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Emerging strategies for breaking the 3D amorphous network of lignin

Saikat Dutta,^{*a} Kevin C.-W. Wu^{*a} and Basudeb Saha^{*bc}

Representing a complex polymeric and amorphous structure arising from the enzymatic dehydrogenative polymerization of three phenylpropanoid monomers, namely sinapyl alcohol, coniferyl alcohol and *p*-coumaryl alcohol, lignin is mainly found as an integral part of the secondary cell walls of lignocellulosic biomass such as plants and some algae. The absence of commercial high-value applications of lignin is mainly due to its heterogeneous molecular structure, which presents formidable challenges for developing depolymerization techniques and adequate structural modifications. Lignin valorization represents an important challenge in biorefinery. In this perspective, emerging trends in lignin valorization to derive chemicals and materials are presented with a major focus on the critical aspects of dehydrogenation/hydrogenolysis, deoxygenation, enzymatic oxidation, and carbonization. In most cases, conversion of suitable lignin model compounds and actual lignin samples are emphasized. A major focus is given to evaluating the nanoscale structure of employed catalysts for dehydrogenation and deoxygenation techniques. Accessing hierarchically porous carbon materials with fiber and particle morphologies via carbonization of lignin is also discussed. By analyzing the current situation in lignin valorization, certain realistic future directions are identified and emphasized.

Received 30th May 2014,
Accepted 1st July 2014

DOI: 10.1039/c4cy00701h

www.rsc.org/catalysis

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1. Introduction

Human beings are desperate to replace sources of energy and materials, *i.e.* replacing petroleum oil with biomass, which has been solely used so far by other living organisms for the production of high-energy compounds such as ATP and a wide range of polymers such as DNA, proteins and



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University, U.S.A., 2006–2008) as a post-doc. He started his own research group in NTU in August 2008. His current interests include the synthesis of porous nanoparticles and thin films with desired structural orientations and functionalities for biomedical and energy-related applications.

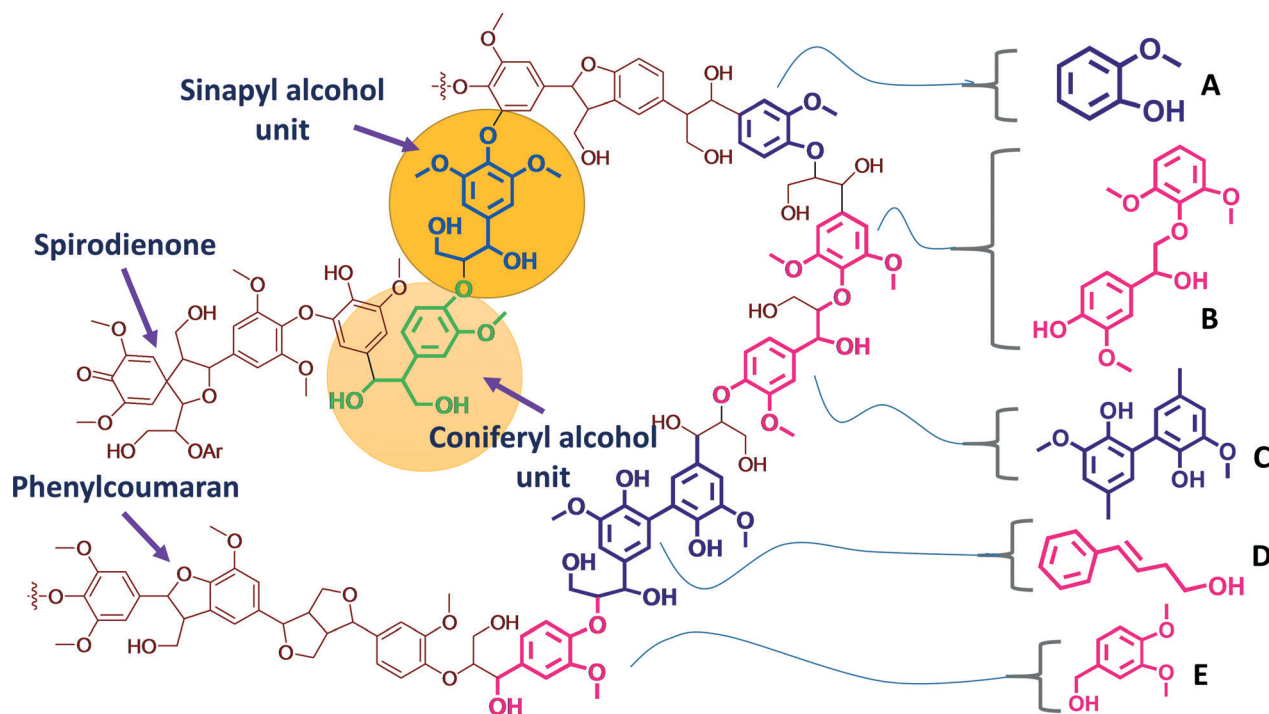


Fig. 1 Schematic depiction of lignin showing various linkages and lignin model compounds. Model (A) phenol and methoxy functionalities, (B) a β -O-4 linkage, (C) a 5-5' linkage, (D) a propyl side chain, and (E) a benzylic group.

polysaccharides for millions of years. Although it is a key component in plant cell walls and most abundant renewable aromatic polymers, lignin is yet to play a significant role as feedstock. Lignin is composed of ~25% of lignocellulosic biomass and it is an amorphous natural polymer consisting of a 3D arrangement of methoxylated phenylpropane.¹ The complex structure of lignin is amorphous, polyaromatic and is incorporated with numerous ether linkages, -OH groups, and methoxy groups. Lignin is regarded as a cross-linked macromolecule composed of three types of monolignols, including

p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, with the proportions depending on the source.² For example, lignin from softwood consists largely of coniferyl units (4-(3-hydroxy-1-propenyl)-2-methoxyphenol) whereas hardwood consists largely of syringol units (2,6-dimethoxyphenol) excluding exceptions. The *p*-coumaryl units without methoxy groups on the aromatic ring are also found in lignin. Moreover, coniferyl, syringol and *p*-coumaryl units are interconnected through various cross-linkages (C-O-C = β -O-4, α -O-4, 4-O-5) and C-C interunit linkages (β -1, β -5, β - β , 5-5), which are formed during the biosynthesis of macromolecular lignin (Fig. 1). The most abundant is the β -O-4 ether linkage.³ It is essential to understand the details of the linkages present in the macromolecular structure in order to design strategies for the selective breaking of these linkages. The essential difference between lignin in hardwood and softwood is the number of methoxy groups on the aryl rings. Hardwood contains two or three methoxy groups per aromatic ring originating from the coniferyl and syringyl alcohol units, however softwood contains only one methoxy groups originating from the polymerization of the coniferyl alcohol.⁴ The common linkage between the monomers is the β -O-4 linkage, which represents approximately 50–65% of all inter subunit bonds (Table 1).

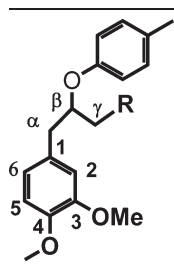
The most abundant linkages are β -O-4 and 5-5', constituting approximately 50–65% and 20–25% of the structure respectively.⁵ Chemical conversion of cellulose and hemicellulose has been extensively studied, while that of lignin remains scarce even though lignin is the most abundant renewable aromatic polymer, constituting up to 15–30% of



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Table 1 Types and frequencies (%) of inter-subunit linkages in softwood and hardwood lignin⁵

	Linkage	Softwood lignin	Hardwood lignin
	β -O-4	49–51	65
	α -O-4	6–8	—
	β -5	9–15	6
	β -1	2	15
	5–5	9.5	2.3
	4-O-5	3.5	1.5
	β - β	2	5.5

the weight and 40% of the energy content of lignocellulosic biomass.^{6,7} As we know, it is its rigid cross-linked structure that renders lignin resistant to chemical degradation.

The catalytic valorization of lignin represents a potentially useful method to access bulk and fine chemicals and there are different approaches *via* chemical routes for developing such processes.⁶ Significantly, disruption of the linkages in lignin represent a potential route for the production of a wide range of aromatic compounds, which are otherwise accessible only from petroleum feedstocks. The utilization of lignin as a feedstock for the production of hydrocarbons also offers a significant opportunity for enhancing the overall operational efficiency, carbon conversion rate, economic viability, and sustainability of biofuel production.⁸ The challenge, however, is the propensity of the aromatic lignin macromolecular assembly to condense and degrade, thereby generating high amounts of relatively intractable solid residues in biorefineries, and paper and pulp industries. Therefore, the depolymerization of lignin and its subsequent conversion to value added products is vital to enhance the profitability of biorefineries.⁹ Among the three main biopolymers that make up the cell wall, lignin is the most recalcitrant. It comprises up to 30% of the plant biomass and is needed for support and water transportation.¹⁰ Furthermore, lignin's high aromatic content is responsible for its high energy content. A number of different linkages occur naturally in the structure of lignin with the most abundant being the β -O-4 ether linkage (Fig. 1).² Therefore, methods to break apart the 3D network of lignin while preserving its aromatic nature promises to provide a valuable stream of chemicals. Previously reported methods to depolymerize lignin include hydrolysis,^{11–13} pyrolysis,^{14,15} catalytic hydrogenation,^{16,17} oxidation,⁵ and hydrocracking.¹⁸ Schinski *et al.* disclosed a process for the hydrotreatment of lignin to yield aromatic products, which required the use of a hydrogen feedstock.^{8,19} Lignin treatment and gasification methods using supercritical water ($T_c = 647.3$ K, $P_c = 221$ bar) have also been reported to primarily form light alkanes and hydrogen,^{20–22} although the disadvantages of these processes include the high reaction temperatures and pressures (often $T = 673$ K and $P = 250$ bar).

