Supplementary information

A low-energy and sustainable pulping technology for eucalypts slabs using deep eutectic solvent

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1. Figures and Tables

Fig. S1. (a-c) The images of commercial pine chips, coarse pulp, screened pulp. (d-f) The images of reed straw, coarse pulp, screened pulp.
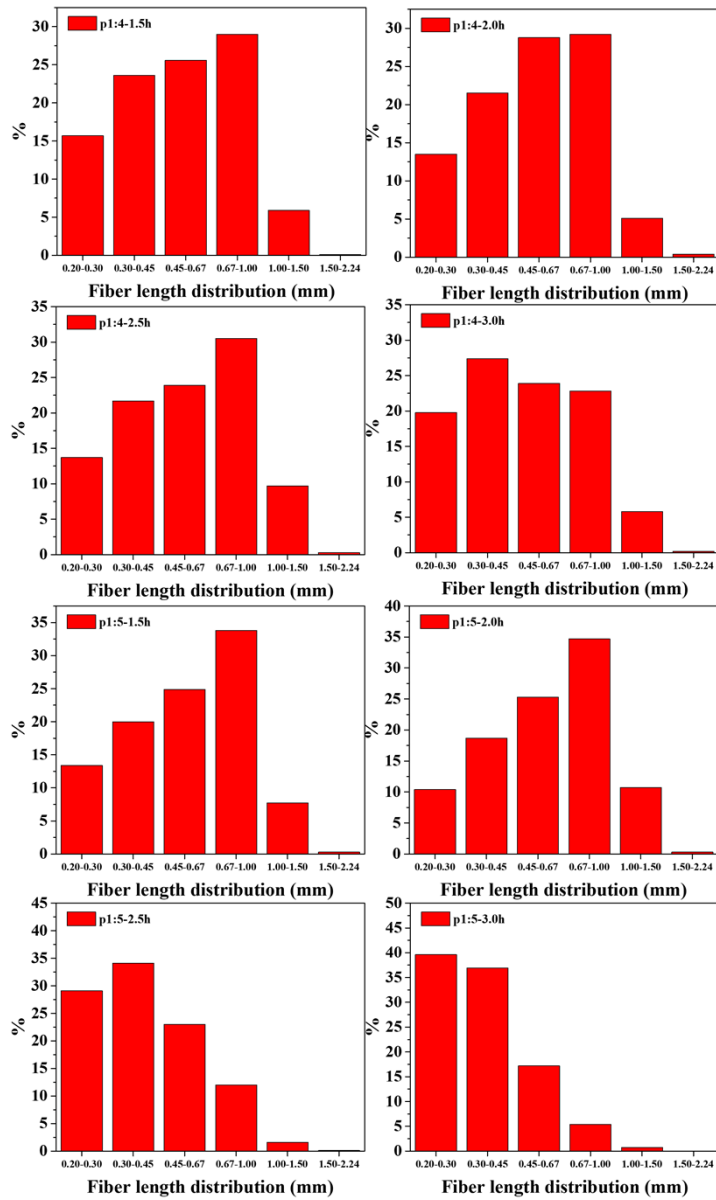
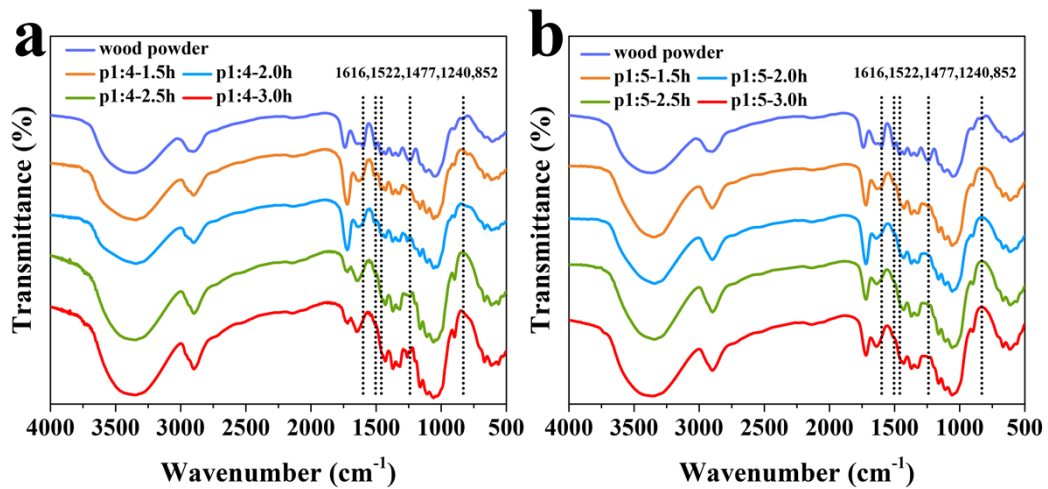**Fig. S2.** The fiber length distribution of DES pulps.

