LOW TEMPERATURE CATALYTIC OZONATION OF ALDEHYDES USING WOOD FLY ASH

by

RANGAN GANGAVARAM

(Under the guidance of James Kastner)

ABSTRACT

Catalytic ozonation of volatile organic compounds (VOCs) using wood fly ash (WFA), an inexpensive waste material, was demonstrated. The kinetics of ozonation of propanal (a model VOC) using WFA were determined in a packed-bed differential reactor system and was compared with two commercially available catalysts, i.e., magnetite and activated carbon. Stable conversions (30-40%) of propanal without significant catalyst decay were obtained in continuous flow experiments (1300 min). The rate law for the catalytic ozonation was determined by studying the effect of ozone and propanal concentration on rate of reaction of propanal. A one-way analysis of variance (ANOVA) test verified that crystalline phases present in WFA contributed to its catalytic activity. A two-tail t-test ($P<0.05$) confirmed that water (humid air and wet catalyst) enhanced the percentage removal of propanal and also the reaction rates.

INDEX WORDS: Catalytic ozonation, Wood fly ash, Propanal, Crystalline phases, Magnetite, Kinetics, Reaction rate

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DEDICATION

This thesis is dedicated to my late grandmother who was always a source of inspiration for me and encouraged me to bring the best out of me. The principles that I imbibed from her have always helped me reach towards my goal.

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CHAPTER 1

FOREWORD

The goal of this research was to develop a low temperature (<100°C) catalytic ozonation process for the removal of aldehydes from exhaust gases. Many aldehydes (odorous volatile organic compounds) are not effectively removed using current air pollution control technologies, such as wet scrubbers. Although effective, catalytic oxidation and regenerative thermal oxidation take place at high temperatures (600-1000°C) and produce large amounts of green house gases such as carbon dioxide (CO_2) and nitrogen oxides (NO_x). The current research describes a catalytic ozonation process for the removal of a wide range of VOCs and Total Reduced Sulfur compounds (TRS) at ambient temperature (23-25°C) in a cost-effective manner by using a waste material, wood fly ash, as a catalyst. Specific objectives were: 1) to design and develop a packed-bed reactor system for the catalytic ozonation of pollutants, 2) to use the system for kinetic studies on propanal (a 3-carbon aldehyde) and 3) to develop a rate law for the catalytic ozonation process facilitating subsequent potential scale-up and industrial use.

This thesis was conducted in the Bioconversion Lab located in the Driftmier Engineering Center at the Athens campus of the University of Georgia. The thesis was organized into four chapters. Chapter two provides background on current air pollution control technologies used for the abatement of pollutants, the specific and detailed objectives of the research, the hypothesis, uniqueness, and novelty of this research. Chapter three covers the design of the catalytic ozonation process, the conversion of propanal using ozone as the oxidizing agent with three

different catalysts namely wood fly ash (WFA), activated charcoal (AC) and magnetite for a range of ozone concentrations and propanal concentrations at different residence times. Chapter four explains the kinetics and the development of rate law for the catalytic ozonation process using the best-fit analysis and also the possibility of scale-up for industrial use.

The standard curve used for calculating inlet and outlet propanal concentrations is presented in Appendix A1. Appendix A2 provides sample calculations for the propanal reaction rates and Appendix A3 describes the determination of rate law. Appendix A4 gives the guidelines for operating and calibrating the Hapsite GC/MS unit. All the chapters in this thesis are prepared in the format suggested by the Graduate School, University of Georgia.

CHAPTER 2

INTRODUCTION AND LITERATURE REVIEW

INTRODUCTION

Air pollution is not a new phenomenon and has been a source of serious concern for centuries. Air pollution is a worldwide environmental issue today. Much of air pollution is directly related to the combustion of fuels for industrial production, transportation, and production of electricity for domestic purposes. In the USA approximately 200 million tons of waste gases are released into the air annually (Mycock et al., 1995). The release of large amounts of toxic gases led to the enactment of the federal Clean Air Act Amendments (CAAA) of 1990, which brought about stricter regulations of air emissions. Today, National Ambient Air Quality Standards have been established for six criteria air pollutants: five primary and one secondary pollutant (Cooper and Alley, 2002). The five primary criteria pollutants are particulate matter less than 10 μm in diameter (PM-10), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), and particulate lead. The secondary criteria pollutant is ozone (O_3). Volatile Organic Compounds (VOCs) and Total Reduced Sulfur Compounds (TRS) are classes of compounds which are not criteria pollutants but are recognized as primary pollutants and are sometimes recognized as Hazardous Air Pollutants (HAPs) because of their large emissions and toxic nature. With increasing population and rapid expansion of industrial production, VOCs and TRS emissions have also increased rapidly.

VOCs have long been regarded as a major source of air pollution due to their harmful effects on human health and on environment. Oxides of nitrogen (NO_x) react with certain VOCs (sometimes called reactive hydrocarbons) in the presence of sunlight to form photochemical oxidants, including ozone. The photochemical oxidants formed are also called photochemical smog (eq.1). Ozone and other oxidants are severe eye, nose, and throat irritants. Severe eye irritation occurs at 100 parts per billion parts (ppb), and severe coughing occurs at 2 parts per

million parts (ppm) (Cooper and Alley, 2002). Also some VOCs are known to be cancinogenic and odoriferous, causing displeasure when exposed to them.

$$NO_x + VOC \xrightarrow{\text{UV rays}} \text{Photochemical Smog} \quad (1)$$

VOCs include not only saturated hydrocarbons but also partially oxidized hydrocarbons (organic acids, aldehydes, ketones) as well as organics containing chlorine, sulfur, nitrogen, or other atoms in the molecule. VOCs are emitted from combustion processes, from industrial processes for the manufacture of organic chemicals, polymers and herbicides, from processes involving painting, printing and degreasing of metals, from rendering operations, and from solvent evaporations. The major constituents that have been qualitatively identified as potential emissions include organic sulfides, disulfides, C-4 to C-7 aldehydes, trimethylamine, C-4 amines, quinoline, dimethyl pyrazine, other pyrazines, and C-3 to C-6 organic acids.

TRS consists of the total sulfur from the following compounds: hydrogen sulfide (H_2S), dimethyl sulfide ($(CH_3)_2S$), and dimethyl disulfide (CH_3SSCH_3). In many cases, H_2S makes up the greatest portion of TRS. These compounds can be detected by their rotten-egg odor and are another important source of air pollution. Sources of TRS include wastewater treatment plants, tanneries, pulp and paper mills, and livestock operations. High-volume low-concentration (HVLC) emissions of VOCs and TRS are odorous, toxic, and can contribute to smog formation (Devai and DeLaune, 1999). These problems coupled with the increasing number of complaints from residential areas in close proximity to TRS-generating industries, have led to the formulation of various odor control rules and EPA air regulations. The increasing problems created by these odorous compounds necessitate the remediation of a wide range of VOCs and TRS generated by these industries. The CAAA calls for techniques that can effectively control air emissions from industrial processes. Commonly both process control to reduce emissions and

end-of-pipe treatment technologies (e.g., chemical wet scrubbers, incinerators, regenerative thermal oxidizers (RTO), catalytic oxidation and biofilters) are used to achieve this objective.

Aldehydes are partially oxidized hydrocarbons which belong to the class of VOCs. They are volatile compounds (sometimes odorous) which are emitted from livestock operations and rendering industries. Recent chemical wet scrubber analysis (Kastner and Das, 2002) of VOCs and TRS, showed close to 100% removal of methanethiol (MT), but only 20 to 80% removal efficiency for aldehydes and 23 to 64% for total VOCs (chlorine dioxide (ClO_2) as the oxidizing agent). Moreover, chlorinated hydrocarbons were identified at the outlets of high-intensity wet scrubbers and chlorinated compounds were identified in the scrubbing solutions because of improper mixing of the reactants (ClO_3, H_2O_2, and H_2SO_4) in the ClO_2 generating systems. Chlorinated hydrocarbons have been found to be persistent in the environment, having a propensity to bioaccumulate and biomagnify in the food chain.

HVLC emissions from many industries (e.g., pulp and paper and wastewater treatment facilities) contain a range of reduced sulfur compounds, such as H_2S, methanethiol and dimethyldisulfide, which are odorous and toxic (Devai and DeLaune, 1999). Regenerative thermal oxidation (RTO) and wet scrubbers are two primary air pollution control technologies used to treat the reduced sulfur compounds (Seiwart, 1997; Kastner and Das, 2002). RTO's have high operating costs, since oxidation occurs at high temperatures (800-1000°C), and produce greenhouse gases (NOx, CO_2) due to combustion of an external carbon source at high temperatures. Wet scrubbers require costly oxidizing chemicals such as ClO_2 or sodium hypochlorite (NaOCl), large amounts of water, and can produce chlorinated hydrocarbons if not properly controlled (Kastner and Das, 2002). A waste-water cost-effective air pollution control

technology for treatment of VOCs and TRS that reduces energy costs, water consumption, and greenhouse gas production is required for many industries.

LITERATURE REVIEW

Several technologies currently exist for controlling air pollution. The type of technology used depends on the types of pollutants to be removed, the cost involved and the overall effect it has on the environment. The following are some of the technologies being used today.

Regenerative Thermal Oxidation (RTOs)

RTOs use the principles of regenerative heat recovery for oxidizing HAPs and CO to remove odorous compounds, to destroy toxic compounds, and to reduce the quantity of photochemically reactive VOCs released to the atmosphere. The process gas with the contaminants enters the RTO and is mixed with air (O_2 in air as the oxidizing agent) after which a flow control valve directs this gas into an energy recovery chamber which preheats the process stream. The process gas and the contaminants are progressively heated as they move toward the combustion chamber. The VOCs are then oxidized to CO_2 and H_2O, releasing energy thereby reducing any auxiliary fuel requirement. The general guidelines suggested for complete destruction of VOCs include high temperatures of 800-1000°C and residence times of 0.2-2.0 s (Buonicore and Davis, 1992). Although RTOs help in the complete elimination of the VOCs, high operating costs and the production of large amounts of greenhouse gases, both from thermal oxidation and burning of fuel for preheating the process gas and contaminants, make them uneconomical and environmentally unsustainable. Moreover, RTOs sometime require SO_2 scrubbing (if sulfur is present).

Wet Scrubbers

Scrubbing is a unit operation in which one or more components of a gas stream are selectively absorbed into an absorbent depending on the solubility of the VOCs. In wet scrubbing, water is the most common choice of absorbent liquor; in special cases, another relatively nonvolatile liquid may be used. A variety of chemicals have been used in wet scrubbers as oxidizing agents, including NaOCl, chlorine gas, ClO_2 and O_3/ NaOCl (Prokop, 1991).

Wet scrubbers are the current air pollution control technology used to treat the reduced sulfur fraction in many emissions (Seiwert, 1997) and also in odor removal at various rendering plants (Kastner and Das, 2002; Prokop 1974, 1985, 1991). NaOCl is considered the most effective scrubbing agent for odor removal, although other oxidants can be used. Recently, ClO_2 has been used as an effective scrubbing agent. However, recent information indicates that the treatment methods used in the rendering industry are ineffective against the aldehyde fraction (VOCs) (Kastner and Das, 2002). ClO_2 reacts rapidly with thiols but has limited activity with other hydrocarbons. This observation indicates that the primary chemical oxidizing agents used in the rendering industry are ineffective against certain fractions of the VOCs. The costly nature of the oxidizing chemicals (ClO_2 or NaOCl) and also their ineffectiveness towards certain fractions of the VOCs requires a novel technology for the abatement of these compounds.

Biofilters

Popular in Europe for more than three decades, biofiltration has only recently become an accepted odor control alternative in North America. Biological odor control employs microorganisms to remove and oxidize compounds from contaminated air. Air streams pass

through a biologically active filter where microorganisms metabolize contaminants, producing carbon dioxide and water vapor. This process is complex and involves the interplay of mass transport (diffusion) and biological degradation. The microorganisms grow in a thin layer of moisture, the biofilm, built around particles of the filter. Contaminated gas is passed through the biofilter and contaminants adsorb onto the biofilm where oxidation occurs. The contaminant is not permanently absorbed/adsorbed to the filter but ultimately gets oxidized to CO_2 and H_2O.

For consistent, reliable performance, close attention must be paid to environmental parameters. Since continuous airflow tends to dry media, biofiltration systems often humidify air before it reaches the filter to maintain moisture levels essential for microbial health. Optimum operating temperatures of 30 to 40 ˚C must be maintained. Oxygen levels are also important and may limit degradation at high VOC loadings since most degradation is aerobic. Microorganisms use the oxygen present in dissolved form in the biofilm. Airflow pH levels must also be considered and possibly controlled. Most microorganisms perform best when pH levels are close to neutral (~pH 7). Nutrients are sometimes added to keep microbes healthy. Finally, synthetic media must be inoculated with microbes prior to operation (organic media, by its nature, usually does not require a separate inoculation step).

Biofilters are another technology which helps in the removal of H_2S and other reduced sulfur compounds. Conventional biofilters have traditionally used wood-based organic media for odor control. These media are inexpensive and provide an excellent environment for supporting microbial activity, but have a short life and lead to high maintenance and operational difficulties. Organic media can provide generally good removal of H_2S, initially but removal rates decline because of low pH environment. In biofilters complete removal of TRS is possible when the filter bed is inoculated with sulfur-degrading bacteria such as *Hyphomicrobium* sp. (Smet and

Van Langenhove, 1998). However, the long-term performance of biofilters is limited due to acidification, accumulation of inhibiting salts, and drying of the filter bed (Inge et al., 2003). Moreover large biofilters with long residence times (15 s – 2 min) are required due to low degradation rates of VOCs.

Catalytic Oxidation

A catalyst is a substance that speeds up a chemical reaction without itself taking part in the reaction. Although catalysts do undergo chemical changes during the course of reaction, these changes are reversible so that the catalyst is not consumed as the reaction proceeds. Catalytic oxidation involves the use of catalysts through which the gaseous molecules diffuse and adsorb onto the surface. The adsorbed gases then are oxidized (e.g. air containing oxygen as the oxidizing agent) on the surface of the catalyst. The catalysts change the mechanism in which the reaction takes place (although the surface reaction mechanisms are still not clear), and thus the reactions proceeds much faster and/or at much lower temperatures (400-600°C for catalytic oxidation using O_2) than with direct thermal oxidation (800-1000°C). Catalytic oxidation of VOCs and gaseous reduced sulfur compounds has been widely studied. Alvim Ferraz et al. (2000) demonstrated that VOC emissions of n-hexane, 2, 3-dimethylbutane, cyclohexane and benzene into the atmosphere can be controlled using activated carbon impregnated with oxides of cobalt and chromium. Kastner et al. (2002) demonstrated the low temperature (23-25 °C) catalytic oxidation of hydrogen sulfide and methanethiol (MT) using wood fly ash (WFA) and coal fly ash (CFA). In other research, activated carbon catalysts have been used for the treatment of gaseous emissions, such as H_2S (Alessandra et al., 1998; Choi et al., 1991) and methyl mercaptan (Dalai et al., 1997; Bashkova et al., 2002). Although catalytic oxidation has been

effective in removing a wide range of VOCs and TRS, there has been limited research on the kinetics of odor-causing compounds such as sulfides, mercaptans, and aldehydes (Kastner et al., 2002; Kastner et al., 2003).

Advanced Oxidation Processes (AOPs)

Advanced oxidation processes have been defined as near ambient temperature processes that involve the generation of highly reactive radical intermediates, especially the hydroxyl radical. These processes show promise for the destruction of hazardous organic substances in municipal and industrial wastes, drinking water, ultra pure water and exhaust gases. Ozone in an alkaline solution ($O_3 + OH^-$), photolysis of ozone (O_3/UV), perozone ($O_3 + H_2O_2$), and catalytic ozonation are the principal existing AOPs known as the most promising processes for industrial effluents. A common objective of the AOPs is to produce a large amount of radicals (especially $OH^{\cdot}$) to oxidize the organic matter. Indeed the hydroxyl is a less selective and more powerful oxidant than molecular ozone, as demonstrated by significantly higher reaction rates in aqueous phase systems.

Catalytic Ozonation

Ozone is a stronger oxidizing agent than molecular oxygen or hydrogen peroxide and reacts with most substances at room temperature. In acid solutions the oxidizing power of ozone is exceeded only by fluorine, the peroxate ion, atomic oxygen, •OH radicals, and a few other such species (Cotton and Wilkinson, 1988). Catalytic ozonation involves the catalytic oxidation of the pollutant using ozone as the oxidizing agent. The most promising application of ozone is in the treatment of polluted streams containing VOCs. The concentration of the contaminants is

generally low, so that only small amounts of ozone are needed. Importantly, the reactivity of ozone is very high (Table 2.1), so that the oxidation can occur close to room temperature for liquid streams. Several research papers have demonstrated that certain VOCs can be catalytically oxidized in the aqueous phase at low temperature when coupled with ozone (Gervasini et al., 2000; Choi et al. 2001; Zaror et al., 2001; Pines and Reckhow, 2002; Kim et al., 2002). Recent research has demonstrated the use of transition metals in catalytic ozonation, primarily for wastewater treatment (Legube and Leitner, 1999; Oyama, 2000). Cobalt (II) catalyzed the oxidation of oxalic acid using O_3 (Pines and Reckhow, 2002), and activated carbon coupled with ozone was also demonstrated to generate •OH free radials and oxidize oxalic acid (Jans and Hogne, 1998; Beltran et al., 2002). Multiple metals (Fe, Mn, Ni, Co, Zn, and Cr) in different forms ranging from salts, solid oxides and deposited metals on supports have been used in the catalytic ozonation (Legube and Leitner, 1999; Pines and Reckhow, 2003). Moreover, catalytic ozonation using noble metal supported catalysts has been shown to significantly reduce operating temperatures required for deep oxidation of VOCs such as toluene and styrene (Gervasini et al., 1996).

Ozone Decomposition in Liquid Phase

The decomposition of ozone in pure water occurs through a complex radical chain mechanism (Wojtowicz, 1996). The sequence is initiated by OH^-.

$$O_3 + HO^- \longrightarrow HO_2^- + O_2^- \quad (2)$$

The propagation steps involve O_2^- radical ions and $HO^\cdot$ radicals (Staehelin and Hoigen, 1982; Buhler et al., 1984; Tomiyasu et al., 1985). In this sequence, O_3^- is a radical ion.

$$HO_2^\cdot \Leftrightarrow O_2^- + H^+ \quad (3)$$

$$O_2^- + O_3 \longrightarrow O_3^- + O_2 \quad (4)$$

$$O_3^- + H^+ \Leftrightarrow HO_3^\cdot \quad (5)$$

$$HO_3^\cdot \longrightarrow HO^\cdot + O_2 \quad (6)$$

$$HO^\cdot + O_3 \Leftrightarrow HO_4^\cdot \quad (7)$$

$$HO_4^\cdot \longrightarrow HO_2^\cdot + O_2 \quad (8)$$

$$\text{NET } 2O_3 \longrightarrow 3O_2 \quad (9)$$

As can be seen, two ozone molecules are decomposed each time the sequence turns over once. The termination steps are (Wojtowicz, 1996)

$$^\cdot HO_4 + {}^\cdot HO_4 \longrightarrow H_2O_2 + 2O_3 \quad (10)$$

$$^\cdot HO_4 + {}^\cdot HO_3 \longrightarrow H_2O_2 + O_3 + O_2 \quad (11)$$

ANALYSIS

The ineffectiveness of wet scrubbers using ClO_2 as the oxidizing agent towards the efficient removal of aldehyde fractions and odor control, the costly nature of alternative oxidizing chemicals like NaOCl, and the expensiveness of RTOs demand an alternative control technology which is cost-effective and can also be applied for a wide range of odor-causing compounds and VOCs.

The research done on catalytic ozonation demonstrates the potential of using catalysts coupled with ozone in packed bed reactors for removal of a wide range of odor-causing compounds from HVLC emissions. Although the cost of O_3 (~ $2/kg, $1/lb; Oyama, 2002) may restrict its use to high-value added substances or operations, the concentration of the contaminants in the exhaust gases is generally low (5-20 ppmv), so that only small amounts of ozone are needed. Ozone also lowers operating temperatures required for propanal oxidation and

allows operation without an additional fuel source. Thus energy costs and CO_2 emissions could be lower allowing for carbon trading. In the destruction of VOCs with ozone alone, selectivity may not seem to be important, since the desired reaction is the complete oxidation of the compounds. However, in many cases where catalysts are not used, partial oxidation products are formed which are not completely mineralized (Oyama, 2000). For example, oxalic, glyoxalic and acetic acids in solution and acetaldehyde in the gas-phase, cannot be completely oxidized by ozone alone. In such cases, the use of catalysts is essential to promote complete oxidation. Unfortunately, there has been limited research on the gas-phase catalytic ozonation of air pollutants and odor-causing compounds such as sulfides, mercaptans, and aldehydes to support the case (Kastner at al., 2002; Kastner et al., 2003). Most research conducted on catalytic ozonation has used activated carbon impregnated with metal oxides and transition metals or solid metal oxides themselves as catalysts; however, these catalysts are expensive for agricultural industries.

