Electronic Supplementary Information (ESI)

Biorefinery approach for lignocellulosic biomass valorisation with acidic ionic liquid

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Data from reactions of wheat straw with aqueous ionic liquid solution

Table S1. The yields of main products, *i.e.* pentoses (sum of arabinose and xylose); furfural; glucose; 5-hydroxymethylfurfural (5-HMF) and acetic acid found in the liquids produced in the biomass reactions.

Entry[a]	$logR_O$	Yield (mol%)[b]				
		Pentoses	Furfural	Glucose	5-HMF	Acetic acid
3	2.45	20.9	0.0	3.1	0.0	36.3
9	3.07	24.7	0.0	2.7	0.4	50.0
5	3.19	26.4	0.0	3.2	0.7	43.5
7	3.19	26.6	0.0	3.2	0.1	50.2
12	3.28	28.7	0.0	2.7	0.3	54.5
11	3.80	43.7	0.1	3.2	0.6	61.2
15	3.92	54.1	0.6	3.6	1.1	73.5
1	3.92	54.5	0.2	4.2	1.2	78.2
13	4.02	56.2	1.1	3.8	1.6	81.2
10	4.53	67.5	2.8	5.1	1.9	85.7
4	4.66	74.4	1.1	5.5	1.4	86.5
6	4.66	67.0	4.5	6.0	2.6	92.4
8	4.76	76.8	3.4	6.4	2.1	91.1
2	5.39	77.5	11.4	8.4	2.5	102.3
14	6.56	59.1	33.2	9.3	2.5	103.4

[a] the entry according to Table 2; [b] For quantification please refer to next sections.

Table S2. The yield of recovered solid (SY) and composition of solid and recovery yields of main components *i.e.* arabinoxylan (sum of xylan and arabinan); acetyl groups; glucan; Klason lignin and ash produced in biomass reactions.

Entry[a]	***logR_O***	**SY wt.%**	**Composition (wt.%)**[b] **(recovery yield (g/100 g of the initial amount present in the feedstock))**[b]				
			Arabinoxylan	**Acetyl groups**	**Glucan**	**Klason Lignin**	**Ash**
native	-	100.0	22.1 (100.0)	2.7 (100.0)	38.5 (100.0)	17.7 (100.0)	10.7 (100.0)
3	2.45	82.7	20.6 (77.1)	1.8 (54.6)	43.2 (92.8)	17.4 (81.1)	3.9 (29.9)
9	3.07	73.2	19.5 (64.7)	1.5 (39.8)	48.8 (92.8)	20.1 (83.1)	4.1 (28.0)
5	3.19	76.0	18.3 (63.1)	1.5 (40.9)	47.4 (93.6)	21.6 (92.9)	3.7 (26.3)
7	3.19	72.6	19.1 (62.7)	1.6 (42.1)	48.5 (91.5)	20.6 (84.6)	3.4 (22.9)
12	3.28	69.9	18.4 (58.3)	0.9 (23.5)	52.3 (94.5)	18.8 (74.2)	4.3 (28.1)
11	3.80	65.7	14.1 (42.0)	0.6 (15.2)	45.9 (78.4)	33.4 (124.0)	4.8 (29.4)
15	3.92	63.8	13.1 (37.9)	0.3 (7.7)	58.1 (96.2)	20.6 (74.1)	5.0 (30.1)
1	3.92	63.5	11.6 (33.2)	0.4 (8.9)	54.9 (90.5)	20.8 (74.6)	5.0 (29.9)
13	4.02	63.3	12.7 (36.4)	0.1 (2.8)	49.1 (80.7)	29.8 (106.5)	5.4 (32.1)
10	4.53	59.6	10.9 (29.5)	0.0 (0.0)	60.7 (93.9)	22.7 (76.4)	2.8 (15.6)
4	4.66	62.2	11.0 (30.8)	0.4 (9.5)	58.1 (93.8)	24.0 (84.3)	4.4 (25.3)
6	4.66	60.0	11.3 (30.6)	0.3 (7.5)	53.5 (83.4)	27.5 (93.1)	4.2 (23.4)
8	4.76	60.3	11.6 (31.7)	0.2 (5.6)	57.8 (90.6)	26.1 (89.1)	4.1 (23.1)
2	5.39	57.4	7.2 (18.8)	0.0 (0.0)	61.9 (92.4)	24.8 (80.5)	5.7 (30.7)
14	6.56	56.3	5.5 (14.0)	0.0 (0.0)	60.4 (88.3)	33.7 (107.4)	6.1 (32.0)

[a] the entry according to Table 2; [b] For quantification please refer to next sections.

