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Catalytic Hydrodehalogenation and Hydrogenation of Halogenated Aromatic Organic Contaminants for Application to Soil Remediation

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Catalytic Hydrodehalogenation and Hydrogenation of Halogenated Aromatic

Organic Contaminants for Application to Soil Remediation

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
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Abstract

The objective of this research was to aid in the development of a new method for removing and destroying soil contaminants. In particular, 1,2,4,5-tetrachlorobenzene (TeCB) was selected for this research. Hydrodehalogenation (HDH) was paired with hydrogenation for remedially destroying TeCB without generating a secondary waste stream in a single batch reactor. Palladium- and rhodium-catalyzed HDH and hydrogenation were applied in a batch reactor at room temperature and moderate hydrogen pressure. Cyclohexane was formed as an end product with benzene as an intermediate reactant.

An analytical method was developed to measure TeCB, benzene, and cyclohexane in a solution of water and ethanol, 50:50 by volume before mixing, by gas chromatography with electron capture detection (ECD) and flame-ionization detection (FID). Experimental data were consistent with a model in which dehalogenation and hydrogenation were considered sequential processes with first order reaction kinetics.

Chapter 1: Introduction, Motivation, and Background

1.1 Introduction to Remedial Extraction and Catalytic Hydrodehalogenation (REACH)

Halogenated organic compounds are encountered consistently throughout the U.S. Environmental Protection Agency's National Priority List (US EPA 2007). Many of these contaminants are chlorinated, such as polychlorinated biphenyls (PCBs), chlorinated benzenes, and chlorinated aliphatic hydrocarbons (Xia et al. 2004, Oxley et al. 2004, Wee 2007). These types of contaminants are extremely harmful to humans as well as the surrounding environment. These contaminants can be found globally and are used in herbicides, insecticides, defoliants, and hydraulic fluids. They are persistent and commonly found in soil media based on being hydrophobic and of relatively low volatility (Wee 2007).

There are various methods for soil remediation on the market today. These include incineration, activated carbon adsorption, and biodegradation (Oxley et al. 2004, Xia et al. 2004, Wee 2007). These methods all have drawbacks and leave room for significant improvement. Incineration carries a high energy cost as well as creating harmful secondary wastes such as highly toxic polychlorinated dibenzo-ρ-dioxins and dibenzofurans (Xia et al. 2004, Hitchman et al. 1994, Menini et al. 2000, Oxley et al. 2004). Activated carbon

adsorption is not a solution as it merely transfers the contaminant onto another medium which still has to be disposed of and is commonly discarded in a landfill. Biodegradation is hard to classify as a means of treatment for hydrophobic halogenated compounds as the rate is very slow (Speitel and Clossman1991, Murena and Gioia 2009) and can generate toxic side products (Murena and Gioia 2009).

A typical schematic for soil remediation found on the EPA website that is applied at Superfund sites for solvent extraction is shown in Figure 1.1. This method employs adsorption of extracted contaminants onto activate carbon.
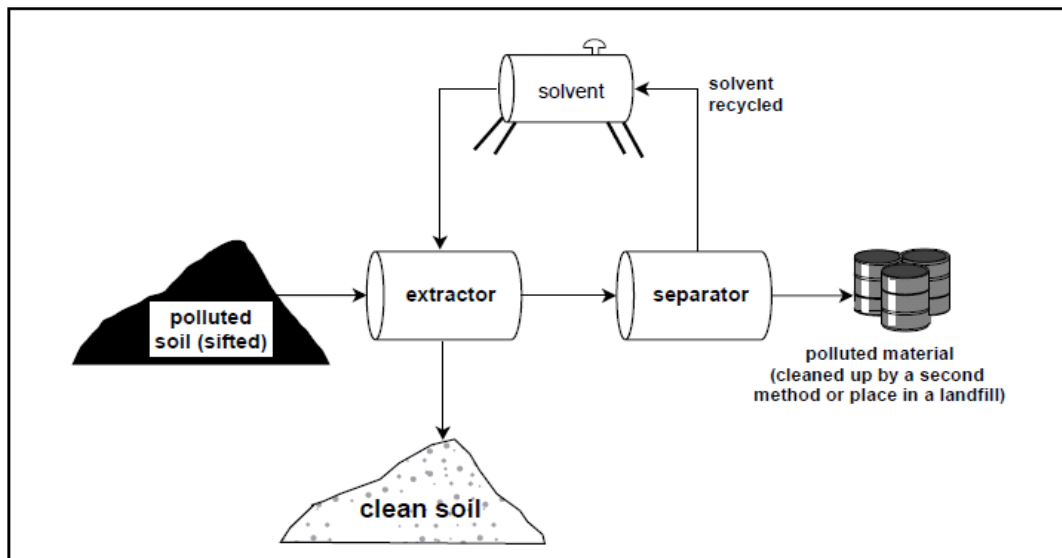
Figure 1.1 EPA Schematic for Soil Remediation by Means of Solvent Extraction. (US EPA, 2001)

As shown, the contaminant is merely moved from the soil to another phase, and then a secondary waste is either treated or disposed of to a landfill. This can lead to further contamination for future generations. The need remains

for a remedial process that cleans the soil effectively and is cost-effective while not generating a secondary pollutant.

In response to this need, Wee and Cunningham (2007) proposed a new technology for soil remediation, REACH, remedial extraction and catalytic hydrodehalogenation (Wee 2007, Wee and Cunningham 2008). The technology that this research is based on demonstrates an innovative approach for soil remediation. The following schematic shows the design approach for REACH. The innovative approach offered by REACH demonstrates that contaminants will be destroyed, not merely transferred from one phase to another. Contaminants will be removed from soil by solvent extraction and then destroyed catalytically.
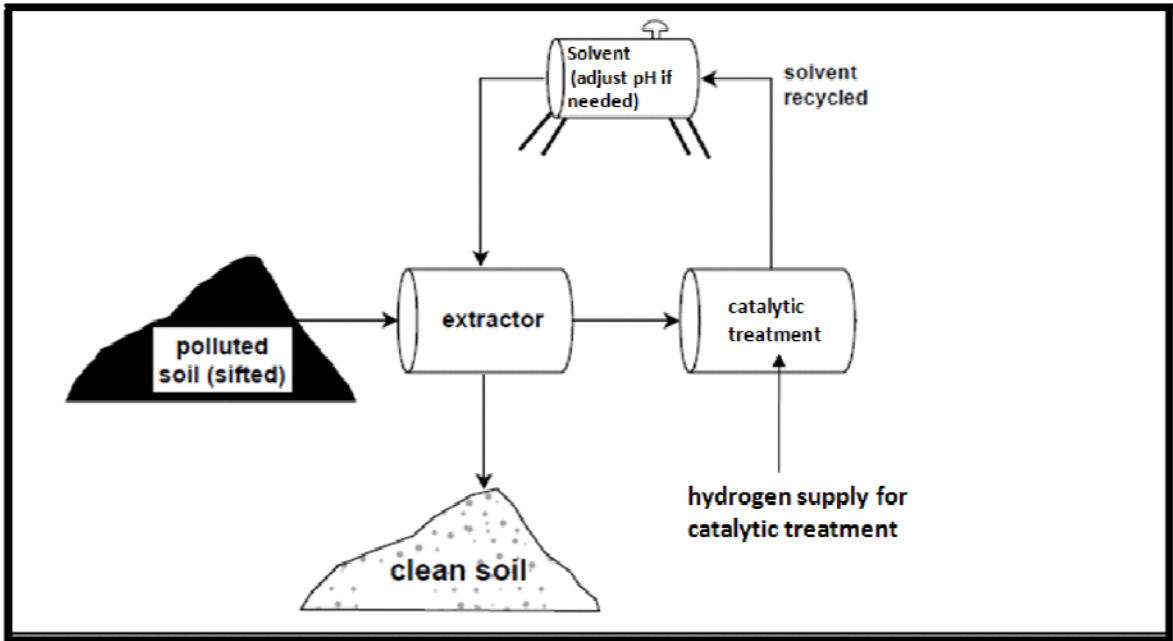
Figure 1.2 Remedial Extraction and Catalytic Hydrodehalogenation (REACH). (Wee 2007)

The approach of REACH is similar to that applied by the EPA, but with a few significant changes. The separator is eliminated, thus a secondary waste stream is not generated. The catalytic reactor will destroy the contaminants on site, eliminating the cost associated with hauling the waste to a landfill or to a facility for treatment.

Wee (2007) and Wee and Cunningham (2008) showed a 50:50 water-ethanol solution to be an appropriate solvent mixture for extracting contaminants from soil. This solvent mixture was also shown effective by Murena and Gioia (2009). Wee and Cunningham (2008) showed that 1,2,4,5-tetrachlorobenzene could be dehalogenated to benzene in a water/ethanol solvent by palladium-catalyzed hydrodehalogenation.

1.2 Background on Catalytic Hydrodehalogenation and Hydrogenation

There have been a wide variety of hydrodehalogenated systems used over the years (Xia et al. 2004, Oxley et al. 2004, Sisak et al. 2003). Reduction is usually mediated by a transition-metal catalyst, such as Pd or Rh, and is often performed under hydrogen pressure or some other reducer (Xia et al. 2004). There are various studies showing application of Pd and Rh as being successful at hydrodehalogenation (Sisak et al. 2003, Wee 2007).

Studies have shown that hydrodehalogenating chlorinated benzenes with a palladium catalyst will form benzene and can result in a build-up of benzene in the solvent (Murena and Gioia 2009, Wee and Cunningham 2008) which can lead to deactivation of the catalyst (Murena and Gioia 2009). Benzene is highly

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toxic to the environment as well and is placed at number six on the 2007 CERCLA priority list of hazardous substances. Therefore, further treatment is required to remove benzene.

Various catalysts have been shown to hydrogenate benzene to cyclohexane (Halligudi et al. 1992, Pellegratta et al. 2002). A Rh catalyst has been shown effective at hydrogenating benzene (Halligudi et al. 1992, Pellegratta et al. 2002) to cyclohexane. Cyclohexane is much more environmentally friendly than benzene.

1.3 Objectives

The research presented here focuses on the catalytic treatment of the extraction solvent. The overall objective of this research is to demonstrate that hydrodehalogenation and hydrogenation can successfully reduce chlorinated benzenes to cyclohexane, thus not generating a secondary waste. A subsidiary objective is to develop an analytic method for detecting and quantifying the target analytes in solutions of water and ethanol.

The primary objective will be achieved by Pd-catalyzed HDH and Rh-catalyzed hydrogenation in a single reactor. The second objective will be achieved by gas chromatography using a Perkin Elmer Clarus 500 GC equipped with an electron capture detector (ECD) and a flame ionization detector (FID).

Chapter 2: Background of Gas Chromatography

2.1 Introduction

Gas chromatography (GC) is implemented in numerous types of analysis such as quantifying concentrations of alcohols, pesticides, and hydrocarbons in environmental samples. Gas chromatography was used in this research to quantify concentrations of TeCB, benzene, and cyclohexane in 50:50 water-ethanol solutions where concentration was unknown.

The objective of this chapter is to discuss the theory of the GC and the importance of the various components so as to understand challenges faced in developing an analytical method for quantifying the target analytes. The methods for quantifying TeCB, benzene, and cyclohexane are also presented in this chapter.

Figure 2.1 shows the various components of a gas chromatograph (GC): the injector, column, and detector. The GC used in this research was a Perkin Elmer Clarus 500 equipped with an electron capture detector (ECD) and a flame-ionization detector (FID). The Clarus 500 is comprised of two split/splitless injectors, two capillary columns, and two detectors, an ECD and a FID.
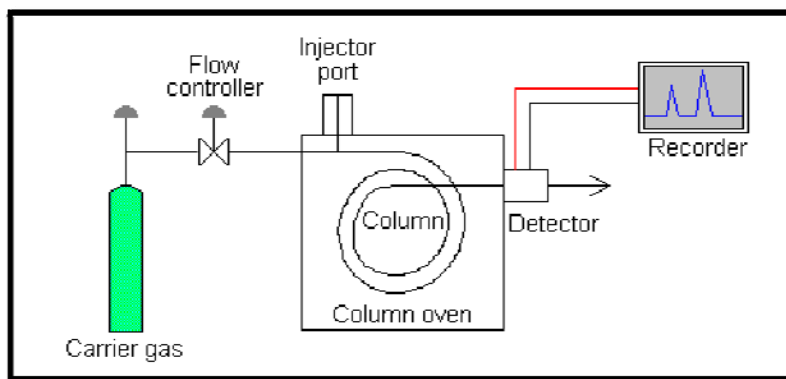
Figure 2.1 Diagram of a Gas Chromatogram (GC). (Sheffield Halem University, 2011)

2.2 Injector

The initial port of a GC is the injector where a sample can be introduced as a liquid or gas. The injector port will vaporize a liquid so that the introduction of the sample to the column will be as a vapor. Injectors are equipped with liners which are open glass tubes where the sample travels to the column. The injector liner can be either narrow or wide bore. A wide bore liner is used in splitless injection and also when attached to a column with a larger inner diameter. A narrow bore liner is for split injection. The application depends on the inner diameter of the column being used. There are various types of injectors. This discussion will be for the split/splitless injector as this is the type of injector that was used in this research.

