

Supporting Information

Renewable co-solvent promoting the selective removal of lignin by increasing of total hydrogen bonds

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Content

S1 Materials	2
S2 Experimental methods	3
S2.1 Pretreatment of CS with sugars platform renewable co-solvent and [BHEM]mesy ..	3
S2.2 Enzymatic hydrolysis of pretreated CS	3
S2.3 Synthesis and purification of ILs	4
S2.4 Analytical methods	4
S2.4.1 Analysis of the components	4
S2.4.2 Characterization of ¹H NMR, ¹³C NMR and ¹H -¹³C HSQC	4
S2.4.3 Characterization of UV	5
S2.4.4 Density and viscosity measurement	5
S2.4.5 Characterization of fourier transform infrared spectroscopy (FT-IR)	5
S2.4.6 Characterization of X-ray diffraction (XRD)	5
S2.4.7 Characterization of scanning electron microscope (SEM)	6
S2.4.8 Yield of glucose	6
S3 Characterization of [BHEM]mesy	6
S4 ¹³C NMR characterization of solvent and ILs-based co-solvent systems	7
S5 FT-IR characterization of solvent and ILs-based co-solvent systems	7
S6 The density of solvent and ILs-based co-solvent systems	8
S7 The viscosity of solvent and ILs-based co-solvent systems	9
S8 FT-IR analysis of regenerated lignin	11
S9 Infrared absorption peak and its attribution	11
S10 ¹³C NMR characterization of neat and recycled of ILs-based co-solvent system	12

S1 Materials

CS were collected in Langfang, Hebei Province. They were air-dried and milled to ≤ 0.125 mm. Then they were washed with neutral detergent to wash away non-structural components in CS and stored in a sealed plastic bag. Methanesulfonic acid was purchased from Sinopharm Group Chemical Reagent Co., Ltd.; N-methyldiethanolamine was purchased from Sinopharm Group Chemical Reagent Co., Ltd.; Ethylene glycol and glycerol were purchased from Sinopharm Group Chemical Reagent Co., Ltd.; Cellulase was purchased from Novozymes (China) Investment Co., Ltd.

S2 Experimental methods

S2.1 Pretreatment of CS with sugars platform renewable co-solvent and [BHEM]mesy

Dried CS (5 wt% of the sugars-based co-solvent and [BHEM]mesy) and sugars-based co-solvent and [BHEM]mesy (10 g) were added into a 50 mL tube. The mixture was then heated at a given temperature and time with magnetically stirring at 700 rpm. After pretreatment, the residue was obtained by filtration and washed with ethanol. The supernatant was obtained by centrifugation (11000 rpm, 3 min). The residue was washed with ethanol and vacuum dried under 50°C. Then it was subjected to components determinations.

S2.2 Enzymatic hydrolysis of pretreated CS

The pretreated CS sample was dissolved in sodium acetate buffer with pH 4.8 and the amount of cellulase was 20 FPU/g cellulose. Then, the enzymatic hydrolysis was carried out at 50°C in a shaker at 200 rpm. Samples were collected at 0, 2, 4, 6, 24 h and centrifuged at 10,000 rpm for 3 min followed by filtration through a 0.22 μ m polyether sulfone membrane (Jinlong, Tianjin Keyilong Experimental Equipment Co., Ltd.). The monosaccharides were determined by high-

performance liquid chromatography (HPLC)

S2.3 Synthesis and purification of ILs

(1) Synthesis: The functional proton-type ILs [BHEM]mesy was synthesized by equal molar mass of methanesulfonic acid added into N-methyldiethanolamine (2 mol) drop by drop under ice bath conditions with methanol (100 mL) as dispersant. Then, the synthesis was carried out for 48 hours at room temperature. After synthesis, methanol was removal by rotary evaporation.

(2) Purification: The mixture after synthesis was purified with ethyl acetate (100 mL) and diethyl ether (100 mL). Subsequently, after removing the organic solvent by rotary evaporation, the ILs was vacuum-dried at 45°C.

