CATALYTIC DESTRUCTION OF LINDANE USING A NANO IRON OXIDE CATALYST

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CATALYTIC DESTRUCTION OF LINDANE USING A NANO IRON

OXIDE CATALYST

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ABSTRACT

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Lindane, also known as gamma hexachlorocyclohexane, is toxic in nature. The objective of this work was to develop an economically viable technology for destruction of lindane into products that are nontoxic in nature. A catalytic approach was chosen for destructing lindane because thermal processes are expensive and can generate toxic products like dioxins. Initially, a set of exploratory experiments (Phase I) were performed using a micro iron oxide particle loaded catalyst (7 cm bed length and 0.92 g Fe₂O₃ loading). The iron oxide catalyst was chosen because results from a previous study done by our group had shown that iron oxide was effective in destroying chlorinated compounds. In phase I, lindane was passed over the catalyst for a period of ten minutes as a lindane-acetone (25 g / 80 ml) mixture at 1.44 g/hr. The results showed that the micro iron oxide catalyst loading and space velocity failed to increase the destruction efficiency of the catalyst. It was decided that perhaps the destruction efficiency will increase if the micro iron oxide catalyst was replaced with a nano iron oxide catalyst.

The second phase of the experiments was performed with a nano iron oxide catalyst (7 cm in bed length and 3% Fe₂O₃ loading). Same amount of lindane-acetone mixture, as in the first phase of experiments, was fed over the catalyst. The results showed that the nano iron oxide catalyst destroyed over 99% of lindane. Once the high destruction efficiency was achieved it was decided to conduct the next set of experiments (Phase III) at a larger scale with the lindane directly fed into the reactor without acetone. This required the design and construction of a solid feed system and a vaporizer that will vaporize lindane into gas phase before it passed over the catalyst. In the third phase, a total of two hundred grams of lindane at a feed rate of 0.2 ± 0.03 g/min in gas phase was passed through two fixed bed catalytic reactors in series that housed nano iron oxides catalysts (catalyst 1 of 7 cm bed length and 7% Fe₂O₃ loading, catalyst 2 of 7 cm bed length and 3.5% Fe₂O₃ loading). The destruction efficiency of the catalyst was found to be 100% for the initial set of experiments. However, as more lindane was passed over the catalyst it was found that the chlorine from lindane was deactivating the catalyst. Chlorine deactivates the catalyst by forming iron chloride on the active sites of the catalyst resulting in a decrease in destruction efficiency. A restoration process was found to activate the catalyst in which water along with air was fed over the catalyst while maintaining the reactor temperature at 650°C. During this process, moisture is adsorbed on the surface of iron chloride and forms the complex (FeCl(OH)) which further reacts with moisture to form ferrous hydroxide. Ferrous hydroxide is then oxidized in the presence of oxygen to form iron oxide. The regenerated iron oxide catalyst was once again effective in destructing lindane. A preliminary cost estimate indicates that if the catalyst can be regenerated five times based on the amount of lindane destroyed during

this study, the process will be economical compared to the other techniques available for lindane destruction and can be implemented at a larger scale.

To avoid a separate process to regenerate the catalyst, experiments should be conducted by passing water along with lindane over the catalyst. In doing so, the destruction of lindane and the regeneration of the catalyst occur simultaneously. This technique will prolong the life of the catalyst.

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LIST OF ABBREVIATIONS AND ANNOTATIONS

- *Fe* Iron
- Fe_2O_3 Iron Oxide
- *HCH*, $C_6H_6Cl_6$ Hexachlorocyclohexane
- *WHO* World Health Organization
- *EPA* Environmental Protection Agency
- *DOT* Department of Transportation
- OSHA Occupational Safety and Health Administration
- *FDA* Food and Drug Administration
- PEL Permissible Exposure Limit
- *KOH* Potassium Hydroxide
- GC/MS Gas Chromatography / Mass Spectrometry
- *TGA* Thermo Gravimetric Analysis
- *DE* Dechlorination Efficiency
- HCB Hexachlorobenzene
- *IUPAC* International Union of Pure and Applied Chemistry
- *ISO* International Organization for Standardization
- *NaOH* Sodium Hydroxide

CHAPTER 1

INTRODUCTION

Lindane, also known as gamma-hexachlorocyclohexane (γ -HCH) [1, 2], gammaxene, and gammallin, is an organochlorine chemical. It is also referred to as "Benzene Hexachloride" (BHC) [2]. Though this designation is incorrect according to International Union of Pure and Applied Chemistry (IUPAC) rules, it has been approved by International Organization for Standardization (ISO) and is widely used.



Figure 1.1. Chemical structure of lindane.

Figure 1.1 shows the chemical structure of lindane. Lindane comprises of 99% of the gamma isomer of HCH, γ -HCH [1]. γ -HCH contains all insecticidal properties. Technical HCH includes varying proportions of alpha, beta, delta, and epsilon HCH isomers. These HCH isomers have proven to have serious short- and long-term health effects [1].

Lindane is the most abundant pesticide in Arctic air and water [3]. Throughout the world, it is abundant in air, water and soil. It is highly stable and travels long distances via atmospheric and oceanic currents.

1.1. Physical and Chemical Properties of Lindane

Lindane is a white solid that evaporates into the atmosphere as a colorless vapor with a slight musty odor [4]. The odor of HCH is technically attributed to its impurities, particularly heptachlorocyclohexane [5]. Lindane is known to be stable in air, light, heat, carbon dioxide, and strong acids. Dehydrochlorination of lindane takes place in the presence of an alkali, forming trichlorobenzene and hydrochloric acid. Dechlorination of lindane ultraviolet radiation forming occurs on exposure to gamma pentachlorocyclohexenes and tetrachlorocyclohexenes. The half-life for the environmental degradation of lindane varies depending on the factors such as climate, type of soil, and depth of application. Under humid and field conditions the half-life is between few days to three years [5]. Lindane is incompatible with strong bases and powdered metals such as iron, zinc, and aluminum. It is also incompatible with oxidizing agents and can undergo oxidation when it comes in contact with ozone. Table 1.1 shows a few more properties of lindane.

Lindane
(1 <i>r</i> ,2 <i>R</i> ,3 <i>S</i> ,4 <i>r</i> ,5 <i>R</i> ,6 <i>S</i>)-1,2,3,4,5,6-
hexachlorocyclohexane
Organochlorine Insecticide
$C_6H_6Cl_6$
200.95
290.85
58 80 0
50-07-7
1.85 g/ml at 20°C
G G G G G G G G G G G G G G G G G G G
112 to 113°C
5.6 mPa at 20°C
Non-explosive
N
Non-manimable
7.3 mg/l at 25°C
7.5 mg/r ut 25 C

Table 1.1. Other Properties of Lindane:

1.2. Uses

The primary applications of Lindane are in agricultural and pharmaceutical sectors. Lindane has been used as an agricultural insecticide since the early 1940s. In agricultural, uses are for seed treatment, foliar applications, and treatment of forests, timber, stored materials or products. In the pharmaceutical sector, lindane was used as a lotion cream to treat scabies infestation, and as a shampoo to treat head and body lice [6]. It is no longer prescribed as drug therapy for these purposes due to its potential risks. Lindane has also been used as an effective household fumigant against flies and cockroaches until it was found to be hazardous to people and pets. It can also be used

against ectoparasites on animals. It affects insects in the form of stomach poison with some fugitive action which kills insects when they inhale its vapor [1]. Lindane is available as a suspension, emulsifiable concentrate, fumigant, seed treatment, wettable and dustable powder, and ultra-low-volume (ULV) liquid [7].

Although lindane has many applications, it has been banned in more than 50 countries due to its adverse effects. It was used in United States and Canada only for medical treatments and was banned for use in agriculture, except for the treatment of preplanting seeds for six crops: barley, corn, oats rye, sorghum and wheat [8] and in 2007 these uses were cancelled [9].

1.3. Environmental Contamination

Environmental Protection Agency (EPA) and World Health Organization (WHO) have classified lindane as "moderately hazardous" due to its adverse effects on human health and environment [2]. The production and agricultural use of lindane are the primary causes of environmental contamination [10]. Large amounts of toxic waste in the form of hexachlorocyclohexane are generated during its production. When lindane is used for agricultural purposes, an estimated 12-30% of it volatilizes into the atmosphere and is later re-deposited by rain. Lindane in soil can leach to the surface and can contaminate drinking water resources [11].

In common with other organochlorine pesticides, lindane is fat soluble, and this fact contributes to its tendency to bioaccumulate through food chains. Lindane residues have been found in the kidneys, livers, and adipose tissue of a wide variety of wild animals and birds. It is considered a highly toxic element to aquatic invertebrates and fish [1].

1.4. Effects on Human Beings

Exposure to large amounts of lindane may harm the human nervous system, producing various symptoms like headache and dizziness. Children can experience convulsions from lindane exposure [12]. Lindane pharmaceuticals cause variety of adverse reactions on human health ranging from skin irritation to seizures. The most common side effects are burning sensations, itching, dryness, and rash [13]. The International Agency for Research on Cancer (IARC) evaluated hexachlorocyclohexanes in 1987 and concluded that it is carcinogenic for human and animals [14]. In contrast, the WHO concluded in 2004 that lindane is not likely to pose a carcinogenic risk to humans [15].

1.5. Regulations

In 1990, the WHO classified lindane as "moderately hazardous" in normal use (on the basis of an LD_{50} of 88 mg/kg in rats). WHO and Food and Agricultural Organization (FAO) in 1975 issued a data sheet on lindane (No.12) dealing with labeling, safe handling, transport, storage, disposal, decontamination, training, and medical supervision of workers, first-aid, and medical treatment [4]. More regulations on lindane are listed below [16].

1.5.1. Department of Transportation (DOT)

Lindane is considered a marine pollutant, and special requirements have been set for marking, labeling, and transporting this material. 1.5.2. Environmental Protection Agency (EPA)

(a) Clean Air Act

National Emissions Standards for Hazardous Air Pollutants: Lindane (all isomers)

is listed as a hazardous air pollutant.

(b) Clean Water Act

Effluent Guidelines: Hexachlorocyclohexane is listed as a toxic pollutant.

Water Quality Criteria: Based on fish or shellfish and water consumption = $0.98 \mu g/l$ for lindane.

(c) Safe Drinking Water Act

Limit: Maximum contaminant level (MCL) = 0.0002 mg/l for lindane.

1.5.3. Food and Drug Administration (FDA)

Maximum permissible level in bottled water = 0.0002 mg/l for lindane.

Action levels for lindane in food and in animal feed range from 0.1 to 0.5 ppm.

