Bachelor's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

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Sustainable Chemical Method of Depolymerizing Lignin into Fine Chemicals

Bachelor's thesis in Bachelor i kjemi
Supervisor: Odd Reidar Gautun
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Sustainable Chemical Method of Depolymerizing Lignin into Fine Chemicals

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Sammendrag

I jakten på bedre utnyttelse av biomasse har interessen for lignin og dens potensielle bruksområder vokst. Som et fornybart materiale kan lignin være en måte å gjøre kjemiindustrien mer bærekraftig ved å erstatte petroleumsbaserte kjemikalier og redusere industriens karbonfotavtrykk. Med gode aromatiske egenskaper har lignin mange bruksområder, men mesteparten av disse krever at ligninet depolymeriseres ned til dens monomerer før det kan brukes videre. Dette hindrer at lignin sitt fulle potensial blir realisert. En av måtene å depolymerisere lignin er på er med kjemikalier som er, på grunn av høy konvertering og selektivitet, det beste alternativet for å gjøre lignin om til verdifulle kjemikalier. For å fremme bærekraft og økonomisk effektivitet bør kostbare og farlige kjemikalier unngås. Denne teksten vurderer flere nye og gamle kjemiske metoder for å finne den beste for depolymerisering og konvertering av lignin til verdifulle kjemikalier. Ulike typer lignin har ulike sammensetninger i makroskala, men i denne teksten vil fokuset være på den beste og mest bærekraftige metoden for å bryte bindingene mellom monomerene i lignin, og for å videre omgjøre det depolymeriserte ligninet til noen utvalgte kjemikalier.

Abstract

In the pursuit of better utilizing biomass, the interest in lignin and its potential uses has grown. As a renewable material sourced from waste biomass it could be a way to make industries more sustainable by replacing petrochemicals and reducing their carbon footprint. Due to its aromatic properties, lignin has a wide variety of applications, many of these however requires lignin to be depolymerized down to its monomers before it can be further processed. This is a major obstacle that prevents lignin to be fully utilized. One of the ways to depolymerize lignin is with chemicals, which is the best option for turning lignin into fine chemicals because of its high conversion and selectivity. To promote sustainability and cost-effectiveness, corrosive and expensive chemicals should to be avoided. This review evaluates several new and old chemical methods and finds the best for the depolymerizing and conversion of lignin into fine chemicals. Different types of lignin have different compositions at a macroscale, but here the focus will be on the best route available today to break the specific polymeric bonds. And to further process the depolymerized lignin into a select few fine chemicals.

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1 Introduction

Due to the carbon imbalance imposed by the unprecedented consumption of oil and natural gas and the impending energy crisis, methods of utilizing the carbon in biomass to right the imbalance is readily needed. Due to this there is an increasing interest in replacing petrochemical products with biodegradeable products made from biomass to have net zero green house gas emissions, like the replacing of plastic products with cardboard or paper based products, like straws[1, 2]. Cardboard and paper among many other things are made from the renewable material cellulose, and in the process of isolating cellulose there is a large amount of one specific biproduct[3]. This is called lignin and is maybe some of the most under-utilized biomass product we have today. With a long list of interesting properties, lignin has potential in the creation of products that are used in food and drinks, food packaging, antimicrobials and as binding agents[2, 4]. However there are challenges to making this sustainable and economically proficient, like depolymerization and avoiding the use of corrosive and expensive chemicals[2].

According to the USA's national institute of medicine 98% of all lignin generated is burned for energy, even though this still achieves net zero green house gas emissions, there are far better ways of valorizing lignin[2, 5]. However most of these ways will first require the lignin to be depolymerized down to its monomers. Chemical depolymerization of lignin has a high selectivity and conversion rate which makes it ideal for producing renewable precursors for fine chemical production[6]. Some of the fine chemicals that can be derived from lignin is vanillin and syringaldehyde, which is closely related to the monomers of lignin. The demand for these chemicals in the food and cosmetics industry is huge and continues to grow. Unfortunately most of these chemicals sold today are derived from petrochemicals. According to Chemical and Engineering news, 85% of the worlds vanillin is produced from petrochemicals, so a viable way of deriving these chemicals from lignin is an important step towards a sustainable future[4, 7]. The objective of this review is to find a way of depolymerizing technical lignin with good selectivity and conversion, and next to use this selectivity to derive precursors for fine chemicals, mainly vanillin. Sustainability and atom economy will be the primary focus when evaluating different methods.

2 Theory

2.1 Lignin

Lignin is a polycyclic biopolymer consisting of aromatic alcohols found in the cell wall of plants[8]. It is one of the most abundant polymers in nature and unlike the straight chains of cellulose, lignin is crosslinked and acts as a flexible binder which is crucial for plants to maintain its mechanical structure. The lignin is found in nature as lignocellulose and is called native lignin as shown in figure 2.1[8].