Lignin is underutilized and the bulk of produced lignin, representing about 70 million metric tons per year, is only employed as a combustible material for its high heat value.⁸

Precise control over the techniques to selectively depolymerize lignin is expected to propel the growth of this field further into new realms of synthetic chemistry focused on utilizing lignin as feedstocks. Templating biomaterials is an active area for harnessing the structural complexity to mimic natural functions,²³ and the disruption of the polymeric structure of lignin is of remarkable interest due to the following reasons: 1) access to a large reservoir of aromatic hydrocarbons, 2) deoxygenation of the ethereal oxygen to obtain hydrocarbons, and 3) access to nanostructured carbon materials or hybrid materials with carbon by the strategic carbonization of lignin in the presence of/or absence of structure/pore directing templates. Considering the above facts, this perspective focuses on describing the structural features of recalcitrant lignin in the woody biomass. Further, we look at the emerging strategies of lignin valorization and its chemical aspects, for example hydrodeoxygenation, synthetic biological methods, and carbonization for novel porous carbon materials. A major emphasis is on the chemicals and material aspects of these techniques, which promise to create significant impact in the lignin valorization field. A lignin model reaction to understand the underlying features of depolymerization and selective cleavage of a bond is described with important recently reported cases covering all emerging lignin valorization techniques. Future prospects of lignin valorization and possible new techniques are also proposed.

2. Emerging lignin valorization techniques

Considering lignin as a renewable reservoir of aromatic building blocks by breaking the complex crosslinked polymeric units *via* selective inter-unit C–O–C bond cleavage and subsequent hydrodeoxygenation of the low molecular weight moieties to aromatic and aliphatic hydrocarbons is an emerging strategy. It can create avenues through the chemical and biological conversion of lignin to chemicals and fuels. Despite the potential, the conversion of lignin to liquid fuels, particularly to aliphatic and aromatic hydrocarbons, has always been a challenging task. Generally, the propensity of the aromatic lignin macromolecular assembly is to condense and degrade, generating high amounts of relatively intractable solid residues in biorefinery processes. Among the recently developed processes, hydrogenolysis of C–O bonds results in a breakdown of high molecular weight components and this process offers phenols as the end product. However, in order to access liquid hydrocarbons, recently the hydrodeoxygenation technique under hydrogenolytic conditions has gained tremendous importance. This technique requires a noble metal nanoparticle catalyst and in most of the cases, biofunctional or bimetallic metal nanoparticles exhibited remarkable performances compared to their mononuclear counterpart. Liquid phase oxidation of lignin, which is mainly dependent on benzylic C–H or C–OH bond transformations to carbonyl groups, usually depends on metal

catalysts,^{6,24} however metal-free catalysts are now also known.²⁵ Enzymatic hydrolysis is a promising strategy for cellulose degradation, and similarly enzymatic oxidation can be considered as a major future prospect for lignin valorization and for the production of aromatics. The essential discovery would be to find lignin sources which have potential to provide ordered porous carbons directly, and among which accessing 3D interconnected porous carbon is one of the major targets. This area of research considers lignin as a major source material for advanced applications and this also offers ample scope for developing non-templating strategies for deriving materials from renewable sources.

2.1 Lignin depolymerization into monomers

Lignin depolymerization (LDP) to form aromatic products under mild conditions is a desired approach for its valorization. So far, hydrolysis, oxidation and reduction are well-established methods, in which aqueous phase alkali hydroxide or carbonate catalysed hydrolysis of C–O–C linkages results in phenol derivatives.^{26–28} Oxidative cleavage of C–H bonds and/or C–C bonds adjacent to C–O–C linkages produces vanillin and/or its analogues.^{29,30} This reaction causes oxidative damage to the aromatic fragments of the lignin, leading to extreme oxidation to form CO_x and H₂O. Besides, vanillin can repolymerize into oligomers, leading to poor recovery of the depolymerization products. Reductive depolymerization has been considered as a promising method of LDP to form phenols. With hydrogenation or hydrogenolysis methods, the C–O–C linkages are selectively cleaved into phenols.³¹ The reduction method may partially avoid the condensation of phenol intermediates into oligomers, a key issue associated with the LDP reaction.³² Kou *et al.* have reported that lignin can be hydrogenated to monomeric phenols over noble metal catalysts mainly consisting of Pt, Ru, Pd and Rh supported on activated carbon under 4 MPa H₂.³³ Zhang *et al.* have shown that woody lignin can be catalytically hydrogenated to form phenolic compounds like guaiacol and syringols.³⁴ Alternative catalysts such as CuCr oxide,³⁵ Co–Mo–S/Al₂O₃,³⁶ activated carbon-, alumina- or silica-supported Ru³⁷ and Pt³⁸ have also been examined to obtain monomeric phenols *via* the hydrogenation of lignin or model compounds. A strategy to convert lignosulfonate into 4-ethylguaiacol and 4-propylguaiacol over heterogeneous nickel catalysts revealed that aryl–O–alkyl bonds (C–O–C) and hydroxyl groups in lignin are hydrogenated to phenols and alkanes, respectively, while preserving the aromatic structure.³⁹ When insoluble solid lignin meets heterogeneous catalysts in common solvents, mass transfer becomes limited and may retard the process. Generally, heterogeneously catalyzed conversion of native lignin fails to address the key chemical aspects of the process and thus the problem is far less elucidated. Fragmentation–hydrogenolysis are the key steps that occur in depolymerizing native lignin into monomeric phenols in alcoholic solvents over nickel-based catalysts (Fig. 2).⁴⁰ The best selectivity toward monomeric phenol

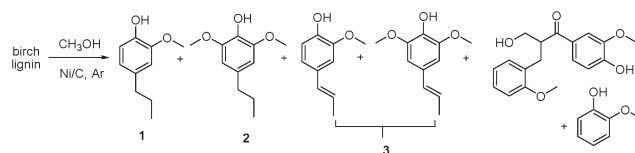


Fig. 2 β -O-4 major products in the lignin-depolymerization reaction over a Ni/C catalyst.

products is >90% from about 50% conversion of birch wood lignin. It has been demonstrated that nickel-based catalysts are highly active and selective in converting native lignin into monomeric phenols such as propylguaiacol and propylsyringol. It has been shown that alcohols act as the nucleophilic reagent for C–O–C cleavage in alcoholysis and function as the source of active hydrogen in the medium. Results of this study confirmed that the conversion of smaller lignin fragments into monomeric phenols undergoes β -elimination dehydration coupled with hydrogenation and subsequent hydrogenolysis.

In the above discussed depolymerization process, the efficiency depends on the CH₃OH solvent coming into contact with an active site on the catalyst to generate an active hydrogen species which is energetically favorable compared to the activation of molecular H₂. A maximum of 54% lignin conversion in methanol can be achieved (Table 2, entry 3) with a total selectivity of 89% for the components containing 4-propylguaiacol (PGol) and 4-propylsyringol (PSol) as major products. The Ni/C system for lignin depolymerization also exhibits a reusability of at least four times with about ~50% lignin conversion in each cycle. Ni forms MeOMe from MeOH and then reforms it into H₂, and therefore CO and CO₂ must be generated in this process as byproducts. The Ni catalyst can be deactivated in the presence of water. Lignin depolymerization from intact biomass currently produces a largely heterogeneous range of molecules, which makes lignin valorization an enormously difficult problem. Even after extensive research effort on lignin conversion over the past seven decades, a selective catalyst that narrows the product range of lignin depolymerization products down to something manageable is yet to be found. The exception is Song's Ni/C-based work,⁴⁰ but deactivation of the Ni/C catalyst in the presence of water and the limitation of the strategy requiring a specific variety of birch wood sawdust are certain downsides of this process.

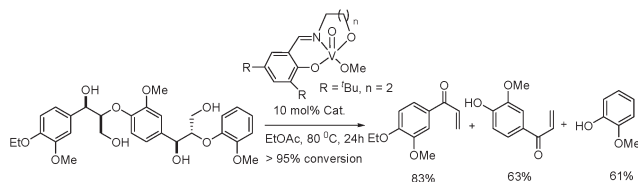
Non-oxidative degradation involving cleavage of β -O-aryloxy bonds in lignin models has been used as a standard system to simplify the development for depolymerization of lignin. Recently, vanadium catalyzed β -O-aryloxy bond cleavage in a lignin model has been reported, which involves the formation of enones as a result of C–O bond cleavage (Fig. 3).⁴¹ Results in this report, reveal the pretreatment and isolation can alter the structure of lignin.

Production of phenols from lignin *via* depolymerization techniques combined with further conversion reactions (hydrogenolysis or cracking) is a challenging task which has been solved *via* catalytic cracking and hydrogenolysis. This

Table 2 Catalytic results of the lignin depolymerization reactions

Entry	Catalyst	Solvent	Conv. (%)	Selectivity (%)			
				1	2	3	Others
1	No catalyst	CH ₃ OH	n.d.	—	—	—	—
2	AC	CH ₃ OH	n.d.	—	—	—	—
3	Ni/C	CH ₃ OH	54	22	67	1	10
4	Ni/C	EtOH	48	25	70	3	2
5	Ni/C	EG	50	25	72	1	2
6	Ni/C	i-PrOH	27	12	37	26	25
7	Ni/C	25% glycerol + H ₂ O	16	16	67	—	17
8	Ni/C	1,4-Dioxane	15	—	6	93	<1
9	Ni/C	1% MOH + H ₂ O	9	31	63	—	6
10	Ni/C	25% MeOH + H ₂ O	22	16	74	—	11
11	Ni/C	Cyclohexane	<1	—	—	—	—
12	Ni/C	MeOH	42	26	71	—	3
13	Ni/SBA-15	MeOH	27	9	18	72	<1
14	Ni/Al ₂ O ₃	MeOH	19	—	18	81	1
15	Cu/C	MeOH	9	—	—	99	1
16	Cu–Cr oxide	MeOH	2	—	—	99	1

Reaction conditions: birch sawdust (2.0 g), catalyst (0.1 g), solvent (40 mL), 200 °C, 6 h, 1 atm Ar. n.d. = not detected. 1. Propylguaiacol, 2. propylsyringol, 3. propenylguaiacol.

