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Revisiting alkaline aerobic lignin oxidation†

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Lignin conversion to renewable chemicals is a promising means to improve the economic viability of lignocellulosic biorefineries. Alkaline aerobic oxidation of lignin has long been employed for production of aromatic compounds such as vanillin and syringaldehyde, but this approach primarily focuses on condensed substrates such as Kraft lignin and lignosulfonates. Conversely, emerging lignocellulosic biorefinery schemes enable the production of more native-like, reactive lignin. Here, we revisit alkaline aerobic oxidation of highly reactive lignin substrates to understand the impact of reaction conditions and catalyst choice on product yield and distribution. The oxidation of native poplar lignin was studied as a function of temperature, NaOH loading, reaction time, and oxygen partial pressure. Besides vanillin and syringaldehyde, other oxidation products include acetosyringone and vanillic, syringic, and p-hydroxybenzoic acids. Reactions with vanillin and syringaldehyde indicated that these compounds are further oxidized to non-aromatic carboxylic acids during alkaline aerobic oxidation, with syringaldehyde being substantially more reactive than vanillin. The production of phenolic compounds from lignin is favored by high NaOH loadings and temperatures, but short reaction times, as the products degrade rapidly, which is further exacerbated by the presence of oxygen. Under optimal conditions, a phenolic monomer yield of 30 wt% was obtained from poplar lignin. Testing a range of catalysts showed that Cu-containing catalysts, such as $CuSO_4$ and $LaMn_{0.8}Cu_{0.2}O_3$, accelerate product formation; specifically, the catalyst does not increase the maximum yield, but expands the operating window in which high product yields are obtainable. We also demonstrate that other native and isolated lignin substrates that are significantly chemically modified are effectively converted to phenolic compounds. Finally, alkaline aerobic oxidation of native lignins was compared to nitrobenzene oxidation and reductive catalytic fractionation, as these methods constitute suitable benchmarks for lignin depolymerization. While nitrobenzene oxidation achieved a somewhat higher yield, similar monomer yields were obtained through RCF and alkaline aerobic oxidation, especially for lignins with a high guaiacyl- and/or p-hydroxyphenyl-content, as syringyl units are more unstable during oxidation. Overall, this study highlights the potential for aerobic lignin oxidation revisited on native-like lignin substrates.

Introduction

Lignin, a heterogeneous aromatic biopolymer, is one of the main constituents of lignocellulosic biomass, comprising 15 to 30% of its weight.[1–4] It is an integral part of terrestrial-plant

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cell walls, where it is responsible for mechanical strength, defence against microbial and insect attack, and preventing the collapse of water-conducting elements.[1–5] Lignin is mainly assembled from three phenyl-propanoid units (p-coumaryl, coniferyl, and sinapyl alcohols), which are linked through C–O and C–C bonds, with β-ether bonds being the most prominent.[1–5] Other important lignin building blocks are p-hydroxycinnamic acids (p-coumaric and ferulic acid), found in herbaceous crops,[6,7] and p-hydroxybenzoic acid, found in feedstocks like poplar and palm.[8,9] These acids are mainly connected to lignin through ester linkages and can account for a significant fraction of the lignin mass.

Due to its aromatic structure, lignin is regarded as a promising source for renewable chemicals.[1–4,10–15] A problem, however, is that traditional lignocellulosic biorefinery pro-

cesses primarily focus on the valorization of the carbohydrates, while the lignin is only utilized for low-value applications (heat and power) without considering the fate of the lignin stream. For instance, pulping processes such as Kraft, sulphite, and organosolv, aim to remove lignin from wood to produce a pure carbohydrate pulp.[16,17] In the production of cellulosic biofuels such as bioethanol, a pretreatment step is applied to disrupt the lignocellulosic cell-wall structure and remove or relocate the lignin, with the primary aim of making the carbohydrates more amenable for biological conversion.[18,19] In these processes, the lignin either ends up in a pretreatment liquor (from which it can be precipitated), or in a residue after enzymatic hydrolysis of the carbohydrates.[10] In most biorefinery processes, the lignin is heavily degraded, which involves cleavage of labile ether bonds (mainly β-O-4 bonds) and condensation of reactive intermediates through C–C bond formation.[3,4,11,20–22] The resulting degraded lignin streams are resistant to depolymerisation and are, therefore, usually incinerated for energy recovery.[10,23] However, to improve the economics and sustainability of lignocellulosic biorefineries, a higher value utilization of the lignin fraction is critical.[10,24]

In this context, strategies to convert lignin into chemicals are receiving increasing attention. Research efforts are directed both toward the development of biorefinery processes in which lignin degradation is avoided,[3,4,14,25] and the development of effective and selective methods to depolymerize the biorefinery lignin streams.[1–4,11–13] Degradation of the lignin structure (C–C bond formation) can, for instance, be prevented through chemical stabilization of the lignin structure during pulping, as in formaldehyde-assisted pulping[26] or reductive catalytic fractionation (RCF).[27–32] In the latter case, pulping is combined with lignin depolymerization and reductive stabilisation of the lignin products. Another option to prevent degradation is to utilize mild conditions, as in the isolation of native-like lignin substrates such as milled wood lignin (MWL), cellulolytic enzyme lignin (CEL), or enzymatic mild acidolysis lignin (EMAL).[33,34] Pretreatment of biomass is often performed through thermochemical methods such as dilute-acid pretreatment (DAP) or hydrothermal pretreatment, which are known to induce significant lignin degradation.[13,19,21] Pretreatment methods that do not use acids or high temperatures, such as deacetylation and mechanical refining (DMR)[35] or anhydrous ammonia pretreatment (AAP),[36,37] likely cause less degradation, and are, thus, expected to generate more reactive lignin streams.

Depolymerization of the resulting lignin streams has been explored *via* reductive, oxidative, acid-catalyzed, base-catalyzed, and thermal methods, and many promising results have been reported.[1–4,11–13] For instance, high yields of phenolic monomers can be obtained through reductive depolymerization, especially from native lignins (as in RCF)[27–32] and other reactive lignins,[26,38] but also from recalcitrant substrates such as Kraft and soda lignin.[39,40] An effective depolymerization method that was recently introduced is acid-catalyzed depolymerization combined with *in situ* stabilization of the products through acetal formation.[41,42] Herein, ethylene glycol forms acetal structures

with the reactive carbonyl functionalities in the side-chains of the phenolic products. Through oxidation, lignin can be selectively converted to valuable chemicals such as aromatic aldehydes, aromatic acids, and aliphatic carboxylic acids.[43–48] Lignin oxidation is mostly performed in alkaline reaction media with oxygen as oxidant (*i.e.*, aerobically),[43,49–61] but has also been successfully performed in acidic solutions, such as diluted inorganic acids[62,63] or concentrated acetic acid,[64] organic solvents,[65] and ionic liquids.[66,67] As alkaline aerobic oxidation enables the selective production of the aromatic aldehydes vanillin and syringaldehyde from lignin, it is performed commercially to produce vanillin from lignosulfonates.[43,44] The production volume has, however, dropped considerably since 1980.

Alkaline lignin oxidation has been extensively studied in the last decade, mainly on condensed lignin substrates such as lignosulfonates[51,59,68–70] and Kraft lignins.[49–53,71] For instance, the influence of process parameters including temperature, oxygen pressure, and NaOH concentration on oxidation of Kraft lignin and lignosulfonates was studied by Rodrigues,[49,50,52] Tarabanko,[54,56,70] and Evtuguin and co-workers.[59] New biorefinery processes, however, enable the generation of more reactive lignins, and, therefore, we decided to examine the alkaline aerobic oxidation of a highly reactive, non-degraded, unmodified substrate, namely native poplar lignin. Oxidation of the entire poplar substrate is likely not relevant from a process perspective (although the carbohydrates are also converted to valuable compounds, *vide infra*), but is performed here to assess the oxidation behaviour of unmodified lignin. We thoroughly investigated the influence of the process parameters and evaluated a series of catalysts on the reaction, in order to gain more insight into the alkaline oxidation process and to clarify some apparent contradictions between previous reports, for instance on the role of the catalysts. Furthermore, we assessed the conversion of other biorefinery lignins and also compared the performance of alkaline aerobic oxidation to RCF for lignin valorisation in a biorefining context.

Results

Oxidation of poplar lignin: parameter investigation

To examine the oxidation of native-like lignin, we performed reactions with poplar sawdust, with a total lignin content (Klason lignin and acid-soluble lignin) of 29.4 wt%. Reactions were performed in 2 M NaOH aqueous solutions under an oxygen partial pressure of 5 bar and a total pressure of 20 bar (He as make-up gas; pressurized at room temperature) for temperatures ranging from 125 to 200 °C and reaction times of 0 to 60 min (the heating time of 30 min is not included in the reaction time). After reaction, the reaction mixture was acidified and extracted with ethyl acetate. The ethyl acetate-extracted phase (EA oil) was derivatized through silylation and subjected to gas chromatography (GC) analysis to quantify the phenolic monomers. The results are shown in Fig. 1. Oxidation of poplar lignin mainly yielded the aromatic alde-
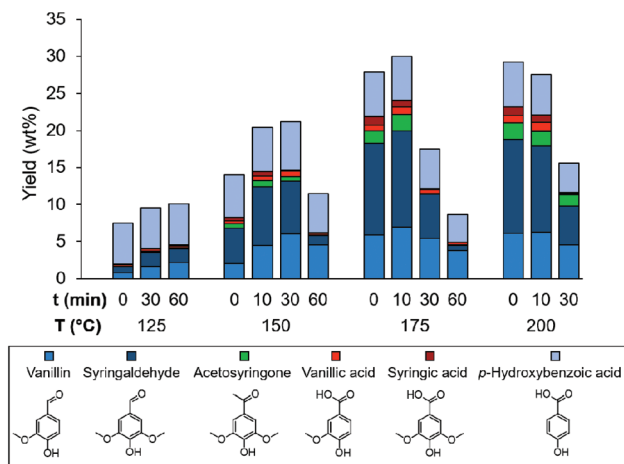
Fig. 1 Phenolic monomer yields (on a lignin basis) from alkaline aerobic oxidation of poplar at various temperatures and reaction times. Reaction conditions: 0.5 g poplar (150 mg lignin), 30 mL of 2 M NaOH aqueous solution, 5 bar O_2 + 15 bar He (at RT).

hydes vanillin and syringaldehyde, along with other compounds such as vanillic and syringic acid, and acetosyringone. These compounds were also obtained in the oxidation of isolated hardwood lignins.[53,58] In addition, *p*-hydroxybenzoic acid was obtained. This compound is not an oxidation product, but is part of the structure of poplar lignin (it is esterified to the γ-OH groups of syringyl structures).[8,9] During the reaction, it was released through hydrolysis of the ester bond. Under these oxidative conditions, the carbohydrates were also transformed. Only under mild oxidation conditions (*e.g.*, low temperature and short reaction time) was some carbohydrate-rich residue preserved, but increasing temperature and reaction time induced almost complete conversion of the substrate. Fig. 2
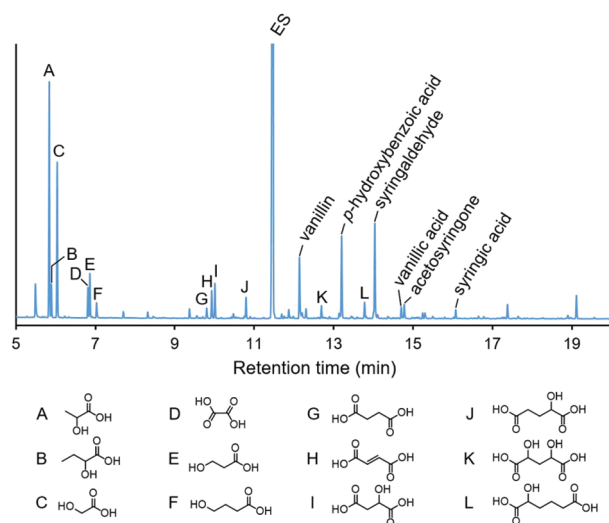

Fig. 2 Gas chromatogram of the silylated EA oil from poplar oxidation at 175 °C for 10 min (2 M NaOH, 5 bar O_2 + 15 bar He at RT). The external standard (ES) is 4-*n*-propylguaiacol.

shows a gas chromatogram of the EA oil after poplar conversion at 175 °C for 10 min. The main carboxylic acids were formic acid and acetic acid (not shown in the chromatogram), followed by lactic acid (A); glycolic acid (B); and smaller amounts of other compounds, such as oxalic acid (D), 3-hydroxy-propionic acid (E), fumaric acid (H), and malic acid (I). Most of these acids originated from the cellulose and hemicellulose in poplar, although some of these also derived from consecutive oxidation of the phenolic compounds (*vide infra*). Thus, the carbohydrate fractions were also converted to valuable compounds during alkaline aerobic oxidation.

