Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

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Tuning the lignin oil OH-content with Ru and Pd catalysts during lignin hydrogenolysis on birch wood

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Liquid reductive processing of birch wood in the presence of commercial Ru/C or Pd/C catalysts yields about 50% of a select set of phenolic monomers and a variety of phenolic di- and oligomers, next to a solid carbohydrate pulp. Changing the catalyst from Ru/C to Pd/C drastically increases the OH-content of the lignin-derived products, in particular for the phenolic monomers.

The essential role of lignin valorisation with regard to the sustainability and economics of a lignocellulosic biorefinery is receiving a lot of awareness.[1-5] While the catalytic conversion of cellulose has already made great progress,[6-15] lignin valorisation remains one of the foremost challenges of new biorefinery strategies. As a promising alternative to conventional lignocellulose delignification methods like Kraft and Organosolv pulping, few groups recently introduced the direct processing of raw lignocellulose substrates under reductive conditions. High yields of low molecular weight lignin compounds were obtained,[16-24] next to a solid carbohydrate pulp, suitable for further processing.[22, 23]

Within this context, our recently presented 'lignin-first' biorefinery processes wood sawdust in methanol at elevated temperature under a mild H_2-pressure in presence of Ru/C.[1] Efficient lignin disassembly of various lignocellulose feedstocks is combined with a very high carbohydrate retention in the pulp. The processability of this pulp towards added-value chemicals was illustrated by its catalytic conversion to sugar polyols using the well-described bifunctional acid/redox approach.[7-11] Moreover, about 90% of lignin is obtained as a "lignin oil", comprising mainly of phenolic monomers like 4-*n*-propylguaiacol and 4-*n*-propylsyringol, next to dimers and small oligomers.

The monomers are relevant in various applications like in aroma components and resins, but can also act as platform molecules for aromatics and other chemicals. In line with the monomers, the di- and oligomers also possess propyl end-chains, yet their phenolic units are predominantly linked by $-CH_2OH$ substituted ethylene

bridges. This results in a higher OH-content per phenolic unit in comparison to that of the monomers. Because certain applications like the production of polyurethanes and polyesters benefit from a high hydroxyl-content,[25] the ability to preserve OH-functionality during wood processing can thus be of paramount importance.

As hydrogenolysis of C-O bonds is metal dependent, higher OH-contents may likely be accomplished by an appropriate choice of
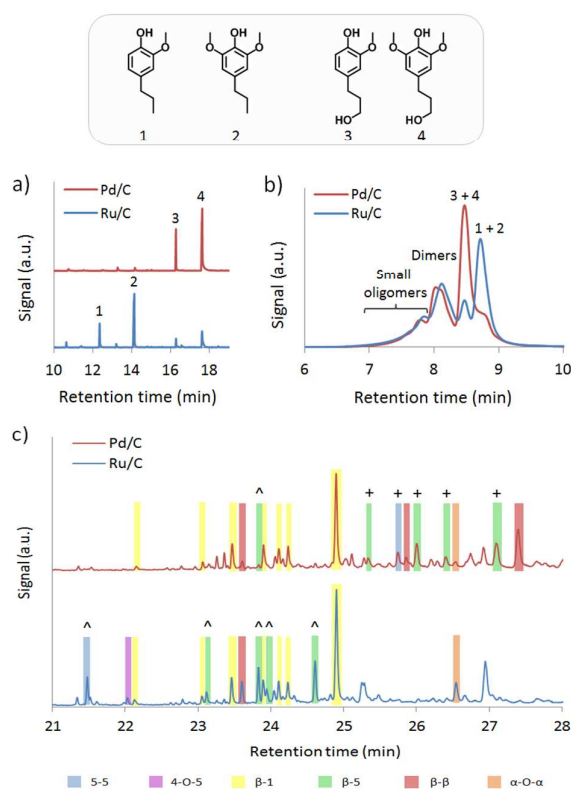
Fig. 1 Comparing the lignin products after the Ru/C and Pd/C catalyzed processing of birch wood in MeOH. a) Peak identification of the monomers *via* GC-MS: **1** (4-*n*-propylguaiacol, PG), **2** (4-*n*-propylsyringol, PS), **3** (4-*n*-propanolguaiacol, PohG) and **4** (4-*n*-propanolsyringol, PohS). b) MW distribution of the 'lignin oil' *via* GPC. c) Peak identification of the dimer *via* GC-MS, ^ represents dimers with propyl end-chains, + represents dimers with propanol end-chains. Reaction conditions: see Table 1.

