Supporting information

Exploiting Deep Eutectic Solvents and Ionic Liquids for the valorization of Chestnut Shell Waste

Elena Husanu, ^{†,+} Angelica Mero, ^{†,+} Jose Gonzalez Rivera, ^{†, ‡} Andrea Mezzetta, [†] Julian Cabrera Ruiz,[§] Felicia D'Andrea, [†] Christian Silvio Pomelli, [†] Lorenzo Guazzelli ^{†,*}

⁺ Department of Pharmacy, University of Pisa, Via Bonanno 33, 56126 Pisa, Italy

[‡] National Institute of Optics, (INO-CNR)–UOS Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy

§ Department of Chemical Engineering, University of Guanajuato, Noria Alta s/n, 36050,

Guanajuato, Gto, Mexico.

* Elena Husanu and Angelica Mero equally contributed to this work.

* corresponding author: lorenzo.guazzelli@unipi.it

Table of content

Schematic representations of hydrolysable and condensed tannins and si	mple
phenolic acids	page S3
Schematic representations of cellulose and hemicellulose	page S4
Schematic representations of Lignin and phenyl propanoid monomers	page S5
¹ H-NMR spectra of prepared DESs and bio-IL pages	s S6-S14
1H-NMR spectra of prepared and recovered ChCI:Oax2H2O	page S15
HPLC chromatogram and retention times of polyphenol standards	page S16
1H-NMR of spectrum of prepared and recovered bio-IL	page S17
Pyrolysis steps using the second derivative method	page S18
HPLC chromatograms of extracts using different DESs pages	s S19-S20
Picture of different Polyphenol extracts in methanol	page S21
TG and DTG simulation results of three-parallel-DAEM model pages	s S22-S23
Yields of extracts obtained using different DESs	page S24
Interval range experimental data Identified by DDTG method to fit the three	e
parallel-DAEM model	page S24
Optimized kinetics parameters of first order three-DAEM-reaction model	page S25



Figure S1. Representative structures of hydrolysable and condensed tannins and simple phenolic acids



Figure S2. a) Cellulose structure with hydrogen bonds and b) an example of hemicellulose structure



Figure S3. a) Typical lignin structure and b) phenyl propanoid monomers



Figure S4. ¹H-NMR spectrum (D₂O, 400 MHz) of ChCl:Oax2H₂O



Figure S5. ¹H-NMR spectrum (D₂O, 400 MHz) of ChCl:CaxH₂O (1:1)



Figure S6. ¹H-NMR spectrum (D₂O, 400 MHz) of ChCl:Ma (1:1)



Figure S7. ¹H-NMR spectrum (D₂O, 400 MHz) of ChCl: But (1:4)



Figure S8. ¹H-NMR spectrum (D₂O, 400 MHz) of ChCI:EG (1:4)



Figure S9. ¹H-NMR spectrum (D₂O, 400 MHz) of ChCl:Mal (1:1)



Figure S10.¹H-NMR spectrum (D₂O, 400 MHz) of ChCl:Glu (1:1)



Figure S11. ¹H-NMR spectrum (D₂O, 400 MHz) of ChCl:Glu(1:2)



Figure S12. ¹H-NMR spectrum (D₂O, 400 MHz) of ChGly



Figure S13. ¹H-NMR spectrum (D₂O, 400 MHz) of ChCI:Oax2H₂O compared with the DES recovered after each extraction cycle (in the enlargement, signals of the methyl groups of the starting DES and of the forming ester side product are shown)



Figure S14. HPLC chromatogram and retention times of polyphenols standards used in this work.



Figure S15. ¹H-NMR spectrum (MeOD, 400 MHz) of ChGly (bottom, red line) compared with the recovered IL (top, green line)



Figure S16. Characteristics of temperature range for the different steps of biomass pyrolysis using the second derivative method.



Figure S17. Chromatogram of extract from ChCI:Ma (1:1)



Figure S18. Chromatogram of extract from ChCI: But(1:4)



Figure S19. Chromatogram of extract from ChCI:Glu (1:2)



Figure S20. Chromatogram of extract from ChCI:Mal 1:1)



Figure S21. Different color of the polyphenol extracts depending on the extraction DES used (form left to right: acid-based, sugar-based and polyol-based DESs). extraction conditions: 24h, 65°C, 1:10 w/w solid to liquid ratio.



Figure S22. TG (a, c) and DTG (b, d) simulation results of three-parallel-DAEM model for CSW and CSWR, respectively. The residuals between the observed and calculated mass data are also plotted for TG curves (a and c).



Figure S23. TG (a, c) and DTG (b, d) simulation results of three-parallel-DAEM model for CRM and LRM, respectively. The residuals between the observed and calculated mass data are also plotted for TG curves (a and c).

Table S1. Yields of extract*

Extraction media	Yield of extracts (%)
MeOH/H ₂ O (70:30)	8.2
ChCl:Oa x2H ₂ O (1:1)	33.7
ChCl:Ma (1:1)	16.7
ChCl:Ca xH ₂ O (1:1)	10.5
ChCl:But (1:4)	12.4
ChCl:EG (1:4)	8.5
ChCl:Glu (1:1)	18.7
ChCl:Glu (1:2)	5.7
ChCl:Malt (1:1)	10.7

*Yield%= (mass of dried phenolic extracts/mass initial mass of chestnut shells waste)*100

Table S2. Interval range experimental data Identified by DDTG method to fit the three parallel

 DAEM model

Sample	Initial Normalized mass from TG	T _o Final Normalized mass from TG		T _f	
CSW	0.9368	435	0.3132	848	
CSWR	0.9904	415	0.3994	820	
CRM	0.9884	415	0.3240	811	
LRM	0.9272	382	0.3673	809	

Sample	Pseudo component	First order reaction model					
		A _i (s ⁻¹)	E _i (kJ/mol)	σ (kJ/mol)	с	Fit (%)	Final O.F. value
CSW	1	3.38x10 ¹³	56.04	13.23	0.0881		0.0585
	2	4.34 x10 ¹⁵	196.51	15.79	0.5248	0.366	
	3	2.57 x10 ¹⁵	257.34	19.35	0.3871	(np=4957)*	
CSWR	1	8.30x10 ¹³	185.77	27.80	0.5207	— 0.499 — (np=4836)*	0.1180
	2	8.63x10 ¹⁴	197.10	4.06	0.4124		
	3	9.45x10 ¹⁵	267.08	16.10	0.0669		
CRM	1	8.63x10 ¹⁵	190.69	21.27	0.2140	– 0.527 – (np=4833)*	
	2	8.78x10 ¹³	189.36	3.27	0.5659		0.1313
	3	1.11x10 ¹⁶	258.74	20.43	0.2202		
LRM	1*	3.57x10 ¹⁴	118.47	29.92	0.1878	0.308	0.043
	2	4.36x10 ¹²	154.40	19.67	0.6657		
	3	9.43x10 ¹⁴	239.64	17.81	0.1465	(1)-0207)	

Table S3. Optimized kinetics parameters of first order three-DAEM-reaction model

• np=number of experimental points used for the fitting

• 1=Hemicellulose, 2=cellulose, 3=lignin, 1*=lignin oligomers