Fig. 1 shows that, especially in oxidation at higher temperatures, the phenolic monomers were rapidly produced, but also quickly consumed through oxidative degradation, resulting in sharp maxima in monomer yield as function of reaction time. The maximum product yield increased with temperature, from 7 wt% at 125 °C up to about 30 wt% at 175 °C, but did not increase further by raising the temperature to 200 °C. The 30 wt% monomer yield obtained after 10 min reaction at 175 °C comprises 24 wt% oxidation products (including 13 wt% syringaldehyde and 7 wt% vanillin) and 6 wt% *p*-hydroxybenzoic acid. As was also observed in the oxidation of condensed lignin substrates such as Kraft lignin,[50,52,59,72] these results show that increasing the reaction temperature enhances the maximum product yield, but also shortens the reaction time needed to reach this maximum, because both the formation and degradation of phenolic monomers are accelerated. Thus, the reaction necessitates careful control of the reaction time. For a high product yield, a very short reaction at high temperature is ideal. However, this is difficult to accomplish with a batch Parr reactor setup, because it requires a long heating time (∼30 min), during which considerable lignin conversion takes place. Using a reactor with a much faster heating rate would likely further enhance the product yield at temperatures above 175 °C.

To examine the oxidative degradation of the phenolic monomers, we performed reactions with vanillin and syringaldehyde at 150 °C for 10 min (Table 1). Syringaldehyde was much more reactive than vanillin, with a conversion of 88%, compared to 31% for vanillin. The higher reactivity of syringyl (S)-type compounds compared to guaiacyl (G)-type compounds observed here is in accordance to previous studies[53,59,60,73] and is obvious from the time-course plots in Fig. 1, which shows a faster degradation of syringaldehyde and syringic acid compared to their guaiacyl analogues.

Both vanillin and syringaldehyde were mainly converted to small carboxylic acids, with formic acid as the main product from vanillin. Syringaldehyde yielded both formic and malonic acid as main products. Malic acid was obtained from syringaldehyde, while this was only scarcely obtained from vanillin. Other products from both aldehydes are acetic acid, glycolic acid, lactic acid, and oxalic acid, although the latter could not be quantified. Vanillin oxidation yielded a small amount of vanillic acid, while reaction with syringaldehyde generated only trace amounts of syringic acid. So although these acids are usually proposed to be derived from vanillin and syringal-

Table 1 Conversion and product yields from alkaline aerobic oxidation of vanillin and syringaldehyde[a]

Substrate	Vanillin	Syringaldehyde
Time (min)	10	10
Conversion (wt%)	31	88 (4)[b]
Yield (wt%)		
Vanillic/syringic acid	2	0
Formic acid	12	28
Acetic acid	3	5
Glycolic acid	1	3
Lactic acid	3	5
Malonic acid	5	31
Malic acid	0	5
Sum	23	76

[a] Reaction conditions: 100 mg substrate, 30 mL of aqueous 2 M NaOH solution, 150 °C, 5 bar O_2 + 15 bar He (at RT). Substrate conversion and vanillic and syringic acid yield were determined *via* GC-FID. The yield of the other acids was determined *via* HPLC. Oxalic acid was observed in both the GC and HPLC analyses, but could not be quantified. [b] Syringaldehyde conversion under inert atmosphere (20 bar He) is indicated in brackets.

dehyde,[68] the majority of vanillic and syringic acid obtained during lignin oxidation is likely produced *via* a different route, such as that proposed by Gierer *et al.*[74]

Subsequently, we assessed the influence of the oxygen pressure on poplar oxidation. Fig. 3a shows the product yields for poplar oxidation in 2 M NaOH at 175 °C, under oxygen partial pressures of 0, 5, and 10 bar (20 bar total pressure). Under inert atmosphere (0 bar oxygen), no oxidation products were obtained (only *p*-hydroxybenzoic acid, which was expected
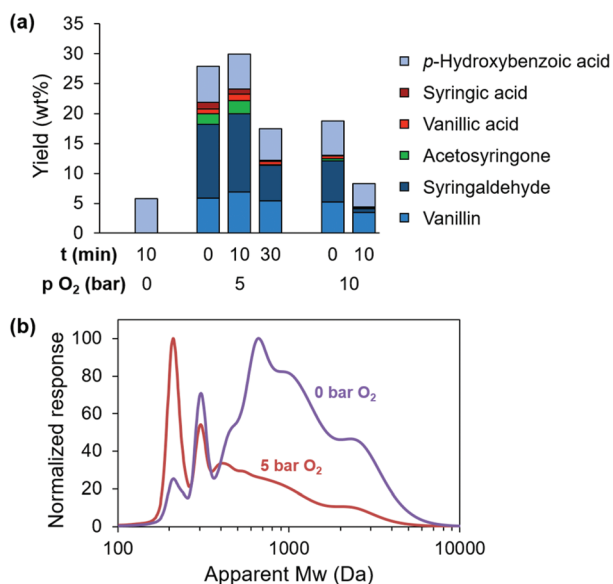

Fig. 3 Impact of oxygen partial pressure (at RT) on phenolic monomer yields (a) and molecular weight distribution of the EA oils (b) obtained from alkaline aerobic oxidation of poplar. The EA oils for GPC analysis were obtained after 10 min reaction and were acetylated prior to analysis. Reaction conditions: 0.5 g poplar, 30 mL of 2 M NaOH aqueous solution, 175 °C, 20 bar total pressure (at RT; He as make-up gas).

from base-catalyzed hydrolysis of ester linkages). Other studies have found that conversion of lignosulfonates in the absence of oxygen yields a considerable amount of depolymerization products (vanillin, syringaldehyde, vanillic acid, and syringic acid),[59,69] but the different functional structure of lignosulfonates compared to native lignin likely facilitates the different chemistry. In contrast, high monomer yields were obtained from reaction under 5 bar oxygen, but increasing the pressure up to 10 bar resulted in a drop in yields. Increasing the oxygen pressure is known to accelerate both product formation and degradation,[50,72] and, therefore, shortens the time needed to reach the maximum product yield. The fact that oxygen facilitates product degradation is also illustrated in Table 1 by the high conversion of syringaldehyde under oxygen (88 wt%), compared to only slight conversion under an inert atmosphere (4 wt%, in brackets). Due to the long heating time, the maximum yield under 10 bar oxygen was likely obtained during the heating period. This again indicates that while oxygen is needed to generate oxidation products from native lignin, rapid heating of the reaction mixture is also critical to avoid subsequent oxidation of the desired products.

In Fig. 3b, the GPC profiles of the EA oils for reaction under inert atmosphere and 5 bar oxygen are depicted. The M_n, M_w, and PD values are provided in Table S1.† The peak at 200 Da corresponds to the aromatic aldehydes and acetosyringone, the peak at 300 Da to the aromatic acids (vanillic, syringic, and *p*-hydroxybenzoic) and the broad signal at higher molecular weights (>350 Da) to the oligomeric products. Reaction under inert atmosphere mainly yielded oligomeric products, while reaction under oxygen primarily generated monomeric products, which underpins the need for oxygen to depolymerize lignin. To further assess the chemical transformations occurring under oxygen and inert atmosphere, poplar and the reaction products (EA oils) were analyzed through HSQC NMR (Fig. 4). Poplar wood showed large peaks of aryl ether (β-O-4), phenylcoumaran (β-5), and resinol units (β–β), while there were almost no aldehyde peaks (Fig. 4a). In the aromatic region, the poplar spectrum mainly displayed signals of guaiacyl (G), syringyl (S), and *p*-hydroxybenzoate (PB) units. The correlation peaks of *p*-hydroxyphenyl units (H2/6) at δ_C/δ_H 128.0/7.2 ppm were extremely small, with the H/G ratio being only 0.0004. This indicates that H-units (other than PB) are only present in minor amounts in poplar. Based on the peak integral, an S/G molar ratio of 1.18 was estimated, which was calculated using both normal and oxidized S components. Besides the S-, G- and H-signals, a clear signal of PB2/6 is present at 131/ 7.71 ppm. The EA oil generated under inert atmosphere contained less resinol and phenylcoumaran units than poplar, and had no aryl ether and cinnamyl alcohol units (Fig. 4b), suggesting, as expected, that β-O-4 linkages were also cleaved under non-oxidative conditions, likely through base-catalyzed transformations. Phenylcoumaran and resinol structures appeared to partially withstand these conditions. In the aromatic region, the PB signal decreased because the ester bonds in PB units were readily saponified to generate *p*-hydroxybenzoic acid, which is evidenced by the phenolic monomer yield
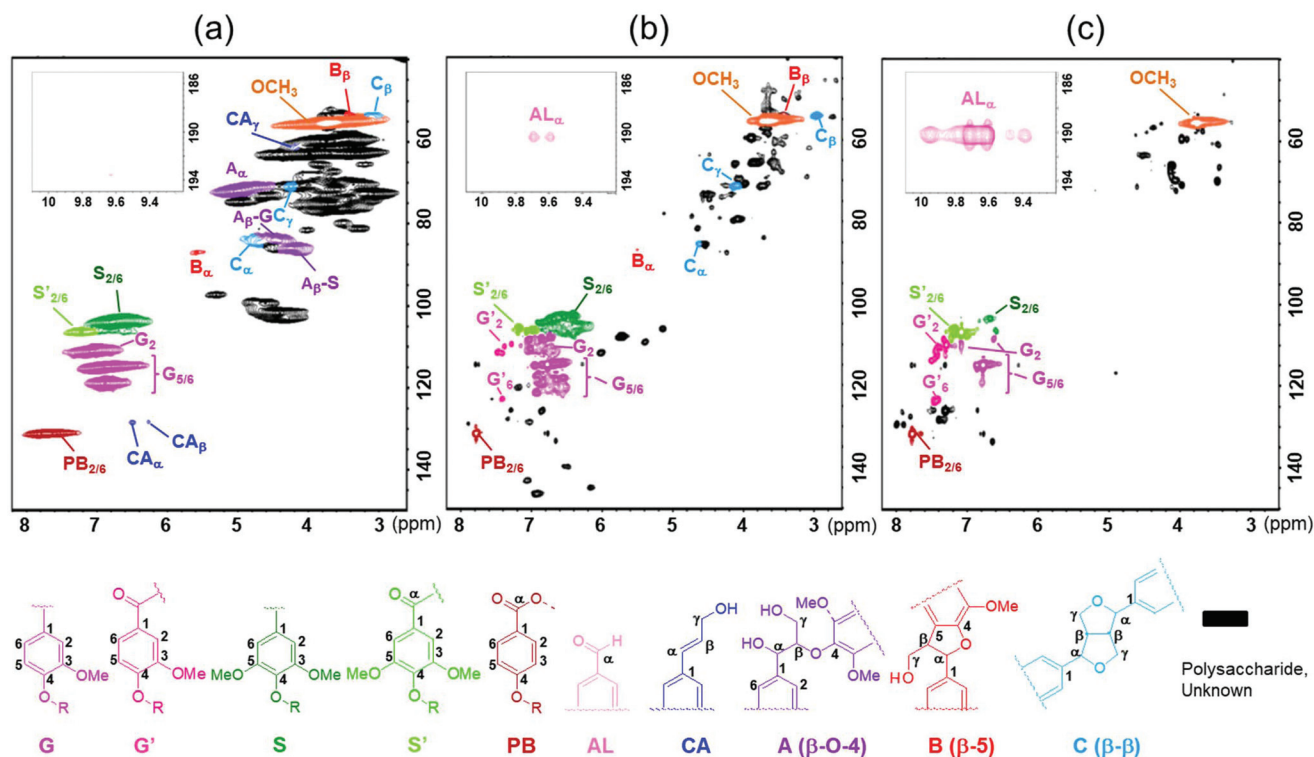
Fig. 4 HSQC NMR spectra of (a) poplar wood, (b) EA oils for poplar conversion under inert atmosphere and (c) 5 bar oxygen. Reaction conditions for (b) and (c): 0.5 g poplar, 30 mL of 2 M NaOH aqueous solution, 175 °C, 10 min, 20 bar He at RT (b) and 5 bar O_2 + 15 bar He at RT (c). G: Guaiacyl, G′: Guaiacyl with $C\alpha$=O, S: Syringyl, S′: Syringyl with $C\alpha$=O, PB: p-Hydroxybenzoate, AL: Benzaldehydes, CA: Cinnamyl alcohol, A: β-Aryl ether (β-O-4), B: Phenylcoumaran (β-5), C: Resinol (β-β).

distribution (Fig. 3a). Also, oxidized guaiacyl unit (G′2) signals at around 110–114/7.4–7.7 ppm and G′6 at 124.5/7.57 ppm clearly appeared, suggesting that α-ketone structures were generated from β-O-4 units under alkaline conditions. The S/G ratio in the EA oil generated under inert atmosphere was 1.73, higher than that in poplar, likely due to base-catalyzed repolymerization of G-units.[3] The spectrum of the EA oil obtained under oxygen exhibited far fewer signals than the spectra of the poplar and the EA oil obtained in absence of oxygen (Fig. 4c). Specifically, there were no β-O-4, phenylcoumaran, resinol, and much fewer carbohydrate peaks. In the aromatic region, the S2/6 and G2/5/6 peaks drastically reduced and the S′2/6 and G′2 signals increased, supporting that 30% of the poplar lignin was degraded into α-ketone monomers by 5 bar O_2 treatment (Fig. 3a). The interunit linkages were thus effectively disrupted under the oxidative conditions. The decrease of aromatic peaks also suggests that some aromatic ring cleavage occurred.[74] The S/G ratio in the EA oil generated under oxygen decreased to 1.14, likely due to a faster oxidative degradation of S-type units compared to G-type units. In addition, the aldehyde peak was much more prominent in the EA oil generated under oxygen than in the oil obtained without oxygen, due to generation of vanillin and syringaldehyde.

