Electronic Supplementary Information

Maleic acid as a dicarboxylic acid hydrotrope for green fractionation of wood at atmospheric pressure and ≤ 100 °C: Mode and utility of lignin esterification

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Calculations

1. Calculation of substrate enzymatic digestibility (SED):

$$SED = c_{glucose} \times 0.05 \times 0.9 / m_{glucan} \times 100\%$$

Here, $c_{glucose}$ is the concentration of glucose in hydrolysate, 0.05 (L) is the volume of hydrolysate, 0.9 is the mass conversion factor between glucan and glucose, m_{glucan} is the mass of glucan in substrate.

2 Calculation of furfural yield:

$$\text{Total furfural yield} = (c_1 \times 0.02 + c_2 \times 0.01) \times 50/15 \times 1.375/(3 \times 0.2299 \times 0.69) \times 100\%$$

$$\text{Pure furfural yield} = (c_1 \times 0.02) \times 50/15 \times 1.375/(3 \times 0.2299 \times 0.69) \times 100\%$$

Here, c_1 is the concentration of furfural in the distillate, c_2 is the concentration of furfural in the dehydrated fractionation liquor, 0.02 (L) and 0.01 (L) is the volume of the distillate and the dehydrated fractionation liquor, respectively. 50/15 is the dilution factor of fractionation liquid to precipitate lignin. 1.375 is the mass conversion factor between xylan and furfural, 3×0.2299×0.69 (g) is the mass of dissolved xylan in spent liquid.

3 Calculation of syringyl and guaiacyl and of interunit linkages:

The total aromatic areas are defined as:

$$I(C9) = 0.5 \times I(S_{2,6}) + 0.5 \times I(S'_{2,6}) + I(S_{cond}) + I(G_2).$$

The content of internal linkages are calculated as:

$$\beta\text{-O-4} = 100 \times [I(\beta\text{-O-4})]/[I(C9)];$$

$$\beta\text{-}\beta = 100 \times [I(\beta\text{-}\beta)]/[I(C9)];$$

$$\beta\text{-5} = 100 \times [I(\beta\text{-5})]/[I(C9)].$$

Content of aromatic units are relative (%):

$$S = 100 \times 0.5 \times [I(S_{2,6})]/[I(C9)];$$

$$S' = 100 \times 0.5 \times [I(S'_{2,6})]/[I(C9)];$$

$$S_{cond} = 100 \times [I(S^*)]/[I(C9)];$$

$$G = 100 \times [I(G_2)]/[I(C9)];$$

The S/G ratio is defined as:

$$S/G = (S + S' + S_{cond})/G.$$

Here, *I* is the integrated area of the crosspeaks in HSQC spectra. Although 2D HSQC are not inherently quantitative, the analysis provides semi-quantitative information about relative quantities of various functionalities based on per 100 Ar units.

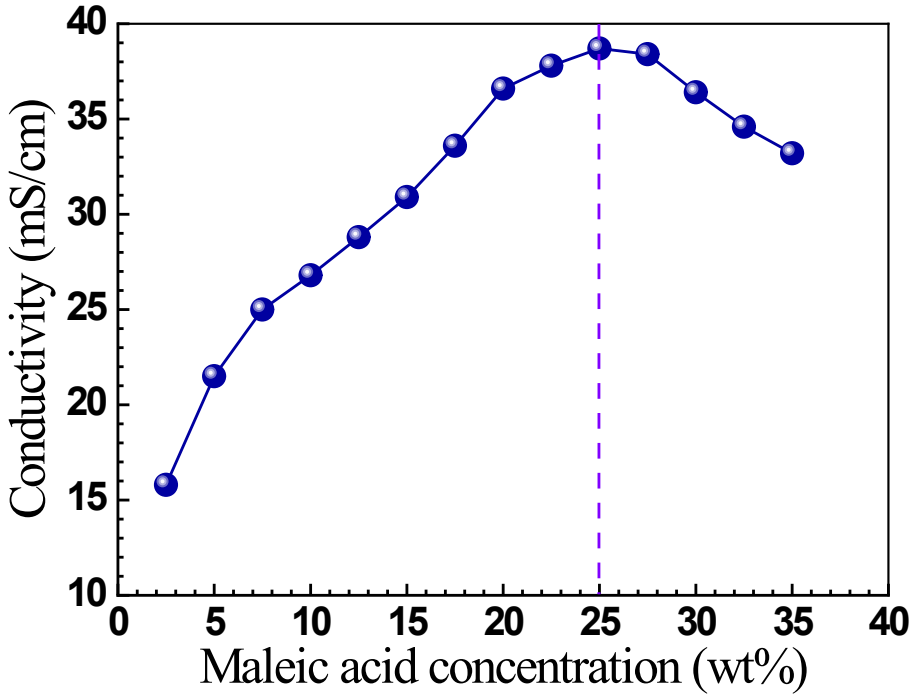

Figure S1. Conductivity of aqueous maleic acid solution as a function of concentration to determine minimal acid concentration.

