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I, Julia E Finer, hereby submit this original work as part of the requirements for the degree of Master of Science in Chemical Engineering.

It is entitled:
Evaluation of the Effect of Dioxygen, Industrial Heterogeneous Palladium Catalyst, pH and Iron Content on the Generation of 3 High-Value Aldehydes from Corn Stover Lignin

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Evaluation of the Effect of Dioxygen, Industrial Heterogeneous Palladium Catalyst, pH and Iron Content on the Generation of 3 High-Value Aldehydes from Corn Stover Lignin

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By

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Abstract

Lignin is the second most abundant biopolymer available in nature after cellulose. Unfortunately, it is often seen as a hindrance to cellulose isolation for cellulosic ethanol production and paper processing instead of a readily available resource for producing high-value chemicals with an aromatic ring in their structure. Many specialty chemicals can be made from wet aerobic oxidation (WAO) of lignin including the valuable aromatic aldehydes vanillin (3-methoxy-4-hydroxybenzaldehyde) and syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde). Lignin is a heterogeneous polymer which varies in its monomer ratios from one plant species to another and therefore will produce different amounts of aldehydes depending on the nature of the feed that is used in the reaction.

Previous research has shown sugar cane bagasse to produce vanillin and syringaldehyde during wet aerobic oxidation and increased yields using a Pd/γ-Al₂O₃ catalyst. However, the production of the most economically valuable compound, syringaldehyde, could be increased by using a different lignin feedstock. Corn stover lignin has more syringyl units than sugar cane bagasse and hypothetically should produce more syringaldehyde. Here, we use lignin from corn stover and report different reactivity trends than those for lignin from sugar cane bagasse. To better understand these findings, we examined the composition of corn stover lignin and the influence of wet aerobic oxidation conditions, both in the presence and absence of a heterogeneous catalyst, in order to understand the impact of these parameters on the reactivity of lignin transformation to aromatic aldehydes. In this study, thermogravimetric analysis (TGA) in air was performed on washed lignin feedstock to identify he percentages of lignin,
celluloses and ash in the lignin. An EDS study (energy dispersive x-ray spectroscopy) of lignin ash confirmed the presence of Fe, known to be catalytically active in catalytic wet aerobic oxidation (CWAO). To confirm Fe’s catalytic activity, Various amounts of Fe(III) nitrate were impregnated onto the lignin feed stock and used in CWAO to determine how iron concentration affected reaction rates and selectivity of aldehydes. The resulting aldehydes were analyzed by GCMS and residual lignin was quantified by TGA in air. The role of pH was also examined to distinguish the roles of dioxygen and hydroxyl ions in CWAO of lignin. A basic economic analysis was used to determine if using wet aerobic oxidation to produce high-value aldehydes is viable at an industrial level.
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I. Introduction and Literature Review

1.1 Introduction

Lignin is the second most abundant biopolymer available in nature, the first being cellulose.\textsuperscript{1,2} It is a readily available source for chemicals which have an aromatic ring in their structure. Many specialty chemicals can be made from the decomposition of lignin including the valuable aromatic aldehydes vanillin (3-methoxy-4-hydroxybenzaldehyde) and syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde).\textsuperscript{3}

Lignin is an unwanted byproduct of both cellulosic plant-based biofuel production and the pulp and paper industry.\textsuperscript{4,5} It is usually sold as a binder or filler or is burned to generate electricity because these are the simplest and cheapest methods for disposal.\textsuperscript{1} Lignin makes an excellent filler because it is a superplasticizer; as an additive, lignin reduces the amount of water needed to increase the workability of the cement.\textsuperscript{6-8} Although burning is a means of lignin disposal, this process also generates enough electricity to cover the energy needed to run papermaking or biofuel facilities.\textsuperscript{9} This disposal method is convenient and helps facilities to save money because of the electricity generated; however, lignin has a greater untapped profit which is its potential as a feedstock for high-value chemicals.

3-methoxy-4-hydroxybenaldehyde (vanillin) and 3,5-methoxy-4-hydroxybenzaldehyde (syringaldehyde) can be produced from lignin using catalytic wet aerobic oxidation (CWAO).\textsuperscript{10-13} Because lignin is used as a feedstock for syringaldehyde and vanillin production and it is a bio-based product, the catalytic wet
aerobic oxidation process can be considered a “green” process. Green processes are promising because they use renewable resources unlike fossil fuel-based technologies. As fossil fuels will be depleted eventually, we will need to find new methods to synthesize chemicals which have become an essential part of everyday life. Green processes are some of the potential technologies which could replace petroleum-based processes in the near future. Also, attaching the label of “made by green process” to products is expected to receive a warmer response from consumers.14

Vanillin is the most recognized of the three aldehydes produced during WAO of lignin. It has a very large market especially in the flavors and fragrances industry, while syringaldehyde has a small but expanding market. The pharmaceutical industry uses both vanillin and syringaldehyde as intermediates in pharmaceutical production processes and as flavorings. These aldehydes are also considered antioxidant, anti-cancer, and anti-inflammatory medicinal spices. Vanillin is also an anti-viral spice.15

Not only is the market large for vanillin, but the price of vanillin is also high. The market value for vanillin produced in the United States in 2006 was 18 USD/kg.16 Syringaldehyde can sell for an even higher price at 32-209 USD/kg depending upon the amount ordered.17-19 Syringaldehyde may fetch such a high price because it has so many constituent groups attached to its benzene ring and is difficult to synthesize in only a few steps with exceptional yields. As will be described later, syringaldehyde can be synthesized from vanillin. The costs of the additional reaction steps to produce syringaldehyde add to the already high price of vanillin. If the lower yields from unreacted feed and byproducts of the reaction are considered, the market value
increases even further. Using this logic helps to explain why the price for syringaldehyde is so much higher than vanillin.

\[ \text{p-hydroxybenzaldehyde} \quad \text{vanillaldehyde} \quad \text{syringaldehyde} \]

**Figure I.1 Aromatic Aldehydes Derived from Lignin Oxidation**

The value of lignin as a potential feedstock for aromatic high-value chemicals, such as vanillin (3-methoxy-4-hydroxybenzaldehyde) and syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde) (**Figure I.1 Aromatic Aldehydes Derived from Lignin Oxidation**) has been overlooked. Vanillin is one of the most important chemicals in the flavors and fragrances industry. Richard Myers lists it as number 97 in his book of *The 100 Most Important Chemical Compounds*. Vanillin makes up 90% of the Vanilla market in the US. It can be produced from black liquor, from a petroleum-based feedstock, or through microbial conversion of natural ferulic acid. Synthetic vanillin has received more widespread use due to the high price of natural vanilla and the growth in demand for the chemical. Natural vanilla is made from the vanilla orchid and is composed of a complex mix of vanillin and other aromatic compounds. For natural vanilla production, the seed pod from the orchid is harvested and cured for 3-6 months under controlled conditions. Because of the length of time needed to cure the vanilla bean and extract the vanilla flavor and because the orchids which produce vanilla beans can only be grown in certain parts of the world including Mexico and
Madagascar, natural vanilla can cost up to 50 times more than vanillin. Worldwide, the market for vanillin is approximately 15,000 MT/year. Currently, the demand for vanillin is increasing around the world as some developing countries, such as China and India have started to adopt western tastes. About 75% of this market is from the vanillin demand for flavoring ice cream and chocolate. Although the main market for vanillin is the flavors and fragrances industry, it is also used as an intermediate in the pharmaceutical and fine chemicals industries. The pharmaceutical drug L-dopa which is used to treat Parkinson’s disease uses vanillin as an intermediate in production. Vanillin is also used to improve the flavor of some drugs to allow for increased palatability when taking the drug orally.

Vanillin can be produced from black liquor and more recently from petroleum-based feedstock. The largest producer of vanillin, Rhodia, uses a variety of processes to produce vanillin. From reading patents filed and exploring their company website, it appears that Rhodia uses ferulic acid from rice bran as a substrate for microbial production of vanillin and also a chemical process using a catechol-based feedstock. Rhodia uses two processes because Rhovanil® Natural, the vanillin produced via fermentation, is classified as a naturally produced aroma chemical and therefore can be sold at a high price, around 700 USD/Kg. Vanillin produced from catechol sells at a much lower price, around 14 USD /Kg, because it is synthetically produced. The third largest producer of vanillin, Borregaard, is the only industrial scale producer of vanillin from black liquor.

Unlike vanillin, syringaldehyde does not have a stable market and is not widely distributed or utilized by commercial ventures. Much of our knowledge regarding
syringaldehyde use as a pharmaceutical intermediate comes from recent patents. One of the patents describes the use of syringaldehyde as an intermediate to produce a drug to treat breast cancer and obesity, neither of which are yet available to consumers. Other patents, which mention syringaldehyde, use it as an enhancer for enzymatic dying of keratin fibers and enzymatic bleaching. Syringaldehyde is also used as an antioxidant, anticancer and anti-inflammatory medicinal spice suggesting that additional commercial applications exist for the compound.

Syringaldehyde can be produced in a number of different ways. Some of the earlier methods of producing syringaldehyde include using pyrogallol-1,3-dimethyl ether, gallic acid or vanillin as starting materials. More recent methods include the use of para-cresol as a starting material.

1.2 Lignin Structure and Sources

Different Types of Lignin

Lignin is the second most abundant natural biopolymer, the first being cellulose. It is produced together with cellulose and can be generally thought of as the cement that holds plant cells together. Although there is no organization to the structure of lignin making it amorphous, it is consistently composed of three individual aromatic building blocks consisting of p-hydroxybenzyl, guaiacyl, and syringyl units which are commonly called, “monolignols”. The precursors of the monolignol units are p-coumaryl, coniferyl, and syringyl, shown in Figure I.2 Phenyl Propane Building Units, which are dehydrogenated by an enzymatic pathway to form the polymer.
Left to right: p-coumaryl, alcohol coniferyl alcohol and syringyl alcohol

Figure I.2 Phenyl Propane Building Units

The percentages of the monolignol units in lignin vary depending on a number of different factors: the plant species, plant cultivation conditions, the age of the plant and the organelle from which the lignin originates all contribute to its composition. Softwoods have G-type lignins meaning that a majority of their lignol units are guaiacyl units. Hardwoods are usually S:G-type, meaning that the majority of the monolignols which make up their lignins are syringyl and guaiacyl units.

