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Renewable chemicals from lignin – A conceptual evaluation of thermochemical processes for production of valuable chemicals from lignin.

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Preface

This thesis is the result of work done in Bergen and Ås during the spring semester of 2016. The thesis concludes my master's degree in Environmental Physics and Renewable Energy, at the Norwegian University of Life Sciences, Department of Mathematical Sciences and Technology.

Signature:

Ås. June 15th, 2016

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Thank you

Abstract

Lignin constitutes about a third of the mass of all woody biomass, and represents a great potential within renewable energy and renewable materials. This thesis consists of an introduction into the nature of lignin, and some of the thermochemical technologies that can be used to convert lignin into valuable chemicals. Those are pyrolysis, hydrothermal liquefaction and solvolysis.

After a review of the experimental literature, some of the chemicals produced by lignin conversion is presented. These are syringol, guaiacol, catechol, vanillin, phenol and BTX (benzene, toluene and xylenes). A selection of 13 experimental reports producing at least one of these products are and evaluated to compare the technically and economically viability of a larger scale production.

The evaluation was done by giving each process scores according to six different criteria. The criteria were reaction temperature, reaction pressure, reaction time, solvent cost, product yield and product cost. All values were calculated per gram of lignin processed. The criteria were then weighted based on importance, and the scores for each process were summarized to find the most promising process.

The evaluation shows that production of BTX by the process described by Thring et al. [1], and production of syringol by the process described by Klamrassamee et al. [2] are the two best candidates for an economically and technically viable process, even though high reaction temperature may be an issue.

Sammendrag

Lignin utgjør omtrent en tredjedel av massen til alt trevirke, og representerer et stort potensial innen fornybar energi og fornybare materialer. Denne masteroppgaven består av en introduksjon til ligninets natur, og noen av de termokjemiske teknologiene som kan brukes til å konvertere lignin til verdifulle kjemikalier. Disse er pyrolyse, hydrotermisk «liquefaction» og solvolyse.

Etter en gjennomgang av den eksperimentelle litteraturen, blir noen av produktene som kan produseres av lignin presentert. Disse er syringol, guaiacol, pyrokatekol, vanillin, fenol og BTX (benzen, toluen og xylener). Et utvalg på 13 eksperimentelle rapporter som produserer minst ett av disse produktene blir så gjengitt, og den økonomiske og tekniske gjennomførbareheten blir vurdert.

Vurderingen ble gjort ved at hver prosess fikk poeng for seks ulike kriterier. Kriteriene var reaksjonstemperatur, reaksjonstrykk, reaksjonstid, kostnader ved løsemiddel, utbyttet av produktet og produktets verdi. Alle verdier ble beregnet per gram lignin prosessert. Kriteriene ble vektet etter viktighet og poengene til hver prosess ble summert for å finne den mest lovende prosessen.

Vurderingen viser at produksjon av BTX med prosessen beskrevet av Thring et al. [1], og produksjon av syringol med prosessen beskrevet av Klamrassamee et al. [2] er de to beste kandidatene for en økonomisk og teknisk gjennomførbare prosess, selv om høye reaksjonstemperaturer kan være en utfordring.

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Abbreviations

BTX	Benzene toluene and xylenes
FA	Formic acid
mL	Millilitre
mmol	millimole
Mt	Megatonne
THF	Tetrahydrofuran
wt%	Percentage by mass

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1. Introduction

One of the great challenges of our time is our dependence on fuels and chemicals from non-renewable fossil sources. In the search for renewable alternatives, biomass has gained increased attention, both as a source of energy, like bioethanol and biodiesel, and as a raw material for renewable materials. In this context lignocellulosic biomass, like wood and wheat straw, represents a huge resource.

Lignocellulosic biomass has been used for energy and materials for ages, but we have not fully taken advantage of the potential that lies in lignin, a major component of lignocellulosic biomass. Lignin is most often considered a low value product or waste in the paper industry, and 95 % of industrial lignin is burned for heat [3]. Better utilization of lignin would generate additional revenue in the biorefinery industry [4], and reduce the demand for fossil based fuels and chemicals [5]. The motivation for this thesis was an interest in the possibilities of replacing chemicals currently produced from petroleum with renewable lignin-derived chemicals.

Research about lignin valorization has increased during the two recent decades, and several routes of valorization exists. Bio-oil from treated lignin can be used as fuel or fuel additive. Lignin could be treated and used as an additive in concrete, to make renewable polymers or to obtain valuable chemicals. These chemicals have applications in the synthesis of pharmaceuticals and new materials.

One of the most well known chemicals that can be produced from lignin is vanillin, a chemical that is a popular flavor used in foods and perfumes. From what I have been able to find in the literature there exist no other commercial production of pure chemicals from lignin. Lignin is a complex structure and forms a complex mixture of products when depolymerized. The development of cost effective conversion of lignin and subsequent product separation and purification is crucial to realize this in an economically viable way.

This thesis will provide an overview of the concepts of lignin chemistry and depolymerization, and highlight some of the laboratory scale attempts to convert lignin to valuable chemical using thermochemical processes. Technological and economical aspects of these processes will be evaluated and discussed. The goal of the evaluation will be finding the process, or processes, most suitable for further testing in a pilot scale.

2. Theory and literature study

2.1 Lignin structure and origin

Lignocellulosic biomass, such as wood,[6] grass and some algae, is composed of its three principal components cellulose, hemicellulose and lignin [7]. The content of lignin varies depending on the type of biomass. Typical lignin contents are in the range of 25-35% for softwoods, 18-25% for hardwoods and 15-19% for wheat straw and switchgrass [8]. Lignin is the earth's largest renewable source of aromatics, and accounts for approximately 30% of the organic carbon in the biosphere [8][9]. Lignin fills the space between cellulose and hemicellulose, and provides rigidity and strength to the plant by holding the cells together and making chemical bonds with cellulose and hemicellulose within the cells. In addition to providing structure, the lignin protects the plant against degradation [8][10].

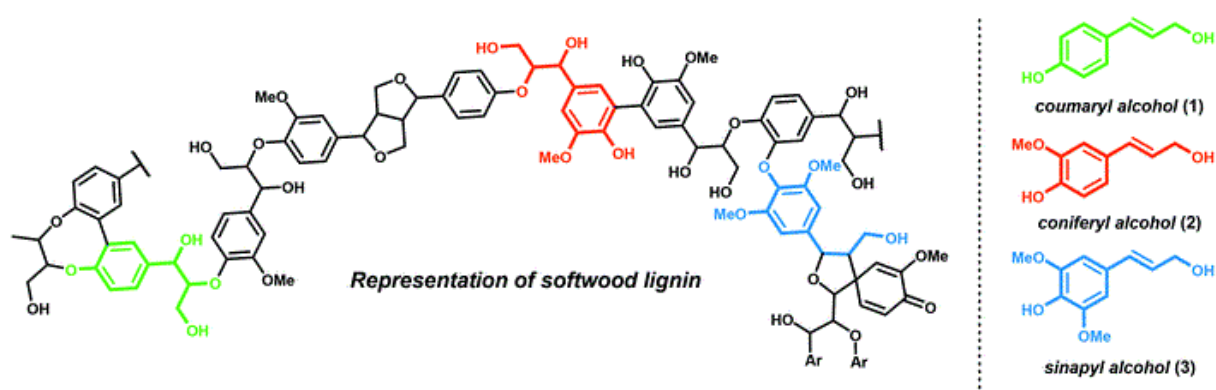


Figure 1. Representation of the structure of softwood lignins and its three main monomers. Reproduced from ref. [11] Published by The Royal Society of Chemistry. Licensed under CC BY-NC 3.0

Table 1. Distribution of the three main monomers in lignin Distribution from [8].

Structural units and their content in lignins [%]			
	Coumaryl alcohol	Coniferyl alcohol	Sinapyl alcohol
Softwood	-	90-95	5-10
Hardwood	-	50	50
Grasses	5	75	25

Lignin is a complex amorphous (non-crystalline) three-dimensional structure. It consists of mainly the three monomers p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, bonded together by C-C or C-O-C ether linkages. A general structure softwood of lignin is shown in Figure 1, along with its three main monomers. The distribution of monomers and linkages differs depending on the type of biomass [8][10]. Table 1 shows the distribution of the tree main monomers in different types of lignocellulosic biomass.

The exact composition and structure of lignin varies with biomass type, even seasonal and growing conditions. To analyze individual components they need to be isolated from the molecule, but the structure of lignin is difficult to modify and requires harsh conditions to be depolymerized [7]. The exact structure of native lignin is not fully understood, and because of the complex nature of the lignin structure and lignin breakdown routes, it is challenging to develop selective conversion processes for valorization of lignin [10][12].

2.2 Lignin separation

To make use of the components in lignocellulosic biomass, they need to be separated from each other. After separation, cellulose, hemicellulose and lignin may be subject to further treatment. A wide range of methods are able to break up lignin, both to enable the extraction of cellulose and hemicellulose, and to depolymerize lignin into smaller constituents that may be further valorized.

The properties of the lignin, and the possibilities for valorization, depends on the origin of the lignin and the process applied for lignin separation [13]. The following subchapters will provide an overview of the relevant lignin separation processes in the context of the paper and biorefinery industry.

2.2.1 Kraft lignin

Kraft lignin, which is also called sulfate or alkali lignin, is obtained from the black liquor from the kraft pulping process [14]. Kraft pulping is the dominant paper pulping process worldwide, accounting for approximately 90% of the total pulping capacity. The kraft process is a stepwise process in which the wood is treated with an aqueous NaOH/Na₂S solution, known as white liquor [8]. The white liquor has a high pH in the range of 13-14, and the treatment is run at 150-180 °C for 0,5-3 hours [8][10][15]. Dissolved lignin, hemicellulose and the chemicals used for the pulping is known as black liquor, and is then separated from the solid cellulose. The black liquor is the delignified by precipitation of the lignin, which is then neutralized with an acidic solution and dried [16].

The kraft process significantly alters the chemical composition and structure of the lignin, introducing new C-C linkages from condensation reactions [17], making the lignin harder to depolymerize further. Kraft lignin has higher contents of phenolic hydroxyl groups than native lignin [17][18]. Because of the use of Na₂S the lignin contains small amounts of sulfur, but a lot less than lignosulfonates. However, kraft lignin is only soluble by strong basic solutions above pH 10, and commercial kraft lignin is often sulfonated to become soluble in water [8][16]. After sulfonation or oxidation kraft lignin can be used in most of the same applications as lignosulfonates [14].

