SUPPORTING INFORMATION

COSMO-RS-Guided selection of DES for the delignification of sugarcane bagasse allowing the integrated recovery of holocellulose and functionalized lignin

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This Supporting Information contains 39 pages, with 26 figures and 16 tables.

S1. SUPPLEMENTARY METHODOLOGY

S1.1 Compositional analysis

S1.1.1 Moisture

The moisture content of SGB (sugarcane bagasse) and SGB-C (complex sugarcane bagasse-with husk) was determined according to the NREL procedure [1]. Ground bagasse samples were placed in porcelain crucibles previously dried at 105 ± 1 °C for 1 h and tared. Portions of ~2.00 g (as-received basis) were weighed in triplicate and dried at 105 ± 1 °C overnight (~16 h) in a forced-air oven. Crucibles were then cooled in a desiccator (30-45 min) and reweighed; when necessary, additional 1 h drying cycles were applied until constant mass (change < 0.1% w w^{-1} between consecutive weighings). Moisture was calculated by Eq. (S1):

$$U = 100 - \left(\frac{m_d}{m_i} \times 100\right) \quad \text{(S1)}$$

where U is the moisture content of the initial sample (%), m_i is initial mass (g) and m_d is dry mass after drying at 105 ± 1 °C. Results were reported as mean ± standard deviation.

S1.1.2 Ash

The ash content of SGB and SGB-C was determined according to the NREL procedure for biomass ash determination [2]. The dry mass was portioned into pre-dried, tared porcelain crucibles. Samples were pre-carbonized at 250 °C for 30 min to avoid flaming losses and then incinerated at 575 °C for 3 h in a muffle furnace. Crucibles were cooled in a desiccator (30-45 min) and weighed. Ash (%), dry basis, was calculated by Eq. (S2):

$$Ash = \frac{m_{ash}}{m_i} \times 100 \quad \text{(S2)}$$

where m_i is the dry mass of the sample (g) used for ashing (after drying at 105 ± 1 °C) and m_{ash} is is the residual inorganic mass after incineration (g) (crucible tare corrected). Results were reported as mean ± standard deviation.

S1.1.3 Water-soluble extractives

The content of hot-water-soluble extractives in SGB and SGB-C was determined by adapting the NREL Determination of Extractives in Biomass (water step) [3]. Approximately 1.00 g of biomass on a dry basis (105 ± 1 °C) were transferred to a glass beaker (150 mL) and mixed with deionized water at a solid-liquid ratio of 1:50 (w v^{-1}). The suspension was heated at 95 ± 5 °C for 1 h under gentle stirring, with the beaker partially covered (watch glass) to

minimize evaporation (add hot water as needed to maintain the S/L ratio). The mixture was then hot-filtered, and the solid residue was washed with hot water (3 x 30 mL). The solid was transferred to pre-dried, tared weighing pans, dried at 105 ± 1 °C to constant mass (cooling in a desiccator between weighing s), and weighed. The hot-water-soluble fraction (%), dry basis, was calculated by Eq. (S3):

$$\text{Water solubles} = \frac{m_0 - m_1}{m_0} \times 100 \quad \text{(S3)}$$

where m_0 is the initial dry mass before extraction and m_1 is the dry mass of the residue after extraction and washing. Results were reported as mean ± standard deviation.

S1.1.4 Holocellulose

The holocellulose content of SGB and SGB-C was determined by adapting the TAPPI UM 249 holocellulose method [4]. Biomass was used *in natura*, adjusted only to dry basis at 105 ± 1 °C (i.e., still containing extractives and hot-water solubles) to enable comparison with solvent-free solubilization. Sintered-glass funnels (ASTM 2 or M, 40-100 μm, ≥150 mL) were washed, dried at 105 ± 1 °C for ≥2 h, and stored in a desiccator until use. In a 500 mL Erlenmeyer, 3.0 g of biomass (dry basis) were combined with 120 mL deionized water; the flask (partially covered with a watch glass) was held in a 70 ± 1 °C water bath. Sodium chlorite (2.50 g) and glacial acetic acid (1.0 mL) were added and the suspension kept for 1 h; the same additions were repeated at 1 h and 2 h, for a total reaction time of 4 h at 70 ± 1 °C. The slurry was then rapidly cooled to 5 ± 1 °C in an ice bath, vacuum-filtered cold through the prepared sintered-glass funnel, and the cake was washed sequentially with two portions of water and one portion of methanol. The solid was dried to constant mass at 105 ± 1 °C in the same sintered-glass funnel (cooling in a desiccator between weighings) and weighed. The holocellulose content, H (%) dry basis) was calculated by Eq. (S4):

$$H = \frac{m_{holo}}{m_0} \times 100 \quad \text{(S4)}$$

where m_0 is the initial dry mass and m_{holo} is the dry mass of the holocellulose solid after the sodium-chlorite/acetic-acid treatment. Results were reported as mean ± standard deviation. In addition to being used to determine H the in SGB (H-SGB) or SGB-C (H-SGB-C), this methodology was also applied to determine H in the solid fractions after delignification with different solvents (See Section 2.4 of the manuscript).

S1.1.5 Klason Lignin

The Klason lignin (L-Klason) content of SGB and SGB-C was determined by adapting the NREL Determination of Structural Carbohydrates and Lignin in Biomass (two-step acid hydrolysis). Biomass was used *in natura*, adjusted only to dry basis at 105 ± 1 °C (i.e., still containing extractives and hot-water solubles) to enable comparison with solvent-free solubilization. Aliquots of ~0.30 g (dry basis) were transferred to suitable vessels; 3.00 mL of 72% H_2SO_4 were added and the mixture was held at 30 ± 1 °C for 60 min with occasional mixing (first hydrolysis). The slurry was then diluted to 4% H_2SO_4 with 84.0 mL of deionized water and subjected to a second hydrolysis at 90 ± 1°C for 3 h in a water bath (vessel partially covered), instead of autoclaving at 121 °C-60 min, to minimize lignin degradation in bagasse. At the end, the mixture was filtered through a tared quantitative paper filter; the residue was washed with hot water to neutrality. The paper filter with the residue was dried at 105 ± 1 °C to constant mass (cooling in a desiccator between weighings) and weighed. The L-Klason (%), dry basis; no ash correction was calculated by Eq. (S5):

$$\text{L-Klason} = \frac{m_L}{w_d} \times 100 \quad \text{(S5)}$$

where m_d is dry mass after drying (g) at 105 ± 1 °C and m_L is the mass of the acid-insoluble, that is lignin fraction (g), on the paper filter (corrected by the filter tare) after drying at 105 ± 1 °C. Results were reported as mean ± standard deviation.

S1.2 Material characterization

S1.2.1 Fourier-transform infrared spectroscopy

Fourier Transform Infrared (FTIR) spectra were obtained using a Spectrum BX model of the Perkin Elmer (USA) in attenuated total reflectance mode The infrared spectra of the materials were obtained in the range of 400 to 4000 cm^{-1}. Each spectrum was obtained from 32 scans of the sample with a resolution of 1 cm^{-1}. The spectra were subjected to intensity normalization (0-1 range), baseline correction, and smoothing using the Savitzky-Golay method (2nd-order polynomial, 15-point window).

S1.2.2 Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) were conducted using an Ultra-High-Resolution Scanning Electron Microscope Tescan Clara-UHR (Czech Republic), equipped with a Bruker-Quantax EDS system (USA). The surface morphology and elemental composition of the materials were evaluated using an

acceleration voltage of 5 keV for SEM and 20 keV for EDS, respectively. Before analysis, approximately 8 mg of the sample was placed on an aluminum support covered with double-sided carbon tape. The sample was then placed in a carbon bath under vacuum to remove possible impurities from the material.

S1.2.3 Thermogravimetric analysis

Thermal stability assessments were carried out using a DTG-60 AH thermogravimetric analyzer (Shimadzu, Japan). For each analysis, approximately 10 mg of each sample of treated and untreated biomass, as well as prepared biochars, were analyzed under an inert atmosphere of N_2 with a gas flow rate of 50 mL min^{-1}. The temperature ranged from 25 to 700 °C, with a heating rate of 10 °C min^{-1}.

S1.2.4 CHNS elemental analysis

The elemental composition (C, H, N, and S) of the lignin fractions was determined by CHNS elemental analysis using a TruSpec 630-200-200 elemental analyzer (LECO Corporation). Approximately up to 10 mg of finely ground and oven-dried sample (micro-scale mode) was weighed into tin capsules and subjected to complete combustion at 1075 °C in an oxygen-rich atmosphere. The resulting combustion gases were subsequently passed through an afterburner maintained at 850 °C to ensure complete oxidation.

Carbon, hydrogen, and sulfur contents were quantified by infrared (IR) absorption detection, whereas nitrogen was determined by thermal conductivity detection (TCD). The results were expressed as weight percentages of each element. All measurements were performed in duplicate, and the reported values correspond to the mean ± standard deviation.

S1.2.5 NMR

^{31}P-NMR analysis was performed according to Meng et al.[13]. The lignin samples were initially dried under vacuum at 40 °C for 6 h to remove residual moisture. Approximately 30 mg of the dried material were then dissolved in 500 µL of a mixture of anhydrous pyridine and $CDCl_3$ (1.6:1, v v^{-1}). Subsequently, 100 µL of a solution containing cyclohexanol (20 mg mL^{-1}), used as internal standard, and chromium (III) acetylacetonate (3.6 mg mL^{-1}), employed as a relaxation agent, prepared in the same solvent mixture, were added to the sample. After that, 100 µL of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) was introduced as phosphitylating reagent. The reaction mixture was thoroughly homogenized and immediately transferred to an NMR tube for analysis using a 400 MHz NMR spectrometer. Quantification of the different hydroxyl groups was carried out according to Eq.(S6):

$$Functional\ group\ (mmol\ g^{-1}\ lignin) = \frac{normalized\ peak\ area}{sample\ weight} \times\ IS\ concentration \times 0.1 \qquad (S6)$$

^{1}H-NMR analysis was performed according to Fernández-Costas et al.[14], in which 50 mg of lignin was dissolved in 750 mm^3 of DMSO-d_6 prior to spectral acquisition. Spectra were acquired using a 30° pulse angle with a relaxation delay of 1 s. A total of 16 scans were collected, with an acquisition time of 6.3 s. Prior to Fourier transformation, the free induction decay (FID) was treated with an exponential line broadening factor of 0.3 Hz.

S1.2.6 Color analysis

The influence of the treatments on the holocellulosic fraction was determined through color analysis using the CIELAB system with a Color Muse colorimeter (Variable, 61 Inc., Chattanooga, TN, USA). In this color space, L* indicates brightness (ranging from 0 = black to 100 = white), a* expresses the transition between green (−a) and red (+a), and b* represents the balance between yellow (−b) and blue (+b). Each treatment was evaluated in triplicate, and the data are presented as mean values accompanied by their standard deviations.

S2. SUPPLEMENTARY FIGURES

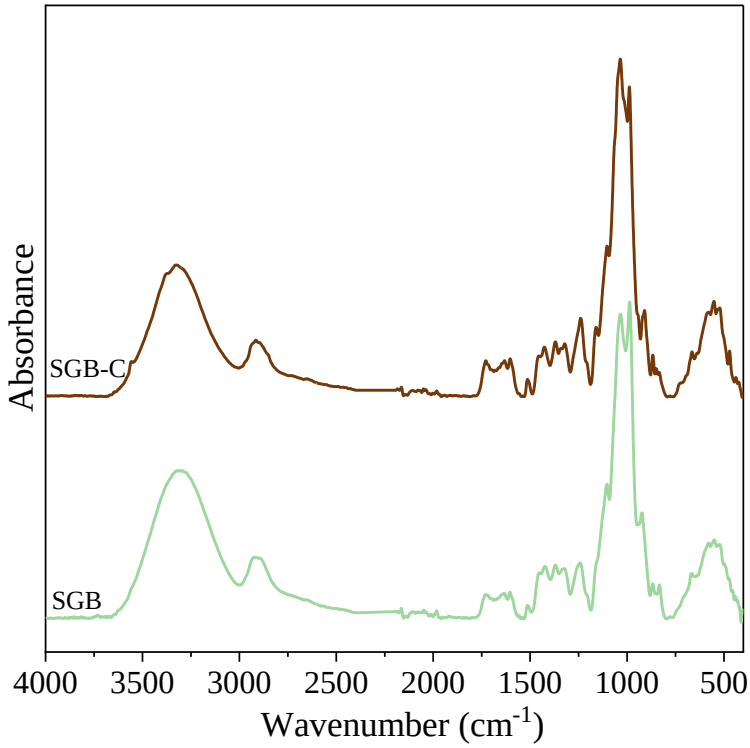


Figure S1. FTIR spectra of SGB and SGB-C. Details on band assignment are shown in Table S7.