S2.4 Analytical methods

S2.4.1 Analysis of the components

The sample about 0.1500-0.1600 g was tested by two-step acid hydrolysis method. First, 1.5 mL 72% H₂SO₄ was added into the sample and it was hydrolyzed in a 30°C shaker for 1 hour. Then, 42 ml deionized water was added into the sample and it was hydrolyzed in a 120°C autoclave for 45 min. After that, it was filtered by sand core glass funnel. Then, the sand core glass funnel was dried in a 100°C for 6 h and the quality of the residue was klason lignin. The filter was adjusted to pH 2 by 8% NaOH solution and the contents of glucose and xylose were determined by HPLC.

S2.4.2 Characterization of ¹H NMR, ¹³C NMR and ¹H -¹³C HSQC

The ¹H NMR, ¹³C NMR and ¹H -¹³C HSQC were recorded on a Bruker Avance III HD 600 instrument at room temperature. The ¹H NMR and ¹³C NMR were operating

at 600 MHz and 150 MHz, respectively. The ^1H - ^{13}C HSQC, approximately 50 mg regenerated lignin sample were dissolved in 0.5 mL DMSO- d_6 . The acquisition parameters were: spectral width of 11 ppm in F2 (^1H) with 1024 data points and 190 ppm in F1 (^{13}C) with 512 data points, 64 scans and 1 s interscan delay.

S2.4.3 Characterization of UV

The sample was diluted 200 times and measured at 190-500 nm by a UV spectrophotometer (UV1901, Shanghai Langguang Technology Co., Ltd.). The scanning interval was 1 nm and the blank sample was deionized water.

S2.4.4 Density and viscosity measurement

The density and viscosity of solvent and ILs-based co-solvent systems were measured by an all-in-one machine comprised of Anton Paar DMATM 5000 M density meter and Anton Paar micro viscometer Lovis 2000 ME at temperature 25-50°C.

S2.4.5 Characterization of fourier transform infrared spectroscopy (FT-IR)

The functional groups of cellulose-rich substrate were measured by Nicolet 380 infrared spectrometer. FT-IR spectra was obtained by the direct transmittance tableted with KBr (sample: KBr = 1:100 ~ 200, w/w). The spectra range was between 4000 and 400 cm^{-1} with a spectral resolution of 4 cm^{-1} .

S2.4.6 Characterization of X-ray diffraction (XRD)

X-Pert PRO MPD multi-function X-ray diffractometer with $\text{CuK}\alpha$ radiation at 40 kV and 30 mA was used to measure the crystallinity. The scanning range was from 5° to 60° at scanning speed of 4°/min.

The crystallinity index (CrI) was calculated according to the formula (1), I_{200}

represents the peak of the maximum intensity at about $2\theta=22.3$, I_{am} is the intensity of amorphous portion of CS at about $2\theta=18.5$.

$$CrI=(I_{200}-I_{am})/I_{200}\times 100 \quad \dots (1)$$

S2.4.7 Characterization of scanning electron microscope (SEM)

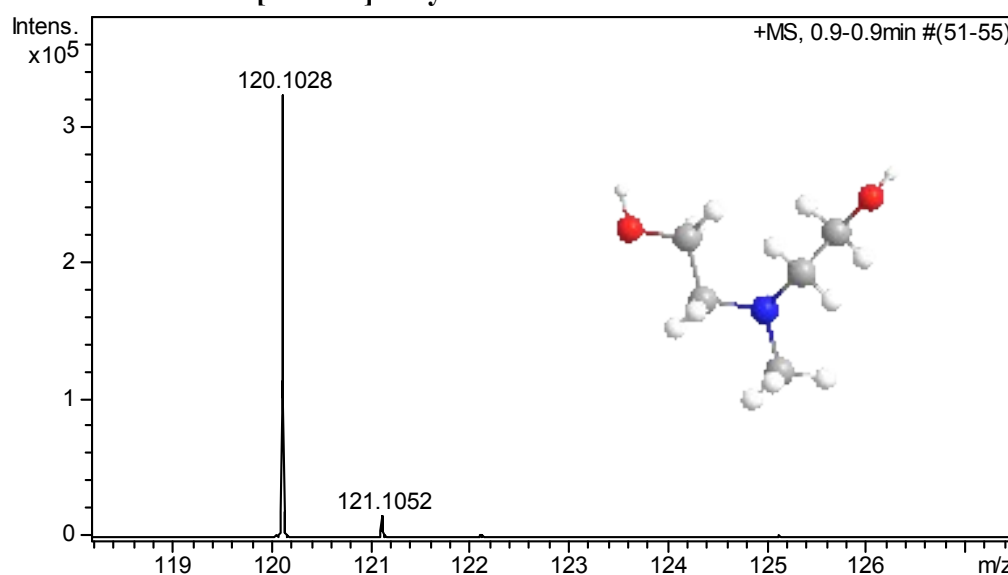
The morphology of samples was characterized by JEOL JSM-6700F cold-field emission scanning electron microscope. A thin layer sample was tiled on the platinum and SEM photos were taken at 5 kV.

