Louisiana State University
LSU Digital Commons

LSU Doctoral Dissertations Graduate School

2010

Iron (III) Oxide and Copper (II) Oxide Mediated Formation of PCDD/Fs from Thermal Degradation of 2-MCP and 1,2-DCBz

Shadrack Kirwa Nganai
Louisiana State University and Agricultural and Mechanical College, sngana1@tigers.lsu.edu

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_dissertations

Part of the Chemistry Commons

Recommended Citation

Nganai, Shadrack Kirwa, "Iron (III) Oxide and Copper (II) Oxide Mediated Formation of PCDD/Fs from Thermal Degradation of 2-MCP and 1,2-DCBz" (2010). *LSU Doctoral Dissertations*. 381.
https://digitalcommons.lsu.edu/gradschool_dissertations/381

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Doctoral Dissertations by an authorized graduate school editor of LSU Digital Commons. For more information, please contactgradetd@lsu.edu.

IRON (III) OXIDE AND COPPER (II) OXIDE MEDIATED FORMATION OF PCDD/Fs FROM THERMAL DEGRADATION OF 2-MCP AND 1,2-DCBz

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Shadrack Kirwa Nganai
B.ED (sc). Kenyatta University, Nairobi, Kenya, 1998
December, 2010

To my loving parents

My late dad Samuel Olenganai
and
My mom Christine Olenganai

Thank you for loving me unconditionally, for the endless support and for being the best parents ever. Thank you for instilling in me the importance of education and for providing me with a solid upbringing that has been a sufficient source of an invaluable set of virtues which have continually guided me well through life. The real value that your great support and love have contributed toward accomplishing this task and my general well-being, is immeasurable. Thank you so much.

ACKNOWLEDGEMENTS

First, I would like to thank my graduate advisor Dr. Barry Dellinger for offering me the opportunity to conduct this research work and be part of his wonderful research group. I am so grateful for his inspirational leadership and all the academic support throughout the entire period of my studies.

A special thanks to Dr. Slawomir Lomnicki who provided me with great assistance in getting started and continually guided me through every step of progress in my research. Without his mentoring, patience and encouragement, I would never have accomplished this task. He was always there to meet and talk about student ideas and sharing his invaluable insight on research challenges. Thank you Dr. Slawo.

I was also fortunate to work in a pleasant, conducive and exciting workplace made possible by the all the graduate students in Dr. Barry Dellinger's group. May each one of them receive my total and deserved appreciation.

Thank you to my committee members for finding time to read my thesis and their invaluable comments.

Finally, I owe my deepest gratitude to my family, especially to my dear mom Christine Jepkorir Olenganai who enormously sacrificed for my education, offered me with constant moral support and always believed in me to accomplish something greater than I could never imagine. I am for ever grateful for her prayers, motivation and all the support during my graduate career.

FOREWORD

The research work reported in five chapters of this Dissertation, investigates surface-mediated reactions associated with the formation of polychlorinated dioxins and furans (PCDD/Fs) from the precursors 1,2-dichlorobenzene and 2-monochlorophenol catalyzed by iron and copper. Chapter one gives an introduction of the present work with a broad view on the occurrence, toxicity and sources of PCDD/Fs. The second chapter describes the experimental section of this work which basically is a descriptive elaboration of the components and design of the System for Thermal Diagnostic Studies (STDS). The results are reported in the third chapter. The discussion part of this dissertation presented in chapter 4 deals with the mechanistic details in the formation of PCDD/Fs observed from the thermal degradation of the precursor reactants 1,2-dichlorobenzene and 2-monochlorophenol. Comparison studies of the catalytic roles of copper versus iron in surface-mediated reactions is explored. In chapter five, a summary of the main findings is presented.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

ABSTRACT

Formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) which occurs inexorably from most thermal and combustion processes constitutes a major toxic component of environmental pollutants. Generally, it is well established that transition metal-mediated reactions account for the majority of PCDD/F emissions from combustion sources. Specifically, both copper and iron ions, which occur abundantly in combustion generated particulate matter, are considered probably the most active in promoting PCDD/F formation typically in the low temperature post-combustion zone and flue gas pollution control devices.

It has also been demonstrated that chlorinated phenols are key intermediates in essentially all pathways of PCDD/F formation. Chlorinated benzenes have been presumed to be potent precursors that form PCDD/Fs and are among the most abundant aromatic compounds in incinerator exhaust. Notably, numerous studies have been reported in regard to surface-mediated processes of PCDD/F formation via *de novo* synthesis and transition metal-mediated processes from reactions of chlorinated phenols. However, few experimental studies have been conducted on chlorinated benzenes.

In addition, even though iron oxide is present at 2-50 times higher concentrations than copper oxide, virtually no studies of the iron oxide mediated formation of PCDD/Fs have been reported in the literature. For this study, PCDD/F formation over iron oxide and copper oxide surfaces were investigated using the reactants 2-MCP and 1,2-DCBz in pure and mixture form. The surface-mediated reactions were studied under pyrolytic and oxidative conditions over a temperature range of 200 to 550 ^{o}C.

For the entire study, simplified model surfaces of 5% copper (II) oxide on silica and 5% iron (III) oxide on silica were used in order to facilitate comparison with previous data from similar experiments performed with pure samples of 2-MCP and 1,2-DCBz. Precursor 2-MCP is useful as a model chlorinated phenol, while 1,2-DCBz was selected because it has been found to be present in high concentration in relation to other congeners of polychlorinated benzenes in combustion exhaust and is nearly isoeletronic with 2-MCP, that provides a basis for comparison of product distributions and yields. Reaction pathways of PCDD/F products as well as the intermediates involved are comprehensively analyzed and discussed.

CHAPTER 1: INTRODUCTION

1.1 General Introduction to PCDD/Fs

Polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofurans (PCDD/Fs) is a group of chlorinated aromatic compounds generated mainly as undesirable by-products from various chemical processes. While there are some natural processes producing PCDD/Fs [1], their contribution is significantly by a weak magnitude in relation to anthropogenic sources [2, 3]. These compounds are commonly termed ‘dioxins’ and have been classified as belonging to the group of persistent organic pollutants (POPs) in the environment [4]. Depending upon the position and number of chlorine atom substituent(s), the dioxin family constitutes a total of 210 congeners of which 75 are polychlorinated dibenzo-*p*-dioxin and 135 are polychlorinated dibenzofuran compounds. These compounds are also characterized by low vapor pressures, high octanol/water partition coefficient (K_{ow}) and very low solubility in water [5]. Their general chemical structures are shown in **Figure 1.1**.

Dibenzo-*p*-dioxin **Dibenzofuran**

Figure 1.1 General Structural Formulas and Substituent Position Numbering for Dibenzo-*p*-dioxin and Dibenzofuran

Dioxins are ubiquitous and persistent in the environment albeit degradation has been observed in catalysis of photolytic and biological processes [6, 7], the reactions responsible are negligibly slow under normal environmental conditions [8, 9]. Because of their persistence, low volatility and lipophilic properties, dioxins can be transported over long distances from local to global scale which increases their environmental impact [10, 11]. Consequently, most PCDD/Fs attach strongly in the particulate matter of soil and sediment with low levels occurring in waste water from paper mills, sewage sludge and water treatment plants [12, 13]. The occurrence of dioxins in vegetation has also been noted as a result of atmospheric deposition process of PCDD/F emissions in air [14, 15]. As fat soluble compounds, dioxins potentially concentrate the food chain occurring in fish, mammalian tissue, and human milk [16].

1.2 Sources of PCDD/Fs

Combustion systems and thermal treatment plants are dominant sources emitting dioxin compounds into the environment [17-21]. For years, incineration has been widely utilized as a preferential method for waste disposal partly due to the advantage of greater volume reduction and ability to conserve energy. Until recently, owing to great advances in combustion research prompting the replacement of old technologies with less polluting combustion equipment, municipal waste combustion (MWC) has been a leading source that contributes significantly to the emission of dioxin compounds [22, 23]. Additionally, the use of cement kilns as an alternative to incineration has been identified as a potential source of PCDD/F emissions [24, 25]. Also, in studies on hazardous-waste-firing industrial boilers/furnaces, release of dioxins was observed [26-28]. Furthermore, dioxins have been detected as effluent products of medical waste incinerators [29], backyard barrel burning of wastes [30], accidental forest fires and in trace amounts from sewage sludge incineration [31, 32].

According to the US Environmental Protection Agency (EPA) report of 2000 on inventory of sources and environmental releases of dioxin-like compounds in the United States, the analysis of dioxin emissions to air from incineration sources in decreasing order were recorded from backyard barrel burning of refuse, medical waste incineration (MWI), municipal waste combustion (MWC), coal-fired utility boilers/furnaces and cement kiln burning of hazardous wastes [33].

Generally, incineration of all kinds is a primary source of dioxin pollution, and ever since the presence of dioxins were first identified in flue gases of an incineration facility in the late 1970s [34], the on-going challenge in combustion research has been focused on proving, characterizing and quantifying combustion parameters that control their formation in order to enable the design of efficient practical combustion equipment to minimize PCDD/Fs emission from incineration processes.

Among sources other than incineration, PCDD/Fs are formed from industrial metallurgical processes such as smelting and sintering [35, 36]. Dioxin releases have also been reported from manufacturing process involving chlorinated aromatic compounds and minimally from reservoir sources mainly soil and sediment over extended timescales [37-39].

1.3 Exposure and Toxicity of PCDD/Fs

Dioxins are highly toxic compounds identified to cause adverse effects in animals and humans. Because dioxins bioaccumulate significantly through the food web in the fatty tissues, human exposure to this compounds is almost entirely by dietary intake of food especially meat, fish, poultry, dairy and other animal fatty products [40]. Evidently, toxicological studies on exposure and effects of environmental hazardous compounds, implicates dioxin and it’s forms in causing a wide range of immunologic, digestive, metabolic and reproductive health disorders [41, 42].

Toxicity of each dioxin congener is estimated basing on the most toxic congener; 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (2,3,7,8-TCDD) [43], which has been identified as a potential promoter of carcinogenesis [44, 45]. As a consequence of increasing environmental concern, over the past three decades studies to investigate their formation mechanisms have been a subject of intense scientific research.

1.4 Formation Mechanism of PCDD/Fs from Combustion and Thermal Processes

There are two general pathways that PCDD/Fs are formed from combustion and thermal processes: 1.) Homogenous, gas phase reactions, and 2.) Heterogeneous, catalytic reactions.

1.4.1 Homogeneous Pathway

Homogeneous route involves gas phase reactions of structurally similar chemical precursors which are observed in post combustion gas at temperature range between 400 and 800 ^{o}C. Even though a wide range of compounds have been identified as potential precursors to PCDD/F formation ranging from simple as C2 aliphatics [46, 47] to complex polymerics such as permethrin [48], the principal precursors established as the most significant are monocyclic chlorinated phenols and chlorinated benzenes. The major mechanistic steps in PCDD/Fs formation from gas phase reactions involving chlorinated phenols and chlorinated benzenes includes: firstly, a self condensation reaction of the precursors through coupling of molecule/molecule, molecule/radical or radical/radical species followed by cyclization and rearrangement of the initial intermediates from the first step to produce PCDD/Fs, and finally chlorination/dechlorination reactions [49].

In the case of chlorinated phenols, the key step involves the formation of phenoxyl radical species which are attributed to principally mediate kinetically favorable homogenous reactions. The proposed gas phase mechanisms of dioxin formation from 2-monochlorophenol as a representative precursor for chlorinated phenols, is shown in **Figure 1.2** [50-52].

As shown in **Figure 1.2**, PCDFs formation from chlorinated phenols under homogenous conditions proceeds exclusively via a pathway that involves condensation of two radicals. The gas phase mechanistic steps for the formation of PCDDs involve the coupling of precursor molecules through radical/radical, molecule/radical or molecule/molecule recombination. Gas phase mechanisms associated with chlorinated benzenes proceeds via the initial step of either the formation of phenyl radical in conditions without oxygen or through formation of phenoxy radical in presence of oxygen. Louw and coworkers observed the formation of significant yields of PCDFs and

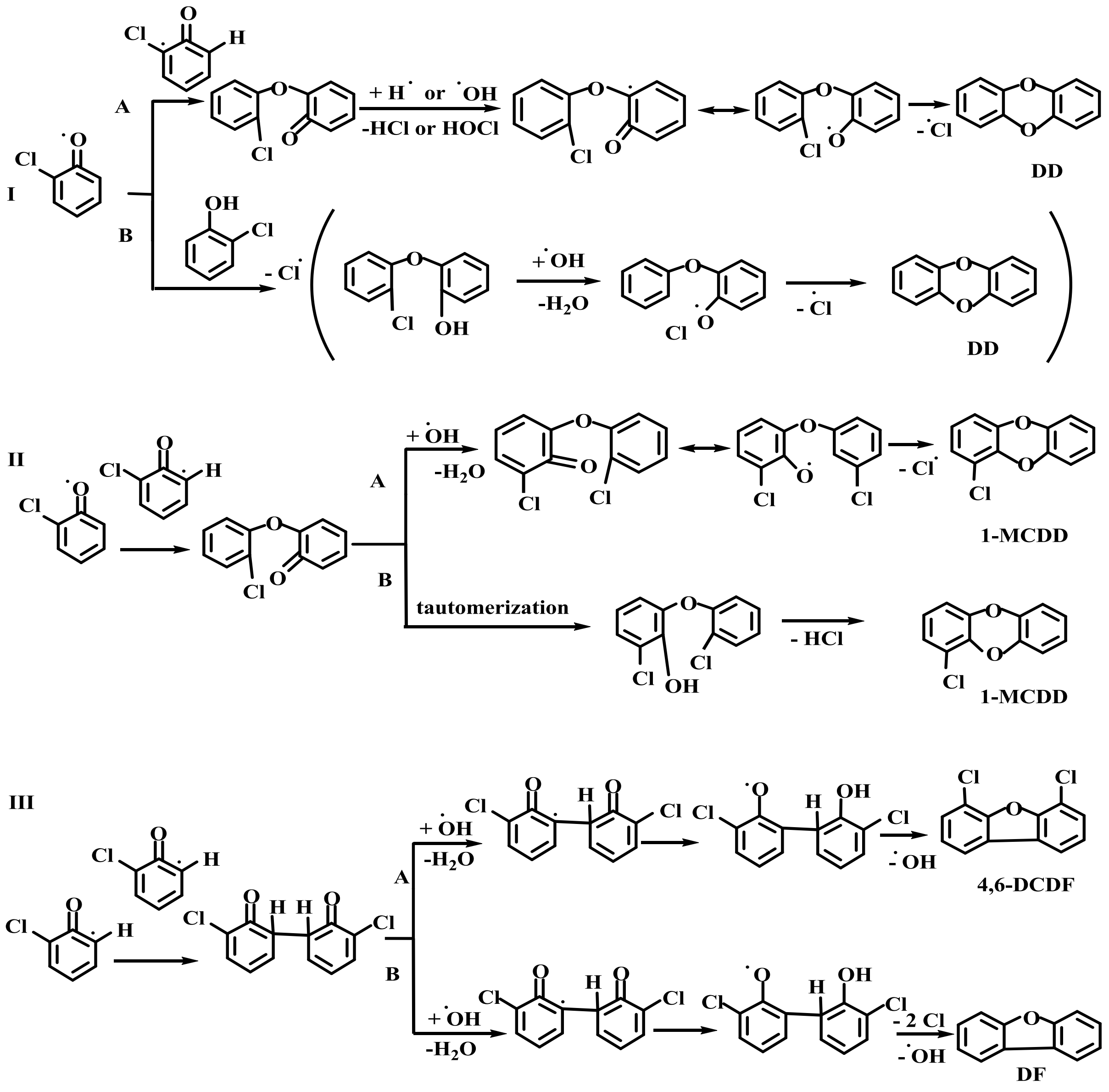


Figure 1.2. IA and IB-Radical-Radical and Radical-Molecule Pathways to DD. IIA and IIB-Radical-Radical Pathways to 1-MCDD. IIIA Radical-Radical Pathways to 4,6-DCDF and IIIB-Radical-Radical Pathways to DF

PCBs from oxidation of chlorinated benzenes above 300 ^{o}C with increased chlorination observed under pyrolytic condition indicated by formation of substantial amounts of highly chlorinated congeners [53]. Unlike the phenoxy radicals, corresponding phenyl radicals propagates gas phase PCDD/Fs formation at comparably slower rate [54]. In addition, both chlorophenyl and chlorophenoxyl radicals have been identified as key intermediates in proposed mechanism for the gas phase formation of PCBs and PCDFs from oxidation of monochlorobenzene [55].

1.4.2 Heterogeneous Pathways

It has been demonstrated that dioxins are formed in almost all combustion processes if there is a source of chlorine, carbon and transition metals to catalyze the condensation and chlorination reactions. Heterogeneous route primarily entails catalytic reactions which are observed in the particle phase at temperature range between 200 and 400 ^{o}C. Most specifically, PCDD/Fs are formed from these reactions as a result of transition-metal catalyzed reactions which may involve particulate carbon by "*de novo*" synthesis or precursors of similar structure by surface-catalyzed synthesis.

I. *De novo* Synthesis

The *de novo* synthesis of dioxins from combustion processes refers to a reaction pathway that involves a certain source of carbon, chlorine, oxygen and hydrogen under suitable temperature, time and catalytic conditions. The carbon source has been suggested to originate from solid carbon matrix in fly ash predominantly through chemical transformation of available graphitic structures in the microcrystalline carbons [56]. Unlike gas phase molecular oxygen that significantly influences the *de novo* synthesis [57], it has been established that hydrogen and chlorine in gas stream have no role in the *de novo* process [58-60]. The source of hydrogen and chlorine has been suggested to be likely from organic and inorganic compounds present in solid carbon or fly ash [61]. Based on the key parameters established for *de novo* synthesis such as organic or inorganic chlorine containing compounds, an oxidizing agent, copper or iron metal ions, a preferable temperature range of 250-450 ^{o}C and solid carbon in the form of graphite layers present in the macro-molecular carbon structure of fly ash [62], there are several observations of dioxin formation that have been attributed to occur through the *de novo* pathway: I.) Emission of PCDD/Fs from chemically unrelated compounds such as cellulose, coal, polystyrene, polyvinyl chloride with inorganic chlorine donors. II.) PCDD/F formation from the cooling of flue gases in the low-temperature post-furnace zone that usually consists of a waste heat boiler and electrostatic precipitator. III.) Dioxins generated from residual carbon and inorganic chlorine in fly ash.

The mechanistic steps of *de novo* synthesis of dioxins from residual carbon in fly ash involve first gas phase molecular oxygen adsorption on the surface containing metal catalysts. In particular, catalytic effect of copper and iron metal species has been observed in the formation of PCDD/F under *de novo* conditions [58, 63-65]. The chemical reactions involved is initiated by dissociative chemisorption process of molecular oxygen on carbon and the metal catalysts [66]. Subsequent transfer of the adsorbed oxygen to a free carbon site within the graphite layers followed by carbon gasification process forms gaseous products mainly carbonmonoxide and carbondioxide [67]. In addition to the formation of carbonmonoxide and carbondioxide as the major gaseous products from the carbon gasification, other minor products that are formed as well include chlorinated benzenes, chlorinated phenols and chlorinated biphenyls [68, 69]. These chlorinated aromatic compounds may potentially undergo condensation reactions leading to formation of dioxins [20, 70].

The halogenations/dehalogenation process on graphite layers and aromatic compounds including DD/F may occur concurrently in the course of the entire *de novo* chemical reactions. Principally, the halogenation process of carbonaceous material such as soot, char and coal proceeds via a substitution reaction of hydrogen by a halogen compound [71, 72]. These halogenation reactions of aromatic compounds and DD/F related structures is mediated by metals in fly ash [73]. Moreover, metal-catalyzed degradation reactions of PCDD/Fs via dechlorination and decomposition routes have been observed to occur during the *de novo* synthesis of dioxins. Huang and Buekens proposed a general mechanistic model for *de novo* synthesis of dioxins in which gaseous reactants first undergo surface adsorption and diffusion processes, then carbon gasification forming CO_2 and CO with also PCDD/F formation through oxygen complexes. The resulting PCDD/Fs potentially decomposes into other products whereas halogenations/dehalogenation reactions occur throughout the entire *de novo* synthesis [74].

II. Surface-Catalyzed Synthesis

Surface-catalyzed synthesis involving structurally similar precursor molecules is a dominant mechanistic pathway in PCDD/F formation [75]. The identifiable precursors such as chlorophenols and chlorobenzenes chemisorb on the surface and undergo chemical reactions through the influence of metal catalysts to form PCDD/Fs. It is believed that surface-mediated processes account for about 70% of all dioxin formation with transition metal oxides and chlorides playing the most important role in PCDD/F formation.

The presence of transition metals has been observed in the fly ash matrix and in flue gas treatment devices of most combustion systems. Transition metals such as copper and iron identified to have a promoting effect [76], while alkali metals such as magnesium and calcium have a suppressing effect [77]. It has been demonstrated that phenols potentially adsorb on the surface via elimination of H_2O to form surface phenolate species. Chlorophenols as potential electron donors, enables an electron transfer process from chlorophenolate to metal cation site (M^{n+}) leading to formation of associated chlorophenoxyl radical and $M^{(n+)-1}$ site. Similar interaction was observed upon adsorption of 2-monochlorophenol and 1,2-dichlorobenzene on a copper (II) oxide surface through elimination of H_2O and HCl, respectively [78, 79]. Moreover, formation of both phenoxy and semiquinone-type radicals was observed from adsorption of a variety of substituted aromatic compounds suspected to be dioxin precursors such as 2-monochlorophenol, catechol, hydroquinone, monochlorobenzene and 1,2-dichlorobenzene on copper (II) oxide surface [80].

In general, the formation of PCDD/F from precursor molecules on metal oxide surfaces appears to proceed through a surface-associated phenoxyl or chlorophenoxyl radical intermediate species. Regarding mechanistic pathways involved in surface-catalyzed synthesis of PCDD/Fs, Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) mechanisms have been proposed [70, 81, 82]. It has been suggested that PCDDs are formed according to E-R mechanism which involves the reaction of an adsorbed species and a gas phase molecule, while formation PCDFs follows an L-H mechanism which involves reaction of two adsorbed species [83]. **Figure 1.4** shows a unified pathway for the formation of PCDD/F in combustion systems involving precursor molecules and transition metal catalysts in the post combustion zone.

1.5 Comparison Studies of PCDD/F Formation from Chlorophenols and Chlorobenzenes

Chlorophenols and chlorobenzenes are the most dominant and direct precursors in formation of dioxins. Ballschmitter and coworkers observed that in reactions involving an aromatic compound with principal flame radicals such as H, OH, O, and O_2H, proceeds via favorable extraction of an H than a Cl [84]. These results imply high concentration of chlorobenzenes and chlorophenols as noted in flue gases. With respect to homogenous pathway in the formation of PCDD/Fs, the focus mainly has been on chlorinated phenols [85-89]. Milligan and Altwicker observed that at relatively high concentration of chlorophenols, the gas phase formation of dioxins was 100 times greater than *de novo* pathway and no PCDFs were detected at shorter residence times [85].

Model experiments involving the reactions of carbon free fly ash and model organic compounds were performed by Addink and Olie [88]. Their findings showed that both

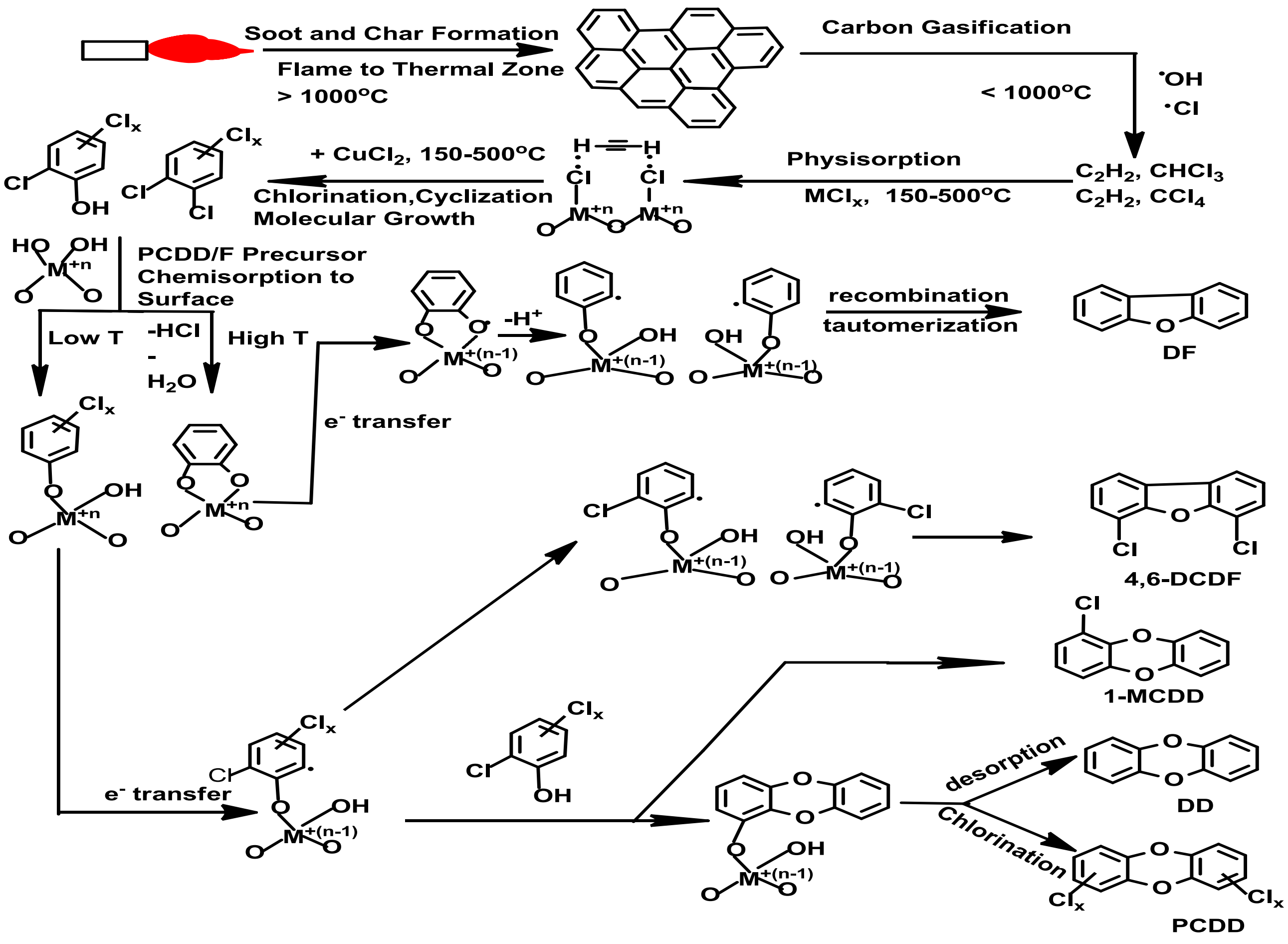


Figure 1.3 Mechanisms of a Unified Pathway for the Formation of PCDD/F in Combustion Systems

chlorophenols and chlorobenzenes undergo condensation to form PCDD/F with the former at a rate of 10-540 times faster than the latter. Although chlorobenzenes have a less favorable rate than chlorophenols in formation of dioxins, their concentration in full scale combustors exceeds that of chlorophenols by a magnitude [90-92], and their propensity to convert into chlorophenols has been noted in some laboratory investigations [93]. In general terms, it has been established that homogenous reactions are mainly related to mechanistic reactions involving precursors and the observed PCDD/F isomer patterns show a significant correlation with initial precursor molecules[89, 94]. Previous studies on homogeneous gas phase reactions in formation of PCDD/Fs from chlorophenols and chlorobenzenes are summarized in **Table 1.1.**

In surface catalysis studies, mechanisms producing dioxins from surface mediated heterogeneous reactions have been widely investigated and the referenced publications are representative [62, 70, 89, 109-111]. It is likely the focus on surface catalyzed synthesis developed as a result of a theoretical model which significantly underestimated the contribution of gas phase formation of dioxins from chlorophenols [112]. However, the findings from this model were later to be discounted on the basis of the lack of directly related experimental data at the time of publication and the failure to incorporate reduced reactivity of phenoxyl radical caused by resonance stabilization. The results from subsequent models estimates homogenous gas phase mechanisms to account for about 30% of PCDD/F emissions from thermal and combustion sources [113, 114].

As a result of numerous studies on surface catalyzed synthesis of PCDD/F, considerable progress has been made toward understanding the mechanistic details that account for their formation in the post combustion zone. Olie and coworkers reviewed the catalytic properties of various metals in formation of PCDD/Fs during incineration of municipal waste and copper was identified to have the strongest catalytic effect in dioxin formation while iron was observed to

Table 1.1 Previous Studies on Homogeneous Gas Phase Formation of PCDD/Fs from Chlorophenols and Chlorobenzenes

Reactant	Author, Title, Journal, Year	Experimental Conditions		Key Findings on PCDD/Fs Formation	Ref
		Type of Reaction	Temperature ^{o}C		
Phenol 2-MCP	Born and co-workers. Formation of dibenzofurans in homogeneous gas-phase reactions of phenols. *Chemosphere* **1989.**	Pyrolysis	455-490 ^{o}C	DF formation observed from phenol and DD detected in mixture of phenol and ortho-CP. With 2-MCP, DD: MCDD: MCDF: DCDF formation observed with yield ratio of about 47:0:2:15.	[95]
2-MCP	Evans and Dellinger. Mechanisms of dioxin formation from the high-temperature pyrolysis of 2-chlorophenol. *Environ. Sci. Technol.* **2003.**	Pyrolysis	300-1000 ^{o}C	DD, 1-MCDD observed was attributed to radical-radical mechanisms. Only DF and no 4,6-DCDF observed and pyrolytic conditions suggested to favor PCDD formation.	[50]
	Evans and Dellinger. Mechanisms of dioxin formation from the high-temperature oxidation of 2-chlorophenol. *Environ. Sci. Technol.* **2005.**	Oxidation	300-1000 ^{o}C	In decreasing order; 4,6-DCDF,DD, 1-MCDD,4-MCDF and DF were the dioxin products observed. Non dioxin products such as naphthalene, chloronaphthalene, 2,4-DCP, 2,6-DCP, MCBz, Bz and phenol were detected.	[51]
	Weber and Hagenmaier. Mechanism of the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans from chlorophenols in gas phase reactions. *Chemosphere* **1999.**	Oxidation	349 ^{o}C	PCDDs observed to form in gas phase via radical mechanisms involving ortho-phenoxyphenols (POPs). PCDFs formed via condensation of polychlorinated dihydroxylbiphenyls (DOHB) as intermediates.	[96]
	Wiater-Protas, and Louw. Gas-phase chemistry of chlorinated phenols - Formation of dibenzofurans and dibenzodioxins in slow combustion. *Eur. J. Org. Chem.* **2001.**	Oxidation	500-550 ^{o}C	Effect of introducing a chlorine substituent on the PCDD/F formation was investigated. Phenol, 2-MCP, 2,4,6-TCP and PeCP observed to have insignificant differences in their rates of conversation . With chlorinated ortho- position, formation of chlorinated DDs was predominant	[97]

Table 1.1 Con'd

Phenol 2-MCP 3-MCP 4-MCP 2,4-DCP 3,4-DCP 2,6-DCP	Yang and Akki, Formation of furans by gas-phase reactions of chlorophenols. *Symp. (Int.) Combust., [Proc.]* **1998.**	Pyrolysis	600 ^{o}C	From pyrolysis of phenol, DF formation was observed and ortho-ortho coupling of phenoxyl radicals proposed as the mechanistic route. Total PCDFs observed from pyrolysis 3-MCP accounted for 0.31% . No PCDDs detected except with 2-MCP. The authors suggest ortho chlorine to be necessary for gas phase formation of PCDD from chlorinated phenols as precursors. From the pyroysis of 2,4 yield, 2,4,6,8-tetraCDF was the primary PCDF product detected while 2 TriCDF, 4 DCDF, 4 MCDF and DF were the secondary products observed. Pyrolysis of 3,4-DCP yielded 1,2,7,8-/2,3,7,8-/1,2,8,9-TetraCDF as primary PCDF products while 6-TriCDF, 6 DCDF, 4 MCDF and DF detected as the secondary products. From the pyrolysis of 2,6-DCP, 2-DCDF, 4-MCDF and DF detected as the secondary products	[98]
3-MCP 2, 6-DCP	Mulholland and coworkers. Temperature dependence of DCDD/F isomer distributions from chlorophenol precursors. *Chemosphere* **2001**	Pyrolysis	300-900 ^{o}C	From the pyrolysis of 3-MCP, formation of 1,7-, 3,7- and 1,9-DCDF via condensation of polychlorinated dihydroxylbiphenyls (DOHB) observed. From pyrolsis of 2,6-DCP, formation of 1,6- and 1,9-DCDD observed through smiles rearrangement. At lower temperatures the formation of isomer 1,6-DCDD was energetically favorable than the 1,9-DCDD formation	[99]
		Oxidation		Higher yields of 1,7-, 3,7- and 1,9-DCDF observed. Strong dependency on steric effects and approach geometries of phenoxyl radical identified to play an important role in PCDF formation.	

Table 1.1 Con’d

2-MCP	Briois, and co-workers. Experimental study on the thermal oxidation of 2-chlorophenol in air over the temperature range 450-900 degrees C. *Chemosphere* **2006.**	Oxidation	450-900 ^{o}C	CO, 2-2 H-pryan-2-one, chlorobenzene, 4-cyclopenten-1,3-dione were observed as the major intermediate products. Above 900^{o}C, 2-CP, CO and other organic byproducts were oxidized to carbon dioxide.	[100]
2,4,6-TCP	Sidhu and coworkers. The homogeneous, gas-phase formation of chlorinated and brominated dibenzo-*p*-dioxin from 2,4,6-Trichlorophenols and 2,4,6-Tribromophenols. *Combustion and Flame* **1995**	Oxidation	300-800 ^{o}C	PCDDs observed with 1,3,6,8- and 1,3,7,9-tetra chlorinated isomers as the dominant PCDDs product. Maximum yield of 0.05% detected for the TCDDs isomers.	[101]
MCBz	Sawerysyn and coworkers. Experimental study on the thermal oxidation of chlorobenzene at 575-825 degrees C. *Chemosphere* **1999.**	Oxidation	575-825 ^{o}C	CO, CH4, C2H2, C2H4,vinyl chloride, vinylacetylene, furane and benzene were observed as the major products. These products are produced by isomerization of phenyl radicals formed from thermal degradation of chlorobenzene.	[102]
	Sommeling and co-workers. Formation of PCDFs during chlorination and oxidation of chlorobenzenes in chlorine/oxygen mixtures around 340^{o}C. *Chemosphere* **1994.**	Oxidation	330-350 ^{o}C	High yields of PCDFs observed via chlorinated phenylperoxyl- and/or phenoxyl radicals reactions with oxygen.	[53]
	Rouzet, and co-workers. The formation of chlorinated aromatic hydrocarbons during high temperature pyrolysis of chlorobenzene. *J. Anal. Appl. Pyrolysis.* **2001.**	Pyrolysis	800-1200 ^{o}C	Formation of polychlorobiphenyls via recombination of phenyl and cholorophenyl radicals observed. Major products dectected included benzene, hydrogen, acetylene and methane. Nathphthalene , chloronathphthalene and acenaphthalene observed as minor products. No PCDD/F compounds observed.	[103]

Table 1.1 Con’d

1,3-DCBz, 1,2,3-TriCBz, 1,2,4,5+1,2,3,4-TeCBz, PentaCBz	Liu and coworkers. Mechanism of PCBs formation from the pyrolysis of chlorobenzenes. *Chemosphere* **2001.**	Pyrolysis	660 ^{o}C	Polychlorinated biphenyls (PCBs) were observed from condensation of chlorobenzenes via chlorophenyl radicals. Lower chlorinated benzenes were observed to produce more PCBs than highly chlorinated isomers. Substantial amounts of PCBs were formed from 1,2,3-trichlorobenzenes. Pyrolysis of 1,2,3,4-tetrachlorobenzene at 280 ^{o}C produced octachlorobiphenyl as the main product.	[104]
CBzs (tri-, tetra-, penta-)	Buser. Formation of polychlorinated dibenzofurans (PCDFS) and dibenzo-para-dioxins (PCDDs) from the pyrolysis of chlorobenzenes. C*hemosphere* **1979.**	Pyrolysis	620 ^{o}C	Significant yields of PCDF were observed in comparison with PCDDs. Presence of chlorophenols noted in all the experimental runs.	[105]
CBz (Bz, mono-, di-, tri-,tetra-,penta-)	Louw and Dorrepaal. Mechanism of vapor-phase chlorination of benzene-derivatives. *Int. J. Chem. Kinet.* **1978.**	Rates of radical formation from CBzs	100-500 ^{o}C	Aryl radials play important role as intermediate in formation of chlorinated products and the relative rate was observed to increase with increasing temperature. PCBs proved to form from gas phase condensation of phenyl radicals.	[106]
MCBz 1,3-DCBz	Ritter, and Joseph. Production of chloro and dichlorobiphenyls, terphenyls, and triphenylenes from pyrolysis of chloro and dichloro-benzenes. . *Organohalogen Compd.* **1990.**	Pyrolysis	800-1010 ^{o}C	Biphenyl, chlorinated biphenyls via cyclohexadienyl intermediate. Terphenyls suggested to form from subsequent additions of biphebyl species while triphelenes were produced from the conversion of o-terphenyl radical.	[107]
CBzs (tri-, tetra-, penta-)	Bleise, and co-workers. Polychlorinated biphenylenes (PCBN) from pyrolysis of chlorobenzenes. Identification and mechanism of formation. *Toxicol. Environ. Chem.* **1997.**	Pyrolysis	500-900 ^{o}C	Formation of polychlorinated biphenylenes and polychlorinated acenaphthalene observed. Traces of naphthalene and chloronapthalene detected. Two reaction pathways proposed: 1.) Involves PCB radicals and cyclization into biphenylenes. 2.) Involves arynes as intermediates via dimerization.	[108]

have a promoting effect but only in high concentrations [73]. Ghorishi and Altwicker studied the combustion of 1,2-dichlorobenzene in heptane in a spouted bed combustor in the presence of sand and quartz [115]. Their results showed PCDD/F formation on quartz which is nearly pure $SiO_{2,}$ to be four times less than the yield observed in presence of sand which contained trace metal oxides such as Fe, Ca, Ti and Mn. Crumett and coworkers studied the reaction benzene in presence of iron (III) chloride catalyst and molar yields of 0.00040% CDD and 0.13% CDF were observed over a wide range of precursor composition and thermal conditions [116]. Previous studies on surface catalyzed synthesis of PCDD/Fs are summarized in **Table 1.2.**

In addition, comparison of data from full-scale systems to those from laboratory scale studies reveals a significant difference in the concentration of precursor species chlorophenols and chlorobenzenes in particular, and the ratio of PCDDs to PCDFs as well. These field and laboratory measurements are summarized in **Table 1.3**.

1.6 Approach to the Present Study of 1,2-Dichlorobenzene and 2-Monochlorophenol

Experimental studies on the formation of dioxins from chlorinated phenols from combustion and other thermal processes are well documented. However, as depicted in **Table 1.3,** the findings from numerous studies involving reactions of chlorophenols strongly implicated as precursors to formation of PCDD/F, shows a wide discrepancy between the PCDD/PCDF ratios where it has been found to be >1 at laboratory experiments designed to emulate incinerator fly ash conditions compared to full scale systems where the ratio is often < 1 in typical incinerator conditions [18]. This inconsistency in the PCDD/PCDF ratios from chlorophenol precursor over fly ash in real incinerators and laboratory reactions which still remains unresolved, suggests alternative species such as chlorobenzenes may be the dominant precursors in PCDD/F formation.

Table 1.2 Previous Studies on Surface-Catalyzed Synthesis of PCDD/Fs

Reactant	**Author, Title, Journal, Year**	**Experimental Conditions**				**Key Findings on PCDD/F Formation**	**Ref**
		Type of Catalyst	**Surface**	**Gas Stream**	**Temperature ^{o}C**		
Phenol 2-MCP 3-MCP 4-MCP	Ryu. Formation of chlorinated phenols, dibenzo-p-dioxins, dibenzofurans, benzenes, benzoquinones and perchloroethylenes from phenols in oxidative and copper(II) chloride-catalyzed thermal process. *Chemosphere* **2008.**	$CuCl_2$	SiO_2	92% N_2 8% O_2	100-425 ^{o}C	Major products observed were chlorinated phenols (CP) benzoquinones (CQ), Chlorinated benzenes (CBz), PCDD/Fs and perchloroethylene (PCE). Ortho- and para- CPs observed to have a greater propensity to form PCDDs.	[117]
	Born, and coworkers. Fly-ash mediated reactions of phenol and Monochlorophenols - Oxychlorination, Deep Oxidation, and Condensation. *Environ. Sci. Technol.* **1993**	$CuCl_2$ and CuO	Fly ash, Al_2O_3, Sand	N_2, O_2, HCl, H_20	150-600 ^{o}C	Oxychlorination increased with increasing HCl concentration implying greater propensity for higher PCDD/Fs yields. Both catalysts observed to promote deep oxidation of phenol.	[118]
2-MCP	Dellinger and Lomnicki. Formation of PCDD/F from the pyrolysis of 2-chlorophenol on the surface of dispersed copper oxide particles. *Proc. Combust. Inst.* **2003.**	CuO	SiO_2	He	200-500 ^{o}C	DD, 1-MCDD and 4,6-DCDF were the PCDD/Fs products observed. L-H mechanisms proposed for the formation of PCDFs while E-R mechanism attributed to the formation of PCDDs.	[119]
	Dellinger and co-workers. Ferric oxide mediated formation of PCDD/Fs from 2-monochlorophenol. *Environ. Sci. Technol.* **2009.**	Fe_2O_3	SiO_2	N_2	200-550 ^{o}C	Major PCDD/F products observed were DF>4,6-DCDF>DD>1-MCDD. Total PCDD/F yields of iron catalyst were 2.5 times higher than in copper compared under identical conditions.	[120]

Table 1.2 Con’d

2-MCP	Dellinger and Lomnicki. A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on a CuO/silica surface. *J. Phys. Chem. A* **2003.**	CuO	SiO_2	20% O_2 80% He	200-500 ^oC	Major PCDD/F products observed were 1-MCDD> 4,6-DCDF> DD. Presence of surface-bound phenoxyl radical attributed to chemisorption of 2-MCP at a copper oxide site and a subsequent electron transfer process.	[82]
	Jean-Pierre and Nicholas. Thermal degradation of 2-chlorophenol promoted by CuCl2 or CuCl: Formation and destruction of PCDD/Fs. *Chemosphere* **2007.**	CuCl and $CuCl_2$.	-	Air	350 ^oC	CuCl was much less efficient in chlorination than $CuCl_2$. Formation PCDDs was predominat particularly with $CuCl_2$ than CuCl. Efficiency of CuCl in PCDD oxidation was observed to be greater than $CuCl_2$.	[121]
2,6-DCP 2,4,6-TCP 2,3,4,6-TetraCP, PentaCP.	Mulholland. Formation of polychlorinated dibenzo-p-dioxins by CuCl2-catalyzed condensation of 2,6 chlorinated phenols. *Combust. Sci. Technol.* **2001**	$CuCl_2$		8% O_2	300-450 ^oC	Total PCDD product yields varied by two orders of magnitude over a range of conditions while only a slight variation in PCDD homologue and isomer distributions was observed. 1,2,3,4,6,8-H_6CDD formed from 2,4,6-TCP and pentaCP was the major PCDD product. PCDD isomer distribution was found to correlate with that observed in typical municipal incinerations.	[122]

Table 1.2 Con'd

PentaCP	Qian and coworkers. Influence of metal oxides on PCDD/Fs formation from pentachlorophenol. *Chemosphere* **2005**	Various Metal Oxides	-	N_2	280 °C	Fe_2O_3, Al_2O_3 and alkali-earth metal oxides were found to have suppressing effect on PCDD/F formation Integrative effect determined by charge to radius ratio controls the suppression efficiency. Metals oxides of Cu, Co, Ti, and Pb had a promoting effect.	[123]
Activated Carbon PAH	Hatanaka and coworkers. Effects of copper chloride on formation of polychlorinated dibenzo-p-dioxins in model waste incineration. *Chemosphere* **2003.**	$CuCl_2$	Fly ash	Air	900 °C	$CuCl_2$ promoted PCDD formation via chlorination effect. Unlike PCDFs, Cu had a less significant effect was in influencing homologue patterns of PCDDs. Formation PCDFs was favored than PCDDs.	[124]
Activated Carbon	Stieglitz and coworkers. On formation conditions of Organohalogen Compd.from particulate carbon of fly-ash. *Chemosphere* **1991.**	$CuCl_2$ and $FeCl_3$	Fly ash	SO_2, HCl, Cl_2	300 °C	PCDD/Fs compounds are formed through a direct ligand transfer of the halogen substituent catalyzed by metals ions (Cu, Fe). Fe(III) also established to promote these reactions as Cu ions although in relatively larger amounts.	[125]
Activated Carbon	Ryan, and Altwicker. Understanding the role of iron chlorides in the de novo synthesis of polychlorinated dibenzo-p-dioxins/dibenzofurans. *Environ. Sci. Technol.* **2004**	$FeCl_2$ $FeCl_3$ FeOCl	12% Al_20_3 48% CaO 40% SiO_2	2% O_2 N_2	300-400 °C	The three different forms of iron investigated promoted the formation of PCDD/Fs. PCDD: PCDF ratios of < 1 was observed. Greater catalytic effect of enhancing PCDD/F formation was observed at about 300 °C.	[65]

Table 1.2 Con'd

Activated Carbon	Addink and co workers, Formation of Polychlorinated Dibenzo-Para-Dioxins Dibenzofurans in the Carbon Fly-Ash System. *Chemosphere* **1991**	-	Fly ash	Air H_2O	200 400 ^oC	PCDD/F formation observed and the highest yields obtained at 350^oC. Congener distribution was dependent on reaction time and temperature.	[126]
^{12} C- and ^{13}C-Carbon	Hell and co-workers. Mechanistic aspects of the *de-novo* synthesis of PCDD/PCDF on model mixtures and MSWI fly ashes using amorphous C-12- and C-13-labeled carbon. *Environ. Sci. Technol.* **2001.**	$CuCl_2$	Fly ash	20% O2 80% He	250-400 ^oC	Two mechanistic pathways proposed to account formation of PCDD/Fs observed: Formation via ^{12} C- and ^{13}C- directly and formation from intermediate monoaromatic rings. The latter mechanism accounted for over 50% of the PCDD/Fs..	[127]
Phenol, 3-MCP, 3,4-DCP, 2,4,6-TCP.	Ryu, and Mulholland. Metal-mediated chlorinated dibenzo-p-dioxin (CDD) and dibenzofuran (CDF) formation from phenols. . *Chemosphere* **2005**	$CuCl_2$		92% N_2 8% O_2	325-450 ^oC	More PCDFs than PCDDs observed. PCDD/F isomer pattern established to be independent with temperature. Steric and electronic factors established to control the chlorination of phenols by $CuCl_2$.	[128]
MCBz	Sidhu and Nakka. Surface catalyzed chlorobenzene transformation reactions in post-combustion zone. *Organohalogen Compd.***2004.**	CuO	Florosil	Air He	300-600 ^oC	Tetrachlroethylene and di- to hexa-chlorobenzenes were the major products observed. No PCDD/Fs, phenols and chlorinated-PAHs were observed.	[129]
MCBz	Kasai, and coworkers. PCDD/Fs formation from mono-chlorobenzene on some metallic oxides. *Organohalogen Compd.*. **2000**	Fe_2O_3 FeOOH MgO Al_2O_3 SiO_2	-	0-5% O_2	200 400 ^oC	Maximum PCDD/Fs amounts observed at 2.5% O_2 concentration at 300 ^oC. Fe_2O_3 catalyzed PCDD/F formation. Catalytic effect of SiO_2 was less significant and ability Al_2O_3 to convert MCB to CPs was also observed.	[130]

Table 1.2 Con'd

MCBz 2-MCP	Kasai, and Nakamura. Formation of PCDD/Fs on iron oxides from chlorobenzene and chlorophenol. *Organohalogen Compd.***1999**	Fe_2O_3 FeOOH	SiO_2	Ar O_2 HCl	100-400 ^oC	Higher yields of PCDD/F products observed at 300 ^oC than at 200^oC. Presence of O_2 favored formation of PCDD/Fs. Chlorination of PCDD/Fs favored at high temperature.	[131]
1,2-DCBz 2,4-DCP	Ghorishi, and Altwicker. Rapid formation of polychlorinated dioxins/furans during the heterogeneous combustion of 1,2-dichlorobenzene and 2,4-dichlorophenol. *Chemosphere* **1996**	SiO_2	-	Air	390-430 ^oC	PCDD/Fs observed from 2,4-DCP were two orders of magnitude higher than 1,2-DCBz. PCDDs to PCDF ratios were less than 1 for both precursors. Dominant congeners for PCDD/F were tetra- from 2,4-DCP and tetra-, hexa- from 1,2-DCBz.	[132]
1,2-DCBz	Ghorishi, and Altwicker. Formation of polychlorinated dioxins, furans, benzenes and phenols in the postcombustion region of a heterogeneous combustor - Effect of bed material and postcombustion temperature. *Environ. Sci. Technol.* **1995.**	Sand and Quartz	-	Air	390-430 ^oC	Catalytic formation of PCDD/Fs and chlorinated benzenes from 1,2-DCBz enhanced by sand was observed. Comparably, catalytic activity on a quartz bed was significantly less. Tetra-CDD/Fs was the dominant congener and formation yields of PCDFs were higher than PCDDs.	[133]
Aliphatic Liquid fuel (C_{10}-C_{13})	Ismo, and coworkers. Formation of aromatic chlorinated compounds catalyzed by copper and iron. *Chemosphere* **1997**	-	$FeCl_3$ $CuCl_2$	-	250 ^oC	Iron and copper added into the fuel promoted formation of PCDD/F. Particle bound concentration of PCDD/F greater than gas phase.	[134]
Bz soot, 1,2-DCBz soot.	Addink and Altwicker. Formation of polychlorinated dibenzo-p-dioxins/dibenzofurans from soot of benzene and *o*-dichlorobenzene combustion. *Environ. Sci. Technol.* **2004**	$CuCl_2$	SiO_2	Air N_2	277-600 ^oC	1,2-DCBz soot was observed to be more active in PCDD/F formation than Bz soot. PCDD: PCDF ratios observed were <1 for both reactants. Soot deposits suggested to be play role in PCDD/F formation in the post combustion zone.	[135]

Chlorobenzenes have been shown in various laboratory investigations to be formed from gas phase pyrolysis of simple chlorinated hydrocarbons [47], *de novo* synthesis of MSW fly ashes [46], and copper catalyzed reactions of ethylene and acetylene [149]. In addition to chlorophenols, chlorobenzenes have been assumed to be precursors of PCDD/Fs.

Table 1.3. Comparison of Concentrations of Chlorobenzenes versus Chlorophenols, and PCDDs versus PCDFs from Full-Scale and Laboratory Measurements

Type of Study	**Total CBzs**	**Total CPs**	**Ratio CBz: CP**	**Total PCDDs**	**Total PCDFs**	**Ratio PCDD: PCDF**	**Ref**
Full- Scale	NA	NA	–	66µg/h	250µg/h	0.264	[22]
	NA	NA	–	500ng/ dscm	2000ng/ dscm	0.25	[136]
	NA	NA	–	2.85-64.12 g/Nm^3	9.39-293.93 g/Nm^3	0.22-0.3	[137]
	NA	NA	–	38.8 wt%	61.3 wt%	0.63	[138]
	NA	NA	–	8mg/hr	40mg/hr	0.2	[139]
	NA	NA	–	885ng/kg	1477ng/kg	0.59	[140]
	445 pptv	110 pptv	4:1	NA	NA	–	[141]
	436.63 pptv	113.45 pptv	3.8:1	0.21 pptv	0.3 pptv	0.7	[142]
	730	970	1:1.3	45	100	0.45	[143]
	NA	NA	–	12.7ng/g	13.62ng/g	0.93	[144]
Laboratory (*De novo* pathway)	NA	NA	–	0.5-1980 (ppm)	2.5-60 (ppm)	0.2-33	[145]
	13900 (ng/g)	1370 (ng/g)	10:1	2046 (ng/g)	8525 (ng/g)	0.24	[69]
	2.15x10^{-3} yield/mol	5.1x10^{-5} yield/mol		1.12x10^{-5} yield/mol	4.67x10^{-4} yield/mol	0.024	[68]
	NA	NA	–	567ng/g	1151ng/g	0.5	[146]
	NA	NA	-	256-1662mg/ sample	1178-5120mg/ sample	0.05-0.93	[65]

NA - not analyzed

Table 1.3 Con'd

	Type of Precursor	PCDDs	PCDFs	Ratio PCDD:PCDF	Ref
Laboratory (Precursor pathway)	2,4,6-Trichlorophenol	232,000 ng/g	10,000 ng/g	23.2	[147]
	2-Monochlorophenol	1.046 yield, %	0.89 yield, %	1.18	[119]
	2,4-Dichlorophenol	4000ng/m^3	12000ng / m^3	0.33	[132]
	1,2-Dichlorobenzene	50ng/m^3	75ng/m^3	0.67	
	2,4,6-Trichlorophenol	0.02-50 wt%	0.1-10 wt%	0.2-33	[145]
	2,3,4,6-Tetrachlorophenol	1.6-10 μg/g	0.8-3.3 μg/g	2-3	[148]

Infact, comparison of the concentrations of PCDD/Fs and various potential precursors as well as other factors in the exhaust of the incinerators indicated that polychlorinated benzenes exhibited the strongest correlation [73, 79, 84, 150, 151]. Studies such as these have led to the common presumption that chlorobenzenes have been experimentally demonstrated to be PCDD/F precursors.

However, few experiemental studies have actually been conducted on chlorinated benzenes [88, 150]. More specifically, pathways of formation due to surface-mediated reactions of low chlorinated benzenes are still not clearly understood. The only study reported on surface catalyzed synthesis of dioxins from chlorobenzenes as the initial reactants was performed in a spouted bed combustor for 1,2-dichlorobenzene from 130 to 430 ^{o}C [132]. Chlorophenols and higher chlorobenzenes were formed and ratio of PCDD/PCDF observed was < 1 implying that the formation of PCDFs was predominant. On the basis of chlorobenzenes also being the most abundant in flue gases of a variety of combustion sources [92], it is somewhat surprising that only limited studies have been devoted to account for their role in the formation of dioxins.

Also, previous research on surface catalyzed synthesis of PCDD/Fs has focused on copper oxide mediated formation from elemental carbon during *de novo* synthesis [56, 145, 152] and mainly on chlorophenols as the precursor molecules [89, 136, 153]. The focus on copper oxide is probably the result of its significant concentration in municipal waste incinerators where PCDD/F were first discovered in combustion systems and the well-known redox activity of copper oxides [75, 114, 154]. However, considering the fact that iron oxide, which is also redox active, is almost always the highest concentration transition metal in combustion systems [155-157], one might expect iron to mediate or catalyze the formation of PCDD/Fs. In addition, the concentration of iron in fly ash and other combustion generated particulate matter is 2-50 times higher than copper. **Table 1.4** summarizes the concentrations of iron versus copper from selected particulate matter.

Table 1.4 Iron and Copper Concentrations in Selected Particulate

Fly ash sources		**Fe (%)**	**Cu (%)**	**Fe/Cu Ratio**	**Ref**
Municipal Solid Waste Incinerators	ESP ash from a stoker-type MSW incinerator	1.0	0.10	10:1	[157]
	ESP ash from incinerator burning MSW	1.2	0.08	16:1	[155]
	Baghouse ash from fluidized-bed MSW incinerator	0.8	0.46	2:1	
	ESP ash from incinerator burning agricultural waste	0.5	0.08	6:1	
Hazardous Waste Incinerators	Ash from rotary kiln burning hazardous waste	1.2	0.23	5:1	[26]
Industrial Boilers and Furnaces	Ash of raw fuels - power poles.	5.1	0.16	31:1	[27]

Table 1.4 Con'd

Co-fired Cement Kilns	Fly ashes from hazardous wastes in cement kilns	0.004	0.00082	49:1	[158]
Airborne particulate matter	World Trade Center (WTC PM.)	5.5	0.20	30:1	[159]
	Urban dust collected in Washington DC.	5.1	0.17	30:1	
Coal Combustion	Ohio blend coal	13	N.A.	-	[156]
	Pittsburg seam coal	19	N.A.	-	
	Wyodak PRB coal.	6	N.A.	-	
	Beulah coal	11	N.A.	-	[160]

N.A - not analyzed

On the basis of the fact that iron is a very effective oxidizing agent, research on the role of iron has most likely focused on destruction rather than formation of PCDD/F[70, 161]. Various formulations of iron have been used to destroy PCDD/Fs and their precursors such as chlorophenols at high temperatures above 400 ^{o}C [162]. Nevertheless, limited studies have been published that have shown presence iron (III) chlorides to promote formation PCDD/F and produced PCDD to PCDF ratios of <<1 in accord with full scale conditions [65, 163]. It is likely that the varying results are due to the ability of iron oxides to act as strong oxidizing agents at elevated temperatures or long residence times while promoting the formation of dioxins at lower temperatures and shorter reaction times.

In summary, the primary goal of the work presented in this dissertation is to develop a better understanding of the mechanistic details involved in the formation PCDD/Fs through the surface catalyzed pathway that synthesizes these pollutants produced mostly from thermal and combustion processes. A comparative approach is adopted not only in examining the role of the precursors 1,2-dichlorobenzene and 2-monochlorophenol that are chosen as representative reactants for chlorobenzenes and chlorophenols respectively, but also the catalytic roles of copper and iron in promoting PCDD/Fs formation in the low temperature post combustion zone.

