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A Route for Lignin and Bio-Oil Conversion: Dehydroxylation of Phenols into Arenes by Catalytic Tandem Reactions**

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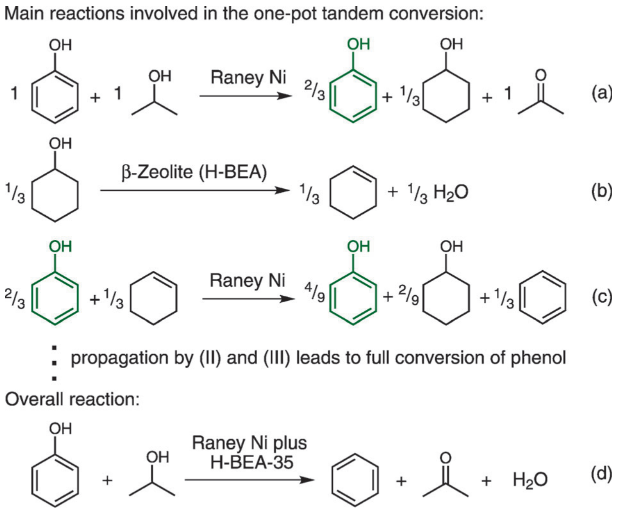
Despite the vast potential for lignin conversion or even for the upgrade of bio-oil,[1,2] the direct dehydroxylation of phenols has remained a very challenging chemical transformation. The Ar−OH bond has a bond dissociation enthalpy of 465 kJ mol^{-1} which is even higher than that of a C−H bond in methane (439 kJ mol^{-1}).[3] The few methods available for phenol dehydroxylation typically require the derivatization of the Ar−OH group with an electron-withdrawing group (EWG) to weaken the C–O bond.[4] As such, the derivatization enables the hydrogenolysis of the C−O[EWG] bond with the use of Pd/C and H_2, thus forming the corresponding arenes.[4] Overall, it is understandably difficult to envision the utilization of these methodologies on a large scale, as required in lignin or bio-oil valorization, since they generate stoichiometric quantities of nonrecyclable waste. Herein we report the first nonderivative method for phenol dehydroxylation yielding arenes under low-severity conditions.[5] We demonstrate this mild procedure as highly useful for the depolymerization of lignin and removal of its oxygen-containing functionalities, in addition to dehydroxylation of phenols. Moreover, the method also appears to be a fundamental finding for the upgrade of bio-oils to monocyclic and bicyclic arenes.

The current approach for phenol dehydroxylation (Scheme 1) consists of coupling the hydrogenation of phenol to cyclohexanol (a) and dehydration of cyclohexanol to cyclohexene (b) with dehydrogenation of cyclohexene to benzene (c). Under H_2 pressure, the combination of steps (a) and (c) in a one-pot procedure is impossible. We demonstrate, however, that steps (a) and (c) become compatible in a one-pot procedure when the reactions are performed by H transfer in the absence of H_2. The one-pot procedure is carried out in the presence of Raney Ni and β-zeolite using 2-propanol (2-PrOH) as an H-donor in a molar ratio of 2-PrOH-to-phenol between 1 and 3. At first sight, the latter condition should limit the hydrogenation of phenol to cyclohexanol (a). However, the conversion of phenol proceeds by the utilization of cyclohexene formed by (b). As it will be discussed here, the reaction (c) is more thermodynamically favorable than (a). Therefore, the limitation of fully converting phenol is circumvented by the propagation of the reaction chain by steps (b) and (c). Accordingly, we henceforth adopt the terms H-transfer initiator and H-transfer propagator for the roles of 2-PrOH and cyclohexene, respectively, in the system.



Scheme 1. Simplified pathway proposed for the dehydroxylation of phenols to arenes by catalytic tandem reactions with concurrent use of Raney Ni and β-zeolite (H-BEA-35). The structure in green corresponds to the unconsumed phenol by steps (a) and (c).