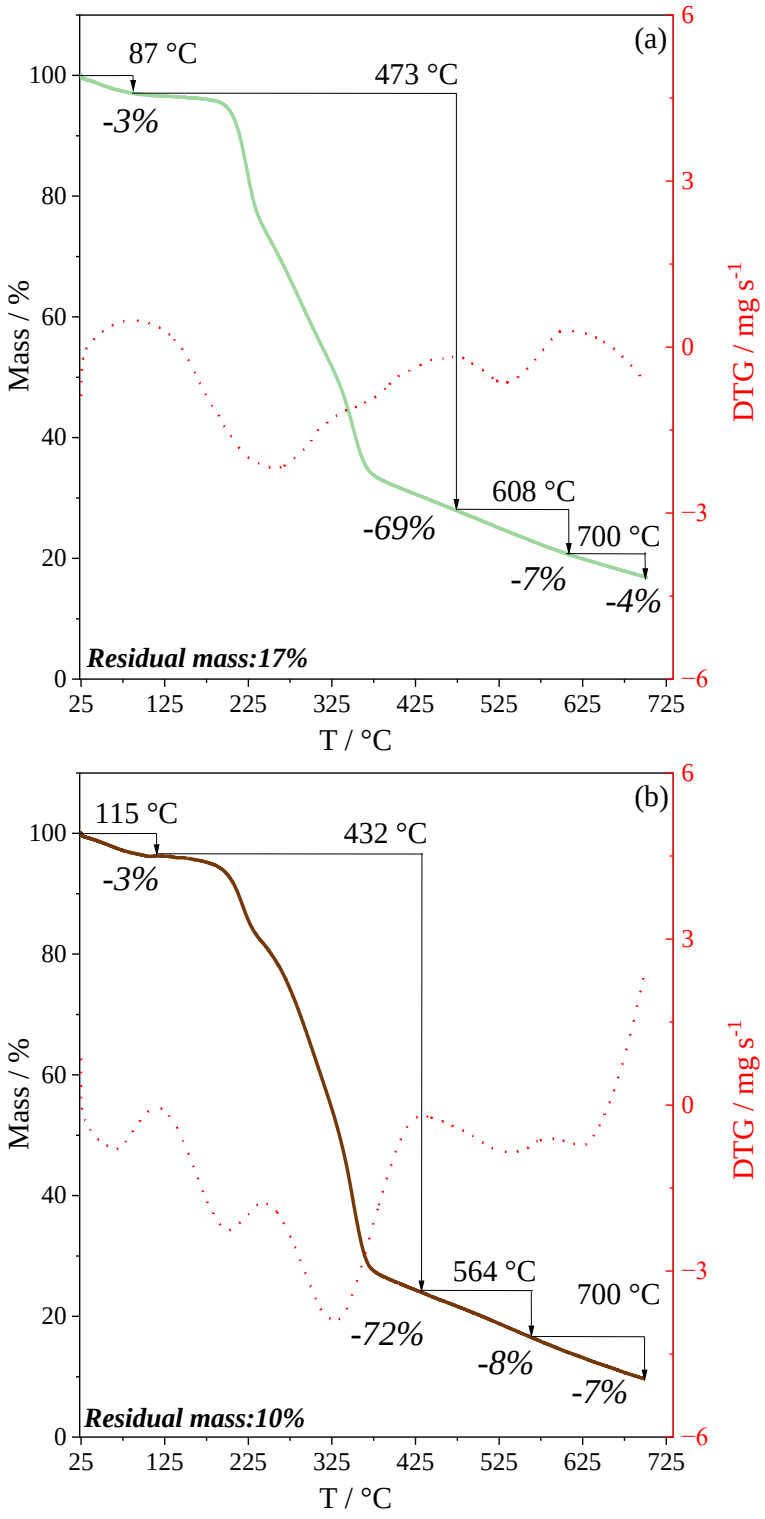


Figure S2. Thermogravimetric analysis (TGA) and derivative (DTG) profiles of (a) SGB and (b) SGB-C.

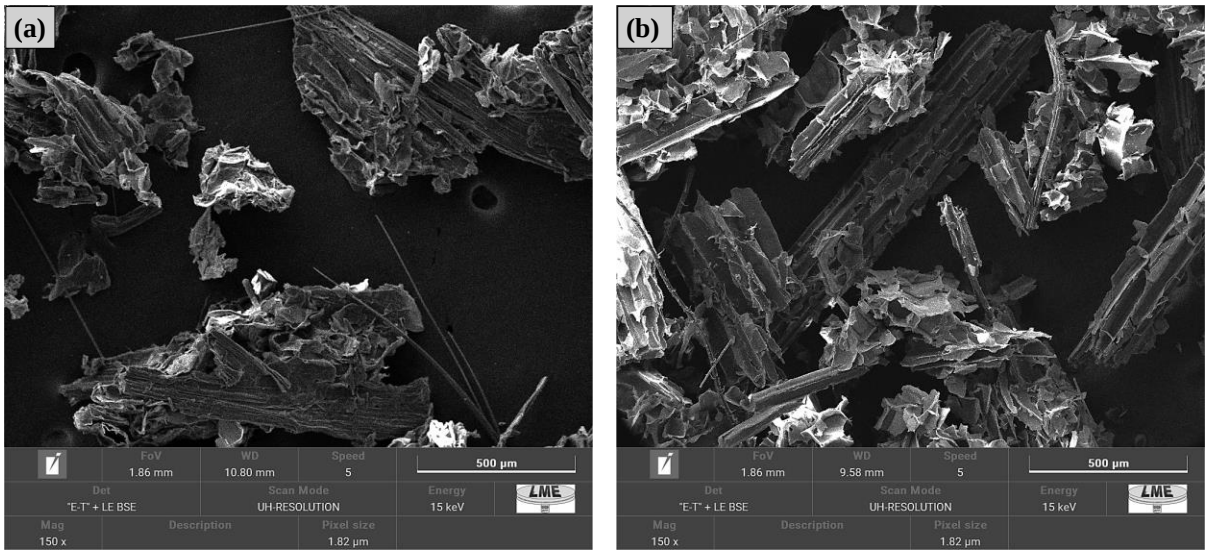


Figure S3. SEM micrographs of (a) SGB and (b) SGB-C.

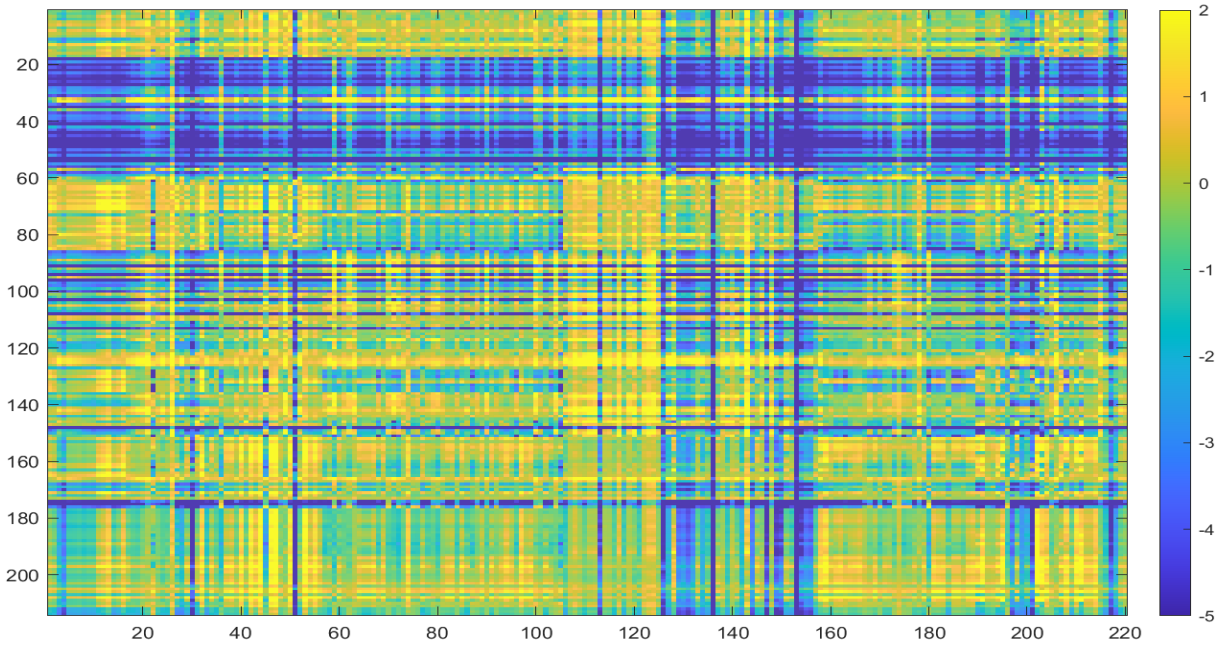


Figure S4. Logarithmic activity coefficients at infinite dilution of GG in DES ln(γ^{∞}) both predicted by COSMO-RS in 47,080 possible HBA:HBD combinations (1:1) at 25 °C.

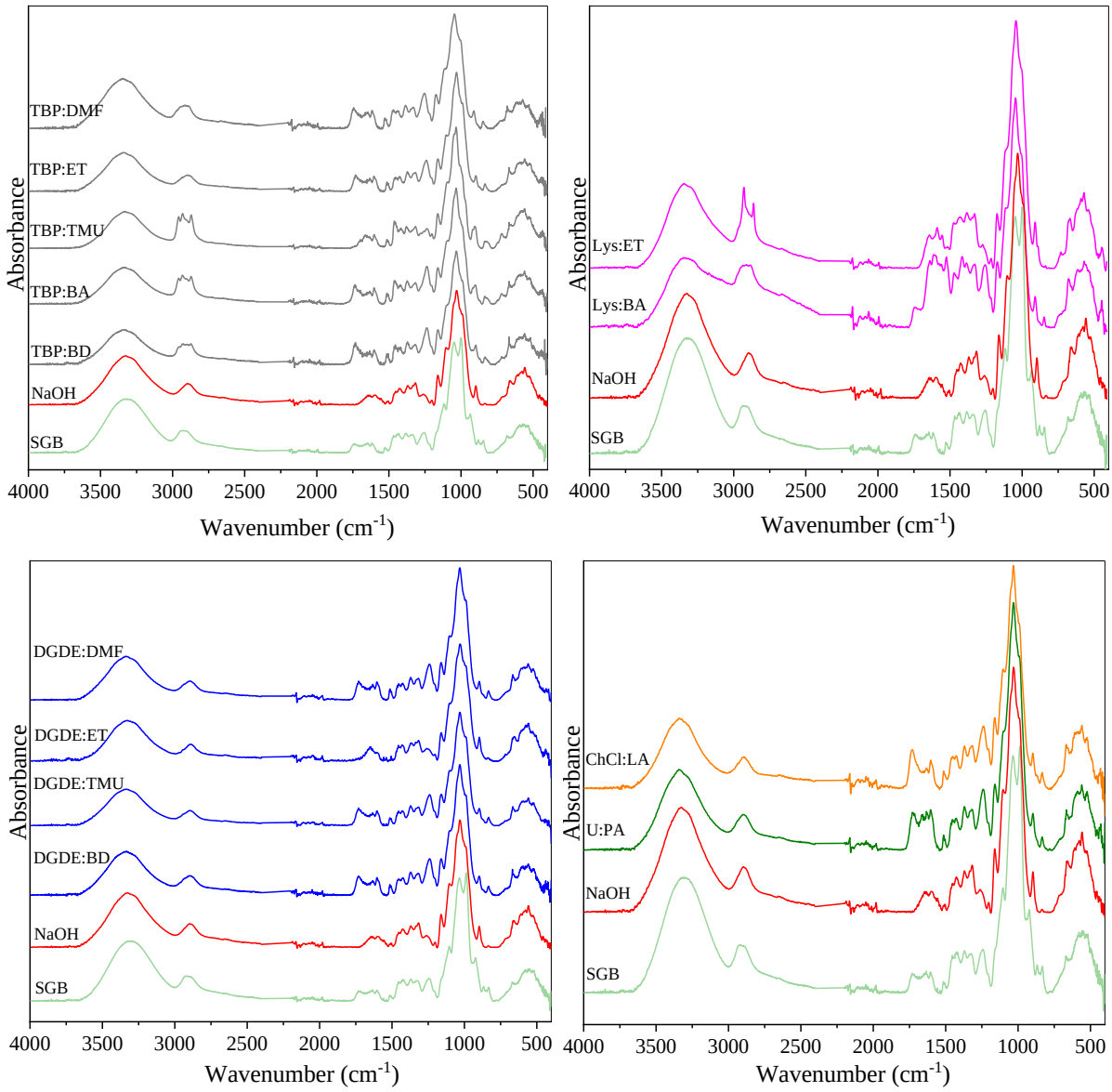


Figure S5. FTIR spectra of the solid fraction after lignin solubilization in the initial screening. Solubilization conditions: 90 ± 1°C for 90 min, 600 rpm, S/L ratio of 1:10, water-free conditions.

