Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps†

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A catalytic lignocellulose biorefinery process is presented, valorizing both polysaccharide and lignin components into a handful of chemicals. To that end, birch sawdust is efficiently delignified through simultaneous solvolysis and catalytic hydrogenolysis in the presence of a Ru on carbon catalyst (Ru/C) in methanol under a H₂ atmosphere at elevated temperature, resulting in a carbohydrate pulp and a lignin oil. The lignin oil yields above 50% of phenolic monomers (mainly 4-n-propylguaiacol and 4-n-propylsyringol) and about 20% of a set of phenolic dimers, relative to the original lignin content, next to phenolic oligomers. The structural features of the lignin monomers, dimers and oligomers were identified by a combination of GC/MS, GPC and 2D HSQC NMR techniques, showing interesting functionalities for forthcoming polymer applications. The effect of several key parameters like temperature, reaction time, wood particle size, reactor loading, catalyst reusability and the influence of solvent and gas were examined in view of the phenolic product yield, the degree of delignification and the sugar retention as a first assessment of the techno-economic feasibility of this biorefinery process. The separated carbohydrate pulp contains up to 92% of the initial polysaccharides, with a nearly quantitative retention of cellulose. Pulp valorization was demonstrated by its chemocatalytic conversion to sugar polyols, showing the multiple use of Ru/C, initially applied in the hydrogenolysis process. Various lignocellulosic substrates, including genetically modified lines of Arabidopsis thaliana, were finally processed in the hydrogenolytic biorefinery, indicating lignocellulose rich in syringyl-type lignin, as found in hardwoods, as the ideal feedstock for the production of chemicals.

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Broader context

There is a growing consensus that lignin valorization is essential for the environmental sustainability and economics of a lignocellulosic biorefinery. The thermal conversion of lignocellulose to renewable gas and bio-oils has been heavily researched and their benefits and challenges for industrial implementation have become clear now. However, to preserve Nature’s highly functionalized materials, milder treatments are required, fractionating lignocellulose into its main components, namely carbohydrates and lignin. Inspired by old delignification processes, many initiatives have been presented to remove lignin, while producing pure hemicellulose and cellulose products. Initially the chemical occurrence of disassembled lignin and its use for the production of chemicals were not a primary concern, but because of the importance of lignin valorization, it is currently one of the foremost challenges of new biorefinery strategies. This work promotes a lignin-first biorefinery approach, converting lignin into useful chemicals during fractionation, while keeping the pulp fraction available for further processing.

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Introduction

Research on the novel ‘biorefinery’ concept has lately received a lot of attention as a sustainable alternative for the current petrochemical industry. Renewable biomass, instead of fossil resources, is herein used to produce heat, power, fuels, chemicals and materials.1–11 Lignocellulose, a sustainable and highly abundant source of biomass, is typically presented as a promising feedstock.2,5 Since its three main components, cellulose, hemicellulose and lignin, are located in the cell wall as a complex rigid matrix, thermal and solvolytic processing is required before the selective conversion towards value-added products is possible.2,3

Numerous lignocellulose conversion efforts have been made, often preferring integrated biorefinery strategies with use of the entire plant because of feasibility reasons. A well-known example is the gasification of lignocellulose to syngas, ultimately generating electricity/heat or leading to the production of chemicals like alkanes, methanol and H2.12 The production of bio-oils via pyrolysis or liquefaction is another option, typically yielding unstable bio-oils, containing hundreds of different oxygenates. These bio-oils can be upgraded catalytically before being used as biofuels.13–17 Through fast-hydrolysis, the production of a high-quality liquid fuel (C4–C8) can be achieved using a single procedure, combining pyrolysis with subsequent catalytic hydrodeoxygenation in the gas phase.18,19 Also, liquefaction in supercritical methanol in the presence of a Cu catalyst was recently demonstrated, resulting in a combustible liquid of complex composition.20,21

One may argue if forthcoming biorefineries should merely focus on the strong defunctionalization of the highly functionalized bio-based (macro)molecules or whether a milder and more selective conversion of Nature’s precious resources to a handful of value-added chemicals is a better research focus. Exploiting the original chemical structure and functionality, hence preserving a high atom efficiency, is probably the best and most encouraging strategy for the creation of value, if technoeconomically applicable.10

Other biorefinery approaches therefore encourage a prior fractionation of the lignocellulose matrix into its different components (i.e. carbohydrates, lignin,...), thereby reducing the complexity of downstream separation and conversion processes. Most lignocellulosic fractionations involve the removal of lignin (delignification), often accompanied by a major part of hemicellulose, to yield a rather pure cellulose substrate. Some of these methods are industrially applied in paper mills or will be used in the production of next generation biofuels like bioethanol as well as biofuel precursors like bio-derived naphtha.2,3,18,19,22–26 Two intriguing fractionation methods were recently introduced that perform a complete solubilisation of the lignocellulose substrate. A mechanocatalytic approach was demonstrated, converting lignocellulose into water soluble oligosaccharides and lignin fragments.27 Further processing can result in various products like sugars,28 furfural,29 or γ-valerolactone,30 next to a lignin precipitate. Interestingly, the sugar processing towards γ-valerolactone has been achieved in a continuous flow mode.10 The second method is based on the promoting effect of γ-valerolactone on the acid-catalyzed saccharification of lignocellulose, enabling very high yields of soluble carbohydrates and a water insoluble lignin fraction.31 However, for all aforementioned fractionation methods, the chemical structure of the obtained lignin precipitates is inevitably degraded to some extent, when compared to that of the original ‘protolignin’.25,26,32–36 Even under relatively mild conditions, such as those used in typical organosolv fractionations, the lignin structure is altered.37–40 Such alterations, amplified in the presence of acid or base, are the result of several side-reactions like the breaking of readily cleavable ether linkages and the formation of new stable C–C bonds.35–39,41 Besides lignin’s recalcitrant behaviour, it also shows a species-specific distribution of bonds and building blocks, further complicating a governable conversion process to a handful of valuable products. Lignin recovery and its subsequent valorization to chemicals have never been of primary concern. Instead, lignin side streams are typically burned for energy recuperation or used in low-value material applications.42,43

