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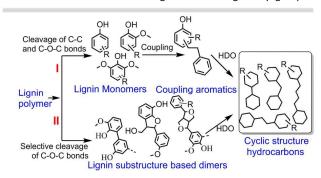# Biomass-derived Lignin to Jet Fuel Range Hydrocarbons via Aqueous Phase Hydrodeoxygenation

Hongliang Wang,[a] Hao Ruan,[a] Haisheng Pei,[a] Huamin Wang,[b] Xiaowen Chen,[c] Melvin P. Tucker,[c] John R. Cort,*[b] and Bin Yang*[a]

A catalytic process, involving the hydrodeoxygenation (HDO) of the dilute alkali extracted corn stover lignin catalysed by noble metal catalyst (Ru/Al$_2$O$_3$) and acidic zeolite (H$^+$-Y), to produce lignin-substructure-based hydrocarbons (C$_7$-C$_{18}$), primarily C$_{12}$-C$_{18}$ cyclic structure hydrocarbons in the jet fuel range, was demonstrated.

Lignin, a main constituent of lignocellulosic biomass (15-30% by weight, 40% by energy), has a great potential in advanced biofuel production in view of its inherent phenylpropane-based structure.[1] The current vision of biorefineries undervalues lignin's potential to address the world's high quality liquid fuel requirements.[2] Despite the potential, selective conversion of lignin has proven to be challenging, mainly due to the heterogeneous, non-hydrolyzable cross-linked structure of lignin and the high reactivity of its degradation intermediates.[3] Several catalytic upgrading routes,[3b, 4] especially hydrodeoxygenation (HDO),[5] have been extensively studied with the aim of producing fuel range hydrocarbons. Sulfided CoMo and NiMo-based catalysts,[6] as well as various supported metal catalysts, such as Pt, Pd, Re, Rh, or Ru based catalysts,[7] were previously used for lignin HDO conversion. Most HDO processes are accompanied by cleavages of both C-O-C and aliphatic C-C bonds in lignin, which result in depolymerizing lignin to monomers that generally contain 6-9 carbon atoms, which have a moderate value in fuel usage.[4a, 8] Although long chain hydrocarbons could be generated via coupling reactions of lignin-degraded monomers (Scheme 1, route I),[9] it requires additional specific catalysts and processes that increase costs. In the process described here, long chain hydrocarbons were produced by maintaining the aliphatic C-C linkages but cleaving ether C-O linkages during HDO, using model compounds as starting m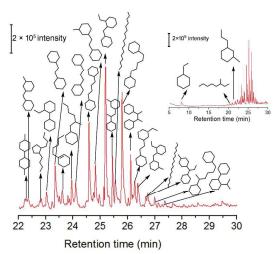aterials.[9b,10] Less effort has been focused on the direct transformation of lignin-degraded oligomers, and dimers to long chain hydrocarbons although these components represent a large portion of lignin-derived intermediates. The predominant linkage between monomers in lignin is the C-O-C bond, which constitutes around two-thirds to three-quarters of the total linkages. Generally, C-O-C bonds have lower bond dissociation energy (~ 218–314 kJ mol^{-1}) than that of C-C single bonds (~ 384 kJ mol^{-1})[11]. Therefore, it is conceptually possible to selectively cleave C-O-C bonds in lignin without disrupting the C-C linkages under controlled reaction conditions. It was calculated that 30%~69% of lignin would be released as dimers if C-O-C linkages in lignin were selectively cleaved without disrupting C-C bonds.[9d, 12] HDO of these lignin substructure-based dimers can directly generate hydrocarbons in the jet fuel range from biomass (Scheme 1, route II).

In this study, the conversion of dilute alkali extracted corn stover lignin into hydrocarbons with carbon numbers in the range of 7~18 was achieved. A remarkable outcome of this approach is the generation of relatively long chain alkyl cyclohexanes by retaining lignin substructures (e.g. dimers) and coupling of lignin-derived monomers and smaller fragments including methyl groups.