Monocotyledonous grasses produce various lignin types. Monocots are one of two major groups of flowering plants, the other being dicots. They have one seed leaf which is produced from the embryo during seed germination, while dicotyledonous plants have two seed leaves. Two large groups of monocotyledonous plants include grasses and grains. Both groups are often used as biomass for alternative chemical and energy processes.
Table I.1 Monolignol Units in Different Crops

<table>
<thead>
<tr>
<th>Source</th>
<th>Monomer Units</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Stover</td>
<td>H 4 G 35 S 61</td>
<td>42</td>
</tr>
<tr>
<td>Wheat Straw</td>
<td>H 5 G 49 S 46</td>
<td>42</td>
</tr>
<tr>
<td>Rice Straw</td>
<td>H 15 G 45 S 40</td>
<td>42</td>
</tr>
<tr>
<td>Flax Fiber</td>
<td>H 4 G 67 S 29</td>
<td>42</td>
</tr>
<tr>
<td>Arundo Donax</td>
<td>H 34 G 60 S 6</td>
<td>40</td>
</tr>
<tr>
<td>Sugarcane Bagasse</td>
<td>H 35 G 38 S 27</td>
<td>43</td>
</tr>
<tr>
<td>Kraft Lignin</td>
<td>H 5 G 94 S 1</td>
<td>44</td>
</tr>
</tbody>
</table>

Variations in lignin structure also occur in bonding orientations between the monolignol units, the most proficient bond being the β-O-4’ bond. Many of the proposed oxidation reactions involve the β-O-4’ bond because it constitutes 45-50% of the bond linkages in softwood lignin and 60-62% of the linkages in hardwoods. Other linkages believed to be found in lignin include: β-5’, β-β’, β-1’, spiradienone, 4-O-5’, dibenzodioxocine, 5-5’ and diphenylmethane (Figure I.3 Linkages found in Lignin Structure). The 5-5’ linkage was found to be 19-27% of the linkages in softwood lignin, while in hardwoods it was found to be less than 10%. The β-5 linkage was found to be 9-12% of the linkages found in spruce softwood lignin, while in hardwoods it was less than 11%. All other linkages are believed to constitute 10% or less of the total linkages in naturally occurring lignin. 36,45
Lignin, cellulose and hemi-cellulose are the main structural components of the plant cell wall. Cellulose, lignin and hemi-cellulose are interwoven which provides excellent structural support for plant cells but is disadvantageous for the uses of these biopolymers as feedstocks for chemical production. The pulp and paper industry has had to battle with the challenge of separating cellulose from lignin and hemi-cellulose for years, often having to use harsh chemicals and extreme conditions to increase pulp brightness. Separating cellulose from the other biopolymers has become especially important in the drive to make biofuels from non-food crops.

Cellulose has been the focus of current research because of its promising outlook as a renewable feedstock for chemicals to replace and/or supplement fuels for transportation. Because of how lignin is associated with crystalline cellulose, it is difficult to achieve high yields of cellulose without using extreme conditions.
Consequently, some efforts have focused on turning off the genes which promote lignin synthesis in order to achieve higher yields of cellulose. Unfortunately, lignin provides structural support, aids in water transportation and contributes to defense responses against invading pathogens; therefore, it is impossible to repress the genes which promote the lignin synthesis pathway without seriously compromising plant productivity and health.\textsuperscript{46}

1.3 Lignin from pulp and paper processing

For commercial utilization of wood for the pulp and paper industry and crops for biofuel production, lignin is an undesirable, unwanted and a limited-value byproduct. The lignin from pulp and paper manufacturing is usually burned to generate electricity to keep the machinery operating or sold as a binder or filler to increase the flowability of materials without the need of adding much water.\textsuperscript{6-9}

Three major methods used in the pulp and paper industry to separate lignin and hemi-cellulose from cellulose are the kraft, lignosulfonate and organosolv processes. The kraft and lignosulfate processes use extreme conditions while the organosolv process is much milder. Kraft and lignosulfonate lignins are currently available commercially, while organosolv lignins are not.\textsuperscript{47}

Kraft lignin is produced by adding large amounts of sodium hydroxide and sodium sulfide to woody biomass at temperatures of 150-180°C for 2 hours.\textsuperscript{36} The resulting slurry, or black liquor, will contain many guaiacol derivatives, eugenol and vanillin in addition to kraft lignin.\textsuperscript{48} The harsh conditions of kraft pulping lead to the lignin being, of lower molecular weight, highly modified and sulfur from the sodium sulfide being
integrated into the structure.\textsuperscript{45} The number-average molecular weight of Norway spruce wood lignin put through kraft pulping to be 1000-3000 Da with the average monomer molecular weight thought to be \textasciitilde180 Da.\textsuperscript{45}

Lignin produced by sulfite pulping is called lignosulfonate lignin. Calcium, sodium, magnesium or ammonium sulfite is used depending on the type of pulping process needed.\textsuperscript{36,47} Like Kraft lignin, lignosulfonate lignin may have sulfur from sulfite integrated into their structure. The resulting average monomer molecular weight is higher at \textasciitilde215 Da for softwoods and \textasciitilde254 Da for hardwoods. A wide range of polymer molecular weights have been reported for lignosulfonates. Lin et al. reports that the polymer molecular weight of softwoods can range from 1000-140,000 Da with the majority lying from 5000-20,000 Da while for hardwoods the weight is lower.\textsuperscript{47} Lange et al. reports that softwood lignosulfonate has a monomer molecular weight of 215-254 Da with the polymer weight being in the range of 36,000-61,000 Da and hardwood lignosulfonate has a monomer molecular weight of 188 Da while the number-average molecular weight of the polymer is 5,700-12,000 Da.\textsuperscript{45} The softwood used in Lange et al.'s data is Norway spruce and aspen wood, while the hardwood is eucalyptus.

Organosolv lignin is produced though woody biomass treatment with organic solvents usually ethanol or methanol at elevated temperatures. The value reported for the monomer molecular weight of lignin after processing is \textasciitilde188 Da with the number-average molecular weight being less than 1000.\textsuperscript{47} As there are no sulfites or sulfates used in the organosolv process, the lignin structure will not contain any additional sulfur.
1.4 Lignin from Cellulosic Ethanol Processing

Cellulosic ethanol production, like pulp and paper processing, also does not utilize lignin in a valuable way. Producers find the process of separating cellulose from lignin and hemi-cellulose to be burdensome and cause lower yields. The inconvenience has led to research on how to genetically alter the makeup of various species of plants to produce less lignin, leading to the creation of sickly plants from lack of ability to carry water and structural support.\(^{46}\) However, unlike pulp and paper processing, it utilizes different methodologies to separate cellulose from lignin and hemi-cellulose because the highly toxic chemicals originally used during pulping are harmful to the microorganisms used downstream during ethanol production. The differing pretreatment process causes the resulting lignin byproduct from cellulosic ethanol production to be different from that of black liquor from pulp and paper processing.

There are multiple pretreatment methods for separating cellulose from hemi-cellulose and lignin including dilute acid, steam explosion, ammonia, milled wood, cellulolytic enzymatic and alkali. Sometimes combinations of these pretreatment methods are used to increase the purity of lignin. The pretreatment method(s) used can affect the lignin polymer size, chemical make-up and bonding and hence affect the lignin’s behavior in potential downstream uses.\(^{45}\)

During the dilute acid process, weak (0.5-1.5%) sulfuric acid is used to cook the biomass at temperatures of 140-210°C from anywhere from 2-80 minutes. A two-stage process is usually used to extract more hemi-cellulose (xylan) from the biomass.\(^{49}\) A monomer molecular weight of ~188 Da has been reported. Because a smaller amount
of sulfur is being used in the pretreatment sulfur does not integrate itself in the structure of the lignin polymer.\textsuperscript{36}

Steam explosion lignin is produced by adding lignin to steam heated to 180-230°C and under pressures of 14-35 bars for 1-20 minutes and then rapidly decreasing the pressure causing an ‘explosion’. The bonds between the biomass components are forcibly broken allowing them to be separated with further extractions. Because the steam explosion process is physical rather than chemical lignin linkages are also broken yielding lower molecular weight lignin polymers.\textsuperscript{36,45} Steam explosion of Japanese white birch wood and larch wood was found to yield lignin polymers of 1100-2300 Da with an average monomer molecular weight of 188 Da.\textsuperscript{45}

Ammonia recycled percolation and ammonia fiber expansion processes both use ammonia to remove lignin from biomass. In ammonia recycled percolation, biomass is added to a reactor with 15\% ammonia solution and heated to 170°C for 90 minutes under a pressure of 23 bars. Kim et al. used ammonia recycled percolation to extract lignin and xylan from cellulose while maintaining the crystallinity of cellulose to allow better enzyme digestibility of cellulose for ethanol production.\textsuperscript{50} Ammonia fiber expansion adds 0.8-1.0 kg of ammonia per kg of dry biomass and increases the temperature of the mixture to 70-90°C depending on the type of biomass used. The mixture is held at these conditions for 5 minutes before the pressure is let down rapidly causing expansion of the biomass fibers.\textsuperscript{51}

Milled wood lignin is a two step process. First, biomass is milled into smaller particles in solvent (e.g. toluene) or under an inert atmosphere (e.g. nitrogen or argon).
Following milling, a neutral solvent (dioxane-water) is used to extract lignin from the other solids. Milled wood lignin is thought to have a lignin structure closest its structure after milling. Milled norway spruce wood lignin was found to have a monomer molecular weight of 198 Da with a number-average molecular weight of 2800-14,200 Da.

Nature already has a way to decompose cellulose and lignin using enzymes which can be found in fungi, protozoa, bacteria or even animals like termites. Cellulolytic enzyme lignin is obtained much in the same way as milled wood lignin except commercially available cellulose-hemicellulase mixtures, with enzymes like those found in nature, are used instead of solvent to isolate the lignin. Cellulolytic enzyme lignin of norway spruce wood has been found to have a monomer molecular weight of ~187 Da with a number-average molecular weight of ~1900 Da.

Alkali or soda processing uses 2-13 wt.% aqueous sodium hydroxide cooked at 120-170°C for 60-90 minutes to separate lignin, cellulose and hemicellulose. After cooking, the biomass fractions can be separated by titrating with acid to pH 6.5 to separate out hemicellulose and pH 1.6 for lignin.

The above mentioned pretreatment methods are only a few of the more well-studied methods. There are many more methods currently being studied with the main goal of maintaining the crystallinity of cellulose while getting rid of as much lignin as possible to improve yield in the down stream process of cellulosic ethanol production. Consequently, lignin structure is sacrificed.
1.5 Lignin Chemistry

Major Reactions and Their Products

There are two other major types of reactions beside oxidation that can break down lignin. The two major reaction mentioned in literature are combustion and pyrolysis. Combustion is used to generate electricity while being an easy way to dispose of lignin, while pyrolysis produces lower molecular weight compounds.

Combustion

Combustion is mainly used for generating electricity from lignin as it has a high heat of combustion at 17.0-29.2 kJ/g, the range occurring because of the variance in composition. Effort has been made to make lignin into a substitute transportation fuel because, while it’s heating value is smaller than ethanol’s, it has ~1.5 times greater heat of combustion than ethanol because of its higher density. Lignin is blended with water, fuel and surfactant and mixed to form a slurry which can be stored for some time before phase separation occurs and it needs to be briefly mixed again. However the slurry, also known as a lignogel, is a non-Newtonian fluid and exhibits transition from laminar to transitional to turbulent flow during batch mixer scale-up, causing larger vessels for mixing to be difficult to design.

