A novel process for the recovery of phenolic compounds from olive mill wastewater

A thesis submitted in partial fulfilment of the requirements for the degree of

Master of Philosophy

by

Conrad Harvey Ralph Gillard

School of Chemical and Biomolecular Engineering
The University of Sydney

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Declaration

This is to certify that to the best of my knowledge, the content of this thesis is my own work. This thesis has not been submitted for any degree or other purposes. I certify that the intellectual content of this thesis is the product of my own work and that all the assistance received in preparing this thesis and sources have been acknowledged.

Conrad Gillard

June, 2016
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Abstract

Requirements for the treatment of wastewater have grown increasingly stringent in recent years, while industrial processes face increasing competition. As a result, there is a great demand for the development of processes that not only treat wastewater, but convert it into value added products. In this thesis, a new process of this nature is proposed. Specifically, a two-stage process is conceived to treat olive mill wastewater (OMW), and produce a concentrated stream of phenolic compounds.

The primary pollutants found in OMW are phenolic acids and other phenolic compounds. These pollutants adversely affect plant, animal and human life. At present, no method to recover these valuable phenolic compounds from OMW is practiced on an industrial scale.

In the first stage of the proposed process, the wastewater stream is heated and pressurised to near critical conditions. Under these conditions, a decarboxylation reaction occurs, converting phenolic acids into phenolic compounds.

In the second stage, phenolic compounds are separated from the aqueous stream, using a heat resistant polydimethylsiloxane membrane. This separation method is capable of producing a permeate with a concentration several orders of magnitude higher than that of the retentate.

This thesis aims to generate the fundamental knowledge necessary for the design of each stage of this process. First, a mechanistic and kinetic study of the decarboxylation reaction was carried out using a flow reactor. Specifically, the effects of residence time and temperature on the conversions of 4-hydroxy benzoic acid, syringic acid and benzoic acid were investigated.

These experiments indicated that the decarboxylation reaction followed an Arrhenius relationship with temperature. The kinetic parameters for the decarboxylation of 4-hydroxy benzoic acid and syringic acid were calculated. However, the reaction rate of benzoic acid under the conditions studied was too low to measure.

The relative magnitudes of these kinetic parameters were consistent with the $S_21$ reaction mechanism. The primary evidence for this conclusion was that the presence of electron
withdrawing groups decreased the activation energy, consistent with the formation of a negatively charged intermediate.

The results of the decarboxylation experiments also suggested that the reaction rate was pressure dependent. However, time constraints prevented a quantitative investigation of this effect.

The separation stage was investigated by carrying out permeation experiments using a membrane apparatus with aqueous solutions of phenol, guaiacol, syringol, catechol and 4-methyl catechol. The effect of temperature on the permeability and partition coefficient of each compound was investigated.

Based on the measurement of permeation rates and partition coefficients, diffusion coefficients were calculated. The diffusion coefficients were observed to be greatly reduced for permeants which possessed a second –OH substituent. The effect of additional hydrogen bonding groups on the diffusion coefficient had not previously been investigated, so this result extended the body of knowledge.

The presence of the heat resistant additive (TiO$_2$) was found to reduce both the partition coefficient and diffusion coefficient compared to a polymer that was identical apart from the presence of the TiO$_2$ additive. The magnitude of the relative decrease in partition coefficient was in agreement with a previously published equation. The decrease in diffusion coefficient was also consistent with results of previous studies, however no equation offering a quantitative prediction had previously been published.
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Nomenclature

4-HBA 4-Hydroxybenzoic acid
A Pre exponential factor
BPR Back Pressure Regulator
$C_i$ Concentration of component $i$
$d_i$ Internal diameter of membrane tubing
D Diffusion coefficient
$E_A$ Activation energy
$F$ Mass flowrate
HPLC High pressure liquid chromatography
$k$ Reaction rate constant
$k_{ov}$ Overall mass transfer coefficient
$k_m$ Membrane mass transfer coefficient
$K$ Partition coefficient
$NMP$ N-methyl-2-pyrrolidone
OMW Olive mill wastewater
$P$ Permeability
PDMS Polydimethylsiloxane
PFD Process flow diagram
PFR Plug Flow Reactor
$R$ Gas constant
$r_1$ Inner radius
$r_2$ Outer radius
SS316 316 stainless steel
$t$ Time
$T$ Temperature
TMEDA Tetramethylethylenediamine
$V$ Volume
$X$ Conversion
Chapter 1

Introduction

The disposal of olive mill wastewater (OMW) is a serious environmental issue in olive oil producing countries, due to its toxic nature. Specifically, the discharge of OMW causes depletion of aquatic oxygen and toxicity toward plant, animal and microbial life [1].

These effects occur because OMW contains phenolic compounds and a high concentration of organic matter [2]. The exact composition of OMW varies with both the agricultural techniques used to grow the olives, and the process used to extract the oil [3]. However, a typical OMW contained 10 g/L of phenolic compounds, including 1 g/L of phenolic acids [4].

A widely used method of disposal is distribution of OMW over agricultural land, known as land-spreading. This practice has been shown to improve soil fertility if carried out in low doses and in appropriate soil types [5, 6]. This improvement in fertility is attributed to the presence of mineral nutrients and organic matter in OMW.

However, high dose or long term land-spreading has been found to reduce the productivity of agricultural land [7, 8, 9]. Due to this issue, the governments of Italy and Israel have enacted laws restricting the quantity of OMW that may be used for land-spreading [10].

Barbera et al [11] comprehensively reviewed the literature and concluded that the presence of phenolic compounds was the main limitation preventing further use of land spreading. As a result, techniques to remove or recover phenolic compounds from OMW have attracted considerable research in recent years.

Rahmainian et al [2] extensively reviewed the existing body of knowledge regarding the removal and recovery of phenols from OMW. A variety of techniques were used to attempt to achieve this transformation, such as porous membrane separation, wet oxidation and microbial decomposition. However, none of these techniques have proved economically viable for industrial use.
To address the above need, this thesis proposes a new process for the recovery of phenolic compounds from OMW. This process is now described.

1.1 Proposed process
The process proposed by this thesis consists of two stages. In the first stage, OMW enters a flow reactor which operates at 200-300°C and a pressure of 200 atmospheres. Under these conditions, water remains in the liquid state and decarboxylation of phenolic acids occurs.

In the second stage, the phenolic compounds are separated from the OMW using a nonporous polydimethylsiloxane membrane. This type of membrane is capable only of separating undissociated phenols from OMW. It is for this reason that the first stage is necessary.

Neither of these techniques have previously been investigated for the recovery of phenolic compounds from OMW. A process flow diagram of the proposed technique is shown in Figure 1.

![Figure 1: PFD of proposed process, consisting of heat treatment stage for decarboxylation of phenolic acids, and membrane separation apparatus for recovery of phenolic compounds from OMW.](image)

The two stages of the process are now described in greater detail.

1.1.1 Decarboxylation reactor
The decarboxylation of phenolic acids will be carried out in a conventional flow reactor, which does not contain any catalyst or enzyme. The general form of this reaction is shown in Figure 2.
The products of this reaction are phenolic compounds that do not contain the carboxylate group. The loss of the carboxylate group greatly decreases the acidity of the molecule, allowing it to permeate the membrane used in the subsequent stage.

### 1.1.2 Membrane separation

The separation of phenolic compounds will be carried out using a nonporous polydimethylsiloxane membrane apparatus. Unlike a porous membrane separator, this technique does not require that a transmembrane pressure difference be maintained.

The membrane apparatus is operated at 60-90°C, as the rate of mass transfer is significantly increased at higher temperatures, as will be described subsequently. In order to ensure the membrane lasts as long as possible without degrading, a blend of PDMS that contains titanium dioxide will be used. This additive was claimed by the manufacturer to enhance the heat resistance of the membrane. This effect has also been reported in the literature [12].

An alkaline solution will be used as the permeate side fluid, in order to ensure that phenolic compounds dissociate after permeating the membrane. The dissociated molecules cannot permeate the membrane, and the driving force is maintained. Han et al [13] used this arrangement to produce a permeate with a phenol concentration two orders of magnitude higher than that of the retentate.

As mentioned previously, olive mill wastewater contains compounds in addition to phenolic acids. Specifically, tannins, mineral salts and catechol bearing polymers are commonly found [3]. It should be noted at the outset that the presence of these substances may influence the operation of the proposed process. For example, certain types of organic matter may undergo reactions at high temperatures that produce undesirable products. This may restrict the range of operating possible conditions for the reactor.
However, it is imperative to first investigate the chemical transformations that form the basis of the proposed process. Should the present work suggest that the process is feasible, the issues arising due to the presence of other compounds will then be investigated. The central objective of this thesis is to generate the fundamental knowledge necessary for the design of each stage of this process.

Having described the motivation for this research and the proposed process, an overview of the structure of this thesis is now given.

1.2 Thesis Structure
In Chapter 2, the literature relating to the hydrothermal decarboxylation of phenolic and transport mechanism within polydimethylsiloxane is reviewed. Knowledge gaps are identified and the specific aims of this thesis are stated.

In Chapter 3, a detailed description of the membrane apparatus that was constructed for this thesis is presented. The flow reactor apparatus, which was built by another researcher, is also briefly described.

In Chapter 4, results of hydrothermal phenolic acid decarboxylation experiments are presented. The Arrhenius parameters are calculated and analysed in order to gain insight into the influence of molecular structure on reactivity. The results are compared with those of another investigation conducted in a gold lined reactor, with the goal of determining the catalytic effect of stainless steel.

In Chapter 5, results of permeation experiments using a heat resistant PDMS membrane are presented. The effects of temperature, concentration and permeant molecular structure on permeability are experimentally investigated. The effect of the presence of the heat resistant additive is investigated by comparing the results of this thesis to those of an investigation that used a PDMS membrane that lacked the TiO$_2$ additive.

In Chapter 6, the conclusions drawn from this thesis are presented. Opportunities for future work are identified, and a course of action for continued investigation of the proposed process is recommended.
In this chapter, the existing body of knowledge regarding the hydrothermal decarboxylation of phenolic acids is reviewed. Following this, the literature relating to the mechanism of transport across PDMS is critically evaluated.

Finally, the literature gaps are identified, and the objectives of this thesis are stated.

2.1 Hydrothermal decarboxylation of phenolic acids
The hydrothermal decarboxylation of phenolic acids has been studied in both the presence and absence of catalysts. The existing body of knowledge regarding each of these fields of research is now critically evaluated. In addition, the ability of predictive models to calculate the rate of reaction is reviewed, in order to determine whether experimental investigations are required.

2.1.1 Uncatalysed decarboxylation
The uncatalysed hydrothermal decarboxylation of phenolic acids was experimentally investigated by several researchers [14, 15, 16, 17]. For all acids studied, the reaction was determined to be irreversible and first order. The rate constant followed an Arrhenius relationship with temperature, and was too slow to measure below 200°C.

Studies into the mechanism of this reaction have reached conflicting conclusions. Segura et al [16] carried out kinetic studies on several phenolic acids, using a glass reactor. These authors concluded that the reaction proceeded via the unimolecular electrophilic substitution reaction mechanism, also known as $S_{E1}$. The general form of this reaction is shown in Figure 3.
Figure 3: Generalised $S_{E1}$ decarboxylation mechanism for phenolic acids

The primary evidence supporting the above mechanism was the observation that the presence of electron withdrawing substituents on the ring reduced the activation energy. This is consistent with the formation of an anionic intermediate, as the negative charge is delocalised due to induction effects. Furthermore, the above mechanism suggests first order kinetics, which was consistent with the experimental observations.

This reaction mechanism was also investigated using computational chemistry [15, 18, 19]. The mechanisms proposed by each study were all significantly different from the $S_{E1}$ mechanism above. Furthermore, the proposed mechanisms conflicted with one another.

For instance, Ruelle et al [18] proposed mechanisms for the hydrothermal decarboxylation of benzoic acid and acrylic acid. Specifically, these authors suggested that a transition state involving two water molecules was formed. Based on this model, activation energies were calculated. As data for the reaction in an aqueous medium was not available, the activation energy from the decarboxylation of benzoic acid in catechol was used as test data. The model predicted an activation energy of 40.1 kcal/mole, whereas the experimental data was 52.2 kcal/mole. Thus the error of this prediction was 23%.

Li and Brill [15] experimentally investigated the rate of hydrothermal decarboxylation of various phenolic acids in the presence and absence of hydrochloric acid. Specifically, reaction rates for mono-, di-, and tri-hydroxy derivatives of benzoic acid were experimentally measured. A computational chemistry model was developed, and the accuracy of the predicted activation energies was assessed. This study found that both the position and number of substituents affected the reactivity. Substituents in the –meta position reduced the reactivity, whereas substituents in the -ortho and -para positions enhanced the reactivity. This trend was consistent with the conventional theory of substituent effects.
The accuracy of the model varied according to the specific acid studied. For the case of 2,4-dihydroxybenzoic acid, the error between the measured and calculated activation energies was 4%. However, for the case of 4-hydroxybenzoic acid, the error was 22%. This study concluded that the reaction mechanism had a transition state in which “at least one” water molecule was involved.

Chuchev and Belbruno [19] developed a model based on computational chemistry for the decarboxylation of salicylic acid. These authors concluded that the mechanism was substantially different to that proposed by Li and Brill, and involved the formation of a ketone-like intermediate. This study did not calculate activation energies based on their reaction mechanism.

Artok and Schobert [17] experimentally investigated the hydrothermal decarboxylation of 4-hydroxybenzoic acid (henceforth, 4-HBA) and benzoic acid using a stainless steel reactor. These acids were exposed to high temperatures and pressures, and their conversion was measured after 30 minutes. As a result, kinetic parameters were not reported.

For the case of benzoic acid, a temperature of 450°C was applied. This study did not report sufficient information to determine the reaction pressure. After 30 minutes, a conversion of 3% was observed. For the case of 4-HBA, the acid was completely converted after exposure to a temperature of 300°C. These results were consistent with those of previous researchers, in that the presence of an electron withdrawing substituent increased the reactivity of the acid.

2.1.2 Catalysed decarboxylation

Due to the high temperatures necessary to achieve decarboxylation, significant research has been focused on developing a catalyst for this reaction. The body of knowledge relating to this field of research is now reviewed.

Acid catalysis

Li and Brill experimentally investigated the rate of decarboxylation of various phenolic acids in acidic aqueous solutions [15]. Hydrochloric acid was added to give a pH of 1.3, which ensured that the phenolic acid remained completely undissociated. The first order rate constant was observed to increase by approximately a factor of two compared to a non-acidified system.
Studies into the mechanism of this reaction have come to conflicting conclusions. Taylor [20] reviewed a large number of early experimental investigations into the decarboxylation of undissociated phenolic acids. The consensus from these studies was that the reaction proceeded via an arenium ion mechanism. The generalised form of this reaction mechanism is shown in Figure 4.

\[ 
\text{H}_2\text{C}=\text{O} + \text{H}^+ \rightarrow [\text{Ph}^+] \rightarrow \text{Ph}^+ + \text{H}_2\text{O} 
\]

*Figure 4: Generalised arenium ion decarboxylation mechanism for phenolic acids*

The evidence for the above mechanism was that the presence of electron donating substituents on the aromatic ring decreased the activation energy. Experiments using isotope effects also supported this mechanism.

However, Gao et al [21] recently published a study in which a different mechanism was proposed, based on modelling with computational chemistry. The proposed mechanism involved a water molecule that acts as a bridge between the hydroxyl hydrogen and carboxyl hydrogen. The activation energies calculated by this study were greater than the observed value by approximately 50%. Due to the poor predictive ability of the study it appears likely that further research is needed before this mechanism is fully understood.

*Metal complexes*

Although not hydrothermal, the use of metal complexes to catalyse decarboxylation of phenolic acids has attracted considerable research. This technique is briefly reviewed here.

The catalytic effects of copper and copper salts on decarboxylation have been studied since the 1960s [22]. The use of these catalysts required that the reaction be carried out in a solvent such as quinolone and in the presence of a ligand.

This technique resulted in a significant increase in reaction rate. For example, Cahiez et al [23] carried out experiments on the decarboxylation of 2-nitrobenzoic acid in NMP using a Cu$_2$O catalyst and TMEDA ligand. A conversion of 99% was achieved after 5 minutes, at a
temperature of 140°C. This is significantly lower than the 200 – 300°C range of temperatures at which the uncatalysed reaction commences.

Complexes of various precious metals have been experimentally investigated and found to catalyse decarboxylation of phenolic acids. These metals include silver [24], gold [25] and palladium [26]. As was the case with copper catalysed decarboxylation, the above techniques require that the reaction is carried out in a solvent such as NMP or quinolone, and in the presence of a ligand.

As the above techniques required that a reaction medium other than water was used, they are not suitable for the enhancement of the proposed process.

Wall effects

Several experimental investigations into the catalytic effect of the material of construction of the reactor wall on the decarboxylation of carboxylic acids were found in the literature [27, 29 – 31]. A common feature of these investigations was that the carboxylic acids studied did not contain an aromatic functional group, so were not phenolic acids. However, due to the presence of the carboxyl group, the behaviour of these acids is anticipated to be similar to that of phenolic acids, and hence is relevant to this thesis.

After critically evaluating this body of research, two overall conclusions were drawn: Firstly, certain wall materials had a significant catalytic effect on the reaction rate. Secondly, for a given reactor wall material, the catalytic effect varied, depending on the identity of the acid.

As an example of the significance of wall effects, Palmer and Drummond [27] carried out a series of experiments on the decarboxylation of acetic acid using reactors constructed from various metals. Specifically, acetic acid was subjected to temperatures of 300 – 440°C in reactors constructed from 321 stainless steel (SS321), gold, titanium, titanium alloy, silica and fused quartz.

The material of the reactor in which the experiments were carried out was found to affect the reaction rate. The SS321 reactor resulted in the highest reaction rate, with an activation energy of 31 kJ/mole. By comparison the silica reactor had the lowest reaction rate, with an activation energy of 286 kJ/mole.
A catalytic wall effect was also reported by McCollom and Seewald [28], who carried out decarboxylation experiments on formic acid in an inert gold lined reactor. The rates observed were significantly lower than those reported from experiments using stainless steel and titanium reactors.

Additionally, Bjerre and Soerensen [29] investigated the effect of corrosion on the catalytic activity of stainless steel on the hydrothermal decarboxylation of formic acid. An experiment was carried out using a stainless steel reactor that had been severely corroded by previous decarboxylation experiments. The experiment was then repeated using a new, uncorroded reactor. The reaction proceeded at a significantly higher rate in the uncorroded tubing.

The variability of wall effects for different acids was demonstrated by Maiella and Brill [30], who studied the hydrothermal decarboxylation of formic and malonic acid in 316 stainless steel (SS316), titanium and 90/10 platinum-iridium reactors. This study found that the decarboxylation of formic acid proceeded at similar rates in the SS316 and titanium reactors, but was faster in the platinum-iridium reactor.

However, for the case of malonic acid decarboxylation, this study found that the material of reactor construction had no effect on the reaction rate. Based on this observation, this study postulated that only monocarboxylic acids are catalysed by the reactor wall material.

Furthermore, Belsky et al [31] decarboxylated 12 acetic acid derivatives in reactors constructed with SS316 and titanium. For 9 out of the 12 acids, the reaction proceeded at the same rate in each reactor. However, for the case of trichloroacetic acid, trifluoroacetic acid and pyruvic acid, the reaction rate was significantly higher in the SS316 reactor.

These authors suggested that the decarboxylation of trichloroacetic acid may have been catalysed due to the well documented reactivity of the chloride ion with SS316. However, these authors were unable to offer an explanation for presence of wall effects for trifluoroacetic acid and pyruvic acid.

2.1.3 Implications for proposed process
In the preceding sections, the literature relating to the hydrothermal decarboxylation of phenolic acids was reviewed. The implications of this research for the proposed process are now discussed.
**Catalytic effects of stainless steel**

In order to design a reactor to carry out the first stage of the proposed process, the reaction kinetics of the decarboxylation of phenolic acids must be known. Specifically, knowledge of the reaction kinetics will enable the calculation of the optimum reactor volume and operating temperature.

Several studies reported that the hydrothermal decarboxylation reactions of some aliphatic carboxylic acids were catalysed by stainless steel [27, 29 – 31]. The hydrothermal decarboxylation of phenolic acids is a very similar reaction, suggesting that it may also be catalysed by stainless steel.

Although the hydrothermal decarboxylation of phenolic acids in stainless steel reactors has been investigated, kinetic parameters of these reactions have not been reported. Consequently, the catalytic effect of stainless steel on the decarboxylation of phenolic acids is presently unknown.

As an industrial scale reactor will most likely be constructed from stainless steel, the development of the proposed process requires that the catalytic effect of this material be determined. As a result, this knowledge gap was selected for investigation in this thesis.

