Supplementary information

Deep eutectic solvent pretreatment for lignin properties improvement and subsequent 4-vinylphenol production: An integrated experimental-modeling investigation†

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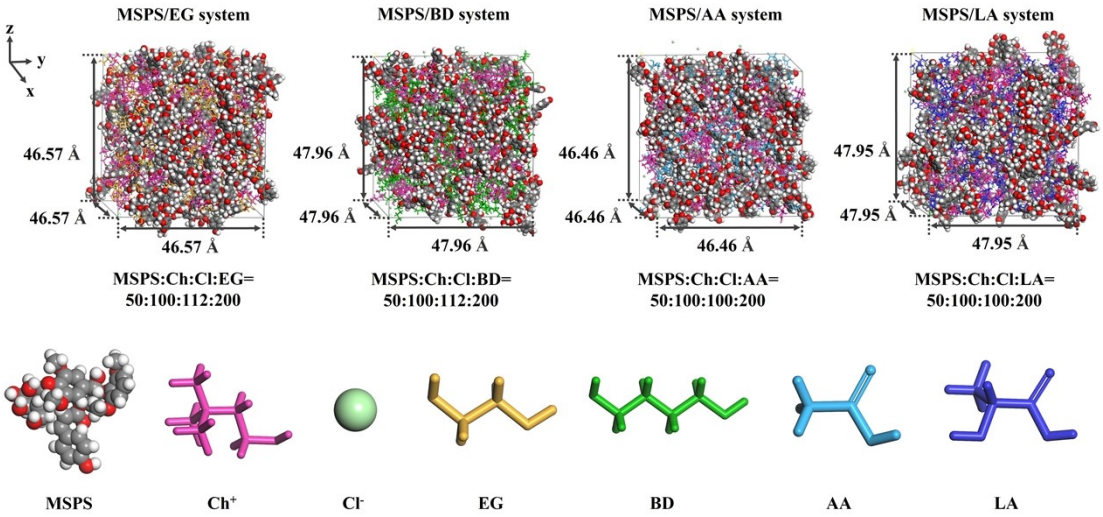

Fig S1. The initial states of different boxes. For the clear view, the MSPS molecule was represented using the CPK style (i.e. grey for carbon, white for hydrogen, and red for oxygen). Choline, EG, BD, AA, and LA were shown by rose-red, yellow, green, celeste, and blue sticks, respectively

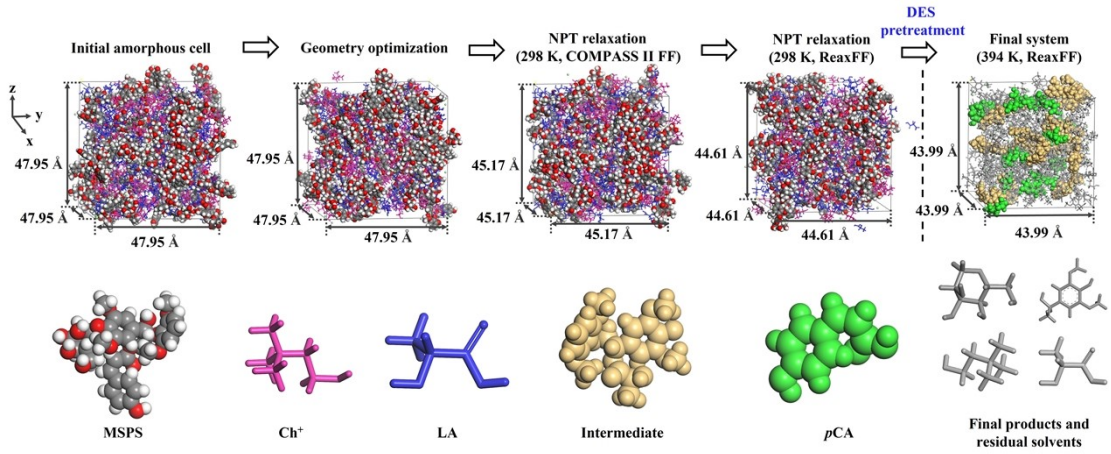

Fig S2. Schematic diagram of simulation procedures by ReaxFF-RMD. The lattice model was achieved from the MSPS/LA system. For convenience, the MSPS molecule was represented using the CPK style (i.e. grey for carbon, white for hydrogen, and red for oxygen). Choline and LA were shown by rose-red and blue sticks, respectively. The intermediate, *p*CA, and various products were presented by ivory CPK, green CPK and light grey sticks, respectively