Factories which produce lignin as a byproduct will generally combust it to generate the electricity needed to run their plants to conserve costs instead of having to use electricity generated off-site. Co-products of combustion include char, which is a thermally stable leftover, and gasses including carbon monoxide, carbon dioxide,
hydrogen and methane. The more extreme the conditions of combustion, the more char produced.

**Pyrolysis**

Pyrolysis of lignin occurs when the lignin is heated in the absence of oxygen. Pyrolysis can be further broken down into thermolysis, hydrogenolysis, gasification and hydrolysis. Hydrogenolysis, or hydrocracking, occurs when hydrogen is added to the reaction. Hydrolysis occurs when water is used in the reaction to break down the lignin polymer. The temperature range over which pyrolysis occurs is large: 120–800°C. The major products from pyrolysis are affected by feedstock type, heating rate, reaction temperatures and additives to the reaction.

One category of thermolysis is base-catalyzed depolymerization, which occurs when a strong base is used during a lignin reaction and the hydroxyl group takes part in driving the reaction. Figure 1.4 displays possible pathways of base-catalyzed depolymerization dependent upon the lignin structure.
**Figure I.4 Reaction pathways of base catalyzed depolymerization of lignin**

**CWAO of Lignin and its products**

**Reaction conditions, types of catalysts (Pd, POM, Fe), products, yields**

Oxidation is the reaction thought to be most favorable for lignin in recent years thanks to the higher value products it produces. Research has also shown the yield of higher value products can be drastically increased with the addition of catalyst. There are many different types of catalyst which are used in conjunction with some type of oxygen donor to produce aldehydes via oxidation. These catalysts are both homogeneous and heterogeneous catalysts. The homogeneous catalysts can be further divided into subcategories including metal salts, metalloporphorins, and polyoxometalates. 

---

B-pathway: phenolic β-O-4 linkages  
C-pathway: formaldehyde formation  
D-pathway: non-phenolic β-O-4 linkages
Metal salts are the simplest of the homogeneous catalysts. Unfortunately, they are non-recyclable and researchers have looked to other recyclable catalysts to use in the reaction instead. Wu et al. found a mixture of CuSO$_4$ and FeCl$_3$ added to their reaction solution gave the best results. They were able to obtain 9.50 wt.% yield of syringaldehyde, 4.70 wt.% vanillin and 0.40 wt.% p-hydroxybenzaldehyde with 73.00 wt.% lignin conversion using wood chips from Populus tremuloides (Aspen) treated with hot water, extracted with NaOH, acidified with H$_2$SO$_4$ and finally washed. The reaction took place in a bomb reactor containing 100 mL 4.375 M NaOH solution with 13.8 bars O$_2$ (at RT), 10 g of lignin, 0.05 g FeCl$_3$ and 0.5 g CuSO$_4$ for a time of 10 minutes. They also believe that under the conditions they used the CuSO$_4$ became Cu(OH)$_2$ and FeCl$_3$ became Fe(OH)$_3$ which both have very low solubility in aqueous solution causing three phases to be present during the reaction.

Metalloporphorin catalysts are biomimetic, meaning they are intended to imitate the enzymes found in nature which break down lignin. They are made by the metallation of a porphyrin with transition metal salt. These catalysts may have Fe, Mn, Ru or Co centers active in selective oxidations. Various structures of metalloporphyrins used in lignin oxidation can be found below in Figure 1.5.
Metalloporphyrin catalysts are known for being selective oxidation catalysts. Fe porphyrins, specifically, are known to cleave the bond between the α and β carbons and oxidize the resulting compound. Crestini et al. compared the oxidation of kraft lignin with a manganese (III) porphyrin catalyst to an iron (III) porphyrin catalyst. They found the manganese (III) porphyrin catalyst were better at degrading kraft lignin than the iron(III) porphyrin catalyst.

Polyoxometalates (POMs) were originally meant to replace chlorine-based bleaches during the pulping stage of papermaking in order to make the process more environmentally friendly, but they have since found a dual purpose in lignin oxidation. Polyoxometalates are different from other oxidative catalysts because they can be used in aerobic or anaerobic conditions. They can adopt a number of different structures and contain various transition metals or other types of catalytic species integrated into their structures. The basic formula of a polyoxometalate building block is $[MO_x]_n$ where M can be Mo, W, V, or Nb and x can be any integer between 4 and 7. Polyoxometalates
can be divided into three categories: heteropolyanions, isopolyanions, and molybdenum blue and molybdenum brown reduced polyoxometalates. The heteropolyanions can be broken up further into various categories by structure. The most common heteropolyanions structures are the Dawson, Keggin, and sandwich-type. We will be focusing on heteropolyanions because they are the largest group and they are, according to Kozhevnikov, the best oxidizers.

Ruuttunen et al. claims that the α-Keggin type polyoxometalates, again part of the heteropolyanion family, are probably the most promising polyoxometalate catalysts in oxidative lignin degradation because they are stable and active over a wide range of pHs and temperatures. The general formula of a keggin-type polyoxometalate is $[XZ_yM_{(12-y)}O_{40}]^{q-}$ where X is P, Si, Ge, B, etc., Z and M are the addendum atoms which are usually the transition metals Mo, W, V, or Nb, q is the charge of the overall structure. They are basically spherical in shape with a XO$_4$ tetrahedron in the center of the structure surrounded by 12 MO$_6$ and/or ZO$_6$ octahedra. The oxygen atoms are what bond the octahedral and tetrahedron structures together.

Voitl et al. used a H$_3$PMo$_{12}$O$_{40}$ catalyst to increase vanillin and methyl vanillate yield. They found that by adding 80% methanol to the reaction solution they could produce methyl vanillate and increase vanillin yield. Anaerobic and aerobic conditions were also tested and the aerobic conditions were found to increase yields.

Heterogeneous catalysts are used for many different applications and are already well established in industry so they are very easy to find and do not have to be specially made. Sales et al. used a 2.85% Pd/γ-Al$_2$O$_3$ catalyst to use as their catalyst in catalytic
wet aerobic oxidation. They decided to use a heterogeneous palladium catalyst because they are stable under extreme conditions. Sales et al. ran reaction with three different temperatures (P O$_2$=5 bar with T=100˚C, 120˚C, 140˚C) and three different oxygen partial pressures (T=120˚C with PO$_2$=2 bar, 5 bar, 10 bar). They used 60 kg/m$^3$ sugar cane bagasse hydrolyzed by Dedine fast hydrolysis as their feed. 2M NaOH was used along with 4.00 wt% catalyst and the total pressure was brought up to 20 bars using N$_2$. Sales et al. found that by using their Pd catalyst they could increase their aldehydes yields 10 fold.$^{10-12}$

Products of oxidation reactions include char, phenolics, aldehydes and aliphatics and various gasses including carbon monoxide, carbon dioxide, methane and hydrogen.

$$\text{products} = \text{char, phenolics, aldehydes and aliphatics and various gasses}$$

![Figure I.6 Alkaline oxidation of phenolics to aldehydes.](image)

Figure I.6 Alkaline oxidation of phenolics to aldehydes.$^{65}$

To produce aldehydes from lignin using wet aerobic oxidation (WAO), extremely alkaline conditions are needed. A pH above 11.5 is required for the negatively charged oxygen atom bound to the fourth carbon in the benzene ring to be favorable in order for
the first step of oxidation to proceed. Figure 1.6, proposed by Gierer et al., shows the reaction mechanism without catalyst.

A mechanism for the catalytic wet aerobic oxidation (CWAO) of lignin using a perovskite-type catalyst with active copper and iron atoms was proposed by Zhang et al. as seen in Figure 1.7. Briefly, to initialize the reaction, a dehydration takes place causing a double bond to form between the α and β carbons of the monolignol creating a phenolate anion. The iron and copper atoms of the perovskite-type catalyst work together to deionize the phenolate anion and then transfer the electron to a free dioxygen molecule causing the dioxygen to become more reactive. The newly formed phenolate radical may now freely resonate between its current structure and a quinone methide radical. While the monolignol is in its quinone form, the activated dioxygen molecule can attack the free radical carbon atom (β-carbon) and form a bond. The anionic oxygen atom can then attack the α-carbon and form a dioxethane structure. The molecule then goes through a synchronous cleavage of the oxygen-oxygen and α-carbon-β-carbon bonds to form resulting in the formation of an aldehyde.
Figure I.7 Proposed mechanism for the Catalytic Wet Oxidation of lignin using \( \text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3 \)

Alternative hypotheses for the reaction path of lignin oxidation have also been published. Tarabanko et al. suggest that the last step of aldehyde formation is retroaldol cleavage, not a synchronous cleavage.\(^{66}\) Wu et al. have proposed that an ionic pathway and a radical pathway exist, as shown in Figure 1.8, for aldehyde formation with iron being active in the ionic pathway and copper being active in the radical pathway.\(^{59}\)
In addition to the main reaction, side reactions and additional reactions take place. Quinones, aceto derivatives, and other molecules may form from side reactions occurring in the reaction scheme in Figure 1.6. Additional oxidation to aldehydes produced in CWAO by free oxygen causes carboxylic acids to form. We want to prevent this additional step to increase the yield of aldehydes.

In the following figures, Gierer et. al displays alternate reactions that can occur during lignin oxidation in an alkaline solution.
The oxidation of lignin in an alkaline solution can proceed in a variety of ways in addition to what is displayed in Figure 1.6. The pathway the reaction takes depends upon which resonant structure the radical is when molecular oxygen attacks.
Figure I.10 Carboxylate formation by oxidation of phenolic keytone.\textsuperscript{65}

Shown in figure 1.10, a phenolic ketone with an anionic $\beta$-carbon is susceptible to dioxygen attack at the $\beta$-carbon. A dioxethane intermediate forms before the bond between the $\alpha$- and $\beta$-carbons is cleaved and the carboxylate is formed. As soon as Hydrochloric acid is added to the basic solution the carboxylate will become a carboxylic acid.
Figure I.11 Pathways of hydroperoxide radical formation from oxidation of a diacetyl anion and anionic phenols in an alkaline solution.\textsuperscript{65}

In an alkaline solution phenolics and 2,3-butenedione exist as anions, allowing for dimolecular oxygen to attack. Hydroperoxide quinones can either lose a hydroxide anion or peroxide radical and form a quinone alcohol or a quinone radical respectively. Hydroperoxide anions are also produced. 2,3-butanedione-2-hydroperoxide anion will form 2,3-butanedione and a hydroperoxide radical in a basic environment.
Figure I.10 Formation of quinone by dehydration

Quinones can form by dehydration of a phenolic with a hydroxyl group on the \( \alpha \)-carbon and a peroxide group on \( C_1 \) in the six-member carbon ring.

Figure I.11 Cleavage of the \( \beta \)-aryl ether bond of lignin in an alkaline solution causing epoxide formation.