Table S3. The yields of main products, *i.e.* pentoses (sum of arabinose and xylose); furfural; glucose; 5-HMF and acetic acid found in liquid from reaction at conditions of 141.0 °C, 57.8 wt.% H_2O and 90.0 min.

Yield (mol%)[a]				
Pentoses	**Furfural**	**Glucose**	**5-HMF**	**Acetic acid**
81.6	11.2	8.8	2.0	105.5

[a] For quantification please refer to next sections.

Table S4. The yield of recovered solid (SY) and composition of solid and recovery yields of main components *i.e.* arabinoxylan (sum of xylan and arabinan); acetyl groups; glucan; Klason lignin and ash produced in biomass reaction at conditions of 141.0 °C, 57.8 wt.% H_2O and 90.0 min.

SY wt%	**Composition (wt.%)[a] (recovery yield (g/100 g of the initial amount present in the feedstock))[a]**				
	Arabinoxylan	**Acetyl groups**	**Glucan**	**KL**	**Ash**
55.8	6.6 (16.7)	0.0 (0.0)	65.6 (95.0)	27.2 (85.7)	6.8 (35.3)

[a] For quantification please refer to next sections.

Table S5. The coefficients of model parameters and their statistical significance.

Model parameters	β_0	β_1	β_2	β_3	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Coefficients	70.36	28.33	2.59	5.95	-34.95	-8.43	-8.20	5.76	2.59	2.69
***p*-value**	0.00	0.00	0.72	0.45	0.01	0.44	0.42	0.74	0.89	0.84
R^2	0.91									

Table S6. Statistical approach of ANOVA performed to data obtained from experimental design.

Source of variation	**DF[a]**	**SS[b]**	**MS[c]**	***F-value***	***p-value***
Regression	9	5400.50	600.06	5.90	0.03
Residual Error	5	508.49	101.70	-	-
Total	14	5908.99	-	-	-

[a] Degrees of freedom; [b] Sum of squares; [c] Mean square;

Table S7. The yields of main products, *i.e.* pentoses (sum of arabinose and xylose); furfural; glucose; 5-HMF and acetic acid found in liquid from reactions at optimal conditions (131.0 °C, 58.7 wt.% H_2O and 88.0 min) with fresh IL and with recovered IL.

Entry	**Yield (mol%)**[a]				
	Pentoses	**Furfural**	**Glucose**	**5-HMF**	**Acetic acid**
Fresh IL	80.5	5.3	7.3	1.7	100.7
Recovered IL	78.5	4.0	5.4	3.2	121.8

[a] For quantification please refer to next sections.

Table S8. The yield of recovered solid (SY) and composition of solid and recovery yields of main components *i.e.* arabinoxylan (sum of xylan and arabinan); acetyl groups; glucan; Klason lignin and ash produced in biomass reactions at optimal conditions (131.0 °C, 58.7 wt.% H_2O and 88.0 min) with fresh IL and with recovered IL.

Entry	**SY Wt.%**	**Composition (wt.%)**[a] (recovery yield (g/100 g of the initial amount present in the feedstock))[a]				
		Arabinoxylan	**Acetyl groups**	**Glucan**	**KL**	**Ash**
Fresh IL	57.8	6.7 (17.6)	0.0 (0.0)	60.6 (90.9)	29.3 (95.7)	3.4 (18.4)
Recovered IL	60.2	9.3 (25.3)	0.0 (0.0)	59.4 (92.9)	23.1 (78.5)	5.2 (29.0)

[a] For quantification please refer to next sections.

Determination of severity factor (*logR$_O$*)

For comparison purposes and to provide a mathematic tool for direct analysis of the influence of three studied parameters a severity factor (*logR$_O$*) for reactions with catalysts was calculated using the following equation: $logR_O = log_{10}\left(e^{\left(\frac{T_r - T_b}{\omega}\right)} \times \Delta t\right)$, where T_r and T_b are absolute reaction temperature and reference temperature when hydrolysis initiates with [emim][HSO_4], respectively, and are expressed in °C, and ω is a dimensionless constant that translates the effect of the temperature in the conversion. Yields of hemicellulose hydrolysis with [emim][HSO_4] obtained in this work were used to estimate the values of T_b and ω.

