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Supporting Information

This version of the ESI (uploaded 07/07/2016) replaces the original version, and updates Fig. S2.

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

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1 Material and methods

1.1 Alkali lignin extraction and purification

Corn stover was provided by Idaho National Laboratory, and was extracted at the National Renewable Energy Laboratory (NREL). Lignin was extracted from 100 kg corn stover using 1100 L of 0.1 mol·L^{-1} NaOH solution at 80 °C for 2 h while being stirred at 30 rpm in a 2000 L horizontal paddle mixer (Eirich, Inc. Gurnee, IL, USA). After extraction, the solids were separated from the liquid by two filter screens (2 mm wire spacing) located in bottom ports of the mixer tank.[1] The crude lignin slurry from the drained dilute alkali extract was precipitated by adding sulfuric acid to bring the pH to 3 and separated from the liquid by centrifugation using the Western States model Q-80 centrifuge. The slurry was then sent to WSU while stored at 4 °C. Upon arrival, 0.1 mol·L^{-1} NaOH solution was added to the filtrate liquor to adjust pH to pH 12. Then 10 wt.% sulfuric acid was added to adjust to pH 3 to precipitate lignin. It was then centrifuged at 10000 g·min^{-1} for 5 min. After disposing of the supernatant, the precipitate was washed with 70 °C DI water followed by centrifugation at 10000 g·min^{-1} for 5 min. The final precipitated technical lignin was freeze-dried and stored at -20 °C before experiments.[2]

1.2 Lignin purity analysis

Lignin purity analysis was conducted based on the procedure developed by Kenji Iiyama et al.[3] 1-2 mg of lignin was dissolved in 2.5 ml of 25 wt.% acetyl bromide (AcBr) in acetic acid solution in a 15 ml vial. The vial was then sealed with a PTFE-coated silicone cap and put in an oven at 70±0.2 °C for 30 min. The vial was shaken every 10 min to improve diffusion. After that, the mixture was cooled and then transferred to a 50 mL volumetric flask, where 2.5 mL of 2 mol·L^{-1} NaOH solution and 0.5 mL of 7.5 mol·L^{-1} $NH_2OH·HCl$ solution were added to the flask. The mixture solution was then diluted to 50 mL with acetic acid. The purity was determined through UV absorption spectrum. The absorptions of the solutions at 280 nm against a blank control without lignin sample were recorded and analyzed using the equation of Morrison as following:

$$\text{Lignin (\%)} = 3.37 \times \text{absorbance/sample concentration (g·L}^{-1}\text{)} - 1.05$$

1.3 Two dimensional (2-D) HSQC NMR spectroscopic analysis of alkali lignin

2-D ^{1}H-^{13}C heteronuclear single quantum coherence (HSQC) NMR was used to characterize the chemical features of the technical lignin and HDO products. Samples of around 50 mg of both the technical lignin and isolated products were individually dissolved in DMSO- d6 (0.75 mL) for NMR spectroscopic studies. The experiments to characterize the compositions of the original technical lignin were conducted on a Varian VNMRS 600 spectrometer equipped with both Varian dual broad band (1-D) and HCN (2-D) probes. Pulsed field gradient coherence selection was used to acquire the 2-D HSQC NMR spectra. The use of spectral editing also allowed for discrimination of methyl and methane signals from methylene signals. 6250 Hz was used for ^{1}H dimensions while 24125 Hz was used for ^{13}C dimensions. The acquisition time is set as 0.199 s for direct observation dimension and 0.0066 s for indirect dimension. And 48 scans were taken per increment. A one-bond ^{1}H–^{13}C J coupling of 150 Hz was used and a total of 2 × 160 increments in t1 were acquired using the gradient echo–anti-echo selection technique for pure phase line shape in F1. The FIDs were zero-filled once to 2048 points in t 2, apodized with a Gaussian function prior to Fourier transformation. Data in t1 were extended by a factor of 2 with linear prediction followed by zero filling to 2 K points, apodizing with a Gaussian function and Fourier transformation.

