Production of Jet Fuel-Range Hydrocarbons from Hydrodeoxygenation of Lignin over Super Lewis Acid Combined with Metal Catalysts

Hongliang Wang,^[a, d] Huamin Wang,^[b] Eric Kuhn,^[c] Melvin P. Tucker,^[c] and Bin Yang^{*[a]}

Super Lewis acids containing the triflate anion [e.g., $Hf(OTf)_4$, $Ln(OTf)_3$, $In(OTf)_3$, $Al(OTf)_3$] and noble metal catalysts (e.g., Ru/C, Ru/Al_2O_3) formed efficient catalytic systems to generate saturated hydrocarbons from lignin in high yields. In such catalytic systems, the metal triflates mediated rapid ether bond cleavage through selective bonding to etheric oxygens while the noble metal catalyzed subsequent hydrocarbons were produced from lignin model compounds by the combined catalysis of $Hf(OTf)_4$ and ruthenium-based catalysts. When a tech-

Introduction

Current biorefineries undervalue lignin's potential by burning it rather than addressing the renewable product requirements of the world. Utilizing lignin feedstock for the production of high energy-density jet fuel and value-added chemicals along with cellulosic ethanol, or other upgradable intermediate chemicals offers a significant opportunity to enhance the overall operational efficiency, carbon conversion efficiency, economic viability, and sustainability of biofuels and chemicals production.^[1] The selective conversion of lignin into well-defined products is hampered by several challenges. The first challenge is derived from lignin's intrinsic heterogeneous and robust structure.^[2] Lignin is randomly coupled from its three monolignols (coniferyl, sinapyl and coumaryl alcohols) through radical processes during construction of the cell wall, which makes lignin a stable, three-dimensional biopolymer that is particularly resistant towards biological or chemical deconstruction and degradation. The second challenge is the high

[a]	Dr. H. Wang, Prof. B. Yang
	Department of Biological Systems Engineering
	Washington State University, Richland, WA 99354 (USA)
	E-mail: bin.yang@wsu.edu
[b]	Dr. H. Wang
	Pacific Northwest National Laboratory
	902 Battelle Boulevard, Richland, WA 99354 (USA)
[c]	E. Kuhn, Dr. M. P. Tucker
	National Bioenergy Center, National Renewable Energy Laboratory
	15013 Denver West Parkway, Golden, CO 80401 (USA)
[d]	Dr. H. Wang
	Current address: Center of Biomass Engineering/College of Agronomy and
	Biotechnology
	China Agricultural University, Beijing, 100193 (PR China)
D	The ORCID identification number(s) for the author(s) of this article can
	be found under https://doi.org/10.1002/cssc.201701567.

nical lignin derived from a pilot-scale biorefinery was used, more than 30 wt% of the hydrocarbons produced with this catalytic system were cyclohexane and alkylcyclohexanes in the jet fuel range. Super Lewis acids are postulated to strongly interact with lignin substrates by protonating hydroxyl groups and ether linkages, forming intermediate species that enhance hydrogenation catalysis by supported noble metal catalysts. Meanwhile, the hydrogenation of aromatic rings by the noble metal catalysts can promote oxygenation reactions catalyzed by super Lewis acids.

reactivity of lignin deconstruction intermediates, which are prone to side reactions to generate stable repolymerized products (e.g., char) through the formation of new C–C bonds, making it difficult to produce high yields of desired products.^[3] The third challenge is principally caused by the complexity of products from lignin.^[4] Unlike cellulose, lignin has no uniform substructure and linkages. Products from lignin are usually highly mixed and very complicated, containing hundreds of compounds with an abundance of functional groups, including methoxy and hydroxyl groups.^[5] The conversion of lignin into well-defined chemicals can support the emergence of biorefineries that integrate more completely into existing markets and can be more profitable, supporting larger scale market penetration.

To fully unlock lignin's potential, at least the aforementioned three challenges should be addressed. For the first challenge, since most of the linkages among lignin's aromatic units contain C-O-C bonds,^[1c] selective cleavage of these C-O-C bonds could effectively depolymerize lignin into aromatic monomers and dimers.^[6] A large proportion of previous research on lignin valorization, including exploring novel catalysts^[7] and employing pre-activation approaches (e.g., by selective pre-oxidation),^[8] has been devoted to cleavage of C–O–C bonds while avoiding harsh conditions. Several strategies to address the second challenge have also been attempted, such as the use of trapping agents, including boric acid,^[9] diols,^[3b] phenol, 2-naphthol, and p-cresol,^[10] to stabilize the reactive species and reduce char formation. A feasible approach to address the third challenge is to rapidly convert lignin or lignin deconstruction intermediates into hydrocarbon fuels (e.g., jet fuel) by using catalytic hydrodeoxygenation (HDO) processing before additional condensation reactions can occur.^[7b, 11] Rapid

