Heterogeneous Catalysis

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Catalytic Biorefining of Plant Biomass to Non-Pyrolytic Lignin Bio-Oil and Carbohydrates through Hydrogen Transfer Reactions**

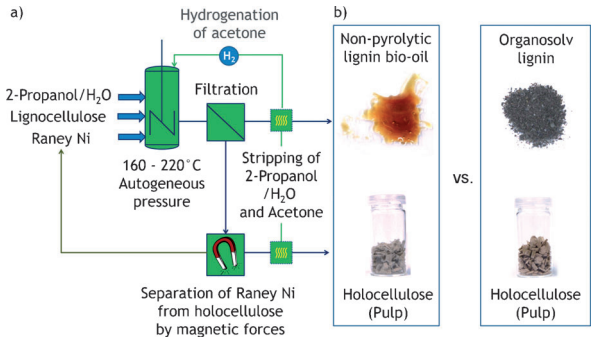
*Paola Ferrini and Roberto Rinaldi**

Dedicated to the MPI für Kohlenforschung on the occasion of its centenary

Abstract: *Through catalytic hydrogen transfer reactions, a new biorefining method results in the isolation of depolymerized lignin—a non-pyrolytic lignin bio-oil—in addition to pulps that are amenable to enzymatic hydrolysis. Compared with organosolv lignin, the lignin bio-oil is highly susceptible to further hydrodeoxygenation under low-severity conditions and therefore establishes a unique platform for lignin valorization by heterogeneous catalysis. Overall, the potential of a catalytic biorefining method designed from the perspective of lignin utilization is reported.*

A new focal point in plant biomass fractionation is mandatory in tackling the challenges of lignin valorization into chemicals and biofuels, thus allowing for the utilization of biomass to its fullest.[1] Current processes for wood pulping produce high-quality cellulosic fibers for paper production; however, they degrade lignin, generating recalcitrant phenolic resins cross-linked by C–C bonds with a high sulfur content (e.g., Kraft lignin and lignosulfonates).[2] Thereby, the conversion of technical lignins into defunctionalized molecules requires extreme conditions for hydrotreatment (e.g., 300–500 °C, 30–100 bar H_2).[2] Recently, the selective cleavage of the typical lignin ether linkages in model compounds was demonstrated in the presence of several classes of homogeneous catalysts under mild conditions.[3] In the field of heterogeneous catalysis, progress towards catalyst design,[4] a better understanding of solvent effects,[5] and densification of hydrodeoxygenation processes by tandem reactions[6] has been achieved. Nonetheless, the migration from lignin models to "real" technical lignins still requires high temperatures (250–300 °C) so that the polymers undergo (non-catalytic) thermolysis, providing suitable lignin fragments for heterogeneously catalyzed reactions.[5a,6g] In effect, an approach for lignocellulose biorefining that directly provides low-molecular-weight lignin intermediates, together with the cellulose and hemicellulose feeds, could hold the key to a new process where the whole plant biomass is efficiently utilized.

Herein, we demonstrate that lignin is solvolytically released from the plant cell wall as fragments having much lower molecular weights (M_w) than currently believed. This feature offers new opportunities for lignin valorization by heterogeneous catalysis. In fact, by simply "cooking" wood in the presence of Raney Ni in 2-propanol (2-PrOH)/H_2O (Scheme 1 a), the lignin fragments directly undergo further depolymerization through catalytic hydrogen transfer reactions. As a result, lignin is obtained as an oil.[7] This new result starkly contrasts with the organosolv process,[8] which isolates lignin as a recalcitrant solid polymer (Scheme 1 b). Remarkably, the non-pyrolytic lignin bio-oil is readily susceptible to further hydroprocessing under low-severity conditions. Moreover, we report the suitability of the pulp (holocellulose) as a raw material for the production of glucose and xylose through enzymatic hydrolysis.



Scheme 1. a) Schematic representation of the catalytic biorefining method. b) Visual comparison of the products obtained by our catalytic biorefining method and those of the organosolv process.

