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Supporting Information

Deep Eutectic Solvent Aqueous Solutions as Efficient Media for the Solubilization of Hardwood Xylans

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Author Contributions

J.C. Conceptualization: Lead; Formal analysis: Lead.

Table S1. Compounds descriptions, CAS number, molecular weight, mass fraction purity, water content and supplier of the DES components investigated.

Compound	Cas number	Mw (g.mol-1)	Purity[a]/wt%	Water content/ wt%	Supplier
Hydrogen Bond Acceptors (HBA)					
Choline Chloride (ChCl)	67-48-1	139.62	99	5.13 ± 0.18	ACROS Organics
Hydrogen Bond Donors (HBD)					
Urea (U)	57-13-6	60.06	>99	0.001 ± 0.00	Panreac
Acetic Acid (AA)	64-19-7	60.05	99	0.01 ± 0.00	Fisher Scientific

[a] as reported by the supplier.

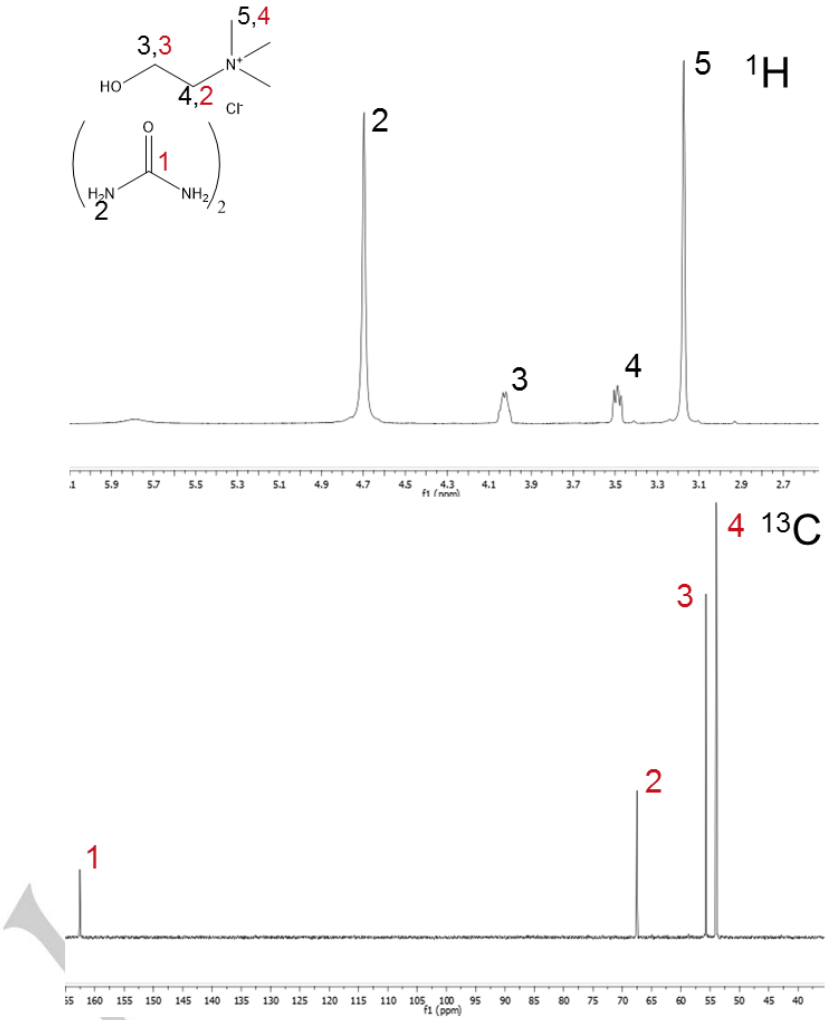

Figure S1. ^{1}H and ^{13}C NMR of ChCl:U (1:2).

^{1}H NMR (D_2O, 300 MHz, [ppm]): δ 5.79 (s, 1H, $N(CH_3)_3CH_2CH_2O\underline{H}$) δ 4.70 (s, 4H, $2x(NH_2)$, δ 4.03 (m, 2H, $N(CH_3)_3CH_2C\underline{H}_2OH$), δ 3.47 (t, 2H, $N(CH_3)_3C\underline{H}_2CH_2OH$), δ 3.17 (s, 9H, $N(C\underline{H}_3)_3$). ^{13}C NMR, (D_2O, 75.47 MHz, [ppm]): δ 162.54 (s, $2x(\underline{C}O(NH_2))$, δ 67.50 (s, $N(CH_3)_3\underline{C}H_2CH_2OH$) , δ 55.72 (s, $N(CH_3)_3CH_2\underline{C}H_2OH$), δ 53.97 (t, J_{CN} = 4.0 Hz, $N(\underline{C}H_3)_3CH_2CH_2OH$).

