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Enhancing the Scrubbing of Chlorinated Compounds from Air Streams

by
Jodi Collins

A thesis submitted to
The Faculty of Graduate Studies and Research
in partial fulfillment of the requirements

for the degree of
Master of Engineering

**Department of Civil and Environmental Engineering
Carleton University, Ottawa
September, 1998**

The Master of Engineering Program in Civil and Environmental
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Department of Civil and Environmental Engineering

The undersigned recommend to the Faculty of Graduate
Studies and Research acceptance of the thesis

**Enhancing the Scrubbing of Chlorinated
Compounds from Air Streams**

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Chair, Department of Civil and
Environmental Engineering

Co-Supervisor, Dr. Wayne Parker

Co-Supervisor, Dr. Kevin Kennedy

Carleton University
Ottawa, Ontario, Canada
September, 1997

Abstract

This research addresses an investigation of mass transfer issues associated with an innovative hybrid process to treat air streams containing chlorinated organics. Three target compounds (dichloromethane (DCM), carbon tetrachloride (CT) and tetrachloroethylene (PCE)) have been selected based upon their range of chemical and physical properties.

Gas-liquid partitioning batch tests clearly demonstrated that aqueous solutions of cosolvents such as propylene glycol will likely require large volumes of cosolvents (i.e. greater than 40% v/v) to substantially reduce the gas phase partitioning of the target compounds. Vegetable oil was identified to be an effective scrubbing solution in removing the target compounds from the air streams and was employed in the continuous flow tests of the bench-scale countercurrent packed column. Removal efficiencies approached 90% for all three target compounds with gas-liquid flow ratios less than 200.

A scrubbing model was developed and compared to the existing Onda correlations, to characterize mass transfer under various operating conditions when water and vegetable oil were employed as scrubbing solutions. It was found that the Onda correlations did not fit the experimental data of vegetable oil very well, hence the existing Onda correlations were modified by assuming that the gas phase resistance was controlling mass transfer.

In order to enhance mass transfer from the oil phase to an aqueous phase a liquid-liquid contacting reactor was proposed. The results of the liquid-liquid reactor suggested that mass transfer could be achieved for compounds that were not highly hydrophobic.

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Glossary

Symbols

ε	= void ratio of packed column
ϕ	= diameter of column (m)
$\gamma_{w,c}$	= activity coefficient in water, cosolvent respectively
$\partial C/\partial x$	= concentration gradient ($\text{mol}\cdot\text{m}^{-4}$)
μ_G	= gas viscosity ($\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$)
ρ_G	= gas density (kg/m^3)
ΔH^0	= enthalpy change at standard state (kJ/mole)
ΔV	= differential volume (m^3)
μ_L	= liquid viscosity ($\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$)
σ_L	= critical surface tension of water (N/m)
μ_L	= liquid viscosity (kg/m sec)
ρ_L	= liquid density (kg/m^3)
ΔS_f	= entropy of fusion of the solute (zero if solute is liquid)
μ_w	= viscosity of water (cp)
A	= surface area of column (m^2)
a_t	= area/volume ratio (m^2/m^3)
C_A	= VOC concentration in air
C_g	= outlet gas concentration of VOC (mg/L)
$C_{g,*}, C_l$	= bulk gas and liquid phase concentration respectively (g/m^3)
C_g	= gas phase conc. that is in equilibrium with bulk liquid conc.
C_{gl}, C_{g2}	= gas concentration in high and low volume systems respectively (EPICS)
C_{gi}, C_{li}	= interface gas and liquid phase concentration respectively (g/m^3)
C_{go}	= inlet gas concentration of VOC (mg/L)
$C_{L,*}$	= outlet liquid concentration of VOC (mg/L)
C_l	= liquid phase conc. that is in equilibrium with bulk gas conc.
C_{l1}, C_{l2}	= liquid concentration in high and low volume systems respectively
C_{li}	= liquid concentration after i number of equilibrations (g/m^3)
C_{lo}	= initial liquid concentration (g/m^3)
C_{Lo}	= inlet liquid concentration of VOC (mg/L)
C_{oil}	= VOC concentration in vegetable oil
C_w	= VOC concentration in water
d	= packing diameter (m)
D_{AB}	= diffusivity of the solute ($\text{m}^2\cdot\text{s}^{-1}$)
D_g	= diffusivity of the solute in the gas phase (m^2/s)
D_l	= diffusivity of the solute in the liquid phase (m^2/s)
d_p	= nominal packing area (m)
ds	= diameter of a sphere having same surface area as unit of packing (m^{-1})
F	= packing factor
g	= gravity (m/sec^2)

G_M	= gas mass loading rate ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
H	= Henry's coefficient ($\text{atm}\cdot\text{mol}^{-1}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$)
H	= Henry's law coefficient of the solute ($\text{m}^3\cdot\text{atm}\cdot\text{mol}^{-1}$)
H_c	= dimensionless Henry's law coefficient
J	= molecular mass transfer flux of solute ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
k	= constant
$K_{A/O}$	= air-oil partitioning coefficient
$K_{A/W}$	= air-water partitioning coefficient
k_g	= mass transfer coefficient for the gas film (m/s)
K_g	= overall mass transfer coefficient based on gas phase concentration (m/s)
K_l	= overall mass transfer coefficient based on liquid phase conc. (m/s)
k_l	= mass transfer coefficient for the liquid film (m/s)
K_{La}	= mass transfer coefficient (sec^{-1})
$K_{W/oct}$	= water-octanol partitioning coefficient
L_M	= liquid mass loading rate ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
M_1, M_2	= total mass in high and low volume systems respectively
MP	= melting point of compound
n	= the total number of equilibrations
P	= partial pressure of the solute (atm)
Q_g	= gas flow rate through packed column (m^3/s)
Q_l	= liquid flow rate through packed column (m^3/s)
R	= universal gas constant, $8.205 \times 10^{-5} (\text{m}^3\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
s	= rate of production of fresh surface per unit area of total surface
t	= time (h)
T	= temperature in (Kelvin)
t_e	= exposure time of bulk phase at the interface
V'_B	= LeBas molal volume of contaminant (cm^3/mol)
V_A	= molar volumes of air ($20.1 \text{ cm}^3/\text{mol}$)
V_B	= molar volume of solute (cm^3/mol)
V_G	= gas volume of closed system (m^3)
V_{g1}, V_{g2}	= volume of gas in high and low volume systems respectively (EPICS)
V_L	= liquid volume of closed system (m^3)
V_{l1}, V_{l2}	= volume of liquid in high and low volume systems respectively
z	= depth of column (m)
Z_g, Z_l	= effective gas and liquid film thickness respectively (m)

Abbreviations

DCM	= dichloromethane
CT	= carbon tetrachloride
PCE	= tetrachloroethylene
GC	= gas chromatograph
BDL	= below detection limit

Chapter 1 – Introduction

1.1 Background

Air streams contaminated with chlorinated organic compounds arise from many different sources including industrial vents, contaminated soil venting off-gases and gas streams from wastewater treatment processes. These contaminated air streams have been a growing concern due to their negative impacts on stratospheric ozone and their carcinogenic effect on the human population.

Existing technologies such as incineration and carbon adsorption have proven to be ineffective or costly and hence a biological process that could overcome these problems would be desirable. Conventional biofiltration processes are aerobic which are not suitable for the degradation of chlorinated organics. Hence, this thesis addresses an investigation of mass transfer issues associated with an innovative hybrid process to treat air streams containing chlorinated organics.

1.2 Overview

The proposed hybrid system involves the transfer of contaminants from the gas phase to the liquid phase in a countercurrent packed bed column. The gas phase is passed upwards through the column and the liquid phase is recirculated downwards over the column packing. The liquid phase containing the chlorinated organics is then transferred to a separate high-rate anaerobic reactor where biodegradation of the

chlorinated compounds will occur. The target compounds investigated within this study included dichloromethane (DCM), carbon tetrachloride (CT) and tetrachloroethylene (PCE).

One uncertainty associated with this system is that many of the chlorinated compounds are relatively insoluble in water as indicated by their high Henry's law coefficients [4]. In this study, alternative scrubbing liquids such as aqueous solutions of organic solvents (i.e. water-propylene glycol, water-methanol, or water-ethanolamine) and a non-aqueous liquid (vegetable oil) were investigated to assess their potential to enhance the solubility of the chlorinated compounds.

The use of vegetable oil as a scrubbing solution presented an additional challenge in transferring the hydrophobic compounds from the non-polar solvent into an aqueous phase for future biological treatment. As a result, a liquid-liquid mass transfer process that would be employed after the packed column was evaluated.

1.3 Objectives

The overall objective of this study was to investigate issues associated with the mass transfer of chlorinated organics from a gas stream to a liquid stream that would be subsequently treated in a biological process.

The specific objectives were to:

- 1) Investigate the solubility enhancing characteristics of selected cosolvents by performing batch tests.
- 2) Characterize scrubbing solutions to be employed in the packed column.

- 3) Design and operate a bench scale countercurrent packed column.
- 4) Develop and apply mass transfer models corresponding to each process condition.
- 5) Design and operate a liquid-liquid mass transfer process.

Chapter 2 - Literature Review

A literature review was undertaken to gain a better understanding of the main principles to be fully examined within this thesis. The sections investigated in the literature review included organic removal processes, gas-liquid partitioning, mass transfer theory and models and, liquid-liquid extraction.

2.1 Organic Removal Treatment Alternatives

A number of processes are currently employed to remove chlorinated compounds from air streams. These technologies include carbon adsorption, thermal incineration, catalytic incineration and biofiltration. The following section describes the advantages and disadvantages associated with each of these treatment alternatives.

2.1.1 Thermal Incineration

Low concentrations of VOCs can be effectively removed through thermal incineration. Destruction efficiencies approaching 99% have been observed with this treatment alternative [19] however, thermal incineration is highly sensitive to fluctuation in flows. An increased flow will cause poor mixing, which will in turn decrease the completeness of combustion. As a result, the combustion chamber temperature falls and the destruction efficiency of the VOCs is decreased [19].

The performance of a thermal incinerator is highly dependent on the combustion chamber temperature. In order to maintain the desired combustion temperature, a

supplementary fuel is required [19]. This leads to the disadvantage of higher operational costs with thermal incineration.

2.1.2 Catalytic Incineration

Catalytic incineration is similar to thermal incineration with the exception that a catalyst is employed to increase the rate of reaction. The catalyst used for combustion is usually a noble metal such as palladium or alumina [30]. Destruction efficiencies in the order of 95% have been observed with catalytic incineration. Higher removal efficiencies are obtainable, but greater catalyst volumes or higher temperatures are required which increase the overall operational costs [19].

Catalytic incineration has the advantage of attaining lower operational costs because the catalyst serves to reduce the temperature at which the reaction takes place, thereby reducing the fuel requirements.

2.1.3 Activated Carbon Adsorbers

High molecular weight, low volatility compounds are strongly adsorbed onto activated carbon. These compounds are so readily adsorbed that it is difficult to remove them during regeneration [19]. Conversely, highly volatile compounds do not adsorb well onto carbon. Removal efficiencies ranging from 95 – 99% have been observed with a wide range of organics with carbon adsorption.

A potential problem associated with carbon adsorption is that if water vapour is present in the air stream the removal efficiency may be significantly reduced. Another

disadvantage of carbon adsorption is the high costs associated with disposing or regenerating the spent carbon [69].

2.1.4 Biofiltration

Biofiltration is an emerging form of treating VOCs in gases using biological treatment. The high biological activity causes the VOCs to become oxidized to form carbon dioxide and water [2]. Biofiltration is mainly used for dilute VOC concentrations. A major advantage to biofiltration is the low operating and capital costs, since microorganisms are used instead of energy or chemicals [2].

One disadvantage of biofiltration is that the moisture within the reactor must be controlled. If the bed becomes dry, the microbial activity is reduced and some of the VOCs may pass through the bed untreated. Biofilters have been found to be effective in removing light and moderate halogenated compounds under aerobic conditions within the biofilter. However, heavily halogenated compounds such as those investigated in this research require anaerobic conditions to be effectively degraded, hence biofiltration would not be suitable.

2.2 Gas-Liquid Partitioning

To investigate and model the fate and transport of organic compounds in the environment, it is essential to have reliable air to water equilibrium partitioning coefficients (also known as Henry's law coefficients). Henry's law coefficients provide useful information in terms of volatilization and absorption of the solute of interest [48]. In

addition, since the partitioning of the target compounds to solutions other than water was unavailable the gas-liquid partitioning principles were therefore fully investigated so that the literature could be extrapolated to this study.

Gas to liquid partitioning was first investigated by William Henry in 1803, when he observed that the amount of gas of a solute, that will dissolve into water, is proportional to the solute's pressure. This observation lead to the renowned Henry's law coefficient.

In general, Henry's law is valid for dilute non-ideal solutions at equilibrium and is expressed as [56]:

$$H = P/C_l \quad (2.1)$$

H = Henry's law coefficient of the solute ($\text{m}^3 \cdot \text{atm} \cdot \text{mol}^{-1}$)

P = partial pressure of the solute (atm)

C_l = liquid phase solute concentration (mol/m^3)

Henry's law coefficients may also be expressed in several dimensionless forms as indicated in equations 2.2 and 2.3:

$$H_c = C_g/C_l \quad (2.2)$$

$$H_c = H/RT \quad (2.3)$$

H_c = Henry's law coefficient (dimensionless)

C_g = gas phase solute concentration (mol/m^3)

R = universal gas constant, $8.205 \times 10^{-5} (\text{m}^3 \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$

T = temperature (Kelvin)

2.2.1 Methods for Determining Henry's Coefficients

There are several methods available to obtain Henry's law coefficients, depending on the degree of accuracy desired. In general, Henry's law coefficients may be found using vapour pressure and solubility data or utilizing experimental techniques.

The two main experimental approaches employed to determine Henry's law coefficients include the static and dynamic equilibration techniques. The dynamic approach employs an air/water exchange method, which utilizes equipment such as a bubble column. Conversely, the static equilibration approach involves the direct measurement of both the gas and liquid phases in a closed environment at equilibrium.

2.2.1.1 Vapour Pressure and Solubility Data

Vapour pressure and solubility data that can be obtained from tables has been used to calculate Henry's law coefficients by slightly modifying equation 2.1. The vapour pressure and the solubility replace the partial pressure and the liquid phase concentration of the solute respectively. This method has been found to be unreliable because of the uncertainties associated with the water solubility data of many organic compounds [40]. Mackay and Shiu [40], suggested that reasonably accurate results could be obtained when the solute's solubility, expressed as a mole fraction, was less than a few percent. In fact, research has shown differences in Henry's law coefficients ranging from 2 to 400%, with no distinct pattern between the varying compounds [4]. It has therefore been recommended to use experimental techniques, to obtain more reliable values for Henry's

law coefficients [40,45]. In addition, the solubility data was unavailable for the solutions that were investigated within this research.

2.2.1.2 Experimental Methods

Mackay and Shiu [40], offered a standard method to experimentally determine Henry's law coefficients. This method involved direct measurement of the gas and liquid concentrations at equilibrium. A difficulty with this method was that typically the compounds of interest had a tendency to have low concentrations within the environment. As a result, the degree of accuracy associated with sampling and analyzing both phases was significantly low. This method is suitable for situations in which the compounds of interest are relatively soluble (such as CO_2) so that the absolute concentrations are more readily measured [40]. In order to alleviate the measurement problems associated with this standard method, other methods have been developed in which only relative concentrations are required to determine Henry's law coefficients [40].

2.2.1.2.1 Batch Air Stripping

Batch air stripping (BAS) is a dynamic method that employs a bubble column to determine Henry's law coefficients. This technique is based upon modeling the process of bubbling air through a liquid containing volatiles and observing the changes in liquid concentration over time as indicated in equation 2.4 [42]. This method assumes equilibrium between the rising gas bubbles and the surrounding liquid, and that the system is completely mixed.

$$-\ln (C_l/C_l^o) = Q_g H/V_l (t-t_o) \quad (2.4)$$

where: C_l = liquid phase concentration ($\text{mol}\cdot\text{m}^{-3}$)

C_l^o = initial liquid concentration ($\text{mol}\cdot\text{m}^{-3}$)

H = Henry's coefficient (dimensionless)

Q_g = gas flow rate (m^3/h)

V_l = liquid volume (m^3)

t = time (h)

t_o = initial time (h)

BAS provides a significant improvement in determining Henry's law coefficients since it requires only relative concentration changes [40]. In this method, Henry's coefficients are determined through regression of a semilogarithmic plot (concentration versus time) and requires only a knowledge of the gas flow rate, liquid volume and temperature [40]. By plotting $-\ln (C_l/C_l^o)$ versus $(t-t_o)$, the slope of the line is equal to $Q_g H/V_l$ and Henry's coefficient can be determined [14].

A potential problem associated with BAS is that in some cases the rising air bubbles within the column may not have reached equilibrium with the surrounding liquid prior to exiting the column. As a result, the assumption of equilibrium is violated [14]. Gossett et al., [23], tried to alleviate the problem of equilibrium by increasing the column height. This action resulted in a counter problem of insufficient mixing within the column.

Mackay and Shiu [40], has found a standard error of 5 % associated with BAS. However, when insoluble compounds were tested it was found that sorption onto the column resulted in an increase in the standard error to 15 %.

Ashworth et al. [4], completed similar studies to determine Henry's law coefficients for 45 compounds, using a batch air stripping technique (BAS). Ashworth et al. [4], concluded that BAS is an accurate method for dilute aqueous solutes with low Henry's law coefficients. It was also observed that when taller columns were used in the BAS process, and lower gas flows were applied, the system was not completely mixed as originally assumed [4].

2.2.1.2.2 Multiple Equilibration Technique

A basic experimental technique has been developed to obtain a sufficiently accurate method for determining Henry's law coefficients that is simple and does not require a special apparatus. The method of statically determining Henry's law coefficients involves the direct measurement of one or both phases of a closed system at equilibrium. If only one phase is directly measured the other phase can be indirectly determined through mass balances of the entire closed system. Researchers have investigated different techniques in order to develop the most accurate method for determining Henry's law coefficients based on the closed system principle.

The multiple equilibration technique as assessed by Munz and Roberts [45], involves the measurement of one phase after the solute was allowed to reach equilibrium within the closed system. The set-up consisted of a syringe containing a volume of liquid spiked with a known concentration of solute. Solute-free air was introduced into the

syringe and the system was allowed to reach equilibrium. One of the phases was analyzed and the remaining gas phase was expelled and immediately replaced with solute-free air. The system was allowed to reach equilibrium again and the procedure was repeated again through multiple equilibrations [45].

Henry's law coefficients may be determined by manipulating a mass balance equation on the system to the form:

$$\log C_{li} = \log C_{lo} - i[\log (1 + (V_G/V_L)H_c)] \quad (2.5)$$

where:

V_L = liquid volume of closed system (m^3)

V_G = gas volume of closed system (m^3)

C_{li} = liquid concentration after i number of equilibrations (g/m^3)

C_{lo} = initial liquid concentration (g/m^3)

From the semi-log plot of liquid concentration versus i , the slope of the line becomes a function of Henry's law coefficient with an intercept being a function of the initial liquid concentration. This method has been successfully employed in the research of both Lamarche and Droste [31], and, Munz and Roberts [45].

2.2.1.2.3 Equilibrium Partitioning in Closed System (EPICS)

The method of Equilibrium Partitioning in Closed Systems (EPICS) was proposed by Lincoff and Gossett [38]. This method, similar to the bubble column, accounts for the

relative concentrations rather than the absolute concentrations. Lincoff and Gossett [38], found that by using EPICS, Henry's law constants could be determined with a coefficient of variation less than 5%.

EPICS involves the addition of equal masses of the organic compounds to serum bottles with differing liquid volumes and associated headspaces [38]. One set of bottles are designated as high volume and contain 100 ml of liquid at all times. The remaining set of bottles are low volume and contain 10 ml of liquid at all times. The two sets of bottles are allowed to reach equilibrium, at which time Henry's law coefficients may be determined based upon measurement of the gas phase concentrations and the use of mass balances [38].

The total mass (M) within each of the high (1) and low (2) volume systems is expressed as:

$$M_1 = C_{l1} V_{l1} + C_{g1} V_{g1} \quad (2.6)$$

$$M_2 = C_{l2} V_{l2} + C_{g2} V_{g2} \quad (2.7)$$

where: M_1, M_2 = total mass in high and low volume systems, respectively
 C_{l1}, C_{l2} = liquid concentration in high and low volume systems, respectively
 C_{g1}, C_{g2} = gas concentration in high and low volume systems, respectively
 V_{g1}, V_{g2} = volume of gas in high and low volume systems, respectively
 V_{l1}, V_{l2} = volume of liquid in high and low volume systems, respectively

At equilibrium, Henry's law applies and equations 2.6 and 2.7 can be rewritten as:

$$M_1 = (C_{g1} V_{l1}) / H_c + C_{g1} V_{g1} \quad (2.8)$$

$$M_2 = (C_{g2} V_{l2}) / H_c + C_{g2} V_{g2} \quad (2.9)$$

Since the same mass of the organic compound is added to the systems at the same temperature but to two different liquid volumes:

$$M_1 = M_2 \quad (2.10)$$

Solving for Henry's law constant yields:

$$H_c = [(C_{g1}/C_{g2})V_{l1} - V_{l2}] / [V_{g2} - (C_{g1}/C_{g2})V_{g1}] \quad (2.11)$$

EPICS employs only knowledge of the ratio of the gas concentrations in the varying volume systems and therefore, the ratio of the peak heights obtained from a gas chromatograph may be used in this method. Gossett [22], suggested that prior to determining Henry's law coefficients, the linearity of each compound should be verified on a gas chromatograph.

The main disadvantage associated with EPICS is that the mass of organic compound added to each system must be exactly equal, so that inaccuracies do not occur. Systematic errors such as adsorption of the organic compound onto the septum may also occur while the closed system is waiting to reach equilibrium [46]. In this case, adsorption must be considered in the analysis of the compounds.

The EPICS method appears to be the most precise method of experimentally determining Henry's coefficients with a coefficient of variance (CV) of 4-5% [38]. Gossett [22], tried to further improve the accuracy by proposing a modification to the original EPICS method. The improved method neglected the assumption of equal solute masses and accounted for volumetric additions through gravimetric analysis. The main difference in the final derived equation was that $M_1 = M_2$ was no longer assumed, instead equations 2.8 and 2.9 are divided by M_1 and M_2 respectively [22]. Solving for Henry's coefficient yields:

$$H_c = (V_{l2} - rV_{l1})/(rV_{g1} - V_{g2}) \quad (2.12)$$

$$r = (C_{g1}/M_1)/(C_{g2}/M_2) \quad (2.13)$$

In this modification of the EPICS method only the ratio of M_1 and M_2 is required and therefore only the relative concentration of stock solution needs to be known. This modification of the original EPICS offered only a slight improvement (CV of 3-4%) over the original method [22]. Upon examining the results yielded from Gossett's tests it was found that the mean CV did not include dichloromethane (DCM) which contributed a significantly high CV of 17-19%. Gossett's reasoning in omitting DCM was due to technical difficulties associated with the integration system within the gas chromatograph. This caused significant tailing, which resulted in higher overall errors for the DCM compound [22].

Gossett [22], also suggested that the modification of the original EPICS method could obtain an even lower mean CV values of 2.5 - 3.5 % if a greater difference between the high and low liquid volumes was used.

It has been found that Gossett's original method of EPICS, provided a sufficient degree of accuracy in determining Henry's law coefficients. EPICS appears to be accurate, simple and requires no special apparatus. EPICS was therefore deemed a suitable method for the determination of gas-liquid partitioning coefficients for the purposes of this research study.

2.2.2 Henry's Law Coefficients Obtained from Research for the Target Compounds

The previously outlined methods to determine Henry's law coefficients have been employed by a number of researchers. Table 2.1 compares the Henry's law coefficients obtained by researchers for the target chlorinated compounds to be investigated in this research.

Mackay and Shiu [40], reported two values for Henry's law coefficients, one was calculated using the vapour pressure and solubility data, whereas the second value was measured experimentally. When comparing the experimental and calculated values obtained by Mackay for DCM it was found that they were comparable. Conversely, it was observed that the calculated Henry's coefficient for carbon tetrachloride (CT) was higher than that reported for the experimentally determined H_c . This observation supports Mackay's conclusion that there is a lack of reliability in the values calculated from vapour pressure and solubility tables, and that experimental techniques should be employed to determine Henry's law coefficients.

The multiple equilibration technique was used by Munz and Roberts [45,46], to determine the Henry's law coefficient for tetrachloroethylene (PCE) and carbon tetrachloride. This method was used because the objective of the study was to quantify slight differences in Henry's law coefficients with the addition of small amounts of cosolvents (methanol and 2-propanol). Munz and Roberts [45,46], concluded that the multiple equilibration technique would provide minimal errors in the results to be obtained for the purposes of his study.

Gossett [22], experimentally determined Henry's law coefficients for DCM, CT and PCE using a modification to the EPICS procedure, as previously outlined. The value

obtained for DCM appeared to be much lower as compared to other researcher's experimental values. Gossett concluded that the substantially higher CV of 17% was attributed to GC integration problems. CVs of less than 4% for Henry's coefficients were obtained for PCE and CT when the modified EPICS method was employed by Gossett.

The original EPICS method was utilized by Ashworth et al.[4], to determine Henry's law coefficients for DCM, CT and PCE. The results of Ashworth exhibited a high degree of accuracy, with a mean CV less than 10%, over the entire temperature range (10 to 30 °C) investigated. Conversely, Robbins et al. [55], employed a static headspace method to determine the Henry's law coefficient for PCE. This method was found to have a CV less than 3%.

Lincoff and Gossett [38], experimentally determined Henry's law constants for 5 compounds, including, DCM and PCE over a range of temperatures from 10 °C to 30 °C. EPICS and BAS techniques were used to determine Henry's law coefficients. Gossett and Lincoff observed that the results obtained from EPICS were comparable to those of the BAS technique. The Henry's law coefficients for the BAS technique were slightly lower than the EPICS results. This difference in Henry's law coefficients appeared to increase at higher temperatures in the BAS method. One exception was found for 1-1-1 trichloroethane, in which there was no difference in H_c between the two techniques. Lincoff and Gossett [38], concluded that the lack of equilibrium which existed in the BAS technique, led to inaccuracies in the experimental results.

A compilation of Henry's coefficients from previous researchers is presented in table 2.1. It can be concluded that overall, the results for the three target compounds vary in accuracy depending on the method employed to determine the Henry's coefficient. It

appears that the Henry's law coefficient for CT was overestimated when it was calculated by solubility and vapour pressure data as obtained by Mackay and Shiu. The BAS technique appeared to be unreliable, since in some cases, the column was not at equilibrium. Conversely, the static equilibration techniques such as EPICS and the multiple equilibration technique appeared to be the most reliable in experimentally determining Henry's law coefficients. A high degree of accuracy for all three compounds to be evaluated in this research was exhibited by the EPICS method.

Table 2.1: Comparison of Dimensionless Henry's Law Coefficients at 25°C (unless otherwise stated)

Dichloromethane (DCM)	Tetrachloroethylene (PCE)	Carbon Tetrachloride (CT)	Reference
0.272		2.16	Mackay et al., 1981 (calc.)
0.256		1.59	Mackay et al., 1981 (exp.)
		0.975 (20°C)	Munz et al., 1986
	0.881	1.09	Munz et al., 1987
0.0895	0.723	1.244	Gossett, 1987
0.121	0.699	1.21	Ashworth et al., 1988
	0.697		Robbins et al., 1993
0.0936	0.5407 (20°C)		Gossett et al., 1984 (EPICS)
0.0819	0.4825 (20°C)		Gossett et al., 1984 (BAS)

2.2.3 Factors Affecting Henry's Law Coefficients

Temperature, concentration and cosolvents have been examined for their influence on Henry's law coefficients. The following section details the influences of these parameters.

2.2.3.1 Effect of Temperature on Henry's Law Coefficients

The laws of thermodynamics predict that Henry's law coefficients will vary with temperature and pressure. If the pressure is kept constant the temperature dependence can be modeled by a van't Hoff type equation [28]:

$$\ln H = \Delta H^0 / RT + k \quad (2.14)$$

where:

- H = Henry's law coefficient (dimensionless)
- ΔH^0 = enthalpy change due to dissolution in water (kcal/kmole)
- k = constant
- R = universal gas constant (1.987 kcal/kmol °K)
- T = temperature (Kelvin)

Experiments have been performed to obtain data that was employed to model the effect of temperature on the Henry's law coefficient using a simplified form of the van't Hoff equation [28] :

$$H = \exp(A - B/T) \quad (2.15)$$

where, A and B are compound specific constants which are experimentally determined.

In general, equation 2.15 accurately models the relationship between Henry's law coefficients and temperature. This was indicated by the high r-squared values obtained from experimental data [2]. Munz and Roberts [45], also modeled the temperature dependence of Henry's coefficients for several different compounds varying in volatility. Munz and Roberts [45], observed an approximate 1.6 factor increase in Henry's law coefficient with a 10°C rise in temperature. This observation demonstrates the strong

effect of temperature on Henry's law coefficient. Munz and Roberts [45], concluded that temperature may be the most important factor that will affect the removal of an organic compound from an air stripper and should be carefully considered in the design process.

2.2.3.2 Effect of Solute Concentration on Henry's Law Coefficients

Munz and Roberts [45], expected that an increase in solute concentration would result in a decrease in Henry's law coefficient and therefore investigated the effect of solute concentration on the solute's Henry's law coefficient. This research examined concentrations ranging from trace levels up to near the solubility limit for carbon tetrachloride, chloroform and hexachloroethane. These compounds have varying degrees of hydrophobicity and are all considered relatively volatile.

In contrast to expectations, it was found that for all solutes investigated, there was no evidence of dependence of Henry's coefficient on the concentration of the solute. Munz and Roberts [45], further validated their results by using a semiempirical thermodynamic model (UNIFAC) that predicts the behavior of compounds in solution. The UNIFAC model predicted a negligible impact of solute concentration with the highest decrease in Henry's law coefficient for chloroform less than 3.5%.

In contrast to Munz and Roberts findings, Gossett et al. [23], found that increasing the solute concentration resulted in an increase in Henry's law coefficients. However, this study was found to contain errors associated with the use of the batch air stripping method that was employed to determine Henry's law coefficient.

In general, it was concluded that there was no significant effect of the concentration of the solute on Henry's law coefficient for the halogenated hydrocarbons.

2.2.3.3 Effect of Mixtures on Henry's Law Coefficients

To verify that there was no impact between mixtures of organic compounds on Henry's coefficients, Gossett et al.[23], prepared aqueous mixtures of tetrachloroethylene, dichloromethane, trichloroethylene, 1-1-1 trichloroethane and chloroform up to a total liquid concentration of 375 mg/L. It was found that the mixture of chlorinated organics had no significant effect on Henry's law coefficient.

Most researchers use the assumption that there are no interactions between organic compounds in a mixture, when the mixtures are relatively comparable in terms of concentrations. By making this assumption stock solutions containing all the organics can be made up in order to reduce analysis time [23]. Another common practice among researchers is to dissolve the slightly soluble organics in methanol prior to mixing with water, to achieve higher stock solution concentrations that are easier to make-up in the laboratory.

2.2.3.4 Effect of Cosolvents on Henry's Law Coefficients

Cosolvents such as methanol, ethanol, 2-propanol and propylene glycol have been employed to increase the solubility of hydrophobic solutes [70]. Yalkowsky and Roseman suggested that by assessing the solute and cosolvent in terms of their polarity and hydrophobicity, the solubility of the compound could be predicted. The hydrophobicity of

compounds has been related to the octanol-water partition coefficient. Yalkowsky and Roseman found that the larger the octanol-water partition coefficient the more hydrophobic the solute or cosolvent hence, it was concluded that the degree of solubility was dependent primarily upon the polarity of the solute and cosolvent [70]. The most common method of measuring polarity is the organic solvent/water partition coefficient, more commonly, the octanol/water partition coefficient. Yalkowsky and Roseman employed the principles of polarity to derive a model that would predict the solubility of a solute by the addition of a cosolvent.

2.2.3.4.1 Log-linear Model

Yalkowsky and Roseman [70], have derived a log linear model for approximating the role of cosolvents in solubilizing non-polar solutes. This derived mathematical approximation assumes that a mixed solvent is simply a linear combination of its component solvents [70].

The equation for the solubility of a solute in water and in pure cosolvent can be expressed by equations 2.16 and 2.17 respectively:

$$\log S_w = \frac{-\Delta S_f(MP-25)}{1364} - \log \gamma_w \quad (2.16)$$

$$\log S_c = \frac{-\Delta S_f(MP-25)}{1364} - \log \gamma_c \quad (2.17)$$

where:

S_w = solubility in pure water (moles/L)

S_c = solubility in pure cosolvent (moles/L)

ΔS_f = entropy of fusion of the solute (zero if solute is liquid, J/moles °K)

MP = melting point of compound

$\gamma_{w,c}$ = activity coefficient in water, cosolvent respectively

The equation for solubility of a solute in a mixed solvent system in which f_c is the volume fraction of cosolvent was therefore determined as:

$$\log S_m = f_c \log S_c + (1-f_c) \log S_w \quad (2.18)$$

Substituting equations 2.16 and 2.17 into equation 2.18 and rearranging, yields:

$$\log S_m = \log S_w + (\log \gamma_c - \log \gamma_w) f_c \quad (2.19)$$

Equation 2.19 depicts an exponential increase in solubility of the mixed solvent system with increasing cosolvent fraction. The solubilizing power σ , as defined by Yalkowsky and Roseman [70], is the slope of the S_m versus f_c plot.

$$\log S_m = \log S_w + \sigma f_c \quad (2.20)$$

For the cosolvent water system the difference between equilibrium activity coefficients in pure cosolvents is constant so that equation 2.19 can be rewritten as [43]:

$$\log \gamma_w - \log \gamma_c = \sigma \quad (2.21)$$

Similarly, for multiple cosolvent systems equation 2.20 may be altered:

$$\log (S_m/S_w) = \sum f_i \sigma_i \quad (2.22)$$

Equation 2.19 may be expressed in terms of Henry's law coefficients:

$$\log (H_m/H_w) \cong f_c \log (H_c/H_w) \quad (2.23)$$

where:

S_m = solubility in mixed solvent system (moles/L)

H_m = Henry's coefficient in mixed solvent system (dimensionless)

H_w = Henry's coefficient in pure water system (dimensionless)

H_c = Henry's coefficient in pure cosolvent system (dimensionless)

In general, the larger the $\log K_{ow}$, the less polar and the more hydrophobic the solute [45]. Most chlorinated compounds typically have a $\log K_{ow} \geq 2$ and are considered non-polar relative to water ($\log K_{ow} \cong -1.4$) [45]. Munz and Roberts [45], concluded from equation 2.23, that for non-polar solutes $H_c/H_w < 1$, it follows that $H_m/H_w < 1$. The subscripts refer to cosolvent (c), water (w) and mixed solvent (m) respectively. This result demonstrates that Henry's law coefficients will always be smaller in a mixed solvent than in pure water (i.e. the solubility will be greater) [45]. This approximation however, will be become less effective with increasing solute polarity [45].