**Fig. 3** β -O-4 vanadium-catalyzed degradation of a trimeric lignin model.

involves the breakdown of molecular components into small fragments *via* the breaking of C–O bonds in a water–alcohol medium, which has been suggested as the major reaction route. For these phenol production processes, tungsten phosphide,⁴² ZrO₂–Al₂O₃–FeO_x,⁴³ and iron oxide⁴⁴ play major roles, respectively. Depolymerization by catalytic alcoholysis of lignin can offer high-value small molecules of carbon C₆–C₁₀ liquid products by using a nanostructured molybdenum carbide catalyst in supercritical ethanol. In this case the advantage is that the lignin fragments can be rapidly stabilized on the surface of the catalyst under supercritical conditions of ethanol.⁴⁵ This recent finding suggests that catalytic alcoholysis is an alternative route to produce value-added chemicals from lignin due to the fact that the release of an active hydrogen atom from an alcohol, *e.g.* methanol, is more facile than from a hydrogen molecule. This approach can be regarded as one of the key strategies to derive organic molecules from lignin degradation.

2.2 Upgradation of lignin monomers

Currently, hydrodeoxygenation (HDO) is receiving more attention. It involves the complete removal of oxygen atoms from the substrate under hydrogenolytic conditions.⁴⁶ Deoxygenation of polyols (*e.g.* glycerol) to form useful organics such as allyl alcohols, propanal, and acrolein is a well-

established method,^{47,48} and several catalytic upgrading routes that involve HDO have been widely studied using monomeric lignin model compounds to produce hydrocarbons.³⁵ HDO is considered as a major tool to upgrade lignin-derived bio-oils and the HDO process involves reactions with hydrogen that produce hydrocarbons and water.⁴⁹ In order to highlight the importance of HDO reactions in bio-oil upgrading, the HDO chemistry of lignin-derived compounds or raw lignin and comparison of the activity of employed catalysts are essential. Solid surfaces that stabilize water–oil emulsions and catalyze reactions at the liquid/liquid interface leading to biphasic HDO, *e.g.* using deposited Pd on a carbon nanotube–inorganic oxide hybrid, are useful for biomass refining as revealed when employed for lignin conversion.⁵⁰ The hybrid solid nanoparticles are capable of simultaneously stabilizing an emulsion and catalyzing reactions in both aqueous and organic phases. In order to remove oxygenate functional groups in phenolic compounds derived from lignin such as vanillin, the HDO of vanillin by nanohybrid emulsions on Pd was studied as a model reaction. The reaction was performed in the aqueous side of the interface and the Pd was deposited in the hydrophilic side. As illustrated schematically in Fig. 4, a range of different products and phase migration processes occur due to the varying extents of the hydrogenation, hydrogenolysis, and decarbonylation reactions of vanillin catalyzed by Pd as the reaction conditions were modified.

The major advantage of this solid-stabilized emulsion method is that a continuous process can be designed in which two homogeneous phases coexist with the emulsion in a layered configuration: oil/emulsion/water. Full conversion can be expected on both sides of the emulsion with a constant removal of oil-soluble products from the top layer and water-soluble products from the bottom layer while the reaction is continuous in the emulsion.

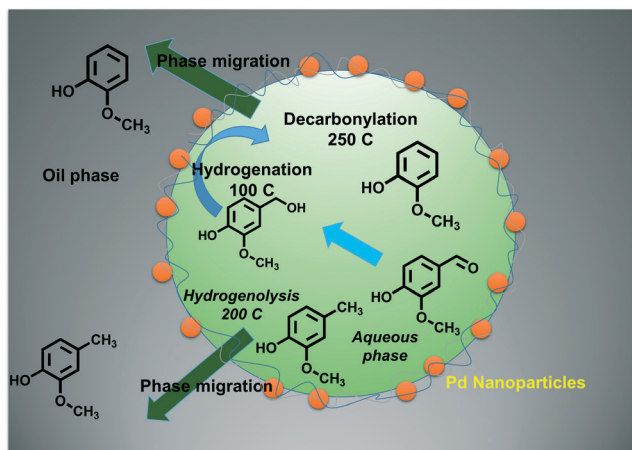


Fig. 4 Schematic illustration of the reactions taking place at the water/oil interface in the solid-stabilized emulsions using vanillin as a lignin model. Depending on the reaction temperature, the prevailing reactions are hydrogenation, hydrogenolysis or decarbonylation, and depending on the relative solubility, the products remain in the aqueous phase or migrate to the oil phase.

In recent years various supported noble metals, such as Ru, Pd, Pt, Rh, and their alloys, have been widely used in aqueous phase non-sulfide-based HDO processes for the conversion of lignin-based monomeric model phenolic substrates to hydrocarbons.^{51–53} A hydrotreatment process of pyrolysis oil fractions has been considered as a promising energy route, however the chemical aspects of the HDO reactions in fast pyrolysis oil have not been investigated in detail even though it has been found that the carbohydrate fraction is very reactive in the HDO of pyrolysis oil. It is important to disclose the chemical aspects of the disassembly/“unzipping” process of lignin involving HDO, which offers the production of value-added products. Recent investigations on model lignin compounds have demonstrated the utilization of ruthenium hydrogenation catalysts and nickel carbene hydrogenation catalysts for the hydrogenolysis of the aromatic CO bonds in aryl ethers, which is important for the generation of fuels and chemical feedstocks from lignin. A study on lignin model compounds revealed the relative reactivity of ether substrates are Ar–O–Ar > Ar–OMe > ArCH₂–OMe (Ar = aryl; Me = methyl).⁵⁴ The conversion of refractory aryl ether biopolymers to hydrocarbons is a formidable challenge to synthetic chemists. Results from this work demonstrated that the selective cleavage of aromatic C–O bonds in the presence of other C–O bonds can be conducted without reduction of the arene units, although the mechanistic issues have not yet been resolved for this nickel system.

Performing HDO to remove covalently bonded oxygen from lignin offers opportunities to not only break apart the complex structure of lignin but also to increase the overall energy density and value of the resulting products. The major complexity is that C–O and C–C bond strengths are comparable, meaning that selective HDO *versus* aromatic hydrogenation is challenging. There have been efforts taken recently to

overcome such critical issues. For example, a bifunctional catalyst constructed from Pd metal nanoparticles on carbon and ZnCl₂ can selectively cleave C–O bonds in a variety of lignin models and lignin under relatively mild conditions (150 °C and 30–300 psi of H₂).⁵⁵ If both Pd/C and Zn²⁺ are present, the benzyl alcohol and aldehyde groups can be selectively deoxygenated in good yields without hydrogenation of the phenyl ring. Most importantly, monomeric lignin surrogates can be deoxygenated depending on the synergy between the Pd/C and Zn²⁺. The β–O–4 linkage of the lignin macro-molecule is the most abundant repeating subunit and selectively cleaving such ether linkages by carrying out HDO using the Pd/C–Zn²⁺ system provides a way of unfolding the complex polymeric structure of lignin into small molecules of fuel value (Fig. 5). In this model, guaiacylglycerol-β-guaiacyl ether was hydrogenated and deoxygenated at 150 °C under 20 bar of hydrogen using Zn/Pd/C in MeOH yielding primarily two products, guaiacol and 2-methoxy-4-propylphenol (Fig. 5, eqn (1)). The catalyst performance was tested for the β–O–4 synthetic lignin polymer (M_n 3390, DP_n 12.1), which underwent cleavage and deoxygenation (Fig. 5, eqn (2)). Extended X-ray Absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) studies confirmed that 30% of the metallic nanoparticles were oxidized and EXAFS studies confirmed that no Pd–Zn bimetallic alloy existed, however at higher temperatures (250 °C) XANES and Pd K-edge suggested a small amount of Pd–Zn alloy formation. The investigation of the chemical aspects of deoxygenation revealed that Zn adsorption on carbon, most likely onto –OH sites, and not forming a Pd–Zn alloy or direct Pd–Zn interactions was very different as revealed from XAS studies. The hypothesis given by the authors based on the evidence was that Zn²⁺ participates in one of two ways, either by activating the substrate by binding to the –OH groups inducing reactivity with Pd–H on the surface *via* a hydrogen spillover, or alternatively, Zn²⁺ ions desorb into solution at the reaction temperature (150 °C). Zinc binds to the substrate and activates its cleavage upon encountering Pd–H sites on the catalyst surface. Once the reaction mixture is cooled, the Zn²⁺ ions are readsorbed onto the C surface. However, Zn/Pd/C was found to be more effective for the cleavage of β–O–4 linkages in lignin molecules and the subsequent HDO of aromatic fragments without any chemical change in the aromatic functional groups.

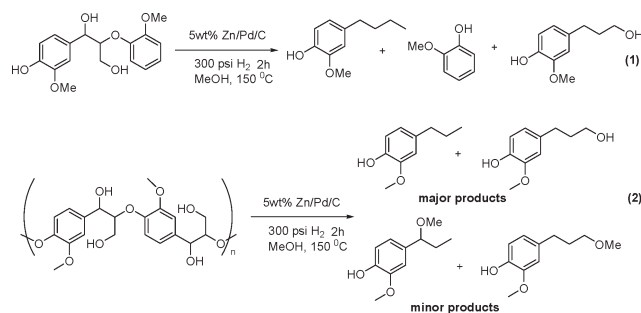


Fig. 5 β–O–4 dimeric and polymeric lignin cleavage and HDO to remove ether oxygen atoms using the Zn/Pd/C system in methanol.

The system is capable of removing alcohol oxygen atoms on the alkyl chains and maintaining valuable aromaticity and thus is useful for cleaving recalcitrant ether bonds of model lignin dimer and polymers.

With the initial development of lignin depolymerization chemistry, deoxygenation *via* the selective hydrogenolysis of C–O bonds has been realized as a key strategy. Dispersed and immobilized nanoscale metal catalysts with dual functionalities play a significant role in the hydrogenolysis of C–O bonds.⁵⁶ In this regard, understanding the nature of the active sites in such bifunctional catalysts and the reaction pathways of C–O bond scission are essential. The superiority of a bimetallic catalyst for the hydrogenolysis of lignin C–O bonds was witnessed in a β -O-4 type C–O bond hydrogenolysis reaction of a lignin model compound, 2-phenoxy-1-phenethanol, with an optimized 85% Ni and 15% Ru composition.⁵⁷ This bimetallic system contained near-surface Ru in the Ni₈₅Ru₁₅ catalyst, however X-ray absorption and photoelectron spectroscopic results suggested that electron-enriched Ni atoms preferentially occupied the surface. Hydrogenolysis results at various temperatures and H₂ pressures led the authors to conclude that enhanced activation of H₂ and the substrate due to electron-rich Ni at the surface was a major factor responsible for the higher activity compared to the single component metal catalysts. Using the Ni₈₅Ru₁₅ system, organosolv lignin from *Betula platyphylla* suk showed that monomeric products can be achieved under the typical reaction conditions as noted in Table 3. In this case, the entire process can be investigated by measuring the intensities of the C–O bond vibration in the guaiacyl unit and the non-conjugated C=O vibration using FTIR spectroscopy. This method of using a NiRu bimetallic system at an optimized ratio of the two metals suggests the importance of such species in other processes which require the prevention of hydrogenation of aromatic rings and where one of the metal components is more active when used as a single metal component.