1.5.4. Occupational Safety and Health Administration (OSHA)

Permissible Exposure Limit (PEL) = 0.5 mg/m^3 for lindane

CHAPTER 2

LITERATURE

Although lindane was useful in agriculture and pharmaceuticals, due to environmental toxicity, there is a great need to find safe ways for its disposal. A number of studies have been conducted to investigate methods for the degradation of chlorinated pollutants via reductive dehalogenation to transform chlorinated organics into their nonchlorinated analogues. Some of the techniques include incineration, chemical methods, catalytic (photo or thermal) and biological degradation. Incineration is the most common available technique, but it has major drawbacks. Incineration generates HCl, may produce toxic products such as dioxins formed in the incinerator at T<750°C, and nitrogen oxides that cause acid rain, and also consumes a lot of energy [17, 18]. Other techniques such as microwave irradiation, а nano-biotechnological treatment, dechlorination of chlorobenzenes using nanoscale Fe particles, and the use of ultrafine Ca-Fe composite oxides for the treatment of hexachlorobenzenes are discussed in the following paragraphs.

2.1. Microwave Irradiation Treatment

The microwave treatment of lindane was carried out via reaction 2.1, in which sodium hydroxide and NiO_x modified sepiolites are used to induce dehydrohalogenation and oxidation.

$$[O] C_6H_6Cl_6 \rightarrow NaCl + CO_2 + H_2O \qquad (Rxn \ 2.1) [NaOH]$$

The above reaction is a dehydrochlorination process in which both hydrogen and chlorine are removed from lindane. The above mechanism is implied by the work of Salvador et al [19]. In the experiments conducted by Salvador et al, lindane was heated in a microwave in the presence of sodium hydroxide at about 300°C. Dehydrochlorination took place, leaving sodium chloride and carbon dioxide as products. Although this microwave treatment is highly efficient (with 97% conversion) for decomposing lindane, the process is practically not possible to implement at a larger scale.

2.2. Degradation of Lindane From Aqueous Solutions Using Nanoparticles

Three methods - physical adsorption, chemical degradation, and bioremediation are typically reported for the removal of lindane from aqueous solutions. Also, it was shown that nanoscale iron particles are very effective for the transformation and degradation of various organochlorine pesticides [20]. In the process involving removal of lindane from aqueous solutions [21], a fungal polymer (used as a stabilizer), was added to a FeSO₄ solution and stirred vigorously under nitrogen atmosphere. To this mixture, Na₂S (1 M, 5 ml) was added drop wise to get a black colloidal suspension of FeS. Then, 1 ml of the solution containing FeS nanoparticle suspensions were added to serum bottles, each 30 ml in capacity containing 9 ml of distilled water supplemented with lindane (at a concentration of 5 mg/l). The bottles were purged with nitrogen, sealed, and then incubated at room temperature (30°C) on a rotary shaker (150 rpm). Samples (100 μ l) were withdrawn from the bottles at 1-hr intervals. Lindane was extracted in HPLC grade hexane (1000 µl) and its concentration was determined by gas chromatography (GC). The results indicated that stabilized FeS nanoparticles degrade 94% of lindane in 8 hours. This nano-biotechnological approach comprising catalytic dechlorination using FeS nanoparticles does not degrade lindane completely in water, as partially degraded intermediates such as trichlorobenzene were detected in the gas chromatographic analysis of the samples. Therefore, an additional treatment, i.e., a microbial degradation in which a bacterial culture (designated as Lin1), was used to remove the remaining lindane in the solution [21]. In this nano-biotechnological process, the catalytic decomposition was not too effective (only 94% of lindane was degraded catalytically), and was very time consuming (~8 hours), and in addition required a separate procedure involving microbial degradation to completely remove lindane from the aqueous solution.

2.3. Dechlorination of Lindane in a Multiphase Catalytic Reduction System

The multi-phase catalytic reduction system consists of a metal catalyst such as 5% Pt/c; 5% Pd/c; or Raney-Ni; a phase transfer agent such as Aliquat 336 (tricaprylmethylammonium chloride), isooctane which acts as the organic phase and an aqueous KOH [22]. Aqueous KOH and Aliquat 336 promote the dehydrochlorination (DHC) step in which both hydrogen and chlorine are removed from the compound and the hydrodechlorination (HDC) step, which involves the removal of chlorine and an addition of hydrogen to the compound. The reactions were conducted in a 25 ml three-necked, round-bottomed reactor. A small amount (10 ml) of isooctane containing 0.2 g of lindane along with 0.0455 g of metal catalyst and 0.103 g of Aliquat 336 was added into the reactor. A small amount (5.7 ml) of the aqueous KOH solution was added to the system along with n-dodecane which served as the GC internal standard. The reactor was

bubbled with H_2 at atmospheric pressure at 10 ml/min and was heated at $50\pm1^{\circ}$ C. Samples of 20 µl volume was periodically drawn from the organic phase (isooctane) during the reaction. The sample that was taken just after the reagents had been added was considered as zero-time point. The samples were shaken with silica to remove Aliquat 336, and filtered with glass wool to remove the catalyst before undergoing GC analysis. Reduction of lindane to trichlorobenzenes and then to benzene was achieved in 5 to 10 minutes via the consecutive DHC-HDC reaction stages shown in Figure 2.2.



Figure 2.1. Catalytic reduction of lindane to benzene via two diverse pathways and the corresponding intermediates [22].

The first step was the base assisted DHC step in which 98% of lindane was converted to trichlorobenzenes. In further steps, catalytic HDC took place in which 90% of trichlorobenzenes was converted to benzene. This process is not economical at a larger scale due to the costs involved with the large quantities of organic solvents, Aliquat 336, KOH and H_2 used in the process. In addition, solvent recovery and catalyst recovery using silica and glass wool needs very good control.

2.4. Dechlorination of Lindane in Subcritical Water

In this process, aliphatic organochlorines are dechlorinated by pure water without the use of catalysts. Dehydrohalogenation of lindane occurs at very low temperatures around 105-200°C [23]. Complete loss of the parent compound occurs at 200°C for lindane in less than 1 hour. All reactions were performed using a static 4 ml cell constructed from an Inconel 600 threaded pipe fitting with end caps. These cells were selected on the basis of their inertness in corrosion tests with subcritical water. For each experiment, 3 ml of water which had been purged with nitrogen for ~ 2 hours to remove dissolved oxygen was poured into the cell, leaving about 1 ml of headspace when the vessel was capped. Initial reactions were performed in water spiked with 10 μ l of an acetone solution of tetrachloroethane (final concentration in water of 1 mM) and lindane (final concentration of 0.57 mM). Reaction cells were heated in a GC oven for 1 hour at 200°C. After heating, the hot cells were immediately removed from the oven and immersed in tap water to quench the reaction. After cooling, each cell was carefully opened and its contents were transferred to a 7 ml vial. Organics were then extracted with three 1 ml aliquots of methylene chloride. 1-Chloronaphthalene was added as an internal standard at a concentration similar to the starting material and the extracts were analyzed by gas chromatography with mass spectrometric detection (GC/MS). The results showed that initially, dehydrohalogenation of lindane occurs to form trichlorobenzenes, followed by subsequent hydrolysis to form chlorophenols, chlorobenzenes and phenol as final products. The use of water under comparatively mild conditions (100-250°C) is

attractive; however, the main disadvantage of this process is the formation of toxic chlorinated phenols as byproducts.

2.5. Dechlorination of Hexachlorobenzene Using Ultrafine Ca-Fe Composite Oxides

In this process, ultrafine CaO and Fe₂O₃ were used as a reagent mix for dechlorination of HCB and was carried out in a small glass tube of 11 cm length and 0.4 cm I.D. [24]. The oxides were grounded into powders of average particle size ~50 μ m. For all reactions, 2 mg of HCB was mixed with 40 mg of the dechlorination reagent and then sealed under atmospheric air and heated in an oven. The reaction temperature was set at 300°C. After the desired heating time, the glass tubes were extracted with 15 ml of hexane twice for 20 minutes each in an ultrasonic extractor. The solution was then washed twice with 10 ml of water and the aqueous and hexane layer were separated. The organic extract was analyzed using GC/MS to measure the parent HCB remaining and the newly-formed lower chlorinated benzenes.

The dechlorination efficiency (DE, %) for the initial HCB is calculated using the following equation:

DE (%) =
$$\left(1 - \frac{\sum_{i=0}^{6} iN_i}{6N_0}\right) \times 100$$

where N_i is the molar number of chlorinated benzene containing *i* chlorine atoms in the molecule and N_0 is the initial molar number of HCB.

The results showed that the percentage of dechlorination increases rapidly in the first 5 minutes and reaches 67%, then increases slowly with further reaction and reaches 97% after 30 minutes of reaction. In the last stage of the reaction, the dechlorination rate tends to decrease; it takes 90 minutes to further increase dechlorination efficiency by 2%.

During this process, 99% of hexachlorobenzenes are destructed using Ca-Fe composite oxides; however, it forms dichlorobenzenes and trichlorobenzenes which are toxic in nature.

2.6. Dechlorination of Hexachlorobenzene by Using Nano-scale Fe Particles

In this process, degradation experiments were conducted to investigate the reaction kinetics of nanoscale Fe and Pd/Fe particles for dechlorination of HCB [25]. During these experiments, 21 ml amber serum vials each containing 15 ml of HCB sample was mixed with around 2 g of nanoscale Fe and nanoscale Pd/Fe particles. The reaction vials were crimp-sealed with Teflon-faced rubber septa and then incubated at 25°C while stirring on a rotary shaker (125 rpm). The samples were extracted with nhexane three times after which the combined organic extracts were concentrated to 1 ml. The extracts were analyzed with an Agilent 6890N gas chromatograph. The results suggested that after 24 hours, the concentration of HCB decreased to 60% by nanoscale Fe particles and 70% by nanoscale Pd/Fe bimetallic particles. It also suggested that the reduction rate of HCB becomes slower after about 24 hours due to the production of hydroxide substances or salt precipitation on the nanoscale Fe and Pd/Fe bimetallic particle surface to reduce the reactive surface. In these experiments using nano Fe particles, a smaller amount of chlorobenzenes was measured, whereas trichlorobenzenes were the dominant byproduct. From the above techniques, it was proven that dechlorination of hexachlorobenzenes can be done in the presence of an iron catalyst.

As part of this study, preliminary studies were conducted with a catalyst investigated in prior dechlorination studies at the University of Dayton Research Institute using a packed bed flow reactor to determine the most promising catalyst. Iron oxide had the highest destruction efficiency and therefore was chosen for further studies to develop an economically and environmentally viable catalyst bed that could be scaled up for a reactor system suitable for commercial use.

CHAPTER 3

EXPERIMENTAL

3.1. Preliminary Experimental Setup Using Micro Iron Oxide (Phase I) and Nano Iron Oxide (Phase II) Catalysts

The experimental setup for the first two phases of the study is shown in Figure 3.1. with details of its components. In this part of the study, the experiments involved heating a fixed bed iron oxide catalyst reactor to a predetermined temperature of 300°C using a furnace comprised of three zones with separate temperature controllers for each zone. The iron oxide catalyst and temperature conditions were chosen because results from a previous study done by our group had shown that iron oxide was effective in destroying chlorinated compounds. Experiments were performed in the first phase with a catalyst loaded with micro iron oxide particles but based on experimental observations that lead to a phase II study with the same system were replaced with a nano iron oxide loaded catalyst. In both phases, lindane was mixed with acetone (both from Sigma Aldrich) in a proportion of 25 g per 80 ml of solvent and was fed into the heated reactor tube at a feed rate of 1.44 g/hr with a syringe infusion pump. The syringe infusion pump which operates by slow turning gears, injected the lindane-acetone solution as droplets.