A split/splitless injector introduces the carrier gas after the sample has been vaporized (if introduced as a liquid) or once the gas sample is introduced. The sample will then be mixed and sent to the column in either its entirety if operated in splitless mode or a portion if in split mode. If in split mode, a portion

of the sample and carrier gas mixture in the injector liner will be exhausted through the split vent.

Operation of split/splitless mode depends on the concentration of analytes. The split method is used when peaks being generated are very wide from long eluting times or when the peak of the analyte is greater than the capability of the detector. This is known as swamping the detector and will result in a peak that is cut off and therefore concentration cannot be determined. Splitless is applied for trace analysis and is the most sensitive. Split mode deals with heavier loads to the column and helps to avoid swamping the detector.

Both applications were applied in this research. Samples that were analyzed by the ECD were injected as liquid and vaporized in the injector. Then a portion of this was split off before entering the column. Samples analyzed by the FID were analyzed in the splitless method.

2.3 Column

In chromatography, there is a mobile phase as well as a stationary phase. The sample solution is introduced to the mobile phase initially by being injected into the injection port where it is volatilized or introduced as a gas. The sample then mixes with the carrier gas, i.e. the mobile phase, and is then sent through the column.

The column is a means of separating the various species and then the separate species pass through the detector where a signal is recorded as a response factor proportionate to the concentration of the species. The most

crucial element in selecting the appropriate column is undoubtedly the stationary phase.

The column is coated by the stationary phase which is a non-volatile liquid. As the mobile phase passes over the stationary phase, the analytes equilibrate or partition back and forth between the mobile and stationary phase. The sorption-desorption process occurs many times as the target analytes move throughout the column, and the resulting retention times will be the result of such interactions. Each analyte is retarded as it migrates through the column according to the interaction with the stationary phase.

One might recall "like dissolves like". This is a fundamental concept with respect to stationary phases. A stationary phase is coated on the inside wall of the column and acts as a solvent for the sample (Grob 1985). The more soluble an analyte is with respect to the stationary phase, the longer the retention time will be as a result of spending a longer amount of time in the stationary phase than in the mobile phase. This can aid in separation as the target analytes will remain in the column longer and at varying amounts of time for different species, resulting in better separation, if the appropriate stationary phase is selected.

In this research, the column selection was simple for TeCB as it is non-polar and the required separation was only between TeCB and an internal standard, TCE. Compounds that are not halogenated are not detected by the ECD and therefore do not control the required separation. A non-polar Db-5MA

capillary column (30m length x 0.53 mm i.d. x 1.5 μm film thickness) (J&W) was selected for use in the analysis of TeCB by GC/ECD.

For the detection of benzene and cyclohexane, the separation proved difficult based on the relatively similar nature between the two compounds. Ethanol complicated the matter by having a similar boiling point as well as being very high in concentration compared to benzene and cyclohexane. Achieving this separation was a crucial component to my contribution in this research. Discussion on this type of separation between benzene, cyclohexane, and high amounts of ethanol could not be found in literature.

Table 2.1 shows stationary phases evaluated for separating benzene and cyclohexane in this research. The selected columns were applied with various oven temperature programs, flow rates, and split ratios in order to try to achieve separation. Various means of introducing the sample as a gas or liquid were tried.

Table 2.1 Columns Employed to Achieve Separation for FID Detection of Benzene and Cyclohexane

Column	Stationary Phase	Polarity	ID (mm)	Film Thickness (µm)	Length (m)
ELITE-5	5% PHENYL 95% DIMETHYLPOLYSILOXANE	NON	0.53	5.0	30
HP5	5% PHENYL 95% DIMETHYLPOLYSILOXANE	NON	0.32	0.25	30
HP 1	100% DIMETHYLPOLYSILOXANE	NON	0.53	3.0	30
RTX 35MS	35% DIPHENYL 65% DIMEHTYL POLYSILOXANE	SLIGHTLY	0.25	0.35	30
RTX 1301	6% CYANOPROPYLPHENYL 94% DIMETHYL POLYSILOXANE	MID	0.25	0.10	15
RTX 1301	6% CYANOPROPYLPHENYL 94% DIMETHYL POLYSILOXANE	MID	0.53	3.0	30
DB - WAX	100% POLYETHYLENE GLYCOL	VERY	0.32	0.25	30

Benzene and cyclohexane are both non-polar compounds. As a first choice, a non-polar column was selected as the ideal candidate for separating these compounds. The Elite-5, HP-5, and HP-1columns were applied. Complete separation was not achieved by these columns between benzene, cyclohexane, and ethanol.

It should be noted that these columns had previously been used. It was not noted for what type of application or over what period of time the columns had been used. Therefore, inadequate separation may be accounted for by a degraded stationary phase rather than an inappropriate stationary phase. Another probable explanation is that the non-polar stationary phase may have

been an inadequate choice since cyclohexane and benzene are very similar in structure and also have a very similar vapor pressure.

Typically in GC analysis, vapor pressure differences would be exploited to give the desired separation, but due to the lack of vapor pressure difference between the benzene and cyclohexane, intermolecular force interactions must be the means for achieving separation. Benzene has a π-electron cloud, which should make it more susceptible to induction effects and possibly dispersion attractions (Poole 2003). Table 2.2 shows the physical and chemical properties of the target analytes.

Table 2.2 Physical and Chemical Properties of TeCB, Benzene, and Cyclohexane. (IPCS INCHEM, 2011)

Chemical	Molecular Weight (g/mol)	Chemical Formula	Water Solubility (g/L)	Vapor Pressure (Pa)
TeCB	215.9	$C_6H_2Cl_4$	2.16 at 25ºC	0.70 at 25 ºC
Benzene	78.11	C_6H_6	0.18 at 25ºC	10,000 at 20ºC
Cyclohexane	84.16	C_6H_{12}	0.0058 at 25ºC	10,300 at 20ºC

The induction force of a dipole depends on the polarizability of the non-polar molecule (Miller 1988). Induction interactions occur between a stationary phase with a permanent dipole and a compound, which forms a dipole as a result of the interaction with the stationary phase. This happens with compounds that are unsaturated such as aromatic compounds like benzene, resulting in a momentary dipole.

Dispersion forces are weak forces that exist which are symmetrical and non-polar. It is believed that this symmetry is distorted due to a momentary polarity. This polarity can attract and be attracted by a similar polarity in a neighboring atom or molecule resulting in a net attraction. Dispersion forces arise from electric, intermolecular fields, which result in the induction of in-phase dipoles. They are present in all phases (Miller 1988).

An RTX-35MS was available and applied towards the separation of benzene and cyclohexane. This column was slightly-polar and therefore would be an ideal choice to exaggerate the intermolecular interactions. Benzene and cyclohexane were readily separated by the slightly-polar column. However, ethanol was eluted with a close retention time to both benzene and cyclohexane. Benzene, cyclohexane, and ethanol had been extracted from the water/ethanol solvent into toluene for injection into the GC. Because ethanol was present in such abundance, high concentrations of ethanol were extracted into toluene. Therefore, ethanol peaks on the GC/FID were very large and obscured the benzene and cyclohexane peaks. Regardless of the split used, I was not able to achieve separation between ethanol, benzene, and cyclohexane.

Instead of extracting the analytes into toluene for liquid analysis I allowed water/ethanol solutions to equilibrate with the headspace (air) in a sealed vial. I then injected some of the headspace into the GC. This reduced the mass of ethanol present in the injected sample. However, the problem was not completely resolved with a slightly-polar column.

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At this point, available columns in the lab that were thought to achieve separation of benzene, cyclohexane, and ethanol had been exhausted. A wide-bore column was originally selected to order, but a smaller, narrow bore column was ordered due to resources. The 15m length of the RTX 1301 and small, inner diameter contributed to inefficient time spent in the column to obtain separation. A slow carrier gas flow rate was employed to try to maximize the retention time, but was not sufficient in achieving adequate time for mass transfer to occur between the mobile phase and stationary phase.

The RTX-1301 brings up the point that separation is not solely dependent upon the selection of the correct stationary phase, but also upon the correct column specifications such as inner diameter, length, and film thickness. A smaller inner diameter will allow the solution to travel faster through the column as will a shorter column. A longer column results in using more carrier gas and a longer analysis time. However, a longer column will aid in better separation as the time of interaction between the stationary phase and mobile phase is increased.

The film thickness of the column proves to be crucial as well. A thicker film thickness increases the active sites for polarizability of hydrocarbons of cyclic and aromatic structure (Krupcik et al. 1994). It has been shown that a thicker film thickness increases the overall polarity of the polysiloxane column (Krupcik et al. 1994).

The small inner diameter and film thickness did not obtain sufficient time for the sample and stationary phase to interact in the 15m RTX-1301 column. This led to only a partial separation of benzene and Cyclohexane. Finally, an RTX-1301 (Restek) column with a wider diameter, thicker film thickness, and 30 meters in length was acquired (Table 2.1). The longer wide-bore column was effective at separating benzene and cyclohexane. Due to the mid-polar nature of the stationary phase, ethanol was readily separated from the target analytes as well.

2.4 Detectors

The GC used for quantifying the target analytes was equipped with two detectors, an ECD and a FID. These detectors will be discussed in more detail.

2.4.1 ECD

The Electron Capture Detector (ECD) has a high sensitivity for compounds containing electronegative elements, such as chlorinated species. The ECD responds to changes in electrical conductivity of gases in an ionization chamber due to the presence of electron acceptor molecules (Braithwaite and Smith 1996). The source electrode has a β-radiation emitter, nickel-63. The high energy electrons produced from the radioactive decay interact with the make-up gas, in our case nitrogen, to produce thermal electrons. These are then collected by the positively polarized collector electrode, producing a baseline signal (Grob 1985). Figure 2.1 shows the cross-section of an ECD detector applied in this research.
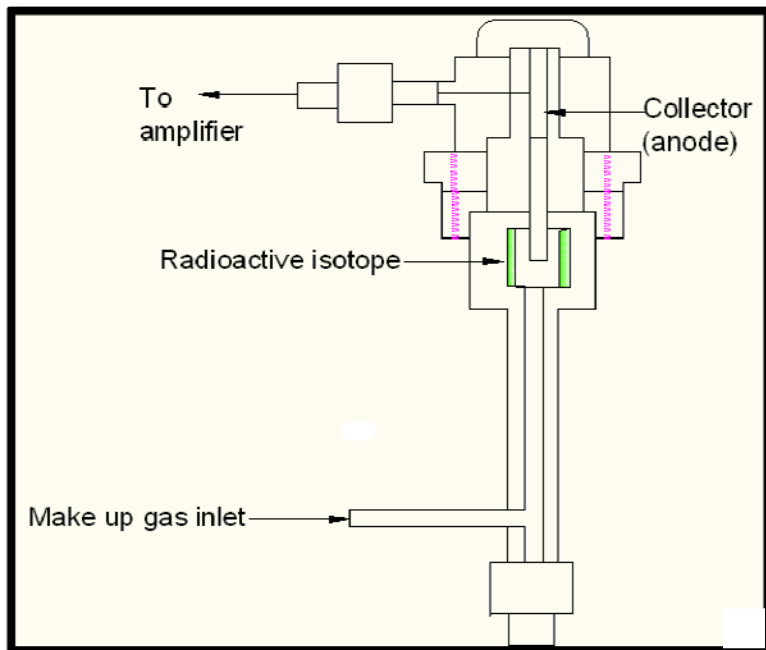
Figure 2.2 Cross-Section of an ECD Detector. (Adapted from Miller 1988)

This signal is electronically processed to form the chromatogram. A chromatogram from the ECD is displayed (Figure 2.2) to show the separation between TCE and TeCB.
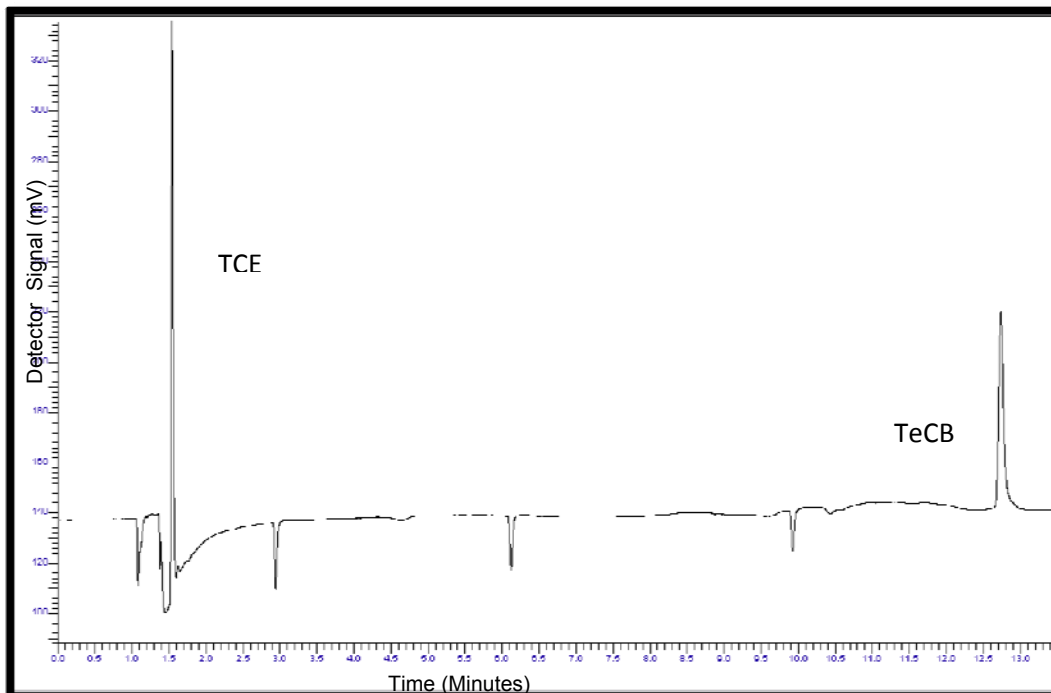
Figure 2.3 ECD Chromatogram of TeCB

The initial peak that elutes is TCE with TeCB having a retention time of approximately 12 minutes. The y-axis is the response of the detector in mV and the x-axis is time in minutes. For this column and method TeCB and TCE will always elute at this time. The method is shown in Table 2.3.

