Supplemental Information

Liquefaction and hydrodeoxygenation of polymeric lignin using a hierarchical Ni micro-reactor catalyst

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h-s), the solid residue after 1h reaction (1.0 h-s), the liquid product after 0.5 h reaction (0.5 h-l), and the liquid product after 1h reaction (1.0 h-l) over Ni/ASA-3 (a, b, c, d) and Ni/ASA-1 (e, f, g, h), respectively, as detected by TOF-MS.

Experiment Section

Chemicals: Corncob lignin (Shandong Longlive Co., Klason lignin content: 80 wt.%), *n*-dodecane (Sinopharm, > 98% GC assay), Na_2SiO_3 (Sinopharm, SiO_2: 4.82 mol·L-1, Na_2O: 1.39 mol·L-1), , $Ni(NO_3)_2·6H_2O$ (Sinopharm, AR), $AlNO_3$ (Sinopharm, AR), Aluminum tri-sec-butoxide (JK, 98%), Tetramethyl orthosilicate (JK, 99%), Aluminum(III) acetylacetonate(JK, 99%), Tetraethyl orthosilicate (JK, 99%), Acetic Acid (Sinopharm, 99%), methanol (Sinopharm,AR), $NH_3·H_2O$ (Sinopharm, AR), urea (Sinopharm, AR), Tetrahydrofuran (J&K, 99.8%, HPLC/spectro,non(BHT), DMSO-d6 (99.9%, Cambridge Isotope Laboratories), Acetone-d6, (99.9%, Cambridge Isotope Laboratories), Chloroform-d (99.8%, Cambridge Isotope Laboratories),. CH_4, Air, H_2 and N_2 gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of macropores-mesopores amorphous-silica-alumina support (ASA-1): An aqueous solution basified to pH = 10 with NaOH was used as starting solutions and heated at 70 °C. The aluminium tri-sec-butoxide and tetramethyl orthosilicate were added under moderate stirring with a Si/Al molar ratio of 9/1 into the solution after mixing well. The resulting gels were homogenized for 1 hour at 70 °C. Then the gels was hydrothermally treated for 72 hours at 80 °C in Teflon cartridges sealed in stainless steel autoclaves, followed by drying.

Synthesis of amorphous-silica-alumina support (ASA-2): the amorphous-silica-alumina (ASA-1) 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 °C for 24 h. Prior to use, it is calcined in flowing air (flowing rate: 100 mL·min-1) at 550 °C for 4 h.

Synthesis of mesopores amorphous-silica-alumina support (ASA-3): ASA-3 were prepared by a co-condensation method. In brief, a desired amount of $Al(NO_3)_3$ and 1.0

g polyvinylpyrrolidone was added to a 700 mL ethanol-water (4:3) solution. After the solution was stirred for 5 min, 6.0 g hexadecyl trimethyl ammonium bromide and 20 mL tetraethyl orthosilicate were added, and the suspension was stirred for another 10 min. Then 120 mL $NH_3 \cdot H_2O$ (25 wt%) was injected dropwise under strong agitation. Stirring vigorously for 72 h, the precipitation was filtrated, washed three times with distilled water and ethanol, and dried at 333 K in air for 12 h. Then the catalyst was calcined at 773 K for 6 h.

Synthesis of the Ni catalysts supported on ASA: The Ni catalysts supported on 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 °C. 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 °C with stirring for 10 h. After cooling down, the solid was filtered, and washed by distilled water. Finally, the samples were dried at 100 °C 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).

Characterizations

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. 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 °C, 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 °C for 12 h, and weighted.

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

Identification of the soluble fraction of molecular weight of acetylated lignin and its hydrodeoxygenated products at different reaction time by gel permeation chromatography and TOF-MS： GPC analysis can refer to the literature. [1] In a typical process, lignin sample (20 mg) was treated with pyridine (2 ml) and acetic anhydride (2 ml) for 48 h at room temperature. The formed solution was added with 10 ml ethyl acetate and anhydrous magnesium sulfate. Then the solid was separated by filtration, the liquid fraction was dried by rotary evaporation at 60 °C. The dried one was added with THF (chromatographically pure), THF was used as an eluent with a flow rate of 1.0 mL/min at 30 °C. The gel permeation chromatography (GPC) consisted of three Waters HPLC columns, a photo-diode array (PDA) detector and a Water 1515 isocratic HPLC pump. The calculation was calibrated with narrowly dispersed linear polystyrene standards. TOF-MS characterization was performed with the mass range of m/z 50-2000 (positive-ion ESI-MS, $m/\Delta m_{50}$ = 60000 at m/z 400).