Figure S2. Stability of aqueous dispersion of LCNFs at 0.2% after standing for two weeks at 4 °C

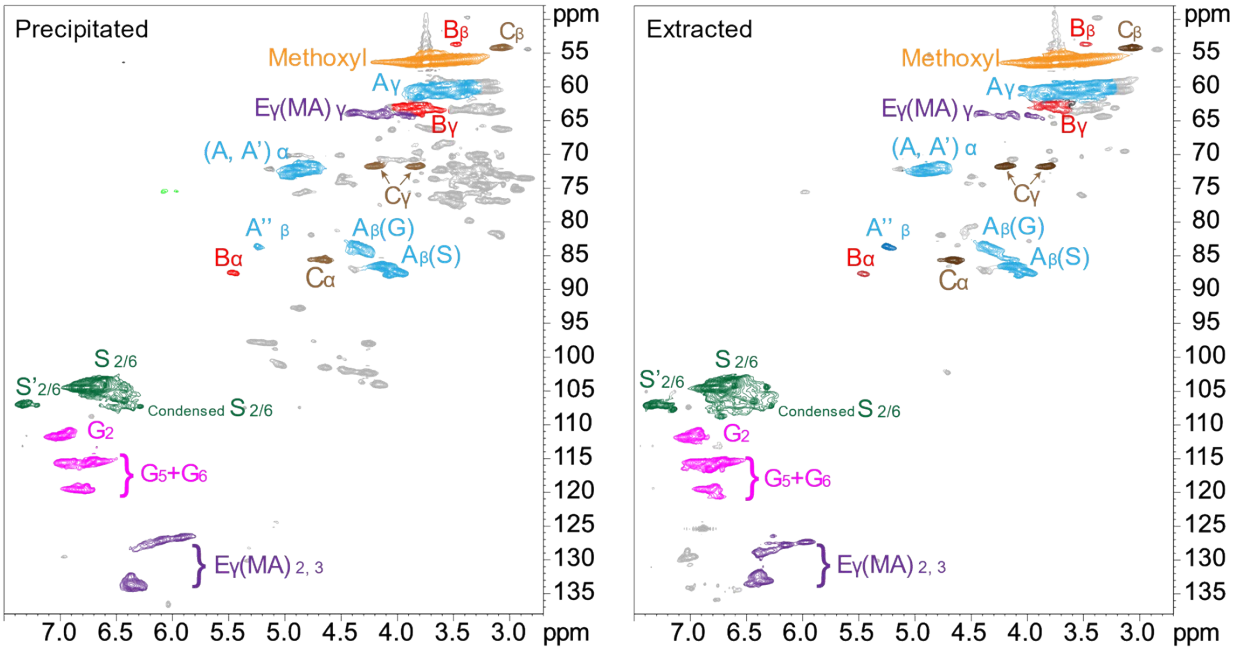

Figure S3. Compariosn of chemical structure of dilution precipitated lignin (left panel) with that of pentanol extratced lignin (right panel) form run M50T100t30 through 2-D NMR HSQC analysis

