Electronic Supplementary Information (ESI)

Ultrasound-Assisted Low-Temperature Catalytic Lignin-first Depolymerization of Pine Wood Biomass to Selectively Produce Propyl Guaiacol

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1. Feedstock Characterization

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1.1. Biochemical Composition Analysis of PW

The extractives-free PW was used to determine the glucans, xylans, acid-soluble lignin and acid-insoluble lignin following the NREL procedure (NREL/TP-510-42618).[1] The preparation of extractives-free biomass is given in the main manuscript (section 2.2.1). Typically, 0.3 g of extractives-free PW was taken in 3 mL of 72% H_2SO_4 and treated at 30 °C for 1 h. 84 mL of water was added to this solution, which resulted in 4% H_2SO_4, and it was further heated at 120 °C for 1 h. After cooling, the acid-treated solution was filtered using a Gooch crucible with sintered disc (G4) to obtain acid-insoluble residue. The filtrate contains acid-soluble lignin and cellulosic monomers. The cellulosic monomers, namely glucans and xylans were quantified using high-performance liquid chromatograph (HPLC) after neutralizing the acid solution using calcium carbonate. The HPLC (Shimadzu 2020) equipped with an amine column (Shim Pack GIST, 250 mm length x 4.6 mm I.D. and 5 μm thickness) was used to quantify the sugar monomers. The mobile phase (CH_3CN: H_2O; 75:25 v/v) was used at 1 mL min^{-1} flow rate with 40 °C column temperature. The refractive index detector was set at 40 °C. The acid-soluble lignin was quantified using UV-Visible spectrometer at 205 nm. Besides, acid-insoluble residue was heated at 575 °C for 18 h to obtain inorganic ash. The amount of acid-insoluble lignin (Klason lignin) was then calculated by subtracting the amount of ash obtained from the acid-insoluble residue that was initially taken.

1.2. Pyrolysis-Gas Chromatograph-Mass Spectrometry (Py-GC/MS) of Klason lignin

The constituents of the Klason lignin were analysed by the means of Py-GC/MS. Pyrolysis of Klason lignin was performed at 500 °C in a Curie point pyrolyzer (JHI-07, Japan Analytical Industry Co.). A microbalance (RADWAG) was used to weigh 0.3 mg of Klason lignin in the Pyrofoil, which was then placed inside a coil of high-frequency oscillator producing an oscillating magnetic field. The induced eddy current generated due to the the oscillating magnetic field causes an increase in the temperature of the pyrofoil until it reaches its rated Curie point temperature. Typically, the heating reate of the sample is ~1000 °C s^{-1}. Further details of the Curie point pyrolyzer are given in Priyadarshi and Vinu.[2] The pyrolysates were analysed in GC/MS with RESTEK, Rxi®-5SIL MS column (30 m length, 0.25 mm i.d., 0.25 μm film thickness). The GC column was maintained at 50 °C for 1 min, then heated to 250 °C at a heating rate of 5 °C min^{-1}. The column was held at 250 °C for 8 min. The temperatures of the injector, interface and the detector were 300 °C, 280°C and 250 °C, respectively. The split ratio was 1:100. The compounds were scanned in the m/z range of 50–500 Da at 70 eV electron ionization voltage. The mass spectra of individual compounds were compared with the NIST library and those with a match factor >85% were considered for semi-quantitative analysis.

