

























299 times higher than those attained with the microwave treatments. Non-reducing sugars for the  
300 NaOH treatment ( $w_B = 3.34\%$  and  $4.64\%$ , respectively) would be similar to those obtained for  
301 a 5 min treatment with choline ChCl/urea, for a 40-50 min treatment with DMAc/NaHCO<sub>3</sub> and  
302 for a 50-60 min treatment with DMAc/CH<sub>3</sub>OK in the case of *E. arborea*; and for a 10 min  
303 treatment with choline ChCl/urea in the case of *C. ladanifer* ( $w_B = 4.64\%$  was much higher than  
304 the values resulting from the polar aprotic solvent-based treatments).

305 For comparison purposes, Table 6 shows the concentration of total sugars and reducing  
306 sugars for corncob (twice higher) and bamboo (ten times higher) [22].

307

308 [Table 5 here]

309 [Table 6 here]

310

### 311 **3.3. Analysis of kinetic data**

312 The kinetic coefficients ( $k$ ) calculated for the different treatments are reported in Table 7. It  
313 may be observed that, in general terms, the highest constants agree with the highest rates of  
314 production. That is, for the ChCl/urea treatment, in addition to the highest concentrations of  
315 lignin and furfural, the highest kinetic constants were also obtained –both for *E. arborea* and *C.*  
316 *ladanifer*–:  $k_{lignin}$  values of 0.296 and 0.175, respectively; and  $k_{furfural}$  values of 0.319 and 0.065,  
317 respectively. Another is the case of 5-HMF and total and reducing sugars, for which the highest  
318 formation kinetics were obtained for the DMAc/CH<sub>3</sub>OK solvent ( $k_{HMF}$  values of 0.488 for *E.*  
319 *arborea* and 0.779 for *C. ladanifer*;  $k_{TS}$  values of 1.404 and 1.778, respectively; and  $k_{RS}$  values  
320 of 0.435 and 0.952, respectively). The difference in the kinetic behavior between furfural and 5-  
321 HMF has to be referred to the different percentages of pentose in the raw materials [23].

322

323 [Table 7 here]

324

### 325 **3.4. On treatment methods and mechanisms**

326 It is known that the use of oxidant acids ( $\text{HNO}_3$ ) for pretreating lignocellulosic biomass  
327 allows the disruption of the association between carbohydrates and lignin [20, 21]. On the other  
328 hand, alkaline treatments ( $\text{NaOH}$ ,  $\text{CH}_3\text{OK}$ ) can also be used to remove lignin and thereby  
329 increase the digestibility of cellulose. Compared to acid and hydrothermal processes, mild  
330 alkaline pretreatments ( $\text{NaHCO}_3$ ) lead to less solubilization of hemicelluloses and less  
331 formation of inhibitory compounds, and they can be operated at lower temperatures [24].

332 Although the solvents under study have the ability to disrupt the hydrogen bond network of  
333 biopolymers, their different mechanisms result in different efficiencies. Further, the lower  
334 performance of DMAc-based systems can be explained by fact that they are disturbed by water  
335 impurities [25].

336 In the DES system,  $\text{ChCl}$  may act as a bridge between the urea and the biomass biopolymers  
337 units to, subsequently, weaken and break the specific linkages into the biopolymer (e.g., the  
338 ether linkages between the phenylpropane units present in lignin, as reported by Alvarez-Vasco,  
339 *et al.* [26]). Another possibility would be that, instead of  $\text{ChCl}$  and urea, the intermediate agents  
340 were choline cation and  $[\text{Cl}(\text{urea})_2]^-$  anion (Figure 1).

341 In the case of DMAc-based systems, the hydroxyl groups of lignocellulosic materials may  
342 interact with a sodium- or potassium-DMAc macrocation via hydrogen bonding bridged by the  
343 bicarbonate or methoxide anions (Figure 4). Sodium or potassium can interact with the carbonyl  
344 oxygen via ion-dipole interaction [27], but for this interaction to take place no biopolymer  
345 bound water can be present. On the contrary, such problem does not occur in the case of the  
346 DES system: since water is linked to urea through hydrogen bonding, the deleterious water  
347 effect is suppressed [28].

