Supplementary Information

Low-pressure flow-through fractionation of *Quercus mongolica* for highly selective cellulose and reactive lignin recovery: a lignocellulosic biorefinery approach

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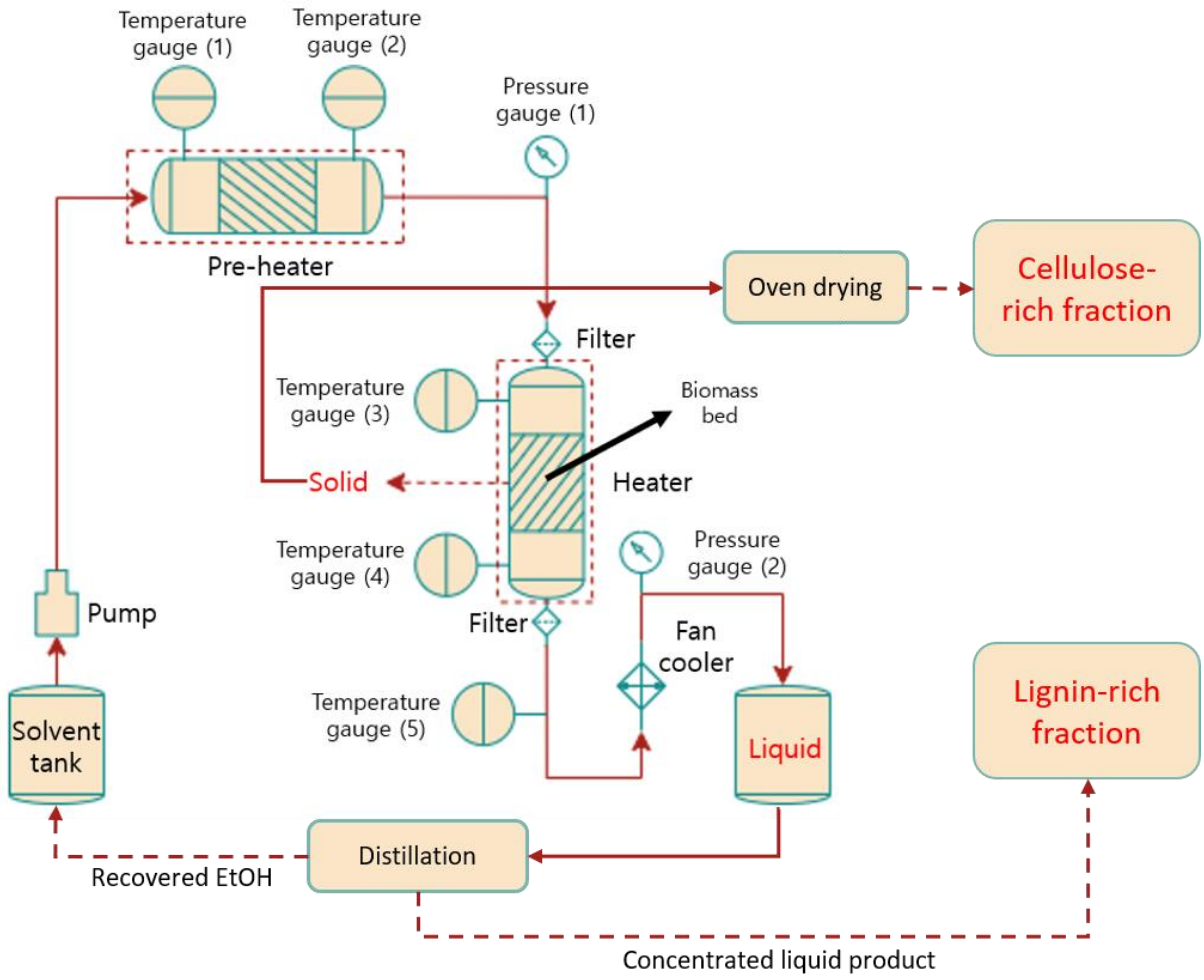


Figure S1. Reactor setup for low-pressure flow-through fractionation.