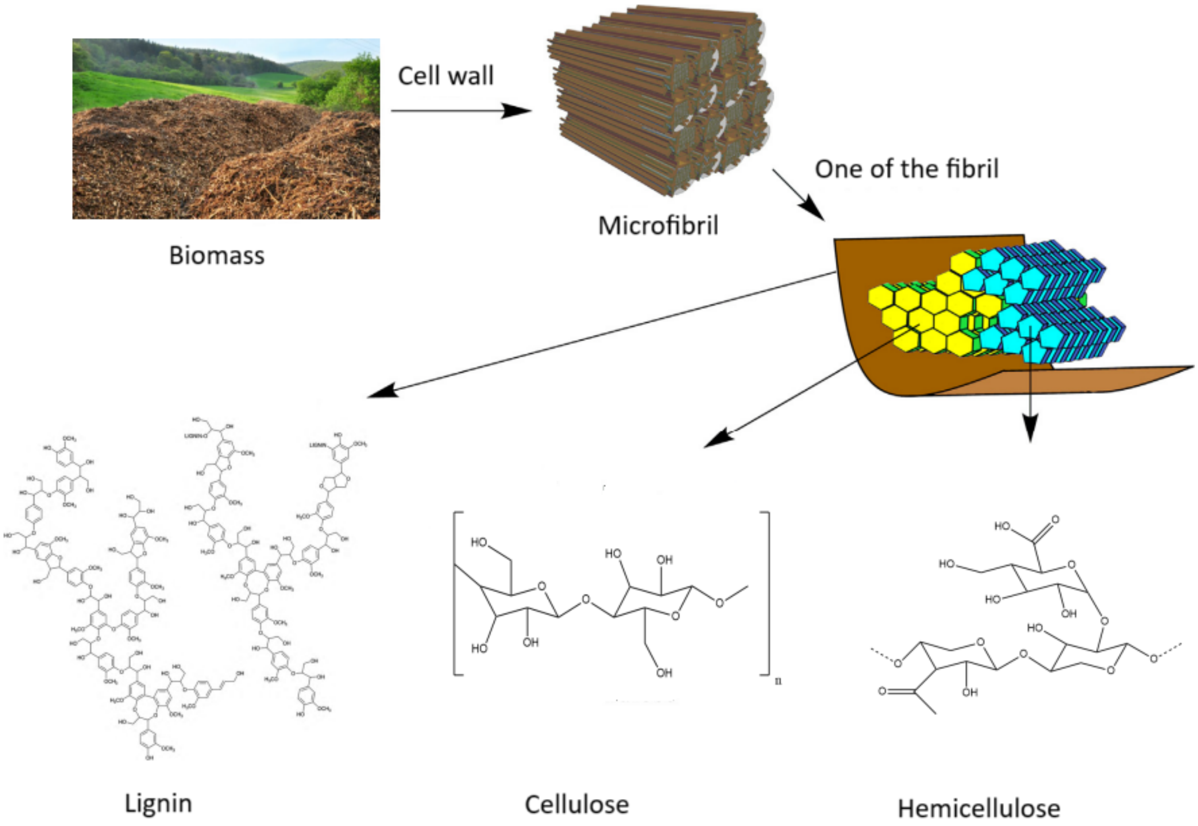

Figure 2.1: Representation of where lignin is found in plants adapted from Chio C et al.[4]

Here the lignin has several covalent bonds to different polysaccharides in plants, mostly hemicellulose and cellulose[4]. When separated, the lignin is called technical lignin and is ready for processing. Technical lignin may have shorter chains as a result of the separation, but has the same structure as native lignin without the bonds to cellulose and hemicellulose as shown in figure 2.2 [9].