348

349

[Figure 4 here]

350

351 Regardless of the chosen method, acid-soluble lignin should be removed to increase  
352 subsequent fermentation process. In agreement to Schwartz and Lawoko [29], a suitable and

353 economical approach would be to use Amberlite XAD-4 resin, which was shown to remove  
354 90% of ASL. Subsequent fermentation of the resin-treated hydrolyzates gave ethanol yields as  
355 high as 97% of theoretical and showed a marked increase in the fermentation rate.

356 The results of this study provide further evidence on the efficiency of microwave-assisted  
357 DES treatment for biomass conversion, previously claimed by other authors: both strategies  
358 exhibit a strong synergism, result in improvements in biomass digestibility and appear to require  
359 much less energy to achieve a satisfactory treatment effectiveness within a very short period  
360 [30]. As compared to common solvents used for biomass conversion, DESs clearly offer notable  
361 advantages, apart from their low cost and low environmental impact, owing to their ability to  
362 produce highly concentrated solutions of HMF or furfural [31]. Moreover, their high H-bond  
363 accepting ability and polarity facilitates lignin degradation and/or extraction from wood fibers  
364 [26]. As regards the concurrent use of microwave irradiation, it can maximize ionic  
365 characteristics and increase molecular polarity of DES [32] and, thus, it can significantly  
366 shorten the reaction time for DES treatment while achieving a similar or even higher degree of  
367 effectiveness compared to DES pretreatment alone [33-35].

368

#### 369 **4. Conclusions**

370 The results suggest that the deep eutectic solvent-based treatment offers an efficient, safe,  
371 sustainable, and cost-effective alternative to conventional methods for the extraction of  
372 bioactive compounds from *C. ladanifer* and *E. arborea* biomass. Samples of these shrubs may  
373 be easily dissolved by a MW-assisted procedure in a ChCl/urea DES to give lignin, furfural, 5-  
374 (hydroxymethyl)furfural and sugars with reasonable yields. Conversely, the DMAc/NaHCO<sub>3</sub>  
375 and DMAc/CH<sub>3</sub>OK solvent exchange systems would be less appropriate due the disruptive  
376 effect of water impurities. Nevertheless, if the aim of treating *C. ladanifer* and *E. arborea*  
377 biomass is to recover sugars for subsequent enzymatic saccharification, the very low 5-HMF  
378 contents attained with the dimethylacetamide systems (especially the CH<sub>3</sub>OK one) make them  
379 highly advantageous as compared to the traditional method using NaOH.

380 A peculiarity of the present work is that the operating conditions led to higher contents of  
381 non-reducing sugars than of reducing sugars. This finding can be useful to modify cured phenol-  
382 formaldehyde resins: whereas reduced sugars cannot be used to modify these resins, non-  
383 reducing sugars can be used to replace a major portion of the adhesive resin. These non-  
384 reducing sugars may also be advantageously used as a starting material in bioprocesses to  
385 produce succinic acid (one of the chemical platforms suggested by the DOE), farnesene  
386 (sesquiterpenes) and sucralose.

387

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394

### 395 **Declaration of interest**

396 The authors have no competing interests to declare.

397

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- 512

513 **Table 1.** Overall chemical composition of *E. arborea* and *C. ladanifer* [14, 36]. Values are given as an  
 514 average of 25 repetitions, followed by the minimum and maximum values in brackets.

	<i>Erica arborea</i>	<i>Cistus ladanifer</i>
<i>Elemental analysis:</i>		
C (%)	51.0 (49.3-52.8)	47.8 (47.5-50.1)
H (%)	6.2 (6.0-6.4)	6.4 (6.0-6.8)
N (%)	1.0 (0.3-1.1)	0.8 (0.3-1.9)
O (by diff., %)	~41.8	~45.0
<i>Vegetal components:</i>		
Cellulose (%)	40.0 (37.3-41.1)	55.0 (54.9-55.7) <sup>†</sup>
Lignin (%)	39.5 (39.3-40.1)	25.3 (24.5-34.2)
Hemi-cellulose (%)	11.0 (9.7-13.8) <sup>‡</sup>	10.2 (10.1-10.9) <sup>‡</sup>
Extractive (%)	9.5 (5.7-11.0)	9.5 (9.4-9.6)
<i>Moisture (wt.%)</i>	26.0	26.8

515 <sup>†</sup> This cellulose content is higher than that of most woods, which is usually in the 35-50% range.