2.2.3.4.2 Previous Studies on the Effect of Cosolvents on Henry's Coefficients

Chen and Delfino [10], investigated the use of cosolvents on 18 polynuclear aromatic hydrocarbons (PAHs) from contaminated soils. The cosolvents used in this study were methanol, ethanol and methyl tert-butyl ether (MTBE). From laboratory results it was found that PAH solubility increased in a log-linear manner with an increase in methanol and ethanol cosolvent fraction. This result was consistent with Yalkowsky's log-linear model. The impact of MTBE exhibited the highest variability from the log-linear

model. Chen and Delfino [10], concluded that methanol and ethanol can significantly increase the solubility of PAHs in a log-linear manner. MTBE appeared to be limited by its aqueous solubility and as a result, its impact deviated from the log-linear model.

Li and Andren [36], examined the solubilities of 4 PCBs (4-chlorobiphenyl, 2-4-6 trichlorobiphenyl, 2-3-4-5 tetrachlorobiphenyl and 2,2',4,4',6,6 hexachlorobiphenyl). To enhance their solubility, cosolvents ranging from completely miscible methanol to octanol were used. In agreement with other researchers, Li and Andren [36], found that methanol increased the solubility for all 4 PCBs in a log-linear manner for cosolvent additions ranging from 5-100% v/v. Figure 2.1 demonstrates a typical log-linear relationship between solubility and cosolvent addition for 2-4-6 trichlorobiphenyl. It was observed that the more hydrophobic the PCB the greater the enhanced solubility effect on the solute. This result was also observed by Munz and Roberts [45].

Figure 2. 1: Effect of Methanol on the Solubility of 2,4,-6 Trichlorobiphenyl (Li and Andren, [36])

In contrast to methanol, Li and Andren [36] observed that the solubility of the PCBs decreased with increasing volume fraction for octanol. Li and Andren [36] suggested that the factors responsible for the increase and decrease in solubility were, the presence of alcoholic hydroxyl groups on the cosolvent and interactions between water and the non-polar alkyl portion of the alcohols. This interaction may alter the water so that the solute is more readily solubilized into the aqueous solution. This theory as proposed by Li and Andren [36], explains the increased solubility of the solutes with methanol addition. The non-polar alkyl portion of the alcohols is believed to cause the decreasing relationship in solubility with octanol fraction addition. Li and Andren [36], proposed that there may be a competition for vacancies in the structured water and that octanol may act as a cosolute competing with the solute for vacancies. This competition may in turn result in a decrease in the solubility of the solute.

Li and Andren [36], performed additional studies to further investigate the impact of alcohols, ranging from methanol to octanol on solubilization. A general trend was observed, that as the alcohol content of the cosolvent increased deviations from the log-linear model increased. As a result, Li and Andren concluded that only low alcohols can be accurately represented by the log-linear model as proposed by Yalkowsky. Li and Andren [36], also found that the solubilization of the solutes increased as the hydrophobicity of the solute increased.

Munz and Roberts [45], examined the effects of two cosolvents, methanol and 2-propanol on the solubility of chloroform, carbon tetrachloride and hexachloroethane. These solutes were selected according to Munz and Roberts [45], because of their strong hydrophobic nature with hexachloroethane being the most non-polar.

Munz and Roberts [45] investigated cosolvents ranging in concentration from 10^{-4} – 10^{-2} mole fraction. It was observed that miscible cosolvents such as methanol and 2-propanol could reduce the solute's Henry's law coefficient by 10% at mole fractions greater than 5×10^{-3} . It was also observed that solubilization was increased for more hydrophobic solutes and the cosolvents [45].

Gossett [22] also performed preliminary studies to examine the effect of methanol on Henry's law coefficient of trichloroethylene (TCE). The methanol concentrations varied from 0.1 % to 5% by volume. Gossett [22] observed that the Henry's law coefficient for TCE was unaffected by methanol addition except at the highest concentration of 5% v/v. At 5% by volume methanol addition, it was observed that the Henry's law coefficient for TCE decreased by approximately 7%.

From the results obtained from previous researchers it was apparent that cosolvents, when used in large quantities increased the solubility of the solute. In addition, when low alcohols were used as cosolvents the solubility of the solutes increased in a log-linear manner. As higher alcohols or less soluble cosolvents were used, deviations from the Yalkowsky's log-linear model were observed and thus the log-linear model became unreliable. It was found that the more hydrophobic (larger K_{ow}) the solute and the cosolvent the greater the effect on increasing the solubility of the solute or decreasing the solute's Henry's law coefficient.

2.3 Mass Transfer

2.3.1 Models of Mass Transfer

The three most widely accepted models that exist to describe mass transfer between the gas and liquid boundaries are the two-film theory by Lewis and Whitman [35], the penetration theory by Higbie [12], and the surface renewal theory proposed by Danckwerts [12].

2.3.1.1 Two-Film Theory

The two film theory was first introduced in 1923 by Whitman [35,12,22,57], to describe mass transfer at an interface in a turbulent system in which a solute is transferred from the gas phase to the liquid phase (figure 2.2). The two film theory consists of an interface separating the gas and liquid films. The flow in both of these films is assumed to be laminar or stagnant. A concentration gradient exists across both the gas and liquid films. Outside the laminar layer, turbulent eddies exist so that the bulk gas and liquid phases are assumed to be completely mixed and no concentration gradient exists in either of the bulk phases [12].

Equilibrium is assumed to exist at the interface between the gas and liquid films and it is assumed that there is no resistance to mass transfer across the interface [12].

Figure 2. 2: Two Film Theory

Mass transfer within each film can be expressed by Fick's Law:

$$J_i = -D_{ABi} \frac{\partial C_i}{\partial x_i} \quad (2.24)$$

J_i = molecular mass transfer flux of solute A into solvent B ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)

i = gas or liquid

D_{AB} = diffusivity of the solute ($\text{m}^2 \cdot \text{s}^{-1}$)

$\partial C / \partial x$ = concentration gradient ($\text{mol} \cdot \text{m}^{-4}$)

It is assumed that steady state exists and hence material does not accumulate at the interface and therefore the mass transfer rates are the same. It is also assumed that the concentration change is linear across the gas and liquid films yielding:

$$J = \frac{D_g}{Z_g} (C_g - C_{gi}) = \frac{D_l}{Z_l} (C_{li} - C_l) \quad (2.25)$$

$$k_g = \frac{D_g}{Z_g} \quad (2.27)$$

$$k_l = \frac{D_l}{Z_l} \quad (2.28)$$

$$J = k_g(C_g - C_{gi}) = k_l(C_{li} - C_l) \quad (2.26)$$

where:

C_g, C_l = bulk gas and liquid phase concentration, respectively (g/m^3)

C_{gi}, C_{li} = interface gas and liquid phase concentration, respectively (g/m^3)

Z_g, Z_l = effective gas and liquid film thickness, respectively (m)

D_l = diffusivity of the solute in the liquid phase (m^2/s)

D_g = diffusivity of the solute in the gas phase (m^2/s)

k_l = mass transfer coefficient for the liquid film (m/s)

k_g = mass transfer coefficient for the gas film (m/s)

Previous attempts that have been made to sample the concentrations at the interface have failed because the sampling devices were large as compared to the film thickness [57]. As a result, it is nearly impossible to determine the interface concentration, however, it is relatively straightforward to determine the bulk gas and liquid concentrations, C_g and C_l respectively.

To accommodate the interface concentrations an overall mass transfer coefficient, accounting for the entire diffusional resistance has been developed.

$$J = k_g(C_g - C_{gi}) = K_g(C_g - C_g^*) \quad (2.29)$$

$$J = k_l(C_{li} - C_l) = K_l(C_l^* - C_l) \quad (2.30)$$

K_g = overall mass transfer coefficient based on gas phase concentration (m/s)

K_l = overall mass transfer coefficient based on liquid phase concentration (m/s)

C_g^* = gas phase concentration that is in equilibrium with bulk liquid concentration

C_l^* = liquid phase concentration that is in equilibrium with bulk gas concentration

If the interface is assumed to be at equilibrium, Henry's law is valid.

$$C_{gi} = C_{li} H_c \quad (2.31)$$

$$C_g^* = C_l H_c \quad (2.32)$$

$$C_l^* = C_g / H_c \quad (2.33)$$

H_c = Henry's constant (dimensionless)

Expanding equations 2.29 and 2.30 and including the interfacial concentrations yields:

$$J = K_g [(C_g - C_{gi}) + (C_{gi} - C_g^*)] \quad (2.34)$$

$$J = K_l [(C_l^* - C_{li}) + (C_{li} - C_l)] \quad (2.35)$$

Substituting equations 2.31-2.33 into equations 2.34 and 2.35 yields:

$$J = K_g [(C_g - C_{gi}) + (C_{li} - C_l) H_c] \quad (2.36)$$

$$J = K_l [(C_g - C_{gi}) / H_c + (C_{li} - C_l)] \quad (2.37)$$

Substituting equation 2.26 into 2.36 and 2.37 yields the overall mass transfer coefficients for the gas and liquid phases, respectively in terms of the individual film coefficients:

$$1/K_g = 1/k_g + H_c/k_l \quad (2.38)$$

$$1/K_l = 1/(k_g H_c) + 1/k_l \quad (2.39)$$

From equation 2.38, mass transfer is considered to be liquid film controlled when its mass transfer coefficient (k_l) is small compared to k_g or Henry's law coefficient is large.

Conversely, mass transfer is considered to be gas film controlled, if its mass transfer coefficient k_g is small compared to the liquid film mass transfer k_l or when Henry's coefficient is small [63].

The reciprocal of the mass transfer coefficient is known as a resistance. The total resistance (R_T) to mass transfer may be expressed on either a gas or liquid phase basis and is the sum of the gas and liquid phase resistances. The total resistance on a liquid basis is expressed in equations 2.40-2.42.

$$R_G = 1/H_c k_g \quad (2.40)$$

$$R_L = 1/k_l \quad (2.41)$$

$$R_T = R_G + R_L \quad (2.42)$$

where: R_G = gas phase resistance

R_L = liquid phase resistance

In summary, the sum of the gas and liquid resistances is the fundamental principle of the two-film theory. The resistance is simply the reciprocal of the respective gas and liquid mass transfer coefficients. The underlying assumptions of the two-resistance theory include that Henry's law must apply and that there is instantaneous phase equilibrium at the interface [23].

2.3.1.2 The Penetration Theory

The penetration theory was initially proposed in 1935 by Higbie, who investigated whether or not a resistance existed at the gas-liquid interface. In the two film theory steady state was assumed to exist at the interface. The penetration theory assumes that small eddies from the bulk phase are continually transported to and from the interface through the laminar layer. The eddies remain at the interface for a definite time interval, after which they are transported back into the bulk phase [12].

This process is governed by unsteady state molecular diffusion as governed by Fick's 2nd law [12,57].

$$\partial C / \partial t = D (\partial^2 C / \partial X^2) \quad (2.43)$$

Assuming uniform bulk concentrations and instantaneous equilibrium at the interface, the average mass transfer over the exposure time is given by:

$$J = 2 (D_1 / \pi t_e)^{1/2} (C_1 - C_{li}) \quad (2.44)$$

t_e = exposure time of bulk phase at the interface

The liquid phase mass transfer coefficient can be represented by:

$$k_l = 2 (D_1 / \pi t_e)^{1/2} \quad (2.45)$$

The penetration theory yields a square root dependence of the mass transfer coefficient on the diffusion coefficient. Conversely, the two film theory exhibits a linear relationship between the mass transfer coefficient and the diffusion coefficient.

2.3.1.3 Surface - Renewal Theory

In 1951 Danckwerts proposed a modification to the penetration theory by suggesting that the exposure time (t_e) of an eddy would not always be the same. As a result, a probability function from time zero to infinity was developed to describe the age distribution of the surface [12].

This relation was found to be of the exponential form:

$$f(t) = se^{-st} \quad (2.46)$$

where: s = rate of production of fresh surface per unit area of total surface. S is independent of age.

The overall transfer rate per unit area when the surface is renewed:

$$J = (C_l - C_{li}) s \sqrt{(D/\pi)} \int_0^\infty t^{-1/2} e^{-st} dt \quad (2.47)$$

$$J = (C_l - C_{li}) s (D/\pi)^{1/2} (2s^{-1/2}) \pi^{1/2}/2 \quad (2.48)$$

$$J = (C_l - C_{li}) \sqrt{(Ds)} \quad (2.49)$$

$$k_l = \sqrt{(Ds)} \quad (2.50)$$

As expected, the final outcome of the derivation yielded the same relationship as the penetration theory. The diffusion coefficient has a square root dependence to the mass transfer coefficient. Researchers have suggested that the derivation behind the final equation for the surface renewal theory is slightly easier to physically visualize [23].

2.3.1.4 Summary of Mass Transfer Models

In summary, the two film theory is a simple model to describe mass transfer across a film by assuming a steady state process of molecular diffusion. The penetration theory

and the surface renewal theory are similar in that both of their final outcomes yield a square root dependence of the mass transfer coefficient on the diffusion coefficient. Conversely, the two film theory exhibits a linear relationship between the mass transfer coefficient and the diffusion coefficient.

Researchers [23,57] have concluded that the two film theory is somewhat simplistic in assuming steady state. In packed towers the conditions are usually quite turbulent and thus the surface renewal model may represent the mass transfer within the tower more accurately [23].

2.3.2 Models for Determining Mass Transfer Coefficients in Packed Towers

Three significant models for predicting mass transfer coefficients in packed towers have been reported. These models are Sherwood and Holloway, Shulman, and Onda. The Sherwood model assumes that the liquid phase resistance controls and neglects the gas phase resistance. The Shulman and Onda models consider both the gas and liquid phase resistances and in turn are called two-resistance models. The following section outlines the theory and equations associated with each model.

2.3.2.1 Sherwood and Holloway Model

Sherwood and Holloway investigated the stripping of carbon dioxide, oxygen and hydrogen from water in a countercurrent packed tower. The tower was loaded with a range of liquid and gas flow rates: $0.27 < L_M < 43 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ and $0.04 < G_M <$

$1.8 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ respectively [59]. The effect of different packings including Raschig rings and Berl saddles was also investigated.

Assuming that the liquid phase controlled mass transfer, the gas phase resistance was neglected. The overall mass transfer coefficient was given as:

$$k_L a / D_L = 10.746 \alpha (0.3048 L_M / \mu_L)^{1-n} (\mu_L / \rho_L D_L)^{0.5} \quad (2.51)$$

where:

$k_L a$ = mass transfer coefficient (s^{-1})

D_L = molecular diffusivity (m^2/s)

L_M = liquid mass loading rate ($\text{kg}/\text{m}^2\cdot\text{s}$)

μ_L = liquid viscosity ($\text{kg}/\text{m}\cdot\text{s}$)

ρ_L = liquid density (kg/m^3)

α, n = empirically determined packing parameters

2.3.2.2 Shulman Model

The Shulman model is a two-resistance model which includes both gas and liquid phase resistances. Shulman et al. [60], attempted to separate the volumetric mass transfer coefficients, $k_G a$ and $k_L a$ from the interfacial area into k_G and k_L so that the effects of specific variables could be determined.

The gas phase mass transfer coefficient expression was obtained from data based on the vaporization of packing prepared from solid naphthalene [60]. The packing used in this study consisted of 1.3 cm – 3.8 cm Raschig rings and 1.3 cm – 2.5 cm Berl saddles. The gas loading rates ranged from 0.14 - 1.4 $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$.

By plotting the data obtained from the naphthalene packings and taking the best fit line, the gas phase mass transfer coefficient was expressed as:

$$(k_g \times d_s)/D_G = 1.195(1 - \varepsilon)^{0.36} \times [(d_s \times G_M)/\mu_G]^{0.64} [\mu_G/(D_G \times \rho_G)]^{0.33} \quad (2.52)$$

The liquid phase mass transfer coefficient expression was obtained from the data of Sherwood and Holloway, describing the desorption of slightly soluble gases from water. The range of liquid loadings covered the same range as previously reported in the studies of Sherwood [59]. The liquid phase mass transfer coefficient was expressed as [60]:

$$(k_L \times d_s)/D_L = 25.1[(d_s \times L_M)/\mu_L]^{0.45} [\mu_L/(D_L \times \rho_L)]^{0.5} \quad (2.53)$$

where: d_s = diameter of a sphere having same surface area as unit of packing (m^{-1})

D_L = diffusivity of solute in liquid ($m^2 \cdot s^{-1}$)

D_G = diffusivity of solute in gas ($m^2 \cdot s^{-1}$)

L_M = liquid mass loading rate ($kg \cdot m^{-2} \cdot s^{-1}$)

G_M = gas mass loading rate ($kg \cdot m^{-2} \cdot s^{-1}$)

μ_L = liquid viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)

μ_G = gas viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)

ρ_L = liquid density (kg/m^3)

ρ_G = gas density (kg/m^3)

ε = void ratio of packed column

Roberts et al., [56], noted that it was quite inconvenient to employ the numerous graphs associated with determining the effective interfacial area for absorption and desorption.

2.3.2.3 Onda Model

The Onda model is the most common model currently used to estimate packed tower mass transfer coefficients in both the gas and liquid phases. Similar to the Shulman model, Onda allows separate estimation of the gas and liquid mass transfer coefficients, in addition to estimating the specific interfacial area for mass transfer. The main assumption associated with the Onda model is that the specific wetted surface area equals the gas-liquid specific interfacial area [49].

Onda defined the specific wetted packing area as a function of the liquid flow rate, the packing properties and the physical properties of the liquid:

$$a_w/a_t = 1 - \exp\{-1.45(\sigma_c / \sigma_L)^{0.75} \times [L_M / (a_t \mu_L)]^{0.1} [L_M^2 a_t / (\rho_L^2 g)]^{-0.05} [L_M^2 / (\rho_L \sigma_L a_t)]^{0.2}\} \quad (2.54)$$

where: a_w = wetted interfacial area (m^2/m^3)

a_t = total packing area (m^2/m^3)

σ_c = critical surface tension with respect to the packing ($\text{kg}\cdot\text{s}^{-2}$)

σ_L = surface tension of the liquid ($\text{kg}\cdot\text{s}^{-2}$)

g = acceleration due to gravity = $9.81 \text{ (m}\cdot\text{s}^{-2}\text{)}$

It can be seen that the wetted surface area is a function of the dimensionless liquid phase Reynolds number, Froude number and Weber number.

Onda also carried out studies involving the absorption of pure CO_2 into water and organic solvents such as methanol and carbon tetrachloride. They used various packings including Rashig rings, Berl saddles, spheres and rods. It was observed that the correlation

for the gas phase mass transfer coefficient in a packed column was accurate with an error of only 20% for water as well as organic solvents [49].

The expression for the liquid phase mass transfer coefficient k_L is shown by equation 2.55 and is valid for liquid mass loading rates of 1- 15 $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$:

$$k_L[\rho_L/(\mu_L g)]^{1/3} = 0.0051 [L_M/(a_w \mu_L)]^{2/3} [\mu_L/(\rho_L D_L)]^{0.5} (a_t d_p)^{0.4} \quad (2.55)$$

The gas phase mass transfer coefficient as derived by Onda is represented by:

$$k_G/(a_t D_G) = 5.23 [G_M/(a_t \mu_G)]^{0.7} [\mu_G/(\rho_G D_G)]^{1/3} (a_t d_p)^{-2} \quad (2.56)$$

Onda suggested that for smaller packing diameters ($< 15 \text{ mm}$) the constant in equation 2.56 should be changed from 5.23 to 2.0.

The overall mass transfer coefficient is represented by:

$$\frac{1}{K_L a} = \frac{1}{H k_G a} + \frac{1}{k_L a} \quad (2.57)$$

2.3.2.4 Evaluation and Verification of the Onda model

The Onda correlations are limited to the range of operating conditions for which they were initially developed. Other researchers have investigated the Onda model's validity by performing studies in which the conditions were not the same as those when the model was initially developed.

Roberts et al., [56], investigated the stripping of six volatile organic solutes, that varied in volatility, in a countercurrent packed column. Two of the compounds of interest included carbon tetrachloride and tetrachlorethylene. Roberts et al. [56], attempted to assess the validity of a two-resistance model by investigating single and two phase

resistance correlation models. The three models Roberts examined included, Sherwood and Holloway, Shulman and the Onda correlations.

It was found that the Onda model offered the best overall fit of the observed and predicted mass transfer coefficients, with a standard deviation of only 21% [56]. This degree of fit was comparable to the original work of Onda [49]. It was also observed that the Shulman model tended to overpredict K_La in the higher range of the observed versus predicted mass transfer rates and underpredict K_La at the lower end of the range. The Sherwood model, as expected, contained a wide range of observed values corresponding to one predicted value [56]. This likely resulted from the assumption that the gas phase resistance was negligible so that the liquid phase resistance was controlling [56].

It was found that the Onda model predicted the decrease in K_La with a decrease in gas flow rate (Q_G), better than the Sherwood and Shulman models. This observation, according to Roberts [56], appeared to be more pronounced with decreasing solute volatility. Conversely, K_La increased with increasing liquid flow rate (Q_L). Again this trend was more pronounced for the more volatile compounds [56].

Gossett et al., [22], examined dichloromethane (DCM), tetrachloroethylene (PCE) and other chlorinated compounds in a stripping tower packed with 2.54 cm polypropylene Pall rings. From their results it was concluded that K_La increased with temperature. It was observed that the compounds with the lowest K_La exhibited the greatest sensitivity to temperature changes.

The Onda model was initially developed and utilized for small diameter packings. In modern technology the packing size in columns has dramatically increased from approximately 1.3 cm to 15.2 cm in full-scale operations. As a result, Narbaitz et al., [17],

investigated the impact of larger packing diameters on the Onda correlation. It was observed that the Onda correlation overestimated K_{La} for larger diameter packings by an average of 40%. A correction equation was developed to accommodate packing diameters larger than 2.5 cm [17]. When this equation was incorporated, the Onda correlation accuracy improved to an average error of only 20% for larger packing diameters. This final result was consistent with Onda's original work. [49].

Most researchers concluded that the Onda model offered the highest accuracy in obtaining values for mass transfer coefficients when compared to the other existing models. Care must be taken however, to ensure that the conditions for which the model was initially developed are consistent with the research conditions. If the operating conditions are not similar then the Onda model must be initially verified.

2.4 Liquid-Liquid Extraction

Liquid-liquid extraction is the separation of the constituents of a liquid solution by contact with another insoluble liquid. In most cases, the two phases are chemically different, which leads to a separation of the components according to physical and chemical properties [66]. In general, there are two types of liquid extractors, those which employ mechanical agitators, and extractors which are mixed by employing the flow of the fluids themselves.

The two primary steps in the liquid extraction process include mixing to increase the interfacial area (and enhance mass transfer), and phase separation. Mass transfer within the column is dependent on the individual film resistances, hence it is a function of the

phase velocities [1]. Mass transfer is also highly dependent on the hydrodynamics within the column, therefore by increasing the turbulence in the column, the interfacial area increases, resulting in an increase in mass transfer. Phase separation is a function of the physical properties of the liquids such as density, viscosity and surface tension and usually becomes the rate limiting step in the liquid extraction process [65].

For the purposes of this research the simplest liquid contacting device, the spray tower, was employed as the liquid-liquid contacting reactor. The spray tower involves an empty shell in which liquids are introduced and withdrawn at the extremities. As a result of the shell being empty, problems sometimes arise in the area of mixing since some of the liquid at the sides of the column may be bypassed or stagnant zones may occur. In order to alleviate this problem Alegret [1], suggested maintaining turbulent conditions within the column.

The traditional approach to designing liquid extractors was to employ a simple countercurrent plugflow assumption such that the concentration driving force was maximized, however for most columns the flow patterns deviated considerable from plugflow. Deckwar et al. [15] suggested that the actual flow pattern within the column, lies somewhere between the extreme cases of plugflow and completely mixed, and therefore the determination of mass transfer data becomes less reliable for scaling up purposes and as a result further research is still required in this area.

2.5. Summary

An investigation of the principles of mass transfer, liquid-liquid extraction, Henry's law coefficients and cosolvency was undertaken. From the compiled research it was found

that the method of equilibrium partitioning in closed systems (EPICS) was an accurate method to determine Henry's coefficients. One objective of this research involved measuring the differences in Henry's law coefficients with cosolvent addition. EPICS was selected as a viable method for this task, since it was simple, accurate and required no special apparatus.

Researchers have also demonstrated the importance of the effects of temperature and cosolvents on Henry's coefficients and therefore these factors should be carefully considered in this research. The effect of solute mixtures and concentrations did not appear to significantly affect Henry's coefficients and thus for efficiency reasons stock solutions of the combined chlorinated compounds may be used in the laboratory.

The principles of mass transfer will be important in this research since the purpose of the study is to transfer chlorinated organics from the gas phase to the liquid phase, to later be treated in an anaerobic reactor. The rate of mass transfer must therefore be accurately determined. From the literature it was found that the Onda model was the most extensively used model to determine mass transfer coefficients. It was also observed that mass transfer coefficients were determined quite accurately ($< 20\%$ error) for studies involving the gas absorption of pure CO_2 into water and organic solvents such as methanol and carbon tetrachloride. However, it is unlikely that existing models such as Onda will describe mass transfer to specific scrubbing solutions other than water. By attempting to examine the relationship between process conditions and mass transfer through the use of a model, the potential for future scale-up of the process may be better addressed.

Chapter 3 - Materials and Methods

3.1 Target Compounds and Cosolvents

The chlorinated compounds that were investigated included dichloromethane (DCM), carbon tetrachloride (CT), and tetrachloroethylene (PCE). These compounds were selected based on their wide range of Henry's law coefficients and molecular make-up (number of chlorine atoms). The cosolvents that were investigated included methanol, propylene glycol, and ethanolamine. Tables 3.1 and 3.2, list the specific properties of the target chlorinated compounds and the cosolvents respectively. In addition, the use of vegetable oil as a possible scrubbing solution was also examined.

Table 3.1: Properties of Chlorinated Target Compounds

Target Compound	Dichloromethane	Carbon Tetrachloride	Tetrachloroethylene
Abbreviation	DCM	CT	PCE
Molecular Formula	CH_2Cl_2	CCl_4	$\text{Cl}_2\text{C}:\text{CCl}_2$
Molecular Weight	84.93	153.82	165.83
Density kg/m^3	1320	1590	1620
Vapour Pressure mmHg @ 20°C	350	91	13
Solubility in water mg/L @ 20°C	20,000	800	200

Reference: Material Safety and Data Sheets

Table 3.2: Properties of Cosolvents

Cosolvent	Ethanolamine	Methanol	Propylene Glycol
Molecular Formula	$\text{HOCH}_2\text{CH}_2\text{NH}_2$	CH_3OH	$\text{CH}_3\text{CHOHCH}_2\text{OH}$
Molecular Weight	61.08	32.04	76.10
Density kg/m^3	1020	790	1040
Vapour Pressure mmHg @ 20°C	0.2	96	N/A

Reference: Material Safety and Data Sheets

3.2 Experimental Methods

3.2.1 Gas - Liquid Partitioning Batch Tests

Batch tests were performed to screen potential scrubbing solutions for use in the packed column. Gossett's EPICS (equilibrium partitioning in closed systems) method was used to determine gas to liquid partitioning coefficients [22]. EPICS involves measuring headspace concentrations in pairs of sealed serum bottles that contain differing liquid volumes, but the same mass of target compounds. EPICS has exhibited a high degree of accuracy in previous studies, and was therefore deemed to be a viable method to determine gas to liquid partitioning coefficients for this study.

3.2.1.1 EPICS Procedure

The following section outlines the EPICS procedure employed to determine a value for the gas to liquid partitioning coefficient. Each EPICS test involved 6, 160 ml serum bottles. Three of the bottles were designated as high volume and contained 100 ml of liquid while the remaining three bottles were low volume and contained 10 ml of liquid.

Each of the 6 bottles was spiked with the same volume of target compound mixture, so that each bottle contained the same mass of target compound. The bottles were then capped with teflon septa and sealed with aluminum crimp caps. The bottles were inverted onto a shaker at room temperature for approximately 24 hours to ensure that equilibrium was reached within the bottle. A 5 ml or 50 μ l headspace sample was then removed using a Hamilton Gastight® glass syringe with a teflon plunger and injected into either the HNU model 311 or HP 5890 gas chromatograph (GC) for quantification of the VOC concentration. It should be noted that both GCs (HP 5890 and HNU model 311) were used for the batch tests. However, the same GC was employed to analyze all the serum bottles for any specific test.

A stock solution that was made up in methanol and contained approximately 5000 mg/L of CT and PCE and 10000 mg/L of DCM was employed in the EPICS test. Each of the serum bottles was spiked with 20 μ l of the stock solution so that the initial aqueous concentrations of CT and PCE were approximately 1 mg/L in the high volume bottles (100 ml), and 10 mg/L for the low volume bottles (10 ml). The sensitivity to DCM was lower on the HP 5890 GC, therefore the initial stock solution was increased to 10000 mg/L to yield concentrations of 2 mg/L and 20 mg/L in the high and low volume system bottles respectively. Table 3.3 summarizes the addition of target compounds to each of the low and high volume systems.

Table 3.3: Addition of Stock Solution into EPICS Serum Bottles

Compound	Stock Solution Conc. (mg/L)	Stock Solution added (μ L)	Low Volume System		High Volume System	
			Liquid Volume (ml)	Conc. mg/L	Liquid Volume (ml)	Conc. mg/L
DCM	10000	20	10.02	20	100.02	2
CT	5000	20	10.02	10	100.02	1
PCE	5000	20	10.02	10	100.02	1

Upon obtaining a gas phase response in peak counts for each compound in the serum bottles, a gas to liquid partitioning coefficient (K_c) was determined as per equation 2.11:

$$K_c = \frac{\left[\left(\frac{C_{g1}}{C_{g2}} \right) V_{l1} - V_{l2} \right]}{\left[V_{g2} - \left(\frac{C_{g1}}{C_{g2}} \right) V_{g1} \right]} \quad (2.11)$$

where:

C_{g1} , C_{g2} - gas concentration in high and low volume systems respectively

V_{l1} , V_{l2} - liquid volume in high and low volume systems (100, 10 ml respectively)

V_{g1} , V_{g2} - gas volume in high and low volume systems (60, 150 ml respectively)

Since the ratios of gas concentrations were used to determine the gas to liquid partitioning coefficient, the ratio of peak counts obtained from the response of the gas

chromatograph was employed. The linearity of each compound on the gas chromatograph was first verified to ensure valid results. The six serum bottles yielded nine values of K_c from which a mean and standard deviation were calculated.

3.2.1.2 Equilibrium Tests

The EPICS procedure assumes that equilibrium between the gas and liquid phases has been attained. To verify that this was occurring in this study, an experiment was performed to ensure that equilibrium was reached within the serum bottles. Gossett [22], reported that compounds with elevated Henry's coefficients took longer to reach equilibrium. It was also found that larger liquid volumes within the serum bottles increased the time to reach equilibrium. To examine the time required to reach equilibrium, 2 serum bottles (160 ml), containing 100 ml of distilled water were spiked with carbon tetrachloride. The bottles were capped with teflon septa and aluminum crimps caps, and were inverted onto a shaker. Headspace samples were taken from each bottle using a 5 ml Hamilton Gastight® glass syringe over a 24 hour period and immediately analyzed on the HNU model 311 GC.

3.2.1.3 Experimental Plan

In the batch tests, equal masses of chlorinated compounds were used for each experiment while the volumes of cosolvent and medium varied. Table 3.4 outlines the various conditions investigated in the batch experiments to determine gas-liquid partitioning coefficients.

Table 3.4: Summary of Gas-Liquid Partitioning Experiments

Test #	Cosolvent / Medium by Volume				
	Water	Methanol	Propylene Glycol	Ethanolamine	Vegetable Oil
1	100 %				
2	80 %	20 %			
3	60 %	40 %			
4	80 %		20 %		
5	60 %		40 %		
6	80 %			20 %	
7	60 %			40 %	
8	70 %		10 %	20 %	
9	60 %		20 %	20 %	
10	80 %				20 %
11	60 %				40 %
12					100 %

At the end of each test the teflon septa and aluminum crimp caps were discarded. The bottles were washed and rinsed twice with methanol. The bottles were allowed to air dry so that any residue of the contaminants would volatilize.

3.2.2 Mass Transfer Column

A packed column with a length of 100 cm, an outer diameter (O.D.) of 10 cm and constructed of stainless steel tubing was employed for continuous flow mass transfer experiments (figure 3.1). The column had a total volume of 8.2 L and was divided into three main sections that were connected by flanges for easy assembly. The bottom section was 25 cm in length, and contained a 1 cm O.D. liquid effluent pipe, that exited directly from the bottom. On one side of the bottom section a 2 cm O.D pipe supplied the contaminated air stream into the column. The contaminated air stream was distributed

evenly over the packing by the way of an air distributor. This consisted of a union cross screwed into a stainless steel elbow, which was welded to a 2 cm O.D. pipe that protruded through the side of the column. The union cross was 6 cm in length and had 4 holes of 1.5 cm O.D, pointing downwards on each end. The configuration of pointing the holes downwards was employed to eliminate any liquid from flowing by gravity through the column into the air distribution and backing up into the air stream.

The middle section was 60 cm in length, with a sample port located halfway up the midsection. The sample port was designed such that a teflon septum and an aluminum crimp cap could be easily removed or inserted as required. The middle section was packed with Intalox™ 13 mm ceramic saddles. The ceramic saddles were selected as a packing material based on availability and to minimize the adsorption of organics.

The top section was 15 cm in length with a 10 cm outer diameter. A liquid distributor was installed 5 cm down from the top of the section to provide an even distribution of flow over the entire packing surface area and to minimize channeling. The configuration of the liquid distributor was similar to that of a shower head. A stainless steel cap was threaded onto the liquid inlet pipe, the cap was allowed to fill with liquid and was drained by gravity through 1.5 mm O.D. holes. The holes on the outer perimeter of the liquid distributor cap of the liquid were placed at 30° angles to provide a complete distribution of liquid on the entire packing surface. A 2 cm stainless steel pipe was welded to the top section to accommodate the exit gas stream. High vacuum grease and teflon-O-rings were used between the three sections to minimize losses by providing a tight seal.

Figure 3. 1: Detail of Packed Column

3.2.2.1 Synthesis of Contaminated Air Stream

A contaminated air stream was synthesized by injecting pure compounds with a syringe pump into the inlet air stream. A Harvard Apparatus model # 55-2226 syringe pump equipped with a 10 ml Becton Dickinson glass syringe (diameter = 14.34 mm) was employed for this purpose. The glass syringe was connected to flexible 3 mm O.D Viton® tubing which was attached to a 22-gauge needle. The needle was inserted into the 2 cm O.D copper inlet pipe by the way of a teflon septa. Upstream of the introduction of the chlorinated compounds, compressed air was metered through a Cole Parmer Flowmeter equipped with tube # N102 -05. The float material within the flowmeter was dependent on the flowrate desired for the specific test. A 3 mm glass float was used for the low flow range (23 -2300 ml/min) and a 3 mm stainless steel float accommodated the higher flow range (580 - 10000 ml/min). As the air flowed through the 2 cm copper pipe, chlorinated organics were introduced into the pipe at a volumetric flowrate of 25 $\mu\text{L}/\text{min}$ – 100 $\mu\text{L}/\text{min}$ depending on the desired concentration for the test. The pure phase compounds were immediately volatilized and carried off by the air stream through the copper pipe into the packed column. To provide sufficient mixing prior to entering the column a 30 cm loop of pipe was installed in the pipe line to increase mixing time. A sample port was installed prior to the column entry to allow sampling of the contaminated air as it entered the column. The sample port was connected directly into the air flow so that a syringe could enter through a teflon septum and sample the air stream. The septum was changed between runs to eliminate leaks.