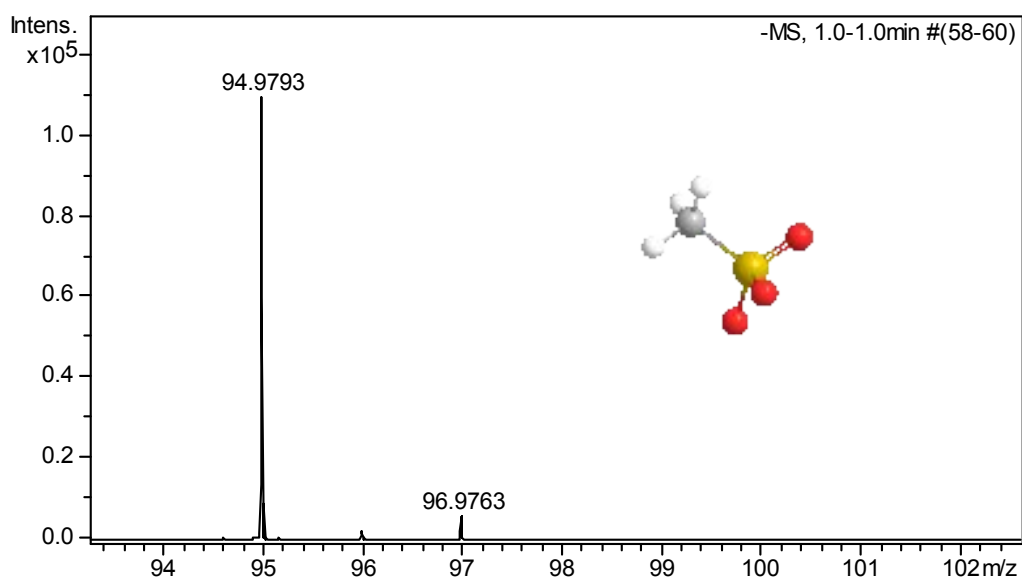
S2.4.8 Yield of glucose

The yield of glucose was calculated according to the Eq. (2). C is the concentration of glucose; V is the volume of enzymatic solution; M is the mass of recovered cellulose-rich; m is the mass of cellulose-rich fractions participating in the enzymatic hydrolysis; M_1 is the total amount of cellulose in the pretreatment raw material; 0.9 is the mass conversion coefficient between glucose and cellulose.

