Supporting Information

Efficient fractionation of pure hemicellulose with high DP from bleached hardwood pulp using $LiBr \cdot 3H_2O$ and co-production of dissolving pulp

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Characterization

The *α*-cellulose content of cellulose samples was characterized according to TAPPI test standard (T203 cm-99). The cellulose sample is extracted consecutively with 17.5% and 9.45% sodium hydroxide solutions at 25 °C. The *α*-cellulose, which is insoluble, is derived by difference. The *α*-cellulose content is determined by calculating the undissolved fraction, which is the difference between the total pulp specimen (100%) and the dissolved fraction (expressed as a percentage).

The degree of polymerization (DP) of cellulose samples was measured in accordance with international standard (ISO 5351/1). The freeze-dried cellulose samples were dissolved in 0.5 M Copper ethylene diamine (CED) at 20 °C for 30 min. Intrinsic viscosities of the solutions were obtained using capillary viscometer, and these values were converted to DP values by the Martin equation, $DP^{0.905} = 0.75[\eta]$.

All the measurements for each test were carried out at least three times, and the average results were reported.

Table S1

Effect of temperature and time of LBTH treatment on hemicellulose removal and yield.

LBTH treatment conditions	Removal rate of hemicellulose (%)	Yield of hemicellulose (%)
25 °C 1 h	66.7±1.2	54.2±1.1
35 °C 1 h	68.1±0.8	60.2±0.7
45 °C 1 h	75.1±1.6	69.9±0.2
55 °C 1 h	79.2±2.0	73.1±2.0
65 °C 1 h	86.9±0.7	75.9±1.6
75 °C 1 h	92.6±1.0	80.3±1.7
85 °C 1 h	94.0±0.2	82.4±3.2
25 °C 5 h	66.6±1.3	62.5±1.3
35 °C 5 h	76.3±2.3	69.4±2.3
45 °C 5 h	85.0±0.6	75.3±2.4
55 °C 5 h	85.5±2.1	82.2±1.8
65 °C 5 h	92.2±2.4	82.0±2.7
75 °C 5 h	94.9±0.2	83.5±2.2
85 °C 5 h	95.2±0.3	84.3±2.9

Table S2

Average molecular weights, *DP* and polydispersity index (*PDI*) (*Mw*/*Mn*) of soluble hemicellulose in ethanol filtrate.

Treatment conditions	*Mw* (g/mol)	*Mn* (g/mol)	*PDI*	*DP*
LBTH (55 °C 5 h)	10060	6000	1.679	45

Table S3

Saccharide components (mean ± standard error) of regenerated hemicellulose.

Treatment conditions	Glucose (%)	Xylose (%)	Arabinose (%)
25 °C 1 h	0.8±0.2	94.2±0.8	3.3±0.7
35 °C 1 h	0.7±0.3	94.7±1.2	3.0±1.3
45 °C 1 h	0.5±0.3	93.5±0.6	3.7±0.8
55 °C 1 h	0.5±0.1	96.5±0.5	2.8±0.7
65 °C 1 h	0.3±0	95.3±1.3	2.8±0.7
75 °C 1 h	0.6±0.2	95.0±2.0	3.1±0.7
85 °C 1 h	0.3±0	97.2±0.8	2.0±0.6
25 °C 5 h	0.4±0	97.3±0.7	2.0±0.3
35 °C 5 h	0.4±0.1	96.5±1.3	2.4±0.3
45 °C 5 h	0.7±0.3	95.3±1.4	2.4±0.3
55 °C 5 h	0.3±0.1	96.9±0.5	2.2±0.3
65 °C 5 h	0.5±0.4	94.5±1.6	2.4±1.9
75 °C 5 h	0.1±0	98.6±0.8	0.8±0.1
85 °C 5 h	0.3±0	97.9±1.5	1.1±0.1

Table S4

Sugar composition, *α*-cellulose content, ash content and degree of polymerization of the obtained dissolving pulp and BHKP.

