Mathematical Modeling of the Solid-Liquid Extraction of Phenolic-Rich Compounds from *Pinus contorta* Bark

by

Gregory Douglas Wright

A thesis submitted in conformity with the requirements for the Degree of Master of Applied Science
Department of Chemical Engineering and Applied Chemistry
University of Toronto

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Abstract

There is an ongoing effort to replace traditional wood adhesives with tree bark-derived resins that use an underutilized biomass residue (tree bark) to reduce the consumption of petroleum-derived chemicals for economic and environmental benefits. A key step in bark-to-resin conversion involves the reactive solid-liquid extraction of phenolic-rich compounds from bark by a caustic solvent. Despite significant work concerning bark conversion, efforts to understand this process were mostly empirical investigations. Therefore, this thesis focuses on developing mechanistic models for the solid-liquid caustic extraction and comparing theoretical predictions with experimental data. Among five types of kinetic behaviour models, it was found that the extended Fick’s law most accurately described the process. Isotherms were proposed to model equilibrium, which was found to have the best fit with the BET isotherm. This thesis work provided valuable insights into the extraction process mechanism that will help with future improvement in equipment design and scaling-up studies.
Acknowledgements

The opportunity to complete an MASc degree has been incredibly rewarding, and I have a list of remarkable individuals and organizations to thank for making the past two years of research, learning, and personal growth possible.

I would like to express my sincere appreciation and gratitude to my supervisors, Dr. Farnood and Dr. Yan, for their support, guidance, and inspiring suggestions, which were beyond critical for the production of this work. Your mentorship allowed me to complete my most challenging project with a keen interest and develop my technical and professional skills and interests far beyond my expectations at the start of this degree.

Thank you to the members of the Bark Biorefinery group, especially Nico, Yong, and Rosanna, who helped me with my experiments and helped me navigate all aspects of graduate work at U of T. My office and lab mates in Wallberg were also fantastic resources throughout this degree. Elina, Krista, Mike, Taofeek, Hanya, and Lei, you made this work possible with your friendship and support.

To the University of Toronto, the Department of Chemical Engineering and Applied Chemistry, NSERC, and the Bark Biorefinery group and its supporters, thank you for this opportunity and for supporting your fantastic students and researchers.

Finally, thank you to my family. Meghan and Fiona, you inspire and motivate me in everything that I do. To my parents, your support and love has given me everything that I have needed to arrive here. To my roommates Julia and Bill, you gave me a home and two unforgettable years in Toronto.
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1 Bark Biorefinery

1-1.0 Introduction

1-1.1 Thesis Overview

Tree bark-derived phenol-formaldehyde (BPF) resin is a type of wood adhesive that aims to replace traditional adhesives in the growing market of engineered wood products. The motivation behind the product's development is two-fold. First, BPF reduces the environmental impact of wood materials by replacing petroleum-derived chemicals in traditional adhesives with bark-derived phenols. Second, BPF uses bark, an underutilized biomass available in large quantities, to create a valuable product which currently must be purchased by companies that already have bark, thus realizing economic benefits.

Bark has a similar composition to wood, but it is unique in that it contains a group of chemicals called extractives, which include polyphenolic molecular structures that are reactive towards formaldehyde. Research at the University of Toronto has successfully taken advantage of this attribute by selectively extracting these compounds and using them to replace phenol, a key component used in traditional resin synthesis. Based on this research, the conversion of bark to resin can be achieved efficiently and safely as it consists of a small number of unit operations at moderate temperatures and pressures, as shown in Figure 1.1. The conversion consists of three primary steps. First, phenolic compounds are extracted from bark by a caustic solvent. Second, the unextracted bark residue is separated from the extractive-rich solvent via filtration. Since the residue is lignocellulosic, it remains suitable for energy recovery, which is the current optimal use for bark. Third, the extractives are reacted with other chemicals to yield the BPF resin.

Figure 1.1: Bark Biorefinery Process Overview
The Bark Biorefinery group, under the direction of Dr. Yan and Dr. Farnood, has conducted research and published several papers outlining the synthesis and characterization of BPF resins. The extraction technique was compared to an alternative liquefaction process in a study that recommended extraction as the choice alternative for resin production[1]. Chemical analysis of the extractives confirmed their suitability for the chosen application[2]. Reaction techniques have also been developed to create BPF-based resins that have similar wet and dry bond strengths to commercial phenol-formaldehyde (PF) resins[3], [4], even when the bark is from mountain pine beetle (Dendroctonus ponderosae) infested lodgepole pine (Pinus contorta), a readily available material since efforts to slow the beetle’s spread include the removal of infested trees[5].

Despite these achievements, efforts to advance the group’s understanding of the bark extraction had halted at empirical investigation and modeling. This is also true in the extended field, where bark extraction analysis has been confined to empirical techniques[6]–[9]. Empirical models are insufficient because they are only valid within the tested experimental levels, and they can only be applied to the exact equipment and procedures used in the experiments. Furthermore, they cannot further one’s understanding of the underlying mechanism of the extraction.

This thesis therefore aims to conduct experiments and model the solid-liquid extraction process mechanistically. The hypotheses are as follows:

1. The kinetics and equilibrium conditions of the extraction can be modeled in terms that are suitable for process scale-up.
2. Mathematical modeling can be used to reveal the extraction’s process mechanism.
3. The kinetic and equilibrium models can be analyzed for process optimization.

These hypotheses are motivated by the goal to design and optimize a scaled-up version of the process, and they represent a vital advancement towards achieving that goal.

The remainder of Chapter 1 expands upon the project motivation and the work to date at the University of Toronto. It also gives background information regarding solid-liquid extraction and wood adhesives. Chapters 2 to 4 are written in the format of a scientific journal. Chapter 2 provides a literature review of modeling and analytical techniques that have been applied to bark extraction in the extended field. In Chapter 3, a range of kinetic models are fit to experimental data to find the effects of temperature and liquid-to-solid ratio over time, to study the mechanism that controls the extraction, and to determine a model that is suitable for scaling-up studies. Chapter 4 applies equilibrium isotherm models to experimental data to further understand the maximum solvent concentration that can be
reached in a batch extraction based on the initial conditions of the solvent and bark. Lastly, Chapter 5 provides the thesis conclusions and suggests future work and recommendations for the project.

1-1.2 Motivation to Study Bark Phenol-Formaldehyde Resins

Phenol formaldehyde (PF) resins are a family of adhesives used to create engineered wood products. These resins occupy a significant industrial market with global sales exceeding 5 million tons per year in 2010[10]. This figure has historically grown in step with the increase in global gross national product. Looking forward, PF resin usage is expected to increase more rapidly as the currently more popular urea formaldehyde (UF) resin falls out of favour because it releases excessive amounts of formaldehyde over time[11]. Therefore, the global market for PF resin is projected to increase at a compound annual growth rate (CAGR) of 5.7% from 2014 to 2019 to reach a value of $19.3 billion[12]. The result is a growing market for bark phenol formaldehyde (BPF) resin.

Despite the common use of synthetic materials for wood adhesive production, natural and renewable adhesives have gained recent attention because of environmental concerns and general interest in sustainable material development. As such, an important motivational factor for this study is interest in renewable yet cost effective materials. PF resins are already more environmentally friendly than the more popular urea-formaldehyde (UF) resins. However, the phenol material used in PF resin synthesis is produced from petroleum products, which bring environmental costs and economic uncertainty[11]. The partial replacement of chemicals used to produce resins with renewable, natural materials will decrease the chemical loading, increase the inherent safety, and reduce the environmental impact of the material.

The second factor motivating this research is a desire to find new applications for bark. Bark is a renewable biomass material that is available in large quantities because it is produced as a waste material when wood logs are converted to forest products. In mills, bark is normally mixed with other woody residues and used as fuel for heat recovery; however, bark has a relatively low heating value, which drops sharply when the material is wet[1]. Although it has a similar composition to wood, it is unique because it contains a group of chemical compounds called extractives. Extractives, including compounds such as fatty acids, terpenes, suberins and tannins[2], accumulate in the bark to protect the organisms from attack sources such as fungi and insects[13]. Tannins, which contain polyphenolic molecular structures, have a higher chemical reactivity toward formaldehyde and can therefore be used to partially replace phenol in phenolic resin synthesis reactions[14], [15].
The potential market for the Bark Biorefinery process and BPF resin spans several sectors in the forestry industry. This range is highlighted in Table 2, which gives examples of industry partners supporting the Bark Biorefinery project at the research level. Applications for phenolic resins such as BPF include plywood, oriented strand board (OSB), medium density fiberboard (MDF), laminated veneer lumber (LVL), particleboard and hardboard insulation, and abrasives[16].

<table>
<thead>
<tr>
<th>Company</th>
<th>Industry Sector</th>
<th>Company Division of Interest</th>
<th>Fiscal 2013 Financial Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tembec</td>
<td>Forestry products (including lumber, pulp, and paper) and chemical products</td>
<td>The Specialty Cellulose Pulp Segment produces specialty pulps and chemicals, including resins.</td>
<td>This segment had CAD $460 million CAD in sales[17].</td>
</tr>
<tr>
<td>Huntsman Corporation</td>
<td>Differentiated chemical products</td>
<td>The Polyurethanes Division produces adhesives and insulation products</td>
<td>This division had revenues of over USD $4.96 billion[18]</td>
</tr>
<tr>
<td>Resolute Forest Products</td>
<td>Forestry products (including wood products, pulp and paper)</td>
<td>The Wood Products Segment processes trees from the forest to consumer products</td>
<td>This segment had sales of CAD $41 million[19].</td>
</tr>
<tr>
<td>Arclin</td>
<td>Differentiated engineering materials and chemical products</td>
<td>The Building &amp; Construction Division produces OSB panels, plywood, MDF, particleboard, resins, and other products</td>
<td>Private company-financial reports are not available. Annual company sales are USD $750 million</td>
</tr>
</tbody>
</table>

1-2.0 Background Information

1-2.1 Research Conducted at the University of Toronto

Research at the University of Toronto has been conducted to transform bark biomass into higher value economically friendly industrial products, such as green adhesives and bio-based foams. One such group of green adhesives are phenol-formaldehyde resins, where bark extractives can be used to replace petroleum-derived phenol.

The bark biorefinery group has conducted research and published several papers outlining the synthesis and characterization of these bark-derived phenol-formaldehyde (BPF) resins. The group has shown itself to be particularly interested in developing a process with bark from lodgepole pine (*Pinus contorta Dougl.*). Although bark is a readily available waste residue from forest mills, there is a pressing
need to develop a process that can use materials from this tree species because of the infestation of mountain pine beetle (D. ponderosae) in Western Canada. Since the outbreak started in the early 1990s, the insect has killed about 50% of the commercial lodgepole pine in the British Columbia[5]. Efforts to slow the beetle’s spread include removing and harvesting infested trees to reduce further attack, thus creating a massive resource of infected lodgepole pine trees.

Under the direction of Dr. Ning Yan, research at the University of Toronto on this subject has led to the development of two types of resin synthesis processes. In the first, bark is liquefied in phenol with an acid catalyst prior to being used in the resin synthesis reaction with formaldehyde and sodium hydroxide[1]. In the second, bark undergoes an extraction process by an alkaline solution prior to being used in the same resin synthesis reaction[2]. Both techniques have produced resins that were further analysed in papers published by the group.

Several key findings can be highlighted from the group’s research. Beetle infestation of lodgepole pine in Western Canada was found to have no negative effect on the bonding properties of the resin produced by the liquefying technique[1]. Extracted material was used in 30, 50 and 70 wt% partial replacement of phenol in the resin synthesis reaction. So, the extractives, crystal phenol, 37% formaldehyde and 40% sodium hydroxide were reacted to produce the final resin[2]. It was found that the 30% phenol replacement resins showed similar dry and wet bond strengths to the commercial PF resin. At 50% phenol replacement, the BPF resins showed similar bonding strength to the lab PF resin, which was slightly less than the commercial resin[2].

The liquefaction and extraction processes were found to have several advantages and disadvantages, which can be discussed by directly comparing results from the group’s research[1]–[4]. The liquefied bark resulted in resin with a better bond strength while the extracted bark led to resin with better thermal stability. Liquefied bark was also found to have more reactive sites towards formaldehyde and better yields (85% for liquefaction compared to 68% for extraction). However, the liquefaction product is only suitable for phenol replacement while the extraction product has broader possibilities. While residue from the liquefaction process is phenolated and difficult to handle, process, or dispose, residue from the extraction process is still composed of cellulose and lignin that can be burned as a fuel or sold as pellets. For these reasons, future research should focus on improving the extraction process.
1.2.2 Solid-Liquid Extraction

This thesis focuses on the extraction step of the resin production process. Solid-liquid extraction, also known as leaching, is the removal of a soluble fraction, in the form of a solution, from an insoluble solid phase. Leaching may result from the solubility of a substance in a liquid or it may be enabled by a chemical reaction. Leaching kinetics are influenced by the rate of extraction of the soluble fraction into the solvent[20].

Leaching systems are distinguished by four categories (shown below). Generally, all four categories are assigned to stipulate a leaching system completely[20].

<table>
<thead>
<tr>
<th>Table 1-2: Leaching system categories</th>
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<tbody>
<tr>
<td><strong>Category:</strong></td>
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<tr>
<td>Types:</td>
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1.2.3 Wood Adhesives

A wood adhesive is a material that is used to make two or more wood pieces adhere together by a cohesive chemical reaction. Phenol-formaldehyde (PF) resins are a family of adhesives that are commonly used in wood products. Manufacturers take advantage of these materials by building products composed of lower quality timber, small dimension wood pieces, or wood process residues that are held together with adhesives, thus realizing economic and environmental benefits [11]. Another benefit is the uniformity of products made with this method since defects naturally present in solid wood are avoided.

PF resins are popular because of their high bond strength and properties that resist damage by water and harsh outdoor temperatures. In fact, more than 70% of wood products use adhesives. The main applications are in construction and furniture materials, including particle boards, fiberboards, plywood, and oriented strand boards (OSBs), whose resin compositions by weight are approximately 20-30%, except for OSBs, which require about 2% resin. [11],[16].
2 Bark Extraction Modeling Literature Review

Chapter Abstract

Solid-liquid extraction has been studied extensively to develop processes that separate or create valuable and renewable products from bark. Since bark is a diverse natural material, and its extracts can be used in a variety of applications, no universal protocol exists for developing and optimizing this type of process. This chapter therefore aims to review the numerous modeling approaches that have been used for solid-liquid bark extraction studies. The review focuses on works that extract the bark for the production of adhesive resins. Bark, solvent, and extract application choices are discussed before the theoretically derived and empirically formulated models are described. Process parameters that affect bark extraction and values that can be measured and optimized are discussed in detail.

2.1 Bark Extraction and Process Modeling

Solid-liquid extraction is commonly used to separate compounds from bark with a liquid solvent. In general, it is done to create a source of sustainable renewable chemicals from bark, an underutilized resource in the forestry industry. The technique has been studied with a substantial variety of barks, solvents, and extraction equipment, and extract applications include pharmaceutical products and adhesive resins.

Process modeling is used to describe a process and predict its response to various disturbances [21]. Modeling is done by analyzing experimental and plant data as the process is influenced by its physical and chemical factors. For example, in extraction, it is key to understand how process factors affect mass transfer and equilibrium conditions because they govern extraction performance [21]. Mathematical models are critically important in process design because performance can be optimized by analysis and manipulation of the models to improve process economics.

Bark contains a diverse range of extractable material, and each combination of bark and solvent type results in different extract products and yield. As a result, there is no universal extraction protocol, and lengthy experiments are required to understand, model, and optimize each bark extraction process. Since no review has been conducted on the subject of modeling bark solid-liquid extraction processes, this chapter aims to identify, discuss, and analyse the numerous modeling approaches that have been used. It separates the models into two main sections based on an important differentiator: whether the
model is theoretically derived or empirically formulated.

Bark extraction falls under the broader heading of active compound extraction from natural materials, and the even broader heading of solid-liquid extraction. Modeling work in these broader fields is more advanced than that for bark extraction alone because of the larger volume of published research. The potential and actual application and extension of that work for bark extraction is the focus of Chapters 3 and 4, and so this review will not include modeling techniques that have not been applied to bark. Broader reviews of solid-liquid extraction in biorefineries are available in the literature [21]–[23].

After searching the literature, 28 papers were deemed appropriate for this review. The majority of the publications use empirical modeling techniques. Only five of the publications use theoretically derived models. This review first identifies topics that are common throughout the articles, which include bark, solvent, and extraction technique choices. Next, theoretically-derived models that have been applied to bark extraction are discussed. Finally, the empirical modeling techniques are reviewed.

2-2.0 Items Common to All Studies

2-2.1 Solvent, Bark, and Process Application Choice

First, the bark, solvent choice, and application of the studies will be discussed. A complete summary of this topic is included in Table B-1 in Appendix B. The studies were found to use a variety of solvents, and several studies included the study of more than one type of solvent. The number of times that each solvent was used in a study is presented below in Figure 2.1. The chemicals listed in the extract choice column vary in concentration from 0 to 100% by volume in water.
The extractive medium is considered a key variable in biomass extraction because the chemical makeup of the medium will directly affect the extract yield and makeup[24]. The most popular solvent choices found in the literature were ethanol, methanol, and acetone. Carbon dioxide was also studied several times with supercritical extraction units, and was combined with ethanol by Domingues et al.[25], [26]. Water has been successfully studied as a solvent for bark extracts[9], and was once declared by Pizzi to be the most suitable extraction solvent for *A. mangium* bark[27]. However, a mixture of alcohol and water has been found to be a better extractive medium for total phenolic content [28]. In one study, a sulfite medium was chosen because it was shown to improve the tannin yield compared to a water extraction[29]. Other choices include ethyl acetate[30], steam[31], hexane[32], a mixture of ethanol and acetic acid[33], and mixtures of multiple polar solvents[8]. Overall, the wide variety of extract choice and concentrations studied in bark extraction optimization over the past several years indicates that no single solvent has been found to consistently outperform other solvents. No extraction study was found to use sodium hydroxide, the extract of choice for Yan et al.’s research.

The publications also study a wide variety of barks. Bark type is normally chosen based on its extractable compounds, and researchers often select bark from trees within their own regions. The bark choice also affects the solvent choice, since that combination determines the extractable components.
Relatively few papers reviewed in this report were applied to resin synthesis. Derkyi et al. published two extraction optimization studies [6], [34] for Pinus caribaea (Caribbean pine) bark to replace phenol in PF resins. Hoong et al. studied Acacia mangium (black wattle) bark extraction for PF resin synthesis [29]. Two of the publications were motivated by the development of modeling techniques [35], [36]. In those cases, bark extraction was chosen only as an example model application. Otherwise, extraction was studied for medicinal purposes, and applications range from antioxidants to remedies for oral cavity affection [37], jaundice [38], inflammation [39] or other maladies. Although these applications differ from resin synthesis, the research is applicable because the authors are attempting to extract the same types of chemicals, such as phenols and tannins, from bark by the most efficient means possible. Although much research has been published on the application of bark extracts for resin synthesis, relatively few study the actual extraction, which speaks to the need to further study this process.

2-2.2 Extraction Equipment

Many types of extraction equipment exist that are suitable for bark extraction. Most of the studies included in this review used a batch process with a single stage. Extraction can be completed by applying a heat source to a beaker [13], a round bottom flask [9], or a container that could perform the same type of task [6], [29], [31], [34], [40]–[42]. At times, more specialized equipment were used for the batch extraction, such as a Soxhlet extractor [9], [43], a reflux extractor [44], an extraction column in a batch mode [40], an Ultraturrax turbo-extractor [8], or an M/K System batch digester, which recirculates liquid over the bark [24]. Variations on the batch extraction process also existed. Some extractions included magnetic stirring [7], shaking [45], [46], and centrifugation [37].

Two types of assisted extraction techniques have also been applied several times to bark extraction modeling studies. In microwave extraction, heating efficiency is improved by applying microwaves [24], [39], [44], [47]. In ultrasonic assisted extraction, stirring and thermal effects are improved by subjecting the process to ultrasonic frequencies [30], [33], [37], [43], [47], [48].

Finally, several modeling studies also used a supercritical solvent in a specialized extraction unit [25], [26], [32], [49]–[51]. Supercritical extraction equipment is more expensive to purchase and operate, but it allows for improved extraction rates with low-impact solvents such as carbon dioxide.
2-3.0 Theoretically-Derived Models Used in Bark Extraction

Theoretically-derived models describe extraction processes with concepts such as desorption of the solute from the solid, diffusion of the solute into the solvent, transfer of the solute across the liquid boundary layer and into the bulk solution, location and distribution of solute in the solid, equilibrium, and solubility[21]. They can be applied when the mass transfer mechanisms and equilibrium are known or they can be used to discover and interpret process mechanisms. Five publications were found to apply theoretically-derived models and concepts to bark extraction, and they are discussed in this section.

2-3.1 Modeling with a Differential Mass Balance

Simeonov et al.[52] modeled the extraction of tannins from oak bark in water with a mass balance in a spherical solid particle undergoing internal diffusion according to Fick’s Law:

\[
\frac{\partial C}{\partial t} = \nabla(-D_{eff} \nabla C) \tag{2-1}
\]

where \( C \) is the concentration of the soluble compound in the solid at time \( t \), and \( D_{eff} \) is the effective diffusivity. Internal diffusion was assumed to be rate limiting for the extraction kinetics because the Biot number was greater than 50. The solid phase equation was balanced with solvent concentration by assuming perfect mixing in the liquid:

\[
\frac{\partial c}{\partial t} = -\frac{V_s}{V_l} \frac{d \bar{C}}{dt} \tag{2-2}
\]

where \( V_s \) and \( V_l \) are the volumes of the solid and liquid phases, respectively, and \( \bar{C} \) is the average concentration of the solid phase at time \( t \).

In this test, the internal porosity of the solid bark was determined by mercury porosimetry several times over the course of the extraction and fit to the following empirical correlation:

\[
\mathcal{E} = p_1 t^{p_2} + p_3 \tag{2-3}
\]

where \( \mathcal{E} \) is the porosity, and \( p_1, p_2, \) and \( p_3 \) are parameters. It was found that the internal porosity and anisotropy of the solid increased during the extraction. Also, the uniformity of the pore size distribution decreased as the extraction progressed.