Table S2. pH of the different tested ILs, individual HBA and HBD, DES and aqueous DES solutions , water and conventional solvent media (NaOH 1.67 M).

Solvent	HBA:HBD	DES/IL content water (%)	pH	Solvent	HBA:HBD	DES/IL content water (%)	pH
NaOH 1.67 M	-	0.0	13.4	ChCl:U	1:2	25	8.13
Choline acetate	-	83.3	8.1			15.0	8.04
Water	-	0.0	5.95			5.0	7.94
ChCl	-	50	7.42		1:1	100.0	10.4
Urea	-	50	7.96			83.3	9.91
ChCl:AA	1:2	100.0	1.01			80.0	9.77
		83.3	1.11			75.0	9.56
		80.0	1.13			50.0	9.05
		75.0	1.26			25.0	8.94
		66.7	1.37			15.0	8.85
		50.0	1.43			5.0	8.74
		35.0	1.98		2:1	100.0	10.58
		25.0	2.01			83.3	10.18
		15.0	2.51			80.0	10.01
		5.0	2.7			75.0	9.87
ChCl:U	1:2	100.0	9.78			66.7	9.71
		83.3	9.12			50.0	9.63
		80.0	8.94			35.0	9.42
		75.0	8.9			25.0	8.98
		66.7	8.86			15.9	8.74
		50.0	8.3			5.0	8.5
		35.0	8.36			5.0	8.5

Table S3. Xylan solubility results for the assays using water, aqueous 1.67 M NaOH, Choline Acetate and ChCl:U (1:2, 1:1, 2:1).

Compound	HBA:HBD	DES/IL content water (%)	Xylan concentration (mg/g)	±deviation
NaOH 1.67 M	-	0	316.47	1.94
Choline acetate	-	83.3	208.61	5.70
Water	-	0	15.48	1.05
ChCl:U	1:2	100	260.40	30.83
		83.3	201.13	11.19
		80	189.21	10.11
		75	171.35	13.70
		66.7	247.74	12.87
		50	304.53	8.71
		35	101.25	23.78
		25	145.08	23.59
		15	91.27	14.12
		5	34.74	1.00
	1:1	100	172.38	9.33
		83.3	145.78	16.71
		80	150.10	18.41
		75	152.36	15.62
		66.7	121.57	23.11
		50	130.43	6.17
		35	125.00	9.74
		25	201.47	24.12
		15	113.92	22.33
		5	165.34	0.60
	2:1	100	148.48	20.63
		83.3	128.98	10.13
		80	141.45	27.61
		75	177.61	8.29
		66.7	174.06	9.90
		50	178.52	28.72
		35	134.98	22.91
		25	201.45	11.17
		15	126.77	28.32
		5	102.31	0.55

Table S4. Xylan solubility results in mg/mL for water, aqueous 1.67M NaOH and ChCl:U.

Solvent	HBA:HBD	DES/IL content water (%)	Xylan concentration (mg/mL)	±deviation
NaOH 1.67 M	-	0	306.30	1.90
Water	-	0	15.48	1.05
ChCl:U	1:2	100	243.49	23.66
		83.3	221.51	20.86
		80	206.39	14.11
		75	188.48	20.10
		66.7	269.02	20.95
		50	320.80	18.35
		35	101.80	23.91
		25	124.07	21.44
		15	91.76	14.20
		5	34.93	1.00
	1:1	100	191.65	10.37
		83.3	160.62	18.41
		80	164.27	20.14
		75	165.07	16.92
		66.7	191.87	18.40
		50	134.79	6.37
		35	115.00	9.80
		25	128.54	23.30
		15	130.41	2.45
		5	166.66	0.67

Table S5. Xylan solubility results for the different temperatures studied.

Compound	HBA:HBD	Temperature (°C)	DES/IL content water (%)	Xylan concentration (mg/mL)	±deviation
ChCl:U	1:2	70	100	228.87	6.43
			83.3	253.46	2.01
			80	300.45	14.23
			75	267.95	26.74
			66.7	168.72	29.80
			50	140.89	19.10
			35	128.07	17.22
			25	68.10	14.62
			15	73.37	0.19
			5	127.40	23.59
		80	100	187.17	11.94
			83.3	232.92	21.91
			80	243.67	19.85
			75	242.91	35.93
			66.7	328.23	28.87
			50	171.74	9.54
			35	78.64	8.02
			25	99.25	12.54
			15	108.91	16.59
			5	129.81	20.19
		90	100	243.49	23.66
			83.3	221.51	20.86
			80	206.39	14.11
			75	188.48	20.10
			66.7	269.02	20.95
			50	320.80	18.35
			35	101.80	23.91
			25	124.07	21.44
			15	91.76	14.20
			5	34.93	1.00
Water	--	70		20.17	4.24
		80		27.01	3.92
		90		15.48	1.05

Table S6. 2^3 factorial planning.

