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Selective production of mono-aromatics from lignocellulose over Pd/C catalyst: the influence of acid co-catalysts

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The 'lignin-first' approach has recently gained attention as an alternative whole biomass pretreatment technology with improved yield and selectivity of aromatics compared with traditional upgrading processes using technical lignins. Metal triflates are effective co-catalysts that considerably speed up the removal of lignin fragments from the whole biomass. As their cost is too high in a scaled-up process, we explored here the use of HCl, H₂SO₄, H₃PO₄ and CH₃COOH as alternative acid co-catalysts for the tandem reductive fractionation process. HCl and H₂SO₄ were found to show superior catalytic performance over H₃PO₄ and CH₃COOH in model compound studies that simulate lignin-carbohydrate linkages (phenyl glycoside, glyceryl trioleate) and lignin intralinkages (guaiacylglycerol- β -guaiacyl ether). HCl is a promising alternative to the metal triflates as a co-catalyst in the reductive fraction of woody biomass. Al(OTf)₃ and HCl, respectively, afforded 46 wt% and 44 wt% lignin monomers from oak wood sawdust in tandem catalytic systems with Pd/C at 180 °C in 2 h. The retention of cellulose in the solid residue was similar.

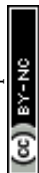
Introduction

Lignocellulosic biomass is the most abundant source of renewable carbon with significant potential for the production of sustainable chemicals and fuels.^{1,2} Together with cellulose and hemi-cellulose, lignin is a main component of land-based biomass. Lignin makes up about 20–35% of the mass of dry biomass.³ It is typically obtained as a by-product in the paper and pulping industry and 2nd generation biorefineries. Such technical lignin is usually contaminated by sulphur, ash, proteins and carbohydrates residue.^{3,4} During biomass separation,

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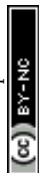
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the lignin structure is altered, rendering technical lignins much less reactive than the native lignin contained in the biomass.^{5–7} Abundant weak ether linkages, such as β -O-4 ones, are replaced by more recalcitrant C–C linkages.⁸ The resulting highly recondensed structure of lignin poses significant challenges for its efficient conversion to chemicals and fuels. Such processes require harsh conditions and typically yield a wide range of aromatic compounds in a low overall yield.^{9–14}

Recent studies have demonstrated that mild depolymerization strategies can also be effective when reactive lignin feedstock rich in β -O-4 ether linkages is used. For instance, a two-step strategy has been developed for aspen lignin, consisting of selective oxidation of the secondary alcohol of β -O-4 linkages followed by a redox-neutral bond cleavage at 110 °C.^{5,15} A similar strategy was also applied to the depolymerization of a reactive dioxasolv birch lignin (an organosolv lignin extracted by 1,4-dioxane) at 80 °C.¹⁶ The use of a hydrosilane reductant and a Lewis acidic ($\text{B}(\text{C}_6\text{F}_5)_3$) catalyst facilitated the conversion of extracted wood lignin into mono-aromatics with a yield of 7–24 wt% at room-temperature.¹⁷ A combination of triflic acid and a heterogeneous Ru or homogeneous Ir catalyst was also effective in depolymerizing dioxasolv lignin in 1,4-dioxane at 140 °C.¹⁸ A similar catalytic system involving the use of a metal triflate and a homogeneous Rh catalyst was employed for the depolymerization of dioxansolv lignins in a 1,4-dioxane/water solvent mixture at 175 °C.¹⁹ Two-step approaches consisting of a mild pretreatment of woody biomass followed by catalytic depolymerization have also been reported.^{20,21} A suitable pretreatment method for the preparation of reactive lignin that preserves high ether linkage content is essential to these mild lignin depolymerization approaches.

An alternative approach is to directly convert the lignin in its native form in the lignocellulosic biomass matrix.^{22–25} For instance, Kou *et al.* reported that lignin in birch wood can be selectively depolymerized to alkylmethoxyphenols in 46 wt% yield in a 1 : 1 (v/v) dioxane/water solvent mixture over carbon-supported noble metal (Pt, Ru, Pd and Rh) catalysts at 200 °C for 4 h.²⁶ Li *et al.* reported the direct catalytic conversion of carbohydrate and lignin fragments from the whole woody biomass into diols and alkylmethoxyphenols in water over a carbon-supported Ni–W₂C catalyst at 235 °C for 4 h.²⁷ Song *et al.* were able to convert about half of the lignin in birch wood into alkylmethoxyphenols in alcohols over a Ni/C catalyst.²² Ferrini, Rinaldi and others reported a catalytic upstream biorefining process that converts lignin from woody biomass into low molecular weight lignin oil and a (hemi-)cellulose-rich pulp over a RANEY® Ni catalyst in a mixture of H₂O/2-propanol.^{23,28} The group of Abu-Omar used a bimetallic Zn/Pd/C catalyst to convert lignocellulosic biomass into two alkylmethoxyphenols and carbohydrate pulp residue in methanol. A yield of 52 wt% of lignin monomers was obtained from birch hardwood after a 12 h reaction at 225 °C.^{24,29} Sels and co-workers reported a lignin-first process that allows simultaneous delignification and reductive depolymerization in the presence of Ru/C or Pd/C in methanol under a H₂ atmosphere at elevated temperature, resulting in a carbohydrate pulp and a lignin oil rich in alkylmethoxyphenol monomers in ~50% yield.^{6,30} The addition of acids, such as H₃PO₄, improved the overall efficiency of the process due to enhanced delignification.³¹ A similar catalytic lignocellulose fractionation process without the addition of external hydrogen or co-catalysts in a 1 : 1 (v/v) ethanol/water solvent mixture was also reported recently.³² Related to these lignin-first or catalytic upstream biorefining processes, we have also demonstrated



a tandem catalytic system that couples delignification and reductive depolymerization of wood lignin in one pot using methanol as a solvent by a combination of Lewis acid metal triflates (*e.g.* $\text{Al}(\text{OTf})_3$) and Pd/C .^{33,34} An important function of the acidic co-catalyst is the efficient extraction of lignin from the biomass, which is a relatively slow step. Conventional Lewis acids, such as AlCl_3 and ZnCl_2 , were found to be less effective in deconstructing lignocellulose compared with metal triflates.^{33,34} Moreover, these conventional Lewis acids are moisture sensitive and tend to decompose in the presence of water generated in etherification and hydrogenolysis. Another drawback is that their recovery and reuse are difficult.