The dependence of the effective diffusivity on concentration was also investigated according to Brunowska’s method to estimate the diffusion coefficient from sorption measurements[53]. It was described by the following correlation:
Where $\bar{D}$ is the dimensionless effective diffusivity, $\varepsilon_0$ and $D_0$ the internal porosity and diffusivity as the concentration of solute in the solid approaches zero, and $\sigma$ is a parameter.

By modeling the effective diffusivity and porosity of the bark over time, three kinetic curves were calculated and compared to the experimental data. In the first, both variables were constant. In the second, both varied according to Equations 2-3 and 2-4, above. In the third, the effective diffusivity was constant and the porosity varied according to Equation 2-3. It was found that the consideration of variable diffusivity and porosity is of greater importance in the initial steep part of the kinetic curve, and that the model where only porosity varies fit experimental data best.

2-3.2 Modeling Supercritical Extraction

Supercritical extraction of *Eucalyptus globulus* with carbon dioxide has been studied by a group at the University of Aveiro[25], [49], [50] by fitting several types of theoretically derived models to experimental data. Supercritical extraction differs from batch extraction because supercritical solvent is passed continuously through the extraction unit containing the biomass. Thus, models developed and applied to these processes are not directly applicable to batch extractions. Modeling work in this area is generally more advanced than batch extraction models because of a push by academia and industry to study sustainable solvents[22].

Domingues et al.[25] tested the fit of four models against experimental data as the pressure, temperature, solvent ethanol content, and carbon dioxide flow rate were varied. The Logistic model (LM), proposed by Martinez et al.[54] predicts the total extraction yield as the solvent exits the reactor (at $z = Z$, the bed height) over time, $t$. It neglects axial dispersion and accumulation in the reactor and assumes that mass transfer depends only on the composition of the solvent:

$$Y(z = Z, t) = \frac{x_0}{\exp(bt_m)} \left(\frac{1 + \exp(bt_m)}{1 + \exp[b(t_m - t)]} - 1\right)$$

(2-5)

where $x_0$ is the initial concentration of extractable material in the solid, and $b$ and $t_m$ are model parameters, where $t_m$ has the physical meaning of the time when the extraction rate reaches a maximum value.

The Desorption model (DSM), developed by Tan and Liou[55], assumes that the mass transfer is described by a first-order kinetic expression:
\[ Y(z = Z, t) = \frac{Q_{CO_2}(1 - \varepsilon)x_0\rho_s}{m_{bark}\varepsilon\rho_{solv}k_d} \left[ 1 - \exp \left( k_d \frac{\varepsilon S_x \rho_{solv} Q_{CO_2}}{\rho_{solv} Q_{CO_2}} \right) \right] \times \exp(-k_d t) - 1 \] (2-6)

where \( k_d \) is the desorption constant, \( Q_{CO_2} \) is the solvent mass flow rate, \( \varepsilon \) is the bed porosity, \( m_{bark} \) is the bark mass, \( S_x \) is the extractor cross-sectional area, and \( \rho_s \) and \( \rho_{solv} \) are the solid and solvent densities, respectively.

The Simple Single Plate (SSPM) model presented by Gaspar et al.[56] assumes that the process is limited by intraparticle diffusion and that there is no fluid phase resistance:

\[ Y(z = Z, t) = x_0 \left[ 1 - \sum_{n=0}^{\infty} \frac{0.8}{(2n + 1)^2} \exp \left( \frac{D_{eff}(2n + 1)^2 \pi^2 t}{\delta^2} \right) \right] \] (2-7)

where the diffusivity is fit along with the plate thickness, \( \delta \), so that the fitting parameter is the ratio \( D_{eff}/\delta^2 \).

Fourth, the Diffusion model (DFM) adopted by Reverchon[57] uses a heat transfer analogy to describe a diffusion-limited mass transfer from spherical particles:

\[ Y(z = Z, t) = x_0 \left[ 1 - \frac{6}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{n^2} \exp \left( -\frac{D_{eff}n^2 \pi^2 t}{R^2} \right) \right] \] (2-8)

Where \( R \) is the particle radius and the fitting parameter is \( D_{eff}/R^2 \).

By fitting these four models to their data, Domingues et al.[25] found that the supercritical extraction was controlled by intraparticle diffusion because the Logistic and Desorption models were consistently outperformed by the Simple Single Plate and Diffusion models. However, external diffusions were also present when the solvent flow rate was low, which worsened the model fits. The Logistic model was found to be inadequate because the \( t_m \) parameter was negative, thus stripping it of its physical meaning in the model. The Desorption model was deemed inadequate because the concentration profiles in the solid are non-uniform, and therefore cannot be accurately described by a single desorption step.

In a later study by the University of Aveiro group, de Melo et al.[49] tested the two diffusion-based models described above (SSPM and DFM) in addition to two different models for the supercritical extraction of *Eucalyptus globulus* with carbon dioxide. The Brunner model assumes that the extraction is limited by a film resistance and that the fluid-solid interface is described by the solute solubility:

\[ n_{tot}(t) = 100 \times \frac{y'Q_{CO_2}\rho_{solv}}{m_{bark}} t \left[ 1 - \exp \left( -\frac{k_f a_0 m_{bark}}{Q_{CO_2}(1 - \varepsilon)\rho_{solv}} \right) \right] \] (2-9)
where $\eta_{tot}$ is the extraction yield in kg per 100 kg of bark, $k_f$ is the convective mass transfer coefficient, $a_0$ is the specific external surface area, and $y^*$ is the solute solubility in the solvent. With the exception of $t$, all terms in this model are constant. The solute removal is therefore constant until the total extractable content is reached.

The second new model tested for the system, proposed by Cocero and Garcia[58], describes the process with film resistance to the mass transport plus a linear equilibrium while ignoring axial and radial dispersion:

$$
\begin{align*}
\varepsilon \frac{\partial y}{\partial t} &= -u \frac{\partial y}{\partial z} - (k_f a)(y - y^*) \\
(1 - \varepsilon) \rho_s \frac{\partial y_s}{\partial t} &= (k_f a)(y - y^*) \\
y^* &= H y_s
\end{align*}
$$

(2-10)

where $y_s$ is the concentration of extractable material in the solid, $y^*$ is the surface equilibrium concentration in the solid, $y$ is the solvent concentration, $(k_f a)$ is the mass transfer coeffient, $u$ is the superficial velocity, and $H$ is the equilibrium constant. The extraction yield can then be found by integrating the concentration of the solvent exiting the reactor over time.

Once again, the diffusion models outperformed the other models in the study. It was therefore reaffirmed that internal diffusion was the most important resistance to the process.

2.3.3 Modeling Based on Solubility

Bark extraction has also been interpreted from the perspective of component solubility. In the supercritical extraction of Eucalyptus globulus, de Melo et al.[50] calculated and analysed solubility and kinetic data for three key triterpenic acids in the bark. The supercritical solvent density and Hildebrand solubility parameter were found to vary significantly with temperature and pressure, which allowed the authors to anticipate that the solubilities of the compounds of interest would also change significantly. The solubilities of those three compounds were estimated by the equilibrium relationship derived from the isofugacity condition[59]:

$$
y^*_i = \frac{P_i^{sat}}{\phi_i^{SCF}} \rho \exp \left[ \frac{V_i^{solid} (P - P_i^{sat})}{RT} \right]
$$

(2-11)

Where $y^*_i$ is the solute solubility, $P_i^{sat}$ is the solute vapor pressure, which was found by the Clausius-Clapeyron equation, $\phi_i^{SCF}$ is the fugacity coefficient found by the Peng-Robinson equation of state, $V_i^{solid}$ is the solute molar volume in the solid state, and $R$ is the universal gas constant.
The ratios of component solubility at different pressures, as well as the ratios of the convective mass transfer coefficient in the extractor and solute flux at different pressures were compared. It was found that increasing the pressure caused the mass transfer coefficient to decrease, but the solubility and solute flux to increase significantly. These properties were used to confirm the experimental results from a theoretical standpoint. However, the relations were derived as ratios at different process conditions, and therefore could not be used to predict the extraction rate at a given set of conditions.

The solubility of bark components were also analysed in the subcritical extraction of betulin from birch bark in water and ethanol[36]. The Hansen three dimensional solubility parameter of Betulin was calculated from its molecular structure. The temperature dependence of that parameter was calculated by a method derived by Jayasri and Yaseen[60]. Also, the Hansen solubility parameters for water and ethanol were calculated over varying temperatures so that the relative energy difference between the solute and solvent could be calculated. This method predicts solute-solvent interactions, which should be maximized to optimize the extraction. In the case of Betulin in water and ethanol, the work confirmed that Betulin is soluble in ethanol between 250 and 325° C, but in ethanol between 50 and 125° C. This method can be used to optimize extraction performance around specific molecules.

2-4.0 Empirical Models Used in Bark Extraction

Empirical modeling techniques are a powerful optimization tool that can be used to analyse a process where the underlying mechanisms are unknown or cannot be suitably described with a theoretically-derived model. They are often applied during the early stages of research when extraction techniques, materials, and equipment are being selected for further study. Twenty-three research papers on the empirical modeling of bark extraction were found and deemed applicable for this review. This section will focus on identifying and comparing several common aspects: first, the parameters that are varied; second, the results that are measured and optimized; and third, the experimental design techniques that are employed. Last, empirical models related to extraction kinetics are discussed.

2-4.1 Process Parameters that are Varied

There are numerous process parameters to consider optimizing in bark extraction. Findings from recently published papers might indicate which variables are considered to have the most significant effect on the extract yield and composition. The parameters varied in the extraction optimization papers are presented below in Figure 2.2. A full summary of what was varied in each study is included in Table B-2 in Appendix B.
Figure 2.2 shows that the time allowed for the extraction, as well as the solvent concentration, temperature, and liquid-to-solid ratio are the most commonly varied parameters in empirical bark extraction studies. In this case, the “solvent concentration” parameter refers to researchers varying both the concentration of the solvent (e.g. changing the %ethanol in an aqueous ethanol solution) and the chemicals present in the extract (e.g. switching from ethanol to methanol, or mixtures of those solvents). These four parameters were repeatedly shown to have a direct effect on the measured extract qualities.

The extraction method was also varied in several studies. This includes varying the number of extraction stages, which was done in two research reports[34], [39]. Derkyi included this parameter in a preliminary test that varied the number of extraction stages but kept all other parameters constant. Although the maximum tannin yield was obtained after a three stage extraction, the author decided that yield was not significantly different enough from a single stage extraction to merit the additional cost and time associated with multi-stage extractions. Thus, single stage extraction was fixed for the process optimization study[34]. Yang varied the number of times the bark was extracted between one and three. Unsurprisingly, the product involved in three extractions was deemed to be optimal. However, the
effect of the triple extraction on the time and cost of the process was not discussed. In other studies, the actual extraction method was modified or changed completely. Brusotti tested both ultrasound-assisted and unassisted extraction[37]. Aspe et al. used batch, Soxhlet, microwave-assisted, and ultrasound-assisted techniques and obtained the highest phenol and tannin yields with the microwave-assisted technique[43]. Cheah et al. studied both supercritical CO\(_2\) extraction and pressurized liquid extraction with hexane and modeled the effect of other process parameters on those extractions separately[32].

Bark chip size was also varied in multiple research reports, though significantly fewer than the four most common parameters. Hoong[29] and Brusotti[37] found that chip size had a significant influence on extraction yield and that smaller particles led to higher tannin extraction yields. Pinelo concluded that reducing particle size might not always increase positive extraction yields, possibly due to packing phenomena and the formation of preferential channels leading to negative effects when working with a certain masses and particle sizes for the biomass[61]. Kaijaluoto et al.[62] found that bark fine crushing was not effective, likely due to the tendency of fine bark material to form a dense clump with poor solvent interaction. These mixed reviews indicate that there is a need to check if varying the chip size will have an effect on a given extraction process.

Another interesting parameter was the plantation site of the trees. This parameter was varied by Hoong et al.[29], and it was concluded that one of the four sites studied had the most potential for tannin extraction. This conclusion shows that uniformity in biomass processing is extremely difficult to achieve due to the great possibilities in the variety of process feeds.

Less commonly studied parameters include the ultrasonic frequency in some ultrasound-assisted extraction studies[33], [48], and the pressure in Cheah’s pressurized liquid extraction[32] and Domingues’ supercritical fluid extraction[26]. Brusotti et al. used a screening design to quickly test the significance of a wider range of parameters such as whether or not light is present or defatting is used in the process[37]. The screening process was used to select a smaller particle size and higher solid:liquid ratio for the more complex factorial experimental design.

### 2-4.2 Measured and Optimized Results

As key process parameters are varied during bark extraction, researchers seeking to optimize the extraction process must choose what values can be measured and improved upon. The extract analysis methods used in the extraction empirical optimization papers are presented below in Figure
2.3. A full summary of what each researcher measured in their study is included in Table B-3 in Appendix B.

In some cases, the measurement should be maximized. For example, the most common extract analysis method involved finding the tannin, phenol, or polyphenol yield or content, which is referred to as “tannin or phenol yield” in the figure below. In other cases, the measurement should be minimized. The sugar content of the extract was found by several researchers who wished to minimize the amount of carbohydrates in the optimized extract solution.

Ten different measurements that researchers have used to analyse extract products are identified in the extraction optimization papers. However, the characteristics of the final biorefinery product, such as the resin, are more important than those of the bark extract. These characteristics cannot be directly predicted by quantitative measurements regarding the extract liquid. Derkyi has attempted to solve this issue by producing resin from extracts with different optimization qualities, thereby deducing the effect of extraction optimization on resin quality[6]. That is, resin was produced from extracts where: (1) only the tannin content was optimized, (2) only the sugar content was optimized, (3) only the Stiasny number was optimized, and (4) these three quantities were simultaneously optimized. This technique stood out as an intelligent approach to designing an extraction process that creates a high quality resin.

![Extract Analysis Methods](image_url)

*Figure 2.3: Extract analysis methods*
Next, the measurement techniques used by the researchers, as identified by Figure 2.3, will be discussed.

2-4.2.1 Stiasny Number Measurement Methods

In several cases, the reactivity of polyphenols and extractives towards formaldehyde is quantified by the Stiasny number, which can therefore provide insight into the potential for the extractives to produce adhesives. The research by Deryki et al. [6], [34] and Pinto et al.[24] directly references the Hillis and Urbach method[63] for obtaining the Stiasny number. Hoong et al. calculated the number by a similar method mentioned by Hillis[29]. The method involves dissolving the dried sample in water and reacting the extractives for 30 minutes under heated conditions with hydrochloric acid and formaldehyde. The resulting precipitate, composed of formaldehyde-condensable tannins, is filtered and dried. The Stiasny number is then expressed as the yield of this precipitate as a percentage of the starting material. Therefore, a higher Stiasny number indicates that the material is more likely to react with formaldehyde.

The Stiasny number quantifies a property that is vital to creating resin since the extractives will be reacted with formaldehyde. It has been used in the past by Yan’s group. Still, it has not been shown to be an absolute predictor of resin quality. For example, Derkyi et al. [6] found that extractives whose Stiasny number and tannin and sugar content were simultaneously optimized formed a better resin than extractives with only the Stiasny number optimized.

2-4.2.2 Phenol or Polyphenol Yield or Content Measurement Methods

The most common property analysed by the extraction optimization papers was the total phenolics of the extract samples. Although the methods used to determine this value differed slightly, the majority referenced and adhered to a variation of the Folin-Ciocalteau method [7], [9], [24], [30], [31], [37], [38], [40], [42], [45], [46], [61]. Several reports referred to the method as described by Singleton and Rossi[64]. This method involves adding the Folin-Ciocalteau agent to solutions of the extract and reacting the solutions with sodium carbonate. Absorbance is then measured and compared to a standard. The standard was found to most commonly be gallic acid, and thus the total phenolic compounds is repeatedly reported in gallic acid equivalents per 100 g of bark or extract[24], [37], [38], [42], [45], [46], [61]. Other authors used the Folin-Ciocalteau method to report the phenol compound content in mg of epicatechin per g of dry plant material[7], and as chlorogenic acid equivalents[9].
Other papers that did not refer to the Folin-Ciocalteu method used similar absorption methods to quantify the phenol or polyphenol content of the samples. The European Pharmacopoeia spectrophotometric method [65] was used by Lonni et al. [8] to report the total phenolics of the samples. The Prussian blue method, used by Yang et al. [39], involves mixing the sample with chemicals such as a ferric chloride solution, potassium ferricyanide and hydrochloric acid before measuring the solution absorbance, and also expresses total polyphenols in gallic acid equivalent units. Last, Jeong et al. [44] used Tintometry based on the Amerine and Ough method [66] to determine the phenol content by spectrophotometry.

The sheer popularity of spectroscopic techniques to analyse the phenol or polyphenol content of the samples speaks to the importance of this analytical method for extraction optimization. Clearly, the total phenol or polyphenol yield should be maximized by the extraction process and the parameters that are varied in the study should be selected to try to maximize this yield.

2.4.2.3 Tannin Yield or Content Measurement Methods

The tannin yield or content of the extract samples was also measured by several papers. This analysis is similar to the phenol or polyphenol yields, though different techniques were chosen by various authors. One technique that was very similar to the total polyphenol content techniques described above was used by Pessoa et al. [41], who reported tannin content as a percent of gallic acid equivalent by subtracting the non-tannin fraction of the sample from the total polyphenol fraction of the sample. Both the total polyphenol and non-tannin fractions were determined by relating the spectroscopic absorbance of the samples to the specific absorbance of gallic acid.

Derkyi et al. [6], [34] used the Roux method [67] to determine tannin content. This method involves filtering a mixture of the extract and slightly chromated hyde powder. The weight gain of the hyde powder expressed as a percentage of the weight of the starting material was equated to the percentage of tannin in the sample.

Last, Brusotti et al. [37] found the amount of condensed tannins by n-butanol-HCl spectrophotometry, which was a variation of the method described by Porter et al. [68]. The extract was mixed with acetone, HCl, 1-BuOH and FeNH₄(SO₄)₂·12H₂O before the absorbance was measured. The condensed tannins content was then expressed as percent delphinidin.
2.4.2.4 Total Yield Measurement Methods

The total yield of extracts from an experiment has been interpreted by researchers either as a means to measure the percent of mass from the original biomass that remains from the starting material or as a means to measure the amount of dryable material that can be found in the extraction liquid produced by the experiment. In the first case, Tham et al. referenced a report by Zhang[69] to calculate the yield by drying the extracts to a constant weight and expressing that mass as a percentage of the starting mass of the samples used in the extraction, as shown in Equation 2-12, below [13]. Alternatively, Pessoa et al. [41] used a gravimetric method described by Harke and Mutschler in the German Pharmacopoeia[70] to measure the dry residue in the extract.

\[
\text{Total extractives Yield (\%) } = \left( \frac{\text{Mass of Water Dried Extracts}}{\text{Mass of Samples Used in Extraction}} \right) \times 100\%
\]  

(2-12)

The second interpretation of extract yield found in the extraction optimization papers aimed to quantify the amount of dryable extractives. For example, Jeong et al. quantified the soluble solid content of the liquid extract, which was expressed as a dry matter percent of the sample obtained from the extraction process[44].

2.4.2.5 Sugar Content or Total Carbohydrates Measurement Methods

The sugar content of the extract samples was also measured by several of the research papers attempting to optimize the bark extraction processes. As opposed to other measurements commonly found in these papers, the aim of the bark extract in this measurement is to minimize the sugar content as the carbohydrates can interfere with future reactions such as the reaction required to produce phenol formaldehyde resin. Derkyi et al. used a modified version of the phenol-sulfuric acid method described by Dubois [71]. The method involves centrifuging the dried extract with a series of chemicals including lead acetate, sulfuric acid before measuring the absorptivity of the solution, which is compared to a glucose standard curve. The total sugar content is reported as an average percent of the oven-dried bark[6], [34]. Pinto et al. measured the total carbohydrates by acid methanolyis as described by Sundberg et al.[72]. This method uses gas chromatography-mass spectrometry (GC-MS) and gas chromatography with a flame ionization detector (GC-FID) to analyse the extract samples. The results are compared to reference monosaccharide samples including rhamnose, xylose, glucuronic acid, glucose, galactose, arabinose, mannose, and galacturonic acid. The total carbohydrate content was the sum of all the monosaccharide quantified and converted to homopolysaccharide[24]. Third, Jeong et al. measured
the reducing sugar content by UV spectrophotometry with the dinitrosalicylic acid method and calculating the results from a glucose standard curve.

Three methods of sugar content, described above, have been found in the extraction optimization papers. Since the literature explains that minimal sugar presence is required to effectively use the extracts for a tannin-formaldehyde resin[6], this analysis should be considered for future work on the subject.

2-4.2.6 Antioxidant Activity Measurement Methods

Antioxidants react through free radical or molecular oxygen quenching, and can delay or inhibit the oxidation processes that occur under the influence of molecular oxygen or reactive oxygen species. Antioxidants are responsible for the defence mechanism of organisms against the pathologies associated to the attack of free radicals, and are associated with the prevention of disease [73]. There are many methods to evaluate the antioxidant capacity of a substance and a range of methods are used in these papers. However, these methods are not relevant to extracts that will be applied to resin synthesis, and will not be discussed.

2-4.2.7 Other Measurements

Several other analytical techniques were found in the extraction optimization papers that cannot be grouped with the above headings. The gel time of the extract solutions was found by Hoong et al. by heating a mixture of the tannin solution and paraformaldehyde powder. This analysis was deemed appropriate because the times could be compared to those of other tannins that have successfully been used for resin synthesis by Pizzi[74]. The authors could then conclude whether or not the gel time range was sufficient for application in plywood and particle boards.