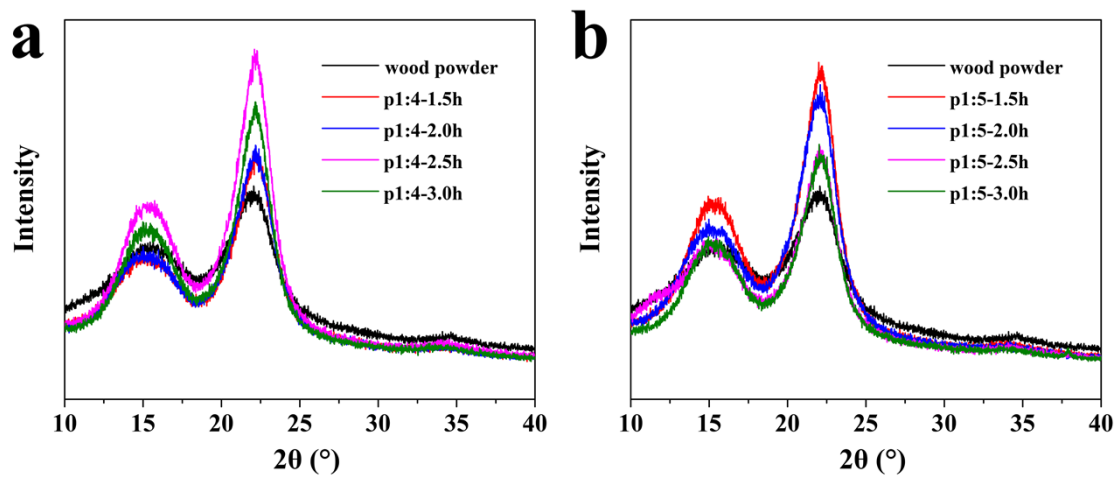**Fig. S3.** (a-b) The FTIR spectra of raw material and screened pulps.

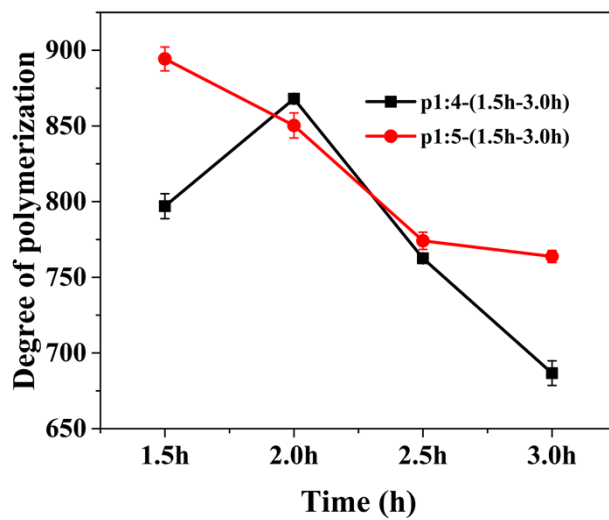**Fig. S4.** (a-b) The XRD spectra of raw material and screened pulps.

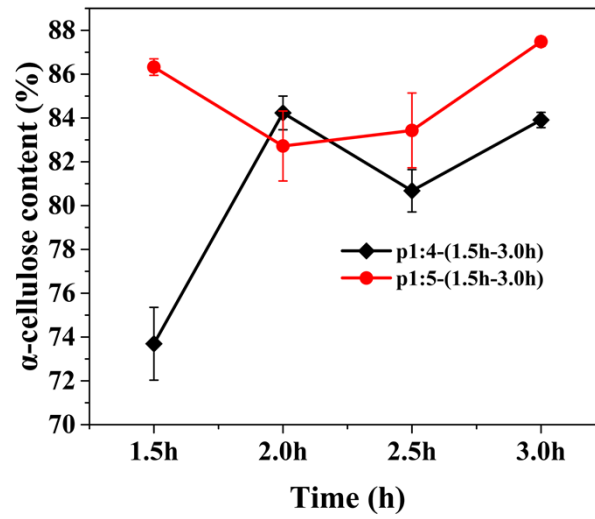**Fig. S5.** The degree of polymerization of screened pulps.