A further interesting feature was reported in the case of a NiAu catalyst for the hydrogenolysis of lignin into phenolic

chemicals with a high selectivity for the β -O-4 type C–O bond hydrogenolysis. An optimum Ni: Au 7: 3 ratio resulted in a 99% conversion of lignin model compound 2-phenoxy-1-phenylethanol, with a maximum of 87% monomer yield when dimers were the reaction intermediates.⁵⁸ The comparative TOFs of the initial hydrogenolysis results confirmed that the more active Ni₇Au₃ catalysts had more active surface sites and an increased dispersion. From the EXAFS, XPS, ICP-MS and UV-Vis experiments, the authors proposed that the structure of the NiAu catalyst would be a Ni-enriched Ni–Au shell encapsulating a Au core (Fig. 6(a)). The exceptional performance of the NiAu catalyst at a Ni: Au ratio of 7: 3 may be related to the unique electronic state of Ni, and an electronic modification of the bimetallic species Ni₇Au₃ can be revealed from the XANES spectra (Fig. 6(b)). The white light intensity of Au increased with increasing Ni loading, pointing to a decreased electron density of Au atoms while interacting with Ni, which results in a concurrent shift of the Ni absorption edge towards a lower energy as the Au content increases. In this case Au acts as an electron donor in the NiAu catalyst, enabling neighboring Ni atoms to be more electron enriched, which is useful for lignin hydrogenolysis. Upon applying the hydrogenolysis reaction of organosolv lignin, the average molecular weight dramatically decreased due to the hydrogenolysis reaction exhibiting complete depolymerization. This case of manipulating the electronic properties of one component of a bimetallic system (Ni) to enhance the overall activity as revealed by spectroscopic studies has a larger implication on future system designs for lignin valorization.

In addition to developing and exploring new combinations of catalysts capable of controlling HDO, studies on oligomeric lignin in order to identify new combinations of catalyst matrixes with multi-catalytic functionalities suitable for the efficient depolymerization of the lignin polymeric framework

Table 3 Organosolv lignin depolymerization over Ni, Ru and Ni₈₅Ru₁₅ catalysts in aqueous medium (reaction conditions: 50 mg of organosolv lignin, 3 mL of aqueous solution containing 0.22 mmol metal and 0.44 mmol PVP, 10 bar H₂)⁴¹

Catalyst	Time (h)	Yield (wt%)			Residual lignin (wt%)
		1	2	3	
Ni	1	0	0	0	46
Ru	1	0.1	0.03	0.03	50
Ni ₈₅ Ru ₁₅	1	0.1	0.6	0.1	58
Ni ₈₅ Ru ₁₅	12	1.4	5.0	0.4	56
Ru	12	0.2	0.06	0.6	38

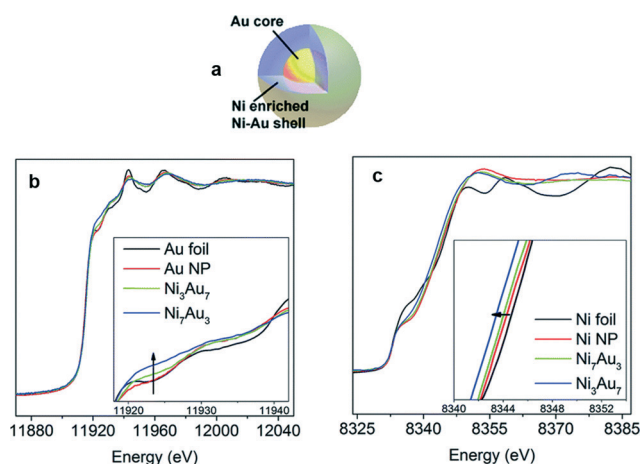


Fig. 6 (a) Proposed structural representation of the NiAu catalyst. (b) Normalized XAS spectra at the AuLIII edge of the Au, Ni₃Au₇ and Ni₇Au₃ catalysts. A spectrum of Au foil was included as a reference. (c) Normalized XAS spectra at the Ni K edge of the Ni, Ni₃Au₇ and Ni₇Au₃ catalysts. A spectrum of Ni foil was included as a reference. (Fig. 6a–c are reproduced with permission from ref. 58, Copyright Royal Society of Chemistry, 2014).

into monomeric intermediates and the subsequent removal of oxygen *via* the HDO process, requires analysis of the inter-unit linkages. For example, a recent study revealed that for technical grade lignin to produce C7 to C9 monomeric lignin intermediates under HDO conditions, a 5% noble-metal (Ru, Rh, Pt)/Al₂O₃ (or C)-zeolyst (*e.g.* NH₄⁺ Z-Y 57277-14-1) catalyst matrix was required.⁵⁹ These multi-functional catalyst matrixes showed promising selectivity for the conversion of lignin to aromatic hydrocarbons (alkyl benzene derivatives) from a wide variety of lignin compounds under HDO conditions in aqueous media. Results show that the Al₂O₃-supported noble metal catalysts are effective in reducing functional groups (*e.g.* methoxyl groups) in lignin aromatic molecules, but are rather inactive for the hydrogenation of the aromatic ring. Thus under HDO conditions, Al₂O₃ supports are preferable over carbon supports. Different HDO conditions with noble metals (Ru, Pt, Rh) and acidic zeolites (CBV 28014 CY 1.6 and NH₄⁺ Z-Y 57277-14-1) in the presence of hydrogen can be used to further improve the yields and selectivity for the production of aromatic hydrocarbons (alkyl benzene derivatives), which can be incorporated into commercial jet fuels to increase the bulk density and lower the cloud point of the fuels. Replacing the acidic zeolite CBV 8014 CY 1.6 with NH₄⁺ Z-Y 57277-14-1 was shown to enhance the aromatic hydrocarbons and the product selectivities with the noble metals Rh and Pt on Al₂O₃ supports under HDO conditions. The high reactivity of technical grade lignin based on their sub-structures (Fig. 7) accounted for their high reactivity as substrates in HDO reactions. The structure of lignin is predominantly comprised of 8-O-4' inter-unit linkages (C-O-C bonds) which would undergo both hydrogenolysis and deoxygenation *via* cleavage and simultaneous removal of oxygen in the presence of a noble metal integrated zeolite catalyst matrix.

Various analyses of lignin model compounds and the distribution of products obtained during the lignin aqueous phase reforming revealed that lignin depolymerization through the disruption of the abundant β-O-4 linkages, and to a lesser extent the 5-5' carbon-carbon linkages, to form monomeric aromatic compounds is well known.⁶⁰ However less effort has been invested in developing selective HDO techniques to access hydrocarbons from lignin or lignin model compounds. In this context, a combined depolymerization and (hydro)-de-oxygenation reaction of lignin in a

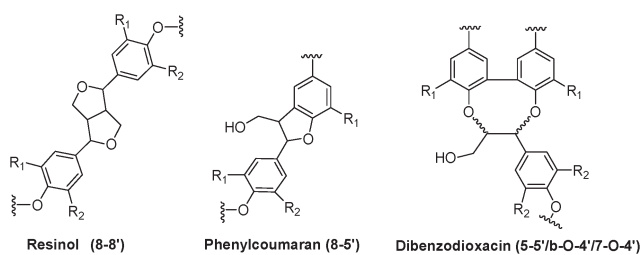


Fig. 7 Inter-unit linkage-based sub-structures of technical grade lignin.

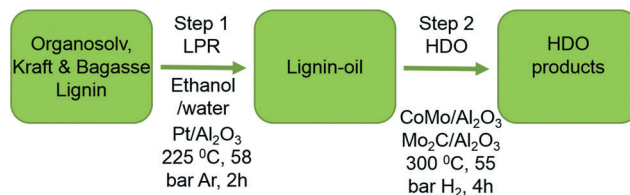


Fig. 8 Two-step approach to the valorization of lignin involving HDO.

single step to access phenolic products over a Pt catalyst with formic acid (H₂ source) can significantly reduce the molecular weight and oxygen content.⁶¹ However, this single-step disassembly of lignin offers monomeric cyclohexyl derivatives and aromatic products.^{62,63}

A combined depolymerization and HDO reaction of lignin in two steps using Pt/Al₂O₃ (ethanol/water) and CoMo/Al₂O₃ under a high pressure of H₂ was reported for the organosolv and kraft lignin. This involves liquid-phase reforming, extraction of lignin-oil and then a HDO step to access the deoxygenated products, *i.e.* mono-oxygenated phenolics (Fig. 8).⁶⁴ Without a pretreatment step, the HDO process with Mo₂C/CNF (carbon nanofiber) on organosolv lignin offers only a small percentage of monomeric phenolic compounds (Fig. 9). In spite of a positive temperature effect on reducing the oxygen content of HDO-derived products, the required level of success for hardwood lignin is yet to be achieved, which must include a convenient pretreatment step.