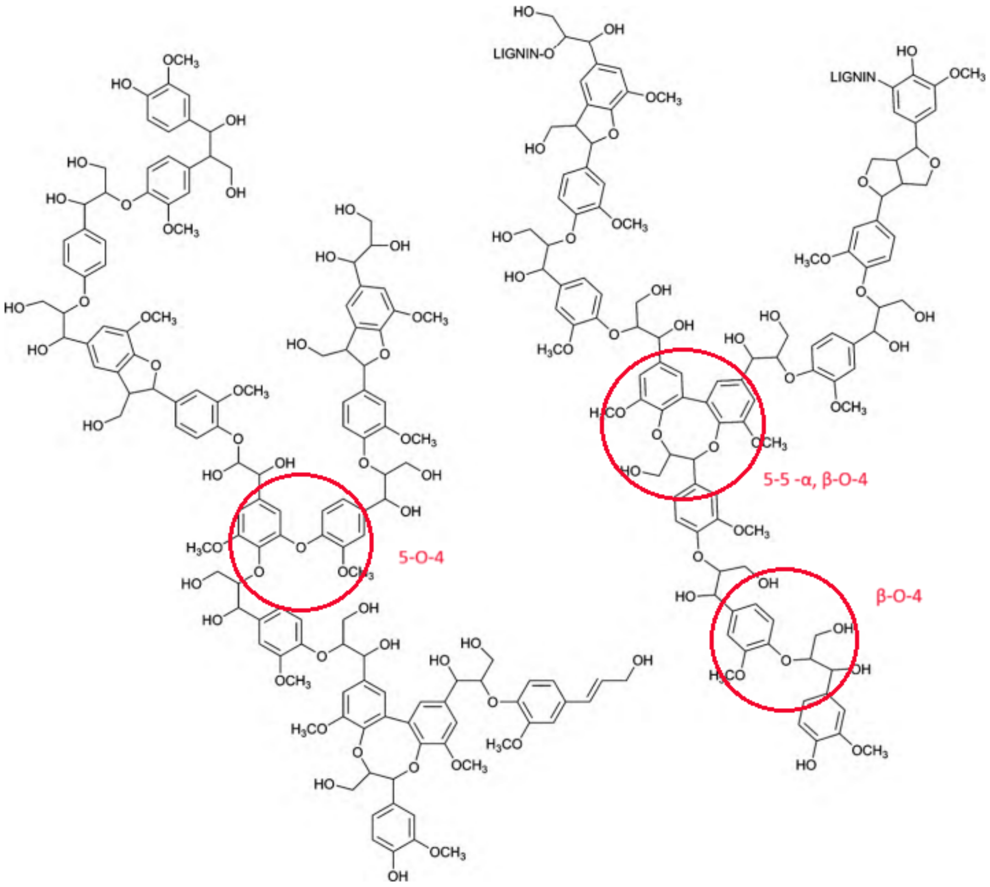

Figure 2.2: Common representation of the structure of lignin with different bonds highlighted adapted from Wang H et al.[6, 9].

Around 98% of all technical lignin produced is used as fuel for power plants, but some is used as binders in tarmac, chelating agents and precursors for fine chemicals [8].

Since the polymer has so many crosslinkages, the exact structure can vary. The most common monomer alcohols found in lignin have been identified as coniferyl(G-unit), sinapyl(S-unit) and paracoumaryl alcohol(H-unit) as shown in figure 2.3[10]. Other monomers such as guaiacyl, sinapyl and ρ-hydroxyphenol can have a significant presence among other, less important, end units, depending on plant species[10].

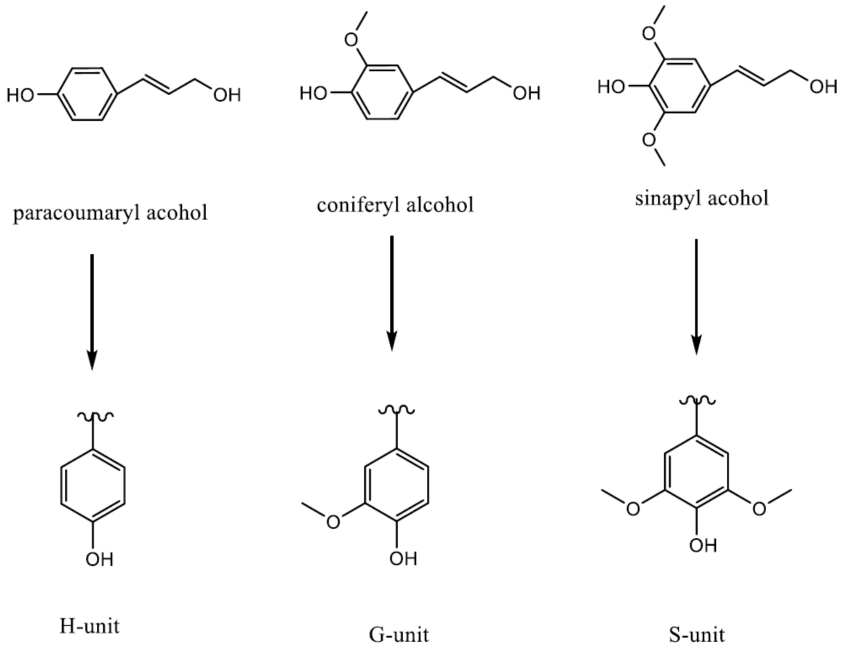

Figure 2.3: Structure of coniferyl alcohol, sinapyl alcohol and paracoumaryl alcohol and their lignin monomer units[4].

Technical lignin is a waste product of many industries who require pure cellulose, like the paper industry[3]. The Kraft process is responsible for 80% of the worlds wood pulp production, which is almost entirely consisting of cellulose fibers and is the main ingredient in paper and cardboard. During this process the bonds between lignin and polysaccharides are broken in a hot mixture of water, NaOH and Na_2S. The lignin left in solution is fractured, contains aliphatic thiol groups, and has a decreased molecular weight compared to lignin in lignocellulose. This lignin can further be sulfonated to produce lignosulfonates, or it can be recovered by precipitation with acid[11].

There are other methods of extracting lignin from lignocellulose such as using organic solvents (organosolv lignin), hydrolysis, pyrolysis, ionic liquids and steam explosion. But these represent a small fraction of the total lignin produced and is mostly used for producing biofuels from biomass[4].

2.2 Ether and Condensed Bond Cleavage

As mentioned before, the exact lignin structure can vary. The representation in figure 2.2 show a generally accepted model of lignin[9]. From this we know that the bonds between the monomers are condensed bonds and ether bonds, and to depolymerize, these bonds needs to be broken. When extracting technical lignin from native lignin, many of these bonds break and form significantly shorter chains. And when the rest of the polymeric bonds are broken the yield, selectivity and conditions greatly vary between techniques.