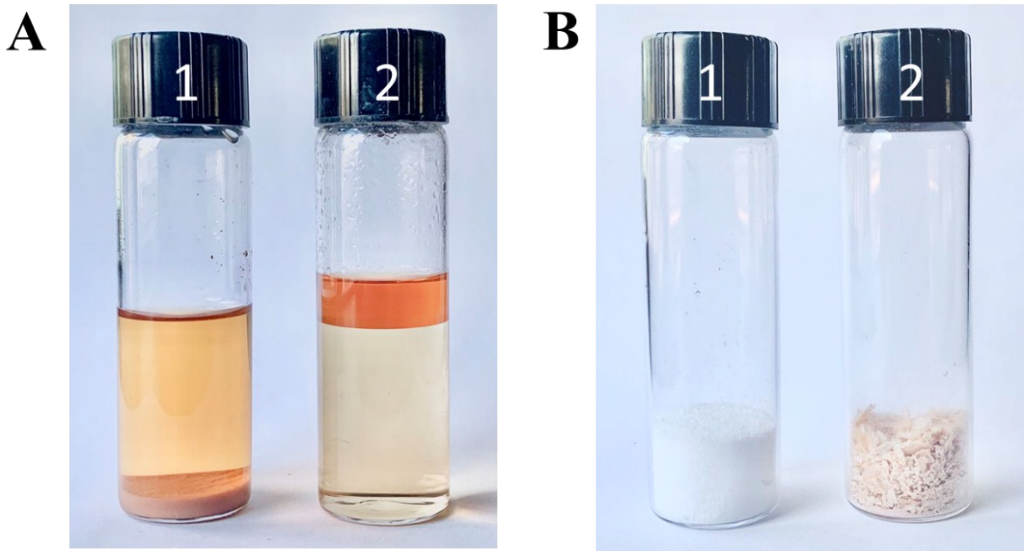

Figure S4. A1: The spent liquor of M50T100t30 diluted to MA concentration 15 wt% to precipitate lignin; A2: After removing precipitated lignin through centrifuging and added 20% (v/v) of n-pentanol to extract remaining dissolved lignin. B1: Fresh MA; B2: MA obtained by evaporating water in the dehydrated fractionation liquor for recycle and reuse.

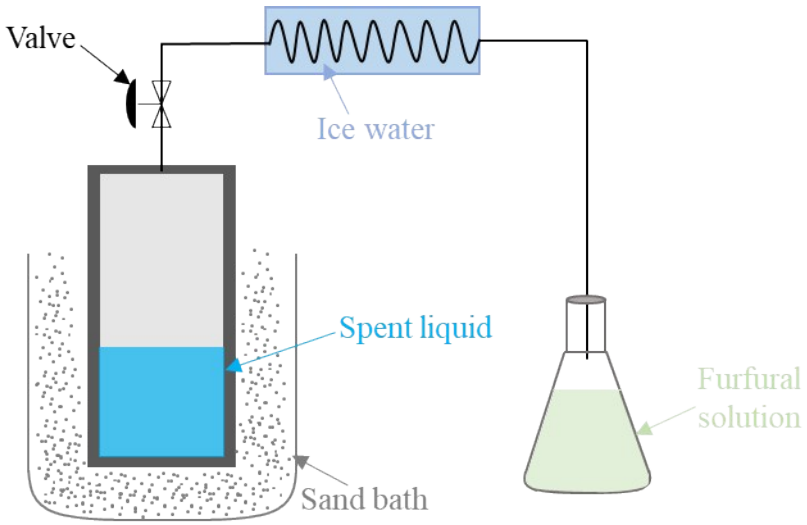

Figure S5. Fractionation liquid after removing lignin is subjected to reactive distillation to dehydrate xylose into furfural and to recycle MA.

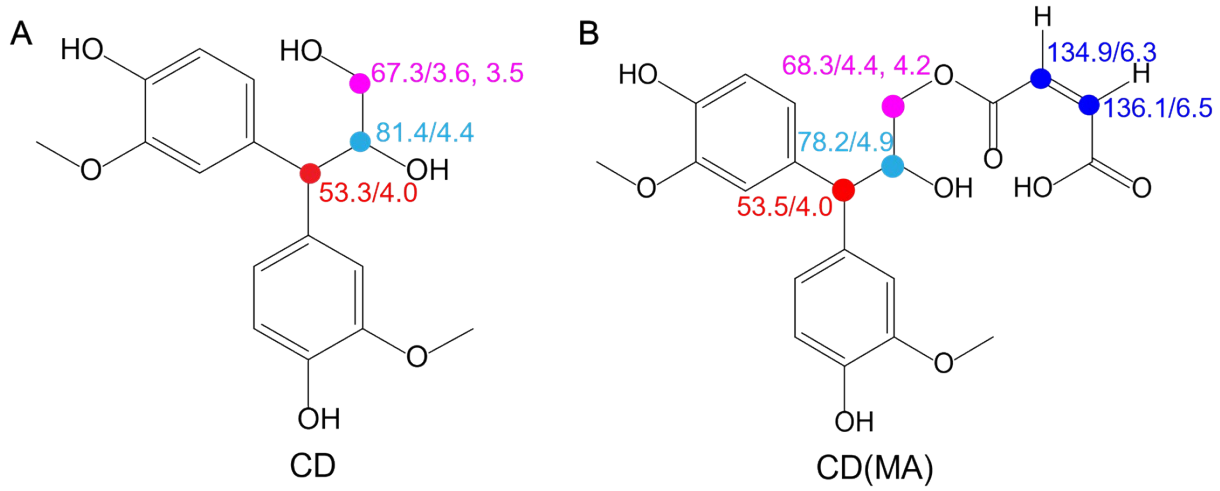

Figure S6. Prediction of ^{13}C and ^{1}H NMR shifts of Eγ and Eγ(MA) by ChemBioDraw Ultra 14.0.