The literature provides different estimates for the total production of kraft lignin, as over 50 Mt per year [18][5], and up to 70 Mt per year [17]. The amount of lignin commercially available is much smaller, less than 100 000 t per year [17][19]. Instead, the lignin is usually burned locally to produce energy to run the pulp mill and for recovery of the pulping chemicals [17]. However, there is a production surplus of kraft lignin, and it is estimated that 8-11 t per year could be valorized without damaging the industry economy [17][5].

2.2.2 Lignosulfonates

Lignosulfonates are lignins obtained from the sulfite pulping process. Sulfite pulping is a set of processes based on aqueous SO_2 and a counter ion such as calcium, magnesium, sodium and ammonium. The process can in principle operate over the whole pH range, dependent by the chemicals used and their dosage. The process is run in a temperature range of 125-180 °C for 1-7 hours [20]. The most common method to separate the lignosulfonates from the pulping liquor is by precipitation of the lignin by addition of lime [14].

The sulfite process is less harsh on the lignin than the kraft process, and the structure of lignosulfonates are more similar to native lignin. The molecular masses in lignosulfonates are higher than in the kraft lignin [16]. During the process the lignin undergoes sulfonation, hydrolysis and condensation [21]. The high sulfur contents makes lignosulfonates highly soluble in water [17].

The sulfite pulping was the main pulping process until the 1940s, when the kraft process became dominant. Since then the production has decreased dramatically to 7 Mt yearly, less than 10% of the pulp production [15][17]. Even though sulfite pulping is a minor pulping method, lignosulfonates are the most important commercial lignins, with a yearly production of about 1 Mt [17][19]. Today lignosulfonates are mostly used as water reducers in concrete, but also has several applications as dispersant and is the source of products used in polymers and flavors. Softwood lignosulfonates has historically been a major source of synthetic vanillin, but now accounts for just 15% of the vanillin synthesis [14][22].

2.2.3 Organosolv lignin

Organosolv pulping is a group of processes based on organic solvents with low boiling temperatures. Solvents used are organic acids as formic acid and acetic acid, and alcohols as methanol and ethanol, often diluted in water.

The Alcell process is the most developed, consisting of three steps. The solvent used is 50% ethanol and the process is run at around 190 °C and 2,8 MPa. The primary liquor is used as secondary liquor in the last previous, while the secondary liquor is then used as tertiary liquor. In this way the wood is cooked in cleaner solvents throughout the process. The primary liquor is then sent to product recovery, where ethanol is recovered used as tertiary liquid, and the lignin is separated by precipitation in a centrifuge. Alcell lignin is soluble in acetone, THF and ethyl acetate, but insoluble in water [8]. The Organocell process consists of two stages. The first one involves 50% methanol and is operated at 170-190 °C for 40-60 min. In the second stage, the methanol content is reduced, and NaOH is added to dissolve the residual lignin at 170 °C for 40-60 min [8]. In acidic organosolv processes lignin is dissolved

in organic acids as formic acid and acetic acid. Different names are used, as Acetosolv, Acetocell, Formosolv and Formacell, depending on the acid and other chemicals used [16]. Delignification is facilitated by the high concentration of hydrogen ions. Acidic organosolv pulping can be run at relatively low temperatures, typically 90-120 °C for 30-90 min with formic acid [8].

The primary advantage of organosolv pulping is the absence or low content of sulfur in the lignin product, making it a more environmentally friendly process [10]. Organosolv lignins are less altered and contain less condensation products than lignosulfonates and kraft lignin, and is very pure and similar to native lignin. This makes it very attractive for valorization into high value chemicals [18]. Furthermore cellulose, hemicellulose and lignin are easily separated into streams, enabling for specific downstream processes for valorization of each component [8][10].

Although research into organosolv processes has increased significantly in the last 10 years, a small amount of organosolv lignin is used commercially [8]. Organosolv pulping produced a pulp of lower quality than the kraft and sulfite processes, and pulping of softwoods in high yields have proven to be difficult. Therefore, organosolv pulping has not been attractive in the pulping industry [8][17]. However, the process has gained interest for its potential in second-generation bio refineries, with raw materials as woody biomass, wheat straw and bagasse. Processes using ethanol and formic acid have been tested in pilot plants, and the organosolv methods are expected to gain more interest in the coming years [17][8].

2.2.4 Soda lignin

Soda pulping is a pulping process that is used in pulping of annual plants and agricultural waste as wheat straw and bagasse, and fiber plants as cotton and hemp. In this separation process, lignin is dissolved by a solution of NaOH at temperatures in the range of 160-170 °C. Since the raw materials contain less lignin than wood, 10-15% NaOH based on the raw material is used [8][20].

The conditions of soda pulping are similar to the kraft process, and except for the absence of sulfur the structure of soda lignin is similar to kraft lignin. However, the lignin removal is lower than in kraft or sulfite pulping, and the use is limited to easily pulped raw materials. Because the lignin is sulfur-free, the process has potential in bio-refineries, and the lignin is attractive for use in polymers. [17][8][15]

2.2.5 Other lignins

Several other methods may be used to obtain lignins. By pyrolysis of lignocellulosic biomass, a carbohydrate-derived bio-oil and a water insoluble phase containing oligomers form partly depolymerized lignin can be obtained. This phase is often called “pyrolytic lignin, but it is important to differentiate between this product and pyrolysis of lignins obtained from other lignocellulose separation processes [8][23].

Steam explosion of biomass is a process wherein biomass is impregnated with steam under high temperature and pressure, followed by a rapid decompression. Catalysts may be used, and the process is often applied to obtain carbohydrates for fermentation [16][24]. However, lignin is also obtained, with properties similar to organosolv lignin [4].

Hydrolysis of lignocellulosic biomass using weak or strong acids are used to separate and hydrolyze cellulose for ethanol production, but also produces a byproduct containing lignin and ash. High concentrations of acid give very effective separation, but also raises issues regarding corrosion [8][4].

2.3 Conversion technologies

The literature offers a wide range of thermochemical methods, most of them involving high temperatures or harsh conditions, to decompose lignin. However good selectivity remains a great challenge [12]. In a broad sense, these treatments can be categorized into lignin cracking or hydrolysis, reductive reactions and oxidative reactions. Reduction reactions are usually used to produce and upgrade bio-oil and fuels, but may also be used to obtain simple aromatics as phenols and benzene, toluene and xylene (BTX). These chemicals may be used as bulk chemicals or further upgraded [10]. Oxidative reactions often produce more complex compounds that may be of value as they are, or used in organic synthesis [10]. The evaluated experimental reports utilized variations of pyrolysis, hydrothermal liquefaction and solvolysis. These methods are described in the following section.

2.3.1 Pyrolysis

Pyrolysis is a common way to decompose biomass, and is done by anaerobic heating of the feedstock. In the absence of oxygen the biomass does not combust, and the process produce a liquid pyrolysis oil as well as some gases and solid char [25][12]. The distribution and composition of these three phases depend on the feedstock, heating rate, final temperature and residence time [3].

The decomposition of cellulose takes place at 220-315 °C, and hemicellulose is pyrolyzed at 315-400 °C. Lignin however, undergoes thermal decomposition over a wider temperature range of 150-900 °C [12]. Most pyrolysis processes are conducted under atmospheric pressures, as high pressures increase the production of char [26]. Pyrolysis of isolated lignin produces more char than pyrolysis of carbohydrates and untreated biomass. This char can cause problems in traditional reactor designs due to clogging of the reactor, and some technical challenges remain in developing continuous systems for pyrolysis of lignin [5][27]. The yields of oil and aromatic chemicals have been reported to be improved with the use of solid catalysts, and in the presence of hydrogen gas [8][5]. Pyrolysis with hydrogen gas pressures is sometimes called hydrolysis, and is used to reduce the oxygen content of bio-oils. High pressures of H₂ are required for the process to be effective [26].

2.3.2 Hydrothermal liquefaction

Several names are used in the literature for reactor mediums involving water under high temperature and pressure conditions. Hot compressed water and high temperature water are both used for water over 200 °C. Subcritical water and supercritical water are used to describe water at conditions just below and over the critical point of water. Depending on the temperature and desired product, these conditions are often called hydrothermal carbonization, hydrothermal liquefaction or hydrothermal gasification [28]. Under normal conditions, water is not likely to react with organics, but

under high temperature the properties of water changes significantly [29]. With increasing temperature, the relative permittivity of water decreases quickly, the water becomes less polar and behaves like an organic solvent. The dissociation of water increases dramatically with higher temperatures, and water is ionized. This increases the rate of both acid- and base-catalyzed reactions [29][28].

Hydrothermal liquefaction of lignocellulosic biomass has shown potential in the production of biofuels. The use of lignin as raw material is less studied, but the number of studies has increased in recent years. Lignin depolymerization have been done in a temperature range of 280-400 °C, with pressures between 20-25 MPa and with residence times between some minutes to several hours. Organic solvents and catalysts are used to improve the depolymerization and selectivity, as well as limiting the formation of char. Common organic solvents are alcohols as ethanol and methanol, phenolic compounds and organic acids. Alkali salts and noble metal catalysts are among the common catalysts used [8][5][30][31].

As the reactions take place in the presence of water, there is no need to dry the feedstock used in hydrothermal liquefaction. This is an advantage compared to some other processes like pyrolysis. The temperatures needed are also lower than those used in fast pyrolysis [31]. However the process needs high pressures, and because of the high specific heat of water the economically viability of the process is dependent on good heat recovery [8][5].

2.3.3 Solvolysis

As mentioned above, organic solvents are sometimes added to improve liquid yields in hydrothermal liquefaction, but many solvents are also used alone or in mixtures with other solvents and catalysts. Among the advantages of solvents are their good heat transfer capability [32], and their ability to stabilize radicals, and thereby limiting the undesired formation of condensed products and chars [5]. Solvents acting as hydrogen donors may greatly improve the depolymerization of lignin through hydrogenolysis [8]. Among the most commonly used solvents are ethanol and methanol, but other alcohols, acetic acid and formic acids are also popular [8][5]. Metal catalysts in solvents have shown to increase the yield of monomers further, while reducing char production [5][33].