**Effect of molecular structure on reactivity**

As discussed previously, the composition of OMW is dependent on factors such as the agricultural techniques used to grow the olives, and the method used to process them. As a result, the composition of OMW produced by each facility is different.

Therefore, the relationship between phenolic acid molecular structure and reactivity is of interest. This would enable the prediction of reaction rates for different OMW components to be predicted, at least qualitatively.

Several attempts to develop predictive models for the reaction rates of phenolic acids were found in the literature [15, 18, 19]. These models utilised computational chemistry, and were designed to predict the kinetic parameters of uncatalysed decarboxylation reactions.

As discussed, it is unknown whether the presence of stainless steel has a catalytic effect on the decarboxylation reaction. If so, these models are not applicable to the proposed system.
Furthermore, the error of the activation energies predicted by each of the models was approximately 23%. This suggests that current modelling techniques are not sufficiently reliable to form the basis of the design of an industrial reactor.

Only one experimental investigation that used a stainless steel reactor to study the hydrothermal decarboxylation of phenolic acids was found in the review of the literature [17]. This study involved benzoic acid and 4-HBA, and found that the presence of an –OH substituent on the phenolic ring resulted in an increased reactivity. However, the effect of additional electronegative substituents has not yet been investigated.

In order to investigate this knowledge gap, kinetic studies of the decarboxylation of 4-HBA and syringic acid will be carried out. Syringic acid differs from 4-HBA only by the presence of two additional methoxy substituents. This acid was selected because a study found that syringic acid, vanillic acid and sinapic acid were the most commonly occurring phenolic acids in OMW [4]. These acids all contain methoxy substituents on the aromatic ring.

The results of this investigation will enable qualitative predictions regarding the reaction rates of other acids, based on their molecular structures. Furthermore, the kinetic parameters obtained may constitute useful test data for future attempts to develop predictive models based on computational chemistry.

Having reviewed the literature relating to the decarboxylation of phenolic acids, the existing body of knowledge relating to the transport mechanism of PDMS will now be critically evaluated.
2.2 Transport mechanism in PDMS
The transport mechanism in nonporous PDMS membranes has been extensively studied by various researchers. Wijmans and Baker [32] reviewed the literature and found that the consensus of these studies was that transport occurs via the solution diffusion mechanism. This mechanism consists of a two-step process, in which the permeant first dissolves into the membrane phase, then diffuses across.

A broad overview of this mechanism is now given. This will be followed by a more detailed analysis of each step in the process, and the factors that affect their magnitudes.

2.2.1 Overview of solution diffusion mechanism
The solution diffusion mechanism differs from the transport mechanisms across porous membranes. In the latter case, transport takes place either by Knudsen Diffusion or Molecular Sieving, depending on the pore size. These mechanisms are selective by permeant size, and rely on a pressure gradient to achieve separation.

By contrast, the driving force for the solution diffusion mechanism is chemical potential. As a result, transport can occur in the absence of a pressure gradient, if a concentration gradient exists. A second key difference is that nonporous membranes are selective on the basis of strength of intermolecular interactions between the permeant and membrane, rather than permeant size. The above transport mechanisms are illustrated in Figure 5.

![Figure 5: Schematic illustrating diffusion mechanisms in membranes of various pore sizes [33]](image)
The mass transfer coefficient \((k_m)\) of a tubular PDMS membrane can be expressed with the following equation, a derivation for which will be given in Chapter 5:

\[
k_m = \frac{KD}{r_1 \ln \left( \frac{r_2}{r_1} \right)} \quad (2.1)
\]

In which \(K\) is the partition coefficient, \(r_1\) and \(r_2\) are the inner and outer radii respectively, and \(D\) is the diffusion coefficient. The physical meanings of these two terms, and the factors that affect them are now discussed. The accuracy of existing predictive models for each parameter are also analysed, in order to determine whether experimental investigations are necessary.

### 2.2.2 Partition coefficient

The partition coefficient is defined as the ratio of the concentrations of a solute in two solvents at equilibrium. As it is used in Equation 2.1, this refers to the ratio of concentrations in the PDMS membrane to the solute on the retentate and permeate sides.

\[
K_i \equiv \frac{C_{i(m)}}{C_{i(f)}} \quad (2.2)
\]

Where \(C_{i(m)}\) and \(C_{i(f)}\) are the concentrations of component \(i\) in the membrane and fluid respectively. Having given a definition of the partition coefficient, the factors that influence the magnitude of this quantity are now investigated.

**Effect of temperature on partition coefficient**

The effect of temperature on the partition coefficient between PDMS and water has been studied extensively [34, 35, 36]. These investigations studied a large number of compounds, and in all cases found that the partition coefficient decreased as temperature increases.

The consensus regarding the underlying cause of this behaviour is that the transfer of organic compounds from water to PDMS is an exothermic process. Therefore, by Le Châtelier’s principle the equilibrium was shifted toward water at higher temperatures. This temperature dependence was found to be exponential.

The significance of this effect has been found to vary for different species. For example in the case of phenanthrene, over a temperature range of 4°C to 30°C, the partition coefficient decreased by approximately 5% [34]. For the case of the benzene, the partition coefficient
decreased by 20% between 12°C to 28°C [35]. Jonker et al [34] hypothesised that the temperature effect was more significant for compounds of greater hydrophobicity.

**Effect of permeant molecular structure on partition coefficient**

The partition coefficient of organic compounds between PDMS and water has been investigated by several researchers [37, 38, 34, 35, 13, 39]. There is no clear consensus regarding the relationship between molecular structure and partition coefficient. However, some investigations provided insights that are relevant to the present work.

Han et al [13] experimentally measured the water-PDMS partition coefficients of several phenolic compounds. The conclusion reached by this study was that the partition coefficient increased with decreasing solubility in water. However, only 5 phenolic compounds were studied in this investigation. As a result this rule of thumb may not be widely applicable.

Brookes and Livingston [40] experimentally measured the partition coefficients of phenolic and non-phenolic aromatic compounds. The results contained several counterexamples to the trend observed by Han et al. For example, chlorobenzene had a lower solubility in water than dichlorobenzene, but a higher partition coefficient. Specifically, chlorobenzene had a solubility of 0.49 g/L and a partition coefficient of 70, whereas dichlorobenzene had a solubility of 0.15 g/L and a partition coefficient of 55. This study did not propose an underlying cause to explain this trend.

Di Filippo and Eganhouse [37] reviewed the literature concerning the water-PDMS partition coefficient, and collected data for hundreds of compounds. These researchers developed an equation to correlate the partition coefficient data with the molecular properties of the permeant.

Specifically, these authors developed this equation by adapting a pre-existing method named the Linear Solvation Energy Relationship (LSER). The LSER method consists of conducting solubility experiments and using regression to obtain values for several parameters that describe characteristics of the molecule. For example, parameters describing the degree of hydrogen bonding and strength of van der Waals interactions are calculated.

The equation developed by Di Filippo and Eganhouse related the published partition coefficient data with the published LSER parameters for various permeants. This equation
involved the use of several fitting parameters that were regressed in order to relate the above two datasets.

By inspection of the magnitudes of the coefficients for each parameter, it was concluded that the characteristics that had the greatest effect on the partition coefficient were: hydrogen bond accepting ability > hydrogen bond donating ability > polarizability > magnitude of London forces.

The model of Di Filippo and Eganhouse has some limitations that will be discussed in a later section. However, the form of this equation provides insights into the relationship between permeant molecular structure and the partition coefficient.

**Effect of additives on partition coefficient**

The literature was reviewed and only one study investigating the effect of additives on the partition coefficient of PDMS was found in the literature. To complement this, investigations into closely related phenomena were also reviewed.

Barrer et al [41] investigated the water-PDMS partition coefficients of various alkanes in additive free PDMS and PDMS containing varying concentrations of silica additive. This study hypothesised that the solubilities of permeants were directly proportional to the volume fraction of PDMS in the polymer:

\[ \sigma = \sigma_r \lambda_r \]  \hspace{1cm} (2.3)

In which \( \sigma \) is the solubility of the filled polymer, \( \sigma_r \) is the solubility of the unfilled polymer, and \( \lambda_r \) is the volume fraction of polymer. This hypothesis based on the assumption that the filler fraction of the polymer did not adsorb any permeant, as it was fully wetted by the surrounding polymer molecules. The above equation was found to accurately describe the results of the investigation, supporting this theory.

Vankelecom et al [42] compared the sorption of organic compounds in unfilled and zeolite filled PDMS. It should be noted that this study measured sorption coefficients rather than partition coefficients. The sorption coefficients were determined by immersing the membrane in a liquid composed purely of the sorbate, and measuring the concentration of the sorbate within the membrane. Whereas partition coefficients involve immersing the membrane in a solution consisting of the permeant and a solvent.
The findings from this study were that the sorption of some compounds was unaffected by the presence of additives, and others were strongly affected. For example, the sorption capacity of 2,3 butadiene into a membrane containing 20 vol % silicalite was measured. This was found to be greater by a factor of 5 compared to that of an unfilled PDMS membrane.

However, the partition coefficient of isoamyl alcohol was observed to decrease by approximately 20%. Notably, this decrease is equal to that predicted by the equation of Barrer et al [41], adding further support to this theory.

Vankelecom et al [42] hypothesised that the cause of this behaviour was that compounds containing functional groups that strongly interacted with the filler were able to adsorb to it. This resulted in additional adsorption sites, thus increasing the uptake of the permeant.

Similarly to the sorption capacity, the partition coefficient is also dependent on the intermolecular forces between the permeant and membrane. As a result it is anticipated that the incorporation of fillers that strongly interact with permeants may increase the partition coefficients of those permeants.

**Predictive models for partition coefficient**

Several investigations that attempt to develop predictive models for the PDMS-water partition coefficient were found in the literature [37, 40, 39, 43]. A common feature of these investigations was that they involved fitting an equation to experimental partition coefficient data, using adjustable parameters.

As a result these equations were only valid for the specific membrane used in the study, because the presence of additives significantly influenced the partition coefficient, as discussed previously. An overview of two of the most rigorous studies into this effect are now given.

As discussed previously, Di Filippo and Eganhouse developed an equation to predict the partition coefficient between PDMS and water based on the molecular characteristics of the permeant [37]. This equation successfully predicted the partition coefficients of hundreds of compounds. However, the equation contained 6 fitting parameters that were regressed based on experiments with a polymer consisting of 100% PDMS.
Chao et al [39] developed an equation for the partition coefficient as a function of the polarizability of organic compounds. This model utilised only 2 fitted parameters, as opposed to 6 for the model of Di Filippo and Eganhouse. However, due to the presence of these fitted parameters, this equation is also limited to use with additive-free PDMS.

Tamai et al [44] used computational chemistry to predict the solubilities of several compounds in PDMS. This was achieved by developing a model of PDMS chains and running molecular dynamics simulations. This approach had the advantage that no fitted parameters were required. A limitation of this approach was that the model developed was of additive-free PDMS. As a result, this approach can only be used to calculate solubilities in additive-free PDMS.

The accuracies of the predictions generated by this approach were mixed. For the case of water, the calculated and experimental values were in close agreement. However, for the case of ethanol the calculated solubility was higher than the experimentally measured solubility by a factor of 5.5.

### 2.2.3 Diffusion mechanism in PDMS

The most rigorous and highly cited investigation into the diffusion mechanism of PDMS was carried out by Watson et al [45]. This investigation was motivated by the observation that the diffusion coefficient was strongly influenced by the nature of functional groups present in the permeant, whereas molecular size was less influential [46].

In the proposed mechanism, diffusion was thought to take place through a series of adsorption and desorption events. This proposed mechanism is a modification of the free volume theory of molecular transport, which posits that the random motion of polymeric chains generates voids in the material. The locations of these voids change continuously as the molecule moves, however the sum of the volumes of these voids, known as the “hole free volume”, remains constant for a given temperature [47].

The permeant is thought to adsorb to the surface of the polymer, within one of the randomly generated voids. After adsorbing to this site, the permeant remains there for a certain dwell time, denoted \( \tau \). After this time, the permeant desorbs and randomly jumps to another adsorption site.
The duration of the dwell time is dependent on the strength of intermolecular forces between the permeant and polymer. The molecule is thought to desorb at such a time when it vibrates with sufficient energy to break this bond. The probability of the molecule accumulating such energy was described with the Arrhenius equation, leading to the following expression for dwell time:

$$\tau = \tau_0 \exp \left( \frac{E}{RT} \right)$$  \hspace{1cm} (2.4)

In which $E$ is the energy of the adsorption bond, and $\tau_0$ is the vibrational frequency of the molecule. The following expression for $\tau_0$ was given:

$$\tau_0 = \frac{h}{kT}$$  \hspace{1cm} (2.5)

In which $h$ is Planck’s constant, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. The above two equations were combined with the following expression for the diffusion coefficient:

$$D = \frac{\lambda^2}{6\tau}$$  \hspace{1cm} (2.6)

In which $\lambda$ represents the mean jump length, which is the distance between adsorption sites. This equation was derived using a statistical mechanical approach [12]. Substituting Equations 2.4 and 2.5 into Equation 2.6 gives the following equation:

$$D = \frac{\lambda^2 kT}{6h} \exp \left( -\frac{E}{RT} \right)$$  \hspace{1cm} (2.7)

The above equation is very similar to that used to describe the interstitial diffusion coefficient. The key difference is that the energy term in the above equation relates to the intermolecular forces between polymer and permeant, rather than the size and shape of the molecule.

Having described the diffusion mechanism in PDMS, the factors that influence the magnitude of this quantity are now investigated.
**Effect of concentration on diffusion coefficient**

Several investigations have been carried out regarding the effect of concentration on the diffusion coefficient of compounds in PDMS [45, 48, 49]. The consensus reached by these studies was that concentration dependence was observed for some permeants, but not for others.

Specifically, permeants that were predicted to have strong intermolecular interactions with the membrane were found to be concentration dependent. In order to predict whether a permeant would have a strong interaction, the molecular structure was examined. The presence of functional groups that would strongly interact with PDMS was found to predict concentration dependence.

This behaviour was predicted by the mechanism proposed by Watson et al [45], which was discussed previously. Having given an overview of the main findings in this area of research, the studies most relevant to this work are now summarised.

Watson et al [45] experimentally determined that the diffusion coefficients of 1-aminobutane, propanone and tetrachloromethane were dependent on concentration. However, the authors did not suggest any rule for determining whether a given molecule would exhibit concentration dependence.

Bennett et al [48] investigated the performance of PDMS membranes for pervaporative separation of organics from aqueous systems. The pervaporation process differs from dialysis in that the shell side is exposed to vacuum conditions, rather than a liquid. After the permeant passes through the membrane it evaporates due to the lower pressure.

Despite this difference in process, some findings of this study are applicable to the present work. This is due to the fact that the pervaporation and dialysis processes are identical except for the conditions on the shell side.

The relevant finding from the above study related to the effect of concentration of phenol on permeability. The concentration of phenol in the treated fluid was varied, and it was observed that the permeability did not change.
Effect of temperature on diffusion coefficient

Numerous researchers have experimentally investigated the effect of temperature on the diffusion coefficient in PDMS for many compounds [13, 50, 51]. The unanimous conclusion from these studies was that the diffusion coefficient follows an Arrhenius relationship with temperature. This is consistent with the theoretical prediction of the mechanism proposed by Watson and Payne [46]. An overview of the studies that are most relevant to this work is now given.

Han et al [13] investigated the effect of temperature on the permeability of PDMS to phenolic compounds, and found that the permeability increased with temperature. Specifically, an Arrhenius relationship was observed. As discussed previously, the partition coefficient was found to decrease with increasing temperature.

Taken together, these trends indicate that for a given increase in temperature, the relative increase in diffusion coefficient is greater than the relative decrease in partition coefficient.

Boscaini et al [50] studied the use of a PDMS membrane for separation of various gaseous compounds, at a range of temperatures. The diffusion coefficients were calculated based on the time taken for the mass flux to reach its steady state value. The findings of this study further supported the theoretical prediction of an Arrhenius relationship between the diffusion coefficient and temperature.

This study also supported the inference that temperature had a more significant effect on the diffusion coefficient than on the partition coefficient. For example, increasing the operating temperature from 25°C to 65°C caused the diffusion coefficient of ethanol to increase by a factor 5.68. By comparison the partition coefficient of the most temperature sensitive permeant, benzene, decreased by 20% between 12°C to 28°C [35].

Effect of permeant molecular structure on diffusion coefficient

The effect of the nature of the permeant species on the diffusion coefficient has been studied by several researchers [45, 52, 13, 53, 49, 54, 55]. A common feature of several of these investigations was that they only studied permeants from a particular class, such as alkanes [13, 53, 49, 54, 55]. The conclusion of these studies was that the diffusion coefficient decreased with increasing molar volume of the permeant.
However, La Pack et al [52] conducted a more rigorous study, in which they experimentally determined the permeability of a PDMS membrane to a variety of compounds. The composition of the membrane was 70 wt % PDMS, 30 wt % fumed silica. Specifically these authors experimented with compounds belonging to different classes such as alkanes, alcohols and chloromethanes.

The key observation from these experiments was that within classes of compounds, the diffusion coefficient decreased linearly with molar volume. For example, between two alkanes, the species with a higher molar volume had a lower diffusion coefficient. However, several alkanes were observed to have a higher diffusion coefficient than bromomethane, despite having a higher molar volume.

In addition, it was found that alcohols did not follow the above trend. This class of compounds did not show any correlation between diffusion coefficient and molar volume. The authors suggested that classes of compounds deviated more strongly from this trend as their capacity for hydrogen bonding increased.

LaPack et al also measured the diffusion coefficients of a series of permeants, each containing a single functional group with the capacity for hydrogen bonding. The conclusion of this series of experiments was that the diffusion coefficient substantially decreased with as the capacity for hydrogen bonding of the functional group increased.

One aspect that was not investigated by LaPack et al was the effect of the presence of multiple functional groups with the capacity for hydrogen bonding. This structural feature is relevant to the proposed process because an analysis of OMW from several facilities found that the two most common phenolic pollutants differed only by the presence of an additional –OH substituent on the aromatic ring [4].

This finding suggested that both monohydroxylated and dihydroxylated species are commonly occurring in OMW. As a result, the influence of the presence of second –OH group on permeability is of relevance to this thesis. Therefore, this knowledge gap was selected for investigation.
Watson et al [45] experimentally investigated the diffusion coefficients of n-alcohols and amines. The results of this investigation were that the diffusion coefficient of the alcohols decreased with molar volume, however the amines showed no clear trend.

This would appear to be contradictory to the results obtained by La Pack et al [52], however it should be noted that the membrane used by Watson et al [45] was of a different composition. Specifically, this membrane did not contain the fumed silica filler that was present in the experiments of La Pack et al [52]. This indicates that the filler had an effect on the diffusion coefficient, which will be discussed in the next section.

The explanation hypothesised by Watson et al [45] was similar to that of La Pack et al [52]. Specifically, it was hypothesised that the amine functional group interacted strongly with the polymer, and this interaction was more significant than molar volume effects.

**Effect of additives on diffusion coefficient**

The literature was surveyed, and two studies that experimentally investigated the effect of additives on the diffusion coefficient were found. Due to the relative scarcity of research on this topic, two additional approaches were used to investigate this effect. First, investigations into the effect of additives on permeability were reviewed. Secondly, data from multiple sources was compared.

Barrer et al [41] experimentally investigated the influence of silica on the diffusion coefficient of PDMS. This was achieved by comparing the diffusion coefficients of an unfilled PDMS membrane and membranes with varying concentrations of silica additive.

The conclusion of this study was that the presence of the additive resulted in a decrease in the diffusion coefficient. The magnitude of this decrease was greater than would be expected if the additive fraction was simply impermeable. This implied that the additive particles effected the surrounding polymer chains. A mechanism for this effect was not proposed by these researchers, but does not appear to be fully understood.

Several studies investigated the effect of additives on the permeability of PDMS membranes [48, 56 - 59]. These investigation reported that the presence of additives significantly affected the permeability. However, a common limitation of these studies was that they did not
determine whether changes in permeability were due to a change in diffusion coefficient or partition coefficient.

However, Hennepe et al [57] proposed a hypothesis regarding the effects of the presence of zeolite fillers on the diffusion coefficient. This investigation found that the permeability of the membrane containing zeolite fillers was greater than that of the unfilled membrane. The authors hypothesised that the cause of this increase was the porous nature of the zeolite fillers. The authors postulated that the porous medium had a lower resistance to diffusion than the dense polymer matrix, resulting in an increased diffusion coefficient. As mentioned, these authors did not experimentally measure the diffusion coefficient.

In order to compare data from multiple sources, the diffusion coefficient of methanol at 25°C was first extracted from a study by La Plack et al [52]. This investigation used a membrane consisting of 70 wt% PDMS and 30 wt% fumed silica. The diffusion coefficient at the above temperature was experimentally measured as $4.2 \times 10^5$ cm$^2$/s.