However, since lignin constitutes the largest direct source of renewable aromatic/phenolic compounds on the Earth, the conversion opportunities towards aromatics but also other chemicals should not be underestimated.22,32,36,44,45 With the emergence of next-generation biofuels, a huge amount of lignin is expected to enter the market and with that, an increased awareness of lignin’s potential.26,46,47 Recent reports have also predicted the essential role of lignin valorization in the economics of lignocellulosic biorefining.22,26 Finding efficient processing routes to convert lignin into valuable products, while maintaining a maximum valorization of the carbohydrate pulp, may thus be regarded essential to strongly expand the economic feasibility and environmental sustainability of the lignocellulosic biorefinery. Numerous efforts have recently led to great progress in the conversion of various types of lignin streams, e.g. originating from pulp- and paper industries and organosolv processes, to valuable chemicals.32,48–57

In our view, a forthcoming biorefinery should deal with the unfavorable fractionation side-effects so as to allow for processing lignin in its most reactive and workable form. Milder solvolytic fractionation conditions, currently under investigation using less acidic or basic compounds, are a valid option to improve the potential valorization of the resulting lignin fraction.3,31,37 However, perhaps the most promising strategy is a fractionation process including catalytic hydrogenolysis in the liquid phase, starting from raw unfractionated lignocellulose. In contrast to previous methods, typically forming a condensed lignin polymer fraction, the thermal and solvolytic disassembly of lignin (delignification) is here immediately followed by the reductive stabilization of lignin’s most reactive intermediates like olefins and carbonyls into a handful of soluble and stable low-molecular-weight phenolic products. This fractionation strategy can be denominated as a ‘lignin-first’ biorefinery, as the valorization of lignin to chemicals is performed before carbohydrate processing. Though being conveyed in the old literature,29–41 its integration in a contemporary biorefinery was only recently discussed by a handful of research groups.62–67 Interestingly, high lignin monomer yields, ranging from 10 to 54%, have thus
Abu-Omar et al. elegantly avoid the use of an external H₂-source, while yielding selective hydrogenolysis of protolignin to 4-n-propylguaiacol and 4-n-propylsyringol. On the other hand, Galkin et al. obtained high yields of 4-(prop-1-enyl) guaiacol and 4-(prop-1-enyl) syringol using Pd on carbon in a water-ethanol solvent system, with formic acid from wood acting as the hydrogen source. Both systems elegantly avoid the use of an external H₂-source, while yielding a solid carbohydrate pulp. Although these studies enable high phenolic monomer yields, other aspects like the degree of delignification, the carbohydrate retention in the pulp or further processing opportunities of the pulp are not studied. Rinaldi et al. proposed RANEY Ni in an isopropanol-water solvent mixture, with isopropanol as the hydrogen donor. High degrees of delignification and carbohydrate retention in the pulp as well as the enzymatic processing of the pulp were demonstrated. The results however also showed the complexity of the low-molecular weight lignin product mixture. Recently Abu-Omar et al. presented a selective hydrogenolysis of protolignin with Zn modified Pd nanoparticles on carbon with external H₂, focusing on the lignin monomers and the enzymatic conversion of the retained pulp.

This paper presents a lignocellulosic fractionation process that results in a high degree of delignification, a selective conversion of lignin towards a handful of useful chemicals and a maximal sugar retention, obtaining a carbohydrate pulp that is applicable for a myriad of downstream processes (Scheme 1). For instance, Li et al. presented a Ni-W₃C/AC catalytic system in water that not only depolymerized lignin, but also converted the carbohydrate fraction into C₂–C₃ diols. However, the presence of all products in the same liquid phase might ultimately complicate product separation, while the integrated carbohydrate conversion reduces the versatility of carbohydrate processing towards other chemicals or materials. Using Ni on carbon as a catalyst and methanol as both solvent and hydrogen donor, Song et al. showed the selective hydrogenolysis of protolignin to 4-n-propylguaiacol and 4-n-propylsyringol. On the other hand, Galkin et al. obtained high yields of 4-(prop-1-enyl) guaiacol and 4-(prop-1-enyl) syringol using Pd on carbon in a water-ethanol solvent system, with formic acid from wood acting as the hydrogen source. Both systems elegantly avoid the use of an external H₂-source, while yielding a solid carbohydrate pulp. Although these studies enable high phenolic monomer yields, other aspects like the degree of delignification, the carbohydrate retention in the pulp or further processing opportunities of the pulp are not studied. Rinaldi et al. proposed RANEY Ni in an isopropanol-water solvent mixture, with isopropanol as the hydrogen donor. High degrees of delignification and carbohydrate retention in the pulp as well as the enzymatic processing of the pulp were demonstrated. The results however also showed the complexity of the low-molecular weight lignin product mixture. Recently Abu-Omar et al. presented a selective hydrogenolysis of protolignin with Zn modified Pd nanoparticles on carbon with external H₂, focusing on the lignin monomers and the enzymatic conversion of the retained pulp.
towards chemocatalytic conversion is successfully illustrated by its conversion to a mixture of sugar polys. Earlier reported bifunctional acid-redox catalysis was applied here,\textsuperscript{72–77} to demonstrate the reusability of the Ru/C catalyst, originally used in the first hydrogenolysis step (Scheme 1).