Scheme 1 a displays an overview of the proposed catalytic biorefining by hydrogen transfer reactions. First, wood pellets and Raney Ni were suspended in an aqueous solution of 2-propanol (2-PrOH, 70 %, v/v).[9] Then, the suspension was heated under mechanical stirring (e.g., at 180 °C for 3 h). The holocellulose fraction or pulp (i.e., cellulose and hemicellulose) was isolated by filtration and washed with the 2-PrOH/water solution. Raney Ni is easily removed from the suspension with a magnet. In our experiments, this catalyst could be reused at least eight times. Finally, the non-pyrolytic lignin bio-oil was isolated by solvent removal from the extracting liquor. Acetone generated by the hydrogen trans-

[*] P. Ferrini, Dr. R. Rinaldi
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany)
E-mail: rinaldi@mpi-muelheim.mpg.de

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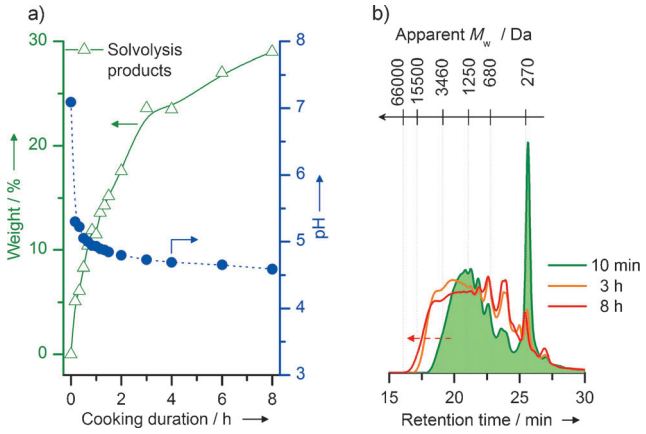


Figure 1. a) Evolution of the amount of product released by solvolysis and the pH value in the extracting medium throughout the organosolv extraction of lignin in 2-PrOH/H_2O (7:3, v/v) at 180 °C. b) Gel permeation chromatograms showing the increase in M_w of the lignin fragments with cooking duration.

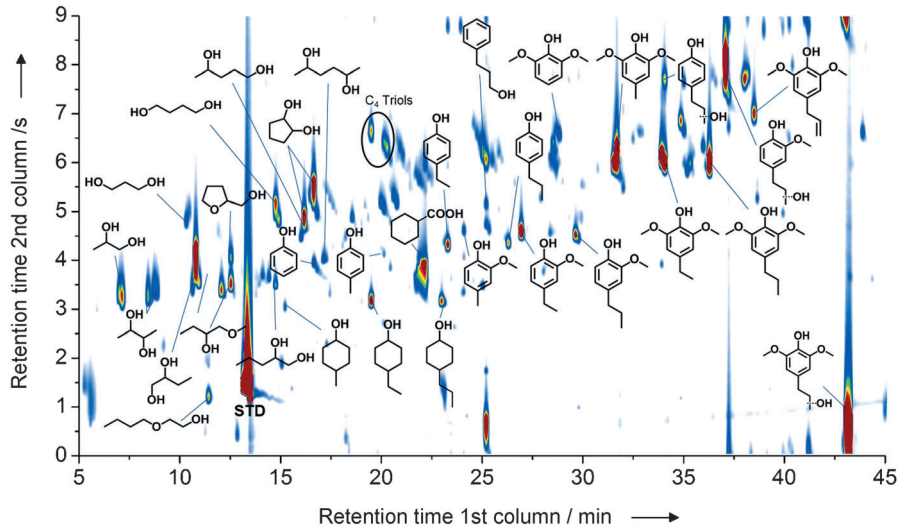


Figure 2. Speciation of the products obtained from the catalytic biorefining of poplar wood in the presence of Raney Ni at 180 °C for 3 h (2-PrOH/H_2O, 7:3, v/v). See Figure S1 and S6 for all GC×GC images of the bio-oils listed in Table 1.

fer processes can be hydrogenated to 2-PrOH in a second, small reactor.[10] This is advantageous because the voluminous lignocellulosic feed is thus processed in the absence of molecular hydrogen. In effect, eventual costs associated with the construction of large reactors are drastically mitigated, as there is no need for a large reactor designed to operate under H_2 pressure.

