

Green Chemistry

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CRITICAL REVIEW

Lignin Transformations for High Value Applications: Towards Targeted Modifications Using Green Chemistry

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Lignin represents a considerable source of renewable and bio-based carbon. Pulping processes enable lignin, together with all components of the lignocellulosic biomass, to enter valorizable streams. A current key objective is to further valorize this versatile aromatic biopolymer, and for that, to go beyond its mere energy use. Despite the emergence of numerous proposals for value-added products coming from lignin, most of them remain at the research stage. The main challenges arise from the complexity and heterogeneity of the lignin structure and resulting molecular properties, the variability of biomass source, pre-treatment processes, growing environment. Keeping in mind that future integrated biorefineries must take into account environmental concerns, lignin processing in accordance with green chemistry principles should first be favoured. From this very perspective, this work proposes to review the most promising current routes towards fractionation and/or depolymerization of lignin. Those should represent sustainable treatment technologies potentially leading to a broad spectrum of marketable lignin-based molecules and products. First, lignin fractionation by selective precipitation using pH as well as green solvents, or by using membrane technologies will be addressed. Then lignin depolymerization will be discussed at length, notably from a catalytic point of view and by hydrogenolysis; the knowledge about the fundamental chemistry stemming from the use of model compounds will be described. Substitution of organic solvents with environmentally harmless supercritical fluids or with negligible vapour pressure ionic liquids is of great interest to modify lignin, and is finally reviewed. Lastly, challenges for integrated biorefineries and for launching new lignin-based compounds and products will be discussed.

1 Introduction

1.1 Lignin and green chemistry

The sustainable production of energy, fuels, products and chemicals from renewable raw materials remains a challenge.^{1–3} Lignocellulosic biomass, including hardwood, softwood and grasses, are an abundant renewable resource mainly composed of cellulose, hemicelluloses and lignin. They constitute a promising alternative to petrochemical fossil resources for the production of biofuels and bio-based products.⁴ The first steps of biorefinery processes are centred on the extraction and recycling of cellulose (into fermentable glucose). These processes used in the production of chemicals or bioenergy leave notably degraded lignin recovered as side-products.⁵ In addition to the steadily increasing second generation biorefineries, the pulp and paper industry extracts cellulose and generates large amounts of technical lignins, mainly

burned in industrial boilers and whose potential is not fully exploited.^{6,7} As a renewable and functionalized resource, however, lignin utilization offers potential in a wide range of industries.

Three major ways of lignin valorization have been considered and investigated: (i) the energy path through power production, green fuels or syngas; (ii) the use as macromolecule; (iii) the production of aromatic compounds for the chemical industry.⁸ Over the past few decades, research on the production of value-added platform or specialty chemicals and alternative fuels from lignin has grown rapidly on account of the importance of lignin in biorefineries. Lignins have found potential applications, either after chemical modifications or as retrieved, as biodispersants, in wood panel products, as emulsifiers, in carbon fibers,⁹ polyurethane foams, automotive brakes, polymer modifiers, adhesives, binders, and epoxy resins for printed circuit boards. They can also be utilized in industry as the principal component of thermoplastic materials.^{4,8} Within the biorefinery context and for economic reasons, the recovery and the non-energetic transformation of lignins have opened up new opportunities. Lignin depolymerization and conversion has a significant potential as a sustainable source for the production of fuels and bulk chemicals, and so as a direct alternative to the petrochemical industry. With its unique polyaromatic structure, a wide variety of bulk and fine chemicals can potentially be obtained from lignin. Those are aromatic compounds as well as fuels that spread on a wide range of market

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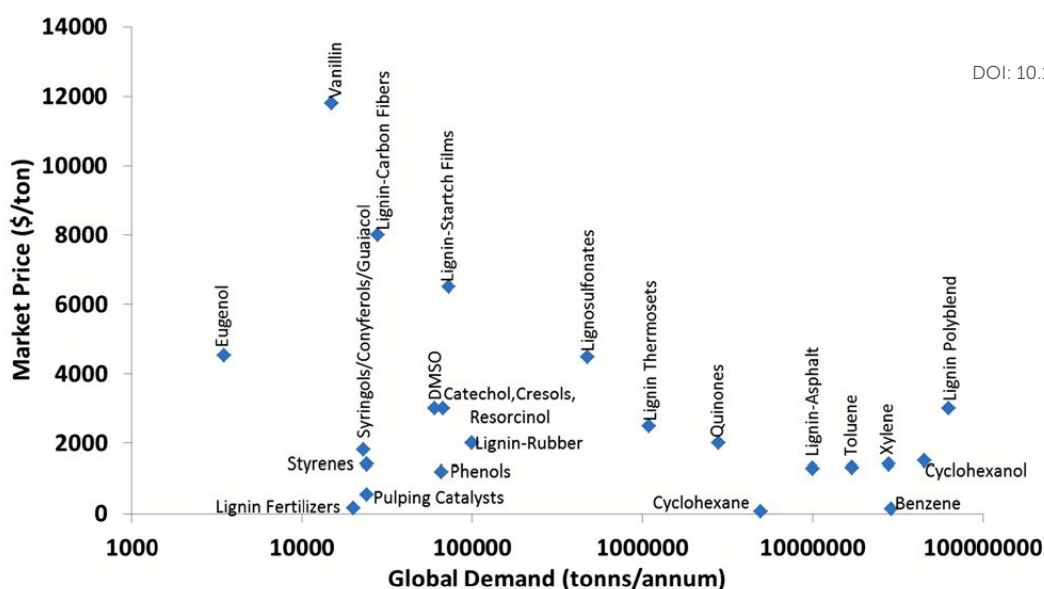
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Fig. 1: Market price vs. demand for lignin. From Varanasi et al.²

demand and prices (Fig. 1), making lignin the major aromatic resource of the bio-based economy and a major challenge for second generation biorefineries of the future. The development of biorefineries is a response to the environmental and sustainability problems encountered by our civilizations. It would therefore be inappropriate to develop this industry through processes – certainly more profitable in the short term but – more polluting, energy-consuming and dangerous. New properties and applications as well as the research of new markets for lignins-derived products consistent with green chemistry principles¹⁰ are therefore capital opportunities to develop a more sustainable chemical industry.

1.2 Chemistry of lignins

In plant cell walls, lignin fills the spaces between cellulose and hemicellulose, acting like a resin that holds the lignocellulose matrix together. Cross-linking with the carbohydrate polymers confers strength and rigidity to the system.¹¹ Lignin is a three-dimensional amorphous polymer consisting of methoxylated phenylpropane structures, and it can thus be regarded as the only abundant source of aromatics found in nature. It is widely accepted that lignin

composition and its content in biomass differ between the types of plants and also between the botanical species and even between trees and morphological parts of the tree. For example, lignin accounts for 30% by weight in softwood, while this share falls to 20–25% in hardwood. Grass lignin only shares 10–15% of the total plant mass.⁴ Lignin biosynthesis follows the phenylpropanoid pathway and is produced by the oxidative polymerization of monolignols catalyzed by laccase, an enzyme containing a copper ion in its reactive centre.¹² Many authors have been interested in this mechanism in order to modify the molecular structure of lignin. Bioengineering of lignins has recently been the subject of a review.⁷ Lignin is composed of three primary units: sinapyl (3,5-dimethoxy-4-hydroxycinnamyl), coniferyl (3-methoxy-4-hydroxycinnamyl) and p-coumaryl (4-hydroxycinnamyl) alcohols, linked through ether and C–C bonds. These three monolignols are also known as syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units, respectively. They all contain a phenyl group and a propyl side-chain; therefore, the typical aromatic unit in lignin is generally called a phenylpropane unit (ppu). These monolignols differ in the number of methoxy groups that are attached to the aromatic moiety; that is, sinapyl alcohol has two methoxy groups, coniferyl alcohol has one methoxy group, and p-coumaryl alcohol has none. The content of each

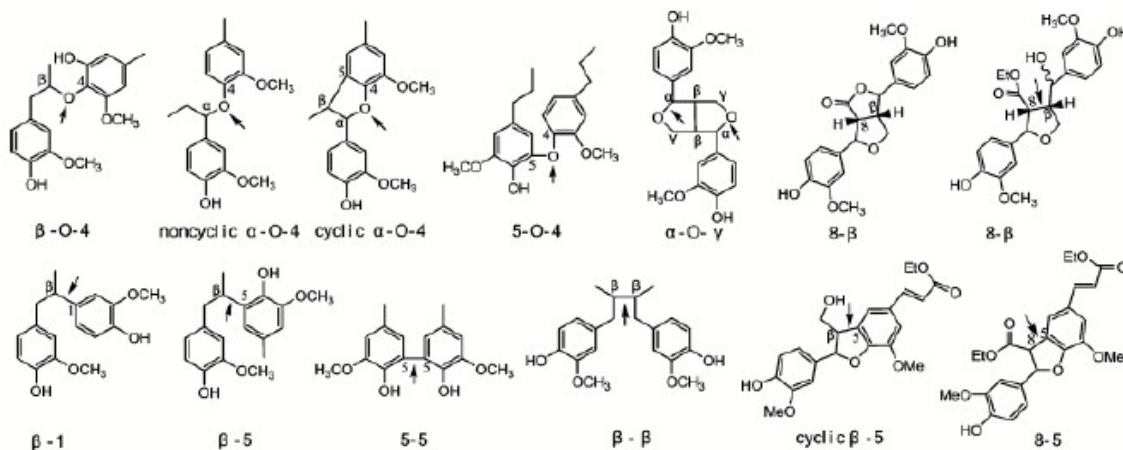


Fig. 2: Typical linkages between the primary units of lignin.

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monolignol in lignin is related to plant taxonomy. Based on the abundance of the three basic units in lignin, these polymers can be classified as G-type (softwood lignin - gymnosperm), GS-type (hardwood lignin - angiosperm), HGS-type (grass lignin), and HG-type (compression wood lignin).¹³ Unlike most natural polymers, lignin molecules are extremely complicated due to their natural variability. Lignin cannot yet be isolated in its native unaltered state and therefore the structure of proto-lignins are still relatively unknown.³ Its structural representations have relied upon the analysis of soluble lignin-derived preparations, such as milled wood, dioxane and kraft lignins.¹⁴ It should be noted that, besides the three primary building blocks of H, G, and S units, some other molecular species can also participate in the formation of the lignin polymer. Non-canonical subunits that have been identified include ferulates (which form linkages between hemicellulose and lignin), coniferaldehyde, sinapaldehyde, 5-hydroxyconiferyl alcohol, and acylated monolignols containing acetate, p-hydroxybenzoate, or p-coumarate moieties.¹⁵

Lignin monolignols are predominantly linked either by ether or by C-C bonds. In native lignin, two-thirds or more of the total linkages are ether bonds, while the other linkages are C-C bonds.

In order to categorize the various types of linkages between two monolignols, the carbon atoms in the aliphatic side chains of the monolignols are labeled as α , β , and γ and those in the aromatic moieties are numbered from 1 to 6. For instance, a β -O-4 linkage represents a bond formed between the β -carbon of the aliphatic side chain and the oxygen atom attached to the C4 position of the aromatic moiety. The major linkages between the structural units of lignin are β -O-4 (β -aryl ether), β - β (resinol), and β -5 (phenylcoumaran). Other linkages include α -O-4 (α -aryl ether), 4-O-5 (diaryl ether), 5-5, α -O- γ (aliphatic ether) and β -1 (spirodienone), etc. (Fig. 2).

1.3 Sources of lignins

The conversion of lignin into valuable products is one way to unleash lignin's potential. There are different sources of lignins as raw materials that can be incorporated into complex transformation processes. These "bulk" lignins originate from the current industry (and mainly from the delignification processes of paper and pulp industry), but in the future they could also come in larger amounts from second-generation biorefineries whose objective is the valorization of all the flows of matter extracted from lignocellulosic biomass (cellulose, hemicellulose and lignins). Technical lignins have been described exhaustively¹⁶ and they can be considered as a potentially interesting raw material, since they are produced in processes dealing with the treatment of lignocellulosic materials. Many technical lignins are readily available in large amounts, such as those obtained from the paper industry (kraft lignin, lignosulphonates and soda lignin). As of 2004, the pulp and paper industry alone produced 50 million tons of extracted lignin. However, by 2010 only approximately 2% of the lignins available (by weight) from the pulp and paper industry was used commercially with the remainder burned as a low-value fuel.¹² In contrast, hydrolysis, organosolv, and ionic liquid lignins constitute currently only a small part of potentially valuable lignins, but are more amenable to valorization processes, thus of higher value (Fig.

3)^{16,17} and with a higher expected growth rate in the future, notably via the development of second generation biorefineries. Lastly, lignin can be utilized in its natural form, proto-lignin, when reacted within raw lignocellulose, without prior pre-treatment to separate out the carbohydrate polymers.

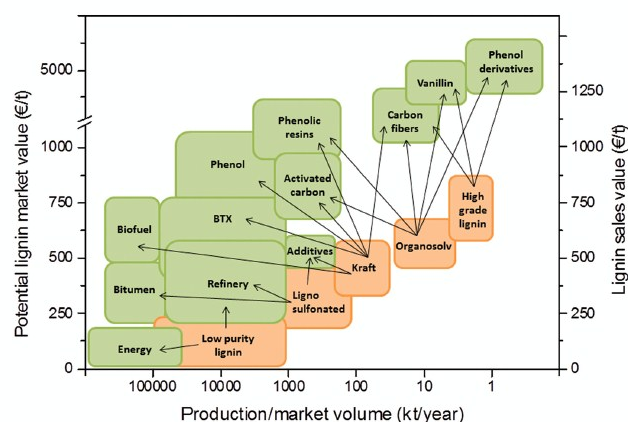


Fig. 3: Potential market value for lignin-based products (orange) and corresponding value-added chemicals (green). From Behling *et al.*¹⁹

1.3.1 Kraft Lignins

Kraft lignin is produced through the sulphate cooking process that entails treating the wood fibers with sodium hydroxide and sodium sulphite at temperatures of 165-175°C for 1-2 hours^{4, 11, 18}. It constitutes about 85% of total world lignin production.¹⁹ During cooking, around 90 to 95% of the lignin contained in the wood is dissolved in the aqueous solution of sodium hydroxide and sodium sulfide.²⁰ Although the Kraft process generates millions of tons of lignin per annum, the process is highly energetically integrated within the pulp process such that paper generation currently depends on lignin as fuel for process heating¹¹. The structural changes in proto-lignin resulting from the Kraft process involve the introduction of thiol groups, stillbene as well as carbohydrate linkages, and the cleavage of β -ether bonds. The resulting lignins contain a high abundance of recalcitrant C-C bonds and phenolic units relative to native and Organosolv lignins¹⁸. Kraft lignin is contaminated with a significant amount of carbohydrates and fatty acids, as well as sulphur (1-3%) as thiol groups¹⁸.

1.3.2 Soda Lignins

Soda lignin originates from soda or soda-anthraquinone pulping processes. Soda based cooking methods are used mainly for cooking of annual crops such as flax, straws, bagasse, and, to some extent, hardwoods.²¹⁻²³ The main difference in comparison to the kraft process is the sulphur-free medium of the cooking liquor.²⁴ The feedstock is digested at 413 – 443 K with aqueous sodium hydroxide, sometimes in the presence of anthraquinone to enhance the stability of the carbohydrates¹⁸. This process effects partial proto-lignin degradation by β -O-4 bond breaking⁴. Resulting lignins from this process have molecular weights 1000-3000 Da, and is usually considered relatively free of impurities (since few additives are utilized)¹⁸.

1.3.3 Lignosulphonates

Lignosulphonates are water-soluble anionic polyelectrolytes that contain a large number of charged groups. Lignosulphonates are obtained as the by-product of sulphite cooking, in which delignification of wood is performed by means of HSO_3^- and SO_3^{2-} ions.^{25, 26} During this process, lignin is sulphonated, degraded, and dissolved. Lignosulphonates are produced in relatively large quantities, around 1 million tons per year as dry solids.^{26, 27} Lignosulphonate lignins usually exhibit a higher average molecular weight than Kraft lignins due to the incorporation of sulphonate groups on the arenes during the process (3–8%)¹⁸. This addition onto lignin makes it a harder substrate for catalytic transformations¹⁸. Furthermore, the sulphite pulping processes involves the cleavage of labile ether bonds (usually targeted in lignin valorization methodologies), loss of methoxyl groups and formation of carbon-carbon bonds⁴. Finally, it should be noted that lignosulphonate lignins often contain up to 30wt% of impurities, ash or remaining carbohydrates¹⁸.

The variety of functional groups on lignosulphonate lignins (phenolic, carboxylic groups, and sulphur containing groups) imply various depolymerisation strategies, and provide unique colloidal properties which allows applications such as dispersing agents, surfactants, adhesives, etc¹⁶. Lignosulphonate lignins are valorized successfully to generate vanillin^{28, 29}.

1.3.4 Organosolv Lignin

In the organosolv pulping process, a mixture of organic solvent/solvents and water is used as a cooking medium²⁴ where organic acids such as H_2SO_4 , HCl, acetic acid, formic acid or peroxyorganic acids can catalyze hydrolysis.³⁰ The most commonly used solvent is ethanol.³¹ Some of these organosolv pulping processes have been commercially registered (FormicoFib®, Alcell®, Acetosolv®, Organocell® and ASAM®) and implemented at industrial scale.^{24, 31–33} The main advantage of the organosolv process is that it forms separate streams of cellulose, hemicelluloses, and lignin, allowing potential valorization of all components of lignocellulosic biomass. The process is generally considered environmentally friendly because it does not use the sulphides and harsh conditions of the kraft or lignosulfonate processes. The resulting lignins have moreover typically very low contents in sulphur and are of higher purity than lignin obtained through other methods, which is a great asset for its valorization to high-value chemicals. Carbohydrate-lignin α -O-4 bonds are broken during pulping, as well as β -O-4 bonds to a small extent.¹⁸ Slight formations of new C-C bonds are observed in resulting lignins, as well as alkoxylation at side chain α -positions. The organosolv lignins eventually lead to generation of low molecular weight lignins. Organosolv lignins are insoluble in water, and hydrophobic.¹⁶ The major disadvantage of this process is the high cost of solvent recovery.^{11, 30}

1.3.5 Ionic-Liquids for Lignin Isolation

There is a growing interest in utilization of ionic liquids for the processing of biomass. Ionic liquids have been described as “green” solvents, being comprised as organic salts that remain as liquids at room temperatures and possess negligible vapour pressure.^{34, 35} Several ionic liquids have been found to be able to fractionate lignocellulosic materials^{36–41} and some biorefinery concepts propose the use of ionic liquids.^{42–44} Lignin from ionic liquids, is not yet available on industrial scale, but has shown potential in applications analogous to those of organosolv and soda lignins¹⁶.

Thus, in addition to an available and low-value by-product of the paper industry that needs to be valorized, lignin can also be considered as a source material whose potential must be fully exploited by biorefineries. Therefore, the pretreatment of lignocellulosic biomass is an important initial step in biorefinery operations. Efficient biomass fractionation is one of the major challenges for the biorefinery, because the complex structure of the plant cell wall and the high crystallinity of cellulose make the feedstock recalcitrant to separation into its components. It is important to stress that the structure of the isolated lignin stream is dependent on the extraction method employed and consequently, affects the types of high-value products obtainable from biomass.¹¹ Sustainable and economic extraction/pretreatment methods that result in consistent types of lignin with high quality and purity are contemporarily highly desirable for integrated biorefinery processes.

1.4 Strategies for lignin transformations

The lignin polymer is susceptible to a wide range of chemical reactions to form valuable products. Apart from its valorization as a polymer or material, lignin can undergo depolymerization reactions towards small molecules with added value. Reactions can be mainly divided into thermal treatments (pyrolysis/gasification), acid/base (neutral) reactions, reduction reactions, and oxidation reactions (Fig. 4). The different conversion pathways of lignins are described in detail in a review published by Pandey and Kim.⁴⁵

Considering lignin as the most abundant renewable source of aromatics, its depolymerization into small aromatics could serve as a ‘drop-in’ replacement to the petrochemical industry. Most studies on the subject aim to depolymerize and to deoxygenate lignins to convert them in sparingly substituted aromatic monomers (such as benzene, toluene and xylenes BTX) which can be directly incorporated in the conventional production cycles of the chemical industry⁴⁶ and resemble fossil fuels.³⁰ It should be noted, however, that biomass is highly functionalized, explaining its poor fuel characteristics. Thus, reducing biomass to fuel-like hydrocarbons in order to burn those, or in order to re-functionalize using known routes, is a waste of energy and means. Rather, sustainable valorization of lignin would allow to harness the inherent functionality of lignin by generating functionalized aromatics.

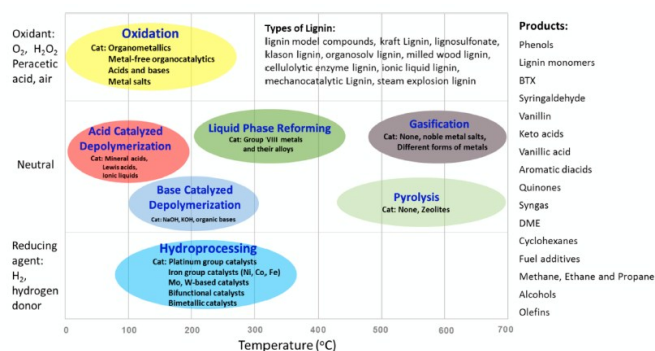


Fig. 4: Summary of processes for conversion of lignin. The abscissa represents the typical temperature range of the lignin conversion processes. Reprinted with permission from Li, C. et al., *Chem. Rev.* 2015, 115 (21), 11559-11624. Copyright 2017 American Chemical Society.³

In most of the oxidative treatment of lignin, a radical chemistry mechanism plays an important role in the production of functionalized aromatics. Oxidation reactions occur at low temperatures, between 0 and 250 °C. They favour the production of aromatic alcohols, aldehydes and acids that are usually target fine chemicals or platform chemicals. Currently, the most significant commercial depolymerization of lignin is performed by the company Borregaard, in Norway, through catalytic oxidation of lignosulfonates to produce vanillin. Syringaldehyde is also often obtained from oxidative depolymerisation of lignin, and is an important precursor in the pharmaceutical industry.⁴⁷ However, oxidation methods suffer poor selectivity due to the difficulty of controlling radical chemistry and repolymerization is also favoured under these conditions.⁴⁸ Lignin heterogeneous catalytic oxidation has recently been extensively reviewed by Behling *et al.*¹⁷

Biocatalysis has also been tested to degrade lignin in an environmentally friendly way. The three main lignin-degrading enzymes are manganese peroxidase, lignin peroxidase and laccase and all function by oxidative treatment.⁴ Van de Pas *et al.*⁴⁹ submitted chemically fractionated lignins to reactions with fungal laccases in order to polymerize small fragments and to modify their surface properties. Laccases are copper-containing enzymes that are able to oxidize phenolic compounds and notably lignins. Whereas laccases naturally contribute to degrade lignin in biomass by depolymerization,⁵⁰ they rather lead to polymerization when applied on concentrated phenolics, through the generation of phenoxy radicals.⁵¹ Indeed, laccase activity on lignin model compounds was investigated⁵² and the potentialities of this enzyme process to obtain various functionalized high-value lignins were reported.^{53, 54} Despite the attractiveness and demonstrated promises of enzymes in lignin modifications at the laboratory, large scale processes remain a challenge. The right enzyme or combination of enzymes require further study. Moreover, the production of laccases would remain a bottleneck towards implementation of viable large scale processes. Combining solvent fractionation of different lignins with further enzyme treatments has been reported. Laccases may be used to modify the physical and chemical properties of lignin through oxidation of its constitutive phenolic compounds,⁴⁹ however this topic that comes under the field of white biotechnology will not be addressed here.