1.7 References

1. Wagner, H.C.; Schramm, K.W.; Hutzinger, O. Biogenic polychlorinated dioxin and furan from trichlorophenol. *Organohalogen Compd.***1990,** *3,* (1026-4892), 453-456.

2. Fiedler, H. Formation and sources of PCDD/PCDF. *Organohalogen Compd.***1993,** *11,* (1026-4892), 221-228.

3. Database of sources of environmental releases of dioxin-like compounds in the United States. In *U.S Environmental Protection Agency,* 2001; Vol. EPA/600/C-01/012.

4. Fiedler, H. National PCDD/PCDF release inventories under the Stockholm convention on persistent organic pollutants. *Chemosphere* **2007,** *67,* (9), S96-S108.

5. Mackay, D., Shiu, W.Y., Ma, K.C. Illustrated handbook of physical–chemical properties and environmental fate for organic chemical, vol. II. polynuclear aromatic hydrocarbons, polychlorinated dioxins, and dibenzofurans. *Lewis Publishers, CRC Press, Boca Raton* **1992,** *II.*

6. Choi, W.; Hong, S. J.; Chang, Y. S.; Cho, Y. Photocatalytic degradation of polychlorinated dibenzo-p-dioxins on TiO2 film under UV or solar light irradiation. *Environ. Sci. Technol.* **2000,** *34,* (22), 4810-4815.

7. Pelizzetti, E.; Minero, C.; Carlin, V.; Borgarello, E. Photocatalytic soil decontamination. *Chemosphere* **1992,** *25,* (3), 343-351.

8. Kearney, P.C.; Woolson, E. A.; Ellingto.C.P. Persistence and metabolism of chlorodioxins in soils. *Environ. Sci. Technol.* **1972,** *6,* (12), 1017-&.

9. Friesen, K.J.; Foga, M. M.; Loewen, M. D. Aquatic photodegradation of polychlorinated dibenzofurans: Rates and photoproduct analysis. *Environ. Sci. Technol.* **1996,** *30,* (8), 2504-2510.

10. Fernandez, P.; Grimalt, J. O. On the global distribution of persistent organic pollutants. *Chimia* **2003,** *57,* (9), 514-521.

11. Simonich, S.L.; Hites, R. A. Global distribution of persistent organochlorine compounds. *Science* **1995,** *269,* (5232), 1851-1854.

12. Ho, A. K.W.; Clement, R. E. Chlorinated dioxins furans in sewage and sludge of municipal water-pollution control plants. *Chemosphere* **1990,** *20,* (10-12), 1549-1552.

13. Orazio, C.E.; Kapila, S.; Puri, R. K.; Yanders, A. F. Persistence of chlorinated dioxins and furans in the soil environment. *Chemosphere* **1992,** *25,* (7-10), 1469-1474.

14. Kaupp, H.; Blumenstock, M.; McLachlan, M. S. Retention and mobility of atmospheric particle-associated organic pollutant PCDD/Fs and PAHs in maize leaves. *New Phytol.* **2000,** *148*, (3), 473-480.

15. Kurokawa, Y.O.; O; Tobiishi, K; Soh, N; Imato, Toshihiko. , Deposition of atmospheric dioxins to the surrogate surfaces to elucidate the uptake pathway by plant leaves and the application of a surrogate surface to long term monitoring. *Organohalogen Compd.***2003,** *61*, 490-493.

16. Fiedler, H.; Cooper, K.; Bergek, S.; Hjelt, M.; Rappe, C.; Bonner, M.; Howell, F.; Willett, K.; Safe, S. PCDD, PCDF, and PCB in farm-raised catfish from southeast United States - Concentrations, sources, and CYP1A induction. *Chemosphere* **1998,** *37*, (9-12), 1645-1656.

17. Brzuzy, L. P.; Hites, R. A. Global mass balance for polychlorinated dibenzo-p-dioxins and dibenzofurans - Response. *Environ. Sci. Technol.* **1996,** *30*, (12), 3647-3648.

18. Thomas, V.M.; Spiro, T. G. The US dioxin inventory: Are there missing sources? *Environ. Sci. Technol.* **1996,** *30*, (2), A82-A85.

19. Fiedler, H. Thermal formation of PCDD/PCDF: A survey. *Environ. Eng. Sci.* **1998,** *15*, (1), 49-58.

20. Huang, H.; Buekens, A. On the mechanisms of dioxin formation in combustion processes. *Chemosphere* **1995,** *31*, (9), 4099-4117.

21. Altwicker, E. R.; Schonberg, J. S.; Konduri, R. K. N. V.; Milligan, M. S. Polychlorinated dioxin furan formation in incinerators. *Hazard. Waste Hazard. Mater***1990,** *7*, (1), 73-87.

22. Giugliano, M.; Cernuschi, S.; Grosso, M.; Aloigi, E.; Miglio, R. The flux and mass balance of PCDD/F in a MSW incineration full scale plant. *Chemosphere* **2001,** *43*, (4-7), 743-750.

23. Altwicker, E.R. Formation of PCDD/F in municipal solid waste incinerators: Laboratory and modeling studies. *J. Hazard. Mater.***1996,** *47*, (1-3), 137-161.

24. Abad, E.; Martinez, K.; Caixach, J.; Rivera, J. Polychlorinated dibenzo-p-dioxin/polychlorinated dibenzofuran releases into the atmosphere from the use of secondary fuels in cement kilns during clinker formation. *Environ. Sci. Technol.* **2004,** *38*, (18), 4734-4738.

25. Karstensen, K.H. Formation, release and control of dioxins in cement kilns. *Chemosphere* **2008,** *70*, (4), 543-560.

26. Addink, R.; Altwicker, E.R. Formation of polychlorinated dibenzo-p-dioxins and dibenzofurans on secondary combustor/boiler ash from a rotary kiln burning hazardous waste. *J. Hazard. Mater.***2004,** *114*, (1-3), 53-58.

27. Skodras, G.; Grammelis, P.; Samaras, P.; Vourliotis, P.; Kakaras, E.; Sakellaropoulos, G. P. Emissions monitoring during coal waste wood co-combustion in an industrial steam boiler. *Fuel* **2002,** *81*, (5), 547-554.

28. Gullett, B. K.; Touati, A.; Lee, C. W. Formation of chlorinated dioxins and furans in a hazardous-waste-firing industrial boiler. *Environ. Sci. Technol.* **2000,** *34*, (11), 2069-2074.

29. Lindner, G.; Jenkins, A. C.; Mccormack, J.; Adrian, R. C. Dioxins and furans in emissions from medical Waste Incinerators. *Chemosphere* **1990,** *20*, (10-12), 1793-1800.

30. Lemieux, P. M.; Lutes, C. C.; Abbott, J. A.; Aldous, K. M. Emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from the open burning of household waste in barrels. *Environ. Sci. Technol.* **2000,** *34*, (3), 377-384.

31. Gullett, B. K.; Touati, A. PCDD/F emissions from forest fire simulations. *Atmos. Environ.* **2003,** *37*, (6), 803-813.

32. Rappe, C.; Andersson, R.; Bonner, M.; Cooper, K.; Fiedler, H.; Howell, F. PCDDs and PCDFs in municipal sewage sludge and effluent from POTW in the State of Mississippi, USA. *Chemosphere* **1998,** *36*, (2), 315-328.

33. *The Inventory of Sources and Environmental Releases of Dioxin-like Compounds in the United State; Report*; EPA/600/p-03/002A; U.S Environmental Protection Agency: Washington DC, **2000.**

34. Olie, K. V., P. L.; Hutzinger, O. Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands. *Chemosphere* **1977,** *6*, (8), 455-9.

35. Buekens, A.; Stieglitz, L.; Hell, K.; Huang, H.; Segers, P. Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry. *Chemosphere* **2001,** *42*, (5-7), 729-735.

36. Wang, T. S.; Anderson, D. R.; Thompson, D.; Clench, M.; Fisher, R. Studies into the formation of dioxins in the sintering process used in the iron and steel industry. 1. Characterisation of isomer profiles in particulate and gaseous emissions. *Chemosphere* **2003,** *51*, (7), 585-594.

37. Kjeller, L. O.; Rappe, C. Time trends in levels, patterns, and profiles for polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls in a sediment core from the baltic proper. *Environ. Sci. Technol.* **1995,** *29*, (2), 346-355.

38. Minh, N. H.; Minh, T. B.; Watanabe, M.; Kunisue, T.; Monirith, I.; Tanabe, S.; Sakai, S.; Subramanian, A.; Sasikumar, K.; Viet, P. H.; Tuyen, B. C.; Tana, T. S.; Prudente, M. S. Open dumping site in Asian developing countries: A potential source of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* **2003,** *37*, (8), 1493-1502.

39. Dyke, P. H.; Amendola, G. Dioxin releases from US chemical industry sites manufacturing or using chlorine. *Chemosphere* **2007,** *67*, (9), S125-S134.

40. Schecter, A.; Cramer, P.; Boggess, K.; Stanley, J.; Papke, O.; Olson, J.; Silver, A.; Schmitz, M., Intake of dioxins and related compounds from food in the US population. *J. Toxicol. Environ. Health, Part A.* **2001,** *63*, (1), 1-18.

41. Kakeyama, M.; Tohyama, C. Developmental neurotoxicity of dioxin and its related compounds. *Ind. Health.***2003,** *41*, (3), 215-230.

42. Peterson, R. E.; Theobald, H. M.; Kimmel, G. L. Developmental and reproductive toxicity of dioxins and related-compounds - cross-species comparisons. *Crit. Rev. Toxicol.***1993,** *23*, (3), 283-335.

43. Rordorf, B. F. Prediction of vapor-pressures, boiling points and enthalpies of fusion for 29 halogenated dibenzo-p-dioxins and 55 dibenzofurans by a vapor-pressure correlation method. *Chemosphere* **1989,** *18*, (1-6), 783-788.

44. Popp, J. A.; Crouch, E.; McConnell, E. E. A weight-of-evidence analysis of the cancer dose-response characteristics of 2,3,7,8-tetrachlorodibenzodioxin (TCDD). *Toxicol. Sci.***2006,** *89*, (2), 361-369.

45. Smith, A. H.; Warner, M. L. Biologically measured human exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin and human cancer. *Chemosphere* **1992,** *25*, (1-2), 219-222.

46. Froese, K. L.; Hutzinger, O. Mechanisms of the formation of polychlorinated benzenes and phenols by heterogeneous reactions of C-2 aliphatics. *Environ. Sci. Technol.* **1997,** *31*, (2), 542-547.

47. Taylor, P. H.; Dellinger, B. Pyrolysis and molecular growth of chlorinated hydrocarbons. *J. Anal. Appl. Pyrolysis.* **1999,** *49*, (1-2), 9-29.

48. Altarawneh, M.; Carrizo, D.; Ziolkowski, A.; Kennedy, E. M.; Dlugogorski, B. Z.; Mackie, J. C. Pyrolysis of permethrin and formation of precursors of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) under non-oxidative conditions. *Chemosphere* **2009,** *74*, (11), 1435-1443.

49. Altarawneh, M.; Dlugogorski, B. Z.; Kennedy, E. M.; Mackie, J. C. Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). *Prog. Energy Combust. Sci.* **2009,** *35*, (3), 245-274.

50. Evans, C. S.; Dellinger, B. Mechanisms of dioxin formation from the high-temperature pyrolysis of 2-chlorophenol. *Environ. Sci. Technol.* **2003,** *37*, (7), 1325-1330.

51. Evans, C. S.; Dellinger, B. Mechanisms of dioxin formation from the high-temperature oxidation of 2-chlorophenol. *Environ. Sci. Technol.* **2005,** *39*, (1), 122-127.

52. Louw, R.; Ahonkhai, S. I. Radical/radical vs radical/molecule reactions in the formation of PCDD/Fs from (chloro)phenols in incinerators. *Chemosphere* **2002,** *46*, (9-10), 1273-1278.

53. Sommeling, P. M., Mulder P., Louw, R. Formation of PCDFs during chlorination and oxidation of chlorobenzenes in chlorine/oxygen mixtures around 340^{o}C. *Chemosphere* **1994,** *29*, 2015-2018.

54. Sommeling, P. M.; Mulder, P.; Louw, R.; Avila, D. V.; Lusztyk, J.; Ingold, K. U. Rate of reaction of phenyl radicals with oxygen in solution and in the gas-phase. *J. Phys. Chem.* **1993,** *97*, (32), 8361-8364.

55. Altarawneh M, D. B., Kennedy EM, Mackie J.C. Mechanisms of PCDFs and PCBs formation from fires: pathways from oxidation of chlorobenzenes. *Seventh Asia-Oceania Symposium on Fire Science and Technology* **2007**.

56. Stieglitz, L.; Zwick, G.; Beck, J.; Roth, W.; Vogg, H. On the de-novo synthesis of PCDD/PCDF on fly-ash of municipal waste incinerators. *Chemosphere* **1989,** *18*, (1-6), 1219-1226.

57. Stieglitz, L. Selected topics on the de novo synthesis of PCDD/PCDF on fly ash. *Environ. Eng. Sci.* **1998,** *15*, (1), 5-18.

58. Stieglitz, L., Vogg, H., Zwick, G., Beck, J., Bautz, H. On formation conditions of Organohalogen Compd.from particulate carbon on fly ash. *Chemosphere* **1991,** *23*, 1255-1264.

59. Altwicker, E. R., Xun, Y., Milligan, M.S. Dioxin formation over fly ash: oxygen dependence, temperature dependence and phase distribution. *Organohalogen Compd.***1994,** *20*, 381-384.

60. Addink, R.; Bakker, W. C. M.; Olie, K. Influence of HCl and Cl-2 on the formation of polychlorinated dibenzo-p-dioxins/dibenzofurans in a carbon/fly ash mixture. *Environ. Sci. Technol.* **1995,** *29*, (8), 2055-2058.

61. Wikstrom, E.; Ryan, S.; Touati, A.; Telfer, M.; Tabor, D.; Gullett, B. K. Importance of chlorine speciation on de novo formation of polychlorinated dihenzo-p-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* **2003,** *37*, (6), 1108-1113.

62. Wikstrom, E.; Ryan, S.; Touati, A.; Gullett, B. K. Key parameters for de novo formation of polychlorinated dibenzo-p-dioxins and dibenzofurans. *Environ. Sci. Technol.* **2003,** *37*, (9), 1962-1970.

63. Weber, P.; Dinjus, E.; Stieglitz, L. The role of copper(II) chloride in the formation of organic chlorine in fly ash. *Chemosphere* **2001,** *42*, (5-7), 579-582.

64. Stieglitz, L.; Zwick, G.; Beck, J.; Bautz, H.; Roth, W. Carbonaceous particles in fly-ash - a source for the de-novo-synthesis of organochlorocompounds. *Chemosphere* **1989,** *19,* (1-6), 283-290.

65. Ryan, S. P.; Altwicker, E. R. Understanding the role of iron chlorides in the de novo synthesis of polychlorinated dibenzo-p-dioxins/dibenzofurans. *Environ. Sci. Technol.* **2004,** *38*, (6), 1708-1717.

66. Kyotani, T.; Yamada, H.; Yamashita, H.; Tomita, A.; Radovic, L. R. Use of transient kinetics and temperature-programmed desorption to predict carbon char reactivity - the case of Cu-catalyzed gasification of coal char in oxygen. *Energy Fuels* **1992,** *6,* (6), 865-867

67. Mckee, D. W. The catalyzed gasification reactions of carbon. *Chem. Phys. Carbon.* **1981,** *16*, 1-118.

68. Stieglitz, L.; Eichberger, M.; Schleihauf, J.; Beck, J.; Zwick, G.; Will, R. The oxidative-degradation of carbon and its role in the de-novo-synthesis of Organohalogen Compd.in fly-ash. *Chemosphere* **1993,** *27*, (1-3), 343-350.

69. Milligan, M. S.; Altwicker, E. The relationship between de-novo synthesis of polychlorinated dibenzo-p-dioxins and dibenzofurans and low-temperature carbon gasification in fly-ash. *Environ. Sci. Technol.* **1993,** *27*, (8), 1595-1601.

70. Addink, R.; Olie, K. Mechanisms of formation and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans in heterogeneous systems. *Environ. Sci. Technol.* **1995,** *29*, (6), 1425-1435.

71. Tobias, H.; Soffer, A. Chemisorption of halogen on carbon .2. thermal reversibility of Cl-2, HCl and H-2 chemisorption. *Carbon* **1985,** *23*, (3), 291-299.

72. Mckee, D. W.; Spiro, C. L. The effects of chlorine pretreatment on the reactivity of graphite in air. *Carbon* **1985,** *23*, (4), 437-444.

73. Olie, K.; Addink, R.; Schoonenboom, M. Metals as catalysts during the formation and decomposition of chlorinated dioxins and furans in incineration processes. *J. Air Waste Manage. Assoc.* **1998,** *48*, (2), 101-105.

74. Huang, H.; Buekens, A. De novo synthesis of polychlorinated dibenzo-p-dioxins and dibenzofurans - Proposal of a mechanistic scheme. *Sci. Total Environ.* **1996,** *193*, (2), 121-141.

75. Dickson, L. C.; Lenoir, D.; Hutzinger, O. Surface-catalyzed formation of chlorinated dibenzodioxins and dibenzofurans during Incineration. *Chemosphere* **1989,** *19*, (1-6), 277-282.

76. Gullett, B. K.; Bruce, K. R.; Beach, L. O. The effect of metal-catalysts on the formation of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran precursors. *Chemosphere* **1990,** *20*, (10-12), 1945-1952.

77. Dickson, L. C.; Lenoir, D.; Hutzinger, O.; Naikwadi, K. P.; Karasek, F. W. Inhibition of chlorinated dibenzo-p-dioxin formation on municipal incinerator fly-ash by using catalyst inhibitors. *Chemosphere* **1989,** *19*, (8-9), 1435-1445.

78. Alderman, S. L.; Dellinger, B. FTIR investigation of 2-chlorophenol chemisorption on a silica surface from 200 to 500 degrees C. *J. Phys. Chem. A* **2005,** *109*, (34), 7725-7731.

79. Alderman, S. L.; Farquar, G. R.; Poliakoff, E. D.; Dellinger, B. An infrared and X-ray spectroscopic study of the reactions of 2-chlorophenol, 1,2-dichlorobenzene, and chlorobenzene with model CuO/silica fly ash surfaces. *Environ. Sci. Technol.* **2005,** *39*, (19), 7396-7401.

80. Lomnicki, S.; Truong, H.; Vejerano, E.; Dellinger, B., Copper oxide-based model of persistent free radical formation on combustion-derived particulate matter. *Environ. Sci. Technol.* **2008,** *42*, (13), 4982-4988.

81. Lippert, T.; Wokaun, A.; Lenoir, D. Surface-reactions of brominated arenes as a model for the formation of chlorinated dibenzodioxins and dibenzofurans in incineration - inhibition by ethanolamine. *Environ. Sci. Technol.* **1991,** *25*, (8), 1485-1489.

82. Lomnicki, S.; Dellinger, B. A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on a CuO/silica surface. *J. Phys. Chem. A* **2003,** *107*, (22), 4387-4395.

83. Lomnicki, S.; Dellinger, B. Formation of PCDD/F from 2-chlorophenol catalyzed by CuO in combustion exhaust, **2003,** pp 141-ENVR.

84. Ballschmiter, K.; Braunmiller, I.; Niemczyk, R.; Swerev, M. Reaction pathways for the formation of polychloro-dibenzodioxins (PCDD) and polychloro-dibenzofurans (PCDF) in combustion processes. 2. Chlorobenzenes and chlorophenols as precursors in the formation of polychloro-dibenzodioxins and polychloro-dibenzofurans in flame chemistry. *Chemosphere* **1988,** *17*, (5), 995-1005.

85. Altwicker, E. R.; Milligan, M. S. Formation of dioxins - competing rates between chemically similar precursors and de-novo reactions. *Chemosphere* **1993,** *27*, (1-3), 301-307.

86. Karasek, F. W.; Dickson, L. C. Model studies of polychlorinated dibenzo-p-dioxin formation during municipal refuse incineration. *Science* **1987,** *237*, (4816), 754-756.

87. Dickson, L. C.; Lenoir, D.; Hutzinger, O. Quantitative comparison of de novo and precursor formation of polychlorinated dibenzo-p-dioxins under simulated municipal solid-waste incinerator postcombustion conditions. *Environ. Sci. Technol.* **1992,** *26*, (9), 1822-1828.

88. Addink, R.; Cnubben, P. A. J. P.; Olie, K. Formation of polychlorinated dibenzo-p-dioxins dibenzofurans on fly-ash from precursors and carbon model compounds. *Carbon* **1995,** *33*, (10), 1463-1471.

89. Milligan, M. S.; Altwicker, E. R. Chlorophenol reactions on fly ash .1. Adsorption desorption equilibria and conversion to polychlorinated dibenzo-p-dioxins. *Environ. Sci. Technol.* **1996,** *30*, (1), 225-229.

90. Blumenstock, M.; Zimmermann, R.; Schramm, K. W.; Kaune, A.; Nikolai, U.; Lenoir, D.; Kettrup, A. Estimation of the dioxin emission (PCDD/FI-TEQ) from the concentration of low chlorinated aromatic compounds in the flue and stack gas of a hazardous waste incinerator. *J. Anal. Appl. Pyrolysis.* **1999,** *49*, (1-2), 179-190.

91. Kaune, A.; Lenoir, D.; Schramm, K. W.; Zimmermann, R.; Kettrup, A.; Jaeger, K.; Ruckel, H. G.; Frank, F. Chlorobenzenes and chlorophenols as indicator parameters for chlorinated dibenzodioxins and dibenzofurans in incineration processes: Influences of various facilities and sampling points. *Environ. Eng. Sci.* **1998,** *15*, (1), 85-95.

92. Zimmermann, R.; Blumenstock, M.; Heger, H. J.; Schramm, K. W.; Kettrup, A. Emission of nonchlorinated and chlorinated aromatics in the flue gas of incineration plants during and after transient disturbances of combustion conditions: Delayed emission effects. *Environ. Sci. Technol.* **2001,** *35*, (6), 1019-1030.

93. Froese, K. L.; Hutzinger, O. Polychlorinated benzene and polychlorinated phenol in heterogeneous combustion reactions of ethylene and ethane. *Environ. Sci. Technol.* **1996,** *30*, (3), 1009-1013.

94. Shin, K. J.; Chang, Y. S. Characterization of polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls, and heavy metals in fly ash produced from Korean municipal solid waste incinerators. *Chemosphere* **1999,** *38*, (11), 2655-2666.

95. Born, J. G. P.; Louw, R.; Mulder, P. Formation of dibenzodioxins and dibenzofurans in homogeneous gas-phase reactions of phenols. *Chemosphere* **1989,** *19*, (1-6), 401-406.

96. Weber, R.; Hagenmaier, H. Mechanism of the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans from chlorophenols in gas phase reactions. *Chemosphere* **1999,** *38*, (3), 529-549.

97. Wiater-Protas, I.; Louw, R. Gas-phase chemistry of chlorinated phenols - formation of dibenzofurans and dibenzodioxins in slow combustion. *Eur. J. Org. Chem.* **2001**, (20), 3945-3952.

98. Yang, Y. Mulholland, J. A.; Akki, U. Formation of furans by gas-phase reactions of chlorophenols. *Symp. (Int.) Combust., [Proc.]***1998,** *Vol. 2*, (27th), 1761-1768.

99. Mulholland, J. A.; Akki, U.; Yang, Y.; Ryu, J. Y. Temperature dependence of DCDD/F isomer distributions from chlorophenol precursors. *Chemosphere* **2001,** *42*, (5-7), 719-727.

100. Briois, C.; Visez, N.; Baillet, C.; Sawerysyn, J. P. Experimental study on the thermal oxidation of 2-chlorophenol in air over the temperature range 450-900 degrees C. *Chemosphere* **2006,** *62*, (11), 1806-1816.

101. Sidhu, S. S.; Maqsud, L.; Dellinger, B.; Mascolo, G. The Homogeneous, gas-phase formation of chlorinated and brominated dibenzo-p-dioxin from 2,4,6-trichlorophenols and 2,4,6-tribromophenols. *Combust. Flame.* **1995,** *100*, (1-2), 11-20.

102. Fadli, A.; Briois, C.; Baillet, C.; Sawerysyn, J. P. Experimental study on the thermal oxidation of chlorobenzene at 575-825 degrees C. *Chemosphere* **1999,** *38*, (12), 2835-2848.

103. Rouzet, G.; Schwartz, D.; Gadiou, R.; Delfosse, L. The formation of chlorinated aromatic hydrocarbons during high temperature pyrolysis of chlorobenzene. *J. Anal. Appl. Pyrolysis.* **2001,** *57*, (2), 153-168.

104. Liu, P.-Y.; Zheng, M.-H.; Zhang, B.; Xu, X.-B. Mechanism of PCBs formation from the pyrolysis of chlorobenzenes. *Chemosphere* **2001,** *43*, (4-7), 783-5.

105. Buser, H. R., Formation of Polychlorinated Dibenzofurans (Pcdfs) and Dibenzo-Para-Dioxins (Pcdds) from the Pyrolysis of Chlorobenzenes. *Chemosphere* **1979,** *8*, (6), 415-424.

106. Dorrepaal, W.; Louw, R. Mechanism of vapor-phase chlorination of benzene-derivatives. *Int. J. Chem. Kinet.* **1978,** *10*, (3), 249-275.

107. Ritter, E. R. B., Joseph W. Production of chloro and dichlorobiphenyls, terphenyls, and triphenylenes from pyrolysis of chloro and dichloro-benzenes. *Organohalogen Compd.* **1990,** *3*, (Combust., Pulp Pap., Chlorine PVC, Soil Workshop, Rem. Action Destr., Gen. Top), 139-42.

108. Bleise, A. D., G.; Schlimper, H.; Gunther, K.; Schwuger, M. J. Polychlorinated biphenylenes (PCBN) from pyrolysis of chlorobenzenes. Identification and mechanism of formation. *Toxicol. Environ. Chem.* **1997,** *60*, (1-4), 87-95.

109. Froese, K. L.; Hutzinger, O. Polychlorinated benzene, phenol, dibenzo-p-dioxin, and dibenzofuran in heterogeneous combustion reactions of acetylene. *Environ. Sci. Technol.* **1996,** *30*, (3), 998-1008.

110. Taylor, P. H. Sidhu., S. S.; Rubey, W. A.; Dellinger, B.; Wehrmeier, A.; Lenoir, D.; Schramm, K. W. Evidence for a unified pathway of dioxin formation from aliphatic hydrocarbons. *Symp. (Int.) Combust., [Proc.]***1998,** *2*, (27), 1769-1775.

111. Ghorishi, S. B.; Altwicker, E. R. Rapid high temperature formation of polychlorinated dioxins and furans in the bed region of a heterogeneous spouted bed combustor: Development of a surface mediated model for the formation of dioxins. *Hazard. Waste Hazard. Mater***1996,** *13*, (1), 11-22.

112. Shaub, W. M.; Tsang, W. Dioxin Formation in incinerators. *Environ. Sci. Technol.* **1983,** *17*, (12), 721-730.

113. Khachatryan, L.; Asatryan, R.; Dellinger, B. Development of expanded and core kinetic models for the gas phase formation of dioxins from chlorinated phenols. *Chemosphere* **2003,** *52*, (4), 695-708.

114. Altwicker, E. R. Some laboratory experimental-designs for obtaining dynamic property data on dioxins. *Sci. Total Environ.* **1991,** *104*, (1-2), 47-72.

115. Altwicker, E. Ghorishi, B. Rapid formation of PCDD/F in the heterogeneous combustion of 1,2-dichlorobenzene and the role of particles. *Organohalogen Compd.***1994,** *20*, ((Dioxin '94)), 293-7.

116. Nestrick, T. J. Lamparski, L. L.; Crummett, W. B. Thermolytic surface-reaction of benzene and iron(III) chloride to form chlorinated dibenzo-p-dioxins and dibenzofurans. *Chemosphere* **1987,** *16*, (4), 777-90.

117. Ryu, J.-Y. Formation of chlorinated phenols, dibenzo-p-dioxins, dibenzofurans, benzenes, benzoquinones and perchloroethylenes from phenols in oxidative and copper(II) chloride-catalyzed thermal process. *Chemosphere* **2008,** *71*, (6), 1100-1109.

118. Born, J. G. P.; Mulder, P.; Louw, R. Fly-ash mediated reactions of phenol and monochlorophenols - oxychlorination, deep oxidation, and condensation. *Environ. Sci. Technol.* **1993,** *27*, (9), 1849-1863.

119. Lomnicki, S.; Dellinger, B. Formation of PCDD/F from the pyrolysis of 2-chlorophenol on the surface of dispersed copper oxide particles. *Proc. Combust. Inst.* **2003,** *29*, 2463-2468.

120. Nganai, S.; Lomnicki, S.; Dellinger, B. Ferric oxide mediated formation of PCDD/Fs from 2-monochlorophenol. *Environ. Sci. Technol.* **2009,** *43*, (2), 368-373.

121. Nicolas, V.; Jean-Pierre, S. Thermal degradation of 2-chlorophenol promoted by CuCl2 or CuCl: Formation and destruction of PCDD/Fs. *Chemosphere* **2007,** *67*, (9), S144-S149.

122. Mulholland, J. A.; Ryu, J-Y. Formation of polychlorinated dibenzo-p-dioxins by CuCl2-catalyzed condensation of 2,6 chlorinated phenols. *Combust. Sci. Technol.* **2001,** *169* (1), 107-126.

123. Qian, Y.; Zheng, M. H.; Liu, W. B.; Ma, X. D.; Zhang, B. Influence of metal oxides on PCDD/Fs formation from pentachlorophenol. *Chemosphere* **2005,** *60*, (7), 951-958.

124. Hatanaka, T.; Imagawa, T.; Takeuchi, A. Effects of copper chloride on formation of polychlorinated dibenzo-p-dioxins in model waste incineration. *Chemosphere* **2003,** *51*, (10), 1041-1046.

125. Stieglitz, L.; Vogg, H.; Zwick, G.; Beck, J.; Bautz, H. On formation conditions of Organohalogen Compd.from particulate carbon of fly-ash. *Chemosphere* **1991,** *23*, (8-10), 1255-1264.

126. Addink, R.; Drijver, D. J.; Olie, K. Formation of polychlorinated dibenzo-p-dioxins dibenzofurans in the carbon fly-ash system. *Chemosphere* **1991,** *23*, (8-10), 1205-1211.

127. Hell, K.; Stieglitz, L.; Dinjus, E. Mechanistic aspects of the de-novo synthesis of PCDD/PCDF on model mixtures and MSWI fly ashes using amorphous C-12- and C-13-labeled carbon. *Environ. Sci. Technol.* **2001,** *35*, (19), 3892-3898.

128. Ryu, J.-Y; Mulholland, J.A. Metal-mediated chlorinated dibenzo-p-dioxin (CDD) and dibenzofuran (CDF) formation from phenols. . *Chemosphere* **2005,** *58*, (7), 977-988

129. Nakka, H. Fullana, A.; Sidhu, S, Surface catalyzed chlorobenzene transformation reactions in post-combustion zone. *Organohalogen Compd.***2004,** *66* (Dioxin 2004), 1124-1129.

130. Kasai, E. K., T.; Nakamura, T.; Shibata, E. PCDD/Fs formation from mono-chlorobenzene on some metallic oxides. *Organohalogen Compd..* **2000,** *46*, 142-145.

131. Kasai, E. K., T; Nakamura, T. Formation of PCDD/Fs on iron oxides from chlorobenzene and chlorophenol. *Organohalogen Compd.***1999,** *41* 187-190.

132. Ghorishi, S. B.; Altwicker, E. R. Rapid formation of polychlorinated dioxins/furans during the heterogeneous combustion of 1,2-dichlorobenzene and 2,4-dichlorophenol. *Chemosphere* **1996,** *32*, (1), 133-144.

133. Ghorishi, S. B.; Altwicker, E. R. Formation of polychlorinated dioxins, furans, benzenes and phenols in the postcombustion region of a heterogeneous combustor -effect of bed material and postcombustion temperature. *Environ. Sci. Technol.* **1995,** *29*, (5), 1156-1162.

134. Ismo, H.; Kari, T.; Juhani, R. Formation of aromatic chlorinated compounds catalyzed by copper and iron. *Chemosphere* **1997,** *34*, (12), 2649-2662.

135. Addink, R.; Altwicker, E. R. Formation of polychlorinated dibenzo-p-dioxins/dibenzofurans from soot of benzene and o-dichlorobenzene combustion. *Environ. Sci. Technol.* **2004,** *38*, (19), 5196-5200.

136. Ryu, J. Y.; Mulholland, J. A.; Kim, D. H.; Takeuchi, M. Homoloque and isomer patterns of polychlorinated dibenzo-p-dioxins and dihenzofurans from phenol precursors: Comparison with municipal waste incinerator data. *Environ. Sci. Technol.* **2005,** *39*, (12), 4398-4406.

137. Mariani, G.; Benfenati, E.; Fanelli, R. Concentrations of PCDD and PCDF in different points of a modern refuse incinerator. *Chemosphere* **1990,** *21*, (4-5), 507-517.

138. Everaert, K.; Baeyens, J. The formation and emission of dioxins in large scale thermal processes. *Chemosphere* **2002,** *46*, (3), 439-448.

139. Duwel, U.; Nottrodt, A.; Ballschmiter, K. Simultaneous sampling of PCDD/PCDF inside the combustion-chamber and on 4 boiler levels of a waste incineration plant. *Chemosphere* **1990,** *20*, (10-12), 1839-1846.

140.Oswego county energy recovery facility. Fulton city New york. *Radian Corporation* **1988**.

141. *The Use of Surrogate Compounds as Indicators of PCDD/F Concentrations in Combustor Stack Gases;* Report EPA-600/R-04-024; U.S Environmental Protection Agency: Washington DC, **2004.**

142. Blumenstock, M.; Zimmermann, R.; Schramm, K. W.; Kettrup, A. Identification of surrogate compounds for the emission of PCDD/F (I-TEQ value) and evaluation of their on-line realtime detectability in flue gases of waste incineration plants by REMPI-TOFMS mass spectrometry. *Chemosphere* **2001,** *42*, (5-7), 507-518.

143. Clement, R. E.; Tosine, H. M.; Osborne, J.; Ozvacic, V.; Wong, G. Gas-chromatographic mass-spectrometric determination of chlorinated dibenzo-p-dioxins and dibenzofurans in incinerator stack emissions and fly-ash - a 13-test study. *Biomed. Environ. Mass Spectrom.* **1988,** *17*, (2), 81-96.

144. Sakai, S. I.; Hayakawa, K.; Takatsuki, H.; Kawakami, I. Dioxin-like PCBs released from waste incineration and their deposition flux. *Environ. Sci. Technol.* **2001,** *35*, (18), 3601-3607.

145. Luijk, R.; Akkerman, D. M.; Slot, P.; Olie, K.; Kapteijn, F. Mechanism of formation of polychlorinated dibenzo-p-dioxins and dibenzofurans in the catalyzed combustion of carbon. *Environ. Sci. Technol.* **1994,** *28*, (2), 312-321.

146. Hagenmaier, H.; Kraft, M.; Brunner, H.; Haag, R. Catalytic effects of fly-ash from waste incineration facilities on the formation and decomposition of polychlorinated dibenzo-p-Dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* **1987,** *21,* (11), 1080-1084.

147. Hell, K.; Stieglitz, L.; Altwicker, E. R.; Addink, R.; Will, R. Reactions of 2,4,6-trichlorophenol on model fly ash: oxidation to CO and CO2, condensation to PCDD/F and conversion into related compounds. *Chemosphere* **2001,** *42*, (5-7), 697-702.

148. Altwicker, E. Milligan, M. S. Dioxin formation from tetrachlorophenol over fly ash under breakthrough conditions. *Organohalogen Compd.***1993,** *11*, (1026-4892), 269-72.

149. Wehrmeier, A.; Lenoir, D.; Sidhu, S. S.; Taylor, P. H.; Rubey, W. A.; Kettrup, A.; Dellinger, B. Role of copper species in chlorination and condensation reactions of acetylene. *Environ. Sci. Technol.* **1998,** *32*, (18), 2741-2748.

150. Stanmore, B. R. The formation of dioxins in combustion systems. *Combust. Flame* **2004,** *136*, (3), 398-427.

151. Pandelova, M.; Lenoir, D.; Schramm, K. W. Correlation between PCDD/F, PCB and PCBz in coal/waste combustion. Influence of various inhibitors. *Chemosphere* **2006,** *62*, (7), 1196-1205.

152. Addink, R.; Altwicker, E. R. Role of copper compounds in the de novo synthesis of polychlorinated dibenzo-p-dioxins/dibenzofurans. *Environ. Eng. Sci.* **1998,** *15*, (1), 19-27.

153. Hatanaka, T.; Imagawa, T.; Takeuchi, M. Effects of copper chloride on formation of polychlorinated dibenzofurans in model waste incineration in a laboratory-scale fluidized-bed reactor. *Chemosphere* **2002,** *46*, (3), 393-399.

154. Altwicker, E. R.; Konduri, R. K. N. V.; Milligan, M. S. The role of precursors in formation of polychlorodibenzo-p-dioxins and polychlorodibenzofurans during heterogeneous combustion. *Chemosphere* **1990,** *20*, (10-12), 1935-1944

155. Cains, P. W.; McCausland, L. J.; Fernandes, A. R.; Dyke, P. Polychlorinated dibenzo-p-dioxins and dibenzofurans formation in incineration: Effects of fly ash and carbon source. *Environ. Sci. Technol.* **1997,** *31*, (3), 776-785.

156. Seames, W. S. An initial study of the fine fragmentation fly ash particle mode generated during pulverized coal combustion. *Fuel Process. Technol.* **2003,** *81*, (2), 109-125.

157. Takasuga, T.; Makino, T.; Tsubota, K.; Takeda, N. Formation of dioxins (PCDDs/PCDFs) by dioxin-free fly ash as a catalyst and relation with several chlorine-sources. *Chemosphere* **2000,** *40*, (9-11), 1003-1007.

158. Kelly, K. E. Beahler, C.C. Burning hazardous wastes in cement kilns: A study of emissions, offsite concentrations, and health effects in Midlothian, Texas. *Environ. Toxicol. Int.* **1993**.

159. McGee, J. K.; Chen, L. C.; Cohen, M. D.; Chee, G. R.; Prophete, C. M.; Haykal-Coates, N.; Wasson, S. J.; Conner, T. L.; Costa, D. L.; Gavett, S. H. Chemical analysis of World Trade Center fine particulate matter for use in toxicologic assessment. *Environ. Health Perspect.* **2003,** *111*, (7), 972-980.

160. Zygarlicke, C. J.; Benson, S. A.; Toman, D. L. Trends in the evolution of fly-ash composition and size during combustion. *Abstr. Papers Am. Chem. Soc.***1990,** *200*, 621-636.

161. Weber, R.; Nagai, K.; Nishino, J.; Shiraishi, H.; Ishida, M.; Takasuga, T.; Konndo, K.; Hiraoka, M. Effects of selected metal oxides on the dechlorination and destruction of PCDD and PCDF. *Chemosphere* **2002,** *46*, (9-10), 1247-1253.

162. Lomnicki, S.; Dellinger, B. Development of supported iron oxide catalyst for destruction of PCDD/F. *Environ. Sci. Technol.* **2003,** *37*, (18), 4254-4260.

163. Ryan, S. P.; Altwicker, E.R. The formation of polychlorinated dibenzo-p-dioxins/dibenzofurans from carbon model mixtures containing ferrous chloride. *Chemosphere* **2000,** *40*, (9-11), 1009-1014.

CHAPTER 2: EXPERIMENTAL

2.1 System for Thermal Diagnostic Studies

A high-temperature, flow-reactor, analytical System of Thermal Diagnostic Studies (STDS), was used to investigate the thermal degradation of the reactants 1, 2–dichlorobenzene and 2-monochlorophenol in their pure and mixed composition under pyrolytic and oxidative conditions. Grant and Rubey have described in detail the design aspects of STDS, its considerable flexibility and versatility for conducting a wide range of thermal diagnostic investigation of organic materials[1]. STDS has been efficiently utilized in thermal analysis involving fast and intense reactions such as in combustion processes[2].

The system is composed of four basic components designed to operate as integrated functional unit. It consists of thermal reactor component served by multiple gas flow paths, conduits and electric connections. The thermal reactor compartment houses a centrally located high temperature furnace (Omega) within an Agilent 6890 gas chromatograph equipped with a control console for precise adjustment of pressure, respective gas flows and oven temperature to ensure uniform temperature throughout transfer paths thus preventing product condensation. The Omega furnace is specifically designed for extreme temperature up to 1200 ^{o}C and controlled by separate temperature controller.

The furnace configuration also allows access for installation of quartz reactors and thermocouples for effective sample introduction and to maintain a well-controlled temperature programmable experimental set up for thermal degradation. **Figure 2.1** shows the Omega furnace that houses the flow reactor inside thermal reactor compartment.

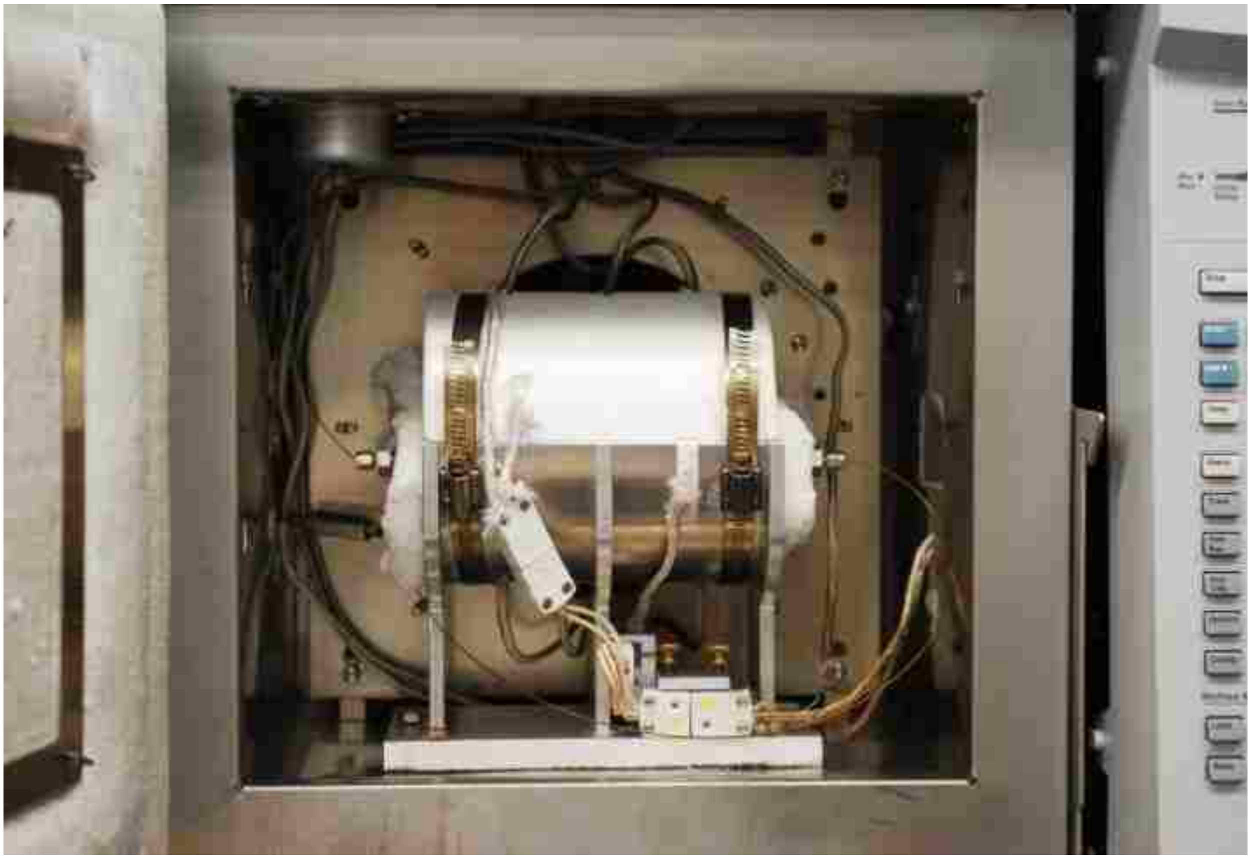


Figure 2.1 Omega Furnace that Houses the Flow Reactor inside the Thermal Reactor Compartment

Downstream the thermal reactor is an in-line gas chromatograph/mass spectrometer (GC/MS) compartment equipped with devices for cryogenic trapping, product separation and detection. Leading to and from the cryogenic trapping component are transfer lines designed to produce nonreactive quantitative transport of organic substances. Identification and quantification of effluent products is accomplished by comprehensive analysis of different reaction products using a mass spectrometer (Agilent 5973 MSD) to generate output chromatographic data for all the products formed. The diagram for System for Thermal Diagnostic Studies (STDS) is depicted in **Figure 2.2.**

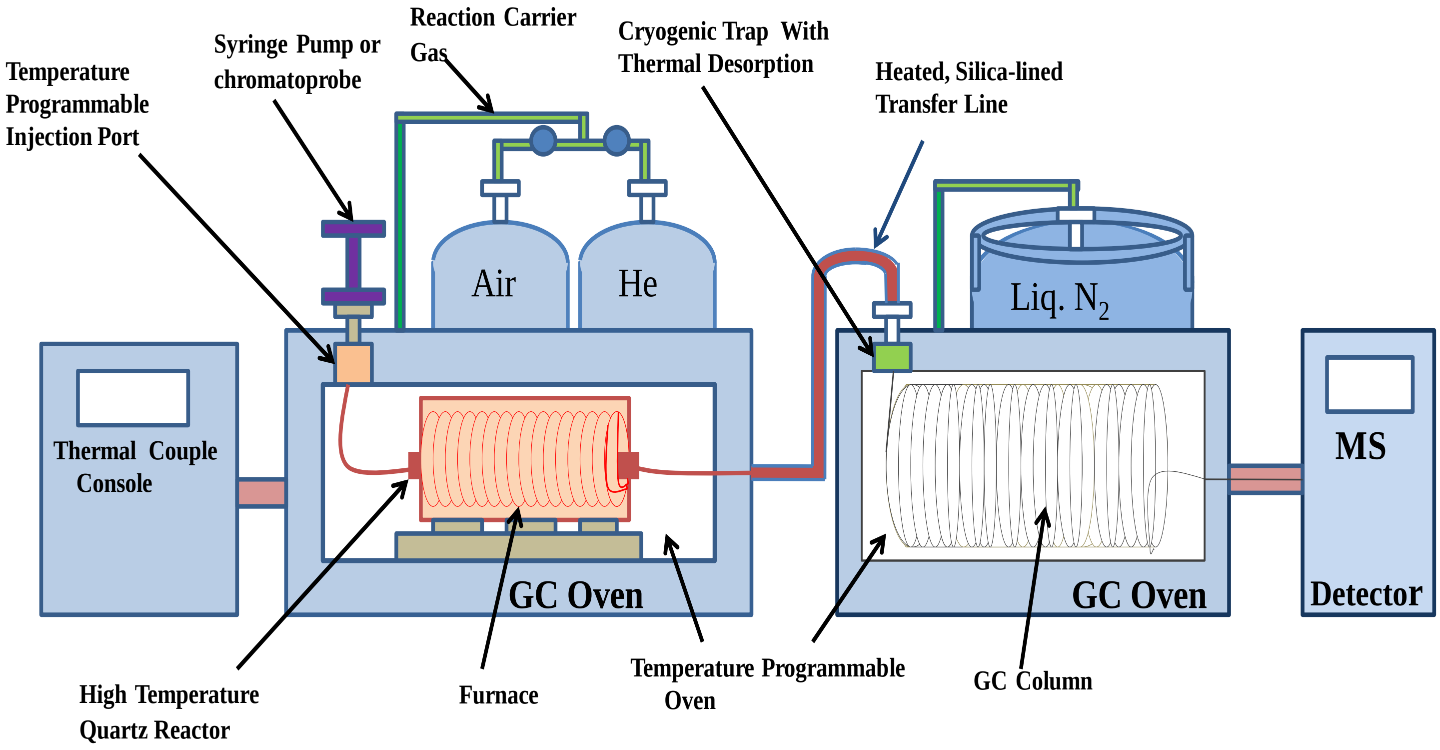


Figure 2.2 System for Thermal Diagnostic Studies

2.2 Experimental Set-up

Experimental set-up was designed so as to maintain a constant concentration of 50ppm for the reactant in gas phase and a contact time for the catalyst bed of 0.01 seconds. The contact time was calculated based on the main flow rate and other physiochemical variables using Equation 1 shown below.

$$\bar{t}_r = \left(\frac{T_o}{T_e}\right)\left(\frac{V_E}{F_o}\right)\left(1 + \frac{P_d}{P_o}\right)$$

(Equation 1)

Where, (seconds) is the mean residence time distribution for gas phase molecules passing through a flow reactor; T_o (Kelvin) is the ambient temperature; T_e is the average exposure temperature within the flow reactor; V_E (m^3) is effective volume of the flow reactor; F_o (m^3/s) is volumetric flow rate; P_o (atm) is ambient pressure; P_d (atm) is a positive differential pressure relative to P_o within the flow reactor.

In order to maintain consistency with previous studies on surface catalysis performed by other members of the group [3-5], a contact time of 0.01 seconds was chosen. Flow rate of 5cc/min was used and the injection rate was varied depending on temperature so as to maintain a gas phase concentration of 50ppm of the sample. **Table 2.1** shows the variation of sample injection rate with experimental temperature.

Table 2.1. Variation of Sample Injection Rates with Temperature

Temperature, ^{o}C	200	250	300	350	400	450	500	550
Injection Rate (µL/min)	0.72	0.58	0.48	0.41	0.36	0.32	0.29	0.26

2.3 Detailed Procedure

Prior to use each day, the STDS is cleaned and baked out using air at a flow rate of 40ml/min for an hour at a furnace temperature of 400^{o}C. The temperature of the oven is set at 400^{o}C whereas the transfer line is first disconnected from the GC/MS and heated at 400^{o}C. The bake out procedure for the GC column is done by setting a temperature of 300^{o}C and holding for an hour before lowering to 120^{o}C for an overnight duration.

Once the STDS has been cleaned and baked out, a blank test at a low temperature that only maintains the sample in gas phase without causing degradation is performed. This is an initial quantitative transport test that is done every morning to test for leaks and verify whether the STDS was cleaned out properly the night before or not. Pure nitrogen was used as the carrier gas under pyrolytic conditions while a mixture 20% oxygen and 80% helium was used for oxidative conditions.

The reaction conditions and details of the procedure for studying the thermal degradation behavior of a sample using the STDS at a single temperature run is described as follows:

i. Set the injection port at a suitable temperature enough to vaporize all of liquid sample into gaseous phase. A temperature of 180^{o}C is ideal.

ii. Place 50mg of the catalytic material between quartz wool plugs in a 0.3-cm-i.d. fused silica reactor in the.

iii. Position well the quartz flow reactor containing the catalyst inside the Omega furnace and tighten all connections gently.

iv. Set the carrier gas flow rate to the desired flow using the mass flow controller and record the effluent flow rate from the transfer line and the splitter using a digital flow meter.

v. Test for leaks at all connections using a leak detector to ensure that initial flow into the STDS equals the output flows of the splitter and transfer line.

vi. Prior to each experiment, oxidize the catalytic material in situ at 450 °C for 1 h at an air flow-rate of 5 cm^3/min to activate the surface.

vii. Set the transfer line temperature and the thermal reactor compartment oven at a temperature of 180^{o}C to maintain the sample in gas phase throughout the entire process of the STDS run.

viii. Set the furnace temperature to the desired temperature using the software that regulates the control box, thermocouple channels and furnace heating.

ix. Program the GC/MS run from an initial set-point temperature of -60^{o}C with a holding time of 35 minutes to 300^{o}C at the rate of 10^{o}C/min for duration of 72 minutes. This set up changes depending on the samples.

x. Program the Agilent MS detector for full scan mode from 15 to 350 amu and turn on the detector after 43 minutes.

xi. Open the liquid nitrogen valve and wait for the GC oven temperature to attain -60^{o}C temperature for cryogenic trapping.

xii. Insert the transfer line into the injection port for GC/MS. When all the temperatures have stabilized and all the flow rates are constant, then sample is ready for injection into the STDS.

xiii. Draw a 0.5µL volume of the sample into a syringe and place the syringe in syringe pump.

xiv. Set the injection rate and insert syringe needle into the injection port of the thermal reactor compartment then start the syringe pump as well as the GC/MS system.

xv. When the set injection runtime completes, stop the syringe pump and remove transfer line from the injection port of the GC/MS.

xvi. Switch off the furnace heating in the thermal compartment and adjust the oven temperature until it cools down adequately to a conveniently low temperature to remove the quartz reactor.

xvii. Replace the spent catalyst with a new catalyst in readiness for the next trial.

xviii. When the entire STDS run is complete, analyze the peaks and repeat the steps for the next experimental run.

2.4. Catalyst Preparation

2.4.1. Preparation of CuO/Silica Catalyst

The method of incipient wetness was used to prepare a catalytic material containing 5% CuO on silica that serves as a surrogate of fly ash. Briefly, the procedure of the method entails the following steps;

- Determine the correct amount of water and silica gel powder that is needed for incipient wetness to occur. The term incipient wetness is used when no bulk water is present and all the added volume is contained in pore structure and/or bound on the surface of the silica.
- Calculate the amount of copper (II) nitrate hemipenta-hydrate $Cu(NO_3)_2.2.5H_2O$ (Aldrich) needed to yield 5% Cu in the CuO/SiO_2 substrate.
- Transfer the calculated amount $Cu(NO_3)_2.2.5H_2O$ into a beaker containing the measured volume of water that is needed for incipient wetness to occur. Stir to dissolve.
- Add the aqueous solution of $Cu(NO_3)_2$ into a beaker containing the correct amount of silica gel powder(Aldrich, grade 923 100-200 mesh wire) and stir to mix well.

- Allow the beaker containing the resulting gel to stand for about 2 hours with occasional stirring at room temperature.
- Place the gel in the oven to dry for about 6 hours at a temperature of 120°C.
- Place the blue-green powder in the furnace and heat at a temperature of 450°C for 12 hours to convert all $Cu(NO_3)_2$ to CuO.
- Grind and sieve the green-black powder and store in a vial for use.

2.4.2 Preparation Fe_2O_3/Silica Catalyst

Basically, preparation of Fe_2O_3/silica catalyst was performed by repeating the procedure described in the preparation of CuO/silica except the use of iron (III) nitrate (Aldrich) instead of copper (II) nitrate. The iron oxide catalyst was prepared using the same method as copper in order to allow direct comparison with results for copper oxide previously published in the literature[3-5]. Accordingly, it was prepared using the same method, materials, and metal oxide concentration. Model fly ashes were used for several reasons. It is very difficult to discern the effect of a specific metal within the complex mixture contained in a typical fly ash generated in a combustion system, and it is impossible to compare the results to those for pure iron or copper oxide. In addition, the combustion-generated fly ashes typically used in these studies are collected at the end of the combustion system after they have been exposed to multiple organics, and their activities might be altered compared to that of fresh, in situ generated fly ashes. Finally, these fly ashes are representative only of the specific system being studied under the operating conditions at the time of collection. Thus, to compare their relative reactivities, we chose to use model systems of pure iron oxide/silica and copper oxide/silica.

Although suboxides of some metals have been reported, the principal oxide of copper or iron in a combustor is expected to be the highest oxidation state. This is due to the high temperature and oxygen-rich environment in the flame in which the metals are vaporized or entrained.

Consequently, our samples of $Fe_2^{(III)}O_3$ and $Cu^{(II)}O$ represent the majority of both metals in most combustion systems [6].

2.5 Quantification and Products Analysis

The products of reaction were analyzed using an in-line Agilent 6890 GC-MSD system. For product separation, a 30-m-long, 0.25-m-i.d., 0.25-µm-film-thickness column was used (Restek RTS 5MX) with a temperature hold at −60 °C for the reaction period, followed by a temperature-programmed ramp from −60 to 300 at 10 °C/min. Detection and quantification of the products were obtained on an Agilent 5973 mass spectrometer, which was operated in the full-scan mode from 15 to 350 amu for the duration of the GC run. The yields of the products were calculated using the expression

$$\text{yield} = \left(\frac{[\text{Product}]A}{[\text{Reactant}]_0}\right)$$

where [product] is the concentration of specific product formed (in moles), $[2\text{-MCP}]_0$ is the initial concentration of 2-MCP (in moles) injected into the reactor, and A is the molar stoichiometric factor (2 in this case, as one PCDD/F molecule is formed from two 2-MCP molecules). Each data point reflects an average result of three experimental runs. All data were plotted using Igor Pro 6.0 (Wave Metrics Inc.) software. The yield curves presented in the graphs are the results of mathematical fits generated by Igor. Quantitative standards were used to calibrate the MS response for all products.

2.6 References

1. Rubey, W. A. G., R. A. Design aspects of a modular instrumentation system for thermal diagnostic studies. *Rev. Sci. Instrum.* **1988,** *59*, (2), 265-9.

2. Oppelt, E. T., Hazardous-waste destruction. *Environ. Sci. Technol.* **1986,** *20*, (4), 312-318.

3. Lomnicki, S.; Dellinger, B. Formation of PCDD/F from the pyrolysis of 2-chlorophenol on the surface of dispersed copper oxide particles. *Proc. Combust. Inst.* **2003,** *29*, 2463-2468.

4. Lomnicki, S.; Dellinger, B. A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on a CuO/silica surface. *J. Phys. Chem. A.* **2003,** *107*, (22), 4387-4395.

5. Evans, C. S.; Dellinger, B. Surface-mediated formation of polybrominated dibenzo-p-dioxins and dibenzofurans from the high-temperature pyrolysis of 2-bromophenol on a CuO/silica surface. *Environ. Sci. Technol.* **2005,** *39*, (13), 4857-4863.