Scheme 1 Proposed routes of depolymerization and Hydrodeoxygenation of biomass-derived lignin to cyclic structure hydrocarbons

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Fig. 1 Product distribution of alkali lignin treated under HDO conditions with Ru/Al$_2$O$_3$ and solid acid zeolite (H$^+$-Y) at 250 °C. Each peak was identified from the GC-MS library and peak areas were used to quantify the products. Reaction conditions: alkali lignin 100 mg, solid acid zeolite 300 mg, Ru/Al$_2$O$_3$ 300 mg, water 30 mL, P$_{H2}$ 4MPa, 4 h, 250 °C.

The NREL dilute alkali extracted corn stover lignin was generated from a pilot-scale dilute alkali deacetylation process.[13] It's compositions and subsequent purification methods are described in the supporting information section. A high catalyst loading approach was applied in the heterogeneous solid-solid catalytic HDO of lignin reactions in order to minimize mass transfer limits.[5a, 9b, 13b, 14] In a typical reaction, 100 mg lignin, 300 mg acid zeolite (H$^+$-Y), 300 mg Ru/Al$_2$O$_3$, and 30 mL water were added into a 100 mL Parr reactor and reacted at 250 °C under 4 MPa H$_2$ for 4 hours. After completion of the reaction, catalysts, together with the solid residues, were separated from the liquid phase by centrifugation and the organic products were extracted using ethyl acetate and were characterized using gas chromatography-mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR).

More than 80 lignin HDO products were detected by GC-MS (Fig. 1). Among these products, the most significant 23~25 hydrocarbons were identified and quantified using *n*-decane as an internal

standard. These products accounted for more than 50% of the total integrated GC peak area for all the detected products derived from lignin. The reaction products were found in three general groups: aromatics, alkyl cyclohexanes, and linear alkanes. They can also be divided into three different groups according to their carbon atom numbers：C$_6$~C$_{11}$，C$_{12}$~C$_{18}$，and C$_{>18}$.

As shown in Figure 1 and Table 1 (entry 1), the products catalysed by Ru/Al$_2$O$_3$ and H$^+$-Y zeolite catalysts were mainly alkyl cyclohexanes with carbon numbers ranging from 12 to 18. A small fraction of aromatics and ring-opening products were also detected. The total yield of the top 23~25 products was calculated to be 21.8 %, with the distributions of C$_{12}$~C$_{18}$ and alkyl cyclohexanes being 84.6 % and 89.8 %, respectively. NMR spectroscopy confirmed that the predominant class of lignin substructure in the product mixture was alkyl cyclohexanes (Figure S1). In recent years, various supported noble metals and their alloys were widely used in aqueous phase reactions as effective non-sulfide-based HDO catalysts for conversion of lignin based model phenolic substrates to hydrocarbons. [9b, 10] However, our results show the existence of characteristic structural features of biomass-derived lignin hydrocarbons in C$_7$–C$_{18}$ jet fuel range through HDO conversion process.

Two control experiments were carried out under identical HDO conditions while using the Ru/Al$_2$O$_3$ and H$^+$-Y acidic zeolite catalysts separately. Results showed that lignin conversion and the total product yield were relatively low (not exceeding 52% and 15%, respectively) when both catalysts were applied individually (Table 1). The lignin conversion with H$^+$-Y acidic zeolite was higher (52%) than that found with Ru/Al$_2$O$_3$ (31%), showing that H$^+$-Y acidic zeolite was more efficient at depolymerizing the lignin polymer. The products were also found to be different. The major products resulting from catalysis with Ru/Al$_2$O$_3$ and acidic zeolite alone were found to be monocyclic alkyl cyclohexanes and phenols, respectively. These results clearly demonstrated that the combined effects of Ru/Al$_2$O$_3$ and acidic zeolite enabled the conversion of the alkali lignin to higher carbon number cyclohexanes in high yield. Zeolite possesses high concentration of active acid sites, thus could