Table 2.3 Detection Method for TeCB

TeCB	
Detector:	ECD
Injection:	Liquid by autosampler
Helium Flow Rate:	3 mL/min
Injected amount:	0.5 µL
Injector Temperature:	230 ºC
ECD Temperature	230 ºC
Attenuation	-2
Split Ratio	40 to 1
Oven Program:	60ºC. Hold for 1 min. Ramp at 5ºC /min to 100ºC. Ramp at 10ºC /min to 115ºC and hold for 3 min.

2.4.2 FID

A cross-section of an FID employed in this detection process is shown in Figure 2.3.
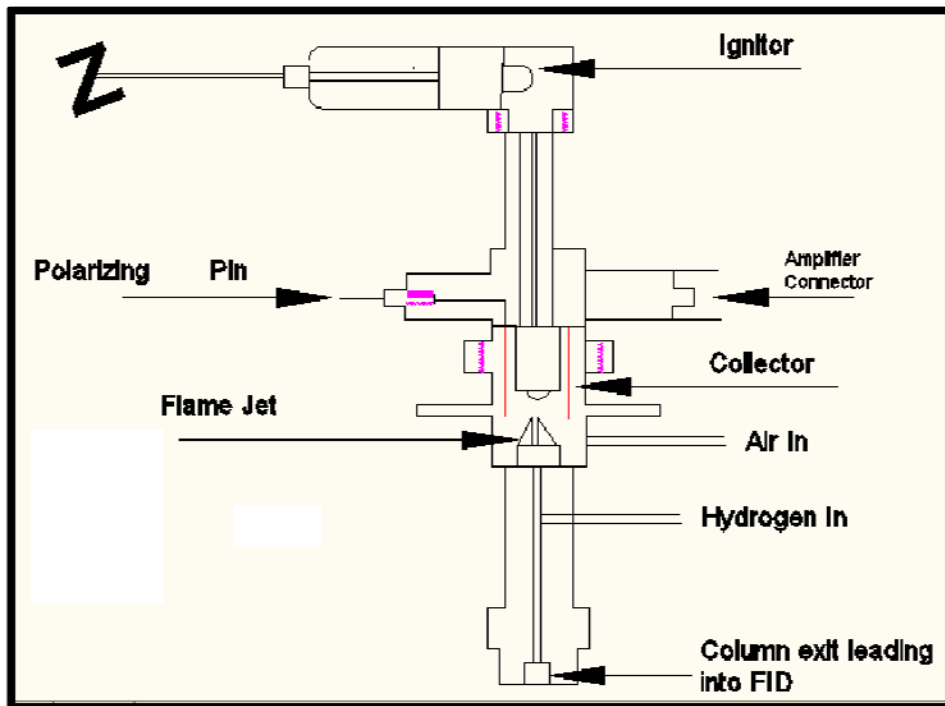
Figure 2.4 Cross-Section of an FID. (Adapted from Grob 1985)

The FID consists of a hydrogen-air flame burning at a small metal jet. There is an electrode located above the flame that collects ions formed from combustion of organic molecules. The hydrogen flows through the column eluent, mixing thoroughly before reaching the jet, where it emerges into the air stream to form the flame. The organic molecules will undergo a series of reactions to produce charged species (Braithwaite and Smith 1996).

A pure hydrogen-air flame will consist of radical species, but not ions. The concept is when organic molecules pass through the flame, ions are formed

proportionately to the amount of carbon atoms present. This is a means of destructive analysis. These ions travel to the collector electrode which is maintained at a negative potential with respect to the flame jet (Braithwaite and Smith1996). An electrical current is observed and recorded, resulting in peaks associated with the organic molecules' concentration.

Figure 2.4 shows the achieved separation between benzene, cyclohexane, and ethanol.
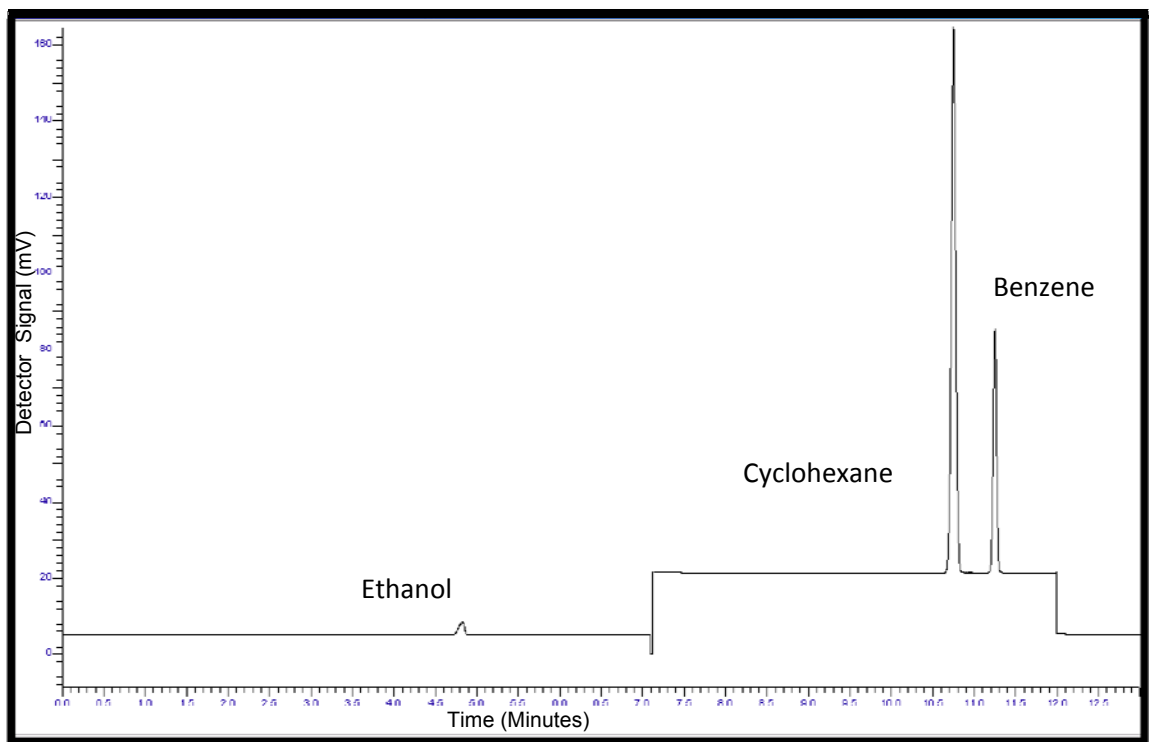
Figure 2.5 Chromatogram from an FID Showing Detection of Ethanol, Cyclohexane, and Benzene

Ethanol elutes at approximately 4.5 minutes, with cyclohexane at 10.6 minutes and benzene at 11.2 minutes. The increased signal at 7 minutes is a timed event that increases the sensitivity of the FID, resulting in detecting the targets at lower concentrations. The method applied here is described in Table 2.4.

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Table 2.4 Detection Method for Benzene and Cyclohexane

Benzene and Cyclohexane	
Detector:	FID
Helium Flow Rate	3 mL/min
Injection:	Manual Headspace
Injected amount:	1 mL
Injector Temperature:	230 ºC
FID Temperature	230 ºC
Attenuation	0
Range	1
Timed Event	At 7 min. Attenuation= -5 and Range =1, Split at 50:1 at 0.5 minutes
Split Ratio	OFF until 0.5 min.
Oven Program:	30ºC. Hold for 8 min. Ramp at 20ºC /min to 130ºC.

2.5 Conclusions

Detection methods were achieved for TeCB, benzene, and cyclohexane. Tables 2.3 and 2.4 show the methods that are employed during this research to detect TeCB on an ECD and benzene and cyclohexane on a FID. The major contribution of this chapter was achieving separation and developing a method of detection for ethanol, benzene, and cyclohexane. Separating benzene, cyclohexane, and high concentrations of ethanol had not been shown in literature by GC analysis.

Chapter 3: Detection Method for TeCB, Benzene, and Cyclohexane Using Gas Chromatography

3.1 Introduction

1,2,4,5-tetrachlorobenzene (TeCB) was the target contaminant selected for this analysis. TeCB is halogenated and hydrophobic and requires a viable means for remediation. The method explored in this thesis is hydrodehalogenation and hydrogenation by catalytic reactions under hydrogen pressure. This will be achieved in a series of reactions:

Hydrodehalogenation of TeCB to Benzene:

- $C_6H_2Cl_4 + 4H_2 \rightarrow C_6H_6 + 4H^+ + 4Cl^-$ (1)

Hydrogenation of Benzene to Cyclohexane:

- $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$ (2)

Net reaction:

- $C_6H_2Cl_4 + 7H_2 \rightarrow C_6H_{12} + 4H^+ + 4Cl^-$ (3)
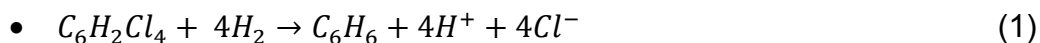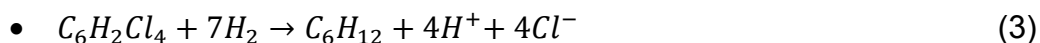
Under the REACH technology, these chemical reactions will take place in a 50:50 water-ethanol mixture. Therefore, in order to evaluate if the proposed REACH technology is working, it is necessary to be able to quantify the concentration of the various compounds in a 50:50 water-ethanol mixture. The

objective of this chapter is to develop a method for quantifying TeCB, benzene, and cyclohexane in a 50:50 water-ethanol mixture by developing calibration plots for each.

3.2 Detection Method for TeCB

Since TeCB is a chlorinated compound, an electron capture detector (ECD) will be employed as the means of detection to make certain the contaminant was successfully destroyed. A calibration plot was obtained in order to determine the concentration of TeCB in a 50:50 water-ethanol solution.

3.2.1 Materials and Methods

3.2.1.1 Chemicals

Ethanol (99.5 %, ACS grade, Aldrich), n-pentane (HPLC grade, Fisher Scientific), 1,2,4,5-tetrachlorobenzene (98%, Sigma-Aldrich), de-ionized water, and trichloroethylene (TCE) (ACS grade, Fisher Scientific) were employed without further purification. A 50:50 mixture of water and ethanol was prepared with de-ionized water and 200 proof (99.5%) ethanol.

Pentane was spiked with TCE as an internal standard. 100 μL of TCE was added to 250 mL of pentane. This gave a stock solution of 588 mg/L of TCE in pentane. 3.4 mL of the pentane stock was then diluted with 200 mL of n-pentane to give 9.8 mg/L of TCE in pentane.

