Supporting Information

Direct Production of Naphthenes and Paraffins from Lignin

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Experiment Section

Chemicals: Corncob lignin (Shandong Longlive Co., Klason lignin content: 80 wt.%), *n*-dodecane (Sinopharm, > 98% GC assay), benzyl phenyl ether (TCI, >98% GC assay), diphenyl ether (Sinopharm, CP), guaiacol (Sinopharm, > 98% GC assay), 4-methylguaiacol (J&K, > 99% GC assay), 4-ethylguaiacol (TCI, > 97% GC assay), 2,6-dimethoxy-4-methylphenol (Alfa Aesar, > 97% GC assay), (2-bromoethyl)-benzene (J&K, > 98% GC assay), phenol (Sinopharm, AR), Na_2SiO_3 (Sinopharm, SiO_2: 4.82 mol·L^{-1}, Na_2O: 1.39 mol·L^{-1}), ZrO_2 (Shanghai maikun Co.), ZnO (Shanghai maikun Co.), TiO_2 (Shanghai maikun Co.), MgO (Shanghai maikun Co.), Al_2O_3 (Shanghai maikun Co.), SiO_2 (Shanghai maikun Co.), NaOH (Sinopharm, AR), hexadecyl trimethyl ammonium bromide (Sinopharm, AR), $Ni(NO_3)_2$·$6H_2O$ (Sinopharm, AR), $AlCl_3$ (Sinopharm, AR), NH_3·H_2O (Sinopharm, AR), urea (Sinopharm, AR), 1,4-dioxane (Sinopharm, AR), benzene (Sinopharm, AR), methylbenzene (Sinopharm, AR), naphthane (Sinopharm, GR), ethanol (Sinopharm, AR), ethylene glycol (Sinopharm, AR), tetrahydrofuran (Sinopharm, AR), dimethyl sulfoxide (Sinopharm, AR), dimethyl sulfoxide-d^6 (J&K, 99.9%). Air, H_2 and N_2 gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of benzyl 2-phenylethyl ether (β-O-4 model compound): phenol (18.8 g, 0.2 mol) and hexadecyl trimethyl ammonium bromide (3.2 g, 0.1 mol) were firstly added into an aqueous solution of NaOH (500 mL, 20 wt.%) with stirring. The mixture was then heated to 60 ℃ with stirring for 0.5 h, and subsequently (2-bromoethyl)-benzene (18.5 g, 0.1 mol) was added. The suspension reacted at 80 ℃ for 12 h. After that, the organic phase was extracted by diethyl ether. The remaining liquid part was evaporated, and further reacted with an aqueous NaOH solution (10 wt.%, 250 mL) at 60 ℃ for 24 h in order to remove the residual phenol. Following the extraction by diethyl ether and sequential evaporation procedures, the final product was purified by distillation under vacuum. Purity: 99.5% (detected by GC), M_w: 198 g·mol^{-1}, Formula: $C_{14}H_{14}O$. The ^1H and ^{13}C NMR spectra are displayed in Fig. S7.

Synthesis of amorphous-silica-alumina support: the amorphous-silica-alumina (ASA) support (containing 10% alumina) was prepared by the co-gelification method. $AlCl_3$ $6H_2O$ and Na_2SiO_3 were used as precursors, and NH_3·H_2O was added into the mixed precursor solutions in order to adjust the pH attaining 8.0. For realizing full decationization, the as-received *co*-gelificated gel was ion-exchanged with CH_3COONH_4 for three-times, and then dried at 100 ℃ for 24 h. Prior to use, it is calcined in flowing air (flowing rate: 100 mL·min^{-1}) at 550 ℃ for 4 h.

Synthesis of the Ni catalysts supported on ZrO_2, ZnO, TiO_2, MgO, SiO_2, Al_2O_3, and ASA: The Ni catalysts supported on ZrO_2, ZnO, TiO_2, MgO, SiO_2, Al_2O_3, and ASA were synthesized by DP method. Nickel nitrate (10.2 g) was firstly dissolved in the deionized water (250 mL), and one part of this solution (210 mL) was suspended with oxide supports (2.0 g) and then heated to 70 ℃. The rest latter solution (40 mL) was dissolved with urea, and then drop-wise added into the former oxide suspension. Afterwards, the mixture was held at 90 ℃ with stirring for 10 h. After cooling down, the solid was filtered, and washed by distilled water. Finally, the samples were dried at 100 ℃ overnight, calcined in flowing air at 400 °C for 4 h (flowing rate = 100 mL·min^{-1}, heating rate: 2 °C·min^{-1}), and reduced in flowing H_2 at 460 °C for 4 h (flowing rate = 100 mL·min^{-1}, heating rate: 2 °C·min^{-1}).

Catalyst characterization

Characterization of lignin raw material: Organic elemental analysis (C, H, N, and S) of lignin was analyzed by the classical oxidation method in a Vario EL III instrument. IR spectrum of lignin was recorded on a Bruker Tensor 27 Fourier transform infrared spectrometer. ^{1}H NMR spectrum of lignin was obtained using a Bruker DPX-400 spectrometer after dissolving the lignin in DMSO-d^6 solution.

Determination of the Klason lignin content in the crude sample: Firstly, the corncob lignin (1.0 g) was extracted by an ethanol-benzene mixture (volume ratio: 1:2) in a Soxlet apparatus for 4 h. Then the as-received sample was dried, and added into a H_2SO_4 solution (15 mL, 72 wt%) at 20 ℃, stayed at stirring for 4 h. Afterwards, the concentrated H_2SO_4 solution was diluted to 3 wt%, and then reacted under reflux with stirring for another 4 h. Finally, the solid was filtered, washed by hot water until neutralized, dried under vacuum at 105 ℃ for 12 h, and weighted.

The Klason lignin content $= \frac{mass_{residue\ soild}}{mass_{corncob\ lignin}} \times 100\%$ (1)

Characterization of Ni catalysts: The Ni contents were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP–AES) with a Thermo IRIS Intrepid II XSP emission spectrometer after dissolving the catalyst in a HF solution. XRD measurement was conducted on a Rigaku Ultima IV X-ray diffractometer (35 kV and 25 mA) using Cu Ka radiation (k = 1.5405 Å). The Brunauer–Emmett–Teller (BET) specific surface areas were measured by using nitrogen adsorption at 77 K on a Belsorp-Max instrument. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) was detected on a Tecnai G^2 f30 microscope. The IR spectra of adsorbed pyridine (IR-Py) were recorded with a Nicolet NEXUS 670 FTIR spectrometer equipped with an in-situ IR cell. The samples were activated in vacuum at 673 K for 1 h before equilibrated with pyridine at 423 K, then evacuated at 423 K for 1 h. For determination of metal dispersion, pulse CO chemisorption was tested on a Micromeritics AutoChem 2910. Prior to test, 50 mg catalyst was reduced in a flow of 100 mL min^{-1} 10 vol% H_2 in He at 500 ℃ for 2 h and then flushed in He for 1 h. After cooled to ambient temperature in He, the CO gas pulses (5 vol% in He) were introduced in a flow of 100 ml min^{-1}. The changes in the CO gas phase concentration were tracked by TCD.

Identification of the soluble fraction of molecular weight of lignin by gel permeation chromatography： The gel permeation chromatography (GPC) consisted of two Waters' HPLC columns, a 2414 refractive index (RI) detector and a Water 1515 isocratic HPLC pump. Tetrahydrofuran was used as the solvent for lignin dissolution and eluent for GPC. The flow-rate was maintained at 1ml min^{-1} with a column temperature of 35 ℃. The calculation was calibrated with narrowly dispersed linear polystyrene standards.