Cooking wood in a solution of 2-PrOH/H_2O (7:3, v/v) at 180 °C initiates many solvolytic processes on hemicellulose and lignin. The deacetylation of hemicellulose decreases the pH value of the liquor (from pH 7 to 4.7; Figure 1a), providing the acid catalyst for solvolytic processes well-known to occur on the α-O-4 lignin linkages and, to a lesser extent, on the β-O-4 linkages (Supporting Information, Scheme S1).[11] Hemicelluloses also undergo partial hydrolysis releasing C_5 and C_6 sugars under weakly acidic conditions.[11a,12] With regard to lignin, we have now found that lignin fragments released in the beginning of the cooking process are distinguishable from those obtained after prolonged cooking times (3 and 8 h), which are commonly found in several variants of the organosolv process. Notably, lignin fragments released after ten minutes display a bimodal distribution of apparent M_w centered at approximately 300 and 1250 Da, whereas the lignin fragments released after cooking for three or eight hours more closely resemble wide monomodal distributions with a considerable fraction of products with M_w greater than 3 kDa (Figure 1b).

As we recently reported, the combination of Raney Ni and 2-PrOH constitutes an outstanding catalytic system for the transfer hydrogenation of phenols, aldehydes, and ketones in addition to the transfer hydrogenolysis of diaryl and aryl alkyl ethers.[13]

Table 1: Comparison of the results obtained from lignin extraction by the organosolv process (entry 1, control experiment) and from the catalytic biorefining by catalytic transfer reactions in the presence of Raney Ni (entries 2–7).[a]

Entry	Solvent	T [°C]	Overall performance descriptors		Isolated fractions relative to initial substrate weight [wt%]		Pulp composition[b] [wt%]			
			Delignification [%][b]	Xylans in the pulps [%]	Lignin	Pulp	Glucans	Xylans	Lignin	Others
	Control experiment									
1	2-PrOH/H_2O (7:3, v/v)	180	77	64	30 (solid)	70	79	11	7	3
	Biorefining with Raney Ni									
2	2-PrOH/H_2O (7:3, v/v)	160	53	82	15 (bio-oil)	81	57	14	14	15
3	2-PrOH/H_2O (7:3, v/v)	180	63	64	25 (bio-oil)	71	68	11	11	10
4	2-PrOH/H_2O (7:3, v/v)	200	83	53	22 (bio-oil)	55	80	9	5	6
5	2-PrOH/H_2O (7:3, v/v)	220	87	41	26 (bio-oil)	52	84	7	4	5
6	2-PrOH	180	40	76	13 (bio-oil)	86	54	13	18	16
7	2-PrOH/MeOH (10:1, v/v)	180	43	82	14 (bio-oil)	92	57	14	17	13

[a] General conditions: poplar wood (16 g, 2 mm pellets), Raney Ni (10 g), solvent mixture (140 mL). [b] In comparison, unprocessed poplar wood contains glucans (53%), xylans (17%), lignin (30%), and other components (1%, dry and ash-free values).

Nonetheless, this catalytic system is not capable of extensively depolymerizing organosolv lignin into defunctionalized products, as we will show later on (Figure 5a). Strikingly, the catalytic system is, however, able to convert the low-molecular-weight lignin fragments released by solvolysis. As a result, lignin is isolated as an oily product. Figure 2 displays a two-dimensional gas chromatography (2D GC × GC) image of the lignin bio-oil obtained from catalytic biorefining in the presence of Raney Ni in 2-PrOH/H_2O (7:3, v/v) at 180 °C for three hours (Table 1, entry 3). In the lignin bio-oil, the volatile components are mostly phenols, aside from a secondary fraction of cyclohexanols, 1,2-cyclohexanediols, and other diols (derived from the hydrogenolysis of hemicellulose sugars, or side reactions involving 2-PrOH). At 300 °C (GC injector temperature), the fraction of volatile components should correspond to approximately 55 wt % of the entire oil sample, as estimated by thermogravimetric analysis (TGA; Figure S9).

To obtain the non-pyrolytic lignin bio-oil in high yields, the effects of temperature and composition of the organic solvent mixture on the fractionation of poplar wood in the presence of Raney Ni were examined. It is worth mentioning that the catalytic biorefining aims at the full delignification of the lignocellulosic matrix. Furthermore, it is highly desirable to retain as much of the xylan content in the pulp as possible, to allow a high recovery of pentoses either through enzymatic catalysis or other emerging methods.[14] Table 1 compares the results of the organosolv process (entry 1) with those of catalytic biorefining processes through hydrogen transfer reactions under various conditions (entries 2–7).

