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Recovering valuable products from the aqueous streams of fast pyrolysis

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Recovering valuable products from the aqueous streams of fast pyrolysis

by

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

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DEDICATION

To my dearest wife, Katie.

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NOMENCLATURE

AAEM	Alkali and Alkaline Earth Metals
ABE	Acetone-Butanol-Ethanol
BCRF	BioCentury Research Farm
BOD	Biological Oxygen Demand
C	Celsius
cm^3	cubic centimeters
cP	centipoise
COD	Chemical Oxygen Demand
DVB	Divinylbenzene
ESP	Electrostatic Precipitator
FC	Folin-Ciocalteu
g	gram
GPC	Gel Permeation Chromatography
HPLC	High Pressure Liquid Chromatography
hr	hour
ISU	Iowa State University
kW	kilowatt
µPa	micropascal
mL	milliliter
mol	mole
M	moles/liter

MIBK	Methyl Isobutyl Ketone
NMR	Nuclear Magnetic Resonance
PDU	Pyrolysis Demonstration Unit
PS	Polystyrene
PS-DVB	Polystyrene – Divinyl Benzene
PNNL	Pacific Northwest National Laboratories
RO	Reverse Osmosis
SAC	Strong-Acid Cation
SBC	Strong-Base Anion
SF	Stage Fraction
TEA	Techno-Economic Analysis
U.S.	United States
WAC	Weak-Acid Cation
WBA	Weak-Base Anion

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ABSTRACT

Many of the biorefineries found in the world operate on a biochemical or thermochemical platform to produce their fuels and chemicals. However, contaminant removal from bio-refineries process and wastewater streams is a mounting issue that needs to be dealt with. Grain ethanol, cellulosic ethanol, hydroprocessing units, and pyrolysis biorefineries all produce process and wastewater streams that must be cleaned prior to releasing them to sewage systems or purified to sequester all valuable products contained within the aqueous matrix. Two major products are found within the aqueous streams of a pyrolysis reactor: levoglucosan and acetic acid. Separating and purifying these valuable compounds would add these commodity chemicals to a bio-refinery's portfolio and reduce the cost of wastewater cleanup.

Fractionation technology developed at Iowa State University separates bio-oil into water soluble sugars, water insoluble phenolic monomers, dimers, and oligomers, and aqueous phases containing water soluble light oxygenates, and carboxylic acids. Productive use of these fractionated bio-oil streams will be important to the development of a bio-refinery based on the fast pyrolysis of biomass.

We have identified a polymeric adsorbent resin that efficiently removes organic contaminants from sugar solutions. It does this by the removal of bio-oil phenolic species which is necessary before the sugars can undergo crystallization or utilization for biological and catalytic upgrading. The resin has high selectivity (affinity) for phenols and other aromatic compounds, high adsorption capacity, low cost, and ease of

regeneration. Our results show a marked sugar purity increase and phenol concentration decrease.

We have also determined that hydrophobic polymeric resins are suitable candidates for adsorption of acetic acid from the aqueous fractions. Among possible resins for chemical adsorption, debittering and anionic resins were selected due to their affinity for phenolic and acetic acid removal, respectively. Both resins have shown favorable results with almost complete removal of their targeted species.

Recovery of acetic acid and other organic species from the aqueous fractions is necessary because it increases the number of chemical products from the bio-oil and reduces the waste water treatment costs associated with the pyrolysis biorefinery. However, the presence of water makes upgrading and simple distillation of this fraction very difficult due to water's high heat capacity and azeotropic properties. Among possible solvents for liquid-liquid extraction, heptanoic acid was selected because of its low water solubility; high boiling point compared to the acetic acid to be distilled from it; and stability during storage. Heptanoic acid extraction of SF5 has shown favorable results with almost complete removal of acetic acid.

CHAPTER I

INTRODUCTION

The world's overdependence of petroleum products is driving the depletion of oil deposits more rapidly each year. It is predicted to rise 60% in the next 25 years if nothing is done to curb its use [1]. Generation of carbon dioxide from fossil fuel consumption is also contributing to global warming and climate change at unprecedented levels [2]. Because of these reasons, finding alternatives to crude oil and its products as well as reducing oil dependency are overarching goals for biorenewable chemists and engineers today [3]. In addition, many governments around the globe are prioritizing finding renewable and sustainable energy sources for their countries. Many of the sources identified by scientists as renewable are in the form of biomass or lignocellulosic material from agriculture, forestry, and aquatic plants [4]. The total energy content of biomass resources is five times that of worldwide crude oil consumption [5]. However, the energy content of biomass is stored in the chemical bonds of the biomass itself, not able to be immediately generated into electricity and put directly on the power grid like wind or solar power.

In the United States (U.S.), 25% of our petroleum supply is imported, or 36% of the total annual consumption of petroleum comes from international sources [6]. Based on 2016 data, 10% of the U.S.'s power now comes from renewable energy [6]. However, much of the opposition to using biomass as renewable sustainable energy comes from the ever-present food versus fuel debate. To put this debate to rest, the U.S. Department of Energy funded the *Billion Ton Study* in 2005, revised in 2011 and 2016. These studies

concluded that more than one billion tons of biomass could be produced, displacing 30% of the U.S.'s petroleum consumption and reducing the importation of foreign petroleum by as much as 67% [7]. Today, the U.S. has a production potential of 1.3 billion dry tons of biomass per year without causing a negative impact to feed, filler, and food production for livestock and humans. In addition, export demands faced by U.S. can still be met [7]. It was also shown in studies at Iowa State University (ISU), and a collaborative study between Purdue and the State University of New York College of Environmental Science and Forestry, that gas and diesel equivalents and blends could be produced at a $2-3 per gallon using biomass in a local biorefinery or cellulosic ethanol plant [8, 9]. In addition, biofuels and biochar produced at these biorefineries would sequester renewable carbon from the atmosphere in a carbon neutral or carbon negative process [10, 11].

Many of the biorefineries found in the world operate on a biochemical or thermochemical platform to produce fuels and chemicals. However, contaminant removal from bio-refineries process and wastewater streams is a mounting issue that needs to be dealt with. Grain ethanol, cellulosic ethanol, hydroprocessing units, and pyrolysis biorefineries all produce process and wastewater streams that must be cleaned prior to releasing them to sewage systems or purified to sequester all valuable products contained within the aqueous matrix. Two major products are found within the aqueous streams of a pyrolysis reactor; levoglucosan and acetic acid. Separating and purifying these valuable compounds would add these commodity chemicals to a bio-refinery's portfolio and reduce the cost of wastewater cleanup.

Biomass Structure

Lignocellulose is commonly used to describe three-dimensional polymeric skeletal structures formed by plants or biomass. Another term used is holocellulose, referring to cellulose and hemicellulose matrices. Hardwoods from deciduous trees, softwoods from coniferous trees, and herbaceous material from grasses and other agricultural biomass have differing compositions from one another. These compositions vary in the percentages of three main structural composites: cellulose, lignin, and hemicellulose [12].

Cellulose

The first of these composites is cellulose, a linear homopolysaccharide of D-glucose (or more specifically β-D-glucopyranose), and ultimately cellobiose, a dimer of glucose [12]. Cellulose, in plant cell walls, comprises around 40-45% of dried biomass weight [13]. These units are linked together in β 1-4 glycosidic bonds and tend to form intra and intermolecular hydrogen bonds. These hydrogen bonded structures or bundles form microfibrils consisting of crystalline and amorphous regions of sugar molecules. Composites of these fibers are known as cellulose fiber [14].

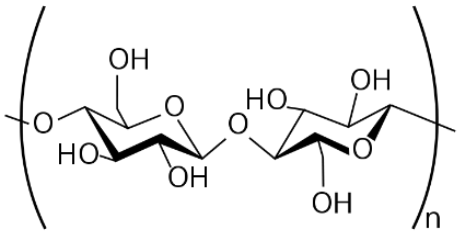

Figure 1. Structure of cellulose illustrating the β 1-4 glycosidic bonds between glucose molecules.

At temperatures above 350°C in pyrolysis, the dominant reaction becomes the depolymerization of cellulose (if it is free of inorganic impurities). Temperatures below

produce more char and cross-linked materials. Temperatures above this point cause cracking reactions of cellulose to produce hydroxyacetaldehydes. The primary thermally depolymerized product of cellulose is levoglucosan, a somewhat thermally stable low volatility anhydrosugar. Its 1,6-anhydroglucofuranose isomer and dimer, cellobiosan, are also produced in varying quantities. [15]

Hemicellulose

Hemicellulose or its main component, xylan, is made up of a large number of heteropolysaccharides formed from hexoses, pentoses, and deoxyhexoses (xylose in the case of xylan) comprising 15-30% of dry wood[13]. The backbone of xylan is β-(1-4)-D-xylopyranose with a multitude of sidechains. These sidechains differ among biomass species. However, the clear majority of these side chains are arabinofuranoses and acetyl groups. Hardwoods and softwoods also differ in their acetyl and acid content. Hardwoods contain much more acid/acetyl residues and are composed primarily of O-acetyl-4-O-methylglucuronoxylan while softwoods contain more O-acetylgalactoflucomannan [16, 17].

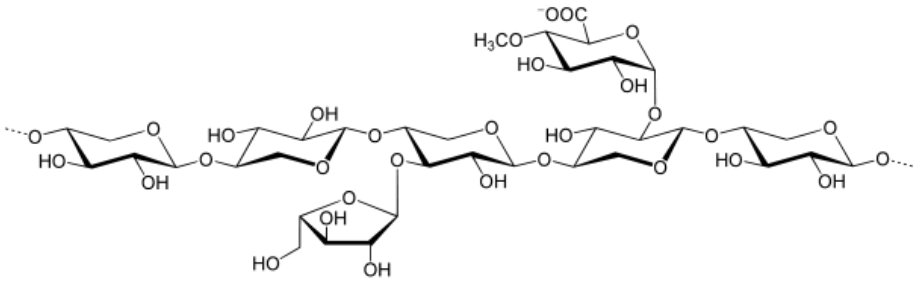

Figure 2. Structure of xylan.

The pyrolysis of hardwoods produces a significantly higher percentage of acetic acid. However, it is known that due to its non-crystalline structure, hemicellulose can more easily be depolymerized. The depolymerization products of hemicellulose include

significant amounts of acetic acid derived from acetyl and 4-*O*-methylflucuronic acid side chains. It has been found that the presence of alkalai and alkaline earth metals inhibit these products [12]. The hydrolysis of hemicellulose yields primarily pentoses, xylose and arabinose. Autohydrolysis (steaming), dilute acid pretreatment (also known as prehydrolysis or acid-catalyzed steam explosion), or sulfur dioxide steaming all aid the breakdown and recovery of hemicellulose-derived compounds [12].

Lignin

The second composite, is lignin, a heterogeneous phenylpropane-based polymer. It makes up the largest non-carbohydrate fraction of lignocellulose; 20-30% [5, 18]. Its structure is composed of three primary monomers or monolignols: paracoumaryl alcohol, coniferyl alcohol, and sinapinyl alcohol. Each of these aromatic compounds has different substituents or moieties including hydroxyl, aldehyde, methoxy groups [12]. It is also known that paracoumaryl alcohol is found more so in herbaceous material while coniferyl alcohol is found in hardwoods in greater quantities.

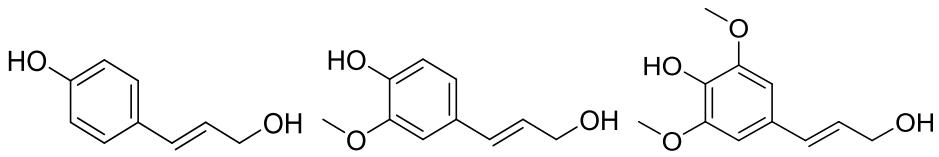

Figure 3. Structures of paracoumaryl alcohol, coniferyl alcohol, and sinapinyl alcohol from left to right; primary monomers which comprise the majority lignin's structure.

The amorphous structure of lignin is very complex and usually only presented in segments. However, lignin has several types of bonds or links in its structure. They are the β-O-4 (most dominant), α-O-4, β-β, β-1, β-5, 5-5, 4-O-5 linkages [19]. Due to the high carbon to oxygen ratio of lignin, it has an energy content similar to bituminous coals [20].

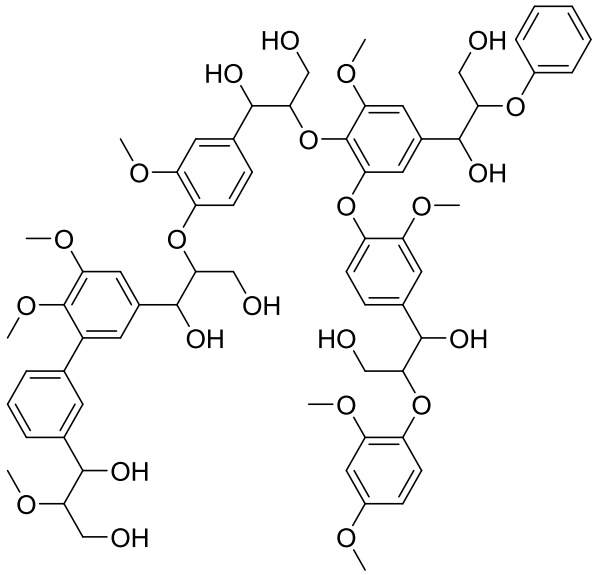

Figure 4. Fragment of lignin's proposed structure.

Lignin and the next and final composite of lignocellulose, hemicellulose, form a non-covalently bonded amorphous sheath that protects the cellulose portion of biomass from pests [12, 17]. This recalcitrance of lignin directly hinders the conversion of biomass to fuels and chemicals using biochemical conversion.

Thermochemical Processing

As mentioned previously, there are two main categories of lignocellulosic material processing: biochemical and thermochemical. Biochemical processing uses enzymes and microorganisms to convert the biomass to usable products. However, the biochemical conversion of cellulosic feedstocks leaves most of the lignin intact [10]. The lignin is then used for low-value applications like process heat through combustion. Thermochemical processes convert much more lignin to valuable products. It uses heat and sometimes catalysts to convert plant material into fuels, chemicals, and electrical power. In thermochemical processes, twenty percent of the lignin is converted to

phenolic monomers while 40% is converted to biochar. The remaining 40% forms phenolic oligomers and other light oxygenates [21, 22]. The monomeric phenols are commonly used for precursor chemicals or upgraded to fuels. Phenolic oligomers can be catalytically cracked to monomeric phenols used for bio-asphalt, binders, resins, and other polymers [23, 24].

There are several main types of thermochemical processes utilized in the biorenewable industry today: gasification, solvent liquefaction, and pyrolysis [25]. Gasification is the heating of biomass to 750-1500°C under almost inert conditions. The products formed are carbon dioxide, carbon monoxide, hydrogen, methane, nitrogen, and a small quantity of hydrocarbons. This mixture is then reformed or partially oxidized to produce synthesis gas or syngas. In solvent liquefaction or solvolysis, the biomass is pyrolyzed in the presence of a solvent. A variety of solvents can be employed, but water is typically used and is known as hydrothermal processing. Of course, based on the solvent used, the temperatures and pressures in the process must be adjusted accordingly.

There are three main forms of pyrolysis in literature. Fast pyrolysis is performed in the absence of oxygen with rapid heating, while autothermal pyrolysis is the rapid heating of biomass in the presence of oxygen. Slow pyrolysis is slow heating in the absence of oxygen.

Fast pyrolysis is the rapid thermal decomposition or conversion of organic compounds or lignocellulosic biomass at mild temperatures (300-600°C), typically in the absence of oxygen [26, 27]. The distribution of products depends on the biomass' composition and the reaction conditions used in the biorefinery. Resonance time, typically 0.5-2 seconds, and temperature, typically 500°C, are used as baselines for most reactors. In addition, the

biomass particle size, the rate and duration of heating, the final temperature achieved, and the process which is used to cool the products all play a role in the distribution of products and their characteristics. The intermediate products of char and non-condensable gases like carbon monoxide, carbon dioxide, hydrogen, and other light hydrocarbons, as wells as condensable vapors like water, methanol, acetic acid, acetone, and heavy hydrocarbons start to form at around 300°C and 400°C [12]. These materials are generally easy to separate (off-gassing or combustion of the gases and cyclone filtration of the biochar) and typically not mixed with bio-oils. The liquid produced (50-78 wt. % yield) at higher temperatures is classified as pyrolysis liquid or bio-oil. It contains all the products of pyrolysis including water, sugars, phenols (monomeric and oligomeric), aldehydes, alcohols, acids (including carboxylic acids), and many other light oxygenated chemical species and moieties. The best description of this material is an emulsion of lignin-derived phenolic monomers/oligomers and carbohydrate-derived light oxygenates in an aqueous phase [12].

Bio-oil cannot be used directly as a transportation fuel today, but it can be used as industrial heating oil. Its diverse composition of molecules with differing molecular weights, high oxygen contents, high acidity of the aqueous phase, high viscosity and low volatility of the phenolic phase, and high reactivity of all the organic phases complicate deoxygenation and upgrading. Typically, these two processes are all that is required to produce petroleum based products. However, bio-oil is a different beast which requires new out-of-the-box thinking applications of techniques from other industries [28]. This suggests that the recovery of high-value chemicals should be the ultimate goal for researchers. The production cost of bio-oil is high when compared to a petroleum

refinery. Bio-oil itself is corrosive and instable during long term storage. However, fuel and value-added chemical production integrated into a biorefinery may be the key to economical and ultimately environmental success and commercial deployment [12].

The majority of lab-scale or pilot-based studies produce a whole bio-oil that contains the liquid components of biomass pyrolysis. However, advancements in fractionation technology have led to bio-oil fractionation systems that can separate the bio-oil into two to six different streams. This fractionation makes separation and upgrading easier because there are fewer chemicals that competing, aiding, or inhibiting reactions like there would be in distillation [29]. Most previous work has been done on a pilot scale system known as the Pyrolysis Demonstration Unit or PDU. This PDU can be operated with either nitrogen as a fluidization gas or air. Nitrogen fluidization of the fluidized bed is what most systems utilize to make their oil. Recent advancements here at ISU have led to an autothermal system which uses air as a fluidization gas. This allows for higher throughput or biomass feeding into the reactor as well as reducing the amount of energy required for heaters. Autothermal operation produces slightly different products from nitrogen fluidized reactors. This is most likely due to the consumption of some molecules as fuel to keep the reactor going. Another change that is evident is more oxygenated compounds dominate the fractions.

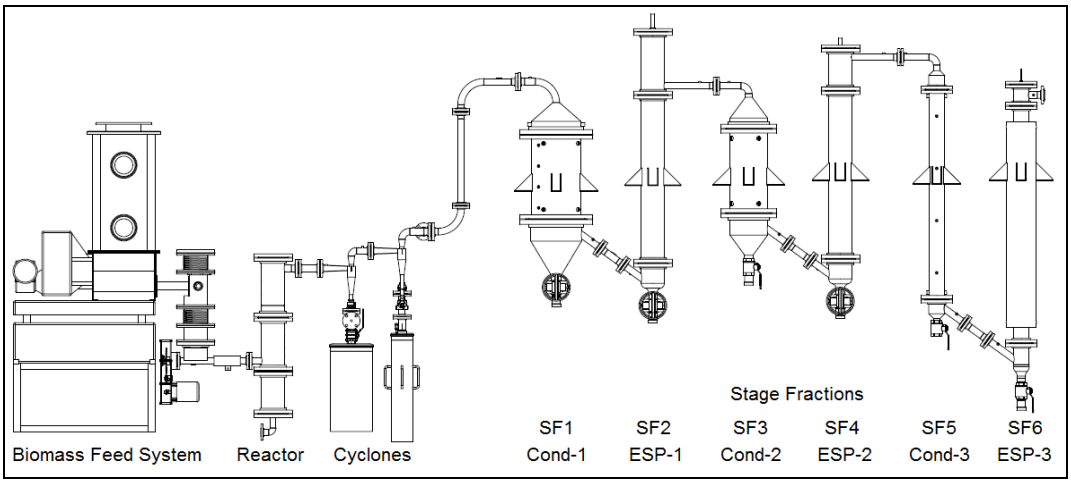

Figure 5. Current schematic of the Pyrolysis Demonstration Unit.

The current iteration of the PDU has three condensers and three electrostatic precipitators (ESP)s paired to separate the pyrolysis stream by dew-points [30, 31]. The first set of condensers and ESPs are labeled as Stage Fraction one (SF1) and SF2. If the pyrolysis is occurring at 500°C, this condenser and ESP set is collecting bio-oil from 125-425°C. The design of the system recovers vapors or highly volatile compounds in the condenser. The ESP recovers aerosols or droplets of higher boiling compounds. Typically, oligomeric phenolic oil and soluble carbohydrates are captured in these first two stage fractions. These tar-like products have a very high viscosity and low volatility. It has been found that a simple 1:1 water wash of SF1 and SF2 yields a carbohydrate rich aqueous phase [32]. Although this wash also entrains slightly soluble phenols and other light oxygenated organics, the vast majority of the oligomeric material remains [33]. Stage Fractions three and four collect the liquid products from 70-125°C. Monomeric phenols abound in these two fractions. These two fractions are the most similar to fuel based products produced at the PDU. Finally, SF5 and SF6 are where the majority of the water from the biomass is collected at 10-70°C. Acetic acid dominates these fractions as the most abundant organic compound.

Acetic Acid

Properties of acetic acid

Acetic acid has been a useful chemical since time immemorial. The first recorded report of acetic acid (ethanoic acid) as vinegar is reported to be dated earlier than 3000 B.C. Ancient Egyptians utilized it to pickle consumables for long term storage. Vinegar is a dilute solution of acetic acid; 3-20% by volume with water. When concentrated it is known as glacial acetic acid; a colorless, liquid, organic compound. It is the second simplest carboxylic acid (next to formic acid) and has a sour taste and acrid smell. Acetic acid is a weak acid (it only partially dissociates in solution) and is corrosive. Acetic acid is miscible with water, alcohols, glycerol, ethers, and carbon tetrachloride. It is insoluble only in carbon disulfide [34]. Its structure contains a methyl ($-CH_3$), carboxyl (=CO), and an acidic hydroxyl (-OH) group. When covalently bonded together, the methyl and carboxyl group are collectively known as an acetyl group.

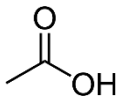

Figure 6. Structure of acetic acid.

Table 1. Acetic Acid Properties [34, 35].

Chemical Formula	$C_2H_4O_2$ (CH_3COOH)
Molecular Weight (g/mol)	60.05
Melting Point (°C)	16.7
Boiling Point (°C)	118
Dissociation Constant	1.75×10^{-5}
Density (liquid) g/mL	1.053
Viscosity (cP)	1.155
pH (1.0M)	2.4
pKa	4.74

Manufacture of acetic acid

Until the late 1800's, acetic acid was derived from sugar fermentation to ethanol and finally, often unwelcome in the brewing process, oxidation to acetic acid. However, with the advent of wood (biomass) distillation (destructive distillation) in the late 19th century, an additional source of acetic acid was achieved. In 1916, the first plant to produce acetic acid chemically, not biologically, was dedicated. This process was based on acetylene hydrated to acetaldehyde, followed by an oxidation with air. This production process boomed with the support of the Tennessee Eastman Company, now a division of Eastman Chemical Company (a division of Eastman Kodak Company) using acetic acid to produce acetic anhydride and diketene [36, 37]. Currently, acetic acid is produced in bulk (75% worldwide) by methanol carbonylation with carbon monoxide[38]. The metal carbonyl containing catalysts used in this carbonylation are iodine, rhodium (Monsanto), and iridium (BP's Cativa) based [39, 40].

Annual acetic acid production in the world is around 2.12 X 10^9 kg, primarily derived from methanol and carbon monoxide. More specifically, the production of acetic acid from fossil fuel begins with the reforming of natural gas or gasification of coal to syngas. This syngas is then catalytically converted to methanol followed by catalytic carbonylation. It sells for $0.79/kg as a commodity chemical. It is also a major product from the pyrolysis of lignocellulosic biomass. However, it is not presently cost effective compared to production from fossil fuels [12, 41].

Biologically, acetic acid is a metabolite from sugar fermentation by several organisms. *Acetobacter aceti*, *Clostridium thermoaceticum*, and *Pachysolen tannophilus*. Their metabolic pathways can be utilized through acetone-butanol-ethanol (ABE)

fermentation. C-5 and C-6 sugars undergo acidogenesis to produce carboxylic acids and then proceed through solventogenesis while converting these acids to solvents such as acetone, butanol, and ethanol. Similarly, unicarbontrophs or acetogens convert carbon dioxide or mixtures of carbon monoxide and hydrogen to fatty acids, including acetic acid. Specifically, *Clostridium ljungdahlii* can co-metabolize carbon monoxide and hydrogen to form acetic acid and ethanol. Some advantages of anaerobic digestion include the use of non-sterile reaction vessels, product separation by outgassing, and simple equipment. Disadvantages are slow reaction rates and yields [12].

Utilization of acetic acid

Acetic acid has many uses in industry. It is important in the manufacture of polymers, most notably, polyvinyl acetate (plastic) and cellulose acetate (films). It is also used in various acetylated compounds, acetate rayon, plastics and rubber in tanning, laundry sour, printing calico and dyeing silk, acidulant and preservative in foods and pharmaceuticals, solvent for gums, resins, and volatile oils. It has even been used as a wart removing agent [34]. Acetylated wood for building also improves stability, including reduced swelling and shrinkage, as well as resistance to biological degradation. Esterification and/or acetylation of wood is usually accomplished with acetic anhydride, a product of acetic acid.

Over 60% of acetic acid (ethanoic acid) is used in the manufacture of vinyl acetate. Vinyl acetate is used as the basis of white glue, the lamination of wallboard, and latex paint. Polymers of vinyl acetate also form safety glass, films, and hot melt adhesives. About 15% of acetic acid produced is used in the production of acetic anhydride, a precursor to cellulose acetate. This compound is used to manufacture

different fibers, plastics, and films. Around 10% of acetic acid demand is for the production of ester solvents for inks, paints, and coatings. Another 10% is used to produce terephthalic acid and dimethyl terephthalate for fibers, resins, paints, coatings, and plastic manufacturing [12].

Levoglucosan

Properties of levoglucosan

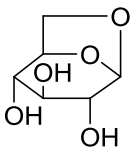

Figure 7. Structure of levoglucosan.

Levoglucosan (1, 6-Anhydro-β-glucopyranose) is an anhydrosugar derived from the pyrolysis of carbohydrates (starch and cellulose). It is an organic compound comprised of a six carbon ring. When purified, it presents itself as colorless crystals. Subsequent hydrolysis of levoglucosan generates glucose.

Table 2. Levoglucosan Properties [42].

Chemical Formula	$C_6H_{10}O_5$
Molecular Weight (g/mol)	162.14
Melting Point (°C)	183
Boiling Point (°C)	384
Density (solid) (g/cm^3)	1.688
Vapor Pressure (μPa)	24.1

Carbohydrates, like levoglucosan, can be classified as polyhydroxy ketones or aldehydes. In addition, the compounds hydrolyzed from them are also called carbohydrates, but more specifically, the smallest units are called monosaccharides. Other degrees of polymerization of these sugars are categorized as disaccharides,

oligosaccharides, and polysaccharides. They are held together by acetal or ketal bonds which can be easily broken by hydrolysis or thermochemical conditions. Many monosaccharides have isomers or epimers. Some isomers are or even contain chiral centers which make them ideal building blocks for the pharmaceutical industry. Chirality is when a molecule is not superimposable on its mirror image. These mirror compounds are known as enantiomers. Upon naming these mirror images, the D- (dextrorotatory) or L- (levorotatory) suffix is applied. In nature, the D- enantiomer dominates and is usually assumed if not specifically stated in literature [12].

Manufacture of levoglucosan

Hydrolysis of polysaccharides produce monosaccharides in an aqueous environment. However, if the thermochemical conversion of polysaccharides occurs in water-scarce gaseous environment, dehydrated sugars or anhydrosugars are produced. This depolymerization effectively produces a monosaccharide missing the water molecule inserted during aqueous-phase hydrolysis. Levoglucosan (1, 6-anhydro-β-D-glucopyranose) is one common anhydrosugar produced from the thermochemical conversion of cellulose (a polymer of glucose) or starch. In fact, the glycosidic bond of cellulose is preferentially cleaved, producing levoglucosan [43]. Levoglucosan degradation is suspected to undergo secondary reactions to form char and light gases, however, the majority of it escapes the reactor by evaporation. This evaporation is possible due to anhydrosugars possessing a small amount of vapor pressure. The β form is so designated due to the hydroxyl unit projecting upward from the anomeric carbon. In addition, monosaccharides can also form substituted furans, tetrahydrofurans, pyrans, and tetrahydropyrans [12, 44]. In the past, vacuum pyrolysis and flash vacuum pyrolysis of

starch, cellulose, lactose have produced levoglucosan (and its more oxidized version, levoglucosenone) [45]. It has been shown that cellulose in the presence of superheated steam at reduced pressure also produces levoglucosan. If the biomass is pretreated with acid, there is a substantial increase in the yield of levoglucosan and other sugars [15, 46-48]. This increase is due to the neutralization of alkali and alkaline earth metals (AAEM) that can catalyze ring scission in the cellulose structure and lead to side products other than levoglucosan [49, 50].