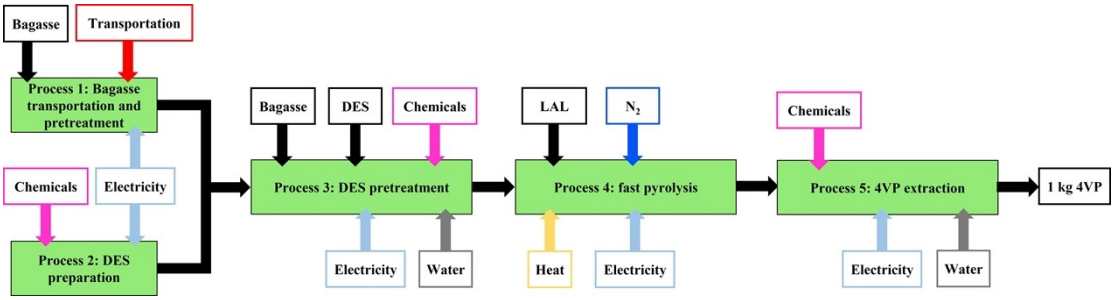

Fig S3. The system boundary of the LCA model for 4VP production

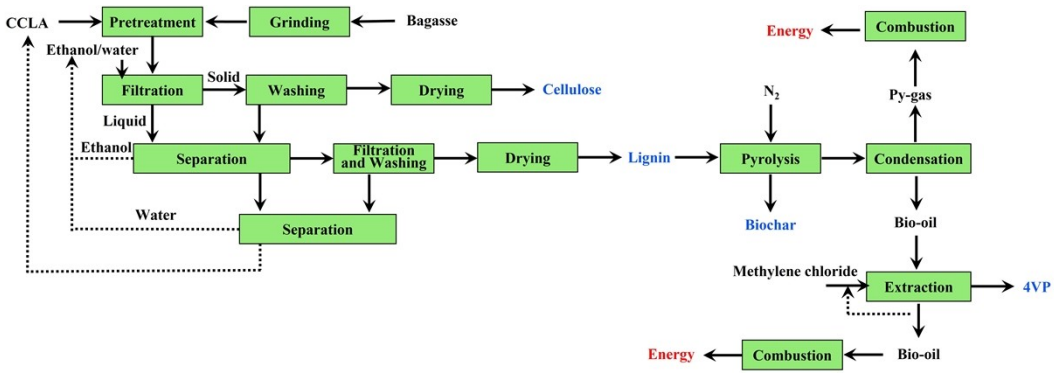

Fig S4. The block diagram of the TEA model for 4VP production

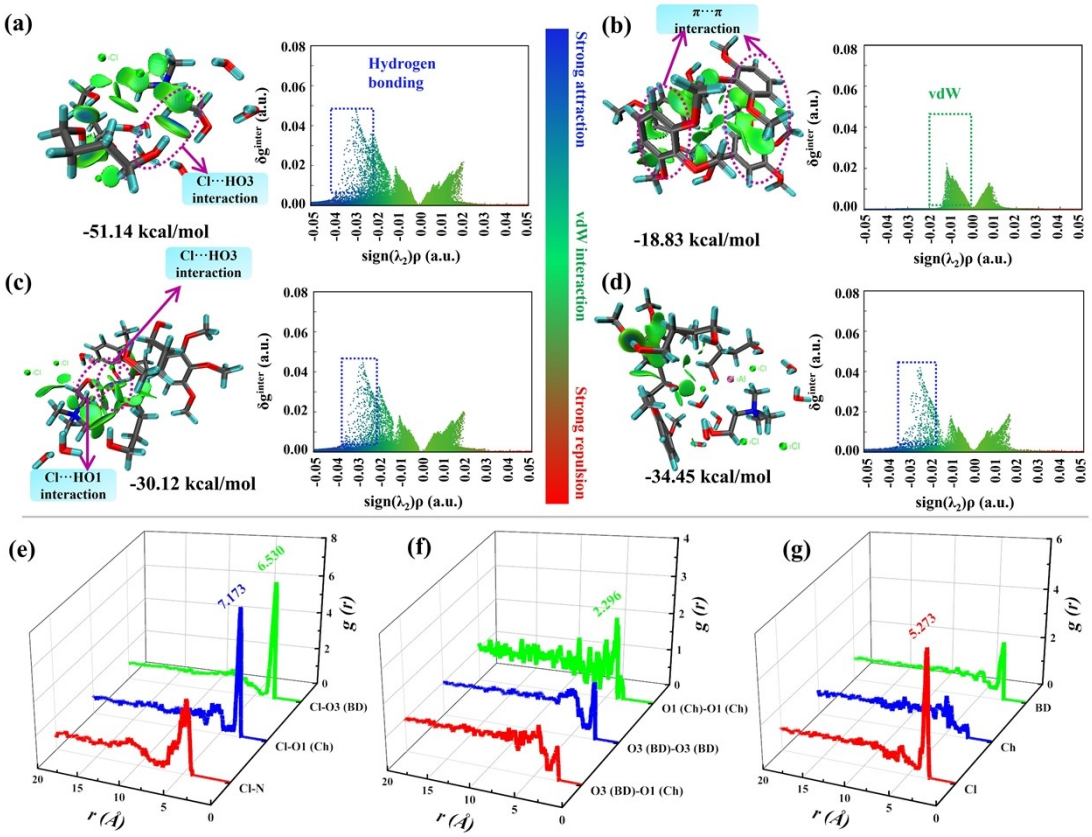

Fig. S5 Isosurfaces (0.005 electrons/Bohr^3), scatter maps, and RDF diagrams of CCBD system. (a) Interactions of ChCl/BD/$AlCl_3$·$6H_2O$; (b) Interactions of double SS molecules; (c) Interactions of ChCl/BD/$AlCl_3$·$6H_2O$ in the presence of SS; (d) Interactions of CCBD and SS; (e) RDF diagrams of nitrogen and oxygen atoms centered around chloride anion; (f) RDF diagrams of oxygen atoms centered around oxygen atoms of BD; (g) Hydroxyl groups of SS centered around chloride anion, hydroxyl group of choline, and hydroxyl groups of BD. Atoms were colored as follows: C (gray), H (cyan), O (red), N (blue), Cl (green), Al (mauve)