ChemSusChem 2017, 10, 1 – 8 Wiley Online Library

These are not the final page numbers! **77**



HDO process reactions, which involve hydrocracking, hydrogenation, and deoxygenation, are necessary to stabilize labile lignin deconstruction intermediates and convert them into fuel-range products before condensation reactions can occur. The use of lignin as a price-competitive source of alternative jet fuel will help meet the growing worldwide demand for renewable jet fuels, while allowing the aviation industry to achieve carbon-neutral growth. Lignin has a relatively high energy density and its conversion products with suitable carbon chain lengths are excellent jet fuel precursors. In addition, conversion of all major chemical compounds from biomass, including lignin, offers a significant opportunity for enhancing the overall profitability of the biorefinery. Despite such potential, the conversion of lignin into biofuels has proven to be challenging.

Acids combined with metals as bifunctional catalytic systems have been used for the HDO conversion of lignin into fuels and have shown very promising performance.^[6] However, most of the acids in these systems are Brønsted acids (e.g., sulfuric acid, phosphoric acid, H-zeolites). Brønsted acids usually have low selectivity on lignin chemical bond cleavage, which leads to low yields of final products.^[5a] Lewis acids exhibit different catalytic performance to Brønsted acids in reactions of C-O bond formation and cleavage.^[12] In many cases, they show better results than Brønsted acids, as they can selectively bond with and activate specific functional groups (e.g., ether bonds and hydroxyl groups) during organic transformations.^[12] Unfortunately, most Lewis acids are water sensitive and can only be used under strictly anhydrous conditions. Thus, this has greatly restricted the use of Lewis acids in catalytic reactions.^[12a] The exploration of water-tolerant Lewis acids for lignin conversion is urgently needed.

Metal triflates are widely used as novel super Lewis acids in organic synthesis, and they are relatively inexpensive and thermally stable, and can be economically recycled.^[12b, 13] Moreover, they are water insensitive, which can keep the catalyst structure stable in water while maintaining the active sites. Several research groups have reported that metal triflates are effective for biomass conversion, especially for lignin depolymerization.^[14] Metal triflates with strong Lewis acidities have been demonstrated effective in catalyzing cleavage of lignin β -O-4 ether bonds, a major ether bond in lignin cross-linkages.^[3b, 15] The strong electron-withdrawing ^-OTf group (CF_3SO_3^-) can make the metals in metal triflates very cationic. The cationic metals can selectively bond with electron-rich atoms (e.g., oxygen atoms in β -O-4 and α -O-4 ether bonds) and promote the cleavage of related chemical bonds.^[14a,c] Moreover, the phenolic hydroxyl groups in lignin can be exchanged with OTf groups, facilitating the removal of oxygen on aromatic rings.

We report herein that metal triflates can be used to replace conventional Brønsted/Lewis acids for the HDO conversion of lignin into hydrocarbons with supported metal cocatalysts. Metal triflates, with different Lewis acidities, were tested in the catalytic systems to pinpoint the catalytic nature of these materials. Several lignin model compounds and technical lignins were employed as reactants to get additional insights into lignin HDO conversion by the combined catalysis of metal triflates and supported noble metals. The objective of this study was to identify feasible combinations of catalysts that address the aforementioned three challenges of lignin utilization in a one-pot process.

Results and Discussion

Guaiacol was selected as a model compound of lignin to test the different catalyst systems to simplify product analysis and provide insight into the reactions. Three different characteristic C–O bonds in guaiacol are common in lignin, that is, C_{methyl} – OAr, C_{aryl} –OMe, and C_{aryl} –OH. The reactions were carried out at 250 °C for 2 h with 4 MPa hydrogen and *n*-octane as the solvent.

In the absence of catalyst, the conversion of guaiacol was low (<8 wt%) and most of the products were catechols. In contrast, 77% of the guaiacol was converted when Ru/Al₂O₃ catalyst was added. The selectivity to hydrocarbon products (cyclohexane, alkylcyclohexanes, and dimers of alkylcyclohexane hydrocarbons) was about 40% whereas the selectivity to oxy-compounds (mainly cyclohexanol and cyclohexane-1,2diol) was close to 60%, suggesting that the catalytic deoxygenation activity of Ru/Al₂O₃ is not high. No aromatic products were detected, indicating Ru/Al₂O₃ had a high aromatic ring hydrogenation catalytic activity under the tested reaction conditions that led to full aromatic ring saturation. Subsequently, several metal triflates were combined separately with Ru/Al₂O₃ with the aim to enhance the HDO performance. The conversion of guaiacol, as well as the selectivity of hydrocarbon products significantly increased when Hf(OTf)₄, Al(OTf)₃, or In(OTf)₃ were added (Table 1, entries 3–6), especially when Hf(OTf)₄ was used, because almost all of the guaiacol was selectively converted into hydrocarbon products.