2.3 Enzymatic oxidation

Generally, chemical methods to depolymerize lignin generate low yields of complex mixtures of products and also results in the formation of insoluble high molecular weight products. Initially, microbial degradation of lignin was investigated primarily in white-rot and brown-rot fungi, depending on the ability of these fungi to produce extracellular lignin peroxidase and Mn peroxidase enzymes for oxidizing lignin. It was revealed that fungi use iron and redox mediators to carry out Fenton oxidation reactions to depolymerize lignin.⁶⁵ Although fungal lignin deconstruction has been studied for a

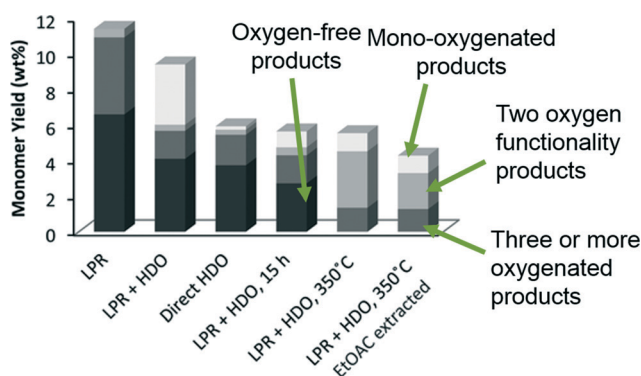


Fig. 9 Yield of monomeric aromatic products after HDO of organosolv lignin-oil over a Mo₂C/CNF catalyst under different conditions.

long time, there is no commercial biocatalytic process involving this technique to date.⁶⁶ Several bacterial strains are also able to break down lignin, including actinobacteria such as *Streptomyces viridosporus*, which produces an extracellular peroxidase, certain pseudomonads, and the anaerobic bacterium *Enterobacter lignolyticus* SCFI. In *Rhodococcus jostii* RHA1, whose genome sequence has been determined, the identification and characterization of peroxidase DypB, which can oxidize lignin models, Kraft lignin, lignocellulose, and Mn^{2+} , has been reported.⁶⁷ Two further bacterial peroxidase enzymes have been reported from *Amycolatopsis* sp. 75iv2: a heme-containing enzyme capable of oxidizing lignin model compounds⁶⁸ and a Dyp2 peroxidase enzyme with higher catalytic activity for Mn^{2+} oxidation.⁶⁹ Synthetic biology is finding importance in designing new biosynthetic routes to alkanol, biodiesel and biofuels with non-fermentative pathways.⁷⁰ It was previously observed that *R. jostii* RHA1 DypB (a lignin oxidizing enzyme) is capable of cleaving a β -aryl ether lignin model compound to produce vanillin and a two-carbon fragment glycoaldehyde. The other aromatic metabolite, 5-carboxyvanillic acid, is a potential intermediate in the biphenyl catabolic pathway and can be decarboxylated to form vanillic acid for growth.⁷¹ This vanillic acid catabolic pathway might be important for lignin breakdown.

For the vanillic catabolic pathway, the production of vanillin from lignin components of lignocellulose using gene deletion is desired and the process can be engineered for the production of aromatic compounds. This concept has the advantage of generating a small number of metabolites in a predictive way, which requires a robust organism for which mutant strain growth to a high cell density also prevents formation of toxic aldehyde metabolites. When a gene deletion strain of *R. jostii* RHA1, where the vanillin dehydrogenase gene has been deleted, is grown on a minimal medium containing 2.5% wheat straw lignocellulose and 0.05% glucose, vanillin is produced as a product.⁷² Hypothetical catabolic pathways in *R. jostii* RHA1 for the breakdown of the β -aryl ether and biphenyl components of lignin based upon the structure of the observed metabolites is depicted in Fig. 10.

Synthetic biology has been used with *Escherichia coli* to engineer new biosynthetic routes to alkanol and biodiesel, but thus far there are limited applications towards biomass deconstruction and little use of other bacterial hosts for synthetic biology. A gene deletion mutant based biocatalytic route to access aromatic chemical-like vanillin from wheat straw lignocellulose is a significant step towards a metabolic engineering based approach.⁷³

2.4 Carbonization

Bulk synthesis of materials for energy storage from renewable sources using scalable technologies is currently desired. Lignin is a major by-product of chemical pulping and is increasingly available for biofuel production, so in spite of the chemical heterogeneity and structural variations, lignin's

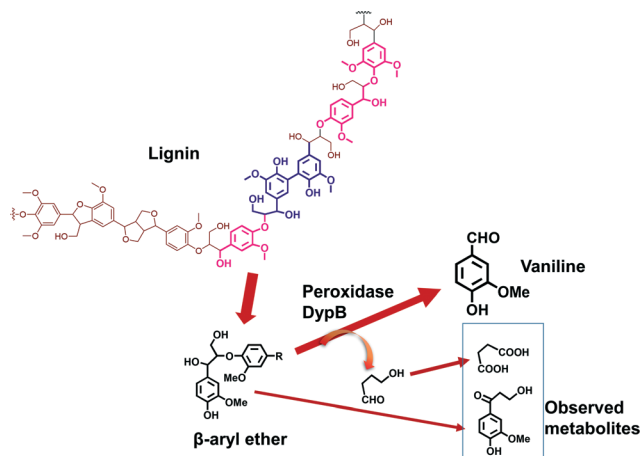


Fig. 10 Hypothetical catabolic pathways in *R. jostii* RHA1 for the breakdown of the β -aryl ether and biphenyl components of lignin based upon the structures of the observed metabolites.

high carbon content and phenolic structure make it an excellent alternative source to carbon materials (Fig. 11). Additionally, high mass retention characteristics of lignin in thermal processing have been witnessed in its conversion to carbon fibers (CFs),^{74,75} porous activated carbon (PAC) particles,^{76–78} and graphitic form of CFs. Lignin based CFs contain comparable mechanical properties to commercial polyacrylonitrile-based CFs for reinforcing composites.

Novel microstructured carbon materials find applications as adsorbents and anode materials in batteries or supercapacitors.⁷⁹ Thus it is highly interesting to discover synthesis techniques to access microstructured carbon materials from lignin involving fiber processing and chemical modifications.

2.4.1 Carbon fibers. The first report on the use of lignin as a precursor for carbon fibers deals with the conversion of lignin into functional polymers to obtain a spinnable material and fibers after thermal stabilization followed by carbonization.⁸⁰ In contrast to the approach based on the use of a binder polymer, a straightforward method to obtain

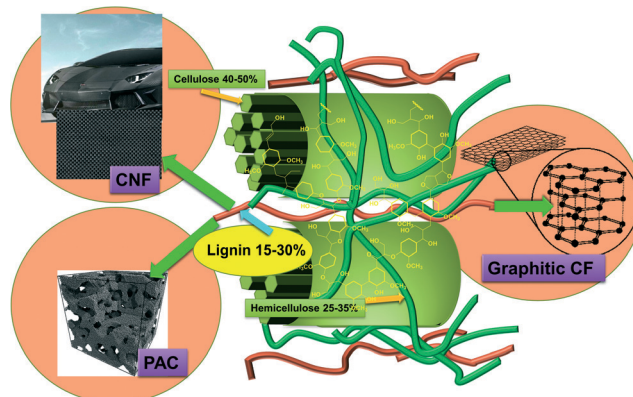


Fig. 11 Pictorial depiction of lignin as a potential source for the various nanostructured carbon materials required for advanced technological applications.

carbon micro and nanofibers by co-electrospinning Alcell lignin solutions at room temperature, followed by thermal stabilization and carbonization reactions to produce carbon fibers has been reported.⁸¹ Alcell lignin electrospun nanofibers (ALFs) were stabilized by thermal treatment in air at room temperature to 200 °C for 24 h, which provides fibers of a similar size and then these were carbonized to obtain carbon nanofibers at 900 °C. The carbon crystallites with a preferred orientation along the fiber axis have smooth fiber surfaces. The fibers remain in the glassy state ($T_g > T$) and the structural organization in the carbon nanofibers was revealed with a Raman spectroscopic study. This confirmed a lower contribution of structural disorder at the higher-temperature and graphitic carbon formation (E_{2g} , 1575 cm^{-1}) confirmed an onset structural organization. The fibers were found to be oxidation resistant and highly microporous. The large micropore volume makes these nanofibers suitable for CO_2 adsorption–desorption processes.

A rapid freezing process of aqueous lignin solution, followed by sublimation of the resultant ice forms a uniform network comprised of individual interconnected lignin nanofibers. Carbonization of that offers a similarly structured carbon nanofiber network.⁸² The rapid freezing process resulted in the elimination of larger spaces and macropores were observed due to the formation of smaller ice crystals. Smaller and uniform fiber diameters were generated due to the more rapid heat removal and uniform cooling rates resulting in lignin and subsequently individual carbon fibers with diameters less than 100 nm (Fig. 12). The fibers tended to have preferential alignment in the direction of the freezing front, which depends on the concentration.

It has been demonstrated that the conventional graphitic anode of lithium ion batteries can be replaced with lignin carbon fibers (LCFs) when synthesized and applied as monolithic fused mats which contain specific charge capacities.⁸³ LCFs carbonized at 1000 °C have specific charge capacities. In this case, irreversible lithium insertion and extraction was witnessed in the more disordered LCFs carbonized at 1000 °C with the smallest nanoscale graphitic domains. The

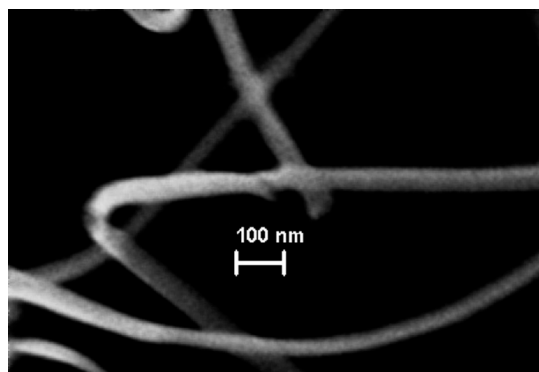


Fig. 12 Scanning electron microscope image of carbon nanofibers. Individual CNFs derived from lignin with diameters of less than 100 nm. (Reproduced with permission from ref. 82, copyright American Chemical Society, 2012).

question is, why do graphitic domains in a carbon fiber enhance the performance of the battery? This happens because the carbonized structure is modulated to yield an active material with an internal mesostructure consisting of a high density, nanoscale crystalline (graphitic) domain surrounded by a continuous, low-density, highly disordered carbon matrix. This amorphous carbon enables facile, isotropic lithium transportation throughout the fiber structures, providing access to charge storage sites within the nanoscale graphitic domains.⁸⁴ It was found that the matrix graphitization increased with the increase in carbonization temperature, *i.e.* the long-range graphite order with no preferential orientation along the fiber axis, as shown in the SEM image of a typical LCF fused mat after carbonization and varying levels of fiber–fiber fusion (Fig. 13) in which the mat densities can be controlled. The mats are excellent anode materials, exhibiting a tunable electrochemical performance suitable for high energy applications. The synthesis method results in an electrically interconnected 3D architecture from the lignin 3D structure and the final carbon fibers act as current collectors and Li insertion materials. This carbonized lignin has a disordered nano-crystalline microstructure.