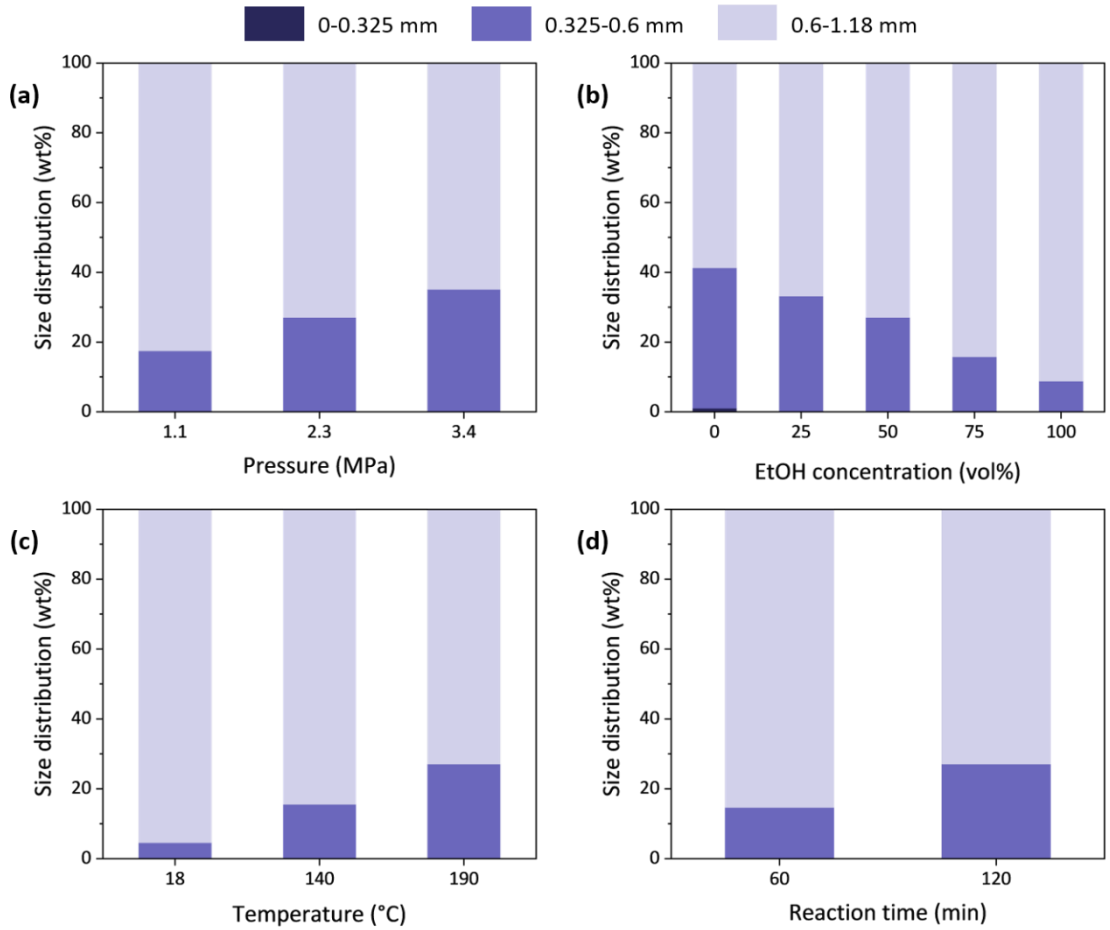
