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Effects of sugars, furans, and their derivatives on hydrodeoxygenation of biorefinery lignin-rich wastes to hydrocarbons

Hongliang Wang,^[a, b] Yuhua Duan,^[d] Qian Zhang,^[e] and Bin Yang*^[a,c]

Abstract: Hydrodeoxygenation of biorefinery lignin-rich wastes to jet fuel hydrocarbons offers a significant opportunity for enhancing the overall operational efficiency, carbon conversion efficiency, economic viability, and sustainability of biofuels production. However, these wastes usually mainly contain lignin with sugars, furans, and their derivatives as "impurities". Although several factors, including reactant structure, solvents, or the decreased ratio of catalyst to reactant, could be responsible for the jet fuel hydrocarbons yield loss, we found evidence that glucose, xylose, and 5-hydroxymethylfurfural dramatically decreased conversion yields. For example, xylose and glucose lowered the final hydrocarbon yield by 78% and 63%, respectively. The results revealed that these compounds could suppress metal catalysts and inhibit lignin depolymerization and hydrodeoxygenation (HDO) reactions thus decrease yields of jet fuel range hydrocarbons from biomass-derived lignin. The first-principles calculations and TGA results from spent catalysts validated these findings.

Efficient utilization of all available carbons from biomass to produce biofuels will be required for an economical process. Catalytic technologies for conversion of biorefinery wastes at high carbon efficiency for maximal biofuel production are critical for enabling a robust biorefinery industry.^[1-3] Biorefinery lignin-rich wastes are the partially dewatered stream containing lignin as well as unconverted biomass components such as sugars, furans, and their derivatives. Such wastes are often burned to supply self-sustaining energy to the biorefinery or discarded. However, the chemical structure of lignin suggest that it not only can be used to produce energy, but also has great potential for production of value-added fuels and chemicals.^[4-8] Unlike conversion of carbohydrates to biofuels,[4-7] effective conversion of lignin and lignin-rich biorefinery wastes still remains challenging.^[8-10] If US replaced 25% of transportation fuels with biofuels by 2030, it will produce around 50 billion gallons of cellulosic ethanol and up to 0.3 billion tons resultant lignin. The amount of lignin wastes will substantially exceed the power demand of the biorefinery

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operation. Efforts are critically needed to transform lignin-rich wastes into higher value products. Lignin depolymerization and subsequent HDO conversion to hydrocarbons under catalytic conditions is one of the most promising approaches for its rational utilization.^[8, 9] The catalytic efficiency as well as the generated products (yield, composition, and distribution) of lignin HDO approach can be regulated by several important factors, such as catalysts, hydrogen pressure, solvents, trapping agents, reaction temperature, and time.^[7, 11-14] Extensive research work on these aspects has been conducted to fully unlock lignin's potential.[15-17] Effects of lignin characteristics, including its origins (softwood, hardwood, or herbaceous plant), molecular weight, and chemical linkages on its HDO conversion also have been extensively studied.^[10,17-21] However, relatively few studies were devoted to the determination of effects of impurities (e.g. sugar, furans, and their derivatives) in lignin-rich wastes on its HDO conversion.

Lignin from biorefinery processes always contains a certain amount of impurities. The majority of these impurities are carbohydrates (sugars) or other derivatives from cellulose and hemicellulose.^[21, 22] Potential effects of sugars, furans, and their derivatives on lignin HDO conversion, including adsorption onto catalysts, reacting with lignin and its degraded intermediates, remain unexplored. In this study, to simulate real lignin degraded intermediates, lignin model compounds were mixed with various sugars to investigate effects of sugars on the HDO conversion of lignin, including on the product compositions and distribution, the efficiency of breaking different C-O-C bonds among lignin interlinkages. Subsequently, to get more insights into effects of sugars on real lignin HDO conversion, HDO reactions of lignin mixed with two typical mono sugars (i.e. glucose and xylose) were investigated. The lignin used in this study was prepared from dilute alkali deacetylation and mechanical refining (DMR) treatment, a biomass deconstruction process developed at the National Renewable Energy Laboratory (NREL).^[23] The catalyst system used here was a combination of a super Lewis acid indium triflate In(OTf)₃ with an inexpensive noble metal based catalyst (Ru/Al₂O₃). It was reported that lignin and its phenol derivatives were successfully converted by the combination of metallic and acidic functions.^[24] Indium triflate was shown being an environmentally friendly, inexpensive, reusable, and watertolerant Lewis acid.^[25] More importantly, it showed high activity in hydrolysis of lignin and its model compounds.[24-27] Ruthenium based catalysts were widely used in lignin HDO conversion, exhibiting high deoxygenation and hydrogenation activities in aqueous solution.[26-29]