Catalytic testing

Catalytic tests of hydrodeoxygenation of lignin: A typical experiment for depolymerization and hydrodeoxygenation of lignin was carried out as follows: lignin (2.0 g), Ni/ASA catalyst (30.1 wt.%, 1.0 g), *n*-dodecane (80 mL) were charged into a batch autoclave (Parr Instrument, 300 mL). The reactor was firstly flushed with H_2 at ambient temperature for three times, and then heated up to 300 ℃ when 6 MPa H_2 was purged, and the reaction started at a stirring speed of

700 rpm. The liquid products were *in situ* sampled during the catalytic run. After reaction, the remaining solid was filtrated and dried at 110 ℃ overnight. During the catalytic run, and then the liquid products were analyzed by GC and MS.

Identification and quantitation of the low molecular-weight products in liquid phase: Liquid products were analyzed on a gas chromatograph (GC) equipped with GC-MS (Shimadzu QP-2010 Ultra). Quantification of liquid yields used undecane as an internal standard. Analysis for gaseous products was performed on a GC equipped with a thermal conductivity detector (TCD) and (TDX-01: 30 cm × 3 mm, TDX-01: 2 m × 3 mm) columns, as well as a flame ionization detector (FID) and a HP-PLOT Q (50 m × 0.53 mm × 25 μm) capillary column.

$$\text{Conversion} = \frac{Total\ solid\ mass_{before\ reaction} - Total\ solid\ mass_{after\ raction}}{\text{mass}_{(raw\ corncob\ lignin)} \times (\text{Klason lignin content})} \times 100\%$$

$$\text{Liquid yield} = \frac{mass_{\text{undecane}} \times \frac{\text{area}_{\text{liquid product}}}{\text{area}_{\text{undecane}}}}{\text{mass}_{(corncob\ lignin\ raw\ material)} \times (\text{Klason lignin content}) \times (theoretical\ yield)} \times 100\%$$

Identification of the high molecular-weight products in liquid phase: HPLC analysis of depolymerization products was performed on Waters (ACQUITY UPLC H-Class) via gradient elution from an ACQUITY UPLC BEH C18 column (50 mm x 2.1 mm x 1.7 μm particle size, Waters) with PDA detector (Waters). Mass spectra were recorded on Waters SQ Detector equipped with a heated electrospray source (ESC I prober, Waters). Mobile phase A consisted of water with 0.1% formic acid and B was acetonitrile. The gradient program at 0.6 ml·min⁻¹ flow rate was: 40% B for 2.8 min, to 80% B over 0.4 min, to 95% B over 0.3 min, and to 1% B over 0.5 min..

Recycling tests of hydrodeoxygenation of lignin: After the each recycling reaction, the catalyst was washed with dimethyl sulfoxide (DMSO) to dissolve the unreacted lignin reactant, and then sequential calcined in air, and reduction in hydrogen before next use. Other detailed procedures were similar to the above-mentioned tests for lignin reactions.

Catalytic tests of hydrodeoxygenation of diverse phenolic monomers and dimers: In a typical procedure, phenolic monomers or dimers (1.0 g), Ni/ASA (30.1 wt.%, 0.2 g), and *n*-dodecane (80 mL) were mixed and charged into a batch autoclave (Parr, 300 mL). After flushing the reactor with H_2 by three times, the reaction was carried out at 300 ℃ in presence of 6 MPa H_2 for 1 h. During the catalytic run, and then the liquid products were analyzed by GC and MS.

Kinetics of benzyl 2-phenylethyl ether (beta-O-4 model compound) conversion: benzyl 2-phenylethyl ether (2.0 g), Ni/ASA (30.1 wt.%, 0.05 g), *n*-dodecane (80 mL) were charged into a batch autoclave (Parr Instrument, 300 mL). After the reactor was flushed with H_2 at ambient temperature for three times, the autoclave was then heated up to 300 ℃ when 6 MPa H_2 was charged, and the reaction was conducted with a stirring speed of 700 rpm. The liquid products were *in situ* sampled every 30 min. during the catalytic run, and then the liquid products were analyzed by GC and MS.

Kinetics of guaiacol conversion: the procedures were similar to those described in the kinetics of benzyl 2-phenylethyl ether conversion, and guaiacol (5.0 g) and Ni/ASA (30.1 wt.%, 0.2 g) was used. The reaction was carried out at 300 ℃

in presence of 6 MPa H_2 at a stirring speed of 700 rpm. The liquid products were in situ sampled every 30 min. During the catalytic run, and then the liquid products were analyzed by GC and MS.

(a) 1H NMR Spectrum

1H NMR information

δ(ppm)	assignment
9.9	Protons in formyl groups
7.5	H-2 and H-6 in aromatic rings with a carbonyl group
7.2	Aromatic protons in p-hydroxyphenyl groups
6.8	Aromatic protons in guaiacyl Protons
6.6	Aromatic protons in syringyl Protons
6.3	α-H in β-O-4 units
5.3	α-H in β-5/α-O-4 units
3.7	Protons in aromatic methoxyl groups
3.3	DMSO(solvent)
2.7	Protons in aliphatic methoxyl groups
2.5	H_2O in solvent
2.3	Aromatic acetate
2.0	Aliphatic acetate
1.4- 0.8	Hydrocarbon contaminant

(b) IR Spectrum

IR information

Wavenumbers (cm^{-1})	Band origin	Wavenumbers (cm^{-1})	Band origin
3408	O-H stretch	1357	aliphatic C-H stretch
3006 2937 2848	C-H stretch (methyl and methylene groups)	1330	G ring plus S ring condensed
1695	C=O stretch(ester groups)	1222	C-C,C-O,C=O stretch
1600	Aromatic skeletal vibrations	1126	C-H in-plane (typical for G rings)
1512	Aromatic skeletal vibrations	1170	C=O stretch(conjugated ester groups)
1461	C-H bending vibrations (methyl and methylene groups)	1031	C-O bending vibrations (primary alcohols)
1423	Aromatic skeletal vibrations	835	C-H out-of-plane(S ring)