The extraction rate was another measurement identified by Yang et al.[39], which was calculated by the equation below, where $D$ is the extraction rate of polyphenols, $V_2$ is the volume of the prepared sample (mL), $C$ is the polyphenols content (µg/mL), $M$ is the quantity of raw material (g) and $V_1$ is the testing volume of the prepared sample (mL). Extraction rate was found to be affected most significantly by the extraction time of the experiment.

$$D(\%) = \left( \frac{C \times V_2}{M \times V_1 \times 1 000 000} \right) \times 100\% \quad (2-13)$$
Some studies aimed to maximize the extraction of a product that was not tannin or phenol, such as Betulin[48], triterpenic acids[26], and oxyresveratrol[33]. Those compounds are not applicable to resin synthesis.

Lastly, the electron-donating ability of the samples were measured by Jeong et al.[44] by a α,α’-diphenyl-β-picrylhydrazyl (DPPH) radical scavenging method, which allows the ability to be expressed as a percentage difference between with the DPPH reagent and without the reagent. Since the researchers aimed to use the extracts for their antioxidant properties, it is unclear if this property would assist the extracts in a resin synthesis process.

2-4.3 Experimental Design and Modeling Techniques

Experimental design requires thoughtful testing and statistical analysis to ensure optimal results. The extraction empirical optimization studies reviewed here draw from a set of concepts that are widely accepted as optimization techniques for multivariable studies in chemical processes[6]. Several concepts must be introduced to understand the experimental design techniques employed in these studies.

A full factorial experiment studies all possible combinations of all levels of the factors that are investigated. This is a strategy where factors are varied together rather than one at a time, and it allows for the most efficient use of data possible[75]. In an extraction process, the factors that are commonly studied have already been discussed, some examples of which are extraction time and temperature. The levels of those factors would then be the extraction time in minutes and temperature in °C that is set for a particular experiment. A factorial experiment is often denoted as a $N^k$ factorial design, where k is the number of factors and N is the number of levels of each factor that is being tested. Experimental design varied in the publications, and included central composite designs[6], [9], [34], Box-Behnken designs[24], [30], [45], and a Taguchi design matrix[32]. Large factorial experiments are often analysed with experimental and statistical software such as Design-Expert[6], [34], [39], Statistica[8], [9], [26], [41], and SPSS[32], [45].

Factorial experiments may also be fractional, which means that some fraction, e.g., one half, of the full factorial experiments are tested to determine the effects that the factors have on the desired outcome of a process[75]. Fractional factorial designs are convenient because the experiments will take less time to complete, though less information will be gathered.
Simpler experimental designs found in the extraction optimisation literature involved varying one parameter at a time while keeping the other parameters constant [13], [31], [38]. The best combination of these parameters was then concluded to be the combination of the values found to individually maximize the measured response. This approach, though simple to design, has been shown to be inferior to analytical experimental design techniques such as a factorial design.

Slightly different approaches were taken by two authors who wanted to narrow down their choice of factors before conducting a factorial experimental technique. Yang first used single factor experiments to determine the major influence factors in the extraction process before moving on to a factorial experiment [39]. Brusotti used a Plackett-Burman screening design to select dominant factors from six choices. This technique determines the coefficients of a linear model for the measured response. The significant factors are those whose coefficients are demonstrably larger than a “dummy” factor that was tested without changing any parameters. The author then used a factorial design for the previously determined significant factors [37]. Both techniques show good judgement and efficiency used to narrow down a long list of parameters to a practical size for a factorial experimental design.

The papers have been shown to employ numerous types of factorial experimental design techniques. All the factorial techniques listed above successfully modeled the extraction processes. So, it may be up to the preference of the experimenter and the time limit of the study to decide which type of technique should be utilised. A central composite design with software-assisted analysis and response surface methodology stands out as a proven and robust technique for process optimization. Model verification, by running an experiment at the optimal conditions determined by the calculated model, also distinguished itself as an intelligent technique that should be included in this type of research.

2-4.4 Empirical Kinetic Models in Bark Extraction

The empirical models discussed up to this point have employed ANOVA and linear least-square regression techniques to determine first, the degree to which process parameters affect outcomes, and second, the form of the mathematical model to describe those findings. However, various empirical models have also been developed so that their formulae match extraction kinetic behaviour, which is how an extraction process at certain conditions behaves over time. These models are especially suitable for assisted extraction, including microwave and ultrasonic techniques, which cannot be effectively described theoretically [76]. The parameters of these models have no physical meaning, and can
therefore only be used to describe the extraction curves empirically rather than the extraction process mechanistically.

While extracting antioxidants from Galician bark and forest biomass, Piwowarska et al. [45] tested three such models originally developed for sorption curves but adapted for extraction processes. They are the Peleg, Elovich, and Page models, shown in Equations 2-14 to 2-16, respectively.

\[ c_t = c_0 \frac{t}{K_1 + K_2 t} \]  
\[ c_t = \frac{1}{\alpha} \ln(\alpha \cdot \beta) + \frac{1}{\alpha} \ln(t) \]  
\[ c_t = e^{kt^n} \]

where \( c_t \) is the solvent concentration at time, \( t \), and \( K_1, K_2, \alpha, \beta, k \) and \( n \) are model parameters.

The model parameters were found via regression and fit to the total phenols content and antioxidant capacity of the extract over time. Peleg’s model was found to best describe the kinetics of the extraction process [45].

2-5.0 Conclusions

A literature review was conducted by identifying and comparing modeling techniques that have been applied to the extraction of compounds from bark. The bark and extract solvent choices in the articles revealed the variety of biomass and solvents that can be used in this type of application. The extraction equipment can also vary from batch and multi-batch units to units facilitated with techniques such as ultrasonic and microwave-assisted extraction, and to units with supercritical solvents flowing continuously past the biomass.

Modeling techniques are vital for enhancing process understanding and optimization. They can be classified based on whether they are derived from theoretical principles or empirical observations. A very limited amount of research has been published that applies theoretically-derived models to bark extraction, and the majority of those studies have been applied to supercritical extraction techniques. Studies have shown that intraparticle diffusion plays a key role in the process because models derived from that assumption have outperformed other models. The solubility of bark components in different solvents has also been analysed, which can be used to target specific extractable components while optimizing the solvent choice and temperature. However, the small number of publications means there is a fundamental lack of understanding with respect to how reactor design, solvent choice, and flow conditions affect the underlying mechanisms of bark extraction, including mass transfer through the solid/liquid boundary layer, intraparticle diffusion, and solubilisation reactions that might occur.
The majority of research that models bark extraction uses empirical techniques. Following the review of related literature, it is clear that this type of study will always be required when looking at a new bark and solvent combination because of the diverse range of extractable components. Empirical modeling techniques are important in early studies to determine suitable process conditions that can be researched with more in-depth techniques. However, very little research has progressed beyond empirical studies.

The empirical works were therefore reviewed to determine key process parameters that should be varied in optimization studies. The process parameters varied in the optimization studies, such as temperature and extraction time, and the measured results, such as the polyphenol yield, provided insight into what parameters should be varied and optimized when studying bark extraction. The final choice for those factors will depend on the extraction equipment choice and process application. Experimental design and statistical analysis techniques employed in the related literature were also discussed and a central composite experimental design would likely be the most robust and efficient method for bark extraction modeling and optimization.
Chapter Abstract

Tree bark extracts have been used in the synthesis of wood adhesives to create a green value-added product from an underutilized resource in the forestry industry. However, research has been limited to empirical attempts to optimize the solid-liquid extraction process. In this work, phenolic-rich compounds were extracted from mountain pine beetle infested lodgepole pine (Pinus contorta) bark via an immersive reactive extraction with a caustic solvent in a batch reactor. To elucidate the process mechanism and provide a basis for process design and scale-up, five types of mathematical models that have been applied successfully in the literature to other solid-liquid extraction processes were fit to experimental data, namely: the shrinking core and rate law models, and the Fick’s law analytical, extended, and solvent balance solutions. Additionally, the extended Fick’s law and rate law models were modified to create new versions of the models that reduce the number of required parameters and increase the fit to experimental results, respectively. It was found that relatively complex shrinking core models, which differentiate between the extraction’s phase transfer, diffusion, and reaction steps, are surpassed in relative fit when compared to homogeneous diffusion-based models derived from Fick’s law. The extraction is most accurately described by the extended Fick’s law model, which indicates a two-stage extraction limited by internal diffusion. This model is suitable for scaling-up studies, for supporting the design of equipment, and even for converting a batch into a continuous process.

3-1.0 Introduction

Traditional wood adhesives such as phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins are produced using synthetic chemicals from the petrochemical industry. Recently, cost-effective renewable adhesives have gained attention due to environmental concerns and interest in sustainable material development[77]. The partial replacement of these chemicals with natural materials will decrease the chemical loading, increase the inherent safety, and reduce the environmental impact of the adhesives.

A further motivation for the formulation of a renewable adhesive is the desire to find new applications for bark, an underutilized source of biomass available in large quantities because it is produced as a waste in pulp and paper, lumber, and wood chip facilities. When a boiler is available, bark can be mixed with other woody residues and burned for heat recovery. Unfortunately, bark has a
relatively low heating value, which drops sharply when it is wet, and renders this use sub-optimal[1]. Although it has a composition similar to that of wood, bark is unique in that it contains a group of chemical compounds called extractives, which include polyphenolic molecular structures that are reactive towards formaldehyde[14], [15]. Renewable adhesives can therefore be made by first, extracting these compounds from bark, and second, reacting the compounds with formaldehyde to synthesize bark-derived phenol-formaldehyde (BPF) resins.

The reactive extraction of phenolic compounds from bark by a sodium hydroxide solvent is therefore studied in this paper to optimize the synthesis of BPF resins. Mountain pine beetle (Dentroctonus ponderosae) infested lodgepole pine (Pinus contorta) bark was chosen because it is a readily available material since efforts to slow the spread of the beetle include the removal of infested trees. This paper aims to build on research by the University of Toronto’s Bark Biorefinery Group, which has studied bark extraction techniques [1], [2] and a reaction techniques that create resins with wet and dry bond strengths similar to those of commercial PF resins [3], [4].

Nonetheless, efforts to advance the group’s understanding of the bark extraction halted at empirical investigation and modeling. In the extended field as well, batch bark extraction analysis has been confined to empirical techniques[6], [7], [9], [13], [24], [29]–[31], [34], [37], [39], [44], [45]. Empirical models are insufficient because they can be applied only to the exact equipment and procedures used in the experiments, and they cannot further understanding of the underlying mechanism of the extraction. Moreover, they are only valid within the tested experimental levels. As a result, they may fail to predict all aspects of the solvent extraction curve, which normally consists of a fast extraction step (washing stage) and a slow extraction step (diffusion stage), as shown in Figure 3.1[76], [78], [79].
This chapter aims to model the bark extraction to meet two primary objectives. First, a mechanistic understanding of the reactive solid-liquid extraction should be gained. Second, since many categories and variations of applicable extraction models exist in the literature, available models should be evaluated and one recommended as most appropriate for this process. Completing these objectives will provide a basis for model-based process design and scale-up.

Model evaluation should be constrained to the characteristics of the bark extraction. Experimental determination of bark extraction yield is a time-consuming and labour-intensive process, which puts pressure on researchers to utilize as few data points as possible. This effect will be escalated with process scale-up. Also, bark is a natural material and is prone to natural deviations in its composition. The models should therefore be evaluated based on relative fit, so that it matches experimental data, parsimony, so that it uses as few parameters as possible, and robustness, so that it does not react excessively to deviations in experimental data.

### 3-2.0 Mathematical Models

Five types of mathematical models that have been applied successfully in the literature to other solid-liquid extraction processes were selected for analysis in this work. As such, the models are not fully derived here. However, the following sections discuss their assumptions, present their final equations, and include references to works where the models are fully derived. Section 3-2.6 presents two new modifications to the models. Model application techniques are presented in the Experimental Section.
3-2.1 Shrinking Core Models

Shrinking core models differentiate the steps of a reactive leaching process. As the process proceeds, the unreacted particle constituents leave an outer porous leached shell for the reactant to diffuse through towards an unleached core, which shrinks with time. The steps involved are: (1) mass transfer of reactant A from the bulk liquid to the outer surface of the particle; (2) pore diffusion of reactant A through the leached shell; (3) chemical reaction at the interface between the leached shell and the unleached core; (4) pore diffusion of the reaction products back through the leached shell; (5) mass transfer of the reaction products back into the bulk liquid surrounding the particle[80]. The rate of the process is controlled by the slowest of these sequential steps[81].

To determine the rate controlling step, experimental data is fit to the integrated rate equation shrinking core models presented in Table 3-1. The model with the best fit is chosen as the rate controlling step. Equations 3-1 to 3-3 fit best in cases where the rate controlling step is one of the previously described shrinking-core model steps. Equations 3-4 and 3-5 alter the model so that it can be applied to a homogeneous process. The shrinking core model has been used for many solid-liquid heterogeneous systems[82]–[89] and plant-based extraction processes with a supercritical solvent[22].

<table>
<thead>
<tr>
<th>Rate-controlling Step</th>
<th>Rate Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film diffusion control</td>
<td>$\frac{t}{t^*} = [X]$</td>
</tr>
<tr>
<td>Diffusion control through the ash or product layer</td>
<td>$\frac{t}{t^*} = \left[1 - 3(1 - X)^2 + 2(1 - X)\right]^2$</td>
</tr>
<tr>
<td>Surface chemical reaction control</td>
<td>$\frac{t}{t^*} = [1 - (1 - X)^3]$</td>
</tr>
<tr>
<td>First-order pseudo-homogeneous model</td>
<td>$\frac{t}{t^*} = -\ln (1 - X)$</td>
</tr>
<tr>
<td>Second-order pseudo-homogeneous model</td>
<td>$\frac{t}{t^*} = (1 - X)^{-1}$</td>
</tr>
</tbody>
</table>

In Table 3-1, $t^*$ is the time for complete dissolution, $\rho_B$ is the molar density of the solid reactant, $R$ is the radius of the solid particle, $k_s$ is the surface reaction rate constant, $k_g$ is the mass transfer coefficient, and $C_{Ag}$ is the concentration of A in the bulk solution. The conversion of the extractable material is denoted by $X$, and determined by Equation 3-6[90].

$$X = \frac{\text{Amount of extracted material in solution}}{\text{Amount of extractable material in the original solid}} (3-6)$$
3-2.2 Fick’s Law Analytical Solution

In the extraction of natural materials, the diffusion of a solute within the solid into the solvent is usually the rate limiting step [91], [92]. Assuming negligible external mass transfer resistance and no change in effective diffusivity with solute concentration, the extraction process model can be simplified to the mass balance in a spherical solid particle, as in Fick’s second law [76]. By further assuming that the spherical particle’s initial concentration is uniform, that extraction causes the concentration to vary only with respect to the particle’s radius, \( r \), and that the particle is uniform in shape with a maximum radius of \( R \), the ordinary differential equations to Fick’s second law can be found [93] and altered to express the concentration of the solute in the extraction solvent at any time: [94]

\[
\ln \left( \frac{c_{\infty} - c}{c_{\infty}} \right) = \ln(E) = -0.498 - \frac{9.87D_{\text{eff}}t}{R^2}
\]

(3-7)

where \( c \) is the concentration of the solute in the solvent at time \( t \), \( c_{\infty} \) is the solvent concentration after infinite time, and \( E \) is the non-extracted fraction of the solute in the sample particle.

This solution was used successfully by Franco et al. [78] to describe the extraction of oil and antioxidant substances from Rosa rubiginosa and by Sprio et al. [95] to describe the extraction of 6-gingerol from Jamaican ginger rhizome.

3-2.3 Fick’s Law with Solvent Balance Model

The solvent balance model balances the release of extractable material from the solids with the solvent concentration. This model shares many assumptions with the previously introduced models. The transport of particles from the solid to the liquid is driven by a diffusion mechanism. The solid particles are spherical in shape and have a uniform and constant radius \( R \) that is independent of moisture content. The diffusion coefficient is constant throughout the extraction. Extraction causes the concentration to vary only with respect to the particle’s radius over time. The solvent in the batch reactor is perfectly mixed and the transfer resistance in the liquid phase is negligible. The initial concentration available for extraction in each experiment is first calculated using the final concentration in the solvent at the end of the experiment [96]. The balance equation for the solid phase comprised of spherical particles is presented in Equation 3-8: [93].

\[
\frac{\partial C}{\partial t} = D_{\text{eff}} \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right)
\]

(3-8)

where \( C \) is the concentration in the solid material at time \( t \) and location \( r \).
The mass balance in the solvent can be expressed by Equation 3-9[97], where the solvent concentration is uniform at any given time:

\[
\frac{\partial c}{\partial t} = -\frac{V_s}{V_l} \frac{d\bar{C}}{dt}
\]  

(3-9)

where \( V_s \) and \( V_l \) are the volumes of the solid and liquid phases, respectively, and \( \bar{C} \) is the average concentration of the solid phase at time \( t \).

The initial and boundary conditions for Equations 3-8 and 3-9 are as follows[97]:

\[
t = 0, \quad C = C_0 \quad \forall r
\]  

(3-10)

\[
t = 0, \quad c = 0
\]  

(3-11)

\[
t > 0, \quad C(r = R) = c
\]  

(3-12)

\[
t > 0, \quad \frac{dC}{dr}_{r=R} = 0
\]  

(3-13)

This method was successfully employed by Wongkittipong et al.[96] and Tsibranska et al.[97] for the extraction of andrographolide and polyphenols, respectively, from different plants.

3-2.4 Fick’s Law Extended Analytical Solution

To improve the traditional Fickian approximation introduced in Section 2.2, Osburn and Katz[98] expanded the equation to include both the washing and diffusion steps of the extraction, as outlined in Figure 3.1. The approach has been used more recently by Hojnik et al. to model the extraction of lutein from Marigold flower petals[99]. For a spherical particle, the equation is:

\[
\frac{c_\infty - c}{c_\infty} = \frac{6}{\pi^2} \left[ f_1 \exp \left( -\frac{\pi^2 D_{eff,1} t}{R^2} \right) + f_2 \exp \left( -\frac{\pi^2 D_{eff,2} t}{R^2} \right) \right]
\]  

(3-14)

where \( D_{eff,1} \) and \( D_{eff,2} \) are the effective diffusivity coefficients of the washing and diffusion stages, respectively, and \( f_1 \) and \( f_2 \) are the fractions of the solute extracted from the washing and diffusion stages, respectively.

3-2.5 Rate Law Model

The extraction of active compounds from plants has also been successfully modeled by applying a second order rate law to the solvent concentration:[100]

\[
\frac{dc}{dt} = k(c - c_\infty)^2
\]  

(3-15)

where \( k \) is the extraction rate constant.
This model also assumes that the extraction proceeds from the diffusion of extracts through the material and into the solution, and that the solvent concentration tends to a constant, saturated value under the same conditions. Furthermore, the solvent is well mixed and has a uniform concentration at any given time.

Linearizing the integration of Equation 3-15 from \( t = 0 \) to \( t \) and \( c = 0 \) to \( c \) yields the following:

\[
\frac{t}{c} = \frac{1}{kc_{\infty}^2} + \frac{t}{c_{\infty}} \tag{3-16}
\]

This model has been successfully used for the extraction of many types of natural materials, including protopine from Fumaria officinalis\[^{100}\], antioxidants from pomegranate marc\[^{101}\], and active constituents from Schisandra chinensis\[^{102}\].

Despite being employed numerously in the analysis of batch solvent extraction kinetics, this model differs from the others presented in this work because it is not derived fundamentally, but rather adapted from rate law theory. Its parameters therefore do not have real physical meaning, and it should not be used for scaling-up or equipment design studies\[^{76}\].

### 3-2.6 Model Modification and Improvement

#### 3-2.6.1 Modification of the Fick’s Law Extended Analytical Solution

The number of variables was reduced for the model introduced in Section 3-2.4 by forcing the solvent concentration function through the origin. That is, the solvent concentration is zero at time equals zero.

This initial condition relates \( f_1 \) and \( f_2 \) by Equation 3-17, and creates a modified model, introduced in Equation 3-18.

\[
f_2 = \left( \frac{\pi^2}{6} - f_1 \right) \tag{3-17}
\]

\[
\frac{c_{\infty} - c}{c_{\infty}} = \left[ \frac{6}{\pi^2 f} \exp \left( -\frac{\pi^2 D_{eff,1} t}{R^2} \right) \right] + \left( 1 - \frac{6}{\pi^2 f} \right) \exp \left( -\frac{\pi^2 D_{eff,2} t}{R^2} \right) \tag{3-18}
\]

where \( f \) is the parameter used to differentiate between the washing and diffusion steps of the extraction.

#### 3-2.6.2 Modification of the Rate Law Model
To improve the fit of the model introduced in Section 3-2.5, the rate order was assumed to be an unknown value, \( n \), and the concentration difference between \( c \) and \( c_\infty \) was reversed:

\[
\frac{dc}{dt} = k(c_\infty - c)^n 
\]  
\[ (3-19) \]

Applying the same boundary conditions as the original rate law model and integrating from \( t = 0 \) to \( t \) and \( c = 0 \) to \( c \) yields the following:

\[
c = c_\infty - (kt(n - 1) + c_\infty^{1-n})^{1/(1-n)}
\]  
\[ (3-20) \]

The model parameters \( k \) and \( n \) can then be found by nonlinear regression. The equilibrium concentration parameter can be found either experimentally or by nonlinear regression.

3-3.0 Experimental Section

3-3.1 Determination of Extraction Yield and Solvent Concentration

Pine beetle-infested *Pinus contorta* bark provided by FPInnovations was ground and sieved to between 0.211 and 0.5 mm (US mesh size 35-70). The bark was extracted with 1 wt% NaOH solution in 50 mL centrifuge tubes, which were submerged in a water bath. The extraction temperatures were 60\(^\circ\)C, 80\(^\circ\)C, and 100\(^\circ\)C, and the liquid-to-solid ratios were 8:1, 10:1, and 12:1 by weight. Prior to submerging the centrifuge tubes, the bark was stirred into the solvent to ensure that all the material was wet, and the samples were again every 15 min until the extraction was stopped. Each extraction condition was run in triplicate.