Table 1. Hydrodeoxygenation of the alkali lignin under various conditions ^{a}

Entry	Catalyst (mg)	Reaction Temperature (^{o}C)	Lignin Conversion (%)	Product distribution (wt. %)						Total Yield (wt.%) ^{c}
				By carbon numbers			By chemical structure			
				C$_{6-11}$	C$_{12}$-C$_{18}$	C$_{>18}$	Aromatics	Alkyl-cyclohexane	Non-cycle alkanes	
1	Ru/Al$_2$O$_3$+zeolite	250	81.03	10.48	84.60	4.92	4.03	89.79	6.18	21.83
2	Ru/Al$_2$O$_3$	250	30.84	63.66	31.76	4.58	9.61	79.10	11.29	9.83
3^b	zeolites	250	52.11	34.08	46.57	19.35	90.17	2.02	7.81	13.66
4	Ru/Al$_2$O$_3$+zeolite	200	45.98	27.85	65.47	6.68	16.64	76.00	7.36	10.64
5	Ru/Al$_2$O$_3$+zeolite	220	67.56	23.04	75.01	1.95	5.72	91.18	3.10	13.29
6	Ru/Al$_2$O$_3$+zeolite	280	92.73	3.31	70.41	26.28	0.63	72.84	26.53	12.25

^{a} Reaction conditions: alkali lignin100 mg, solid acid zeolite (H$^+$-Y) 300 mg, Ru/Al$_2$O$_3$ 300 mg, water 30mL, P$_{H2}$ 4MPa, 4 h, T=250 °C. ^{b} The main products were found to be phenols with high oxygen content. ^{c} Refers to the total yield of the top 23~25 products.

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not only effectively depolymerize lignin into monomers and dimers via hydrolysis of the C-O-C bonds, but also could couple the monomers into dimers via alkylation or dimerization reactions.[9a] Ruthenium-based catalysts, together with acidic zeolites, showed promising synergistic activity and efficiency in the hydrodeoxygenation reactions consistent with the conversion of the monomer and dimer intermediates of lignin into cyclohexanes via complete removal of oxygen groups and hydrogenation of the aromatic rings observed in this study. [9a, 15]

The molecular weight distribution of the alkali lignin was calculated from the gel permeation chromatography (GPC) curves based on pre-calibration with polystyrene standards. The alkali lignin had a relatively broad MW distribution with apparent estimated weight average ($\bar{M}w$) and number average ($\bar{M}n$) molecular weights centered at 2590 Da and 1410 Da, respectively, which were lower than that of ball-milled corn stover lignin (typically >3850 Da).[16] The corresponding polydispersity value ($\bar{M}w/\bar{M}n$) of the alkali lignin was also found higher (1.84) than that of ball-milled lignin (1.03) [13b, 17]

Two-dimensional heteronuclear single quantum coherence (2-D^{1}H-^{13}C HSQC) NMR was used to elucidate the compositions and structure of the alkali lignin, including different aromatic units and inter-unit linkages (see supporting material Fig. S2). Results showed the conservation of native mono-lignol components (G and S) with abundance of cinnamyl alcohol end groups in the alkali lignin. The ratios of the three aromatic units and the percentages of their inter-unit linkages were calculated from the relative peak areas[18] (Table S2). Both the ball-milled lignin and alkali lignin were mainly composed of S and G subunits, accounting for nearly 90% of the total subunits found by NMR. However, the percentage of β-O-4 linkages in alkali lignin (43%) was lower than that in the ball-milled lignin (58%), suggesting some β-O-4 linkages were cleaved during the lignin extraction and purification processes. On the other hand, β-5 linkages in the alkali lignin (44%) were found to be much higher than that in ball-milled lignin (27%), indicating most of C-C bonds remained stable.