Figure S1. (a) ^{1}H NMR spectrum (using DMSO-d[6] as solvent) and (b) Infrared spectrum of lignin.
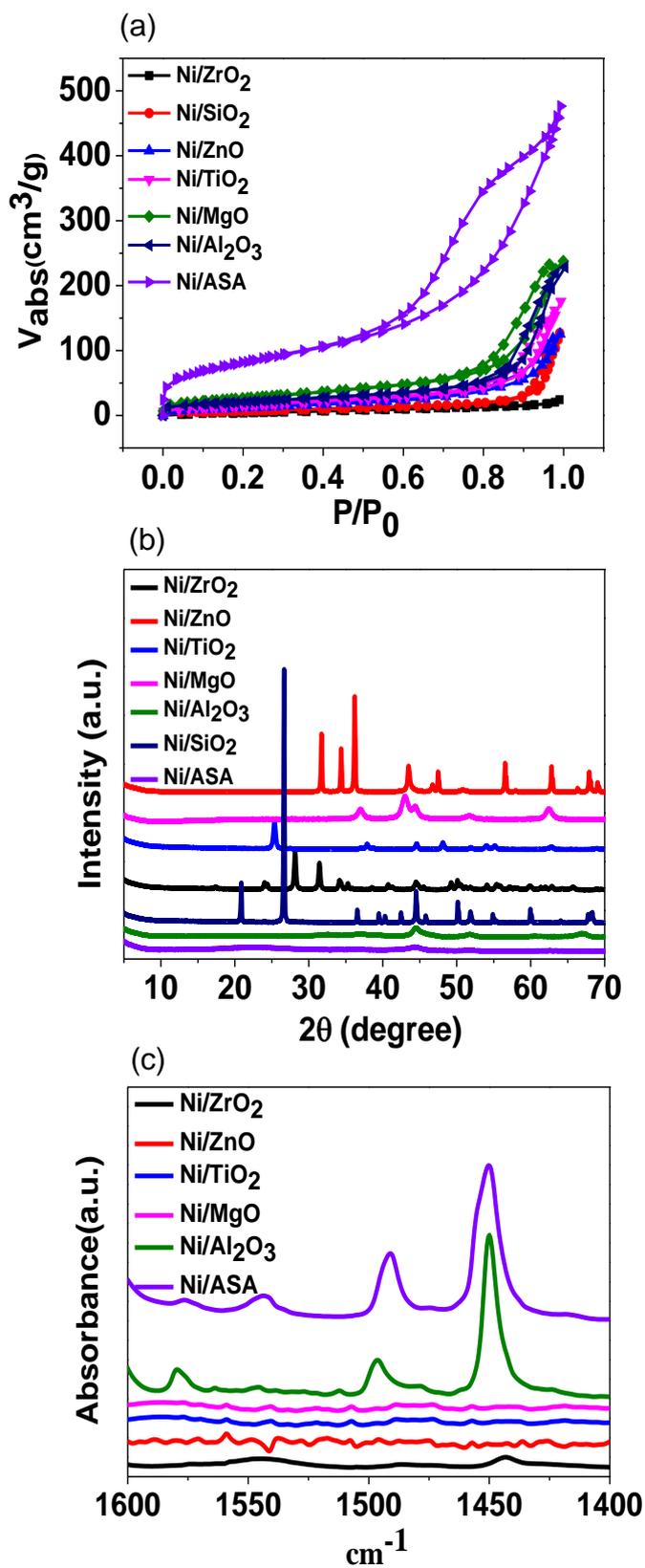
Figure S2. (a) N_2 adsorption and desorption isotherms (b) XRD patterns and (c) the IR spectra of adsorbed pyridine of supported Ni catalysts.

(a) — Phenolic monomers chromatogram with labeled peaks: 0.48, 0.55, 0.62, 0.98 ($M_w = 186$), 1.73 ($M_w = 340$), 2.07 ($M_w = 356$), 2.19 ($M_w = 396$), 2.43 ($M_w = 414$), 3.01 ($M_w = 494$), 3.63 ($M_w = 630$), 3.72 ($M_w = 782$)

(b) Time = 0.98 min
(c) Time = 1.73 min
(d) Time = 2.07 min
(e) Time = 2.19 min
(f) Time = 2.43 min
(g) Time = 3.01 min

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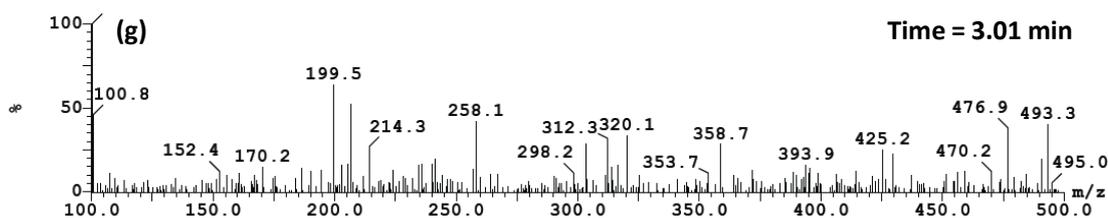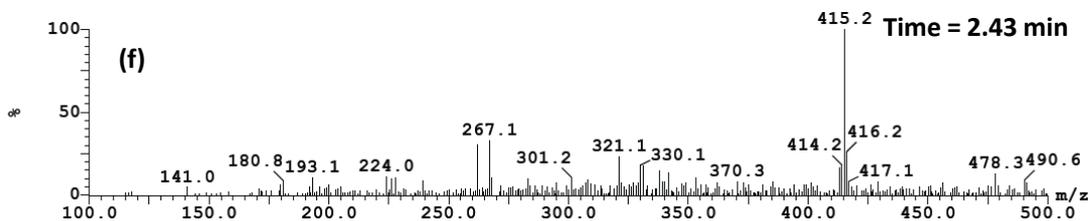