

Supplementary Materials

Poplar Lignin structural changes during extraction in γ -valerolactone (GVL)

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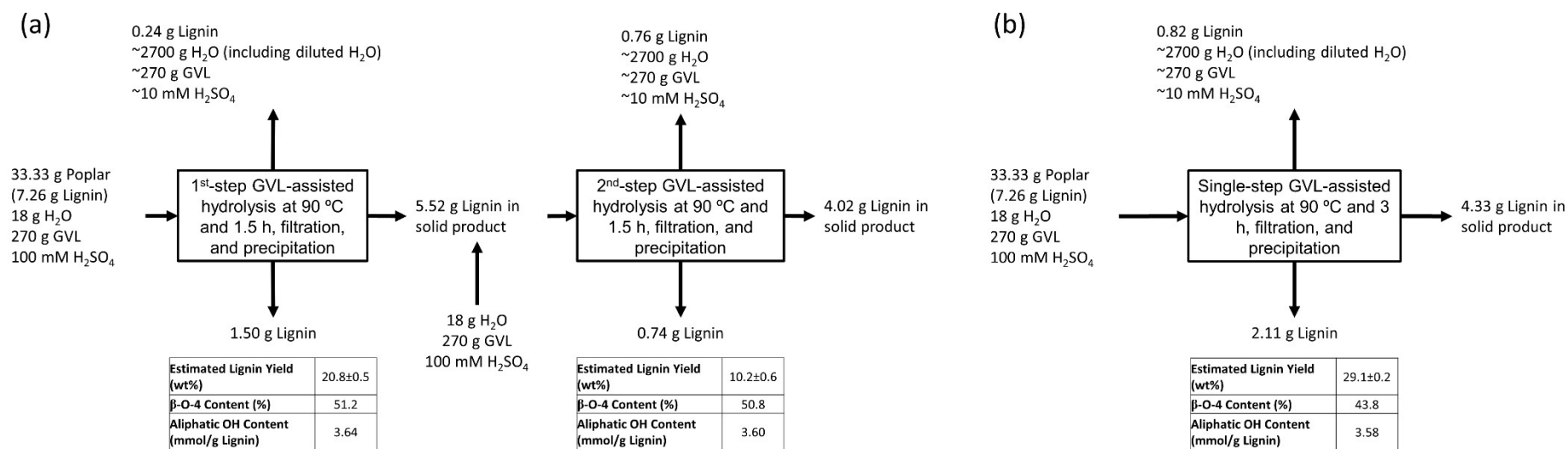


Figure S1. Process flow diagram of poplar GVL-assisted hydrolysis with corresponding lignin qualities in (a) two-step process at 90 °C and 1.5h and (b) single-step process at 90 °C and 3h.