Table S1 Chemical composition of MAHF fractionated WIS and their corresponding fractionation liquors under different conditions. The numbers if the parenthesis are percentages of the component retained in WIS or percentages of wood xylan converted to xylose.

Sample	WISs[1]				Spent liquor		
	Solids Yield (%)	Klason Lignin (%)	Glucan (%)	Xylan (%)	Glucose (g/L)	Xylose (g/L)	Acetic acid (g/L)
Birch		19.5	39.96	22.99			
M50T80t60	76.4	19.3 (75.4)	48.8 (93.3)	19.3 (64.0)	0.26	2.93 (11.2)	1.34
M60T80t60	71.9	18.5 (68.1)	48.5 (87.2)	18.0 (56.4)	0.35	6.15 (23.5)	1.43
M70T80t60	66.0	15.9 (53.8)	52.2 (86.3)	14.8 (42.5)	0.36	12.5 (47.9)	1.69
M50T90t60	65.7	18.4 (61.9)	51.5 (84.6)	15.6 (44.5)	0.41	4.74 (18.1)	2.05
M60T90t30	64.0	15.8 (51.9)	55.3 (88.6)	14.0 (39.0)	0.68	9.73 (37.2)	1.67
M50T100t30	64.7	15.4 (51.5)	58.4 (94.5)	11.0 (31.0)	0.20	9.46 (36.2)	2.68
M50T100t60	56.4	17.5 (50.6)	59.2 (83.5)	12.2 (29.9)	0.75	16.8 (64.4)	3.31
M50T100t90	57.5	16.0 (47.2)	58.1 (83.6)	10.7 (26.8)	0.79	16.9 (64.7)	3.20
M50T100t120	54.3	16.0 (44.6)	57.8 (78.6)	11.8 (27.9)	0.98	17.2 (65.8)	3.20
M70T100t15	60.3	17.7 (54.7)	58.6 (88.2)	11.5 (30.1)	0.46	13.2 (50.3)	1.72

Table S2 Comparison of maleic acid hydrotropic fractionation to other pretreatment methods for enzymatic saccharification of wood.

Wood	Fractionation condition	Xylan; lignin removal (%)	Enzyme loading (FPU/per g glucan)	Substrate enzymatic digestibility (SED) @ 72 h (%)	Method and Source
Birch fibers	Maleic acid = 50 wt% T = 100 °C t = 60 min	70 ; 49	CTec 3 = 10 (or 6 FPU/g solids)	89 ± 3	Maleic Acid Hydrotrope This study
Poplar NE222 fibers	*p*-TsOH = 50 wt% T = 90 °C t = 112 min	80 ; 84	CTec 3 = 20	93 ± 2	Aromatic Acid Hydrotrope [1]
Poplar NE222 fibers	*p*-TsOH = 75 wt% T = 80 °C t = 20 min	81 ; 86	CTec 3 = 10 20	59 87	Aromatic acid Hydrotrope [2]
Birch particles (2 mm)	Acetone = 50 wt% + H_2SO_4 @ 3.9 g/L T = 140 °C t = 120 min	92 ; 86	Accelerase TRIO = 14 (or 10 FPU/g solids)	~ 90	Acetone Organosolv [3]
Birch chips	Na_2CO_3 = 26.5 g/L T = 120 °C t = 1200 min Steam H_2SO_4 = 5 g/L T = 200 °C t = 5 min	~100 ; NA ~100 ; NA	Celluclast 1.5 L = 10 FPU/g solids + Novozymes 188	~ 95 ~ 95	Alkaline Oxidation & Steam Explosion [4]
Poplar NE222 chips	T = 160 °C; t = 58 min H_2SO_4 = 0.2 %; @ $NaHSO_3$ = 0 % (Dilute acid) @ $NaHSO_3$ = 1.3 % (SPORL)	78 ; 3 84 ; 31	CTec 3 = 10	52 80	SPORL & Dilute Acid [5]

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