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† Electronic supplementary information (ESI†) available. See DOI:…

the metal catalyst. In particular Pd, when compared to Ru, has a lower activity to alcohol hydrogenolysis.[26, 27] Also, during lignocellulose processing, a higher selectivity towards hydroxyl-rich lignin monomers was observed earlier with Pd catalysts. Unfortunately, only very little information is available on the chemical structure of the di- and oligomer products, whereas sustainable aspects like the degree of delignification, carbohydrate pulp retention and solvent stability are not discussed.[17-19, 24]

This communication therefore endorses an effective tuning of the overall lignin oil OH-content by processing birch sawdust in methanol at elevated temperature under a mild H_2 atmosphere with Pd/C. Next to the OH-content, several sustainable aspects, as mentioned above, will be discussed and compared with the Ru/C benchmark. Also, both a high degree of delignification and a high carbohydrate retention remain essential criteria.

The product fractions, obtained after reductive processing of birch wood with Ru/C and Pd/C catalysts are compared in Table 1. Except for the type of catalyst, identical conditions were applied (ESI†). The liquid product yields are very similar for both catalysts, showing a high selectivity towards a handful of *p*-substituted *o*-methoxy phenolic monomers. Next to a monomer yield of 50%, which is close to the expected theoretical maximum yield of birch lignin (discussed in ESI†), 15% of phenolic dimers and a rest fraction of short oligomers are obtained. This way the total degree of delignification amounts to about 90% for both catalysts.

Although the lignin product yields are very similar for Ru/C and Pd/C, the obtained chemical structures differ substantially. This is

Table 1 Comparison of the results after lignin hydrogenolysis on birch wood with a Ru/C and Pd/C catalyst.[a]

	Ru/C	Pd/C
Lignin fraction		
Delignification (wt%)	85	90
Monomer yield (C%)	48	49
PG + PS selectivity (%)[b,c]	75	4
PohG + PohS selectivity (%)[b,c]	19	91
Dimer yield (C%)	13	15
# OH's in lignin oil (mmol/g)	7.9	9.7
# OH's per monomer unit	1.5	1.9
Carbohydrate fraction		
C5 retention (C%)	69	81
C6 retention (C%)	93	94
Total sugar retention (C%)	85	89
Composition of the gas phase (vol%)		
H_2	92.7	94.2
N_2	3.4	4.1
CH_4	1.1 (0.08)[d]	0.2 (0.01)[d]
CO	1.9 (0.13)[d]	0.9 (0.05)[d]
Maximum loss of methanol into carbonaceous gases (mol%)[d]	0.21	0.06