Initially in this study, guaiacol was selected as a lignin model compound for the investigation of effects of carbohydrates and their derivatives (i.e. glucose, xylose, 5-HMF, cellulose) on lignin HDO conversion. Six types of HDO main products were detected (Table 1). Product **6** was mainly alkylphenols and alkylcyclohexanols. Although addition of 10 mol% glucose in the reactant did not significantly change the amount of guaiacol

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converted, it strongly affected the product distribution. As listed in Table 1 run 1~2, the selectivity of the primary product (product 1, 1,2-benzenediol) with 10 mol% glucose addition was much higher than that with pure guaiacol as reactant. Meanwhile, without addition of any sugars, the selectivity of aromatic ring hydrogenated products (product 3~5) was moderate. However, with the addition of 10 mol% glucose, the selectivity of these products became fairly low. These results indicated that the existence of glucose had significant effects on the further conversion of 1,2-benzenediol to aromatic ring saturated products although it showed small effect on the conversion of guaiacol to 1,2-benzenediol.

Since both In(OTf)₃ and Ru/Al₂O₃ can catalyze guaiacol to 1.2-benzenediol reactions, but only Ru/Al₂O₃ can catalyze 1.2benzenediol to products 3~5, the inhibition of 1,2-benzenediol to aromatic ring saturated products in run 2 is likely due to the deactivation of Ru/Al₂O₃ by glucose or its derivatives. To test this hypothesis, In(OTf)₃ and Ru/Al₂O₃ were tested separately. Results showed that, when In(OTf)₃ was used alone, the addition of 10 mol% glucose in the reactants had little effect on both quaiacol conversion and product distribution. 1,2-benzenediol was found to be the dominant product with both catalysts. When the glucose content increased to 30 mol%, the guaiacol conversion slightly decreased 3.9%. Further increasing the glucose content to 60 mol%, the guaiacol conversion dropped 14.4%. These results suggested that glucose had little effect on the acidic conversion of guaiacol. However, under the catalysis of Ru/Al₂O₃, both guaiacol conversion and the product distribution changed obviously with the addition of glucose. The conversion

Table 1. HDO conversion of guaiacol with carbohydrates and their derivatives^[a]

Run	Catalysts	Carbohydrates	Conversion	Product selectivity (C %)					
			(wt.%)	1	2	3	4	5	6
1	In(OTf)₃+ Ru/Al₂O₃		72.5	26.1	10.3	15.1	22.4	22.6	3.5
2	In(OTf)₃+ Ru/Al₂O₃	Glucose (0.1mmol)	68.2	55.2	14.2	4.6	8.7	7.6	9.7
3	In(OTf)₃	,	65.6	85.3	12.6	N.R.	N.R.	N.R.	2.1
4	In(OTf)₃	Glucose (0.1mmol)	64.9	88.9	8.2	N.R.	N.R.	N.R.	2.9
5	In(OTf)₃	Glucose (0.3mmol)	61.7	90.5	5.0	N.R.	N.R.	N.R.	4.5
6	In(OTf)₃	Glucose (0.6mmol)	51.2	94.5	3.7	N.R.	N.R.	N.R.	1.8
7	Ru/Al ₂ O ₃	· _ /	79.3	10.2	6.7	26.7	17.4	30.5	8.5
8	Ru/Al ₂ O ₃	Glucose (0.1mmol)	55.3	36.8	15.3	11.9	16.6	14.1	5.3
9	Ru/Al ₂ O ₃	Glucose (0.3mmol)	30.1	48.2	10.7	9.0	11.3	10.3	10.5
10	Ru/Al ₂ O ₃	Xylose (0.1mmol)	48.6	39.9	16.1	9.8	17.1	11.0	6.1
11	Ru/Al ₂ O ₃	5-HMF (0.1mmol)	41.7	45.3	18.9	7.5	9.3	9.5	9.5
12	Ru/Al ₂ O ₃	Cellulose	64.1	28.3	11.9	19.6	14.5	23.6	2.1