6. Sarofim, A. F.; Howard, J. B.; Padia, A. S. Physical transformation of mineral matter in pulverized coal under simulated combustion conditions. *Combust. Sci. Technol.* **1977,** *16*, (3-6), 187-204.

CHAPTER 3: RESULTS[*]

3.1 Iron Catalyzed Thermal Degradation of 2-Monochlorophenol

3.1.1 Results under Pyrolytic Conditions

The temperature dependence of the surface-mediated pyrolysis of 2-MCP over Fe_2O_3/SiO_2 and the yields of major organic products are presented [1]. At the lowest temperature studied of 200 °C, about 90% of the 2-MCP undergoes surface mediated decomposition. Above 350 °C, the reaction rapidly accelerates, resulting in almost complete degradation of 2-MCP by 500 °C. Apart from the lower molecular weight products, not analyzed quantitatively in this study (CO, CO2, C2 and C3 organics), the main products were chlorophenols and chlorobenzenes. The yields of chlorophenols were generally higher than those of chlorobenzenes and included 2,4- and 2,6-dichlorophenol (2,4- + 2,6-DCP) with a maximum yield of 0.49% at 450 °C, 2,3,6- and 2,4,6-trichlorophenol (2,3,6- + 2,4,6-TCP) with a maximum yield of 7.0% at 250 °C, and phenol with a maximum yield of 1.3% at 450 °C.

Among chlorobenzene products, the yields of hexachlorobenzene (HxCBz), with a 0.94% maximum yield at 500 °C and tetrachlorobenzenes (1,2,3,4- + 1,2,3,5-TeCBz), with a 1.4% maximum yield at 500 °C were the highest. Other chlorobenzenes detected were monochlorobenzene (MCBz), with a <0.10% yield at 250 °C; 1,2,4- and 1,2,3-trichlorobenzene (1,2,4- + 1,2,3-TriCBz), with a 0.26% maximum yield at 450 °C; and pentachlorobenzene (PeCBz), with a<0.10% yield at 350 °C. Benzene (Bz) was formed with a constant yield of ~0.10% from 300-550 °C. **Figure 3.1** and **Figure 3.2** depicts the yields of chlorophenols and chlorobenzenes respectively, from the pyrolysis of 2-MCP over an Fe_2O_3/silica surface.

---

[*] Portions of this chapter reprinted by permission of American Chemical Society, Journal of Environmental Science & Technology

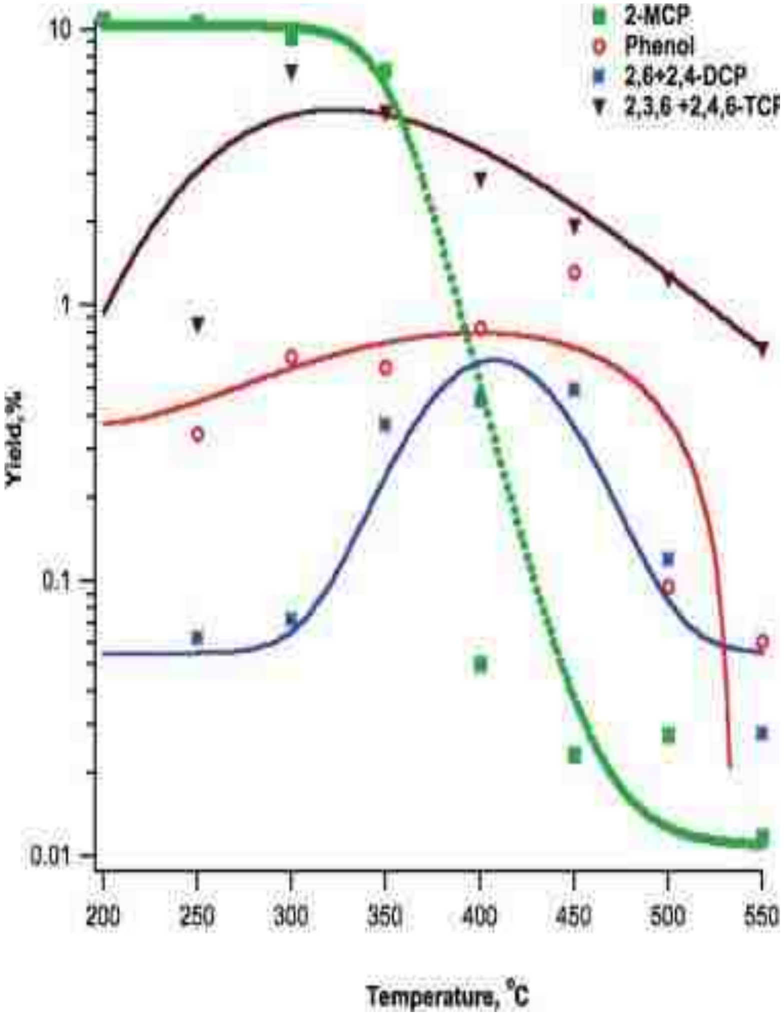


Figure 3.1. Yields of Phenols from the Pyrolysis of 2-MCP over an Fe_2O_3/Silica Surface

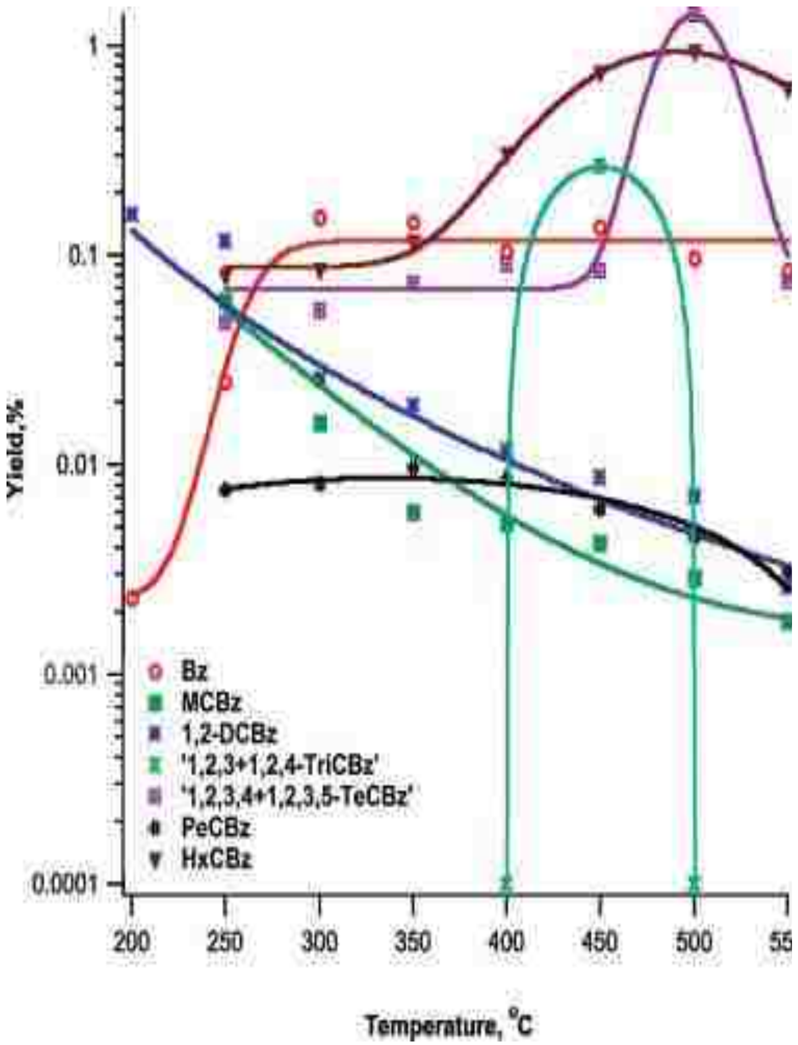


Figure 3.2. Yields of Chlorobenzenes from the Pyrolysis of 2-MCP over an Fe_2O_3/Silica Surface

At 200-250 °C, significant yields PCDD/Fs were observed, comparable to the yields of chlorinated benzenes. Dibenzo-*p*-dioxin (DD), 1-monochlorodibenzo-*p*-dioxin (1-MCDD), 4,6-dichlorodibenzofuran (4,6-DCDF), and dibenzofuran (DF) were all detected as the products of 2-MCP pyrolysis over Fe_2O_3/silica surface. The maximum yields of 4,6-DCDF and 1-MCDD were 0.32% and 0.093% at 300 and 350 °C, respectively, whereas DD and DF exhibited maximum yields of 0.22% and 0.40% at 450 and 500 °C, respectively. Chloronaphthalene, naphthalene, and biphenyl were also detected in trace quantities, with yields that increased with increasing temperature to a maximum at 450-500 °C. **Figure 3.3** shows the PCDD/F yields from the pyrolysis of 2-MCP over an Fe_2O_3/silica surface.

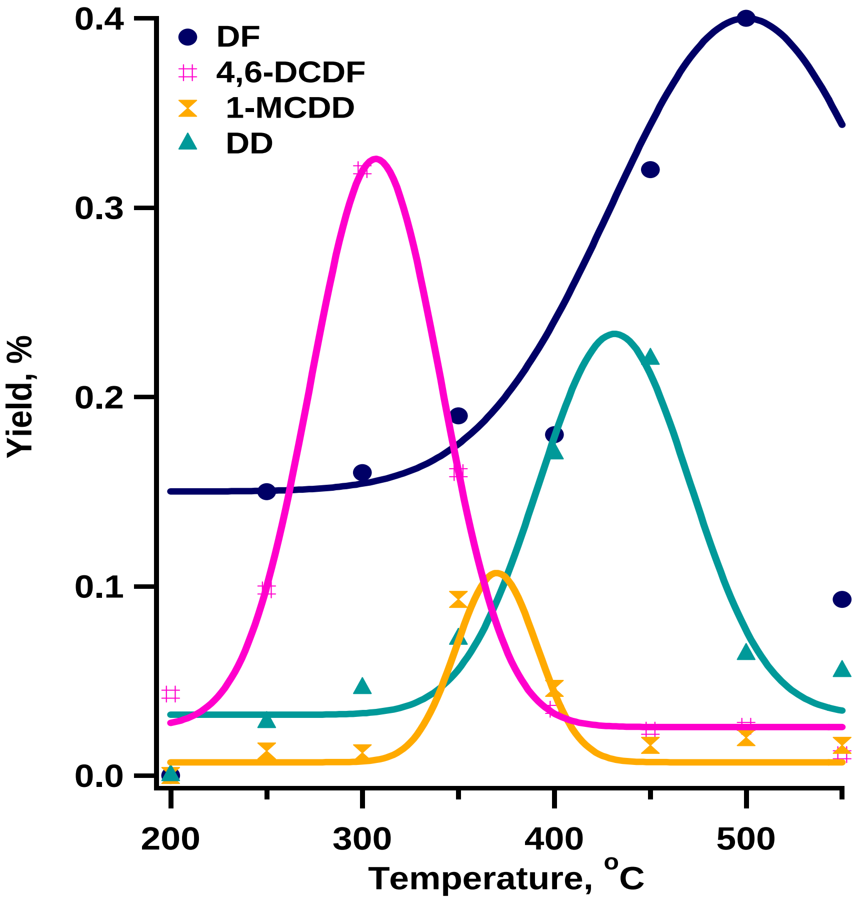


Figure 3.3. PCDD/F Yields from the Pyrolysis of 2-MCP over an Fe_2O_3/Silica Surface

Table 3.1 Dioxin and Non-Dioxin Products from Pyrolysis of 2-Monochlorophenol over Fe_2O_3/Silica Surface

	Reaction Temperature, °C							
Products	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**
Benzene	**0.0023**	**0.025**	**0.15**	**0.14**	**0.11**	**0.14**	**0.096**	**0.084**
Monochlorobenzene	**bdl**	**0.061**	**0.016**	**0.0060**	**0.0053**	**0.0042**	**0.0029**	**0.0018**
1,2-Dichlorobenzene	**0.16**	**0.12**	**0.026**	**0.019**	**0.012**	**0.0087**	**0.0071**	**0.0026**
1,2,3 +1,2,4-Trichlorobenzene	**bdl**	**bdl**	**bdl**	**bdl**	**0.26**	**bdl**	**bdl**	**bdl**
1,2,3,4 +1,2,3,5-Tetrachlorobenzene	**bdl**	**0.048**	**0.055**	**0.073**	**0.090**	**0.084**	**1.4**	**0.074**
Pentachlorobenzene	**bdl**	**0.0076**	**0.0081**	**0.0097**	**0.0085**	**0.0062**	**0.0045**	**0.0031**
Hexachlorobenzene	**bdl**	**0.080**	**0.085**	**0.11**	**0.30**	**0.74**	**0.94**	**0.63**
Chloronaphthalene	**bdl**	**0.018**	**0.022**	**0.057**	**0.087**	**0.17**	**0.24**	**0.18**
Naphthalene	**bdl**	**0.0072**	**0.0080**	**0.011**	**0.015**	**0.035**	**0.075**	**0.069**
Biphenyl	**0.0057**	**0.0050**	**0.0061**	**0.0097**	**0.021**	**0.049**	**0.0042**	**0.0058**
Phenol	**bdl**	**0.34**	**0.65**	**0.59**	**0.82**	**1.3**	**0.096**	**0.060**
2-Monochlorophenol	**11**	**11**	**9.4**	**7.1**	**0.050**	**0.023**	**0.028**	**0.012**
2,4+2,6-Dichlorophenol	**bdl**	**0.062**	**0.073**	**0.37**	**0.45**	**0.49**	**0.12**	**0.028**
2,3,6+2,4,6-Trichlorophenol	**0.85**	**7.0**	**5.0**	**2.9**	**1.9**	**1.3**	**0.70**	**bdl**
Dibenzofuran	**bdl**	**0.15**	**0.16**	**0.19**	**0.18**	**0.32**	**0.40**	**0.093**
Dibenzo-*p*-dioxin	**bdl**	**0.028**	**0.046**	**0.072**	**0.17**	**0.22**	**0.064**	**0.055**
1-Monochlorodibenzo-*p*-dioxin	**bdl**	**0.013**	**0.012**	**0.093**	**0.046**	**0.016**	**0.020**	**0.016**
4,6-Dichlorodibenzofuran	**0.043**	**0.098**	**0.32**	**0.16**	**0.035**	**0.024**	**0.026**	**0.011**

bdl- Below Detection Limit

3.1.2 Results under Oxidative Conditions

The temperature dependence of the surface-mediated oxidation of 2-MCP over Fe_2O_3/SiO_2 and the yields of major organic products are presented. Significant catalytic degradation of the reactant occurred with 11% of the initial amount of 2-MCP remaining undestroyed at 200 ^{o}C; the lowest temperature studied. Rapid and accelerated conversion was observed at above 300 °C, achieving almost complete degradation of 2-MCP by 400 °C.

Although not all products formed from thermal decomposition of 2-MCP were analyzed quantitatively such as CO, CO_2, C2 and C3 organics, chlorophenols and chlorobenzenes were the main products observed. Chlorophenols were formed at comparably higher yields than those of chlorobenzenes and included phenol with a maximum yield of 3.5% at 300 °C, 2,4- and 2,6-dichlorophenol (2,4- + 2,6-DCP) with a maximum yield of 3.0% at 300 °C, and 2,3,6- and 2,4,6-trichlorophenol (2,3,6- + 2,4,6-TCP) with a maximum yield of 6.2% at 350 °C.

Chlorobenzene products observed were monochlorobenzene (MCBz), with a maximum yield of 0.014% at 450 °C, 1,2-dichlorobenzene (1,2-DCBz) with yield of 0.22% at 250 °C, 1,2,3- and 1,2,4- trichlorobenzene (1,2,4-+ 1,2,3-TriCBz), with a 0.26% maximum yield at 450 °C and 1,2,3,4- and 1,2,3,5-tetrachlorobenzenes (1,2,3,4- + 1,2,3,5-TeCBz, with a 0.048% maximum yield at 350 °C. Other chlorobenzenes observed were hexachlorobenzene (HxCBz), with yield of <0.01% at 500 °C and pentachlorobenzene (PeCBz), with a maximum yield of 0.085% at 450 °C. The formation benzene (Bz) increased gradually with increase in temperature reaching a maximum yield of 0.036% at 550 °C. **Figure 3.4** and **Figure 3.5** depicts the yields of chlorophenols and chlorobenzenes respectively, from the oxidation of 2-MCP over an Fe_2O_3/silica surface.

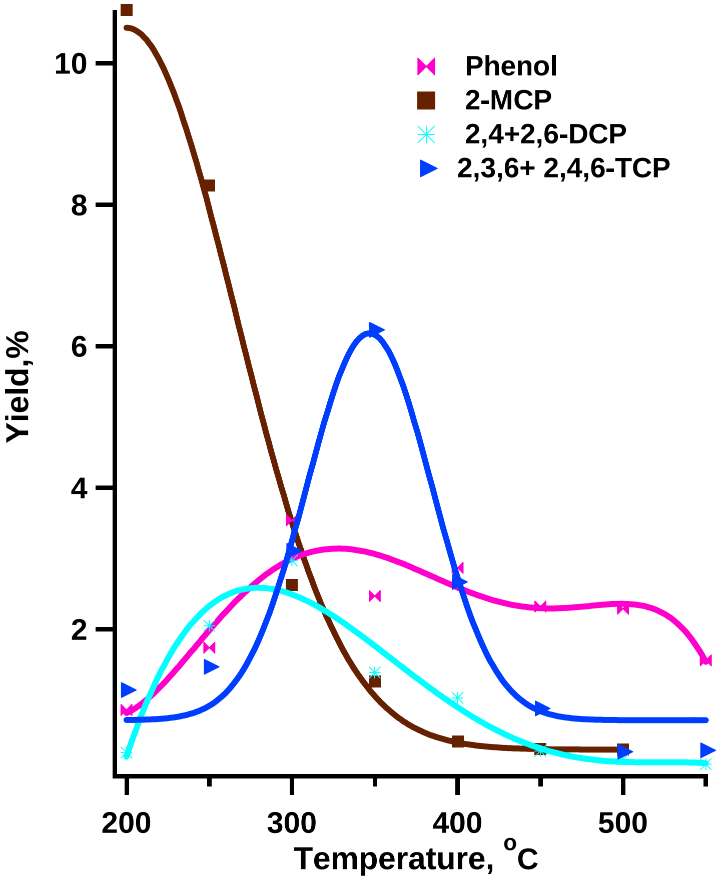


Figure 3.4. Yields of Phenols from the Oxidation of 2-MCP over an Fe_2O_3/Silica Surface

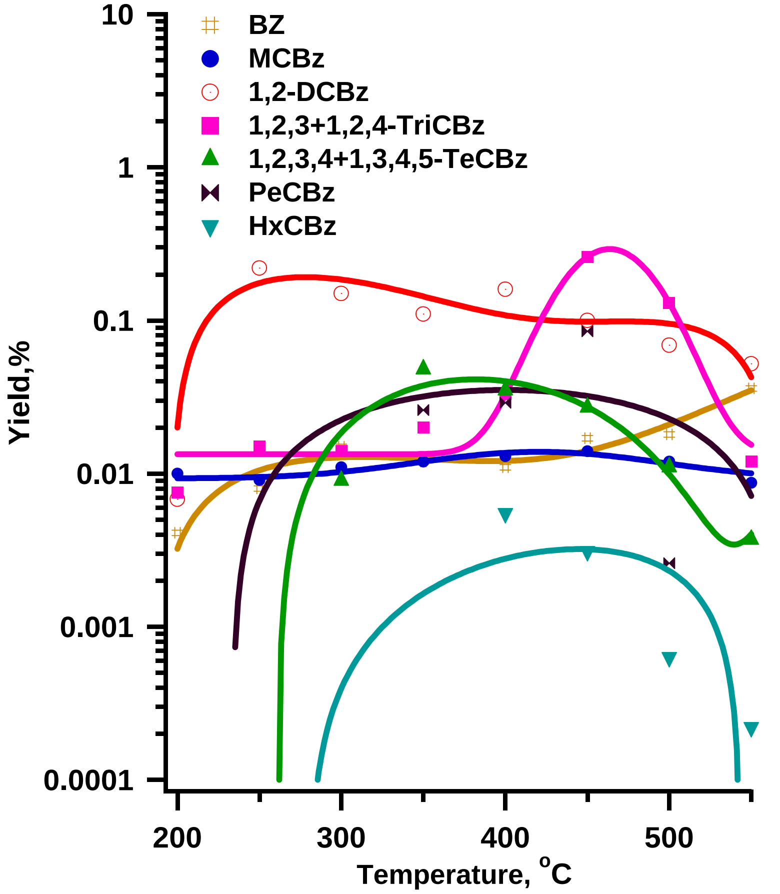


Figure 3.5. Yields of Chlorobenzenes from the Oxidation of 2-MCP over an Fe_2O_3/Silica Surface

Among other non-dioxin products formed from thermal oxidative degradation of 2-MCP were chloronaphthalene with a maximum yield of 0.041% at 400 °C, naphthalene with a maximum yield of 0.89% at 400 °C and biphenyl with a maximum yield of 0.10% at 300 °C. Benzoquinone (BQ), catechol (CT), chlorobenzoquinone (CQ) and chlorocatechol (CC) were also detected in trace quantities, with relatively higher yields formed at 300-400 °C.

The PCDD/F products observed from pyrolysis of 2-MCP over Fe_2O_3/Silica surface were dibenzo-*p*-dioxin (DD), 1-monochlorodibenzo-*p*-dioxin (1-MCDD), 4,6-dichlorodibenzofuran (4,6-DCDF), and dibenzofuran (DF). The maximum yields of 4,6-DCDF and 1-MCDD were 0.41% and 0.45% at 250 and 350 °C, respectively, whereas DD and DF exhibited maximum yields of 0.49% and 0.33% at 500 °C and 450 °C, respectively. **Figure 3.6** shows the PCDD/F yields from the oxidation of 2-MCP over an Fe_2O_3/silica surface.

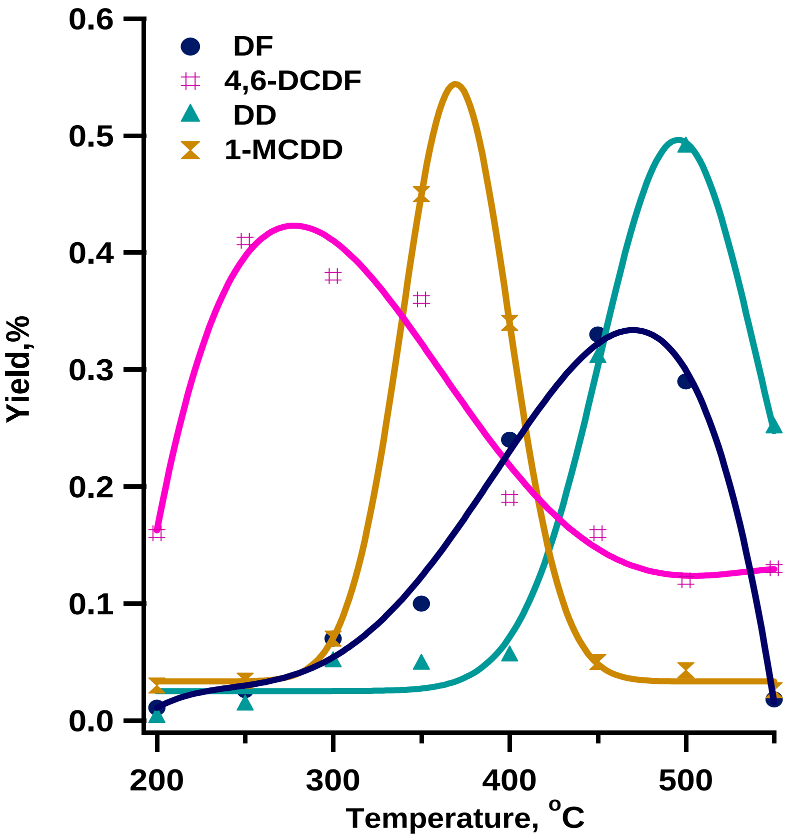


Figure 3.6. PCDD/F Yields from the Oxidation of 2-MCP over an Fe_2O_3/Silica Surface

Table 3.2 Dioxin and Non-Dioxin Products from Oxidation of 2-Monochlorophenol over Fe_2O_3/Silica Surface

Products	Reaction Temperature, °C							
	200	250	300	350	400	450	500	550
Benzene	0.0041	0.0080	0.015	0.012	0.011	0.017	0.018	0.036
Monochlorobenzene	0.010	0.0091	0.011	0.012	0.013	0.014	0.012	0.0087
1,2-Dichlorobenzene	0.0068	0.22	0.15	0.11	0.16	0.10	0.069	0.052
1,2,3 +1,2,4-Trichlorobenzene	0.0075	0.015	0.014	0.020	0.033	0.26	0.13	0.012
1,2,3,4 +1,2,3,5-Tetrachlorobenzene	bdl	bdl	0.0090	0.048	0.035	0.027	0.011	0.0037
Pentachlorobenzene	bdl	bdl	bdl	0.026	0.029	0.085	0.0026	bdl
Hexachlorobenzene	bdl	bdl	bdl	bdl	0.0055	0.0031	0.00063	0.00022
Chloronaphthalene	0.014	0.024	0.019	0.028	0.041	0.027	0.022	0.013
Naphthalene	0.47	0.49	0.62	0.68	0.89	0.71	0.042	0.0077
Biphenyl	0.023	0.053	0.10	0.061	0.057	0.043	0.032	0.0082
Phenol	0.86	1.7	3.5	2.5	2.9	2.3	2.3	1.6
2-Monochlorophenol	11	8.3	2.6	1.3	0.41	0.31	0.30	0.21
2,4+2,6-Dichlorophenol	0.26	2.1	3.0	1.4	1.0	0.28	0.16	0.094
2,3,6+2,4,6-Trichlorophenol	1.1	1.5	3.1	6.2	2.7	0.88	0.27	0.29
Benzoquinone	0.00051	0.0072	0.0053	0.013	0.0086	0.0049	0.0024	0.0020
Chlorobenzoquinone	bdl	0.0061	0.0096	0.014	0.016	0.012	0.0084	0.0055
Catechol	0.00022	0.0011	0.0014	0.0023	0.00098	0.00028	0.00019	0.000078
Chlorocatechol	bdl	0.000096	0.00014	0.00041	0.00050	0.00053	0.000056	0.000035
Dibenzofuran	0.011	0.026	0.070	0.10	0.24	0.33	0.29	0.018
Dibenzo-p-dioxin	0.0025	0.013	0.050	0.048	0.055	0.31	0.49	0.25
1-Monochlorodibenzo-p-dioxin	0.030	0.034	0.070	0.45	0.34	0.050	0.043	0.026
4,6-Dichlorodibenzofuran	0.16	0.41	0.38	0.36	0.19	0.16	0.12	0.13

bdl- Below Detection Limit

3.2 Copper Catalyzed Thermal Degradation of 1,2-Dichlorobenzene

3.2.1 Results under Pyrolytic Conditions

The results for the thermal degradation of 1,2-DCBz decomposition under pyrolytic conditions are presented in **Table 3.3**. 65% of the 1,2-DCBz was decomposed by 200 ^{o}C. 1,2,3- and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), which was a 0.40% impurity in the 1,2-DCBz, decomposed to 0.13 % at 200 ^{o}C. Benzene (Bz), monochlorobenzene (MCBz), 1,2,3,4-and 1,2,3,5-tetrachlorobenzenes (1,2,3,4+1,2,3,5-TeCBzs), phenol, and 2-monochlorophenol (2-MCP) were detected in yields of 0.0043%, 0.49%, 0.0049 %, 0.093%, and 0.010%, respectively at 200 ^{o}C. Additionally, the yields of Bz, trichlorobenzenes (1,2,3-+1,2,4-TriCBzs), tetrachlorobenzenes (1,2,3,4+1,2,3,5-TeCBzs), pentachlorobenzene (PeCBz), phenol, and 2-monochlorophenol (2-MCP) increased with increasing temperature, achieving maximum of 0.024% at 500 ^{o}C, 10% at 400 ^{o}C, 1.0% at 350 ^{o}C, 0.18% at 350 ^{o}C, 0.64% at 500 ^{o}C, and 0.027% at 350 ^{o}C, respectively. The yield of MCBz decreased with increasing temperature to below detection limit (0.00010%) at 550 ^{o}C. The yields of the chlorinated benzenes from the decomposition of 1,2-DCBz are depicted in **Figure 3.7.** Dichlorophenols (2,4-+2,6-DCP) were observed with a yield of 0.013% at 500 ^{o}C. The yields of the chlorophenols from the decomposition of 1,2-DCBz are shown in **Figure 3.8**. Biphenyl and naphthalene achieved maximum yields of 0.030% at 300-500 ^{o}C and 0.13% at 450 ^{o}C, respectively.

The formation profiles of the PCDD/F products are depicted in **Figure 3.9**. No dibenzo-*p*-dioxin (DD) or other PCDDs were detected. However, 4,6-dichlorodibenzofuran (4,6-DCDF) and dibenzofuran (DF) were observed with maximum yields of 0.21% at 350 ^{o}C and 0.51% at 450 ^{o}C, respectively.

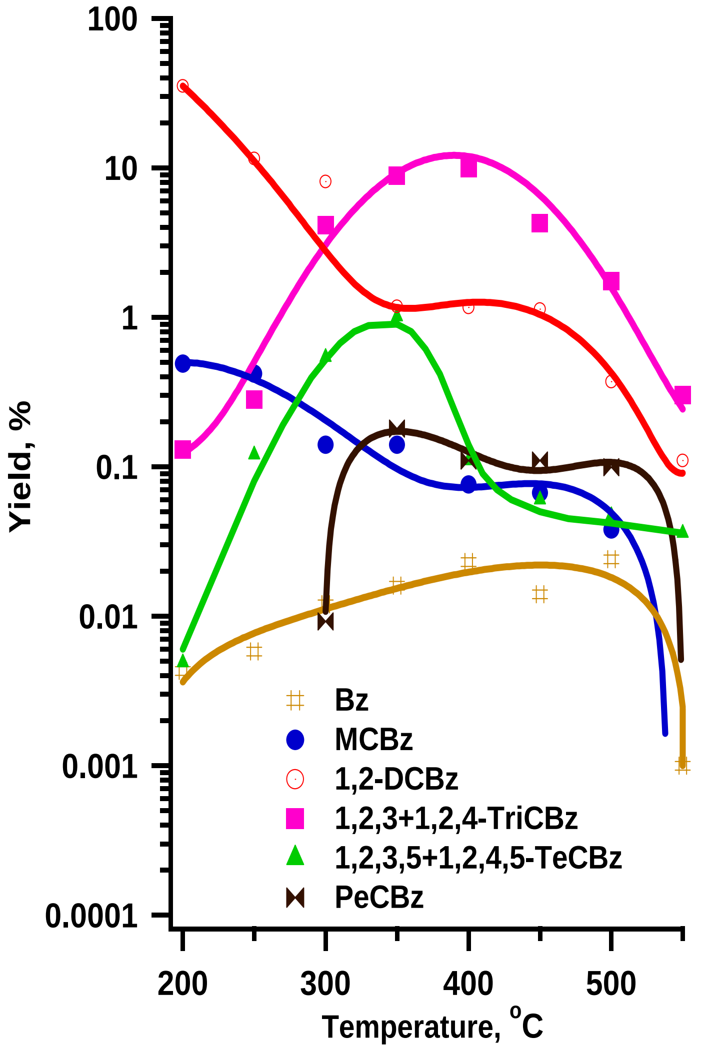


Figure 3.7. Product Yields of Chlorobenzenes from the Pyrolysis of 1,2-DCBz over CuO/Silica Surface

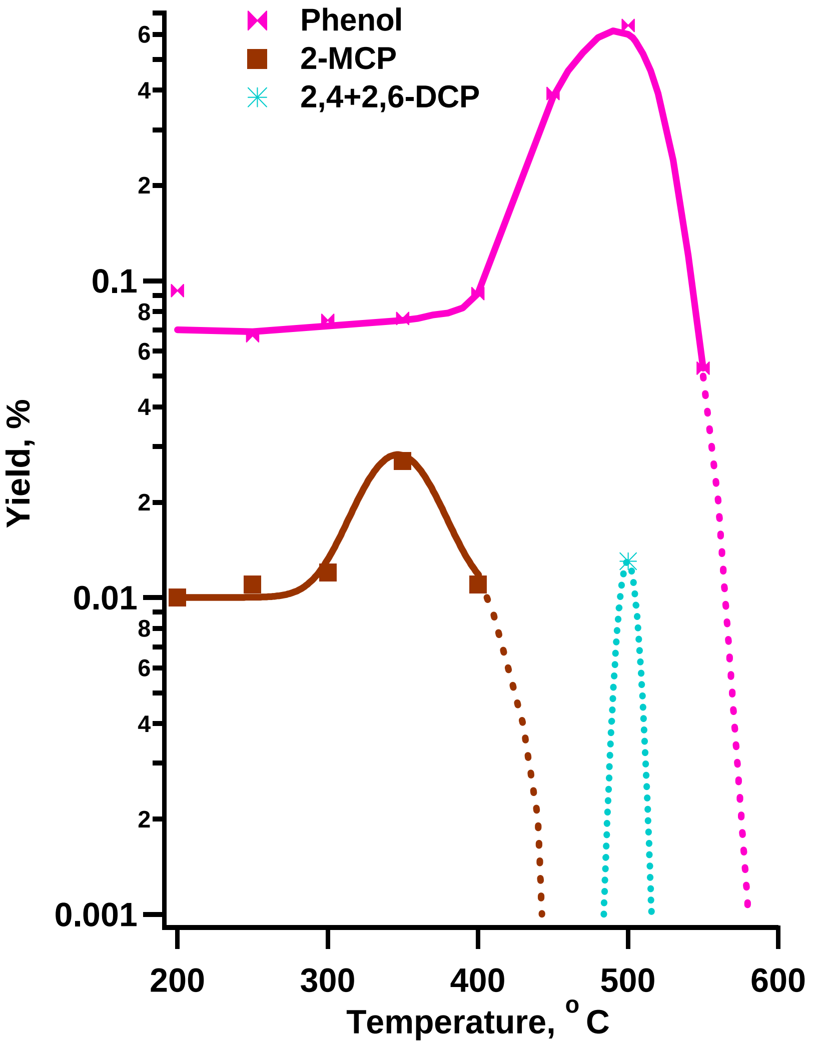


Figure 3.8. Product Yields of Chlorophenols from the Pyrolysis of 1,2-DCBz over CuO/Silica Surface

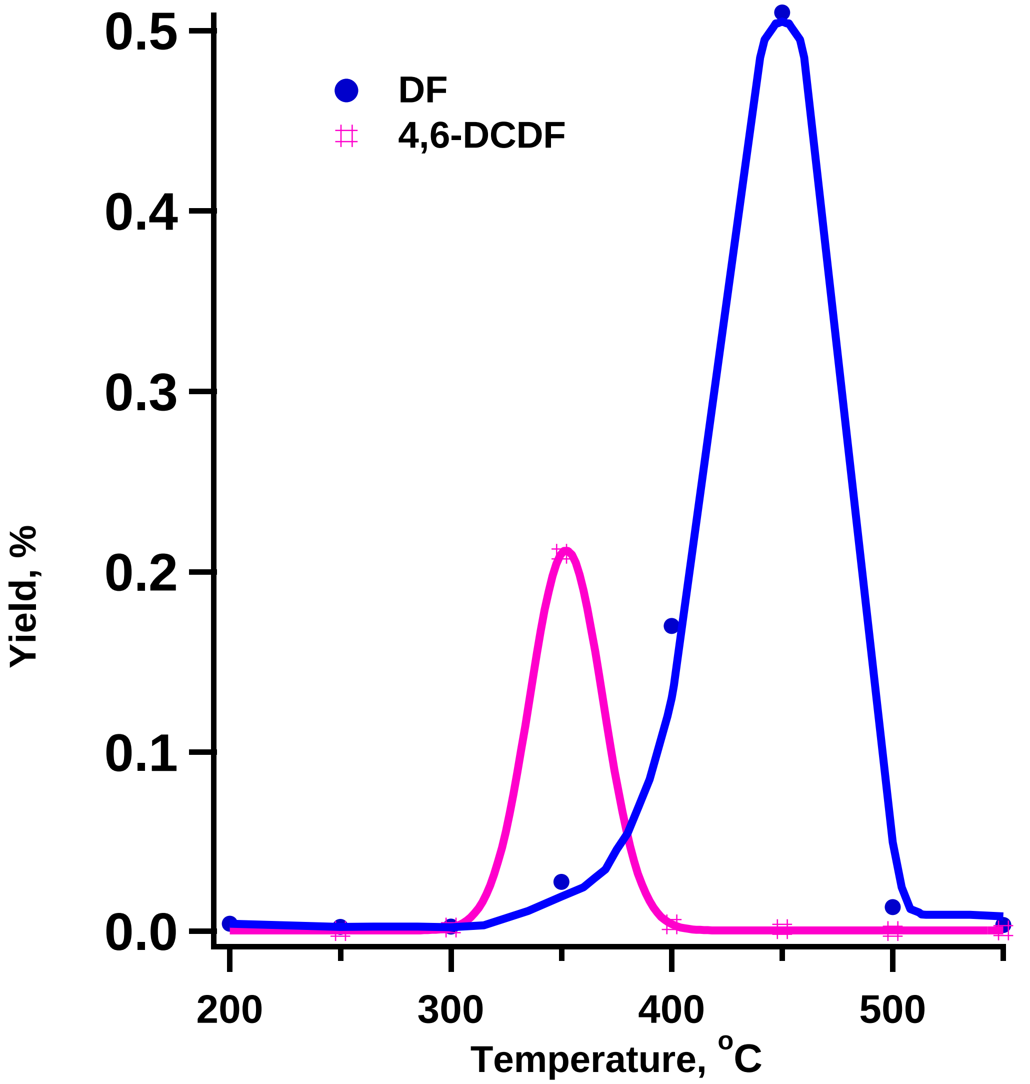


Figure 3.9. Yields of PCDD/Fs from the Pyrolysis of 1,2-DCBz over CuO/Silica Surface

Table 3.3 Dioxin and Non-Dioxin Products from Pyrolysis of 1,2-Dichlorobenzene over CuO/Silica Surface

	Reaction Temperature, ^{o}C							
Products	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**
Benzene	**0.0043**	**0.0058**	**0.012**	**0.016**	**0.023**	**0.014**	**0.024**	**0.0010**
Monochlorobenzene	**0.49**	**0.42**	**0.14**	**0.14**	**0.076**	**0.067**	**0.038**	**bdl**
1,2-Dichlorobenzene	**35**	**12**	**8.1**	**1.2**	**1.2**	**1.1**	**0.37**	**0.11**
1,2,3 +1,2,4-Trichlorobenzene	**0.13**	**0.28**	**4.1**	**8.9**	**10**	**4.3**	**1.7**	**0.30**
1,2,3,4 +1,2,3,5-Tetrachlorobenzene	**0.0049**	**0.12**	**0.54**	**1.0**	**0.11**	**0.060**	**0.047**	**0.036**
Pentachlorobenzene	**bdl**	**bdl**	**0.0092**	**0.18**	**0.11**	**0.11**	**0.099**	**bdl**
Biphenyl	**0.0017**	**0.0047**	**0.030**	**0.019**	**0.024**	**0.021**	**0.030**	**0.0044**
Naphthalene	**0.013**	**0.012**	**0.015**	**0.026**	**0.052**	**0.13**	**0.024**	**0.0059**
Phenol	**0.093**	**0.067**	**0.075**	**0.076**	**0.091**	**0.39**	**0.64**	**0.053**
2-Monochlorophenol	**0.010**	**0.011**	**0.012**	**0.027**	**0.011**	**bdl**	**bdl**	**bdl**
2,4+2,6-Dichlorophenol	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**0.013**	**bdl**
Dibenzofuran	**0.0049**	**0.0031**	**0.0033**	**0.028**	**0.17**	**0.51**	**0.014**	**0.0041**
4,6-Dichlorodibenzofuran	**bdl**	**0.00080**	**0.0027**	**0.21**	**0.0046**	**0.0018**	**0.00080**	**0.0012**

bdl- Below Detection Limit

3.2.2 Results under Oxidative Conditions

The major products from the thermal degradation of 1,2-DCBz under oxidative conditions are presented in **Table 3.4**. 27% of the initial amount of 1,2-DCBz was unreacted at 200 ^{o}C. 1,2,3- and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), which was a 0.40% impurity in the 1,2-DCBz, increased to 1.5% at 200 °C achieving a maximum yield of 3.3% at 250 °C. Benzene (Bz), monochlorobenzene (MCBz), 1,2,3,4- and 1,2,3,5- tetrachlorobenzenes (1,2,3,4+1,2,3,5 TeCBzs), were detected with maximum yields of 0.21% at 450 °C, 0.15% at 250 °C, 0.11 % at 450 °C, respectively. Pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) were observed with maximum yields of 0.11% at 550 °C and <0.010 at 450-550 °C, respectively. The yields of the chlorinated benzenes from the decomposition of 1,2-DCBz over CuO/silica surface under oxidative conditions are depicted in **Figure 3.10.**

Phenolic products formed were phenol, with a maximum yield of 1.7 % at 500 °C, and 2-monochlorophenol (2-MCP) which increased with increasing temperature, achieving maximum of 0.16% at 250 ^{o}C, 0.22% at 300-350 ^{o}C, 0.36% at 450 ^{o}C, and 0.086% at 500 ^{o}C, respectively. Dichlorophenols (2,4-DCP+2,6-DCP) and 2,3,6-+ 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) were observed with maximum yields of 1.3% at 400 ^{o}C and 0.67% at 350 ^{o}C, respectively. The yields of the chlorophenols from the decomposition of 1,2-DCBz over CuO/silica surface under oxidative conditions are depicted in **Figure 3.11.**

Among other non-dioxin products detected were biphenyl, naphthalene and chloronaphthalene which achieved maximum yields of 0.037% at 450 ^{o}C, 0.13% at 450 ^{o}C, and 0.024% at 500 ^{o}C respectively. Trace amounts of benzoquinone and catechol were observed across the entire temperature range studied from 200 to 550 ^{o}C.

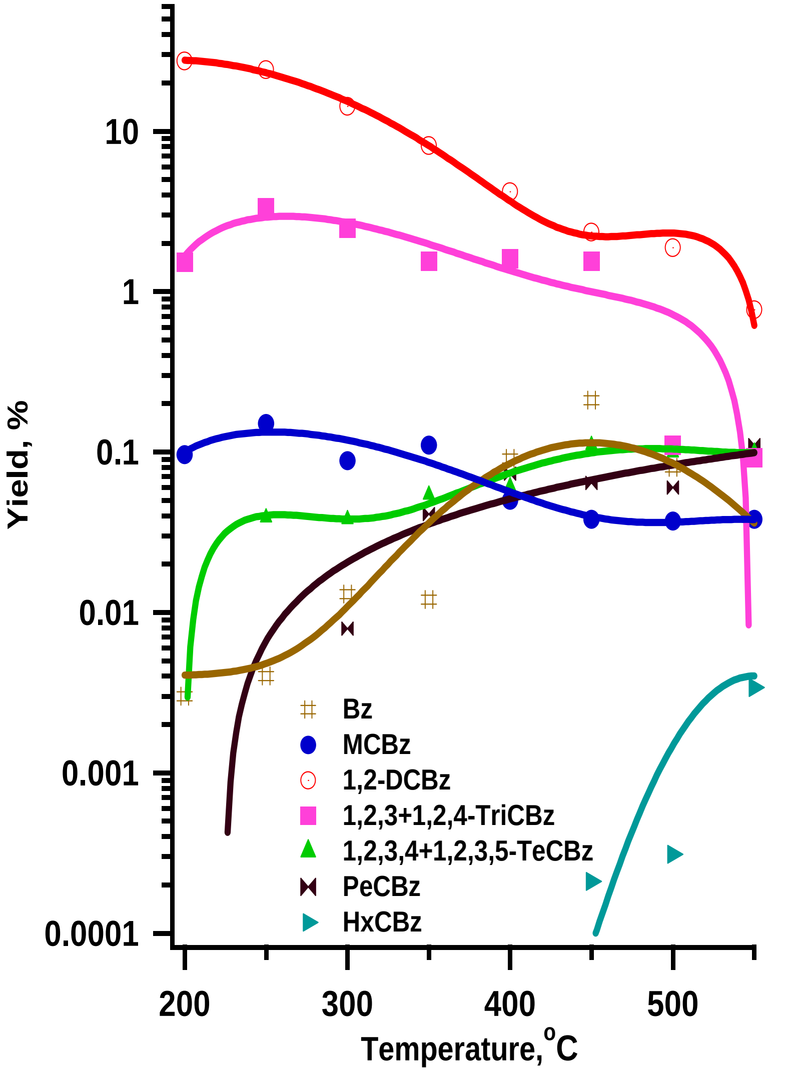


Figure 3.10. Product Yields of Chlorobenzenes from the Oxidation of 1,2-DCBz over CuO/Silica Surface

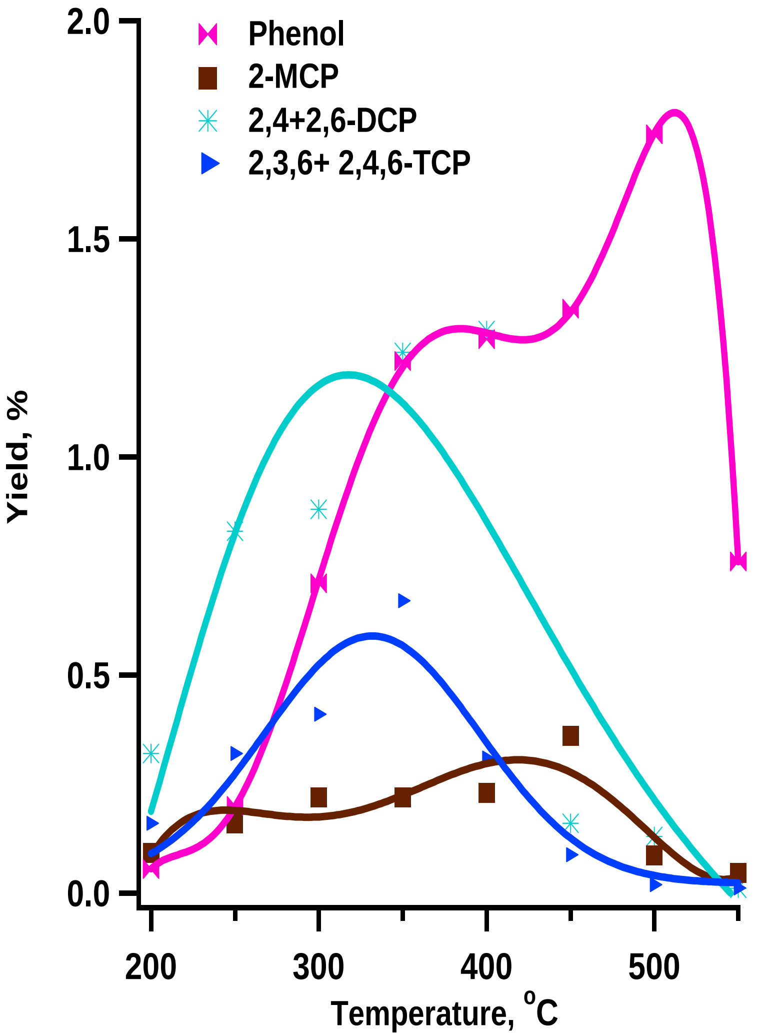


Figure 3.11. Product Yields of Chlorophenols from the Oxidation of 1,2-DCBz over CuO/Silica Surface

The formation yields of the PCDD/F products detected are shown in **Figure 3.12**. Dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF) were formed with maximum yields of 0.30% at 500 ^{o}C and 0.091% at 250 ^{o}C, respectively. No dibenzo-p-dioxin (DD) or other PCDD/Fs products were detected.

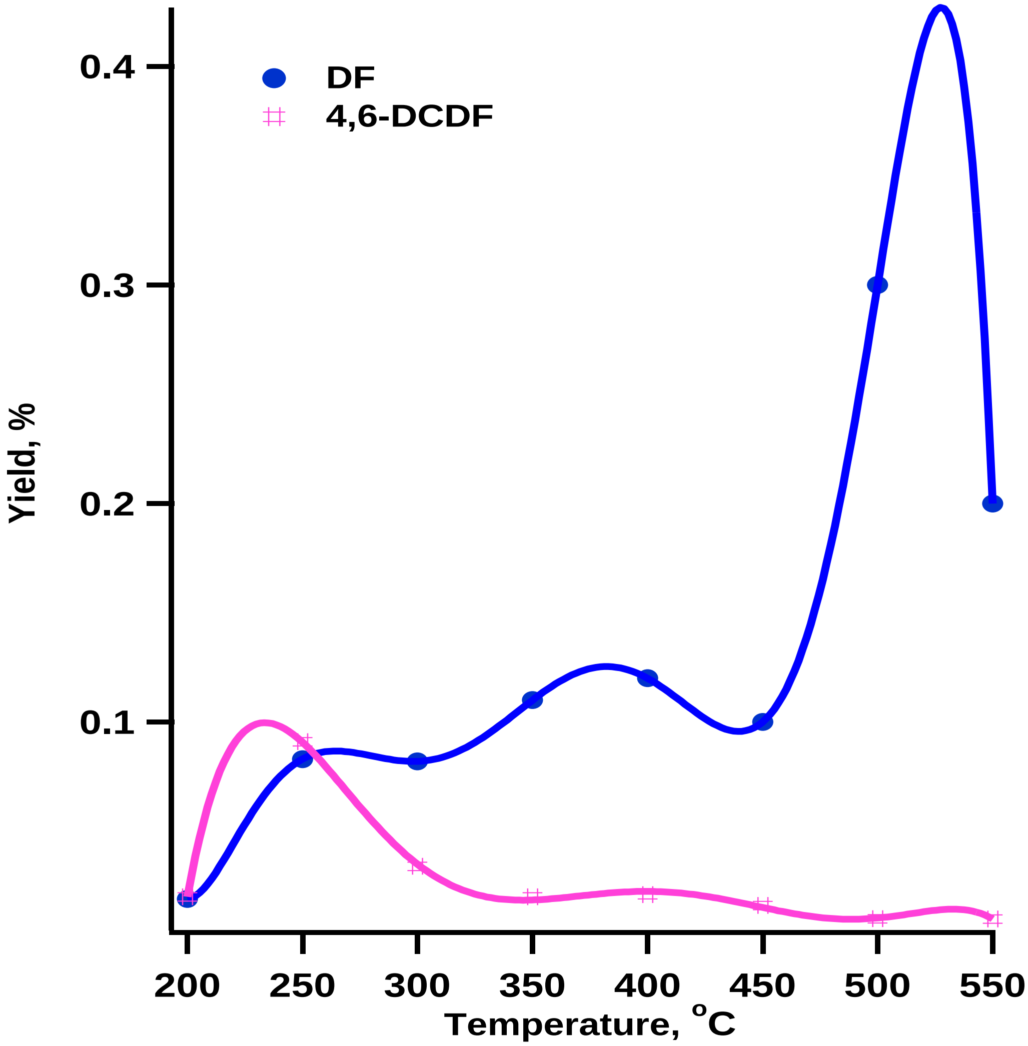


Figure 3.12. Yields of PCDD/Fs from the Oxidation of 1,2-DCBz over CuO/Silica Surface

Table 3.4 Dioxin and Non-Dioxin Products from Oxidation of 1,2-Dichlorobenzene over CuO/Silica Surface

	Reaction Temperature, ^{o}C							
Products	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**
Benzene	**0.0030**	**0.0040**	**0.013**	**0.012**	**0.091**	**0.21**	**0.080**	**0.031**
Monochlorobenzene	**0.096**	**0.15**	**0.088**	**0.11**	**0.050**	**0.038**	**0.037**	**0.038**
1,2-Dichlorobenzene	**27**	**24**	**14**	**8.1**	**4.2**	**2.3**	**1.9**	**0.77**
1,2,3 +1,2,4-Trichlorobenzene	**1.5**	**3.3**	**2.5**	**1.5**	**1.6**	**1.5**	**0.11**	**0.092**
1,2,3,4 +1,2,3,5-Tetrachlorobenzene	**bdl**	**0.039**	**0.038**	**0.054**	**0.061**	**0.11**	**0.099**	**0.10**
Pentachlorobenzene	**bdl**	**bdl**	**0.0079**	**0.041**	**0.073**	**0.064**	**0.060**	**0.11**
Hexachlorobenzene	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**0.00021**	**0.00031**	**0.0034**
Naphthalene	**0.021**	**0.047**	**0.058**	**0.080**	**0.10**	**0.13**	**0.096**	**0.084**
Chloronaphthalene	**0.00043**	**0.0050**	**0.014**	**0.015**	**0.020**	**0.023**	**0.024**	**0.019**
Biphenyl	**0.0052**	**0.0062**	**0.011**	**0.026**	**0.033**	**0.037**	**0.029**	**0.027**
Phenol	**0.055**	**0.20**	**0.71**	**1.2**	**1.3**	**1.3**	**1.7**	**0.76**
2-Monochlorophenol	**0.092**	**0.16**	**0.22**	**0.22**	**0.23**	**0.36**	**0.086**	**0.047**
2,4+2,6-Dichlorophenol	**0.32**	**0.83**	**0.88**	**1.2**	**1.3**	**0.16**	**0.13**	**0.011**
2,3,6+2,4,6-Trichlorophenol	**0.16**	**0.32**	**0.41**	**0.67**	**0.31**	**0.088**	**0.019**	**0.012**
Benzoquinone	**0.00029**	**0.00050**	**0.00051**	**0.00062**	**0.00076**	**0.0011**	**0.00081**	**0.00023**
Catechol	**0.0000075**	**0.000036**	**0.00039**	**0.000094**	**0.000031**	**0.000063**	**0.000050**	**0.000014**
Dibenzofuran	**0.019**	**0.083**	**0.082**	**0.11**	**0.12**	**0.10**	**0.30**	**0.20**
4,6-Dichlorodibenzofuran	**0.020**	**0.091**	**0.034**	**0.020**	**0.021**	**0.016**	**0.010**	**0.0099**

bdl- Below Detection Limit

3.3. Iron Catalyzed Thermal Degradation of 1,2-Dichlorobenzene

3.3.1 Results under Pyrolytic Conditions

The results for the thermal degradation of 1,2-DCBz under pyrolytic conditions are presented in **Table 3.5.** At 200 °C, 58% of the 1,2-DCBz was decomposed. 1,2,3- and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), which accounted for a 0.40% of the initial 1,2-DCBz concentration as impurity, decomposed to 0.13 % at 200 ^{o}C. The yield of monochlorobenzene (MCBz) increased with increasing temperature with yield of 0.0080%, at 200 °C, 0.017%, at 300 °C, 0.54% at 400 °C and 1.7% at 500-550 °C. Benzene (Bz), trichlorobenzenes (1,2,3-+1,2,4), tetrachlorobenzenes (1,2,3,4+1,2,3,5 TeCBzs), phenol, and 2-monochlorophenol (2-MCP) were detected in maximum yields of 0.0035%, 0.13%, 0.0034%, 0.27%, and 0.020%, respectively at 200 ^{o}C. The maximum yields of pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) were 0.011% at 500 ^{o}C and 0.17% at 450 ^{o}C, respectively. The yields of the chlorobenzenes from the decomposition of 1,2-DCBz under pyrolytic conditions over Fe_2O_3/silica surface are depicted in **Figure 3.13.**

The formation of biphenyl increased initially with increasing temperature from 0.0030% at 200 °C reaching a maximum yield of 0.35% at 400 °C then decreasing to 0.022% by 550 °C. Formation of naphthalene achieved a maximum yield of 0.36% at 400 °C and declined drastically at elevated temperatures to 0.0036% at 550 °C. The yields of phenol, and 2-MCP increased with increasing temperature, achieving maximum of 0.72% at 300 ^{o}C, and 0.067% at 400 ^{o}C, respectively. The formation of 2,4- and 2,6-dichlorophenols (2,4-+2,-6DCP) increased with increasing temperature with yield of 0.020% at 200 ^{o}C and attained a maximum yield of 0.49% at 450 °C. The yields of the chlorophenols from the decomposition of 1,2-DCBz over Fe_2O_3/silica surface under pyrolytic conditions are depicted in **Figure 3.14.**

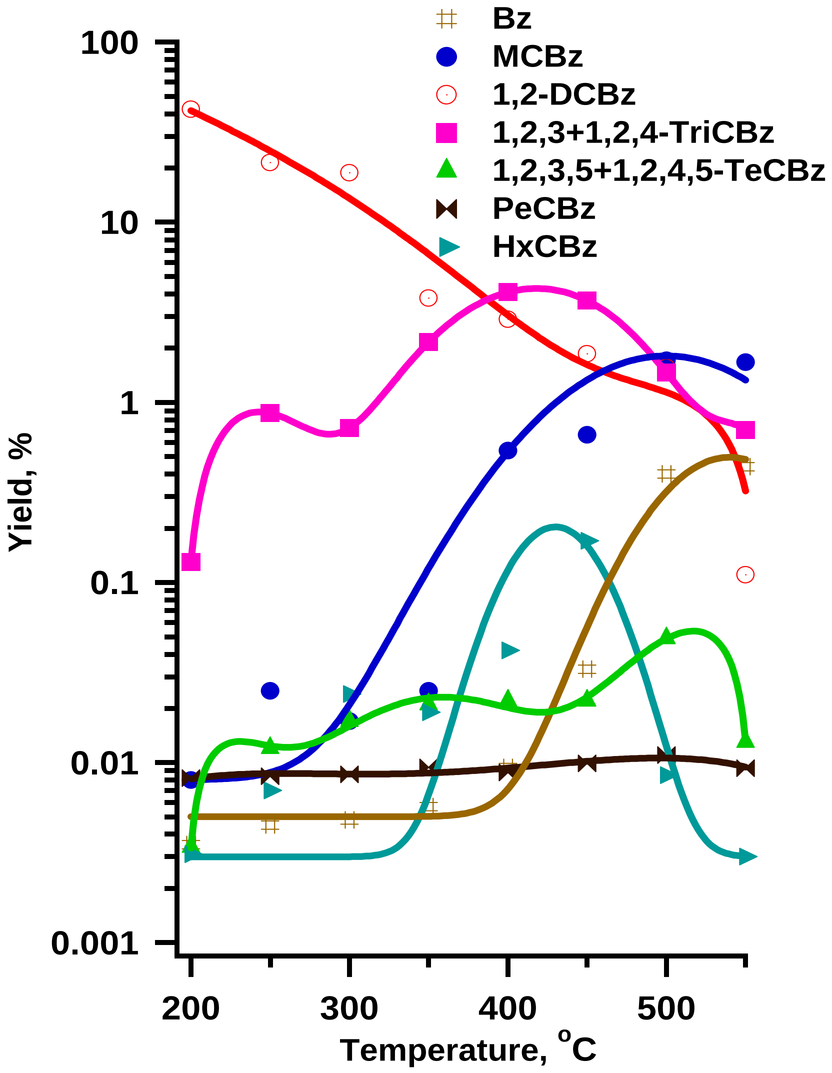


Figure 3.13. Product Yields of Chlorobenzenes from the Pyrolysis of 1,2-DCBz over Fe_2O_3/Silica Surface

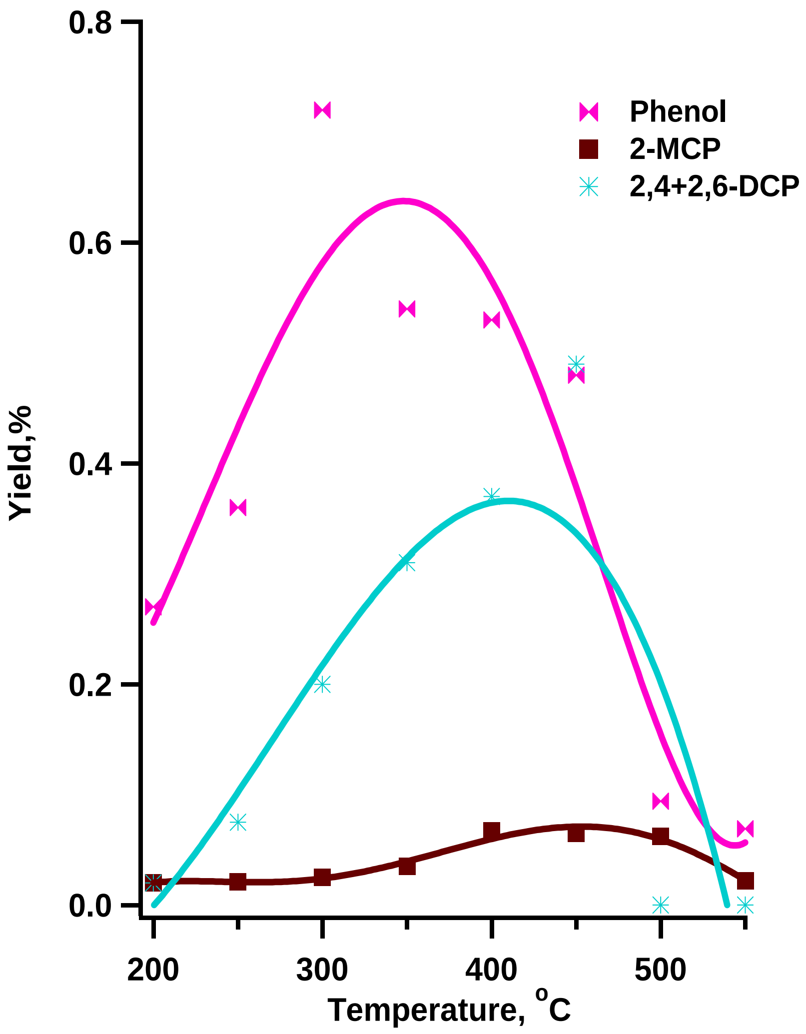


Figure 3.14. Product Yields of Chlorophenols from the Pyrolysis of 1,2-DCBz over Fe_2O_3/Silica Surface

The formation of PCDD/F products from thermal decomposition of 1,2-DCBz under pyrolytic conditions over Fe_2O_3/silica surface are depicted in **Figure 3.15**. No dibenzo-*p*-dioxin (DD) or other PCDDs were detected. However, 4,6-dichlorodibenzofuran (4,6-DCDF) and dibenzofuran (DF) were both observed with equal maximum yields of 0.070% at 300 °C and 400 °C, respectively.