400 ml/min from an air cylinder into the heated reactor. Due to the hot gas flow, the droplets vaporized and transported freely through the reactor. The reactor tube was made of glass and housed a foam catalyst bed loaded with iron oxide particles in the middle zone with glass wool plugs on either side to hold the catalyst in place. The reactor tube was 29 inches in length, 1.5 inches in O.D. and 1.402 inches in I.D.



Figure 3.1. Experimental setup of lindane experiment.

- 1. LINDBERG FURNACE
- 2. REACTOR TUBE
- 3. OUTLET GAS VENTING TUBE
- 4. FLOW METER (ROTAMETER)
- 5. IMPINGER
- 6. XAD TRAP GLASS TUBE
- 7. TEFLON FITTINGS
- 8. STAINLESS STEEL FITTING

- 9. THERMOCOUPLE READOUT
- 10. TEMPERATURE CONTROLLERS
- 11. IRON OXIDE CATALYST
- 12. PRESSURE GAUGE
- 13. SYRINGE
- 14. SYRINGE INFUSION PUMP
- 15. ALUMINUM STAND
- 16. AIR INLET FROM CYLINDER

The mass flow rates of reactants were chosen to represent near-stoichiometric conditions based on the product distribution given in Rxn 3.1.

$$C_6H_6Cl_6 + 5.5O_2 + 20.7N_2 \rightarrow 5CO_2 + CO + 6HCl + 20.7N_2$$
 (Rxn 3.1)

For each experiment, the flue gas from the reactor was passed through a glass tube containing a pre-cleaned XAD trap. XAD traps were made with 8-inch long, ¹/₂ inch O.D. glass tubes. Each tube was filled with a 5 cm long bed of pre-cleaned XAD (Amberlite XAD-2 resin from Supelco) to trap the compounds exiting the reactor. An impinger was placed behind the XAD trap to capture the break through products from the XAD trap. Rotameters were placed at the gas cylinder outlet (i.e. before inlet of reactor) and behind the impinger to measure the gas flow rates through the reactor and to make sure there are no leaks in the system. Leaks were checked by passing helium through the reactor using a helium leak detector. After the completion of the experiment, the traps are taken out and the recovery / internal standards are injected into the trap, extracted and analyzed using GC/MS to characterize the effluents from the reactor. The details of the XAD preparation, extraction and analysis are described later.

3.2. Experimental Setup for Phase III

The experimental setup for the third phase consisted of a feeding unit, two reactors, a carbon trap and inlet/outlet flow meters that were assembled in series. High temperature valves were positioned appropriately for sampling flue gas using XAD sorbent traps/bags, and for flow routing (see Figure 3.2). A schematic of the experimental system is shown in Figure 3.2 and a photograph of the experimental setup is shown in Figure 3.3. The various reactor components and operation of the experimental system is described in detail.



Figure 3.2. Schematic of the experimental setup for phase III experiment.



Figure 3.3. Photograph of the experimental setup.

3.2.1. Feeding Unit

The feeding unit consisted of a cylindrical tube with a beveled end at the outlet of the tube, a blade and a piston both driven by two independent DC motors, and a vaporizer. The cylindrical tube 9 inches in length and 1 inch in I.D. was packed with lindane to a predetermined weight (~84 g of lindane) to maintain the packing density required for a constant feed rate. A piston at the inlet of the cylindrical tube, driven by a DC motor attached to a threaded rod assembly displaced lindane from the tube outlet. A blade that was driven along the beveled edge of the cylindrical tube with another DC motor sliced the lindane into a funnel with a 0.5 inch I.D. tube connected to a heated vaporizer at the bottom of the feeding unit. The vaporizer was a 14.5 inch long tube with a 1.5 inch O.D. maintained at a temperature of $230\pm10^{\circ}$ C with its outlet connected to the inlet of the first reactor. Thermo gravimetric analysis (TGA) indicated that to ensure complete transport of the gaseous feed at the air/mass flow rates investigated, a temperature greater than $\sim 215^{\circ}$ C had to be maintained in the entire experimental system. Therefore, taking into consideration possible non uniformities in temperature, the vaporizer was maintained at $230\pm10^{\circ}$ C. During each experiment, lindane was continuously fed into the vaporizer at a feed rate of 0.2 ± 0.03 g/min. The feed rates were measured before and after each set of experiments to account for the impact on experimental observations from possible differences in lindane packing when refilling the cylindrical feeding tube in the feeding unit. To assist the transport of lindane sliced from the cylindrical feeding tube to the vaporizer and thereafter to the first reactor, and to reduce vaporized lindane from flowing back into the solid feed lines and clogging it, the

air flow inlet was directed to the tip of the beveled end of the cylindrical feeding tube in the feeding unit to help transport the lindane into the vaporizer.

3.2.2. Reactors

The first five experiments were performed using glass tubes as reactors and the subsequent experiments were performed using 316 stainless steel tubes. The reactor tubes were each 29 inches long with an O.D. of 1.5 inches and an I.D. of 1.402 inches. A nano iron oxide catalyst was kept in the middle of each reactor. Two different catalysts were used in the two reactors: a 7 cm long catalyst bed containing ~1.5 g of Fe₂O₃ (7% catalyst loading) was placed in the first reactor and a second catalyst also of 7 cm bed length containing ~0.75 g Fe₂O₃ (3% catalyst loading) was placed in the second reactor. The catalysts were held in place by glass wool plugs placed on either side of the catalysts. The total length of the bed was ~11 cm. A schematic of the reactor tube is shown in Figure 3.4. Based on TGA observations, all valve assemblies and transfer lines between/after reactors were heated to temperatures of $230\pm10^{\circ}$ C to prevent condensation of reactants and products which could lead to clogging. During experiments, both reactors were maintained at 300°C using two three-zone furnaces with individual temperature controllers for each zone.



Figure 3.4. A schematic of the reactor tube.

3.2.3. Carbon Trap

A carbon trap (filled with activated carbon from Sigma Aldrich) was placed at the end of the second reactor valve assembly to prevent any toxic effluent from escaping into the laboratory exhaust. The toxic organic effluent coming out from the second reactor was collected in the carbon trap and the remaining gas was passed to the exhaust.

3.2.4. Rotameter

Two rotameters, one at the inlet to the feeding unit and a second at the end of the carbon trap, were kept to measure the inlet and outlet flows. During the experiment, flow rates were checked every 10 minutes to check for leaks and to ensure that a constant gas flow rate was maintained throughout the experiment. During experiments, a total gas flow rate of 400 ml/min was maintained through the reactors connected in series.

3.2.5. XAD Trap

XAD traps were made with 8 inch long, ¹/₂ inch O.D. glass tubes. Each tube was filled with a 5 cm long bed of pre-cleaned XAD (Amberlite XAD-2 resin from Supelco) to trap the compounds exiting the reactor. Two XAD traps were connected to the sampling valves at the end of each reactor and the exhaust gas was sampled consecutively for 1 minute at 10 minute intervals. After sampling, the traps are removed, recovery / internal standards are injected into the trap, extracted and analyzed using GC/MS as described later.

3.3. XAD Trap Preparation, Extraction and Analysis

3.3.1. Cleaning XAD Using Soxhlet Extraction

Before preparing the sampling traps with XAD, the XAD was cleaned by Soxhlet extraction. The XAD was put into the thimble of the Soxhlet extractor and the thimble

was placed inside the extractor. The XAD was then extracted with methylene chloride for 48 hrs. Once the extraction process was finished, XAD was dried and used in the traps for the experiments.

3.3.2. Extraction from XAD

To capture and characterize effluents from the reactors, glass tubes containing pre-cleaned XAD resins were kept at the end of the catalytic reactors. Upon completion of the experiment, the XAD-traps are removed from the system for extraction. In all three phases, a recovery / internal standard mixture of 100 µl containing d-phenanthrene and d-acenaphthylene (200 µg each) was injected into the XAD before extraction. A recovery / internal standard is injected to the sampling trap to correct for losses during extraction and concentration steps as well as to account for dilution effects during GC/MS analysis. A total of 40 ml of dichloromethane was added to each XAD trap to extract the products by solvent extraction. A sample of 2 ml was taken from the 40 ml extract for analysis of lindane conversion and the rest (38 ml) was concentrated to 2 ml using nitrogen gas and stored for the analysis of byproducts using GC/MS.

3.3.3. GC-MS Analysis

The products were analyzed by GC/MS using an Agilent Technologies 6890N GC System and 5973 Inert Mass Selective Detector. A DB-5 60 m chromatographic column was used for separation in this analysis. The injector was maintained at 340°C prior to injection. A total of 1 μ l of the sample was injected and trapped at the head of the column. The oven temperature was initially maintained at 40°C and after a 5 min hold time was increased to 300°C at a rate of 5°C/min. The mass spectrometer was used in full scan mode was

used when determining unknown compounds in the sample over the selected mass range. The selective ion mode was used to record the ion current of selected masses that is characteristic of the compound of interest over the expected retention time window. The principal ions of the compounds of interest were used to determine areas from the chromatograms. In this case, the products of interest were primarily lindane, chlorobenzenes, and chlorophenols. The recovery / internal standards were then used to quantify recovery losses that occurred during extractions. The products were quantified using a point calibration of standards. All data from GC/MS analysis is given in the appendix (Appendices A and B).
CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results of catalytic destruction of lindane (γ -HCH) into nontoxic products are presented and analyzed from the three different phases of this study conducted to develop an economically viable technology for lindane destruction. The three phases involved three sets of experiments for the destruction of lindane into nontoxic products. Catalytic treatment of organic phase lindane was performed in the first two sets of experiments (Phase I and II). In the first phase, lindane destruction was done using a micro iron oxide particle-loaded catalyst and the results obtained are discussed in Section 4.1. The results showed that the micro catalyst was inefficient in destroying lindane, hence, the micro-sized catalyst particles were then replaced with nano-sized particles in the next set of experiments (Phase II). Experiments conducted with the nano iron oxide catalyst are discussed in Section 4.2. In Section 4.3, the results from the third phase of experiments conducted with lindane in gas phase using nano iron oxide catalyst are discussed (Phase III).

4.1. Destruction of Lindane Using Micro Iron Oxide Catalyst

Lindane was treated catalytically with an iron oxide catalyst under conditions chosen from results of prior exploratory studies where different catalyst and experimental conditions were investigated. In the first phase of this study, experiments were conducted with micro size (non-nano) iron oxide particle loaded catalysts. Three catalysts shown in Figure 4.1 were used to determine the catalyst efficiency, impact of catalyst loading, and space velocity. For each experiment, a lindane-acetone mix (25 g / 80 ml of solvent) was injected at a feed rate of 1.44 g/hr for 10 min while passing air at a flow rate of 400 ml/min with the reactor at a temperature of 300°C. After each 10 min experiment, the system was flushed with air for an additional 20 min to ensure that the reactor tube was free of residual lindane by maintaining the air flow rate at 400 ml/min and reactor temperature at 300°C. During the experiment and while flushing the system, the effluents from the reactor were captured on a XAD sorbent bed to determine destruction efficiency and to characterize effluents for products from decomposition.