In the control experiment, a reddish-brown solid (lignin with a minor fraction of hemicellulose sugars) was obtained in 30 wt % yield. Extensive delignification of the substrate was achieved (77 %; Table 1, entry 1). Furthermore, a considerable fraction (64 %) of the xylan content was retained in the pulp.

When the temperature at which poplar wood was subjected to Raney Ni suspended in 2-PrOH/H_2O (7:3, v/v) for three hours was increased from 160 to 220 °C, the yield of non-pyrolytic oil increased from 15 to 26 wt % (Table 1, entries 2–5). The delignification increases (from 53 to 87 %) with the process temperature (from 160 to 220 °C). Furthermore, the remaining xylan content in the pulp decreases (from 82 to 41 %). The experiments performed in 2-PrOH or 2-PrOH/MeOH (10:1, v/v) led to the lowest delignification of poplar wood (40–43 %; entries 6 and 7) at 180 °C for 3 h. These results clearly show that the presence of water in the extracting medium improves the delignification of the substrate and therefore increases the yield of lignin bio-oil. Apparently, water is needed to guarantee the transport of the liquor into the wood pellets, to enable lignin extraction.

Figure 3a displays the gel permeation chromatograms obtained from organosolv lignin and non-pyrolytic lignin bio-oil samples. The non-pyrolytic lignin bio-oils show products with lower apparent M_w values than organosolv lignin. Furthermore, the distribution of apparent M_w values continually shifts towards lower values with an increase in the process temperature. These results clearly demonstrate that lignin is further depolymerized; most importantly, the formed

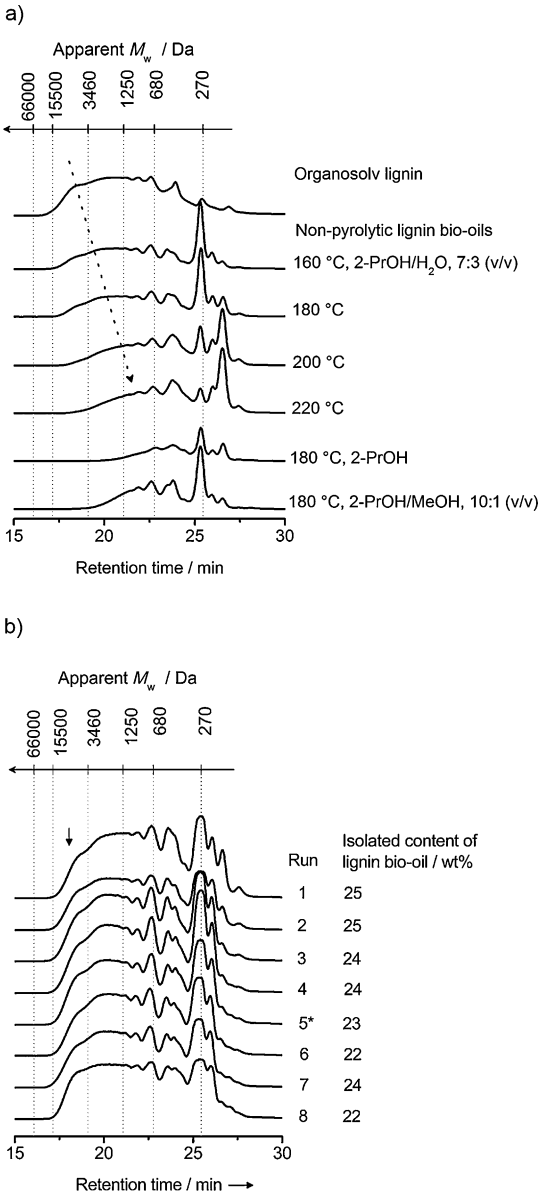


Figure 3. a) Gel permeation chromatograms of organosolv lignin and non-pyrolytic bio-oils obtained under various conditions (Table 1). b) Corresponding chromatograms of the bio-oil samples obtained from catalytic biorefining with recycled Raney Ni (eight successive reactions) in 2-PrOH/H_2O (7:3, v/v) at 180 °C for 3 h. The * indicates that the catalyst was reconditioned in 2-PrOH under autogeneous pressure at 200 °C for 4 h.

fragments do not undergo repolymerization, as was observed in the organosolv process (Figure 1b).