**Experimental section**

For a list of all used chemicals and materials as well as a more complete description of the experimental procedures, the reader is kindly referred to the ESL.\textsuperscript{†}

In a typical catalytic hydrogenolysis experiment, 2 g of birch sawdust (Betula pendula from Ecobois, Ghent), 0.3 g of Ru/C and 40 mL of methanol were loaded into a 100 mL stainless steel batch reactor (Parr Instruments Co.). The reactor was sealed, flushed with N\textsubscript{2} and pressurized with 3 MPa H\textsubscript{2} at room temperature (RT). The mixture was stirred at 700 rpm and the temperature was increased to 523 K (\textsim 10 K min\textsuperscript{−1}) at which the pressure reached \textsim 12 MPa (\textsim 6.5 MPa at 473 K) and the reaction was started. After reaction, the autoclave was cooled in water and depressurized at RT.

To analyze the lignin monomers, a weighed amount of external standard (2-isopropylphenol) was added and mixed in the reactor.\textsuperscript{78–80} GC/MS was used to identify the phenolic amide (MSTFA), was introduced to increase their volatility before GC analysis.78–80 GC/MS was used to identify the phenolic monomers, a weighed amount of external standard (2-isopropylphenol) was added and mixed in the reactor. The reactor content was filtered and a sample of the filtrate was used for GC analysis. To analyze the dimers, a derivatization step, via trimethylsilylation with N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA), was introduced to increase their volatility before GC analysis.78–80 GC/MS was used to identify the phenolic mono- and dimers, while gel permeation chromatography (GPC) and 2D HSQC NMR were applied for qualitative analyses of the lignin oil. To determine the degree of delignification, the raw filtered methanol product mixture was evaporated and a brown lignin oil was obtained. The lignin oil was subjected to threefold liquid–liquid extraction using dichloromethane (DCM) and water to separate the soluble lignin- and sugar-derived products. Finally the DCM-extracted phase was dried to obtain the ‘DCM lignin oil’. The weight of the DCM lignin oil is then used to determine the degree of delignification (based on Klason lignin weight). A corrected value was added in the results, to account for the expected presence of birch extractives in the DCM lignin oil. The sugar retention was based on the amount of sugars in the lignocellulose substrates and in the carbohydrate pulp after hydrogenolysis, using a standard total sugar procedure, adapted with hydrolysis conditions for cellulose-rich materials.\textsuperscript{81–83}

The chemocatalytic conversion of the carbohydrate pulp was demonstrated in a hydrolytic hydrogenation experiment. The carbohydrate pulp (\textsim 1.4 g including 0.3 g Ru/C) was mixed with tungstosilicic acid (0.5 g) and water (50 mL) in a 100 mL stainless steel batch reactor (Parr Instruments Co.). The reactor was sealed, flushed with N\textsubscript{2} and subsequently pressurized with 5 MPa H\textsubscript{2} at RT. The mixture was stirred at 700 rpm and the temperature was increased to 463 K (\textsim 13 K min\textsuperscript{−1}), at which the pressure reached \textsim 7 MPa and the reaction was started. After reaction, the autoclave was rapidly cooled in water and depressurized at RT. A sample of the reaction product was taken and centrifuged. External standard (myo-inositol) was added to the supernatant and dried under vacuum, after which it was derivatized via trimethylsilylation and analyzed by GC.

**Table 1** Comparison of the results after the hydrogenolysis of birch wood under varying reaction conditions\textsuperscript{a}

| Entry | \(t\) (h) | Birch (g mL\textsuperscript{−1}) | Phenolic product yields\textsuperscript{b} (C%) | Sugar retention\textsuperscript{c} (%) |
|-------|----------|-------------------------------|---------------------------------|------------------|
|       |          |                               | PG + PS\textsuperscript{d} | Total monomers | Dimers | Delignification\textsuperscript{e} (wt%) | C6 | C5 | Total |
| 1     | 6        | 6.05                          | 41 (79)                       | 52               | 16    | 92 (79)                      | 95 | 47 | 78    |
| 2\textsuperscript{b} | 6        | 6.05                          | 17 (70)                       | 25               | 11    | <            | <3 | <1 | 1     |
| 3\textsuperscript{c} | 6        | 6.05                          | 0.9 [12]                      | 8                | 9     | 95 [82]                      | 86 | 68 | 79    |
| 4\textsuperscript{d} | 6        | 6.05                          | 38 (77)                       | 43               | 16    | 78 (65)                      | 97 | 84 | 92    |
| 5     | 3        | 0.05                          | 42 (84)                       | 50               | 18    | 83 (80)                      | 95 | 56 | 81    |
| 6     | 0.5      | 0.05                          | 33 (84)                       | 39               | 18    | 81 (68)                      | 96 | 67 | 86    |
| 7\textsuperscript{e} | 3        | 0.05                          | 49 (92)                       | 51               | 14    | 98 (85)                      | 94 | 63 | 83    |
| 8\textsuperscript{f} | 3        | 0.05                          | 45 (87)                       | 40               | 17    | 92 (79)                      | 99 | 65 | 87    |
| 9\textsuperscript{g} | 3        | 0.05                          | 30 (62)                       | 48               | 15    | 92 (79)                      | 93 | 83 | 90    |
| 10\textsuperscript{h} | 3        | 0.25                          | 44 (87)                       | 50               | 14    | 94 (81)                      | 90 | 52 | 77    |
| 11\textsuperscript{i} | 3        | 0.25                          | 44 (89)                       | 49               | 15    | 92 (79)                      | 92 | 55 | 79    |