Cellulose readily depolymerizes during pyrolysis at temperatures of 350-600°C, yielding levoglucosan and other anhydrosugars. Levoglucosan is most notably used as a marker or chemical tracer for forest fires. Its low vapor pressure allows for its vaporization or formation of aerosols in gases produced during these events. Because of this, paleochemists use levoglucosan to monitor climate change due to fires from natural disasters.

Utilization of levoglucosan

Levoglucosan is utilized for its chiral center in the pharmaceutical and polymer industry [51, 52]. The internal acetal ring makes the molecule structurally rigid and locked in conformation. Mainly, the polymers produced contain unhydrolyzable glucose or dextrin-like polymers: 1, 6-α-glycans, polyurethanes, polyfunctional epoxide resins, and non-ionic surfactants. Specifically, levoglucosan has found use as a glycosyl donor in polysaccharide construction [15, 53]. It is also found in a complex ligand attached to platinum metal, "DIOXOP," which is a leukemia inhibiting agent and growth promoting substance for (+)-Biotin and Vitamin H. Levoglucosan also makes appearances in

macrolide antibiotics: nonesin, rosaramycin, and rifamycin [15]. It also is used for the formulation of insecticides and sugar alcohols.

Most bacteria cannot ferment anhydrosugars directly, however some species of yeasts and fungi can convert levoglucosan to ethanol utilizing their glycolysis pathway. The hydrolysis of levoglucosan protonates C1 and C6 carbons and results in the cleavage of the C1-oxygen bond and the addition of a water molecule to form glucose. Typically, sulfuric acid will aid in hydrolysis (Johnston), but a solid acid catalyst like a sulfonic acid-type resin is used in industry [54].

Interestingly, when ingested, levoglucosan does not convert to another compound because the human body cannot metabolize its locked structure. It is currently an expensive specialty chemical ($80-260/gram), however the price is decreasing. Typically, levoglucosan is produced by the fast-pyrolysis of acid-treated lignocellulose in yields of 20-30%. These yields can easily be obtained if metal ions like potassium can be removed or deactivated prior to pyrolysis. Some microorgansims, including some yeasts, can metabolize and ferment levoglucosan to citric acid or ethanol [12, 15].

Levoglucosan and other monosaccharides from pyrolysis can also be upgraded to specialty chemicals using aqueous phase processing or fermented via microorganisms using hybrid processing [55-57].

Research Goal

The ultimate goal of this research and dissertation is accomplish and describe the processes to reduce phenolic content and capture carbon from process and wastewater streams.

Dissertation Organization

This dissertation is composed of four chapters in addition to the Introduction (*Chapter 1*) and Conclusions and Future Work (*Chapter 6*). This dissertation will focus on the recovery of value-added materials from the two previously stated aqueous streams; the carbohydrate-rich stream from water extraction of SF1 and SF2 bio-oil fractions and the solubilized acetate stream from SF5 and SF6 bio-oil fractions. For simplification, SF2 and SF5 were chosen as the fractions to be studied due to higher contents of desirable compounds (pyrolytic sugar and acetic acid).

Chapter 2 is a literature review of some separations methodology for pyrolytic sugar and acetic acid. It also reviews mixing thermodynamics, adsorption theory and methodology, and some technoeconomics of the processes.

Chapter 3 is a manuscript discussing the results of the purification of pyrolytic sugar using resin technology. This is the first work done using hydrophobic polymeric resin to separate pyrolytic sugars from an aqueous stream generated from a fast pyrolyzer with fractionation technology.

Chapter 4 reveals and in-depth look at the characterization of SF5 from different feedstocks and pyrolyzer conditions. It provides a baseline for future researchers with which to compare their results. This chapter also details a liquid-liquid extraction of SF5 with a fatty acid, heptanoic acid. Based on the water content of SF5 (and SF6) it is imperative to capture all the carbon content in the aqueous phase prior to water treatment.

Chapter 5 outlines a set of experiments utilizing resin technology to separate acetic acid from SF5. A set of resins was selected to adsorb phenols and/or acetic acid from the final two stage fractions of the fast pyrolyzer system. This work descries the

equilibrium and kinetic adsorption of phenols and acetic acid. Adsorption isotherms, mass transfer coefficients, and activation energies were also calculated. Linear, Langmuir, and Freundlich models were also applied to determine appropriate fit to the data for comparison between resins.

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CHAPTER 2

LITERATURE REVIEW

As products of fast pyrolysis, acetic acid and levoglucosan are valuable chemicals to collect and utilize in in the quest to generate an economically feasible bio-oil through fractionation. It is imperative that these materials along with others be isolated from the process and wastewater streams to lower costs of the bio-refinery and increase the portfolio of products produced. Through separation and purification, these components can be further utilized as finished goods or raw materials for fermentation or upgrading.

There are a multitude of ways to separate and purify acetic acid and levoglucosan. This chapter is by no means an exhaustive review, but a subset of this vast information that was found to be informative to direct laboratory research. It details acetic acid and levoglucosan separation and purification citing some of the barriers faced and accomplishments made by scientists in the field.

Barriers for Purification and Upgrading of Acetic Acid and Levoglucosan

There are three major groups of fermentation inhibitors in bio-oil. Aliphatic acids (acetic, formic, and levulinic acid), furan derivatives like furfural and 5-hydroxymethylfurfural (5-HMF), and phenolic compounds (phenol, p-hydroxybenzoic acid, and vanillin) are all major species that researchers target for removal from bio-oils for use or to aid in purification and upgrading.

Acetic acid acts as an inhibitor to fermentation above a threshold of 0.5g/L [1]. Hardwoods release 6-10g/L of acetic acid from dilute acid pretreatment of biomass while

softwoods release 2-4g/L due to their lack of acetate groups in their structure. Steam can easily remove acetic acid produced during pretreatment. Despite obtaining acetic acid, a disadvantage of pretreatment is the requirement of neutralization of the acidified biomass. Typically, inexpensive calcium hydroxide (lime) is employed as a base, but it produces calcium sulfate (gypsum) as product. Gypsum, a solid, is of low value and adds to the waste stream of the refinery [2]. Other forms of pretreatment are ammonia fiber explosion and the use of organic solvents. These have distinct advantages and drawbacks. Evaporation, over-liming with calcium hydroxide, activated carbon adsorption, solvent extraction, enzymatic detoxification, and ion exchange resins are just some of the explored methods for the removal of inhibitors or detoxification of bio-oil. Water and phenolic compounds also are a major barrier to acetic acid sequestration.

For carbohydrates, dilute acid hydrolysis of biomass can be performed at high temperatures which causes decomposition of cellulosic sugars and yields acetic acid and furfural [2-4]. Levoglucosan is also converted to glucose in this case. Hydrolysis can also be performed enzymatically [5]. In addition, the breakdown products from the hydrolysis of hemicellulose, acetic acid and furfural, inhibit fermentation. Traditional detoxification methods such as the addition of activated carbon, organic solvent extraction, ion exchange resins, ion exclusion membranes, molecular sieves, over-liming, steam stripping, and fermentation organism adaptation can be costly [6]. For instance, in order to use the hydrolyzed material, at least enzymatically, the sulfuric acid used as the hydrolysis acid must be neutralized. This is commonly performed with calcium hydroxide, also producing gypsum. In pyrolysis, as discussed in the previous chapter, water soluble inhibitors like furans and phenols complicate levoglucosan purification.

Our group has explored many of these avenues in researching acetic acid and levoglucosan. The most common methods employed by researchers will be described herein. Two of these methods will specifically be highlighted in later chapters of this manuscript: organic solvent extraction and adsorption resins.

Acetic Acid

Acetic acid separation and purification can be divided into five main areas: distillation, extraction, precipitation, membrane separation, and chromatography. There are also a few hybridized processes and novel approaches that will also be mentioned. As stated in the introductory chapter, acetic acid has been utilized throughout history. However, since its production both synthetically and biologically, researchers have been trying to find ways to sequester every percent of material produced [7, 8].

Distillation

Distillation is probably the most prominent way to separate/purify volatile compounds. Distillation depends on differences in boiling points which may require utilizing azeotroping or entraining compounds and reactive distillation in some instances to obtain pure chemicals or cuts [9]. In essence, it is a method of separating mixtures based on differences in volatilities. Depending on water content and chemical composition, the difficulty varies greatly.

The structure of organic acids make is so that the carbonyl has a strong electron-withdrawing or induction effect, contributing to hydrogen bonding. Also, a dimeric effect occurs with hydrogen bonding between two carboxylic acids, where one acidic proton on one molecule will make a hydrogen bond with another carboxylic acid's

carbonyl oxygen. Most acids have a higher boiling point than water, making both reactive and extractive distillations competitive for organic acid removal. However, vacuum distillation is commonly used for industrial applications for cost reduction purposes.

Today, the synthesis of glacial acetic acid is usually performed using the BP's CATIVA process. In this process, methanol is carbonylated by carbon monoxide in the presence of an iridium catalyst. The glacial acetic acid is purified by flash distillation, drying, a light ends distillation, and finally a heavy ends distillation. The impurities consisting of formic acid, aldehydes, and water are removed by successive distillation. Other impurities are acetaldehyde, acetone, and methyl ethyl ketone. These can further react through aldol condensation or multi-carbon alkyl iodides created by the iodide catalyst promotor in the process.

Although needed in the CATIVA process at concentrations of <5%, water is not a large part of the final stream. Many impurities have also been reduced by using an iridium catalyst rather than the first generation rhodium catalyst developed by Monsanto. It becomes cost prohibitive if large quantities of water are to be removed along with other light oxygenates due to diminishing returns of the desired material (acetic acid) each round. The same is true with SF5 and SF6 bio-oil fractions from fast pyrolysis of biomass. Water content is high and acetic acid concentration is low, making distillation difficult.

Distillation is effective at high concentrations of organic acids, but inefficient at low concentrations. It becomes even more inefficient when the azeotropic point is neared.

Entrainers

Many researchers have used entrainers to extract acetic acid. Entrainers essentially aid in distillation, by carrying along other chemicals that may be difficult to distill into the vapor phase.

One research team [10] explored the use of six different solvents or entrainers to aid with their distillation: methyl *tertiary*-butyl ether, isopropyl acetate, *n*-propyl acetate, ethyl acetate, methyl propyl ketone, and methyl isobutyl ketone (MIBK). They found that originally it took 280 kW per 100/kg/hr to distill a 10 wt. % acetic acid solution. However, when any of these entrainers listed were used, the power usage dropped to 260 kW. The same result occurred when they distilled 35 wt. % acetic acid. The power required for the rectification column dropped from 260 kW to 180 kW. Methyl *tertiary*-butyl ether was also used for the "dehydration" agent of acetic acid by Li et al. [11]. They used multi-effect pressurized distillation, azeotropic distillation, and liquid-liquid extraction methods in their study. Other solvents tested were ethylene dichloride, propyl acetate, butyl acetate, vinyl acetate, isobutyl acetate, and diisopropyl ether. By using this multitude of methods and solvents, Li was able to formulate a Techno-Economic Analysis (TEA) on acetic acid recovery systems.

Ethyl acetate, diethyl ether, and hexane were used to successfully extract acetic acid by Jipa et al. [12]. Interestingly, they suggested that for acetic acid concentrations lower that 40%, liquid-liquid extractions should be used based on economic calculations. Solutions in the range of 50-70% should be ideal candidates for extractive distillation. Kalaichelvi agrees with this assessment and suggests solutions ranging from 40-70%

should be distilled using entrainment. They used ethyl acetate and MIBK as their solvents [13].

Many other teams have used a variety of solvents to aid with distillation. A patent filed by Berg in 1987 used carboxylic acids ranging from hexanoic to neodecanoic to extract formic acid from an acetic acid solution [14]. Gadekar et al. used benzene, ethyl acetate, and toluene as entrainers [15]. Mahfud and coworkers employed a tetrahydrofuran and trioctylamine system to extract organic acids from bio-oil [16]. Heterogeneous azeotropic distillation was utilized to extract acetic acid from water using *p*-xylene by Pirola et al. [17].

Reactive Distillation

In efforts to remove acetic acid from solution by synthesis of a new compound, Bianchi et al. esterified acetic acid with butanol creating butyl acetate. This is a reversible process and the organic acid was obtained after hydrolysis [18]. Saha and fellow researchers also used *n*-butanol to reactively distill butyl acetate from a 30% acetic acid solution [19]. It was also found that isoamyl alcohol can be used to create a suitable ester for distillation as well. Interestingly, in this study, the esters were cleaved using an acidic ion-exchange resin.

Although easily and simply performed, recovery and concentration of a desired carboxylic acid product can represent up to 60% of the cost of the process [11].

Liquid-liquid extractions

Distribution coefficients of carboxylic acids between aqueous and organic phases are quite low. However, if extractants are added, separation becomes easier. These low coefficients are due to acid dissociation in aqueous solutions and the formed ionic species

having low solubility in non-polar solvents. For example, the distribution coefficient with ether and acetic acid in solution with water is 0.14 whereas an extractant (aliphatic amine salt) that complexes with acetic acid yields a value of 1.97 [20, 21].

Liquid-liquid extractions are a very common method used to separate compounds by their relative solubility in immiscible liquids. There are three main types of extractions: solvent, reactive / complexing, and ionic liquid.

Solvent extractions are a low-energy consuming, efficient separation technology. They are very robust and can even be used for in situ product removal. Extractions have many attractive attributes, but the cost of solvents and complexing agents must be carefully calculated. Although it is best to recover all materials for reuse, a slight drop in recovery yield will be seen over time due to laboratory error.

Jipa et al. [12] used ethyl acetate, diethyl ether, diethyl ether-hexane to separate acetic acid from fermentation broths. It was found that ethyl acetate had a better effect than the other two methods employed. As already stated, they found that solutions that contain less than 40% acetic acid are ideal candidates for liquid-liquid extraction. Haque et al. [22] agree with these findings and employed the used of n-butanol, isobutanol, amyl alcohol, ethyl acetate, and ethyl ether to extract acetic acid from an aqueous solution. Ince and Kirbaslar used butyl acetate to extract acetic acid. They also performed a literature review on current solvents in use for extractions [23]. An exhaustive literature review was also performed by the Environmental Protection Agency (EPA) on every historical solvent used to extract acetic acid and their efficiencies [24]. Finally, Ijmker and fellow researchers [25] employed the use of long-chain fatty acids, specifically

heptanoic acid, to extract dilute acetic acid from an aqueous solution. This extraction will be discussed more in depth in the second research chapter of this dissertation.

Reactive and complexing extractions

Reactive extractions convert the desired product to another compound for easier extraction. Typical examples are esterification and hydrolysis. The products of these reactions are then separated by a rectification column, enhancing their efficiency. Common extractants employed today are phosphorus compounds, hydrocarbon solvents, and aliphatic amines. Aliphatic amines are currently the go to chemical for separating organic acids from aqueous solutions. Reactive liquid-liquid extractions can also be classified as reactive distillations, however the initial compound forming reaction is typically done at lower temperatures than distillation.

Reactive extraction or separation intensification, operates between chemical (solute and extractant) and physical phenomena (diffusion and solubilization). It's based on interfacial and bulk reactions between the solute and extractant. Fundamentally, the extractant could be the solvent itself or could be soluble in the solvent phase. When dealing with the physical phenomena side, a solvent must possess low solubility in another phase, as well as have high selectivity and chemical inertia (so to reduce solute loss) [26, 27]. Extracted compounds that are the products of reactive distillation could be: chelates, solvated compounds, ion-pair compounds, or any compounds that are physically bound to another. On the other hand, extractants could be: chelating agents, organophosphoric compounds, solvating agents (including reactive organic solvents), and cyclic derivatives such as crown ethers and calixarenes. Of course, the solubility, mass

transfer limiting step and reaction type/rate/mechanism all play a role in reactive extraction [20].

Organophosphoric derivatives, aliphatic amines and their salts also greatly increased the success at distillation of carboxylic acids [20, 26-31]. Eggeman et al. successfully formed an amine complex with acetic acid in a fermentation broth and were able to extract the resulting pure compound [32]. Similarly, Lei also used a tributylamine complex with great success [33]. However, both of these research teams used patents from 1943 and 1983 detailing this same complex for use with acetic acid extraction [34, 35].

Golob and coworkers also formed a complex with acetic acid using trioctylphosphine oxide. However, they found that using this method was only economically feasible with the acetic acid concentration was greater than that of 3% [36].

Ionic liquid

Ionic liquid extractions utilize ionic liquids or organic salts for separation. These salts are non-volatile, non-flammable, and liquid over a wide range of temperatures. They are considered green chemicals and are chemically stable, have low viscosities, and high densities when compared to organic solvents. Ionic liquids possess the properties of high distribution coefficients and selectivity, low miscibility with the mother liquor, and non-toxicity. They possess highly sought after attributes for chemical processes today. For these reasons, ionic liquids are considered to be short cycle, or allow for faster mass transfers between phases. Smirnova et al. [37] used an ionic liquid in conjunction a crown ether for the separation of amino acids.

Interestingly, most of the data obtained suggest that acidity in reactive extraction processes control the separation efficiency [20].

Precipitation

Precipitation is a tried and true method to efficiently recover organic acids from fermentation broth. Typically, the broth is filtered to remove any impurities. Then, if sufficiently concentrated, calcium carbonate or calcium hydroxide is added until precipitation of the carboxylic acid salt occurs. Finally, after filtration, sulfuric acid is added to acidify the salt to obtain the carboxylic acids. Despite the ease of these steps, a low value salt, calcium sulfate (gypsum) is formed and has to be disposed of. In an effort to reduce calcium waste, ammonia has been gaining traction in the scientific community as a precipitation agent [38]. Ammonia is used to form ammonium acetate, which can be concentrated. The salt is then pressurized with carbon dioxide, reforming the acetic acid and ammonia.

In spite of the disadvantage of salt formation, there are three main advantages to organic acid precipitation. First, there are no phase transitions to separate. Product purity is high in addition to highly selective towards specific compounds [7]. However, in the case of bio-oil there are more compounds other than the carboxylic acids that precipitate when pH is changed. Typically, phenols are one of these species. Once the compounds drop out of solution, it is very difficult to utilize them for end products and they can hinder further purifications down the line.

Membrane separations

A membrane is a thin barrier which permits adaptable and selective mass transport of materials (solvents or solutes) across a barrier. This barrier achieves physical

separation and enrichment of the solvent (permeate) and solute (retentate) streams. For this reason, high purities and yields can be obtained. There are six major areas of interest in membrane separations: electrodialysis, reverse osmosis, nanofiltration, ultrafiltration, microfiltration, and pervaporation [39-42].

Membranes are usually made of organic polymers and inorganic ceramic materials. Polymeric membranes usually have less membrane resistance and thus, higher flux or permeability. They are usually cheaper than ceramic membranes as well. However, chemical and thermal stability is poor [43]. Membrane separations are high-energy consuming, usually requiring pumps and a vacuum. The membranes are very expensive and can foul easily. The separation efficiency also decreases as organic acid concentration increases [44, 45]. Electrical or chemical potential is what drives membrane separations [46].

Of these six methods, pervaporation is in use in our research group to recover organic acids from the acetate streams of the PDU. It is of interest because it allows for the separation of close-boiling substances, especially azeotropic species. However, fluxes, or permeabilities of pervaporation membranes are less than that 2,000 g/(m^2*h) which limits more development in this area of industry [41, 47].

Borneman et al. [48] utilized a polyethersulfone / polyvinylpyrrolidone membrane to separate polyphenols and pigment from apple juice. They found that its performance was better than a cellulose membrane. Kujawski et al. [49] also separated phenols using a membrane. However, the matrix was wastewater stream that contained acetone and phenol. The authors suggest that a hybrid system coupled with resin technology would provide better separation. Polyphenols were separated from cocoa seeds using

membranes by Sarmento et al. [50]. Han et al. [51] used an anion exchange membrane and found that it exhibited better performance that ion exchange resin.

A microporous polypropylene substrate with a sodium alginate active layer was able to separate 80% acetic acid aqueous solution at 50°C by Zhang et al. [52]. Manzak and Sonmezoglu used an emulsion type liquid membrane, a surfactant, a carrier, and a sodium carbonate additive; 86% of the total acetic acid in a solution was able to be separated in ten minutes [53]. Teella et al. [54] utilized a reverse osmosis membrane and nanofiltration to separate acetic acid. However, the resin kept fouling with guaiacol, damaging the membrane.

Novel acetic acid separations

Lou et al. [55] performed a solvent free extraction to extract acetic acid. Utilizing head space technology, they were able to purify small quantities of acetic acid. Rasrendra [56] used a continuous contact separator (centrifugal) to separate acetic acid with aliphatic tertiary amines (trioctylamine) mixed with 2-ethyl hexanol. However, this system only removed water efficiently. Many phenolics and light oxygenates were extracted with the acid. Carbon dioxide at 40 bar was used to acidify a fermentation broth that had calcium acetate in the mixture. Reyhanitash et al. [57] then used an ionic liquid and trioctylamine in n-octanol to extract the 1% acetic acid in solution.

In a simple experimental setup, Usman et al. [58] sonicated a model system of acetic acid, water, and ethyl acetate. It was found that sonication of the mixture, enabled the extraction of acetic acid in the ethyl acetate layer. Dickey et al. [59] utilized vaporization by an ultrasonic spray nozzle and condensation of an acetol and acetic acid

mixture to try and separate the two compounds. Despite the effort, separation was unable to be achieved.

Van Osch and coworkers [60] successfully used deep eutectic solvents that enabled hydrophobic interactions between decanoic acid, acetic acid, and ammonium salts. Similarly, Yao et al. [61] formed hydrophobic micelles made of tributylphosphate, a mixture of glycols, and dimethione and used them in a cloud point extraction of acetic acid.

Fractional freezing also is a method of acetic acid purification. Acetic acid freezes at 16.6°C while water freezes at 0°C. Water can be decanted from this binary system quite easily. The eutectic point at -26.7°C where the solution's individual components look crystalline gives rise to the name glacial acetic acid. Although incorrect, some sources regard fractional freezing as the derivation of glacial acetic acid's namesake.

Chromatography

Finally, chromatography is a viable option to separate carboxylic acids from different media. This will be the topic of chapter five. This method relies on ion-exchange or adsorptive properties of the resin chosen for a study. Resins are a porous polymer that are an insoluble matrix (or support structure) in the form of small microbeads. The microbeads' porosities allow for a large surface area on or in which compounds can absorb and adsorb. Some are designed to be used in amino acid synthesis by binding the first amino acid of a peptide sequence and anchoring it until all remaining amino acids have been added [62].

When selecting a resin, a researcher looks for one that is stable, insoluble, requires a low amount of energy for adsorption (or desorption), has a good selectivity or selectivity, and will not cause a phase separation of the eluent or stirred batch. In addition, the properties of high capacity, quick (and low consumption) regeneration time, are all beneficial traits when selecting a resin [63].

There are two main categories of resin available to researchers today: macroporous adsorption resin and ion-exchange resins. Macroporous adsorption resins rely on hydrogen bonding, dipole ion interactions, and van der Waal's forces to adsorb materials. Ion-exchange resins are often substituted with acidic or basic groups. Their exchange ions, particle size, and degree of cross-linking all play a role in their binding properties [64]. The specific properties of the macroporous and ion-exchange resins used in this manuscript will be detailed in the third and fifth chapters.

A disadvantage to chromatography is the generation of a large amount of liquid volume. Usually, this volume will have to be removed using a lot of the bio-refinery's energy. Ion-exchange resins will also consume large amounts of salts for regeneration. Both resins suffer that their exchange capacity will be diminished over time with repeated use [65].

Macroporous Resin

Yagyu et al. also utilized resins to form ethyl acetate from ethanol in what they called catalytic dehydrative esterification [66]. This allowed for polystyrene (PS)-supported sulfonic acids or homogenous salts to aid in continuous extraction of acetic acid.

Although not technically manufactured resins, a more natural type of adsorbent material is activated carbon. Ahsan et al. had success in separation of acetic acid using activated carbon as well as an amine based resin resulting in a 66-84% yield after desorption with sodium hydroxide. They also found that tertiary amine functionalized resins are better at adsorption than secondary and primary amines [67, 68]. Anasthas and Gaikar utilized tertiary and quaternary amine modified polystyrene-divinylbenzene (PS-DVB) to separate acetic acid from solution of ethanol and ethyl acetate [69].

Polyvinylpyrrolidone has been used with great success in the brewing industry as a clarifying agent [70]. It was also used by Anderson and Sowers [71] to bind plant phenols. Gray [72] also used polyvinylpyrrolidone to adsorb polyphenols. Depending on the molecular weight of the resin and the amount of crosslinking; this versatile resin material can function as a clarifying agent (acting as a nucleation site for precipitation) or as packed filter bed with higher crosslinked species.

Ion-Exchange Resin

As discussed earlier, Saha [19] used ion-exchange resin to cleave butyl acetate to yield acetic acid. Chen et al. [73] used ion-exchange resins (both anion and cation-based) to separate model compound solutions of monosaccharides, organic acids, and phenolic compounds. Organic acids were converted to salts by Patton et al. [74] and then ion-exchange resins were used to produce the acidic species again after separation. Sukhbaatar et al. [75] used a free base (quaternary ammonia) ion-exchange resin to convert insoluble calcium acid salts to a soluble sodium salt after calcium oxide precipitation.

Interestingly, in order to reduce the liquid volume required for resin purification, Cabrera et al. [76] used alcohol and pressurized carbon dioxide to desorb adsorbed organic acid salts. This was done by creating a carbonic acid that would replace the adsorbed salt. Once pressure was released, the carbonic acid would easily evaporate.

Levoglucosan

As suggested in many dissertations and journal articles, the recovery of pyrolytic sugars from bio-oil and their subsequent conversion into liquid drop-in fuels and high value products is a viable approach to the economic success of bio-oil refineries [77-81]. High value products from the phenols could include green diesel, adhesives, resins, as well as asphalt. It has been suggested that the soluble carbohydrates could provide a good substrate for fermentation [82, 83]and the phenolic oligomers could be utilized as a substitute for bitumen in asphalt binders [84].

Levoglucosan or more generally, carbohydrate separation and purification can be divided into four main areas: 1) precipitation, crystallization, and extraction, 2) derivatization, 3) high pressure chromatography, and 4) low pressure chromatography. Of course, there are many novel and hybrid processes as well. This section will discuss separation and purification as it relates to unprotected/neutral carbohydrates. There are also different techniques and opportunities available to the researcher for unprotected/charged and protected carbohydrates.

Precipitation, crystallization, and extraction

Simple precipitation of carbohydrates has occurred with additions of ammonium sulfate, polyethylene glycol, trichloroacetic acid, or water-miscible organic solvents.

Typically, a form of separation or purification has already been performed. In most cases the process preceding precipitation or crystallization is the removal of ionic and hydrophobic constituents by resin technology. These technologies will be discussed further in this section [85].

Due to the limited solubility of carbohydrates in mixtures of aqueous/organic matrices; additions of organic solvents (ethanol or acetone) to aqueous solutions of carbohydrates induce precipitation or crystallization. The concentration of solvent is increased until the cloud point. The cloud point is the point at which a clear solution becomes cloudy. The aqueous/organic solution is then cooled to 4°C and left overnight. In most cases where the matrix is devoid of crystallization inhibitors, crystal formation occurs. Amorphous precipitations will also be found depending on the sugar in question. It is important to note, monosaccharides and disaccharides will crystallize. Polysaccharides will be recovered as precipitates. The crystals or precipitations can be recovered by filtration or centrifugation [86].

Markande et al. [87] performed studies on the purity required by a sugar solution to begin nucleation and crystallization. It has also been found by our group that trituration with cold methanol induces crystallization from an amorphous mass of cleaned pyrolytic sugar (the product of chapter three). If precipitation does not occur, rotary evaporation of the sample will aid in water removal and help with the purification.

Simple extraction with water also yields a carbohydrate (levoglucosan) rich solution [88]. However, some fermentation inhibitors and other resinous products are slightly water soluble. This is due to the polarity of bio-oils. Carbonyl species along with alcohols, esters and phenols contribute to this polarity. Rover has found, however, as

increasing amounts of water is added, phase separation occurs between the polar compounds (including sugars) and the non-polar compounds (lignin-derived) [80, 89, 90]. Bennett et al. [91] has also phase separated their pyrolysis oil. However, after separation, hydrolysis was performed and then a water extraction was used to obtain the hydrolyzed sugars [91]. Saccharification, then filtration was demonstrated by Kaldstrom et al. to obtain pyrolytic sugars [92]. Peniston [93] performed a water extraction followed by over-liming to purify his sugar rich solution.