LBTH Treatment conditions	*DP*	*α*-cellulose %	Ash %	Xylan %
25 °C 1 h	800.3	97.0	0.09	4.9±2.0
35 °C 1 h	817.9	97.3	0.15	2.5±1.0
45 °C 1 h	878.0	95.8	0.24	3.6±0.5
55 °C 1 h	880.7	96.8	0.13	2.9±0.8
65 °C 1 h	875.8	97.2	0.15	3.8±0.7
75 °C 1 h	809.1	98.1	0.12	1.3±0.6
85 °C 1 h	789.4	96.5	0.11	3.4±0.7
25 °C 5 h	801.2	97.4	0.16	3.6±1.4
35 °C 5 h	864.8	95.2	0.15	3.9±2.0
45 °C 5 h	844.2	96.9	0.30	2.5±0.5
55 °C 5 h	901.7	97.2	0.24	2.4±1.1
65 °C 5 h	916.4	97.4	0.18	3.4±0.3
75 °C 5 h	850.5	97.2	0.12	0.8±0.6
85 °C 5 h	794.6	96.4	0.07	2.4±1.0
BHKP	902.2	-	-	16.7±1.3

Table S5

The quality of the resulting pulp with the recycled LBTH under optimal conditions (55 °C, 5 h).

Recycle times	*DP*	*α*-cellulose %	Ash %	Xylan %
0	901.7	97.2	0.24	2.4±1.1
1	898.1	97.0	0.3	2.5±0.7
2	903.5	96.8	0.24	2.4±0.3
3	883.0	96.6	0.26	2.1±1.3
4	894.2	96.6	0.18	2.5±1.0
5	897.6	96.3	0.24	2.3±1.1

Table S6

Comparison of the methods for fractionation of hemicellulose.

Methods	Treatment conditions	Removal rate of hemicellulose %	Yield of hemicellulose %	Methods of solvent recovery	Recovery rate of solvent %
Phosphotungstic acid (PTA)-cold caustic[1]	25°C /90°C 30 min	79.2	NA	Filtration and evaporation	＞86
Brønsted acidic DESs (BDESs)[2]	80°C 6 h	NA	36.3	Evaporation of anti-solvent	＞90
γ-valerolactone (GVL)/water[3]	135°C 2 h	93	NA	Evaporation /Conversion of the filtrate(glucose/xylose)	NA
Ionic liquid (EmimAc) /water[4]	60°C 2 h	61.2	NA	Evaporation of anti-solvent	NA
LBTH (this study)	55 °C 5 h	85.5	82.2	Evaporation of anti-solvent	>90

Note: a, calculated based on the composition of the obtained dissolving pulp; NA, not reported.

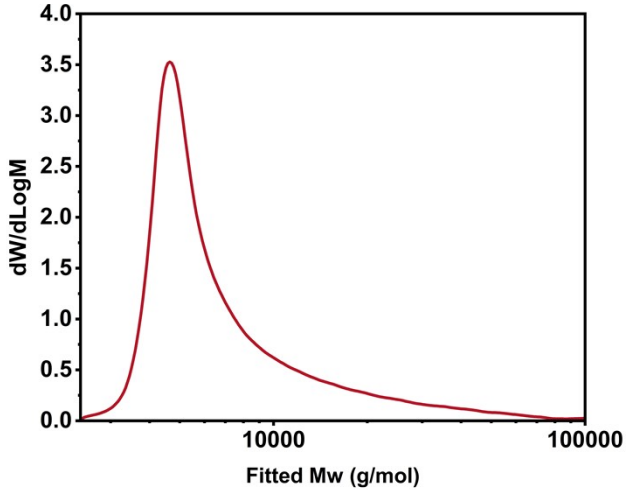

Fig. S1 Molecular weight distribution of the collected soluble hemicellulose with the LBTH treatment condition of 55°C for 5 h.