Characterization of the Ni catalysts and parent materials: 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 ºC 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. 2D HSQC and $_{13}$C NMR spectra were measured at 500 MHz in d$_6$-DMSO (or Acetone-d$_6$, and Chloroform-d) using TMS signal.

Identification and Quantitation of the products: 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.

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

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

Catalytic testing

Catalytic tests of hydrodeoxygenation of lignin: A typical experiment for depolymerization and hydrodeoxygenation of lignin was carried out as follows: lignin, Ni/ASA catalyst, *n*-dodecane (80 mL) were charged into a batch autoclave. The reactor was firstly flushed with H$_2$ at ambient temperature for three times, and then heated up to 300 °C 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 °C overnight. During the catalytic run, and then the liquid products were analyzed by GC and MS.

In situ-IR tests of hydrodeoxygenation of lignin: Firstly, the well mixed Ni/ASA and lignin (S/C=4:0.5) is coated on the tube made of CaF_2. Then, the solvent (dodecane) is pumped into the reaction cell and filled with 2 MPa H_2 before heated up to 300 °C. The IR spectrum is acquired at each five minutes to record the changes of the lignin structures.

NMR detecting the products from the hydrodeoxygenation of lignin with kinetic reactions: lignin (4.0 g), Ni/ASA catalyst (0.5 g), *n*-hexane (80 mL) were charged into a batch autoclave, and reacted at 300 °C and 6 MPa H_2 with different reaction time. After reaction of 0.5h or 1h, the reacted liquid and solid phase can be achieved by filtration, respectively. The liquid products from the hydrodeoxygenation of lignin were obtained by drying the solvent at 70 °C. The remaining solid phase may consist of the catalyst, the unconverted lignin, and the depolymerized oligomers. The solid catalyst was removed by filtration of the dissolved solid phase using the dioxane. The gained solid products in the dioxane was distilled at 102 °C to eliminate the dioxane and then the solid products from the hydrodeoxygenation of lignin were obtained. In the NMR tests, DMSO-d_6 was used to dissolve the lignin and the derived solid-phase products, while, the liquid products were dissolved by using the mixed solvents of DMSO-d_6：Acetone-d_6：Chloroform-d (2:1:1).
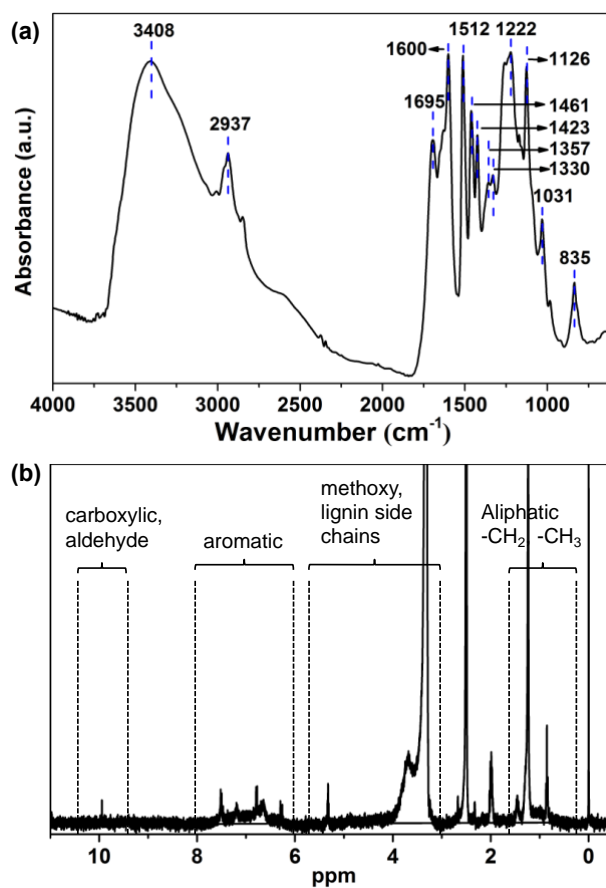
Figure S1. Characterization of lignin by (**a**) infrared spectrum and (**b**) 1H-NMR spectrum using DMSO as solvent.
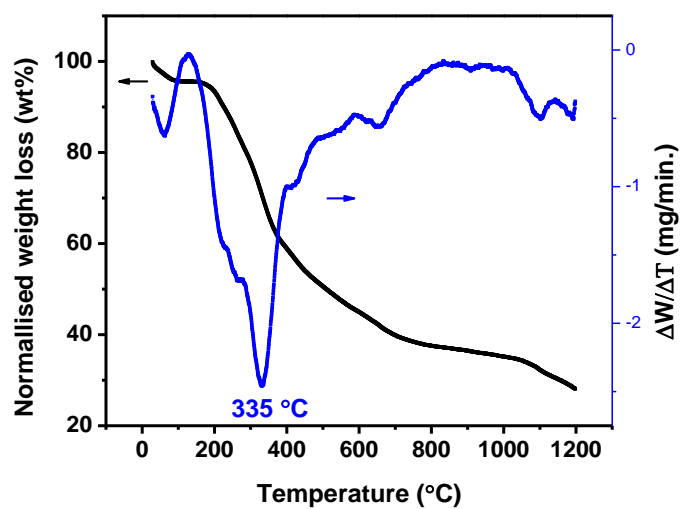
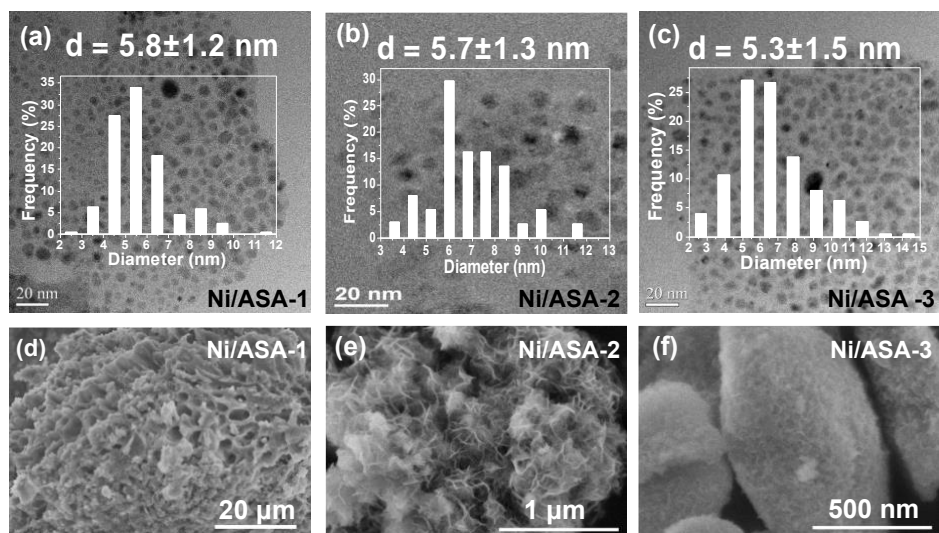**Figure S2.** Thermogravimetric analysis of lignin in the atmosphere of nitrogen at the heating rate of 10 °C/min.