Wood fly ash (WFA), an inexpensive waste material is produced in large volumes in the USA (75 million tons/yr). The physical and chemical properties (Tables 2.2 and 2.3) of the ash indicate catalytic potential given the high surface area (~ 45 m^2/g) and the presence of crystalline phases typically associated with catalytic activity (Kastner et al., 2003). Mullite ($3Al_2O_3 \cdot 2SiO_2$), magnetite (Fe_3O_4), and hematite (Fe_2O_3 possibly with small amounts of other metals such as V, Mn, Cu, Co substituting for Fe) were identified in WFA and have been reported to catalyze the oxidation (O_2 only) of TRS or other VOCs at temperatures significantly greater than 25˚C. Recent research has demonstrated that wood fly ash can catalytically oxidize H_2S, ethanethiol, and methanethiol (Kastner et al., 2002). Given its high surface area, metal and carbon content,

and the presence of crystalline phases, WFA may have potential as an inexpensive environmental catalyst.

Magnetite and hematite have been shown to catalyze the formation of •OH free radicals from H_2O_2 and the subsequent oxidation of organic compounds by the hydroxyl free radical (Kwan and Voelker, 2003). Moreover, activated carbon supported with Fe_2O_3 and MnO_2-Fe_2O_3 was shown to catalytically decompose O_3; however a mechanism was not proposed (Heisig et al., 1997). Activated carbon in various forms has been utilized as adsorbents and/or catalysts in the catalytic oxidation of TRS and VOCs (Choi et al., 2001). Finally, metal oxides (e.g., Fe_2O_3) in soil and on supported catalysts have been suggested to generate •OH or other surface radicals and subsequently oxidize adsorbed organic compounds. (Legube and Leitner, 1999; Oyama, 2000).

Given the expensive nature of activated carbon and other supported catalysts, we theorize that WFA (or other inexpensive waste materials) with high metal content and surface area, and the presence of crystalline phases could act as inexpensive catalytic oxidizer of reduced sulfur compounds ("odor") and volatile organic compound (VOC) removal when coupled with O_3. It is theorized that the ash or selective crystalline phases in the ash may act to catalyze the formation of free radicals from ozone in the presence of water and subsequently catalyze the oxidation of a wide range of odor-causing compounds and VOCs or provide a catalytic site for direct oxidation via O_3. Moreover, the OH radical is less selective and has higher rate constants for organic compounds when compared to O_3 alone (Table 2.4).

Commercially available magnetite (Sigma-Aldrich), activated carbon (AC, Sigma-Aldrich) (Table 2.5), and magnetically separated crystalline phases present in WFA will be used as the benchmark catalysts in the catalytic ozonation experiments. Reaction rates obtained from

WFA and synthetic magnetite will be compared to determine if the crystalline phases present in WFA catalyze the oxidation of propanal and in turn result in higher reaction rates.

HYPOTHESIS

(1) Catalytic ozonation will oxidize gas-phase aldehydes at high reaction rates and low temperatures (ambient temperatures).

(2) WFA contains active phases that will catalytically oxidize aldehydes (and other VOCs) in the presence of O_3.

(3) Reaction between O_3 and aldehydes in the presence of catalyst is a surface phenomenon involving chemisorption of ozone and the aldehyde molecule, decomposition of ozone into free radicals in the presence of water, and subsequent oxidation of the aldehyde by the free radical to partially oxidized intermediates or complete oxidation to CO_2 and H_2O.

OBJECTIVES

1. Develop methods to demonstrate and enhance the catalytic ozonation of aldehydes. Propanal, found in traces in the exhaust gases from rendering streams, will be used as the model compound for the study.
2. Study the effect of catalyst structure and physical properties on the catalytic ozonation process. Experiments will be designed to determine the effect of surface area and catalyst type in the kinetics of propanal oxidation. Four catalytic materials, WFA, AC, synthetic magnetite (Fe_3O_4), and magnetically separated ash will be used as catalysts in the study.
3. Measure the kinetics of the catalytic ozonation process (including decay if it occurs) and to test the effect of the following parameters on aldehyde oxidation rates:

a. Ozone concentration

b. Aldehyde concentration

c. Residence Time

d. Type of catalyst

By realizing these objectives, we can develop a cost-effective process which will help in the abatement of not only the above mentioned aldehydes but also other VOCs and TRS.

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Table 2.1. Summary of heterogeneous reactions of ozone (Data from Oyama, 2000)

Substrates	Catalysts	Reaction Conditions	Products	Rate (mol/ m^2.
Ethanol Propanol Isopropanol	γ-Al_2O_3 SiO_2	293-363 K	Ketones, Aldehydes, CO_2	1.7×10^{-9}
Ethanol	MoO_3/Al_2O_3	300-550 K	Acetaldehyde,	0.9×10^{-9}
	MnO_2/Al_2O_3		CO_2	1.9×10^{-9}
Benzene	MnO_2	383-353 K	CO, CO_2	1.5×10^{-9}
	γ-Al_2O_3/Fe-oxide			1.7×10^{-7}
	γ-Al_2O_3/Cu-oxide			3.7×10^{-7}
Benzene	γ-Al_2O_3/Ni-oxide	296 K	CO, CO_2	3.8×10^{-7}
	γ-Al_2O_3/Mn-oxide			1.3×10^{-7}
Dichloromethane Tetrachloroethylene *p*-chlorotoluene	Pt/ Al_2O_3 Pd/ Al_2O_3 $BaCuCrO_x$	323-473 K	Mostly CO_2	___
Cyclohexane	γ-Al_2O_3/Mn-oxide	296 K	CO,CO_2	1.2×10^{-6}

Table 2.2. Physical and chemical properties of WFA

Properties	WFA (Mean $\pm$ SD)
Surface Area, m^2/g	44.89 $\pm$ 8.34
pH	12.13 $\pm$ 0.17
Bulk Density, g/cm^3	0.54
Carbon, % (dry basis)	18.75 $\pm$ 1.87
Selected Elements (ppm)	Range
Co	4.5 – 5.2
Cu	32.0 – 39.0
Mn	500.0 – 584
Mo	2.2 – 2.7
Ni	18 – 19
Fe	6,600 – 8,300

Table 2.3. Particle size distribution of WFA.

Particle Size range (μ)	% of particles (by mass) in the range
> 600	5.69
600-425	2.40
425-150	9.99
150-75	12.89
< 75	69.73

The percentages of particles in the ranges measured add up to 100.7 owing to small calculation errors

Table 2.4. Ozonation rate constants and OH rate constants for some organic compounds in liquid phase.

Solute	k_{O3} (M^{-1} s^{-1})	$k_{OH^{\cdot}}$ (M^{-1} s^{-1}) x 10^{-9}[a]
Benzene	2 ± 0.4	7.8
Nitrobenzene	0.009 ± 0.02	3.9
Toluene	14 ± 3	3.0
m-xylene	94 ± 20	7.5
Formic acid	5 ± 5	1.3
Formate ion	100 ± 20	3.2
Acetic acid	(<3 x 10^{-5})	1.6
Salicylic acid	<500	2.2

[a] $k_{OH^{\cdot}}$ read as cell value times 10^9. e.g. $7.8x10^9$

Table 2.5. Physical properties of magnetite and activated carbon

Properties	Magnetite	Activated Carbon
Surface Area, m^2/g	1.7905 ± 0.464	424.95 ± 52.33
Pore Volume, mL/g	5.0792 ± 0.7472	0.429 ± 0.0273

CHAPTER 3

CATALYTIC OZONATION OF PROPANAL USING WOOD FLY ASH, ACTIVATED CARBON AND MAGNETITE[1]

[1]Rangan, G. V. and Kastner, J.R. To be submitted to the Journal of Environmental Science and Technology

ABSTRACT

The feasibility of using wood fly ash, a waste material, as an inexpensive catalyst in the catalytic ozonation of propanal (an odorous volatile organic compound) has been demonstrated. Extended continuous catalytic ozonation of propanal indicated that wood fly ash could be used continuously without significant catalyst decay (1300 min) and resulted in measurable propanal oxidation (30-40%, 2 g of catalyst, 2.3 s residence time). There was not a significant increase in reaction rate (2.2 vs. 3.1 x 10^{-9} mol g^{-1} s^{-1}) with an increase in ozone concentration (75 -175 ppmv) in case of WFA but there was a two-fold increase in the case of magnetite in the same ozone range. The presence of water in the form of humid air and wet catalyst significantly increased the percent conversion, by about 50%, when compared to that without the presence of water. In the case of wood fly ash, the reaction rate increased three fold with water when compared to no water (1.15 to 3.68 x 10^{-9} mol g^{-1} s^{-1}) in case of WFA. High specific surface area and presence of crystalline phases played vital role for WFA as a catalyst. Apart from propanal and ozone concentrations, the catalyst type used had a significant role in the reaction rates obtained.

KEY WORDS: Propanal, aldehyde, catalytic ozonation, wood fly ash, activated charcoal, Magnetite, low-temperature oxidation, odor.

INTRODUCTION

Air pollution is not a new phenomenon, and has been a source of serious concern for centuries. Air pollution is a worldwide environmental issue today. Much of air pollution is directly related to the combustion of fuels for industry, transportation, and production of electricity for domestic purposes. In the USA, approximately 200 million tons of waste gases are released into the air annually (Mycock et al., 1995). The release of large amounts of toxic gases led to the enactment of the federal Clean Air Act Amendments (CAAA) of 1990, which brought about stricter regulations of air emissions. Volatile Organic Compounds (VOCs) and Total Reduced Sulfur Compounds (TRS) are classes of compounds which are recognized as Hazardous Air Pollutants (HAPs) due to the large volume emissions and toxic nature. With increasing populations and rapid expansions of industrial production, the emissions of VOCs and TRS have also increased rapidly.

VOCs have long been regarded as a major source of air pollution due to their harmful effects on human health and on environment. Oxides of nitrogen (NO_x) react with certain VOCs (sometimes called reactive hydrocarbons) in the presence of sunlight to form photochemical oxidants, including ozone. The photochemical oxidants formed are also called photochemical smog (eq.1). Ozone and other oxidants are severe eye, nose, and throat irritants. Severe eye irritation occurs at 100 parts per billion (ppb), and severe coughing occurs at 2.0 parts per million (ppm) (Cooper and Alley, 2002) when exposed to ozone. Also some VOCs are known to be cancerous and odoriferous, causing displeasure when exposed to them.

$$\text{VOC} + NO_x \xrightarrow{\text{UV rays}} \text{Photochemically} \qquad (1)$$

VOCs include not only saturated hydrocarbons, but also partially oxidized hydrocarbons (organic acids, aldehydes, ketones), as well as organics containing chlorine, sulfur, nitrogen, or other atoms in the molecule. VOCs are emitted from combustion processes, industrial processes for the manufacture of organic chemicals, polymers and herbicides, processes involving painting, printing and degreasing of metals, rendering operations and solvent evaporations. The major constituents that have been qualitatively identified as potential emissions include organic sulfides, disulfides, C-4 to C-7 aldehydes, trimethylamine, C-4 amines, quinoline, dimethyl pyrazine, other pyrazines, and C-3 to C-6 organic acids (Cooper and Alley, 1999).

TRS consists of the total sulfur from the following compounds: hydrogen sulfide (H_2S), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS). In some cases, H_2S makes up the greatest portion of TRS. These compounds can be detected by their rotten-egg odor and are another important source of air pollution. Sources of TRS include wastewater treatment plants, pulp and paper operations, tanneries, and livestock operations. High volume low concentration emissions (HVLC) of VOCs and TRS are odorous, toxic at high concentrations, and can contribute to smog formation (Devai and DeLaune, 1996). These problems coupled with the increasing number of complaints from residential areas in close proximity to TRS-generating industries have led to the formulation of various odor control rules and EPA air regulations. The increasing problems created by these odorous compounds necessitate the remediation of a wide range of VOCs and TRS generated by these industries. The CAAA calls for techniques that can effectively control air emissions from industrial processes. Commonly both process control to reduce emissions and end of pipe treatment technologies like wet scrubbers, incinerators, regenerative thermal oxidizers (RTO), catalytic oxidation and biofilters are used to achieve this objective.

Aldehydes are partially oxidized hydrocarbons which belong to the class of VOCs. They are odorous compounds which are emitted from livestock operations and rendering industries. Recent wet scrubber analysis of VOCs and TRS using chlorine dioxide (ClO_2) as the oxidizing agent to achieve high destruction efficiencies, showed close to 100% removal of methanethiol (MT), but only 20 to 80% removal efficiency for aldehydes and 23 to 64% for total VOCs (Kastner and Das, 2002). Moreover chlorinated hydrocarbons were identified at the outlets of high-intensity wet scrubbers and chlorinated compounds were identified in the scrubbing solutions because of improper mixing of the reactants (ClO_3, H_2O_2, and H_2SO_4) in the ClO_2 generating systems. Chlorinated hydrocarbons have found to be persistent in the environment, propensity to bioaccumulate and biomagnify in the food chain.

High-volume low-concentration emissions from many industries (e.g., pulp and paper and wastewater treatment facilities) contain a range of reduced sulfur compounds, such as H_2S, MT and DMDS, which are odorous and toxic at high concentrations (Devai and DeLaune, 1999). Regenerative thermal oxidation (RTO) and wet scrubbers are two primary air pollution control technologies used to treat the reduced sulfur compounds (Seiwart, 1997; Kastner and Das, 2002). RTO's have high operating costs, since oxidation occurs at high temperatures (760-870°C), and produce greenhouse gases (NOx, CO_2) due to combustion of an external carbon source at high temperatures. Wet scrubbers require costly oxidizing chemicals, such as ClO_2 or sodium hypochlorite (NaOCl), large amounts of water, and can produce chlorinated hydrocarbons if not properly controlled (Kastner and Das, 2002). The ineffectiveness of wet scrubbers towards the aldehyde fraction demands a cost-effective air pollution control technology for treatment of VOCs and TRS that reduces energy costs, water consumption, and greenhouse gas production.

Catalytic oxidation using ozone, as the oxidizing agent is a commonly used treatment technology in wastewater treatment and treating polluted streams containing VOCs. Ozone is a stronger oxidizing agent than molecular oxygen or hydrogen peroxide and reacts with most substances at room temperature. In acid solutions the oxidizing power of ozone is exceeded only by fluorine, the peroxate ion, atomic oxygen, •OH radicals, and a few other such species (Cotton and Wilkinson, 1988). The concentration of the contaminants is generally low, so that only small amounts of ozone are needed. Importantly, the reactivity of ozone is very high (Table 3.1), so that the oxidation can occur close to the room temperature for both liquid and gaseous streams. Several research papers have demonstrated that certain VOCs can be catalytically oxidized in the aqueous phase at low temperature when coupled with ozone (Gervasini et al., 2000; Choi et al. 2001; Zaror et al., 2001; Pines and Reckhow, 2002; Kim et al., 2002). Recent research has demonstrated the use of transition metals in catalytic ozonation, primarily for wastewater treatment (Legube and Leitner, 1999; Oyama, 2000). Cobalt (II) catalyzed the oxidation of oxalic acid using O_3 (Pines and Reckhow, 2002), and activated carbon coupled with ozone was also demonstrated to generate •OH free radials and oxidize oxalic acid (Jans and Hogne, 1998; Beltran et al., 2002). Multiple metals (Fe, Mn, Ni, Co, Zn, and Cr) in different forms ranging from salts, solid oxides and deposited metals on supports have been used in the catalytic ozonation (Legube and Leitner, 1999; Pines and Reckhow, 2003). Moreover, catalytic ozonation using noble metal supported catalysts has been shown to significantly reduce operating temperatures required for deep oxidation of VOCs such as toluene and styrene (Gervasini et al., 1996).

The research performed on catalytic ozonation demonstrates the potential of using catalysts coupled with ozone in packed bed reactors for removal of wide range of odor-causing

compounds from HVLC emissions. Although the cost of O_3 (~ $2/kg, $1/lb; Oyama, 2000) may restrict its usage to high-value added substances or operations, the concentration of the contaminants in the exhaust gases is generally low (5-20 ppmv), so that only small amounts of ozone are needed. In destruction of VOCs with ozone alone, selectivity may not seem to be important, as the desired reaction is the complete oxidation of the compounds. In many cases where catalysts are not used, partial oxidation products (Oyama, 2000) are formed which are not completely mineralized. For example, oxalic, glyoxalic and acetic acids in solution and acetaldehyde in the gas-phase cannot be completely oxidized by ozone alone. In such cases, the use of catalysts is essential to promote complete oxidation. Unfortunately, there has been limited research on the gas-phase catalytic ozonation of air pollutants and odor-causing compounds such as sulfides, mercaptans, and aldehydes. Most research conducted on catalytic ozonation used activated carbon impregnated with metal oxides and transition metals or solid metal oxides themselves as catalysts which are expensive. There is a need for an inexpensive catalytic material which has high surface area, optimum pore volume, metal and metal oxide content and high carbon content which can catalyze the ozonation of a wide range of VOCs and odor-causing compounds.

Wood fly ash (WFA), a cheap waste material, is produced in large volumes in the USA (75 million tons/yr). The physical and chemical properties (Table 3.2, 3.3) of the ash indicated catalytic potential given the high surface area (~ 45 m^2/g) and the presence of crystalline phases typically associated with catalytic activity (Kastner et al., 2003). Mullite ($3Al_2O_3 \cdot 2SiO_2$), magnetite (Fe_3O_4), and hematite (Fe_2O_3 possibly with small amounts of other metals such as V, Mn, Cu, Co substituting for Fe) were identified in WFA and have been reported to catalyze the oxidation (O_2 only) of TRS or other VOCs at temperatures significantly greater than 25˚C.

Recent research has demonstrated that wood fly ash can catalytically oxidize H_2S, ethanethiol and methanethiol (Kastner eat al., 2002). Given its high surface areas, metal, carbon content and low cost, WFA could potentially be used as a low cost catalyst.

Magnetite and hematite have been shown to catalyze the formation of •OH free radicals from H_2O_2 and the subsequent oxidation of organic compounds by the hydroxyl free radical (Kwan and Voelker, 2003). Moreover, activated carbon supported with Fe_2O_3 and MnO_2-Fe_2O_3 was shown to catalytically decompose O_3, however a mechanism was not proposed (Heisig et al., 1997). Activated carbon in various forms has been utilized as an adsorbent and/or catalyst in the catalytic oxidation of TRS and VOCs (Choi et al., 2001). Finally, metal oxides (e.g., Fe_2O_3) in soil and on supported catalysts have been suggested to generate •OH or other surface radicals and subsequently oxidize adsorbed organic compounds (Legube and Leitner, 1999; Oyama, 2000).

Given the expensive nature of activated carbon and other metal oxides, alternatively we theorize that WFA (or other inexpensive waste materials) given the high metal content, the surface area and the presence of crystalline phases could act as an inexpensive catalytic oxidizer of reduced sulfur compounds ("odor") and volatile organic compound (VOC) removal when coupled with O_3. It is theorized that the ash or selective crystalline phases in the ash may act to catalyze the formation of free radicals (•OH radicals) from ozone in the presence of water and subsequently catalyze the oxidation of a wide range of odor-causing compounds and VOCs or provide a catalytic site for direct oxidation via O_3. Moreover, •OH radical is less selective and has higher rate constants for organic compounds when compared to O_3 (Table 3.4).

Commercially available Magnetite (Sigma-Aldrich), a crystalline phase present in WFA will also be used as one of the catalysts in the catalytic ozonation as a benchmark. Reaction rates

obtained from WFA and magnetite will be compared to find out if the crystalline phases present in WFA catalyze the oxidation of propanal using ozone and in turn result in higher reaction rates. AC (Sigma-Aldrich) which has been widely used in catalytic ozonation will also be used as a benchmark for the research.

Propanal, a 3-carbon aldehyde will be used as the model compound in the catalytic ozonation research with all the three catalysts (WFA, AC, and magnetite). The objective of the research is to evaluate the effectiveness of WFA to catalyze the oxidation of propanal and compare the results with benchmark catalysts (AC and synthetic magnetite). Based on the conversion data of propanal obtained, the kinetics and rate law for the catalytic ozonation of propanal will be developed and the reaction rates obtained with all the three catalysts would be compared. Based on the results obtained, it is possible that catalytic ozonation using inexpensive waste materials can be extended to a wide range of VOCs and odor-causing compounds thus eliminating the need for more than one control technology in eliminating the pollutants at various exhaust gas treatment facilities.