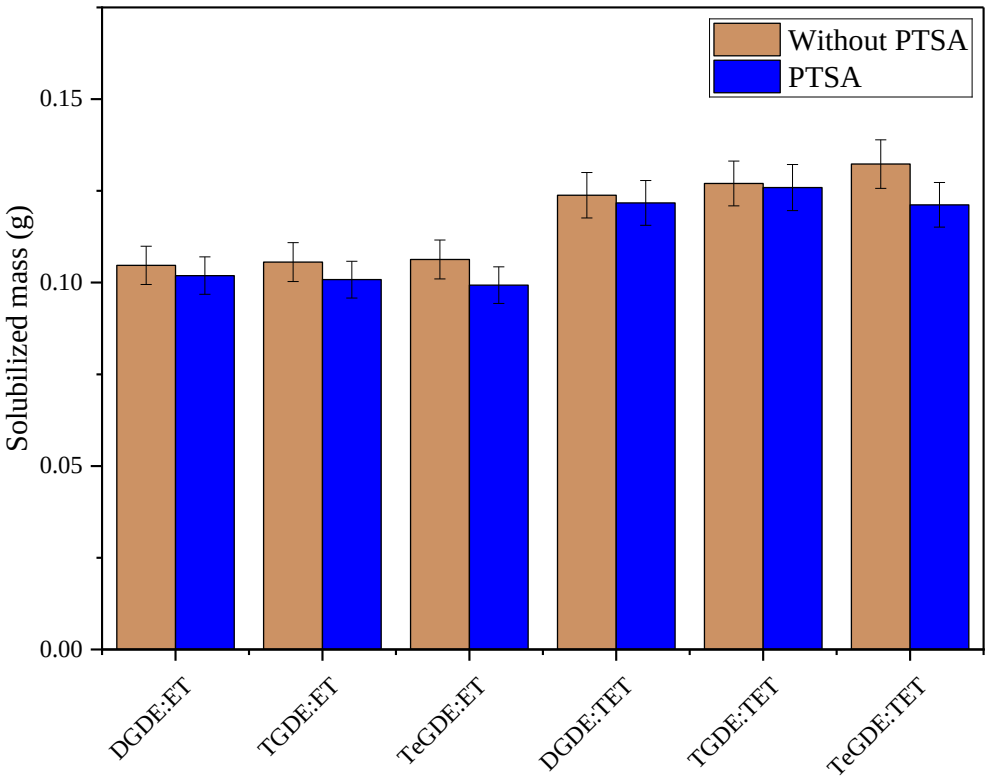


Figure S6. Solubilized mass of SGB using different DES with and without PTSA, evidencing chain-length effect. Solvents preparation: 1:1 molar ratio, 0.005 M PTSA, 80 ± 1 °C, 30 min, stirring. Solubilization conditions: 90 ± 1 °C for 90 min, 600 rpm, S/L ratio of 1:10, under water-free conditions.

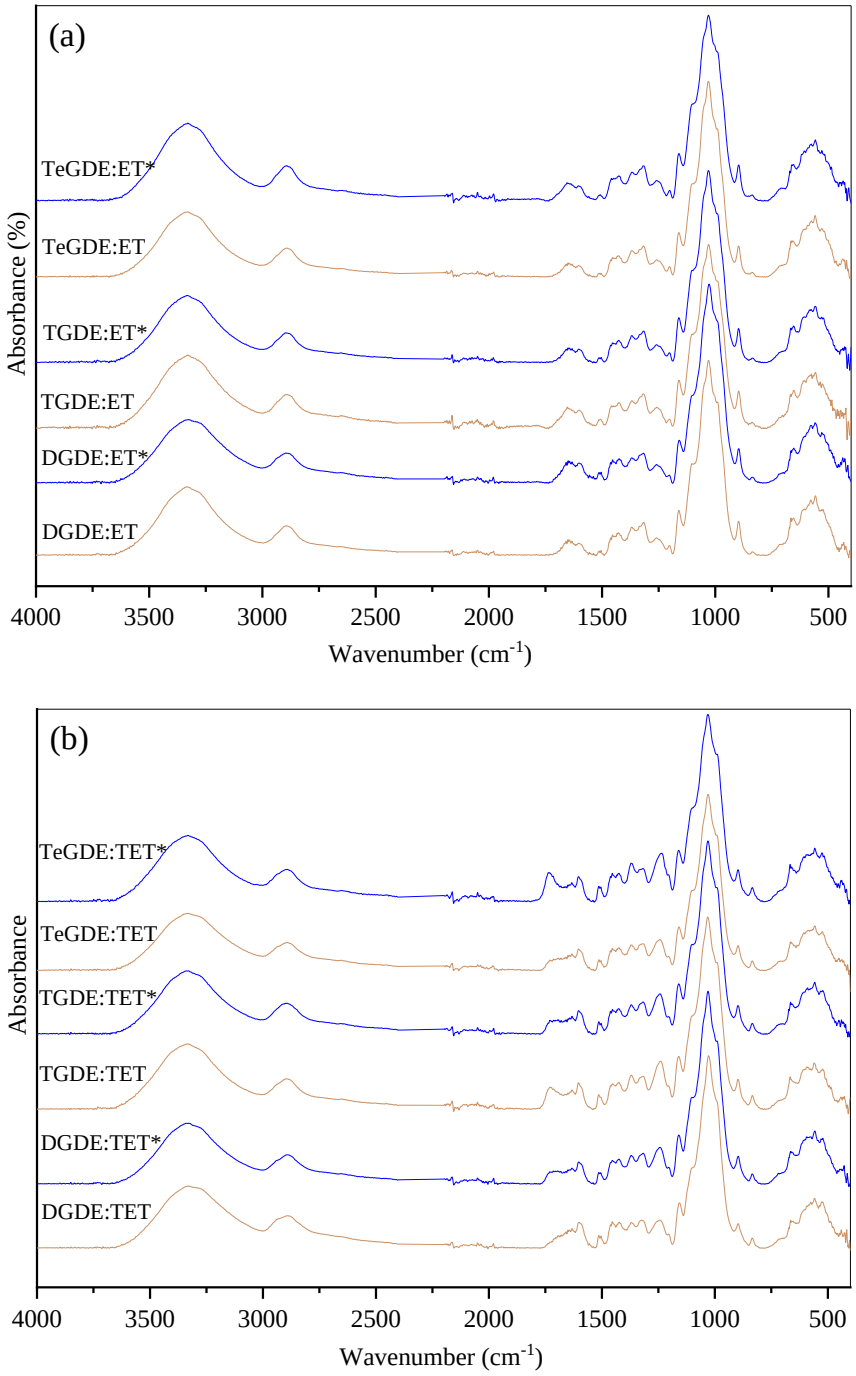


Figure S7. FTIR spectra of the solid fractions obtained after treatment with different solvent systems, highlighting the chain-length effect: (a) ethanolamine as HBD and (b)triethanolamine. Solvent preparation: 1:1 molar ratio, 0.005 M PTSA, 80 ± 1 °C, 30 min under stirring. Delignification conditions: 90 ± 1 °C, 90 min, 600 rpm, S/L ratio 1:10, under water-free conditions. *Addition of PTSA.

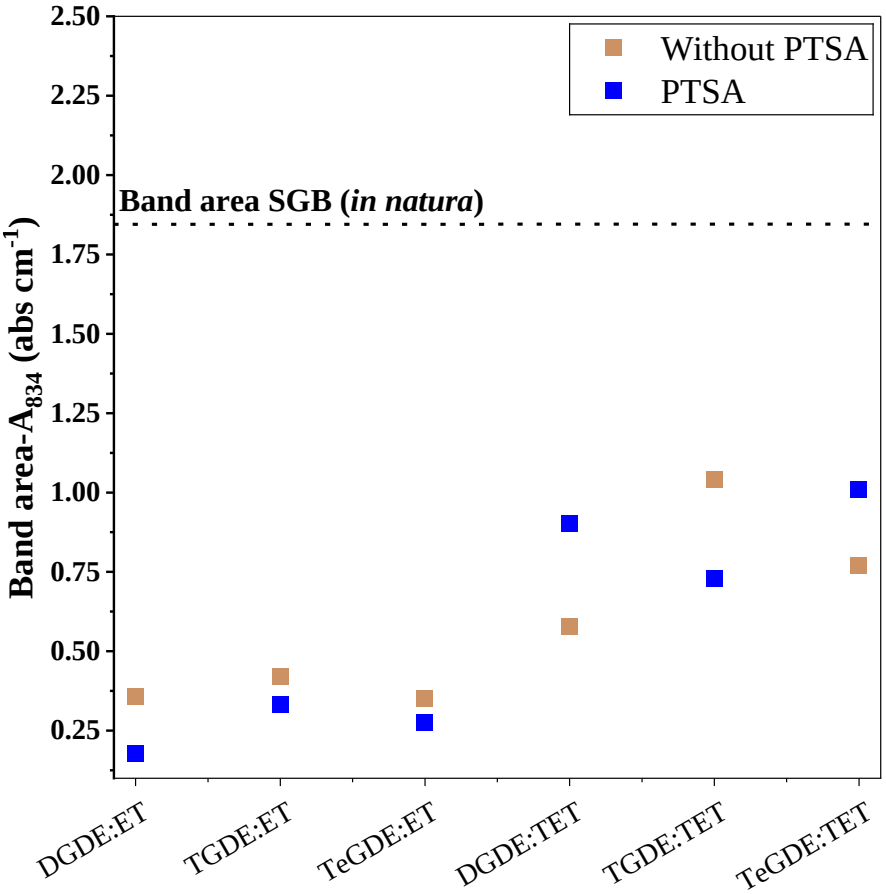


Figure S8. Band area at 834 cm^{-1} (from FTIR spectra in Fig. S7), highlighting chain-length effect and comparison with raw SGB.

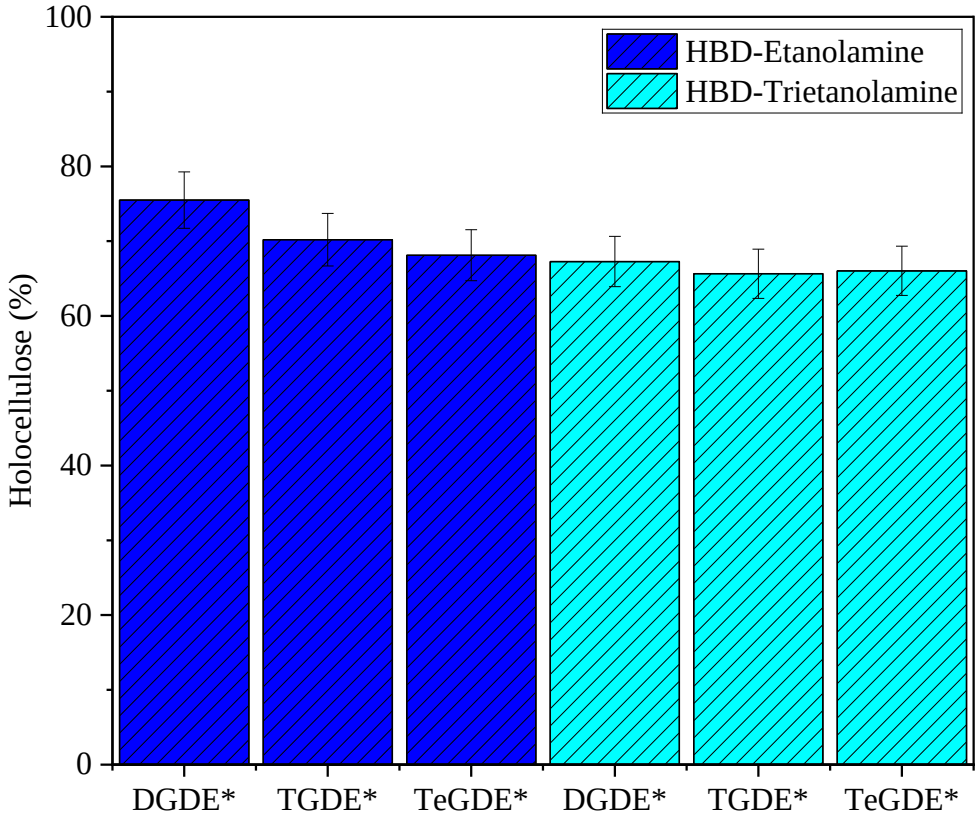


Figure S9. The holocellulose content, *H* quantified in the solid fractions obtained after treatment with different solvent systems, as presented in Figures S6, S7, and S8. *Addition of PTSA.

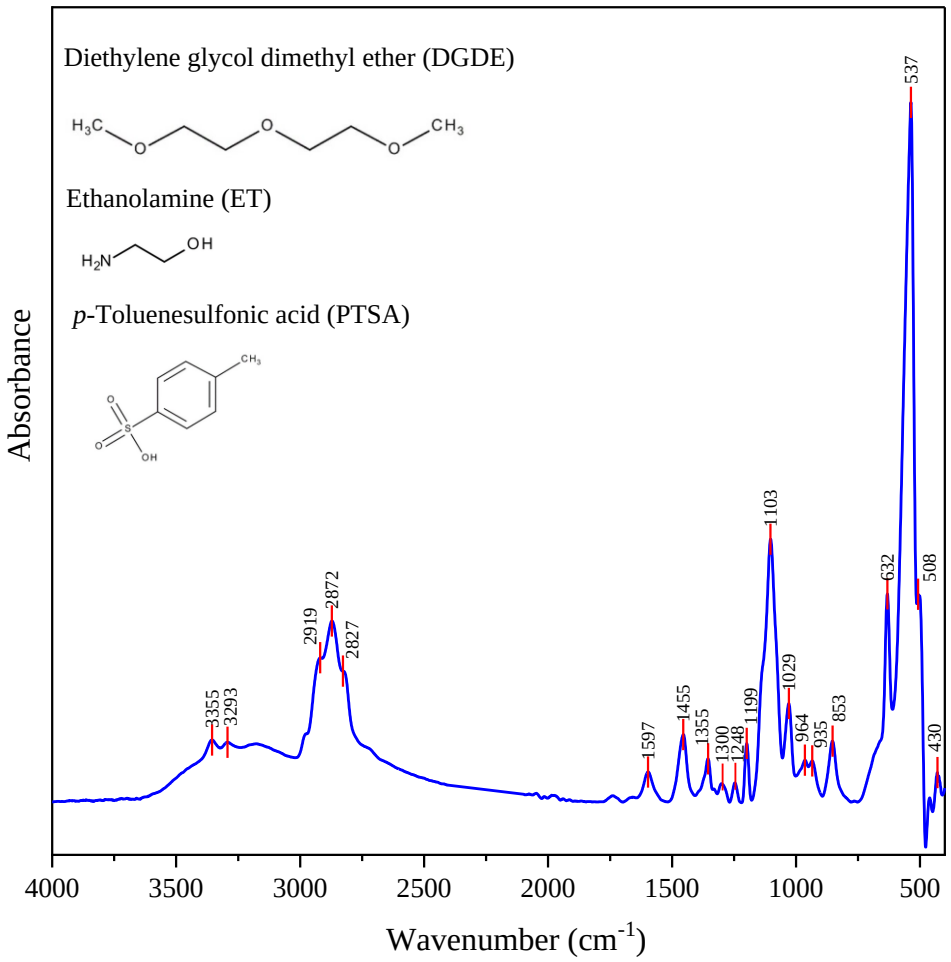


Figure S10. FTIR spectrum of the DGDE:ET solvent. Preparation conditions: molar ratio 1:1 and PTSA concentration of 0.005 M, at 80 ± 1 °C for 30 min under stirring.