Figure S3. TEM images of Ni/ASA and its Ni particle size distributions, and SEM images of Ni/ASA. Ni/ASA-1 **(a, d)**, Ni/ASA-2 **(b, e)**, and Ni/ASA-3 **(c, f).**
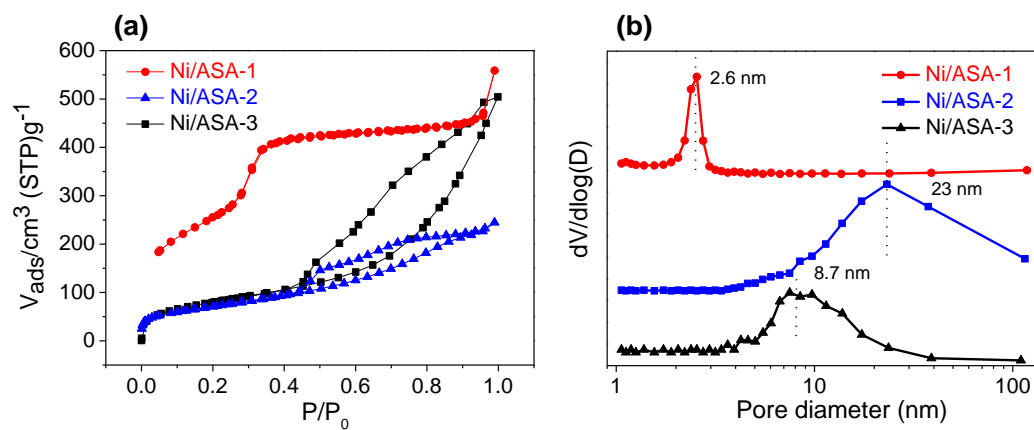
Figure S4. The nitrogen desorption data of three Ni/ASA catalysts. **(a)** The nitrogen adsorption-desorption curves; **(b)** the pore size distributions.
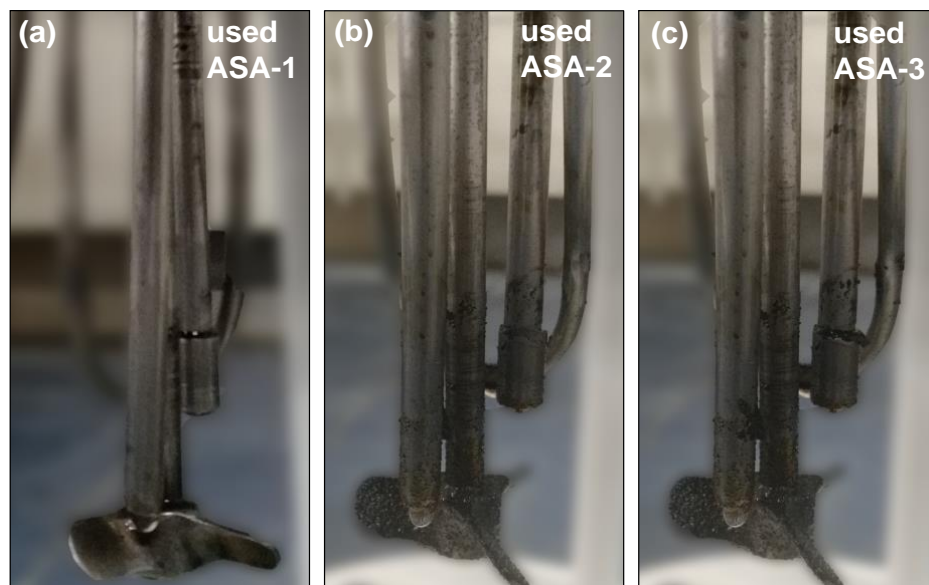