2.4 Separation of products

Lignin depolymerization at high temperatures produce complex phenolic mixtures, making selective separation into pure chemicals is a big challenge [34]. Thus product separation is often a more extensive process than the process of converting biomass [35]. Except for the established production of vanillin from liginosulfonates, no industrial process of separating valuable compounds from lignin oils have been found in the literature [36], and very few separation strategies are proposed. Attempts at separation and purification are reported in the litterature. Pyrolysis oil from birch bark are reported to have been separated into 16 subtractions by vacuum distillation, and the syringol rich fraction purified to 92,3 wt%. However, few of the reported attempts manage to obtain products with high purity. More often, the separation yields fractions containing different chemicals with similar properties, which are challenging to separate. An example is Barta et al. who depolymerized organosolv lignin. Column chromatography gave a fraction of three catechols which could not be

separated by further attempts of chromatography or distillation, and a second fraction containing a fourth catechol [37].

Methods commonly used when separating bio-oils is solvent extraction, column chromatography and distillation. Solvent extraction may be done with water, alkaline solutions, alcohols or other organic solvents to dissolve targeted components of the product mix. Products are then separated into two different phases. Solvent extraction and filtering, precipitation or centrifugation are common ways to separate solids, heterogeneous catalysts, residual lignin and high-weight oligomers. Industrial scale use may be uneconomical, as large volumes of solvents are needed. Column chromatography is based on the oil components different absorption onto a stationary phase, often silica gel or aluminum oxide [23]. As the components flow through the stationary phase they gain different speeds, will exit the column at different times. Column chromatography is economical, but is best suited for compounds of high value, because of low processing rates. Distillation separates components based on their different volatilities. Steam distillation and vacuum distillation lowers the operating temperature, and reduces decomposition of compounds [23].

2.5 Product monomers from conversion of lignin

The rest of chapter 2 is dedicated to introductions to the main products produced in the studied reports, their main production routes and industrial applications. Production of syringol was studied based on its high value, and the fact that it was one of the major products in many experimental reports. Guaiacol production was studied because it was one of the major products in many reports, reported in relatively high wt% yields by some authors, and because of its potential in the flavor and fragrance industry. Phenol was studied due to its many applications in the synthetic industry. Catechol production was reported with high yields, and studied due to its use as a building block in the chemical industry. Vanillin was natural to evaluate, since vanillin production from lignin is an established industry. BTX was not produced in many reports, but in relatively high yields in one report. This process was evaluated due to the products wide range of applications, and the fact that they were not among the most common products from conversion of lignin.

2.5.1 Syringol

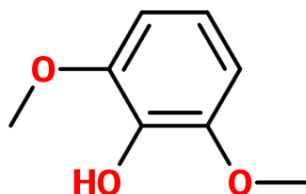


Figure 2. Molecular structure of syringol

Syringol is present in wood smoke and contributes to the aroma of smoked meat [38][39]. As syringol is present in the lignin structure, it is a common product from thermal decomposition of lignin, especially from hardwood lignins [4][40]. Together with guaiacol, it is a product of primary degradation of lignin, and is further degraded at higher temperatures [41].

2.5.2 Guaiacol

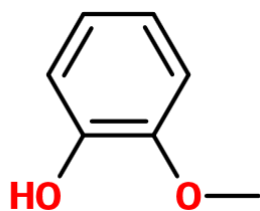


Figure 3. Molecular structure of guaiacol.

Guaiacol is used as an intermediate in production of flavors, fragrances and pharmaceuticals. It is present in many essential oils, and is found as a flavor in foods as roasted coffee and also contributes to the taste of smoked meat [42][43][39]. Petrochemical guaiacol is used to produce vanillin, and this synthetic vanillin accounts for about 85% of the global vanillin supply [22].

In the industry, guaiacol is synthesized by several methods involving methylation of catechol [42]. Guaiacol is present in the lignin structure, and is one of the organic compounds produced by hydrolysis of ether-bonds during hydrothermal degradation of lignin [4][5].

2.5.3 Catechol (pyrocatechol).

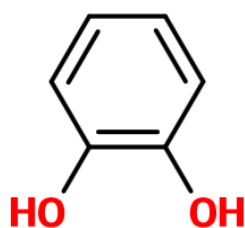


Figure 4. Molecular structure of catechol.

Catechol is among other phenols important intermediates in chemical industries and is as a building block in production of a wide spectrum of products [31][44]. The global consumption of catechol in 1990 was estimated to be about 20 000 tons per year, where 50% were assumed to be used as a starting material for insecticides and 35-40% for perfumes and pharmaceuticals [42].

Most catechol is currently produced by hydroxylation of phenol with peroxides, with catalysts at temperatures between 40-90 °C [42][45]. Catechol can be produced along with other organic compounds as guaiacol and phenol during hydrothermal degradation of lignin, due to hydrolysis of ether-bonds [5]. Vuori and Bredenberg [46] suggested that catechol is an intermediate in production of phenol from guaiacol. Petrocelli and Klein [47] investigated pyrolysis of kraft lignin, and found catechol to likely be formed by decomposition of guaiacols, especially at long residence times.

2.5.4 Vanillin

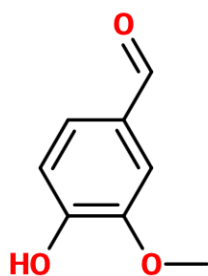


Figure 5. Molecular structure of vanillin.

Vanillin is the most important constituent of natural vanilla flavor, which has been used in food for centuries [48]. Vanillin is widely used as a sweetener or flavor enhancer in chocolate, ice cream, beverages, cakes and candy, and as aroma in perfumes and cosmetics. It is used as a starting material in the production of several pharmaceutical products and have many applications in the chemical industry [49][50].

Vanillin is present in vanilla beans at about 2% concentrations, and can be extracted by water, alcohol or other organic solvents [49]. However, the global demand far exceeds the supply of vanilla beans [16] [48]. By 2004, natural vanilla was much more expensive than synthetic vanillin, and constituted less than 5% of the world market.

Currently, the most common way to produce vanillin is by condensation of guaiacol with glyoxylic acid [49]. In 2004, 85% of all synthetic vanillin was synthesized from guaiacol [22]. Vanillin is also produced by oxidation of the lignosulfonate wastes from the sulfite pulping process in the paper industry [16][48][49]. This method accounts for 15% of the global vanillin supply. Borregaard in Norway is the only major producer of vanillin from lignin, and is overall the second largest supplier of synthetic vanillin [22][18].

Several attempts have been done to produce vanillin from kraft lignin, but the yield have been low, and no commercial technology is available yet [6][12]. Historically, vanillin has been produced by oxidation by isoeugenol, but this process is no longer widely used [49].

2.5.5 Phenol

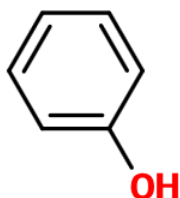


Figure 6. Molecular structure of phenol.

Phenol is an important starting material in the production of a wide range of polymers and resins. The major use of phenol, accounting for over one third of the global phenol consumption of 7,3 Mt per year in 2003, is production of Bisphenol A. Bisphenol A is used in the production of high grade

polycarbonates, used in CD's and the automotive industry, and epoxy resins used in automotive and electronic coatings. The second largest application of phenol is production of low cost phenolic resins with formaldehyde, used in the plywood and automotive industry [51][52]. Phenol can be used in the production of several phenolic chemicals, like catechol [42].

Phenol is to some extent recovered from coal tar, but most phenol is synthesized. Almost all of the synthetic phenol is produced by oxidation of cumene (isopropylbenzene), a process in which acetone is produced as a co-product. Phenol is produced by oxidation of toluene, with benzoic acid as an intermediate product, but this method is mostly considered less economical than oxidation of cumene, and it accounts for just 4% of the total synthetic phenol capacity [51][52][53].

2.5.6 Benzene, toluene and xylene (BTX)

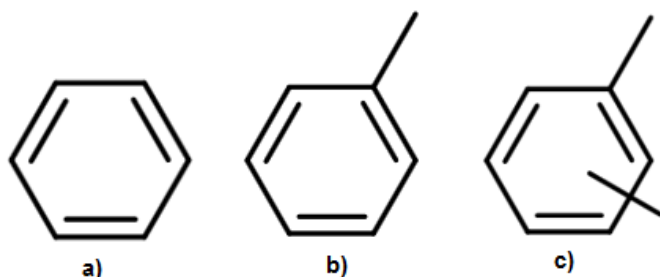


Figure 7. The molecular structures of a) benzene, b) toluene and c) xylenes.

Benzene, toluene and xylenes (BTX) are mostly produced by reforming of naphthalenes in the petroleum industry [1], where they are produced together with other aromatics. Recently, developments have been made to produce BTX from pyrolysis of light hydrocarbons [53]. They are among the most important aromatic compounds in the chemical industry [54]. Most reformat is directly blended into gasoline, and not separated into its constituents [53]. Both toluene and xylenes have high octane numbers, and are used as additives in gasoline [1]. 94% of toluene is produced by reforming, and only 10-15% of the toluene produced in the USA is isolated. This is mostly used as solvent and in productions of benzene and styrene, while some is used as an additive to increase octane number of gasoline. Toluene solvent use represents 12% of the chemical demand in the USA [53]. Besides octane boosting, the main application of xylenes are use as solvents in the paints and coating industry [54]. Benzene is not a desired additive to gasoline due to its toxicity, but can be used to produce fine chemicals, ethylbenzene cumene and cyclohexane being the most common [1][55].

3. Method

To map the current state of research into lignin valorization into chemicals, a literature study of experimental reports and reviews was conducted. Over 100 experimental reports were collected, most of them published after 2010. Only reports providing product yields in wt% based on lignin were used. This was done to ensure all reports were suitable for comparison and further evaluation. A selection of chemical products were chosen based on the following criteria: The product had to be produced in several reports, so that different processes could be compared. The product had to be produced in significant yields in at least one of the reports, making recovery of the product easier, and increasing the potential production volume. Some consideration was given to the price and applicability of the product.

To compare the technical and economical aspects, each process was evaluated according to 6 criteria. The processes were given a score from 0-100 for each criterion. The scores were linearly scaled to the range of parameter values (yield, product price etc.), so that the maximum value among the processes would correspond to a score of 100, and the lowest value corresponded to a score of 0. The criteria were given weights to balance their influence on technical and economical viability. As the reported experiments were conducted with different amounts of initial lignin, scores were calculated per gram of lignin processed.

Table 2. Criteria selected to evaluate processes by, and their respective weights.