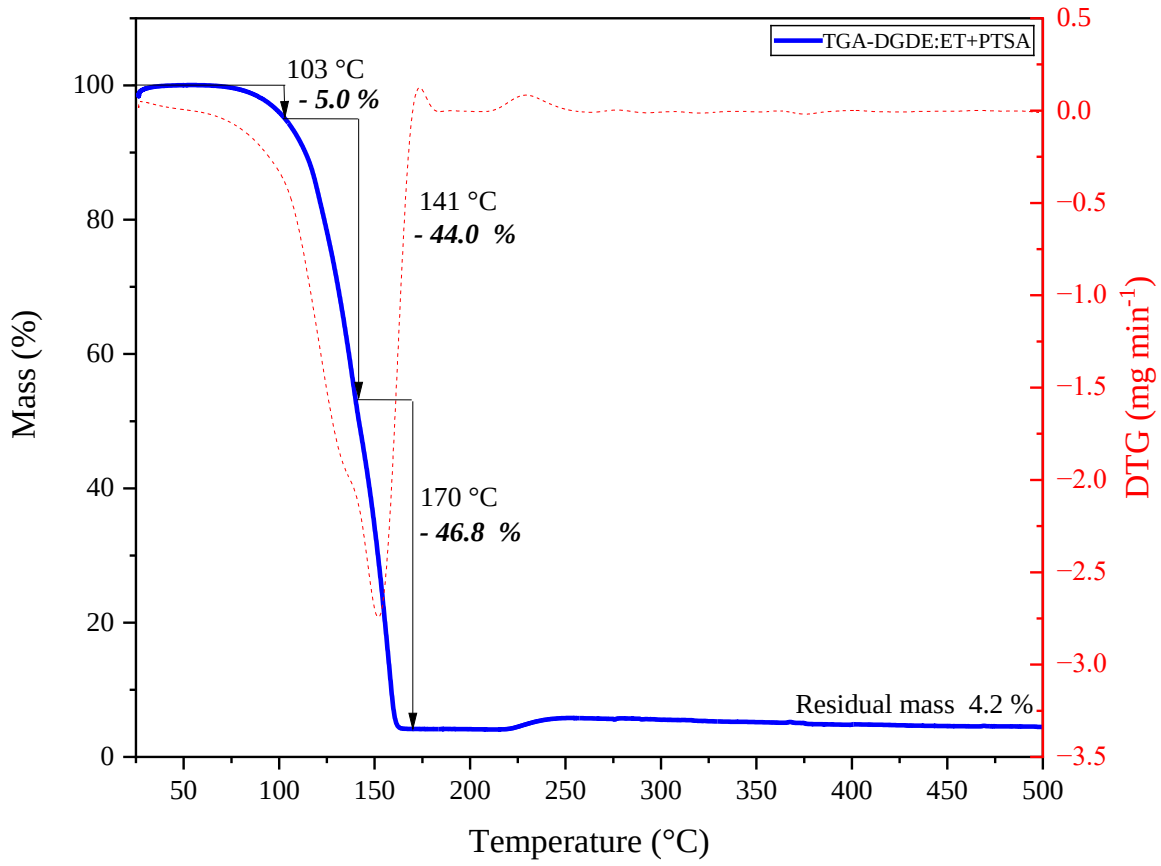


Figure S11. TGA and DTG profiles of the DGDE:ET+PTSA solvent. Preparation conditions: molar ratio 1:1 and PTSA concentration of 0.005 M, at 80 ± 1 °C for 30 min under stirring.

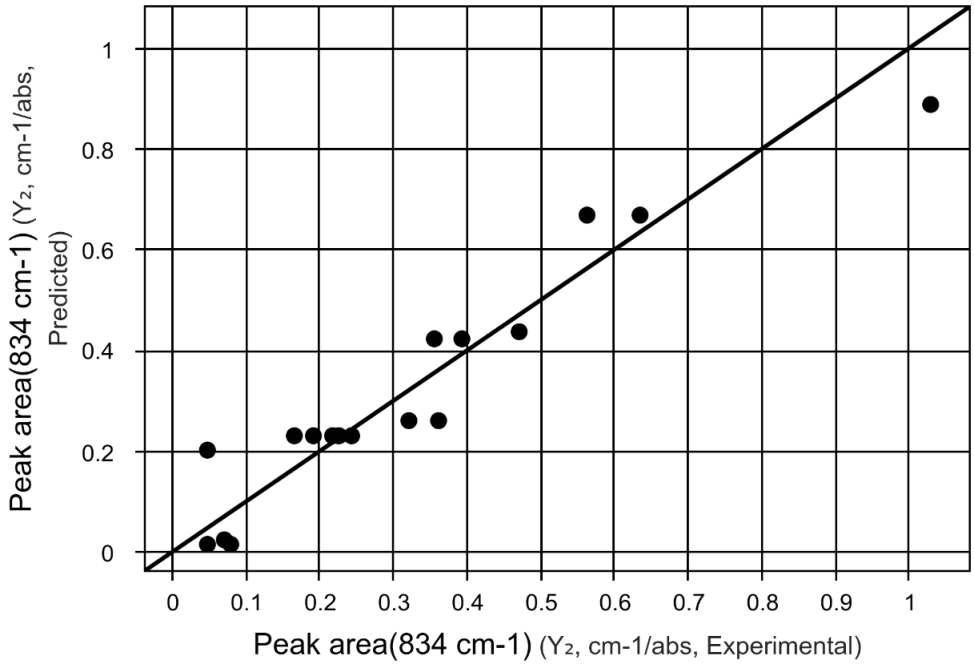


Figure S12. Predicted versus experimental values of band area at 834 cm^{-1} (Y_2), obtained from the fitted response surface model. The solid line represents the ideal correlation (y = x).

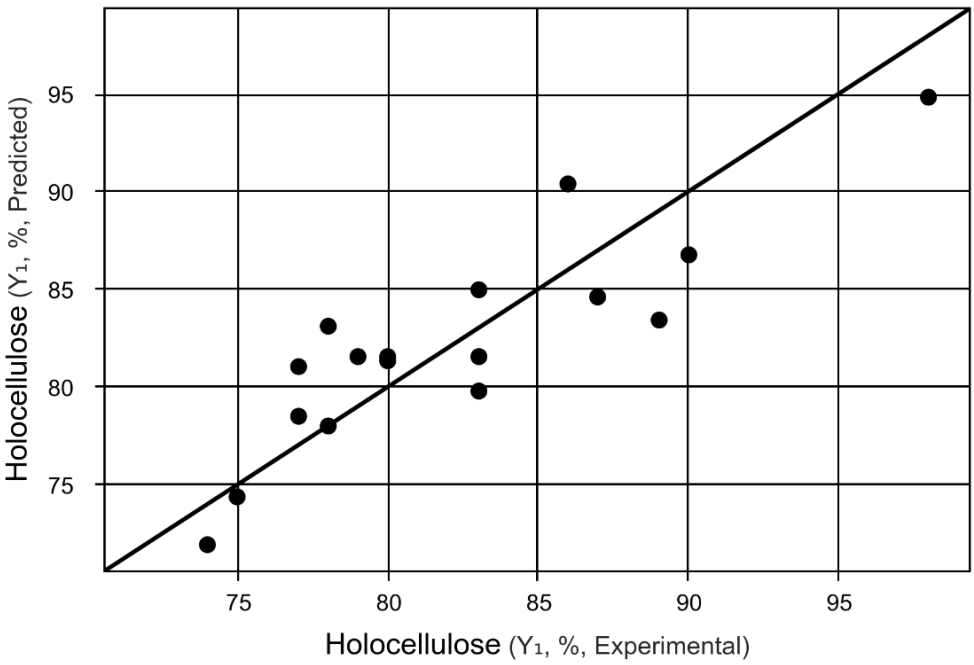


Figure S13. Predicted versus experimental values of holocellulose content, *H* (Y_1), obtained from the fitted response surface model. The solid line represents the ideal correlation (y = x).

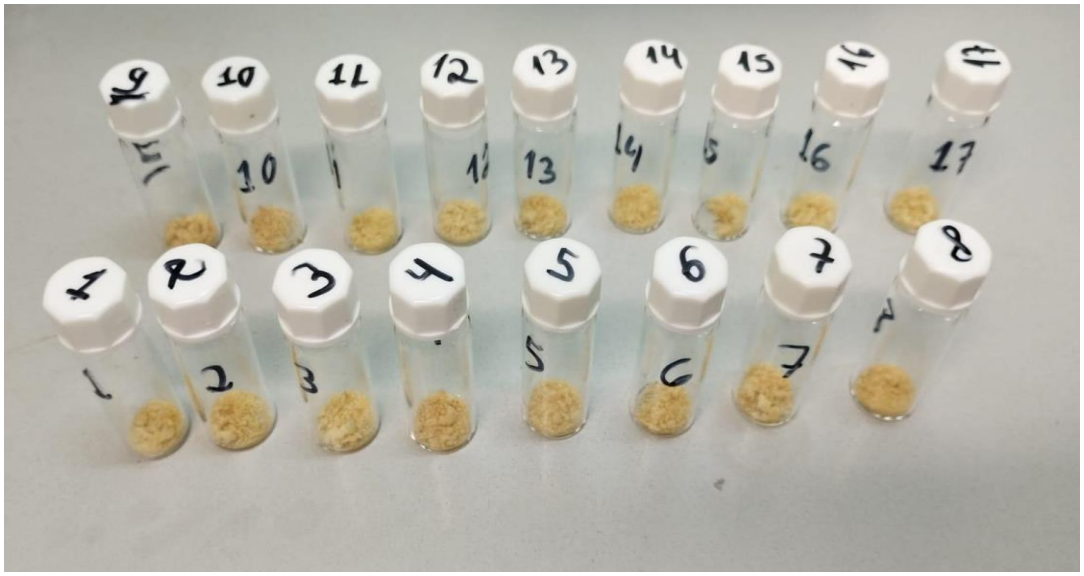


Figure S14. Solid fraction obtained after each run of the experimental design.

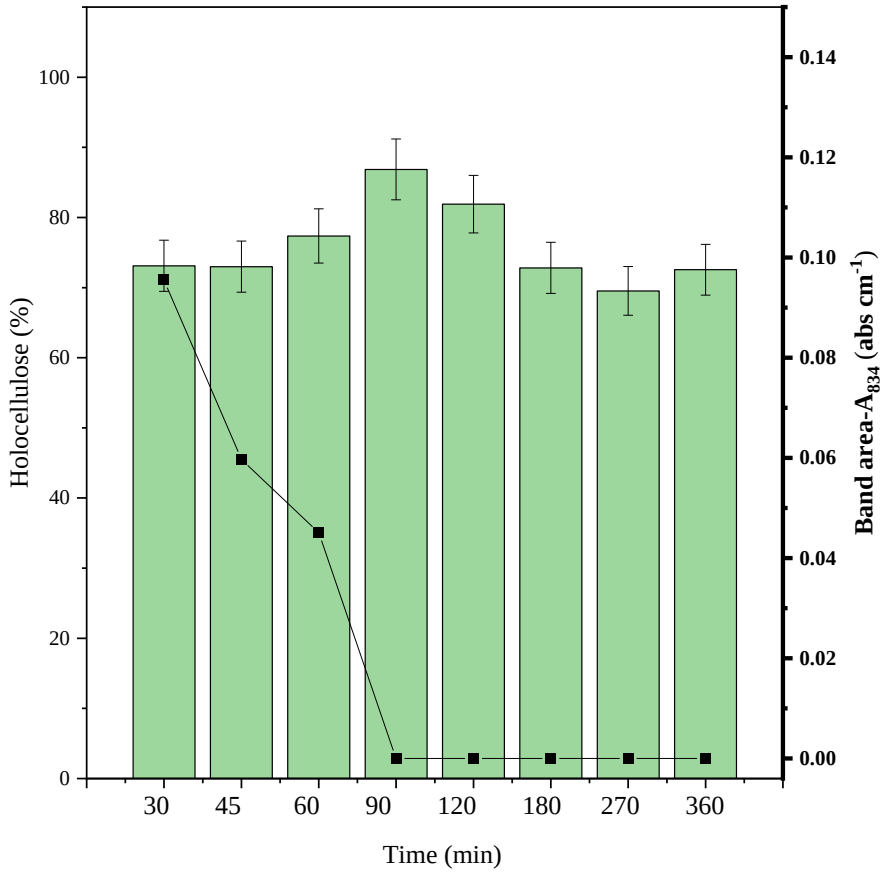


Figure S15. *H* (bars) and A_{834} (dot-line) for the solid fractions obtained after treatment with DGDE:ET+PTSA as a function of the reaction time.

