## Fractionation of woody biomass at mild conditions using bifunctional phenol-4-sulfonic acid as catalyst and lignin solvent

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Fig. S1 Photos of poplar chips.



**Fig. S2** Correlation between the adsorbed amount of the aqueous 72% PSA solution and poplar chip weight.



Fig. S3 Disintegration of softened poplar chip using a glass rod.



Fig. S4 Bleaching of cellulose fibres using alkali hydrogen peroxide.



Fig. S5 Effects of the PSA concentration on the proton concentration and the lignin isolation.



Fig. S6 Effect of the PSA/poplar (oven dry) weight ratio on the lignin isolation.



Fig. S7 Effect of the PSA/phenol weight ratio on the lignin isolation.



**Fig. S8** Effect of the length of poplar chip (width: 1.5 cm, thickness: 0.3 cm) on its lignin isolation by PSA (60 °C, 2 h, PSA/poplar chip=19).



**Fig. S9** Effect of the thickness of poplar chip (length: 1.5 cm, width: 1.5 cm) on its lignin isolation by PSA (60 °C, 2 h, PSA/poplar chip=19).



**Fig. S10** Effect of the width of poplar chip (length: 1.5 cm, thickness: 0.3 cm) on its lignin isolation by PSA (60 °C, 2 h, PSA/poplar chip=19).



Fig. S11 Fractionation of a larger poplar chip by PSA.



**Fig. S12** Manual disintegration (at the defibration point) vs magnetic stirring (at 200 rpm) for the lignin isolation during fractionation of poplar chip at 60 °C.



Fig. S13 Photos of birch and pine chips and their lignin isolations by PSA.



**Fig. S14** Photos of fractionated poplar slices by sulfuric acid with different concentrations at 60 °C for 2 h. A: 0.8 M, B: 1.6 M, C: 2.4 M, D: 3.2 M, E: 4 M, F: 4.8 M, G: 5.6 M, H: 7.2 M.



**Fig. S15** Optical microscope photos of microcrystalline cellulose powder (Avicel) and cellulose fibres (CF) after incubated with the aqueous 72% PSA solution at 60 °C for 2 h.







Fig. S16 Colour development of lignin under varied fractionation conditions.



Fig. S17 Schematic illustration of the reactions of PSA with lignin.



Fig. S18 Partial charge diagram of phenol.



Fig. S19 Partial charge diagram of PSA.



Fig. S20 Partial charge diagram of ethanol.



Fig. S21 Photos of fresh and spent PSA.



Fig. S22 Electrostatic potential surface diagram of PSA.