Other technologies, such as pyrolysis of lignin (typically at 450-700 °C) are based on a radical mechanism to produce a liquid product known as “bio-oil”. Liquid-phase reforming (typically at 250-400 °C) has been attempted for lignin conversion in which hydrogen and light gases were produced from the lignin. Gasification is the process that creates synthesis gas (CO and H₂) from a range of real lignin feedstocks and model compounds. Although pyrolysis and gasification have the advantage of being applicable to a wide range of different lignins, the variability of products obtained from these processes is limited and possess minimal value addition potential. Moreover those processes are highly energy intensive.

Depolymerization reactions catalyzed by both acid (typically at 0-200 °C) and base (100-300 °C) break the C–O or C–C linkages between lignin units to offer small segments including monomeric phenols. Ionic liquids and supercritical fluid treatments of lignin have harnessed the basic or acidic properties of these solvents to simultaneously utilize them as catalysts and depolymerize lignins. Integration of these strategies with hydroprocessing or oxidation can be attempted for lignin conversion.

Hydroprocessing involves thermal reduction in the presence of a hydrogen source at temperatures typically ranging from 100 to 350 °C in the presence of a catalyst. The major challenge with this strategy lies in selectively cleaving inter-unit lignin C–O and C–C bonds versus hydrogenating the aromatics, which would be a waste of reducing equivalents. Thus, development of technical and cost-effective depolymerization strategies with new, selective and robust catalysts specifically designed for lignin has now attracted ever-increasing attention. A lot of research has also been devoted to hydrodeoxygenation of generated aromatics from lignin, involving the removal of the extensive functionality of the lignin subunits to form simpler monomeric compounds such as phenols, benzene, toluene, or xylene (BTX). These aromatic compounds can then be hydrogenated to alkanes or used as platform chemicals in the synthesis of fine chemicals through technology already available in the petroleum industry.¹¹ Furthermore, the use of a reducing environment has the advantage of quenching any generated radicals in situ, thus preventing undesirable repolymerization and charring. The increased selectivity from these approaches removes the necessity of purifications and increases process sustainability. Although hydroprocessing of lignins already shows a lot of potential towards generating industrially relevant processes, the applicability of catalytic methods to the wide range of lignin molecular properties remains a challenge. Fundamentally, there remains a lack of understanding of mechanisms leading to lignin depolymerisation. Technically, lignin insolubility in most organic solvents prevents reaching mechanistic understandings, but also limits the applicability of known chemical transformations. The source of hydrogen is also a major concern in hydroprocessing technologies, since most is still currently obtainable from the petroleum industry and thus non-renewable. The use of ionic liquids (as both solvent and catalyst) and the performance of supercritical fluids, in particular of reforming alcohols, in lignin depolymerisation have the potential to solve the aforementioned problems.

Whereas several pathways for lignin valorization exist as evidenced above, perhaps a more rewarding strategy would involve the consideration of the entire system, rather than viewing lignin as a

simple starting material to be transformed. Lignin should instead be considered as one interlinked component of complex systems that are future bio-refineries. In addition, increasing concern with environmental externalities and dwindling fossil resources reinforce the necessity of reaching such sustainable systems via the application of the principles of green chemistry.

In this context, two promising approaches retain our attention. First, an approach that already demonstrates a lot of potential is the 'lignin-first' strategy – whereby lignin is valorized from raw lignocellulose directly, rather than from isolated lignins resulting from other carbohydrate valorization processes (such as the pulp and paper industry). This approach is promising as lignin is attacked in its proto-lignin state, thereby reducing the potential variability in lignin structure, limiting the amount of catalyst poisoning impurities and simplifying lignin-product yield and composition. Surprisingly, however, very few efforts have focused on the tandem delignification-depolymerization of lignin in unfractionated lignocellulose.

Overall, a lignin-first strategy making use of catalytic hydrogenolysis shows promise for utilization within an integrated bio-refinery, with high lignin monomer yields, often enhanced product selectivity, and a processable versatile carbohydrate pulp. A lignin-first valorization process with reasonable energy inputs that uses economic and abundant catalysts and provides full delignification with a selective product distribution, and that is applicable to various biomass sources, however, has still not been realized. We believe the use of supercritical fluids and ionic liquids should prove extremely useful in combination with hydroprocessing technologies to generate even more sustainable and efficient lignin-first technologies.

Since lignin-first methodologies are still in development stage, a second important approach towards the valorization of lignin will reside in novel sustainable fractionation methodologies. As such, disperse technical lignins can be refined towards reproducible smaller and cleaner lignins, which undergo more facile depolymerisation towards target molecules.

We will thus first review sustainable fractionation technologies for lignin, then focus our investigations on mechanistic details of hydroprocessing technologies, along with the use of supercritical fluids, and finally the utilization of ionic liquids as both solvents and catalysts in lignin valorization.

2 Fractionation by ultrafiltration and by selective precipitation

Lignin varies across feedstocks in amount and in the ratio of H/G/S subunits in the polymer. Moreover, depending on many factors, individual biorefineries may target different arrays of products in addition to fuels and thus use different, and possibly changing, biomass processing schemes.⁵⁵ Whatever the pulping or biorefinery process, the resulting effluents contain dissolved lignin as a complex polydispersed mixture of high molecular weight heteropolymers fragmented at varying degrees, with uncertain reactivity. According to the physico-chemical parameters used, fragments may recombine through condensation reactions to form

molecules with higher mass,⁵⁶ adding to the already wide distribution of the molecular masses within a lignin fraction. Such variability and heterogeneity restricts the options for high value applications of lignin,⁵⁷ since the chemical industry is built largely on the use of uniform and consistent raw materials. Indeed specific properties intended for designated uses are more likely to arise from polymers with narrow mass distribution around a specific average value.⁵⁸⁻⁶²

So technologies will need to be developed to precondition lignin to make its properties and reactivity patterns more stable, consistent, and uniform. Advanced separation technologies for lignins based on size-selective or functional group-selective processes are therefore needed both for upstream separation of lignin from biomass and downstream separation of lignin products.

One challenging approach would be to separate lignin used for production of chemicals from the biomass early in biorefinery operations, using mild methods to conserve the structure.⁸ Different purification and fractionation soft processes may be applied to technical lignins in order to target specific average molecular masses and to reduce the polydispersity, enabling the supply of more standardized flows of material to the chemical industry. Fractions with narrow lignin populations may find applications as such in various sectors, but they can also be an important source of raw material for further reactions, notably depolymerization.

2.1 Fractionation by precipitation with pH

Pulping black liquors contain high amounts of lignin dissolved in a dark aqueous solution, which is highly alkaline due to the salts from the process. Other processes may also involve alkali-extraction of lignins from wood⁶² and non-wood biomass.^{57, 63-65} A convenient and common method to recover the lignin is to precipitate it by acidification. This can be achieved using carbon dioxide,⁶⁶ phosphoric acid,⁶⁴ sulfuric acid,^{62, 63, 67} hydrochloric acid,⁵⁷ acetic acid⁶⁴ or spent acid from chlorine dioxide generation.⁶⁸ Once precipitated, the lignin can be recovered by mechanical filtration and then washed until the desired purity is reached. In order to avoid redissolving solid lignin, the washing solution should not have a pH higher than the one reached during precipitation in the black liquor.⁶⁹

Lignin dissolves very well at alkaline pH due to the ionization of its weakly acidic phenolic and carboxyl groups, whose negative charges create electrostatic repulsion between molecules. Decreasing the pH of the liquor will progressively protonate these groups, which will gradually lower the existing electrostatic interactions within the aqueous solution. Concurrently van der Waals and other hydrophobic forces will dominate, leading to a progressive self-aggregation of the lignin macromolecules, and consequently to a colloidal precipitation.^{70, 71} The addition of acid will progressively increase the bulk of precipitated lignin and the mass recovered will follow a sigmoid shape against pH resembling a titration curve.^{63, 72} For instance, decreasing the pH of brewer's spent grain black liquor to 2.15 with concentrated sulfuric acid, resulted in the recovery of 81.4% of the lignin.⁷² The final precipitation pH affects not only the amount of recovered lignin, but also the characteristics of the

product, such as the molecular mass distribution, the composition and namely the content in hydroxyl groups, and the resulting physical properties.⁶⁴ It was reported that the content in methoxyl groups in softwood kraft lignin decreases with the yields of precipitated lignin.⁷³

Carbon dioxide can be used to decrease the pH in black liquors. The gas can be sparged into the kraft cooking liquor⁷⁴ or applied pressurized in a vessel,⁷⁵ enabling to reach a pH around 9.5. Thus only a small part of the total lignin is precipitated and it appeared to be of high average molecular mass. As a general rule, larger lignin molecules have a lower solubility and higher pKa values, and they precipitate first when the lignin loses stability.⁷⁰ So the average molecular mass of the recovered lignin should decrease with the precipitation pH, and at the same time the dispersity should increase. However in practice, such a decrease was not clear neither on black liquor of oil palm empty fruit bunch fibre pulping⁶⁴ nor on black liquor from *Miscanthus sinensis* soda pulping.⁶³ According to the latter, it may be explained by a recovery of impurities such as hemicelluloses and silicates present in the raw material.

Together with pH, lowering temperature or increasing ionic strength also lead to higher lignin recovery yields.^{73, 76} So, adding acid to strongly alkaline black liquors until the pH reaches a determined value constitutes a simple way to selectively precipitate lignin and so to fractionate the broad range of molecules. The mass yields increase with the dispersity of the final product, and concurrently the specificity of the lignin obtained decreases. The fractions thus obtained may exhibit varied polymeric structures and composition, and even different macromolecular aspects, such as the color.^{63, 72}

Based on pH-mediated precipitation, a process was developed and a demonstration plant was set up. This so called LignoBoost Process consists of the acidification of black liquor with CO₂ then the filtration of the recovered lignin and its washing after re-dispersion.^{76, 77} However here the lignin obtained is to be used as a biofuel, more efficient than the black liquor.⁷⁸

2.2 Membrane technologies to recover lignin populations

Membrane technologies are a convenient and non chemical-consuming mean to reach a mechanical separation of lignin from industrial black liquors. Together with their low energy needs and their excellent fractionation capability, membrane processes have the qualities to become key separation units in biorefineries.^{79, 80} Thus, ultrafiltration allows selective extractions of lignin fractions with specific thermo-mechanical properties, which can be matched to the intended end uses.⁸¹

Ultrafiltration membranes may be used for lignin extraction directly from black liquors, without any prior treatment or pH and temperature alterations.⁸²⁻⁸⁴ Besides separation of lignin and cooking chemicals, the membrane cut-off offers the possibility to control the molecular mass of the lignin fraction recovered. Ultrafiltration and nanofiltration membranes have been tested in the last decade to isolate kraft lignin, whereas ultrafiltration has been used to isolate lignosulfonates from spent liquor in sulfite pulp mills for decades.^{59, 85} Such membranes can be made of

polystyrene, of polyethersulfone,⁶⁵ or of ceramic⁸⁰ with different cut-offs, enabling to fractionate the lignin into a high molecular mass retentate, and a lower molecular mass permeate.

Using a ceramic membrane with a cut-off of 15 kDa on kraft black liquors at a high flux, retention of 35% of the total lignin was achieved.⁸⁶ When tested on the black liquor taken directly from a continuous digester, *i.e.* at 145 °C, ceramic membranes (15 and 5 kDa cut-offs) exhibited higher fluxes, but the retention of lignin was lower than below 100 °C.⁸² Applying membranes with a cut-off of 15 or 5 kDa to process industrial black liquors from spruce/pine, birch and *Eucalyptus globulus*, yielded permeates which, for each wood species, gave lignins lowly contaminated with carbohydrates and ash.⁸⁷ A hybrid ultrafiltration/nanofiltration process for hardwood black liquor was tested.⁷⁹ More precisely, the permeate from ultrafiltration (performed at 90 °C) with a 15 kDa cut-off ceramic membrane, was concentrated by nanofiltration (at 60 °C, due to limited chemical stability of the membrane) with a 1 kDa cut-off polymeric membrane. Most of the hemicellulose was retained by the ultrafiltration membrane, yielding a permeate with a minor amount of xylan, the major hemicelluloses component in hardwood pulping liquor. Furthermore, concerning the hemicellulose present in black liquor, it was shown that lowering beforehand its content reduced considerably the filtration resistance.⁷⁷

The efficient fractionations of kraft lignin reached by ultrafiltration, lead to clear differences in composition and physico-chemical properties of the fractions obtained. Besides the neat differences in polymer mass distribution, low-molecular mass fractions accumulate sulfur-containing compounds and they tend to contain more phenolic hydroxyl groups, and fewer aliphatic hydroxyl groups. The thermo-mechanical properties (notably glass-transition temperatures) of these lignin fractions were shown to vary accordingly to their average molecular mass.⁸¹

The main issue with using membranes to recover lignin is the fouling that occurs quite fast.⁸⁸ So the maintenance has to be meticulous and steady cleaning cycles have to be planned. A convenient methodology is to rinse first with an available cheap alkaline solution (for instance the permeate), then thoroughly with

an alkaline cleaning agent and finally with water.^{80, 84} The cost estimates of kraft lignin recovery by ultrafiltration using ceramic membranes⁸⁵ evidenced realistic prices in line with medium- to high-value-added lignins. And this, taking into account the membrane costs, lifetime and cleaning.^{77, 81, 83} The production costs of the combined ultrafiltration/nanofiltration proposed by Jönsson *et al.*⁷⁹ were equivalent to those of an ultrafiltration alone (33 € per ton of lignin in 2008). So, these economical aspects indicate seemingly good prospects for industrial applications of this technique.

2.3 Fractionation in green solvents

Green solvents should minimize the environmental impact resulting from their use in a process. In order to measure the "greenness" of solvents (or solvent mixtures), Capello *et al.*⁸⁹ proposed a framework combining the assessment of potential hazards of chemicals with the quantification of emissions to the environment as well as resource use over the full life-cycle of a solvent (*i.e.* life-

cycle assessment). Thus it was established that methanol, ethanol or alkanes (heptane, hexane) are environmentally preferable solvents, whereas the use of dioxane, acetonitrile, acids, formaldehyde, and tetrahydrofuran is not recommendable. Moreover based on a solvolysis case study, methanol-water or ethanol-water mixtures appeared favourable compared to pure alcohol or propanol-water mixtures.⁸⁹

Standing as an alternative to kraft pulping, although it has been operating on a smaller scale, the Alcell® process is an ethanol-water solvent pulping of hardwood. It generates sulphur-free lignin and it appears to be an environmentally friendly process. However the so-called Alcell® lignin is a heterogeneous mixture with a rather broad molecular weight distribution. So, as with lignins from other processes, an efficient solvent fractionation may be reached only by additional extractions on the recovered lignin.⁶⁰ Lignin fractions may be extracted with solvents of increasing hydrogen-bonding capability. More precisely, lignin dissolved in a polar solvent can be progressively precipitated upon gradual additions of a selected miscible but nonpolar solvent.⁹⁰ The limitations here come from the straight set of available solvents offering only few possibilities of fractionation: this was rectified to some extent by using solvent mixtures between two successive extraction steps with two different solvents.^{45, 86}

Solvent extraction was found to fractionate lignin according to the molecular mass: low molecular-mass lignin is dissolved in the organic solvents, whereas the higher molecular-mass lignin is not. For instance, isolated acetone fractions of lignin were rather homogeneous with narrow molecular mass distributions.⁹¹

The different works on lignin extraction by solvents evidenced that the average molecular mass of the isolated fractions increases with increasing hydrogen bonding capacity and polarity of the solvents.⁹² This can be quantified using the solubility parameter, which is a useful numerical estimate of the degree of interaction between materials, and that gives for instance a good indication of solubility of polymers in a solvent.⁹³ The details for the calculation of solubility parameters for different lignins (from softwood, hardwood, grass and wheat straw) were reported.⁹⁴ Mörck *et al.*⁹⁵ used a series of solvents to extract both softwood and hardwood kraft lignins in an order of an increasing solubility parameter, whereas Wang *et al.*⁹² did the same on kraft-anthraquinone lignin obtained from *Eucalyptus pellita*. In the latter work, lignins with the lowest molecular mass were extracted in low yield with hydrophobic solvents like hexane and diethylether, moreover the content of β -O-4 structure was higher in the high molecular mass fractions obtained and the thermal stability increased with the average mass.⁹² Gosselink *et al.* extracted different kraft and soda lignins in water sequentially with dichloromethane, propanol, methanol and methanol/dichloromethane (v/v 7/3). They noticed that the lignin-carbohydrate complexes present in commercial technical lignins are poorly soluble in organic solvents.⁹⁶ Methacanon *et al.* determined that a ratio of 1:5 (lignin:solvent) and an extraction time of 1 h were adequate.⁵⁸ They obtained the best extractions yields on kraft black liquor with acetone and methanol, whereas dichloromethane gave the fraction with lowest average mass. Although life cycle assessment gives a rather reasonable score for dichloromethane, as a chlorinated solvent is

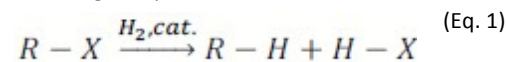
preferably to be avoided.⁹⁷ Quesada-Medina *et al.* extracted almond shell lignin with mixtures water-solvent (acetone, ethanol and dioxane-water) at temperatures higher than 150 °C.⁹⁸ The mixture that led to the highest lignin extraction was composed of a 75% volume of solvent, and the best lignin extraction conditions were at 210 °C during 40 min for the acetone and ethanol series, and 25 min for the dioxane series. Boeriu *et al.* focused more on the “greenness” of solvent extraction on industrial lignins, and notably by working at ambient temperature.⁹⁴ Thus they obtained from softwood, hardwood, grass and wheat straw lignins, fractions with low molecular mass and with narrow dispersity by using ethyl acetate and acetone-water solution containing 30 and 50% acetone, while insoluble fractions with very high mass were obtained in low yield from acetone-water solutions with 50, 70 and 90% acetone. They also reported that lignin-carbohydrate complexes can be isolated by extraction with acetone:water 10:90. Once lignin is recovered from the bulk of industrial liquors and fractionated using above-mentioned soft processes, fractions with a composition more or less controlled can be utilized for further reactions, notably towards depolymerization.

3 Reduction to modify lignins

3.1 Hydroprocessing

Most reports on the hydrotreatment of biomass-derived feeds are focused on bio-oil production and subsequent upgrading (hydrodeoxygenation - HDO) to achieve useful transportation fuels. Hydrodeoxygenation is thus employed to increase the thermal stability and volatility of the oil and to reduce viscosity, through oxygen removal, lowering hydrogen/carbon ratios and decreasing the molecular weight.¹¹ Hydroprocessing involves thermal reduction of the feed by hydrogen and is intimately linked to the presence of catalysts. Today, it is one of the most popular and efficient strategies applied in deconstruction of lignin into components such as low depolymerized lignin, phenols, and other valuable chemicals, and upgrading of the small compounds to hydrocarbon fuels. Most of the scientific studies carried out on the “lignin first” strategy have also been carried out under hydroprocessing conditions, that particularly suit the approach. Three main kinds of reaction occur during catalytic hydroprocessing: hydrogenolysis, hydrodeoxygenation (HDO) and hydrogenation.

Hydrogenolysis describes a chemical reaction whereby carbon-carbon or carbon-heteroatom bonds are cleaved by hydrogen according to Eq. 1:



Generally, the X represents an alkyl chain or other functional group containing heteroatoms (OH, SH, NH₂, OR, NR, etc.). Hydrogenolysis is an important reaction for lignin upgrading – particularly in cleaving of C–O bonds – which occurs between 90 and 200 °C. In the generation of fuels and chemicals, selective hydrogenolysis of aliphatic C–O bonds is preferred, while the aryl C–O bonds are far less active, and require high temperatures and/or high hydrogen

pressures. The harsh hydrogenolysis conditions lead to undesired hydrogenation of aromatic rings. In addition to the studies carried out on model compounds (see below), investigations of the action of catalysts such as NiRu, NiRh and NiPd – used in aqueous medium for the transformation of lignin to monophenols – have also been performed.^{4, 99, 100} Mechanistic investigations indicated that the synergistic effects could be attributed to three factors: (1) increased fraction of catalytically active surface atoms, (2) improved H₂ and substrate activation capability, and (3) inhibited benzene ring hydrogenation. Besides the catalyst, the solvent plays also a key role in directing the selectivity and, thus, it must be taken into consideration in the design of catalytic systems for conversion of lignin by hydrogenolysis of C-O ether bonds.¹⁰⁰⁻¹⁰² The bond dissociation enthalpies (BDE) of the ether linkages reveal the order of bond strengths: α -O-4 < β -O-4 < 4-O-5. The strongest ether linkage, 4-O-5, and C-C bond 5'-5, have BDEs of *ca.* 330 and 490 kJmol⁻¹, respectively, higher than those of the β -O-4 linkages. Therefore, the hydrogenolysis of the weak ether linkages, α -O-4 and β -O-4, is the most enthalpy-favorable strategy for the hydrogenolysis of lignin towards simpler molecules.

HDO is considered the most efficient method for bio-oil upgrading. In the future, HDO may provide economical routes for the production of fuels from bio-oils, but for now this reflects a prospect rather than a technological reality. The bio-oils that can be formed from lignocellulosic biomass require massive chemical modifications to be useful as fuels in today's petroleum-based infrastructure. Bio-oils derived from lignin have such high oxygen contents that oxygen removal is an essential processing goal. Removal of oxygen from bio-oils by reactions with H₂ that form water and deoxygenated compounds are called HDO reactions. There are numerous reports of catalytic HDO of lignin-derived bio-oils and compounds found in bio-oils, including the conversions of such compounds with catalysts that are not selective for HDO.¹⁰³ Most studies on HDO are based on lignin model compounds and occur between 150 and 320 °C by using monometallic catalysts as well as bimetallic catalyst or bifunctional catalyst.⁴

Hydrogenation is performed either by treating lignin in an active hydrogen-donating solvent or in gaseous hydrogen.⁴⁵ In this case, hydrogenation is a chemical reaction which employs a pair of hydrogen atoms to reduce or saturate organic compounds. The double or triple carbon-carbon bonds, as well as C=O bonds, are saturated during hydrogenation and increase the percentage of H in the final products. The selectivity for hydrogenation towards aromatic C=C, linear C=C, C=O, C=C, etc. varies drastically due to the different nature of catalysts and is controllable via fine manipulation of the catalyst system and of reaction conditions. Generally, hydrogenation occurs with hydrogenolysis simultaneously, or is included in the process of hydrogenolysis, HDO, and other upgrading methods. Compared to pyrolysis, liquefaction or oxidation, hydrogenolysis of lignins leads to higher net conversion, higher yields of monophenols, and less char formation by quenching any generated radicals *in situ*.¹⁰⁴ However, many authors have reported repolymerization or condensation reactions that occurred during hydrothermal lignin depolymerization.^{45, 105} Polymerization takes place simultaneously with acidolysis and both those reaction pathways have the same intermediate state, namely, a carbenium ion, generated at the α -

carbon atom. The ether bond in the intermediate can then be cleaved (depolymerized) or attacked by an adjacent aromatic ring forming stable carbon-carbon bond (polymerized).^{4, 106}

Some strategies can be implemented to limit lignin repolymerization and the appearance of char during hydroprocessing.