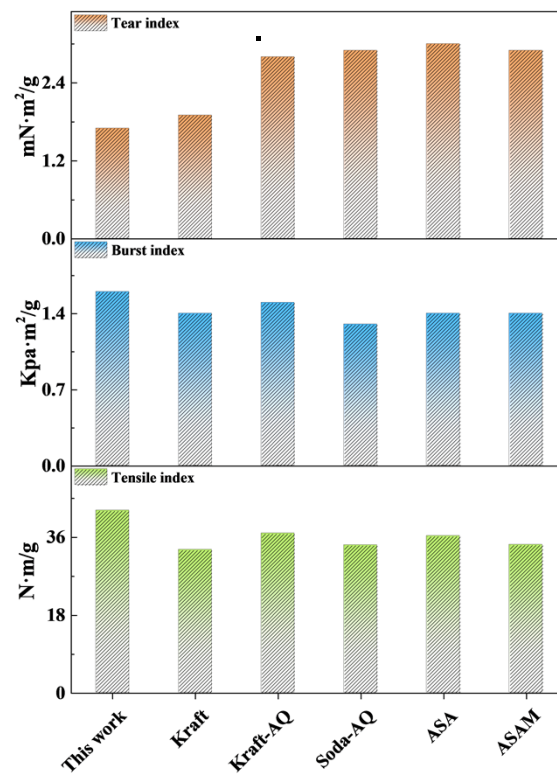**Fig. S6.** The α-cellulose content of screened pulps.

Fig. S7. The tear index, burst index, and tensile index of the handsheets of unbeaten eucalypts pulp cooked by different methods.
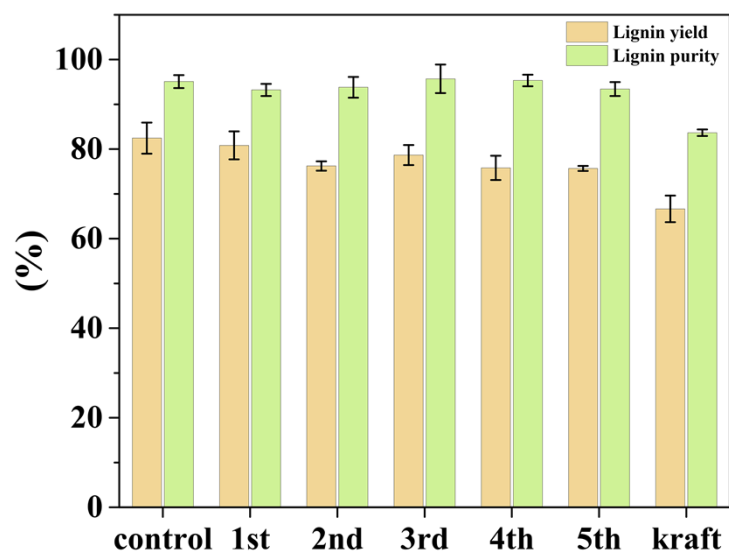
Fig. S8. The yield and purity of DES lignin and kraft lignin.
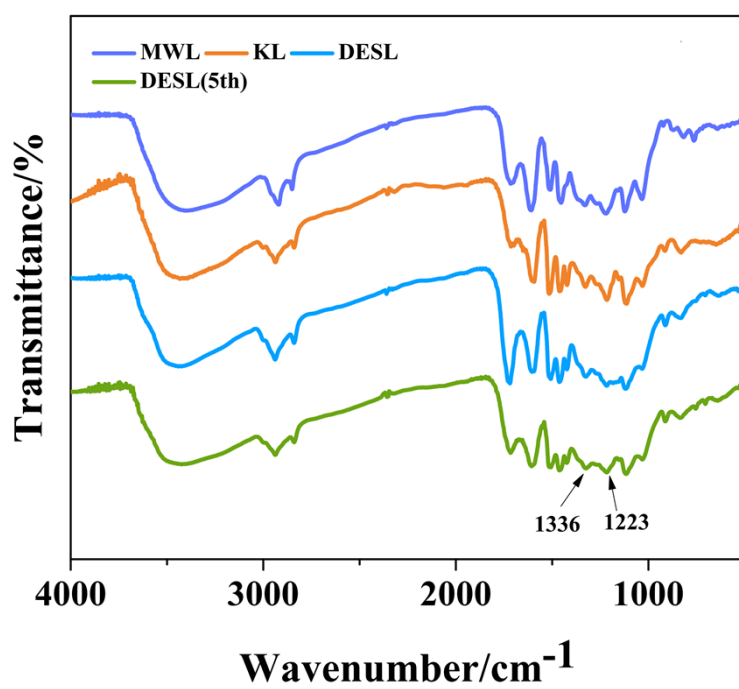
Fig. S9. The FTIR spectra of lignin fractions.
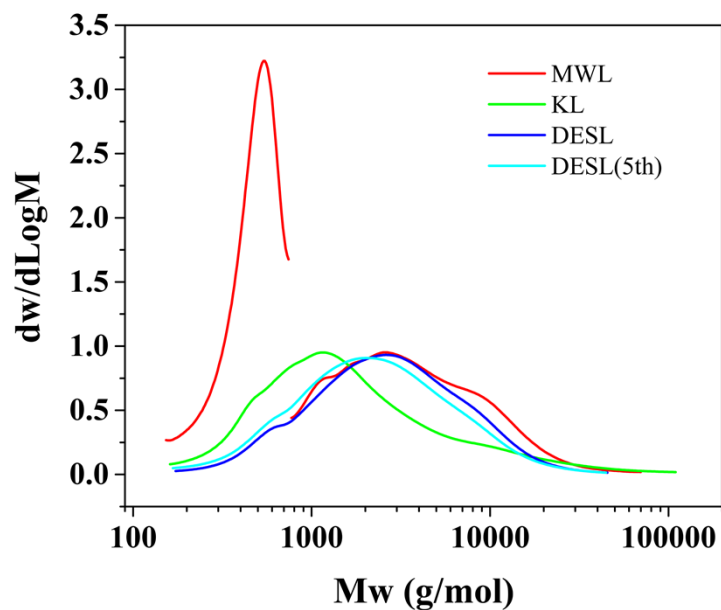
Fig. S10. Molecular weight distribution of lignin fractions.
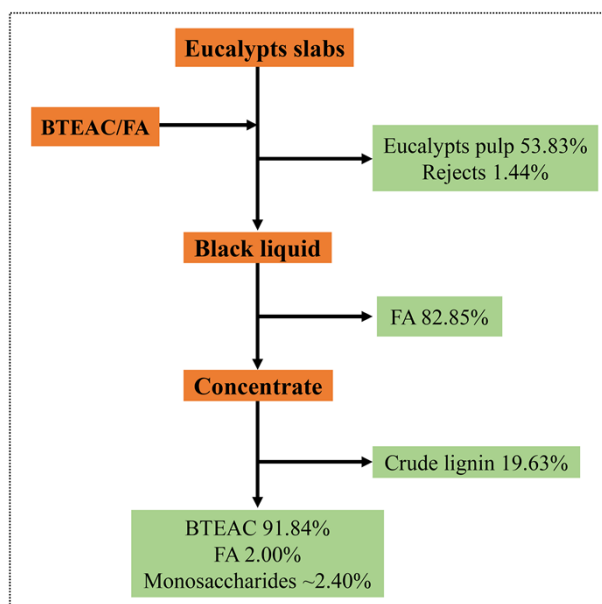
Fig. S11. The mass balance diagram of DES pulping process. (Monosaccharides mainly include xylose and glucose. Their content in black liquid is determined by ion chromatography.)