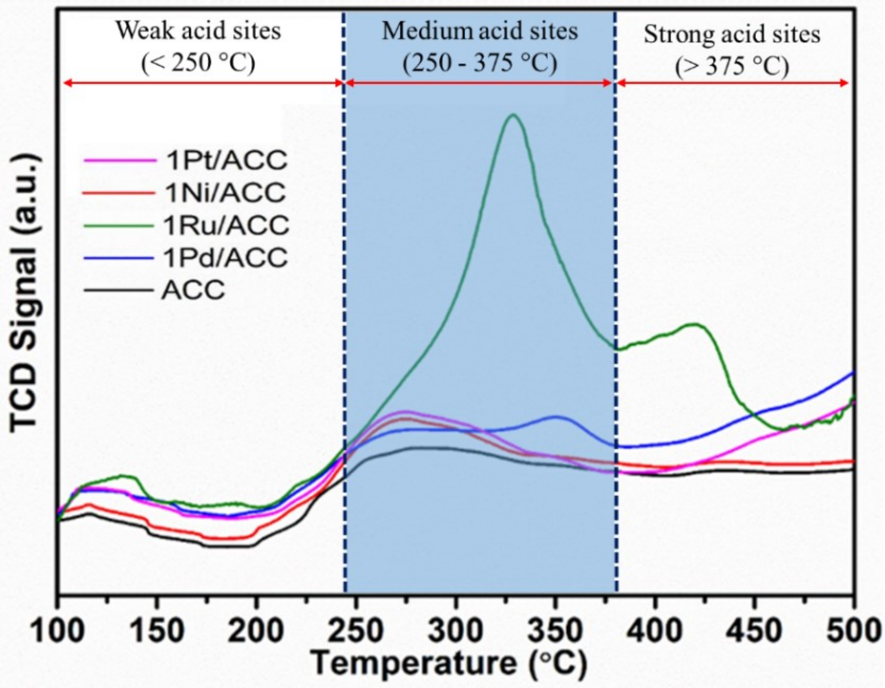

Fig. S1. NH_3-TPD profiles of the support and metal-loaded catalysts.

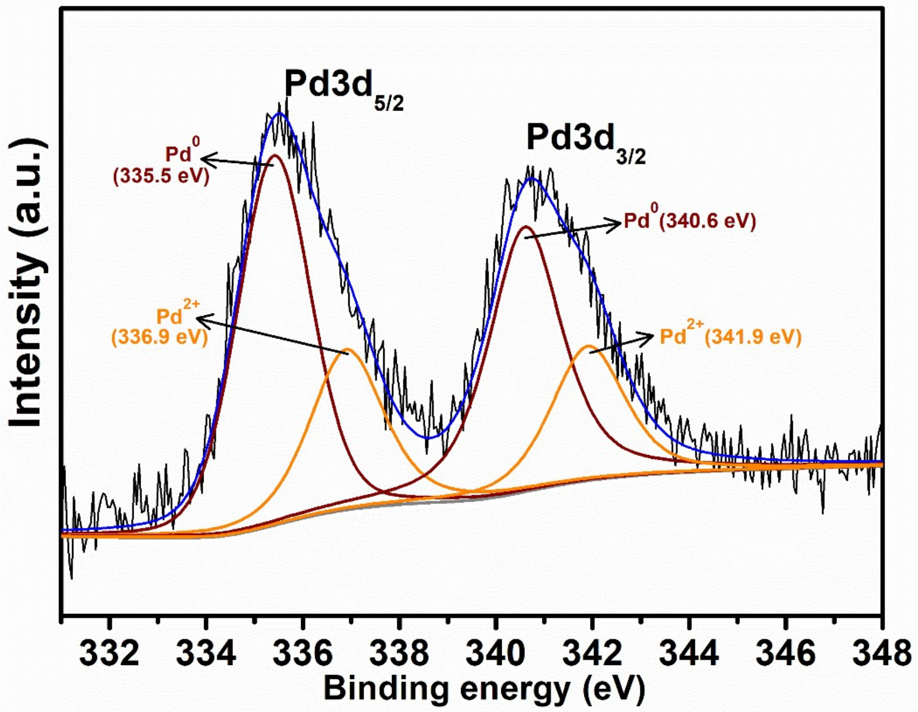

Fig. S2. XPS of Pd3d in 1Pd/ACC catalyst.