MATERIALS AND METHODS

Catalyst Characterization

Wood fly ash from a pulp mill was used in this study. The physical and chemical characteristics of the fly ash, including pH, surface area, bulk density, and the elemental composition were previously determined (Table 3.2, 3.3; Kastner and Das, 2002). Activated carbon and synthetic magnetite, two commercially available catalysts were obtained from Sigma-Aldrich and used as benchmarks in this research. Limited data about their physical and chemical properties were available (Table 3.5).

Continuous Flow Studies for the Catalytic Ozonation of Propanal

The catalytic ozonation of the propanal was studied in a continuous flow packed bed reactor system (Figure 3.1) at ambient temperature and atmospheric pressure. Compressed air or N_2 (2.5 - 3 L/min) was first passed through a bubble column (5.0 cm i.d., 30 cm length, Pyrex) to humidify the air or N_2 (100% humidity) and then mixed with propanal (97% purity, Sigma-Aldrich) using a syringe pump (Cole-Parmer 74900-30). Propanal (4-15 ppmv) was injected using a Becton Dickinson syringe (plastipak 10 cc, 14.48 mm i.d.) via a tee (stainless steel, Swage-Lok) into the main airflow from the bubble column. The air-propanal mixture was passed through a static mixer (2.5 cm i.d. and 30 cm length, 50 mm diameter glass beads, Pyrex) and then transported down through the packed-bed reactive column (2.5 cm i.d., 30 cm length, Pyrex). An ozone generator (OL100H/DS, Yanco Industries Ltd., B.C., Canada), utilizing a high frequency corona discharge, was used with a medium grade tank of oxygen (99.9%, National Welders, NC) to generate the ozone required for the experiments. Ozone was added via a tee into the air-propanal stream after the static bed mixer, approximately 2 inches from the packed bed reactor inlet. Mass flow controllers (UNIT UFC-8100) were used to control the flow rates of air/N_2 (2.5–3 L/min) and ozone (400–700 mL/min). The catalysts used in the process were distributed on glass wool and packed over a defined height in the reactor. Tees (stainless steel, Swage-Lok) with septum were installed at the inlet and outlet of the packed-bed reactor column for sampling. All tubing used was 6.35 mm (i.d.) Teflon with fittings constructed of stainless steel (Swage-Lok). Threaded Teflon plugs with an O-ring were used at the end of each column for an airtight fit.

The catalytic ozonation of propanal was performed at different residence times (τ = 1-5 s) to see if external mass transfer limited the reaction process. The residence time of the gas mixture in the packed-bed reactor was calculated using the following equation:

$$\tau = ResidenceTime = \left(\frac{packingvolume}{Q} \right) = \left(\frac{HA}{Q} \right)$$

where, Q is the gas flow rate (2.5-3 L/min), H is the height of packing (5-7 cm) and A is the cross sectional area of the reactor.

Ozone Decomposition

The continuous flow reactor system was also to measure ozone decomposition in an empty bed, in the presence of glass wool only, and glass wool plus WFA (2 – 2.5 g). In this case, WFA was distributed throughout the entire column (30 cm) and the residence time based on the entire column ranged from 2.3-2.8 s for all experiments.

MEASUREMENT OF ACTIVITY

Analytical Methods

The physical and chemical properties of the catalysts such as pH, surface area (BET-Brunauer- Emmett-Teller method using N_2 – Nova 3000 Quantachrome, Boyton Beach FL), bulk density, and elemental composition were determined.

In the continuous flow experiments, a bench top GC/MS units (Hapsite Inficon, East Syracuse, NY)) were used to measure the inlet and outlet propanal concentrations at the packed bed reactor. Gas samples were drawn directly from tees at the inlet and the outlet of the column for a defined flow rate of the propanal- air mixture. The gas samples were analyzed under isothermal conditions (70° C).

The mass spectrometer consisted of an ionizer (70 eV), a mass selector (1- 300 AMU), and an ion detector (scan rate 1000 AMU/sec @ 10 points per AMU). Two internal standards, 1, 3, 5-tris (trifluoromethyl) benzene (100 ppmv) and bromopentafluorobenzene (50 ppmv) were used to tune the Hapsite GC/MS and were injected with each gas sample. The Hapsite GC/MS was tuned before each analysis or every twelve hours. Selective ion monitoring (SIM) was used to improve the sensitivity of the propanal used in the experimental analysis. In the SIM mode mass/charge ratios of the corresponding propanal (for e.g. 58 in the case of propanal) and the internal standard (m/z 69) were selectively scanned.

Standard Curve

Standard curves for propanal were prepared from liquid standards in the range of 0-100 ppmv. A known volume of propanal was mixed with a known volume of air in a tedlar sample bag (SKC, Houston, TX) and analyzed using the Hapsite GC/MS. The corresponding peak area of the propanal and the internal standard were measured and the peak area ratio (peak area of propanal/peak area of internal standard) was calculated. The same procedure was repeated for different concentrations of propanal in the range of 0-100 ppmv. Finally the standard curve was obtained by plotting the concentration of propanal against the corresponding peak area ratio. The standard curve obtained was used for the further analysis of the inlet and outlet concentrations of propanal.

Ozone Analysis

The concentration of ozone in the inlet and outlet of the decomposition and catalytic ozonation experiments was measured using an IN-USA 2000 ozone analyzer, via UV absorption

at 254 nm (Model IN-2000-L2-LC, 0.01 ppmv resolutions in the 0-100 ppmv range). The inlet ozone concentration ranged from 86-95 ppmv in the decomposition experiments and 75-175 ppmv in the catalytic ozonation experiments of propanal. The ozone analyzer was also used to calibrate the ozone generator and confirm the generators capability of producing a defined ozone concentration. Ozone concentrations above 100 ppmv were calculated based on the manufacturer's calibration data and dilution of the O_3 gas with main airflow. The UV lamp present in the ozone analyzer was calibrated before the start of each experiment or once in 12 hours for continuous studies.

Methods of Modeling

The kinetics of catalytic oxidation was studied based on the following premises:

(i) In order that the experimental data could be used in the kinetic analysis, potential external and internal mass transfer resistance had to be ruled out.

(ii) Due to the inability to obtain to VOC concentrations along the length of the reactor column, a differential reactor with a small amount of catalyst was used and hence a low conversion of reactant was obtained.

(iii) To reduce the relative error caused by using an approximate rate equation for calculating the reaction rate, average concentrations of inlet and outlet reactants should be adopted.

(iv) To reduce relative error caused by using an approximate rate equation for calculating reaction rate of a differential reactor, average concentrations of inlet and outlet reactants should be adopted.

(v) The heat of reaction in the packed-bed reactor did not increase the temperature and thus the temperature across the reactor was assumed to be constant (isothermal) and equal to the room temperature (23-25°C).

(vi) The plug flow model was assumed regarding the flow of the gases in the reactor.

With the above constraints, the method of modeling catalytic ozonation of propanal over WFA, AC and magnetite catalysts is depicted as follows:

A mole balance for propanal over the catalyst bed in a packed-bed reactor gives the following equation:

$$F_{RI}\,dX = (-r)dW \qquad (1)$$

where F_{RI} is the molar feed rate of propanal in mole/s, X the fractional conversion of propanal, (-r), the reaction rate of catalytic ozonation of propanal in mole $g^{-1}s^{-1}$ and W the mass of catalyst in grams. X is defined as follows:

$$X = \left(\frac{F_{RI} - F_R}{F_{RI}}\right) = \left(\frac{C_{RI} - C_{RO}}{C_{RI}}\right) \qquad (2)$$

where F_R is the molar rate of propanal in mole s^{-1} in the outlet, C_{RI} and C_{RO} are inlet and outlet propanal concentrations in mol cm^{-3}. The percentage conversion is obtained by multiplying X by 100. Equation 1 can be rearranged as

$$-r = F_{RI}\left(\frac{dX}{dW}\right) = C_{RI}\upsilon\left(\frac{dX}{dW}\right) \qquad (3)$$

where C_{RI} is the inlet concentration of propanal in mol cm^{-3} and v the volumetric flow rate of gas in cm^3/s. Theoretically, the reaction rate of propanal can be calculated from the above equation provided $\left(\frac{dX}{dW}\right)$ is known. However, it is well known that the concentration, and thus the value

of $\left(\frac{dX}{dW}\right)$, along the axial position of the packed-bed reactor, is hard to measure. To overcome this difficulty, a differential reactor is commonly used.

When a differential reactor is employed, the approximate rate of catalytic incineration of propanal can be estimated by:

$$-r = F_{RI}\left(\frac{X}{W}\right) = C_{RI}\upsilon\left(\frac{X}{W}\right) \qquad (4)$$

where W is the mass of catalyst used in the differential reactor and X the fractional conversion of propanal at the outlet of reactor. As mentioned before, for the best fit of the kinetic models, when (-*r*) is to be correlated to the concentrations of species involved in the reaction, the average concentration of outlet (C_{RO}) and inlet (C_R, defined as ½ [C_{RI} + C_{RO}]) should be adopted.

RESULTS AND DISCUSSION

Propanal Oxidation

A series of experiments were conducted to confirm that ozone and a catalyst were necessary to oxidize propanal (Figure 3.2). First an experiment was conducted to see if propanal (14-15 ppmv) could be catalytically oxidized by oxygen alone. Average percentage conversion of approximately 6% was obtained over a time period of 253 min at a residence time of 2.5 s. The very low percentage conversion which was statistically insignificant indicated that catalytic oxidation (O_2 at low temperatures ~25°C) is not an effective control technology for treating the aldehyde fractions (propanal) although catalytic oxidation be effective in treating certain VOCs and odorous compounds at high temperatures (400-600°C).

Since propanal could not be catalytically oxidized by oxygen, the oxidizing capability of ozone was tested. A control experiment was run at room temperature to see if propanal could be oxidized by ozone alone (no catalyst), since Ozone being a better oxidizing agent than molecular oxygen. Analysis of the propanal inlet and outlet concentration at regular intervals indicated similar concentrations of propanal during a time period of 150 min and thus practically no oxidation of propanal (~ 15 ppmv) for an ozone concentration of 95 ppmv and a residence time of 2.3 s. The ineffectiveness of ozone alone indicated that a catalyst was necessary for the oxidation of propanal. Before an experiment was performed with WFA as the catalyst material, another experiment was conducted to see if glass wool (support material for WFA) would act as a catalyst in the experiment. The percent conversions of propanal (14-15 ppmv) obtained in this experiment were approximately 6-8% over a time period of 160 min. Based on the inlet and outlet concentrations of propanal over the time period of the experiment, there was no statistical evidence to prove that glass wool played a role in the oxidation of propanal and hence the effect of glass wool in the catalytic ozonation of propanal when used as the support material for WFA can be neglected.

Finally, WFA supported on glass wool was used in the ozonation of propanal (14-20 ppmv) with 90-100 ppmv of ozone and a residence time of 2.74 s. Over the 229 min period for which the experiment was conducted (229 min), the percent conversion varied between 26-45% with an average conversion of 34%. The varying response in the percentage conversions could be because of the fluctuations in propanal flow and any experimental errors. This clearly indicated that ozone, combined with a catalyst was responsible for the partial or complete oxidation of propanal.

Assessment of Influence of Mass Transfer Resistance on the Reaction Rate

According to the premises mentioned before, the experimental data could not be used in a kinetic analysis if external and internal mass transfer resistance were present. For the assessment of mass transfer resistance, we conducted the catalytic ozonation of propanal using a defined mass of catalyst (2.5 g), ozone concentration of 95 ppmv and propanal concentration of 30 ppmv for different residence times between 1 to 4.5 s. The residence times were set by varying the flow rates of the gas mixture entering the packed-bed reactor. As seen in the fig 3.3, reaction rate (calculated using the model mentioned in the premise) for the catalytic ozonation of propanal using WFA and magnetite was independent of the residence time (or flow rates). Although the percentage conversions varied at each residence time, the overall reaction rate at each residence time for each of the catalyst did not vary much indicating that resistance due to mass transfer can be ignored. Based on the above analysis, the following kinetic studies were all conducted under the assumption of negligible mass transfer resistance. If external mass transfer was rate limiting, there would either be an increase or decrease in the reaction rates with increasing residence times.

Ozone Decomposition

A continuous flow reactor system was used to measure ozone decomposition in an empty bed in the presence of glass only and glass wool plus wood ash (2 g). In this case, the wood ash was distributed throughout the entire column (30 cm) and the residence time based on the entire column ranged from 2.3-2.8 s for all experiments. The transient kinetics of ozone decomposition on wood ash (ozone alone) indicated a high initial reaction rate (0.27 mg/g.min or 1.88×10^{-9} mol m^{-2} s^{-1}) and subsequent decline (Figure 3.4). Compared to controls (empty and glass wool only)

the initial ozone decomposition rate was significantly higher and comparable to initial rates measured using activated carbon (0.25 mg/g.min). The initial decomposition rate is also comparable to that of n-type metal oxides (Oyama, 2000) like CeO_2 (~2.6 $x10^{-9}$ mol m^{-2} s^{-1}), Cr_2O_3 (~ 2.4$x10^{-9}$ mol m^{-2} s^{-1}), V_2O_5 (~ 1.5$x10^{-9}$ mol m^{-2} s^{-1}), MoO_3, and CuO (both ~ 1 $x10^{-9}$ mol m^{-2} s^{-1}). The metal oxides listed have been used in ozone decomposition in a number of situations, such as in the destruction of ozone generated by photocopiers and destruction of ozone in the air entering the cabin section of vehicles and air planes.

However, within 3 hours of the ozone decomposition experiment, the fractional conversion declined from 0.96 to 0.15 and the O_3 reaction rate declined from 1.88$x10^{-9}$ to 2.08$x10^{-10}$ mol m^{-2} s^{-1} (Figure 3.5). These data suggest that a stable surface oxide may form that saturates the surface and prevents further oxidation of O_3 without the presence of a VOSC or VOC capable of being oxidized and subsequently regenerating the surface. The surface oxides formed could be utilized in the oxidation of the pollutant compound there by regenerating the surface and hence leading to continuous decomposition of ozone on the surface of WFA. Given the high initial decomposition rate, these results suggest that WFA could be used as a catalyst with ozone to generate surface oxides or other reactive species for the oxidation of propanal.

Continuous Catalytic Ozonation of Propanal

In order to determine if the packed-bed reactor system could be used in the continuous conversion of propanal without any significant catalyst decay and reduction in propanal conversion, an air-propanal-ozone mixture was passed through the packed bed reactor containing 2.5 g of WFA wetted with 1.5 g DI water, and impregnated on glass wool. A stable conversion of 30-40% (Figure 3.6) was observed over a period of 1300 hours. The generation and the

subsequent utilization of the active species formed due to ozone decomposition in the water film on the catalytic surface could be the reason behind the continuous oxidation of propanal. The surface oxides formed on the surface of the catalysts could potentially oxidize propanal thereby regenerating the surface for further generation of active species. The stable conversion indicated that WFA could be used for continuous studies on catalytic ozonation of propanal without any significant catalyst decay.

Effect of Reactant Concentration on the Rate of Catalytic Ozonation of Propanal

Figure 3.7 shows the effect of propanal concentration on the rate of reaction at different ozone levels (75-175 ppmv). We can see from the Figure that for a given ozone concentration, the propanal reaction rate increased with propanal concentration in the range of 5-15 ppmv. On the other hand, the rate of reaction did not vary much at a constant propanal concentration and varying ozone concentrations except for magnetite for which there was an appreciable increase in the rate of reaction (figure 3.8). Thus we conclude that the rate of reaction for a given catalyst is affected mainly by the concentration of propanal and not by ozone.

Effect of Ozone Concentration on Catalytic Ozonation of Propanal

As discussed above, Fig. 3.8 shows that for a given propanal concentration, increasing the ozone concentration results in only a small increase in the rate of reaction of propanal. In the case of WFA, for a propanal concentration of 15 ppmv, increase in ozone concentration increased the reaction rate by approximately 1.4x from 2.218×10^{-9} mol g^{-1} s^{-1} to 3.1095×10^{-9} mol g^{-1} s^{-1}. But for magnetite, there was 2x increase in the reaction rate for change increase in concentration from 75 ppmv to 175 ppmv for the same propanal concentration. The two fold

increase of reaction rate in the case of magnetite when compared to only 50% increase in WFA could be attributed to the availability of more active sites in synthetic magnetite which in turn lead to higher ozone decomposition rate when compared to WFA. In WFA, crystalline phases of magnetite are present in traces and the distribution of transition metals on the surface is also uneven owing to less increase in reaction rate with increase in ozone concentration.

Effect of Water on Catalytic Ozonation of Propanal

Table 3.6 shows the effect of water on the catalytic ozonation of propanal. As hypothesized, water played a vital role in the conversion/ decomposition of propanal and this can be observed based on the reaction rates for the conversion of propanal with and without water. At a fixed propanal concentration of 15 ppmv and two ozone concentrations 75 and 95 ppmv, the propanal-O_3 stream was made to pass through two packed bed reactors with 2.5 g of WFA in one of them and 2.5 g of AC in the other. In both cases, the percentage conversion of propanal without water was approximately 10% when compared to 18-19% conversion with water using WFA and approximately 24% using AC for both the ozone concentrations. In case of WFA, the reaction rate increased more than three times from 1.15×10^{-9} to 3.68×10^{-9} mol g^{-1} s^{-1} for an ozone concentration of 95 ppmv. In case of AC, the reaction rate increased from 1.17×10^{-9} to 2.96×10^{-9} mol g^{-1} s^{-1} for the same ozone concentration. The higher reaction rates (Table 3.6) with water indicate the presence of multiple mechanisms which lead to the formation of active species on the surface of the catalyst which in turn help in the oxidation of propanal. The higher reaction rates are also in accordance with the ozone decomposition experiments conducted (Fig 3.5), where in the initial ozone decomposition rates were higher. But as hypothesized earlier, the continuous utilization of the surface oxides formed for the oxidation of propanal led to a

continuous oxidation (700-800 min) of propanal without much decline in the reaction rate. The low reaction rates without water suggest lack of reaction or slight reaction due to no formation of active species owing to ozone decomposition.

DISCUSSION

The formation of active species is the key point in any study for the catalytic ozonation of pollutants. In this research also, the transient kinetics study of ozone decomposition on WFA was vital for the oxidation of propanal. The high initial reaction rates (with WFA) when compared to the controls (glass wool and empty reactor) indicated that ozone decomposed on the catalyst in the presence of the water film. But the subsequent decline in the decomposition rates raised questions about the catalytic decay of WFA. The study on the continuous oxidation of propanal (1300 min) with a stable conversion (36-40%) led to the conclusion that the decline in the ozone decomposition rate was due to the saturation of the catalytic surface with surface oxides and the subsequent utilization of surface oxides for the oxidation of propanal led to the regeneration of the catalytic surface.

The percentage conversions and reaction rates obtained for various ozone and propanal concentrations indicate that WFA is an effective catalyst for the oxidation/decomposition of propanal. The physical and chemical properties of the ash indicated catalytic potential given the high specific surface area (~45 $m^2 g^{-1}$) and the presence of crystalline phases typically associated with catalytic activity. The effect of crystalline phases on the catalytic ozonation can be observed based on the fact that the reaction rate for the catalytic ozonation of propanal with magnetite was approximately two times (3.12×10^9 mol g^{-1} s^{-1} to 5.94 mol g^{-1} $s^{-1)}$ when compared to that of WFA for a propanal concentration of 15 ppmv and ozone concentration of 175 ppmv.

Magnetite and hematite have been shown to catalyze the formation of OH free radicals from H_2O_2 and the subsequent oxidation of organic compounds by the hydroxyl free radical. The higher reaction rates obtained with catalyst wetted with water proves the point that crystalline phases in WFA did result in the formation of active species (not known) due to ozone decomposition in the water film on the catalyst surface and result in the higher oxidation rates of propanal. Hence water played a vital role in the catalytic ozonation of propanal.

AC with a high carbon content and surface area is has been shown previously to decompose O_3 when supported with Fe_2O_3 and MnO_2-Fe_2O_3. In the current research, although no metal oxides were impregnated on AC, the high reaction rates obtained for the catalytic ozonation of propanal indicates that carbon present in the AC acts as an adsorbent for propanal thereby leading to chemisorption of pollutant which then reacts with the surface oxides present and in turn result in the oxidation of propanal. The high carbon content (19%, dry basis) contributed to the catalytic activity, potentially by increasing the adsorptive capacity of the organic pollutant (propanal). Activated carbon impregnated with platinum (Pt) was shown to significantly increase the catalytic ozonation of *p*-chlorobenzoic acid (*p*CBA) relative to platinum dispersed on aluminum in liquid phase reactions (14).