Structural modification of lignin with different ester groups results in a precursor which is highly compatible with the melt processing technique for fiber extrusion and further conversion into microstructured carbons by oxidative stabilization and subsequent carbonization.⁸⁵ Acid anhydride modification of lignin hydroxyl groups (acyl substitution) under neutral conditions and over a long reaction time (6 h) can be carried out. Most of the available (phenolic and aliphatic) hydroxyl groups of lignin are esterified, however the polymeric structural characteristics of lignin are not changed throughout the modification process. It is interesting that the surface areas of the resulting carbon materials fall in the range of commercial graphitic carbon materials. Phthalic anhydride modified lignin contains a relatively high microscale porosity compared to unmodified lignin based carbon fibers (Fig. 14). This modification influences the underlying meso- and microstructure development and pore creation, and the carbonization temperature can be adjusted to access carbons with either more graphitic or disordered structures.

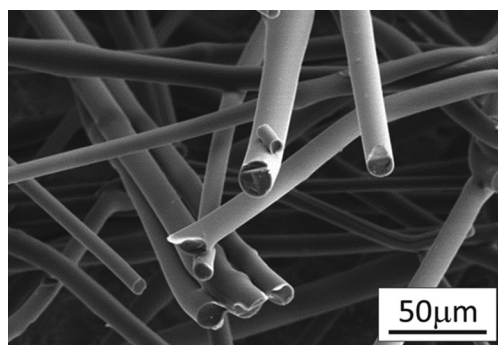


Fig. 13 SEM image of varying levels of fiber–fiber fusion in LCF mats. (Reproduced with permission from ref. 83, copyright Wiley-VCH, 2014).

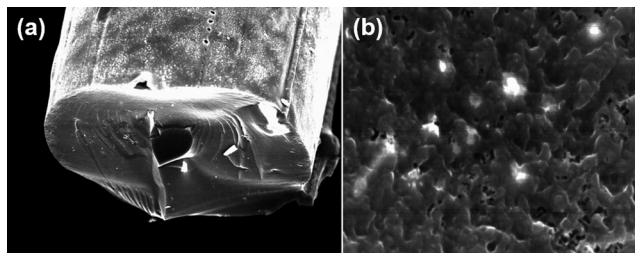


Fig. 14 Scanning electron microscope image of carbon fibers (a) from phthalic anhydride modified lignin and (b) showing the micro scale porosity of phthalic anhydride modified lignin. (Reproduced with permission from ref. 85, copyright RSC, 2013).

A method for producing ultrafine (100–500 nm) highly porous activated carbon fibers (ACFs) has been reported. This involves the electrospinning of aqueous solutions of predominantly alkali lignin (low sulfone content), followed by the simultaneous carbonization and activation.⁸⁶ The major advantage of this process is the simultaneous carbonization and activation reactions in a single heating step, which results in a range of micropore to mesopore dominant ACFs with superior specific surface areas and porosities tuned by varying the contents of alkali hydroxides. The use of the electrospinnable PEO carrier as one ninth of the AL_{1s} made the mixture electrospinnable into fibers. Interestingly, size variation of the fibers in the 100–300 nm and 300–500 nm range when using NaOH and KOH, respectively, can also be achieved (Fig. 15). The decreased fiber sizes are generally attributed to the increased charges of the solutions and the improved charge dissipation from the added electrolytes in the electrospinning process.

This approach offers highly porous and high specific surface area ACFs containing both mesopores and micropores with different size proportions and slit-like micropores at 0.1 impregnation ratio. These develop into a network of larger mesopores connected or embedded within the

micropores matrix by narrow necks as the ratio increased to 0.3 and 0.5, along with the increase of mesopores.

Production of carbon fibers by mixing carbon nanotubes with the carbonaceous precursor to generate carbon nanotube composite fibers depends on the chemical modification of the carbonaceous precursors. In this case, anhydride compounds play a special role making functionalized lignin suitable for fiber production.⁸⁷ These carbon fibers derived from lignin contain controllable turbostatic disorder, which is controllable by the choice of functional agents and the aspect ratio. In addition, fibers can be derived with desired transport and interfacial properties. These lignin derived fibers found potential applications in Li-ion batteries.

Melt-spinning has already been proven as a suitable technique to access carbon fibers. Lignin was modified chemically and blended with poly(lactic acid) (PLA) before melt-spinning into lignin fibers.⁸⁸ This pre-carbonization functionalization involves butyration to form ester functional groups in place of the polar hydroxyl (–OH) groups. This enhances the miscibility of lignin with PLA. Microstructure analyses (SEM and TEM) of the carbon fibers produced from lignin/PLA blends revealed the composition dependent microporous structure inside the fine fibers (Fig. 16). The microvoids in the cross section of all fibers, which are absent in pure lignin-derived fibers, are produced by PLA after carbonization and the size of the microvoids decreased with the increase in lignin content.

A strategy for porous core construction has been reported for the controlled co-electrospinning and carbonization method of lignin and cellulose, which produces core-shell carbon fibers with cellulose nanofibrils (CNFs) and a porous core. After carbonization, a hollow fiber structure was obtained with an increased surface area and porosity.⁸⁹ It is advantageous to increase the surface area and porosity *via* the co-electrospinning method as it provides an improved

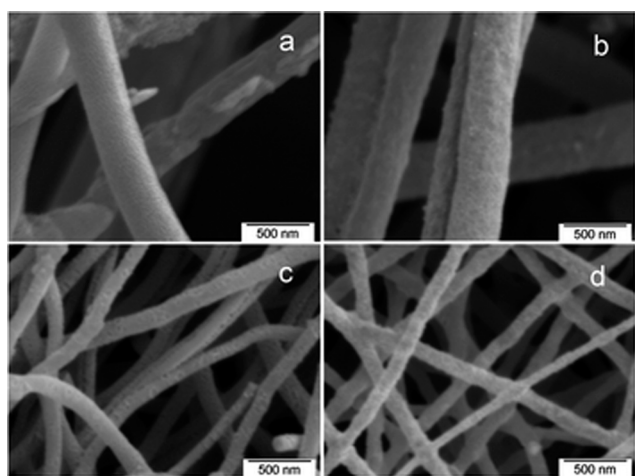


Fig. 15 SEM images of AL_{1s}-PEO hybrid fibers with NaOH (a, b) and KOH (c, d). (Reproduced with permission from ref. 86, copyright RSC, 2014).

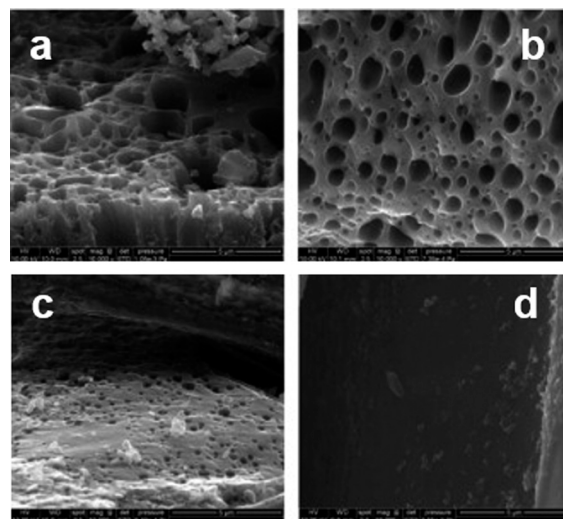


Fig. 16 SEM images of cross-sections of carbon fibers from B-lignin/PLA blends: (a) 50/50; (b) 75/25; (c) 90/10; (d) 100/0. (Reproduced with permission from ref. 88, copyright Elsevier, 2014).

platform for various interactions between the fibers and their surrounding environments, which potentially enhances the performance of the fibers for advanced applications. Core-shell CNF-lignin/PAN fibers exhibit relatively smooth surfaces where the porous core consists of a CNF network and the shell consists of lignin and LAN. The differences between a lignin based hollow fiber (lignin/PAN) and a CNF-lignin based core-shell fiber (CNFs-lignin/PAN) can be easily seen in the cross sectional surfaces as shown in Fig. 17.

In the past and currently, phenolic resin has been broadly applied as a source of activated carbon fibers (ACFs), and lignin with a phenyl-propane structure, similar to the phenol-formaldehyde resin, is found to be ideal replacement to prepare phenolic resin. Furthermore, application of this resin to fabricate lignin-based carbon materials with controllable surfaces, pore structures and physical properties are desired.

2.4.2 Microporous carbon. Nanostructured carbon materials with a hierarchical pore arrangement are considered to be one of the most appropriate electrode materials for high-performance electrochemical capacitors. The ordered mesopore networks of these materials provide shorter diffusion pathways along the carbon particles, which enhances the diffusivity of molecules and/or ions to make the inner surface more accessible than the microporous activated carbons. The presence of certain oxygen surface groups on carbon materials can contribute significantly to the performance by improving the wettability of the surface and enhancing the pseudocapacitance. Preparation of hierarchically porous carbon materials from biomass sources is an emerging area needing further investigation. The technique to access such novel nanostructured carbon materials majorly depends on the nanocasting technique using a hard or soft template. Microporous carbon with a 3D connected and ordered pore structure can be produced by liquid phase impregnation (LPI) with a carbon precursor over a porous zeolite and the template is traditionally removed by HF washing. To prepare ultraporous carbon, the use of a zeolite template and lignin as a carbon precursor to obtain zeolite-template carbon (ZTC) containing finger prints of zeolite has been achieved recently.⁹⁰ This lignin derived ZTC contained a bimodal pore structure where the microporosity resulted from both the removal of the zeolite walls and the lignin carbonization, and a mesoporous network originated as a

result of the incomplete pore filling of the hard template. The interesting part is to analyse the origin of the mesoporosity for the template carbon materials, which replicates both the external and internal morphology of the corresponding zeolite crystals.