Hf(OTf)₄, as a strong Lewis acid, was tested alone in the conversion of guaiacol. Interestingly, guaiacol conversion was not high (58%) and oxy-compounds (phenols and alkylphenols) were detected as the major products. It should be noted that the oxy-compounds (aromatics) obtained by using Hf(OTf)₄ were different from those (cyclohexanols) formed by using Ru/ Al_2O_3 catalysis. These results suggest that Ru/Al_2O_3 is a catalyst not only for hydrogenation reactions, but also partly for oxygen-removal reactions. It has also been demonstrated that the hydrogenation of aromatic rings is favorable for the removal of ring-associated oxy groups. $^{\mbox{\tiny [16]}}$ Usually, sp^2 hybrid Caromatic-O bonds have 80-100 kJ mol⁻¹ higher bond dissociation energy than sp³ hybrid C–O bonds. The hydrogenation of the aromatic rings can destroy the aromaticity of the reactant and change the sp² hybrid C_{aromatic}-O bonds into sp³ hybrid C-O bonds and thus facilitate the removal of oxygen on aromatic rings. Some dimer products were detected by using Hf(OTf)₄ only, which were also aromatics. The total selectivity of the GC-MS detectable products catalyzed by Hf(OTf)₄ was less than 100%, indicating that some high molecular weight products existed, most probably produced from condensation and polymerization reactions. When no Ru-based catalysts were present, the conversion of lignin deconstruction intermediates into char instead of hydrocarbon products increased, since these in-



CHEMSUSCHEM Full Papers

 Table 1. HDO conversion of guaiacol with different metal triflate/supported noble metal catalyst systems.^[a]



Entry	Catalyst	Conversion [wt %]	hydrocarbon monomers	Product selectivity [C hydrocarbon dimers	%] oxy-compounds	Total hydrocarbon yield [C%]
1	none	<8	N.D.	N.D.	96.0	N.D.
2	Ru/Al ₂ O ₃ only	77	38.2	2.4	59.4	31.3
3	Ni(OTf)₂+Ru	86	49.9	3.6	46.5	46.0
4	Al(OTf)₃+Ru	91	78.1	10.2	11.7	80.4
5	Hf(OTf)₄+Ru	>99	82.6	17.4	N.D.	>99.9
6	In(OTf)₃+Ru	>99	71.9	18.7	9.4	91.0
7	ZnCl ₂ +Ru	83	45.6	3.1	51.3	40.4
8	AlCl₃+Ru	87	46.6	4.8	48.6	44.7
9	Hf(OTf)₄ only	58	2.0	6.3	68.0	1.2
10	Hf(OTf) ₄ +Pd	>99	75.0	13.7	11.3	88.7
11	Hf(OTf)₄+Pt	89	65.9	14.6	19.5	72.1
12 ^[b]]	Hf(OTf)₄+Ru	> 99	84.5	15.5	N.D.	>99.9
13 ^[c]	H₃PO₄+Ru	84	55.2	2.3	42.5	48.3
14 ^[d]	HY+Ru	87	60.3	7.9	31.8	59.3

termediates are aromatic oxy-compounds with high polymerization reactivity under Lewis acid catalysis, increasing C–C bond formation through alkylation and aldol condensation reactions.