Experiments to characterize product mixtures were conducted on a Varian Inova 500 equipped with a Nalorac z-axis pulsed-field gradient triple-resonance HCNP probe. 600 µL deuterated DMSO (Cambridge Isotope Laboratories) was used as the solvent. The resulting liquid sample was placed in 5 mm Wilmad 535-PP NMR tubes. NMR spectra were collected at 25° C. Samples contained 0.05% (v/v) TMS for chemical shift referencing. Separate HSQC spectra of the aliphatic and aromatic regions were collected using the BioPack gChsqc pulse sequence, with ^{1}H spectral width of 17 ppm and ^{13}C spectral widths of 120 or 60 ppm for the aliphatic and aromatic regions, respectively. Spectra were collected with 1024 points (Varian parameter np) and 51 ms acquisition time with 128 or 256 transients and 128 or 96 complex points in the indirect dimension, for aliphatic and aromatic spectra, respectively. Adiabatic WURST decoupling was applied during acquisition. Delay times t_{CH} and lambda for $1/4*J_{CH}$, were 1.8 ms and 1.6 ms for aliphatic spectra, and 1.45 ms and 1.3 ms for aromatic spectra, respectively. Reference one-dimensional ^1H spectra were collected with 32k points and 128 transients. HSQC spectra were processed and analyzed with Felix 2007 (FelixNMR, Inc) or MestreNova 6.0.4 (Mestrelab Research), with matched cosine-bell apodization and sine-bell squared apodization in the indirect dimension, 2X zero filling in both dimensions, and forward linear prediction of 30% more points in the indirect dimension. One-dimensional ^1H spectra were processed with no apodization or linear prediction and 2X zero filling.

1.4 Gel permeation chromatography and molecular weight calculation

The technical lignin samples were acetylated to enable dissolution in tetra-hydrofuran (THF) for GPC analysis. The acetylation was conducted by stirring the lignin sample with 2 mL of acetic anhydride-pyridine (1/1, v/v) at room temperature for 24 hours. Then, the lignin samples were dissolved in THF and analyzed using an Agilent 1200 LC with UV detector. A 20 μL sample was injected after filtration through a 0.45 μm membrane filter. The GPC analysis was conducted through a 4-column sequence of Waters TM Styragel columns (HR0.5, HR2, HR4 and HR6) at 1.00 $mL \cdot min^{-1}$ flow rate. The UV detector was set to 280 nm. Polystyrene standards were used for calibration. Win GPC Unity software (Version 7.2.1, Polymer Standards Service USA, Inc.) was used to collect data and determine molecular weight profiles.[2]

1.5 HDO reaction in a Parr reactor

A 100 mL Parr reactor was used for HDO catalysis experiments. 30 mL of DI water was used as the solvent for reaction while certain amounts of the NREL purified lignin, Nobel-metal catalyst (Ru/Al_2O_3), and solid acid (H^+ Z-Y) were added into the reactor. After sealing the vessel, H_2 was used to flush out the air in the reactor for at least 3 times and then the reactor was pressurized to 4 MPa at room temperature. The reactor was then heated to reach the reaction temperature where the reaction time was started. After the various reaction times, the vessel was plunged into cold water to cool. The headspace gas was then exhausted and the volume was measured using water displacement method. A gas sample was extracted and analyzed by GC-MS for qualitative and quantitative analysis. Then 5 μL of *n*-decane was added in to the reactor as an internal standard. By mixing the internal standard with the reaction liquids within the reactor using the stirring motor, the loss of liquid during transferring was measured. After mixing, 30 mL of ethyl acetate was injected and used to wash the interior of the reactor including the reactor headplate. Then all the liquid phase and solid residues were transferred into a centrifuge tube. By mixing the two phases, the products were extracted into the organic phase. Then a sample was acquired from the organic phase for GC/MS analysis. For GC/MS analysis, the response factor for each product was standardized with the use of efficient carbon number (ECN) [4] which enabled the calculation of compounds without pure standards. Lignin conversion, the mass yield of each product and the selectivity were calculated as following:

Lignin conversion=

$$\frac{Carbon\ content\ in\ original\ lignin - carbon\ content\ in\ residue\ solid}{Carbon\ content\ in\ original\ lignin} \times 100\%$$