Experiment	χ_1	χ_2	χ_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
18	0	0	0
19	0	0	0
20	0	0	0

Table S7. Coded levels of independents variables used in the first and second factorial planning.

Studied parameters	Symbol	Level				
		Axial	Factorial	Central	Factorial	Axial
		-1.68	-1	0	1	1.68
Concentration (wt%)	C	8.0	25.0	50.0	75.0	92.0
Temperature (°C)	T	63.2	70.0	80.0	90.0	96.8
HBA:HBD Ratio	R	21.9	33.3	50.0	66.7	78.1

Table S8. Experimental data and response surface predicted values of the factorial planning.

Experiment	C (wt%)	T (°C)	Ratio S/L	Experimental xylan solubility (mg/g)	Predicted xylan solubility (mg/g)	Relative deviation (%)
1	25.0	70.0	33.30	68.10	94.68	-26.58
2	75.0	70.0	33.30	267.95	243.20	24.75
3	25.0	90.0	33.30	124.07	108.52	15.55
4	75.0	90.0	33.30	188.48	156.12	32.36
5	25.0	70.0	66.70	40.61	64.36	-23.74
6	75.0	70.0	66.70	83.18	90.11	-6.93
7	25.0	90.0	66.70	201.45	217.58	-16.13
8	75.0	90.0	66.70	177.61	142.41	35.20
9	8.0	80.0	50.00	138.69	104.24	34.45
10	92.0	80.0	50.00	119.19	165.86	-46.67
11	50.0	63.2	50.00	162.09	138.59	23.50
12	50.0	96.8	50.00	158.42	194.14	-35.72
13	50.0	80.0	21.94	113.48	136.77	-23.28
14	50.0	80.0	78.06	110.85	99.79	11.06
15	50.0	80.0	50.00	166.27	144.25	22.02
16	50.0	80.0	50.00	149.72	144.25	5.47
17	50.0	80.0	50.00	156.67	144.25	12.43
18	50.0	80.0	50.00	180.49	144.25	36.24
19	50.0	80.0	50.00	105.50	144.25	-38.74
20	50.0	80.0	50.00	109.00	144.25	-35.25

Table S9. Regression coefficients of the predicted second-order polynomial model from factorial planning.

	Regression coefficients	Standard deviation	t-student (10)	P-value
Interception	2.8660	1.0138	2.8268	<0.05
Time	0.0105	0.0054	1.9299	0.08244
Concentration	6.5025	0.8912	7.2963	<0.05
Solid-liquid ratio	-20.5519	9.3240	-2.2041	0.05207
Time^2	0.0000	0.00001	-1.3810	0.19733
Concentration^2	-2.2092	0.2916	-7.5758	<0.05
Solid-liquid ratio^2	73.6479	32.6225	2.2575	<0.05
Time × Concentration	-0.0003	0.0023	-0.1192	0.90747
Time × Solid-liquid ratio	-0.0116	0.0252	-0.4575	0.65702
Solid-liquid ratio × Concentration	1.7420	4.1330	0.4214	0.68231

Table S10. ANOVA data for the xylan solubility obtained from the RSM design.

	Sum of squares	Degrees of freedom	Mean square	F-value	P-value
Regression	34783.05	9	3864.783	2.525512	0.082590
Residuals	15302.97	10	1530.297		
Total	50086.01				