Lignin from different species of plants can be very different and the amount of condensed bonds (5-5 and β-1 linkages) and ether bonds (α-O-4 and β-O-4) can change (see figure 2.2)[12]. But in most species the lignin has more ether bonds than condensed bonds, and in these ether bond the most important one to break to depolymerize lignin is the β-O-4 linkage, which is also closely related to yield of vanillin from lignin[13].

2.3 Chemically Catalysed and Assisted Lignin Depolymerization

2.3.1 Acid and Base Catalysed Lignin Depolymerization

Acid catalysed hydrolysis is a common way of cleaving ether bonds, and in depolymerization of lignin it has been used since 1943[14]. Alcoholysis and hydrolysis both work catalysed by different acids such as hydrochloric and sulfuric acid. These methods break β-O-4 bonds by supplying H^+ ions to the solution and forming H_3O^+ on the ether bond, thus making it unstable and prone to breakage. Newer methods still use alcoholysis with ethanol and formic acid as reactants, in this reaction the temperature is 380 °C and pressure is 25 MPa. With wheat straw lignin the major products were methoxyphenols and catechols with a yield of around 2 wt.%[6, 15].

Base catalysis is somewhat simpler, sodium hydroxide is the only reactant needed and under temperatures around 300 °C and high pressures, it can break β-O-4 bonds[6]. Here the aryl-alkyl bonds present in lignin have a six-membered transition state catalyzed by cation adducts formed by the sodium ions during the reaction[16, 17]. Adduct ions are formed by an interaction between a precursor ion, in this case sodium ions, and one or more atoms in solution[18]. Because of these cation adducts the ratio between lignin and base is very important to form the right amount of adducts. Different sources of lignin require different reaction conditions, and some can have other alkali metal-bases as reactants to increase selectivity and yield. It was also found that by treating reaction mixture with boric acid after the reaction had taken place the yield of phenols and phenolic compounds increased. In general the main products from this depolymerization method of lignin is guaiacol and catechol from steam explosion hemp and softwood lignin, syringol from organosolv lignin and pyrocatechol from Kraft lignin with yields averaging 2 wt.%[6].

2.3.2 Oxidative and Reductive Methods of Lignin Depolymerization

Oxidative or reductive methods of lignin depolymerization can be effective at breaking ether bonds. Perovskite is a common catalyst class for hydrocarbon oxidation and can be used to depolymerize lignin, these can have a very high lignin conversion rate of around 40-60 wt.%[19, 20]. Reductive methods with H_2 gas and a catalyst can also have a high yield of phenols, benzene, toulene and xylene at 5-20 wt. %[20]. Other oxidation methods can be used to directly produce vanillin from the lignin polymer. The Korea Institute of Energy

Research investigated the oxidation of lignin with hydrogen peroxide using a copper and manganese catalyst. This resulted in a vanillin yield of around 6% at a temperature below 200 °C which is promising, but when trying to increase the yield they discovered over-oxidation of vanillin to vanillic acid[21]. Both oxidative and reductive depolymerization has a significant risk of over-oxidation/reduction, which in addition to an already low selectivity lowers it even more[20].

2.3.3 Metal Catalysed Lignin Depolymerization

Metal catalysts is a common way of decreasing the activation energy of reactions, and in lignin depolymerization it's no different. In 2019, the Chinese Academy of Sciences achieved a bio-oil yield of 82% when using nickel nanoparticles inlaid in lignin-derived carbon[22]. Solid acid catalysts can also be used with a very good yield of bio-oil, specially with $SiO_2 - Al_2O_3$, which achieved a conversion of 60%[23]. This is promising for depolymerization, but if a high selectivity of lignin monomers is wanted this method would not be suitable. Metal catalysts can be used in combination with acid or base depolymerization methods to lower the harsh conditions and have a better selectivity, but the yield would still be quite low at around 2 wt.%. A method using organosolv lignin and formic acid did get a better yield, but at temperatures over 300 °C[6].

Nickel based catalysts on activated carbon in combinations with other metals like Pt, Pd and Cu show good potential with a yield of guaiacol at 10 % with mild conditions from lignosulfonate[24]. And a pure nickel catalyst on a carbon bearer at mild conditions in reaction with birch sawdust lignin gave a yield of 12 and 36 % of propenylguaiacol and propenylsyringol respectively.

The problem however with nickel catalysts in combination with lignosulfonates is poisoning of the catalyst or creation of hydrogen sulfite, this prevents recyclability of the catalyst and creates poisonous biproducts[6].

This is solved with metal sulfides acting as catalysts during hydrogenolysis process of lignosulfonates, these metal compounds are sulfur-tolerant and has a high selectivity[25]. Here a selectivity for guaiacol monomers is achieved with a 4-propylguaiacol yield of upto 60% at 230 °C and a H_2 pressure of 5 MPa. When recycling the chosen catalyst it was discovered that 700 °C is the optimal temperature[25].

