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Lignin depolymerisation strategies: towards valuables chemicals and fuels

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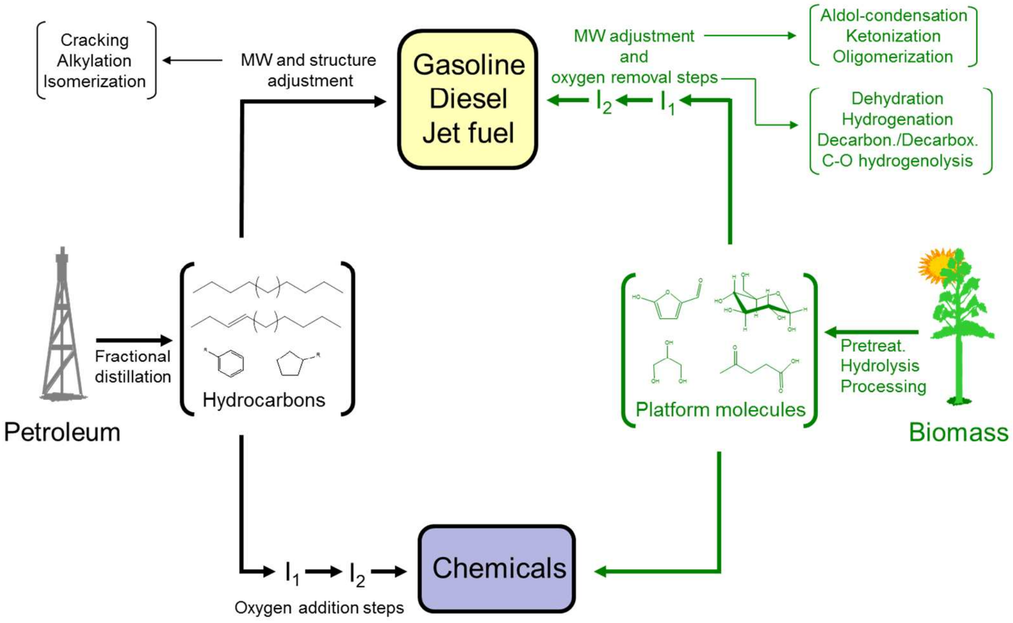
Abstract

Research on lignin deconstruction has recently become ae center of interest for scientists and companies worldwide, racing towards harvesting fossil-fuel like aromatic compounds which are so durably put together by plants as a product of millions of years of evolution. The natural complexity and high stability of lignin bonds (also as an evolutionary adaptation by plants) makes lignin depolymerization a highly challenging task. Several efforts have been directed towards a more profound understanding of the structure and composition of lignin in order to devise pathways to break down the biopolymer into useful compounds. The present contribution aims to provide an overview of key advances in the field of lignin depolymerisation . Protocols and technologies will be discussed as well as critically evaluated in terms of possibilities and potential for further industrial implementation.

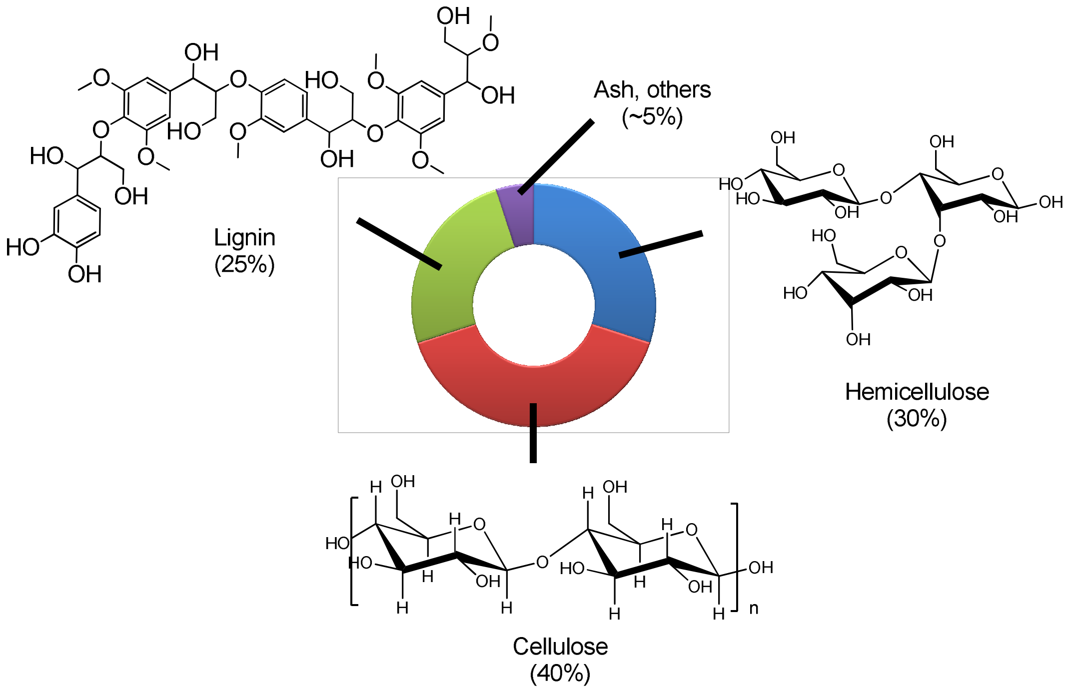
Introduction

Recent trends and patterns within the energy sector predict a remarkable increase in energy demand (over 60%) by 2030[1]. Society will also experience a daunting panorama of challenges with food availability and safety, water, and resources distribution. Despite joint efforts from scientists, politicians, bureaucrats and related divisions, there is still a very urgent need to come up with more sustainable energy alternatives to meet the present demands. Biomass has emerged in recent years as a highly attractive renewable source of chemicals, materials and fuels. It is widely believed that their mere abundance can facilitate the switch to a bio-based economy to replace the petrol-based industry that we have relied upon for the past 70+ years[2]. However, the proposed transition to a bio-based industry requires an extensive reconsideration and rethinking of feedstock processing strategies because of the differences in structure, composition and complexity of biomass as compared to crude oil (Scheme 1).[2]



Scheme 1. Biomass vs petroleum processing to fuels and chemicals. Reproduced with permission from the Royal Society of Chemistry.[2]

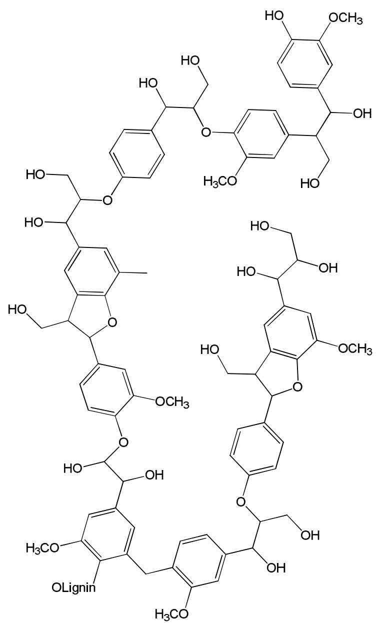
Lignocellulosics comprise three markedly different profitable fractions (Scheme 2). Hemicellulose is composed of C5 and C6 polysaccharides,having important applications for biofuels production (e.g. bioethanol) and for the generation of valuable chemical intermediates (e.g. furfural).[3] Cellulose is comparably considered as one pf the most abundant biopolymers on earth comprising linear β(1➔4) glucose chain links. Cellulosecan be also deconstructed into valuable products such as biofuels (e.g. bioethanol and lignocellulosic fuels-alkyl valerates-), and platform chemicals (including levulinic and formic acids, gamma-valerolactone and derived products).[4] Lignin is the third major component in lignocellulosics, being the most underutilized fraction.Lignin has been traditionally employed for heat and power purposes through combustion in the pulp and paper industry due to its high calorific value.



Scheme 2. Proportion of hemicellulose (30-35%), cellulose (40-45%) and lignin (25-30%) as lignocellulose components (Adapted from reference 3)

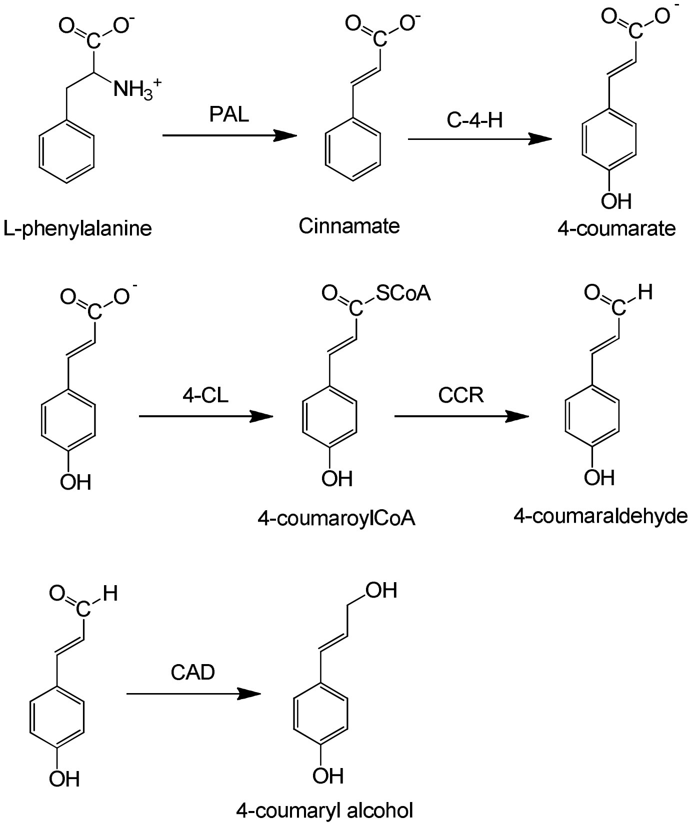
Lignin is a complex and recalcitrant phenolic macromolecule comprising phenylpropane type-units (scheme 3). Due to its highly irregular polymeric structure, it is resistant to microbial attack and can prevent water from destroying the polysaccharide-protein matrix of plant cells.