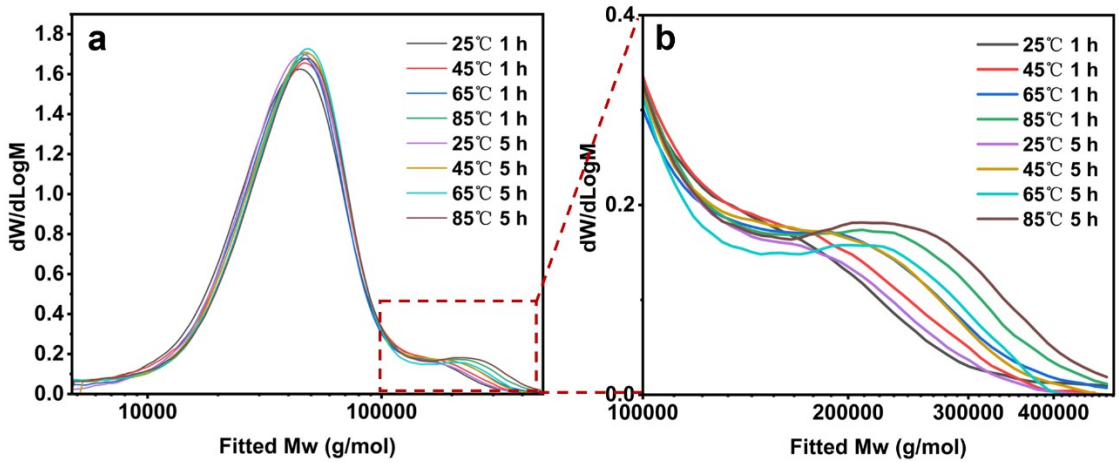

Fig. S2 Molecular weight distribution diagram of regenerated hemicellulose.

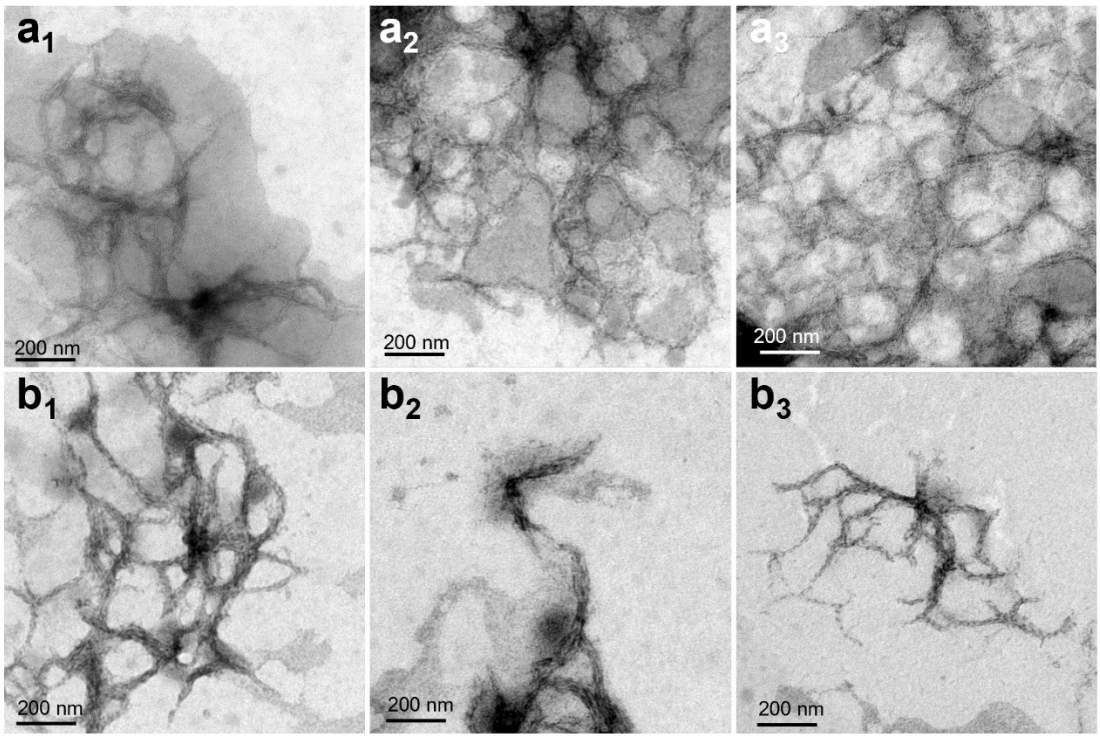

Fig. S3 TEM photographs of regenerated hemicellulose treated in LBTH at 55 °C (a) and 75 °C (b) for 5 h, respectively.