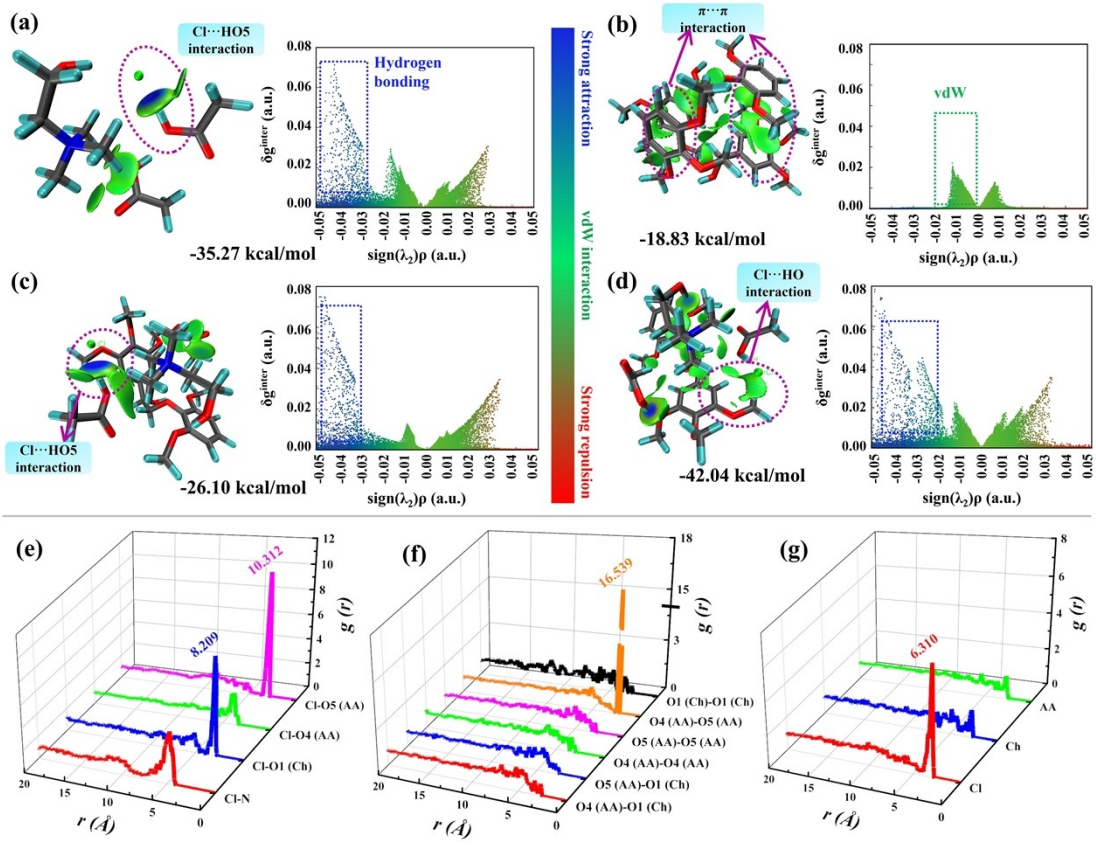

Fig. S6 Isosurfaces (0.005 electrons/Bohr^3), scatter maps, and RDF diagrams of CCAA system. (a) Interactions of ChCl/AA; (b) Interactions of double SS molecules; (c) Interactions of ChCl/AA in the presence of SS; (d) Interactions of CCAA and SS; (e) RDF diagrams of nitrogen and oxygen atoms centered around chloride anion; (f) RDF diagrams of oxygen atoms centered around oxygen atoms of AA; (g) Hydroxyl groups of SS centered around chloride anion, hydroxyl group of choline, and hydroxyl groups of AA. Atoms were colored as follows: C (gray), H (cyan), O (red), N (blue), Cl (green), Al (mauve)