Criteria:	Weight:
Product wt% yield ^a	0,25
Product value per kg ^a	0,20
Reaction temperature per gram of lignin	0,175
Reaction pressure per gram of lignin	0,175
Reaction time per gram of lignin	0,10
Solvent cost per gram of lignin	0,10
Sum	1,00

^a Processes were given negative scores for these two criteria, and positive scores for the rest

The criteria and their weighting are given in Table 2. High scores on product yield and product price would increase the potential income or make the separation and purification process easier. Therefore, processes were given negative scores on these criteria. Processes were given positive scores on the rest of the criteria, as they would increase cost and technical challenges. With this approach, the process with the highest score would be the least promising.

As product yields influence the potential income, and the complexity of separation, this criteria was given the highest weight. Since the sales value of the product must at least cover the expenses of production, product value was also given a relatively high weight. A high temperature represent a cost by the need for power for heating, and expenses due to increased heat loss and corrosion on equipment. High pressures also exert great strains on the equipment, and together with temperature is determines much of the costs related to reaction conditions and equipment. Reaction temperature and pressure were given medium and equal weights. Long reaction times reduces income as it affects

the throughput of the process, but is most important when the conversion process is the bottleneck in the process stream. Therefore reaction time was given a relatively low weight. Solvents adds costs to materials needed for the process, and may require extra separation and recovery. However, extensive separation will probably be required regardless of solvent use. Solvent use was given a relatively low weight.

4. Summary of experimental reports

4.1 Syringol from lignin

Klamrassamee et al. [2], isolated lignin from eucalyptus wood by an organosolv method using methyl isobutyl ketone and methanol solvents, water and sulfuric acid. The lignin was then depolymerized in a tube reactor with water at 250 °C, 0,1 MPa, for 60 minutes with and without the presence of a solid catalyst. The catalysts used were MCM-41, ZrO₂-MCM-41, SBA-15, ZrO₂-SBA-15 and NiMo/Al₂O₃ catalysts. Then the effect of reaction temperature was tested with the MCM-41 and SBA-15 catalysts, at 200, 250, 300 and 350 °C. Finally, these two catalysts were tested at 300 °C in a methanol/water mixture (50/50 wt%). Product yields were found for both an aqueous and THF soluble fraction, and the total syringol yields for all reaction conditions are given in Table 3.

Table 3. Total of syringol wt% yields in the aqueous and THF-soluble fraction,, for various catalysts, temperatures and reaction medium combinations. 0,1 MPa pressure and 60 minutes reaction time.

Solvent:	Catalyst:	Temperature [°C]:			
		200	250	300	350
Water	No catalyst	---	1,85	---	---
-	MCM-41	0,10	6,58	15,06	15,46
-	ZrO ₂ -MCM-41	---	6,59	---	---
-	SBA-15	0,29	7,28	18,80	16,85
-	ZrO ₂ -SBA-15	---	5,51	---	---
-	NiMO/Al ₂ O ₃	---	5,96	---	---
Methanol/water	MCM-41	---	---	20,41	---
-	SBA-15	---	---	23,03	---

There were small differences in the aqueous fraction yields for the different catalysts, but char formation significantly decreased using the MCM-41 and SBA-15 catalysts. All catalysts increased the syringol yields in both the aqueous fraction and the residual lignin fraction. Using the MCM-41 catalyst, the syringol yields in both fractions increased with temperature, but at a low rate between 300 and 350 °C. The syringol yields using SBA-15 also followed this trend, but decreased between 300 and 350 °C. At 250 °C the highest syringol yield in the aqueous fraction were given by MCM-41, while the highest yield in the residual fraction, and the highest total yield, were given by SBA-15. The addition of methanol gave an increase of syringol for both MCM-41 and SBA-15. The highest syringol yield, in both the aqueous fraction and residual lignin was obtained with SBA-15 and methanol, giving a total yield of 23,03 wt%.

Long et al. [56], performed depolymerization of pine lignin with base catalyst MgO in various solvents and investigated the effect of temperature, reaction time and catalyst dosage. The pyrolysis pressure was not reported. The lignin was separated using a process involving ethanol and acidic ionic liquid. The solvents used as reaction medium were water, ethanol, methanol, water/methanol mix and tetrahydrofuran (THF). First the effects of solvents were tested with 40 ml of solvent at 250 °C with 3,0 mmol of MgO and a reaction time of 30 minutes. The effect of catalyst dosage was investigated with 40 ml THF at 250 °C and 30 minutes reaction time. The effect of reaction temperature was investigated with 4 mmol of MgO, THF reaction medium and a reaction time of 30 min. Finally, the effect of reaction time was investigated with 4 mmol MgO, 40 mL of THF at 250 °C. The results are shown in Table 4

Table 4. Syringol wt% yields and effect of (a) solvents, (b) catalyst dosages, (c) temperatures and (d) reaction times.

(a) Effect of solvent					
Conditions: 40 mL solvent, 3 mmol MgO, 250 °C, 30 min					
Solvent:	EtOH	MeOH	MeOH/Water	THF	Water
Yield:	1,19	1,24	1,32	1,45	0,52

(b) Effect of MgO catalyst dosage						
Conditions: 40 mL THF, 250 °C, 30 min						
Dosage [mmol]:	0	1	2	3	4	5
Yield:	0,4	0,7	1,5	1,4	1,4	1,3

(c) Effect of temperature					
Conditions: 40 mL THF, 4 mmol MgO, 30 min					
Temperature [°C]:	220	230	240	250	280
Yield:	0,9	1,2	1,5	1,4	1,2

(d) Effect of reaction time					
Conditions: 40 mL THF, 4 mmol MgO, 250 °C					
Time [min]:	15	30	45	60	
Yield:	1,3	1,4	1,3	1,1	

THF gave the highest syringol yield, while all solvents gave higher yields than water alone. Yields increased with the addition of MgO catalyst, but the effect stopped with at 2 mmol, and the yield slightly decreased for higher doses. The lignin conversion and monomer yield continued to increase up to 4 mmol of catalyst. The yield increased greatly then the temperature was raised from 220 °C to 240 °C, but then was reduced at 250 °C while the monomer yield was at its highest. Reaction time had little influence on syringol yields, but longer times reduced the total monomer yield. The fraction of solids increased with longer reaction times and catalyst dosage over 4 mmol, because of repolymerization of oligomer products.

Kim et al. [57], tested conversion of lignin Protobind 1000 in supercritical alcohols with and without catalysts. Protobind 1000 is a soda lignin made from herbaceous crops as wheat straw and sarkanda grass. The alcohols used were methanol, ethanol and isopropanol. The catalysts used were 5 wt% Pt, Pd, Ru and Ni supported on activated carbon. The reactor was initially pressurized to 3 MPa with hydrogen before the polymerization was conducted at 350 °C for 40 min. The maximum recorded pressures were 19 MPa for the methanol experiments, 15 MPa for the ethanol experiments and 13 MPa for the isopropanol experiments. Syringol yields for all experiments are shown in Table 5.

Table 5. Syringol wt% yields after depolymerization of Protobind 1000 with different supercritical alcohols and catalysts. Conditions: 0.5 g lignin, 20 mL alcohol, 0.025 g of 5 wt% metal on carbon catalyst, 350 °C.

Catalyst:	Reaction medium:		
	Methanol	Ethanol	Isopropanol
No catalyst	1,17	1,02	1,05
Pt/C	1,32	1,21	0,99
Pd/C	1,19	1,09	0,92
Ru/C	1,11	1,11	0,92
Ni/C	1,07	1,09	0,98
Max. pressure [MPa]	19	15	13

Compared to depolymerization without catalyst, all catalysts gave higher yields of lignin-oil and less char in all alcohols. The highest oil yields were achieved by the Pt/C and Pd/C catalysts, while the yield just increased just a few percent using Ni/C, compared with no catalyst. With all catalysts used, methanol gave the lowest oil yield, while isopropanol gave the lowest oil yield without catalyst. Syringol yields varied by less than a half percent, but considering the oil yields there was a high selectivity towards syringol when using methanol as solvent. The highest selectivity towards syringol was obtained in methanol without catalyst.

4.2 Guaiacol from lignin

Ohra-aho and Linnekoski [58], investigated catalytic fast pyrolysis of Indulin AT kraft lignin, acetone-extracted lignin from scots pine wood chips, and Avicel microcrystalline cellulose. The catalysts used where the two zeolite based catalysts HZSM-5 and Zeolite Y, and two palladium on carbon catalysts 5% Pd/C and 10% Pd/C. Pyrolysis was performed at 600 °C for 2 s, at an unspecified pressure. The lignin and wood chips were pyrolyzed with and without the different catalysts, while the cellulose was pyrolyzed with HZSM-5 only. The products were analyzed by gas chromatography-mass spectrometry, and the results was normalized to 100%.

Table 6 shows the normalized guaiacol yields. Both the guaiacol and total aromatic yield was higher for kraft lignin than for scots pine wood, both with and without catalysts. Although pyrolysis of cellulose with HZSM-5 did produce some aromatic compounds, no guaiacol was found. The scots pine wood contained only 27% lignin and produced more guaiacol than the kraft lignin relative to lignin content. However, aromatics could also be produced by the cellulose in the scots pine wood. In general, a high content of oxygen rich guaiacyl units, that are typical of native wood, were formed from scots pine wood. The highest guaiacol yield was obtained from kraft lignin using Y-zeolite catalyst, even though this catalyst gave the lowest aromatic yield from kraft lignin. Pyrolysis of scots pine wood

showed the same tendency, with Y-zeolite giving the lowest yield of aromatics but the highest guaiacol yield from scots pine wood.

Table 6. Normalized guaiacol wt% yields after pyrolysis with and without catalysts of scots pine wood and kraft lignin, with HZSM-5 for cellulose. Pyrolysis at 600 °C for 2 s. 1:1 mass ratio of sample and catalyst.

Raw material:	Catalyst:				
	No catalyst	HZSM-5	Y-zeolite	5% Pd/C	10% Pd/C
Scots pine wood	6,6	5,7	16,4	9,1	13,4
Kraft lignin	22,4	14,1	28,4	20,8	23,9
Cellulose	---	0,0	---	---	---

Choi and Meier [59] performed fast pyrolysis of Lignoboost kraft lignin with and without HZSM-5, FCC and Olivine catalysts. Product yields given in Table 7 were calculated after pyrolysis of 40 mg lignin with 40 mg of catalyst, at 470 °C pyrolysis temperature and an unspecified pressure. The materials were heated to the pyrolysis temperature during 40 s, and pyrolyzed for 80 s.