Figure S16. Kinetics of delignification, showing the solid fraction obtained at different reaction times: (1) 30 min, (2) 45 min, (3) 60 min, (4) 90 min, (5) 120 min, (6) 180 min, (7) 270 min, and (8) 360 min. Conditions: DGDE molar fraction = 0.1 (ET predominance), T = 100 ± 1 °C, [PTSA] = 0.03 M, S/L =1:10.

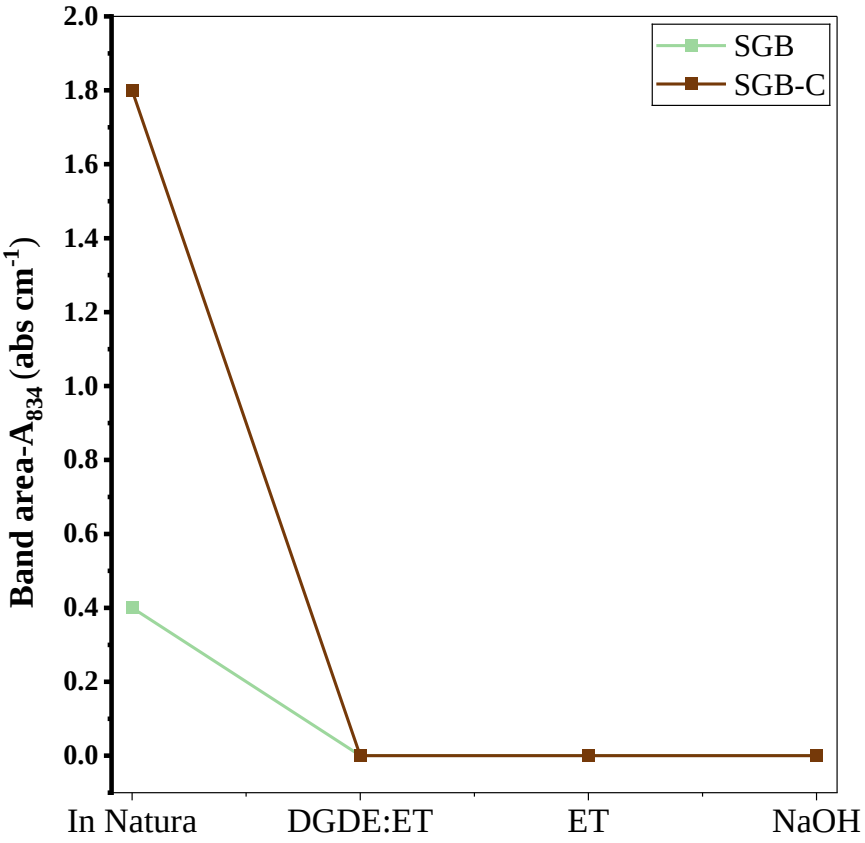


Figure S17. Band $A_{834\ of}$ the solid fraction from delignification assays under optimal conditions, comparing SGB and SGB-C.

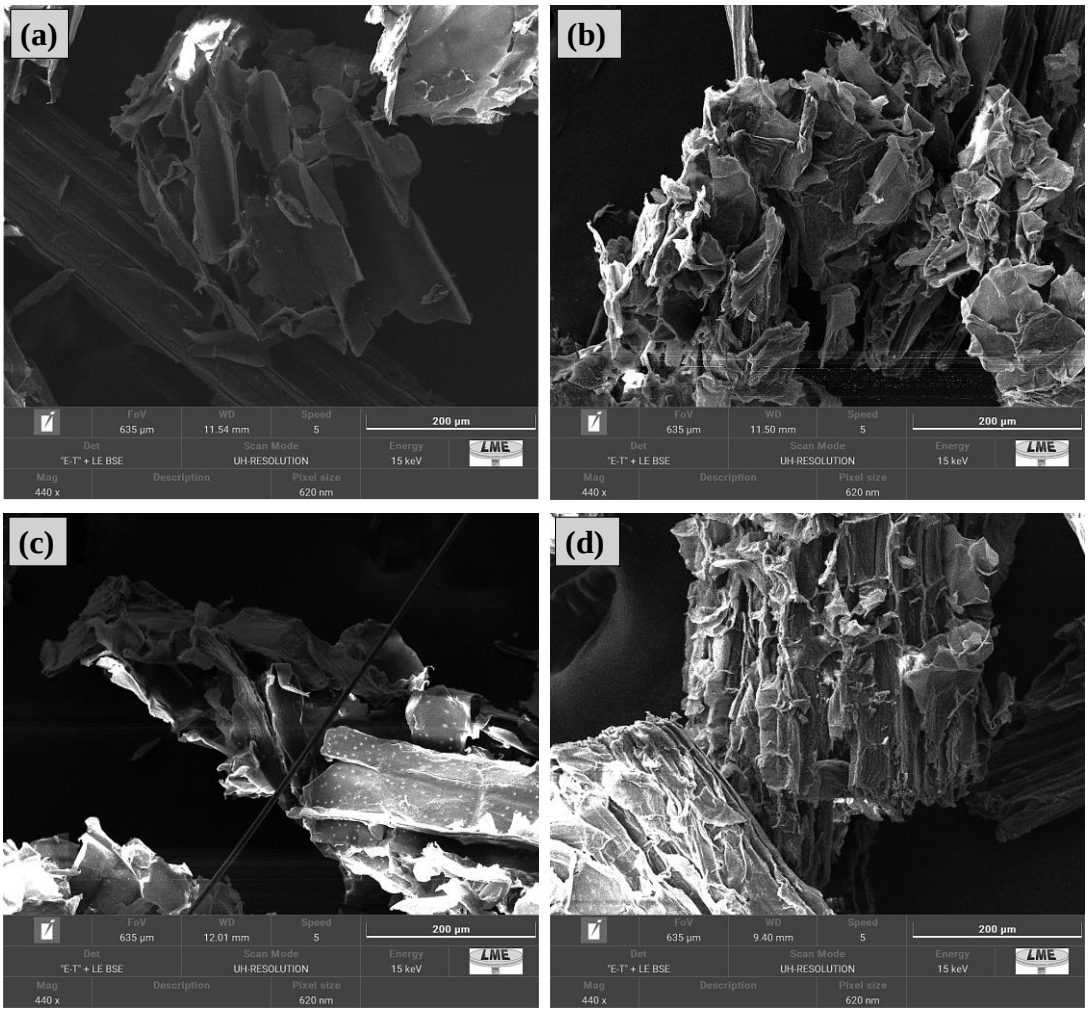


Figure S18. SEM images of holocellulosic fractions obtained from SGB-C: (a) H-SGB-C; (b) H-DGDE:ET+PTSA; (c) H-ET+PTSA; and (d) H-NaOH. H-denotes the holocellulosic fraction recovered using each solvent or the conventional method for H-SGB-C.

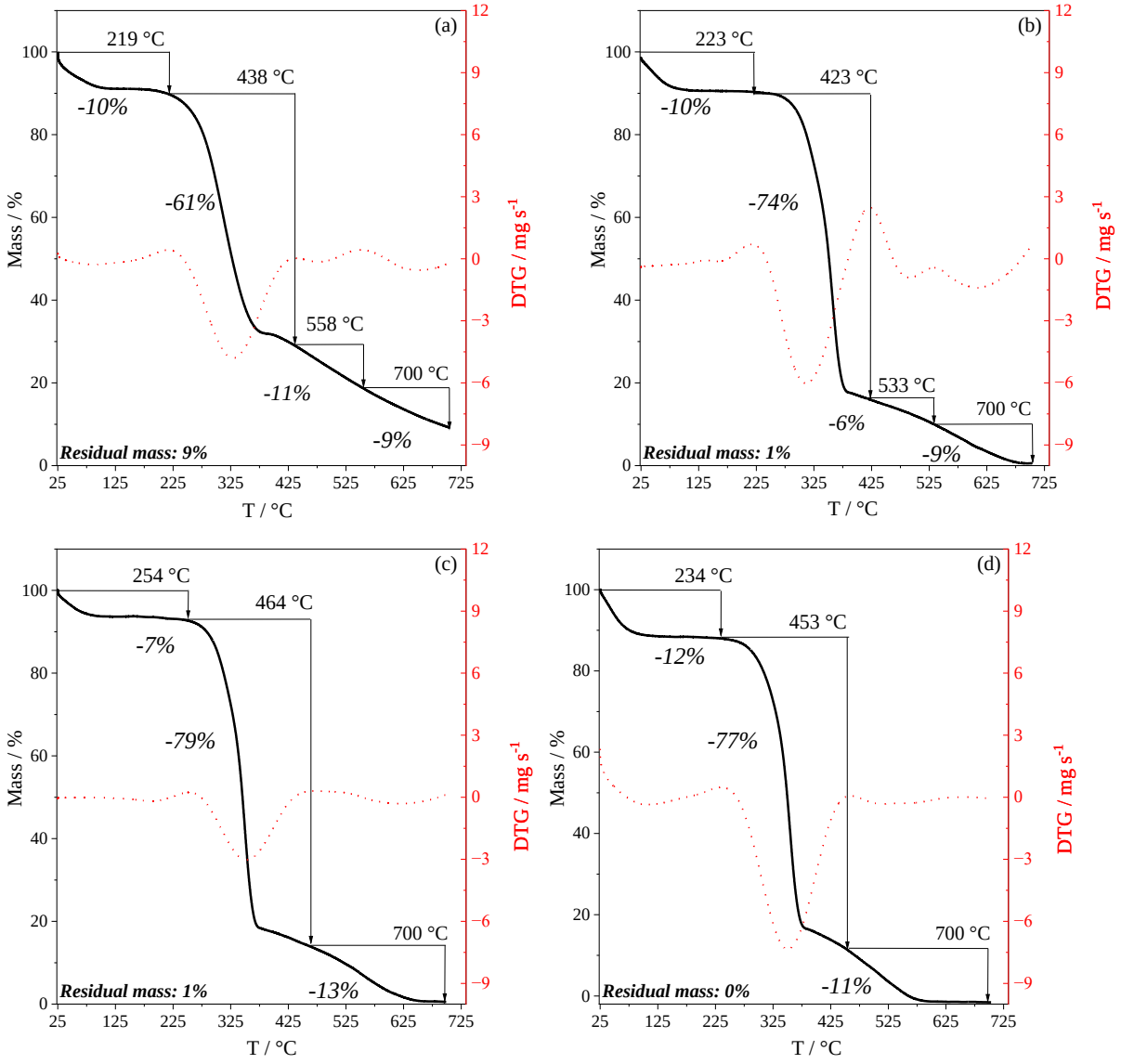


Figure S19. TGA and DTG profiles of holocellulosic fractions obtained from SGB: (a) H-SGB-C; (b) H-DGDE:ET+PTSA; (c) H-ET+PTSA; and (d) H-NaOH. H-denotes the holocellulosic fraction recovered using each solvent or the conventional method for H-SGB.