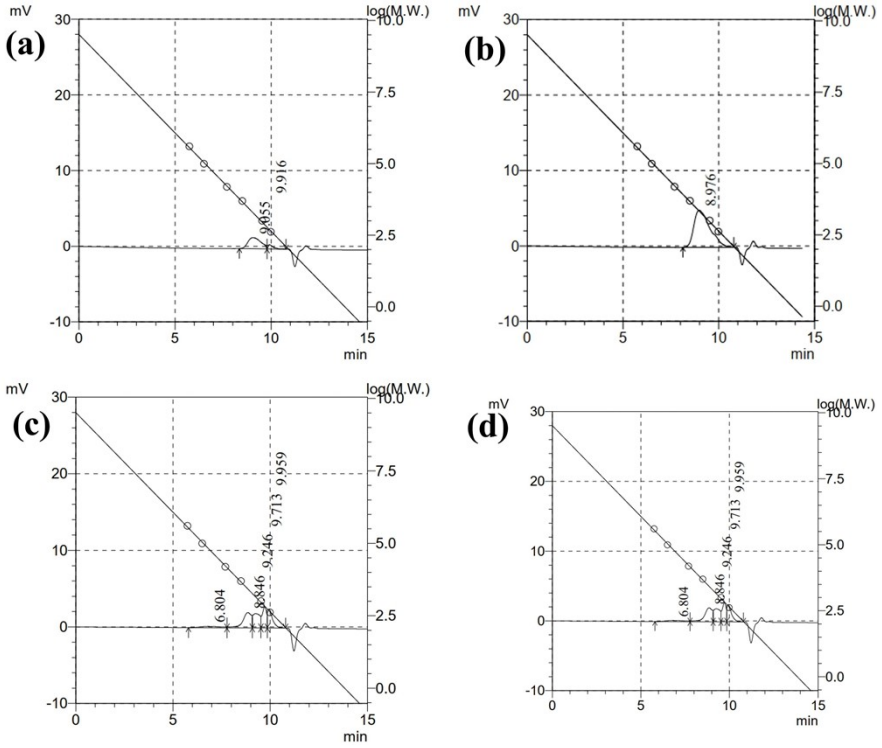

Fig. S7 The GPC curves of DESLs

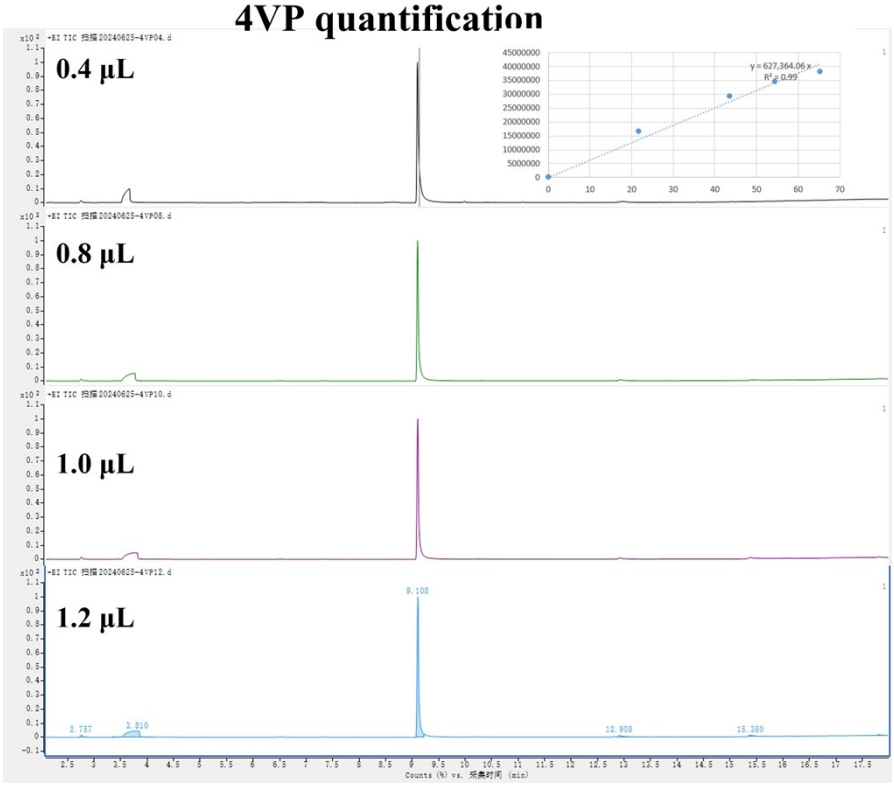

Fig. S8 The calibration curves of 4VP

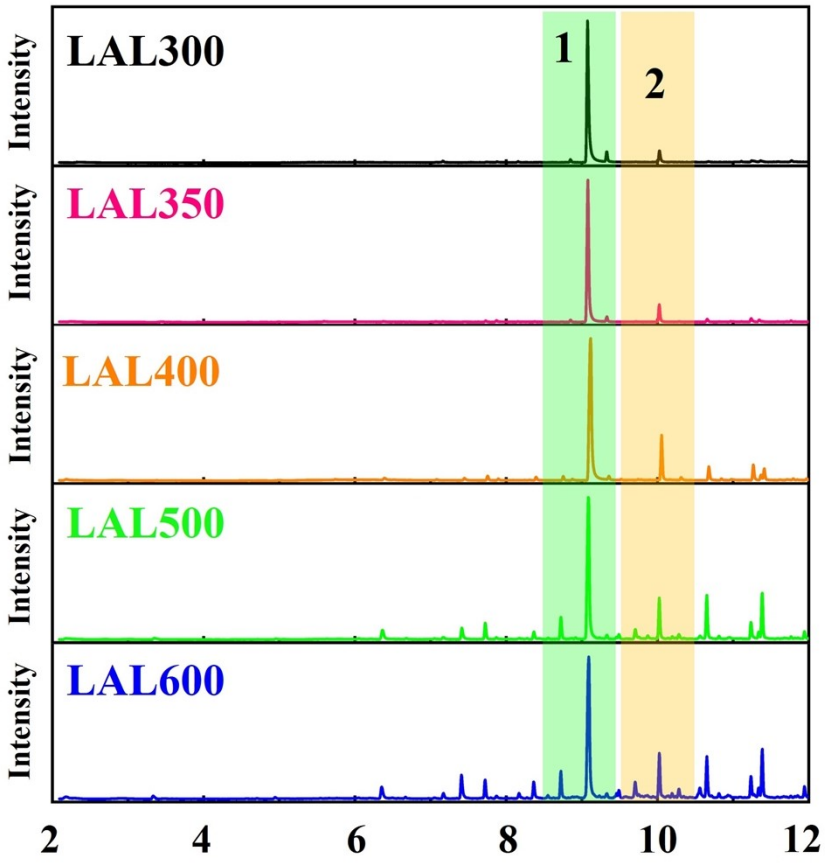

Fig. S9 Typical ion chromatograms from fast pyrolysis of LAL at different temperatures

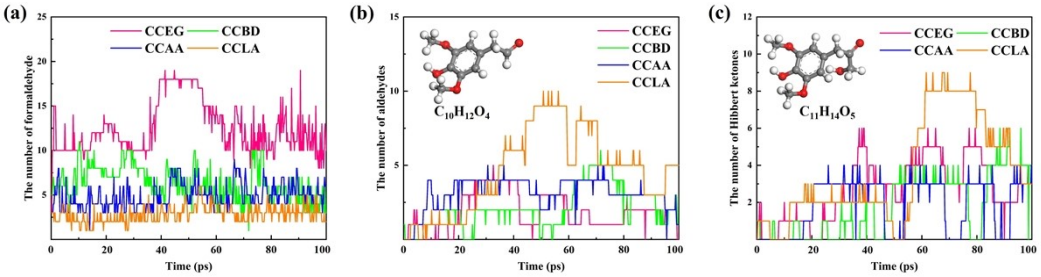

Fig. S10 Variations in the intermediate molecules as a function of reaction duration. (a) The distribution of formaldehyde molecule; (b) The distribution of aldehydes molecule; (c) The distribution of Hibbert ketones