In our endeavor to design this methodology, we found that three parameters are key for achieving both high conversion of phenols and high selectivity for arenes: 1) the type of the solid acid (SA), 2) the molar ratio of 2-PrOH to substrate ("n"), and 3) the weight ratio of solid acid to Raney Ni (SA/Ni). An initial screening of SA revealed the following order of selectivity for benzene at about 90 % conversion of phenol: Na-BEA-35 (17 %) $\approx$ γ-Al_2O_3 (18 %) $<$ SiO_2-Al_2O_3 (28 %) $\ll$ H-ZSM-5 (49 %) $\ll$ H-MOR-40 (73 %) $<$ H-BEA-35 (79 %, details provided in Tables S1–S2 in the Supporting Information). Accordingly, we chose the concurrent use of H-BEA-35 and Raney Ni to examine the effect of the parameters n and SA/Ni on the reaction. The results are listed in Table 1.

Yields of benzene of up to 82 % are achieved with $1.5 \leq n \leq 2.5$ (Table 1, entries 5 and 7). An increase in the parameter n from 2.5 to 4 (entries 7 and 8) decreased the selectivity for benzene (from 81 to 58 %). In addition, the selectivity for cyclohexane increased (from 14 to 32 %). Only when using substochiometric quantities of 2-PrOH ($n < 3$) is the utilization of cyclohexene as an H-donor a required condition for achieving a full conversion of phenol. The ability of cyclo-

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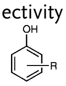
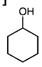
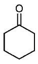
Table 1: Results of the phenol dehydroxylation.[a]

Entry	n [mol/mol]	SA/Ni [wt/wt]	Conv. [%]	C Selectivity [%][b] 				
1	0	0.133	33	25	0.3	8	0	0.3
2[c]	1.5	0.133	90	74	9	3	0	0.4
3	1.0	0.133	73	73	11	7	0	0
4	1.5	0.083	98	79	9	4	0	0
5	1.5	0.133	100	82	9	2	0	0
6	1.5	0.250	92	71	9	10	0	0
7	2.5	0.133	100	81	14	0	0	0
8	4.0	0.133	100	58	32	0	0	0.2
9[c]	4.5	0	99	4	1	0	76	16
10[c]	2.25[d]	0	100	[e]	[f]	0	61	23

[a] General reaction conditions: phenol (2 mmol), 2-PrOH, n-$C_{16}H_{34}$ (7 mL, solvent), $T = 433$ K, 4 h. [b] For a complete list of products, see Table S3 in the Supporting Information. [c] Reaction time: 0.5 h. [d] H-donor: cyclohexene. Absolute content (in mmol): [e] C_6H_6 (3.2) and [f] C_6H_{12} (1.4).

hexene to serve as an H-donor was demonstrated by the conversion of phenol with Raney Ni and cyclohexene at 433 K for 0.5 hours. As shown in entries 9 and 10 of Table 1, the reaction using cyclohexene achieved similar results to that using 2-PrOH.

With regard to the quantity of H-BEA-35 (Table 1, entries 4–6), SA/Ni = 0.133 is the optimal ratio for the full conversion of phenol into benzene in high yields (entry 5). Using a higher quantity of H-BEA-35 decreased both conversion of phenol (from 100 to 92 %) and the selectivity for benzene (from 82 to 71 %; entries 5 and 6). This phenomenon is caused by two plausible reasons. First, as detected by GC-MS, the depletion of transferable hydrogen through the pathway 2-PrOH→propene→propane starts to become important in the experiment listed in entry 6 of Table 1. Second, the depletion of the H-transfer initiator can also proceed by the alkylation or etherification of phenol with 2-PrOH, as indicated by an increase in the overall selectivity for C_9–C_{10} products (from 3 to 13 %, see entries 5 and 6 in Table S3 in the Supporting Information) by altering the H-BEA to Raney-Ni ratio from 0.133 to 0.250.

Throughout the tandem conversion of phenol into benzene, several intermediates are formed, and they play different roles in the system. While acetone and cyclohexanone act as H-acceptors, cyclohexanol and cyclohexene serve as H-donors. Concurrently, side reactions (e.g., hydrogenation of cyclohexene, and dehydration of 2-PrOH followed by hydrogenation of propene) may also take place, thus leading to the depletion of transferable H-content. To shed light on possible pathways occurring in the one-pot conversion, the Gibbs free energy for hypothetical gas-phase reactions at 433 K under 1 bar were calculated (for the complete dataset, see Table S5 in the Supporting Information).