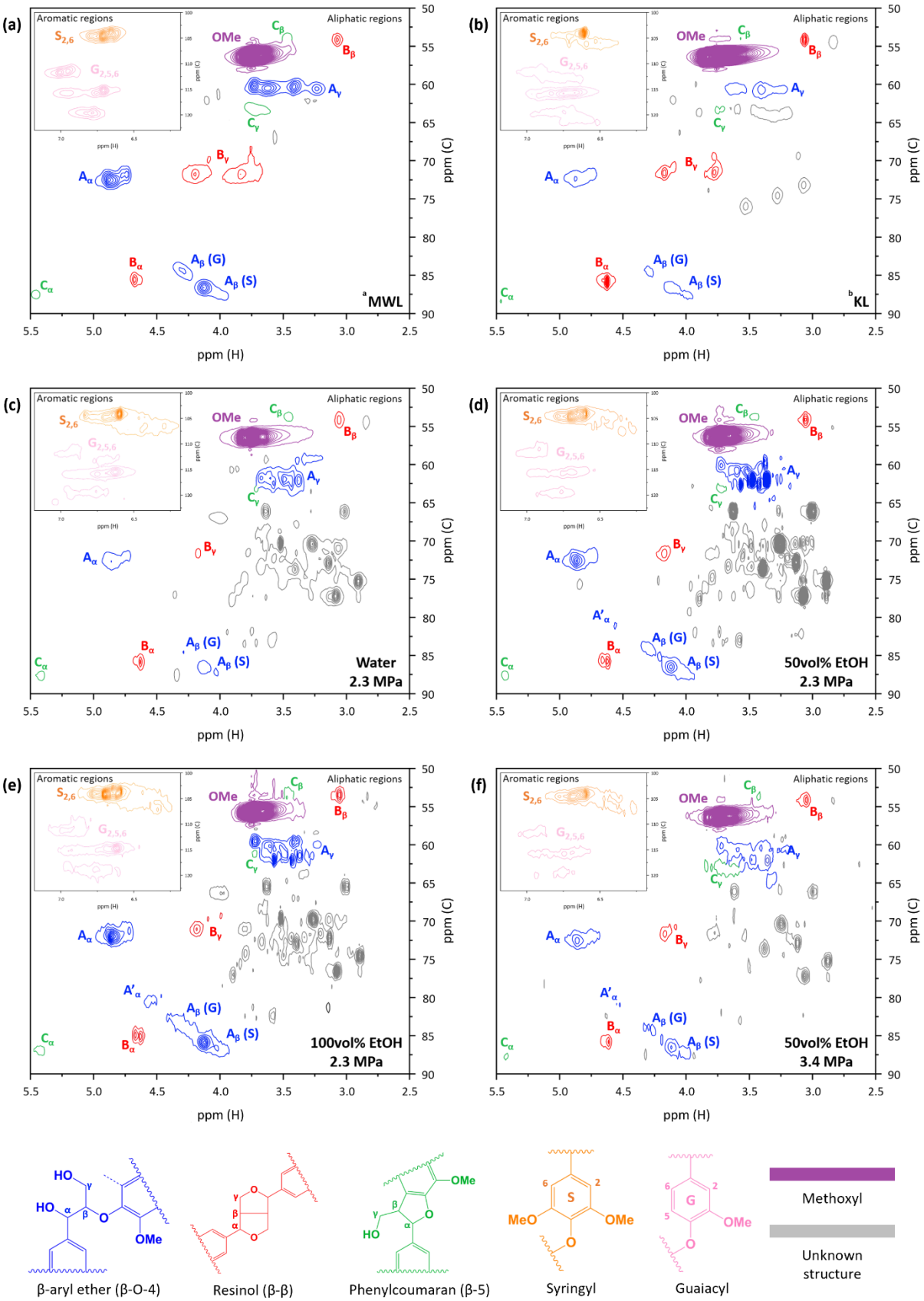