Figure 4.1. Micro catalysts used in this study: (1) 7 cm bed length and 0.92 g Fe_2O_3 loading (2) 5 cm bed length and 0.65 g Fe_2O_3 loading (3) 5.5 cm bed length and 0.25 g Fe_2O_3 loading.

The destruction efficiency of the micro size iron oxide particle loaded catalyst was investigated using catalyst 1 by conducting two experiments. A lindane-acetone mix was injected into the system for two 10 min intervals at a flow rate of 1.44g/hr. The percentage of lindane destruction was determined and is shown in Figure 4.2.



Figure 4.2. Efficiency of catalyst 1 (0.92 g Fe_2O_3 loading / 7 cm bed length) with time.

As shown in figure 4.2, the destruction efficiency of lindane was found to be ~79% for the first 10 minutes and ~65% for the next 10 minutes. Then, the impact of catalyst loading was investigated using catalyst 2 (5 cm bed length and 0.65 g Fe₂O₃ loading) and catalyst 3 (5.5 cm bed length and 0.25 g Fe₂O₃ loading) to verify whether catalyst loading had any impact on lindane destruction. Figure 4.3 is a graphical representation of catalyst loading vs. destruction efficiency. The destruction efficiency of lindane was found to be ~76% with both catalysts 2 and 3. The results indicate that perhaps the 0.5 cm increased length in catalyst 3 (and hence increased residence time) compared to catalyst 2 had an effect on destruction efficiency similar to the increased loading (0.4 g additional loading) in catalyst 2.



Figure 4.3. Effect of catalyst loading on destruction efficiency.

Since the catalyst loading had no impact on the destruction efficiency of lindane in the previous experiment, the effect of residence time was investigated by comparing the destruction efficiencies of catalysts 1 and 2. As Figure 4.4 shows, the destruction efficiency of lindane is ~78% for catalyst 1 and ~76% for catalyst 2. This indicates that an increased residence time (slower space velocity) had only negligible gains. This slight increase in destruction efficiency observed with catalyst 1 could very well be within experimental uncertainty and indicates that an increase in residence time had either none or negligible gains in destruction efficiency.



Figure 4.4. Impact of space velocity vs. destruction efficiency.

When Lindane is thermally treated, it is known to yield CO, CO₂, water, and HCl with trace quantities of chlorinated and non chlorinated organics. Therefore, for the current study the catalyst was also expected to convert lindane into CO, CO₂, water, HCl and trace quantities of nonchlorinated and chlorinated semi-volatile/volatile compounds such as chlorobenzenes, chlorophenols, and chlorinated dioxins and furans. The untreated lindane and other semi-volatile compounds from the catalytic decomposition of lindane sampled onto XAD traps were extracted and analyzed using GC/MS for chlorobenzene yields. The chlorobenzene yields determined are shown in Figures 4.5 through 4.7 as percentages (%) based on mass of lindane fed into the reactor.



Figure 4.5. Impact of catalyst efficiency on chlorobenzene yields from lindane with catalyst 1 (0.92 g Fe_2O_3 / 7 cm bed length): (a) monochlorobenzene (b) dichlorobenzene (c) trichlorobenzene.



Figure 4.6. Impact of catalyst loading on chlorobenzene yields from lindane with catalyst 2 (0.65 g Fe₂O₃ / 5 cm bed length) and catalyst 3 (0.25 g Fe₂O₃ loading / 5.5 cm bed length) (a) monochlorobenzene (b) dichlorobenzene (c) trichlorobenzene.



Figure 4.7. Impact of space velocity on chlorobenzene yields from lindane with catalyst 1 (0.92 g $Fe_2O_3 / 7$ cm bed length) and catalyst 2 (0.65 g $Fe_2O_3 / 5$ cm bed length).

The results from this phase of the study indicate that only ~78% of lindane was destroyed and that significant amounts of monochlorobenzenes, dichlorobenzenes, and trichlorobenzenes are formed as byproducts during the destruction of lindane when compared to the amount of lindane destructed, which shows that a micro catalyst is inefficient in destroying lindane. As the changes in the catalyst loading and space velocity failed to increase lindane destruction efficiency, micro-sized catalyst particles were replaced with nano-sized particles in the next series of experiments.

4.2. Destruction of Lindane Using Nano Iron Oxide Catalyst

As the second phase of this study, experiments similar to the ones using the micro catalyst were conducted with a foam bed nano catalyst, 7 cm in bed length and 3% Fe_2O_3 loading using the same experimental setup and experimental conditions (air flow, reactor temperature and lindane feed rate). The only difference was that in these experiments, the particle size of the catalyst was nano whereas a micro-sized catalyst was used in earlier experiments. The catalyst efficiency was investigated using the nano particle loaded catalyst where a lindane-acetone mix was injected into the system for 10 min. Again, after each 10 min experiment, the system was flushed with air for an additional 20 min. A

total of 12 experiments were conducted. The experiments showed that the catalyst efficiency was relatively high and remained the same as opposed to the micro catalyst. The catalyst efficiency and the chlorobenzene yields as percentages (%) based on mass of lindane fed into the reactor are shown in Figures 4.8 through 4.11.



Figure 4.8. Efficiency of nano-catalyst (3 wt% Fe_2O_3 loading / 7 cm bed length) with time.



Figure 4.9. Impact of nano-catalyst (3 wt% Fe_2O_3 loading / 7 cm bed length) efficiency on monochlorobenzene yields with time.



Figure 4.10. Impact of nano-catalyst (3 wt% Fe_2O_3 loading / 7 cm bed length) efficiency on dichlorobenzene yields with time.



Figure 4.11. Impact of nano-catalyst (3 wt% Fe_2O_3 loading / 7 cm bed length) efficiency on trichlorobenzene yields with time.

As Figure 4.8 shows, the catalyst efficiency for all 12 experiments is ~99%, which is relatively high when compared to the micro iron oxide catalyst. This proves that nano iron oxide is more efficient than micro iron oxide catalyst in destroying lindane. The impact of oxygen on the destruction of lindane was then investigated by replacing 25% of the air flow with nitrogen, thereby effectively decreasing the amount of oxygen in the system. The results indicate that even at lower oxygen levels the catalyst maintained its destruction efficiency and that oxygen has no impact on the destruction of Lindane (see Figure 4.12). It is possible that the oxygen in the Fe₂O₃ catalyst may have compensated for the oxygen deficiency.



Figure 4.12. Impact of oxygen on lindane destruction for nano-catalyst of 3 wt% Fe_2O_3 loading / 7 cm bed length.

The effect of moisture was also investigated by introducing water into the suspended particle stream. Water in the amount of 5% by volume was added into the lindane-acetone solution, but it had no impact on lindane destruction as it still remained above 99% (see Figure 4.13).



Figure 4.13. Impact of water on lindane destruction for nano-catalyst of 3 wt% Fe_2O_3 loading / 7 cm bed length.

From the above results, it can be clearly observed that the nano catalyst was more efficient than the micro catalyst and that a high destruction efficiency was achieved. It was decided to conduct the next phase of experiments at a larger scale with solid lindane directly fed and vaporized in to the reactor without acetone.

4.3. Phase III: Destruction of Lindane in Gas Phase Using Nano Iron Oxide Catalyst

In the first two sets of experiments (Phase I and II), lindane was mixed with an acetone solution before it was introduced into the reactor. To avoid the use of an additional solvent and to destroy larger amounts of lindane (~10 x scale up), a new experimental setup was designed and another set of experiments (Phase III) were performed with the total gas flow rates and reactor temperatures maintained as in the previous two phases of the study. The experimental conditions for this third phase of the study are listed in Table 4.1.

The first lindane destruction experiment (Experiment 1) was conducted using a lindane feed rate of ~0.225 g/min with an air flow rate of 400 ml/min. In addition to the XAD traps that were used to sample the semi volatiles exiting the reactors, an attempt was made to sample HCl by connecting impingers containing 15 ml of deionized (D.I.) water (commercially available for human consumption) to the back of the XAD traps. The flow rate of air exiting the impingers was measured to verify that the air flow rate was constant while sampling. The measured air flow rates were found to be significantly lower and the air flow had to be increased to maintain the required flow rate (400 ml/min) during sampling. The XAD traps analyzed after feeding ~21 g of lindane showed a lindane destruction efficiency of ~36% for the first reactor and ~63% for the second

reactor (Figure 4.14, 21 g). It was later determined that the reduced flow rate was due to leaks at the impinger connections and by increasing the flow rate during sampling, the flow inside both reactors was increased. Therefore, it was concluded that the low destruction efficiencies observed during the first set of experiments was due to the low residence times for lindane destruction. From the D.I. water sample collected, a 10 ml sample was titrated using a phenolphthalein indicator by adding (~10 ml) a 0.02 N solution of NaOH. When titrated to determine the HCl content, the water samples from the impingers showed only trace levels (<0.002 ppm) of HCl.

•	Reaction g	as flow rate	Lindane	~ Amount	
	Oxygen (ml/min)	Air (ml/min)	feed rate (g/min)	of mass fed (g)	
Experiment 1	-	400	0.225	21	
Experiment 2	-	400	0.195	16	
Experiment 3	-	400	0.195	15	
Experiment 4	100	300	0.215	7	
Experiment 5	100	100 300 0.215		6	
Experiment 6*	100	300	0.215	2	
Experiment 7	100	300	0.175	4	
Experiment 8	200	200	0.175	2	
Experiment 9	200	200	0.200	11	
Experiment 10	200	200	0.168	7	
Experiment 11	200	200	0.185	19	
Experiment 12	200	200	0.191	13	
Experiment 13	200	200	0.210	21	
Experiment 14	200	200	0.188	19	
Experiment 15	200	200	0.185	19	
Experiment 16	200	200	0.218	21	
Experiment 17	200	200	0.218	5	
Experiment 18	200	200	0.220	4	

Table 4.1. Experimental Conditions:

*No samples were obtained, experiment was discontinued!

For Experiment 2, impinger leaks were fixed and samples were collected as in experiment 1. The lindane feed rate for the second experiment was ~0.195 g/min and the air flow was maintained at 400 ml/min. Again, leaks were detected in the system, one at the inlet of reactor 1 and the other at the outlet of reactor 2 before the sampling port. Therefore, the low destruction efficiencies observed during the Experiment 2 (see Figure 4.14) are due to leaks in the system. The water samples from the impingers of the second experiment titrated to determine the HCl content showed levels similar to experiment 1 (<0.002 ppm). After Experiment 2, all system leaks were fixed and the first attempt was made to regenerate the catalyst in reactor 1 (Regeneration 1) since the decreased efficiency was attributed to leaks or a decrease in efficiency or a combination of both. To regenerate the catalyst, reactors 1 and 2 were maintained at 500°C and 300°C, respectively and air was passed for 36 hrs at a flow rate of 400 ml/min (Table 4.2).