3. Summary and outlook

We have reviewed recent work on a number of emerging strategies of lignin valorization including depolymerization reactions to form monomers, further upgradation of the monomers, enzymatic oxidation and carbonization. Among these, depolymerization *via* hydrogenolysis of lignin into monomers has been the key strategy. However with the development of nano-scale catalysts, selective deoxygenation *via* the hydrogenolysis of β -O-4 type C-O bonds has emerged as a challenging target for further upgradation of the monomers obtained *via* lignin depolymerization. Emerging strategies of enzymatic oxidation of lignin have been reviewed with limited cases, along with covering the potentials of lignin for the production of carbon materials with a wide range of nanostructures.

As a resource of nanomaterials, biopolymers have many advantages and can be extracted industrially on a large scale, for example lignin from kraft pulping.⁹¹ Some of the current approaches show that lignin can be a versatile source to obtain a wide range of high quality nanostructured carbon fibers, which are emerging materials for electrochemical energy storage applications. This article has also analyzed the scope of the deoxygenation techniques for the upgradation of lignin-derived aromatic functionalized monomers and its successful recent outcomes for accessing high value deoxygenation products containing an intact aromatic ring. However, lignin depolymerization from intact biomass currently produces a largely heterogeneous range of molecules, which makes lignin valorization an enormously difficult problem. Such cleavage strategies for polymeric units consisting of aromatic fragments demonstrate the careful selection of reactive molecules or nanoparticles capable of selectively cleaving biomass lignin. This results in a successful route to disrupt the recalcitrance of lignin under controlled conditions to generate value from lignin and make the carbohydrate fraction more reactive for hydrolysis. Enzymatic strategies involving synthetic biological processes with appropriate enzymes are currently evolving and have a lot to offer. In nature, lignin is slowly degraded by white-rot fungi such as *Phanerochaete chrysosporium*, which provides an extracellular lignin peroxidase enzyme to begin the degradation process. Manganese peroxidase and laccase enzymes are also capable of lignin breakdown to form initial breakdown products such as phenylpropanoid dimers, which can be further degraded *via* aromatic meta-cleavage pathways and this is carried out in nature by soil bacteria. Certain studies that contain huge potential to change the face of lignin valorization are envisaged as follows:

1) Accessing non-pyrolytic lignin bio-oil by developing new depolymerization strategies are essential since lignin-bio-oil

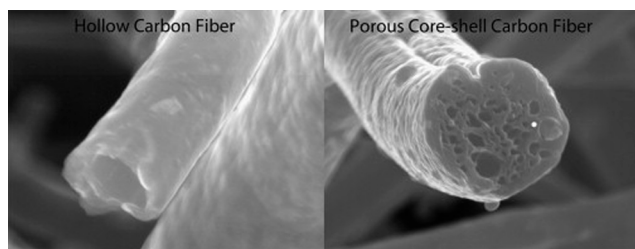


Fig. 17 SEM images of hollow and porous core-shell carbon fibers derived from lignin/PAN and CNF-lignin/PAN, respectively. (Reproduced with permission from ref. 89, copyright Elsevier, 2013).

is extremely amenable to HDO for further upgradation, and therefore a catalytic biorefining method can be established. Transfer hydrogenation in alcohol media has been found to be a potential strategy as discussed earlier in this article. New hydrogen transfer strategies under mild conditions will be investigated for the future development of the depolymerization process to access the lignin-oil-fraction. Efficient strategies would enable us to proceed by avoiding the use of recalcitrant solid polymers obtained from the organosolv process.

2) Establishing the role of the bimetallic alloy system for selective C–O bond hydrogenolysis is one of the fundamental interests related to lignin valorization and its chemical aspects. The development of strong and effective homogeneous catalysts for HDO is something that is not often investigated recently. This topic has significant scope for developing new lignin chemistry. Moreover, in HDO reactions of naturally occurring lignin species, the important features of the lignin surface and their role is yet to be revealed. The HDO process is to be studied extensively in the future, in addition to designing and improving conventional methods of lignin depolymerization.

3) Identifying new bacterial lignin degraders and test enzymes like manganese peroxidase and laccase in the solution phase and immobilized phase. The mechanism of lignin cleavage by enzymes is an interesting area to explore. Polysaccharide monooxygenase enzyme AA9 (GH61) is also another candidate for lignin valorization.⁹² In this respect, bacterial peroxidase enzymes are potential compounds which are capable of oxidizing lignin.⁹³ This article highlights this part to convey the message that experts in biology have a major role to play in the near future for the gene specific or gene altered enzyme specific disruption of biopolymer chains of lignin. Apart from exploring new oxygenase enzymes, novel nanomaterial-enzyme composites and enzyme encapsulated nanoscale materials as biocatalysts should be explored and this offers a potential area to develop lignin chemistry.

4) The strategy of exemplifying the potential of different rigid templates such as hierarchical zeolites and large pore metal-organic frameworks can be extensively tested for accessing hierarchical porous carbon (HPC) materials by infiltration of lignin as the carbon source. Novel strategies to obtain carbon using lignin as a carbon precursor have plenty to offer for designing and developing energy storage devices. In order to develop strategies for chemical modification or chemical conversion of lignin, it is of high importance to consider the bonds which are to be cleaved.

Acknowledgements

SD and KWC Wu thank the Ministry of Science and Technology (MOST), Taiwan (101-2628-E-002-015-MY3, 101-2623-E-002-005-ET, 101-2923-E-002-012-MY3, 103-2811-E-002-018 and 103-2218-E-002-101), National Taiwan University (101R7842 and 102R7740), and the Center of Strategic Materials Alliance for Research and Technology (SMART Center) of National

Taiwan University (102R104100) for funding support. BS acknowledges the Center for direct Catalytic Conversion of Biomass to Biofuels (C3Bio), an Energy Frontier Research Center funded by the U. S. Department of Energy, Office of Science, and Office of Basic Energy Sciences under award number DE-SC0000997 for the financial support.

Notes and references

- 1 A. S. Mamman, J.-M. Lee, Y.-C. Kim, I. T. Hwang, N.-J. Park, Y. K. Hwang, J.-S. Chang and J.-S. Hwang, *Biofuels, Bioprod. Biorefin.*, 2008, 2, 438–454.
- 2 R. E. Hage, N. Brosse, L. Chrusciel, C. Sanchez, P. Sannigrahi and A. Ragauskas, *Polym. Degrad. Stab.*, 2009, 94, 1632–1638.
- 3 H. H. Nimz, *Angew. Chem., Int. Ed. Engl.*, 1974, 13, 313–321.
- 4 E. Adler, *Wood Sci. Technol.*, 1977, 11, 169–218.
- 5 G. Chatel and R. D. Rogers, *ACS Sustainable Chem. Eng.*, 2014, 2, 322–339.
- 6 J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, 110, 3552.
- 7 J. Holladay, J. F. White, J. J. Bozell and D. Johnson, DOE Report, *Top Value-Added Chemicals from Biomass, Volume II*, 2007.
- 8 D. D. Laskar, B. Yang, H. Wang and J. Lee, *Biofuels, Bioprod. Biorefin.*, 2013, 7, 602–626.
- 9 H. Yang, R. Yan, H. Chen, D. H. Lee and C. Zheng, *Fuel*, 2007, 86, 1781–1788.
- 10 J. R. Regalbuto, *Science*, 2009, 325, 822–824.
- 11 V. M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li and J. A. Lercher, *Chem. – Eur. J.*, 2011, 17, 5939–5948.
- 12 B. G. Janesko, *Phys. Chem. Chem. Phys.*, 2014, 16, 5423–5433.
- 13 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.
- 14 Z. Ma, E. Troussard and J. A. Van Bokhoven, *Appl. Catal., A*, 2012, 423–424, 130–136.
- 15 P. F. Britt, A. C. Buchanan, M. J. Cooney and D. R. Martineau, *J. Org. Chem.*, 2000, 65, 1376–1389.
- 16 G. S. Macala, T. D. Matson, C. L. Johnson, R. S. Lewis, A. V. Iretskii and P. C. Ford, *ChemSusChem*, 2009, 2, 215–217.
- 17 Z. Li, M. Garedew, C.-H. Lam, J. E. James, D. J. Miller and C. M. Saffron, *Green Chem.*, 2012, 14, 2540–2549.
- 18 R. W. Thring and J. Breau, *Fuel*, 1996, 75, 795–800.
- 19 W. L. Schinski, A. E. Kuperman, J. Han and D. G. Nae, US 2009/0218061A0218061, 2009.
- 20 M. Saisu, T. Sato, M. Watanabe, T. Adschiri and K. Arai, *Energy Fuels*, 2003, 17, 922–928.
- 21 M. Osada, T. Sato, M. Watanabe, T. Adschiri and K. Arai, *Energy Fuels*, 2004, 18, 327–333.
- 22 M. Osada, N. Hiyoshi, O. Sato, K. Arai and M. Shirai, *Energy Fuels*, 2007, 21, 1854–1858.
- 23 J. Huang, X. Wang and Z. L. Wang, *Nano Lett.*, 2006, 6, 2325–2331.

