Flexibilization of Biorefineries: Tuning Lignin Hydrogenation by Hydrogen Partial Pressure

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Materials

Phenol (Aldrich, 99.5%), Hexadecane (Aldrich, 99%), Penta (Aldrich, 95%), Ethyl acetate (Aldrich, 99.7%), Dichloromethane (Aldrich, 99%), Ni/SiO$_2$ (Strem, 64%), trioctylphosphine (Aldrich, 97%), Dioctylehter (Aldrich, 99%), were purchased and used as received.

Catalyst preparation

The commercial Ni/SiO$_2$ catalyst was converted into Ni$_2$P/SiO$_2$ using trioctylphosphine (TOP). The synthesis was performed under absolute air-free conditions using standard schlenk line techniques. In a standard procedure, 0.2 g of the commercial Ni/SiO$_2$ was placed in a schlenk tube together with 3 ml dioctylether (DOE) and 6 ml trioctylphosphine (equal to a Ni:P ratio of 0.1) under argon atmosphere. After careful oxygen removal, the dispersion was heated to 300 °C under argon atmosphere and kept at this temperature for 6 h. After the dispersion was cooled down to room temperature, the catalyst was washed three times with 20 ml isopropanol. The separation was done by centrifugation. Finally, the catalyst was dried at 60 °C under vacuum overnight. The final catalyst has a BET surface of 10 m$^2$/g, the Ni weight and P weight contents are 46% and 17 %, respectively.

HDO of model compounds

For each catalytic reaction on a model compound, the corresponding quantity of substrate (3 mmol), hexadecane (internal standard GC, 20 mg) and pentane (2 mL) were placed into the reactor vessel (a quartz inlet with 33 mL volume in the autoclave). The catalytic conversion was carried out under different pressure (measured at r.t.) of H$_2$ as indicated and at temperatures of 573 K, for the specified times. After the reaction, the reactor was placed in an ice-bath. The resulting product liquid was dissolved in dichloromethane to obtain a homogenous solution. MgSO$_4$ was used to remove water from the product mixture before analysis by GC. All samples were analyzed using a (DB-624 30 m, 0.32mm ID, d$_f$/0.25 µm) column with an Agilent 6850 gas chromatograph. The temperature program began at 35 °C for 2 min, then the temperature was increased at a rate of 10 °C min$^{-1}$ to 90 °C, kept there for 1 min, then increased to 150 °C at 10 °C min$^{-1}$, and afterward to 250 °C at 50 °C min$^{-1}$, followed by an isothermal step at a temperature of 250 °C for 1 min. The conversion, selectivity and the mass balance were determined according to the following equations:
Conversion = \( \frac{n_{t=0}^{\text{substrate}} - n_{t=0}^{t_i}}{n_{t=0}^{\text{substrate}}} \times 100 \% \)

Selectivity = \( \frac{n_{t=0}^{t_i}}{n_{t=0}^{\text{substrate}} - n_{t=0}^{t_i}} \times 100 \% \)

Ring balance = \( \frac{\sum n_{t=0}^{t_i}}{n_{t=0}^{\text{substrate}}} \times 100 \% \)

The hydrogen, hydrogen in water and hydrogen in the product were calculated based on the product distribution. The deuteriation of the phenol was performed in the same way. The deuteriation number in each product was identified by mass spectrometry, and the average D-numbers were calculated, as shown in Table S3.

**Thermal pyrolysis of organosolv Lignin**

The preparation of the organosolv lignin is described elsewhere in detail. (1) Briefly, 10 g of organosolv lignin was placed in the oven under argon. Then it was heated to 600 °C within 10 min, and the generated compounds were swept with argon and condensed by a mixture of acetone and dry ice. Afterward, the product was obtained by washing the pipe with methanol, and the methanol was removed by evaporation. The yield of the oil product is around 50 wt.%. 

**HDO of the mixture obtained by the pyrolysis of organosolv lignin**

For hydrodeoxygenation (HDO) reactions of the pyrolysis oil (200 mg), catalyst (100 mg), and pentane (2 mL) were placed into stainless steel, home-made pressure reactor vessel (a quartz inlet with 33 mL volume in the autoclave). The experiments were performed under 5/8/20 bar \( \text{H}_2 \) pressure, measured at r.t. before reaction. The reaction was conducted at 473 K for 2 h, then at 573 (613) K, for 18 h. After the reaction, the reactor was quenched by immersion in an ice-bath. \( \text{MgSO}_4 \) was added to adsorb the water in the product, and the solid was removed by filter paper. By using rotary evaporation at 313 K and 50 mbar, the solvent was removed; the resultant liquid product was obtained and weighed, and roughly 70 wt.% yield is obtained. Then the product was treated with dichloromethane (2 mL), to obtain a homogeneous solution before GCMS. The quantitative and qualitative analysis of final products are listed in appendix B-D. Since most product compounds are hydrocarbons, their response factors can be regarded as the same. In this manner, the area shown in the appendix is equal to the concentration of different compounds.
Sample analysis with Orbitrap Elite

Upgraded pyrolysis oil was diluted with dichloromethane to a final concentration of 250 μg ml\(^{-1}\) and used without further treatment. Mass Spectra was recorded on a research-type Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with commercially available atmospheric pressure chemical ionization (APCI). The spectra were collected in positive mode. For the measurements, each sample was infused with a flow rate of 20 μl min\(^{-1}\), evaporated at 350 °C with the sheath and auxiliary gas flow of 20 and 10 (arbitrary units), respectively. APCI current was set as 5 kV. Mass spectra were collected using full scan mode with mass window 100 \(\leq m/z \leq 1000\) and resolving power \(R= 480,000\) (full-width half-maximum at \(m/z \approx 400\)). In each case, a total of 200 scans was recorded in reduced mode and summed up before data analysis. Peak assignment was performed using Composer64 (v 1.5.0, Sierra Analytics, Modesto, CA, USA) after internal recalibration according to the following constraints: \(C_{0-200}H_{0-1000}N_{0-2}O_{0-30}S_{0-2}, 0 \leq DBE \leq 60\) and \(\pm 2.0\ ppm\).