The diffusivity of methanol at 26°C through an unfilled PDMS membrane was extracted from a study by Watson et al [45]. The value in this case was $3.0 \times 10^6$ cm$^2$/s. The fact that these two values differed by approximately one order of magnitude indicated that the presence of additives had a strong effect on the diffusion coefficient.

*Predictive Models for diffusion coefficient*

Several attempts to develop predictive models for the diffusion coefficient were found in the literature. The majority of these investigations used molecular dynamics simulation to predict diffusion coefficients [60 – 63]. In addition, one investigation developed a simple equation based on the molecular properties of the permeant, which is now described.

LaPack et al [52] developed an equation that successfully predicted the diffusion coefficients of a large number of compounds in a membrane consisting of 69 wt % PDMS and 31 wt % fumed silica. This equation was a function of the Hildebrand solubility parameter of the permeant, the partition coefficient between polymer and filler, and the volume fraction of filler.

A limitation of this method was that it involved the use of an adjustable parameter that was regressed from permeability experiments with the above membrane. As discussed
previously, the presence of additives was found to have a significant effect on the diffusion coefficient. As a result this equation can only be used to predict the permeability of compounds to the membrane used in the study.

Furthermore, the above predictive equation was tested by Han et al [13]. These authors experimentally measured diffusion coefficients and compared them to those predicted by the equation. The predicted values were lower than the measured values by one order of magnitude.

Of the molecular dynamics based predictive models, that of Makrodimitri & Economou [60] was successful at predicting the diffusion coefficients of the largest number of compounds. This model extended the work of the other investigations in this field to include higher molecular weight compounds.

This investigation did not require any fitted parameters to be regressed from experimental permeation data. A single constant, the Lennard Jones parameter for CH₃ was fitted based on the density of PDMS at room temperature.

This model was successful in predicting the diffusion coefficients of several substances. However, a limitation of this study was that the authors did not propose a method of extending the model for blends of PDMS that contained additives. Therefore, at present this method is not capable of predicting the diffusion coefficients of compounds in PDMS that contains additives.

2.2.4 Implications for proposed process

In the preceding sections, the literature relating to the permeation of phenolic compounds through PDMS was reviewed. The implications of this body of knowledge for the proposed process are now discussed.

Effect of TiO₂ additive

In order to design a membrane separation apparatus to carry out the second stage of the proposed process, the rate of permeation of phenolic compounds must be known. Specifically, knowledge of pollutant permeabilities will enable the calculation of the optimum membrane surface area and operating temperature.
Several researchers have developed predictive models to calculate the permeability of phenolic compounds through PDMS [13, 52, 60-63]. However, these models are only valid for PDMS that does not contain additives.

Several studies from the literature reported that additives significantly influenced the transport properties of PDMS membranes [41, 48, 56 - 59]. The proposed process uses a membrane containing a TiO$_2$ additive, in order to improve heat resistance.

As a result, the permeabilities of phenolic compounds through a PDMS membrane containing a TiO$_2$ additive are unknown. Therefore, it was decided to experimentally investigate this knowledge gap in this thesis.

**Effect of molecular structure on permeability**

As the composition of OMW is highly variable, a method of predicting the relative permeabilities of different phenolic compounds is of interest for the design of the proposed process. As discussed previously, existing predictive models are not applicable due to the presence of the TiO$_2$ additive.

As a result, this knowledge gap was selected for investigation in this thesis. Specifically, an experimental investigation will be carried out to determine molecular descriptors that correlate with the partition and diffusion coefficients.

Specifically, a previous study found that the PDMS-water partition coefficient was negatively correlated with the water solubility of the permeant [13]. Due to the influence of the TiO$_2$ filler, it is not clear if this trend is applicable to the membrane used in the proposed process. As a result, this knowledge gap was selected for experimental investigation in this thesis.

Additionally, the effect of the presence of a second –OH substituent on the aromatic ring will be investigated. This relationship has not been previously studied. However, the presence of a single substituent with the capacity for hydrogen bonding was found to substantially decrease the diffusion coefficient. As a result, it was hypothesised that the presence of an additional hydrogen bonding substituent may further reduce the diffusivity.

This particular structural feature was selected for study because an analysis of OMW from several plants found that the two most common phenolic pollutants differed in structure only by the presence of an additional –OH substituent [4].
2.3 Knowledge gaps and objectives
From the preceding literature review it is clear that several gaps exist in the body of knowledge relating to the proposed process. The knowledge gaps identified are as follows:

I) In order to design the decarboxylation reactor with an appropriate residence time, the reaction rate must be known. However, at present no study has investigated the existence or extent of the catalytic effect of stainless steel on decarboxylation of phenolic acids.

II) As the composition of OMW is highly variable, knowledge of the reaction mechanism would be beneficial, as this would allow for predictions regarding the relative reaction rates of different phenolic acids. Due to the unknown catalytic influence of stainless steel, the reaction mechanism is also currently uncertain.

III) In order to design a membrane separation apparatus with appropriate surface area, the membrane permeability must be known. However, at present no study has investigated the influence of TiO$_2$ additives on PDMS permeability.

IV) Due to the variable composition of OMW, knowledge of the molecular descriptors that correlate with permeability would be beneficial, as this would enable predictions regarding the relative permeabilities of different phenolic compounds. Due to the unknown influence of TiO$_2$ additives, this trend is unclear.

V) Several attempts to develop predictive models for the decarboxylation reaction rate were found in the literature. However, these studies had conflicting results and inconsistent accuracy. Also, attempts to predict the permeability of PDMS to various compounds have not yet been extended to blends containing additives. As a result, an experimental approach is required to address the previous knowledge gaps.

This thesis aims to generate the fundamental scientific knowledge necessary to evaluate the viability of the proposed process. Furthermore, many attempts to develop predictive models for the decarboxylation reaction rate and permeability of PDMS have used data from literature sources to evaluate the model accuracy. Therefore, the experimental data reported in this thesis may accelerate the development of such models.

Based on the aim of this thesis, and the above knowledge gaps, the following objectives of this thesis were proposed:
1. Determine whether stainless steel has a catalytic effect on the hydrothermal decarboxylation of 4-HBA.
2. Determine the influence of methoxy substituents on the hydrothermal reactivity of phenolic acids in the presence of stainless steel.
3. Quantify the effect of TiO$_2$ additives on the diffusion and partition coefficients of PDMS membranes.
4. Identify molecular descriptors that correlate with the diffusion and partition coefficients of phenolic compounds in heat resistant PDMS.
Chapter 3

Experimental Apparatus Design

In order to study the reactions of phenolic acids, a micro-flow reactor was used. This apparatus is described fully elsewhere [64], however a brief description and details of operation are given in this Chapter.

In order to study the transport properties of heat resistant PDMS, an apparatus utilising a tubular membrane submerged in a bottle of water was designed. The water in the bottle was periodically sampled and the concentration of permeate was measured using HPLC. In this Chapter the experimental apparatus is described, and the analytical technique is detailed. Furthermore, a claim in the literature regarding the accuracy of this type of experimental setup is critically analysed.

Following this, the experimental apparatus and method used to measure the permeability of the membrane to water was described.

Finally, the experimental method used to measure the PDMS-water partition coefficients of phenolic compounds was described.
3.1 Design of micro-flow reactor

The micro flow reactor was built by Dr Asanka Rahubadda Kankanamge and Mr Sergio Londono. A comprehensive description of the design and operation of this apparatus is given in Dr Kankanamge’s PhD thesis [64]. As a result, this thesis contains only a brief overview, and the interested reader is directed to the above work for further details.

The purpose of the micro flow reactor was to subject aromatic acid solutions to high temperature and high pressure conditions for a precisely controlled length of time. The apparatus was configured as shown in Figure 6.

**Figure 6: Schematic of continuous flow microreactor [64]**

An aromatic acid solution of known concentration was prepared using Millipore water. In order to minimise the time taken to bring this solution to the required temperature, a direct contact heating method was used.

This was achieved with the use of two HPLC pumps. The first pump drew its feed from a Millipore water reservoir, and was capable of providing flowrates of up to 25 mL /min. The outlet of this pump was a stainless steel Swagelok tube, around which a heating cable was wrapped. This heating cable was powered by a DC power supply. A thermocouple entered this tube via a watertight fitting in order to measure the fluid temperature at the outlet.
The second HPLC pump drew its feed from the test solution reservoir, and had a maximum flowrate of 10 mL/min. The outlet of this pump was a tee junction, in which the preheated water was combined with the test solution. This direct contact mixing enabled rapid heating of the test solution.

Immediately after mixing, the combined streams entered the reactor, which consisted of a coiled stainless steel tube of known volume. This coil was also wrapped with a heating wire that was attached to a DC power supply. The reactor was thermally insulated from the environment with glass wool. A thermocouple entered the reactor in order to measure the fluid temperature.

The outlet of the reactor was a stainless steel tube, which connected to a back pressure regulator (BPR). The purpose of the BPR was to maintain the desired pressure in the reactor. The outlet of the BPR was a PEEK tube, the outlet end of which was located above a beaker, into which the liquid products flowed.

### 3.1.1 Experimental Procedure

Once again, a detailed operating procedure is available in Dr Kankanamge’s PhD thesis. Hence only a brief overview is given here.

A solution of known acid concentration was first made up. Specifically, a known mass of 4-hydroxy benzoic acid, syringic acid or benzoic acid was dissolved in Millipore water. These acids were all purchased from Sigma Aldrich.

Initially, the test solution pump was configured to draw its feed from a second reservoir of Millipore water. The pump was set to the flowrate that was required to achieve the desired residence time. The water pump was then turned on and set to the required flowrate.

The BPR was then adjusted to achieve the correct operating pressure. The preheater was then turned on and set to the voltage required to achieve the desired temperature.

After the preheater temperature had stabilised, the oven was turned on. After the reactor temperature had stabilised at the required value, the inlet of the first HPLC pump was switched, so that it began pumping the test solution, rather than Millipore water.

The test solution was allowed to flow through the reactor, while it was maintained at the correct pressure and temperature for 10 minutes. A sample was then taken.
The temperature was then adjusted to the next value to be investigated, by changing the power settings of the preheater and reactor. The flowrate was not adjusted when the temperature was changed, as it was found that this increased the time taken for the reactor temperature to stabilise. As a result, the residence times changed slightly with each new temperature.

3.2 Design of membrane characterisation experimental apparatus

A schematic of the experimental setup used to investigate the behaviour of the membrane is shown in Figure 7. In brief, a solution of known concentration was passed through a tubular membrane that was submerged in a bottle of water. The solute permeated through the membrane into the water in the bottle, which was periodically sampled and analysed using HPLC.

![Figure 7: Schematic of membrane separation apparatus](image)

A Varian ProStar HPLC pump was used to transport the test solution through the tubular membrane. The inlet to this pump was a flexible length of tubing that was placed either in the volumetric flask containing the test solution, or in a beaker of deionized water.

The outlet port of the pump was connected to a 1/16 inch stainless steel Swagelok tube. This tube passed through a beaker containing water that was mounted on a heater stirrer. The
The purpose of this water bath was to preheat the test solution. After passing through the preheating bath, the tube entered the stripping solution bottle.

Immediately above the surface of the liquid inside the bottle, a fitting was attached to the steel tubing. This fitting was used to join a known length (1 m) of polydimethylsiloxane tubing to the steel tube, forming a watertight seal. The PDMS tubing was submerged in the stripping fluid. The outlet of the PDMS tubing was joined to a second section of stainless steel tubing using a second fitting.

The polydimethylsiloxane tubing was bought from Silex. The blend of polymer used for this work contained a proprietary additive designed to improve the heat resistance of the material. The internal diameter of the tube was 3 mm and the wall thickness was 0.5 mm.

The stripping solution bottle was mounted on a heater stirrer with an automatic temperature controller. The temperature probe for this control system entered the stripping bottle through a specially designed opening in the bottle cap. The opening was designed to be a snug fit around the thermocouple, to minimize the evaporation of any volatile species.

The outlet of the final section of stainless steel tubing was connected to a waste bottle into which the fluid was discharged. All tubing and fittings used in this apparatus were purchased from Swagelok. The entire apparatus was housed in a fume cupboard in order to prevent the emission of hazardous fumes to the laboratory.

### 3.2.1 Experimental Procedure

The goal of the experiments using this apparatus was to investigate the effect of various factors on the mass transfer coefficient of the membrane. In order to achieve this, a solution of known concentration of solute was first made up.

Specifically, a solution was made up using Millipore water and a known mass of either phenol, guaiacol, catechol or 4-methyl catechol. Phenol, catechol and guaiacol were bought from Sigma Aldrich. 4-methyl catechol was bought from AK scientific.

Initially, the inlet of the HPLC pump was placed in the Millipore water beaker. The pump was then turned on and set to the desired flowrate. The preheating bath was then turned on and set to the desired temperature. The stirrer function of this bath was also turned on, and set
to 120 RPM. The temperature of this heating bath was monitored using the inbuilt temperature indicator on the heater stirrer.

The HPLC pump had a built in pressure gauge and display, with an accuracy of 0.1 bar. When the pump was turned on, the reading on this display remained at 1 atmosphere. This indicated that the pressure drop developed by the passage of the liquid through the apparatus was below 0.1 bar.

The heater stirrer on which the stripping solution bottle was mounted was then turned on, and set to the desired temperature and stirrer frequency. The temperature of the stripping solution was monitored using the temperature indicator.

When the heating bath and stripping side solution temperatures remained steady at the appropriate value, a sample was taken from the stripping solution bottle. Sampling was carried out using a syringe to aspirate approximately 1 mL liquid from the stripping solution bottle. This was then transferred to a HPLC vial to be tested.

After taking the initial sample, the inlet tube of the HPLC pump was then transferred to the volumetric flask that contained the test solution. At this point a timer was started, and further samples were taken after 30, 60, 90 and 120 minutes. The same technique described above was used to take these samples.

After the experiment was completed, the apparatus was cleaned by pumping Millipore water through the membrane for 30 minutes. During this 30 minute cleaning session the stripping solution was replaced with Millipore water several times. Different solutes were used in subsequent experiments so that any residual contamination could be easily detected by examination of the chromatograms.

The selection of operating temperature, agitation frequency, solute concentration and flowrate will be discussed in detail in Chapter 5.

3.2.2 Design Calculations

In order to calculate the mass transfer coefficient, it was necessary to determine the area of the tube that was available for mass transfer. This is not simply equal to the surface area of the tube that is submerged by water, as part of the tube is in contact with the glass wall, and hence cannot take part in mass transfer. This concept is illustrated in Figure 8.
Several studies have utilised an experimental apparatus consisting of a length of tubing loosely arranged inside a vessel, similar to the setup used in the present work [11, 13]. These studies all assumed that the entire tube area was available for mass transfer, but did not provide any justification for this assumption. In order to address this shortcoming of the literature, the fraction of surface area available for mass transfer was investigated.

First, an experiment was carried out in order to determine the force exerted by the tubing as a result of the tube elasticity, and pressure of the tube side fluid. Water was pumped through the tube at the same flowrate that was used in the permeation experiments. The tubing was removed from the glass bottle and placed on a lab bench in a horizontal orientation. An object weighing 500 g was then placed on top of the tubing.

As a result, the tubing deformed, with the height of the loops of tubing decreasing from 5 cm to 1 cm. The final height was lower than the diameter of the glass bottle used in the permeation experiments, 4 cm. This experiment is shown in Figure 9.
In order to determine the magnitude of the forces exerted by the tubing, a free body diagram of the tubing was first developed. The forces acting on the tube are the weight force due to the object, denoted $F_W$, and the normal force exerted by the lab bench, $F_N$. The weight of the tubing itself was ignored.

The experimental apparatus is known to be in a state of mechanical equilibrium. Applying Newton’s Second Law of Motion:

$$\sum F_y = F_N - F_W = 0 \quad (3.1)$$

Solving for $F_N$:

$$F_N = F_W \quad (3.2)$$

Using the definition of weight, the magnitude of $F_W$ was calculated:
\[ F_w = mg \]  

\[ F_w = 0.5 \, kg \times 9.81 \, N/kg \]  

\[ F_w = 4.9 \, N \]  

Substituting the Equation 3.4 into Equation 3.2:

\[ F_N = 4.9 \, N \]  

In the next step of the analysis, a free body diagram of the section of the tube wall that was in contact with the lab bench was developed. A sketch illustrating the section that is being analysed is presented in Figure 11.

\[ \text{Figure 11: Diagram highlighting deformation of tubing against lab bench} \]

The forces acting on this section of tubing are the normal force exerted by the lab bench, \( F_N \), the force exerted on the tube walls due to the pressure of the lumen side fluid, \( F_{P1} \), and the force exerted on the wall by the elasticity of the tube as it tends to regain its original shape, \( F_{E1} \).

The elastic force occurs due to both the tendency of the tubing to regain its circular cross sectional profile, and the tendency of the tubing to return to a straight, rather than looped arrangement. The magnitude of this force is very complex to calculate. However, as will be shown, it is not necessary to calculate this magnitude. A free body diagram of this section of tubing is presented in Figure 12.
Applying Newton’s Second Law of Motion:

\[ \sum F_y = F_N - F_{E1} - F_{P1} = 0 \quad (3.6) \]

Solving for \( F_N \):

\[ F_N = F_{E1} + F_{P1} \quad (3.7) \]

Substituting Equation 3.6 into Equation 3.2:

\[ F_W = F_{E1} + F_{P1} \quad (3.8) \]

Finally, a free body diagram of the object that was placed on top of the tubing was developed. The forces acting on the body are the weight force, \( F_W \), and the pressure and elastic forces exerted by the tubing, \( F_{P2} \) and \( F_{E2} \). This free body diagram is presented in Figure 13.
Figure 13: Free body diagram of weight that was placed on top of tubing

Applying Newton’s Second Law of Motion:

$$\sum F_y = F_{E2} + F_{P2} - F_W = 0$$ \hspace{1cm} (3.9)

Solving for $F_W$:

$$F_W = F_{E2} + F_{P2}$$ \hspace{1cm} (3.10)

Substituting Equation 3.4 into Equation 3.10:

$$F_{E2} + F_{P2} = 4.9 \, N$$ \hspace{1cm} (3.11)

Equation 3.11 will now be used to analyse the experimental apparatus to determine the area of tubing in contact with the bottle wall.

Analysis of experimental apparatus

The strategy that will be employed to determine whether the area of the tube that is in contact with the wall of the bottle is significant is as follows. An upper limit for the contact area will be calculated, and the fraction of the total area that this represents will be calculated. If this maximum value is insignificant, it can be concluded that the real value is also insignificant.
In order to simplify the analysis it was assumed that the tubing is symmetrical and has two locations of contact with the walls of the bottle, on the left and right hand sides. These are denoted $A_{W1}$ and $A_{W2}$ respectively.

A free body diagram was developed to analyse the forces acting on the section of tube wall that was in contact with the left hand side of glass bottle. The section of the tube wall that is being analysed is analogous to that shown in Figure 11. The forces consist of the elastic force, the force due to the pressure inside the tube, and the normal force from the wall of the bottle. This free body diagram is presented in Figure 14.