Table 3.1 Chemicals

Chemicals or Catalyst	Specification	Company
1,2,4,5-tetrachlorobenzene	98%	Sigma-Aldrich
Benzene	>99%, ACS grade	Sigma-Aldrich
Cyclohexane	99+%, ACS grade	Sigma-Aldrich
n-Pentane	HPLC grade	Fisher Scientific
Trichloroethylene	ACS grade	Fisher Scientific
Ethanol	99.50%	Sigma-Aldrich
De-ionized water	> 18.2 MΩ*cm	Barnstead

3.2.1.2 Stock Solution of TeCB

50 mg of 1,2,4,5-tetrachlorobenzene was dissolved in 20 mL of ethanol, resulting in a stock solution of 2500 mg/L. The stock was kept in a 20 mL borosilicate glass vial enclosed by a cap and stored in the freezer. The stock solution would last approximately two weeks before having to make up a new stock. The stock solution was diluted down into known, varying concentrations in a 50:50 water-ethanol solution.

3.2.2 Analysis

2 mL of a known concentration of TeCB in a 50:50 water-ethanol solution were placed in a 5 mL borosilicate glass vial with 2 mL of n-pentane spiked with TCE as an internal standard. The vials were secured with a screw cap. The vials were then shaken vigorously on a shaker table for one hour in order to transfer

the target analyte to n-pentane. The partitioning of TeCB to pentane was a crucial step due to the solvent being comprised of water as water can hasten the degradation of the stationary phase of a column.

The vials then sat for an hour before being analyzed on the GC/ECD, allowing for equilibration. One mL of the n-pentane phase was drawn off and placed in a Perkin Elmer GC autosampler amber glass vial. The pentane containing the TCE and TeCB was analyzed according to the procedure described in Chapter 2.

3.2.3 Calibration Plot for TeCB Using an ECD

The following calibration plot was constructed by analyzing various samples of known concentration. TCE was used as an internal standard to give a peak area ratio to account for the error associated with the autosampler. There is approximately a 10% error associated with an autosampler (Miller 1988). The peak area of TeCB was divided by the peak area of the TCE to give a ratio for peak areas to correct for any loss of TeCB during sampling or at the sample inlet of the GC. The x-axis shows the concentration of TeCB in the 50:50 water-ethanol solution.
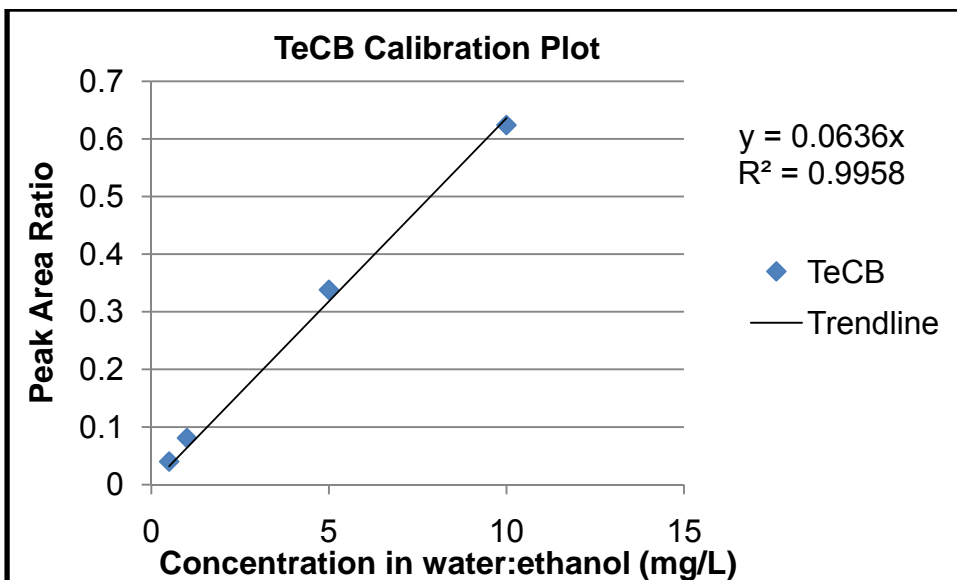
Figure 3.1 TeCB Calibration Plot

3.3 Detection Method for Benzene and Cyclohexane

A method of detection was needed for benzene and cyclohexane to affirm the mass balance and to show that TeCB was hydrodehalogenated and benzene was hydrogenated. Benzene and cyclohexane were detected and quantified by means of a flame-ionization detector (FID).

3.3.1 Materials and Methods

3.3.1.1 Chemicals

Ethanol (99.5 %, ACS grade, Aldrich), benzene (99%, ACS grade, Sigma-Aldrich), cyclohexane (99%, ACS grade, Sigma-Aldrich), and de-ionized water were employed without further purification. A 50:50 mixture of water and ethanol was prepared with de-ionized water and 200 proof (99.5%) ethanol. The specifications for these chemicals are shown in Table 3.1.

3.3.1.2 Stock Solutions of Benzene and Cyclohexane

Stock solutions of benzene and cyclohexane were made up independently. 200 µL of each were combined with 100 mL of ethanol to create a stock solution of 1560 mg/L of cyclohexane in ethanol and 1760 mg/L of benzene in ethanol. The stock solutions were kept in 200 mL glass jars and stored in the freezer fitted with a glass top. The stock solutions would last for a week before having to be remade. The stock solutions were then diluted down with a known amount of water and ethanol resulting in standards of benzene and cyclohexane in 50:50 water-ethanol mixtures.

3.3.2 Analysis

2 mL of each standard were placed in a 5 mL borosilicate vial and enclosed by a cap with a piercable septa. The vials were shaken vigorously over the course of an hour and then equilibrated for 24 hours before analysis by gas chromatography. Then, 1 mL of headspace was drawn off and injected into the GC. Analysis was preformed according to the method described in Chapter 2.

3.3.3 Calibration Plot for Benzene and Cyclohexane

The calibration plots for benzene and cyclohexane were constructed by analyzing samples of known concentration and plotting the peak areas against the known concentration in solution. The peak area ratio was quantified by taking the area of the analyte peak, benzene or cyclohexane, and dividing it by the area of the ethanol peak. Ethanol acted as an internal standard and aided in

correcting the error of slight differences of sample being manually injected to the

GC.
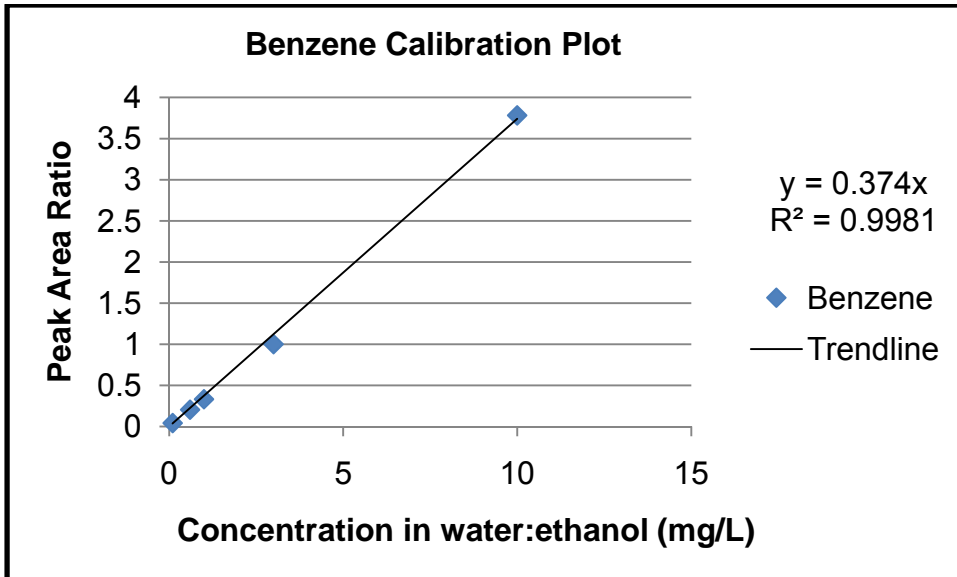
Figure 3.2 Benzene Calibration Plot
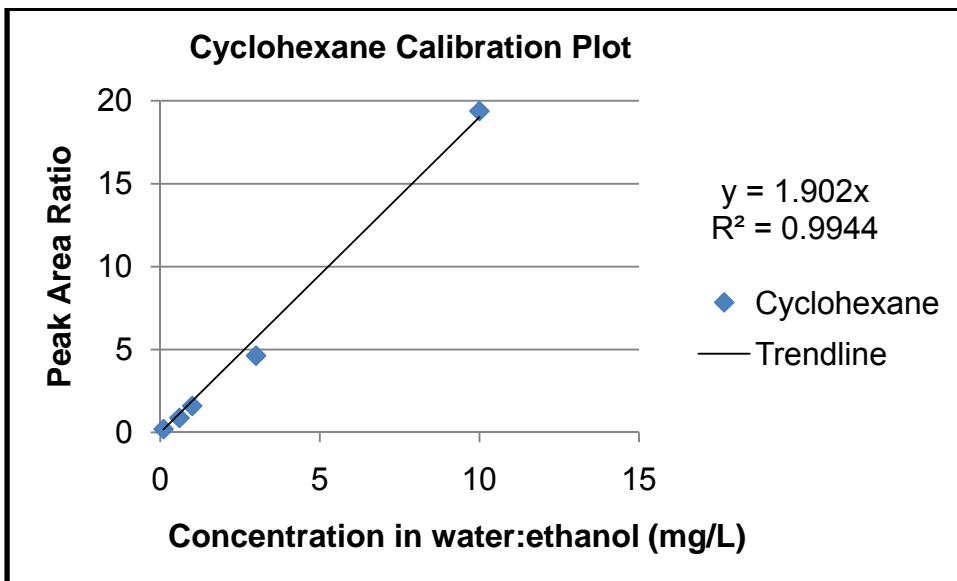
Figure 3.3 Cyclohexane Calibration Plot

It is worth mentioning the peak areas for cyclohexane were significantly larger than those for benzene. This phenomenon occurs because cyclohexane is much less soluble in water (see Table 2.2) and has a slightly higher vapor pressure than benzene; therefore more cyclohexane partitions to the gas phase.

3.4 Conclusion

A method was developed for quantifying TeCB, benzene, and cyclohexane by way of gas chromatography. The calibration plots each show the linear equation that corresponds with the trendline as well as the square of the correlation coefficient (R^2). R^2 has a value between 0 and 1, with 1 indicating a perfect linear fit. The calibration plots for the individual chemicals are quite linear, as shown by the square of the correlation coefficient (R^2), which was approximately 0.99 for each. Since this value is very close to 1, the calibration curve is a good fit and will serve for quantifying concentrations of unknown samples. Concentrations of unknown samples are estimated by measuring the peak area ratios, then calculating the concentration of the analytes via the equations shown in Figures 3.1-3.3.

Chapter 4: Individual Batch Reactor Analysis for Hydrodehalogenation of TeCB and Hydrogenation of Benzene

4.1 Introduction

As the long-term goal of this research is to develop a process that can be implemented at contaminated sites, a desired end-product needs to be achieved. The first step in destroying the halogenated organic contaminant is through hydrodehalogenation. Palladium was successfully employed and benzene was formed as a result of HDH (Wee and Cunningham, 2008). However, this is not a desired end product as benzene is a known carcinogen and harmful to the environment.

A second catalyst, rhodium, is needed to hydrogenate benzene to cyclohexane. In this Chapter, I conduct these reactions in separate batch reactors, initially with palladium to hydrodehalogenate TeCB, and finally in a separate reactor with rhodium to hydrogenate benzene to cyclohexane, to demonstrate the feasibility of the individual reactions.

The goal of this chapter is to show the feasibility of the separate reactions. This was achieved through a series of batch reactor experiments. The first set of experiments conducted show the HDH of TeCB. TeCB was spiked into a mixture of 50:50 water-ethanol, then hydrodehalogenated to benzene through Pd-

catalyzed HDH. The second set of experiments was to show the hydrogenation of benzene where benzene was spiked into a mixture of 50:50 water-ethanol, then hydrogenated to cyclohexane through Rh-catalyzed halogenation in a batch reactor. Several reaction times were varied to estimate reaction kinetics.

4.2 Methods and Materials

4.2.1 Chemicals and Catalysts

The chemicals employed in this research are summarized in Table 3.1. Different catalysts are commercially available. A supported palladium catalyst and a supported rhodium catalyst were selected for this research, each supported on alumina (Al_2O_3). Table 4.1 shows the characteristics of the catalyst employed during this research.

Table 4.1 Catalysts

Catalyst	Specification	Company
Rh-on-Al_2O_3 catalyst	0.5% Rh by weight, 3.2 mm pellets	Sigma-Aldrich
Pd-on-Al_2O_3 catalyst	5% Pd by weight, 3.2 mm pellets	Sigma-Aldrich

The content of the catalyst specified by the manufacturer is assumed to be accurate. The catalysts were used without further treatment. No special effort was given to prevent the catalyst from contacting air.

