Biomass Hot Paper

International Edition: DOI: 10.1002/anie.201610405 German Edition: DOI: 10.1002/ange.201610405

Catalysis Meets Nonthermal Separation for the Production of (Alkyl)phenols and Hydrocarbons from Pyrolysis Oil

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Abstract: A simple and efficient hydrodeoxygenation strategy is described to selectively generate and separate high-value alkylphenols from pyrolysis bio-oil, produced directly from lignocellulosic biomass. The overall process is efficient and only requires low pressures of hydrogen gas (5 bar). Initially, an investigation using model compounds indicates that $MoC_s/$ C is a promising catalyst for targeted hydrodeoxygenation, enabling selective retention of the desired Ar—OH substituents. By applying this procedure to pyrolysis bio-oil, the primary products (phenol/4-alkylphenols and hydrocarbons) are easily separable from each other by short-path column chromatography, serving as potential valuable feedstocks for industry. The strategy requires no prior fractionation of the lignocellulosic biomass, no further synthetic steps, and no input of additional (e.g., petrochemical) platform molecules.

Mirroring the petroleum-based economy, it is crucial for a bio-based economy to maximize the revenue obtained from both fuels and chemicals.^[1] 4-Alkylphenols are unique candidate value-added products for targeted extraction from pyrolysis bio-oil, with the potential to serve as replacements for petroleum-derived phenols in applications such as nonionic surfactants, lubricant additives, phenolic resins, polymer additives, and agrochemicals.^[2] Annual worldwide production of all alkylphenols exceeds 450 000 metric tons, and the cost of raw materials is the largest single contributor to total manufacturing costs (60–80 %).^[3] One reasonable procedure is to separate the holocellulose and lignin fractions, followed by depolymerization and dehydration to the desired chemicals.^[1h,4] However, in this manner, the cost of pre-separation

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the author(s) of this article can be found under: http://dx.doi.org/10.1002/anie.201610405.

Angew. Chem. Int. Ed. 2017, 56, 1-7

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is considered excessive. Therefore, for application at a largescale biorefinery, a strategy based on the pyrolysis of whole biomass is still preferred.^[1i] Thermal pyrolysis is one important technology for lignocellulosic (LC) biomass deconstruction, whereby high-temperature treatment yields a bio-oil on the second timescale.^[5] Although the depolymerization of LC biomass during pyrolysis leads to the formation of high-value aromatic chemicals, relatively little attention has been devoted to the extraction of high-value species from the pyrolysis oil, mostly because of the expense associated with the separation of complex mixtures of highly oxygenated species.^[6]

4-Alkylphenol species are resistant to dehydroxylation, owing to the high dissociation energies of Ar–OH bonds.^[7] The constituents of LC pyrolysis bio-oil contain an array of both aliphatic and aromatic C–O-bonded substituents. Considering nonthermal separation (e.g. industrial flash chromatography), a strategy centered around selective hydrodeoxygenation (SHDO) of aliphatic C–O bonds, whilst leaving Ar–OH substituents intact, would be highly advantageous. In this way, the high-value-added alkylphenol species could be generated through pyrolysis, SHDO, and nonthermal separation steps while retaining the hydrocarbons as a fuel fraction.

In the following, we present a novel strategy, consisting of three steps, to convert LC biomass into alkylphenols and hydrocarbons (Figure 1). The SHDO of pyrolysis oil is catalyzed by molybdenum carbide supported on carbon under low H₂ pressures, whereby exploitation of the high Ar-OH bond energy enables selective cleavage of other oxygen-containing functional groups found in the pyrolysis bio-oil. For a wide range of highly oxygenated compounds, the valuable phenolic moiety is preserved throughout the course of the SHDO process. This step is followed by simple and economic separation of phenol and alkylphenol species from the upgraded product mixture. The resulting product mixtures after SHDO are primarily composed of a monolignol-derived (alkyl)phenol fraction and a hydrocarbon fraction. These fractions are easily separated by means of a short-path silica gel column (solvent I: n-hexane, solvent II: ethyl acetate; Figure 1). As a third step, after flash chromatographic separation, the generated hydrocarbons and ethyl acetate solution may be re-applied to the extraction of additional (alkyl)phenols after the next SHDO cycle.