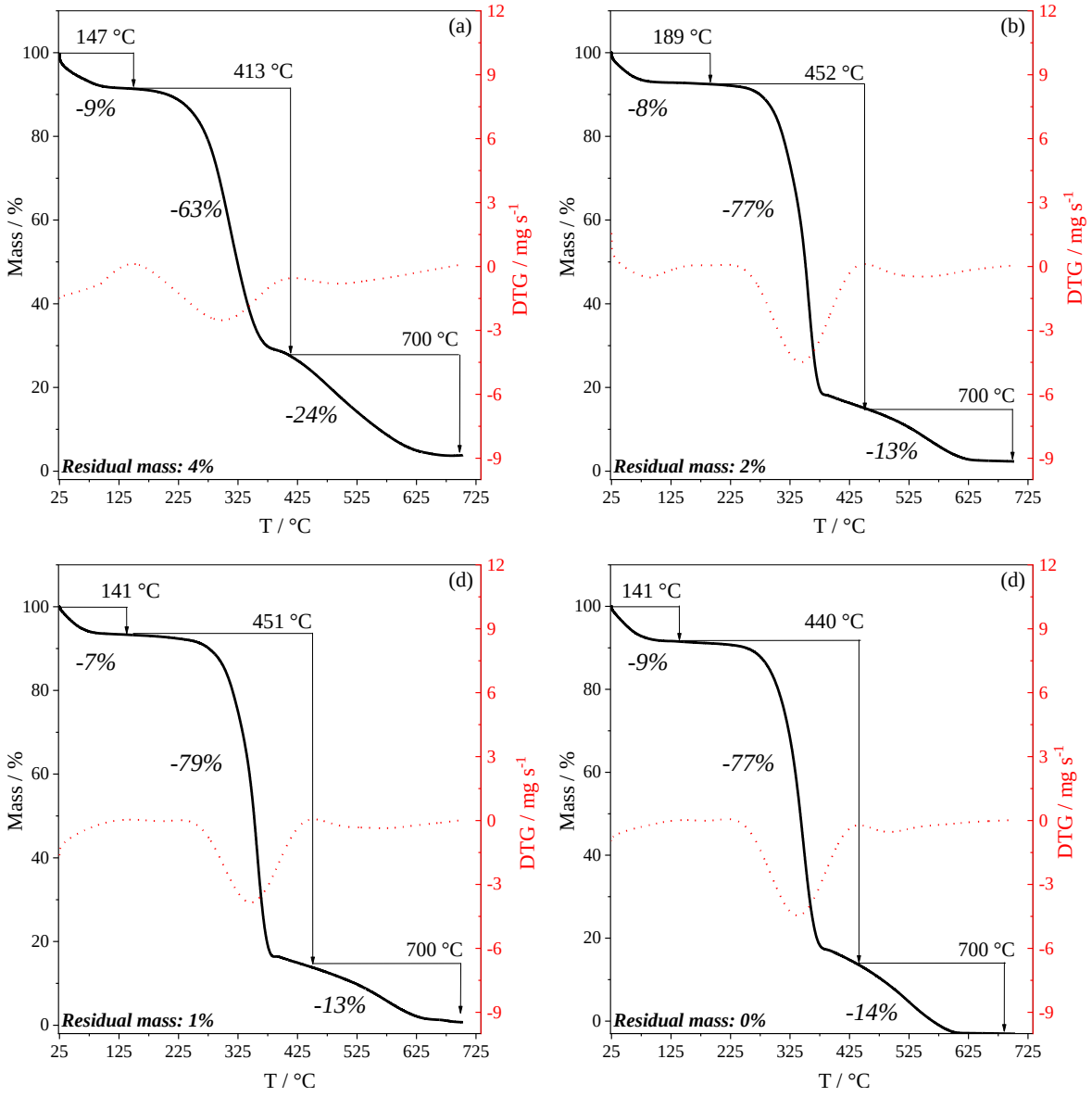


Figure S20. TGA and DTG profiles of holocellulosic fractions obtained from SGB-C: (a) H-SGB-C; (b) H-DGDE:ET+PTSA; (c) H-ET+PTSA; and (d) H-NaOH. H-denotes the holocellulosic fraction recovered using each solvent or the conventional method for H-SGB-C.

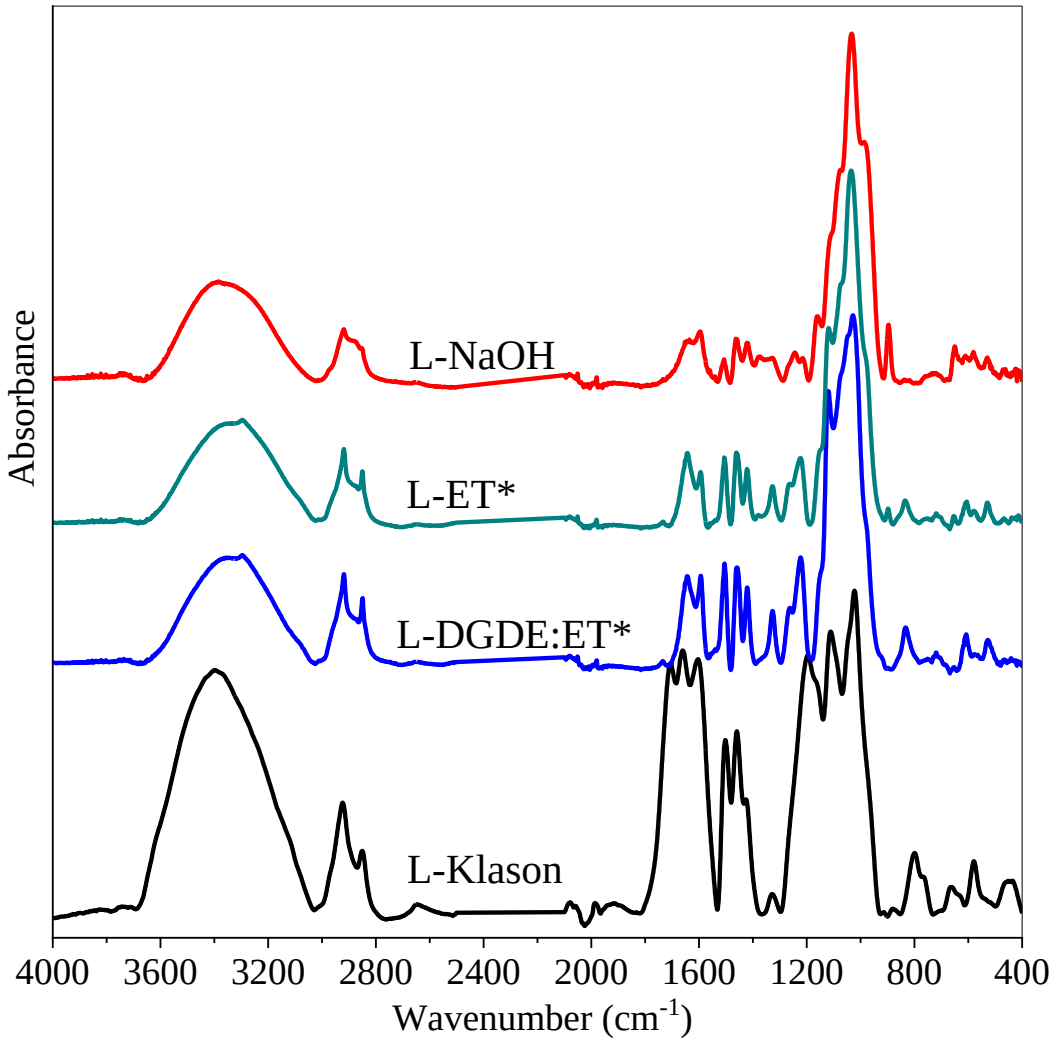


Figure S21. FTIR spectra of lignin from SGB-C. L-X denotes the lignin recovered using each solvent X or obtained by the Klason method. *Addition of PTSA.

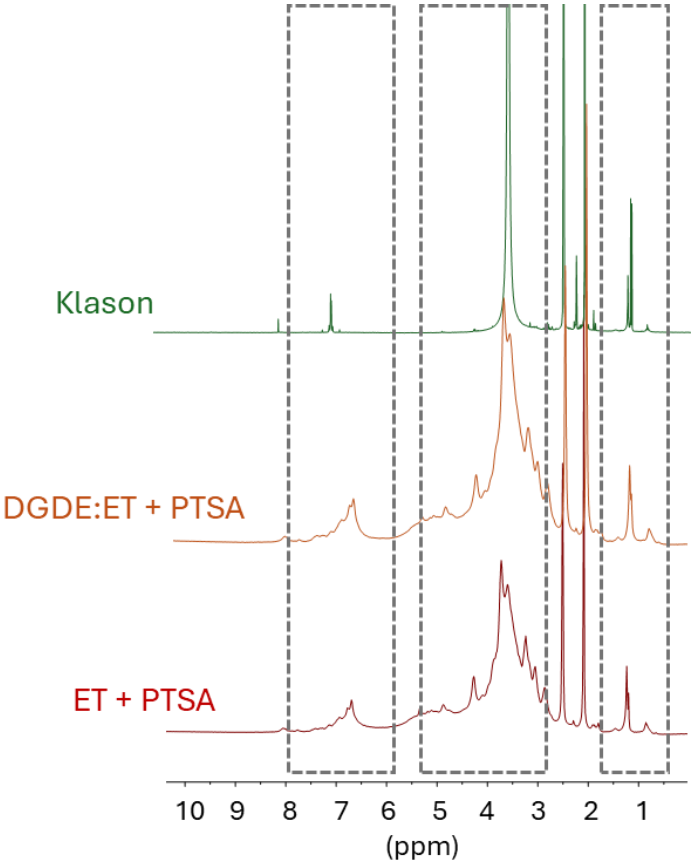


Figure S22. ^{1}H NMR spectra of Klasson, DGDE:ET + PTSA and ET + PTSA lignin samples.

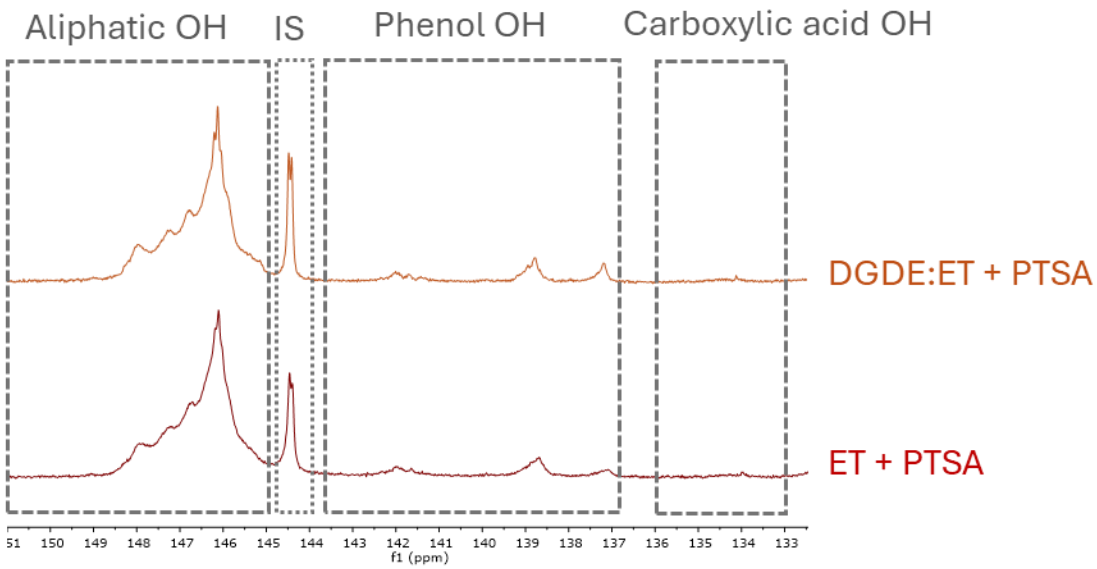


Figure S23. ^{31}P-NMR spectra of, DGDE:ET + PTSA and ET + PTSA lignin samples.

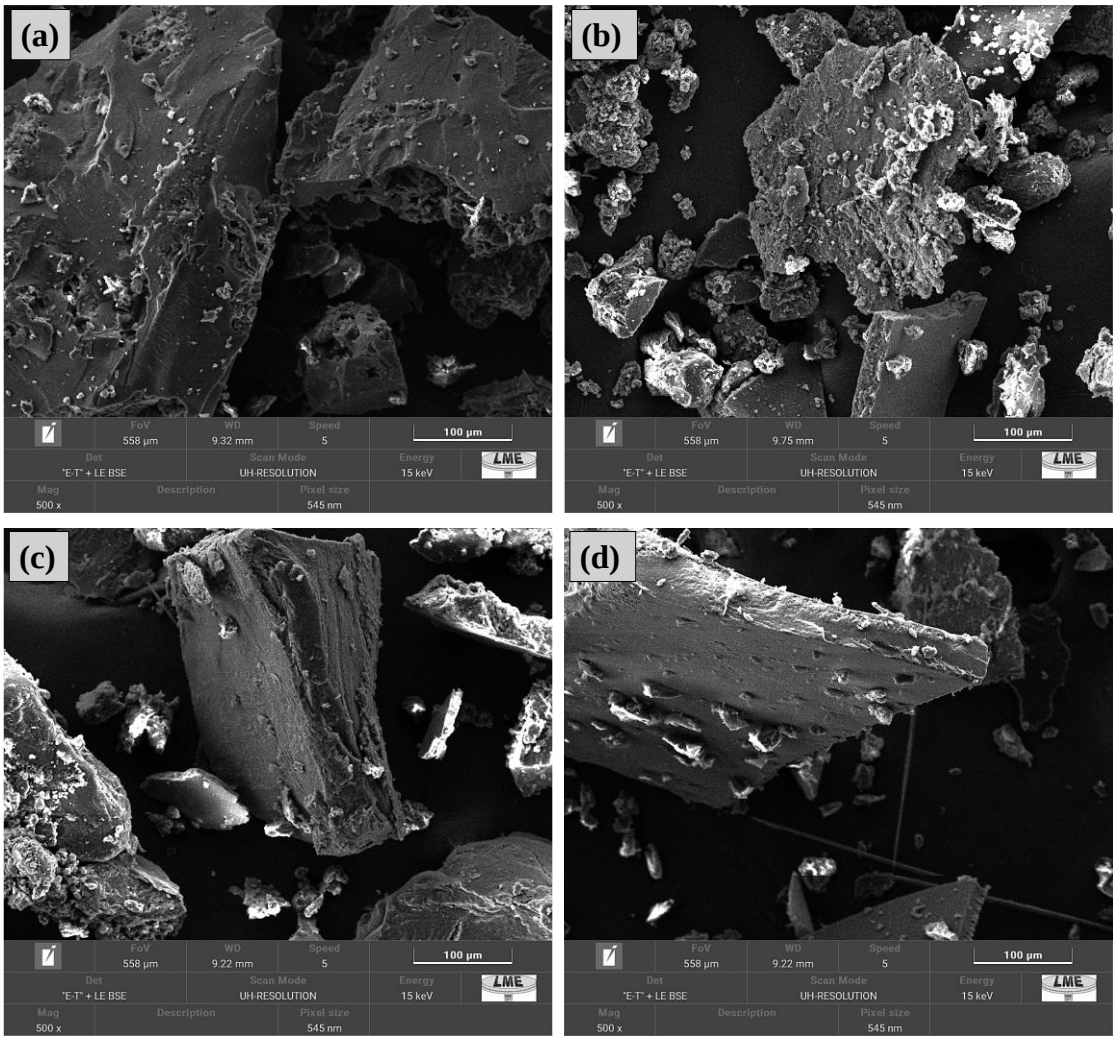


Figure S24. SEM images of lignins from SGB-C: (a) L-Klason; (b) L-DGDE:ET+PTSA; (c) L-ET+PTSA; and (d) L-NaOH. L-denotes the lignin recovered using each solvent or obtained by the Klason method.