Figure S5. The coking state after reaction over Ni/ASA-1 **(a)**, Ni/ASA-2 **(b)**, and Ni/ASA-3 **(c)**. General conditions: lignin (4.0 g), Ni catalyst (0.5 g), 300 ˚C, 6 MPa H_2, dodecane (80 mL), 160 min., stirring at 700 rpm.
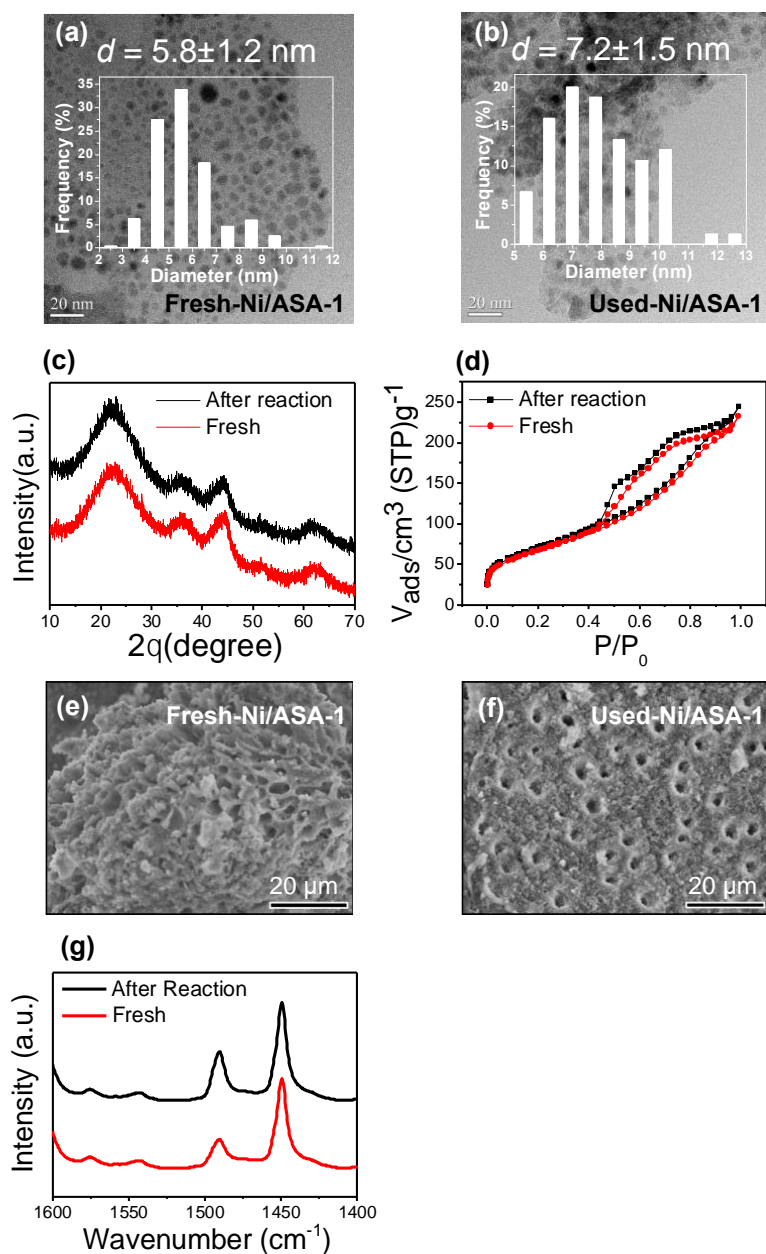
Figure S6. The characterizations of fresh Ni/ASA-1 and used Ni/ASA-1 for **(a, b)** TEM images, **(c)** XRD patterns, **(d)** N_2 adsorption and desorption