3.2.2.2 Experimental Description

Figure 3.2, displays the set-up of the continuous flow experimental apparatus. The synthesized contaminated air stream flowed directly into the bottom section of the column as previously described. The contaminated gas stream flowed upwards through the packed column and the treated gas stream exited through the top of the column.

The scrubbing solution was pumped into the top of the column and removed from the bottom of the column by Cole Parmer model # 7553-80 peristaltic pumps with speeds ranging from 1 - 100 rpm. Masterflex® Viton® tubing with a 1 cm O.D was used for both the liquid inlet and liquid outlet. The liquid flowrates ranged from 10 - 200 ml/min. Outlet liquid samples were collected into 40 ml amber bottles and immediately capped with a teflon cap and stored at 4°C prior to analysis on the HP 5890 GC.

3.2.2.3 Experimental Conditions

Prior to starting a run, the 10 ml Becton Dickinson glass syringe was filled with a mixture of equal parts, by volume, of the pure phase target chlorinated compounds. The bench air supply valve was opened all the way and the flow was adjusted to the desired flow rate for the specific run. Inlet and outlet gas samples were taken to ensure that there were minimal losses in the column. After obtaining three reproducible gas inlet samples with minimal changes in concentration, the liquid scrubbing solution was introduced into the column from the influent reservoir. Inlet and outlet gas samples were taken periodically to ensure steady state conditions were obtained within the packed column. After steady state conditions were reached within the column, 25 ml of water or water

cosolvent mixture samples (depending on the scrubbing solution employed in the run) were collected in 40 ml amber bottles. The liquid samples were sealed with a teflon septa, capped and allowed to reach equilibrium. All tests were run at ambient temperature including the scrubbing solutions. If the samples were not analyzed the same day, they were stored at 4°C overnight until analysis the following day. A 50 µl headspace sample was taken from each bottle using a Hamilton Gastight® syringe and injected into the HP 5890 gas chromatograph. If vegetable oil was employed as the scrubbing solution the 40 ml amber bottle was completely filled to the top and stored at 4°C overnight prior to analysis.

After each column test, the liquid pump was turned off, and the remaining liquid in the column was allowed to drain by gravity to the effluent reservoir. The inlet gas was sampled at the end of the run to ensure that the operating conditions within the column did not fluctuate through the run. The range of gas to liquid flow ratios (Q_G/Q_L) investigated ranged from 6-1221. Table 3.5 presents the experimental conditions evaluated in the packed column. The column was cleaned with detergent to remove any oil residue left on the packing or column sides.

Table 3.5: Summary of Experimental Conditions Evaluated in the Packed Column

Run #	Scrubbing Solution	Q_G (ml/min)	Q_L (ml/min)	Q_G/Q_L
		ml/min	ml/min	
40	40 % propylene glycol	1535	100	15
41	40 % propylene glycol	1535	100	15
46	40 % propylene glycol	1535	60	26
48	40 % propylene glycol	1535	200	8
1	vegetable oil	3612	60	60
2	vegetable oil	3612	60	60
3	vegetable oil	5850	60	98
5	vegetable oil	5850	10	585
12	vegetable oil	1535	60	26
13	vegetable oil	8540	60	142
14	vegetable oil	12607	60	210
15	vegetable oil	12211	10	1221
16	vegetable oil	8540	10	854
17	vegetable oil	8540	100	85
18	vegetable oil	8540	100	85
20	vegetable oil	12607	60	210
21	vegetable oil	6264	60	104
22	vegetable oil	1349	60	22
24	vegetable oil	1136	100	11
28	vegetable oil	10396	60	173
29	vegetable oil	10396	60	173
30	vegetable oil	10396	60	173
31	vegetable oil	12607	60	210
32	vegetable oil	1136	60	19
33	vegetable oil	1136	100	11
49	vegetable oil	1535	60	26
50	vegetable oil	1535	100	15
51	vegetable oil	3612	60	60
52	vegetable oil	5850	60	98

Table 3.5: Cont... Summary of Experimental Conditions Evaluated in the Packed Column

Run #	Scrubbing Solution	Q_G (ml/min)	Q_L (ml/min)	Q_G/Q_L
7	water	5850	60	98
9	water	1535	60	26
10	water	1535	100	15
11	water	1535	200	8
25	water	1136	100	11
26	water	1136	60	19
27	water	1136	200	6
34	water	1136	60	19
35	water	1136	100	11
36	water	1136	200	6
37	water	3118	200	16
38	water	4917	200	25
39	water	6708	200	34
42	water	1535	100	15
43	water	1535	200	8
44	water	1535	60	26
45	water	4740	200	24
47	water	1535	60	26

Figure 3.2: Experimental Set-up of Packed Column

3.2.3 Liquid-Liquid Contacting Reactor

A glass column was employed in an attempt to transfer the relatively hydrophobic compounds from vegetable oil, generated in the packed column, into an aqueous phase for future biological treatment.

3.2.3.1 Liquid-Liquid Partitioning Experiments

Batch tests were performed to determine water-oil partitioning coefficients for the three target compounds to assist in modeling mass transfer in the liquid-liquid contacting reactor.

Table 3.6 outlines the procedure employed for the liquid-liquid partitioning tests. A 30 ml volume of clean vegetable oil was carefully measured into a 40 ml amber bottle. A known volume of pure phase target compound was introduced into each bottle by way of a 10 μ l Hamilton Co. glass syringe as depicted in table 3.6. The three replicate bottles were then completely filled to the top with distilled water, capped with a Teflon lined septum and inverted onto a shaker overnight.

The following day 1ml of the water phase was transferred from the 40 ml amber bottle into a 2 ml glass bottle and sealed with an aluminum crimp cap and teflon septum. The bottle was inverted overnight and a 50 μ l headspace sample was injected into the HP 5890 GC for quantification of the VOC concentration in the water phase by employing Henry's law coefficient and the gas phase concentration. The oil phase of the 40 ml bottle was analyzed as described in section 3.3.4. The ratio of the water concentration to the oil concentration yielded the liquid-liquid partitioning coefficient.

Table 3.6: Procedure employed in Liquid-Liquid Batch Tests (40 ml bottle)

Target Compound	Volume Oil (ml)	Volume Water (ml)	Initial VOC Concentration in Oil (mg/L)	Volume of Pure Phase Required (μ l)
DCM	30	10	200	4.55
CT			650	12.26
PCE			500	11.36

3.2.3.2 Experimental Description

A 13 L glass column with a length of 150 cm and an outer diameter of 10 cm was utilized for the liquid-liquid mass transfer experiments. The top of the column was fastened with a glass cap and secured with metal clamps. Clean water was withdrawn from a reservoir and pumped into the top of the column by way of a Cole Parmer model # 7553-80 peristaltic pump with speeds ranging from 1-600 rpm. A combination of 1 cm copper pipe and Masterflex® Tygon tubing was used for the water inlet. A stainless steel liquid distributor was installed 20 cm down from the top of the column to provide adequate distribution of the clean water over the oil surface. The configuration of the liquid distributor cap was similar to that of the packed column. The cap had an outer diameter of 7.5 cm and was 5 cm thick. The cap contained holes 2 mm in diameter that allowed the water to drain by gravity over the top of the oil surface to increase mass transfer. The holes on the outer perimeter were placed at 30° angles to ensure complete water distribution. The column was run in both semi-batch and continuous modes. Figures 3.3 and 3.4 describe the typical experimental set-up employed in the semi-batch and continuous flow glass column experiments.

Figure 3.3: Experimental Set-up of Liquid-Liquid Contacting Reactor in Semi-Batch Mode

Figure 3.4: Experimental Set-up of Liquid-Liquid Contacting Reactor in Continuous Mode

3.2.3.3 Semi-Batch Mode Experimental Conditions

When the column was operated in batch mode a known volume of oil contaminated with VOCs, generated from the packed column was pumped into the bottom of the column using 1 cm Masterflex® Viton tubing. Clean water was allowed to trickle over the oil layer, and being more dense than the oil, passed downwards to form a separate phase below the oil layer. The column was filled with water at a constant rate until the liquid volume within the column was approximately 10 L. When the liquid level was approximately 30 cm from the top of the column, the water beneath the oil layer was pumped out at the same rate as the fresh water was being pumped in, thereby maintaining a constant liquid level. All semi-batch and continuous flow tests were run for 3 hours including the time to fill the column. The flowrate of clean water over the contaminated oil was evaluated over a range from 112 ml/min to 400 ml/min. The initial volume of contaminated oil pumped into the column was assessed over a range from 1000 ml to 4000 ml. The concentrations of target compounds in the oil that were employed in the glass column were typical of those generated from the packed column. Table 3.7 presents the experimental conditions employed in the semi-batch runs of the liquid-liquid reactor.

Table 3.7: Summary of Operating Conditions Employed in Semi-Batch Experiments

Run #	Initial Oil Volume (ml)	Water Flow Rate Q_w (ml/min)
1	2300	225
2	2100	225
3	2100	225
4	4000	225
5	1000	225
6	2000	115
7	2000	400

3.2.3.4 Continuous Flow Experiments

The continuous flow experiments were carried out in a fashion similar to the semi-batch mode experiments. A modification of the column allowed fresh contaminated oil to be introduced to and withdrawn from the column at the same rate. A known volume of contaminated oil was initially pumped into the column and clean water was pumped into the top of the column thereby allowing the column to fill. The time for the fill mode ranged from 30 to 45 min depending on the water flow rate. When the column was full, the effluent water stream was pumped out of the column to maintain a constant liquid level. At this time, fresh contaminated oil was introduced into the top of the existing oil and withdrawn out of the bottom of the oil layer to maintain a constant volume of oil in the reactor. This mode of operation was representative of that expected to be employed when the packed and the liquid-liquid contacting reactor would be working simultaneously. Each test was run for approximately three hours including the fill time. Sampling of both the oil and water streams was performed periodically. Table 3.8 presents the operating conditions employed in the continuous flow experiments of the liquid-liquid reactor.

Table 3.8: Summary of Operating Conditions Employed in Continuous Flow Experiments

Run #	Initial Oil Volume (ml)	Water Flow Rate Q_w (ml/min)	Oil Flow Rate Q_o (ml/min)
1	2000	200	25
2	1000	200	25
3	2000	200	10
4	2000	100	25
5	2000	350	25
6	2000	200	5

3.2.3.5 Sampling

25 ml water effluent samples were collected every 30 minutes for three hours and were placed into 40 ml glass amber bottles. The 40 ml amber bottles were verified by filling them with a known volume of water to ensure that they were exactly 40 ml. The water samples were sealed with a teflon septum and plastic cap and were allowed to reach equilibrium. A 50 μ l headspace sample was taken from each bottle using a Hamilton Gastight® syringe and was manually injected into the HP 5890 gas chromatograph for analysis.

For the continuous flow experiments only, oil effluent samples were collected in 40 ml sample bottles every 30 minutes for three hours. Three replicate samples of the initial oil were taken prior to starting each run and stored in 40 ml amber bottles. Some water was present in the oil, and hence after each run, the oil and water layers were allowed to completely separate overnight and three final oil samples were collected in 40 ml bottles and analyzed. If the samples were not analyzed the same day, they were stored at 4°C overnight until analysis the following day. At the end of each run the column was drained and cleaned using detergent to remove any excess oil on the sides of the column.

3.3 Analytical Methods and Equipment

The target chlorinated organics were analyzed on two different gas chromatographs, a Hewlett Packard model 5890 equipped with an electron capture detector (ECD) and a HNU model 311 equipped with a photoionization detector (PID).

3.3.1 HP 5890 Gas Chromatograph

The HP 5890 gas chromatograph was equipped with an electron capture detector (ECD) and a DB624 capillary column. The column was 30 m long with an internal diameter of 0.33 mm. The detector was operated at a temperature of 300°C and the inlet temperature was 200°C. The carrier gas employed in the HP 5890 GC was helium at a flow of 200 ml/min. The operating conditions for the GC were as follows:

Initial Temperature	30°C for 5 minutes
Rate increase	10°C/minute
Final Temperature	35°C
Final Time	4 minutes
Rate increase	20°C/minute
Final Temperature	140°C
Final Time	1 minute

Under these operating conditions table 3.9 lists the elution times obtained for the chlorinated target compounds.

Table 3.9: Approximate Retention Times of VOCs on HP 5890 GC

Target Chlorinated Compound		
DCM	CT	PCE
3.4 min	7.7 min	13.5 min

3.3.2 HNU Model 311 Gas Chromatograph

The HNU Model 311 gas chromatograph was equipped with a photoionization detector and employed nitrogen as the carrier gas at a flow of 40 ml/min. The column was 244 cm long with an outer diameter of 3 mm, constructed of stainless steel, and filled with 60/80 Carbopack B 1% sp-1000. An 11.7 eV lamp was employed in this chromatograph. The oven temperature was maintained isothermal at a temperature of 200°C, while the detector and injector temperatures were 140 °C. Table 3.10 depicts the specific retention times for the three compounds of interest on the HNU 311 GC. Figures 3.5 and 3.6 depict typical integrator results obtained by the HP 5890 and HNU model 311 GCs, respectively.

Regular maintenance of both GCs included changing the septum after repeated injections and periodically baking the column overnight to remove any traces of contaminants left on the column that could interfere with the results.

Table 3.10: Approximate Retention Times of VOC's on HNU 311

Target Chlorinated Compound		
DCM	CT	PCE
1.04 min	2.39 min	8.28 min

3.3.3 Linearity Tests and Standard Curves

Prior to commencing experimentation the response of both GCs were examined to verify that linear behavior was observed for all the compounds to be investigated. For the HNU model 311 GC several standards were prepared by spiking a 160 ml serum bottle containing 100 ml of distilled water with a mixture of the chlorinated organics of interest. A 5 ml headspace sample was withdrawn from the 160 ml serum bottle using a 5 ml

Hamilton Gastight® glass syringe and was manually injected directly into the HNU GC for analysis. The second bottle was similarly prepared but diluted by a factor of 10 and the procedure was repeated, so that the concentrations tested covered a range of values from the detection limit to the highest concentration anticipated in the experimental runs. A plot of peak count versus the mass of organic for each compound was prepared, the best fit line was drawn and the coefficient of determination (R^2) was determined to assess linearity of the GC's detector.

For the continuous flow mass transfer tests actual concentrations were required for the target compounds. Standard curves were made for each compound on both GCs. A stock solution containing 1000 mg/L of the target compounds was made up in methanol. Repeated dilutions of the stock solution were made up in water to reflect the concentrations that were to be obtained in the experiments. Tables 3.11 and 3.12 depict the procedure employed to determine standard curves for each target compound, made up in 40 ml bottles. Appendix A presents the standard curves obtained for each target compound from the HP 5890 and HNU model 311 GCs.

Care was taken to minimize systematic errors such as transferring the same mass of the stock solution to each of the 6 serum bottles. In addition, all headspace samples were injected into the GCs using either a 5 ml or 50 μ l Hamilton glass Gastight® syringe. It was suspected that some of the sample may have absorbed onto the needle and may be carried over into the next injection. In order to minimize this error the removable needle was taken off the syringe between runs and placed in the oven for approximately 10 minutes to remove any traces of VOCs from the needle. It was also found that when the

smaller syringe (50 μ l) was employed, if the septum had been recently changed the first few injections resulted in a blocked needle from the septum. It was necessary to periodically clean the needle with a cleaning wire to ensure that no blockage had occurred.

Table 3.11: Stock Solution Concentration of 1000 mg/L for each Target Compound (40 ml bottle)

Target Compound	Density (kg/m ³)	Liquid Concentration (g/ml)	Mass (g)	Volume required (μ l)
DCM	1320	1.32	0.04	30.3
CT	1590	1.59	0.04	25.2
PCE	1620	1.62	0.04	24.7

Table 3.12: Dilution Table of Stock Solution (40 ml bottles)

Diluted Liquid Conc. (mg/L)	Stock Solution Conc. (mg/L)	Volume of Stock Solution (ml)	Volume of Liquid (ml)	Volume of Headspace (ml)
10	1000	0.25	25	15
1	1000	0.025	25	15
0.1	1000	0.0025	25	15
0.01	1000	0.00025	25	15

3.3.4 Sample Preparation for Analysis of VOC's in Oil

An analytical method was developed to determine the concentration of VOCs in vegetable oil. In this method, a 0.125 ml sample of vegetable oil containing VOCs, was injected with a 1 ml glass syringe into a 160 ml serum bottle that had been filled with 100 ml of methanol. The bottle was sealed with a rubber septum and an aluminum crimp cap. This resulted in a volumetric dilution of 1:800. The bottle was placed on a shaker and it was observed that within an hour the oil had dissolved in the methanol. A 1 μ l liquid sample was withdrawn from the methanol solution with a 10 μ l Hamilton Co. glass syringe and injected into the HP 5890 GC for analysis.

Figure 3. 5: Typical Integrator Printout from HP 5890 GC

=====
 External Standard Report
 =====

Sorted By : Retention Time
 Calib. Data Modified : 9/23/97 11:55:17 AM
 Multiplier : 1.0000
 Dilution : 1.0000
 Uncalibrated Peaks : compound name not specified

Signal 1: ECD1 B,
 Results obtained with enhanced integrator!

RetTime [min]	Sig	Type	Area counts*s	Amt/Area	Amount [ng/ul]	Grp	Name
1.396	1	PV	2119.42627	0.00000	0.00000		
1.771	1	VB	1.10303e5	0.00000	0.00000		
3.381	1	PB	438.77612	0.00000	0.00000		
3.499	1		-	-	-		
6.900	1		-	-	-		
7.587	1	BB	6.01468e4	7.37602e-6	4.43644e-1		
10.616	1		-	-	-		
13.448	1	PB	5.41369e4	7.69341e-6	4.16497e-1		

Totals : 8.60141e-1

Figure 3. 6: Typical Integrator Printout from HNU Model 311 GC

DATE TIME
01/28/98 15:53:09

NOISE = 14
BASELINE = 728

SEARCH MODE RESULTS			
PK#	HEIGHT	AREA	TIME
1	2013	27106	1:06
2	2040	28898	2:42
3	131387	3426359	8:34

3.3.5 Flowmeter Calibration

The gas flow rate through the packed column was measured with a Cole Parmer Flowmeter tube # N102 -05. The float material within the flowmeter was dependent on the flowrate desired for the specific test. A 3.2 mm glass float was used for the low flow range (23 -2300 ml/min) and a 3.2 mm stainless steel float accommodated the higher flow range (580 - 10000 ml/min).

It was found that the flows measured by the Cole Parmer Flowmeter were slightly lower than expected. A verification of the flows was performed by employing a Barner Tri-Sense velocity meter. The velocity was measured at both the inlet and outlet of the 2 cm copper pipe under varying flow rates. The modified gas flows were calculated and a calibration curve was prepared for the modified gas flows. Appendix B contains the modified calibration curves employed for both float materials investigated within the study.

Chapter 4 – Results/Discussion

4.1 Gas-Liquid Partitioning Tests

4.1.1 Equilibrium Test

Preliminary tests were performed to ensure that equilibrium was reached within each of the serum bottles prior to analysis. Figure 4.1 presents the measured concentrations of CT in the headspace as a function of time.

Gossett et al. [23], found that it took longer for compounds with elevated Henry's coefficients to reach equilibrium. It was also found that higher liquid volumes increased the time to equilibrium. Both of these observations were considered in this study. CT, with a Henry's coefficient of 1.2 was employed in a high liquid volume system of 100 ml in order to determine the maximum time to reach equilibrium. From figure 4.1, it was evident that it took approximately 4 hours to reach equilibrium. Since the serum bottles employed in the subsequent tests were prepared one day and put on the shaker overnight before analysis the following day; it was assumed that they were at equilibrium. The bottles were not kept on the shaker for longer than 24 hours since previous research has found that sorption may occur onto the teflon septa over extended periods of time [23].

Figure 4.1: Equilibrium Test for EPICS Method Employing CT

4.1.2 EPICS Results

Gas-liquid partitioning coefficients for the target compounds were determined using Gossett's EPICS method with varying volumes of cosolvents and vegetable oil in water at room temperature. Table 4.1 presents a typical EPICS data set obtained for CT in 40% methanol solution. The remaining data obtained from the EPICS tests are presented in Appendix C.

Table 4.1: Typical Data Set for EPICS Test (CT in 40 % methanol solution)

Sample #	Peak count	COV %	Partitioning Coefficient (L/L)
H1	2509842		0.128
H2	3141992		0.140
H3	2676040	11.8 %	0.180
L1	9262182		0.185
L2	8780845		0.201
L3	7505629	10.6%	0.255
			0.142
			0.155
			0.199
	AVG=		0.176
	STDEV=		0.040

(COV = (stdev/mean)*100)

Where:

H_i – high volume bottle (100 ml of liquid, 60 ml of headspace) for replicates 1,2,3 respectively

L_i – low volume bottle (10 ml liquid, 150 ml headspace) for replicates 1,2,3 respectively

Employing equation 2.11, 9 values for the gas-liquid partitioning coefficients were determined for each test, the average and standard deviation were calculated. The standard deviation and mean were also calculated for both the high and low volume bottles separately and the coefficients of variance (COV) were reported in table 4.1 to

investigate the variability in the EPICS method. The variability in the peak counts for the low and high volume bottles resulted in an overall average COV of 12.9 %. PCE in 20 % vegetable oil exhibited the highest COV of all the partitioning tests. Higher COVs were typically observed with lower gas-liquid partitioning coefficients such as PCE in vegetable oil.

The gas-liquid partitioning coefficients that were obtained from the EPICS tests are summarized in tables 4.2-4.4.

Table 4.2: Gas to Liquid Partitioning Coefficients Obtained from EPICS for DCM

Cosolvent	Partition Coefficient (L/L)	Standard Deviation
100 % water	0.189	0.027
20 % methanol	0.084	0.053
40 % methanol	0.181	0.097
20 % propylene glycol	0.090	0.040
40 % propylene glycol	N/A	
20 % vegetable oil	0.026	0.029
100 % vegetable oil	0.013	0.012
20 % ethanolamine	0.231	0.037
40 % ethanolamine	0.296	0.073
20 % propylene glycol, 10 % ethanolamine	0.218	0.066
20 % propylene glycol, 20 % ethanolamine	0.227	0.041

N/A – data not available

Table 4.3: Gas to Liquid Partitioning Coefficients Obtained from EPICS for CT

Cosolvent	Partition Coefficient (L/L)	Standard Deviation
100 % water	1.038	0.071
20 % methanol	1.238	0.733
40 % methanol	0.176	0.040
20 % propylene glycol	0.958	0.310
40 % propylene glycol	0.188	0.065
20 % vegetable oil	0.019	0.014
100 % vegetable oil	0.004	0.005
20 % ethanolamine	0.607	0.173
40 % ethanolamine	N/A	
20 % propylene glycol, 10 % ethanolamine	0.481	0.113
20 % propylene glycol, 20 % ethanolamine	0.344	0.070

Table 4.4: Gas to Liquid Partitioning Coefficients Obtained from EPICS for PCE

Cosolvent	Partition Coefficient (L/L)	Standard Deviation
100 % water	1.186	0.272
20 % methanol	0.517	0.050
40 % methanol	0.217	0.090
20 % propylene glycol	0.821	0.580
40 % propylene glycol	0.159	0.064
20 % vegetable oil	0.026	0.090
100 % vegetable oil	0.001	-
20 % ethanolamine	0.598	0.134
40 % ethanolamine	0.498	0.164
20 % propylene glycol, 10 % ethanolamine	0.347	0.096
20 % propylene glycol, 20 % ethanolamine	0.272	0.059

4.1.2.1 Results of DCM from EPICS

From table 4.2 the gas to liquid partition coefficient of DCM in water alone was comparable to previous research [40,4,22,55]. Table 2.1 summarized partition coefficients for DCM in water in the range of 0.082-0.272. This was comparable to the partition coefficient of 0.189 obtained in this study.

The batch experiments for DCM demonstrated that increasing the cosolvent addition of either methanol or propylene glycol, resulted in a modest decrease in the gas-liquid partition coefficient. One anomaly was observed when 40% methanol was employed, the gas-liquid partition coefficient increased slightly from 0.084 to 0.181. This result was not consistent with the literature, which indicated that with increasing cosolvent addition, the gas-liquid partition coefficient would be decreased. The standard deviation for this particular test was slightly higher than those obtained for the other DCM batch tests. The analytical method was relatively insensitive to lower chlorinated compounds such as DCM, and as a result the peaks produced for DCM were not always reproducible,

which may serve as an explanation for the increased standard error. GC integrator problems with the use of DCM were also encountered by Munz [45]. Munz [45], did not find any conclusive answers to the problem of higher standard errors with DCM in comparison to the other compounds investigated and therefore omitted the results obtained for DCM.

When ethanolamine or mixtures of ethanolamine and propylene glycol were used, the gas to liquid partitioning coefficients for DCM slightly increased from that in water alone. Ethanolamine appeared to be the factor which resulted in an increase in DCM's partitioning coefficient. When vegetable oil was used as a medium the gas-liquid partitioning coefficients decreased by approximately one order of magnitude.

4.1.2.2 Results of CT from EPICS

From table 4.3 the gas-liquid partitioning coefficient of CT in water alone was found to be 1.038. This value was within the range of literature values which varied from 0.975-1.244 at 20°C [40,45,46,4]. The results of the batch tests for CT demonstrated that as cosolvent addition was increased the gas to liquid partitioning coefficient decreased. This was observed for all tests, with the exception of 20 % methanol in which the gas to liquid partitioning coefficient increased as compared to water alone. The standard deviation associated with this specific test was substantially higher in this experiment hence, it was difficult to differentiate this value from that of water.

Propylene glycol and methanol appeared to decrease the gas to liquid partition coefficient to approximately 20 % of the value for water alone when the highest cosolvent

concentration of 40% by volume was employed. When mixtures of 20% propylene glycol with 10% or 20% ethanolamine were used the partitioning coefficients (0.481 and 0.344, respectively) were further reduced from than that of 20% v/v propylene glycol (0.958). The gas-liquid partitioning coefficient for 20% propylene glycol was higher than those observed in the 20% propylene glycol, 20% ethanolamine mixture. The observation of enhanced solubility with cosolvent mixtures was consistent with the results of Yalkowsky's solubility theory.

The most dramatic decrease in partitioning coefficients was observed with vegetable oil. When 100% v/v vegetable oil was employed the partitioning coefficient was reduced to 0.004. This value was approximately 3 orders of magnitude less than the value in water alone. This result would indicate that if vegetable oil were to be used in the packed column, CT should readily partition to the liquid phase.

4.1.2.3 Results of PCE from EPICS

From table 4.4 the gas-liquid partitioning coefficient of PCE in water was found to be 1.186. The values obtained from the literature were found to be slightly lower ranging from 0.4825-0.881 [48,22,4,55,23]. The results for PCE that were obtained from the batch tests, demonstrated that as the cosolvent concentration was increased the gas to liquid partitioning coefficient decreased. From the three selected cosolvents of methanol, propylene glycol and ethanolamine; 40% v/v propylene glycol caused the highest reduction in partition coefficient to a value approximately 15% of the value in water. Other researchers such as Li et al. [36] and Munz [45] have also observed this inverse relationship between gas-liquid partition coefficients and cosolvent addition. These

researchers also noted that the more hydrophobic the chlorinated compound, the greater the enhanced solubility effect.

100 % vegetable oil exhibited the lowest partition coefficient, reducing the value by 4 orders of magnitude relative to that in water alone. PCE was the most hydrophobic of the three target compounds and exhibited the lowest gas-liquid partition coefficient in oil of the three target compounds. This observation was consistent with the work of Munz [45], which suggested that the more hydrophobic the compound the greater the solubilization effect in vegetable oil.

4.1.2.4 Summary

From the batch tests it was observed that typically as the cosolvent fraction was increased the gas-liquid partitioning coefficient decreased. One anomaly occurred with the results of DCM, the partitioning coefficient in ethanolamine and ethanolamine mixtures increased over that of water alone. For all three target compounds the most evident reduction in the gas to liquid partitioning coefficients was observed with vegetable oil.

In general, the results of the batch tests demonstrated that high volumes of aqueous cosolvents would be required in a continuous flow system, and hence it was elected to evaluate an alternative scrubbing solution. Vegetable oil was identified as a possible scrubbing solution since it is readily available, inexpensive, environmentally acceptable, and has the potential for recycle in a hybrid system. The results from the batch experiments clearly demonstrated that the target compounds strongly partition to vegetable oil and hence vegetable oil was deemed a viable scrubbing solution to be further

researched within this study. Although the cosolvents did not appear to dramatically enhance the solubility of the VOCs, 40 % propylene glycol was also selected from the range of cosolvents to be further investigated within the continuous flow studies in the packed column.

4.2 Mass Transfer Column

4.2.1 Continuous Flow Tests

The continuous flow mass transfer tests examined the impact of gas and liquid flow rates as well as scrubbing solution composition on the removal of chlorinated contaminants from air streams. All tests employed either water, Canola vegetable oil, or an aqueous solution of propylene glycol as the scrubbing solution.

4.2.1.1 Steady-State Condition

Prior to conducting the mass transfer tests in the continuous flow system, preliminary tests were conducted to ensure steady-state conditions were reached within the column. Figure 4.2 presents a typical graph showing the time required to reach steady-state within the packed column. In general, it took approximately 25 minutes to reach steady-state conditions and all subsequent tests were operated for at least this long prior to sampling. In addition, since the time to steady state was a function of the flowrates, sampling of the gas phase was performed in each subsequent test to ascertain steady-state conditions.

Figure 4.2: Typical Graph of Time to Steady State in Packed Column ($Q_G = 3807$ ml/min, $Q_L = 60$ ml/min)

4.2.1.2 Mass Balances

Preliminary mass balances were performed on the packed column to assess the validity of the results. Initially, it was found that most mass balances did not exhibit complete closure. As a result, the gas flows were verified with a Barner Tri-sense velocity meter. It was found that the gas flows measured by the Cole-Parmer flow meter were slightly lower than those obtained with the velocity meter. A modified calibration curve for the Cole-Parmer flowmeter was obtained and is presented in Appendix B for the stainless steel and glass floats respectively. Employing the modified gas flows it was found that the mass balances exhibited a higher degree of closure on the overall system. Tables 4.5 and 4.6 present typical preliminary mass balances on the original and modified data respectively for DCM when 40 % propylene glycol was employed as a scrubbing solution.

From tables 4.5 and 4.6 it was evident that the modified gas flows resulted in a higher percent mass balance closure on the system. The modification to the gas flows was therefore employed for all the packed column data.

Table 4.5: Original Preliminary Mass Balance for DCM on Packed Column

Q_G ml/min	Q_L ml/min	C_{gin} mg/L	C_{gout} mg/L	C_{Lout} mg/L	M_{in} mg/min	M_{out} Liquid mg/min	M_{out} Gas mg/min	M_{out}/M_{in} %
977	100	9.11	6.04	35.03	8.90	3.85	5.90	109
977	100	9.11	6.34	36.88	8.90	3.69	6.19	111
977	100	9.11	6.87	48.43	8.90	4.84	6.71	130
977	100	9.11	6.27	45.79	8.90	4.58	6.12	120

Table 4.6: Modified Mass Balance for DCM on Packed Column

Q_G ml/min	Q_L ml/min	C_{gin} mg/L	C_{gout} mg/L	C_{Lout} mg/L	M_{in} mg/min	M_{out} Liquid mg/min	M_{out} Gas mg/min	M_{out}/M_{in} %
1535	100	9.11	6.04	35.03	13.99	3.50	9.27	91
1535	100	9.11	6.34	36.88	13.99	3.69	9.73	96
1535	100	9.11	6.87	48.43	13.99	4.84	10.55	110
1535	100	9.11	6.27	45.79	13.99	4.58	9.62	101

After modifying the data in terms of the gas flows, it was observed that some of the data still did not exhibit mass balance closure. After a thorough analysis it was found that some of data had exceeded equilibrium between the gas and liquid phases at the base of the column, perhaps as a result of analytical errors in determining gas phase concentrations.

It was observed that CT and PCE in water and DCM in oil exceeded equilibrium at the base of the column. To alleviate this problem, the equilibrium liquid concentrations at the column effluent were calculated using the gas-liquid partitioning coefficient. A mass balance around the system was then performed and the gas phase outlet concentration was calculated. The modified outlet gas concentrations were employed for the remainder of the data analysis on the data that had exceeded equilibrium. Appendix D presents the raw data of the three target compounds for the various scrubbing liquids under the differing process conditions. Tables 4.7 and 4.8 present a sample analysis for modifying the outlet gas concentrations when equilibrium was exceeded for CT in water.

Table 4.7: Typical Analysis for Modifying the Outlet Gas Concentrations for CT in Water

Q_G ml/min	Q_L ml/min	C_{gin} mg/L	C_{gout} mg/L	C_{Lout} mg/L	C_{Lout} (equilib) mg/min
1535	60	11.46	9.73	28.17	9.55
1535	60	11.46	9.46	32.56	9.55
1535	60	11.46	8.87	42.17	9.55

Table 4.8: Modified Outlet Gas Concentration for CT in Water (partitioning coefficient in water $K_c = 1.2$)

Q_G ml/min	Q_L ml/min	C_{gin} mg/L	C_{gout} mg/L	C_{Lout} mg/L
1535	60	11.46	11.09	9.55

From tables 4.7 and 4.8 it was observed that the corrected outlet gas concentration (C_{gout}) resulted in only a slight deviation from the measured outlet gas concentrations. This result was typical for all three compounds and the modified and measured gas concentrations are presented in Appendix D for the varying process conditions. It should be noted that only the gas concentrations were employed in the subsequent analysis of mass transfer coefficients and removal efficiencies.

4.2.1.3 Water

Appendix J presents the coefficients of determination and the equations of the line associated with the assumed trendlines for the applicable figures obtained in chapters 4 and 5. When water was employed as the scrubbing solution within the packed column, the removal efficiencies varied for the three compounds. Figure 4.3 presents the three target compounds steady state removal efficiencies as function of gas velocity for a constant liquid velocity of 0.025 m/min. From figure 4.3, DCM appeared to be removed to the greatest extent when water was employed as a scrubbing solution. DCM removal

approached 90 % in water at the lowest gas velocity of 0.14 m/min. As the gas velocity was increased the removal efficiency for DCM decreased to approximately 8%.

PCE and CT removals also decreased with increasing gas velocity. PCE decreased in removal from 25 % to 4.3 % for gas velocities ranging from 0.14 m/min – 0.83 m/min. CT exhibited the lowest removals of the three compounds with removals ranging from 10.3 % to 3.3 % for gas velocities ranging from 0.14 m/min to 0.83 m/min. These results suggest that high removals would be difficult to achieve for the more hydrophobic compounds such as CT and PCE.

