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Catalytic Hydrodechlorination

Bijan F. Hagh
Graduate Research Assistant
Department of Chemical Engineering
University of California
Los Angeles, CA 90024

David T. Allen
Associate Professor
Department of Chemical Engineering
University of California
Los Angeles, CA 90024

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Abstract

Chlorinated organics are among the most significant and widespread toxic materials in the environment. Because chlorinated organics are very difficult to destroy by incineration, new technologies must be developed for recycling or destroying these materials. A process for recycling chlorinated organics that has been under development at the UCLA Engineering Research Center for Hazardous Substances Control is catalytic hydrodechlorination (HDC). Catalytic HDC has potential applications in recycling of agricultural chemical wastes, in PCB and PCP remediation and in oil recycling. All of these applications involve hydrogenating a carbon-chlorine bond. Therefore, this chapter will focus on the basic chemistry of HDC.

Our initial efforts in catalytic HDC of chlorinated organics were focused toward identifying a suitable catalyst. A catalyst screening study in a batch autoclave reactor was performed in order to identify catalysts with a high dechlorination activity that would also be relatively unaffected by the wide variety of functionalities present in waste streams. Hydroprocessing catalysts used in heavy oil upgrading were logical candidates for robust dechlorination activity. Noble metal catalysts were also screened. Chlorobenzene and 1,2-dichlorobenzene were used as model compounds in the screening study. Presulfided NiMo supported on Al₂O₃ showed excellent dechlorination activity with both compounds. Reduced Pd supported on Al₂O₃ also showed good activity with chlorobenzene but was less successful with dichlorobenzene.

Based on these early results, presulfided NiMo supported on Al₂O₃ was used in all subsequent experiments. A fixed bed, continuous-flow micro-reactor was constructed. Unlike the batch autoclave used in the catalyst screening, this reactor system allowed the determination of reaction mechanisms and reaction rates. These data on rates and mechanisms can be used to design and optimize a commercial reactor. The dechlorination reactions of chlorobenzene have been examined in the new reactor system and the results indicate that the NiMo

catalyst retains its remarkable activity over at least several days. Current work is focusing on the interactions between denitrogenation reactions and dechlorination reactions. These competing and interacting reaction pathways are particularly important in oil recycling and agricultural chemical recycling.

INTRODUCTION

This chapter will focus on the hydrodechlorination of chlorinated organics. This chemistry has applications in agricultural chemical manufacturing, oil recycling and PCB remediation as described below.

Chemical manufacturing

Chlorinated aromatics are widely used in pesticides and other agricultural chemicals. Often, only certain isomers of these chlorinated hydrocarbons have desirable properties. Since the synthesis processes employed are not completely stereospecific, the treatment and recycle of undesirable isomers poses an important waste minimization problem. Catalytic hydrodechlorination is being explored as a source reduction method, with the case study of chloropyridines in mind. Chlorinated pyridines are a major agricultural chemical. Only a few of the over 200 chloropyridine isomers are useful products, so in manufacturing chloropyridines, many streams are recycled internally. Still, a significant amount of these materials end up in tars that must be incinerated. These materials are a logical candidate for hydrodechlorination. Preliminary results on the hydroprocessing reactions of chloropyridines will be presented later in this chapter.

Oil recycling

Oil recycling is becoming a large industry. Recyclers typically separate lighter components from waste oils using conventional distillation, then treat the residue using catalytic hydroprocessing. A difficult problem facing recyclers is catalyst deactivation due to the reaction of NH₃ and HCl, producing NH₄Cl. The NH₃ and HCl are products of denitrogenation and dechlorination reactions. Part of the data presented in this chapter will address the interaction of these reaction pathways.

PCB remediation

One of the most significant applications of catalytic hydroprocessing is PCB remediation. Polychlorinated biphenyls, commonly called PCBs, are a group of chlorinated organic compounds in which one to ten chlorine atoms are attached to biphenyl. PCBs have extremely high thermal and chemical stability. They are relatively nonflammable and have excellent electrical insulating characteristics. The physical properties of PCBs make them highly useful in numerous commercial applications, including dielectric fluids in capacitors and transformers, heat transfer fluids, hydraulic fluids, lubricating and cutting oils. PCBs were commercially produced as complex mixtures beginning in 1929 and are not known to occur naturally. Commercial mixtures were synthesized by chlorination of biphenyl with chlorine gas over a metal chloride catalyst. The production of PCBs ceased in 1977 with a total worldwide production of PCBs estimated to be 2.4 billion pounds.