[a] Reaction conditions: ngualacot+ncarbohydrate=1 mmol, 0.05 mmol In(OTf)₃, 0.025 mmol Ru as 5 wt.% Ru/Al₂O₃, 1 ml water as solvent. T=250 °C, t=2 h, PH₂=580 psi. N.R. means no product observed.

of guaiacol decreased from 79% to 55% when 10 mol% glucose was added. Further increase of the glucose content to 30 mol% led to a sharp decrease of guaiacol conversion to 30%. Meanwhile, the selectivity of aromatic ring saturated products obviously dropped when glucose was added (run 8~9).

To evaluate the influence of other common carbohydrates or their derivatives on guaiacol HDO conversion under Ru/Al₂O₃ catalysis, xylose, 5-hydroxymethylfurfural (HMF), and cellulose were mixed separately with guaiacol under identical reaction conditions, and results are summarized in Table 1, run 10~12. Both xylose and HMF significantly suppressed the catalytic activity of Ru/Al₂O₃. The addition of cellulose also decreased the HDO catalytic activity of Ru/Al₂O₃ although not as strong as the mono sugars and HMF. Results showed that the inhibition ability of carbohydrates on Ru/Al2O3 decreased as follows: 5-HMF>xylose>glucose>cellulose. This sequence appears to be in line with the amount of products containing aromatic furan ring that formed from those carbohydrates under the reaction conditions. HMF is a dehydration product of hexose and a furanbased compound, which can compete with guaiacol to adsorb onto the surface of ruthenium nanoparticle and thus suppress the HDO conversion of guaiacol.^[18] Xylose comes from hemicellulose, and it can be easily converted into furfural (also contains an aromatic furan ring) under hydrothermal or acidic conditions. Compared with xylose, glucose and cellulose are more difficult to be converted to furan-based compounds. Meanwhile, previous studies also reported the suppression of catalytic hydrogenation activities of metals by furan compounds.[21, 22, 30]

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Table 2. HDO conversion of lignin dimers over the combined catalysis of In(OTf) ₃ and Ru/Al ₂ O ₃ ^[a]										
Entry	Reactant	Conversion (wt.%)			Selectivity (C%)	A				
1		56.3	55.3	11.7	25.4		1.9			
2 ^b		36.8								
	DPE		80.3	7.4	8.2	2.6	0.8			
3		>99								
	BPE		33.9	27.1	14.7	11.3	8.6			
4 ^b		84.6	41.0		21.0	9.7				
	BPE T		11.0	19.6		9.1	6.3			
5		>99					\bigcirc			
	VGE		27.4	18.4	16.9	15.4	11.8			
6 ^[b]		78.6					0.1			
	VGE		33.6	15.1	18.3	14.5	3.1			

Reaction conditions: 0.05 mmol In(OTf)₃, 0.025 mmol Ru as 5 wt.% Ru/Al₂O₃, 1 ml water as solvent. T=250 °C, t=2 h, P_{H2}=580 psi. [a] guaiacol 1 mmol. [b]guaiacol 0.9 mmol, glucose 0.1 mmol.

In addition to the conversion of guaiacol, effects of sugars on the HDO conversion of several lignin dimers, which contain typical ether linkages of lignin and are usually generated during lignin HDO, were further explored to provide more fundamental insights in sugar effects on lignin HDO. Since β -O-4, α -O-4, 4-O-5 bonds are the most abundant C-O-C bonds in lignin linkages, diphenyl ether (DPE), benzyl phenyl ether (BPE), and veratrylglycero- β -guaiacyl ether (VGE) (Table 2) were chosen to represent aryl-O-aryl (4–O–5), aryl-O-benzyl (α-O-4), and aryl-Oalkyl (β-O-4) linkages, respectively, to test effects of sugars on the breakage of a wide range of C-O-C bonds under lignin HDO conversion conditions. These model compounds cover various C-O bond strengths in lignin, typically with bond dissociation enthalpy (BDE): $4-O-5 > \alpha - O-4 > \beta - O-4$. The conversion of these model compounds and the selectivity of their top five products are listed in Table 2.