Table 4.2. Regeneration Conditions:

	Temperature (°C)		Lindane	Air Flow	Additive	Time
	Reactor 1	Reactor 2	Fed (g)	(ml/min)	Soln. (ml)	(hrs)
REGENERATION 1	500	300	0-37	400	-	36
REGENERATION 2	500	300	37-52	400	60 ml/min (CH ₃ OH soln for 5.5 hrs)	36
REGENERATION 3	800	300	52-59	400	60 (CH ₃ OH soln for 5.5 hrs)	36
REGENERATION 4	500	300	59-67	400	55 (H ₂ O)	24
REGENERATION 5	500	300	67-71	800	55 (H ₂ O)	24
REGENERATION 6	500	300	73-84	800	72 (H ₂ O)	24
REGENERATION 7	500	300	85-91	800	78 (H ₂ O)	24
REGENERATION 8	500	300	92-110	400	76 (H ₂ O)	24
REGENERATION 9-12	500	300	112-182	400	78 (H ₂ O)	24
REGENERATION 13	800	500	182-183	800	78 (H ₂ O)	24
REGENERATION 14	500	500	184-203	400	-	72
REGENERATION 15	650	650	204-208	400	681 (0.95ml/m in) (H ₂ O)	12

After Regeneration 1, Experiment 3 was performed with a lindane feed rate of ~0.195 g/min and an air flow rate of 400 ml/min. The inlet and outlet flow rates were checked every 10 minutes for leaks and to ensure that a constant gas flow rate was maintained throughout the experiment. For this and subsequent experiments, the impingers were removed to prevent leaks and accompanying artifacts, and only semi-volatiles were sampled using the XAD traps. Samples analyzed from the third experiment showed that fixing all the system leaks increased the destruction efficiency of lindane to \geq 95% for both reactors (Figure 4.14). A literature review showed that methanol solution

had been used to wash and restore an iron oxide catalyst [20]. Therefore, to further improve the efficiency of reactor 1 from 95% to 100%, the catalyst was regenerated (Regeneration 2) by using a syringe pump to inject a methanol solution (50% v/v) into the reactor. A total of 60 ml of methanol was injected over a period of 5.5 hrs with reactor 1 at 500°C and reactor 2 at 300°C and air was passed at a flow rate of 400 ml/min for 36 hrs (Table 4.2).

To determine if the observed <100% lindane destruction efficiency in the system was due to an oxygen starved condition, Experiment 4 was conducted after Regeneration 2 by feeding lindane at ~0.215 g/min into the reactor (~7 g) with an increased flow of oxygen into the system. The oxygen in the reactors was increased by introducing oxygen at a flow rate of 100 ml/min and decreasing the air flow rate from 400 ml/min to 300 ml/min to maintain comparable residence times. By introducing additional oxygen into the system, the destruction efficiency increased to ~100% after the first and second reactors (Figure 4.14).

Based on the regeneration conditions used in the study where a methanol solution was used to restore the catalyst to prolong the catalyst efficiency at 100%, the catalyst in reactor 1 was regenerated (Regeneration 3) by increasing reactor 1 temperature to 800°C with reactor 2 at 300°C. Similar to Regeneration 2, while a methanol solution (50% v/v) was injected into the reactor system (a total of 60 ml) over a period of 5.5 hrs (Table 4.2), air was passed into the reactor at a flow rate of 400 ml/min for 36 hrs. After Regeneration 3, Experiment 5 was conducted by feeding lindane at ~0.215 g/min into the reactor (~6 g), with an air flow rate of 300 ml/min and oxygen flow rate of 100 ml/min. Destruction efficiency was determined to be ~100% after the first and second reactors (see Figure 4.14). However, when the reactors were opened after Experiment 5 to determine the external condition of the catalyst, it was observed that the reactor 1 tube had deformed from heating reactor 1 to a temperature 800°C above the melting point of the glass reactor tube during Regeneration 3. Although the deformed glass tube in reactor 1 appeared to be intact, crystalline lindane deposits were observed outside the reactor housing. Therefore, care should be taken when interpreting the destruction efficiency observed from Experiment 5 because of possible experimental artifacts.

After Experiment 5, both glass reactor tubes were replaced with 316 stainless steel tubes and the same catalyst used in the previous experiments was positioned at the center of the tubes. Experiment 6 was initiated with a lindane feed rate of ~0.215 g/min (~2 g) with air and O_2 flow rates of 300 and 100 ml/min, respectively. However, samples were not obtained and the experiment was aborted as the temperature in reactor 1 was accidently increased to 500°C from 300°C (Table 4.1).

In an attempt to avoid the use of the additional solvent methanol during the regeneration process, only water was used for Regeneration 4. Regeneration 4 was performed with reactors 1 and 2 at 500°C and 300°C, respectively. During regeneration, the air flow rate was increased to 800 ml/min and 55 ml of water was injected into the reactor over 24 hrs (Table 4.2). The air flow rate was increased assuming the increased presence of oxygen would assist in restoring and prolonging the active sites of the catalyst during regeneration, as well as assist in flushing out any lindane accumulated inside the reactor assembly. After Regeneration 4, Experiment 7 was performed using a lindane feed rate of ~0.175 g/min (a total feed of ~4 g) with air and O_2 flow rates of 300 ml/min and 100 ml/min, respectively. In addition to the XAD samples collected, volatile

samples were collected by connecting gas sample bags to the back of the XAD sorbent traps. The gas samples collected in the bags were then evacuated through impingers containing 15 ml of D.I. water. The water samples were stored for later analysis. The destruction efficiency was determined to be ~85% after the first reactor and ~100% after the second reactor (Figures 4.14 and 4.15). The decrease in destruction efficiency of the first reactor catalyst could be due to either attempting to regenerate the catalyst at a higher temperature (800°C) during Regeneration 3 (where the maximum temperature the catalyst could withstand had not been evaluated before and the high efficiency observed in Experiment 5 could have been due to leaks in the deformed glass reactor) or the fact that the catalyst efficiency had decreased because it had not been regenerated successfully using the regeneration techniques attempted.

After Experiment 7, Regeneration 5 was performed under conditions similar to Regeneration 4 with reactor 1 at 500°C and reactor 2 at 300°C, and an air flow rate of 800 ml/min with water (55 ml) fed into the reactor for 24 hrs (Table 4.2). For Experiment 8, the oxygen flow rate was increased from 100 ml/min to 200 ml/min and the air flow rate was decreased from 300 ml/min to 200 ml/min to determine whether a further increase in the amount of oxygen flowing into the system would enhance the catalytic destruction of lindane. During Experiment 8, ~2 g of lindane was fed at a rate of ~0.175 g/min and similar to Experiment 7, both XAD and gas sample bags were collected for analysis. Although the oxygen content was increase in the lindane destruction efficiency was observed (Figure 4.15). Experiment 9 was performed at conditions similar to Experiment 8 (Table 4.1) by feeding a total of ~11 g of lindane at a rate of ~0.2 g/min.

Samples analyzed from Experiment 9 showed a small increase (<5%) in the destruction efficiency of reactor 1 when compared to Experiment 8, with reactor 2 maintaining the same destruction efficiency of ~100% (Figure 4.15). The increase in efficiency during Experiment 9 or the lack of it during Experiment 8, despite an increase in the oxygen flow during both experiments, could be due to changes in the feed rates that occurred during the experiments from partial choking of the lindane feeder. To determine the effects of the increased oxygen flow on yields of other toxic organic pollutants formed during the catalytic decomposition of lindane, samples from select experiments were analyzed for chlorobenzenes and chlorinated dioxins and furans. Although the effect of the increased oxygen flow on lindane destruction efficiency was inconclusive, the increased oxygen flow durins and furans. Therefore, for subsequent experiments, the increased oxygen flow rate of 200 ml/min was used with an air flow rate of 200 ml/min similar to Experiments 8 and 9 (Table 4.1).

After Experiment 9, Regeneration 6 was performed with reactor 1 at 500°C and reactor 2 at 300°C, and an air flow rate of 800 ml/min with an increased amount of water (72 ml compared to Regenerations 4 and 5) fed into the reactor for 24 hrs (Table 4.2). Experiment 10 conducted with a lindane feed rate of ~0.168 g/min (a total feed of ~7 g) initially showed a destruction efficiency of ~93% after the first reactor and then decreased to ~77% after a total lindane feed of ~5 g. However, the efficiency after reactor 2 remained ~100% throughout the experiment (Figure 4.15).



Figure 4.14. Destruction efficiency of lindane for experiments 1 through 7, and regenerations 1 through 4.

It was suspected that the Cl expected to be formed during the lindane destruction was reducing the catalyst efficiency. Therefore, to understand the effects and mechanism leading to the decrease in the efficiency of the catalyst, the water samples collected by passing the gas collected in the sample bags from Experiment 7 through 10 were titrated. All the samples titrated showed only trace levels of chlorine ions (~4.25 x 10^{-4} g/min) compared to the amount of lindane destroyed by the catalyst (Av. ~0.2 g/min).



Figure 4.15. Destruction efficiency of lindane for experiments 7 through 12, and regenerations 5 through 8.



Figure 4.16. Total chlorobenzene yields from experiments 3 through 5 and 9 after reactor 1 (shown as -1) and after reactor 2 (shown as -2) sampled at 10 minute intervals.

To verify that the lindane fed by the feeding unit was being transported into the reactor tube, after the experiment the heated tube of the feeding unit and reactor 1 were disassembled and the catalyst in reactor 1 was removed. Then, the inside of both the reactor tube and the feeding unit heated vaporizer tube were washed with acetone. When the catalyst was removed from the reactor tube, pitting-type corrosion was observed inside of the tube wall at the location of the catalyst with general corrosion observed on the surface downstream of the catalyst inside of the reactor tube. The reactor wash was filtered using a pre-cleaned quartz filter to remove corroded metal particles in the wash, concentrated, and analyzed using GC/MS. Only lindane was detected. Lindane detected in the reactor wash (~0.85 g) was <1% of the total mass of lindane fed into the reactor during the experiments (~91 g).

After the reactor wash, the catalyst removed from the first reactor tube was first Soxhlet extracted with methanol and then with acetone for 24 hrs at ~4 cycles/hr. Methanol was used since it had been used in a previous study to wash and restore an iron oxide catalyst and acetone was used due to the low solubility of lindane in methanol to determine if lindane or any other methanol insoluble compounds were trapped on the catalyst. The extract with methanol had solid residue that was filtered using a pre-cleaned quartz filter with a filtering efficiency of up to 0.3 µm. Both samples were then concentrated for GC/MS analysis. After concentrating, a reddish-brown ultra-fine residue that appeared to be nano iron oxide particles washed away from the surface of the catalyst was observed at the bottom of the sample vial containing the extract from methanol. The mass of the nano iron oxide particles found in the catalyst wash sample was estimated to be <1% of the total iron oxide present in the catalyst. The GC/MS analysis showed that the catalyst sample washed with methanol contained a small quantity of lindane (~0.0003 g) and a bulk of chlorophenols, chloropyridnes, and oxygenated chlorine compounds. After the catalyst was extracted and the reactor tube washed, the reactor tube was replaced with a new stainless steel reactor tube and the system was reassembled and checked for leaks before conducting the seventh regeneration.