Figure 4.4 presents the steady state removal efficiencies of the three target compounds as a function of the liquid velocity at a constant gas velocity of 0.2 m/min. From figure 4.4, all three of the target compounds removal efficiencies increased with increasing liquid velocity. This observation characterizes the effect of liquid velocity on the removal of the target compounds. DCM exhibited the highest removal efficiencies ranging from 27% to 90% for the entire liquid velocity range of 0.007 m/min to 0.02 m/min. CT and PCE exhibited substantially lower removals ranging from 3.26% to 10.34% and 6% to 18.6% respectively for flows in the range of 0.007 m/min to 0.25 m/min. The results of PCE and CT suggested that even at the highest liquid velocities of 0.025 m/min the removal efficiencies were still quite low, hence an alternative scrubbing liquid would be required to effectively remove the target compounds from the air streams.

Figures 4.5-4.7 present the steady state removal efficiencies of the three target compounds as a function of the gas-liquid flow ratios and as a function of the inlet gas concentrations. As expected, the inlet concentrations appeared to have no effect on the

overall removal efficiencies of the three target compounds. From figures 4.5-4.7 the removal efficiencies decreased with increasing gas-liquid flow ratios.

It was observed that CT was removed to the least extent of the three target compounds. The highest removal efficiency for CT approached only 15% at the lowest gas-liquid flow ratios. From figure 4.7 it was observed that the results of PCE rapidly decreased from 25% to 2% for gas-liquid flow ratios ranging from 8-98.

The gas to liquid flow range of 1-40 was investigated to the greatest extent when water was employed as the scrubbing solution. Several tests examined the higher gas-liquid flow range to a limit of approximately 99. At the highest gas to liquid flow range it was found that the removal efficiencies were at their lowest, therefore most of the continuous flow tests for water were operated at a gas to liquid flow range of 1-40.

The trends exhibited in removal efficiencies were consistent with that which would be predicted by their Henry's law coefficients. DCM had the lowest Henry's law coefficient of the three compounds, which would indicate that it would have the highest partitioning to water as depicted in figures 4.3 and 4.4. The Henry's law coefficient for CT was the highest of the three compounds, which explains the lowest removals efficiency with water.

The results with water alone as scrubbing solution confirm the hypothesis that water alone would not be desirable as a scrubbing solution for hydrophobic compounds such as PCE and CT due to the large quantities of water that would be required to obtain substantial removals of these target compounds.

Figure 4.3: Steady State Removal Efficiencies in Water as a Function of the Gas Velocity (Constant Liquid Velocity = 0.025 m/min) for DCM, CT and PCE

Figure 4.4: Steady State Removal Efficiencies in Water as a Function of the Liquid Velocity (Constant Gas Velocity = 0.2 m/min) for DCM, CT and PCE

Figure 4.5: Removal of DCM in Water as a Function of Gas-Liquid Flow Ratio

Figure 4.6: CT Removal in Water as a Function of Gas-Liquid Ratio

Figure 4.7: PCE Removal in Water as a Function of the Gas-Liquid Ratio

4.2.1.4 Propylene Glycol

Propylene glycol exhibited the highest potential in reducing the gas to liquid partitioning coefficient among the cosolvents investigated in the batch tests. Propylene glycol, at a volumetric fraction of 40%, was investigated as an alternative scrubbing solution to water. Figures 4.8 and 4.9 present the removal efficiencies obtained in the packed column as a function of the liquid velocity and gas-liquid flow ratio respectively.

The results of these continuous flow experiments were consistent with the results obtained in the batch tests for CT and PCE. It was hypothesized and confirmed in the batch tests that employing a cosolvent such as 40% propylene glycol, would further enhance the solubility of the VOCs in the air stream over water alone. From figure 4.8, at the highest liquid velocity of 0.025 m/min, CT and PCE exhibited an increase in removal efficiencies from 10 % to 38 % and from 18% to 50% respectively when 40% propylene glycol was employed as the scrubbing solution over water alone. In contrast to the batch tests, when water alone was employed as a scrubbing solution the removal efficiencies for DCM were substantially higher at 90% than that of 65% observed when a 40% propylene glycol solution was employed.

One possible explanation for the inconsistency with DCM may lie in the physical properties associated with the cosolvents mixtures as compared to water. Propylene glycol was much more viscous than water alone, and a higher surface tension was exhibited by the cosolvent which might have influenced the wetted surface area, hence influencing the extent of VOC removal.

From figure 4.9 it was evident that for all three target compounds, as the gas-liquid flow ratio was increased, the removal efficiency of the target compounds decreased. At the lowest gas-liquid flow ratio of 8 the highest removal efficiency obtained was approximately 65% for DCM. CT was removed to the least extent at the lowest gas-liquid flow ratio, approaching a removal of only 40%, whereas, PCE removal approached approximately 55% at this ratio.

The results from the continuous flow tests indicated that large volumes of cosolvents would be required to effectively remove the target compounds from the air streams. From an economic perspective an alternative scrubbing solution to water and cosolvents was therefore investigated.

Figure 4.8: VOC Removal in 40 % Propylene Glycol as a Function of Liquid Velocity (Constant Gas Velocity = 0.12 m/min)

Figure 4.9: VOC Removal in 40 % Propylene Glycol as a Function of Gas-Liquid Flow Ratio

4.2.1.5 Oil

From the batch tests it was found that the VOCs strongly partitioned to vegetable oil. These results suggested that vegetable oil may be a suitable medium for scrubbing VOCs and concentrating them into a liquid phase. Vegetable oil was therefore employed as an alternative scrubbing solution in the packed column under varying gas and liquid flowrates.

The results from the continuous flow tests employing vegetable oil as a scrubbing solution are presented in figures 4.10-4.14. Figures 4.10-4.12 depict the steady state removal efficiencies as a function of gas to liquid flow ratios. From figures 4.10-4.12 it was evident that there was no effect of the inlet concentrations on the removal efficiencies of the target compounds. In general, much higher removal efficiencies among the target compounds were observed when vegetable oil was employed as a scrubbing solution. PCE was removed to the greatest extent with efficiencies approaching 90% for gas to liquid ratios as high as 1221. Greater than 85% removal efficiencies were observed for CT for gas to liquid flow ratios as high as 200. DCM was removed to a lesser extent than the two other target compounds with removal efficiencies ranging from 90% to 35% for gas to liquid flow ratios ranging from 9-210 respectively.

Removal efficiencies, as a function of the liquid velocity are presented in figure 4.13. The removal efficiency of DCM increased from 8% to 85% as the liquid velocity was increased from 0.001 to 0.012 m/min. CT and PCE also exhibited increasing removals with increasing liquid velocity from 69% to 95% and 92% to 99% respectively, with liquid velocities ranging from 0.001 m/min to 0.012 m/min. CT and PCE appeared to reach a

plateau in terms of removals at a liquid flow rate of 0.008 m/min. This may suggest that the maximum achievable removal efficiency had been attained in the packed column. There may have been some short-circuiting within the column that could have resulted in deviations from ideal conditions.

Figure 4.14 presents the removal efficiencies as function of the gas velocity in the continuous flow tests. From figure 4.14 it was evident that as the gas velocity increased the removal efficiencies of all three target compounds decreased. DCM removal decreased from 90% to approximately 35% as the gas velocity increased from 0.7 m/min to 1.50 m/min. CT and PCE also exhibited a modest decrease in removal efficiencies from 95% to 75% and from 99% to 90% respectively as the gas velocity increased from 0.2 m/min to 1.5 m/min.

The removal efficiencies were consistent with theory, the most non-polar compound (PCE) was the most readily removed and was relatively independent of the gas and liquid flows. Conversely the most polar compound (DCM) was removed to the least extent. High removals for all compounds were obtained when the gas to liquid flow ratio was less than 200. These results demonstrate that vegetable oil is a highly effective scrubbing agent for non-polar organic compounds.

Figure 4.10: DCM Removal in Oil as a Function of Gas-Liquid Flow Ratio

Figure 4.11: CT Removal in Oil as a Function of Gas-Liquid Flow Ratio

Figure 4.12: PCE Removal in Oil as a Function of Gas-Liquid Flow Ratio

Figure 4.13: VOC Removal in Oil as a Function of Liquid Velocity
(Constant Gas Velocity = 1.05 m/min)

Figure 4.14: VOC Removal in Oil as a Function of Gas Velocity
(Constant Liquid Velocity = 0.007 m/min)

4.2.1.6 Summary

Vegetable oil appeared to be the most viable liquid solution for scrubbing VOCs from air streams. Vegetable oil demonstrated relatively high removal efficiencies for a range of polarities. Vegetable oil was the most effective scrubbing solution employed in removing VOCs from the air stream and concentrating them in a liquid stream for future treatment. High removal efficiencies were obtained when vegetable oil was employed as a scrubbing solution at both low and relatively high gas-liquid flow ratios.

The results of the continuous flow experiments demonstrate the importance of selecting a scrubbing agent that is appropriate for removing specific compounds from an air stream. Air streams such as the one synthesized for this study are especially challenging when the compounds vary in hydrophobicity. Under optimal process conditions high removal efficiencies may be obtained.

4.3 Liquid-Liquid Contacting Reactor

The use of vegetable oil as a scrubbing solution was found to be advantageous since it provided high partitioning of the compounds from the gas phase to the liquid phase. In addition, by employing a separate phase as a scrubbing solution there is a potential for recycle back to the scrubbing column, thereby reducing the consumption of vegetable oil and minimizing the overall operational costs of the system. However, employing vegetable oil as a scrubbing solution presented an additional challenge in the process design of the overall hybrid system, which included the high rate anaerobic

reactor. In order to further treat the concentrated oil stream the relatively hydrophobic compounds need to be transferred from the non-polar solvent into an aqueous phase. Oil-water mass transfer was assessed in this study using a liquid-liquid contacting reactor. The results from the liquid reactor could then be employed to assess mass transfer in an anaerobic reactor that incorporated this process.

4.3.1 Liquid – Liquid Partitioning Tests

Batch tests were performed to determine water–oil partitioning coefficients for the three target compounds that could then be employed to assist in modeling the liquid-liquid mass transfer process.

Mass balances were initially performed around the system for all three target compounds (table 4.9) to ensure confidence in the batch test results. The mass balances on CT and PCE exhibited nearly complete closure for the first two replicates of the liquid-liquid partitioning test. When mass balances were performed around the system for DCM there appeared to be a substantially higher increase in the water VOC concentration in comparison to the oil VOC concentration. The mass balances for DCM could not be closed for any of the three replicate tests.

Table 4.9: Results of Mass Balance Closure for Water-Oil Partitioning Tests

	Actual Mass VOC in bottle (mg)	Mass Water (mg)	Mass Oil (mg)	Mw +Mo (mg)	Mass Balance % Closure
DCM	6.01	15.20	3.16	18.36	305.5
	6.01	15.31	3.17	18.48	307.5
	6.01	21.88	1.42	23.29	387.5
CT	19.49	1.91	16.47	18.38	94.3
	19.49	2.59	18.95	21.54	110.5
	19.49	2.28	9.34	11.62	59.6
PCE	18.40	0.24	16.78	17.01	92.4
	18.40	0.33	19.26	19.59	106.5
	18.40	0.30	9.65	9.95	54.1

The liquid-liquid partitioning coefficient was calculated as:

$$K_{w/o} = \frac{C_w}{C_{oil}} \quad (4.1)$$

where: $K_{w/o}$ = water – oil partitioning coefficient

C_w = VOC concentration in water

C_{oil} = VOC concentration in vegetable oil

The data obtained for the three target compounds was applied to equation 4.1 to determine values for the water-oil partitioning coefficients. The water-oil partitioning coefficient obtained for DCM was substantially higher than anticipated, and therefore based on these results and the mass balance analysis it was elected to omit the experimental results for DCM.

A water-oil partitioning coefficient for DCM was required to effectively model DCM in the liquid-liquid reactor. Since the experimental values were questionable an approximate water–oil partitioning coefficient for DCM was estimated from the gas-water

partitioning coefficient and gas-oil partitioning coefficient previously obtained in the batch tests.

$$K_{A/w} = \frac{C_A}{C_w} \quad (4.2)$$

$$K_{A/o} = \frac{C_A}{C_{oil}} \quad (4.3)$$

where:

- $K_{A/w}$ = air-water partitioning coefficient
- $K_{A/o}$ = air-oil partitioning coefficient
- $K_{w/oct}$ = water-octanol partitioning coefficient
- C_w = VOC concentration in water
- C_A = VOC concentration in air
- C_{oil} = VOC concentration in vegetable oil

Rearranging equations 4.2 and 4.3 for C_w and C_{oil} respectively and substituting into equation 4.1 yields:

$$K_{w/o} = \frac{K_{A/o}}{K_{A/w}}$$

Table 4.10 summarizes the results obtained for the water-oil partitioning coefficients that were calculated and measured along with the water-octanol partition

coefficients for the three target compounds. Barbari [8], suggested that the partitioning of VOCs to octanol was similar to the partitioning to oils. The experimental water-oil partitioning coefficients obtained for the three target compounds appeared to be consistent with the published water-octanol values for DCM and PCE (table 4.10). However, the water-octanol partition coefficient for CT was approximately 1 order of magnitude smaller than the experimental water-oil partitioning coefficient.

As expected the most hydrophobic compound (PCE) exhibited the lowest water-oil partitioning coefficient. The least hydrophobic compound (DCM) was found to have the highest water-oil partitioning coefficient. These results would suggest that of the three target compounds PCE would partition to the least extent from the oil phase into the water phase in the liquid-liquid reactor.

Table 4. 10: Summary of Partitioning Coefficients

Partition Coefficient	DCM		CT		PCE	
	Average	Std. Dev	Average	Std. Dev	Average	Std. Dev
$K_{A/w}$	0.189	0.027	1.038	0.071	1.186	0.272
$K_{A/o}$	0.013	0.012	0.004	0.005	0.001	-
exp. $K_{w/o}$	-	-	0.042	0.005	0.005	0.001
calc. $K_{w/o}$	0.069	-	0.039	-	0.001	-
$K_{w/oct}$	0.056	-	0.002	-	0.002	-

4.3.2 Semi-batch Tests

Semi-batch tests were initially employed in the liquid-liquid contacting reactor to assess mass transfer without oil entering or leaving the process. Table 4.11 presents the conditions investigated for the semi-batch tests. In this method a known volume of contaminated oil was introduced into the column and the column was then allowed to fill with fresh water. The time to fill the column ranged between 45 min and 1 hour depending on the water flow rate.

A series of experiments were performed with the liquid-liquid mass transfer process operating in a batch mode. Figures 4.15 and 4.16 present the typical results obtained in the semi-batch tests for CT and PCE concentrations in water, respectively, as a function of time for run #3. From these graphs it is evident that the water concentration in the column was initially higher during the fill mode, and this was likely due to the fact that the dilution factor was higher in the column after it was completely filled resulting in lower VOC water concentrations. Immediately after the column was filled and water was allowed to exit the column, the concentration quickly decreased from approximately 1 mg/L to 0.3 mg/L for CT and from 0.56 mg/L to 0.15 mg/L for PCE. After 2 hours the target compound concentration in water appeared to reach pseudo steady state conditions. All subsequent tests were therefore run for approximately 3 hours including the fill time.

Figure 4.15: Typical Graph of Semi-Batch Test- Equilibrium VOC Water Concentrations for CT (Volume oil = 2100 ml, $Q_w = 225$ ml/min)

Figure 4.16: Typical Graph of Semi-Batch Test - Equilibrium VOC Water Concentrations for PCE (Oil Volume = 2100 ml, $Q_w = 225$ ml/min)

Similar to the liquid-liquid batch test the water concentrations of PCE were an order of magnitude smaller than those of CT. These results were consistent with the findings of the water-oil partitioning coefficients, which indicated a very low partition coefficient between water and oil for hydrophobic PCE.

Table 4.11 presents the removal efficiencies obtained from the semi-batch tests. The removal efficiencies were calculated based on the initial oil concentration at the beginning of each test and the final VOC concentration in the oil at the end of the test. The results from the semi-batch tests exhibited low removals from the oil phase to the water phase. The lowest removals were exhibited by PCE for all test conditions. CT was removed from the oil phase to the greatest extent at the highest liquid flowrates with a removal approaching only 10 % at the highest liquid flowrate of 400 ml/min. The oil volume within the column appeared to exhibit no impact on the overall removal efficiencies of CT and PCE.

Figure 4.17 presents the removal of CT and PCE respectively from the oil phase to the water phase as a function of liquid flowrate. From figure 4.17 it is evident that as the water flow rate was increased the removal of the target compounds from the oil phase to the water phase also increased. The results for DCM were not presented for the semi-batch tests because the concentrations obtained from the GC during the oil analysis were below the detection limit.

The concentration of target compounds in the water phase in the liquid-liquid reactor indicated that mass transfer was occurring between the oil and water phases. It was expected that if the column were run in a continuous mode, in which fresh

Figure 4.17: Removal Efficiencies of VOCs from Oil as a function of the Water Flow Rate in the Semi-Batch Tests after 3 hours

contaminated oil was introduced at a constant rate the mass transfer of the VOCs from the oil phase to the water phase could be further enhanced.

Table 4.11: Pseudo Steady State Removal Efficiencies Obtained in the Liquid-Liquid Contacting Reactor Semi-Batch Experiments (13 L column volume, 3 hour contact time)

Run #	Oil Volume (ml)	Water Flowrate, Q_w (ml/min)	% Removal CT	% Removal PCE
1	2300	225	13.5	11.6
2	2100	225	19.6	8.7
3	2100	225	7.1	3.9
4	4000	225	12.8	4.2
5	1000	225	10.8	5.3
6	2000	110	5	1.3
7	2000	400	9.3	5.2

4.3.3 Continuous Flow Tests

The liquid-liquid contacting reactor was run in a continuous mode with various water and oil flow rates. Table 4.12 presents the conditions investigated for the continuous flow tests. Similar to the semi-batch tests a known volume of contaminated oil was introduced into the column and the column was filled to a constant level with clean water. After the fill mode was completed water was allowed to exit the bottom of the column at the same rate as fresh water was sprayed over the oil layer. Contaminated oil was introduced and withdrawn from the initial contaminated oil layer at a constant rate.

Each test was run for 3 hours including the time to fill. After examining the data obtained for these tests it was found that not all the tests had actually achieved steady state conditions. Figure 4.18 depicts a typical graph of the target compound concentrations in the water phase as a function of time. From the graph it is evident that that DCM had not obtained steady state by the end of the test. Conversely, the plateauing

trend exhibited by CT and PCE suggested that these compounds have achieved steady state within the 3 hour time. The data sets were therefore examined with the objective of identifying those that had achieved steady state. Removal efficiencies were computed for the runs that had achieved steady state and are subsequently discussed. All of the data sets were employed in the estimation of mass transfer coefficients. Table 4.13 presents the results of the steady state test for the continuous flow experiments.

For the six experiments it was found that steady state conditions for PCE were reached for all test conditions. The steady state removal efficiencies are presented in table 4.14. As expected it was found that the more hydrophobic compound PCE, was removed to the least extent, whereas the removal efficiencies of CT were approximately one order of magnitude higher than PCE. The DCM concentration in water appeared to be higher than expected, but these results lacked confidence since a closure of mass balance on the system was not achieved.

Table 4.12: Conditions Investigated in Continuous Flow Tests

Run #	Water Flow Rate Q_w (ml/min)	Oil Flow Rate Q_o (ml/min)	Initial Oil Volume V_o (L)
1	200	25	2
2	200	25	1
3	200	10	2
4	100	25	2
5	350	25	2
6	200	5	2

Figure 4.18: Typical Graph of Continuous Flow Liquid-Liquid Extraction Experiments Testing for Steady State Conditions
(Run # 1 - $Q_w = 200$ ml/min, $Q_o = 25$ ml/min)

Table 4. 13: Results of Steady State Analysis (3 hour runs)

Run #	DCM	CT	PCE
1	Not at Steady State	Not at Steady State	Steady State Condition
2	Steady State Condition	Steady State Condition	Steady State Condition
3	Not at Steady State	Not at Steady State	Steady State Condition
4	Not at Steady State	Not at Steady State	Steady State Condition
5	Steady State Condition	Steady State Condition	Steady State Condition
6	Steady State Condition	Steady State Condition	Steady State Condition

Figure 4.19 demonstrates the increasing relationship between the water flow rate and the rate of removal of PCE from the oil into the water phase. At the highest water flow rate of 350 ml/min PCE demonstrated a removal efficiency of 5.8 %. In contrast, for CT at water flow rates ranging from 200 – 350 ml/min, the removal efficiencies ranged from 45.0 % to 80.3% respectively.

Table 4.14: Steady State Removal Efficiencies from Continuous Flow Experiments

Run #	CT	PCE
1	-	3.08
2	45.26	4.48
3	-	5.47
4	-	2.16
5	80.27	5.76
6	N/A	17.47

Figure 4.19: Steady State PCE Removal Efficiencies for the Continuous Flow Liquid-Liquid Extraction Tests as a Function of Liquid Flow Rate

4.3.4 Summary

The water-oil partitioning batch tests demonstrated that a higher degree of partitioning from the oil to the water phase was obtainable for the less hydrophobic compounds. It was observed that PCE did not partition well from the oil to the water phase a result of being highly hydrophobic. These results were consistent with the findings of the continuous flow tests, in which PCE exhibited the lowest removal efficiencies. It was initially assumed that if the liquid-liquid column was operated for a minimum of 3 hours, that steady state conditions were obtainable. The results from the continuous flow tests however indicated that not all the compounds were at steady state conditions. To accurately characterize liquid-liquid mass transfer within the reactor a dynamic liquid-liquid model was developed.

Chapter 5 – Model Development and Application

5.1 Model Development for Scrubber

The scrubbing model was developed to estimate mass transfer coefficients from the continuous flow experiments in the packed column. These observed mass transfer coefficients will assist in the comparison of existing mass transfer models and allow for effective scale-up of the hybrid process. Figure 5.1 presents a schematic of the packed column employed in the continuous flow tests and describes some of the nomenclature used in the modeling. The gas phase was passed upwards from the bottom of the column and exited at the top. The liquid phase was passed downwards over the column packing and exited at the top. Since the gas and liquid flows were countercurrent a sign convention was assumed with the downwards direction assumed to be positive.

Figure 5. 1: Packed Column Schematic

5.1.1 Mass Balances

Gas and liquid phase mass balances on the target compound were performed around the packed column. Steady state conditions and perfect plug flow were assumed to prevail within the column. The accumulation term in the mass balance equations was therefore zero.

$$\Delta V \frac{\partial C_g}{\partial t} = \Delta V \frac{\partial C_l}{\partial t} = 0$$

Assuming a cross-sectional slice of thickness (dz) the following expression can be developed based upon a mass balance of the liquid phase.

$$0 = Q_l C_{L_{o_z}} - Q_l C_{L_{z+\Delta z}} + A dz K_L a \left(C_L - \frac{C_g}{H} \right) \quad (5.1)$$

The source/sink term represents the degree to which the system is out of equilibrium which is known as the driving force, and is responsible for mass transfer within the packed column [30]. For an incremental slice, $C_{L_o} - C_L = dC_L$ and the mass balance equation was simplified to:

$$\boxed{\frac{dC_L}{dz} = \frac{-AK_L a}{Q_l} \left(C_L - \frac{C_g}{H} \right)} \quad (5.2)$$

where:

Q_l	= liquid flow rate through packed column (m^3/s)
Q_g	= gas flow rate through packed column (m^3/s)
C_{L0z}	= inlet liquid concentration of VOC (mg/L)
$C_{Lz+\Delta z}$	= outlet liquid concentration of VOC (mg/L)
C_{g0z}	= inlet gas concentration (mg/L)
$C_{gz+\Delta z}$	= outlet gas concentration (mg/L)
H	= dimensionless Henry's law coefficient
A	= cross-sectional area of column (m^2)
z	= depth of column (m)
dC/dz	= concentration gradient (mg/L/m)
K_La	= mass transfer coefficient (sec^{-1})
ΔV	= differential volume (m^3)

A similar analysis was performed on the gas phase to yield equation 5.3.

$$\boxed{\frac{dC_g}{dz} = -\frac{AK_La}{Q_g} \left(C_L - \frac{C_g}{H} \right)} \quad (5.3)$$

Employing:

$$k_1 = \frac{AK_La}{Q_l} \quad \text{and} \quad k_2 = \frac{AK_La}{Q_g}$$

Equations 5.2 and 5.3 were rewritten to yield:

$$\boxed{\frac{dC_L}{dz} = -k_1 C_L + \frac{k_1}{H} C_g} \quad (5.4)$$

$$\boxed{\frac{dC_g}{dz} = -k_2 C_L + \frac{k_2}{H} C_g} \quad (5.5)$$

Appendix H presents the manipulation and simplification involved in simultaneously solving differential equations 5.4 and 5.5. The principal equations employed in the model are summarized below.

$$\boxed{C_{gout} = C_1 + C_2} \quad (H-11)$$

$$\boxed{C_L = \frac{C_1}{H} + \frac{k_1}{k_2} C_2 \exp\left(\frac{k_2}{H} - k_1\right)z} \quad (H-12)$$

$$\boxed{C_1 = -C_2 H \frac{k_1}{k_2} + C_{Lo} H} \quad (H-9)$$

$$\boxed{C_2 = \frac{C_{go} - C_{Lo} H}{\left[-\frac{k_1 H}{k_2} + \exp\left(\frac{k_2}{H} - k_1\right)L \right]}} \quad (H-10)$$

5.2 Development of Liquid-Liquid Mass Transfer Model

A model was developed to describe liquid–liquid mass transfer within the liquid–liquid contacting reactor. The liquid–liquid model was developed as a dynamic model since some of the continuous flow data had not attained steady state conditions as previously assumed. The model was applied to the data obtained from the continuous flow experiments from the liquid–liquid reactor. Figure 5.2 presents a schematic of the liquid–liquid contacting reactor employed in the continuous flow tests and describes some of the nomenclature used in the modeling.

Figure 5. 2: Schematic of Liquid-Liquid Reactor Employed in Continuous Flow Experiments

5.2.1 Mass Balances

Water and oil mass balance equations were developed around the liquid–liquid column assuming the oil and water layers were completely mixed to yield equations 5.6 and 5.7.

$$V_w \frac{dC_w}{dt} = -Q_w C_w + V_o K_L a \left(C_o - \frac{C_w}{K_p} \right) \quad (5.6)$$

$$V_o \frac{dC_o}{dt} = Q_o C_o^o - Q_o C_o - V_o K_L a \left(C_o - \frac{C_w}{K_p} \right) \quad (5.7)$$

where:

- Q_o = oil flow rate (ml/min)
- V_o = volume of oil (ml)
- C_o = concentration of VOC in the oil phase (mg/L)
- K_{wo} = partition coefficient between water and oil phase
- Q_w = water flow rate (ml/min)
- V_w = volume of water (ml)
- C_w = concentration of VOC in the water phase (mg/L)
- $K_L a$ = mass transfer coefficient (1/sec)

The liquid-liquid model was solved by writing equations 5.6 and 5.7 in terms of an explicit finite difference scheme and solving them simultaneously.

$$V_w \frac{(C_w^t - C_w^{t-\Delta t})}{\Delta t} = -Q_w C_w^{t-\Delta t} + V_o K_L a \left(C_o^{t-\Delta t} - \frac{C_w^{t-\Delta t}}{K_{w/o}} \right) \quad (5.8)$$

$$V_o \frac{(C_o^t - C_o^{t-\Delta t})}{\Delta t} = Q_o C_o^o - Q_o C_o^{t-\Delta t} - V_o K_L a \left(C_o^{t-\Delta t} - \frac{C_w^{t-\Delta t}}{K_{w/o}} \right) \quad (5.9)$$

Mass transfer coefficients between the water and oil phases were estimated for the intermediate column under various water and oil flow rates. The steady state data

employed a simplified version of the liquid-liquid model. The dynamic liquid-liquid model was employed to determine observed mass transfer coefficients from all of the other data.

5.3 Application of Scrubbing Model

The previously described scrubbing model was calibrated to data obtained from the packed column under varying gas and liquid flow rates when water and vegetable oil were employed as scrubbing solutions. Mass transfer coefficients were fitted to both the water and vegetable oil experimental data. These observed mass transfer coefficients obtained from the scrubbing model were then compared to those estimated by the Onda correlations to characterize the effect of operating conditions on mass transfer within the packed column.

5.3.1 Fitting of Mass Transfer Coefficients to Water Data

Water was initially employed as a scrubbing solution in the packed column. Appendix F presents the observed mass transfer coefficients calculated for the three target compounds under various gas and liquid flow rates.

As discussed in chapter 4, the data obtained for DCM in water did not appear to exceed equilibrium at the base of the column therefore the experimental values were directly employed in the scrubbing model. An iterative approach was employed to estimate the best fit mass transfer coefficient for DCM. The best fit mass transfer coefficient was determined by minimizing the sum of squares between observed and predicted outlet gas phase concentrations and by iterating on an assumed mass transfer coefficient.

Since the experimental data for PCE and CT in water appeared to exceed equilibrium conditions at the base of the packed column, the outlet gas concentrations were corrected for equilibrium conditions and were then employed to the model. It should be noted that the inlet gas samples were the same for the replicates of each run and in turn only one outlet gas concentration could be calculated. Therefore, only one mass transfer coefficient could be determined for each run, hence a mean could not be calculated as in the case of DCM in water.

Figure 5.3 presents the mass transfer coefficients that were estimated from the experimental data for the three target compounds as a function of the gas velocity and at a constant liquid velocity of 0.025 m/min. From figure 5.3, it appears that as the gas velocity was increased the mass transfer coefficients for CT and PCE slightly decreased. Overall the decrease in mass transfer coefficients for CT and PCE were relatively minor, hence this may suggest that the mass transfer coefficients for CT and PCE were relatively independent of the gas flows. This result was consistent with the two-resistance theory that suggested that mass transfer of compounds with higher partitioning coefficients would be primarily liquid phase controlled. Similarly, the least volatile compound DCM, would be more likely to be gas phase controlled which would explain the increasing dependence on the gas velocity in figure 5.3.

Figure 5.4 presents the observed mass transfer coefficients as a function of the liquid velocity at a constant gas velocity of 0.189 m/min for the three target compounds. As the liquid velocity was increased the mass transfer coefficients also increased for all three target compounds. PCE appeared to have the highest mass transfer coefficient of 2.71×10^{-2} 1/sec at the highest liquid velocity of 0.025 m/min. Whereas, DCM exhibited

the lowest mass transfer coefficient of 2.38×10^{-3} 1/sec of the three compounds. Similar to the results of Roberts et al. [56], the dependence on the liquid flow rates was more pronounced with the higher volatility compounds such as PCE and CT. This relationship was less dependent for compounds with lower partitioning coefficients as exhibited by DCM. These results were consistent with figure 5.3. Mass transfer of the more volatile compounds, CT and PCE was more dependent on the liquid velocities which would suggest that they may be liquid phase controlled. DCM, however demonstrated less of a dependence on the liquid velocity which would indicate that it is gas phase controlled as previously suggested.

Figure 5.3: Observed Mass Transfer Coefficients in Water as a Function of Gas Velocity (Constant Liquid Velocity = 0.025 m/min)

Figure 5.4: Observed Mass Transfer Coefficients in Water as a Function of Liquid Velocity (Constant Gas Velocity = 0.189 m/min)

5.3.1.2 Oil Data

The scrubbing model was also applied to oil as a scrubbing liquid and the relationship between mass transfer and operating conditions was investigated with vegetable oil. In a similar fashion to the water data, the outlet gas concentrations for DCM were modified to avoid exceeding equilibrium conditions at the base of the column, hence one specific mass transfer coefficient was obtained for each run from the scrubbing model. The data obtained for CT and PCE did not exceed equilibrium, therefore the best fit mass transfer coefficient was determined by minimizing the sum of squares between the observed and predicted outlet gas concentrations.

Appendix F presents the observed mass transfer coefficients at various process conditions when vegetable oil was employed as a scrubbing solution. Limited mass transfer data was available for the DCM because the gas concentrations were below the analytical method's detection limit.

Figure 5.5 presents the observed mass transfer rate coefficients for the three target compounds as a function of the gas velocity at a constant liquid velocity of 0.007 m/min. For all three compounds it was evident that as the gas velocity was increased the observed mass transfer coefficient also increased. PCE, having the lowest gas-liquid partitioning coefficient in oil exhibited the lowest mass transfer coefficient of 9.01×10^{-5} 1/sec at a gas velocity of 1.556 m/min. DCM exhibited the highest mass transfer coefficient at 1.86×10^{-2} sec⁻¹ at a gas flow velocity of 0.445 m/min. CT had a mass transfer coefficient of 8.73×10^{-4} 1/sec at a gas velocity of 1.56 m/min. The mass transfer rate coefficients for DCM were the maximum $K_L a$ values obtained within the column when vegetable oil was employed as a scrubbing solution because the minimum outlet gas concentration as

calculated by employing equilibrium conditions was applied to the model. The increasing relationship between mass transfer coefficients and gas velocity for all three compounds would suggest that the gas phase resistance may be controlling for the target compounds when oil was employed as a scrubbing solution.

Figure 5.6 presents the observed mass transfer coefficients for CT and PCE as a function of the liquid velocity at a constant gas velocity of 1.05 m/min. The mass transfer coefficients for DCM as a function of liquid velocity were not included because of limited data associated with varying liquid flow rates. From figure 5.6 it is evident that as the liquid flow rate was increased the mass transfer coefficients slightly increased. It was observed that the mass transfer coefficient was less dependent on increases in liquid velocity for PCE (lowest gas-liquid partitioning coefficient in oil). The observed mass transfer rate coefficients for CT ranged from 5.33×10^{-4} 1/sec to 5.64×10^{-4} 1/sec for liquid flow rates ranging from 0.0012 m/min – 0.012 m/min respectively. PCE mass transfer rate coefficients ranged from 6.89×10^{-5} 1/sec to 8.87×10^{-5} 1/sec liquid velocities ranging from 0.0012 m/min – 0.012 m/min. These results were consistent with the batch tests and the two-resistance theory. All three target compounds were observed to partition to the greatest extent to the oil phase, which would result in low gas-oil partitioning coefficients. This would suggest that the gas phase was controlling, hence there was only a slight dependence on the liquid velocities as compared to the increased dependence with the gas velocities on the mass transfer rate coefficients.

Figure 5.5: Observed Mass Transfer Coefficients in Oil for the Target Compounds as a Function of Gas Velocity (Constant Liquid Velocity = 0.007 m/min)

Figure 5.6: Observed Mass Transfer Coefficients in Oil as a Function of Liquid Velocity (Constant Gas Velocity $V_g = 1.05$ m/min)

5.3.2 Comparison of Observed Mass Transfer Coefficients to Onda Predictions

The Onda correlations are most commonly employed to estimate mass transfer coefficients in packed columns. The feasibility of employing these correlations to this application was assessed by comparing the Onda predicted mass transfer coefficients with those calculated from experimental data. The relationship between predicted and observed mass transfer coefficients was investigated for both scrubbing liquids.