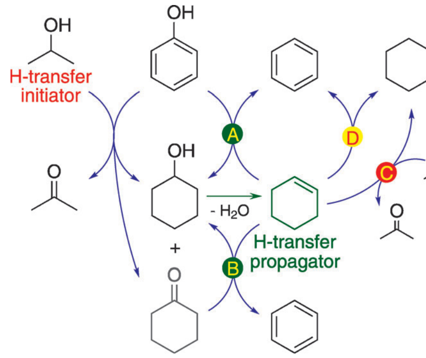
The data in Table 2 shows several important features. First, the conversion of one mole of phenol into cyclohexanol using cyclohexene is markedly much more exergonic than that utilizing 2-PrOH or cyclohexanol [Eqs. (1)–(6)]. Moreover, cyclohexane cannot serve as an H-donor in the hydrogenation of phenol because this reaction is highly endergonic at 433 K [Eq. (7)]. Second, the dehydration of cyclohexanol [Eq. (8)] is more favorable than that of 2-PrOH by -9 kJ mol^{-1} [Eq. (19)]. This favorability is one of the key factors accounting for the atom-efficient utilization of 2-PrOH as an H-transfer initiator because it prevents 2-PrOH from dehydrating to propene. Third, phenol and cyclohexanone are much better H-acceptors than acetone in the conversion of cyclohexene into benzene, since the reactions using cyclohexanone or phenol are more exergonic than that utilizing acetone, by about -16 kJ mol^{-1} [Eqs. (9)–(12)]. Consequently, the transfer hydrogenation of acetone should take place preferentially after the full conversion of phenol. Finally, the hydrogenation of cyclohexene or propene ranks among of the most exergonic reactions regardless of the H-donor [Eqs. (13)–(18)]. The transfer hydrogenation of cyclohexene with 2-PrOH is the most favorable reaction in the system [$\Delta_r G = -53$ kJ mol^{-1}, Eq. (13)]. Hence, the amount of H-donor initiator must be carefully controlled to avoid the shift of selectivity towards cyclohexane.

The energetics of the reactions indicate four highly favorable pathways consuming cyclohexene (Scheme 2). Pathways A and B [Eq. (9) and (10), respectively] lead to the H-transfer propagation upon formation of benzene, while pathways C and D [Eq. (13) and (15), respectively] result in depletion of transferable H-content upon formation of cyclohexane.

Pathway A involves the hydrogenation of phenol to cyclohexanol using cyclohexene as the H-transfer propagator,

Table 2: Gibbs free energy of gas-phase reactions at 433 K, 1 bar.