516 <sup>‡</sup> These hemicellulose contents are lower than those of most woods, which usually range from 20% to 30%.

517

518 **Table 2.** Mass fraction ( $w_B$ , in %) for lignin, furfural and 5-HMF in hydrolysates after MW-assisted deep  
 519 eutectic solvent or polar aprotic solvent extraction. The tests were performed in triplicate, and  
 520 standard deviations were <5 %, except in those cases in which the furan compounds yields were below  
 521 1.5 % (in which the standard deviations were higher, up to 10 %).

Treatment	Time (min) <sup>†</sup>	<i>Erica arborea</i>			<i>Cistus ladanifer</i>		
		$w_{\text{lignin}}$	$w_{\text{furfural}}$	$w_{\text{5HMF}}$	$w_{\text{lignin}}$	$w_{\text{furfural}}$	$w_{\text{5HMF}}$
MW-assisted ChCl/urea DES extraction	1	0.52	1.00	0.25	0.48	1.05	0.23
	5	0.82	1.13	0.34	0.69	1.38	0.33
	10	1.25	1.30	0.39	0.93	1.45	0.36
	20	1.35	1.73	0.59	1.03	1.58	0.45
	30	1.63	2.59	0.65	1.22	1.94	0.49
	40	1.67	2.70	0.65	1.28	2.13	0.58
	50	1.79	2.69	0.75	1.40	2.26	0.63
MW-assisted DMAc/NaHCO <sub>3</sub> extraction	60	1.80	2.74	0.82	1.26	2.33	0.77
	1	0.33	0.97	0.22	0.42	0.92	0.20
	5	0.45	1.02	0.23	0.58	1.06	0.21
	10	0.47	1.08	0.24	0.59	1.16	0.24
	20	0.55	1.18	0.25	0.61	1.20	0.26
	30	0.69	1.26	0.27	0.62	1.23	0.28
	40	0.80	1.37	0.28	0.70	1.25	0.28
MW-assisted DMAc/CH <sub>3</sub> OK extraction	50	0.85	1.43	0.33	0.79	1.29	0.29
	60	0.90	1.46	0.34	0.78	1.30	0.29
	1	0.52	0.62	0.00	0.46	0.62	0.05
	5	0.69	0.93	0.02	0.64	0.80	0.05
	10	0.90	1.08	0.02	0.68	1.06	0.07
	20	0.98	1.43	0.06	0.73	1.29	0.09
	30	0.99	1.42	0.11	0.76	1.25	0.09
40	1.04	1.37	0.12	0.77	1.16	0.10	
50	1.07	1.36	0.15	0.80	1.30	0.11	
60	1.10	1.35	0.18	0.82	1.23	0.13	

522 <sup>†</sup> This time refers to the isothermal treatment time. It should be noticed that the heating and cooling ramps also  
 523 contribute to the thermal budget (i.e., for  $t=0$  min, there would be a non-zero production of lignin, furfural and 5-  
 524 HMF due to heating and cooling ramps).

525 **Table 3.** Mass fractions ( $w_B$ , in %) for acid soluble lignin (ASL), furfural, 5-HMF, total sugars (TS),  
 526 reducing sugars (RS) and non-reducing sugars (NRS) in the hydrolysates after a 60 min treatment for the  
 527 MW-assisted ChCl/urea, DMAc/NaHCO<sub>3</sub> and DMAc/CH<sub>3</sub>OK media.