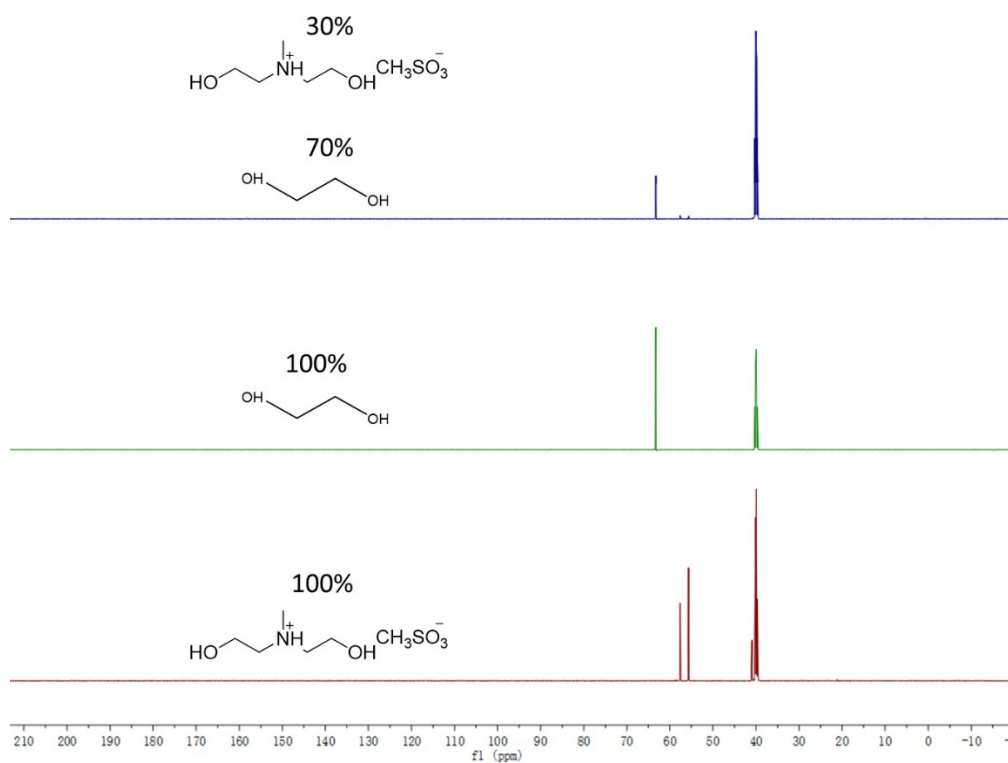
$$\text{Glucose yield (\%)}=C*V*(M/m)/(M_1/0.9)*100 \quad \dots(2)$$