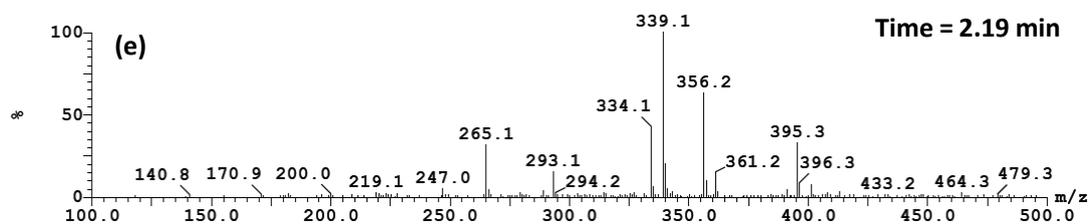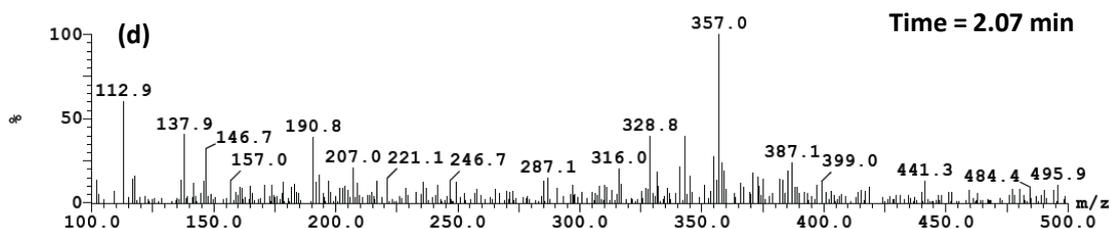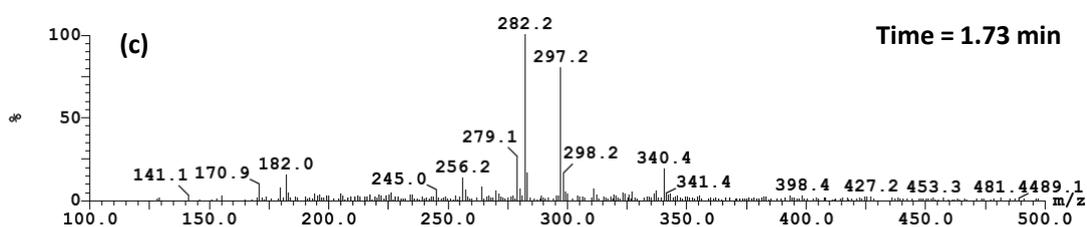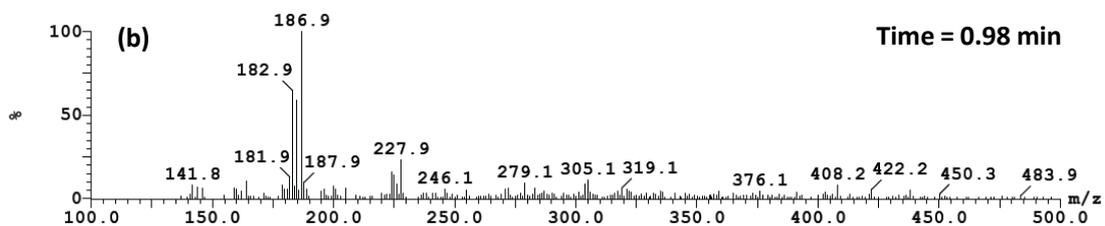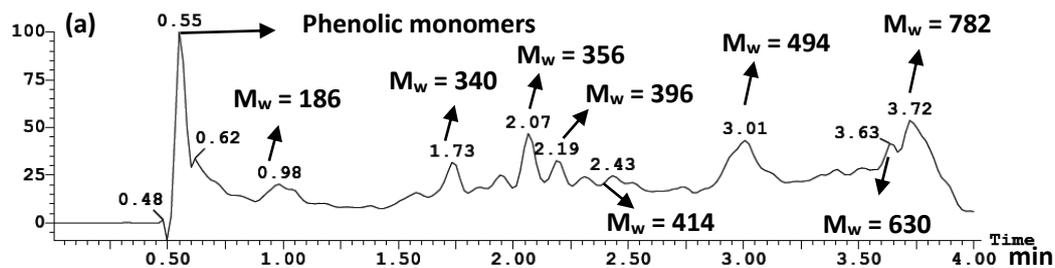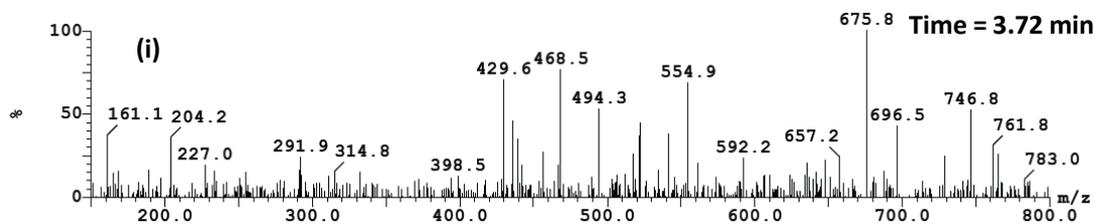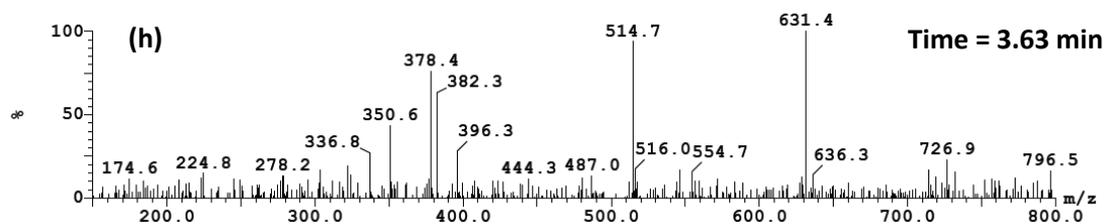
Figure S3. (a) HPLC spectrum for analyzing the liquid product, (b)-(h) HRMS (ESI) mass spectra obtained at retention times of (b) 0.98 min, (c) 1.73 min, (d) 2.07 min, (e) 2.19 min, (f) 2.43 min, (g) 3.01 min, (h) 3.63 min, (i) 3.72 min.
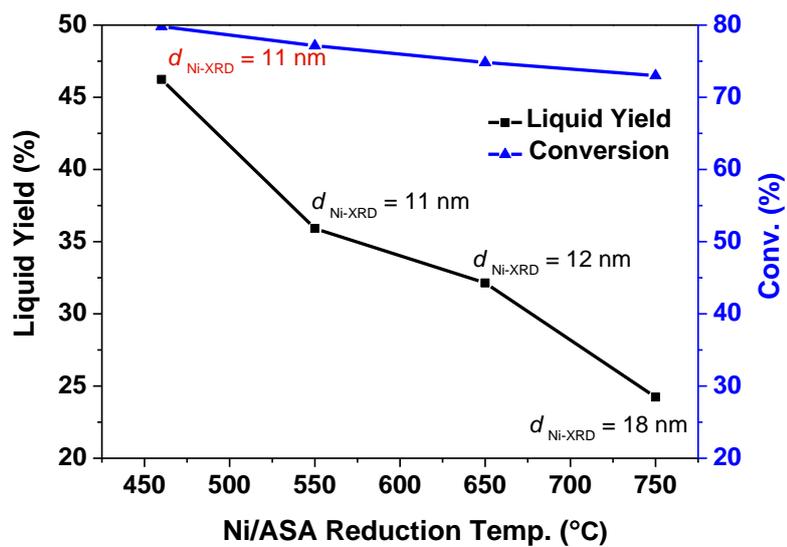
Figure S4. Influence of Ni/ASA reduction temperature towards the lignin conversion and the liquid yield. General conditions: lignin (2.0 g), Ni/ASA catalyst (30.1 wt.%, 1.0 g), 300 ℃, 6 MPa H_2, dodecane (80 mL), 160 min., stirring at 700 rpm.