Once cleavage of the \( \beta \)-aryl ether bond occurs the charged oxygen will form an epoxy structure to stabilize itself. In an alkaline solution anionic hydroxyl groups can attack the \( \alpha \)-carbon causing epoxide formation.
A hydration followed by a rearrangement will form a phenolic radical and a methyl phenolic radical.

**Oxygen sources for lignin oxidation**

There are many different sources of oxygen for the oxidation of lignin including ozone, dioxygen, hydrogen peroxide, metal oxides, and nitrobenzene. Nitrobenzene is a known carcinogen, so it has not been utilized in recent research except to determine the monolignol fractions in various lignins. Nitrobenzene is also much more expensive than oxygen sources, such as $\text{H}_2\text{O}_2$ and $\text{O}_2$. Metal oxides are not recoverable and must be disposed of after they have been used so they would not be an appropriate choice for an industrial process. The three remaining sources: ozone, dioxygen, and hydrogen peroxide have been the mostly widely utilized because they are considered to be environmentally friendly. The two latter-mentioned sources are the most popular because ozone is corrosive, is hard to store and decomposes easily.

**Chemistries Known to Produce Value-Added Molecules**

Catalytic wet aerobic oxidation is not the only reaction known to produce value-added molecules; however, it is known to produce the highest. Pyrolysis, base-catalyzed depolymerization and pulping technologies are all known to produce value-
added molecules from lignin. Instead of value-added molecules being produced by these chemistries Hartley and Keene suggest that p-hydroxybenzaldehyde, vanillin and syringaldehyde pre-exist in graminaceous plant cell walls and are released as their salt form during treatment with sodium hydroxide. This concept could also be applied to pyrolysis; trace amounts of p-hydroxybenzaldehyde, vanillin and syringaldehyde were all found in pyrolysis product.

**Existing and Potential Applications of Lignin**

As a complex polymer, lignin is a versatile entity. Known for its strength and resistance to breakage, as it is the main structural support in rigid biomass, lignin is usually mixed into things to increase their integrity including cement and plastics. It can also be used as a dispersant. Applications of lignin may vary depending on the pretreatment method used to purify the lignin and additional reactions. Most applications involve lignins acting as structural modifiers, dispersants or carriers.

The largest market for lignosulfate use worldwide is as filler in concrete. Lignin makes excellent filler because it is a superplasticizer; as an additive, lignin reduces the amount of water needed to increase the workability of the cement. Lignosulfonates can also be used as cement retarders while using cement in oil wells to achieve zonal isolation. The conditions of oil well are extreme with large temperature ranges and high pressures which can cause cement to harden to quickly or make the hardening time unpredictable. Lignosulfonate addition will increase the drying time of the cement allowing it to be poured in the correct location.
Adding lignosulfonates to metal complexes which provide essential metals to plants allows for easier application. When metal complexes are applied directly to plant leaves, leaf scorch may occur. However when lignosulfonates are adding they protect the leaf from any scorching that may occur while allowing the plant to absorb nutrients. Metal complexes may also be added to the soil with lignosulfonates to be absorbed through the plant roots. Lignosulfonate addition will prevent degradation and allow the micronutrients to be available for a longer period of time in the soil.\textsuperscript{47,73}

Lignins being polymers themselves have been added to synthetic polymers to improve their properties and decrease costs. Adhesives, foams, films, rubber and resin additives and polyblends have all been attempted with lignin as an additive. When the right amount of lignin is added to a plastic polymer, the strength and flexibility of the polymer can increase.\textsuperscript{74}

Lignosulfonates and kraft lignin can be used as dispersants, grinding aids and binders in various applications including: dye manufacturing, pesticide production and ink manufacturing.\textsuperscript{47} Lignosulfonates can also be added to utility water in industrial plants as dispersants: preventing settling of salts and other particulates which may cause scaling, biofilm formation and fouling of instrumentation.

There are numerous other applications of lignins including: as expanders for lead-acid batteries, in leather tanning, as flotation and wetting aids in ore processing, as sacrificial agents in enhanced oil recovery, as precipitating agents in protein recovery, in de-icing formulations, as wood preservatives and as glue in plywood.\textsuperscript{47,75}
Motivation for WCAO

Previous studies including Sales’s\textsuperscript{10-12} of a heterogeneous catalyst and Zhang’s\textsuperscript{13} study of a perovskite catalyst did not address the yields of aldehydes affected by the feedstock choice for desired aldehyde products, as both groups used what was readily available to them. All lignins are made up of the same 3 monolignols but they are randomly arranged and the percentages of each can vary from plant to plant. Also, both groups used further reactions to obtain pure lignin feedstock which further changed the lignin structure and polymer size. In addition, we want to explore the possibility of base catalyzed depolymerization occurring at the same time as wet catalytic oxidation and the affect that the concentration of the base has on lignin degradation. Furthermore, we wanted to address the possible participation of naturally occurring iron in the reaction. Iron is known to be active in WCAO and it is naturally occurring in plant material. We increased the reaction temperature to 140˚C instead of 120˚C because iron becomes much more active at 140˚C.\textsuperscript{59}

1.6 Research Objectives

The main objective of this project is to explore an economically feasible process to produce and purify syringaldehyde and vanillin from corn stover lignin oxidation.

To accomplish this task, the following specific objectives will be pursued:

1. Investigate how the continuous addition of molecular oxygen to the reactor affects the aldehyde yield.
2. Investigate the effect of the addition of an industrial heterogeneous palladium catalyst on aldehyde selectivity and yields.
3. Investigate if naturally occurring iron is a selective catalyst for aldehyde production.

4. Conduct an analysis to understand the role of NaOH in the reaction. Is base catalyzed depolymerization occurring at 140°C and what is the effect of NaOH concentration?
II. Chapter 2

2.1 Experimental

*Materials*

Corn stover lignin was obtained from the National Renewable Laboratory (NREL) in Colorado. According to the MSDS from NREL, the lignin was isolated by first cooking corn stover in a weak (1.4% sulfuric acid) acid. The resulting slurry was then dewatered and neutralized. A cellulose enzyme was added to the dewatered and neutralized slurry to reduce the cellulose into glucose. The byproducts of the enzymatic reaction were washed to remove ethanol and residual sugars and then dried to produce the product that we received from NREL. The lignin byproduct that NREL send contains 66% w/w of water, 10% w/w cellulose and 24% w/w lignin and may contain trace sulfurs from cooking the original corn stover feed in weak sulfuric acid.

98% p-hydroxybenzaldehyde, 99% 3-methoxy,4-hydroxybenzaldehyde 98+% 3,5-methoxy,4-hydroxybenzaldehyde and 98+% Fe(NO$_3$)$_3$•9H$_2$O were purchased from Alfa Aesar. HPLC grade chloroform stabilized with 0.75% ethanol, 12.1N hydrochloric acid ACS plus Grade and ACS grade sodium hydroxide were purchased from Fisher Scientific. 5% Pd/γ-Alumina ESCAT$^{\text{TM}}$ 1241 was purchased from Strem Chemicals who sell bench top quantities of industrial BASF catalysts.

*Methods*

Corn stover lignin was used as feedstock because it has the most syringyl units (Table I.1 Monolignol Units in Different Crops) and was expected to produce more
syringaldehyde during CWAO. It is also convenient that corn stover should be readily available in the Midwestern United States because corn is a major crop in the region.\textsuperscript{76}

To rid the lignin of any excess sugars and sulfurs to prepare it for reaction, it was dried in an 80°C oven, ground into a fine powder with a mortar and pestle, and then washed twice with DI water. During the first wash, lignin was stirred and heated for 30 minutes, then allowed to sit until it settled to the bottom of the flask. The top water layer was then taken off and disposed of. DI water was again added for the second wash and stirred and heated for 30 minutes. After the second 30 minutes of washing, the lignin was dried by vacuum filtration and then left in the 80°C oven over night. The lignin was ground into a powder a second time and stored in the 80°C oven to keep it dry until it was needed for reaction.

Reactions

Reactions were run in a Parr 5500 50 mL stainless steel reactor with a heating jacket and Parr 4848 reactor controller. Lignin was added to reactor at 60 Kg/m\textsuperscript{3} or 1.8 g per 30 mL 2 M NaOH. 2 M NaOH was used ensure solubility of the lignin in the aqueous solution. If catalyst was used, 3 g/L of catalyst was also added to the reactant solution. The reaction was initially run at 140°C with 15 bars of N\textsubscript{2} and 5 bars of O\textsubscript{2} (5 bars N\textsubscript{2} for N\textsubscript{2} reactions) for a specified amount of time. While the reactor was heating to temperature, the reaction solution was stirred and 12 bars of N\textsubscript{2} was added (15 bars once reactor reached reaction temperature). Once the reactor reached a stable temperature (20 minutes was the standard for each reaction), 5 bars of oxygen, or additional nitrogen for the N\textsubscript{2} reactions, was added to the reactor initializing the start of
the reaction time. The oxygen valve was left open to allow a continuous flow of oxygen into the reactor as the oxygen was used up in the reaction. Once the reaction time ended, stirring was stopped and the reactor was dumped into an ice bath to cool quickly. The reactor was depressurized while cooling. After the reactor was cool enough to touch (~70°C), it was opened. The reactant solution was transferred to a 100 mL beaker via glass pipet to prepare for HCl titration.

To insolublize the unreacted lignin and allow it to be mechanically removed, the reactant solution was titrated to a pH of 2 using 12.1 M HCl indicated by the color change seen in Figure II.1 Color change of lignin by titration of lignin reactant solution with 12.1 M NaOH to pH 2 indicating a change in the exposed functional groups of the unreacted lignin causing insolubilit. A Sensorex 200C pH electrode was used to measure the pH. After titrating, the reaction solution was poured into 15 mL centrifuge tubes and centrifuged for 1 hour to separate the residual lignin from the reactant solution.
The reactant solution was decanted into a 100 mL graduated cylinder to measure the volume of solution finally obtained from the reaction. The solution was then poured into a 100 mL beaker with a stir bar and mixed for 15 minutes to ensure a homogeneous solution. 8.4 mL of solution was taken while stirring. The leftover lignin pellets were rinsed out of the centrifuge tube with DI water into 100 mL beakers and put into the 80°C oven to dry overnight.

The 8.4 mL of reaction solution was extracted with 30 mL of chloroform stabilized with 0.75% ethanol from Fisher. The separatory funnel was shaken for 1 minute before allowing the phases to separate and settle. The chloroform phase was taken off of the bottom into a 100 mL beaker and allowed to evaporate off overnight in the negative
pressure flow hood. The aqueous phase was added back to the original solution and put in the 80°C oven to evaporate off the water.

The leftover solids were redissolved in a known volume 50% ethanol solution and pipetted into a 0.5 mL micro-centrifuge tube to freeze in an -80°C freezer until they could be analyzed.