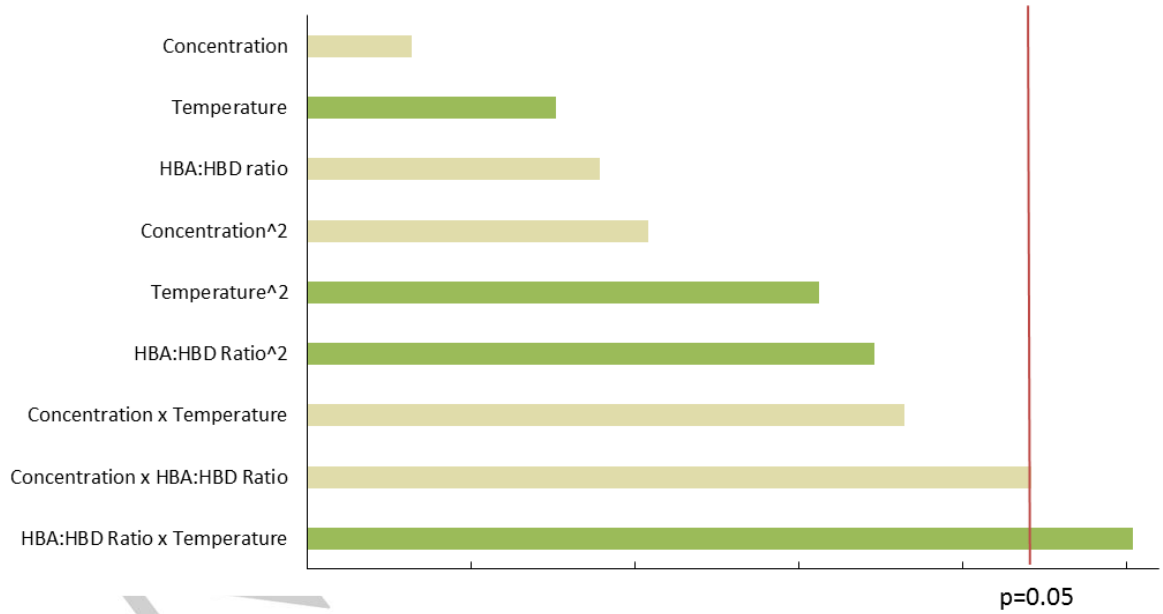

Figure S2. Pareto chart for the standardized main effects (positive ( ) and negative ( )) in the factorial planning for xylan solubility. Vertical line indicates the statistical significance of the effects.

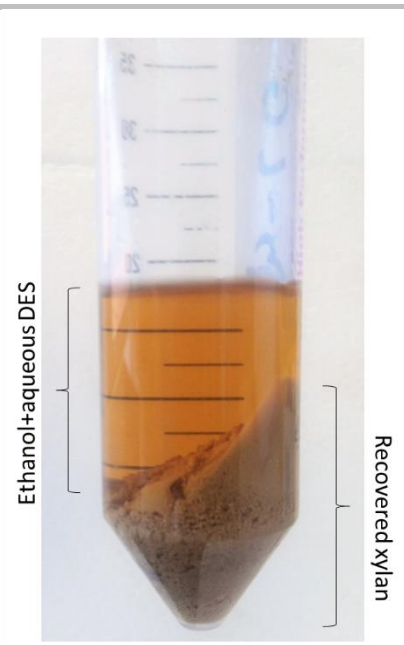

Figure S3. Photo of the recovered xylan after precipitation with ethanol.

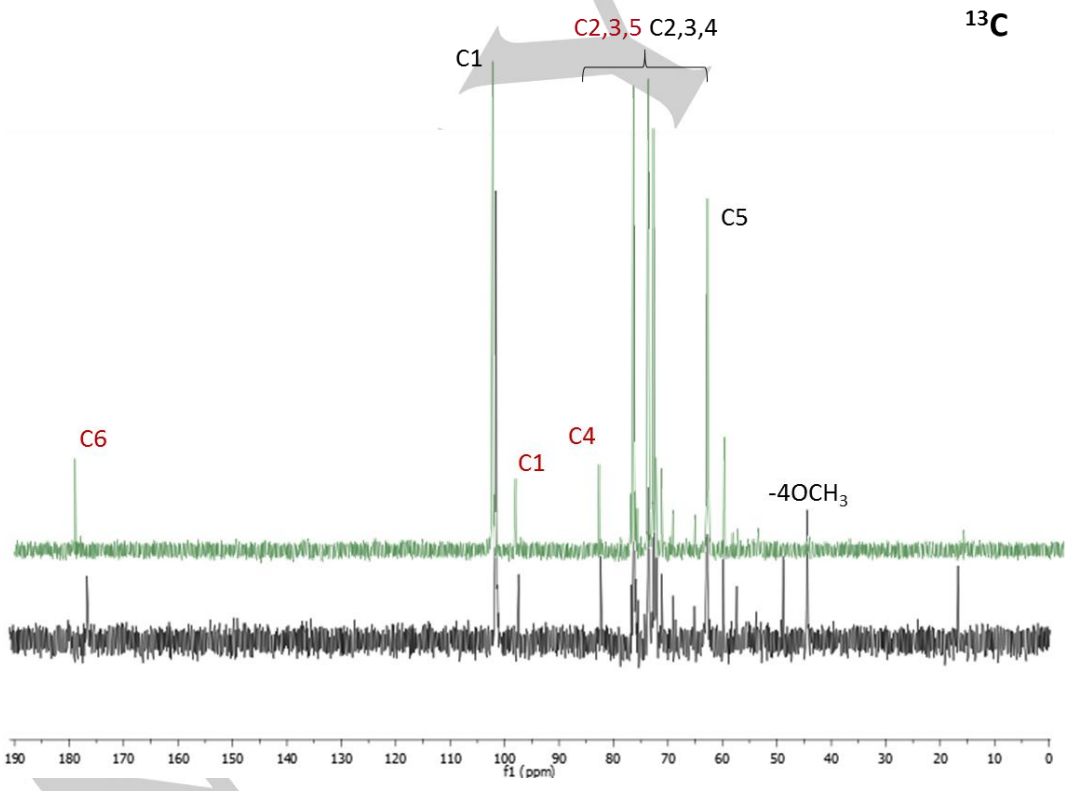

Figure S4. ^{13}C NMR juxtaposed spectra for original xylan (—) and recoverd xylan (—) after dissolution in ChCl:Urea (1:2) at 90 °C. The carbons corresponding to X^a are in black and the carbons corresponding to U^b are in red.