2.3.4 Ionic Liquid Assisted Lignin Depolymerization

Ionic liquids are salt that usually have a melting point below 100 °C and are characterized by an extremely low vapor pressure, these properties make them useful in a myriad of applications in electrochemistry, catalysis and more[26]. They have also been investigated for potentially being able to break β-O-4 bonds under mild conditions. Many different ionic liquids have been investigated, but cost is a major hurdle for these methods[4, 27, 28]. Some reasearchers have managed to use relatively cheap ionic liquids without co-catalysts to break β-O-4 bonds in lignin model compounds, but it still requires tweaking to work on actual lignin[29].

Unfortunately ionic liquids are quite expensive and recycliability is of great concern. Due to $\pi - \pi$ interactions between ionic liquids and aromatic substances, separation of lignin monomer is difficult[6]. Despite these concerns, there are areas of lignin valorization where ionic liquid liquids can be of much more use. Native lignin is usually treated according to the Kraft process as mentioned before, but with ionic liquid the native lignin can be dissolved and separated. Liu et al. reportedly used a liquid composed of choline chlorine and oxalic acid dihydrate at 80 °C assisted with microwaves at 800 W to efficiently cleave lignin-carbohydrate bonds. After only 3 minutes there were high purity lignin oligomers in solution and undissolved pure cellulose with potential to make nanocellulose and other products[30]. Other methods have been developed using different ionic liquids and they all represent good treatment methods for native lignin. However regarding ionic liquid assisted lignin depolymerization there are still complications that need to be addressed before it's viable[30, 31].

2.3.5 Supercritical Fluid Assisted Lignin Depolymerization

Supercritical fluids are solvents subjected to extremely high pressure and temperature and can have properties similar to both liquid and gas, this makes it an interesting medium for chemical reactions[32]. Supercritical fluids have been investigated in the past as a medium for base catalysed lignin depolymerization, but this proved that supercritical fluids had no significant impact[33]. However recently supercritical fluids have been found to affect lignin in a way that's beneficial when quantifying lignin depolymerization products[34]. Further in 2020 Ivakhnov et al. depolymerized alkaline lignin in supercritical 2-propanol which resulted in 74% lignin conversion at 450 °C[35]. These results are promising, but supercritical fluids require a significant investment even at a small scale. This makes it a low researching priority when compared to other cheaper and less demanding methods[4, 32].

2.4 Synthesis of Fine Chemicals from Lignin Monomers

Vanillin and many other aromatic substances has a variety of applications as additives in food and cosmetics among other industries, and the demand for these chemicals is huge[36–38]. Lignin monomers are heavily substituted aromatics, and after a successful depolymerization these monomers could be turned into a myriad of different substances[37]. To promote green chemistry, sustainability and profitability, an efficient process with a high yield is desired[39]. The monomers as explained earlier can vary depending on depolymerization method, so ideally a method should yield monomers that is relatively close to the end product to maximise efficiency. Guaiacol and guaiacol derivatives is an abundant product of many lignin depolymerization methods and it's the most common starting point for synthesising vanillin. Vanillin and syringaldehyde, which are closely related as shown in figure 2.4, are valuable fine chemicals that can be a great way to valorize lignin when synthesised from it[40].

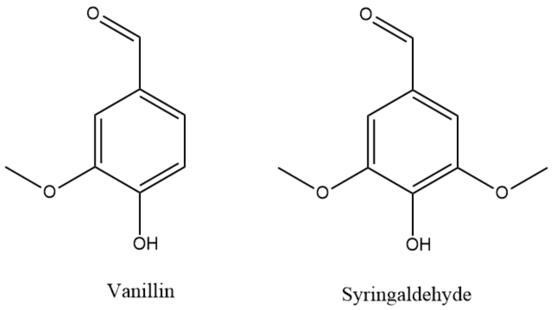

Figure 2.4: Vanillin and syringaldehyde structure representation.

Natural vanilla comes from many different vanilla orchids originating from Mesoamerica, evidence suggests it was first cultivated by Totonac indians who used it for its aroma and flavour[41]. The conquistador Cortez was the first to import it to Spain, and later the rest of europe, together with cocoa after supposedly being served a chocolate drink with added vanilla flavouring in 1520 by an aztec tribe[42]. It quickly spread across Europe and grew in popularity. Gobley was the first to isolate vanillin in 1852 from the vanilla orchid and determined that it was the primary component of the vanilla flavour. Vanillin was first synthesised in 1875 by oxidation of eugenol, extracted from clove oil, and was made available in France and North America[42].

In the 1930s it was discovered that lignosulfonates had a selectivity towards vanillin and companies started manufacturing vanillin from sulphite liquor, a biproduct of pulp production[43]. This production of vanillin became continuously more profitable and grew fast, but this stopped in the early 1990s by a growing concern of the corrosive and harmful wastes that came from processing the lignosulfonates which halted the interest and growth. At the same time petroleum was used more and more as a source of different chemicals and became increasingly cheaper. This, the failure to address the environmental concerns of the lignin-to-vanillin process, and the normalization of burning waste lignin from pulp production caused the closing of every major lignin-to-vanillin chemical plant except Borregaards biorefinery in Sarpsborg, Norway[43]. Today this biorefinery stands for 15% of the global supply of vanillin while 85% is synthesised from petrochemicals and less than 1% is harvested naturally from vanilla orchids[7].