In a patent, Arnulf [94] performed a liquid-liquid extraction using water and then a subsequent distillation and crystallization of levoglucosan from pyrolytic degradation products using MIBK. Similarly, using the same solvent system, Moens over-limed pyrolysis oil and then purified levoglucosan using successive MIBK and ethyl acetate extractions and washes [95, 96]. Ethanol / water extraction of polyphenols was successful by Nawaz et al. to isolate sugars from pyrolysis oil [97]. Organic solvents were also employed by Wang et al. for extraction of sugars and furans. The solvents tested were ethyl acetate, ethanol, methanol, dichloromethane, and diols. In addition, High Pressure Liquid Chromatography (HPLC) was also used to separate the sugars from the furan constituents [98, 99]. Lian et al, used ethyl acetate and bio-diesel blends to extract the sugar fraction. This fraction was then hydrolyzed followed by a detoxification and neutralization by activated carbon and barium sulfate [100].

Derivatization

The goal of derivatization in organic chemistry is to positively identify a compound or class of compounds. However, in analytical chemistry, derivatization improves detection and facilitates separation. Improved detection can be obtained by

adding ultraviolet active chromophores, radio, and fluorescent labels. Gel Permeation Chromatography (GPC), reversed phase HPLC, and ion-exchange HPLC can be utilized to separate sugars that have been derivatized. Biotinylated (biotin derivatized) can be separated by reversed-phase HPLC or affinity chromatography [101-108].

With sugars, the most common way to add these labels is through reductive amination. However, the saccharide must be a reducing sugar. Levoglucosan is not a reducing sugar as its reducing end is locked in the bridge of the compound.

Abou-Yousef and Hassan [109] used acidic resin and 2-butanone solvent to extract sugars from the aqueous phase of bio-oil. Then, MIBK and formic acid were used to convert the sugars to furan derivatives.

Ruiz-Matute et al. [110] converted different classes of sugars to various derivatives. They converted common neutral sugars to ethers, esters, oximes, alditol acetates, aldonitriles, and dithioacetals. Amino and iminosugars were also targeted materials. Sugar acids were acetylated, reductively hydrolyzed, and turned into trimethylsilyl and heptafluorobutyrate derivatives. This group also looked at the characteristics of the Maillard reaction (browning reaction) vs. Amadori compounds (rearrangements of the Maillard reaction) and their intermediates.

High pressure chromatography

GPC using an HPLC is often employed to separate many carbohydrate species. Carbohydrate detection on these systems use refractive index, <200 nm ultraviolet absorbance, viscosity, pulsed amperimetric, and post-column derivatization for identification.

It has been found that fractionation by anion-exchange HPLC can be successful at pH 13 for separating sugars. At this pH, hydroxyl groups on carbohydrates can be ionized [102, 104]. Subsequent neutralization yields the carbohydrate product.

As previously mentioned, Wang et al. utilized HPLC systems for the separation of sugars and furans [98, 99]. Johnston et al. also developed a robust method for separation and identification of water soluble and hydrolysable pyrolytic sugars [111]. This method is currently employed in our laboratory today.

Low pressure chromatography

Low pressure chromatography is considered to be a passive process. Many neutral (uncharged) carbohydrates can be recovered using ion-exchange resins, hydrophobic (macroporous) resins (PS-based), or membrane separation. Most ionic impurities can be removed using an ion-exchange resin. The neutral carbohydrate itself will elute while the ionic contaminants will remain bound to the resin. Similarly, hydrophobic resins will adsorb hydrophobic material on porous PS beads, allowing the hydrophilic carbohydrate to pass through. As with all resins, their capacity must be determined prior to scaling. However, desalting steps may be required when using ion-exchange resins.

Additionally, gel permeation, partition, and affinity chromatography can be considered passive chromatography when not coupled with HPLC. Low pressure GPC is almost generally restricted to small samples. Many of the samples eluted through the low resolution column require a phenol-sulfuric acid or anthrone assay for identification [112]. Thin layer chromatography can also be used to separate multiple carbohydrates in a complex mixture [113].

Activated carbon was used by Otero et al. [114]and Caqueret et al. [115] to remove polyphenols from solutions with sugar present. As discussed earlier, polyvinylpyrrolidone was also used as a gel-like resin for phenol complexation [70]. Damnjanovic et al. [116] utilized β and ZSM-5 zeolites as adsorbents for sugar and phenol separation.

Modified resins were also employed to separation sugar from bio-oil. Amide functionalized resins were used in a patent by Ford for phenol removal [117]. Zhang et al. [118] also used aminated resins for adsorption of phenol. Acrylic backbone resins were also synthesized and demonstrated to remove phenols from solution. Phenols in apple juice concentrate were removed by Kammerer et al. [119]. Zeng et al. [120] prepared methylmethacrylate / DVB and ethylene glycol / dimethacrylate resins to remove phenols from wastewater.

PS-DVB resins were used by many research teams for phenol removal like Diez et al. [121], Otero et al. [114], and Chen et al. [73]. Palikova adsorbed anthocyanins from honeysuckle plants. Anthocyanins are flavonoids or pigments the change color depending on pH. A common experiment with flavonoids are their employment as pH indicators from red cabbage anthocyanins. Wang et al. [122] and Scordino et al. [123] also adsorbed anthocyanins . In addition, hydroxycinnamic acids were adsorbed as well [123]. Antioxidants were removed from winery waste by Soto et al. [124]. Zhang et al. [118, 125] also performed studies on competitive binding between compounds in complex phenolic mixtures based on pore size and cross-linking properties.

Interestingly, mycotoxins, a notoriously difficult toxin to remove from raw materials were removed by PS-DVB resin by Shan et al. [126].

Novel levoglucosan separations

Taking advantage of the slight vapor pressure of anhydrosugars, Oja and Suuberg [127] used sublimation to isolate anhydrosugars from model compound matrices.

Chromatography

Chromatography, or the separation of materials through a medium, was first described by Tswett in 1906 [128]. The actual separation depends upon differences in migration velocities due to chemical potentials across phase boundaries (gas, liquid, and solid) and partitioning behavior between the mobile and stationary portions of the chromatography system. The migration velocities of the solutes can also be affected by attraction forces to the solid phase: adsorption, complex formation, ion/ligand exchange, electrostatic effects, steric effects, and interactions between other solutes (salting-out).

Separation efficiency depends on column loading and resolution of the compound of interest (lack of overlapping or co-elution). Water is a commonly used solvent because it is environmentally benign, non-hazardous, inexpensive, and relatively easy to separate many compounds. Gradients with water, pH buffer, and organic solvents can also be employed in some cases.

Adsorption

Adsorption is the adhesion of molecules on a solid surface. In chromatography, this adhesion is usually a reversible process, however, it can be irreversible as well. As discussed earlier, weak interactions such as van der Waals forces, hydrogen bonding, hydrophobic-hydrophilic interactions, complex formation, and ion/ligand exchange aid the adhesion of molecules on the surface. This adhesion is what allows for the slowing of

migration velocities in chromatography. The higher the attraction or adhesion forces, the less eluent volume is required for a separation.

Size-exclusion

Size exclusion chromatography or GPC is based on the hydrodynamic radii of molecules. Large molecules are excluded from entering the pores of the solid phase and elute first. Smaller molecules enter the pores of the solid phase and take longer to navigate through the solid phase's network of void space. The degree of swelling of the solid phase (equivalent to the size of the pores) depends on the extent of cross-linking between solid phase materials.

Different types of size exclusion solid phases are dextran cross-linked with epichlorohydrin, agarose, cross-linked polyacrylamide [129]. There are some neutral stationary phases as well. These stationary phases are functionalized Polystyrene-Divinylbenzene (PS-DVB) resins and silica packed columns [130].

Ion-exclusion

Ion-exclusion is the electrostatic repulsion between charged solution ions with the groups on the solid surface or stationary phase. The repulsion between negative ions in solution and negative ions on the stationary phase causes positive ions to stay in solution to maintain electroneutrality. This electroneutrality zone forms a membrane or Donnan effect membrane. This membrane is only permeated by neutral, non-ionized species. The size or radius of the membrane is dictated by ionic strength of the solution. Ion-exchange not based on interchange of ions but partitions due to ion-exclusion and other interactions [131].

The structure of ion-exclusion stationary phases is mainly polymeric beads that can be non-porous or porous. Non-porous beads form gel type consistencies and have higher capacity [132]. They are also usually lower in price. Zeolites and silicates can also form ion-exclusion stationary phases [133]. These stationary phases are microporous and less sensitive to fouling.

A subset of ion-exclusion chromatography is ion-exchange chromatography. There are four groups of resins utilized in ion-exchange chromatography based on functionality of the resin backbone: strong-acid cation (SAC), weak-acid cation (WAC), strong-base anion (SBA), and weak-base anion (WBA).

SAC resins are functionalized with sulfonic acid and are typically inexpensive [6]. The backbone of these resins are typically PS cross-linked with 2-20% DVB [134]. The amount of crosslinking affects the capacity and shrinking/swelling behavior of the separation. Their only drawback is that they susceptible to degradation by oxidation. One fact of note is when sulfonic acid is neutralized with calcium, it enables it to form complexes with carbohydrates [135].

WAC resins are functionalized with a carboxylic group. Their backbones are polyacrylic or polymethacrylic acid structures cross-linked with DVB. These resins are also susceptible to oxidation.

SBA have a quaternary ammonium functionality while WBA has a polyamine moiety, usually consisting of a pyridine, imidazole, or tertiary amine functionality. Both are PS or acrylic-based.

Review Summary

This manuscript will detail 1) the polymeric macroporous resin adsorption of phenols from a pyrolytic sugar solution to obtain purified levoglucosan, 2) liquid-liquid extraction of acetic acid with long chain fatty acids, and 3) ion-exchange resin adsorption of acetic acid.

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CHAPTER 3

PURIFICATION OF PYROLYTIC SUGAR FROM BIO-OIL FRACTIONS

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Abstract

Productive use of all streams of fractionated bio-oil will be important to the development of a biorefinery based on the fast pyrolysis of biomass. Fractionation technology separates bio-oil into water soluble sugars, water insoluble phenolic monomers, dimers, and oligomers, and aqueous phases containing water soluble, light oxygenates. The major species in our first two stage fractions are water soluble sugars and water insoluble phenols. An aqueous phase extraction removes the majority of the pyrolytic sugars, however phenolic monomers are slightly soluble in water depending on the phenolic species. Removal of the phenolic monomers from the aqueous phase is necessary before the sugars can undergo crystallization or utilization for biological and catalytic upgrading.

The primary goal of this research is to demonstrate the effectiveness of a polymeric resin adsorbent for the removal of bio-oil phenolic species from the aqueous phase extraction of the second stage fraction of fractionated fast pyrolysis bio-oil. We have identified a polymeric adsorbent resin, Sepabeads SP207, which sufficiently cleans or purifies the sugar solution. Our results show an increase of sugar purity to 97.64 ± 0.65 wt. % on a dry basis (db) from 56.58 ± 0.65 wt. % db in the raw pyrolytic sugar syrup. The resin has high selectivity (affinity) for phenols and other aromatic

compounds, high adsorption capacity, low cost, and ease of regeneration [1]. Phenol concentrations of the pyrolytic sugar syrup have been reduced from 33.59 ± 4.37 wt. % to 0.82 ± 0.11 wt. % utilizing this resin technology. Some sugar is adsorbed by the resin, but can easily be recovered by regeneration. Resin purification of the pyrolytic sugar stream has shown favorable results with almost complete removal of the sugar impurities.

Introduction

The Department of Energy has identified a series of platform chemicals that could be derived from biorenewables as well as secondary chemicals that could be used to replace commodity chemicals in the near future [2, 3]. One chemical platform identified is carbohydrates. Our research group has taken a unique route to make carbohydrates a viable option to produce secondary or commodity chemicals while producing a wide variety of other platform chemicals.

Cellulosic sugar can be produced through acid or enzymatic hydrolysis, solvent liquefaction, or pyrolysis [3-8]. We employ the thermochemical conversion of lignocellulosic biomass by fast pyrolysis to produce bio-oil and bio-oil products. Fast pyrolysis is the thermal depolymerization and decomposition of lignocellulosic biomass, typically in the absence of oxygen. Traditionally, a whole bio-oil is produced from fast pyrolysis by condensing all vapors and aerosols together as one product [9-11]. However, fast pyrolysis can be coupled with a fractionating bio-oil recovery system to create another option towards the utilization of biomass [12, 13]. This fast pyrolysis bio-oil could be upgraded to a fuel, drop-in fuel, or precursor for plastics [14].

The process yielded 7.8 wt. % and 15.9 wt. % soluble carbohydrates on a biomass basis for untreated and passivated alkaline earth metals, respectively [5]. The

carbohydrates produced in this method could be a viable pathway for the production of cheaper sugars [15]. Conventionally produced bio-oil has very little sugar content [16]. This is because naturally occurring alkalai and alkaline earth metals (AAEM) catalyze the fragmentation of five and six membered sugar rings during pyrolysis. This process directly competes with thermal cracking of glycosidic bonds in polymeric carbohydrate chains which would directly produce sugars. However, this can be alleviated by passivation [4]. In addition to the low sugar concentrations already produced due to AAEMs, the vast majority of the sugars produced this way are diluted or effectively emulsified with water and other light molecular weight pyrolytic products (i.e. whole bio-oil).

Traditional fast pyrolysis yields whole bio-oil, consisting of an emulsion of lignin-derived phenolic compounds in an aqueous phase of mostly carbohydrate-derived compounds, including sugars and anhydrosugars [4]. Our Pyrolysis Demonstration Unit (PDU) condenses gaseous pyrolysis products according to vapor pressure and molecular weight. The fractionating bio-recovery system is a six Stage Fraction (SF) system that collects monomeric water soluble sugars (WSS) and phenol monomers, a water-insoluble phenolic monomers, dimers, and oligomers in the first two stage fractions, SF1 and 2 or a Condenser (Cond) and an Electrostatic Precipitator (ESP). These first two stages of the reactor typically condense 30-50 wt. % of the produced bio-oil. Water, furans, aldehydes, and organic acids are also present in low concentrations. The remaining four SF's allow for separation of monomeric phenols, furans, aldehydes, carboxylic acids, and water produced in the fast pyrolysis reactor. As evidenced by these separations, this

system allows for the generation of specific cuts or targeting of specific chemical species in bio-oil. The targeted cut in this article is pyrolytic sugar.

However, utilizing bio-oil fractionation technology, a simple liquid-liquid water extraction of the first two stage fractions or "heavy ends" affords sugar-rich aqueous portions and phenolic rich raffinates (a viscous mixture of high-boiling compounds). The aqueous layer is simply decanted from the raffinate and condensed to pyrolytic sugar syrup for long-term storage (**Figure 1**). Typical sugar concentration of this syrup is 50 wt. % on a dry basis. This pyrolytic sugar syrup is comprised of primarily the anhydrosugar levoglucosan; in addition to lower concentrations of other sugars like cellobiosan, xylose, galactose, and mannose.

Figure 1. Condensed pyrolytic sugar syrup. Its consistency is similar to food-grade maple syrup that is reddish-orange in color.

Water-soluble contaminants or inhibitors such as phenols complicate thermochemical upgrading and inhibit fermentation [17-20]. High temperature upgrading or distillations lead to polymerization due to the presence of highly reactive functional groups on water-soluble phenolic compounds [21]. Crystallization is also not readily

effective due to the large array of concentrations and types of compounds in the pyrolytic syrup mixture. It has been found that this sugar syrup can be detoxified with base and successfully utilized by ethanoligenic *E. coli* [19, 20]. Recent research has informed us that phenol content must be below 0.3 wt. % to not inhibit microbe fermentation [19]. It has also been investigated that activated carbon can clean this stream [22, 23]. Some activated carbon purifications require many successive passes through a carbon plug or turbulent mixing [24]. The majority of sugar purification has been done with solvent extractions (including deep eutectic solvents) [25-27]. Adjustments of the pH to bio-oil fractions have also been attempted [28-30] as well as adsorption on zeolites [31]. Recent applications in resin technology allow for further purification of the sugar stream [32-41]; some requiring only one pass through a column prior to upgrading to remove phenolic content. Utilizing an adsorbent resin (which can be easily regenerated) that has affinity for these contaminants will enable us to obtain a purified pyrolytic sugar mixture devoid of the majority of these compounds except sugars. Combining this technology with fractionation holds the key to sugar purification. It allows for the purification to a simpler or less chemically complex mixture, when compared to whole bio-oil.

The goal of this research is to investigate the use of resins to purify the sugar stream by removing phenolic compounds and producing a substrate suitable for fermentation and/or upgrading. In addition, in the case of levoglucosan, further purification of the sugars may yield the building blocks of green solvents and chiral platforms for pharmaceuticals [42, 43].

Materials and Methods

Bio-oil was produced using a fluidized-bed fast pyrolysis development unit operated at 500°C with a bio-oil recovery system consisting of multiple stages. Nitrogen was used as the fluidizing agent. Red oak (*Quercus rubra*; Wood Residual Solutions of Montello, WI) was used as our feedstock. The feed rate was 6 kg hr^{-1}. Stages 1, 3, and 5 were water-cooled condensers operated at progressively lower temperatures to collect bio-oil according to condensation temperatures of different compounds or moieties in the vapor stream. Stages 2, 4, and 6 were electrostatic precipitators (ESPs) that collected the aerosols. Steady state was achieved for five hours. Further operational information can be found in previous literature [12, 13].

Stage Fraction 2 (SF2) derived from this system was mixed with 18.2MΩ water (1:1 w/w). The suspension was stirred manually, placed on a shaker table (MaxQ 2506, Thermo Scientific, Hanover Park, IL) for 30 min at 250 oscillations min^{-1} and centrifuged (AccuSpin 1R, Thermo Scientific, Hanover Park, IL) at 2561 g force for 30 min. The water-soluble (sugar-rich) solution was decanted. This solution was condensed to syrup using a Heidolph rotary evaporator at 40°C with 1mbar vacuum (Heidolph, Germany). This syrup was stored at 5°C in a polypropylene container.

A column (Chemglass CG-1189-21; 24/40 joint, 2’’I.D. x 24’’ with a fritted disc) was wet-packed with slurry of 500g of Sepabeads SP207 (Sigma Aldrich, St. Louis, Missouri) and 18.2MΩ water. The adsorption resin, Sepabeads SP207, was chosen due to its selectivity (affinity) for phenols and other aromatic compounds, high adsorption capacity, low cost, and ease of regeneration [1]. According to manufacturer data the resin has a bromine modified polystyrene / divinylbenzene backbone. Three column

volumes of water (3 x 500) were eluted through the column to remove any manufacturing residues. Column volume (CV) was determined by CV = (interstitial volume + resin particle volume + resin pore volume). Alternatively, CV= (resin slurry mass / resin slurry density). An HPLC pump was used to backflush the column at 100mL/min. Back flushing was performed until all air pockets were absent and the resin beads were flowing freely. Water was allowed to elute through the column using gravity. The meniscus of the water level was stopped just above the topmost layer of the resin.

A 30% solution of pyrolytic sugar syrup in water (25g pyrolytic syrup / 83g water) was carefully added to the column without disturbing the column bed using a pipette. The fluid in the column eluted at a steady rate of 2 column volumes hr^{-1} (16.6 ml min^{-1}). A Brix refractometer (with a range of 0-32°Bx) calibrated at 22°C with a sucrose solution was used to monitor sugar content in the eluent stream in °Bx. One degree Brix is one gram of sucrose in 100 grams of solution. Water was added batch-wise to the inlet of the column to prevent the resin from drying over the course of the experiment. It was initially added after the meniscus of the 30% sugar solution was just above the topmost layer of resin. Once sugar presence was determined (25 minutes), a round bottom flask was placed under the outlet of the column and used to collect the sugar-rich product. Sugar content reached its peak at 27°Bx and then diminished to 1°Bx. Collection stopped at this point. Three column volumes of water were required for the elution of the sugar. The aqueous pyrolytic sugar solution was condensed by rotary evaporation at 40°C under full vacuum (1 mbar). The condensed sugar was put directly into a 5°C cooler and crystallization occurred over the course of 16 hours. A mixture of amorphous material

and crystalline masses were obtained with a consistency similar to crystallized table honey.

The adsorbent resin was regenerated by five column volume elutions with methanol. The resin was also successfully regenerated by repeated washing with clean methanol in a soxhlet apparatus.

Volatile characterization was determined by a Bruker GC with a Flame Ionization Detector (GC-FID) 430 (Bruker Corporation, Bruker Daltonics, Inc., Fremont, CA) and a Zebron ZB-1701 (60 m × 0.250 mm and 0.250µm film thickness) GC capillary column (Phenominex, Torrance, CA). Galaxie and Compass software was used for data analysis. Samples (0.2g) were dissolved in 0.8g of HPLC grade methanol to make 20% solutions. The samples were filtered with Whatman 0.45µm Glass Microfiber syringe filters into GC vials. Injection volume for analysis was 1µL with a split ratio of 1:20. The 1177 injection port and FID were held at 280°C and 300°C, respectively. The oven temperature of GC was ramped from 35(3 min hold time) to 280°C (4 min hold time) at a heating rate of 5°C min^{-1}.

A Gas Chromatograph with Mass Spectrometer and Flame Ionization Detector (Agilent 7890B GC-MS/FID, Santa Clara, CA) was used to analyze the volatiles. The gas chromatograph was equipped with two identical ZB-1701 (60 m × 0.250 mm and 0.250µm film thickness) capillary columns (Phenominex, Torrance, CA) for separation of the products. One column was connected to the MS and the other was connected to the FID. The injection port and FID detector in the GC were both held at 300°C. Helium carrier gas flow was 1 mL min−1. Injection volume for analysis was 1µL with a split

ratio of 1:20. The oven temperature of GC was ramped from 35(3 min hold time) to 280°C (4 min hold time) at a heating rate of 5°C min^{-1}.

Moisture determination was performed by using an MKS 500 Karl Fisher Moisture Titrator (Kyoto Electronics Manufacturing Co., LTD, Kyoto, Japan). The percent moisture of the bio-oil samples was determined using an average of a minimum of three trials and a 95% confidence interval.

Sugar quantification was performed using a Dionex Ultimate 3000 (Sunnyvale, CA) HPLC system coupled with a Shodex refractive index (New York, NY). The software used to control the instrument and evaluate the samples was Dionex Chromeleon version 6.8. Water (18.2MΩ) was the eluent used at a flow rate of 0.2 $mLmin^{-1}$ on a Hyperez XP Carbohydrate (Thermo Fisher Scientific) column for hydrolysable sugars (HSS) and 0.6 $mLmin^{-1}$ on an Aminex 87P (Bio-Rad, Hercules, CA) column for water soluble sugars at 50°C and 75°C respectively. Sixty mg of pyrolytic sugar was dissolved in 6mL of 0.4M sulfuric acid in a capped conical glass reactor vial with a stir bar. This closed vial was reacted at 125°C for 44 minutes. After cooling, the sample was filtered into vials for analysis. The water soluble sugars were diluted to 10 $mgmL^{-1}$ using water. Water was dispensed using an electronic repeater pipette (Eppendorf North America, Inc., Hauppauge, NY). All samples were filtered through Whatman 0.45µm Glass Microfiber syringe filters prior to analysis [19, 44]. The standards used for sugar analysis were cellobiose, cellobiosan, levoglucosan, glucose, xylose, galactose, mannose, and sorbitol. Cellobiose and sorbitol were purchased from Acrōs Organics and had purities of ≥99.0 and ≥98.5%, respectively. Cellobiosan (98.9%), levoglucosan (99%), galactose (≥99%), and mannose (99%) were purchased

from Sigma-Aldrich (St. Louis, Missouri). Glucose and xylose were purchased from Thermo Fisher Scientific and had purities ≥98%, and Quantum Analytics [44]. Four significant figure results are reliable in these methods.

Carboxylic acid content was determined by Ion Chromatography (IC) using a Dionex ICS3000 (Thermo Scientific®, Sunnyvale, CA). The system was equipped with a conductivity detector and an Anion Micromembrane Suppressor AMMS-ICE300. The suppressor regenerant used was 5 mM tetrabutylammonium hydroxide (TBAOH) at a flow rate of 4–5 mL min^{-1}. The eluent used was 1.0 mM heptaflourobutyric acid with an IonPac® ICE-AS1 4 × 50 mm guard column and IonPac® ICE-AS1 4 × 250 mm analytical column with a flow rate of 0.120 mL min^{-1} at 19°C. The software used was Dionex Chromeleon version 6.8. The bio-oil samples were prepared using 6 mL deionized water and 1.5 mL of HPLC grade methanol. The samples were filtered using Whatman 0.45µm Glass Microfiber syringe filters.

Determination of phenolic content based on gallic acid equivalents (GAE) was measured at 765 nm with a Varian Cary 50 UV–visible spectrophotometer (Agilent Technologies Inc., Santa Clara, CA) using Cary WinUV (Agilent Technologies Inc., Santa Clara, CA) Simple Reads module software. The Folin-Ciocalteu method employed was based on the procedure developed in our department [45].

Results and Discussion

For typical column purification the rule of thumb is 1:20 for wet loading and 1:40 for dry loading [46]. Most experiments used 1:20 wet loading as described in the experimental section. In addition, elution at two column volumes per hour is necessary for adequate separation and purification for crystallization.

Upon elution of the sugar mixture through the column the carbohydrates that eluted accounted for 91.2 ± 0.16 wt. % of the total sugars while 8.78 ± 0.08 wt. % were adsorbed (18.9 ± 0.16 wt. % of the adsorbed material). The cleaned sugar accounted for 53.5 ± 0.92 wt. % of the initial sample to be purified, while 46.5 ± 0.92 wt. % was adsorbed by the resin. Subsequent washes with water allowed recovery of the sugars with only a slight decrease in purity. Regeneration of the resin with methanol allowed recovery of 97.3 ± 3.84 wt. % of the pyrolytic syrup mass and 98.6 ± 2.07 wt. % of the sugar content when both partitions are combined. All values are on a dry basis. Moistures for the raw pyrolytic sugar, cleaned pyrolytic sugar, and the adsorbed material (phenols) were 74.4 ± 1.43 wt. %, 11.4 ± 3.24 wt. %, and 13.0 ± 2.69 wt. % respectively.

Table 1. Adsorption efficiency (recovery) of the resin is listed here as mass balances of the pyrolytic sugar syrup.

	Recovery wt. %	**Sugar Content wt. %**
Cleaned Pyrolytic Syrup	53.5 ± 0.92	96.6 ± 4.94
Adsorbed Material	46.5 ± 0.92	18.9 ± 0.16

The initial concentrations of quantified sugars prior to purification was 56.4 ± 0.65 wt. % on a dry basis (db). After resin purification sugar concentrations were 97.6 ± 0.65 wt. % db. Vendor recommendations state that two column volumes (CV)s of water are effective at retrieving most of the carbohydrate portion. **Figure 2** details the sugar composition of the raw and cleaned pyrolytic sugar samples.

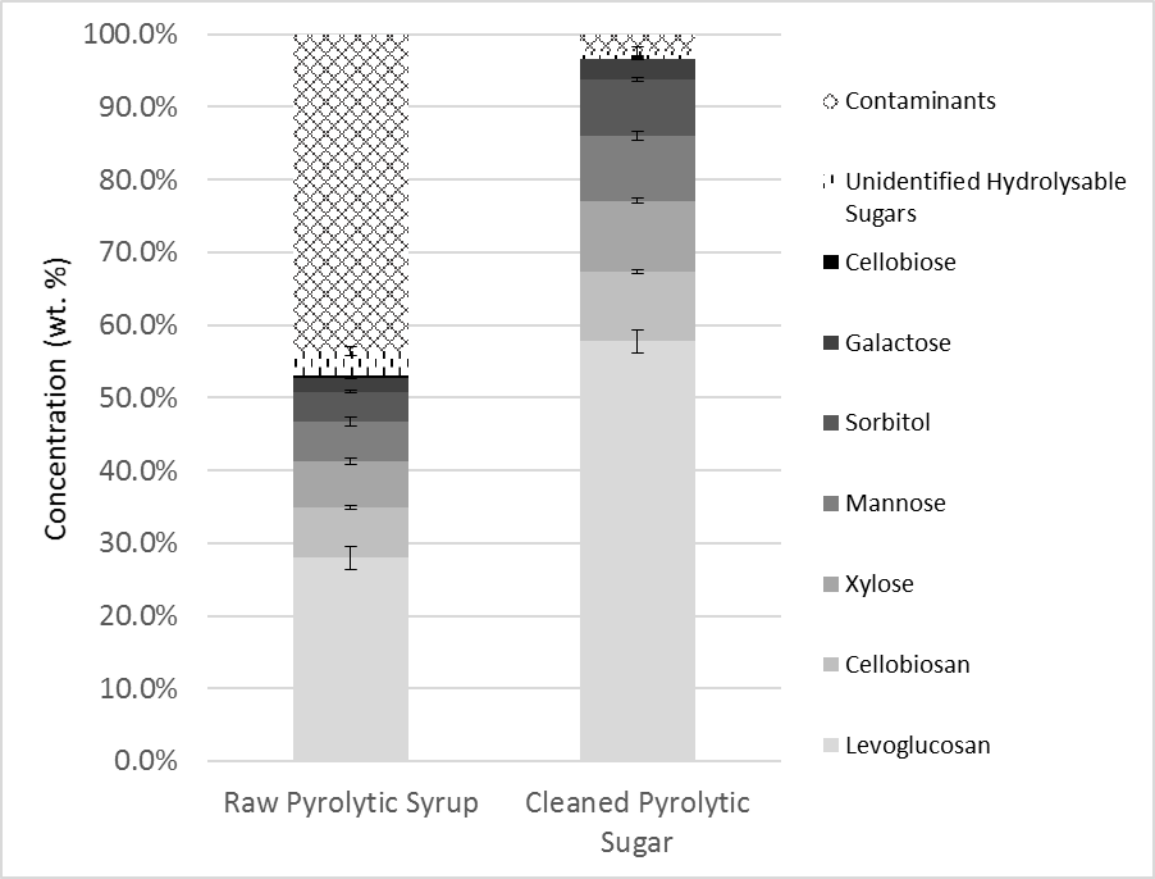

Figure 2. Pyrolytic sugar composition (wt. %) of the raw and cleaned sugar samples are listed on a dry basis. Unidentified hydrolysable sugars were determined by subtracting total water soluble sugars from total hydrolysable sugar results. Table S1 in the supporting information contains the numerical data.