Accounting for almost 30% of organic carbon within the biosphere, lignin has an intriguing biosynthesis. Although extensive research has been reported in the literature to prove its origins, only a small part of this very complex biomolecule is well understood. Until now, it is not very clear if monolignols (the monomer units of lignin) are polymerized in an organized manner like most biomolecules or if they are randomly attached together inside the cytoplasm using a radical pathway.[5] Eleven recognized enzymes are involved in the conversion of L-phenylalanine to primary monolignols. These have been recently targeted for down-regulation to engineer plants with reduced lignin contents.[5] Recent studies have demonstrated that lignin biosynthesis and structure can be more tuneable than in principle expected as to the introduction of several variations in both aromatic rings and side chains. Such flexibility could be potentially useful to future "recalcitrance" design in lignins as well as to facilitate its fractionation in lignocellulosics to establish lignin biorefineries. For further information on lignin biosynthesis and characterization, readers are kindly referred to the recent overview by Ragauskas *et al.* and references contained therein.[5]

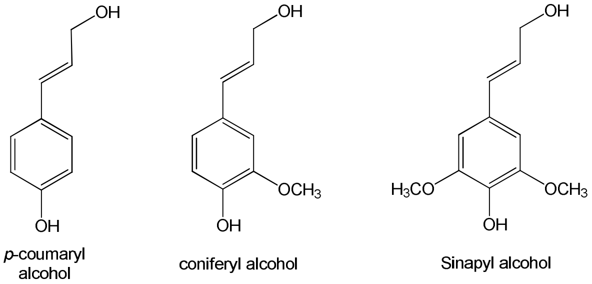


Scheme 3. Representative fragment of the proposed structure of lignin which illustrates its remarkable complexity with a large abundance of aromatic hydrocarbons.

Monolignols are believed to come from a phenylalanine (or tyrosine) precursor which underwent extensive modifications. Certain enzymes involved in such modifications have been isolated but the detailed function of many of them in key steps has not been elucidated (Scheme 4). Lignin is mainly composed of three different monolignol monomers, methoxylated to various degrees, namely *p*-coumaryl, coniferyl and sinapyl alcohols (Scheme 5).[5-6] These lignols are incorporated into lignin aromatic cores in the form of phenyl propanoids, namely p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively. Different types of lignins (i.e., softwood, hardwood, grasses) contain different amounts of methoxy groups depending on how much of each of the three alcohols has been incorporated into the lignin macromolecules.



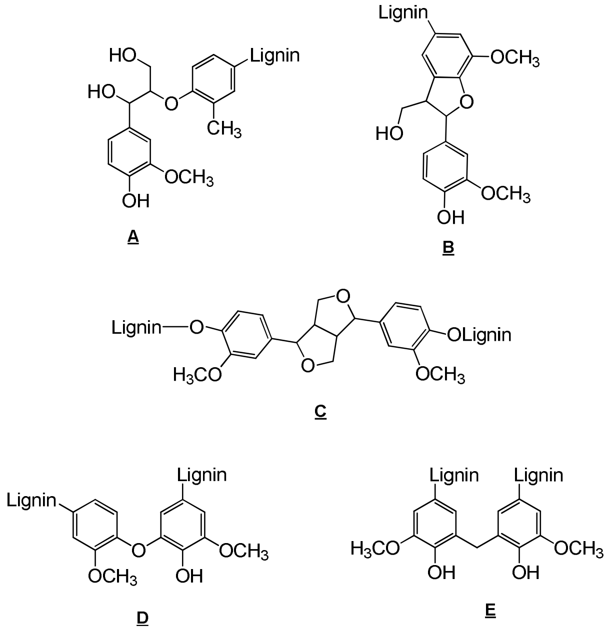
Scheme 4. Proposed biosynthesis of coumaryl alcohol using the enzymes Phenylalanine ammonia-lyase (PAL), Cinnamate 4-hydroxylase (C-4-H), 4-coumarate:Coenzyme A ligase (4CL), Cinnamoyl-Coenzyme A reductase (CCR), Cinnamyl alcohol dehydrogenase (CAD).



Scheme 5. Structures of the building block monomeric aromatic precursors of lignin.

The synthesis of guaiacyl and syringyl alcohols is believed to branch out from the intermediates of 4-coumaryl alcohol synthesis (see pathway shown on Scheme 4). Examples include the hydroxylation, methoxylation (at the *ortho* position relative to the hydroxyl) and subsequent thioamidation of coniferyl alcohol to form feruloyl-CoA which lead to the formation of guaiacyl alcohol. Further upstream modifications eventually produce sinapyl alcohol. Unlike common biopolymers including chitosan and cellulose, lignins additionally have different monomer units, bonding linkages (>20 known bonding patterns) and a highly branched structure, making it one of the strongest and most complex biopolymers known.

Structural elucidation studies of lignin so far revealed that 50% of its components are aromatic hydrocarbons which can be a potentially attractive source of fuels and chemicals[7]. Based on the bonding pattern, 45-48% in native lignin are β-O-4 ether bonds (Scheme 6A) while more than 12% are β-5 phenylcoumaran bonds (Scheme 6B). Smaller percentages belong to β-β' pinoresinol (Scheme 6C), diphenyl ether 4-O-5'(Scheme 6D), and β-1' diphenyl methane (Scheme 4E).[8] The common bonding patterns in lignin are thus usually C-O-C bonds which exist either as ethers or as part of a furan ring.



Scheme 6. Five typical bonding patterns in a lignin biopolymer structure

Different forms of lignin are also found in different plant species– a fact that adds to the difficulty of valorizing lignin into useful chemicals and fuels-. To illustrate the important evolutionary role of lignin in the survival of many plant species, grasses have been shown to have a unique lignin subunit based on *para*-coumaric acid esterified with hydroxycinnamyl subunits.[9] Esterification of different sub-units in this case is important to the grass to add more structural durability, so that they become less susceptible to destruction by terrestrial animals.

Why is it difficult to degrade lignin? The lignin-rush

The composition, structure and abundance of lignin clearly evidences that such a durable biopolymer could become the next player of the renewable energy industry. Based on its potential, lignin deconstruction has become the *gold-rush* for several academics worldwide, with recent stimulus from experienced scientists in the field.[10] The fierce competition in lignin depolymerisation is illustrated by the staggering increase in the number of publications in the topic of *lignin depolymerisation* over the past four years (Figure 1).

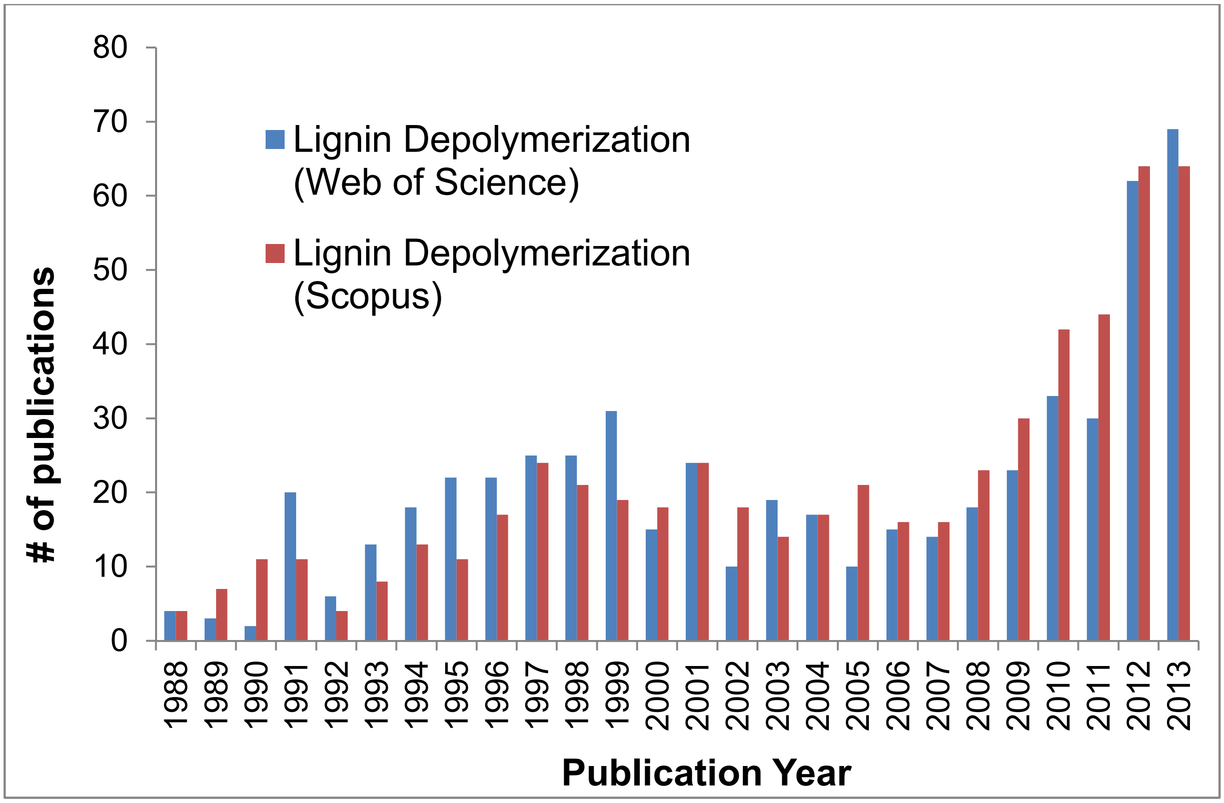


Figure 1. Staggering interest in lignin depolymerisation over the past four years. (Source: ISI, Web of Science, Scopus).