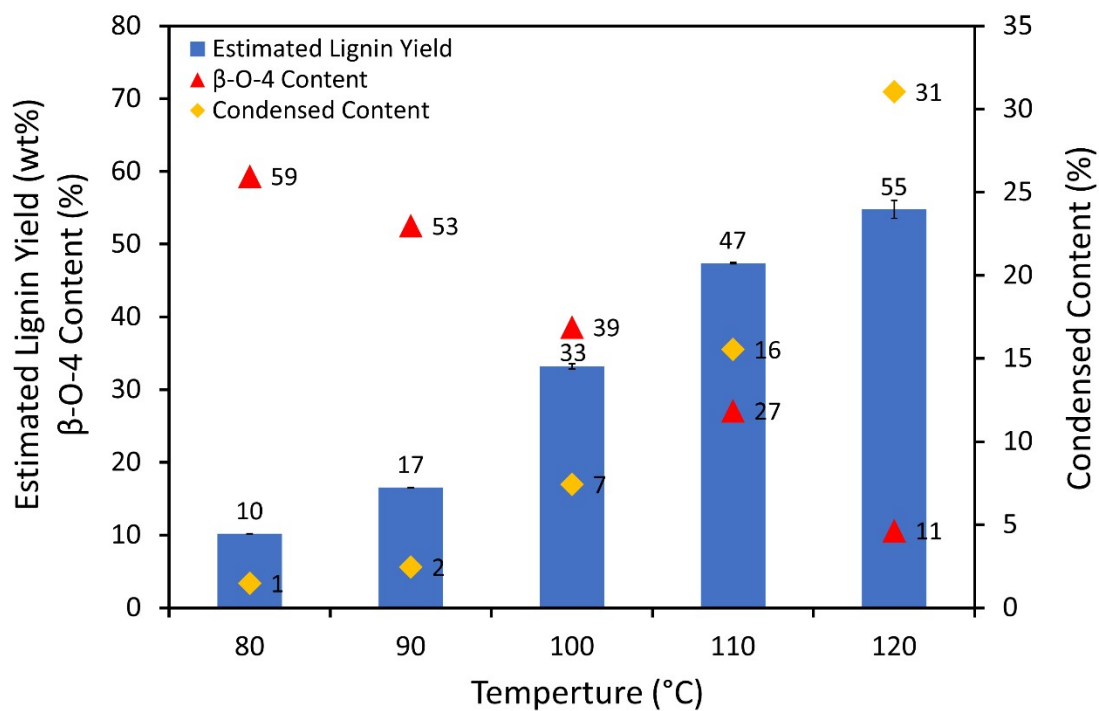


Figure S2. Lignin yields (poplar) were estimated on a basis of CASA-quantified lignin content in the extracted poplar. All data points were obtained in duplicates using 90wt.% GVL and H₂O mixture (9:1, w/w) and 100mM H₂SO₄ at 80–120°C and 1hr.

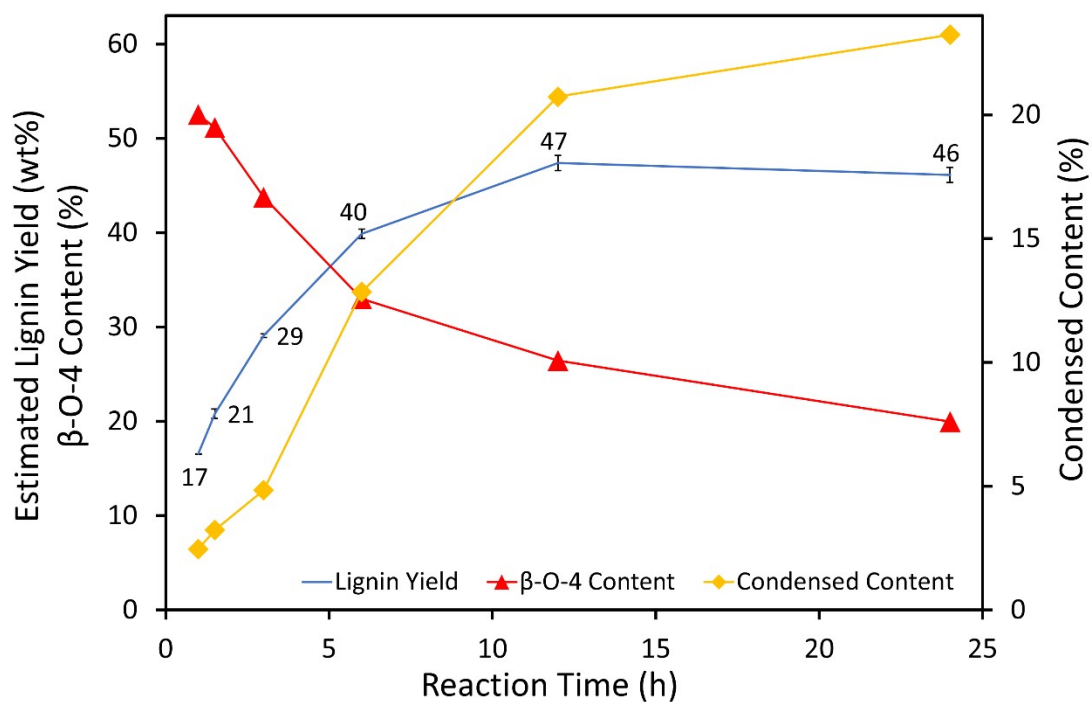


Figure S3. Lignin yields (poplar) were estimated on a basis of CASA-quantified lignin content in the untreated poplar. All data points were obtained in duplicates using 90wt.% GVL and H₂O mixture (9:1, w/w) and 100mM H₂SO₄ at 90 °C and 1–24h.