In this work, we explore a range of Brønsted acid co-catalysts, such as HCl , H_2SO_4 , H_3PO_4 and CH_3COOH , as alternatives to the benchmark $\text{Al}(\text{OTf})_3$ catalyst. The main goal was to identify a suitable and cheaper acid co-catalyst that helps in the delignification of the biomass but leaves the (hemi)cellulose part as much as possible unconverted. The strategy of this work is to evaluate the performance of these acids as co-catalysts in the cleavage of model compounds relevant to carbohydrate–lignin interlinkages and lignin intralinkages. Finally, oak wood sawdust is used to verify the trends and establish the potential of these cheap acid co-catalysts to replace $\text{Al}(\text{OTf})_3$.

Results and discussion

The catalytic process

Fig. 1 illustrates the overall concept of the tandem catalytic system for the valorization of lignin from woody biomass. Metal triflates are effective in the extraction of lignin from the lignocellulosic matrix by cleaving phenyl glycoside, phenyl ether and ester lignin–carbohydrate intralinkages.^{31,32} These lignin fragments are then disassembled by Pd -catalyzed hydrogenolysis reactions involving molecular hydrogen. Metal triflates strongly promote the reductive fractionation of lignocellulose, thus shortening the time needed to obtain a high lignin monomer yield.^{31,32} The metal triflates are also active for the depolymerization of some of the ether bonds in these lignin fragments and they also modify the performance of the Pd/C catalyst used to depolymerize these fragments. In a typical experiment (2000 mg of birch wood sawdust, 200 mg of Pd/C , 15 mg of aluminum triflate

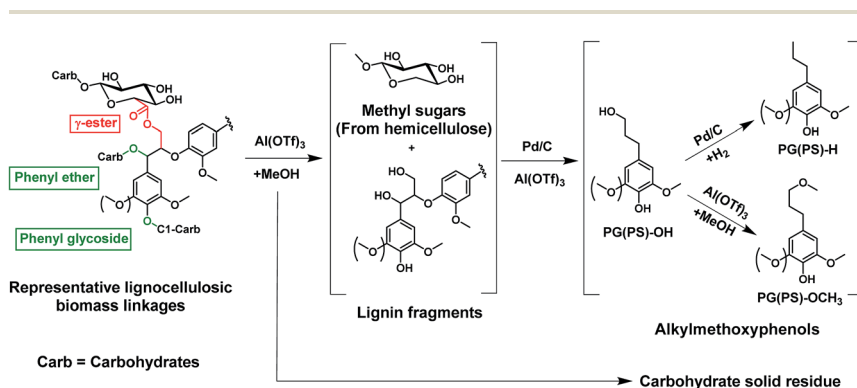
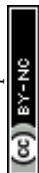


Fig. 1 The cleavage of representative linkages between carbohydrates and lignin (phenyl glycoside, benzyl ether and γ -ester) by a tandem metal triflate and Pd/C catalyst system.



(Al(OTf)₃), 40 ml of methanol, 180 °C, 2 h, 30 bar H₂), the yield of C₉ lignin monomers was 45 wt% (based on 23.6 wt% lignin content of birch wood). The main products are 4-*n*-propylsyringol (PS-H), 4-*n*-propanolsyringol (PS-OH) and 4-*n*-methoxy propyl syringol (PS-OCH₃), and their corresponding guaiacyl counterparts, namely PG-H, PG-OH and PG-OCH₃. The formation of PS-OCH₃ and PG-OCH₃ is caused by the etherification of the propanol side-group with methanol catalyzed by the Al(OTf)₃ Lewis acid catalyst. The lignin monomers distribution can be controlled by varying the ratio of Pd/C to Al(OTf)₃. A higher Pd/Al ratio results in more PS/G-OH and PS/G-H, and less PS/G-OCH₃ products.³⁴

Fig. 2 shows a detailed analysis of the composition of birch wood, the solid residue and the product oil after upgrading by a combination of Pd/C and Al(OTf)₃. The solid residue is comprised mainly of cellulose, hemicellulose and a small amount of lignin together with the Pd/C catalyst. About 56 wt% of the hemicellulose and 81 wt% of the lignin were released from the raw birch wood and, respectively, converted into predominantly methyl xylose and monoaromatics. The cellulose fraction was nearly all unconverted as evident from the unchanged cellulose content.

For the comparison of this optimized catalyst system to common Brønsted acid catalysts, we used another hardwood oak sawdust (125–300 μm) as the starting material. The amount of Pd/C was reduced from 200 mg to 100 mg. The amount of acid was equivalent to the amount of Al(OTf)₃ (0.0316 mmol, 15 mg). The effect of the acid concentration was also investigated by increasing the amount of acid to 4, 16 and 32 times the standard concentration. For the model compound studies, the same concentrations of acids were used.