Typically, an HDO reaction of pyrolysis bio-oil proceeds in two stages: 1) initial low-temperature treatment eliminates reactive functional groups (e.g. ketone, aldehyde, alcohol or alkenyl groups), and 2) subsequent reaction under high pressures of hydrogen cleaves phenolic substituents (e.g. phenyl alkyl ethers, diphenyl ethers, benzofuran linkages, and Communications



Figure 1. A simplified representation of the strategy for the production of high-value, low-volume chemicals (alkylphenols) and low-value, high-volume fuels from LC biomass: Thermal pyrolysis of the biomass to pyrolysis oil; Low-pressure selective hydrodeoxygenation (SHDO) of the bio-oil affords mixtures of alkylphenols/phenol and hydrocarbons; Hydrocarbon and alkylphenol/phenol fractions are separated over silica, using *n*-hexane and ethyl acetate.

phenol Ar-OH bonds) by hydrogenation and hydrodeoxygenation pathways.^[8] For the proposed strategy, it is crucial to selectively maintain the phenolic hydroxy group, whilst simultaneously cleaving phenyl alkyl ether and diphenyl ether bonds.^[7a,b,9] To explore catalysts for this selective reaction, we selected o-methoxyphenol (guaiacol) as a simple lignin model compound, because it incorporates both the phenyl alkyl ether and the phenolic functional groups. Table 1 reveals several important trends regarding the performance of some catalysts, selected based on literature data,^[10] for the conversion of guaiacol. First, Pt/C showed high activity for direct hydrogenation of guaiacol to 2-methoxycyclohexan-1-ol. Second, Ni₂P/C and Ni₂P/SiO₂ resulted in relatively high anisole yields (although anisole hydrogenolysis could generate phenol). Third, PtCo/C exhibited undesirably high activity for the hydrogenation of the aromatic ring to cyclohexanol and cyclohexanone. Last, the deficit in the "ring balance" with Ru/TiO₂ indicates the possible formation of coke, thus contributing to the low yield of phenol. Interestingly, of the investigated catalysts, molybdenum carbide supported on carbon, MoC_x/C , clearly exhibited the greatest selectivity towards phenol (Table 1).^[10b] In fact, the selectivity towards phenol by HDO of guaiacol over MoC_x/C was promisingly high (75% yield at 99% conversion). Under HDO conditions, guaiacol may be expected to undergo either "direct" HDO to phenol or anisole or ("indirect") full hydrogenation to 2-methoxycyclohexan-1-ol followed by HDO (Scheme 1).^[7c,11] However, the predominance of



Scheme 1. Various possible HDO pathways of guaiacol.

a guaiacol \rightarrow phenol \rightarrow benzene HDO pathway with MoC_x/C allows kinetic control (low pressure, low temperature). Previous investigations demonstrated that benzene is the primary product from the reaction of guaiacol under high hydrogen pressure and high temperature (25–30 bar, 350–400 °C), and considerable selectivity to phenols was observed using alcohol solvents without hydrogen.^[10b,12] In contrast, here the phenolic group is preserved under low hydrogen pressure and low temperature (5 bar, 300 °C). Therefore, MoC_x/C was selected as the most promising candidate for further investigation.

Despite the observed selectivity towards phenol from guaiacol with MoC_x/C , it was nevertheless important to determine whether other varieties of (primarily aliphatic) C–O bonds can be cleaved under the same reaction conditions while retaining the phenolic hydroxy group. Accordingly, HDO reactions were performed on a selection of additional model compounds, of varying complexity, over MoC_x/C (Table 2). In general, the MoC_x/C catalyst demon-

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Cat.	X [%]		Ring balance [%] ^[b]							
		OH	OH	\bigcirc	0-	o	OH	OH OH	\bigcirc	
Pt/C*	50	1	4	3	3	5	18	29	20	91
PtCo/C*	99	12	2	5	0	30	40	0	1	90
Ni ₂ P/SiO ₂	83	20	0	16	8	0	0	0	49	92
Ni₂P/C	36	36	1	23	17	0	0	0	8	95
Ru/TiO ₂	94	14	3	37	2	6	2	0	7	74
MoC _x /C	99	76	8	3	7	0	0	0	0	97

Table 1: Conversions and product distributions of different catalysts in the screening test, for HDO of o-methoxyphenol (guaiacol).^[a]

[a] Reaction conditions: substrate (1 mmol), *n*-hexadecane (internal standard, 20 mg), catalyst (100 mg), and solvent (2 mL) at 300 °C (" \star " denotes 250 °C) and 5 bar pressure of H₂ (25 °C) for 2 h. [b] As the SHDO performed on guaiacol leads to demethoxylation, the C-balance is given relative to the C₆-ring products.