**Reactions with Palladium Catalyst**

Reactions were run the same way as oxygen reactions with the exception of 5 wt.% (0.09 g/30mL 2M NaOH) of 5% Pd/γ-Alumina industrial catalyst (Escat™ 1241) from BASF being added to the reaction.

**Lower pH Nitrogen Reactions**

Reaction with lower pH were run the same way as regular nitrogen reactions except 3 mL of 2 M NaOH and 27 mL DI water were used to achieve a 0.2 M NaOH (pH ~12.8) solution to use during the lignin reaction.

**Iron Impregnation of Lignin for Iron Runs**

6 grams of corn stover lignin was weighed out per impregnation batch. 0.13 grams and 0.26 grams of Fe(NO$_3$)$_3$•9H$_2$O was weighed out and dissolved in DI water to make Fe2X and Fe3X samples respectively. Iron content of the original lignin was determined by SEM-EDS and then it was doubled for the Fe2X and tripled for the Fe3X samples. Iron was impregnated on the Corn Stover lignin by incipient wetness impregnation. After impregnation the lignin was left in the 80°C oven overnight. The lignin was then ground into a powder with a mortar and pestle and then put into a glass vial to store
until it was needed for reaction. Reactions using these lignin samples impregnated with iron were run the same way as stated for the lignin run under 5 bars of oxygen. All lignin samples impregnated with iron were left to stir at room temperature for 5 minutes to let iron migrate out of the lignin before heating up under 15 bars of nitrogen for 20 minutes and then running with an additional 5 bars of oxygen for 30 minutes.

**Evaluation of Reaction Products**

**Concentration Curves**

Reaction products and the yields of the three aldehydes were analyzed by a Shimadzu GCMS QP-5000 equipped with a GC-17A, a SLB-5ms capillary column from Suppelco that was 30 m in length with a 0.25 mm inner diameter and a 0.5 μm film thickness and a quadrapole MS. Curves were made from samples of known concentrations of the three aldehydes to be quantified. Aldehyde peak identity was confirmed by MS. The injection port temperature of the GC was set to 230°C and the interface to 230°C. The column temperature was initially set at 140°C and held for 1 minute before ramping to 280°C at 25°C/min (Figure II.2 GCMS concentration curves for first method: 140°C for 1 minute then ramping to 280°C at 25°C/min. The aldehydes shown are: A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde). The method used had to be changed for samples run later because of decreasing peak separation and increased sensitivity over time. Consequently, the initial column temperature was decreased to 100°C and the ramp speed decreased to 16°C/min to slow the rate at which the compounds traveled through the column (Figure II.3 GCMS concentration curves for second method: 100°C for 1 minute then ramping to 280°C at 16°C/min. The aldehydes shown are: A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde).
Figure II.2 GCMS concentration curves for first method: 140°C for 1 minute then ramping to 280°C at 25°C/min. The aldehydes shown are: A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde.
Figure II.3 GCMS concentration curves for second method: 100˚C for 1 minute then ramping to 280˚C at 16˚C/min. The aldehydes shown are: A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde

**Partition Coefficients**

The concentrations of aldehydes detected by GCMS were adjusted to actual concentrations produced from the reaction based upon preliminary testing of the partition coefficients of all three aldehydes between 8.4 mL of reactant solution and 30 mL of chloroform. In preliminary testing, known concentrations of aldehydes were dissolved in 7 mL of 2 M NaOH and then titrated down to a pH of 2 with 1.4 mL of 12.1
M HCl. The solution was then extracted with 30 mL of Chloroform, by shaking for 1 minute, letting both phases separate and then taking off the bottom layer and letting the chloroform evaporate off overnight. The solids were redissolved in 1:1 ethanol:water solution and then run through the GCMS. The concentrations after chloroform extraction were compared to the concentrations originally added to the sodium hydroxide solution to obtain the partition coefficients. A table (Table II.1 Partitions for various concentrations of vanillin(V), syringaldehyde(S) and p-hydroxybenzaldehyde(H). STDev for individual runs are from multiple GCMS runs while average STDev is the standard deviation of all runs.) of the partitions and their standard deviations can be seen below. Table II.2 Partitions of each concentration averaged and the standard deviation for the averaged runs shows the partition averages of each concentration tested. No changes were seen in the partition as related to the concentration of aldehydes in solution so it was decided to use one average partition for all concentrations.

Table II.1 Partitions for various concentrations of vanillin(V), syringaldehyde(S) and p-hydroxybenzaldehyde(H). STDev for individual runs are from multiple GCMS runs while average STDev is the standard deviation of all runs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P-hydroxybenzaldehyde % Recov’d</th>
<th>STDev</th>
<th>Vanillin % Recov’d</th>
<th>STDev</th>
<th>Syringaldehyde % Recov’d</th>
<th>STDev</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) 1 g/L</td>
<td>80.39%</td>
<td>3.42%</td>
<td>85.36%</td>
<td>2.10%</td>
<td>99.41%</td>
<td>2.79%</td>
</tr>
<tr>
<td>2) 1 g/L</td>
<td>79.61%</td>
<td>0.69%</td>
<td>88.23%</td>
<td>0.76%</td>
<td>96.92%</td>
<td>0.92%</td>
</tr>
<tr>
<td>3) 1 g/L</td>
<td>79.60%</td>
<td>2.16%</td>
<td>86.91%</td>
<td>1.27%</td>
<td>97.24%</td>
<td>2.46%</td>
</tr>
<tr>
<td>4) 3 g/L</td>
<td>82.15%</td>
<td>0.57%</td>
<td>82.59%</td>
<td>1.08%</td>
<td>95.56%</td>
<td>1.45%</td>
</tr>
<tr>
<td>5) 3 g/L</td>
<td>82.47%</td>
<td>0.57%</td>
<td>89.26%</td>
<td>0.46%</td>
<td>94.14%</td>
<td>1.30%</td>
</tr>
<tr>
<td>1) 5 g/L</td>
<td>83.11%</td>
<td>0.80%</td>
<td>89.10%</td>
<td>1.40%</td>
<td>96.69%</td>
<td>2.73%</td>
</tr>
<tr>
<td>2) 5 g/L</td>
<td>83.56%</td>
<td>0.67%</td>
<td>89.23%</td>
<td>1.02%</td>
<td>98.22%</td>
<td>1.23%</td>
</tr>
<tr>
<td>4) 5 g/L</td>
<td>82.95%</td>
<td>1.44%</td>
<td>89.44%</td>
<td>1.91%</td>
<td>95.08%</td>
<td>2.16%</td>
</tr>
<tr>
<td>Average</td>
<td>81.73%</td>
<td>1.62%</td>
<td>87.52%</td>
<td>2.45%</td>
<td>96.66%</td>
<td>1.71%</td>
</tr>
</tbody>
</table>
Table II.2 Partitions of each concentration averaged and the standard deviation for the averaged runs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P-hydroxybenzaldehyde</th>
<th>Vanillin</th>
<th>Syringaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Recov’rd</td>
<td>STDev</td>
<td>% Recov’rd</td>
</tr>
<tr>
<td>1 g/L Average</td>
<td>79.86%</td>
<td>0.45%</td>
<td>86.83%</td>
</tr>
<tr>
<td>3 g/L Average</td>
<td>82.31%</td>
<td>0.23%</td>
<td>85.92%</td>
</tr>
<tr>
<td>5 g/L Average</td>
<td>83.21%</td>
<td>0.32%</td>
<td>89.26%</td>
</tr>
</tbody>
</table>

**Dry Lignin Characterization**

Insoluble lignin was also measured to show how aldehyde production compared with lignin degradation. The lignin pellets left after centrifugation and decanting of the reactant solution were washed out of the centrifuge tubes and into 100 mL beakers and left to dry in the 80°C oven. After drying, they were weighed, scraped out of the beakers and ground to a powder with a mortar and pestle. The powder samples were analyzed by a SDT Q600 Thermogravimetric analyzer (TGA) from TA Instruments (ramp 10°C/min to 650°C in air) to determine the amounts of unreacted, non-water soluble lignin and cellulosics left over after reaction. The peak deconvolution software, Fityk 0.9.8, was used to determine the weight loss caused by each biopolymer. The individual peaks for pure components run on TGA are shown in Figure II.4 Lignin, cellulose and hemicellulose TGA peaks. Peak shapes from this graph were used to find the best curve fit. SplitGaussian was used for cellulose while SplitPearson7 was used for hemicelluloses and lignin. Starting lignin was also analyzed by this method to determine the amounts of each biomass in the initial lignin sample.
Ash Analysis

After TGA, ash remained. To determine if there were any metals present in the ash which could be catalytically active in the reaction, an elemental analysis was performed. A FEI XL30 ESEM (Environmental Scanning Electron Microscope) was used to analyze the ash by EDS (Energy Dispersive X-ray Spectroscopy). To prepare samples for analysis, lignin was placed in an alumina calcinations dish and put in an oven ramping to 650˚C at 10˚C/min to simulate the same conditions used during TGA. Samples from TGA were too small to use so lignin had to be prepared in larger quantities. After ash was obtained individual dies were prepared by placing double stick carbon tape on the die surface and dipping the carbon tape into the lignin ash. Excess ash was removed using pressurized air. Samples were coated with a palladium and gold mixture and run under higher vacuum because of the uncertainty of what would be present in the sample. EDS was performed at lower magnification because of the heterogenous
nature of the ash particles. Table II.3 Comparison of different elemental analysis of corn stover ash. (1) SEM-ESD elemental analysis of corn stover. (2) X-ray Fluorescence Spectroscopy of corn stover fast pyrolysis char.\textsuperscript{80} shows the results of analysis and compares existing data.\textsuperscript{80}

Table II.3 Comparison of different elemental analysis of corn stover ash. (1) SEM-ESD elemental analysis of corn stover. (2) X-ray Fluorescence Spectroscopy of corn stover fast pyrolysis char.\textsuperscript{80}

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt. %</th>
<th>Element</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4.6%</td>
<td>Al</td>
<td>5.0%</td>
</tr>
<tr>
<td>Ca</td>
<td>2.5%</td>
<td>Ca</td>
<td>11.1%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1%</td>
<td>Cl</td>
<td>2.4%</td>
</tr>
<tr>
<td>Cu</td>
<td>0.9%</td>
<td>Cu</td>
<td>0.0%</td>
</tr>
<tr>
<td>Fe</td>
<td>2.6%</td>
<td>Fe</td>
<td>5.3%</td>
</tr>
<tr>
<td>K</td>
<td>0.0%</td>
<td>K</td>
<td>10.8%</td>
</tr>
<tr>
<td>Mg</td>
<td>0.2%</td>
<td>Mg</td>
<td>5.0%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0%</td>
<td>Mn</td>
<td>0.3%</td>
</tr>
<tr>
<td>Na</td>
<td>0.7%</td>
<td>Na</td>
<td>0.6%</td>
</tr>
<tr>
<td>P</td>
<td>0.0%</td>
<td>P</td>
<td>2.1%</td>
</tr>
<tr>
<td>S</td>
<td>0.0%</td>
<td>S</td>
<td>0.3%</td>
</tr>
<tr>
<td>Si</td>
<td>88.6%</td>
<td>Si</td>
<td>57.1%</td>
</tr>
</tbody>
</table>

After finding that iron was present at decent quantities, two different amounts of iron were impregnated onto lignin to test how they would affect the oxidation reaction. To determine the actual amount of iron present in the initial iron sample SEM-EDS was again used. The procedure for preparing samples for analysis was much the same as stated above except for two differences: (1) No coating was used on the samples
because of the low percentage of metals present in the sample and (2) The instrument was used in environmental mode because it was felt a higher vacuum was not required to analyze the samples.