Influence of acid co-catalysts: model compound studies

The selective cleavage of lignin-carbohydrate bonds and lignin-lignin ether bonds is essential for the one-pot reductive fractionation process. Typical linkages between lignin and carbohydrates in woody biomass are phenyl glycoside, benzyl ether and γ-ester bonds.³⁵ With the purpose of understanding the role of acid in the delignification of woody biomass, we selected phenyl glycoside (PG) and glyceryl trioleate (GT) as model compounds, representing phenyl glycosidic and γ-ester type linkages, respectively. The reactions were conducted at 160 °C for 2 h in a small autoclave of 12 ml. When Pd/C was used without an acid co-catalyst, the

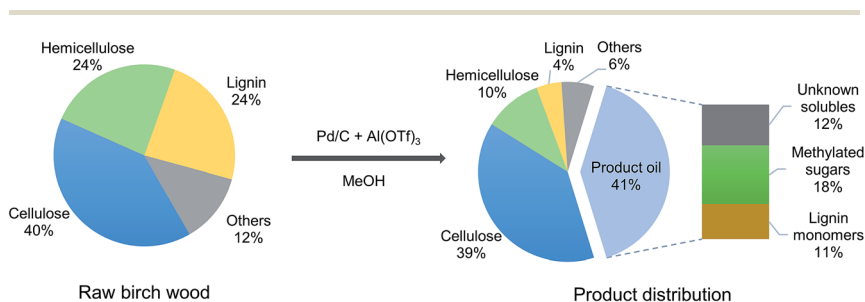
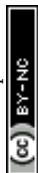


Fig. 2 Composition of birch wood, the carbohydrate residue and product oil mixture after reductive fractionation over a tandem Al(OTf)₃ and Pd/C catalyst system. (Reaction conditions: 2000 mg of extracted birch wood sawdust (125–300 μm), 200 mg of 5 wt% Pd/C, 15 mg of Al(OTf)₃, 40 ml of methanol, 30 bar H₂, stirring speed: 500 rpm, 2 h.)



conversions of PG and GT were 22% and 5%, respectively (Fig. 3). Methanol is nearly inactive in converting PG.³⁴ The conversion of PG is mainly due to hydrogenation and hydrogenolysis reactions catalyzed by the Pd/C catalyst (Fig. 3a). Hydrogenation of ester bonds typically requires high reaction temperature and hydrogen pressure.³⁶ GT can be converted in methanol by trans-esterification catalyzed by the weak acidity of methanol under sub-critical conditions.¹⁶ Trans-esterification can be significantly enhanced by an acid. The use of $\text{Al}(\text{OTf})_3$ is very effective in cleaving the phenyl glycosidic bond of PG. The overall product yield of phenol-derivatives is 75% after a 2 h reaction at 160 °C. $\text{Al}(\text{OTf})_3$ also shows a high activity towards ester bond cleavage in GT with a 80% yield of methyl octadecanoate, the product of ester bond cleavage.

The use of acids resulted in similar or higher conversions of PG (Fig. 3). Increasing the HCl concentration led to higher conversions and suppressed aromatic ring hydrogenation. Nearly all the PG was converted when H_2SO_4 was the co-catalyst. In this case, all the aromatic products were hydrogenated. H_3PO_4 is very effective in catalyzing the cleavage of the phenol-glycoside bond in PG and it also strongly suppresses aromatic ring hydrogenation. Acetic acid was the least effective acid and phenol was the only product observed from the phenyl part of the reactant.

The conversion of GT was less efficient with HCl and larger amounts were needed to obtain a similar conversion as that obtained for PG. H_2SO_4 was nearly as active as the metal triflate in cleaving the GT model reactant. H_3PO_4 and CH_3COOH were much less active in cleaving the ester bond in GT. Overall, these data show that cleaving the phenyl glycosidic bond is more facile than cleaving the ester bond. The substantial difference ($\sim 70\%$) between PG and GT conversion observed for H_3PO_4 cannot be explained by the small activity difference ($\sim 20\%$) observed when only the Pd/C catalyst was used. Accordingly, we conclude that strong acids, such as HCl and H_2SO_4 , are required to catalyze trans-esterification, while a weak acid (H_3PO_4) is sufficient to catalyze trans-etherification of the phenyl glycosidic bond. The use of CH_3COOH as a co-catalyst is not efficient. It appears that acetic acid suppresses the cleavage of the bonds compared to the reference case. A tentative explanation could be that esterification between

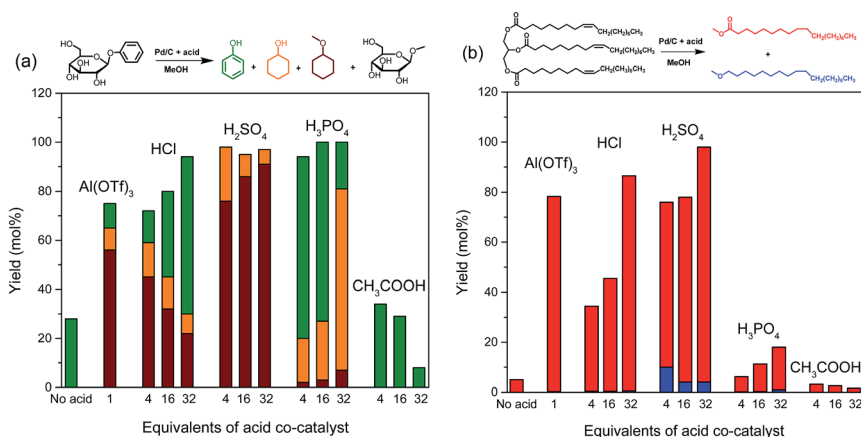
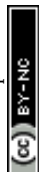


Fig. 3 Reactions of (a) phenyl glycoside (PG) and (b) glyceryl trioleate (GT) in methanol over Pd/C and/or different acid co-catalysts at 160 °C for 2 h in 30 bar H_2 .



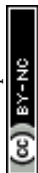
CH_3COOH and methanol decreases the acidity. In line with this, we observed the formation of methyl acetate by GC-FID. Based on these results, we conclude that HCl and H_2SO_4 acids are potential co-catalysts for the lignin-first approach.