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Entry	Substrate	<i>t</i> [h]	X [%]	Main products and selectivity [%]	Ring balance [%] ^[c]
1	<i>n</i> -octanol	2	93	<i>n</i> -C ₈ H ₁₈ 97	97
2	OH	2	99	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	95
3	OH	2	8	100	100
4	OH	8	27	96	99
5	OH OH	2	99	$\begin{array}{cccc} OH & O & OH & OH \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ 76 & 7 & 8 & 3 & 3 \\ \hline \end{array}$	97
6	0	4	73	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	92
7 ^[b]		2	26		98
8 ^[b]		8	83		98
9 ^[b]	_00_	2	89	$\begin{array}{c} OH \\ \downarrow \\ 52 \end{array} \begin{array}{c} OH \\ 10 \end{array} \begin{array}{c} OH \\ \downarrow \\ 9 \end{array} \begin{array}{c} OH \\ \downarrow \\ 0 \end{array} \begin{array}{c} OH \\ \downarrow \\ \downarrow \\ 0 \end{array} $	94
10 ^[b]	_00	8	91	$\begin{array}{c} OH \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	88
]] ^[b]	€ Contraction (Contraction)	2	28		98
12 ^[b]	⊂⊂°>	8	91		89

Table 2: Identified products evolving from low-pressure HDO of different model compounds over MoC,/C.^[a]

[a] Reaction conditions: substrate (1 mmol), *n*-hexadecane (internal standard, 20 mg), catalyst (100 mg), and solvent (2 mL) at 300 °C under 5 bar H_2 pressure (25 °C) for the given time. [b] Reaction conditions: substrate (0.5 mmol), *n*-hexadecane (internal standard, 20 mg), catalyst (100 mg), and solvent (2 mL) at 300 °C under 5 bar H_2 pressure (25 °C) for the given time. [c] As the HDO performed on guaiacol leads to demethoxylation, the C-balance is given relative to the C₆-ring products.

strated the ability to retain Ar–OH bonds, while selectively cleaving the other oxygen-containing functional groups. Aliphatic C–O bonds (i.e. in 1-octanol and cyclohexanol) were cleaved within 2 hours of reaction. HDO reactions on model compounds incorporating diphenyl ether, phenyl alkyl ether, and benzofuran moieties (entries 7, 9, and 11) primarily resulted in the corresponding phenol and alkoxy-(alkyl-)phenol species. Although conversions were low within 2 hours of reaction time, an extension to 8 hours led to an increase in conversion, and the promising selectivity towards the targeted product(s) was still observed. However, the yield of the intermediate phenol was reduced with longer reaction times (entries 3 and 4). A compromise between the degree of HDO and the phenol yield must, therefore, be found by adjustment of reaction time.

To demonstrate the feasibility of the strategy, MoC_x/C catalyzed SHDO reactions on a pyrolysis bio-oil obtained from oak wood were performed (H₂ pressure 5 bar, 300 °C). To ensure a high degree of HDO, reactions were carried out for a duration of 8 hours at 300 °C, and were expected to lead to a somewhat increased arene yield instead of the targeted phenol products. Two-dimensional (2D) GC×GC images

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from each stage of the process are shown in Figure 2. The 2D GC×GC image of untreated bio-oil (prior to SHDO) demonstrates that the oil consisted of furan species, aldehydes, ketones, and lignin-derived phenolic compounds (Figure 2a).^[13] Similar to the reactions performed on model compounds, SHDO brought about cleavage of aliphatic C-O bonds of the bio-oil to form alkanes. Likewise, hydrodeoxvgenation at Ar-OR and Ar-O-Ar bonds took place selectively without saturation of the aromatic ring. By contrast, hydrogenolysis of stronger Ar-OH bonds was disfavored under the reaction conditions. The identified compounds were mainly phenol, 4-(alkyl)phenols, and hydrocarbons (Figure 2b). A product mass yield of 38% was obtained after SHDO, corresponding to a total carbon yield of approximately 68%.