Finally, we assessed the impact of the NaOH concentration on poplar oxidation. Fig. 5 shows the monomer yields for oxi-
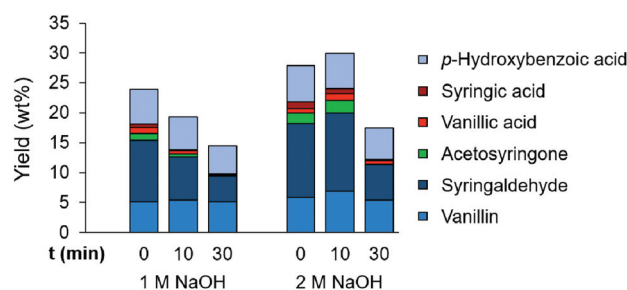

Fig. 5 Impact of NaOH concentration on the phenolic monomer yields from alkaline aerobic oxidation of poplar. Reaction conditions: 0.5 g poplar, 30 mL of 1 or 2 M NaOH aqueous solution, 175 °C, 5 bar O_2 + 15 bar He (at RT).

dation at 175 °C under 5 bar oxygen partial pressure in 1 and 2 M NaOH solutions. In line with previous studies on Kraft lignin and lignosulfonates,[43,50,54,71] the highest monomer yields were obtained in 2 M NaOH. A high NaOH concentration is suspected to be necessary to facilitate lignin oxidation, *viz.* for ionization of the phenolic hydroxyl groups[43,44] and likely also for the conversion of reactive intermediates (see Discussion),[43,54–57] and to retard degradation of the phenolic compounds.[43,72] For instance, Rodrigues *et al.* showed that raising the pH of the reaction solution over 12 significantly slows down the oxidative degradation of vanillin.[72] On the

other hand, utilizing an NaOH concentration that is too high (*e.g.*, 4 M) causes operational problems such as salt deposition and fouling in the reactor, and, therefore, a 2 M concentration is usually advised.[43]

Catalytic oxidation of poplar: catalyst screening and examination of the catalyst effect

Alkaline oxidation of lignin is often performed in the presence of a catalyst. The catalyst is suggested to facilitate lignin oxidation through electron abstraction (oxidation) of the phenolate groups to phenoxy radicals, after which the catalyst is reoxidized by oxygen (thus completing the redox cycles).[43,59,75] The catalyst is usually $CuSO_4$ or another metal salt, but also solid catalysts such as metal oxides and noble metal catalysts have been studied. Numerous studies have shown that the catalyst accelerates product formation and also raises the maximum product yield,[58–60,76–80] although a few studies did not observe an increase in maximum product yield.[50,71] To verify the catalyst effect in alkaline lignin oxidation, we first compared the catalytic activity of a range of reported catalysts in the alkaline oxidation of poplar. The oxidation was performed in 2 M NaOH at 150 °C under 5 bar oxygen for 0 min. Fig. 6a shows the catalytic results for reactions with metal salts. The uncatalyzed reaction reached a total monomer yield of 14 wt%, including 8 wt% oxidation products (without *p*-hydroxybenzoic acid). The latter yield is used as benchmark and is indicated with a dashed line. $CuSO_4$ reached the highest yield of oxidation products (17 wt%), followed by $CoCl_2$ and $MnCl_2$ (11–12 wt%). Reactions with $FeCl_3$ and $Cr_2(SO_4)_3$ achieved approximately the same yields as the uncatalyzed run. The superior catalytic performance of $CuSO_4$ is likely due to the intermediate reduction potential of Cu^{2+} (-0.16 V for the CuO/Cu_2O redox pair at pH 14), as was postulated by Tarabanko *et al.* to be sufficient for oxidation of lignin to aldehydes with limited subsequent oxidation of aldehydes.[57] The promising performance of Cu relative to other metals explains why it is a commonly used catalyst in alkaline lignin oxidation.[50,58,59,68,70] Regarding the Co, Mn, and Fe salts, Lin *et al.* also found that Co and Mn salts improve lignin oxidation,[78,79] while $FeCl_3$ had no effect on the reaction.[80] This can be explained by the fact that Fe^{3+} cannot abstract an electron from the phenolate groups and, thus, cannot follow the oxidation–reduction cycles.[75] However, some studies reported that $FeCl_3$ facilitates lignin oxidation, which was attributed to the formation of O_2–Fe–lignin complexes that act as oxygen carriers that can attack the lignin.[58,60,75] These studies also showed that $CuSO_4$ and $FeCl_3$ exert a synergistic effect on the oxidation. However, in this work, no further increase in product yield was observed with the addition of $FeCl_3$ to $CuSO_4$ (Fig. 6a).

In Fig. 6b, the catalytic results for a range of oxide-based catalysts are depicted. A series of oxides, perovskites, and noble metal catalysts were tested. Co_3O_4 is a commonly used oxidation catalyst,[81,82] and CuO has been used frequently in lignin oxidation, either in the absence (itself being the oxidant)[83,84] or presence of oxygen.[60,75] The use of perovskites is based on the work of Lin and co-workers, who found that
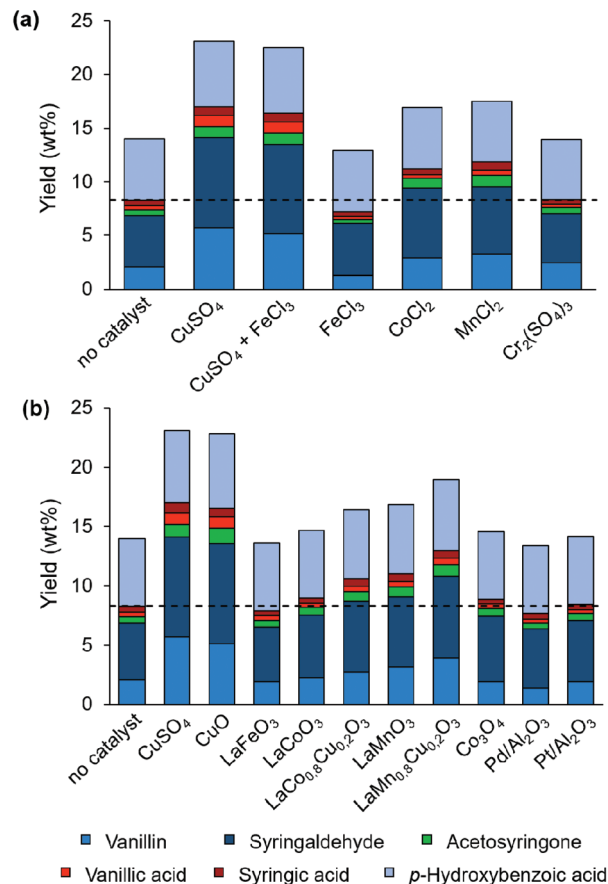

Fig. 6 Phenolic monomer yields from oxidation of poplar with various metal salts (a) and oxide-based catalysts (b). Reaction conditions: 0.5 g poplar, 30 mL of 2 M NaOH aqueous solution, 40 µmol metal salt or 10 mg solid catalyst, 150 °C, 0 min (the reactor was quenched when reaching the reaction temperature, 30 min heating time), 5 bar O_2 + 15 bar He (at RT). The dashed line indicates the yield of oxidation products obtained in the uncatalyzed reaction (8 wt%).

Co-, Mn-, and Fe-based perovskites significantly enhanced the product yields in alkaline lignin oxidation, and that their performance can be further improved by Cu doping.[77–80] Sales *et al.* showed that Pd/Al_2O_3-catalyzed lignin oxidation enabled much higher product yields than uncatalyzed oxidation,[76] while Villar *et al.* observed that the use of Pt/Al_2O_3 had an adverse effect on the product yield.[71] In poplar oxidation, the highest yield was achieved with CuO (17 wt%), similar to the yield obtained with $CuSO_4$. Following oxidation with Co_3O_4, Pd/Al_2O_3, and Pt/Al_2O_3, no increase in product yield was observed compared to the uncatalyzed reaction. To test the catalytic activity of perovskites, we prepared Fe-, Co-, and Mn-based perovskites through sol–gel synthesis and confirmed their perovskite crystal structure *via* XRD (Fig. S1†). The highest yield was obtained when poplar was oxidized with $LaMnO_3$, while the use of $LaFeO_3$ or $LaCoO_3$ resulted in no or a very minor yield increase compared to the uncatalyzed reaction. In line with the results of Lin *et al.*, the catalyst performance could be enhanced by doping the perovskites with Cu

(see results for $LaCo_{0.8}Cu_{0.2}O_3$ and $LaMn_{0.8}Cu_{0.2}O_3$). The highest yield of oxidation products was achieved with $LaMn_{0.8}Cu_{0.2}O_3$ (13 wt%).

To elucidate the catalytic behaviour of the perovskite catalysts, some physicochemical properties were determined. Fig. 7a shows the specific surface area, determined by N_2 physisorption, and Fig. 7b the temperature programmed reduction (TPR) profiles, which provide valuable information about the reducibility of oxidation catalysts.[85,86] A high specific surface area is advantageous because more active surface sites are available, while a high catalyst reducibility facilitates the oxidation (electron abstraction) of the lignin. Regarding the Cu-free perovskites, $LaMnO_3$ exhibited a considerably higher specific surface area than $LaFeO_3$ and $LaCoO_3$ (22 vs. 6–9 m^2 g^{-1}), which can explain its higher catalytic activity. The TPR profiles indicated a negligible hydrogen uptake for $LaFeO_3$, in line with the very low reducibility of Fe^{3+}.[80,87] $LaMnO_3$ showed a higher hydrogen consumption, which can be attributed to reduction of Mn^{4+} to Mn^{3+} at lower temperature and Mn^{3+} to Mn^{2+} at higher temperature.[79,88,89] The highest hydrogen consumption was observed for $LaCoO_3$, due to reduction of Co^{3+} to Co^{2+} at lower temperature (300–450 °C) and Co^{2+} to Co^0 at higher temperature (500–650 °C).[88,90] Although $LaMnO_3$ showed a much lower hydrogen consumption than $LaCoO_3$, its reduction started at lower temperature (the maximum of the first TPR signal of $LaMnO_3$ and $LaCoO_3$ was at about 320 °C and 380 °C, respectively), which might also have contributed to its higher activity in lignin oxidation. Incorporation of Cu in $LaMnO_3$ and $LaCoO_3$ did not affect the specific surface area of the catalysts (Fig. 7a), but clearly lowered the temperature at which reduction takes place (Fig. 7b). The first TPR signal (at about 200–350 °C) is due to both Cu^{2+} and Mn^{4+}/Co^{3+} reduction.[88] The higher activity of the Cu-doped catalysts is,

thus, attributed to their easier reducibility, which can also explain the high activity of CuO.[89]

Due to their high catalytic activity, $CuSO_4$ and $LaMn_{0.8}Cu_{0.2}O_3$ were further used to examine the influence of the catalyst in alkaline aerobic oxidation. First, the conversion of poplar was studied with $CuSO_4$ at 150 °C and 175 °C at times ranging from 0 to 60 min. The monomer yields for catalyzed and uncatalyzed oxidation are depicted in Fig. 8. At both temperatures, $CuSO_4$ accelerated product formation and retarded product degradation, compared to uncatalyzed oxidation, but did not increase the maximum monomer yield. As shown in Fig. 8c and d, $LaMn_{0.8}Cu_{0.2}O_3$ exerted the same effect on the product yields. So, although addition of a catalyst does not enhance the product yield, it accelerates the reaction and widens the time window in which a high product yield is obtained, which makes the process less time sensitive. $LaMn_{0.8}Cu_{0.2}O_3$ was further employed in oxidation of other substrates, as discussed in the next section.