(a) Pictures of feedstock, catalyst, and liquid product

(b) *In situ* sampling products at 250 ° C, 4 MPa H_2
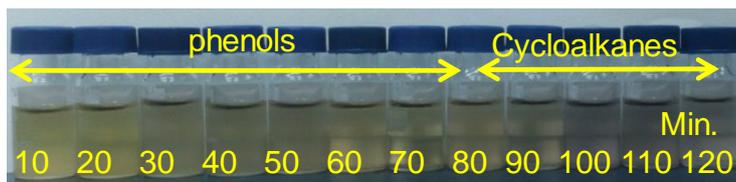
(c) *In situ* sampling products at 300 ° C, 6 MPa H_2

Figure S5. Illuminative images for (a) feedstock, catalyst, and liquid product, (b) *in situ* sampling the liquid products at 250 ℃ in presence of 4 MPa H_2, (c) *in situ* sampling the liquid products at 300 ℃ in presence of 6 MPa H_2.

Figure S6. Production of C$_5$ and C$_6$ compounds from conversion of (a) cellulose and (b) hemicellulose.
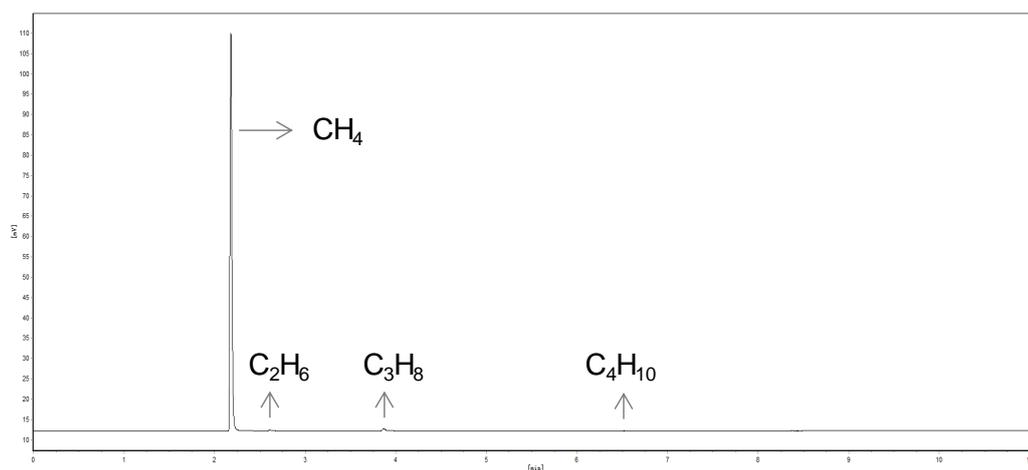
Figure S7 Gas phase products from catalytic conversion of lignin over Ni/ASA catalyst. General conditions: lignin (2.0 g), Ni/ASA catalyst (30.1 wt.%, 1.0 g), 300 ℃, 6 MPa H_2, dodecane (80 mL), 160 min., stirring at 700 rpm.
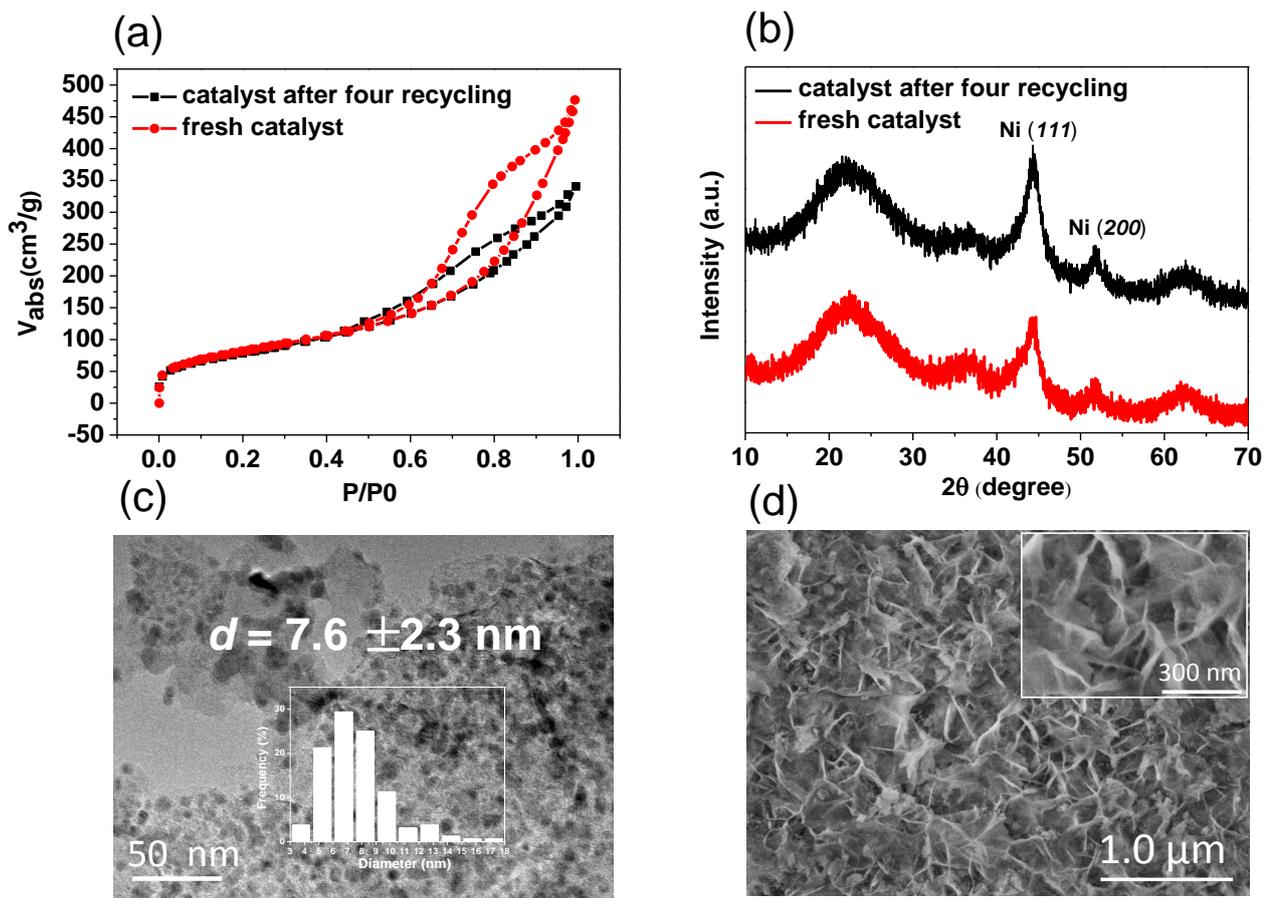
Figure S8. Characterization of the selected Ni/ASA catalyst after four recycling measurements, by a) N$_2$ adsorption and desorption isotherms, b) XRD, c) TEM and d) SEM images.