Model compound conversion=

$$\frac{Weight\ of\ initial\ model\ compounds - weight\ of\ remaining\ model\ compounds}{Weight\ of\ initial\ model\ compounds} \times 100\%$$

$$Yieldx\ (wt.\%) = \frac{\frac{Mass\ \ of\ decane}{142} \times \frac{areax/\ ECNx}{area\ of decane/\ 10} \times MWx}{Mass\ lignin}$$

$$\text{Selectivity}_x = \frac{Yieldx}{Yield\ of\ total\ caculated\ products} \times 100\%$$

$$Toal\ product\ yield = \sum_{1}^{n} Yieldx_n$$

$$n = \ 23{\sim}25\ (for\ technical\ lignin)$$

$$n = \ 6\ (for\ \ lignin\ model\ compounds)$$

1.6 GC-MS analysis

After ethyl acetate extraction, the organic phase was analyzed by GC-MS. 1 μL of sample was injected with 0.6 $\text{mL}\cdot\text{min}^{-1}$ of He (carrier gas) into a DB-5 (30 m length × 250 μm I.D. × 0.25 μm film thickness, J&W Scientific) capillary column installed in an Agilent Technologies 7890A GC that was set at splitless mode. The GC oven was set to maintain 45°C for 2 min, then heated to 200 °C at the rate of 15 °C per min then held at 200 °C for another 1 min. After that, the oven was heated up to 300 °C at the rate of 10 °C per min and held for 5 min. Eluting compounds were determined using a MS (Agilent Technologies 5975C) inter XL EI/CI MSD with a triple axis detector, and matched to NIST GC-MS libraries.[2]

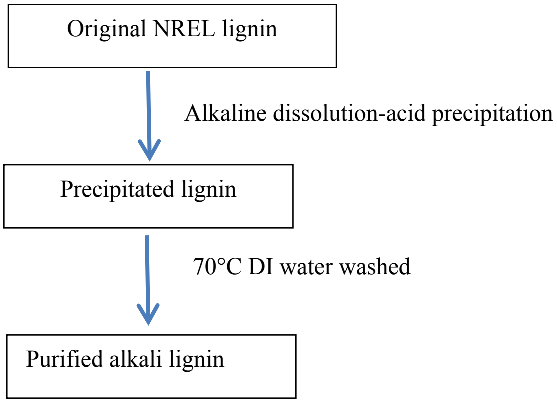
1.7 Total carbon analysis

A Shimadzu TOC-V Analyzer was used for the quantification of the total carbon content of NREL alkali extracted lignin, solid residues, and the HDO reaction products. After extraction, oil phase products were obtained after removing the ethyl acetate solvent by vacuum rotary evaporation at 50 °C. The aqueous phase was freeze-dried and analyzed with TOC analyzer. The solids were washed with hot DI water and dried, before analyzing using the TOC analyzer.

2 Additional results

2.1 Technical lignin purification

The original NREL lignin contains carbohydrates, including 20.66% glucose and 11.19% xylose as shown in Table S1. In order to avoid the influence of carbohydrates during the HDO process, the original NREL lignin was first dissolved in 0.1M NaOH solution and then was precipitated by titrating with sulfuric acid to pH 3. Then the precipitated lignin was washed with 40°C DI water as shown in Scheme.S1. Through alkaline dissolution-acid precipitation treatment, the carbohydrate content in the lignin samples were dramatically decreased to 2.28 % glucose and 3.31% xylose. In order to thoroughly remove carbohydrates, protein and inorganic salts, the precipitated lignin was further washed with 70°C DI water. Thus, the amount of carbohydrates was further decreased to lower than 2 wt.%. Through purification, the purity of NREL lignin was significantly increased from 60.00 % of the original NREL lignin A to 81.24 % of the final technical lignin C (Scheme S1).



Scheme S1 The schematic of purification process for NREL alkali lignin

Two lignin purity analytic methods were compared, including UV analytic method (see section 1.2) and Klason lignin method (NREL LAP "Determination of structural carbohydrates and lignin in biomass [5]"). There was no obvious difference found between these two methods, and the final purity of hot DI water washed lignin reached to approximately 81%.