Given the high selectivity of the SHDO reaction, the product mixture was subsequently separated nonthermally using a short-path flash silica gel column, exploiting the differences in polarity of the aliphatic and phenol derivatives. Hydrocarbons were extracted by eluting with n-hexane (Figure 2d), followed by extraction of the phenolic species using ethyl acetate (Figure 2c). The n-hexane solution of hydrocarbons may be recycled as the solvent for a second SHDO reaction cycle. Alternatively, the reclaimed *n*-hexane and ethyl acetate solvents could be used for subsequent separation of SHDO product mixtures. In this manner, the requirement for input of solvents is minimized, and the targeted phenol (and aliphatic) products may be concentrated, thus enhancing the efficiency and economy of the process. Since no compounds of higher polarity than phenol-(s) were present (Figure 2b), all compounds were washed out by either *n*-hexane or ethyl acetate. Therefore, no compounds were lost as a result of reversible adsorption on the silica column during separation.

A 2D GC × GC analysis of the ethyl acetate fraction after nonthermal separation demonstrated that the solution predominantly contained the desired alkylphenol/phenol products (Figure 2c). The overall yields (calculated from starting pyrolysis bio-oil) of alkylphenols and phenol were 2.5 and 1.0%, respectively (see Table S3 in the Supporting Information). Considering the total mass yield is 38%, the yield of other compounds, hydrocarbons, remains as 35 wt %. One may always argue that these yields appear to be too low to be industrially relevant. However, vanillin, a specialty chemical produced on a scale of 70000 ton per year, is obtained at comparable yields by current industrial processes based on oxidation of lignosulfonates.^[4a] Moreover, the overall yield of 3.5% of high-value-added, isolated phenolic compounds nears the current market distribution of chemicals and fuels obtained from petroleum. Furthermore, the yield could be expected to increase by either applying a feedstock with higher lignin content or an even more selective catalyst.

In addition to the target products, minor quantities of oxygenated species (e.g., guaiacol, 4-methylguaiacols, 4-ethylguaiacols) were detected (see Table S3; Figure 2c). Our approach renders 4-alkylphenols as the primary compounds of the final product mixture.^[14] The para isomers are known to boil at temperatures 10-20°C higher than analogous ortho compounds, which would likely facilitate separa-



Retention time over 1st column / mir

 $\textit{Figure 2.}~GC {\times} GC {-} FID$ traces highlighting volatile products obtained at different stages of the process. a) Starting pyrolysis bio-oil from oak wood. b) After selective HDO reaction with MoC_x/C. c) Content of the ethyl acetate fraction. d) Content of n-hexane fraction, after chromatographic separation using *n*-hexane and ethyl acetate eluents (smearedout tail at high retention time in the first column results from impurities in the n-hexane).

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. א א These are not the final page numbers! tion of the main products, *p*-alkylphenols, from the mixture.^[15] Alternatively, as was recently demonstrated by Verboekend et al., hydrocracking of 4-alkylphenols is another feasible strategy to obtain high purity phenol.^[16]

In conclusion, we have demonstrated a new strategy, consisting of pyrolysis of LC biomass, SHDO, and nonthermal separation, thus rendering high-value alkylphenols and hydrocarbons as isolated fractions. Instead of the preseparation of lignin and holocellulose, the low-cost nonthermal separation of the product mixture can easily be undertaken in our system to afford the desired alkylphenols from lignin, thus serving as an important potential feedstock for industry. The integrated procedure could offer significant economic benefits relative to a simple biomass-to-fuel strategy, on account of both the decreased hydrogen consumption and the high value of the (alkyl)phenol products. The extent of this contribution to profitability is hard to assess without a more detailed process layout, but the result of this development represents an attractive approach for generating value-added products from LC biomass. In fact, our main consideration upon proposing a process involving selective catalysis in conjunction with nonthermal separation of products of distinct polarities is that, if a process beginning with pyrolysis oil to produce (nonpolar, high yield, low value) fuels were designed, the large-scale application of such a process could very well work synergistically with the production of (oxygenated, low yield, but high value) chemical specialties. This hypothesis directly mirrors the petrochemical industry, in which a similar synergy between fuel and chemical production has enabled the petrochemical and chemical industries to be success stories of the modern global economy.