Gas Chromatography – Flame Ionization Detection (GC-FID) results show the unpurified pyrolytic sugar syrup contained 22.2 ± 0.80 wt. % quantified volatiles. It was found that upon resin purification, quantified volatile content is reduced to 5.05 ± 0.66 wt. %. Quantified and identified compound categories are listed in **Figure 3**. All trials showed a total GC volatiles loss between 58-78 wt. % in cleaned pyrolytic sugar samples.

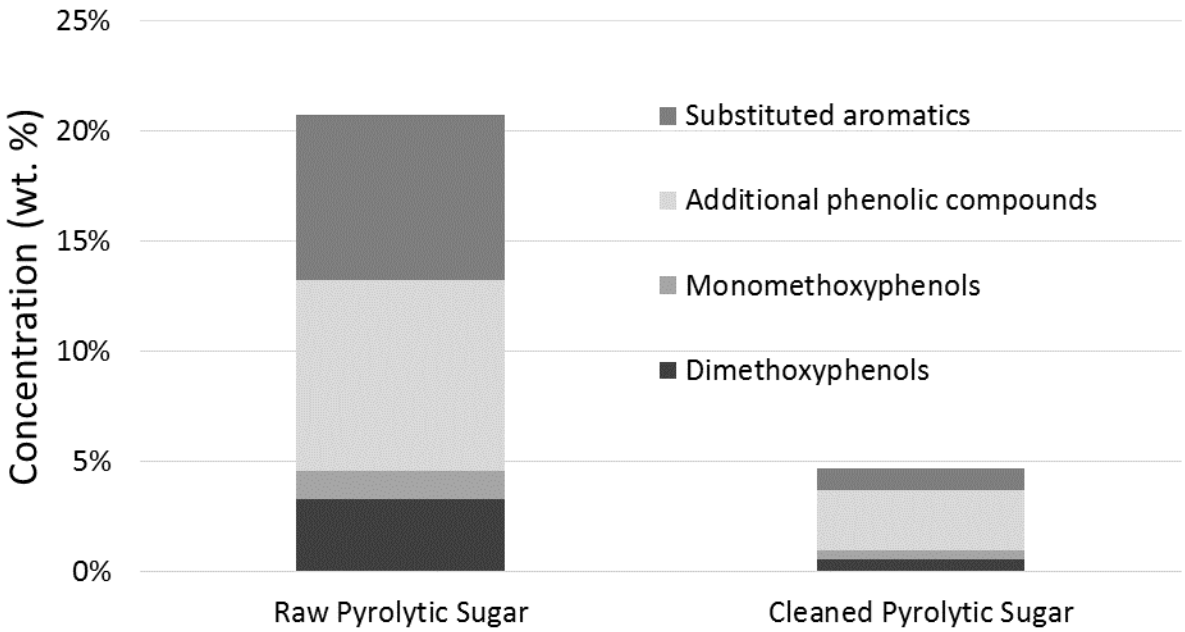

Figure 3. Quantified characterized contaminants by category found in raw pyrolytic sugar syrup and cleaned pyrolytic sugars. Table S2 in the supporting information specifies each category's compounds for GC-FID. Gas Chromatography – Mass Spectrometry (GC-MS) qualitative data is listed in Table S3.

Folin-Ciocalteu results also reveal a significant drop in phenolic content. Initial phenolic content based on gallic acid equivalents is 33.6 ± 4.37 wt. %. Following purification, phenolic content was only 0.82 ± 0.11 wt. %. This colorimetric assay allows for quantification of phenolic and polyphenolic antioxidants [45].

Total organic acid content showed a major loss as well after resin purification, 4.15 ± 0.57 wt. % to 2.25 ± 0.11 wt. %. Removal of organic acids was not expected, but aided greatly in total product purification.

Unidentified compounds accounted for 17.2 wt.% of the raw sugar sample. This was due to water insoluble material and non-volatiles (higher molecular weight compounds) which could not be analyzed. These materials were evident by their plating on the walls of the column (and storage containers). Despite this, all the mass of the cleaned pyrolytic sugar sample was identified (**Table 2**).

Table 2. Values listed are the mass balances of major components in raw and cleaned pyrolytic sugar. Unaccounted mass in the raw sugar is due to non-volatiles and water insolubles.

	Raw Pyrolytic Sugar	**Cleaned Pyrolytic Sugar**
Total Sugar wt.%	56.4	97.6
GC Volatile wt.%	22.2	5.05
Total Organic Acid wt.%	4.15	2.3
Total Quantified wt.%	**82.8**	**105**
Water Insoluble / Non-volatile wt.%	17.2	0.00
Total wt.%	**100**	**105**

Regeneration of the resin with methanol was successful. Four repeated uses of the same resin material showed no loss in adsorptivity of phenol upon subsequent filtration trials.

Upon water removal, concentration, and cooling of the purified sugars, crystallization occurred. The ease of crystallization is a good indicator of the purity of a substance [46].

Conclusion

Purification of a pyrolytic sugar-rich fraction from bio-oil was achieved by removing the phenolic content. Utilization of a polymeric resin adsorbent (SP207) for the removal of phenolic impurities yields a potentially value-added product. The resin utilized has high selectivity (affinity) for phenols and other aromatic compounds, high adsorption capacity, low cost, and ease of regeneration. The value added product is a cleaned mixture of 97.64 wt. % sugar stream that has had the phenolic content removed. This mixture could be further upgraded chemically and/or possibly utilized directly by microorganisms without passivation of any remaining phenols, furans, aldehydes, organic acids, and other "contaminants" or "inhibitors." In addition, in the case of levoglucosan

(obtained in 57.78 wt. %), further conversion of the sugars may yield the building blocks of green solvents and chiral platforms for pharmaceuticals.

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Supporting Information

Table S1. Pyrolytic sugar composition (wt. %) of the raw and cleaned sugar samples are listed on a dry basis. Unidentified hydrolysable sugars were determined by subtracting total water soluble sugars from total hydrolysable sugar results.

	Raw Pyrolytic Sugar	**Cleaned Pyrolytic Sugar**
Levoglucosan wt.%	27.99 ± 1.65	57.78 ± 4.68
Cellobiosan wt.%	6.85 ± 0.52	9.62 ± 0.52
Xylose wt.%	6.38 ± 0.72	9.72 ± 1.01
Mannose wt. %	5.56 ± 1.65	8.96 ± 0.79
Sorbitol wt.%	4.08 ± 0.24	7.67 ± 0.72
Galactose wt.%	1.88 ± 0.48	2.89 ± 0.32
Cellobiose wt. %	0.30 ± 0.09	0.00 ± 0.00
Unidentified Hydrolysable Sugars wt.%	3.34 ± 3.75	<1.00 ± 1.00
Total Sugar wt.%	**56.38 ± 0.65**	**97.64 ± 0.65**

Table S2. The compounds listed are GC-FID quantified and identified compounds found in pyrolytic sugar syrup and cleaned pyrolytic sugars. Compounds with (-) are not present. Some values may have increased in the cleaned sample due to concentration by removal of the volatiles by the resin.

	Raw	**Cleaned**
Dimethoxyphenols		
2,6-dimethoxyphenol	0.19%	0.04%
3',5'-dimethoxy-4'-hydroxyacetophenone	1.92%	0.15%
4-allyl-2,6-dimethoxyphenol	0.48%	-
4-methyl-2,6-dimethoxyphenol	0.71%	0.35%
Monomethoxyphenols		
2-methoxy-4-propylphenol	0.29%	-
2-methoxy-4-vinylphenol	0.19%	0.08%
4-ethyl-2-methoxyphenol	-	0.10%
m,p-cresol	0.10%	0.06%
o-cresol	0.10%	0.01%
vanillin	0.61%	0.18%
Additional phenolic compounds		
2,4-dimethylphenol	0.29%	-
2,5-dimethylphenol	0.22%	-
2,6-dimethylphenol	-	0.07%
2-ethylphenol	0.10%	0.18%
3,4-dimethylphenol	0.29%	-
3,5-dimethylphenol	0.19%	0.48%
3-ethylphenol	0.22%	-

Table S2 Continued

4'-hydroxy-3'-methoxyacetophenone	0.87%	0.34%
4-vinylphenol	6.35%	1.60%
phenol	0.10%	0.05%
Substituted aromatics		
1,2,3-trimethoxybenzene	0.45%	-
1,2,4-trimethoxybenzene	0.45%	-
1,2-benzenedimethanol	0.87%	-
2,3-dimethoxytoluene	-	0.02%
2,5-dimethoxybenzylalcohol	0.96%	-
2-methylanisole	0.29%	0.18%
3,4-dimethoxytoluene	1.51%	0.23%
3'4'-dimethoxyacetophenone	0.38%	-
3-methylanisole	1.38%	0.08%
4-ethoxystyrene	0.48%	-
4-vinylanisole	-	0.06%
anisole	0.74%	0.07%
ethylbenzene	-	0.36%
m-xylene	-	0.11%
o-xylene	0.77%	0.07%
styrene	0.74%	0.18%

Table S3. The compounds listed in this table are qualitative GC-MS results. Compounds marked with (*) are present, while compounds with (-) were not detected. All compound matches were above 60% probability.

	Raw	**Cleaned**
1-(1,1-dimethylethyl)-cyclohexanecarboxylic acid	*	-
1-(2,4,6-trihydroxyphenyl)-2-pentanone	*	-
1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone	*	-
1,2:3,4-di-O-ethylboranediyl-cyclobutane	*	-
1,2-cyclopentanedione	*	-
1,4:3,6-dianhydro-α-D-glucopyranose	*	*
1,4-pentadien-3-one	*	-
1,7-dimethyl-3-phenyltricyclo[4.1.0.0(2,7)]hept-3-ene	*	-
1-methyl-1-ethoxycyclobutane	*	-
1-methyl-8-propyl-3,6-diazahomoadamantan-9-ol	*	-
1-propyl-3,6-diazahomoadamantan-9-ol	*	-
2-(1-hydroxybut-2-enylidene)cyclohexanone	*	-
2-(2-butoxyethoxy)ethyl 2-methylbutanoate	-	*
2-(4-nitrobutyryl)cyclooctanone	*	-

Table S3 Continued

2(5H)-furanone	*	-
2,2,4,4-tetramethyl-3-pentanol	*	-
2,2-diethyl-3-methyl-oxazolidine	*	*
2,3,4-trimethoxybenzoic acid	*	-
2,3-anhydro-d-mannosan	*	-
2,5-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one	*	-
2,5-monoformal-l-rhamnitol	-	*
2,6-dimethoxy-4-(2-propenyl)-phenol	*	-
2-ethyl-1,1'-biphenyl	*	-
2-ethyl-5-propylcyclopentanone	-	*
2-ethylbutyric acid, cyclohexylmethyl ester	*	-
2-ethylbutyric acid, tetrahydrofurfuryl ester	*	-
2-ethylhexanal	*	-
2H-pyran-2,6(3H)-dione	*	-
2-hydroxy-2-cyclopenten-1-one	-	*
2-hydroxymethyl-6-methoxytetrahydropyran-3-ol	*	-
2-methoxyfuran	*	-
2-methoxyphenol	*	-
2-methyl-5-oxo-proline, methyl ester	-	*
3-(1,3-dihydroxyisopropyl)-1,5,8,11-tetraoxacyclotridecane	*	-
3,4-diethyl-(Z,Z)-2,4-hexadienedioic acid, dimethyl ester	*	-
(E)-2-methoxy-5-(1-propenyl)-phenol	*	-
3,5-dimethylpyrazole	*	-
3-ethyl-2-hydroxy-2-cyclopenten-1-one	*	-
3-furaldehyde	-	*
3-hydroxy-2-methyl-2-cyclopenten-1-one	*	-
3-methyl-2-cyclopenten-1-one	*	-
3-oxo-2-propyl-heptanoic acid, methyl ester	-	*
3-tert-butyl-4-hydroxyanisole	*	-
4-(2,2-dimethylpropanoate)-1,3,5-trideoxy-3-nitro-d-xylitol	-	*
4-ethoxy-cyclohexanone	*	-
4-hydroxy-2-butenoic acid, methyl ester	-	*
4-hydroxy-3,5,5-trimethyl-4-(3-oxo-1-butenyl)-2-cyclohexen-1-one	*	-
4-hydroxy-3,5-dimethoxybenzaldehyde	*	-
5-heptyldihydro-2(3H)-furanone	*	-
5-hydroxymethyldihydrofuran-2-one	*	*
acetaldehyde	*	-
butanedioic acid, monomethyl ester	*	*
creosol	*	-

Table S3 Continued

D-allose	*	*
D-fucose	-	*
estra-1,3,5(10)-trien-17β-ol	*	-
ethane-1,1-diol dipropanoate	-	*
furyl hydroxymethyl ketone	*	-
lactose	*	*
methyl 2,3-anhydro-β-d-ribofuranoside	*	-
methyl 4-O-acetyl-2,3,6-tri-O-ethyl-α-d-galactopyranoside	-	*
methyl 6-O-[1-methylpropyl]-β-d-galactopyranoside	-	*
methylenecyclopropanecarboxylic acid	*	*
methyl-α-D-xylofuranoside	-	*
N-methyl-2-propenamide	-	*
N-methylvaleramide	*	-
O,O-di(pivaloyl)-ethylene glycol	*	*
O-α-D-glucopyranosyl-(1→3)-β-D-fructofuranosyl-α-D-glucopyranoside	*	-
propanal	*	*
propane-1,1-diol dipropanoate	*	-
propanoic acid	*	-
propanoic acid, anhydride	*	*
valeric anhydride	-	*

CHAPTER 4

CHARACTERIZATION AND SEPARATION OF ACETATE FROM THE AQUEOUS PHASE OF BIO-OIL

Patrick H. Hall, Marjorie R. Rover, Patrick A. Johnston,
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Abstract

Productive use of all streams from fast pyrolysis reactors will be important to their profitable operation. The condensable products of fast pyrolysis can be recovered as separate fractions of heavy ends, intermediates, and an aqueous phase. Whereas the heavy ends contain sugars and phenolic oil and the intermediates contains phenolic monomers and furans, the aqueous phase consists mostly of carboxylic acids (10 wt.%) and several other light oxygenates (30 wt.%). However, the presence of water (60 wt.%) makes upgrading and simple distillation of this fraction very difficult due to water's high heat capacity and azeotropic properties.

The primary goal of this research is to recover acetic acid and other organic species from the aqueous phase, which increases the number of chemical products from the bio-oil and reduces waste water treatment costs associated with the pyrolysis biorefinery. We have determined that long chain fatty acids are suitable candidates for cleaning this waste water stream. Among possible solvents for the liquid-liquid extraction, heptanoic acid was selected because of its low water solubility; high boiling point compared to the acetic acid to be distilled from it; and stability during storage. Heptanoic acid extraction of SF5 has shown favorable results with almost complete removal of acetic acid.

This technique was also successful when used to recover acetic acid from an acetosolv product stream. Surprisingly, many other light oxygenates were extracted in our aqueous stream. These extractions yielded concentrated organic solutions, possible starting materials for catalytic cracking reactors, which were distilled from the heptanoic acid.

The secondary goal of this research is to perform a complete characterization and compare three aqueous streams derived from nitrogen fluidized pyrolysis or conventional pyrolysis, auto-thermal pyrolysis, and pretreated auto-thermal pyrolysis of two feed stocks; red oak and corn stover. It is imperative to characterize all components of the aqueous streams in order to better understand what is required for purification. These insights will allow informed decisions to isolate specific chemical species to recover all carbon from the aqueous stream.

Introduction

Productive use of all streams from pyrolysis streams will be important to their profitable operation. The condensable products of fast pyrolysis can be recovered as separate fractions of heavy ends, intermediates, and an aqueous phase. Whereas the heavy ends contain sugars and phenolic oil and the intermediates contains phenolic monomers and furans, the aqueous phase consists mostly of carboxylic acids (10 wt.%), water (60 wt.%), and several other light oxygenates (30 wt.%).

Fast pyrolysis is the thermal decomposition of lignocellulosic biomass. It is usually performed in the absence of oxygen, however, recent developments in our research group have led to an autothermal fast pyrolysis process [1]. The composition of the aqueous fraction from autothermal systems also differs when varying feedstocks,

pretreatments. However, water soluble organic compounds must be removed prior to wastewater treatment.

As stated, water and acetic acid, zeotropic compounds, are present in this acetate fraction. Both compounds form azeotropic mixtures with other compounds in the fraction. Most readers of this manuscript are familiar with azeotropic mixtures; where the boiling point of azeotroping compounds can be lower or higher than that of the pure compound's boiling point. Typically, in distillations, this is useful to entrain higher boiling substances with lower boiling point compounds that are highly volatile [2-9]. A Dean-Stark apparatus is typically employed in these azeotropic distillations. For example, water is easily removed with toluene as an entrainer when using this apparatus. However, removal of large amounts of water is not economically feasible. Conversely, compounds that form a zeotropic mixture, like that of water and acetic acid; should easily be separated by distillation due to their boiling points at 100°C and 118°C, respectively. Zeotropic mixtures never have the same vapor phase and liquid phase composition. In the case of water and acetic acid, separations require expensive progressive/successive distillations (known as rectification columns industrially) [10]. However, this is not the case with the acetate fraction, where other light oxygenates can cause an azeotrope to occur. When vacuum distillation of the acetate fraction was performed on site, only 25% of the compounds distilled successfully (which included acetic acid and water). The other portion formed a polymeric mass upon further heating, losing the valuable carbon sources. Another compounding problem with water/acetic acid mixtures is that many common acetate salts are completely soluble in water and will not precipitate, nor can be extracted. However, recently, some work has been done in this area [11-13].

Although many refineries separate acetic acid by successive distillation or rectification, it becomes economically infeasible to remove large volumes of water through distillation. Other methods of water removal employed by industry and other researchers are as follows; evaporation/sublimation, resin/membrane separation or adsorption, desiccation, and solvent extraction [4, 14-16]. Evaporation / sublimation are slow processes unless heated (evaporation) or frozen and removed by vacuum (sublimation) with costly power. Resin adsorption and membrane separation, or more widely known as reverse osmosis (RO) or pervaporation are successful in the removal of acetic acid from water. Resin adsorption of acetic acid will be discussed more in detail in the next chapter of this dissertation. In the case of membrane separation or RO, the system removes impurities from water instead of the removal of water through tiny ceramic pores. Desiccation is a technique reserved for small amounts of water. Typically, magnesium sulfate, sodium sulfate, or molecular sieves are utilized in these cases. Recently, it has been shown in literature that fatty acid extraction of carboxylic acids is successful [17]. Carboxylic acids have been known to dimerize due to their hydrogen bonding donor and acceptor pairs [17, 18]. These dimers are considered complexed compounds in equilibria (**Figure 1**). Although expensive and there is a risk of low solvent recovery, this chapter will focus on solvent extraction of the acetate fraction using a fatty acid, heptanoic acid. It is surmised that a selective solvent will extract acetic acid and other light oxygenates from the light ends stream from pyrolysis and industrial applications.

The primary goal of this research is to recover acetic acid and other light organic species from the aqueous phase, which increases the number of chemical products from

the bio-oil and reduces waste water treatment costs associated with the pyrolysis biorefinery. We have determined that long chain fatty acids are suitable candidates for extraction of acetic acid while excluding water. Among possible solvents for this liquid-liquid extraction, heptanoic acid was selected because of its low water solubility; high boiling point compared to the acetic acid to be distilled from it; and stability during storage. Heptanoic acid extraction of the acetate fraction has shown favorable results with almost complete removal of acetic acid. Distillation of the extract should afford acetic acid and other light oxygenates with water content greatly reduced.

The secondary goal of this research is to perform a complete characterization and compare aqueous streams derived from two feedstocks pyrolyzed under three distinctive pyrolysis conditions. It is imperative to characterize all components of the aqueous streams in order to better understand what is required for purification [19-21]. These insights will allow informed decisions to isolate specific chemical species to recover all carbon from the aqueous stream.

Proximate and ultimate analysis will be coupled by Karl-Fischer moisture analysis to determine water content, volatiles, fixed carbon, and ash. GC-FID and GC-MS will be utilized to analyze the volatiles through both quantification and qualification. Ion Chromatography and Total Acid Number/Modified Acid Number (TAN/MAN) coupled with pH will be used to quantify acid content. Folin-Ciocalteu will be used to quantify phenolic content. Finally, IR and ^{31}P-NMR analysis will allow for a thumbprint of each bio-oil to be ascertained.

Theory

Acetic acid and its salts are known to be highly hydrophilic or soluble in water. Solubility is an intrinsic characteristic property of a substance. Solubility is also a useful means with which to separate components in a mixture. This can be done by taking advantage of their differences in solubility in certain solvent systems. Partitioning describes the movement of components of a mixture from one phase to another when an immiscible solvent is added. Partition law is an extension of Nernst's distribution law and Henry's Law. Nernst's law describes the distribution of a solute in two immiscible solvents. Henry's law (**Equation 1**) states that:

$$K = \frac{m}{p} \qquad \textbf{(1)}$$

K is the constant, where *m* is the mass of gas dissolved per unit volume and *p* is the pressure at constant temperature. When dealing with only a liquid- based system, both *m* and *p* can be replaced by concentrations C_1 and C_2 to give **Equation 2**:

$$K = \frac{C_2}{C_1} \qquad \textbf{(2)}$$

Essentially, this ratio describes the concentration of a molecule in an organic phase versus the concentration of the same component in an aqueous phase at equilibrium. The model system typically described is octanol (C_2)/ water (C_1).

Another extension that can be made from this equation is the lipophilicity or partition of an organic compound in an organic / water system (**Equation 3**). It can be described as:

$$\log P = \log\left(\frac{[unionized\ compound]_{org}}{[unionized\ compound]_{aq}}\right) \qquad \textbf{(3)}$$

This can be further extrapolated to the distribution coefficient which takes into account both unionized and ionized compounds (**Equation 4**). This equation plays a role when applications must be compared that have differing pHs.

$$\log D = \log\left(\frac{[ionized\ compound]+[unionized\ compound]_{org}}{[ionized\ compound]+[unionized\ compound]_{aq}}\right) \quad \textbf{(4)}$$

Log P and *D* values can easily be compared between different systems.

Of course, the Henderson-Hasselbalch relation (**Equation 5**) can be applied in these situations to aid in calculations of the acid dissociation constant (**Equation 6**).

$$pH = pK_a + \log\left(\frac{[H^-]}{[HA]}\right) \quad \textbf{(5)}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \textbf{(6)}$$

A more simplified way to look at dissociation, partition, and complexation and their corresponding equilibria is shown in **Figure 1**.

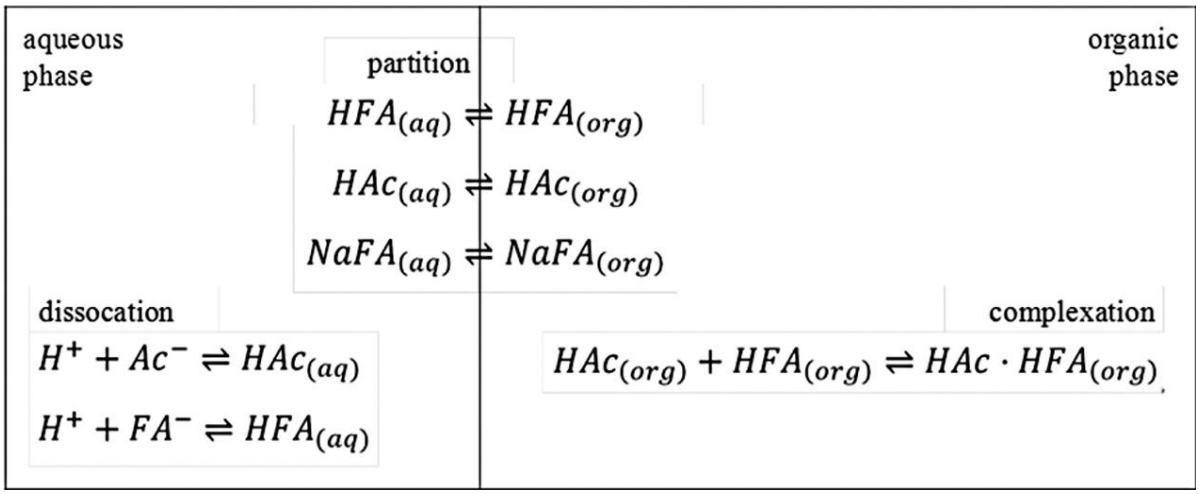

Figure 1. Equilibria in extraction of acetic acid from an aqueous solution using fatty acids as the solvent [17].

The Hansen solubility parameter essentially says like dissolves like which is a simplification of the Hildebrand solubility parameter. In other words, the dispersion

forces, intermolecular forces, and hydrogen bond energy all must be similar for a compound to be completely soluble in another.

Materials and Methods

Production of bio-oil

Fractionated bio-oil was produced using fluidized-bed fast pyrolyzers operated at 500°C with multi-stage bio-oil recovery systems. One pyrolyzer used a six-fraction recovery system while a second pyrolyzer, used a four-fraction recovery system. The samples were produced under diverse operating conditions, as detailed in **Table 1** [1]. Red oak (*Quercus rubra*; Wood Residual Solutions of Montello, Wisconsin) and corn stover (*Zea mays ssp. mays*; BioCentury Research Farm of Boone, Iowa) were used as feedstock. The bio-oil for part one of this study (heptanoic acid extraction) was produced using nitrogen fluidization or conventional pyrolysis with no pretreatment and a feed rate of six kg/hr.

The autothermal bio-oil was also produced on the six fraction system. Autothermal pyrolysis was performed to maximize pyrolytic sugar production [22]. However, the pretreated autothermal bio-oil was produced on the four-fraction system. Pretreated autothermal samples were produced to add enthalpy of pyrolysis [1, 23]. Despite this difference, the aqueous fractions of both systems were used in this study. The rest of this chapter will refer to only the acetate or aqueous fraction to allow for comparisons unless it is specifically stated otherwise. Operational information and the PDU diagram can be found in previous literature [20, 24].

Table 1. Feed rate and equivalence ratios for six fast-pyrolysis runs used in this study.

		Equivalence Ratio	Feed Rate (kg/hr)
Red Oak	Conventional	0	6
	Autothermal	0.071	23
	Pretreated Autothermal	0.07	0.25
Corn Stover	Conventional	0	5
	Autothermal	0.098	23
	Pretreated Autothermal	0.1	0.25

Extraction of the acetate fraction

Twenty-five milliliters of SF5 was extracted with increasing ratios of heptanoic acid ranging from 1:1 to 1:25 SF5 to heptanoic acid. The liquid-liquid extraction was performed at room temperature using a separatory funnel (**Figure 2**).

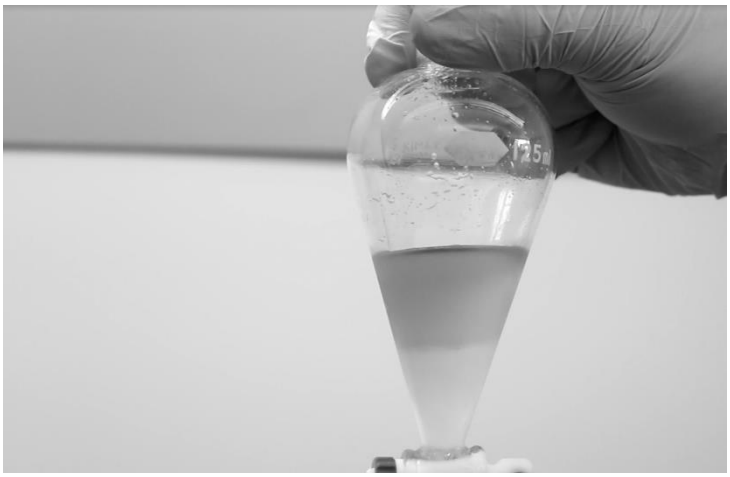

Figure 2. Heptanoic acid extraction of SF5. The topmost layer is heptanoic acid with the extracted organic portion, the bottom layer is immiscible material, comprised primarily of water.