5.3.2.1 Onda Correlations

The Onda correlations were employed to determine predicted values for the mass transfer coefficients, $(K_L a)$ based on independent empirical equations for gas and liquid phase resistances (k_l and k_g). In addition, the interfacial area for mass transfer (a) was assumed to be approximately equal to the specific wetted area (a_w) [50]. Tables 5.1 - 5.3 list the parameters and constants required in the calculation of the Onda correlations. The liquid properties employed in the Onda equations were dependent on the scrubbing solution used in the continuous flow experiments.

Table 5.1: Parameters required for Onda Correlation

Parameter	Symbol	Units
Liquid density	ρ_L	kg/m^3
Liquid viscosity	μ_L	kg/m sec
Gravity	g	m/sec^2
Liquid diffusivity	D_L	m^2/sec
Nominal packing diameter	d_p	m
Critical surface tension of water	σ_L	N/m
Gas diffusivity	D_G	m^2/sec
Gas density	ρ_G	kg/m^3
Gas viscosity	μ_G	kg/m sec
Henry's coefficient	H	dimensionless
Packing Characteristics		
Intalox™ ceramic saddles		
Packing diameter	d	m
Packing factor	F	dimensionless
Area/volume ratio	a_t	m^2/m^3
Diameter of column	ϕ	m
Temperature	T	$^{\circ}\text{C}$
Area of column	A	m^2

Table 5. 2: Constants Employed in the Onda Model Related to Packing Material [30]

Parameter	Value
Intalox™ ceramic saddles	
σ_c	0.061 N/m
d	0.013 m
F	200
ϕ	0.1016 m
T	20 $^{\circ}\text{C}$
A	0.008103 m^2
a_t	623 m^2/m^3

Table 5.3: Physical Properties of Liquid Employed in Onda Correlation

Property	Water	Reference	Vegetable Oil	Reference
Density (kg/m ³)	998.2	LaGrega et al. [30]	911.4	Coupland and McClements [13]
Viscosity (kg/m s)	1.002 x 10 ⁻³	LaGrega et al. [30]	73 x 10 ⁻³	Coupland and McClements [13]
Surface Tension(N/m)	0.0729	LaGrega et al. [30]	0.030	Chemfinder [73]

note: all properties at 20°C

The Onda correlations were initially developed based on absorption of hydrogen and carbon dioxide by water. Three dimensionless groups including the Weber, Reynolds and Froude numbers were employed in the correlation to determine the specific wetted area. Each dimensionless group was raised to an empirically determined exponent. The Onda correlations have been found to be accurate within $\pm 20\%$ for saddles, spheres and rods with materials of ceramic, glass and PVC [50].

The Onda correlations as presented in chapter 2 were:

$$a_w = a_t \left[1 - \exp \left[-1.45 \left(\frac{\sigma_c}{\sigma} \right)^{0.75} (\text{Re})^{0.1} (\text{Fr})^{-0.05} (\text{Web})^{0.2} \right] \right] \quad (2.54)$$

$$\text{Web} = \left(\frac{L^2}{\rho_L \sigma a_t} \right)$$

$$\text{Re} = \left(\frac{L}{a_t \mu_L} \right)$$

$$\text{Fr} = \left(\frac{L^2 a_t}{\rho_L^2 g} \right)$$

$$k_l = \frac{\left[0.0051 \left(\frac{L}{a_w \mu_L} \right)^{2/3} \left(\frac{\mu_L}{\rho_L D_L} \right)^{-0.5} (a_i d_p)^{0.4} \right]}{\left(\frac{\rho_L}{\mu_L g} \right)^{1/3}} \quad (2.55)$$

$$k_g = a_i D_g \left[5.23 \left(\frac{G}{a_i u_G} \right)^{0.7} \left(\frac{\mu_G}{\rho_G D_g} \right)^{1/3} (a_i d_p)^{-2} \right] \quad (2.56)$$

$$\frac{1}{K_{L a}} = \frac{1}{H k_G a_w} + \frac{1}{k_L a_w} \quad (2.57)$$

The packing employed in this study was 13 mm Intalox™ ceramic saddles. As suggested by Onda [50], for packing material less than 15 mm the coefficient in equation 2.56 was changed from 5.23 to 2.

5.3.2.2 Estimating Liquid Diffusivities in Water and Vegetable Oil

The Hayduk and Laudie method was employed to estimate the liquid diffusivities of the target compounds in water and vegetable oil [39]. The Hayduk estimation method was recommended by other researchers [32, 23] based on its high accuracy, low number of input parameters and simple calculations involved in estimating liquid diffusivities. Equation 5.10 describes the relationship employed to estimate diffusivity of the solutes in water.

$$D = \frac{13.26 \times 10^{-5}}{\mu_w^{1.14} V_B^{0.589}} \quad (5.10)$$

where: D = diffusion coefficient (cm^2/sec)

μ_w = viscosity of water (cp)

V'_B = LeBas molal volume of contaminant (cm^3/mol)

This method does not include a separate temperature term because it was incorporated into the viscosity term. The molal volumes of the contaminant were estimated from the LeBas method [39] and are presented in tables 5.4 and 5.5. Appendix G presents sample calculations for determining gas and liquid diffusivities.

Table 5.4: Additive Volume Increments for the Calculation of Molal Volumes by the LeBas and FSG Methods [39]

Atom	V_B Increments (cm^3/mol)	V'_B Increments (cm^3/mol)
C	16.5	14.8
H	1.98	3.7
Cl	19.5	24.6

Table 5.5: Molecular Weight and Molal Volumes Employed in the LeBas and FSG methods [39]

Compound	Molecular Weight (g/mol) - M_B	Molal Volume V_B - (cm^3/mol)	Molal Volume V'_B - (cm^3/mol)
DCM	84.93	57.48	71.4
CT	153.82	94.5	113.2
PCE	165.83	111	128.0

The Hayduk and Laudie estimation method was empirically developed for estimating liquid diffusivities of organic compounds in water [39]. Since no other method was readily available for determining liquid diffusivities in vegetable oil, the method of Hayduk and Laudie was employed using the viscosity of oil. It was assumed the calculated diffusivity of VOC's in oil would be sufficiently accurate for the purposes of this study. A

recommendation for future work could be to experimentally determine the liquid diffusivity of the organic compounds in oil, since this task was not within the scope of this study.

5.3.2.3 Estimating Gas Diffusivities in Air

The method of Fuller, Schettler and Giddings (FSG) was used to estimate the gas diffusion coefficient of the target compounds [39]. According to researchers [23,32], the FSG method was found to be the most accurate method for estimating gas diffusivities of non-polar gases at low to moderate temperatures [39]. The FSG method is described by equations 5.11 and 5.12.

$$D_{B,A} = \frac{10^{-3} T^{1.75} \sqrt{M_r}}{P (V_A^{1/3} + V_B^{1/3})^2} \quad (5.11)$$

where:

- D_{BA} = gas diffusivity (cm²/sec)
- V_A = molar volume of air (20.1 cm³/mol)
- V_B = molar volume of solute (cm³/mol)
- P = pressure (1 atm)
- T = temperature (°K)
- M_A = molecular weight of air (28.97 g/mol)
- M_B = molecular weight of solute (g/mol)

where:

$$M_r = \frac{(M_A + M_B)}{M_A M_B} \quad (5.12)$$

Table 5.6 provides a summary of the gas and liquid diffusivities that were calculated for use in the Onda correlations for both water and vegetable oil.

Table 5. 6: Summary of Gas and Liquid Diffusivities in Water and Vegetable Oil

Diffusivity (m ² /sec)	DCM	CT	PCE
D _G – Gas Diffusivity	1.029 x10 ⁻⁵	7.942 x 10 ⁻⁶	7.379 x10 ⁻⁶
D _{Lw} – Diffusivity in Water	1.071 x10 ⁻⁹	8.163 x10 ⁻¹⁰	7.593 x10 ⁻¹⁰
D _{LO} - Diffusivity in Oil	8.063 x10 ⁻¹²	6.146 x10 ⁻¹²	5.717 x10 ⁻¹²

5.3.2.4 Comparison of Observed and Predicted Mass Transfer Coefficients

By rearranging and simplifying equation H-6 (Appendix H) the observed mass transfer coefficient was represented by equation 5.13 The observed mass transfer coefficient could then be compared to predicted mass transfer coefficient as determined by Onda.

$$K_L a = \frac{\ln \frac{(C_{go} - C_1)}{C_2}}{A \left(\frac{1}{Q_g H} - \frac{1}{Q_l} \right) L} \quad (5.13)$$

Figures 5.7-5.9 present the observed and predicted mass transfer coefficients in water as a function of the liquid velocity at a constant gas velocity of 0.19 m/min. From figures 5.7-5.9 it can be seen that the mass transfer coefficients increased with increasing liquid velocities. After examining the Onda predicted mass transfer coefficients it was observed that the higher volatility compounds, CT and PCE exhibited an increase in $K_L a$ with increasing gas flow rate, but at the higher range of gas flow rates the relationship between gas flow and mass transfer coefficients became less dependent on the gas flows.

These results were also observed with the work of Roberts [56]. This observation was consistent with the proposed 2-resistance theory which suggested the lower volatility compounds such as DCM would be gas phase controlling. It was also observed that the Onda predicted mass transfer coefficients were substantially lower than the observed values for CT and PCE. It was suspected that when equilibrium conditions were approached the sensitivity to error in the terms of the mass transfer coefficients increased. This observation was also observed by Roberts [56], who noted that as equilibrium conditions were approached the error associated with $K_L a$ became very large, approaching infinity in some cases. The DCM data appeared to be modeled quite well by Onda. It was hypothesized that if the experimental data had not approached or exceeded equilibrium conditions the Onda model would represent the data quite accurately as found by other researchers [23,31,56].

Figures 5.10-5.12 present the observed and predicted mass transfer coefficients in oil as a function of the gas velocity at a constant liquid velocity of 0.007 m/min. From figures 5.10-5.12, it can be seen that the observed and predicted mass transfer coefficients for all three target compounds increased with increasing gas velocity. In general, the observed mass transfer coefficients in vegetable oil were not predicted very well by the Onda correlations. The Onda correlations appeared to be fairly insensitive to fluctuations in the gas flows rates when oil was employed as the scrubbing solution. The following section describes modifications to the Onda correlations so that mass transfer of the VOCs to oil may be modeled more effectively for the purposes of scale-up of the hybrid process.

Figure 5.7: Observed and Predicted Mass Transfer Coefficients in Water for DCM as a Function of Liquid Velocity
(Constant Gas Velocity = 0.19 m/min)

Figure 5.8: Observed and Predicted Mass Transfer Coefficients in Water for CT as a Function of Liquid Velocity
(Constant Gas Velocity = 0.19 m/min)

Figure 5.9: Observed and Predicted Mass Transfer Coefficients in Water for PCE as a Function of Liquid Velocity
(Constant Gas Velocity = 0.19 m/min)

Figure 5.10: Predicted and Observed Mass Transfer Coefficients for DCM in Oil as a Function of the Gas Velocity
(Constant Liquid Velocity = 0.007 m/min)

Figure 5.11: Predicted and Observed Mass Transfer Coefficients for CT in Oil as a Function of the Gas Velocity (Constant Liquid Velocity = 0.007 m/min)

Figure 5.12: Predicted and Observed Mass Transfer Coefficients for PCE in Oil as a Function of the Gas Velocity (Constant Liquid Velocity = 0.007 m/min)

5.3.3 Modification of Onda Correlation for Oil

Although the Onda correlations were not developed for scrubbing solutions such as vegetable oil, an attempt was made to characterize mass transfer by employing the Onda correlations to vegetable oil, for purposes of future scale-up. It was hypothesized that the empirically determined Onda correlations could be slightly modified to accommodate other scrubbing solutions such as vegetable oil in modeling mass transfer within the packed column. As previously observed, the Onda correlations did not fit the oil mass transfer data very well. The Onda correlations employ a number of empirical coefficients and it was not possible to calibrate all of the coefficients with the existing data set. In the previous analysis it was observed that the gas phase resistance appeared to be dominating mass transfer. Hence it was elected to focus on the empirical constant in equation 2.56, as it was believed that this would have the greatest impact on the correlation predictions.

$$k_g = a_i D_g \left[5.23 \left(\frac{G}{a_i u_G} \right)^{0.7} \left(\frac{\mu_G}{\rho_G D_g} \right)^{1/3} (a_i d_p)^{-2} \right] \quad (2.56)$$

When the overall gas liquid phase resistances were calculated with the original Onda correlations it was found that the liquid phase resistance controlled mass transfer (>90% for all target compounds). This observation was not consistent with the results of figures 5.5 and 5.6 which demonstrated that the mass transfer coefficients were relatively independent of the liquid velocity and, that there was a strong dependence between the gas velocity and the mass transfer coefficients, suggesting gas phase resistance control. It

was therefore suspected that the original liquid phase resistance, was not correct when vegetable oil was employed as a scrubbing solution and was therefore discarded from the Onda correlations so that the main emphasis was put on the gas phase resistance. By recalibrating the model in this manner the observed mass transfer coefficients were better modeled by the modified Onda correlations.

Figures 5.13-5.15 present the predicted and observed mass transfer coefficients when the gas phase resistance was assumed to be controlling (liquid phase resistance discarded) and the empirical constant was modified. These values were arrived at by minimizing the sum of squares between the observed and predicted mass transfer coefficients through an iterative approach. Table 5.7 lists the modified equations for the Onda correlations for each compound corresponding to figures 5.13-5.15.

From table 5.7, it was observed that the compound with the lowest gas-liquid partitioning in oil (PCE) exhibited the smallest change from the original Onda correlations, aside from assuming gas phase control. DCM, the highest gas-liquid partitioning coefficient in oil exhibited the most substantial modification from the original Onda by changing the constant in front of the gas phase resistance from 2 to 35.2. The results suggest that CT and PCE were likely gas phase controlled and hence the omission of the liquid phase resistance was probably valid. In contrast, DCM may have some component of liquid phase control, hence the liquid phase resistance may also have to be modified to accommodate this observation.

Other attempts to modify the original Onda included Gossett [23], attempting to derive relationships for the temperature dependence of mass transfer instead of employing the temperature corrected parameters of viscosity, density etc., directly into the Onda

correlations. Gossett [23], made no attempt to modify specific components of the gas and liquid phase resistances, however, the constants in front of each of the expressions were modified similar to this study. The results of Gossett's study indicated that no simple modification could be made to model the temperature dependence of Onda by simply changing the constants of the gas and liquid phase resistances. Gossett concluded that the results of modifying the original Onda could not consistently improve the predictive ability of the Onda correlations.

Further investigation is required in the area of modifying the existing Onda correlations for other scrubbing solutions such as vegetable oil. One possible method of investigation would be to select compounds that are gas phase controlling (i.e low gas-liquid partition coefficient) or compounds that liquid phase controlling (ie. high gas-liquid partition coefficient). By selecting such compounds the resistances could be investigated separately by performing gas or liquid phase controlling tests.

Figure 5.13: Modified Onda for DCM in Oil, Mass Transfer Coefficients vs. Gas Velocity
(Constant Liquid Velocity = 0.007 m/min)

Figure 5.14: Modified Onda for CT in Oil, Mass Transfer Coefficients vs. Gas Velocity
(Constant Liquid Velocity = 0.007 m/min)

Figure 5.15: Modified Onda for PCE in Oil, Mass Transfer Coefficients vs. Gas Velocity
(Constant Liquid Velocity = 0.007 m/min)

Table 5. 7: Modified Onda Correlations gas and liquid resistances

<p><u>Original Onda</u></p> $k_L = \frac{\left[0.005 \left(\frac{L}{a_w \mu_L} \right)^{2/3} \left(\frac{\mu_L}{\rho_L D_L} \right)^{-0.5} (a_t d_p)^{0.4} \right]}{\left(\frac{\rho_L}{\mu_L g} \right)^{1/3}}$	$k_G = a_t D_g \left[2.0 \left(\frac{G}{a_t \mu_G} \right)^{0.7} \left(\frac{\mu_G}{\rho_G D_g} \right)^{1/3} (a_t d_p)^{-2} \right]$
<p><u>Modified Onda -DCM</u></p> <p>omission of liquid phase resistance</p>	$k_G = a_t D_g \left[35.2 \left(\frac{G}{a_t \mu_G} \right)^{0.7} \left(\frac{\mu_G}{\rho_G D_g} \right)^{1/3} (a_t d_p)^{-2} \right]$
<p><u>Modified Onda - CT</u></p> <p>omission of liquid phase resistance</p>	$k_G = a_t D_g \left[1.89 \left(\frac{G}{a_t \mu_G} \right)^{0.7} \left(\frac{\mu_G}{\rho_G D_g} \right)^{1/3} (a_t d_p)^{-2} \right]$
<p><u>Modified Onda - PCE</u></p> <p>omission of liquid phase resistance</p>	$k_G = a_t D_g \left[2.0 \left(\frac{G}{a_t \mu_G} \right)^{0.7} \left(\frac{\mu_G}{\rho_G D_g} \right)^{1/3} (a_t d_p)^{-2} \right]$

5.4 Application of Liquid-Liquid Model

The liquid-liquid model was calibrated primarily for the steady state data in the semi-batch tests and continuous flow tests by simplifying equations 5.6 and 5.7. The previously described liquid-liquid model was also calibrated for the data in the continuous flow tests that had not obtained steady state by employing a finite difference approach (equations 5.8 and 5.9) and solving for the outlet VOC water concentration. For both cases the sum of squares of the differences between the observed and predicted outlet water concentrations were minimized and the mass transfer coefficient for each process condition was calculated through an iterative approach.

5.4.1 Fitting of Mass Transfer Coefficients to Semi-Batch Experiments

The liquid-liquid model was initially calibrated with the data obtained from the semi-batch experiments. Table 5.8 summarizes the pseudo steady state mass transfer coefficients obtained under various process conditions for the semi-batch tests. Appendix I presents a summary of the standard error calculated for each mass transfer coefficient obtained in the liquid-liquid reactor. Although steady state conditions can not be theoretically obtained in batch experiments, the changes in the VOC water concentrations were minimal over time, hence pseudo steady state conditions were assumed to simplify analysis. The data for DCM was not presented for the semi-batch tests because the concentrations were below the detection limit of the analytical method. From table 5.8 it was evident that overall, CT exhibited higher mass transfer coefficients for all the operating conditions investigated with the exception of run #7 in which the highest water flow rate was employed.

Table 5.8: Mass Transfer Coefficients Obtained from Pseudo Steady State Conditions in the Semi-Batch Experiments with the Liquid-Liquid Reactor

Run #	Water Flow Rate Q_w (ml/min)	Initial Oil Volume (ml)	CT (1/sec)	PCE (1/sec)
1	225	2300	5.83×10^{-6}	4.90×10^{-6}
2	225	2100	5.45×10^{-6}	2.82×10^{-6}
3	225	2100	1.57×10^{-6}	6.20×10^{-7}
4	225	4000	3.67×10^{-7}	1.88×10^{-7}
5	225	1000	1.53×10^{-6}	1.19×10^{-6}
6	110	2000	4.90×10^{-7}	4.15×10^{-7}
7	400	2000	6.83×10^{-7}	1.19×10^{-6}

Figure 5.16 presents the mass transfer coefficients as a function of the oil volume within the column for CT and PCE. From figure 5.16 it was evident that as the volume of oil increased the mass transfer coefficients of CT and PCE exhibited a modest decrease.

Figure 5.17 presents the mass transfer coefficients of CT and PCE as a function of the water flow rate within the liquid-liquid column. From figure 5.17 it was evident that as the water flow rate increased the mass transfer coefficient increased for PCE. The results for CT were inconclusive since the mass transfer coefficients exhibited a sharp increase with increasing flow rates at flows of 110 ml/min to 225 ml/min. The mass transfer coefficient then exhibited a decrease with flows of 225 ml/min to 400 ml/min. These results suggest that the water phase resistance may be dominating mass transfer for PCE, since the water-oil partitioning coefficient for PCE is very small. This phenomena was further assessed in the continuous flow experiments.

Figure 5.16: Mass Transfer Coefficients as a Function of the Oil Volume in the Semi-Batch Tests ($Q_w = 225$ ml/min)

Figure 5.17: Mass Transfer Coefficients as a Function of the Water Flow Rate in the Semi-Batch Tests (Oil Volume = 2 L)

5.4.1 Fitting of Mass Transfer Coefficients to Continuous Flow Experiments

The mass transfer rate coefficients in the liquid-liquid model were also calibrated with the continuous flow data obtained in the liquid-liquid reactor. Appendix E presents the raw data associated with the semi-batch and continuous flow experiments. Table 5.9 presents a summary of the mass transfer coefficients obtained for the continuous flow data. As previously mentioned in chapter 4, not all of the runs had obtained steady state conditions hence, the runs that were at steady state have been noted.

Table 5.9: Mass Transfer Coefficients from Continuous Flow Tests in Liquid-Liquid Reactor

Run #	Water Flow Rate Q_w (ml/min)	Oil Flow Rate Q_o (ml/min)	DCM (1/sec)	CT (1/sec)	PCE (1/sec)
1	200	25	1.24×10^{-4}	1.46×10^{-4}	$*2.27 \times 10^{-5}$
2	200	25	$*2.52 \times 10^{-4}$	$*4.02 \times 10^{-4}$	$*2.93 \times 10^{-5}$
3	200	10	1.16×10^{-4}	1.08×10^{-4}	$*6.70 \times 10^{-6}$
4	100	25	1.26×10^{-4}	1.25×10^{-4}	$*7.67 \times 10^{-6}$
5	350	25	$*2.03 \times 10^{-4}$	$*1.77 \times 10^{-4}$	$*1.01 \times 10^{-5}$
6	200	5	$*1.16 \times 10^{-4}$	$*9.17 \times 10^{-5}$	$*1.33 \times 10^{-5}$

*steady state runs

From the data of table 5.9 it was observed that the lowest mass transfer coefficients were exhibited by PCE under all process conditions. The difference between the mass transfer coefficients of DCM and CT in the continuous flow experiments were minimal for all the runs investigated. These results were consistent with the water-oil partitioning coefficients obtained from the batch tests for DCM and CT being 0.07 and 0.04 respectively. PCE, the most hydrophobic compound did not partition well from the oil phase to the water and hence, the liquid-liquid contacting reactor process would require further improvement for highly hydrophobic compounds such as PCE.

Figure 5.18 presents the mass transfer coefficients observed in the liquid-liquid column as a function of the oil flow rate. From figure 5.18, DCM and CT mass transfer coefficients appeared to increase with increasing oil flow rate. This would suggest that the oil phase resistance may be controlling mass transfer over the water resistance. CT and DCM exhibited the highest water-oil partitioning coefficients over PCE, from the two resistance theory, the water resistance may be negligible as compared to the dominating oil phase resistance. PCE, appeared to be fairly insensitive to fluctuations in the oil flows, supporting the hypothesis that it may be water phase controlled.

Figure 5.19 presents mass transfer coefficients for the three target compounds as a function of the water flow rate in the liquid-liquid column. The mass transfer coefficient for CT increased from 1.25×10^{-4} to 1.77×10^{-4} 1/sec for increasing flows of 100 ml/min to 200 ml/min. Similarly, DCM appeared to be fairly insensitive to increased water flows at the lower range of 100 ml/min to 200 ml/min, but appeared to increase more rapidly at the highest water flow of 350 ml/min. From figure 5.19, it was observed that PCE was fairly insensitive to water flow rates.

It was observed that the mass transfer coefficients obtained in the semi-batch and continuous flow experiments were not consistent. There was approximately one order of magnitude difference between mass transfer coefficients in the two experiments. These results may suggest that the liquid-liquid model did not accurately assess physical conditions occurring within the reactor. The assumption of a completely mixed system may not have been entirely true under the varying flowrates and hence, the model should be reevaluated to verify the physical processes occurring within the liquid-liquid column. The liquid-liquid model attempted to characterize only the potential for employing a

liquid-liquid contacting reactor within the hybrid system to transfer the relatively hydrophobic compound from a non-polar solvent into an aqueous phase for future biological treatment. The liquid-liquid contacting reactor appears to be a feasible method to transfer the VOCs from the oil phase to the aqueous phase for subsequent treatment in the anaerobic reactor. However, highly hydrophobic compounds such as PCE would require further measures to enhance mass transfer from the oil to the water phase. Further methods to enhance mass transfer may include the addition of an emulsifier that is non-toxic, non-biodegradable and inexpensive, increasing the mixing of the water and oil layers by the way of an agitator or adding a packing material to the column to increase surface area for mass transfer. Another method to increase mass transfer may be to incorporate separate stages into the overall system in which relatively high hydrophobic compounds would be treated slightly differently from less hydrophobic compounds.

In order to simulate the operation of the mass transfer packed column in conjunction with the liquid-liquid contacting reactor which was directly incorporated into the anaerobic reactor, a combined model was developed and simulations were performed.

Figure 5.18: Mass Transfer Coefficients as a function of the Oil Flow Rate in the Continuous Flow Tests ($Q_w = 200$ ml/min, Volume of Oil = 2000 ml)

Figure 5.19: Mass Transfer Coefficients as a Function of the Water Flowrate for the Continuous Flow Tests ($Q_o = 25$ ml/min, Volume of Oil - 2000 ml)

5.5 Simulation of Combined Mass Transfer Model

The packed column and the liquid-liquid contacting reactor mass transfer models were combined to form one joint steady state model. An attempt was made to characterize the impact of gas and liquid flows on the mass transfer coefficients for future scale up of the hybrid process.

This study focused primarily on the first phase of the hybrid process, in which contaminated VOCs were transferred from the gas phase to a liquid phase by way of packed column. The liquid phase was then transferred into an aqueous solution by way of a liquid-liquid contacting reactor for further biological treatment in an anaerobic reactor. It was believed that the second stage may be achieved without a separate liquid-liquid reactor, by maintaining minimal aqueous-phase concentrations through the anaerobic reactor and by designing the mass transfer process appropriately. The following combined model attempts to synthesize the final hybrid system.

Figure 5.20 presents a schematic of the joint system in which the liquid-liquid reactor was incorporated directly into the anaerobic reactor. The packed column was referred to as system 1, hence all nomenclature associated with the packed column employs the subscript 1. Similarly, the anaerobic reactor was labeled system 2 and therefore all nomenclature associated with the anaerobic reactor employed subscript 2.

The symbols in the joint model are defined as follows:

$V_{oil(2)}$ = volume of contaminated oil initially introduced into system 2

$Q_{l(1)}$ = liquid flowrate in packed column (ml/min)

$Q_{g(1)}$ = gas flowrate in packed column (ml/min)

$Q_{w(2)}$ = water flow rate in anaerobic reactor (ml/min)

$Q_{oil(2)}$ =oil flowrate in anaerobic reactor (ml/min)

$K_{La(1)}$ = mass transfer coefficient of VOCs from gas to oil in packed column (1/sec)

$K_{La(2)}$ = mass transfer coefficient of VOCs from oil to water in anaerobic reactor (1/sec)

$C_{lin(1)}$ = inlet VOC liquid concentration in packed column (mg/L)

$C_{gin(1)}$ = inlet VOC gas concentration in packed column (mg/L)

$C_{lout(1)}$ = outlet VOC liquid concentration in packed column (mg/L)

$C_{gout(1)}$ = outlet VOC gas concentration in packed column (mg/L)

$C_{lin(2)}$ = inlet VOC liquid concentration in anaerobic reactor (mg/L)

$C_{lout(2)}$ = outlet VOC liquid concentration in anaerobic reactor (mg/L)

$C_{wout(2)}$ = outlet VOC water concentration in anaerobic reactor (mg/L)

Typical mass transfer coefficients calculated in the continuous flow tests of the packed column and liquid-liquid reactor were employed in the joint simulation for each target compound. The mass transfer coefficients for the packed column were determined by employing the modified Onda correlations which assumed that the gas phase resistance controlled. A typical gas flow (typical of full scale plant) of 1 m³/min was assumed to enter the packed column. A gas-liquid ratio of 20 was assumed, hence all liquid flows within the system could be determined. Assuming typical inlet gas concentrations into the packed column ($C_{gin(1)}$) of 0.34 mg/L, 0.19 mg/L and 0.37 mg/L for DCM, CT and PCE respectively, all other gas and liquid concentrations were calculated by the model for both columns assuming a best case scenario. The best case scenario assumed that all the VOCs were fully degraded within the anaerobic reactor hence, the outlet water concentration was approximately zero.

Tables 5.10-5.12 present a typical simulation of the combined model for each target compound. The combined model assumed steady state conditions in both the packed column and the anaerobic reactor. The purpose of the simulation was to determine the volume of oil required in the anaerobic system so that the two processes could be sized appropriately. An initial inlet target compound liquid concentration of 1 mg/L into the packed column was assumed and the system was solved iteratively by maintaining a 95 % removal efficiency within the packed column to yield a new value for the inlet liquid concentration ($C_{lin(1)}$). This new inlet liquid concentration was the maximum value that the packed column could accommodate to achieve a 95% removal efficiency. A second iteration was performed through the anaerobic reactor by assuming that the outlet oil concentration ($C_{l out(2)}$) was less or equal to the maximum value allowed in the packed column and the oil volume was determined through an iterative process.

From tables 5.10-5.12 it was observed that the oil volume required varied from 3746 L to 1793 L for DCM and PCE respectively. It was suspected that a large oil volume would be required in the anaerobic reactor to accommodate the process for PCE, however, PCE exhibited the smallest oil volume requirement for the system. The results obtained from the joint simulations were consistent with the gas-oil partitioning coefficients in the packed column. PCE which exhibited the lowest gas-oil partitioning coefficient, was removed to the greatest extent in the packed column, hence it was able to accommodate higher inlet liquid concentrations, as observed in table 5.12. It was evident that the major factor that influenced the overall oil volume in the anaerobic reactor was the degree of partitioning between the gas and oil phases within the packed column.

Table 5.10: Simulation of Joint Model for DCM

Constants

$Z(0) =$	0 m
$Z(L) =$	2 m
Area =	1 m^2
$K(\text{DCM}) =$	0.0132 (air/oil)
diameter	1.1287 m

Parameter	Units	Value	Comment
G/L ratio		20	
V oil (2)	L	3754.6	iterate
$Q_l(1)$	ml/min	50000	input
$Q_l(1)$	m^3/s	8.33E-04	
$Q_g(1)$	ml/min	1000000	input
$Q_g(1)$	m^3/s	1.67E-02	
$Q_w(2)$	ml/min	50000	input
$Q_w(2)$	m^3/s	8.33E-04	
$Q_{oil}(2)$	ml/min	50000	input
$Q_{oil}(2)$	m^3/s	8.33E-04	
$K_L a(1)$	1/sec	1.16E-02	(estimated modified Onda)
$K_L a(2)$	1/sec	4.00E+00	input
$C_{lin}(1)$	mg/L	1.29	iterate
k_1		13.92	$AK_L a/Q_l$
k_2		0.70	$AK_L a/Q_g$
C_2		6.33E-35	
C_1		0.02	
$C_{gin}(1)$	mg/L	0.34	input
$C_{lout}(1)$	mg/L	7.75	
$C_{gout}(1)$	mg/L	0.017	
%Removal in gas		95.00	
$C_{lin}(2) \text{ oil}$	mg/L	7.75	equal to $C_{lout}(1)$
$C_{lout}(2)$	mg/L	1.29	
$C_{win}(2)$	mg/L	0.00	clean water
$C_{wout}(2)$	mg/L	0.00	best case scenario

Table 5.11: Simulation of Joint Model for CT

Constants

$Z(0) =$	0 m
$Z(L) =$	2 m
Area =	1 m^2
$K \text{ (CT)} =$	0.004 (air/oil)
diameter	1.1287 m

Parameter	Units	Value	Comment
G/L ratio		20	
$V_{\text{oil}} (2)$	L	2929.4	iterate
$Q_l (1)$	ml/min	50000	input
$Q_l (1)$	m^3/s	$8.33\text{E-}04$	
$Q_g (1)$	ml/min	1000000	input
$Q_g (1)$	m^3/s	$1.67\text{E-}02$	
$Q_w (2)$	ml/min	50000	input
$Q_w (2)$	m^3/s	$8.33\text{E-}04$	
$Q_{\text{oil}} (2)$	ml/min	50000	input
$Q_{\text{oil}} (2)$	m^3/s	$8.33\text{E-}04$	
$K_L a (1)$	1/sec	$1.59\text{E-}04$	(estimated modified Onda)
$K_L a (2)$	1/sec	$2.00\text{E+}00$	input
$C_{\text{lin}} (1)$	mg/L	1.85	iterate
k_1		0.19	$AK_L a/Q_l$
k_2		0.01	$AK_L a/Q_g$
C_2		$2.27\text{E-}03$	
C_1		0.01	
$C_{\text{gin}} (1)$	mg/L	0.19	input
$C_{\text{l out}} (1)$	mg/L	5.46	
$C_{\text{g out}} (1)$	mg/L	0.009	
%Removal in gas		95.000	
$C_{\text{l in}} (2)_{\text{oil}}$	mg/L	5.46	equal to $C_{\text{l out}} (1)$
$C_{\text{l out}} (2)$	mg/L	1.85	
$C_{\text{w in}} (2)$	mg/L	0.00	clean water
$C_{\text{w out}} (2)$	mg/L	0.00	best case scenario

Table 5.12: Simulation of Joint Model for PCE

Constants

$Z(0) =$	0 m
$Z(L) =$	2 m
Area =	1 m ²
K (PCE) =	0.0006 (air/oil)
diameter	1.1287 m

Parameter	Units	Value	Comment
G/L ratio		20	
V oil (2)	L	1793.1	iterate
$Q_l (1)$	ml/min	50000	input
$Q_l (1)$	m ³ /s	8.33E-04	
$Q_g (1)$	ml/min	1000000	input
$Q_g (1)$	m ³ /s	1.67E-02	
$Q_w (2)$	ml/min	50000	input
$Q_w (2)$	m ³ /s	8.33E-04	
$Q_{oil} (2)$	ml/min	50000	input
$Q_{oil} (2)$	m ³ /s	8.33E-04	
$K_L a (1)$	1/sec	2.40E-05	(estimated modified Onda)
$K_L a (2)$	1/sec	3.03E-01	input
$C_{in} (1)$	mg/L	25.75	iterate
k1		0.03	$AK_L a / Q_l$
k2		0.00	$AK_L a / Q_g$
C_2		3.09E-03	
C_1		0.02	
$C_{gin} (1)$	mg/L	0.37	input
$C_{l out} (1)$	mg/L	32.78	
$C_{g out} (1)$	mg/L	0.018	
%Removal in gas		95.000	
$C_{l in} (2)$ oil	mg/L	32.78	equal to C_l out (1)
$C_{l out} (2)$	mg/L	27.75	
$C_{w in} (2)$	mg/L	0.00	clean water
$C_{w out} (2)$	mg/L	0.00	best case scenario

The joint model provides useful insight into the feasibility of operating the proposed hybrid system to effectively remove VOCs from contaminated airstreams. It was found that there is a high potential for the overall process to remove chlorinated compounds that vary in hydrophobicity hence, further research should be continued in this area.

Chapter 6 - Conclusions and Recommendations

This research investigated the issues associated with the mass transfer of chlorinated organics from a gas stream to a liquid stream that would be subsequently treated in an anaerobic reactor.