2.2 Results and Discussion

The lignin degradation over reaction time is shown in Figure II.5 Lignin degradation over reaction time with P O\textsubscript{2}: 5 bar, P N\textsubscript{2}: 15 bar (for N\textsubscript{2} runs P N\textsubscript{2}: 20 bar) at T=140˚C and with a 5% Pd/\gamma-Al\textsubscript{2}O\textsubscript{3} (Escat) from BASF. The O\textsubscript{2} and Pd wt.\% converted lignin graphs are identical while the N\textsubscript{2} wt.\% converted lignin graph shows lower conversion overtime. We can conclude from this observation that O\textsubscript{2} addition increases lignin degradation; however, Pd catalyst addition has no effect on lignin conversion.

It is also observed from Figure II.5 Lignin degradation over reaction time with P O\textsubscript{2}: 5 bar, P N\textsubscript{2}: 15 bar (for N\textsubscript{2} runs P N\textsubscript{2}: 20 bar) at T=140˚C and with a 5% Pd/\gamma-Al\textsubscript{2}O\textsubscript{3} (Escat) from BASF that initial lignin wt.\% converted at time 0 min is not zero. During the 20 minute reactor heating period 40-55 wt.\% of lignin is degrading which is a significant amount. Most likely, what is occurring is base-catalyzed depolymerization since the lignin reaction solution was heated under 15 bars N\textsubscript{2} in a 2M NaOH solution. Although it is suggested that base-catalyzed depolymerization and wet aerobic oxidation work together to break the lignin down, it would be preferable to not have 40-55\% of the lignin already reacted before starting wet aerobic oxidation. A possible solution to decrease initial lignin degradation is a faster heat-up method.
The heating time was standardized at 20 minutes because it was the amount of time all reactions took to reach $140^\circ C \pm 2^\circ C$. The way heating of the reactor was controlled was the heating element only switched off when the reactor reached the target temperature. This caused the reactor temperature to overshoot by $>10^\circ C$ at the $10^\circ C/min$ heating rate, because no cooling element was installed. To prevent overshooting, the operator started heating up the reactor at $20^\circ C/min$ and then switched to $10^\circ C/min$ at $100^\circ C$. Once the reactor reached $125^\circ C$ the operator turned the heating element off and let the temperature continue to increase slowly. The reactor temperature would reach $138^\circ C$ and then the operator would switch the heating element back to the $10^\circ C/min$ rate. This procedure would keep the reactor around the desired temperature, but, unfortunately, took a lot of time and control over the heating jacket temperature was difficult to maintain.
Using a batch reactor and submerging said reactor in an oil bath pre-heated to the reaction temperature may decrease required heat-up time. However, using a batch reactor will limit the amount of oxygen available for the reaction and heating up the reactor will still require a lot of time for larger reactors. A better possible solution to decrease lignin degradation by base-catalyzed depolymerization is to start the oxidation reaction while the reactor is at room temperature and include the heating up time in the total reaction time. Precautions will need to be taken to make sure the temperature ramp during oxidation is consistent between trials.

**Comparison of yields and selectivity**

For the experiments displayed in below in Figure II.8 Aldehyde yield over time for A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde. Conditions were P O₂: 5 bar and P N₂: 15 bar (for N₂ runs P N₂: 20 bar) at T=140˚C and with a 5% Pd/γ-Al₂O₃ (Escatter™ 1241) from BASF., it was decided to use a different definition of % yield than usually reported in literature. The aldehydes produced in the reactions are each from one of the three precursors as such the following definition of yield will be used to present data:

\[
\%\text{yield} = \frac{\text{mol aldehyde}}{\text{mol monolignol in lignin}}
\]

To calculate the mols of monolignol in lignin, the molecular weights of the lignin alcohol precursors were used Table II.4 Molecular weights of lignin alcohol precursors. Each molecular weight was multiplied by the percentage of each monolignol in the lignin type to create an average monolignol molecular weight. The
weight of lignin converted was divided by the average monolignol molecular weight and then multiplied by the monolignol percentage to get mols monolignol in lignin.

**Table II.4 Molecular weights of lignin alcohol precursors.**

<table>
<thead>
<tr>
<th>Monolignol</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-coumaryl alcohol</td>
<td>150</td>
</tr>
<tr>
<td>coniferyl alcohol</td>
<td>180</td>
</tr>
<tr>
<td>sinapyl alcohol</td>
<td>210</td>
</tr>
</tbody>
</table>

**Table II.5 Wet aerobic oxidation reactions from previous research with calculated % yield**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lignin Type</th>
<th>Reaction Conditions</th>
<th>Products</th>
<th>% Yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.85% Pd/γ-Al₂O₃</td>
<td>Totally hydrolyzed sugar-cane bagasse</td>
<td>2M NaOH, 120°C, 5 bar O₂, 15 bar N₂, semi-batch reaction, 30 min</td>
<td>p-Hydroxybenzaldehyde, Vanillin, Syringaldehyde</td>
<td>39.5% 27.3% 42.0%</td>
<td>10-12</td>
</tr>
<tr>
<td>2.85% Pd/γ-Al₂O₃</td>
<td>Totally hydrolyzed sugar-cane bagasse</td>
<td>2M NaOH, 140°C, 5 bar O₂, 15 bar N₂, semi-batch reaction, 15 min</td>
<td>p-Hydroxybenzaldehyde, Vanillin, Syringaldehyde</td>
<td>77.5% 45.4% 67.6%</td>
<td>10-12</td>
</tr>
<tr>
<td>No catalyst</td>
<td>Totally hydrolyzed sugar-cane bagasse</td>
<td>2M NaOH, 120°C, 5 bar O₂, 15 bar N₂, semi-batch reaction, 30 min</td>
<td>p-Hydroxybenzaldehyde, Vanillin, Syringaldehyde</td>
<td>1.4% 2.6% 1.8%</td>
<td>10-12</td>
</tr>
</tbody>
</table>
LaCu$_{0.2}$Fe$_{0.8}$O$_3$

**Need to Synthesize**

<table>
<thead>
<tr>
<th>Enzymatic hydrolysis of steam-explosion cornstalks</th>
<th>2M NaOH, 120°C, 5 bar O$_2$, 15 bar N$_2$, Semi-batch reaction, 30 min</th>
<th>p-Hydroxybenzaldehyde, Vanillin, Syringaldehyde</th>
<th>62.6% 16.3% 20.4%</th>
</tr>
</thead>
</table>

H$_3$PMo$_{12}$O$_{40}$

**Commercially Available**

<table>
<thead>
<tr>
<th>Kraft Lignin</th>
<th>20% v. H$_2$O/80% v. CH$_3$OH, 170°C, Bomb reactor, 20 min</th>
<th>Vanillin, Methyl Vanillate</th>
<th>0.19% 0.14%</th>
</tr>
</thead>
</table>

To be able to compare previous data with the data presented in this research previous results have been changed to match the definition of yield used in this study as seen in Table II.5 seen in Table II.5. Wet aerobic oxidation reactions from previous research with calculated % yield. Only one study used corn stover lignin however it was prepared differently than the corn stover used in this study.
Figure II.6  Reactions were run at 120°C with a 2.85% Pd/γ-Al₂O₃ catalyst at 4 wt.%, 2 M NaOH, PO₂=5 bars, PN₂ = 15 bars and initial lignin concentration of 60 kg/m³. A) lignin consumption, B) vanillin yield, C) syringaldehyde yield and D) p-hydroxybenzaldehyde yield.¹¹
Figure II.7 Sales et al.’s reaction data. Reactions were run at 140°C with a 2.85% Pd/γ-Al₂O₃ catalyst at 4 wt.%, 2 M NaOH, PO₂=5 bars, PN₂ = 15 bars and initial lignin concentration of 60 kg/m³.¹¹
Figure II.8 Aldehyde yield over time for A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde. Conditions were P O₂: 5 bar and P N₂: 15 bar (for N₂ runs P N₂: 20 bar) at T=140˚C and with a 5% Pd/γ-Al₂O₃ (EscaT™ 1241) from BASF.

In Figure II.8 Aldehyde yield over time for A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde. Conditions were P O₂: 5 bar and P N₂: 15 bar (for N₂ runs P N₂: 20
bar) at T=140˚C and with a 5% Pd/γ-Al₂O₃ (Escat™ 1241) from BASF. A. p-hydroxybenzaldehyde looks to be present in high yields. However, since the p-hydroxyphenyl group constitutes only 4% of the total monomer units present in corn stover, the actual amount of p-hydroxybenzaldehyde present is not large. An improvement in p-hydroxybenzaldehyde yield is seen in Figure II.8 Aldehyde yield over time for A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde. Conditions were P O₂: 5 bar and P N₂: 15 bar (for N₂ runs P N₂: 20 bar) at T=140˚C and with a 5% Pd/γ-Al₂O₃ (Escat™ 1241) from BASF. A with O₂ addition, however with Pd catalyst addition the %yields decrease which may be attributed to degradation caused by the catalyst. Over time, all three p-hydroxybenzaldehyde curves tend to level off. This type of behavior is consistent with the results in Sales et al. and Zhang et al.’s work.¹⁰⁻¹³

Vanillin displays improvement in % yield with O₂ addition like p-hydroxybenzaldehyde (Figure II.8 Aldehyde yield over time for A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde. Conditions were P O₂: 5 bar and P N₂: 15 bar (for N₂ runs P N₂: 20 bar) at T=140˚C and with a 5% Pd/γ-Al₂O₃ (Escat™ 1241) from BASF. B). However, with Pd catalyst addition there is increased product degradation. Vanillin shows the same decrease in yield overtime due to degradation like Sales et al. and Zhang et al. find.¹⁰⁻¹³