![Free body diagram of section of tube wall in contact with left hand side of bottle wall](image)

*Figure 14: Free body diagram of section of tube wall in contact with left hand side of bottle wall*

The experimental apparatus is known to be in a state of mechanical equilibrium. Applying Newton’s Second Law of Motion:

$$\sum F_x = F_N - F_E - F_P = 0$$  \hspace{1cm} (3.12)

Solving for $F_N$:

$$F_N = F_E + F_P$$  \hspace{1cm} (3.13)

Hooke’s Law states that the magnitude of the force required to compress an elastic body is proportional to the magnitude of the deformation. Recall that the height of the tubing after the weight force was applied was 1 cm, and the diameter of the glass bottle was 4 cm.
Therefore, the sum of the elastic and pressure forces exerted by the tubing on the weight is greater than the forces exerted against the sides of the glass bottle. That is:

\[ F_E + F_P < F_{E2} + F_{P2} \] (3.14)

The goal of this analysis is to estimate an upper limit for the force exerted by the tubing against the bottle walls. Therefore, in order to be conservative, it was assumed that the sum of the elastic and pressure forces exerted against the bottle wall was equal to the sum of the forces exerted by the tubing against the weight:

\[ F_E + F_P = F_{E2} + F_{P2} \] (3.15)

Substituting Equation 3.11 into Equation 3.15:

\[ F_E + F_P = 4.9N \] (3.16)

Substituting Equation 3.16 into Equation 3.13:

\[ F_N = 4.9N \] (3.17)

The force due to the pressure of the liquid inside the tube is calculated using the definition of pressure:

\[ P \equiv F_P / A \] (3.18)

Solving for \( F_P \):

\[ F_P = P A_{W1} \] (3.19)

Substituting Equation 3.19 into Equation 3.13:

\[ F_N = F_E + P A_{W1} \] (3.20)

Solving for \( A_{W1} \):

\[ A_{W1} = \frac{F_N - F_E}{P} \] (3.21)

As mentioned, the force exerted due to the elasticity of the tube, \( F_E \) is very complex to calculate. However, by inspection of Equation 3.21 it is apparent that the maximum value of \( A \) occurs when \( F_E \) is zero. Therefore, to simplify the analysis, and ensure that the upper limit for contact area was calculated, it was assumed that this was the case:
\[ F_E = 0 \quad (3.22) \]

Substituting equation 3.22 into equation 3.21:

\[ A_{W1} = \frac{F_N}{P} \quad (3.23) \]

As mentioned in Section 3.2.1, the pressure of the liquid inside the tube was measured as 1 atmosphere by the HPLC pumps built in pressure gauge. This value was substituted into Equation 3.23. Equation 3.17 was also substituted into Equation 3.23, and the following value was calculated for \( A_{W1} \):

\[ A_{W1} = \frac{4.9 \ N}{101,325 \ N/m^2} \]

\[ A_{W1} = 4.84 \times 10^{-5} \ m^2 \quad (3.24) \]

Recall that the above analysis is based on the assumption that there are two locations in which the tube contacts the bottle wall, \( A_{W1} \) and \( A_{W2} \). As the tubing is symmetrical, these contact areas are also equal:

\[ A_{W1} = A_{W2} = 4.84 \times 10^{-5} \ m^2 \quad (3.25) \]

Therefore the total contact area is given by:

\[ A_W = A_{W1} + A_{W2} = 9.68 \times 10^{-5} \ m^2 \quad (3.26) \]

The total surface area of the tube was then calculated, based on its cylindrical geometry:

\[ A_T = \pi DL \quad (3.27) \]

\[ A_T = \pi \times 0.004 \ m \times 1 \ m \]

\[ A_T = 0.0126 \ m^2 \]

The ratio of wall contact area to total tube surface area was then calculated:

\[ R = \frac{A_W}{A_T} = \frac{9.68 \times 10^{-5} \ m^2}{0.0126 \ m^2} \]

\[ R = 0.0077 \]

Therefore, the fraction of the tube wall that is in contact with the walls of the bottle is < 0.77% of the total surface area. This is not a significant fraction of the total area, and will be ignored.
3.3 Design of membrane water permeability experiments
The water permeability of the membrane used in this work was experimentally investigated. A 10 g/L saline solution was prepared using NaCl purchased from Sigma Aldrich. The solution was aspirated with a syringe and transferred into the interior of a section of membrane tubing. The tubing was then placed in a sample bottle containing Millipore water, as shown in Figure 15. Aluminium foil was used to form an airtight seal over the opening of the bottle.

![Diagram of experimental setup for water permeability of membrane experiments](image)

Figure 15: Schematic of experimental setup for water permeability of membrane experiments
This concentration gradient acted as a driving force for osmosis of water into the tube from the bottle. The initial water level within the sample bottle was marked, and the apparatus was left in a fume cupboard for 96 hours. After this time the apparatus was inspected, and the water level compared to the initial marking.

A decrease in the water level would indicate that transport of water from the bottle side to tube side had occurred. The occurrence of this transport would imply that the membrane was permeable to water. If the level remained unchanged, this would imply that the membrane was impermeable to water.

3.4 Design of partition coefficient experiments
The PDMS-water partition coefficients of several phenolic compounds were measured using the method of Brookes and Livingstone [40].
A known mass of PDMS tubing was placed inside a glass sample bottle. The bottle was then filled to the top with a solution of known concentration, leaving a minimal airgap. The bottle was then sealed by screwing on the metal cap, and was shaken to ensure good mixing.

The bottle was then placed in a temperature controlled environment for 48 hours. Specifically, the sample bottle was placed in either an oven, a cupboard in a temperature controlled laboratory or a refrigerator.

After 48 hours, the bottle was removed from the temperature controlled environment and the aqueous phase concentration was measured. This was achieved by taking a sample from the solution, and using the analytical techniques that will be described subsequently. The ratio of the concentration of the compound within the PDMS to the concentration of the compound in the aqueous phase was then calculated using the following equation.

\[ K = \left( \frac{C_0}{C_{eq}} - 1 \right) \cdot \frac{V_F}{V_M} \]  

(3.29)

In which \( C_0 \) is the initial concentration of the solution expressed as w/v, \( C_{eq} \) is the concentration measured after 48 hours, \( V_F \) is the volume of the solution, and \( V_M \) is the volume of the membrane.

It should be noted that to prove that equilibrium had been reached, measurement of the liquid phase concentration should be carried out several at several time intervals. However, the study of Brookes and Livingstone [40] found that 48 hours was significantly longer than required to reach equilibrium. As a result, the same approach was taken in this work, in order to simplify the experimental procedure.

3.5 Analytical Methodology
All samples taken in these experiments were analysed using an HPLC system bought from Agilent Australia. Specifically, a MicroSorb C18 column and a ProStar 335 PDA detector were used to identify and determine the concentration of solutes.

The details of the isocratic method are as follows. The mobile phase consisted of 3.3 g/L acetic acid and methanol (70%/30% by volume) with a flowrate of 0.4 mL / minute. The injection volume was 10 µL. The UV detector was operated at a wavelength of 215 nm. The column temperature was 308 K. The running times were 20-30 minutes depending on the compounds to be detected.
Using this configuration, clear separation was obtained for all compounds studied, as will be seen in the subsequent chapters.

3.6 Summary
This chapter described the experimental apparatus used in this work, and showed rigorous design calculations for the membrane apparatus. The experimental method and analytical methodology are also described here. The subsequent chapters will present, analyse and discuss the experimental results that were obtained using these experimental techniques.
Chapter 4

Decomposition of phenolic acids under subcritical water conditions

The first stage of the process proposed by this thesis consists of subjecting OMW to high pressure and high temperature conditions. Under these conditions, phenolic acids (which are a pollutant found in OMW) are known to undergo decarboxylation reactions. The products of these reactions are non-acidic phenolic compounds. This treatment is necessary because the second stage of the process utilises a nonporous PDMS membrane to separate pollutants from OMW. This membrane is not capable of separating acidic compounds.

In order to design a reactor with an appropriate volume to carry out this process, the kinetics of the decarboxylation reaction must be known. The composition of OMW is highly variable, so the relationship between molecular structure and reactivity is also of practical interest.

For economic reasons, stainless steel is generally preferred as the material of construction for industrial reactors. Previous studies have found that stainless steel catalysed the hydrothermal decarboxylation of some non-phenolic carboxylic acids. As the decarboxylation of phenolic acids is an extremely similar reaction, it was hypothesised that stainless steel may also catalyse this reaction. The kinetics of the hydrothermal decarboxylation of phenolic acids in a stainless steel reactor have not previously been investigated.

In order to address this knowledge gap, a reactor constructed from 316 stainless steel was used to experimentally investigate the reactivity of 4-hydroxybenzoic acid (4-HBA). The measured rate of reaction was compared to that reported by a previous study in which the reactivity of 4-HBA was studied in a gold lined reactor.

In addition to practical applications, these experiments will also extend the existing body of fundamental knowledge on this topic. Specifically, past studies have found that some
decarboxylation reactions are catalysed by stainless steel and others are not. The reason for this behaviour is not currently understood. The results of these experiments will enable further testing of hypotheses regarding the cause of this behaviour.

The mechanism by which the decarboxylation reaction proceeds has also been studied in the absence of a catalyst. However, the influence of stainless steel on this reaction mechanism is unknown. As a result, the influence of additional electronegative substituents is unclear. In order to investigate this knowledge gap, an experimental kinetic study of the decarboxylation of syringic acid was undertaken. Syringic acid differs from 4-HBA only by the presence of two additional methoxy substituents, and is a commonly occurring phenolic pollutant in OMW. In order to gain further insight into the influence of electronegative substituents, the reactivity of benzoic acid was also investigated.
4.1 Methodology

The experiments in this chapter were carried out using the flow reactor described in Chapter 3. The identification and quantification of products was achieved using HPLC, as described in Chapter 3. An overview of these methods is given here.

Solutions containing syringic acid, 4 Hydroxy Benzoic Acid (4-HBA), or benzoic acid were processed with the flow reactor. These solutions were initially a pale yellow colour. After processing, the solutions were either yellow or colourless. No solids were generated during these reactions.

In general it is uncommon for reaction rate laws to vary due to the presence of uncoupled chemical reactions in the same system. However, the mechanism of these reactions is not well understood, so it is possible that catalytic or other effects may occur. In order to avoid these complicating factors, the reaction rates of each acid were studied individually. That is, solutions containing only a single acid were prepared, and passed through the reactor.

The products of these reactions were found to be phenol, syringol, 3-methoxy catechol and pyrogallol. These were identified using HPLC with a visible light spectrum detector as described in Chapter 3. These products were clearly separated, as will be shown in chromatograms later in this Chapter.

A mass balance was carried out for these experiments, which will also be described in detail subsequently. The discrepancy was < 6% for all experiments, indicating that all significant reactions were identified.
4.2 Results

4.2.1 Syringic acid conversion
Aqueous solutions containing 1.013 g/L of syringic acid were subjected to subcritical conditions using the flow reactor as described in Chapter 3. The reaction temperatures ranged from 230°C to 310°C and the residence time was varied between 8.5 and 30 seconds. The pressure was maintained at 200 bar for all experiments.

These experiments were repeated in duplicate, and the average difference between the repeats was found to be < 5%. The conversion of syringic acid after exposure to the above conditions is shown in Figure 16. The data points represent the average value of the two repeats.

![Figure 16: Conversion of syringic acid as a function of residence time and reaction temperature at a constant pressure of 200 bar in a tubular flow reactor](image)
In order to determine the reaction order, a subset of the above experiments was repeated, using a lower initial concentration of syringic acid. Specifically, the set of experiments investigating the effect of residence time on conversion at 270°C was repeated using an initial concentration of 0.5006 g/L. This was approximately 50% lower than the original initial concentration. The results of the lower initial concentration experiments were within 5% of those obtained from the original experiments.

The observation that the rate of conversion was independent of the initial concentration suggested that the reaction was first order. For each temperature investigated, a first order rate constant was calculated based on the measured conversion data. The process by which the first order rate constants were calculated is now described.

### 4.2.1.1 Calculation of first order rate constant

By definition, the rate of reactant disappearance for a first order reaction can be mathematically expressed with the following equation:

\[ r = kC \]  
(4.1)

For a flow reactor, the time rate of change of reactant concentration is related to the rate of disappearance by the following equation:

\[ \frac{dC}{dt} = -r \]  
(4.2)

Substituting Equation 4.2 into Equation 4.1:

\[ \frac{dC}{dt} = -kC \]  
(4.3)

Integrating between initial concentration, \( C_0 \) and concentration at time \( t \), denoted \( C_1 \):

\[ \int_{C_0}^{C_1} \frac{dC}{C} = \int_0^t -k \, dt \]

\[ \ln \frac{C_1}{C_0} = -kt \]

Rearranging:

\[ \frac{C_1}{C_0} = e^{-kt} \]  
(4.4)

Recall the definition of conversion, \( X \):
\[ X \equiv 1 - \frac{C_1}{C_0} \]  

(4.5)

Rearranging:

\[ \frac{C_1}{C_0} = 1 - X \]  

(4.6)

Substituting Equation 4.6 into Equation 4.4:

\[ 1 - X = e^{-kt} \]  

(4.7)

Solving Equation 4.3 for \( kt \):

\[ \ln(1 - X) = -kt \]

\[ -\ln(1 - X) = kt \]  

(4.8)

Therefore, plotting \(-\ln(1 - X) vs t\) will yield a straight line with a gradient of \( k \). This relationship is shown in Figure 17.
Figure 17: Pseudo first order kinetics of syringic acid disappearance at various temperatures in water at a constant pressure of 200 bar

The trend lines shown in Figure 17 were obtained by linear regression, using Microsoft Excel’s inbuilt chart function. The high coefficient of determination for each trend line indicated that the first order reaction assumption closely matched the experimental data.

By inspection of the above plot, the following first order reaction coefficients for each temperature were read off:
Table 1: First order rate constants for decarboxylation of syringic acid at various temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( k ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>0.00627</td>
</tr>
<tr>
<td>250</td>
<td>0.0105</td>
</tr>
<tr>
<td>270</td>
<td>0.0215</td>
</tr>
<tr>
<td>290</td>
<td>0.0400</td>
</tr>
<tr>
<td>310</td>
<td>0.0767</td>
</tr>
</tbody>
</table>

By inspection of the above table it was observed that with every 20°C increase in reaction temperature, the rate constant approximately doubled. This observation suggested that the temperature dependence of the reaction rate constant followed an Arrhenius relationship.

In order to quantify this temperature dependence, values for the Arrhenius parameters were calculated based on the above data. The process by which values for activation energy and the pre-exponential factor were calculated will now be described.

4.2.1.2 Calculation of activation energy and pre-exponential factor

Recall the Arrhenius equation:

\[
k = Ae^{-E_A/RT}
\]  

(4.9)

Rearranging:

\[
\ln(k) = \ln(Ae^{-E_A/RT})
\]

\[
\ln(k) = \ln(A) + \ln(e^{-E_A/RT})
\]

\[
\ln(k) = \ln(A) - E_A/RT
\]  

(4.10)

Thus plotting \( \ln(k) \) against \( 1/T \) will yield a straight line with a gradient of \( -E_A/R \) and a \( y \) intercept of \( \ln(A) \). This relationship is shown in Figure 18.
Figure 18: Arrhenius plot of rate constants for hydrothermal decarboxylation of syringic acid

The trend line shown in Figure 18 was obtained by linear regression, using Microsoft Excel’s inbuilt chart function. The high coefficient of determination indicates that the Arrhenius equation accurately described the experimental data.

Based on the gradient and y intercept of the above trend line, the activation energy was determined to be 77,300 J/mole. The natural logarithm of the frequency factor was determined to be 13.32.

4.2.1.3 Identification of products

The products of the reaction were analysed with HPLC, and one additional peak was detected. A typical chromatogram of the products of this experiment is shown in Figure 19. This additional peak was identified as syringol.
Figure 19: Typical chromatogram from syringic acid experiments

The molecular structures of syringic acid and syringol are as follows:

![Molecular structures of syringic acid and syringol](image)

Figure 20: Molecular structures of syringic acid (L) and syringol (R)

By inspection of the above structures, it was deduced that carbon dioxide was evolved during the reaction. Based on this insight, the following balanced reaction was proposed.

![Balanced reaction](image)

Figure 21: Balanced reaction for decarboxylation of syringic acid to syringol

The mechanism of the above reaction will be discussed at a subsequent point in this Chapter.

4.2.1.4 Secondary reaction

At high temperatures and long residence times, the chromatograms of the product samples showed an additional peak, suggesting a secondary reaction had occurred.
Figure 22: Chromatogram from syringic acid experiments, showing additional peak

This compound was identified as 3-methoxy catechol, which has the following molecular structure.

![Molecular structure of 3-methoxy catechol](image)

Figure 23: Molecular structure of 3-methoxy catechol

By inspection of the above molecular structure, it was deduced that one of syringol’s methoxy groups had been replaced by a hydroxyl group. Based on this observation, the following balanced reaction was proposed.

![Balanced reaction for demethoxylation of syringol to 3-methoxy catechol](image)

Figure 24: Balanced reaction for demethoxylation of syringol to 3-methoxy catechol

Due to the lack of kinetic data, a mechanism was not proposed for this reaction.
4.2.1.5 Tertiary reaction
By inspection of the structure of 3-methoxy catechol, it was observed that this molecule contained a methoxy substituent. It was hypothesized that at longer residence times, this methoxy group would also be substituted by a hydroxyl group.

In order to test this hypothesis, a solution of 3-methoxy catechol was prepared and passed through the flow reactor. The products were analysed using HPLC, and the chromatogram showed a second peak.

![Chromatogram](image)

*Figure 25: Chromatogram from 3-methoxy catechol experiment, showing additional peak*

This peak was identified as pyrogallol, which has the following structure.

![Pyrogallol structure](image)

*Figure 26: Molecular structure of pyrogallol*

Hence the hypothesis that the methoxy group would be substituted by a hydroxyl group was confirmed. Based on this observation, and the molecular structures of the reactant and product, the following balanced reaction was proposed.
Figure 27: Balanced reaction for demethoxylation of 3-methoxy catechol to pyrogallol

As the above reaction only occurred in trace amounts, the mechanism was not investigated.

4.2.1.6 Mass balance
In order to assess whether any other reactions had occurred that were not identified, a mass balance was formulated. The following equation was used to calculate the mass that was unaccounted for. The secondary and tertiary reactions were not included in this calculation, as the amounts of the products formed were insignificant.

\[
Mass\ Loss = Syringic\ Acid_{Initial} - (Syringic\ Acid_{Final} + M(Syringol) + M(CO_2))
\]  

(4.11)

The mass of CO₂ evolved was not directly measured. This was calculated based on the stoichiometry of the above reaction, using the following formula:

\[
CO_2 = Syringol \times \frac{MW_{CO2}}{MW_{Syringol}}
\]  

(4.12)

The mass loss was expressed as a percentage of the initial reactant.

\[
Mass\ Loss\ Percentage = \frac{Mass\ Loss}{Syringic\ Acid_{Initial}} \times 100\%
\]  

(4.13)
The mass loss percentage was calculated for each individual experiment using the above formula. The average of these values for each reaction temperature were calculated, and are shown in Figure 28.

![Figure 28: Mass balance for syringic acid experiments](image)

The average percentage mass loss was < 6% for each set of experiments. The mass loss was consistently positive, indicating that some mass was not accounted for. This unaccounted mass is thought to be due to human error during the experimental process.

For example, the sampling process was carried out under a spigot in order to prevent fumes escaping into the laboratory. As a result, a small fraction of the products may have evaporated from the solution. The amount lost through this process is not expected to be large, as the boiling points of phenol and syringol are 181.7 °C and 261.0 °C respectively. Another possibility is that the reactor may have exhibited imperfect mixing, resulting in some products being held up.

These errors are sufficiently small that the kinetic parameters that were calculated previously are not significantly affected. Having investigated the behaviour of syringic acid, attention was then turned to 4-hydroxy benzoic acid.
4.2.2 4-Hydroxy benzoic acid conversion

The behaviours of 4-Hydroxy Benzoic Acid (henceforth, 4-HBA) and syringic acid were investigated using similar methods. Aqueous solutions containing 1.0134 g/L of 4-HBA were subjected to high pressure and high temperature conditions using the flow reactor as described in Chapter 3. The reaction temperatures ranged from 230°C to 310°C and the residence time was varied between 15 and 30 seconds. The pressure was maintained at 200 bar for all experiments.

These experiments were repeated in duplicate, and the average difference between the repeats was found to be < 5%. The conversion of 4-HBA after exposure to the above conditions is shown in Figure 29. Each data point represents the average of the two repeats.

![Figure 29: Conversion of 4-HBA as a function of residence time and reaction temperature at a constant pressure of 200 bar in a tubular flow reactor](image)
Similarly to the case of the syringic acid experiments, the results of the above experiments were consistent with the occurrence of an irreversible, first order reaction.

In order to test the hypothesis that the reaction was first order, a subset of the above experiments was repeated using a lower initial concentration of 4-HBA. Specifically, the set of experiments investigating the effect of residence time on conversion at 250°C was repeated using an initial concentration of 0.5017 g/L. This represented a 50% decrease compared to the original initial concentration. The results of these experiments were within 5% of those obtained from the original experiments.

In order to quantify the rate of reaction, first order rate constants were calculated for each temperature based on the experimental data.
4.2.2.1 Calculation of first order reaction rate constants

The first order rate constants were calculated using the process described in Section 4.2.1. Figure 30 shows a plot of $-\ln(1 - X)$ vs $t$ for the above results.