With the purpose of gaining insight into the performance of the acid co-catalyst in the depolymerization of lignin fragments, guaiacylglycerol- β -guaiacyl ether (GG) was used as a model substrate. GG is the most suitable model for the most abundant (50–65%) β -O-4 ether linkage in native lignin.¹⁴ For this reason and also because it is readily available, GG is frequently used in mechanistic studies on lignin deconstruction.^{5,16,18,37–39} The reactions were performed under the same conditions as the previous model compound reactions (160 °C, 2 h). Without acid, Pd/C is already active in cleaving the β -O-4 ether linkage in GG. The product of the ether bond cleavage, guaiacol, is obtained in 40% yield (Fig. 4). A combination of Pd/C and $\text{Al}(\text{OTf})_3$ resulted in a higher conversion ($\sim 60\%$) of the β -O-4 ether bond. Interestingly, at the lowest HCl concentration, the yield ($\sim 20\%$) was lower than in the Pd-only case. Although a higher HCl concentration slightly improved the GG conversion, the overall product yields remain lower than for Pd/C. In contrast, the use of H_2SO_4 is already effective in low concentrations. At a higher concentration, the yield of GG conversion products decreased. Similar trends were found when H_3PO_4 or CH_3COOH were the co-catalyst (Fig. 4). Notably, the combination of 4 or 16 equivalents of CH_3COOH and Pd/C shows superior performance in cleaving the ether bond of GG ($\sim 65\%$).

In line with the results of PG conversion (Fig. 3a), the addition of acid promoted the hydrogenation activity of Pd/C. With $\text{Al}(\text{OTf})_3$, the guaiacol selectivity was about 50% – the remainder being methylated and ring-saturated products such as 1,2-dimethoxycyclohexane and a small amount of methoxycyclohexane (Fig. 4). The promoting effect for hydrogenation is stronger with H_2SO_4 : nearly all of the guaiacol-derived products are ring saturated. On the other hand, such a promoting effect was not apparent with HCl , H_3PO_4 and CH_3COOH as co-catalysts, different from the results obtained during PG conversion (Fig. 3a). During PG conversion, the addition of HCl or H_3PO_4 yielded more ring-saturated phenol-derivatives (Fig. 3a). The difference is the higher stability of the aromatic



Fig. 4 Reactions of guaiacylglycerol- β -guaiacyl ether (GG) in methanol over Pd/C and/or different acid co-catalysts at 160 °C for 2 h in 30 bar H_2 .



ring in guaiacol compared with phenol.⁴⁰ This was confirmed by carrying out two separate hydrogenation reactions using guaiacol and phenol as the reactant under identical conditions (Pd/C, 160 °C, 30 bar H₂, 2 h). With guaiacol as the reactant, the use of Pd/C resulted in a conversion to ring-saturated products of 61%, while all the phenol was converted to methoxycyclohexane (Fig. 5a).

A tentative explanation for the promoting effect of acid co-catalysts on the aromatic ring hydrogenation by Pd/C is the removal of hydroxyl groups by their methylation catalyzed by acids. We have shown earlier that hydroxyl groups (*e.g.* as in propanol and sugars) suppress hydrogenation of aromatic rings.³³ This is further supported by two additional experiments in which guaiacol was converted in the presence and absence of an equivalent mass of glucose. Fig. 5b shows the yield of the ring-hydrogenated products as a function of reaction time. The results attest to the lower rate of aromatic ring hydrogenation in the presence of sugars. This result confirms that hydroxyl-rich substrates hinder the hydrogenation activity of Pd/C, presumably by hindering specific adsorption models of the aromatic rings on the Pd surface that would lead to complete ring saturation.³³ In the presence of an acid, the hydroxyl groups are readily converted into methoxy groups in the methanol solvent. This is also supported by the formation of substantial amounts of methylated cyclic products when PG and GG were converted with Pd/C and Al(OTf)₃ or H₂SO₄ as co-catalysts (Fig. 3a and 4).

Based on these results, we conclude that combinations of Pd/C and H₂SO₄ or HCl are effective in cleaving two different types of lignin-carbohydrate (phenyl glycosidic and ester) as well as lignin-lignin (β -O-4 ether) linkages. The combination of Pd/C and weak H₃PO₄ acid is only active in cleaving the phenyl glycosidic bond and β -O-4 ether bonds, and not in the cleavage of ester type lignin-carbohydrate linkages. CH₃COOH, the weakest among the tested acids, is not effective in cleaving any of the lignin-carbohydrate linkages.

Oak sawdust upgrading

With these model compound experiment results in hand, we evaluated the performance of the acids as co-catalysts in the upgrading of oak wood. In a typical

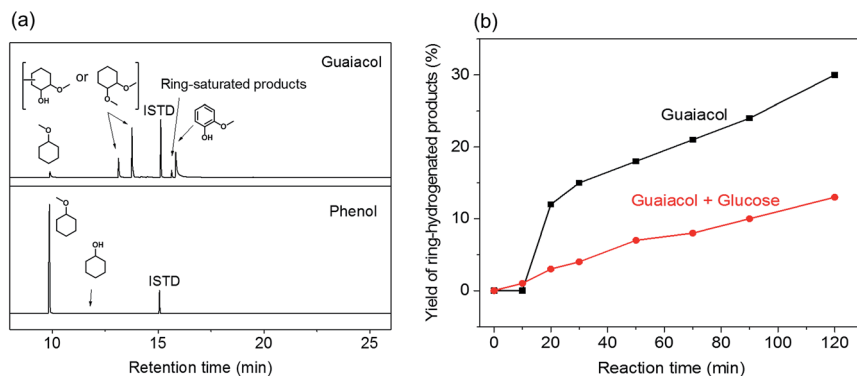


Fig. 5 (a) Gas chromatograms of the reactions in methanol using phenol and guaiacol as model substrates; (b) yield of ring-hydrogenated products obtained from the hydrogenation reaction of guaiacol (black) and guaiacol + glucose (red) in methanol (conditions: 50 mg of substrate, 30 ml of methanol, 10 mg of Pd/C, 160 °C, 2 h, 30 bar H₂).

experiment, 2000 mg of extracted oak wood sawdust, 100 mg of 5 wt% Pd/C and different equivalents of acid (1 equivalent = 0.0316 mmol) were added to a 100 ml autoclave together with 40 ml of methanol (180 °C, 2 h, 30 bar H₂). The acid concentration was the same as in the model compound experiments. An aliquot of the reaction mixture was analyzed by GC-MS and GC-FID to quantify the lignin monomers and methylated sugars. Some of the reaction mixtures were also analyzed by gel permeation chromatography (GPC). Table 1 summarizes the overall results of the tandem-catalyzed reductive fractionation of oak sawdust using different acid co-catalysts under different conditions.