Unlike Hf(OTf)₄, Al(OTf)₃, or In(OTf)₃, the addition of Ni(OTf)₂ showed minimal improvement in guaiacol HDO conversion, with half of the products being oxy-compounds. The differences in the catalytic behaviors of the tested metal triflates may lie in the differences of the effective charge density of their metal ions.^[13b, 14d] In general, the Lewis acidity of metal triflates increased with the effective charge density of their central metal cations. The effective charge density of the metal ions in $Hf(OTf)_4$, $Al(OTf)_3$, and $In(OTf)_3$ is higher than that in $Ni(OTf)_2$, which means that the Lewis acidity of Hf(OTf)₄, Al(OTf)₃, and In(OTf)₃ is stronger than that of Ni(OTf)₂. Catalysts with higher Lewis acidities are more effective in activating chemical bonds, for example, C-O bonds, and achieve highly efficient cleavage of these bonds through proton transfers. To further verify this hypothesis, metal chlorides, including ZnCl₂ and AlCl₃, were used in combination with Ru/Al₂O₃ to test the hypothesis. Results were unsatisfactory. The conversion of guaiacol was incomplete and almost half of the products were oxy-compounds. Although AlCl₃ and Al(OTf)₃ have the same cation and a similar pH in solution, their catalytic results are quite different, indicating that neither cation nor Arrhenius acidity is the decisive factor affecting the reactivity. The effective charge density of metal cations plays an important role in the reactions. Anions in Lewis acids could influence the effective charge densities of the central metal ions, and thus influence the Lewis acidity, which relates to the strengths of the substrate-catalyst interactions. AI^{3+} in $AI(OTf)_3$ is more cationic than it is in AlCl₃, so the Lewis acidity of Al(OTf)₃ is stronger than AlCl₃. Metals in strong Lewis acids have a strong interaction with oxygen atoms in ether bonds, and they can effectively activate and cleave these bonds. The effective cleavage of ether bonds by strong Lewis acids can form intermediate species that can be converted on Ru/Al_2O_3 more efficiently through hydrogenation and deoxygenation reactions. Brønsted acids, including H_3PO_4 and HY zeolite, were also used to replace metal triflates. Both guaiacol conversion and hydrocarbon product yields were low. The different performances of Brønsted acids to Lewis acids are probably because Lewis acids can selectively interact with oxygens in the reactant, achieving highly efficient cleavage of the ether bond and oxygen removal with the accompaniment of Ru/Al_2O_3 hydrodeoxygenation catalysis.

As indicated above, both strong Lewis acids and Ru/Al₂O₃ are essential for achieving high yields of hydrocarbons in guaiacol HDO conversions. Ru-based catalysts have been widely used for lignin conversion. Ru, as compared with other noble metals, is less expensive and has superior HDO catalytic activity.^[17] In addition, other noble metals commonly used in hydrogenation reactions were explored to replace Ru/Al₂O₃. Pd/Al₂O₃ and Pt/Al₂O₃ combined with Hf(OTf)₄ were tested in the reactions (Table 1, entries 10-12). Both supported noble metal catalysts improved their catalytic behavior in the presence of Hf(OTf)₄. The conversion of guaiacol and the selectivity to deoxygenated products were close to those when catalyzed by Ru/Al₂O₃. Moreover, other supports besides Al₂O₃ were also tested in this reaction. Activated carbon (C) was chosen to replace Al₂O₃, which has a degree of Lewis acidity. The loading of Ru in Ru/C was the same as that in Ru/Al₂O₃ and similar HDO results were obtained.



Effects of solvents on guaiacol HDO conversion were investigated next (Figure 1). Guaiacol conversion was nearly 90% and the yield of hydrocarbon products was about 60% when no solvent was added. About 10 mol% of oxy-compounds (mainly



Figure 1. Effects of solvents on the HDO conversion of guaiacol. Reaction conditions: guaiacol (2.5 mmol), Hf(OTf)₄ (1 mol%), Ru (0.8 mol%; as 5 wt% Ru/Al₂O₃), solvent (1 mL), T=250 °C, t=2 h, $P_{H_2}=4$ MPa. Control: guaiacol (5 mmol), Hf(OTf)₄ (1 mol%), Ru (0.8 mol%; as 5 wt% Ru/Al₂O₃), no solvent. *n*-octane + water means 90 wt% *n*-octane mixed with 10 wt% water.

cyclohexanol and 2-cyclohexylcyclohexanol) were obtained. No other products were detected by GC-MS. The conversion of guaiacol and the yield of hydrocarbon products were quite low when the reactions were carried out in water. This result is probably due to the low solubility of guaiacol in water and the instability of Ru/Al₂O₃ in hot water. Although methanol and dichloromethane led to relatively high conversion of guaiacol, the yields of hydrocarbons in these solvents were low. Products, mainly various oxy-compounds, obtained in water, methanol, and dichloromethane were quite complicated. n-Octane was found to be an excellent solvent for the reactions. Guaiacol was completely converted into hydrocarbons in *n*-octane. The use of a suitable solvent such as *n*-octane was found to be better than the control reactions for the following reasons: i) Catalysts, temperature, and pressure are more stable within solvents; ii) the dissolution and transportation of H₂ are superior; iii) these solvents hold the reactant, intermediates, and products in solution.^[13b] Since it is difficult and costly to remove all water from biomass feedstocks, 10 wt% of water was mixed with n-octane as the mixed solvent, whereby approximately 100% guaiacol conversion was observed and the yield of hydrocarbons was acceptable. The good performance of these catalyst systems in *n*-octane may result from greater H₂ solubility, better heat and mass transfer, and less adverse impact to the catalysts (e.g., non-active for competitive adsorption). The use of *n*-octane or other inexpensive hydrocarbon solvents is especially beneficial for the current catalytic systems since these hydrocarbons can be directly used as fuel without expensive separation.

