Supporting Information

Improved production of 5-hydroxymethylfurfural in acidic deep eutectic solvents using microwave-assisted reactions

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Process optimization – response surface methodology (RSM)

In a 2^k surface response methodology there are *k* factors that contribute to a different response, and the data are treated by a second order polynomial equation according to equation S1:

$$y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum_{i<j} \beta_{ij} X_i X_j \qquad \text{(S1)}$$

where y is the response variable and β_0, β_i , β_{ii} and β_{ij} are the adjusted coefficients for the intercept, linear, quadratic and interaction terms, respectively, and X_i and X_j are independent variables. This model allows the drawing of surface response curves and through their analysis the optimal conditions can be determined (1). The 2^3 factorial planning has been defined by the central point (zero level), the factorial points (1 and −1, level one) and the axial points (level α) The axial points are encoded at a distance α from the central point, according to equation S2:

$$\alpha = (2^k)^{1/4} \qquad \text{(S2)}$$

Table S1. 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

χ_1 – time; χ_2 – temperature; χ_3 – GVL concentration;

Table S2. Experimental data attained.

Experiment	χ_1	χ_2	χ_3	HMF yield (%)
1	2.0	120.0	5.00	75.19
2	4.0	120.0	5.00	85.72
3	2.0	140.0	5.00	67.94
4	4.0	140.0	5.00	81.78
5	2.0	120.0	15.00	93.16
6	4.0	120.0	15.00	80.80
7	2.0	140.0	15.00	68.82
8	4.0	140.0	15.00	69.18
9	1.3	130.0	10.00	44.18
10	4.7	130.0	10.00	94.65
11	3.0	113.2	10.00	66.84
12	3.0	146.8	10.00	73.44
13	3.0	130.0	1.60	70.80
14	3.0	130.0	18.40	80.67
15	3.0	130.0	10.00	86.81
16	3.0	130.0	10.00	90.21
17	3.0	130.0	10.00	84.10
18	3.0	130.0	10.00	90.84
19	3.0	130.0	10.00	83.57
20	3.0	130.0	10.00	81.33

χ_1 – time; χ_2 – temperature; χ_3 – GVL concentration;

Table S3. 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**
Time (min)	t	1.3	2.0	3.0	4.0	4.7
Temperature (°C)	T	113.20	120.0	130.0	140.0	146.8
GVL (wt.%)	GVL	1.6	5.0	10.0	15.0	18.4

Table S4. Regression coefficients of the predicted second-order polynomial model from factorial planning for the dependable variable of 5-HMF yield.

	Regression coefficients	**Standard deviation**	**t-student (10)**	**P-value**
Interception	85.91	4.216	20.373	< 0.05
Time	7.121	2.799	2.544	0.237
Time^2	-4.4522	2.728	-1.632	0.133
Temperature	-2.643	2.799	-0.944	< 0.05
Temperature ^{2}	-4.194	2.728	-1.537	0.155
GVL	1.312	2.799	0.468	0.649
GVL^2	-2.213	2.728	-0.811	0.436
Time × Temperature	2.004	3.655	0.548	0.595
Time × GVL	-4.546	3.655	-1.243	0.241
GVL × Temperature	-3.0970	3.6552	-0.847	0.416

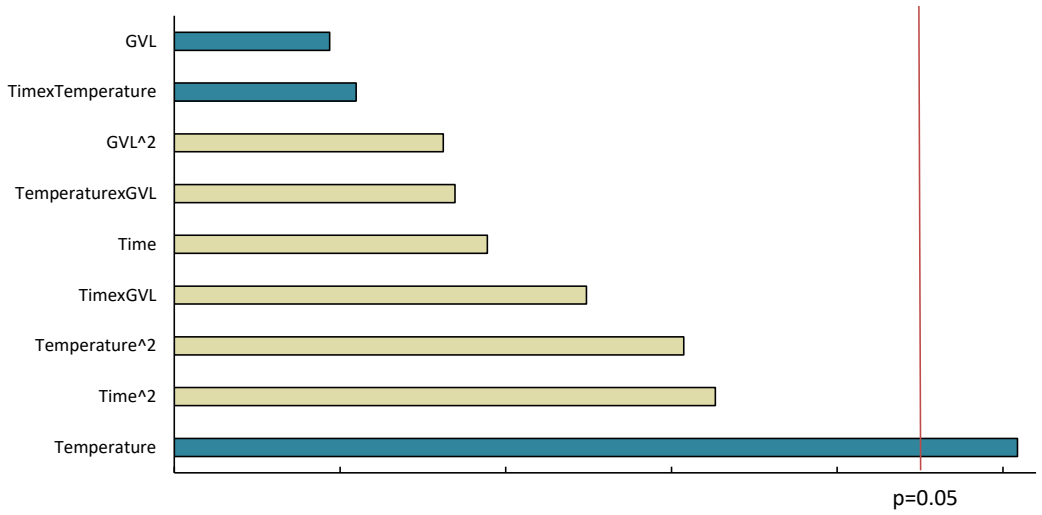

Figure S1. Pareto chart for the standardized main effects (positive ( ) and negative ( )) in the factorial planning for furfural yield optimization. Vertical line indicates the statistical significance of the effects.