\textsuperscript{a} Reaction conditions: 2 g of birch sawdust (particle size 0.25–0.50 mm; composition: 19.5 wt% lignin, 2.5 wt% extractives, 39.3 wt% C\textsubscript{6} sugars, and 20.7 wt% C\textsubscript{5} sugars), 0.3 g of 5% Ru/C, 40 mL of methanol, 523 K and 3 MPa H\textsubscript{2} at RT (\textsim 12 MPa at 523 K).\textsuperscript{3} 40 mL of water as the solvent, no delignification value due to the complete dissolution of lignocellulose.\textsuperscript{4} Reaction without catalyst.\textsuperscript{5} Reaction temperature 473 K (\textsim 6.5 MPa).\textsuperscript{6} 1 MPa H\textsubscript{2} at RT.\textsuperscript{7} Atmospheric pressure of N\textsubscript{2} at RT.\textsuperscript{8} Reuse of the catalyst (0.3 g) after liquid–liquid (methanol/decane) separation of Ru/C and the carbohydrate fraction.\textsuperscript{9} 10 g of birch sawdust in 40 mL of methanol and 1 g of 5% Ru/C.\textsuperscript{10} Reaction performed in a 600 mL batch reactor with 60 g of birch sawdust in 240 mL of methanol, and 6 g of 5% Ru/C.\textsuperscript{11} Yields are carbon-based, assuming a birch protolignin carbon content of 64 wt% (ESI). Primary products are 4-\textit{p}-propyguaiacol (PG) and 4-\textit{p}-proplysyringol (PS), PS/PG ratios vary around 3, and values in parentheses refer to the selectivity of both products based on the total phenolic monomer yield.\textsuperscript{3} Based on the weight of the dichloromethane (DCM) extracted fraction, specified in the text as ‘DCM lignin oil’, and the Klason lignin weight. These values slightly overestimate the real delignification degree due to the concomitant removal of other extractives. Values in parentheses are corrected for the weight of these birch extractives.\textsuperscript{3} Based on the amount of carbon in the sugar fractions of birch sawdust and the produced carbohydrate pulps (ESI).

**Results and discussion**

**Catalytic delignification of birch wood**

Initial catalytic reactions were executed using birch sawdust as a benchmark hardwood substrate and Ru/C as the solid redox catalyst typically at 3 MPa H\textsubscript{2} (RT) and 523 K (Table 1). All reactions in Table 1 show 4-\textit{p}-propyguaiacol (PG) and 4-\textit{p}-proplysyringol (PS)
as main compounds, with a PS/PG ratio of around three, being in close agreement with the syringyl/guaiacyl ratio of birch wood lignin.\(^8\)\(^4\) Besides PG and PS, other monomers like 4-\(n\)-propylguaiacol, 4-ethylsyringol, 4-\(n\)-propylsyringol, 4-\(n\)-propanolguaiacol and 4-\(n\)-propanolsyringol were identified (see Fig. 1a). A more detailed monomer distribution for all experiments in Table 1 is presented in the ESI,\(^\dagger\) Table S1. Next to the lignin monomer yields, also the dimer yields, the degree of delignification and the retention of sugars in the carbohydrate pulp, as defined in the Experimental section and the ESI,\(^\dagger\) are listed in Table 1.

Entries 1 and 2 compare the results for reactions in methanol and water, respectively, as commonly used solvents in lignocellulose pretreatment and lignin valorization. With methanol, more than 90% of lignin was solubilized, yielding 52% phenolic monomers with a selectivity of 79% towards PG and PS. Next to monomers, a phenolic dimer yield of 16% was obtained, totaling a well-defined lignin product yield of almost 70% to phenolic mono- and dimers. The nature of the dimer structures is discussed below. Furthermore, a total carbohydrate pulp retention as high as 78% was obtained in methanol, the retention of C6 sugars being almost quantitative as opposed to a 47% retention for C5 sugars. The higher retention of C6 sugars compared to C5 sugars in the pulp is due to a better protection of glucose (C6) in the crystalline cellulose structure, while C5 sugars like xylose in the amorphous hemicellulose are more prone to solvolysis. The released C5 sugars mainly appear in methanol as the corresponding methyl sugars, which may be useful in the detergent and soap industries, or could be hydrolyzed readily into the C5 sugar. Hence, with birch sawdust, the primary sugar product in methanol was methylated xylose, corresponding to 33% of the initial carbon in hemicellulose. In addition, the acetyl groups in hemicellulose, representing about 3 to 4 wt% of birch,\(^8\)\(^5\) were entirely removed and appeared in the methanol phase as methyl acetate, an interesting bio-derived solvent\(^8\)\(^6\) and precursor for chemicals like acetic anhydride and vinyl acetate.\(^8\)\(^7\)–\(^8\)\(^9\) Separation of methyl acetate and methanol is common practice in industry.\(^8\)\(^9\) In comparison with methanol, the use of water in entry 2 resulted in a lower phenolic monomer yield of 25% and a complete dissolution of the carbohydrate fraction (no pulp remaining). The carbohydrates mainly appeared as water soluble polyols. For the envisioned biorefinery concept, water is thus not a suitable solvent.

Next, the essential role of Ru/C is demonstrated in entry 3. Without catalyst a phenolic monomer yield of only 8% and a dimer yield of 9% were obtained when using the conditions from entry 1. The much higher monomer yield with Ru/C is likely due to an efficient hydrogenolysis of most of the ether-bonds between phenolic units, combined with a reductive stabilization of reactive intermediates. This prevents repolymerization reactions leading to new stable C–C bonds within the lignin structural network. The product spectrum of the uncatalyzed reaction indeed shifts towards phenolic compounds with unsaturated C2-chains (ESI,\(^\dagger\) Table S1). Lowering of the reaction temperature to 473 K (entry 4) resulted in a higher retention of the C5 sugars (here 84%), corresponding to a total pulp retention of 92%, with only a small decrease in the phenolic monomer yield as well as in the delignification efficiency. A similar trend is observed by lowering the contact time at 523 K (entries 5 and 6), leading to a
monomeric phenol yield of 50% after 3 h and 39% after 0.5 h, along with a C6/C5 sugar retention in the pulp of 95/56 and 96/67, respectively. During a shorter reaction time, the selectivity to PG and PS within the monomeric fraction increased slightly to 84%. The gas chromatogram in Fig. 1a illustrates the monomer distribution for entry 5. Moreover, gas analysis, showing low amounts of CO and methane (ESI,† Table S2), reveals a minor loss of carbon in the gas phase, indicating a high stability of the solvent, methanol, in the presented biorefinery process.