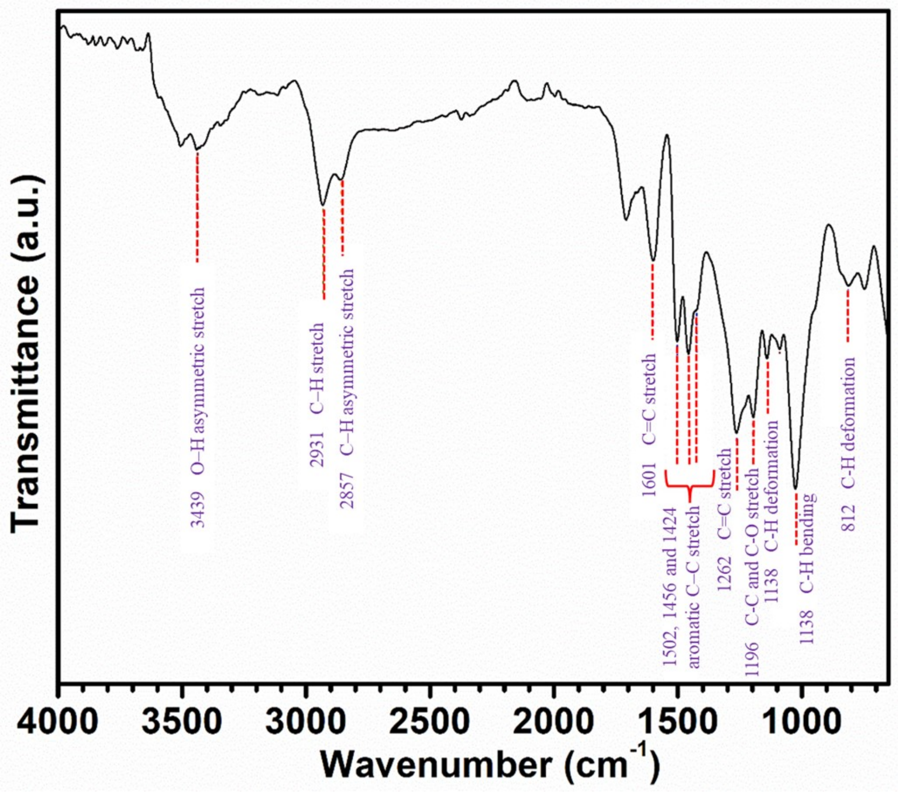

Fig. S3. FTIR spectrum of Klason lignin.

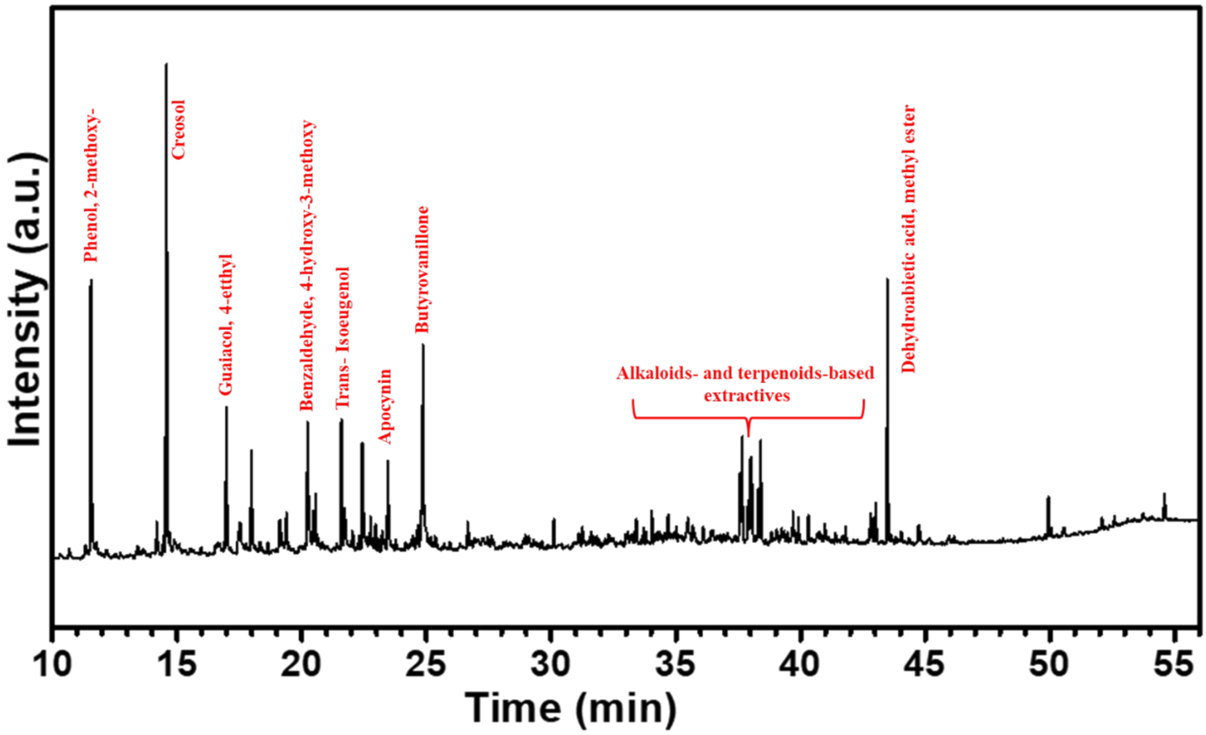

Fig. S4. Py-GC/MS of Klason lignin at 500 °C.