Computational details

The DFT calculations were performed using the projected augmented wave (PAW) formalism and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional as implemented in the Vienna ab initio simulation package (VASP). (2-5) The transition states were localized using the climbing image nudged elastic band method (CI-NEB) (6) and dimer method (7) as implemented in the Transition State Tools for VASP (VTST) (8) and verified with frequency calculations.

Model

The Ni\(_2\)P-0001-A surface determined previously as the thermodynamically most stable surface (9) was modeled with the 3x2 supercell to minimize the lateral interaction between periodic images (Figure S2). Slab model consisting of 5 atomic layers and a vacuum region of 13 Å was used together with the 3x2x1 \(k\)-points grid based on Monkhorst-Pack scheme. (10) The positions of atoms in the bottom layer were fixed in all calculations. The lattice constants were optimized to \(a=17.71\) Å, \(b=11.80\) Å, \(c=18.85\) Å, \(a=\beta=90^\circ\) and \(\gamma=120^\circ\) and kept unchanged for all calculations. The most stable adsorption complex of phenol is on the nickel trimer (Ni\(_3\)) where phenol lies parallel to the surface (Figure S2 d); this complex is characterized by the adsorption energy \(-0.83\) eV. Hydrogen atoms could adsorb on the nickel trimers next to phenol: dissociative adsorption of \(\frac{1}{2} \text{H}_2\) is exothermic \((-0.64\) eV) if there is just one H atom per Ni\(_3\) (H in the hollow
site, Figure S2 d) while the dissociative adsorption of the second H atom on Ni$_3$ is almost energy neutral (on the bridge sites, Figure S2e).

**Figure S1.** a) Gibbs free energy ($\Delta$G$_r$) of the phenol hydrotreatment; b) selectivity and conversion of PhOH by hydrotreatment at different H$_2$ pressures; (Reaction condition: 3mmol phenol, 2 mL Pentane and 20 mg hexadecane at different hydrogen pressures, t = 180 min); c) and d) distribution of the main products from the phenol hydrotreatment at different H$_2$ pressures (6 and 15, respectively) as a function of time; (Reaction condition: 3mmol phenol, 2mL Pentane and 20 mg hexadecane at different hydrogen pressures).
Results

Each reaction shown in Figure 2a (main text) consists of two elementary steps, each corresponding to the transfer of one H atom between the surface and the reactant. Calculations were performed under the assumption that hydrogen on the surface is at the equilibrium with the gas phase H\textsubscript{2}. At lower $p_{\text{H}_2}$ hydrogen adsorbs at hollow sites while at higher $p_{\text{H}_2}$ hydrogen adsorbs at bridge sites. It is assumed that after each elementary step, the hydrogen on the surface is equilibrated with the gas phase. The computational strategy is shown for the first elementary step of phenol hydrogenation in Figure S3. At lower $p_{\text{H}_2}$ hydrogen occupies only the hollow sites (denoted 1 H\textsuperscript{*} and corresponding reaction path shown in red in Figure S3). The H atom at the hollow site interacts with the adjacent phenol, corresponding transition state (TS) is localized, and the geometry of the resulting reaction intermediate (denoted FS) is found. At this point, there is no hydrogen on the Ni\textsubscript{3} adjacent to the adsorbed intermediate. Surface equilibration is
assumed, and an H-atom is added to the hollow site before the next reaction step takes place. The same strategy was adopted for the higher $p_{\text{H}_2}$ modeled with two H atoms at the bridge sites of Ni$_3$ (denoted 2 H* and depicted in blue in Figure S3). At the end of the first elementary step, there is just one hydrogen left on Ni$_3$ (at the hollow site), and surface equilibration with the gaseous H$_2$ is assumed before the next reaction step is investigated. A similar strategy is adopted for the dehydrogenation steps: upon the transfer of H from any intermediate to the surface, the surface equilibration is assumed (hydrogen is taken away from the surface to the gas phase). The activation barriers calculated as described above are summarized in Table S4.

**Figure S3.** First elementary step of phenol hydrogenation on the Ni$_2$P surface (energies are in eV). For lower surface hydrogen coverage (1 H*) and higher surface hydrogen coverage (2 H*) the barriers and reaction energies are depicted in red and blue, respectively. Energy zero is defined as bare surface and molecules in the gas phase. See Figure S2 for the color scheme. The results for the second reaction step (from B to C or E) are depicted in Figure S4.
Figure S4. The critical reaction steps $B \rightarrow C$ (hydrogenation of aromatic ring) and $B \rightarrow E$ (deoxygenation) for low and high hydrogen pressures. For low hydrogen pressure (part a, one H atom on the hollow site of the Ni$_3$ trimer), barriers for deoxygenation step $B \rightarrow E$ are lower than those for hydrogenation of aromatic ring $B \rightarrow C$. For high hydrogen pressure (part b, two H atoms on bridge sites of the Ni$_3$ trimer), the barriers for deoxygenation step are higher than those for
aromatic ring hydrogenation. Energy zero is defined as the bare surface and molecules in the gas phase (see caption of Figure S2 for color scheme).

**Figure S5.** The distribution of the other products for phenol HDO at different H$_2$ pressures: 6 bar (left) and 15 bar (right) as a function of time.

**Figure S6.** a) and b) hydrogen distribution during phenol hydrotreatment at 6 bar and 15 bar partial hydrogen pressure.
Figure S7. The rate-determining activation barriers of the individual reaction steps calculated for low (a) and high (b) surface hydrogen coverages (in eV), respectively.