[a] Reaction conditions: 2 g extracted birch sawdust (composition: 19.5 wt% Klason lignin, 41/21 wt% C6/C5 sugars), 0.2 g catalyst, 40 mL methanol, 523 K, 3 h and 3 MPa H_2 at RT (~12 MPa at 523 K). See ESI† for definition of all parameters. [b] Primary products listed in the caption of Fig. 1, S/G ratios vary around 3. [c] Selectivity within the monomer fraction. [d] Values in brackets relate the amount of gaseous compound to the initial amount of MeOH (mol%). Summation gives the maximum loss of MeOH to carbonaceous gasses.
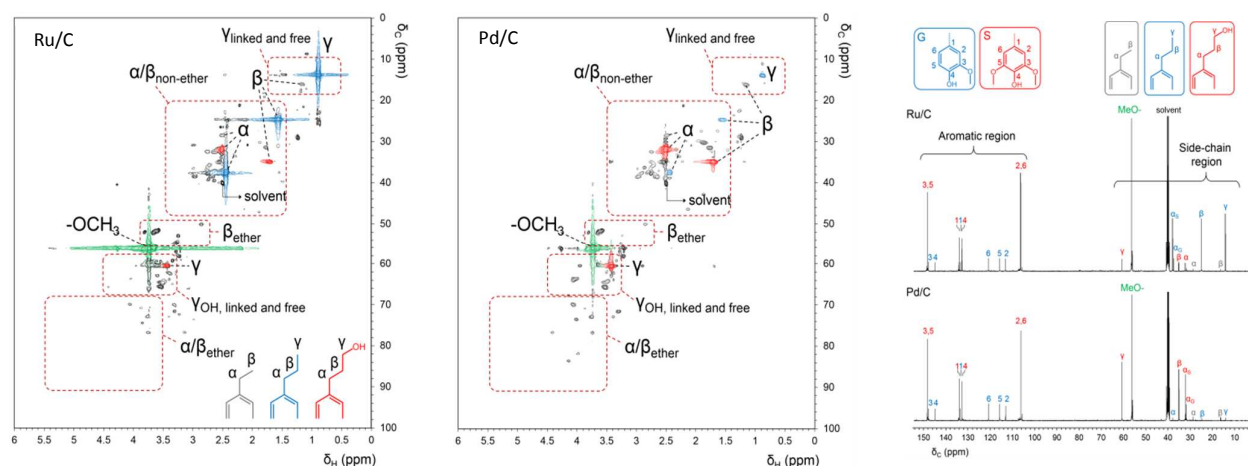
illustrated by the gas chromatographic analyses (GC) in Fig. 1a and supported by the data in Table 1. Wood processing with Ru/C preferentially forms *para*-propyl phenolics, showing a combined selectivity of 75% towards 4-*n*-propylguaiacol (PG) and 4-*n*-propylsyringol (PS), whereas the presence of Pd/C favours the formation of *para*-propanol phenolics with a notable 91% selectivity towards 4-*n*-propanolguaiacol (PohG) and 4-*n*-propanolsyringol (PohS). This difference in selectivity is further substantiated by gel permeation chromatography (GPC, see Fig. 1b). The largest peak for Ru/C represents the monomers, PG and PS, whereas the largest fraction for Pd/C has a shorter retention time, assigned to PohG and PohS, in accord with their larger molecular structure. The MW distribution of the di- and oligomers seems less dependent on the type of catalyst, though a slight shift towards larger dimers with Pd/C is apparent, likely also due to a higher OH-content.

Indeed, GC-MS analysis of the phenolic dimers clearly shows their different chemical structures depending on the catalyst (Fig. 1c; peak identification in ESI†, Fig. S1). The identified phenolic dimers are predominantly linked via β-1 bonds, followed by β-5, and to a lesser extent by 5-5 and β-β bonds. Though the distribution of β-1 bound dimers, indicated in yellow, is very similar for both catalysts, the dimers with β-5 and 5-5 linkages show remarkable structural differences. Lignin hydrogenolysis with Ru/C favourably produces phenolic dimers with *n*-propyl end-chains (indicated with ^), whereas the presence of Pd/C yields structurally identical dimers, yet with a higher abundance of *n*-propanol end-chains (indicated with +) at higher retention times.

In an effort to further elucidate the lignin-derived chemical structures and functionalities, for both catalysts the 'lignin oils' were characterized by 2D HSQC, ^{13}C and ^{1}H NMR and compared. The aromatic region of the [13]C (Fig. 2) and 2D HSQC (Fig. S2, ESI†) NMR spectra is very similar for both lignin oils, pointing to a high chemical stability of both guaiacyl and syringyl units under the applied conditions. On the other hand, the side chain region of the HSQC spectra of both oils, highlighted in Fig. 2, shows several differences. The correlation signals of ethyl, propyl and propanol side chains as well as methoxy groups are marked in colour. Various regions are defined that include C_α-H_α, C_β-H_β and C_γ-H_γ correlation signals of side-chains that form inter-unit linkages via C-C bonds (like β-1, β-5 or β-β) and/or ether bonds (like β-O-4, α-O-4, α-O-α or α-O-γ). All signals were assigned, based on an extensive set of ChemDraw NMR predictions, and if possible were verified with available literature data.[1]