A stock solution of 1,2,4,5-tetrachlorobenzene with concentration of 2500 mg/L was prepared by dissolving 50 mg of TeCB in 20 mL of ethanol in a 20 mL clear borosilicate glass vial. The vial containing the stock solution was capped with a PTFE-lined septum and kept in the freezer to minimize volatilization.

A stock solution of benzene was prepared with a concentration of 1760 mg/L in ethanol by dissolving 200 µL of benzene in 100 mL of ethanol. The benzene stock was kept in a 200 mL glass jar fitted with a glass cap and kept in the freezer to minimize volatilization.

4.2.2 Catalytic Reaction Studies

In this research, all catalytic reactions were carried out in a Parr 3911 hydrogenation apparatus (Parr Instrument Company, Moline, IL, USA).
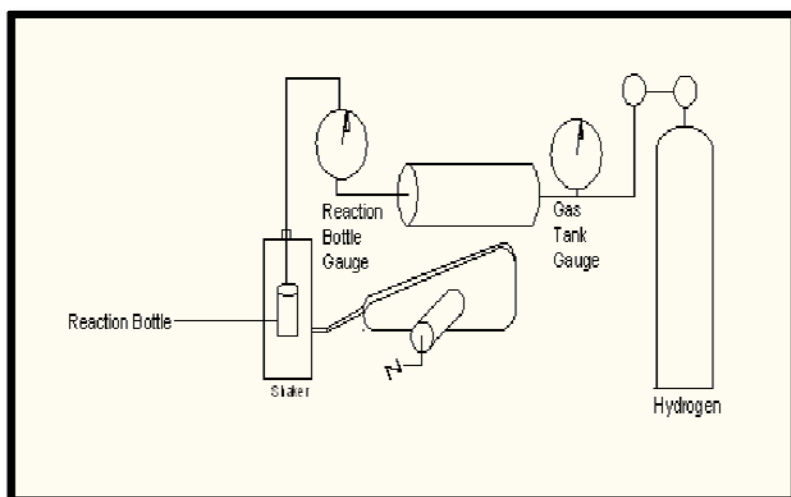
Figure 4.1 Diagram of the Hydrogenation Apparatus

A hydrogen cylinder with ultra-grade hydrogen gas was connected to a 4 L hydrogen tank. The 4 L hydrogen tank is pressurized to the desired reaction pressure. The valve connecting the hydrogen cylinder to the hydrogen tank is closed before the reaction is initiated. This is a safety precaution so as to not have a runaway reaction. The 4 L hydrogen tank is connected to a 500 mL reactor bottle. The reactor bottle is sitting on a shaker table that will shake the reactor bottle at 200 rpm while the reaction is running. The reaction bottle is

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shaken vigorously over the course of reaction. This minimizes any mass-transfer limitations as the reactor solution is well mixed. The valve between the reactor bottle and 4 L hydrogen tank is kept open during the course of the reaction to supply a constant source of hydrogen.

The experiments were conducted as follows. A 300 mL mixture of 50:50 water-ethanol was transferred to a 500 mL reaction bottle. The required amount of stock solution was added to the bottle in order to spike the reactor with either TeCB or benzene. Two initial samples were then taken to affirm the initial concentration of the contaminant in question. If TeCB was being analyzed, 2 mL were drawn off and placed a 5.0 mL borosilicate glass vial with 2 mL of n-pentane spiked with TCE. The vials were enclosed with a screw cap. This was done for each sample. If benzene or cyclohexane were being measured, 2 mL were placed in a 5.0 mL borosilicate glass vial and enclosed with a pierceable septa screw cap.

The desired amount of catalyst was then added to the reaction bottle. The bottle was then placed in the hydrogenation reactor and air in the bottle was removed by filling the bottle with hydrogen gas to at least 35 psig and venting.

The venting procedure was repeated three times to ensure removal of air from the headspace. The headspace of the bottle was then filled with hydrogen gas to 50 psig and shaking was initiated. The reactor vessels for the hydrogenation apparatus have a limit of 60 psi.

The reactions were run at room temperature as it is important in making the application feasible for on-site remediation as well as minimizing the associated cost. The hydrogenation reactor is designed to shake at 200 rpm to ensure complete mixing. After shaking for the desired amount of time, the reactor was stopped, and samples were taken for analysis.

4.2.3 Sampling and Analysis

At the end of each hydrogenation run, the shaker was stopped and vented. An appropriate amount of solution was filtered with Whatman glass microfiber filters. Two filtered samples were taken for analysis and were prepared as in the initial analysis depending on the chemical being measured.

4.2.4 Control Experiments

For each set of experimental conditions, two control tests were conducted to verify that any observed disappearance of contaminant was due to reduction. The first control experiment was conducted in exactly the same fashion as described above with the exception that no catalyst was added to the reaction bottle. The reaction vessel was spiked with the desired compound. This determines the loss of TeCB, benzene, and cyclohexane due to volatilization. The experiment for determining the volatilization for TeCB was run over the course of three hours. The individual experiments for benzene and cyclohexane was run for ten hours.

The second control test was to investigate the loss due to sorption on to the surface of the catalyst. The second type of control experiment was performed

by placing equimolar amounts of TeCB, benzene, and cyclohexane in the reactor with both palladium and rhodium catalyst present. Nitrogen gas was used in place of hydrogen in this control test to determine the amount of contaminant that was sorbed onto the surface of the catalyst.

The volatilization control experiment showed no net loss for either TeCB or benzene over the course of 10 hours. Cyclohexane showed a 13% loss from volatilization. The sorption test shows 100% loss of benzene, 20% loss for TeCB, and 0% loss for cyclohexane.

4.3 Results and Discussion for HDH of TeCB

For HDH tests, 0.2 grams of palladium catalyst was placed in the reactor vessel before running the reactions to give 0.67 g/L of catalyst in solution. The 50:50 water-ethanol solution was spiked with 1.2 mL of TeCB stock solution to give a TeCB concentration of 10 mg/L in the reactor vessel. Various reaction times were run in order to qualitatively show the hydrodehalogenation of TeCB.

A material balance was performed on the batch reactor. The assumptions were that the reactor is well mixed and the reactor volume is the entire reactor contents. The reactor volume for the experiments conducted was 300 mL and did not change over the course of the reaction.

Recall the basic material balance equation:

- $\{Rate\ of\ Accumulation\ of\ Component\ j\} =$

  $\{Rate\ of\ inflow\ of\ Component\ j\} - \{Rate\ of\ outflow\ of\ Component\ j\} +$

  $\{Rate\ of\ generation\ of\ Component\ j\} -$

  $\{Rate\ of\ consumption\ of\ Component\ j\}$

Based on the assumptions, the material balance for batch reactor conditions is:

- $$\frac{d(C_T)}{dt} = R_T \tag{4}$$

where C_T is the concentration of TeCB in solution and R_T is the rate of hydrodehalogenation of TeCB. The reaction is simply

- $$C_6H_2Cl_4 + 4H_2 \xrightarrow{Pd} C_6H_6 + 4H^+ + 4Cl^- \tag{5}$$
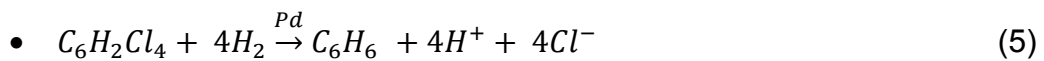
Let the reaction rate be given by a simple first order rate expression where

- $$r_1 = k_1 C_T \tag{6}$$

where r_1 is the reaction rate of hydrdehalogenation of TeCB and k_1 is the reaction rate coefficient.

The material balances are then

- $$\frac{dC_T}{dt} = R_T = -r_{1=} - k_1 C_T \tag{7}$$

for TeCB and

- $$\frac{dC_B}{dt} = R_B = r_1 = k_1 C_T \tag{8}$$

for benzene, where R_B is the reaction rate for the formation of benzene. The material balances can easily be solved, yielding:

$$C_T = C_{T0}e^{-k_1 t}$$ (9)

for TeCB and

$$C_B = C_{T0}(1 - e^{-k_1 t})$$ (10)

for benzene. Plotting the natural log of $\frac{C_T}{C_{T0}}$ versus time gives an estimated value for k_1 based on observed data. Figure 4.1 shows the estimated value of k as 0.11 hours^{-1}.
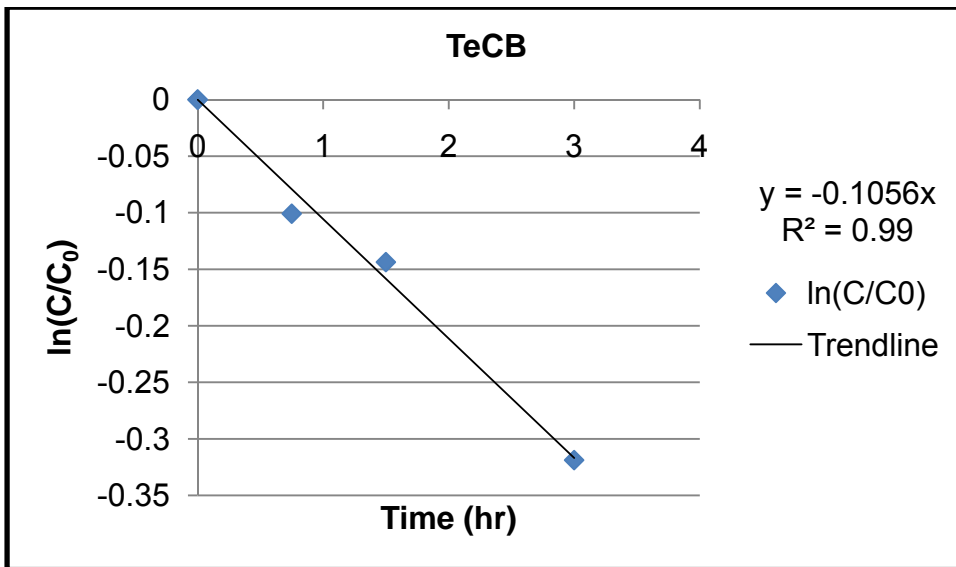
Figure 4.2 Estimate for the Reaction Rate Coefficient for HDH of TeCB

Using the material balance and estimate for k_1 based on experimental data predicted concentrations for TeCB and benzene were calculated. These predicted concentrations were plotted against experimental data shown in Figure 4.3. A plot using a k_1 of 0.30 hours^{-1} gave a better fit than a plot with 0.10 hours-1

as shown in Figure 4.4. An estimate of 0.30 hours^{-1} will be used as the reaction rate coefficient k_1.
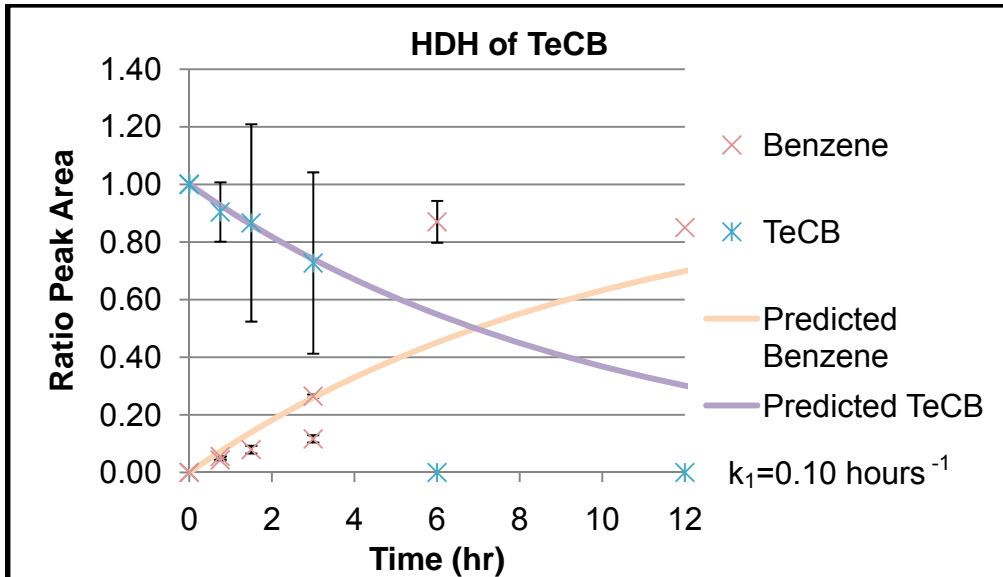
Figure 4.3 First Order Kinetic Model for HDH of TeCB
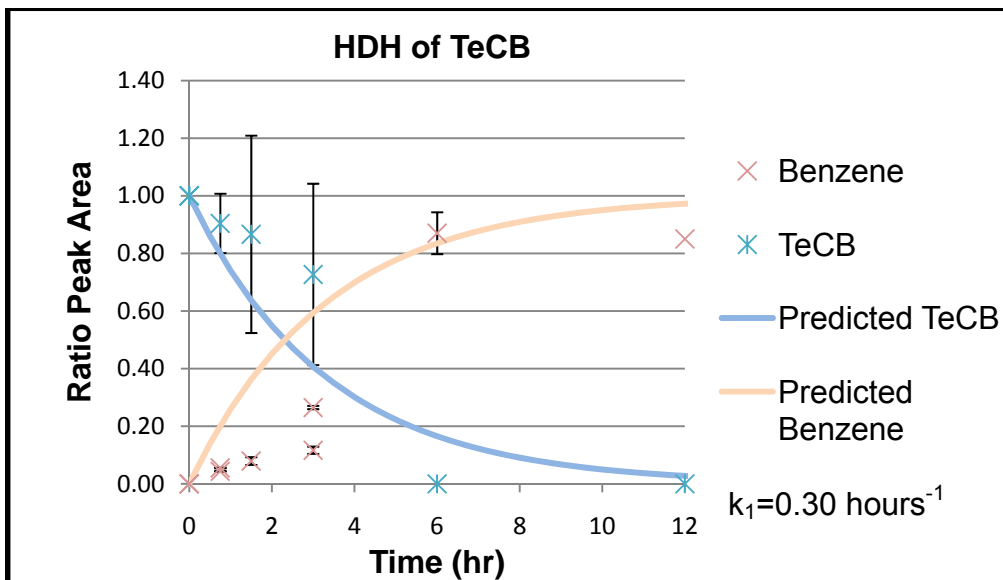
Figure 4.4 First Order Kinetic Model for HDH of TeCB with k_1=0.30 Hours^{-1}

The analytical model shows that the reactions are consistent with first order reaction kinetics. Table 4.2 shows a summation of the fraction of mass recovered for TeCB and benzene. This helps to show if the mass balance was closed.

