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Electronic Supplementary Information (ESI)

Relevance of the acidic 1-butyl-3-methylimidazolium hydrogen sulphate ionic liquid in the selective catalysis of biomass hemicellulose fraction

Ana V. Carvalho,[1,2] André M. da Costa Lopes[1,2] and Rafał Bogel-Łukasik[1]*

[1] Laboratório Nacional de Energia e Geologia, Unidade de Bioenergia, 1649-038 Lisboa, Portugal,

[2] LAQV/REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

* Corresponding author: phone: +351210924600 ext. 4224; fax: +351217163636; email: rafal.lukasik@lneg.pt

1. Statistical modelling

The pre-treatment reaction conditions for production of xylose and furfural were subject of statistical modelling. In order to optimise the effect of the principal independent variables (temperature (X_1) and time (X_2)) on efficiency of xylan hydrolysis into xylose (Y_1) and arabinan and xylan to furfural (Y_2), the Doehlert experimental designs were employed as presented in Tables 1, 2 and 3.

Table 1. Pre-treatment temperatures and times studied in this work and respective coded levels for statistical modelling.

T	*t*	Coded levels (xylose)		Coded levels (furfural)	
(°C)	(min)	X_1	X_2	X_1	X_2
85	113.3	-0.67	+0.87	-	-
100	70.0	-0.33	0.00	-	-
115	26.7	0.00	-0.87	-1.00	-
	113.3	0.00	+0.87	-1.00	0.00
130	70.0	+0.33	0.00	-0.50	-
	156.6	+0.33	-	-0.50	+0.87
145	26.7	+0.67	-0.87	0.00	-
	113.3	+0.67	+0.87	0.00	0.00
160	70.0	-	-	+0.50	-0.87
	156.6		-	+0.50	+0.87
175	63.3	-	-	+1.00	-1.00
	163.3		-	+1.00	+1.00
	113.3		-	+1.00	0.00

Table 2. Doehlert experimental design applied for the corresponding experimental responses Y_1 (xylan hydrolysis to xylose).

Run	Coded variables		Response
	X_1	X_2	Y_1
A	-0.33	0.00	1.9
B	0.33	0.00	18.9
C	0.00	0.87	15.4
D	0.00	-0.87	4.5
E	-0.67	0.87	0.0
F	0.67	-0.87	12.9
G	0.67	0.87	3.8

Table 3. Doehlert experimental design applied for the corresponding experimental responses Y_2 (sum of arabinan and xylan conversion to furfural).

Run	Coded variables		Response
	X_1	X_2	Y_2
A	-0.50	-0.87	14.3
B	-1.00	0.00	3.1
C	0.00	0.00	26.1
D	1.00	0.00	34.4
E	0.50	0.87	36.2
F	0.50	-0.87	30.7
G	-0.50	0.87	23.4
H	1.00	1.00	15.6
I	1.00	-1.00	30.6

The statistical significance of estimated effects on both Y_1 and Y_2 responses was checked by analysis of variance (ANOVA) presented in Table 4. The p-values indicated the statistical significance ($p<0.05$) of the estimated relations between variables within a 95 % confidence interval for obtained coefficients. Model analysis by the coefficient of multiple determinations (R^2) indicated that the relevance of the dependent variables in the model was well fitted to explain the behaviour variation because R^2 value is near the unity.

Table 4. Parameters of the polynomial models representing the studied response Y_1 (xylan hydrolysis to xylose) and Y_2 (hemicellulose sugar hydrolysis to furfural); The adequacy of the models to fit the sets of data was performing using Fisher test (F-test) for the effectiveness.

Model parameters (MP)	Y_1		Y_2	
	MP	*p*	*MP*	*p*
β_0	13.82	0.01	30.16	0.00
β_1	19.77	0.02	12.89	0.01
β_2	7.04	0.04	2.81	0.40
β_{12}	-18.29	0.03	-7.94	0.12
β_{11}	-32.00	0.03	-13.70	0.05
β_{22}	-5.19	0.16	-3.36	0.49
F-test				
Effectiveness of the parameters	16.23		5.49	
Significance level	0.06		0.06	
R^2	0.99		0.93	

2. Optimisation results

The experimental results at the optimum conditions for both xylose and furfural formation are shown in Tables 5 and 6.