The HSQC spectra in Fig. 2 only show low intensity signals in the region of C_α-H_α and C_β-H_β signals of ether-linked side-chains (marked with α/β_ether), illustrating a nearly complete ether dissociation of the original protolignin. Accordingly, a large number of intense signals is monitored in the α/β_non-ether region, corresponding to C_α-H_α and C_β-H_β signals of free side-chains or C-C-linked side-chains. In line with the chromatographic analysis of the phenolic mono- and dimers, the Ru/C HSQC spectrum shows very intense C_α-H_α, C_β-H_β and C_γ-H_γ correlation signals (marked in blue), typically assigned to propyl substituents, whereas the Pd/C-spectrum exhibits very intense propanol signals (marked in red).

The difference in product distribution is even more clear in the one dimensional proton decoupled ^{13}C NMR (Fig. 2) and ^{1}H NMR spectra (Fig. S3, ESI†). The propyl C_α, C_β and C_γ and H_α, H_β and H_γ

Fig. 2 Comparing the lignin oils, obtained after lignin hydrogenolysis of birch wood with Ru/C (left) and Pd/C (middle) *via* 2D HSQC NMR analysis and ^{13}C-NMR analysis (right).

signals dominate in the Ru/C spectra, whereas the corresponding propanol signals are clearly prominent in the Pd/C spectra. The ability to tune the product selectivity and hence the lignin oil properties, is therefore concluded.

With the above information, one should expect a higher lignin oil OH-content, when operating the reductive wood processing in presence of Pd/C. Based on polyester and polyurethane chemistry, such OH-functionalities are often essential in the production of polymers.[25] Therefore, monitoring the OH-content, here by ^{1}H-NMR analysis after acetylation of the lignin oil (Fig. S4, ESI†), is a helpful measure to judge the usefulness of the lignin oil for such applications. The ^{1}H NMR spectra for both catalysts clearly show equally intense acetylated phenolic OH-signals (normalized per weight lignin oil), demonstrating the low reactivity of the phenol entity. On the other hand, the signal of acetylated aliphatic OH-groups is much more pronounced in the Pd/C ^{1}H NMR spectrum, resulting in a clearly higher lignin oil OH-content after Pd/C processing, compared to that of the Ru/C catalyzed reaction. The measured OH-density for Pd/C and Ru/C (respectively 10 *vs.* 8 mmol/g), corresponds roughly to 1.9 and 1.5 OH-functionalities per phenolic unit, when assuming an average MW of 203 and 197 g/mol for the phenolic units in the Pd/C and Ru/C lignin oil. Taking into account their equal level of phenolic OH-groups, there is a difference of about a factor of two in their aliphatic OH-content.

To pinpoint better the events that determine selectivity, an adsorption experiment was first conducted. However, Ru/C and Pd/C both showed a very low adsorption of PG and PohG (Table 2, ESI†), making it unlikely that adsorption phenomena are the main cause for their highly contrasting product selectivity. Next, contact times were varied by changing the catalyst-to-biomass ratio from 0.05 to 0.15. Results are presented in Table S1 and Fig. S5a (ESI†). With Ru/C, a higher catalyst contact time leads to the formation of mainly PG and PS, their combined selectivity increasing from 57% to 84%. This indicates the disassembly of protolignin into PohG and PohS, prior to Ru/C catalyzed C-O hydrogenolysis. As Pd/C has a low C-O hydrogenolysis activity,[26, 27] PohG and PohS remain stable in solution, irrespective of the catalyst content (Fig. S5b, ESI†).

Despite focusing extensively on the obtained lignin products and the difference in selectivity between Ru/C and Pd/C, the sugar retention in the solid pulp is equally important, as to valorize the carbohydrates *via* downstream processing. The sugar pulp retention is slightly higher with the Pd/C catalyst, mainly due to the higher hemicellulose retention of 81% in presence of Pd/C, compared to 69% with Ru/C. This observation can currently not be explained and should be further investigated. Interestingly, the solubilized sugars mainly appear in their protected methyl ether form. As shown in Fig. S6 in the ESI†, the conversion to smaller C2-C4 sugars (e.g. *via* hydrogenolysis, retro-aldol condensation or decarbonylation) almost doesn't occur. Methyl-xylopyranoside is the main sugar-derived product, representing about 30% of the solubilized C5-sugars. Also small amount of methyl-glucopyranoside and methyl-furanoses were observed (Fig. S6, ESI†). Likely, the rest of the solubilized fraction is comprised of di- and oligomeric sugars.