Treatment	<i>Erica arborea</i>						<i>Cistus ladanifer</i>					
	ASL	Furfural	5-HMF	TS	RS	NRS	ASL	Furfural	5-HMF	TS	RS	NRS
ChCl:urea DES	1.80 aA	2.74 aA	0.82 aA	9.19 aA	0.41 aA	8.78 aA	1.26 aB	2.33 aB	0.77 aA	8.45 aA	0.33 aB	8.13 aA
DMAc/NaHCO <sub>3</sub>	0.90 bA	1.46 bA	0.34 bA	3.74 bA	0.34 bA	3.40 bA	0.78 bB	1.30 bB	0.29 bB	3.22 bB	0.23 bB	2.99 bB
DMAc/CH <sub>3</sub> OK	1.10 cA	1.35 bA	0.18 cA	3.80 bA	0.44 aA	3.36 bA	0.82 bB	1.23 bA	0.13 cB	2.90 bB	0.36 aB	2.54 bB

528 \* Means followed by the same lowercase letter within each column are not significantly different at p<0.05 by  
 529 Tukey's test. Means of the same product (viz. ASL, furfural, 5-HMF, TS, RS or NRS) followed by the same  
 530 uppercase letter for *E. arborea* and *C. ladanifer* are not significantly different at p<0.05 by Tukey's test. All values  
 531 are presented as the average of three repetitions.  
 532

533 **Table 4.** Comparative measurements of soluble lignin, furfural and 5-HMF in the hydrolysates ( $w_B$ , in %).  
 534 Tests were performed in triplicate, and standard deviations were <10 % in all cases.

Component	Solvent	Shrubs		Native cellulose	Hardwoods	References
		<i>E. arborea</i>	<i>C. ladanifer</i>			
Lignin	ChCl/urea	0.52-1.80	0.48-1.4			
	DMAc/NaHCO <sub>3</sub>	0.33-0.90	0.42-0.79		1.43	Chi, <i>et al.</i> [15]
	DMAc/CH <sub>3</sub> OK	0.52-1.10	0.46-0.82			
	NaOH	2.25	1.31			
Furfural	ChCl/urea	1.00-2.74	1.05-2.33	2.30-5.25		da Silva <i>et al.</i> [20]
	DMAc/NaHCO <sub>3</sub>	0.97-1.46	0.92-1.30			
	DMAc/CH <sub>3</sub> OK	0.62-1.43	0.62-1.30			
	NaOH	0.40	0.19			
5-HMF	ChCl/urea	0.25-0.82	0.23-0.77	0.23-0.87		da Silva <i>et al.</i> [21]
	DMAc/NaHCO <sub>3</sub>	0.22-0.34	0.20-0.29			
	DMAc/CH <sub>3</sub> OK	0.00-0.18	0.05-0.13			
	NaOH	0.52	0.47			

535

536

537

538 **Table 5.** Total sugars (TS), reducing sugars (RS) and non-reducing sugars (NRS) mass fractions ( $w_B$ , in  
 539 %) for the MW-assisted ChCl:urea, DMAc/NaHCO<sub>3</sub> and DMAc/CH<sub>3</sub>OK treatments as a function of  
 540 exposure times. Tests were performed in triplicate, and standard deviations were <5 %.

Treatment	Time (min) <sup>†</sup>	<i>Erica arborea</i>			<i>Cistus ladanifer</i>		
		$w_{TS}$	$w_{RS}$	$w_{NRS}$	$w_{TS}$	$w_{RS}$	$w_{NRS}$
MW-assisted ChCl:urea DES extraction	1	2.94	0.17	2.76	3.33	0.12	3.21
	5	3.54	0.20	3.34	3.97	0.14	3.84
	10	4.04	0.27	3.78	4.86	0.23	4.63
	20	6.45	0.28	6.17	6.36	0.23	6.13
	30	8.15	0.31	7.84	7.03	0.28	6.75
	40	8.44	0.35	8.09	8.06	0.29	7.77
	50	8.83	0.40	8.43	8.09	0.30	7.79
	60	9.19	0.41	8.78	8.45	0.33	8.13
MW-assisted DMAc/NaHCO <sub>3</sub> extraction	1	0.45	0.17	0.29	0.39	0.11	0.29
	5	0.61	0.18	0.43	0.40	0.11	0.28
	10	0.75	0.22	0.53	0.57	0.12	0.45
	20	2.46	0.25	2.21	2.44	0.19	2.25
	30	3.29	0.28	3.01	2.44	0.19	2.25
	40	3.33	0.28	3.05	2.60	0.20	2.40
	50	3.68	0.30	3.37	2.70	0.23	2.47
	60	3.74	0.34	3.40	3.22	0.23	2.99
MW-assisted DMAc/CH <sub>3</sub> OK extraction	1	0.28	0.16	0.11	0.12	0.12	0.00
	5	0.71	0.19	0.52	0.26	0.13	0.13
	10	1.05	0.28	0.77	0.63	0.16	0.47
	20	2.63	0.30	2.33	2.21	0.26	1.94
	30	3.27	0.36	2.91	2.39	0.28	2.11
	40	3.32	0.37	2.95	2.64	0.29	2.35
	50	3.48	0.42	3.06	2.82	0.33	2.49
	60	3.80	0.44	3.36	2.90	0.36	2.54