Following extraction, the alkaline-soluble fraction of each mixture was separated from the remaining bark with grade 42 Whatman filter paper held on a Buchner funnel that led to a vacuumed flask. Next, the samples were washed with hot water until the washing liquid ran clear, and dried at 65\(^\circ\)C to a constant weight. The extraction yield (dry basis) was then calculated by the equation below:

\[
Yield \text{ (\%)} = \left(1 - \frac{m_e - m_f}{m_b}\right) \times 100\%
\]  
\[ (3-21) \]

where \( m_e \) is the dried weight of the extracted bark and filter together, \( m_f \) is the dried weight of the filter, and \( m_b \) is the dried weight of the bark prior to extraction.

The initial moisture content of the bark used for the extraction experiments was found by drying 1 g samples of the material at 65\(^\circ\)C to a constant weight. The ground bark was kept in a re-sealable storage bag and was thoroughly mixed before samples were taken so that their uniformity was ensured.
The concentration at a given time was calculated by multiplying the average yield and the initial dry weight of the bark, and dividing that value by the solution volume used in the experiment. The concentration was assumed to be equal throughout the well-mixed bulk solvent.

3.3.2 Model Parameter Estimation Methods

For the shrinking core models, the linearized equations presented in Table 1 were fit to the experimental data and model fit was analysed by the coefficient of determination ($R^2$) values. To fit the the Fick’s law analytical solution model, a linear regression was used for Equation 7 to determine ($D_{eff}/R^2$) by plotting $\ln (E)$ versus time, where $c_\infty$ was determined experimentally.

For the Fick’s law with solvent balance model, the particle radius was discretized in space with second-order finite differences. Finite difference equations of the same order were used for the boundary equations. The equations were solved with the Crank-Nicolson method. The initial concentration available for each extraction was calculated using the final concentration in the solvent at equilibrium. The effective diffusivity was then modified to fit the experimental points using a simple dichotomy algorithm to maximize the model fit.

The Fick’s law extended analytical solution model was also fit with linear regression. Since the first term on the right-hand-side of Equation 3-14 is not significant during the diffusion stage, $D_{eff,2}$ and $f_2$ were found from the linear regression of the plot $\ln (E)$ versus time, where $c_\infty$ was determined experimentally. In the early extraction stage, the second term on the right-hand-side of Equation 3-14 approaches unity, and a plot of $\ln \left(\frac{E \pi^2}{6} - f_2\right)$ versus time yielded $D_{eff,1}$ and $f_1$. The modified version of this model was fit with the same technique.

The rate law model was fit by plotting $\frac{t}{c}$ versus $t$ according to Equation 3-16. The slope and y-intercept of the resulting linear regression determined the parameters $k$ and $c_\infty$.

Two modifications of the rate law model were tested. In modification A, the extraction kinetic order and rate constant were found by nonlinear regression, and the equilibrium concentration was found experimentally. In modification B, the extraction kinetic order, rate constant, and equilibrium concentration were all found experimentally. MATLAB’s nlinfit function was used for nonlinear regression.

The performance of the models was analysed by the average absolute relative deviation (AARD), given in Equation 3-22.
where \( N \) is the number of experimental values, \( C_{\text{exp}} \) is an experimental concentration value, and \( C_{\text{calc}} \) is the concentration predicted by the model.

### 3-4.0 Results and Discussion

#### 3-4.1 Effect of Temperature

Extraction curves were found experimentally for every combination of liquid-to-solid ratios of 8, 10, and 12:1 and temperatures of 60°, 80°, and 100° C, thus forming nine complete extraction curves. The results are first analysed in Figure 3.2, which displays experimental results for a solid-to-liquid ratio of 10:1. The error bars represent the standard deviation of the measured yields on a dry basis, which were tested in triplicate.

The curves follow the expected shape for a batch extraction, which was shown in Figure 3.1. The initial mass transfer from the bark is fast because the surface layers of the bark have been mechanically damaged during the grinding and the solute is simply washed into the solvent. This stage is therefore called the washing stage. Next, the extraction slows as the solute must diffuse into the particles during the slower diffusion stage. Third, a final equilibrium concentration is reached.

Also as expected, the equilibrium concentration of the solvent increases with temperature, from a 32.75% yield at 60° C to a 43.74% yield at 100° C. This effect has been confirmed empirically for bark extraction in several studies[6], [24], [34], [40]. This effect has been attributed to a reduction in solvent viscosity and the resulting improved ability to wet the plant matrix and solubilise the target extractives, to the added thermal energy that encourages extractive diffusion, and to the softening of plant tissue that may weaken the phenol-protein and phenol-polysaccharide interactions in the powdered bark[34], [39]. The diffusion of extractives from the bark to the solvent occurs quickly, with at least 60% and 75% of the extraction completed within 5 and 30 min, respectively. No appreciable changes were found after 4 hr. At 60 and 80° C, equilibrium is nearly reached after 2 hr. At 100° C, equilibrium is reached after just 1 hr.
Figure 3.2: Influence of temperature on extraction yield for experiments conducted with a 10:1 liquid-to-solid ratio at 60°C (blue), 80°C (red), and 100°C (green). Error bars represent the standard deviations of triplicate experiments.

3.4.2 Effect of Liquid-to-Solid Ratio

Figure 3.3 displays the experimentally determined extraction curves for liquid-to-solid ratios of 8, 10, and 12 to 1 at 80°C, where error bars represent the standard deviation of the measured yields, which were tested in triplicate. Again, all the plots show a classical behaviour. The final extraction yields and rates increase with increasing liquid-to-solid ratios, which has also been shown empirically for bark extraction[6, 7, 24, 34].
Figure 3.3: Influence of liquid-to-solid ratio on extraction yield for experiments conducted at 80° C with a liquid-to-solid ratio of 8:1 (blue), 10:1 (red), and 12:1 (green). Error bars represent the standard deviations of triplicate experiments.

3-4.3 Shrinking Core Models

To further understand the underlying mechanism of the reactive extraction between the bark and sodium hydroxide, shrinking core models were applied to the experimental data because they differentiate the steps of reactive extractions, as described in Section 3-2.1. The $R^2$ values generated by applying each model to all experimental data are presented in Table 3-2.

Table 3-2: Shrinking core model fit results

<table>
<thead>
<tr>
<th>Model</th>
<th>Average $R^2$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Reaction</td>
<td>0.745</td>
</tr>
<tr>
<td>Film Diffusion</td>
<td>0.689</td>
</tr>
<tr>
<td>Ash Diffusion</td>
<td>0.795</td>
</tr>
<tr>
<td>1st Order Pseudo-Homogeneous</td>
<td>0.773</td>
</tr>
<tr>
<td>2nd Order Pseudo-Homogeneous</td>
<td>0.836</td>
</tr>
</tbody>
</table>

Since the ash diffusion model has a better average fit than the chemical reaction or film diffusion models, it is likely that this step has the greatest impact on the overall extraction rate. The poor fit for the film diffusion model shows that the solvent mixing conducted during the experiments sufficiently rendered that step insignificant. The 2nd order pseudo-homogeneous model reaches
achieved the best average fit, with an $R^2$ value of 0.836. The process is therefore best interpreted as a single homogeneous step rather than a series of steps or a clear rate-limiting step.

None of these models were found to match the experimental data with sufficient accuracy to confidently identify one as appropriate for process design or prediction for this bark extraction. As a comparison, successful application of these models in the literature generally results in an $R^2$ value of at least 0.85 for one of the models, and is frequently as high as 0.98 [82], [83], [89], [90], [103]. Overall, the shrinking core models support the conclusion that homogeneous models are most appropriate for this process.

### 3.4.4 Model Fit and Use of Parameters

The remaining models were applied to experimental data to analyze their fit, parsimony, and robustness, and to identify their advantages and disadvantages. To analyze model parsimony, Table 3-3 identifies the parameters required for each model. The table also presents the AARD values for each model over all nine extraction curves. AARD values were calculated for each point in time that the extraction yield was found. The washing, diffusion, and equilibrium stages are generalized to identify stages of the extraction where the models fit experimental data particularly well or poorly. Note that the stages started and finished at different times in each extraction curve because they are affected by the temperature and liquid-to-solid ratio of the process. The average AARD values over all experimental data are also presented as a final means to compare model fit. The AARD values are colour-coded to assist data interpretation.
Table 3-3: Number of parameters required for each model, and AARD values over time calculated for all extraction curves. Where necessary, “Original” and “Modified” are truncated to “O.” and “M.”, respectively.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>240</th>
<th>360</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ficks Analytical</td>
<td>$c_\infty, D_{eff}$</td>
<td>21.04</td>
<td>23.78</td>
<td>20.25</td>
<td>18.65</td>
<td>10.28</td>
<td>2.52</td>
<td>2.54</td>
<td>0.51</td>
<td>0.21</td>
<td>11.09</td>
</tr>
<tr>
<td>Solvent Balance</td>
<td>$C_0, D_{eff}$</td>
<td>23.80</td>
<td>8.15</td>
<td>4.19</td>
<td>6.28</td>
<td>10.36</td>
<td>8.98</td>
<td>4.19</td>
<td>0.64</td>
<td>0.19</td>
<td>7.42</td>
</tr>
<tr>
<td>Extended Fick’s Analytical Solution</td>
<td>O.</td>
<td>$c_\infty, D_{eff,1}, D_{eff,2}, f_1, f_2$</td>
<td>2.06</td>
<td>4.12</td>
<td>4.71</td>
<td>1.97</td>
<td>2.19</td>
<td>0.90</td>
<td>0.38</td>
<td>1.08</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>M.</td>
<td>$c_\infty, D_{eff,1}, D_{eff,2}, f$</td>
<td>11.13</td>
<td>5.96</td>
<td>5.81</td>
<td>2.35</td>
<td>2.31</td>
<td>1.46</td>
<td>1.10</td>
<td>0.54</td>
<td>0.26</td>
</tr>
<tr>
<td>Rate Law</td>
<td>O.</td>
<td>$c_\infty, k$</td>
<td>36.92</td>
<td>18.07</td>
<td>7.78</td>
<td>2.57</td>
<td>3.15</td>
<td>4.75</td>
<td>2.54</td>
<td>0.63</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>M. A</td>
<td>$c_\infty, k, n$</td>
<td>7.59</td>
<td>2.86</td>
<td>6.15</td>
<td>3.52</td>
<td>2.20</td>
<td>2.92</td>
<td>2.89</td>
<td>3.97</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td>M. B</td>
<td>$c_\infty, k, n$</td>
<td>4.85</td>
<td>2.44</td>
<td>4.21</td>
<td>3.23</td>
<td>2.11</td>
<td>2.71</td>
<td>1.95</td>
<td>1.60</td>
<td>1.18</td>
</tr>
</tbody>
</table>

**Colour Coding Legend (%)**
3.4.4.1 Fick’s Law Analytical Solution

The Fick’s analytical solution model approximates the extraction as a single step with an effective diffusivity that controls the process. Table 3-3 shows that, with only two parameters required, this model is among the most parsimonious tested in this study. Conversely, the average AARD values are higher than every other model.

The parity diagram for all experimental data for this model is presented in Figure 3.4. Since the equilibrium concentrations were determined experimentally for this model, the fit is relatively good once equilibrium is reached. At 100° C, the model fits sufficiently well, but at 60° and 80° C, the model significantly underpredicts the solvent concentration in the first hour of the extraction, which is confirmed in Table 3-3.

![Figure 3.4: Parity diagram for the Fick’s law analytical solution model for liquid-to-solid ratios of 8:1 (squares), 10:1 (diamonds), and 12:1 (triangles), and temperatures of 60° (blue), 80° (green), and 100° C (red).](image-url)
This model’s strongest attributes are its small number of model parameters and ease of application. However, the experimental extraction curves pose a significant challenge because the solvent reaches a high concentration after a very short time before growing to an equilibrium concentration at a much slower rate in the diffusion stage. At 60° and 80° C, this model’s range of curves is not sufficient for this process because of the bad fit to experimental data. Yet, at 100° C, Table 3-4 shows that the model fit is comparable to the modified extended Fick’s analytical solution and rate law models, which require four and three parameters, respectively, as shown in Table 3-3. The increased temperature therefore reduces the slowing effect of the diffusion stage, and allows the complete process to be accurately predicted by this model. The excellent fit and parsimony suggest that this is an excellent candidate for process modeling at 100° C.

Table 3-4: Average AARD values for the Fick’s law analytical solution model for each temperature tested

<table>
<thead>
<tr>
<th>Temperature (° C)</th>
<th>Average AARD Values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3.60</td>
</tr>
<tr>
<td>80</td>
<td>13.7</td>
</tr>
<tr>
<td>60</td>
<td>15.9</td>
</tr>
</tbody>
</table>

3.4.4.2 Fick’s Law Solvent Balance

The solvent balance model improves on the first analytical solution to Fick’s law by balancing the release of extractable material from the solids with the solvent concentration. It is especially comparable to the previous model because they both require only two model parameters. In this model, parameters were calculated by a second order finite difference approximation with the Crank-Nicolson method. The particle radius was estimated to be 355 µm by assuming an even particle size distribution between the sieve sizes. The bark density was found experimentally to be 0.311 g/mL.

Figure 3.5 shows the parity diagram for all the experimental data for this model. Along with Table 3-3, the figure confirms that the model fit is significantly improved during the fast washing step compared to the previous model. However, it overestimates the yield during the diffusion step of the extraction. The overall fit is improved compared to the previous model, but not as impressive as the upcoming models.
3.4.3 Extended Fick’s Law Analytical Solution and Modification

The extended Fick’s law analytical solution divides the extraction into two stages and assigns an effective diffusivity coefficient to each stage. Table 3-3 shows that by increasing the number of parameters to the highest among the tested models, this solution achieves the best average fit. The two extraction stages follow the sharp slope transformation in the experimental results, thereby providing strong evidence that the bark extraction follows the classical behaviour of plant extraction processes, as shown by the parity diagram for the model in Figure 3.6.
Figure 3.6: Parity diagram for the extended Fick’s law analytical solution model for liquid-to-solid ratios of 8:1 (squares), 10:1 (diamonds), and 12:1 (triangles), and temperatures of 60° (blue), 80° (green), and 100° C (red).

To reduce the number of parameters required for this model and combat its most obvious disadvantage, the model parameters that define the fraction of solute extracted in each stage were combined into a single parameter by forcing the model curve through the origin. The parity diagram for this modification is shown in Figure 3.7.
Figure 3.7: Parity diagram for the modified extended Fick’s law analytical solution model for liquid-to-solid ratios of 8:1 (squares), 10:1 (diamonds), and 12:1 (triangles), and temperatures of 60° (blue), 80° (green), and 100° C (red).

The modified model remains among the better performing models in this study, but the above figure and Table 3-3 show that the fit to experimental data at the start of the extraction is noticeably reduced. This is unfortunate because a further potential advantage of the modified model is that it is forced through the origin, and therefore begins predicting solvent concentration at time equals zero rather than at time greater than zero. The modified model shows that this condition is difficult to apply to the bark extraction. Still, it is likely that the loss of model fit would be reduced for an extraction whose yield increases more moderately during its washing stage. Also, if a process is constrained so that yields cannot be experimentally determined very early in the extraction, the modification could improve prediction between process start-up and the first measurable yield.

The high number of parameters also causes the model fitting to become more complicated and time-consuming. Within the constraints of this type of extraction, where data acquisition is labour-intensive, leading to fewer experimental points, and results are prone to natural deviation due to the natural material, this model is vulnerable to experimental errors. For example, if one data point is too
high or too low due to experimental error, this model may wrongly predict the shift from the first extraction stage to the second due to the sudden slope change.

Yet, the excellent fit of this model and its modification confirms that this extraction consists of a fast extraction step (washing stage) and a slow extraction step (diffusion stage), as is common in the batch extraction of active compounds from plants[76]. It was shown in Section 3-4.4.1 that the extraction can be accurately described as a single extraction step at 100° C by the Fick’s analytical solution model, but this is likely due to a shortened diffusion stage that can be modeled as the solvent concentration approaches its equilibrium value. Mechanistically, this extended model describes the process most accurately by identifying the dominant mechanism in the complex, multi-step extraction. This suggests that bark particle size and shape will have a significant effect on the extraction kinetics, which should be considered in future studies.

3-4.4.4 Rate Law Model and Modifications

The performances of the rate law model and its variants are compared in detail for experiments carried out at a liquid-to-solid ratio of 10:1 at 80° C in Figure 3.8.

![Figure 3.8: Kinetics of extraction and model fit for the rate law model and its modifications for a liquid-to-solid ratio of 10:1 at 80° C. Symbols represent experimental, and lines calculated model data: original rate law model (red), modification A (green), and modification B (purple).]
The original rate law model assumes second order extraction kinetics. Although the extraction rate constant and equilibrium concentration were found by linearizing the model, the above figure and Table 3-3 show that the model underestimates the concentration at the beginning of the extraction and overestimates the concentration before equilibrium is reached, especially in the 45 – 60 min range. As a result, it was necessary to modify the model.

In modification A, the extraction kinetic order was assumed to be unknown, and it was found along with the rate constant by nonlinear regression. The equilibrium concentration was determined experimentally and included in the model, as with the models described in Sections 3-4.4.1 and 3-4.4.3. In this case, the prediction accuracy was increased during the first hour of the extraction, but the model underestimated the concentration when equilibrium was achieved experimentally (from 120 to 360 minutes).

In modification B, the extraction kinetic order, rate constant, and equilibrium concentration were all found by nonlinear regression. The model fit surpasses that for the earlier variants; however, the equilibrium concentration parameter was increased to a value significantly than the true experimental value to compensate for the increased kinetic order. Since the parameter increased on average by 20% compared to the observed equilibrium concentration, it no longer represents a true mechanistic value, and the model will fail to predict the extraction performance as time increases from 360 minutes.

Modification B also lacks robustness because it is overly sensitive to minor shifts in experimental data and willing to drastically alter its parameter values to fit every experimental point. For example, the rate constant values range from $1.0 \times 10^{-2}$ to $3.8 \times 10^{-3}$ in the original rate law model, but from $1.1 \times 10^{-3}$ to $3.3 \times 10^{-11}$ in modification B. Modification A is therefore the best performing model due to its parsimony, ease of application, average fit, and robustness.

However, as stated previously in Section 3-2.5, this model differs from the others in this work in that it is not derived fundamentally, but rather adapted from rate law theory. Despite being suitable for this application, it therefore does not meet this study’s objective to provide a basis for model-based process design and scale-up[76].

**3-5.0 Conclusions**

This chapter aimed to experimentally determine and model extraction curves for ground lodgepole pine bark in 1 wt% NaOH. Its goals were first, to gain a mechanistic understanding of the
reactive solid-liquid extraction, and second, to evaluate available mechanistic models and determine an optimal model for the process to provide a basis for process design and scale-up. Model evaluation was based on relative fit, parsimony, and robustness, and constrained to account for the extraction’s limitations: that bark is a natural material prone to natural variations, and extraction yield data acquisition is labour-intensive and time-consuming, pressuring researchers to collect fewer data points.

Experiments yielded nine extraction curves at all combinations of 8:1, 10:1, and 12:1 liquid-to-solid ratios at 60°, 80°, and 100° C. Extraction yield increases with increasing temperature and liquid-to-solid ratio, but extract concentration in the solvent decreases with increasing liquid-to-solid ratio. Since the extracts are separated from the solvent by evaporation, temperature should be preferably varied over liquid-to-solid ratio to optimize extract yield in support of overall process efficiency and economics.

Mechanistically, shrinking core models, which differentiate the extraction’s phase transfer, diffusion, and reaction steps, were outperformed in terms of relative fit by homogeneous diffusion-based models derived from Fick’s law, which therefore identify the dominant mechanism of the extraction. The diffusion consists of two stages before equilibrium is reached: a fast washing stage, and a slower diffusion stage.

The sharp initial slope of the extraction and the sudden shift to its second stage are difficult to fit with the most parsimonious Fickian models: the Fick’s analytical solution and solvent balance models, which require only two model parameters, underestimate the washing and diffusion stage yields, and overestimate the diffusion stage yields, respectively. Conversely, the least parsimonious model, the extended Fick’s analytical solution, fits the extraction results most accurately with five parameters. The exception is at 100° C, where the higher temperature accelerates the slower diffusion stage of the extraction so that the entire process can be described by the more parsimonious Fick’s analytical solution model. This model, in addition to the extended Fick’s analytical solution model at 60° and 80° C, most accurately describe the extraction mechanism and fit the experimental data. Since these models are derived fundamentally and include parameters with real physical meaning, they are suitable for scaling-up studies, for supporting the design of equipment, and even for converting a batch into a continuous process.

The rate law model was also tested against the extraction data. Two modifications were presented to improve the model by adding a parameter. The modification that finds all three parameters with nonlinear regression fits the experimental data excellently, but overpredicts the equilibrium concentration. The modification that requires an experimentally determined equilibrium concentration, which is called modification A, is parsimonious, flexible enough to have good relative fit,
and robust enough to not significantly change its parameter values if natural deviations or experimental error are present in the data; however, it does not provide insight into the process mechanism and should not be used for scaling-up studies.
Chapter Abstract

Mathematical models have been used to describe the kinetics of batch solid-liquid extractions, and are important for the extraction of active compounds from plants. However, attempts to analyse the equilibrium conditions of these processes have been limited to qualitative or empirical descriptions. This chapter therefore proposes isotherms to model equilibrium conditions for the batch extraction of phenolic compounds from mountain pine beetle infested lodgepole pine (*Pinus contorta*) bark. It was found that BET isotherms fit the experimental data well, which suggests a multilayer solubilisation of the bark material. At 60° C, the BET isotherm was modified to improve its fit by adding a new model parameter. Also, increasing the extraction temperature was found to increase the amount of extractable material in the bark. The isotherms were used to model the effect of an increasing liquid-to-solid ratio on the extraction yield and solvent concentration. The equilibrium models can also be combined with kinetic extraction models, and were therefore found to improve process design analysis capabilities. The isotherms are a meaningful improvement over past attempts to model equilibrium in batch solid-liquid extractions.