Table 7. Guaiacol wt% yields with various catalysts, after fast pyrolysis of 40 mg lignin with 40 mg catalyst at 470 °C.

	Catalyst			
	No catalyst	HZSM-5	FCC	Olivine
Guaiacol yield:	10,999	7,469	14,032	13,109
Liquid yield:	30,0	32,8	32,7	30,1

Pyrolysis with the FCC and Olivine catalysts gave guaiacol yields approximately 3% and 2,1% higher than without catalyst. HZSM-5 gave the highest liquid yields, but the guaiacol yield was approximately 3,5% lower than for pyrolysis without catalyst. Pyrolysis at 560 °C showed a small increase in liquid yields with FCC, Olivine and with no catalyst. The liquid yield was reduced by increasing the amount of FCC to 160 mg, but showed no significant change for the same increase of HZSM-5 and Olivine. No individual components were identified in these tests.

Onwudili and Williams [60], depolymerized alkali (kraft) lignin in a batch reactor with subcritical water at 265 °C, 6,5 MPa and at reaction times of 1 h, 3 h and 6 h. The depolymerization was also run in the presence of formic acid as a hydrogen donor and capping agent to stabilize reactive intermediates, and in the presence of formic acid and Pd/C catalyst for hydrodeoxygenation. Table 8 shows the guaiacol yields for the different reaction conditions.

Table 8. Guaiacol wt% yields from lignin depolymerization in water at 265 °C and 6,5 MPa, at different reaction times, with and without the addition of formic acid (FA) and Pd/C catalyst. 1,0 g lignin, 60 mL deionized water. When used, 1,0 g FA, 0,5 g Pd/C.

Reaction time [h]	Reactant mixture		
	Lignin	Lignin + FA	Lignin + FA + Pd/C
1	2,4	10,8	5,0
3	7,6	12,6	9,1
6	12,2	4,1	2,9

The liquid yields increased when formic acid, or formic acid and Pd/C were added. The effect was larger when formic acid was the only additive. The same tendency was true for guaiacol. Without catalyst or formic acid, Guaiacol yields increased with reaction time. When formic acid, or catalyst and formic acid was added, the yields increased in the first three hours before they decreased considerably between 3-6 hours.

4.3 Catechol from lignin

Onwudili and Williams [60] produced catechol as described in chapter 4.2. Table 9 shows the catechol yields for the different reaction conditions.

Table 9. Catechol wt% yields from lignin depolymerization in water at 265 °C and 6,5 MPa, at different reaction times, with and without the addition of formic acid (FA) and Pd/C catalyst (5 wt% Pd). 1,0 g lignin, 60 mL deionized water. When used, 1,0 g FA, 0,5 g Pd/C.

Reaction time [h]	Reactant mixture		
	Lignin	Lignin + FA	Lignin + FA + Pd/C
1	0	2,8	1,8
3	3,7	7,7	7,1
6	5,3	17,9	13

The result show that catechol production increased over time for all reactant mixtures. The addition of formic acid increased catechol production significantly, and the effect was greater for longer reaction times. Compared with depolymerization without formic acid, the catechol yield was slightly more than 2 times higher after 3 hours, and almost 3.5 times higher after 6 hours. Addition of Pd/C catalyst and formic acid also increased catechol yields, but to a less degree than adding just formic acid, especially for longer reaction times. As mentioned in chapter 4.2, total liquid yields also increased with the addition of formic acid. Experiments with lignin and Pd/C catalyst were also executed, but no product yields were reported. For all reaction times, the liquid yield was lower than for reactions with lignin and formic acid.

Wahyudiono et al. [61] reported catechol yields up to 30,5%. They used alkaline (kraft) lignin in a batch reactor with sub- and supercritical water at 350 °C and 400 °C, respectively, at 25 MPa pressure. The catechol yields for the different reaction conditions are given in Table 10.

Table 10. Catechol wt% yields from lignin depolymerization in sub- and supercritical water at different reaction times and 25 MPa pressure. 0,1 g lignin.

Reaction temperature [°C]	Reaction time [min]					
	5	15	30	60	120	240
350	21,5	26,0	30,5	26,0	20,0	17,0
400	10,5	25,0	18,0	5,5	1,0	0,5

Catechol yields were consistently higher in the subcritical reaction at 350 °C and 25 MPa. At 350 °C the catechol yield rapidly increased during the first 5 minutes, and continued to increase to a

maximum of 30,5% at 30 minutes. After its maximum, the yield gradually decreased with time and reached 17% after 240 minutes. At 400 °C the catechol yield reached its maximum value of 25% after 15 minutes, and then decreased to 0,5% after 240 minutes.

The report also investigated the effect of water density on product yields. The catechol yield decreased with increasing water density at 350 °C, and at 400 °C for reaction times over 15 minutes. At 400 °C, the higher water density increased the production of catechol in the first minutes and increased the maximum yield, but not enough to exceed the yields at 350 °C.

Liguori and Barth [62], tested depolymerization of several lignins in water, with formic acid and Nafion SAC-13 acid in the presence of various palladium catalysts. The lignins tested were lignin from acidic hydrolysis (#1), lignin from enzymatic hydrolysis (#2), the enzymatic lignin pretreated with SO₂ (#3), lignin from acidic hydrolysis (#4), lignin from strong acid hydrolysis (#5) and desulfonated kraft lignin (#6). Palladium catalysts tested were 10% Pd/C, 30% Pd/C, PD(OH)₂/C, PD(OAc)₂, Pd-PEPPSI-iPr and Pd/Lindlar. All experiments were run at 300 °C and at a calculated pressure of 9,6 MPa. First, lignin #1 was tested for different reaction times, with different amounts of 10% Pd/C catalyst and Nafion SAC-13. Addition of additional formic acid and catalyst was conducted after 2 hours in some of the runs. Table 11 shows the different scenarios and the catechol yields.

Table 11. Catechol wt% yields after depolymerization of 1000 mg acidic hydrolysis lignin (#1) in 12 mL of water, with different amounts of Nafion SAC-13, and for varying initial/added amounts of 10% Pd/C catalyst and formic acid. 300 °C and 9,6 MPa

10% Pd/C [mg] (initial + added after 2 h)	Formic Acid [mL] (initial + added after 2 h)	Nafion SAC-13 [mg]	Reaction time:	Catechol yield:
20 + 0	0,5 + 0	200	2	2,0
100 + 0	0,5 + 0,5	200	4	2,4
100 + 0	0,5 + 0,5	200	21	3,7
20 + 20	0,5 + 0,5	130	4	2,1

The variation of dosages and reaction times only slightly altered the catechol yield, and the same was true for the reported yields of other phenolics (guaiacol and resorcinol). The rest of the lignins were tested with 0,5 mL of formic acid, 12 mL of water, 20 mg of 10% Pd/C catalyst. Table 12 shows catechol yields from the different lignins.

Table 12. Catechol wt% yields after depolymerization of different lignins at 300 °C and 9,6 MPa in 12 mL water and in the presence of 0,5 mL formic acid, 10% Pd/C and Nafion SAC-13. 2 h reaction time.

Lignin type:	Lignin amount [mg]	10% Pd/C amount [mg]	Nafion SAC-13 amount [mg]	Catechol yield:
Enzymatic lignin (#2)	1000	20	130	1,8
SO ₂ – treated enzymatic lignin (#3)	1000	20	130	4,2
Acidic hydrolysis lignin (#4)	1000	20	200	2,6
Strong acidic hydrolysis lignin (#5)	1000	20	130	1,9
Desulfonated kraft lignin (#6)	1028	22	130	4,7

The origin of the lignins had a great influence on catechol yields. Desulfonated kraft lignin gave the highest yield, and constituted nearly half of the three quantified monomers. The yields from the SO₂ – treated enzymatic yield gave almost equal yields, and constituted 90% of the quantified monomers.

Finally, the effect of different palladium catalyst were tested for 2 h with acid hydrolysis lignin (#1), 12 mL of water, 0,5 mL of formic acid and 130 mg of Narion SAC-13. Table 13 shows the resulting catechol yields.

Table 13. Catechol wt% yields after depolymerization of acidic hydrolysis lignin with different palladium catalysts, with 12 mL water, 0,5 mL formic acid and 130 mg Nafion SAC-13. 2 h reaction time at 300 °C and 9,6 MPa.

Catalyst:	Catalyst amount [mg]:	Lignin amount [mg]:	Catechol yield:
Pd/Lindlar	23	1000	3,1
Pd/C^a	20	1000	1,8
Pd(OH)₂/C	32	1000	2,5
Pd-PEPPSI-Ipr	30	954	2,8
PD(OAc)₂	37	1000	1,9

a) 10% Pd/C and 30% Pd/C gave the same results

Under these conditions, Pd/Lindlar gave the highest catechol yields, while Pd-PEPPSI-Ipr gave the highest yield of quantified monomers (7,7%). Of all the experiments executed, the highest catechol yield was obtained with desulfonated kraft lignin and 10% Pd/C catalyst, with a reaction time of 2 h.

4.4 Vanillin from lignin

Erdocia et al. [63], investigated the production of aromatic chemicals during alkaline nitrobenzene oxidation of three different organosolv lignins from olive tree pruning. Nitrobenzene oxidation is a common method used for lignin characterization [64]. Acetosolv lignin extraction was carried out at 130 °C for 90 min, with a 90 wt% acetic acid solution and 0,2% of HCl as catalyst in a solid-liquid ratio of 1:10. Formosolv extraction was done under the same conditions as the acetosolv treatment, but with 80 wt% of formic acid. Then a combined acetosolv and acetosolv extraction was done with the same conditions and a mix of formic acid, acetic acid and water in the ratios of 30:60:10 respectively. Nitrobenzene oxidation was performed with 50 mg of lignin in a sodium hydroxide and nitrobenzene solution and left at 175 °C for 2,5 hours at an unspecified pressure. Table 14 shows the vanillin yields from the process for the three different lignins, as well as the total yield of phenolic acids and aldehydes.

Table 14. Vanillin wt% yields for three different organosolv lignins after nitrobenzene oxidation. Conditions described above.

Lignin:	Acetosolv	Formosolv	Aceto-formosolv
Vanillin yields:	10,37	4,61	7,55

The lignin extraction with formic acid degraded the lignin more than extraction with acetic acid or a mix of formic and acetic acid, as the product compounds had a lower average mass. There were

significant differences between the vanillin yields, from 7,55% for the combined acetosolv and formosolv lignin, to 10,37% for the acetosolv lignin. As all lignins were treated the same way after extraction, it is evident that the lignin pulping process had a great influence on product distribution. Yields of only five products were identified.