Due to the consumer habit of picking natural products over synthetic products, natural vanillin can be sold at a higher price than synthetic vanillin[43]. EU regulations state that a product can be labeled as natural if the raw materials and process of making the product is natural, otherwise it has to be labeled as synthetic or artificial. This is a powerful incentive for companies to shift back to making vanilla from lignin again to increase the value of the product, if there is a viable way of doing so[43].

Vanillin is the main ingredient in the flavour we recognise as vanilla and is used in a myriad of different foods and drinks. Especially chocolate and ice cream production has a big demand for it since they consist of 0.1 to 0.9 w% vanillin[43]. It can also be used as a pharmaceutical intermediate for other aromatic compounds like syringaldehyde which is very closely related to vanillin. It can also be a product of over-oxidation when oxidizing lignin directly[44].

Traditionally, vanillin is synthesised from guaiacol and other chemicals abundant in petroleum. The most used method of synthesising vanillin from guaiacol is the Riedel process where guaiacol and glyoxylic acid reacts to make vanilylmandelic acid as shown in figure 2.5[43]. The vanilylmandelic acid is then submitted to an oxidative decarboxylation using copper(II) oxide/hydroxide as a catalyst. Glyoxylic acid is used in almost every process where vanillin is made from guaiacol because of its region-selectivity towards the para position. The Riedel process achieves a yield of 74% which is good, but not ideal from a perspective of atom economy[43]. This is attributed to the Canizarro reaction where glyoxylic acid in an alkaline solution reacts to form glycolic acid and oxalic acid as shown in figure 2.6[45].

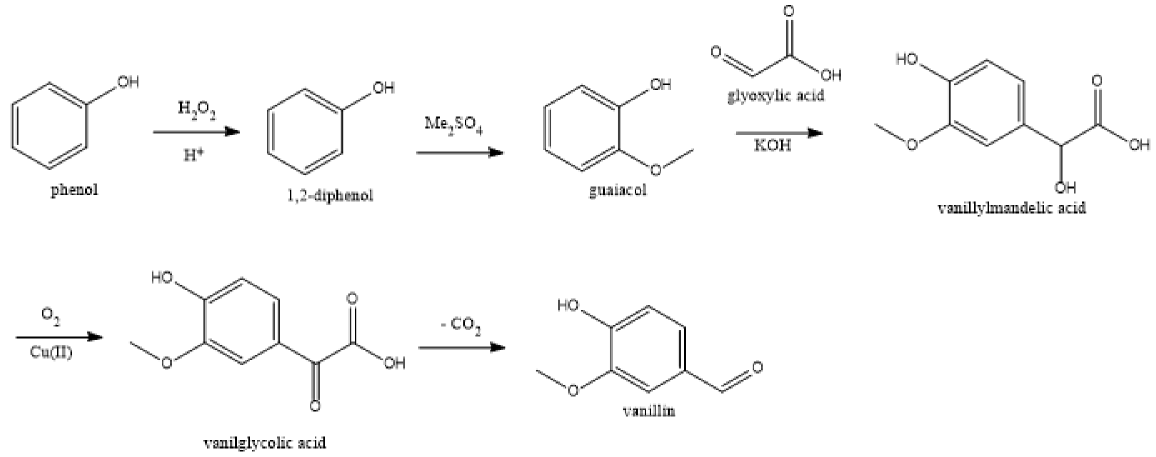

Figure 2.5: The Riedel process adapted from Fache et al.[43].

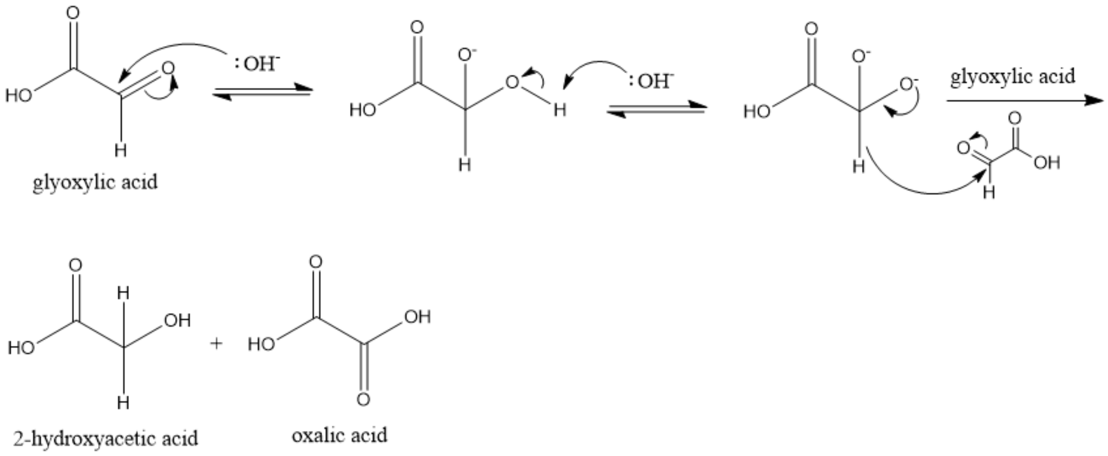

Figure 2.6: The Cannizzaro reaction between two glyoxylic acid molecules under basic conditions[45].