Table S1 The reaction conditions and pulp yield of DES pulping

Feedstock	Time	Temperature	Solid-liquid ratio	BTEAC/FA	Coarse pulp yield	Screened pulp yield
Pine	150 min	130 ℃	1:7	1:5	68.32%	64.29%
Reed straw	50 min	130 ℃	1:7	1:5	60.25%	39.95%

Table S2 The crystallinity index (CrI) and CrI/cellulose content ratios of DES pulps and raw material.

Sample label	CrI (%)	CrI/cellulose content
wood powder	46	1.06
p1:4-1.5h	64	0.89
p1:4-2.0h	66	0.80
p1:4-2.5h	71	0.81
p1:4-3.0h	71	0.78
p1:5-1.5h	69	0.88
p1:5-2.0h	68	0.77
p1:5-2.5h	65	0.73
p1:5-3.0h	67	0.72

Table S3 The content of lignin linkages and the degree of condensation of lignin

Samples	β-O-4	β-β	β-5	Degree of condensation
MWL	48.04%	13.73%	3.92%	-
KL	14.29%	10.20%	-	79.59%
DESL	5.11%	6.57%	-	65.69%
DESL(5th)	4.42%	6.19%	-	66.37%

2. Supplementary method

2.1. Chemical composition analysis

The lignin content of pulp and the purity of lignin were analyzed by acid hydrolysis according to the standard method recommended in National Renewable Energy Laboratory Technical Report. Briefly, 0.3 g of extractives free sample was first stirred at 30 ℃ for 1 h in 3 mL of 72% H_2SO_4 solution. Upon completion of the hydrolysis, the acid was diluted to 4% concentration by adding 84 mL of distilled water. Then, the dilution was hydrolyzed in an autoclave for 1 h at 121 ℃. After cooling down to near ambient temperature, the suspension was filtered. The acid insoluble lignin content was calculated by the mass of solid residues. The acid soluble lignin content was determined by an ultraviolet spectrophotometer (UV-2600, Shimadzu, Japan) at 240 nm wavelength. The lignin content was the sum of the acid soluble lignin content and the acid insoluble lignin content.