541 <sup>†</sup> This time refers to the isothermal treatment time. It should be noticed that the heating and cooling ramps also  
 542 contribute to the thermal budget (i.e., for  $t=0$  min, there would be a non-zero production of TS, RS and NRS due to  
 543 heating and cooling ramps).  
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546 **Table 6.** Comparison of the sugar mass fractions ( $w_B$ , in %) in the lignocellulosic biomass hydrolysates  
 547 from *E. arborea* and *C. ladanifer* studied herein with values reported by other authors for corncob and  
 548 bamboo.

Component	Solvent	Shrubs		Corncob	Bamboo	References
		<i>E. arborea</i>	<i>C. ladanifer</i>			
Total sugars ( $w_{TS}$ )	ChCl/urea	2.94-9.19	3.33-8.45	18.6-20.9		Procentese, <i>et al.</i> [37]
	DMAc/NaHCO <sub>3</sub>	0.45-3.74	0.39-2.70			
	DMAc/CH <sub>3</sub> OK	0.28-3.80	0.12-2.90			
	NaOH	4.63	5.64			
Reducing sugars ( $w_{RS}$ )	ChCl/urea	0.17-0.41	0.12-0.33		3.4	Wu, <i>et al.</i> [38]
	DMAc/NaHCO <sub>3</sub>	0.17-0.34	0.11-0.23			
	DMAc/CH <sub>3</sub> OK	0.16-0.44	0.12-0.36			
	NaOH	1.29	1.00			
Non-reducing sugars ( $w_{NRS}$ )	ChCl/urea	2.76-8.75	3.21-8.13			
	DMAc/NaHCO <sub>3</sub>	0.29-3.40	0.28-2.99			
	DMAc/CH <sub>3</sub> OK	0.11-3.36	0.00-2.54			
	NaOH	3.34	4.64			

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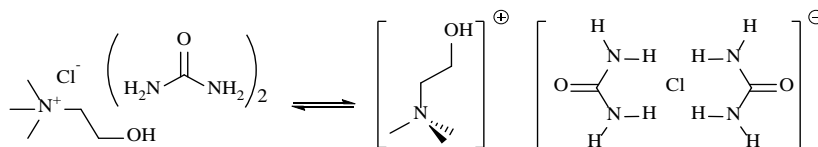
551 **Table 7.** Kinetic coefficients ( $k$ ), correlation coefficients ( $r^2$ ) and initial concentration of each sample ( $H_0$ )  
 552 determined from the concentration as a function of time for lignin, furfural, 5-HMF, total sugars and  
 553 reducing sugars production from the hydrolysis of *E. arborea* and *C. ladanifer* lignocellulosic biomass.