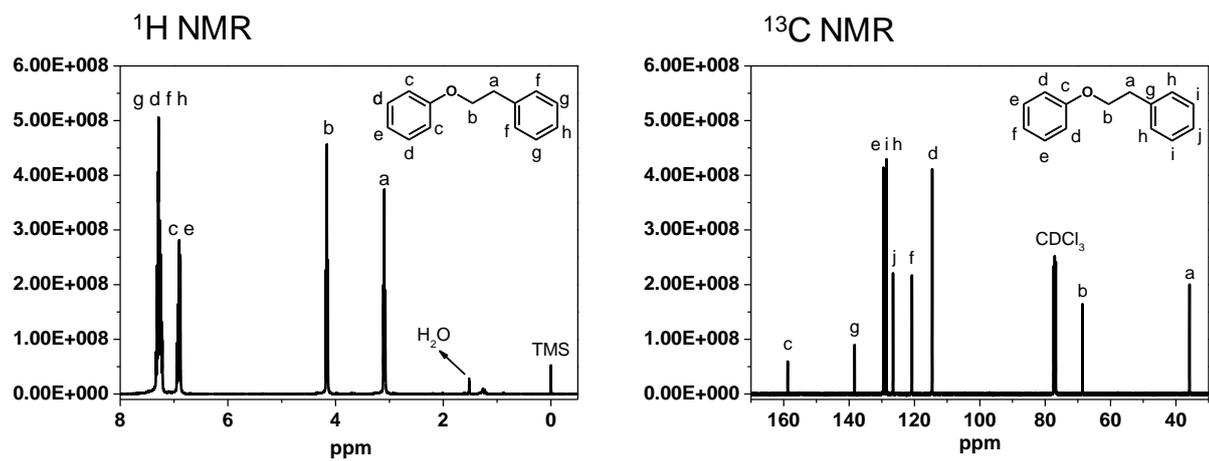
Figure S9. The ^{1}H NMR and ^{13}C NMR spectra of benzyl 2-phenylethyl ether (β-O-4 model compound).
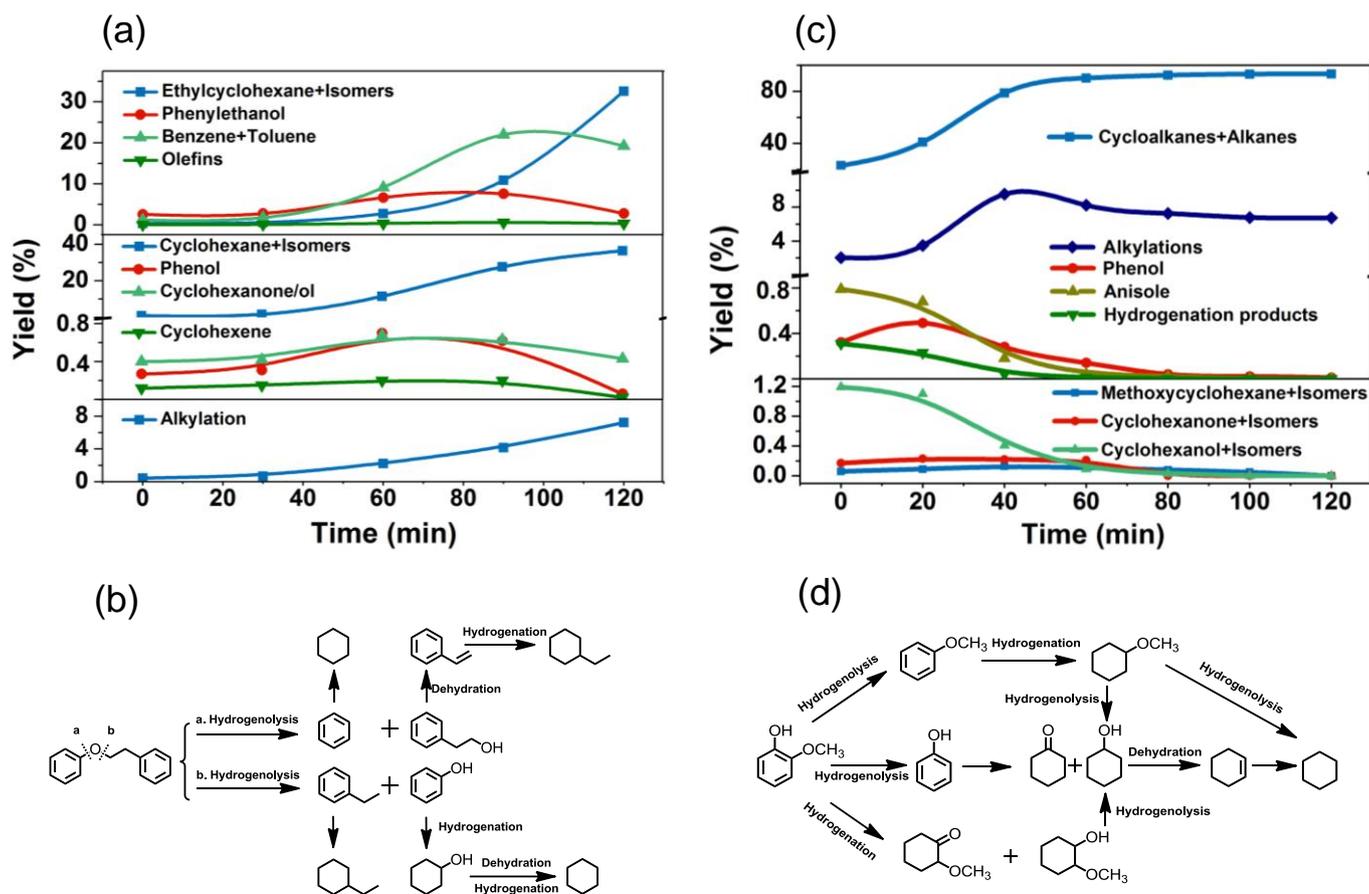
Figure S10. (a) Kinetics of phenolic dimer conversion to cycloalkanes over Ni/ASA. (b) Reaction steps in benzyl 2-phenylethyl ether conversion over Ni/ASA. Conditions: benzyl 2-phenylethyl ether (2.0 g), Ni/ASA catalyst (30.1 wt.%, 0.05 g), dodecane (80 mL), 300 ℃, 6 MPa H_2, 160 min., stirring at 700 rpm. (c) Kinetics of phenolic monomer conversion to cycloalkanes over Ni/ASA, (d) Reaction steps in guaiacol hydrodeoxygenation to cycloalkanes on Ni/ASA. Conditions: guaiacol (5.0 g), Ni/ASA catalyst (30.1 wt.%, 0.2 g), dodecane (80 mL), 300 ℃, 6 MPa H_2, stirring at 700 rpm.
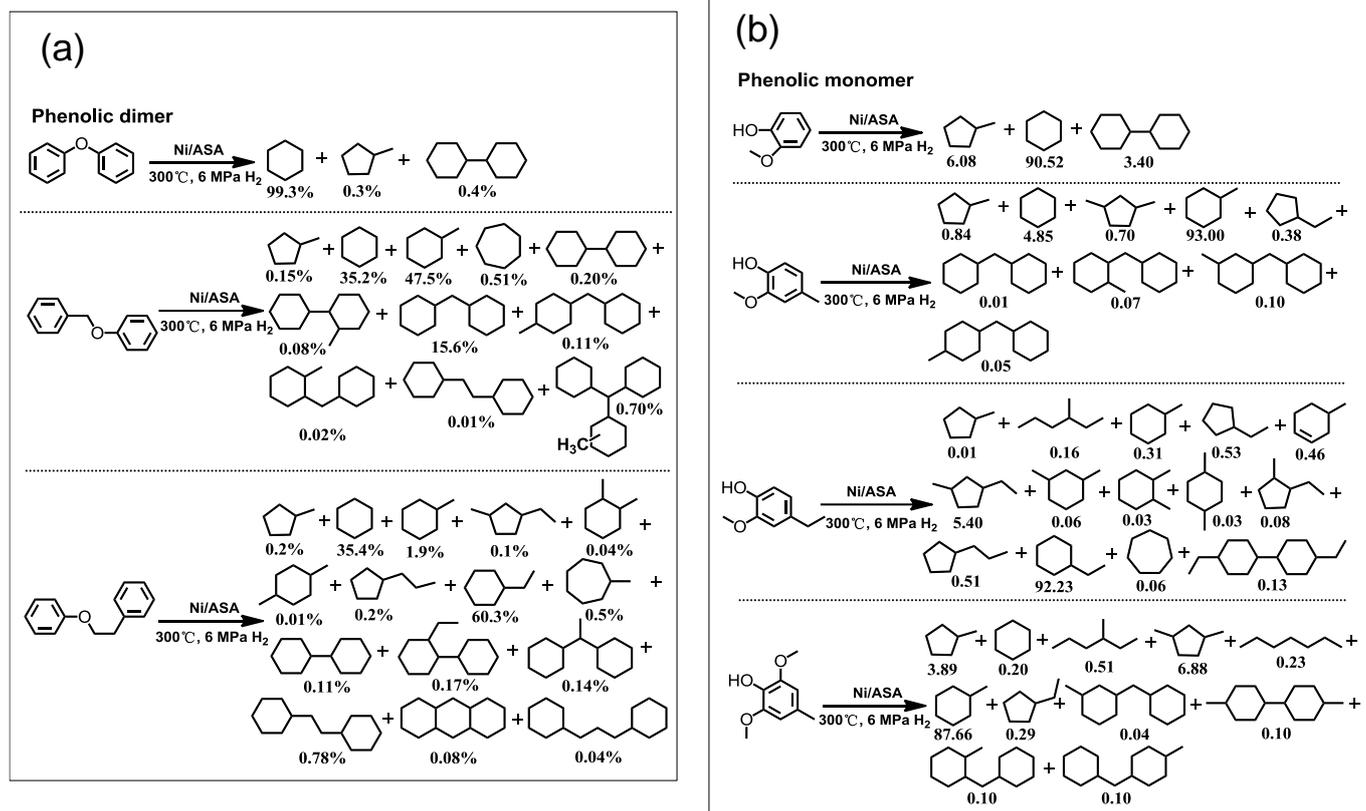
Figure S11. (a) Phenolic dimers and (b) phenolic monomers hydrodeoxygenation with Ni/ASA. Conditions: phenolic monomer and dimer model compound (1.0 g), Ni/ASA (30.1 wt.%, 0.2 g), 80 mL dodecane, 300 ℃, 6 MPa H_2, 160 min., stirring at 700 rpm.