The addition of capping agents such as phenol could prevent repolymerization as well as char formation during hydrolysis.⁴⁵ Capping agents also enhance the yields of low molecular weight liquid products by stabilizing the phenolic compounds. Boric acid has also been shown to suppress addition and condensation reactions of initial products generated during hydrolysis.¹⁰⁷ Char formation can also be minimized with increasing alkali concentration, demonstrating that condensation reactions between the lignin fragments are greatly reduced by small concentrations of alkali in solution during hydrolysis.^{107, 108}

When hydrogenolysis is privileged, hydrogenolysis, hydrodeoxygenation and repolymerization reactions usually take place and compete intensely, especially when temperature increases. The source and the structure of lignin can be important. Organosolv lignin was more sensitive to hydrogenolysis than dealkaline lignin and sodium lignosulfonates, due to its high unsaturation degree and low molecular weight. In all cases the depolymerization products with unsaturated carbonyl groups were prone to repolymerize.¹⁰⁹

The operating conditions may be oriented to promote the occurrence of methylation reaction during hydrogenolysis. Methylation seems to stabilize the depolymerization products and suppress the further repolymerization.¹⁰⁹

The products targeted can also be oriented. Generally, aliphatic alcohols are more stable than phenolic compounds due to the saturated structure. Therefore, the exploitation of a novel and efficient strategy for the hydrogenolysis of phenolic oligomers to more inert aliphatic alcohols would be a promising approach for the comprehensive utilization of lignin with reduced char formation.¹⁰⁴

It was also demonstrated than during hydrogenolysis with gaseous hydrogen, depolymerization and char formation depends on the hydrogen partial pressure.⁴⁵ High partial pressure of hydrogen suppresses char formation and promotes depolymerization.

Furthermore, some catalysts emerged to play a significant role in minimizing char formation and favoring the required hydrogenolysis, dehydration, and hydrogenation stages without reducing the aromatic rings.¹⁰¹ Generating catalysts able to limit repolymerization and char formation, while guaranteeing efficient lignin depolymerization during hydroprocessing is an appealing challenge that needs further in-depth studies in the field of catalysis. However, until now research on catalysts has been primarily targeted on depolymerization and bio-oil production.

Recently, zero-valent metals (Al, Fe, Mg, and Zn) were reported to be active for hydrogenation of the C=O groups within the bio-oil at ambient temperature and pressure to increase the chemical stability (pH value) of the obtained bio-oil.² Investigations of the action of combination of catalysts such as Ni-Ru, Ni-Rh and Ni-Pd,

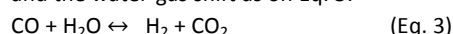
used in aqueous medium for the conversion of lignin to monophenols have also been performed.^{99, 100}

Advances in catalytic methods have helped to improve selectivity and increasingly there are reports of promising catalysts based on earth-abundant metals. Some of these are bio-inspired, for example a Mn-dependent enzymatic transformation that converts kraft lignin to monomeric species. Bio-based approaches have also been used as pretreatments, helping to reduce char formation in subsequent thermal processing. Chemical treatments, particularly HDO and hydrogenolysis reactions, have been developed using first-row transition metals. Approaches based on heterogeneous Ni catalysts have been shown to produce lower-weight lignin oligomers and bio-oils from isolated lignins. A Ni catalyst has also been demonstrated to selectively convert isolated lignins to monomers via solvolysis and hydrogenolysis. Supported catalysts based on Cr, Fe, Cu, and Ni have also been shown to deoxygenate lignin model compounds sometimes under remarkably mild conditions of temperature and pressure.¹¹⁰ Ni species have also shown promise for hydrogenolytic cleavage of aromatic ethers in model compounds. Vanadium catalysts were demonstrated to promote C-O bond cleavage in organosolv lignins under mild conditions. Porous metal oxides (PMOs) based on hydrotalcite-like precursors have exhibited potential for hydrogenolysis and hydrogenation reactions with no- or minimal formation of char, therefore improving the efficiency of lignin conversion and helping prevent catalyst deactivation.¹¹¹

In particular, previous works revealed that a copper-doped porous metal oxide (Cu-PMO) was capable of very selective transformations. The Cu-PMO catalyst has the advantage of being composed entirely of earth-abundant materials and of operating at very low loading of Cu (0.3 mol%). Compared to other earth-abundant metal catalysts, Cu-PMO is resilient to phenolic units, is able to accommodate electron-rich and sterically hindered substrates and is recyclable up to 11 times before noticing a decrease in activity.^{101, 110, 111} Cu-PMO also catalyzes methanol reforming, according to Eq. 2:



and the water-gas shift as on Eq. 3:



The resulting H_2 provides the reducing equivalents necessary both to cleave the aromatic ethers and for further reduction and deoxygenation.^{102, 112} Thus, the Cu-PMO catalyst is effective in converting low-molecular weight lignin – in methanol with an added pressure of H_2 – into mixture of aromatic products in high yield, without char formation¹⁰¹ and in relatively mild conditions while preserving aromatic structures.¹¹³ Unlike ethanol, methanol also seems to preserve the aromatic nature of hydrogenolysates.^{114, 115}

New integrated processes must go through the development of such catalysts.

Currently, only few fundamental mechanistic studies are carried out directly on the lignin, because of their excessive sizes and their wide polydispersity. Therefore, hydrogenolysis of lignin is studied through model compounds, which represent an appealing method to identify and understand the precise mechanism of action of tested catalysts.

3.2 Model Compound Hydrogenolysis: Mechanistic Insights

Insights Online
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3.2.1 Catalytic reductive treatment of lignin model compounds with hydrogen

The use of lower molecular mass lignin model compounds circumvents the variability of lignin and its insolubility in most organic solvents.¹¹ Such substrates contain linkages that mimic those found in lignin, yet they are much easier to handle experimentally. Lignin model compounds are usually classified according to the type of lignin linkage being exemplified in the substrate (Fig. 2). Most model compounds are dimers (two basic aromatic units), and fall into the category of aryl ethers, with β -O-4 models being the most prevalent, followed by α -O-4 and 5-O-4.¹¹ Due to lesser linkage abundance within lignins and higher robustness, especially in reductive conditions, C-C models such as 5-5' substrates are much less studied.¹¹⁶

Lignin model compound reactivity gives insight into that of lignin itself. These compounds are also obtained upon depolymerisation of lignin and understanding their reactivity is important for the development of selective lignin degradation pathways.¹¹ As such, finding pathways to obtain value-added products from lignin degradation compounds themselves is likewise advantageous. Overall, lignin model compounds allow a more rapid methodology development, through fast screening of reaction conditions. More importantly, using model compounds permits mechanistic understanding of selected methods, since there are fewer variables to consider when working with the models as opposed to the polymer, and experimental techniques are facilitated. Mechanistic understanding of developed methodologies is crucial for lignin depolymerisation, particularly due to the variable lignin structure, and it should allow rapid tailoring of reaction conditions towards specific products of interest.

As evidenced above, hydroprocessing shows great potential for the generation of valuable aromatic chemicals with ubiquitous applications.¹¹⁷ Additionally, using reductive conditions versus pyrolysis or oxidative methods will promote the generation of novel aromatic chemicals. These new substrates will catalyse the development of modern products and processes based on a renewable carbon source. Reductive approaches advantageously limit the formation of char and repolymerization by quenching phenoxide radicals and other unsaturated moieties responsible for these processes.^{17, 117}

As evidenced by prior studies, however, particularly with model compounds, selective breakage of lignin bonds versus reductions of arenes or undesired cleavage of aliphatic C-O bonds is difficult to achieve with catalytic reductive methods.^{117, 118} Elucidating mechanisms of successful catalytic reductive depolymerisations of lignin thus becomes crucial for the empowerment of further sustainable methodology developments.

The present section thus highlights new methodologies and mechanistic findings from catalytic reductive treatment of lignin model compounds with H_2 . Hydrogenolysis of aryl ether model compounds is primarily considered, as the β -O-4, α -O-4 and 4-O-5 linkages together are the most abundant bonds found in lignin and have been widely studied. We focus on heterogeneous

methodologies due to their facile recyclability and wider implementation in industry.

3.2.2 Nickel-based heterogeneous catalysts

In 1937, Sauer and Adkins¹¹⁹ showed the selective hydrogenolysis of butyl oleate or butyl erucate to the corresponding unsaturated alcohols with ZnCrO and CuCrO in the presence of H₂ pressure at elevated temperatures. The same reaction on hardwood lignin, however, did not display the same selectivity, providing mixture of substituted cyclohexanol compounds.¹²⁰ Hydrogenolysis selectivity was achieved ten years later with lignin, utilizing Raney-Ni in the presence of base, thereby promoting Ni reduction and preventing repolymerization, to yield mixtures of substituted phenolics.^{121, 122} Since then, a lot of efforts have been devoted to the development of Ni-based catalysts, not solely due to its potential high selectivity and activity, but also thanks to its abundant and inexpensive nature as a transition metal.

The study of the selectivity of hydrogenolysis versus hydrogenation, relevant to the depolymerisation of lignin, where hydrogenolysis is more advantageous (yielding aromatic value-added chemicals), started in 1935. Sauer¹²³ reported the hydrogenolysis of various ethers using Raney-Ni under H₂ pressure.

Interestingly, Chandler and Sasse¹²⁴ reported that Raney-Ni gave mixtures of benzene and cyclohexanol upon reduction of diphenyl ether at atmospheric pressures. Jackson and Sasse¹²⁵ had earlier obtained similar results by effecting the reaction in refluxing methanol. Performing the reaction at room temperature increased the prevalence of phenol over cyclohexanol in the product stream.¹²⁵ The authors propose a mechanism involving the initial adsorption of the ether on the catalyst through the oxygen atom, followed by the fission of one of the carbon-oxygen bonds to provide a more stable hydrocarbon anion and phenol, with the latter subsequently undergoing hydrogenation to cyclohexanol.

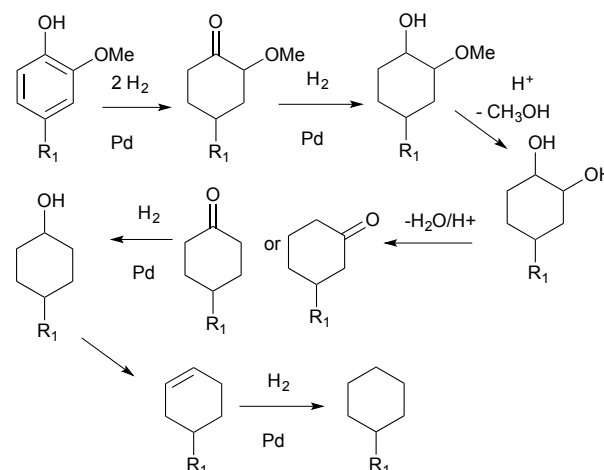
Then it was found that the use of a hydrocracking catalyst, Ni-Mo/SiO₂-Al₂O₃, in a fixed bed reactor at 250–350 °C and 5 MPa H₂, left phenol and *o*-cresol relatively unreacted.¹²⁶ Anisole and guaiacol, however, underwent reaction at the alkyl ether bond readily. Interestingly, guaiacol did not undergo hydrogenation, however anisole furnished comparatively high amounts of alkanes under the same conditions.

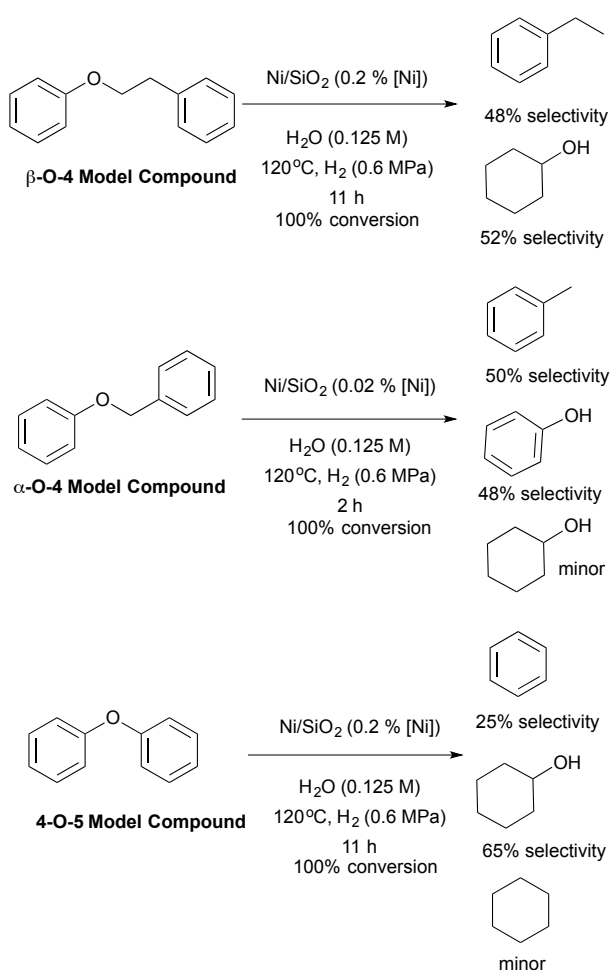
More recently, it was shown that Raney-Ni, in combination with Nafion/SiO₂ and in the presence of 4 MPa H₂ in aqueous medium, was capable of performing HDO of bio-derived phenols and anisoles to hydrocarbons and methanol¹²⁷. They indicate that Raney-Ni acts as a hydrogenation catalyst, while the Nafion/SiO₂ component acts as a Brønsted solid acid for the hydrolysis and dehydration reactions. In effect, the group previously demonstrated the

mechanism of this reaction using Pd/C in the presence of H₃PO₄ (H⁺) and H₂ pressure (Scheme 1).¹²⁸ Using anisole as a representative example, hydrogenation of the arene is thought to occur first, followed by hydrolysis of the methoxy substituent on the formed cyclohexanone, yielding methanol and a substituted cyclohexanol. Dehydration occurs, yielding an enol that is subsequently hydrogenated. Further dehydration and hydrogenation furnish the final hydrocarbon product.

The Lercher group also investigated the HDO of phenol in water using Ni/HZSM-5¹²⁹ or Ni/HZSM-5-Al₂O₃.¹³⁰ Both perform efficiently, providing cyclohexane with 5.0 MPa H₂ at 473 K in a few hours. Lewis acidity of the Al₂O₃ binder stabilizes a ketone intermediate, thus inhibiting its hydrogenation to the corresponding alcohol. The alumina doped catalyst, however, still showed much higher rates in phenol hydrogenation (fivefold higher), as well as higher rates for overall phenol HDO. The authors indicated that the Ni(0) particles on Ni/HZSM-5-Al₂O₃ are much smaller and three-fold more dispersed, enhancing reactivity. In the case of HZSM-5 supported Ni, however, the porous nature of the support was shown to allow cyclohexanol to diffuse and react, thereby leading to a very high rate of conversion for this substrate (by changing the concentration of monomers in the aqueous phase and taking advantage of LeChatelier's principle).¹²⁹ Phenol hydrogenation is reported to be the rate-limiting step. Lercher and coworkers¹²⁹ also demonstrate the hydrogenolysis and hydrogenation of β-O-4, α-O-4 and 4-O-5, as well as 5-5' model compounds in water at 523 K and with 5 MPa H₂, yielding substituted alkanes with minor amounts of aromatic products.

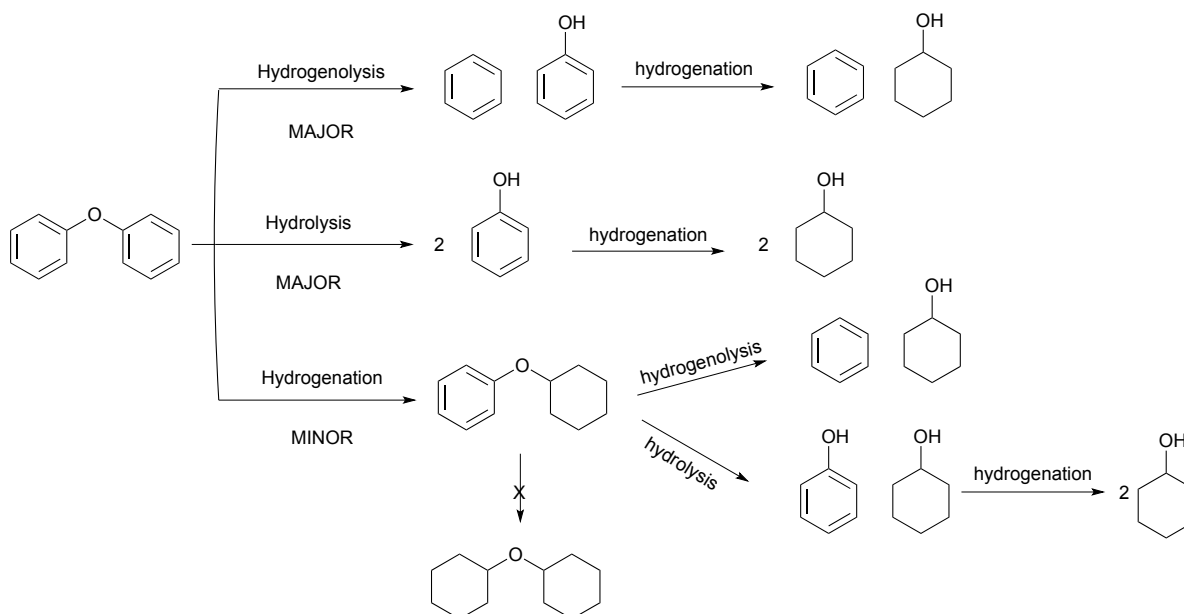
Scheme 1: Mechanism of Pd/C and H₃PO₄ mediated HDO of anisole, as determined by Lercher and co-workers.



Scheme 2: Ni/SiO₂ mediated aqueous aryl ether cleavage.

Later, the C-O bond cleavage of α -O-4, β -O-4 and 4-O-5 model compounds with a silica-supported Ni catalyst was disclosed, in aqueous media at 120 °C and 6 bar of H₂ (Scheme 2).¹³¹ Moderate selectivity for hydrogenolysis over hydrogenation is observed. The

mechanism for β -O-4 and α -O-4 is thought to occur through first hydrogenolysis of the model compound, furnishing phenol and ethylbenzene or toluene, followed by hydrogenation of phenol to the corresponding cyclohexanol. In contrast, both ethylbenzene and toluene are hardly converted to the cyclohexane hydrogenation product. The authors remind the importance of the adsorption of phenol on the Ni/SiO₂ surface, and of the markedly different solubility of phenol versus ethylbenzene and toluene in water, limiting the ability of the latter to react. Interestingly, the 4-O-5 substrates demonstrate a different reactivity pathway. At initial reaction time, both hydrogenolysis and hydrogenation products are observed, whereas for the α -O-4 and β -O-4 substrates only the cleavage has occurred. Cyclohexylphenylether and dicyclohexylether are very recalcitrant to cleavage under the reaction conditions. The authors hypothesize that, in parallel to Ni/SiO₂ mediated hydrogenolysis of the diaryl ether, hydrolysis also occurs, producing two molecules of phenol (Scheme 3). This hypothesis is consistent with the bond strength of the different type of ethers: α -O-4 (weakest) < β -O-4 < 4-O-5 (strongest). Since 4-O-5 has such a slow hydrogenolysis rate, hydrolysis can compete. After verification that Ni is the active site for reactivity, surprisingly no reaction occurs with 4-O-5 in the absence of H₂. This implies that H₂ would thus be necessary even for hydrolysis. This is thought to occur through the addition of H or OH radicals from water, rather than through the addition of 2 H radicals from H₂. Investigation of the H₂ pressure effect on reactivity showed that, although there is an increase of conversion with increased pressure, there is an optimal H₂ pressure after which increasing the pressure actually induces a decrease in reactivity. This was attributed to the competition of H₂ for active sites with the substrates. Note that this behaviour is not observed with A-O-4 substrates, as these possess such a high rate of reaction and necessitate less Ni active sites. Investigation of the effect of H₂ pressure also reveals mechanistic differences between the three types of linkages: higher H₂ pressure favors hydrogenation over hydrogenolysis for 4-O-5 and β -O-4, but for α -O-4, the hydrogenolysis barrier is much lower than

Scheme 3: Parallel hydrogenolysis and hydrolysis for the cleavage of 4-O-5 model compounds with H₂ catalysed by Ni/SiO₂.

hydrogenation and thus the former always dominates. Song *et al.* reported the use of Ni over activated carbon in ethanol with 2 MPa H₂ at 393 K for the hydrogenolysis of dibenzyl ether to toluene in quantitative yield.¹³² Phenylbenzylether, however, is only partially converted to phenol and toluene under the same conditions (62% conversion).¹³² Their strategy is capable of converting lignosulfonate into phenols without disturbing the arenes. The authors propose that Ni(0) sites on the catalyst are the active sites for the hydrogenolysis of aryl alkyl ether bonds to phenols and for the hydrogenolysis of hydroxyls at side chains into alkanes. Then the effect of the catalyst on hydrocracking behaviour of phenethyl-phenyl-ether (PPE), a β -O-4 model compound were demonstrated.¹³³ Ni on carbon was prepared using three different carbothermal reduction temperatures under Ar (450 °C, 400 °C and 300 °C), and the efficiency and selectivity of the three catalysts were compared to Pd/C, Ru/C and Ni/C-H for the hydrogenolysis of PPE. Ru/C, Pd/C and Ni/C-H show ether cleavage selectivities of 40%, 69% and 85%, respectively, versus arene hydrogenation.

In contrast, Ni/C-C showed an ether cleavage selectivity of > 99%, with 44% retention of aromaticity (versus 0% retention with other catalysts). Although smaller particle size is often correlated with higher catalytic activity, the authors note that particle size is higher in Ni/C-H ($d = 20$ nm) than Ni/C-C ($d = 13$ nm), even though the former has higher hydrogenation capabilities. The carbothermal method used to reduce the Ni/C-C catalyst, however, is demonstrated to generate Ni particles which possess a close interaction with the carbon support, leading to a potential increase in electron mobility within the catalyst, which may result in Ni bearing a partial negative charge. Benzene hydrogenation is known to occur over positive charges on the surface of metal nanoparticles, thus in Song's Ni/C-C catalyst arene hydrogenation may be limited from a lack of these positive charges, increasing selectivity for ether hydrogenolysis.

The effect of solvents on the hydrogenolysis of diphenyl ether with Raney-Ni was studied with 50 bar of H₂ at 90 °C.¹⁰⁰ The Lewis acidity of the solvent was a crucial variable in determining catalytic activity, with Raney-Ni being most active for hydrogenolysis and hydrogenation in non-basic solvents (such as alkanes). In basic solvents, such as methanol, THF or dioxane, the activity of Raney-Ni is reduced, but gratifyingly the catalyst becomes more selective for hydrogenolysis than hydrogenation.