Table S1 Compositions of lignin samples

Sample	Glucose %	Xylose%	Galactose%	Arabinose%	K-lignin%	ash%
Original NREL lignin	20.66	11.19	1.48	2.81	60.00±0.37	11.23±0.72
Purified alkali lignin	0.51	0.44	0.25	0.36	81.24±0.24	15.67±0.28

2.2 HDO products in ethyl acetate phase characterized by NMR

After ethyl acetate extraction, the ethyl acetate oil phase was dried under vacuum and then dissolved in DMSO-d6. The most prominent peaks found in the 2-D ^1H-^{13}C HSQC spectra are consistent with monoalkylated cylcohexane species. Correlations in HMBC spectra confirmed these assignments. A number of weaker aromatic resonance peaks as well as an Ar-OCH_3 peak were observed, but aside from the methyl groups these did not coincide with the starting lignin, indicating that some modification occurred.

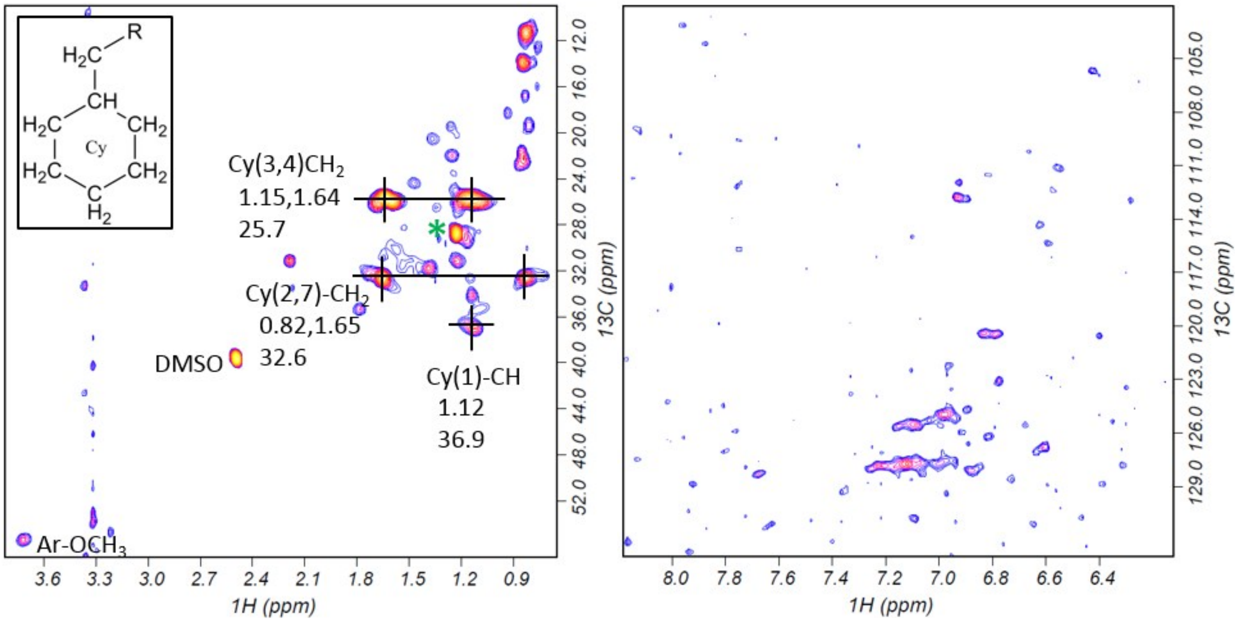


Fig. S1. HSQC spectra (left aliphatic region, right aromatic region) of ethyl acetate oil phase in DMSO.

2.3 Alkali lignin characterization by NMR

Lignin compositions and structure, including different aromatic units and their inter-unit linkages, were determined by two dimensional heteronuclear single quantum coherence (2-D-HSQC) NMR. Generally, ^{1}H-^{13}C HSQC spectrum of lignin can be divided into three regions: aliphatic, aliphatic oxygenated and aromatic regions, as shown in Fig. S2 a, and the latter two regions are of particular importance for lignin structure analysis. Information on lignin side chains， including structural types and distribution of inter-unit bonding patterns, can be found in the aliphatic oxygenated region.[6] The aromatic region can indicate the compositions of aromatic units and differences in the *p*-hydroxyphenyl : guaiacyl : syringyl (H :G: S) distributions in the lignin. As shown in Fig. S2 b, mainly four inter-unit linkages of the technical lignin, including β-ether (β-O-4) units A, phenylcoumaran (β-5) units B, resinol (β-β) units C, and spirodienone (β-1) units D, could be readily assigned and quantified by ^{1}H-^{13}C HSQC NMR. The relative concentrations of each linkage could be calculated from the relative volumes of the contour peaks. Fig. S2 c shows the aromatic region of the technical lignin. It indicates the composing units of the lignin were much more complicated, involving all the three constitutional units (H, G, S), and their integral ratios (H: G: S) can be obtained readily by integrating the contours.