$LaMn_{0.8}Cu_{0.2}O_3$-catalyzed oxidation of other substrates

In addition to poplar, we subjected other lignocellulosic feedstocks, viz. high-S poplar, pine, and corn stover to alkaline aerobic oxidation with $LaMn_{0.8}Cu_{0.2}O_3$. Fig. 9 shows the monomer yields for oxidation at 175 °C for 0 min under 5 bar oxygen partial pressure. From wild-type (WT) poplar, a 31 wt% monomer yield was obtained, comprising 25 wt% oxidation products. Oxidation of transgenic poplar with a high S-lignin content (high-S poplar; line F5H-64-E)[91,92] resulted in a higher selectivity towards S-type compounds (syringaldehyde, acetosyringone, and syringic acid) than WT poplar, but the yield of oxidation products was only a little higher (29 vs. 25 wt%) and the total monomer yield was the same (31 wt%). This is quite unexpected because a higher S content in lignin results in a higher β-ether content,[93,94] and, therefore, should enable a higher monomer yield. However, the maximum attainable monomer yield was likely limited due to the fast oxidative degradation of S-type compounds. High-S poplar oxidation also generated p-hydroxybenzoic acid, but with a considerably lower yield than WT poplar (2 vs. 6 wt%).

The oxidation of pine yielded only G-type compounds (vanillin, acetovanillone, and vanillic acid), in line with the lignin composition of softwoods, with high selectivity towards vanillin. While the maximum product yield was obtained at a reaction time of 0 min for all other substrates (Table S2† for the monomer yields after 0 and 10 min), the maximum yield from pine (22 wt%) was reached after 10 min, which indicates that oxidation of G-rich lignin occurs more slowly than oxidation of S-rich lignin. In oxidation of corn stover, p-coumaric acid, ferulic acid, and p-hydroxybenzaldehyde were obtained, along with the previously described products. Similar to p-hydroxybenzoic acid in poplar, the hydroxycinnamic acids p-coumaric and ferulic acid were not produced through lignin oxidation, but through alkaline hydrolysis of ester bonds. These compounds were obtained in 9 and 2 wt% yield, respectively, with the total monomer yield being 27 wt%.
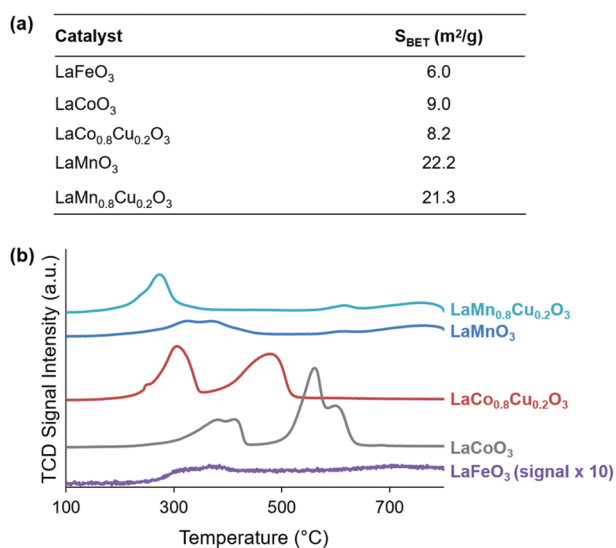

(a) Catalyst	S_{BET} (m²/g)
$LaFeO_3$	6.0
$LaCoO_3$	9.0
$LaCo_{0.8}Cu_{0.2}O_3$	8.2
$LaMnO_3$	22.2
$LaMn_{0.8}Cu_{0.2}O_3$	21.3

Fig. 7 Brunauer−Emmett−Teller specific surface areas (S_{BET}) obtained from N_2 adsorption isotherms (a) and H_2-TPR profiles (b) of the perovskite catalysts.
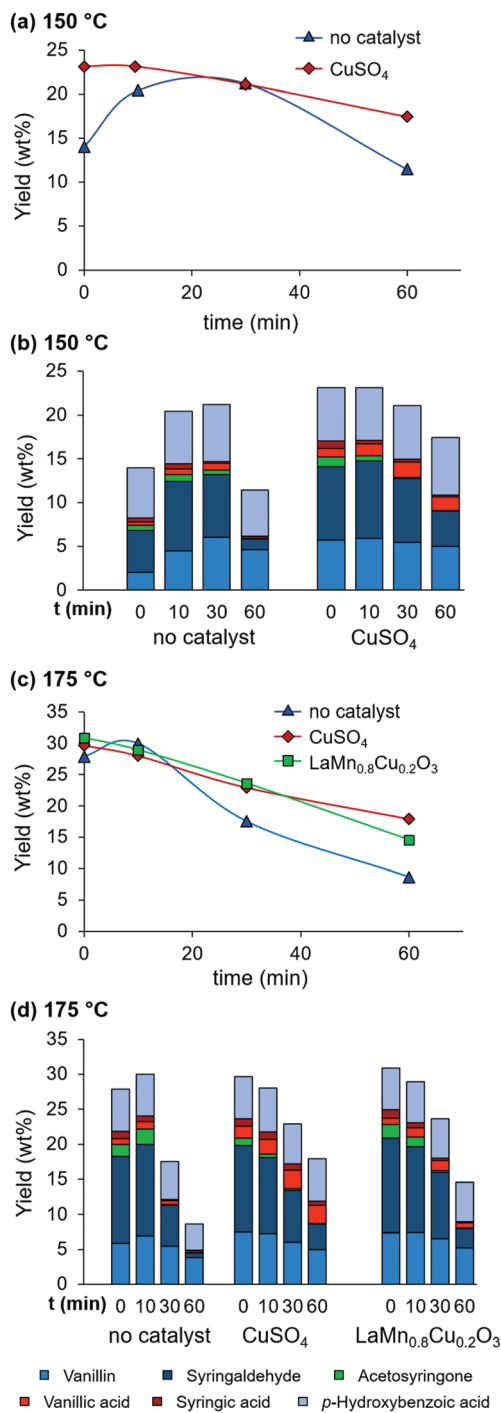
Fig. 8 Phenolic monomer yields from uncatalyzed and catalyzed oxidation of poplar wood at 150 °C (a and b) and 175 °C (c and d). Panels a and c depict the total monomer yield, while the yields of the individual compounds are indicated in panels b and d. Reaction conditions: 0.5 g poplar, 30 mL of 2 M NaOH aqueous solution, 40 μmol CuSO$_4$ or 10 mg LaMn$_{0.8}$Cu$_{0.2}$O$_3$, 5 bar O$_2$ + 15 bar He (at RT).

Fig. 9 Monomer yields (on lignin basis) from LaMn$_{0.8}$Cu$_{0.2}$O$_3$-catalyzed oxidation of various lignocellulosic feedstocks and isolated lignins. Reaction conditions: 0.5 g lignocellulose (95–150 mg lignin), 150–300 mg isolated lignin (140–160 mg lignin) or 15 g corn stover AAP-AE liquor (150 mg lignin), 30 mL of 2 M NaOH aqueous solution (for reaction with the corn stover AAP-AE lignin, 15 mL of the liquor (0.1 M NaOH) was combined with 15 mL of a 3.9 M NaOH aqueous solution to obtain 30 mL of a 2 M NaOH solution), 10 mg LaMn$_{0.8}$Cu$_{0.2}$O$_3$, 175 °C, 0 min (10 min for pine), 5 bar O$_2$ + 15 bar He (at RT).

Fig. 10 GPC profiles of the lignocellulose oxidation products. The reaction conditions are indicated in the caption of Fig. 9.

The molecular weight distribution of the oxidation products from the lignocellulosic feedstocks is depicted in Fig. 10 (see Table S1† for M_n, M_w and PD values). For the woody substrates, the peaks at about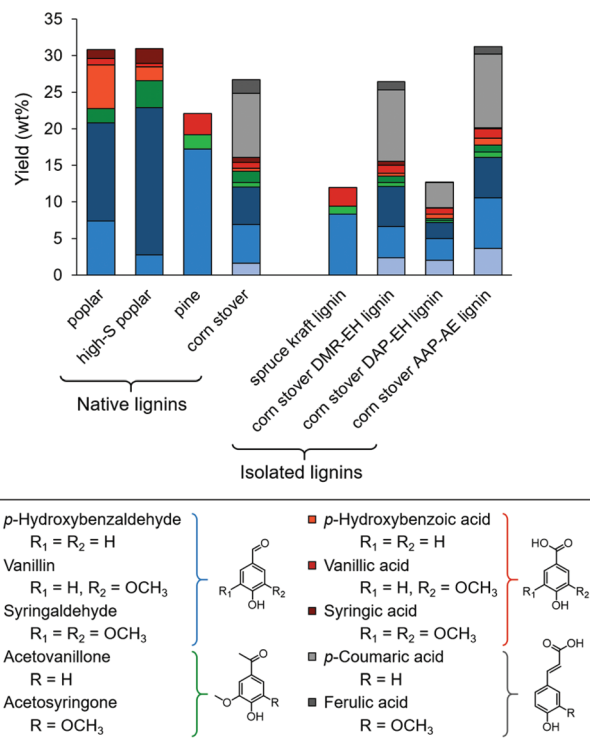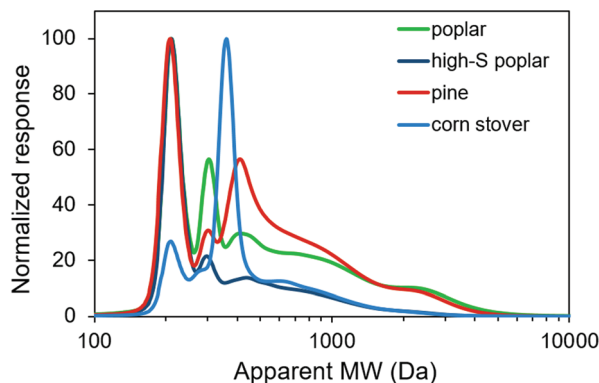 200 and 300 Da correspond to the mono-meric compounds. The signal of the oligomeric compounds (>350 Da) decreased in the following order: pine > WT poplar > high-S poplar. The GPC profile of the corn stover oxidation product showed a large peak at 350–400 Da, corresponding to the hydroxycinnamic acids.

In addition to the native lignins, we examined the oxidation of a range of isolated lignins, comprising one softwood lignin (spruce Kraft lignin) and three herbaceous lignins (corn stover DMR-EH, DAP-EH, and AAP-AE lignin) (Fig. 9). The results not only indicated the potential of oxidation to yield phenolic products from these substrates, but also made it possible to evaluate the impact of the isolation method on the structural integrity of the lignin, by comparing the results of the native and isolated lignins for the same (or similar) feedstocks. Oxidation of spruce Kraft lignin, an isolated softwood lignin, yielded 12 wt% monomers, with a very similar monomer distribution as from pine oxidation. The monomer yield, however, was much lower, which is due to the degraded state of the Kraft lignin structure. Next, three isolated corn stover lignins were subjected to oxidation, which enabled a direct evaluation of the isolation method on the reactivity of lignin toward depolymerization. Oxidation of DMR enzymatic hydrolysis residue (DMR-EH lignin) from corn stover rendered a similar monomer yield (27 wt%) and monomer distribution as corn stover oxidation, thus, indicating that the original lignin reactivity is well preserved during the mechanical pretreatment and enzymatic hydrolysis steps. On the other hand, oxidation of dilute acid-pretreated enzymatic hydrolysis residue (DAP-EH lignin) from corn stover generated a much lower monomer yield (13 wt%), indicating that the lignin structure is significantly degraded during DAP. The individual yield of most monomers was lower than in oxidation of corn stover or DMR-EH lignin, but the main difference is observed for the hydroxycinnamic acids. The *p*-coumaric acid yield was only 3 wt% and almost no ferulic acid was obtained, compared to a *p*-coumaric and ferulic acid yield of 10 and 1 wt%, respectively, for corn stover DMR-EH lignin. These acids were likely removed during the DAP step, as aqueous acid can also hydrolyse ester bonds. Lastly, we tested alkaline-extracted lignin from anhydrous ammonia-pretreated corn stover (AAP-AE lignin) in the reaction. The ammonia pretreated corn stover was treated with a 0.1 M NaOH aqueous solution, which extracted 70 wt% of the lignin. A portion of this alkaline extraction liquor was subsequently combined with a concentrated NaOH solution to obtain a 2 M NaOH aqueous solution, and subjected to oxidation. The monomer distribution was quite similar to that from corn stover and DMR-EH lignin oxidation, while the monomer yield was even higher (31 wt% on extracted lignin basis). However, in oxidation of corn stover and DMR-EH lignin, the yields were based on the entire corn stover lignin fraction (given that no lignin is lost during DMR-EH), while in oxidation of AAP-AE lignin, only the extracted lignin was considered (*i.e.*, 70 wt% of the total lignin). Taking into account the extracted lignin yield, 22 wt% of the original corn stover lignin was converted to phenolic monomers through AAP-AE and oxidation. Although this yield is somewhat lower than the yields from raw corn stover and corn stover DMR-EH lignin (27 wt%), it can be concluded that AAP-AE is also an effective method to isolate a highly reactive lignin substrate from corn stover.