Other emerging methods has been investigated such as a cobalt based catalyst that oxidizes 4-methylguaiacol into vanillin with a 100% conversion and a 90% selectivity[46]. But the use of this in the context of lignin valorization heavily depends on the precursor 4-methylguaiacol being easily attainable as a lignin depolymerization product. And synthesis of 4-methylguaiacol from guaiacol has proven to be difficult because of low selectivity and a formation of biproducts[47]. Another method uses sodium glyoxylate over a novel silica encapsulated magnesium hydroxide catalyst to form vanillylmandelic acid[48]. Additional procedures have been developed for synthesis of vanillin from guaiacol without using glyoxylic acid, but it would seem that it's almost impossible to achieve the same yields as the Riedel process[49, 50]. Zeolites has been used as a shape-selective catalyst for the Reimer-Tiemann reaction of guaiacol and chloroform providing great selectivity but with a relatively low conversion[49]. Another method is using a non regioselective Vilsmeier-Haack reaction to make both vanillin and isovanillin. They achieved a vanillin yield of 68% and an isovanillin yield of 28%[50].

3 Discussion

Depolymerization of lignin has been investigated for a long time with the first article being published in 1943[14]. It's a very interesting polymer with many uses, but the cheaper and more widely available petroleum is favoured as a source of chemicals and many industries in which lignin could have been used, choose this option instead. However with the growing focus on sustainability, lignin has received a great deal of attention. To replace petroleum it needs to have a cost-effective and environmentally friendly way of achieving the same results[2].

3.1 Challenges of Lignin Depolymerization

Lignin is a sustainable source of aromatic chemicals only if there is a equally sustainable way of extracting it[39]. It's already known that increasing temperature is a common way of breaking chemical bonds, and in this case it can be an effective method of breaking the polymeric bonds in lignin with temperatures upwards of 450 °C in an oxygen-poor environment[4]. However at such high temperatures the process becomes wasteful, so ideally to promote sustainability the temperatures would be lowered as much as possible with catalysts while still being able to depolymerize lignin[4]. Ether bonds have many traditional chemical ways of being broken, but it's essential for large scale manufacturing that it's done as effectively as possible[51]. Ideally there would be a method that can easily break many of the bonds between monomers in lignin while also being affordable and reusable. Numerous methods have been applied to lignin model compounds, which are usually a dimer connected with similar bonds to that between lignin monomers. But good results with model compounds won't necessarily translate directly to good results with lignin[6]. This is important to keep in mind especially with new methods of lignin depolymerization where unexpected problems may arise when trying to upscale and apply it to lignin. This is maybe most prevalent in ionic liquid assisted depolymerization where is works extremely well on lignin model compounds, but encounters a major problem of separation due to $\pi - \pi$ interactions when using it on lignin[6].

3.2 Vanillin Synthesis and Applications

Vanillin is a chemical that has been and still is of great importance in food and cosmetics[2]. It's interesting to see how lignin and vanillin has been so closely related since the 1930s, and that lignin was used a raw material for vanillin synthesis long before petroleum was[43]. The environmental concerns causing the industry to shift towards petroleum as a raw material is almost ironic, but perhaps it was a good choice that the old methods of the 1990s was retired. Today's methods are better in almost every way, and hopefully this can help the industry shift back from petroleum[43].

Lignin can potentially be depolymerized straight into vanillin, but at a relatively low yield, so a method of converting the guaiacol monomer to vanillin is needed[13]. The Riedel process is the most used way of making synthetic vanillin from guaiacol or phenol and in this, and many other similar processes, glyoxylic acid is used to add the aldehyde group to guaiacol[43]. Glyoxylic acid is favoured because of its high selectivity towards the para position on guaiacol. However the Cannizzaro effect can affect the yield by around 20%, especially since a basic solution can promote this effect[43]. The Cannizzaro reaction is a disproportionation reaction of two molecules of a non-enolizable aldehyde to produce a carboxylic acid and a primary alcohol as shown in figure 2.6, a basic environment will shift the equilibrium towards the alcohol and carboxylic acid[45]. For the Riedel process this means that the glyoxylic acid is destroyed and cannot be used, this is problematic since many lignin depolymerization methods rely on basic conditions[6]. A neutralization step could be added but this may cause some of the lignosulfonate precipitate out of solution[52].

To improve the atom economy of making vanllin from guaiacol is would be preferable to avoid the use of glyoxylic acid and circumvent the Cannizzaro effect, and there are options for this. Although the reactions can't seem to achieve the same yield as the Riedel process and other similar methods, they can have much better conversions of over 90%. Huang et al. achieved a vanillin yield of 68% and a isovanillin yield of 28% with a total conversion of 96% without using glyoxylic acid[43, 50]. Isovanillin does not have the same aromatic properties as vanillin, but is still used as a precursor for pharmaceuticals like morphine among others[53].