Animal studies with commercial mixtures of PCBs have shown a variety of chronic toxic effects including birth defects, high offspring mortality rates, liver damage, and enlargement of the liver, kidneys, and heart (Ackerman and Scinto, 1983). PCB contaminated cooking oil caused a total of 1,291 "Yusho" patients in 1968 in western Japan. Clinical tests done on the patients showed low birth weights, chloracne and liver damage. The realization of the widespread distribution of PCBs in the environment and growing knowledge of their hazards led Monsanto, the world's largest producer of PCBs, to cease all production in 1977. Growing evidence of the problem of PCB contamination prompted a public outcry which culminated in the United States in 1976 with the regulation of PCBs by the Toxic Substances Control Act (TSCA). The TSCA banned the manufacture and use of PCBs in other than a totally enclosed manner by January of 1979, and a complete ban on manufacture, processing and distribution in commerce of PCBs by July of 1979. Section 6e of TSCA required the Environmental Protection Agency (EPA) to regulate the disposal of PCBs already in use.

Large amounts of PCB containing products such as transformer oils and capacitors are in service. These devices are subject to or are currently awaiting disposal.

Disposal of PCB contaminated products has generally been limited to incineration, although some chemical degradation processes (e.g. the Goodyear process) are permitted in the United States. Some of the problems associated with PCB incineration are listed below.

- The chlorine atoms are effective flame retardants. They tend to quench the hydrogen free radicals which propagate the reactions in the incinerator. Therefore, it is difficult to achieve complete combustion.
- Incinerators have high operating cost due to high operating temperatures (1200°C-1600°C).
- The combustion stack gases present a severe corrosion problem at the high operating temperatures.
- The problem of greatest concern is the generation of products of incomplete combustion, which are formed in trace quantities. When PCBs are burned, dioxins and chlorinated dibenzofurans (CDBF) can be formed. Other materials contained in the stack effluents include HCl, CO, CO₂, NO_x and O₂. Removing these materials from the stack gases can be very difficult and expensive.
- Currently there are only three licensed incinerator units in the United States (Texas, North Carolina and Tennessee); therefore, PCB wastes from the rest of the country must be transported to those sites. As a result there are backlogs at the sites and the transportation of the wastes can be very dangerous and expensive.

A number of chemical methods have been proposed for the treatment of PCB-contaminated materials. The best known of these include a sodium naphthalide method (Goodyear's) and a sodium-amine method (PCBX).

1. Goodyear Sodium Naphthalide Process

Goodyear Tire and Rubber Co. developed a chemical treatment process for PCB transformer and heat transfer fluids. Major steps in the process are shown in Figure 1. Preparation of the reagent begins with the dispersion of molten sodium in hot oil, to produce highly reactive, finely dispersed droplets of liquid sodium. Agitation is continued while the mixture is rapidly cooled to room temperature, causing the sodium droplets to solidify into fine, bright spheres. A solution of naphthalene and tetrahydrofuran is then added to the mixture to form sodium naphthalide. Additional stirring for 1-4 hours results in a homogeneous solution. The sodium naphthalide breaks the carbon-chlorine chemical bonds to produce sodium chloride and hydrogen ions. The reaction takes less than 5 minutes at room temperature and a minimum ratio of 50 moles of naphthalide to 100 moles of chlorine is required to remove 98% of the PCBs from a standard heat transfer fluid containing 82 ppm of PCBs.

A number of concerns have hampered the widespread use of this process. Extreme caution is necessary with reactions involving metallic sodium. Hydrogen is rapidly generated when sodium makes contact with water. During the water quench step, water must be added in small amounts over a long period to minimize possible hydrogen release. Nitrogen or a similar inert gas is used as a blanket to prevent the formation of potentially explosive hydrogen/oxygen mixtures. Furthermore, EPA has classified naphthalene as a restricted compound. The costs of this process are reported to be about \$2.75/gal to reduce PCB concentrations from 500 ppm to zero (Fradkin and Barisa, 1982).