In this regard, the viability of recovering hydrocarbons and aromatics from lignin has been under intense investigation over the past years. In spite of its apparent abundance, lignin deconstruction still has not reached even pilot plant scale because of the difficulties both on the depolymerization itself and the product separation. Furthermore, the structural variability of lignin in different plant species prevents the development of a generally applicable depolymerisation protocol for lignins. As an example, groundbreaking studies such as those from Sergeev and Hartwig[11] who developed an elegant protocol for the selective Ni-catalysed hydrogenolytic cleavage of C-O bonds in aryl ethers of lignin model compounds may not be useful in a complex actual system. For a reaction protocol to work in industry, in this case, many issues such as lignin repolymerisation, structural variability and product separation efficiency should be carefully addressed.

Several further studies and efforts have been devoted to depolymerize lignin, however, from the point of view of the authors, current chemical methods are not very successful in providing effective, environmentally sound and simple strategies to recover the aromatic monomers. This contribution aims to explore the various strengths and weaknesses of different depolymerisation studies of lignin reported in the scientific literature. A critical analysis of every method's industrial viability is also provided on a case by case basis. We aim to provide our own evaluation on their respective simplicities, pros and cons, and potential for future development. In light of these premises, this work does not aim to consider the extensive work conducted with lignin model compounds since we believe that catalysts tested with lignin model compounds will not necessarily be effective for complex lignin samples. For further information on recent overviews on lignin depolymerisation, readers are kindly referred to recent key contributions in the field.[12]

Lignin Deconstruction strategies

General considerations

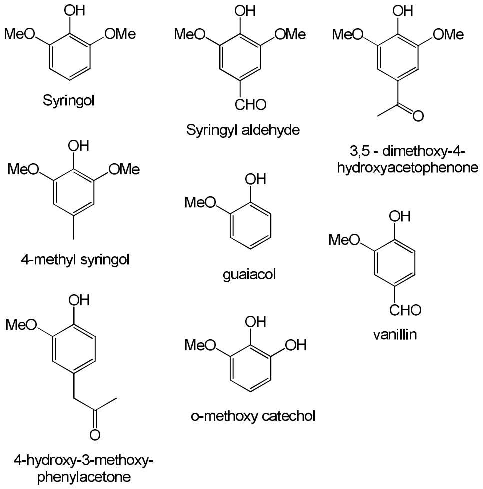
There are generally two main approaches for lignin depolymerization: pyrolysis, *oxidation* and *hydrotreating* (hydrogenolysis, deoxygenation).[7, 12] In some cases, enzymatic depolymerization methods have also been described. However, depolymerisation processes are often not too well understood in terms of mechanism. Analyzing current general methodologies and recent protocols, there are two main considerations that should be taken into account for lignin valorisation purposes: **1) maximisation of the activity and stability of the catalyst under the chosen conditions (as mild as possible),** bearing in mind the bulky nature of the biomass source and the reaction conditions and **2) more importantly, the repolymerisation and self-condensation capability of lignin under processing conditions** (due to the formation of radicals[12] and/or C-C bond forming self-condensation reactions in acidic media[15]) which eventually leads to a complex pool of re-condensed aromatics.[7, 12]

In other cases, when depolymerisation is achieved under generally harsh reaction conditions (high hydrogen pressures, temperatures >400ºC), it produces a range of products composed mainly of simple aromatics. [7, 12, 13-15] Another important aspect to consider for lignin depolymerisation is the addition of hydrogen to the products. In some cases, reduction caused by hydrogen is not avoided and cannot be controlled. This hydrogenation side reaction becomes more prominent in the presence of a metal in the system as it could act as a surface for the reduction.[16] It is critical that these issues on product quality and hydrogen economy be addressed to obtain a clean valorization strategy for lignin. Previous work and results in this field point to a general consensus that catalytic hydrogenolysis is a valuable approach to unravel many structural insights about lignin through the detection of the identity of the lignin degradation products. In any case, the design of an active and stable system able to work under mild reaction conditions will offer a significant step forward in lignin deconstruction strategies. Chemical and enzymatic depolymerisation strategies have been developed in recent years aiming to recover the aromatic monomers in lignin. Relevant literature examples mostly related to hydrotreating technologies that advance the understanding of lignin deconstruction will be subsequently discussed in the next sections. While thermochemical (e.g. pyrolysis) and oxidative protocols can contribute to lignin depolymerisation, these will be not discussed in detail in this contribution.

Chemical depolymerisation

Homogeneous Acid/Base-catalyzed deconstruction

A popular lignin depolymerisation strategy involves the utilization of a strong base to carry-out the fragmentation and separation of different monomers (and their respective isomeric structures). Parameters in a base-catalyzed depolymerisation (BCD) affect heavily the products formed after the reaction.[17] Sodium hydroxide is a common homogeneous base catalyst, in aqueous media at high temperatures in the 240-340°C range. Simple aromatic products (Scheme 7) were obtained at a temperature of 300 °C, 250 bar pressure, 2% (w/w) NaOH and 5% (w/w) starting lignin material and 4 minute optimum residence time.[17] According to the reported mass balance, 11.5% of the starting materials were converted to oils after only 4 minutes, while most of the reaction mixture was unreacted lignin.



Scheme 7. Various phenolic products of NaOH-catalyzed hydrolysis of lignin at 300°C, and 250 bar.

The base-catalyzed depolymerisation (BCD) reaction not only cleaves susceptible lignin monomer linkages, but also other functional groups (such as methoxy groups) attached to the aromatic rings. For this study at least, both pressure and reaction times have been shown to favor the formation of lignin oligomers. Higher temperatures are also not encouraged for lignin depolymerization since the molecule tends to get completely degraded (to form both coke and gases). From this study alone, it is evident that the process of depolymerizing lignin lies on a proper selection of reaction parameters.

A more upscale and directed approach for this depolymerisation is the use of a dedicated reactor system that can form different easy to separate products. A continuous flow instrument can be a promising methodology to synergistically produce a range of products from lignin.[18] In this example, 10% kraft lignin solution with 5% NaOH was placed in a 30 m continuous flow reactor, heated in the temperature range 270-315°C and pressurized up to 130 bar. Products were recovered at a much cooler outlet of the reactor and subsequently characterised and quantified using GC-FID and GC-MS. Separation of oligomers from monomers was conducted via simple precipitation (e.g. acidification until pH = 1), and subsequently followed by liquid-liquid extraction. Results show that there is a negative correlation between monomer depolymerisation, gas formation and oligomer formation implying that lignin depolymerisation takes place in a step-wise manner starting from the cleavage of select sites (ether bonds being most susceptible to acid/base hydrolysis) to form oligomeric residues and then followed by the cleavage of oligomers into their respective monomers.

The isolation of lignin monomers can be highly favored in a strongly basic solution because this pH will also prevent the products from reforming into longer polymers. However, these BCD reactions have high activation energies. Due to high temperature (>300°C) and pressure requirements (>200 bar) of the reaction, the formation of side products cannot be controlled making the final mixture hard to purify.

To address the issue of reaction conditions, deconstruction of lignin may be performed under milder reaction conditions in the presence of an acid catalyst. Recently, depolymerisation of lignin using 10 wt.% of formic acid in conjunction with 77 wt.% of ethanol at high temperatures was reported.[19] The suggested lignin depolymerisation pathway involved mainly deoxygenation reactions of methoxyphenols and catechols to produce stable phenols in the liquid phase. The main reaction pathways are strongly dependent on the chemical structure of the utilized lignin.[19]

Aside from lignin depolymerisation, acid catalysts also facilitate the fractionation of lignocellulosic materials, separating lignin from cellulose and hemicellulose. Using an acid reflux set-up (dilute H_2SO_4 and water as a solvent), hemicelluloses and celluloses from wheat straw can be separated on the first step while lignin can be fractionated in the second acid reflux reaction (2N H_2SO_4) in the presence of ethanol as a solvent.[20] Interestingly, 50% of the hemicelluloses were selectively hydrolyzed after the first reflux, while >70% of lignin was removed from the mixture on the second step.

The efficiency of a fractionation procedure is important if we aim to harvest value-added chemicals from wood or other lignocellulosic sources, since this will also allow for utilization of the sugar components of the material. These sugar components may be used as a fermentation feedstock to produce biofuels, dicarboxylic acids (which are precursors of many important fine chemicals), alcohols, etc. The lignin fraction, on the other hand, can be processed to produce aromatic hydrocarbons for fuel and chemical applications.