To conclude, various parameters, determining the severity of the reaction conditions, need to be well-balanced to optimize the phenolic monomer yield, the product selectivity and the degree of delignification as well as the carbohydrate pulp retention. Based on the aforementioned results, the reaction conditions from entry 5 were used for the following experiments.

Several potential constraints were additionally tested to anticipate the technical and economic feasibility of an industrial implementation. Interestingly, a reaction executed at reduced H2 pressure (1 MPa at RT) showed a similar catalytic performance (entry 7). Here, birch wood is efficiently delignified, yielding 51% of phenolic monomers with up to 92% of PG and PS, while the retention of C6 sugars is nearly complete and 63% for the C5 sugars. The use of N2 at atmospheric pressure, thus implying methanol or lignocellulose itself as a reducing source, also proved to be possible, in agreement with previous reports.63,64,90 However, in our hands the phenolic monomer yield was considerably lower (entry 8) than when executed under a H2 atmosphere. Crucial for the viability of the biorefinery is also the reusability of the Ru/C catalyst. Ru/C was separated from the carbohydrate pulp by a liquid–liquid extraction as described in the ESI.† In entry 9, the recycled catalyst showed a phenolic monomer yield of 48%, very similar to the 50% obtained with a fresh catalyst. A shift in selectivity towards more propanol-substituted compounds is reported in the literature.101–104 Many C–H cross-signals in the HSQC spectrum are well reported in literature like those of the main substructures (2D) heteronuclear single quantum coherence (HSQC) NMR analysis (Fig. 2b). This technique is a powerful tool for the identification of lignin structural features like interunit linkages,101–104 Many C–H cross-signals in the HSQC spectrum are well reported in literature like those of the main substructures present in native lignin, viz. p-coumaryl, coniferyl and sinapyl.

Chemical composition of the lignin oil

Liquid–liquid extraction of the raw lignin oil with DCM and water was applied to remove the soluble sugar-derived products prior to a detailed analysis of the chemical composition. Next to the earlier discussed phenolic monomers, the isolated birch ‘DCM lignin oil’ (see Experimental section) also contains a set of dimers and some small oligomers. This can be derived from the GPC chromatogram in Fig. 2a (blue line), which shows two major signals, at circa 200 and 450 g mol−1 (based on poly-styrene standards), suggesting a successful depolymerization mainly towards monomers and dimers. In an effort to elucidate their chemical structure, both GC/MS as well as NMR analyses were conducted on the DCM lignin oil.

Before GC/MS analysis, the DCM lignin oil was first derivatized via trimethylsilylation to improve the volatility of the dimers. The identification of these dimers was supported by literature78–80 and the results are presented in the chromatographic analysis in Fig. 1b. The first observation is the absence of ether bonds in the present dimer fraction, except for a minor signal at 22.2 min, representing compound 2 with a relatively stable 4-O-5 ether bond.91,92 This suggests a nearly complete hydrogenolysis of the ether bonds, present in the original protolignin structure. Taking into account the ether function density of a typical birch lignin and assuming that most C–C bonds are not broken under the applied conditions, one can estimate that the previously determined monomer yield of about 50% is close to the expected theoretical maximum monomer yield of birch wood, as discussed in the ESI.† 45,62–64

Within the identified dimer fraction, the largest part of C–C linkages is represented by β-1 bonds, followed by β-5 and to a lesser extent 5–5 bonds, as illustrated in the structures of compounds 1 to 12 in Fig. 1b. These interunit linkages also represent the most important C–C bonds in birch lignin.22,85 Although β–β linkages are also common in birch lignin, no dimers with this bond were identified in the product mixture. Most dimers thus comprise two phenol units which are p,p′- or o,p′-coupled by an ethylene bridge. Remarkably, the bridge is either unsubstituted (as in 3–5, 8, and 9) or contains a –CH2OH substituent (as in 6, 7, and 10–12), whereas a –CH3 substituent was never analyzed. Moreover, unlike the monomers, the dimers always possess at least two hydroxyl groups, making them favourable candidates as building blocks for a broad range of polymers (e.g. polyureethanes, polysteres, polycarbonates).93–100
alcohol units, while connected through various interunit linkages such as β-O-4, phenylcoumaran, resinol, β-1, spirodienone, dibenzodioxocin and 4-O-5. The oxygenated side chain region of the HSQC spectra, represented in the δC/δH region of 50–95/2.5–6 ppm, gives useful information about these interunit linkages. In lignin depolymerization studies, HSQC NMR is often used to examine the cleavage of ether bonds by following the decrease in intensity of C–H correlation signals related to substructures with ether bonds. Upon depolymerization however, also new correlation signals appear, attributed to chemical structures in which the original ether bonds between the phenol units are broken, but the C–C bonds remain. Breaking of α-O-4 in a phenylcoumaran unit for example results in a substructure of two phenol units linked by a β-5 bond (Scheme 2). Such structures were also identified by GC/MS in the dimer fraction of the ‘DCM lignin oil’, shown in Fig. 1b (see structures 5, 7, 9, and 11). Unfortunately, only little information is available about C–H correlation signals in a HSQC spectrum of lignin samples solely comprising C–C interunit linkages. Predictions via ChemDraw of δC and δH chemical shifts of a range of lignin substructures (ESI,† Table S3) were therefore performed, and were sufficiently accurate, compared to literature values, to be helpful in the identification of structures and functionalities (ESI,† Table S3). A plot of the
In order to characterize the di- and oligomer fractions in the DCM lignin oil, the oil was first extracted with hexane to remove most of the apolar monomers, together with a small part of the short apolar oligomers like the dimers 1, 2, 3, 5, and 9 in Fig. 1b. The separation of the mono- from the oligomeric fraction is clearly demonstrated by GPC analysis (Fig. 2a) of the DCM lignin oil, the hexane extracted phase and the residue after hexane extraction (hexane residue). The corresponding HSQC spectra of the hexane-extracted phase (ESI,† Fig. S5) shows the expected C–H correlation signals of the earlier identified monomers with mainly propyl and some ethyl side chains as the dominant signals. The HSQC spectra of the DCM lignin oil and the hexane residue, containing most of the oligomers, are displayed in Fig. 2b and c. The correlation signals of ethyl, propyl and propanol side-chains, the methoxy groups and the guaiacyl and syringyl structures are marked in colour. For each fraction, additional 1H-, 13C- and DEPT-NMR spectra are provided in the ESI,† Fig. S6–S8. In the side-chain region of the spectra (Fig. 2b top and c top), the Cα-H2 and Cβ-H3 correlation signals of substructures with ether bonds are very small or even absent (region marked with α/βether), indicating that most of the ether bonds in β-O-4, phenylcoumaran, resinol and spirodienone structures have indeed been broken, in agreement with the GC/MS structural analysis. Instead, especially for the hexane residue, a number of signals were observed in the δc/δh 22–48/1.4–3.4 ppm region (marked with α/βnonether). According to the Chemdraw NMR, these signals can be assigned as Cα–Cβ and Cβ–H3 correlation signals of structures with β, β-1 and β-β C–C bonds, but without ether bonds. The δc/δh 58–68/3.2–4.5 ppm region further shows Cγ–H3 correlation signals of linked (via C–C and ether bonds) or free propanol side chains (marked with γether). As more signals can be observed in this region than in the δc/δh 0.5–1.5 ppm region, corresponding to Cβ–H3 correlation signals of linked or free propyl side chains (marked with γether), it is suggested that rather the propanol side-chains instead of the propyl units act as bridging groups between phenol units (like in the dimers 6, 7, and 10–12 in Fig. 1b). The propyl side-chains are mainly present as free side chains in the different compounds. These NMR results corroborate the earlier GC/MS structure analysis, in which propyl-type bridges were also not observed (Fig. 1b). Next to propanol groups, also ethyl side chains represent a significant fraction of the bridges between the phenol units in the oligomer fraction (see dimer structures 3, 4, 5, 8, and 9 in Fig. 1b). These ethyl-bridges are likely formed by Cβ–Cβ bond cleavage in original propanol-type linkages, which may proceed via retro-condensation or direct hydrogenolysis chemistry.59,107,108