As shown in Table 2, HDO conversion of DPE was 56.3% and the yield of aromatic ring hydrogenated products was 24%. The moderate conversion of DPE under the carried reaction conditions was probably due to the high bond dissociation enthalpy of 4–O–5 ether bond. DPE conversion dropped to about 37% when 10 mol% glucose was added. At the meantime, the selectivity of aromatic ring hydrogenated products significantly decreased. Since α –O-4 ether bond has a relatively low bond

dissociation enthalpy, complete conversion of BPE was achieved when no sugar was added. However, when 10 mol% of glucose was added, the conversion of BPE decreased to about 85%. The addition of glucose also changed the product distribution of BPE HDO conversion. The selectivity of incomplete hydrogenated products (aromatics) significantly increased to 88% from 34% when glucose was added. Similar results were obtained from HDO conversion of VGE with β-O-4 structure, the most prevalent ether bond in lignin interlinkages. The existence of glucose not only decreased the VGE conversion but also lowered the selectivities of deoxygenated and fully hydrogenated products. Results obtained from HDO conversion of lignin dimers with glucose were consistent with those obtained from HDO conversion of guaiacol, revealing that sugars affected the hydrogenolysis and hydrogenation activities of the catalysis system.

In addition, effects of sugars (glucose or xylose) on HDO conversion of technical lignin were investigated. The conversion of lignin and the total yield of products are depicted in Figure 1(a). The generated GC-MS detectable products are shown in Figure 1(b). Results showed that the addition of 10 wt% sugars (either glucose or xylose) obviously hindered HDO conversion of lignin, and they showed greater effects on lignin than on lignin model compounds. Compared to the conversion of lignin model

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compounds, the conversion of technical lignin decreased more rapidly after sugars were added. The macromolecular form of technical lignin that is disadvantageous in the competitive adsorption on the metal catalyst can be the primary cause for the loss in hydrocarbons yield from HDO of technical lignin although several factors, including reactant structure, solvents, or the decreased ratio of catalyst to reactant, can be responsible. Furthermore, xylose was more inhibitory than glucose in terms of decreasing hydrocarbon yield. Xylose and glucose lowered the final hydrocarbon yield by 78% and 63%, respectively. Moreover, we found the color of the ethyl acetate extraction solution with the addition of sugar was quite different from that without sugar, as shown in Figure 1(c). The ethyl acetate extraction solution of products from lignin without adding sugars appeared faint yellow. On the contrary, with the addition of sugars, the ethyl acetate extraction solution of products turned brownish black. This is probably due to the production of humins from the added sugars under the reaction conditions. Humins can also absorb on the catalyst surface and thus decrease its catalytic activities.



 $\label{eq:Figure 1. Effects of sugars on lignin HDO conversion. Reaction conditions: 0.1 mmol In(OTf)_3, 0.05 mmol Ru as 5 wt.% Ru/Al_2O_3, 1.2 ml water as solvents. T=250 °C, t=4 h, P_{H2}=580 psi. A: 100 mg lignin; B: 90 mg lignin + 10 mg glucose; C: 90 mg lignin + 10 mg xylose.$

Based on the obtained results, potential mechanism of effects of carbohydrates and their derivatives on lignin conversion over catalysis of Ru/Al₂O₃ is proposed and depicted in Scheme 1. Furan-based compounds, including 5-HMF and furfural generated from carbohydrates through depolymerization and dehydration, competitively adsorb on the Ru metal particles with lignin, and thus prevent lignin from hydrogenolysis depolymerization. The adsorption of furan-based compounds on Ru also hinders HDO conversion of depolymerized lignin intermediates. Moreover, humins formed from the polymerization of furan-based compounds and other carbohydrate derivative products plausibly cover the Ru particle surface and thus deactivate the metal catalyst.