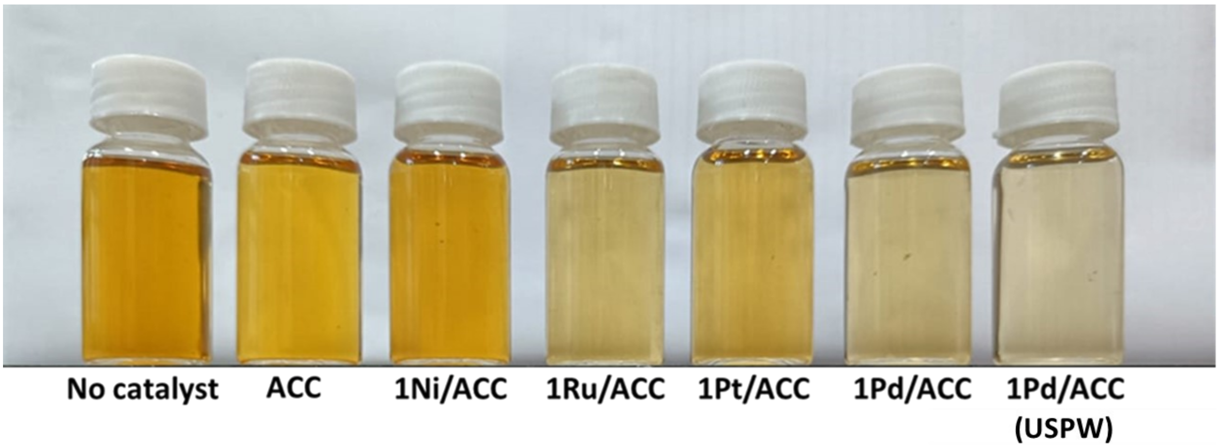

Fig. S5. Snapshot showing the colour change of lignin monomer oil obtained using different catalysts.

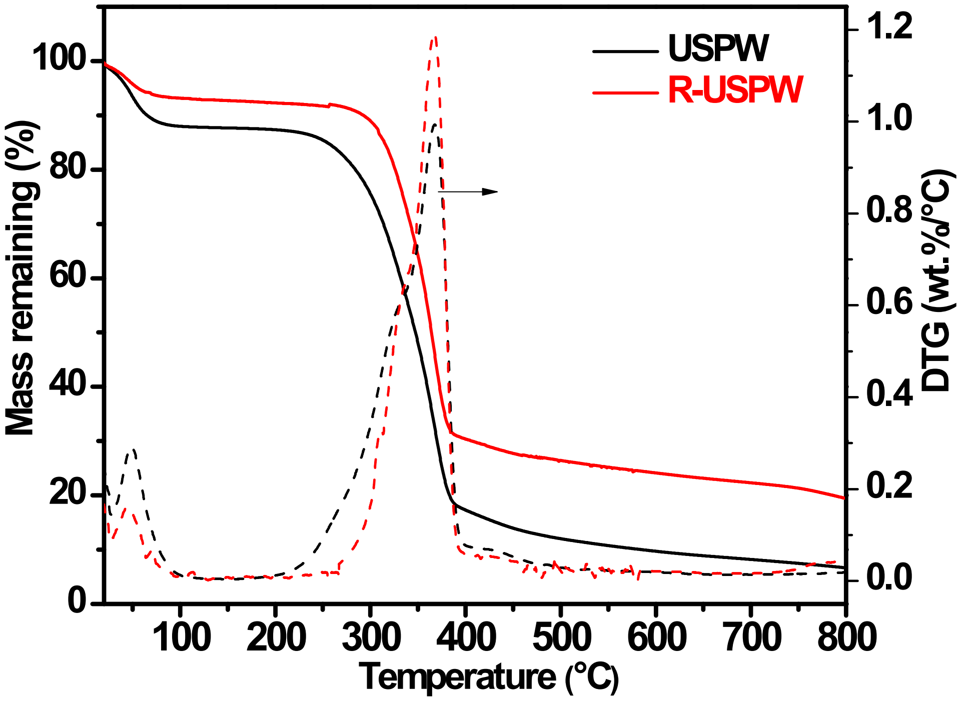

Fig. S6. Thermogravimetric analysis of USPW and the solid pulp obtained from the Pd/ACC catalyzed RCF of USPW.