Figure S8. Proposed phenol hydrotreating reaction pathways by deuterium at 573K under low and high pressure.
Figure S9. GC-MS chromatography of the final products from hydrotreatment at 20 (a), 8 (b), and 5 (c) bar pH₂, at 573K (20 and 8 bar) and 613K (5 bar). The ratios between selected aromatic and aliphatic products are shown in Table (d).

Figure S10. Relative intensity distributions of various classes assigned in the positive-ion APCI Orbitrap mass spectra of lignin, lignin pyrolysis products and products of hydrogenation at 5, 8 and 20 bar (from top to bottom). The relative intensity is based on the ratio between the intensity of each class and the total intensity calculated by summing all assigned categories in each mass spectra. The fully colored section of the bars represent protonated cations, [M+H]⁺ while the white background sections represents radical ions, M⁺.
Table S1. Selectivity of the products and conversion of HDO of phenol over Ni$_2$P/SiO$_2$ at different H$_2$ pressure (a, up = 6 bar; b, down = 15 bar). Based on the fact that the mass balance is around 98-103% and no other products were detected, the selectivities were modified to a sum = 100%.

| Time / min | Benzene | Cyclohexane | Cyclohexene | Cyclohexanone | Cyclohexanol | Sum (saturates) | X(Phenol) | Conversion |
|------------|---------|-------------|-------------|---------------|--------------|----------------|-----------|------------|
| 5          | 49%     | 17%         | 0%          | 22%           | 12%          | 51%            | 2%        | 2%         |
| 10         | 47%     | 31%         | 0%          | 12%           | 10%          | 53%            | 16%       | 16%        |
| 20         | 54%     | 32%         | 2%          | 8%            | 5%           | 46%            | 37%       | 37%        |
| 40         | 62%     | 32%         | 1%          | 3%            | 2%           | 38%            | 62%       | 62%        |
| 90         | 63%     | 34%         | 0%          | 2%            | 1%           | 37%            | 63%       | 63%        |
| 180        | 72%     | 28%         | 0%          | 1%            | 0%           | 28%            | 75%       | 75%        |

| Time / min | Benzene | Cyclohexane | Cyclohexene | Cyclohexanone | Cyclohexanol | Sum (saturates) | X(Phenol) | Conversion |
|------------|---------|-------------|-------------|---------------|--------------|----------------|-----------|------------|
| 5          | 45%     | 17%         | 1%          | 15%           | 22%          | 55%            | 9%        | 9%         |
| 10         | 20%     | 49%         | 1%          | 8%            | 23%          | 80%            | 45%       | 45%        |
| 20         | 19%     | 57%         | 1%          | 6%            | 17%          | 81%            | 77%       | 77%        |
| 40         | 20%     | 78%         | 1%          | 0%            | 1%           | 80%            | 100%      | 100%       |
| 90         | 12%     | 88%         | 0%          | 0%            | 0%           | 88%            | 100%      | 100%       |
Table S2. Selectivity of the products and conversion of HDO of phenol over Ni$_2$P/SiO$_2$ at different D$_2$ Pressure (3, 6 and 15 bar). Based on the fact that the mass balance is around 97-101% and no other products were detected, the selectivities were modified to a sum = 100%.

| Time / min | Benzene | Cyclohexane | cyclohexene | Selectivity | Cyclohexanone | Cyclohexanol | Sum (saturates) | Conversion X(Phenol) |
|-----------|---------|-------------|-------------|-------------|---------------|--------------|-----------------|---------------------|
| 10        | 47%     | 24%         | 0%          | 13%         | 17%           | 52%          | 6%              |
| 20        | 46%     | 28%         | 0%          | 9%          | 16%           | 54%          | 18%             |
| 40        | 59%     | 34%         | 0%          | 5%          | 2%            | 41%          | 41%             |

| Time / min | Benzene | Cyclohexane | cyclohexene | Selectivity | Cyclohexanone | Cyclohexanol | Sum (saturates) | Conversion X(Phenol) |
|-----------|---------|-------------|-------------|-------------|---------------|--------------|-----------------|---------------------|
| 10        | 37%     | 30%         | 0%          | 10%         | 23%           | 63%          | 18%             |
| 20        | 47%     | 39%         | 0%          | 6%          | 7%            | 54%          | 42%             |
| 40        | 58%     | 37%         | 0%          | 3%          | 2%            | 42%          | 68%             |

| Time / min | Benzene | Cyclohexane | cyclohexene | Selectivity | Cyclohexanone | Cyclohexanol | Sum (saturates) | Conversion X(Phenol) |
|-----------|---------|-------------|-------------|-------------|---------------|--------------|-----------------|---------------------|
| 10        | 31%     | 46%         | 0%          | 6%          | 17%           | 69%          | 37%             |
| 20        | 29%     | 57%         | 0%          | 2%          | 12%           | 71%          | 85%             |
| 40        | 26%     | 72%         | 0%          | 0%          | 2%            | 75%          | 98%             |
Table S3. Deuteration degree of D-benzene and D-cyclohexane resulted from the reaction Ni_2P/SiO_2 at different D_2 pressure (a, top = 3 bar; b, middle = 6 bar; b, bottom = 15 bar).