Table 4.2 Summation of Mass Fractions for TeCB and Benzene for HDH

Time (hrs)	TeCB (C_T/C_0)	Benzene (C_B/C_0)	Cyclohexane (C_c/C_0)	Total (C/C_0)
0	1	0	0	1
0.75	0.9	0.06	0	0.96
0.75	*	0.04	0	*
1.5	0.87	0.08	0	0.95
3	*	0.12	0	*
3	0.74	0.26	0.01	1.01
6	0	0.87	0.02	0.89
12	0	0.92	0.03	0.95

The columns marked by * for TeCB were for runs where an irregular baseline disrupted quantifying TeCB. The average mass recovered, based on samples where all three analytes were quantified, was 95%.

4.4 Results and Discussion for Hydrogenation of Benzene

Initially 0.8 grams of rhodium catalyst was used and the reaction was run for 24 hours to observe if complete hydrogenation of benzene would occur. There was still benzene left in solution after 24 hours. 0.9 g was successful at completely hydrogenating benzene over the course of a 24 hour period and was selected as the appropriate amount of catalyst. The rhodium catalyst concentration in solution was 3 g/L. The reactor was spiked with 0.5 mL of the

benzene stock solution to give 2.9 mg/L of benzene in 50:50 water-ethanol

solution. Various reaction times were run in order to develop a qualitative model

for the hydrogenation of benzene. Each reaction time was run twice.

A similar material balance from that performed on the batch reactor for

HDH of TeCB was performed for the hydrogenation reaction of benzene.

The hydrogenation reaction for benzene is simply

- $C_6H_6 + 3H_2 \xrightarrow{Rh} C_6H_{12}$ (11)

Let the reaction rate be given by a simple first order rate expression where

- $r_2 = k_2 C_B$ (12)

where r_2 is the reaction rate of hydrogenation of benzene, C_B is the concentration

of benzene in the 50:50 water-ethanol solution, and k_2 is the reaction rate

coefficient.

The material balances are then

- $\frac{dC_B}{dt} = R_B = -r_2 = -k_2 C_B$ (13)

for benzene where R_B is the reaction rate of hydrogenation and

- $\frac{dC_C}{dt} = R_C = r_2 = k_2 C_B$ (14)

for cyclohexane, where R_C is the reaction rate for the formation of cyclohexane

and C_C is the concentration of cyclohexane in solution. The material balances

can be solved easily to give

- $C_B = C_{B0}e^{-k_2 t}$ (15)

for benzene and

- $C_C = C_{B0}(1 - e^{-k_2 t})$ (16)

for cyclohexane. Plotting the natural log of $\frac{C_B}{C_{B0}}$ versus time gives an estimated

value for k_2 based on observed data. Figure 4.1 shows the estimated value of k_2

as 0.39 hours^{-1}.

Benzene

$y = -0.3935x$
$R^2 = 0.8669$

◆ Benzene
— Trendline

y-axis: ln(C/C₀) — $\ln(C/C_0)$
x-axis: Time (hr)
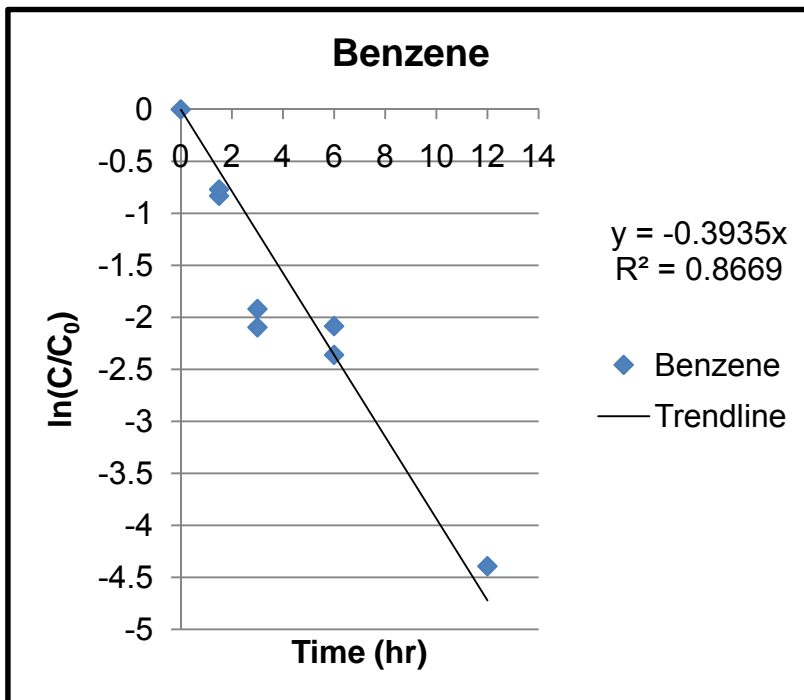
Figure 4.5 Estimate of the Reaction Rate Coefficient for the Hydrogenation of Benzene

The following figure displays the experimental data obtained for the

hydrogenation of benzene plotted with the predicted values of benzene and

cyclohexane according to the material balance and the estimate for the reaction rate coefficient of 0.39 hours^{-1} for k_2.
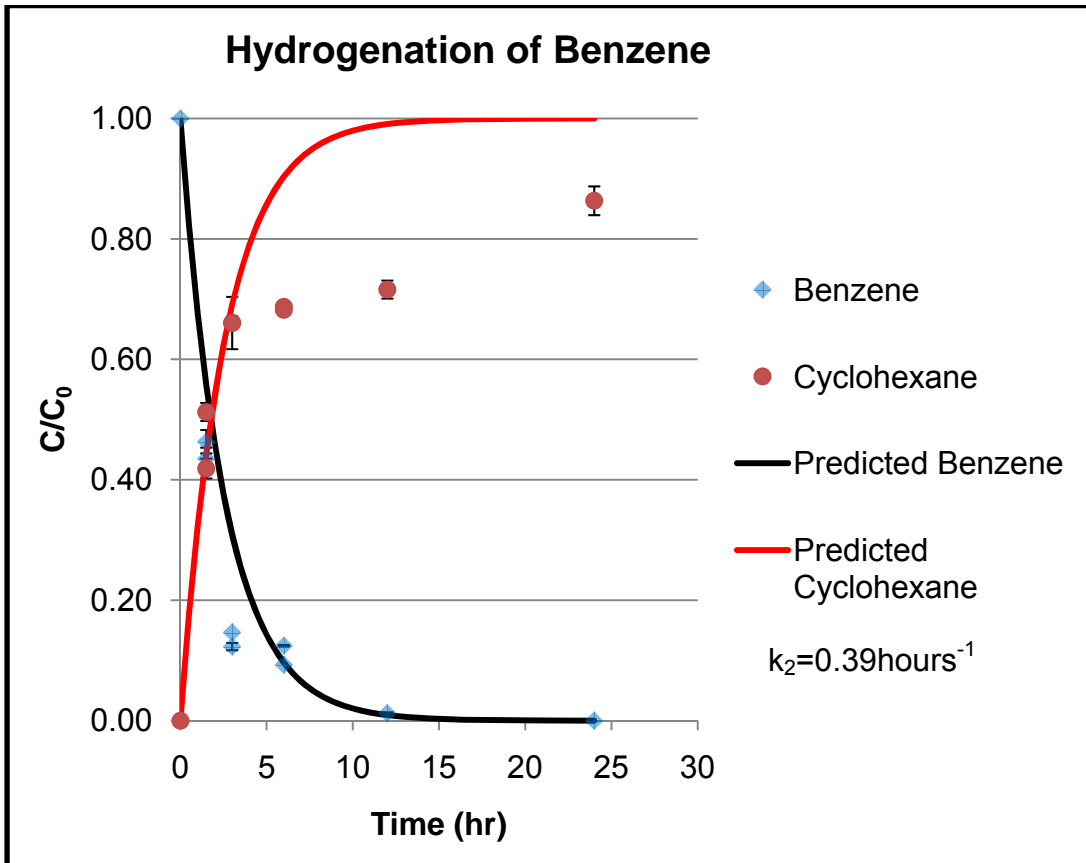
Figure 4.6 Hydrogenation of Benzene

A summation of the fraction of mass in solution for benzene and cyclohexane is shown in Table 4.3. The final column gives a total of recovered benzene and cyclohexane. On average 83% of the initial mass of benzene was recovered either as cyclohexane or as unreacted benzene.

Table 4.3 Summation of Mass Fractions for the Hydrogenation of Benzene

Time (hr)	Benzene (C_B/C_0)	Cyclohexane (C_C/C_0)	Total (C/C_0)
0	1	0	1
1.5	0.44	0.42	0.85
1.5	0.46	0.51	0.98
3	0.12	0.66	0.78
3	0.15	0.66	0.81
6	0.12	0.69	0.81
6	0.09	0.68	0.78
12	0.01	0.72	0.73
24	0.00	0.86	0.86

4.5 Conclusion

The data show that for the hydrodehalogenation and hydrogenation reactions the experimental data are consistent with a first order kinetic model. The generation of cyclohexane from hydrogenation shows that the model seems to fit well during the initial disappearance of benzene, but then deviates from the trend as more cyclohexane formation was predicted that observed. This may be due to sorption of cyclohexane onto the catalyst surface, or that time for diffusion from the catalyst surface had not been reached. The most likely contributing factor to lower concentrations of cyclohexane in solution than predicted is volatilization of cyclohexane as shown by the control tests.

The HDH reaction of TeCB was the last experiment performed in the lab. The palladium catalyst had been opened for several months at the point of this last experiment. Based on the slow HDH of TeCB, I believe the catalyst had lost activity from oxidation. Comparing reaction times from when I had initially

received the catalyst to the reaction times observed from these last experiments I had run, it becomes apparent that the catalyst had lost activity, presumably from oxidation because it had not previously been used. The mechanism of loss of activity could be confirmed by regenerating the catalyst by reduction under hydrogen pressure and re-running the experiments to observe if a higher reaction rate is achieved. If the reaction rate increased after reduction under hydrogen pressure, than it could be confirmed that the catalyst had oxidized and had been successfully regenerated.

Chapter 5: Dual-Catalyst Batch Reactor Analysis for Hydrodehalogenation and Hydrogenation of TeCB Using Pd and Rh Catalysts

5.1 Introduction

The long-term objective of REACH is to design a new remediation technology for soil that allows for full-scale treatment without generating a secondary waste. The goal of this thesis research is to demonstrate that TeCB can be fully converted to cyclohexane. This should ideally be completed in a single reactor versus a series of batch reactors. The goal of this chapter is to determine if TeCB will be destroyed and cyclohexane formed in a single batch reactor when both Pd and Rh are present. I refer to this as a "dual-catalyst" reactor to distinguish it from the individual reactors considered in Chapter 4.

5.2 Methods and Materials

5.2.1 Chemicals and Catalysts

The chemicals employed in this research are summarized in Table 3.1. Refer to Table 4.1 for a description of catalysts used in this research. A 50:50 mixture of water and ethanol was prepared using de-ionized water and 200 proof (99.5%) ethanol. 5% (wt.) Pd-on-Al_2O_3 and 0.5% (wt.) Rh-on-Al_2O_3 catalyst were employed and the content of the catalyst specified by the manufacturer is assumed to be accurate. The catalysts were used in the hydrodehalogenation

and hydrogenation reactions without further treatment. No special effort was given to prevent either catalyst from contacting air.