4-1.0 Introduction

Batch solid-liquid extraction techniques have been widely explored and applied to a variety of processes, for example, in the extraction of active compounds from plants[76]. In developing extraction techniques, mathematical models should be used to understand and optimize extraction performance, which is controlled by both mass transfer kinetics and equilibrium conditions[21]. Popular models, including analytical solutions to Fick’s law[94], [98] and the rate law model[76], [100], [101] highlight the importance of equilibrium conditions by including the \( c_\infty \) parameter, which is the concentration of the solute in the extraction solvent after infinite time, i.e., at equilibrium[76]. That parameter therefore has an essential role in determining the performance and economics of solid-liquid extraction operations.

Despite this prominence, investigation regarding of the \( c_\infty \) parameter has been insufficient. It has been discussed in terms of what process parameters can be manipulated to alter its value, but analysis has fallen short of a mechanistic model. For example, Xu et al. reported that solvent choice can be used to maximize the equilibrium extraction yield[104]. Franco et al. reported that solvent-to-liquid
ratio can be increased to an optimum to maximize the equilibrium yield, but increasing the ratio beyond that optimum will not have a significant effect on the yield[78]. Stanisaviljevic et al. reported that equilibrium is reached faster, though at a lower value, if the solvent-to-feed ratio is lowered[105]. Also, ultrasonic-assisted extractions have been found to enhance the equilibrium extraction yield[76]. Rate law models, which predict solvent concentration over time by the difference between the final equilibrium and present solvent concentrations, are often paired with empirical models to predict \( c_\infty \) as a function of a parameter such as particle size or temperature [100]–[102]. Still, this analysis is limited to certain extraction conditions and can be improved.

To address this knowledge gap, modeling techniques for supercritical fluid extraction processes were examined because they are generally more advanced than batch extraction models due to a push to study sustainable solvents[106]. Equilibrium is modeled in these works by functions called isotherms, which describe the equilibrium established for the solute distribution between the fluid and the solid surface. This is expressed in terms of: (1) concentration of the liquid and (2) solute loading on the solid, expressed as mass, moles, or volume of adsorbate per unit mass or per unit adsorbent surface area[80]. For example, Goto et al. used a linear isotherm for the extraction of peppermint oil by supercritical \( \text{CO}_2 \) in a continuous flow reactor[107]. Peker et al.[108] and Cocero et al.[58] also used linear isotherms to model supercritical extractions of caffeine and oil seeds, respectively. Finally, Kassing et al. found that a Langmuir isotherm governs the extraction of pepper[109].

This chapter therefore aims to use isotherms to model the equilibrium relationship between the solute loading on a solid and the solute concentration in the solvent of a batch solid-liquid extraction. This will be done for the batch extraction of phenolic compounds from mountain pine beetle (\( \text{Dentroctonus ponderosae} \)) infested lodgepole pine (\( \text{Pinus contorta} \)) bark by a sodium hydroxide solvent. This is being studied to synthesize wood adhesives from the extracts, thus creating an eco-friendly product from bark, an underutilized source of biomass in the forestry industry.

The equilibrium isotherms will be determined experimentally by modeling the extraction as the desorption of extractable material from material that is absolutely not soluble in the chosen solvent. Experiments will be conducted at different temperatures to find the initial amount of extractable material in the bark and the equilibrium solvent concentrations at various liquid-to-solid ratios. The isotherm models will provide insight into the process mechanism and allow for prediction of the equilibrium conditions, thereby allowing one to model the effect of an increasing liquid-to-solid ratio on the process yield and solvent concentration.
4-2.0 Mathematical Models

Many types of equilibrium isotherm models exist. Three models that pertain to this study, as shown in the results and discussion section, are introduced in Section 4-2.1, namely: the Langmuir, anti-Langmuir, and Brunauer-Emmett-Teller (BET) isotherms. Section 4-2.2 introduces two new modifications to the BET isotherm to improve the model fit to experimental data by adding model parameters.

4-2.1 Equilibrium Isotherm Models

A wide variety of single component isotherms have been developed to describe equilibrium relationships in adsorption/desorption processes. The following is an introduction to three isotherms that will be tested against experimental data for the bark extraction.

The Langmuir isotherm assumes a monolayer saturation of the available adsorption sites on the stationary phase. The solid phase loading gradually reaches the saturation capacity with increasing solute concentration in the liquid phase. The isotherm equation is expressed as:

\[ q_{eq} = \frac{q_s K_L c_{eq}}{(1 + K_L c_{eq})} \]  

where \( q_{eq} \) is the solid phase loading at equilibrium, \( q_s \) is the solid phase loading at saturation, also called the saturation capacity, \( K_L \) is the adsorption equilibrium constant, and \( c_{eq} \) is the liquid phase concentration[110].

In an anti-Langmuir isotherm, the solid phase loading increases gradually towards infinity as the solute concentration in the liquid phase increases. The isotherm equation is expressed as:

\[ q_{eq} = \frac{q_s K_L c_{eq}}{(1 - K_L c_{eq})} \]  

In this case, the parameter \( q_s \) no longer has the physical meaning of a saturation capacity. The fluid phase concentration is limited to the range of 0 to 1/\( K_L \)[110].

The Brunauer-Emmett-Teller (BET) isotherm expands on the Langmuir isotherm for multilayer adsorption. The behaviour resembles a Langmuir isotherm at lower solute concentrations and passes through an inflection point before behaving like the anti-Langmuir isotherm as solute concentration increases:

\[ q_{eq} = \frac{q_s K_L^a c_{eq}}{(1 - K_L^b c_{eq})(1 - K_L^b c_{eq} + K_L^a c_{eq})} \]
where $K_L^a$ represents the equilibrium constant for adsorption on the bare solid phase surface, and $K_L^b$ is the constant for subsequent layers. Typically, $K_L^a$ is greater than $K_L^b$. If $K_L^b$ reduces to zero, the isotherm equation reduces to the Langmuir isotherm. If $K_L^b$ and $K_L^a$ are equal, the isotherm equation reduces to the anti-Langmuir isotherm. The fluid phase concentration is limited to an upper bound of $1/K_L^b[110].$

The general shapes of these three isotherms are compared in Figure 4.1, below.

![Solute Concentration in Liquid Phase](image)

**Figure 4.1:** Adsorption isotherms showing three different behaviours: (a) Langmuir, (b) anti-Langmuir, and (c) BET

### 4-2.2 Modification of the Equilibrium Isotherm Models

To improve the isotherm fit to experimental data, two modifications to the BET isotherm were developed. The modifications are similar to the BET isotherm in that they describe Langmuirian behaviour at lower solute concentrations before passing through an inflection point and exhibiting anti-Langmuirian behaviour as solute concentration increases. In the first modification, a new degree of freedom was added to the model by including the full equations for the Langmuir and anti-Langmuir sections:

$$q_{eq} = \frac{q_LK_Lc_{eq}}{1 + K_Lc_{eq}} + \frac{q_ALK_ALc_{eq}}{1 - K_ALc_{eq}}$$  \hspace{1cm} (4-4)$$

where $q_L$ and $K_L$ are the equilibrium constants related to the Langmuir section, and $q_AL$ and $K_AL$ are the equilibrium constants related to the anti-Langmuir section.

In the second modification, another degree of freedom was added to the model by shifting the anti-Langmuir section of the model horizontally:

$$q_{eq} = \frac{q_LK_Lc_{eq}}{1 + K_Lc_{eq}} + \frac{q_ALK_AL(c_{eq} - H)}{1 - K_AL(c_{eq} - H)}$$  \hspace{1cm} (4-5)$$
where $H$ is the horizontal shift parameter.

### 4-3.0 Experimental Section

#### 4-3.1 Determination of Equilibrium Concentration and Loading

Pine beetle-infested *Pinus contorta* bark was extracted with 1 wt% NaOH via the method described in Section 3-2.1. The extraction was carried out for five hours at 60° and 80° C and for three hours at 100° C to ensure that equilibrium was reached. The liquid-to-solid ratio was varied from 5:1 to 40:1.

The equilibrium extraction yield and concentration were also found by the methods described in Section 3-2.1. The equilibrium loading of extractable material on the unextractable material was found by Equation 4-6:

$$q_{eq} = \frac{m_{extractables}}{m_{unextractables}}$$

where $m_{extractables}$ is the dry mass of extractable bark material, and $m_{unextractables}$ is the mass of bark material that cannot be extracted no matter how high the liquid-to-solid ratio, or how many extractions the bark undergoes at a given temperature.

The initial amount of extractable material was found by extracting the bark multiple times until the extraction became ineffective. The bark was first extracted at a liquid-to-solid ratio of 40:1, and further extractions were conducted at liquid-to-solid ratios of either 20:1 or 15:1. All extraction experiments were brought to equilibrium.

#### 4-3.2 Isotherm Parameter Estimation and Analysis

The isotherm models were fit to experimental data by nonlinear regression with MATLAB’s nlinfit function. Initial guesses for parameters were found by linearizing the Langmuir and anti-Langmuir sections of the experimental data. The performances of the models were analysed by the average sum of absolute error:

$$EABS = \frac{1}{n} \sum_{i=1}^{n} |q_{meas} - q_{calc}|$$

(4-7)
where \( \text{EABS} \) is the average sum of absolute error term, \( n \) is the number of experimental data points, \( q_{\text{meas}} \) is the experimental equilibrium loading value, and \( q_{\text{calc}} \) is equilibrium loading value predicted by the model.

### 4-4.0 Results and Discussion

#### 4-4.1 Initial Amount of Extractable Material

The initial amount of extractable material in the bark was found by repeatedly extracting the bark until the yield approached one percent, which is close to the approximate experimental error, as determined by the standard deviation between the triplicate experiments. The amount of extractable material in the bark was found to increase with increasing temperature from 43% at 60° C to 65% at 100° C. As a result, the initial loading of extractable material per mass of unextractable material also increases with increasing temperature. The result at 100° C is consistent with a previous study by the group, which found the total extractable yield to be 68% in a boiling water bath[2].

<table>
<thead>
<tr>
<th>Temperature (° C)</th>
<th>Total Extraction Yield</th>
<th>Initial Loading of Extractable Material [g/g] (dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>43.44%</td>
<td>0.77</td>
</tr>
<tr>
<td>80</td>
<td>60.28%</td>
<td>1.52</td>
</tr>
<tr>
<td>100</td>
<td>65.00%</td>
<td>1.86</td>
</tr>
</tbody>
</table>

The increasing initial loading of extractable material means that the faster extraction kinetics at higher temperatures found in the previous chapter are not only because of a faster diffusion process, but because more material is solubilised at higher temperatures. This is likely due to a combination of several phenomena. First, the increasing temperature allows the system to surpass activation energy requirements for new solubilisation reactions between the solvent and the bark. Second, the increasing temperature increases the solubility of the solvent so that more bark components are able to dissolve into the solvent.

To further validate this finding, earlier research conducted on this topic by Tanguay et al. was reviewed. In this work, the same bark sample and solvent were combined in an extraction while the temperature, liquid-to-solid ratio, and extraction time were varied to study the process empirically. Additionally, the bark residue composition was analysed and modeled empirically.
The empirical models determined by Tanguay et al. were manipulated so that the bark residue lignin composition was predicted when the same yield was reached at 60°, 80° and 100° C. This test was completed three times: at the lowest and highest yields that could be reached by all three temperatures as defined by the empirical models, and at a yield between those values. The results are displayed in Table 4-2, below.

Table 4-2: Predicted effect of temperature on bark residue composition at various yield values.

<table>
<thead>
<tr>
<th>Yield [dry basis]</th>
<th>60° C</th>
<th>80° C</th>
<th>100° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.2%</td>
<td>20.29%</td>
<td>18.88%</td>
<td>17.53%</td>
</tr>
<tr>
<td>36.0%</td>
<td>19.54%</td>
<td>17.28%</td>
<td>16.99%</td>
</tr>
<tr>
<td>40.9%</td>
<td>18.43%</td>
<td>16.37%</td>
<td>15.73%</td>
</tr>
</tbody>
</table>

The above table shows that as temperature increases, lignin in the residue decreases when the extraction yield is the same. Lignin is the largest polymeric phenolic component in bark, and these results confirm that more lignin components are being solubilised as the temperature is increased. As a result, the amount of extractable material in the bark depends on extraction temperature. This was also confirmed by Kaijaluoto et al., who found that increasing temperature caused compounds with higher molecular weight to dissolve during the extraction of spruce bark [62]. Similarly, Gironi et al [40] found that chestnut tree wood polyphenol solubility increased with increasing temperature of water and ethanol solvents.

4.4.2 Equilibrium Modeling

Experimental isotherm equilibrium data were found by varying the liquid-to-solid ratio of the extraction. The lower limit, a ratio of 5:1, was chosen because the bark absorbs approximately all of the solvent at this ratio, resulting in very little bulk solvent. The upper limit, 40:1, was restricted by the experimental apparatus. Data points beyond that ratio represent results from bark that was extracted multiple times, i.e., until the extractions became ineffective. The experimental results are shown in Figures 4.2 – 4.4, below.
Figure 4.2: Experimental equilibrium isotherm results for the bark and solvent system at 60°C. Data labels present the liquid-to-solid ratios, and values in parentheses present the number of times the bark had been extracted. Error bars represent the standard deviations of triplicate experiments.

Figure 4.3: Experimental equilibrium isotherm results for the bark and solvent system at 80°C. Data labels present the liquid-to-solid ratios, and values in parentheses present the number of times the bark had been extracted. Error bars represent the standard deviations of triplicate experiments.
Figure 4.4 Experimental equilibrium isotherm results for the bark and solvent system at 100° C. Data labels present the liquid-to-solid ratios, and values in parentheses present the number of times the bark had been extracted. Error bars represent the standard deviations of triplicate experiments.

The experiments clearly indicate a BET-like isotherm for the system. At 100° C, an anti-Langmuir isotherm also appears to be suitable. The experimental results are discussed in greater detail alongside the models in Figure 4.6.

Next, the BET isotherm for liquid-solid systems and its modifications presented in Section 4-2.2 were fit to the experimental data. The model modifications were developed in an attempt to fit the experimental data with greater accuracy by adding degrees of freedom to the standard BET model. The model parameters were found by nonlinear regression with MATLAB’s nlinfit function because first, nonlinear estimation gives better fit and more authentic results than linearization[111], and second, all of the models could be fit with the same technique. The models at 60° C are presented below.
Figure 4.5: Comparison of standard BET model (blue), its first modification (green), and its second modification (purple) for the isotherm at 60° C.

The above figure shows that the original BET isotherm fits the experimental data reasonably well, but that its fit is noticeably improved in the first modification. The second modification mostly improves the fit near the origin of the isotherm; however, adding a fifth degree of freedom to the model no longer forces the model to the origin. This departure from reality, as well as the lack of significant improvement in the model led to its dismissal as a possible model from the system.

The fit of the models is presented quantitatively in Table 4-3, by the average sum of absolute error, which has been employed in the literature for isotherm modeling studies[112]. This metric was chosen over relative error values (which were used in the previous chapter) because the relative values were skewed by the data points close to the origin, where insignificant absolute differences were amplified to massive relative differences because of the low experimental bark loading value.

Table 4-3: Sum of absolute error values for the BET models, where BET_m1 and BET_m2 are the first and second modification, respectively.

<table>
<thead>
<tr>
<th>Model</th>
<th>Average Sum of Absolute Error ($\times 10^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature</td>
</tr>
<tr>
<td></td>
<td>BET</td>
</tr>
<tr>
<td></td>
<td>BET_m1</td>
</tr>
<tr>
<td></td>
<td>BET_m2</td>
</tr>
</tbody>
</table>
Table 4-3 shows that adding a new parameter in the first model modification significantly improves the model fit at 60° C. However, the improvement is less significant at 80° and 100° C, and the modification is not warranted at these temperatures. Therefore, the original BET model best predicts the system at these temperatures, but the first modified model should be selected at 60° C. At 100° C, the Langmuir isotherm also appears appropriate, however, as stated in Section 4-2.1, the Langmuir isotherm is a special case of the BET model where $K_L^b$ reduces to zero. Since that parameter was found to be greater than zero by nonlinear regression, the BET model is best. The experimental and predicted concentration values are compared in a parity diagram in Figure 4.6.

Figure 4.6: Parity diagram for the BET modification 1 model at 60° C, and the original BET model at 80° and 100° C

Figure 4.6 shows that the first BET modification isotherm has excellent fit at 60° C. At 80° and 100° C, the original BET isotherm models also have excellent fit. The main source for the lack of fit are the data points near the origin of the isotherm. It is possible that the true initial amount of extractable
material in the bark at each temperature could be slightly higher than the results presented in this chapter. Assuming that the bark could be extracted further beyond the last experimental value would improve the fit of the isotherms near the origin. However, the final assumed amount of unextracted material would not be based on experiments, and this approach was deemed inappropriate. This source of lack-of-fit is less significant at 60°, where the modified model improves the fit near the origin.

Numerous other isotherms not introduced in Section 4-2.1 were also compared to the experimental data. Adsorption isotherms listed in review articles on the subject were considered[112]. However, no isotherm model was found to outperform the BET model and the modification presented above.

On a theoretical basis, the BET fit provides an understanding of the nature of the desorption phenomenon: multilayer extraction of material. Application of this isotherm to numerous solid/liquid systems stands as strong evidence that it is appropriate for the bark extraction[113]. It therefore accurately describes the dominant mechanism in this extraction. However, it is limited in that it doesn’t account for the reactions between the sodium hydroxide and the bark components. It would not be able to account for a change in the initial solvent concentration.

Although the isotherm was originally developed for gas phase adsorption, it was reworked for solid/liquid systems with an important difference: the \( q_s \) parameter no longer has the real physical meaning of saturation capacity solid loading[113]. This alteration affirms the decision to modify the BET further by adding a new degree of freedom and selecting that modification to describe the bark extraction process at 60° C.

4-4.3 Batch, Multi-Batch, and Continuous Operation Design

Elucidation of the bark extraction equilibrium behaviour also provides insight into optimizing a batch or multi-batch counter-current or cross-current process by combining the material balance of the system with the equilibrium relationship. The material balance is:

\[
q_0 S + c_0 L = q_1 S + c_1 L
\]  

(4-8)

where \( S \) is the mass of undissolvable bark \([g]\), \( L \) is the solvent volume \([mL]\), \( q \) is the loading of soluble material onto the unextractable bark \([g/g]\), \( c \) is the solvent concentration \([g/mL]\) and the subscripts 0 and 1 represent the initial and final streams of the process, respectively.

The mass balance can be rearranged to form an operating line, which defines the solid and liquid phase compositions as the system moves towards equilibrium:
The operating line may also be drawn with the feed point \( F = (c_0, q_0) \) and the slope \( = \frac{L}{S} \). Combining the material balance with the equilibrium relationship yields their intercept, \( E \), which gives the final equilibrium loading and concentration values of the system[80]. In this case, \( \frac{L}{S} \) is the ratio of solvent volume to dry unextractable mass, as defined by the axes of the equilibrium relationship. This value can be converted to the liquid-to-solid ratio referred to throughout this thesis, which is the ratio of solvent mass to initial air dry bark mass.

The equilibrium curves show that batch extraction yield increases with increasing the liquid-to-solid ratio. However, the yield increase begins to diminish as the equilibrium curve flattens out and approaches the y-axis. The optimal first extraction in a multi-batch extraction would therefore reduce the bark loading to the point where the equilibrium curve begins to flatten out. Subsequent extractions would then be able to reduce the bark loading beyond that flattened section.

Using a higher liquid-to-solid ratio to increase the extraction yield also has a negative effect: the extract concentration in the solvent decreases, which increases the cost of separation. To study this effect, and the need to balance the yield increase with the concentration decrease, the equilibrium isotherms were used to plot the predicted percent increase in yield and decrease in concentration as the liquid-to-solid ratio increases from 5:1. Figure 4.7 shows that an optimal liquid-to-solid ratio would be in the range of 10 to 15:1 at 60° C, but 15 to 20:1 at 80° and 100° C. True optimization would also consider the costs of the solvent, of separating the solvent from the extract, and of purchasing and operating the extraction equipment. In a multi-batch operation, optimization would also require process knowledge of solvent retention in the underflow residue because that solvent would move on with the underflow.
This type of process design offers several advantages. First, one does not have to assume process ideality, which is the case where all of the solute is dissolved by the solvent[80]. Combining the kinetic model selected in Chapter 3 and the equilibrium model selected in this chapter would allow the designer to consider the time required for the process. The extraction units could then be halted before equilibrium is reached if that was found to improve the economics of the process.

Analysis of the extraction equilibrium behaviour is also an important step towards designing for continuous operation. Some continuous extraction equipment could even be designed with a multibatch simulation that incorporates the kinetic and equilibrium models and process knowledge regarding solvent retention in the underflow. For example, the Rotocell or Carousel extractor loads the biomass onto fixed trays in a rotating wheel. Each tray is mixed with solvent before the solvent of each tray is pumped to the next tray while the wheel rotates the trays with the solid material in the opposite direction, thus achieving counter-current continuous operation[114]. Other types of continuous extraction equipment, including the Hildebrandt, De Danske Sufferfabriker (DDS), and Bonotto Extractors[114], keep the countercurrent biomass and solvent streams in continuous contact. In that case, the operating line would run parallel to the equilibrium curve.
4-5.0 Conclusions

This chapter aimed to use isotherms to model equilibrium in the batch solid-liquid extraction of phenolic compounds from mountain pine beetle infested lodgepole pine bark. Its goals were first, to find suitable isotherm models, second, to provide insight into the extraction mechanism, and third, use the models to predict the effect of an increasing liquid-to-solid ratio on the process yield and solvent concentration.

As extraction temperature increased from 60° to 100° C, the amount of extractable material in the bark increased from 43% to 65% on a dry basis. Increasing the temperature therefore allows more bark components to be solubilised by the solvent, and causes the initial loading of extractable material to increase. It was confirmed that higher temperatures cause more lignin to be extracted, which is a polymeric phenol compound.

The extraction resulted in BET equilibrium behaviour for a liquid/solid system. At 60° C, a modified isotherm model with a fourth parameter was proposed and selected as most appropriate. At 80° and 100° C, the original BET isotherm is most appropriate. This behaviour suggests that the process mechanism consists of a multilayer extraction phenomenon. Therefore, it has been found that isotherms
are appropriate for modeling the equilibrium between the loading of soluble material on a solid and the solute concentration in the solvent in a solid-liquid extraction.