Figure 3b shows gel permeation chromatograms of the products obtained when the Raney Ni catalyst was reused eight times. The amount of isolated lignin bio-oil remained at 23 ± 2 % throughout the recycling experiments. As indicated by the arrow, the formation of products with apparent M_w values from 3.4 to 15.5 kDa was quite stable throughout the recycling experiment. Nonetheless, during the fifth and eighth run, a more prominent signal is noticeable within this M_w range. Reconditioning Raney Ni in 2-PrOH at 200 °C for

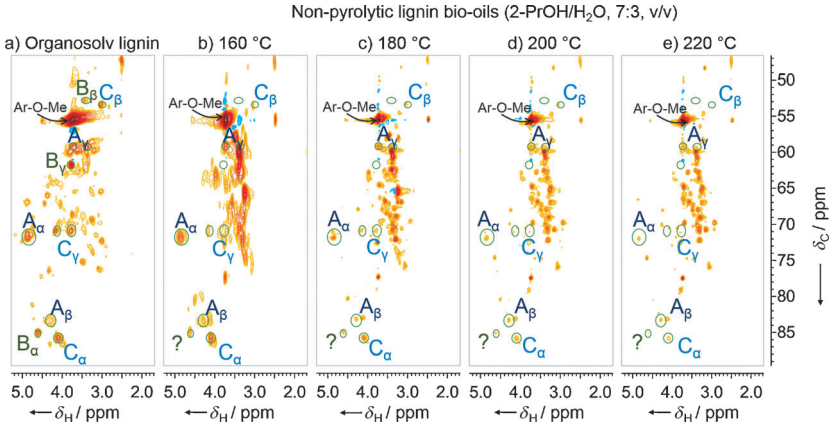
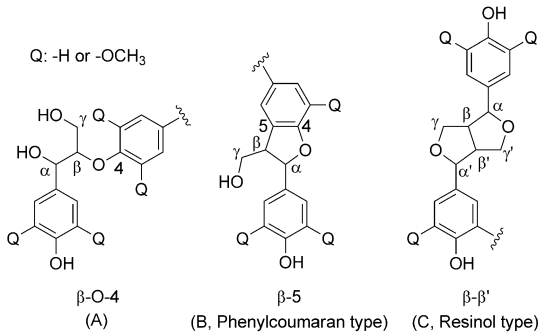


Figure 4. 2D HSQC NMR spectra of a) organosolv lignin and b–e) non-pyrolytic lignin bio-oils obtained from fractionation by catalytic transfer hydrogenation at various temperatures. Arrows indicate the missing fingerprint signals B_β and B_γ.

four hours under autogeneous pressure was effective in regenerating the performance capabilities with respect to the apparent M_w distribution obtained for the sixth and seventh use of the catalyst.

To gain further information on the conversion of the lignin fraction as a function of the process temperature, 2D HSQC NMR spectra of organosolv lignin and bio-oils that were obtained by the catalytic biorefining in 2-PrOH/H_2O (7:3, v/v) at temperatures between 160 and 220 °C were examined (Figure 4). Several 2D HSQC NMR methods have been developed to shed light on the structural complexity of lignins.[15] Overall, the set of correlation signals A_α, A_β, and A_γ fingerprint the β-O-4 linkage types, while B_α, B_β, and B_γ fingerprint the phenylcoumaran subunits (containing an α-O-4 ether linkage and a β-5 C–C bond), and C_α, C_β, and C_γ fingerprint the resinol subunits (with a β-β′ C–C linkage). The aryl methoxy groups are identified by the cross signal at δ_C, $\delta_H = 55.6$ ppm, 3.7 ppm.



The HSQC spectrum of the organosolv lignin shows the fingerprint correlation signals for the β-O-4 ether linkages and the phenylcoumaran and resinol subunits (Figure 4a). Surprisingly, the absence of the fingerprint signals B_β and B_γ in the bio-oil spectra indicates that the phenylcoumaran substructures have been converted throughout the catalytic biorefining process even under low-severity conditions (e.g., 160 °C). In turn, the cross signals that are characteristic of β-O-4 ether linkages and resinol subunits were found in the HSQC spectra of the lignin bio-oils (Figure 4b–e). The ratio A_α/C_α decreases with cooking temperature as follows: Organosolv 180 °C (1.6) ≈ catalytic biorefining at 160 °C (1.6) > 180 °C (1.5) > 200 °C (1.3) > 220 °C (1.2). This observation suggests that the β-O-4 linkages are more reactive than the resinol subunits towards reductive processes in the presence of Raney Ni. The disappearance of the β-O-4 linkages is directly associated with the depolymerization of the released lignin fragments. However, the disappearance of the phenylcoumaran and resinol substructures does not necessarily imply depolymerization. For these linkages, both C–O and C–C bond scissions are required for the depolymerization.