2. Sunohio PCBX Process

PCBX is a chemical destruction process. The chemical reactions are still proprietary information, but they probably involve organic sodium compounds in an amine solvent. The chlorine substituents in PCBs are converted to sodium chloride, while the organic portion of the PCB molecule, the biphenyl nucleus, is converted to polymeric solids which are insoluble in water.

The various parts of a mobile unit are illustrated in Figure 2. The mobile processing unit is permitted to decontaminate 600 gal/hr of transformer oils containing up to 2600 ppm of PCBs. The EPA requires that the residual PCB concentration be under two ppm.

Since the PCBX process reduces the PCB concentration in cycles, the economics of the process are less favorable than Goodyear's. For example, three cycles are required to decrease the PCB concentration to 0.6% of the original contamination, e.g. from 1000 ppm to 6 ppm. This process also involves the use of sodium in a potentially toxic solvent, so it possesses many of the same drawbacks as the Goodyear process. At present, costs are estimated at \$3/gal if the transformer oil is reusable, and \$7/gal is new oil is needed (Fradkin and Barisa, 1982).

3. Catalytic Hydrodechlorination as an Alternative Disposal Method

Catalytic hydrodechlorination can be used as an alternative disposal method for PCBs. The advantages of catalytic hydrodechlorination of PCBs over current incineration practices are listed below.

• Catalytic dechlorination can be effective at a much lower operating temperature than incineration (350°C vs. 1200°C to 1600°C).

- The biphenyl product would have value as fuel additives, and could be recovered rather than burned.
- The effluent from the catalytic dechlorination unit could be monitored much more closely than the effluent from an incinerator.
- The formation of dioxin, CDBF, NO_x, CO and CO₂ are virtually eliminated. The mechanisms for the formation of dioxin from combustion reactions are poorly understood, but it is obvious that a source of oxygen is necessary. Catalytic hydrodechlorination requires no supply of oxygen: therefore, dioxin is unlikely to be produced.
- The greatest advantage of catalytic hydrodechlorination is its capability of being moved to or located at the site where the PCB wastes are being stored.

The operating costs of catalytic dechlorination appear to be lower than any of the present disposal technologies. During the past year, UOP has begun marketing the proprietary HDC technology for treating PCB laden transformer fluids (Kalnes and James, 1988). Their process is shown in Figure 3. The remainder of this chapter will describe the work done in our laboratory over the past three years on HDC chemistry. The work is presented as three steps.

- Various catalysts were screened for hydrodechlorination activity using chlorobenzene and dichlorobenzene as model compounds.
- 2. The most promising catalyst from the screening study was studied in a continuous flow micro-reactor. Catalyst lifetimes, reaction mechanisms, reaction rates and the effects of various contaminants were studied.
- 3. Using the experimental data obtained above, the suitability of HDC for processing a variety of wastes will be discussed.

PROCESS CHEMISTRY

Some of the reactions involved in hydrodechlorination of waste streams are shown in Figure 4. Note that the reactions frequently involve the cleavage of an aromatic carbon-chlorine bond. The goals of our work on process chemistry are to identify active catalysts, quantify reaction rates and elucidate reaction mechanisms. Our progress to date is summarized in this section on Process Chemistry.

Catalyst Screening Study

The goal of the catalyst screening study was to identify catalysts with a high dechlorination activity that would also be relatively unaffected by the wide variety of functionalities present in toxic waste streams. Hydroprocessing catalysts used in heavy oil upgrading were logical candidates for robust dechlorination activity, since the carbon-chlorine bond energy is within the range of bond energies susceptible to hydrotreatment (Hendrickson et al., 1970). Noble metal and nickel catalysts have also been reported to have good hydrodechlorination activity (Dini et al., 1975; LaPierre et al., 1978a,1978b; Coq et al., 1985,1986).