Table S1. Pyrolysate composition from Klason lignin at 500 °C.

Entry	**Compound name**	**Formula**	**Relative area %**
	Guaiacyl-based compounds		
1	Phenol, 2-methoxy-	$C_7H_8O_2$	8.6
2	Creosol	$C_8H_{10}O_2$	12.4
3	Guaiacol, 4-ethyl-	$C_9H_{12}O_2$	3.8
4	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	2.8
5	3-Allyl-6-methoxyphenol	$C_{10}H_{12}O_2$	0.8
6	Phenol, 2-methoxy-4-propyl-	$C_{10}H_{14}O_2$	1.3
7	4-Hydroxy-3-methoxy-benzaldehyde	$C_8H_8O_3$	4.1
8	Trans-Isoeugenol	$C_{10}H_{12}O_2$	3.9
9	Phenol, 2-methoxy-4-propyl-	$C_{10}H_{14}O_2$	1.1
10	Phenol, 2-methoxy-4-(1-propenyl)-	$C_{10}H_{12}O_2$	0.6
11	acetovanillone	$C_9H_{10}O_3$	3.3
12	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	$C_9H_{10}O_4$	0.5
13	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_{10}H_{12}O_3$	2.4

14	Acetosyringone	$C_{11}H_{14}O_5$	0.9
15	Butyrovanillone	$C_{11}H_{14}O_3$	5.9
	Hydroxyl-based compounds		
16	1,2-Benzenediol, 4-methyl-	$C_7H_8O_2$	0.6
	Alkaloids- and terpenoids-based extractive compounds		
17	1H-Indene, 3-ethenyl-2,3-dihydro-1,1-dimethyl-	$C_{13}H_{16}$	1.1
18	7-Methoxy-1-naphthol	$C_{11}H_{10}O_2$	0.7
19	2-Propen-1-one, 3-(4-methylphenyl)-1-phenyl-	$C_{16}H_{14}$	0.5
20	Phenanthrene, 2,3,4,4a,9,10-hexahydro-1,4a-dimethyl-7-(1-methylethyl)-, (s)-	$C_{19}H_{26}$	0.6
21	Methyl isopropyl phenanthrene	$C_{18}H_{18}$	1.9
22	Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-1,1,4a-trimethyl-7-(1-methylethyl)-, (4as-trans)-	$C_{20}H_{30}$	4.9
23	4-epi-Dehydroabietinol acetate	$C_{22}H_{32}O$	3.2
24	Simonellite	$C_{19}H_{24}$	1.2
25	Dehydroabietic acid	$C_{20}H_{28}O_2$	0.7
26	17-Methylandrosta-5,7,9(11)-trien-17-ol acetate	$C_{22}H_{32}O_2$	0.6
27	8-Isopropyl-1,3-dimethylphenanthrene	$C_{19}H_{20}$	0.8
28	Dibenz[d,f]cycloheptanone, 2,3,9-trimethoxy-	$C_{18}H_{18}O_4$	1
29	Dehydroabietic acid, methyl ester	$C_{21}H_{30}O_2$	6.1
30	2,2'-(Alpha-methylbenzylidene)bis(5-methylfuran)	$C_{18}H_{18}O_2$	0.6
	Fatty acid-based extractive compounds		
31	1-Dodecanol	$C_{12}H_{26}O$	0.6
32	1-Tridecene	$C_{13}H_{26}$	0.6
33	1-Pentadecene	$C_{15}H_{30}$	1
34	Hexadecane	$C_{16}H_{34}$	0.8
35	11-Methyltricosane	$C_{24}H_{50}$	0.6
36	Hexadecanal	$C_{16}H_{32}O$	0.6
37	5β-cholestan-3α-ol, methyl ether	$C_{28}H_{50}O$	1
38	Cholesta-3,5-dien-7-one	$C_{27}H_{42}O$	0.7
	Others		
39	1,5-Cyclooctadiene, 3,4,7,8-tetrakis(1-methylethylidene)-	$C_{20}H_{28}$	1.1
40	Harmol, bis(ethyl)-	$C_{16}H_{18}N_2O$	0.7

Reference

1 A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, and D. Crocker, *NREL-Protocols* (NREL/TP-510-42618), 2008, 1–18.

2 S. Priyadarshi and R. Vinu, *Energy Fuels*, 2022, **36**, 12144–12159.