Table S1a. Typical composition and organic elemental analysis of lignin.

Component (wt. %)	Residual sugar	Ash	Water	Lignin
Sample	3	12	5	80

Element (wt. %)	C	H	N	S	O [a]
Sample	62.4	5.34	0.45	-	31.8

[a] The remaining part is calculated to be the oxygen content.

Table S1b. The element composition and theoretical yield calculated from lignin.

$C_{10}H_{10.3}O_{3.8} \rightarrow C_9H_{7.3}O_{2.8}(OCH_3)_{1.0}$	Theoretical yield: C_9H_{18} = 66 wt.%
Lignin unit M_w = 191 g·mol^{-1}	H_2O = 32 wt.%
Assumed that it contains one −OCH$_3$ group in the lignin unit	CH_4 = 8.4 wt.%

Table S2. Depolymerization of lignin with Ni-based catalysts in dodecane.[a]

Cat.	Ni-wt.%[b]	S_{BET}[c] $(m^2\ g^{-1})$	Acid conc. $(m\text{mol}\ g^{-1})$[d] B	L	$d_{Ni\text{-}XRD}$ (nm)	Solid conv. (%)[e]	Liquid yield (%)[f]	Rate $(g_{lig}\cdot g_{cat}^{-1}\cdot h^{-1})$	Liquid product selectivity (%) Cycloalkanes/ Alkanes	Aromatics/ Olefins	Phen-ols	Alcohols /Ketones
None	-	-	-	-	-	-[g]	2	0.02	-	-	100	-
Ni/ZrO$_2$	33.9	27	0	0.023	18	41	5	0.30	1	3	76	21
Ni/ZnO	26.7	47	0	0	23	40	7	0.28	8	1	88	3
Ni/TiO$_2$	24.9	62	0	0	21	39	8	0.30	7	2	88	3
Ni/MgO	29.2	99	0	0	17	37	10	0.29	8	4	85	3
Ni/SiO$_2$	28.9	32	-	-	39	36	5	0.32	5	1	86	8
Ni/Al$_2$O$_3$	26.0	75	0	0.199	12	43	11	0.27	14	1	65	19
Ni/ASA[h]	30.1	292	0.107	0.246	11	78	18	0.58	72	2	13	13

[a] Condition: lignin (2.0 g), Ni catalysts (30.1 wt.%, 1.0 g), dodecane (80 mL), 250 °C, 4 MPa H$_2$, 160 min., stirring at 700 rpm.

[b] The Ni loading refers to the value: weight (metal) / weight (support).

[c] The BET surface area is obtained by N$_2$ sorption.

[d] The acid concentration is determined by IR spectra of adsorbed pyridine. B: Brönsted acid site, L: Lewis acid site.

[e] The conversion value refers to the weight loss of solid lignin before and after reaction.

[f] The liquid yield is calculated by area normalization using undecane as an internal standard.

[g] Serious coke is formed.

[h] Amorphous-silica-aluminum (ASA) contains 10 wt.% alumina.

Table S3. The liquid products, their retention time, and relative contents after lignin conversion. Conditions: Lignin (2.0 g), Ni/ASA (30.1 wt.%, 1.0 g), dodecane (80 mL), 250 ℃, 4.0 MPa H₂, 160 min., stirring at 700 rpm.
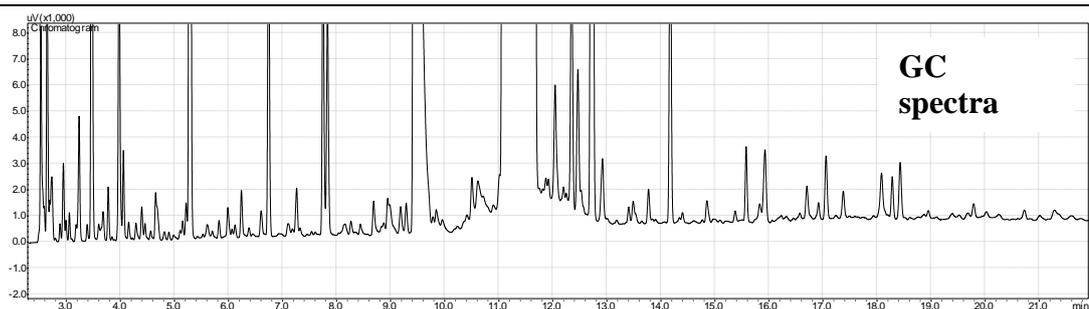
No.	Retention time [min]	Compound	Yield (%)	No.	Retention time [min]	Compound	Yield (%)
1	2.528		0.67	47	7.26		0.19
2	2.882		0.04	48	7.324		0.03
3	2.944		0.23	49	7.831		0.80
4	2.992		0.05	50	8.266		0.15
5	3.055		0.08	51	8.439		0.04
6	3.179		0.04	52	8.685		0.13
7	3.235		0.37	53	8.873		0.05
8	3.385		0.04	54	8.944		0.13
9	3.466		2.56	55	8.98		0.12
10	3.599		0.05	56	9.044		0.03
11	3.65		0.03	57	9.183		0.11
12	3.68		0.09	58	9.287		0.11
13	3.774		0.14	59	10.503		0.18
14	3.845		0.01	60	10.615		0.41
15	3.975		1.14	61	11.016		0.09