The reactivity and structural features of alkali lignin could be considered as one of the key factors for selective production of the obtained C_{12}-C_{18} cyclohexanes.[9d, 13b] The β-5 structures in the alkali lignin implied that dimers with C-C bond linkages could be released after all the C-O-C bonds in lignin are cleaved, and then be ready to be transformed into higher carbon number cycloalkanes that retain some characteristics of the substructures of the original alkali lignin. For example, 5-5' substructure of lignin can result in bi(cyclohexane) derivative products; β-5 and β-1 substructures can be converted into 1,2-dicyclohexylethane analogues; β-β substructures can form 1,4-dicyclohexylbutane. All these products were found in the reaction shown in Figure 1.

To test this hypothesis, the mechanism of the HDO reaction was explored using several lignin model compounds chosen to represent C-C bonds (Table 2, entries 1–3) under the similar reaction conditions to the alkali-extracted lignin. Results showed high selectivity (95.5%) for aromatic ring hydrogenation of 1,2-diphenylethane to give the saturated product 1,2-dicyclohexylethane with no C-C bond cleavage (Table 2, entry 1). Bicyclohexane was detected as a minor product (3.4%), indicating

Table 2. Hydrodeoxygenation of lignin model compounds.[a]

Entry	Sub.	Conv.(%)	Selectivity (%)					
1		>99.0	95.5	3.40	0.40	0.40	0.20	0.01
2		>99.0	83.00	5.00	5.00	3.00	3.00	1.00
3		>98.0	51.13	0.52	12.91	5.18	3.70	2.50
4		>98.0	20.35	15.56	13.20	12.86	5.33	4.36

[a] Reaction conditions: model compound 100 mg, solid acid zeolite (H$^+$-Y) 300 mg, Ru/Al$_2$O$_3$:300 mg, water 30mL, P_{H2}:4 MPa, t=4 h, T=250 °C

that a small amount of rearrangement and C-C bond cleavage occurred during the reaction. In addition, the total yield of all the ring-opening products was approximately 1%, indicating the C-C bonds in aromatic rings were less susceptible to cleavage. 2,2'-biphenol, representing the 5-5' aryl-aryl linkages in lignin, was also used as a substrate in the reaction. After HDO reaction, it was found that not only the aromatic rings were saturated but also the hydroxyl groups on the rings had been removed. The substrate was converted to a bicyclohexane with high selectivity (83%). It further demonstrates that the carbon skeleton structure of the starting material could be preserved during the HDO catalysis process. Results showed that HDO of dehydrodi-isoeugenol (Table 2, entries 3), which resembles phenylcoumaran linkages (β-5 linkage), led to cleavage of C-O-C bonds, hydrogenation of aromatic rings and removal of oxygen-containing groups, while leaving C-C bonds mostly intact.

The alkali lignin with lower molecular weight and higher ratios of condensed structures (e.g. β-5) showed the tendency toward the formation of higher carbon number alkyl cyclohexanes. Some of the products, such as 1,5-dicyclohexylpentane and other cyclopentane derivatives, did not have similar structures like the lignin-derived dimers, implying that these products were not directly derived from lignin substructures but required rearrangement, coupling, or insertion reactions that presumably involved C-C bond formation and cleavage. Guaicyl-(4-O-methyl)-beta-guiacylether (Table 2 entry 4) represents the key features of β-O-4 linkages encountered in lignin. Its HDO products were much more complicated, including various dicyclohexylalkanes and alkyl cyclohexanes. Almost all the β-O-4 bonds were found cleaved after the reaction, suggesting that this catalytic system could effectively break alkyl-aryl ether bonds. More importantly, it was discovered that the majority of the products were bicyclohexanes, which indicated that the coupling of the monomers released from the cleavage of β-O-4 bonds occurred.