Table 5. Analysis of the liquid fraction produced in experiments performed at the optimum conditions for xylose and furfural production.

T (°C)	t (min)	Yield (% w/w) of xylose[a]	arabinose[b]	furfural[c]	glucose[d]	HMF[e]	acetic acid[f]	formic acid[g]	levulinic acid[h]
125	82.1	16.7	10.9	7.6	0.9	1.1	40.8	0.0	0.0
161	104.5	0.0	0.0	30.7	0.9	1.4	67.9	0.9	2.1

a) $\frac{[xylose]}{[xylan]_{untreated\ biomass}} \times 100$; b) $\frac{[arabionse]}{[arabinan]_{untreated\ biomass}} \times 100$; c) $\frac{[glucose]}{[glucan]_{untreated\ biomass}} \times 100$; d) $\frac{[furfural]}{([xylan]+[arabinan])_{untreated\ biomass}} \times 100$; e) $\frac{[HMF]}{[glucan]_{untreated\ biomass}} \times 100$; f) $\frac{[acetic\ acid]}{[acetyl\ groups]_{untreated\ biomass}} \times 100$; g)

$$\frac{[formic\ acid]}{([xylan] + [arabinan] + [glucan])_{untreated\ biomass}} \times 100 \quad ; \qquad \text{h)}$$

$$\frac{[levulinic\ acid]}{([xylan] + [arabinan] + [glucan])_{untreated\ biomass}} \times 100 \quad .$$

Table 6. Analysis of the solid produced from wheat straw pre-treatment at optimum conditions for xylose and furfural production obtained from statistical modelling.

T (°C)	t (min)	Solid composition (% w/w)[a]							Total recovery yield (%) of	
		xylan	arabinan	acetyl	glucan	lignin	ash	SY (%)	hemicellulose	cellulose
125	82.1	12.4	0.3	0.5	55.3	20.1	6.1	64.4	54.5	81.1
161	104.5	0.0	0.0	1.0	47.5	40.5	6.4	62.8	38.4	71.4