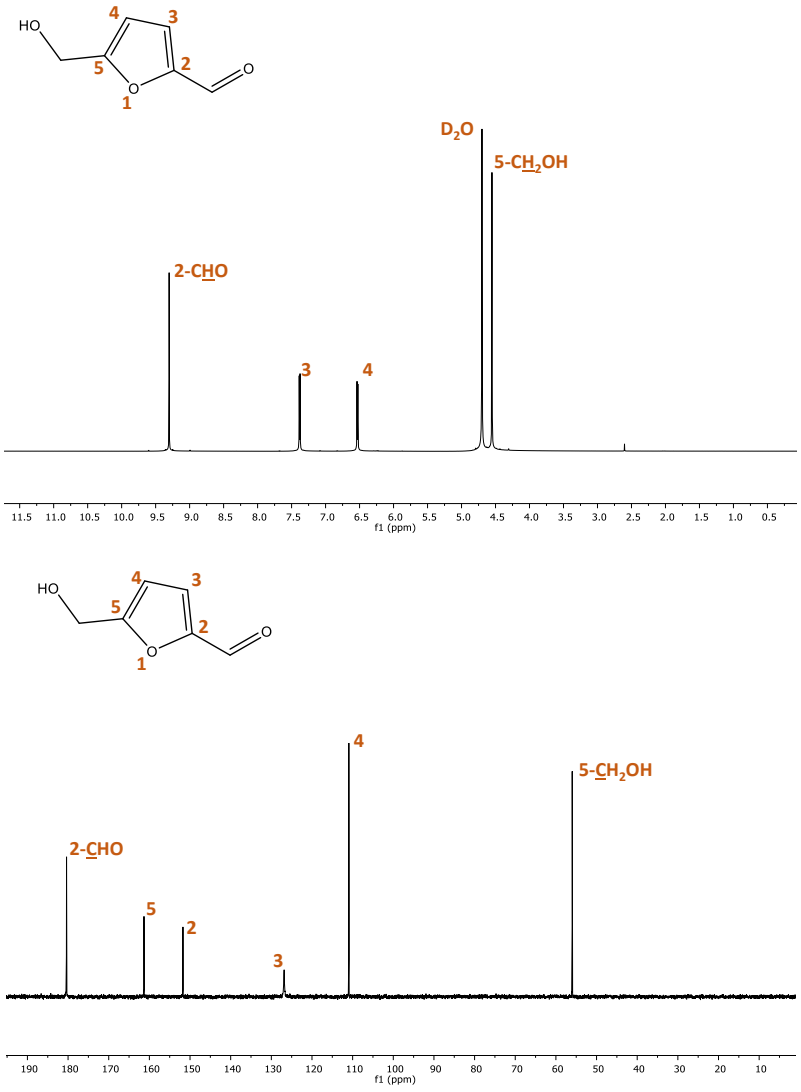

Figure S2. ^{1}H and ^{13}C NMR spectra of the recovered 5-HMF.

^{1}H NMR (D_2O, 300 MHz, [ppm]): δ 9.30 (d, 1H, 2-C<u>H</u>=O), 7.38 (d, 1H, H-3), 6.53 (dd, 1H, H-4), 4.55 (d, 2H, 5-C<u>H</u>$_2$OH). ^{13}C NMR (D_2O, 75.47 MHz, [ppm]): δ 180.38 (2-<u>C</u>H=O), 161.32 (C-5), 151.74 (C-2), 126.86 (C-3), 11.93 (C-4), 55.99 (5-<u>C</u>H$_2$OH).

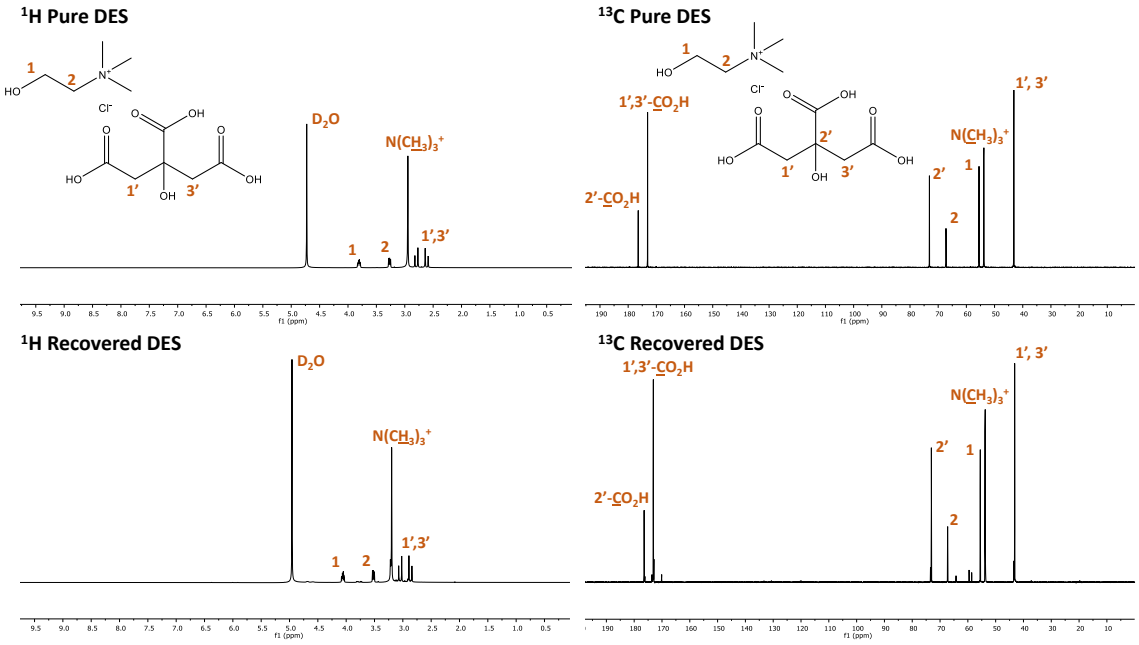

Figure S3. ^{1}H and ^{13}C NMR spectra of the pure and recovered [Ch]Cl:CA.