Finally, increasing the liquid-to-solid ratio causes the final extraction yield to increase significantly at lower ratios before the yield return begins to diminish. The isotherm shape allows for the design of batch or multibatch processes that balance the addition of solvent with the returns of extract yield and decreased solvent concentration. Furthermore, the equilibrium model and kinetic model from Chapter 3 can potentially be combined with data concerning solvent retention in the solid residue to simulate multi-batch and even continuous counter-current operation with certain extraction units.
5 Conclusions and Future Work

5.1 Conclusions and Contributions

This thesis demonstrates a comprehensive study in which mathematical models are applied to the solid-liquid extraction of phenolic compounds from mountain pine beetle infested lodgepole pine bark for the substitution of petroleum-derived phenol in bio-based PF resin formulations. The experiments and modeling work were completed to advance the Bark Biorefinery group’s ability to scale up and optimize the extraction process. The major conclusions and contributions of this thesis study are summarized as follows:

1. Kinetic Modeling

To analyse the kinetic behaviour of the extraction, five types of models were tested and evaluated based on their fit, parsimony, and robustness. Those models were the shrinking core and rate law models, and the Fick’s law analytical, extended, and solvent balance solutions. Additionally, the extended Fick’s law and rate law models were modified to create new versions of the models that reduce the number of required parameters and increase the fit to experimental results, respectively. To the best of the author’s knowledge, this is the first time that the extraction of phenolic compounds from bark by a caustic solvent has been analysed with fundamentally-derived models.

At 60° and 80° C, the extraction is most accurately described by the extended Fick’s law analytical solution. At 100° C, the more parsimonious Fick’s law analytical solution is most appropriate. The model forms are shown in Table 5-1, below. The model parameters change with temperature and liquid-to-solid ratio.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Model Form</th>
</tr>
</thead>
</table>
| 60° and 80° C   | \[
\frac{c_{\infty} - c}{c_{\infty}} = \frac{6}{\pi^2} \left[ f_1 \exp \left( -\frac{\pi^2 D_{eff,1} t}{R^2} \right) + f_2 \exp \left( -\frac{\pi^2 D_{eff,2} t}{R^2} \right) \right] \]
| 100° C          | \[
\ln \left( \frac{c_{\infty} - c}{c_{\infty}} \right) = -0.498 - \frac{9.87 D_{eff} t}{R^2} \]

The modified extended Fick’s law analytical solution model successfully increased the model parsimony, but reduced its fit to experimental data. It was therefore not selected as most appropriate.
The rate law model also accurately described the extraction. Its modification where the equilibrium concentration was found experimentally and the other parameters were found by nonlinear regression improved the fit of the model. However, these models differed from the other models tested in this thesis in that they are adapted from rate law theory rather than derived fundamentally. They were not selected as most appropriate because they are not appropriate for scaling-up studies.

2. Equilibrium Modeling

Isotherms were proposed to model the equilibrium between the loading of soluble material on the insoluble bark mass and the solute concentration in the solvent. The Brunauer-Emmett-Teller (BET) isotherm for liquid/solid systems fits the experimental data excellently, and was selected as most appropriate for the extraction. At 60° C, the yield increase with increasing liquid-to-solid ratio was relatively slow, so the BET isotherm was modified by adding a fourth parameter to improve its fit to the experimental data. The model forms are shown in Table 5-2, below. The isotherms are a major improvement over past attempts to model equilibrium in batch solid-liquid extractions in the extended field, which were limited to qualitative or empirical descriptions.

Table 5-2: Final equilibrium model forms

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Model Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>60° C</td>
<td>[ q_{eq} = \frac{q_L K_L c_{eq}}{1 + K_L c_{eq}} + \frac{q_AL K_AL c_{eq}}{1 - K_AL c_{eq}} ]</td>
</tr>
<tr>
<td>80° and 100° C</td>
<td>[ q_{eq} = \frac{q_s K_L^a c_{eq}}{(1 - K_L^b c_{eq})(1 - K_L^b c_{eq} + K_L^a c_{eq})} ]</td>
</tr>
</tbody>
</table>

3. Process Mechanism

The modeling work resulted in several new findings regarding the mechanism of the extraction. Shrinking core models were used to differentiate the extraction’s phase transfer, diffusion, and reaction steps, and the diffusion step was determined to be rate limiting. However, these models were outperformed by homogeneous diffusion-based models derived from Fick’s law, which therefore identify the dominant mechanism of the extraction. The diffusion consists of two stages before equilibrium is reached: a fast washing stage, and a slower diffusion stage. At 100° C, the higher
temperature accelerates the slower diffusion stage so that the full extraction can be described by one stage. This can be attributed to the thermal energy that encourages the extractive diffusion and the lowered solvent viscosity that improves its ability to wet the plant matrix and solubilise the target extractives. The equilibrium modeling work found that the process is analogous to multi-layer solubilisation of material from unextractable bark material.

4. Process Design and Optimization

For this extraction, an optimal process will operate at a temperature as close as possible to the solvent’s boiling point because of two primary benefits. First, extraction kinetics increase with increasing temperature, as described above. Second, the amount of extractable material, and therefore, the possible yield, increases with increasing temperature as the solvent solubility increases and more activation energy barriers for solubilisation reactions are surpassed. Increasing the extraction temperature was confirmed to increase the amount of lignin being extracted, which is a polymeric phenolic bark component.

The equilibrium isotherm models were used to predict the returns of increasing yield and decreasing concentration as the liquid-to-solid ratio is increased. True process optimization would require economic data related to the costs of the solvent and of extract and solvent separation, but the analysis showed that optimal liquid-to-solid ratio would be in the range of 10 to 15:1 at 60° C, but 15 to 20:1 at 80° and 100°C.

Finally, since the models selected above are derived fundamentally and include parameters with real physical meaning, they are suitable for scaling-up studies, for supporting the design of equipment, and even for converting a batch into a continuous process.
5-2.0 Future Work

The completion of this thesis work resulted in several recommendations for future work on the project. They are described below.

1. Conduct future process development work at 100° C
   
   Future studies should be conducted at a single temperature so that the research can focus on process modeling. A temperature close to the boiling point of the solvent should be chosen because it increases both the extraction kinetics and the available extractable material. Since the extract and solvent are separated by evaporation, the solvent will have to be brought to this temperature after the extraction regardless of the extraction temperature. Therefore, operating the extraction at a high temperature should not significantly increase the energy requirements of the overall process.

2. Conduct scale-up studies
   
   The extraction must be tested with full-scale bark, and eventually, pilot-scale equipment. Bark milling is time-consuming and expensive, so the process should be designed with bark sourced directly from an industrial debarker. This will change several aspects of the model, especially the geometry of the extracted material and the rate of diffusion. Also, the solvent can already be at the target temperature when it is charged into the extraction unit. Several studies can be referred to for direction[49], [115]–[117].

3. Measure solvent concentration directly
   
   Solvent concentration determination for this thesis was time consuming and labour intensive. When the process scale is increased, small samples of the bulk solvent can be taken at different times during the extraction without significantly affecting the process. A method for determining the solvent concentration directly from the solvent should be used, such as HPLC or spectrophotometry. Extraction curves could then be generated from a single extraction experiment as opposed to than having to conduct a new experiment for each measurement of solvent concentration.

4. Determine solvent retention in the solid underflow
   
   The question of liquid retention in the underflow for this extraction, i.e., after filtration, is yet to be studied. The mass ratio of liquid to solid in the underflow, referred to as the retention ratio, depends
on the properties of the phases and the equipment used, and, according to Seader et al.[80], is best
determined from experience or tests with prototype equipment. Generally, if the viscosity of the liquid
phase increases with increasing solute concentration, the mass ratio of the liquid-to-solid in the
underflow increases because the solid retains more liquid[80].

\[
Retention\ Ratio = \frac{Mass\ of\ Solvent\ and\ Extract\ in\ Raffinate}{Mass\ of\ Dry\ Solid\ Residue\ in\ Underflow}
\]

The distribution of solute between the raffinate and extract streams is commonly expressed by the partition coefficient:

\[
K = \frac{c_B}{c_R}
\]

where \( K \) is the partition coefficient, \( c_B \) is the solute concentration in the extract solvent, and \( c_R \) is the
solute concentration in the raffinate, which is retained in the underflow liquid residue. These values are
depicted in Figure 5.1, below.

![Solid Feed, F
Insoluble A
Solute B

Liquid Solvent, S
Extract Liquid C

Overflow, V
Extract Liquid

Underflow, U
Retained Liquid (Raffinate)

Retention Ratio

Figure 5.1: Retention ratio and partition coefficient in solid-liquid extraction

The partition coefficient is often independent of the solute concentration, but deviation from
that guideline has been observed in some systems. It is also normally determined experimentally[21].

The relationship between the extract-rich solvent condition and underflow retention should be
determined to advance the group’s modeling capabilities. Experiments should be performed with full-
scale bark. The effects of solvent concentration (\( c \)) and bark loading (\( q \)) should be found on the
retention ratio and partition coefficient.
5. Develop a model that incorporates both extraction kinetics and equilibrium behaviour

A model should be developed that simultaneously incorporates the kinetic and equilibrium behaviour discovered in this thesis. This model will provide a more accurate and unified representation of the extraction.

6. Convert to a continuous process

Compared to batch extractors, continuous units produce a higher yield in a shorter time and require less solvent[21], [106]. It will therefore be vital to design a continuous extractor and use the modeling techniques developed with the batch extraction experiments to model and optimize the continuous process[115], [118].

7. Develop a multi-component model

A multi-component model simulates the extraction of different components from a solid compound[119]. This could be developed for the bark extraction process because of the diverse range of compounds that are being extracted, for example, compounds that are soluble in water, and compounds that require sodium hydroxide to be solubilised. This increased level of detail would be valuable if one type of extractable component was found to be particularly productive or counter-productive in the resin synthesis process.

8. Study chemical recovery for the extraction

Chemical recovery is vital for most industrial chemical processes. After separating the solvent and extract, the solvent should be condensed and its composition determined to study its suitability for recycling.

9. Study residue use for the extraction

Determining the best possible use for the solid bark residue will also be important for evaluating process economics. The residue might be sold as hog fuel for industrial boilers, or it might be suitable as a feed for other processes in the forestry industry. These options should be researched and evaluated.
10. Model the washing process

After the leaching stage, some extract-rich solvent is retained in the wet bark. Washing is the process where water is used to separate that remaining solvent from the bark. In this thesis, washing was simply conducted until the water ran clear. However, it should be studied more thoroughly and modeled so that an optimal washing process can be designed that minimizes the required amount of water.
References Cited


Appendix A: Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{(i)}$</td>
<td>Solvent constituent in the extraction</td>
</tr>
<tr>
<td>AARD</td>
<td>Average absolute relative deviation</td>
</tr>
<tr>
<td>$B_{(s)}$</td>
<td>Solid reactant in the extraction</td>
</tr>
<tr>
<td>$b$</td>
<td>Stoichiometric coefficient in the reactive extraction</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration of solute in the solvent</td>
</tr>
<tr>
<td>$c_{0}$</td>
<td>Initial concentration of solute in the solvent</td>
</tr>
<tr>
<td>$c_{1}$</td>
<td>Final concentration of solute in the solvent</td>
</tr>
<tr>
<td>$c_{\infty}$ or $c_{eq}$</td>
<td>Concentration of solute in the solvent after infinite time AKA equilibrium concentration</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration of solute in the solid</td>
</tr>
<tr>
<td>$\bar{C}$</td>
<td>Average concentration of the solid phase</td>
</tr>
<tr>
<td>$C_{Ag}$</td>
<td>Concentration of A in the bulk solution</td>
</tr>
<tr>
<td>$C_{calc}$</td>
<td>Concentration predicted by the model</td>
</tr>
<tr>
<td>$C_{exp}$</td>
<td>Experimental concentration value</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Solute concentration at the interface of the particle</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Initial extractable solute concentration of the solid</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Plate thickness</td>
</tr>
<tr>
<td>$D_{eff}$</td>
<td>Effective diffusivity coefficient</td>
</tr>
<tr>
<td>$D_{eff,1}$</td>
<td>Effective diffusivity during the fast (washing) extraction stage</td>
</tr>
<tr>
<td>$D_{eff,2}$</td>
<td>Effective diffusivity during the slow (diffusion) extraction stage</td>
</tr>
<tr>
<td>$\bar{D}$</td>
<td>Dimensionless effective diffusivity</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Porosity</td>
</tr>
<tr>
<td>$E$</td>
<td>Equilibrium point at the intersection of the equilibrium bark loading and solvent concentration</td>
</tr>
<tr>
<td>$\bar{E}_{ABS}$</td>
<td>Average sum of absolute error</td>
</tr>
<tr>
<td>$f_1$</td>
<td>Fraction of solute extracted during the fast (washing) extraction stage</td>
</tr>
<tr>
<td>$f_2$</td>
<td>Fraction of solute extracted during the slow (diffusion) extraction stage</td>
</tr>
<tr>
<td>$f$</td>
<td>Parameter to differentiate the washing and diffusion steps of the extraction</td>
</tr>
<tr>
<td>$F$</td>
<td>Feed point at the intersection of the initial bark loading and solvent concentration</td>
</tr>
<tr>
<td>$\eta_{tot}$</td>
<td>Extraction yield in kg per 100 kg of bark</td>
</tr>
<tr>
<td>$H$</td>
<td>Horizontal shift equilibrium model parameter</td>
</tr>
<tr>
<td>$k$</td>
<td>Extraction rate constant</td>
</tr>
<tr>
<td>$k_d$</td>
<td>Desorption constant for a supercritical extractor</td>
</tr>
<tr>
<td>$k_f$</td>
<td>Mass transfer coefficient</td>
</tr>
<tr>
<td>$k_a$</td>
<td>Mass transfer coefficient</td>
</tr>
<tr>
<td>$k_s$</td>
<td>Surface reaction rate constant</td>
</tr>
<tr>
<td>$K_{AL}$</td>
<td>Adsorption equilibrium constant</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$K_L$</td>
<td>Adsorption equilibrium constant</td>
</tr>
<tr>
<td>$K_L^a$</td>
<td>Equilibrium constant for adsorption on the solid phase surface</td>
</tr>
<tr>
<td>$K_L^b$</td>
<td>Equilibrium constant for adsorption for subsequent layers</td>
</tr>
<tr>
<td>$L$</td>
<td>Solvent volume</td>
</tr>
<tr>
<td>$n$</td>
<td>Extraction rate order</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of experimental values</td>
</tr>
<tr>
<td>$m_{extractables}$</td>
<td>Dry mass of extractable bark material</td>
</tr>
<tr>
<td>$m_{unextractables}$</td>
<td>Dry mass of unextractable bark material</td>
</tr>
<tr>
<td>$M$</td>
<td>Mass of solute transferred from the particle</td>
</tr>
<tr>
<td>$M_\infty$</td>
<td>Total mass of solute transferred after infinite time</td>
</tr>
<tr>
<td>$p_1$, $p_2$, and $p_3$</td>
<td>Internal porosity model parameters</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$q_0$</td>
<td>Initial loading of soluble material on the bark</td>
</tr>
<tr>
<td>$q_1$</td>
<td>Final loading of soluble material on the bark</td>
</tr>
<tr>
<td>$q_{AL}$</td>
<td>Equilibrium constant related to the anti-Langmuir section of a BET curve</td>
</tr>
<tr>
<td>$q_{calc}$</td>
<td>Equilibrium loading value predicted by a model</td>
</tr>
<tr>
<td>$q_{eq}$</td>
<td>Solid phase loading at equilibrium</td>
</tr>
<tr>
<td>$q_L$</td>
<td>Equilibrium constant related to the Langmuir section of a BET curve</td>
</tr>
<tr>
<td>$q_{meas}$</td>
<td>Experimental equilibrium loading value</td>
</tr>
<tr>
<td>$q_s$</td>
<td>Solid phase loading at saturation</td>
</tr>
<tr>
<td>$Q_{CO_2}$</td>
<td>Solvent mass flow rate for a supercritical extractor</td>
</tr>
<tr>
<td>$r$</td>
<td>Radial position in a spherical particle</td>
</tr>
<tr>
<td>$R$</td>
<td>Radius of the solid particle</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Coefficient of determination</td>
</tr>
<tr>
<td>$\rho_B$</td>
<td>Molar density of the solid reactant</td>
</tr>
<tr>
<td>$\rho_S$</td>
<td>Solid density</td>
</tr>
<tr>
<td>$\rho_{solv}$</td>
<td>Solvent density</td>
</tr>
<tr>
<td>$S$</td>
<td>Mass of unextractable bark</td>
</tr>
<tr>
<td>$S_X$</td>
<td>Cross-sectional area of a supercritical extractor</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$t^*$</td>
<td>Time to complete dissolution</td>
</tr>
<tr>
<td>$V_l$</td>
<td>Volume of the liquid phase</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Volume of the solid phase</td>
</tr>
<tr>
<td>$\phi_i^{SCF}$</td>
<td>Fugacity coefficient</td>
</tr>
<tr>
<td>$x_0$</td>
<td>Initial concentration of extractable material in the solid in a supercritical extractor</td>
</tr>
<tr>
<td>$X$</td>
<td>Conversion of extractable material</td>
</tr>
<tr>
<td>$Y$</td>
<td>Total extraction yield for a supercritical extractor</td>
</tr>
<tr>
<td>$z$</td>
<td>Supercritical extractor horizontal position</td>
</tr>
</tbody>
</table>
### Appendix B: Tables from the Literature Review

#### Table B-1: Summary of the application, bark, and extract choices in the extraction modeling papers

<table>
<thead>
<tr>
<th>Paper</th>
<th>Application</th>
<th>Bark or Biomass</th>
<th>Extract Choice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspe et al., 2011</td>
<td>Pharmacy</td>
<td><em>Pinus radiata</em> (Monterey Pine) bark</td>
<td>Acetone</td>
</tr>
<tr>
<td>Bocalandro et al., 2012</td>
<td>Pharmacy</td>
<td><em>Pinus radiata</em> (Monterey Pine) bark</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Brusotti et al., 2010</td>
<td>Pharmacy</td>
<td><em>Bridelia grandis</em> (Doando) bark</td>
<td>Acetone and Methanol</td>
</tr>
<tr>
<td>Cheah et al., 2010</td>
<td>Pharmacy</td>
<td><em>Magnolia officinalis</em> (Magnolia) bark</td>
<td>Hexane and Supercritical Carbon Dioxide</td>
</tr>
<tr>
<td>Chen et al., 2009</td>
<td>Pharmacy</td>
<td><em>Betula platyphylla</em> (Japanese White Birch) bark</td>
<td>Ethanol</td>
</tr>
<tr>
<td>de Melo et al., 2012</td>
<td>Pharmacy</td>
<td><em>Eucalyptus globulus</em> (Tasmanian Blue Gum) bark</td>
<td>Supercritical Carbon Dioxide</td>
</tr>
<tr>
<td>de Melo et al., 2014</td>
<td>Pharmacy</td>
<td><em>Eucalyptus globulus</em> (Tasmanian Blue Gum) bark</td>
<td>Supercritical Carbon Dioxide</td>
</tr>
<tr>
<td>Derkyi et al., 2011</td>
<td>Resin</td>
<td><em>Pinus caribaea</em> (Caribbean pine) bark</td>
<td>Acetone and Ethanol</td>
</tr>
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<td>Supercritical Carbon Dioxide modified with Ethanol</td>
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<td>Pharmacy</td>
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Table B-3: Summary of measured results in the extraction empirical modeling papers

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<th>Molecular Weight</th>
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Appendix C: Full Model Derivation, Equations, and MATLAB Scripts for Parameter Estimation

In Chapter 3, mathematical models that have been applied successfully in the literature to other solid-liquid extraction processes were selected for analysis. As such, the models were not fully derived. This appendix therefore presents the full model derivations and includes MATLAB scripts used for parameter estimation so that readers can better follow, validate, or extend the work in this thesis. Unlike the derivations, the methods for parameter estimation are included in full detail in the main chapters of the thesis. This appendix is organized by model type.

Fick’s Law Analytical Solution

Assuming negligible external mass transfer resistance and no change in effective diffusivity with solute concentration, the extraction process model can be simplified to the mass balance in a spherical solid particle, as in Fick’s second law[76]:

\[
\frac{\partial C}{\partial t} = \nabla (D_{eff} \nabla C)
\]

where \( C \) is the solution concentration at time \( t \), and \( D_{eff} \) is the effective diffusivity or diffusion coefficient of the solute.

By further assuming that the spherical particle’s initial concentration is uniform, that extraction causes the concentration to vary only with respect to the particle’s radius, \( r \), and that the particle is uniform in shape with a maximum radius of \( R \), the initial and boundary conditions can be written as follows:

\[
\begin{align*}
    t &= 0, & C &= C_0 \quad \forall r \\
    t &> 0, & C &= C_i = 0 \quad r = R \\
    t &> 0, & \frac{\partial C}{\partial r} &= 0 \quad r = 0
\end{align*}
\]

where \( C_0 \) is the initial solute concentration of the particle and \( C_i \) is the solute concentration at the interface of the particle. The ordinary differential equation for spherical particles is then expressed as:[93]
\[ \frac{C - C_0}{C_i - C_0} = 1 + \left[ \frac{2R}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{\pi nr}{R} \exp \left\{ -\frac{D_{eff} n^2 \pi^2 t}{R^2} \right\} \right] \]

Then, the total amount of diffusing substance leaving the sphere is:

\[ \frac{M}{M_\infty} = 1 - 6 \frac{1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left\{ -\frac{D_{eff} n^2 \pi^2 t}{R^2} \right\} \]

The above equation is simplified by assuming that only the first term of the series is significant. It is further altered to express the concentration of the solute in the extraction solvent at any time, \( c \), to yield the following: [94]

\[ \ln \left( \frac{c_\infty - c}{c_\infty} \right) = \ln (E) = -0.498 - \frac{9.87 D_{eff} t}{R^2} \]

where \( c \) is the solvent concentration at time \( t \), \( c_\infty \) is the solvent concentration after infinite time, and \( E \) is the inverse of the non-extracted fraction of the solute in the sample particle.