Figure 2. The calculated adsorption energies (E_{ads}) of molecules on Ru (0001) surface (a) and adsorption geometries of 5-HMF; (b) and phenol; (c) on Ru (0001) surface.

To prove the proposed mechanism (Scheme 1), we performed first-principles density functional theory (DFT) calculations on molecules produced from carbohydrates (furfural, 5-HMF, Levulinic acid) and from lignin (guaiacol, phenol, cresol) adsorption on Ru (0001) surface. The obtained adsorption energies (E_{ads}) of these molecules as well as two example adsorption configurations are shown in Figure 2. Results show that the calculated E_{ads} of molecules produced from carbohydrates are higher than those of molecules produced from lignin, which means phenol-based molecules produced from lignin have weaker interaction with Ru catalyst than those furanbased molecules produced from carbohydrates. When furanbased molecules co-exist as impurity with lignin, they competitively bind with catalysts thus reduce the interaction of phenol-based molecules with catalysts, preventing further depolymerization and HDO conversion of lignin as depicted in Scheme 1. Comparing Figure 2(b) with 2(c), results indicate that in furan-based molecules, mainly the O of carboxyl group binds with Ru (0001) surface while in phenol-based molecules, the C of benzene ring binds with Ru surface. The calculated bond-length of O-Ru in furan-based configurations is 0.1-0.2 Å shorter than those of C-Ru bonds in phenol-based adsorption systems. These results indicate that the active sites of Ru (0001) surface are competitively occupied by furan-based molecules, blocking the

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phenol-based molecules to bind with the catalyst surface. Such poisoning effects caused by furans and their derivatives suppress the lignin HDO conversion as observed in Figure 1.



Figure 3. Thermogravimetric analysis (TGA) of spent catalysts. 1: fresh Ru/Al₂O₃; 2: Ru/Al₂O₃ after reacting with guaiacol; 3: Ru/Al₂O₃ after reacting with furfural; 4: Ru/Al₂O₃ after reacting with HMF; 5: Ru/Al₂O₃ after reacting with glucose.

Furthermore, thermogravimetric analysis (TGA) of spent catalysts was carried out to determine the carbon deposition on Ru/Al₂O₃. These catalysts were collected from HDO reactions by using guaiacol, glucose, HMF, and furfural as reactants, separately, under identical HDO reaction conditions. The conversion of these compounds as well as the selectivity of products were also analyzed. The dehydration of glucose to HMF was quite slow, and the yield of HMF and its hydrogenated products (mainly bishydroxymethyl-tetrahydrofuran) was lower than 20%. Most of glucose was converted into sorbitol (with a yield of 47 %) under the reaction conditions. While, the formation of char from glucose is obviously higher than that from other reactants as indicated by TGA in Figure 3. Char or humins could be formed from glucose directly or from its dehydration intermediates. When HMF and furfural were used separately as reactants, the major products were found to be bishydroxymethyltetrahydrofuran (with a yield of 63%) and hydroxymethyltetrahydrofuran (with a yield of 76 %), respectively. The formation of char from HMF and furfural is lower than that from glucose but higher than that from guaiacol as shown in Figure 3. These results indicate that glucose, HMF, and furfural are more easily to form char or humins than guaiacol under the tested HDO reaction conditions. Char or humins from carbohydrates covers the metal surface of Ru/Al₂O₃ and deactivates the catalyst.

Conclusions

Valorization of biorefinery lignin-rich wastes improves the carbon efficiency of the entire process, thus is an attractive but challenging topic for economic biorefinery design. Sugars and their derivatives (e.g. HMF) co-exist as impurities with lignin in biorefinery lignin-rich wastes. Negative effects of these compounds on lignin HDO conversion were found in this study. They could hinder lignin from hydrogenolysis depolymerization as well as further prevent lignin depolymerized intermediates (monomers and dimers) from hydrogenation and deoxygenation conversion. Such mechanism was further validated by first-principles DFT calculations and thermogravimetric analysis of

spent catalysts. Compared with acidic catalyst $(In(OTf)_3)$, metal catalyst (Ru/Al_2O_3) was more sensitive to sugars. The generated furan-based products and humins from sugars are responsible for the negative effects since these products can competitively absorb on the metal surface of catalysts and block the absorption of lignin and its degraded intermediates. The findings of this study suggest that the development of lignin catalytic system should fully consider the influence of sugar impurities, and robust catalysts that are insensitive to sugars and their derivatives should be developed for effective lignin conversion.