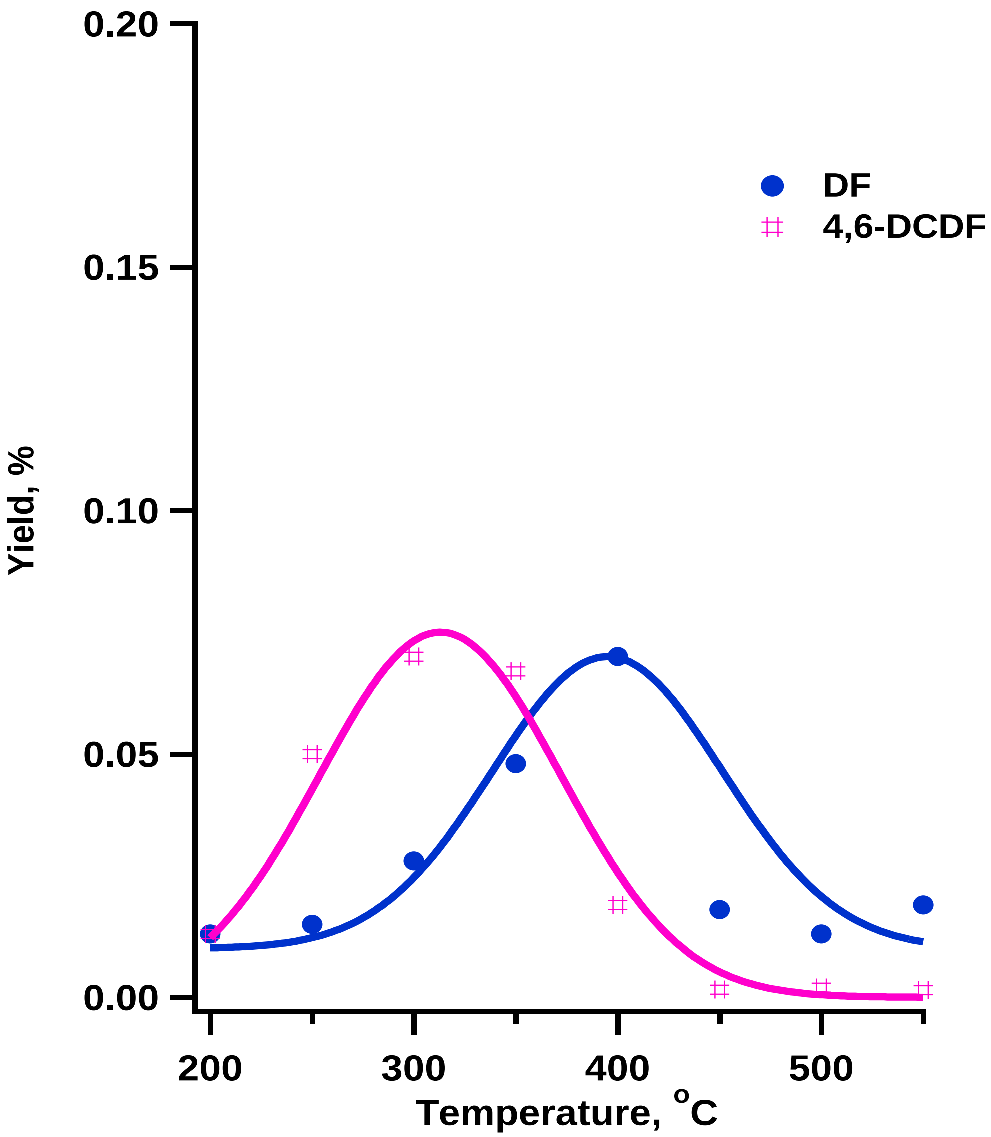


Figure 3.15 Yields of PCDD/Fs from the Pyrolysis of 1,2-DCBz over Fe_2O_3/Silica Surface

Table 3.5 Dioxin and Non-Dioxin Products from Pyrolysis of 1,2-Dichlorobenzene over Fe_2O_3/Silica Surface								
	Reaction Temperature, ^oC							
Products	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**
Benzene	**0.0035**	**0.0045**	**0.0048**	**0.0057**	**0.0094**	**0.033**	**0.40**	**0.44**
Monochlorobenzene	**0.0080**	**0.025**	**0.017**	**0.025**	**0.54**	**0.66**	**1.7**	**1.7**
1,2-Dichlorobenzene	**42**	**21**	**19**	**3.8**	**2.9**	**1.9**	**1.6**	**0.11**
1,2,3 +1,2,4-Trichlorobenzene	**0.13**	**0.87**	**0.72**	**2.2**	**4.1**	**3.7**	**1.5**	**0.70**
1,2,3,4 +1,2,3,5-Tetrachlorobenzene	**0.0034**	**0.012**	**0.017**	**0.021**	**0.022**	**0.022**	**0.049**	**0.013**
Pentachlorobenzene	**0.0082**	**0.0084**	**0.0086**	**0.0094**	**0.0088**	**0.0099**	**0.011**	**0.0093**
Hexachlorobenzene	**0.0031**	**0.0070**	**0.024**	**0.019**	**0.042**	**0.17**	**0.0085**	**0.0030**
Naphthalene	**0.0090**	**0.0091**	**0.010**	**0.025**	**0.36**	**0.34**	**0.0074**	**0.0036**
Biphenyl	**0.0030**	**0.0092**	**0.053**	**0.17**	**0.35**	**0.11**	**0.075**	**0.022**
Phenol	**0.27**	**0.36**	**0.72**	**0.54**	**0.53**	**0.48**	**0.094**	**0.069**
2-Monochlorophenol	**0.020**	**0.021**	**0.025**	**0.035**	**0.067**	**0.065**	**0.062**	**0.022**
2,4+2,6-Dichlorophenol	**0.020**	**0.075**	**0.20**	**0.31**	**0.37**	**0.49**	**bdl**	**bdl**
Dibenzofuran	**0.013**	**0.015**	**0.028**	**0.048**	**0.070**	**0.018**	**0.013**	**0.019**
4,6-Dichlorodibenzofuran	**0.013**	**0.050**	**0.070**	**0.067**	**0.019**	**0.0016**	**0.0020**	**0.0015**
bdl- Below Detection Limit								

3.3.2. Results under Oxidative Conditions

The results for the thermal degradation of 1,2-DCBz under oxidative conditions are presented. 74% of the initial amount of 1,2-DCBz was decomposed at 200 ^{o}C and 1,2,3- and 1,2,4-trichlorobenzenes (1,2,3+ 1,2,4-TriCBz), which formed a 0.40% impurity in the 1,2-DCBz, first decomposed to 0.26 % at 200 °C then increased gradually to a maximum yield of 0.99% at 350 °C. Benzene (Bz), monochlorobenzene (MCBz), tetrachlorobenzenes (1,2,3,4+1,2,3,5 TeCBzs), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) were detected with maximum yields of 0.15% at 350 °C, 0.097% at 450 °C, 0.13% at 400 °C, 0.21% at 350 °C and 0.020% at 250 °C, respectively. The yields of the chlorobenzenes from the decomposition of 1,2-DCBz over an Fe_2O_3/silica surface under oxidative conditions are depicted in **Figure 3.16.**

The yields of phenol, and 2-monochlorophenol (2-MCP) increased with increasing temperature, achieving a maximum of 1.5% at 400 ^{o}C, and 0.24% at 500 ^{o}C, respectively. The maximum yields of 2,4-, and 2,6-dichlorophenols (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenols (2,3,6+2,4,6-TCP) observed were 1.3% at 500 °C, and 0.40% at 400 ^{o}C, respectively. **Figure 3.17** depicts the profiles of chlorophenol products from oxidation of 1,2-DCBz over an Fe_2O_3/silica surface.

Less significant yields of biphenyl, chloronaphthalene and naphthalene were detected with maximum yields of 0.035%, 0.031%, and 0.32%, respectively at 350 ^{o}C. Trace amounts of bezoquinone (BQ) and catechol (CT) were detected both achieving maximum yields of <0.010% at 350-400 °C. The yields of PCDD/F products from thermal oxidation of 1,2-DCBz over an Fe_2O_3/silica surface are depicted in **Figure 3.18**. No dibenzo-*p*-dioxin (DD) or other PCDDs were detected. However, 4,6-dichlorodibenzofuran (4,6-DCDF) and dibenzofuran (DF) were observed with maximum yields of 0.36% at 300 ^{o}C and 0.23% at 450 ^{o}C, respectively.

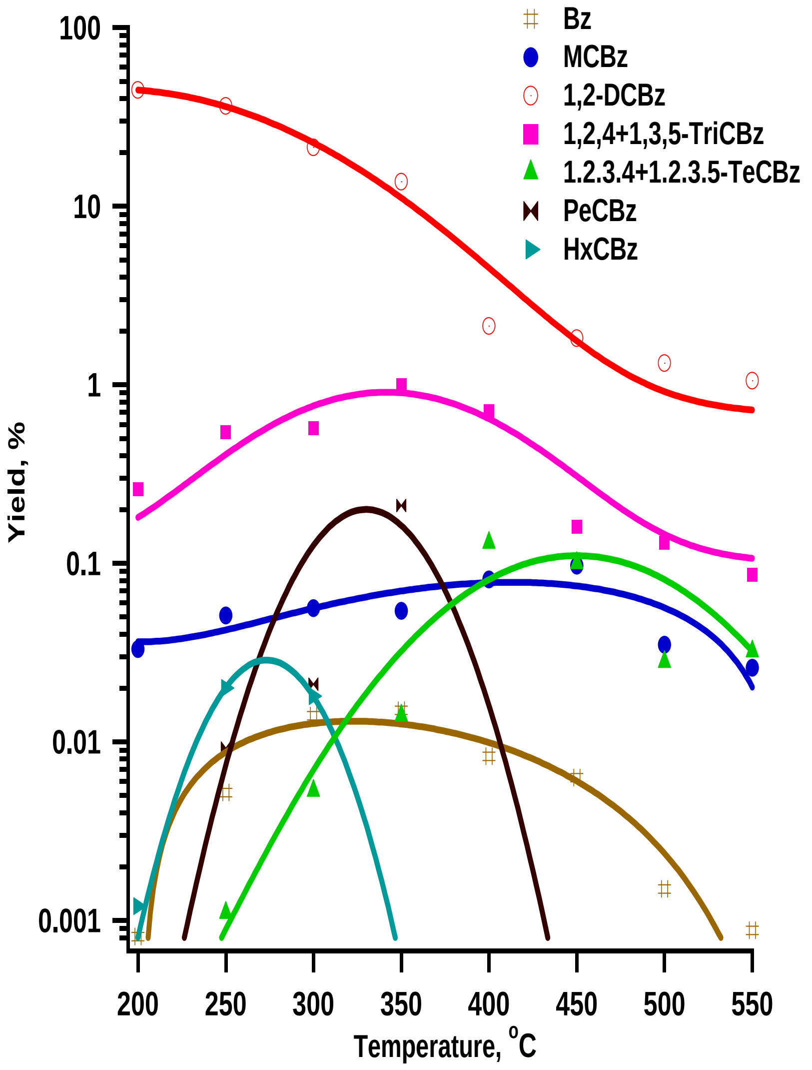


Figure 3.16 Product Yields of Chlorobenzenes from the Oxidation of 1,2-DCBz over Fe_2O_3/Silica Surface

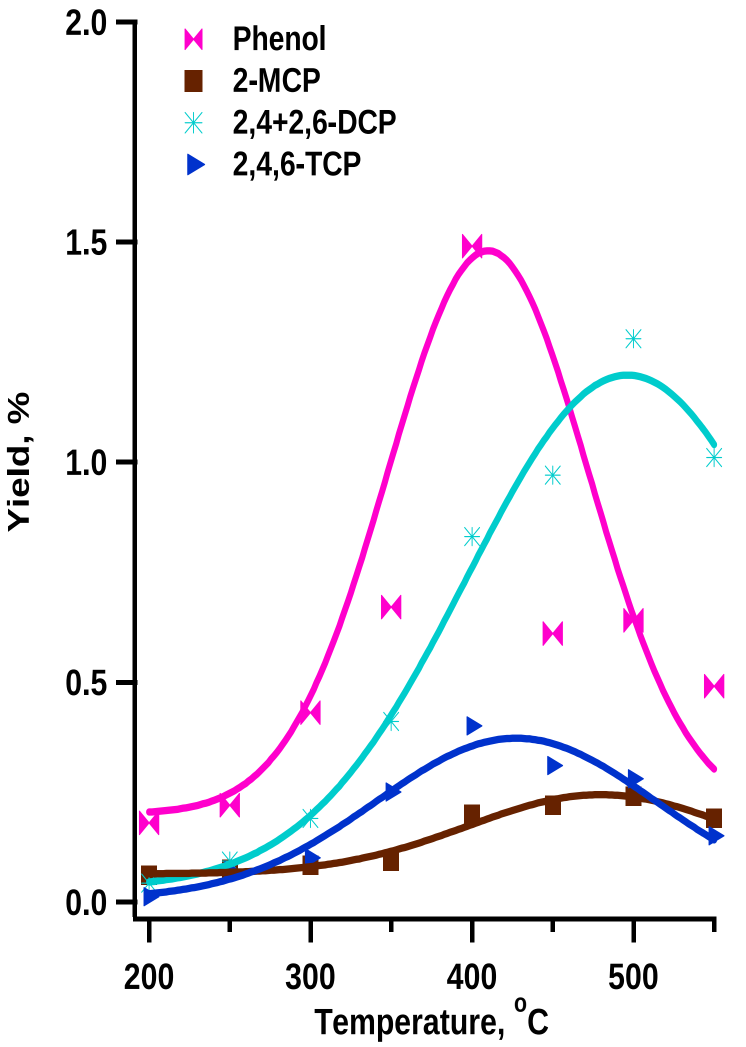


Figure 3.17. Product Yields of Chlorophenols from the Oxidation of 1,2-DCBz over Fe_2O_3/Silica Surface

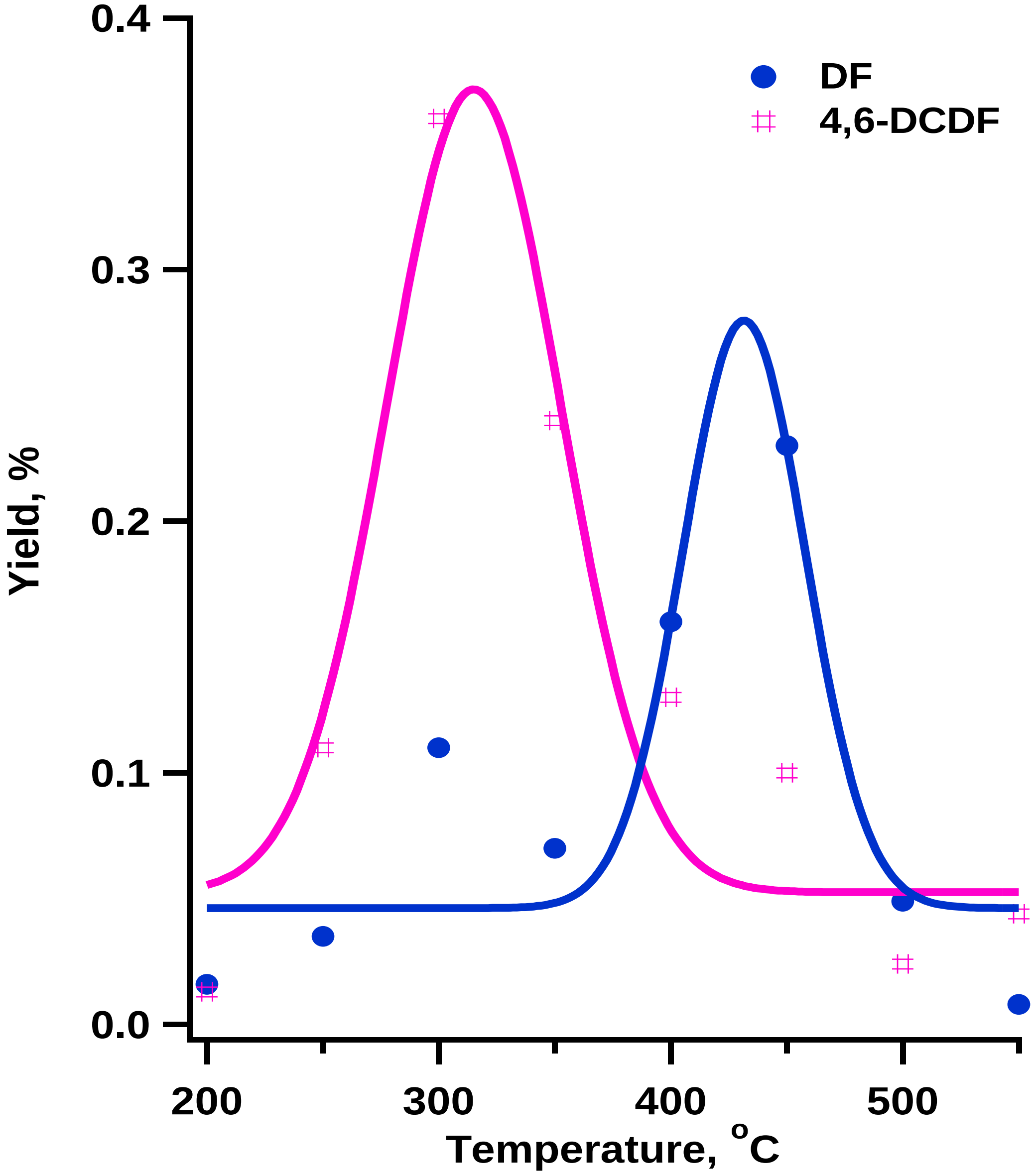


Figure 3.18 Yields of PCDD/Fs from the Oxidation of 1,2-DCBz over Fe_2O_3/Silica

Table 3.6 Dioxin and Non-Dioxin Products from Oxidation of 1,2-Dichlorobenzene over Fe_2O_3/silica Surface

	Reaction Temperature, °C							
Products	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**
Benzene	**0.00081**	**0.0052**	**0.014**	**0.015**	**0.0083**	**0.0063**	**0.0015**	**0.00088**
Monochlorobenzene	**0.033**	**0.051**	**0.056**	**0.054**	**0.081**	**0.097**	**0.035**	**0.026**
1,2-Dichlorobenzene	**26**	**22**	**21**	**14**	**2.1**	**1.8**	**0.92**	**0.65**
1,2,3 +1,2,4-Trichlorobenzene	**0.26**	**0.54**	**0.57**	**0.99**	**0.71**	**0.16**	**0.13**	**0.086**
1,2,3,4 +1,2,3,5-Tetrachlorobenzene	**bdl**	**0.0011**	**0.0053**	**0.014**	**0.13**	**0.10**	**0.028**	**0.032**
Pentachlorobenzene	**bdl**	**0.0092**	**0.021**	**0.21**	**bdl**	**bdl**	**bdl**	**bdl**
Hexachlorobenzene	**0.0012**	**0.020**	**0.018**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**
Naphthalene	**0.066**	**0.21**	**0.25**	**0.32**	**0.15**	**0.090**	**0.049**	**0.057**
Chloronaphthalene	**0.0087**	**0.017**	**0.023**	**0.031**	**0.010**	**0.0078**	**0.0068**	**0.0079**
Biphenyl	**0.013**	**0.031**	**0.019**	**0.035**	**0.020**	**0.0075**	**0.0020**	**0.00092**
Benzoquinone	**bdl**	**0.00036**	**0.0014**	**0.0036**	**0.0018**	**0.0016**	**0.00063**	**0.00014**
Catechol	**bdl**	**0.000022**	**0.000092**	**0.00011**	**0.00033**	**0.00019**	**0.000060**	**0.000014**
Phenol	**0.18**	**0.22**	**0.43**	**0.67**	**1.5**	**0.61**	**0.64**	**0.49**
2-Monochlorophenol	**0.061**	**0.075**	**0.083**	**0.093**	**0.20**	**0.22**	**0.24**	**0.19**
2,4+2,6-Dichlorophenol	**0.043**	**0.093**	**0.19**	**0.41**	**0.83**	**0.97**	**1.3**	**1.0**
2,3,6+2,4,6-Trichlorophenol	**0.012**	**0.071**	**0.10**	**0.25**	**0.40**	**0.31**	**0.28**	**0.15**
Dibenzofuran	**0.016**	**0.035**	**0.11**	**0.070**	**0.16**	**0.23**	**0.048**	**0.0080**
4,6-Dichlorodibenzofuran	**0.013**	**0.11**	**0.36**	**0.24**	**0.13**	**0.10**	**0.024**	**0.044**

bdl- Below Detection Limit

3.4. Copper Catalyzed Thermal Degradation of 2-Monochlorophenol and 1,2-Dichlorobenzene Mixtures

3.4.1 Results under Pyrolytic Conditions

I. Results from a 1:10 Mixture of 2-MCP and 1,2-DCBz, Respectively

At 200 °C, 89% and 35% of 2-MCP and 1,2-DCBz respectively, were decomposed. Chlorobenzenes products formed were monochlorobenzene (MCBz), 1,2,3- and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4- and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz) pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) with maximum yields of 4.9% at 200 °C, 13% at 300 °C, 12% at 350 °C, 0.13% at 500 °C and 0.021% at 350 °C, respectively. Benzene formation increased with increasing temperature achieving a maximum yield of 0.11% at 400 °C. **Figure 3.19** depicts the yields of chlorobenzenes observed from pyrolytic thermal degradation a 1: 10 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface.

Chlorophenols products observed includes phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 3.3% at 350 °C, 2.6% at 300 °C, and 1.2% at 350 °C, respectively. The yields of chlorophenols observed from pyrolytic thermal degradation of a 1: 10 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface are depicted in **Figure 3.20.** Other non-dioxins observed were naphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) with maximum yields of 0.39% at 250 °C, 0.080% at 400 °C, 0.026% at 350 °C and < 0.010% at 250 °C, respectively.

Dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF) were the only PCDF products formed at maximum yields of 0.23% at 400 °C and 0.25% at 350 °C, respectively. Low yields of dibenzo-*p*-dioxin (DD) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) were detected at maximum yields of 0.14% at 200 °C to 300 °C, and 0.062% at 250 °C, respectively.

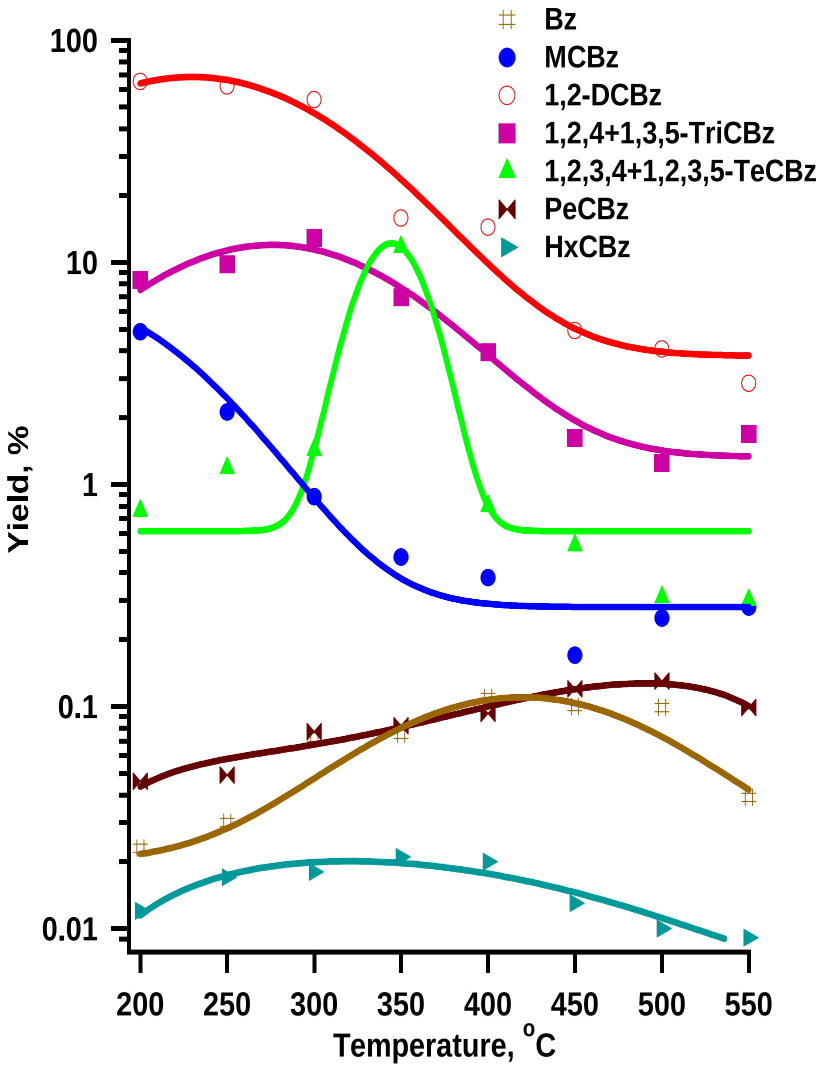


Figure 3.19 Product Yields of Chlorobenzenes from the Pyrolysis of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

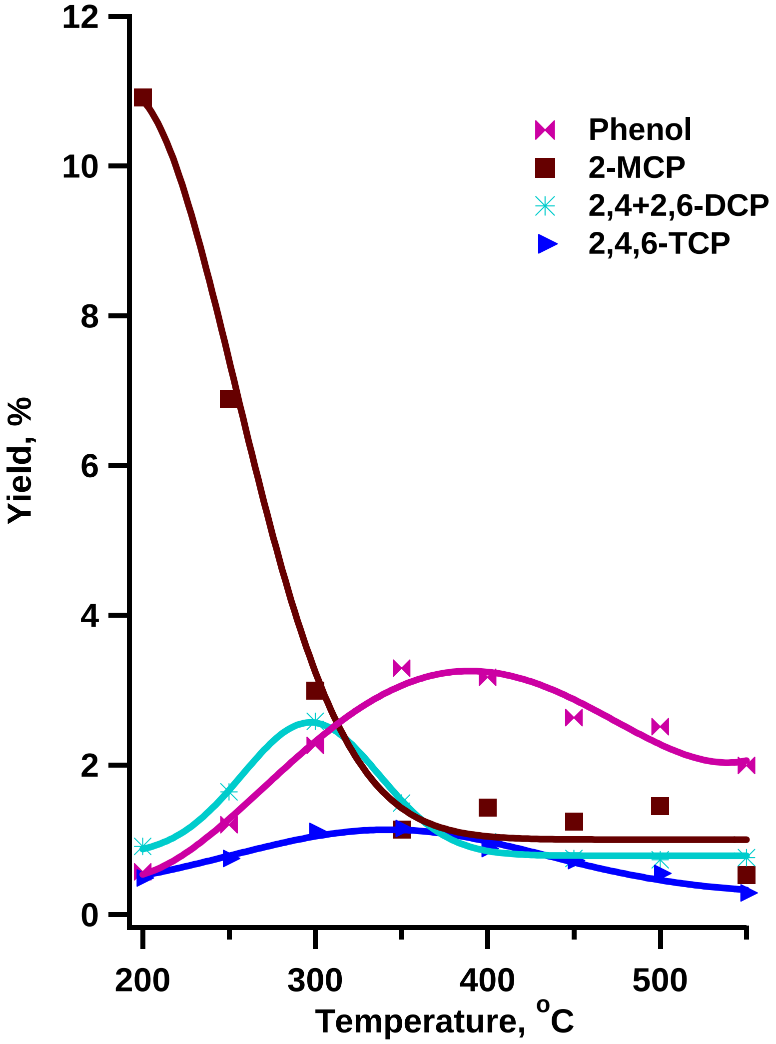


Figure 3.20 Product Yields of Chlorophenols from the Pyrolysis of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

Dibenzo-*p*-dioxin (DD) was not detected at temperature above 300 °C and 1-monochlorodibenzo-p-dioxin (1-MCDD) was below detection limit at temperatures exceeding 450 °C. The total yield of PCDF products for the whole temperature range studied was 4x higher than PCDDs. The yields of dioxin products observed from pyrolytic thermal degradation of a 1:10 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface are depicted in **Figure 3.21.**

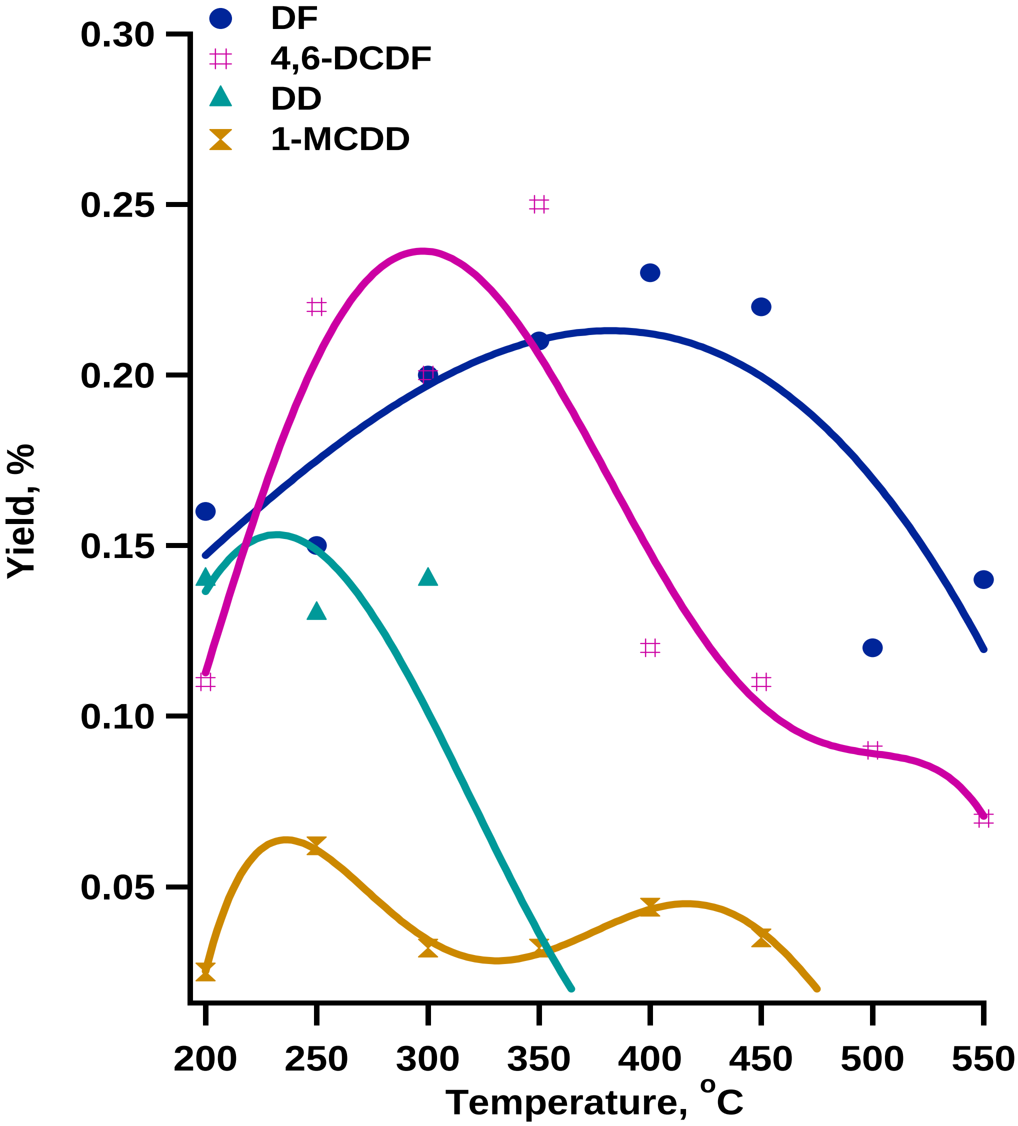


Figure 3.21 Product Yields of PCDD/Fs from the Pyrolysis of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

II. Results from a 1:1 Mixture ratio of 2-MCP and 1,2-DCBz, Respectively

Decomposition at 200 °C achieved 60% and 55% destruction of 2-MCP and 1,2-DCBz, respectively. Monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) were the chlorobenzenes observed with maximum yields of 1.9% at 200 °C, 10% at 300 °C, 1.6% at 300 °C, 0.29% at 450 °C and 0.087% at 350 °C, respectively. Yield of benzene (Bz) increased with increasing temperature reaching a maximum yield of 0.18% at 450 °C. **Figure 3.22** depicts the yields of chlorobenzenes observed from pyrolytic thermal degradation a 1: 1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface.

Phenolic products observed includes phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 2.2% at 350 °C, 8.1% at 300 °C, and 5.7% at 350 °C, respectively. Other non-dioxins observed were naphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) with maximum yields of 0.62% at 350 °C, 0.13% at 350-400 °C, 0.21% at 500 °C and < 0.01% at 350 °C, respectively. The yields of chlorophenols observed from pyrolytic thermal degradation of a 1: 1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface are depicted in **Figure 3.23.**

Significant yields of PCDD/Fs were observed from thermal degradation of a 50:50 mixture of 2-MCP and 1,2-DCBz. Dibenzo-*p*-dioxin (DD) was initially detected at 250 °C and increased to achieve a maximum yield of 0.18% at 350 °C. Formation of 4,6-dichlorodibenzofuran (4,6-DCDF) was not detected below 300 °C and increased reaching a maximum yield of 0.36% at 500 °C. Other dioxin products observed were dibenzofuran (DF) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) with maximum yields of 0.30% at 500 °C and 0.048% at 400 °C, respectively.

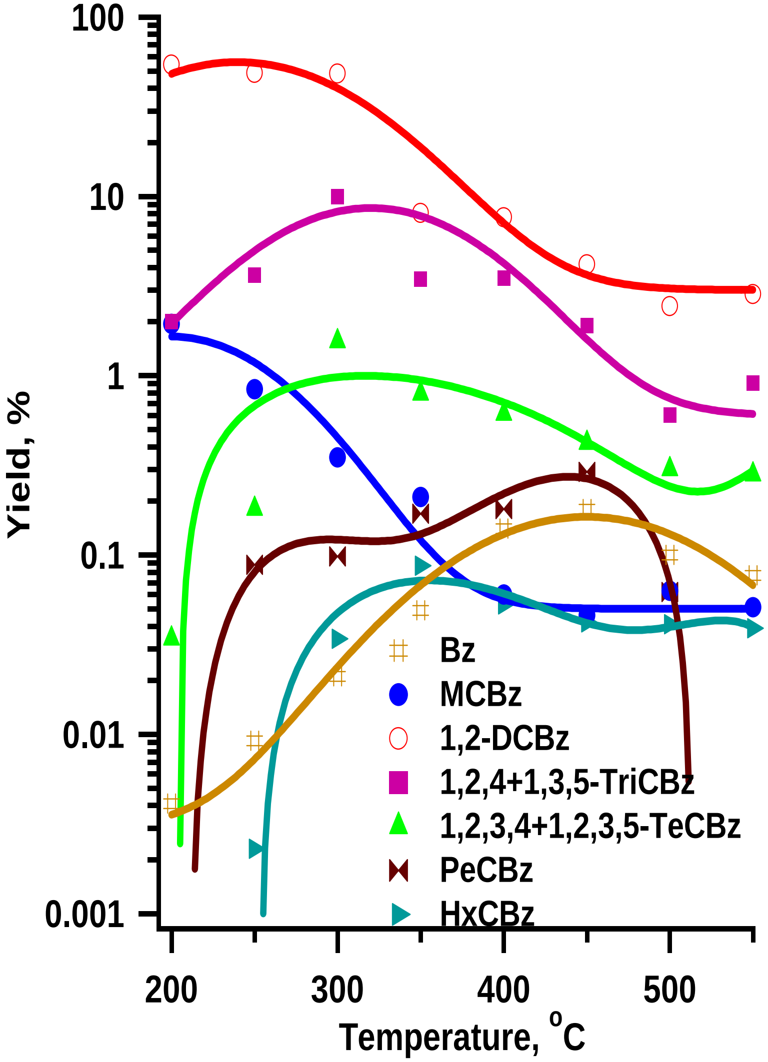


Figure 3.22 Product Yields of Chlorobenzenes from the Pyrolysis of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

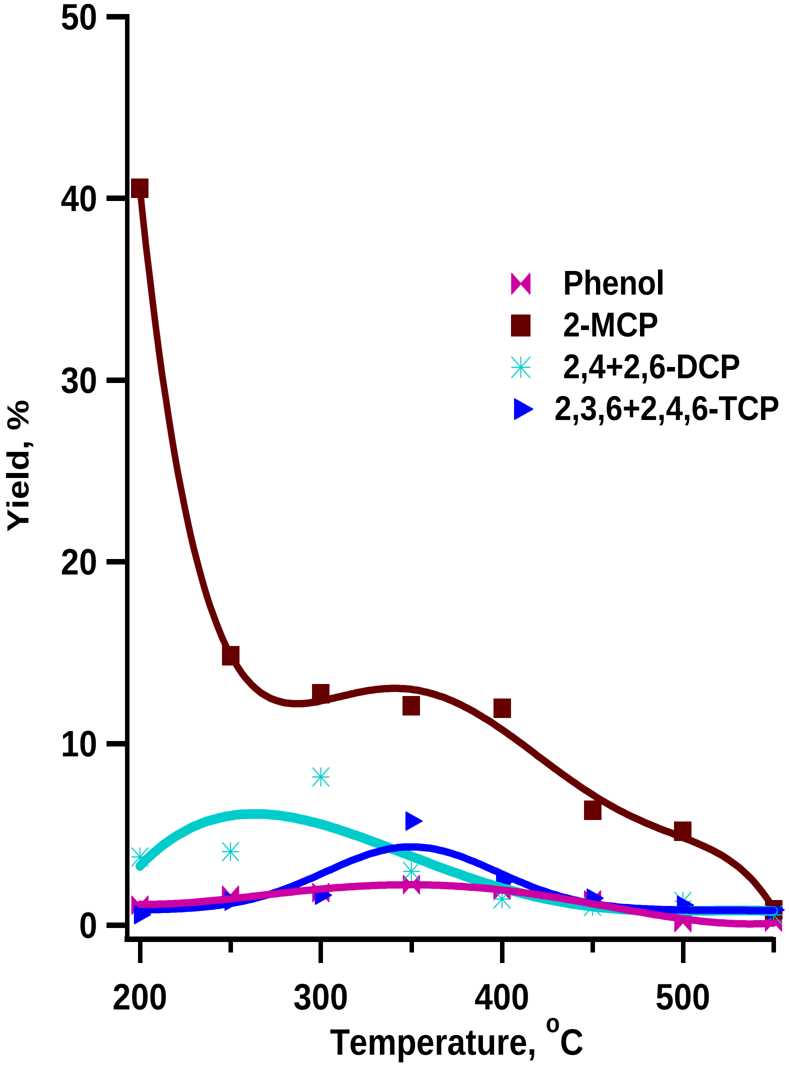


Figure 3.23 Product Yields of Chlorophenols from the Pyrolysis of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

The total yield of PCDFs observed from 200 °C to 500 °C, was 11x higher than the total yields of PCDDs detected. The product yields of dioxins observed from pyrolytic thermal degradation of a 1: 1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface are depicted in **Figure 3.24.**

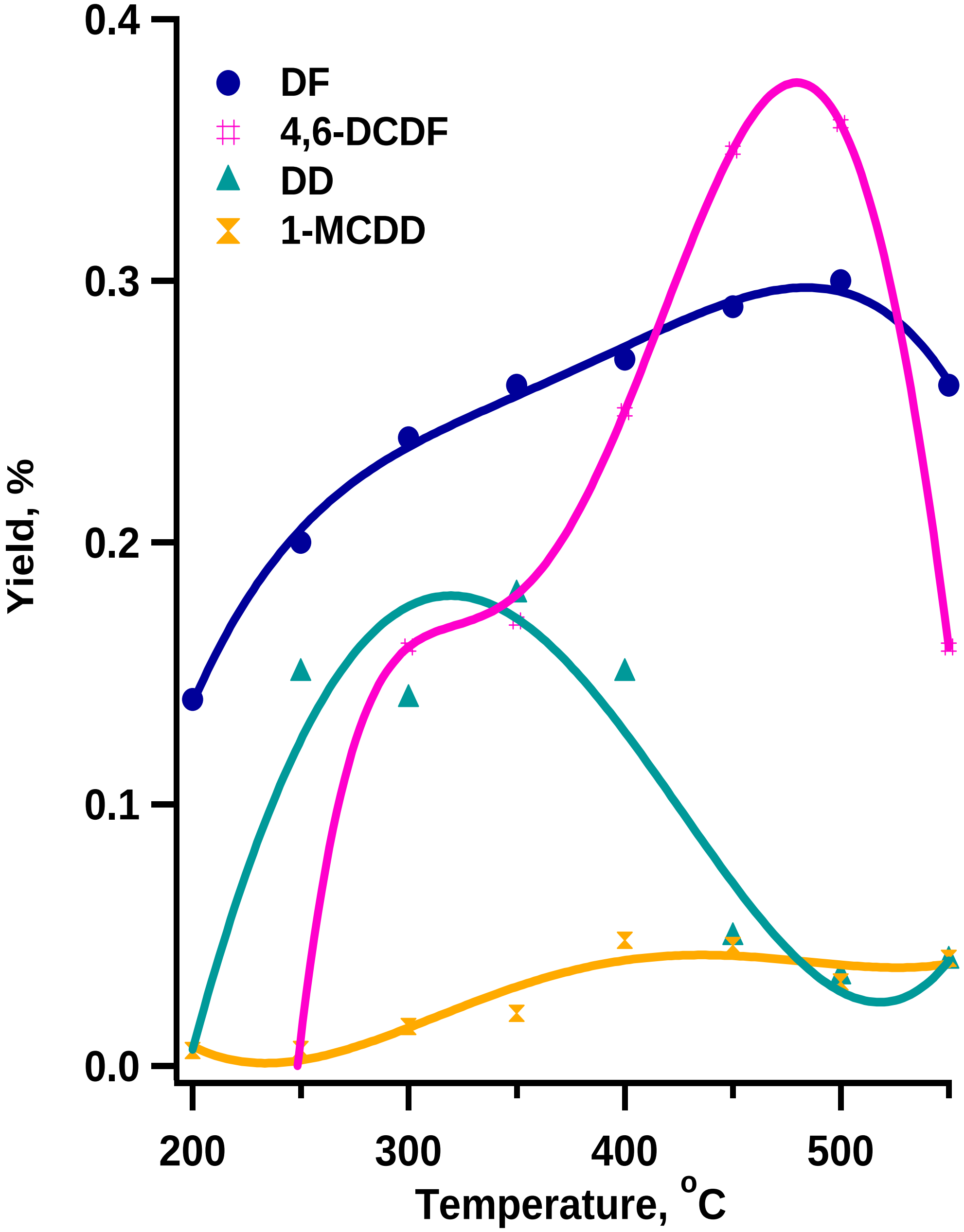


Figure 3.24 Product Yields of PCDD/Fs from the Pyrolysis of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

III. Results from a 10:1 Mixture of 2-MCP and1,2-DCBz, Respectively

The thermal degradation of 2-MCP and 1,2-DCBz tracked one another increasing gradually with rising temperature achieving 96% and 98% destruction at 550 °C, respectively. Benzene (Bz) yield increased from 0.11% at 200 °C to 0.33% at 300 °C and remained fairly constant before declining to 0.19% at 450 °C. Chlorobenzenes formed includes monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) with maximum yields of 1.4% at 250 °C, 1.9% at 350 °C, 0.92% at 400 °C, 0.081% at 450 °C and 0.067% at 250 °C, respectively. **Figure 3.25** depicts the yields of chlorobenzenes observed from pyrolytic thermal degradation of a 10:1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface.

Phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) were the chlorophenol products detected with maximum yields of 9.8% at 400 °C, 4.8% at 350 °C, and 3.2% at 300 °C, respectively. Naphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) were the other non-dioxins products formed with maximum yields of 1.2% at 400 °C, 0.054% at 350 °C , 0.019% at 250 °C and < 0.01% at 300 °C, respectively. The yields of chlorophenols observed from pyrolytic thermal degradation of a 10: 1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface are depicted in **Figure 3.26.**

The formation of PCDD/F products was observed from the lowest temperature of this study at 200 °C to 550 °C. The dioxin products detected were dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF), dibenzo-*p*-dioxin (DD) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) with maximum yields of 0.19% at 450 °C, 0.17% at 250 °C, 0.15% at 400 °C and 0.091% at 300 °C, respectively.

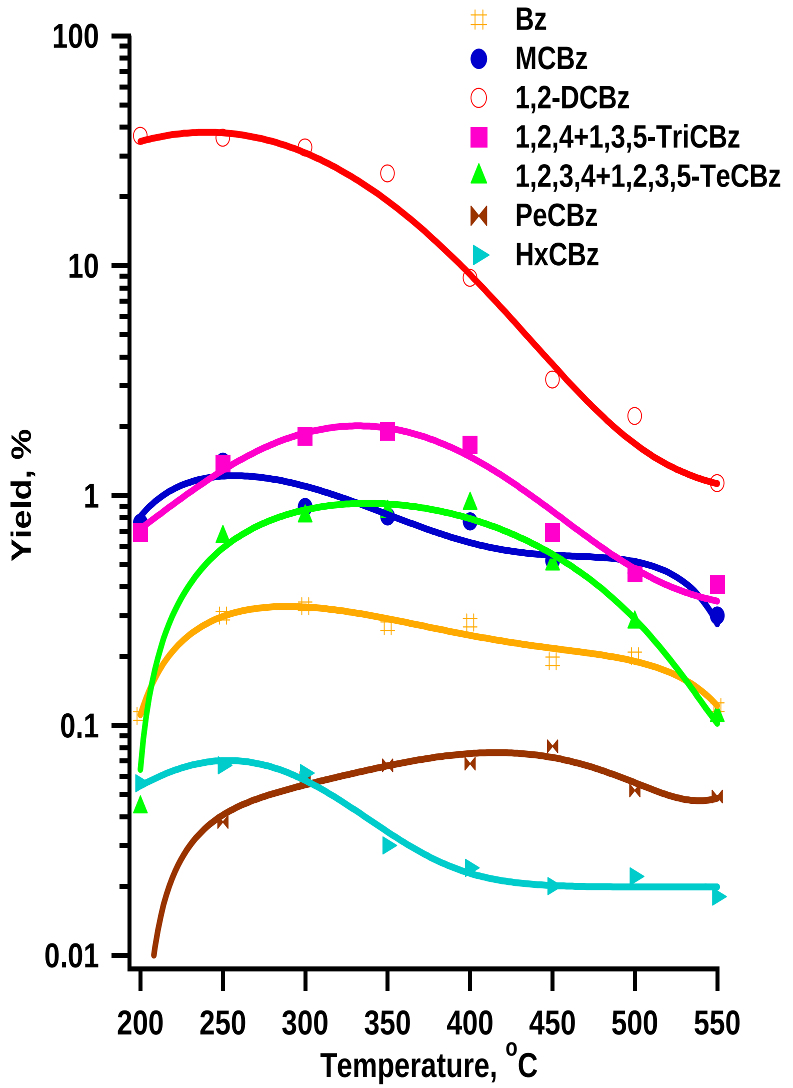


Figure 3.25 Product Yields of Chlorobenzenes from the Pyrolysis of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

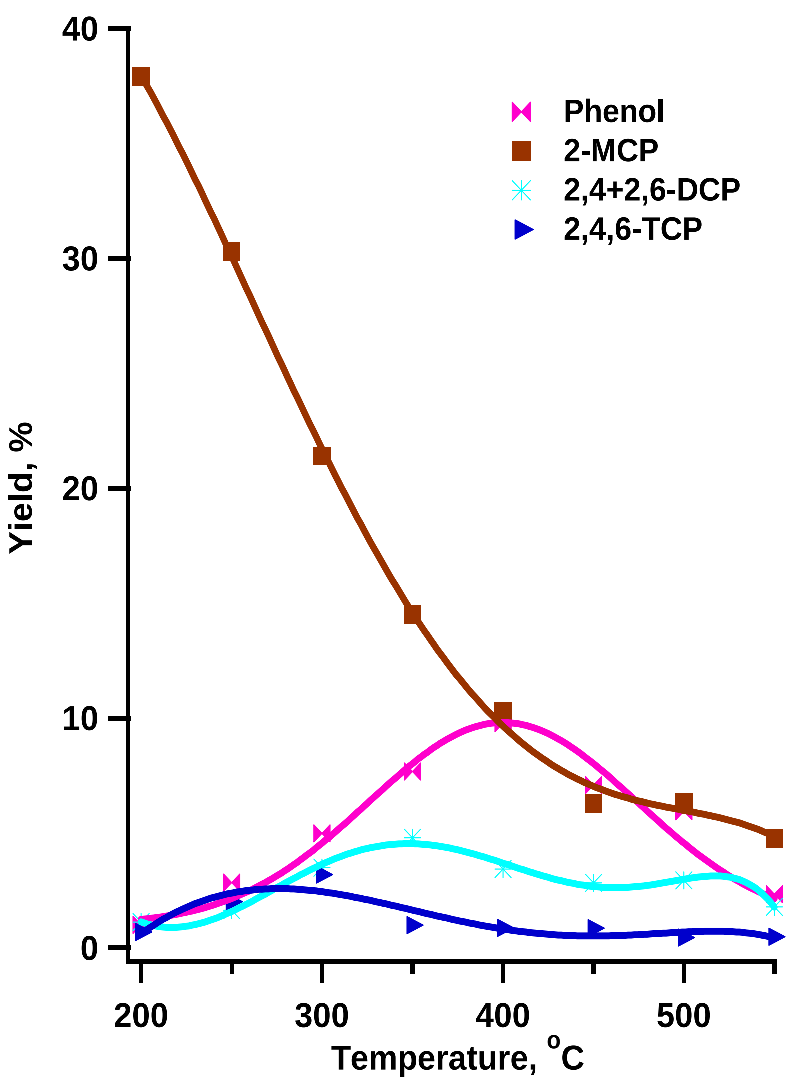


Figure 3.26 Product Yields of Chlorophenols from the Pyrolysis of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

The formation of PCDD/F products was observed from the lowest temperature of this study at 200 °C to 550 °C. The dioxin products detected were dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF), dibenzo-*p*-dioxin (DD) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) with maximum yields of 0.19% at 450 °C, 0.17% at 250 °C, 0.15% at 400 °C and 0.091% at 300 °C, respectively. PCDD/F product yields observed from pyrolytic thermal degradation of a 10: 1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface are depicted in **Figure 3.27.** The PCDD to PCDF ratio observed was 0.63 **Table 3.7 and Table 3.8** depicts dioxin and non-dioxin products, respectively from pyrolysis of 1,2-dichlorobenzene and 2-monochlorophenol mixtures over CuO/silica surface.