Results obtained from HDO of alkali lignin and model compounds provided more insights in the lignin HDO process. First, the most types of C-O-C bonds, especially the β-O-4 bond, were

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cleaved effectively either by hydrogenolysis over Ru/Al_2O_3 catalysis or by zeolite H^+-Y hydrolysis, and the bulk lignin polymer structure was fragmented into lignin substructures based aromatic monomers and dimers. Then, these monomers and dimers could undergo dehydration, demethoxylation, and hydrogenation reactions to remove oxygen and saturate the aromatic ring. During the oxygen removal and aromatic ring hydrogenation reactions, most of the C-C bonds remained stable and the carbon skeleton structures of these products were largely unchanged. Moreover, some of the monomers coupled to form dimers and some methylation occurred presumably by methyl groups derived from HDO of aryl methyl ethers. Thus, products obtained from HDO of lignin were mainly alkyl cyclohexanes with 12~18 carbon atoms.

The resulting solid products residues were collected and analysed by 2-D HSQC NMR after dissolution in a DMSO solvent (Figure S3). The ^1H and ^{13}C chemical shifts suggest that the material is a saturated aliphatic hydrocarbon similar to the oil products although it is probably solid and insoluble in ethyl acetate due to polymerization. Additionally, the effects of reaction temperature on alkali lignin conversion and product distribution were studied. As shown in Table 1, the conversion of lignin was low at 200 °C, and a relatively high portion of aromatics with carbon number ranging from 6~12 was found in the oil products. Increasing the reaction temperature significantly improved the lignin conversion. Meanwhile, aromatic products, such as cresol and guaiacol, were decreased and more cyclohexane derivatives with carbon number between 12~18 were formed. However, the total calculated yield of the products was found to decrease when the temperature was raised to 280 °C. Meanwhile, more ring-opened products, mainly linear alkanes, were detected at the higher reaction temperature (280 °C). In order to better monitor the reaction, gases were collected and analysed after the reaction. The main gas products detected were CH_4, CO and CO_2. The total yield of these products at 250 °C was about 3.7 wt.%, and it increased significantly to 7.4 wt.% when the reaction temperature increased to 280 °C, indicating that higher reaction temperatures could promote C-C bond hydrogenolysis reactions, thus resulting in low molecular weight products. The carbon balance was calculated after analysing carbon contents in oil, aqueous, solid and gas phases (Table S3). The change of product distribution with reaction time was investigated (Figure S5). Results suggested that C_{12}~C_{18} cycloalkanes were the dominant products at all stages of the HDO reactions.

Conclusions

Our results showed that characteristic structural features of biomass-derived lignin permit conversion to C_7–C_{18} jet fuel range hydrocarbons through catalysis by noble metal catalyst (Ru/Al_2O_3) and acidic zeolite (H^+-Y). The H^+-Y type of zeolites that possess large-pore structure and contain high concentrations of active acid sites could effectively disrupt the lignin polymer into oligomers via selectively cleaving C-O-C bonds. Lignin deconstruction can also be partially done on the metal catalyst. Ruthenium-supported Al_2O_3, together with the H^+-Y zeolite, showed promising activity and high efficiency in HDO reactions, which could not only have a synergistic effect on oxygen removal from lignin-degraded intermediates, but also could couple the monomers into dimers via alkylation or

dimerization reactions to produce a wide variety of alkyl cyclohexane species that are commonly found in jet fuel blend stocks. An advantage of this approach is that the carbon chain substructures of lignin can be largely retained and new C-C bonds can be also generated. Therefore, lignin-substructure-based C_{12}-C_{18} cyclohexanes are plausibly generated through the cleavage of C–O–C bonds without disrupting the C–C linkages (β–β', β–5' and 5'–5'') in the lignin structure and/or through coupling reactions of degraded lignin monomer. The overall carbon yield was 38.3% (Table S2). In addition, NMR spectroscopy revealed distributions of aliphatic hydrocarbons rather than aromatic lignin intermediate structures in solid residues after product separation, indicating the high efficiency of the HDO transformations.

Acknowledgements

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