Without a catalyst, the reaction mixture contains only 6 wt% C9 lignin monomers (entry 1). A large amount (1655 mg) of solid biomass residue was obtained (83 wt% based on the mass of the starting biomass). This solid residue was subjected to further analysis to determine the Klason lignin content. The results show that delignification is about 35 wt%, suggesting that methanol is not effective in extracting lignin from woody biomass at 180 °C. The low monomer yield and high solid residue retention obtained in the blank experiment are caused by the low degree of delignification and lignin depolymerization. By adding the Pd/C catalyst, the lignin monomer yield increased to 19 wt%, with PS-H, PS-OH and PG-OH as the main products (Table 1 entry 2, Fig. 6a). The improved yield is mainly due to the enhanced lignin depolymerization. Besides, the extent of delignification was also found to be slightly increased (57 wt%) compared with the blank reaction (entry 1, 35 wt%). This could be due to the fact that Pd/C is also effective in cleaving the phenyl glycosidic linkage. However, the delignification is limited by the poor accessibility of the solid biomass for the solid Pd/C catalyst.

In the benchmark case using 1 equivalent of Al(OTf)₃ as the co-catalyst, the yield of lignin monomers increased substantially. A yield of 40 wt% C9 lignin monomer was obtained after a 1 h reaction at 180 °C and the yield increased to 46 wt% after 2 h (entry 3). The delignification degree is 82 wt%. The C9 lignin monomers are mainly PS-H, PS-OH and PS-OCH₃, and small amounts of PG-H, PG-OH and PG-OCH₃ (Fig. 6a). Apart from these mono-aromatics, an amount of 274 mg of methylated C5 sugars was formed. No cellulose-derived C6 sugars nor sugar degradation products were observed. Sugar degradation was only observed when a larger amount of metal triflate was used, consistent with our earlier work.³⁴ For instance, some aliphatic ketones, such as 2,5-hexanedione, and esters, such as the methyl ester of levulinic acid, were observed when 3 equivalents of Al(OTf)₃ were used in combination with 200 mg of Pd/C for the reductive fractionation of birch wood sawdust at 180 °C for 2 h.³⁴ The incomplete mass balance is due to the presence of lignin dimers and oligomers, which were not identified. Their formation was confirmed by GPC analysis (*vide infra*).

The influence of other acid co-catalysts was evaluated under identical conditions. The use of small amounts of HCl did not improve the lignin monomer yield compared with the Pd/C-only case (entries 4–5). However, larger amounts improved the yields of lignin monomers and also increased the amount of methylated C5 sugars (entries 6–7). With the largest amount of HCl, the lignin monomer yield was 44 wt% (entry 7). The amount of solid residue and the monomeric lignin product distribution (Fig. 5a) are very similar to the results obtained with Al(OTf)₃.

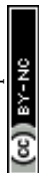




Table 1 Influence of different acid co-catalysts on the tandem-catalyzed reductive fractionation of oak sawdust over Pd/C in methanol at 180 °C

Entry	Catalyst	Acid co-catalyst		pH ^a	Solid residue mass (mg)		Delignification ^c (wt%)	Lignin monomers yield ^e wt% (mg)			Methyl C5 sugars (mg)	Total yield (wt%)
		Type	Amount (mmol)		Amount ^b (mg)	Delignification ^c (wt%)		0 h ^d	1 h	2 h		
1	—	—	—	6.6	1655	35	1	5	6 (26)	4	84	
2	Pd/C	—	—	6.6	1619	57	4	14	19 (81)	4	85	
3	Pd/C	Al(OTf) ₃	0.0316 (1×)	3.4	1175	82	18	40	46 (206)	274	83	
4	Pd/C	HCl	0.0316 (1×)	3.0	1546	N/A	4	11	14 (62)	5	81	
5	Pd/C	—	0.126 (4×)	2.2	1422	N/A	6	15	18 (78)	20	76	
6	Pd/C	—	0.506 (16×)	1.7	1211	N/A	12	21	23 (100)	133	72	
7	Pd/C	—	1.011 (32×)	1.4	1148	75	21	41	44 (194)	249	80	
8	Pd/C	H ₂ SO ₄	0.0316 (1×)	2.9	1562	N/A	4	9	10 (44)	5	81	
9	Pd/C	—	0.126 (4×)	2.2	1017	76	23	31	35 (153)	257	71	
10	Pd/C	—	0.506 (16×)	1.7	328	N/A	28	35	40 (176)	46	28	
11	Pd/C	H ₃ PO ₄	0.0316 (1×)	3.6	1761	N/A	1	6	13 (55)	20	92	
12	Pd/C	—	0.126 (4×)	3.1	1600	N/A	3	9	13 (55)	19	84	
13	Pd/C	—	0.506 (16×)	2.8	1448	N/A	3	13	17 (75)	30	78	
14	Pd/C	—	1.011 (32×)	2.6	1358	69	5	14	26 (117)	31	77	
15	Pd/C	CH ₃ COOH	0.0316 (1×)	5.0	1598	N/A	4	10	15 (65)	5	83	
16	Pd/C	—	0.126 (4×)	4.1	1577	N/A	3	8	10 (41)	6	81	
17	Pd/C	—	0.506 (16×)	3.7	1639	N/A	1	5	8 (35)	7	84	
18	Pd/C	—	1.011 (32×)	3.5	1649	40	1	4	6 (26)	3	84	

^a pH values were measured at room temperature using an electronic pH meter after replacing 20 vol% of the acidic methanol solution with water. ^b Mass of the residue excluding Pd/C catalyst. ^c Delignification was determined by analyzing the Klason lignin content of the solid residue, assuming the Pd/C is homogeneously mixed with the biomass residue. ^d Heating time (30 min). ^e Lignin yield is based on the acid-insoluble (Klason) lignin content (22.4 wt%) of the pre-extracted oak sawdust.