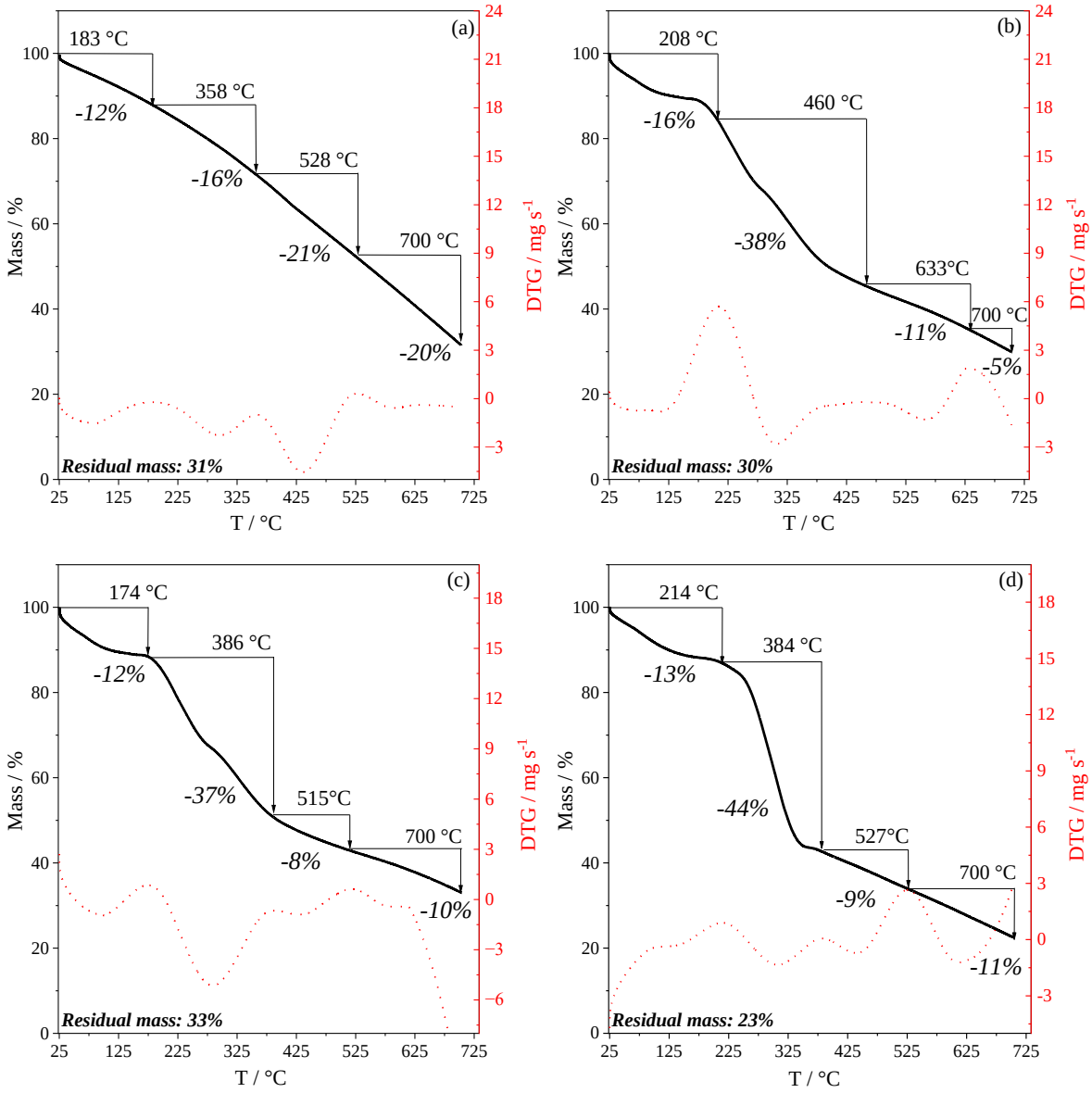


Figure S25. TGA and DTG profiles of lignins from SGB: (a) L-Klason; (b) L-DGDE:ET+PTSA; (c) L-ET+PTSA; and (d) L-NaOH. L-denotes the lignin recovered using each solvent or obtained by the Klason method.

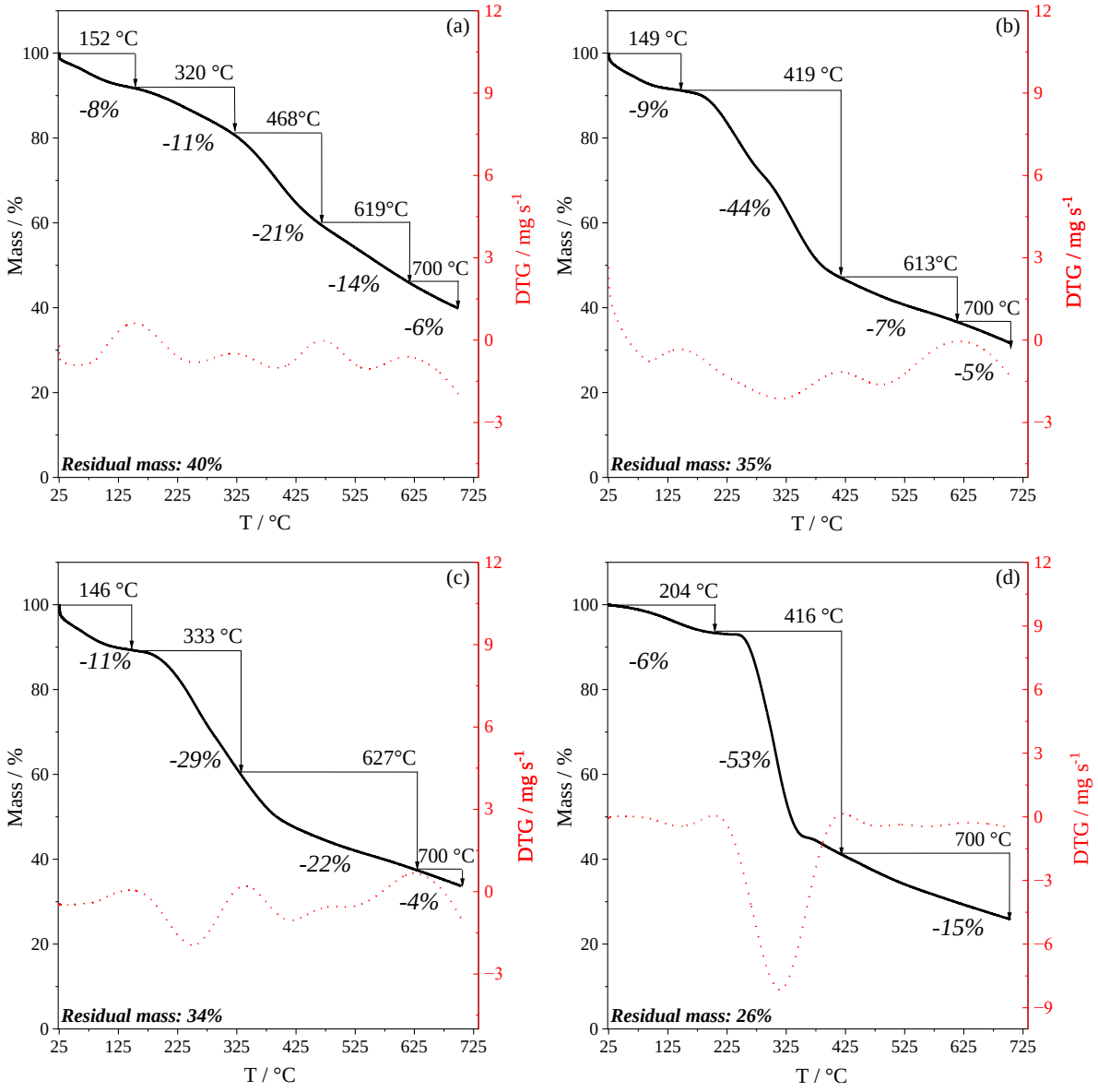
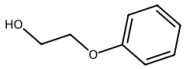
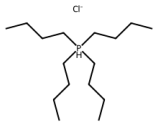
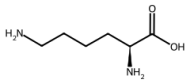
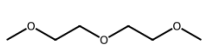
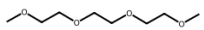
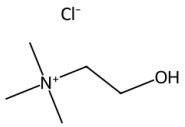
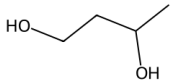
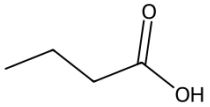
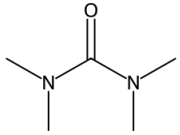


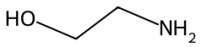
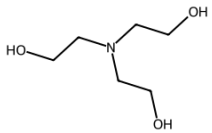
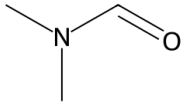
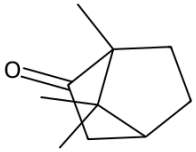
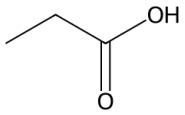
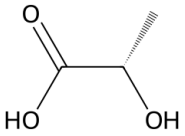
Figure S26. TGA and DTG profiles of lignin from SGB-C: (a) L-Klason; (b) L-DGDE:ET+PTSA; (c) L-ET+PTSA; and (d) L-NaOH. L-denotes the lignin recovered using each solvent or obtained by the Klason method.

S3. SUPPLEMENTARY TABLES

Table S1. Chemical structure, CAS number, mass purity and supplier of the compounds used as HBA or HBD in this work.

Compound	Chemical structure	Abbreviation	Purity	Supplier	CAS number
HBA					
2-Phenoxyethanol		2-PE	99.0%	Sigma-Aldrich	122-996
Tetrabutylphosphonium chloride		TBP	95.0%	Iolitec	
L-Lysine		Lys	98.0%	Acros Organics	56-87-1
Potassium carbonate	—	PC	99.0%	Sigma Aldrich	584-08-7
Diethylene glycol dimethyl ether		DGDE	99.5%	Sigma-Aldrich	111-96-6
Triethylene glycol dimethyl ether		TGDE	99.0%	Alfa Aesar	112-49-2

Tetraethylene glycol dimethyl ether		TeGDE	99.0%	Acros Organics	143-24-8
Choline chloride		ChCl	98.0%	Acros Organics	67-48-1
HBD					
(±)-1,3-Butanediol		BD	99.5%	Sigma-Aldrich	107-88-0
Trioctylphosphine oxide		TPO	99.0%	ThermoScientific	78-50-2
Butyric acid		BA	PA	Sigma-Aldrich	107-92-6
Tetramethylurea		TMU	99.0%	Alfa Aesar	632-22-4

Ethanolamine		ET	98.0%	Merck	141-43-5
Triethanolamine		TET	98.0%	Alfa Aesar	102-71-6
N,N-Dimethylformamide		DMF	99.8%	Honeywell	68-12-2
(1R)-(-)-Fenchone		Fen	98.0%	Aldrich	7787-20-4
Propionic acid		PA	99.0%	Acros Organics	79-09-4
L-(+)-Lactic acid		LA	92.0%	Sigma-Aldrich	79-33-4

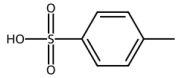
Others					
p-Toluenesulfonic Acid Monohydrate		PTSA	>98.5%	Sigma-Aldrich	6192-52-5
Sodium hydroxide (Pellets)	—	NaOH	98.0%	Fisher	1310-73-2

Table S2. Summary of DES formation and water solubility for selected HBA:HBD.