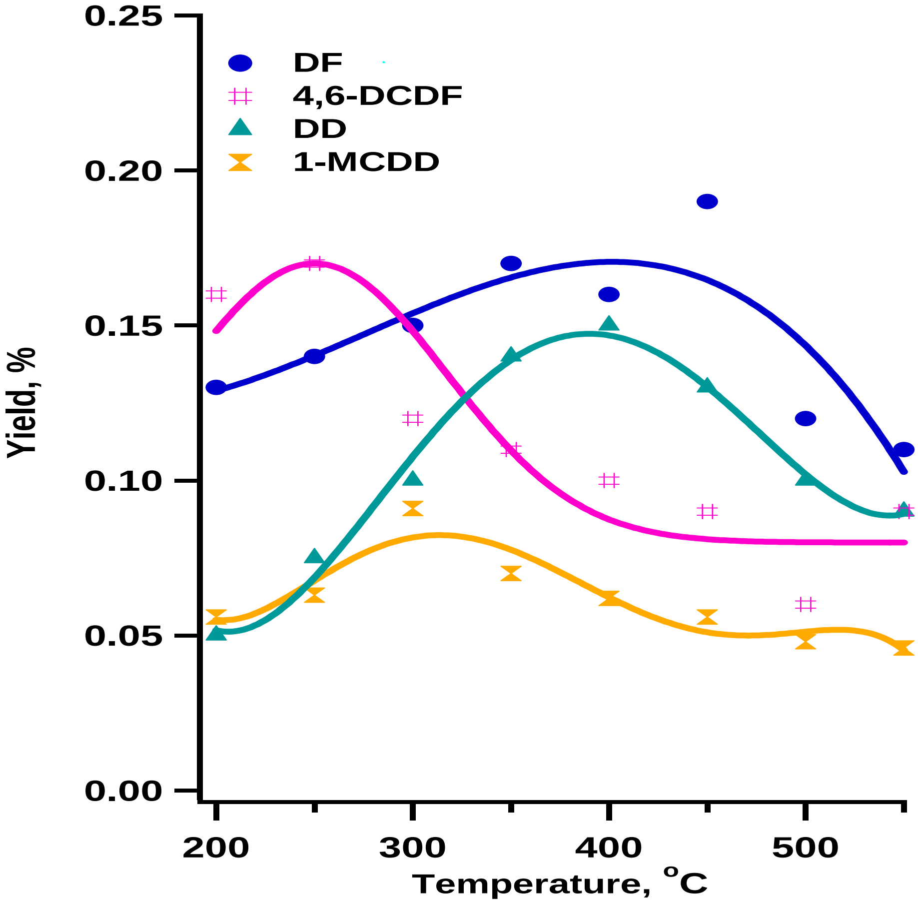


Figure 3.27 Product Yields of PCDD/Fs from the Pyrolysis of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

Table 3.7 Non-Dioxin Products from Pyrolysis of 1,2-Dichlorobenzene and 2-Monochlorophenol Mixtures over CuO/Silica Surface

Non-Dioxin Products		2-MCP/1,2-DCBz	Reaction Temperature, °C							
			200	250	300	350	400	450	500	550
1	Benzene	0.1	0.023	0.030	0.073	0.075	0.11	0.10	0.099	0.039
		1.0	0.0041	0.0092	0.021	0.049	0.14	0.18	0.10	0.077
		10	0.11	0.30	0.33	0.27	0.28	0.19	0.20	0.12
2	Monochlorobenzene	0.1	4.9	2.1	0.88	0.47	0.38	0.17	0.25	0.28
		1.0	1.9	0.84	0.35	0.21	0.060	0.046	0.063	0.051
		10	0.76	1.4	0.89	0.81	0.77	0.52	0.46	0.30
3	1,2-Dichlorobenzene	0.1	65	62	54	16	14	5.0	4.1	2.9
		1.0	54	49	48	8.1	7.6	4.2	2.4	2.9
		10	37	36	33	25	8.8	3.2	2.2	1.1
4	1,2,3+1,2,4-Trichlorobenzene	0.1	8.4	9.8	13	6.9	3.9	1.6	1.3	1.7
		1.0	2.0	3.6	10	3.5	3.5	1.9	0.60	0.91
		10	0.69	1.4	1.8	1.9	1.7	0.69	0.46	0.41
5	1,2,3,4+1,2,3,5-Tetrachlorobenzene	0.1	0.76	1.2	1.4	12	0.80	0.53	0.31	0.30
		1.0	0.034	0.18	1.6	0.79	0.61	0.42	0.30	0.28
		10	0.044	0.66	0.81	0.85	0.92	0.50	0.28	0.11
6	Pentachlorobenzene	0.1	0.046	0.049	0.077	0.082	0.093	0.12	0.13	0.099
		1.0	bdl	0.088	0.098	0.17	0.18	0.29	0.062	bdl
		10	bdl	0.038	0.059	0.067	0.068	0.081	0.052	0.049
5	Hexachlorobenzene	0.1	0.012	0.017	0.018	0.021	0.020	0.013	0.010	0.0091
		1.0	bdl	0.0023	0.034	0.087	0.053	0.042	0.041	0.039
		10	0.056	0.067	0.062	0.030	0.024	0.020	0.022	0.018
6	Phenol	0.1	0.57	1.2	2.3	3.3	3.2	2.6	2.5	2.0
		1.0	1.1	1.7	1.8	2.2	1.9	1.4	0.13	0.16
		10	1.0	2.8	5.0	7.7	9.8	7.1	5.9	2.3
7	2-Monochlorophenol	0.1	11	6.9	3.0	1.1	1.4	1.2	1.5	0.53
		1.0	41	15	13	12	12	6.3	5.2	0.85
		10	38	30	21	15	10	6.3	6.3	4.8

Table 3.7 Con’d

8	**2,4+2,6-Dichlorophenol**	**0.1**	**0.91**	**1.6**	**2.6**	**1.5**	**0.97**	**0.75**	**0.73**	**0.76**
		1.0	**3.8**	**4.1**	**8.1**	**2.9**	**1.4**	**1.0**	**1.3**	**0.55**
		10	**1.1**	**1.6**	**3.5**	**4.8**	**3.4**	**2.8**	**2.9**	**1.8**
9	**2,3,6+2,4,6-Trichlorophenol**	**0.1**	**0.49**	**0.75**	**1.1**	**1.2**	**0.88**	**0.72**	**0.55**	**0.29**
		1.0	**0.57**	**1.3**	**1.6**	**5.7**	**2.4**	**1.5**	**1.1**	**0.83**
		10	**0.68**	**2.0**	**3.2**	**0.99**	**0.86**	**0.85**	**0.45**	**0.48**
10	**Naphthalene**	**0.1**	**0.34**	**0.39**	**0.22**	**0.21**	**0.20**	**0.19**	**0.18**	**0.20**
		1.0	**0.44**	**0.34**	**0.46**	**0.62**	**0.21**	**0.17**	**0.11**	**0.063**
		10	**0.39**	**1.0**	**0.98**	**1.1**	**1.2**	**0.68**	**0.37**	**0.26**
11	**Chloronapthalene**	**0.1**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**
		1.0	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**
		10	**0.10**	**0.13**	**0.18**	**0.15**	**0.13**	**0.11**	**0.088**	**0.054**
12	**Biphenyl**	**0.1**	**0.0056**	**0.035**	**0.077**	**0.079**	**0.080**	**0.070**	**0.045**	**0.032**
		1.0	**0.019**	**0.063**	**0.095**	**0.13**	**0.13**	**0.12**	**0.032**	**0.038**
		10	**0.026**	**0.052**	**0.053**	**0.054**	**0.039**	**0.028**	**0.024**	**0.019**
13	**Benzoquinone**	**0.1**	**0.011**	**0.020**	**0.023**	**0.026**	**0.015**	**0.014**	**0.0087**	**0.0056**
		1.0	**0.0047**	**0.0084**	**0.013**	**0.016**	**0.018**	**0.017**	**0.021**	**0.019**
		10	**0.014**	**0.019**	**0.017**	**0.015**	**0.014**	**0.015**	**0.011**	**0.0039**
14	**Catechol**	**0.1**	**0.00070**	**0.0010**	**0.0011**	**0.0013**	**0.00078**	**0.00074**	**0.00086**	**0.00055**
		1.0	**0.00023**	**0.0012**	**0.0015**	**0.0017**	**0.0012**	**0.00091**	**0.00028**	**0.00049**
		10	**0.0013**	**0.0014**	**0.0015**	**0.00081**	**0.00077**	**0.00067**	**0.00043**	**0.00038**

bdl- Below Detection Limit

Table 3.8 Dioxin Products from Pyrolysis of 1,2-Dichlorobenzene and 2-Monochlorophenol Mixtures over Fe_2O_3/Silica Surface

Dioxin Products		**2-MCP/1,2-DCBz**	**Reaction Temperature, ^oC**							
			200	**250**	**300**	**350**	**400**	**450**	**500**	**550**
1	**DF**	**0.1**	**0.16**	**0.15**	**0.20**	**0.21**	**0.23**	**0.22**	**0.12**	**0.14**
		1.0	**0.14**	**0.20**	**0.24**	**0.26**	**0.27**	**0.29**	**0.30**	**0.26**
		10	**0.13**	**0.14**	**0.15**	**0.17**	**0.16**	**0.19**	**0.12**	**0.11**
2	**DD**	**0.1**	**0.14**	**0.13**	**0.14**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**
		1.0	**bdl**	**0.12**	**0.12**	**0.18**	**0.15**	**0.049**	**0.060**	**0.040**
		10	**0.050**	**0.075**	**0.10**	**0.14**	**0.15**	**0.13**	**0.10**	**0.090**
3	**1-MCDD**	**0.1**	**0.062**	**0.032**	**0.032**	**0.044**	**0.035**	**bdl**	**bdl**	**bdl**
		1.0	**0.0059**	**0.0062**	**0.015**	**0.020**	**0.048**	**0.046**	**0.032**	**0.041**
		10	**0.056**	**0.063**	**0.091**	**0.070**	**0.062**	**0.056**	**0.048**	**0.046**
4	**4,6-DCDF**	**0.1**	**0.11**	**0.22**	**0.20**	**0.25**	**0.12**	**0.11**	**0.090**	**0.070**
		1.0	**bdl**	**bdl**	**0.16**	**0.17**	**0.25**	**0.35**	**0.36**	**0.16**
		10	**0.16**	**0.17**	**0.12**	**0.11**	**0.10**	**0.090**	**0.060**	**0.090**

bdl- Below Detection Limit

3.4.2 Results under Oxidative Conditions

I. Results from a 1:10 Mixture of 2-MCP and 1,2-DCBz, Respectively

At 200 °C, 82% and 49% of 2-MCP and 1,2-DCBz respectively, were decomposed. Chlorobenzenes products formed were monochlorobenzene (MCBz), 1,2,3+1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4+1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) with maximum yields of 1.6% at 200 °C, 6.1% at 350 °C, 4.1% at 400 °C, 0.30% at 400 °C and 0.081% at 400 °C, respectively. Benzene (Bz) formation increased with increasing temperature achieving a maximum yield of 0.098% at 450 °C. **Figure 3.28** depicts the yields of chlorobenzenes observed from thermal degradation of a 1: 10 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface under oxidative conditions.

Chlorophenols products detected includes phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 6.3% at 350 °C, 2.4% at 350 °C, and 2.8% at 400 °C, respectively. The yields of chlorophenols observed from thermal degradation of a 1: 10 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface under oxidative conditions are depicted in **Figure 3.29**. Other non-dioxins observed were naphthalene, chloronaphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) with maximum yields of 0.78% at 400 °C, 0.37% at 400 °C, 0.071% at 350 °C, 0.035% at 350 °C and < 0.010% at 300 °C, respectively.

Dioxin products detected were dibenzofuran (DF), 4,6-dichlorodibenzofuran (4,6-DCDF), dibenzo-*p*-dioxin (DD) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) at maximum yields of 0.51% at 500 ^{o}C 0.36% at 250 ^{o}C, 0.16% at 450 ^{o}C , and 0.23% at 300 °C, respectively.

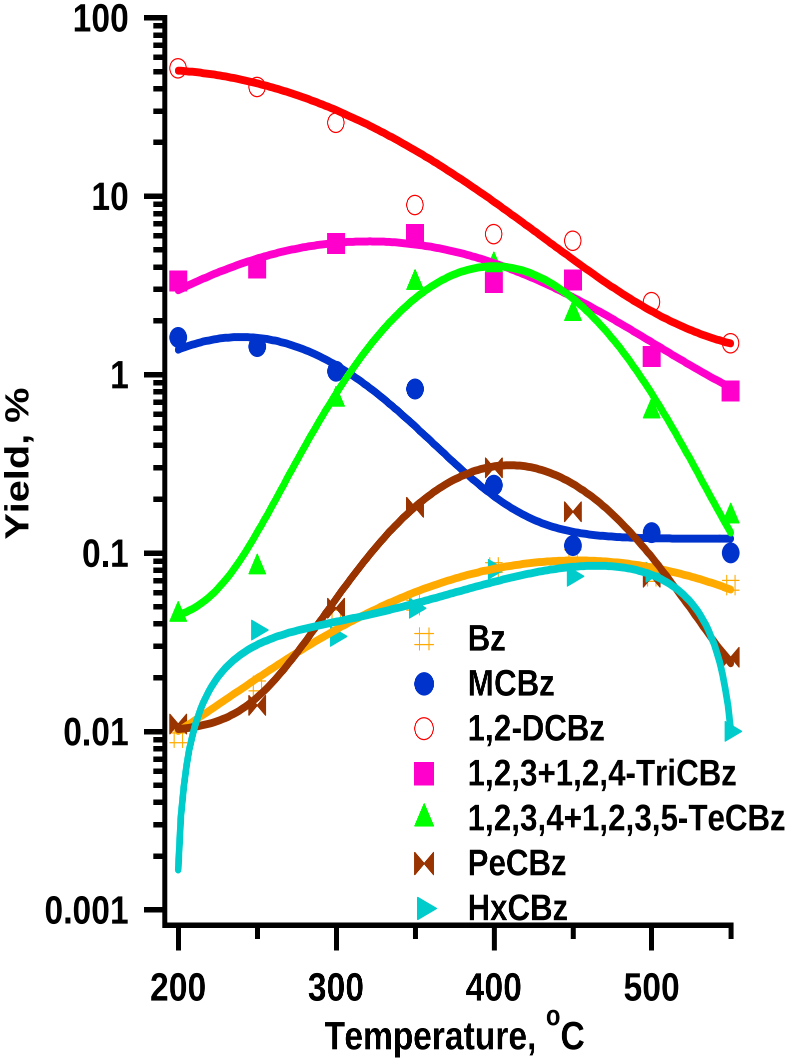


Figure 3.28 Product Yields of Chlorobenzenes from the Oxidation of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

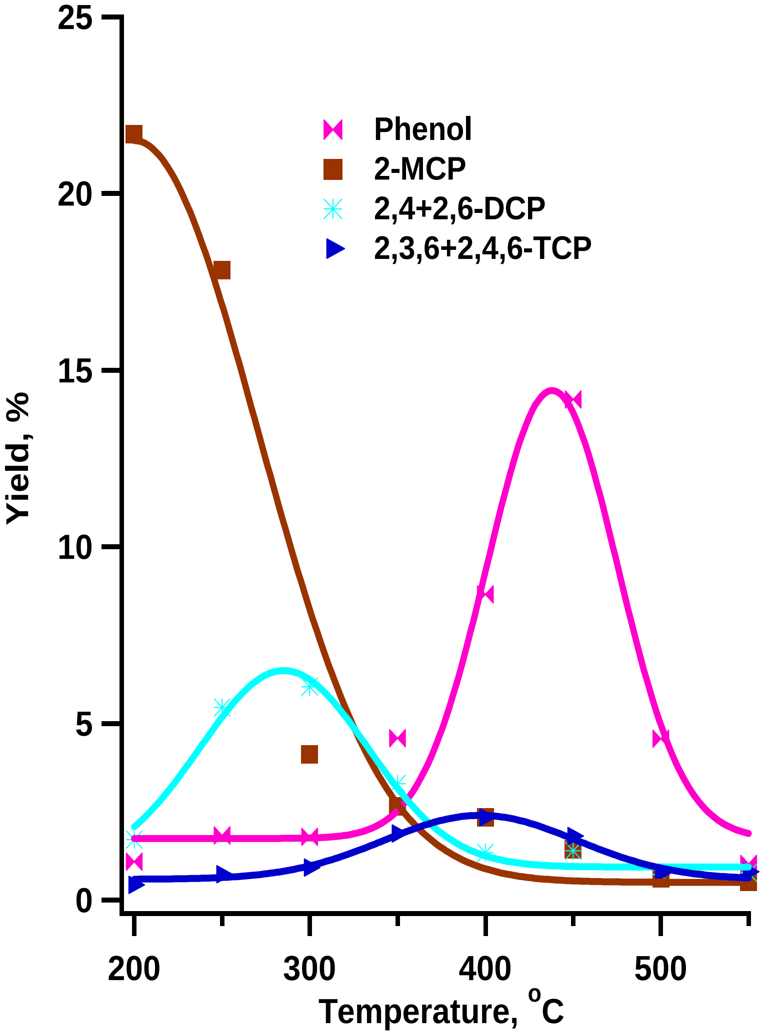


Figure 3.29 Product Yields of Chlorophenols from the Oxidation of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

The total yield of PCDF products for the whole temperature range studied was about 3.5x higher than PCDDs. The yields of dioxin products observed from thermal degradation of a 1:10 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface under oxidative conditions are depicted in **Figure 3.30.**

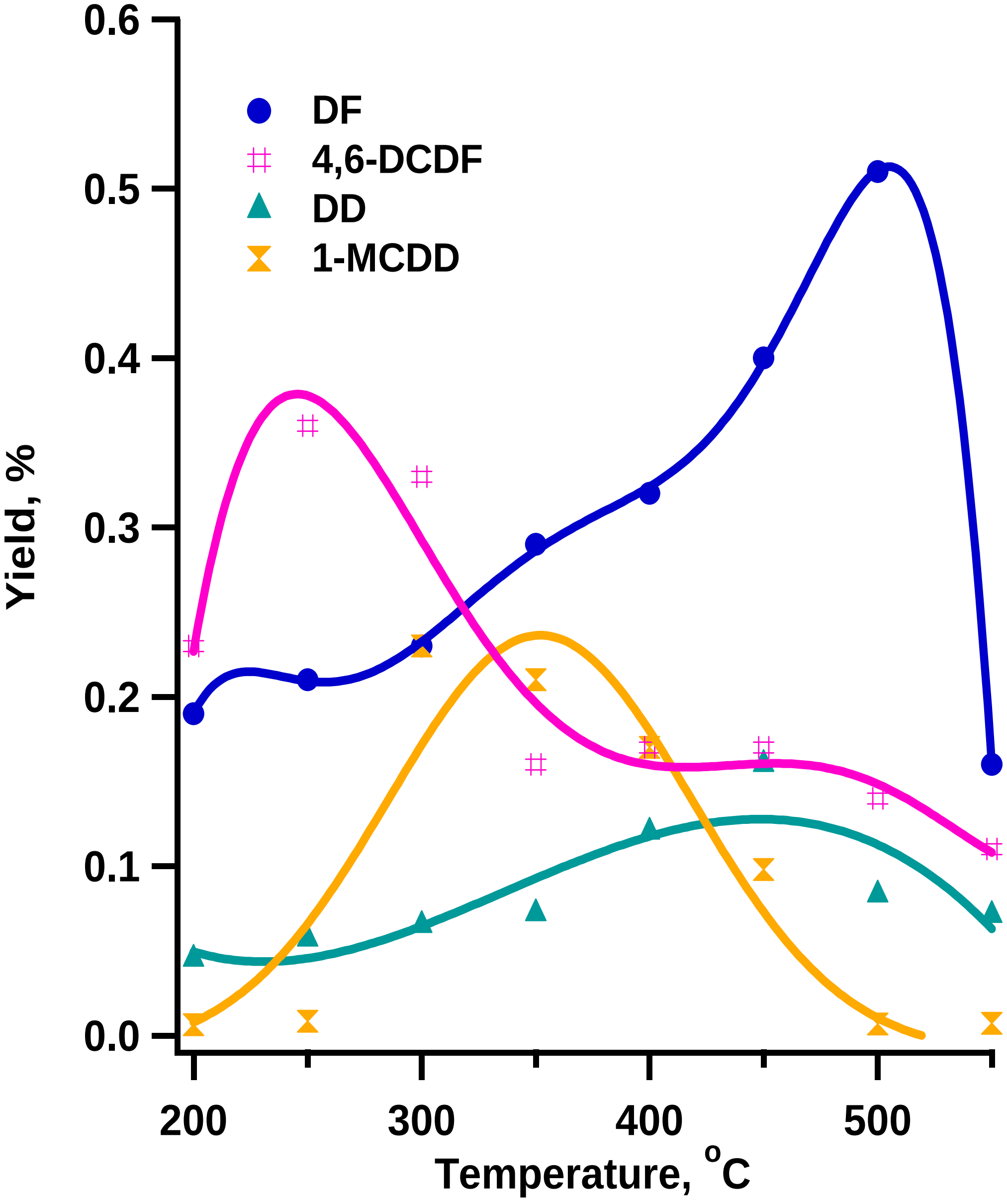


Figure 3.30 Product Yields of PCDD/Fs from the Oxidation of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

II. Results from a 1:1 Mixture of 2-MCP and 1,2-DCBz, Respectively

Thermal decomposition at 200 °C achieved 78% and 52% destruction of 2-MCP and 1,2-DCBz, respectively. Monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) were the chlorobenzenes products observed with maximum yields of 1.8% at 200 °C, 4.2% at 400 °C, 1.4% at 450 °C, 0.38% at 450 °C and 0.080% at 350 °C, respectively. Formation of benzene (Bz) increased with increasing temperature reaching a maximum yield of 0.11% at 450 °C. **Figure 3.31** depicts the yields of chlorobenzenes observed from thermal degradation of a 1: 1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface under oxidative conditions.

Chlorophenols products observed includes phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 14% at 450 °C, 6.0% at 300 °C, and 2.3% at 400 °C, respectively. The yields of chlorophenols observed from thermal degradation of a 1: 1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface under oxidative conditions are depicted in **Figure 3.32**. Other non-dioxins observed were naphthalene, chloronaphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) with maximum yields of 0.91% at 450 °C, 0.11% at 400 °C, 0.23% at 400 °C, 0.063% at 250 °C and < 0.010% at 300 °C, respectively.

Significant yields of PCDD/Fs were observed from thermal degradation of a 50:50 mixture of 2-MCP and 1,2-DCBz. Dibenzo-*p*-dioxin (DD) was formed across the entire temperature range of this study with a maximum yield of 0.28% at 400 °C. 1-monochlorodibenzo-*p*-dioxin (1-MCDD) was initially detected at 250 ^{o}C and its yield increased with increasing temperature to achieve a maximum yield of 0.31% at 350 °C**.**

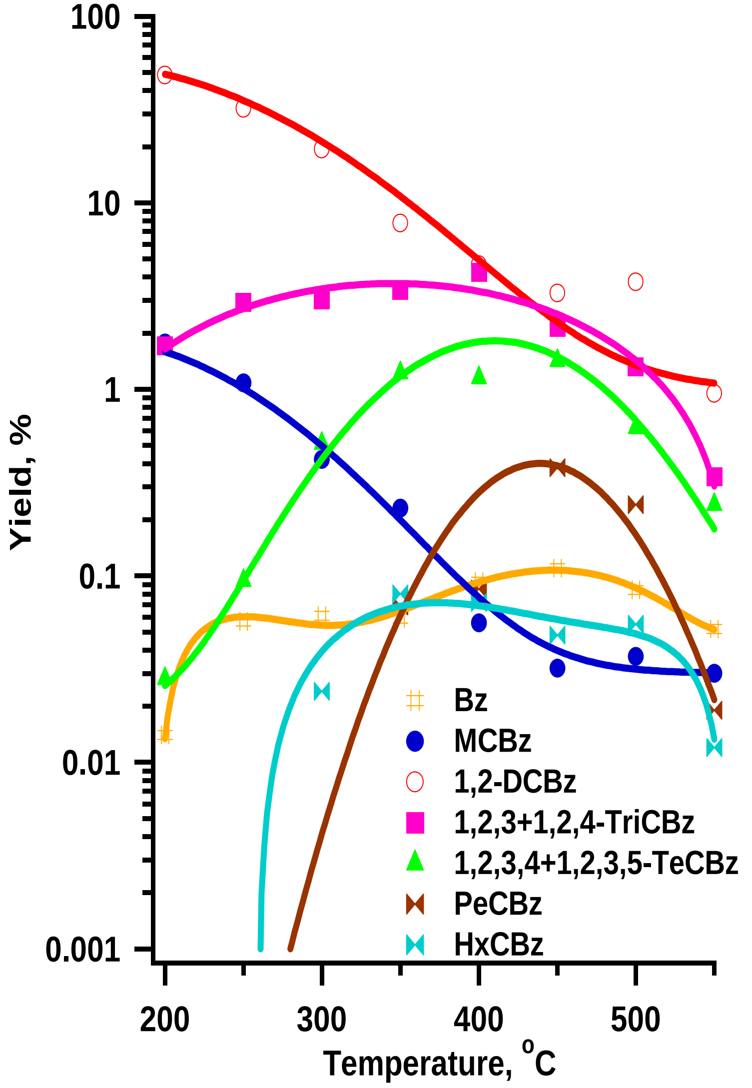


Figure 3.31 Product Yields of Chlorobenzenes from the Oxidation of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

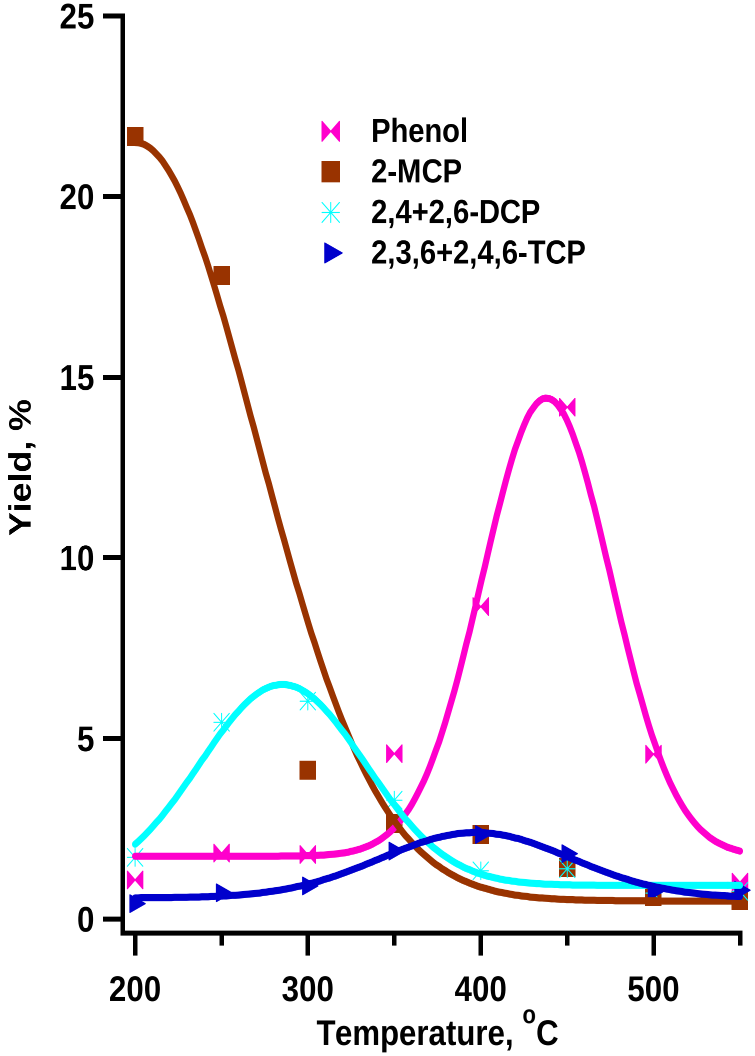


Figure 3.32 Product Yields of Chlorophenols from the Oxidation of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

Other dioxin products observed were dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF) with maximum yields of 0.56% at 400 °C and 0.41% at 250 °C, respectively. The total yields of PCDFs observed from 200 °C to 550 °C, were 2x greater than the total yields of PCDDs detected. The yields of dioxin products observed from thermal degradation of a 1:1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface under oxidative conditions are depicted in **Figure 3.30.**

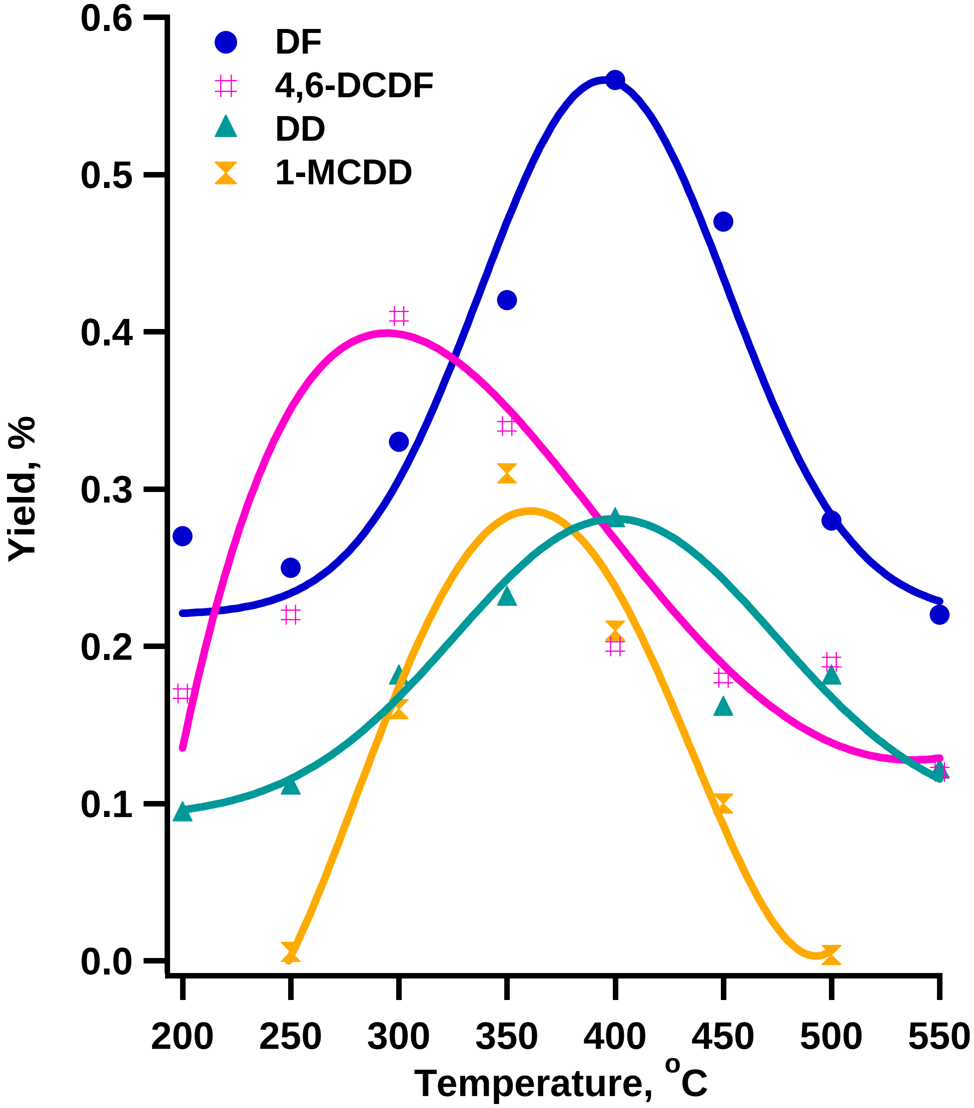


Figure 3.33 Product Yields of PCDD/Fs from the Oxidation of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

III. Results from a 10:1 Mixture of 2-MCP and 1,2-DCBz, Respectively

The thermal degradation of 2-MCP and 1,2-DCBz tracked one another increasing gradually with rising temperature achieving 97% and 98% destruction at 550 °C, respectively. Benzene yield increased from 0.085% at 200 °C to reach a maximum yield of 0.20% at 300 °C and decreased to 0.090% at 450 °C. Chlorobenzenes formed includes monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) with maximum yields of 1.3% at 200 °C, 3.2% at 300-350 °C, 1.4% at 400 °C, 0.24% at 400 °C and 0.058% at 350 °C, respectively. **Figure 3.34** depicts the yields of chlorobenzenes observed from thermal degradation a 10:1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface under oxidative conditions.

Phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) were the chlorophenol products detected with maximum yields of 16% at 400 °C, 5.3% at 300 °C, and 3.2% at 350 °C, respectively. The yields of chlorophenols observed from thermal degradation of a 10:1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface under oxidative conditions are depicted in **Figure 3.35**. Naphthalene, chloronaphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) were other non-dioxins products observed forming with maximum yields of 1.4% at 400 °C, 0.28% at 400 °C, 0.22% at 350 °C , 0.083% at 300 °C and < 0.010% at 300 °C, respectively.

The formation of PCDD/F products was observed from the lowest temperature of the study at 200 °C to 550 °C. The dioxin products detected were dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF), dibenzo-*p*-dioxin (DD) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) with maximum yields of 0.33% at 400 °C, 0.31% at 350 °C, 0.31% at 400 °C and 0.37% at 350 °C, respectively.

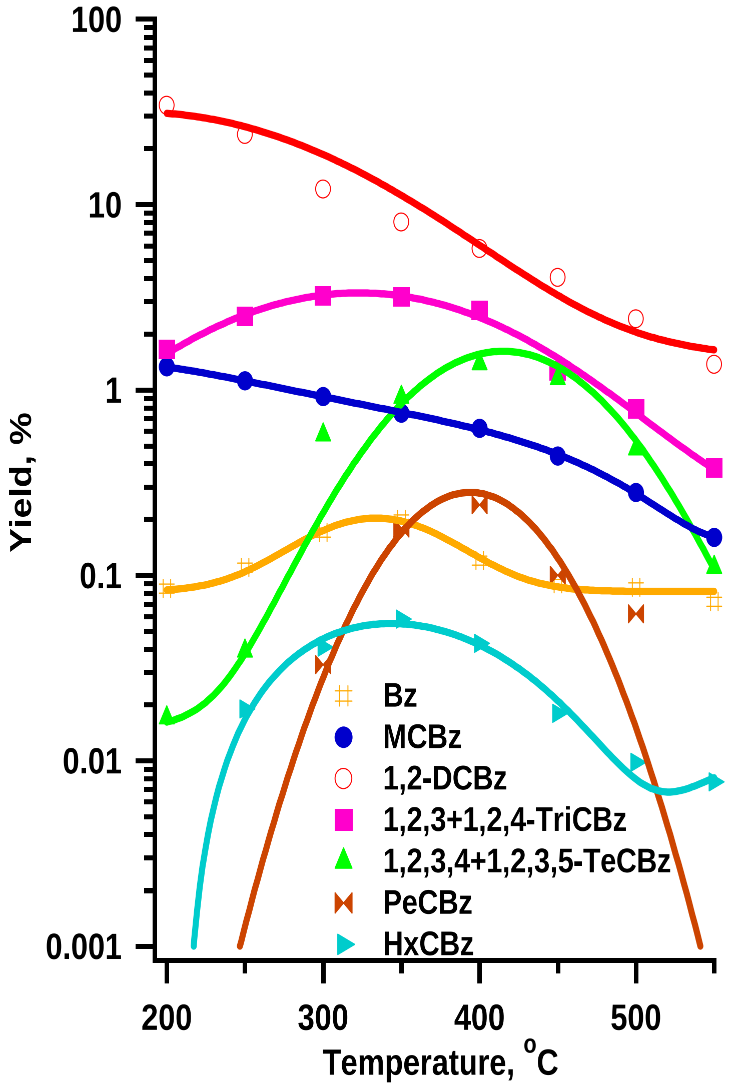


Figure 3.34 Product Yields of Chlorobenzenes from the Oxidation of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

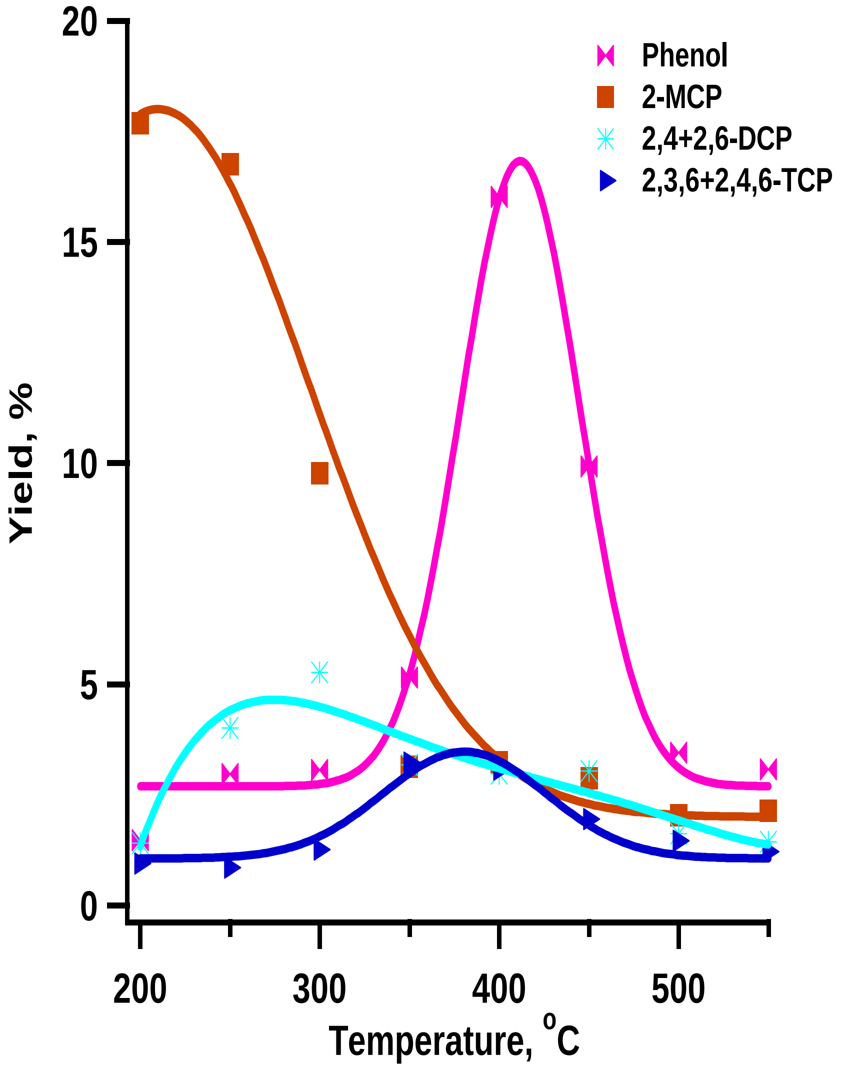


Figure 3.35 Product Yields of Chlorophenols from the Oxidation of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

The PCDD to PCDF ratio observed was 0.78. The yields of dioxin products observed from thermal degradation of a 10:1 mixture of 2-MCP and 1,2-DCBz, respectively over copper oxide/silica surface under oxidative conditions are depicted in **Figure 3.36.** The temperature dependence of the thermal degradation of 2-MCP and 1,2-DCBz mixture over a CuO/silica surface under oxidative conditions and the yields of dioxin and non-dioxin products are presented in **Table 3.9 and 3.10.**

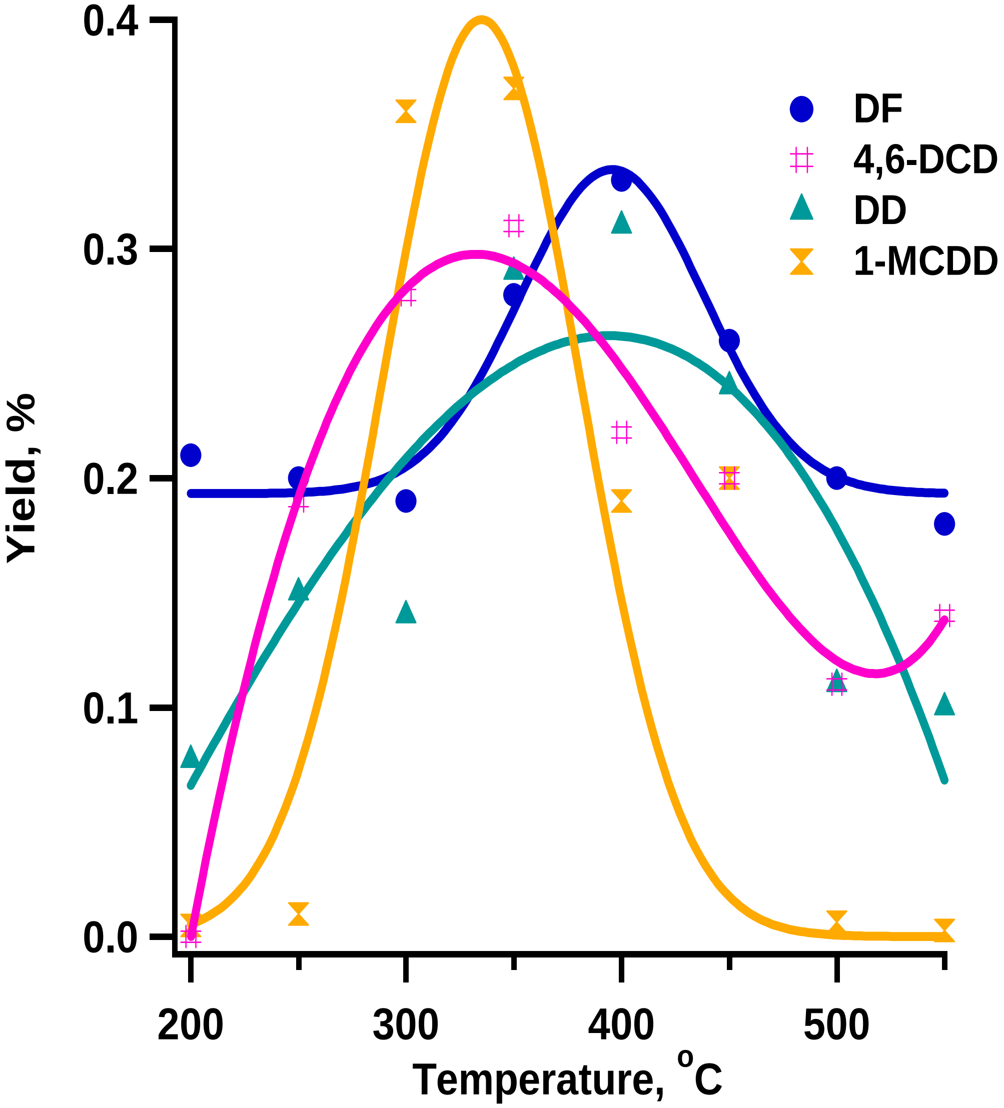


Figure 3.36 Product Yields of PCDD/Fs from the Oxidation of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over CuO/Silica Surface

Table 3.9 Non-dioxin Products from Oxidation of 1,2-Dichlorobenzene and 2-Monochlorophenol Mixtures over CuO/Silica Surface

Non-Dioxin Products		2-MCP/1,2-DCBz	Reaction Temperature, ^oC							
			200	250	300	350	400	450	500	550
1	Benzene	0.1	0.0092	0.018	0.045	0.051	0.083	0.098	0.074	0.066
		1.0	0.014	0.057	0.061	0.059	0.093	0.11	0.084	0.052
		10	0.085	0.11	0.17	0.20	0.12	0.090	0.086	0.072
2	Monochlorobenzene	0.1	1.6	1.4	1.0	0.83	0.24	0.11	0.13	0.10
		1.0	1.8	1.1	0.42	0.23	0.056	0.032	0.037	0.030
		10	1.3	1.1	0.92	0.75	0.62	0.44	0.28	0.16
3	1,2-Dichlorobenzene	0.1	52	41	26	8.9	6.1	5.6	2.5	1.5
		1.0	48	32	19	7.8	4.7	3.3	3.8	0.95
		10	34	24	12	8.0	5.8	4.0	2.4	1.4
4	1,2,3+1,2,4-Trichlorobenzene	0.1	3.4	3.9	5.4	6.1	3.3	3.4	1.3	0.81
		1.0	1.7	2.9	3.0	3.4	4.2	2.1	1.3	0.34
		10	1.7	2.5	3.2	3.2	2.7	1.3	0.79	0.38
5	1,2,3,4+1,2,3,5-Tetrachlorobenzene	0.1	0.045	0.083	0.72	3.3	4.1	2.2	0.62	0.16
		1.0	0.028	0.094	0.51	1.2	1.2	1.4	0.62	0.24
		10	0.017	0.039	0.57	0.91	1.4	1.2	0.48	0.11
6	Pentachlorobenzene	0.1	0.011	0.014	0.049	0.18	0.30	0.17	0.073	0.026
		1.0	bdl	bdl	bdl	0.069	0.085	0.38	0.24	0.019
		10	bdl	bdl	0.033	0.18	0.24	0.10	0.062	bdl
5	Hexachlorobenzene	0.1	bdl	0.037	0.034	0.049	0.081	0.074	0.078	0.010
		1.0	bdl	bdl	0.024	0.080	0.072	0.048	0.055	0.012
		10	bdl	0.019	0.041	0.058	0.043	0.018	0.0098	0.0077
6	Phenol	0.1	1.3	1.5	2.9	6.3	2.6	2.4	2.5	1.3
		1.0	1.1	1.8	1.8	4.6	8.7	14	4.6	1.0
		10	1.5	3.0	3.1	5.2	16	9.9	3.5	3.1
7	2-Monochlorophenol	0.1	18	12	3.5	1.8	1.2	1.3	0.98	0.64
		1.0	22	18	4.1	2.7	2.3	1.4	0.62	0.51
		10	18	17	9.8	3.1	3.2	2.9	2.0	2.1

Table 3.9 Con’d

8	**2,4+2,6-Dichlorophenol**	**0.1**	**0.76**	**1.6**	**2.3**	**2.4**	**1.1**	**1.1**	**0.81**	**0.61**
		1.0	**1.7**	**5.5**	**6.0**	**3.3**	**1.3**	**1.4**	**0.72**	**0.77**
		10	**1.4**	**4.0**	**5.3**	**3.2**	**3.0**	**3.0**	**1.6**	**1.4**
9	**2,3,6+2,4,6-Trichlorophenol**	**0.1**	**0.54**	**0.68**	**1.1**	**1.7**	**2.8**	**2.5**	**1.6**	**0.81**
		1.0	**0.43**	**0.73**	**0.92**	**1.9**	**2.3**	**1.8**	**0.77**	**0.80**
		10	**0.95**	**0.86**	**1.3**	**3.2**	**3.1**	**2.0**	**1.5**	**1.2**
10	**Naphthalene**	**0.1**	**0.13**	**0.41**	**0.61**	**0.36**	**0.78**	**0.44**	**0.51**	**0.23**
		1.0	**0.35**	**0.46**	**0.49**	**0.59**	**0.67**	**0.91**	**0.72**	**0.57**
		10	**0.21**	**0.91**	**0.84**	**0.93**	**1.4**	**1.2**	**0.74**	**0.33**
11	**Chloronapthalene**	**0.1**	**bdl**	**bdl**	**bdl**	**0.21**	**0.37**	**bdl**	**bdl**	**bdl**
		1.0	**bdl**	**0.016**	**0.043**	**0.068**	**0.11**	**0.056**	**bdl**	**bdl**
		10	**0.0012**	**0.0063**	**0.016**	**0.091**	**0.28**	**0.067**	**0.042**	**0.018**
12	**Biphenyl**	**0.1**	**0.0073**	**0.011**	**0.033**	**0.071**	**0.061**	**0.034**	**0.013**	**0.0083**
		1.0	**0.027**	**0.039**	**0.080**	**0.14**	**0.23**	**0.11**	**0.091**	**0.025**
		10	**0.035**	**0.031**	**0.052**	**0.22**	**0.083**	**0.044**	**0.016**	**0.010**
13	**Benzoquinone**	**0.1**	**0.0085**	**0.0094**	**0.012**	**0.035**	**0.0078**	**0.0059**	**0.0031**	**0.0018**
		1.0	**0.0072**	**0.016**	**0.063**	**0.018**	**0.0082**	**0.0044**	**0.0022**	**bdl**
		10	**0.010**	**0.018**	**0.083**	**0.076**	**0.011**	**0.0069**	**0.0037**	**0.0014**
14	**Catechol**	**0.1**	**0.0030**	**0.0034**	**0.0051**	**0.00087**	**0.00061**	**0.00014**	**bdl**	**bdl**
		1.0	**0.0011**	**0.0019**	**0.0066**	**0.0051**	**0.0021**	**0.0015**	**0.00063**	**bdl**
		10	**0.0067**	**0.0072**	**0.0089**	**0.0043**	**0.0017**	**0.00072**	**0.00054**	**0.00039**

bdl- Below Detection Limit

Table 3.10 Dioxin Products from Oxidation of 1,2-Dichlorobenzene and 2-Monochlorophenol Mixtures over CuO/Silica Surface

Dioxin Products		**2-MCP/1,2-DCBz**	**Reaction Temperature/^{o}C**							
			200	**250**	**300**	**350**	**400**	**450**	**500**	**550**
1	**DF**	**0.1**	**0.19**	**0.21**	**0.23**	**0.29**	**0.32**	**0.40**	**0.51**	**0.16**
		1.0	**0.27**	**0.25**	**0.33**	**0.42**	**0.56**	**0.47**	**0.28**	**0.22**
		10	**0.21**	**0.20**	**0.19**	**0.28**	**0.33**	**0.26**	**0.20**	**0.18**
2	**DD**	**0.1**	**0.045**	**0.057**	**0.065**	**0.072**	**0.12**	**0.16**	**0.083**	**0.071**
		1.0	**0.093**	**0.11**	**0.18**	**0.23**	**0.28**	**0.16**	**0.18**	**0.12**
		10	**0.077**	**0.15**	**0.14**	**0.29**	**0.31**	**0.24**	**0.11**	**0.10**
3	**1-MCDD**	**0.1**	**0.0063**	**0.0084**	**0.23**	**0.21**	**0.17**	**0.098**	**0.0067**	**0.0072**
		1.0	**bdl**	**0.0056**	**0.16**	**0.31**	**0.21**	**0.10**	**0.0038**	**bdl**
		10	**0.0049**	**0.0098**	**0.36**	**0.37**	**0.19**	**0.20**	**0.0062**	**0.0027**
4	**4,6-DCDF**	**0.1**	**0.23**	**0.36**	**0.33**	**0.16**	**0.17**	**0.17**	**0.14**	**0.11**
		1.0	**0.17**	**0.22**	**0.41**	**0.34**	**0.20**	**0.18**	**0.19**	**0.12**
		10	**bdl**	**0.19**	**0.28**	**0.31**	**0.22**	**0.20**	**0.11**	**0.14**

bdl- Below Detection Limit

3.5. Iron Catalyzed Thermal Degradation of 2-Monochlorophenol and 1,2-Dichlorobenzene Mixtures

3.5.1 Results under Pyrolytic Conditions

I. Results from a 1:10 Mixture of 2-MCP and 1,2-DCBz, Respectively

The thermal degradation of a 1:10 mixture of 2-MCP and 1,2-DCBz achieved about 86% and 47% destruction at 200 °C, respectively. Among chlorobenzene products formed were monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) with maximum yields of 1.1% at 450 °C, 9.4% at 350 °C, 1.2 % at 400-450 °C, 0.066% at 350 °C and 0.048% at 550 °C, respectively. The yield of benzene (Bz) increased with increasing temperature reaching a maximum yield of 0.29% at 350 °C. **Figure 3.37** depicts the yields of chlorobenzenes observed from thermal degradation a 1: 10 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under pyrolytic conditions.

Phenolic products observed includes phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 2.3% at 300 °C, 10% at 300 °C, and 3.3% at 350-400 °C, respectively. The yields of chlorophenols observed from thermal degradation of a 1:10 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under pyrolytic conditions are depicted in **Figure 3.38**. Other non-dioxins observed were naphthalene, chloronapthalene, biphenyl, benzoquinone (BQ) and catechol (CT) with maximum yields of 0.94% at 400 °C, 0.14% at 350 °C, 0.11% at 350 °C, 0.018% at 300 °C and < 0.010% at 350 °C, respectively.

Major PCDD/F products observed were dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF) formed at maximum yields of 0.33% at 450 °C and 0.28% at 250 °C, respectively. The only PCDD product observed; 1-monochlorodibenzo-*p*-dioxin (1-MCDD), was initially detected

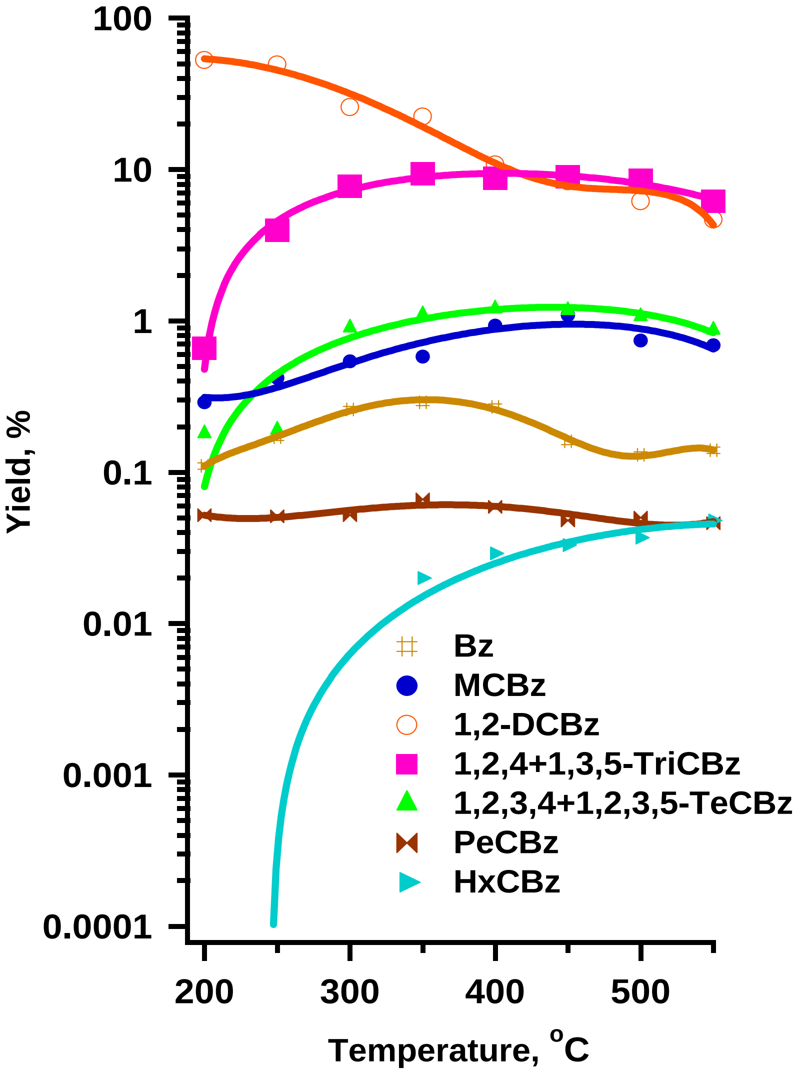


Figure 3.37 Product Yields of Chlorobenzenes from the Pyrolysis of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

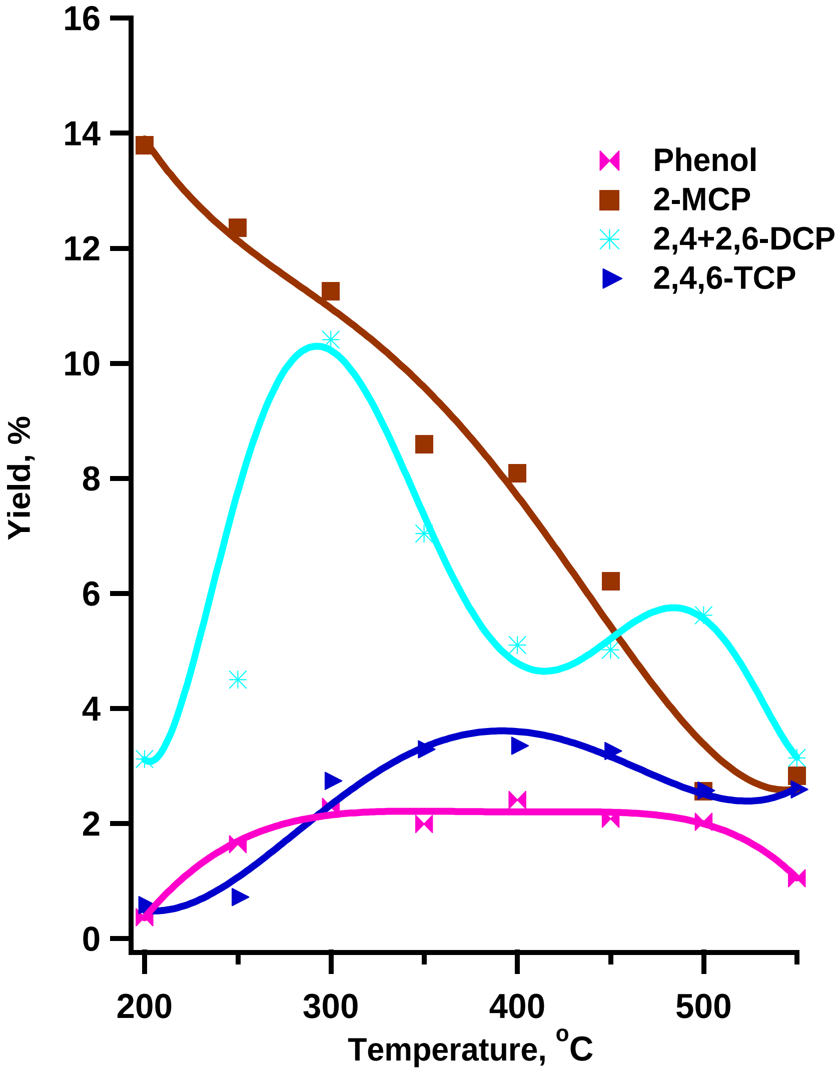


Figure 3.38 Product Yields of Chlorophenols from the Pyrolysis of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

at 250 °C and increased with increasing temperature achieving a maximum yield of 0.098% at 350 °C. PCDD to PCDF ratio observed was 0.24. The yields of dioxin products observed from thermal degradation of a 1:10 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under pyrolytic conditions are depicted in **Figure 3.39.**

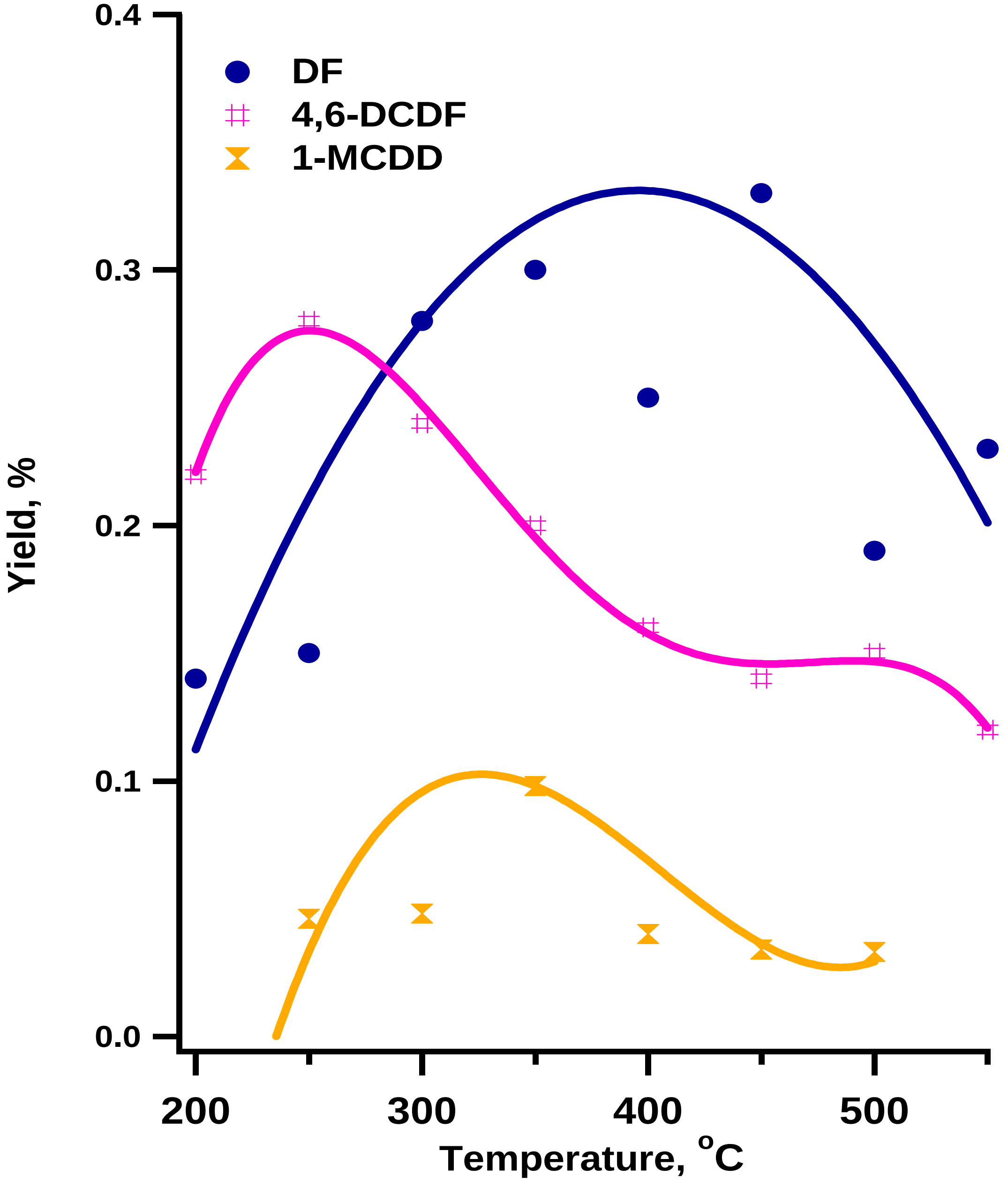


Figure 3.39 Product Yields of PCDD/Fs from the Pyrolysis of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

II. Results from a 1:1 Mixture of 2-MCP and 1,2-DCBz, Respectively

Thermal degradation of 2-MCP and 1,2-DCBz tracked each other from the initial temperature at 200 °C and the rate accelerated gradually achieving 99% destruction at 450 °C for both reactant components. At 200 °C, chlorobenzene products observed were monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), and pentachlorobenzene (PeCBz) with formation yields of 0.39%, 1.6%, 0.14%, and 0.042%, respectively. Yield of benzene (Bz) increased with increasing temperature reaching a maximum yield of 0.23% at 450 °C. **Figure 3.40** depicts the yields of chlorobenzenes observed from thermal degradation a 1: 1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under pyrolytic conditions.