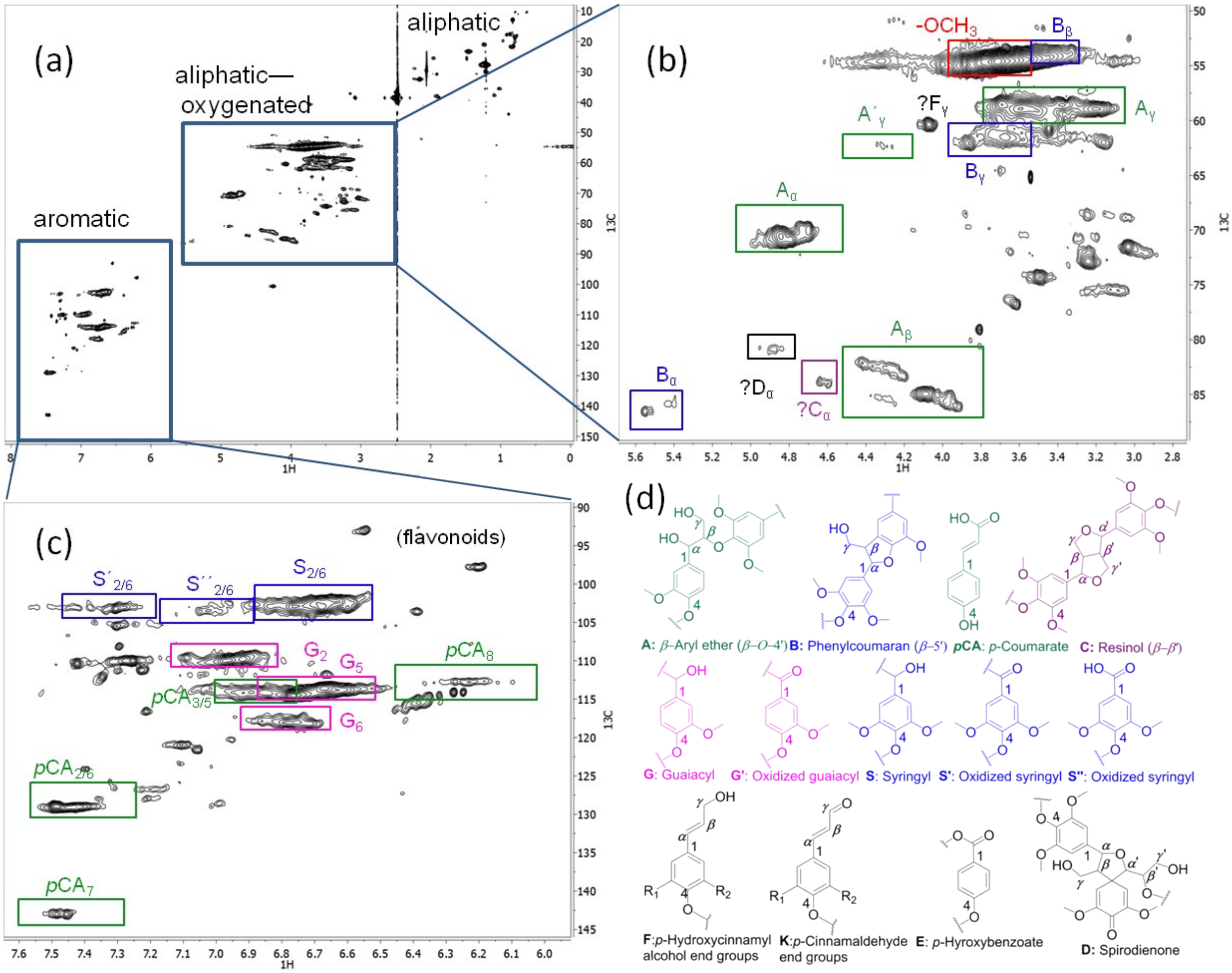


Fig. S2 2-D ^{13}C–^{1}H correlation (HSQC) spectra of alkali lignin

2.4 Distributions of aromatic units and their inter-unit linkages in lignins

Table S2. Aromatic units and their inter-unit linkages in lignins determined by NMR ^{a}

Sample	Composing units (%)			Inter-unit linkages (%)			
	S	G	H	β-O-4	β-5	β-β	β-1
Ball-milled lignin [b]	36	50	14	58	27	10	5
Alkali lignin	40	48	12	43	44	9	4

[a] Assuming β-O-4, β-5, β-β and β-1 add up to 100%.