Chlorobenzene and 1,2-dichlorobenzene were used as model compounds due to their simplicity, availability and their presence as contaminants in many waste streams. The catalysts used for the screening study were NiMo, CoMo, NiW and Pd supported on Al₂O₃. The catalysts used in this study and the pretreatment applied are listed in Table 1. The screening study was performed in a batch autoclave reactor. Complete experimental details are available from the authors.

The results of chlorobenzene hydrodechlorination experiments are summarized in Table 2. The catalysts with the highest chlorobenzene conversion were then used to dechlorinate 1,2-dichlorobenzene. These experiments were carried out to determine the steric effects of the chlorine atoms. The results of the experiments with 1,2-dichlorobenzene are summarized in

Table 3. The total absence of chlorocyclohexane and cyclohexane among the reaction products clearly indicated that chlorine atoms are removed before any hydrogenation of the aromatic ring occurs.

The catalyst screening study can be summarized as follows. First, presulfided NiMo supported on Al₂O₃ showed excellent dechlorination activity with both chlorobenzene and 1,2-dichlorobenzene. Reduced Pd supported on Al₂O₃ also showed good activity with chlorobenzene but was less successful with dichlorobenzene. In addition, the pretreated catalysts generally showed better dechlorination than untreated catalysts.

Reaction Rates and Mechanisms

The data collected in the batch autoclave reactor provided a reasonable basis for selecting a hydrodechlorination catalyst, however, the data were inadequate for designing a commercial process. Therefore, a high pressure, continuous-flow microreactor system was constructed to provide the mechanistic and rate data crucial for process design. This reactor system can be used for catalyst lifetime studies and can be operated at differential conversions. Operating under differential conditions (see, for example, Levenspiel, 1972) is essential for determining rate expressions which in turn determine the optimum reaction conditions.

The microflow differential reactor system shown in Figure 5 consists of a one liter stirred autoclave (rated for 2000 psi at 230°C), a tubular fixed bed reactor (1/4 inch diameter Hastelloy-C tubing), a 250 microliter sampling valve (Hastelloy-C), and two 500 ml pressure vessels (rated for 2000 psi at 232°C). The stirred autoclave is used to saturate the feed to the reactor with hydrogen, assuring that both the chlorinated organic and the molecular hydrogen are in the same phase. The feed to the reactor typically contains 0.01-0.05 weight fraction of reactant (e.g. chlorobenzene) in hexadecane saturated with dry, oxygen-free hydrogen at a controlled temperature and pressure. This saturated mixture is then pumped at a controlled

rate over a heated reactor bed. The bed consists of a catalyst section, preceded and followed by inert alundum sections. The temperature of the catalytic section of the reactor was controlled within $\pm 3^{\circ}$ C as measured by a thermocouple inserted directly in the catalyst bed. The product stream is sampled by using a high pressure sampling valve. Depending on the degree of corrosivity, the product stream is stored in either a 500 ml stainless steel vessel or a 500 ml Hastelloy-C vessel. These vessels are used to maintain back pressure in the system and are periodically drained to maintain a constant reactor pressure. Products are quantified using gas chromatography; gas chromatography/mass spectroscopy is used to identify products. It must be emphasized that these reaction conditions are designed to elucidate process chemistry. They are *not* designed to achieve complete dechlorination or to represent actual waste mixtures. Demonstration of HDC on actual waste streams has been done, however, and is reported by Kalnes and James (1988).

In any study of catalytic rates and mechanisms, precautions must be taken to insure that the data actually represents the chemistry occurring on the catalyst surface. Thus, a number of preliminary experiments were performed to address mass transfer effects, the catalytic properties of the reactor walls and packing materials and the catalyst stability. These experiments are briefly described below.

Effects of Reactor Walls, Packing Materials and Carrier Solvent

The reactor walls and the thermocouple which measured temperature in the reaction zone both contain traces of Ni, and thus could serve as catalysts. To determine whether these materials were catalyzing dechlorination, a 0.0216 weight fraction chlorobenzene solution in n-hexadecane was pumped through a reactor filled with only the alundum packing material. At a flow rate of 1.6 cm³/min and at a reactor temperature of 350°C less than 0.1% of the chlorobenzene was dechlorinated. At the same conditions, a reactor containing 0.04 g of catalyst dechlorinates 30% of the chlorobenzene fed. Thus, the reactor and packing materials

do not play a significant role in the dechlorination reactions.