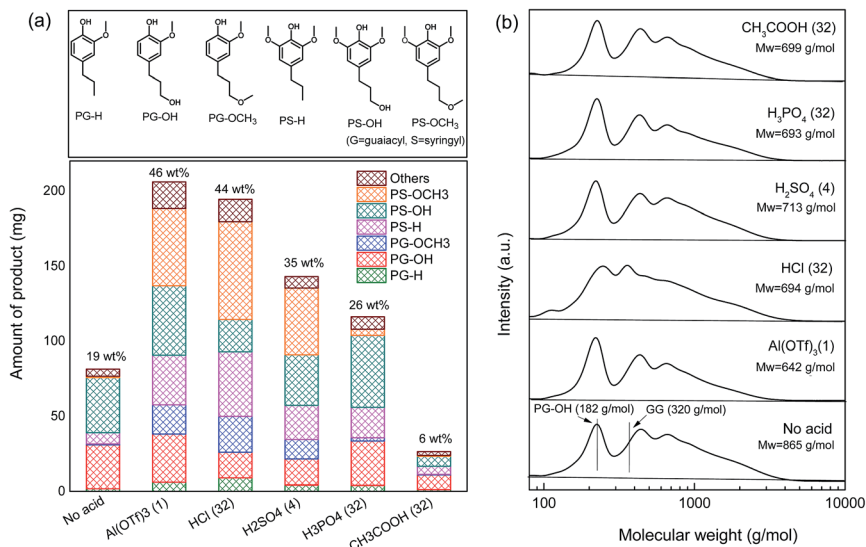


Fig. 6 (a) Lignin monomeric product distributions and (b) GPC chromatograms of the reaction mixtures obtained from the reactions over Pd/C in combination with different acid co-catalysts at 180 °C for 2 h. (Conditions: 2000 mg of pre-extracted oak sawdust, 100 mg of Pd/C, 30 bar H₂, 40 ml of methanol; 1 eqv. = 0.0316 mmol of acid; the numbers on top of the bars in (a) are the lignin monomer yields; GPC results of two reference compounds (GG: guaiacylglycerol- β -guaiacyl ether and PG-OH: 4-*n*-propanolguaiacol) are included.)

At the lowest concentration, H₂SO₄ hardly affected the conversion as with HCl (entry 8). The lignin monomer yield increased drastically to 35 wt% when 4 equivalents of H₂SO₄ were used (entries 9–10). The lignin monomeric product distribution and the amount of residue (1017 mg) are very similar to the best result obtained with HCl (1148 mg, 32 eqv., entry 7) and the Al(OTf)₃ reference

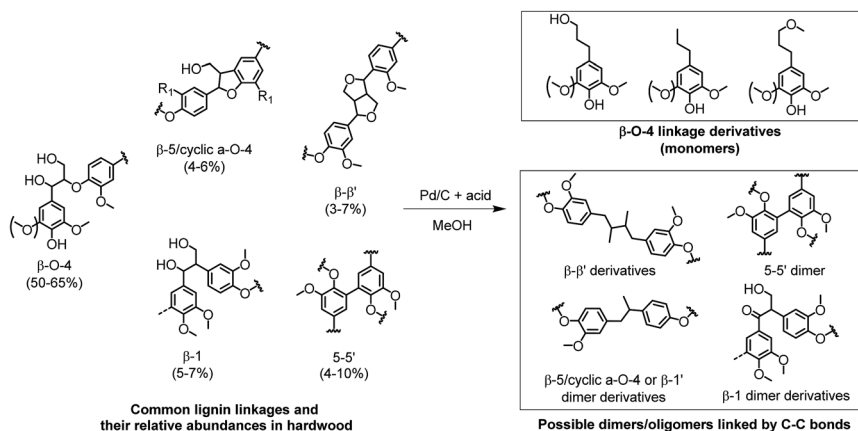
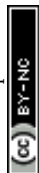


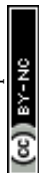
Fig. 7 Formation of lignin monomers and proposed dimers and oligomers in the process of reductive fractionation of lignin from woody biomass. (The proposed structure and relative abundances are based on the literature.^{14,22,25})



(1175 mg, entry 3). The delignification degree in this case is 76 wt%. Although increasing the dosage of H_2SO_4 acid resulted in a slightly higher yield of lignin monomers (40 wt%), much less solid residue was left, suggesting that a significant fraction of cellulose was converted. Moreover, darkening of the solution and the very low mass balance (28 wt%) point to humin formation from the released C6 sugars. These findings limit the use of high concentrations of H_2SO_4 .

The influence of H_3PO_4 was minor with lignin monomer yields below 20 wt% (entries 11–13). Moreover, it is seen that the solid carbohydrate residue is decreasing with increasing H_3PO_4 content. The lignin monomer yields are even lower than the reference case without H_3PO_4 (19 wt%, entry 2). A maximum yield of 26 wt% lignin monomers was achieved after a 2 h reaction at 180 °C at the highest H_3PO_4 concentration (entry 14). The yield is slightly lower than the one reported in the literature.³¹ It was reported that the addition of 2.5 g L⁻¹ (equal to 27.8 equivalents) H_3PO_4 in combination with Pd/C resulted in a lignin monomer yield of approximately 40 mol%, compared with the yield obtained from the neutral methanol solvent (26 mol%) at 200 °C using pre-extracted poplar sawdust feedstock. This difference could be caused by the lower reaction temperature (180 °C vs. 200 °C), the different feedstock (oak vs. poplar sawdust) and the different calculation methods (wt% vs. mol%). Nevertheless, it can be said that the addition of an appropriate amount of H_3PO_4 improves the overall efficiency of the reductive fractionation process. Yet, compared with $\text{Al}(\text{TOF})_3$ and the other stronger Brønsted acids (HCl and H_2SO_4), the promoting effect of H_3PO_4 is less pronounced. Our model compound experiments show that the combination of H_3PO_4 and Pd/C is active in cleaving the phenyl glycosidic lignin–carbohydrate and β -O-4 ether types of lignin–lignin linkages, but less active in cleaving the ester type lignin–carbohydrate linkages. We surmise that part of the lignin (linked by ester bonds) might not be effectively extracted from the biomass matrix. This is further confirmed by the relatively low degree of delignification (68 wt%), revealed by the compositional analysis of the solid residue obtained at the highest H_3PO_4 concentration. Furthermore, we observed that the lignin monomers are mostly non-etherified products, such as PS-H, PS-OH and PG-OH (Fig. 6a). Also, a small amount of methylated C5 sugars was formed. These results indicate that methylation/etherification is not occurring due to the low acidity of H_3PO_4 (entries 11–14). It is known that sugars and their derivatives (e.g. 5-HMF, furfural) can condense with each other and lignin-derived products under acidic conditions into humins.^{41,42} Methylation stabilizes sugars.^{43,44} In our earlier work, it was also confirmed that methylation of the lignin phenolic intermediates plays a key role in hindering repolymerization of lignin fragments and avoiding char formation.¹² Accordingly, we argue that the low rate of etherification might be another reason for the lower efficiency of H_3PO_4 .