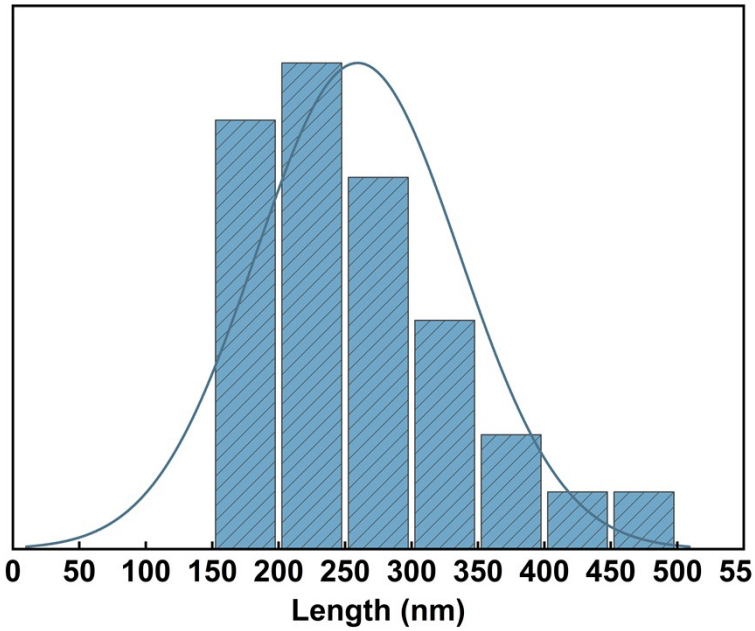

Fig. S4 Length distribution of regenerated hemicellulose in TEM images.

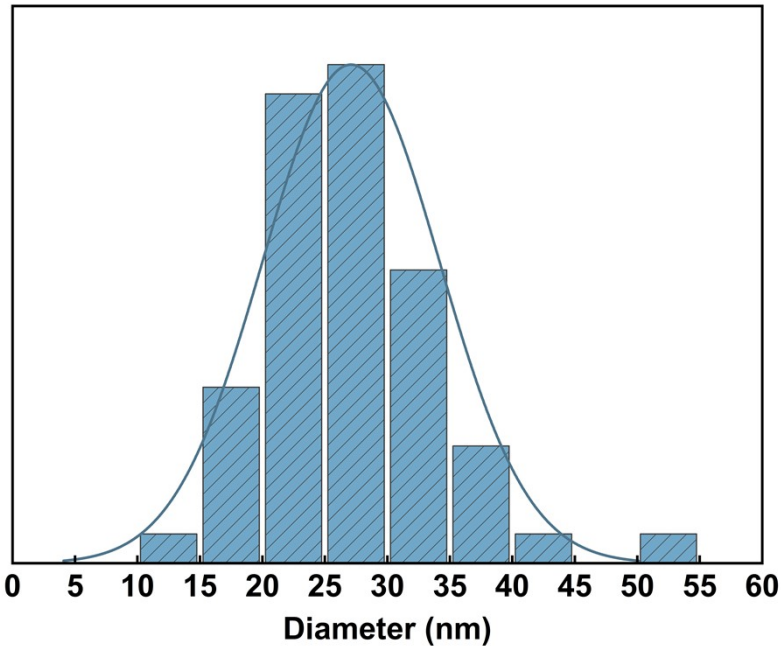

Fig. S5 Diameter distribution of regenerated hemicellulose in TEM images.

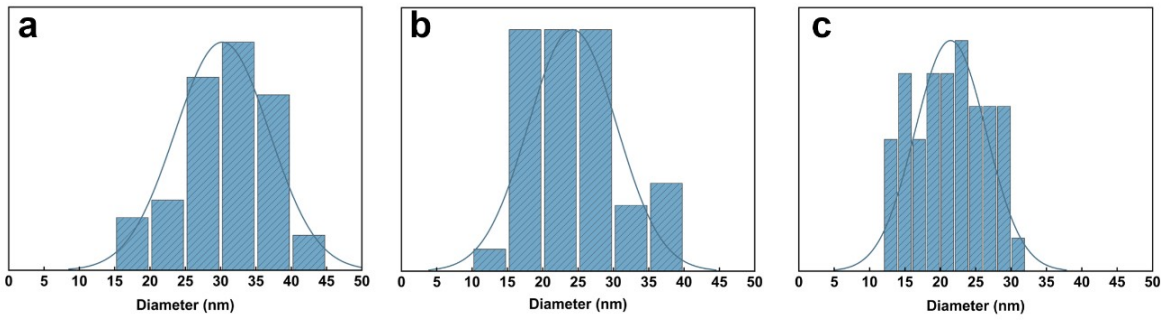

Fig. S6 Diameter distribution of regenerated hemicellulose at different LBTH treatment temperatures (25 °C (a), 55 °C (b), 85 °C (c)) in SEM.