S3 Characterization of [BHEM]mesy

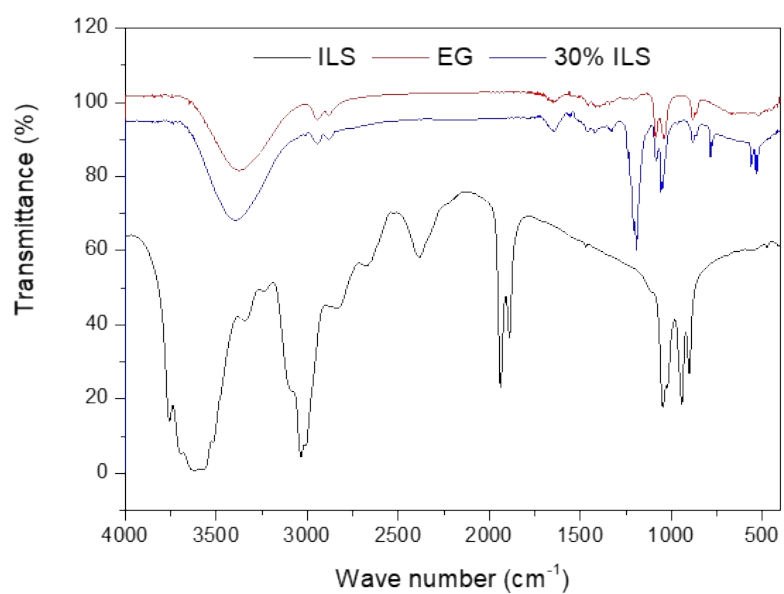




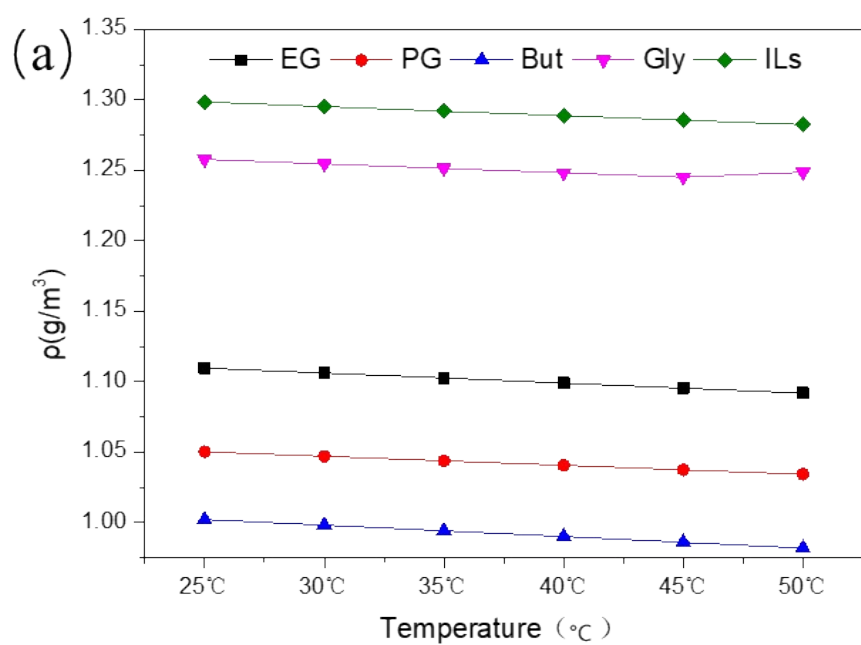
S4 ^{13}C NMR characterization of solvent and ILs-based co-solvent systems

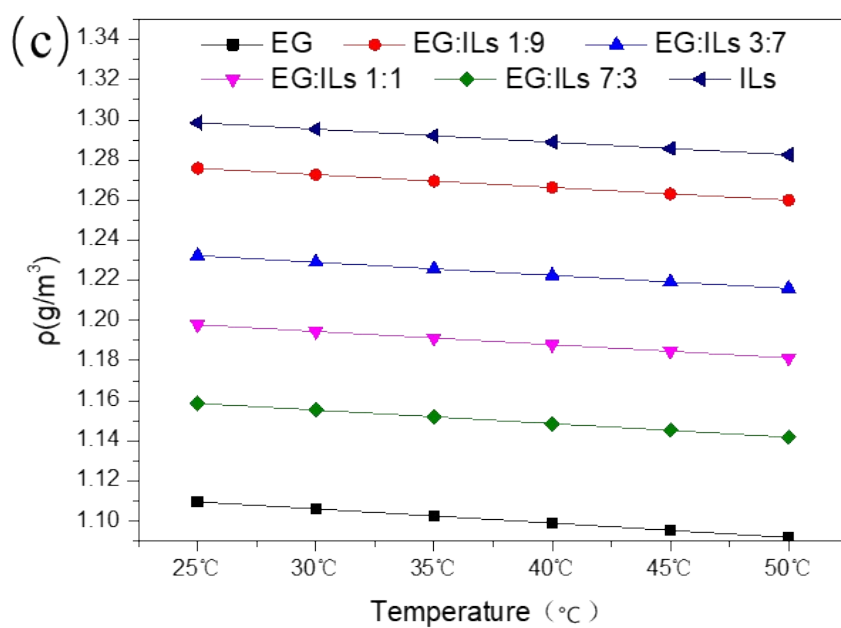
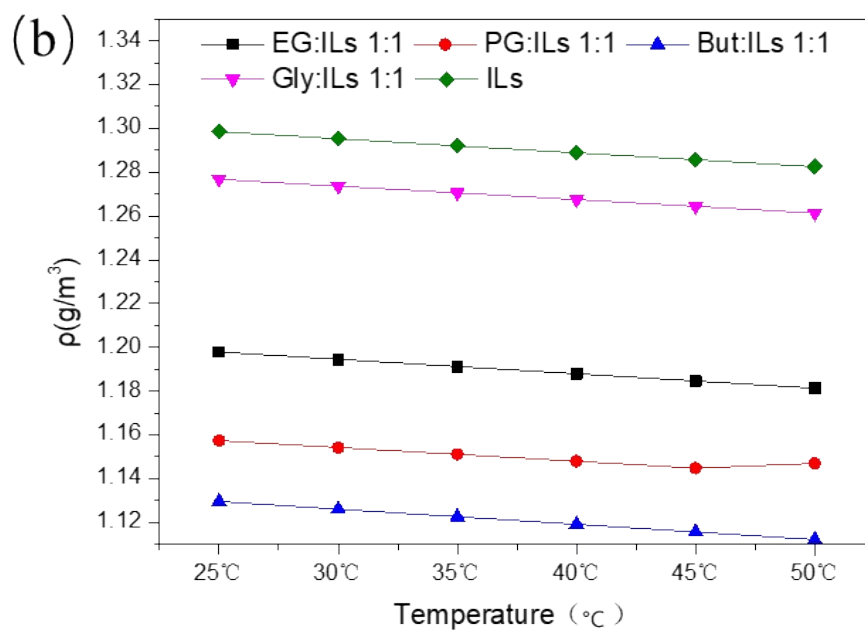