**Fick’s Law with Solvent Balance Model**

This model balances the release of extractable material from the solids with the solvent concentration. This model shares many assumptions with the models introduced in the earlier sections. The transport of particles from the solid to the liquid is driven by a diffusion mechanism. The solid particles are spherical in shape and have a uniform and constant radius \( R \) that is independent of moisture content, i.e., wetness of the bark. The diffusion coefficient is constant throughout the extraction. Extraction causes the concentration to vary only with respect to the particle’s radius over time. The solvent in the batch reactor is perfectly mixed and the transfer resistance in the liquid phase is negligible. The initial concentration in each experiment is first calculated using the final concentration in the solvent at the end of the experiment[96]. The balance equation for the solid phase is[93]:

\[ \frac{\partial C}{\partial t} = D_{eff} \left( \frac{\partial^2 C}{\partial r^2} + \frac{2 \partial C}{r \partial r} \right) \]

The mass balance in the solvent can be expressed by the next equation[97], where the solvent concentration is uniform at any given time[97].
\[ \frac{\partial C}{\partial t} = -\frac{V_s}{V_l} \frac{d\bar{C}}{dt} \]

where \( V_s \) and \( V_l \) are the volumes of the solid and liquid phases, respectively, and \( \bar{C} \) is the average concentration of the solid phase at time \( t \), which is calculated by the following:

\[ \bar{C} = \frac{3}{R^3} \int_0^R C(r) \cdot r^2 \cdot dr \]

The initial and boundary conditions for these equations are as follows:

\[ t = 0, \quad C = C_0 \quad \forall r \]
\[ t = 0, \quad c = 0 \]
\[ t > 0, \quad C(r = R) = c \]
\[ t > 0, \quad \frac{dC}{dr_{r=R}} = 0 \]

The particle radius was discretized in space with second-order finite differences. For the boundary equations, finite difference equations of the same order were used. The equations were solved with the Crank-Nicolson method. In this method, a second-order approximation is achieved by approximating the derivatives at \( t = 0 + \frac{1}{2} \). These approximations are shown below. The solid balance is approximated with the following:

\[ \frac{\partial C}{\partial t} = \frac{C_i^{0+1} - C_i^0}{\Delta t} = \frac{C_i^0 - C_i^0}{\Delta t} \quad \text{O}(h^2) \]

\[ \frac{\partial^2 C}{\partial r^2} = \frac{1}{2} \left( \frac{C_{i-1}^0 - 2C_i^0 + C_{i+1}^0}{(\Delta r)^2} + \frac{C_{i-1}^{0+1} - 2C_i^{0+1} + C_{i+1}^{0+1}}{(\Delta r)^2} \right) \quad \text{O}(h^2) \]

\[ \frac{\partial C}{\partial r} = \frac{1}{2} \left( \frac{C_{i+1}^0 - C_{i-1}^0 + C_{i+1}^{0+1} - C_{i-1}^{0+1}}{2\Delta r} \right) \quad \text{O}(h^2) \]

Similarly, the liquid balance is approximated with the following:

\[ \frac{\partial c}{\partial t} = \frac{c^{0+1} - c^0}{2 \left( \Delta t \right)} = \frac{c^{0+1} - c^0}{\Delta t} \quad \text{O}(h^2) \]
The differential boundary condition is approximated with a forward-derivative approximation:

\[
\frac{d\bar{C}}{dt} = \frac{\bar{C}^{0+1} - \bar{C}^0}{\Delta t} \quad 0(h^2)
\]

The average concentration in the solid is approximated with trapezoidal integration:

\[
I = h \left( \frac{1}{2} f(x_1) + \sum_{i=2}^{n-1} f(x_i) + \frac{1}{2} f(x_n) \right)
\]

where \( I \) is the integral of the function \( f(x) \), which has been discretized into \( n \) nodes separated by a distance of \( h \).

The MATLAB script for parameter estimation for this model is included below. This script is for the extraction curve at 60° C and a liquid-to-solid ratio of 8:1. A different script was used for each extraction curve.

```matlab
% DIFFUSION FROM A SPHERE
% Crank-Nicholson method
% Attempt 3 - Wongkittipong & Prat Equations

% define parameters
format long

R = 0.000355; % total radius of a particle [meters]
tf = 380; % time length of simulation [minutes]
V_s = 6.431847; % volume of solid [mL]
V_l = 15.94; % volume of liquid [mL]
Deff = 2.13E-9; % effective diffusivity [m^2/min]
C_initial = 107.24; % initial concentration throughout the particle [kg/m^3]

% select a grid size
delr = 0.00001; % splitting up nodes along sphere radius
delt = 0.01; % splitting up time nodes

m = round(R/delr-1); % number of internal nodes
r = [0:delr:R]'; % this is our grid along sphere
rint = [delr:delr:R-delr]'; % internal node grid along sphere
C = C_initial*ones(size(r)); % initial concentrations
C_int = C(2:end-1);
```
A=zeros(m);
%set up first row in A
A(1,1)= (1/delt) + Deff/(delr^2) ; %Ci
A(1,2)= -Deff/(2*(delr^2)) - Deff/(2*delr*rint(1)); %Ci+1
%set up last row in A
A(m,m-1)= -Deff/(2*(delr^2)) + Deff/(2*delr*rint(end)); %Ci-1 %at the last point, ri = R, the last point of r
A(m,m) = (1/delt) + Deff/(delr^2); %Ci
for i = 2:m-1 %iterates
    p1= Deff/(2*(delr^2));
    p2= Deff/(rint(i)*2*delr);
    p3= 1/delt;
    A(i,i-1)= -p1+p2 ; %Ci-1
    A(i,i)=p3+2*p1 ; %Ci
    A(i,i+1)= -p1-p2 ; %Ci+1
end

[L,U] = lu(A); % luse LU decompose, since we need to solve this repeatedly

%Begin making table with row1 = time, row 2 = Cliquid
TABLE=[0:delt:tf];;
[rT cT]=size(TABLE);
TABLE = [TABLE;zeros(rT,cT)];

for j = 2:(tf/delt+1)
    %Make b of knowns:
b=zeros(size(rint));
    %at this point, C goes all the way from r = 0 to r = R
    for i = 1:m %countint internal nodes
        p1= Deff/(2*(delr^2));
        p2= Deff/(rint(i)*2*delr);
        p3= 1/delt;
        b(i)=(p1-p2)*C(i)+(p3-2*p1)*C(i+1)+(p1+p2)*C(i+2);
    end
% find new Cinternal
y=L\b;
Cintnew=U\y;

% Find average value of current C
Ctimesr2=C.*(r.^2);
n=length(Ctimesr2);
Int=dellr*(0.5*Ctimesr2(1)+sum(Ctimesr2(2:n-1))+0.5*Ctimesr2(n));
CAvg=(3/(R^3))*Int;

% start building solvent balance equation
Cintnewtimesr2=Cintnew.*(rint.^2);
Clq=(1/(1+(Vs/Vl)*(1.5/(R))*dellr))*(TABLE(2,(j-1))+(Vs/Vl)*CAvg-
(Vs/Vl)*(3/(R^3))*dellr*sum(Cintnewtimesr2)); % in the first iteration, Clq=0, but then it is the current's C(end)

% find new C(r=0) value with the B.C.
Czeronew=(1/3)*(4*Cintnew(1)-Cintnew(2));

% Construct Cnew of Cinternal and boundary C's
Cnew = [Czeronew; Cintnew; Clq];
TABLE(2,j)=Cnew(end);
C=Cnew;
end

plot(TABLE(1,:),TABLE(2,:))
hold on

% Compare to results
% time=[2 5 10 15 30 60 120 240 360]; % time in min
% exresultsConc=[24.1789658 28.03274373 29.2661597 31.50215054 31.89687798 33.07905895 35.50280131 35.98308765 35.96917856]; % conc in kg/m^3
% format short e
% Compare = [time; exresultsConc ; TABLE(2,201) , TABLE(2,501) , TABLE(2,1001), TABLE(2,1501), TABLE(2,3001), TABLE(2,6001), TABLE(2,12001), TABLE(2,24001),TABLE(2,36001)];
Compare = [Compare; abs(Compare(3,:)-Compare(2,:))./Compare(2,:)]
To plot the results for this model, the following script was used:

```matlab
AARD = mean(Compare(4,:))
plot(time,exresultsConc,'rx')
```

```matlab
t_exp = [2 5 10 15 30 60 120 240 360];
C_exp_8_6 = [24.179 28.0327 29.2662 31.5022 31.8969 33.0791 35.5028 35.9831 35.9692];
C_exp_8_8 = [24.3674 28.9097 32.4639 32.9587 36.6206 36.621 38.8546 41.5406 41.5276];
C_exp_8_0 = [24.4373 30.709 36.6562 41.6091 45.2057 48.3931 48.3261 48.4588 48.6304];
C_exp_10_8 = [21.5954 23.6645 25.8806 26.243 29.3689 34.3829 36.9307 37.6838 38.1607];
C_exp_10_0 = [22.0949 26.5858 30.7584 37.8029 40.1662 43.5126 43.7355 43.2321 43.5906];

figure(1)
plot(t_exp,C_exp_8_6,'bd',t_exp,C_exp_8_8,'rs',t_exp,C_exp_8_0,'g^',T8_60(1,:),T8_60(2,:),'b-','T8_80(1,:),T8_80(2,:),'r-','T8_100(1,:),T8_100(2,:),'g-')
title('Fick''s Law with Solvent Balance Model, 8 to 1 Liquid-to-Solid Ratio')
legend('60{\circ} C, Experimental','80{\circ} C, Experimental','100{\circ} C, Experimental','60{\circ} C, Model','80{\circ} C, Model','100{\circ} C, Model')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(2)
plot(t_exp,C_exp_10_6,'bd',t_exp,C_exp_10_8,'rs',t_exp,C_exp_10_0,'g^',T10_60(1,:),T10_60(2,:),'b-','T10_80(1,:),T10_80(2,:),'r-','T10_100(1,:),T10_100(2,:),'g-')
```
Fick's Law Extended Analytical Solution

This model is derived identically to the Fick's Law Analytical Solution model, except it is extended to yield its final equation:

\[
\frac{c_\infty - c}{c_\infty} = \frac{6}{\pi^2} \left[ f_1 \exp \left( \frac{-\pi^2 D_{eff,1} t}{R^2} \right) + f_2 \exp \left( \frac{-\pi^2 D_{eff,2} t}{R^2} \right) \right]
\]

Rate Law Model

The extraction of active compounds from plants has also been successfully modelled by applying a second order rate law to the solvent concentration[100]:

\[
\frac{dc}{dt} = k(c - c_\infty)^2
\]

where \( k \) is the second order extraction rate constant. This model also assumes that extraction proceeds from the diffusion of extracts through the material and into the solution, and that the solvent concentration tends to a constant, saturated value under the same conditions. Furthermore, the solvent
is well mixed and has a uniform concentration at any given time. Integrating the above equation from \( t = 0 \) to \( t \) and \( c = 0 \) to \( c \) yields the following:

\[
c = \frac{c_\infty^2 kt}{1 + c_\infty kt}
\]

Then, that can be linearized to obtain the equation below, which is fit to experimental data by plotting \( \frac{t}{c} \) versus \( t \). The slope and \( y \)-intercept of the resulting linear regression are used to determine the parameters \( k \) and \( c_\infty \).

\[
\frac{t}{c} = \frac{1}{kc_\infty^2} + \frac{t}{c_\infty}
\]

The MATLAB script to find the parameters for the rate law model modifications is included below. This script is for the extraction curve at 60° C and a liquid-to-solid ratio of 8:1. A different script was used for each extraction curve.

%8 to 1
%60 C
%A = n = 2
%B = n,k solved, Cinf is known from experiments
%C = n,k,Cinf solved
t=[2 5 10 15 30 60 120 240 360]; %time experimental
c=[24.1789658 28.03274373 29.26615973 31.50215054 31.89687798 33.07905895 35.50280131 35.98308765 35.96917856];
format shorte
%var = [k n]
cinf = 35.99; %start with this one known, from earlier models (not as found with model 4a though)
var01=[0.010392, 2]; %initial guess for k and n, from model 4
func1 = @(var1,t) cinf - (((var1(2)-1).*var1(1).*t)+((cinf).^(1-var1(2)))).^(1./(1-var1(2))));
fits1 = nlinfit(t,c,func1,var01)
%var = [k n cinf]
var02=[0.010392, 2,35.99]; %initial guess for k, n, and cinf from model 4
func2 = @(var2,t) var2(3) - (((var2(2)-1).*var2(1).*t)+((var2(3))).^(1-
var2(2))) .^(1./(1-var2(2)));
fits2 = nlinfit(t,c,func2,var02)

format short
cm1 = func1(fits1,t);
cm2 = func2(fits2,t);
TABLE = [t;c;cm1;cm2];
TABLE = [TABLE; abs(TABLE(3,:)-TABLE(2,:))./TABLE(2,:); abs(TABLE(4,:)-TABLE(2,:))./TABLE(2,:)]
AARD1 = mean(TABLE(5,:))
AARD2 = mean(TABLE(6,:))

To plot the results for this model, the following script was used:

```matlab
%Storing k,n,Cinf for the rate law model

t_exp = [2 5 10 15 30 60 120 240 360];
C_exp_8_6 = [24.179 28.0327 29.2662 31.5022 31.8969 33.0791 35.5028 35.9831 35.9692];
C_exp_8_8 = [24.3674 28.9097 32.4639 32.9587 36.6206 36.621 38.8546 41.5406 41.5276];
C_exp_8_0 = [24.4373 30.709 36.6562 41.6091 45.2057 48.3931 48.3261 48.4588 48.6304];
C_exp_10_8 = [21.5954 23.6645 25.8806 26.243 29.3689 34.3829 36.9307 37.6838 38.1607];
C_exp_10_0 = [22.0949 26.5858 30.7584 37.8029 40.1662 43.5126 43.7355 43.2321 43.5906];
```
%8_60
    cinf8_6 = 35.99;
    var8_6a = [1.632300E-03  2.963600E+00];
    var8_6b = [1.882500E-06  4.966000E+00  4.069200E+01];
%8_80
    cinf8_8 = 41.55;
    var8_8a = [5.122600E-04  3.063800E+00];
    var8_8b = [5.323400E-08  5.501100E+00  4.957200E+01];
%8_100
    cinf8_0 = 48.64;
    var8_0a = [5.692700E-03  2.119400E+00];
    var8_0b = [1.139400E-03  2.544700E+00  5.086000E+01];
%10_60
    cinf10_6 = 32.75;
    var10_6a = [3.615800E-04  3.442700E+00];
    var10_6b = [4.953900E-11  7.731900E+00  4.339200E+01];
%10_80
    cinf10_8 = 38.17;
    var10_8a = [1.646600E-04  3.346200E+00];
    var10_8b = [2.656000E-11  7.212800E+00  5.272600E+01];
%10_100
    cinf10_0 = 43.74;
    var10_0a = [4.844900E-03  2.184600E+00];
    var10_0b = [6.206100E-04  2.739000E+00  4.634800E+01];
%12_60
    cinf12_6 = 28.13;
    var12_6a = [7.474700E-04  3.312400E+00];
    var12_6b = [5.961900E-09  6.778500E+00  3.501300E+01];
%12_80
    cinf12_8 = 34.99;
    var12_8a = [8.818000E-05  3.562500E+00];
    var12_8b = [3.310800E-11  7.293100E+00  4.762700E+01];
%12_100
    cinf12_0 = 39.46;
    var12_0a = [2.207200E-03  2.408800E+00];
    var12_0b = [4.381300E-05  3.458800E+00  4.397700E+01];

tplot=[2:1:360];
%funcs for 8_60
func1_8_6 = @(var8_6a,t) cinf8_6 - (((var8_6a(2)-1).*var8_6a(1).*t)+((cin8_6).^((1-var8_6a(2))).^(1./(1-var8_6a(2)))));
func2_8_6 = @(var8_6b,t) var8_6b(3) - (((var8_6b(2)-1).*var8_6b(1).*t)+((var8_6b(3)).^(1-(1-var8_6b(2))).^(1./(1-var8_6b(2)))));

m8_6 = func2_8_6([0.010392,2,36.23188], tplot);
m8_6a = func1_8_6(var8_6a, tplot);
m8_6b = func2_8_6(var8_6b, tplot);

%funcs for 8_80
func1_8_8 = @(var8_8a,t) cinf8_8 - (((var8_8a(2)-1).*var8_8a(1).*t)+((cin8_8).^((1-var8_8a(2))).^(1./(1-var8_8a(2)))));
func2_8_8 = @(var8_8b,t) var8_8b(3) - (((var8_8b(2)-1).*var8_8b(1).*t)+((var8_8b(3)).^(1-(1-var8_8b(2))).^(1./(1-var8_8b(2)))));

m8_8 = func2_8_8([0.005573,2,41.841], tplot);
m8_8a = func1_8_8(var8_8a, tplot);
m8_8b = func2_8_8(var8_8b, tplot);

%funcs for 8_100
func1_8_0 = @(var8_0a,t) cinf8_0 - (((var8_0a(2)-1).*var8_0a(1).*t)+((cin8_0).^((1-var8_0a(2))).^(1./(1-var8_0a(2)))));
func2_8_0 = @(var8_0b,t) var8_0b(3) - (((var8_0b(2)-1).*var8_0b(1).*t)+((var8_0b(3)).^(1-(1-var8_0b(2))).^(1./(1-var8_0b(2)))));

m8_0 = func2_8_0([0.0086881,2,49.01961], tplot);
m8_0a = func1_8_0(var8_0a, tplot);
m8_0b = func2_8_0(var8_0b, tplot);

%funcs for 10_60
func1_10_6 = @(var10_6a,t) cinf10_6 - (((var10_6a(2)-1).*var10_6a(1).*t)+((cin10_6).^((1-var10_6a(2))).^(1./(1-var10_6a(2)))));
func2_10_6 = @(var10_6b,t) var10_6b(3) - (((var10_6b(2)-1).*var10_6b(1).*t)+((var10_6b(3)).^(1-(1-var10_6b(2))).^(1./(1-var10_6b(2)))));

m10_6 = func2_10_6([0.007198,2,33.0666], tplot);
m10_6a = func1_10_6(var10_6a, tplot);
m10_6b = func2_10_6(var10_6b, tplot);
%funcs for 10_80
func1_10_8 = @(var10_8a,t) cinf10_8 - (((var10_8a(2)-1).*var10_8a(1).*t)+((cinf10_8).^(1.-var10_8a(2))).^(1./(1.-var10_8a(2))));
func2_10_8 = @(var10_8b,t) var10_8b(3) - (((var10_8b(2)-1).*var10_8b(1).*t)+((var10_8b(3)).^(1.-var10_8b(2))).^(1./(1.-var10_8b(2))));

m10_8 = func2_10_8([0.004681,2,38.61004] , tplot);
m10_8a = func1_10_8(var10_8a,tplot);
m10_8b = func2_10_8(var10_8b,tplot);

%funcs for 10_100
func1_10_0 = @(var10_0a,t) cinf10_0 - (((var10_0a(2)-1).*var10_0a(1).*t)+((cinf10_0).^(1.-var10_0a(2))).^(1./(1.-var10_0a(2))));
func2_10_0 = @(var10_0b,t) var10_0b(3) - (((var10_0b(2)-1).*var10_0b(1).*t)+((var10_0b(3)).^(1.-var10_0b(2))).^(1./(1.-var10_0b(2))));

m10_0 = func2_10_0([0.009417391,2,43.85964912] , tplot);
m10_0a = func1_10_0(var10_0a,tplot);
m10_0b = func2_10_0(var10_0b,tplot);

%funcs for 12_60
func1_12_6 = @(var12_6a,t) cinf12_6 - (((var12_6a(2)-1).*var12_6a(1).*t)+((cinf12_6).^(1.-var12_6a(2))).^(1./(1.-var12_6a(2))));
func2_12_6 = @(var12_6b,t) var12_6b(3) - (((var12_6b(2)-1).*var12_6b(1).*t)+((var12_6b(3)).^(1.-var12_6b(2))).^(1./(1.-var12_6b(2))));

m12_6 = func2_12_6([0.008342,2,28.238222] , tplot);
m12_6a = func1_12_6(var12_6a,tplot);
m12_6b = func2_12_6(var12_6b,tplot);