Equation		$\Delta_r G$ (433 K) [kJ mol^{-1}]
H-donors in the hydrogenation of phenol		
1	$C_6H_5OH_{(g)} + 1.5\,C_6H_{10(g)} \rightarrow C_6H_{11}OH_{(g)} + 1.5\,C_6H_{6(g)}$	-50
2	$C_6H_5OH_{(g)} + C_6H_{10(g)} \rightarrow C_6H_{10}O_{(g)} + C_6H_{6(g)}$	-33
3	$C_6H_5OH_{(g)} + 3\,i\text{-}C_3H_7OH_{(g)} \rightarrow C_6H_{11}OH_{(g)} + 3\,C_3H_6O_{(g)}$	-24
4	$C_6H_5OH_{(g)} + 2\,i\text{-}C_3H_7OH_{(g)} \rightarrow C_6H_{10}O_{(g)} + 2\,C_3H_6O_{(g)}$	-16
5	$C_6H_5OH_{(g)} + 2\,C_6H_{11}OH_{(g)} \rightarrow 3\,C_6H_{10}O_{(g)}$	0
6	$C_6H_5OH_{(g)} + {}^{2}/_{3}\,C_6H_{12(g)} \rightarrow C_6H_{10}O_{(g)} + {}^{2}/_{3}\,C_6H_{6(g)}$	8
7	$C_6H_5OH_{(g)} + C_6H_{12(g)} \rightarrow C_6H_{11}OH_{(g)} + C_6H_{6(g)}$	12
Dehydration of cyclohexanol		
8	$C_6H_{11}OH_{(g)} \rightarrow C_6H_{10(g)} + H_2O_{(g)}$	-22
H-acceptors in the conversion of cyclohexene into benzene		
9	$C_6H_{10(g)} + 2\,C_6H_{10}O_{(g)} \rightarrow C_6H_{6(g)} + 2\,C_6H_{11}OH_{(g)}$	-33
10	$C_6H_{10(g)} + {}^{2}/_{3}\,C_6H_5OH_{(g)} \rightarrow C_6H_{6(g)} + {}^{2}/_{3}\,C_6H_{11}OH_{(g)}$	-33
11	$C_6H_{10(g)} + C_6H_5OH_{(g)} \rightarrow C_6H_{6(g)} + C_6H_{10}O_{(g)}$	-33
12	$C_6H_{10(g)} + 2\,C_3H_6O_{(g)} \rightarrow C_6H_{6(g)} + 2\,i\text{-}C_3H_7OH_{(g)}$	-17
Depletion of the transferable H-content		
13	$C_6H_{10(g)} + i\text{-}C_3H_7OH_{(g)} \rightarrow C_6H_{12(g)} + C_3H_6O_{(g)}$	-53
14	$C_6H_{10(g)} + C_6H_{11}OH_{(g)} \rightarrow C_6H_{12(g)} + C_6H_{10}O_{(g)}$	-45
15	$C_6H_{10(g)} \rightarrow {}^{2}/_{3}\,C_6H_{12(g)} + {}^{1}/_{3}\,C_6H_{6(g)}$	-41
16	$C_3H_{6(g)} + 0.5\,C_6H_{10(g)} \rightarrow C_3H_{8(g)} + 0.5\,C_6H_{6(g)}$	-46
17	$C_3H_{6(g)} + i\text{-}C_3H_7OH_{(g)} \rightarrow C_3H_{8(g)} + C_3H_6O_{(g)}$	-37
18	$C_3H_{6(g)} + C_6H_{11}OH_{(g)} \rightarrow C_3H_{8(g)} + C_6H_{10}O_{(g)}$	-29
19	$i\text{-}C_3H_7OH_{(g)} \rightarrow C_3H_{6(g)} + H_2O_{(g)}$	-13



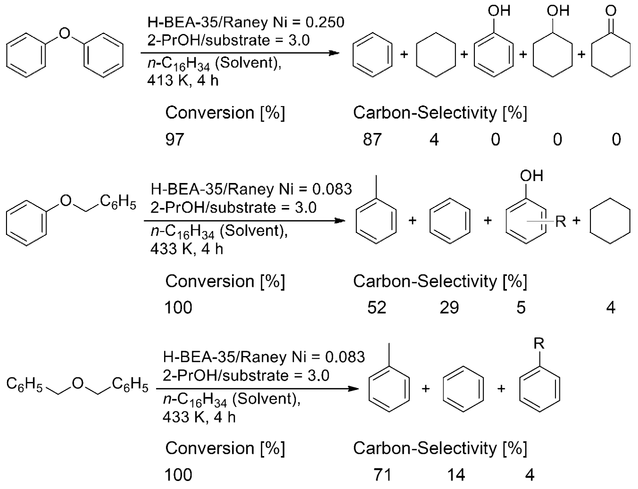
Scheme 2. Proposed pathways A–D based on reaction energetics (see Table 2). Arrows in blue indicate the reactions catalyzed by Raney Ni, and the arrow in green indicates the dehydration step catalyzed by H-BEA-35. The stoichiometry was omitted for clarity (refer to Table 2 for the reaction stoichiometry).