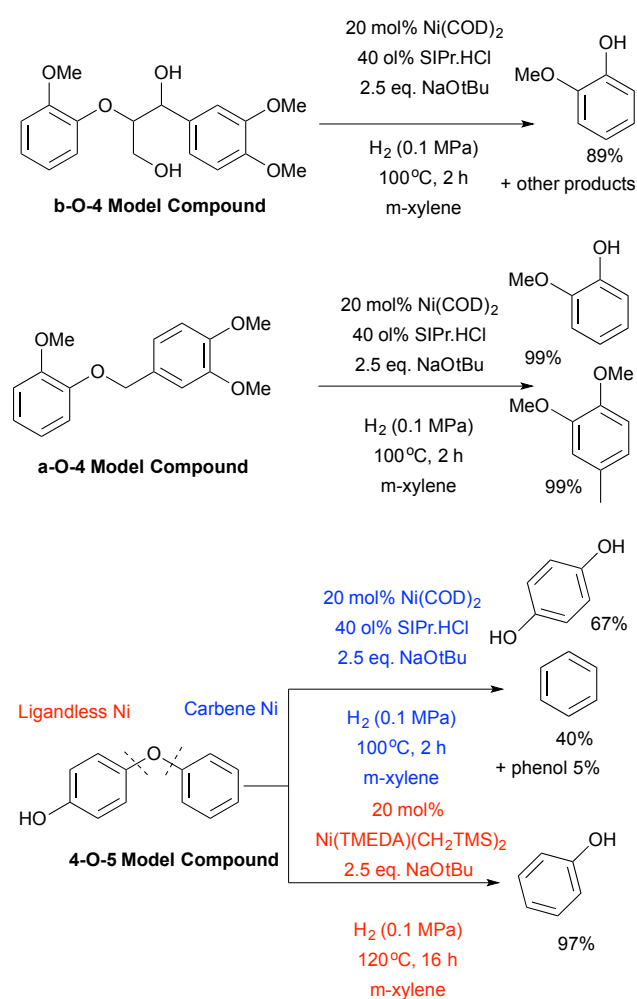
Similarly, Lercher and co-workers published mechanistic investigations of benzyl phenyl ether (BPE) cleavage with supported Ni (on HZSM-5 or SiO₂) in aqueous and apolar phases,¹³⁴ supported by DFT calculations. An ionic mechanism by which BPE is thought to occur through hydrogenolysis if metal sites and H₂ are present, with hydrolysis playing a minor role in the presence of acidic sites (such as HZSM-5 support). In apolar solvents, the mechanism also proceeds through hydrogenolysis, suppressing the pyrolysis/radical pathways occurring in the absence of metals. Analogous considerations of the cleavage of diaryl ethers in the aqueous phase revealed that hydrolysis and hydrogenolysis compete over Ni/SiO₂ in the aqueous phase with diphenyl ether.¹³⁵ The rate-

determining step was found to be C-O cleavage over Ni. Interestingly, di-*p*-tolyl ether forms *p*-cresol and toluene exclusively, suggesting hydrogenolysis is the exclusive route of ether cleavage.

In 2011, the homogeneous Ni-catalyzed cleavage of aryl and benzyl ether bonds was published.¹³⁶ The use of Ni(COD)₂ with an NHC ligand (SIPr), over 2 equivalents of base and 1 bar H₂ effected selective cleavage of β -O-4, α -O-4 and 4-O-5 bonds in 2 to 16 hours at 80-100 °C. It was found that the carbene Ni showed a preference for electron deficient arenes, and selectively reduced diaryl ethers in the presence of aryl-alkyl ethers. Impressively, this catalyst was also shown to be compatible with other hydride sources, such as DIBAL-H, Et₃SiH, or LiAl(OtBu)₃H. Later it was discovered that the carbene ligand could be excluded (Scheme 4).¹³⁷ Starting with pre-catalyst Ni(CH₂TMS)₂(TMEDA), with 1 bar H₂ and 2.5 equivalents of tBuONa, diaryl ethers and benzyl ethers are selectively and efficiently converted to the corresponding phenolic and aryl products. Interestingly, the novel heterogeneous Ni catalyst displays orthogonal reactivity to that of its homogeneous carbene counterpart. In effect, 'ligandless' Ni displays a bias towards electron-rich arenes. Furthermore, this trend also applies to different C_{Ar}-O bonds within the same ether, with preferred hydrogenolysis of the most electron-rich side of exemplary diaryl ether as shown in Scheme 4. In contrast, the carbene-ligated Ni selectively cleaves the C_{Ar}-O bond that is most electron poor within a molecule. Although the 'ligandless' Ni discussed above shows great promise, it did not convert very electron-rich models more alike lignin itself, even at higher temperatures.¹³⁸ The lack of activity at higher temperatures was attributed to the aggregation of Ni particles, and the deposition of Ni on supported carbon overcame that issue, allowing reactivity at higher temperatures.

Despite tremendous progress achieved towards utilization of Ni for the selective hydrogenolysis of aryl ether bonds relevant to lignin, heterogeneous supported Ni catalysts still exhibit low turnover numbers for the hydrogenolysis of β -O-4 bonds, the most abundant linkage in lignin.¹³⁹ Thus, the group strived to elucidate the relationship between the activity and selectivity and the electronic and geometric properties of Ni catalysts by comparing the activity of 13 monometallic catalysts (Ru, Rh, Pd, Pt, Ir, Ag, Au, Cu, Fe, Co, Ni, Re and Sn) and 12 bimetallic NiM catalysts in the conversion of 2-phenoxy-1-phenylethanol.¹⁴⁰ Amongst the monometallic catalysts, Ni was found to possess the highest selectivity towards ether hydrogenolysis (furnishing both aryl and cyclohexane monomer derivatives), but not the highest activity. Coupling with Au furnished the highest activity and selectivity towards monomers, out of all NiM catalysts studied. The structure of the Ni₇Au₃ catalyst consists of an Au core and a Ni-enriched shell, with Au acting as an electron donor, enabling neighbouring Ni atoms to be electron-enriched.

The authors found that hydrogenation of a surface intermediate was a kinetically important step, and studied the hydrogenation of adsorbed phenoxy, showing that Au destabilizes such intermediates, thus decreasing the activation energy barrier of hydrogenation. Finally, the Ni₇Au₃ catalyst is also capable of cleaving methoxylated β -O-4 model compounds, as well as an α -O-4



Scheme 4: Ni-mediated aryl ether cleavage.

and a 4-O-5 model with high resulting monomer yields. Encouraged by findings of very high activity of NiAu, the authors then went on to study three other NiM catalysts (M = Ru, Rh, and Pd) in a subsequent study.⁹⁹ The Ni₈₅Ru₁₅ catalyst showed activity at 100 °C and only 1 bar H₂ pressure in β-O-4 cleavage towards monomers (aromatic and alkanes). The authors attribute the activity and selectivity enhancement to three factors: (1) an increased number of surface atoms leading to increased activity, (2) an enhanced H₂ and substrate activation due to electron enriched Ni, and (3) inhibition of benzene ring hydrogenation due to electron enriched Ni.

In a similar manner, the synergistic effect of Titanium Nitride and Ni for the hydrogenolysis of aryl ethers was investigated, and good conversions towards both aromatic and aliphatic monomers were obtained at 12 bar H₂, 100–150 °C in ethanol over a few minutes in a flow system.^{141, 142} TiN is proposed to partially oxidize at high temperature during catalyst calcination, by electron transfer from Ni to TiN. This will result in an electron deficient Ni which can effectively bind ethers through oxygen, and enhance the hydride transfer to the arene during reductive elimination. The authors do not exclude a mechanism in which Ni activates hydrogen while Ti activates ethers. This catalyst was later applied to the

depolymerization of kraft lignin towards oligomers and aromatic monomers in mild conditions and short residence times.¹⁴³

The authors published then the effect of base on the hydrogenolysis of a β-O-4 model compound (and lignin itself).¹⁴³ With their Ni₇Au₃ catalyst, the authors observed a dramatic increase in activity as pH increased to 13, but above which the particles started to aggregate, causing a loss in efficiency. Interestingly, the selectivity towards aromatic monomers also increases at higher pH. At higher pH, phenolics exist as phenolates, with lower solvation energy than the corresponding neutral molecules. Thus, the energy required for surface absorption and hydrogenation over the catalyst is relatively increased compared with the neutral species, explaining in part why higher pH limit hydrogenation of monomers. Because hydrogenation of all aromatics (not just phenolics) is limited at higher pH, the authors propose that coordination of the aromatic ring on the catalyst surface is hindered in the presence of base due to the latter's competitive absorption on the catalyst surface. Importantly, other bases, such as triethylamine, exhibit negligible effects, indicating that –OH is important and reinforcing the claim that base binds competitively to the catalyst surface.

In 2014, Zaheer and coworkers¹⁴⁴ achieved selectivity for hydrogenolysis, with no observed arene hydrogenation, by utilizing a catalyst composed of integrated Ni nanoparticles on porous SiC composites. The resulting material can be tailored by careful choice of starting reagents, and the most active (starting from intermediate molecular-mass compounds) showed micro and mesopores, a large surface area (527 m²g^{−1}) and Ni nanoparticles with average size of 2.7 nm. The reactions were performed first on benzylphenyl ether (BPE), in water, at 6 bar H₂ and 90 °C, with the addition of KOtBu (1 equivalent) and TBAB (0.3 equivalent) to circumvent the lack of solubility of BPE in water, and providing full conversion towards phenol and toluene selectively. Analogous results were obtained with β-O-4 and 4-O-5 model compounds.

Overall, the following observations can be made for the hydrogenolysis of ethers in lignin model compounds with Ni:

- (1) Using heterogeneous Ni, efficient ether hydrogenolysis can be achieved with mild reaction conditions (80–150 °C, 1–20 bar H₂, in aqueous or alcohol solvents)
- (2) Ether cleavage efficiency is in accordance with calculated BDEs as: benzylphenyl ether (most labile) > benzylalkyl ether > diphenyl ether (most robust)
- (3) Prevention of over reduction of arenes towards alkanes remains unachieved, even at mild reaction conditions, except in a select example
- (4) Reaction pH plays a crucial role in efficiency and selectivity, with (Lewis and Brønsted) basic media generally promoting hydrogenolysis over arene hydrogenation and decreasing efficiency.

3.2.3 Copper-based heterogeneous catalysts

Ni has been extensively studied as a promising transition-metal catalyst for aryl ether cleavage and lignin depolymerisation, especially with H₂ pressure as reductant. Copper, however, has not been as widely investigated, despite its readily available and inexpensive nature. Copper's inability to efficiently perform arene

hydrogenation is an advantage for the selective hydrogenolysis of ethers without the over reduction of aromatics during lignin depolymerization.

The catalytic properties of a bimetallic NiCu catalyst supported on $\text{ZrO}_2\text{-SiO}_2$ were investigated versus the corresponding monometallic Ni analogue.¹⁴⁵ Cu was applied to Ni as a promoter, reducing the reduction temperature of Ni, while silica was added to the more traditional ZrO_2 support to increase its surface area. Moreover the incorporation of Cu introduces strong acid sites, and blocks the porosity of the support material. Overall, guaiacol reduction at 300 °C, with 50 bar H_2 in 8 h demonstrated that the addition of Cu changed the product selectivity, enhancing the formation of methylated products while limiting cyclohexane formation. The acidity of the catalyst is thought to increase activation of the aryl ether bond through the oxygen, cleaving heterolytically and generating a positively charged methyl group, which can be transferred to other substrates. Increased temperature is shown to decrease HDO, while increasing intermolecular polymerization.

It was demonstrated that Cu(0) on acidic zeolite support was capable of hydrogenolysis of aromatic aldehydes to the corresponding hydrocarbons,¹⁴⁶ similar to ether cleavage, and without arene hydrogenation. Results were contrasted with corresponding Cu and Ni on alumina (both showing smaller surface areas). With Cu on alumina, no arene hydrogenation was observed, whereas analogous Ni did produce some methylcyclohexane from the reduction of benzaldehyde at 120 °C and 20 bar H_2 pressure. Both the benzylalcohol and toluene are observed from this reaction, but more acidic Cu-HZSM-5 enhances selectivity towards toluene. H_2 spillover is proposed to contribute to enhance hydrogenation ability of Cu-HZSM-5, along with acidic activation of the C-O bond targeted. The authors report that all Cu is reduced to Cu(0) during the reaction, and that the average Cu particle size is of 21 nm, bigger than the pore diameters and thus located outside the pores.

Cu on alumina and magnesia-alumina was later demonstrated to perform hydrogenolysis of two β -O-4 model compounds with no loss of aromaticity under 25 bar H_2 at 150 °C in 21 h.¹⁴⁷ Unfortunately, ether hydrogenolysis efficiency remained low, with concurrent deoxygenation of benzylic ketones/alcohols, thereby competing with aryl-alkyl ether hydrogenolysis. Introducing basic sites on the catalyst support was found to hinder HDO (magnesia-alumina support). The authors also investigated pre-reduced, Cu(0) on alumina and magnesia-alumina, showing that hydrogenolysis is enhanced in the same conditions when started with a pre-reduced catalyst. The efficiency of deoxygenation of resulting intermediate benzylic alcohol is also enhanced. Regrettably, the catalyst suffers from deactivation after several cycles, possibly from coking or poisoning of the catalyst by byproduct adsorption.

Anastas and co-workers¹⁰¹ successfully utilized a similar Cu-based catalyst for the depolymerisation of lignin selectively towards four major catechols. Instead of being deposited on alumina or magnesia alumina, the catalyst is formed by coprecipitation of the corresponding Cu, Mg and Al salts, yielding a hydrotalcite-like structure that is subsequently calcined in air forming a Cu-doped porous metal oxide (Cu-PMO). Catechol formation is proposed to occur through hydrogenolysis of β -O-4 bonds, with further

hydrogenolysis, dehydration and hydrogenation of the intermediates.

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Although Cu shows promise towards selective hydrogenolysis over hydrogenation, applied to lignin depolymerisation,¹¹³ very few studies have been directed towards mechanistic understanding of ether cleavage with hydrogen gas. Overall, we observe that copper can promote the reduction and enhance the selectivity of Ni, and more acidic supports of Cu enhance both hydrogenolysis and HDO reactions.

Very few other transition metals have been investigated for their ability to activate H_2 and cleave ethers without arene hydrogenation. Transition metal phosphides have shown ability to perform hydrodesulfurization and hydrodenitrogenation, but were only recently demonstrated to perform HDO.¹⁴⁸ The same team utilized a FeMoP heterogeneous catalyst, in combination with 21 bar H_2 , in decane at 400 °C, to perform aryl ether cleavage of (2-phenoxyethyl)benzene towards benzene and ethyl benzene. Interestingly, with lower reaction temperatures, selectivity to benzene decreases, and increased amounts of cyclohexane are observed.

3.2.4 Palladium-based heterogeneous catalysts

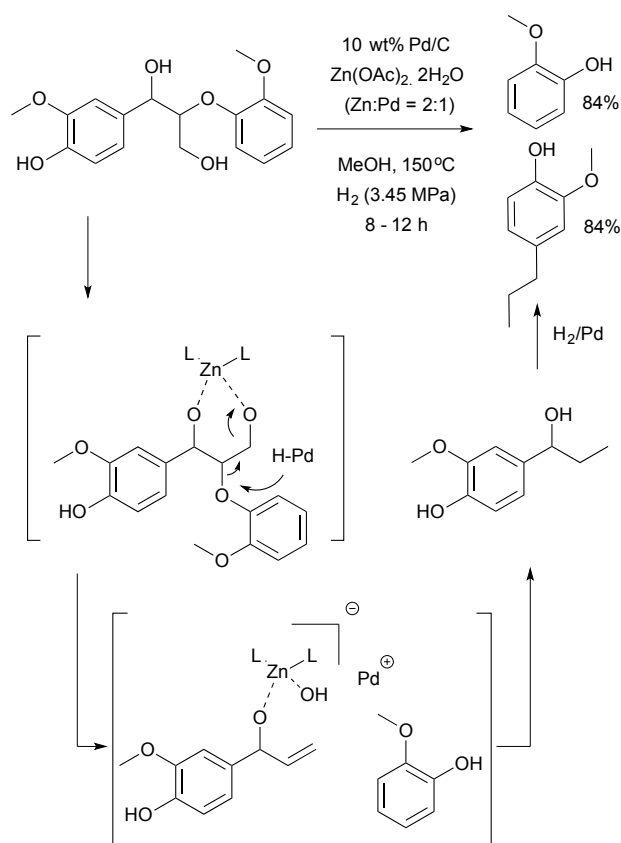
Noble metals are well known for their ability to activate H_2 at relatively mild reaction conditions, and have thus been widely applied to the reductive cleavage of lignin-relevant ethers, despite their cost and environmental disadvantage.

Pd/C, Rh/C, Ru/C and Pt/C were investigated to depolymerize white birch wood sawdust, in a mixture of water and dioxane, under 40 bar H_2 at 200 °C, in the presence of phosphoric acid (H_3PO_4) towards four aromatic monomers (guaiacylpropane, guaiacylpropanol, syringylpropane, and syringylpropanol).¹⁴⁹ Platinum was found to be the most effective catalyst, and Rh performed more selectively. Their process was completely inhibited in the presence of NaOH, and the authors propose that rate enhancement with acid may be due to acid activation of the catalyst or acid-catalysed dehydration. In fact, Pd/C, in the presence of H_3PO_4 , is capable of HDO of phenolics, through a hydrogenation/dehydration mechanistic sequence.¹²⁸ This came after the report of selective phenol hydrogenation to cyclohexanone with supported Pd in the presence of a Lewis acid (AlCl_3 , ZnCl_2).¹⁵⁰ Later, it was also shown that solid Brønsted acids, such as HZSM-5, can promote HDO in combination with Pd/C, and cleave β -O-4, α -O-4, 4-O-5 ethers while retaining all C-C linkages (such as 5-5').¹⁴⁷ While Brønsted acid sites promote HDO through dehydration,^{128, 151} alkylation can be achieved in the presence of La^+ cations in dual Pd/C and H/La-BEA catalysis.¹⁵²

Then a bimetallic Pd/Zn catalyst was synthesized, capable of cleavage and HDO of ethers relevant to lignin.¹⁵³ Although Pd/C in combination with ZnCl_2 in dichloromethane at 80 °C and 5-30 bar H_2 had shown only phenolic hydrogenation¹⁵⁰, it is not observed in methanol at 150 °C under 300 psi of H_2 with pre-made or *in situ* generated (from Pd/C and ZnCl_2) Pd/Zn/C catalyst. Instead, the catalyst promotes hydrogenolysis of benzyl alcohols and aldehydes, and is able to cleave β -O-4 bonds without arene hydrogenation. The authors report that Pd-Zn interactions are absent in the catalyst, with Zn ions instead interacting with the carbon support. They propose that Zn^{2+} ions activate the substrate via OH-binding,

inducing reactivity with Pd-H on surface via H-spillover, or that these ions are desorbed from the carbon support in solution and activate the substrate before its encounter with Pd-H entities. In a subsequent report,¹⁵⁴ the synergistic effect of Pd/C and Zn²⁺ is evaluated in more detail. Zn is proven to perform more than simple Lewis activation of the substrate, and to be crucial for removal of the C_γ hydroxyl of β-O-4 compounds. A mechanism is proposed involving the formation of a Zn-containing six-membered ring, activating the substrate for reaction with Pd-H (Scheme 5).

Because Pd is so efficient at reductions, including hydrogenation of arenes, it can be combined with other metals such as Fe,¹⁵⁵ or active supports such as metal-organic frameworks (MOF),¹⁵⁶ to enhance its selectivity towards aryl ether cleavage. The bimetallic Pd-Fe/OMC catalyst cleaves benzyl phenyl ether with 84% selectivity for aromatics (versus 39% selectivity for Pd/OMC).¹⁵⁵ It is proposed that electron-deficient Fe atoms adsorb ether bonds readily, which then reacts with Pd-H species. The interaction of Pd and Fe increases the electron density at Pd, and decreases its ability to adsorb hydrogen, thus decreasing the arene hydrogenation capability of the catalyst.¹⁵⁵ Pd supported on MOF UiO-66 ([Zr₆O₄(OH)₄(CO₂)₁₂] linked by 1,4-benzenedicarboxylic acid) furnishes cresol from vanillin in the presence of hydrogen (0.5 MPa) in aqueous media quantitatively, due to the hydrogenation capability of Pd and the acidic sites of the support promoting the hydrogenolysis of the intermediate benzyl alcohol.¹⁵⁶



Scheme 5: Proposed mechanism of the synergistic Pd/Zn catalyzed β-O-4 cleavage with H₂.

Overall, Pd is found to be extremely efficient for reductions, and the lack of selectivity for aryl ether cleavage can be offset by combining Pd catalysis with Brønsted or Lewis acid activation.

As Pd-based catalysts, Ruthenium has been applied towards the reductive valorization of biomass, with good efficiency but limited selectivity.^{143, 157, 158} Brønsted acid sites (such as on HSZM-5 supports),¹⁵⁷ in combination with Ru and H₂ pressure, promote HDO through dehydration. A bimetallic Ru-W catalyst, supported on Si-Al, is capable of aryl ether and phenolic cleavage.¹⁵⁹ The authors propose a mechanism by which the substrate is adsorbed onto Lewis acid sites on the support or W moieties of the catalyst before being reduced by Ru particles.¹⁵⁹

In conclusion, heterogeneous catalysts circumvent the added difficulty of separating the catalyst from product stream and are typically very robust entities, thus finding facile applicability on industrial scales. Although they are easier to handle and generally possess many active sites, heterogeneous catalysts tend to suffer from a lack of selectivity. Ni and Pd are very efficient at cleaving aryl ether bonds, and their lack of selectivity can be offset by combining with other metals, or tailoring the metal support as Brønsted and Lewis acids.

H₂ gas provides the advantage of potentially being derived from renewable sources. Other reductive strategies, however, have been applied to the study of lignin depolymerization, for example by using silanes with or without transition metals.¹¹⁸ Another promising reductive catalytic method involves hydrogen transfer from alcohols, with the advantage that these terminal reductants can be derived from biomass (methanol, ethanol)^{110, 118, 160} and concomitantly utilized as solvents. These reactions typically utilize supercritical conditions to reach significant reforming equilibria.

3.3 Hydroprocessing and “lignin first” approach

In the mid-20th century, copper chromite was applied to the hydrogenation of maple wood.¹⁶¹ Raney-Nickel was utilized on wheat straw and aspen wood, achieving complete lignin solubilization and the isolation of aromatic compounds in modest yields,¹⁶² and 40-51% pulp yield after reductive treatment. Pepper et al. studied the effect of the metal catalyst on lignin degradation from spruce wood.¹⁶³ Using small amounts of Ra-Ni, Pd/C, Rh/C or Rh/Al₂O₃, 4-propyl-guaiacol and dihydroconiferyl alcohol are obtained almost exclusively after depolymerization of most of the lignin (67-87% of Klason lignin). When high amounts of Ra-Ni are utilized, or when Ru/C or Ru/Al₂O₃ is used, cyclohexyl derivatives are obtained from hydrogenolysis. Aspen poplar wood meal was subjected to analogous reaction conditions with Rh/C in the 1980s, achieving 75% lignin solubilization at 195°C in 5 hours under 34.5 bars of H₂ and yielding monomeric and dimeric phenolic products.¹⁶⁴ Most of these early reports targeted the elucidation of the lignin structure.