6.1 Conclusions

The results of the gas-liquid partitioning batch tests and the continuous flow experiments in the packed column clearly demonstrated that aqueous solutions of cosolvents such as propylene glycol will likely require large volumes of cosolvents (i.e. greater than 40% v/v) to substantially reduce the gas phase partitioning of the target VOCs.

Vegetable oil was identified to be an effective scrubbing solution in removing the target compounds from the air streams. PCE, the most hydrophobic of the three compounds exhibited the lowest gas-oil partitioning coefficient, reducing the value by 4 orders of magnitude over water alone. Similarly, the gas-oil partitioning coefficient for CT was reduced by 3 orders of magnitude over water alone. DCM, the least hydrophobic of three target compounds exhibited the lowest partition coefficient with 100% vegetable oil in comparison to all other cosolvents investigated. The results of the batch tests provided conclusive evidence that the target compounds strongly partition to vegetable oil and hence, vegetable oil was further investigated as a scrubbing solution in the packed column experiments.

A bench-scale countercurrent packed column was designed and operated under various scrubbing liquids and gas-liquid ratios to characterize mass transfer and removal efficiencies. Water, 40% v/v propylene glycol and vegetable oil were employed as scrubbing solutions. The results obtained from the continuous flow tests suggested that high removal efficiencies for all three compounds (90%) could be obtained when vegetable oil was employed as a scrubbing solution with gas-liquid flow ratios less than 200.

A scrubbing model was developed and compared to the existing Onda correlations, to characterize mass transfer under various operating conditions when water and vegetable oil were employed as scrubbing solutions. The relationship between predicted and observed mass transfer coefficients was assessed for both scrubbing solutions. It was found that the Onda correlations did not fit the experimental data of vegetable oil very well, hence the existing Onda correlations were modified by assuming that the gas phase resistance was controlling mass transfer. The assumption appeared to be valid for the compounds with the lower gas-oil partitioning coefficients (CT and PCE). DCM appeared to have some component of liquid phase control as expected, since it had the highest gas-oil partition coefficient of the three target compounds hence, the liquid phase resistance may also have to be modified to accommodate this observation.

In order to enhance mass transfer from the oil phase to an aqueous phase a liquid-liquid contacting reactor was proposed. The results of the liquid-liquid reactor suggested that mass transfer could be achieved for compounds that were not highly hydrophobic such as PCE. DCM and CT exhibited comparable mass transfer coefficients, as a result of their similar water-oil partitioning coefficients. PCE demonstrated the lowest mass transfer coefficients in the liquid-liquid reactor of the three target compounds, this result was

consistent with its low partitioning coefficient from oil-water. The liquid-liquid model employed in this study has limitations and was tending to oversimplify the flow conditions occurring in the reactor, hence a more complex liquid model may be required to further assess mass transfer in the contacting reactor.

A combined mass transfer model was developed and simulated for the three target compounds to synthesize the hybrid process. The liquid-liquid reactor could be directly incorporated into the anaerobic reactor if the two mass transfer processes were sized appropriately. From the combined model simulations, the major factor that influenced the overall oil volume in the anaerobic reactor was the degree of partitioning between the gas and oil phases within the packed column. The hybrid system appears to be a feasible alternative for removing VOCs from air streams in industrial processes, and research should therefore be continued in this area.

6.2 Recommendations

In order to minimize errors associated with exceeding equilibrium in the scrubbing column further research is required to accurately establish the air-oil partitioning coefficients.

Further work is also required to increase mass transfer in the liquid-liquid reactor for hydrophobic compounds such as PCE. Research to enhance mass transfer from the oil-phase to the water phase could include, the addition of emulsifiers (non-biodegradable and non-toxic to microorganisms), addition of packing in the column to increase the interfacial surface area for mass transfer or rapid agitation in the form of a mixer.

Other recommendations include further investigation into modifying the Onda correlations to scrubbing solutions other than water and determining more precise values for the physical properties of oil such as liquid diffusivities.

The liquid-liquid model was developed based on the assumption that the column was completely mixed however, inconsistencies with the semi-batch and continuous flow mass transfer data suggest that perhaps the flow conditions within the model were not modeled accurately. Further research is required to develop a more precise model to effectively assess mass transfer within the liquid-liquid reactor.

Chapter 7 - References

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Appendix A

Linearity of Detectors / Standard Curves

The detectors of both the HP 5890 and the HNU model 311 GCs were verified for linearity. Concentrations ranging from 10 mg/L to 0.01 mg/L were prepared for dichloromethane, carbon tetrachloride and tetrachloroethylene as outlined in chapter 3. A 50 μ l or 5 ml headspace sample was taken from each bottle and injected into the GC and the peak count corresponding to the concentration was recorded. A graph of peak counts versus chlorinated organic concentration was prepared for each compound on each GC. The line of best fit was determined for each compound:

$$y = mx + b$$

where: y = peak counts obtained from GC

x = mass injected in to GC

m = slope

b = intercept

The coefficient of determination, r^2 was determined for each compound. Figures A.1- A.9 depict the standard curves obtained for each compound. It should be noted that the HP 5890 GC was not very sensitive to DCM and as a result higher concentrations were used in obtaining a standard curve.

Three sets of standard curves were obtained for the three target compounds. The first set of curves obtained from the HP 5890 GC were utilized to analyze liquid samples,

by measuring the VOC concentration in the headspace of a 40 ml bottle. Each 40 ml bottle contained 25 ml of the liquid of interest and 15 ml of headspace. A 50 μ l headspace sample was injected into the HP 5890 GC using a 50 μ l Hamilton Gastight® syringe.

The second set of curves obtained from the HNU model 311 GC were employed for gas samples taken directly from the inlet and outlet of the packed column and immediately injected into the GC for analysis. The second set of standards were prepared similarly to the first set, with the exception that a 5 ml headspace sample from the 40 ml amber bottle was injected into the HNU model 311 GC. By performing a mass balance on the bottle the approximate gas concentration was obtained for a range of concentrations to be investigated within the study.

The third set of curves were employed in the analysis of the oil samples. As discussed in the section entitled analytical methods, the oil samples were made up in 160 ml serum bottles containing 100 ml of methanol. A standard curve employing various concentrations made up in 100 ml of methanol were made to represent typical concentrations obtained in the sample bottles. It should be noted that for the third set of curves the actual VOC concentration was multiplied by a dilution factor of 800. It was found that when making up standard curves for each GC, a higher degree of accuracy was obtainable when the sample method was similar to the procedure employed for making up the standards.

Table A.1 summarizes the equations employed to yield the gas and liquid concentrations for each target compound on the HP 5890 and HNU 311 GCs. The coefficient of determination (r^2) for the three sets of standard curves approached unity for all the graphs. The high r^2 obtained from the graphs demonstrated that the best fit line was well represented by the trendline.

Table A.1: Summary of Equations and Coefficients of Determination obtained from the Standard Curves

Target Compound	GC	Intercept	Slope	r^2	Conc.	Sample
DCM	HP 5890	-43.722	34.398	1	liquid	50 μ l headspace
CT	HP 5890	917.59	9279	0.9854	liquid	50 μ l headspace
PCE	HP 5890	1015.1	22054	0.9960	liquid	50 μ l headspace
DCM	HNU 311	24968	13191	0.9999	gas	5 ml gas sample
CT	HNU 311	3480.8	30330	0.9815	gas	5 ml gas sample
PCE	HNU 311	10223	204782	0.9901	gas	5 ml gas sample
DCM	HP 5890	219.41	717.76	0.9972	liquid (oil)	1 μ l liquid sample
CT	HP 5890	4011.2	126533	0.9993	liquid (oil)	1 μ l liquid sample
PCE	HP 5890	197.21	129505	0.9999	liquid (oil)	1 μ l liquid sample

Figure A.1: Standard Curve for DCM on HP 5890 GC

Figure A.2: Standard Curve for CT on HP 5890 GC

Figure A.3: Standard Curve for PCE on HP 5890 GC

Figure A.4: Standard Curve for DCM on HNU model 311 GC

Figure A.5: Standard Curve for CT on HNU model 311 GC

Figure A.6: Standard Curve for PCE on HNU model 311 GC

Figure A.7: Standard Curve for DCM in methanol on HP 5890 GC (oil sample analysis)

Figure A.8: Standard Curve for CT in methanol on HP 5890 GC (oil sample analysis)

Figure A.9: Standard Curve for PCE in methanol on HP 5890 GC (oil sample analysis)

Appendix B

Figure B-1: Flowmeter Calibration Curve for Glass Float

Figure B-2: Flowmeter Calibration Curve for Stainless Steel Float

Appendix C

100% WATER

Table C-1: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1	62226272		1.066
H2	58325536		1.174
H3	59244640		1.091
		3.4	
L1	60050624		0.950
L2	56991040		1.042
L3	59305408		0.971
		2.7	0.976
			1.072
			0.998
	AVG=		1.038
	STDEV=		0.071

Table C-2: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1	50369216		1.490
H2	43471680		1.395
H3	40991104		1.511
		10.8	
L1	40855264		1.119
L2	42203232		1.055
L3	40578944		1.133
		2.1	1.006
			0.950
			1.018
	AVG=		1.186
	STDEV=		0.219

Table C-3: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1	164029		0.232
H2	135775	9.4	0.210
H3	153447		0.202
L1	416897		0.173
L2	445008		0.156
L3	457049		0.149
		4.7	0.210
			0.189
			0.182
	AVG=		0.189
	STDEV=		0.027

Appendix C

20 % METHANOL

Table C-4: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1	1471312		0.919
H2			0.720
H3			2.077
L1	1544200		
L2	1785422		
L3	1027870		
		26.6	
	AVG=		1.238
	STDEV=		0.733

Table C-5: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1	3026014		0.570
H2			0.471
H3			0.511
L1	4252712		
L2	4813280		
L3	4563898		
		6.2	
	AVG=		0.517
	STDEV=		0.050

Table C-6: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1	2668		0.146
H2			0.051
H3	2221		
		12.9	
L1	9084		
L2	15547		
L3			
		37.1	0.107
			0.030
	AVG=		0.084
	STDEV=		0.053

Appendix C

40 % METHANOL

Table C-7: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1	2509842		0.128
H2	3141992		0.140
H3	2676040		0.180
		11.8	
L1	9262182		0.185
L2	8780845		0.201
L3	7505629		0.255
		10.7	0.142
			0.155
			0.199
	AVG=		0.176
	STDEV=		0.040

Table C-8: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1	2689134		0.109
H2	3219918		0.135
H3	4171526		0.208
		22.4	
L1	10860088		0.149
L2	9610976		0.181
L3	7341328		0.274
		19.2	0.224
			0.269
			0.404
	AVG=		0.217
	STDEV=		0.090

Table C-9: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1	28556		0.239
H2	11881		0.259
H3	26256		0.283
		40.6	
L1	71250		0.048
L2	67505		0.055
L3	63740		0.062
		5.6	0.210
			0.228
			0.249
	AVG=		0.181
	STDEV=		0.097

Appendix C

20% PROPYLENE GLYCOL

Table C-10: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1	4255		1.189
H2	3151		0.997
H3			1.425
		21.1	
L1	3870		0.706
L2	4261		0.605
L3	3528		0.823
		9.4	
	Average =		0.958
	Stdev=		0.310

Table C-11: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1	32685		0.831
H2	22745		0.739
H3	25131		1.877
		19.3	
L1	36375		0.467
L2	39032		0.420
L3	23838		0.921
		24.5	0.544
			0.488
			1.100
	Average =		0.821
	Stdev=		0.459

Table C-12: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1	8823		0.041
H2	15292		0.036
H3	13283		0.046
		26.6	
L1	55891		0.130
L2	58794		0.119
L3	53753		0.139
		4.5	0.101
			0.092
			0.109
	AVG=		0.090
	STDEV=		0.040

Appendix C

40% PROPYLENE GLYCOL

Table C-13: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1	5533907		0.200
H2	5914778		0.265
H3	4516883		0.134
		13.6	
L1	15493224		0.222
L2	12876792		0.293
L3	19881888		0.149
		22.0	0.145
			0.194
			0.093
	AVG=		0.188
	STDEV=		0.065

Table C-14: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1	4080109		0.154
H2	4333059		0.245
H3	2925021		0.135
		19.9	
L1	13454720		0.170
L2	10000384		0.269
L3	14552920		0.150
		18.8	0.086
			0.145
			0.073
	AVG=		0.159
	STDEV=		0.064

Table C-15: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1			
H2			
H3			
L1			
L2			
L3			
	AVG=		
	STDEV=		

Appendix C

20% VEGETABLE OIL

Table C-16: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1	130493		0.042
H2	94416		0.026
H3	110257		0.034
		16.2	
L1	823339		0.010
L2	949036		
L3	883042		0.005
		7.1	0.024
			0.011
			0.017
	AVG=		0.019
	STDEV=		0.014

Table C-17: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1	37989		0.001
H2	19573		
H3	133655		
		96.1	
L1	375858		
L2	456861		
L3	733435		
		35.9	0.199
			0.145
			0.059
	AVG=		0.027
	STDEV=		0.089

Table C-18: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1	4812		0.043
H2	3090		0.026
H3	3668		0.085
		22.7	
L1	30027		0.002
L2	35201		
L3	22284		0.027
		22.3	0.016
			0.003
			0.046
	AVG=		0.027
	STDEV=		0.029

Appendix C

100% VEGETABLE OIL

Table C-19: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1	24894		0.000
H2	23664		0.008
H3			0.009
		3.6	
H4	248839		
H5	221948		0.005
H6	220641		0.005
		6.9	
	AVG=		0.004
	STDEV=		0.005

Table C-20: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1	3400		
H2	BDL		
H3	BDL		0.001
L1	36561		
L2	39205		
L3	33732		
		7.5	
	Average =		0.001
	Stdev=		

Table C-21: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1	29204		0.029
H2	22049		0.008
H3	22022		0.032
		16.9	
L1	207335		0.004
L2	261744		
L3	200210		0.007
		15.1	0.004
			0.007
	Average =		0.013
	Stdev=		0.012

Appendix C

20% ETHANOLAMINE

Table C-22: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1	3273		0.842
H2	2155		0.754
H3	2691		0.836
		20.7	
L1	3614		0.434
L2	3862		0.393
L3	3630		0.432
		3.7	0.612
			0.552
			0.608
	Average =		0.607
	Stdev=		0.173

Table C-23: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1	20637		0.636
H2	18713		0.840
H3	15666		0.675
		13.7	
L1	27063		0.545
L2	22815		0.715
L3	26066		0.578
		8.8	0.415
			0.539
			0.440
	Average =		0.598
	Stdev=		0.135

Table C-24: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1	4505		0.276
H2	3536		0.275
H3	4114		0.260
		12.0	
L1	10218		0.190
L2	10244		0.190
L3	10637		0.179
		2.3	0.240
			0.240
			0.226
	Average =		0.231
	Stdev=		0.037

Appendix C

40% ETHANOLAMINE

Table C-25: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1			
H2			
H3			
L1			
L2			
L3			
	Average =		
	Stdev=		

Table C-26: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1			
H2	23018		
H3	17387		
		19.7	
L1	26643		0.778
L2	32990		0.553
L3	36050		0.482
		15.0	0.499
			0.361
			0.316
	Average =		0.498
	Stdev=		0.164

Table C-27: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1	3396		0.262
H2			0.245
H3			0.379
L1	7963		
L2	8322		
L3	6234		
		14.9	
	Average =		0.296
	Stdev=		0.073

Appendix C

10% ETHANOLAMINE 20% PROPYLENE GLYCOL

Table C-28: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1	6376		0.551
H2	4829		0.581
H3			0.613
		19.5	
L1	9158		0.361
L2	8847		0.380
L3	8552		0.400
		3.4	
	Average =		0.481
	Stdev=		0.113

Table C-29: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1	31274		0.362
H2	33345		0.223
H3	40362		0.288
		13.6	
L1	59172		0.399
L2	81510		0.246
L3	68982		0.317
		16.0	0.534
			0.329
			0.422
	Average =		0.347
	Stdev=		0.096

Table C-30: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1	6564		0.185
H2	6608		0.166
H3	9482		0.169
		22.1	
L1	19327		0.187
L2	20700		0.168
L3	20443		0.171
		3.6	0.324
			0.292
			0.298
	Average =		0.218
	Stdev=		0.066

Appendix C

10% ETHANOLAMINE 20% PROPYLENE GLYCOL

Table C-31: Carbon Tetrachloride

Sample #	Peak count	COV %	Henry's Constant
H1			
H2	5613		
H3	4804		
		11.0	
L1	9774		0.410
L2	9398		0.436
L3	11832		0.308
		12.7	0.325
			0.345
			0.244
	Average =		0.345
	Stdev=		0.070

Table C-32: Tetrachloroethylene

Sample #	Peak count	COV %	Henry's Constant
H1			
H2	34195		
H3	33302		
		1.9	
L1	67085		0.343
L2	76695		0.281
L3	93124		0.209
		16.7	0.330
			0.270
			0.200
	Average =		0.272
	Stdev=		0.059

Table C-33: Dichloromethane

Sample #	Peak count	COV %	Henry's Constant
H1			
H2	9307		
H3	7594		
		14.3	
L1	22409		0.252
L2	22338		0.253
L3	20860		0.281
		4.0	0.184
			0.185
			0.206
	Average =		0.227
	Stdev=		0.041

Appendix D

Raw Data from Packed Column for DCM

Run #	scrubbing solution	QG ml/min	QG Actual ml/min	Velocity m/min	QL ml/min	QG/QL	Peak Count Cg in	Conc. mg/L Cg in	Peak Count Cg out	Conc. mg/L Cg out	Conc. mg/L Cl out	Modified Cgout mg/L
48	40 % propylene glycol	977	1535.47	0.189	200	8	788827	5.79	315239	2.20		
48	40 % propylene glycol	977	1535.47	0.189	200	8	788827	5.79	291413	2.02		
40	40 % propylene glycol	977	1535.47	0.189	100	15	1227235	9.11	821435	6.04		
40	40 % propylene glycol	977	1535.47	0.189	100	15	1227235	9.11	861055	6.34		
40	40 % propylene glycol	977	1535.47	0.189	100	15	1227235	9.11	931094	6.87		
40	40 % propylene glycol	977	1535.47	0.189	100	15	1227235	9.11	851770	6.27		
46	40 % propylene glycol	977	1535.47	0.189	60	26	363055	2.56	319771	2.23		
52	oil	5807	8899.29	1.098	200	44	315049	2.20	6022	BDL	197.15	
52	oil	5807	8899.29	1.098	200	44	315049	2.20	4719	BDL	169.16	
54	oil	5057	8540.28	1.054	100	85	315049	2.20	26273	0.01	169.16	0.22
54	oil	5057	8540.28	1.054	100	85	315049	2.20	31661	0.05	169.16	0.22
54	oil	5057	8540.28	1.054	100	85	315049	2.20	33403	0.06	169.16	0.22
29	oil	6110	10395.87	1.283	60	173	386456	2.74	84179	0.45	169.16	1.76
29	oil	6110	10395.87	1.283	60	173	386456	2.74	166060	1.07	210.80	1.52
52	oil	3807	5850.09	0.722	60	98	557537	4.04	26574	0.01	210.80	1.88
52	oil	3807	5850.09	0.722	60	98	557537	4.04	21133	BDL	310.56	0.85
52	oil	3807	5850.09	0.722	60	98	557537	4.04	31097	0.05	310.56	0.85
28	oil	6110	10395.87	1.283	60	173	662166	4.83	257518	1.76	310.56	3.04
28	oil	6110	10395.87	1.283	60	173	662166	4.83	261777	1.80	371.58	2.69
51	oil	2339	3611.98	0.446	60	60	665317	4.85	9689	BDL	371.58	
51	oil	2339	3611.98	0.446	60	60	665317	4.85	7151	BDL	373.42	
51	oil	2339	3611.98	0.446	60	60	665317	4.85	12202	BDL	373.42	
31	oil	7365	12607.43	1.556	60	210	737285	5.40	301929	2.10	373.42	3.62
31	oil	7365	12607.43	1.556	60	210	737285	5.40	81244	0.43	415.38	3.42
33	oil	855	1135.51	0.140	100	11	786748	5.77	50314	0.19	415.38	
3	oil	3807	5850.09	0.722	60	98	787537	5.78	235692	1.60	444.23	1.22
3	oil	3807	5850.09	0.722	60	98	787537	5.78	201661	1.34	444.69	1.22
3	oil	3807	5850.09	0.722	60	98	787537	5.78	227057	1.53	444.69	1.22
3	oil	3807	5850.09	0.722	60	98	787537	5.78	219568	1.48	444.69	1.22
3	oil	3807	5850.09	0.722	60	98	787537	5.78	242824	1.65	444.69	1.22
20	oil	7365	12607.43	1.556	60	210	789744	5.80	414198	2.95	444.69	3.68

Appendix D

Raw Data from Packed Column for DCM

Run #	scrubbing solution	QG ml/min	QG Actual ml/min	Velocity m/min	QL ml/min	QG/QL	Peak Count Cg in	Conc. mg/L Cg in	Peak Count Cg out	Conc. mg/L Cg out	Conc. mg/L Cl out	Modified Cgout mg/L
50	oil	977	1535.47	0.189	100	15	793308	5.82	899	BDL		
50	oil	977	1535.47	0.189	100	15	793308	5.82	131873	0.81	448.05	
49	oil	977	1535.47	0.189	60	26	793308	5.82	456	BDL	448.05	
49	oil	977	1535.47	0.189	60	26	793308	5.82	738	BDL	448.05	
14	oil	7590	13003.93	1.605	60	217	824081	6.06	125375	0.76	448.05	3.99
30	oil	6110	10395.87	1.283	60	173	909688.5	6.71	566669	4.11	466.00	4.02
30	oil	6110	10395.87	1.283	60	173	909688.5	6.71	628196	4.57	515.92	3.73
16	oil	5057	8540.28	1.054	10	854	935925	6.91	544182	3.94	515.92	6.30
32	oil	855	1135.51	0.140	60	19	959535	7.08	93908	0.52	531.22	
32	oil	855	1135.51	0.140	60	19	959535	7.08	36191	0.09	544.99	
32	oil	855	1135.51	0.140	60	19	959535	7.08	21118	BDL	544.99	
13	oil	5057	8540.28	1.054	60	142	997670	7.37	293676	2.04	544.99	3.55
5	oil	3807	5850.09	0.722	10	585	1183777	8.78	655823	4.78	567.23	7.82
5	oil	3807	5850.09	0.722	10	585	1183777	8.78	342821	2.41	675.75	7.63
1	oil	2339	3611.98	0.446	60	60	1218415	9.05	177284	1.15	675.75	
24	oil	855	1135.51	0.140	100	11	1339268.5	9.96	35632	0.08	695.95	
24	oil	855	1135.51	0.140	100	11	1339268.5	9.96	30098	0.04	766.43	
15	oil	7140	12210.94	1.507	10	1221	1482493	11.05	672863	4.91	766.43	10.42
15	oil	7140	12210.94	1.507	10	1221	1482493	11.05	1102185	8.17	849.95	10.35
2	oil	2339	3611.98	0.446	60	60	1533952	11.44	337069	2.37	849.95	
2	oil	2339	3611.98	0.446	60	60	1533952	11.44	199005	1.32	879.95	
2	oil	2339	3611.98	0.446	60	60	1533952	11.44	238836	1.62	879.95	
2	oil	2339	3611.98	0.446	60	60	1533952	11.44	395564	2.81	879.95	
18	oil	5057	8540.28	1.054	100	85	1572975	11.74	206480	1.38	879.95	1.43
18	oil	5057	8540.28	1.054	100	85	1572975	11.74	233373	1.58	902.71	1.17
18	oil	5057	8540.28	1.054	100	85	1572975	11.74	263331	1.81	902.71	1.17
22	oil	855	1135.51	0.140	60	19	1659347	12.39	337408	2.37	902.71	
22	oil	855	1135.51	0.140	60	19	1659347	12.39	67326	0.32	953.08	
21	oil	3765	6263.51	0.773	60	104	1677682	12.53	434370	3.10	953.08	3.40
21	oil	3765	6263.51	0.773	60	104	1677682	12.53	514825	3.71	963.77	3.30
21	oil	3765	6263.51	0.773	60	104	1677682	12.53	504614	3.64	963.77	3.30

Appendix D

Raw Data from Packed Column for DCM

Run #	scrubbing solution	QG ml/min	QG Actual ml/min	Velocity m/min	QL ml/min	QG/QL	Peak Count Cg in	Conc. mg/L Cg in	Peak Count Cg out	Conc. mg/L Cg out	Conc. mg/L Cl out	Modified Cgout mg/L
36	water	855	1135.51	0.140	200	6	246957	1.68	124522	0.75		
44	water	977	1535.47	0.189	60	26	461107	3.31	339861	2.39		
44	water	977	1535.47	0.189	60	26	461107	3.31	570457	4.14		
45	water	3079	4740.18	0.585	200	24	591838	4.30	295985	2.05		
45	water	3079	4740.18	0.585	200	24	591838	4.30	264296	1.81		
45	water	3079	4740.18	0.585	200	24	591838	4.30	254519	1.74		
47	water	977	1535.47	0.189	60	26	788827	5.79	553557	4.01		
47	water	977	1535.47	0.189	60	26	788827	5.79	564794	4.09		
47	water	977	1535.47	0.189	60	26	788827	5.79	188109	1.24		
34	water	855	1135.51	0.140	60	19	852228.5	6.27	1001446	7.40		
34	water	855	1135.51	0.140	60	19	852228.5	6.27	873999	6.44		
36	water	855	1135.51	0.140	200	6	917957	6.77	277962	1.92		
35	water	855	1135.51	0.140	100	11	920630	6.79	282425	1.95		
35	water	855	1135.51	0.140	100	11	920630	6.79	391164	2.78		
37	water	1980	3117.99	0.385	200	16	921023.5	6.79	644895	4.70		
26	water	855	1135.51	0.140	60	19	1084556	8.03	933295	6.89		
26	water	855	1135.51	0.140	60	19	1084556	8.03	811145	5.96		
25	water	855	1135.51	0.140	100	11	1146528	8.50	392255	2.78		
25	water	855	1135.51	0.140	100	11	1146528	8.50	1083752	8.03		
25	water	855	1135.51	0.140	100	11	1146528	8.50	1259050	9.36		
42	water	977	1535.47	0.189	100	15	1467804	10.94	724333	5.30		
42	water	977	1535.47	0.189	100	15	1467804	10.94	714576	5.23		
42	water	977	1535.47	0.189	100	15	1467804	10.94	430711	3.08		
43	water	977	1535.47	0.189	200	8	1548138	11.55	265839	1.83		
43	water	977	1535.47	0.189	200	8	1548138	11.55	329025	2.31		
43	water	977	1535.47	0.189	200	8	1548138	11.55	317435	2.22		
7	water	3807	5850.09	0.722	60	98	1571063	11.72	1109578	8.22		
27	water	855	1135.51	0.140	200	6	2097012	15.71	380742	2.70		
27	water	855	1135.51	0.140	200	6	2097012	15.71	275547	1.90		
9	water	977	1535.47	0.189	60	26	2280898	17.10	875842	6.45		
11	water	977	1535.47	0.189	200	8	2290153	17.17	116252	0.69		
10	water	977	1535.47	0.189	100	15	2290153	17.17	819858	6.03		
38	water	3001	4917.19	0.607	200	25	5944766	44.88	536827	3.88		
38	water	3001	4917.19	0.607	200	25	5944766	44.88	560778	4.06		

Appendix D

Raw Data from Packed Column for C_T

Run #	scrubbing solution	QG ml/min	QG actual ml/min	Velocity V (ml/min)	QL ml/min	QG/QL	Peak Count Cg in	Cone. mg/L Cg in	Peak Count Cg out	Conc. mg/L Cg out
47	40 % propylene glycol	977	1535.47	0.19	200	8	409236	13.38	321033	10.47
47	40 % propylene glycol	977	1535.47	0.19	200	8	409236	13.38	254105	8.26
40	40 % propylene glycol	977	1535.47	0.19	100	15	687231	22.54	443885	14.52
40	40 % propylene glycol	977	1535.47	0.19	100	15	687231	22.54	475839	15.57
40	40 % propylene glycol	977	1535.47	0.19	100	15	687231	22.54	526639	17.25
40	40 % propylene glycol	977	1535.47	0.19	100	15	687231	22.54	444745	14.55
46	40 % propylene glycol	977	1535.47	0.19	60	26	283422	9.23	280408	9.13
29	oil	6110	10395.87	1.28	60	173	110725.5	3.54	18393	0.49
29	oil	6110	10395.87	1.28	60	173	110725.5	3.54	15998	0.41
28	oil	6110	10395.87	1.28	60	173	186306	6.03	29249	0.85
28	oil	6110	10395.87	1.28	60	173	186306	6.03	32456	0.96
31	oil	7365	12607.43	1.56	60	210	223782.5	7.26	42561	1.29
31	oil	7365	12607.43	1.56	60	210	223782.5	7.26	20905	0.57
31	oil	7365	12607.43	1.56	60	210	302144.25	9.85	20905	0.57
20	oil	7365	12607.43	1.56	60	210	242285	7.87	69848	2.19
14	oil	7590	13003.93	1.60	60	217	243855	7.93	45311	1.38
30	oil	6110	10395.87	1.28	60	173	292176.5	9.52	66993	2.09
13	oil	5057	8540.28	1.05	60	142	377495	12.33	24981	0.71
5	oil	3807	5850.09	0.72	10	585	386474	12.63	134412	4.32
5	oil	3807	5850.09	0.72	10	585	386474	12.63	166353	5.37
5	oil	3807	5850.09	0.72	10	585	386474	12.63	105631	3.37
24	oil	855	1135.51	0.14	100	9	433936	14.19	59669	1.85
24	oil	855	1135.51	0.14	100	11	433936	14.19	29961	0.87
3	oil	3807	5850.09	0.72	60	98	476692	15.60	15978	0.41
3	oil	3807	5850.09	0.72	60	98	476692	15.60	13018	0.31
3	oil	3807	5850.09	0.72	60	98	476692	15.60	15237	0.39

Appendix D

Raw Data from Packed Column for CT

Run #	scrubbing solution	QG ml/min	QG actual ml/min	Velocity V (m/min)	QL ml/min	QG/QL	Peak Count Cg in	Conc. mg/L Cg in	Peak Count Cg out	Conc. mg/L Cg out	Conc. mg/L Cl out	Modified Cgout mg/L
3	oil	3807	5850.09	0.72	60	98	476692	15.60	13496	0.33		
3	oil	3807	5850.09	0.72	60	98	476692	15.60	17362	0.46		
18	oil	5057	8540.28	1.05	100	85	501034	16.40	19161	0.52		
18	oil	5057	8540.28	1.05	100	85	501034	16.40	21126	0.58		
18	oil	5057	8540.28	1.05	100	85	501034	16.40	22148	0.62		
15	oil	7140	12210.94	1.51	10	1221	556218	18.22	163459	5.27		
15	oil	7140	12210.94	1.51	10	1221	556218	18.22	241582	7.85		
33	oil	855	1135.51	0.14	100	11	573997	18.81	12940	0.31		
33	oil	855	1135.51	0.14	100	11	573997	18.81	4805	0.04		
1	oil	2339	3611.98	0.45	60	60	579219	18.98	21759	0.60		
2	oil	2339	3611.98	0.45	60	60	583002	19.11	37619	1.13		
2	oil	2339	3611.98	0.45	60	60	583002	19.11	19467	0.53		
2	oil	2339	3611.98	0.45	60	60	583002	19.11	17246	0.45		
2	oil	2339	3611.98	0.45	60	60	583002	19.11	21385	0.59		
17	oil	5057	8540.28	1.05	100	85	599688	19.66	19324	0.52		
16	oil	5057	8540.28	1.05	10	854	602347	19.75	194947	6.31		
32	oil	855	1135.51	0.14	60	19	643480	21.10	62871	1.96		
32	oil	855	1135.51	0.14	60	19	643480	21.10	14901	0.38		
32	oil	855	1135.51	0.14	60	19	643480	21.10	4897	0.05		
21	oil	3765	6263.51	0.77	60	104	684061	22.44	60872	1.89		
21	oil	3765	6263.51	0.77	60	104	684060.5	22.44	55131	1.70		
21	oil	3765	6263.51	0.77	60	104	684060.5	22.44	54680	1.69		
12	oil	977	1535.47	0.19	60	26	965644	31.72	3190	BDL		
23	oil	855	1135.51	0.14	100	9	1065316	35.01	9793	0.21		
22	oil	855	1135.51	0.14	60	19	1165047	38.30	12274	0.29		
22	oil	855	1367.27	0.17	60	23	1165047	38.30	232694	7.56		
45	water	3079	4740.18	0.58	200	24	135069	4.34	127292	4.08	3.62	4.19
45	water	3079	4740.18	0.58	200	24	135069	4.34	142430	4.58	3.62	4.19

Appendix D

Raw Data from Packed Column for CT

Run #	scrubbing solution	QG ml/min	QG actual ml/min	Velocity V (m/min)	QL ml/min	QG/QL	Peak Count Cg in	Conc. mg/L. Cg in	Peak Count Cg out	Conc. mg/L. Cg out	Conc. mg/L. Cj out	Modified Cgout mg/L.
45	water	3079	4740.18	0.58	200	24	135069	4.34	148618	4.79	3.62	4.19
44	water	977	1535.47	0.19	60	26	161584	5.21	139061	4.47	4.34	5.04
44	water	977	1535.47	0.19	60	26	161584	5.21	258818	8.42	4.34	5.04
47	water	977	1535.47	0.19	60	26	351084	11.46	298507	9.73	9.55	11.09
47	water	977	1535.47	0.19	60	26	351084	11.46	290251	9.46	9.55	11.09
47	water	977	1535.47	0.19	60	26	351084	11.46	272658	8.87	9.55	11.09
37	water	1980	3117.99	0.38	200	16	413884	13.53	402304	13.15	11.28	12.81
38	water	3001	4917.19	0.61	200	25	413884	13.53	290062	9.45	11.28	13.07
38	water	3001	4917.19	0.61	200	25	413884	13.53	261606	8.51	11.28	13.07
39	water	4017	6707.59	0.83	200	34	413884	13.53	28898	0.84	11.28	13.20
25	water	855	1135.51	0.14	100	11	415761	13.59	98730	3.14	11.33	12.60
25	water	855	1135.51	0.14	100	11	415761	13.59	101488	3.23	11.33	12.60
25	water	855	1135.51	0.14	100	11	415761	13.59	143041	4.60	11.33	12.60
36	water	855	1135.51	0.14	200	6	494393	16.19	418301	13.68	13.49	13.81
36	water	855	1135.51	0.14	200	6	494393	16.19	407757	13.33	13.49	13.81
35	water	855	1135.51	0.14	100	11	535207	17.53	135715	4.36	14.61	16.24
35	water	855	1135.51	0.14	100	11	535207	17.53	166289	5.37	14.61	16.24
7	water	3807	5850.09	0.72	60	98	590216	19.35	543288	17.80	16.12	19.18
7	water	3807	5850.09	0.72	60	98	590216	19.35	443849	14.52	16.12	19.18
34	water	855	1135.51	0.14	60	19	603668	19.79	326002	10.63	16.49	18.92
34	water	855	1135.51	0.14	60	19	603668	19.79	309445	10.09	16.49	18.92
43	water	977	1535.47	0.19	200	8	712323	23.37	444826	14.55	19.48	20.83
43	water	977	1535.47	0.19	200	8	712323	23.37	537445	17.61	19.48	20.83
43	water	977	1535.47	0.19	200	8	712323	23.37	601427	19.71	19.48	20.83
42	water	977	1535.47	0.19	100	15	712323	23.37	640317	21.00	19.48	22.10
42	water	977	1535.47	0.19	100	15	712323	23.37	472155	15.45	19.48	22.10
42	water	977	1535.47	0.19	100	15	712323	23.37	352134	11.50	19.48	22.10
26	water	855	1135.51	0.14	60	19	791964.5	26.00	945337	31.05	21.66	24.85
26	water	855	1135.51	0.14	60	19	791964.5	26.00	597261	19.58	21.66	24.85