a) The oven-dried solid phase composition; SY ¬ solid yield

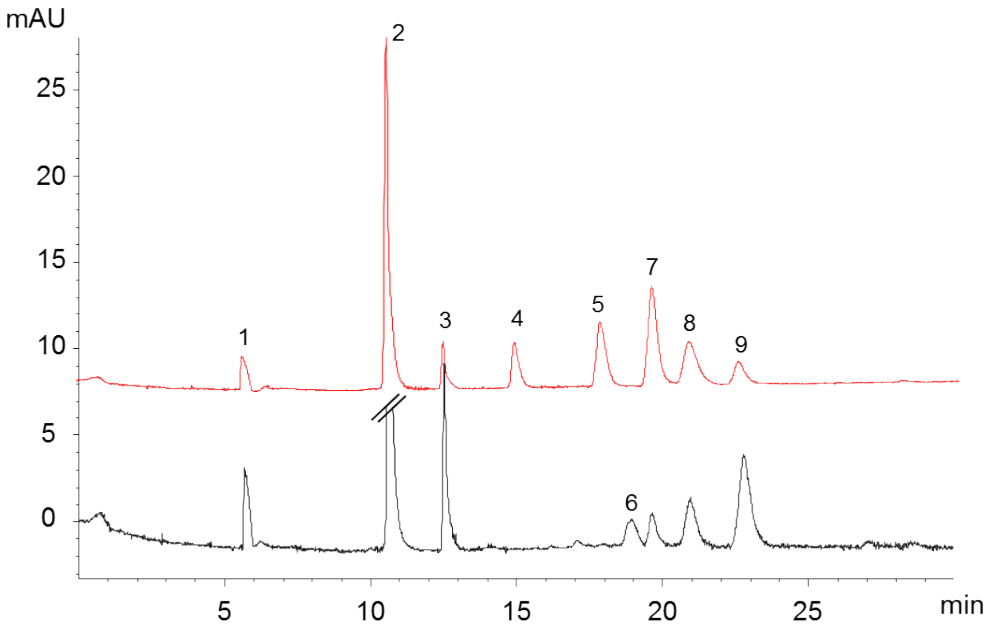

Figure 1. CE electropherograms recorded at 270 nm demonstrating the detection and separation of [bmim][HSO_4], furans and sugars of standard solution (red) and liquid phase from a pre-treatment sample (black). Analytes: 1) [bmim][HSO_4]; 2) furfural; 3) HMF; 4) sucrose (internal standard); 5) cellobiose; 6) unidentified compound; 7) glucose; 8) arabinose; and 9) xylose.

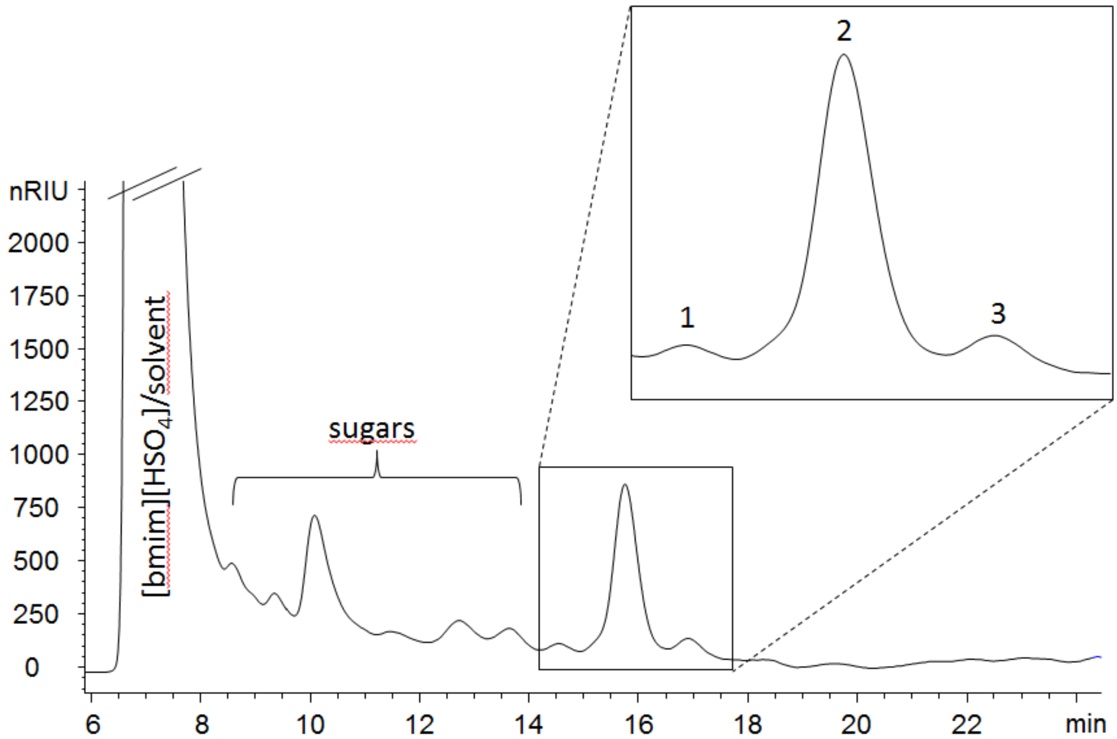

Figure 2. HPLC chromatogram acquired with refractive index detector demonstrating the separation of [bmim][HSO_4], sugars and organic acids of liquid phase from a pre-treatment sample. Analytes: 1) formic acid; 2) acetic acid; and 3) levulinic acid.