%funcs for 12_80
func1_12_8 = @(var12_8a,t) cinf12_8 - (((var12_8a(2)-1).*var12_8a(1).*t)+((cinf12_8).^(1.-var12_8a(2))).^(1./(1.-var12_8a(2))));
func2_12_8 = @(var12_8b,t) var12_8b(3) - (((var12_8b(2)-1).*var12_8b(1).*t)+((var12_8b(3)).^(1.-var12_8b(2))).^(1./(1.-var12_8b(2))));

m12_8 = func2_12_8([0.003778,2,35.3369] , tplot);
m12_8a = func1_12_8(var12_8a,tplot);
m12_8b = func2_12_8(var12_8b,tplot);
```matlab
%funcs for 12_100
func1_12_0 = @(var12_0a,t) cinf12_0 - (((var12_0a(2)-1).*var12_0a(1).*t)+((cinf12_0).^((1-var12_0a(2))))).^(1./(1-var12_0a(2))));
func2_12_0 = @(var12_0b,t) var12_0b(3) - (((var12_0b(2)-1).*var12_0b(1).*t)+((var12_0b(3)).^(1-var12_0b(2))))).^(1./(1-var12_0b(2))));

m12_0 = func2_12_0([0.006850485,2,39.68253968] , tplot);
m12_0a = func1_12_0(var12_0a,tplot);
m12_0b = func2_12_0(var12_0b,tplot);

figure(1)
plot(t_exp,C_exp_8_6,'bd',t_exp,C_exp_8_8,'rs',t_exp,C_exp_8_0,'g^',tplot,m8_6,'b-',tplot,m8_8,'r-',tplot,m8_0,'g-')
title('Rate Law Model, 8 to 1 Liquid-to-Solid Ratio')
legend('60\{\textdegree} C, Experimental','80\{\textdegree} C, Experimental','100\{\textdegree} C, Experimental','60\{\textdegree} C, Model','80\{\textdegree} C, Model','100\{\textdegree} C, Model')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(2)
plot(t_exp,C_exp_8_6,'bd',t_exp,C_exp_8_8,'rs',t_exp,C_exp_8_0,'g^',tplot,m8_6a,'b-',tplot,m8_8a,'r-',tplot,m8_0a,'g-')
title('Rate Law Model Modification A, 8 to 1 Liquid-to-Solid Ratio')
legend('60\{\textdegree} C, Experimental','80\{\textdegree} C, Experimental','100\{\textdegree} C, Experimental','60\{\textdegree} C, Model','80\{\textdegree} C, Model','100\{\textdegree} C, Model')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(3)
plot(t_exp,C_exp_8_6,'bd',t_exp,C_exp_8_8,'rs',t_exp,C_exp_8_0,'g^',tplot,m8_6b,'b-',tplot,m8_8b,'r-',tplot,m8_0b,'g-')
title('Rate Law Model Modification B, 8 to 1 Liquid-to-Solid Ratio')
```
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(4)
plot(t_exp,C_exp_10_6,'bd',t_exp,C_exp_10_8,'rs',t_exp,C_exp_10_0,'g^',tplot,m10_6,'b-',tplot,m10_8,'r-',tplot,m10_0,'g-')
title('Rate Law Model, 10 to 1 Liquid-to-Solid Ratio')
legend('60\{circ\} C, Experimental','80\{circ\} C, Experimental','100\{circ\} C, Experimental','60\{circ\} C, Model','80\{circ\} C, Model','100\{circ\} C, Model')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(5)
plot(t_exp,C_exp_10_6,'bd',t_exp,C_exp_10_8,'rs',t_exp,C_exp_10_0,'g^',tplot,m10_6a,'b-',tplot,m10_8a,'r-',tplot,m10_0a,'g-')
title('Rate Law Model Modification A, 10 to 1 Liquid-to-Solid Ratio')
legend('60\{circ\} C, Experimental','80\{circ\} C, Experimental','100\{circ\} C, Experimental','60\{circ\} C, Model','80\{circ\} C, Model','100\{circ\} C, Model')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(6)
plot(t_exp,C_exp_10_6,'bd',t_exp,C_exp_10_8,'rs',t_exp,C_exp_10_0,'g^',tplot,m10_6b,'b-',tplot,m10_8b,'r-',tplot,m10_0b,'g-')
title('Rate Law Model Modification B, 10 to 1 Liquid-to-Solid Ratio')
legend('60\{circ\} C, Experimental','80\{circ\} C, Experimental','100\{circ\} C, Experimental','60\{circ\} C, Model','80\{circ\} C, Model','100\{circ\} C, Model')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(7)
plot(t_exp,C_exp_12_6,'bd',t_exp,C_exp_12_8,'rs',t_exp,C_exp_12_0,'g^',tplot,m12_6,'b-',tplot,m12_8,'r-',tplot,m12_0,'g-')
title('Rate Law Model, 12 to 1 Liquid-to-Solid Ratio')
legend('60\{circ\} C, Experimental','80\{circ\} C, Experimental','100\{circ\} C, Experimental','60\{circ\} C, Model','80\{circ\} C, Model','100\{circ\} C, Model')
xlabel('Time [min]')

%%%
ylabel('Concentration [kg/m$^3$]')

figure(8)
plot(t_exp,C_exp_12_6,'bd',t_exp,C_exp_12_8,'rs',t_exp,C_exp_12_0,'g^',tplot,m12_6a,'b-',tplot,m12_8a,'r-',tplot,m12_0a,'g-')
title('Rate Law Model Modification A, 12 to 1 Liquid-to-Solid Ratio')
legend('60$\circ$C, Experimental','80$\circ$C, Experimental','100$\circ$C, Experimental','60$\circ$C, Model','80$\circ$C, Model','100$\circ$C, Model')
xlabel('Time [min]')
ylabel('Concentration [kg/m$^3$]')

figure(9)
plot(t_exp,C_exp_12_6,'bd',t_exp,C_exp_12_8,'rs',t_exp,C_exp_12_0,'g^',tplot,m12_6b,'b-',tplot,m12_8b,'r-',tplot,m12_0b,'g-')
title('Rate Law Model Modification B, 12 to 1 Liquid-to-Solid Ratio')
legend('60$\circ$C, Experimental','80$\circ$C, Experimental','100$\circ$C, Experimental','60$\circ$C, Model','80$\circ$C, Model','100$\circ$C, Model')
xlabel('Time [min]')
ylabel('Concentration [kg/m$^3$]')

figure(10)
plot(t_exp,C_exp_8_6,'bd',tplot,m8_6b,'b-',tplot,m8_6a,'k-',tplot,m8_6b,'m-')
title('Rate Law Model Comparisons, 8 to 1 Liquid-to-Solid Ratio, 60$\circ$C')
legend('Experimental','Rate Law Model','Modification A','Modification B')
xlabel('Time [min]')
ylabel('Concentration [kg/m$^3$]')

figure(11)
plot(t_exp,C_exp_8_8,'rs',tplot,m8_8b,'m-',tplot,m8_8a,'k-')
title('Rate Law Model Comparisons, 8 to 1 Liquid-to-Solid Ratio, 80$\circ$C')
legend('Experimental','Rate Law Model','Modification A','Modification B')
xlabel('Time [min]')
ylabel('Concentration [kg/m$^3$]')

figure(12)
plot(t_exp,C_exp_8_0,'g^',tplot,m8_0b,'m-',tplot,m8_0a,'k-')
title('Rate Law Model Comparisons, 8 to 1 Liquid-to-Solid Ratio, 100$\circ$C')
legend('Experimental','Rate Law Model','Modification A','Modification B')
xlabel('Time [min]')
ylabel('Concentration [kg/m$^3$]')
figure(13)
plot(t_exp,C_exp_10_6,'bd',tplot,m10_6,'b-',tplot,m10_6a,'k-',tplot,m10_6b,'m-')
title('Rate Law Model Comparisons, 10 to 1 Liquid-to-Solid Ratio, 60\(\circ\) C')
legend('Experimental','Rate Law Model','Modification A','Modification B')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(14)
plot(t_exp,C_exp_10_8,'rs',tplot,m10_8,'r-',tplot,m10_8a,'k-',tplot,m10_8b,'m-')
title('Rate Law Model Comparisons, 10 to 1 Liquid-to-Solid Ratio, 80\(\circ\) C')
legend('Experimental','Rate Law Model','Modification A','Modification B')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(15)
plot(t_exp,C_exp_10_0,'g^',tplot,m10_0,'g-',tplot,m10_0a,'k-',tplot,m10_0b,'m-')
title('Rate Law Model Comparisons, 10 to 1 Liquid-to-Solid Ratio, 100\(\circ\) C')
legend('Experimental','Rate Law Model','Modification A','Modification B')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(16)
plot(t_exp,C_exp_12_6,'bd',tplot,m12_6,'b-',tplot,m12_6a,'k-',tplot,m12_6b,'m-')
title('Rate Law Model Comparisons, 12 to 1 Liquid-to-Solid Ratio, 60\(\circ\) C')
legend('Experimental','Rate Law Model','Modification A','Modification B')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(17)
plot(t_exp,C_exp_12_8,'rs',tplot,m12_8,'r-',tplot,m12_8a,'k-',tplot,m12_8b,'m-')
title('Rate Law Model Comparisons, 12 to 1 Liquid-to-Solid Ratio, 80\(\circ\) C')
legend('Experimental','Rate Law Model','Modification A','Modification B')
xlabel('Time [min]')
ylabel('Concentration [kg/m^3]')

figure(18)
plot(t_exp,C_exp_12_0,'g^',tplot,m12_0,'g-',tplot,m12_0a,'k-',tplot,m12_0b,'m-')
Equilibrium Isotherms

The MATLAB script to find the parameters for the equilibrium models is included below. This script is for the extraction curve at 60° C. A different script was used for each temperature.

```
% nlinfit for isotherm models
% T = 60 C

% Liq to Solv ratios:
% 5, 8, 10, 12, 30, 40, 20(2)
format long e

c = [0.041365468 0.035976133 0.032704374 0.028053422 0.017617149 0.012118828 0.009083254 0.002190314 0.001129985 0.000893779]
q = [0.381738113 0.230557286 0.157207758 0.139282252 0.109955444 0.088996110 0.089434420 0.041673492 0.018217193 8.18572E-05];

%BET Original
% var = [qs, Ka, Kb]
var1 = [0.5 500 13]; % initial guesses
func1 = @(var,c) (var(1).*var(2).*c)./(1-var(3).*c).*(1-(var(3).*c)+(var(2).*c));
fits1 = nlinfit(c,q,func1,var1);
c_BET = [0:0.001:0.042];
q_BET = func1(fits1,c_BET);

figure(1)
pplot(c,q,'x')
hold on
plot(c_BET,q_BET,':')
title('Original BET')
```
%%BET Modification 1
%var = [qL, KL, qAL, KAL]
var2 = [0.138 182 0.019 23.6]; %initial guesses, based on each being linearized
func2 = @(var,c) var(1).*var(2).*c./(1+(var(2).*c)) + (var(3).*var(4).*c)./(1-(var(4).*c));
fits2 = nlinfit(c,q,func2,var2);
q_BET_m1 = func2(fits2,c_BET);
figure(2)
plot(c,q,'bd')
hold on
plot(c_BET,q_BET_m1,'b-')
legend('Experimental','BET Modification 1 Model')
xlabel('Solvent Concentration, c [g/mL]')
ylabel('Bark Loading, q [g/g]')

%%BET Modification 2
%var = [qL, KL, qAL, KAL, H]
var3 = [0.138 49 0.0675 33.1 0.017];
func3 = @(var,c) var(1).*var(2).*c./(1+(var(2).*c)) + (var(3).*var(4).*(c-var(5)))./(1-(var(4).*(c-var(5))));
fits3 = nlinfit(c,q,func3,var3);
q_BET_m2 = func3(fits3,c_BET);
figure(3)
plot(c,q,'x')
hold on
plot(c_BET,q_BET_m2,'-')
title('BET Modification 2 (5 parameters)')

figure(4)
plot(c,q,'rd',c_BET,q_BET,'-';c_BET,q_BET_m1,'-',c_BET,q_BET_m2,'-')
xlabel('Solvent Concentration, c [g/mL]')
ylabel('Bark Loading, q [g/g]')
legend('Experimental','BET Isotherm','BET Modification 1','BET Modification 2')

%%%% Absolute Error Work
format short
qm_BET = func1(fits1,c);
qm_BET_m1 = func2(fits2,c);
qm_BET_m2 = func3(fits3,c);

TABLE = [c ; q ; qm_BET; qm_BET_m1; qm_BET_m2];
TABLE = [TABLE; abs(TABLE(3,:)-TABLE(2,:)) ; abs(TABLE(4,:)-TABLE(2,:))
     ; abs(TABLE(5,:)-TABLE(2,:))];

% Switching to sum of absolute error because points close to origin throw
% off the relative aspect

AE_BET = sum(TABLE(6,:))
AE_BET_m1 = sum(TABLE(7,:))
AE_BET_m2 = sum(TABLE(8,:))

%c%%%&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&%&
%Operating line

c_opt = 0.033
q_eq_opt = func2(fits2,c_opt);

op_c = [0 c_opt]; %initial and equilibrium
op_q = [0.768 q_eq_opt] ; %initial and equilibrium

figure(5)
plot(c_BET,q_BET_m1,'b-',op_c,op_q,'k-')
legend('BET Modification 1 Model','Operating Line')
xlabel('Solvent Concentration, c [g/mL]')
ylabel('Bark Loading, q [g/g]')

% %var = [qs, Ka, Kb]
% var = [0.5 500 13]; %initial guesses --> how to find?
% func1 = @(var,c) (var(1).*var(2).*c)./((1-
   var(3).*c).*(1-(
   (var(3).*c)+(var(2).*c)))) %BET isotherm
% fits = nlinfit(c,q,func1,var)
% %
% c_mod = [0:0.001:0.05];
% q_mod= func1(fits,c_mod)
% %
% plot(c,q,'x')
% hold on

The script used to model the effect of liquid-to-solid ratio on process yield and solvent concentration is shown below for the data at 60° C:

```matlab
% Optimization of yield and concentration, 60 C
% use first modification to BET model
fits2 = [0.1099 204.6935 0.0331 21.6598]
func2 = @(var,c) var(1).*var(2).*c./(1+(var(2).*c)) + (var(3).*var(4).*c)./(1-(var(4).*c));

format short
c_eq = [0.0413:-0.0001:0.0183]; % works well for linear x axis
q_eq = func2(fits2,c_eq);

TABLE = [c_eq ; q_eq ; zeros(5,length(c_eq))];

c0 = 0;
q0 = 0.7680;
SL_fact = (1/1.00363252)*(2/1.066948); % divide equilibrium plot L/S by this to get paper L/S = (mL liq/g liq)*(g air dry/g unextractable)

%TABLE = [ceq ; q_eq ; L/S ratio (mass to air-dry-mass) ; Liq. Volume (mL) % ; Yield (g) ; %increase in yield ; %decrease in conc.]

for i = 1:length(TABLE)
    TABLE(3,i) = ((TABLE(2,i)-q0)/(TABLE(1,i)-c0))*(-1/SL_fact);
    TABLE(4,i) = TABLE(3,i)*2*(1/1.00363252); % volume solvent used in a 2 g sample
    TABLE(5,i) = TABLE(1,i)*TABLE(4,i); % (g solute/mL solvent) * (mL solvent) = Yield (g) for a 2 g sample brought to eq.
    TABLE(6,i) = 100*(TABLE(5,i) - TABLE(5,1))/TABLE(5,1); % percent increase in yield
    TABLE(7,i) = -100*(TABLE(1,i) - TABLE(1,1))/TABLE(1,1); % percent decrease in concentration
end

TABLE;
```
[ax h1 h2] = plotyy(TABLE(3,:),TABLE(6,:),TABLE(3,:),TABLE(7,:));

xlabel('Liquid-to-Solid Ratio')
ylabel(ax(1),''Increase in Yield Compared to 5:1'') %left y-axis
ylabel(ax(2),''Decrease in Concentration Compared to 5:1'') %right y-axis
%ylabel(ax(2),''decrease in concentration compared to 5:1'')

% figure(1)
% plot(c_eq,q_eq)
%
% figure(2)
% plot(TABLE(3,:),TABLE(6,:))
% xlabel('Liquid-to-Solid Ratio')
% ylabel('Increase in yield compared to 5:1')
%
% figure(3)
% plot(TABLE(3,:),TABLE(7,:))
% xlabel('Liquid-to-Solid Ratio')
% ylabel('Decrease in concentration compared to 5:1')
Appendix D: Extra Figures and Tables

The figures and tables generated during the completion of this work but not included in the main body of the thesis are presented here. They are organized according to model type. They include model parameter and fit estimate values and extraction curve figures.

Extraction Yield Results:

![Extraction Yield, 8 to 1 Liquid-to-Solid Ratio](image1)

![Extraction Yield, 10 to 1 Liquid-to-Solid Ratio](image2)
Shrinking Core Models:

<table>
<thead>
<tr>
<th>Liquid-to-solid ratio</th>
<th>Temperature (° C)</th>
<th>Chemical Reaction</th>
<th>Film Diffusion</th>
<th>Ash Diffusion</th>
<th>1st Order Pseudo-Homogeneous</th>
<th>2nd Order Pseudo-Homogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 to 1</td>
<td>60</td>
<td>0.62</td>
<td>0.6912</td>
<td>0.6839</td>
<td>0.7404</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.71</td>
<td>0.7279</td>
<td>0.673</td>
<td>0.735</td>
<td></td>
</tr>
<tr>
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<td>100</td>
<td>0.722</td>
<td>0.8221</td>
<td>0.7841</td>
<td>0.8455</td>
<td></td>
</tr>
<tr>
<td>10 to 1</td>
<td>60</td>
<td>0.721</td>
<td>0.8321</td>
<td>0.7658</td>
<td>0.9028</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.7386</td>
<td>0.8283</td>
<td>0.823</td>
<td>0.735</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.7393</td>
<td>0.8133</td>
<td>0.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 to 1</td>
<td>60</td>
<td>0.7423</td>
<td>0.7986</td>
<td>0.8304</td>
<td>0.8994</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.717</td>
<td>0.8121</td>
<td>0.7959</td>
<td>0.9038</td>
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<tr>
<td></td>
<td>100</td>
<td>0.7393</td>
<td>0.8133</td>
<td>0.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Values</td>
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<td>0.7453</td>
<td>0.6886</td>
<td>0.7947</td>
<td>0.7725</td>
<td>0.8355</td>
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</tbody>
</table>

Fick’s Law Analytical Solution Model:

<table>
<thead>
<tr>
<th>Liquid-to-solid ratio</th>
<th>Temperature (° C)</th>
<th>$c_\infty$ [kg m$^{-3}$]</th>
<th>$\frac{D_{eff}}{R^2} \times 10^5$ [s$^{-1}$]</th>
<th>AARD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 to 1</td>
<td>60</td>
<td>35.99</td>
<td>5.72</td>
<td>15.94</td>
</tr>
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<td></td>
<td>80</td>
<td>41.55</td>
<td>5.15</td>
<td>14.66</td>
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<td>48.64</td>
<td>13.41</td>
<td>2.40</td>
</tr>
<tr>
<td>10 to 1</td>
<td>60</td>
<td>32.75</td>
<td>3.77</td>
<td>17.21</td>
</tr>
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</tr>
<tr>
<td></td>
<td>100</td>
<td>43.74</td>
<td>13.16</td>
<td>2.33</td>
</tr>
<tr>
<td>12 to 1</td>
<td>60</td>
<td>28.13</td>
<td>5.93</td>
<td>14.72</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>34.19</td>
<td>3.33</td>
<td>12.85</td>
</tr>
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<td>100</td>
<td>39.46</td>
<td>6.75</td>
<td>6.07</td>
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</table>
Fick's Law Analytical Solution Model, 8 to 1
Liquid-to-Solid Ratio

Fick's Law Analytical Solution Model, 10 to 1
Liquid-to-Solid Ratio
Fick’s Law with Solvent Balance Model

<table>
<thead>
<tr>
<th>Liquid-to-solid ratio</th>
<th>Temperature (°C)</th>
<th>$C_0$ [kg m$^{-3}$]</th>
<th>$D_{eff} \times 10^9$ [s$^{-1}$]</th>
<th>AARD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8 to 1</strong></td>
<td>60</td>
<td>107.24</td>
<td>2.13</td>
<td>6.68</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>123.80</td>
<td>1.47</td>
<td>7.96</td>
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<tr>
<td></td>
<td>100</td>
<td>144.44</td>
<td>1.11</td>
<td>2.41</td>
</tr>
<tr>
<td><strong>10 to 1</strong></td>
<td>60</td>
<td>117.61</td>
<td>0.95</td>
<td>9.73</td>
</tr>
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<td></td>
<td>80</td>
<td>137.34</td>
<td>0.71</td>
<td>10.55</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>157.52</td>
<td>1.04</td>
<td>3.61</td>
</tr>
<tr>
<td><strong>12 to 1</strong></td>
<td>60</td>
<td>118.70</td>
<td>1.06</td>
<td>9.50</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>147.63</td>
<td>0.65</td>
<td>11.81</td>
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<tr>
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<td>165.44</td>
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</table>
Fick's Law Extended Analytical Solution and Modification

<table>
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<th>Liquid-to-solid ratio</th>
<th>Temperature (° C)</th>
<th>$c_\infty$ [kg m$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Original</td>
</tr>
<tr>
<td>8 to 1</td>
<td>60</td>
<td>35.99</td>
</tr>
<tr>
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<td>48.64</td>
</tr>
<tr>
<td>10 to 1</td>
<td>60</td>
<td>32.75</td>
</tr>
<tr>
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<td>80</td>
<td>38.17</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>43.74</td>
</tr>
<tr>
<td>12 to 1</td>
<td>60</td>
<td>28.13</td>
</tr>
<tr>
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<td>34.99</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>39.46</td>
</tr>
<tr>
<td>Liquid-to-solid ratio</td>
<td>Temperature (°C)</td>
<td>AARD (%)</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------</td>
<td>----------</td>
</tr>
<tr>
<td></td>
<td>Original</td>
<td>Modified</td>
</tr>
<tr>
<td>8 to 1</td>
<td>60</td>
<td>1.40</td>
</tr>
<tr>
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<td>80</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>2.70</td>
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</tr>
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<td>1.81</td>
</tr>
<tr>
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<tr>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquid-to-solid ratio</th>
<th>Temperature (°C)</th>
<th>( \frac{D_{eff,1}}{R^2} \times 10^4 )</th>
<th>( \frac{D_{eff,2}}{R^2} \times 10^5 )</th>
<th>( \frac{D_{eff,1}}{R^2} \times 10^4 )</th>
<th>( \frac{D_{eff,2}}{R^2} \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Original</td>
<td>Modified</td>
<td>Original</td>
<td>Modified</td>
</tr>
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<td>3.68</td>
<td>15.74</td>
<td>3.68</td>
</tr>
<tr>
<td></td>
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<td>4.61</td>
<td>1.60</td>
<td>8.40</td>
<td>2.13</td>
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Fick's Law Extended Analytical Solution Model,
8 to 1 Liquid-to-Solid Ratio

Fick's Law Extended Analytical Solution Model,
10 to 1 Liquid-to-Solid Ratio
Fick’s Law Extended Analytical Solution Model,
12 to 1 Liquid-to-Solid Ratio

Modified Fick’s Law Extended Analytical Solution
Model, 8 to 1 Liquid-to-Solid Ratio
Modified Fick's Law Extended Analytical Solution
Model, 10 to 1 Liquid-to-Solid Ratio

Modified Fick's Law Extended Analytical Solution
Model, 12 to 1 Liquid-to-Solid Ratio
## Rate Law Model and Modifications

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Rate Law Model, 8 to 1 Liquid-to-Solid Ratio
Equilibrium Isotherm Models

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