Under the reaction conditions of guaiacol conversion reported herein, several other lignin model compounds with a broad range of functional groups and linkages were tested. Most of the C–O bonds, including the ether bonds and C–OH bonds, were cleaved efficiently, although a small amount of C–O–C bonds in diphenyl ether remained stable (Table 2, entry 3). Ether bonds in methoxy groups, as well as in α -O-4 (entry 2) and β -O-4 linkages (entry 4), were completely cleaved. Almost all oxygen atoms in these model compounds were removed. High yields of hydrocarbon products were obtained from all of the tested model compounds. Moreover, most of the ring structures, side carbon chains, and carbon linkages between aromatic rings (Table 2, entry 5) in these reactants remained after the reactions, indicating that the catalytic systems had little effect on the carbon skeleton.

The HDO conversion of corn stover lignin obtained from dilute alkali deacetylation and mechanical refining (DMR) treatment, an alternative biomass deconstruction process developed at the National Renewable Energy Laboratory (NREL), was investigated. This technology has been shown to produce highly digestible pretreated solid residues and result in highconcentration sugar syrups (ca. 230 g L⁻¹ fermentable monomeric sugars) and high sugar yields (up to 90% cellulose to glucose) with commercial enzyme preparations at high solid loadings (up to 30 wt% insoluble solids).^[6a] Potential valueadded streams produced in the DMR process are the "nativelike" and tractable lignin residues isolated from the deacetylation process and enzymatic hydrolysis. These lignin streams can be converted into fuels and chemicals instead of being burned to produce electricity, thus increasing a biorefinery's revenues. A large portion (ca. 80%) of the lignin is carried all the way through enzymatic hydrolysis as insoluble solids in the DMR process. After purification, the DMR lignin was characterized by using 2D NMR spectroscopy. The inter-unit linkages among the aromatic units of the DMR lignin were found to be about 43, 44, 9, and 4% for β -O-4, β -5, β - β , and β -1, respectively.[6a]

The HDO conversion of DMR lignin was initially tested with Ru/Al_2O_3 as catalyst at 250 °C under 4 MPa hydrogen pressure for 4 h (Figure 2a). The yield of hydrocarbon products was low (< 5 wt%). An additional large portion of products was found to be oxy-compounds, mainly including the derivatives of cy-clohexanone and cyclohexanol. When Hf(OTf)₄ was used alone, the yield of hydrocarbon products was negligible (Figure 2b). The majority of the products from DMR lignin by the catalysis of Hf(OTf)₄ was found to be phenols and alkylphenols. More



Figure 2. Hydrocarbon yields from DMR lignin in HDO conversion under different conditions. Reaction conditions: lignin (50 mg), *n*-octane (1 mL), $T = 250 \degree$ C, t = 4 h, $P_{H_2} = 4$ MPa. Catalysts: a) 10 mg Ru/Al₂O₃. b) 15 mg Hf(OTf)₄. c) 10 mg Ru/Al₂O₃ + 15 mg Hf(OTf)₄. d) 10 mg Ru/Al₂O₃ + 15 mg Hf(OTf)₄ in 1 mL *n*-octane containing 10 wt% water as solvent. e) No catalyst was added.

www.chemsuschem.org





than 30 wt% of hydrocarbon products was obtained from DMR lignin HDO conversion by using the combined catalysis of Ru/Al_2O_3 and $Hf(OTf)_4$. This yield was about six times that obtained by using Ru/Al₂O₃ alone, demonstrating that Hf(OTf)₄ provided significant synergistic effects with Ru/Al₂O₃ in the conversion of technical lignin into hydrocarbons. Moreover, the majority of the hydrocarbon products produced with the combined catalysts was found to maintain ring structures and mainly contained 9-18 carbon atoms, suitable for fuel usage (Figure 3). Additionally, when mixed solvents containing 90 wt% *n*-octane and 10 wt% water was used to replace pure *n*-octane, the yield of hydrocarbon products remained similar. Negligible amount of hydrocarbon products was generated when no catalyst was added (Figure 2e). The yield of other lignin depolymerization products, such as monomer and dimer aromatics, was also quite low (< 10 wt %). The stability and reusability of metal triflates were proven very good.^[13b, 14a] A slight efficiency loss in hydrocarbon production from lignin was found when the catalysts were reused, and this was probably due to the formation of some clusters in the Ru-based catalyst.