Very recently, select research groups have focused their attention on the valorisation of native lignin, by performing lignin depolymerisation on whole lignocellulosic biomass.¹⁶⁵ This ‘lignin-first’ approach removes the added complexity introduced by the

above mentioned pre-treatment steps, and circumvents the problematic incorporation of catalyst poisoning impurities (such as sulphur) before lignin valorisation. This approach results in a tunable bio-oil composed of substituted aromatics, and varying process conditions can allow for various pulp valorisation strategies.¹⁶⁶ This very promising approach has paradoxically been subject to few researches so far.

The majority of more recent reports make use of precious metals such as Pd/C and Ru/C, under hydroprocessing conditions. Kou et al. developed a two-step process for the valorization of lignocellulosic biomass into fuel^{149, 164}, subjecting white birch sawdust to Pt/C catalysis under H₂ pressure (40 bars) at 200 °C, in acidic dioxane-water, providing high yields of aromatic monomeric (46.4wt%) and dimeric (12wt%) products. Galkin and Samec obtained 2-methoxy-4-(prop-1-enyl)phenol in 23% yield from pine wood and 2,6-dimethoxy-4-(prop-1-enyl)phenol in 49% yield from birch wood by using a combination of organosolv pulping (EtOH/H₂O) and Pd-catalyzed reduction at 195 °C in 1 h¹⁶⁵. Both cellulose and hemicellulose can be recovered from the process. Lignin, however, was converted in 54-98% yield w/w, and the resulting bio-oil exhibits monomeric (58-62%) and dimeric/oligomeric products.

Abu-Omar et al. reported the doping of Pd/C with Zn to promote lignin depolymerization within genetically modified poplar (enhanced in syringyl content), yielding a single product: dihydroeugenol¹⁶⁷. The reaction is run at 225 °C under 34.5 bars of H₂ in methanol, giving up to 54% of phenolic products and 85% of sugars in the carbohydrate residue, and is amenable to white birch, eucalyptus and pine valorizations. In addition, the authors further process the carbohydrate residue by cellulose enzyme digestion, giving 95% of glucose, and in another instance subject it to fast pyrolysis yielding mainly cellobiosan.

Sels and coworkers recently reported Ru/C catalysed reductive fractionation of lignocellulose into phenolic monomers and dimers and a carbohydrate pulp¹⁶⁸. Birch sawdust was treated in methanol under H₂ (30 bars) at 250 °C for 3 hours, giving 93% delignification and 81% carbohydrate retention, with a lignin-derived bio-oil containing 50% phenolic monomers and 18% aromatic dimers. Interestingly, this strategy shows poor performance on Organosolv lignin (3% phenolic monomers and 6% dimers). The methodology is applicable to other substrates with varying degrees of delignification (56-86%) and phenolic monomer yields (21-44%). Switching the catalyst from Ru/C to Pd/C dramatically increases the OH content of the bio-oil obtained from birch wood, although very similar overall liquid product yields are obtained in otherwise identical conditions¹⁶⁸. The authors successively processed the carbohydrate pulp towards polyols via a known protocol^{169, 170} by taking advantage of the residual Ru/C present in the pulp. Later, the effect of base or acid on this Pd/C catalyzed process was studied evidencing the ability of acid (H₃PO₄) to catalyse alcoholysis of hemicellulose under the reaction conditions while enhancing delignification, generating a cellulose rich pulp, a lignin-oil with high monomer yield, and a fraction containing methylated carbohydrates¹⁷¹. Alkaline conditions, however, promote repolymerization, loss of hydroxyl groups (generating C8 versus C9 phenolics) and promote cellulose loss from the carbohydrate pulp.

For both economic (political) and environmental reasons, earth-abundant metals should be favoured for catalysis. In that case, lignin-first strategies have relied on the use of nickel, again under hydroprocessing conditions. For example a Ni-W2C/AC catalyst performs aqueous depolymerization of lignin in untreated birch wood, at 235 °C and 60 bar H₂, into monophenols (46.5% based on lignin), simultaneously converting the carbohydrates into diols with up to 75.6% yield.¹⁷² The authors report that the source of lignocellulose has a significant effect with phenolic yields in the range of 10-40% for poplar, beech, yate, xylosma, basswood and ashtree. Pine, bagasse and yate performed very poorly under the reaction conditions, attributed to differences in lignin base unit proportions and the increased presence of sulfur in some feeds. The simultaneous valorization of whole lignocellulose is accompanied by some drawbacks. Namely, all products are present in the same liquid phase, necessitating complicated isolation procedures, and the depolymerization of the carbohydrate fractions reduces the potential versatility of their processing.¹⁶⁸

Song et al.¹³³ successfully utilized Ni/C to convert birch wood lignin into propylguaicol and propylsyringol in methanol at 200 °C under 1 atm Ar. A high selectivity of 90% towards these two products is achieved at 50% delignification. A mechanism by which lignin is first fragmented into smaller species via alcoholysis, followed by conversion with Ni/C into monomeric phenols is proposed. The authors hypothesize that most of the cellulose and hemicellulose remains in the residue after reaction, and show that cellulose, crystalline cellulose and cellobiose are unaffected under the reaction conditions. This process was later expanded to poplar and eucalyptus wood,¹⁷³ showing that lower Ni/C loadings afforded the propenyl equivalents of propylguaicol and propylsyringol from all wood substrates, with yields from <10% to >30%.

Ferrini and Rinaldi¹⁷⁴ later demonstrated concomitant delignification and depolymerization of lignin in poplar wood with Ra-Ni in 2-propanol at 160-220 °C, with up to 77% delignification and 64% retention of the xylan content in the pulp. The resulting bio-oil, however, is a complex mixture of aromatic and aliphatic monomers, as well as diols from hemicellulose degradation.

Abu-Omar et al. use Ni/AC to depolymerize untreated Miscanthus, in methanol at 225 °C under H₂ (5-30 bars)¹⁷⁵. Under higher H₂ pressure, higher yields of monomeric products are obtained (69%), mostly propylphenols. With lower hydrogen pressure, the unsaturated analogues can be obtained, albeit in lower overall yield (30%). The process generates a carbohydrate residue, which can be converted to furfural and levulinic acid (in 53-76% yields) using FeCl₃.

Overall, a lignin-first strategy making use of catalytic hydrogenolysis shows promise for utilization within an integrated bio-refinery, with high lignin monomer yields, often enhanced product selectivity, and a processable carbohydrate pulp. A process with reasonable energy inputs that uses economic and abundant catalysts and provides full delignification with a selective product distribution, and that is applicable to various biomass sources has still not been realized.

3.4. Alternatives heating technologies

Usually, lignin depolymerization studies are carried out in conventional reactors (stirred or not) which are resistant to pressure. Several authors have recently considered microwaves as an alternative heating technology and probably the most interesting and "greenest" way to convert lignin. Microwave-

assisted lignin conversion to renewable fuels and chemical has recently been reviewed¹⁷⁶ and allows concluding that microwave-assisted technology is an effective method for significantly reducing reaction time and improving the yields and selectivity of target products. By reducing the heating time and boosting energy absorption, microwaves technology also improves the overall process efficiency.¹⁷⁷ Microwaves may also be used for reactions in the presence of ionic liquids (see below).¹⁷⁸

Microwave-assisted lignin conversion technologies can be grouped into two major pathways. The first group includes the microwave-assisted pyrolysis of lignin without oxygen, under high temperatures, and with or without catalysts. The second group includes different microwave-assisted solvolysis technologies under mild conditions, with or without catalysts.¹⁷⁶

In the second case, microwave technology has thus been able to demonstrate its effectiveness on the conversion of sulfonated¹⁷⁹, black liquor^{180, 181}, alkali¹⁸² lignins or of lignocellulosic¹⁸³⁻¹⁸⁶ materials to phenolic compounds.

It has also been evidenced that the phenolic products obtained after the degradation of lignins were different from those obtained by electrical heating, in aqueous media¹⁷⁹ or in hydrogen donating solvents.^{105, 108} To our knowledge, no clear mechanism has been proposed to explain such discrepancies.

If the heating technique is likely to influence the type of products obtained, it has also been shown that a same catalyst may favor the appearance of different products if used in a conventional reactor or in microwaves.¹⁷⁹

Even if the mechanism of lignin solvolysis under microwaves heating is ambiguous and could limit its large-scale application, microwaves technologies still represent another step towards the development of fully sustainable and “green” methodologies of low environmental impact for lignin depolymerization.¹⁰⁸

4 Supercritical fluids to modify lignin

4.1 Supercritical fluids to modify lignin

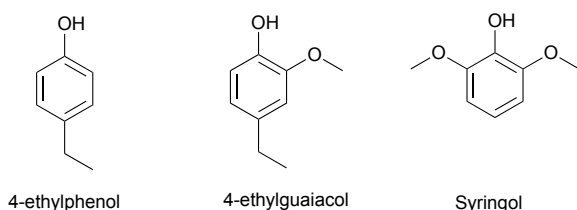
Supercritical fluids (SCFs) are substances above their critical temperature (T_c) and critical pressure (P_c) and below the pressure needed for condensation. As defined by Himmelblau, the critical condition for the gas-liquid transition is the established physical condition at which density of both liquid and gas coexist and becomes indistinguishable.¹⁸⁷ Under supercritical conditions, SCFs have unique physico-chemical properties, such as gas-like diffusivity and viscosity, and liquid-like density, which are completely different from gas and liquid at ambient conditions. Also the solvation power of SCFs is lower in comparison to ordinary liquids modifying both selectivity and reactivity of the processes. In general, at gas-like densities, the fluid is hardly able to dissolve other substances, whereas at liquid-like densities, the molecules of SCF can reasonably easily interact with the molecules of other compounds and drive them into gas phase. Slight changes of temperature and pressure near to the critical point of the system are enough to achieve a significant variation of density allowing several properties,

such as solubility, partition coefficient, dielectric constant and ionic products of SCFs to be tailor-made.¹⁸⁸ Besides, low surface tension and high diffusivities of SCFs, promote the diffusion of these substances into the pores of lignocellulosic biomass structure, whereas their liquid-like density endorses the dissolution of biomass components. The above-mentioned properties as well as a possibility to easy manipulation of these properties enhance the potential of SCFs to promote the depolymerization of lignin into its monomers. Among several solvents proposed for supercritical delignification and lignin depolymerization, the most sustainable ones are: water ($T_c = 374.2\text{ }^\circ\text{C}$; $P_c = 221\text{ bar}$), ethanol ($T_c = 243.1\text{ }^\circ\text{C}$; $P_c = 64\text{ bar}$), methanol ($T_c = 240.0\text{ }^\circ\text{C}$; $P_c = 79.6\text{ bar}$) and carbon dioxide ($T_c = 31.0\text{ }^\circ\text{C}$; $P_c = 74\text{ bar}$). Mixtures of solvents, such as water/alcohols,¹⁸⁹⁻¹⁹² carbon dioxide/water,¹⁹³ carbon dioxide/water/alcohol,^{194, 195} mostly under subcritical conditions, have also been used for this purpose.

4.2 Supercritical H₂O

In spite of intensive research carried out to establish the mechanism and to optimise the depolymerization of lignin with supercritical water (scH₂O), the precise lignin depolymerization pathway remains unclear mostly due to the specific and complex structure of lignin polymer and the competition between radical and ionic reactions. According to literature reports, in scH₂O medium, lignin is firstly decomposed through the hydrolysis and dealkylation into low molecular weight fragments with highly reactive functional groups, *e.g.* formaldehyde and phenolic compounds (guaiacols, anisoles and catechols).^{196, 197} Higher molecular weight fragments are formed through the cross-linking between above-referred fragments and residual lignin.¹⁹⁶ Kleinert and Barth¹⁹⁸ reported that the combination of highly reactive radicals promotes condensation reactions leading to the formation of re-condensed aromatics products with high molecular weight, called char or tar. Consequently, it limits the content of low molecular weight phenolic compounds. An alternative approach to overcome the above-referred recombination of highly reactive radical reaction intermediates is the employment of reactive additives to scH₂O processes. Phenol has attracted attention as capping agent because it possesses unique radical scavenging properties limiting the formation of undesired multiple condensed compounds.^{197, 199} Man *et al.*¹⁹⁷ investigated the depolymerization of lignin in scH₂O/phenol mixtures at 400 °C. Little char formation (up to 20 wt. %) was found due to “obstruction” of active fragments (*e.g.* formaldehyde) and capping of active sites by excess of phenol.^{196, 197} Also, Roberts *et al.*²⁰⁰ have reported that char formation in base-catalysed lignin hydrolysis can be greatly diminished by adding boric acid as capping agent. Besides the promising results obtained in a presence of phenol or boric acid, their use can be questionable because of environmental, health and safety concerns related to those chemicals. In scH₂O medium, lignin is rapidly converted into a wide range of products, mainly low molecular weight compounds (*e.g.* phenol, guaiacol, catechol, *o*-cresol, *m*-cresol, and catechol) and gases (*e.g.* H₂, CO₂ and CH₄).^{106, 201, 202} A quick formation of phenolic products indicates that ether bonds present in lignin are easily cleaved under scH₂O.²⁰¹ Catechol

is one of the main products obtained in depolymerization of lignin with yields in the range of 11–28 wt.%, depending on the lignin source and reaction severity.^{106, 203} Wahyudiono *et al.*²⁰⁴ explored the effect of scH_2O medium (370–420 °C) on the decomposition of catechol as a lignin model compound. They found that changing the temperature and pressure influences the reaction rate of phenol production. Additionally, higher water density promotes the hydrolysis rate of either ether or C–O bonds of lignin, probably due to variation of degree of ionic dissociation of water as the pressure changes with temperature. Sato *et al.*²⁰⁵ also investigated the effect of water densities on the decomposition of 2-isopropylphenol through dealkylation into phenol and propene and arrangement of 2-isopropylphenol propyl functional group into 2-propylphenol. The liquid products from decomposition of 2-isopropylphenol in scH_2O are depicted in Scheme 6. The authors stated that the rate constant for dealkylation increased almost proportionally with an increase of water density, whereas reaction rate for rearrangement did not change significantly with the water density.²⁰⁵



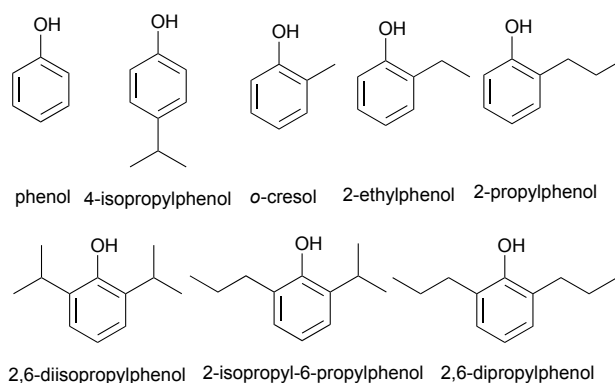
Scheme 6. Examples of liquid products obtained from decomposition of 2-isopropylphenol in scH_2O at 400 °C.

4.3 Supercritical alcohols

Recently, alcohols such as ethanol,^{193, 206–209} and methanol,^{210, 211} have become popular solvents for the supercritical depolymerization of lignin. The main reason for this is the rapid heat transfer and high solubility.²¹² In the context of green chemistry, it should be noted that methanol and ethanol have been considered as the most environmentally preferable alcohols.⁸⁹ Additionally, these alcohols can act as H_2 donors, making them a suitable reaction medium for lignin depolymerization processes. In addition, Song *et al.* suggested that alcohol molecules can work as nucleophiles to prompt C–O–C bond cleavage *via* alcoholysis reaction acting as a source of hydrogen.²¹³ Specifically, ethanol does not only act as H_2 donor solvent but also as capping agent and formaldehyde scavenger, inhibiting re-polymerisation reactions.^{115, 214}

Lignin depolymerization processes in presence of supercritical alcohols can be categorised into two main groups: base-catalysed²⁰⁶ and hydrogenolysis. Hydrogenolysis, in turn, can be divided into the following strategies: (i) presence of molecular H_2 and metal catalysts;¹⁹¹ (ii) presence of a metal catalyst and H_2 donor solvent, such as formic acid;²¹⁵ and (iii) depolymerization characterised by the production of H_2 from the reforming of the solvent in a presence of noble metal catalysts.¹⁰² The yield and product distribution in the lignin bio-oil is strongly influenced by the adopted depolymerization strategy and lignin source, as depicted in Table 1. Miller *et al.*²⁰⁶ studied a wide range of bases and demonstrated that stronger alkalis, *e.g.* NaOH, KOH, enhance the

lignin conversion yields in comparison (on molar basis) to weaker bases, *e.g.*, LiOH. As mentioned above, several hydrogenolysis strategies have been used to explore lignin depolymerization. Kim *et al.*²¹⁶ tested different alcohols, including ethanol, methanol and 2-propanol, as solvents under supercritical conditions in the depolymerization of a commercial Asian lignin (Protobind 1000) at 350 °C for 40 min with four types of catalysts supported on activated carbon (Pt/C, Pd/C, Ru/C and Ni/C) in the presence of 30 bar H_2 . In this case, ethanol was the preferred alcohol along with Pt/C resulting in a high lignin-oil yield of 77.4 wt. % composed by low molecular weight phenols as shown in Scheme 7.



Scheme 7. Examples of low molecular weight phenols of Pt/C-catalysed hydrolysis of a commercial Asian lignin (Protobind 1000) in supercritical ethanol at 350 °C, 30 bar of initial H_2 pressure for 40 min.

The use of hydrogen donor solvent, *e.g.* formic acid, for the depolymerisation and hydrogenolysis of switchgrass lignin with supercritical ethanol and 20 wt. % Pt/C catalyst at 350 °C (no pressure information given) has been investigated by Xu *et al.*²¹⁵ who reported a higher yield in monomeric phenols and enhanced H/C and O/C molar ratios. Additionally, formic acid was previously found to promote the stabilisation of aromatic radicals under supercritical conditions through *in-situ* hydrogen production.²¹⁷ Considering the green chemistry concept, it is preferred to avoid the addition of acids due to their significant high environmental impact.⁸⁹ Besides, the use of additional reagents, such as formic acid, constitutes an important drawback to be addressed in an effort to scale up this technology to industrial level. On the other hand, using formic acid as a source of renewable hydrogen permits to avoid the use of H_2 gas. Ma *et al.* reported the catalytic depolymerization of kraft lignin in supercritical ethanol over activated-carbon-supported α -molybdenum carbide catalyst (α -MoC1–x/AC) under N_2 at 280 °C and 105 bar of pressure.²¹⁸ The main products were aromatics, such as phenols and phenyl alcohols, aliphatics (C_8 – C_{10} esters and C_6 alcohols), oligomers and char. Ethanol was reported to provide higher liquid product yield in comparison to methanol, isopropanol or water, with complex relations between lignin source, solvent and operational parameters. The addition of H_2 instead of N_2 was found to have a negative effect on the formation of the low-molecular-mass products. In opposition, Wang and Rinaldi¹⁰⁰ reported that supercritical 2-propanol, due to its great H_2 transfer properties, is one of the best solvent options in the catalytic degradation of

organosolv lignin and lignin model compounds at 300 °C and in presence of Raney Ni catalyst. Huang *et al.*²¹⁹ investigated the depolymerization of soda lignin in supercritical ethanol using Cu-Mg-Al catalyst. At the respective optimal conditions, under 340 °C for 4 h with 20 wt % Cu and having a (Cu+Mg)/Al in a ratio of 4, resulted in 34 wt % of monomers with no char formation. In this work, ethanol acted as both solvent and alkylation agent, reacting with alcohols, aldehydes and esters. Additionally, the combination of Cu with alkali sites promotes ethanol dehydrogenation, which in consequence produced H₂ needed for dehydrogenation and HDO reactions. Supercritical methanol together with Cu-doped porous catalysts has been reported to avoid the formation of char, with production of H₂ from the reforming of solvent.²¹⁰

4.4 Supercritical CO₂

One of the most recent strategies reported in literature for lignin depolymerization involves the presence of supercritical CO₂ (scCO₂) in water and water/alcohol mixtures. CO₂ as additional component in the mixture, can significantly enhance the yield and selectivity of particular valuable, low molecular-mass products. In general, scCO₂ increases the accessibility of solvents to organic matter improving the effectiveness of the process. Specifically, Schrems *et al.*¹⁹⁴ evaluated the presence of scCO₂ in water/ethanol mixture in delignification pathways during organosolv pulping using lignin model compounds. This work allows concluding that scCO₂ adds value to the process by speeding up the conversion of lignin model compounds. For example, the decomposition rate of 2-methoxy-4-(1-hydroxyethyl)phenol at 140 °C with scCO₂ was faster than the reaction rate at 180 °C in the absence of CO₂. According to the authors, this result can be explained by the decrease of solvent polarity, which promotes the formation of neutral *p*-quinone methide intermediate and the destabilisation of polar transition states and ionic intermediates as well. Thus, scCO₂ does not only affect the solubility and diffusivity but also changes the reaction pathways and energy activation parameters and kinetics of the pulping process.¹⁹⁴ Also, Numan-Al-Mobin *et al.*¹⁹³ evaluated the presence of scCO₂ in subcritical water, which consists in the acid-catalysed treatment, by the formation of acidic environment, at 300 °C, 221 bar for 10 min of residence time, *in lieu* of typical mineral acid-based depolymerization. The authors reported that appreciable guaiacols yields (60%) were achieved using this approach. Given that mild temperatures are preferable to increase CO₂ solubility and, consequently the reaction selectivity, it is likely that this approach might be more amenable for lignin depolymerization process in comparison to *e.g.* scH₂O.

4.5 Overview of key supercritical fluid strategies for lignin depolymerisation

Table 1 depicts some of the supercritical fluids strategies, feedstocks, main products and yields from the most representative literature reports included in this review. It constitutes an overview of key strategies in using supercritical fluids for lignin depolymerisation, and shows a need for improvements regarding yields, products, operational conditions (*e.g.* milder conditions) and catalysts yet to be optimized. Supercritical water technologies face

numerous engineering challenges, which should be taken into consideration before engaging them in a depolymerization of lignin. One of the main tasks is the requirement of specialized equipment able to withstand high temperatures and pressures. Besides, due to high acidity and high level of dissolved oxygen, scH₂O may lead to equipment corrosion problems. Additionally, due to high temperatures and pressures required, scH₂O processes are energy-demanding. A process using scCO₂ for lignin depolymerization appears possibly more viable than scH₂O, since CO₂ requires milder temperatures. Supercritical alcohols show a great potential as reaction medium for lignin depolymerization, however there is still a lack of detailed information about their influence on obtaining phenolic compounds with high yields. Understanding the solvent effect in lignin depolymerization is highly desirable to allow designing active and stable systems working under mild reaction conditions that could provide a significant advance in the lignin depolymerization strategies with supercritical alcohols.