Ohra-Aho and Linnekoski [58] performed catalytic fast pyrolysis as described in chapter 4.2. The lignins used were acetone-extracted organosolv lignin from scots pine wood and the kraft lignin Indulin AT.

Table 15. Vanillin wt% yields (normalized to 100%) after pyrolysis with and without catalysts of scots pine wood and kraft lignin, with HZSM-5 for cellulose. Pyrolysis at 600 °C for 2 s, 100 µg of raw material.

Raw material:	Catalyst:				
	No catalyst	HZSM-5	Y-zeolite	5% Pd/C	10% Pd/C
Scots pine wood	11,6	5,3	6,5	4,4	4,2
Kraft lignin	3,7	3,2	1,3	2,6	2,4

Yields from pyrolysis are shown in Table 15. Vanillin and other oxygen rich guaiacyl units are typical for native wood lignin, and were produced in greater amounts from the scots pine lignin than the kraft lignin, especially without catalyst. All catalysts reduced the yield of vanillin and oxygen rich guaiacyl units. This deoxygenation effect of the catalyst was most significant for the scots pine lignin. The total yield of aromatic products was overall lower for the scots pine lignin, and the lowest aromatic yield was obtained without catalyst. Therefore, pyrolysis of scots pine lignin without catalyst had a good selectivity towards vanillin.

Rodrigues Pinto et al. [64] investigated the yields from different types of lignin after oxidation with O₂ and NaOH. Three types of lignin were tested, pine kraft lignin from Westvaco, LignoBoost softwood kraft lignin and organosolv beech lignin from Fraunhofer Germany. 30 g of lignin was dissolved in 500 mL of a solution containing 40 g of NaOH. The reactor was heated to 120 °C and pressurized to 0,97 MPa with a continuous O₂ partial pressure of 0,3MPa. Every 5 minutes, samples were taken and the reactor temperature was measured. The vanillin yields and reaction times for the three lignins are shown in Table 16.

Table 16. Maximum vanillin wt% yields and corresponding reaction time and reactor temperature, under alkaline oxidation of different lignins. Conditions described above.

	Lignin type and supplier:		
	Kraft, Westvaco	Kraft, LignoBoost	Organosolv, Fraunhofer
Max. vanillin yield:	4,4	3,1	1,2
Time [min]:	25	40	25
Temperature [°C]:	129	133	135

For all the three lignins, vanillin was produced from the start of the reaction and reached a concentration maximum, before the yield slowly declined. The Westvaco kraft lignin gave the highest vanillin yield and the organosolv lignin gave the lowest. The same was true for the total yield of the seven identified products. Both kraft lignins were made from softwood, and vanillin was the major low

molecular weight phenolic product. Vanillin was also produced from the hardwood organosolv lignin, but in smaller amounts than syringaldehyde.

Voitl and Von Rohr [65] produced vanillin by acidic oxidation of kraft lignin in aqueous methanol. 1 g of the kraft lignin Indulin AT was dried and added into a mix of 9,128 g of a polyoxometalate catalyst, 20 mL of H₂O and 80 mL of methanol. The reactor was pressurized with O₂ to 1,08 MPa at 22 °C, heated to 170 °C during 18,5 min and kept at 170 °C for 20 minutes. 11 runs of the experiment was performed, and the vanillin yields are presented in Table 17.

Table 17. Vanillin wt% yields after acidic oxidation of kraft lignin. Conditions described above.

Run:	1	2	3	4	5	6	7	8	9	10	11
Vanillin yield:	2,3	3,6	3,0	3,6	3,2	3,6	3,6	3,6	3,8	3,5	3,7

The vanillin yield started at 2,3%, but stabilized on ca. 3,6% during the 6 first runs. The monomer product extraction, with chloroform, was not sufficient to completely recover monomeric products, but these could be extracted in the next run. The combined yield of vanillin and methyl vanillate stabilized on 7%. The catalyst showed no sign of deactivation, but after 11 runs, 40% of the catalyst had left the system through the solid product fraction.

4.5 Phenol from lignin

Onwudili [66], conducted hydrothermal conversion of alkali (kraft) lignin. Experiments were done with three different reaction mixtures: Lignin in water, lignin in formic acid and water, and lignin with Pt/Al₂O₃ catalyst in formic acid and water. The mixtures were exposed to two different two-stage conditions. In condition #1, the reactor was heated to 265 °C and kept at this temperature for 1 hour, before the reactor was heated to 350 °C and kept at this temperature for 5 hours. In condition #2, the reactor was kept at 256 °C for 5 hours, and 350 °C for 1 hour. Maximum reactor pressures were measured as 6,5 MPa at 265 °C, and 20,0 MPa at 350 °C. Phenol yield are given in Table 18.

Table 18. Phenol wt% yields from lignin depolymerization at different reaction conditions and reactant mixtures. 1,0 g lignin, 60 mL deionized water. When used: 1,0 g FA, 0,5 g Pd/Al₂O₃. Condition 1: 1 hour at 265 °C, 5 hours at 350 °C. Condition 2: 5 hours at 265 °C, 1 hour at 350 °C.

Reaction conditions:	Reactant mixture		
	Lignin	Lignin + FA	Lignin + FA + Pd/Al ₂ O ₃
Condition #1	0,4	4,5	0
Condition #2	4,0	17,3	12,0

When no formic acid was used, the solid yields were relatively high, 41,8% and 36,6% for condition #1 and #2, respectively. The phenol yields were relatively low. The addition of formic acid dramatically reduced the solid yields down to around 5%, based on lignin and formic acid. The phenol yields increased, especially when the temperature was kept at 265 °C for 5 hours. However, the gas

yields also increased dramatically, to between 50-60% for all experiments where formic acid was present. With both conditions, the addition of catalyst increased the formation of both gas and solids. Phenol production was reduced for both temperature conditions, and no phenol was produced at condition #1.

Wahyudiono et al. [61], depolymerized alkaline (kraft) lignin in a batch reactor at 25 MPa pressure. The reaction was carried out in sub- and supercritical water at 350 °C and 400 °C, respectively. The catechol yields from the report are given in Table 10, and the phenol yields are given in Table 19.

Table 19. Phenol w% yields from lignin depolymerization in sub- and supercritical water at different reaction times and 25 MPa pressure. 0,1 g lignin..

Reaction temperature [°C]	Reaction time [min]					
	5	15	30	60	120	240
350	0	0,2	0,9	1,3	1,9	2,5
400	4,5	5,3	6,0	7,2	8,1	8,7

The phenol yields were considerably higher at 400 °C than 350 °C. The yields increased at the highest rate in the first minutes, and then slowly increased for longer reaction times. The catechol yields reached their maximum after 15 and 30 minutes, at 350 °C and 400 °C respectively. As the rate of catechol degradation slowed down, the production rate of phenol and other phenolics slowed down.

The report also investigated the effect of water density on product yields at both temperatures. Increased water density gave slightly higher phenol yields, but any significant improvement were only achieved for the longest reaction times. After 240 minutes, the difference between highest and lowest phenol yields were 0,9% at 350 °C, and 3% at 400 °C.

4.6 BTX from lignin

Thring et al. [1] depolymerized Alcell organosolv lignin in a fixed bed reactor. The Alcell lignin was a hardwood lignin extracted with aqueous ethanol. Experiments were run with 2 g of HZSM-5 catalyst, a 1:2 weight ratio solution of Alcell lignin in acetone. Lignin was depolymerized for 30 minutes at temperatures in the range of 500-650 °C and with weight hourly space velocities (WHSV) in the range of 2,5-7,5 h⁻¹. Table 20 shows the yields of benzene, toluene and xylenes, as well as liquid yields and the total BTX yields.

Gas and liquid yields increased with temperature up to a combined maximum at 600 °C with a WHSV of 2,5 h⁻¹. The liquid yield was at its maximum at 550 °C and decreased with higher temperature, while the production of gas increased. Toluene was the most abundant product under all conditions, while benzene yields were relatively low. The authors suggested that low benzene yields were due to high rates of alkylation reactions. Combined, the BTX compounds constituted a significant percentage of the aromatic products in the liquid, and good selectivities towards BTX were obtained at a temperature of 550 °C and a WHSV of 5 h⁻¹.

Table 20. wt% yields of benzene, toluene and xylenes, liquid yields and total BTX yields after depolymerization of organosolv lignin in 1:2 lignin-acetone. 2 g HZSM-5 catalyst.

Temperature [°C]:	500	550		600		650
WHSV [h ⁻¹]:	5	5	2,5	5	7,5	5
Liquid yield:	39	43	34	30	22	11
Benzene	3,4	4,0	3,2	4,1	3,2	1,6
Toulene	13,0	15,8	10,5	12,7	9,2	4,8
Xylenes	12,3	14,2	8,5	6,8	5,5	2,3
BTX total	28,7	34,0	22,2	23,6	17,9	8,7

5. Evaluation of processes and discussion

5.1 Product yields

Product yields presented in Table 21 were either given as wt% based on initial amount of lignin in the reports, or estimated from graphs presented in the reports.

Table 21. Reported wt% yields from evaluated reports, and their scores

Product	Report	Product yield [wt%]	Scores
Syringol	Klamrassamee et al. [2]	23,03	-66
	Long et al. [56]	1,5	-1
	Kim et al. [57]	1,32	0
Guaiacol	Ohra-aho and Linnekoski [58]	28,4 ^a	-83
	Choi and Meier [59]	14,032	-39
	Onwudili and Williams [60]	12,6	-35
Catechol	Onwudili and Williams [60]	17,9	-51
	Wahyudiono et al. [61]	30,5	-89
	Liguori and Barth [62]	4,7	-10
Vanillin	Erdocia et al. [63]	10,37	-28
	Ohra-aho and Linnekoski [58]	11,6 ^b	-31
	Rodrigues Pinto et al. [64]	4,4	-9
	Voitl and Von Rohr [65]	3,8	-8
Phenol	Onwudili [66]	17,3	-49
	Wahyudiono et al. [61]	8,7	-23
BTX	Thring et al. [1]	34 ^c	-100

a) Kraft lignin raw material.

b) Scots pine raw material.

c) Total yield of benzene, toluene and xylenes

The highest yielding product was the mixture of benzene, toluene and xylenes. The mixture was considered as a single product for the scoring, and the BTX yield given in Table 21 was calculated as a sum of their individual yields.