Oxidative depolymerisation

The use of oxidants and/or oxidising protocols is not a generally adopted practise for lignin depolymerisation despite several available relevant studies on oxidation protocols mostly for lignin model compounds. Oxidative cracking of lignin could be an interesting possibility to consider due to the large presence of hydroxyl groups in lignin. Aromatic aldehydes and carboxylic acids are formed as main products from oxidative degradation of lignin.[21] Metal oxides and hydrogen peroxide have been considered for these purposes. Vanillin is obtained as a major product in oxidative deconstruction of lignin with yields in the range of 5-15 wt% with respect to the lignin source. Most reported protocols involve the use of homogenous conditions (e.g. alkali or mineral acids) combined with hydrogen peroxide,[21] the use of homogeneous heteropolyacid catalysts and in some cases combination of metals (Cu^{2+}, Fe^{3+}, etc.) under high temperatures and pressures. In some cases, oxidation of lignin may not be ideal as they produce radicals that lead to partial re-polimerisation and form more complex lignin structures. For more information on oxidative protocols, readers are kindly referred to the recent general overviews on oxidative lignin depolymerisation.[7, 12]

Interestingly, a recent report from the group of Stahl and coworkers may point out the way forward in the field of oxidative depolymerisation of lignin.[21] An efficient organocatalytic method based on the chemoselective aerobic oxidation of secondary benzylic alcohols for lignin model compounds (with an extension to Aspen lignin with a S:G 2:1 ratio) was reported. The catalytic system consisting of 4-acetamido TEMPO (5 mol%) in combination with mineral acids such as HNO_3 and HCl (10 mol% each) could achieve the selective oxidation of a range of lignin model compounds including important ketones and acids (e.g. vanillin, vanillic and veratric acids) under mild reaction conditions after 24 h reaction. Coupling oxidations with C-C bond cleavage (using an alkali/H_2O_2 system) was also preliminarily introduced for a particular benzylic ketone which could be converted into veratric acid (88% yield) and guaiacol (42% yield) at complete conversion of starting material. The protocol was also extended to the selective oxidation of Aspen lignin in which NMR data proved the successful oxidation of most S and G units to their benzylic ketone analogues. Only a small fraction (<10%) of unoxidised beta-S ether units were found to be present. The simplicity of the metal-free system, mild reaction conditions and possibilities to scale-up (already proved for larger scale reactions up to 10 g) can make this protocol potentially suitable for larger-scale industrial processes.

In summary, base catalyzed depolymerisations require the use of high temperatures and pressures. The difficulty of such process relates to the fact that at much higher temperatures, depolymerisation usually generates a significant amount of gases aside from the large number of side products that prevent the formation of monomeric aromatic hydrocarbons.

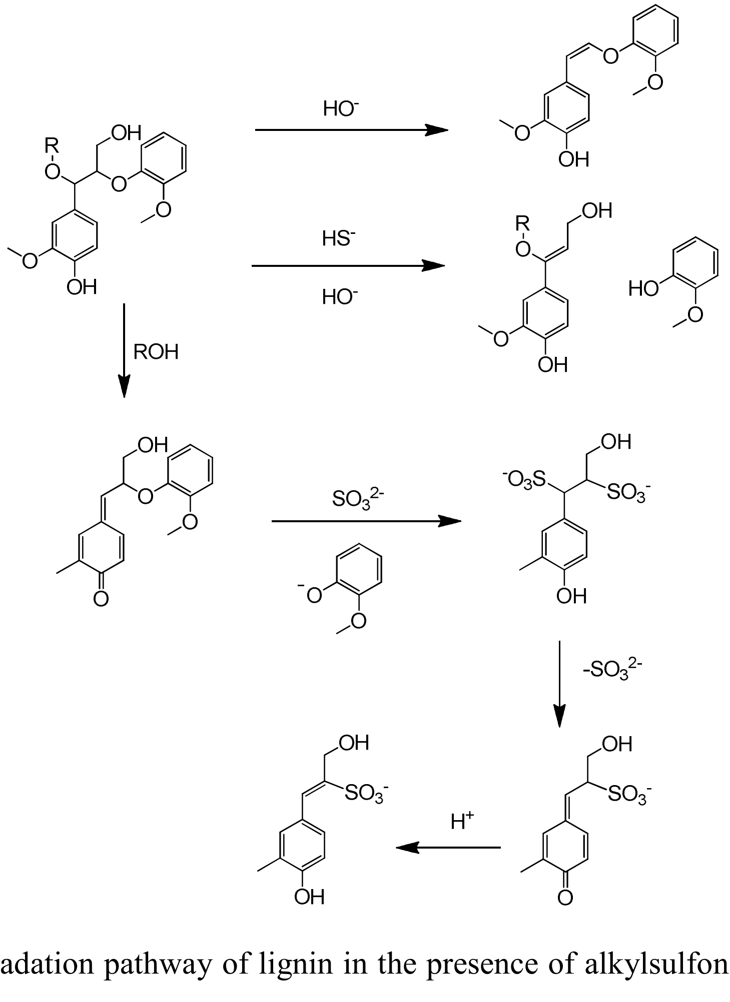
On the other hand, the acid catalysed process appears to be a mild and kinetically favored method. The technique is also able to facilitate the fractionation of celluloses, hemicelluloses, and lignin by destroying cavities that enclose cellulose in lignocellulosic materials. In principle, the addition of an acid can also promote acidolytic cleavage of C-C and C-O bonds within the complex lignin structure as previously suggested.[22] These features of an acid-assisted reaction may provide a promising avenue in the development of an integrated biorefinery concept.[5, 23] However, the efficiency of the acid-catalyzed was only tested for tannins. Its ability to depolymerize lignin, which is a more complex feedstock, has yet to be demonstrated in literature reports.

Oxidative depolymerisation strategies can be comparatively useful for the production of chemicals (e.g. aromatic acids, aldehydes) where the aromatic moieties are fully preserved as well as potentially room for ring-opened organic acids (e.g. under ozonolysis conditions). However, in spite of the very recent promising reports,[21] significant issues need to be addressed in terms of 1) yields to products, 2) recombination/repolymerisation of lignin and 3) feasibility of product separation and/or isolation (especially for low quantities of generated products). The highest reported yields to oxidative products from lignin are ca. 10-11%, with average yields to products including vanillin in the 3-5 wt.% range.[24]

Ionic-Liquid Catalyzed Depolymerisation

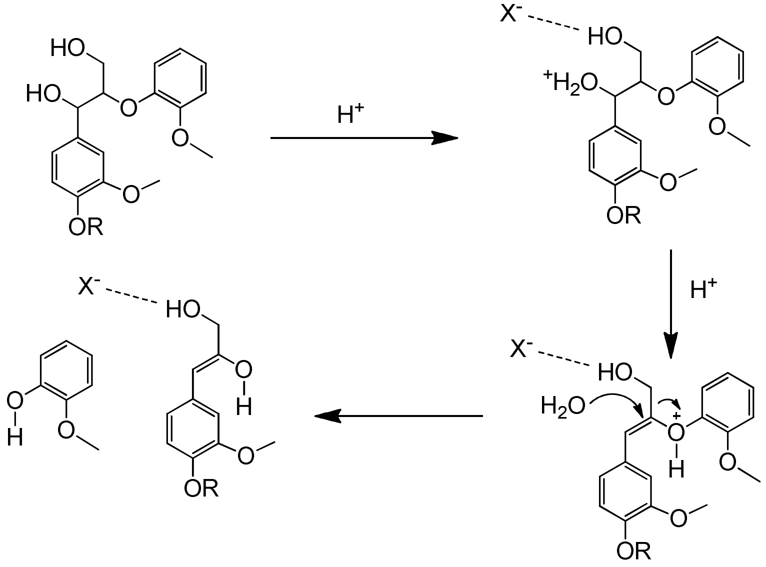
In spite of intensive research conducted to ascertain the mechanism and optimise lignin deconstruction with acid and base catalysts, the separation and downstream processing of depolymerised lignin remains a significant challenge. The use of ionic liquids (ILs) for deconstruction of lignocellulosic biomass can also be an interesting alternative to conventional chemical depolymerisation. ILs are composed of ionic organic/inorganic salts that are liquid at low temperatures (<100ºC) and which possess interesting properties including low vapour pressures, chemical and thermal stabilities and the ability to dissolve a wide range of compounds. ILs have been considered as new generation of *green* solvents in spite of some controversy around their green credentials and environmental hazards.[25]

Understanding the role of various IL cations and anion is important in the design of efficient lignin depolymerisation strategies using ILs. Recently, it has been shown that anions mostly affect the structural integrity of the lignin biopolymer while cations only have spectator roles.[26] In terms of reducing the polydispersity of lignin, alkylsulfonate anions are the most effective followed by lactates, acetates, chlorides, and phosphates (decreasing strength: alkylsulfonates>Lactate>Acetate>Chloride>Phosphate).[26] This trend in anion activity is mainly explained by the nucleophilicity of the electronegative atom present in those species. In the case ofalkylsulfonates, the depolymerisation is believed to occur via sulfite addition to one of the lignin unsaturations outside of the aromatic system, after liberation of the alcohol (Scheme 9). However, studies with lignin model compounds have shown that these anionic effects are also caused by the strength of their respective coordination with the hydrogen in the hydroxyl groups present in the backbone of lignin and lignin-like structures.[27]



Scheme 9. The degradation pathway of lignin in the presence of alkylsulfonate anions is caused by the ability of sulphite groups to act as nucleophiles. The main driving force of this reaction is the formation of relatively stable alcohols.[26]

As shown in Scheme 10, this coordination with hydrogen stabilizes the electronic environment of the compound and directs the nucleophilic attack of water at the double bond carbon. However, we believe that the more important property in considering an IL anion for lignin depolymerisation should be nucleophilicity since the anion can possibly attack highly electron deficient protonated C-O bonds.