To demonstrate the higher susceptibility of the lignin bio-oil to undergo further hydrodeoxygenation compared to organosolv lignin, we chose to resubject the lignin bio-oil and to subject organosolv lignin (both obtained by cooking wood at 180 °C) to Raney Ni in 2-PrOH in the absence of molecular hydrogen at 160 °C for 18 hours.

2D GC × GC images of the products obtained from non-pyrolytic bio-oil and organosolv lignin and photographs of the reaction media after 18 h are shown in Figure 5. The experiment performed on organosolv lignin led to a product mixture containing phenols, aside from cyclohexanols and 1,2-cyclohexanediols as secondary products. However, the reaction medium stayed turbid. In fact, a substantial fraction of the substrate (45 %) remained as a solid polymer. Moreover, the volatile products at 300 °C were estimated to amount to 40 wt % by TGA (Figure S9). In contrast, the lignin bio-oil was fully converted into colorless products. The 2D GC × GC image shows a greater number of products, which correspond to at least 85 wt % of the content vaporized in the GC injector at 300 °C, as estimated by TGA (Figure S9). The conversion of the lignin bio-oil produced cyclohexanols, 1,2-cyclohexanediols, and bicyclic compounds as the major products (see Figure S7 and S8 for details).

Obviously, biorefining of lignocellulosic materials should also be able to provide a carbohydrate fraction suitable for the production of sugars. To examine the susceptibility of the pulp to enzymatic hydrolysis, the pulp was treated with a commercial preparation of glycoside hydrolyses (Celluclast, Novozymes) at 45 °C (pH 4.5, acetate buffer).

Figure 6 compares the glucose and xylose yields resulting from enzymatic saccharification of the pulps. For the production of glucose, the pulps obtained by the catalytic biorefining process at 160 or 180 °C showed lower susceptibility to enzymatic hydrolysis than the organosolv pulp. This feature is most likely due to the fact the pulps obtained from catalytic biorefining at 160 or 180 °C have a higher lignin content (14 and 11 %, respectively) than the organosolv pulp (7 %, Table 1). However, the catalytic biorefining methods at 200 and 220 °C produced holocelluloses with low lignin contents (5 and 4 %, respectively). These pulps were as susceptible to enzymatic hydrolysis as the organosolv pulp. For the production of xylose, a similar trend to that for