Experimental Section

Chemicals and materials: All the chemicals used in this research are commercially available and used as received without any treatment. In(OTf)₄, glucose, xylose, HMF, cellulose (Avicel) were purchased from Sigma-Aldrich. Ru/Al₂O₃ (reduced) was purchased from Alfa Aesar. Lignin model compounds, including guaiacol, diphenyl ether, and benzyl phenyl ether, were purchased from Fisher Scientific. Lignin β -O-4 model compounds were purchased from GreenLignol, LLC. Lignin was obtained from National Renewable Energy Laboratory (NREL) via dilute alkali deacetylation and mechanical Refining (DMR) treatment. All other chemicals were purchased from Fisher Scientific.

Hydrodeoxygenation conversion of lignin model compounds and lignin: A specific amount of lignin or lignin model compounds, catalysts, and water (1 ml or 1.2 ml) with or without sugars addition were added to a 3 mL dry glass sleeve. The sleeve was placed into a high-throughput 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 pressured with 580 psi H₂ at room temperature. The reactor was heated to 250 °C and maintained for 2 or 4 hours depending on the substrate. The metal plate of the high-throughput reactor was shaking (shaking frequency: 200 r/min) during the reaction to improve the mass transfer. After each run, the reactor was cooled to room temperature to terminate reactions. The glass sleeve was removed from the high-throughput reactor and the liquids were separated from the solids by centrifugation (8000 r/min for 10 min). The liquid was extracted with 5 ml ethyl acetate. The solids were extracted with 3 mL ethyl acetate. The ethyl acetate extraction was combined and diluted in a 20-mL volumetric flask. Certain amount of vanillin and 3-methylheptane were added as internal standards for aromatics and hydrocarbons, respectively, in GC analysis.

Analysis of HDO products: The ethyl acetate diluted liquid samples were analysed by GC and GC-MS in an Agilent Technologies 7890A GC system with a DB-5 capillary column (30 m length × 250 μ m l.D. × 0.25 μ m film thickness, J&W Scientific) in the split-less mode. Typically, 1 μ l sample was injected with 0.6 ml min⁻¹ of He as the carrier gas into the GC system. The injection port temperature was set at 300 °C. The GC oven was programmed to 45 °C and maintained for 6 min. Then the temperature was raised at the rate of 10 °C/min until it reached 300 °C and maintained at 300 °C 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 using NIST libraries. For model compounds, the conversion of reactants and the selectivity of the products were calculated using the internal standard method based on the following formulas:

For the conversion of technical model compounds:

 $Conversion\% = \frac{Weight of reactant converted}{Weight of reactant added} \times 100\%$

$$\label{eq:Yield of hydrocarbon A\%} \begin{split} & \text{Yield of hydrocarbon A\%} = \frac{\text{Carbon atoms in hydrocarbon A}}{\text{Carbon atoms in hydrocarbon A}} \times 100\% \\ & \text{Selectivity of hydrocarbon A\%} = \frac{\text{Carbon atoms in hydrocarbon A}}{\text{Total carbon atoms in products}} \times 100\% \end{split}$$

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For technical lignin, the calculations of conversion was based on the weight change of lignin before and after HDO reaction. The yield of lignin HDO products was calculated by the effective carbon number (ECN) approach.^[31] 3-methylheptane was added as internal standard. The top 20 products were calculated to determine the total yield of HDO products.