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#	RT	Structure	Value	#	RT	Structure	Value
16	4.055		0.24	62	12.043		0.52
17	4.152		0.05	63	12.199		0.07
18	4.222		0.00	64	12.347		1.07
19	4.288		0.06	65	12.464		0.65
20	4.394		0.10	66	12.919		0.32
21	4.454		0.05	67	13.181		0.02
22	4.559		0.02	68	13.403		0.06
23	4.652		0.14	69	13.487		0.12
24	4.676		0.08	70	13.771		0.15
25	4.814		0.03	71	13.903		0.02
26	4.897		0.02	72	14.4		0.05
27	4.984		0.02	73	14.606		0.01
28	5.104		0.02	74	14.767		0.01
29	5.15		0.05	75	14.852		0.11
30	5.215		0.11	76	14.972		0.04
31	5.284		7.06	77	15.198		0.01
32	5.525		0.01	78	15.376		0.04
33	5.606		0.06	79	15.506		0.00
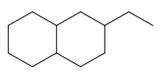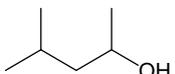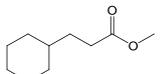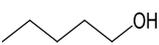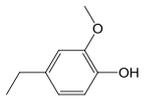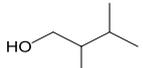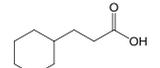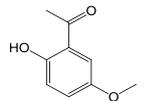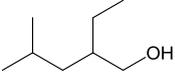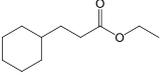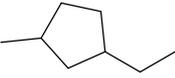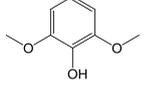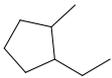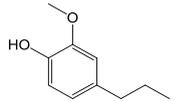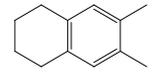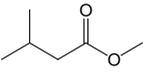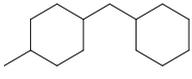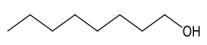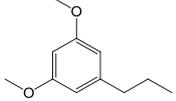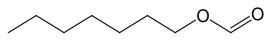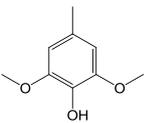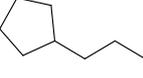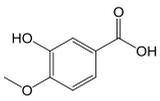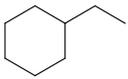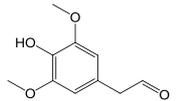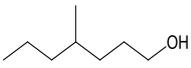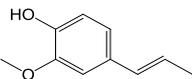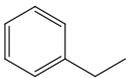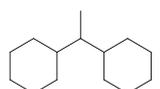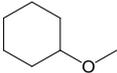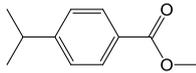
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34	5.701		0.03	80	15.828		0.11
35	5.824		0.05	81	15.926		0.37
36	5.987		0.10	82	16.228		0.10
37	6.065		0.02	83	16.453		0.01
38	6.121		0.04	84	16.57		0.03
39	6.238		0.15	85	16.701		0.14
40	6.379		0.03	86	16.754		0.01
41	6.447		0.01	87	17.055		0.26
42	6.603		0.10	88	17.239		0.01
43	6.74		1.17	89	17.375		0.11
44	6.935		0.02	90	18.082		0.25
45	7.103		0.07	91	18.428		0.26
46	7.184		0.03	92	19.787		0.48
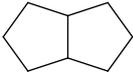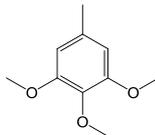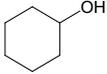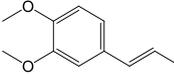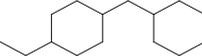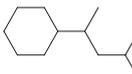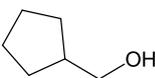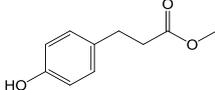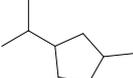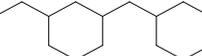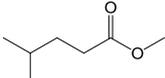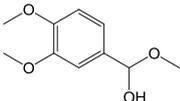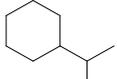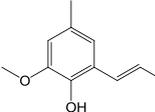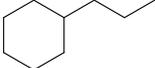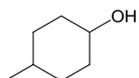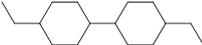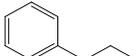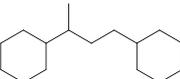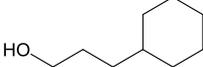
Table S4. The liquid products, their retention time, and relative contents after lignin conversion. Conditions: Lignin (2.0 g), Ni/ASA (30.1 wt.%, 1.0 g), dodecane (80 mL), 300 ℃, 6.0 MPa H$_2$, 160 min., stirring at 700 rpm.
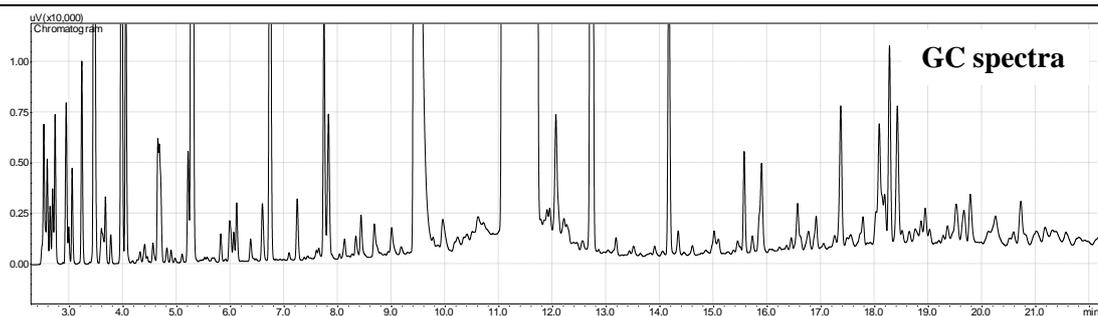
No.	Ret. time [min]	Compound	Yield (%)	No.	Ret. time [min]	Compound	Yield (%)
1	2.522		0.50	42	7.243		0.25
2	2.586		0.32	43	7.440		0.04
3	2.686		0.20	44	7.601		0.04
4	2.732		0.46	45	7.645		0.45
5	2.939		0.52	46	7.824		0.28
6	2.986		0.12	47	8.030		0.02
7	3.050		0.27	48	8.124		0.11
8	3.230		0.61	49	8.335		0.13
9	3.458		4.51	50	8.432		0.20
10	3.596		0.20	51	8.680		0.23
11	3.670		0.22	52	9.002		0.18
12	3.770		0.09	53	9.180		0.04
13	3.969		2.94	54	9.954		0.39
14	4.049		1.05	55	12.061		0.65

23

#	Value	Structure	%		#	Value	Structure	%
15	4.177		0.01		56	13.181		0.08
16	4.261		0.01		57	13.508		0.08
17	4.316		0.05		58	13.90		0.04
18	4.401		0.08		59	14.049		0.79
19	4.448		0.02		60	14.339		0.04
20	4.555		0.07		61	14.604		0.02
21	4.647		0.75		62	15.009		0.12
22	4.815		0.05		63	15.088		0.09
23	4.892		0.04		64	15.447		0.30
24	4.968		0.01		65	15.721		0.08
25	5.098		0.03		66	15.891		0.29
26	5.210		0.39		67	16.225		0.01
27	5.282		18.59		68	16.359		0.03
28	5.438		0.01		69	16.563		0.25
29	5.480		0.01		70	16.767		0.08
30	5.563		0.04		71	17.047		0.17
31	5.690		0.04		72	17.367		0.71
32	5.818		0.10		73	17.552		0.12
33	5.907		0.01		74	18.084		0.61
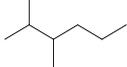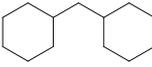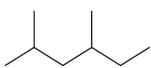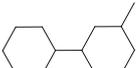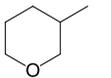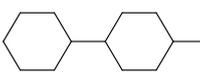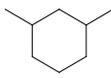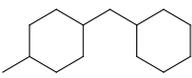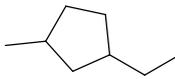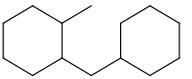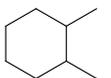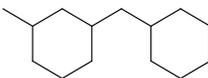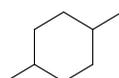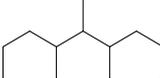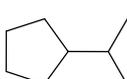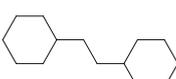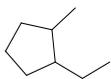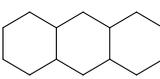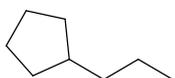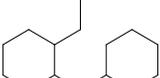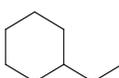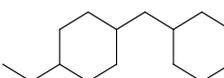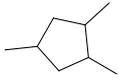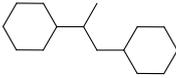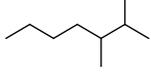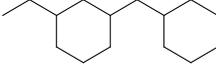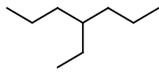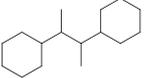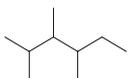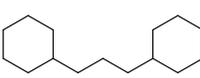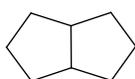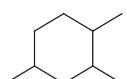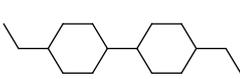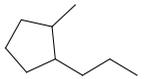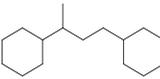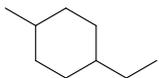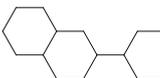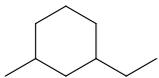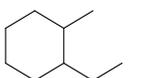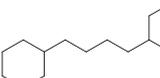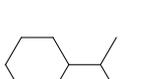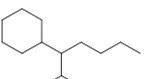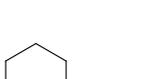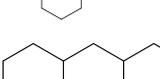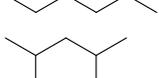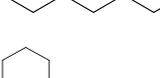
34	5.986		0.21	75	18.421		0.50
35	6.060		0.10	76	18.445		0.45
36	6.375		0.09	77	18.864		0.21
37	6.418		0.02	78	18.941		0.28
38	6.594		0.24	79	19.519		0.44
39	6.735		3.25	80	19.662		0.21
40	6.924		0.01	81	20.250		0.44
41	7.091		0.03	82	20.721		0.35