A second concern was that the solvent n-hexadecane might react, interfering with product analysis. At the most severe reaction conditions used in this work, less than 2% of the n-hexadecane underwent cracking reactions and none of the products interfered with the analysis of the dechlorination reaction products.

Mass Transfer Effects

The rate of a catalytic reaction can depend not only on the rate of the reaction on the catalyst surface, but also on the rate at which reactant molecules arrive at the surface. To accurately measure surface reaction rates, the reactor must be able to deliver reactant molecules to the catalyst surface much faster than the surface reaction can consume them. Two mass transfer processes can be important. The first, transport of reactants to the catalyst pellet surface, was examined theoretically in this work and was found to have no effect. The second, transport of reactants within the catalyst pores, was examined experimentally by varying the size of catalyst pellets. The results shown in Table 4 indicate that there were no intraparticle mass transfer effects.

Catalyst Stability

The catalyst activity remained relatively constant throughout the course of the experiments. Figure 6 shows hydrodechlorination rate as a function of time on stream. Because H_2S is frequently used in hydroprocessing to maintain catalyst activity, experiments were run both with and without H_2S . The presence of H_2S did not significantly affect catalyst lifetimes but did lower reaction rates slightly.

Dechlorination Rate Studies

The rate of the hydrodechlorination reaction will depend on the concentration of the reactants, on the reaction temperature and possibly on the concentrations of the products. The rate data shown in Table 5 can be used to provide a preliminary assessment of the hydrodechlorination rate. The rate appears to be linearly proportional to chlorobenzene concentration and the temperature dependence of the rate is consistent with an activation energy of 10 kcal/gmol. These data point to either mass transfer or reactant adsorption as the rate limiting step for dechlorination. Since experiments described earlier in this section seem to rule out mass transfer effects, we tentatively conclude that adsorption of reactants onto the catalyst controls the rate of surface reaction.

Hydroprocessing of Chloropyridines

The hydroprocessing reactions of chloropyridines were examined to assess the ability of HDC to treat waste streams containing both nitrogen and chlorine atoms. The presence of both nitrogen and chlorine in a waste stream may present problems since the hydroprocessing products NH₃ and HCl can combine to form NH₄Cl. The ammonium chloride can sublime, plugging process lines and fouling the catalyst.

The hydroprocessing reactions of 3-chloropyridine were examined. Preliminary results indicate that the dechlorination reaction is much faster for chloropyridine than for chlorobenzene. Some of the pyridine resulting from the dechlorination reacts further. Plugging of the reactor is not a problem at reactor conditions, however, as the product stream cools down after leaving the reactor, precipitation and plugging become a serious problem. Additional work is planned to further investigate these preliminary findings.

Summary of Process Chemistry

At moderate conversions, the dechlorination reaction is very selective, with very little

hydrogenation of the aromatic ring. At the high conversions necessary for waste processing, some ring hydrogenation does occur, as reported by Kalnes and James (1988).

- The rate limiting step in the catalytic hydrodechlorination of chlorobenzene appears to be adsorption of chlorobenzene onto the catalyst site. This process has an apparent activation energy of 10 kcal/mol.
- Hydrodechlorination over a Ni/Mo catalyst at 300-350°C is a very fast reaction.
 Although adsorption appears to be the rate limiting reaction step, in a commercial reactor, mass transfer rates will probably control the overall dechlorination rate.
- Dechlorination of waste streams containing organic nitrogen compounds can be very difficult. Reaction products from simultaneous dechlorination and denitrogenation can plug process lines.
- All of the experiments described in this chapter have used liquid phase reactants at high pressure. The dechlorination reactions can proceed at low pressure, if the hydrogen to chlorine molar ratio remains greater than 1 (La Pierre et al., 1978). The role of the high pressure is to insure that enough hydrogen reaches the catalyst.