S5 FT-IR characterization of solvent and ILs-based co-solvent systems

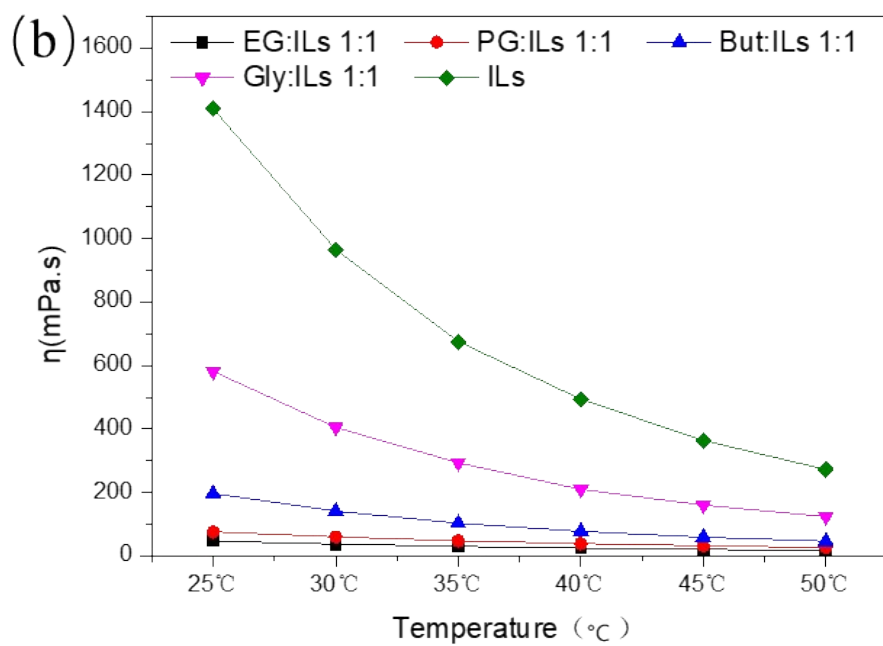
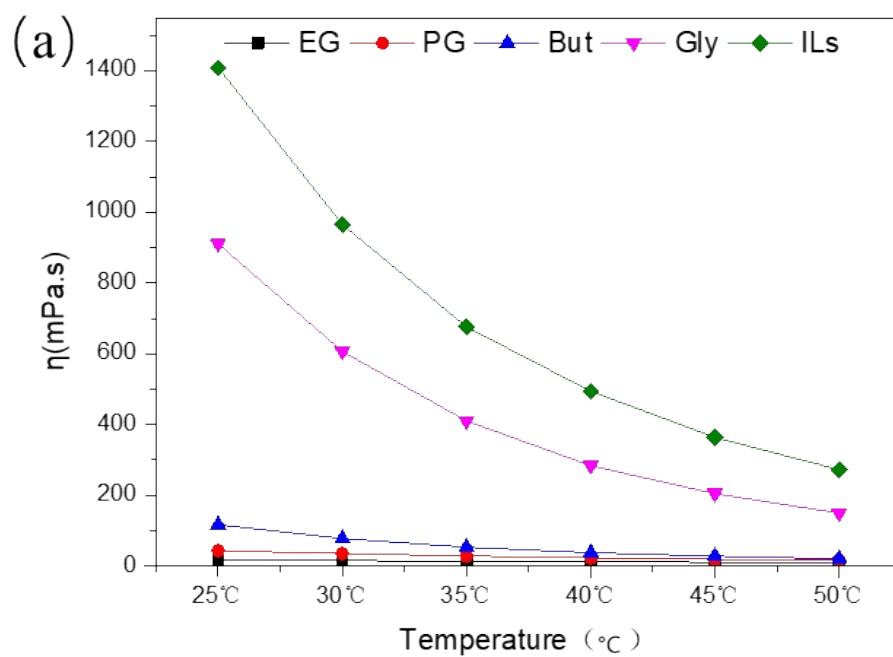