Regeneration 7 was performed with reactor 1 at 500°C and reactor 2 at 300°C, and an air flow rate of 800 ml/min with water (78 ml) fed into the reactor for 24 hrs (Table 4.2). Experiment 11 was then conducted using a lindane feed rate of ~0.185 g/min (~19 g) with both air and oxygen flow rates at 200 ml/min (Table 4.1). During Experiment 11, a gas sample exiting the XAD trap at the end of the first reactor was passed into a beaker containing 125 ml of D.I. water for 2 min to determine the HCl content exiting reactor 1. Similar to the observations from Experiments 1, 2 and 7 through 10, the chlorine ion content from Experiment 11 that was determined using a chlorine ion analyzer showed a low level of chlorine ions (1.56×10^{-4} g/min). In addition, Experiment 11 showed that the first catalyst efficiency decreased from ~77% in Experiment 10 to ~58%, and the second catalyst efficiency decreased to ~98% and remained constant throughout the experiment (Figure 4.15).

Regeneration 8 was performed with reactors 1 and 2 at 500°C and 300°C, respectively, and an air flow rate of 400 ml/min with water (76 ml) fed into the reactor for 24 hrs (Table 4.2). The air flow rate was reduced from 800 ml/min to 400 ml/min to increase the residence time of the oxygen in the reactor during Regeneration 8, as the additional air flow did not successfully regenerate the catalyst. Experiment 12 was conducted by feeding lindane at ~0.191 g/min into the reactor (~13 g) with both air and O₂ flow rates maintained at 200 ml/min each (Table 4.1). From Experiment 12 it could be observed that the catalyst destruction efficiency further decreased to $\sim 46\%$ for the first reactor and 92% for second reactor (Figure 4.17). We were unable to effectively regenerate the catalyst either because the techniques used to regenerate the catalyst were inadequate or due to a decrease in nano iron oxide that was washed away during Soxhlet extraction of the catalyst. This could not only reduce the effectiveness of the regeneration but also the efficiency of the catalyst. Despite attempts to regenerate the catalyst in reactor 1, a steady decrease in catalyst efficiency (reactor 1) was observed throughout the last experiments (Figure 4.15). This increased the amount of lindane entering the second reactor and therefore caused the efficiency of the catalyst in the second reactor to

gradually decrease and the lindane exiting the second reactor to increase. The lindane exiting the second reactor condensed and completely clogged the retaining screen in the carbon trap at the end of Experiment 12. The gradual buildup of lindane at the carbon trap can lead to an increase in back pressure that can lead to sampling artifacts. After Experiment 12, the clogged carbon trap was replaced and the next regeneration (Regeneration 9) was performed.



Figure 4.17. Destruction efficiency at 112 to 212 g of feed, for experiments 12 through 18 and regenerations 9 through 15.

During Regeneration 9, reactors 1 and 2 were at 500°C and 300°C, respectively, the air flow rate was at 400 ml/min, and a total of 79 ml of water was fed into the reactor for 24 hrs (Table 4.2). Experiment 13 was conducted by feeding lindane into the reactor at a flow rate of ~0.21 g/min with air and O_2 flow rates maintained at 200 ml/min each (Table 4.1). Experiment 13 showed that the destruction efficiency in the first reactor increased to ~70% and the second reactor catalyst efficiency remained at ~90% throughout the experiment and later decreased significantly to ~37% for the first reactor and to ~79% for the second reactor (Figure 4.17) at the end of the experiment (after a total of ~21 g). Since the efficiency of the catalyst in the first reactor was very low, another attempt was made to regenerate the catalyst (Regeneration 10).

During Regeneration 10, reactors 1 and 2 were kept at 500°C and 300°C, respectively, the air flow rate was at 400 ml/min and a total of 78 ml of water was fed into the reactor for 24 hrs (Table 4.2). Experiment 14 had a lindane feed rate of ~0.188 g/min (~19 g) and air and O_2 flow rates of 200 ml/min each (Table 4.1). At the start of Experiment 14 (~the first 10 minutes), the temperature control of the first reactor malfunctioned and the temperature increased to ~850°C and had to be reset to 300°C before continuing the experiment. Although the temperature in reactor 1 increased for a relatively short period (~30 min) to a temperature above normal regeneration temperatures, the high temperature may have affected the efficiency of the catalyst. However, Experiment 14 showed an increase in the destruction efficiency (to ~60%) for the first catalyst compared to Experiment 13 and therefore an increase in the second catalyst efficiency since the amount of lindane entering the second reactor decreased.

During the experiment, as more lindane was fed into the system the second catalyst efficiency gradually decreased to ~86% (Figure 4.17).

The increase in catalyst efficiency after both Regenerations 9 and 10 indicated a partial restoration of the catalyst. Although the last three attempts at catalyst regeneration were conducted under similar conditions (8 through 10), it is believed that a similar effect from regeneration was not observed because the carbon trap clogged during Experiment 12. Since the exhaust gas analyzed during the experiments showed only trace levels of chlorine ions, it was hypothesized that the chlorine formed during the lindane destruction process was deactivating the catalyst by forming iron chloride. To validate the hypothesis, the exhaust during the regeneration had to be analyzed for the chlorine ion content. Accordingly, Regeneration 11 was performed at conditions similar to Regenerations 8 through 10). During the regeneration, reactors 1 and 2 were kept at 500°C and 300°C, respectively, and a total of 78 ml of water was fed into the reactor with an air flow rate of 400 ml/min over 24 hrs (Table 4.2). All of the gas exiting the carbon trap behind the reactors was passed through a beaker containing 125 ml of D.I. water and later analyzed for Cl ions. Again, the chlorine ion analysis showed a low Cl ion content (2.5 ppm); however, it was later determined that sampling the gas exiting the coal trap resulted in erroneous Cl content since most of the HCl could have been absorbed by the coal in the trap. Therefore, Experiment 15 was performed before attempting to regenerate and validate this hypothesis.

Experiment 15 was conducted with a lindane feed rate of ~0.185 g/min and air and O_2 flow rates were kept at 200 ml/min each (Table 4.1). Experiment 15 showed a further increase in efficiency of reactor 1 to ~71% at the beginning of the experiment and after destroying a total of ~19 g of lindane, gradually decreased in efficiency to ~39%. Initially, the second catalyst showed a small gain in efficiency from the increased efficiency of the first reactor but efficiency decreased by <5% at the end of the experiment (Figure 4.17, 163 to 182 g).

To determine the mechanism of regeneration, Regeneration 12 was performed by isolating reactor 2 and passing the entire gas exiting reactor 1 through 100 ml of D.I. water. During Regeneration 12, reactor 1 was at 500°C and 78 ml of water was fed into the reactor with an air flow rate of 400 ml/min over 24 hrs (Table 4.2). The D.I. water sample from Regeneration 12 was analyzed for chlorine ions and showed a higher chlorine yield (17.31 ppm) than the previous observations. This observation supported the hypothesis that the chlorine ions formed during the lindane destruction process were deactivating the catalyst by chlorinating iron oxide and that the iron chloride formed was reconverted to iron oxide during regeneration. However, when compared to the lindane mass fed to the reactor or the Fe_2O_3 loading of the catalyst, the chlorine yield indicated that the attempted regeneration technique did not effectively restore the catalyst. To further understand a possible mechanism of regeneration, a liquid-to-liquid extraction (LLE) was performed on the D.I. water using 100 ml of methylene chloride. This was repeated three times and the methylene chloride extract was then concentrated together and analyzed using GC/MS. Only lindane was detected in the sample from LLE.

Since Regeneration 12 indicated that the catalyst was not restored and no attempt had been made to restore the catalyst in reactor 2, Regeneration 13 was performed with the temperatures of reactors 1 and 2 increased to 800°C and 500°C, respectively. During Regeneration 13, 78 ml of water was fed into the reactor at an increased air flow rate of 800 ml/min for 24 hrs (Table 4.2). After the two consecutive regenerations (Regenerations 12 and 13), Experiment 16 was conducted by feeding lindane into the reactor at ~0.218 g/min (~21 g) with air and O_2 flow rates maintained at 200 ml/min each (Table 4.1). Experiment 16 showed that the destruction efficiency of the first reactor had increased to ~52%, but the efficiency of the second reactor had decreased to ~70% compared to Experiment 15. After feeding ~16 g, the first catalyst efficiency decreased by ~5% and the second catalyst efficiency decreased by ~20% (Figure 4.17). The results also showed that attempting to regenerate both catalysts concurrently affected the efficiency of the second reactor because the regeneration technique attempted was inadequate to counter the impact from the first reactor. As hypothesized before, it is believed that the HCl/Cl ions in effluents from the first reactor deactivated the active sites of the second catalyst.

Although the observations from the attempted regenerations and experiments supported the hypothesis that chlorine from lindane destruction was deactivating the catalyst, no technique to successfully restore the catalyst had been determined. Another attempt was made to concurrently restore both catalysts (Regeneration14). For Regeneration 14, both reactors were maintained at 500°C and air was passed at a flow rate of 400 ml/min without feeding any water into the system for 72 hrs (Table 4.2). Regeneration 14 was performed to determine whether the catalyst could be restored if only oxygen was available in the system over an extended regeneration time (72 vs. 24 hrs).

After Regeneration 14, Experiment 17 was performed by feeding lindane into the reactor at ~0.218 g/min (~5 g) with air and O_2 flow rates kept at 200 ml/min each (Table

4.1). The destruction efficiencies increased in reactor 1 by $\sim 5\%$ and in reactor 2 by $\sim 16\%$ (Figure 8, Experiment 17). Since no significant increase in efficiency was observed in the first catalyst, another technique widely used in the steel manufacturing industry known as the Ruthner process was attempted (Regeneration 15) [26]. During Regeneration 15, both reactors 1 and 2 were maintained at 650°C and water was fed at 0.95 ml/min (681 ml) with an air flow rate of 400 ml/min for 12 hrs (Table 4.2). The reactor temperatures and the amount of water fed into the reactors during the regeneration were based on the Ruthner process, which is used commercially. To determine whether the catalyst was regenerated, the exhaust from the second reactor was passed through D.I. water (450 ml) and analyzed for Cl ions. The chlorine ion analysis showed 0.85 g (1700 ppm) in the exhaust gas and only lindane was detected in a LLE performed on the water sample. The high chlorine ion yield observed from the regeneration was comparable to the mass of Cl that could have deactivated the estimated mass of iron in both catalyst and confirmed the hypothesis that chlorine was deactivating the catalyst. To further validate the hypothesis and confirm the regeneration of the catalyst, Experiment 18 was performed.