Acknowledgments

This work was conducted within the framework of the CASCATBEL project funded by the European Commission (Grant Agreement No. 604307). R.R. and F.S. are grateful for funding provided by the Excellence Cluster "Tailor-Made Fuels from Biomass" (DFG).

Conflict of interest

The authors declare no conflict of interest.

Keywords: biomass · gas chromatography · hydrocarbons · molybdenum · phenols

D. W. Kicklighter, A. C. Gurgel, T. W. Cronin, S. Paltsev, B. S. Felzer, X. Wang, A. P. Sokolov, C. A. Schlosser, *Science* **2009**, *326*, 1397–1399; f) J. Fargione, J. Hill, D. Tilman, S. Polasky, P. Hawthorne, *Science* **2008**, *319*, 1235–1238; g) C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, *Science* **2012**, *337*, 695–699; h) Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, *447*, 982–985; i) A. V. Bridgwater, D. Meier, D. Radlein, *Org. Geochem.* **1999**, *30*, 1479–1493.

- [2] a) S. Czernik, A. V. Bridgwater, *Energy Fuels* 2004, *18*, 590–598;
 b) D. Mohan, C. U. Pittman, P. H. Steele, *Energy Fuels* 2006, *20*, 848–889.
- [3] J.-S. Kim, Bioresour. Technol. 2015, 178, 90-98.
- [4] a) R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijnincx, B. M. Weckhuysen, Angew. Chem. Int. Ed. 2016, 55, 8164–8215; Angew. Chem. 2016, 128, 8296; b) P. C. A. Bruijnincx, R. Rinaldi, B. M. Weckhuysen, Green Chem. 2015, 17, 4860–4861; c) C. Kropf, N. Bode, D. Bedrunka, R. Rinaldi, H. J. Estevez Rivera, US Patent 20,150,337,237, 2015.
- [5] a) U. Zoller, P. Sosis, Handbook of Detergents, Part F, Vol. 142, CRC, Boca Raton, FL, 2008; b) G. Anson Roy in Handbook of Detergents, Part F, CRC, Boca Raton, FL, 2008, pp. 49–67.
- [6] a) J. N. Chheda, G. W. Huber, J. A. Dumesic, Angew. Chem. Int. Ed. 2007, 46, 7164–7183; Angew. Chem. 2007, 119, 7298–7318;
 b) N. Meine, R. Rinaldi, F. Schüth, ChemSusChem 2012, 5, 1449–1454; c) P. Ferrini, R. Rinaldi, Angew. Chem. Int. Ed. 2014, 53, 8634–8639; Angew. Chem. 2014, 126, 8778–8783.
- [7] a) E. Furimsky, Appl. Catal. A 2000, 199, 147–190; b) H. Wang, J. Male, Y. Wang, ACS Catal. 2013, 3, 1047–1070; c) C. Zhao, Y. Kou, A. A. Lemonidou, X. Li, J. A. Lercher, Angew. Chem. Int. Ed. 2009, 48, 3987–3990; Angew. Chem. 2009, 121, 4047–4050; d) S. Crossley, J. Faria, M. Shen, D. E. Resasco, Science 2010, 327, 68–72; e) C. Zhao, J. A. Lercher, Angew. Chem. Int. Ed. 2012, 51, 5935–5940; Angew. Chem. 2012, 124, 6037–6042; f) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, Chem. Rev. 2010, 110, 3552–3599; g) X. Wang, R. Rinaldi, Angew. Chem. Int. Ed. 2013, 52, 11499–11503; Angew. Chem. 2013, 125, 11713–1171; h) Z. Luo, Y. M. Wang, M. He, C. Zhao, Green Chem. 2015, 17, 433–441.
- [8] a) R. H. Venderbosch, A. R. Ardiyanti, J. Wildschut, A. Oasmaa, H. J. Heeres, J. Chem. Technol. Biotechnol. 2010, 85, 674–686; b) E. Baker, D. Elliott in Research in Thermochemical Biomass Conversion, Springer, Heidelberg, 1988, pp. 883–895; c) P. Grange, E. Laurent, R. Maggi, A. Centeno, B. Delmon, Catal. Today 1996, 29, 297–301.
- [9] D. C. Elliott, *Energy Fuels* **2007**, *21*, 1792–1815.
- [10] a) S. T. Oyama, X. Wang, Y. K. Lee, W. J. Chun, J. Catal. 2004, 221, 263–273; b) S. Boullosa-Eiras, R. Lødeng, H. Bergem, M. Stöcker, L. Hannevold, E. A. Blekkan, Catal. Today 2014, 223, 44–53; c) R. C. Nelson, B. Baek, P. Ruiz, B. Goundie, A. Brooks, M. C. Wheeler, B. G. Frederick, L. C. Grabow, R. N. Austin, ACS Catal. 2015, 5, 6509–6523; d) J. He, C. Zhao, J. A. Lercher, J. Am. Chem. Soc. 2012, 134, 20768–20775; e) T. I. Korányi, Z. Vít, J. B. Nagy, Catal. Today 2008, 130, 80–85.
- [11] Y.-B. Huang, L. Yan, M.-Y. Chen, Q.-X. Guo, Y. Fu, Green Chem. 2015, 17, 3010–3017.
- [12] a) J. Engelhardt, Z. Cao, G.-H. Wang, R. Rinaldi, F. Schüth, unpublished results; b) R. Ma, K. Cui, L. Yang, X. Ma, Y. Li, *Chem. Commun.* 2015, *51*, 10299–10301; c) E. Santillan-Jimenez, M. Perdu, R. Pace, T. Morgan, M. Crocker, *Catalysts* 2015, *5*, 424; d) P. M. Mortensen, J.-D. Grunwaldt, P. A. Jensen, A. D. Jensen, *ACS Catal.* 2013, *3*, 1774–1785; e) J. Chang, T. Danuthai, S. Dewiyanti, C. Wang, A. Borgna, *ChemCatChem* 2013, *5*, 3041–3049.
- [13] a) H. Yang, R. Yan, H. Chen, D. H. Lee, C. Zheng, *Fuel* 2007, *86*, 1781–1788; b) Q. Zhang, J. Chang, T. Wang, Y. Xu, *Energy Convers Manage*. 2007, *48*, 87–92.