According to a Chinese Standard GB/T266.10-1995, the holocellulose was prepared for subsequent component test. In brief, 2 g of sample was added into 65 mL of distilled water, 0.5 mL of acetic acid (99%), and 0.75 g of sodium chlorite (80%). The mixture was heated at 75 °C for 1 h under stirring. The above operation was repeated 5 times to remove lignin completely. The mixture was then filtered to obtain holocellulose.

The cellulose and hemicellulose contents were determined by NaOH treatment. Then, 1 g of holocellulose was mixed with 100 mL of 0.5 mol/L NaOH solution. The mixture was heated for 3.5 h in a water bath at 80 °C. The solid residues were separated through vacuum filtration to obtain cellulose. The mass of hemicelluloses is the difference between the mass of holocellulose and cellulose.

2.2. α-cellulose content analysis

First, 2 g of holocellulose was mixed with 15 mL of 175 g/L NaOH solution with a gentle stirring for 1 min to form uniform paste. Second, another 15 mL of 175 g/L NaOH solution was added into the paste with a gentle stir for 1 min. Thirdly, the mixture was placed in a water bath at 20 ± 0.5 °C for 43 min. After reaction, 30 mL of distilled water was added into the mixture with a gentle stirring for 1 min, and then the solid residue was separated through filtration. Afterwards, the solid residue was washed three times with 25 mL of 95 g/L NaOH solution for 2-3 min under weak vacuum filtration condition. Then, the solid residue was completely soaked in 2 mol/L acetic acid solution for 5 min after it was washed by distilled water to neutral. Finally, the solid residue was washed to neutral by distilled water again.

$$\alpha\text{ - cellulose content }(\%) = \frac{\text{Mass of }\alpha\text{ - cellulose}}{\text{Mass of holocellulose}} \times 100 \quad \text{(Eq 1)}$$

2.3. Degree of polymerization analysis

First, 0.3 g of sample was dispersed in 25 mL of distilled water, and then 25 ml of copper ethylenediamine solution (1.0 M in H_2O) was added into the mixture. Second, the mixture was shaken vigorously until the fibers were completely dissolved. Thirdly, the mixture was placed in a water bath at 25 ± 0.1 °C for 5 min. Finally, the degree of polymerization of pulp was tested by a Nordic standard viscometer.

2.4. Kraft pulping process

Kraft pulping was implemented in a laboratory digester. The mass ratio of water to wood chips was

fixed at 6:1. The effective alkali was 25% (expressed as Na_2O) and the sulfidity was 20% (expressed as Na_2O). The heating time, from room temperature (25 °C) to the maximum temperature (160 °C) was specified as 1.0 h, and the soaking time at the maximum temperature was 2.0 h.

2.4. Semi-quantitative analysis of lignin fractions

The relative content of the substructures is described as content per 100 aromatic units. Where IC9 represents the integral value of the aromatic ring, $IS_{2,6}$ is the integral value of the $S_{2,6}$, IG_2 is the integral value of the G_2, IX is the integral value of the α-position of A (β-O-4), B (β-β), and C (β-5)[1], $IS_{condensed}$ is the integral value of the $S_{condensed}$[2, 3].

$$IC9 = 0.5IS_{2,6} + IG_2 \text{ (Eq 2)}$$

$$IX\% = IX/IC9 × 100\% \text{ (Eq 3)}$$

$$\text{Condensation ratio} = IS_{condensed}/ IC9 × 100\% \text{ (Eq 4)}$$

2.5. Calculation of energy consumption in DES cooking process

Generally, A 10 L digester could produce about 1 Kg of DES pulp. The power computation of DES cooking was calculated by a formula proposed by Wang et al [4] . A simple ratio of power to temperature was proposed by Wang et al. When the heating power was 600 W, the hotplate could achieve 340 °C. Thus, the power required to maintained a temperature of 130 °C was determined to be 229.4 W. Therefore, the energy consumption of DES cooking was 229.4 W × 2.0 h = 0.458 KW·h. According to the data of World Nuclear Association, the CO_2 emissions was 0.375 Kg CO_2/ Kg pulp[5].

References

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