Scheme 10. Mechanism of lignin depolymerisation under acidic conditions showing the effect of IL anions.

One of the most important advantages of some ionic liquids in lignin depolymerisation relates to their ability to act as both an acidic catalyst and a solvent. 1-H-3-methylimidazolium chloride can promote acidolytic cleavage of β-O-4 linkages in lignin over a relatively mild temperature range (110-150°C). The mechanism of depolymerisation using this acidic IL is similar to that proposed under conventional acid-catalyzed conditions. Firstly, protonation (or coordination) of the ether linkages takes place, followed by subsequent attack of water (or any other nucleophile present in the system). A similar IL, 1-ethyl-3-imidazolium chloride, has also been shown to simultaneously depolymerize both lignin and cellulose to form a myriad of products including phenols, alcohols, and sugars. With lignocellulosics, the advantage of using IL is illustrated by their ability to also fractionate/separate different lignocellulose components, similar to other acidic catalysts.[27-29]

Another advantage of using IL relates to their ability to dissolve relatively larger amounts of the starting polymer (500 g Lignin/kg ionic liquid). However, lignin conversions are very low in most reported depolymerisation studies.[29] To exploit this important property of ILs and to further increase the yield, transition metal catalysts are often co-utilised in conjunction with IL to influence lignin depolymerisation via oxidation.[8]

An example to illustrate the role of transition metals is the use of $CoCl_2 \cdot 6H_2O$ with 1-ethyl-3-methylimidazolium diethylphosphate ionic liquid in the presence of molecular oxygen. Using simple ATR-IR studies, oxidation was found to take place prior to depolymerisation, therefore controlling lignin pre-functionalization.[30] In a separate study, the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate along with $Mn(NO_3)_2$ showed excellent conversion in lignin depolymerisation (yields of up to 66.3%, from 11 g starting materials) after 24 h at 100 °C under 84×10^5 Pa air pressure.[31] Oxidizing the substituents outside the aromatic ring will help in the deconstruction by intermediate stabilisation via resonance.

However, in spite of the promising achievements of IL-promoted lignin deconstruction (even *dissolution* rather than *deconstruction or depolymerisation*), the utilization of ionic liquids for industrial applications is still in its infancy due to several drawbacks including costs and investment, environmental hazards, recyclability, etc. From detailed technologies in this contribution, we believe IL-assisted lignin depolymerisation has only minor prospects to become industrially feasible. Further details on the use of ILs for lignin oxidation have been recently compiled in an extensive and excellent overview by Rogers *et al.* [29]

Heterogeneously catalyzed depolymerisation

Heterogeneously catalyzed depolymerisation strategies have evolved as promising deconstruction strategies in spite of the mass transfer limitations from the bulk lignin molecules to the catalyst surface. Interestingly, recent reports have illustrated the utilization of supported transition metal catalysts (e.g. Ni) in lignin depolymerisation.

Most reported studies with heterogeneous catalysts also deal with the hydrodeoxygenation of the lignin fragments via hydrogenolytic cleavage of C-C and C-O lignin bonds using: 1) hydrogen-donor systems (e.g. alcohols) with *in-situ* generated hydrogen and 2) the use of moderate to high pressure molecular hydrogen. This section will also briefly include the topic on selected oxidative heterogeneously catalyzed protocols for lignin deconstruction.

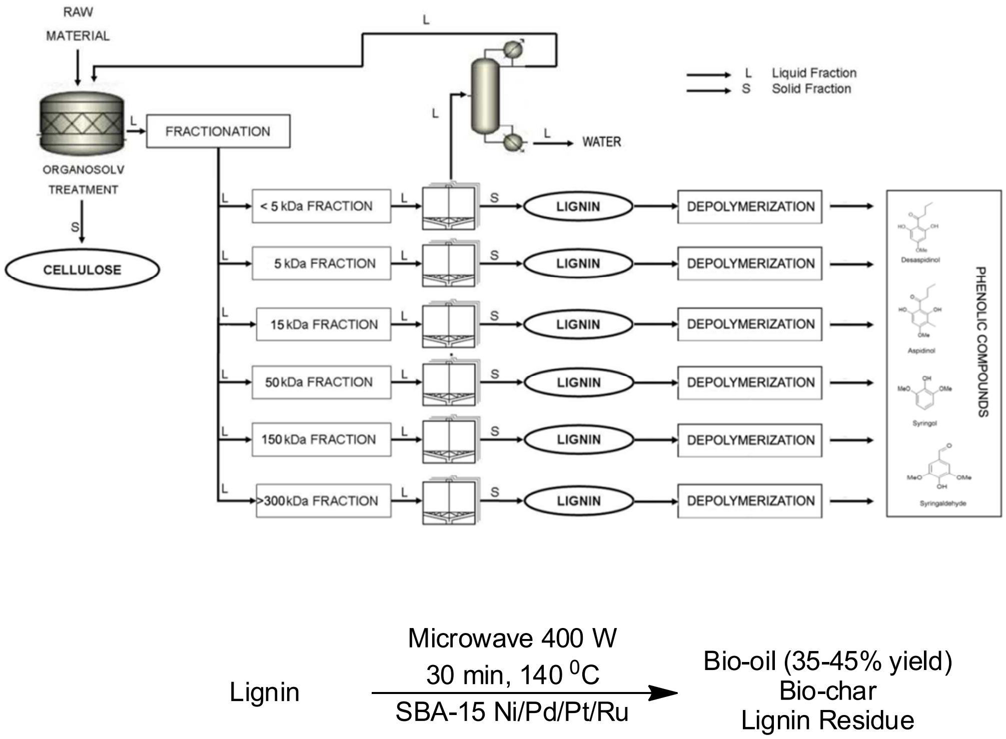
Transfer hydrogenation systems (in-situ generated hydrogen or hydrogen-free)

Oxygen removal steps increase the energy density of complex biomass molecules, often decreasing their chemical reactivity. Oxygen is generally removed upon deoxygenation from biomass in the form of H_2O and/or CO_x species (CO and CO_2) by means of various catalytic processes including hydrogenation, C-O hydrogenolysis, dehydration and decarboxylation and decarbonylation. However, these deoxygenation steps have often been associated with significant consumption of expensive and fossil-fuel derived hydrogen which negatively affects the carbon footprint of the process. In some cases, hydrogen from renewable sources has also been used.[32]

Studies from our group were originally aimed to avoid the utilization of external hydrogen consumption added in hydrogenolysis by using renewable H_2 sources (i.e. formic acid co-generated with levulinic acid from cellulose depolymerisation)[22, 33]. The proposed methodology for lignin deconstruction was based on a formic acid-mediated microwave assisted approach using a mechanochemically synthesized bifunctional Ni nanocatalyst. [22, 33]

The bifunctional Ni nanoparticle-aluminosilicate/formic acid system was rationally designed from a fundamental understanding that 1) maximises the activity of the metal sites, as supported nanoparticles synthesized by ball milling (mechanochemistry) have been proved to predominantly deposit on the external surface of a support; being highly active and accessible even at very low loadings[22, 33] and 2) minimises repolymerisation and related recombination reactions using a mild hydrogenolytic approach under reducing conditions combined with acidolytic cleavage of lignin by both formic acid and the acid sites of Al-SBA-15. These conditions can quench radicals and unstable intermediates formed during depolymerisation avoiding, at the same time, the addition of hydrogen in the systems. Formic acid was previously reported to increase the yield of aromatic monomers by stabilizing aromatic radicals under supercritical conditions.[14] The support was selected due to its good (hydro) thermal stability, large surface area and its high acidity. Different hydrogen donating solvents (e.g. tetralin, isopropanol, formic acid) were also utilized in the protocol to maximize *in-situ* hydrogen production.

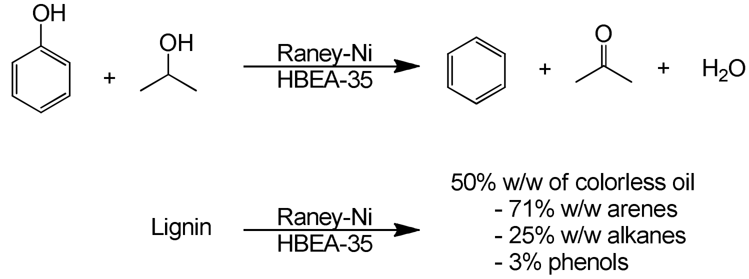
The Ni-based catalyst with formic acid was found to provide optimum depolymerisation results as compared to noble metals including Rh, Ru, Pd and Pt.[22] In this way, several mg of simple aromatic compounds including syringaldehyde, vanillin, aspidinol and deaspidinol could be produced per gram of organosolv lignin under mild reaction conditions (typically a maximum of 40% yield to aromatics after ca. 30 min under microwave irradiation at 150^{o}C). Importantly, the protocol could be extended to a range of lignin fractions of different molecular weights, which could be deconstructed to a pool of aromatics[22, 33] (Scheme 11).



Scheme 11. Lignin purification and fractionation followed by heterogeneously catalyzed depolymerization using supported Ni nanomaterials to simple aromatics. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission from reference 33b.

The catalyst was also found to be reusable under the investigated reaction conditions, and fairly stable in terms of Ni sintering and deactivation.[22, 33] In spite of obtaining fairly good monomer product yields (35 to 45%) under optimized conditions, the separation of a complex product mixture and the utilization of an expensive formic acid reagent are key points to address in order to bring this technology to industrial applications.