isotherms, **(e, f)** SEM images, **(g)** The Brönsted and Lewis acids by the Py-IR.
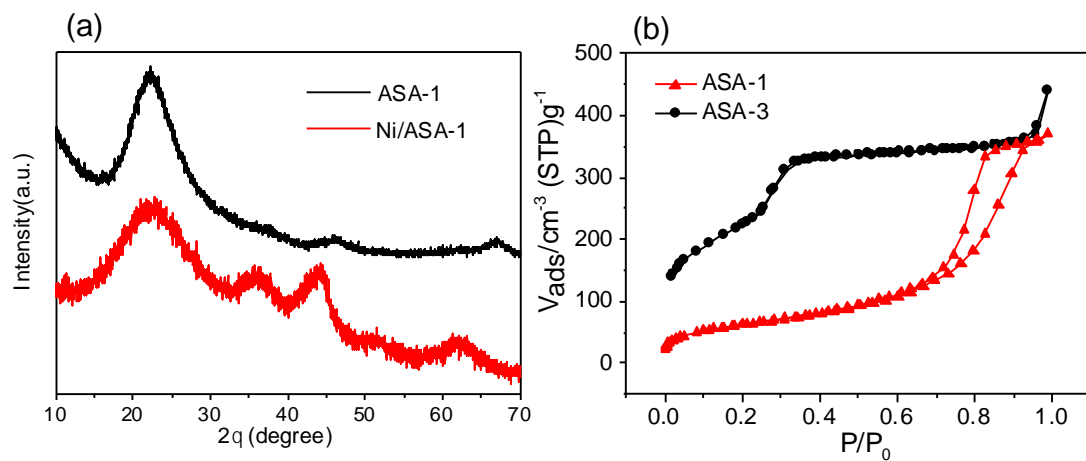
Figure S7. (**a**) XRD patterns of ASA-1 and Ni/ASA-1. (**b**) N_2 adsorption and desorption isotherms of ASA-1 and ASA-3.
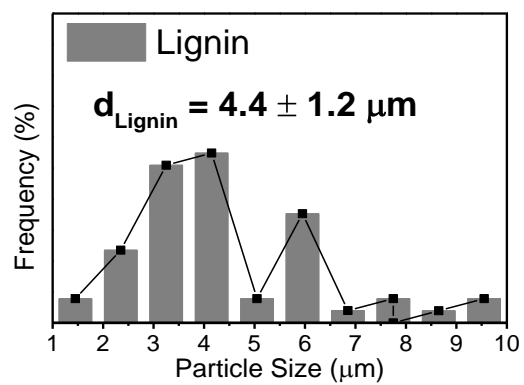
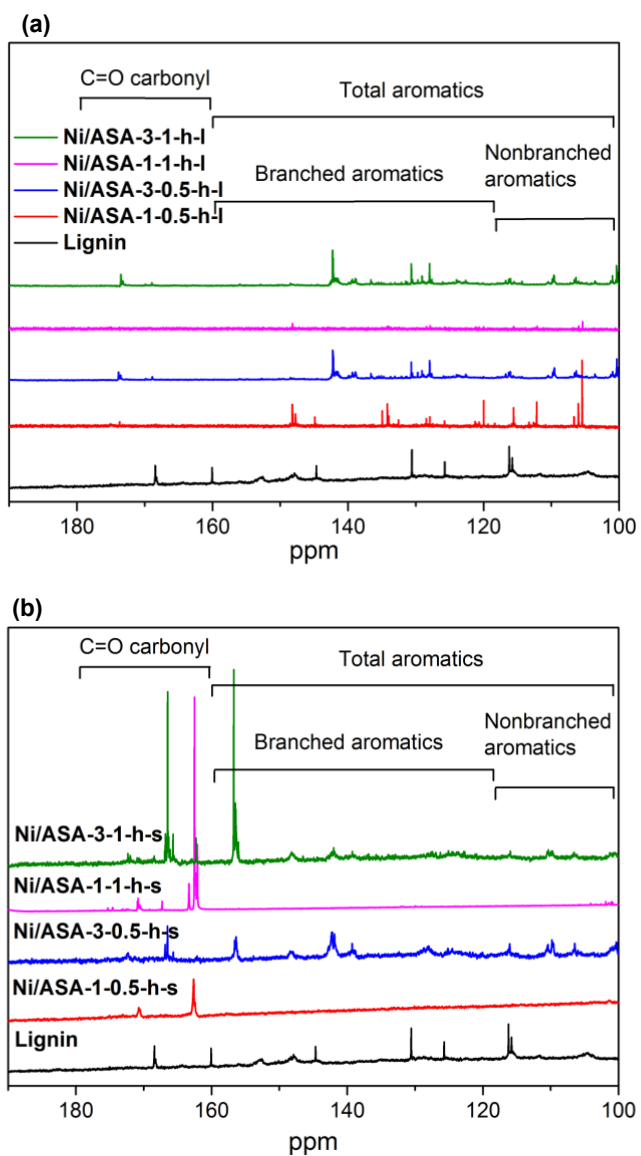**Figure S8.** The size distributions of lignin particles calculated from the SEM image.