- 24 H. Lange, S. Decina and C. Crestini, *Eur. Polym. J.*, 2013, **49**, 1151–1173.
- 25 Y. Gao, J. Zhang, X. Chen, D. Ma and N. Yan, *ChemPlusChem*, 2014, **79**, 825.
- 26 T. Radoykova, S. Nenkov and K. Stanulov, *Chem. Nat. Compd.*, 2010, **46**, 807–808.
- 27 Wahyudiono, M. Sasaki and M. Goto, *Fuel*, 2009, **88**, 1656–1664.
- 28 S. Karagöz, T. Bhaskar, A. Muto and Y. Sakata, *Fuel*, 2004, **83**, 2293–2299.
- 29 T. Voith and P. Rudolf von Rohr, *ChemSusChem*, 2008, **1**, 763–769.
- 30 K. Stärk, N. Taccardi, A. Bösmann and P. Wasserscheid, *ChemSusChem*, 2010, **3**, 719–723.
- 31 J. Zakzeski, A. L. Jongerius, P. C. A. Bruijninx and B. M. Weckhuysen, *ChemSusChem*, 2012, **5**, 1602–1609.
- 32 R. W. Coughlin and F. Davoudzadeh, *Nature*, 1983, **303**, 789–791.
- 33 N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. T. Liu and Y. Kou, *ChemSusChem*, 2008, **1**, 626–629.
- 34 C. Z. Li, M. Y. Zheng, A. Q. Wang and T. Zhang, *Energy Environ. Sci.*, 2012, **5**, 6383–6390.
- 35 E. E. Harris, J. D'Ianni and H. Adkins, *J. Am. Chem. Soc.*, 1938, **60**, 1467–1470.
- 36 A. L. Jongerius, R. Jastrzebski, P. C. A. Bruijninx and B. M. Weckhuysen, *J. Catal.*, 2012, **285**, 315–323.
- 37 J. M. Nichols, L. M. Bishop, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2010, **132**, 12554–12555.
- 38 R. C. Runnebaum, T. Nimmanwudipong, D. E. Block and B. C. Gates, *Catal. Sci. Technol.*, 2012, **2**, 113–118.
- 39 Q. Song, F. Wang and J. Xu, *Chem. Commun.*, 2012, **48**, 7019–7021.
- 40 Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu and J. Xu, *Energy Environ. Sci.*, 2013, **6**, 994–1007.
- 41 J. M. W. Chan, S. Bauer, H. Sorek, S. Sreekumar, K. Wang and F. D. Toste, *ACS Catal.*, 2013, **3**, 1369–1377.
- 42 X. Ma, Y. Tian, W. Hao, R. Ma and Y. Li, *Appl. Catal., A*, 2014, **481**, 64–70.
- 43 T. Yoshikawa, T. Yagi, S. Shinohara, T. Fukunaga, Y. Nakasaka, T. Tago and T. Masuda, *Fuel Process. Technol.*, 2013, **108**, 69–75.
- 44 T. Yoshikawa, S. Shinohara, T. Yagi, N. Ryumon, Y. Nakasaka, T. Tago and T. Masuda, *Appl. Catal., B*, 2014, **146**, 289–297.
- 45 R. Ma, W. Hao, X. Ma, Y. Tian and Y. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 7310.
- 46 S. Dutta, *ChemSusChem*, 2012, **5**, 2125–2127.
- 47 J. Yi, S. Liu and M. M. Abu-Omar, *ChemSusChem*, 2012, **5**, 1401–1404.
- 48 M. Shiramizu and F. D. Toste, *Angew. Chem.*, 2012, **124**, 8206–8210 (*Angew. Chem., Int. Ed.*, 2012, **51**, 8082–8086).
- 49 M. Saidi, F. Samimi, D. Karimipourfard, T. Niianwudipong, B. C. Gates and M. R. Rahimpour, *Energy Environ. Sci.*, 2014, **7**, 103–129.
- 50 S. Crossley, J. Faria, M. Shen and D. E. Resasco, *Science*, 2009, **327**, 68–72.
- 51 J. Wildschut, M. Iqbal, F. H. Mahfud, I. Melian-Cabrera, R. H. Venderbosch and H. J. Heeres, *Energy Environ. Sci.*, 2010, **3**, 962–970.
- 52 J. Wildschut, I. Melian-Cabrera and H. J. Heeres, *Appl. Catal., B*, 2010, **99**, 298–306.
- 53 F. D. Mercader, M. J. Groeneveld, S. R. A. Kersten, C. Geantet, G. Toussaint, N. W. J. Way, C. J. Schaverien and K. J. A. Hogendoorn, *Energy Environ. Sci.*, 2011, **4**, 985–997.
- 54 A. G. Sergeev and J. F. Hartwig, *Science*, 2011, **332**, 439–443.
- 55 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, *Chem. Sci.*, 2013, **4**, 806–813.
- 56 N. Yan and P. J. Dyson, *Curr. Opin. Chem. Eng.*, 2013, **2**, 178–183.
- 57 J. Zhang, J. Teo, X. Chen, H. Asakura, T. Tanaka, K. Teramura and N. Yan, *ACS Catal.*, 2014, **4**, 1574–1583.
- 58 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.
- 59 D. D. Laskar, M. P. Tucker, X. Chen, G. L. Helms and B. Yang, *Green Chem.*, 2014, **16**, 897–910.
- 60 J. Zakzeski and B. M. Weckhuysen, *ChemSusChem*, 2011, **4**, 369–378.
- 61 W. Y. Xu, S. J. Miller, P. K. Agrawal and C. W. Jones, *ChemSusChem*, 2012, **5**, 667–675.
- 62 K. Barta, T. D. Matson, M. L. Fetting, S. L. Scott, A. V. Iretskii and P. C. Ford, *Green Chem.*, 2010, **12**, 1640–1647.
- 63 T. D. Matson, K. Barta, A. V. Iretskii and P. C. Ford, *J. Am. Chem. Soc.*, 2011, **133**, 14090–14097.
- 64 A. L. Jongerius, P. C. A. Bruijninx and B. M. Weckhuysen, *Green Chem.*, 2013, **15**, 3049–3056.
- 65 D. W. S. Wong, *Appl. Biochem. Biotechnol.*, 2010, **157**, 174–209.
- 66 T. D. H. Bugg, M. Ahmad, E. M. Hardiman and R. Rahmanpour, *Nat. Prod. Rep.*, 2011, **28**, 1883–1896.
- 67 M. Ahmad, J. N. Roberts, E. M. Hardiman, R. Singh, L. D. Eltis and T. D. H. Bugg, *Biochemistry*, 2011, **50**, 5096–5107.
- 68 M. E. Brown, M. C. Walker, T. G. Nakashige, A. T. Iavarone and M. C. Y. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 18006–18009.
- 69 M. E. Brown, T. Barros and M. C. Y. Chang, *ACS Chem. Biol.*, 2012, **7**, 2074–2081.
- 70 S. Atsumi, T. Hanai and J. C. Liao, *Nature*, 2008, **451**, 86–90.
- 71 X. Peng, E. Masai, H. Kitayama, K. Harada, Y. Katayama and M. Fukuda, *Appl. Environ. Microbiol.*, 2002, **68**, 4407–4415.
- 72 P. D. Sainsbury, E. M. Hardiman, M. Ahmad, H. Otani, N. Seghezzi, L. D. Eltis and T. D. H. Bugg, *ACS Chem. Biol.*, 2013, **8**, 2151–2156.
- 73 J. W. Lee, D. Na, J. M. Park, J. M. Lee, S. Choi and S. Y. Lee, *Nat. Chem. Biol.*, 2012, **8**, 536–546.
- 74 J. F. Kadla, S. Kubo, R. A. Venditti, R. D. Gilbert, A. L. Compere and W. Griffith, *Carbon*, 2002, **40**, 2913–2920.
- 75 J. L. Braun, K. M. Holtman and J. F. Kadla, *Carbon*, 2005, **43**, 385–394.

- 76 J. Hayashi, A. Kazehaya, K. Muroyama and A. P. Watkinson, *Carbon*, 2000, **38**, 1873–1878.
- 77 V. Fierro, V. Torne-Fernandez and A. Celzard, *Microporous Mesoporous Mater.*, 2007, **101**, 419–431.
- 78 K. Babel and K. Jurewicz, *Carbon*, 2008, **46**, 1948–1956.
- 79 W. E. Tenhaeff, O. Rios, K. More and M. A. McGuire, *Adv. Funct. Mater.*, 2013, **24**, 86–94.
- 80 S. Kubo, Y. Uraki and Y. Sano, *Carbon*, 1998, **36**, 1119–1124.
- 81 M. Lallave, J. Bedia, R. Ruiz-Rosas, J. Rodríguez-Mirasol, T. Cordero, J. C. Otero, M. Marquez, A. Barrero and I. G. Loscertales, *Adv. Mater.*, 2007, **19**, 4292–4296.
- 82 J. Spender, A. L. Demers, X. Xie, A. E. Cline, M. A. Earle, L. D. Ellis and D. J. Neivandt, *Nano Lett.*, 2012, **12**, 3857–3860.
- 83 W. E. Tenhaeff, O. Rios, K. More and M. A. McGuire, *Adv. Funct. Mater.*, 2014, **24**, 86–94.
- 84 M. Park, X. C. Zhang, M. D. Chung, G. B. Less and A. M. Sastry, *J. Power Sources*, 2010, **195**, 7904–7929.
- 85 S. Chatterjee, A. Clingenpeel, A. McKenna, O. Rios and A. Johs, *RSC Adv.*, 2014, **4**, 4743–4753.
- 86 S. Hu and Y.-L. Hsieh, *J. Mater. Chem. A*, 2013, **1**, 11279–11288.
- 87 O. Rios, W. E. Tenhaeff, C. Daniel, N. J. Dudney, A. Johns, G. Alexander and F. S. Baker, *US Pat.*, 2014/0038034 A1, 2014.
- 88 M. Thunga, K. Chen, D. Gewell and M. R. Kessler, *Carbon*, 2014, **68**, 159–166.
- 89 X. Xu, J. Zhou, L. Jiang, G. Lubineau, Y. Chen, X.-F. Wu and R. Piere, *Mater. Lett.*, 2013, **109**, 175–178.
- 90 R. Ruiz-Rosas, M. J. Valero-Romero, D. Salinas-Torres, J. Rodríguez-Mirasol, T. Cordero, E. Morallon and D. Cazorla-Amoros, *ChemSusChem*, 2014, **7**, 1458.
- 91 Z. Schniepp, *Angew. Chem., Int. Ed.*, 2012, **52**, 1096–1108.
- 92 J. Hu, V. Arantes, A. Pribowo, K. Gourlay and J. N. Saddler, *Energy Environ. Sci.*, 2014, **7**, 2308.
- 93 M. E. Brown, M. C. Walker, T. G. Nakashige, A. T. Lavarone and M. C. Y. Chang, *J. Am. Chem. Soc.*, 2011, **133**, 18006–18009.