![Figure 30: Pseudo first order kinetics of syringic acid disappearance at various temperatures in water at a constant pressure of 200 bar](image)

The trend lines shown in Figure 30 generally had a high coefficient of determination. However, the experiments carried out at 230°C had a coefficient of determination of 0.84, which was the lowest of all the temperatures investigated. One possible explanation for this observation is that the conversions at this temperature were the lowest. Thus, random error will have a greater significance at this temperature than at any other.
By inspection of the above plot, the first order reaction coefficients for each temperature are as follows:

Table 2: First order rate constants for decarboxylation of 4-HBA at various temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>k (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>0.00287</td>
</tr>
<tr>
<td>250</td>
<td>0.00701</td>
</tr>
<tr>
<td>270</td>
<td>0.0194</td>
</tr>
<tr>
<td>290</td>
<td>0.0400</td>
</tr>
<tr>
<td>310</td>
<td>0.0871</td>
</tr>
</tbody>
</table>

From the above results it was observed that the rate constant increased by a factor of approximately 2.5 with every 20°C increase in reaction temperature. Based on this observation it was hypothesised that the rate constant followed an Arrhenius relationship with temperature. In order to quantify this temperature dependence, values for the Arrhenius parameters were calculated based on the above experimental data.
4.2.2.2 Calculation of Arrhenius parameters

The Arrhenius parameters were calculated using the process described in Section 2.2. A plot of \( \ln(k) \) against \( 1/T \) is shown in Figure 31.

\[
y = -12580x + 19.14 \quad R^2 = 0.9987
\]

**Figure 31: Arrhenius plot of rate constants for hydrothermal decarboxylation of syringic acid**

Based on the gradient and y intercept of the above trend line, the activation energy was determined to be 104,600 J/mole. The natural logarithm of the frequency factor was determined to be 19.14.

4.2.2.3 Product identification

The products of the reaction were analysed with HPLC, and one additional peak was detected. A typical chromatogram of the products of this experiment is shown in Figure 32. This additional peak was identified as phenol.
The molecular structures of 4-HBA and phenol are as follows:

\[
\begin{align*}
\text{4-HBA} & : \quad \text{HO}_2\text{C-phenol} \\
\text{Phenol} & : \quad \text{HO-phenol}
\end{align*}
\]

By inspection of the above structures, it was deduced that carbon dioxide was also evolved during the reaction. Based on this insight, the following balanced reaction was proposed.

\[
\text{4-HBA} \rightarrow \text{Phenol} + \text{CO}_2
\]

Based on the stoichiometry of the above reaction, a mass balance was carried out.
4.2.2.4 Mass balance
The mass loss occurring during these experiments was calculated in order to determine if any other reactions had occurred. This was achieved using Equation 4.11 to 4.13 by adapting, them to the reactant (4-HBA) and products (phenol and CO2) involved here.

The average percentage mass losses for the experiments carried out at each reaction temperature are shown in Figure 35:

![Percentage Mass Loss vs. Temperature Graph](image)

**Figure 35: Mass balance for 4-HBA experiments**

As was the case with syringic acid, the values were consistently positive, indicating that some mass was not accounted for. The mass loss was <5% for all reaction temperatures. These losses are also thought to result from accumulation in the reactor, or experimental errors while taking samples.

These errors were sufficiently small as to not significantly affect the calculated kinetic parameters.

4.2.3 Benzoic acid conversion
The stability of benzoic acid was investigated in a similar manner to the other acids. Aqueous solutions containing 1.0134 g/L of benzoic acid were subjected to subcritical conditions using the flow reactor as described in Chapter 3.
Benzoic acid was subjected to the most severe conditions permitted by the experimental apparatus, 310°C and 30 seconds residence time. Under these conditions, no reaction was observed. That is, the conversion of benzoic acid was 0%. Based on this observation, the remaining temperatures were not experimentally investigated, as it was clear that no reaction would occur.

4.3 Discussion
The results presented in this chapter were analysed, in order to investigate the knowledge gaps identified in the objectives of this thesis. Specifically, the reactivities of each species were compared, in order to determine a reaction mechanism. Also, the results from this study were compared to those from a literature study which was conducted in a gold reactor, in order to determine the catalytic effect of stainless steel.

4.3.1 Comparison of reactivities of species
The reactivities of the three acids studied in this thesis are summarised in the following table.

Table 3: Arrhenius parameters for decarboxylation of syringic acid, 4-HBA and benzoic acid

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_A$ (J/mole)</th>
<th>$\ln(A)$ (–)</th>
<th>Number of Substituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syringic Acid</td>
<td>77,300</td>
<td>13.32</td>
<td>3</td>
</tr>
<tr>
<td>4-HBA</td>
<td>104,600</td>
<td>19.10</td>
<td>1</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>–</td>
<td>–</td>
<td>0</td>
</tr>
</tbody>
</table>

The reactivities of syringic acid and 4-HBA can also be compared by plotting the first order rate constants as a function of temperature. This is presented in Figure 36.
Figure 36: First order reaction rate constants of syringic acid and 4-HBA as a function of temperature

Figure 36 illustrates that at lower temperatures, the rate of reaction is higher for syringic acid than for 4-HBA. However, at a reaction temperature of 290°C, the rate of reaction is the same for both acids. At 310°C the rate of reaction for 4-HBA exceeds that of syringic acid. This reflects the fact that at high temperatures, the exponential term of the Arrhenius equation becomes less significant, and the pre-exponent becomes the dominant term.

Having compared the reactivities of the species, the influence of molecular structure on reactivity is investigated.

4.3.2 Influence of molecular structure on reactivity

From Table 3, it was observed that the activation energy decreased as the degree of substitution increased. This trend was compared with the current body of knowledge regarding the reaction mechanism of hydrothermal decarboxylation of phenolic acids.

As mentioned in the literature review, several conflicting theories regarding the reaction mechanism of hydrothermal decarboxylation have been proposed. Segura et al [16] proposed that the reaction took place via the S_{E1} mechanism, in which a carbanionic intermediate is formed. To illustrate this mechanism, the decarboxylation of syringic acid via the S_{E1} reaction mechanism is shown in Figure 37.
A trend predicted by the $S_{E1}$ mechanism is that electronegative substituents stabilise the carbanionic intermediate through resonance and inductive effects. Recall that the molecular structure of syringic acid differed from that of 4-HBA only by the presence of two additional methoxy groups in the -meta positions. These functional groups are strongly electronegative. The results of this thesis were consistent with this trend, as the activation energy of syringic acid was found to be approximately 30% lower than that of 4-HBA.

A second prediction of the $S_{E1}$ mechanism is that the reaction is first order. This is because the first step, the loss of the carboxyl group, has the highest energy barrier, as it causes a loss of aromaticity. As this step involves a single substrate molecule, the $S_{E1}$ mechanism suggests a first order reaction rate. This prediction was consistent with the experimental observations of this thesis.

Two other reaction mechanisms were proposed by Li and Brill [15] and Chuchev and Belbruno [19]. These authors both developed models using computational chemistry in order to predict the rate constants of the decarboxylation of certain phenolic acids. However these studies did not give a prediction for the relative reaction rates of syringic acid and 4-HBA, so their accuracy cannot be assessed here. However, the reaction rates measured in this thesis may prove to be useful as test data for the further development of these models.

Having discussed the influence of molecular structure on reactivity, the catalytic effect of stainless steel is now investigated.
4.3.3 *Catalytic effect of stainless steel*

As discussed previously, in order to determine the catalytic effect of stainless steel, the kinetic data from the present investigation was compared with literature values.

Specifically, the first order rate constants for 4-HBA decarboxylation reported by Li and Brill [15] were compared with those calculated in the present investigation. This comparison is presented in Figure 38. To enable the reader to compare these datasets more easily, Figure 38 does not show all rate constants that were calculated in the present study. Rather, only the rate constants at temperatures that were also reported in the literature were shown.

![Figure 38: Comparison of first order reaction rates of 4-HBA decarboxylation from this thesis and Li and Brill [15]](image)

As shown in Figure 38, the rate constants calculated in the current study were slightly lower than those reported in the literature. Interestingly, this indicated that the reaction occurred more rapidly in the literature experiments, which were carried out in a gold lined reactor.

The above data indicate that the reaction rate reported by the literature study was approximately 15% greater than that measured in the present study. As discussed previously, the margin of error for the present study was 5%, so this difference is significant.

One possible explanation for this result is that neither gold nor SS316 catalysed the reaction, and the difference in rate constants is attributable to the different operating pressures used.
by the two sets of experiments. Specifically, the operating pressure of the present study was 200 bar, whereas that of the literature study was 275 bar.

No investigation into the effect of pressure on the reaction rate of phenolic acid decarboxylation was found in the literature. For this reason a pressure dependency was not anticipated. Had this pressure dependency been anticipated, the system pressure in this work would have been set to that used in the literature study. The operating pressure of this work was selected as 200 bar because the BPR used in the experimental apparatus became more difficult to adjust at higher pressures.

Several investigations reported that certain aqueous phase reactions are accelerated at increased pressures. Specifically, the reaction rates of Michaels-type reactions [65, 66], substitution of alkyl halides [67] and Diels-Alder reactions [65, 68] were all found to increase at higher pressures.

The pressure dependency of aqueous reaction rates is most commonly expressed in terms of an activation volume [69], using an equation that is similar to the Arrhenius equation:

\[
\Delta V^* = -RT(\partial \ln k / \partial p)_T
\]

4.14

In which \( \Delta V^* \) is the activation volume. The physical meaning of this quantity is the difference in partial molar volume between the transition state and the reactants:

\[
\Delta V^* = V^* - V_R
\]

4.15

For reactions in which the activation volume is positive, the volume of the solution increases as the reactants form the transition state, causing an increase in system pressure. For this reason, higher system pressures inhibit reactions with positive activation volumes. Conversely, reactions with negative activation volumes are accelerated at higher system pressures.

The magnitude of this effect varies depending on the specific reaction, however a rule of thumb is that the reaction rate doubles with every kilobar increase in pressure [69]. Combining this rule with the exponential dependency demonstrated by Equation 4.14 and assuming a constant activation volume, an estimate for the increase in reaction rate was made. The system pressure of the literature study was 75 bar above that of the present study.
Based on the above approximation, this pressure difference was expected to result in an increase in reaction rate in the order of 5%.

However, the simplifying assumption of constant activation volume is inaccurate, as activation volume is pressure dependent. This due to the fact that the transition state is more dense than the reactants, and is thus less compressible [68, 69]. As a result, the activation volume decreases at higher pressures. In general, plots of the logarithm of reaction rate against pressure have a concave down shape [69]. Hence the 5% estimate above is likely too low, and the observed increase of 15% is consistent with typical values.

It should be noted that Dunn et al [70] studied the effect of pressure on the hydrothermal decarboxylation of benzoic acid at a temperature of 400°C and various pressures. The reaction rate was found to increase at higher pressures. However, this study differed from the present work in that the experimental conditions used were in the supercritical phase. The observed pressure dependence is likely due to the compressible nature of supercritical water. Consequently, the results of this study neither contradict nor support those obtained by this thesis. They are mentioned here only to ensure that readers who are aware of this study are informed that a disparate phenomenon has been observed in the present work. Hence, the pressure dependence of the hydrothermal decarboxylation reaction in the subcritical regime is a new observation, and extended the body of knowledge on this topic.

The above hypothesis, that the reaction was pressure dependent, could be tested by conducting experiments at a range of pressures. However, due to time constraints this hypothesis was not experimentally tested in this thesis.

4.3.4 Application of results to treatment of OMW
In order to illustrate the application of the above results to the treatment of OMW, an example design calculation is now presented. A literature study analysed the compositions of OMWs from several facilities, and found that vanillic acid and syringic acid were the most commonly occurring phenolic acid pollutants [4].

These acids both contain 2 or more electron withdrawing substituents on the aromatic ring. As a result, the rate constants for the decarboxylation of each these acids are expected to be greater than or equal to that of 4-HBA. Thus, by assuming their rate constants are equal to that of 4-HBA, a conservative sizing calculation for the reactor can be made.
The percentage removal of phenolic acids that is necessary to ensure that landspreading does not have detrimental agricultural effects must be determined by experimentation. However, to illustrate the design process, a value of 99% will be assumed.

The design equation for a PFR (assumed to be appropriate for modelling the tubular micro-flow reactor used) is as follows:

\[
V = -\frac{\ln(1 - X) \cdot F_{A0}}{k \cdot C_{A0}} \tag{4.16}
\]

In which \( V \) is the reactor volume, \( X \) is the desired conversion, \( F_{A0} \) is the initial mass flowrate of reactants, \( k \) is the rate constant, and \( C_{A0} \) is the initial reactant concentration. The magnitude of the rate constant increases with the temperature of operation, and thus a higher operating temperature will decrease the reactor volume.

However, a higher operating temperature will require a greater heating energy requirement. In a production environment, the operating temperature would be determined by an economic analysis, weighing the cost of reactor construction against heating energy requirements.

For this example, an operating temperature of 310°C, and a flowrate of 1 m³/hour (density of reactant A being considered equal to 1) were assumed. Based on these specifications, the reactor volume was calculated. To do so, the mass flowrate of reactants was first calculated:

\[
F_{A0} = \dot{V} \cdot C_{A0} = \frac{1 \text{ m}^3 \cdot 1 \text{ hour}}{3600 \text{ s}} \cdot \frac{1000 \text{ L}}{1 \text{ m}^3} \cdot \frac{1 \text{ g}}{1 \text{ L}} = 0.278 \text{ g/s} \tag{4.17}
\]

The reactor volume was then calculated by substituting the above value into Equation 4.16:

\[
V = -\frac{\ln(1 - 0.99) \cdot 0.278 \text{ g/s}}{0.0871 \text{ s}^{-1} \cdot 1000 \text{ g/m}^3} = 0.0147 \text{ m}^3 \tag{4.18}
\]

Based on this reactor volume, the required residence time was calculated:

\[
\tau = \frac{V}{Q} \tag{4.19}
\]

In which \( Q \) is the total volumetric flowrate (assumed constant along the reactor):

\[
\tau = \frac{0.0146 \text{ m}^3}{0.000278 \text{ m}^3/\text{s}} = 52.56 \text{ s} \tag{4.20}
\]
Flow reactors with residence times similar to this are commonly used in industrial scale facilities. This suggests that the construction and operation of such a reactor is feasible.

In order to ascertain the economic viability of the proposed process, an analysis of the overall process must be undertaken. Such an analysis would require data from experiments conducted with samples of OMW. As this data is not presently available, this further analysis will not be undertaken in this thesis.

4.4 Summary

The reactivities of syringic acid, 4-HBA and benzoic acid were investigated. Specifically, aqueous solutions containing these compounds were prepared, and were then exposed to temperatures of 250 – 310°C and a pressure of 200 bar.

The nature of the reactions that occurred were investigated. It was determined that syringic acid first underwent decarboxylation to form syringol. Syringol then underwent demethoxylation to form 3-methoxy catechol. 3-methoxy catechol underwent demethoxylation to form pyrogallol.

For the case of 4-HBA, decarboxylation occurred, which produced phenol. Benzoic acid did not undergo any reaction even at the most severe conditions that were possible using the experimental apparatus.

The rates of conversions of syringic acid and 4-HBA did not change when the experiments were repeated with an initial concentration that was 50% lower. This suggested that the reactions were first order. First order rate constants were calculated for each temperature, and were found to accurately describe the concentration profiles.

The dependence of the rate constants on temperature was then quantified by fitting Arrhenius parameters to the data. The activation energy and natural logarithm of the pre-exponent for syringic acid were found to be 13.32 and 77,300 J/mole respectively. For the case of 4-HBA, the activation energy and natural logarithm of the pre-exponent were calculated as 104,600 J/mole and 19.10 respectively.

A mass balance was calculated for each set of experiments. For the case of syringic acid < 6% of the mass was unaccounted for. For the case of 4-HBA the discrepancy was <5%. The small magnitude of these errors indicates that all significant reactions were identified.
Furthermore, the errors are sufficiently low that they do not significantly affect the kinetic parameters that were calculated.

The effect of the number of substituents on the stability of the molecule was analysed. It was found that the activation energy of the acids increased in the order of Syringic Acid < 4-HBA < Benzoic acid. This trend indicated that the activation energy decreased with the degree of substitution. This was consistent with an $S_{E1}$ mechanism, which posits the formation of an anionic intermediate. The electron withdrawing substituents enabled the negative charge to be delocalised, rather than confined to the aromatic ring. This increased the stability of the anionic intermediate, thus reducing the activation energy of the reaction.

Finally, the catalytic activity of SS316 was investigated by comparing the results of this study to those from a study conducted in a gold reactor. The reaction rates in the present study were found to be 15% lower than those of the literature study. This change in reaction rate is thought to be due to an unanticipated pressure dependency of the reaction. This pressure dependency had not previously been observed, and hence extended the existing body of knowledge on this topic. This pressure dependency obscured the catalytic effect.
Chapter 5

Effect of permeant molecular structure and TiO$_2$ additive on PDMS permeability

The process proposed by this thesis utilises a heat resistant PDMS membrane to separate phenolic compounds from OMW. In order to design a membrane separation apparatus with appropriate surface area, the rate at which phenolic compounds permeate the membrane must be known. As the composition of OMW is highly variable, knowledge of the relationship between molecular structure and permeability is also of interest.

In addition to the practical applications of this work, the experiments undertaken in this Chapter will address several gaps in the existing body of fundamental knowledge. For instance, a previous investigation reported that phenolic compounds containing a functional group with the capacity for hydrogen bonding had significantly lower diffusion coefficients than those that did not. However, the impact of the presence of multiple hydrogen bonding functional groups had not been previously investigated.

In order to address this knowledge gap, the permeabilities of phenolic compounds containing varying numbers of −OH substituents were investigated. Specifically, the permeabilities of phenol, guaiacol, catechol and 4-methyl catechol were experimentally determined. The partition coefficient of each compound was also experimentally measured. Based on these values, the diffusion coefficient of each compound was back calculated. The magnitudes of the diffusion coefficients were compared, to determine the effect of the presence of multiple hydrogen bonding groups.

A second knowledge gap was investigated, relating to the partition coefficients of phenolic compounds between water and PDMS. A previous study utilising additive free PDMS found that partition coefficients were negatively correlated with the water solubility of the
permeant. The applicability of this trend to PDMS containing TiO$_2$ had not previously been studied. In order to investigate this knowledge gap, the correlation between the partition coefficients measured in this work and the water solubility of the permeants was examined.

A third knowledge gap, relating to the effect of TiO$_2$ on the transport behaviour of PDMS, was also investigated. Specifically, previous investigations found that the permeability of additive free PDMS exhibited Arrhenius dependence on temperature. The permeabilities of the above compounds were measured over a range of temperatures, and Arrhenius parameters were calculated, to determine if this equation was applicable.

Furthermore, the Arrhenius parameters of phenol were compared to those reported by a study that was conducted using a membrane that was identical except for the absence of TiO$_2$. The partition coefficient and diffusion coefficient of phenol were also compared to those values reported in the literature study. In this manner, the influence of the TiO$_2$ additive on these quantities was investigated.

Finally, previous studies involving additive free PDMS reported that the rate of permeation was independent of tube side concentration. The permeabilities of solutions of various concentrations were experimentally measured, in order to determine whether the TiO$_2$ additive altered this transport property.
5.1 Methodology
Solutions containing phenol, guaiacol, catechol or 4-methyl catechol were passed through the membrane apparatus. These solutes permeated the membrane into a stripping solution, which was sampled periodically. A detailed description of the membrane apparatus is given in Chapter 3.

The concentrations of phenolic compounds in the stripping solution were determined using HPLC with a visible light spectrum detector. Each compound showed a distinct peak. The specifics of the HPLC system are presented in Chapter 3.

The membrane apparatus was operated in such a manner as to ensure that the membrane was the limiting mass transfer resistance. The process by which the appropriate operating conditions were determined is described in the results section of this Chapter.
5.2 Results and discussion

5.2.1 Calculation of overall mass transfer coefficient

In order to investigate the effect of the incorporation of TiO$_2$ on the permeability of PDMS, it was necessary to calculate the overall mass transfer coefficient of the system. In order to illustrate the calculation process, a typical experiment is now described.

Aqueous solutions containing 0.5 g/L of guaiacol were pumped through the lumen side of the tubular heat resistant PDMS membrane using the experimental procedure described in Chapter 3. Over time, the concentration of guaiacol in the stripping solution increased. The temperature of operation was maintained at 25°C, the agitation rate was 250 rpm, and the tube side flowrate was 8 mL/min.

These experiments were repeated in duplicate. The average difference between the repeats was < 5%. Figure 39 shows the concentration of guaiacol in the samples taken from the stripping solution, as a function of time. Each data point represents the average of the two measurements.

![Figure 39: Concentration of guaiacol in stripping solution of membrane separation apparatus as a function of running time. Operating temperature = 298K, tube side concentration = 0.5g/L, agitation rate = 250 RPM, flowrate = 8 mL/min](image)

In order to calculate the overall mass transfer coefficient from the above measurements, an equation for the stripping solution concentration as a function of time and overall mass transfer coefficient was derived. This derivation is presented in Appendix A, and lead to the following equation:
\[ C_S = C_{T0} - C_{T0} \cdot \exp \left( \frac{F \cdot t}{V_S} \cdot \left( \exp \left( \frac{-k_{OV}2\pi r_1 L}{F} \right) - 1 \right) \right) \]  

(5.1)

In the above equation, \( C_S \) is the stripping solution concentration at time \( t \), \( C_{T0} \) is the initial tube side concentration, \( F \) is the volumetric flowrate, \( V_S \) is the volume of the stripping solution, \( k_{OV} \) is the overall mass transfer coefficient, \( r_1 \) is the inner radius of the tube and \( L \) is the length of the tube.