Appendix D

Raw Data from Packed Column for C'T

Run #	scrubbing solution	QG ml/min	QG actual ml/min	Velocity V (m/min)	QL ml/min	QG/QL	Peak Count Cg in	Conc. mg/L Cg in	Peak Count Cg out	Conc. mg/L Cg out
27	water	855	1135.51	0.14	200	6	844974	27.74	669312	21.95
27	water	855	1135.51	0.14	200	6	844974	27.74	773812	25.40
11	water	977	1535.47	0.19	200	8	1042482	34.26	498267	16.31
10	water	977	1535.47	0.19	100	15	1042482	34.26	559529	18.33
9	water	977	1535.47	0.19	60	26	1048878	34.47	702339	23.04

Appendix D

Raw Data from Packed Column for PCIE

Run #	scrubbing solution	QG		QG actual		QL	QG/QL	Peak Count		Conc. mg/L		Peak Count		Conc. mg/L	
		ml/min	ml/min	ml/min	ml/min			Cg in	Cg out	Cg in	Cg out	Cg in	Cg out	Cg in	Cg out
48	40 % propylene glycol	977	1535.4742	200	8	2440254	11.87	1246842	6.04						
48	40 % propylene glycol	977	1535.4742	200	8	2440254	11.87	979320	4.73						
40	40 % propylene glycol	977	1535.4742	100	15	6171291	30.09	4024310	19.60						
40	40 % propylene glycol	977	1535.4742	100	15	6171291	30.09	4082048	19.88						
40	40 % propylene glycol	977	1535.4742	100	15	6171291	30.09	4149300	20.21						
40	40 % propylene glycol	977	1535.4742	100	15	6171291	30.09	3702419	18.03						
46	40 % propylene glycol	977	1535.4742	60	26	2104710	10.23	1681720	8.16						
46	40 % propylene glycol	977	1535.4742	60	26	2104710	10.23	1750215	8.50						
46	40 % propylene glycol	977	1535.4742	60	26	2104710	10.23	1958560	9.51						
29	oil	6110	10395.872	60	173	1245559	3.24	349129	0.89						
29	oil	6110	10395.872	60	173	1245559	3.24	43890	0.09						
29	oil	6110	10395.872	60	173	1245559	3.24	196509.5	0.49						
28	oil	6110	10395.872	60	173	1544951.5	4.02	106920	0.26						
28	oil	6110	10395.872	60	173	1544951.5	4.02	77059	0.18						
28	oil	6110	10395.872	60	173	1544951.5	4.02	91989.5	0.22						
52	oil	3807	5850.0922	60	98	909867	4.39	8324	BDL						
14	oil	7365	12607.433	60	210	2043785	5.32	621993	1.60						
30	oil	6110	10395.872	60	173	2273807	5.93	96906	0.23						
30	oil	6110	10395.872	60	173	2273807	5.93	57538	0.13						
30	oil	6110	10395.872	60	173	2273807	5.93	77222	0.18						
31	oil	7365	12607.433	60	210	2390617.5	6.23	372601	0.95						
31	oil	7365	12607.433	60	210	2390617.5	6.23	132880	0.32						
31	oil	7365	12607.433	60	210	2390617.5	6.23	252740.5	0.64						
20	oil	7365	12607.433	60	210	2485177	6.48	108587	0.26						
51	oil	2339	3611.9794	60	60	1389654	6.74	81857	0.35						
51	oil	2339	3611.9794	60	60	1389654	6.74	4829	BDL						
51	oil	2339	3611.9794	60	60	1389654	6.74	BDL	BDL						
13	oil	5057	8540.2754	60	142	2654866	6.92	42909	0.09						
18	oil	5057	8540.2754	100	85	3981197	10.39	170450	0.42						
18	oil	5057	8540.2754	100	85	3981197	10.39	89167	0.21						

Appendix D

Raw Data from Packed Column for PCIE:

Run #	scrubbing solution	QG ml/min	QG actual ml/min	QL ml/min	QG/QL	Peak Count Cg in	Conc. mg/L Cg in	Peak Count Cg out	Conc. mg/L Cg out
18	oil	5057	8540.2754	100	85	3981197	10.39	37906	0.08
3	oil	3807	5850.0922	60	98	4102941	10.71	300776	0.76
3	oil	3807	5850.0922	60	98	4102941	10.71	137396	0.34
3	oil	3807	5850.0922	60	98	4102941	10.71	76144	0.18
3	oil	3807	5850.0922	60	98	4102941	10.71	59603	0.13
3	oil	3807	5850.0922	60	98	4102941	10.71	72549	0.17
50	oil	977	1535.4742	100	15	2277825	11.04	3876	BDL
49	oil	977	1535.4742	60	26	2277825	11.04	5385	BDL
50	oil	977	1535.4742	100	15	2277825	11.07	47523	0.10
49	oil	977	1535.4742	60	26	2277825	11.07	32790	0.03
5	oil	3807	5850.0922	10	585	4290666	11.20	731587	1.89
5	oil	3807	5850.0922	10	585	4290666	11.20	360907	0.92
15	oil	7140	12210.938	10	1221	5244305	13.70	684539	1.77
21	oil	3765	6263.513	60	104	5438621	14.21	402588	1.03
16	oil	5057	8540.2754	10	854	5586037	14.59	428812	1.10
2	oil	2339	3611.9794	60	60	5867749	15.33	599447	1.55
2	oil	2339	3611.9794	60	60	5867749	15.33	271588	0.69
2	oil	2339	3611.9794	60	60	5867749	15.33	334946	0.85
2	oil	2339	3611.9794	60	60	5867749	15.33	59753	0.13
17	oil	5057	8540.2754	100	85	6389212	16.70	598096	1.54
21	oil	3765	6263.513	60	104	6448969	16.85	130783	0.32
21	oil	3765	6263.513	60	104	6448969	16.85	32466	0.06
32	oil	855	1135.511	60	19	6982787.5	18.25	1004435	2.60
32	oil	855	1135.511	60	19	6982787.5	18.25	499643	1.28
32	oil	855	1135.511	60	19	6982787.5	18.25	2310669	6.02
33	oil	855	1135.511	100	11	7346593	19.20	371249	0.95
33	oil	855	1135.511	100	11	7346593	19.20	671275	1.73
33	oil	855	1135.511	100	11	7346593	19.20	521262	1.34
1	oil	2339	3611.9794	60	60	4447145	21.69	50674	0.11
32	oil	855	1135.511	60	19	638010.333	16.67	414403.6667	1.06
24	oil	855	1135.511	100	11	10906827	28.52	2292429	5.98
24	oil	855	1135.511	100	11	10906827	28.52	1379890	3.59

Appendix D

Raw Data from Packed Column for PCIE

Run #	scrubbing solution	QG ml/min	QG actual ml/min	QL ml/min	QG/QL	Peak Count Cg in	Conc. mg/L Cg in	Peak Count Cg out	Conc. mg/L Cg out	Conc. mg/L Cl out	Modified Cgout mg/L
12	oil	977	1535.4742	60	26	11015057	28.80	168463	0.42		
22	oil	855	1349.473	60	22	12527312	32.76	4850295	12.67		
22	oil	855	1135.511	60	19	12527312	32.76	719273	1.86		
15	oil	7140	12210.938	10	1221	5244305	13.70	579591	1.49		
45	water	3079	4740.1834	200	24	664601	3.20	559575	2.68	4.56	3.00
45	water	3079	4740.1834	200	24	664601	3.20	650111	3.12	4.56	3.00
45	water	3079	4740.1834	200	24	664601	3.20	731390	3.52	4.56	3.00
47	water	977	1535.4742	60	26	1963835	9.54	1486835	7.21	13.63	9.01
47	water	977	1535.4742	60	26	1963835	9.54	1607602	7.80	13.63	9.01
47	water	977	1535.4742	60	26	1963835	9.54	1225272	5.93	13.63	9.01
44	water	977	1535.4742	60	26	2317451	11.27	1607378	7.80	16.10	10.64
44	water	977	1535.4742	60	26	2317451	11.27	1568401	7.61	16.10	10.64
35	water	855	1135.511	100	11	5086793	13.29	694436	1.79	18.98	11.62
42	water	977	1535.4742	100	15	3120922	15.19	2282687	11.10	21.70	13.78
42	water	977	1535.4742	100	15	3120922	15.19	2866490	13.95	21.70	13.78
42	water	977	1535.4742	100	15	3120922	15.19	1659717	8.05	21.70	13.78
37	water	1980	3117.986	200	16	5944766	15.53	5043327	13.17	22.19	14.11
38	water	3001	4917.1922	200	25	5944766	15.53	4554111	11.89	22.19	14.63
38	water	3001	4917.1922	200	25	5944766	15.53	4074236	10.64	22.19	14.63
38	water	3001	4917.1922	200	25	5944766	15.53	4314173.5	11.27	22.19	14.63
39	water	4017	6707.5874	200	34	5944766	15.53	3426359	8.94	22.19	14.87
36	water	855	1135.511	200	6	6042667	15.79	3234166	8.44	22.56	11.82
36	water	855	1135.511	200	6	6042667	15.79	1295154	3.37	22.56	11.82
7	water	3807	5850.0922	60	98	6057336	15.83	5614295	14.67	22.61	15.60
7	water	3807	5850.0922	60	98	6057336	15.83	4285625	11.19	22.61	15.60
43	water	977	1535.4742	200	8	3608367	17.57	2331335	11.33	25.10	14.30
43	water	977	1535.4742	200	8	3608367	17.57	2867492	13.95	25.10	14.30
43	water	977	1535.4742	200	8	3608367	17.57	3280554	15.97	25.10	14.30
34	water	855	1135.511	60	19	8404658	21.97	2247898	5.86	31.39	20.31
34	water	855	1135.511	60	19	8404658	21.97	1483970	3.86	31.39	20.31
34	water	855	1135.511	60	19	8404658	21.97	1865934	4.86	31.39	20.31
35	water	855	1135.511	100	11	8404658	21.97	1674952	4.36	31.39	19.21

Appendix D

Raw Data from Packed Column for PCI:

Run #	scrubbing solution	QG ml/min	QG actual ml/min	QL ml/min	QG/QL	Peak Count Cg in	Conc. mg/L Cg in	Peak Count Cg out	Conc. mg/L Cg out	Conc. mg/L Cl out	Modified Cgout mg/L
9	water	977	1535.4742	60	26	9809751	25.65	7643671	19.98	36.64	24.22
11	water	977	1535.4742	200	8	9853753	25.76	4604082	12.02	36.80	20.97
10	water	977	1535.4742	100	15	9853753	25.76	3990025	10.42	36.80	23.37
27	water	855	1135.511	200	6	11735151.5	30.69	4824961	12.60	43.84	22.96
27	water	855	1135.511	200	6	11735151.5	30.69	3625805	9.46	43.84	22.96
25	water	855	1135.511	100	11	12187141	31.87	1772490	4.61	45.53	27.86
25	water	855	1135.511	100	11	12187141	31.87	3926518	10.25	45.53	27.86
25	water	855	1135.511	100	11	12187141	31.87	3147930	8.21	45.53	27.86
35	water	855	1135.511	100	11	12187141	31.87	1134597	2.95	45.53	27.86
26	water	855	1135.511	60	19	12197289.5	31.89	3967432	10.36	45.56	29.49
26	water	855	1135.511	60	19	12197289.5	31.89	1734853	4.52	45.56	29.49

Appendix E - Liquid-Liquid Contacting Reactor Semi-Batch Data

Run #: 1
Date: 02-Mar-98
Liquid flow rate (ml/min): 225
Start time: 1:00pm
End time: 3:00pm
Total time running (hours): 2
Total volume of water passed (l): 27
Initial volume of oil added to colt: 2300

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
50 ul gas sample injected into GC

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
15	299.9	9.99	45865	4.84	16.348476	65649.2	2.93	9.89118
30	64.7	3.15	17394.8	1.78	11.9863312	32316	1.42	9.58017
45	59.1	2.99	12411.7	1.24	12.5420696	24589.1	1.07	10.82283
60	BDL		8877.8	0.86	11.5812949	13773.4	0.58	7.809787
75	BDL		9103.4	0.88	14.8868999	16625	0.71	11.94419
90	BDL		47056.7	4.97	100.691559	74819.8	3.35	67.76753
120	BDL		8391.1	0.81	21.7463919	15784.2	0.67	18.08133

Oil samples
(160 ml bottle, 60 ml headspace, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	PCE peak count	conc. mg/L
start	481.5	299.53	52619.8	388.8688	67968.7	542.17192
end	BDL		46070.4	336.4736	60076.5	479.03432

Appendix E - Liquid-Liquid Contacting Reactor Semi-Batch Data

Run #: 2
Date: 05-Mar-98
Liquid flow rate (ml/min): 225
Start time: 11.56pm
End time: 12.56pm
Total time running (hours): 2
Total volume of water passed (l): 27
Initial volume of oil added to coil: 2100

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
50 ul gas sample injected into GC

time (min)	DCM peak count	conc. mg/L	CT peak count	Mass mg onc. mg/L	PCE peak count	Mass mg onc. mg/L
15	60.20	3.02	38737.50	4.08	38230.80	1.69
30			29416.60	3.07	33772.10	1.49
45			16947.00	1.73	18806.20	0.81
60			9801.00	0.96	13296.00	0.56
75			21732.10	2.24	17725.60	0.76
90			8140.80	0.78	10614.70	0.44
105			5622.20	0.51	3894.00	0.13
120			14302.10	1.44	13408.20	0.56
	Average	3.02		1.53		0.68

Oil samples
pace, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM peak count	conc. mg/L	CT peak count	PCE peak count
start sample 1	337.60	135.07	63285.80	58872.70
start sample 3	318.20	112.90	54973.30	61380.00
Average start	327.90	123.99	59129.55	60126.36
end sample 1	301.80	94.16	50437.30	65431.40
end sample 2	323.10	118.50	46174.20	44353.70
Average end	312.46	106.33	48306.76	54892.56

Run #:	3
Date:	11-Mar-98
Liquid flow rate (ml/min):	225
Start time:	8:57am
End time:	11:57am
Total time running (hours):	3
Total volume of water passed (L	40.5
Initial volume of oil added to coil	2100

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
50 μ l gas sample injected into GC

	time (min)	DCM peak count	conc. mg/L	C.T peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
	30			10248.60	1.01	6.79	13327.10	0.56	3.77
	60			5888.40	0.54	7.23	7795.20	0.31	4.15
	90			4825.20	0.42	8.53	6028.80	0.23	4.60
	120			2788.80	0.20	5.44	3949.70	0.13	3.59
	180			4700.70	0.41	16.51	4915.10	0.18	7.16
	240			3360.60	0.26	14.22	3231.60	0.10	5.43
		Average			0.37				0.19

Oil samples
pace, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM	CT	PCE	conc. mg/L	peak count	conc. mg/L	peak count	conc. mg/L	peak count
start sample 2	286.10	53339.60	394.63	76.22	53339.60	394.63	68153.00	543.65	
start sample 3	324.90	60923.50	455.30	120.56	60923.50	455.30	75953.10	606.05	
Average start	305.50	57131.55	424.96	98.39	57131.55	424.96	72053.05	574.35	
end sample 1	213.80	52889.90	391.03		52889.90	391.03	67868.60	541.37	
end sample 3		53842.40	398.65		53842.40	398.65	70607.70	563.28	
Average end	213.80	53356.15	394.84		53356.15	394.84	69238.15	552.33	

Run #:	4
Date:	12-Mar-98
Liquid flow rate (ml/min):	225
Start time:	9:20
End time:	12:20
Total time running (hours):	3.00
Total volume of water passed (l	40.5
Initial volume of oil added to coli	4000

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
50 ul gas sample injected into GC

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
30			11642.20	1.16	7.80	9797.30	0.40	2.69
60			4707.50	0.41	5.51	6911.20	0.27	3.61
90			3428.90	0.27	5.48	6815.90	0.26	5.33
120			1519.00	0.06	1.75	1043.90		
180			1795.30	0.09	3.83	2535.20	0.07	2.79
240			2564.80	0.18	9.59	3443.40	0.11	5.95
	Average			0.20			0.18	

Oil samples
pace, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM	CT	PCE
	peak count	peak count	peak count
	conc. mg/L	conc. mg/L	conc. mg/L
start sample 2	332.80	66457.00	80470.50
start sample 3	384.00	72260.50	99018.30
Average start	358.40	69358.75	89744.40
end sample 1	239.90	60481.10	77263.60
end sample 2	208.00	61558.00	76970.20
end sample 3			614.18
Average end	223.95	61019.55	77116.90
		456.07	615.36

Appendix E - Liquid-Liquid Contacting Reactor Semi-Batch Data

Run #: 5
 Date: 16-Mar-98
 Liquid flow rate (ml/min): 225
 Start time: 8:42
 End time: 11:59
 Total time running (hours): 3.28
 Total volume of water passed (l): 44.32
 Initial volume of oil added to cell: 1000

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
 50 ul gas sample injected into GC

time (min)	DCM peak count	conc. mg/	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
30			5042.30	0.44	3.00	8215.40	0.33	2.20
60			3181.80	0.24	3.29	6787.40	0.26	3.53
90			3257.80	0.25	5.11	6520.70	0.25	5.06
120			2533.60	0.17	4.70	5656.70	0.21	5.68
180			3474.90	0.28	11.16	5742.50	0.21	8.68
240			1959.80	0.11	6.07	2807.10	0.07	3.90
257			1653.90	0.08	4.59	2801.50	0.08	4.68
	Average			0.19			0.18	

Oil samples
 pace, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM peak count	conc. mg/	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
start sample 2	306.30	99.30	61913.40	463.22	75258.20	600.49		
start sample 3	316.10	110.50	63326.00	474.52	75867.70	605.36		
Average start	311.20	104.90	62619.70	468.87	75562.95	602.93		
end sample 1	148.60	-80.93	64401.40	483.12	80026.20	638.63		
end sample 2			44433.00	323.37	60291.30	480.75		
end sample 3	231.20	13.47	60064.90	448.43	74321.30	592.99		
Average end	189.90		56299.77	418.31	71546.27	570.79		

Appendix E - Liquid-Liquid Contacting Reactor Semi-Batch Data

Run #:	6
Date:	March/20/98
Liquid flow rate (ml/min):	115
Start time:	11:20
End time:	2:20
Total time running (hours):	3.00
Total volume of water passed (l)	20.70
Initial volume of oil added to cell	2000

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
50 μ l gas sample injected into GC

	time (min)	DCM peak count	conc. mg/ L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
	30			10519.90	1.03	3.57	15628.10	0.66	2.29
	60			4941.30	0.43	2.99	8215.40	0.33	2.25
	90			3288.80	0.26	2.64	6125.10	0.23	2.40
	120			3634.60	0.29	4.04	6172.40	0.23	3.23
	180			1906.20	0.11	2.21	3417.80	0.11	2.26
	240			2291.80	0.15	4.09	4016.70	0.14	3.76
		Average			0.38			0.28	

Oil samples
 pace, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM		CT		POE	
	peak count	conc. mg/l	peak count	conc. mg/L	peak count	conc. mg/L
start sample 2	342.8	141.02	51948.8	383.50	52543.5	418.77
	329.90	126.27	72276.60	546.12	69817.80	556.96
	324.70	120.33	71148.00	537.09	70743.10	564.37
Average start		129.21	65124.47	488.91	64368.13	513.37
end sample 1	203.70		59447.80	443.49	61868.80	493.37
end sample 2	254.30		64686.40	485.40	71731.80	572.28
end sample 3					57035.40	454.71
Average end	229.00		62067.10	464.45	63545.33	506.78

Run #:	7
Date:	March 24/98
Liquid flow rate (ml/min):	400
Start time:	9:04
End time:	11:34
Total time running (hours):	2.50
Total volume of water passed (l)	60.00
Initial volume of oil added to colt	2000

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
50 μ l gas sample injected into GC

[illegible]

Oil samples
space, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM		CT		PCE	
	peak count	conc. mg/L	peak count	conc. mg/L	peak count	conc. mg/L
start sample 2	395.10	200.79	88809.90	678.39	103349.10	825.22
start sample 3	313.40	107.42	66498.70	499.90	81681.30	651.87
Average start		154.10	77654.30	589.14	92515.20	738.54
end sample 1	313.40	107.42	76934.00	583.38	93718.80	748.17
end sample 2	262.40	49.13	65000.40	487.91	82140.80	655.55
end sample 3	225.10	6.50	70559.40	532.39	87369.80	697.38
Average end	266.97	54.35	70831.27	534.56	87743.13	700.37

Appendix E - Liquid-Liquid Contacting Reactor Continuous Flow Data

Run #: 1
 Date: 13-May-98
 Water flow rate (ml/min): 200
 Oil flow rate (ml/min): 25
 Start time: 10:47
 End time: 1:47
 Total time running (hours): 3 hours with recycle
 Total volume of water passed: 36
 Initial volume of oil added: 2000

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)

50 ul gas sample injected into GC

Water Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60	5083.80	149.06	291947.60	31.36	376.37	46913.20	2.08	24.97
90	6222.10	182.16	313132.30	33.65	605.65	42107.60	1.86	33.54
120	7000.70	204.79	327312.60	35.18	844.22	41915.60	1.85	44.51
150	7560.70	221.07	371569.10	39.95	1198.36	40950.00	1.81	54.32
180	8091.30	236.50	393884.60	42.35	1524.61	41532.70	1.84	66.14
Average		198.72		36.50			1.89	
Sum					4549.20			223.48

Oil Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60	393.00	198.39	83202.10	633.53	950.29	58451.20	466.03	5592.38
90	381.80	185.59	86386.80	659.00	1482.76	62775.80	500.63	9011.32
120	435.80	247.30	83101.40	632.72	1898.16	57201.20	456.03	10944.77
150	205.80	0.00	48888.30	359.02	1346.31	38380.70	305.47	9164.04
180	449.40	262.85	85561.20	652.40	2935.80	62248.00	496.41	17870.63
Average		178.83		587.33			444.91	
Sum					8613.33			52583.13

Oil samples

ce, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	PCE peak count	conc. mg/L
start sample 1	479.40	297.13	82850.10	630.71	60850.40	485.23
start sample 2	503.30	324.45	87372.00	666.89	62241.10	496.35
Average start	491.35	310.79	85111.06	648.80	61545.75	490.79
end sample 1	925.20	806.62	85723.50	653.70	62355.60	497.27
end sample 2	443.90	256.56	87136.50	665.00	61443.60	489.97
Average end	684.55	531.69	86430.00	659.35	61899.60	493.62

Appendix E - Liquid-Liquid Contacting Reactor Continuous Flow Data

Run #: 2
 Date: 14-May-98
 Water flow rate (ml/min): 200
 Oil flow rate (ml/min): 25
 Start time: 9:17
 End time: 12:17
 Total time running (hours): 3 ours with recycle)
 Total volume of water passed (L): 38
 Volume of oil added to column: 1000

(40 ml bottles, 25 ml liquid sample, 15 ml headspace)

3 ul gas sample injected into GC

Water Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60	5467.40	160.22	413518.10	44.47	533.59	99781.00	4.48	53.74
90	6429.70	188.19	328887.40	35.45	638.16	56035.40	2.49	44.91
120	4881.40	143.18	325828.70	35.02	840.38	50529.70	2.25	53.88
150	7132.50	208.62	382844.70	41.16	1234.81	63215.80	2.82	84.61
180	5906.30	172.98	350316.80	37.65	1355.57	61005.50	2.72	97.93
	Average	174.64		38.75			2.95	
				Sum	4602.51			335.07

Oil Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60	327.40	123.42	82290.40	626.23	939.35	63578.70	507.05	6084.62
90	373.90	176.56	98749.20	757.90	1705.28	74324.30	593.02	10674.30
120	386.70	191.19	82771.60	630.08	1890.25	64662.00	517.32	12415.64
150	468.40	284.58	91872.70	702.89	2635.85	68241.30	544.35	16330.58
180	358.10	158.50	68184.30	513.38	2310.23	52694.30	419.98	15119.16
	Average	186.85		646.10			516.34	
				Sum	9480.96			60624.31

Oil samples

space, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	PCE peak count	conc. mg/L
start sample 1	574.20	405.47	113211.30	873.60	80505.10	642.46
start sample 2	387.30	191.87	66046.60	496.28	51695.50	411.99
Average start	480.75	298.67	89628.95	684.94	66100.30	527.22
end sample 1	444.10	256.79	99603.90	764.74	72493.50	578.37
end sample 2	408.10	215.65	87724.20	669.70	69861.70	557.32
Average end	426.10	236.22	93664.05	717.22	71177.60	567.84

Appendix E - Liquid-Liquid Contacting Reactor Continuous Flow Data

Run #: 3
 Date: 21-May-98
 Water flow rate (ml/min): 200
 Oil flow rate (ml/min): 10
 Start time: 9:45
 End time: 12:45
 Total time running (hours): 3
 Total volume of water passed: 36
 Initial volume of oil added to column: 2000

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
 50 ul gas sample injected into GC

Water Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60	2737.60	80.86	179102.70	19.20	230.44	28949.50	1.27	15.20
90	3448.40	101.52	166017.10	17.79	320.27	16083.80	0.68	12.30
120	3497.50	102.95	138602.80	14.84	356.12	12866.30	0.54	12.90
150	4543.30	133.35	215339.30	23.11	693.25	18082.40	0.77	23.22
180	5216.70	152.93	238797.60	25.64	922.91	17270.40	0.74	26.53
Average		114.32		20.12			0.80	
Sum					2522.99			90.15

Oil Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60			39935.80	287.40	172.44	32746.40	260.39	3124.72
90			49713.50	365.62	329.06	38339.30	305.14	5492.46
120			40273.40	290.10	348.12	37623.20	299.41	7185.79
150			23041.80	152.24	228.37	19618.90	155.37	4661.21
180			26809.30	182.38	328.29	23999.20	190.42	6854.97
Average				255.55			242.15	
Sum					1406.27			27319.15

Oil samples

100 ml methanol, 1 ul liquid sample injected into GC

time	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	PCE peak count	conc. mg/L
start sample 1	591.40	425.13	41290.60	298.24	38499.20	306.42
start sample 2			40257.80	289.97	34947.40	278.00
Average start	591.40	425.13	40774.20	294.10	36723.30	292.21
end sample 1						
end sample 2		column drained	-			
Average end						

Appendix E - Liquid-Liquid Contacting Reactor Continuous Flow Data

Run #: 4
 Date: 22-May-98
 Water flow rate (ml/min): 100
 Oil flow rate (ml/min): 25
 Start time: 7:50
 End time: 11:50
 Total time running (hours): 3 hours with recycle)
 Total volume of water passed (l): 18
 Initial volume of oil added to col: 2000

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
 50 ul gas sample injected into GC

Water Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60	5051.60	148.13	561365.80	60.40	362.40	60125.70	2.68	16.08
90	5224.30	153.15	377534.00	40.59	365.29	41836.80	1.85	16.66
120	5361.20	157.13	274184.70	29.45	353.40	26935.30	1.18	14.10
150	6000.40	175.71	241630.70	25.94	389.13	37623.30	1.66	24.90
180	5827.00	170.67	226726.20	24.34	438.04	31183.10	1.37	24.62
	Average	160.96		30.08			1.75	
				Sum	1908.25			96.37

Oil Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60			40556.10	292.36	438.54	33979.00	270.25	1621.53
90			42304.10	306.34	689.27	37832.80	301.08	2709.76
120			40764.30	294.02	882.07	35902.10	285.64	3427.67
150			42881.60	310.96	1166.11	36345.20	289.18	4337.76
180			45677.00	333.33	1499.97	40552.90	322.85	5811.22
	Average			307.40			293.80	
				Sum	4675.97			17907.94

Oil samples
 pace, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	PCE peak count	conc. mg/L
start sample 1	275.40	63.99	48603.50	356.74	40545.80	322.79
start sample 2						
Average start	275.40	63.99	48603.50	356.74	40545.80	322.79
end sample 1			47310.90	346.40	42761.50	340.51
end sample 2						
Average end			47310.90	346.40	42761.50	340.51

Appendix E - Liquid-Liquid Contacting Reactor Continuous Flow Data

Run #: 5
 Date: 26-May-98
 Water flow rate (ml/min): 350
 Oil flow rate (ml/min): 25
 Start time: 9:17
 End time: 12:17
 Total time running (hours): 3 ours with recycle)
 Total volume of water passed (63
 Initial volume of oil added to col 2000

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)

50 ul gas sample injected into GC

Water Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60	3324.60	97.92	353666.20	38.02	798.33	45943.70	2.04	42.78
90	2767.40	81.72	157310.50	16.85	530.92	19681.80	0.85	26.66
120	1898.50	56.46	107382.80	11.47	481.90	18219.80	0.78	32.76
150	3321.30	97.83	225142.80	24.16	1268.65	33033.00	1.45	76.22
180	2554.40	75.53	176730.50	18.95	1193.69	21877.00	0.95	59.59
	Average	81.89		17.86			1.21	
				Sum	4273.49			238.02

Oil Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60			34267.40	242.05	363.07	31608.10	251.29	5277.03
90			33443.40	235.46	529.78	31881.90	253.48	7984.54
120			41367.80	298.85	896.56	35721.80	284.20	11936.26
180			37422.30	267.29	1202.80	32571.80	259.00	16316.79
	Average			237.85			226.97	
				Sum	3538.26			46077.50

Oil samples

pace, 100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	PCE peak count	conc. mg/L
start sample 1			40163.70	289.22	33593.20	267.17
start sample 2			42947.70	311.49	40518.80	322.57
Average start			41556.70	300.36	37056.00	294.87
end sample 1			34388.20	243.02	43179.40	343.86
end sample 2						
Average end			34388.20	243.02	43179.40	343.86

Appendix E - Liquid-Liquid Contacting Reactor Continuous Flow Data

Run #: 6
 Date: 27-May-98
 Water flow rate (ml/min): 200
 Oil flow rate (ml/min): 5
 Start time: 9:17
 End time: 12:17
 Total time running (hours): 3 hours with recycle)
 Total volume of water passed (l): 36
 Initial volume of oil added to column: 2000

Sampling of headspace (40 ml bottles, 25 ml liquid sample, 15 ml headspace)
 50 ul gas sample injected into GC

Water Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60	2548.30	75.35	516026.90	55.51	666.16	54075.80	2.41	28.87
90	2398.30	70.99	173199.50	18.57	334.20	44634.90	1.98	35.60
120	2262.50	67.05	141185.50	15.12	362.80	26722.40	1.17	27.98
150	2145.40	63.64	155948.50	16.71	501.23	27222.70	1.19	35.65
180	2380.90	70.49	227302.90	24.40	878.31	37998.60	1.68	60.37
	Average	69.50		18.70			1.50	
				Sum	2742.71			188.47

Oil Outlet samples

time (min)	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	Mass mg	PCE peak count	conc. mg/L	Mass mg
60			40849.30	294.70	88.41	40176.80	319.84	3838.04
90			31830.60	222.56	100.15	31829.10	253.06	4554.99
120			17175.80	105.32	63.19	17007.80	134.48	3227.63
150			30351.60	210.72	158.04	33632.00	267.48	8024.35
180								
	Average			208.33			243.71	
				Sum	409.79			19645.02

Oil samples
 (100 ml methanol, 1 ul liquid sample injected into GC)

time	DCM peak count	conc. mg/L	CT peak count	conc. mg/L	PCE peak count	conc. mg/L
start sample 1			34388.20	243.02	43179.40	343.86
start sample 2						
Average start			34388.20	243.02	43179.40	343.86
end sample 1			38860.10	278.79	38339.40	305.14
end sample 2			38933.50	279.38	38989.40	310.34
Average end			38896.80	279.08	38664.40	307.74

Appendix F

Table F-1: Observed and Predicted Mass Transfer Coefficients for DCM with Water as the Scrubbing Solution

Run#	Cg inlet (mg/L)	Ql (ml/min)	Vl (m/min)	Qg (ml/min)	Vg (m/min)	Qg/Ql	Kla Onda (1/sec)	Kla Observed (1/sec)
26	8.03	60	0.007	1135.51	0.140	18.93	5.57E-04	1.39E-04
26	8.03	60	0.007	1135.51	0.140	18.93	5.57E-04	1.39E-04
34	6.27	60	0.007	1135.51	0.140	18.93	5.57E-04	
34	6.27	60	0.007	1135.51	0.140	18.93	5.57E-04	
9	17.10	60	0.007	1535.47	0.189	25.59	5.93E-04	
44	3.31	60	0.007	1535.47	0.189	25.59	5.93E-04	
44	3.31	60	0.007	1535.47	0.189	25.59	5.93E-04	
47	5.79	60	0.007	1535.47	0.189	25.59	5.93E-04	6.63E-04
47	5.79	60	0.007	1535.47	0.189	25.59	5.93E-04	6.63E-04
47	5.79	60	0.007	1535.47	0.189	25.59	5.93E-04	6.63E-04
7	11.72	60	0.007	5850.09	0.722	97.50	7.09E-04	
25	8.50	100	0.012	1135.51	0.140	11.36	7.78E-04	1.28E-04
25	8.50	100	0.012	1135.51	0.140	11.36	7.78E-04	1.28E-04
25	8.50	100	0.012	1135.51	0.140	11.36	7.78E-04	1.28E-04
35	6.79	100	0.012	1135.51	0.140	11.36	7.78E-04	1.44E-03
35	6.79	100	0.012	1135.51	0.140	11.36	7.78E-04	1.44E-03
10	17.17	100	0.012	1535.47	0.189	15.35	8.35E-04	1.02E-03
42	10.94	100	0.012	1535.47	0.189	15.35	8.35E-04	7.60E-02
42	10.94	100	0.012	1535.47	0.189	15.35	8.35E-04	7.60E-02
42	10.94	100	0.012	1535.47	0.189	15.35	8.35E-04	7.60E-02
27	15.71	200	0.025	1135.51	0.140	5.68	1.20E-03	1.52E-03
27	15.71	200	0.025	1135.51	0.140	5.68	1.20E-03	1.52E-03
36	1.68	200	0.025	1135.51	0.140	5.68	1.20E-03	8.23E-04
36	6.77	200	0.025	1135.51	0.140	5.68	1.20E-03	8.23E-04
11	17.17	200	0.025	1535.47	0.189	7.68	1.31E-03	8.34E-03
43	11.55	200	0.025	1535.47	0.189	7.68	1.31E-03	2.38E-03
43	11.55	200	0.025	1535.47	0.189	7.68	1.31E-03	2.38E-03
43	11.55	200	0.025	1535.47	0.189	7.68	1.31E-03	2.38E-03
37	6.79	200	0.025	3117.99	0.385	15.59	1.53E-03	7.12E-04
45	4.30	200	0.025	4740.18	0.585	23.70	1.65E-03	4.46E-03
45	4.30	200	0.025	4740.18	0.585	23.70	1.65E-03	4.46E-03
45	4.30	200	0.025	4740.18	0.585	23.70	1.65E-03	4.46E-03
38	4.32	200	0.025	4917.19	0.607	24.59	1.65E-03	1.90E-04
38	4.32	200	0.025	4917.19	0.607	24.59	1.65E-03	1.90E-04