Figure S2. Particle size distribution of the cellulosic product from organosolv flow-through fractionation as a function of (a) pressure, (b) solvent concentration, (c) temperature, and (d) reaction time.


(a)
Aromatic regions
Aliphatic regions
OMe
C_β
B_β
A_γ
C_γ
B_γ
A_α
B_α
A_β (G)
A_β (S)
C_α
[a]MWL
(b)
[b]KL
(c)
Water
2.3 MPa
(d)
50vol% EtOH
2.3 MPa
(e)
100vol% EtOH
2.3 MPa
(f)
50vol% EtOH
3.4 MPa
ppm (H)
ppm (C)

β-aryl ether (β-O-4)
Resinol (β-β)
Phenylcoumaran (β-5)
Syringyl
Guaiacyl
Methoxyl
Unknown structure

Figure S3. 2D-HSQC NMR spectra of (a) MWL[a], (b) KL[b], and fractionated lignin with (c) water (2.3 MPa), (d) 50vol% EtOH (2.3 MPa), (e) 100vol% EtOH (2.3 MPa), and (f) 50vol% EtOH (3.4 MPa). [a]Milled wood lignin; [b]Kraft lignin

The primary signals were assigned based on the literature,[29,50] and the detected linkages are depicted above (Fig. S3), including the inter-unit linkages β-O-4 aryl ether (A), resinol (β–β, B), and phenylcoumaran (β-5, C). The cross-signals of C_α–H_α in the β-O-4 substructure are explicitly located at δ_C/δ_H 72.5/4.87. The cross-signals at δ_C/δ_H 84.3/4.30 and 86.6/4.12 are attributed to C_β–H_β correlations linked to G and S units in the β-O-4 substructure, respectively. Meanwhile, the resinol (β–β, B) signals were also detected, and the C_α–H_α, C_β–H_β, and C_γ–H_γ correlations were observed at δ_C/δ_H 85.6/4.67, 54.1/3.07, 71.7/4.19, and 3.83, respectively. Moreover, the phenylcoumaran (β-5, C) signals were found at C_α–H_α (δ_C/δ_H 87.5/5.45), C_β–H_β (δ_C/δ_H 53.7/3.46), and C_γ–H_γ (δ_C/δ_H 57.9/3.75).

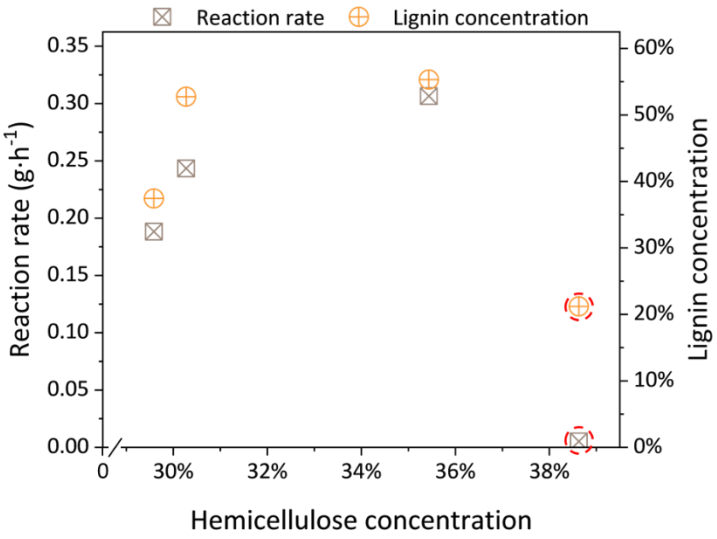


Figure S4. Enzymatic hydrolysis rate of hemicellulose in lignin-rich fraction.

Table S1. Comparison of fractionation results from the existing literature.

Biomass Sources	System	Solvent	Catalyst	Pressure	Temperature	Duration	Delignification (%)	Total β-O-4	References
Willow wood	Batch	94 wt% EtOH	-	-	190 °C	180 mins	39.6	-	[14]
Wheat straw	Batch	60 vol% EtOH	30 mM H_2SO_4	-	190 °C	60 mins	75.8	-	[10]
Poplar	Batch	60 vol% EtOH	1.25 wt% H_2SO_4	-	180 °C	60 mins	84.0	2.0	[28]
Eucalyptus residues	Batch	50 vol% EtOH	1,000 mM H_2SO_4	-	190 °C	120 mins	79.0	-	[11]
Pinus radiata	Batch	50 vol% EtOH	-	-	210 °C	75 mins	81.8	-	[15]
Pinus taeda	Flow-through	50 vol% EtOH	-	19.0 MPa	170 °C	120 mins	84.9	-	[35]
Corn stover	Flow-through	H_2O	-	2.5 MPa	190 °C	30 mins	75.0	-	[31]
Beech wood	Flow-through	95 vol% EtOH	180 mM H_2SO_4	0.6 MPa	120 °C	120 mins	73.0	43.0	[6]
Quercus mongolica	Flow-through	50 vol% EtOH	-	2.3 MPa	190 °C	120 mins	87.9	20.8	**This study**