Table S11. ^{13}C NMR peak identification of the original and recovered xylans.[1]

(D_2O, 75.47 MHz, [ppm])	**Assignments**							
	1	2	3	4	5_{eq}	5_{ax}	6	$-OCH_3$
X[a]	101.6	73.6	74.3	75.9	62.9	62.9		
U[b]	97.5	72.2	72.2	82.4	72.2		176.7	59.8

X[a] – (1→4)-β-D-Xylp, U[b] – 4-*O*-Methy-α-D-GlcpA.

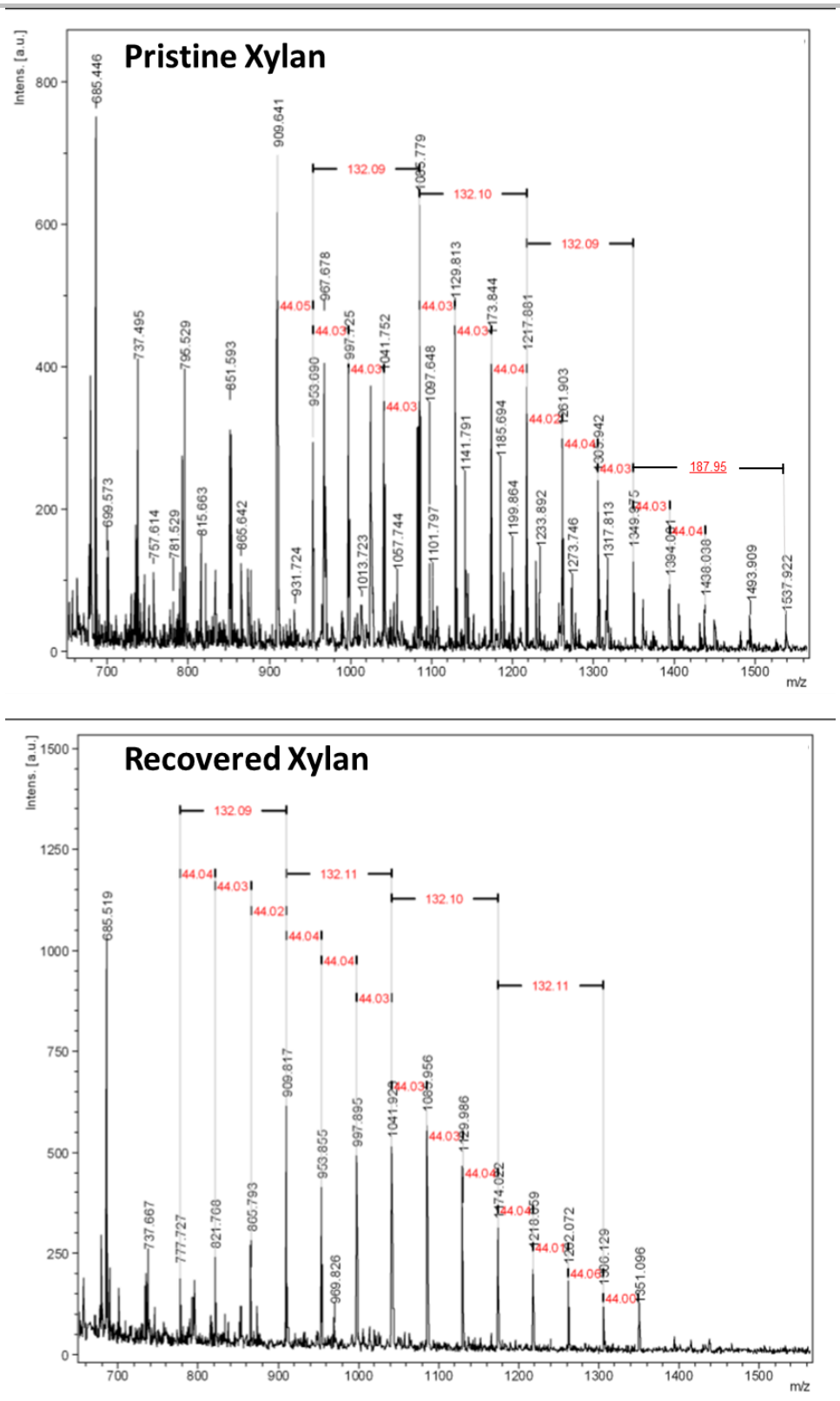

Figure S5. MALDI-ToF/GC spectra for pristine and recovered xylan.[2]