Figure 3. GC-MS spectrum of DMR lignin HDO products from the combined catalysis of Ru/Al_2O_3 and $Hf(OTf)_4$.



Conclusions

High yields of hydrocarbons with the carbon numbers in the jet fuel range were obtained from technical lignin or lignin model compounds by the combined catalysis of strong Lewis acids [e.g., Hf(OTf)₄, Al(OTf)₃, or In(OTf)₃] and supported ruthenium catalysts (e.g., Ru/Al₂O₃ or Ru/C) in a simple one-pot process. Almost all of the C-O bonds, including ether bonds and C-OH bonds, were found to be cleaved in the tested lignin model compounds. Meanwhile, oxygen in these compounds was efficiently removed while the carbon skeletal structures were retained. Sufficient evidence is presented to show that strong Lewis acids had synergistic effects in combination with Ru/Al₂O₃ on HDO conversion of lignin and its model compounds. The HDO reactions in these catalytic systems were enhanced by using *n*-octane as solvent. These results highlight the potential for an efficient HDO catalytic process to produce jet fuel from biorefinery lignin waste streams.

Experimental Section

Chemicals and materials

All the chemicals used in this research are commercially available and used as received without further purifications. Metal triflates, including Hf(OTf)₄, Ln(OTf)₃, ln(OTf)₃, Al(OTf)₃, and Ni(OTf)₂ (OTf= trifluoromethanesulfonate group), were purchased from Sigma–Aldrich. Reduced catalysts, including Ru/Al₂O₃, Pd/Al₂O₃, Pt/Al₂O₃, and Ru/C, were purchased from Alfa Aesar. Lignin model compounds, including guaiacol, 4-ethyl-2-methoxyphenol, benzyloxy benzene, diphenyl ether, and 1,1'-biphenyl, were purchased from Fisher Scientific. Lignin β -O-4 model compounds were purchased from GreenLignol, LLC. Zeolite HY (CBV 400) was purchased from Zeolyst International. Corn stover lignin was obtained by the National Renewable Energy Laboratory (NREL) through dilute alkali deacetylation and mechanical refining (DMR) treatment. All other chemicals were purchased from Fisher Scientific.

Hydrodeoxygenation conversion of lignin model compounds and lignin

In a typical reaction, lignin (50 mg) or lignin model compounds (2.5 mmol), catalysts, and solvents (1 mL), as needed, were added to a 3 ml dry glass sleeve. The sleeve was placed into a highthroughput batch reactor (PNNL-SA-117072) at the Bioproducts, Science & Engineering Laboratory. The reactor was sealed and purged with H₂ three times to exclude air, and then pressurized with 4 MPa H₂ at room temperature. The reactor was heated to 250 °C and heating was maintained for 2 or 4 hours, depending on the substrate. The metal plate of the high-throughput reactor was shaken at a rate of 80 counts min⁻¹ during the reaction to improve the mass transfer. After each run, the reactor plate was cooled to room temperature to terminate the reaction by removing the heat. (WARNING! Use caution when handling and venting the reactor and glass sleeves; the reaction mixtures containing Ru/C and organic solvents are extremely catalytically reactive, flammable, and pyrophoric when exposed to air). The glass sleeve was removed from the high-throughput reactor and the liquids were separated from the solids by centrifugation (8000 rmin^{-1} for 10 min). The liquid was diluted with methanol in a 10 mL volumetric flask. The solids were washed with an additional 10 mL methanol and centrifuged. The methanol phase was combined in the volumetric flask. A small quantity of 3-methylheptane (0.2 mmol) was added into the diluted liquid solution and used as the internal standard in GC analysis.

Analysis of HDO products

The methanol-diluted liquid samples were analyzed by GC and GC-MS in an Agilent Technologies 7890A GC system with a DB-5 capillary column (30 m length \times 250 µm I.D. \times 0.25 µm film thickness; J&W Scientific) in the splitless mode. Typically, a 1 µL sample was injected with 0.6 mL min⁻¹ of He used as the carrier gas into the GC system. The injection port temperature was set at 300 °C. The GC oven was programmed to 32 °C for 10 min. Then the temperature was raised at a rate of 10 °C min⁻¹ until it reached 300 °C and was held at this temperature for 2 min. Eluting compounds were detected with a MS (Agilent Technologies 5975C) inert XL El/Cl MSD with a triple axis detector, and compared by using NIST libraries. The calculations of conversion and selectivity of lignin model compounds were based on carbon, and the calculations of conversions and selectivity of technical lignin were based on weight.