With CH_3COOH as the co-catalyst, a lignin monomer yield of 15 wt% was obtained at the lowest concentration (entry 15), which is close to the yield obtained in the case of the Pd/C catalyst. When the concentration was increased, the lignin monomer yield decreased significantly (entries 15–18). The lignin products were mostly non-etherified PS-OH, PS-H and PG-OH (Fig. 5). The amount of solid residue was nearly unchanged, suggesting that the delignification could not be improved by increasing the amount of CH_3COOH . Analysis of the Klason lignin content of the solid residue showed that 40 wt% lignin was released from the woody biomass at the highest CH_3COOH concentration. Based on the decreasing



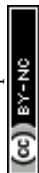
lignin monomer yield and unchanged solid residue yield, we infer that the addition of CH_3COOH negatively affects the lignin conversion, consistent with the model compound results. The lack of delignification and etherification is likely the cause of the low lignin monomer yield.

Based on the lignin monomer yields and the solid carbohydrate residue, lignin oil samples obtained from the following experiments were subjected to GPC analysis: no acid, $\text{Al}(\text{OTf})_3$ (1 eqv.), HCl (32 eqv.), H_2SO_4 (4 eqv.), H_3PO_4 (32 eqv.) and CH_3COOH (32 eqv.). Fig. 6b shows the results of the GPC analysis. Surprisingly, all of the selected lignin oils gave very similar results. Three broad peaks were observed related to lignin monomers, dimers and oligomers. For all the acid-catalyzed lignin oil samples, the molecular weights (M_w) were between 642 g mol^{-1} ($\text{Al}(\text{OTf})_3$) and 713 g mol^{-1} (H_2SO_4 (4 eqv.)), which are slightly lower than the molecular weight for the Pd/C -only case (865 g mol^{-1}). This confirms that the addition of acid contributes to lignin depolymerization.³⁴ The dimers and oligomers are likely to be linked by strong C–C bonds. The possible formation of dimers and oligomers is shown in Fig. 7. These C–C linkages either originate from the native structure (e.g. β -1, 5-5') or they derive from the cleavage of some ether linkages (e.g. β - β' , β -5/cyclic α -O-4). The cleavage of C–C linkages requires a higher temperature. Accordingly, the fraction of ether linkages (typically 50–65% β -O-4 ether linkages in hardwood) puts an upper limit on the lignin monomers yield.

In brief, the most promising replacement of $\text{Al}(\text{OTf})_3$ is HCl , which is able to obtain a 44 wt% yield of lignin monomers from oak wood sawdust in reductive fractionation using Pd/C at 180°C in 2 h. A drawback of the use of HCl is corrosion of the process equipment, which will add to the overall cost of biomass upgrading. The alkylmethoxyphenols resulting from this approach can be used in the fragrance industry (e.g. dihydroeugenol) or upgraded to other valuable base chemicals, such as (alkyl)phenols. One challenge in this lignin-first approach is that the metal catalyst ends up in the solid residue. A solution is to separate the delignification step and hydrogenolysis steps. This approach has been demonstrated in a recent study.³³ The resulting carbohydrate solid residue is an ideal starting material for the paper industry and can also be used in the production of biobased chemicals, such as ethanol, levulinic acid, and γ -valerolactone.

Conclusions

We explored Brønsted acids as alternatives to $\text{Al}(\text{OTf})_3$ co-catalysts in the tandem reductive delignification of biomass to aromatics using Pd/C as the hydrogenolysis catalyst. The main role of the acid catalyst is to delignify lignocellulosic biomass, while Pd/C cleaves the ether bonds in the released lignin fragments. The solid residue in this process is a cellulose-rich fraction that also contains some hemicellulose and lignin. We systematically compared HCl , H_2SO_4 , H_3PO_4 and CH_3COOH as co-catalysts for the tandem reductive fractionation of woody biomass in methanol using Pd/C at 180°C for 2 h. Model compound experiments (PG, GT and GG) show that the combinations of Pd/C and strong Brønsted acids (H_2SO_4 and HCl) are suitable to cleave phenyl glycosidic and ester type lignin-carbohydrate linkages as well as lignin-lignin (β -O-4 ether) linkages. The combination of Pd/C and the weaker acid H_3PO_4 was only able to cleave phenyl glycosidic bonds and β -O-4 ether bonds but not ester type lignin-carbohydrate



linkages. CH_3COOH is not effective in cleaving the model lignin-carbohydrate linkages. These model compound results explain the better catalytic performance of $\text{Al}(\text{OTf})_3$, HCl and H_2SO_4 compared to H_3PO_4 and CH_3COOH for the upgrading of oak wood biomass. The poor performance of the latter two weak acids is due to their low activity in delignification. The most promising replacement of $\text{Al}(\text{OTf})_3$ is HCl . Under optimum conditions, a 44 wt% yield of lignin monomers was obtained from oak wood sawdust, similar to the result obtained with the metal triflate.