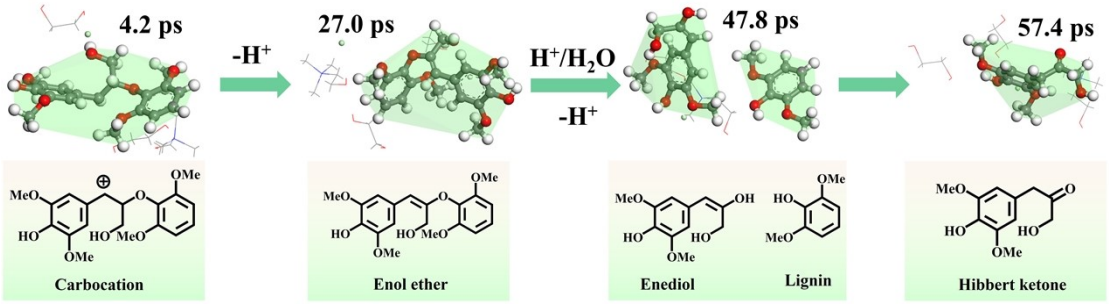

Fig. S11 The formation process of Hibbert ketone during ReaxFF-RMD simulation

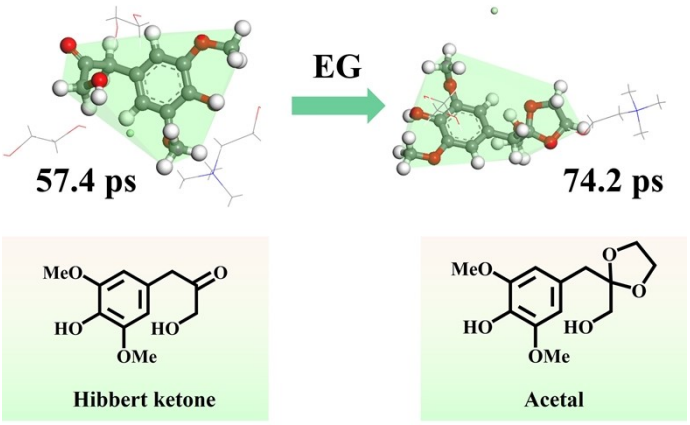

Fig. S12 The acetalization process of Hibbert ketone

Table S1 The list of abbreviations

Name	Abbreviation	Name	Abbreviation
Deep eutectic solvent	DES	CCBD lignin	BDL
4-vinylphenol	4VP	CCAA lignin	AAL
Lignin-carbohydrate complexes	LCCs	CCLA lignin	LAL
p-coumaric acid	*p*CA	Double enzymatic lignin	DEL
DES lignins	DESLs	Net present value	NPV
Quantum chemical	QC	Dynamic payback period	DPP
Density functional theory	DFT	Internal rate of reture	IRR
Reactive force field	ReaxFF	Net production cost	NPC
Molecular dynamics	RMD	Minimum selling price	MSP
Radial distribution function	RDF	Total capital investment	TCI
Hirshfeld partition method	IGMH	Total direct cost	TDC
Life cycle assessment	LCA	Total indirect cost	TIDC
Techno-economic analysis	TEA	Land use cost	LC
ChCl/EG DES	CCEG	Working capital	WC
ChCl/BD DES	CCBD	Total operating cost	TOC
ChCl/AA DES	CCAA	Total variable operating cost	TVOC
ChCl/LA DES	CCLA	Total fixed operating cost	TFOC
CCEG lignin	EGL		

Table S2 One-way ANOVA tests on lignin yields

Source of variation	SS[1]	df[2]	MS[3]	*F*-value	*P*-value	$F_{critical}$
Between groups	862.93	4	215.73	22.86	0.00	3.48
Within groups	94.39	10	9.44			
Total	957.32	14				

[1]SS: sum squared error;

[2]df: degrees of freedom;