HBA:HBD	Final condition[b]	Formation (DES)	Solubility (H_2O)
2-PE:BD	2h - 80°C - 0%[a]	✓	✕
2-PE:BA	2h - 80°C - 0%	✓	✕
2-PE:TMU	2h - 80°C - 0%	✓	✕
2-PE:TPO	2h - 80°C - 0%	✓	✕
2-PE:ET	2h - 80°C - 0%	✓	✕
2-PE:DMF	2h - 80°C - 0%	✓	✕
2-PE:Fen	2h - 80°C - 0%	✓	✕
TBP:BD	**2h - 80°C - 0%**	✓	✓
TBP:BA	**2h - 80°C - 0%**	✓	✓
TBP:TMU	**2h - 80°C - 0%**	✓	✓
TBP:TPO	2h - 80°C - 0%	✕	✕
TBP:ET	**2h - 80°C - 0%**	✓	✓
TBP:DMF	**2h - 80°C - 0%**	✓	✓
TBP:Fen	2h - 80°C - 0%	✓	✕
Lys:BD	3h - 80°C - 20%	✕	✕
Lys:BA	**3h - 80°C - 20%**	✓	✓
Lys:TMU	3h - 80°C - 20%	✕	✕
Lys:TPO	3h - 80°C - 20%	✕	✕
Lys:ET	**3h - 80°C - 20%**	✓	✓
Lys:DMF	3h - 80°C - 20%	✕	✕
Lys:Fen	3h - 80°C - 20%	✕	✕
PC:BD	3h - 80°C - 20%	✕	✕
PC:BA	3h - 80°C - 20%	✕	✕
PC:TMU	3h - 80°C - 20%	✕	✕
PC:TPO	3h - 80°C - 20%	✕	✕
PC:ET	3h - 80°C - 20%	✕	✕
PC:DMF	3h - 80°C - 20%	✕	✕
PC:Fen	3h - 80°C - 20%	✕	✕
DGDE:BD	**1h - 80°C - 0%**	✓	✓
DGDE:BA	1h - 80°C - 0%	✓	✕
DGDE:TMU	**1h - 80°C - 0%**	✓	✓
DGDE:TPO	1h - 80°C - 0%	✕	✕
DGDE:ET	**1h - 80°C - 0%**	✓	✓
DGDE:DMF	**1h - 80°C - 0%**	✓	✓
DGDE:Fen	1h - 80°C - 0%	✓	✕

[a]Percentage of water in the system. [b]Step 1: Heated 1 h at 60, 80, 90, and 100 °C with variation ± 1 °C (no water); step 2: If no DES, add water (5-20% w/w), heat 1 h at 80 ± 1 °C. The solvents highlighted in bold were selected for the initial delignification screening of SGB.

Table S3. 2^3 factorial planning for RSM methodology.

Run	Coded variables*		
	X_1	X_2	X_3
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
9	-1.68	0	0
10	1.68	0	0
11	0	-1.68	0
12	0	1.68	0
13	0	0	-1.68
14	0	0	1.68
15	0	0	0
16	0	0	0
17	0	0	0

* X_1 - DGDE molar fraction; X_2 - Temperature; X_3 - PTSA concentration (mol L^{-1})

Table S4. Coded levels of variables in the RSM factorial design.

Independent variables	Axial	Factorial	Central	Factorial	Axial
	-1.682	-1	0	1	1.682
X_1 - DGDE molar fraction	0.0	0.2	0.5	0.8	1.0
X_2 - Temperature (°C)	70	76	85	94	100
X_3 - PTSA concentration (mol L^{-1})	0.0	0.02	0.05	0.08	0.1

Table S5. Compositional analysis of SGB and SGB-C.

Component	SGB(%)	SGB-C(%)
Water[a]-soluble extractives	44.0 ± 1.0	23.2 ± 4.1
H[b]	34.0 ± 5.0	49.0 ± 2.5
L-Klason	14.5 ± 4.7	21.8 ± 3.9
Moisture	2.60 ± 0.03	1.70 ± 0.10
Ash	1.09 ± 0.04	1.16 ± 0.04
Others	3.79	3.71

[a]Temperature 95 ± 5°C.; [b]Holocellulose content (Cellulose + Hemicellulose); [c] Lignin Klason.

Table S6. FTIR band assignments of SGB and SGB-C (corresponding to Figure S1).

SGB (cm^{-1})	SGB-C (cm^{-1})	Vibrational Mode	Possible Component	Ref
3305	3326	O-H stretching	Cellulose/Hemicellulose/Lignin	[5, 6]
2924	2915	C-H stretching	Cellulose	[5, 6]
1729	1732	C=O stretching	Hemicellulose	[5, 6]
1640	1635	O-H bending or C-O stretching	Cellulose/Hemicellulose/Lignin	[7, 8]
1600	1603	C=C aromatic ring stretching	Lignin	[5, 6]
1511	1512	C=C aromatic ring stretching	Lignin	[5, 6]
1455	1460	C=O-aromatic ring stretching	Lignin	[9]
1422	1429	Symmetric C-H deformation	Cellulose/Hemicellulose	[10]
1366	1376	Symmetric C-H deformation	Cellulose/Hemicellulose	[10]
1324	1331	C-O stretching	Cellulose	[5, 6]
1240	1242	C-O-C ether linkage	Hemicellulose	[5, 6]
1104	1103	O-H bending	Cellulose/Hemicellulose	[8]
1035	1035	C-O stretching	Cellulose/Hemicellulose	[8]
987	988	C-O-C alicyclic structures	Hemicellulose	[11]
923	910	C-O stretching vibration	Cellulose/Hemicellulose	[8]
870	867	C-H out-of-plane bending	Lignin	[5, 6, 9]
834	835	C-H out-of-plane bending	Lignin	[5, 6, 9]
672	661	Out-of-plane C-H bending (aromatic)	Lignin/Cellulose/Hemicellulose	[7, 8]
582	586	Aromatic ring/metal-oxygen vibrations	Lignin / Mineral traces	[7, 8, 12]
549	552	Phenolic C-O/skeletal deformation	Lignin / Inorganic components	[7, 8]
519	521	Metal-O and Si-O/ lattice modes	Mineral components / Additives	[7, 8, 12]

Table S7. Experimental design matrix and responses for DGDE:ET(DES) system.

Run	DGDE molar fraction	T (°C)	[PTSA] (M)	Holocellulose-*H* (%)	Band area-A_{834} (abs cm^{-1})
1	0.2	76	0.02	80.0	0.3201
2	0.8	76	0.02	75.0	0.6338
3	0.2	94	0.02	83.0	0.0474
4	0.8	94	0.02	78.0	0.3924
5	0.2	76	0.08	90.0	0.3625
6	0.8	76	0.08	83.0	0.5622
7	0.2	94	0.08	86.0	0.0802
8	0.8	94	0.08	89.0	0.3568
9	0.0	85	0.05	98.0	0.0482
10	1.0	85	0.05	78.0	1.0288
11	0.5	70	0.05	77.0	0.4712
12	0.5	100	0.05	87.0	0.0703
13	0.5	85	0.0	74.0	0.2253
14	0.5	85	0.1	77.0	0.2439
15	0.5	85	0.05	79.0	0.2177
16	0.5	85	0.05	83.0	0.1665
17	0.5	85	0.05	80.0	0.1924
	Mean			82.55	0.35
	Standard Deviation			6.65	0.26
	Mean Run 15-17			80.57	0.19
	Standard Deviation			1.56	0.02

Table S8. Regression models and statistical parameters obtained from the RSM for the studied variables.

Response	Unit	Model	R^2	Fcal	Fcal/pure error	Ftab
Y_1 - Holocellulose content	wt.%	$Y_1 = 81.51 - 3.49x_1 + 2.62x_1^2 + 1.82x_2 + 2.71x_3 - 1.79x_3^2$	0.76	6.8	3.7	2.45
Y_2 - Peak area (834 cm^{-1})	abs cm^{-1}	$Y_2 = 0.23 + 0.20x_1 + 0.11x_1^2 - 0.12x_2$	0.91	45.1	12.3	2.56

Table S9. Additional responses monitored during optimization.

Run	**Solubilized mass (g)**	**Colour**
1	0.0996	0.75
2	0.1073	0.75
3	0.0924	0.75
4	0.0989	0.75
5	0.097	0.75
6	0.1087	0.75
7	0.0915	0.75
8	0.1001	0.75
9	0.0882	0.50
10	0.1117	0.75
11	0.1049	0.75
12	0.0923	0.75
13	0.0958	0.75
14	0.0977	0.75
15	0.0972	0.75
16	0.0956	0.75
17	0.0972	0.75
Mean	0.1	0.73
Standard Deviation	0.01	0.06
Mean Run 15-17	0.1	0.75
Standard Deviation	0.0	0.0

Table S10. ANOVA for Holocellulose (Y_1).

Source	SQ	df	MS	Fcal	p-value
Regression	471	5	94	6.8	0.0041
Residual	153	11	14		
Lack of fit	144	9	16	3.7	0.2308
Pure error	9	2	4		
Total	624	16			
R^2	0.76				

SQ: Sum of Squares, total variation of a factor or error; df: Degrees of Freedom, number of independent observations; MS: Mean Square, SQ divided by df; Fcal: Calculated F value, ratio of factor to error MS; p-value: probability of obtaining an equal or greater F, assuming the null hypothesis is true.

Table S11. ANOVA for A_{834} (Y_2).

Source	SQ	df	MS	Fcal	p-value
Regression	0.934	3	0.311	45.1	<0.0001
Residual	0.090	13	0.0069		
Lack of fit	0.088	11	0.0080	12.3	0.0778
Pure error	0.0013	2	0.0007		
Total	1.024	16			
R^2	0.91				

SQ: Sum of Squares, total variation of a factor or error; df: Degrees of Freedom, number of independent observations; MS: Mean Square, SQ divided by df; Fcal: Calculated F value, ratio of factor to error MS; p-value: probability of obtaining an equal or greater F, assuming the null hypothesis is true.

Table S12. Elemental surface composition of materials obtained from EDS analysis, derived from SGB.

Material	Element (weight %)					
	O	S	Cl	N	Na	Si
H-SGB[a]	94.71	-	5.29	-	-	-
H-DGDE:ET+PTSA	100	-	-	-	-	-
H-ET+PTSA	100	-	-	-	-	-
H-NaOH	100	-	-	-	-	-
L-Klason[b]	63.94	36.06	-	-	-	-
L- DGDE:ET+PTSA	65.75	5.23	-	29.02	-	-
L-ET+PTSA	62.55	5.35	-	32.10	-	-
L-NaOH	79.85	-	-	-	17.66	2.49

[a]Holocellulose sample from SGB. [b]Lignin of method Klason.

Table S13. Elemental surface composition of materials obtained from EDS analysis, derived from SGB-C.

Material	Element (weight %)					
	O	S	Cl	N	Na	Si
H-SGB-C[a]	95.31	-	4.69	-	-	-
H-DGDE:ET+PTSA	100	-	-	-	-	-
H-ET+PTSA	100	-	-	-	-	-
H-NaOH	100	-	-	-	-	-
L-Klason[b]	91.67	8.33	-	-	-	-
L- DGDE:ET+PTSA	52.41	21.47	-	26.12	-	-
L- ET+PTSA	50.26	20.60	-	29.13	-	-
L- NaOH	78.06	-	-	-	12.31	9.62

[a]Holocellulose sample from SGB-C. [b]Lignin of method Klason.

Table S14. CHNS elemental analysis of materials derived from SGB (or SGB-C).

Material	Element (weight %)				
	C	H	N	S	O[b]
SGB					
L-Klason[a]	53.5 ± 0.3	4.77 ± 0.01	0.5 ± 0.1	0.8 ± 0.2	40.4 ± 0.4
L-DGDE:ET+PTSA	45.6 ± 0.2	6.0 ± 0.2	3.71 ± 0.07	1.7 ± 0.4	43.0 ± 0.5
L-ET+PTSA	44.2 ± 0.5	6.3 ± 0.1	3.66 ± 0.08	1.9 ± 0.3	43.9 ± 0.6
SGB-C					
L-Klason[a]	55.3 ± 0.1	4.83 ± 0.03	0.595 ± 0	0.949 ± 0	38.3 ± 0.1
L-DGDE:ET+PTSA	49.3 ± 0.8	6.29 ± 0.03	4.08 ± 0.03	1.44 ± 0.04	38.9 ± 0.8
L-ET+PTSA	46.6 ± 0.5	6.4 ± 0.3	2.8 ± 0.1	0.7 ± 0.4	43.5 ± 0.7
L-NaOH	45.72 ± 0.08	5.79 ± 0.04	0.5 ± 0.2	0.049 ± 0.01	47.9 ± 0.2

[a]Lignin of method Klason. [b]The oxygen content was calculated by difference, and the associated uncertainty was estimated by error propagation of the elemental deviations. L-NaOH for SGB-C was not performed due to insufficient material availability.

Table S15. Distribution of hydroxyl functionalities from ^{31}P-NMR.

Chemical Shift (ppm)	Assignment	Content (mmol g^{-1})	
		DGDE:ET + PTSA	ET + PTSA
145.4 – 150.0	Aliphatic OH	4.68	5.01
137.6 – 144.0	Phenolic OH	0.30	0.48
133.6 – 136.0	Carboxylic Acid OH	0.05	0.02

Table S16. **C**omparative Index after treatment with different solvent systems.

System	Precipitated lignin[a] (%)	Holocellulose (%)	Comparative Index[b]
SGB			
DGDE:ET+PTSA	51.00	89.26	4.75
ET+PTSA	56.00	94.17	9.60
NaOH	40.95	87.25	3.21
SGB-C			
DGDE:ET+PTSA	37.00	84.13	2.33
ET+PTSA	37.00	86.32	2.71
NaOH	44.65	88.40	3.85

[a]The L-Klason content determined by compositional analysis was used as the 100% reference basis.; [b]Calculated according to Eq. 6 of the manuscript.

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