[b] Ball-milled lignin was prepared from corn stover by using the method from the reference.[14]

2.5 Characterization of HDO solid residues by NMR

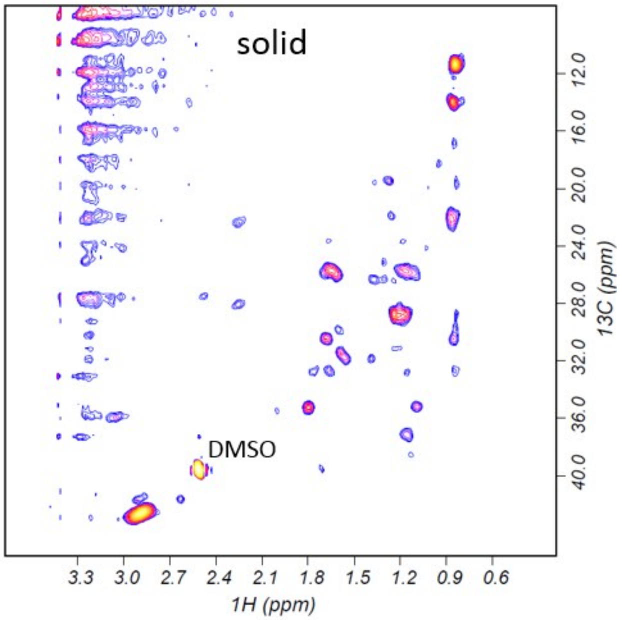


Fig. S3. HSQC spectra (aliphatic region) of DMSO-soluble solid residues

DMSO-soluble materials in the solid residues were also characterized by 2-D HSQC NMR. Mainly aliphatic peaks were observed, and the chemical shifts observed are consistent with main oil products that were adhered to the solid after the oil was removed.

2.6 Carbon balance in HDO of alkali lignin

Table S3 Carbon balance in HDO of alkali lignin[a]

$C_{\text{Alkali lignin}}$ (mg)	$C_{\text{Oil product}}$ (mg)	$C_{\text{Aqueous products}}$ (mg)	$C_{\text{Solid products}}$ (mg)	$C_{\text{Gas products}}$ (mg)	Carbon Balance (%)
53.2±0.32	20.36±0.57	13.19±0.68	10.10±0.35	2.87±0.21	87±2.12

[a] Reaction conditions: lignin100 mg, solid acid zeolite (H^+-Y, 57277-14-1) 300 mg, Ru/Al_2O_3 300 mg, water 30mL, P_{H2} 4MPa, 4 h, T=250 °C. C_{A} means the carbon content in substance A, e.g. $C_{\text{Alkali lignin}}$ means carbon content in alkali lignin.

The mass balance is relatively low probably due to the heterogeneity nature of biomass-derived lignin. In addition, some low boiling point products might have been removed from the ethyl acetate extract during the rotary vacuum evaporation process, which may also cause experimental errors in the carbon content calculation. The gas volume was determined by water displacement method. Results showed that negligible amounts of CO_2 and CH_3OH were found dissolved in water.

2.7 Effects of reaction time on HDO of technical lignin

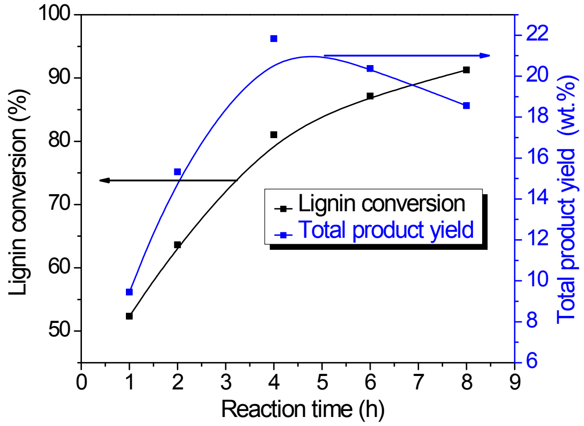


Fig. S4. Effects of reaction time on the lignin conversion and the total product yields. Reaction conditions: lignin100 mg, solid acid zeolites (H^+-Y,57277-14-1) 300 mg, Ru/Al_2O_3:300 mg, Water: 30 mL, P_{H2}:4MPa, T=250 °C.