Future Work

Because of the wide applicability of catalytic hydroprocessing, future work will be directed toward on determining relative rates of dechlorination for a wide variety of chlorinated organics. These data will help define the limits of HDC applicability. Further, our preliminary work has indicated that the presence of some functionalities, such as nitrogen groups, makes dechlorination impractical. Identification of troublesome functionalities will also be a major focus of our continuing work.

CONCLUSIONS

Catalytic hydrodechlorination (HDC) is a potential treatment method for a variety of waste streams, including PCBs, agricultural chemicals and waste oils. Although some applications are still in the conceptual phase, the technology has been demonstrated for PCB remediation and a few petrochemical waste streams (Kalnes and James, 1988). The goals of this chapter have been to present the basic process chemistry and to discuss the implications of the chemistry in the design of commercial scale units. The main conclusions to be drawn from the work to date are that dechlorination is a viable process for many waste streams, however, the presence of certain combinations of compounds makes dechlorination impractical.

ACKNOWLEDGMENT

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Table 1. Catalysts Selected for Screening

Catalyst	Composition	Pretreatment
CoMo on γAl ₂ O ₃	(3.1% Co, 7.5% Mo)	None
CoMo on γAl ₂ O ₃	(3.1% Co, 7.5% Mo)	10% H ₂ S in H ₂ at 350°C for >1 hour
NiMo on γAl ₂ O ₃	(2.0% Ni, 7.0% Mo)	None
NiMo on γAl ₂ O ₃	(2.0% Co, 7.0% Mo)	10% H ₂ S in H ₂ at 350°C for >1 hour
NiW on γAl ₂ O ₃ , HR354	(2.7% Ni, 18.3% W)	3% H ₂ S in H ₂ at 350°C, >2 hours
CoMo on γAl ₂ O ₃ , HR306	(2.4% Co, 9.3% Mo)	3% H ₂ S in H ₂ at 350°C, >2 hours
NiMo on γAl ₂ O ₃ , HR348	(2.2% Co, 10.75% Mo)	3% H ₂ S in H ₂ at 350°C, >2 hours
Pd on γAl ₂ O ₃	(0.5% Pd)	None
Pd on yAl ₂ O ₃	(0.5% Pd)	H ₂ at 400°C, >4 hours

Table 2. Dechlorination Activity of Screened Catalysts

Catalyst	Reaction Temperature (°C)	Reaction Time (hr)	H ₂ /Chloro- benzene Molar Ratio	Chlorobenzene to Catalyst Weight Ratio	Chlorobenzene Conversion (%)
Presulfided NiMo on γAl ₂ O ₃	350	1	2.60	1.0	99.2
Reduced Pd on γAl ₂ O ₃	352	1	2.60	1.0	99.6
Untreated NiMo on γAl ₂ O ₃	350	1	2.60	1.0	23.8
Untreated Pd on γAl ₂ O ₃	352	1	2.60	1.0	95.1
Presulfided HR306	352	1	2.60	1.0	84.5
Presulfided HR348	352	1	2.60	1.0	98.7

Table 3. Dechlorination Activity and Selectivity

Catalyst	Reaction Temperature (°C)	H ₂ /Dichloro- benzene Molar Ratio	Dichlorobenzene Conversion (%)	Benzene/ Chlorobenzene Selectivity (%)
Presulfided NiMo on γAl ₂ O ₃	350	2.9	96.92	97.62
Untreated NiMo on γAl ₂ O ₃	350	2.9	72.13	72.02
Presulfided CoMo on γAl ₂ O ₃	350	2.9	16.69	9.99
Reduced Pd on γAl ₂ O ₃	350	2.9	96.90	61.50

In all runs, a reaction time of 1 hour and a dichlorobenzene/catalyst ratio of 1.0 ml/g were used.