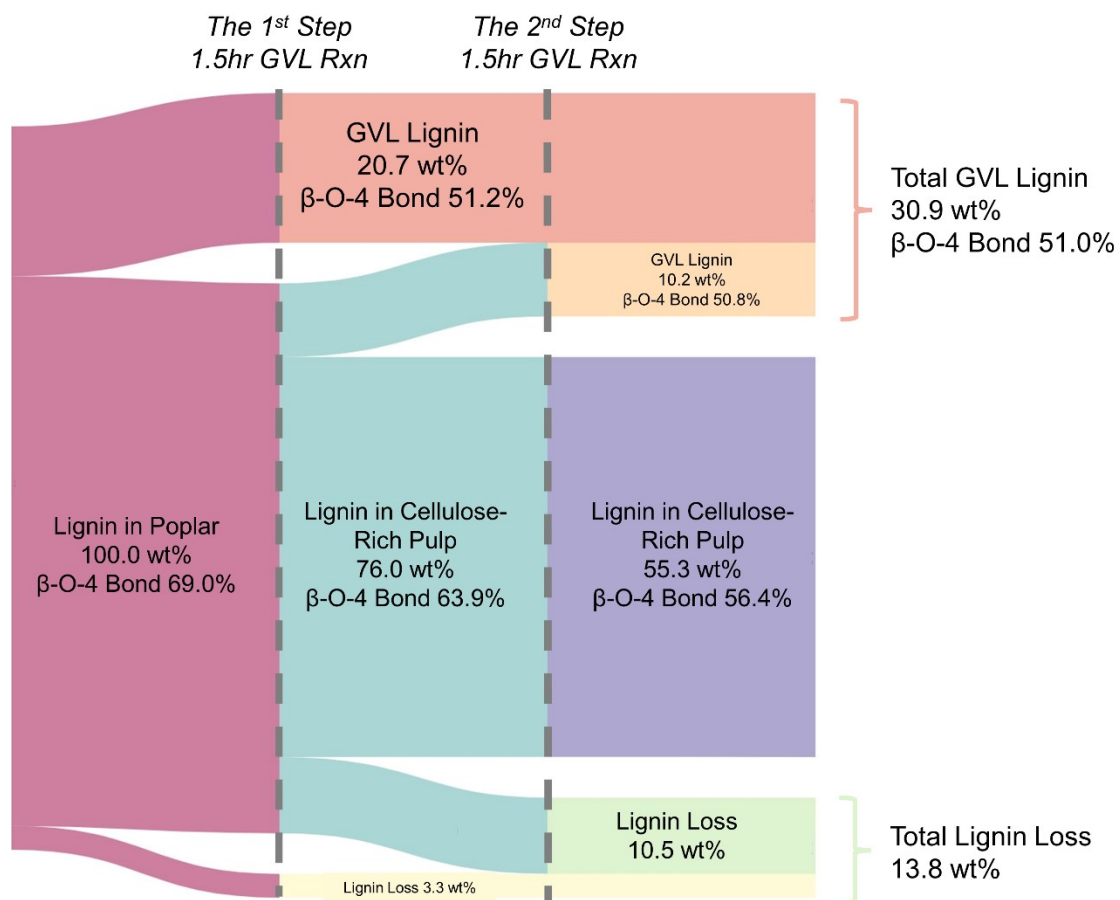


Figure S4. Sankey diagram of lignin mass balance during GVL pretreatment at 90 °C and 2 × 1.5 h, as measured by CASA-lignin analysis.

Table S1. Other primary types of bonds existed in GVL lignin.

Temperature (°C)	80	80	90	100	110	120
Time (h)	6	1	1	1	1	1
β-5 (%)	2.81	3.39	3.48	2.31	1.94	2.15
β-β (%)	3.14	2.84	3.25	4.55	4.36	4.22
Temperature (°C)	90	90	90	90	90	90
Time (h)	1	1.5	3	6	12	24
β-5 (%)	3.48	3.49	2.71	2.14	2.73	1.99
β-β (%)	3.25	3.66	3.97	3.72	4.51	4.56

Table S2. The contents of different types of hydroxyl groups existed in the GVL lignin obtained in the 1 h reaction at different temperature.

Temperature (°C)	80	90	100	110	120
Aliphatic OH (mmol/g Lignin)	3.67	3.69	3.47	2.35	1.59
C₅-substituted OH (mmol/g Lignin)	0.32	0.51	0.90	0.87	1.10
Guaiacyl OH (mmol/g Lignin)	0.52	0.47	0.46	0.47	0.51
<i>p</i>-Hydroxyphenyl OH (mmol/g Lignin)	0.64	0.60	0.64	0.46	0.32
Carboxylic acid OH (mmol/g Lignin)	0.41	0.37	0.29	0.28	0.15

Table S3. The contents of different types of hydroxyl groups existed in the GVL lignin obtained in the 90 °C reaction for different reaction times.

Reaction Time (h)	1	1.5	3	6	12	24
Aliphatic OH (mmol/g Lignin)	3.69	3.64	3.58	3.48	2.99	1.90
C₅-substituted OH (mmol/g Lignin)	0.51	0.50	0.81	1.05	1.23	1.23
Guaiacyl OH (mmol/g Lignin)	0.47	0.48	0.36	0.52	0.52	0.41
<i>p</i>-Hydroxyphenyl OH (mmol/g Lignin)	0.60	0.67	0.62	0.62	0.56	0.31
Carboxylic acid OH (mmol/g Lignin)	0.37	0.43	0.34	0.37	0.34	0.24