3.3 Chemical Catalysts for Sustainable Lignin Depolymerization

To evaluate a process for sustainability, all chemicals and conditions needs to meet specific requirements, this includes cost and environmental impact. Expensive and corrosive chemicals, harsh conditions and elements with low availability will make a process less desirable, including how recyclable and reusable a chosen catalyst is[39].

Acid and base catalysted lignin depolymerization is an old and reliable method, especially base deploymerization is easy, cheap and robust[4, 6]. Because of this and its ability to dissolve native lignin and separate it from cellulose and hemicellulose, NaOH and other bases is widely used today in the Kraft process[11]. Unfortunately it has some of the worst conversion of all the methods reviewed here at around 2 wt.%[4, 6]. These methods are cost-effective, but since it leaves a lot of unreacted lignin it's undesirable from a biomass utilization perspective. This is in addition to having relatively harsh temperature and pressure conditions[11].

Oxidative and reductive methods are promising, but both are imprinted with problems when trying to scale up or increase yield. Reduction without co-catalysts usually has extreme reaction conditions at temperatures around 300°C and pressures exceeding 100 MPa[20]. Both these methods are also sensitive to the amount of cross-linkages the lignin can have which limits what lignin extraction methods it's compatible with and it's commercial capability[20]. Currently these usually give a yield of around 10%, but when trying to increase yield, the increasing reactant concentration resulted in an over-oxidation or -reduction of products[6, 20]. This limits selectivity and hinders these methods to be widely applicable. Nevertheless these methods, oxidation in particular, require far less harsh conditions than most other methods of lignin depolymerization and uses catalysts than can be easily recycled. In spite of failing to have high selectivity and conversion which lowers the value from a biomass utilization perspective, it can still be a good option for specific cases with mild conditions and readily available reactants[6].

Many metal catalysts has good properties for promoting lignin depolymerization, but usually metal catalysts has problems with cost and recyclability[4, 6]. The most effective catalysts are often made from expensive and rare metals like palladium or platinum, so for the method to be conducted at large scale it would need a significant investment. For this to be avoided, other metals can be used but usually at the cost of effectiveness. However nickel is found to have as good or even better properties for lignin depolymerization than the noble metals, showing good yields of bio-oil. This is also true for silicon and aluminium[22, 23].

Furthermore there have been many studies on the use of nickel for depolymerizing lignin into specific monomers, and in combination with lignosulfonate it can get good yields of guaiacol and other guaiacol derivatives[6, 25]. Using lignosulfonate as a source for lignin is a great way of valorizing the waste from pulp and paper production, and guaiacol is the perfect precoursor for synthesis of vanillin[43]. Using sulfur and water-tolerant catalysts based on an earth-abundant metal that can be recycled and reused multiple times may be the best solution for depolymerizing waste lignin into valuable chemicals. It does come with somewhat harsh conditions requiring 230 C, a H_2 pressure of 5 MPa and recycling the catalyst at 700 °C. But this is tolerable considering the yield and wide application[25].

Both ionic liquid assisted and supercritical fluid assisted lignin depolymerization methods typify as being effective, but at a high-cost[4, 6]. Supercritical fluid has good recyclability and yields, however being supercritical it needs a great deal of specialized equipment and extreme conditions to be effective. Despite recent advances making Supercritical fluids energy-efficient and calling it "The solvent of the future", the drawbacks far outweigh the benefits for supercritical assisted lignin depolymerization[32, 35]. Ionic liquid is the most promising of the the two by having very good yields from lignin and lignin model compounds with mild conditions[6]. But significant drawbacks are presented when upscaling with the extreme cost of these chemicals and difficulty in recycling and separation[30, 31]. Despite this it excels in dissolving and separating native lignin from cellulose and hemicellulose, and can be a good alternative to the Kraft process for the treatment of lignocellulosic biomass. It has big potential in the future and is worth keeping an eye on, but for now it’s not as viable as many other lignin depolymerization methods[4, 30].

4 Conclusion

This review found that reduction with H_2 gas and a metal catalyst made from nickel and modified to be sulfur-tolerant is the best way to deplolymerize lignin into vanillin and syringaldehyde precursors guaiacol and guaiacol derivatives using lignosulfonate as the source of lignin. Vanillin and syringaldehyde are valuable chemicals in high demand and are good ways to valorize lignin. It was also found that the best way of making vanillin from guaiacol is a nonregioselective Vilsmeier-Haack reaction where both vanillin and isovanillin are made with excellent conversion. Lignosulfonate is selective towards vanillin, so to use metal catalysts to valorize waste lignin from the Kraft process by producing vanillin starting materials is the best option to better utilize lignin. Other methods were shown to have promise like ionic liquid assisted lignin depolymerization and supercritical fluid assisted lignin depolymerization, but these ultimately did not meet requirements of cost-effectiveness and scalability. They might be relevant in the future, especially ionic liquids not just for lignin depolymerization, but also for the conversion of native lignin to technical lignin. For now however metal catalysts as a standalone reactant or in combination with other methods is the best and most sustainable chemical way to depolymerize lignin into fine chemicals.

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