Table 4. Intraparticle Mass Transfer Effects

Catalyst	Rate of Chlorobenzene Disappearance (10 ⁴ mole/CB/g cat-min)		
Particle Size (µm)	300°C	350°C	
<250	4.2 ± 1.4	20.5 ± 3.0	
250-355	4.3 ± 1.0	17.0 ± 4.1	

Table 5. Dechlorination Rate Data

Chlorobenzene Conc. (mole/l) ^a	Hydrogen Conc. (mole/l) ^a	H ₂ S Conc (mole/l) ^a	Rate of Chloro- benzene disappearance (10 ⁴ mole/g cat-min)		
Experiments at 300°C					
0.08969 0.2084 0.04779	0.3073 0.2436 0.2570	0 0 0	4.2 ± 1.4 8.8 ± 5.2 1.80 ± 0.08		
Experiments at 325°C					
0.1904 0.04578 0.09966	0.2352 0.2493 0.2935	0 0 0.02307	6.4 ± 2.9 3.3 ± 2.3 10.8 ± 1.8		
Experiments at 350°C					
0.09822 0.1838 0.04484 0.08632	0.2543 0.2263 0.2385 0.2475	0 0 0 0.02268	20.5 ± 3.0 11.5 ± 4.3 $6.5 \pm 10.$ 17.3 ± 2.0		

<sup>a - concentrations are calculated at reactor conditions.
b - error bands are based on 95% confidence limits.</sup>

FIGURE CAPTIONS

- Figure 1. Goodyear Process
- Figure 2. PCBX Process
- Figure 3. Process Flow Diagram for Hydrodechlorination (Kalnes and James, 1988)
- Figure 4. Process Chemistry for Hydrodechlorination
- Figure 5. Hydrodechlorination Microreactor
- Figure 6. Catalyst Activity Over a 12 Hour Dechlorination Run

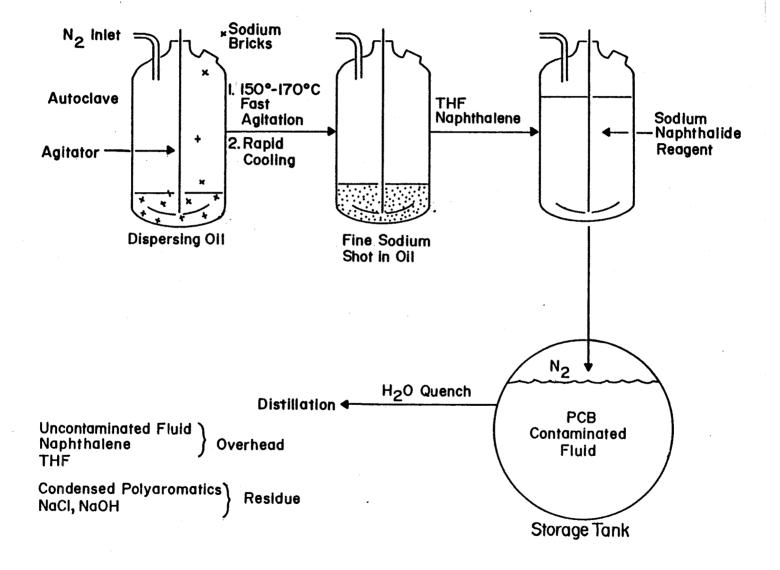


Figure 1. Goodyear Process

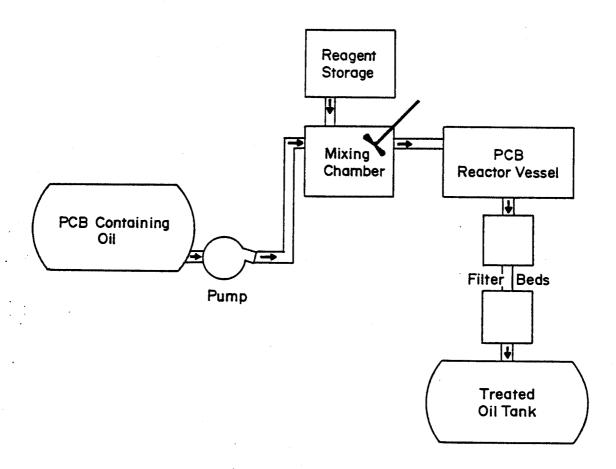


Figure 2. PCBX Process

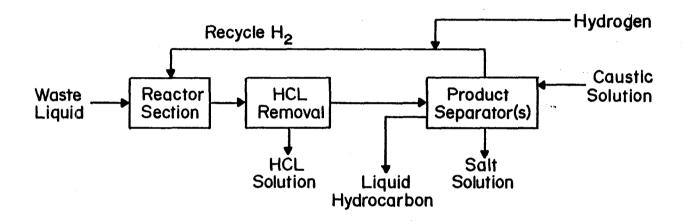


Figure 3. Process Flow Diagram for Hydrodechlorination (Kalnes and James, 1988)