Rinaldi *et al.* also performed several studies on the combination of transfer hydrogenation (using isopropanol) and hydrogenolysis with a Raney-Nickel in combination with an acidic beta-zeolite using lignin model compounds and organosolv lignin.[34] The proposed approach was conducted at reasonable temperatures (150-240°C) and reaction times (4 h). Preliminary results for lignin deconstruction indicate the cleavage of ether linkages and demethoxylation of phenol units (in addition to dehydroxylation of phenol intermediates) as observed by heteronuclear (^{13}C-^{1}H) HSQC 2D NMR (Figure 2).[34] No catalyst stability/reusability studies were provided in this work, particularly for the case of lignin valorization.



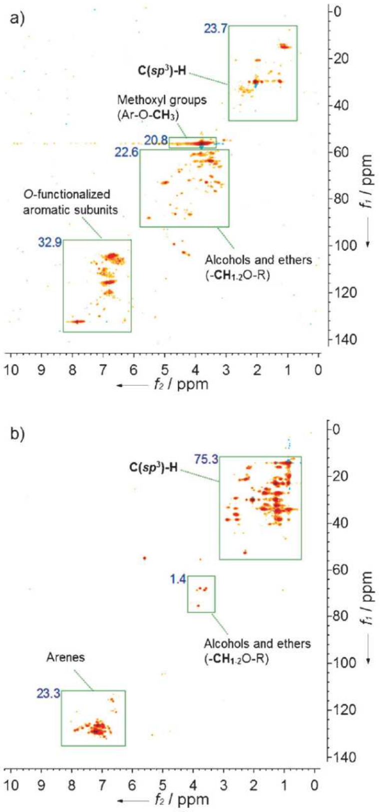
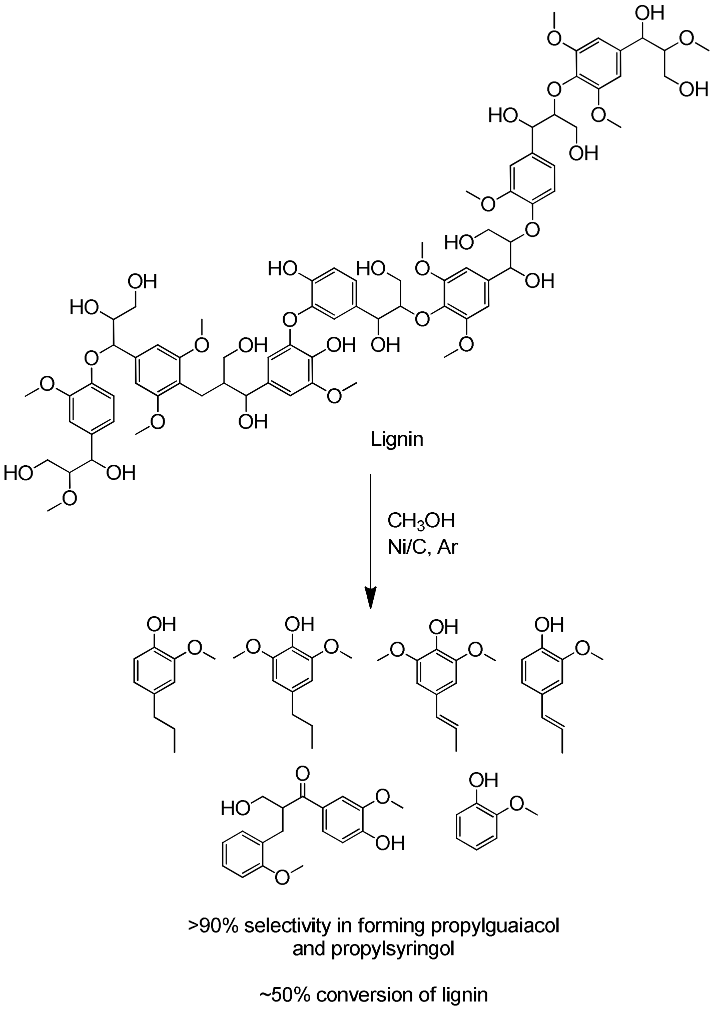


Figure 2. Catalytic tandem reaction between a phenol and 2-propanol in the presence of a reducing reagent (Raney-Ni) and oxidant (HBEA-35). The protocol was able to form mostly arenes, alkanes, and phenols. HSQC 2D NMR experiments were able to provide insights into lignin products as compared to parent organosolv lignin. Copyright by Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission from reference 34.

In parallel to the mentioned studies but of relevance to a better understanding of lignin deconstruction strategies related Ni-based magnetically separable systems have also been designed for the depolymerisation of native birch wood lignin to monomeric phenols.[35] The proposed methodology was conducted in methanol and other alcohols (e.g. ethanol and ethylene glycol) at moderate temperatures (200°C) and moderate time of reaction (typically 6 h) under

Argon (in the absence of hydrogen) to achieve conversions of ca. 50% at >90% selectivity to propylguaiacol and propylsyringol (Scheme 12). Promising findings show that birch lignin could be first fragmented into smaller oligomeric compounds followed by subsequent hydrogenolysis of the generated compounds into monomeric phenolics.

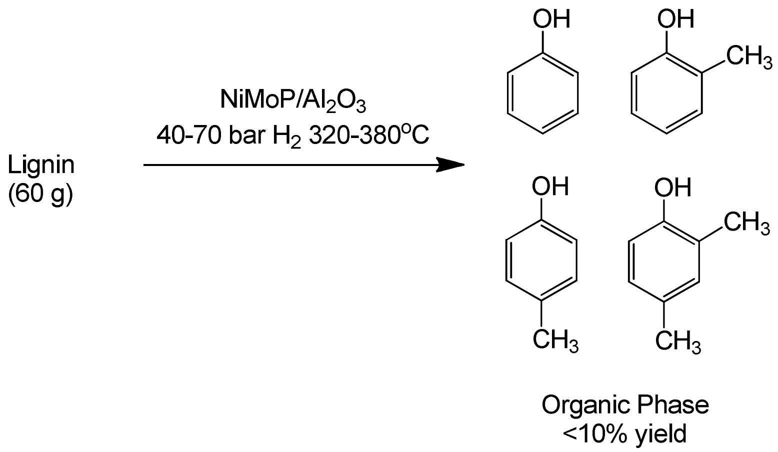


Scheme 12. Valorization of wood lignin using a Ni-based catalyst with methanol as a hydrogen solvent, selectively forming phenolic aromatic compounds.

Most interestingly, the authors also proved using isotopic tracing experiments that the addition of hydrogen in the systems (even at high pressures of 50 bar H_2) did not influence lignin conversion. These results support previous evidences by other groups[22, 33] that alcohols can in fact provide the active hydrogen species to promote the depolymerisation of lignin. Mechanistic insights provided in this work suggest that alcohols act as nucleophiles to induce C-O-C bond cleavage via alcoholysis as well as provide the source of active hydrogen most probably via hydrogen transfer under the reaction conditions.[34, 35] The conversion of smaller lignin fragments into monomers is believed to follow a beta-elimination dehydration mechanism coupled with hydrogenation for C_{alpha} and C_{beta} and subsequent hydrogenolysis for the C_{gamma}. The magnetically separable Ni/C system was also highly stable and reusable under the investigated conditions, preserving its initial activity after four uses.

Hydrogen pressurized systems

Protocols based on pressurized molecular hydrogen systems using different catalysts have also been recently developed using a range of catalysts. Following previous work on Ni-derived catalysts, NiMoP/γ-Al_2O_3 materials have also been used to break down lignin into monomeric units.[36] Lignin was depolymerized in a semi-continuous flow reactor at high temperatures 320-380°C and 40-70 bar hydrogen pressure in the presence of the Ni-modified catalyst (17.0% MoO_3, 2.95% NiO, and 5.71% P_2O_5).[36] The proposed methodology generated products in three different phases. The aqueous phase was composed of deoxygenation and dehydration products with low quantities of phenol. Comparatively, the organic phase mainly comprised aromatics and gaseous products mostly related to carbon dioxide and carbon monoxide from decarboxylated lignin fragments (Scheme 13).

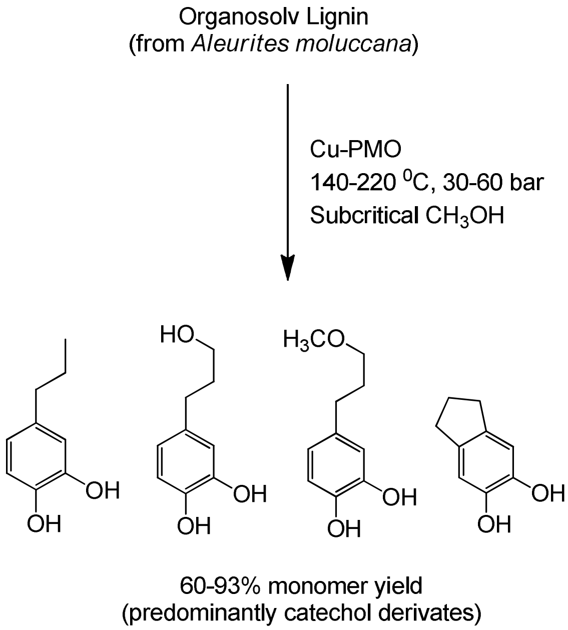


Scheme 13. Depolymerization of lignin materials using Nickel/Aluminum catalysts forming phenolic compounds in <10% yields.[36]

This study also illustrates the influence of reaction conditions with respect to depolymerization products. The catalyst was found to play a vital role in the cleavage of two monomer units as evidenced by changes in the composition of the organic and aqueous phases at increasing catalyst loadings. Low quantities of aromatics, and high temperatures and hydrogen pressures (Scheme 13) are the main limitations of the proposed technology.