Component	Solvent	<i>E. arborea</i>			<i>C. ladanifer</i>			References
		$k$	$r^2$	$H_0$	$k$	$r^2$	$H_0$	
Soluble lignin	ChCl/urea	0.2959	0.9707	0.0320	0.1752	0.9479	0.0321	
	DMAc/NaHCO <sub>3</sub>	0.2118	0.8583	0.0321	0.0088	0.8646	0.0321	
	DMAc/CH <sub>3</sub> OK	0.0348	0.9745	0.0321	0.0042	0.9831	0.0320	
Furfural	ChCl/urea	0.3192	0.8214	0.0320	0.0649	0.8900	0.0321	0.2712 (macauba pulp) [21]
	DMAc/NaHCO <sub>3</sub>	0.0011	0.8500	0.0321	0.0001	0.9905	0.0321	
	DMAc/CH <sub>3</sub> OK	0.0433	0.8908	0.0321	0.0309	0.8782	0.0320	
5-HMF	ChCl/urea	0.3844	0.9025	0.0320	0.3296	0.8365	0.0321	0.2729 (macauba pulp), 0.0810 (macauba shell) [21]
	DMAc/NaHCO <sub>3</sub>	0.0025	0.6806	0.0321	0.0013	0.9240	0.0321	
	DMAc/CH <sub>3</sub> OK	0.4883	0.8024	0.0321	0.7798	0.8367	0.0320	
Total sugars	ChCl/urea	0.3778	0.8704	0.0100	0.1605	0.9149	0.0100	
	DMAc/NaHCO <sub>3</sub>	1.4143	0.8309	0.0100	1.3890	0.8024	0.0100	
	DMAc/CH <sub>3</sub> OK	1.4044	0.8928	0.0100	1.7780	0.8634	0.0100	
Reducing sugars	ChCl/urea	0.3005	0.8780	0.0667	0.5469	0.9137	0.0668	
	DMAc/NaHCO <sub>3</sub>	0.1600	0.8976	0.0668	0.6234	0.8339	0.0668	
	DMAc/CH <sub>3</sub> OK	0.4351	0.9132	0.0668	0.9528	0.8690	0.0668	

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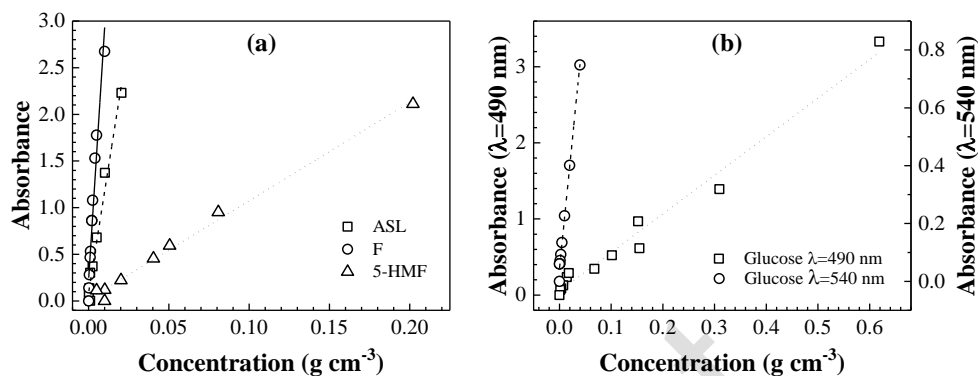
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**Figure 1.** DES of ChCl and urea where a [choline]<sup>+</sup> cation is energetically competitive with [Cl(urea)<sub>2</sub>]<sup>−</sup>.

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**Figure 2.** (a) Calibration curves for furfural (F), acid-soluble lignin (ASL) and 5-(hydroxymethyl)-