CONCLUSION

The physical and chemical properties of WFA like high specific surface area, presence of crystalline phases (mullite, hematite and magnetite) and presence of wide range of transition metals contribute to catalytic activity of WFA, thereby demonstrating its potential as an inexpensive catalyst.

Its effectiveness in the oxidation of propanal (VOC) and H_2S, MT and DMDS (odorous compounds; Kastner and Das, 2002) can make it a potentially good catalyst in the oxidation of wide range of VOCs and odorous compounds from exhaust gases in rendering, paper and pulp and many other industries.

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Table 3.1. Summary of heterogeneous reactions of ozone (Data from Oyama, 2000)

Substrates	Catalysts	Reaction Conditions	Products	Rate (mol/ m^2.
Ethanol	γ-Al_2O_3		Ketones,	
Propanol	SiO_2	293-363 K	Aldehydes,	1.7×10^{-9}
Isopropanol			CO_2	
Ethanol	MoO_3/Al_2O_3	300-550 K	Acetaldehyde,	0.9×10^{-9}
	MnO_2/Al_2O_3		CO_2	1.9×10^{-9}
Benzene	MnO_2	383-353 K	CO, CO_2	1.5×10^{-9}
	γ-Al_2O_3/Fe-oxide			1.7×10^{-7}
	γ-Al_2O_3/Cu-oxide			3.7×10^{-7}
Benzene	γ-Al_2O_3/Ni-oxide	296 K	CO, CO_2	3.8×10^{-7}
	γ-Al_2O_3/Mn-oxide			1.3×10^{-7}
Dichloromethane	Pt/ Al_2O_3			
Tetrachloroethylene	Pd/ Al_2O_3	323-473 K	Mostly CO_2	___
p-chlorotoluene	$BaCuCrO_x$			
Cyclohexane	γ-Al_2O_3/Mn-oxide	296 K	CO,CO_2	1.2×10^{-6}

Table 3.2. Physical and chemical properties of WFA

Properties	WFA (Mean ± SD)
Surface Area, m^2/g	44.89 ± 8.34
pH	12.13 ± 0.17
Bulk Density, g/cm^3	0.54
Carbon, % (dry basis)	18.75 ± 1.87
Selected Elements (ppm)	Range
Co	4.5 – 5.2
Cu	32.0 – 39.0
Mn	500.0 – 584
Mo	2.2 – 2.7
Ni	18 – 19
Fe	6,600 – 8,300

Table 3.3. Particle size distribution of WFA.

Particle Size range (μ)	% of particles (by mass) in the range
> 600	5.69
600-425	2.40
425-150	9.99
150-75	12.89
< 75	69.73

The percentages of particles in the ranges measured add up to 100.7 owing to small calculation errors

Table 3.4. Ozonation rate constants and OH rate constants for some organic compounds in liquid phase.

Solute	k_{O3} ($M^{-1} s^{-1}$)	$k_{OH^{\cdot}}$ ($M^{-1} s^{-1}$)*10^{-9}[a]
Benzene	2 ± 0.4	7.8
Nitrobenzene	0.009 ± 0.02	3.9
Toluene	14 ± 3	3.0
m-xylene	94 ± 20	7.5
Formic acid	5 ± 5	1.3
Formate ion	100 ± 20	3.2
Acetic acid	(<3 x 10^{-5})	1.6
Salicylic acid	<500	2.2

[a] $k_{OH^{\cdot}}$ read as cell value times 10^9. e.g. 7.8x10^9

Table 3.5. Physical properties of magnetite and activated carbon

Properties	Magnetite	Activated Carbon
Surface Area, m^2/g	1.7905 ± 0.464	424.95 ± 52.33
Pore Volume, mL/g	5.0792 ± 0.7472	0.429 0.7472 0.0273

Table 3.6. Effect of water on the catalytic ozonation of propanal using wood fly ash and activated carbon.

Ozone Concentration (ppmv)	Wood Fly Ash Reaction Rate x 10^{9*} (mole g^{-1} s^{-1})		Activated Carbon Reaction Rate x 10^{9*} (mole g^{-1} s^{-1})	
	With water	Without water	With water	Without water
75	2.33±0.3	1.67±0.2	3.07	1.22±0.16
95	3.68±0.4	1.15±0.2	2.96	1.17±0.17

*reaction rate to be read as (value in the cell) $x10^{-9}$; e.g., $2.33x10^{-9}$ for WFA with water at 75 ppmv.

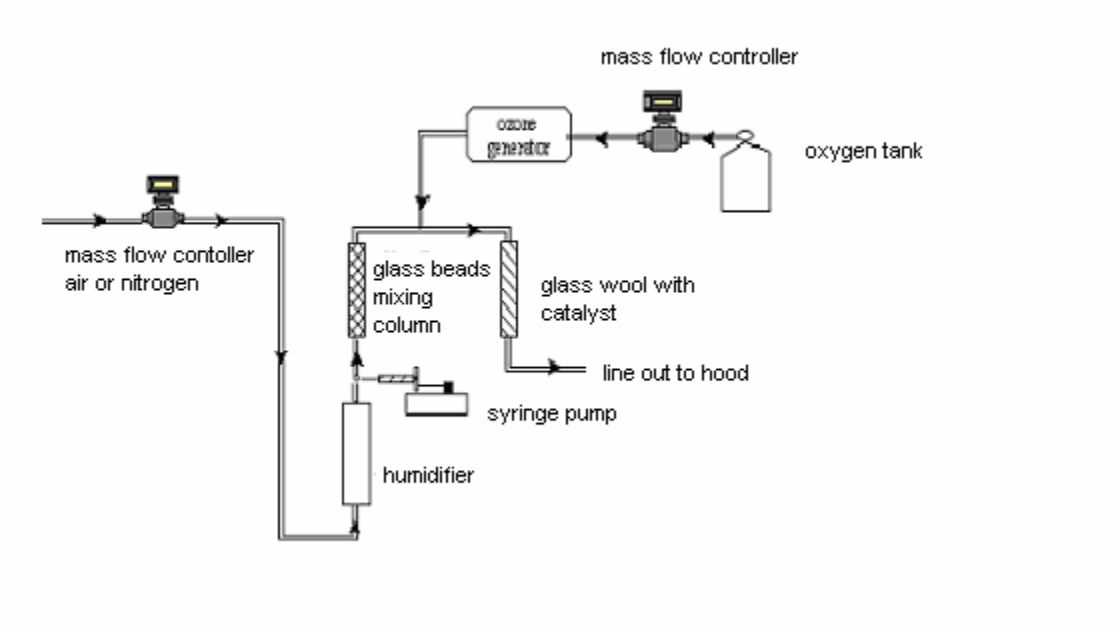

Figure 3.1: Experimental set up for the catalytic ozonation of aldehydes in a packed bed reactor column.

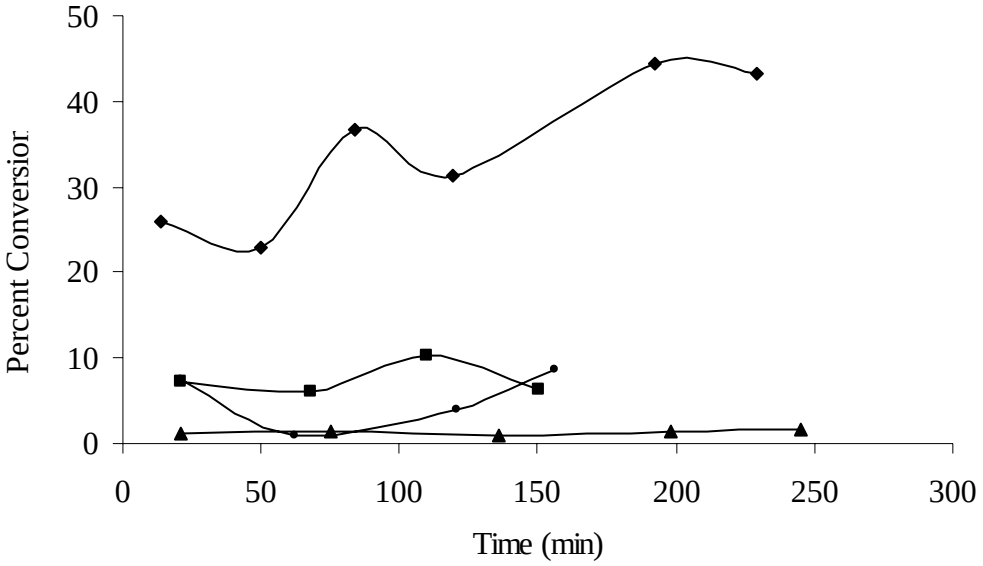

Figure 3.2. Comparison between catalytic oxidation using WFA, ozonation, catalytic ozonation using glass wool and catalytic ozonation using WFA, of propanal (14-15ppmv) at room temperature. • Catalytic oxidation of at a residence time of ~2.5 s with WFA (2.5 g) as catalyst, ▲ oxidation of propanal (14-15 ppmv) using ozone (90-100 ppmv) alone at a residence time of 2.3 s, ♦catalytic oxidation of propanal using WFA (2.5 g) and ozone (90-100 ppmv) at a residence time of 2.74 s, ■ Catalytic oxidation of propanal using glass wool and ozone (90-100 ppmv) at a residence time of 2.74 s.

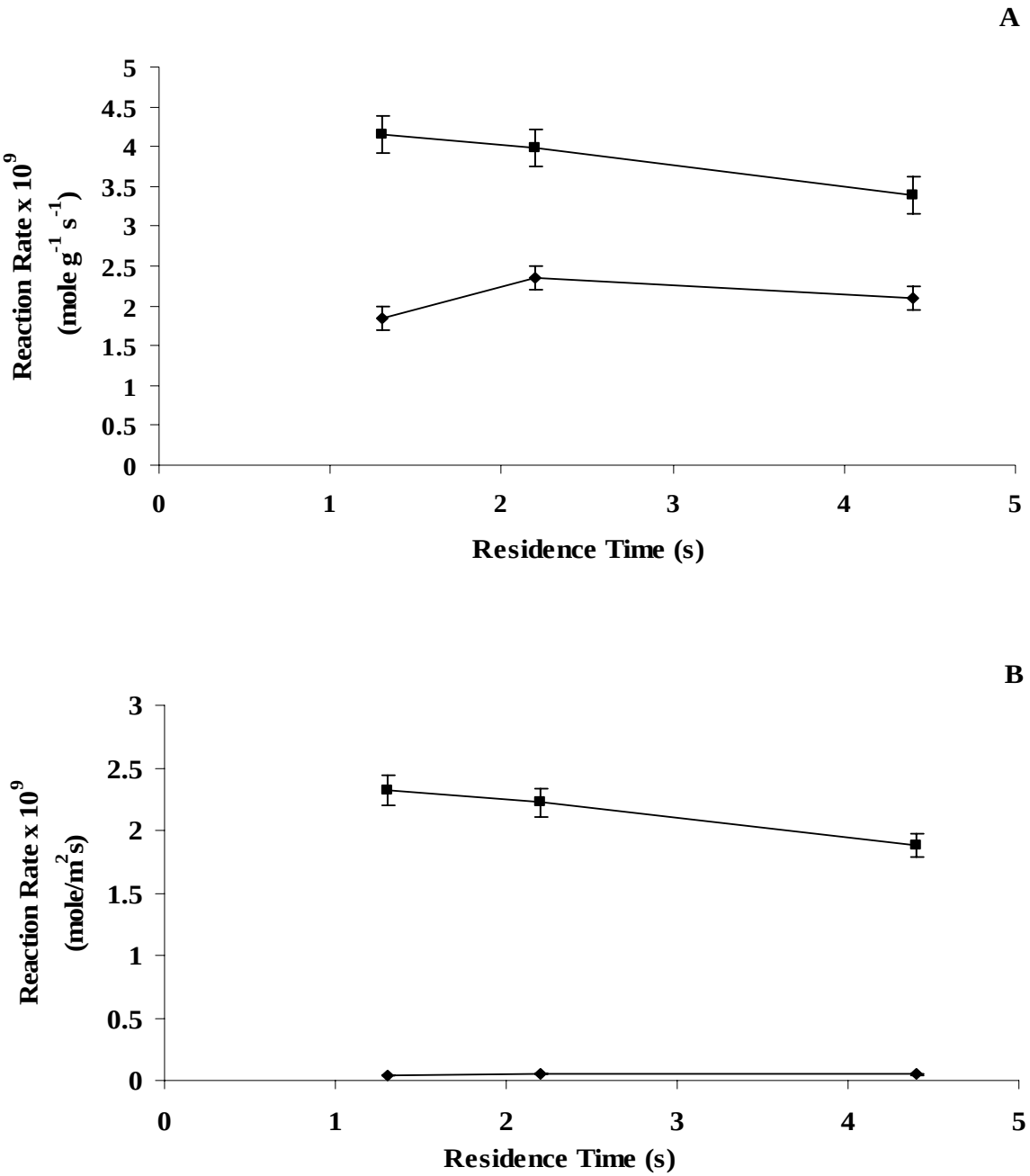

Figure 3.3: Assessment of mass transfer resistance. Effect of residence time (RT) on the reaction rate of catalytic ozonation of propanal using Magnetite (■) and WFA (♦) for an ozone oncentration of 95 ppmv and propanal concentration of 15 ppmv using 2.5 g of catalyst. A) Reaction rate in mole/g/s, B) reaction rate in mole/m^2/s. Bars denote standard errors.

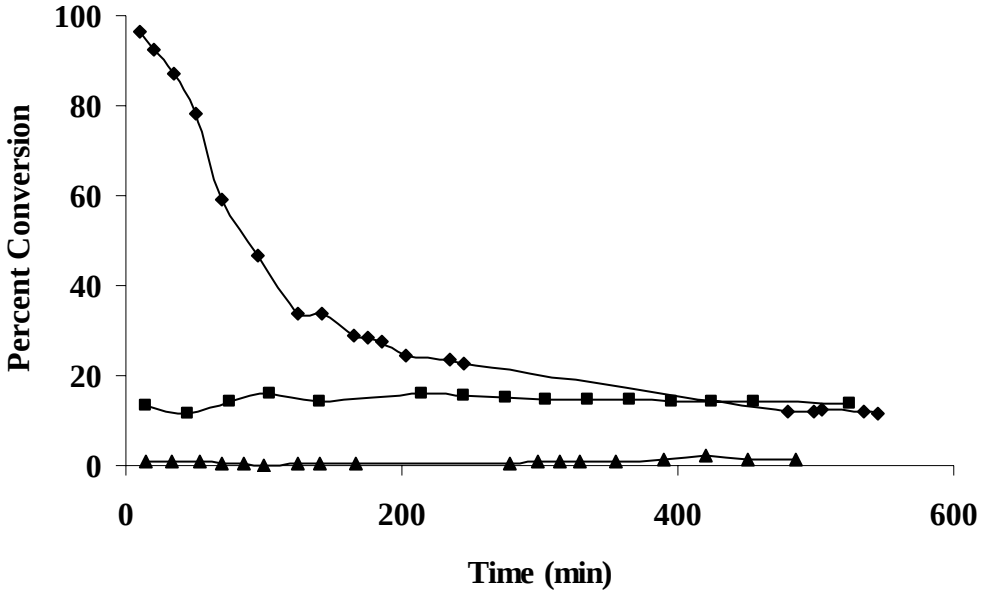

Figure 3.4. Ozone decomposition in an empty reactor (▲), the presence of glass only (■) and wood ash dispersed in glass wool (◆) using a reactor packed with 2 g of wood ash (25% moisture) at 23-25°C in an approximate 2.75 residence time.

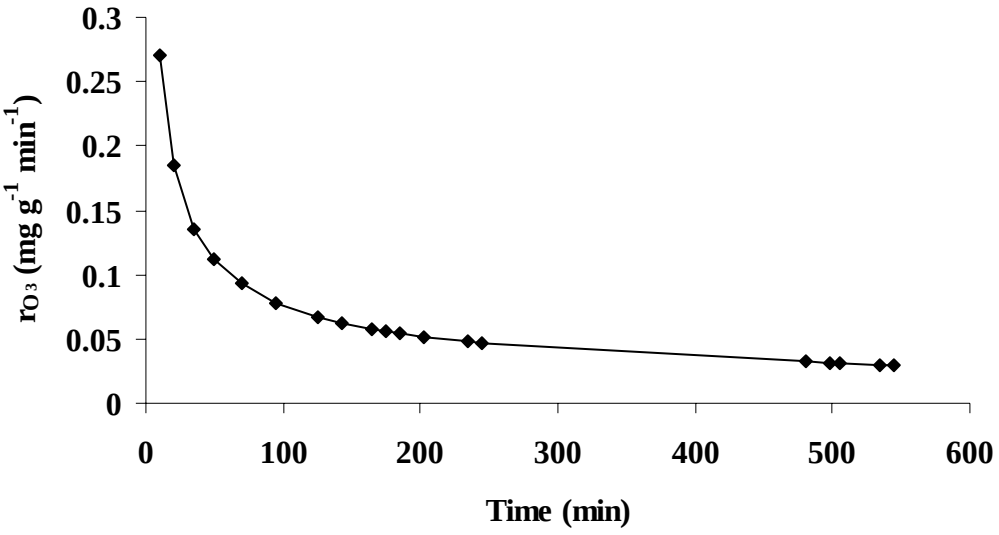

Figure 3.5. Reaction rate versus Time for decomposition of ozone on 2 g WFA (25% moisture) impregnated on glass wool in a packed bed reactor column at 23°C for a residence time of 2.75 s.

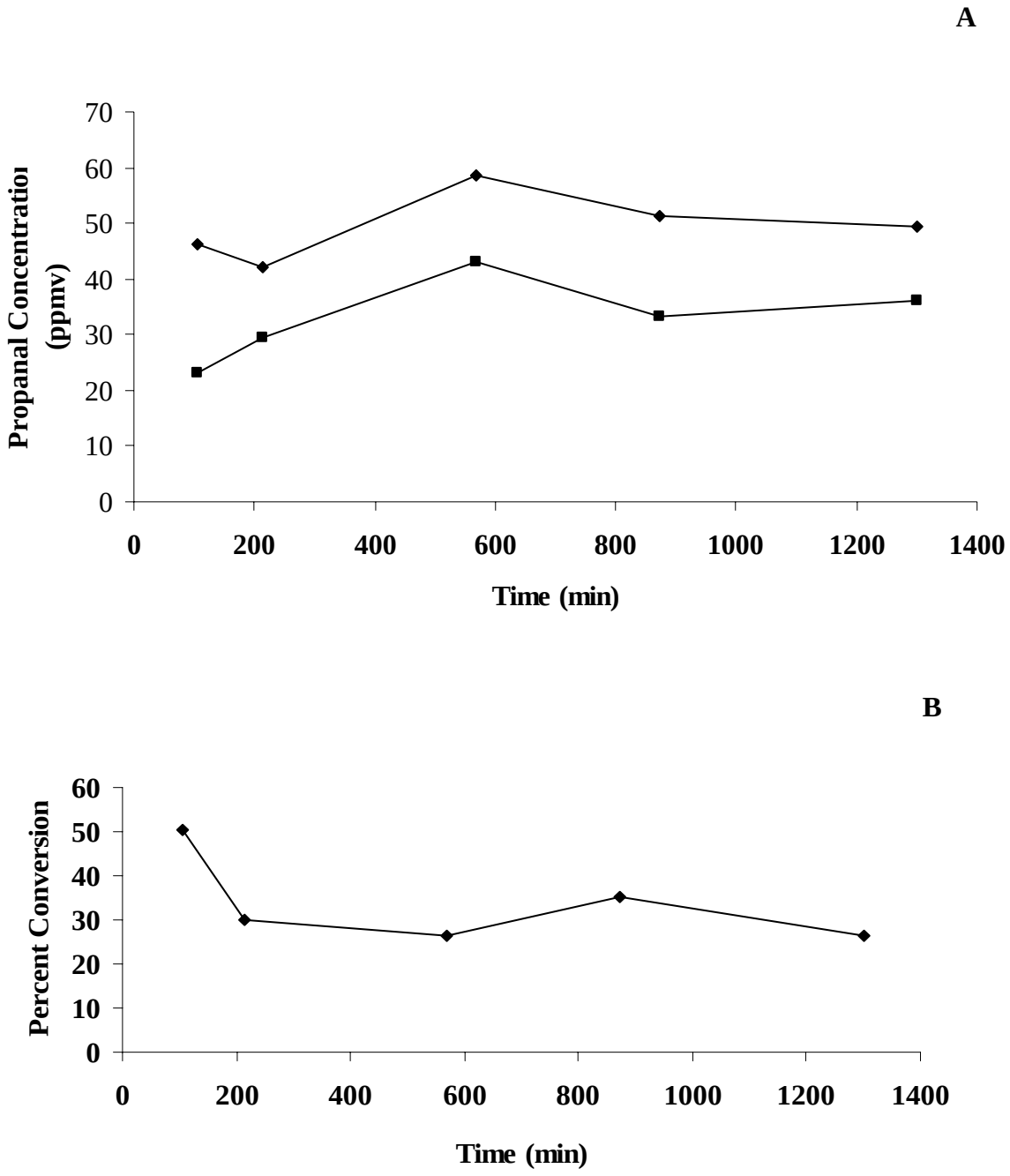

Figure 3.6. Continuous conversion of propanal for 1300 hours using 2.5 g of WFA, 42-49 ppmv of propanal and 90-100 ppmv of ozone. A. Inlet and outlet concentrations of propanal during the 1300 hrs. B. Percentage conversion of propanal during the continuous conversion.