For lignin model compounds [Eqs. (1)–(3); HC = hydrocarbon]:

$$Conversion \% = \frac{\text{Reactant converted}}{\text{Reactant added}} \times 100\%$$
(1)

Yield of HC
$$\mathbf{A}$$
 % = $\frac{C \text{ atoms in HC } \mathbf{A}}{C \text{ atoms in reactant}} \times 100\%$ (2)

$$\label{eq:Selectivity to HC A \%} \begin{split} & \text{Selectivity to HC A \%} = \frac{\text{C atoms in HC A}}{\text{Total C atoms in products}} \times 100\% \end{split} \tag{3}$$

For the conversion of technical lignin [Eqs. (4)–(6)]:

$$Conversion \% = \frac{\text{Weight of reactant converted}}{\text{Weight of reactant added}} \times 100\%$$
(4)

$$\label{eq:Yield of HC A } \ensuremath{\mathbb{Y}} \ensuremath{\mathsf{Y}} = \frac{\ensuremath{\mathsf{W}} \ensuremath{\mathsf{eight of HC A produced}}}{\ensuremath{\mathsf{Weight of reactant added}}} \times 100\% \tag{5}$$

Total HC yield
$$\% = \sum_{x=1}^{20} \text{Yield}(x) \times 100\%$$
 (6)

Metal triflate recycling

After reaction, solvents and hydrocarbon products were removed from the reaction mixture by rotary evaporation. The residue was separated by extraction with water and ethyl acetate. Most of the initial metal triflates was found in the water phase. After filtration, water was removed from the filtrate by rotary evaporation under vacuum. The residue (mainly metal triflate) was redissolved in *n*-octane and used in a new reaction under standard conditions.

Acknowledgements

This work was supported by the National Renewable Energy Laboratory Subcontract # AEV-6–52054-01 under Prime U.S. Department of Energy (DOE) Award # DE-AC36-08G028308, and the Sun Grant-U.S. Department of Transportation (DOT) Award # T0013G-A-Task 8 with the Bioproducts, Science & Engineering Laboratory and Department of Biological Systems Engineering at Washington State University. This work was performed in part at the Wil-



liam R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the U.S. DOE's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory, operated for the DOE by Battelle. The authors would like to thank Ms. Heather Job and Ms. Marie S. Swita, who helped us to conduct the highthroughput experiments and to collect part of the GC-MS data for this project.

Conflict of interest

The authors declare no conflict of interest.

Keywords: biomass conversion · fuels · hydrocarbons hydrodeoxygenation · metal triflates

- [1] a) 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; b) D. D. Laskar, B. Yang, H. Wang, J. Lee, Biofuels Bioprod. Biorefin. 2013, 7, 602-626; c) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, Chem. Rev. 2010, 110, 3552-3599.
- [2] a) S. Stiefel, C. Marks, T. Schmidt, S. Hanisch, G. Spalding, M. Wessling, Green Chem. 2016, 18, 531-540; b) T. Saito, J. H. Perkins, F. Vautard, H. M. Meyer, J. M. Messman, B. Tolnai, A. K. Naskar, ChemSusChem 2014, 7, 221 - 228
- [3] a) L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph, J. S. Luterbacher, Science 2016, 354, 329-333; b) P. J. Deuss, M. Scott, F. Tran, N. J. Westwood, J. G. de Vries, K. Barta, J. Am. Chem. Soc. 2015, 137, 7456-7467.
- [4] a) C. W. Lahive, P. J. Deuss, C. S. Lancefield, Z. Sun, D. B. Cordes, C. M. Young, F. Tran, A. M. Slawin, J. G. de Vries, P. C. Kamer, J. Am. Chem. Soc. 2016, 138, 8900-8911; b) S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. De Meester, W. Huijgen, W. Dehaen, C. Courtin, Energ. Environ. Sci. 2015, 8, 1748-1763.
- [5] a) C. Li, X. Zhao, A. Wang, G. W. Huber, T. Zhang, Chem. Rev. 2015, 115, 11559-11624; b) H. Wang, T. Deng, H. Ruan, X. Hou, J. R. Cort, B. Yang, Green Chem. 2016, 18, 2802-2810.
- [6] a) H. Wang, H. Ruan, H. Pei, H. Wang, X. Chen, M. P. Tucker, J. R. Cort, B. Yang, Green Chem. 2015, 17, 5131-5135; b) N. Yan, C. Zhao, P. J. Dyson, C. Wang, L. T. Liu, Y. Kou, ChemSusChem 2008, 1, 626-629.