In Fig. 11, the molecular weight distribution of the isolated lignins (a) and their oxidation products (b) is displayed (see Table S1† for M_n, M_w and PD values). The GPC profiles of the isolated lignins and the oxidation products are plotted together in Fig. S2† for each lignin substrate. Spruce Kraft lignin, corn stover DMR-EH, and DAP-EH lignin exhibited a high molecular weight (Fig. 11a) and were clearly converted to low-molecular-weight products (200–4000 Da) by oxidation (Fig. 11b). Similar to Fig. 10, the main peaks were present at 200 Da, corresponding to the aromatic aldehydes and acetovanillone and -syringone (especially for spruce Kraft lignin), and 350–400 Da, corresponding to the hydroxycinnamic acids (for the corn stover lignins). In contrast to the other isolated lignins, corn stover AAP-AE lignin exhibited a low molecular weight (Fig. 11a). The GPC profile showed a large signal at 350–400 Da, indicating that the lignin in the AAP-AE liquor was mainly composed of 'free' (hydrolyzed) hydroxycinnamic acids. Oxidation of the AAP-AE lignin enabled the conversion of other lignin structures in the liquor to small monomeric compounds, as indicated by the signal strength at 200 Da (Fig. 11b and Fig. S2†).

Besides phenolic compounds, alkaline aerobic oxidation of the lignocellulosic feedstocks and isolated lignins also generated a large amount of aliphatic carboxylic acids, which derived from both the lignin and the carbohydrate fractions. While this study only focuses on the lignin fraction in the reactions with the lignocellulosic feedstocks (and, therefore, only looks at the phenolic compounds), the fate of the entire substrate is of interest in the reactions with the isolated lignins, because these rep-
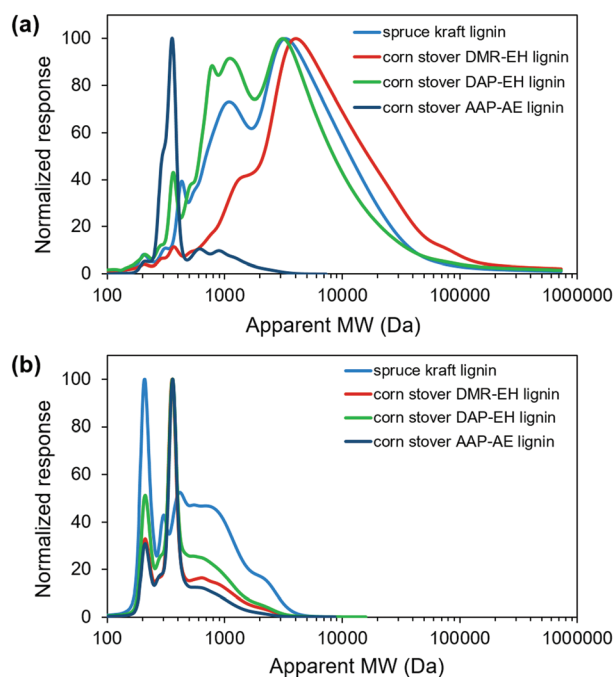

Fig. 11 GPC profiles of the isolated lignins (a) and oxidation products of the isolated lignins (b). The reaction conditions used to obtain the oxidation products are indicated in the caption of Fig. 9.

resent highly relevant feedstocks for chemical production. The mixed carboxylic acid stream that is obtained in addition to the lignin products could, for instance, be separated into individual acids analogously to recovery of acids from fermentation broth,[95] or they could be upgraded biologically to other value-added products.[96] In Table 2, the yields of phenolic compounds and aliphatic carboxylic acids (on total substrate basis) are indicated. Spruce Kraft lignin has a very high lignin content (93 wt%) and, thus, almost all carboxylic acids derived from the lignin fraction. On the other hand, the isolated corn stover lignins have a much lower lignin content (30–63 wt%) and contain a significant fraction of carbohydrates (15–33 wt%). Thus, for these substrates, the carboxylic acids originated from both the lignin and carbohydrates. Besides the phenolic monomer compounds, spruce Kraft lignin oxidation mainly yielded formic acid and smaller amounts of acetic, glycolic, lactic, malonic, and oxalic acid (the lattermost was not quantified). Only traces of succinic acid and no malic acid were obtained. The carboxylic acid distribution was, thus, rather similar to that from vanillin oxidation (Table 1). A total product yield of 39 wt% was obtained. In oxidation of the corn stover lignins, formic acid was also the main product, followed by acetic, glycolic, and lactic acid. Malonic and malic acid were minor products (2–3 wt% yield), while succinic acid was only present in trace amounts. Also some oxalic acid was obtained from these lignins, although not quantified. Remarkably, AAP-AE lignin oxidation generated similar amounts of formic and acetic acid, while the acetic acid yield was much lower than the formic acid yield for the other corn stover lignins. The total quantified product yields from the corn stover lignins amounted to 46–49 wt%. Thus, a targeted valorization strategy can be rationally designed for up to half of the substrate mass.

Comparison of lignocellulose alkaline aerobic oxidation with nitrobenzene oxidation and RCF

Through alkaline aerobic oxidation, the native lignin in lignocellulosic feedstocks can be effectively converted to phenolic monomers. To evaluate the effectiveness of this depolymerization method, we compared alkaline aerobic oxidation to nitrobenzene oxidation and reductive depolymerization. Nitrobenzene oxidation is commonly used for lignin characterization, as it enables an effective depolymerization of lignin into phenolic monomers.[51,53,83] However, as the oxidant (nitrobenzene) and its products are harmful, nitrobenzene oxidation is only relevant from a characterization perspective. Reductive depolymerization of native lignin, which is usually termed RCF when applied to whole biomass, enables very high (close-to-theoretical) monomer yields from native lignin (based on ester and β-O-4 ether cleavage).[3,11,13,14] Both of these methods constitute suitable benchmarks for alkaline aerobic oxidation. It should be noted that while RCF is an appropriate method to valorize the entire lignocellulose substrate (i.e., both the lignin and carbohydrates; the latter are largely retained in a pulp that can be used for further processing), alkaline aerobic oxidation is likely not, as the carbohydrates are converted into a complex mixture of aliphatic carboxylic acids. Therefore, alkaline aerobic oxidation and RCF are solely compared at the lignin level here.

Fig. 12 depicts the monomer yields obtained through alkaline aerobic oxidation (Ox; same results as in Fig. 9), nitrobenzene oxidation (Ox[NB]) and RCF (Red). Only poplar was subjected to nitrobenzene oxidation. The same products and a similar product distribution were obtained as in alkaline aerobic oxidation of poplar, but a rather higher total monomer yield was achieved (35 vs. 31 wt%). RCF was applied to all lignocellulose substrates in Fig. 9, and was performed with Pd/C in methanol at 225 °C under hydrogen pressure. The main products were propanolguaiacol and -syringol, with minor products being guaiacol and syringol with a propyl, propenyl, methoxypropyl, or ethyl side-chain (these compounds are combined under 'other guaiacols' and 'other syringols'). The p-hydroxybenzoic acid in poplar and high-S poplar was converted to methyl p-hydroxybenzoate (through esterification) and phenol (through decarboxylation)[97] and the p-coumaric

Table 2 Product yield from alkaline aerobic oxidation of isolated lignin on total substrate basis[a]

Substrate	Spruce Kraft lignin	Corn stover DMR-EH lignin	Corn stover DAP-EH lignin	Corn stover AAP-AE lignin[b]
Substrate mass (mg)	150	300	250	520
Lignin content (wt%)	93	53	63	30
Lignin mass (mg)	140	160	158	154
Yield (wt%)				
Phenolic compounds	12	14	8	9
Formic acid	15	13	16	11
Acetic acid	4	4	5	11
Glycolic acid	3	7	6	6
Lactic acid	3	7	5	7
Malonic acid	2	2	3	2
Succinic acid	<1	<1	<1	<1
Malic acid	0	2	2	2
Sum	39	49	46	49

[a] Reaction conditions: 30 mL of 2 M NaOH aqueous solution, 10 mg LaMn$_{0.8}$Cu$_{0.2}$O$_3$, 175 °C, 0 min, 5 bar O$_2$ + 15 bar He (at RT). The yield of phenolic compounds and other acids was determined via GC-FID and HPLC, respectively. Oxalic acid was observed in both the GC and HPLC analyses, but could not be quantified. [b] 15 mL of the AAP-AE liquor (0.1 M NaOH, containing 520 mg solids and 154 mg lignin) was combined with 15 mL of a 3.9 M NaOH aqueous solution to obtain 30 mL of a 2 M NaOH solution.
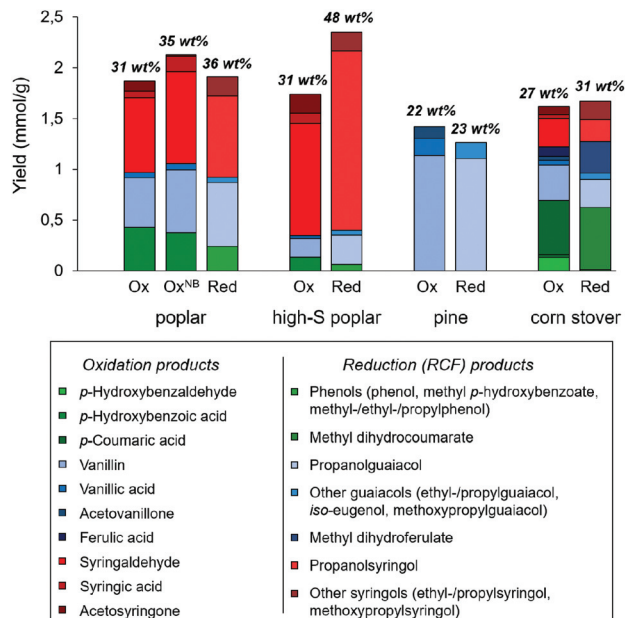
Fig. 12 Monomer yields (on lignin basis) from alkaline aerobic oxidation (Ox), nitrobenzene oxidation (Ox^{NB}) and reductive catalytic fractionation (Red) of various lignocellulosic substrates. Syringyl (S)-, guaiacyl (G)- and p-hydroxyphenyl (H)-type products are indicated in red, blue and green, respectively. Reaction conditions for alkaline aerobic oxidation: 0.5 g lignocellulose (95–150 mg lignin), 30 mL of 2 M NaOH aqueous solution, 10 mg LaMn$_{0.8}$Cu$_{0.2}$O$_3$, 175 °C, 0 min (10 min for pine), 5 bar O$_2$ + 15 bar He (at RT). Reaction conditions for nitrobenzene oxidation: 0.5 g poplar, 27 mL of 2 M NaOH aqueous solution, 3 mL nitrobenzene, 170 °C, 120 min. Reaction conditions for reduction: 1 g lignocellulose, 30 mL methanol, 0.1 g Pd/C, 225 °C, 6 h, 30 bar H$_2$ (at RT).

and ferulic acid in corn stover were converted to methyl dihydrocoumarate and dihydroferulate (through side-chain hydrogenation and esterification, respectively).[28] Because the monomeric compounds produced through oxidation and reduction are different and, thus, have different molecular weights, the product yields cannot be compared on weight basis. Therefore, the yields presented in Fig. 12 are indicated on a molar basis (mmol g^{-1}). The total monomer yields on weight basis are also shown.

For poplar, pine, and corn stover, alkaline aerobic oxidation and reduction achieved comparable monomer yields. Also, starting from poplar and corn stover, a similar distribution of S-, G-, and p-hydroxyphenyl (H)-type compounds (indicated in red, blue, and green, respectively, in Fig. 12) was obtained through both methods. Pine conversion yielded only G-type products. For corn stover, reduction generated a significantly higher yield of p-coumaric acid (as methyl dihydrocoumarate) and ferulic acid (as methyl dihydroferulate) than oxidation, while the total yield of H- and G-type products was fairly similar. This can be explained by the fact that these acids were further transformed to other H- and G-type products during oxidation,[61] while they were stabilized during reduction (as methyl dihydrocoumarate and dihydroferulate). Oxidation achieved a considerably lower monomer yield than reduction

only for high-S poplar. The main difference was in the S-type products. This yield difference is likely due to the low stability of S-type compounds during oxidation, while they are stable under reductive conditions. These results show that an effective oxidative depolymerization is especially difficult for S-rich lignins.

Discussion and conclusions

Consistent with previous work, we have shown that alkaline oxidation is an effective lignin depolymerization strategy for both native and technical lignins, provided that the latter are not overly degraded in upstream operations. Up to about 30 wt% aromatic monomers can be achieved, depending on the substrate and conditions, with short reaction times, high temperatures, and high NaOH concentrations being favourable. Addition of Cu-based catalysts does not appear to improve phenolic monomer yields, but makes the process less sensitive to reaction time.