Appendix F

Table F-2: Observed and Predicted Mass Transfer Coefficients for CT
with Water as the Scrubbing Solution

Run#	Cg inlet (mg/L)	Ql (ml/min)	Vl (m/min)	Qg (ml/min)	Vg (m/min)	Qg/Ql	Kla Onda (1/sec)	Kla Observed (1/sec)
34	19.79	60	0.007	1135.51	0.140	18.93	6.29E-04	6.68E-03
34	19.79	60	0.007	1135.51	0.140	18.93	6.29E-04	6.68E-03
26	26.00	60	0.007	1135.51	0.140	18.93	6.29E-04	6.09E-03
26	26.00	60	0.007	1135.51	0.140	18.93	6.29E-04	6.09E-03
44	5.21	100	0.012	1135.51	0.140	11.36	9.19E-04	6.51E-03
44	5.21	100	0.012	1135.51	0.140	11.36	9.19E-04	6.51E-03
47	11.46	100	0.012	1135.51	0.140	11.36	9.19E-04	6.53E-03
47	11.46	100	0.012	1135.51	0.140	11.36	9.19E-04	6.53E-03
47	11.46	100	0.012	1135.51	0.140	11.36	9.19E-04	6.53E-03
9	34.47	200	0.025	1135.51	0.140	5.68	1.52E-03	6.04E-03
7	19.35	200	0.025	1135.51	0.140	5.68	1.52E-03	6.10E-03
7	19.35	200	0.025	1135.51	0.140	5.68	1.52E-03	6.10E-03
25	13.59	200	0.025	1135.51	0.140	5.68	1.52E-03	1.16E-02
25	13.59	60	0.007	1535.47	0.189	25.59	6.43E-04	1.16E-02
25	13.59	60	0.007	1535.47	0.189	25.59	6.43E-04	1.16E-02
35	17.53	60	0.007	1535.47	0.189	25.59	6.43E-04	1.15E-02
35	17.53	60	0.007	1535.47	0.189	25.59	6.43E-04	1.15E-02
42	23.37	60	0.007	1535.47	0.189	25.59	6.43E-04	1.04E-02
42	23.37	60	0.007	1535.47	0.189	25.59	6.43E-04	1.04E-02
42	23.37	100	0.012	1535.47	0.189	15.35	9.43E-04	1.04E-02
10	34.26	100	0.012	1535.47	0.189	15.35	9.43E-04	1.04E-02
36	16.19	100	0.012	1535.47	0.189	15.35	9.43E-04	2.57E-02
36	16.19	100	0.012	1535.47	0.189	15.35	9.43E-04	2.57E-02
27	27.74	200	0.025	1535.47	0.189	7.68	1.57E-03	2.15E-02
27	27.74	200	0.025	1535.47	0.189	7.68	1.57E-03	2.15E-02
43	23.37	200	0.025	1535.47	0.189	7.68	1.57E-03	2.44E-02
43	23.37	200	0.025	1535.47	0.189	7.68	1.57E-03	2.44E-02
43	23.37	200	0.025	3117.99	0.385	15.59	1.66E-03	2.44E-02
11	34.26	200	0.025	4740.18	0.585	23.70	1.70E-03	2.17E-02
37	13.53	200	0.025	4740.18	0.585	23.70	1.70E-03	2.25E-02
45	4.34	200	0.025	4917.19	0.607	24.59	1.71E-03	2.18E-02
45	4.34	200	0.025	4917.19	0.607	24.59	1.71E-03	2.18E-02
38	13.53	60	0.007	5850.09	0.722	97.50	6.80E-04	2.18E-02
38	13.53	60	0.007	5850.09	0.722	97.50	6.80E-04	2.18E-02
39	13.53	200	0.025	6707.59	0.828	33.54	1.73E-03	2.13E-02

Appendix F

Table F-3: Observed and Predicted Mass Transfer Coefficients for PCE with Water as the Scrubbing Solution

Run#	Cg inlet	Ql	Vl	Qg	Vg	Qg/Ql	Kla Onda	Kla Observed
	(mg/L)	(ml/min)	(m/min)	(ml/min)	(m/min)		(1/sec)	(1/sec)
34	21.97	60	0.007	1135.51	0.140	18.93	5.61E-04	6.97E-03
34	21.97	60	0.007	1135.51	0.140	18.93	5.61E-04	6.97E-03
26	31.89	60	0.007	1135.51	0.140	18.93	5.61E-04	7.02E-03
26	31.89	60	0.007	1135.51	0.140	18.93	5.61E-04	7.02E-03
47	9.54	60	0.007	1535.47	0.189	25.59	5.81E-04	6.85E-03
47	9.54	60	0.007	1535.47	0.189	25.59	5.81E-04	6.85E-03
9	25.65	60	0.007	1535.47	0.189	25.59	5.81E-04	6.79E-03
7	15.83	60	0.007	5850.09	0.722	97.50	6.38E-04	6.23E-03
7	15.83	60	0.007	5850.09	0.722	97.50	6.38E-04	6.23E-03
35	21.97	100	0.012	1135.51	0.140	11.36	8.07E-04	1.26E-02
25	31.87	100	0.012	1135.51	0.140	11.36	8.07E-04	1.25E-02
25	31.87	100	0.012	1135.51	0.140	11.36	8.07E-04	1.25E-02
25	31.87	100	0.012	1135.51	0.140	11.36	8.07E-04	1.25E-02
35	31.87	100	0.012	1135.51	0.140	11.36	8.07E-04	1.25E-02
42	15.19	100	0.012	1535.47	0.189	15.35	8.41E-04	1.19E-02
42	15.19	100	0.012	1535.47	0.189	15.35	8.41E-04	1.19E-02
42	15.19	100	0.012	1535.47	0.189	15.35	8.41E-04	1.19E-02
10	25.76	100	0.012	1535.47	0.189	15.35	8.41E-04	1.19E-02
36	15.79	200	0.025	1135.51	0.140	5.68	1.30E-03	3.00E-02
36	15.79	200	0.025	1135.51	0.140	5.68	1.30E-03	3.00E-02
27	30.69	200	0.025	1135.51	0.140	5.68	1.30E-03	3.00E-02
27	30.69	200	0.025	1135.51	0.140	5.68	1.30E-03	3.00E-02
43	17.57	200	0.025	1535.47	0.189	7.68	1.37E-03	2.71E-02
43	17.57	200	0.025	1535.47	0.189	7.68	1.37E-03	2.71E-02
43	17.57	200	0.025	1535.47	0.189	7.68	1.37E-03	2.71E-02
11	25.76	200	0.025	1535.47	0.189	7.68	1.37E-03	2.73E-02
37	15.53	200	0.025	3117.99	0.385	15.59	1.50E-03	2.39E-02
45	3.2	200	0.025	4740.18	0.585	23.70	1.56E-03	2.27E-02
45	3.2	200	0.025	4740.18	0.585	23.70	1.56E-03	2.27E-02
45	3.2	200	0.025	4740.18	0.585	23.70	1.56E-03	2.27E-02
38	15.53	200	0.025	4917.19	0.607	24.59	1.57E-03	2.27E-02
38	15.53	200	0.025	4917.19	0.607	24.59	1.57E-03	2.27E-02
38	15.53	200	0.025	4917.19	0.607	24.59	1.57E-03	2.27E-02
39	15.53	200	0.025	6707.59	0.828	33.54	1.60E-03	2.21E-02

Appendix F

Table F-4: Observed and Predicted Mass Transfer Coefficients for DCM in Oil

Run #	Cg in (mg/L)	Ql (ml/min)	Vl (m/min)	Qg (ml/min)	Vg (m/min)	Qg/Ql	Kla Onda (1/sec)	Kla Observed (1/sec)
5	8.78	10	0.001	5850.09	0.722	585.01	6.94E-07	
5	8.78	10	0.001	5850.09	0.722	585.01	6.94E-07	
16	6.91	10	0.001	8540.28	1.054	854.03	6.94E-07	
15	11.05	10	0.001	12210.94	1.507	1221.09	6.94E-07	
15	11.05	10	0.001	12210.94	1.507	1221.09	6.94E-07	
32	7.08	60	0.007	1135.51	0.140	18.93	2.84E-06	1.77E-03
32	7.08	60	0.007	1135.51	0.140	18.93	2.84E-06	1.77E-03
32	7.08	60	0.007	1135.51	0.140	18.93	2.84E-06	1.77E-03
22	12.39	60	0.007	1135.51	0.140	18.93	2.84E-06	1.77E-03
22	12.39	60	0.007	1135.51	0.140	18.93	2.84E-06	1.77E-03
49	5.82	60	0.007	1535.47	0.189	25.59	2.85E-06	2.67E-03
49	5.82	60	0.007	1535.47	0.189	25.59	2.85E-06	2.67E-03
12	14.39	60	0.007	1535.47	0.189	25.59	2.85E-06	2.67E-03
51	4.85	60	0.007	3611.98	0.446	60.20	2.86E-06	1.86E-02
51	4.85	60	0.007	3611.98	0.446	60.20	2.86E-06	1.86E-02
51	4.85	60	0.007	3611.98	0.446	60.20	2.86E-06	1.86E-02
1	9.05	60	0.007	3611.98	0.446	60.20	2.86E-06	1.86E-02
2	11.44	60	0.007	3611.98	0.446	60.20	2.86E-06	1.86E-02
2	11.44	60	0.007	3611.98	0.446	60.20	2.86E-06	1.86E-02
2	11.44	60	0.007	3611.98	0.446	60.20	2.86E-06	1.86E-02
2	11.44	60	0.007	3611.98	0.446	60.20	2.86E-06	1.86E-02
52	4.04	60	0.007	5850.09	0.722	97.50	2.87E-06	
52	4.04	60	0.007	5850.09	0.722	97.50	2.87E-06	
52	4.04	60	0.007	5850.09	0.722	97.50	2.87E-06	
3	5.78	60	0.007	5850.09	0.722	97.50	2.87E-06	
3	5.78	60	0.007	5850.09	0.722	97.50	2.87E-06	
3	5.78	60	0.007	5850.09	0.722	97.50	2.87E-06	
3	5.78	60	0.007	5850.09	0.722	97.50	2.87E-06	
3	5.78	60	0.007	5850.09	0.722	97.50	2.87E-06	
21	12.53	60	0.007	6263.51	0.773	104.39	2.87E-06	
21	12.53	60	0.007	6263.51	0.773	104.39	2.87E-06	
21	12.53	60	0.007	6263.51	0.773	104.39	2.87E-06	
13	7.37	60	0.007	8540.28	1.054	142.34	2.87E-06	
29	2.74	60	0.007	10395.87	1.283	173.26	2.87E-06	
29	2.74	60	0.007	10395.87	1.283	173.26	2.87E-06	
28	4.83	60	0.007	10395.87	1.283	173.26	2.87E-06	
28	4.83	60	0.007	10395.87	1.283	173.26	2.87E-06	
30	6.71	60	0.007	10395.87	1.283	173.26	2.87E-06	
30	6.71	60	0.007	10395.87	1.283	173.26	2.87E-06	
31	5.40	60	0.007	12607.43	1.556	210.12	2.87E-06	
31	5.40	60	0.007	12607.43	1.556	210.12	2.87E-06	
20	5.80	60	0.007	12607.43	1.556	210.12	2.87E-06	
14	6.06	60	0.007	13003.93	1.605	216.73	2.87E-06	
33	5.77	100	0.012	1135.51	0.140	11.36	4.24E-06	1.59E-03
24	9.96	100	0.012	1135.51	0.140	11.36	4.24E-06	1.59E-03
24	9.96	100	0.012	1135.51	0.140	11.36	4.24E-06	1.59E-03
50	5.82	100	0.012	1535.47	0.189	15.35	4.26E-06	2.27E-03
50	5.82	100	0.012	1535.47	0.189	15.35	4.26E-06	2.27E-03
54	2.20	100	0.012	8540.28	1.054	85.40	4.29E-06	
54	2.20	100	0.012	8540.28	1.054	85.40	4.29E-06	
54	2.20	100	0.012	8540.28	1.054	85.40	4.29E-06	

Table F-4: Observed and Predicted Mass Transfer Coefficients for DCM in Oil

Run #	Cg in (mg/L)	Ql (ml/min)	Vl (m/min)	Qg (ml/min)	Vg (m/min)	Qg/Ql	Kla Onda (1/sec)	Kla Observed (1/sec)
18	11.74	100	0.012	8540.28	1.054	85.40	4.29E-06	
18	11.74	100	0.012	8540.28	1.054	85.40	4.29E-06	
18	11.74	100	0.012	8540.28	1.054	85.40	4.29E-06	
52	2.20	200	0.025	8899.29	1.098	44.50	7.38E-06	
52	2.20	200	0.025	8899.29	1.098	44.50	7.38E-06	

Appendix F

Table F-5: Observed and Predicted Mass Transfer Coefficients for CT in Oil

Run #	Cg in (mg/L)	Ql (ml/min)	VI (m/min)	Qg (ml/min)	Vg (m/min)	Qg/Ql	Kla Onda (1/sec)	Kla Observed (1/sec)
5	12.63	10	0.001	5850.09	0.722	585.01	9.21E-07	
5	12.63	10	0.001	5850.09	0.722	585.01	9.21E-07	
5	12.63	10	0.001	5850.09	0.722	585.01	9.21E-07	
16	19.75	10	0.001	8540.28	1.054	854.03	9.43E-07	5.33E-04
15	18.22	10	0.001	12210.94	1.507	1221.09	9.62E-07	
15	18.22	10	0.001	12210.94	1.507	1221.09	9.62E-07	
32	21.10	60	0.007	1135.51	0.140	18.93	2.59E-06	5.31E-05
32	21.10	60	0.007	1135.51	0.140	18.93	2.59E-06	5.31E-05
32	21.10	60	0.007	1135.51	0.140	18.93	2.59E-06	5.31E-05
22	38.30	60	0.007	1135.51	0.140	18.93	2.59E-06	3.92E-05
22	38.30	60	0.007	1367.27	0.169	22.79	2.65E-06	3.92E-05
12	31.72	60	0.007	1535.47	0.189	25.59	2.68E-06	
1	18.98	60	0.007	3611.98	0.446	60.20	2.91E-06	2.04E-04
2	19.11	60	0.007	3611.98	0.446	60.20	2.91E-06	2.04E-04
2	19.11	60	0.007	3611.98	0.446	60.20	2.91E-06	1.98E-04
2	19.11	60	0.007	3611.98	0.446	60.20	2.91E-06	1.98E-04
2	19.11	60	0.007	3611.98	0.446	60.20	2.91E-06	1.98E-04
3	15.60	60	0.007	5850.09	0.722	97.50	3.03E-06	3.69E-05
3	15.60	60	0.007	5850.09	0.722	97.50	3.03E-06	4.19E-04
3	15.60	60	0.007	5850.09	0.722	97.50	3.03E-06	4.19E-04
3	15.60	60	0.007	5850.09	0.722	97.50	3.03E-06	4.19E-04
3	15.60	60	0.007	5850.09	0.722	97.50	3.03E-06	4.19E-04
21	22.44	60	0.007	6263.51	0.773	104.39	3.04E-06	2.99E-04
21	22.44	60	0.007	6263.51	0.773	104.39	3.04E-06	2.99E-04
21	22.44	60	0.007	6263.51	0.773	104.39	3.04E-06	2.99E-04
13	12.33	60	0.007	8540.28	1.054	142.34	3.10E-06	5.59E-04
29	3.54	60	0.007	10395.87	1.283	173.26	3.14E-06	1.52E-03
29	3.54	60	0.007	10395.87	1.283	173.26	3.14E-06	5.16E-04
28	6.03	60	0.007	10395.87	1.283	173.26	3.14E-06	4.60E-04
28	6.03	60	0.007	10395.87	1.283	173.26	3.14E-06	4.60E-04
30	9.52	60	0.007	10395.87	1.283	173.26	3.14E-06	3.37E-04
31	7.26	60	0.007	12607.43	1.556	210.12	3.17E-06	8.73E-04
31	7.26	60	0.007	12607.43	1.556	210.12	3.17E-06	8.73E-04
31	7.26	60	0.007	12607.43	1.556	210.12	3.17E-06	8.73E-04
20	7.87	60	0.007	12607.43	1.556	210.12	3.17E-06	3.70E-04
14	7.93	60	0.007	13003.93	1.605	216.73	3.18E-06	6.46E-04
24	14.19	100	0.012	1135.51	0.140	11.36	3.60E-06	3.69E-05
24	14.19	100	0.012	1135.51	0.140	11.36	3.60E-06	3.69E-05
33	18.81	100	0.012	1135.51	0.140	11.36	3.60E-06	7.41E-05
33	18.81	100	0.012	1135.51	0.140	11.36	3.60E-06	7.41E-05
23	35.01	100	0.012	1135.51	0.140	11.36	3.60E-06	8.15E-05
18	16.40	100	0.012	8540.28	1.054	85.40	4.35E-06	5.24E-04
18	16.40	100	0.012	8540.28	1.054	85.40	4.35E-06	5.24E-04
18	16.40	100	0.012	8540.28	1.054	85.40	4.35E-06	5.24E-04
17	19.66	100	0.012	8540.28	1.054	85.40	4.35E-06	5.64E-04

Appendix F

Table F-6: Observed and Predicted Mass Transfer Coefficients for PCE in Oil

Run #	Cg in (mg/L)	Ql (ml/min)	Vl (m/min)	Qg (ml/min)	Vg (m/min)	Qg/Ql	Kla Onda (1/sec)	Kla Observed (1/sec)
5	11.20	10	0.001	5850.09	0.722	585.01	8.77E-07	3.12E-05
5	11.20	10	0.001	5850.09	0.722	585.01	8.77E-07	
16	14.59	10	0.001	8540.28	1.054	854.03	9E-07	6.89E-05
15	13.70	10	0.001	12210.94	1.507	1221.09	9.2E-07	9.54E-05
15	13.70	10	0.001	12210.94	1.507	1221.09	9.2E-07	1.07E-04
32	18.25	60	0.007	1135.51	0.140	18.93	2.1E-06	3.95E-06
32	18.25	60	0.007	1135.51	0.140	18.93	2.1E-06	3.95E-06
32	18.25	60	0.007	1135.51	0.140	18.93	2.1E-06	3.95E-06
32	16.67	60	0.007	1135.51	0.140	18.93	2.1E-06	6.38E-06
22	32.76	60	0.007	1135.51	0.140	18.93	2.1E-06	3.74E-06
22	32.76	60	0.007	1349.47	0.167	22.49	2.2E-06	3.74E-06
49	11.04	60	0.007	1535.47	0.189	25.59	2.29E-06	4.36E-05
49	11.07	60	0.007	1535.47	0.189	25.59	2.29E-06	1.92E-05
12	28.80	60	0.007	1535.47	0.189	25.59	2.3E-06	1.33E-05
51	6.74	60	0.007	3611.98	0.446	60.20	2.65E-06	2.22E-05
51	6.74	60	0.007	3611.98	0.446	60.20	2.65E-06	
51	6.74	60	0.007	3611.98	0.446	60.20	2.65E-06	
2	15.33	60	0.007	3611.98	0.446	60.20	2.6E-06	2.21E-05
2	15.33	60	0.007	3611.98	0.446	60.20	2.6E-06	2.21E-05
2	15.33	60	0.007	3611.98	0.446	60.20	2.6E-06	2.21E-05
2	15.33	60	0.007	3611.98	0.446	60.20	2.6E-06	2.21E-05
1	21.69	60	0.007	3611.98	0.446	60.20	2.6E-06	3.96E-05
52	4.39	60	0.007	5850.09	0.722	97.50	2.80E-06	6.61E-05
3	10.71	60	0.007	5850.09	0.722	97.50	2.80E-06	4.36E-05
3	10.71	60	0.007	5850.09	0.722	97.50	2.80E-06	4.36E-05
3	10.71	60	0.007	5850.09	0.722	97.50	2.80E-06	4.36E-05
3	10.71	60	0.007	5850.09	0.722	97.50	2.80E-06	4.36E-05
21	14.21	60	0.007	6263.51	0.773	104.39	2.8E-06	3.47E-05
21	16.85	60	0.007	6263.51	0.773	104.39	2.8E-06	4.69E-05
21	16.85	60	0.007	6263.51	0.773	104.39	2.8E-06	4.69E-05
13	6.92	60	0.007	8540.28	1.054	142.34	2.90E-06	8.07E-05
29	3.24	60	0.007	10395.87	1.283	173.26	2.95E-06	4.21E-05
29	3.24	60	0.007	10395.87	1.283	173.26	2.95E-06	4.21E-05
29	3.24	60	0.007	10395.87	1.283	173.26	2.95E-06	4.21E-05
28	4.02	60	0.007	10395.87	1.283	173.26	2.95E-06	6.61E-05
28	4.02	60	0.007	10395.87	1.283	173.26	2.95E-06	6.61E-05
28	4.02	60	0.007	10395.87	1.283	173.26	2.95E-06	6.61E-05
30	5.93	60	0.007	10395.87	1.283	173.26	2.95E-06	7.98E-05
30	5.93	60	0.007	10395.87	1.283	173.26	2.95E-06	7.98E-05
30	5.93	60	0.007	10395.87	1.283	173.26	2.95E-06	7.98E-05
14	5.32	60	0.007	12607.43	1.556	210.12	2.99E-06	3.23E-05
31	6.23	60	0.007	12607.43	1.556	210.12	2.99E-06	6.31E-05
31	6.23	60	0.007	12607.43	1.556	210.12	2.99E-06	6.31E-05
31	6.23	60	0.007	12607.43	1.556	210.12	2.99E-06	6.31E-05
20	6.48	60	0.007	12607.43	1.556	210.12	2.99E-06	9.01E-05
33	19.20	100	0.012	1135.51	0.140	11.36	2.8E-06	6.15E-06
33	19.20	100	0.012	1135.51	0.140	11.36	2.8E-06	6.15E-06
33	19.20	100	0.012	1135.51	0.140	11.36	2.8E-06	6.15E-06
24	28.52	100	0.012	1135.51	0.140	11.36	2.8E-06	4.12E-06
24	28.52	100	0.012	1135.51	0.140	11.36	2.8E-06	4.12E-06
50	11.04	100	0.012	1535.47	0.189	15.35	3.06E-06	4.36E-05
50	11.07	100	0.012	1535.47	0.189	15.35	3.06E-06	1.48E-05
18	10.39	100	0.012	8540.28	1.054	85.40	4.03E-06	6.80E-05
18	10.39	100	0.012	8540.28	1.054	85.40	4.03E-06	6.80E-05
18	10.39	100	0.012	8540.28	1.054	85.40	4.03E-06	6.80E-05
17	16.70	100	0.012	8540.28	1.054	85.40	4.03E-06	4.69E-05

Appendix G

Sample Calculations

Sample Calculation of diffusivity of DCM in water:DCM – dichloromethane – CH_2Cl_2

$$T = 20\text{ }^\circ\text{C} + 273 = 293\text{ K}$$

$$\mu_w = 1.002\text{ cp}$$

Molal Volume

$$C = 1 \times 14.8$$

$$H = 2 \times 3.7$$

$$Cl = 2 \times 24.6$$

$$V'_B = 71.4\text{ cm}^3/\text{mol}$$

$$D = \frac{13.26 \times 10^{-5}}{(1.002\text{ cp})^{1.14} \left(71.4 \frac{\text{cm}^3}{\text{mol}} \right)^{0.589}}$$

$$D_{\text{DCM}} = 1.0708 \times 10^{-9}\text{ m}^2/\text{sec}$$

Sample Calculation of diffusivity of DCM in air:

$$M_r = \frac{28.97 + 84.93}{28.97 \times 84.93}$$

$$M_r = 4.629 \times 10^{-2}$$

$$C = 1 \times 16.5$$

$$H = 2 \times 1.98$$

$$Cl = 2 \times 19.5$$

$$V_B = 57.48\text{ cm}^3/\text{mol}$$

$$D_{DCM} = \frac{10^{-3} 293^{1.75} \sqrt{4.629 \times 10^{-2}}}{(20.1^{1/3} + 57.48^{1/3})^2}$$

$$D_{DCM} = 1.0296 \times 10^{-5} \text{ m}^2/\text{sec}$$

Sample Calculation for EPICS test

The following presents a sample calculation of the gas-liquid partitioning coefficient for CT with 40 % methanol addition. The calculation employs equation 2.11 and the data from table 4.1, using the first high and low volume system bottles (H1 and H2).

$$K_c = \frac{\left[\left(\frac{2509842}{9262182} \right) 100 \text{ ml} - 10 \text{ ml} \right]}{\left[150 \text{ ml} - \left(\frac{2509842}{9262182} \right) 60 \text{ ml} \right]}$$

$$K_c = 0.128$$

All other gas-liquid partitioning coefficients were determined similarly to the above sample calculation.

Appendix H

H.1 Solving Differential Equations for Scrubber Model

The following section presents the manipulation and simplification involved in simultaneously solving the differential equations 5.4 and 5.5. For simplicity purposes, the principal equations employed in the model were clearly outlined.

Differentiating equation 5.5 yields:

$$\frac{d^2 C_g}{dz^2} = \frac{k_2}{H} \frac{dC_g}{dz} - k_2 \frac{dC_L}{dz} \quad (\text{H-1})$$

Substituting 5.4 into H-1:

$$\frac{d^2 C_g}{dz^2} = \frac{k_2}{H} \frac{dC_g}{dz} - k_2 \left(-k_1 C_L + \frac{k_1}{H} C_g \right) \quad (\text{H-2})$$

Solving equation 5.5 in terms of C_L yields:

$$C_L = \frac{C_g}{H} - \frac{1}{k_2} \frac{dC_g}{dz} \quad (\text{H-3})$$

Substituting equation H-3 into H-2:

$$\frac{d^2 C_g}{dz^2} = \frac{k_2}{H} \frac{dC_g}{dz} - k_2 \left(-k_1 \left(\frac{C_g}{H} - \frac{1}{k_2} \frac{dC_g}{dz} \right) + \frac{k_1}{H} C_g \right) \quad (\text{H-4})$$

Simplifying yields:

$$\frac{d^2 C_g}{dz^2} = \frac{dC_g}{dz} \left(\frac{k_2}{H} - k_1 \frac{dC_g}{dz} \right)$$

$$\boxed{\frac{d^2 C_g}{dz^2} = \frac{dC_g}{dz} \left(\frac{k_2}{H} - k_1 \right)} \quad (\text{H-5})$$

Solving the differential equation of equation H-5 yields the following general solution,

$$r^2 - r \left(\frac{k_2}{H} - k_1 \right) = 0$$

where : r = roots of the general solution

The roots are therefore: $r = 0$

$$r = \frac{k_2}{H} - k_1$$

The general solution in terms of the gas concentration can be written as:

$$\boxed{C_g = C_1 + C_2 \exp \left(\left(\frac{k_2}{H} - k_1 \right) z \right)} \quad (\text{H-6})$$

Differentiating equation H-6:

$$\frac{dC_g}{dz} = \left(\frac{k_2}{H} - k_1 \right) C_2 \exp \left(\left(\frac{k_2}{H} - k_1 \right) z \right) \quad (\text{H-7})$$

Substituting equation H-7 and H-6 into 5.5 yields:

$$\left(\frac{k_2}{H} - k_1\right) C_2 \exp\left(\frac{k_2}{H} - k_1\right) z = \frac{k_2}{H} C_1 + \frac{k_2}{H} C_2 \exp\left(\frac{k_2}{H} - k_1\right) z - k_2 C_L \quad (\text{H-8})$$

Figure H- 1: Boundary Conditions on the system

$$\text{Boundary Conditions: } C_{lo} = C_l \quad z = 0 \quad (\text{i})$$

$$C_g = C_{go} \quad z = L \quad (\text{ii})$$

Using boundary condition (i) and equation H-8 yields:

$$\left(\frac{k_2}{H} - k_1\right) C_2 = \frac{k_2}{H} C_1 + \frac{k_2}{H} C_2 - k_2 C_{Lo}$$

Simplifying:

$$C_1 = -C_2 H \frac{k_1}{k_2} + C_{Lo} H \quad (H-9)$$

Substituting equation H-9 into H-6:

$$C_g = C_2 \left(-\frac{k_1}{k_2} H \right) + H C_{Lo} + C_2 \exp \left(\frac{k_2}{H} k_1 \right) z$$

Rearranging for C_2 and using the boundary equation (ii) yields:

$$C_2 = \frac{C_{go} - C_{Lo} H}{\left[-\frac{k_1 H}{k_2} + \exp \left(\frac{k_2}{H} k_1 \right) L \right]} \quad (H-10)$$

At $z = 0$,

$$C_{gout} = C_1 + C_2 \quad (H-11)$$

Rearranging equation H-7 and solving for C_L ,

$$C_L = \frac{C_1}{H} + \frac{k_1}{k_2} C_2 \exp \left(\frac{k_2}{H} k_1 \right) \quad (H-12)$$

The above method of simultaneously solving the differential equations was also employed for the liquid phase equations as a verification to ensure the equations were accurate.

Appendix I

Standard Error on Liquid-Liquid Mass Transfer Coefficients

Table I-1: Mass Transfer Coefficients Obtained from Pseudo Steady State Conditions in the Semi-Batch Experiments with the Liquid-Liquid Reactor

Run #	CT (1/sec)	PCE (1/sec)
1	$5.83 \times 10^{-6} \pm 3.61 \times 10^{-6}$	$4.90 \times 10^{-6} \pm 1.98 \times 10^{-6}$
2	$5.45 \times 10^{-6} \pm 1.23 \times 10^{-7}$	$2.82 \times 10^{-6} \pm 5.97 \times 10^{-7}$
3	$1.57 \times 10^{-6} \pm 2.62 \times 10^{-7}$	$6.20 \times 10^{-7} \pm 1.29 \times 10^{-7}$
4	$3.67 \times 10^{-7} \pm 1.14 \times 10^{-7}$	$1.88 \times 10^{-7} \pm 7.53 \times 10^{-8}$
5	$1.53 \times 10^{-6} \pm 1.93 \times 10^{-7}$	$1.19 \times 10^{-6} \pm 2.40 \times 10^{-7}$
6	$4.90 \times 10^{-7} \pm 1.16 \times 10^{-7}$	$4.15 \times 10^{-7} \pm 8.52 \times 10^{-8}$
7	$6.83 \times 10^{-7} \pm 1.10 \times 10^{-7}$	$1.19 \times 10^{-6} \pm 1.25 \times 10^{-7}$

Table I-2: Mass Transfer Coefficients from Continuous Flow Tests in Liquid-Liquid Reactor

Run #	DCM (1/sec)	CT (1/sec)	PCE (1/sec)
1	$1.24 \times 10^{-4} \pm 1.61 \times 10^{-5}$	$1.46 \times 10^{-4} \pm 1.63 \times 10^{-5}$	$*2.27 \times 10^{-5} \pm 9.40 \times 10^{-6}$
2	$*2.52 \times 10^{-4} \pm 2.27 \times 10^{-6}$	$*4.02 \times 10^{-4} \pm 7.55 \times 10^{-6}$	$*2.93 \times 10^{-5} \pm 2.50 \times 10^{-5}$
3	$1.16 \times 10^{-4} \pm 5.58 \times 10^{-21}$	$1.08 \times 10^{-4} \pm 1.06 \times 10^{-6}$	$*6.70 \times 10^{-6} \pm 2.08 \times 10^{-6}$
4	$1.26 \times 10^{-4} \pm 1.30 \times 10^{-6}$	$1.25 \times 10^{-4} \pm 4.47 \times 10^{-6}$	$*7.67 \times 10^{-6} \pm 5.12 \times 10^{-6}$
5	$*2.03 \times 10^{-4} \pm 1.66 \times 10^{-20}$	$*1.77 \times 10^{-4} \pm 2.98 \times 10^{-5}$	$*1.01 \times 10^{-5} \pm 1.33 \times 10^{-5}$
6	$*1.16 \times 10^{-4} \pm 4.70 \times 10^{-21}$	$*9.17 \times 10^{-5} \pm 7.93 \times 10^{-6}$	$*1.33 \times 10^{-5} \pm 5.22 \times 10^{-6}$

*steady state runs

Appendix J

List of Equations and Coefficients of Determination (r^2) Corresponding to Figures

Figure #	Equation	r^2
Figure 4.3 (DCM)	$y = -120.58x + 97.99$	0.793
Figure 4.3 (CT)	$y = -10.94x + 10.28$	0.342
Figure 4.3 (PCE)	$y = 3.53x^{-1}$	1.000
Figure 4.4 (DCM)	$y = 53.73 \ln(x) + 286.94$	0.757
Figure 4.4 (CT)	$y = 362.72x - 1.05$	0.561
Figure 4.4 (PCE)	$y = 753.88x + 2.00x10^{-5}$	1.000
Figure 4.5	$y = -3.05x + 105.97$	0.873
Figure 4.6	$y = -8.29 \ln(x) + 27.09$	0.820
Figure 4.7	$y = 32.82e^{-0.07x}$	0.951
Figure 4.8 (DCM)	$y = 44.10 \ln(x) + 225.44$	0.965
Figure 4.8 (CT)	$y = 28.56 \ln(x) + 150.52$	0.684
Figure 4.8 (PCE)	$y = 33.17 \ln(x) + 178.98$	0.898
Figure 4.9 (DCM)	$y = -2.99x + 80.88$	0.874
Figure 4.9 (CT)	$y = -2.19x + 69.97$	0.909
Figure 4.9 (PCE)	$y = -2.14x + 60.57$	0.851
Figure 4.10	$y = 7692.00x^{-1}$	1.000
Figure 4.11	$y = 136.42x^{-0.097}$	0.586
Figure 4.14 (DCM)	$y = 56.95x^{-1}$	1.000
Figure 4.14 (CT)	$y = -9.29x + 99.32$	0.410
Figure 4.14 (PCE)	$y = 93.08x^{0.0158}$	0.013
Figure 5.3 (DCM)	$y = 0.002 \ln(x) + 0.006$	0.948
Figure 5.3 (CT)	$y = -0.001 \ln(x) + 0.021$	0.346
Figure 5.3 (PCE)	$y = 0.021x^{-0.176}$	0.973
Figure 5.5 (DCM)	$y = 0.057x - 0.007$	0.994
Figure 5.5 (CT)	$y = 0.0004x^{1.09}$	0.725
Figure 5.5 (PCE)	$y = 5.00x10^{-5}x^{1.01}$	0.783
Figure 5.11	$y = 0.0004x^{1.07}$	0.766
Figure 5.12	$y = 5.00x10^{-5}x^{1.01}$	0.783

IMAGE EVALUATION TEST TARGET (QA-3)

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