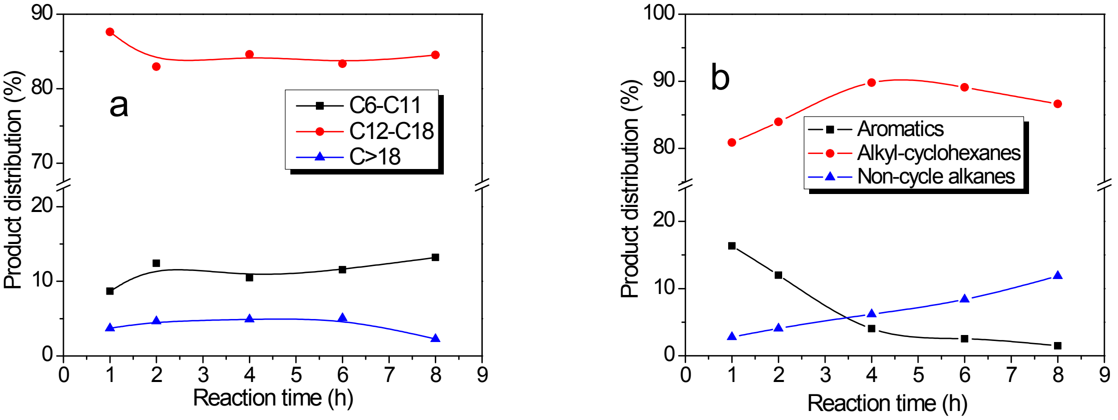


Fig. S5. Effects of reaction time on product distributions. Reaction conditions: lignin100 mg, solid acid zeolites (H^+ -Y, 57277-14-1) 300 mg, Ru/Al_2O_3 300 mg, water 30 mL, $P_{H2=}$4 MPa, 250 °C.

Increasing the reaction time initially increased the ratio of C>18 products, followed by a decrease with time. This result indicates that most of the C>18 products were produced from the lignin degradation intermediates with relatively low stability and were easier to further hydrogenate. The yield of C6~C11 products increased with reaction time, indicating that the hydrogenolysis of higher molecular weight products occurred during the HDO process. Fig. S5 (b) shows that the aromatic content decreased as reaction times increased, indicating this catalyst system has good selectivity for hydrogenation of the aromatic rings. Fig. S5 (b) also shows that the ratio of non-cyclic linear hydrocarbon products increased with longer reaction times, indicating that ring-opening reactions increased at longer time reactions.

2.8 Catalyst preparation and properties.

γ-Al_2O_3 (BET surface area = 200 m^2 /g) supported 5 wt.% Ru (Reduced) catalyst was bought from Sigma-Aldrich, and used as received without further treatment. Zeolite-Y (Z-Y) was bought from Zeolyst International®. The properties of Z-Y catalyst are listed in **Table S4**.

Table S4. Properties of Z-Y[1].

Type	SiO_2/Al_2O_3 Mole Ratio	Nominal Cation Form	Na_2O Weight %	Unit Cell Size, Å	Surface Area, m^2/g
CBV 100	5.1	Sodium	13.0	24.65	90

[1] Data was provided by Zeolyst International®

Z-Y was used in its H^+ Z-Y form in our research. The synthesis of H^+ Z-Y from Na^+ Z-Y was carried out as follows:

① 15.076 g Na^+ Z-Y was added into 200 mL NH_4NO_3 solution (1 mol/L), and exchanged at 25 °C for 24 h.

② After exchanging, the solid was separated by filtration and rinsed thoroughly by DI water. Then, it was dried in an oven at 90 °C for 12 h, transformed to NH_4^+ Z-Y.

③ The obtained NH_4^+ Z-Y was finally calcinated at 550 °C for 4 h to make H^+ Z-Y.

4. References

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