5 Ionic liquids to modify lignin

5.1 Ionic liquids

The use of ionic liquids (ILs) for biomass processing has been thoroughly developed as green and efficient technology over the properties,²²⁰ such as high thermal stability, negligible vapour last years.^{39, 43, 221} Composed exclusively by ions and possessing melting point lower than 100 °C, ILs have unique physicochemical pressure, wide polarity, acidity and basicity ranges, and good solvent power, which allow to selectively modify biomass and to reach a wide range of products in the frame of the biorefinery concept.⁵¹ Lignin is one of the targets in biomass processing and several ILs have demonstrated an exceptional ability to dissolve this macromolecular fraction.²²²⁻²²⁴ Extraction of lignin from lignocellulosic biomass and further recovery, as high purity fraction, has been successfully achieved.^{48, 225, 226} Furthermore, conversion of macromolecular lignin into aromatic products can also be performed in ILs when assisted by catalysts,²²⁷⁻²²⁹ but the need of both catalyst and IL recovery can be technically and economically challenging. Lately, George *et al.*²³⁰ mentioned that some ILs have the potential to play both solvent and catalyst roles by dissolving and transforming lignin without additional catalyst. The acidity and basicity of ILs, the importance of cation and anion, the reaction conditions and the presence of water are determinant factors in lignin depolymerization process solely mediated by ILs.

5.2 Acidity and basicity of ILs and their effect on the cleavage of lignin bonds

Lignin depolymerisation can be achieved by using acidic catalysts (*e.g.* organic and inorganic acids) with the ability to perform hydrolysis of several types of covalent linkages existing in lignin. Therefore, examination of the ability of acidic ILs for the same purpose was tackled in various works.²³¹⁻²³⁶

In early studies, reaction of lignin model compounds, such as guaiacylglycerol- β -guaiacyl ether (GG) and veratrylglycerol- β -guaiacyl ether (VG), with acidic ILs were performed by Ekerdt and co-workers.^{232, 234} The acidic property of 1-H-3-methylimidazolium chloride ([Hmim][Cl]) provided the ability to disrupt β -O-4 linkages

in both GG and VG model compounds releasing guaiacol as main product. Approximately 70 mol% conversion into guaiacol was attained after reaction at 150 °C of both GG and VG with [Hmim][Cl]. The authors suggested a reaction mechanism starting with dehydration process. Afterwards, the acidic environment promoted by IL allows acidic character of water molecules, thus participating in the direct hydrolysis of β -O-4 linkages present in GG and VG. However, as side products Hibbert's ketones were also produced.²³⁴ In another work, guaiacol and unstable intermediates were formed after reacting similar lignin model compound with both acidic 1-(4-sulfobutyl)-2,3-dimethylimidazolium triflate ([pSO₃Hmim][OTf]) and 1-(4-sulfobutyl)-2,3-dimethylimidazolium triflate ([bSO₃Hmim][OTf]).²³⁶ Furthermore, cleavage of α -O-4 ether linkages was attained using other acidic ILs, *i.e.* 1-carboxymethyl-3-methylimidazolium tetrafluoroborate ([mCOOHmim][BF₄]), 1-carboxymethyl-3-methylimidazolium chloride ([mCOOHmim][Cl]), 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulphate ([bSO₃Hmim][HSO₄]) and 1-butyl-3-methylimidazolium hydrogensulphate ([bmim][HSO₄]), when reacted with benzyl phenyl ether (BPE).¹⁷⁸ Conversion of 83.1 % of BPE into phenol, as major product, and an array of secondary compounds, such as benzyl alcohol, 2-benzylphenol and 4-benzylphenol was successfully obtained after 10 min of microwave-assisted reaction. Moreover, [bmim][HSO₄] was also capable to mediate demethylation of guaiacol into catechol.¹⁷⁸

As a proof of concept, depolymerization of oak lignin using [Hmim][Cl] as solvent and catalyst was accomplished and presented elsewhere.²³¹ The obtained results showed a decrease of lignin molecular weight, caused by cleavage of alkyl-aryl ether linkages present in lignin.²³¹ However, products from lignin breaking down were not disclosed in this study. A different approach of liquefaction of sugarcane bagasse (250 °C) with [bSO₃Hmim][HSO₄] in catalytic amounts (1 mmol) allowed simultaneous delignification and depolymerization of lignin into low molecular weight fractions.²³⁵ This process yielded 13.5 wt% of volatile aromatic compounds originated from lignin. From the mechanistic point of view, the presence of acidic IL firstly breaks down lignin ether bonds, such as β -O-4 and 4-O-5, forming structural units *i.e.* *p*-coumaryl, coniferyl and sinapyl alcohol and their dimers. Afterwards, several side reactions, also catalysed by [bSO₃Hmim][HSO₄], take place to form a variety of aromatic compounds.²³⁵

Although IL acidity is relevant to hydrolyse lignin, in general, acidic ILs lack the ability to form strong hydrogen bonds with macromolecular components of biomass. On the contrary, highly alkaline ILs, such as 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) and 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), are able to dissolve practically entire biomass, thus they are more commonly used in lignocellulosic feedstock processing.^{43, 60, 237, 238} Therefore, a strong need to understand the chemical transformations of lignin in this type of ILs has been raising in last years, especially if related to [emim][OAc].^{230, 239-247}

Lignin model compound, GG, was again an object of study and its transformation at 120 °C using [Cl] and [OAc] imidazolium-based ILs was scrutinised.²⁴⁰ In all cases, production of enol ether (EE) was observed as a result of GG dehydration. EE is generally unstable in pulping and acidolysis processes, but surprisingly it presented

stability in the ILs examined.²⁴⁰ This phenomenon demonstrates that chemical character and selectivity of ILs is crucial to obtain and stabilise specific compounds derived from lignin. The production of EE instead of guaiacol is an opposite effect to that aforementioned with acidic ILs. In fact, ILs with [Cl] and [OAc] cations were not able to hydrolyse the β -O-4 ether linkage of GG to form guaiacol, precisely because of the lack of anion acidity. Nevertheless, Singh and co-workers^{239, 241} suggested that chemical properties of [emim][OAc] might be changed from alkaline to acid when increasing temperature from 120 °C to 160 °C. They justify this by a release of the acidic proton in C2 position of IL imidazolium ring with temperature increase. This acidic behaviour was referred to mediate the disruption of β -O-4 ether linkage in lignin. Precisely, at the highest temperature studied, a high content of guaiacyl monomers, such as guaiacol and allyl guaiacol, were detected suggesting an acidic cleavage behaviour of IL medium.¹¹ At the lowest temperature, the alkaline environment allows to break 8-aryl ether bonds in lignin.²⁴¹ However, it is worth mentioning that these conclusions were conceived on the basis of the reaction between [emim][OAc] and biomass, but not pure lignin. One of the key differences in this case can be the fact that biomass autohydrolysis products, such as acetic acid, might be formed at 160 °C participating in the cleavage of β -O-4 ether linkages. Therefore, the acidic and alkaline temperature dependence of [emim][OAc] is debatable and it shall be supported with further research.

Although the mechanism is not fully understood, cleavage of aryl ether bonds in lignin with high basicity ILs was reported in other literature reports.^{243, 245, 246} The behaviour of [emim][OAc] in lignin depolymerization was deeply scrutinised, by performing chemical characterisation and quantitative analysis of generated products through 2D NMR spectroscopy, elemental analysis and gel permeation chromatography.²⁴³ The results disclosed 4 main phenomena occurring in lignin macromolecule when in contact with [emim][OAc]: i) depolymerization; ii) dehydration; iii) demethoxylation; and iv) condensation. The first phenomenon was characterised by hydrolysis of β -O-4 ether linkage as well as carbon-carbon bonds, such as β - β' and β -5'. Similar results were also reported with 1-butyl-3-methylimidazolium acetate ([bmim][OAc]).^{245, 247} A decrease of aliphatic hydroxyl groups in treated sample and consequent formation of conjugated double bonds indicated a dehydration reaction. The demethoxylation was monitored by the reducing content of methoxyl groups in treated lignin.^{243, 247} This phenomenon was also observed in another study, in which 45 mol% and 50 mol% of methoxyl groups were removed from original lignin using [emim][OAc] and [bmim][Cl], correspondingly.^{245, 246} Finally, condensation was confirmed by an increase of the average molecular weight when compared to that of original lignin.^{243, 247} All these reactions allowed a decrease of polydispersity of treated lignin leading to more homogeneous molecular structures.^{243, 246} Furthermore, using [emim][OAc] is possible to produce a more linear lignin, due to disruption of dibenzodioxocin linkages associated to lignin branching.²⁴⁴ This allows to establish a new strategy of production of biopolymers derived from lignin.

Lignin source	Solvents	Experimental conditions			Catalyst	Main products/Results	Yields	Ref.
		T (°C)	p (bar)	t (min)				
"Alkaline" lignin	water	400	250	600	-	Catechol, phenol, <i>m,p</i> -cresol and <i>o</i> -cresol and char	Catechol 26.2 wt. %, phenol 11.8 wt. %, <i>m,p</i> -cresol 7.0 wt. % and <i>o</i> -cresol 4.0 wt. %	106
Poplar alkali lignin (AL) and corncob to corncob residue lignin (XRL)	water	375	221	30	-	Char and gases formation; Phenol and 4-ethylphenol produced from corncob residual lignin; Guaiacol and 2,6-dimethoxyphenol produced from Poplar alkali lignin	Phenolic yield from XRL and AL: 140 and 90 mg/g of dry lignin, respectively; Char: up to ~250 mg/g dry lignin for XRL and AL; Gas: <5%	203
Commercial lignin (Protobind 1000)	ethanol and molecular H ₂	350	30 ^a	40	Pt/C	4-ethylphenol, guaiacol, 4-ethylguaiacol, and syringol; Gases (H ₂ , CH ₄ , CO and CO ₂)	Lignin oil: 77.4 wt. %; Char: 3.7 wt. %; Gases: ~20 wt. %	216
Indulin-AT (Kraft lignin)	methanol and molecular H ₂	320	35 ^a	480	S-NiW/AC ^c	No char formation; Neither competing aromatic ring hydrogenation or repolymerization of char was observed	Monomers: 28 wt. % of which 76 % of the products were alkylphenolics and guaiacolics	248
Asian lignin (AL), Organosolv (OL) and Inbicon lignins (LI)	<i>tert</i> -butanol and molecular H ₂	350	30 ^a	40	Pt/C	Effective hydrodeoxygenation was observed; Gases (CO, CO ₂ and CH ₄) ^b and char.	4-ethylphenol and 4-ethyl guaiacol: 1.4 wt. % from AL; syringol, 4-methylsyringol, 4-propylsyringol: 1.9 wt. %, 1.1 wt. % and 1.4 wt. %, respectively, from OL; Low yield of aliphatic phenols from LI; Char: up to 12.7 wt. % from AL.	249
Organosolv switchgrass lignin	ethanol and formic acid ^c	350	- ^d	240	Pt/C	Identified monomers; Phenol, <i>p</i> -cresol, guaiacol, <i>p</i> -methylguaiacol, <i>p</i> -ethylguaiacol, <i>p</i> -propylguaiacol, and homovanillyl alcohol	Monomers: 21 wt. %; Char: 28 wt. %	215
Protobind 1000 lignin (from wheat straw soda pulping)	ethanol and water	400	375-400	240	Al(OTf) ₃	Aliphatic and aromatic hydrocarbons, condensation products and saturated oxygenates; No char formation	100% lignin conversion; Selectivity - aliphatics: 67 wt. %; monoaromatics: 18 wt. %; naphthalenes: 5 wt. %	250
Kraft lignin (KL) and organosolv lignins (OL)	acetone	350	100 ^a	60	FHUDS-2 ^e	Lower amount of aliphatic hydroxyl groups and higher amount of aromatic hydroxyl groups in the depolymerised lignin products	Depolymerization yield for KL and OL > 95 wt. %	251
Alkali lignin	water and scCO ₂	300	221	10	-	Higher content of the volatile fraction in the scCO ₂ -treated samples; ScCO ₂ promoted the β-O-4 bond cleavage	Guaiacols: 60 % in CO ₂ vs. 37 % in N ₂ ^f	193

^a initial H₂ pressure, final pressure was 150 bar; ^b H₂ was included in the compositional analysis of gas fraction due to the presence of high amounts of residual H₂ in the reactor; ^c used as hydrogen donor; ^d Autogenous pressure; ^e NiMoW-based commercial hydrogenation catalyst; ^f used as standard system with pressure equal to this of CO₂.

5.3 Influence of cation and anion on the depolymerization process

ILs are design solvents with easily tuneable properties.³⁵ Therefore, studying different combinations of cations and anions in lignin

depolymerization is recommendable in order to set the desirable physicochemical properties of ILs. Several works evaluated and ranked ILs regarding their catalytic power towards lignin.^{230, 232, 247, 252}

Ekerdt and co-workers²³² studied the effect of the acidity of several imidazolium-based ILs in the cleavage of β -O-4 ether linkage in lignin model compounds to produce guaiacol. Using Hammett acidity function, ILs were ranked according to their acidity: [Hmim][Cl] > 1-H-3-methylimidazolium tetrafluoroborate ([Hmim][BF₄]) > 1-H-3-methylimidazolium hydrogensulphate ([Hmim][HSO₄]) \approx 1-H-3-methylimidazolium bromide ([Hmim][Br]) \approx [bmim][HSO₄]. Although the most acidic ([Hmim][Cl]) IL demonstrated the highest guaiacol yield, a lack of correlation between acidic power and guaiacol yield was observed for other examined ILs. Hence, they suggested that acidity of IL solely does not represent a mean to evaluate the effectiveness of cleavage of β -O-4 ether linkage. The ability of IL anion to establish strong hydrogen bonds with hydroxyl groups present in lignin or in lignin model compounds was referred to contribute strongly to effective bond cleavage. This property was better correlated with guaiacol production than IL acidity.²³² Furthermore, size of ions could also obstruct the catalytic ability of ILs. For instance, less acidic [bmim][HSO₄] demonstrated better catalytic performance in lignin depolymerization than more acidic [bSO₃Hmim][HSO₄]. It was suggested that higher steric hindrance of butyl sulfonic acid is determinant for a less efficient catalytic performance of this IL.¹⁷⁸ However, when using catalytic amount of ILs, the acidity strength is more relevant for lignin depolymerization as reported elsewhere.²³³ In this context, [bSO₃Hmim][HSO₄] was the most efficient in reducing the average molecular weight of lignin in comparison to other tested acidic ILs, including [bmim][HSO₄]. The enhanced performance of this IL can be explained by the simultaneous acidity of both cation and anion.²³³

There are also contradictory reports regarding depolymerization and condensation effects during lignin dissolution in different types of ILs.^{243, 247, 252} Two of these reports state that strongly alkaline imidazolium-based ILs, such as [emim][OAc] and [bmim][OAc], lead to cleavage of β - β' and β -5' bonds. In another work, this phenomenon was not observed for alkaline cholinium-based ILs, *i.e.* cholinium lysinate ([Ch][Lys]) or cholinium glycinate ([Ch][Glc]).²⁴⁷ On the contrary, condensation reactions favouring the formation of novel β - β' and β -5' bonds in lignin structure was achieved using these cholinium-based ILs.²⁴⁷ The veracity of this statement must be confirmed, once it implicates the alkaline character of both types of ILs. However, temperature range settled in these studies is considerably different which could compromise a fair comparison of presented results. Nevertheless, a profound research on the effect and influence of IL cation on depolymerization/condensation reactions must be made.

Other studies focused on the selectivity of lignin depolymerization. ILs with different anions depolymerise lignin through restrict reactions increasing the selectivity towards certain compounds.^{178, 247} The cleavage of BPE α -O-4 and guaiacol C-O linkages was studied by testing 29 ILs.¹⁷⁸ In both cases the acidity was the key factor for the successful breaking down of bonds in lignin model compounds. However, strongly acidic [mCOOHmim][BF₄], which promoted the highest BPE conversion, barely disintegrated C-O from guaiacol to

produce catechol. In contrast, [bmim][HSO₄] showed elevated efficiency in both reactions.¹⁷⁸ Therefore, it can be concluded that one IL can be very efficient in lignin depolymerization however the selectivity is low and *vice versa*.²⁴⁷

A non-conventional, strongly alkaline IL, such as butyl-1,8-diazabicyclo[5.4.0]undec-7-enium chloride ([DBUC₄][Cl]), also demonstrated both lignin dissolution²⁵³ and depolymerization ability.²⁵⁴ Contrary to other chloride ILs, [DBUC₄][Cl] demonstrated an improved stabilisation of lignin, dissolving it at mild temperatures such as 105 °C.²⁵³ This achievement is chiefly attributed to alkaline property of [Cl] anion, but a special contribution in the stabilisation of lignin aromatic units was mediated by [DBUC₄] cation.²⁵³ By increasing temperature from 150 to 250 °C, [DBUC₄][Cl] was also able to depolymerise lignin through cleavage of β -O-4 ether linkages. The depolymerization performed by this IL impressively favoured the formation of oligomers mainly constituted by catechol units.²⁵⁴

5.4 Other parameters affecting lignin depolymerization in ILs

Besides the catalytic performance of ILs, depolymerization of lignin is also governed by other factors, such as temperature, residence time and presence of water. Among those, temperature is the most influent parameter and must be controlled to effectively depolymerise lignin and to avoid side reactions simultaneously. For instance, in the treatment of eucalyptus and switchgrass with [emim][OAc], an increase of temperature from 120 °C to 160 °C determined a preferential structural cleavage of syringyl units from native lignin in detriment of guaiacyl units. This phenomenon was regarded as a change of solvatochromic properties of lignin units in a presence of IL, influenced by temperature increase.²⁴¹ Furthermore, the kinetics of the process towards certain products can be controlled thermally. The processing of different types of lignocellulosic biomass with [emim][OAc] at 120 °C allowed formation of vanillin, which at high temperature (*e.g.* 160 °C) went through cleavage of methyl ketone group producing guaiacol.¹⁰ In general, increasing temperature enhances the hydrolysis of lignin by ILs, but selectivity to produce particular products could be compromised.

Although less influencing parameter, residence time correlates well with temperature in case of depolymerization efficiency and selectivity.²⁵⁵ An increase of residence time leads to structural modifications of lignin mainly in the cleavage of β -O-4 bonds, which is significantly enhanced.²⁵⁵ This type of linkage practically disappears after treating lignin with 1-butylimidazolium hydrogen sulphate ([bHim][HSO₄]) at 120 °C for 12 h. In contrast, β - β and β -5 linkages were maintained stable for an 8 h-treatment, but further increase of residence time to 12 h allowed chemical alterations of those bonds. Furthermore, a drastic increase of residence time could lead to re-polymerisation of lignin fragments through condensation reactions.²⁵⁵

The presence of water is sometimes overlooked, but it strongly influences the activity of IL for lignin depolymerization. In fact, the process of depolymerization through hydrolysis reaction requires water. In absence of water, hydrolysis of lignin with ILs was verified to be quenched specially when dried lignin was used.²³¹ Therefore, highly reactive ILs *per se* may not be able to depolymerise lignin if

water is absent in the system. Furthermore, the presence of water alters the acidity and basicity of the IL medium.²⁵² For acidic ILs, such as 1-butyl-3-methylimidazolium methylsulphonate ([bmim][MeSO₃]), adding water allows to control the pH of the medium for a precise lignin depolymerization without carbonization of the raw material. In case of strongly alkaline [bmim][Cl], an appropriate amount of water (30 wt.%) improves the interaction through π - π stacking between the benzene ring of aromatic lignin and IL cation, enhancing cleavage of β -O-4 linkages and helps to avoid condensation reactions.²⁵²

5.5 The challenge in ILs recovery and products separation

The recovery of reagents and downstream processing are key aspects of every process. In case of ILs this is even more challenging once strong interactions are established between ILs, lignin and lignin-derived products. For instance, in the processing of *Miscanthus* biomass a carbohydrate-free lignin with low sulphur contents was efficiently isolated, but approximately 6-9 wt.% IL was simultaneously recovered in the sample. Even with additional washing steps, IL was not completely removed from the recovered lignin.²⁵⁵ The incomplete recovery of ILs is probably one of the main disadvantages on their application in biomass and lignin processing. The price of ILs in contrast to other solvents and catalysts mentioned in this review is still higher. Therefore, yield recoveries near 100% are highly desirable either due to economic or environmental issues. Fewer concerns can be given to the reuse of IL since several works have demonstrated a success in this issue.^{178, 234, 256}

The separation and purification of aromatic and phenolic products from IL is even more intriguing. A recent study revealed the use of compressed CO₂ as anti-solvent of lignin-derived products.²⁴⁵ After lignin depolymerization with [bmim][OAc], compressed CO₂ is added and it forms carboxylate zwitterions (imidazolium-2-carboxylate), which disrupts the hydrogen-bond network between IL and lignin-originated products. Moreover, a selective precipitation of products can be accomplished by monitoring the pressure of CO₂.²⁴⁵ Another approach considered the application of polymeric resins and supercritical CO₂ to extract phenolic compounds resulting from wheat straw lignin depolymerization mediated by [emim][OAc].⁵² Polymeric resins, such as Amberlite XAD-7, allowed to concentrate phenolic compounds and to remove a vast amount of IL. A final purification step was attained with extraction of several phenolic compounds using supercritical CO₂, taking in advantage the negligible solubility of ILs in this sustainable solvent.⁵²

6 Conclusions and next challenges for “green” lignin and derivatives

The way to a global sustainable development is through the establishment of solutions which reduce the rapid consumption of fossil resources, which are not renewable (petroleum, natural gas, coal, minerals). A forward looking approach is the stepwise conversion of large parts of the global economy into a sustainable

biobased economy with bioenergy, biofuels, and biobased products as its main pillars.²⁵⁷ The creation of complete and integrated biorefining industries, based on the valorization of plant resources, implies the development of lignin valorization processes with the same concerns and therefore should be designed considering the principles of green chemistry.^{10, 258, 259}

Different valorizations for lignins can be considered. Several cost-effective examples of use of macromolecular lignin have already been demonstrated.²⁶⁰ In the future, one of the most interesting and challenging concepts seems to be the conversion of lignins to aromatic monomers. This strategy allows satisfying the industry needs in hydrocarbons but also allows a complete exploitation of lignin's structural potential. Hydroprocessing is certainly the most interesting way for lignins conversion into aromatic monomers. Three elements appear us crucial to continue the development of integrated hydroprocessing pathways: (i) Imagining chemical demand differently, (ii) Improving the theoretical knowledge of hydroprocessing, (iii) Developing effective new technologies, new equipment and new catalysts at lower costs.

6.1 Think differently

Direct and efficient conversion of lignin to discrete molecules or classes of high volume, low molecular weight aromatic molecules is an attractive goal. As petroleum resources diminish and prices increase, this goal is very desirable, and is perhaps the most challenging and complex of the lignin technological barriers. It has long been recognised that there is a need for both “high-volume and low value” and “low-volume and high-value” applications in order to achieve full economic use of isolated lignins.⁷ Bringing high-volume aromatics efficiently and selectively from a material as structurally complex and diverse as lignin becomes a challenging but viable long-term opportunity.²⁶¹ Most of the developed lignin hydroprocessing technologies therefore target the production of aromatic bulks (BTX), which are directly incorporable in the conventional petrochemical processes (possibly with a valorization under low-weight compounds in syngas). This pathway seems more interesting than gasoline production which requires very strict conditions of hydroprocessing, mainly through extensive and energy-intensive HDO.^{45, 103} The aim of this step is to yield fungible transportation fuels or refinery feedstock blends³⁰ but it does not fully exploit the aromatic potential of lignin. In the integrated biorefineries scenario, the BTX pathway seems the most commonly accepted and expected.²⁶¹ However, two problems arise, the first one being related to the BTX toxicity and ecotoxicity. Additionally, using energy and resources to transform lignin into bulk - before using them again to turn bulks into chemicals - makes sense only if no other alternative exists. Thus transforming benzene to phenol increases the market price of the product by 50%.⁴⁶ If the idea of producing BTX from lignin to reincorporate them into conventional production cycles seems appealing, it does have obvious energy, financial and environmental costs. In this context, the valorization of oxygenated aromatic compounds obtained from lignins (Organosolv, if possible) by a softer hydroprocessing (less energy- and H₂-consuming), is a very interesting way. From these and

beyond the well-known example of vanillin,²⁶² the creation and design of new compounds (either platform chemicals or end products) with new properties and applications as well as the research of new markets for these products are capital opportunities to develop an industry more consistent with green chemistry. Creating the regulatory and market environment necessary for increased development and use of these biobased products is also fundamental. Improve resources and end-products distribution pathways to make them more sustainable are key points too.