| D_2/O = 1.4 | Benzene | Time / min | Cyclohexane | Time / min |
|-------------|---------|------------|-------------|------------|
|             |         | 10 20 40   | D0 D1 D2 D3 D4 D5 D6 D7 D8 D9 D10 D11 D12 |         |
| 0           | D0      | 25% 27% 16% | D0          | 5% 2% 1%   |
| 1           | D1      | 37% 40% 33% | D1          | 4% 14% 9%  |
| 2           | D2      | 25% 24% 29% | D2          | 13% 22% 14%|
| 3           | D3      | 11% 8% 16%  | D3          | 17% 25% 18%|
| 4           | D4      | 2% 1% 5%   | D4          | 20% 19% 18%|
| 5           | D5      | 0% 0% 1%   | D5          | 18% 12% 18%|
| 6           | D6      | 1%         | D6          | 12% 5% 12% |
| 7           | D7      |            | D7          | 7% 1% 7%   |
| 8           | D8      |            | D8          | 3% 0% 3%   |
| 9           | D9      |            | D9          | 1%         |
| 10          | D10     |            | D10         | 0%         |
| 11          | D11     |            | D11         |            |
| 12          | D12     |            | D12         |            |
| Average Dn  |         | 1.27 1.17 1.63 | Average Dn | 4.05 3.08 3.97 |

| D_2/O = 2.8 | Benzene | Time / min | Cyclohexane | Time / min |
|-------------|---------|------------|-------------|------------|
|             |         | 10 20 40   | D0 D1 D2 D3 D4 D5 D6 D7 D8 D9 D10 D11 D12 |         |
| 0           | D0      | 13% 9% 8%  | D0          |            |
| 1           | D1      | 28% 29% 27% | D1          | 1% 1%      |
| 2           | D2      | 28% 33% 36% | D2          | 4% 6%      |
| 3           | D3      | 20% 21% 22% | D3          | 10% 13%    |
| 4           | D4      | 9% 7% 7%   | D4          | 2% 17% 21% |
| 5           | D5      | 2% 1% 1%   | D5          | 11% 21% 23%|
| 6           | D6      |            | D6          | 20% 19% 18%|
| 7           | D7      |            | D7          | 23% 15% 11%|
| 8           | D8      |            | D8          | 21% 9% 5%  |
| 9           | D9      |            | D9          | 14% 4% 2%  |
| 10          | D10     |            | D10         | 7% 0%      |
| 11          | D11     |            | D11         | 3%         |
| 12          | D12     |            | D12         |            |
| Average Dn  |         | 1.88 1.92 1.95 | Average Dn | 7.39 5.36 4.93 |

| D_2/O = 7   | Benzene | Time / min | Cyclohexane | Time / min |
|-------------|---------|------------|-------------|------------|
|             |         | 10 20 40   | D0 D1 D2 D3 D4 D5 D6 D7 D8 D9 D10 D11 D12 |         |
| 0           | D0      | 10% 5% 2%  | D0          |            |
Table S4. Activation barriers of elementary steps calculated for lower and higher surface hydrogen coverages (1 H* and 2 H*, respectively). Some reaction intermediates show chemical bonding between C6 ring and the surface and such intermediates are denoted with the *.

| Reaction steps | $\Delta E^\dagger(1\text{H}^*)$/eV | $\Delta E^\dagger(2\text{H}^*)$/eV |
|----------------|-----------------------------------|-----------------------------------|
| Phenol hydrogenation |                                   |                                   |
| ![Reaction 1](image1.png) | 1.67 | 1.11 |
| ![Reaction 2](image2.png) | 1.56 | 1.02 |
| ![Reaction 3](image3.png) | 1.43 | 0.50 |
| ![Reaction 4](image4.png) | 1.04 | 0.47 |
| ![Reaction 5](image5.png) | 1.27 | 0.50 |
| ![Reaction 6](image6.png) | 0.68 | 0.09 |
**OH elimination**

\[
\text{Cyclic C}_6 \text{ hydrogenation/dehydrogenation}
\]

| Reaction |.activation | rate constant |
Table S5: Selectivity of the products and conversion of different model compounds hydrotreatment over Ni\(_2\)P/SiO\(_2\) at different H\(_2\) Pressure (6 and 15 bar). (Reaction conditions: substrate containing 3mmol O (3 mmol Anisole, 1.5 mmol guaiacol or 4-propyl guaiacol, and 1 mmol 2,6 dimethoxyphenol), 2mL Pentane and 20 mg hexadecane at different hydrogen pressures, t = 240 min).

| Substrate | Hydrogen Pressure / bar | X / % | S / % | S / % | HDO Degree / % |
|-----------|-------------------------|-------|-------|-------|----------------|
|           | 6                       | >99   | 22    | 76    | 98             |
|           | 15                      | >99   | 83    | 16    | 99             |
|           | 6                       | >99   | 23    | 73    | 96             |
|           | 15                      | >99   | 95    | 2     | 97             |
|           | 6                       | 93    | 13    | 77    | 94             |
|           | 15                      | >99   | 93    | 5     | 98             |
|           | 6                       | 88    | 27    | 58    | 90             |
|           | 15                      | >99   | 93    | 6     | 99             |
**Table S6**: Hydrotreating of phenolic compounds at different hydrogen pressures reported in literatures.