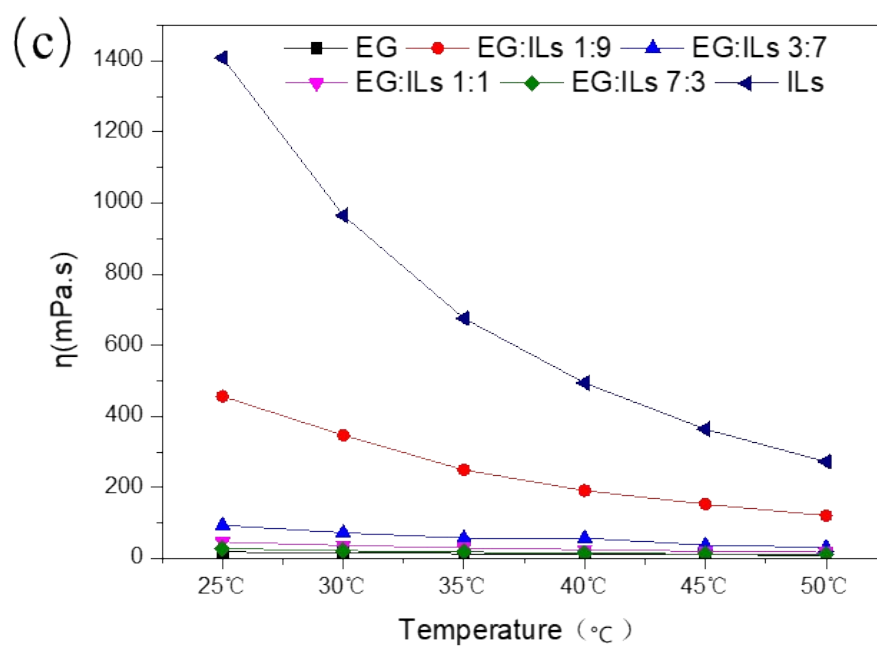
S6 The density of solvent and ILs-based co-solvent systems