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a) R. Rinaldi, F. Schüth, *Energy Environ. Sci.* 2009, 2, 610–626;
 b) E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gärtner, J. A. Dumesic, *Science* 2008, 322, 417–421;
 c) P. Anbarasan, Z. C. Baer, S. Sreekumar, E. Gross, J. B. Binder, H. W. Blanch, D. S. Clark, F. Dean Toste, *Nature* 2012, 491, 235– 239; d) G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* 2005, 308, 1446–1450; e) J. M. Melillo, J. M. Reilly,



- [14] A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan, C. E. Wyman, *Science* **2014**, *344*, 1246843.
- [15] H. Fiege, H.-W. Voges, T. Hamamoto, S. Umemura, T. Iwata, H. Miki, Y. Fujita, H.-J. Buysch, D. Garbe, W. Paulus in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2000.

[16] D. Verboekend, Y. Liao, W. Schutyser, B. F. Sels, *Green Chem.* 2016, 18, 297–306.

Manuscript received: October 24, 2016 Revised: December 6, 2016 Final Article published:



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Catalysis Meets Nonthermal Separation for the Production of (Alkyl)phenols and Hydrocarbons from Pyrolysis Oil



Out of the woods: Selective hydrodeoxygenation of lignocellulose-derived pyrolysis bio-oil, catalyzed by MoC_x/C , affords value-added alkylphenol (and phenol) products and hydrocarbons. The strategy requires no prior fractionation of the lignocellulosic biomass, no further synthetic steps, and no input of additional petrochemical platform molecules.