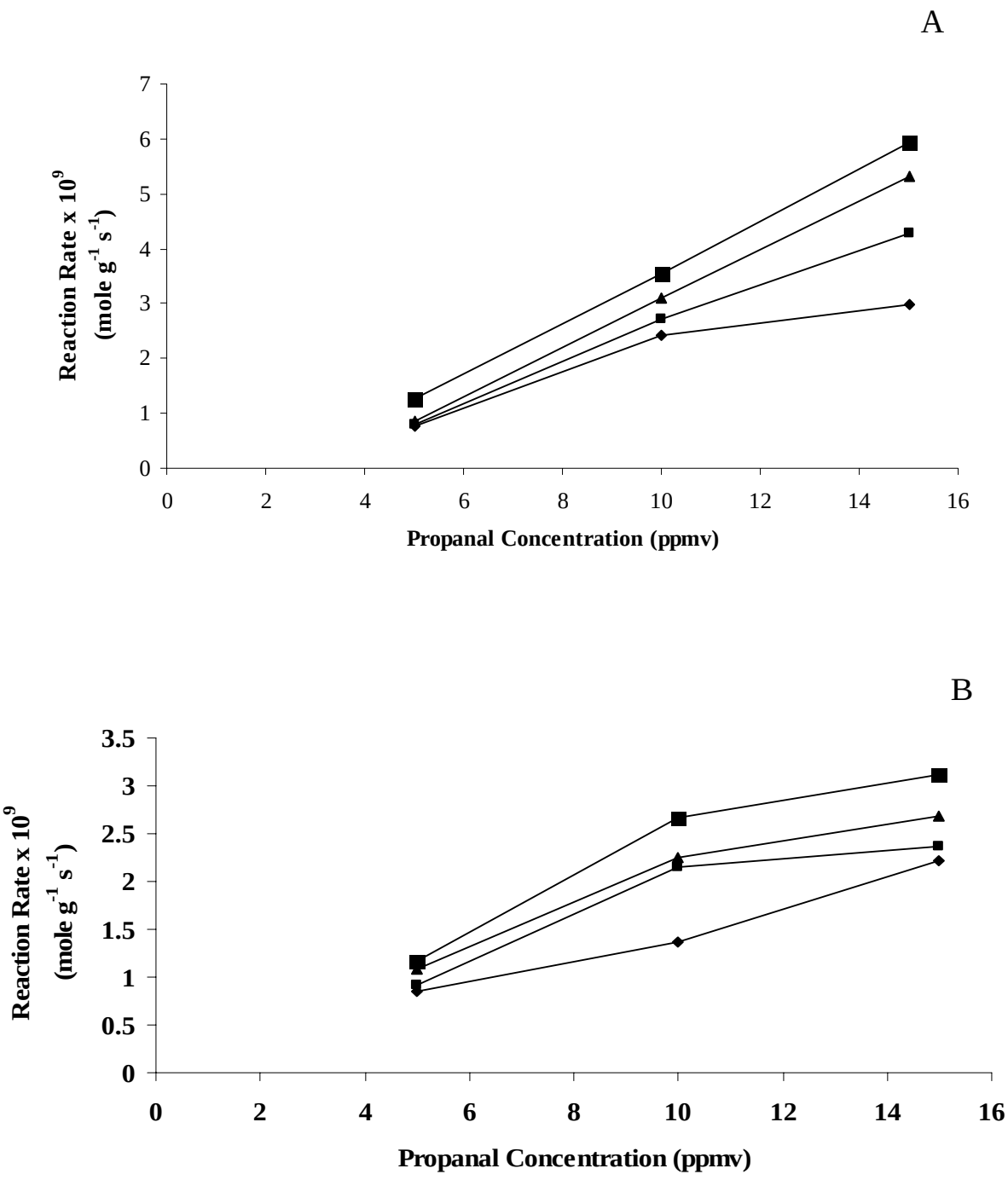

Figure 3.7. Effect of propanal concentration on the catalytic ozonation of propanal using four different ozone concentrations: ■ 175 ppmv ▲ 145 ppmv, ▪ 95 ppmv ♦ 75 ppmv at room temperature (23-25°C) for A) magnetite and B)WFA.

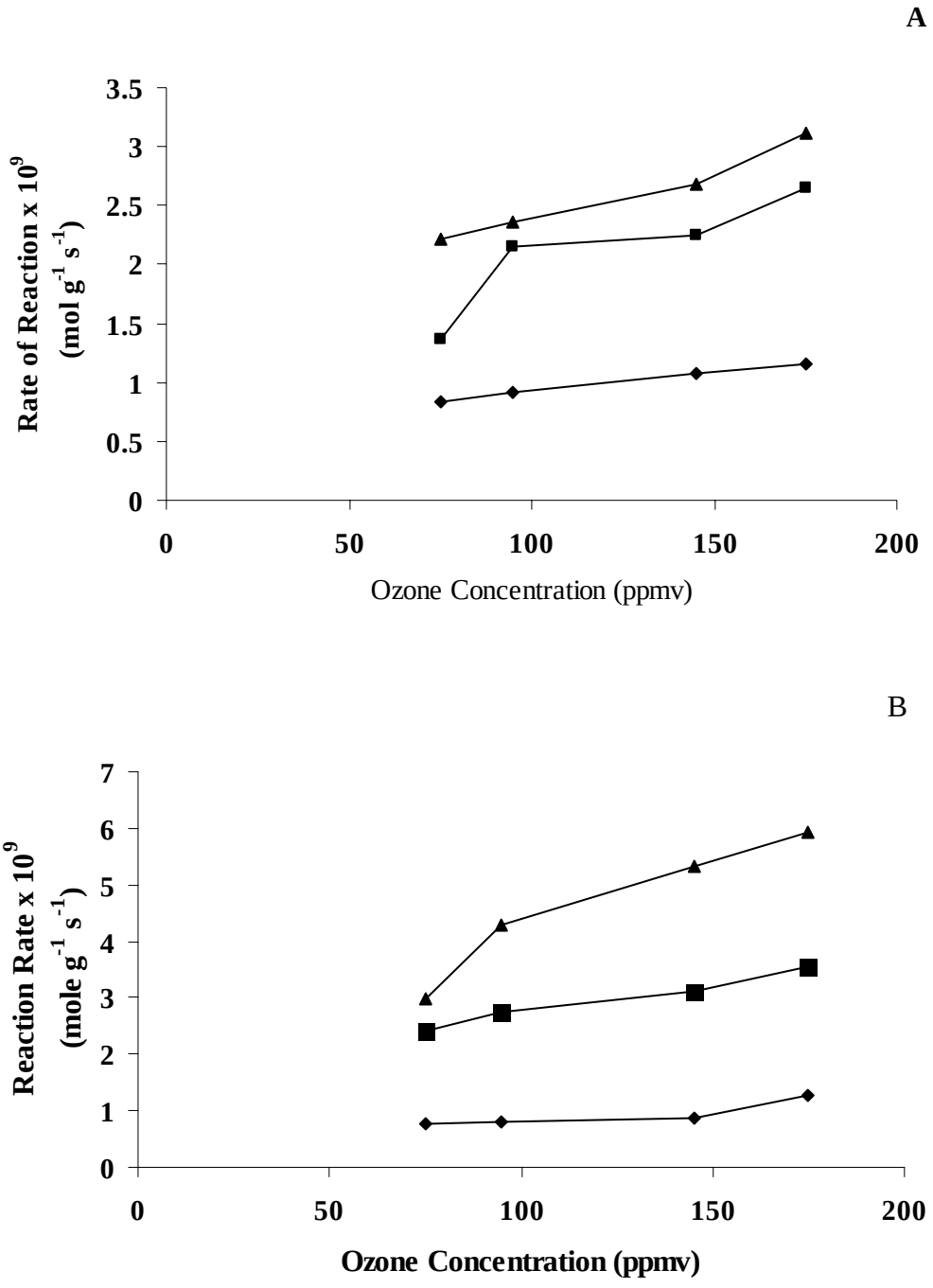

Figure 3.8: Effect of ozone concentration and propanal concentration (♦5 ppmv, ■ 10 ppmv, ▲15 ppmv) on the catalytic ozonation of propanal using 2.5 g of WFA (A) and magnetite (B)

CHAPTER 4

CATALYTIC OZONATION KINETICS OF PROPANAL AND REACTOR DESIGN[2]

[2]Rangan, G. V. and Kastner, J.R. To be submitted to the Journal of Environmental Science and Technology

ABSTRACT

In this study, the kinetics of catalytic ozonation of propanal was investigated by varying reaction conditions including propanal concentration, ozone concentration, and catalyst type. The power law model was applied to best fit the experimental results obtained using wood fly ash (WFA) and magnetite as catalysts. The reaction expression of the power rate law model for WFA (r_w) and magnetite (r_m) were respectively; $-r_w = k_w' (C_R)^{0.879}$ and $-r_m = k_m' (C_R)^{1.479}$, where k_w', and k'_m are pseudo first order rate constants with values 2.48E-10 g^{-1} s^{-1} (moles ozone)$^{-1}$ and 7E-11 g^{-1} s^{-1} (moles ozone)$^{-1}$ respectively, and C_R is the inlet propanal concentration in moles/cm^3. The high R^2 values (0.823 for WFA and 0.901 for magnetite) obtained for the regression models using both the catalysts indicated that the power law model appropriately described the kinetics of catalytic ozonation for both the catalysts. Crystalline phases (mainly magnetite and hematite) present in the WFA played a significant role in the catalytic ozonation of propanal. General linear regression analysis performed on reaction rates obtained from crystalline phases separated from WFA, WFA itself and magnetite at 95 ppmv (parts per million by volume) of ozone and 10 ppmv propanal indicated that crystalline phases separated from WFA had significantly higher reaction rate (~ 2x mol $g^{-1}s^{-1}$) than that of WFA and was similar to reaction rate measured for synthetic magnetite. The catalytic activity of WFA was comparable to that of commercially available catalysts and could be attributed to the presence of crystalline phases in WFA.

KEY WORDS: Catalytic ozonation, propanal, power-rate law model, wood ash, magnetite, hematite. crystalline phases.

INTRODUCTION

Air pollution is not a new phenomenon, and has been a source of serious concern for centuries. Air pollution is a worldwide environmental issue today. Much of air pollution is directly related to the combustion of fuels for industrial production, for transportation, and for production of electricity for domestic purposes. In the USA, approximately 200 million tons of waste gases are released into the air annually (Mycock et al., 1995). The release of large amounts of toxic gases led to the enactment of the federal Clean Air Act Amendments (CAAA) of 1990, which brought about stricter regulations of air emissions. Volatile Organic Compounds (VOCs) and Total Reduced Sulfur Compounds (TRS) are classes of compounds which are recognized as Hazardous Air Pollutants (HAPs) because of their large emissions and toxic nature. With increasing populations and rapid expansions of industrial production, the emissions of VOCs and TRS have also increased rapidly.

VOCs have long been regarded as a major source of air pollution due to their harmful effects on human health and on environment. Oxides of nitrogen (NO_x) react with certain VOCs (sometimes called reactive hydrocarbons) in the presence of sunlight to form photochemical oxidants, including ozone. The photochemical oxidants formed are also called photochemical smog (1). Also some VOCs have known to be cancerous and odoriferous, causing displeasure when exposed to them.

$$NO_x + VOC \xrightarrow{\text{UV rays}} \text{Photochemical Smog} \qquad (1)$$

VOCs are emitted from combustion processes, from industrial processes for the manufacture of organic chemicals, polymers and herbicides, from processes involving painting, printing and degreasing of metals, from rendering operations and from solvent evaporations. The major constituents that have been qualitatively identified as potential emissions include organic

sulfides, disulfides, C-4 to C-7 aldehydes, trimethylamine, C-4 amines, quinoline, dimethyl pyrazine, other pyrazines, and C-3 to C-6 organic acids.

TRS consists of the total sulfur from the following compounds: hydrogen sulfide (H_2S), dimethyl sulfide (DMS), dimethyl disulfide (DMDS). H_2S makes up the greatest portion of TRS. These compounds can be detected by their rotten-egg odor and are another important source of air pollution. Sources of TRS include wastewater treatment plants, tanneries, and livestock operations. High volume low concentration emissions (HVLC) of VOCs and TRS are odorous, toxic at high concentrations, and can contribute to smog formation (Devai and DeLaune, 1996). These problems coupled with the increasing number of complaints from residential areas in close proximity to TRS-generating industries have led to the formulation of various odor control rules and EPA air regulations. The increasing problems created by these odorous compounds necessitate the remediation of a wide range of VOCs and TRS generated by these industries. The CAAA calls for techniques that can effectively control air emissions from industrial processes. Commonly both process control to reduce emissions and end of pipe treatment technologies like wet scrubbers, incinerators, regenerative thermal oxidizers (RTO), catalytic oxidation and biofilters are used to achieve this objective.

High volume low concentration (HVLC) emissions from many industries (e.g., pulp and paper mills, rendering plants and wastewater treatment facilities) contain a range of reduced sulfur compounds, such as H_2S, MT and DMDS, which are odorous and toxic at high concentrations (Devai and DeLaune, 1999). Regenerative thermal oxidation (RTO) and wet scrubbers are two primary air pollution control technologies used to treat the reduced sulfur compounds (Seiwart, 1997; Kastner and Das, 2002). RTO's have high operating costs, since oxidation occurs at high temperatures (760-870°C), and produce greenhouse gases (NOx, CO_2)

due to combustion of an external carbon source at high temperatures. Wet scrubbers require costly oxidizing chemicals, such as ClO_2 or sodium hypochlorite (NaOCl), large amounts of water, and can produce chlorinated hydrocarbons if not properly controlled (Kastner and Das, 2002). Moreover wet scrubbers using ClO_2 as the oxidizing agent were ineffective towards the aldehyde fraction. Catalytic oxidation helps in the complete removal of VOCs and TRS but at high temperatures (600-800°C). There is a need for a cost-effective air pollution control technology for treatment of VOCs and TRS that reduces energy costs, water consumption, and greenhouse gas production.

Catalytic oxidation using ozone as the oxidizing agent is a commonly used treatment technology in waste water treatment and treating polluted streams (liquid) containing VOCs. Ozone is a stronger oxidizing agent than molecular oxygen or hydrogen peroxide and reacts with most substances at room temperature. In acid solution the oxidizing power of ozone is exceeded only by fluorine, the peroxate ion, atomic oxygen, •OH radicals, and a few other such species (Cotton and Wilkinson, 1988). The concentration of the contaminants is generally low, so that only small amounts of ozone are needed. Importantly, the reactivity of ozone is very high (Table 4.1), so that the oxidation can occur close to the room temperature for both liquid and gaseous streams. Several research papers have demonstrated that certain VOCs can be catalytically oxidized in the aqueous phase at low temperature when coupled with ozone (Gervasini et al., 2000; Choi et al. 2001; Zaror et al., 2001; Pines and Reckhow, 2002; Kim et al., 2002). Recent research has demonstrated the use of transition metals in catalytic ozonation, primarily for wastewater treatment (Legube and Leitner, 1999; Oyama, 2000). Cobalt (II) catalyzed the oxidation of oxalic acid using O_3 (Pines and Reckhow), and activated carbon coupled with ozone was also demonstrated to generate OH free radials and oxidize oxalic acid (Jans and Hogne,

1998; Beltran et al., 2002). Multiple metals (Fe, Mn, Ni, Co, Zn, and Cr) in different forms ranging from salts, solid oxides and deposited metals on supports have been used in the catalytic ozonation (Legube and Leitner, 1999; Pines and Reckhow, 2003). Moreover, catalytic ozonation using noble metal supported catalysts has been shown to significantly reduce operating temperatures required for deep oxidation of VOCs such as toluene and styrene (Gervasini et al., 1996).

Previous research done on catalytic ozonation demonstrates the potential of using catalysts coupled with ozone in packed bed reactors for removal of wide range of odor-causing compounds from HVLC emissions. Although the cost of O_3 (~ \$2/kg, \$1/lb) may restrict its usage to high-value added substances or operations, the concentration of the contaminants in the exhaust gases is generally low (5-20 ppmv), so that only small amounts of ozone are needed. In destruction of VOCs with ozone alone, selectivity may not seem to be important, as the desired reaction is the complete oxidation of the compounds. In many cases where catalysts are not used, partial oxidation products (Oyama, 2000) are formed which are not completely mineralized. For example, oxalic, glyoxalic and acetic acids in solution and acetaldehyde in the gas-phase cannot be completely oxidized by ozone alone. In such cases, the use of catalysts is essential to promote complete oxidation. Unfortunately, there has been limited research on the gas-phase catalytic ozonation of air pollutants and odor-causing compounds such as sulfides, mercaptans, and aldehydes (Kastner at al., 2002; Kastner et al., 2003) to support the case. Most research conducted on catalytic ozonation used activated carbon impregnated with metal oxides and transition metals or solid metal oxides themselves as catalysts which are expensive. There is a need for a cheap catalytic material which has high surface area, pore volume, metal and metal

oxide content and high carbon content which can catalyze the ozonation of a wide range of VOCs and odor-causing compounds.

Aldehydes are partially oxidized hydrocarbons which belong to the class of VOCs. They are odorous compounds which are emitted from livestock operations and rendering industries. Recent wet scrubber analysis (Kastner and Das, 2002) of VOCs and TRS using chlorine dioxide (ClO_2) as the oxidizing agent to achieve high destruction efficiencies, showed close to 100% removal of methanethiol (MT), but only 20 to 80% removal efficiency for aldehydes and 23 to 64% for total VOCs. Moreover chlorinated hydrocarbons were identified at the outlets of high-intensity wet scrubbers and chlorinated compounds were identified in the scrubbing solutions because of improper mixing of the reactants (ClO_3, H_2O_2, and H_2SO_4) in the ClO_2 generating systems. Chlorinated hydrocarbons have found to be persistent in the environment, propensity to bioaccumulate and biomagnify in the food chain.

Wood fly ash (WFA), a cheap waste material is produced in large volumes in the USA (75 million tons/yr). The physical and chemical properties (Table 4.2, 4.3) of the ash indicated catalytic potential given the high surface area (~ 45 m^2/g) and the presence of crystalline phases typically associated with catalytic activity (Kastner et al., 2003). Mullite ($3Al_2O_3$ •$2SiO_2$), magnetite (Fe_3O_4), and hematite (Fe_2O_3 possibly with small amounts of other metals such as V, Mn, Cu, Co substituting for Fe) were identified in WFA and have been reported to catalyze the oxidation (O_2 only) of TRS or other VOCs at temperatures significantly > 25˚C. Recent research has demonstrated that wood fly ash can catalytically oxidize H_2S, ethanethiol and methanethiol (Kastner at al 2002). Given its high surface areas, metal, carbon content and inexpensiveness WFA can be of significant use as a catalyst.

Magnetite and hematite have been shown to catalyze the formation of •OH free radicals from H_2O_2 and the subsequent oxidation of organic compounds by the hydroxyl free radical (Kwan and Voelker, 2003). Moreover, activated carbon supported with Fe_2O_3 and MnO_2-Fe_2O_3 was shown to catalytically decompose O_3, however a mechanism was not proposed (Heisig et al., 1997). Activated carbon in various forms has been utilized as adsorbent and/or catalyst in the catalytic oxidation of TRS and VOCs (Choi et al, Primavera et al). Finally, metal oxides (e.g., Fe_2O_3) in soil and on supported catalysts have been suggested to generate •OH or other surface radicals and subsequently oxidize adsorbed organic compounds. (Legube and Leitner, 1999; Oyama, 2000).