Experimental section

Chemicals and materials

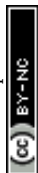
Oak wood sawdust was obtained from Houtzagerij Mennen (<http://www.houtzagerijmenn.nl>). Birch wood was obtained from the Energy Research Center of Netherlands (ECN). 5 wt% Pd/C, $\text{Al}(\text{OTf})_3$ ($\geq 99\%$), CH_3COOH ($\geq 99\%$) and H_3PO_4 (85 wt% in water) were purchased from Sigma Aldrich. HCl (37 wt% in water) was purchased from Merck Emsure. H_2SO_4 (95–97%, 99.99% trace metals basis) was purchased from Merck Emsure. 4-*n*-Propanolguaiacol (PG-OH) was purchased from TCI. 4-*n*-Propylsyringol (PS-H) and 4-*n*-methoxy propyl syringol (PS- OCH_3) were recovered from the reaction mixture; the detailed procedure can be found in our previous work.³³ These phenolic compounds were used to determine the weight response factors relative to *n*-dodecane. Glyceryl trioleate ($\geq 97.0\%$), phenyl β -D-glucopyranoside ($\geq 97\%$) and benzyl phenyl ether were purchased from Sigma Aldrich. Guaiacylglycerol- β -guaiacyl ether (GG, $\geq 97\%$) was purchased from TCI. Extra-dry absolute methanol was purchased from Biosolve. All the other commercial chemicals were analytical grade and were used without further purification.

Feedstock pretreatment

Oak wood sawdust was obtained in the sawdust form and sieved to obtain particles with sizes between 150 μm and 300 μm . The wood sawdust was subjected to a Soxhlet extraction with water (~ 4 h) followed by ethanol (~ 4 h) to remove extractives. After extraction, the feedstock particles were dried at 105 $^\circ\text{C}$ overnight for the catalytic reaction.

Catalytic activity measurements

In a typical reaction experiment, the autoclave was charged with a suspension of 2000 mg of feedstock, 100 mg of Pd/C (5 wt% Pd loading), a certain amount of acid (e.g. 0.0316 mmol of $\text{Al}(\text{OTf})_3$) and 30 μl of *n*-dodecane internal standard in 40 ml of methanol. The reactor was sealed and purged with nitrogen and hydrogen several times sequentially. After leak testing, the pressure was brought to 30 bar with hydrogen and the reaction mixture was heated to the reaction temperature under continuous stirring at 500 rpm within 0.5 h. A sampling valve was installed, which allowed the removal of liquid samples during the reaction. About 0.4 ml solutions were taken out from the autoclave during the reaction and analysed directly by GC-MS. After the reaction, the heating oven was removed and the reactor was cooled to room temperature in an ice-water bath. After releasing the pressure, the autoclave was opened and the mixture was collected and



combined with the solution obtained from washing the autoclave with methanol. The collected reaction mixture was filtered by using a filter crucible (porosity 4) under vacuum. The carbohydrate and Pd/C solid residue was left in air to dry for one day to determine the amount of all-solid residue. In some cases, the solid residue was further subjected to a two-stage acid hydrolysis to determine the Klason lignin content following the protocol described earlier.³³

An autoclave with a volume of 12 ml was used for the reactions with the model compounds. In a typical run, 25 mg (PG, GT and GG) of model compound, 10 mg of Pd/C and 10 μ l of *n*-dodecane internal standard were added to 5 ml of methanol, which contained a certain amount of acid (the same concentrations as the corresponding woody biomass reactions described above). After sealing, purging and checking for leaks, the autoclave was heated to 160 °C and maintained at that temperature for 2 h. After the reaction, an aliquot of $\sim$ 1 ml was taken from the reaction mixture and directly analysed by GC-MS without dilution following filtration with a 0.45 μ m syringe filter. In the experiments involving guaiacol and phenol model compounds, a 100 ml Parr autoclave was used as the reactor, which allows sampling during the reaction. In a typical run, 50 mg of reactant (guaiacol, phenol and glucose), 10 mg of Pd/C, and 30 μ l of *n*-dodecane internal standard were added to the reactor together with 30 ml of methanol. The reaction was operated at 160 °C for 2 h.

Product analysis and characterization

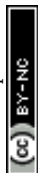
The liquid phase products were analysed by a Shimadzu 2000 GC-MS system equipped with a RTX-1701 column (60 m $\times$ 0.25 mm $\times$ 0.25 μ m) and a flame ionization detector (FID) together with a mass spectrometer (MS) detector. For the lignin monomers, the product peaks were identified using MS and by authentication with reference compounds. All the quantitative analyses of the liquid phase products were based on GC-FID. Experimentally determined weight response factors (RF) were used for calculation relative to *n*-dodecane, which was the internal standard. For some of the commercially unavailable compounds (side-products obtained in small amounts), the RF of PS-OCH₃ was used for quantification. The yield of lignin monomers was calculated using following equation:

$$\text{Yield of monomers (wt\%)} = (\text{weight of monomers})/(\text{weight of starting feedstock} \times \text{Klason lignin weight percentage in oak wood}) \times 100\%$$

For the model lignin compound reactions (PG, GT and GG), the FID response factors were calculated using the Effective Carbon Number (ECN) method⁴⁵ to determine the relative response factors corrected by the molecular weight of the compounds relative to *n*-dodecane, which served as the internal standard.

Gel permeation chromatography (GPC)

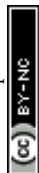
GPC analyses were performed using a Shimadzu apparatus equipped with two columns in series (Mixed-C and Mixed-D, polymer laboratories) and a UV-Vis detector at 254 nm. The column was calibrated with polystyrene standards. Analyses were carried out at 25 °C using THF as the eluent at a flow rate of 1 ml min⁻¹. For the lignin residue analysis, the sample was prepared at



a concentration of 2 mg ml⁻¹. All the samples were filtered using a 0.45 µm filter membrane prior to injection.

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