For the conversion of technical lignin:

 $\frac{Conversion\%}{Weight of reactant converted} \times 100\%$

$$\label{eq:Yield of hydrocarbon A%} \begin{split} & \underline{\mathsf{Weight of hydrocarbon A produced}}_{Weight of reactant added} \times 100\% \end{split}$$

Total hydrocarbon yield= $\sum_{x=1}^{20}$ Yieldx

DFT Calculation details: The calculations performed in this work are based on first-principles DFT with plane-wave basis sets and pseudopotentials to describe the electron-ion interactions. The Vienna ab-initio simulation package (VASP, https://www.vasp.at) was employed to calculate molecules adsorption on Ru (0001) surface. In this study, all calculations were done using the PAW pseudo-potentials and the PBE exchange-correlation functional. The plane-wave basis sets were used with a plane-wave cutoff energy of 500 eV and a kinetic energy cutoff for augmentation charges of 644.9 eV. The 6x6 Ru (0001) surface was created from optimized Ru crystal with space group P63/mmc (#194). To reduce the calculation cost, a three-layer Ru (0001) surface slab (108 atoms) with 20 Å vacuum separation was used in our calculation. Compared to the model in ref. ^[22], our model has larger surface area to eliminate the unexpected interactions between adsorbed molecules due to the periodicity. During adsorption calculation, the bottom layer of Ru was fixed as bulk material. The molecules were introduced on the surface for adsorption. During calculations, the lattice dimension was fixed. Except for the bottom layer of Ru, all atoms in the supercell were relaxed to the equilibrium configurations. A 3x3x1 k-point sampling grids were applied in all adsorption calculations while for pure molecule systems a 4x4x4 k-point sampling grids were used. The valence electrons contain s and p orbitals for H, C and O atoms, s, p, and d orbitals for Ru atoms. The adsorption energy (Eads) is defined as Eads = (ERu(0001) + EMol) - ERu-Mol, where ERu-Mol, ERu(0001) and EMol are the DFT energies of the optimized molecule adsorbed on Ru (0001) surface slab, pure Ru (0001) surface slab, and the single molecule in 20x20x20 Å supercell, respectively.

HDO of guaiacol, glucose, furfural, HMF. HDO reactions using guaiacol, glucose, HMF, and furfural as reactants, separately, were conducted under identical HDO reaction conditions as listed in Table 1. In order to collect enough catalysts for TGA, the scale of these reactions was magnified 5 times and reacted in a 10 mL batch reactor (5 mmol reactant, 0.25 mmol ln(OTf)₃, 0.125 mmol Ru as 5 wt.% Ru/Al₂O₃, 5 ml water as solvent). The conversion of glucose, HMF, and furfural, and the selectivity of generated products were analyzed by HPLC following an external standard method.

Analysis of Spent catalysts: The spent catalysts were subjected to thermogravimetric analysis (TGA) to determine the carbon deposition after HDO reactions. All catalysts were collected after being reused for three times, and thoroughly washed by deionized water and then dried at 65 °C before TGA testing. TGA was conducted by a Setaram Setsys thermogravimetric analyser. The TG system was calibrated with calcium oxalate monohydrate for temperature readings prior to experiments. In each run, approximately 5 mg of spent Ru/Al₂O₃ catalysts were put in an alumina crucible, and then the following experimental procedure was used: (a) the TGA system was purged with N₂ for 10 min and then the furnace temperature was increased from room temperature to 30 °C with the heating rate of 1 °C min⁻¹; (b) the temperature of 800 °C with a heating rate of

10 °C min⁻¹ under the same atmosphere; (c) when it reached the final temperature, the run was stopped and the temperature of the furnace was decreased to room temperature. The blank experiments were conducted following the exact same procedure as above using empty crucible to compensate for the output drift of the thermobalance, respectively. All of these experiments were duplicated.

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Keywords: Lignin • Hydrodeoxygenation • impurities • Hydrocarbons• furan compounds

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Entry for the Table of Contents

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Effects of impurities on hydrodeoxygenation (HDO) of lignin to hydrocarbons: Valorization of biorefinery lignin-rich wastes is challenging but necessary for an economical process. This study revealed that sugars, furans, and their derivatives as "impurities" in such wastes could suppress metal catalysts and inhibit lignin depolymerization and HDO reactions thus decrease yields of jet fuel range hydrocarbons from biomass-derived lignin.



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