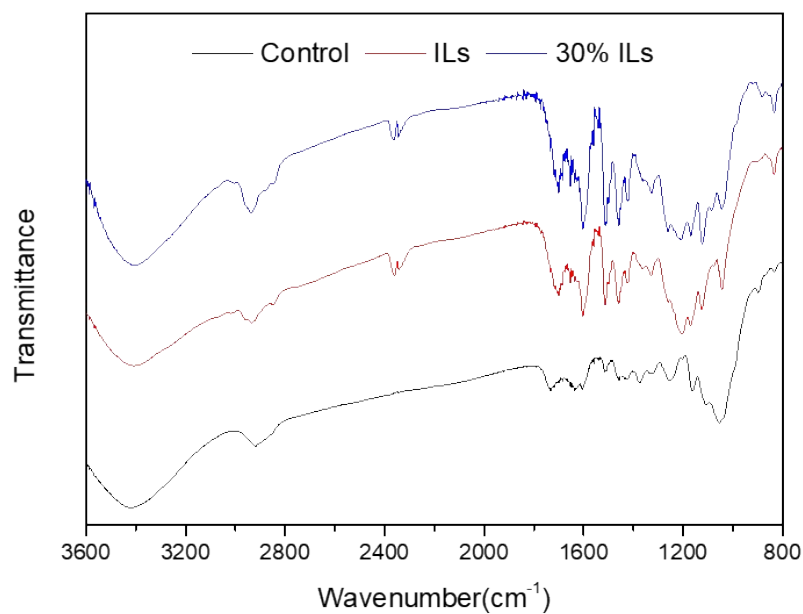


S7 The viscosity of solvent and ILs-based co-solvent systems





S8 FT-IR analysis of regenerated lignin

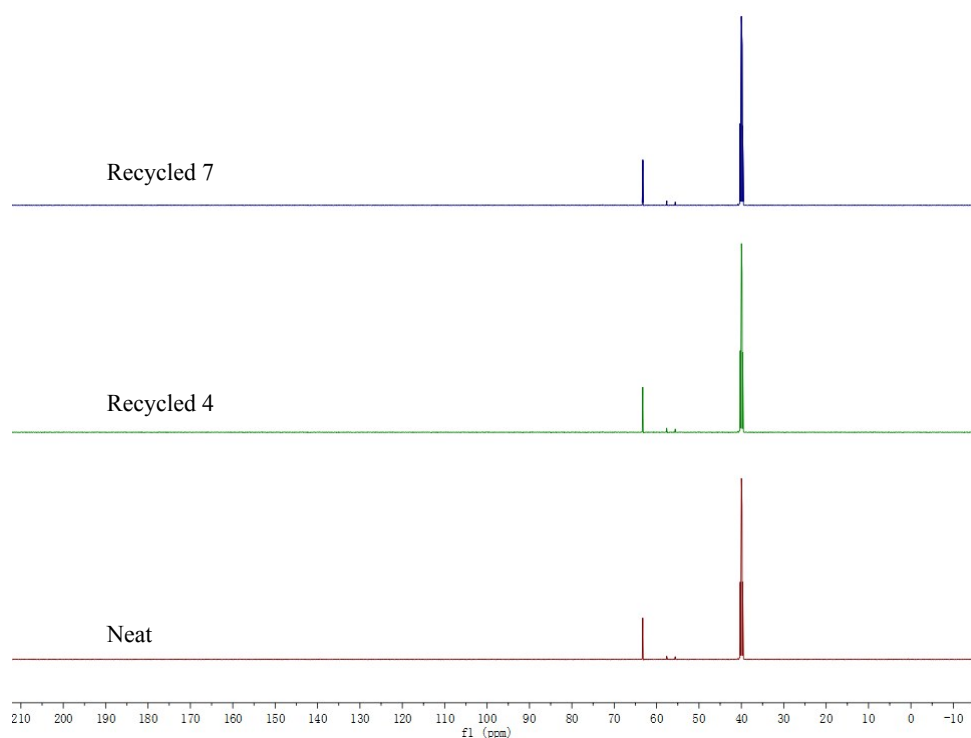


S9 Infrared absorption peak and its attribution

Attribution	Wavenumber (cm ⁻¹)
Aromatic C-H out-of-plane deformation	835
Aromatic C-H in plane deformation	1043
Guaiacyl C-H in plane deformation	1126

Phenolic hydroxyl C-O stretching vibration	1155
Guaiacyl C-O stretching vibration	1265
Syringyl C-O stretching vibration	1328
Aromatic skeletal vibrations	1427
C-H deformations in CH ₃ and CH ₂	1452
Aromatic skeletal vibrations	1514
Aromatic skeletal vibrations	1604
Conjugated carboxyl stretching vibration	1654
Non-conjugated carboxyl stretching vibration	1703
Methoxy C-H stretching vibration	2860
C-H stretching vibration in CH ₃ and CH ₂	2931
O-H stretching vibration	3394

S10 ¹³C NMR characterization of neat and recycled of ILs-based co-solvent system



S11 FT-IR characterization of neat and recycled of ILs-based co-solvent system