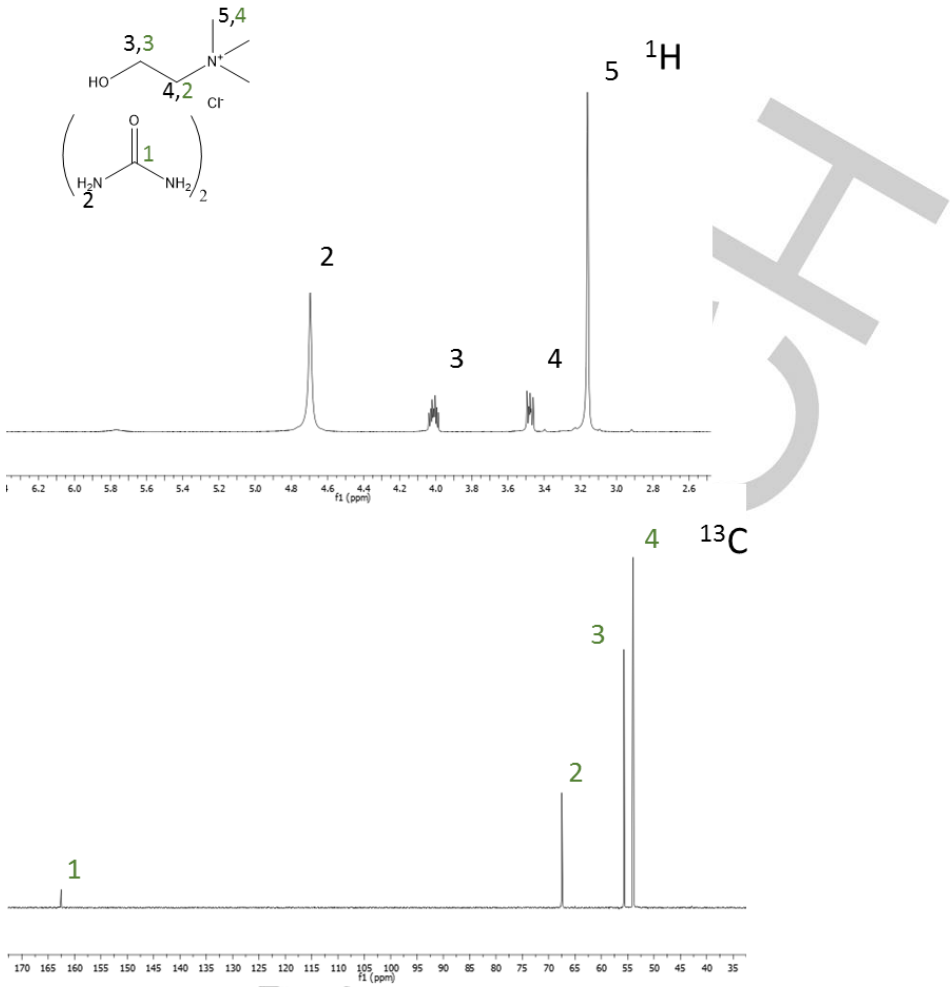

Figure S6. ^{1}H and ^{13}C NMR spectra for the reclycled ChCl:U (1:2**).**

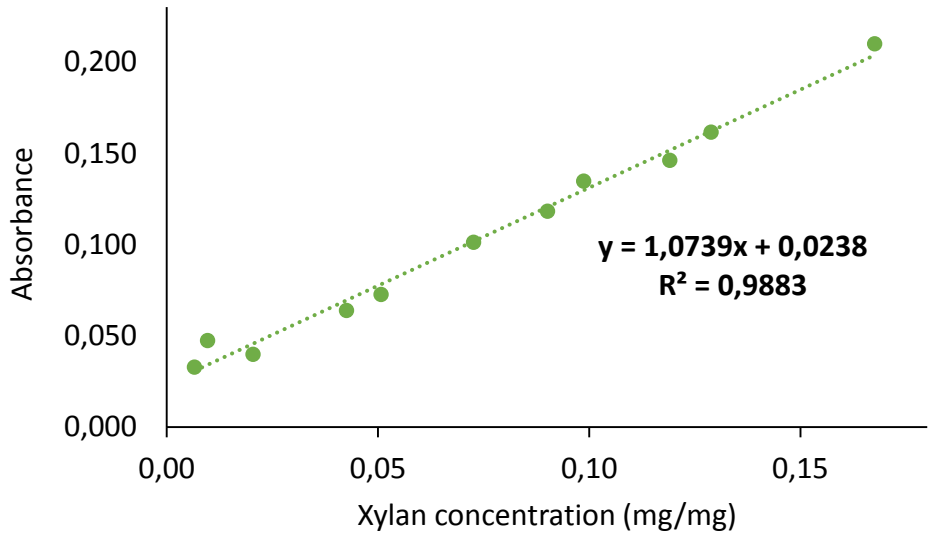

Figure S8. Calibration curve for xylan dissolved in Choline Acetate.