The phenolic products observed includes phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 3.2% at 300 °C, 14% at 350 °C, and 9.4% at 350 °C, respectively. The yields of chlorophenols observed from thermal degradation of a 1: 1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under pyrolytic conditions are depicted in **Figure 3.41**. Other non-dioxins observed were naphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) with maximum yields of 1.9% at 450 °C, 0.061% at 350 ^{o}C, 0.18% at 300 °C and < 0.010% at 400 ^{o}C, respectively. Trace amounts of chlorocatechol (CC) and chlorobenzoquinone (CQ) were observed at yields < 0.010% from 300 to 400 ^{o}C.

High yields of PCDD/Fs were observed from thermal degradation of a 50:50 mixture of 2-MCP and 1,2-DCBz. Dibenzo-*p*-dioxin (DD) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) were the only PCDD products observed with maximum yields of 0.30% at 300 °C and 0.12% at 300 °C, respectively. PCDF products observed were dibenzofuran (DF) and

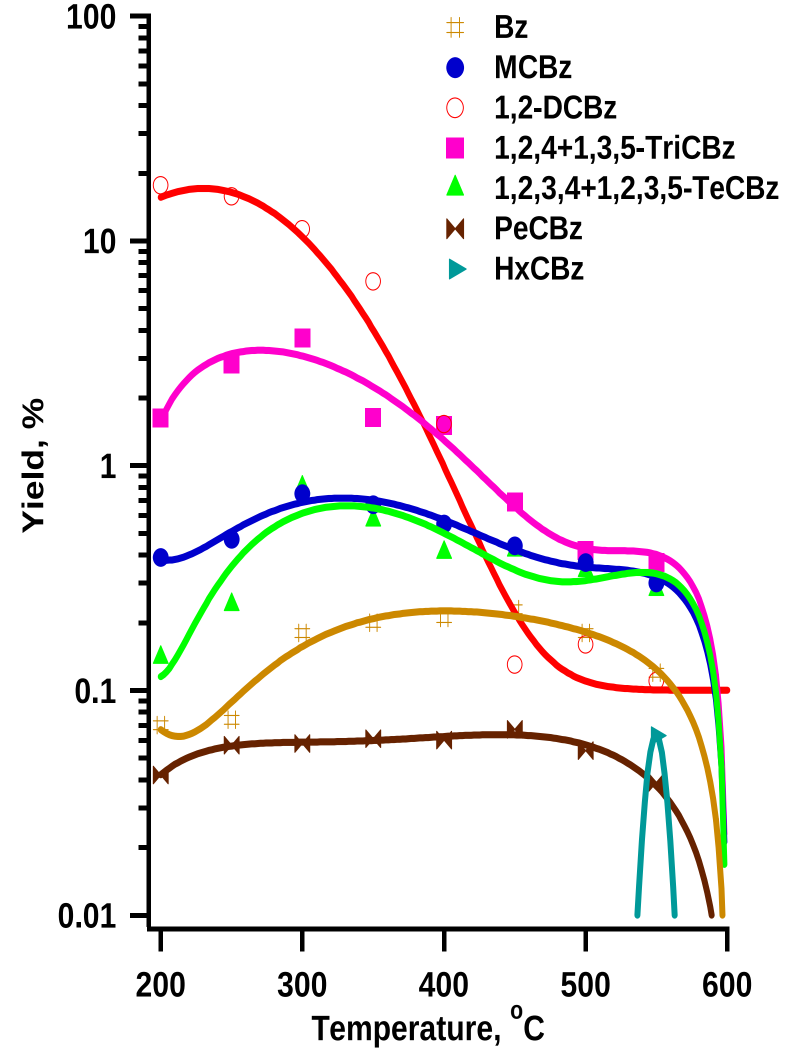


Figure 3.40 Product Yields of Chlorobenzenes from the Pyrolysis of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

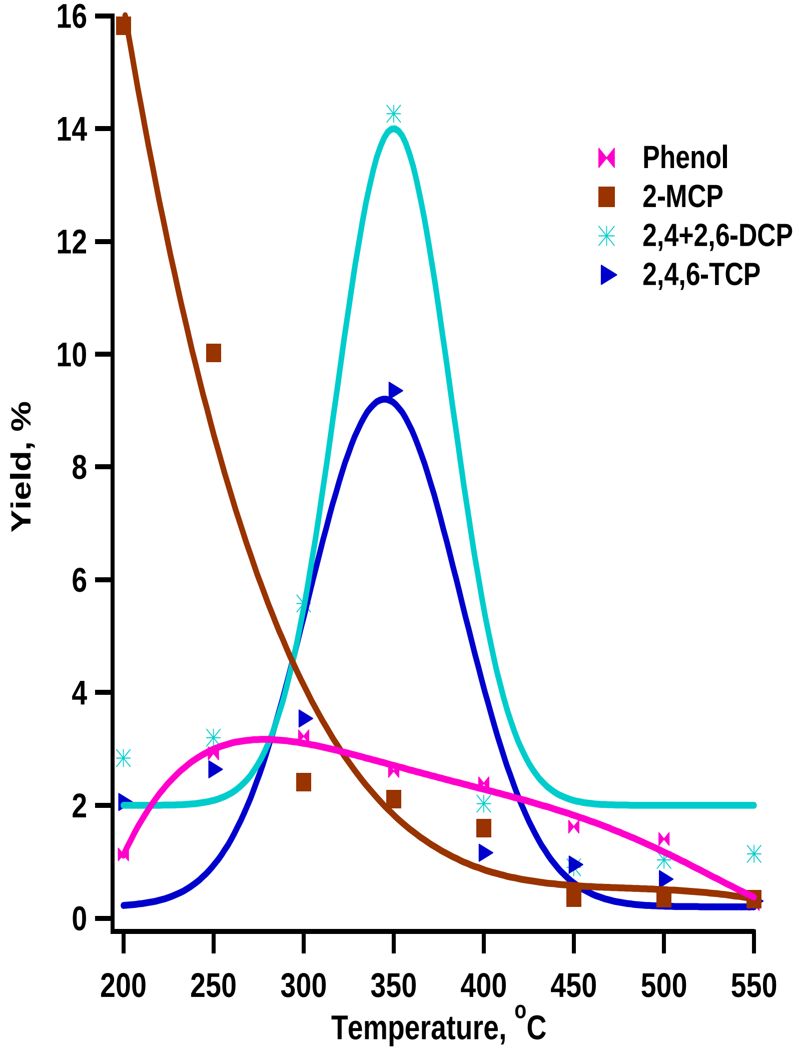


Figure 3.41 Product Yields of Chlorophenols from the Pyrolysis of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

4,6-dichlorodibenzofuran (4,6-DCDF) formed with maximum yields of 0.27% at 450 °C and 0.46% at 350 °C, respectively. The total yield of PCDFs observed from 200 °C to 500 °C, was 2x higher the total yields of PCDDs detected. The yields of dioxin products observed from thermal degradation of a 1:1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under pyrolytic conditions are depicted in **Figure 3.42.**

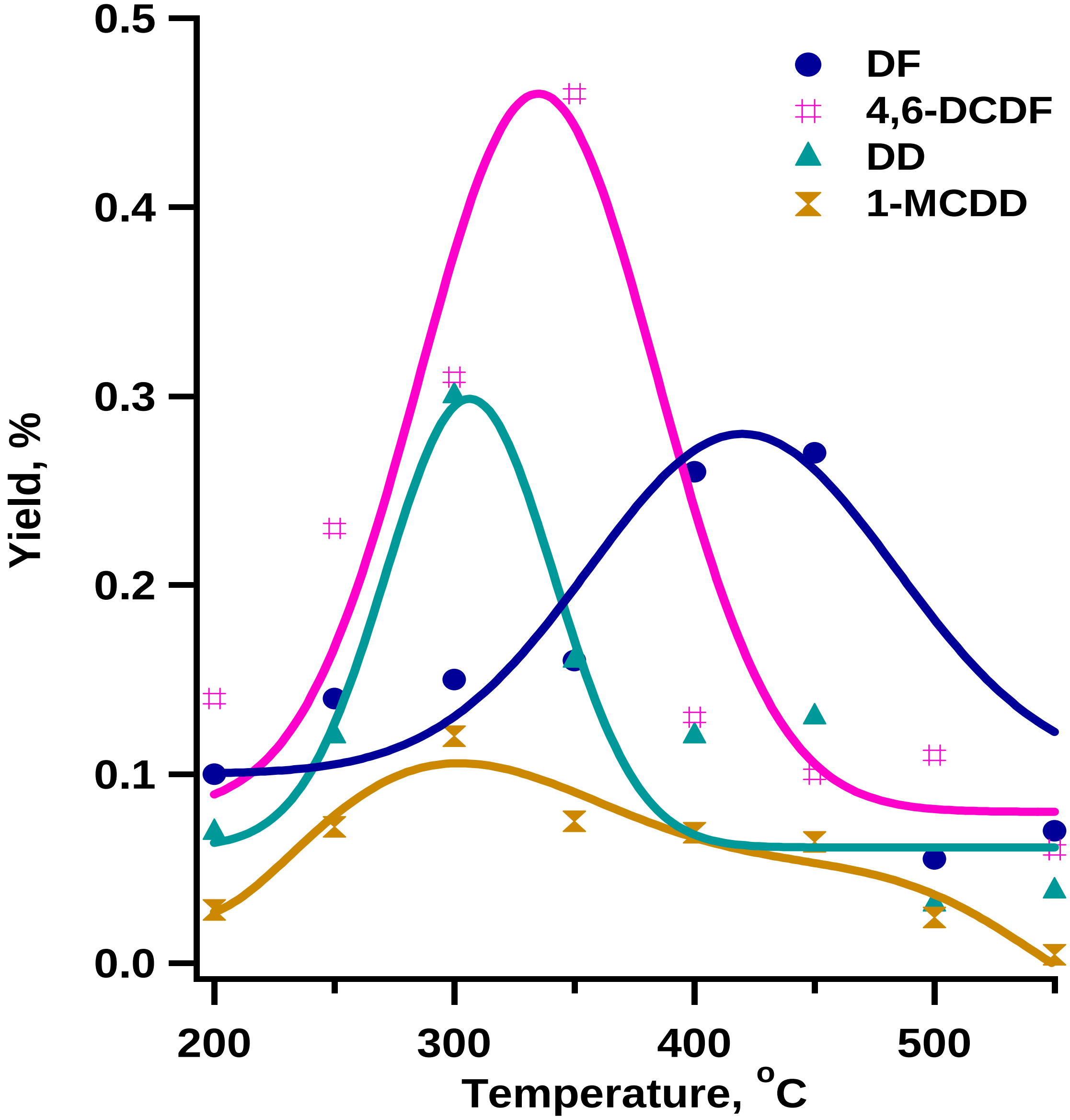


Figure 3.42 Product Yields of PCDD/Fs from the Pyrolysis of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

III. Results from a 10:1 Mixture of 2-MCP and 1,2-DCBz, Respectively

Significant thermal degradation of 2-MCP and 1,2-DCBz was observed even at low temperature reaching about 82% and 73% destruction at 200 °C, respectively. Formation of benzene (Bz) increased with increasing temperature achieving a maximum yield of 0.39% at 450 °C. Chlorobenzene products observed includes monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) with maximum yields of 0.84% at 350 °C, 3.2% at 300 °C, 2.4% at 450 °C, 0.13% at 450 °C and 0.19% at 450 °C, respectively. **Figure 3.43** depicts the yields of chlorobenzenes observed from thermal degradation a 10: 1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under pyrolytic conditions.

Chlorophenol products detected were phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 16% at 300 °C, 7.6% at 250 °C, and 1.3% at 400 °C, respectively. The yields of chlorophenols observed from thermal degradation of a 10: 1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under pyrolytic conditions are depicted in **Figure 3.44.**

Additionally, naphthalene, chloronaphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) were formed with maximum yields of 1.1% at 250 °C, 0.16% at 500 °C, 0.090% at 450 °C, 0.021% at 250 °C and < 0.010% at 300 °C, respectively. Other non-dioxin products detected were chlorobenzoquinone (CQ) and chlorocatechol (CC) with maximum yields of 1.0% at 250 °C and <0.010% at 500 °C, respectively.

PCDD/Fs products were observed across the whole temperature range studied from 200 °C to 550 °C. The dioxin products detected were dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF), dibenzo-*p*-dioxin (DD) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) with

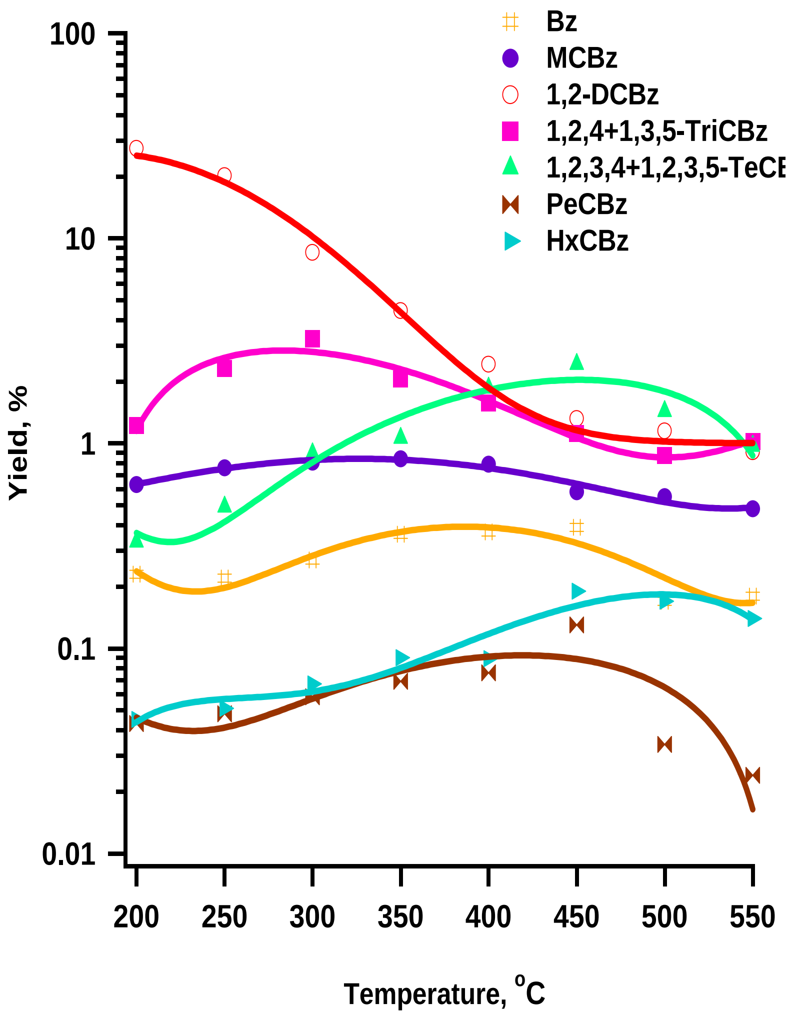


Figure 3.43 Product Yields of Chlorobenzenes from the Pyrolysis of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

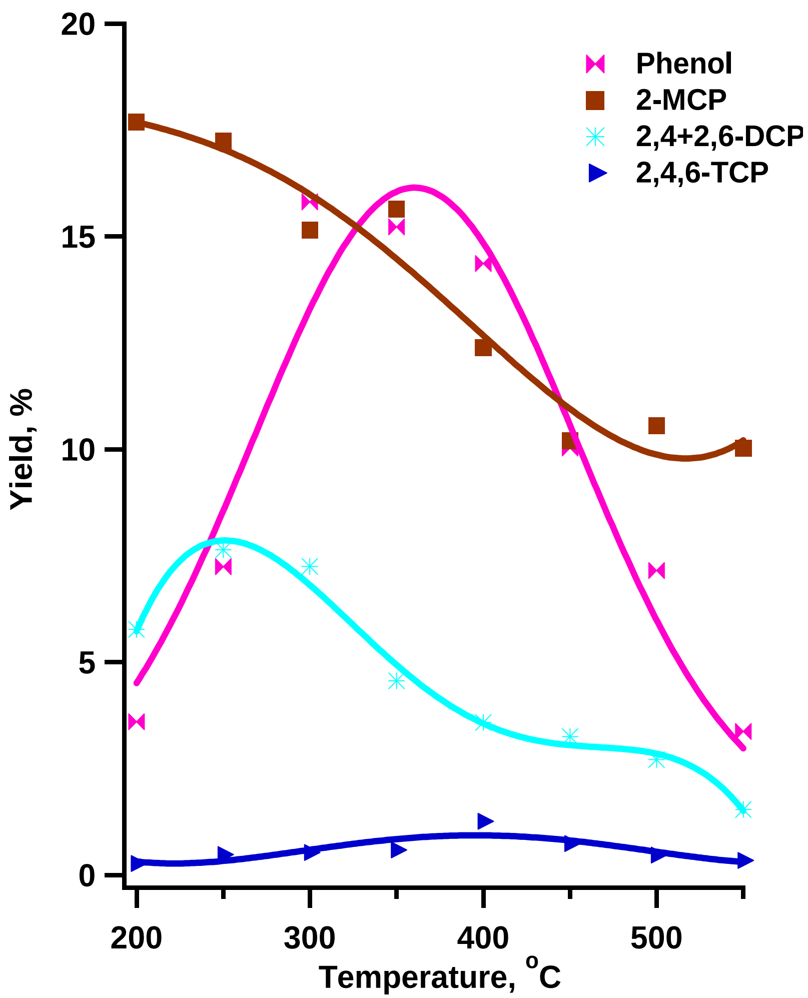


Figure 3.44 Product Yields of Chlorophenols from the Pyrolysis of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

maximum yields of 0.37% at 400 °C, 0.46% at 400 °C, 0.28% at 500 °C and 0.20% at 300 °C, respectively. The PCDD to PCDF ratio observed was 0.64. The yields of dioxin products observed from thermal degradation of a 10:1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under pyrolytic conditions are depicted in **Figure 3.45.** The temperature dependence of the pyrolytic thermal degradation of 2-MCP and 1,2-DCBz mixture over a Fe_2O_3/silica surface and the yields of dioxin and non-dioxin products are presented in **Table 3.12 and Table 3.13.**

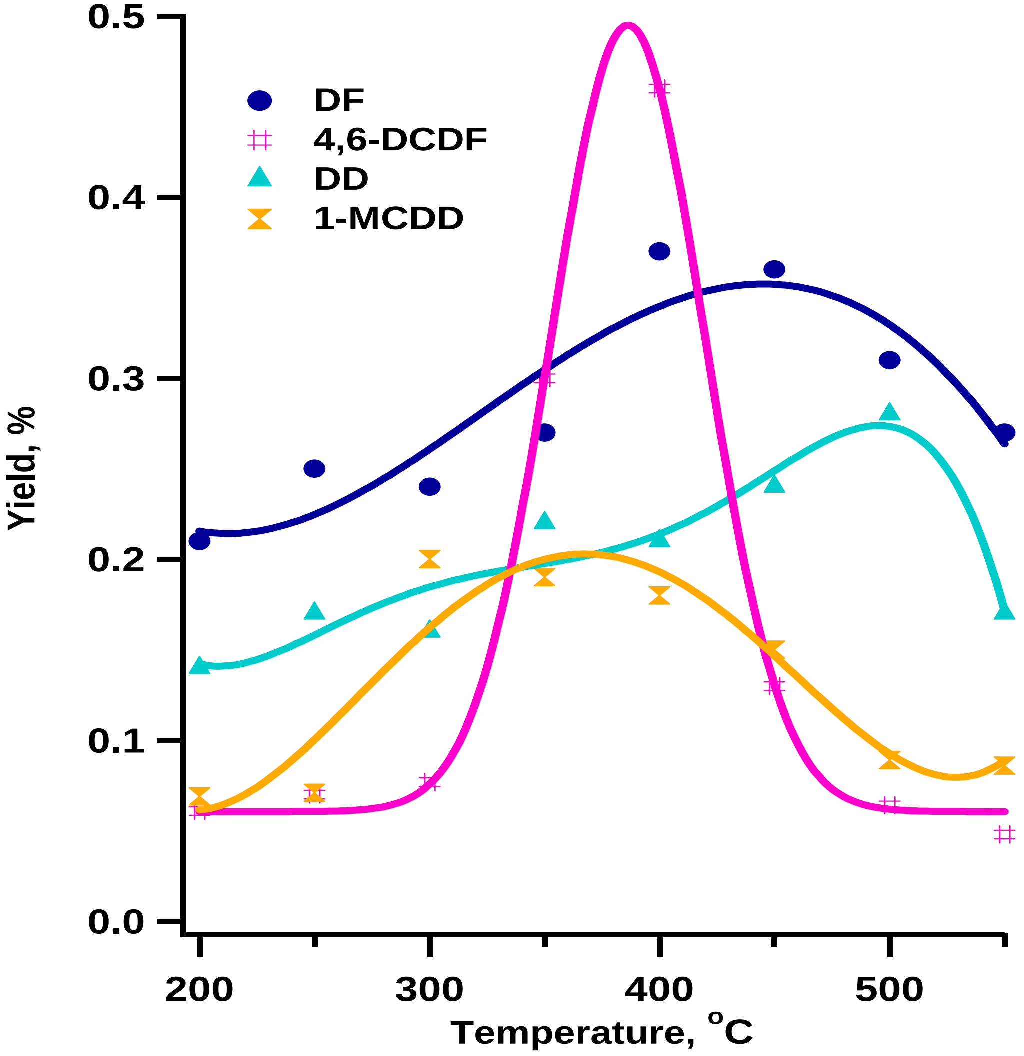


Figure 3.45 Product Yields of PCDD/Fs from the Pyrolysis of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

Table 3.11 Non-Dioxin Products from Pyrolysis of 1,2-Dichlorobenzene and 2-Monochlorophenol Mixtures over Fe_2O_3/Silica Surface

Non-Dioxin Products		2-MCP/1,2-DCBz	Reaction Temperature, ^oC							
			200	250	300	350	400	450	500	550
1	Benzene	0.1	0.11	0.17	0.26	0.29	0.27	0.16	0.13	0.14
		1.0	0.070	0.074	0.18	0.20	0.21	0.23	0.18	0.12
		10	0.23	0.22	0.27	0.36	0.37	0.39	0.17	0.18
2	Monochlorobenzene	0.1	0.29	0.42	0.54	0.58	0.93	1.1	0.74	0.69
		1.0	0.39	0.47	0.75	0.67	0.55	0.44	0.37	0.30
		10	0.63	0.76	0.81	0.84	0.79	0.58	0.55	0.48
3	1,2-Dichlorobenzene	0.1	53	49	26	22	11	8.3	6.2	4.7
		1.0	18	16	11	6.6	1.5	0.13	0.16	0.11
		10	27	20	8.5	4.4	2.4	1.3	1.2	0.91
4	1,2,3+1,2,4-Trichlorobenzene	0.1	0.66	4.0	7.7	9.4	8.8	8.9	8.5	6.2
		1.0	1.6	2.8	3.7	1.6	1.5	0.69	0.42	0.37
		10	1.2	2.3	3.2	2.1	1.6	1.1	0.87	1.0
5	1,2,3,4+1,2,3,5-Tetrachlorobenzene	0.1	0.18	0.19	0.9	1.1	1.2	1.2	1.1	0.87
		1.0	0.14	0.24	0.80	0.57	0.41	0.42	0.34	0.28
		10	0.33	0.49	0.89	1.1	1.9	2.4	1.4	0.97
6	Pentachlorobenzene	0.1	0.052	0.051	0.052	0.066	0.059	0.048	0.050	0.046
		1.0	0.042	0.057	0.058	0.061	0.060	0.067	0.054	0.039
		10	0.043	0.048	0.058	0.069	0.076	0.13	0.034	0.024
5	Hexachlorobenzene	0.1	bdl	bdl	bdl	0.020	0.029	0.033	0.037	0.048
		1.0	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.063
		10	0.045	0.051	0.067	0.09	0.089	0.19	0.17	0.14
6	Phenol	0.1	0.37	1.6	2.3	2.0	2.4	2.1	2.0	1.1
		1.0	1.1	3.0	3.2	2.6	2.4	1.6	1.4	0.25
		10	3.6	7.2	16	15	14	10	7.2	3.4
7	2-Monochlorophenol	0.1	14	12	11	8.6	8.1	6.2	2.6	2.8
		1.0	16	10	2.4	2.1	1.6	0.36	0.35	0.33
		10	18	17	15	16	12	10	11	10

Table 3.11 Con'd

8	**2,4+2,6-Dichlorophenol**	**0.1**	**3.1**	**4.5**	**10**	**7.0**	**5.1**	**5.0**	**5.6**	**3.1**
		1.0	**2.8**	**3.2**	**5.6**	**14**	**2.0**	**0.90**	**1.0**	**1.1**
		10	**5.8**	**7.6**	**7.3**	**4.6**	**3.6**	**3.3**	**2.7**	**1.5**
9	**2,3,6+2,4,6-Trichlorophenol**	**0.1**	**0.58**	**0.72**	**2.7**	**3.2**	**3.3**	**3.3**	**2.6**	**2.6**
		1.0	**2.1**	**2.6**	**3.5**	**9.4**	**1.2**	**0.95**	**0.69**	**0.30**
		10	**0.27**	**0.48**	**0.53**	**0.59**	**1.3**	**0.74**	**0.47**	**0.34**
10	**Naphthalene**	**0.1**	**0.071**	**0.22**	**0.26**	**0.63**	**0.94**	**0.89**	**0.63**	**0.33**
		1.0	**0.17**	**0.26**	**0.24**	**0.25**	**0.32**	**1.9**	**0.75**	**0.24**
		10	**0.70**	**1.1**	**0.92**	**0.83**	**0.81**	**0.38**	**0.31**	**0.30**
11	**Chloronapthalene**	**0.1**	**0.079**	**0.085**	**0.13**	**0.14**	**0.11**	**bdl**	**bdl**	**bdl**
		1.0	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**
		10	**0.077**	**0.10**	**0.11**	**0.12**	**0.13**	**0.14**	**0.16**	**0.092**
12	**Biphenyl**	**0.1**	**0.038**	**0.046**	**0.079**	**0.11**	**0.078**	**0.047**	**0.049**	**0.028**
		1.0	**0.037**	**0.045**	**0.055**	**0.061**	**0.046**	**0.039**	**0.040**	**0.035**
		10	**0.038**	**0.043**	**0.055**	**0.065**	**0.077**	**0.090**	**0.076**	**0.045**
13	**Benzoquinone**	**0.1**	**0.013**	**0.014**	**0.018**	**0.016**	**0.015**	**0.014**	**0.014**	**0.011**
		1.0	**0.11**	**0.13**	**0.18**	**0.16**	**0.058**	**0.069**	**0.035**	**0.043**
		10	**0.0050**	**0.021**	**0.017**	**0.018**	**0.019**	**0.015**	**0.013**	**0.011**
14	**Catechol**	**0.1**	**0.00062**	**0.0012**	**0.0017**	**0.0018**	**0.0014**	**0.0016**	**0.00081**	**0.00083**
		1.0	**bdl**	**0.00091**	**0.0016**	**0.0023**	**0.0030**	**0.0023**	**0.0021**	**0.0022**
		10	**0.00038**	**0.0017**	**0.0018**	**0.0016**	**0.0015**	**0.00097**	**0.00091**	**0.00087**
15	**Chlorobenzoquinone**	**0.1**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**
		1.0	**bdl**	**bdl**	**bdl**	**0.0089**	**bdl**	**bdl**	**bdl**	**bdl**
		10	**0.45**	**1.0**	**0.27**	**0.12**	**0.09**	**0.041**	**0.033**	**0.034**
16	**Chlorocatechol**	**0.1**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**
		1.0	**bdl**	**bdl**	**0.00063**	**0.0013**	**0.00028**	**bdl**	**bdl**	**bdl**
		10	**0.0020**	**0.0017**	**0.0021**	**0.0022**	**0.0026**	**0.0028**	**0.0039**	**0.0019**

bdl- Below Detection Limit

Table 3.12 Dioxin Products from Pyrolysis of 1,2-Dichlorobenzene and 2-Monochlorophenol Mixtures over Fe_2O_3/Silica Surface

Dioxin Products		2-MCP/1,2-DCBz	Reaction Temperature, ^{o}C							
			200	**250**	**300**	**350**	**400**	**450**	**500**	**550**
1	**DF**	**0.1**	**0.14**	**0.15**	**0.28**	**0.30**	**0.25**	**0.33**	**0.19**	**0.23**
		1.0	**0.10**	**0.14**	**0.15**	**0.16**	**0.26**	**0.27**	**0.055**	**0.070**
		10	**0.21**	**0.25**	**0.24**	**0.27**	**0.37**	**0.36**	**0.31**	**0.27**
2	**DD**	**0.1**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**	**bdl**
		1.0	**0.069**	**0.12**	**0.30**	**0.16**	**0.12**	**0.13**	**0.031**	**0.038**
		10	**0.14**	**0.17**	**0.16**	**0.22**	**0.21**	**0.24**	**0.28**	**0.17**
3	**1-MCDD**	**0.1**	**bdl**	**0.046**	**0.048**	**0.098**	**0.04**	**0.034**	**0.033**	**bdl**
		1.0	**0.028**	**0.072**	**0.12**	**0.075**	**0.069**	**0.064**	**0.024**	**0.0044**
		10	**0.069**	**0.071**	**0.20**	**0.19**	**0.18**	**0.15**	**0.089**	**0.086**
4	**4,6-DCDF**	**0.1**	**0.22**	**0.28**	**0.24**	**0.20**	**0.16**	**0.14**	**0.15**	**0.12**
		1.0	**0.14**	**0.23**	**0.31**	**0.46**	**0.13**	**0.10**	**0.11**	**0.060**
		10	**0.061**	**0.070**	**0.077**	**0.30**	**0.46**	**0.13**	**0.064**	**0.048**

bdl- Below Detection Limit

3.5.2 Results under Oxidative Conditions

I. Results from a 1:10 Mixture of 2-MCP and 1,2-DCBz, Respectively

The thermal degradation of a 1:10 mixture of 2-MCP and 1,2-DCBz achieved 85% and 54% destruction at 200 °C, respectively. Among chlorinated benzenes formed were monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) with maximum yields of 0.47% at 350 °C, 4.5% at 300 ^{o}C, 2.7 % at 450 °C, 0.33% at 500 °C and 0.091% at 400 °C, respectively. The yield of benzene increased with increasing temperature reaching a maximum yield of 0.31% at 350°C. **Figure 3.46** depicts the yields of chlorobenzenes observed from thermal degradation a 1: 10 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under oxidative conditions.

Phenolic products observed includes phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 4.4% at 450 °C, 6.5% at 300 °C, and 1.7% at 350 °C, respectively. The yields of chlorophenols observed from thermal degradation of a 1: 10 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under oxidative conditions are depicted in **Figure 3.47.**

Other non-dioxins observed were naphthalene, chloronapthalene, biphenyl, benzoquinone (BQ) and catechol (CT) with maximum yields of 0.71% at 350 °C, 0.025% at 450 °C, 0.090% at 350 °C, 0.018% at 300 °C and 0.026% at 250 °C, respectively.

PCDD/F products observed were dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF), dibenzo-*p*-dioxin (DD), and 1-monochlorodibenzo-*p*-dioxin (1-MCDD), at maximum yields of 0.58% at 400 °C, 0.32% at 250 °C, 0.20% at 450 °C and 0.25% at 350 °C, respectively.

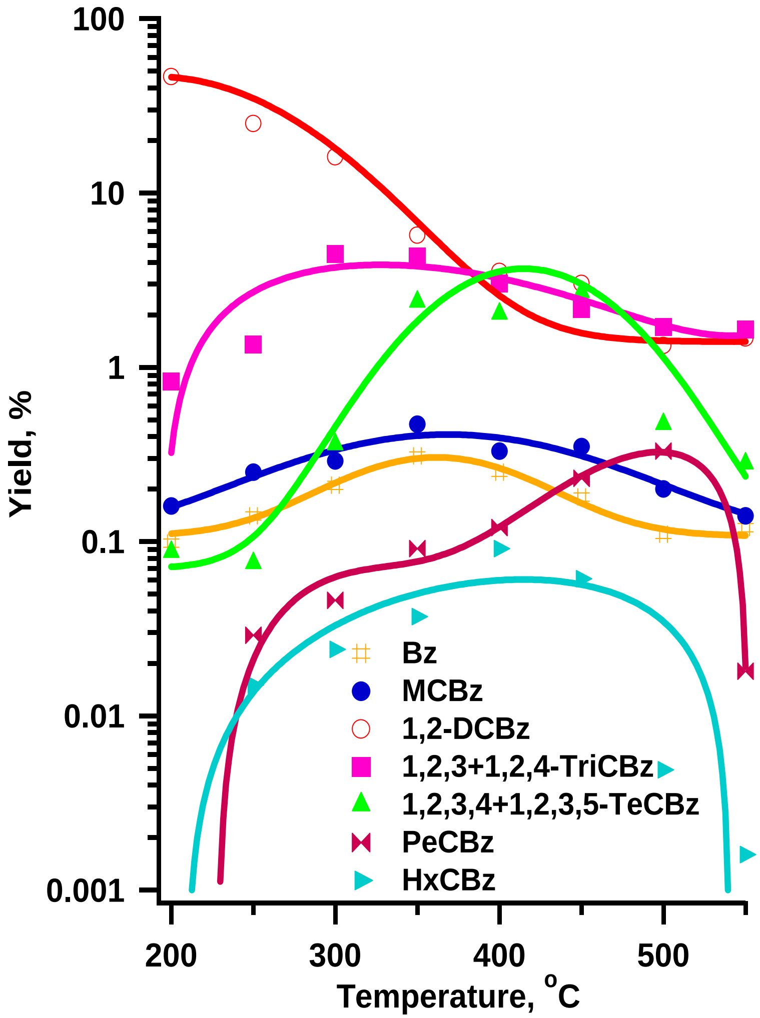


Figure 3.46 Product Yields of Chlorobenzenes from the Oxidation of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

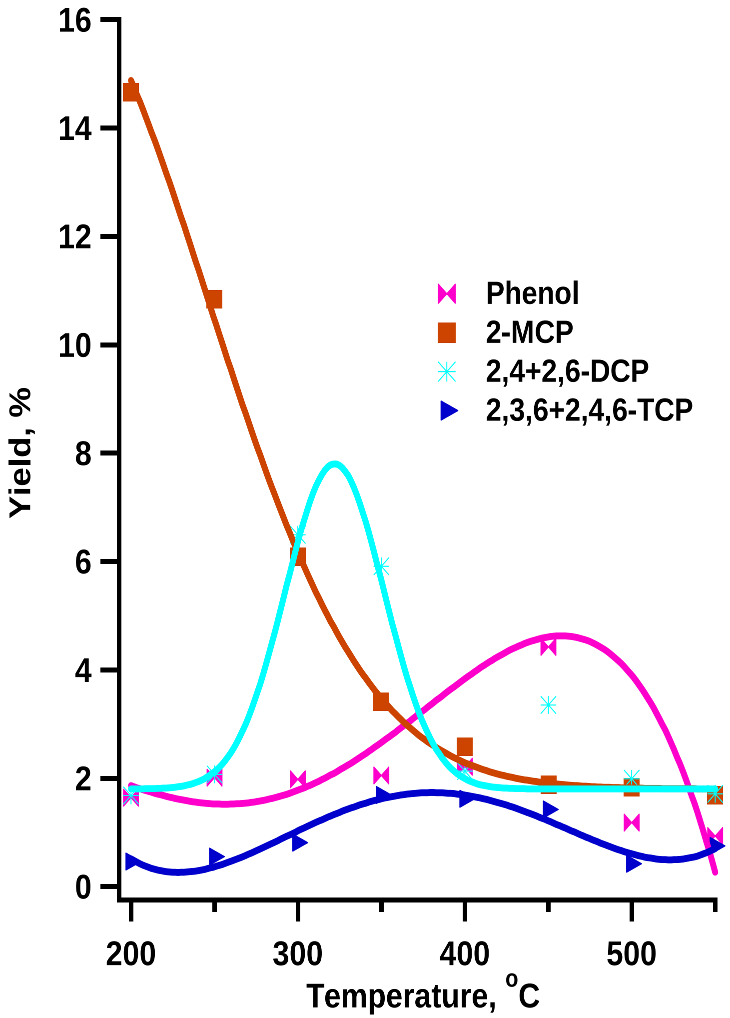


Figure 3.47 Product Yields of Chlorophenols from the Oxidation of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

PCDD to PCDF ratio observed was 0.33. The yields of dioxin products observed from thermal degradation of a 1:10 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under oxidative conditions are depicted in **Figure 3.48.**

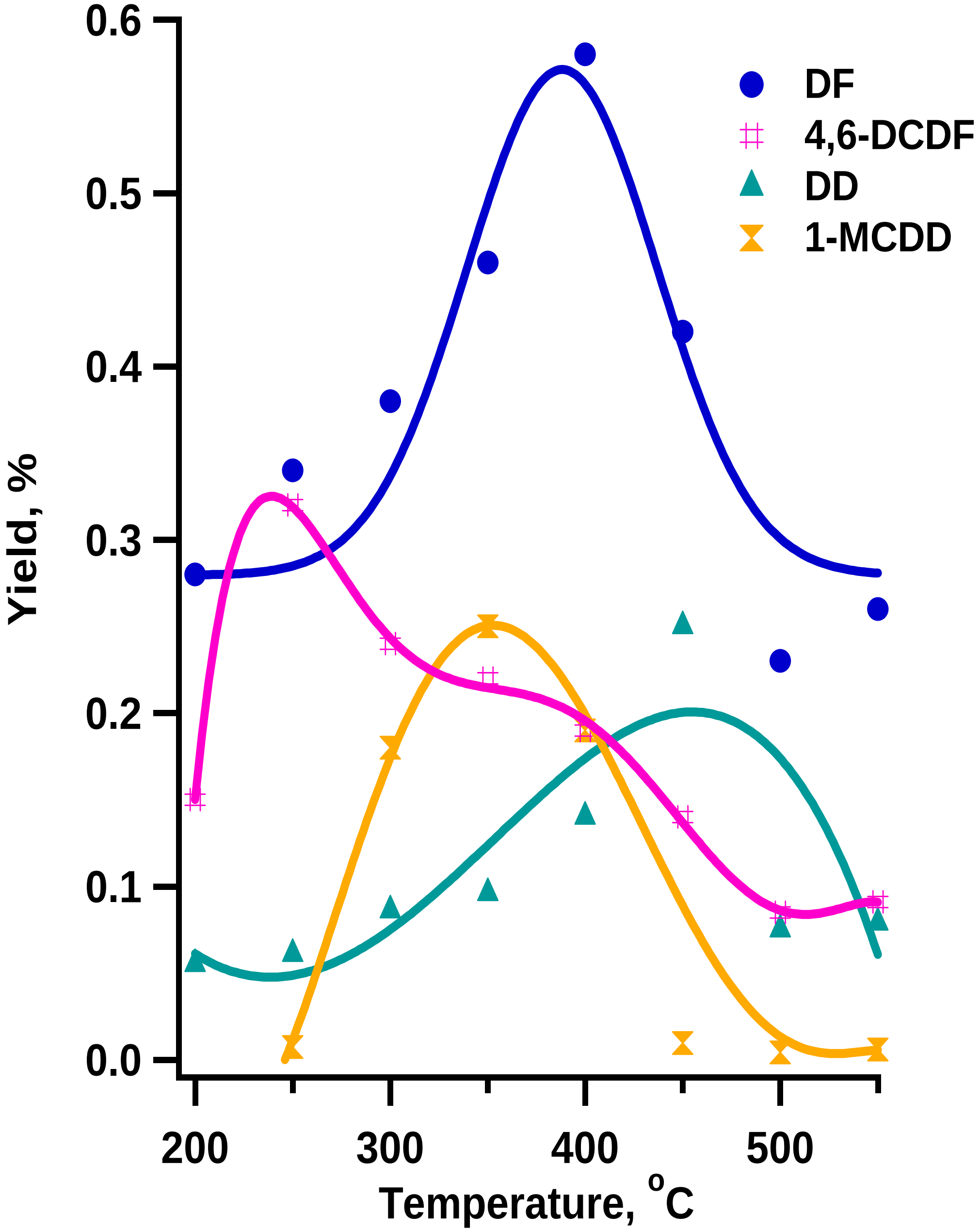


Figure 3.48 Product Yields of PCDD/Fs from the Oxidation of a 1: 10 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

I. Results from a 1:1 Mixture of 2-MCP and 1,2-DCBz, Respectively

Thermal degradation of an equal part mixture of 2-MCP and 1,2-DCBz tracked each other from the initial temperature at 200 °C and the rate accelerated gradually both achieving about 98% destruction at 500 °C. Chlorobenzene products observed were monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), and pentachlorobenzene (PeCBz), and Hexachlorobenzene with maximum yields of 0.43% at 300 °C, 3.6% at 350 °C, 1.4% at 400 °C, 0.21% at 350 °C and 0.014% at 400 °C, respectively. Yield of benzene (Bz) increased with increasing temperature reaching a maximum yield of 0.30% at 350 °C. **Figure 3.49** depicts the yields of chlorobenzenes observed from thermal degradation a 1: 1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under oxidative conditions

The phenolic products observed includes phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 11% at 400 °C, 8.8% at 350 °C, and 2.3% at 450 °C, respectively. The yields of chlorophenols observed from thermal degradation of a 1:1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under oxidative conditions are depicted in **Figure 3.50.**

Other non-dioxin products observed were naphthalene, chloronaphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) with maximum yields of 1.4% at 350 °C, 0.46% at 450 °C, 0.12% at 350 °C, 0.078% at 350 °C and 0.018% at 300 °C, respectively.

High yields of PCDD/Fs were observed from thermal degradation of a 50:50 mixture of 2-MCP and 1,2-DCBz. Dibenzo-*p*-dioxin (DD) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) were the only PCDD products observed with maximum yields of 0.26% at 400 ^{o}C and 0.27% at 350 °C, respectively. PCDF products observed were dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF) forming with maximum yields of 0.53% at 450 °C and 0.35%

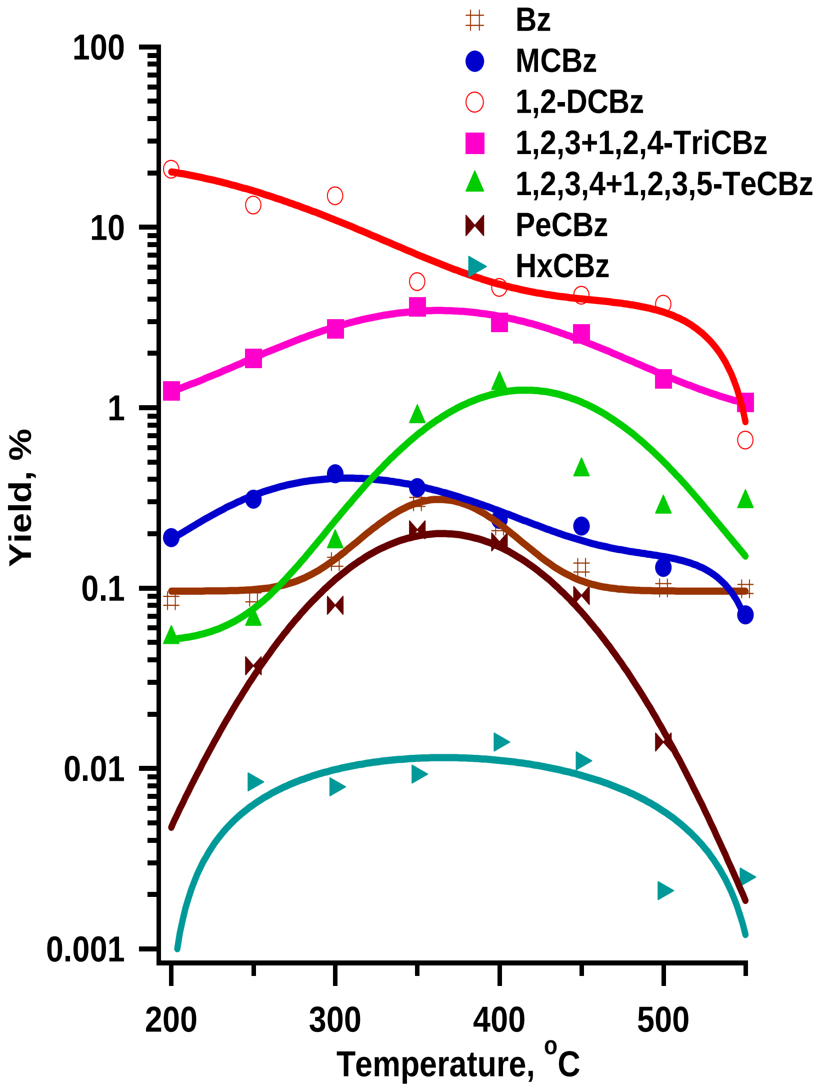


Figure 3.49 Product Yields of Chlorobenzenes from the Oxidation of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

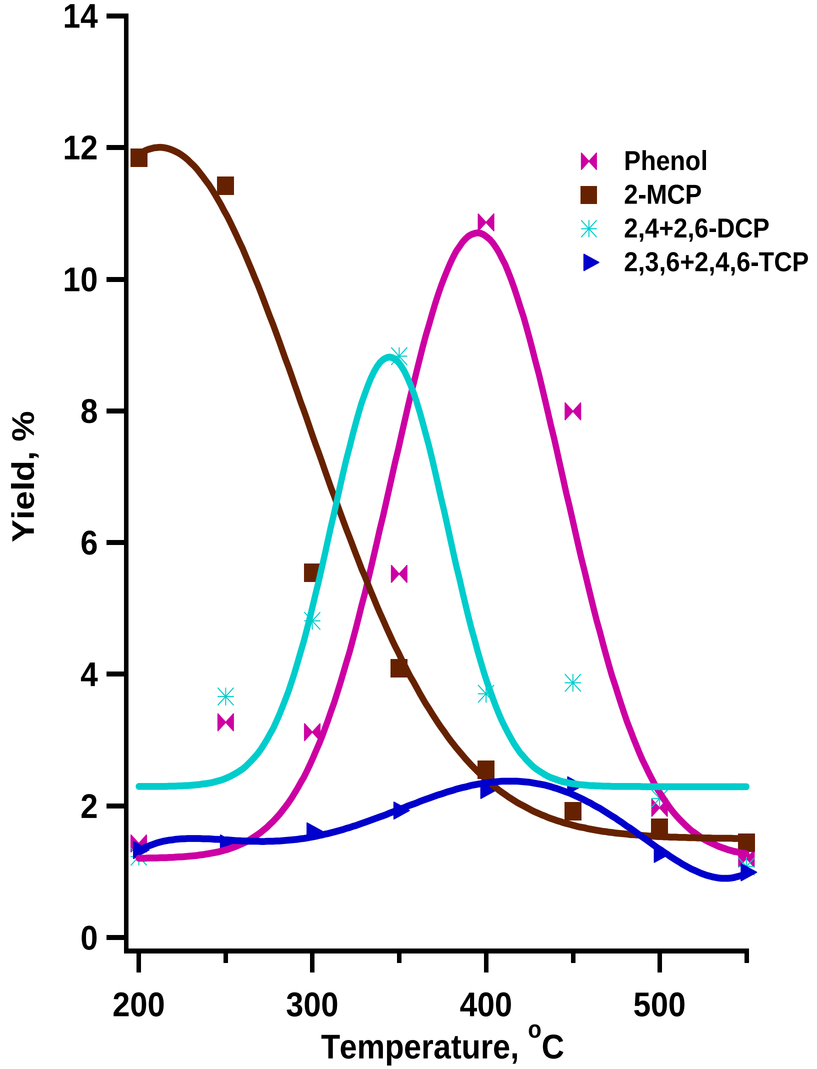


Figure 3.50 Product Yields of Chlorophenols from the Oxidation of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

at 300 °C, respectively. The total yield of PCDFs observed from 200 °C to 550 °C, was about 2.2x higher the total yields of PCDDs detected. The yields of dioxin products observed from thermal degradation of a 1:1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under oxidative conditions are depicted in **Figure 3.51.**

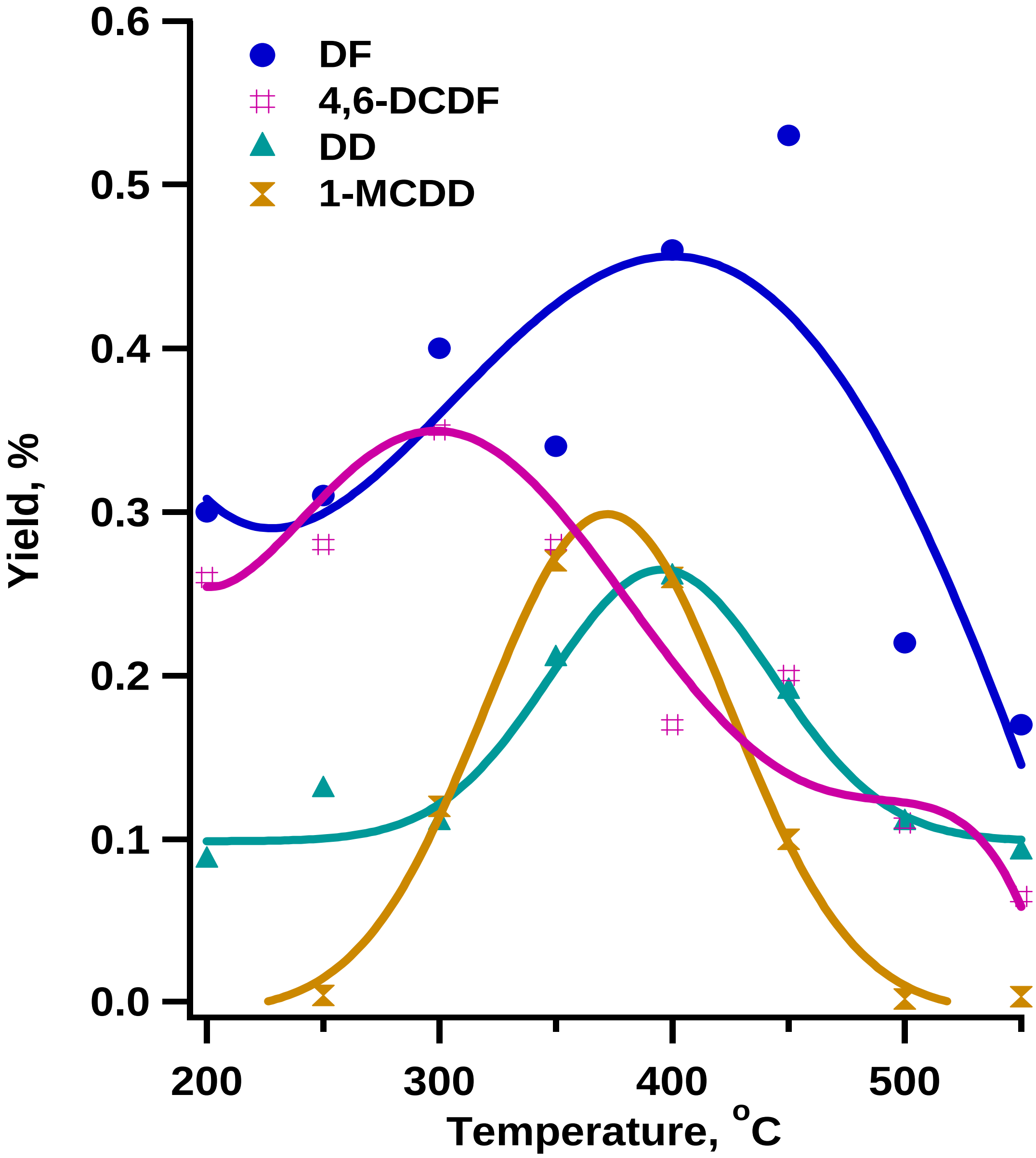


Figure 3.51 Product Yields of PCDD/Fs from the Oxidation of a 1: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

II. Results from a 10:1 Mixture of 2-MCP and 1,2-DCBz, Respectively

Thermal degradation of 2-MCP and 1,2-DCBz occured significantly even at low temperature reaching about 88% and 76% destruction at 200 °C, respectively. Formation of benzene (Bz) increased with increasing temperature achieving a maximum yield of 0.34% at 400 °C. Chlorobenzene products observed includes monochlorobenzene (MCBz), 1,2,3-, and 1,2,4-trichlorobenzene (1,2,3+1,2,4-TriCBz), 1,2,3,4-, and 1,2,3,5-tetrachlorobenzene (1,2,3,4+1,2,3,5-TeCBz), pentachlorobenzene (PeCBz) and hexachlorobenzene (HxCBz) with maximum yields of 0.56% at 350 °C, 3.3% at 300 °C, 1.2% at 400 °C, 0.26% at 450 °C and 0.075% at 450 °C, respectively. **Figure 3.49** depicts the yields of chlorobenzenes observed from thermal degradation a 10: 1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under oxidative conditions

Phenolic products detected were phenol, 2,4-, and 2,6-dichlorophenol (2,4+2,6-DCP) and 2,3,6-, and 2,4,6-trichlorophenol (2,3,6+2,4,6-TCP) with maximum yields of 15% at 450 °C, 7.5% at 350 °C, and 3.7% at 400 °C, respectively. The yields of chlorophenols observed from thermal degradation of a 10: 1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under oxidative conditions are depicted in **Figure 3.53.**

In addition, naphthalene, chloronaphthalene, biphenyl, benzoquinone (BQ) and catechol (CT) were formed with maximum yields of 1.8% at 400 °C, 0.38% at 450 °C, 0.10% at 450 °C, 0.081% at 300 °C and 0.038 % at 300 °C, respectively.

Dioxin products were observed over the entire temperature range of the study from 200 °C to 550 °C. PCDD/F products detected were dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF), dibenzo-*p*-dioxin (DD) and 1-monochlorodibenzo-*p*-dioxin (1-MCDD) with maximum yields of 0.41% at 450 °C, 0.46% at 250 °C, 0.32% at 400 °C and 0.36% at 350 °C, respectively.