An initial guess was made for the value of \( k_{OV} \). Specifically, a value of \( 3.1 \times 10^{-7} \) m/s was used, as this value was reported by Han et al [13] as the mass transfer coefficient for the permeation of phenol through a similar membrane at 50°C. The above equation was then used to calculate the predicted values of \( C_S \) after 30, 60, 90 and 120 minutes. Based on these predicted values the sum of square error was calculated, using the following equation:

\[ SSE = \sum (C_{S,C} - C_{S,M})^2 \]  

(5.2)

In which \( C_{S,C} \) is the stripping solution concentration calculated with Equation 5.1, and \( C_{S,M} \) is the measured concentration.

Excel Solver was then used to find a value of the overall mass transfer coefficient that resulted in a minimum sum of squared error between the measured and calculated concentrations of the stripping solution.

Using the technique described above, \( k_{OV} \) was calculated for the permeation of a 0.5 g/L guaiacol solution at 25°C, with an agitation rate of 250 rpm, and a tube side flowrate of 8 mL/min. A value of \( 3.9 \times 10^{-7} \) m/s was found, which was in the same order as that reported for phenol by Han et al [13]. The predicted and measured stripping solution concentrations are compared in Figure 40.
Figure 40: Calculated and measured concentrations of guaiacol in stripping solution as a function of running time. Operating temperature = 298K, tube side concentration = 0.5g/L, agitation rate = 250 RPM, flowrate = 8 mL/min

As illustrated by Figure 40, the predicted values were in close agreement with the measured values. To further quantify the goodness of fit, the mean absolute percentage error was calculated, using the following formula:

\[
MAPE = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{n_i - v_i}{v_i} \right|
\]

In which \(n_i\) is the predicted value and \(v_i\) is the measured value. For the data in the above experiment, the MAPE was 4.8%. As the predicted values were within 5% of the measured values, it was concluded that the equation for stripping solution concentration as a function of time accurately described the experimental data.

The above calculation process was repeated to determine the overall mass transfer coefficient for all permeation experiments in this study. However, the objective of this thesis is to investigate the membrane transport properties. As a result, it was necessary to determine the contribution of the membrane to the overall mass transfer resistance. The method used to achieve this is now described.

5.2.2 Calculation of membrane mass transfer coefficient

The resistance in series model gives the following expression for the overall mass transfer coefficient for this apparatus:
\[
\frac{1}{k_{OV}} = \frac{1}{k_l} + \frac{1}{k_m} + \frac{1}{k_s}
\] (5.4)

In which \(k_l\) denotes the mass transfer coefficient of the tube side fluid, \(k_s\) is the mass transfer coefficient of the stripping solution, and \(k_m\) is the mass transfer coefficient of the membrane.

It is possible to estimate \(k_l\) and \(k_s\) using correlations based on the hydrodynamic conditions of each compartment, and calculate \(k_m\) based on the measured value of \(k_{OV}\). However, these correlations are only accurate to within 5–10\%, meaning that this would introduce additional error into the estimation of \(k_m\).

To avoid this issue, \(k_m\) was determined using the following approach. The hydrodynamic conditions of the tube and stripping solution fluids were manipulated such that the resistance to mass transfer of these fluids was greatly lower than that of the membrane. This strategy was taken from previous investigations reported in the literature [48, 13].

Guaiacol was selected as the compound to be used for these experiments. The reason for this selection was that a set of preliminary experiments suggested that guaiacol had the highest permeability of all compounds studied in this investigation. This result was confirmed by experiments that will be presented later in this Chapter. Thus, a set of operating conditions that resulted in membrane-limited mass transfer for the permeation of guiacol would also result in membrane-limited mass transfer for the other compounds.

In order to manipulate the tube side mass transfer resistance, the flowrate of the fluid was varied. Several experiments were carried out, in which the tube side flowrate was varied, and all other parameters were kept constant. For each experiment the overall mass transfer coefficient was calculated using the process described in Section 5.2.1. The results of these experiments are shown in Figure 41.
Figure 41: Effect of tube side flowrate on overall mass transfer coefficient of guaiacol through heat resistant PDMS: 
Operating temperature = 298K, tube side concentration = 0.5g/L, agitation rate = 250 RPM

From Figure 41, the following trends were observed. As the tube side flowrate was increased up to a value of 5 mL / min, the overall mass transfer coefficient also increased. When the flowrate was increased beyond this value the overall mass transfer coefficient remained constant.

This indicated that at flowrates greater than 5 mL / min, the tube side fluid was not the controlling resistance to mass transfer. As a result, a flowrate of 7 mL / min was selected for the subsequent experiments in this study.

The effect of the stripping fluid agitation rate was investigated by carrying out two additional permeation experiments, using agitation rates of 250 and 375 RPM. A 0.5 g/L guaiacol was used, and a flowrate of 7 mL/min was selected, based on the result of the previous experiments.
The difference in overall mass transfer coefficients measured by these two experiments was below 3%. This indicated that the overall mass transfer coefficient remained constant at agitation rates of 250 RPM or higher.

Based on the above results, the subsequent experiments in this work were carried out using an agitation rate of 250 RPM and a flowrate of 7 mL/min. Under these conditions, the overall mass transfer coefficient was equal to the membrane mass transfer coefficient.

Implicit in the above analysis was the assumption that the membrane did not permit transport of water. This assumption was experimentally tested.

5.2.3 Water permeability of membrane
The water permeability of the membrane was investigated using the experimental process described in Chapter 3.

After 96 hours the water level in the sample bottle was unchanged, indicating that the membrane was impermeable to water. This result validated the assumption on which the method used for the calculation of the membrane mass transfer coefficient was based.

Having confirmed the validity of the mass transfer calculation method, the effect of permeant molecular structure on the diffusion and partition coefficients was experimentally investigated.

5.2.4 Effect of permeant molecular structure on permeability
Aqueous solutions containing either guaiacol, phenol, catechol or 4-methyl catechol were prepared. These compounds were selected in order to test the hypothesis stated earlier in this thesis: That the presence of multiple hydrogen bonding groups caused a reduction in the diffusion coefficient. The molecular structures of these compounds are shown in Figure 42.

![Molecular structures of guaiacol, phenol, 4-methyl catechol and catechol](image)

*Figure 42: Molecular structures of (from left to right) guaiacol, phenol, 4-methyl catechol and catechol*
The permeability of the membrane to each of the 4 compounds was experimentally determined using the membrane apparatus, at an operating temperature of 298K. For each experiment, a solution containing only one compound was used. This was done to avoid the effect of interaction between solutes.

Due to the large difference in mass transfer coefficients, it was necessary to use different tube side concentrations for each permeant. This was done to ensure that sufficient permeation occurred to produce a measurable concentration in the stripping solution. For example, the concentration of guaiacol used in the above experiments was 0.5 g/L. For the case of catechol, a concentration of 20 g/L was used.

The use of different concentrations for each permeant seemingly introduces a second manipulated variable, that could be responsible for part of the observed difference in permeabilities. However, a subsequent set of experiments was carried out, which found that concentration had no effect on the mass transfer coefficient. These experiments will be presented at a later point in this work.

For each experiment, the mass transfer coefficient was calculated as described in Section 2.2. These values were converted to permeabilities using Equation 5.5, the derivation of which is presented in Appendix B.

\[ P = k_m r_1 \ln \left( \frac{r_2}{r_1} \right) \]  \hspace{1cm} (5.5)

In the above equation, \( P \) denotes the permeability, \( r_2 \) and \( r_1 \) are the outer and inner radii respectively, and \( k_m \) is the membrane mass transfer coefficient.

The results of these experiments are presented in Table 4.

<table>
<thead>
<tr>
<th>Permeant</th>
<th>( k_m \times 10^7 \text{ (m/s)} )</th>
<th>( P \times 10^{10} \text{ (m}^2/\text{s}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guaiacol</td>
<td>3.91</td>
<td>0.905</td>
</tr>
<tr>
<td>Phenol</td>
<td>2.16</td>
<td>0.499</td>
</tr>
<tr>
<td>4-Methylcatechol</td>
<td>0.00750</td>
<td>0.0173</td>
</tr>
<tr>
<td>Catechol</td>
<td>0.00323</td>
<td>0.00747</td>
</tr>
</tbody>
</table>

Table 4: Mass transfer coefficients for guaiacol, phenol, 4-methyl catechol and catechol in heat resistant PDMS at 298K
From the results in Table 4, it was observed that the mass transfer coefficients of guaiacol and phenol were significantly greater than those of 4-methylcatechol and catechol. For example at 298K, the mass transfer coefficient for catechol was $3.23 \times 10^{-9} \text{ m/s}$. At the same conditions, the mass transfer coefficient for guaiacol was greater by a factor of over 100, having a value of $3.91 \times 10^{-7} \text{ m/s}$.

In order to investigate the cause of this difference in permeability, the partition coefficient and diffusion coefficient were determined for each species. The diffusion coefficients of permeants within PDMS are problematic to measure directly. As a result, the partition coefficient of each compound between water and heat resistant PDMS was measured, and the diffusion coefficient was back-calculated.

5.2.5 Effect of permeant molecular structure on partition coefficients
The PDMS-water partition coefficients of each compound were measured at 298 K using the method described in Chapter 3. Based on these results, and the previously measured values of $P$, the diffusion coefficient of each permeant was calculated using the relation $D = P/K$. These results are presented in Table 3.

<table>
<thead>
<tr>
<th>Permeant</th>
<th>$P \times 10^{10} (\text{m}^2/\text{s})$</th>
<th>$K (-)$</th>
<th>$D \times 10^{10} (\text{m}^2/\text{s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guaiacol</td>
<td>0.905</td>
<td>0.673</td>
<td>1.34</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.499</td>
<td>0.310</td>
<td>1.61</td>
</tr>
<tr>
<td>4-Methylcatechol</td>
<td>0.0173</td>
<td>0.225</td>
<td>0.0769</td>
</tr>
<tr>
<td>Catechol</td>
<td>0.00747</td>
<td>0.057</td>
<td>0.131</td>
</tr>
</tbody>
</table>

These results indicated that the both the partition and diffusion coefficients of catechol and 4-methylcatechol were significantly lower than those of both phenol and guaiacol. These results illustrated the root cause of the earlier observation that the permeabilities of guaiacol and phenol were significantly greater than those of catechol and 4-methylcatechol: both the partition coefficients and diffusion coefficients of catechol and 4-methylcatechol were significantly lower than those of phenol and guaiacol.
The above results were also compared to the existing body of knowledge. Specifically, the above data was used to test the hypothesis of Han et al [13] who suggested that PDMS-water partition coefficients were negatively correlated with the water solubility.

The water solubilities of the compounds studied in this work were obtained from the literature [71-74] and used to develop the plot shown in Figure 43.

![Figure 43: Correlation between PDMS-Water partition coefficients at 298K and water solubilities for Guaiacol, Phenol, 4-methyl Catechol and Catechol at 298K](image)

By inspection of Figure 43 it was apparent that the compounds studied in this thesis also displayed a negative correlation between partition coefficient and water solubility. Thus these results were consistent with the existing body of knowledge.

The molecular characteristics that influence water solubility are well known. Polarity and capacity for hydrogen bonding are positively correlated with solubility, whereas molecular size is negatively correlated. Thus the fourth objective of this thesis, to identify molecular descriptors to predict the relative magnitudes of partition coefficients, was achieved.

Having successfully determined a set of molecular descriptors that correlated with the partition coefficient, the relationship between molecular structure and the diffusion coefficient was investigated.
5.2.6 Effect of permeant molecular structure on diffusion coefficients

From Table 5 it was observed that the diffusion coefficients of guaiacol and phenol were significantly lower than those of 4-methylcatechol and catechol. This was thought to be attributable to the fact that catechol and 4-methylcatechol each contain two alcohol functional groups.

As discussed in the literature review, LaPack et al [52] found that the diffusive flow of permeants was greatly hindered by the presence of functional groups with a high capacity for hydrogen bonding. These authors hypothesised that these functional groups underwent strong intermolecular interactions with the polymer chains, thus facing a higher energy barrier to desorb from adsorption sites.

It was hypothesised at the outset of this work that the presence of additional hydrogen bonding groups would further reduce the diffusion coefficient. The above results supported this hypothesis.

The effect of the number of functional groups with a capacity for hydrogen bonding on diffusivity has not previously been researched. Thus these results extended the existing body of knowledge.

Having investigated the relationship between molecular structure and the diffusion and partition coefficients, the fourth objective of this thesis was achieved. Attention was then turned to the third objective, investigating the influence of the presence of the TiO$_2$ additive on these properties.

5.2.7 Influence of TiO$_2$ additive on partition coefficient

Han et al [13] measured the permeability and partition coefficient of a PDMS membrane to phenol at 223K, and back calculated the diffusion coefficient. The membrane studied was identical to that used in this thesis, except for the absence of the TiO$_2$ additive.

In order to compare the behaviour of the two membranes, the permeability and partition coefficient of the membrane used in this work was measured at 223K. The results of these experiments are presented in Table 6, along with the data published by Han et al.
Table 6: Permeabilities, partition coefficients and diffusion coefficients of phenol at 223K as measured by this work and by the study of Han et al [13]

<table>
<thead>
<tr>
<th>Researcher</th>
<th>$P \times 10^{10}$ (m$^2$/s)</th>
<th>$K$ (-)</th>
<th>$D \times 10^{10}$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>1.04</td>
<td>0.242</td>
<td>4.31</td>
</tr>
<tr>
<td>Han et al [13]</td>
<td>1.34</td>
<td>0.250</td>
<td>5.36</td>
</tr>
</tbody>
</table>

The results shown in Table 6 indicated that the presence of the TiO$_2$ additive resulted in a decrease in the partition coefficient of 3.2%. This result was compared to the existing body of knowledge on this topic.

As discussed in the literature review, Barrer et al [41] experimentally investigated several blends of PDMS, each containing a different volume percentage of fumed silica. Based on these experiments, a linear relationship between the partition coefficient and the volume fraction of PDMS was proposed. This was thought to be attributable to two factors. Firstly, the monomeric nature of the fumed silica suggests that absorption of permeants would not occur. Secondly, the surface of the additive was thought to be fully occupied by the polymer, preventing adsorption.

The molecular structure of TiO$_2$ is similar to that of fumed silica, as TiO$_2$ is a metal dioxide, and fumed silica (SiO$_2$) is a dioxide of a semimetal. Thus sorption of phenol by the TiO$_2$ additive was not expected to occur. As a result, the relationship proposed by Barrer et al [41] was expected to apply to the polymer studied in this thesis.

In order to calculate the volume fraction of PDMS in the membrane used in the present work, the densities of PDMS, fumed silica and TiO$_2$ were extracted from the literature [75 – 77]. The following equation was then used to calculate the volume fraction:

$$\lambda_1 = \frac{\frac{X_1}{\rho_1}}{\frac{X_1}{\rho_1} + \frac{X_2}{\rho_2} + \frac{X_3}{\rho_3}}$$

(5.6)

In which $\lambda_1$ is the volume fraction of PDMS, $X_1$, $X_2$ and $X_3$ are the mass fractions of PDMS, fumed silica and TiO$_2$ respectively and $\rho_i$ is the mass density of component $i$. As discussed, the membrane used in this thesis consisted of 65% (wt/wt) PDMS, 30% (wt/wt) fumed silica and 5% (wt/wt) TiO$_2$. The volume fraction of PDMS was calculated using the above equation.
The volume fraction of PDMS in the membrane used in the literature study was also calculated.

\[
\lambda_1 = \frac{0.65}{\frac{965 \text{ kg/m}^3}{0.3} + \frac{0.05}{2,200 \text{ kg/m}^3} + \frac{0.05}{4,240 \text{ kg/m}^3}} = 0.820 
\]

Based on the equation of Barrer et al [41], the expected decrease in partition coefficient between the membranes was calculated as follows.

\[
\lambda_{1,\ell} = \frac{0.65}{\frac{0.7}{965 \text{ kg/m}^3} + \frac{0.3}{2,200 \text{ kg/m}^3}} = 0.842 
\]

The predicted decrease in partition coefficient of 2.61% was similar to the observed decrease of 3.2%. This suggested that TiO\(_2\) did not have strong intermolecular interactions with phenol, which was expected based on the molecular structures. Thus, the result of this thesis was consistent with the existing body of knowledge.

In order to gain further insight into the influence of the TiO\(_2\) additive on PDMS permeability, the effect on the diffusion coefficient was investigated.

**5.2.8 Influence of TiO\(_2\) additive on diffusion coefficient**

In this thesis, the diffusion coefficient of phenol at 223 K was calculated as \(4.31 \times 10^{10} \text{ m}^2/\text{s}\). The value reported by Han et al [13] was \(5.36 \times 10^{10} \text{ m}^2/\text{s}\), indicating that the additive reduced the diffusion coefficient by 19.5%. This result was compared to the existing body of knowledge on this topic.

As discussed in the literature review, permeants are thought to diffuse through the PDMS matrix by a process of adsorption and desorption between randomly generated void spaces. Barrer et al [41] hypothesised that impermeable fillers hinder diffusion as they do not form such void spaces, and also restrict the motion of surrounding polymer chains.

An exception to the above effect has been reported for the case of porous additives, which can increase the permeability of the membrane [57]. As the TiO\(_2\) additive studied in this thesis...
was nonporous, the observation that the diffusion coefficient decreased was consistent with the existing body of knowledge.

Additionally, the mechanism by which additive molecules influence the surrounding polymer chains is not fully understood. The extent to which the diffusion coefficient was decreased by the presence of TiO$_2$ is therefore a useful result for future works that seek to elucidate this mechanism.

In order to gain a more detailed understanding of the effect of the TiO$_2$ additive and permeant molecular structure on the permeability of PDMS, the temperature dependence of membrane permeability was investigated.

### 5.2.9 Temperature dependence of membrane permeability

In order to investigate the effect of temperature on the membrane mass transfer coefficient, a set of experiments was carried out using an aqueous guaiacol solution with a concentration of 0.5 g/L. For each experiment, the temperature of operation was adjusted by changing the set points on the temperature controllers as described in Chapter 3.

The temperature of the system was varied from 298K to 338K. All other variables were kept constant. In order to isolate the effect of the membrane on the rate of permeation, the agitation rate and tube side flowrate values that were determined in the previous experiments were used.

Each experiment was repeated in duplicate, and had an average difference of < 5%. The results of this set of experiments are presented in Figure 44. Each data point represents the average of the two repeats.
Figure 44: Effect of temperature on overall mass transfer coefficient for guaiacol permeation. Agitation rate = 250 RPM, tube side concentration = 0.5g/L, tube side flowrate = 8 mL/min

From Figure 44 it was observed that the permeability was significantly affected by temperature, which was consistent with Arrhenius dependency. Based on these measurements, Arrhenius parameters were calculated and the goodness of fit of the Arrhenius equation was examined.

5.2.9.1 Calculation of Arrhenius parameters
The Arrhenius relationship of membrane permeability was mathematically formalised:

\[ P = P_0 e^{-E_A/RT} \]  \hspace{1cm} (5.10)

In which \( P_0 \) is the frequency factor, and \( E_A \) is the activation energy of permeation.

Rearranging:

\[ \ln(P) = \ln(P_0 \cdot e^{-E_A/RT}) \]
\[ \ln(P) = \ln(P_0) + \ln(e^{-E_A/RT}) \]
\[ \ln(P) = \ln(P_0) - \frac{E_A}{RT} \]  \hspace{1cm} (5.11)

Thus, plotting \( \ln(P) \) against \( 1/T \) yields a straight line with a gradient of \(-E_A/R\) and a \( y \) intercept of \( \ln(P_0) \). The above mass transfer coefficients were converted to permeabilities using Equation 5.5 and plotted in Figure 45.
The trend line shown in Figure 45 was obtained by linear regression, using Microsoft Excel’s inbuilt chart function. Based on the gradient and y intercept of the above trend line, the activation energy was determined to be 24,397 J/mole. The natural logarithm of the frequency factor was determined to be -13.20. The high coefficient of determination indicated that the Arrhenius equation accurately described the experimental data.

In order to determine the influence of TiO$_2$ on the temperature dependence of permeability, the above result was compared to a similar study. Han et al [13] studied the permeability of phenolic compounds through a membrane that was identical to that used in this thesis, except for the absence of the TiO$_2$ additive. These authors reported an Arrhenius relationship between permeability and temperature. Thus, the presence of TiO$_2$ did not alter fact that the membrane permeability exhibited an Arrhenius dependence.