[3]MS: mean squared error

Table S3 One-way ANOVA tests on lignin purities

Source of variation	SS[1]	df[2]	MS[3]	*F*-value	*P*-value	$F_{critical}$
Between groups	434.42	4	108.61	42.76	0.00	3.48
Within groups	25.40	10	2.54			
Total	459.82	14				

[1]SS: sum squared error;

[2]df: degrees of freedom;

[3]MS: mean squared error

Table S4 One-way ANOVA tests on 4VP yields under different DESs

Source of variation	SS[1]	df[2]	MS[3]	*F*-value	*P*-value	$F_{critical}$
Between groups	81.14	4	20.29	8.86	0.002	3.48
Within groups	22.90	10	2.29			
Total	104.04	14				

[1]SS: sum squared error;

[2]df: degrees of freedom;

[3]MS: mean squared error

Table S5 One-way ANOVA tests on 4VP yields under different temperatures

Source of variation	SS[1]	df[2]	MS[3]	*F*-value	*P*-value	$F_{critical}$
Between groups	205.97	4	51.49	15.97	0.00	3.48
Within groups	32.25	10	3.22			
Total	238.22	14				

[1]SS: sum squared error;

[2]df: degrees of freedom;

[3]MS: mean squared error

Table S6 The main costs of major equipment

Components	Purchase cost (US$)	Installed factor	Installed cost (US$)
Feedstock	□	□	□
Conveyor	5.62E+04	1.08	6.06E+04
Pulverizer	1.18E+05	1.08	1.27E+05
Dryer	5.98E+03	1.09	6.53E+03
Feeding system	6.58E+04	1.08	7.10E+04
DES pretreatment	□	□	□
Reactor	1.40E+06	1.5	2.10E+06
Filtration system	3.38E+05	1.7	5.74E+05
Evaporator system	6.80E+05	1	6.80E+05
Heat exchanger	2.05E+05	2.2	4.51E+05
Conveyor	2.02E+04	1.05	2.11E+04
Dryer	8.06E+03	1.09	8.78E+03
Lignin pyrolysis	□	□	□
Reactor	1.04E+06	1.69	1.76E+06
Pump	3.46E+03	2.29	7.92E+03
Distillation	2.54E+05	2.4	6.11E+05
Storage tank	3.74E+04	2	7.49E+04
Evaporator system	8.02E+04	1	8.02E+04
Dryer	8.06E+03	1.09	8.78E+03
Heat exchanger	5.42E+04	2.2	1.19E+05
N_2 plant	5.66E+05	□	5.66E+05

Table S7 Main ^{13}C-^{1}H cross signals in the 2D-HSQC spectra

Label	δ_C/δ_H (ppm)	Assignments
OMe	55.430/3.640	C-H in methoxyl
γ	59.980/3.440	C_γ-H_γ in β-O-4 structure
γ′	65.110/4.210	C_γ-H_γ in γ-acylated β-O-4 structure
α	72.855/4.910	C_α-H_α in β-O-4 structure
α′	81.900/4.920	C_α-H_α in α-etherified β-O-4 structure
β	84.355/4.275	C_β-H_β in β-O-4 structure linked to S units
$S_{2,6}$	104.360/6.650	$C_{2,6}$-$H_{2,6}$ in syringyl units
$S'_{2,6}$	107.210/7.200	$C_{2,6}$-$H_{2,6}$ in oxidized syringyl units
G_2	110.240/6.850	C_2-H_2 in guaiacyl units
G_5	116.240/6.720	C_5-H_5 in guaiacyl units
G_6	119.440/6.800	C_6-H_6 in guaiacyl units
$pCA_{2,6}$	130.100/7.500	$C_{2,6}$-$H_{2,6}$ in *p*CA structures
FA_α	146.100/7.400	C_α-H_α in ferulate units
pCA_α	146.100/7.400	C_α-H_α in *p*CA structures