Second to BTX, the highest yielding processes were production of catechol by Wahyudiono et al. [61], and the guaiacol produced by Ohra-aho and Linnekoski [58], both with yields close to 30 wt%.

A challenge when comparing the reports were the different methods used to calculate the products yields. For example, Ohra-aho and Linnekoski [58] normalized the yields to 100%. This may have resulted in an overestimation of the yields. As no mass balance was provided, the magnitude of this error was impossible to evaluate. The reports described the quantification methods they used with a varying degree of detail. To the best of my understanding, all reports except Ohra-aho and Linnekoski used fairly reliable methods, and yields were used as reported.

5.2 Product value

Prices of chemicals, shown in Table 22, were collected from the website of Sigma-Aldrich. As benzene, toluene and xylenes were offered in packages based on volume rather than weight, the prices per kg were calculated using densities supplied in the product documentations. Most chemicals were offered in different quantities and purities. Chemical products were chosen so that the purities were among the highest available, while comparable by being close to each other. Bulk chemicals offered in quantities close to 1 kg were preferred over small quantities or chemicals for very special applications.

Table 22. Prices for chemicals offered by Sigma-Aldrich, product IDs and purities, and the calculated scores for the product value criterion.

Chemical product	Sigma-Aldrich product ID	Purity	Price [NOK/kg]	Score
Syringol	D135550 (10*100 g)	99%	9902,50	-100
Guaiacol	W253200 (1 kg)	≥ 99%	501,50	0
Catechol	C9510 (1 kg)	≥ 99%	1593,75	-12
Vanillin	V1104 (2*500 g)	99%	1793,50	-14
Phenol	185450 (2*500 g)	≥ 99%	612,00	-1
BTX	-	-	544,36 ^a	0
Benzene	319953 (1 L)	≥ 99,0%	684,67 ^b	-
Toluene	179418 (1 L)	≥ 99,5%	394,05 ^b	-
Xylenes	247642 (1 L)	≥ 99,5%	672,09 ^b	-

a) Calculated using the component prices and distribution in the mixture obtained in [1].

b) Calculated based on densities supplied by Sigma-Aldrich

Syringol was clearly the most valuable product, with a price more than five times higher than vanillin, which was the second most valuable chemical. However, food grade syringol was also available at a 98% purity for 4088,50 NOK/kg. The big price difference may have been due to increased cost of purification at such high purities. The 98% syringol was offered in 1 kg packages, but it seemed unlikely that a quantity discount or less packaging would result in a price difference of this magnitude. However, even at a reduced purity, syringol was twice as valuable as vanillin.

The value of BTX was calculated based on the price of purified chemicals and the distribution obtained by Thring et al. [1]. Because of this approach, the price represented the value of the products if they were to be separated, and not the value of the BTX mixture. The value of the mixture would most likely be lower than the one calculated, as it would be less refined.

5.3 Process temperature

Operating temperature for each process is given in Table 23, together with scores calculated from the respective temperatures divided by the amount of lignin processed.

The scores given to the report by Ohra-aho and Linnekoski [58] were far beyond the predetermined 0-100 range. The combination of a very small lignin amount of 100 µg and high temperature of 600 °C gave a stunning 6 000 000 °C/g. If that value were to be used as a reference for the maximum score of 100, all the other processes would get a score of 0. Therefore, the second highest temperature per gram of lignin was used as reference to the highest score.

Table 23. Operating temperatures for evaluated processes and scores given based on amount of lignin.

Chemical product	Report	Process temperature [°C]	Scores:
Syringol	Klamrassamee et al.[2]	300	73
	Long et al. [56]	240	41
	Kim et al. [57]	350	59
Guaiacol	Ohra-aho and Linnekoski [58]	600	512382 ^a
	Choi and Meier [59]	470	100
	Onwudili and Williams [60]	265	22
Catechol	Onwudili and Williams [60]	265	22
	Wahyudiono et al. [61]	250	30
	Liguori and Barth [62]	300	25
Vanillin	Erdocia et al. [63]	175	30
	Ohra-aho and Linnekoski [58]	600	512382 ^a
	Rodrigues Pinto et al. [64]	120	0
	Voitl and Von Rohr [65]	170	15
Phenol	Onwudili [66]	350 ^b	30
	Wahyudiono et al. [61]	400	34
BTX	Thring et al. [1]	550	28

a) Range purposely set lower to enable better comparison of other processes.

b) Maximum temperature (5 h at 265 °C, then 1 h at 350 °C).

The pyrolysis done by Ohra-aho and Linnekoski [58] was of an analytical nature, and was therefore not suitable for production of any significant volume. This was mainly due to the small amount of lignin processed per run, and the amount of work and downtime that would be required to clean and reload the equipment between each run.

Next to the process used in the Ohra-aho and Linnekoski report, the process with the highest operating temperature was the production of BTX by Thring et al. [1]. However, this process got a temperature per lignin score of only 28, while the highest scoring process was the guaiacol producing process used by Choi and Meier [59]. The main cause for this was the difference in lignin processed. The operating temperatures used in these two reports were higher than, or close to, the maximum temperatures of some reactor materials [67].

For the report by Onwudili [66], the maximum temperature was used for scoring, as this was the temperature the equipment had to withstand. However, if the average temperature of 279 °C were to be used, the score would better reflect the costs associated with maintaining the operating temperature.

The three lowest operating temperatures were reported by Rodrigues Pinto et al. [64], Voith and Von Rohr [65] and Erdocia et al. [63], all three producing vanillin as the main product. The two first mentioned processes also got the lowest scores based on grams of lignin, while production of guaiacol and catechol by the method used by Onwudili and Williams [60] got the third best score.

5.4 Pressure

As for temperature, the pressure scores were calculated per gram of lignin. Unfortunately, the pressure was not given in several of the reports, so estimations were made for the evaluation. The pressures that were used are shown in Table 24, and a note is made for those who were estimated. Due to the low amount of lignin used in the report by Ohra-aho and Linnekoski [58], the pressure per gram of lignin was 1000 MPa. Again, using this as a reference for maximum score would make comparison of the other reports difficult. Therefore, the pressure per gram of lignin from the report by Kim et al. [57] was used as maximum.

Table 24. Operating pressures for evaluated processes and their scores based on amount of lignin processed.

Chemical product	Report	Pressure [MPa]	Scores
Syringol	Klamrassamee et al. [2]	0,1	1
	Long et al. [56]	6 ^a	32
	Kim et al. [57]	19	100
Guaiacol	Ohra-aho and Linnekoski [58]	0,1 ^a	2634 ^c
	Choi and Meier [59]	0,1 ^a	1
	Onwudili and Williams [60]	6,5	17
Catechol	Onwudili and Williams [60]	6,5	17
	Wahyudiono et al. [61]	25	66
	Liguori and Barth [62]	9,6	25
Vanillin	Erdocia et al. [63]	0,1 ^a	0
	Ohra-aho and Linnekoski [58]	0,1 ^a	2634 ^c
	Rodrigues Pinto et al. [64]	0,97	0
	Voith and Von Rohr [65]	1,08	3
Phenol	Onwudili [66]	20 ^b	53
	Wahyudiono et al. [61]	25	66
BTX	Thring et al. [1]	0,1	0

a) Estimated pressures.

b) Maximum pressure. (6,5 MPa at 265 °C, 20 MPa at 350 °C)

c) Range purposely set lower to enable better comparison of other processes.

The reports by Choi and Meier [59], and Ohra-aho and Linnekoski [58] did not report the pressure at which they performed pyrolysis. Both used fast pyrolysis, which most commonly is performed under atmospheric pressure [26][68]. For that reason 0,1 MPa was assumed as pressure for the evaluation of those two reports, though the actual pressures used might have been higher.

Long et al. [56] did not report any pressure for their process. To obtain estimate an operating pressure, atmospheric pressure was assumed before heating. The saturated vapor of THF at 240 °C was found to be 3,6 MPa [69]. The pressure during operation was most likely higher due to production of gas. To avoid underestimation, an estimated reactor pressure of 6 MPa was used for scoring.

Erdocia et al. [63], did not report the pressure at which they did nitrobenzene oxidation of lignin. According to the report “59 mg of lignin were placed in a tube with sodium hydroxide and nitrobenzene and left at 175 °C for 2,5 h”. As neither sealing of the tube or applied O₂ pressure was mentioned, atmospheric pressure was assumed.

Despite low estimated pressure, the process used by Ohra-aho and Linnekoski [58] got the highest cost score. As for temperature, this was due to the low amount of lignin. The calculation of pressure per gram of lignin helped the differentiation between processes running at similar high or medium pressures. However as running a process at atmospheric pressure rarely would add any cost, it could be argued that the amount of lignin is of less importance, and that the Ohra-aho and Linnekoski process got an unfairly high score.

The second highest score was given to the process from Kim et al. [57] where lignin was depolymerized under a 19 MPa pressure. The highest pressure applied where used in the production of catechol and phenol by Wahyudiono et al. [61], but this process got a lower score because a higher amount of processed lignin.

The processes with the lowest pressures were Klamrassamee et al. [2], Ohra-aho and Linnekoski [58], Choi and Meier [59], Erdocia et al. [63] and Thring et al. [1], who all operated at atmospheric pressures.

5.5 Time

All the evaluated processes except the production of BTX in Thring et al. [1] were batch experiments. For those processes, the times presented in Table 25 were the residence times at which each chemical product reached its maximum concentration in the product mixture. In the report by Thring et al. the depolymerization was done for 30 minutes in a continuous flow reactor, during which 1,67 grams of lignin was processed.

Table 25. Reactor run times and scores based on lignin amount.

Chemical product	Report	Time [min]	Scores
Syringol	Klamrassamee et al.[2]	60	48
	Long et al. [56]	30	17
	Kim et al. [57]	40	22
Guaiacol	Ohra-aho and Linnekoski [58]	0,033	92
	Choi and Meier [59]	1,33	1
	Onwudili and Williams [60]	180	50
Catechol	Onwudili and Williams [60]	180	100
	Wahyudiono et al. [61]	240	67
	Liguori and Barth [62]	120	32
Vanillin	Erdocia et al. [63]	150	84
	Ohra-aho and Linnekoski [58]	0,033	92
	Rodrigues Pinto et al. [64]	25	0
	Voitl and Von Rohr [65]	20	6
Phenol	Onwudili [66]	360	100
	Wahyudiono et al. [61]	240	67
BTX	Thring et al. [1]	30 ^a	5

a) Not residence time.