These results provide some insight into the puzzling and sometimes contradictory results of previous work. First, because short reaction times are required and reactors are typically pressurized with O$_2$ or air at room temperature, the heating rate of the reactors is a critical parameter that could significantly affect results across experimental setups. For example, Wu *et al.* employed a system that could be heated from room temperature to 170 °C in 3–5 min[60,75] In contrast, other configurations, including the one used here, were limited by a 30 min heating time, which we show allows the reaction to proceed to a significant extent. The reaction during heating is likely due to both hydrolysis of ether and ester bonds in the alkaline solution and oxidation reactions. Few monomers, such as the ester-linked p-hydroxybenzoic acid, are produced while heating without oxygen, as indicated in Fig. 3, but significant monomer production is evident by the time the reactors reach reaction temperature when they are heated under 5 bar O$_2$. These results are consistent with Rodrigues *et al.*, who showed that pine Kraft lignins produce minimal vanillin under non-oxidizing alkaline hydrolysis conditions, but that vanillin is both rapidly produced and consumed when O$_2$ is present.[50] On the other hand, Pacek *et al.* found significant vanillin production without O$_2$ from Na-lignosulfonates.[69] In future work, it would be useful to assess the influence of introducing the oxidizing atmosphere before and after heating the reactor, although it is expected that heating in absence of oxygen will induce lignin degradation through base-catalyzed transformations, as illustrated by the loss of β-ether structures in the reaction under inert atmosphere (see Fig. 4) and, therefore, lower the product yields. While not typically reported, the stirring rate, which affects the gas–liquid mass transfer of O$_2$ into solution, may also influence reported yields, though Pacek *et al.* found vanillin yields in lignosulfonate oxidation were relatively insensitive to agitation, at least for stirring speeds above 500 rpm at pH $\geq$ 12.[69]

Second, the observation in the literature that a catalyst sometimes increases lignin monomer yields and other times does not may be due to both heating rate (with/without O_2) and lignin chemistry. Lignin in the native biomass substrates explored here has a high reactivity even without catalyst, and while some catalysts appear to have a substantial effect at lower temperatures and short reaction times (150 °C, 0 min in Fig. 6 and 8a), the apparent benefit is not as prominent at higher temperatures or intermediate reaction times. At longer reaction times, monomer yields are again higher with catalyst than without, though overall yields are again lower. There are at least three mechanisms by which the catalyst could lead to these trends, which would be sensitive to the chemistry of the substrate. First, the catalyst may be breaking lignin linkages that are not broken (or not broken as quickly) without a catalyst, leading to higher aldehyde yields initially. Second, as the aldehyde-producing linkages in the lignin are consumed, the catalyst may preserve the aldehyde products, inhibiting their degradation. Third, the catalyst may preferentially shuttle active oxygen species to other reactions (*e.g.*, converting carboxylic acids to CO_2), reducing the O_2 pressure in the reactor and leading to slower aldehyde degradation. The first mechanism is difficult to prove because the HSQC NMR spectra are somewhat ambiguous. The second mechanism is unlikely, as preliminary results suggest that Cu catalysts increase the rate of degradation of vanillin and syringaldehyde. In the third mechanism, the reactor pressure should decrease more during the reaction with catalyst as more O_2 is consumed. However, in our reactions, the reactor pressures with and without catalyst were similar, rendering the third mechanism unlikely, as well. Therefore, the catalytic trends cannot yet be explained, and further research efforts are needed to understand the role of the catalyst.

Third, further study is needed regarding the congruence of monomeric product yields in oxidative and reductive lignin depolymerization approaches. RCF has been proposed to cleave mainly inter-unit ether and ester linkages, generating stabilized products. On the other hand, aromatic monomers are rapidly degraded under alkaline oxidation conditions, with loss of aromaticity as a primary contributor. This, combined with the much shorter reaction times in alkaline oxidation, indicates that the reported maximum aromatic monomer yields are more snapshots of a much more dynamic reaction system than an indication that both depolymerization strategies attack the same functional linkages (although there is clear NMR evidence that ester and β-O-4 linkages do not survive either process).[28–30]

Fourth, and similarly, further study is needed to conclusively elucidate the mechanism of alkaline oxidation with and without catalysts. Several mechanisms have been proposed in literature, comprising both radical and ionic pathways.[48,54–57,74,75] The requirement of a highly alkaline solution can in part be rationalized on the basis of deprotonating phenolic functional groups and maintaining alkalinity in the presence of produced acids. However, even in presence of the produced acids, which constitute much less than 0.5 M

of neutralizing equivalents, deprotonation of the phenolic groups should still be possible at much lower NaOH concentrations than 2 M, as the pK_a of phenolic groups is around 10–11.5 at 25 °C.[43] Thus, the need for high alkalinity likely indicates a critical step in the depolymerization that depends on deprotonation of different functional groups with higher pK_a. According to the mechanism proposed by Tarabanko *et al.* (Fig. S3†), a high alkalinity is necessary for deprotonation of certain reaction intermediates and retro-aldol cleavage of a cinnamaldehyde-like intermediate to obtain the final aromatic aldehydes and acetophenone-like products.[54–57] The mechanism involving retro-aldol cleavage is supported by the fact that the kinetics of vanillin formation from lignin are similarly affected by the pH of the reaction medium as oxidation of vanillideneacetone, which is a representative compound for the cinnamaldehyde-like intermediate. Furthermore, this mechanism can also explain the formation of the acetophenone-derived products, and is, therefore, considered to be a plausible mechanism for alkaline lignin oxidation. However, a more conclusive elucidation of the reaction mechanism likely requires a combined experimental (model compound) and computational study, as was previously performed to verify the mechanism of acid- and base-catalyzed lignin conversion.[22,98]

Finally, alkaline oxidation requires a different workup procedure than reductive approaches, such as RCF. Reductive methods are usually performed in low-boiling reaction solvents, which can be easily removed and recycled by distillation. The products exhibit similar functionality and polarity, implying that separations will have to rely on differences in molecular weight and/or boiling point between monomers, dimers, and oligomers. Alkaline oxidation, on the other hand, yields a highly alkaline reaction solution containing a mixture of phenolics (aromatic aldehydes, aromatic acids, acetophenone-like compounds, and oligomer fragments) and aliphatic carboxylic acids. Isolation of the phenolics from the reaction is typically performed through acidification and extraction with organic solvents.[43,44,99] This procedure, however, requires large amounts of acid and organic solvent, and generates a significant amount of highly saline wastewater. To avoid extraction of the acidified solution with organic solvents, alternatives such as extraction with supercritical CO_2 or adsorption of the phenolics on zeolites or macroporous resins have been examined.[43,44,99] To circumvent the acidification of the entire reaction mixture, strategies to directly isolate the phenolates from the mixture, such as extraction with specific solvents (*e.g.*, butanol), adsorption on cation-exchange resins (in the Na^+ or H^+ form), or ultrafiltration to remove high-molecular-weight lignin fragments, have been investigated.[43,44,99] Despite advances being made, further research is necessary to enable a more sustainable isolation of the phenolic products from the reaction solution, and, in addition, separation of individual products from the phenolics mixture. For instance, separating vanillin in high purity requires an elaborate purification procedure, involving crystallization, extraction, and distillation steps. However, an advantage of alkaline oxidation compared

to reductive procedures is that the market for certain oxidation products, such as vanillin, is well established, while the market for reductively produced monomers is smaller and/or less-defined.

Materials and methods

Chemicals and materials

N,O-Bis(trimethylsilyl)trifluoroacetamide (BSFTA), pyridine (anhydrous, +99%), dichloromethane (+99%), nitrobenzene (+99%), 2-isopropylphenol (+98%), HCl (37%), 4-propylguaiacol (+99%), citric acid (+99%), spruce Kraft lignin (alkali lignin; 93.2 wt% lignin content), Na_2SO_4 (+99%), Pt/Al_2O_3 (5 wt%), Pd/Al_2O_3 (5 wt%), CuO nanopowder, $La(NO_3)_2 \cdot 6H_2O$ (+99%), $Co(NO_3)_2 \cdot 6H_2O$ (+99%), $CuSO_4 \cdot 5H_2O$ (+99%), $FeCl_3$ (+99%), $MnCl_2$ (+99%), $CoCl_2 \cdot 6H_2O$ (+97%), $Cr_2(SO_4)_3 \cdot xH_2O$ (+99%), were all purchased from Sigma-Aldrich. NaOH (99%), acetone (+99%), tetrahydrofuran (THF, Baker, HPLC grade), methanol (+99%) and ethyl acetate (+99%) were purchased from Fischer Scientific. $Fe(NO_3)_3 \cdot 9H_2O$ (98%), $Mn(NO_3)_2 \cdot 4H_2O$ (99%), $Cu(NO_3)_2 \cdot 3H_2O$ (99%), Co_3O_4 nanopowder (99%) were purchased from Alfa Aesar. H_2SO_4 was purchased from Ricca Chemical Company.

The poplar wood used for this project was obtained from a farm in Alexandria, Minnesota, provided through the USDA Northern Research Station in Rhinelander, Wisconsin. The poplar sawdust was extracted with both water and ethanol for 24 h. The total lignin content (Klason lignin and acid-soluble lignin) of the (extractives-free) poplar sawdust is 29.1 wt%. Pine sawdust was provided by Idaho National Laboratory (total lignin content of 29 wt%). Corn stover was provided by Idaho National Laboratory (total lignin content of 15.1 wt%). The genetically engineered high-S poplar line (F5H-64-E) was originally produced as described by Franke *et al.*[91] and was provided by Carl Huetteman (Managing Director, C3Bio, Purdue University) (total lignin content of 22.9 wt%).[92] The preparation of corn stover DMR-EH and DAP-EH lignin is described elsewhere (total lignin content of 52.8 and 67.3 wt%, respectively).[100] Corn stover AAP-AE lignin was prepared as described elsewhere.[36] Briefly, 50 g milled corn stover was treated with anhydrous ammonia (3 g g^{-1} corn stover) in a stainless steel Parr batch reactor at 130 °C for 60 min. After evaporation of the ammonia, alkali extraction was performed by treating the pretreated corn stover in an Erlenmeyer flask with 500 mL of a 0.1 M NaOH solution at 25 °C for 2 h. The insoluble material was subsequently separated by centrifugation. The separated solid was mixed with 30 mL of deionised water and the obtained slurry was centrifuged again. This step was repeated twice, and the two wash fractions were added to the supernatant from the first centrifugation, making up the corn stover AAP-AE liquor. A portion of this liquor was neutralized with H_2SO_4 and freeze-dried to determine the total solids concentration (34.4 g L^{-1}, corrected for Na_2SO_4 weight) and lignin concentration (10.3 g L^{-1}).

Oxidation experiments

Alkaline aerobic oxidation reactions were performed in a Parr multi-batch reactor system. 30 mL of a NaOH aqueous solution (deionized water; typically 2 M concentration), substrate and catalyst were added to 75 mL reactor cups (type 316 stainless steel). The reactors were closed and stirring was performed using magnetic stir bars at 800 rpm. Next, the reactors were flushed with high-pressure He (three cycles), pressurized with He, and further pressurized with O_2 to achieve a total pressure of 20 bar. The applied He pressure depended on the targeted O_2 partial pressure and was typically 15 bar (corresponding with an O_2 partial pressure of 5 bar). The reactors were then heated to the desired temperature (heating time of 30 min), at which point the reaction was started (*i.e.*, reaction time was set to 0 min). After reaction, the reactors were quenched in water and depressurized at room temperature.

For the nitrobenzene oxidation reactions of poplar, 27 mL of a 2 M NaOH aqueous solution, 3 mL nitrobenzene and 0.5 g poplar were added to the reactor cups. After flushing with He, the reactors were heated to 170 °C and left at this temperature for 120 min.

Cautionary remark: Using highly alkaline solutions at high temperature can cause stress corrosion cracking in stainless steel pressure vessels. Therefore, Monel 400 pressure vessels were purchased for future research.

Work-up procedure

For GC analysis, the following procedure was performed in duplicate for each reaction: 5 mL of the reaction solution was added to a 15 mL glass vial, acidified with concentrated HCl to pH < 2 and extracted with ethyl acetate (4 × 5 mL). The nitrobenzene oxidation reaction mixtures were first extracted with dichloromethane (3 × 5 mL) before acidification. The ethyl acetate was evaporated with a rotavap, resulting in a brown lignin oil (EA oil). 25 mg of 4-*n*-propylguaiacol was added as a standard and 7 mL acetone was added to solubilize the EA oil and standard. 200 μL of this solution was added to a GC vial and subsequently dried under vacuum. Next, 1 mL of pyridine and 100 μL of BSTFA were added, the vial was sealed, thoroughly shaken and left for 24 h before GC analysis.

For GPC and NMR, the remainder of the reaction solution (~20 mL) was acidified and extracted with ethyl acetate in a separatory funnel (4 × 25 mL). The ethyl acetate phase was dried with $NaSO_4$ and the ethyl acetate evaporated using a rotavap, yielding the EA oil.