5.2.2 Stock Solution

A stock solution of TeCB was prepared with a concentration of 2500 mg/L in ethanol by dissolving 50 mg of 1,2,4,5-tetrachlorobenzene in 20 mL of ethanol in a 20 mL borosilicate vial with a PTFE-lined septa cap and kept in the freezer to minimize volatilization.

5.2.3 Reaction Studies

In this research, all hydrodehalogenation and hydrogenation reactions were carried out in a Parr 3911 hydrogenation apparatus (Parr Instrument Company, Moline, IL, USA). The experiments were conducted as follows.

A 300 mL mixture of 50:50 water-ethanol was transferred to a 500 mL reaction bottle. 1.2 mL of TeCB stock solution was added to the reactor vessel. Two initial samples were then taken to affirm the initial concentration of TeCB, predicted to be 10 mg/L. The desired amount of rhodium- and palladium-catalyst was then added to the reaction bottle. The same amount of catalyst shown in the single batch reactor studies was used, 0.67 g/L for the palladium catalyst and 3 g/L for the rhodium catalyst.

The bottle was then placed in the hydrogenation reactor and air in the bottle was removed by filling the bottle with hydrogen gas to at least 35 psig and venting. The venting procedure was repeated three times to ensure air from the

headspace had been removed. The headspace of the bottle was then filled with hydrogen gas to 50 psig and shaking was initiated. The hydrogenation reactor is designed to shake at 200 rpm to ensure complete mixing. After shaking for the desired amount of time, the reactor was stopped, and samples were taken for analysis. The reaction was run at room temperature and 50 psig under hydrogen pressure.

5.2.4 Sampling and Analysis

At the end of each run, the shaker was stopped and vented. An appropriate amount of solution was filtered using Whatman glass microfiber filters. Four filtered samples were taken to be analyzed, two of which were analyzed on the ECD to detect any remaining TeCB, and two of which were analyzed on the FID for quantifying the amount of benzene and cyclohexane generated.

5.2.5 Control Experiments

The results for control experiments described in Chapter 4 were used to determine loss of TeCB, benzene, and cyclohexane from sorption and volatilization in this experiment in order to close the mass balance.

5.3 Results and Discussion

A material balance was performed on the batch reactor. The assumptions are the reactor is well mixed and the reactor volume is the entire reactor contents. The reactor volume for the experiments conducted was 300 mL

and did not change over the course of the reaction. Recall the basic material balance equation:

- $\{Rate\ of\ Accumulation\ of\ Component\ j\} =$

  $\{Rate\ of\ inflow\ of\ Component\ j\} - \{Rate\ of\ outflow\ of\ Component\ j\} +$

  $\{Rate\ of\ generation\ of\ Component\ j\} -$

  $\{Rate\ of\ consumption\ of\ Component\ j\}$

Based on the assumptions and the material balance being performed on a batch reactor where the inflow and outflow are 0, the following equation is achieved:

- $\dfrac{d(C_j)}{dt} = R_j$ \hfill (17)

where C_j is the concentration for the compound that is being observed in a 50:50 water-ethanol solution and R_j is the reaction rate of that compound. There are two reactions in series:

- $C_6H_2Cl_4 + 4H_2 \xrightarrow{Pd} C_6H_6 + 4H^+ + 4Cl^-$ \hfill (18)

- $C_6H_6 + 3H_2 \xrightarrow{Rh} C_6H_{12}$ \hfill (19)
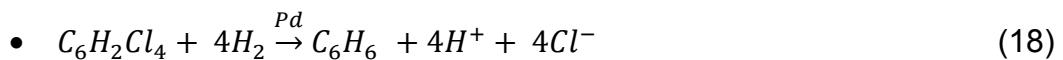
Let the reaction rates be given by simple, first order rate expressions where

- $r_1 = k_1 C_T$ \hfill (20)

- $r_2 = k_2 C_B$ \hfill (21)

where r_1 is the reaction rate of HDH of TeCB and r_2 is the reaction rate of hydrogenation of benzene. The material balances are as follows.

TeCB:

- $$\frac{dC_T}{dt} = R_A = -r_1 = -k_1 C_{TeCB} \tag{22}$$

Benzene:

- $$\frac{dC_B}{dt} = R_B = r_1 - r_2 = k_1 C_{TeCB} - k_2 C_{Benzene} \tag{23}$$

Cyclohexane:

- $$\frac{dC_C}{dt} = R_C = r_2 = k_2 C_B \tag{24}$$

The material balance for TeCB can be solved easily to give

- $$C_T = C_{T0} e^{-k_1 t} \tag{25}$$

Solving the material balance for benzene becomes slightly more challenging. The solved ODEs for benzene and cyclohexane are:

- $$C_B = \frac{k_1}{k_2 - k_1} C_{T0} (e^{-k_1 t} - e^{-k_2 t}) \tag{26}$$

- $$C_C = C_{T0} (\frac{k_1}{k_2 - k_1} e^{-k_2 t} - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_2 - k_1}{k_2 - k_1}) \tag{27}$$

The material balances were used to make estimates for k_1 and k_2 based upon reaction data and then plotted against the reaction data to see if reactions followed first order kinetics. Using the material balance for TeCB to solve for k_1

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was accomplished by plotting the natural log of C/C_0 against time. Figure 5.1 shows k_1 was determined to be 0.66 hours $^{-1}$.
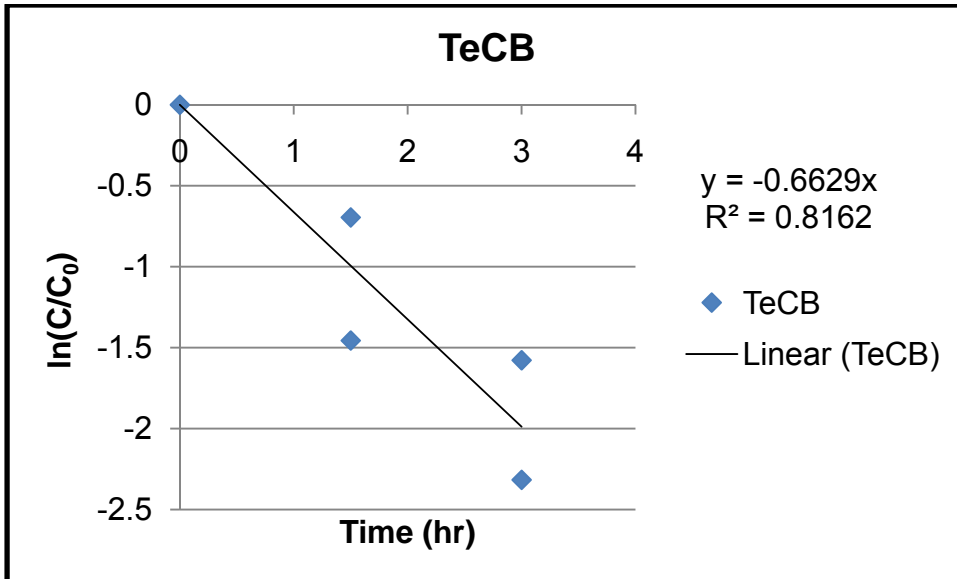
Figure 5.1 Estimate for k_1 for the Hydrodehalogenation of TeCB

Plotting observed data for TeCB in Figure 5.2 shows that the estimate for k_1 is reasonable.
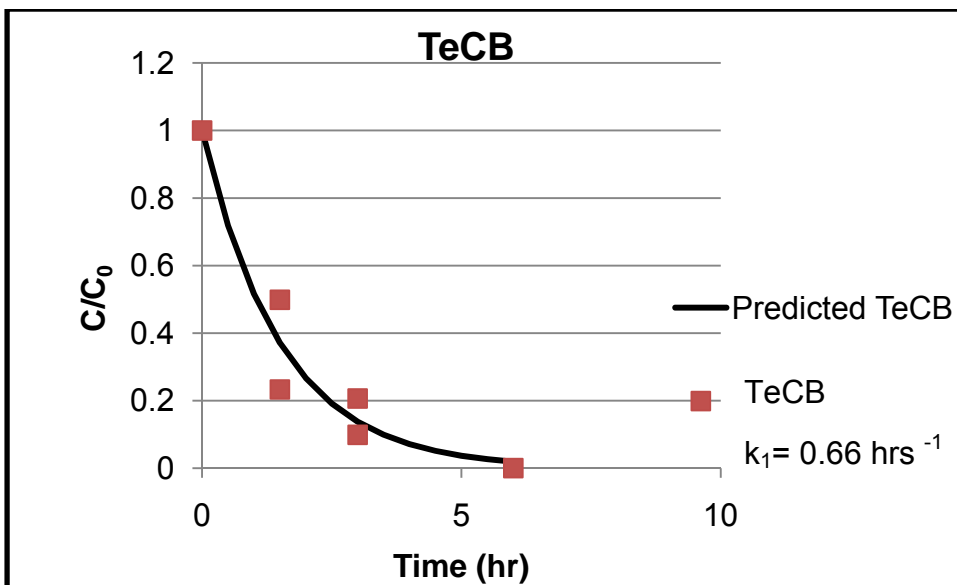
Figure 5.2 Experimental Data for the Hydrodehalogenation of TeCB Plotted Against Predicted Values of TeCB with k_1 Estimated as 0.66 Hours $^{-1}$

The experimental data were then plotted to show the reactions for the hydrodehalogenation of TeCB. Figure 5.3 shows the disappearance of 1,2,4,5-TeCB during the dehalogenation reaction, forming benzene, and then the hydrogenation reaction happening in series, resulting in the consumption of benzene and formation of cyclohexane as the end product. A value of 0.60 hours^{-1} gave a better fit overall than 0.66 hours^{-1} for k_1.
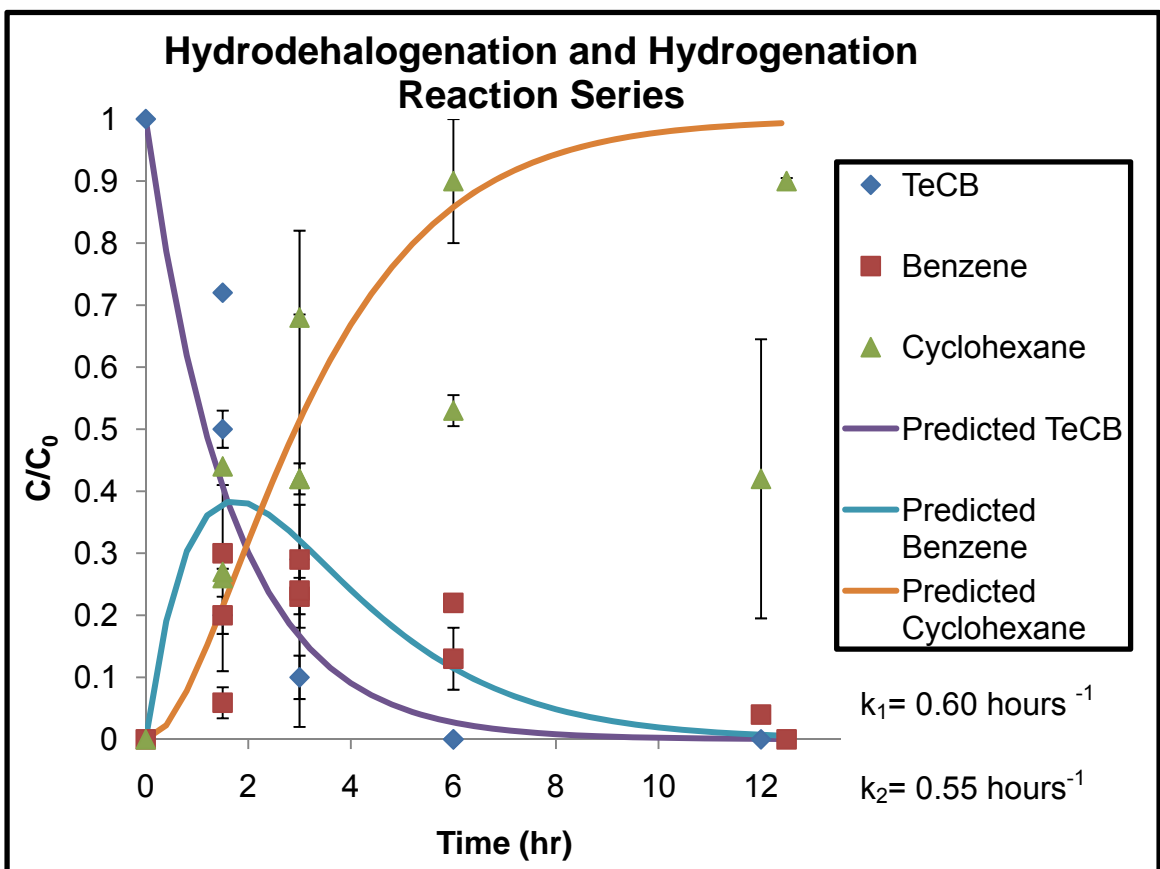
Figure 5.3 Reaction Data for Hydrodehalogenation & Hydrogenation of TeCB with Estimates for the Rates of Reaction.