| Lines | Model compound | Catalyst | Hydrogen pressures /bar | Aliphatic Selectivity/ % | Aromatic Selectivity/ % | HDO / % | Reference |
|-------|----------------|----------|-------------------------|--------------------------|-------------------------|---------|-----------|
| 1     | Phenol         | Ni,P/SiO₂| 6                       | 28                       | 72                      | >99     | Our work  |
| 2     | Phenol         | Ni,P/SiO₂| 15                      | 88                       | 12                      | >99     | Our work  |
| 3     | Propyl Phenol  | Pt/H-ZSM-5| 1                       | 99                       | <1                      | >99     | Ohta, Yamamoto et al. Chem. Commun., 2015 |
| 4     | Phenol mixture | Ru/SZ    | 2                       | -                        | 92                      | >92     | Luo, Wang et al. Green Chem., 2016 |
| 5     | Phenol         | Ru/H-ZSM-5| 2                       | 23                       | 78                      | ~85     | Luo, Zheng et al. Green Chem., 2016 |
| 6     | Phenol         | MoO₃     | 5                       | 0-22                     | 74-97                   | >95     | Zhang, Tang et al. Catal. Today, 2019 |
| 7     | Phenol         | Co/SiO₂  | 10                      | 45                       | 54                      | ~93     | Mochizuki, Chen et al. Appl. Catal. B-Environ., 2014 |
| 8     | Phenol mixture | Ru-WOₓ/ZrO₂| 10                      | 80-95                    | -                       | ~99     | Jiang, Hu et al. ACS Sustain. Chem. Eng., 2018 |
| 9     | Phenol         | Pd/MOFI40| 10                      | 74                       | 4                       | ~18     | Chen, He et al. ChemCatChem, 2018 |
| 10    | Phenol         | Pd/MOFI40| 20                      | 80                       | 3                       | ~42     | Chen, He et al. ChemCatChem, 2018 |
| 11    | Phenol         | Ru-WOₓ/SiAl| 20                     | 11                       | 81                      | >92     | Huang, Yan et al. Green Chem., 2015 |
| 12    | Methyl phenol  | Co-MoS₂  | 30                      | >99                      | >99                     | >99     | Liu, Robertson et al. Nat. Chem., 2017 |
| 13    | Methyl phenol  | NiMoW    | 30                      | 6                        | 94                      | >99     | Wang, Wu et al. Catal. Commun., 2013 |
| 14    | Phenol         | Pd/C+H2ZSM5| 40                     | 99                       | N/A                     | 99      | He, Zhao et al. J. Catal., 2014 |
| 15    | Methyl phenol  | MoS₂     | 40                      | 7-42                     | 57-93                   | -       | Wang, Zhang et al. Ind. Eng. Chem. Res., 2014 |
| 16    | Phenol         | Ru/H-ZSM-5-OM| 40                   | >99                      | 0                       | 94      | Wang, Zhang et al. ACS Catal., 2015 |
| 17    | Phenol         | Pd/C+H₂PO₄| 50                      | 99                       | 0                       | >92     | Zhao, Kou et al. Angew. Chem. Int. Ed., 2009 |
| 18    | Phenol         | Pd/Al₂O₃| 50                      | 86                       | N/A                     | ~40     | Zhao, He et al. J. Catal., 2011 |
| 19    | Phenol         | NiCo/H-ZSM-5| 50                     | 94                       | 6                       | 99      | Huynh, Armbruster et al. ChemCatChem, 2014 |
| 20    | Phenol         | PtCo/NOMC| 100                     | 99                       | N/A                     | >99     | Wang, Cao et al. Angew. Chem. Int. Ed., 2016 |
| 21    | Phenol         | Ni/ZrO₂  | 100                     | 92                       | 8                       | 88      | Mortensen, Grunwaldt et al. ACS Catal., 2013 |
| 22    | Phenol         | Ru@SILP-1.00| 120                    | >99                      | N/A                     | 95      | Luska, Migowski et al. Angew. Chem. Int. Ed., 2015 |
| 23    | Anisole        | Ru/W/SIO₂| 5 bar N₂                | 0                        | >99                     | >99     | Meng, Yan et al. Sci. Adv., 2019 |
| 24    | Phenol         | Ru/W/SIO₂| 5 bar N₂                | 0                        | 0                       | 0       | Meng, Yan et al. Sci. Adv., 2019 |
| 25    | Phenol         | Ru/W/SIO₂| 5 bar N₂                | 0                        | 0                       | 0       | Meng, Yan et al. Sci. Adv., 2019 |
| 26    | Lignin         | Pt/H-ZSM-5| 17(650°C)               | 0                        | ~7(yield)               | -       | Jan, Marchand et al. Energ. Fuel., 2015 |
| 27    | Lignin         | Pt/H-ZSM-5| 17(300°C)               | ~1(yield)                | 0                       | -       | Jan, Marchand et al. Energ. Fuel., 2015 |

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Appendix A: Pyrolysis Organosolv Lignin

31.08.2017
File: 134567b-00.raw
Analyse: ZHC-2B-010-03
STF: Zhengwen, Cao

Messung: GC-MS
Ionisierung: GC-EI
Spektrometer: ISQ
Länge: 30
Temp.: 30-3-70-6-250-5
GC-Nr.: -
MS-Nr.: 13176
Auswerter: Margold (2242)

| No. | MW  | Comment                         |
|-----|-----|---------------------------------|
| 1   | 60  | Compare Q100611: Acetic acid     |
| 2   | 152 | Compare NJ332797: 3,4-Dimethoxytoluene |
| 3   | 152 | Compare NJ352827: 3,5-Dimethoxytoluene |
| 4   | 124 | Compare Q117172: Phenol, 2-methoxy- |
| 5   | 128 | Compare NJ135426: 2-Methoxy-6-methylphenol |
| 6   | 166 | Similar NJ6254: Phenol, 3-methoxy-2,5,6-trimethyl- |
| 7   | 122 | Compare Q116320: Phenol, 2,5-dimethyl- |
| 8   | 152 | Similar NJ352788: 2,3-Dimethoxytoluene |
| 9   | 138 | Compare NJ233910: Phenol, 2-methoxy-4-methyl- |
| 10  | 152 | Compare NJ332797: 3,4-Dimethoxytoluene |
| 11  | 94  | Compare NJ133909: Phenol         |
| 12  | 152 | Compare NJ135148: Phenol, 4-ethyl-2-methoxy- |
| 13  | 122 | Compare Q116289: Phenol, 2-ethyl- |
| 14  | 122 | Compare NJ291090: Phenol, 2,3-dimethyl- |
| 15  | 108 | Compare Q109321: Phenol, 2-methyl- |
**Angegebene Mol.-Gewichte u. Massenzahlen basieren auf dem häufigsten Isotop der Elemente**