as shown in Scheme 1. Nonetheless, the formation of cyclohexanone always takes place to a certain extent when the transfer hydrogenation of phenol is performed with a low amount of 2-PrOH (e.g., Table 1, entry 9). Thus, pathway B also contributes to the formation of benzene upon reduction of cyclohexanone to cyclohexanol [Eq. (9)]. The pathways A and B are concurrent in the system because of similar reaction energetics [Eq. (9) and (10)]. In turn, when performing the experiment with high amounts of 2-PrOH ($n>4$), the undesirable pathway C is observed [Eq. (13)]. Lastly, pathway D [Eq. (15)], which is even more exergonic than pathways A and B, is also prone to occur in the system. Despite this, pathway D is partially hindered by the extremely low concentration of cyclohexene in the reaction medium. Indeed, cyclohexene was not detected in the product mixtures obtained by experiments with concurrent use of Raney Ni and H-BEA.

The consideration of these four pathways leads to three very distinct situations regarding the selectivity for benzene. If pathways A and B are followed, a yield of 100 % benzene would most probably be achieved. Next, if only pathway C is followed, the transferable hydrogen would be fully used for the formation of cyclohexane. Finally, if only pathway D is observed, the conversion of one mole cyclohexene into benzene and cyclohexane ($^1/_3$ mol:$^2/_3$ mol, respectively) would enable a maximum yield of 33 % benzene. We conclude from the data in Table 1 that pathways A and B are predominant over pathways C and D in experiments carried out with $1.5 \leq n \leq 2.5$, as indicated by high selectivity for benzene (82 %; Table 1, entries 5 and 7). However, pathway C starts to be predominant at $n>4$, as demonstrated by the marked decrease in the selectivity of benzene (from 82 to 58 %) in addition to the increase in the selectivity for cyclohexane (from 9 to 32 %; Table 1, entry 8).

Previously, we found that Raney Ni is an extremely active catalyst for hydrogen transfer reactions and, in particular, shows a considerably high chemoselectivity for transfer hydrogenolysis of diaryl, aryl alkyl, and dibenzyl ethers.[6] This feature is key when one considers its utilization in lignin conversion. In the presence of Raney Ni with 2-PrOH as both a solvent and an H-donor, the hydrogenolysis of diphenyl ether generates phenol and benzene. Nonetheless, under the reaction conditions, phenol undergoes hydrogenation yielding cyclohexanol, thus wasting hydrogen.[6–7]

Alternatively, Scheme 3 shows that the concurrent use of Raney Ni and H-BEA-35 allows the hydrogenolysis of ether linkages to proceed without the formation of saturated products. So far, such high selectivity for arenes was achieved only in the presence of homogeneous catalysts,[8] unsupported metal nanoparticles,[9] or a Pd/Zn/C catalyst.[10] However, these approaches are not able to dehydroxylate phenols. Through our current approach, however, diphenyl ether, phenyl benzyl ether, and dibenzyl ether were fully converted with high selectivity for arenes (80–90 %; Scheme 3).



Scheme 3. HDO of diphenyl ether, benzyl phenyl ether, and dibenzyl ether. See Table S4 in the Supporting Information for full list of products.

Inspired by the results obtained from the experiments with model compounds, we applied the methodology to the conversion of real raw materials, that is, bio-oil and organosolv lignin. Bio-oil was prepared by pyrolysis of pinewood. To remove lower alcohols and carboxylic acids, bio-oil was washed with saturated $KHCO_3$. The extraction of carboxylic acids is needed because they poison Raney Ni.[6] The isolated fraction contains furans and methoxyphenols, as revealed by GC × GC-MS analysis (Figure 1 a). Applying the catalytic procedure to the fractionated bio-oil leads to arenes and saturates forming the major products (Figure 1 b). A yield of about 50 wt % colorless oil was isolated after rotary evaporation of n-pentane at 313 K under reduced pressure (50 mbar). Semi-quantitative analysis by GC × GC-FID indicates that 71 wt % of the detected products are arenes, 26 wt % alkanes, and 3 wt % phenols. Similar results to those with bio-oil were obtained with lignin (Figure 1 c), with a yield of about 40 wt % of an isolated colorless oil (78 wt % of the detected products are arenes, 18 wt % alkanes, and only 4 wt % are phenols).