Given the expensive nature of activated carbon and other metal oxides, alternatively we theorize that WFA (or other inexpensive waste materials) given the high metal content, the surface area and the presence of carbon could act as an inexpensive catalytic oxidizer of reduced sulfur compounds ("odor") and volatile organic compound (VOC) removal when coupled with O_3. It is theorized that the ash or selective crystalline phases in the ash may act to catalyze the formation of free radicals (OH radicals) from ozone in the presence of water and subsequently catalyze the oxidation of a wide range of odor-causing compounds and VOCs or provide a catalytic site for direct oxidation via O_3. Moreover, OH radical is less selective and has higher rate constants for organic compounds when compared to O_3 (Table 4.4).

Commercially available Magnetite (Sigma-Aldrich, Table 4.5), a crystalline phase present in WFA would also be used as one of the catalysts in the catalytic ozonation as a benchmark. Reaction rates obtained from WFA and magnetite would be compared to find out if the crystalline phases present in WFA catalyze the formation of free radicals from ozone and in

turn result in higher reaction rates. Propanal, a 3-carbon aldehyde would be used as the model compound in the catalytic ozonation research with all the three catalysts (WFA, and magnetite).

The basic objective of the research is to determine the kinetics of catalytic ozonation and to develop a rate law to predict the kinetics and for reactor design. The specific objectives of this study are:

- Develop a rate law for WFA and magnetite using the reaction rate data obtained from four different ozone concentrations (75, 95, 145, and 175 ppmv) and three propanal concentrations (5, 10, 15 ppmv).
- Separate crystalline phases from WFA and use them as catalyst for ozonation of propanal.
- Compare the reaction rate data obtained from separated crystalline phases with that of WFA, synthetic magnetite, and activated carbon.

After developing a rate-law for the WFA and magnetite, the possibilities of scaling-up the catalytic ozonation process will be discussed, as well as the different catalytic and reactor designs for an industrial setting.

MATERIALS AND METHODS

Catalysts

Wood ash from a pulp mill was used in this study. The physical and chemical characteristics of the fly ash, including pH, surface area, bulk density, and the elemental composition were previously determined (Table 4.2 and 4.3) (Kastner and Das, 2002). Activated carbon and magnetite, two commercially available catalysts were obtained from Sigma-Aldrich, Table 4.5) and used as benchmarks in this research.

Separation of Crystalline Phases from WFA

Magnetic crystalline phases (magnetite, mullite and hematite) were separated manually from WFA by using laboratory magnetic bars. The magnetic bars were passed over a known amount of catalyst and the material attracted to the magnetic bar was knocked off till only the crystalline phases remained attached to the bars. The process was repeated until most of the crystalline phase material in the given amount of catalyst was separated. The percentage separation achieved using this process was 8.85% (by mass). Although not an efficient method, the separation technique was used in order to determine the effect of the crystalline phases in WFA on its catalytic activity.

Surface Area Analysis

The Brunauer-Emmett-Teller (BET) method using N_2 and a Nova 2000 Quantachrome was used to determine the surface area of the separated crystalline phases from WFA as well as the pure magnetite catalysts. An average value of the duplicates from a 6-point BET method was used to determine the final surface area and pore volume.

Continuous Flow Studies for the Catalytic Ozonation of Propanal

The catalytic ozonation of propanal was studied in a continuous flow packed bed reactor system (Figure 4.1) at ambient temperature (23-25°C) and atmospheric pressure. Compressed air or N_2 was first passed through a bubble column (5.0 cm i.d., 30 cm length, Pyrex) to humidify the air or N_2 (100% humidity) and then mixed with propanal (97% purity, Sigma-Aldrich) metering in by a syringe pump (Cole-Parmer 74900-30). Propanal (4-15 ppmv) was injected using a Becton Dickinson syringe (plastipak 10 cc, 14.48 mm i.d.) via a tee (stainless steel,

Swage-Lok) into the main airflow from the bubble column. The air-propanal mixture was then passed through a static mixer (2.5 cm i.d. and 30 cm length, 50 mm diameter glass beads, Pyrex) and then transported down through the packed-bed reactive column (2.5 cm i.d., 30 cm length, Pyrex). An ozone generator (OL100H/DS, Yanco Industries Ltd., B.C., Canada), utilizing a high frequency corona discharge, was used with a medium grade tank of oxygen (99.9%, National Welders, NC) to generate the ozone required for the experiments. Ozone was added via a tee into the air-propanal stream after the static bed mixer, approximately 5 cm from the packed bed reactor inlet. Mass flow controllers (UNIT UFC-8100) were used to control the flow rates of air/N_2 and ozone. The catalysts used in the process were distributed on glass wool and packed over a specified height in the reactor. Tees (stainless steel, Swage-Lok) with septum were installed at the inlet and outlet of the packed-bed reactor column for sampling. All tubing used was 6.35 mm (i.d.) Teflon with fittings constructed of stainless steel (Swage-Lok). Threaded Teflon plug with an O-ring was used at the end of each column for an airtight fit.

The catalytic ozonation of propanal was performed at different residence times (τ = 1-5 s) to see if external mass transfer limited the reaction process. The residence time of the gas mixture in the packed-bed reactor was calculated using the following equation:

$$\tau = \mathrm{Re}\,sidenceTime = \left(\frac{packingvolume}{Q}\right) = \left(\frac{H.A}{Q}\right)$$

where, Q is the gas flow rate (2.5-3 L/min), H is the height of packing (5-7 cm) and A is the surface area of the packed bed.

MEASUREMENT OF ACTIVITY

Analytical Methods

In the continuous flow experiments, bench top GC/MS units (Hapsite Inficon, East Syracuse, NY)) was used to measure the inlet and outlet concentrations of the propanal from the packed bed reactor. Gas samples were sampled directly from tees at the inlet and the outlet of the column for a defined flow rate of the propanal- compressed air mixture. The gas samples were analyzed under isothermal conditions (70° C).

The mass spectrometer used consisted of an ionizer (70 eV), a mass selector (1- 300 AMU), and an ion detector (scan rate 1000 AMU/sec @ 10 points per AMU). Two internal standards, 1, 3, 5-tris (trifluoromethyl) benzene (100 ppmv) and bromopentafluorobenzene (50 ppmv) were used to tune the Hapsite GC/MS and were injected with each gas sample. The Hapsite GC/MS was tuned before each analysis or every twelve hours. Selective ion monitoring (SIM) was used to improve the sensitivity of the propanal used in the experimental analysis. In the SIM mode mass/charge ratios of the corresponding propanal (for e.g. 58 in the case of propanal) and the internal standard (m/z 69) were selectively scanned.

Ozone Analysis

The concentration of ozone in the inlet and outlet of the decomposition and catalytic ozonation experiments was measured using an IN-USA 2000 ozone analyzer, using UV absorption model (Model IN-2000-L2-LC, 0.01 ppmv resolutions in the 0-100 ppmv range). The ozone concentrations ranged from 75-175 ppmv in the catalytic ozonation experiments of propanal. The ozone analyzer was also used to calibrate the ozone generator and confirm the generators capability of producing a defined ozone concentration. Ozone concentrations above

100 ppmv were calculated based on the manufacturer's calibration data and dilution of the O_3 gas with main airflow. The UV lamp present in the ozone analyzer was calibrated before the start of each experiment or once in 12 hours incase of continuous studies.

Methods of Modeling

The kinetics of catalytic oxidation was studied based on the following premises:

(i) In order that the experimental data could be used in the kinetic analysis, potential external and internal mass transfer resistance had to be ruled out.

(ii) Due to the inability to obtain to VOC concentrations along the length of the reactor column, a differential reactor with a small amount of catalyst was used and hence a low conversion of reactant was obtained.

(iii) To reduce the relative error caused by using an approximate rate equation for calculating the reaction rate, average concentrations of inlet and outlet reactants should be adopted.

(iv) To reduce relative error caused by using an approximate rate equation for calculating reaction rate of a differential reactor, average concentrations of inlet and outlet reactants should be adopted.

(v) The heat of reaction in the packed-bed reactor did not increase the temperature and thus the temperature across the reactor was assumed to be constant (isothermal) and equal to the room temperature (23-25°C).

(vi) The plug flow model was assumed regarding the flow of the gases in the reactor.

With the above constraints, the method of modeling catalytic ozonation of propanal over WFA, AC and magnetite catalysts is depicted as follows:

A mole balance for propanal over the catalyst bed in a packed-bed reactor gives the following equation:

$$F_{RI}\,dX = (-r)dW \tag{1}$$

where F_{RI} is the molar feed rate of propanal in mole/s, X the fractional conversion of propanal, (-r), the reaction rate of catalytic ozonation of propanal in mole $g^{-1}s^{-1}$ and W the mass of catalyst in grams. X is defined as follows:

$$X = \left(\frac{F_{RI} - F_R}{F_{RI}}\right) = \left(\frac{C_{RI} - C_{RO}}{C_{RI}}\right) \tag{2}$$

where F_R is the molar rate of propanal in mole s^{-1} in the outlet, C_{RI} and C_{RO} are inlet and outlet propanal concentrations in mol cm^{-3}. The percentage conversion is obtained by multiplying X by 100. Equation 1 can be rearranged as

$$-r = F_{RI}\left(\frac{dX}{dW}\right) = C_{RI}\upsilon\left(\frac{dX}{dW}\right) \tag{3}$$

where C_{RI} is the inlet concentration of propanal in mol cm^{-3} and v the volumetric flow rate of gas in cm^3/s. Theoretically, the reaction rate of propanal can be calculated from the above equation provided $\left(\frac{dX}{dW}\right)$ is known. However, it is well known that the concentration, and thus the value of $\left(\frac{dX}{dW}\right)$, along the axial position of the packed-bed reactor, is hard to measure. To overcome this difficulty, a differential reactor is commonly used.

When a differential reactor is employed, the approximate rate of catalytic incineration of propanal can be estimated by:

$$-r = F_{RI}\left(\frac{X}{W}\right) = C_{RI}\upsilon\left(\frac{X}{W}\right) \tag{4}$$

where W is the mass of catalyst used in the differential reactor and X the fractional conversion of propanal at the outlet of reactor. As mentioned before, for the best fit of the kinetic models, when (-*r*) is to be correlated to the concentrations of species involved in the reaction, the average concentration of outlet (C_{RO}) and inlet (C_R, defined as ½ [C_{RI} + C_{RO}]) should be adopted.

RESULTS AND DISCUSSION

Assessment of Best Fit for the Experimental Data

The reaction equation for the oxidation of propanal using ozone and a catalyst is as follows:

$$\text{Propanal} + O_3 \xrightarrow{\text{Catalyst}} \text{Products} \qquad (5)$$

The reaction rate of Eq. (5) may depend upon concentrations of propanal, ozone and also the catalyst used. But since the concentration of ozone (75-175 ppmv) is much higher than the required amount for complete oxidation of propanal (5-15 ppmv), we ignore the influence of O_3 concentration on the reaction rate. A regression model analysis (Appendix D) to verify the effect of the combined and individual effect of propanal and O_3 concentration on the reaction rate was performed. The parameter estimate of ozone obtained was close to zero (0.007) and also the R^2 value using the R^2 selection method was very low (0.153) for ozone. The low R^2 value and the parameter estimate for ozone indicated that it did not have a significant effect on the rate of reaction. Hence the reaction rate was assumed to be a function of propanal concentration. The power law model was applied to best fit the experimental data obtained from the catalytic ozonation of propanal using WFA and synthetic magnetite. Although mechanistic models like Langmuir-Hinshelwood help in determining catalytic and heterogeneous mechanisms, the basic problems associated with such models are that one has to choose between such mechanisms as

molecular or atomic adsorption, and single- or dual-site reaction determining the rate law. In order to choose between one of these mechanisms, we need to have information regarding the intermediates and/or by-products formed. Since sufficient information was not available to choose between the mechanisms, a simple empirical model like power-rate law was used. Moreover, it is good practice to use the simplest model that can best fit the data compared to more complicated models as the magnitude of experimental errors will mask the differences predicted by the various mechanisms (Levenspiel, 1999).

Power Law Model

The power-rate law model was applied to best fit the experimental data obtained from the catalytic ozonation of propanal using WFA and magnetite. By using this law we can express the reaction rate of propanal as follows:

$$-r = kC_{O_3}{}^{m} C_R{}^{n} \approx k' C_R{}^{n} \qquad (6)$$

where k is the intrinsic rate constant, k' the approximate rate constant equals to kC_{O_3} while C_{O_3} and C_R are the concentrations of ozone and propanal (both in moles cm^{-3}), and, m and n are the orders of the reaction with respect to ozone and propanal respectively.

From the results of linear fitting experimental data with Eq. (6) i.e. plotting Ln ($-r$) vs. Ln (C_R) via the regression method, the reaction order n and the rate constant k were calculated at various ozone concentrations from the slope and intercept. Results of plotting Ln ($-r$) vs. Ln (C_R) for WFA and magnetite are shown in Figure 4.2. The regression analysis using Ln ($-r$) as the single dependent variable results in an R^2 value of 0.823 and 0.901 for WFA and magnetite respectively. The rate constants and the order were calculated from the parameter estimates for

the intercept and Ln (C_R). The rate law thus calculated for WFA and magnetite respectively are as follows:

$$-r_w = k_w' (C_R)^{0.879} \quad (7)$$

$$-r_m = k'_m (C_R)^{1.479} \quad (8)$$

where k_w', and k'_m are pseudo first order rate constants with values 2.48E-10 g^{-1} s^{-1} (moles ozone)$^{-1}$ and 7E-11 g^{-1} s^{-1} (moles ozone)$^{-1}$ respectively, and C_R is the inlet propanal concentration in moles/cm^3. The linearity of the plots (high R^2 values) suggests that the power-rate law model is an appropriate model for simulating the catalytic oxidation of propanal using WFA and magnetite over the range of ozone concentration (75-175 ppmv) and propanal (5-15 ppmv) tested.

From the rate laws obtained for WFA and magnetite we can observe that the order of the reaction with respect to propanal is higher for magnetite when compared to WFA (1.479 versus 0.879). Figure 4.3 shows that for given ozone concentration, higher concentrations of propanal result in a higher reaction rate and the increase in the rate is highly linear. In the case of WFA (Figure 4.3), although the reaction rate increases with increase in propanal concentrations for a given ozone concentration, it appears that for higher ozone concentrations, the increase in rate with propanal is not linear and for very high propanal concentrations, the reaction rate may not vary much (because the reaction order is less than 1). This implies that with the given packed-bed reactor system, WFA is best at lower propanal concentrations. Fortunately, the typical aldehyde concentration from industrial emissions is also low (5-20 ppmv) and hence WFA would be a suitable catalyst for the removal of aldehydes.

Effect of Crystalline phases in WFA on the Catalytic Ozonation of Propanal

The catalytic activity of WFA has been attributed to its physical and chemical properties namely high surface area, carbon content and presence of crystalline phases. Also previous research on catalytic ozonation in liquid phase demonstrated that ozone decomposed in the presence of magnetite and hematite and that activated carbon impregnated with metals and metal oxides (Legube and Leitner, 1999; Oyama, 2000) enhanced the catalytic ozonation of VOCs. In order to verify if the crystalline phases (magnetite, mullite and hematite) present in WFA significantly contributed to the catalytic activity of WFA, a continuous catalytic ozonation experiment was conducted using crystalline phases separated from WFA as the catalyst (O_3 95 ppmv, propanal 10 ppmv, room temperature, 23-25°C). Figure 4.4 shows the comparison of the reaction rates obtained for crystalline phases, WFA, and magnetite under the same conditions. It can be clearly observed that the crystalline phases separated from WFA had higher reaction rates when compared to WFA, and the reactions rates are almost similar to that of magnetite. The general linear regression procedure using the Tukey's studentized range test for reaction rate indicates that the crystalline phases have a greater catalytic activity than WFA. The test also indicates that no significance difference between reaction rates of separated crystalline phases and synthetic magnetite can be inferred.

On analyzing the separated crystalline phases for the surface area and pore volume using the BET method (Nova-2000, Quantachrome), it was observed that their surface area (~ 3.7 m^2/g) was similar to that of magnetite (~ 2 m^2/g). Also visual inspection of the optical microscopic images (figure 4.5) of crystalline phases and synthetic magnetite indicated similar topography. The similar reaction rates obtained using magnetite and crystalline phases along with the surface area analysis and the microscopic images suggest that the catalytic activity of

WFA is due to the crystalline phases present in the ash. More quantitative analysis using XRD diffraction technique should be performed in the future to determine the composition of the separated crystalline phases to verify this theory.

Problems in Finding the Mechanisms

In heterogeneous reactions where more than one phase is present, apart from the stated chemical reaction taking place, the movement of material from one phase to the other must be considered in the rate equation. Thus, the rate expression in general will incorporate mass transfer terms in addition to the usual chemical kinetics term. These mass transfer terms are different in type and magnitude in different kinds of heterogeneous systems. Hence no single rate expression has general application. Moreover in the current study of the ozonation of propanal, the complete reaction is not known because of the inability to detect any byproducts and our inability to measure intermediates formed at the surface of the catalysts due to the ozonation of propanal. This process of finding an appropriate mechanism is complex. Even if a mechanism is proposed, to prove that we have such a mechanism, we must show that the family of curves representing the rate equation of the favored mechanism fits the data so much better than the other families that all others can be rejected. With the large number of parameters (three to seven) that can be chosen arbitrarily for each rate-controlling mechanism, a very extensive experimental program is required, using very precise and reproducible data, which in itself quite a problem. We should bear in mind that it is not good enough to just select the mechanism that best fits the data. Any difference in fit may be explained entirely in terms of experimental error and in statistical terms these differences may not be “significant”. Unfortunately, if a number of alternative mechanisms fit the data equally well, we must recognize that the equation selected

can only be considered to be one of good fit and not the only one that represents reality. With this in mind, there is no reason why a power-rate law model would not be sufficient to explain the mechanism involved in the catalytic ozonation of propanal. Moreover, it is simple and verified easily. Hence, the scope of this research was limited to the power law model although heterogeneous reactions models like Langmuir-Hinshelwood and Mars Van-Krevelen have been used previously.

Scale-up of Catalytic Ozonation Process for Industrial Setting

The lab scale catalytic ozonation of propanal was performed in a packed reactor (2.5 cm i.d. and 30 cm length) with flow rates ranging from 3-4 LPM. The typical flow rates of the exhaust gases (containing aldehydes and other VOCs) that are treated in the rendering industry are on the order of 30,000-40,000 ft^3/min (CFM) or higher. The experimental set up and results obtained in the lab scale catalytic ozonation may not be appropriate for scale up for industrial purposes. Some of the important considerations that need to be made when scale up of a lab scale process.

- Pressure drop across the reactor
- Distributing large amounts of catalyst in the reactor (Catalyst design)
- Reactor design
- Mass and heat transfer considerations.

Because of the small particle sizes associated with the catalysts used (WFA, <600 μm; magnetite, < 5 μm), the problems related to pressure drop would be the most significant and this would in turn increase the energy requirement of the reactor system. Therefore alternative reactor

and catalyst designs are necessary for processing of heterogeneously catalyzed gas-liquid reactions.

Reactor Design

Given the rate-law and the kinetics for catalytic ozonation of propanal using WFA and magnetite, we need design equation which would help us determine the size of the reactor and mass of the catalyst required in order to initially size the reactor. The design equations for determining the catalyst mass based on a given gas flow rate, VOC concentration and fractional conversion can be obtained by assuming a differential packed-bed reactor. A mole balance (equation 9) performed on the VOC (A) over a catalyst mass ΔW can be used to determine the mass of catalyst required (equation 13)

$$F_A(W) - F_A(W + \Delta W) + r_A(\Delta W) = 0 \tag{9}$$

$$-\left(\frac{dF_A}{dW}\right) = -r_A \tag{10}$$

$$F_{AO}\left(\frac{dX}{dW}\right) = -r_A \tag{11}$$

$$W = F_{AO}\int_0^X \frac{dX}{-r_A} \tag{12}$$

$$W = C_{AO}\upsilon\int_0^X \frac{dX}{-r_A} \tag{13}$$

By using the rate law for WFA (equation 7) and the design equation for determining the mass of catalyst (equation 13), the mass of WFA for hypothetical values of X=0.95, C_{AO}=15 ppmv and ν=30,000 CFM was calculated to be approximately 600 kg. Given the typical flow

rates of 30,000-50,000 CFM in rendering industries, approximately 600-1000 kg of WFA is required to achieve a 95% removal of aldehyde (s).

In order to calculate the approximate height of the reactor required to distribute the WFA, we can use the bulk density data (mass of catalyst used/volume of packing) from the experiments conducted. For a bulk density of 0.15 g/cm^3 (2.5g of WFA in 35 cm^3 reactor volume, packed density used in experiments) and a reactor size of 7 ft i.d and 12 ft height (typical sizes of wet scrubbers), the height of reactor required to distribute 600 kg of WFA is approximately 1.07 ft. Although the height determined is only an approximation, it could be help in obtaining a rough estimate of the size of the reactor required for the scale-up. Apart from using the packed-bed reactor system, other reactor designs could potentially be used for scaling up the catalytic ozonation process.