1. $\text{B}3228(16:23)$

2. $\text{B}4799(24:21)$

3. $\text{B}4921(24:58)$

4. $\text{B}4986(25:18)$

**SIS1: Q100611 60**

**SIS1: NJ332797 152**

**SIS1: NJ352827 152**

**SIS1: Q117172 124**
| No. | MW  | Comment |
|-----|-----|---------|
| 16  | 136 | Compare Q125628: Phenol, 2-ethyl-6-methyl- |
| 17  | 164 | Similar NJ291308: Phenol, 2-methoxy-4-[(1-propenyl)-, (Z)- | |
| 18  | 154 | Compare Q142516: Phenol, 2,6-dimethoxy- |
| 19  | 164 | Compare Q5454: PHENOL, 2-METHOXY-3- (2-PROPENYL)- |
| 20  | 168 | Compare NJ1098121: 1,2,4-Trimethoxybenzene |
| 21  | 182 | Compare U121122: a13047 WAX–WA–027–01 |
| 22  | 140 | Compare NJ118675: 1,2-Benzenedioli, 3-methoxy- |
| 23  | 138 | Compare NJ236759: 3-Methoxy-5-methylphenol |
| 24  | 152 | Compare Q139931: Benzaldehyde, 4-hydroxy-3-methoxy- |
| 25  | 154 | Similar E56950: |
| 26  | 124 | Compare NJ113391: 1,2-Benzenedioli, 3-methyl- |
| 27  | 110 | Compare Q109906: 1,2-Benzenedioli |
| 28  | 194 | Compare Q75808: PHENOL, 2,6-DIMETHOXY-4- (2-PROPENYL)- |
| 29  | 124 | Compare NJ113391: 1,2-Benzenedioli, 3-methyl- |
| 30  | 152 | Compare Q139877: Benzoic acid, 4-hydroxy-, methyl ester |
| 31  | 182 | Compare Q173361: Benzaldehyde, 4-hydroxy-3,5-dimethoxy- |

Zoom 2

RI44/206

30:00
32:00
34:00
36:00
38:00
40:00
42:00
44:00

16 17 18 20 22 23 24 25 26 27 29 30 31

**SIS1: Q125628 136**

*1

10 20 30 40 50 60 70 80 90 100 110 120 130 140

134567b-00 * ZHC-2B-010-03/GC–MS/GC–EI/ISQ/DB-WAXETR/30/30-3-70-6-250-5/-/13176/

15 27 39 55 65 77 91 103 121 131 149

**SIS1: NJ291308 164**

*1

10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

134567b-00 * ZHC-2B-010-03/GC–MS/GC–EI/ISQ/DB-WAXETR/30/30-3-70-6-250-5/-/13176/

15 27 39 55 65 77 91 103 121 131 149

**B5933 (30:06)**

**B6014 (30:30)**
Angebene Mol.-Gewichte u. Massenzahlen basieren auf dem häufigsten Isotop der Elemente

*** Angegebene Mol.-Gewichte u. Massenzahlen basieren auf dem häufigsten Isotop der Elemente ***
Angegebene Mol.-Gewichte u. Massenzahlen basieren auf dem häufigsten Isotop der Elemente ***

**B8177 (41:28)**

**B8197 (41:34)**

**SIS1: Q139877 152**

**SIS1: Q173361 182**

134567b-00 * ZHC-ZB-010-03/GC-MS/GC-EI/ISQ/DB-WAXETR/30/30-3-70-6-250-5/-/13176/

134567b-00 * ZHC-ZB-010-03/GC-MS/GC-EI/ISQ/DB-WAXETR/30/30-3-70-6-250-5/-/13176/*1
Übersichtsanalyse der Probe, Auswertung ohne Lösungsmittelbereich (3,1min bis 3,4min)  
Zuordnung nach GC/MS 13310 und 13837 ZHC-ZB-010-04 ELNA: 3610  
MS-Zuordnung nur vergleichbar mit Komponenten, keine gesicherten Angaben  
prozentuale Ergebnisse ungenau durch Überlagerungen mit anderen Peaks  