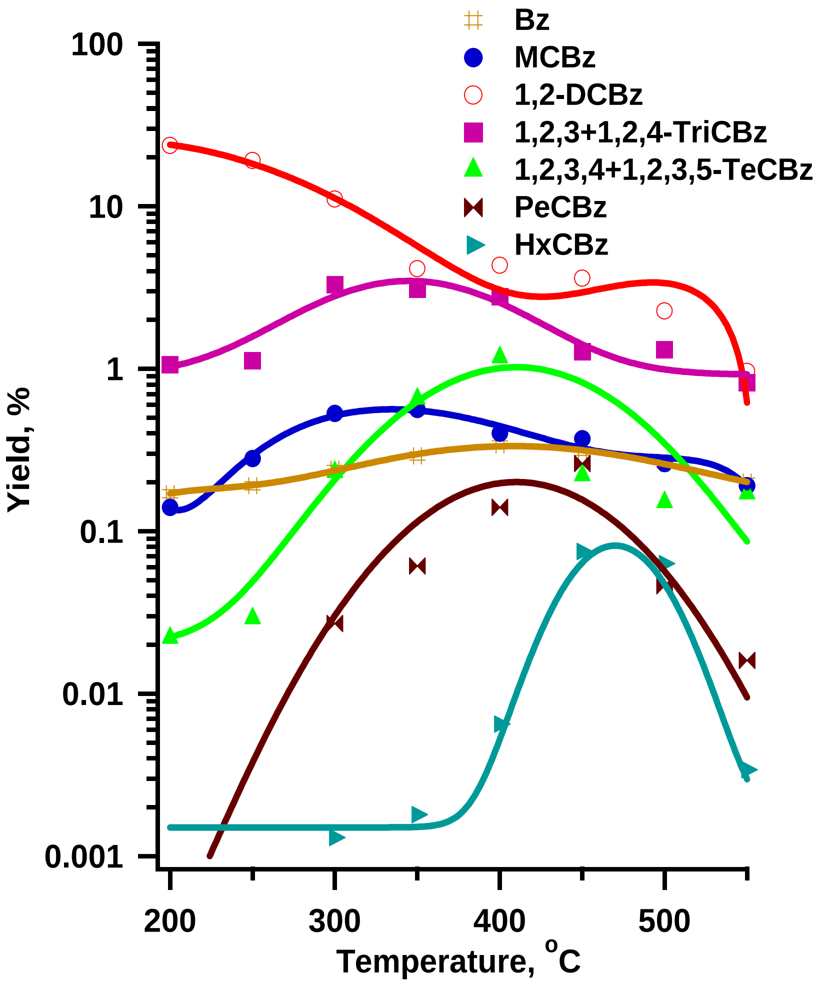


Figure 3.52 Product Yields of Chlorobenzenes from the Oxidation of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

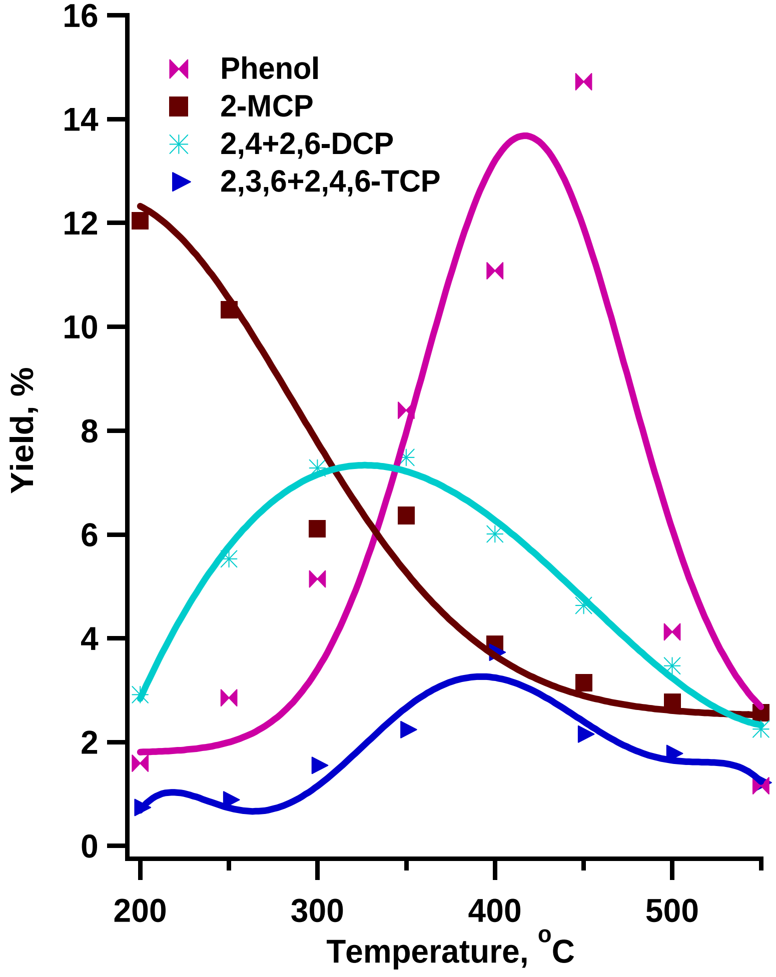


Figure 3.53 Product Yields of Chlorophenols from the Oxidation of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

The PCDD to PCDF ratio observed was 0.62. The yields of dioxin products observed from thermal degradation of a 10:1 mixture of 2-MCP and 1,2-DCBz, respectively over iron oxide/silica surface under oxidative conditions are depicted in **Figure 3.54.** The temperature dependence of thermal degradation of 2-MCP and 1,2-DCBz mixture over a Fe_2O_3/silica surface under oxidative conditions and the yields of dioxin and non-dioxin products are presented in **Table 3.14 and 3.15.**

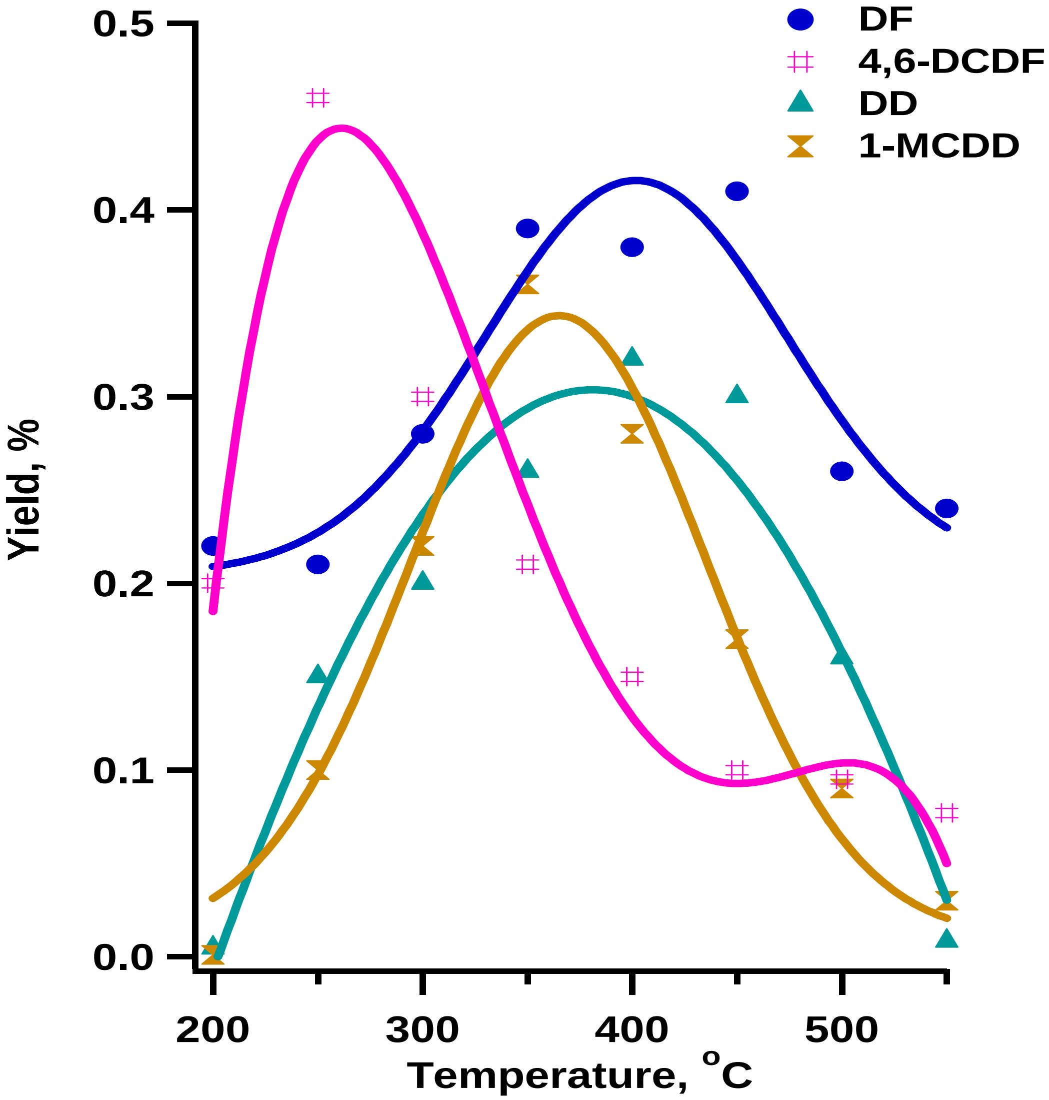


Figure 3.54 Product Yields of PCDD/Fs from the Oxidation of a 10: 1 Mixture of 2-MCP and 1,2-DCBz, Respectively over Fe_2O_3/Silica Surface

Table 3.13 Non-Dioxin Products from Oxidation of 1,2-Dichlorobenzene and 2-Monochlorophenol Mixtures over Fe_2O_3/Silica Surface

Non-Dioxin Products		2-MCP/1,2-DCBz	Reaction Temperature, °C							
			200	250	300	350	400	450	500	550
1	Benzene	0.1	0.098	0.14	0.21	0.31	0.25	0.18	0.11	0.12
		1.0	0.085	0.089	0.14	0.30	0.22	0.13	0.10	0.099
		10	0.17	0.19	0.24	0.29	0.34	0.31	0.26	0.20
2	Monochlorobenzene	0.1	0.16	0.25	0.29	0.47	0.33	0.35	0.20	0.14
		1.0	0.19	0.31	0.43	0.36	0.24	0.22	0.13	0.071
		10	0.14	0.28	0.53	0.56	0.40	0.37	0.26	0.19
3	1,2-Dichlorobenzene	0.1	46	25	16	5.7	3.5	3.0	1.3	1.5
		1.0	21	13	15	5.0	4.6	4.2	3.7	0.66
		10	24	19	11	4.1	4.3	3.6	2.3	0.96
4	1,2,3+1,2,4-Trichlorobenzene	0.1	0.83	1.4	4.5	4.3	3.0	2.2	1.7	1.6
		1.0	1.2	1.9	2.7	3.6	3.0	2.6	1.4	1.1
		10	1.1	1.1	3.3	3.1	2.8	1.3	1.3	0.82
5	1,2,3,4+1,2,3,5-Tetrachlorobenzene	0.1	0.087	0.075	0.36	2.4	2.0	2.7	0.47	0.28
		1.0	0.053	0.067	0.18	0.89	1.4	0.45	0.28	0.30
		10	0.022	0.029	0.23	0.65	1.2	0.22	0.15	0.17
6	Pentachlorobenzene	0.1	bdl	0.029	0.046	0.091	0.12	0.23	0.33	0.018
		1.0	bdl	0.037	0.08	0.21	0.18	0.091	0.014	bdl
		10	bdl	bdl	0.027	0.061	0.14	0.26	0.046	0.016
5	Hexachlorobenzene	0.1	bdl	0.015	0.024	0.037	0.091	0.061	0.0049	0.0016
		1.0	bdl	0.0084	0.0079	0.0093	0.014	0.011	0.0021	0.0025
		10	bdl	0.00090	0.0013	0.0018	0.0065	0.075	0.063	0.0034
6	Phenol	0.1	1.6	2.0	2.0	2.1	2.2	4.4	1.2	0.93
		1.0	1.4	3.3	3.1	5.5	11	8.0	2.0	1.2
		10	1.6	2.9	5.1	8.4	11	15	4.1	1.2
7	2-Monochlorophenol	0.1	15	11	6.1	3.4	2.6	1.9	1.8	1.7
		1.0	12	11	5.5	4.1	2.6	1.9	1.7	1.4
		10	12	10	6.1	6.4	3.9	3.1	2.8	2.6

Table 3.13 Con'd

8	**2,4+2,6-Dichlorophenol**	**0.1**	**1.7**	**2.1**	**6.5**	**5.9**	**2.1**	**3.4**	**2.0**	**1.7**
		1.0	**1.2**	**3.7**	**4.8**	**8.8**	**3.7**	**3.9**	**2.1**	**1.1**
		10	**2.9**	**5.5**	**7.3**	**7.5**	**6.0**	**4.6**	**3.8**	**2.3**
9	**2,3,6+2,4,6-Trichlorophenol**	**0.1**	**0.46**	**0.55**	**0.81**	**1.7**	**1.6**	**1.4**	**0.69**	**0.75**
		1.0	**1.3**	**1.4**	**1.6**	**1.9**	**2.2**	**2.3**	**1.3**	**0.99**
		10	**0.74**	**0.89**	**1.6**	**2.1**	**3.7**	**2.2**	**1.8**	**1.2**
10	**Naphthalene**	**0.1**	**0.15**	**0.19**	**0.32**	**0.71**	**0.63**	**0.68**	**0.42**	**0.22**
		1.0	**0.26**	**0.56**	**0.67**	**1.4**	**1.1**	**0.82**	**0.29**	**0.31**
		10	**0.14**	**0.80**	**1.2**	**1.2**	**1.8**	**1.0**	**0.64**	**0.19**
11	**Chloronapthalene**	**0.1**	**0.0051**	**0.0069**	**0.0060**	**0.0088**	**0.013**	**0.025**	**0.0073**	**0.0048**
		1.0	**bdl**	**0.0084**	**0.028**	**0.076**	**0.33**	**0.46**	**0.054**	**0.0077**
		10	**0.0065**	**0.082**	**0.13**	**0.10**	**0.28**	**0.38**	**0.029**	**0.018**
12	**Biphenyl**	**0.1**	**0.027**	**0.049**	**0.069**	**0.090**	**0.051**	**0.036**	**0.015**	**0.018**
		1.0	**0.016**	**0.044**	**0.036**	**0.12**	**0.071**	**0.058**	**0.028**	**0.024**
		10	**0.041**	**0.061**	**0.073**	**0.065**	**0.079**	**0.10**	**0.057**	**0.020**
13	**Benzoquinone**	**0.1**	**0.0024**	**0.0047**	**0.018**	**0.013**	**0.0084**	**0.0023**	**0.0011**	**0.0018**
		1.0	**0.025**	**0.068**	**0.076**	**0.078**	**0.053**	**0.0064**	**0.0049**	**0.0030**
		10	**0.034**	**0.093**	**0.081**	**0.012**	**0.0079**	**0.0083**	**0.0037**	**0.0039**
14	**Catechol**	**0.1**	**0.0028**	**0.0075**	**0.026**	**0.0071**	**0.0022**	**0.00092**	**0.00041**	**0.00025**
		1.0	**0.0035**	**0.0088**	**0.018**	**0.0034**	**0.0012**	**0.0010**	**0.00036**	**0.00018**
		10	**0.0057**	**0.0070**	**0.038**	**0.0079**	**0.0062**	**0.00085**	**0.00067**	**0.00040**

bdl- Below Detection Limit

Table 3.14 Dioxin Products from Oxidation of 1,2-Dichlorobenzene and 2-Monochlorophenol Mixtures over Fe_2O_3/Silica Surface

			Reaction Temperature, ^oC							
Dioxin Products		**2-MCP/1,2-DCBz**	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**
1	**DF**	**0.1**	**0.28**	**0.34**	**0.38**	**0.46**	**0.58**	**0.42**	**0.23**	**0.26**
		1.0	**0.30**	**0.31**	**0.40**	**0.34**	**0.46**	**0.53**	**0.22**	**0.17**
		10	**0.22**	**0.21**	**0.28**	**0.39**	**0.38**	**0.41**	**0.26**	**0.24**
2	**DD**	**0.1**	**0.055**	**0.061**	**0.086**	**0.096**	**0.14**	**0.20**	**0.075**	**0.079**
		1.0	**0.087**	**0.13**	**0.11**	**0.21**	**0.26**	**0.19**	**0.11**	**0.092**
		10	**0.0047**	**0.15**	**0.20**	**0.26**	**0.32**	**0.30**	**0.16**	**0.0083**
3	**1-MCDD**	**0.1**	**bdl**	**0.0073**	**0.18**	**0.25**	**0.19**	**0.0095**	**0.0041**	**0.0058**
		1	**bdl**	**0.0045**	**0.12**	**0.27**	**0.26**	**0.10**	**0.0023**	**0.0037**
		10	**0.0010**	**0.10**	**0.22**	**0.36**	**0.28**	**0.17**	**0.090**	**0.030**
4	**4,6-DCDF**	**0.1**	**0.15**	**0.32**	**0.24**	**0.22**	**0.19**	**0.14**	**0.085**	**0.091**
		1	**0.26**	**0.22**	**0.35**	**0.28**	**0.17**	**0.20**	**0.11**	**0.065**
		10	**0.20**	**0.46**	**0.30**	**0.21**	**0.15**	**0.10**	**0.095**	**0.077**

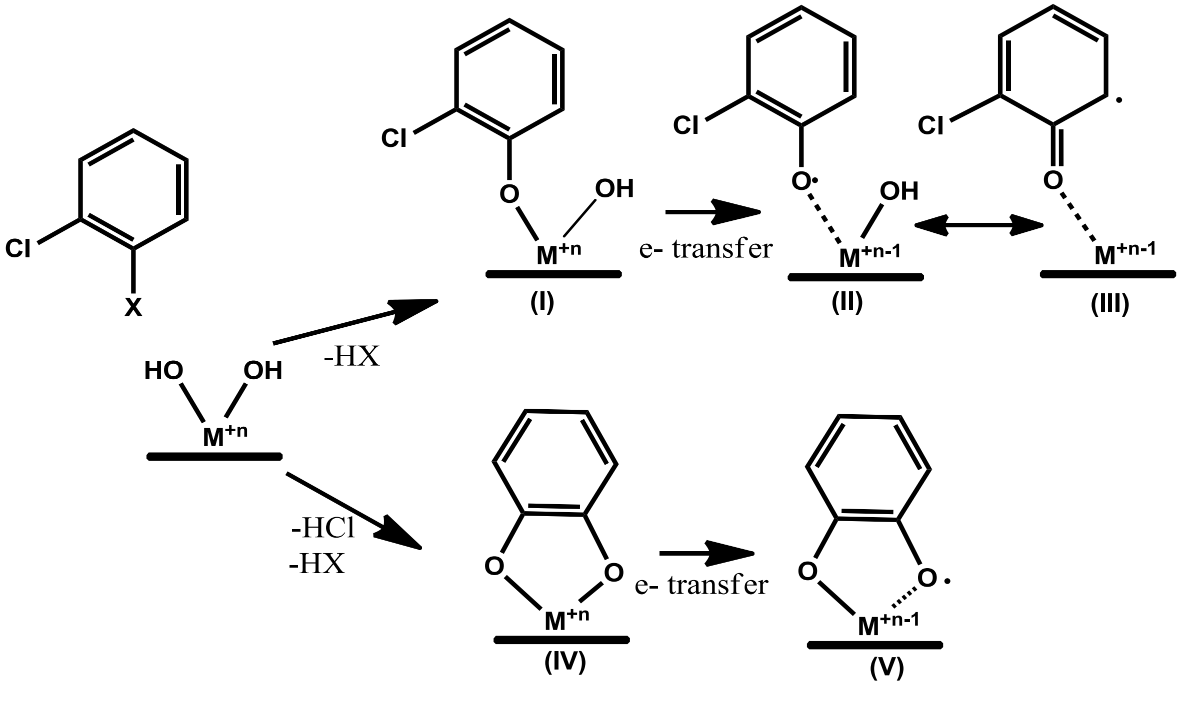
bdl- Below Detection Limit

3.6 References

1. Nganai, S.; Lomnicki, S.; Dellinger, B. Ferric oxide mediated formation of PCDD/Fs from 2-monochlorophenol. *Environ. Sci. & Technol.* **2009,** *43*, (2), 368-373.

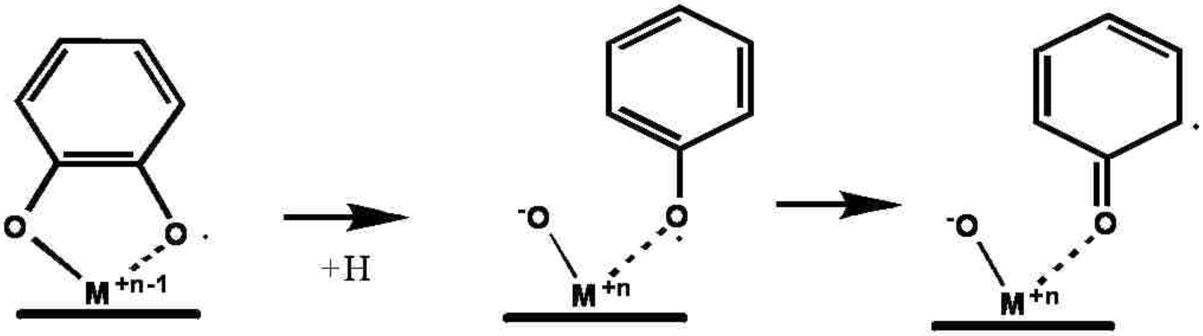
CHAPTER 4: DISCUSSION

The formation of dioxin and non-dioxin products from transition metal-mediated reactions is initiated by chemisorption of the chemical precursors on the surface. Previous studies have demonstrated using FTIR spectroscopy that chlorinated phenols and chlorinated benzenes chemisorb on the surface of copper oxide[1]. Subsequent elimination of water and/or HCl above 150 °C leads to the formation of a chemisorbed phenoxide [2]. Hydroxyl groups are present on almost every terminal plane of metal oxides as a completion of unsatisfied charges and valences of metal ions at terminal positions [3-5]. Iron oxide is no different than other metal oxides, and its interaction with gas-phase substituted aromatic precursor molecules is expected to be similar to that of copper oxide. **Scheme 4.1** depicts two general pathways of formation of surface-associated radicals from chlorobenzenes (x=Cl and y=Cl) and chlorophenols (x=OH and y=Cl) transition metal surface.



Scheme 4.1 Parallel Pathways of Formation of Surface-Associated Radicals from Chlorobenzenes (x=Cl and y=Cl) and Chlorophenols (x=OH and y=Cl)

Furthermore, the bidentate species **(IV), (Scheme 4.1)** potentially undergoes transition metal-mediated thermal decomposition at higher temperatures via cleavage at one carbon-oxygen bond to form phenoxyl radicals in both its oxygen-centered and carbon-centered structures as depicted in **Scheme 4.2**.



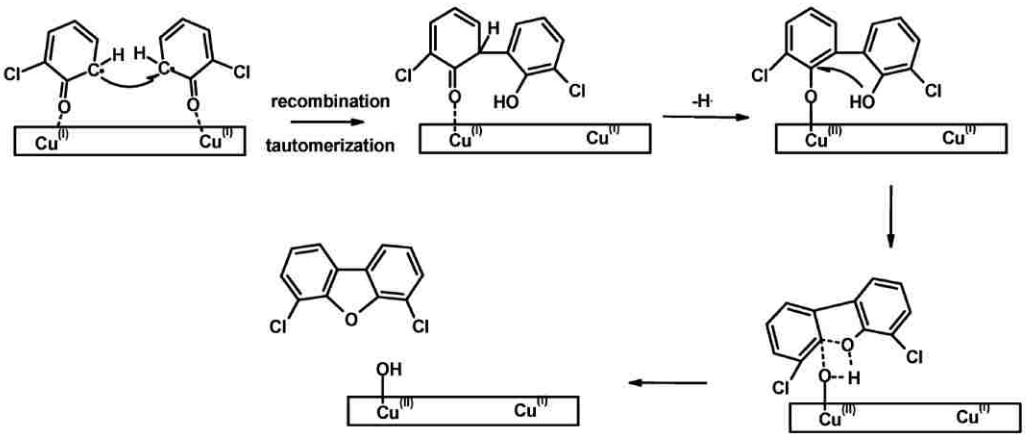
Scheme 4.2 Formation of Oxygen- and Carbon-Centred Phenoxyl Radicals from Chemisorbed Chemical Precursors

These transformations are manifested by appearance of non-chlorinated products such dibenzofuran and phenol with maximum formation yields at temperatures above 450 ^{o}C versus other products at 250 to 350 ^{o}C.

4.1 Mechanistic Aspects of Dioxin Formation from 2-Monochlorophenol over CuO/Silica Surface

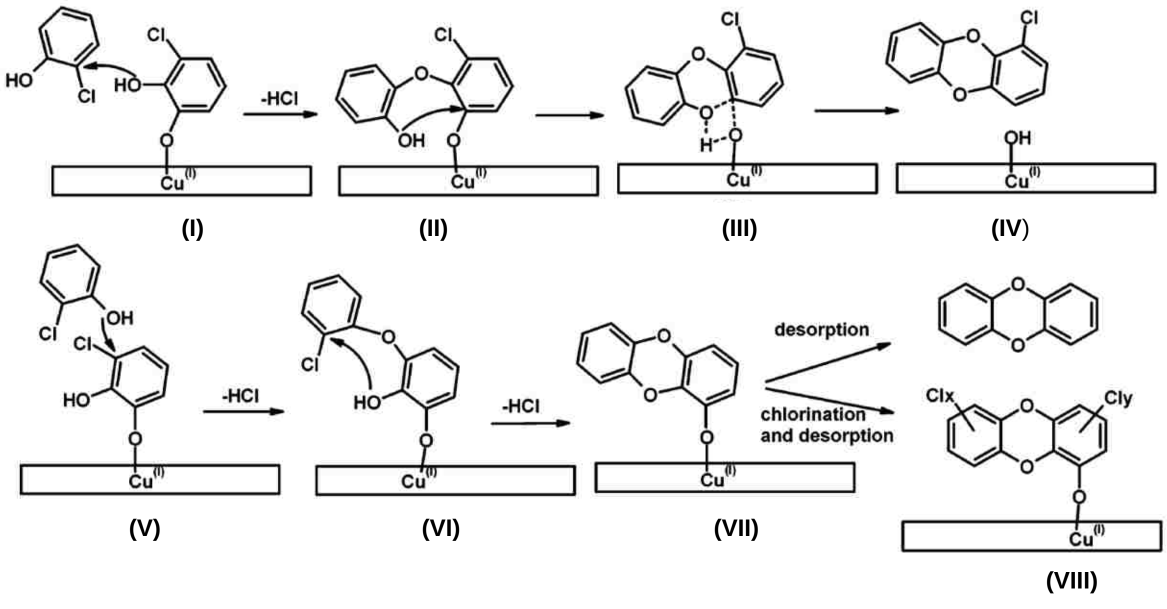
Based on previous experimental results over CuO/silica surface, two pathways of chemisorption have been identified for chlorophenols: (1) elimination of H_2O (upper path in **Scheme 4.1**) and (2) elimination of both H_2O and HCl (lower path in **Scheme 4.1** [6]. It has been demonstrated previously using electron paramagnetic resonance spectroscopy (EPR) [6] and X-ray absorption near-edge spectroscopy (XANES) [5] that, in the case of CuO, the resulting chemisorbed species, **I** and **IV**, are subject to electron transfer between the adsorbed molecule and metal center (Cu^{2+} for CuO), resulting in the formation of persistent free radicals, species **II**, **III**, and **V**, that are associated with the concomitantly formed reduced metal centers (Cu1+ for

CuO) [6, 7]. It has also been previously proposed on the basis of the results of a study with 2-MCP over CuO/silica system in which PCDFs formation exhibited a negative rate order with respect to 2-MCP concentration whereas PCDDs exhibited rate orders ranging from 0.5 to 1 [8], that PCDFs are produced as a result of Langmuir-Hinshelwood (L-H) mechanism while PCDDs are formed according to Eley-Rideal (E-R) mechanism. **Scheme 4.3** summarizes the previously identified L-H mechanism in the formation of 4,6-DCDF from reaction of two surface-associated, carbon-centered chlorophenoxyl radicals.



Scheme 4.3. Proposed Langmuir-Hinshelwood Mechanism for 4,6-DCDF Formation

In addition, two plausible E-R pathways which have previously been proposed for the formation of PCDDs on CuO/silica surface are depicted in **Scheme 4.4** [9, 10]. The chemisorbed chlorophenoxyl radical reacts with terminal oxygen and tautomerizes to surface species (**I**) shown in **Scheme 4.4**. [11]. Gas phase 2-MCP can react with species (**I**) at one of the two sites (a) the site of hydroxyl substitution or (b) the site of chlorine substitution. When 2-MCP reacts with species (**I**) at hydroxyl substituted site, intermediate species (**II**) is formed and HCl is eliminated in the process. Consequently, cyclic transition of species (**II**) allows for 1-MCDD to be desorbed from the surface. Additionally, when gas phase 2-MCP reacts with species (**I**) at chlorine substituted site, again with HCl elimination, species (**IV**) is formed. Further elimination of HCl from resulting species (**IV**) and ring closure process leads to formation of surface bound DD or species (**VII**) **Scheme 4.4** that can then be desorbed or potentially undergo further chlorination to form PCDDs.



Scheme 4.4 Copper Oxide-Mediated 1-MCDD and DD Formation

4.2 Comparison of the Mechanisms of Dioxin Formation from 2-Monochlorophenol over Fe_2O_3/Silica versus CuO/Silica

The yields of PCDD/Fs from oxidation of 2-MCP was 3x greater over Fe_2O_3/silica than CuO/silica. The formation of DD, 1-MCDD, and 4,6-DCDF from 2-chlorophenoxyl radical is likely by similar mechanisms previously described for the reaction of 2-MCP over CuO/silica surface. **Figure 4.1** depicts a comparison of PCDD/Fs yields from the oxidation of 2-MCP over Fe_2O_3/silica and CuO/silica surfaces.

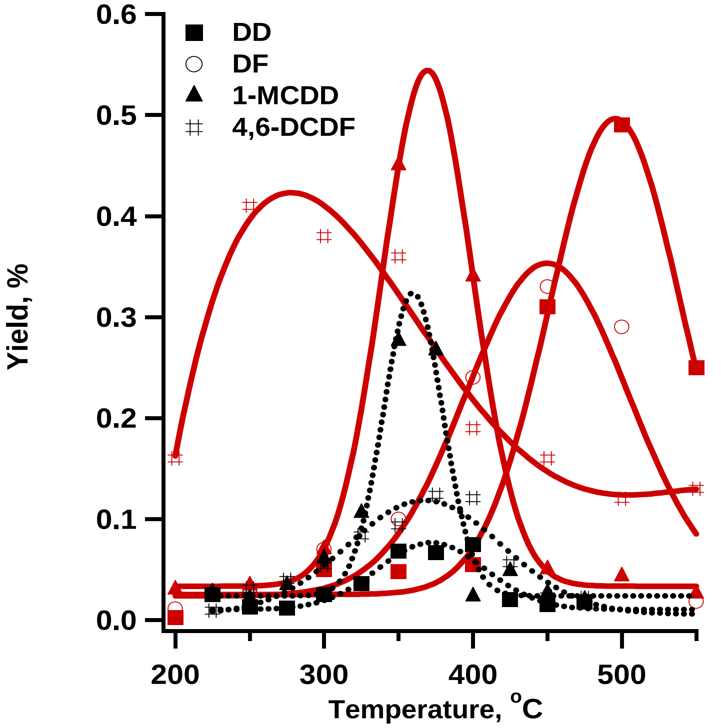


Figure 4.1 Comparison of PCDD/Fs Yields from the Oxidation of 2-MCP over Fe_2O_3/Silica (—) and CuO/Silica (·····) Surfaces

A significant shift in temperature range of maximum yield 4,6-DCDF formation is observed between 250 to 300 °C for iron and from 350 to 400 °C for copper. This observation can be attributed to stronger catalytic properties of iron than copper which consequently leads to greater concentration of chemisorbed species even at relatively lower temperatures.

Furthermore, a comparison of the results from pyrolysis of 2-MCP over iron oxide versus previous data over copper oxide is presented in **Figure 4.2**.

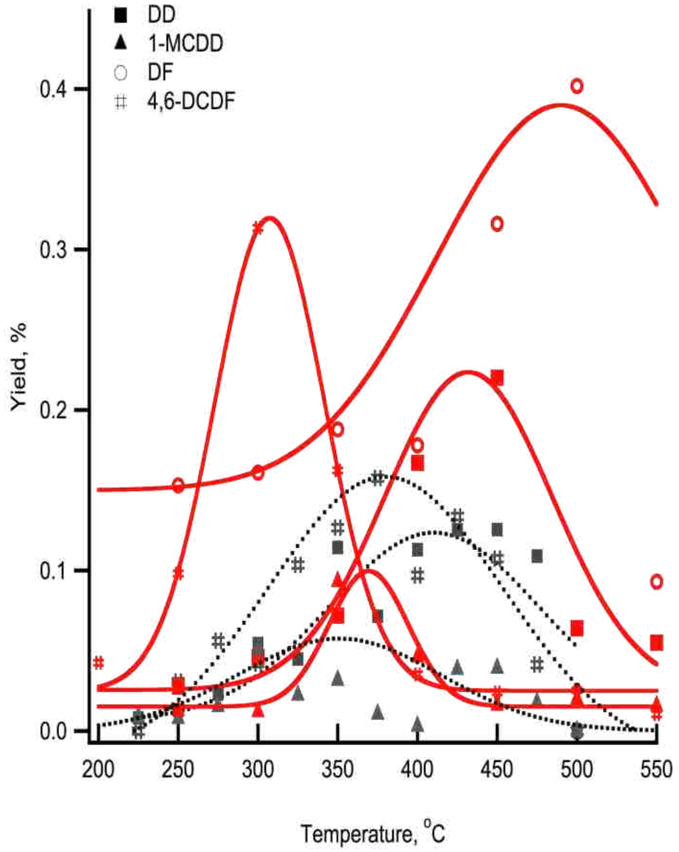
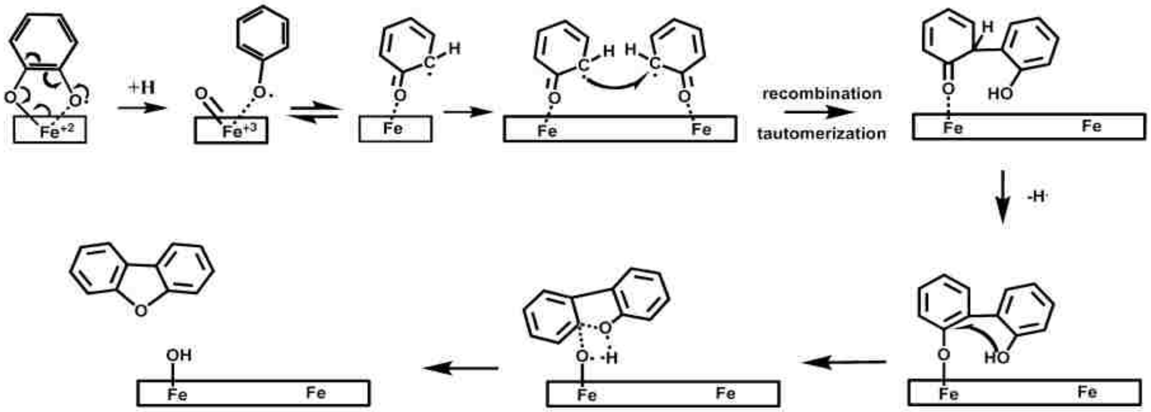


Figure 4.2. Comparison of PCDD/Fs Yields from the Pyrolysis of 2-MCP over Fe_2O_3/Silica (—) and CuO/Silica (······) Surfaces

In comparison, the maximum yield of total PCDD/Fs is 2.5x greater over iron oxide than over copper oxide. As depicted in **Figure 4.2.**, PCDFs over iron oxide were the dominant products, with 4,6-DCDF which is formed from 2-chlorophenoxyl radical dominating at temperatures less than 350 °C and DF which is formed from phenoxyl radical dominating above 350 □C. In contrast, for copper oxide, the PCDD and PCDF product yields were comparable. DF was not observed for copper oxide at all, and the only PCDD/F products detected for 2-chlorophenoxyl reactions were DD, 1-MCDD, and 4,6-DCDF.

A notable difference in PCDD/F products observed is the formation of DF over Fe_2O_3/silica which was not observed over CuO/silica surface [9]. This observation can be attributed to the favorable formation of the bidentate species intermediate **V** depicted in **Scheme 4.1** over iron than copper. **Scheme 4.2** depicts the mechanism of the resulting surface-associated phenoxyl radical, **VI**, through back-electron transfer and subsequent conversion to the keto mesomer. Two of the surface-associated keto mesomers then react to form DF as depicted in **Scheme 4.5.**



Scheme 4.5 Mechanism of Dibenzofuran Formation over of Fe_2O_3/Silica Surface

In addition, more PCDFs than PCDDs were predominantly formed over iron than copper surface. This observation may imply iron facilitates a faster rate of chemisorption of the reactant species consequently resulting in greater concentration and stability of the chlorophenoxyl and phenoxyl species on the surface than copper.

4.3 Comparison of the Mechanisms of Dioxin Formation from 1,2-Dichlorobenzene versus 2-Monochlorophenol over CuO/Silica

Significant yields of PCDFs and lack of PCDD formation were observed from the surface-mediated reactions of 1,2-DCBz over CuO/silica both under pyrolytic and oxidative conditions. **Figure 4.2** depicts a comparison of the PCDD/F yields from oxidation of 1,2-DCBz and 2-MCP over CuO/Silica surface.

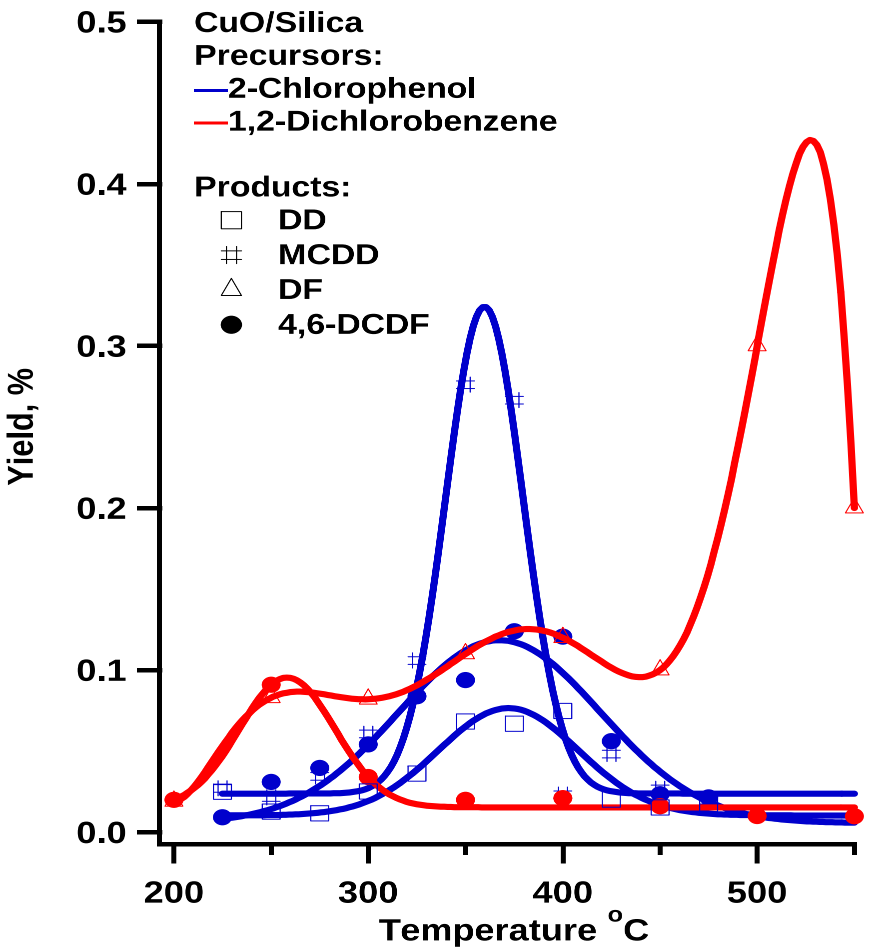


Figure 4.3. Comparison of PCDD/F Yields from Oxidation of 1,2-DCBz (red lines) and 2-MCP (blue lines) over CuO/Silica Surface

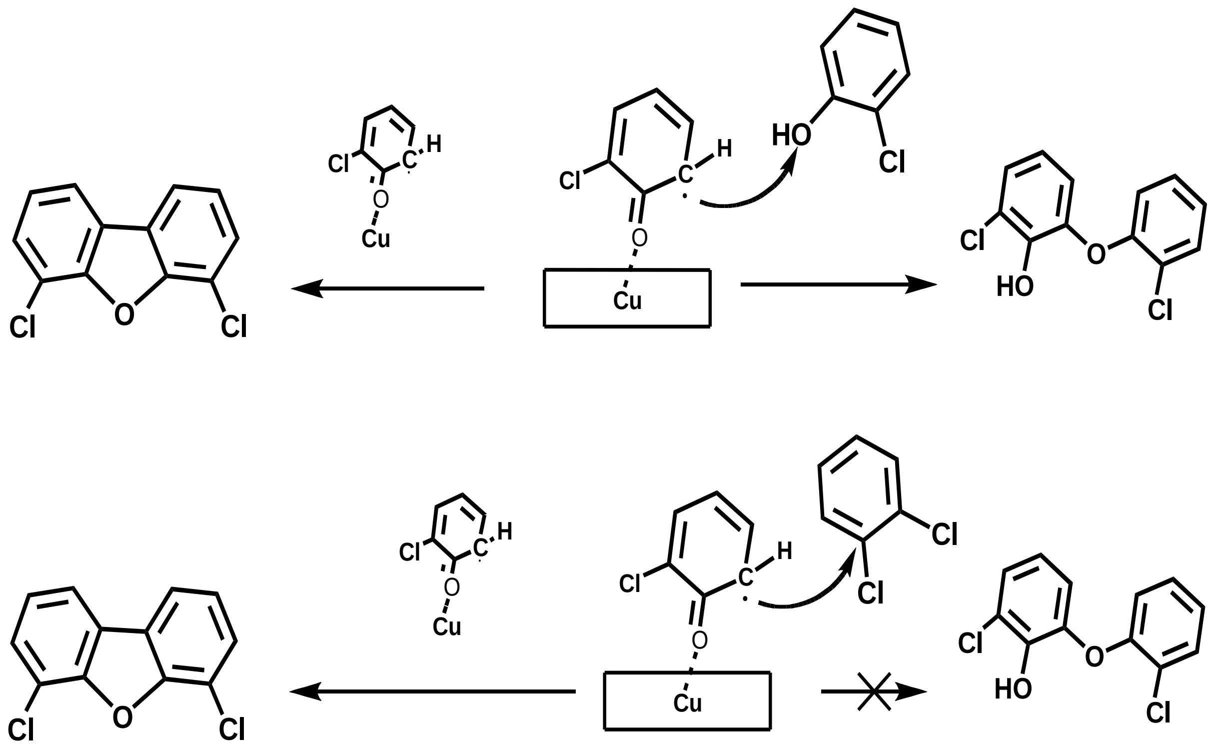
The high yields of PCDFs and lack of formation of PCDD observed in our laboratory study has important implications concerning PCDD to PCDF ratios observed in the full-scale combustion systems. Previous laboratory studies of chlorophenols have not been able to reproduce the low PCDD to PCDF emissions. Since the concentration of chlorobenzenes in the exhaust of waste incinerators typically exceeds that of chlorophenols by at least an order of magnitude[12-15], and PCDD to PCDF ratio for our 1,2-DCBz studies is < 0.01 (based on a PCDD detection limit of 0.003%), the PCDD to PCDF emission ratio from full scale combustors is expected to be <<1 based on our 2-MCP and 1,2-DCBz oxidation and pyrolysis studies [13, 16].

Since this theory relies on the concentration of chlorobenzenes being greater than that of chlorophenols, it is natural to ask why this is true. The combustion of the chlorine-containing materials results in the formation of chlorinated benzenes through the condensation reaction of C2 and C4 fuel or waste fragment [17]. It is generally assumed that chlorinated phenols are formed by similar reactions or gas-phase oxidation of chlorinated benzenes. However, there are no laboratory or field data demonstrating the formation of chlorophenols via gas-phase reactions. Since we were able to observe the formation of chlorinated phenols from chlorinated benzenes over a copper and iron oxide surfaces, it is possible that the chlorophenols observed in the exhaust result from the surface mediated transformation of chlorinated benzenes. In fact, the observed ratio of chlorobenzenes to chlorophenols of ~10:1 observed in our studies correlates with the ratios observed in municipal waste incinerator exhausts of 10:1-100:1[12-15].

In addition, the majority of the research studies on the surface mediated formation of PCDD/Fs have concentrated on the chlorophenols as the precursors [18-21]. Our recent studies have indicated that both PCDDs and PCDFs can be formed over a copper oxide surface from 2-MCP with yields of 0.3-0.5% [7, 9, 22]. However, as was the case for other reported laboratory studies of chlorinated phenols, the PCDD to PCDF ratio was > 1 which is not in agreement with ratios measured in full-scale combustors where the PCDD/PCDF was observed to be <<1 [23-25] .

This disagreement is a subject of vigorous discussion within the dioxin research community. We demonstrated previously that the reaction of 2-MCP over an Fe_2O_3/silica surface resulted in a PCDD to PCDF ratio of 0.38, which led to the proposal that iron oxide mediated reactions could be an explanation for the low PCDD to PCDF ratios observed in full-scale combustors [26]. We have also postulated that when chlorinated phenols are the reactant, the surface radical-radical condensation reaction that forms PCDF is inhibited by a competitive reaction between the gas phase chlorophenols and surface bound radicals that instead form dichloro-, hydroxy-, biphenyl ether as shown in **Scheme 4.6** [9] . We suggested that if chlorobenzenes rather than chlorophenols were the reactant, the competitive reaction would not occur and higher PCDF yields (and lower PCDD to PCDF ratios) would be observed. Competitive reaction of gas-phase chlorophenol with a surface radical forms dichloro-, hydroxy diphenyl ether rather than PCDFs. When the reactant is a chlorobenzene, the competitive reaction is slow and PCDFs may be formed. Our 1,2-DCBz data support this hypothesis, as only PCDFs and no PCDDs are formed. The competing reaction product, dichloro-, hydroxy-diphenyl ether was also not observed. Moreover, the yields of PCDFs **(DF +DCDF)** from the pyrolysis of 1,2-DCBz were ~3x higher than the combined PCDD and PCDF yields **(DD+MCDD+DCDF)** for the reaction of 2-MCP over copper oxide under the same conditions as shown in **Figure 4.4**.

An important difference between 2-MCP and 1,2-DCBz reactions is best illustrated in **Figure 4.4.** Notably, unlike 2-MCP presence of two temperature maxima for the PCDD/F and other products at ~350 °C and 450-550 °C is observed for 1,2-DCBz. This can be attributed to the differences in the chemisorption reactions of 2-MCP and 1,2-DCBz [6].



Scheme 4.6. Comparison of Surface Reactions of Gas-phase Chlorophenols (upper pathway) and Chlorobenzenes (lower pathway)

4.4 Comparison of the Mechanisms of Dioxin Formation from 1,2-Dichlorobenzene versus 2-Monochlorophenol over Fe_2O_3/Silica versus CuO/Silica

The low temperature thermal degradation of 1,2-DCBz over supported iron catalyst formed high yields of PCDFs and no PCDDs observed. The yield of dioxin products from pyrolysis of 2-MCP over CuO/silica were 4x higher than the dioxin yields from pyrolysis of 1,2-DCBz over Fe_2O_3/silica surface. This observation can be attributed to the favorable rate of chemisorption of 2-MCP as demonstrated previously in our XANES studies on adsorption mechanisms of 2-MCP and 1,2-DCBz on CuO/silica surface [5].

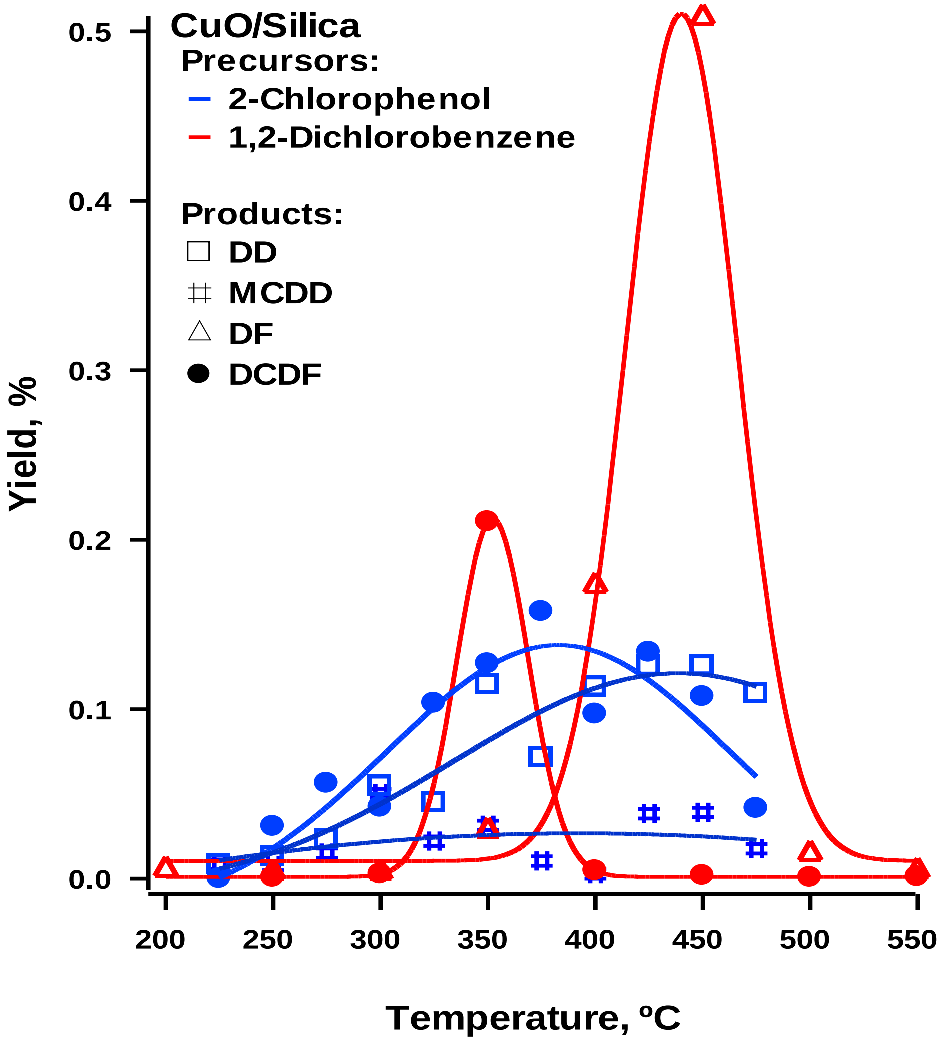


Figure 4.4. PCDD/Fs Yields from the Pyrolysis of 1,2-DCBz (red lines) and 2-MCP (blue lines) over Copper Oxide/Silica

Figure 4.5 presents a comparison of PCDD/F yields from pyrolysis of 2-MCP over CuO/silica and pyrolysis of 1,2-DCBz over Fe_2O_3/silica surface. Furthermore, the role of iron and copper as effective catalysts that promote PCDD/F was also observed from reactions of 1,2-DCBz in both excess oxygen and in low oxygen conditions. For instance, **Figure 4.6** depicts a comparison of the yields of dioxin products obtained from oxidation of 1,2-DCBz over copper oxide and iron oxide surfaces.

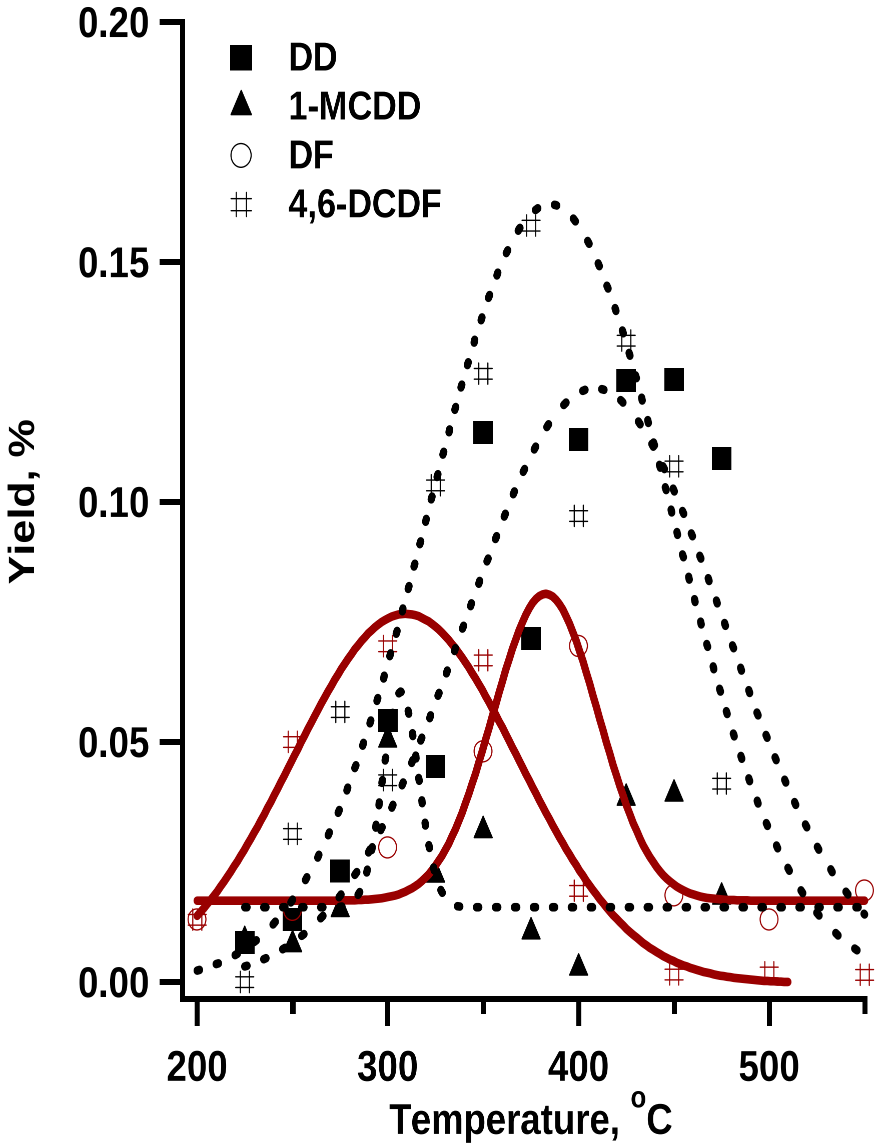


Figure 4.5 Comparison of PCDD/F Yields from Pyrolysis of 2-MCP over CuO/Silica (···) and Pyrolysis of 1,2-DCBz over Fe_2O_3/Silica(-) Surface

The total maximum yields of PCDD/Fs are 1.5x greater over iron oxide than over copper oxide. In contrast to the results from 2-MCP over iron oxide and copper oxide surface, oxidation of 1,2-DCBz over both metal catalysts resulted in lack of PCDDs formation and PCDFs were the dominant products with 4,6-DCDF achieving its maximum yields at temperatures below 350 °C.

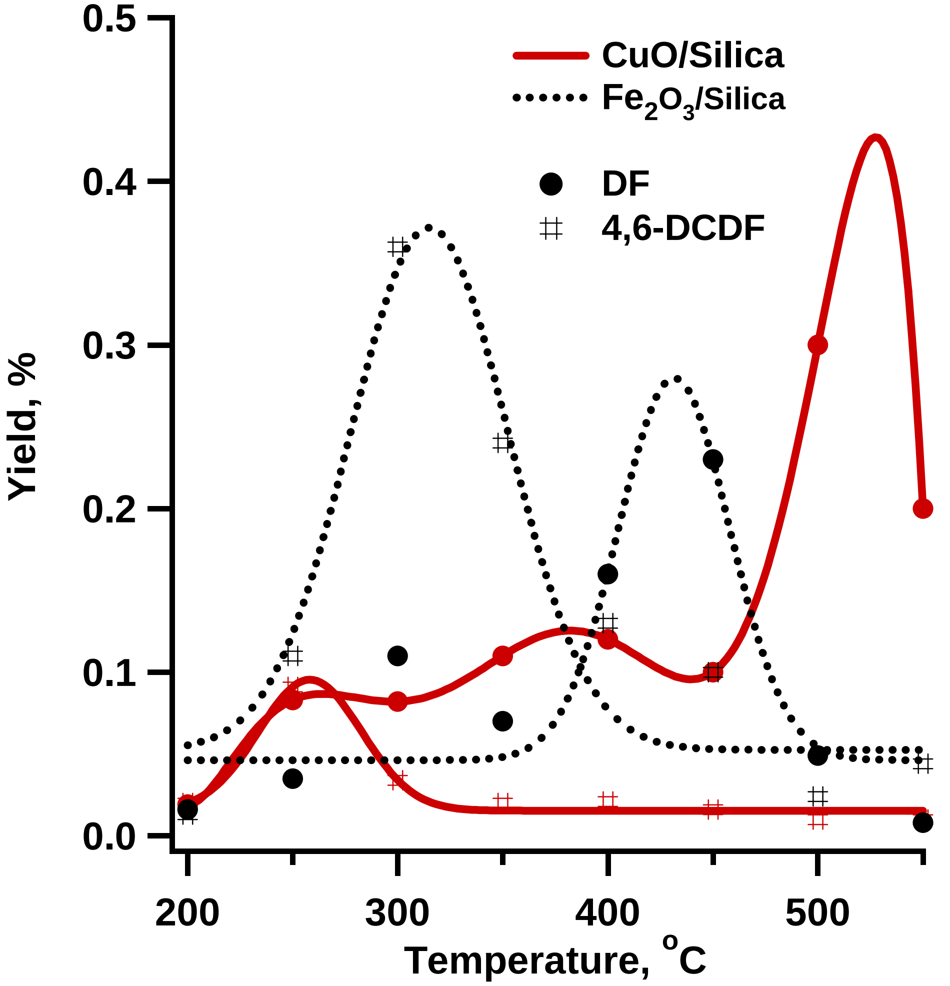


Figure 4.6. Comparison of PCDD/Fs Yields from the Oxidation of 1,2-DCBz over Fe_2O_3/silica and CuO/silica Surfaces

Additionally, no significant difference was observed in the temperature dependence of DF formation which peaked at above 350 °C for both copper oxide and iron oxide. Similar trend was observed involving reactions pure 1,2-DCBz as explained in **Section 4.2** and **Section 4.3.** However, it is notable as shown in **Figure 4.7** that the yields of DF and 4,6-DCDF dropped drastically at above 500 °C over iron oxide than over CuO. This observation can be attributed to stronger oxidative properties of iron which dominates at higher temperatures resulting in destruction rather than formation of dioxin products.