HYDROPROCESSING REACTIONS

Chloropyridine Dechlorination

$$\bigcirc$$
 + H₂ catalyst \bigcirc + HCI

Waste Oil Upgrading

Figure 4. Process Chemistry for Hydrodechlorination

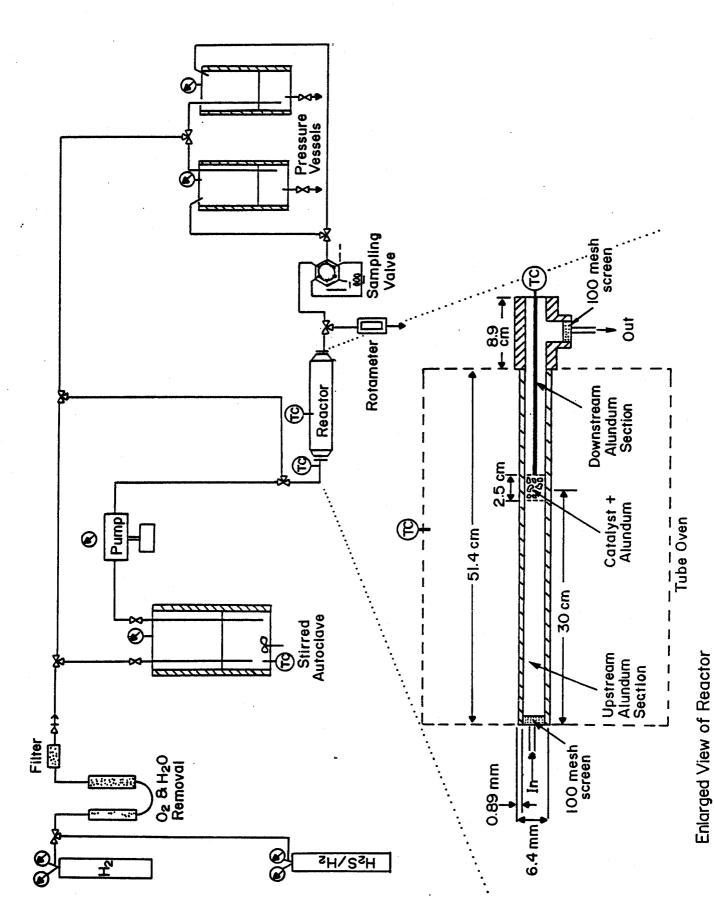


Figure 5. Hydrodechlorination Microreactor

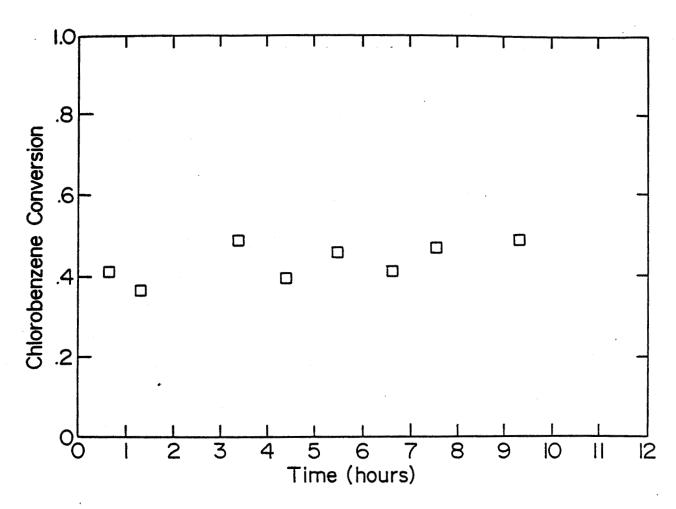


Figure 6. Catalyst Activity Over a 12 Hour Dechlorination Run