The run time from Thring et al. [1] did not represent the time the lignin were present inside the reactor, and should not be used in calculation or comparison of the kinetics of lignin conversion. Nevertheless, all the times presented in Table 25 represented how long the reactor was run to achieve the given product yield. Therefore, the run time from Thring et al. and residence times from the other reports were used to calculate cost scores.

As for temperature and pressure, the pyrolysis in Ohra-aho and Linnekoski [58] got a high score due to the low amount of lignin. Even though the pyrolysis time of 2 seconds was much shorter than other times used, the process got the second highest score. It could be argued that a short process time would be preferred, and that the process therefore deserved a lower score. However, because of the cleaning and reloading issues mentioned earlier the time required to produce any meaningful volume of chemicals made this process very impractical.

Second to Ohra-aho and Linnekoski, Choi and Meier [59] reported the process with the shortest reaction time. This method processed more lignin than Ohra-aho and Linnekoski, but would still suffer the same impracticalities related to downtime for refilling. The best score was given to Rodrigues Pinto et al. [64], mainly due to the high amount of lignin that were processed. The methods used by Thring et al [1] and Voitl and Von Rohr [65] also got good scores.

The process reported by Onwudili and Williams [60], got the highest score of 100 for production of catechol, while the production of guaiacol with the same method got a score of 50. The reason for this difference was that catechol and guaiacol reached their maximum yields at different times. As guaiacol yields decreased over time, the catechol yields increased, most likely due to conversion from guaiacol to catechol [46][60].

5.6 Solvent cost

To evaluate the cost of solvents, prices were collected from Sigma-Aldrich in the same manner as the prices for product chemicals. Table 26 shows the prices found for the solvents used all processes.

Table 26. Prices for solvents offered by Sigma-Aldrich, their purity and product ID.

Solvent	Sigma Aldrich product ID	Purity	Price [NOK/L]
Water, deionized	38796 (1L)	100 %	103,70
Formic acid	33015 (1L)	≥ 98 %	340,00
Methanol	34860 (1L)	≥ 99,9 %	259,25
Tetrahydrofuran	186562 (1L)	≥ 99,9 %	909,50
Nitrobenzene	252379 (1L)	≥ 99,0 %	981,75
Acetone	270725 (1L)	≥ 99,9 %	392,55

The costs of solvents were calculated per gram of lignin, and the scores are presented in Table 27.

Table 27. Solvents used in the reports and their score based on cost per gram of lignin processed.

Chemical product	Report	Solvent	Scores:
Syringol	Klamrassamee et al.[2]	Water/Methanol	1 ^a
	Long et al. [56]	Tetrahydrofuran	100
	Kim et al. [57]	Methanol	14
Guaiacol	Ohra-aho and Linnekoski [58]	-	0
	Choi and Meier [59]	-	0
	Onwudili and Williams [60]	Water/Formic acid	9
Catechol	Onwudili and Williams [60]	Water/Formic acid	9
	Wahyudiono et al. [61]	Water	1 ^b
	Liguori and Barth [62]	Water/Formic acid	2
Vanillin	Erdocia et al. [63]	Nitrobenzene	- ^c
	Ohra-aho and Linnekoski [58]	-	0
	Rodrigues Pinto et al. [64]	Water	2
	Voitl and Von Rohr [65]	Water/Methanol	34
Phenol	Onwudili [66]	Water/Formic acid	3
	Wahyudiono et al. [61]	Water	1 ^a
BTX	Thring et al. [1]	Acetone	1

a) Based on volumes calculated using densities supplied by Sigma-Aldrich

b) Based on the volume of the reactor

c) Amount not given

The report by Wahyudiono et al.[61] did not report the amount of water used, but as the reactor size was 5 mL, this volume was used for the scoring. The decision to assume the maximum volume did not influence the score in any significant way, as the process got a score of 1.

Erdocia et al. did not report the amount of nitrobenzene used for oxidation, and no information was found about the volume of the tube in which the oxidation was carried out. Due to the high cost of nitrobenzene, a relatively low amount would have to be used to make the solvent cost of the process computable with the best processes in the comparison. Though nitrobenzene is an effective oxidant, it is known to cause cancer [70]. Historically, the volumes of nitrobenzene used in nitrobenzene benzene oxidation of lignin have been too high for industrial applications [71].

As they did not use any solvents, several of the reports naturally got a zero score. Only 4 reports got a score over 4. Of them, the scores given to Long et al. [56] and Voitl and Von Rohr [65] stood out because of their relatively high scores. Compared to the lower scoring processes, they both used large volumes of solvents per gram of lignin. For Long et al. the high price of THF increased the cost additionally, and the process got the highest score.

5.7 Weighting and summation of scores

In Table 28 the score given to each process for all criteria are presented for easy comparison. For each criterion, the best scoring and worst scoring processes are marked with green and red scores, respectively. Table 29 shows the weighted scores and the sum of weighted scores given to each reported process. Again, green and red scores are given to the best and worst processes respectively.

Table 28. Scores given to all process reports, for each criterion. Best score within each criterion marked with green, worst scores with red.

Product	Report	Criteria:					
		Product yields	Product value	Temperature ^a	Pressure ^a	Reaction time ^a	Solvent cost ^a
Syringol	Klamrassamee et al.[2]	-66	-100	73	1	48	1
	Long et al. [56]	-1	-100	41	32	17	100
	Kim et al. [57]	0	-100	59	100	22	14
Guaiacol	Ohra-aho and Linnekoski [58]	-83	0	512382	2634	92	0
	Choi and Meier [59]	-39	0	100	1	1	0
	Onwudili and Williams [60]	-35	0	22	17	50	9
Catechol	Onwudili and Williams [60]	-51	-12	22	17	100	9
	Wahyudiono et al. [61]	-89	-12	30	66	8	1
	Liguori and Barth [62]	-10	-12	25	25	32	2
Vanillin	Erdocia et al. [63]	-28	-14	30	0	84	- ^b
	Ohra-aho and Linnekoski [58]	-31	-14	512382	2634	92	0
	Rodrigues Pinto et al. [64]	-9	-14	0	0	0	2
	Voitl and Von Rohr [65]	-8	-14	15	3	6	34
Phenol	Onwudili [66]	-49	-1	30	53	100	3
	Wahyudiono et al. [61]	-23	-1	34	66	67	1
BTX	Thring et al. [1]	-100	0	28	0	5	1

a) Per gram of lignin

b) Solvent amount not given

Table 29. Weighted scores given to process reports for each criterion and the weighted sum of scores for each process. Best score within each criterion marked with green, worst scores with red.

Product	Report	Weights:	Criteria:					Sum:	
			Product yields	Product value	Temperature ^a	Pressure ^a	Reaction time ^a		Solvent cost ^a
			0,25	0,2	0,175	0,175	0,1	0,1	1
Syringol	Klamrassamee et al.[2]		-17	-20	13	0	5	0	-19
	Long et al. [56]		0	-20	7	6	2	10	4
	Kim et al. [57]		0	-20	10	18	2	1	12
Guaiacol	Ohra-aho and Linnekoski [58]		-21	0	89667	461	9	0	90116
	Choi and Meier [59]		-10	0	18	0	0	0	8
	Onwudili and Williams [60]		-9	0	4	3	5	1	4
Catechol	Onwudili and Williams [60]		-13	-2	4	3	10	1	3
	Wahyudiono et al. [61]		-22	-2	5	12	1	0	-7
	Liguori and Barth [62]		-3	-2	4	4	3	0	7
Vanillin	Erdocia et al. [63]		-7	-3	5	0	8	- ^b	4 ^c
	Ohra-aho and Linnekoski [58]		-8	-3	89667	461	9	0	90126
	Rodrigues Pinto et al. [64]		-2	-3	0	0	0	0	-5
	Voitl and Von Rohr [65]		-2	-3	3	1	1	3	3
Phenol	Onwudili [66]		-12	0	5	9	10	0	12
	Wahyudiono et al. [61]		-6	0	6	12	7	0	18
BTX	Thring et al. [1]		-25	0	5	0	1	0	-20

a) Per gram of lignin

b) Solvent amount not given

c) Sum calculated without any value for solvent cost

For the report by Erdocia et al. [63] the weighted sum was calculated without any value for solvent cost, and could therefore not be fully compared with the other reports.

After scoring and weighting, the production of BTX of Thring et al. [1] got the best total score. The main contribution to the total score was given by the full score for BTX yields. The scores for the rest of the criteria were relatively low. Because the scores were calculated per gram of lignin the temperature score did not reflect the cost of equipment that can withstand a temperature of 550 °C. An advantage of the process is its continuous flow. However, the HZSM-5 zeolite catalyst used showed signs of deactivation after 30 minutes. However, the cost of catalyst purchase and processing was not studied here.

The second best scored process, with a score only 1 point lower than Thring et al. was the production of syringol done by Klamrassamee et al. [2]. The main contribution to the score was made by the relatively high value of syringol, but the high yield also contributed significantly. The process got relatively low weighted scores for pressure, reaction time and solvent cost, but the operational temperature of 300 °C gave a high temperature score. The effect of reaction time on syringol production was not investigated. The authors did not report any catalyst deactivation during the 60-minute run.

The process used by Rodrigues Pinto et al. [64] for production of vanillin were among the best processes within four criteria. In spite of this, the process was not among the very best when scores were summarized. The price of vanillin got a low score because of its low price relative to syringol. However, it was the second most valuable product, and the process should not be disregarded because of its low value score. However the vanillin yields were low, and separation would be difficult.

The process used by Ohra-aho and Linnekoski [58] got the highest sum of scores. Calculated per gram of lignin, the temperature and pressure used were much higher than the values obtained for the other processes.

Some of the studied processes produced products with yields that probably were too low to be practically separated. Yields below 5 wt% were given by Liguori and Barth [62], Long et al. [56], Kim et al. [57], Rodrigues Pinto et al. [64] and Voitl and Von Rohr [65].

6. Conclusions

Based on the method described in chapter 3 and the assumptions described in chapter 5, the most technically and economically viable processes were:

1. Production of benzene, toluene and xylenes by catalytic solvolysis of Alcell lignin as described by Thring et al.[1]
2. Production of syringol by catalytic hydrothermal liquefaction/solvolysis of organosolv lignin as described by Klamrassamee et al.[2]

For both processes, the main cost and technical challenges are attributed to high operating temperatures.

7. References

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