The yields of 40–50 wt % of the isolated oils correspond, indeed, to high carbon yields (70–80 %), since the C-content of the substrates (lignin, 59 % and bio-oil, 70 %) is much

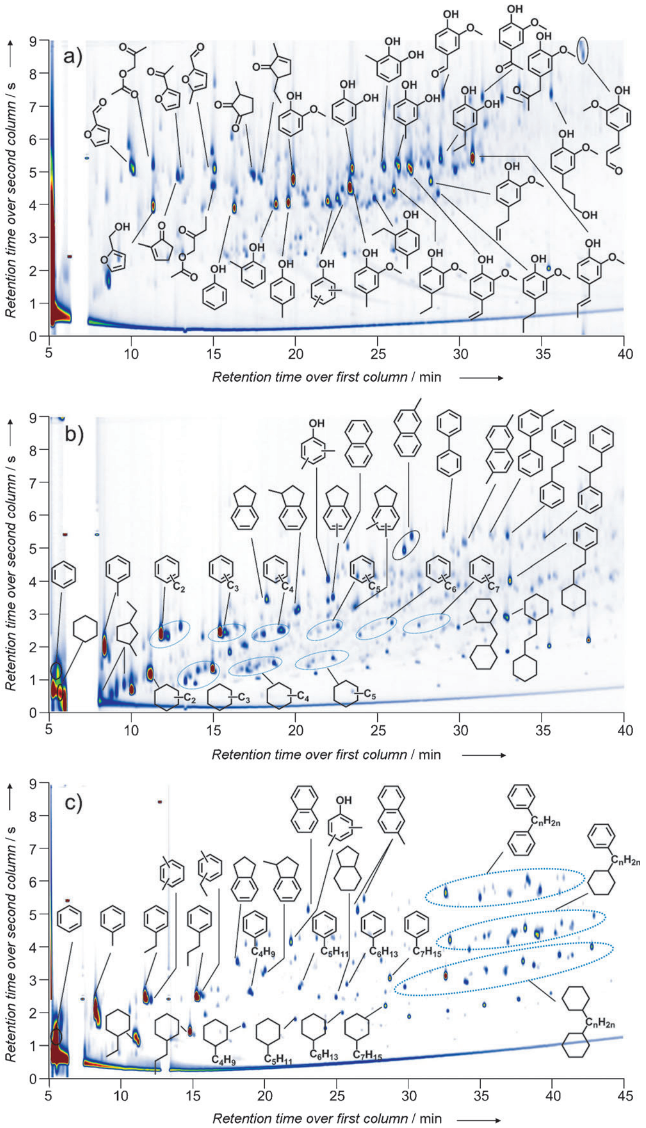


Figure 1. GC×GC-MS of fractionated bio-oil before (a) and after (b) transfer HDO. c) Volatile products from organosolv lignin. Reaction conditions: Raney Ni (0.6 g), H-BEA-35 (0.050 g), substrate (0.1 g), 2-PrOH (0.50 g), *n*-pentane (7 mL) processed at 433 K for 2 h and sequentially at 493 K (bio-oil) or 513 K (lignin) for an additional 2 h.