Similarly, a 5% Pd/C system was also utilized in the hydrogenolysis of isolated *Pinus Radiata* lignin to its aromatic monomers (temperature around 200°C, 35 bar hydrogen and 5-24 h reaction time).[37] Lignin conversions of 80-90% with high selectivities to dihydroguiacyl alcohol, 4-propylguaiacol, dimers and oligomers (linked with β-5, 5-5, 4-*O*-5 and β-1 bond-types) were obtained as a bio-oil after lignin depolymerisation. No catalyst reusability studies were presented or further insights into the role of the catalyst on lignin deconstruction but the presence of large quantities of hydrogen suggest that the metal catalysts mainly act as an active surface for the reduction.

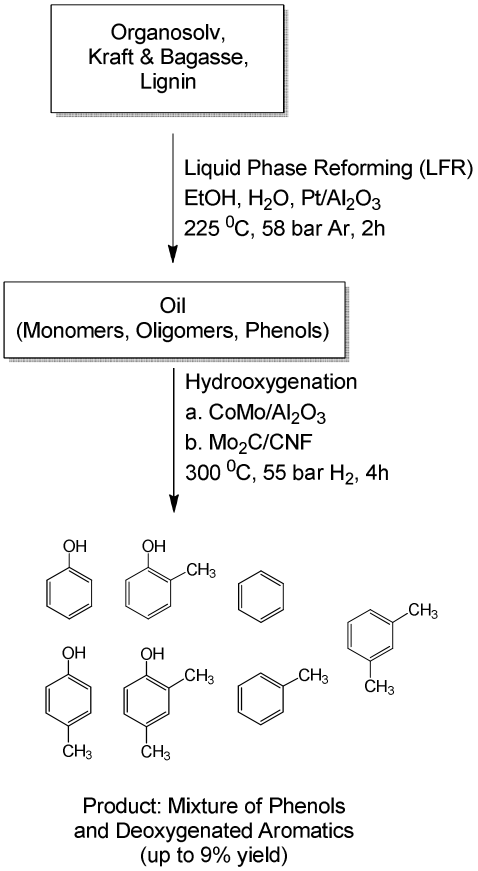
In another example, a developed Cu-doped hydrotalcite (Cu-PMO) catalyst has been successfully utilised in the depolymerisation of isolated lignin from candlenut biomass under mild temperatures (140-220°C) and high hydrogen pressures (30-60 bar) in subcritical methanol[38], following previous studies from the group. Under the reported conditions, organosolv lignin was converted into valuable monomeric compounds (predominantly catechol derivatives, Scheme 14) and some oligomers with yields ranging from 60-93%.



Scheme 14. Depolymerisation strategy involving the use of porous metal oxides (PMO) in subcritical methanol to produce lignin monomers composed mainly of catechol derivatives.[38]

No char formation was also observed in the systems. However, the stability and reusability of the catalyst particularly under subcritical methanol were not addressed in this work.

So far, one-step heterogeneously catalysed hydrogenolytic processes using molecular hydrogen have been developed for lignin deconstruction into simple aromatics. In order to advance not only with lignin depolymerisation but in further processing/upgrading of generated valuable products from lignin, an innovative two-step approach has been devised entailing: a) lignin depolymerization in liquid-phase reforming (LFR) over a 1% Pt/ γ-Al_2O_3 catalyst at 225 °C in alkaline ethanol-water and b) subsequent hydrodeoxygenation of the lignin-oil obtained after LFR under $CoMo/Al_2O_3$ and Mo_2C/CNF (carbon nanofiber) at 300°C (Scheme 15).[39] The LFR step involves the catalytic cracking of large lignin fragments into shorter polymeric chains and monomer units with a yield of up to 9% (w/w) from native lignin. The second step involves a heterogeneous hydrodeoxygenation of lignin to form more reduced products with higher potential energy. This two-step approach is particularly interesting because it directly provides access to gasoline components such as Benzene, Toluene, and Xylene (BTX) via two-step catalytic depolymerisation and hydrodeoxygenation.[39, 40] It is also important to highlight that directly harvesting highly deoxygenated monomer components of lignin (BTX) is a significantly challenging process. However, this approach involving two processes is far from simple, requires intensive reaction conditions (high hydrogen pressures and temperatures) and provides low yields to products. An interesting alternative can be the combination of hydrotreating in hydrogen donor solvents in a similar way to technologies proposed for coal liquefaction studies.[40] Work related to lignin liquefaction and upgrading via hydroconversion have been attempted using sulfided NiMo catalysts in a batch reactor using wheat straw soda lignin (Protobind 1000) under tetralin/hydrogen pressure. Excellent mass and carbon balances (96-98 wt.%), with high liquid yields (>70 wt.% at 80% maximum lignin conversion) could be obtained for lignin/tetralin 30/70 ratios at 350ºC and 80 bar H_2.[40]



Scheme 15. Novel lignin depolymerization method involving a two-step recovery of phenolic and deoxygenated aromatic compounds.[40]

Heterogeneously catalyzed oxidative protocols

A number of oxidative heterogeneously catalyzed protocols of lignin have also been developed as alternatives to hydrotreating protocols. Supported metal oxides and/or metal complexes in conjunction with molecular oxygen (occasionally also hydrogen peroxide) generally employed to deconstruct lignin-containing materials into valuable aldehydes, ketones and acids. Typical catalytic systems reported in this aim include noble metal-containing materials (e.g. Pd-alumina, Pt-based materials), perovskite-type mixed oxides of La/Mn (Fe, Cu) and supported bimetallic systems (e.g. Cu/Pd-alumina or silica) metal organic frameworks (e.g.

Co-ZIF, only for lignin model compounds).[24] In some cases, photocatalytic and electrocatalytic oxidation protocols have been developed, with promising results. A synergistic combination of photo-electrocatalysis using a three-electrode iridium oxide system coupled with UV light provided ca. 92% lignin oxidation as compared to a 66% using an analogous single electrochemical approach.[24] A range of lignin-containing feedstocks have been utilized as starting materials, ranging from hardwood to softwood lignins as well as lignocellulosics (e.g. straw, bagasse and corn stalks). For a full account of heterogeneously catalyzed oxidative methodologies for lignin depolymerisation, readers are kindly referred to recent reviews on the topic.[7, 12, 24] The most extended and general issues of the use of oxidative protocols again relate to their low yields to products (<10 wt.%) for reactions generally conducted under high oxygen pressures (>30 bar), moderate to high temperatures (150-300ºC) as well as often high pH (11-13).[7, 12, 24]

Although heterogeneous catalysts for lignin degradation are already available, they have also important drawbacks in their industrial implementation due to reusability issues. Since the usual products of the reaction range from alcohols to aromatic compounds, solid catalysts remain very susceptible to surface saturation and deactivation.

Enzymatic Depolymerisation strategies

Chemical methods of lignin degradation have shown that one of the main challenges in deconstructing lignin relates to catalyst selectivity. Due to the randomness of lignin structures, it is also difficult to develop a general catalyst that can specifically cleave C-O-C bonds to form functional aromatic compounds, and prevent repolymerisation.[41] Enzymatic deconstruction of lignin is somewhat a less developed field. However, there are interesting studies with some fungi showing some remarkable tolerance towards lignin.

Phanerochaete chrysosporium is a common fungus widely studied for the degradation of lignin. During the late 1970s, it was observed that this fungus produces a lignin peroxidase enzyme that can deconstruct the molecule in the presence of both nitrogen and carbon sources.[41] This organism is also able to produce lignin-degrading enzymes even without lignin, implying that these enzymes assume a primary function in the organism. A recent comprehensive analysis of the genes of this fungus reveals a wide array of genes encoding for oxidases, peroxidases and hydrolytic enzymes[42] dependent to Mn metal. Metals such as Zn, Ca, and Mn directly influence the activity of these enzymes as evidenced by the large decrease in the conversion when these ions were reduced.[43]

A similar fungus, *Pycnoporus cinnabarinus,* can also produce peroxidases composed of Laccase enzymes with similar lignolytic activities.[44] Recent studies on organisms producing similar enzymes show that these have a substrate-specific region. These studies do not only contribute to the biological understanding of the metabolism of these organisms, more importantly, they can lead to the development of effective microbial methods to deconstruct lignin. These organisms are however limited by the feedback mechanisms typically used by enzymes to down-regulate their activities. Because of this, latest research on microbial lignin degradation has been focused on the use of a microbial consortium that can operate in a synergistic manner to produce lignin monomers. Very recent work in this area showed the development of a sludge-derived bacterial consortium able to degrade 60% of the lignin present in reeds at 30 °C for 15 days.[45] Interestingly, oleaginous *Rhodococci* was recently utilised to convert organosolv lignin into lipids up to 4.08%.[46] The metabolic route from lignin to lipid bioconversion is composed of four steps, namely digestion and degradation of low molecular weight lignin fractions, followed by the conversion to protocatechuate susbstrates with aromatic ring opening enzymes, aromatic ring degradation via catabolic routes (e.g. β-ketoadipate pathway) to acetyl-CoA, and lastly biosynthesis to triacylglycerols (TAG).[46] The fatty acid profile revealed that the major product of the biosynthesis is palmitic acid (ca. 40%), stearic (23%) and oleic (17%) acids, with minor contents of hexa- and heptadecenoic acids (around 10% each). In spite of low lipid yields, the protocol holds a remarkable promise in diversifying lignin conversion to valuable compounds other than aromatics for fuels and chemicals. The production of fatty acids is particularly attractive because these can be readily converted into biodiesel. For further information in the field of enzymatic lignin depolymerisation, readers are kindly referred to recent key overviews and discussion.[47]