Comparison of iron oxide and copper oxide mediated formation of PCDD/Fs from pyrolysis of 1,2-DCBz under identical conditions are depicted in **Figure 4.7**.

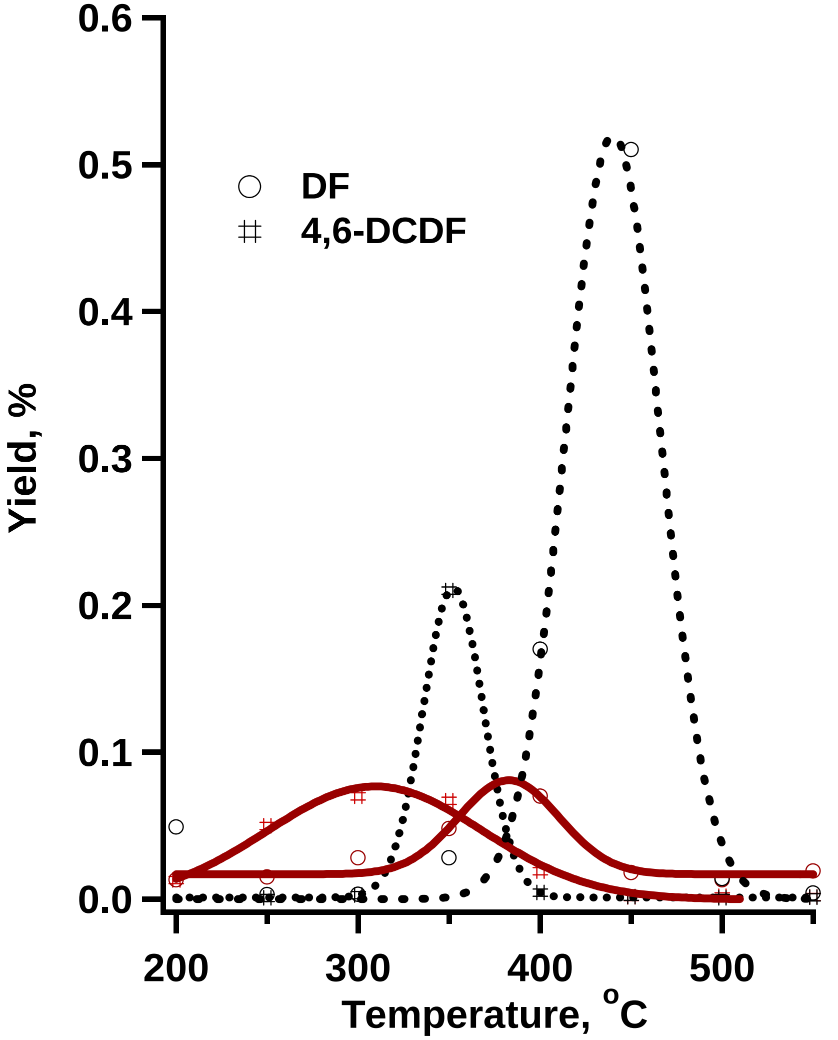


Figure 4.7. Comparison of PCDD/F Yields from the Pyrolysis of 1,2-DCBz over CuO/Silica (···) and Fe_2O_3/Silica(-) Surface

Formation of significant yields of PCDFs, which were the only dioxin products detected, was observed from 250 to 400 ^oC. Unlike the case with CuO/silica system where PCDFs peaked within a narrow temperature window, formation of both DF and 4,6-DCDF over Fe_2O_3/silica was observed over a relatively broader temperature range.

In contrast, the total yields of PCDD/Fs over copper were 2x higher than iron. In addition, the total yields of benzene and phenol were 2x higher over Fe_2O_3/silica than CuO/silica implying most probably that dechlorination as well as oxidative properties of iron may be responsible. A notable observation from thermal degradation of 1,2-DCBz over Fe_2O_3/silica was the formation of significant yields of DF and no higher chlorinated PCDFs were observed suggesting that no surface induced chlorination occurred. It is possible that the formation of surface bidendate species which undergoes further transformation to form phenoxyl radical was predominant at temperatures above 400 ^oC as reflected by the high yield formation of phenol and DF. High yields of PCDFs and no PCDDs observed contributed to a low PCDD to PCDF ratio of 0.06 and 0.07 for oxidative and pyrolytic conditions, respectively. On the basis of the concentration of chlorinated benzenes in incinerator effluent that reportedly exceeds those of chlorinated phenols by at least an order of magnitude [14-17], the low PCDD to PCDF ratio (<<1) observed from thermal degradation of 1,2-DCBz over Fe_2O_3/silica surface is consistent with the data of full-scale systems.

4.5 Comparison of Mechanistic Aspects of PCDD/F Formation from a Mixed 2-Monochlorophenol/1,2-Dichlorobenzene System

The comparison of PCDFs versus PCDDs over iron oxide and copper oxide surfaces from thermal degradation of a mixed system of 2-MCP and 1,2-DCBz are depicted in **Figure 4.8** and **Figure 4.9.** More PCDFs than PCDDs were formed in all the three mixture variations of 2-MCP/1,2-DCBz studied.

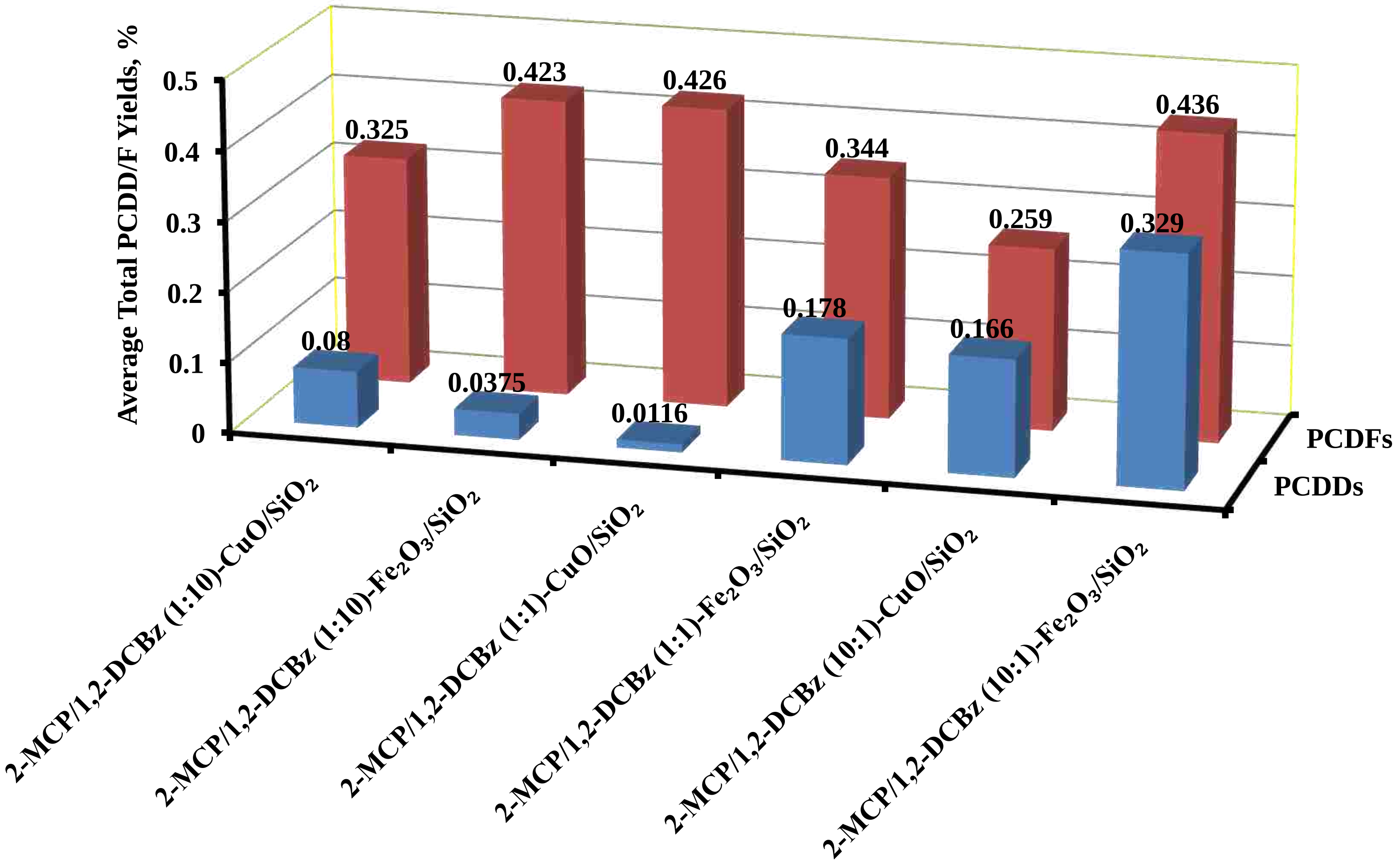


Figure 4.8 Average Total PCDDs and PCDFs from Pyrolysis of a Mixed 2-MCP/1,2-DCBz System

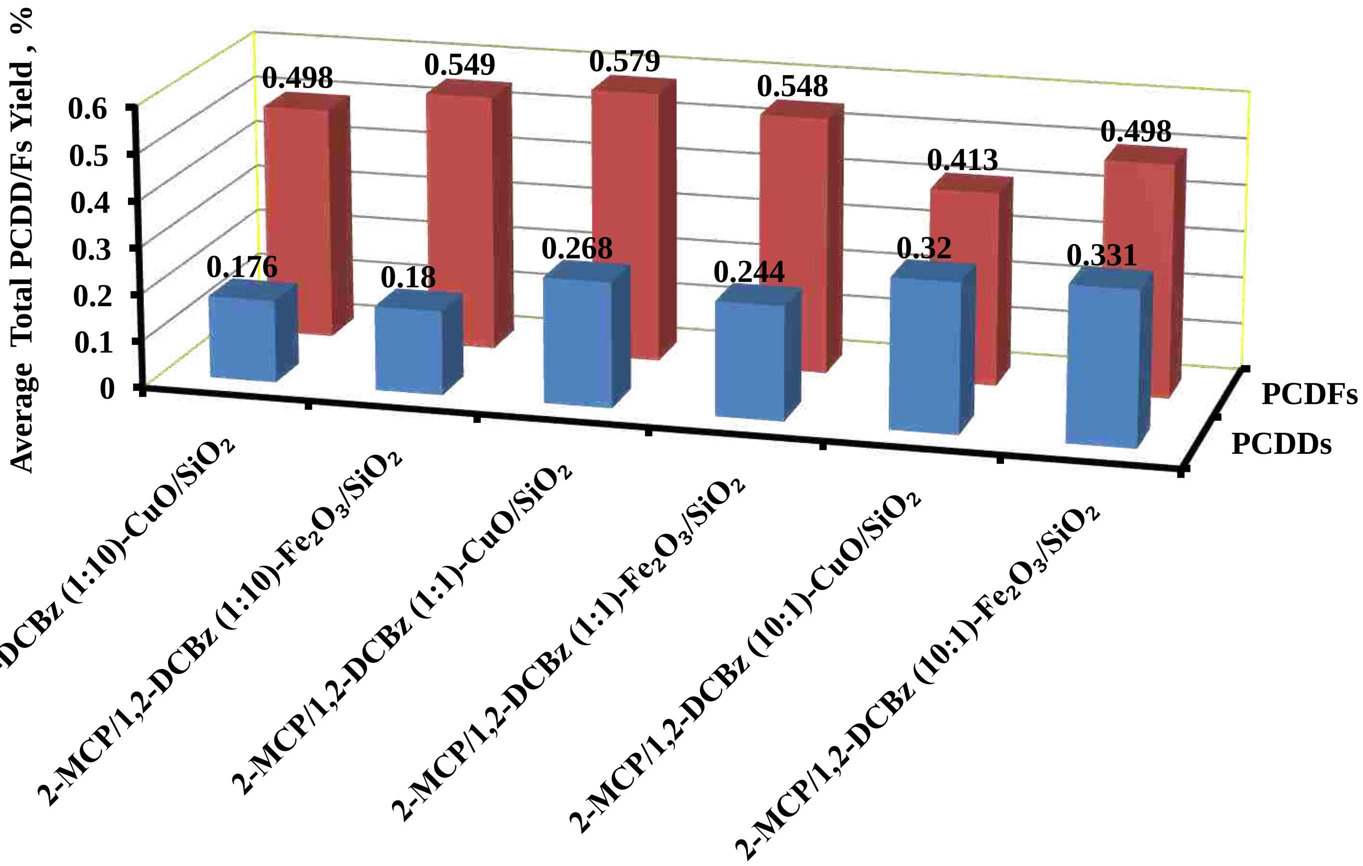


Figure 4.9 Average Total PCDDs and PCDFs from Oxidation of a Mixed 2-MCP/1,2-DCBz System

It has been suggested that chlorophenols bind preferentially with surfaces and thus even low concentrations of gas-phase chlorophenols in full scale systems could result in PCDDs. In fact, our research confirms chlorophenols preferentially bond through the hydroxyl substituent which might suggest that chlorophenols compete successfully with chlorobenzenes for adsorption sites. Furthermore, the observations from laboratory studies of mixed chlorobenzene/chlorophenol systems indicate PCDFs formation was in greater yields than PCDDs under both pyrolytic and oxidative conditions.

The yields of PCDFs from 1,2-DCBz and in chlorobenzenes/chlorophenols mixed systems has substantial environmental implications. These results suggest that formation of PCDF from chlorobenzenes is most likely a source of low PCDD to PCDF ratios in full scale combustors**.** Additionally, the observed low PCDD to PCDF ratios from mixed systems which simultaneously contain chlorophenols and chlorobenzenes can be attributed to chlorobenzenes which form only PCDFs and inhibits formation of PCDDs from chemisorbed chlorophenols. On overall, the PCDD to PCDF emission ratio from full scale combustors is expected to be <<1 based on these data from thermal degradation of 2-MCP and 1,2-DCBz in pure and in mixed systems [14,15].

4.6 References

1. Alderman, S. L.; Dellinger, B. FTIR investigation of 2-chlorophenol chemisorption on a silica surface from 200 to 500 degrees C. *J. Phys. Chem. A.* **2005,** *109*, (34), 7725-7731.

2. Alderman, S. L.; Farquar, G. R.; Poliakoff, E. D.; Dellinger, B. An infrared and X-ray spectroscopic study of the reactions of 2-chlorophenol, 1,2-dichlorobenzene, and chlorobenzene with model CuO/silica fly ash surfaces. *Environ. Sci. Technol.* **2005,** *39*, (19), 7396-7401.

3. Bandara, J.; Mielczarski, J. A.; Kiwi, J., I. Adsorption mechanism of chlorophenols on iron oxides, titanium oxide and aluminum oxide as detected by infrared spectroscopy. *Appl Catal B-Environ.* **2001,** *34*, (4), 307-320.

4. Lomnicki, S.; Dellinger, B., Formation of PCDD/F from the pyrolysis of 2-chlorophenol on the surface of dispersed copper oxide particles. *Proc. Combust. Inst.* **2003,** *29*, 2463-2468.

5. Farquar, G. R.; Alderman, S. L.; Poliakoff, E. D.; Dellinger, B., X-ray spectroscopic studies of the high temperature reduction of Cu(II)0 by 2-chlorophenol on a simulated fly ash surface. *Environ. Sci. Technol.* **2003,** *37*, (5), 931-935.

6. Lomnicki, S.; Truong, H.; Vejerano, E.; Dellinger, B. Copper oxide-based model of persistent free radical formation on combustion-derived particulate matter. *Environ. Sci. Technol.* **2008,** *42*, (13), 4982-4988.

7. Khachatryan, L.; Lomnicki, S.; Dellinger, B. An expanded reaction kinetic model of the CuO surface-mediated formation of PCDD/F from pyrolysis of 2-chlorophenol. *Chemosphere* **2007,** *68*, (9), 1741-1750.

8. Lomnicki, S.; Dellinger, B. Development of supported iron oxide catalyst for destruction of PCDD/F. *Environ. Sci. Technol.* **2003,** *37*, (18), 4254-4260.

9. Lomnicki, S.; Dellinger, B. A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on a CuO/silica surface. *J. Phys. Chem. A.* **2003,** *107*, (22), 4387-4395.

10. Evans, C. S.; Dellinger, B. Surface-mediated formation of PBDD/Fs from the high-temperature oxidation of 2-bromophenol on a CuO/silica surface. *Chemosphere* **2006,** *63*, (8), 1291-1299.

11. Evans, C. S.; Dellinger, B. Surface-mediated formation of polybrominated dibenzo-p-dioxins and dibenzofurans from the high-temperature pyrolysis of 2-bromophenol on a CuO/silica surface. *Environ. Sci. Technol.* **2005,** *39*, (13), 4857-4863.

12. Kim, K. S.; Hong, K. H.; Ko, Y. H.; Kim, M. G. Emission characteristics of PCDD/Fs, PCBs, chlorobenzenes, chlorophenols, and PAHs from polyvinylchloride combustion at various temperatures. *J. Air Waste Manage. Assoc.* **2004,** *54*, (5), 555-562.

13. Zimmermann, R.; Blumenstock, M.; Heger, H. J.; Schramm, K. W.; Kettrup, A. Emission of nonchlorinated and chlorinated aromatics in the flue gas of incineration plants during and after transient disturbances of combustion conditions: Delayed emission effects. *Environ. Sci. Technol.* **2001,** *35*, (6), 1019-1030.

14. Wienecke, J.; Kruse, H.; Wassermann, O. Organic-compounds in the waste gasification and combustion process. *Chemosphere* **1992,** *25*, (4), 437-447.

15. *The Use of Surrogate Compounds as Indicators of PCDD/F Concentrations in Combustion Stack Gases*; Report EPA-600/R-04-024; U.S. Environmental Protection Agency: Washington, DC, **2004.**

16. Blumenstock, M.; Zimmermann, R.; Schramm, K. W.; Kaune, A.; Nikolai, U.; Lenoir, D.; Kettrup, A. Estimation of the dioxin emission (PCDD/FI-TEQ) from the concentration of low chlorinated aromatic compounds in the flue and stack gas of a hazardous waste incinerator. *J. Anal. Appl. Pyrolysis* **1999,** *49*, (1-2), 179-190.

17. Taylor, P. H.; Dellinger, B. Pyrolysis and molecular growth of chlorinated hydrocarbons. *J. Anal. Appl. Pyrolysis* **1999,** *49*, (1-2), 9-29.

18. Mulholland, J. A. R., J.Y. Formation of polychlorinated dibenzo-p-dioxins by CuCl2-catalyzed condensation of 2,6 chlorinated phenols. *Combust. Sci. Technol.* **2001,** 107-126.

19. Lomnicki, S.; Lichtenberger, J.; Xu, Z. T.; Waters, M.; Kosman, J.; Amiridis, M. D. Catalytic oxidation of 2,4,6-trichlorophenol over vanadia/titania-based catalysts. *Appl Catal B-Environ* **2003,** *46*, (1), 105-119.

20. Hell, K.; Stieglitz, L.; Altwicker, E. R.; Addink, R.; Will, R. Reactions of 2,4,6-trichlorophenol on model fly ash: oxidation to CO and CO2, condensation to PCDD/F and conversion into related compounds. *Chemosphere* **2001,** *42*, (5-7), 697-702.

21. Born, J. G. P.; Louw, R.; Mulder, P. Formation of dibenzodioxins and dibenzofurans in homogenous gas-phase reactions of phenols. *Chemosphere* **1989,** *19*, (1-6), 401-406.

22. Dellinger, B.; Lomnicki, S.; Khachatryan, L.; Maskos, Z.; Hall, R. W.; Adounkpe, J.; McFerrin, C.; Truong, H. Formation and stabilization of persistent free radicals. *Proc. Combust. Inst.* **2007,** *31*, 521-528.

23. Milligan, M. S.; Altwicker, E. R. Chlorophenol reactions on fly ash .1. Adsorption desorption equilibria and conversion to polychlorinated dibenzo-p-dioxins. *Environ. Sci. Technol.* **1996,** *30*, (1), 225-229.

24. Addink, R.; Olie, K. Mechanisms of formation and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans in heterogeneous systems. *Environ. Sci. Technol.* **1995,** *29*, (6), 1425-1435.

25. Fiedler, H. Thermal formation of PCDD/PCDF: A survey. *Environ. Eng. Sci.* **1998,** *15*, 49-58.

26. Nganai, S.; Lomnicki, S.; Dellinger, B. Ferric oxide mediated formation of PCDD/Fs from 2-monochlorophenol. *Environ. Sci. Technol.* **2009,** *43*, (2), 368-373.

CHAPTER 5: SUMMARY

Transition metal-mediated reactions of chemical precursors which constitute a dominant pathway of PCDD/Fs formation from combustion sources were investigated in this study and the influence of various combustion parameters has been addressed as well. The results from this study reveals significant differences in the role of iron versus copper as metal catalysts that promote PCDD/F formation, the contributions from chlorinated benzenes versus chlorinated phenols in PCDD/F emissions, and the overall impact in product yields and distribution under excess oxygen conditions versus pyrolytic conditions. The potential pathways to PCDD/F formation were proposed to account for the product yields and distribution observed from the experiments performed. Based on these results and findings from other similar studies previously reported in the literature, some general conclusions can be drawn.

5.1 Oxidation versus Pyrolysis

The addition of oxygen had a profound effect in both product yields and distribution from thermal degradation of the selected chemical precursors whether in pure or mixture form. In particular, PCDD/F formation was in general greater under excess oxygen conditions than under pyrolytic conditions for all the experiments performed using 2-MCP and 1,2-DCBz. This finding can be attributed to accelerated rate of thermal decomposition of the chemical precursors due to rapid reactions involving hydroxyl radicals and regeneration of adsorption sites on the metal catalyst surfaces leading to higher concentration of surface-bound phenoxyl and chlorophenoxyl radicals. **Figure 5.1** summarizes the effect of the presence of oxygen on the total yields of PCDD/Fs from chemical precursors studied on copper and iron metal catalyst surfaces.

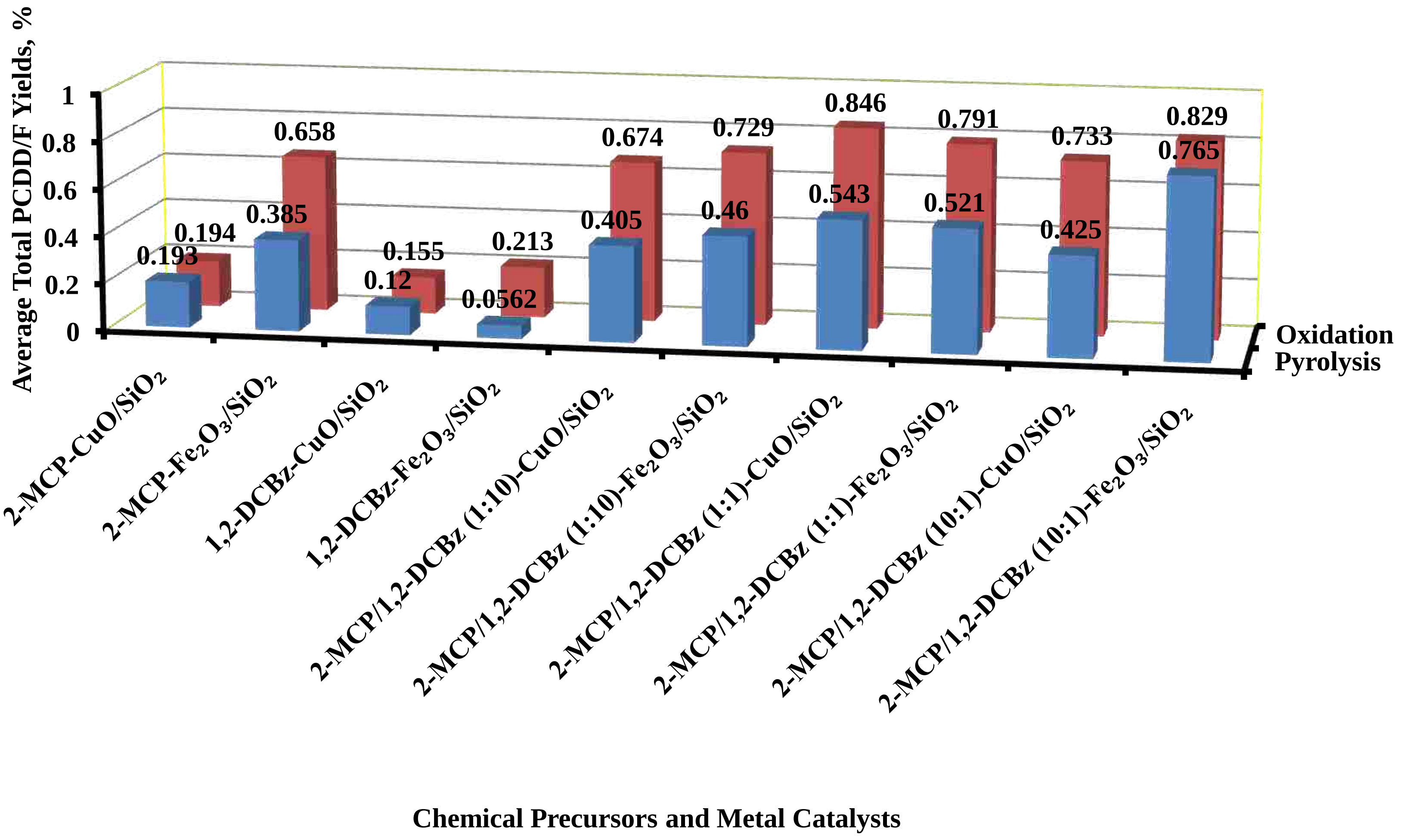


Figure 5.1 Comparison of Total Yields of PCDD/Fs from the Surface-Mediated Pyrolysis and Oxidation of Pure and Mixture Samples of 1,2-DCBz and 2-MCP Precursors on CuO/Silica and Fe_2O_3/Silica Surface Catalysts

In addition, the previously identified possible intermediates in the formation of PCDD/Fs such as catechol and benzo-*o*-quinone [1, 2], were formed at higher yields under oxidative conditions than under pyrolytic conditions. The formation yields of BQ and CT peaked at relatively low temperatures of 250 to 300 ^{o}C and dropped drastically at temperatures above 350 ^{o}C where significant yields of DD and 1-MCDD were formed. This observation is consistent with our previous experiments in which derivative products of catechol and benzoquinones were identified as likely intermediates in formation of PCDDs [3]. Moreover, this finding is further supported by the yields of PCDDs which generally increased with addition of oxygen by a greater magnitude for all experiments performed in these studies than those of PCDFs.

For all the experiments performed as depicted in **Figure 5.1,** the significant increase in the formation of dioxin products with addition of oxygen when compared to less oxygen conditions, may also result from enhanced hydrogen abstraction process by hydroxyl radicals from reaction intermediates. Additionally, the resulting increase in hydrogen abstraction process and high concentration of radicals under excess oxygen conditions, also facilitated formation of slightly higher yields of polycyclics such as naphthalene, chloronapthalene and biphenyl observed generally under oxidative than pyrolytic conditions.

Formation of polychlorinated phenols occurred generally in greater yields under excess oxygen conditions than pyrolytic conditions, suggesting enhanced degree of chlorination process. This observation implies that the presence of oxygen is affecting the chlorination of other products. However, gas phase concentration of polychlorinated benzenes and dechlorination products such as unchlorinated phenols, unchlorinated benzenes were comparable for both oxidative and pyrolytic conditions.

5.2 Catalytic Roles of Iron versus Copper

The majority of laboratory studies of the surface-mediated formation of PCDD/Fs have focused on copper and copper oxide [4-8]. The results from these studies clearly indicate that iron is also a mediator of the formation of PCDD/Fs. For both 2-MCP and 1,2-DCBz studies, comparison of PCDD/F product yields over copper oxide and iron oxide surfaces under otherwise identical conditions reveals that iron is a stronger promoter in PCDD/Fs formation than copper.

In particular, when 2-MCP is the reactant, the main differences in PCDD/F formation over copper and iron oxides surfaces result from different chemisorption mechanisms. On the basis of our previous reactions of pure 2-MCP over copper oxide [3, 9] and iron oxide [10], it is clear that for copper oxide the chemisorption at the hydroxyl constituent through the upper pathway as depicted in **Scheme 4.1** to form 2-chlorophenoxyl radical is dominant. In the case of iron oxide, the two plausible chemisorption processes of 2-MCP dominates: (1) the upper pathway showed in **Scheme 4.1** where 2-chlorophenoxyl radical is formed and (2) the lower pathway in **Scheme 4.1** where the bidentate species is formed. The 2-chlorophenoxyl radical proceeds to form 4,6-DCDF, whereas the bidentate species reacts further at temperatures above 350 °C to produce phenoxyl radical that forms DF[10]. Consequently, more PCDFs than PCDDs are observed iron mediated surface reactions of 2-MCP in contrast to copper mediated surface reactions 2-MCP where PCDDs are predominantly formed.

In addition, when transition metal-mediated studies on thermal degradation of 1,2-DCBz over CuO/silica and Fe_2O_3/silica surfaces are compared, the total yields of PCDFs for Fe_2O_3/silica were 1.4x greater than for CuO/silica and the total yields of phenolic products were 1.2x higher for Fe_2O_3/silica than for CuO/silica system. Clearly iron exhibited a strong catalytic effect in promoting the formation of PCDFs than copper and given its abundant occurrence in high concentration that exceeds those of copper by 2-50x in combustion exhaust [11-15], this further supports the possibly dominant role of iron PCDD/F emissions in full-scale systems.

5.3 Correlating Observed PCDD/F Yields with Full-Scale Emissions

Majority of the previous research work on surface-catalyzed synthesis of PCDD/Fs via the precursor pathway have focused primarily on their formation from chlorinated phenols [16-20]. However**,** the low PCDD to PCDF ratio observed in full scale systems [21, 22], have not been reproducible at laboratory studies of chlorinated phenols. In contrast to results for studies of chlorinated phenols, our experimental studies on chlorinated benzenes have produced high yields PCDFs and low PCDD to PCDF ratios in agreement with data of full-scale. In these studies low PCDD to PCDF ratios <1 were observed particularly from chlorobenzenes due generally high yields of PCDFs and low or lack of PCDDs formation. Because chlorinated benzenes are observed in incinerator effluents with concentrations that are greater than those of chlorinated phenols by at least an order of magnitude [22, 23], this results suggests that formation of primarily PCDFs from chlorinated benzenes is likely to be a source of low PCDD to PCDF ratios in full-scale combustors.

An overall comparison of studies of chlorinated phenols with studies of chlorinated benzenes indicates that chlorinated phenols chemisorb more preferentially at a faster rate on surfaces than chlorinated benzenes [24, 25]. However, chlorinated benzenes have been reported to form predominantly from surface catalyzed reactions involving simple hydrocarbons such as ethane and ethylene [26, 27] and copper catalyzed molecular growth reactions of C2 and C4 fragments [28]. In addition, we have experimentally demonstrated in a previous article on formation of surface bound persistent free radicals (PFRs) such as phenoxyl and chlorophenoxyl radicals on copper oxide surface from substituted phenols were also formed from chlorinated benzenes as well [2]. Thus, even though chlorinated phenols form PCDDs in greater yields than chlorinated benzenes in fly ash [24], the occurrence of chlorinated benzenes in comparably high concentration than chlorinated phenols in effluent gases of combustion system [22] and strong correlation between chlorinated benzenes with emission profiles of PCDD/Fs in full-scale combustors [23, 29-31], implies that chlorinated benzenes significantly contribute to formation of PCDD/Fs from combustion sources. However, it has also been reported at elevated temperatures that thermal degradation of chlorinated benzenes under oxidative conditions results into some fractions converting to other substituted aromatics [32, 33]. Due to the lack of sufficient data that supports the potential of chlorinated benzenes to convert significantly into chlorinated phenols from gas phase reactions, it is unclear whether gas phase reactions of chlorinated benzenes are the most dominant in the formation of PCDD/Fs in full-scale combustors.

In summary, formation of chlorinated phenols from 1,2-DCBz over both copper oxide and iron oxide surfaces under both pyrolytic and oxidative conditions, suggests that additional attention and more research should be conducted for a better understanding of the mechanism of transition metal-mediated transformation of chlorinated benzenes into chlorinated phenols and further implications on the formation of PCDD/F in combustion systems.

5.4 Concluding Remarks

Iron and copper oxide surfaces can both mediate the formation of PCDD/Fs in the post flame cool zones of combustion systems under both pyrolytic and oxidative conditions. Of course, most combustion systems have regions of pyrolysis and oxidation, various pollutants that can participate in competitive co-adsorption and fly ash that is more complex than the simple iron oxide/ silica and copper oxide/silica substrates used in this study, all of which can lead to varied results. However, for the simplified, comparable conditions presented in this work, the data suggest that iron could potentially play a more important role than copper. Because the total

PCDD/F yield was on average 1.5x higher for iron oxide than for copper oxide, this implies that iron contributes more significantly in PCDD/Fs emissions than copper.

It should be pointed out that many other factors can affect the reactivity of copper or iron in the combustion systems; however, because both of the metals are subject to such limitations, the overall yield factors between copper and iron should still be valid. Furthermore, as presented in this study, iron oxide promotes PCDF formation over PCDD formation, as well as partial dechlorination that has not been observed for copper oxide. The PCDD/PCDF ratios in our laboratory studies particularly with iron oxides were generally in far better agreement with typical field measurements in which the PCDD/PCDF ratio is much less than 1 [34, 35]. The bidentate chemisorption of the precursor molecules on transition metal oxide surface promotes loss of additional chlorine in the pathway of PCDF formation. This is also in agreement with typical full-scale results in which the homologue class distribution of PCDFs is typically shifted to one less chlorine than the homologue class distribution for PCDDs [36, 37].

Mechanistic aspects have been elucidated to account for the differences in product yields and distribution, the discrepancy in PCDD to PCDF ratios between laboratory and full-scale measurements as well as the role of chlorobenzene versus chlorophenols as precursor molecules to PCDD/F formation. In addition, comparison of catalytic roles of copper and iron in surface mediated reactions have been investigated and proposed mechanisms to better understand the PCDD/F emissions from combustion systems have been developed.

It is possible that the role of iron in PCDD/F formation has been overlooked because iron is highly oxidative above 500 °C, resulting in destruction rather than formation of PCDD/Fs and other chlorinated hydrocarbons. Laboratory experiments over the temperature range typically used for studies of copper might have missed the PCDD/F formation window for iron. The potential role of other transition metals present in fly ash merits additional study as well.

The observation of the formation of PCDD/Fs over iron oxide surfaces suggests that additional studies of the impact of iron in combustion-generated particulate matter should be conducted. These include laboratory studies using variable size and concentration of supported iron catalyst; addition of relatively high-concentration species such as water, SO*x*, and NO*x* that can also adsorb on surfaces; use of more complex fly ash samples; and field studies. Development of new reaction kinetic models for the formation of PCDD/Fs over iron would be particularly useful, as the current models significantly overpredict PCDD concentrations but underpredict PCDF concentrations in full-scale combustion systems based solely on copper mediated reactions of chlorophenols [8].

5.5 References

1. Truong, H.; Loranicki, S.; Dellinger, B. Mechanisms of molecular product and persistent radical formation from the pyrolysis of hydroquinone. *Chemosphere* **2008,** *71*, (1), 107-113.

2. Lomnicki, S.; Truong, H.; Vejerano, E.; Dellinger, B. Copper oxide-based model of persistent free radical formation on combustion-derived particulate matter. *Environ. Sci. Technol.* **2008,** *42*, (13), 4982-4988.

3. Lomnicki, S.; Dellinger, B. A detailed mechanism of the surface-mediated formation of PCDD/F from the oxidation of 2-chlorophenol on a CuO/silica surface. *J. Phys. Chem. A.***2003,** *107*, (22), 4387-4395.

4. Stieglitz, L.; Zwick, G.; Beck, J.; Roth, W.; Vogg, H. On the de-novo synthesis of PCDD/PCDF on fly-ash of municipal waste incinerators. *Chemosphere* **1989,** *18*, (1-6), 1219-1226.

5. Luijk, R.; Akkerman, D. M.; Slot, P.; Olie, K.; Kapteijn, F. Mechanism of formation of polychlorinated dibenzo-p-dioxins and dibenzofurans in the catalyzed combustion of carbon. *Environ. Sci. Technol.* **1994,** *28*, (2), 312-321.

6. Addink, R.; Altwicker, E. R. Role of copper compounds in the de novo synthesis of polychlorinated dibenzo-p-dioxins/dibenzofurans. *Environ. Eng. Sci.* **1998,** *15*, (1), 19-27.

7. Hatanaka, T.; Imagawa, T.; Takeuchi, M. Effects of copper chloride on formation of polychlorinated dibenzofurans in model waste incineration in a laboratory-scale fluidized-bed reactor. *Chemosphere* **2002,** *46*, (3), 393-399.

8. Khachatryan, L.; Lomnicki, S.; Dellinger, B. An expanded reaction kinetic model of the CuO surface-mediated formation of PCDD/F from pyrolysis of 2-chlorophenol. *Chemosphere* **2007,** *68*, (9), 1741-1750.

9. Lomnicki, S.; Dellinger, B. Formation of PCDD/F from the pyrolysis of 2-chlorophenol on the surface of dispersed copper oxide particles. *Proc. Combust. Inst.* **2003,** *29*, 2463-2468.

10. Nganai, S.; Lomnicki, S.; Dellinger, B. Ferric oxide mediated formation of PCDD/Fs from 2-monochlorophenol. *Environ. Sci. Technol.* **2009,** *43*, (2), 368-373.

11. Addink, R.; Altwicker, E. R. Formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans on secondary combustor/boiler ash from a rotary kiln burning hazardous waste. *J. Hazard. Mater.* **2004,** *114*, (1-3), 53-58.

12. Skodras, G.; Grammelis, P.; Samaras, P.; Vourliotis, P.; Kakaras, E.; Sakellaropoulos, G. P. Emissions monitoring during coal waste wood co-combustion in an industrial steam boiler. *Fuel* **2002,** *81*, (5), 547-554.

13. Cains, P. W.; McCausland, L. J.; Fernandes, A. R.; Dyke, P. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans formation in incineration: Effects of fly ash and carbon source. *Environ. Sci. Technol.* **1997,** *31*, (3), 776-785.

14. Seames, W. S. An initial study of the fine fragmentation fly ash particle mode generated during pulverized coal combustion. *Fuel Process. Technol.* **2003,** *81*, (2), 109-125.

15. Zygarlicke, C. J.; Benson, S. A.; Toman, D. L. Trends in the Evolution of Fly-Ash Composition and Size during Combustion. *Abstr. Pap. Am. Chem. S.* **1990,** *200*, 14-Fuel.

16. Hell, K.; Stieglitz, L.; Altwicker, E. R.; Addink, R.; Will, R. Reactions of 2,4,6-trichlorophenol on model fly ash: oxidation to CO and CO2, condensation to PCDD/F and conversion into related compounds. *Chemosphere* **2001,** *42*, (5-7), 697-702.

17. Nicolas, V.; Jean-Pierre, S. Thermal degradation of 2-chlorophenol promoted by CuCl2 or CuCl: Formation and destruction of PCDD/Fs. *Chemosphere* **2007,** *67*, (9), S144-S149.

18. Lomnicki, S.; Lichtenberger, J.; Xu, Z. T.; Waters, M.; Kosman, J.; Amiridis, M. D. Catalytic oxidation of 2,4,6-trichlorophenol over vanadia/titania-based catalysts. *Appl Catal B-Environ.* **2003,** *46*, (1), 105-119.

19. Born, J. G. P.; Mulder, P.; Louw, R. Fly-ash mediated reactions of phenol and monochlorophenols - oxychlorination, deep oxidation, and condensation. *Environ. Sci. Technol.* **1993,** *27*, (9), 1849-1863.

20. Ryu, J. Y. Formation of chlorinated phenols, dibenzo-*p*-dioxins, dibenzofurans, benzenes, benzoquinnones and perchloroethylenes from phenols in oxidative and copper (II) chloride-catalyzed thermal process. *Chemosphere* **2008,** *71*, (6), 1100-1109.

21. Blumenstock, M.; Zimmermann, R.; Schramm, K. W.; Kaune, A.; Nikolai, U.; Lenoir, D.; Kettrup, A. Estimation of the dioxin emission (PCDD/FI-TEQ) from the concentration of low chlorinated aromatic compounds in the flue and stack gas of a hazardous waste incinerator. *J. Anal. Appl. Pyrol.* **1999,** *49*, (1-2), 179-190.

22. Zimmermann, R.; Blumenstock, M.; Heger, H. J.; Schramm, K. W.; Kettrup, A. Emission of nonchlorinated and chlorinated aromatics in the flue gas of incineration plants during and after transient disturbances of combustion conditions: Delayed emission effects. *Environ. Sci. Technol.* **2001,** *35,* (6), 1019-1030.

23. Wienecke, J.; Kruse, H.; Wassermann, O. Organic-compounds in the waste gasification and combustion process. *Chemosphere* **1992,** *25,* (4), 437-447.

24. Ghorishi, S. B.; Altwicker, E. R. Rapid formation of polychlorinated dioxins/furans during the heterogeneous combustion of 1,2-dichlorobenzene and 2,4-dichlorophenol. *Chemosphere* **1996,** *32,* (1), 133-144.

25. Alderman, S. L.; Farquar, G. R.; Poliakoff, E. D.; Dellinger, B. An infrared and X-ray spectroscopic study of the reactions of 2-chlorophenol, 1,2-dichlorobenzene, and chlorobenzene with model CuO/silica fly ash surfaces. *Environ. Sci. Technol.* **2005,** *39,* (19), 7396-7401.

26. Froese, K. L.; Hutzinger, O. Polychlorinated benzene and polychlorinated phenol in heterogeneous combustion reactions of ethylene and ethane. *Environ. Sci. Technol.* **1996,** *30,* (3), 1009-1013.

27. Froese, K. L.; Hutzinger, O. Polychlorinated benzene, phenol, dibenzo-p-dioxin, and dibenzofuran in heterogeneous combustion reactions of acetylene. *Environ. Sci. Technol.* **1996,** *30,* (3), 998-1008.

28. Taylor, P. H.; Dellinger, B. Pyrolysis and molecular growth of chlorinated hydrocarbons. *J. Anal. Appl. Pyrolysis***1999,** *49,* (1-2), 9-29.

29. Kaune, A. L., D.; Nikolai, U.; Kettrup, A. Estimating concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the stack gas of a hazardous waste incinerator from concentrations of chlorinated benzenes and biphenyls. *Chemosphere* **1991,** *29,* (9-11), 2083-96.

30. Kim, K. S.; Hong, K. H.; Ko, Y. H.; Kim, M. G. Emission characteristics of PCDD/Fs, PCBs, chlorobenzenes, chlorophenols, and PAHs from polyvinylchloride combustion at various temperatures. *J. Air Waste Manage. Assoc.* **2004,** *54,* (5), 555-562.

31. *The Use of Surrogate Compounds as Indicators of PCDD/F Concentrations in Combustion Stack Gases*; Report EPA-600/R-04-024; U.S. Environmental Protection Agency: Washington, DC, **2004.**

32. Ritter, E.; Bozzeli, J. W. Chlorobenzene and dichlorobenzene reactions in hydrogen and in hydrogen oxygen mixtures. *Hazard. Waste Hazard. Mater.* **1990,** *7,* (1), 103-115.

33. Fadli, A.; Briois, C.; Baillet, C.; Sawerysyn, J. P. Experimental study on the thermal oxidation of chlorobenzene at 575-825 degrees C. *Chemosphere* **1999,** *38,* (12), 2835-2848.

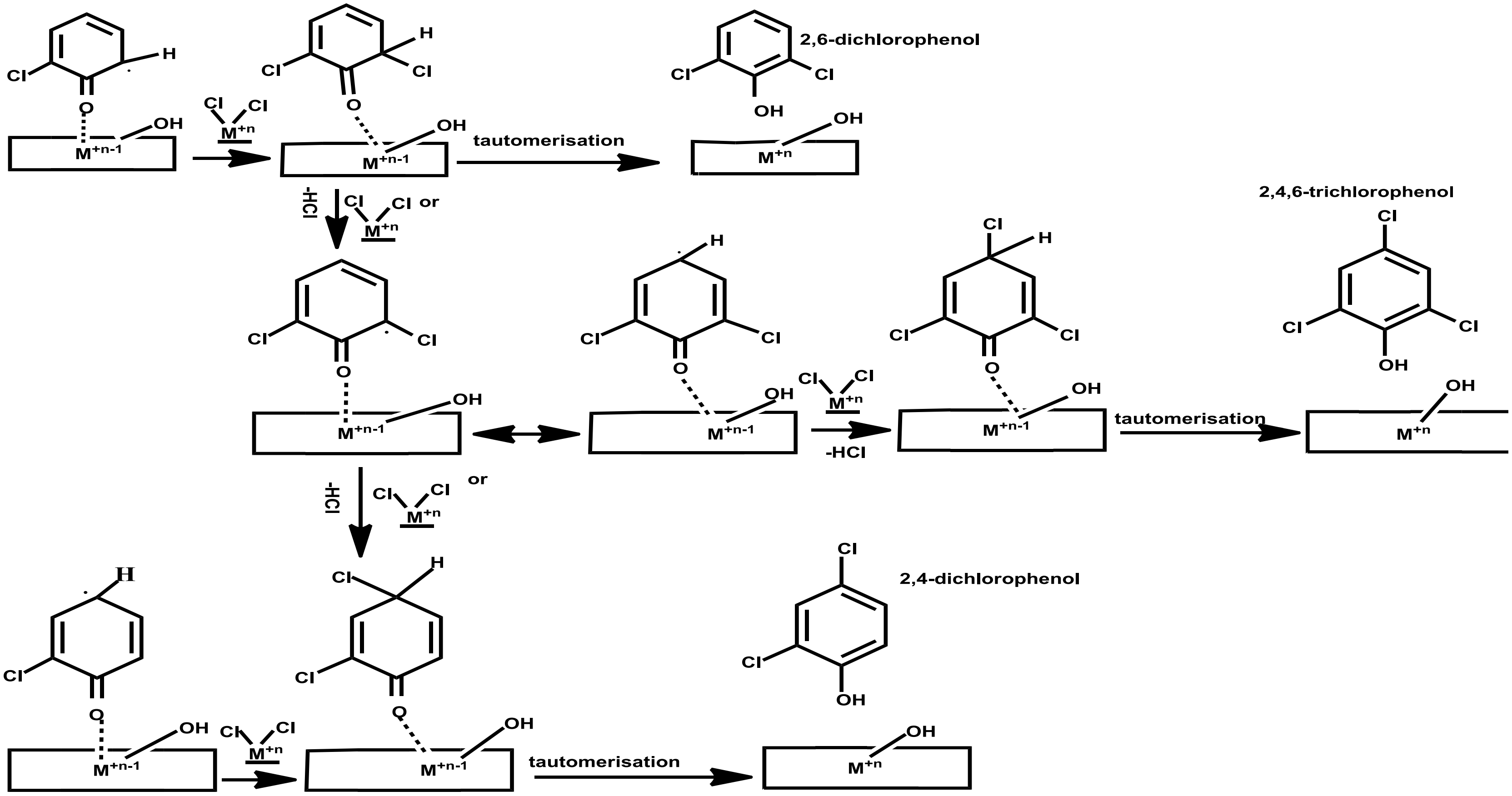
34. Altwicker, E. R.; Schonberg, J. S.; Konduri, R.; Milligan, M. S. Polychlorinated dioxin/ furan formation in incinerators. *Hazard. Waste Hazard. Mater.* **1990,** *7,* (1), 73-87.

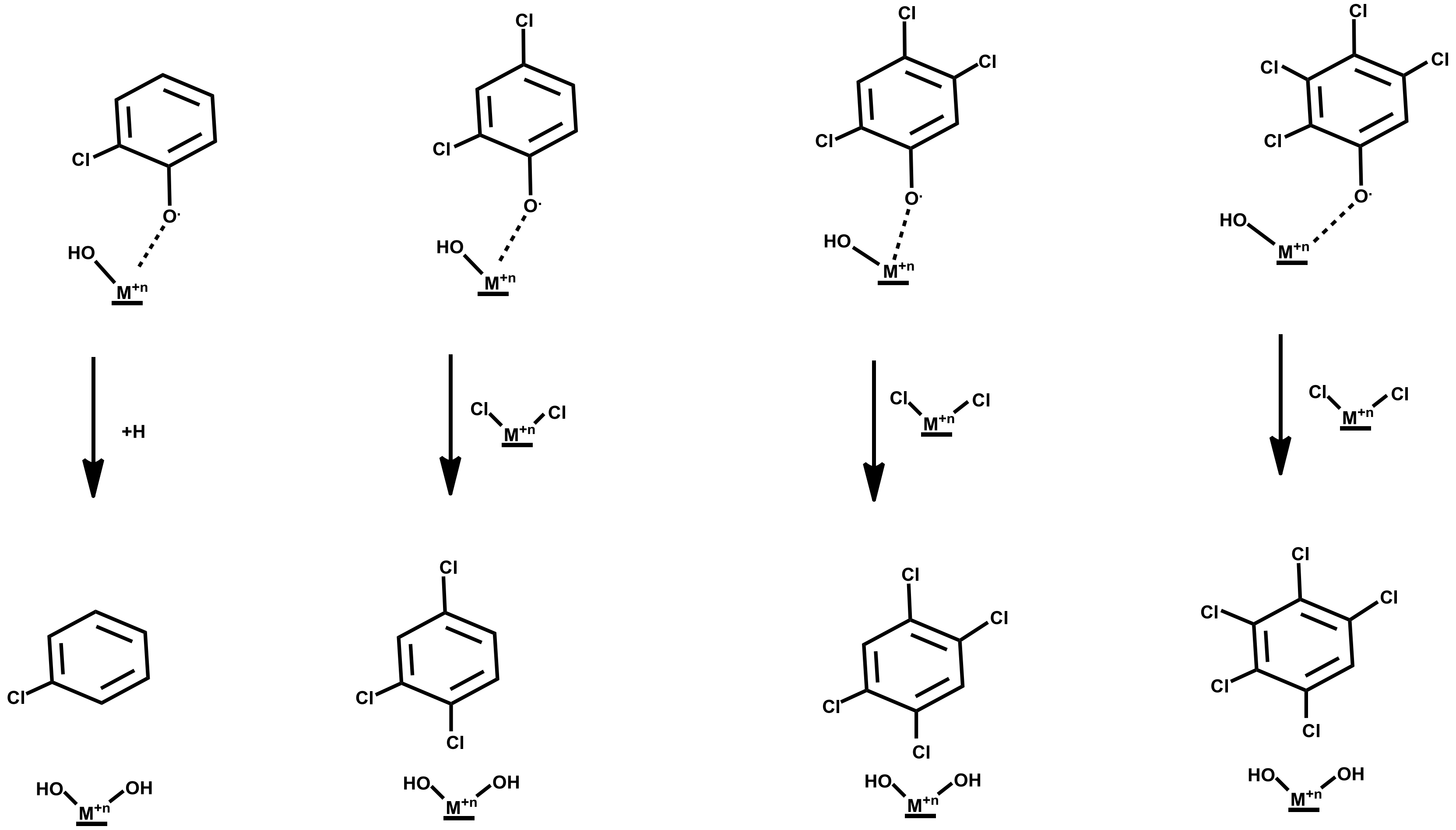
35. Karasek, F. W.; Dickson, L. C. Model Studies of polychlorinated dibenzo-*p*-dioxin formation during municipal refuse incineration. *Science* **1987,** *237*, (4816), 754-756.

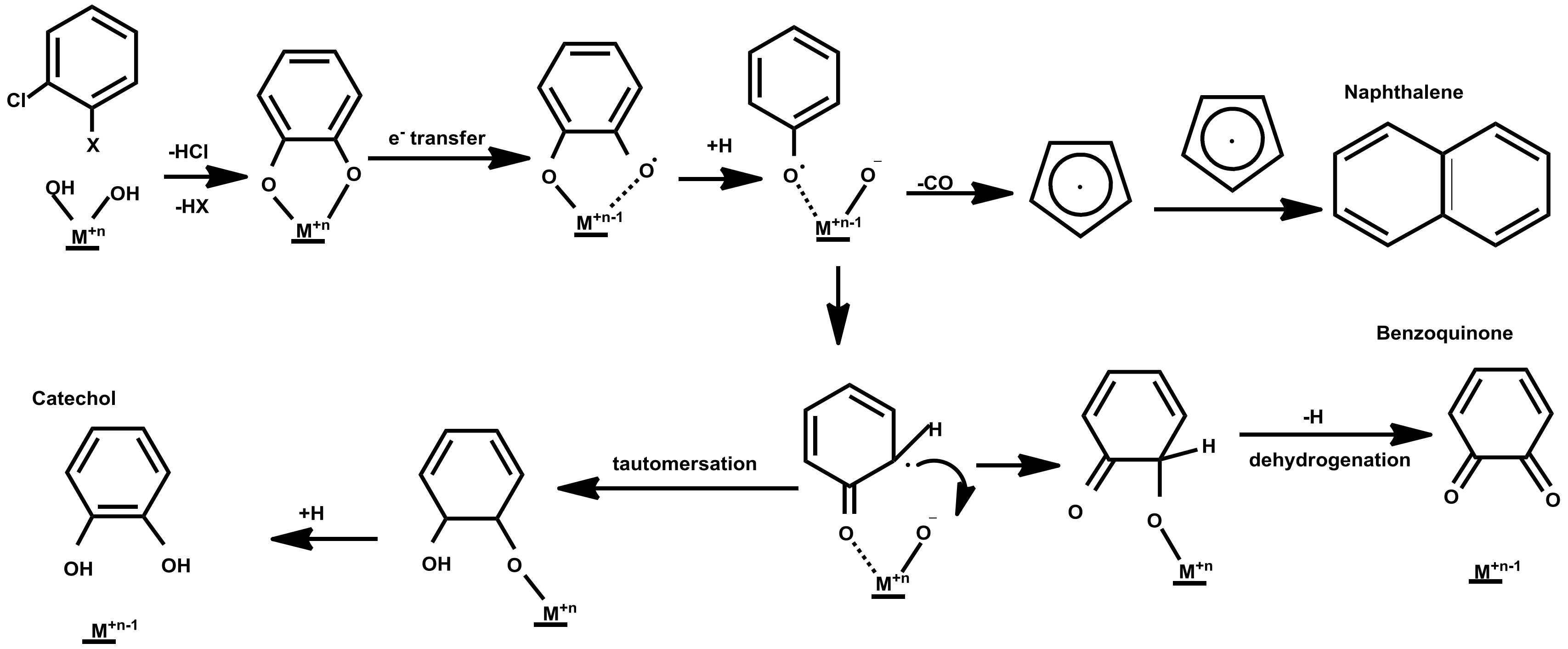
36. Ryu, J. Y.; Mulholland, J. A.; Kim, D. H.; Takeuchi, M. Homoloque and isomer patterns of polychlorinated dibenzo-*p*-dioxins and dihenzofurans from phenol precursors: Comparison with municipal waste incinerator data. *Environ. Sci. Technol.* **2005,** *39*, (12), 4398-4406.

37. Iino, F.; Imagawa, T.; Gullett, B. K. Dechlorination controlled polychlorinated dibenzofuran isomer patterns from municipal waste incinerators. *Environ. Sci. Technol.* **2000,** *34*, (15), 3143-3147.

APPENDIX 1. PROPOSED MECHANISMS FOR THE FORMATION OF NON-DIOXIN PRODUCTS




Cl
O·
HO
M+n
+H
OH


Cl
X
OH
OH
M+n
-HCl
-HX
O
O
M+n
e- transfer
O
O·
M+n-1
+H
O·
O−
M+n-1
-CO
Naphthalene
Benzoquinone
Catechol
OH
OH
M+n-1
+H
OH
O
M+n
tautomersation
H
O
O−
M+n
H
O
O
M+n
-H
dehydrogenation
O
O
M+n-1

APPENDIX 2. COPYRIGHT PERMISSIONS

AMERICAN CHEMICAL SOCIETY LICENSE
TERMS AND CONDITIONS

This is a License Agreement between Shadrack Nganai and American Chemical Society ("American Chemical Society") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by American Chemical Society, and the payment terms and conditions.

License Number: 2480951485487

License Date: Aug 02, 2010

Licensed content publisher: American Chemical Society

Licensed content publication: Environmental Science & Technology

Licensed content title: Ferric Oxide Mediated Formation of PCDD/Fs from 2-Monochlorophenol

Licensed content author: Shadrack Nganai et al.

Licensed content date: Jan 1, 2009

Volume number: 43

Issue: number 2

Type of Use: Thesis/Dissertation

Format: Print and Electronic

Portion: 50% or more of original article

Title of the thesis / dissertation: IRON (III) OXIDE AND COPPER (II) OXIDE MEDIATED FORMATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND FURANS FROM THERMAL DEGRADATION OF 1,2-DICHLOROBENZENE AND 2-MONOCHLOROPHENOL

LIMITED LICENSE: Publisher hereby grants to you a non-exclusive license to use this material. Licenses are for one-time use only with a maximum distribution equal to the number that you identified the licensing process; any form of republication must be completed within 60 days from the date hereof (although copies prepared before then may be distributed thereafter).

VITA

Shadrack Kirwa Nganai was born in November 1974, in Eldoret, Republic of Kenya. He earned a Bachelor of Education degree in chemistry with a minor in mathematics on October 16 1998 at Kenyatta University, Nairobi, Kenya. After a six year period of teaching and mentoring in Kenyan High Schools, he went on to pursue a doctoral degree in environmental physical chemistry in August 2004 at Louisiana State University, Baton Rouge, Louisiana. His research was under the direction of Dr. Barry Dellinger, Patrick F. Taylor Chair and Director of Intercollege Environmental Cooperative. He will receive his Doctor of Philosophy degree in December 2010. He is grateful to God for all his achievements in life.