The aromatic region of the HSQC spectra (Fig. 2b bottom and c bottom) clearly shows the correlation signals of free guaiacyl- and syringyl-units (marked in color). However, in their vicinity, a set of other signals was observed, especially in the hexane residue, indicative of compounds with varying chemical environments close to the guaiacyl and syringyl C–H entities. This is most likely due to C–C linkages between side-chains, between side-chains and aromatic rings or between aromatic rings. In the spectrum of the hexane residue, three signals were unambiguously assigned to C–H entities of guaiacyl units involved in β-5 and β-1 bonds, in accordance with the literature (Fig. 2c bottom, as the dimer structure 3–12 in Fig. 1b).109

The 2D HSQC NMR analysis showed a high content of hydroxyls in the phenolic oligomers of the hexane residue. Such a high content is of paramount importance to their potential use in the synthesis of e.g., polyurethanes and polyesters.90–95 The quantification of the OH-content, following a reported acetylation method using 1H-NMR analysis (ESI,† Fig. S9) demonstrates a remarkably high OH-content of 8.83 mmol g−1, corresponding to 1.47–1.87 OH-groups per phenolic unit, assuming an average phenol monomer MW in the oligomer structure of 166 to 212 g mol−1, respectively. Such a high OH-content thus corroborates the real potential of the produced polar lignin oligomers in several future polymer applications.

Comparison with different lignocellulosic feedstocks

Now that the nature and the benefits of the catalytic system have been demonstrated and the main products have been analyzed, it is equally important to comprehend the impact of the lignocellulose structure variability. Reaction parameters as in entry 5 (Table 1) were used for the comparison of feedstocks. First, the advantage of using a raw lignocellulose material instead of a separated lignin stream is demonstrated. Ethanol organosolv lignin from birch (EOL) was chosen because of its high-purity (viz. sulfur-free, low in residual carbohydrates and ash).37–40 Compared with the former results on birch wood, a low yield of phenolic monomers (3%) and dimers (6%) was obtained (Table 2, entries 1 and 2). Most likely, an altered chemical lignin structure, i.e. a decreased content of ether bonds and an increased amount of C–C bonds compared to protolignin, is responsible for the limited degree of depolymerization with EOL. This result is further supported by GPC analysis of initial and reacted EOL, only showing a small shift towards smaller components (Fig. 3). For the production of high-value chemicals from an isolated lignin like the EOL used
Table 2  Comparison of several lignocellulose substrates in the reductive delignification processa and the second step carbohydrate conversionb

| Entry | Substrate | PG + PS% | Total monomers | Dimers | Delignification% | Total sugar retention% | Total sugar polylol yield% |
|-------|-----------|----------|----------------|--------|-----------------|------------------------|--------------------------|
| 1     | Birch     | 42 (84)  | 50             | 18     | 93 (80)         | 81                     | 74                       |
| 2     | EOL birch | 1.7 (59) | 3              | 6      | —               | —                      | —                        |
| 3     | Poplar    | 33 (75)  | 44             | 16     | 86 (65)         | 85                     | 52                       |
| 4     | Softwood  | 17 (83)  | 21             | 15     | 56 (40)         | 78                     | 63                       |
| 5     | Miscanthus| 12 (43)  | 27             | 8      | 63 (36)         | 85                     | 59                       |

a Reaction conditions: 2 g of substrate, 0.3 g of 5% Ru/C, 40 mL of methanol, 3 h, 3 MPa H2 at RT (~12 MPa at 523 K). b Reaction conditions: carbohydrate pulp fraction + Ru/C catalyst from step 1, 0.5 g of H4[Si(W3O10)4]2 · xH2O, 50 mL of water, 16 h, 463 K, 3 MPa H2 at RT (~7 MPa at 463 K). c 1 g of ethanol organosolv lignin from birch (EOL), reaction conditions for the production of EOL are given in the ESI, Table S5. d Pine–spruce mixture. e A definition of the presented parameters is provided in the caption of Table 1 and in the ESI. PS/PG ratios are provided in the ESI, Table S4. f Yields are based on the amount of carbon in the obtained carbohydrate fraction (procedure in the ESI).