After optimization of the correct ratio, 25 mL of SF5 was extracted using three sequential washes (150mL x 3) of heptanoic acid (1:6). Each separation step was allowed to equilibrate for one hour for phase separation. The heptanoic acid extracts were combined and distilled using short path and vacuum distillations to recover acetic

acid (and other carboxylic acids) and light oxygenates. The same methods were employed using octanoic acid (and other acids) as extractants during preliminary testing.

Characterization of the acetate fraction

Samples were analyzed in triplicate on all available related instrumentation.

Quantitative and qualitative analysis of calibrated volatiles was performed by a Bruker GC with a Flame Ionization Detector (GC-FID) 430 (Bruker Corporation, Bruker Daltonics, Inc., Fremont, CA) and a Zebron ZB-1701 (60 m × 0.250 mm and 0.250µm film thickness) GC capillary column (Phenominex, Torrance, CA). Galaxie and Compass software was used for data analysis. Samples (0.2g) were dissolved in 0.8g of HPLC grade methanol and filtered with Whatman 0.45µm glass microfiber syringe filters into GC vials. Injection volume for analysis was 1µL with a split ratio of 1:20. The 1177 injection port and FID were held at 280°C and 300°C, respectively. The oven temperature of GC was held at 35 for three minutes, increased to 280°C at a heating rate of 5°/min, and then held for four minutes. Calibration compounds were entered into the software using a six-point linear fit with an R^2 greater than 0.98 for each compound.

Qualitative analysis of the all volatiles was performed using an Agilent 7890B Gas Chromatograph with Mass Spectrometer and Flame Ionization Detector (GC-MS/FID, Santa Clara, CA). The GC was equipped with two identical ZB-1701 (60 m × 0.250 mm and 0.250µm film thickness) capillary columns (Phenominex, Torrance, CA) for separation of the products. One column was connected to the MS and the other was connected to the FID. The injection port and FID detector in the GC were both held at 300°C. Helium carrier gas flow was 1 mL/min. Injection volumes, split ratio, and oven program were the same as the GC-FID to allow for comparisons.

Moisture determination was performed by using a Kyoto MKS 500 Karl Fisher Moisture Titrator (Kyoto Electronics Manufacturing Co., LTD, Kyoto, Japan). The percent moisture of each bio-oil sample was determined using an average of a minimum of three trials and a 95% confidence interval.

A Dionex ICS3000 Ion Chromatograph (IC) (Thermo Scientific®, Sunnyvale, CA) was utilized to determine carboxylic acid content. The system was equipped with a conductivity detector and an Anion Micromembrane Suppressor AMMS-ICE300. The suppressor regenerant used was 5mM tetrabutylammonium hydroxide (TBAOH) at a flow rate of 3 mL min^{-1}. The eluent used was 1.0mM heptaflourobutyric acid with an IonPac® ICE-AS1 4 × 50 mm guard column and IonPac® ICE-AS1 4 × 250 mm analytical column with a flow rate of 0.120 mL min^{-1} at 19°C. The software used was Dionex Chromeleon version 6.8. The bio-oil samples were prepared using deionized water (variable amounts) and 1.5 mL of HPLC grade methanol for dilution. The samples were filtered using Whatman 0.45µm glass microfiber syringe filters.

Phenolic content based on gallic acid equivalents (GAE) was measured at 765nm with a Varian Cary 50 UV–visible spectrophotometer (Agilent Technologies Inc., Santa Clara, CA) using Cary WinUV (Agilent Technologies Inc., Santa Clara, CA) Simple Reads module software. The Folin-Ciocalteu method employed was based on the procedure developed internally [25].

Nuclear Magnetic Resonance (NMR) analysis and quantification was performed using a Bruker AVIII-600 (Agilent Technologies, Inc., Santa Clara, CA) narrow bore 14.1 tesla/600MHz magnet. Two probes: a normal geometry $^{2}H/^{1}H$/BB BBFQ SmartProbe capable of tuning to ^{109}AG-^{19}F on the broadband channel and an inverse

geometry $^{2}H/^{1}H/^{13}C$/BB inverse probe with a dedicated ^{13}C channel and ^{109}AG-^{19}F range on the broadband channel were installed on the instrument. Topspin 3.0 (Agilent Technologies, Inc., Santa Clara, CA) was used for data acquisition and MNova (MestReNova, Escondido, CA) software was used for data processing. A Pacific Northwest National Labs (PNNL) method utilized for ^{31}P quantification was followed [26]. A slight modification was made from the PNNL method in number of scans and d1 (delay). The number of scans was changed from 128 to 16 and d1 was changed from 25 seconds to 10 seconds.

Ultimate analysis was conducted using an Elementar elemental analyzer (vario MICRO cube). At 900 °C, the sample was combusted and the products of carbon dioxide, water, nitric oxide, were characterized by a thermal conductivity detector. The weight percentages of the C, H, and N were calculated based on the amount of the combustion products calibrated by a rice flour standard (EA Consumables; Pennsauken, NJ). Approximately 5 mg of sample was inserted into the combustion chamber for the analysis. Results were reported on a wet ash basis as well as a dry ash-free basis for comparison.

A Nicolet iS10 (Thermo Fisher Scientific Inc., Waltham, MA) with a Smart iTR accessory was used for Fourier Transform Infrared (FTIR) analysis. Acquisition of the sample was obtained with OMNIC software. The background was collected before every sample.

Total Acid Number (TAN) and Modified Acid Number (MAN) were determined by potentiometric titration. The instrument used was a Metrohm 798 Titrino instrument. The method employed for TAN was based on ASTM D664 using 50% toluene, 49.5% 2-

propanol, and 0.5% water as the sample solution. The titrant was 0.1M potassium hydroxide in 2-propanol. For MAN determination, a solution of 75mL methanol and 5mL dimethylformamide (DMF) were used instead of the solution prepared for TAN.

Determination of pH was performed using a Mettler-Toledo pH meter equipped with a InLab Expert Pro probe. Calibration standards of 4.01, 7.01, and 10.01 pH were used to standardize the probe prior to use.

Proximate analysis was performed using a Mettler-Toledo Thermogravimetric Analyzer (TGA)/Differential Scanning Calorimetry (DSC) instrument. The method employed was based on ASTM D5142 – 09 with 100mg samples. The sample was heated from 25 to 105°C at 10K/min to remove any low boiling compounds. Then the sample was held at 105°C for 40 minutes to allow the water to fully vaporize. Again, heating was ramped from 105 to 900°C at 10K/min to remove volatiles and held at 900°C for 20 minutes in order to calculate fixed carbon. After which, the nitrogen environment was switched to air for 30 minutes to determine ash content. The sample was analyzed by integration using STARe software.

Results and Discussion

Extraction of the acetate fraction

Figure 3 shows the moisture content of a 1:1 extraction of SF5 using three fatty acids; hexanoic, heptanoic, and octanoic.

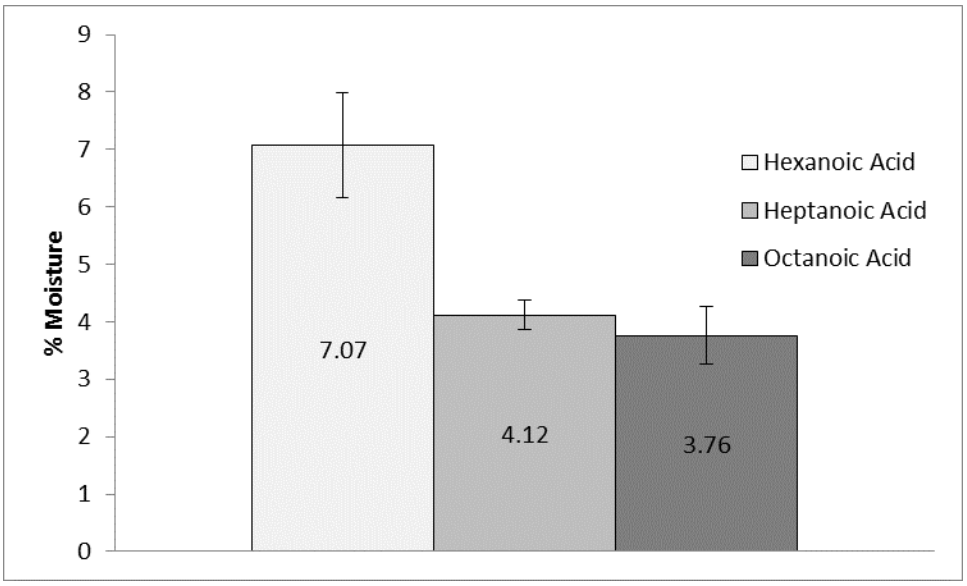

Figure 3. Moisture content of a 1:1 extract of SF5 with three different fatty acids.

Results show that hexanoic acid is slightly more hydrophilic or miscible with water in SF5 than heptanoic and octanoic acids, thereby extracting more water from the fraction. **Table 2** also verifies these results.

Table 2. Miscibility of organic acids with water [27].

	Miscibility in Water (g/100 mL) @25°C
Ethanoic Acid (Acetic)	miscible
Propanoic Acid	miscible
Butanoic Acid	miscible
Pentanoic Acid	4.97
Hexanoic Acid	1.082
Heptanoic Acid	0.2419
Octanoic Acid	0.068

In order to determine extraction efficiency, the aqueous portion of the same solutions used for the results in **Figure 3** were tested for acetic acid content. The results are listed in **Figure 4**.

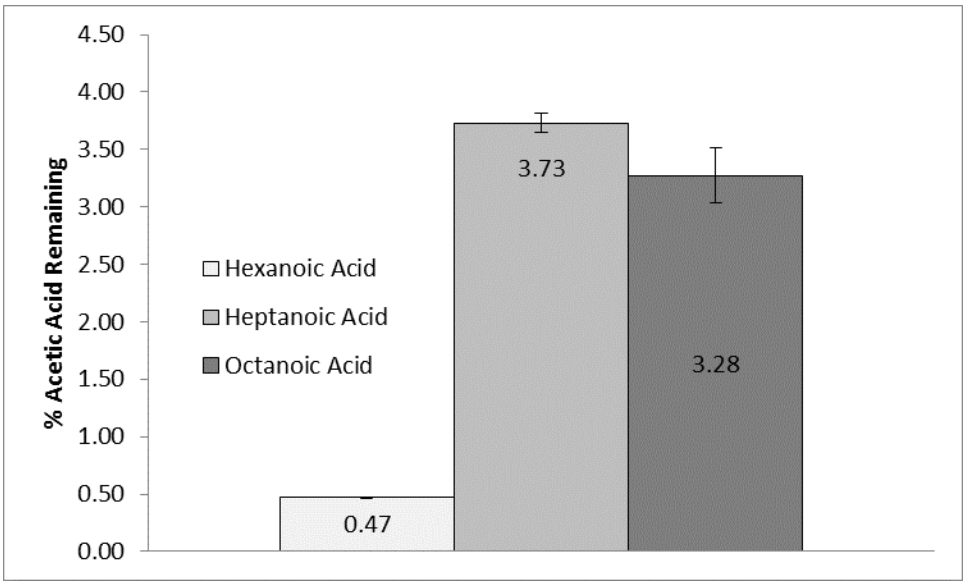

Figure 4. Acetic acid content remaining in the aqueous phase after a 1:1 extraction with three different organic acids.

Interestingly, hexanoic acid performed the best and extracted the most acetic acid. The original solution contained 9.6 wt.% acetic acid. The extraction efficiency was 95.07%. Heptanoic and octanoic acids did not perform as well with 61.15% and 65.83% efficiency respectively. However, based on water extracted and acetic acid extraction efficiency, it was decided to continue the experimentation with heptanoic acid. Twenty-five mL samples of SF5 were extracted with increasing quantities of heptanoic acid (1:1….1:25) as shown in **Figure 5**. At a ratio of 1:25 SF5 to heptanoic acid, 625mL of heptanoic acid extracted all but 0.92 wt.% acetic acid remaining. If the trend continues, the figure suggests that it would take 886mL to sequester all acetic acid.

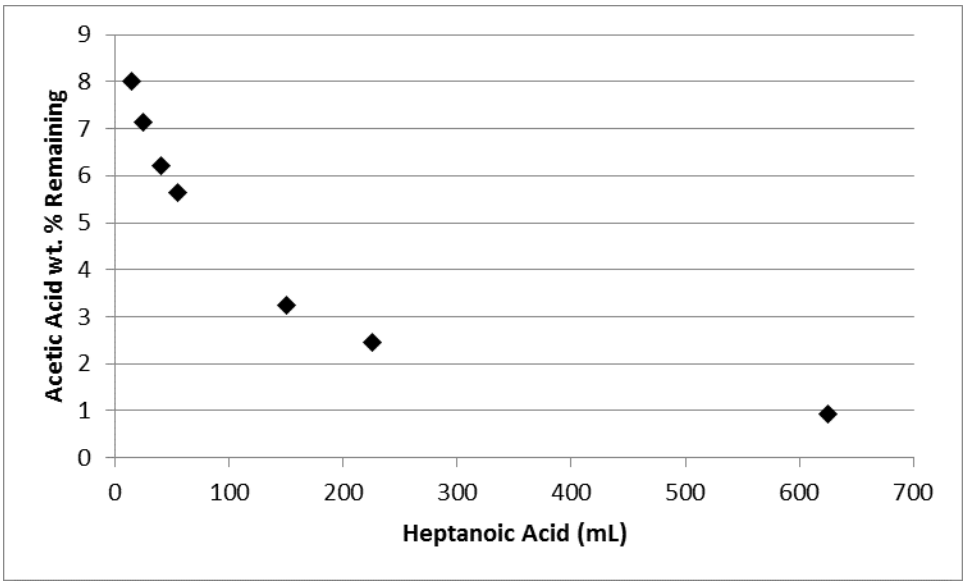

Figure 5. Extractions results showing remaining acetic acid in 25mL SF5 using increasing volumes of heptanoic acid as the extract solvent.

Of course, due to diminishing returns and price, it would not be economically feasible to continue with single extractions. At the time of this dissertation, heptanoic acid costs $46.30/100mL. If a linear extrapolation of the first points is generated, a more suitable quantity of heptanoic acid is suggested: 150mL of heptanoic acid or a ratio of 1:6. Multiple extractions (150mL) with heptanoic acid of the same volume (25mL) of SF5 yielded the best results with the least amount of solvent used (**Figure 6 and Table 3**).

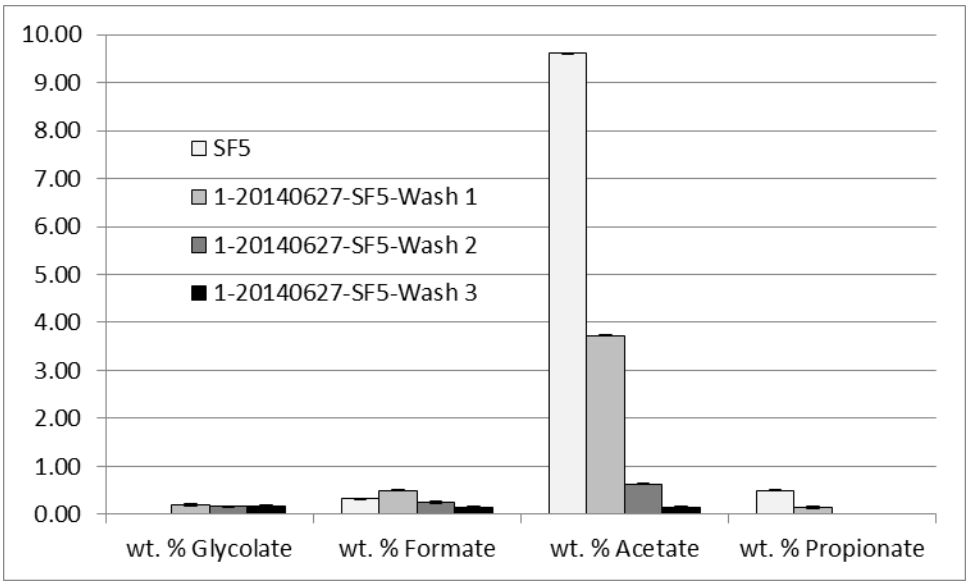

Figure 6. Three extractions of 25mL SF5 using 3 x 150mL heptanoic acid showed decreasing amounts of each quantified organic acid.

Table 3. Acetic acid remaining and cumulative percent of acetic acid extracted after each extraction with heptanoic acid.

	Acetic Acid wt. % Remaining	Cumulative % Acetic Acid Extracted
SF5	9.60	-
SF5-Extract 1	3.73	67.7
SF5-Extract 2	0.63	93.4
SF5-Extract 3	0.14	98.5

As shown in **Table 3**, acetic acid was recovered at 98.5% efficiency, however, acetic acid and other light oxygenates are now in 450mL (150 x 3) of heptanoic acid. Interestingly, if the equilibria coefficients (*K*) were calculated for each extraction, there is a dramatic increase in the coefficient for the second extract (1.57, 4.92, 3.5). This is most likely due to extraction of other light oxygenates in the first extraction. This is not an issue now that water has been reduced drastically and distillation can be used to separate the solutes from the solvent. The boiling points of acetic acid (118°C) and heptanoic acid (223°C) afford clean distillation cuts. Simple short path and vacuum distillation were used to separate the heptanoic acid. Almost all the solvent was recovered (99%) after

distilling to 118°C. Acetic acid content in the distillation products ranged from 5-24 wt.% in all trials. In one successful trial, the distilled product contained 22.9 wt.% acetic acid, 4.0 wt.% propionic acid, 0.18 wt.% formic acid, 69.1 wt.% other light oxygenates, and 3.84 wt.% water (down from 69.02 wt. % water). GC-MS analysis of this cut revealed these light oxygenate compounds: acetol, furfural, furfuryl alcohol, phenol, 2,6-dimethoxyphenol, 2(5H)-furanone, 3-methyl-1,2-cyclophentanedione, guaiacol, vanillin, and 5-(hydroxymethyl) furfural. Analysis of the solvent revealed only heptanoic acid, its dimers, and anhydrides which are from its initial production (97% purity). All compound matches were above 60% probability.

This extraction scheme was also applied to industrial acetic acid streams. An organic insoluble lignin hemicellulose stream (3.95% acetic acid) and an organic soluble lignin stream (10.4% acetic acid) were extracted with heptanoic acid, yielding the same results as SF5 (**Figures 7 and 8**).

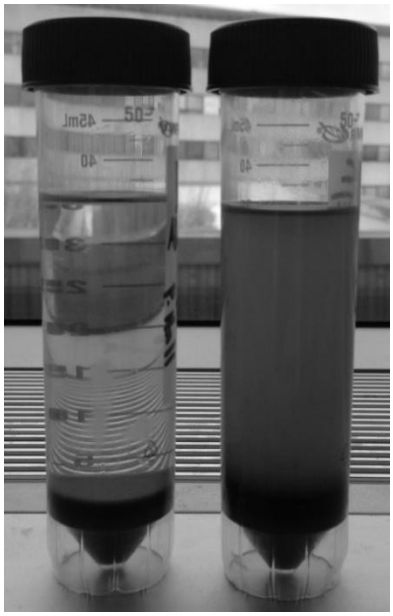

Figure 7. Separation and extraction of an organic insoluble lignin hemicellulose stream (left) and an organic soluble lignin stream (right) with heptanoic acid. Solid insoluble compounds (most likely lignin) as well as the aqueous phase were on the bottom of each centrifuge tube.

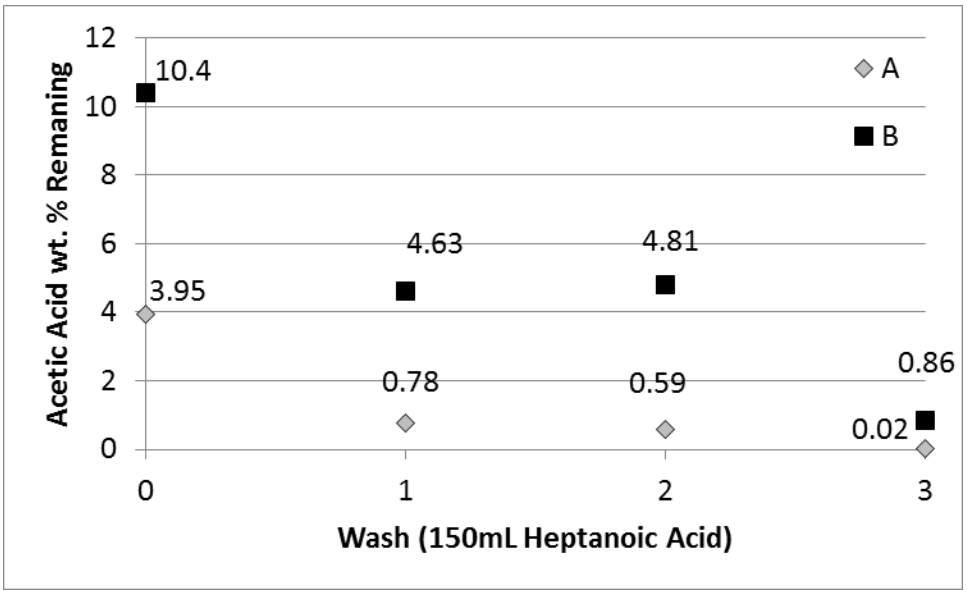

Figure 8. Acetic acid remaining in an organic insoluble lignin hemicellulose stream (A) and an organic soluble lignin stream (B) with successive heptanoic acid extractions.

This technique was also successful when used to recover acetic acid from an acetosolv product stream. Surprisingly, many other light oxygenates were extracted in both SF5 and the acetosolv product stream. These yielded concentrated organic solutions that were distilled by other researchers from the heptanoic acid suitable for catalytic cracking to aromatics.

Despite the positive results, when this liquid-liquid extraction process was applied to autothermal and pretreated autothermal bio-oil, it was not as effective liquid-liquid extraction from water. Higher percentages of water were extracted. In some cases, a liquid bilayer was not formed, only an emulsion. Trials using octanoic acid were performed and some were successful, but did not yield statistically significant values to warrant a solvent change. In order to understand the difference between conventional, autothermal, and pretreated autothermal bio-oils and their corresponding feedstocks, a characterization study was performed.

Acetate fraction characterization

GC-FID results showed that autothermal bio-oil has statistically the same amount of volatiles as conventional bio-oil. However, pretreated autothermal reveals more volatile compounds (**Figure 9**). This can be attributed to the fact that the pretreatment may help more with the catalytic breakdown of lignocellulosic material rather than just thermal degradation.

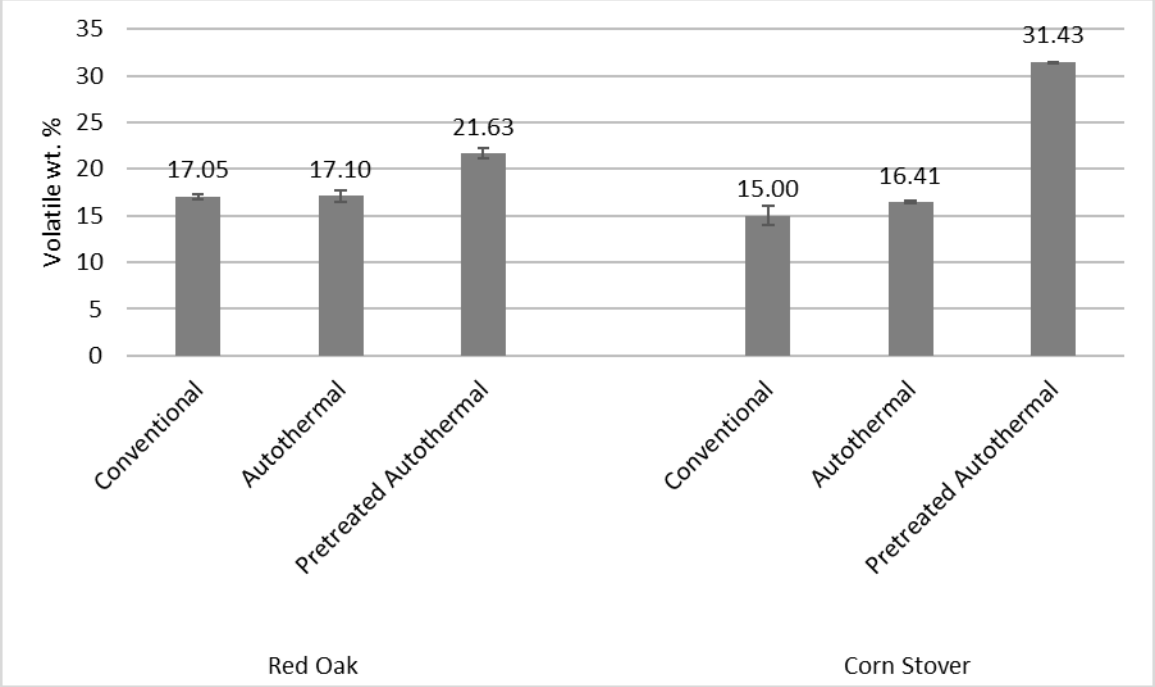

Figure 9. GC-FID volatiles present in six different types of the acetate fraction of bio-oil.

Table 4 lists compounds present in three or more of the bio-oils characterized by GC-MS in this study. A full listing of all compounds identified is in the supporting information of this manuscript (Table S1). All compound matches were above 60% probability. Two interesting compounds identified are DL-arabinose and limonene dioxide. DL-arabinose is a sugar and made its way to the final aqueous fractions rather than remaining with the majority of the sugars in SF1 and SF2. Limonene dioxide is a derivative of limonene, a chiral terpene that smells like oranges. Like other chiral

compounds, limonene (and limonene dioxide) would be ideal target compounds to use for future work.

Table 4. GC-MS results of six acetate fraction bio-oils. An "X" denotes presence of the compound.

	Red Oak			Corn Stover		
	Conventional	**Autothermal**	**Pretreated Autothermal**	**Conventional**	**Autothermal**	**Pretreated Autothermal**
(E)-2-hexen-1-ol	X	X		X		
1-acetylcyclohexene	X	X		X	X	
1-hydroxy-2-propanone	X		X	X	X	
2,4-dimethylfuran	X	X			X	
2-decenoic acid	X	X	X			X
acetic acid	X	X	X	X	X	X
DL-arabinose	X	X				X
furfural	X	X	X			X
limonene dioxide	X			X	X	

Figure 10 shows the results of the moisture analysis. The water content in acetate fraction is very similar except for corn stover, pretreated bio-oil. This may have occurred due to differences in the fractionation system and more water being separated in previous fractions.

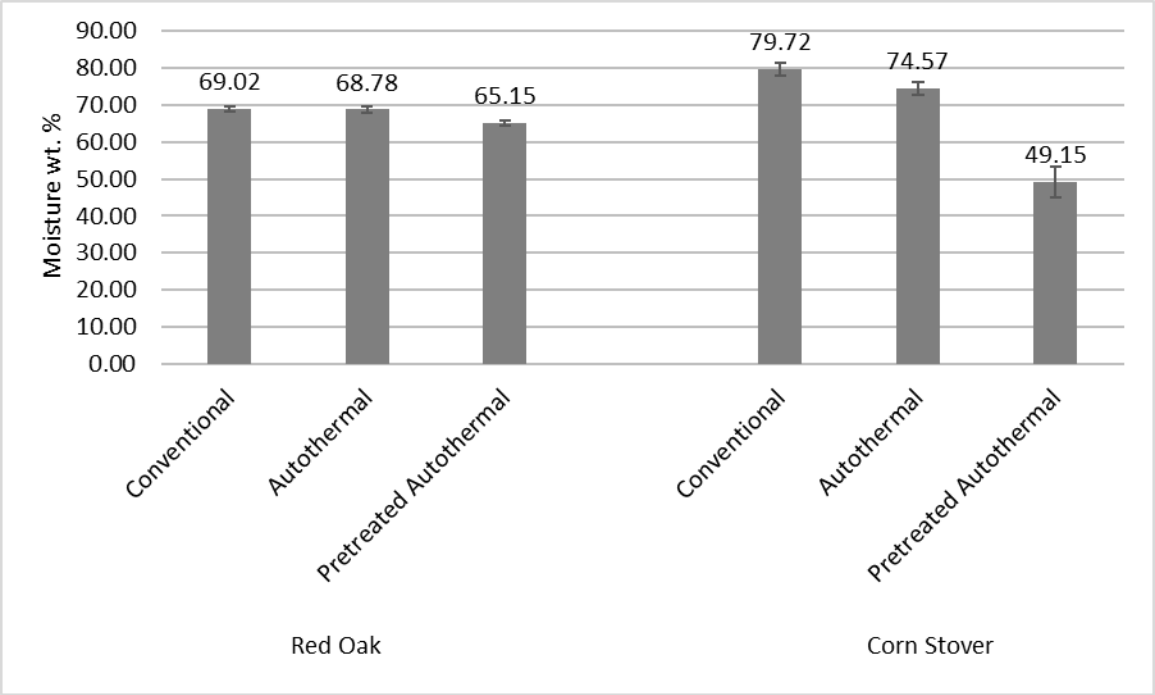

Figure 10. Moisture wt.% of the aqueous fraction of bio-oils.