The value of T_b was attained by applying the equation below obtained from Doehlert experimental design (section 2.4 of the article) for all the hemicellulose hydrolysis experiments examined. The point (x,0,0) represents the value of T_b and by solving the equation obtained from experimental design in the following form $Y = 77.01 + 30.83X_1 - 0.59X_2 - 0.62X_1X_2 - 21.20{X_1}^2 - 11.00{X_2}^2$, where Y is the percentage of hemicellulose hydrolysis and X_1, X_2 are the temperature (°C) and H_2O content (wt%), respectively. The result gave T_b= 80.25 °C.

The value of ω was attained by representation of the experimental results using the following equation: $Y = mX + B$, where $Y = \ln\left(-\ln\left(1 - \alpha\right)\right)$, where α is the hydrolysis of hemicellulose and X is the severity factor calculated in the following manner: $X = logR_O = log_{10}\left(R_{oheating} + R_{oisothermal}\right)$, where $R_{oheating}$ is the severity factor for heating and $R_{0isothermal}$ is the severity factor for isothermal condition process. Hence the value of ω was 7.2, obtained by maximization of R^2.

Therefore, *logR$_O$* for each reaction was calculated through the following equation:

$$logR_O = log_{10}\left(e^{\left(\frac{T_r - 80.25}{7.2}\right)} \times \Delta t\right)$$

Calculations of the yields of products in the liquid samples

$$pentose\ yield\ (mol\%) = \frac{m_{pentose}}{m_{arabinoxylan_{native}}} \times \frac{132}{150} \times 100$$

$$glucose\ yield\ (mol\%) = \frac{m_{glucose}}{m_{glucan_{native}}} \times \frac{162}{180} \times 100$$

$$furfural\ yield\ (mol\%) = \frac{m_{furfural}}{m_{arabinoxylan_{native}}} \times \frac{132}{96} \times 100$$

$$HMF\ yield\ (mol\%) = \frac{m_{5-HMF}}{m_{glucan_{native}}} \times \frac{162}{126} \times 100$$

$$acetic\ acid\ yield\ (mol\%) = \frac{m_{acetic\ acid}}{m_{acetyl\ group_{native}}} \times \frac{59}{60} \times 100$$

native means the amount of fraction in native biomass

Calculations of the recovery yields in the solid phase samples

$$solid\ recovery\ yield\ (wt.\%) = \frac{m_{dry\ biomass_{initial}}}{m_{dry\ biomass_{after\ reaction}}} \times 100$$

$$arabinoxylan\ recovery\ yield\ (wt.\%) = \frac{m_{arabinoxylan}}{m_{arabinoxylan_{native}}} \times 100$$

$$acetyl\ groups'\ recovery\ yield\ (wt.\%) = \frac{m_{acetyl\ groups}}{m_{acetyl\ groups_{native}}} \times 100$$

$$glucan\ recovery\ yield\ (wt.\%) = \frac{m_{glucan}}{m_{glucan_{native}}} \times 100$$

$$lignin\ retained\ in\ the\ solid\ (wt.\%) = \frac{m_{lignin}}{m_{lignin_{native}}} \times 100$$

$$ash\ recovery\ yield\ (wt.\%) = \frac{m_{ash}}{m_{ash_{native}}} \times 100$$

native means the amount of fraction in native biomass; *initial* means the amount of biomass used in the reaction; *after reaction* means the amount of biomass recovered after the reaction with IL;

Calculations of the solid phase samples' composition

$$arabinoxylan\ content\ (wt.\%) = \frac{m_{arabinoxylan}}{m_{recovered\ biomass}} \times 100$$

$$acetyl\ groups\ content\ (wt.\%) = \frac{m_{acetyl\ groups}}{m_{recovered\ biomass}} \times 100$$

$$glucan\ content\ (wt.\%) = \frac{m_{glucan}}{m_{recovered\ biomass}} \times 100$$

$$lignin\ content\ (wt.\%) = \frac{m_{lignin}}{m_{recovered\ biomass}} \times 100$$

$$ash\ content\ (wt.\%) = \frac{m_{ash}}{m_{recovered\ biomass}} \times 100$$