With 15%, the dimer yield was however comparable with that of the hardwoods. As expected, the mono- and dimer products of softwood almost exclusively contained G-units, as opposed to the high S-content in the mono- and dimers from hardwoods (Fig. 4a and ESI, Table S4 and S5 and Fig. S10). Softwood conversion also led to higher amounts of 5-5 bonded dimers (ESI, Table S10) in agreement with its nearly exclusive formation from G-moieties.

Finally, miscanthus grasses resulted in an intermediate degree of delignification as well as an intermediate monomer yield, with the formation of two specific phenolic monomers, assigned to the methanolyis and side-chain hydrogenation of p-coumaric and ferulic acid (ESI, Fig. S11). Both acids are typically present in grasses.38,39,113

These results suggest a direct correlation between the lignin building block composition and its tendency to depolymerize into mono-, di- and oligomers. Fig. 4b shows the total phenolic monomer yield after hydrogenolysis of each feedstock as a function of its syringyl (S) content in the DCM lignin oil (ESI, Table S4). This was determined by integrating the H2,6,G 2 and S2,6 correlation signal in the aromatic region of the HSQC spectra.114 It becomes clear that a higher S-content in the DCM lignin oil is directly correlated with a higher phenolic monomer yield as well as a more efficient delignification (Table 2). This is in accordance with earlier results, obtained for Kraft pulping, in which a higher S-content in lignin also resulted in a more efficient wood delignification.115–117

To avoid the influence of species-specific properties rather than the type of lignin building block, similar feedstock tests were conducted on a single species. To that end, Arabidopsis thaliana (arabidopsis) genotypes were used that have lignin with a contrasting S-content. The Arabidopsis genes ferulate 5-hydroxylase (F5H1) and caffeic acid O-methyltransferase (COMT) are crucial in the biosynthesis of S-units. Consequently, the corresponding mutants, F5H1-2 and COMT-1, are rich in G-units and have only traces of S-units.70,118,119 On the other hand, over-expression of F5H1 (CAH:F5H1) resulted in plants with high S-content and low G-content.118,120,121 Finally, wild-type Arabidopsis plants have a G/S ratio of about 2/1.70 The lignin content and the monomer composition of each line, determined by thioacidolysis, are shown in the ESI, Table S6. The monomer product distribution has been added in the
Thus, a comparison of the hydrogenolytic results of several lignocellulosic feedstocks emphasizes the importance of a smart feedstock choice. The results suggest that hardwoods and genetically engineered plants with a high S-content are the preferred substrates for the lignin-first biorefinery.

**Valorization of carbohydrate pulps to chemicals**

In the context of a sustainable and economically viable biorefinery, the valorization of protolignin can only be justified when the remaining carbohydrate pulp is also readily processable towards value-added products. As the recent literature already describes the simultaneous fermentation of hexoses and pentoses towards ethanol, an enzymatic conversion process can be envisioned in analogy with the next generation bio-ethanol industry. Powder X-ray diffraction patterns of the original birch wood and the isolated carbohydrate pulp after catalytic delignification, compared in the ESI,† Fig. S12, indicate the presence of crystalline cellulose in both samples. Although a larger set of parameters needs to be evaluated, this observation already suggests that paper production might be possible.

Next to biofuels and paper, a third valorization option is the chemocatalytic conversion of the pulp towards high-value commodity chemicals. Here, the presence of the Ru/C catalyst in the carbohydrate pulp was exploited and a conversion towards sugar polyols, based on a bifunctional catalytic system from Geboers et al., was demonstrated. Hereto, tungstosilicic acid and water were mixed with an isolated pulp fraction and subsequently heated to 463 K under external H₂ pressure. The hydrolytic power of the acid is used to convert cellulose into glucose and hemicellulose into mainly xylene and in smaller amounts into arabinose and mannose. The released sugars are then hydrogenated to their respective sugar alcohols in the presence of the Ru/C catalyst. Fig. 5 shows the obtained yields of sugar polyols as a function of the reaction time. The product distribution and the general chemical structure of the products are displayed as well. After 8 h, a sugar polyol yield of 70% was obtained, starting from the pulp of entry 5, Table 1 (dotted lines), despite the presence of residual lignin. Sorbitol, xylitol and their anhydrous analogues constitute the main product fraction. Mannitol and arabinitol as well as the smaller polyols erythritol, threitol, glycerol, propylene glycol and ethylene glycol complete the remaining fraction. A maximal total yield of 74%, accompanied by a shift towards anhydrous products, was achieved at a longer reaction time of 16 h. The valorization potential of the obtained carbohydrate fraction from the other lignocellulose substrate was also demonstrated, resulting in somewhat lower yields between 52 and 63% of sugar polyols (entries 3–5, Table 2).

To further improve the selectivity towards xylitol and sorbitol, the reaction rate was enhanced by subjecting the carbohydrate pulp to a ballmill procedure (ESI†), prior to its catalytic conversion. This procedure is known to improve the reactivity of cellulose towards chemical reactions. The crystallinity of the carbohydrate pulp was altered, as illustrated by XRD in the ESI,† Fig. S12. The results are represented by the thin lines
Brief economic assessment

To illustrate the economic valorization potential of the proposed biorefinery scheme, the future revenues from the conversion of birch wood are roughly estimated in Table 3. The calculations are based on the concentrated 600 mL reaction (entry 11, Table 1) for the lignin derived products and the concentrated carbohydrate conversion (thick lines, Fig. 5) for the sugar derived products, combined with current market information. Since the cost of transportation limits the volumes in which woody biomass can be economically collected, processing of such a geographically dispersed feedstock is best accomplished at moderate-sized facilities centered in regions where lignocellulose waste or crops is generated or easily transported e.g., harbors. We here show that a process volume, similar to that of a medium sized paper mill (~200 kton lignocellulose per year)\(^{130,131}\) can be sufficient to produce valuable sugar- and lignin-based chemicals in an economically profitable way at a realistic production scale for each product.