Table 5. Ion Chromatography values wt.% of acetate fraction of bio-oil.

		Glycolic	Formic	Acetic	Propionic
Red Oak	Conventional	0.02	0.32	7.75	0.17
	Autothermal	0.02	0.38	7.76	0.17
	Pretreated Autothermal	0.16	0.48	6.03	0.13
Corn Stover	Conventional	0.05	0.10	3.49	0.26
	Autothermal	0.08	0.29	4.10	0.34
	Pretreated Autothermal	0.16	1.32	4.79	0.14

In the preceding table, **Table 5**, organic acid weight percentages are reported. The corn stover acetic acid values are lower than the red oak values because red oak or hardwoods have more acetyl groups in the hemicellulose than herbaceous material like corn stover.

Phenolic content based on gallic acid equivalents is reported in **Figure 11**. Surprisingly, both pretreated autothermal bio-oils have triple the quantity of phenols.

This is most likely due to separation differences with the different fractionation systems. The temperature cuts may have been designed differently for phenols in each system.

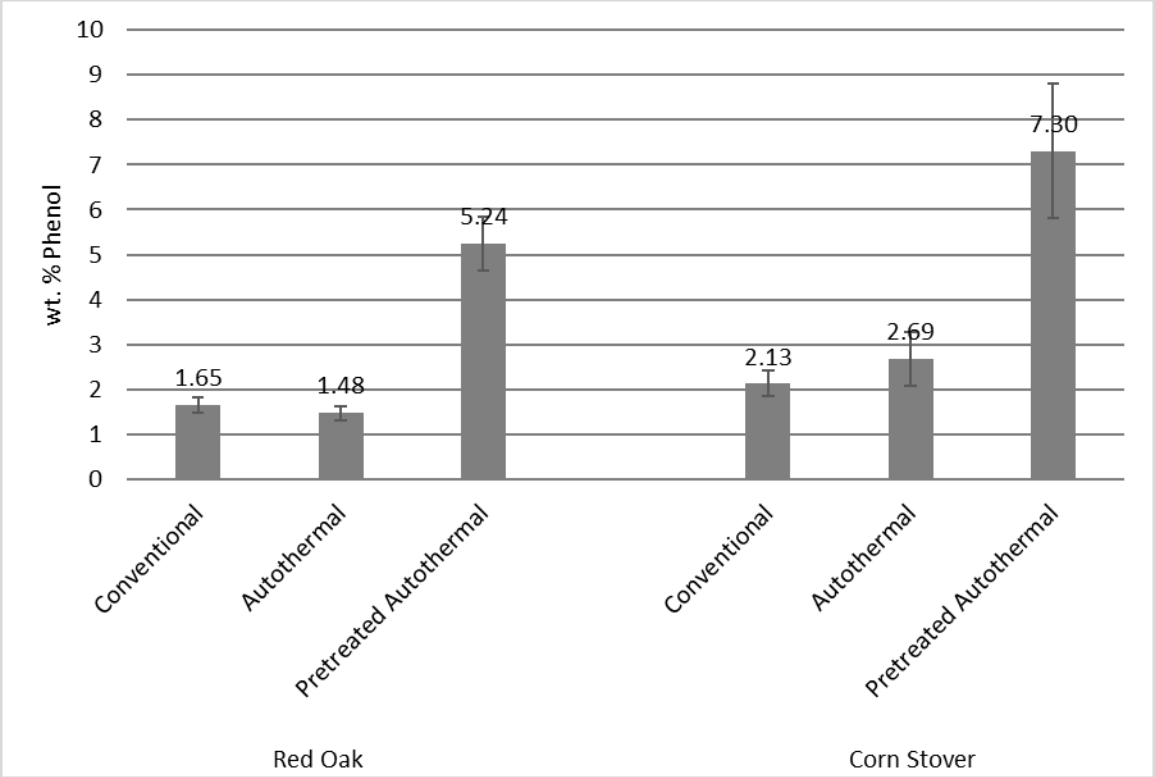

Figure 11. Folin-Ciocalteu results detailing the differences in phenols of the acetate fraction of different bio-oils.

^{31}P-NMR analysis was performed on the acetate fractions of different types of bio-oil. The samples were phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) to allow for quantification (mmol/g) of the hydroxyl group substitution of aliphatic, phenolic, and carboxylic groups in the bio-oil samples (**Figure 12** and **Figure 13**).

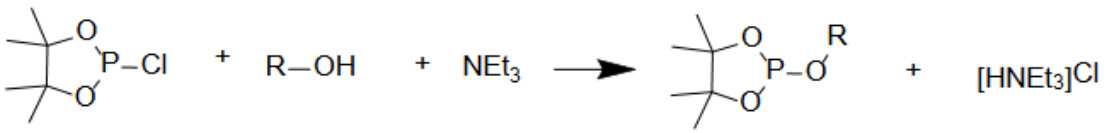

Figure 12. Phosphitylation of the hydroxyl groups of bio-oil.

Surprisingly, the bio-oils are very similar when using NMR for quantification. Autothermal pretreated corn stover had the highest quantity of aliphatic and phenolic hydroxyl groups while red oak bio-oil from nitrogen-fluidized or conventional pyrolysis had the highest amount of carboxylic acid based hydroxyl groups. This suggests that pretreated lignocellulose from corn stover is more easily broken down to phenolic monomers in autothermal conditions. The higher hydroxy-carboxylic acid functionalities in red oak pyrolysis oil can easily be attributed to the hardwood hemicellulose composition.

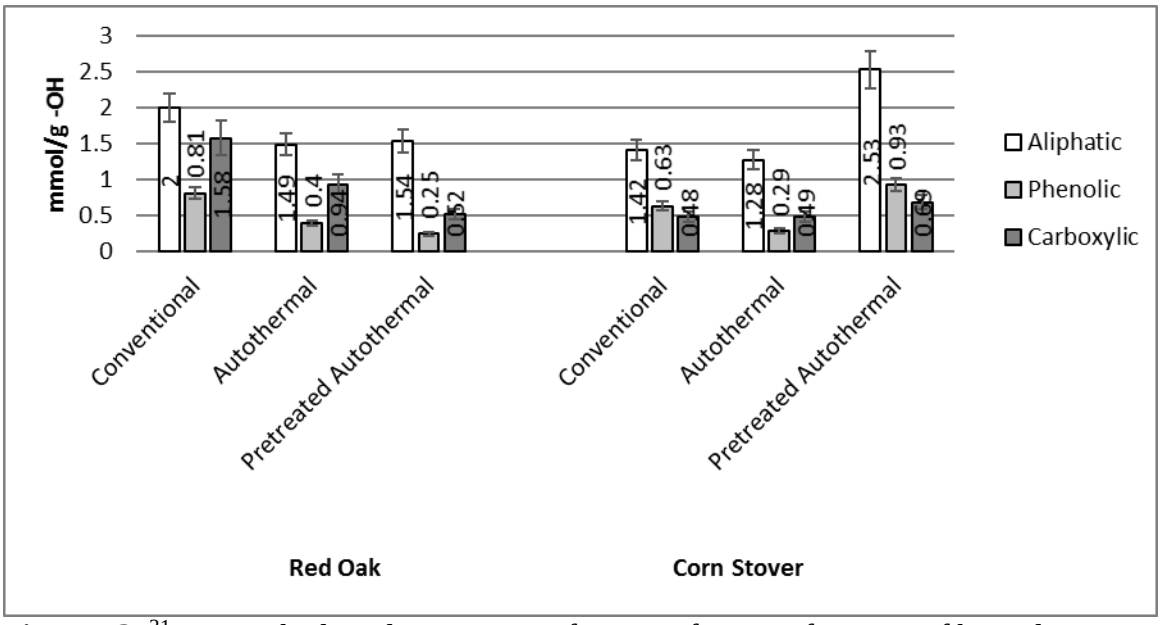

Figure 13. ^{31}P-NMR hydroxyl group quantification of acetate fractions of bio-oil.

Ultimate analysis of the fractions revealed higher values of carbon for oil from autothermal pyrolysis. This can be attributed to the fractionation system and pyrolysis regime. Specifically, fewer fractions yield a higher carbon content per fraction. **Table 6** reports dry, ash-free values and oxygen by difference. **Table 7** is on a wet, ash basis so oxygen content cannot be calculated since water is included in the hydrogen percentage. The small hydrogen percentage in the dry, ash-free analysis is due to variation in water

content between samples tested by Karl-Fisher and the samples tested by ultimate analysis despite thorough mixing.

Table 6. Ultimate analysis acetate fraction characterization on a dry, ash-free basis and oxygen by difference.

		N	C	H	S	O
Red Oak	Conventional	0.50	44.08	0.19	0.03	55.20
	Autothermal	0.76	42.67	0.90	0.02	55.65
	Pretreated Autothermal	1.08	50.00	1.90	0.19	46.82
Corn Stover	Conventional	1.50	47.63	0	0.06	61.21
	Autothermal	0.93	43.02	0	0.03	62.63
	Pretreated Autothermal	0.63	48.37	0.35	0.23	50.42

Table 7. Ultimate analysis characterization on a wet, ash basis of the acetate fractions.

		N	C	H	S
Red Oak	Conventional	0.15	13.62	7.73	0.01
	Autothermal	0.23	13.19	7.92	0.01
	Pretreated Autothermal	0.38	17.29	7.90	0.07
Corn Stover	Conventional	0.30	9.57	6.77	0.01
	Autothermal	0.23	10.84	6.62	0.01
	Pretreated Autothermal	0.32	24.53	5.64	0.11

In FT-IR, the carbonyl region (1640 cm^{-1}) of the pretreated autothermal red oak and the autothermal corn stover showed less carbonyl functionality. In addition, the -OH group (3400 cm^{-1}) also was less intense. These results differ from the other results previously stated. However, FTIR is very sensitive to homogeneity of the sample and may not be representative of the entire sample. The overlaid spectra are located in the supporting information (Figures S1 and S2).

Total Acid Number and Modified Acid Number (Phenolics and Carboxylic Acids) results agreed with F-C and IC test results (**Figure 14**). Phenolic content is higher in the pretreated autothermal samples. Carboxylic acid content also agrees because acyl groups are less plentiful in herbaceous material compared to hard woods.

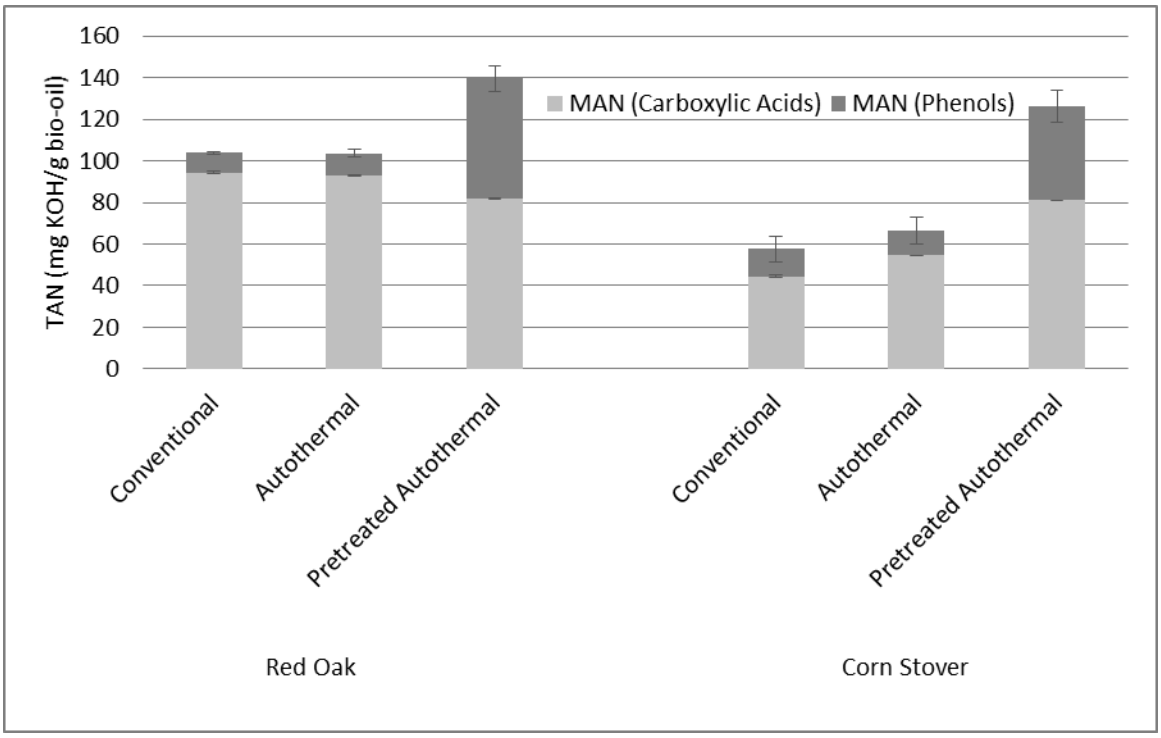

Figure 14. TAN and MAN values for the acetate fractions. Both phenolic and carboxylic acid MAN values contribute to the TAN value.

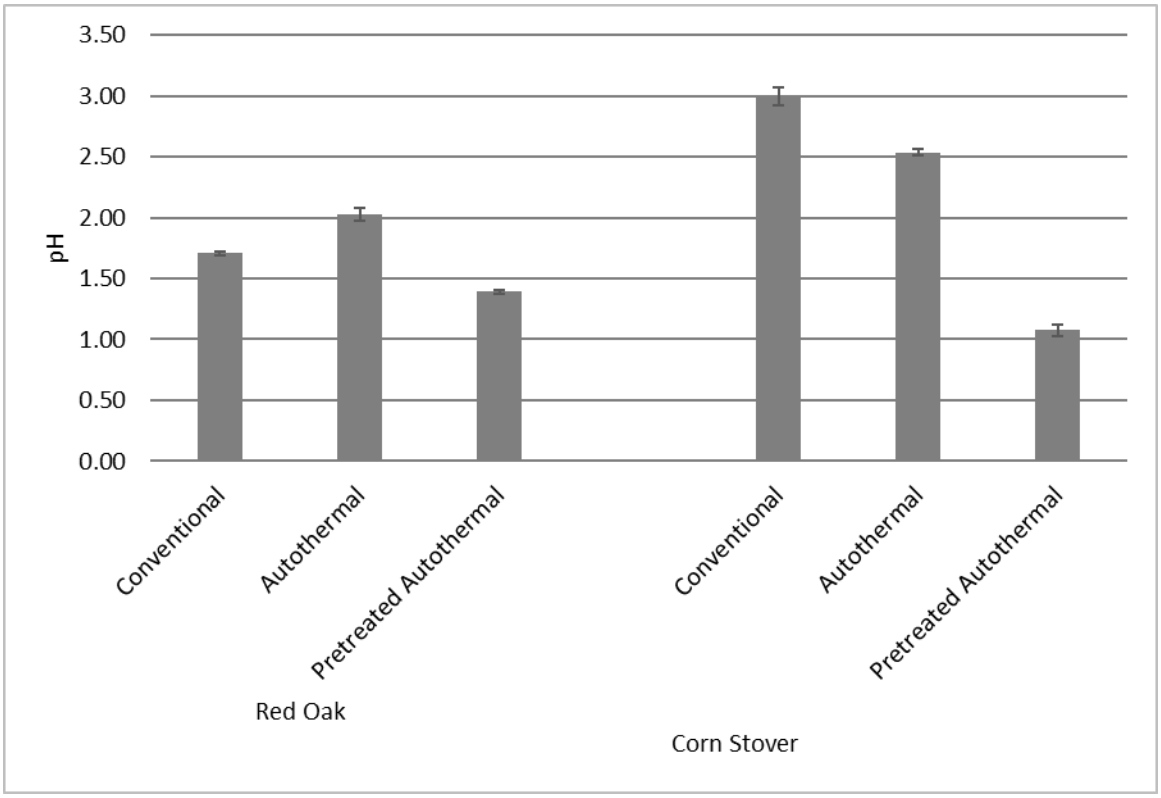

Figure 15. pH values obtained from the acetate fractions.

Figure 15 reveals that pH correlates well with water content. The smaller the water content, the lower the pH. This also corresponds well with TAN/MAN and F-C values as well. Phenols and other acidic compounds contribute to pH.

Table 8. Proximate analysis results of the acetate fraction. All values are in weight percent.

		Moisture (from KF)	Volatiles (from Difference)	Fixed Carbon	Ash
Red Oak	Conventional	69.02	30.69	0.29	0.08
	Autothermal	68.78	30.59	0.39	0.32
	Pretreated Autothermal	65.15	31.70	2.87	0.28
Corn Stover	Conventional	79.72	20.15	0.21	0.19
	Autothermal	74.57	24.81	0.62	0.23
	Pretreated Autothermal	49.15	46.05	4.77	0.14

Proximate analysis results are reported in **Table 8**. Moisture values from Karl Fisher were used to calculate the volatiles by difference. The reason being, the majority of the volatiles had already evaporated prior to the water content integration on the software. The volatiles results are different from GC-FID values, but the trend is the same. This is most likely sampling error. Interestingly, fixed carbon values from the pretreated sample are a lot higher, this is most likely due to the pretreatments employed. Surprisingly, the ash content of the corn stover samples is not as high as was expected. Typically, corn stover ash content is higher due to metals content from the soil.

Personal communication [28] has revealed that an acidification with a strong acid of the SF5 prior to extraction will yield better results. The acidification should help with ionization of acetic acid in an aqueous solution and enable better partitioning. Temperature of the extraction may also play a role (an increase would be a negative interaction by reducing hydrogen bonding). Further tests need to be performed on the waste water stream from the separation process to determine its chemical and biological oxygen demands. It is hypothesized that this waste water retains little organic content, greatly reducing waste water treatment.

Conclusion

Long chain fatty acids were able to extract acetic acid from the aqueous phase of bio-oil while excluding water. Among possible solvents for this liquid-liquid extraction, heptanoic acid was selected because of its low water solubility; high boiling point compared to the acetic acid to be distilled from it; and stability during storage. Heptanoic acid extraction of the acetate fraction (1:6) has shown favorable results with almost complete removal of acetic acid (98.5% efficient) in three washes or extractions. The

water content was reduced from 69.02 to 3.84 wt.%. This technique was also successful when used to recover acetic acid from three industrial acetate streams. Surprisingly, many other light oxygenates were extracted in the extract streams. These streams yielded concentrated organic, solutions that could be distilled from the heptanoic acid, suitable for catalytic cracking to aromatics.

However, when attempts were made to extract autothermal and pretreated autothermal acetate fractions from bio-oil, emulsions, not bilayers would form. If two separable layers would form, higher percentages of water were extracted. This unexpected result encouraged a full characterization study. This study did not reveal notable chemical differences between the acetate fractions. The main differences can be attributed to feed stock and the pyrolysis system on which the bio-oil was generated. Typically, the red oak contained for carboxylic acid functionality than corn stover attributed to the fact that hard woods contain more acyl groups than herbaceous material in the hemicellulose. More compounds were present in the pretreated autothermal acetate fractions. This difference is most likely due to differences in the fractionation system between two pyrolyzers. Chemically, all acetate streams should extract equally as well.

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Supporting Information

Table S1. GC-MS compounds present in six acetate fractions from red oak and corn stover using different pyrolysis regimes. All compound matches were above 60% probability.

	Red Oak			Corn Stover		
	Conventional	Autothermal	Pretreated Autothermal	Conventional	Autothermal	Pretreated Autothermal
(1R,2S,5R)-1'-(butyn-3-one-1-yl)menthol			X			
(E)-2-hexen-1-ol	X	X		X		
(E)-5,9-dimethyl-5,8-decadien-2-one				X		
(E)-acetate-9-tetradecen-1-ol	X	X				
(propoxymethyl)oxirane			X		X	
(Z)-3,4-dimethyl-3-hexen-2-one				X		
1-(1-methylethoxy)-2-propanol						X
1-(acetyloxy)-2-butanone					X	
1,1,1-trimethoxyethane						X
1,1-dimethoxyethane		X				
1,1'-oxybis-2-propanol			X			
1,4-dimethylpyrazole		X				
1-acetylcyclohexene	X	X		X	X	
1b,5,5,6a-tetramethyl-octahydro-1-oxa-cyclopropa[a]inden-6-one	X					
1-hydroxy-2-butanone				X		
1-hydroxy-2-propanone	X		X	X	X	
1-methoxy-3-hydroxymethylheptane				X		
1-methylbutylhydroperoxide		X		X		
1-propanol				X		
1-propoxy-2-propanol		X			X	
2-(2-isopropenyl-5-methyl-cyclopentyl)-acetamide						X
2-(2-methoxyethoxy)ethanol			X			
2,3-bis(methylene)-1,4-butanediol				X	X	
2,4-dimethylfuran	X	X			X	
2,6-dimethoxyphenol				X		
2-buten-1-ol					X	

Table S1 Continued

2-decenoic acid	X	X	X			X
2-deoxy-D-galactose						X
2-dodecenoic acid			X			
2-ethyl-4-(3-oxiranylpropyl)-1,3,2-dioxaborolane			X			
2-ethylidene-6-methyl-3,5-heptadienal				X		X
2-heptanone						X
2'-hexyl-, methyl ester-[1,1'-bicyclopropyl]-2-octanoic acid			X			
2-methylene-acetate-1-butanol					X	
2-nonen-1-ol					X	
2-oxa-7-thia-tricyclo[4.3.1.0(3,8)]dec-10-yl ester-acetic acid			X			
3,3-dimethoxy-2-butanone						X
3,4,5,5-tetramethyl-2-cyclopenten-1-one		X	X			
3-hepten-1-ol					X	
3-hydroxydodecanoic acid						X
3-nonynoic acid				X	X	
3-O-benzyl-d-glucose						X
4,5-diethyl-2,3-dihydro-2,3-dimethylfuran			X			
4,7-dimethyl-5-decyne-4,7-diol		X				
4-ethoxy-2-butanone			X			
4-hydroxycyclohexanone			X			
4-O-β-D-galactopyranosyl-β-D-glucopyranose			X			X
6-methyl-5-hepten-2-ol	X	X				
6-oxa-bicyclo[3.1.0]hexan-3-ol					X	
7-oxo-octanoic acid						X
8-methylenecyclooctene-3,4-diol					X	
9-oxabicyclo[6.1.0]nonan-4-ol			X			
acetic acid	X	X	X	X	X	X
cis-cyclohexene-3,5-diol			X			
DL-arabinose	X	X				X
ethyleneglycol-diglycidylether	X					
furfural	X	X	X			X
glycolaldehyde-dimethylacetal						X
limonene dioxide	X			X	X	
naphtho[2,3-b]thiophene						X
propylene carbonate	X					X
R-limonene			X			X
tetrahydro-2,5-dimethoxyfuran						X

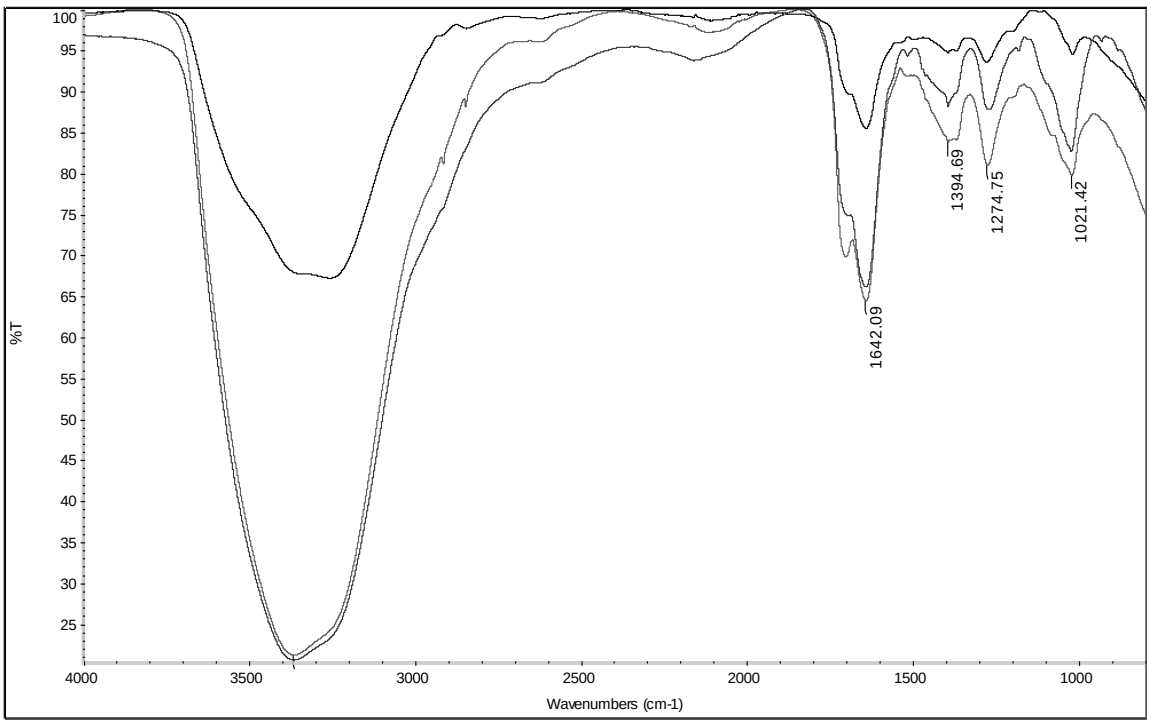

Figure S1. Compiled red oak bio-oil FTIR spectra. The less intense trace is the pretreated autothermal sample.

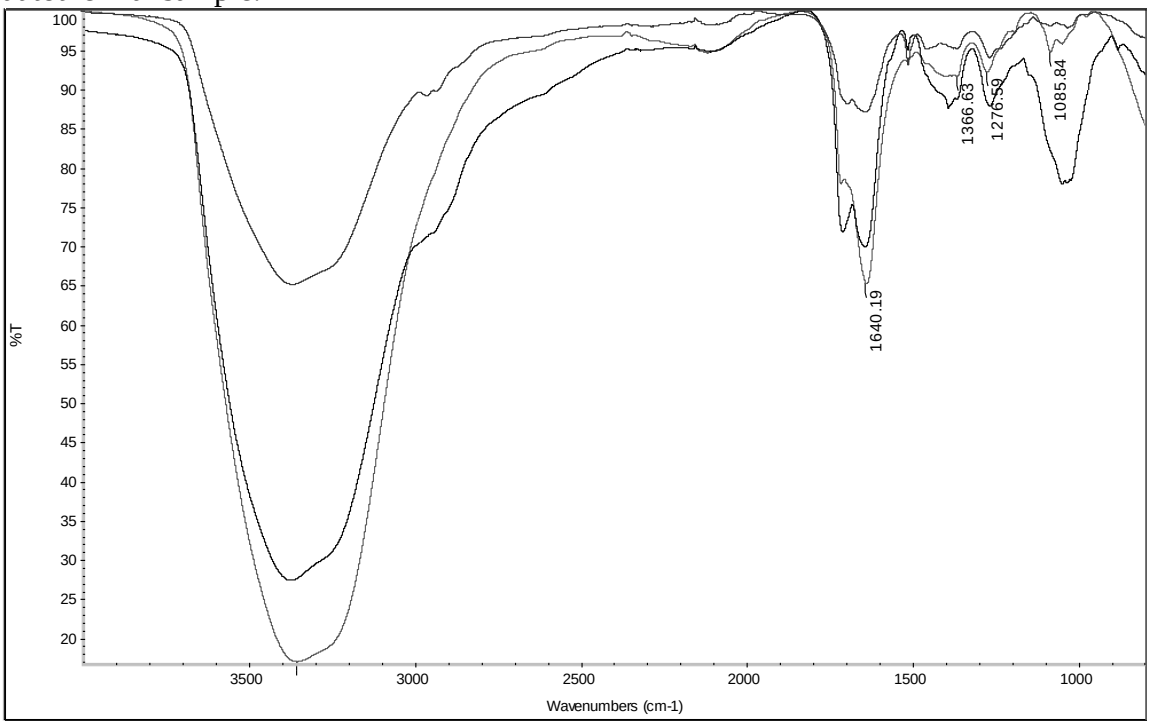

Figure S2. Compiled corn stover bio-oil FTIR spectra. The less intense trace is the autothermal sample.

CHAPTER 5

ADSORPTION RATES AND CAPACITY OF DEBITTERING AND ANIONIC RESINS TO RECOVER ORGANICS FROM THE AQUEOUS STREAM OF FAST PYROLYSIS

Patrick H. Hall, John P. Stanford, Marjorie R. Rover,
Ryan G. Smith, and Robert C. Brown

Abstract

Productive use of all streams from a fast pyrolysis reactor will be important to their profitable operation. The condensable products of fast pyrolysis can be recovered as separate fractions of heavy ends, intermediates, and an aqueous phase. The aqueous phase consists mostly of carboxylic acids (10 wt.%) and several other light oxygenates (30 wt.%). However, the presence of water (60 wt.%) makes upgrading and simple distillation of this fraction very difficult due to water's high heat capacity and azeotropic properties.