In order to gain a further understanding of the effect of temperature on permeability, the permeabilities of guaiacol, phenol, 4-methyl catechol and catechol were measured at a range of temperatures. These results are shown in Figure 46.
Figure 46: Effect of temperature on overall mass transfer coefficient: $P = 1 \text{ atm, } C_0 \text{ Guaiacol} = 0.5 \text{ g/L, } C_0 \text{ Phenol} = 1.0 \text{ g/L, } C_0 \text{ 4-Methylcatechol} = 20.0 \text{ g/L, } C_0 \text{ Catechol} = 20.0 \text{ g/L, tube side liquid flowrate} = 8 \text{ mL/min, agitation rate} = 250 \text{ RPM}$

In order to further compare the permeabilities of these species, Arrhenius parameters were calculated. This was achieved by first developing a Van’t Hoff plot, shown in Figure 47.

Figure 47: Van’t Hoff plot of PDMS permeability to Guaiacol, Phenol, 4-Methylcatechol and Catechol.
By inspection of Figure 47 it was observed that the Arrhenius equation accurately described the behaviour of all the permeants. Using the calculation process described in Section 5.2 (Equations 5.5 and 5.11), the Arrhenius parameters shown in Table 7 were calculated for each permeant.

**Table 7: Activation energies and pre-exponential factors for the permeation of guaiacol, phenol, 4-methylcatechol and catechol in heat resistant PDMS**

<table>
<thead>
<tr>
<th>Permeant</th>
<th>$E_A$ (kJ/mole)</th>
<th>$\ln(P_0)$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>21.97</td>
<td>-14.847</td>
</tr>
<tr>
<td>4-Methylcatechol</td>
<td>29.24</td>
<td>-15.281</td>
</tr>
<tr>
<td>Catechol</td>
<td>30.35</td>
<td>-15.621</td>
</tr>
</tbody>
</table>

From the data in Table 7 it was observed that the activation energies of guaiacol and phenol were significantly lower than those of 4-methylcatechol and catechol. In order to determine the cause of this difference, the temperature dependence of the diffusion and partition coefficients were investigated.

**5.2.10 Temperature dependence of partition coefficient**

The partition coefficient of each compound was measured over a range of temperature, using the experimental process described in Chapter 3. The results are shown in Figure 48.
From Figure 48 it was observed that the partition coefficients exhibited an exponential dependency on temperature. For instance, the partition coefficient of guaiacol approximately halved with every 30K increase in temperature. This trend is consistent with the observation of Chen and Pawliszyn [35] who proposed an Arrhenius relationship between partition coefficient and temperature:

$$K = K_0 e^{-E_K/RT} \quad (5.12)$$

In order to determine whether the results of this thesis were consistent with this observation, a Van’t Hoff plot was developed. Specifically, plotting $\ln(K)$ against $1/T$ will yield a straight line with a gradient of $-E_K/R$ and a $y$ intercept of $\ln(K_0)$. This plot is presented in Figure 49.
By inspection of Figure 49 it was observed that the Arrhenius equation accurately described the behaviour of the compounds. The coefficient of determination was greater than 0.98 for all compounds, with the exception of 4-methylcatechol for which it was 0.93.

Using the calculation process described in Section 5.2 (Equations 5.5 and 5.11), the Arrhenius parameters shown in Table 8 were calculated for each permeant.
Table 8: Activation energies and pre-exponential factors for the partitioning of guaiacol phenol, 4-methylcatechol and catechol in heat resistant PDMS

<table>
<thead>
<tr>
<th>Permeant</th>
<th>$E_K$ (kJ/mole)</th>
<th>$\ln(K_0)$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guaiacol</td>
<td>12.37</td>
<td>5.40</td>
</tr>
<tr>
<td>Phenol</td>
<td>7.38</td>
<td>4.18</td>
</tr>
<tr>
<td>4-Methylcatechol</td>
<td>13.29</td>
<td>7.02</td>
</tr>
<tr>
<td>Catechol</td>
<td>11.39</td>
<td>7.15</td>
</tr>
</tbody>
</table>

From the data in Table 8 it was observed that the activation energy for guaiacol was greater than that of phenol, and the activation energy of 4-methyl catechol was greater than that of catechol. This trend is consistent with the observation of Chen and Pawliszyn [35] who noted that larger molecules exhibited greater partition coefficient temperature dependence.

In order to continue the investigation of the temperature dependence of permeability, the influence of temperature on the diffusion coefficients was investigated.

5.2.11 Temperature dependence of diffusion coefficient

Based on the previous permeability and partition coefficient measurements, the diffusion coefficients at each temperature were calculated. These values are shown in Figure 50.

Figure 50: Diffusion coefficients in heat resistant PDMS as a function of temperature for Guaiacol, Phenol, 4-methyl catechol and Catechol
From Figure 50, an exponential relationship between temperature and diffusion coefficient was again observed (note that the y axis has a logarithmic scale). This increase in diffusion coefficient with temperature was consistent with previous research [13, 50, 51]. The Arrhenius dependency on temperature was mathematically stated:

\[ D = D_0 e^{-\frac{E_D}{RT}} \]  

(5.13)

A Van’t Hoff plot was developed in order to determine the Arrhenius parameters for each compound.

By inspection of Figure 51 it was apparent that the Arrhenius equation accurately described the temperature dependence of the diffusion coefficients. The following Arrhenius parameters were calculated for each permeant.

**Figure 51:** Van’t Hoff plot of diffusion coefficient in heat resistant PDMS for Guaiacol, Phenol, 4-methyl catechol and Catechol

By inspection of Figure 51 it was apparent that the Arrhenius equation accurately described the temperature dependence of the diffusion coefficients. The following Arrhenius parameters were calculated for each permeant.
Table 9: Activation energies and pre-exponential factors for the diffusion of guaiacol phenol, 4-methylcatechol and catechol in heat resistant PDMS

<table>
<thead>
<tr>
<th>Permeant</th>
<th>$E_D$ (kJ/mole)</th>
<th>$\ln(D_0)$ (–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guaiacol</td>
<td>36,770</td>
<td>-7.799</td>
</tr>
<tr>
<td>Phenol</td>
<td>29,870</td>
<td>-10.45</td>
</tr>
<tr>
<td>4-Methylcatechol</td>
<td>41,740</td>
<td>-8.471</td>
</tr>
<tr>
<td>Catechol</td>
<td>42,540</td>
<td>-8.263</td>
</tr>
</tbody>
</table>

From the above table it was observed that the activation energies of guaiacol and phenol were significantly lower than those of 4-methyl catechol and catechol. As discussed previously, this is thought to be attributable to the presence of two $-\text{OH}$ substituents on the former two compounds. These groups increase the strength of intermolecular reactions between the permeant and polymer, thus increasing the activation energy for diffusion.

It was also observed that the activation energy for guaiacol was greater than that of phenol, and the activation energy of 4-methylcatechol was greater than that of catechol. This is thought to be due to the fact that larger molecules require a greater input of thermal energy in order to vibrate with sufficient energy to desorb from adsorption sites.

The results of the previous two sections can also be used to determine the root cause of the in activation energies of permeation. Specifically, it was observed that guaiacol and phenol had lower activation energies than 4-methyl catechol and catechol. Comparison of the magnitudes of the activation energies of partitioning and diffusion reveal that the diffusion process activation energies are greater by a factor of approximately 3.

For example, the activation energies of partitioning and diffusion for guaiacol were 12.37 kJ/mole and 36.77 kJ/mole respectively. This indicates that the diffusion coefficient is more sensitive to changes in temperature than the partition coefficient. Hence the cause of the above mentioned observation is that the activation energies of diffusion of guaiacol and phenol are also lower. This in turn is attributable to the presence of one $-\text{OH}$ substituent on the aromatic ring of these compounds, as opposed to two on that of 4-methyl catechol and catechol.
Having investigated the temperature dependence of permeation, the effect of concentration on the mass transfer coefficient was investigated. This was undertaken in order to gain further insight into the effect of the TiO$_2$ additive on the transport properties of PDMS.

### 5.2.12 Effect of concentration on permeability

Solutions of different concentrations were prepared, and used to carry out permeation experiments using the procedure described previously.

For the cases of guaiacol and phenol, the concentration was varied from 0.5 g/L to 8 g/L and 16 g/L respectively. These maximum concentrations represented 50% and 20% of the saturation concentrations at room temperature respectively. For the case of catechol and 4-methyl catechol, constraints on the amount of chemicals available restricted the maximum concentrations used to 20 g/L.

The above concentration ranges were selected considering the typical phenolic compound concentrations found in OMW. As noted in the literature review, a typical total phenolic concentration was approximately 10 g/L. Therefore the maximum concentrations selected for these experiments were likely to exceed those found in OMW.

All other experimental operating variables were kept constant. The results of these experiments are shown in Figure 52.
From the above results it was apparent that concentration did not affect the permeability of any species studied in this investigation.

No investigations were found in the literature regarding the effect of concentration on the permeability of PDMS containing heat resistant additives. However, Bennett et al [48] directly measured the effect of concentration on permeability in PDMS functionalised with 20% acetate. These experiments were conducted at 70°C over a concentration range of up to 50 g/L. Over this concentration range, no concentration dependence was observed.

Furthermore, a study of the pervaporative separation of phenol from water found that the phenol flux was linearly dependent on concentration [78], indicating concentration
independent permeability. These experiments were conducted over a concentration range of up to 3 g/L, using additive free PDMS.

The concentration dependence of guaiacol, catechol and 4-methyl catechol did not appear to have been previously studied. As a result, the results of this thesis extended the existing body of knowledge on this topic.

Watson et al [45] observed that the diffusion coefficient of 1 amino-butane was highly concentration dependent, whereas those of 1-propanone and tetrachloromethane did not vary significantly. These authors attributed this behaviour to the occurrence of strong intermolecular interactions between the permeant and polymer. The results of this thesis are consistent with this theory, as the permeants studied in this work were not expected to strongly interact with the polymer, based on their molecular structures.

5.2.13 Influence of TiO$_2$ additive on concentration dependence of permeability

The result observed in this thesis, that the presence of the TiO$_2$ additive did not cause concentration dependence, may be attributable to the fact that TiO$_2$ is a non-polar molecule. According to the theory of Watson et al [45], concentration dependence occurs due to the presence of strong intermolecular interactions.

Non-polar compounds would not be expected to interact strongly with the permeants studied in this work, due to the polar nature of the –OH groups. Hence the results of this thesis were consistent with the existing body of knowledge.

5.3 Application of results to treatment of OMW

In order to illustrate the application of the above results to the treatment of OMW, an example design calculation is now presented. A literature study analysed the compositions of OMW samples from several facilities, and found that the typical concentration of phenolic compounds in OMW was 10 g/L. Tyrosol and hydroxytyrosol were the most commonly occurring phenolic pollutants [4].

These compounds contain one and two hydroxyl substituents respectively. In order to be conservative, and simplify the analysis, it will be assumed that the permeabilities of each compound are equal to that of 4-methyl catechol. The solubilities of tyrosol and hydroxytyrosol are lower than that of 4-methyl catechol, so this is likely an underestimate.
The percentage removal of phenolic compounds that is necessary to ensure that landspreading does not have detrimental agricultural effects must be determined by experimentation. However, to illustrate the design process, a value of 99% will be assumed.

The following equation was used to calculate the volume of membrane tubing required in order to achieve this level of removal. The derivation of this equation is presented in Appendix C.

\[
V = \frac{\ln \left( \frac{r_2}{r_1} \right) \cdot F \cdot \ln \left( \frac{C_T}{C_{T0}} \right) \cdot r_1^2}{-2P}
\]  

(5.14)

In which \( V \) is the membrane volume, \( r_2 \) and \( r_1 \) are the outer and inner radii respectively, \( F \) is the volumetric flowrate, \( C_{T0} \) and \( C_T \) are the initial and final phenol concentrations respectively, and \( P \) is the membrane permeability.

The magnitude of the permeability increases with the temperature of operation, and thus a higher operating temperature will decrease the length of membrane tubing required. However, a higher operating temperature will require a greater heating energy requirement. In an industrial setting, the optimum operating temperature would be determined by an economic analysis, weighing the cost of reactor construction against heating energy requirements. For the purpose of this example, an operating temperature of 65°C was selected.

A smaller radius would reduce the overall membrane volume. However, narrower membranes are more easily fouled and blocked. The determination of the optimum radius would require experimental investigation. For the purpose of this example, an inner radius of 0.9 mm was assumed.

A thinner membrane wall will increase the mass transfer coefficient, and hence reduce the length of tubing required. However, as wall thickness decreases, the strength of the membrane also decreases, increasing the probability of breakage. The determination of the optimum thickness would require experimentation. For this example, a wall thickness of 0.1 mm was selected, as this is commercially available [79]. An OMW flowrate of 1 m\(^3\) was assumed.
The above values were used to calculate the required volume of tubing:

\[
V = \ln\left(\frac{1.0 \text{ mm}}{0.9 \text{ mm}}\right) \cdot \frac{1 \text{ m}^3/\text{hour} \cdot \text{hour}/3600 \text{s} \cdot \ln\left(\frac{0.1 \text{ g/L}}{10 \text{ g/L}}\right) \cdot (0.0009 \text{ m})^2}{-2 \cdot 6.97 \times 10^{-12} \text{ m}^2/\text{s}} = 7.8 \text{ m}^3
\]

Membrane modules with volumes of this magnitude are frequently encountered in industrial settings. This suggests that the construction and operation of such an apparatus is feasible.

The economic viability of this process cannot be determined until the above mentioned parameters are determined, via experimentation. This data is not yet available, so this analysis will not be undertaken in this thesis.

5.4 Summary
The behaviour of the PDMS membrane containing a TiO\(_2\) additive was studied in this chapter. The behaviour was largely similar to that of additive free PDMS. Permeability followed an exponentially positive relationship with temperature. This was due to the significant increase in the diffusion coefficient with temperature, which outweighed a smaller decrease in partition coefficient.

The presence of the TiO\(_2\) additive did not introduce water permeability to the membrane. Also, the additive did not introduce concentration dependence of permeabilities for any of the compounds studied. This was thought to be attributable to the non-polar nature of TiO\(_2\), which was hence not expected to strongly interact with the permeants studied in this thesis.

The presence of the TiO\(_2\) additive was found to decrease the diffusion coefficient of phenol at 323K by 19.5%. This was thought to be attributable to two effects. Firstly, the TiO\(_2\) additive did not form void spaces, and so was not available for free volume diffusion. Secondly, the additive was thought to reduce the mobility of the surrounding polymer chains, further hindering diffusion. The mechanism by which additives effect the bulk polymer behaviour is not fully understood. Therefore, this result may aid future attempts to determine this mechanism.

The partition coefficient of the membrane containing the TiO\(_2\) additive decreased by 3.2% compared to a membrane that was identical except for the absence of the additive. An equation developed by a previous study suggested that for an inert filler, the decrease in partition coefficient was expected to be equal to the decrease in volume fraction of the
polymer. The decrease in volume fraction was 2.6% meaning that this result was consistent with the existing body of knowledge.

Permeants which contained a second alcohol functional group exhibited greatly reduced rates of diffusion. This was attributed to strong intermolecular interactions between the permeant and silica molecules. The effect of the number of alcohol functional groups on the diffusion coefficient had not previously been studied, so this result extended the body of knowledge.

Permeants with a greater water solubility were found to have a lower partition coefficient. This was consistent with the results of a previous study. Furthermore, the partition coefficients of permeants with larger molecular masses were found to be more strongly effected by temperature. This result was consistent with that reported by a previous study.

The experiments described in this chapter delivered fundamental insights regarding the effect of molecular structure on the relative rates of permeation of phenolic compounds, and the effect of the presence of a TiO₂ additive on the transport behaviour of the membrane. This knowledge is essential for the design of membrane separation apparatuses specified to olive mill wastewaters of various compositions.
Conclusions and Recommendations

In this thesis a two stage process for the treatment of olive mill wastewater was proposed. The first stage of the proposed process consisted of subjecting OMW to a heat treatment process. The objective of this stage was to decarboxylate phenolic acids, which are an important pollutant in OMW. The second stage of the proposed process consisted of passing the OMW through a membrane separation apparatus, in order to recover phenolic compounds.

Fundamental studies of both stages were carried out, in order to generate the new knowledge necessary for their design. A flow reactor developed by a previous researcher was used to investigate the first stage of the process, and a membrane apparatus was fabricated in order to investigate the second stage.

The conclusions drawn from these investigations are presented in this Chapter, along with the recommendations for future work.

6.1 Conclusions

6.1.1 Hydrothermal decarboxylation of phenolic acids
A review of the literature showed that stainless steel catalysed the hydrothermal decarboxylation of certain aliphatic carboxylic acids. However, the existence of a catalytic effect on the hydrothermal decarboxylation of phenolic acids had not previously been investigated. Due to the industrial importance of stainless steel as a material of construction, this knowledge gap was selected for investigation. Furthermore, the relationship between molecular structure and reactivity was not fully understood. This knowledge gap was also selected for investigation, due to the variable composition of OMW.

In order to investigate the catalytic effect of stainless steel, experiments were carried out using a flow reactor that was built by a previous researcher. 4-hydroxybenzoic acid (4-HBA) was selected as a reactant, as reliable literature data obtained from experiments conducted in a gold-lined reactor was available for this compound. A series of experiments were carried out in order to determine the first order reaction rate constants, and Arrhenius parameters.
The activation energies measured by this thesis were found to be greater than those reported by the literature study. This unexpected result was thought to be attributable to the fact that the operating pressure used in this thesis was lower than that in the literature study. Due to the discovery of this unanticipated confounding factor, the catalytic effect of stainless steel on the decarboxylation reaction was not determined.

The pressure dependence of the hydrothermal decarboxylation of phenolic acids had not previously been investigated. Thus, the result of this thesis extended the existing body of knowledge on this topic, and may have implications for the design of industrial reactors to achieve this transformation. Due to time constraints, the quantification of this effect was not studied in this thesis.

In order to gain insight into the relationship between molecular structure and reactivity, several acids with varying degrees of substitution were experimentally investigated. Specifically, benzoic acid and syringic acid were studied, in addition to 4-HBA. The relative reaction rates of the acids were consistent with the $S_{E1}$ mechanism, which was proposed by previous studies undertaken in non-catalytic environments.

The kinetics of syringic acid had not previously been reported in the literature. As a result, the parameters determined by this investigation may constitute useful test data for the development of predictive models for the activation energies of decarboxylation reactions. Furthermore, syringic acid is one of the most commonly occurring pollutants in OMW. Hence this result also has practical significance.

6.1.2 Separation of phenolic compounds with heat resistant PDMS

A review of the literature relating to PDMS revealed that the influence of heat resistant additives on permeability had not been studied. Furthermore, the relationship between molecular structure and permeability was not fully understood.

As the permeability of PDMS is improved at high temperatures, the knowledge gap relating to the effect of heat resistant additives on permeability was selected for further study. In addition, the relationship between molecular structure and permeability was also selected for investigation. This was motivated by the variability of the composition of OMW.

A membrane separation apparatus was fabricated to investigate the separation of phenolic alcohols from aqueous solutions using a PDMS membrane containing a TiO$_2$ additive.
Specifically, experiments were carried out to investigate the influence of molecular structure on permeability. The influence of the TiO$_2$ was also determined by comparing the results of this investigation to those of a study that used a membrane that was identical except for the absence of the TiO$_2$ additive.

In order to investigate the influence of the heat resistant additive (TiO$_2$), permeation experiments were carried out using phenol. This permeant was selected because a previous investigation had studied phenol permeation through a membrane that was identical to that used in this thesis, except for the absence of the TiO$_2$ additive.

The presence of TiO$_2$ was found to reduce the partition coefficient and diffusion coefficient of phenol. The magnitude of the decrease in partition coefficient was consistent with the prediction of an equation proposed by previous researchers.

The mechanism by which the presence of additives decreased the diffusion coefficient has been studied in the literature, but is not fully understood. Thus the magnitude of the decrease in diffusion coefficient may be a useful result for studies that seek to determine this mechanism.

The relationship between permeant molecular structure and permeability was experimentally investigated by measuring the permeabilities of compounds containing 1 and 2 –OH groups. The partition coefficients of all permeants were found to be negatively correlated with water solubility. This result was consistent with the results of previous studies.

The presence of the second –OH group was found to greatly reduce the diffusion coefficient. This result was consistent with previous studies which demonstrated that the presence of groups with the capacity for hydrogen bonding inhibited the diffusion of compounds. However, the effect of multiple hydrogen bonding groups had not previously been studied. Thus this result extended the existing body of knowledge.

6.2 Recommendations for future work
The results of this thesis suggested that the rate of phenolic acid decarboxylation was affected by pressure. A survey of the literature indicated that the effect of pressure on this reaction had not been experimentally investigated previously. Therefore, an experimental
investigation, in which pressure was varied systematically is recommended to address this knowledge gap. Furthermore, such an investigation would have industrial implications for the design of reactors.