Gas chromatography (GC) analysis

For quantitative analysis of the volatile fraction, the duplicate samples were analyzed on an Agilent GC (6890 series) equipped with a HP5-column and a flame ionization detector (FID). The following operating conditions were used: injection temperature of 260 °C; column temperature program: 50 °C, 2 min hold, 10 °C min^{-1} to 280 °C, 5 min hold; detection temperature of 300 °C. Sensitivity factors of the reagents and products were obtained by calibration with commercial stan-

dards. When using lignocellulosic feedstocks and isolated lignins, the product yields were calculated on a weight basis using the following equation:

$$Yield = \frac{mass_{product}}{mass_{substrate,\ initial} \times substrate\ lignin\ content} \times 100\ wt\%$$

In the experiments with vanillin and syringaldehyde (Table 1), the conversion and yield were calculated as follows:

$$Conversion = \frac{mass_{substrate,\ inital} - mass_{substrate}}{mass_{substrate,\ inital}} \times 100\ wt\%$$

$$Yield = \frac{mass_{product}}{mass_{substrate,\ inital}} \times 100\ wt\%$$

The yields and conversions indicated in the manuscript constitute the average of the yields from the duplicate samples. The standard deviation was always less than 1%. Selected reactions were performed in triplicate, with the standard deviation being less than 1%. Qualitative analysis of the product solution was performed by analyzing the samples on an Agilent GC (6890 series) equipped with a HP5-column and a 5973N MS detector (Agilent Technologies). The following operating conditions were used: injection temperature of 260 °C; column temperature program: 50 °C, 2 min hold, 10 °C min⁻¹ to 280 °C, 5 min hold; MS transfer line temperature: 280 °C.

HPLC analysis

High-performance liquid chromatography (HPLC) analysis was performed to quantify the aliphatic carboxylic acids in the reaction mixture. Before HPLC analysis, a 1 mL reaction sample was acidified with concentrated HCl to pH < 2 and filtered with a 0.45 μm nylon membrane syringe filter. The samples were analyzed on an Agilent HPLC (1100 series, Santa Clara, CA, USA) outfitted with a refractive index detector and using an Aminex HPX-87H (300 × 7.8 mm) organic acid column and Cation H⁺ guard cartridge (Biorad Laboratories, Hercules, CA, USA). The column was maintained at 65 °C with mobile phase consisting of 0.05 N sulfuric acid with a flow rate of 0.6 mL min⁻¹. The mobile phase was prepared from 10 N sulfuric acid (Ricca Chemical Company, Arlington, TX, USA). Analytes were identified by comparing retention times and spectral profiles with pure standards.

Gel permeation chromatography (GPC) analysis

GPC analysis was performed to assess the molecular weight distribution of the aromatic lignin oxidation products. The EA oils and the lignin substrates (20 mg) were acetylated in a mixture of pyridine (0.5 mL) and acetic anhydride (0.5 mL) at 40 °C for 24 h with stirring. The reaction was terminated by addition of methanol (0.5 mL). The acetylation solvents were then evaporated from the samples at 40 °C under a stream of N₂ gas. Additional methanol was added in 1 mL increments during N₂ drying to assist in removing the remaining acetylation solvents by converting any remaining acetic anhydride to methyl acetate. The samples were further dried overnight in a

vacuum oven at 40 °C. The dried, acetylated samples were dissolved in THF. The dissolved samples were filtered (0.2 μm nylon membrane syringe filters) before GPC analysis. GPC analysis was performed using an Agilent HPLC with 3 GPC columns (Polymer Laboratories, 300 × 7.5 mm) packed with polystyrene-divinylbenzene copolymer gel (10 μm beads) having nominal pore diameters of 10⁴, 10³, and 50 Å. The eluent was THF and the flow rate 1 mL min⁻¹. An injection volume of 25 μL was used. The HPLC was attached to a diode array detector measuring absorbance at 260 nm (bandwidth 80 nm). Retention time was converted into molecular weight (MW) by applying a calibration curve established using polystyrene standards of known molecular weight (1 × 10⁶ to 580 Da) plus toluene (92 Da). The detection method is mainly sensitive to aromatics, while other (sugar and lignin-derived) products only contribute little to the signal.

NMR analysis

Heteronuclear Single Quantum Coherence (HSQC) nuclear magnetic resonance (NMR) spectra were acquired for the EA oils and poplar wood. The EA oil (80 mg) was dissolved in 0.5 mL of deuterated acetone. The MWL (100 mg) was dissolved into 0.5 mL of d_6-DMSO/d_5-pyridine (4:1, v/v). Spectra were acquired on a Bruker 400 MHz spectrometer using a BBO probe with Z gradient, with 1024 points and a sweep width of 15 ppm in the F2 (¹H) dimension and 512 points and 220 ppm of sweep width in the F1 (¹³C) dimension. The delay time was 1.5 s. TMS was used as an internal reference for the oil samples and DMSO peak (δ_H 2.5, δ_C 39.51 ppm) for the MWL. Peak assignment was performed according to the literature.[101–103]

Synthesis and characterization of the perovskite catalysts

For the synthesis of the LaCoO₃, LaFeO₃, and LaMnO₃ perovskite catalysts, 15 mmol of La(NO₃)₂·6H₂O (6.495 g), 15 mmol of either Co(NO₃)₂·6H₂O (4.3655 g), Fe(NO₃)₃·9H₂O (6.06 g) or Mn(NO₃)₂·4H₂O (3.765 g), and 45 mmol citric acid (8.645 g) were added to a 200 mL glass beaker together with 120 mL deionized water. For the LaCo₀.₈Cu₀.₂O₃ and LaMn₀.₈Cu₀.₂O₃ catalysts, 12 mmol of either Co(NO₃)₂·6H₂O (3.492 g) or Mn(NO₃)₂·4H₂O (g) and 3 mmol Cu(NO₃)₂·3H₂O (0.7248 g) were combined with 15 mmol La(NO₃)₂·6H₂O, 45 mmol citric acid, and 120 mL deionised water. The mixture was stirred with a magnetic stirring bar, heated to 90 °C and left until most of the water was evaporated and a gel remained. The sample was subsequently dried at 100 °C overnight and calcined at 650 °C for 6 h (5 °C min⁻¹ heating rate). XRD was performed on a Rigaku Ultima IV X-ray diffraction system using Cu Kα radiation, with operating voltage and current of 40 kV and 44 mA, respectively, scan speed of 5° min⁻¹, and point spacing of 0.02°. N₂ physisorption was carried out at 77 K with a Quantachrome Quadrasorb SI instrument, with outgassing under vacuum at 350 °C for a minimum of 12 h before analysis, and equilibration time of 30 s for both adsorption and desorption. Temperature programmed reduction (TPR) was performed on an AMI-390 (Altamira Instruments) system

equipped with a thermal conductivity detector (TCD) to measure hydrogen consumption during a temperature ramp. A molecular sieve was placed before the TCD to trap water coming from the catalyst bed. Approximately 100 mg of catalyst was loaded between quartz wool plugs into a quartz U-tube reactor. A thermocouple located in the furnace wall was used to control the experiment temperature and another thermocouple located on top quartz wool plug monitored the sample temperature. A pretreatment step consisting of heating in 10% O_2/He at 10 °C min^{-1} up to 500 °C, followed by holding for 30 min, was performed *in situ*. TPR experiments were then carried out in 35 sccm of 5% H_2/Ar with a ramp rate of 10 °C min^{-1} from 100 to 800 °C.

RCF experiments

RCF experiments were performed in a Parr multi-batch reactor system. 30 mL of methanol, 1 g of substrate and 100 mg of Pd/C catalyst were added to the 75 mL reactor cups. The reactors were closed and stirring was performed (800 rpm). The reactors were flushed with high-pressure He (three cycles), pressurized with 30 bar H_2, heated to 225 °C (heating time of 30 min) and left at this temperature for 6 h. After reaction, the reactors were quenched in water and depressurized at room temperature. The reaction solutions were subsequently filtered to separate the pulp and catalyst from the liquor. The liquors were dried in a rotavap and the resulting brown oils were subjected to a three-fold liquid–liquid extraction with dichloromethane and water. The dichloromethane phase, containing the lignin products, was dried, 40 mg 2-isopropylphenol was added as a standard and 7 mL acetone was added to solubilize the standard and lignin products. The resulting mixtures were quantitatively and qualitatively analysed by GC-FID and GC-MS, respectively. The operating conditions of the GC-FID and GC-MS, and the yield calculations were the same as described for the oxidation reactions.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

References

1 C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chem. Rev.*, 2015, **115**, 11559–11624.

2 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.

3 W. Schutyser, T. Renders, S. Van den Bosch, S. F. Koelewijn, G. T. Beckham and B. F. Sels, *Chem. Soc. Rev.*, 2018, **47**, 852–908.

4 Z. Sun, B. Fridrich, A. de Santi, S. Elangovan and K. Barta, *Chem. Rev.*, 2018, **118**, 614–678.

5 R. Vanholme, B. Demedts, K. Morreel, J. Ralph and W. Boerjan, *Plant Physiol.*, 2010, **153**, 895–905.

6 A. U. Buranov and G. Mazza, *Ind. Crops Prod.*, 2008, **28**, 237–259.

7 R. Vanholme, K. Morreel, C. Darrah, P. Oyarce, J. H. Grabber, J. Ralph and W. Boerjan, *New Phytol.*, 2012, **196**, 978–1000.

8 F. Lu, S. D. Karlen, M. Regner, H. Kim, S. A. Ralph, R.-C. Sun, K.-i. Kuroda, M. A. Augustin, R. Mawson, H. Sabarez, T. Singh, G. Jimenez-Monteon, S. Zakaria, S. Hill, P. J. Harris, W. Boerjan, C. G. Wilkerson, S. D. Mansfield and J. Ralph, *BioEnergy Res.*, 2015, **8**, 934–952.

9 F. Lu, J. Ralph, K. Morreel, E. Messens and W. Boerjan, *Org. Biomol. Chem.*, 2004, **2**, 2888–2890.

10 A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan and C. E. Wyman, *Science*, 2014, **344**, 709.

11 R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijnincx and B. M. Weckhuysen, *Angew. Chem., Int. Ed.*, 2016, **55**, 8164–8215.

12 S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. da Costa Lopes, R. M. Lukasik and P. T. Anastas, *Green Chem.*, 2017, **19**, 4200–4233.

13 W. Schutyser, T. Renders, G. Van den Bossche, S. Van den Bosch, S.-F. Koelewijn, T. Ennaert and B. F. Sels, in *Nanotechnology in Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA, 2017, pp. 537–584, DOI: 10.1002/9783527699827.ch23.

14 T. Renders, S. Van den Bosch, S. F. Koelewijn, W. Schutyser and B. F. Sels, *Energy Environ. Sci.*, 2017, **10**, 1551–1557.

15 L. Shuai and B. Saha, *Green Chem.*, 2017, **19**, 3752–3758.

16 M. Ragnar, G. Henriksson, M. E. Lindström, M. Wimby, J. Blechschmidt and S. Heinemann, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000, DOI: 10.1002/14356007. a18_545.pub4.

17 P. Sannigrahi and A. J. Ragauskas, in *Aqueous Pretreatment of Plant Biomass for Biological and Chemical Conversion to Fuels and Chemicals*, John Wiley & Sons, Ltd, 2013, pp. 201–222, DOI: 10.1002/9780470975831.ch10.

18 S. P. S. Chundawat, G. T. Beckham, M. E. Himmel and B. E. Dale, *Annu. Rev. Chem. Biomol. Eng.*, 2011, **2**, 121–145.

19 P. Kumar, D. M. Barrett, M. J. Delwiche and P. Stroeve, *Ind. Eng. Chem. Res.*, 2009, **48**, 3713–3729.

20 J. Gierer, *Wood Sci. Technol.*, 1985, **19**, 289–312.

21 Y. Pu, F. Hu, F. Huang and A. J. Ragauskas, *BioEnergy Res.*, 2015, **8**, 992–1003.

22 M. R. Sturgeon, S. Kim, K. Lawrence, R. S. Paton, S. C. Chmely, M. Nimlos, T. D. Foust and G. T. Beckham, *ACS Sustainable Chem. Eng.*, 2014, **2**, 472–485.

23 J. Lora, in *Monomers, Polymers and Composites from Renewable Resources*, ed. M. N. B. Gandini and M. N. Belgacem, Elsevier, Amsterdam, 2008, pp. 225–241.

24 R. Davis, L. Tao, E. Tan, M. Biddy, G. Beckham, C. Scarlata, J. Jacobson, K. Cafferty, J. Ross and J. Lukas, *Process design and economics for the conversion of ligno-cellulosic biomass to hydrocarbons: dilute-acid and enzymatic deconstruction of biomass to sugars and biological conversion of sugars to hydrocarbons*, Report NREL/TP-5100-60223, National Renewable Energy Laboratory (NREL), Goldon, CO (US), 2013.

25 L. Shuai and B. Saha, *Green Chem.*, 2017, **19**, 3752–3758.

26 L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph and J. S. Luterbacher, *Science*, 2016, **354**, 329–333.

27 M. V. Galkin and J. S. M. Samec, *ChemSusChem*, 2016, **9**, 1544–1558.

28 E. M. Anderson, R. Katahira, M. Reed, M. G. Resch, E. M. Karp, G. T. Beckham and Y. Roman- Leshkov, *ACS Sustainable Chem. Eng.*, 2016, **4**, 6940–6950.