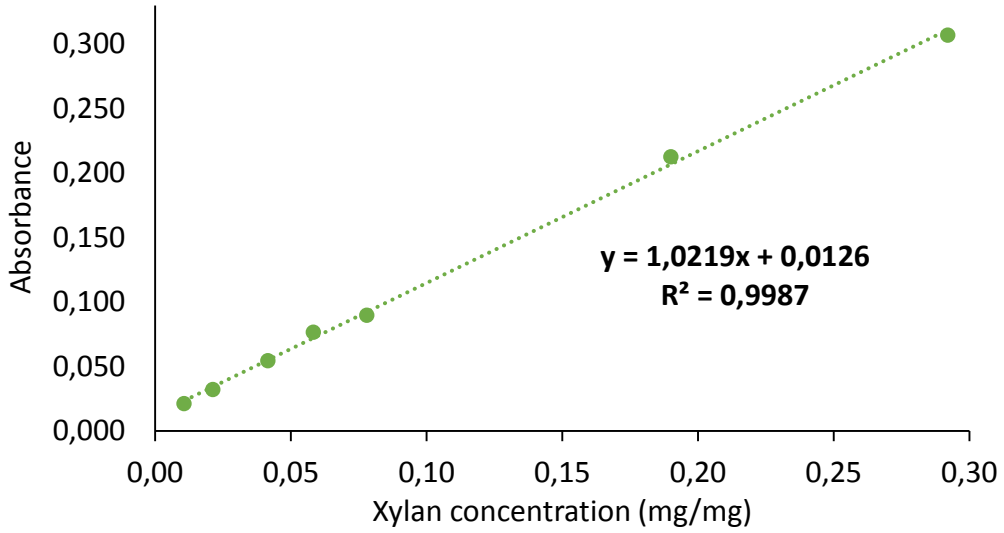

Figure S9. Calibration Curve for xylan dissolved in ChCl:U.

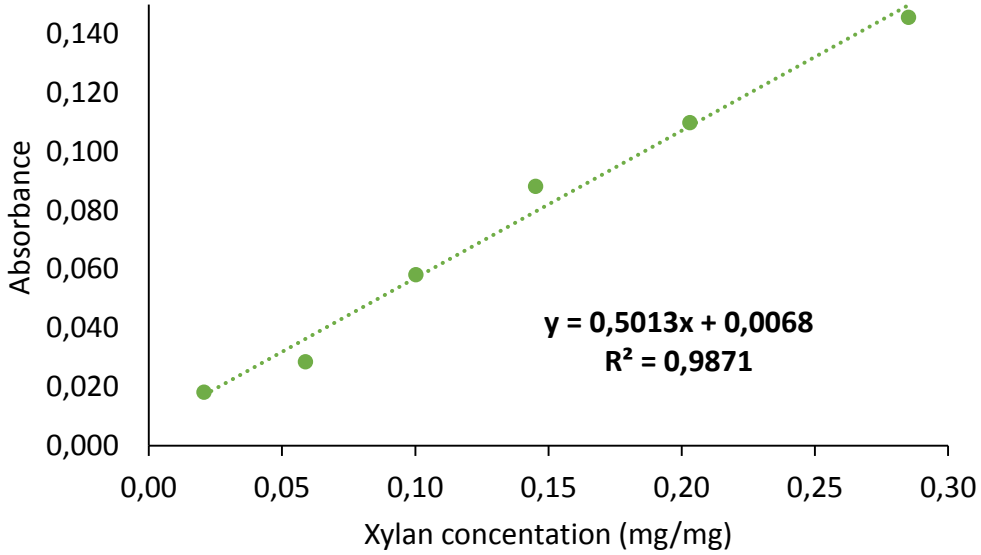

Figure S10. Calibration curve for xylan dissolved in aqueous 1.67M NaOH.