Due to the influence of pressure, the catalytic effect of stainless steel on phenolic acid decarboxylation was obscured. In order to address this knowledge gap, it is recommended that experiments are carried out in stainless steel and gold lined reactors at equal pressures.

The question of whether kinetic isotope effects exist for the decarboxylation reactions of phenolic acids was not investigated in this work. However, such an investigation may generate further insight into the reaction mechanism. As such, this is recommended as an area for future investigation.

As discussed in Chapter 4, there is a possibility that the reaction rate constants measured in this work may not apply to a system containing a mixture of phenolic acid reactants. While interactions of this type are uncommon for the case of uncoupled reactions, this was not investigated experimentally in this work due to a lack of time. This effect is of importance to the proposed process as olive mill wastewater contains a mixture of phenolic compounds. Therefore, this topic is suggested as an area for future work.

The presence of TiO$_2$ was found to significantly reduce the diffusion coefficient of phenol. The mechanism by which additives hinder diffusion been investigated but is not fully understood. In order to address this knowledge gap, the development of a model based on computational chemistry is recommended. This approach has previously been used to successfully determine the causes of other aspects of membrane behaviour. The magnitude of the decrease in diffusion coefficient measured by this thesis would constitute suitable test data for validation of such a model.

One aspect of the relationship between permeant molecular structure and diffusion coefficient that was not investigated in this thesis was the effect of relative positioning of substituents. Knowledge of the magnitude of this effect may allow for further qualitative predictions to be made regarding the relative permeabilities of phenolic compounds. In order to address this knowledge gap, it is recommended that the diffusion rates of several phenolic compounds containing two hydroxyl substituents are measured. Specifically, it is
recommended that compounds which differ only by the relative positioning of these substituents are selected.

Overall, the results of this thesis suggest that the proposed process is capable of recovering phenolic compounds from OMW. It is recommended that this process be investigated further by treating a sample of OMW obtained from an industrial facility. A key outcome of this investigation would be an increased understanding of the influence of other components of OMW on each stage of the process. Such an investigation would also enable an economic evaluation of the proposed process.
References


71. 4-Methyl-1,2-benzenediol. (2015, October 9). Retrieved from http://foodb.ca/compounds/FDB008861


The following section describes the derivation of an equation for the stripping solution concentration as a function of time and overall mass transfer coefficient. This equation was used to calculate the overall mass transfer coefficient based on stripping solution concentration measurements.

The style of the diagrams used in the following analysis is adapted from that found in the textbook “Fundamentals of heat and mass transfer” by Bergman, Incropera and DeWitt [80].

**Phenol balance on tube**

The first step in this analysis was to carry out a phenol balance on the tubular membrane.

The following diagram represents a cross section of a volume element of the polydimethylsiloxane tubing.

![Diagram of cross section of volume element of membrane tubing](image)

**Figure 53: Diagram of cross section of volume element of membrane tubing**

In the above diagram, \( F_{P,In} \) and \( F_{P,Out} \) represent the mass flowrates of phenol into and out of the volume element respectively, \( \dot{n}_P \) represents the rate of permeation of phenol through the wall of the membrane, and \( d_i \) represents the inner diameter of the tubing.

By inspection of the Figure 53, the following expression is derived for the mass balance of phenol:
Analysing for the case of steady state operation:

\[ F \cdot C_{T,In} - F \cdot C_{T,Out} - \dot{n}_p = 0 \]  \hspace{1cm} (A1)

In which \( C_{T,In} \) and \( C_{T,Out} \) represent the concentration of phenol at the inlet and outlet of the volume element respectively. The overall mass transfer coefficient is defined as the ratio of the mass transfer rate to the product of the area and concentration difference between each side of the boundary:

\[ k_{OV} = \frac{\dot{n}_p}{A\Delta C_p} \]  \hspace{1cm} (A2)

Where \( k_{OV} \) is the overall mass transfer coefficient, \( \dot{n}_p \) is the molar flowrate of phenol that permeates the membrane, \( A \) is the area of the volume element, and \( \Delta C_p \) is the difference in phenol concentration between the shell and lumen sides.

From the above relationship, the following expression is obtained for the rate of permeation of phenols through the membrane:

\[ \dot{n}_p = k_{OV} A (C_{T,In} - C_S) \]  \hspace{1cm} (A3)

In which \( C_S \) is the concentration of phenol in the stripping solution. The area available for mass transfer can be calculated based on the cylindrical geometry of the tubing:

\[ \dot{n}_p = k_{OV} 2\pi r_1 L (C_{T,In} - C_S) \]  \hspace{1cm} (A4)

In which \( r_1 \) is the internal radius, and \( L \) is the length of the tubing. As discussed in Chapter 3, the fraction of the tube area that is in contact with the walls of the bottle is insignificant, meaning that the above equation can be used without modification. Substituting Equation A4 into Equation A1:

\[ F \cdot C_{T,In} - F \cdot C_{T,Out} - k_{OV} 2\pi r_1 L = 0 \]  \hspace{1cm} (A5)

Rearranging:
\[
\frac{F \cdot (C_{T,\text{out}} - C_{T,\text{in}})}{L} = -k_{OV}2\pi r_1(C_{T,\text{in}} - C_S)
\]  

(A6)

As \( L \) approaches 0 the partial derivative of tube side phenol concentration with respect to tube length is obtained:

\[
\lim_{L \to 0} \frac{F \cdot (C_{T,\text{out}} - C_{T,\text{in}})}{L} = F \cdot \frac{\partial C_T}{\partial L} = -k_{OV}2\pi r_1(C_T - C_S)
\]

(A7)

Rearranging:

\[
F \cdot \frac{\partial C_T}{(C_T - C_S)} = -k_{OV}2\pi r_1 \, \partial L
\]

(A8)

Integrating between the limits of tube side concentration at \( L = 0 \), denoted \( C_{T0} \) and tube side concentration at \( L \), denoted \( C_T \):

\[
F \cdot \int_{C_{T0}}^{C_T} \frac{\partial C_T}{C_T - C_S} = -k_{OV}2\pi r_1 \int_0^L \partial L
\]

\[
F \cdot \ln \left( \frac{C_T - C_S}{C_{T0} - C_S} \right) = -k_{OV}2\pi r_1 L
\]

(A9)

Solving for \( C_T - C_S \):

\[
\frac{C_T - C_S}{C_{T0} - C_S} = \exp \left( \frac{-k_{OV}2\pi r_1 L}{F} \right)
\]

\[
C_T - C_S = (C_{T0} - C_S) \exp \left( \frac{-k_{OV}2\pi r_1 L}{F} \right)
\]

(A10)

The above equation will be used subsequently, when formulating an expression for the mixed second order partial derivative.

Equation AA4 was also used to derive the partial derivative of phenol permeation rate with respect to length. Rearranging Equation A4:
\[
\frac{\dot{n}_p}{L} = k_{OV} 2\pi r_1 (C_{T, in} - C_S)
\]  \hspace{1cm} \text{(A11)}

Taking the limit of \( L \) approaches 0 the partial derivative of permeation rate with respect to tube length is obtained:

\[
\lim_{L \to 0} \frac{\dot{n}_p}{L} = \frac{\partial \dot{n}_p}{\partial L} = k_{OV} 2\pi r_1 (C_T - C_S)
\]  \hspace{1cm} \text{(A12)}

In order to complete the derivation of the mixed second order partial derivative, a phenol balance on the stripping solution was carried out.

**Phenol balance on stripping solution**

The following diagram represents the stripping solution beaker at initial state and after a time period, \( \Delta t \) has elapsed:

![Diagram of change in stripping solution concentration over one time step](image)

*Figure 54: Diagram of change in stripping solution concentration over one time step*

By inspection of the above figure, the following expression is derived for the mass balance of phenol in the stripping solution:

\[
\begin{bmatrix}
\text{Initial Mass of phenol} \\
\text{of phenol}
\end{bmatrix} + \begin{bmatrix}
\text{Permeation of phenol}
\end{bmatrix} = \begin{bmatrix}
\text{Final Mass of phenol}
\end{bmatrix}
\]
Denoting the initial mass of phenol in the stripping solution as $M_{S0}$, and the mass of phenol in the stripping solution at time $\Delta t$ as $M_S$:

\[ M_{S0} + \dot{n}_P \Delta t = M_S \]

\[ M_S - M_{S0} = \dot{n}_P \Delta t \]  \hspace{1cm} (A13)

Recall that the mass of solute in a solution is given by the product of the solute concentration, $C_i$ and the volume of the solution, $V$:

\[ M_i = C_i V \]

Therefore:

\[ (C_S - C_{S0})V_S = \dot{n}_P \Delta t \]

\[ V_S \frac{(C_S - C_{S0})}{\Delta t} = \dot{n}_P \]  \hspace{1cm} (A14)

As $\Delta t$ approaches 0, the partial derivative of stripping solution concentration with respect to time is given:

\[ \lim_{\Delta t \to 0} V_S \frac{(C_S - C_{S0})}{\Delta t} = V_S \frac{\partial C_S}{\partial t} = \dot{n}_P \]  \hspace{1cm} (A15)

We now have sufficient equations to formulate the mixed second order partial derivative.

**Formulation of mixed second order partial derivative**

Substituting Equation A15 into Equation A12:

\[ \frac{\partial}{\partial L} \left( V_S \frac{C_S}{\partial t} \right) = k_{OV} 2\pi r_1 (C_T - C_S) \]

\[ V_S \frac{\partial^2 C_S}{\partial t \partial L} = k_{OV} 2\pi r_1 (C_T - C_S) \]

\[ \frac{\partial^2 C_S}{\partial t \partial L} = k_{OV} 2\pi r_1 \frac{(C_T - C_S)}{V_S} \]  \hspace{1cm} (A16)

Substituting Equation A10 into Equation A16:
\[
\frac{\partial^2 C_S}{\partial t \partial L} = \frac{k_{OV} 2\pi r_1 (C_{T0} - C_S)}{V_S} \cdot \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \tag{A17}
\]

A double integration was then used to derive an analytical equation for \( C_S \). Taking the definite integral with respect to \( L \) between bounds of 0 and \( C_s \), and 0 and \( L \):

\[
\frac{\partial}{\partial t} \int_0^{C_s} \frac{k_{OV} 2\pi r_1 (C_{T0} - C_S)}{V_S} \cdot \int_0^L \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \, dL
\]

\[
\frac{d}{dt} (C_S)|_0^{C_S} = \frac{k_{OV} 2\pi r_1 (C_{T0} - C_S)}{-k_{OV} 2\pi r_1 V_S} \cdot \left( \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \right) \bigg|_0^L
\]

\[
\frac{dC_S}{dt} = \frac{-F \cdot (C_{T0} - C_S)}{V_S} \cdot \left( \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \right) - \exp(0)
\]

\[
\frac{dC_S}{dt} \cdot \frac{1}{C_{T0} - C_S} = \frac{-F}{V_S} \cdot \left( \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \right) - 1
\]

\[
\int_0^{C_s} \frac{1}{(C_S - C_{T0})} \, dC_S = \int_0^t \frac{F}{V_S} \cdot \left( \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \right) - 1 \, dt
\]

\[
\ln \left( \frac{C_S - C_{T0}}{-C_{T0}} \right) \bigg|_0^{C_s} = \left( \frac{F}{V_S} \cdot \left( \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \right) - 1 \right) \bigg|_0^t
\]

\[
\ln \left( \frac{C_S - C_{T0}}{-C_{T0}} \right) = \frac{Ft}{V_S} \cdot \left( \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \right) - 1
\]

\[
\frac{C_S - C_{T0}}{-C_{T0}} = \exp \left( \frac{Ft}{V_S} \cdot \left( \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \right) - 1 \right)
\]

\[
C_S - C_{T0} = -C_{T0} \cdot \exp \left( \frac{Ft}{V_S} \cdot \left( \exp \left( -\frac{k_{OV} 2\pi r_1 L}{F} \right) \right) - 1 \right)
\]

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\[ C_S = C_{T0} - C_{T0} \cdot \exp \left( \frac{Ft}{V_S} \cdot \left( \exp \left( \frac{-k_{OV}2\pi r_1 L}{F} \right) - 1 \right) \right) \]  

Equation A19 gives the concentration of phenol in the stripping solution after time \( t \).
Appendix B

The following section describes the derivation of an equation for permeability as a function of overall mass transfer coefficient and inner and outer tube radius.

Derivation of permeability equation

As discussed in the literature review, the solution diffusion model states that transport across the membrane occurs by Fickian diffusion. As a result, $k_m$ can be derived starting from Fick’s first law of diffusion:

$$J = D \frac{dC}{dx} \quad (B1)$$

Where $J$ is flux, $D$ is the diffusion coefficient, $C$ is concentration and $x$ is displacement. Using a cylindrical coordinate system, this has the following form:

$$J = D \frac{dC}{dr} \quad (B2)$$

Where $r$ is displacement in the radial direction. The definition of flux is as follows:

$$J = \frac{\dot{m}}{a} \quad (B3)$$

For a cylindrical section:

$$J = \frac{\dot{m}}{2\pi r L} \quad (B4)$$

Substituting into expression for $D$:

$$D \frac{dC}{dr} = \frac{\dot{m}}{2\pi r L} \quad (B5)$$

Solving for $dC$:

$$dC = \frac{\dot{m}}{2\pi r LD} dr \quad (B6)$$

Integrating between limits of $C = C_{1(m)}$ at inner surface of the membrane ($r_1$), and $C = C_{2(m)}$ at outer surface of the membrane ($r_2$):

$$\int_{C_1}^{C_2} dC = \frac{\dot{m}}{2\pi LD} \int_{r_1}^{r_2} \frac{dr}{r} \quad (B7)$$
\[ C_{2(m)} - C_{1(m)} = \frac{\dot{m}}{2\pi LD} \ln\left(\frac{r_2}{r_1}\right) \]  \hfill (B8)

At equilibrium, the concentration of permeant at the surface of the membrane is related to the concentration in the fluid adjacent to the surface by the partition coefficient, which is defined as:

\[ K_i \equiv \frac{C_{i(m)}}{C_{i(f)}} \]  \hfill (B9)

Where \( C_{i(f)} \) is the concentration of component \( i \) in the fluid adjacent to the membrane.

This allows the Equation B8 to be stated in terms of the concentrations on the fluid sides of the membrane:

\[ K_C T - K_C S = \frac{\dot{m}}{2\pi LD} \ln\left(\frac{r_2}{r_1}\right) \]  \hfill (B10)

Rearranging Equation B10 gives:

\[ \frac{KD}{\ln\left(\frac{r_2}{r_1}\right)} = \frac{\dot{m}}{2\pi L(C_T - C_S)} \]  \hfill (B11)

Dividing both sides by \( r_1 \):

\[ \frac{KD}{r_1 \ln\left(\frac{r_2}{r_1}\right)} = \frac{\dot{m}}{2\pi r_1 L(C_T - C_S)} \]  \hfill (B12)

Recall that the RHS of Equation B12 is the definition of the mass transfer coefficient, as described in Equation A2. Therefore, the mass transfer coefficient can be expressed with the following equation:

\[ k_m = \frac{KD}{r_1 \ln\left(\frac{r_2}{r_1}\right)} \]  \hfill (B13)

The quantity \( KD \) is also known as the permeability of the membrane, denoted \( P \). Using this notation:

\[ k_m = \frac{P}{r_1 \ln\left(\frac{r_2}{r_1}\right)} \]  \hfill (B14)
This form is convenient, as the values of the diffusion coefficient and partition coefficient cannot be individually determined from the mass transfer experiments. Solving for permeability:

\[ P = k_m r_1 \ln \left( \frac{r_2}{r_1} \right) \]  

(B15)

The above expression was used to convert the mass transfer values into permeabilities. These permeability values were then used to calculate Arrhenius parameters.
Appendix C

The following section describes the derivation of an equation for the volume of a tubular membrane required to achieve a given separation.

Phenol balance on tube

The first step in this analysis was to carry out a phenol balance on the tubular membrane.

The following diagram represents a cross section of a volume element of the polydimethylsiloxane tubing.

![Diagram of cross section of volume element of membrane tubing](image)

**Figure 55: Diagram of cross section of volume element of membrane tubing**

In the above diagram, $F_{P,\text{In}}$ and $F_{P,\text{Out}}$ represent the flowrates of phenol into and out of the volume element respectively, $\dot{n}_p$ represents the rate of permeation of phenol through the wall of the membrane, and $d_i$ represents the inner diameter of the tubing.

By inspection of the above figure, the following expression is derived for the mass balance of phenol:

$$
\begin{bmatrix}
\text{Inlet flow of phenol} \\
\text{Outlet flow of phenol} \\
\text{Permeation of phenol}
\end{bmatrix}
- 
\begin{bmatrix}
\text{Accumulation of phenol}
\end{bmatrix}
= 0
$$

Analysing for the case of steady state operation:

$$
F \cdot C_{T,\text{In}} - F \cdot C_{T,\text{Out}} - \dot{n}_p = 0
$$  \hspace{1cm} (C1)
In which $C_{T,\text{In}}$ and $C_{T,\text{Out}}$ represent the concentration of phenol at the inlet and outlet of the volume element respectively. The overall mass transfer coefficient is defined as the ratio of the mass transfer rate to the product of the area and concentration difference between each side of the boundary:

$$k_{OV} = \frac{\dot{n}_P}{A\Delta C_p}$$  \hspace{1cm} (C2)

Where $k_{ov}$ is the overall mass transfer coefficient, $\dot{n}_P$ is the molar flowrate of phenol that permeates the membrane, $A$ is the area of the volume element, and $\Delta C_p$ is the difference in phenol concentration between the shell and lumen sides.

From the above relationship, the following expression is obtained for the rate of permeation of phenols through the membrane:

$$\dot{n}_P = k_{OV} A (C_{T,\text{In}} - 0)$$  \hspace{1cm} (C3)

In which $C_s$ is the concentration of phenol in the stripping solution. The area available for mass transfer can be calculated based on the cylindrical geometry of the tubing:

$$\dot{n}_P = k_{OV} 2\pi r_1 L C_{T,\text{In}}$$  \hspace{1cm} (C4)

In which $r_1$ is the internal radius, and $L$ is the length of the tubing. As discussed in Chapter 3, the fraction of the tube area that is in contact with the walls of the bottle is insignificant, meaning that the above equation can be used without modification. Substituting Equation 4 into Equation 1:

$$F \cdot C_{T,\text{In}} - F \cdot C_{T,\text{Out}} - k_{OV} 2\pi r_1 L C_{T,\text{In}} = 0$$  \hspace{1cm} (C5)

Rearranging:

$$\frac{F \cdot (C_{T,\text{Out}} - C_{T,\text{In}})}{L} = k_{OV} 2\pi r_1 C_{T,\text{In}} = 0$$  \hspace{1cm} (C6)
As \( L \) approaches 0 the partial derivative of tube side phenol concentration with respect to tube length is obtained:

\[
\lim_{L \to 0} \frac{F \cdot (C_{T,\text{Out}} - C_{T,\text{In}})}{L} = F \cdot \frac{\partial C_T}{\partial L} = k_{ov} 2\pi r_1 C_T
\]  

(C7)

Rearranging:

\[
F \cdot \frac{\partial C_T}{C_T} = -k_{ov} 2\pi r_1 \partial L
\]  

(C8)

Integrating between the limits of tube side concentration at \( L = 0 \), denoted \( C_{T0} \) and tube side concentration at \( L \), denoted \( C_T \):

\[
F \cdot \int_{C_{T0}}^{C_T} \frac{\partial C_T}{(C_T - C_S)} = -k_{ov} 2\pi r_1 \int_0^L \partial L
\]

\[
F \cdot \ln \left( \frac{C_T}{C_{T0}} \right) = -k_{ov} 2\pi r_1 L
\]  

(C9)

Solving for \( L \):

\[
L = \frac{F \cdot \ln \left( \frac{C_T}{C_{T0}} \right)}{-k_{ov} 2\pi r_1}
\]  

(C10)

Recall that the mass transfer coefficient of a membrane as a function of the membrane permeability and inner and outer radii is given by the following equation:

\[
k_m = \frac{P}{r_1 \ln \left( \frac{r_2}{r_1} \right)}
\]  

(C11)

Equation C11 was substituted into Equation C10:

\[
L = \frac{\ln \left( \frac{r_2}{r_1} \right) \cdot F \cdot \ln \left( \frac{C_T}{C_{T0}} \right)}{-2\pi \cdot P}
\]  

(C12)
As the tube has a cylindrical geometry, its volume is given by the following equation:

\[ V = L \cdot \pi \cdot r_1^2 \]  

(C13)

Equation C12 was substituted into Equation C13 in order to give an equation for the membrane volume required to achieve a given removal of solute.

\[ V = \frac{\ln \left( \frac{r_2}{r_1} \right) \cdot F \cdot \ln \left( \frac{C_T}{C_{T0}} \right) \cdot r_1^2}{-2P} \]  

(C14)