Thermal deconstruction

To make the process cleaner and more efficient, the degradation of lignin into phenolics was accomplished *in situ* after the fractionation in 65% ethanol. In the absence of acid/base catalyst, lignin depolymerisation (523 K and 90 minutes) was performed hydrothermally where products such as 4-ethylphenol, 4-vinylphenol, guaiacol, 4-ethylguaiacol, and 4- vinylguaiacol were obtained in <70% yields.[10] For further information on the thermo(chemical) degradation of lignin, readers are kindly referred to recent literature overviews and key references on the topic.[13, 48] Recent work on integrating hydrolysis and thermal deconstruction via pyrolysis of lignocellulosics pointed out that combining the two processes does not necessarily produce more usable carbon as compared to pyrolysis alone.[49] These findings have relevant implications in the current debate for lignin (and biomass in general) processing and conversion to both chemicals and fuels. As the authors pointed out, the thermal deconstruction of biomass is a very important field of research that should not be overshadowed by the more applied researches only aimed to quick commercialization.

Summary of key processes and technologies for lignin depolymerisation

Table 1 summarises some of the conditions, starting materials, products and yields from most of the key literature reported results including in this contribution, which clearly highlight that only with selected examples there is plenty of room for improvements in terms of yields, products and technologies (e.g. catalysts) yet to be developed in lignin depolymerisation.

Table 1. Summary of key depolymerization strategies and conditions (selected publications)

Catalyst	Conditions	Starting Material	Products	Yield	Ref.
Vanadyl complexes	10 wt.% catalyst, MeCN, 80ºC, air, 24 h	Organosolv lignin	Monomers	<10%, monomers (>95% yield using model compounds)	50
NaOH (5% w/w)	Continuous flow, 270-315 °C, 130 bar	Kraft Lignin	Gas fraction, MeOH, CH_3COOH, formic acid, monomers	19.1 % monomers	7
-	523 K, 90 min, Hydrothermal conditions	Organosolv Lignin	4-ethylphenol, 4-vinylphenol, 4-ethylguaiacol 4-vinylguaiacol	70%	10

Ni-W_2C	4h, hydrogen pressure, 235^oC	Crude lignocellulose	Monophenols	46.5 %	15
NaOH (2% w/w)	300 °C, 250 bar, Boric Acid as capping agent	Organosolv Lignin	Monomers and Oligomers	up to 85% monomer yield (with Boric acid)	17
4-acetamido TEMPO(5 mol%)/ HNO_3-HCl (20 mol%)	1 atm O_2, 45ºC, 24 h	Lignin models + Aspen lignin (S:G 2:1)	Ketones and acids	80-95% for lignin models, not reported for Aspen lignin	21
Methylimidazolium chloride	110-150 °C	Oak Wood Lignin	Phenols, Alcohols, Sugars	(decrease in MW observed)	28
Methylimidazolium diethylphosphate; $Mn(NO_3)_2$	84 x 105 Pa; 24 h, 100 °C	Beech lignin	predominantly 2,6-dimethoxy-1,4-benzoquinone	11.5%	31
Ni-SBA15	0.5h, 150 ^oC, microwave irradiation	Organosolv lignin (O. europea)	35-45	Monomers (mesitol, syringaldehyde, aspidinol, desaspidinol)	33
Ni-Raney + H-BEA zeolite	4 h 150^oC (2h) + 240^oC (2h), alcohols	Organosolv lignin	40-50	78% arenes, 18% alkenes, 4% phenols	34
Ni/C	6h, 200^oC, air, methanol	Birch sawdust	50	Propylguaiacol, propylsyringol	35
Cu-PMO	8-20 h $140\text{-}220^oC$, 30-60 bar hydrogen	Organosolv lignin (A. moluccana)	60-93	Catechol derivates and some oligomers	38
Pd/C	2-24 h, 195 ^oC	Organosolv lignin, wood, steam-exploded fiber	79-89	Dihydroconiferyl alcohol, 4-propylguaiacol, dimers, oligomers	36
1. 1% Pt/Al_2O_3; 2. CoMo/Al_2O_3/Mo_2C /CNF	225 °C (EtOH, H_2O); 300 °C	Organosolv lignin, Kraft, Sugarcane	Alkylated phenol, guaiacol,	11 %, 9%, 5% (organosolv, kraft, bagasse	39

		Bagasse	syringol	respectively)	
Bacterial consortium	30 °C, 15 days	Oil Palm Empty Fruit Bunch Fiber	Monomers	60% (monomers);	45

Future prospects and conclusions

Lignin valorisation methods to produce high added value phenolic compounds have recently attracted a great deal of attention from the scientific community. The present contribution has been aimed to highlight a series of important processes and technologies for lignin depolymerisation that can significantly contribute to a future bio-based economy and discusses several innovative sustainable methodologies for advanced catalysts to be employed in future lignin biorefineries.

Selected examples for this contribution clearly exemplify the challenges and inherent difficulties of deconstructing a complex and highly recalcitrant biopolymer such as lignin. Most catalysts provide the catalytic surface for different bond cleavage to happen either via protonation/deprotonation, nucleophilic attack, hydrogenolysis, etc. In principle, a clear advantage of heterogeneous over homogeneous/IL systems relates to their simple separation and recyclability which however needs to be addressed on a case by case basis depending on conditions and strategies. In fact, only a few selected heterogeneous protocols have been investigated in detail for catalyst stability and recyclability in lignin depolymerisation.[22, 33, 35] Furthermore, the mass transfer from lignin feedstocks to the catalytic surface can be a significant issue and lead to reduced yields to products.[22, 33, 38, 39]

Hydrotreating methodologies have significant potential for future development, particularly with recent reports that large hydrogen pressures in the system do not seem to have any significant influence on lignin depolymerisation yields.[35] These highly controversial findings have to be critically considered and addressed in any reported protocols that use alcohols (e.g. methanol, ethanol, isopropanol, etc.) in conjunction with high temperatures and hydrogen pressures. In any case, several advances have already been reported in the field.

Based on these premises, the complexity of the lignin structure and the production of a mixture that is difficult to purify (e.g. substituted phenols, alcohols, etc) are the main reasons why lignin biorefineries are not yet established. [5, 7, 12, 38] We believe that the current direction towards the development of a lignin-based biorefinery should fundamentally address an efficient separation and/or purification (both green and not energy intensive) and diversification towards chemical and fuels as end products from lignin If current separation methods are employed, the entire process will be very costly One possibility to perform a good separation is through supercritical fluid extraction.[14]

Another challenge relates to the fact that most products of lignin depolymerisation are highly oxygenated species. Because of this, the energy potential of these compounds is generally low enough so that they cannot be directly used as fuels. Methods mentioned in the previous sections show that depolymerisation and hydrodeoxygenation can be performed at the same time. However, based on the profile of the product mixtures formed, oxygenated products still dominate the reaction mix. The way forward in future research certainly relates to the development of advanced catalytic tandem reaction systems by combining more efficiently depolymerisation and deoxygenation steps. [33, 38, 39]

Another important issue to address relates to the critical point of the selectivity in hydrotreating processes to perform lignin depolymerization and C-O bond hydrogenolysis without reducing the aromatic core. Under high hydrogen pressures and high temperatures, noble metal-based catalytic systems are well known to fully hydrogenate the aromatic rings in lignin-model compounds leading to cyclic alcohols and cycloalkanes.[49] However, different designer catalytic systems based on comparatively cheaper and active transition metals (e.g. Ni) have been reported to selectively cleave C-C and C-O bonds in lignin without affecting aromatic rings.[22, 33-35] On the other hand, process engineering and design towards mild depolymerisation conditions (e.g. low temperatures, ambient/low pressures) and process intensification (i.e. continuous flow reactions) can offer more controllable systems in which activities can be fine-tuned depending on the designed catalytic system.

In the light of these premises, it is clear that 1) the design of advanced materials based on cheaper, more selective and water tolerant transition metal containing catalysts (e.g. Ni) and 2) processes under mild reaction conditions and low hydrogen pressures (e.g. hydrogen-transfer) can be the way forward to control C-C and C-O bond cleavage and hydrogenation processes in hydrotreating systems.[7, 22, 33]

Lignin recovery and valorization may only effectively reach the market if a cheap, efficient and green protocol is developed for lignin depolymerisation if: 1) an advanced deconstruction method with high efficiency is developed ; 2) an effective and cost-competitive separation/purification/isolation of valuable products is proposed; 3) relatively mild reaction conditions are used; and 4) a scalable continuous flow process is used with the possibility to diversify between end products (as in a biorefinery concept).

Regardless of the industrial benefits of the implementation of lignin biorefinery concepts, which we might only see on a longer term basis, we hope this contribution can serve as a momentum and stimulus to both academia and industry (e.g. pulp and paper companies) to join efforts in promoting joint ventures for lignin deconstruction with a potential for additional revenues in industrial facilities. Scientists around the world should also join forces in this fascinating crusade of lignin depolymerisation aiming to set multidisciplinary teams to come up with more innovative solutions for a betterment of future generations.

Acknowledgments

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