29 E. M. Anderson, M. L. Stone, R. Katahira, M. Reed, G. T. Beckham and Y. Román-Leshkov, *Joule*, 2017, **1**, 613–622.

30 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.

31 S. Van den Bosch, T. Renders, S. Kennis, S.-F. Koelewijn, G. Van den Bossche, T. Vangeel, A. Deneyer, D. Depuydt, C. M. Courtin, J. Thevelein, W. Schutyser and B. F. Sels, *Green Chem.*, 2017, **19**, 3313–3326.

32 I. Kumaniaev, E. Subbotina, J. Savmarker, M. Larhed, M. V. Galkin and J. S. M. Samec, *Green Chem.*, 2017, **19**, 5767–5771.

33 A. Guerra, I. Filpponen, L. A. Lucia, C. Saquing, S. Baumberger and D. S. Argyropoulos, *J. Agric. Food Chem.*, 2006, **54**, 5939–5947.

34 E. Capanema, M. Balakshin, R. Katahira, H.-m. Chang and H. Jameel, *J. Wood Chem. Technol.*, 2015, **35**, 17–26.

35 X. Chen, E. Kuhn, E. W. Jennings, R. Nelson, L. Tao, M. Zhang and M. P. Tucker, *Energy Environ. Sci.*, 2016, **9**, 1237–1245.

36 A. Mittal, R. Katahira, B. S. Donohoe, S. Pattathil, S. Kandemkavil, M. L. Reed, M. J. Biddy and G. T. Beckham, *ACS Sustainable Chem. Eng.*, 2017, **5**, 2544–2561.

37 L. da Costa Sousa, M. Foston, V. Bokade, A. Azarpira, F. Lu, A. J. Ragauskas, J. Ralph, B. Dale and V. Balan, *Green Chem.*, 2016, **18**, 4205–4215.

38 J. S. Luterbacher, A. Azarpira, A. H. Motagamwala, F. C. Lu, J. Ralph and J. A. Dumesic, *Energy Environ. Sci.*, 2015, **8**, 2657–2663.

39 X. Huang, T. I. Koranyi, M. D. Boot and E. J. M. Hensen, *Green Chem.*, 2015, **17**, 4941–4950.

40 A. Narani, R. K. Chowdari, C. Cannilla, G. Bonura, F. Frusteri, H. J. Heeres and K. Barta, *Green Chem.*, 2015, **17**, 5046–5057.

41 P. J. Deuss, C. S. Lancefield, A. Narani, J. G. de Vries, N. J. Westwood and K. Barta, *Green Chem.*, 2017, **19**, 2774–2782.

42 P. J. Deuss, M. Scott, F. Tran, N. J. Westwood, J. G. de Vries and K. Barta, *J. Am. Chem. Soc.*, 2015, **137**, 7456–7467.

43 P. C. Rodrigues Pinto, E. A. Borges da Silva and A. E. Rodrigues, in *Biomass Conversion: The Interface of Biotechnology, Chemistry and Materials Science*, ed. C. Baskar, S. Baskar and R. S. Dhillon, Springer Berlin Heidelberg, Berlin, Heidelberg, 2012, pp. 381–420, DOI: 10.1007/978-3-642-28418-2_12.

44 M. Fache, B. Boutevin and S. Caillol, *ACS Sustainable Chem. Eng.*, 2016, **4**, 35–46.

45 R. Behling, S. Valange and G. Chatel, *Green Chem.*, 2016, **18**, 1839–1854.

46 R. S. Ma, M. Guo and X. Zhang, *ChemSusChem*, 2014, **7**, 412–415.

47 A. G. Demesa, A. Laari, I. Turunen and M. Sillanpaa, *Chem. Eng. Technol.*, 2015, **38**, 2270–2278.

48 R. Ma, Y. Xu and X. Zhang, *ChemSusChem*, 2015, **8**, 24–51.

49 J. D. P. Araújo, C. A. Grande and A. E. Rodrigues, *Chem. Eng. Res. Des.*, 2010, **88**, 1024–1032.

50 A. L. Mathias and A. E. Rodrigues, *Holzforschung*, 1995, **49**, 273–278.

51 P. C. R. Pinto, C. E. Costa and A. E. Rodrigues, *Ind. Eng. Chem. Res.*, 2013, **52**, 4421–4428.

52 C. Fargues, Á. Mathias and A. Rodrigues, *Ind. Eng. Chem. Res.*, 1996, **35**, 28–36.

53 P. C. Rodrigues Pinto, E. A. Borges da Silva and A. E. Rodrigues, *Ind. Eng. Chem. Res.*, 2011, **50**, 741–748.

54 V. E. Tarabanko and D. V. Petukhov, *Chem. Sustainable Dev.*, 2003, **11**, 655–667.

55 V. E. Tarabanko, Y. V. Hendogina, D. V. Petuhov and E. P. Pervishina, *React. Kinet. Catal. Lett.*, 2000, **69**, 361–368.

56 V. E. Tarabanko, D. V. Petukhov and G. E. Selyutin, *Kinet. Catal.*, 2004, **45**, 569–577.

57 V. Tarabanko and N. Tarabanko, *Int. J. Mol. Sci.*, 2017, **18**, 2421.

58 Q. Xiang and Y. Y. Lee, *Appl. Biochem. Biotechnol.*, 2001, **91**, 71–80.

59 S. G. Santos, A. P. Marques, D. L. D. Lima, D. V. Evtuguin and V. I. Esteves, *Ind. Eng. Chem. Res.*, 2011, **50**, 291–298.

60 G. Wu, M. Heitz and E. Chornet, *Ind. Eng. Chem. Res.*, 1994, **33**, 718–723.

61 G. Lyu, C. G. Yoo and X. Pan, *Biomass Bioenergy*, 2018, **108**, 7–14.

62 T. Voitl and P. R. von Rohr, *ChemSusChem*, 2008, **1**, 763–769.

63 H. Werhan, J. M. Mir, T. Voitl and P. R. von Rohr, *Holzforschung*, 2011, **65**, 703–709.

64 W. Partenheimer, *Adv. Synth. Catal.*, 2009, **351**, 456–466.

65 J. Mottweiler, M. Puche, C. Räuber, T. Schmidt, P. Concepción, A. Corma and C. Bolm, *ChemSusChem*, 2015, **8**, 2106–2113.

66 K. Stark, N. Taccardi, A. Bosmann and P. Wasserscheid, *ChemSusChem*, 2010, **3**, 719–723.

67 R. Prado, A. Brandt, X. Erdocia, J. Hallet, T. Welton and J. Labidi, *Green Chem.*, 2016, **18**, 834–841.

68 H.-R. Bjørsvik and F. Minisci, *Org. Process Res. Dev.*, 1999, **3**, 330–340.

69 A. W. Pacek, P. Ding, M. Garrett, G. Sheldrake and A. W. Nienow, *Ind. Eng. Chem. Res.*, 2013, **52**, 8361–8372.

70 V. E. Tarabanko, N. A. Fomova, B. N. Kuznetsov, N. M. Ivanchenko and A. V. Kudryashev, *React. Kinet. Catal. Lett.*, 1995, **55**, 161–170.

71 J. C. Villar, A. Caperos and F. García-Ochoa, *Wood Sci. Technol.*, 2001, **35**, 245–255.

72 C. Fargues, Á. Mathias, J. Silva and A. Rodrigues, *Chem. Eng. Technol.*, 1996, **19**, 127–136.

73 V. S. Sultanov and A. F. A. Wallis, *J. Wood Chem. Technol.*, 1991, **11**, 291–305.

74 J. Gierer, *Wood Sci. Technol.*, 1986, **20**, 1–33.

75 G. Wu and M. Heitz, *J. Wood Chem. Technol.*, 1995, **15**, 189–202.

76 F. G. Sales, L. C. A. Maranhão, N. M. Lima Filho and C. A. M. Abreu, *Ind. Eng. Chem. Res.*, 2006, **45**, 6627–6631.

77 H. Deng, L. Lin and S. Liu, *Energy Fuels*, 2010, **24**, 4797–4802.

78 H. Deng, L. Lin, Y. Sun, C. Pang, J. Zhuang, P. Ouyang, J. Li and S. Liu, *Energy Fuels*, 2009, **23**, 19–24.

79 H. Deng, L. Lin, Y. Sun, C. Pang, J. Zhuang, P. Ouyang, Z. Li and S. Liu, *Catal. Lett.*, 2008, **126**, 106.

80 J. Zhang, H. Deng and L. Lin, *Molecules*, 2009, **14**, 2747.

81 V. S. Kshirsagar, J. M. Nadgeri, P. R. Tayade and C. V. Rode, *Appl. Catal., A*, 2008, **339**, 28–35.

82 V. R. Mate, A. Jha, U. D. Joshi, K. R. Patil, M. Shirai and C. V. Rode, *Appl. Catal., A*, 2014, **487**, 130–138.

83 J. C. Villar, A. Caperos and F. García-Ochoa, *J. Wood Chem. Technol.*, 1997, **17**, 259–285.

84 J. M. Pepper, B. W. Casselman and J. C. Karapally, *Can. J. Chem.*, 1967, **45**, 3009–3012.

85 J. Zhu, H. Li, L. Zhong, P. Xiao, X. Xu, X. Yang, Z. Zhao and J. Li, *ACS Catal.*, 2014, **4**, 2917–2940.

86 S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyrat, S. Laassiri and H. Alamdari, *Chem. Rev.*, 2014, **114**, 10292–10368.

87 P. Ciambelli, S. Cimino, S. De Rossi, L. Lisi, G. Minelli, P. Porta and G. Russo, *Appl. Catal., B*, 2001, **29**, 239–250.

88 L. Lisi, G. Bagnasco, P. Ciambelli, S. De Rossi, P. Porta, G. Russo and M. Turco, *J. Solid State Chem.*, 1999, **146**, 176–183.

89 F. Patcas, F. C. Buciuman and J. Zsako, *Thermochim. Acta*, 2000, **360**, 71–76.

90 M. Crespin and W. K. Hall, *J. Catal.*, 1981, **69**, 359–370.

91 R. Franke, C. M. McMichael, K. Meyer, A. M. Shirley, J. C. Cusumano and C. Chapple, *Plant J.*, 2000, **22**, 223–234.

92 R. Meilan and C. Ma, in *Agrobacterium Protocols*, ed. K. Wang, Humana Press, Totowa, NJ, 2007, vol. 2, pp. 143–151, DOI: 10.1385/1-59745-131-2:143.

93 Y. Mottiar, R. Vanholme, W. Boerjan, J. Ralph and S. D. Mansfield, *Curr. Opin. Biotechnol.*, 2016, **37**, 190–200.

94 M. V. Galkin, A. T. Smit, E. Subbotina, K. A. Artemenko, J. Bergquist, W. J. J. Huijgen and J. S. M. Samec, *ChemSusChem*, 2016, **9**, 3280–3287.

95 P. O. Saboe, L. P. Manker, W. E. Michener, D. J. Peterson, D. G. Brandner, S. P. Deutch, M. Kumar, R. M. Cywar, G. T. Beckham and E. M. Karp, *Green Chem.*, 2018, **20**, 1791–1804.

96 D. R. Vardon, M. A. Franden, C. W. Johnson, E. M. Karp, M. T. Guarnieri, J. G. Linger, M. J. Salm, T. J. Strathmann and G. T. Beckham, *Energy Environ. Sci.*, 2015, **8**, 617–628.

97 T. Renders, W. Schutyser, S. Van den Bosch, S.-F. Koelewijn, T. Vangeel, C. M. Courtin and B. F. Sels, *ACS Catal.*, 2016, **6**, 2055–2066.

98 S. Dabral, J. Engel, J. Mottweiler, S. S. M. Spoehrle, C. W. Lahive and C. Bolm, *Green Chem.*, 2018, **20**, 170–182.

99 M. I. F. Mota, P. C. Rodrigues Pinto, J. M. Loureiro and A. E. Rodrigues, *Sep. Purif. Rev.*, 2016, **45**, 227–259.

100 R. Katahira, A. Mittal, K. McKinney, X. Chen, M. P. Tucker, D. K. Johnson and G. T. Beckham, *ACS Sustainable Chem. Eng.*, 2016, **4**, 1474–1486.

101 H. Kim and J. Ralph, *Org. Biomol. Chem.*, 2010, **8**, 576–591.

102 S. D. Mansfield, H. Kim, F. Lu and J. Ralph, *Nat. Protoc.*, 2012, **7**, 1579.

103 L. da Costa Sousa, M. Jin, S. P. S. Chundawat, V. Bokade, X. Tang, A. Azarpira, F. Lu, U. Avci, J. Humpula, N. Uppugundla, C. Gunawan, S. Pattathil, A. M. Cheh, N. Kothari, R. Kumar, J. Ralph, M. G. Hahn, C. E. Wyman, S. Singh, B. A. Simmons, B. E. Dale and V. Balan, *Energy Environ. Sci.*, 2016, **9**, 1215–1223.