Experiment 18 was conducted with a lindane feed rate of 0.22 g/min (~4 g) and with air and O_2 flow rates of 200 ml/min each (Table 4.1). Although chlorine estimates indicated that the catalyst should have been regenerated successfully, the destruction efficiencies of both the first and second reactors only increased by ~15% and ~5%, respectively, to an average catalyst efficiency of ~70% (Figure 4.17). Therefore, to determine the condition of the two catalysts, the reactors were disassembled and the catalysts removed. Analysis of the surface areas of the two catalysts showed that the surface areas had decreased in the first catalyst by 99% and second catalyst by 95%.

Also, the ICP analysis of the catalyst showed a strong bonding of the iron coated to the aluminum silicate of the catalyst. Therefore, it is believed that the thermal cycling and the elevated temperatures (in excess of 550°C, typical glass/silica softening temperatures) used during the regenerations may have caused the decrease in the active surface area of the catalyst. Despite the loss of surface area of the catalyst to >99%, the Fe₂O₃ mass loaded on the catalyst was able to maintain an efficiency of ~70%. Therefore, the observations from this study suggest that an increase in catalyst loading will be more likely to enable the catalyst. Also, feeding excess oxygen and water during the experiment could inhibit catalyst deactivation by simultaneously regenerating the active sites similar to a process that is observed during catalyst regeneration (Rxn 4.1 through 4.6)

Based on the observations of this study and the physical effects that could contribute to the decrease in catalyst efficiency, a kinetic mechanism has been proposed to explain the deactivation and regeneration of the catalyst.

4.4. Catalyst Deactivation

The chlorine from lindane destruction reacts with iron oxide and forms iron chloride on the surface of the catalyst. At low levels of oxygen and water in the reactor, the chlorine on the iron surface blocks the active oxidation sites and thereby inhibits the dissociative adsorption of oxygen and water vapor. The poisoning effect of chlorine on the activity of iron catalyst is strong.

4.5. Catalyst Activation Through Regeneration

During regeneration of the catalyst, a volume of 681 ml of water at a flow rate of 0.95 ml/min along with air at a flow rate of 400 ml/min was fed through the heated reactors containing the catalysts. Regeneration of iron oxide catalyst occurs as in the Ruthner process as:

$$FeCl_2 + H_2O + \frac{1}{4}O_2 \rightarrow \frac{1}{2}Fe_2O_3 + 2 HCl$$
 (Rxn 4.1)

The proposed mechanism for Rxn 1 is shown below.

Moisture is adsorbed on the surface of iron chloride and forms the complex (FeCl(OH)).

$$FeCl_2 + H_2O \rightarrow (FeCl(OH))_{comp} + HCl$$
 (Rxn 4.2)

The complex further reacts with moisture present in the gas phase and forms ferrous hydroxide which is a stable compound when compared to iron chloride.

$$(FeCl(OH))_{comp} + H_2O \rightarrow Fe(OH)_2 + HCl$$
 (Rxn 4.3)

Oxygen in the gas phase is adsorbed on the surface of the catalyst and splits into adsorbed oxygen molecules,

$$O_{2 g} \rightarrow O_{2 ads}$$
 (Rxn 4.4)

$$O_{2 ads} \rightarrow O_{ads}$$
 (Rxn 4.5)

but due to the high temperature and the presence of oxygen, ferrous hydroxide is oxidized and forms the more stable ferric oxide.

$$Fe(OH)_2 + \frac{1}{2} Oads \rightarrow \frac{1}{2} Fe_2O_3 + H_2O$$
 (Rxn 4.6)

4.6. Economics

The following calculations and analysis will provide insight into economics of the process. In the current system, on average 94% of lindane fed into the reactor was destroyed using two catalysts each having a length of 7 cm and an I.D. of 3.4 cm

involving 12 restorations for catalyst 1. A gas flow rate of 400 ml/min (200 ml/min air + 200 ml/min oxygen) was maintained during the experiment. To commercialize the process, considering two catalysts used in the process as a single catalyst, and calculating its volume

Length of the catalyst = $2 \times 7 \text{ cm} = 14 \text{ cm}$

I.D of the catalyst = 3.4 cm

Area of the catalyst = $3.14 \times 1.7 \times 1.7 = 9.0746 \text{ cm}^2$

Volume of the catalyst = $3.14 \times 1.7 \times 1.7 \times 14 = 127 \text{ cm}^3$

Lindane flow rate during the experiments = 12 g/hr

Total amount of time lindane fed over the catalyst = 17 hrs

Total amount of lindane fed over the catalyst = $17 \times 12 = 204 \text{ g}$

Destructed amount of Lindane = 197 g

127 cm³ of catalyst volume is required for destructing 197 g of lindane.

197 g	0.004523 ft3			
1 ton	?			

Volume of catalyst required to destroy 1 ton of lindane = $(10^{6} \times 0.004523)/197$

$$= 23 \text{ ft}^{3}$$

If we consider a cost of \$30 per 1 ft3 of catalyst, then cost estimated to destroy 1 ton of lindane is \$690. To reduce this cost to \$200 per ton of lindane, we must be able to regenerate the catalyst 4 times and can be achieved with the restoration process discussed above.

It was estimated that lindane destruction by incineration and other heating techniques costs around \$1000 per ton of lindane. Therefore, the destruction of lindane using nano iron oxide catalyst is economical when compared to other destruction techniques of lindane.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

The results of the study show that use of a nanoparticle-loaded catalyst bed is the most efficient to destruct lindane when compared to a micro particle loaded catalyst. During these experiments, ~200 g of lindane was destroyed using two catalysts in series. It was found that chlorine from lindane deactivated the catalyst by forming iron chloride on its active sites. Injecting excess water along with air proved to be effective in restoring the actives sites by converting iron chloride to iron oxide and thereby prolonging the life of the catalyst. Contrary to the observation made with a micro particle loaded catalyst, the study indicates that with the nanoparticle catalyst, an increase in catalyst loading would increase destruction efficiency.

To further validate observations of this study, it is recommended that the experiments be repeated with the technique identified in Regeneration 15 to see how much more lindane could be efficiently dechlorinated. It is also recommended that water be introduced into the reactor with lindane to see if it will prolong the life of the catalyst. Also recommended is an effort to design a system and perform studies to destroy lindane at a larger feed rate. The design of a recommended scale up system is given in appendix C.

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APPENDICES

Names	Graph X-axis	Conditions	Lindane (ml/br)	Weight of Lindane (gms)	Air Flow Rate (ml/hr)
Standard		Conditions	(111/111)	0.1	
OM 1-1a	1st 10 Min	4 6/400	4.6	0 239583333	400
OM 1-22	2nd 10 Min	4.6/400	4.6	0.239583333	400
OM 2 1a	1st 10 Min	4.6/400	4.0	0.239583333	400
OM 2-1a	1st 10 Min	4.6/400	4.0	0.229585555	400
OM 5-1a	1st 10 Min.	4.6/400	4.0	0.239583333	400
OM 5-1a	1st 10 Min.	4.6/400	4.0	0.239383333	400
OM 5-2a	2nd 10 Min.	4.6/400	4.0	0.239383333	400
OM 5-3a	3rd 10 Min.	4.6/400	4.0	0.239583535	400
OM 5-4a	4th 10 Min.	4.6/400	4.6	0.239583333	400
OM 5-5a	Sth 10 Min.	4.6/400	4.6	0.239583333	400
OM 5-6a	6th 10 Min.	4.6/400	4.6	0.239583333	400
OM 5-7a	7th 10 Min.	4.6/400	4.6	0.239583333	400
OM 5-8a	8th 10 Min.	4.6/400	4.6	0.239583333	400
OM 5-9a	9th 10 Min.	4.6/400	4.6	0.239583333	400
OM 5-10a	10th 10 Min.	4.6/400	4.6	0.239583333	400
OM 5-11a	11th 10 Min.	4.6/400	4.6	0.239583333	400
OM 5-12a	12th 10 Min.	4.6/400	4.6	0.239583333	400
OMN1-1A	1st 10 Min.	4.6/100/300	4.6	0.239583333	100+300
OMN1-2A	2nd 10 Min.	4.6/100/300	4.6	0.239583333	100+300
OMR-1A	1st 10 Min.	4.6/400	4.6	0.239583333	400
OMR-2A	2nd 10 Min.	4.6/400	4.6	0.239583333	400
OMW1-A	1st 10 Min.	4.6/400	4.6	0.239583333	400
OMW2-A	2nd 10 Min.	4.6/400	4.6	0.239583333	400
OMW3-A	3rd 10 Min.	4.6/400	4.6	0.239583333	400
OMAW1A	1st 10 Min.	4.6/400	4.6	0.239583333	400
OMAW2A	2nd 10 Min.	4.6/400	4.6	0.239583333	400
1-HRE-A	1ST 1 HOUR	4.6/400	4.6	1.4375	400
1-HRSJKF	2ND I HOUR	4.6/400	4.6	1.4375	400

Appendix A: List of % Destruction of Lindane.

Areas		Area Ratio		
Lindane	Int Std		Mass of Lindane	
219	188	219/188	Remaining	% Destruction
56804931	638046	89.02952295		
45522297	2011788	22.62778036	0.050832083	78.7831307
44599835	1190529	37.46219958	0.084156802	64.87368274
59962997	2405067	24.93194452	0.056008263	76.62263821
38961584	1541738	25.27120951	0.056770403	76.30452742
0	2639975	0	0	100
2322792	2655831	0.874600831	0.001964743	99.1799332
961102	1957608	0.490957332	0.001102909	99.53965535
1144354	2471596	0.463002044	0.001040109	99.56586754
1918374	4332241	0.442813315	0.000994756	99.58479744
3117689	3044337	1.024094573	0.002300573	99.03976084
1258760	2520977	0.499314353	0.001121683	99.53181942
609942	3421695	0.178257267	0.000400445	99.83285762
291412	2229760	0.130692092	0.000293593	99.87745696
4234969	2539159	1.667862863	0.003746764	98.43613347
550869	2925469	0.18830109	0.000423008	99.82344006
782743	2466076	0.317404249	0.000713031	99.70238687
528961	2265843	0.233449979	0.000524433	99.78110634
1248729	2833547	0.440694649	0.000989997	99.58678401
1755043	3352598	0.523487457	0.001175986	99.50915358
1697457	2525465	0.672136418	0.001509918	99.36977334
342947	1610975	0.21288164	0.000478227	99.80039218
1512522	2377456	0.636193477	0.001429174	99.40347512
2604763	2629393	0.990632819	0.002225403	99.07113616
1317344	2656496	0.495895345	0.001114002	99.53502524
15004	2747938	0.005460094	1.22658E-05	99.99488036
45929810	2611279	17.58900906	0.039512756	97.25128654
250504139	3328872	75.25195892	0.169049449	88.24003834
251285072	3104894	80.93193262	0.181809202	87.35240334
78274	2177436	0.035947784	8.07548E-05	
9372442	2722778	3.4422351	0.007732795	
			0.007813549	96.73869242
37082622	2143252	17.30203541	0.038868085	