There is improved %yield with O₂ addition for syringaldehyde just like the other two aldehydes (Figure II.8 Aldehyde yield over time for A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde. Conditions were P O₂: 5 bar and P N₂: 15 bar (for N₂ runs P N₂: 20 bar) at T=140˚C and with a 5% Pd/γ-Al₂O₃ (Escat™ 1241) from BASF. C). Figure II.8 Aldehyde yield over time for A) p-hydroxybenzaldehyde, B) vanillin and C)
syringaldehyde. Conditions were P O₂: 5 bar and P N₂: 15 bar (for N₂ runs P N₂: 20 bar) at T=140°C and with a 5% Pd/γ-Al₂O₃ (Escat™ 1241) from BASF. C displays little difference between the O₂ curve and the Pd curve. However, the maximum % yield for Pd occurs at the first reaction time point, 15 minutes, and only decreases as reaction time increases. Because there are no time points between 0 and 15 minutes we cannot ascertain whether the % yield at 15 minutes is the actual maximum. Sales et al.’s results for 140°C, shown in Figure II.7 Sales et al.’s reaction data. Reactions were run at 140°C with a 2.85% Pd/γ-Al₂O₃ catalyst at 4 wt.%, 2 M NaOH, PO₂=5 bars, PN₂ = 15 bars and initial lignin concentration of 60 kg/m³.¹¹, display the same behavior where the 15 minute reaction time point is the maximum yield seen. The shift in reaction time for maximum % yield for the Pd catalyst agrees with syringyl units and syringaldehyde being much more reactive than guaicyl units and vanillin to oxygen.⁸¹

Sales et al.’s results greatly differ from the results seen in Figure II.8 Aldehyde yield over time for A) p-hydroxybenzaldehyde, B) vanillin and C) syringaldehyde. Conditions were P O₂: 5 bar and P N₂: 15 bar (for N₂ runs P N₂: 20 bar) at T=140°C and with a 5% Pd/γ-Al₂O₃ (Escat™ 1241) from BASF. Sales et al. found aldehyde yield was improved greatly by palladium catalyst addition, while this study found palladium catalyst addition did not have any effect upon aldehyde yield, and may have even increased degradation reactions, produced from the reaction.¹⁰⁻¹² There are a couple of factors which could have contributed to these results including the molecular weights of the lignin polymers and the percentages of lignols in each lignin type.

The sugarcane bagasse Sales et al. used was prepared pretreated with a different method than the corn stover used in this study. Dedine Fast Hydrolysis was used to
completely hydrolyze the sugarcane bagasse. While in this study weak acid cooking followed by enzymatic reaction of cellulose to glucose was used to decrease cellulose content. The corn stover was then dried, ground with a mortar and pestle, washed twice, dried and ground a final time. As discussed in the background about different pretreatment methods, the two different pretreatment methods used could have changed the lignins’ structure and therefore cause different reactivity. The different pretreatment methods also cause variability in the lignin polymer size. According to Kang et al., lower molecular weight lignins will produce higher aldehyde yields because they expose more precursors for the oxidation reaction. \(^{82}\)

**pH Effect on Lignin Conversion and Aldehyde Yield**

![Bar graph showing pH effect on lignin conversion and aldehyde yield]
Figure II.9 Effect of pH under a nitrogen atmosphere. Conditions were P N$_2$: 20 bar at T=140˚C for 30 minutes. pH 12.8 was made by using 0.2M NaOH while pH 14 used 2 M NaOH. A) lignin consumed and B) % yield of aldehydes

Figure II.9 Effect of pH under a nitrogen atmosphere. Conditions were P N$_2$: 20 bar at T=140˚C for 30 minutes. pH 12.8 was made by using 0.2M NaOH while pH 14 used 2 M NaOH. A) lignin consumed and B) % yield of aldehydes shows the impact of pH on lignin conversion and product yield. Higher pH increased the lignin consumed (Figure II.9 Effect of pH under a nitrogen atmosphere. Conditions were P N$_2$: 20 bar at T=140˚C for 30 minutes. pH 12.8 was made by using 0.2M NaOH while pH 14 used 2 M NaOH. A) lignin consumed and B) % yield of aldehydes) while it also increased aldehyde yields (Figure II.9 Effect of pH under a nitrogen atmosphere. Conditions were P N$_2$: 20 bar at T=140˚C for 30 minutes. pH 12.8 was made by using 0.2M NaOH while pH 14 used 2 M NaOH. A) lignin consumed and B) % yield of aldehydes). It is believed that the reaction occurring is base catalyzed depolymerization. Studies on
base catalyzed depolymerization are run at temperatures higher (160-300°C) than what was run in this study.\textsuperscript{57,83} Evidence of OH consumption in the reaction can be proven because, after reaction the pH, of the 0.2M NaOH runs decreased to a pH of \(~10.48\) (range 10.44-10.52) and the pH of the 2M NaOH runs decreased to pH 13.75.

As can be seen from the low yields in Figure II.9 Effect of pH under a nitrogen atmosphere. Conditions were P N\textsubscript{2}: 20 bar at T=140°C for 30 minutes. pH 12.8 was made by using 0.2M NaOH while pH 14 used 2 M NaOH. A) lignin consumed and B) % yield of aldehydes B, aldehydes are not major products of this reaction. The largest peak from the GCMS for both pHs, shown in Figure II.9 GC chromatogram showing peaks from 30 minute reactions run under N\textsubscript{2} atmosphere, is the 2,3-dihydrobenzofuran peak which was not quantified. The second largest peak differed depending on the pH. Acetosyringone was the second largest peak for the N\textsubscript{2} reactions run with 2 M NaOH while 2-methoxy-4-vinylphenol was the second largest for the lower pH reactions.
Figure II.9 GC chromatogram showing peaks from 30 minute reactions run under N$_2$ atmosphere

*Fe impact on Lignin conversion and Aldehyde Yield*

<table>
<thead>
<tr>
<th>% Lignin Consumed (g/g)</th>
<th>0.97 wt.% Fe</th>
<th>2.91 wt.% Fe</th>
<th>4.01 wt.% Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>70%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>76%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>82%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>84%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>86%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>88%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>92%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A. 0.97 wt.% Fe  2.91 wt.% Fe  4.01 wt.% Fe
Figure II.10 Impact of Fe on lignin conversion. Conditions were P O\textsubscript{2}: 5 bar and P N\textsubscript{2}: 15 bar (for N\textsubscript{2} runs P N\textsubscript{2}: 20 bar) at T=140˚C for a duration of 30 minutes. A) % lignin consumption and B) % aldehydes yield.

From Figure II.10 Impact of Fe on lignin conversion. Conditions were P O\textsubscript{2}: 5 bar and P N\textsubscript{2}: 15 bar (for N\textsubscript{2} runs P N\textsubscript{2}: 20 bar) at T=140˚C for a duration of 30 minutes. A) % lignin consumption and B) % aldehydes yield. The impact of iron on the reaction can be seen. Greater lignin conversion occurs with increased iron loading suggesting that iron is catalytically active. However, with increased iron loading, a decrease in aldehyde % yield is seen. This means that iron is likely active but not selective for aldehydes under the reaction conditions used. To increase aldehydes yield, a lignin source with low ash content would be preferred. The corn stover lignin used had an ash content of ~15%. An alternative would be to leach the iron out of the corn stover lignin; however this method may change the lignin structure.
Lignin vs. Cellulose conversion

Figure II.11 Comparison of % conversion for all biomass species. Conditions were P \( \text{O}_2 \): 5 bar and P \( \text{N}_2 \): 15 bar (for \( \text{N}_2 \) runs P \( \text{N}_2 \): 20 bar) at T=140˚C for a duration of 30 minutes.

Figure II.12 Comparison of oxidation reactions with decreasing \( \text{O}_2 \) pressure and with constant \( \text{O}_2 \) pressure. Conditions were P \( \text{O}_2 \): 13.8 bar (cold pressure) at T=170˚C with 0.5 wt% \( \text{FeCl}_3 \) catalyst. Displays the % conversion of all biomass species over reaction time. Lignin and Cellulose conversion looks to be unaffected by Pd catalyst addition. On the other hand, the Pd catalyst and \( \text{O}_2 \) curves for hemi-cellulose are different. After 30 minutes the Pd catalyst degrades the hemi-cellulose more than just \( \text{O}_2 \). Also, all biomass species are consumed during the reaction.
**Biphasic System**

A biphasic system has been looked into as a possible way to decrease aldehyde degradation over time and improve aldehyde yields. The difficulty in doing this is that O₂ will not differentiate between phases so another oxidant would need to be used that would favor the aqueous phase. Also, an organic phase which has a great partition coefficient at the reaction conditions and low solubility in water, while being economical is needed. This study used chloroform as the organic phase as it had the best partition coefficient for aldehydes of most common organic solvents. Unfortunately, chloroform is not an ideal solvent to use under the reaction conditions employed in this study as it reacts with NaOH.

Alternative to a biphasic system to decrease aldehyde degradation is to decrease the oxygen partial pressure over time. Wu et al. found that if they decreased the oxygen partial pressure overtime while their reaction was occurring they could decrease aldehyde degradation (Figure II.12 Comparison of oxidation reactions with decreasing O₂ pressure and with constant O₂ pressure. Conditions were P O₂: 13.8 bar (cold pressure) at T=170°C with 0.5 wt% FeCl₃ catalyst.). Reactions run as batch instead of semi-batch see decreased oxygen partial pressure overtime because of O₂ consumption.
To decrease additional reactions and increase product yield, the oxidation reaction pathway must be maximized while decreasing additional oxidations and also minimizing reactions driven by hydroxyl involvement. Unfortunately, the environment must be alkaline for oxidation of lignin to take place as seen in figure 1.6. A possible solution may be to pretreat lignin so that its polymer size is a smaller molecular weight exposing more lignol precursors in addition to increasing the temperature and increasing oxygen availability to force an oxidation reaction to occur. Sales et al. found increasing the reaction temperature and increasing the oxygen availability in the atmosphere to improve aldehyde concentration in the reaction solution. Increasing the oxygen
percentage in the lignin reaction also causes the lignin to be consumed quicker.\textsuperscript{11,12} Reaction time should also be decreased and the reaction solution should promptly be cooled to room temperature or lower and titrated with HCl to a neutral or acidic pH to prevent additional reactions from occurring.

\textit{Economic Analysis}

Part of this research involves the economics of the process. Since a goal of this research is to eventually create an industrial process from the results of this research an economic analysis is necessary.

Currently there is no process industrial process to convert lignin into high value chemicals. Figure 2.14 displays a process flow diagram of a hypothetical industrial sized plant which would use catalytic wet aerobic oxidation to convert powdered lignin into high value chemicals and includes a process to isolate vanillin and syringaldehyde from the waste liquor.