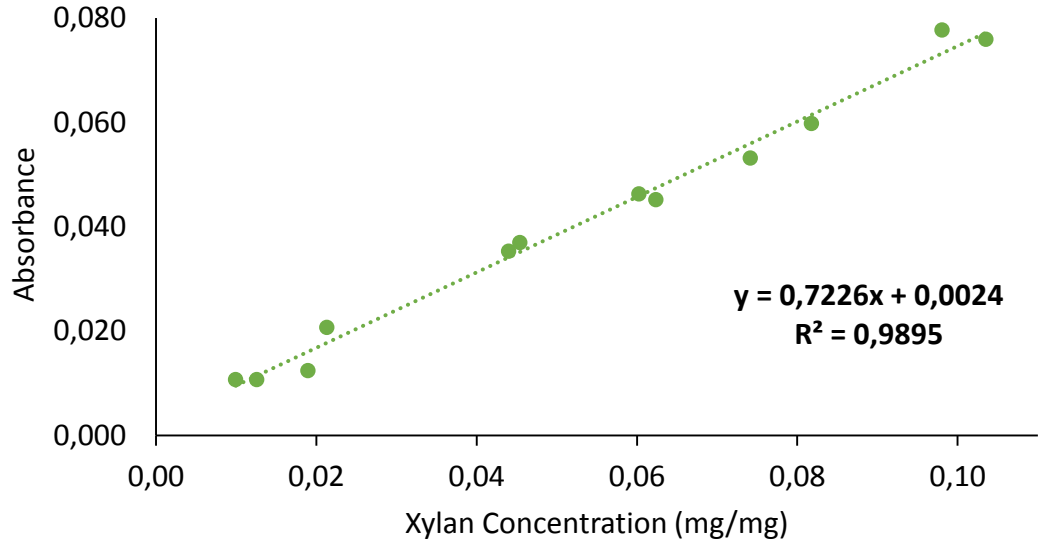

Figure S11. Calibration curve for xylan dissolved in aqueous aqueous ChCl.

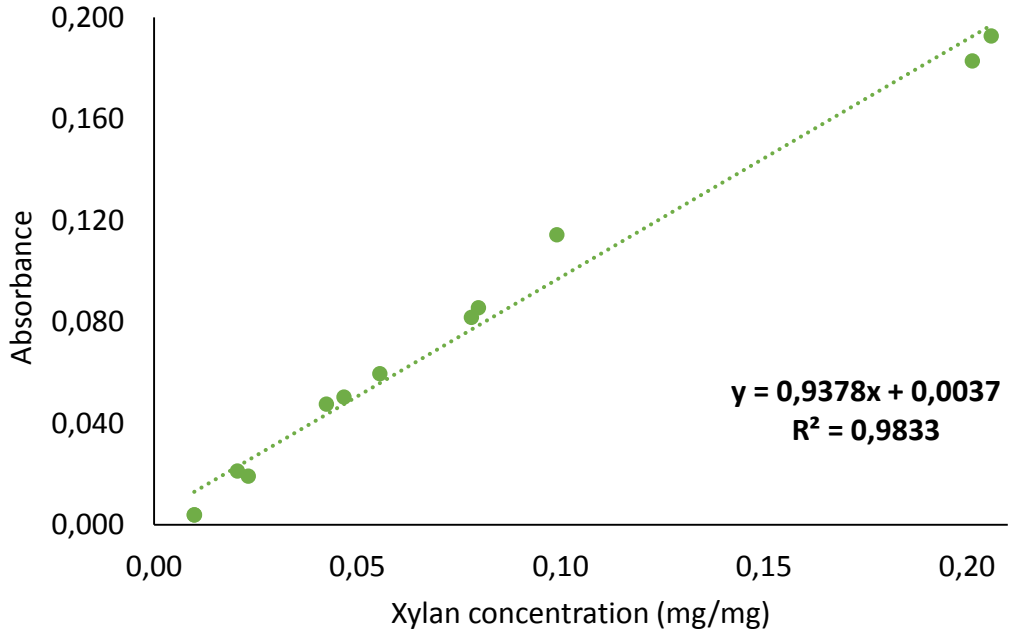

Figure S12. Calibration curve for xylan dissolved in aqueous aqueous Urea.

Table S12. Values for the statistic test using confidence interval of 95% for the calibration curves calculated.

Solvent	Slope	standard deviation (error) of the gradient, Sm	Confidence interval of the gradient, Cm	Correlation coefficient, R	Correlation coefficient square, R^2	t Stat	P-value
Choline Acetate	1.074	0.069	0.046	0.982	0.964	21.804	4.23E-09
ChCl:U	0.977	0.016	0.016	0.999	0.999	61.983	2.07E-08
NaOH	0.502	0.029	0.032	0.993	0.987	17.385	6.43E-05
ChCl only	0.718	0.023	0.011	0.995	0.989	30.777	3.08E-11
Urea only	0.937	0.039	0.028	0.991	0.983	24.286	3.19E-10

References

[1] S. N. Sun, T. Q. Yuan, M. F. Li, X. F. Cao, F. Xu, Q. Y. Liu, *Cellul. Chem. Technol.* **2012**, *46*, 165–176.

[2] Y. Nakahara and K. Yamauchi, *J Wood Sci* **2014**, *60*, 225–231.