| No. | Ret.Time | area-% | Peak Name                                |
|-----|----------|--------|------------------------------------------|
| 4   | 3,00     | 5,21   | MG:72;1 2-Methylbutan                   |
| 5   | 3,48     | 0,45   | MG:70;3 1-Penten                        |
| 12  | 4,31     | 0,25   | MG:84;4 Methylcyclopentan               |
| 15  | 4,75     | 6,29   | MG:78;5 Benzol                          |
| 16  | 4,93     | 4,16   | MG:84;6 Cyclohexan                      |
| 25  | 6,07     | 1,28   | MG:100;7 Heptan                         |
| 26  | 6,70     | 4,97   | MG:98;8 Methylcyclohexan                |
| 28  | 7,17     | 0,42   | MG:98;9 Ethylcyclopentan                |
| 33  | 8,16     | 9,93   | MG:92;10 Toluol                         |
| 46  | 10,88    | 10,99  | MG:114;11 Octan                         |
| 52  | 12,68    | 2,57   | MG:112;12 Ethylcyclohexan               |
| 58  | 14,16    | 4,23   | MG:106;13 Ethylbenzol                   |
| 60  | 14,80    | 2,42   | MG:106;14 α-Xylo                        |
| 70  | 16,83    | 0,86   | MG:106;15 1,2-Dimethylbenzol            |
| 84  | 21,75    | 1,81   | MG:128;16 (1-Methyl)-Cyclohexan          |
| 91  | 23,37    | 4,15   | MG:120;17 Propylbenzol                  |
| 94  | 24,33    | 1,75   | MG:120;18 1,2,3-Trimethylbenzol         |
| 100 | 26,28    | 0,34   | MG:120;1 Cumol                          |
| 105 | 28,13    | 0,23   | MG:120;2 1,2,3-Trimethylbenzol          |
| 107 | 28,57    | 0,09   | MG:140;3 unknown structure              |
| 110 | 29,35    | 0,06   | MG:112;4 unknown structure              |
| 111 | 29,69    | 0,13   | MG:140;5 Trans-1,4-diethyliclohexan     |
| 112 | 30,09    | 0,13   | MG:134;6 (2-Methylpropyl)-Benzol        |
| 113 | 30,37    | 0,22   | MG:134/ 140;7 unknown structure         |
| 114 | 30,84    | 0,13   | MG:122;8 1-Methoxy-3-methylbenzol      |
| No. | Ret.Time min | area-% % | Peak Name                                      |
|-----|--------------|----------|-----------------------------------------------|
| 119 | 32.53        | 0.58     | MG:118;10 2,3-Dihydro-1H-Indene               |
| 123 | 34.45        | 0.18     | MG:140;11 Butylcyclohexan                     |
| 126 | 35.53        | 0.40     | MG:134;12 1-Methyl-3-(1-methylethyl)-benzol   |
| 127 | 35.85        | 0.84     | MG:134;13 1-Methyl-4-propylbenzol             |
| 128 | 36.40        | 0.53     | MG:134;14 Butylbenzol                         |
| 159 | 44.15        | 0.40     | MG:148;18 (1,1-Dimethyl(propyl)-Benzol         |
| 167 | 45.46        | 0.53     | MG:128;19 Naphthalene                         |
| 179 | 47.20        | 0.23     | MG:146;21 Cyclopentylbenzol                   |
| 196 | 48.96        | 0.68     | MG:142;22                                     |
| 200 | 49.32        | 0.54     | MG:142/160;23 unknown structure               |
| 214 | 50.76        | 0.32     | MG:154;24 1,1'-Biphenyl                      |
| 218 | 51.37        | 0.53     | MG:174;25 (Cyclohexylmethyl)-Benzol           |
| 221 | 51.69        | 0.49     | MG:168;28 1,1'-Methylenebisbenzol             |
| 235 | 53.31        | 0.48     | MG:188;28 Cyclohexylethylbenzol + overlapping |
| 247 | 54.49        | 0.56     | MG:196;29 unknown structure                   |
| 260 | 55.63        | 0.38     | MG:210;30 unknown structure                   |
| 262 | 55.82        | 0.50     | MG:240/180;31                                 |
| 271 | 56.74        | 0.22     | MG:178;32 Benz(a)azulene + overlapping MG:224 |

291 peaks out of 334 (total area percentage = 28.58%) are below threshold.

Instrument parameters:
- Column: 30.0 m
- Temperature: 220/30 1/min 70 10/min 320, 5 min isol 350
- Gas: 0.60 bar Helium
- Sample size: 0.2 µL
Übersichtsanalyse der Probe, Auswertung ohne Lösungsmittelbereich (3,1min bis 3,8min)
Zuordnung nach GC/MS 13287 und 13832 ZHC-ZB-010-04 ELNA: 3610
MS-Zuordnung nur vergleichbar mit Komponenten, keine gesicherten Angaben
prozentuale Ergebnisse ungenau durch Überlagerungen mit anderen Peaks

| No. | Ret.Time min | area-% % | Peak Name                                      |
|-----|--------------|-----------|------------------------------------------------|
| 3   | 3.00         | 8.46      | MG:72;1 2-Methylbutan                          |
| 10  | 4.75         | 4.48      | MG:78;3 Benzol                                 |
| 11  | 4.92         | 10.91     | MG:84;4 Cyclohexan                             |
| 22  | 6.07         | 1.23      | MG:100;5 Heptan                                |
| 24  | 6.69         | 11.95     | MG:98;6 Methylcyclohexan                       |
| 25  | 7.16         | 0.64      | MG:98;7 Ethylcyclopentan                       |
| 29  | 8.15         | 4.86      | MG:92;8 Methylbenzol                           |
| 35  | 9.22         | 0.96      | MG:112;9 trans-1,3-Dimethylcyclohexan          |
| 42  | 10.84        | 6.44      | MG:114;10 Octan                                |
| 48  | 12.67        | 5.61      | MG:112;11 N-(Diphenylmethyl)-Acetamid          |
| 53  | 14.17        | 1.78      | MG:106;12 Ethylbenzol                          |
| 55  | 14.92        | 0.94      | MG:106;13 p-Xylo                                |
| 64  | 17.43        | 0.92      | MG:126;14 1-Ethyl-2-methylcyclohexan           |
| 70  | 19.27        | 0.73      | MG:126;15 1-Ethyl-4-methylcyclohexan           |
| 78  | 21.74        | 4.46      | MG:126;16 (1-Methyl)ethyl-Cyclohexan           |
| 83  | 23.38        | 1.78      | MG:120;17 Propylbenzol                         |
| 85  | 24.36        | 0.61      | MG:120;18 1,2,3-Trimethylbenzol                |
| 90  | 26.32        | 0.15      | MG:120;1 (1-Methylethyl)-Benzol                |
| 94  | 27.81        | 0.52      | MG:94/124;2 Phenol + overlapping unknown structure |
| 95  | 28.26        | 0.40      | MG:140;3 Menthan                              |
| 98  | 28.55        | 0.17      | MG:140;4 (2-Methylpropyl)-Cyclohexan          |
| 99  | 29.67        | 0.27      | MG:140;5 unknown structure                    |
| 101 | 30.34        | 0.32      | MG:140/134;6 Menthan + unknown structure       |
| 102 | 30.83        | 0.33      | MG:122;7 1-Methoxy-3-methylbenzol             |
| 103 | 31.13        | 0.14      | MG:140;8 unknown structure                    |
| No. | Ret. Time | area-% | Peak Name |
|-----|-----------|--------|-----------|
| 106 | 32,56     | 0,25   | MG:118;9 1-Propenylbenzol |
| 108 | 33,24     | 0,12   | MG:140;10 (1-Methylpropyl)-Cyclohexan |
| 109 | 34,43     | 0,50   | MG:140;11 unknown structure |
| 113 | 35,88     | 0,32   | MG:134;12 1-Methyl-2-propylbenzol |
| 114 | 36,42     | 0,28   | MG:134/138;13 unknown structure |
| 115 | 36,88     | 0,40   | MG:108;14 2-Methylphenol |
| 177 | 48,34     | 0,38   | MG:146;19 Tetrahydroiminaphthalen |
| 181 | 48,87     | 0,47   | MG:142/146/168;20 unknown structure |
| 185 | 49,32     | 0,21   | MG:142/160;21 unknown structure |
| 188 | 49,69     | 0,36   | MG:160;22 Cyclohexylbenzol |
| 201 | 51,08     | 0,45   | MG:180;24 1,1'-Methylenebiscyclohexan |
| 203 | 51,36     | 0,49   | MG:174;25 (Cyclohexylmethyl)-Benzol |
| 219 | 53,14     | 0,81   | MG:194;26 unknown structure |
| 220 | 53,30     | 0,38   | MG:188;27 (2-Cyclohexylethyl)-Benzol |
| 226 | 53,92     | 0,24   | MG:208;28 |