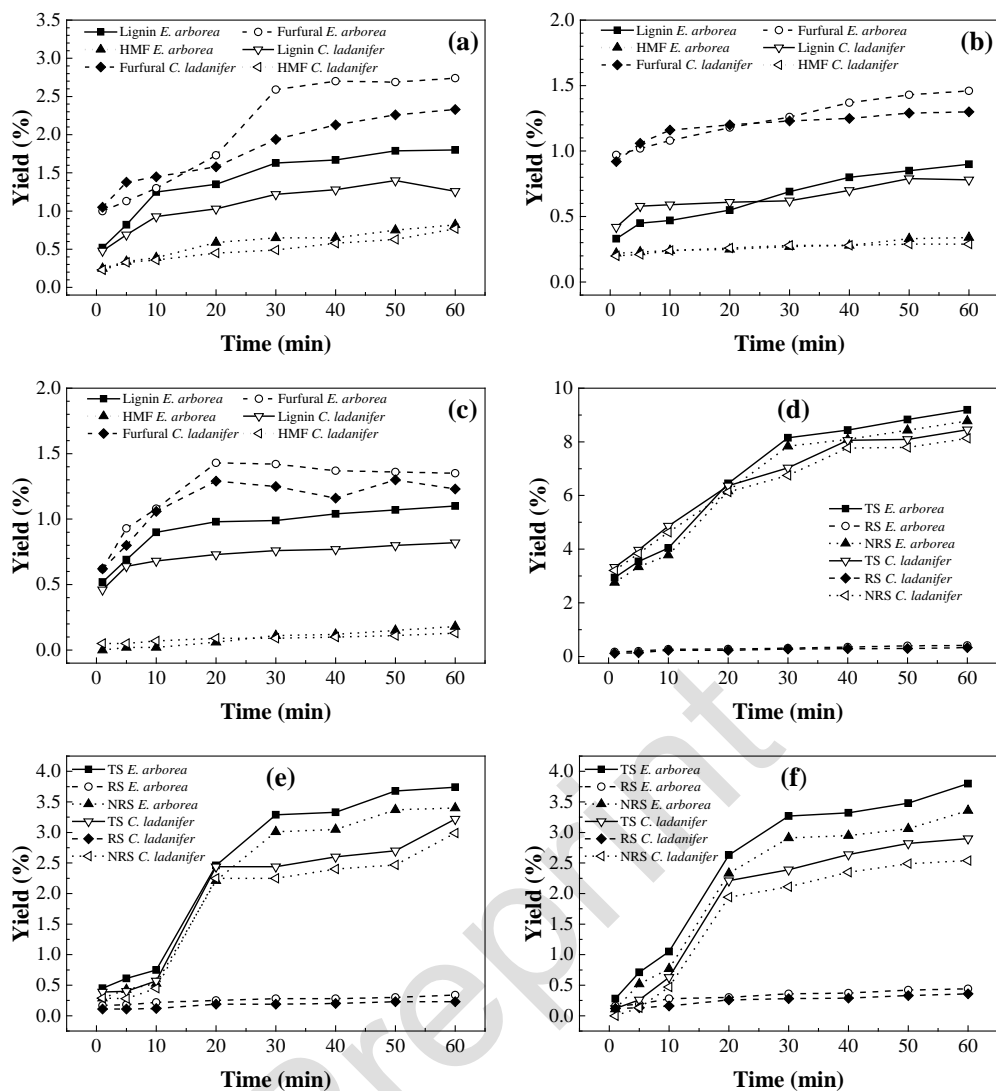
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furfural (5-HMF) concentrations. (b) Calibration curves for glucose concentration. Each data point was

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the mean of three determinations. Standard deviation bars were omitted for clarity.

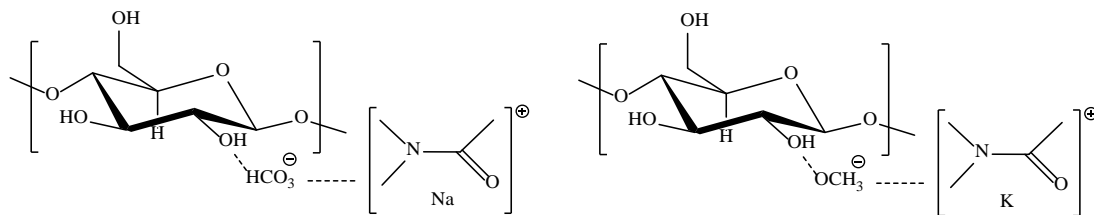




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564 **Figure 3.** Lignin, furfural and 5-HMF yields for the *E. arborea* and *C. ladanifer* lignocellulosic biomass  
 565 hydrolysates after: (a) MW-assisted ChCl/urea extraction; (b) MW-assisted DMAc/NaHCO<sub>3</sub> extraction;  
 566 and (c) MW-assisted DMAc/CH<sub>3</sub>OK extraction. Total, reducing and non-reducing sugars in the  
 567 hydrolysates after: (d) MW-assisted ChCl/urea treatment; (e) MW-assisted DMAc/NaHCO<sub>3</sub> treatment;  
 568 and (f) MW-assisted DMAc/CH<sub>3</sub>OK treatment.

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571 **Figure 4.** Proposed interaction between DMAc-NaHCO<sub>3</sub> and DMAc-CH<sub>3</sub>OK solvents and sugar polymer