Areas		Area Ratio		
Lindane	Int Std		Mass of Lindane	
Graph x-axis	164	219/164	Remaining	% Destruction
56804931	33447	1698.356534		
45522297	1416371	32.14009394	0.003784847	98.42023798
44599835	1864493	23.92062346	0.002816914	98.82424449
59962997	2073499	28.91874894	0.003405498	98.57857475
38961584	2276013	17.11834862	0.002015872	99.15859247
0	2227566	0	0	100
2322792	2162843	1.073953126	0.00012647	99.94721265
961102	1985376	0.484090671	5.7007E-05	99.97620579
1144354	2123932	0.538790319	6.34484E-05	99.97351718
1918374	3180360	0.603193978	7.10327E-05	99.97035158
3117689	2234123	1.39548673	0.000164334	99.93140851
1258760	1859322	0.676999465	7.97241E-05	99.96672387
609942	2431335	0.250867116	2.95423E-05	99.98766928
291412	1772974	0.16436338	1.93556E-05	99.99192115
4234969	2103371	2.013419886	0.000237102	99.90103563
550869	2135471	0.257961358	3.03778E-05	99.98732059
782743	1977645	0.395795504	4.66092E-05	99.98054571
528961	1968726	0.268681879	3.16402E-05	99.98679365
1248729	2251669	0.554579292	6.53078E-05	99.97274111
1755043	2538288	0.691427844	8.14232E-05	99.96601468
1697457	1823383	0.930938261	0.000109628	99.95424217
342947	1376584	0.249129003	2.93377E-05	99.98775472
1512522	1596664	0.947301373	0.000111555	99.95343789
2604763	1938324	1.343822292	0.00015825	99.93394794
1317344	1935518	0.680615732	8.01499E-05	99.96654612
15004	1954420	0.007676958	9.04045E-07	99.99962266
45929810	1589467	28.8963596	0.003402861	99.76327921
250504139	2334133	107.3221359	0.012638352	99.12081032
251285072	2281437	110.1433316	0.012970578	99.0976989

		Areas						
		Chloro Benzenes						
Names	Graph x- axis	164	mcl	dcl	tcl	tecl	pcl	
standard		33447	2436671	2436671	2436671	2436671	2436671	
OM 1-2a	1st 10 Min.	1416371	101753765	103844135	26385345	0	0	
OM 1-1a	2nd 10 Min.	1864493	117605137	201853318	70842683	0	0	
OM 2-1a	1st 10 Min.	2073499	98595355	139070139	44447437	0	0	
OM 3-1a	1st 10 Min.	2276013	107771393	104708107	24697434	0	0	
OM 5-1a	1st 10 Min.	2227566	80639075	23726062	6866100	0	0	
OM 5-2a	2nd 10 Min.	2162843	120824246	170600048	104238090	0	0	
OM 5-3a	3rd 10 Min.	1985376	104033456	147669402	79234775	0	0	
OM 5-4a	4th 10 Min.	2123932	107190252	133561605	70871265	0	0	
OM 5-5a	5th 10 Min.	3180360	130601301	178320947	109668913	0	0	
OM 5-6a	6th 10 Min.	2234123	120257781	188582455	130062734	0	0	
OM 5-7a	7th 10 Min.	1859322	131038553	149359774	71681855	0	0	
OM 5-8a	8th 10 Min.	2431335	114593300	128738640	41006712	0	0	
OM 5-9a	9th 10 Min.	1772974	106933709	116381005	42126286	0	0	
OM 5-10a	10th 10 Min.	2103371	111169034	147791648	140986079	0	0	
OM 5-11a	11th 10 Min.	2135471	114701389	142742908	102807370	0	0	
OM 5-12a	12th 10 Min.	1977645	103528233	119594887	53733495	0	0	
OMN1-1A	1st 10 Min.	1968726	120976947	100111784	32268672	0	0	
OMN1-2A	2nd 10 Min.	2251669	122922284	98610761	36852934	0	0	
OMR-1A	1st 10 Min.	2538288	113302344	157904008	127219050	0	0	
OMR-2A	2nd 10 Min.	1823383	117652330	152183551	48266494	0	0	
OMW1-A	1st 20 Min.	1376584	126142057	148787505	64600793	0	0	
OMW2-A	2nd 20 Min.	1596664	112185417	100449221	54101606	0	0	
OMW3-A	3rd 20 Min.	1938324	110141659	126723891	101149991	0	0	
OMAW1A	1st 10 Min.	1935518	142142326	192182669	65408312	0	0	
OMAW2A	2nd 10 Min.	1954420	213275172	29201507	1181256	0	0	
1-HRE-A	1ST 1 HOUR	1589467	136451695	327387817	103660452	0	0	
1-HRSJKF	2ND I HOUR	2334133	111594530	550292241	280548038	0	0	
1- HRSJK2A	3RD I HOUR	2281437	1526408	584682162	835203792	0	0	
TESTJK1A	1st trap	1654851	12445532	0	0	0	0	
TESTJK2A	2nd trap	1953077	181919145	115292137	79658000	0	0	
testjkfinal1	1st 10 Min.							
TESTJK3A	1st trap	1445683	37610445	139040685	279773496	0	0	
TESTJK4A	2nd trap	1386119	116304022	5855799	0	0	0	
testjkfinal2	2nd 10 Min.							

Appendix B: Chlorobenzene Yield Calculations.

					W_{α} : -1-4	Walt	Weister	Weister
Areas Ratios					of	of	of	of
					mcl	dCL	tCL	lindane
mcl/164	dcl/164	tcl/164	tecl/164	pcl/164	(GMS)	(GMS)	(GMS)	(GMS)
72.852	72.852	72.852	72.852	72.852				
71.841	73.317	18.629	0.000	0.000	0.109	0.111	0.028	0.240
63.076	108.262	37.996	0.000	0.000	0.096	0.165	0.058	0.240
47.550	67.070	21.436	0.000	0.000	0.072	0.102	0.033	0.240
47.351	46.005	10.851	0.000	0.000	0.072	0.070	0.016	0.240
36.201	10.651	3.082	0.000	0.000	0.055	0.016	0.005	0.240
55.864	78.878	48.195	0.000	0.000	0.085	0.120	0.073	0.240
52.400	74.379	39.909	0.000	0.000	0.080	0.113	0.061	0.240
50.468	62.884	33.368	0.000	0.000	0.077	0.096	0.051	0.240
41.065	56.069	34.483	0.000	0.000	0.062	0.085	0.052	0.240
53.828	84.410	58.216	0.000	0.000	0.082	0.128	0.088	0.240
70.477	80.330	38.553	0.000	0.000	0.107	0.122	0.059	0.240
47.132	52.950	16.866	0.000	0.000	0.072	0.080	0.026	0.240
60.313	65.642	23.760	0.000	0.000	0.092	0.100	0.036	0.240
52.853	70.264	67.029	0.000	0.000	0.080	0.107	0.102	0.240
53.712	66.844	48.143	0.000	0.000	0.082	0.102	0.073	0.240
52.349	60.473	27.170	0.000	0.000	0.080	0.092	0.041	0.240
61.449	50.851	16.391	0.000	0.000	0.093	0.077	0.025	0.240
54.592	43.795	16.367	0.000	0.000	0.083	0.067	0.025	0.240
44.637	62.209	50.120	0.000	0.000	0.068	0.095	0.076	0.240
64.524	83.462	26.471	0.000	0.000	0.098	0.127	0.040	0.240
91.634	108.085	46.928	0.000	0.000	0.139	0.164	0.071	0.240
70.262	62.912	33.884	0.000	0.000	0.107	0.096	0.051	0.240
56.823	65.378	52.184	0.000	0.000	0.086	0.099	0.079	0.240
73.439	99.293	33.794	0.000	0.000	0.112	0.151	0.051	0.240
109.125	14.941	0.604	0.000	0.000	0.166	0.023	0.001	0.240
85.847	205.973	65.217	0.000	0.000	0.130	0.313	0.099	1.438
47.810	235.759	120.194	0.000	0.000	0.073	0.358	0.183	1.438
0.669	256.278	366.087	0.000	0.000	0.001	0.389	0.556	1.438
7.521	0.000	0.000	0.000	0.000	0.011	0.000	0.000	
93.145	59.031	40.786	0.000	0.000	0.142	0.090	0.062	
					0.153	0.090	0.062	0.240
26.016	96.176	193.523	0.000	0.000	0.040	0.146	0.294	
83.906	4.225	0.000	0.000	0.000	0.127	0.006	0.000	
					0.167	0.153	0.294	0.240

mcl/weight of lindane	dcl/weight of lindane	tcl/weight of lindane	
			graph x-axis
0.400052352	0.686635778	0.240982517	
0.455643055	0.46500352	0.118150903	1st 10 Min.
0.400052352	0.686635778	0.240982517	2nd 10 Min.
0.301580959	0.425384197	0.135954688	1st 10 Min.
0.300317093	0.291780903	0.068822174	1st 10 Min.
0.229597022	0.06755327	0.019549283	1st 10 Min.
0.354307538	0.500271137	0.305669948	2nd 10 Min.
0.332339186	0.471736024	0.253118772	3rd 10 Min.
0.320085483	0.398834129	0.211631773	4th 10 Min.
0.260448892	0.35561279	0.218704918	5th 10 Min.
0.341395192	0.535359482	0.369230096	6th 10 Min.
0.446987908	0.509483746	0.244515233	7th 10 Min.
0.298927395	0.335826844	0.106969863	8th 10 Min.
0.382528288	0.4163236	0.15069613	9th 10 Min.
0.335211758	0.445641168	0.425120105	10th 10 Min.
0.34066404	0.423947575	0.305338709	11th 10 Min.
0.3320181	0.383544333	0.172324905	12th 10 Min.
0.389734307	0.322515965	0.103955413	1st 10 Min.
0.346240101	0.277760864	0.103805129	2nd 10 Min.
0.283106142	0.394551365	0.317879517	1st 10 Min.
0.409236088	0.529347792	0.167887803	2nd 10 Min.
0.581177088	0.685511962	0.297636662	1st 20 Min.
0.44562974	0.399010508	0.214905692	2nd 20 Min.
0.360393155	0.414651671	0.33097163	3rd 20 Min.
0.465776418	0.629750179	0.214332002	1st 10 Min.
0.692107724	0.094762969	0.003833341	2nd 10 Min.
0.090745994	0.217726375	0.068938468	1ST 1 HOUR
0.050537919	0.249211359	0.127052051	2ND I HOUR
0.000707232	0.270901498	0.38697599	3RD I HOUR
			1st trap
			2nd trap
0.638457608	0.374396359	0.258679091	1st 10 Min.
			1st trap
			2nd trap
0.697165067	0.636780314	1.227396242	2nd 10 Min.



Appendix C: Design of a Recommended Scale Up System.