The development of inexpensive and "green" techniques for purification and fractionation of raw material and products will also have to accompany research on these new molecules and their potential new markets. Beside the products obtained from lignins which requires high purity components, another approach may however be considered. Strassberger *et al.*²⁶² foresee a major market segment for aromatic "cocktails" more focused on the "function" than on the "structure" or "purity". For example, the linear alkylated benzenes (LABs) can be used for some application such as surfactant production. This "cocktail" strategy is obviously highly compatible with the "lignin first" approach.

6.2 Improve understanding

The few studies on the hydrogenolysis of lignins mainly targeted the optimization of the reaction settings (temperature, pressure, time) or the testing of a new catalyst.^{2, 261} The development of industrial production of aromatic compounds from lignin must also be considered through the understanding of the impacts of different inputs on the products. The influence of lignin structure on yields and composition of the oils obtained after hydrogenolysis should also be the subject of further studies. The relationship between structure and properties is a key point and has already been studied extensively for other macromolecules than lignins.²⁶³⁻²⁶⁶ Adapting the kind of lignocellulosic raw materials used to target a specific chemical production seems very important in the design of integrated biorefineries and the tailoring of original chemicals and products. The barriers that would need to be overcome are to develop knowledge of the lignin material in link with the mechanism of action of a catalyst that would allow a selective cleavage of bonds bearing determined structure monomeric lignins. This aspect should certainly not be overlooked.

6.3 New technologies, new equipment and new catalyst at lower costs

A tremendous array of products is potentially obtainable with lignin valorization, and considerable effort has been placed in developing processes that could produce valuable compounds. The realization of fully integrated biorefinery schemes for lignin valorization requires the right technology (including separation technologies), the right equipment and new catalysts to perform desired transformations as well as an improvement of efficiency and performance in conversion.

Despite significant progress and promising results with supercritical lignin depolymerization, it is notorious that there is room for improvement in terms of yields and selectivities. Focus on the design and optimization of operational conditions e.g. mild

temperatures and low pressures, and process intensification through the use of continuous mode reactors would tune the reaction pathways resulting in improved final yields. Additionally, further investigation in the recovery and reuse of catalysts would be highly desirable. Notwithstanding all the above-referred advantages of using SCFs, the need of specialized equipment able to stand such temperatures and pressures represents a huge bottleneck in terms of capital costs (CAPEX). Surely, this has been jeopardizing the investigation and development of SCF in lignin depolymerization.

In the case of ionic liquids, a major point that now needs resolution is the development of low energy and "green" separation to isolate each compound and catalyst after reaction. The coupling between heterogeneous catalysts and ionic liquid media should constitute a promising strategy to improve the extraction and separation aspects.

Whether the technique uses ionic liquids, supercritical fluids or hydroprocessing, the development of new heterogeneous catalysts is probably the most critical point for the development of integrated biorefineries. The biomass source and pretreatment method dictate the requirements of the catalyst in terms of robustness, selectivity, activity, and recyclability. For example, dirtier feedstreams require more robust catalysts, which often has implications on the type of processes that can be realistically employed. Knowledge of the types of catalysts available, their characteristics, and the types of transformations that they perform are thus essential for the development of efficient biorefineries.¹² Catalysis is the basis for many improvements in sustainable chemical transformations, facilitating the use of reduced energy and material inputs for processes that society requires.¹¹ However catalysts' synthesis either employs several equivalents of toxic reagent or is energy intensive. Thus, easily synthesized green catalysts based on earth abundant elements could provide promising solutions for the large-scale applications of catalytic hydrogenation and hydrogenolysis.¹¹⁰ The development of new green catalyst can also favour specific breaking of C-C and C-O bonds leading to a very selective depolymerisation that could produce a series of aromatic complex not likely to be obtained through conventional techniques and thus opening new opportunities for upgrading.

Anyway, the one-track thinking is not recommended and different alternatives and all the valorization pathways must be investigated.

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Notes and references

1. F. A. Wobiwo, T. H. Emaga, E. Fokou, M. Boda, S. Gillet, M. Deleu, A. Richel and P. A. Gerin, *Biomass Conversion and Biorefinery*, 2017, **7**, 167-177.
2. F. Awedem Wobiwo, V. K. Alleluya, T. H. Emaga, M. Boda, E. Fokou, S. Gillet, M. Deleu and P. A. Gerin, *Energy for Sustainable Development*, 2017, **37**, 60-65.
3. M. F. T. Deumaga, T. H. Emaga, R. Tchokouassom, C. Vanderghem, M. Aguedo, S. Gillet, N. Jacquet, S. Danthine, D. Magali and A. Richel, *Biomass Conversion and Biorefinery*, 2015, **5**, 409-416.
4. C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chemical Reviews*, 2015, **115**, 11559-11624.
5. M. Simon, Y. Brostaux, C. Vanderghem, B. Jourez, M. Paquot and A. Richel, *Journal of Chemical Technology & Biotechnology*, 2014, **89**, 128-136.
6. N. Jacquet, L. Desquay, B. Jadot, T. Kenne, N. Villani, G. Maniet, P.-L. Bombeck, S. Gillet and A. Richel, *Biotechnol. Agron. Soc. Environ.*, 2015, **19**, 197-203.
7. R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijninx and B. M. Weckhuysen, *Angewandte Chemie International Edition*, 2016, **55**, 8164-8215.
8. J. E. Holladay, J. F. White, J. J. Bozell and D. Johnson, *Top Value Added Chemicals from Biomass, Volume II- Results of Screening for Potential Candidates from Biorefinery Lignin*, Pacific Northwest Laboratory (PNNL), Richland WA (US), 2007.
9. I. Norberg, Y. Nordström, R. Drougge, G. Gellerstedt and E. Sjöholm, *Journal of Applied Polymer Science*, 2013, **128**, 3824-3830.
10. P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, 1998.
11. J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius and B. M. Weckhuysen, *Chemical Reviews*, 2010, **110**, 3552-3599.
12. S. Nanayakkara, A. F. Patti and K. Saito, *Green Chemistry*, 2014, **16**, 1897-1903.
13. F. G. Calvo-Flores and J. A. Dobado, *ChemSusChem*, 2010, **3**, 1227-1235.
14. N. G. Lewis and E. Yamamoto, *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, 1990, **41**, 455-496.
15. R. Vanholme, K. Morreel, J. Ralph and W. Boerjan, *Current Opinion in Plant Biology*, 2008, **11**, 278-285.
16. A. Vishtal and A. Kraslawski, *BioResources* 2011, **6**, 3547-3568.
17. R. Behling, S. Valange and G. Chatel, *Green Chemistry*, 2016, **18**, 1839-1854.
18. M. V. Galkin and J. S. M. Samec, *ChemSusChem*, 2016, **9**, 1544-1558.
19. A. Tejado, C. Peña, J. Labidi, J. M. Echeverría and I. Mondragon, *Bioresource Technology*, 2007, **98**, 1655-1663.
20. F. S. Chakar and A. J. Ragauskas, *Industrial Crops and Products*, 2004, **20**, 131-141.
21. B. Saake and R. Lehen, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000, DOI: 10.1002/14356007.a15_305.pub3.
22. S. González-García, M. Teresa Moreira, G. Artal, L. Maldonado and G. Feijoo, *Journal of Cleaner Production*, 2010, **18**, 137-145.
23. A. Rodríguez, R. Sánchez, A. Requejo and A. Ferrer, *Journal of Cleaner Production*, 2010, **18**, 1084-1091.
24. J. Gullichsen, C. J. Fogelholm, H. Paulapuro, S. P.-I. Yhdistys, T. A. o. t. Pulp and P. Industry, *Papermaking Science and Technology: Book 6A , 6B: Chemical Pulping*, Fapet Oy, 1999.
25. J. Fan and H. Zhan, *Chinese Journal of Chemical Engineering*, 2008, **16**, 407-410.
26. A. Gandini and M. N. Belgacem, *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Amsterdam, 2008.
27. N.-E. E. Mansouri and J. Salvadó, *Industrial Crops and Products*, 2006, **24**, 8-16.
28. A. Rahimi, A. Ulbrich, S. S. Stahl and J. J. Coon, *Nature*, 2014, **515**, 249-252.
29. Borregaard Business Areas, <http://www.borregaard.com/Business-Areas>, (accessed 07/06/2017, 2017).
30. D. D. Laskar, B. Yang, H. Wang and J. Lee, *Biofuels, Bioproducts and Biorefining*, 2013, **7**, 602-626.
31. F. Xu, J.-X. Sun, R. Sun, P. Fowler and M. S. Baird, *Industrial Crops and Products*, 2006, **23**, 180-193.
32. M. Wang, M. Leitch and C. Xu, *European Polymer Journal*, 2009, **45**, 3380-3388.
33. A. P. Klein, E. S. Beach, J. W. Emerson and J. B. Zimmerman, *Journal of Agricultural and Food Chemistry*, 2010, **58**, 10045-10048.
34. C. Chiappe and D. Pieraccini, *Journal of Physical Organic Chemistry*, 2005, **18**, 275-297.
35. M. J. Earle and K. R. Seddon, *Pure and Applied Chemistry*, 2000, **72**, 1391-1398.
36. N. Muhammad, Z. Man and M. A. Bustam Khalil, *European Journal of Wood and Wood Products*, 2012, **70**, 125-133.
37. P. Mäki-Arvela, I. Anugwom, P. Virtanen, R. Sjöholm and J. P. Mikkola, *Industrial Crops and Products*, 2010, **32**, 175-201.
38. W. O. S. Doherty, P. Mousavioun and C. M. Fellows, *Industrial Crops and Products*, 2011, **33**, 259-276.
39. A. Brandt, J. Grasvik, J. P. Hallett and T. Welton, *Green Chemistry*, 2013, **15**, 550-583.
40. S. P. Magalhaes da Silva, A. M. da Costa Lopes, L. B. Roseiro and R. Bogel-Lukasik, *RSC Advances*, 2013, **3**, 16040-16050.
41. A. M. da Costa Lopes, K. G. João, D. F. Rubik, E. Bogel-Lukasik, L. C. Duarte, J. Andreus and R. Bogel-Lukasik, *Bioresource Technology*, 2013, **142**, 198-208.
42. M. FitzPatrick, P. Champagne, M. F. Cunningham and R. A. Whitney, *Bioresource Technology*, 2010, **101**, 8915-8922.

43. A. M. da Costa Lopes, K. G. Joao, A. R. C. Morais, E. Bogel-Lukasik and R. Bogel-Lukasik, *Sustainable Chem. Processes*, 2013, **1**, 3/1-3/31, 31 pp.
44. A. M. da Costa Lopes, M. Brenner, P. Falé, L. B. Roseiro and R. Bogel-Lukasik, *ACS Sustainable Chemistry & Engineering*, 2016, **4**, 3357-3367.
45. M. P. Pandey and C. S. Kim, *Chemical Engineering & Technology*, 2011, **34**, 29-41.
46. J. v. Haveren, E. L. Scott and J. Sanders, *Biofuels, Bioproducts and Biorefining*, 2008, **2**, 41-57.
47. P. C. Rodrigues Pinto, E. A. Borges da Silva and A. E. Rodrigues, in *Biomass Conversion: The Interface of Biotechnology, Chemistry and Materials Science*, eds. C. Baskar, S. Baskar and R. S. Dhillon, Springer Berlin Heidelberg, Berlin, Heidelberg, 2012, DOI: 10.1007/978-3-642-28418-2_12, pp. 381-420.
48. N. Jacquet, G. Maniet, C. Vanderghem, F. Delvigne and A. Richel, *Industrial & Engineering Chemistry Research*, 2015, **54**, 2593-2598.
49. D. v. d. Pas, A. Hickson, L. Donaldson, G. Lloyd-Jones, T. Tamminen, A. Fernyhough and M.-L. Mattinen, *Bioresources*, 2011, **6**, 1105-1121.
50. Q. Chen, M. N. Marshall, S. M. Geib, M. Tien and T. L. Richard, *Bioresource Technology*, 2012, **117**, 186-192.
51. T. K. Lundell, M. R. Mäkelä and K. Hildén, *Journal of Basic Microbiology*, 2010, **50**, 5-20.
52. M. Lahtinen, K. Kruus, H. Boer, M. Kemell, M. Andberg, L. Viikari and J. Sipilä, *Journal of Molecular Catalysis B: Enzymatic*, 2009, **57**, 204-210.
53. T. Kudanga, G. S. Nyanhongo, G. M. Guebitz and S. Burton, *Enzyme and Microbial Technology*, 2011, **48**, 195-208.
54. S. Witayakran and A. J. Ragauskas, *Enzyme and Microbial Technology*, 2009, **44**, 176-181.
55. J. E. Holladay, J. J. Bozell, J. F. White and D. Johnson, *Top Value-Added Chemicals from Biomass Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin*, 2007.
56. G. Gellerstedt, A. Majtnerova and L. Zhang, *Comptes Rendus Biologies*, 2004, **327**, 817-826.
57. G. Wang and H. Chen, *Separation and Purification Technology*, 2013, **105**, 98-105.
58. P. Methacanon, U. Weerawatsophon, M. Thainthongdee and P. Lekpittaya, *Kasertat Journal: Natural Sciences*, 2010, **44**, 680-690.
59. M. Zhou, X. Qiu, D. Yang and H. Lou, *Journal of Dispersion Science and Technology*, 2006, **27**, 851-856.
60. M. N. Vanderlaan and R. W. Thring, *Biomass and Bioenergy*, 1998, **14**, 525-531.
61. H. Yoshida, R. Mörck, K. P. Kringstad and H. Hatakeyama, *Journal of Applied Polymer Science*, 1990, **40**, 1819-1832.
62. M. N. Anglès, J. Reguant, R. Garcia-Valls and J. Salvadó, *Wood Science and Technology*, 2003, **37**, 309-320.
63. A. García, A. Toledano, L. Serrano, I. Egüés, M. González, F. Marín and J. Labidi, *Separation and Purification Technology*, 2009, **68**, 193-198.
64. R. Sun, J. Tomkinson and J. Bolton, *Polymer Degradation and Stability*, 1999, **63**, 195-200.
65. G. Wang and H. Chen, *Separation and Purification Technology*, 2013, **120**, 402-409.
66. R. Alen, E. Sjostrom and P. Vaskikari, *Cellul. Chem. Technol.*, 1985, **19**, 537-541.
67. A. Abächerli and F. Doppenberg, *Journal*, 2001.
68. M. F. Davy, V. C. Uloth and J. N. Cloutier, *Pulp Pap. Can.*, 1998, **99**, 35-39.
69. F. Öhman, H. Theliander, P. Tomani and P. Axegard, *Journal*, 2013.
70. M. Norgren, H. Edlund, L. Wagberg, B. Lindstrom and G. Annergren, *Colloids Surf., A*, 2001, **194**, 85-96.
71. M. Norgren, H. Edlund and L. Wagberg, *Langmuir*, 2002, **18**, 2859-2865.
72. S. I. Mussatto, M. Fernandes and I. C. Roberto, *Carbohydr. Polym.*, 2007, **70**, 218-223.
73. W. Zhu and H. Theliander, *Bioresources*, 2015, **10**, 1696-1714.
74. L. Kouisni, Y. Fang, M. Paleologou, B. Ahvazi, J. Hawari, Y. Zhang and X.-M. Wang, *Cellul. Chem. Technol.*, 2011, **45**, 515-520.
75. M. Nagy, M. Kosa, H. Theliander and A. J. Ragauskas, *Green Chem.*, 2010, **12**, 31-34.
76. W. Zhu, G. Westman and H. Theliander, *J. Wood Chem. Technol.*, 2014, **34**, 77-97.
77. H. Wallmo, H. Theliander, A. S. Joensson, O. Wallberg and K. Lindgren, *Nord. Pulp Pap. Res. J.*, 2009, **24**, 165-171.
78. P. Tomani, *Cellul. Chem. Technol.*, 2010, **44**, 53-58.
79. A.-S. Joensson, A.-K. Nordin and O. Wallberg, *Chem. Eng. Res. Des.*, 2008, **86**, 1271-1280.
80. O. Wallberg, A.-S. Jönsson and R. Wimmerstedt, *Desalination*, 2003, **156**, 145-153.
81. O. Sevastyanova, M. Helander, S. Chowdhury, H. Lange, H. Wedin, L. Zhang, M. Ek, J. F. Kadla, C. Crestini and M. E. Lindström, *Journal of Applied Polymer Science*, 2014, **131**, n/a-n/a.
82. O. Wallberg and A.-S. Jönsson, *Desalination*, 2006, **195**, 187-200.
83. O. Wallberg, A. Holmqvist and A.-S. Jönsson, *Desalination*, 2005, **180**, 109-118.
84. O. Wallberg, A.-S. Jönsson and R. Wimmerstedt, *Desalination*, 2003, **154**, 187-199.
85. A.-S. Joensson and O. Wallberg, *Desalination*, 2009, **237**, 254-267.
86. A. Holmqvist, O. Wallberg and A. S. Joensson, *Chem. Eng. Res. Des.*, 2005, **83**, 994-999.
87. I. Brodin, E. Sjöholm and G. Gellerstedt, *Holzforchung*, 2009, **63**, 290-297.
88. A. Toledano, A. García, I. Mondragon and J. Labidi, *Separation and Purification Technology*, 2010, **71**, 38-43.
89. C. Capello, U. Fischer and K. Hungerbuehler, *Green Chem.*, 2007, **9**, 927-934.
90. C. Cui, R. Sun and D. S. Argyropoulos, *ACS Sustainable Chem. Eng.*, 2014, **2**, 959-968.
91. J. Ropponen, L. Rasanen, S. Rovio, T. Ohra-aho, T. Liitia, H. Mikkonen, D. van de Pas and T. Tamminen, *Holzforchung*, 2011, **65**, 543-549.
92. K. Wang, F. Xu and R. Sun, *Int. J. Mol. Sci.*, 2010, **11**, 2988-3001.
93. C. M. Hansen, *Prog. Org. Coat.*, 2004, **51**, 77-84.
94. C. G. Boeriu, F. I. Fitigau, R. J. A. Gosselink, A. E. Frissen, J. Stoutjesdijk and F. Peter, *Ind. Crops Prod.*, 2014, **62**, 481-490.
95. R. Moerck, H. Yoshida, K. P. Kringstad and H. Hatakeyama, *Holzforchung*, 1986, **40**, 51-60.