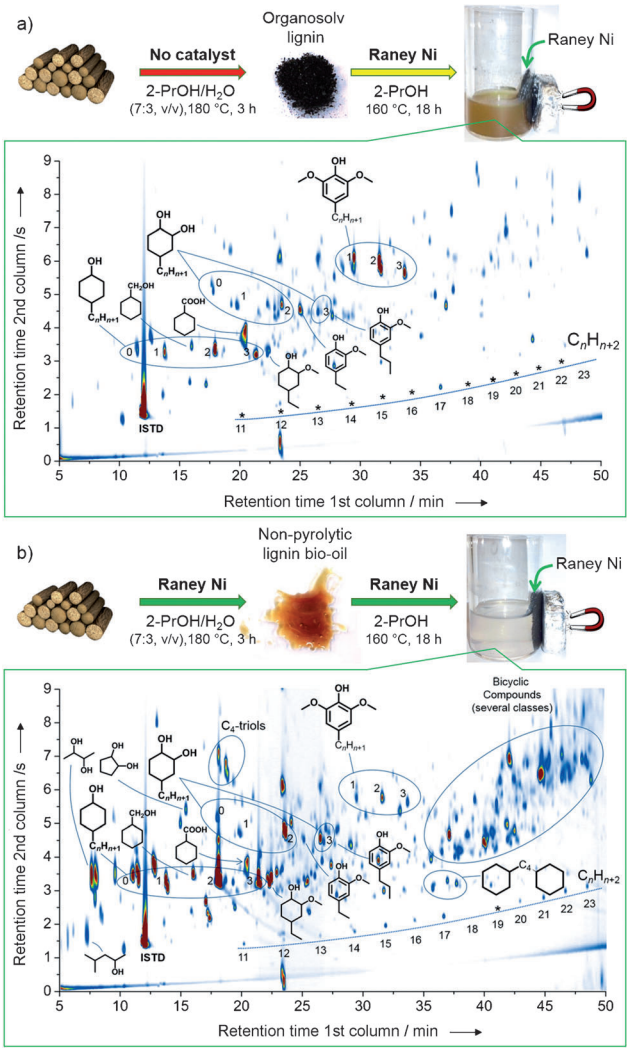


Figure 5. Products obtained by the further processing of a) organosolv lignin and b) non-pyrolytic lignin bio-oil through catalytic transfer hydrogenation in the presence of Raney Ni at 160 °C for 18 h. The numbers indicate the values of "*n*". For a detailed speciation of the mixture components by GC×GC–MS, see Figures S7 and S8.

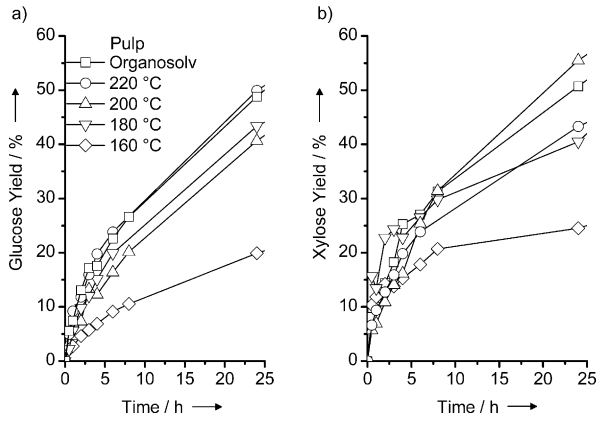


Figure 6. Enzymatic hydrolysis of the pulps obtained by the organosolv process and by fractionation through catalytic hydrogen transfer in 2-PrOH/H_2O (7:3, v/v) at 160, 180, 200, or 220 °C for 3 h. Reaction conditions: substrate (equivalent to 1 g of cellulose), Celluclast (350 U g^{-1} substrate), pH 4.5 (acetate buffer), 45 °C.

glucose formation was observed (Figure 6b). However, catalytic biorefining at 220 °C generated a pulp that released a smaller amount of xylose than the organosolv pulp when subjected to xylanases (which are also present in commercial enzymatic preparations).

In summary, we have developed a catalytic biorefining method that is able to convert lignin into a non-pyrolytic bio-oil whilst providing pulp susceptible to enzymatic hydrolysis. Non-pyrolytic lignin bio-oil is a phenolic feed amenable to further reduction through hydrogen transfer reactions in the presence of Raney Ni and 2-PrOH under unprecedented low-severity conditions. The pulp obtained by this method has a low lignin content and thus may be a suitable raw material for the production of biofuels, chemicals, or paper. Moreover, as lignin decomposes over a broad temperature range,[16] lignin also poses problems for the optimization of working conditions for the catalytic pyrolysis of biomass. In effect, the catalytic pyrolysis route[17] could also benefit from pulps with low lignin contents. Altogether, it was demonstrated that biorefining displays a clear potential for lignin valorization. Aside from a high-quality carbohydrate fraction, this new biorefining method rendered a non-pyrolytic lignin bio-oil that could well be utilized as a feedstock for emerging routes for the production of alkanes[6a,c,d] or arenes.[6f]

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[9] We chose 2-PrOH as a solvent and a hydrogen donor because primary alcohols (e.g., methanol and ethanol) were found to deactivate Raney Ni when used as the solvent and hydrogen donor. Interestingly, in the presence of 2-PrOH, methanol (at concentrations as high as 10 vol%) partially inhibits Raney Ni. However, the catalyst is not deactivated. For further information, see Ref. [13].

[10] For the catalytic biorefining of poplar wood in the presence of Raney Ni in 2-PrOH/water (7:3, v/v) at 180 °C, approximately 5 mol% of the 2-PrOH content were converted into acetone. This value corresponds to about 5 mol of acetone per kg of poplar wood.

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