Slurry Reactors

In a slurry reactor, small catalyst particles (1-200 μm) are suspended in the liquid by either a mechanical stirrer or by the gas flow. Slurry reactors can be operated batch-wise, as well as (semi-) continuous. When the catalyst particles are sufficiently large to form a distinct third phase, a continuously operated slurry reactor is also called a three-phase fluidized bed. In some cases, the gas-liquid mixture is injected as a jet at high velocity to promote mixing and total utilization of the pure gas reactant. To assure a strong internal liquid circulation, a draft tube may be installed inside the reactor.

The catalyst load in slurry reactors is limited by the agitation power of the mechanical stirrer or by the gas flow. However, the small dimensions of the catalyst particles provide catalyst utilization factors that approach unity. Due to substantial mixing, high conversions can be realized by the staging of several reactors only. Temperature control is relatively simple due

to the large amount of liquid present and the possibility to install coolers inside the reactor. One of the most difficult aspects of these reactors is the catalyst filtration step. However, in case of rapid catalyst deactivation, continuous catalyst removal and regeneration is crucial and slurry reactors are likely to be applied.

The slurry reactor is widely implemented in the fine chemical and pharmaceutical industry for selective catalytic hydrogenations. Since in these industries, multipurpose manufacturing is an important issue, the operation is most often batch or semi-continuous. Bubbling slurry reactors are particularly employed in fermentation processes (Biardi and Baldi, 1999). Three-phase fluidized beds have been applied industrially in coal liquefaction.

Trickle Bed Reactor

Trickle-bed reactors are the most widely used type of three-phase reactors. The gas and liquid flow co-currently/counter-currently over a fixed bed of catalyst particles. Approximate dimensions of trickle-bed reactors are 10 m in height and 2 m in diameter. Trickle-bed reactors are employed in the petroleum, petrochemical and chemical industries, in waste water treatment and biochemical and electrochemical processing (Al-Dahhan et. al., 1997).

In contrast to a usual slurry operation, the trickle-bed reactor has advantages, a catalyst separation is not required, a high catalyst-liquid ratio can be used, and a high gas-liquid interfacial area can be obtained. Due to the low oxygen solubility in the liquid reaction mixture, a high gas-liquid-solid interfacial area is more important than the catalyst activity. On the other hand, hydrodynamic impact (wetting efficiency) can have a controlling role at low liquid velocities typical of the wastewater treatment processes. The three-phase trickle-bed reactor performance was confirmed by many authors (El-Hisnawi et al.,1982; TukaË and Hanika, 1999). Based on reaction conditions used, namely temperature, the reaction between dissolved

gaseous and liquid reactants can be limited by their mass transport. However, if the reaction is a gas-limited one, the gaseous reactant can easily access catalyst pores in the non-wetted dry areas in the bed and, consequently, a higher reaction rate is usually observed with a decreased external catalyst wetting. The above analysis is based on an assumption that particles in trickle beds are always internally wetted.

An alternative for scale-up studies is the use of trickle beds diluted with fines (inert particles, by an order of magnitude smaller than the catalyst pellets). The Absence of liquid spreading due to the application low liquid velocities in laboratory reactors is compensated by fines which provide additional contact points for solids over which liquid films flow. This improves liquid spreading and helps to achieve the same liquid-solid contacting in laboratory reactors as obtained industrial units at higher superficial liquid velocities. Fines decouple the hydrodynamics and kinetics and provide an estimate of the true catalyst performance in industrial reactor by improving wetting and catalyst utilization in a laboratory-scale unit at space velocities identical to those in industrial reactors.

Honeycomb Reactor

Honeycomb reactors are a slight modification of the catalyst monolith reactors which are used as catalyst afterburners in automobiles. In the honeycomb reactors, process feed streams flows through square channels (Figure 4.7), and the reaction takes place on the surface of the plates. Depending on the desired conversions and the flow rates of the process feed, using the design equation (equation 13) of the packed-bed reactor the required amount of catalyst can be calculated and the inner surface of the square channels can be coated with the catalyst.

Catalyst Designs

With pressure drop being a major concern in the reactor design, the shape and size of the catalyst used plays an important role in the scale-up of the catalytic process. The current powdered form of WFA which was distributed on glass wool in the laboratory experiments might not be suitable in the industrial scenario due to pressure drop in the reactor. Therefore alternative ways of distributing the catalyst are necessary.

One way of distributing the catalyst could be by generating catalyst pellets with WFA or crystalline phases separated from WFA, and packing the reactor column. The catalysts generated should have a large void volume such that its shape and size would allow for uniform mechanical packing and little flow restriction. Figure 4.6 shows activated carbon pellets made from peanut hulls used in bio-oil generation via pyrolysis. Another way of distributing the catalyst could be by coating the surface of the pellets with WFA or crystalline phases thereby offering minimal restriction to the flow of the gases.

CONCLUSIONS

Under the reaction conditions of this study, using a differential reactor and WFA catalyst, the fitness of the power law model, was assessed. The high R^2 values associated with the rate laws for WFA and magnetite indicates that the power law appropriately describes the kinetics of propanal catalytic ozonation. Other significant conclusions that could be drawn were:

- WFA has catalytic activity similar to other commercial catalyst used in VOC removal, since the reaction rates measured were of the same magnitude as that cited in literature.

- WFA is best used at lower propanal concentrations (5-10 ppmv) because the reaction order is less than one. For magnetite, an increase in propanal concentration results in higher reaction rates.
- The reaction rates were calculated based on a differential reactor design and then used to develop a rate-law, so higher conversions and reaction rates could be realized.
- Crystalline phases present in WFA played a significant role in the catalytic activity of propanal as hypothesized. Higher reaction rates where obtained by using crystalline phases separated from WFA when compared to WFA itself, and activated carbon.
- The reaction rates obtained with the separated crystalline phases were similar to that of synthetic magnetite and their surface areas were also similar.

BENEFITS

In this study, the possibility of reusing wood fly ash as an inexpensive catalyst in the catalytic ozonation of propanal has been successfully demonstrated. This research will facilitate the successful control of aldehyde emission from rendering plants using a cost-effective process. Also this process can be further applied for the emission control of various other VOCs and TRS. This process also has many benefits when compared to the currently used technologies.

1. Both volatile sulfur (Kastner and Das, 2002) and organic compounds (i.e. aldehydes) can be oxidized.
2. Only water vapor is needed for the catalytic ozonation process, thus significantly reducing the need for water usage compared to wet scrubbers.

3. A waste material may potentially be used as the catalyst, thus reducing costs.
4. Easy separation of crystalline phases from WFA suggests that separated crystalline phases could be used to significantly increase its catalytic activity.
5. Also separated crystalline phases could be used to coat other catalytic materials like activated carbon pellets or they themselves could be pelletized thus generating new catalysts.
6. Residence times for the reaction could be very short (<5 s), thus requiring small reactors, similar in size (or smaller) than the currently used scrubbers (if ozone is converted to $OH^{\bullet}$, catalytic ozonation of VOCs are much faster than ozonation alone).
7. Ozone systems currently in place at many rendering plants (where aldehydes are emitted) could be utilized for the process.

FUTURE WORK

Although it has been identified that crystalline phases in the WFA play a significant role in the catalytic ozonation of propanal, the mechanism involved is not clear. Future work should be focused on identifying potential mechanisms and also the by-products and intermediates formed in the course of the reaction. An XRD analysis of the separated crystalline phases should be performed in order to identify the major components.

A mass balance on the total material involved in the ozonation process should be performed in order to understand the stoichiometry of the reactions place in the reactor system. Since the experiments were performed at room temperature (23-25°C) and the typical temperatures in industries might vary between 30-40°C, the effect of temperature on the catalytic ozonation process should be determined.

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Table 4.1. Summary of heterogeneous reactions of ozone

Substrates	Catalysts	Reaction Conditions	Products	Rate (mol/ m^2.
Ethanol Propanol Isopropanol	γ-Al_2O_3 SiO_2	293-363 K	Ketones, Aldehydes, CO_2	1.7×10^{-9}
Ethanol	MoO_3/Al_2O_3	300-550 K	Acetaldehyde,	0.9×10^{-9}
	MnO_2/Al_2O_3		CO_2	1.9×10^{-9}
Benzene	MnO_2	383-353 K	CO, CO_2	1.5×10^{-9}
	γ-Al_2O_3/Fe-oxide			1.7×10^{-7}
	γ-Al_2O_3/Cu-oxide			3.7×10^{-7}
Benzene	γ-Al_2O_3/Ni-oxide	296 K	CO, CO_2	3.8×10^{-7}
	γ-Al_2O_3/Mn-oxide			1.3×10^{-7}
Dichloromethane Tetrachloroethylene *p*-chlorotoluene	Pt/ Al_2O_3 Pd/ Al_2O_3 $BaCuCrO_x$	323-473 K	Mostly CO_2	___
Cyclohexane	γ-Al_2O_3/Mn-oxide	296 K	CO,CO_2	1.2×10^{-6}

Table 4.2. Physical and chemical properties of WFA

Properties	WFA (Mean $\pm$ SD)
Surface Area, m^2/g	44.89 ± 8.34
pH	12.13 ± 0.17
Bulk Density, g/cm^3	0.54
Carbon, % (dry basis)	18.75 ± 1.87
Selected Elements (ppm)	Range
Co	4.5 – 5.2
Cu	32.0 – 39.0
Mn	500.0 – 584
Mo	2.2 – 2.7
Ni	18 – 19
Fe	6,600 – 8,300

Table 4.3. Particle size distribution of WFA.

Particle Size range (μ)	% of particles (by mass) in the range
> 600	5.69
600-425	2.40
425-150	9.99
150-75	12.89
< 75	69.73

The percentages of particles in the ranges measured add up to 100.7 owing to small calculation errors

Table 4.4. Ozonation rate constants and OH rate constants for some organic compounds in liquid phase.

Solute	k_{O3} ($M^{-1} s^{-1}$)	$k_{OH^{\cdot}}$ ($M^{-1} s^{-1}$)*10^{-9}[a]
Benzene	2 ± 0.4	7.8
Nitrobenzene	0.009 ± 0.02	3.9
Toluene	14 ± 3	3.0
m-xylene	94 ± 20	7.5
Formic acid	5 ± 5	1.3
Formate ion	100 ± 20	3.2
Acetic acid	(<3 x 10^{-5})	1.6
Salicylic acid	<500	2.2

[a] $k_{OH^{\cdot}}$ read as cell value times 10^9. e.g. 7.8x10^9

Table 4.5. Physical properties of magnetite and activated carbon

Properties	Magnetite	Activated Carbon
Surface Area, m^2/g	1.7905 ± 0.464	424.95 ± 52.33
Pore Volume, mL/g	5.0792 ± 0.7472	0.429 0.7472 0.0273

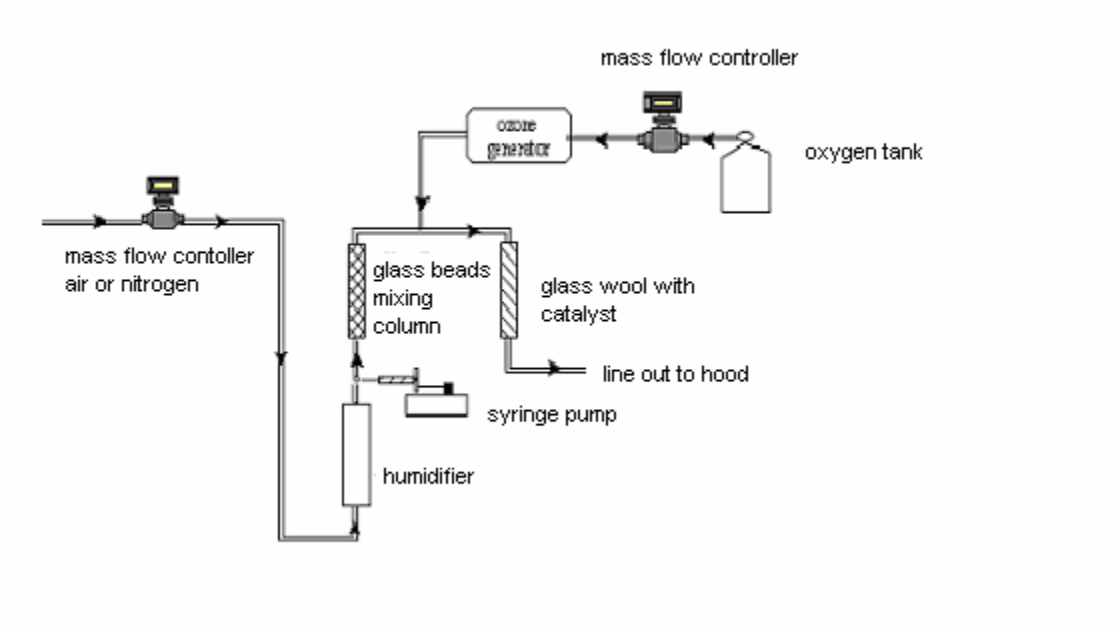

Figure 4.1: Experimental set up for the catalytic ozonation of aldehydes in a packed bed reactor column

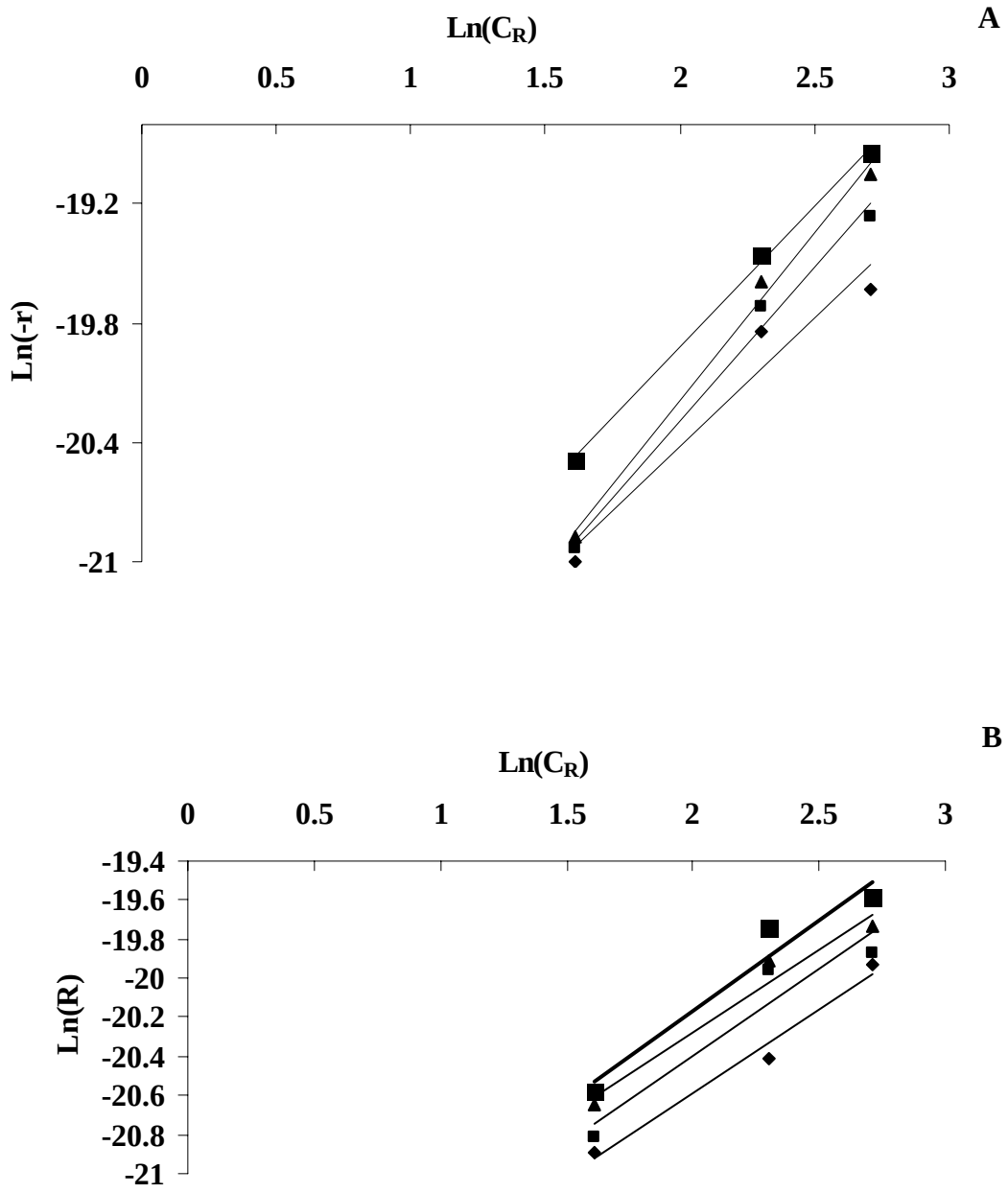

Figure 4.2. Ln (-*r*) versus Ln (C_R) for four different ozone concentrations (■ 175 ppmv, ▲ 145 ppmv, ■ 95 ppmv ♦75 ppmv) using magnetite (A) and wood fly ash (B).

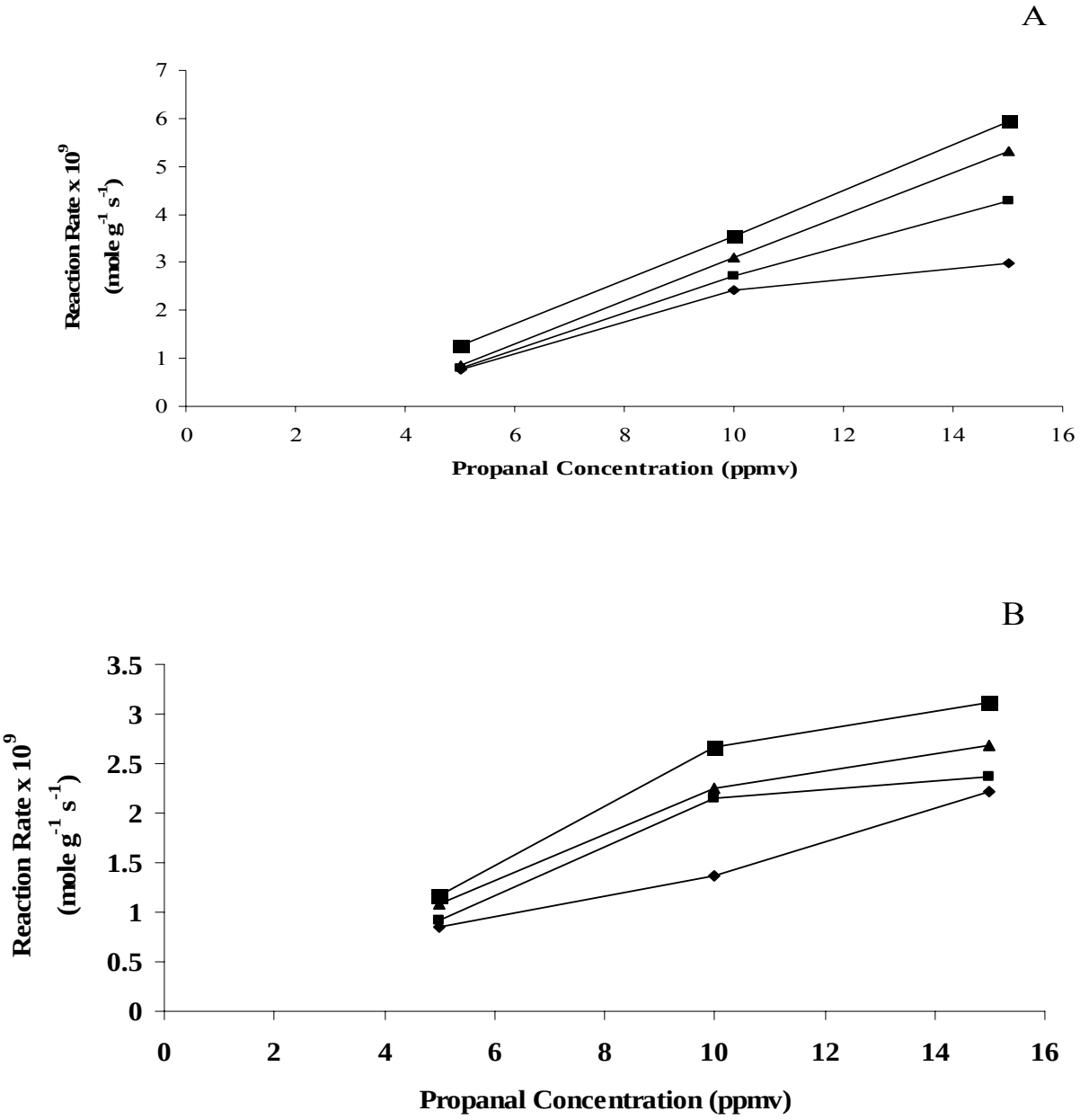

Figure 4.3. Effect of propanal concentration on the reaction rate of propanal for four different ozone concentrations (■ 175 ppmv, ▲ 145 ppmv, ■ 95 ppmv ♦ 75 ppmv) using A) magnetite and B) wood fly ash.