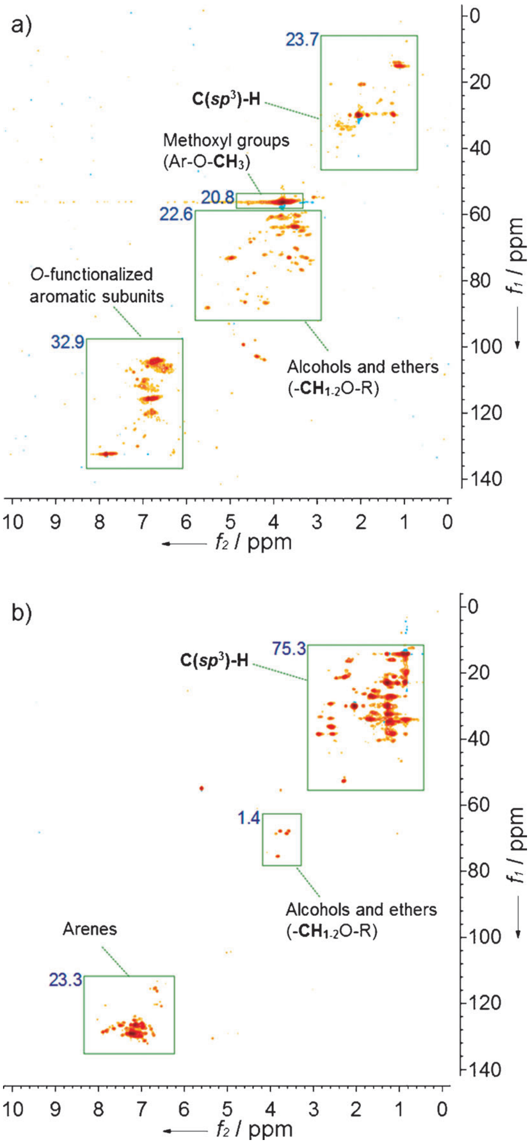


Figure 2. a) HSQC 2D NMR experiments on organosolv lignin (in [D$_6$]acetone:D$_2$O 90:10, v/v). and b) HSQC 2D NMR experiments on lignin products (in [D$_6$]acetone). Values in blue indicate the relative integration values of H-atoms (sum: 100).

lower than that of the isolated oils (80–90 %). In addition to that, the C-content of lignin or bio-oil cannot be fully transferred into the isolated oils because a substantial part of the O-content is removed by demethoxylation, which easily proceeds in the presence of Raney Ni by H-transfer hydrogenolysis.[6] Hence, the elimination of methanol contributes to an apparent lower carbon yield of upgraded oils relative to the initial C-content of the substrates.

To gain conclusive evidence that the procedure leads to cleavage of ether linkages and demethoxylation of the phenol units, in addition to the dehydroxylation of the phenol intermediates, heteronuclear (^{13}C-^{1}H) HSQC 2D NMR experiments were performed.[11] The HSQC spectrum obtained from organosolv lignin (Figure 2 a) shows four distinct regions and corresponding integrals for the H atoms (sum to 100 H): 1) aliphatic C_{sp^3}–H (23.7 H), 2) methoxy groups (Ar-OCH$_3$, 20.8 H), 3) alcohols and ethers (22.6 H), and 4) O-functionalized aromatic units (32.9 H). In turn, the HSQC spectrum of the lignin products (Figure 2 b) clearly demonstrates that methoxy groups (>0.1 H) and the ether linkages (1.4 H) were almost fully removed, while characteristic signals for aliphatic C_{sp^3}–H (75.3 H) and arenic C_{sp^2}–H (23.3 H) were substantially enhanced. Overall, these results confirm that the methoxy and phenolic functionalities of lignin are removed, and arenes in addition to alkanes are the products formed.

In conclusion, the present study demonstrates a new route for the conversion of bio-oil and lignin into arenes. The conversion of lignin to yield low boiling point arenes instead of high boiling phenols could greatly facilitate the valorization of lignin products by conventional refinery processes. Moreover, the unprecedented high selectivity for arenes, obtained under low-severity conditions, provides a new route, which is in stark contrast to emerging approaches for the catalytic upgrade of bio-oil[12] or other methods using H-transfer, such as direct coal liquefaction and catalytic disassembly of lignin or biomass in supercritical MeOH,[13] that are performed under extremely harsh conditions (50–200 bar, 573–773 K). Further development of the current methodology may provide a fundamental platform for innovative industrial processes for bio-oil and lignin valorization. Finally, the mixture of arenes and aliphatics could very well serve as valuable bio-additives to synthetic fuels produced by the Fischer–Tropsch process, which lacks the aromatic and branched hydrocarbons required for high-performance of fuels for aviation and Otto engines.

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[1] "Top Value-Added Chemicals from Biomass, Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin": J. E. Holladay, J. F. White, J. J. Bozell, D. Johnson, available from http://www1.eere.energy.gov/bioenergy/pdfs/pnnl-16983.pdf. In this insightful report, the conversion of lignin into simple arenes is highlighted as "very desirable, and is perhaps the most challenging and complex of the lignin technology barriers" (on page 26, section "8. Aromatic Chemicals").

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