Starting from a substrate cost of 50–100 euros per ton of birch, a significant profit on the total revenue was calculated. For example, with the here obtained yields of cellulose to sorbitol/ sorbitans and hemicellulose to xylitol and methyl acetate, a rather conservative price estimation of about 600 euros can be generated from 1 ton of birch wood. This corresponds to an added value of 6 to 12 times the feedstock cost. When the roughly estimated revenues from lignin products like alkylated phenols as well as multifunctional di- and oligomers are taken into account, e.g. as a substitute resource of phenolic resins, the revenue for one ton of wood reach up to 800 euros. This theoretical exercise thus shows that lignin valorization can potentially amount to a 30–40% improvement in the economics of the presented lignocellulose biorefinery.

Though the presented values are based on optimized lab-scale experiments at the sub-liter scale, the results are promising and encouraging for future demonstration at the pilot scale. Such an exercise will allow an estimation of the installation and process costs, which next to the product valorization, will evidently play a key role in the success of a lignin-first biorefinery. In the near future, pilot scale experiments should deliver more accurate data.

**Conclusion**

A catalytic lignocellulose biorefinery process is presented, valorizing both polysaccharide and lignin components into a handful of chemicals. The selective delignification of lignocellulose in methanol through simultaneous solvolysis and catalytic hydrogenolysis, resulted in a lignin oil, rich in phenolic monomers next to di- and short oligomers. At the same time a processable carbohydrate pulp was obtained, with an almost quantitative retention of the original cellulose and a large fraction of the hemicellulose. Several key parameters, like temperature, reaction time, substrate particle size, reactor loading and the choice of solvent and gas, were examined as a first assessment of the techno-economic feasibility of the biorefinery process. The proposed biorefinery scheme was further investigated using other lignocellulose substrates, including genetically modified lines of *Arabidopsis thaliana*. The results led to a
description of the preferred lignocellulose feedstock, being a feedstock rich in S-type lignin.

More specifically, the reductive fractionation of birch sawdust in the presence of Ru/C resulted in a delignification up to 90%, 50% being converted into phenolic monomers and about 20% to a family of phenolic dimers, while retaining 80% of the carbohydrates in a processable pulp. Acetyl groups are completely removed from the hemicellulose backbone as methyl acetate, a relatively safe and environmentally friendly solvent and chemical precursor. The resulting methoxylated alkylphenols can be used in applications of aromatic products, like for example sorbitol, xylitol and sorbitans. High yields of these chemicals were achieved by chemocatalytic conversion of the carbohydrate pulp, while reusing the Ru/C catalyst from the hydrogenolysis reaction.

Characterization efforts of the dimers in the lignin oil reveal the presence of Ru/C resulted in a delignification up to 90%, 50% being converted into phenolic monomers and about 20% to a family of phenolic dimers, while retaining 80% of the carbohydrates in a processable pulp. Acetyl groups are completely removed from the hemicellulose backbone as methyl acetate, a relatively safe and environmentally friendly solvent and chemical precursor. The resulting methoxylated alkylphenols can be used in applications of aromatic products, like for example sorbitol, xylitol and sorbitans. High yields of these chemicals were achieved by chemocatalytic conversion of the carbohydrate pulp, while reusing the Ru/C catalyst from the hydrogenolysis reaction.

Processing lignocellulosic biomass in the proposed biorefinery thus results in 5 valuable product groups, being C5 and C6 polyols, methyl acetate, alkyl phenolic monomers and some larger phenolic oligomer products, which represent about 80% of the convertible fraction of the lignocellulosic feedstock.

To conclude a brief economic assessment was made as a first evaluation of the economic feasibility of the proposed biorefinery process. High revenues may be obtained and the added value of lignin valorization is shown to be substantial. Though the experiments were run at the lab-scale, they are encouraging to demonstrate the technology on a larger scale. To further improve the process economy, the use of cheaper catalysts, a smart catalyst regeneration as well as a continuous flow design are advised. Inspired by recent articles,63,65,66 additional research is now in progress to develop an inexpensive nickel-based biorefinery process in line with the ‘lignin-first’ concept.

Next to the lignin oil, a carbohydrate pulp is obtained, useful for the traditional pulp and paper industry or for biofuel production, but it can also be valorized into bio-based chemicals, like for example sorbitol, xylitol and sorbitans. High yields of these chemicals were achieved by chemocatalytic conversion of the carbohydrate pulp, while reusing the Ru/C catalyst from the hydrogenolysis reaction.

Processing lignocellulosic biomass in the proposed biorefinery thus results in 5 valuable product groups, being C5 and C6 polyols, methyl acetate, alkyl phenolic monomers and some larger phenolic oligomer products, which represent about 80% of the convertible fraction of the lignocellulosic feedstock.

To conclude a brief economic assessment was made as a first evaluation of the economic feasibility of the proposed biorefinery process. High revenues may be obtained and the added value of lignin valorization is shown to be substantial. Though the experiments were run at the lab-scale, they are encouraging to demonstrate the technology on a larger scale. To further improve the process economy, the use of cheaper catalysts, a smart catalyst regeneration as well as a continuous flow design are advised. Inspired by recent articles,63,65,66 additional research is now in progress to develop an inexpensive nickel-based biorefinery process in line with the ‘lignin-first’ concept.
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