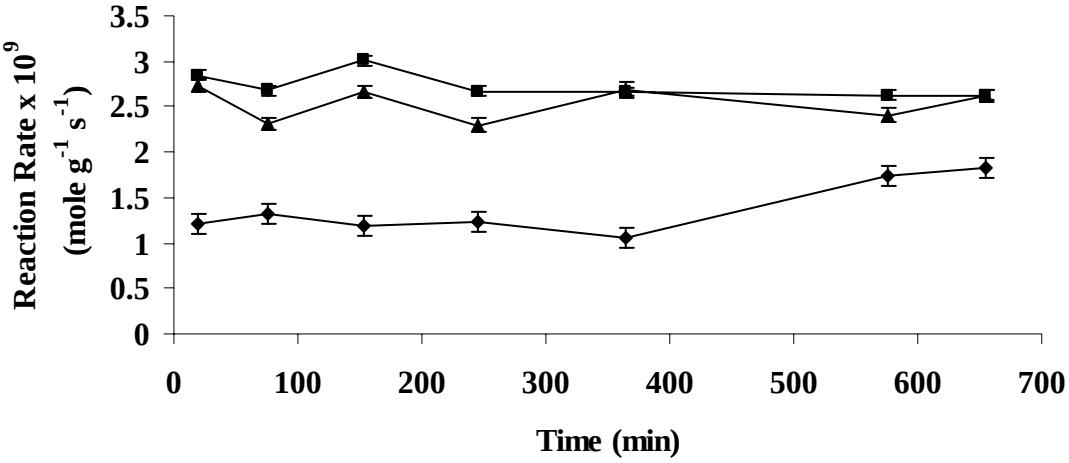

Figure 4.4. Comparison of reaction rates for the catalytic ozonation of propanal (10 ppmv) and ozone (95 ppmv) at 23-25°C using ■ magnetite, ▲ crystalline phases separated from WFA and ♦ WFA.

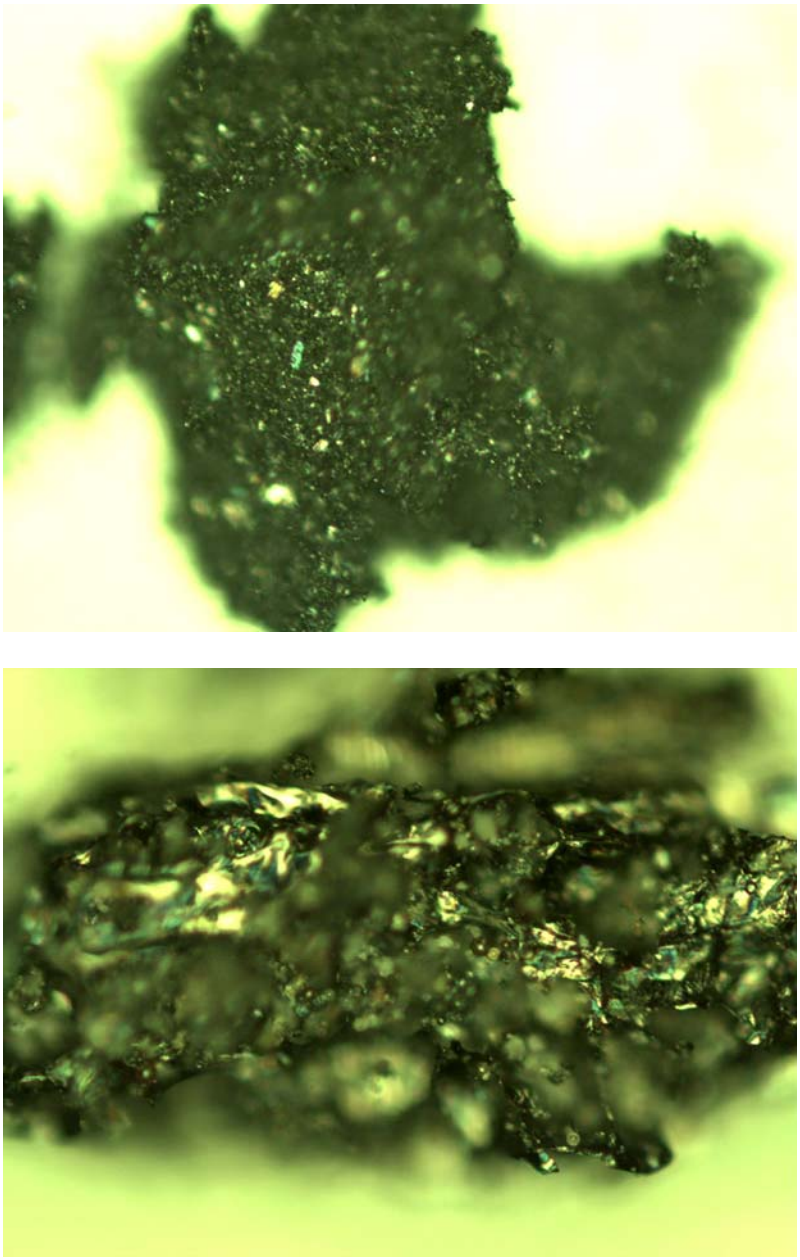

Figure 4.5. Optical Microscope photo image (20x) of magnetite (top) and crystalline phases separated from WFA (bottom).

Figure 4.6. Activated carbon pellets generated from peanut hulls used in bio-oil generation via pyrloysis.

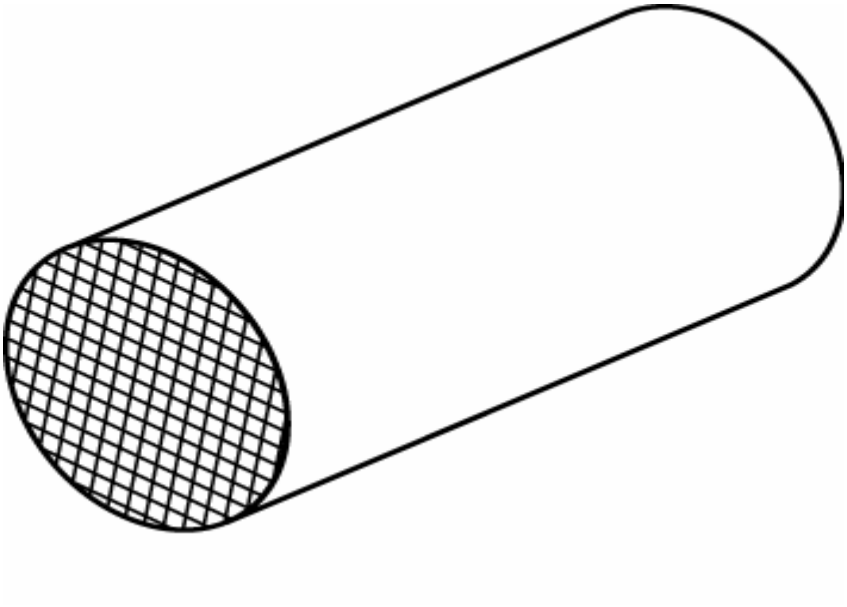

Figure 4.7. Structural design of a honeycomb reactor. (Photo courtesy H. Scott Fogler, Elements of Chemical Reaction Engineering.

CHAPTER 5

CONCLUSIONS, BENEFITS AND FUTURE WORK

CONCLUSIONS

Under the reaction conditions of this study, using a differential reactor and three catalysts: wood fly ash (WFA), synthetic magnetite, and activated carbon (AC), the following conclusions can be drawn:

- WFA has catalytic activity at par with other commercial catalyst used in VOC removal as the reaction rates obtained are of the same order as that cited in literature.
- WFA is best used at lower propanal concentrations (5-10 ppmv) because the reaction order is less than one.
- For magnetite, an increase in propanal results in higher reaction rates.
- The reaction rates were calculated based on a differential reactor design and then used to develop a rate-law, so higher conversions and reaction rates could be realized.
- Crystalline phases present in WFA played a significant role in the catalytic activity of propanal as hypothesized. Higher reaction rates where obtained by using crystalline phases separated from WFA when compared to WFA itself.
- The reaction rates obtained with the crystalline phases were similar to that of magnetite and also their surface areas were also similar.

BENEFITS

In this study, the possibility of reusing wood fly ash as an inexpensive catalyst in the catalytic ozonation of propanal has been successfully explored. This research will facilitate the successful control of aldehyde emission from rendering plants using a cost-effective process.

Also this process can be further applied for the emission control of various other VOCs and TRS. This process also has many benefits when compared to the currently used technologies.

1. Both volatile sulfur (Kastner and Das, 2002) and organic compounds (i.e. aldehydes) can be oxidized.
2. Only water vapor is needed for the catalytic ozonation process thus significantly reducing the need for water usage compared to wet scrubbers.
3. A waste material (WFA, activated carbon from peanut hulls) may potentially be used as the catalyst, thus reducing costs.
4. Easy separation of crystalline phases from WFA suggests that separated crystalline phases could be used to further enrich WFA and hence increasing its catalytic activity.
5. Also separated crystalline phases could be used to coat other catalytic materials like activated carbon pellets or they themselves could be palletized thus generating new catalysts.
6. Residence times for the reaction could be very short (<5 s), thus requiring small reactors, similar in size to the currently used scrubbers (if ozone is converted to $OH^{\bullet}$, catalytic ozonation of VOCs are much faster than ozonation alone).
7. Ozone systems currently in place at many rendering plants (where aldehydes are emitted) could be utilized for the process.

FUTURE WORK

Although it has been identified that crystalline phases in the WFA play a significant role in the catalytic ozonation of propanal, the mechanism involved is not clear. Future work should be focused on identifying potential mechanisms and also the by-products and intermediates

formed in the course of the reaction. An XRD analysis of the separated crystalline phases should be performed in order to identify the major components.

A mass balance on the total material involved in the ozonation process should be performed in order to understand the stoichiometry of the reactions place in the reactor system. Since the experiments were performed at room temperature (23-25°C) and the typical temperatures in industries might vary between 30-40°C, the effect of temperature on the catalytic ozonation process should be determined.

Appendix A. Standard Curve generation for Propanal

A standard curve for propanal (gas phase) in the range of 0-100 ppmv was prepared from liquid standards. A known volume of propanal (liquid phase) was mixed with a known volume of air and the final mixture thus obtained was assumed to be in gaseous phase owing to the low concentration of propanal in the liquid phase. The mixture was analyzed using the GC/MS. The respective peak areas of propanal and the internal standard (mixture of 1, 3, 5-tris (trifluoromethyl) benzene, 100 ppmv and bromopentafluorobenzene, 50 ppmv) were measured and the peak area ratio (peak area of aldehyde / peak area of internal standard) was calculated. The same procedure was repeated for different concentrations of propanal in the range of 0-100 ppmv. Finally the standard curve (figure A.1.1) was obtained by plotting the concentration of propanal against the corresponding peak area ratio. The standard curve obtained was used for the further analysis of the inlet and outlet concentrations of propanal in the catalytic ozonation experiments and periodically confirmed throughout the course of study.

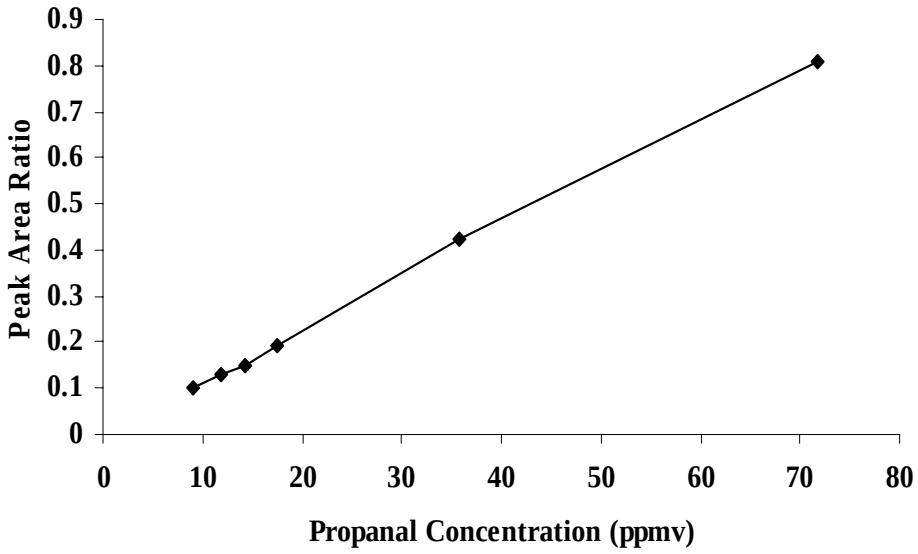

Figure A.1. Standard Curve for propanal generated by using GC/MS (Hapsite, Inficon)

Appendix B. Sample calculation for determining the reaction rates for a given propanal concentration

The overall reaction rate was calculated from the measured fractional conversion, mass of the ash, volumetric gas flow rate, inlet mole fraction, pressure, and temperature using the following equation.

$$-r = Q\left(\frac{P}{RT}\right)y\left(\frac{X}{W}\right)$$

where,

- r = reaction rate mole g^{-1} min^{-1}

Q = total gas flow rate (air + propanal + ozone), L min^{-1}

y = mole fraction of propanal in the inlet

X = fractional conversion of propanal = $(C_{in} - C_{out})/ C_{out}$

C_{in} = propanal concentration at the inlet of the packed-bed reactor

C_{out} = propanal concentration at the outlet of the packed-bed reactor system

W = mass of the ash (g)

P = pressure, atm

R = ideal gas constant, L-atm mol^{-1} K^{-1}

T = Temperature, K

MW = molecular weight of propanal

The sample calculations for an inlet propanal concentration of 14.791 ppmv, ozone concentration of 75 ppmv, total gas flow rate of 3.4 L min^{-1} (air: 2.7 L min^{-1} + oxygen: 700 mL min^{-1}), catalyst weight of 2.5 g and propanal fractional conversion of 0.192.

Inlet propanal moles calculation

Using the ideal gas law,

$$PV = n_{propanal} RT$$

Where,

P = 1 atm

V = volume of propanal in a gas mixture of 3.4 L (on a minute basis)

= $((14.791 * 3.4)/10^6)$ L

R = 0.08206 L-atm mol^{-1} K^{-1}

T = 296 K (room temperature)

$n_{propanal}$ = PV/RT = $((14.791 * 3.4)/10^6) * (1/ (0.08206*296))$ = 1.976 E-06 moles

Propanal mole fraction in the total inlet gas mixture

The inlet gas mixture contains air, oxygen, ozone and propanal. In order to calculate the mole fraction of propanal in the gas mixture, the number of moles of each gas present in the mixture was first calculated.

$n_{02} = PV_{02}/ RT = (1*0.7)/ (0.08206*296)$ = 0.031 moles

$n_{03} = PV_{03}/ RT$

where,

$V_{03} = ((75*3.4)/ 10^6)$ = 0.000255 L

$n_{03} = (1*0.000255)/ (0.08206*296)$ = 8.71 E-06 moles

$n_{air} = (1*2.7)/ (0.08206*296)$ = 0.120373

$y_{propanal} = n_{propanal}/ (n_{propanal} + n_{02} + n_{03} + n_{air})$

= 1.976 E-06/ (1.976 E-06 + 0.031 + 0.000255 + 8.71 E-06)

= 2.07 E-06

Calculation of reaction rate

$-r = Q*(P/RT)*y*(X/W)$

$= 3.4 \times (1/ (0.08206*296))*2.07 \text{ E-}06*(0.192/58)$

$= 1.4 \text{ E-}07 \text{ mol } g^{-1} \text{ min}^{-1}$ or $2.33 \text{ E-}09 \text{ mol } g^{-1} \text{ s}^{-1}$

Appendix C. Rate law determination for Wood Fly Ash

The rate law for the catalytic ozonation of propanal was determined by varying the concentrations of propanal, ozone and also using different catalysts. The rate law for WFA was determined by varying propanal in the range of 5-15 ppmv and ozone in the range of 75-175 ppmv. The reaction equation for the oxidation of propanal using ozone and a catalyst is as follows:

$$Propanal + O_3 \xrightarrow{\text{catalyst}} Products$$

The power law was applied to best fit the experimental data obtained from the catalytic ozonation of propanal. By using this law we can express the reaction rate of propanal as follows:

$$-r = kC_{O3}{}^{m} C_R{}^{n} \approx k'C_R{}^{n}$$

where k is the intrinsic rate constant, k' the approximate rate constant equals to kC_{O3} while C_{O3} and C_R are the concentrations of ozone and propanal (both in moles cm^{-3}), and, m and n are the orders of the reaction with respect to ozone and propanal respectively. The concentration of ozone was assumed to be constant since it was higher and in excess relative to propane concentration. In order to verify if this assumption was valid, linear regressional analysis (SAS Output 1) for the dependency of ozone and propanal concentration on the rate of reaction was performed. The low r-square value (0.1530) for ozone and the very low parameter estimate of ozone (0.00740) indicates that ozone concentration does not have a significant effect on the rate of reaction when compared to propanal concentration (r-square-0.7532, parameter estimate-0.15925). Therefore the assumption that ozone concentration is constant over the time of reaction is valid.

The regressional analysis of the Ln (P) and Ln (-r) data (Table A.C.1) resulted in a moderately good r-square value of 0.8230 suggesting a good linear fit of the data and the order of

the reaction and rate constant were determined from the parameter estimates of Ln (P) and the intercept (SAS Output 2).

Table A.C.1. Experimental data for the determination of rate-law for catalytic ozonation of propanal using wood fly ash.

Observation	**Ozone Concentration (ppmv)**	**Propanal Concentration (ppmv)**	**Reaction Rate*10^9 $-r$, (mol g^{-1} s^{-1})**	**Ln(P)**	**Ln($-r$)***
1	75	5	0.842	1.61	-20.895
2	95	5	0.918	1.61	-20.810
3	145	5	1.080	1.61	-20.640
4	175	5	1.160	1.61	-20.570
5	75	10	1.370	2.31	-20.410
6	95	10	2.150	2.31	-19.960
7	145	10	2.250	2.31	-19.910
8	175	10	2.660	2.31	-19.750
9	75	15	2.220	2.71	-19.930
10	95	15	2.360	2.71	-19.870
11	145	15	2.680	2.71	-19.740
12	175	15	3.110	2.71	-19.590

*Calculation for reaction rate (r) is as shown in Appendix 2.

SAS Output 1. Regressional Analysis for dependency of rate of reaction (r) on ozone and propanal concentration

The REG Procedure
Dependent Variable: r

Analysis of Variance

Source	DF	Sum of Squares	Mean Squares	F value	Pr>F
Model	2	6.10230	3.05115	43.49	<0.0001
Error	9	0.63138	0.07015		
Corrected Total	11	6.73369			

Paramter Estimates

Root MSE	0.26487	R-square	0.90962
Dependant Mean	1.90000	Adj. R-square	0.8854
Coeff. Var	13.94030		

Variable	DF	Parameter Estimate	Standard Error	T value	Pr>|t|
Intercept	1	-0.59871	0.31120	-1.92	0.0865
Ozone	1	0.00740	0.00193	3.83	0.0040
Propanal	1	0.15925	0.01873	8.50	<.0001

The REG Procedure
Dependent Variable: r

R-Square Selection Method

Model	R-Square	Variables in Model
1	0.7352	Propanal
1	0.1530	Ozone

SAS Output 2. Regressional Analysis of Ln (P) versus Ln (-*r*) data for determining the rate-law for catalytic ozonation of propanal using wood fly ash

The REG Procedure
Dependent Variable: Ln (-*r*)

Analysis of Variance

Source	DF	Sum of Squares	Mean Squares	F value	Pr>F
Model	1	1.918905	1.91805	46.49	<0.0001
Error	10	0.41257	0.04126		
Corrected Total	11	2.33062			

Root MSE	0.20312	R-square	0.8230
Dependant Mean	-20.17292	Adj. R-square	0.8053
Coeff. Var	-1.00689		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T value	Pr>|t|
Intercept	1	-0.59871	0.31120	-1.92	<0.0001
Ln (P)	1	0.87944	0.12898	6.82	<0.0001