96. R. J. A. Gosselink, J. E. G. van Dam, E. de Jong, E. L. Scott, J. P. M. Sanders, J. Li and G. Gellerstedt, *Holzforschung*, 2010, **64**, 193-200.
97. R. K. Henderson, C. Jimenez-Gonzalez, D. J. C. Constable, S. R. Alston, G. G. A. Inglis, G. Fisher, J. Sherwood, S. P. Binks and A. D. Curzons, *Green Chem.*, 2011, **13**, 854-862.
98. J. Quesada-Medina, F. J. Lopez-Cremades and P. Olivares-Carrillo, *Bioresour. Technol.*, 2010, **101**, 8252-8260.
99. J. Zhang, J. Teo, X. Chen, H. Asakura, T. Tanaka, K. Teramura and N. Yan, *ACS Catal.*, 2014, **4**, 1574-1583.
100. X. Wang and R. Rinaldi, *ChemSusChem*, 2012, **5**, 1455-1466.
101. K. Barta, G. R. Warner, E. S. Beach and P. T. Anastas, *Green Chem.*, 2014, **16**, 191-196.
102. T. D. Matson, K. Barta, A. V. Iretskii and P. C. Ford, *J. Am. Chem. Soc.*, 2011, **133**, 14090-14097.
103. M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B. C. Gates and M. R. Rahimpour, *Energy Environ. Sci.*, 2014, **7**, 103-129.
104. J. Long, Y. Xu, T. Wang, Z. Yuan, R. Shu, Q. Zhang and L. Ma, *Applied Energy*, 2015, **141**, 70-79.
105. A. Toledano, L. Serrano and J. Labidi, *Journal of Chemical Technology & Biotechnology*, 2012, **87**, 1593-1599.
106. Wahyudiono, M. Sasaki and M. Goto, *Chem. Eng. Process.*, 2008, **47**, 1609-1619.
107. O. Y. Abdelaziz, D. P. Brink, J. Prothmann, K. Ravi, M. Sun, J. García-Hidalgo, M. Sandahl, C. P. Hultberg, C. Turner, G. Lidén and M. F. Gorwa-Grauslund, *Biotechnology Advances*, 2016, **34**, 1318-1346.
108. A. Toledano, L. Serrano, J. Labidi, A. Pineda, A. M. Balu and R. Luque, *ChemCatChem*, 2013, **5**, 977-985.
109. R. Shu, J. Long, Y. Xu, L. Ma, Q. Zhang, T. Wang, C. Wang, Z. Yuan and Q. Wu, *Bioresour. Technology*, 2016, **200**, 14-22.
110. L. Petitjean, R. Gagne, E. S. Beach, D. Xiao and P. T. Anastas, *Green Chem.*, 2016, **18**, 150-156.
111. G. Warner, T. S. Hansen, A. Riisager, E. S. Beach, K. Barta and P. T. Anastas, *Bioresour. Technol.*, 2014, **161**, 78-83.
112. G. S. Macala, T. D. Matson, C. L. Johnson, R. S. Lewis, A. V. Iretskii and P. C. Ford, *ChemSusChem*, 2009, **2**, 215-217.
113. S. Gillet, L. Petitjean, M. Aguedo, C.-H. Lam, C. Blecker and P. T. Anastas, *Bioresour. Technol.*, 2017, **233**, 216-226.
114. X. Huang, T. I. Koranyi, M. D. Boot and E. J. M. Hensen, *ChemSusChem*, 2014, **7**, 2276-2288.
115. X. Huang, T. I. Koranyi, M. D. Boot and E. J. M. Hensen, *Green Chem.*, 2015, **17**, 4941-4950.
116. M. D. Karkas, B. S. Matsuura, T. M. Monos, G. Magallanes and C. R. J. Stephenson, *Org. Biomol. Chem.*, 2016, **14**, 1853-1914.
117. M. Zaheer and R. Kempe, *ACS Catal.*, 2015, **5**, 1675-1684.
118. P. J. Deuss and K. Barta, *Coord. Chem. Rev.*, 2016, **306**, 510-532.
119. J. Sauer and H. Adkins, *J. Am. Chem. Soc.*, 1937, **59**, 1-3.
120. E. E. Harris, J. D'anni and H. Adkins, *J. Am. Chem. Soc.*, 1938, **60**, 1467-1470.
121. J. M. Pepper and H. Hibbert, *J. Am. Chem. Soc.*, 1948, **70**, 67-71.
122. C. P. Brewer, L. M. Cooke and H. Hibbert, *J. Am. Chem. Soc.*, 1948, **70**, 57-59.
123. E. M. Van Duzee and H. Adkins, *J. Am. Chem. Soc.*, 1935, **57**, 147-151.
124. G. S. Chandler and W. H. F. Sasse, *Aust. J. Chem.*, 1963, **16**, 20-30.
View Article Online
DOI: 10.1039/C7GC01479A
125. G. D. F. Jackson and W. H. F. Sasse, *J. Chem. Soc.*, 1962, DOI: 10.1039/jr9620003746, 3746-3751.
126. J. B. Bredenberg, M. Huuska, J. Raty and M. Korpio, *J. Catal.*, 1982, **77**, 242-247.
127. C. Zhao, Y. Kou, A. A. Lemonidou, X. Li and J. A. Lercher, *Chem. Commun. (Cambridge, U. K.)*, 2010, **46**, 412-414.
128. C. Zhao, Y. Kou, A. A. Lemonidou, X. Li and J. A. Lercher, *Angew. Chem., Int. Ed.*, 2009, **48**, 3987-3990, S3987/3981-S3987/3986.
129. C. Zhao and J. A. Lercher, *Angew. Chem., Int. Ed.*, 2012, **51**, 5935-5940, S5935/5931-S5935/5913.
130. C. Zhao, S. Kasakov, J. He and J. A. Lercher, *J. Catal.*, 2012, **296**, 12-23.
131. J. He, C. Zhao and J. A. Lercher, *J. Am. Chem. Soc.*, 2012, **134**, 20768-20775.
132. Q. Song, F. Wang and J. Xu, *Chem. Commun. (Cambridge, U. K.)*, 2012, **48**, 7019-7021.
133. Q. Song, J. Cai, J. Zhang, W. Yu, F. Wang and J. Xu, *Chinese Journal of Catalysis*, 2013, **34**, 651-658.
134. J. He, L. Lu, C. Zhao, D. Mei and J. A. Lercher, *J. Catal.*, 2014, **311**, 41-51.
135. J. He, C. Zhao, D. Mei and J. A. Lercher, *J. Catal.*, 2014, **309**, 280-290.
136. A. G. Sergeev and J. F. Hartwig, *Science (Washington, DC, U. S.)*, 2011, **332**, 1263.
137. A. G. Sergeev, J. D. Webb and J. F. Hartwig, *J. Am. Chem. Soc.*, 2012, **134**, 20226-20229.
138. F. Gao, J. D. Webb and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2016, **55**, 1474-1478.
139. N. Yan and G. Zhang, *Abstract Pap. Am. Chem. Soc.*, 2014, **247**, 220.
140. J. Zhang, H. Asakura, J. van Rijn, J. Yang, P. Duchesne, B. Zhang, X. Chen, P. Zhang, M. Saeys and N. Yan, *Green Chem.*, 2014, **16**, 2432-2437.
141. V. Molinari, G. Clavel, M. Graglia, M. Antonietti and D. Esposito, *ACS Catal.*, 2016, **6**, 1663-1670.
142. V. Molinari, C. Giordano, M. Antonietti and D. Esposito, *J. Am. Chem. Soc.*, 2014, **136**, 1758-1761.
143. H. Konnerth, J. Zhang, D. Ma, M. H. G. Precht and N. Yan, *Chem. Eng. Sci.*, 2015, **123**, 155-163.
144. M. Zaheer, J. Hermannsdoerfer, W. P. Kretschmer, G. Motz and R. Kempe, *ChemCatChem*, 2014, **6**, 91-95.
145. X. Zhang, T. Wang, L. Ma, Q. Zhang, Y. Yu and Q. Liu, *Catal. Commun.*, 2013, **33**, 15-19.
146. X. Kong and L. Chen, *Catal. Commun.*, 2014, **57**, 45-49.
147. Z. Strassberger, A. H. Alberts, M. J. Louwerse, S. Tanase and G. Rothenberg, *Green Chem.*, 2013, **15**, 768-774.
148. D. J. Rensel, S. Rouvimov, M. E. Gin and J. C. Hicks, *J. Catal.*, 2013, **305**, 256-263.
149. N. Yan, C. Zhao, P. J. Dyson, C. Wang, L.-t. Liu and Y. Kou, *ChemSusChem*, 2008, **1**, 626-629.
150. H. Liu, T. Jiang, B. Han, S. Liang and Y. Zhou, *Science (Washington, DC, U. S.)*, 2009, **326**, 1250-1252.
151. C. Zhao and J. A. Lercher, *ChemCatChem*, 2012, **4**, 64-68.
152. C. Zhao, W. Song and J. A. Lercher, *ACS Catal.*, 2012, **2**, 2714-2723.
153. T. H. Parsell, B. C. Owen, I. Klein, T. M. Jarrell, C. L. Marcum, L. J. Hauptert, L. M. Amundson, H. I. Kenttamaa,

- F. Ribeiro, J. T. Miller and M. M. Abu-Omar, *Chemical Science*, 2013, **4**, 806-813.
154. I. Klein, C. Marcum, H. Kenttamaa and M. M. Abu-Omar, *Green Chem.*, 2016, **18**, 2399-2405.
155. J. K. Kim, J. K. Lee, K. H. Kang, J. C. Song and I. K. Song, *Appl. Catal., A*, 2015, **498**, 142-149.
156. F. Zhang, S. Zheng, Q. Xiao, Y. Zhong, W. Zhu, A. Lin and M. Samy El-Shall, *Green Chem.*, 2016, **18**, 2900-2908.
157. W. Zhang, J. Chen, R. Liu, S. Wang, L. Chen and K. Li, *ACS Sustainable Chem. Eng.*, 2014, **2**, 683-691.
158. Z. Luo, Y. Wang, M. He and C. Zhao, *Green Chem.*, 2016, **18**, 433-441.
159. Y.-B. Huang, L. Yan, M.-Y. Chen, Q.-X. Guo and Y. Fu, *Green Chem.*, 2015, **17**, 3010-3017.
160. K. Barta and P. C. Ford, *Acc. Chem. Res.*, 2014, **47**, 1503-1512.
161. J. R. Bower, Jr., L. M. Cooke and H. Hibbert, *J. Am. Chem. Soc.*, 1943, **65**, 1192-1195.
162. J. M. Pepper, C. J. Brounstein and D. A. Shearer, *J. Am. Chem. Soc.*, 1951, **73**, 3316-3319.
163. J. M. Pepper and Y. W. Lee, *Canadian Journal of Chemistry*, 1969, **47**, 723-727.
164. K. Sudo, D. J. Mullord and J. M. Pepper, *Can. J. Chem.*, 1981, **59**, 1028-1031.
165. M. V. Galkin and J. S. M. Samec, *ChemSusChem*, 2014, **7**, 2154-2158.
166. R. E. Key and J. J. Bozell, *ACS Sustainable Chem. Eng.*, 2016, **4**, 5123-5135.
167. T. Parsell, S. Yohe, J. Degenstein, T. Jarrell, I. Klein, E. Gencer, B. Hewetson, M. Hurt, J. I. Kim, H. Choudhari, B. Saha, R. Meilan, N. Mosier, F. Ribeiro, W. N. Delgass, C. Chapple, H. I. Kenttamaa, R. Agrawal and M. M. Abu-Omar, *Green Chemistry*, 2015, **17**, 1492-1499.
168. S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan and B. F. Sels, *Energy Environ. Sci.*, 2015, **8**, 1748-1763.
169. J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blochouse, P. Jacobs and B. Sels, *Chemical Communications*, 2010, **46**, 3577-3579.
170. J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs and B. Sels, *Green Chemistry*, 2011, **13**, 2167-2174.
171. T. Renders, W. Schutyser, S. Van den Bosch, S.-F. Koelewijn, T. Vangeel, C. M. Courtin and B. F. Sels, *ACS Catalysis*, 2016, **6**, 2055-2066.
172. C. Li, M. Zheng, A. Wang and T. Zhang, *Energy Environ. Sci.*, 2012, **5**, 6383-6390.
173. I. Klein, B. Saha and M. M. Abu-Omar, *Catal. Sci. Technol.*, 2015, **5**, 3242-3245.
174. P. Ferrini and R. Rinaldi, *Angew. Chem., Int. Ed.*, 2014, **53**, 8634-8639.
175. U. P. Agarwal and R. H. Atalla, 1995.
176. W. Yunpu, D. A. I. Leilei, F. A. N. Liangliang, S. Shaoqi, L. I. U. Yuhuan and R. Roger, *Journal of Analytical and Applied Pyrolysis*, 2016, **119**, 104-113.
177. S. U. Lee, K. Jung, G. W. Park, C. Seo, Y. K. Hong, W. H. Hong and H. N. Chang, *Korean Journal of Chemical Engineering*, 2012, **29**, 831-850.
178. J. Pan, J. Fu, S. Deng and X. Lu, *Energy Fuels*, 2014, **28**, 1380-1386.
179. H. G. Kim and Y. Park, *Industrial & Engineering Chemistry Research*, 2013, **52**, 10059-10062.
180. C. Dong, C. Feng, Q. Liu, D. Shen and R. Xiao, *Bioresour. Technology*, 2014, **162**, 136-141. DOI: 10.1039/C7GC01479A
181. D. Shen, N. Liu, C. Dong, R. Xiao and S. Gu, *Chemical Engineering Journal*, 2015, **270**, 641-647.
182. X. Ouyang, G. Zhu, X. Huang and X. Qiu, *Journal of Energy Chemistry*, 2015, **24**, 72-76.
183. J. Xu, J. Jiang, C. Hse and T. F. Shupe, *Green Chemistry*, 2012, **14**, 2821-2830.
184. J. Xie, J. Qi, C. Hse and T. F. Shupe, *Journal of Forestry Research*, 2015, **26**, 261-265.
185. A. Toledano, L. Serrano, A. Pineda, A. A. Romero, R. Luque and J. Labidi, *Applied Catalysis B: Environmental*, 2014, **145**, 43-55.
186. X.-p. Ouyang, Y.-d. Tan and X.-q. Qiu, *Journal of Fuel Chemistry and Technology*, 2014, **42**, 677-682.
187. H. F. Johnson, *AIChE Journal*, 1967, **13**, 1042-1237.
188. J. W. King and K. Srinivas, *J. Supercrit. Fluids*, 2009, **47**, 598-610.
189. Y. Ye, Y. Zhang, J. Fan and J. Chang, *Ind. Eng. Chem. Res.*, 2012, **51**, 103-110.
190. Z. Yuan, S. Cheng, M. Leitch and C. Xu, *Bioresour. Technol.*, 2010, **101**, 9308-9313.
191. S. Cheng, C. Wilks, Z. Yuan, M. Leitch and C. Xu, *Polym. Degrad. Stab.*, 2012, **97**, 839-848.
192. S. Cheng, I. D'Cruz, M. Wang, M. Leitch and C. Xu, *Energy Fuels*, 2010, **24**, 4659-4667.
193. A. M. Numan-Al-Mobin, K. Voeller, H. Bilek, E. Kozliak, A. Kubatova, D. Raynie, D. Dixon and A. Smirnova, *Energy Fuels*, 2016, **30**, 2137-2143.
194. M. Schrems, F. Liebner, M. Betz, M. Zeilinger, S. Boehmdorfer, T. Rosenau and A. Potthast, *J. Wood Chem. Technol.*, 2012, **32**, 225-237.
195. H. Lv, L. Yan, M. Zhang, Z. Geng, M. Ren and Y. Sun, *Chem. Eng. Technol.*, 2013, **36**, 1899-1906.
196. M. Saisu, T. Sato, M. Watanabe, T. Adschiri and K. Arai, *Energy Fuels*, 2003, **17**, 922-928.
197. X. Man, K. Okuda, S. Ohara, M. Umetsu, S. Takami and T. Adschiri, *J. Jpn. Inst. Energy*, 2005, **84**, 486-490.
198. M. Kleinert and T. Barth, *Chem. Eng. Technol.*, 2008, **31**, 736-745.
199. Z. Fang, T. Sato, R. L. Smith, H. Inomata, K. Arai and J. A. Kozinski, *Bioresour. Technol.*, 2008, **99**, 3424-3430.
200. V. M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li and J. A. Lercher, *Chem. - Eur. J.*, 2011, **17**, 5939-5948.
201. T. L.-K. Yong and Y. Matsumura, *Ind. Eng. Chem. Res.*, 2012, **51**, 11975-11988.
202. B. Zhang, H.-J. Huang and S. Ramaswamy, *Appl. Biochem. Biotechnol.*, 2008, **147**, 119-131.
203. W. Jiang, G. Lyu, S. Wu, L. A. Lucia, G. Yang and Y. Liu, *BioResources*, 2016, **11**, 5660-5675.
204. Wahyudiono, M. Sasaki and M. Goto, *Fuel*, 2009, **88**, 1656-1664.
205. T. Sato, G. Sekiguchi, M. Saisu, M. Watanabe, T. Adschiri and K. Arai, *Ind. Eng. Chem. Res.*, 2002, **41**, 3124-3130.
206. J. E. Miller, L. Evans, A. Littlewolf and D. E. Trudell, *Fuel*, 1999, **78**, 1363-1366.
207. M. Nagy, K. David, G. J. P. Britovsek and A. J. Ragauskas, *Holzforchung*, 2009, **63**, 513-520.
208. Z. Tang, Y. Zhang and Q. Guo, *Ind. Eng. Chem. Res.*, 2010, **49**, 2040-2046.
209. J.-Y. Kim, S. Oh, H. Hwang, T.-s. Cho, I.-G. Choi and J. W. Choi, *Chemosphere*, 2013, **93**, 1755-1764.

210. K. Barta, T. D. Matson, M. L. Fettig, S. L. Scott, A. V. Iretskii and P. C. Ford, *Green Chem.*, 2010, **12**, 1640-1647.
211. J. Tsujino, H. Kawamoto and S. Saka, *Wood Sci. Technol.*, 2003, **37**, 299-307.
212. D. S. Brands, K. Pontzen, E. K. Poels, A. C. Dimian and A. Bliek, *J. Am. Oil Chem. Soc.*, 2002, **79**, 85-91.
213. Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu and J. Xu, *Energy Environ. Sci.*, 2013, **6**, 994-1007.
214. J. Zakzeski, A. L. Jongerius, P. C. A. Bruijninx and B. M. Weckhuysen, *ChemSusChem*, 2012, **5**, 1602-1609.
215. W. Xu, S. J. Miller, P. K. Agrawal and C. W. Jones, *ChemSusChem*, 2012, **5**, 667-675.
216. J.-Y. Kim, J. Park, U.-J. Kim and J. W. Choi, *Energy Fuels*, 2015, **29**, 5154-5163.
217. R. J. A. Gosselink, W. Teunissen, J. E. G. van Dam, E. de Jong, G. Gellerstedt, E. L. Scott and J. P. M. Sanders, *Bioresour. Technol.*, 2012, **106**, 173-177.
218. R. Ma, W. Hao, X. Ma, Y. Tian and Y. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 7310-7315.
219. X. Huang, C. Atay, T. I. Koranyi, M. D. Boot and E. J. M. Hensen, *ACS Catal.*, 2015, **5**, 7359-7370.
220. J. P. Hallett and T. Welton, *Chem. Rev. (Washington, DC, U. S.)*, 2011, **111**, 3508-3576.
221. A. M. da Costa Lopes and R. Bogel-Lukasik, *ChemSusChem*, 2015, **8**, 947-965.
222. Y. Wang, L. Wei, K. Li, Y. Ma, N. Ma, S. Ding, L. Wang, D. Zhao, B. Yan, W. Wan, Q. Zhang, X. Wang, J. Wang and H. Li, *Bioresour. Technol.*, 2014, **170**, 499-505.
223. D. Glas, C. Van Doorslaer, D. Depuydt, F. Liebnier, T. Rosenau, K. Binnemans and D. E. De Vos, *J. Chem. Technol. Biotechnol.*, 2015, **90**, 1821-1826.
224. Y. Pu, N. Jiang and A. J. Ragauskas, *J. Wood Chem. Technol.*, 2007, **27**, 23-33.
225. N. Sun, M. Rahman, Y. Qin, M. L. Maxim, H. Rodriguez and R. D. Rogers, *Green Chem.*, 2009, **11**, 646-655.
226. S. S. Y. Tan, D. R. MacFarlane, J. Upfal, L. A. Edye, W. O. S. Doherty, A. F. Patti, J. M. Pringle and J. L. Scott, *Green Chem.*, 2009, **11**, 339-345.
227. S.-Y. Jia, B. J. Cox, X.-W. Guo, Z. C. Zhang and J. G. Ekerdt, *Ind. Eng. Chem. Res.*, 2011, **50**, 849-855.
228. B. Zhang, C. Li, T. Dai, G. W. Huber, A. Wang and T. Zhang, *RSC Adv.*, 2015, **5**, 84967-84973.
229. S. Nanayakkara, A. F. Patti and K. Saito, *ACS Sustainable Chem. Eng.*, 2014, **2**, 2159-2164.
230. A. George, K. Tran, T. J. Morgan, P. I. Benke, C. Berruoco, E. Lorente, B. C. Wu, J. D. Keasling, B. A. Simmons and B. M. Holmes, *Green Chemistry*, 2011, **13**.
231. B. J. Cox and J. G. Ekerdt, *Bioresour. Technol.*, 2012, **118**.
232. B. J. Cox, S. Jia, Z. C. Zhang and J. G. Ekerdt, *Polym. Degrad. Stab.*, 2011, **96**, 426-431.
233. J. Long, X. Li, B. Guo, L. Wang and N. Zhang, *Catal. Today*, 2013, **200**, 99-105.
234. S. Jia, B. J. Cox, X. Guo, Z. C. Zhang and J. G. Ekerdt, *ChemSusChem*, 2010, **3**, 1078-1084.
235. J. Long, W. Lou, L. Wang, B. Yin and X. Li, *Chem. Eng. Sci.*, 2015, **122**, 24-33.
236. M. Scott, P. J. Deuss, J. G. de Vries, M. H. G. Precht and K. Barta, *Catal. Sci. Technol.*, 2016, **6**, 1882-1891.
237. A. M. da Costa Lopes, K. G. Joao, E. Bogel-Lukasik, L. B. Roseiro and R. Bogel-Lukasik, *J. Agric. Food Chem.*, 2013, **61**, 7874-7882.
238. A. Brandt, J. P. Hallett, D. J. Leak, R. J. Murphy and T. Welton, *Green Chem.*, 2010, **12**, 672-679. [View Article Online](https://doi.org/10.1039/C7GC01479A)
239. P. Varanasi, P. Singh, M. Auer, P. D. Adams, B. A. Simmons and S. Singh, *Biotechnology for Biofuels*, 2013, **6**, 14.
240. S. Kubo, K. Hashida, T. Yamada, S. Hishiyama, K. Magara, M. Kishino, H. Ohno and S. Hosoya, *J. Wood Chem. Technol.*, 2008, **28**, 84-96.
241. P. Varanasi, P. Singh, R. Arora, P. D. Adams, M. Auer, B. A. Simmons and S. Singh, *Bioresour. Technol.*, 2012, **126**.
242. S. Singh, P. Varanasi, P. Singh, P. D. Adams, M. Auer and B. A. Simmons, *Biomass Bioenergy*, 2013, **54**, 276-283.
243. J.-L. Wen, T.-Q. Yuan, S.-L. Sun, F. Xu and R.-C. Sun, *Green Chem.*, 2014, **16**, 181-190.
244. N. Sathitsuksanoh, K. M. Holtman, D. J. Yelle, T. Morgan, V. Stavila, J. Pelton, H. Blanch, B. A. Simmons and A. George, *Green Chem.*, 2014, **16**, 1236-1247.
245. X. Sun, C. Huang, Z. Xue, C. Yan and T. Mu, *Energy Fuels*, 2015, **29**, 2564-2570.
246. Y. Qu, H. Luo, H. Li and J. Xu, *Biotechnol. Rep. (Amst)*, 2015, **6**, 1-7.
247. Y.-X. An, N. Li, H. Wu, W.-Y. Lou and M.-H. Zong, *ACS Sustainable Chem. Eng.*, 2015, **3**, 2951-2958.
248. A. Narani, R. K. Chowdari, C. Cannilla, G. Bonura, F. Frusteri, H. J. Heeres and K. Barta, *Green Chem.*, 2015, **17**, 5046-5057.
249. J.-Y. Kim, J. Park, H. Hwang, J. K. Kim, I. K. Song and J. W. Choi, *J. Anal. Appl. Pyrolysis*, 2015, **113**, 99-106.
250. B. Guevenatam, E. H. J. Heeres, E. A. Pidko and E. J. M. Hensen, *Catal. Today*, 2016, **269**, 9-20.
251. Z. Yuan, M. Tymchyshyn and C. Xu, *ChemCatChem*, 2016, **8**, 1968-1976.
252. B. Yan, K. Li, L. Wei, Y. Ma, G. Shao, D. Zhao, W. Wan and L. Song, *Bioresour. Technol.*, 2015, **196**, 509-517.
253. A. Diop, A. Hadj Bouazza, C. Daneault and D. Montplaisir, *BioResources*, 2013, **8**, 4270-4282, 4213 pp.
254. A. Diop, K. Jradi, C. Daneault and D. Montplaisir, *BioResources*, 2015, **10**, 4933-4946.
255. A. Brandt, L. Chen, B. E. van Dongen, T. Welton and J. P. Hallett, *Green Chem.*, 2015, **17**, 5019-5034.
256. Y.-X. An, M.-H. Zong, H. Wu and N. Li, *Bioresour. Technol.*, 2015, **192**, 165-171.
257. B. Kamm, P. R. Gruber and M. Kamm, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000, DOI: 10.1002/14356007.i04_i01.pub2.
258. P. T. Anastas, T. C. Williamson, D. Hjerresen and J. J. Breen, *Environ. Sci. Technol.*, 1999, **33**, 116A-119A.
259. P. T. Anastas, L. G. Heine and T. C. Williamson, *Green Chemical Syntheses and Processes*, American Chemical Society, 2000.
260. F. H. M. Graichen, W. J. Grigsby, S. J. Hill, L. G. Raymond, M. Sanglard, D. A. Smith, G. J. Thorlby, K. M. Torr and J. M. Warnes, *Ind. Crops Prod.*, 2016, DOI: 10.1016/j.indcrop.2016.10.036, Ahead of Print.
261. J. Holladay, J. Bozell, J. White and D. Johnson, in *DOE Report PNNL-16983*, 2007.
262. Z. Strassberger, S. Tanase and G. Rothenberg, *RSC Adv.*, 2014, **4**, 25310-25318.
263. G. Sébastien, B. Christophe, A. Mario, L. Pascal, P. Michel and R. Aurore, *Carbohydrate Polymers*, 2014, **108**, 159-168.

Journal Name

ARTICLE

264. S. Gillet, M. Simon, M. Paquot and A. Richel, *Biotechnol., Agron., Soc. Environ.*, 2014, **18**, 97-107.
265. S. Gillet, C. Blecker, M. Paquot and A. Richel, *C. R. Chim.*, 2014, **17**, 386-401.
266. S. Gillet, M. Aguedo, R. Petrut, G. Olive, P. Anastas, C. Blecker and A. Richel, *Int. J. Biol. Macromol.*, 2017, **96**, 550-559.

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