The primary goal of this research is to recover acetic acid and other water soluble organic species from the aqueous phase, which increases the number of chemical products from the bio-oil and reduces waste water treatment costs associated with the pyrolysis biorefinery. We have determined that hydrophobic polymeric resins are suitable candidates for cleaning this waste water stream. Among possible resins for chemical adsorption, debittering (SP70) and anionic (A21) resins were selected due to their affinity for phenolic and acetic acid removal, respectively. Both resins have shown favorable results with almost complete removal of their targeted species. Regeneration of the resins allow for recovery of the adsorbed materials through desorption. Using a debittering resin could allow for a concentrated phenolic/light oxygenate stream to be

catalytically upgraded while generating a suitable dilute acetic acid stream for utilization in fermentation where phenolic content must be below 0.01 wt%. Our studies have also shown anionic resins to be an effective tool for the production of acetate salts through regeneration which can be used for either fermentation or anti-icing agents such as calcium magnesium acetate (CMA).

In addition to column elution experiments to calculate adsorption values; breakthrough curves, adsorption isotherms, and kinetic adsorption parameters were also determined. These adsorption parameters can be further implemented to scale up this process for a biorefinery.

Introduction

Second generation bio-fuels based on lignocellulosic materials frequently suffer from low yields and lack of product separation. This is especially evident with the aqueous streams of these processes. The streams typically contain compounds that could be utilized rather than neutralized and discarded in waste water. In order to sequester these useful materials from aqueous streams, researchers are focusing on volatile fatty acids like acetic acid, their enrichment in fermentation broth, and various separation methods such as pervaporation, solvent extraction, reactive separation, and resin adsorption [1-5].

Acetic acid is produced in large quantities (9-12 wt. %) in Stage Fraction Five (SF5) and Six (SF6) of the PDU. However, there are large volumes of water and other light oxygenates associated with these fractions. Therein lies the one of the barriers of acetic acid separation, light oxygenates. Of course, water being the other barrier to producing a pure concentrated acetic acid stream. However, to tackle this complex

mixture, we are treating this as a binary separation; acetic acid removal from water a soluble organic substrate.

The goal of this project is recovery of acetic acid from the acetate stream of a pyrolysis bio-refinery. The approach to this goal is two-fold; utilization of pyrolysis fractionation technology and the separation of acetic acid from light oxygenates using resin technology to generate a dilute acetic acid. The purification of acetic acid from SF5 and SF6 can be performed using an acid or phenol selective polymeric resin. A resin with a higher adsorption capacity and adsorption rate (as compared to other resins) for phenols and other light oxygenates) or acetic acid, will be used for the purification of SF5 and SF6. Desorption with sodium hydroxide should theoretically yield a dilute sodium acetate stream, devoid of phenolic inhibitors. This neutralized sodium acetate stream would be an ideal candidate for fermentation to methane or it could be acidified and extracted using the procedure described in the previous chapter of this manuscript.

Several types of adsorbents have been explored for the removal of organic species from water, particularly in wastewater treatment [6]. These adsorbents include polymeric resins, natural ash and biomaterial products like zeolites and activated carbon [7]. This chapter focuses on the use of polymeric resin adsorbents due to their low cost, ease of regeneration and use, and scalability lending themselves to larger industrial processes. Specific polymeric resins were chosen for this study because several literature studies suggest they are good adsorbents for acetic acid and/or phenol and light oxygenate analogues.

This study uses adsorption theory; employing isotherms (linear, Langmuir, and Freundlich), kinetic adsorption profiles, and breakthrough values (Wheeler-Jonas) of

acetic acid and phenolics to determine the best resin for carbon capture from the acetate stream. Although these compounds are present in SF6 as well, this study only focuses on SF5, as current SF6 fractions produced, have variable baselines of chemical quantities.

Resin Structure and Properties

There are six resins in this study that are representative of the types available to a researcher today. They are listed in **Table 1**.

Table 1. Properties of resins in this study.

Resin	**SP207**	**SP70**	**A21**	**A21($^-$OH)**	**IR120(H^+)**	**IR120(Na^+)**
Polymer	PS/DVB	PS/DVB	S/DVB	S/DVB	S/DVB	S/DVB
Functionality	Bromine	None	Dimethyl -amine	Dimethyl-ammonium hydroxide	Sulfonic acid	Sulfonate
Matrix	Porous	Porous	Macro -porous	Macro -porous	Gel	Gel
Particle Diameter (avg. mm)	0.4	0.25	0.55	*	0.73	0.7
Density (g/cm^3)	1.18	1.01	0.33	*	1.28	1.28
Surface Area (m^2/g)	650	700	35	*	NA	NA
Pore Radius (Å)	105	70	55	*	NA	NA
Pore Volume (cm^3/g)	1.2	1.5	0.1	*	NA	NA
Exchange capacity (meq/g)	NA	NA	4.7 ; *	*	1.9 ; 4.4	*

The backbones or polymeric structure of the resin beads in this study are generally Polystyrene (PS)/Divinylbenzene (DVB), but manufacturers will sometimes consider the quantity of crosslinking and label resins as simply styrene-based. The functionality of the backbone also plays a vital role in the properties of the resin and how they perform in a trial, i.e. brominated, weak free base, or strong acid. Typically, the classification of microporous (gel), mesoporous (porous), and macroporous is based on

pore size of 2-20Å, 20-500Å, and >500Å, respectively [8]. However, manufacturers will make mesoporous and microporous resins synonymous or exchange one for the other.

Sepabeads SP207 resin was made viable by researchers collecting water soluble molecules from wastewater [9, 10]. It is strongly hydrophobic, dense, nonionic, and has a large capacity when compared to similar resins. Its high density when compared to other resins is due to its bromine functionalized PS/DVB backbone. This modification allows the polymer to remain on the bottom of solutions and/or columns and not float. This property is useful for upflow fluidized bed applications and column packing material [11-13]. Sepabeads SP70 resin is almost identical to its analogue, SP270. The single difference is that its backbone is unmodified, making this resin less dense and therefore able to float on aqueous solutions. However, once the resin has adsorbed compounds, it sinks in the solution and remains there until regeneration. SP70 is typically used for debittering of juices and other food products, notably orange juice. The debittering process removes polyphenols, furanolactones, and flavonoids which contribute to the acidic taste. It has also been utilized for purification of molasses [14-18].

Amberlyst A21 resin is a weak base anion exchange resin. Like SP70, it was developed for the removal of acidic materials from aqueous streams. The resin itself is shipped as a free base, functionalized with a dimethylamine group. Researchers can leave this as a free base or modify the structure with acidic or alkaline solution through solvent conditioning to form an amine salt. This neutralization helps adsorb or exchange different target compounds. A21 is generally used to remove acidic materials from organic solvents like phenol and hydroquinone from benzene. Researchers have found

success in making both hydroxide (A21($^{-}$OH) and chloride (A21($^{-}$Cl) salts of this resin to exchange carboxylic acids and carbohydrates from aqueous solution [19].

Amberlite IR120(H^{+}) is a strong acid cation exchange resin. Its backbone has been functionalized with sulfonic acid. Typically, this acidic resin is used for water demineralization like potassium removal from tap water or decalcification. It also aids in removal of toxic heavy metals in waste water treatment plants. However, recently, it has become known for separation of amino acids at low pHs [20, 21]. It cation analogue Amberlite IR120(Na^{+}) is generally used for water softening and demineralization.

Theory

Breakthrough Curves

A simple, robust method is needed for estimating the amount of resin required in the column to reduce contaminant levels below the threshold above which they are toxic to the microorganisms used in the proposed fermentations. The Wheeler-Jonas equation (**Equation 1**), originally developed to predict gaseous contaminant breakthrough times for activated carbon filters, will be used for this estimation [22-27]. The Wheeler-Jonas equation is derived from a fluid continuity equation incorporating simple, first-order adsorption kinetics. As such, it should find utility in predicting adsorption of low-level contaminants (phenolics) from a liquid stream. The Wheeler Equation can be written as a semi-logarithmic expression for the exiting concentration from an adsorption filter as a function of time:

$$\rho_b ln\left[\frac{C_{in}-C_{out}(t)}{C_{out}}\right] = -\left(\frac{k_v C_{in}}{W_e}\right)t + \left(\frac{k_v M}{Q}\right) \qquad \textbf{(1)}$$

where ρ_b = bulk density of the resin
C_{in} = entering concentration of contaminant
$C_{out}(t)$ = exiting concentration of contaminant at time t
k_v = reaction rate associated with contaminant adsorption on the resin
W_e = equilibrium absorption capacity of the contaminant on the resin
M = mass of resin
Q = volumetric flow rate of the sugar solution through the resin column

The parameters k_v and W_e depend upon the type of sorbent, contaminant and flow rate of the adsorption process. These parameters can be determined by periodically measuring the outlet concentrations from a column as a function of time and plotting $\rho_b ln\left[\frac{C_{in}-C_{out}}{C_{out}}\right]$ vs. time. The slope of the linear portion of this plot and the y-intercept are related to k_v and W_e as follows:

$$k_v = \left(\frac{Intercept \cdot Q}{M}\right) \qquad \textbf{(2)}$$

$$W_c = \left(\frac{Intercept}{|Slope|}\right)\frac{C_{in}Q}{M} \qquad \textbf{(3)}$$

Rearranging **Equation 1** for the mass of resin *M*, substituting the values of k_v and W_e determined by **Equations 2 and 3**, and specifying the desired breakthrough time for the maximum allowable contaminant level exiting the column (C_{out}), the resin column can be appropriately sized.

Adsorption and quantitation of phase equilibria

Adsorption, at its core, is a mass transfer process which occurs at the interface between two phases. This includes the adhesion of components of a liquid solution onto that of a solid surface. When in solution, the solid surface itself is in a state of unsaturation (with a higher surface energy) requiring a balancing or equilibrium to be established [28].

The relationship between the amount of adsorbate in solution and the adsorbate adsorbed can be described by adsorption isotherms. The curve generated by relating the concentration of a solute on an adsorbent (q) to the concentration of the solute in a solution (c) is known as an adsorption isotherm. Of course, this equilibrium can be changed easily with temperature, among other factors (including pressure, surface area, and activation of a solid adsorbent). The shape of this curve generated also sheds light on whether an adsorbent (resin in this case) is chemical interaction limited and what type of adsorption is occurring; chemisorption and physisorption, to name two. Although there is no definitive separation and both processes can occur simultaneously; chemisorption involves both hydrogen bonding and covalent bonding, and charge transfer. Physisorption describes intermolecular force attractions like van der Waals and dispersion forces, and dipole-dipole interactions. The mass of adsorbed species adsorbed or (q) can be calculated from the concentration change in the liquid phase by **Equation 4**; where V is the volume of solution, M is the mass of dry adsorbate or resin, and c_o and c_e are the initial and equilibrium concentration of the analyte, respectively.

$$q = \frac{V(c_o - c_e)}{M} \qquad \textbf{(4)}$$

As stated earlier, chromatographic separation is based on the partitioning of compounds between the stationary and mobile phase. This partitioning or equilibria can also be quantified by adsorption isotherms. There are many types of isotherms, but three of the most common are used in this chapter: Linear, Langmuir, and Freundlich. Their isotherm shapes are shown in **Figure 1**.

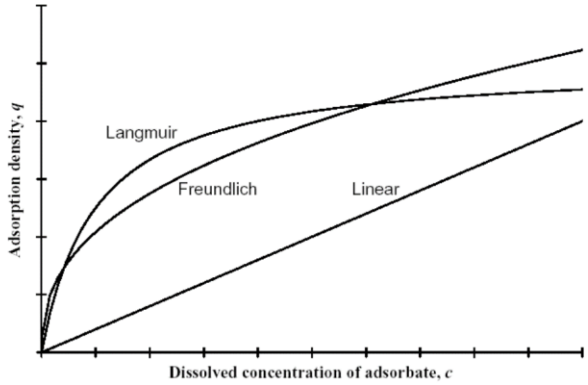

Figure 1. General isotherms; linear, Langmuir, and Freundlich can describe the relationship between concentration of a compound in solution vs. its adsorbed concentration [29].

Adsorption isotherms

The simplest isotherm model is the linear isotherm. The concentration (q) of a compound in equilibrium at its concentration in the liquid phase is expressed in **Equation 5**.

$$q = K \cdot c \qquad \textbf{(5)}$$

$$q = H \cdot c \qquad \textbf{(6)}$$

Although not used in this work, **Equation 5** can also be written as **Equation 6** using the Henry constant of adsorption (H). For linear chromatography, the retention of a compound is independent on its concentration. The linear isotherm model can be applied when concentrations are low, but quickly breaks down when concentrations are higher. Interestingly, the shape of the elution band of a compound with a linear relationship to its stationary phase in chromatography is described as symmetrical or Gaussian. If plotted, the linear isotherm yields the linear isotherm parameter (K) as the slope. The R^2 value helps give insight to the degree of linearity for comparison purposes. The units of q are usually in g/g or mg/g, depicting the grams of material adsorbed (adsorbate) per grams of adsorbent. The units of c are usually in g/mL or g/L.

Non-linear isotherms are more typical in chromatography, especially with adsorbents. A Langmuir isotherm, or Type I isotherm, (**Equation 7**) is a classic example of a non-linear isotherm.

$$q = \frac{Q_m K_L c}{1 + K_L c} \qquad \textbf{(7)}$$

It can also be rewritten in linear form as **Equation 8** shows:

$$\frac{c}{q} = \frac{1}{Qm} c + \frac{1}{K_L Q_m} \qquad \textbf{(8)}$$

The inverse of the slope of the line (Q_m) is the maximum loading capacity of the resin at equilibrium. It is also listed as q^* or q_{max} in literature and is the plateau of the Langmuir isotherm. K_L is the Langmuir affinity parameter or fit of the line to the slope. R^2 is also used as a test for linearity in **Equation 8**. Of course, **Equation 7** can also be solved using software like MATLAB, which will be described later. In multicomponent mixtures, the solutes compete for adsorption sites; contributing to the shape of the Langmuir isotherm model. Typically, this model's shape is convex upward, but convex downward isotherms also exist when exclusion takes place or the Donnan effect occurs [30]. The shape of the elution band in a Langmuir isotherm is a sharp uptick or spike followed by an elongated tail [31]. The Langmuir model also assumes monolayer coverage of an adsorbent making all adsorption sites equally probable in a second order reaction [32].

If the fit still does not describe equilibrium relationship, the Freundlich equation is used (**Equation 9**).

$$q = K_F c^{1/n} \qquad \textbf{(9)}$$

Like the Langmuir isotherm, the Freundlich isotherm can be rearranged for linear plotting (**Equation 10**).

$$\log(q) = \log(K_F) + \frac{1}{n}\log(c) \qquad \textbf{(10)}$$

K_F is the Freundlich adsorption capacity parameter while *n* is the affinity parameter (which can be determined from the slope). The affinity parameter describes the fit of the line to the model and the intensity of the adsorption. It can roughly be used to determine how well the equilibrium relationship follows the Freundlich parameter; much like R^2 for linear fits. For *n* values greater than one, it suggests a favorable isotherm, whereas larger *1/n* values mean a stronger adsorption. It must be noted, however, that the Langmuir isotherm has a rational basis while the Freundlich isotherm is an empirical equation.

Adsorption kinetics and activation energy

The mass transfer coefficient (*k*) or rate can be determined using a pseudo-first order (**Equation 11**) or pseudo-second order equation (**Equation 12**) [33].

$$\frac{dq}{dt} = k_1(q^* - q_t) \qquad \textbf{(11)}$$

$$\frac{dq}{dt} = k_2(q^* - q_t)^2 \qquad \textbf{(12)}$$

A rearrangement of **Equation 11** yields a linear function of first order kinetics as shown in **Equation 13** and **Equation 14,** both give the same result. The linear function of second order kinetics is **Equation 15**.

$$\ln\left(\frac{1}{\frac{q_t}{q^*}-1}\right) = -k_1 t \qquad \textbf{(13)}$$

$$\log(q^* - q_t) = \log(q_t) - \frac{k_1}{2.303}t \qquad \textbf{(14)}$$

$$\frac{1}{(q^*-q_t)} = \frac{1}{q^*} + k_2 t \qquad \textbf{(15)}$$

Plotting these functions gives the mass transfer coefficients (k_1 and k_2) as the slopes.

From this, activation energy (or sensitivity to temperature) can be determined from the Arrhenius equation (**Equation 16**) and its linear analogue (**Equation 17**).

$$k = Ae^{-Ea/(RT)} \quad \textbf{(16)}$$

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A) \quad \textbf{(17)}$$

R is the universal gas constant, T is temperature, A is the frequency of collisions, and E_a is the activation energy.

Adsorption thermodynamics

Although, not specifically a target value in this study, Gibbs free energy (**Equation 18**) or its energy for a system at equilibrium (**Equation 19**) can be calculated and is related to the Arrhenius equation by the Eyring Equation (**Equation 20 and 21**). It can be linearized as well (**Equation 22**).

$$\Delta G = \Delta H - T\Delta S \quad \textbf{(18)}$$

$$\Delta G = -RT\ lnK \quad \textbf{(19)}$$

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}} \quad \textbf{(20)}$$

$$ln\frac{k}{T} = \frac{\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \quad \textbf{(21)}$$

$$lnK = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \textbf{(22)}$$

The variables: K is the thermodynamic equilibrium constant, T is the temperature, $\Delta H^{\ddagger}$ is the enthalpy of activation, k_B is the Boltzmann constant, h is Plank's constant, $\Delta S^{\ddagger}$ is the entropy of activation, and $\Delta G^{\ddagger}$ is Gibb's energy of activation. If Gibbs free energy is negative the adsorption is a spontaneous process. If enthalpy is negative, adsorption is an exothermic process [34].

Mass transfer

Mass transfer plays a role in adsorption. However, when characterizing resin for the optimization of adsorption, it is important to remove mass transfer from the equation.

One way to do this is to constantly have the resin particles or the solution in motion. This way, the diffusion boundary layers of resin particles are at their smallest, allowing adsorption to occur faster. Diffusion in an adsorption setting can be described by **Figure 2** and **Equations 23** and **24** and also Fick's Law (flux = diffusivity of a concentration in a location) [35].

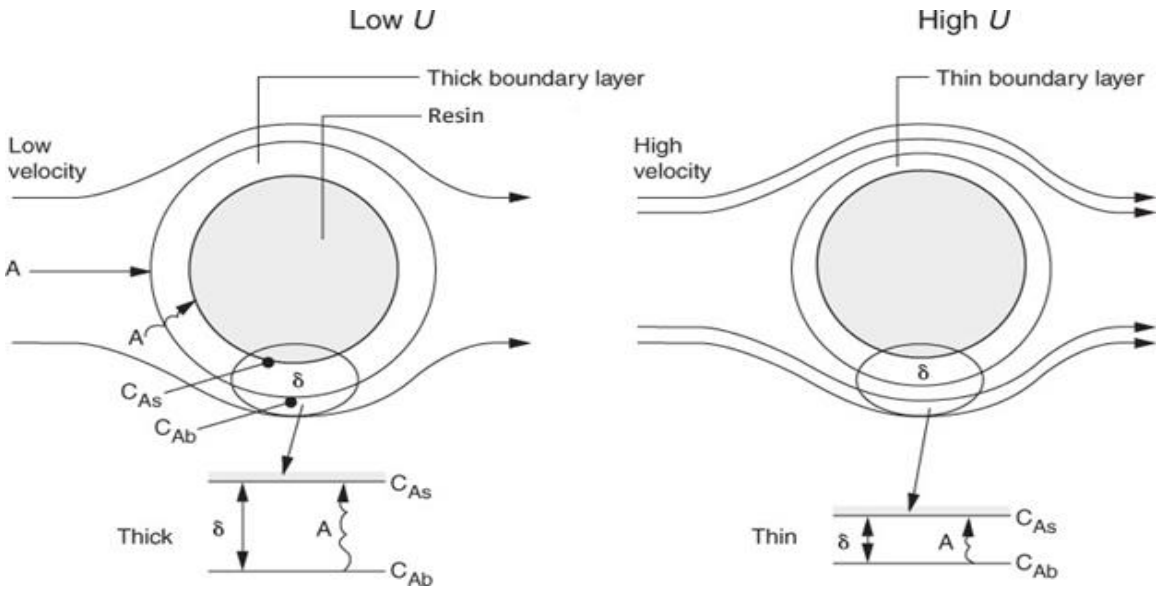

Figure 2. Diffusion through the external boundary layer [36].

$$Rate = k_C(C_{Ab} - C_{As}) \qquad \textbf{(23)}$$

Solution A, at bulk concentration C_{Ab} must diffuse through the boundary layer δ to the external surface of the resin where the concentration is C_{As}. As shown in **Equation 23**, the mass transfer coefficient (k_c) is a function of hydrodynamic conditions; fluid velocity U and particle diameter D_p.

$$k_C = \frac{D_{AB}}{\delta} \qquad \textbf{(24)}$$

The mass-transfer coefficient is inversely proportional to the boundary layer thickness δ and directly proportional to the diffusion coefficient (**Figure 3**). In other words, when fluid velocity is slow, the mass transfer coefficient is small and limits the reaction. If the

fluid velocity is fast, the mass transfer rate is increased and the boundary layer is thinner. If the velocity is very fast, the boundary layer thickness δ offers no resistance. This also occurs when the particle size is increased, the boundary layer becomes smaller.

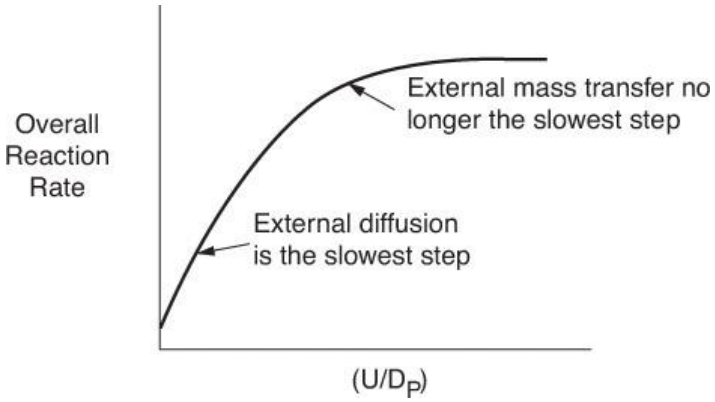

Figure 3. Effect of particle size and fluid velocity on reaction rate [36].

Once external diffusion is no longer the rate limiting step. Internal diffusion is the slowest rate limiting step. As shown in **Figure 4**, reactant A diffuses at concentration C_{As} into the resin's interior at concentration C_A. Size of the resin bead plays a role on how long diffusion takes, if it occurs at all (in the case of larger particles). Larger resins typically adsorb only on the outside of the bead, while smaller resin particles allow for faster diffusion of compounds internally. If internal diffusion is fast enough and the boundary layer is small, mass transfer no longer limits adsorption as described in **Equation 25**.

$$Rate = k_r C_{As} \qquad \textbf{(25)}$$

The rate constant (k_r) increases as resin particle size decreases in solution of concentration C_{As}.

Figure 4 shows internal diffusion (a) of a small particle that size is no longer the slowest step (b). The surface adsorption and desorption now limit the rate of reaction (if velocity of the fluid is fast as previously described).

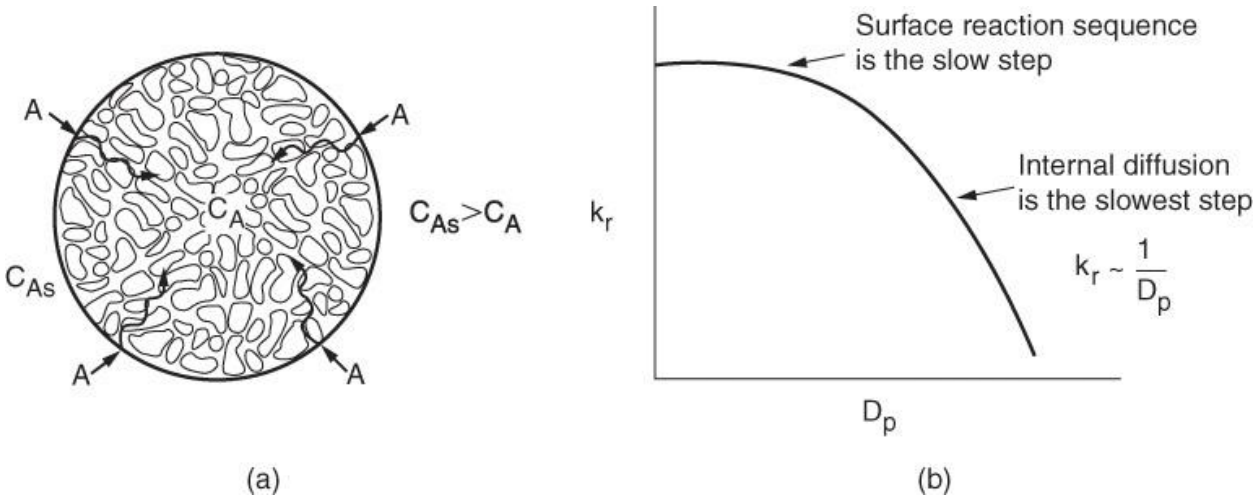

Figure 4. Internal diffusion of a resin particle and rate dependency as a function of particle diameter (D_p) [36].

Materials and Methods

Bio-oil

Fractionated bio-oil was produced using a fluidized bed fast pyrolyzer operated at 500°C with a multi-stage bio-oil recovery system. Autothermal operation was employed using air as a fluidizing agent. Red oak (*Quercus rubra*; Wood Residual Solutions of Montello, Wisconsin) was used as feedstock. Stage fractions 1, 3, and 5 were collected using water-cooled condensers operated at progressively lower temperatures. These temperatures enabled collection of bio-oil according to condensation temperatures of different compounds. Stages 2, 4, and 6 were electrostatic precipitators (ESPs) that collected the aerosols. Further operational information and the PDU diagram can be found in previous literature and the introduction of this manuscript [37-39].

Resins

Sepabeads SP207 and SP70, Amberlite IR120(H^+) and IR120(Na^+), and Amberlyst A21 resins were purchased from Sigma Aldrich (St. Louis, Missouri) and dried for three days at 60°C to remove sorbed water content. Amberlyst A21($^-$OH) was

prepared by mixing the resin with 1M sodium hydroxide at room temperature for one hour. The resin was filtered and dried for three days at 60°C [19].

Room temperature isotherms

Vials containing 10mL of SF5 with a range of concentrations (0%, 6.25%, 12.5%, 50%, and 100%) and 0.5g of swollen resin were shaken for 24 hours at room temperature. Prior to adding the SF5 solution, the weighed dried resin was rewetted to swell it to its original moisture content with 2-3 drops of water.

Column elution

A column (24/40 joint, 1''I.D. x 18'' with a fritted disc) was wet-packed with slurry of 100g of Amberlyst A21 (Sigma Aldrich, St. Louis, Missouri) and 18.2MΩ water. Three column volumes of water were eluted through the column to remove any manufacturing residues. Column volume (CV) was determined by CV = (interstitial volume + resin particle volume + resin pore volume). Alternatively, CV= (resin slurry mass / resin slurry density). An HPLC pump was used to backflush the column at 100mL/min. Back flushing was performed until all air pockets were absent and the resin beads were flowing freely. Water eluted through the column using gravity. The meniscus of the water level was stopped just above the topmost layer of the resin.

SF5 was carefully added to the column without disturbing the column bed using a pipette. The fluid in the column eluted at a steady rate of 2 column volumes hr^{-1} (4.6 ml min^{-1}) using an HPLC pump. SF5 was added batch-wise to the inlet of the column to prevent the resin from drying over the course of the experiment. Samples were taken once per minute after the void volume of water had eluted. Once acetic acid presence was determined using pH paper, the elution and sample collection was terminated.

Room temperature kinetics

Fifty mL of SF5 was stirred at 200 rpm with five grams of swelled (previously dried) resin. Aliquots were taken at time intervals from 0-300 minutes.

Analytical testing

Phenolic content, based on gallic acid equivalents (GAE), was measured at with a Varian Cary 50 UV–visible spectrophotometer (Agilent Technologies Inc., Santa Clara, CA) using Cary WinUV (Agilent Technologies Inc., Santa Clara, CA) Simple Reads module software at 765nm. The Folin-Ciocalteu method used was based on a previous procedure [40].

Carboxylic acid composition was determined by a Dionex ICS3000 Ion Chromatograph (IC) (Thermo Scientific®, Sunnyvale, CA). The system utilized a conductivity detector and an Anion Micromembrane Suppressor AMMS-ICE300. The suppressor regenerant used was 5mM tetrabutylammonium hydroxide (TBAOH) at a flow rate of 3 mL min^{-1}. The eluent was 1.0mM heptaflourobutyric acid with an IonPac® ICE-AS1 4 × 50 mm guard column and IonPac® ICE-AS1 4 × 250 mm analytical column with a flow rate of 0.120 mL min−1 at 19°C. Dionex Chromeleon version 6.8 was used for data analysis. The bio-oil samples were prepared using deionized water (variable amounts) and 1.5 mL of HPLC grade methanol for dilution. The samples were filtered using Whatman 0.45μm glass microfiber syringe filters.