![Process Flow Diagram of Hypothetical Industrial Sized Lignin Catalytic Wet Air Oxidation Plant](image)

\textbf{Figure II.13 Process Flow Diagram of Hypothetical Industrial Sized Lignin Catalytic Wet Air Oxidation Plant}

To start the process, a premixed 2 M NaOH solution will enter a heat exchanger and recycle until it reaches 100°C and the previous batch in the reactor, or the proceeding
vessel, has been pumped into the acidification vessel. The preheated 2 M NaOH will then be pumped into the reactor. Next, the powdered lignin will be released into the reactor and mixed into the 2 M NaOH solution. The pressure inside the reactor will be increased to 20 bars total using 5 bars of O₂ and 15 bars of N₂ and the temperature of the solution will be increased to 140°C using electric coils. The reaction will be run for 30 minutes before being transferred to the acidification tank. The pressure will not be decreased because it will help transfer the solution to the next vessel. Using a hydrochloric acid solution, the pH of the reaction solution will be decreased to a pH of 4.5 to prepare for the extraction step. Once the pH is decreased to 4.5, the solution will be pumped into the next vessel which contains a non-polar macroporous resin and will adsorb vanillin and syringaldehyde in the quantities of 96.2% and 94.7% respectively after 2 hours. The vessel will be cooled with cooling water to maintain a temperature of 290°C. After 2 hours of allowing the macroporous resin to adsorb vanillin and syringaldehyde in the reactant solution, the rest of the solution will be drained out and ethanol will be added to desorb the vanillin and syringaldehyde. For further purification the vanillin will be extracted with supercritical CO₂ in the next vessel. The supercritical CO₂ solution will be further extracted with supercritical CO₂ to further purify the vanillin. The ethanol solution with a majority of syringaldehyde in it will have the ethanol taken off, redissolved in water and will be extracted with chloroform for further purification. CO₂ and chloroform will be allowed to vaporize to crystallize the vanillin and syringaldehyde.

**Table II.6 Theoretical number of vessels required in for the process of reaction and separation**

| Number of Reactors | 6 |

---

64
<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acidification Tanks</strong></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Macroporous Resin Adsorption Tanks</strong></td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Super critical CO&lt;sub&gt;2&lt;/sub&gt; Extraction Tanks</strong></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Settler and Separation Tanks</strong></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Chloroform Extraction Tanks</strong></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Crystallization w/Chloroform Tanks</strong></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CO&lt;sub&gt;2&lt;/sub&gt; Extraction Tanks</strong></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Crystallization CO&lt;sub&gt;2&lt;/sub&gt; Tanks</strong></td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table II.7 Time requirement per reaction batch**

<table>
<thead>
<tr>
<th>Time per Batch</th>
<th>Maintenance Time (days)</th>
<th>Batches per Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 minutes</td>
<td>36.5</td>
<td>15768.0</td>
</tr>
</tbody>
</table>

**Table II.8 Total volume of reactors**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume of Reactors</strong></td>
<td>5.45 m&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Volume of Liquid in Reactors</strong></td>
<td>4.36 m&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Volume of Liquid in Reactors</strong></td>
<td>4363.32 L</td>
</tr>
</tbody>
</table>

**Table II.9 Theoretical high-value aldehyde yield and profit.**

<table>
<thead>
<tr>
<th>Theoretical Yield Calculation</th>
<th>p-Hydroxybenzaldehyde</th>
<th>Vanillin</th>
<th>Syringaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/L</td>
<td>Not Recovering</td>
<td>0.2943</td>
<td>0.3638</td>
</tr>
<tr>
<td>%Recovered</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Product</td>
<td>Returns ($/Kg)</td>
<td>g/Batch</td>
<td>$/Batch</td>
</tr>
<tr>
<td>p-Hydroxybenzaldehyde</td>
<td>$ 1.40</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>Vanillin</td>
<td>$ 18.00</td>
<td>1,284.13</td>
<td>23.11</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>$ 102.00</td>
<td>1,587.38</td>
<td>161.91</td>
</tr>
<tr>
<td>Totals:</td>
<td>$ 185.03</td>
<td>$ 2,917,501.28</td>
<td></td>
</tr>
</tbody>
</table>

**Table II.10 Raw material requirements per batch and yearly.**

<table>
<thead>
<tr>
<th>Raw Material Costs</th>
<th>Batch Amount</th>
<th>Amount/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Hydroxide</td>
<td>349.07 Kg</td>
<td>5,504,070.33 Kg</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>318.52 Kg</td>
<td>5,022,464.18 Kg</td>
</tr>
<tr>
<td>Process Water</td>
<td>3619.81 L</td>
<td>57,077,209.31 L</td>
</tr>
<tr>
<td>Sewer</td>
<td>3619.81 L</td>
<td>57,077,209.31 L</td>
</tr>
</tbody>
</table>
Tables 2.6-2.11 show that raw material costs are far greater than profit from selling vanillin and syringaldehyde. The profits from vanillin and syringaldehyde do not cover the cost of hydrochloric acid required to change the pH of the reactant solution to 4. Chloroform, ethanol and macroporous resin were assumed to be recovered with a loss of 5% for each reuse to keep down costs. Chloroform requirement was reduced from 112,860,668.54 Kg/year to 5,649,833.13 Kg/year, ethanol was reduced from 57,077,209.31 L/year to 2,874,493.40 L/year and macroporous resin was reduced from 344,900.93 Kg/year to 17,369.73 Kg. However, this cost saving measure did not decrease the costs of raw materials to a profitable range.

<table>
<thead>
<tr>
<th>Raw Material Costs</th>
<th>Unit Costs</th>
<th>Metric Costs</th>
<th>$/Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Hydroxide</td>
<td>$ 0.05/lb²⁵</td>
<td>$ 0.11/Kg</td>
<td>$ 606,719.90</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>$ 0.24/lb²⁵</td>
<td>$ 0.53/Kg</td>
<td>$ 2,656,883.55</td>
</tr>
<tr>
<td>Process Water</td>
<td>$ 0.0013/L ²⁶</td>
<td>$ 0.0013/L</td>
<td>$ 73,855.05</td>
</tr>
<tr>
<td>Sewer</td>
<td>$ 0.00010/L ²⁶</td>
<td>$ 0.00010/L</td>
<td>$ 55,779.93</td>
</tr>
<tr>
<td>Lignin</td>
<td>$ 80.00/MT ²⁷</td>
<td>$ 0.08/Kg</td>
<td>$ 330,244.22</td>
</tr>
<tr>
<td>Nitrogen gas</td>
<td>$ 6.00/251 CF²⁸</td>
<td>$ 0.0011/Kg</td>
<td>$ 316.45</td>
</tr>
<tr>
<td>Oxygen gas</td>
<td>$ 6.00/230 CF²⁸</td>
<td>$ 0.0010/Kg</td>
<td>$ 123.17</td>
</tr>
<tr>
<td>Chloroform</td>
<td>$ 0.26/lb¹⁶</td>
<td>$ 0.57/Kg</td>
<td>$ 3,238,494.98</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$ 2.23/gal²⁹</td>
<td>$ 0.59/Kg</td>
<td>$ 5,080,123.90</td>
</tr>
<tr>
<td>Macroporous Resin</td>
<td>$ 3000.00/MT²⁴</td>
<td>$ 3.00/Kg</td>
<td>$ 558,093.84</td>
</tr>
<tr>
<td><strong>Total Consumable Costs</strong></td>
<td></td>
<td></td>
<td>$ 12,600,634.99</td>
</tr>
</tbody>
</table>
Increased percent yield, a new economically conservative process and/or an increased selling price for high-value aldehydes need to occur for the process to become more economically viable. Another way to increase economic viability is to look at other high-value chemicals WAO produces; however additional separation steps would also be needed to purify these additional products and add costs. Acetosyringone is the most promising to look at as a high-value chemical as it is worth more than Syringaldehyde at $7,900/Kg. Instead of looking at other high-value chemicals produced during WAO, syringaldehyde and vanillin prices could be increased to $550-$650Kg to cover raw material costs. The only way this would be able to be done is to market vanillin and syringaldehyde as natural products. Solutions to how the cost of producing high-value aldehyde can be decreased need to be investigated to make the process profitable.

2.3 Conclusions

This study compared a N$_2$ atmosphere with an atmosphere of a partial pressure of 5 bars of O$_2$ and the PO$_2$ atmosphere with 5% Pd/γ-Al$_2$O$_3$ addition. Adding a partial pressure of 5 bars of O$_2$ greatly increased aldehydes yields yet, addition of the Pd catalyst did not affect lignin degradation and may have increased the rate of aldehyde degradation.

pH was found to play a major role during reaction under a N$_2$ atmosphere. OH is an active species, driving a depolymerization reaction and reducing lignin into smaller molecules. Increasing the amount of base present in the reaction will increase aldehydes consumption and also increase aldehydes yield.
Iron, which is one of the species found in biomass ash, is catalytically active in the catalytic wet aerobic oxidation reaction. Increased iron loading will increase lignin consumption. Unfortunately, increased iron loading decreases aldehyde yield due to increased aldehyde degradation.

All biomass species were affected by O$_2$ addition which caused them to break down over the reaction time. However, Pd catalyst addition did not increase degradation of lignin or cellulose. Hemicellulose was the only biomass component affected by Pd catalyst addition.

A biphasic reaction is most likely economically infeasible. An alternative may be to use a batch reactor during wet aerobic oxidation so the free O$_2$ will decrease overtime leaving a lesser amount to react with highly reactive syringyl derivatives.

Currently wet aerobic oxidation is not an economically feasible process. To be closer to being able to use WAO on lignin to produce high-value aldehydes on an industrial scale, improvements need to be made to improve yield, change the process to decrease raw materials costs and/or look into selling additional products produced by WAO.
References


17. Xu A. 40 drums at 25kgs per drum syringaldehyde, 4-NITRO N-METHYLPHTHALIMIDE, diaminopyridine  march 10, 2011. 


28. Tagmose TM, Olesen PH, Hansen TK, inventors; Novo NA, Tagmose TM, Olesen

29. Vollmond T, inventor; Novo NA, assignee. Fabric Treated with Cellulase and
Oxidoreductase. 1999.

30. Schneider P, Damhus T, inventors; Novo NA, assignee. Enhancers Such as
Acetosyringone. 1999.

Hair. 2002.

32. Andrean H, Lagrange A, inventors; L'Oreal SA, assignee. Dyeing Method Using a
Specific Cationic Derivative and a Compound Selected Among a Specific Aldehyde, a
Specific Ketone, a Quinone and a Di-imino-isoindoline or 3-amino-isoindolone
Derivative. 2003.


46. Shi X. Transcriptional repression of lignin biosynthesis by two maize transcription factor family in monocots. . 2010.


75. Li R, Chung Y, Sattely E, Billington S. Completely biobased lignin adhesives for plywood applications. . 2013.

76. USDA. 2011 corn planted, USDA-NASS. 

77. Pinto PCR, da Silva, Eduardo A. Borges, Rodrigues AE. Comparative study of solid-phase extraction and Liquid-Liquid extraction for the reliable quantification of high value added compounds from oxidation processes of wood-derived lignin. *Ind Eng Chem Res*. 2010;49(23):12311-12318.


83. Olarte MV. *BASE-CATALYZED DEPOLYMERIZATION OF LIGNIN AND HYDRODEOXYGENATION OF LIGNIN MODEL COMPOUNDS FOR ALTERNATIVE FUEL PRODUCTION.* [Doctor of Philosophy]. Georgia Institute of Technology; 2011.


86. Butler County Water & Sewer. Industrial rate wizard.