- [7] a) T. H. Parsell, B. C. Owen, I. Klein, T. M. Jarrell, C. L. Marcum, L. J. Haupert, L. M. Amundson, H. I. Kenttaemaa, F. Ribeiro, J. T. Miller, M. M. Abu-Omar, Chem. Sci. 2013, 4, 806-813; b) R. Ma, W. Y. Hao, X. L. Ma, Y. Tian, Y. D. Li, Angew. Chem. Int. Ed. 2014, 53, 7310-7315; Angew. Chem. 2014, 126, 7438-7443; c) Q. Song, F. Wang, J. Y. Cai, Y. H. Wang, J. J. Zhang, W. Q. Yu, J. Xu, Energ. Environ. Sci. 2013, 6, 994-1007.
- [8] a) C. S. Lancefield, O. S. Ojo, F. Tran, N. J. Westwood, Angew. Chem. 2015, 127, 260-264; b) A. Rahimi, A. Ulbrich, J. J. Coon, S. S. Stahl, Nature 2014, 515, 249-252.
- [9] V. M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li, J. A. Lercher, Chem. Eur. J. 2011, 17, 5939-5948.
- [10] J. B. Li, G. Henriksson, G. Gellerstedt, Bioresour. Technol. 2007, 98, 3061 -3068.
- [11] a) X. Y. Wang, R. Rinaldi, Angew. Chem. Int. Ed. 2013, 52, 11499-11503; Angew. Chem. 2013, 125, 11713-11717; b) Q. Xia, Z. Chen, Y. Shao, X. Gong, H. Wang, X. Liu, S. F. Parker, X. Han, S. Yang, Y. Wang, Nat. Commun. 2016, 7, 11162; c) X. Cui, A.-E. Surkus, K. Junge, C. Topf, J. Radnik, C. Kreyenschulte, M. Beller, Nat. Commun. 2016, 7, 11326.
- [12] a) S. Kobavashi, K. Manabe, Acc. Chem. Res. 2002, 35, 209-217; b) T. L. Lohr, Z. Li, T. J. Marks, Acc. Chem. Res. 2016, 49, 824-834.
- [13] a) Z. Li, R. S. Assary, A. C. Atesin, L. A. Curtiss, T. J. Marks, J. Am. Chem. Soc. 2014, 136, 104-107; b) H. J. Song, J. Deng, M. S. Cui, X. L. Li, X. X. Liu, R. Zhu, W. P. Wu, Y. Fu, ChemSusChem 2015, 8, 4250-4255.
- [14] a) R. Jastrzebski, S. Constant, C. S. Lancefield, N. J. Westwood, B. M. Weckhuysen, P. C. Bruijnincx, ChemSusChem 2016, 9, 2074-2079; b) P. J. Deuss, C.W. Lahive, C.S. Lancefield, N.J. Westwood, P.C. Kamer, K. Barta, J. G. de Vries, ChemSusChem 2016, 9, 2974-2981; c) L. Yang, Y. Li, P. E. Savage, Ind. Eng. Chem. Res. 2014, 53, 2633-2639; d) R. S. Assary, A. C. Atesin, Z. Li, L. A. Curtiss, T. J. Marks, ACS Catal. 2013, 3, 1908-1914; e) J. Degenstein, S. R. Kamireddy, M. P. Tucker, Y. Ji, Int. J. Agric. Biol. Eng. 2013, 6, 54-62.
- [15] X. Huang, O. M. Morales Gonzalez, J. Zhu, T. I. Koranyi, M. D. Boot, E. J. M. Hensen, Green Chem. 2017, 19, 175-287.
- [16] a) X. Zhu, L. L. Lobban, R. G. Mallinson, D. E. Resasco, J. Catal. 2011, 281, 21-29; b) H. Wang, M. Feng, B. Yang, Green Chem. 2017, 19, 1668-1673
- [17] a) C. Michel, P. Gallezot, ACS Catal. 2015, 5, 4130-4132; b) J. Zhang, J. Teo, X. Chen, H. Asakura, T. Tanaka, K. Teramura, N. Yan, ACS Catal. 2014, 4, 1574-1583.

Manuscript received: August 19, 2017 Revised manuscript received: October 11, 2017 Version of record online:

7

ChemSusChem 2017, 10, 1-8

FULL PAPERS

H. Wang, H. Wang, E. Kuhn, M. P. Tucker, B. Yang*

Production of Jet Fuel-Range Hydrocarbons from Hydrodeoxygenation of Lignin over Super Lewis Acid Combined with Metal Catalysts



The biggest Lewiser: Super Lewis acids and noble metals form an efficient catalytic system that can overcome the energy barrier for conversion of lignin into high yield jet-fuel range hydrocarbons. Metal triflates mediate rapid ether bond cleavage through selective bonding to the etheric oxygen, whereas the noble metal catalyzes the subsequent hydrogenation reaction, eliminating functional groups.

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim **K** These are not the final page numbers!