269 peaks out of 309 (total area percentage = 25.28%) are below threshold.

Instrument parameters:

- Column: 30,0 m
- Temperature: 220/30 1/min 70 10/min 320, 5 min iso/350
- Gas: 0,60 bar Helium
- Sample size: 0,2 µL

H. Hausser
Übersichtsanalyse der Probe, Auswertung ohne Lösungsmittelpeak (DCM)
Zuordnung nach GC/MS 14113 ZHC-ZB-010-07 ELNA:3818
MS-Zuordnung nur vergleichbar mit Komponenten, keine gesicherten Angaben
prozentuale Ergebnisse ungenau durch Überlagerungen mit anderen Peaks

| No. | Ret.Time  | area-% | Peak Name                              |
|-----|-----------|--------|----------------------------------------|
|     | min       |        |                                        |
| 12  | 3,44      | 1,47   | MG:70;3 Cyclopentan                    |
| 17  | 4,26      | 0,29   | MG:84;4 Methylcyclopentan              |
| 20  | 4,88      | 3,67   | MG:84;5 Cyclohexan                     |
| 27  | 6,01      | 0,30   | MG:100;6 Heptan                        |
| 29  | 6,63      | 3,89   | MG:98;7 Methylcyclohexan               |
| 30  | 7,10      | 0,17   | MG:98;8 Ethylcyclopetan                |
| 39  | 9,14      | 0,47   | MG:112;9 1,3-Dimethylcyclohexan        |
| 44  | 10,21     | 0,14   | MG:112;10 1,2-Dimethylcyclohexan       |
| 45  | 10,75     | 2,44   | MG:114;11 Octan                        |
| 49  | 12,57     | 1,70   | MG:112;12 Ethylcyclohexan              |
| 62  | 17,30     | 0,46   | MG:126;13 1-Ethyl-3-methylcyclohexan   |
| 68  | 19,13     | 0,22   | MG:126;14 1-Ethyl-2-methylcyclohexan   |
| 75  | 21,59     | 1,38   | MG:126;15 Isopropylcyclohexan          |
| 92  | 28,11     | 0,19   | MG:140;16 m-Menthane                   |
| 95  | 29,50     | 0,13   | MG:140;17 1,2-Diethylcyclohexan        |
| 104 | 34,26     | 0,18   | MG:140;18 Buthylcyclohexan             |
| 109 | 36,10     | 0,11   | MG:138;19 Decahydrornaphthalen         |
| 121 | 41,79     | 0,10   | MG:154;20 1-Ethyl-2-propylcyclohexan   |
| 126 | 42,62     | 0,12   | MG:152;21 Decahydro-2-methylnaphthalen|
| 131 | 43,58     | 0,07   | MG:152;22 1-Methyldecahydronaphthalen  |
| 135 | 44,44     | 0,08   | MG:154;23 Pentylcyclohexan             |
| 165 | 48,07     | 0,08   | MG:180;24 overlapping with 168, 166 unknown structure |
| 172 | 48,91     | 0,06   | MG:166;25 (Cyclopentylmethyl)-Cyclohexan |
| 178 | 49,55     | 0,09   | MG:166;26 1,1'-Bicyclohexyl            |
| 191 | 51,03     | 0,22   | MG:180;27 1,1'-Methylenbiscyclohexene  |
| No. | Ret.Time | area-% | Peak Name                                      |
|-----|----------|--------|-----------------------------------------------|
| 202 | 51,96    | 0,09   | MG:194:28 1-((Cyclohexyl)methyl)-4-Methylcyclohexan |
| 213 | 53,09    | 0,30   | MG:212:29 unknown structure                   |
| 221 | 53,87    | 0,12   | MG208:30                                      |
| 229 | 54,74    | 0,12   | MG:222:31 4-Methyl-4′-propyl-1,1′-bicyclohexyl  |
| 241 | 56,11    | 0,09   | MG:236:32 unknown structure                   |

251 peaks out of 281 (total area percentage= 81,27 %) are below threshold.

Instrument parameters:
- **Column:** 30,0 m
- **Temperature:** 220/30 1/min 70 10/min 320, 5min iso/ 350
- **Gas:** 0,60 bar  Helium
- **Sample size:** 0,2 µL

M. Masa – Ed