Table S8 Major chemical species generated from the fast pyrolysis of DESLs

No.	R.T. (min)	Aromatic products	GC peak area								
			DEL	EGL	BDL	AAL	LAL	LAL300	LAL350	LAL500	LAL600
1	6.39	phenol	-	1478086	1463334	402848	805217	-	-	2515987	3470169
2	7.45	2-methyl phenol	1120475	452260	326657	680859	751901	-	-	551660	1306960
3	7.63	4-methyl phenol	-	-	-	-	-	-	-	2523718	5532358
4	7.72	guaiacol	-	795980	680523	571607	1110312	-	-	2849336	3554747
5	8.39	4-ethyl phenol	-	1567280	838254	-	939811	-	-	1393240	3810885
6	8.76	creosol	-	-	326500	-	908162	-	-	3675898	5180163
7	9.12	4-vinyl phenol	17826905	25603046	27332748	38150641	54832243	6220401	23238146	36007657	42811583
8	9.71	3-methoxy catechol	-	520086	843335	409907	-	-	-	1972690	3919425
9	10.06	4-vinyl guaiacol	4477689	3344049	3660021	5532855	10075609	446006	2283211	7165140	9448841
10	10.68	syringol	-	1927960	1494268	2191709	3246017	-	383857	7489982	8529552
11	11.27	eugenol	1258503	256926	392669	1306089	3594078	110880	543324	3261427	4516623
12	11.41	4-methyl syringol	-	1047333	1096543	1624945	2700340	88351	401217	8023861	10279669

Table S9 The inputs and outputs on the basis of production of 1 kg 4VP

□	EGL	BDL	AAL	LAL	Unit
Process 1 Bagasse transportation and pretreatment					
Inputs					
Bagasse	24.43	23.75	19.33	12.58	kg
Transportation	1.68E-02	1.63E-02	1.33E-02	8.64E-03	kg*km
Deionized water	73.29	71.25	57.99	37.74	kg
Electricity	15.10	14.63	11.53	6.81	kWh
Outputs					
Dried bagasse	19.54	19.00	15.46	10.07	kg
Waste water	73.29	71.25	57.99	37.74	kg
Process 2 DES preparation					
Inputs					
ChCl	101.50	81.60	83.10	44.00	kg
EG	90.00				kg
BD		105.30			kg
$AlCl_3$	3.90	3.10			kg
AA			71.50		kg
LA				56.70	kg
Electricity	3.42	3.33	2.71	1.76	kWh
Outputs					
DES	195.40	190.00	154.60	100.70	kg
Process 3 DES pretreatment					
Inputs					
Bagasse (from process 1)	19.54	19.00	15.46	10.07	kg
DES (from process 2)	195.40	190.00	154.60	100.70	kg
Ethanol	256.90	249.80	203.30	132.40	kg
Deionized water	325.70	316.70	257.70	167.80	kg
Electricity	10.26	9.98	8.12	5.29	kWh
Outputs					
DESLs	3.50	3.28	2.35	1.63	kg
Cellulose	13.39	12.27	8.26	4.98	kg
Waste water	39.08	38.00	30.92	20.14	kg
Process 4 Fast pyrolysis					
Inputs					
DESLs (from process 3)	3.50	3.28	2.35	1.63	kg
Electricity	4.67	4.38	3.14	2.18	Wh
Natural gas	0.43	0.40	0.29	0.20	m^3

Outputs					
Bio-oil	3.39	3.18	2.28	1.58	kg
Bio-char	0.07	0.07	0.05	0.04	kg
Process 5 4VP extraction					
Inputs					
Bio-oil (from process 4)	3.39	3.18	2.28	1.58	kg
Methylene chloride	6.75	6.33	4.54	3.14	kg
Deionized water	6.30	5.91	4.23	2.93	kg
Electricity	1.15	1.07	0.77	0.53	Wh
Outputs					
4VP	1.00	1.00	1.00	1.00	kg
Waste water	1.35	1.27	0.91	0.63	kg

Table S10 Environmental impacts of DES pretreatment and pyrolysis process

impact category	EGL	BDL	AAL	LAL	Unit
Fossil fuels depletion	953.44	935.86	889.15	776.75	MJ eq
Global warming	64.30	64.52	65.86	60.22	kg CO_2 eq
Ozone layer depletion	6.06E-06	6.02E-06	6.06E-06	5.34E-06	kg CFC-11 eq
Human toxicity	32.12	32.35	33.28	30.31	kg 1,4-DB eq
Fresh water ecotoxicity	29.01	29.51	31.46	28.98	kg 1,4-DB eq
Marine ecotoxicity	53980.15	54031.79	54460.99	49304.81	kg 1,4-DB eq
Terrestrial ecotoxicity	0.17	0.17	0.19	0.17	kg 1,4-DB eq
Photochemical oxidation	0.03	0.03	0.03	0.02	kg C_2H_4 eq
Acidification	0.50	0.51	0.55	0.50	kg SO_2 eq
Eutrophication	0.35	0.36	0.40	0.37	kg PO_4^{3-} eq