In addition, methyl acetate was observed in methanol after wood processing with both catalysts, its amount advocating a complete conversion of the initial acetate groups in birch wood hemicellulose. An efficient separation of this azeotropic mixture of methanol and methyl acetate could offer an additional revenue for the biorefinery.[1]

Sustainable process practice not only requires an optimal use of the feedstock, but also strongly benefits from an on-site integration of the produced chemicals like the solvent and hydrogen. Several schemes might be imagined to generate a 'bio-methanol' to feed the presented lignin-first biorefinery, for example by selective demethoxylation of typical phenolic monomers.[4, 18, 28] However, also other biobased solvents, like bio-ethanol from carbohydrate fermentation, can be envisioned. Irrespective of the choice of the solvent, its recuperation in the biorefinery has to be demonstrated and its chemical stability in the catalytic reductive environment should be considered. Therefore gas formation after wood processing was monitored and the results are summarized in Table 1. Also, reference reactions were performed in absence of wood, to isolate the contribution of solvent consumption into gasses (see Table S3, ESI†). For both catalysts, low quantities of CH_4 and CO in the order of 1 vol% were analyzed. The former is likely obtained *via* catalytic methanation with consumption of H_2, whereas the latter likely results from endothermic solvent reforming or decarbonylation of wood compounds. Most notable is the

enormous influence of wood to reduce the (undesired) methanation activity of Ru/C. In absence of wood, 28.3 vol% of CH_4 was analyzed in the gas phase, compared to 1.1 vol% in presence of wood. This indicates that Ru/C prefers the reductive catalysis with wood, likely lignin, over reaction with abundant solvent molecules. As expected, methanation activity is low with Pd/C,[29] showing 5 times less CH_4 in the gas phase after wood processing compared to Ru/C. The origin of CO is less straightforward, but comparing the results from reactions with and without wood suggests that at least a part is due to methanol reforming. However, the decarbonylation from wood compounds cannot be excluded.

With regard to sustainability, an on-site production of H_2 is also important for future biorefineries. Although APR of oxygenates,[30] co-generation of formic acid like in levulinic acid schemes[6, 8, 11] as well as H-transfer, for instance with MeOH[20] or 2-propanol,[22] are relevant options, it is important to mention the relatively low H_2-consumption of roughly 2-3 kg per tonnage of wood with Pd/C processing, producing about 550 kg of carbohydrate pulp, 100 kg of phenolic monomers and 75 kg of di- and oligomers. In addition, both catalysts do not require a high H_2-pressure. Ru/C yields 50% monomers with a 92% selectivity towards PG and PS at 10 bar initial H_2-pressure (Table S1 & Fig. S5a, ESI†). Interestingly, starting from 1 bar N_2, a monomer yield of 40% and an 87% selectivity to PG and PS is still obtained. Though for Pd/C, the total monomer yield is not strongly influenced by the H_2-pressure, it has a remarkable impact on the monomer selectivity. At 10 bar initial H_2-pressure, a maximal selectivity towards PohG and PohS (91%) is obtained, while in absence of external H_2, 4-ethylguaiacol and 4-ethylsyringol become major co-products, reaching a combined selectivity of 42% within the monomer fraction (Fig. S5b, ESI†). Likely, in the absence of H_2, free surface sites on Pd foresee C-C hydrogenolysis, e.g., through consecutive dehydrogenation/ decarbonylation, converting primary alcohols into alkanes shortened by one C- atom.[31]

In summary, selective disassembling of birch sawdust is demonstrated in methanol under mild reductive conditions in presence of a redox catalyst. High phenolic monomer yields close to the theoretical maximum were obtained, next to di- and oligomers and a carbohydrate pulp. Finally, the phenolic product selectivity can be tuned by choice of catalyst, Pd/C being preferred when a lignin oil with a high OH-content is required.

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