Figure S9. ^{13}C NMR spectra of **(a)** lignin and the depolymerized liquid products and **(b)** lignin and the depolymerized solid products over Ni/ASA-1 and Ni/ASA-3.
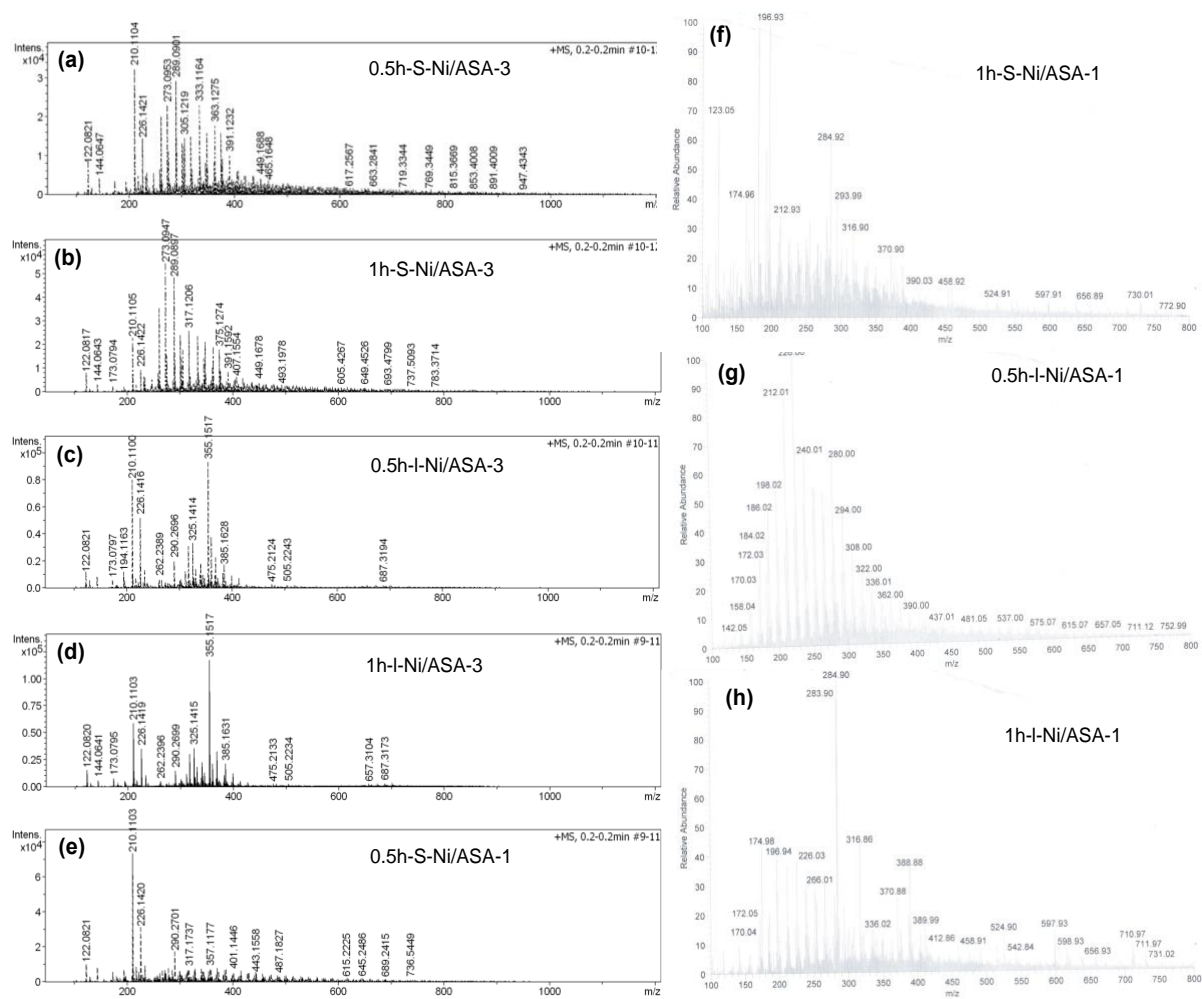
Figure S10. Molar mass of the solid residue after 0.5h reaction (0.5 h-s), the solid residue after 1h reaction (1.0 h-s), the liquid product after 0.5 h reaction (0.5 h-l), and the liquid product after 1h reaction (1.0 h-l) over Ni/ASA-3 (**a, b, c, d**) and Ni/ASA-1 (**e, f, g, h**), respectively, as detected by TOF-MS.

Table S1. 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 S2. The element composition and theoretical yield calculated from lignin.

	Theoretical yield: C_9H_{18} = 54.1 wt.%
$C_{10}H_{10.3}O_{3.8} \rightarrow C_9H_{7.3}O_{2.8}(OCH_3)_{1.0}$	
Lignin unit M_w = 191 g·mol^{-1}	
Assumed that it contains one $-OCH_3$ group in the lignin unit	H_2O = 32 wt.%
	CH_4 = 8.4 wt.%

Reference:

(1) Pettolino, F.A.; Walsh, C.; Fincher, G.B.; Bacic, A. Determining the polysaccharide composition of plant cell walls. *Nat. Protoc*, **2012**, *7*, 1590–1607.