MATLAB Code

A MATLAB code was generously provided by Dr. John Stanford and utilized for calculation of Q_m, K_L, K_F, and n isotherm parameters; the maximum loading capacity,

Langmuir affinity parameter, Freundlich capacity parameter, and Freundlich affinity parameter, respectively. It is located in the supporting information.

Results and Discussion

Column elution experiments were performed with SP70 and A21(-OH) resins to determine breakthrough times of phenols and acetic acid. A21(-OH) resin was found to have a very large particle diameter after swelling when the components from SF5 were adsorbed. One trial shattered the glass chromatography column due to excessive swelling. A second trial with a stronger glass column disallowed flow of solvents once SF5 reached the resin. Due to these reasons, A21 resin was tested in its place. SP70 resin elution data is reported in **Figure 5** and A21 in **Figure 6**.

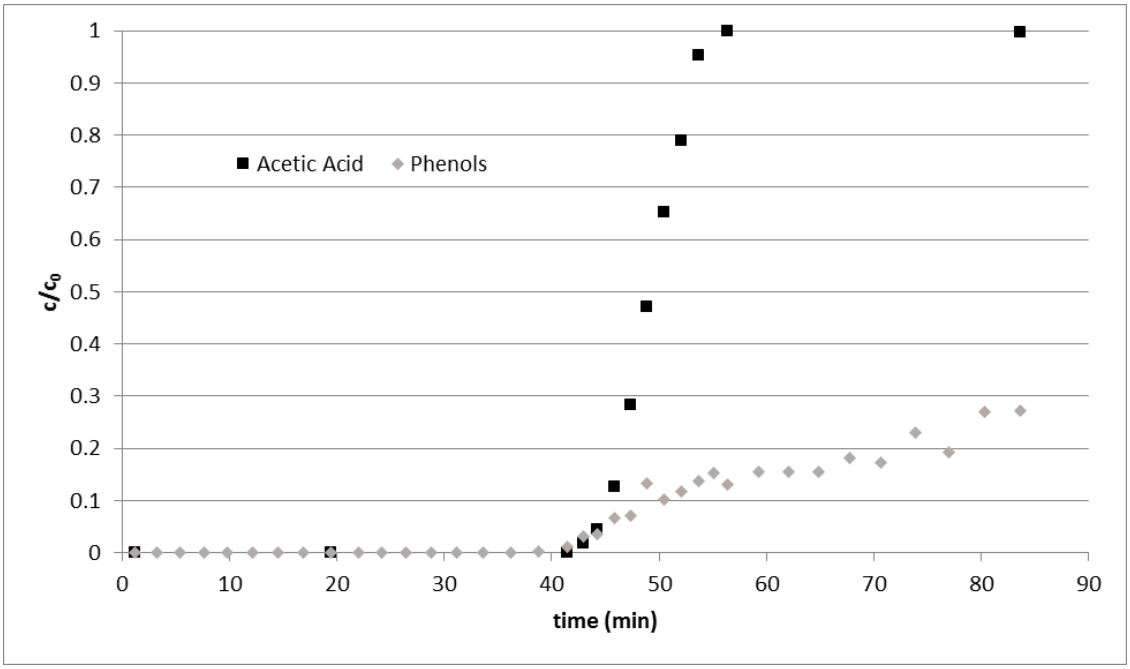

Figure 5. SP70 column elution data. Phenols and acetic acid break through at the same time.

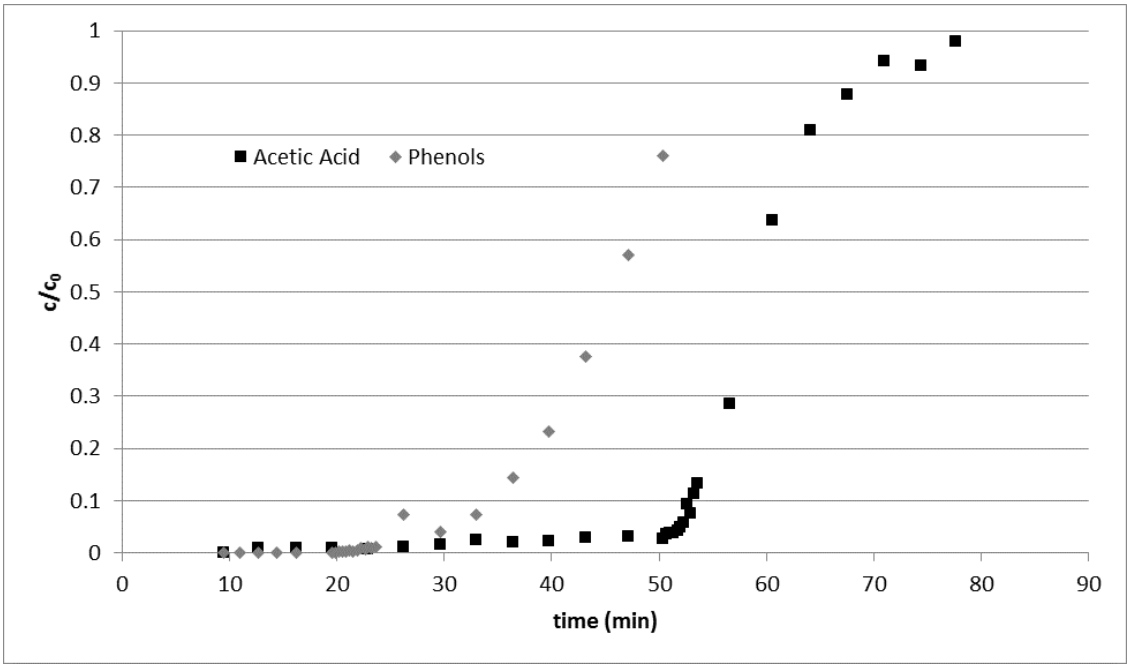

Figure 6. A21 column elution data. Phenol breakthrough was much sooner than acetic acid.

As shown in **Figure 5**, it was found that phenols and acetic acid broke through at the same time. After much consideration and data comparison it was determined that this was serendipitous as SP70 has a relatively high capacity for phenol adsorption when compared to acetic acid, which has adsorption close to zero. Manufacturer specification cites SP70 as a good phenol absorbent. Another interesting feature of this figure is acetic acid fully saturates the resin (where $c/c_o = 1$), while phenolics only reach 20% of their final challenging concentration. This would suggest that the phenolics are not adsorbing strongly, possibly due to pH. **Figure 6** yields results more in line with what is expected in breakthrough data. A21 is an ion-exchange resin which would suggest that acetic acid interacts more with the resin structure, slowing down its elution and breakthrough. The results back up this claim.

Wheeler-Jonas breakthrough data was also obtained and listed in **Table 2**. W_e (adsorption capacity) and k_v (adsorption rate) were calculated using **Equations 2 and 3**.

One interesting feature of the previous two figures, is if an integral is taken of the negative space prior to (left) of each curve to the y-axis, it should roughly equal the adsorption capacity of the resin (W_e).

Table 2. Wheeler Jonas breakthrough data.

	Acetic Acid		Phenols	
Resin	We (g/g)	kv (min^{-1})	We (g/g)	kv (min^{-1})
SP70	0.098	0.792	0.018	0.586
A21	0.07	1.23	0.01	1.34

Although originally intended to optimize adsorbents, this data does not match other values obtained in this study, despite flow rates remaining constant. Upon further review, it was found that flow rate and ultimately mass transfer plays a major role in this data, as described in the diffusion diagram, **Figure 2**. It was determined that the Wheeler-Jonas equation breaks down when "leaching" causes mathematical asymmetry of the breakthrough curve [41]. Due to the breakthrough of both compounds at the same time in SP70, further research in this study only looks at A21 resin.

The six resins (SP207, SP70, A21, A21($^{-}$OH), IR120(H^{+}), and IR120(Na^{+})) were tested with varying concentrations of SF5 (0, 6.25, 12.5, 25, 50, and 100%) at room temperature. Values of q were calculated and plotted versus concentration. **Figures 7 and 8** are representative plots (A21 resin).

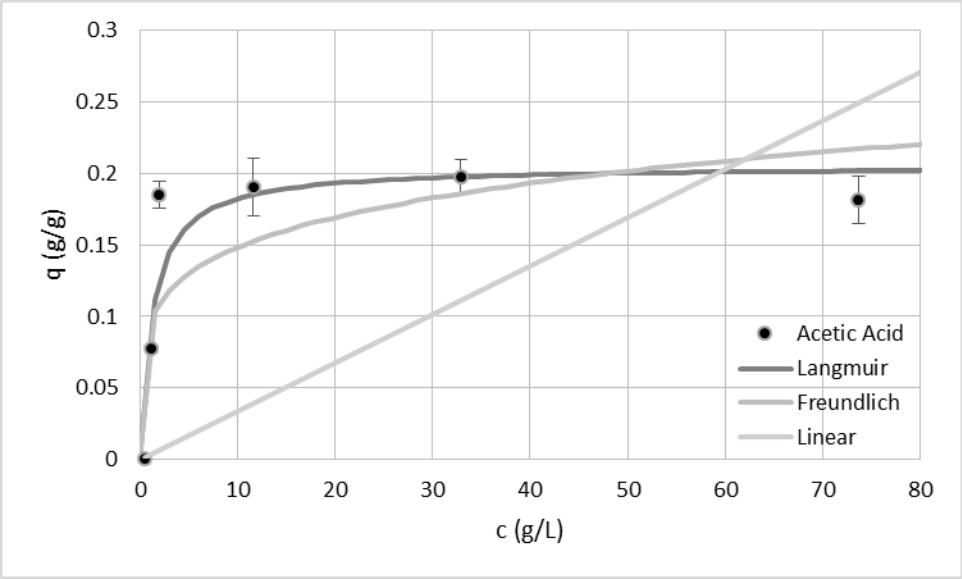

Figure 7. Isothermal adsorption plots of q vs c for acetic acid on A21 resin.

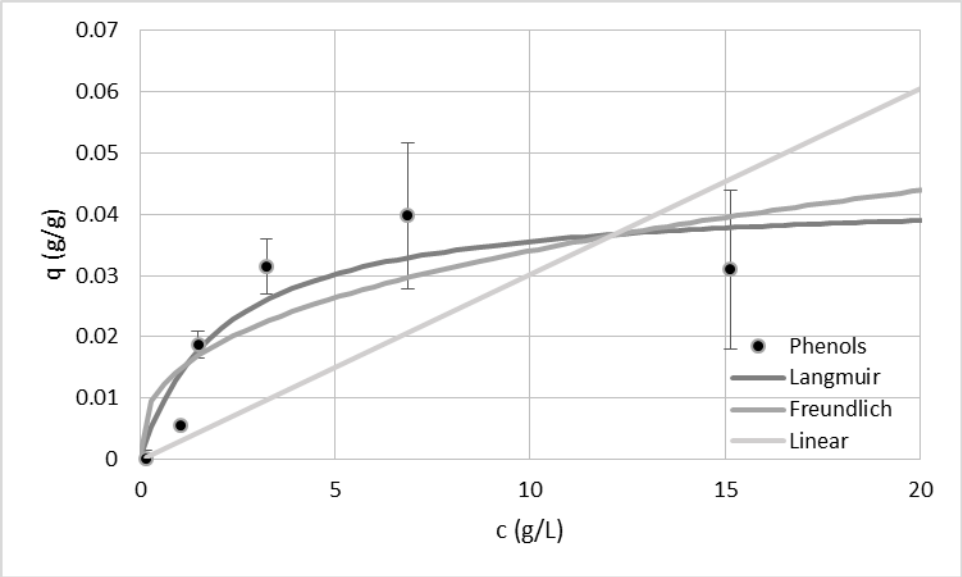

Figure 8. Isothermal adsorption plots of q vs c for phenols on A21 resin.

As can be deduced from the shape of these plots; they are not linear.

However, as reported in the introduction of this chapter, linearization of the Langmuir and Freundlich can be performed. This was completed, but more accurate results were obtained using the previously reported MATLAB code. All linear values of *K* were

obtained using Excel. **Table 3** lists the results from these calculations from Excel and MATLAB.

Table 3. Adsorption values of K, K_L, Q_m, K_F, and n for phenols and acetic acid on each resin.

		Linear		Langmuir			Freundlich		
		K	R^2	K_L	Q_m	R^2	K_F	n	R^2
SP207	*Phenols*	0.0026	0.50	**1.1924**	**0.0472**	0.94	0.0228	3.3704	0.82
	Acetic Acid	**0.0007**	0.96	0.0017	0.4267	0.96	0.0007	1.0174	0.96
SP70	*Phenols*	0.0072	0.85	**0.2346**	**0.1141**	0.97	0.0242	1.8953	0.95
	Acetic Acid	**0.0008**	0.98	-	-	-	0.0005	0.9102	0.98
A21	*Phenols*	0.0018	0.42	**0.4680**	**0.0432**	0.84	0.0147	2.7306	0.68
	Acetic Acid	0.0014	0.23	**0.7963**	**0.2053**	0.79	0.0956	5.2396	0.53
A21($^-$OH)	*Phenols*	0.0055	0.71	-	-	-	**0.1260**	**2.1693**	0.87
	Acetic Acid	0.0030	0.59	**0.1476**	**0.2954**	0.88	0.0670	2.8910	0.81
IR120(H^+)	*Phenols*	0.0019	0.88	**0.2826**	**0.0243**	0.97	0.0061	1.9902	0.96
	Acetic Acid	0.0001	0.46	**0.0689**	**0.0730**	0.69	0.0095	2.1346	0.61
IR120(Na^+)	*Phenols*	0.0002	0.20	-	-	-	**0.0031**	**3.4145**	0.45
	Acetic Acid	**0.0001**	0.80	-	-	-	-	-	-

Values in the table that are bolded are the highest R^2 values of the series. The values of K are similar to distribution coefficients and also reveal the shape of the isotherm curves. They are the ratios of the concentration of a compound on the solid phase versus the concentration of a compound in the liquid phase. Q_m is essentially the threshold concentration of a compound before no more compound of that type can adsorb. Values of n that are greater than one are unfavorable isotherms. However, smaller values of n indicate stronger adsorption properties of a compound, due to 1/n (from **Equation 6**). Values obtained that exceeded the threshold (both low and high) of the MATLAB parameters are indicated with a (-).

The highest capacity for phenols was shown in SP70 resin, while the highest capacity for acetic acid was A21($^{-}$OH) resin. Both forms IR120 resin produced erratic results, suggesting that a sulfonic acid (or sulfonate) functionalized resin does not adsorb either species, which was expected.

As discussed earlier in the theory section, temperature plays a role in adsorption. For acetic acid; as temperature increases, adsorption increases on A21 ion-exchange resin (**Figure 9**). The converse is true for phenols; as temperature increases, adsorption decreases (**Figure 10**). All plots show the Langmuir adsorption isotherm fitting.

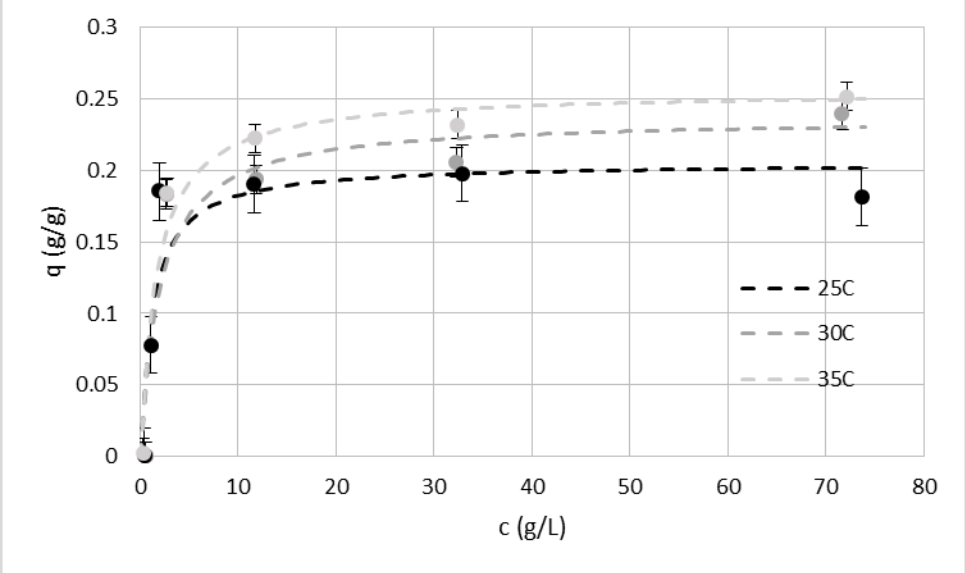

Figure 9. Acetic acid adsorption at 25, 30, and 35°C.

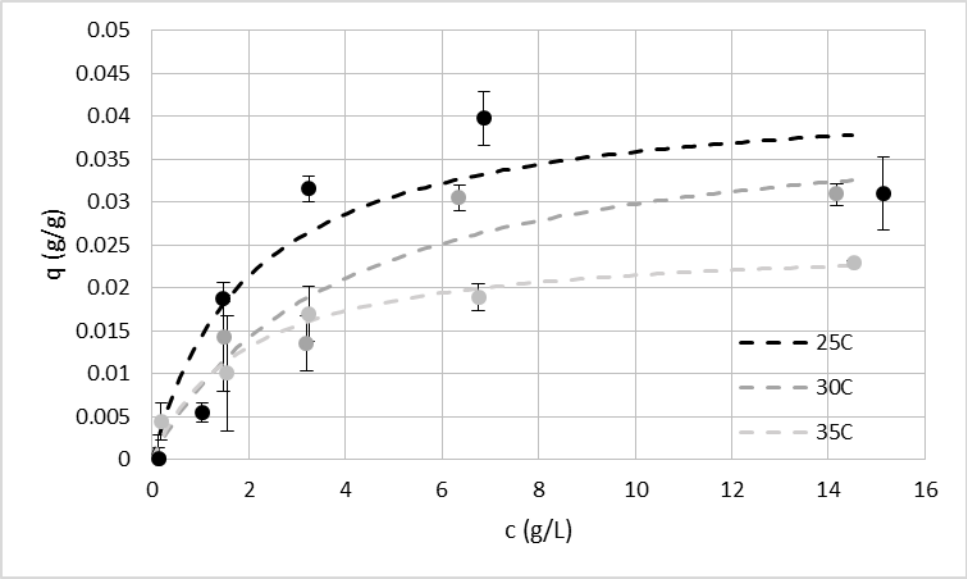

Figure 10. Phenolic adsorption at 25, 30, and 35°C.

Kinetic rates were also able to be calculated using a stirred bath at 25, 30, and 35°C for both acetic acid and phenolics on A21 resin. **Figure 11** shows the rate of adsorption for acetic acid.

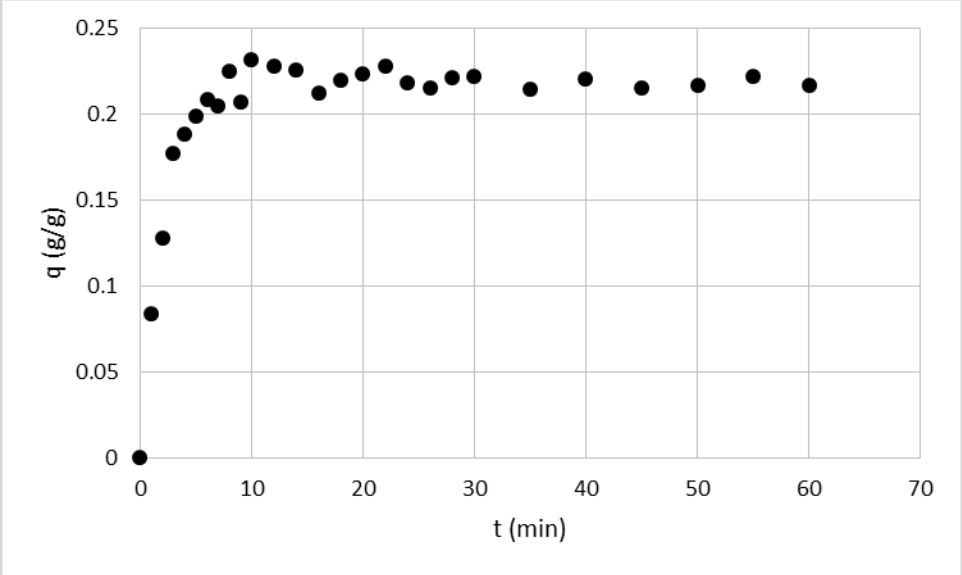

Figure 11. Grams of acetic acid per gram of resin adsorbed per minute at 25°C.

The stirring continued for 300 minutes and no change was observed after about 30 minutes. As shown in **Figure 11**, adsorption occurs in the first 10 minutes before

adsorption capacity is reached. If data points within these 10 minutes are plotted with **Equations 10 or 11** versus time, the rate of adsorption can be calculated with the slope, if the function is linear. If the function is not linear, as in the case of phenolics, a second order equation must be used instead (**Equation 12**) [42]. Since the phenolics are not linear, it suggests that there is no interaction with the resin, which would be expected with ion-exchange. Rates (k_1) for acetic acid at 25, 30, and 35°C were 0.0842, 0.0888, and 0.0923 $g \cdot g^{-1} min^{-1}$, respectively. Rates (k_2) for phenolics were 1.73, 2.40, and 2.59 $g \cdot g^{-1} min^{-1}$, respectively. This fast of rate suggests that adsorption and desorption were occurring very quickly, which aligns well with the breakthrough of phenolics in the column elution study.

Plotting the natural log of these rates versus the inverse of temperature (K) yields the activation energy of adsorption (E_a). Adsorbing acetic acid takes 0.0778 kJ/mol while phenolics take 0.350 kJ/mol. Both activation energies are under 40 kJ/mol which suggests that both adsorptions are physisorptive processes. Interestingly, based on literature, pseudo-first order rate constants are used in adsorption applications with pollutants in wastewater. On the other hand, pseudo-second order rate constants are used for adsorption of metals, dyes, and other organic compounds [43].

Conclusion

Amberlyst A21 ion-exchange resin proved to be the best candidate for the adsorption of acetic acid from the SF5 fraction of bio-oil among six types of adsorptive resin. This is based on its equilibrium adsorption capacity of greater than 0.2 grams of acetic acid per gram of resin. Other factors, such as breakthrough times for phenols and

acetic acid, temperatures of adsorption for both species, rates of adsorption, and activation energies, were also calculated for A21 resin.

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Supporting Information

MATLAB Code

```
1   % John Stanford
2   clc;  clear all; close all;
3   % Load Data
4   data = xlsread('Excel Data File','Sheet1');
5   phenolics_conc = data(1:6,1); % g phenol / L solution
6   phenolics_ads = data(1:6,2); % g phenolics / g resin (dry)
7
8   % Fitting data
9   x = phenolics_conc; y = phenolics_ads;
10  langmuirFun = @(b,x) (b(1).*b(2).*x)./(1+b(1).*x);
11  freundlichFun = @(a,x) a(1).*x.^(1/(a(2)));
12  start_Langmuir = [.2; 200];
13  start_Freundlich = [1 1];
14  w = [1 1 1 1 1 1];% weighting for SF5 - SP207 data
15  langmuir_fit_nlm = fitnlm(x,y,langmuirFun,start_Langmuir,'Weight',w);
16  freundlich_fit_nlm = fitnlm(x,y,freundlichFun,start_Freundlich,'Weight',w);
17
18  % Calculating model
19  xx = linspace(0,.1,101)';
20  K_langmuir = langmuir_fit_nlm.Coefficients(1,1); K_L =
    table2array(K_langmuir)
21  Qm =  langmuir_fit_nlm.Coefficients(2,1); Qm = table2array(Qm)
22  K_Freundlich = freundlich_fit_nlm.Coefficients(1,1); K_F =
    table2array(K_Freundlich)
23  n =  freundlich_fit_nlm.Coefficients(2,1); n = table2array(n)
24  Q_langmuir_calc = K_L*Qm*xx./(1+K_L*xx);
25  Q_freundlich_calc = K_F*xx.^(1/n);
26
27  % Plotting
28  figure1 = figure(1);
29  plot(xx,Q_langmuir_calc,'k--')
30  hold on
31  plot(xx,Q_freundlich_calc,'b--')
32  plot(phenolics_conc, phenolics_ads,'o')
33  xlabel('Conc (g/mL)'); ylabel('Q_e (g/g)');
```

Line five is the spreadsheet location of concentration values (c) in grams of phenol or acetic acid per L of solution, while line 6 is the spreadsheet location of the mass of adsorbed material (q) in grams of phenol or acetic acid per gram of dry resin.

Lines 10 and 11 (as well as 24 and 25) utilize the Langmuir and Freundlich equations, respectively. Lines 12 and 13 are educated guesses for possible values for Q_m, K_L, and K_F for Langmuir and Freundlich isotherms. Supplying these values enables the program to compute results faster. Line 19 designates the range and number of points for the plot that is generated. This line, especially the range, may need modification when dealing with large data sets. Although not important for calculations, lines 29, 31, and 32 allow for customization of the plots. As is written above, line 29 codes a black dashed line for Langmuir fits. Line 31 codes a blue dashed line for Freundlich fits. Line 30 plots a point as "o" for an experimental value. The rest of the code should be self-explanatory for a reader that is familiar with isotherm equations.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The overall goal of this research was to find solutions for contaminant removal in process and wastewater streams from biorefineries. Two chemicals found in these streams, levoglucosan and acetic acid, were selected as target compounds for separation and purification.

Chapter Three

Chapter three investigated the purification of a pyrolytic sugar-rich aqueous phase produced from fractionated bio-oil. Phenolic removal from the process water was achieved. Utilization of a polymeric resin adsorbent (SP207) for the removal of phenolic impurities yielded a potentially value-added product. The resin utilized had a high selectivity (affinity) for phenols and other aromatic compounds, high adsorption capacity, low cost, and ease of regeneration. The value-added product is a cleaned mixture of 97.64 wt. % sugar stream containing levoglucosan that has had the phenolic content removed.

This mixture could be further upgraded chemically and/or possibly utilized directly by microorganisms without passivation of any remaining phenols, furans, aldehydes, organic acids, and other "contaminants" or "inhibitors." In addition, in the case of levoglucosan (obtained in 57.78 wt. %), further conversion of the sugars may yield the building blocks of green solvents and chiral platforms for pharmaceuticals. Catalytic cracking and chemical/biological conversion of the "contaminants" and

"inhibitors" adsorbed by the resin to finished fuels and chemicals may also be investigated in future work.

Chapter 4

Chapter four determined that long chain fatty acids are suitable candidates for extraction of acetic acid while excluding water. Among possible solvents for this liquid-liquid extraction, heptanoic acid was selected because of its low water solubility; high boiling point compared to the acetic acid to be distilled from it; and stability during storage. Heptanoic acid extraction of the acetate fraction (1:6) has shown favorable results with almost complete removal of acetic acid (98.5% efficient) in three washes or extractions. The water content was reduced from 69.02 to 3.84 wt.%. This technique was also successful when used to recover acetic acid from three industrial acetate streams. Surprisingly, many other light oxygenates were extracted in the extract streams. These streams yielded concentrated organic, solutions that could be distilled from the heptanoic acid, suitable for catalytic cracking to aromatics.

However, when attempts were made to extract autothermal and pretreated autothermal acetate fractions from bio-oil, emulsions, not bilayers would form. If two separable layers would form, higher percentages of water were extracted. This result led to a full characterization study. This study did not reveal chemical differences between the acetate fractions. The main differences can be attributed to feed stock and the pyrolysis system on which the bio-oil was generated. Chemically, all acetate streams should extract equally as well.

Personal communication with industry partners has revealed that an acidification with a strong acid of the SF5 prior to extraction will yield better results. The

acidification should help with ionization of acetic acid in an aqueous solution and enable better partitioning. Temperature of the extraction may also play a role (an increase would be a negative interaction by reducing hydrogen bonding).

Chapter Five

Chapter five determined that Amberlyst A21 ion-exchange resin is the best candidate for the adsorption of acetic acid from the SF5 fraction of bio-oil among six types of adsorptive resin. This is based on its equilibrium adsorption capacity of greater than 0.2 grams of acetic acid per gram of resin. Other factors, such as breakthrough times for phenols and acetic acid, temperatures of adsorption for both species, rates of adsorption, and activation energies, were also calculated for A21 resin.

Desorption with sodium hydroxide should theoretically yield a dilute sodium acetate stream, devoid of phenolic inhibitors. This neutralized sodium acetate stream would be an ideal candidate for fermentation to methane or it could be acidified and extracted using the procedure described in the previous chapter of this manuscript.

The three research chapters of this manuscript show much potential in larger applications of contaminant removal from biorefinery process and wastewater. Resin technology, coupled with fractionation and extraction, is a powerful tool in the crusade to reduce the world's overdependence on petroleum products.