Qualitatively the figure shows the dehalogenation of TeCB and the hydrogenation of benzene. Initially during the reaction sequence, TeCB is disappearing as benzene is formed. As benzene is formed it is hydrogenated to

cyclohexane. Qualitatively the experimental data show what we expected, that TeCB would be hydrodehalogenated and benzene would be hydrogenated. The experimental data are consistent with first order reaction kinetics. However, the estimates for the reaction rate coefficients are hard to determine accurately because of the variability in data for each reaction time.

The formation of benzene does not seem to follow the reaction rate found by estimating it upon observed hyrdodehalogenation of TeCB. A closer fit yields a significantly lower value for the reaction rate coefficient for the formation reaction while keeping the reaction rate coefficient the same for the hydrogenation (consumption) reaction. Figure 5.4 shows the prediction of a lower reaction rate coefficient for benzene formation to yield a better fit for the superimposed reaction series.
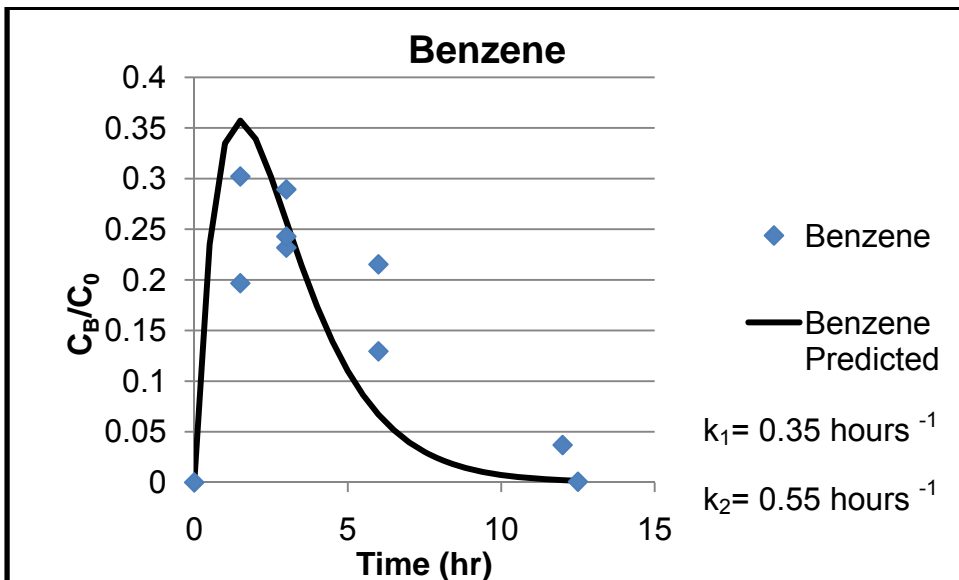
Figure 5.4 Estimated Values for the Reaction Rate Coefficients of the Hydrodehalogenation & Hydrogenation Reactions Based on Experimental Data Observed for Benzene

The observed data for benzene may be hard to fit by this method as diffusion and sorption on the catalyst surface were not taken into account. A more developed model that describes the data set was not implemented based on the variability of data for the separate reaction times.

Notice the best fit obtained for the generation of cyclohexane shown in Figure 5.5 results in different reaction rate coefficients than that for benzene. The fit for the experimental data for cyclohexane shows that the hydrodehalogenation reaction rate coefficient is kept the same as that estimated for the overall reaction series, but a greater hydrogenation reaction rate coefficient yields a better fit for cyclohexane.

Again, the estimated reaction rates are hard to determine from the data sets. Notice that the reaction is nearly completed by 6 hours, but as cyclohexane remains in solution, there is a decline in the concentration observed. Based on the control test where 13% of cyclohexane had volatilized, it can be estimated that the mole fraction of cyclohexane recovered would be 87. This is consistent with what was observed in Figure 5.5, taking into account the data points that follow the predicted curve.
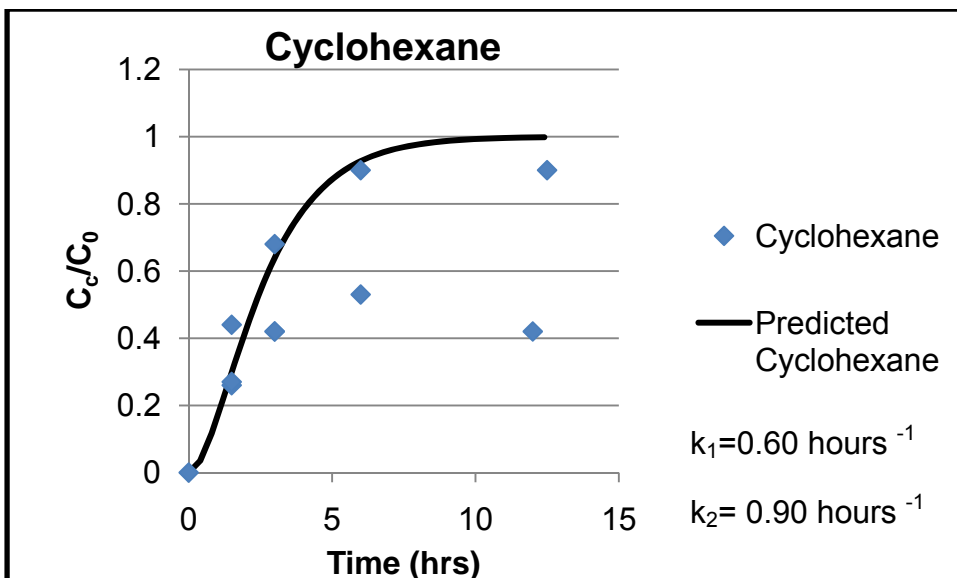
Figure 5.5 Estimated Values for the Reaction Rate Coefficients of the Hydrodehalogenation & Hydrogenation Reactions Based on Experimental Data Observed from the Formation of Cyclohexane

It should be determined for each individual reaction time if loss of TeCB can be accounted for by being converted to cyclohexane and benzene. Table 5.2 shows a list of the different reaction times and the associated mass fraction for the reactant and products. A summation of the mass fraction for the analytes that could be quantified indicated that loss of TeCB was due to being converted to benzene and cyclohexane with an average recovery of 90%.

Table 5.1 Summation of Mass Fractions for Dual-Catalyst Batch Reactor

Time (hr)	TeCB (C_T/C0)	Benzene (C_B/C0)	Cyclohexane (C_C/C0)	Total (C/C_0)
1.5	0.73	0.06	0.26	1.05
1.5	0.20	0.30	0.40	0.91
1.5	0.50	0.20	0.27	0.96
3	0.10	0.29	0.68	1.07
3	*	0.23	0.42	*
3	0.29	0.24	0.42	0.95
6	0.00	0.22	0.53	0.74
6	0.00	0.13	0.90	1.03
12	0.00	0.04	0.42	0.46
12.5	*	0.00	0.89	*

This table shows the ratio of reactant or product left after the reaction to that of the initial concentration of TeCB. This shows overall that the disappearance of TeCB was due to being converted to benzene and cyclohexane because the summation of the fractions is near one for each individual reaction time. Items marked by * indicate that a reading could not be measured due to an error associated with the GC.

The pH was measured at the beginning and ending of each run by litmus paper. This showed an initial pH of 7 and a pH of 6 at the end of each reaction time. This is not an accurate measurement of pH as the detection level was 6.0. A low pH is expected as HCl will form in solution (Xia et al. 2004). A buffering agent will be needed to raise the pH. Care must be taken on the selection of an appropriate buffer as some buffers have been shown to limit the catalytic activity (Xia et al. 2004).

5.4 Conclusion

The hydrodehalogenation of TeCB and hydrogenation of benzene was successful at a hydrogen pressure of 50 psig using both a palladium and rhodium catalyst. The data show that the reactions are consistent with a first order kinetics model. An estimate of the reaction rate coefficient for the dehalogenation reaction was approximately 0.60 hours^{-1} and 0.55 hours^{-1} for the hydrogenation reaction.

Increasing the pressure is the most likely means to increasing the reaction rate. Rhodium-catalytic hydrogenation of benzene is performed at higher temperatures and pressures (Aresta et al. 2008, Halligudi et al. 1992) than shown in this research.

Increasing the rhodium weight percent in solution in order to try to achieve complete conversion faster than 12 hours would also be a way to increase the reaction rate, but is probably not as cost-effective as increasing the hydrogen pressure. A solvent with a higher ratio of water to ethanol may be needed to increase the activity of the catalysts, but this is not ideal as it will decrease the amount of contaminant removed from soil.

It is not recommended to increase the palladium weight percent as it is believed that there was more palladium-catalyst than needed. This conclusion is drawn from comparing observed data from the reactions where only rhodium catalyst was present and yielded a reaction rate coefficient of 0.39 hours $^{-1}$ to that

where both palladium and rhodium-catalyst were present and the reaction rate

for hydrogenation of benzene was increased to 0.55 hours^{-1}.

Chapter 6: Summary, Conclusions, and Future Work

6.1 Summary and Conclusions

The research presented in this thesis qualitatively shows that TeCB can be hydrodehalogenated to benzene and that benzene will then be hydrogenated to cyclohexane in a single batch reactor in the presence of palladium and rhodium catalysts, while under mild hydrogen pressure and at room temperature. Hydrogenation of benzene at 50 psi is lower than that found in literature while also being at room temperature. Often hydrogenation of benzene takes place at higher temperatures and pressure. The data shown are consistent with a sequential first-order reaction model. The estimates for k_1 and k_2 for a dual-catalyst batch reactor are 0.60 hours^{-1} and 0.55 hours^{-1}.

The estimates for k_1 and k_2 for the individual batch reactors were 0.30 hours^{-1} for k_1 and 0.39 hours^{-1} for k_2. The separate estimates for k_1 cannot be compared as the activity of the palladium catalyst may have changed over time. Observed conversion of TeCB was lower at the end of my experiments even when running with similar operating conditions, which may indicate loss of Pd activity.

There is approximately a 40% difference between the observed k_2 values in the dual-catalyst batch reactor with palladium and rhodium and that of the

individual reactor with only rhodium catalyst present. Palladium is known to hydrogenate benzene as well. This may have increased the effective reaction rate coefficient. However, the data set for the individual reaction times had significant internal variability. It is hard to draw conclusions on the reaction rate coefficient because of this. The variability in data could possibly have occurred from the temperature increasing over the course of reaction as both reactions are exothermic. Keeping a consistent reactor temperature would most likely lead to a tighter data fit and less variability in the data.

Another significant contribution of this research was developing the analytical methods for analyzing and quantifying TeCB, benzene, and cyclohexane in solutions of high ethanol concentration. This had not been shown in the literature and was the most challenging aspect of this research.

6.2 Future Work

Future work will need to include trying to minimize the overall reaction time needed to reduce TeCB to cyclohexane. Increasing the hydrogen pressure and/or temperature have been shown to decrease the reaction time needed for hydrogenation reactions (Halligudi 1992, Pellegrata 2001). However, it is preferable from a practical standpoint to keep a moderate pressure and run the reactions at room temperature.

A different support for the catalysts may increase catalytic activity, as might running the catalytic reactions homogenously where the catalyst is dissolved in solution. The reactions in this research were heterogeneous and the

catalysts used in these experiments were pellets. The pH will also need to be investigated as HCl is expected to form. It will need to be determined how this affects the activity of the catalyst.

Scaling up the reactor design and performing a cost analysis on the design will need to compare current technology with this new method to demonstrate feasibility. The cost of catalyst will be the major factor in whether this technology is competitive. Rhodium is the rarest precious metal, making it the most costly, and is commonly mined in South Africa and Ontario, Canada (Hilliard 2001). Palladium is also rare. Ore deposits are found in Russia, South Africa, Canada, and Montana (Hilliard 2001). The price of such precious metal has historically been seen to vary greatly over time (Hilliard 2001). A method for recovering and regenerating the catalyst will need to be developed in order to make this process feasible for full-scale application. Determining the number of times the catalyst can be reused, as well as how many tons of soil can be treated by this method, will determine the feasibility.

The REACH technology has a way to come before it can be implemented as a continuous system for full-scale soil remediation. This research has furthered the technology by investigating the catalytic treatment in batch reactors to demonstrate TeCB being fully converted to cyclohexane.

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