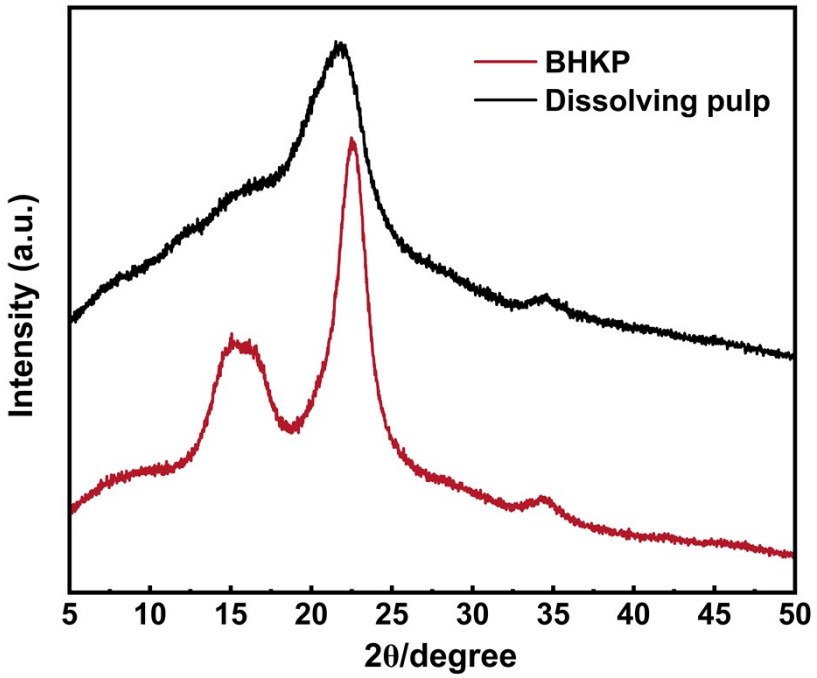

Fig. S7 XRD patterns of BHKP before and after LBTH treatment.

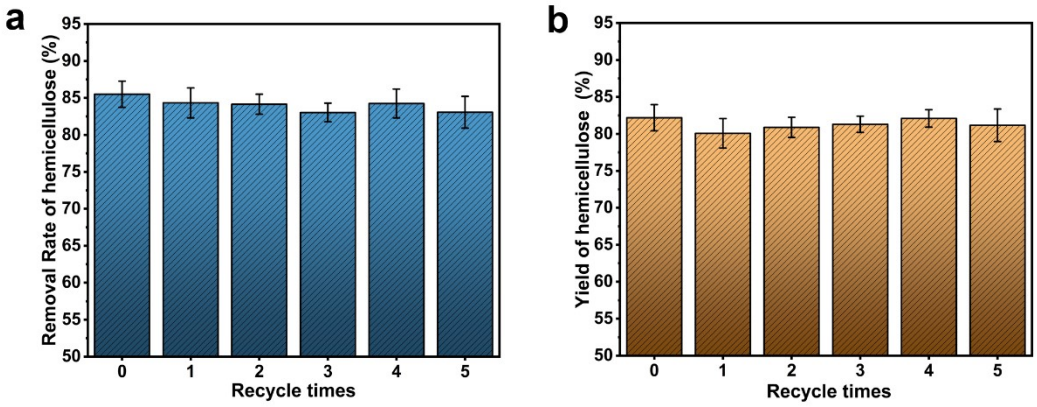

Fig. S8 Removal rates (a) and yields (b) of hemicelluloses with the recycled LBTH under optimal conditions (55 °C, 5 h).

Reference:

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2. J. Yang, W. Zhang, Y. Wang, M. Li, F. Peng and J. Bian, *Carbohydr Polym*, 2022, **278**, 118992.
3. B. Yang, S. Zhang, H. Hu, C. Duan, Z. He and Y. Ni, *Separation and Purification Technology*, 2020, **248**, 117071.
4. B. Yang, X. Qin, H. Hu, C. Duan, Z. He and Y. Ni, *Cellulose*, 2020, **27**, 9653-9661.