Electronic Supplementary Information (ESI)

Effective conversion of biomass into bromomethylfurfural, furfural, and depolymerized lignin in lithium bromide molten salt hydrate of a biphasic system

Chang Geun Yoo,^a Shuting Zhang^a and Xuejun Pan^{*a}

^a Department of Biological Systems Engineering, University of Wisconsin-Madison, Madison, WI 53706 USA

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Process optimization

Preliminary tests indicated that cellulose could be effectively converted into BMF in molten lithium bromide hydrate solution (LiBr·3H₂O), and reaction temperature, time, and hydrobromic acid (HBr, cocatalyst) loading were the primary reaction parameters affecting BMF yield. To maximize BMF yield, these variables were optimized through an experiment matrix of 20 runs (see Table S1), designed by response surface methodology (RSM). Based on our preliminary results, the three variables were optimized within the ranges of 0.00-0.30 mL HBr (0-0.26 M in aqueous phase), 30-210 min, and 90-150 °C. All experiments were conducted with 0.2 g cellulose, 10 mL LiBr 3H₂O solution, and 20 mL solvent (DCM), as described in the experimental section. The experimental results are presented in Figure 1. In summary, the results indicated that the acid co-catalyst (HBr) was critical, and no BMF (or very little) was formed without HBr loading. However, too much HBr resulted in low BMF yield, presumably because the acid catalyzed the degradation and condensation of BMF. Sufficient reaction time was necessary to ensure satisfactory BMF yield, but extending reaction increased the risk of BMF degradation and condensation. Similarly, increasing reaction temperature till 125 °C promoted BMF yield, but higher temperature had a negative effect on BMF yield. Through the RSM optimization, suggested optimal reaction conditions were 125 °C, 0.181 mL HBr loading (equivalent to 1.29 w/v% (0.16 M) of HBr in aqueous phase), and 126 min. The optimization results were fitted into a regression model (Equation S1 in supporting materials). Detail statistical analysis is presented in supporting material (see Table S2). Using the model, the predicted maximum BMF yield from cellulose was 94% (molar yield). Verification trials were run in triplicate under the suggested optimal reaction conditions, and the experimental BMF yield was 90.3% (average of the triplicate, Table S3).



Fig. S1 Experimental set-up for the biphasic system used in this study

Note. Left: Oil bath and stainless steel reactor; Right: Stainless steel reactor with Teflon liner (50 mL internal volume) and magnetic stirring bar.



Fig. S2 Images of the biphasic system after the conversion of biomass

Note. Upper layer: BMF and FF in organic phase (DCM); Bottom layer: Molten LiBr hydrate; Between layers: lignin.



Fig. S3 (a) ¹H and (b) ¹³C NMR spectra of BMF from cellulose with internal standard (pyrazine)



Fig. S4 2D ¹³C-¹H HSQC NMR spectra of furan-based products produced from biomass (corn stover) with internal standard (pyrazine)

Two-dimensional (2D) ${}^{13}C{}^{-1}H$ heteronuclear single quantum coherence (HSQC) pulse program (ns = 8, ds = 16, d1 = 1 s) was also conducted to identify and quantify the mixture of furan-based products from biomass (Fig. S2). Detailed peak assignments of BMF and furfural are below:

2D NMR peak assignments for BMF (500 MHz, CDCl₃): ¹H NMR (CDCl₃): δ = 4.46 (2 H), 6.55 (1 H), 7.16 (1 H), 9.59 (1 H) ppm; ¹³C NMR (CDCl₃): δ = 21.8, 112.3, 122.2, 153.0, 156.4, 177.9 ppm

2D NMR peak assignments for CMF (500 MHz, CDCl₃): ¹H NMR (CDCl₃): δ = 4.62 (2 H), 6.60 (1 H), 7.22 (1 H), 9.65 (1 H) ppm; ¹³C NMR (CDCl₃): δ = 36.1, 111.6, 122.1, 152.2, 155.3, 177.1 ppm

2D NMR peak assignments for furfural (500 MHz, CDCl₃): ¹H NMR (CDCl₃): δ = 6.63, 7.22, 7.73, 9.66 ppm; ¹³C NMR (CDCl₃): δ = 112.7, 121.8, 148.3, 153.1, 177.9 ppm



Fig. S5 (a) GC-MS chromatograms of BMF and CMF from cellulose in biphasic system with LiBr and (b) GC-MS spectra of HMF and CMF from cellulose in biphasic system with LiCl

Run	HBr loading*	Reaction time	Reaction temp.	BMF yield
#	mL	min	°C	Molar %
1	0.05	180	140	48.30
2	0.05	60	140	39.95
3	0.15	120	90	38.78
4	0.05	180	100	28.16
5	0.15	120	120	89.36
6	0.00	120	120	0.00
7	0.15	120	120	89.27
8	0.15	120	120	89.00
9	0.15	120	150	76.77
10	0.25	60	100	23.75
11	0.30	120	120	80.00
12	0.15	120	120	88.35
13	0.25	60	140	73.17
14	0.5	60	100	4.47
15	0.25	180	140	55.73
16	0.15	210	120	65.29
17	0.15	30	120	14.44
18	0.15	120	120	89.01
19	0.15	120	120	88.99
20	0.25	180	100	70.47

Table S1 Experimental design using RSM and results for BMF production from cellulose

* HBr concentration was 48%.

Through the optimization, the predicted BMF yield as a function of HBr loading, reaction temperature, and reaction time is given below (**Equation S1**):

BMF yield = $-650.68 + 734.30 \times$ HBr loading + 2.42 × Reaction time + 7.97 × Reaction temp. - 8.28E-3 × Reaction time × Reaction temp. -1855.04 × HBr loading² - 5.17E-3 × Reaction time² - 0.027 × Reaction temp.² [S1]

The statistical significance of the model equation was evaluated by the F-test for ANOVA (Table S3). The model F-value of 19.39 implies that the model is significant. Very small p-value (p<0.0001) also indicates the significance of the model. In this model, single terms including A, B, and C, interaction term BC, and quadric terms (A^2 , B^2 , and C^2) are significant terms (less than 0.05 of "Prob>F").

Source	Sum of Squares	df	Mean Square F-Value p-value (F		p-value (Prob > F)	
Model	16559.36	7	2365.63	19.39	< 0.0001	Significant
A-HBr loading	3295.38	1	3295.38	27.02	0.0002	
B-Reaction time	1514.59	1	1514.59	12.42	0.0042	
C-Reaction temp.	1735.43	1	1735.43	14.23	0.0027	
BC	790.03	1	790.03	6.48	0.0257	
A^2	3546.41	1	3546.41	29.07	0.0002	
B^2	3569.39	1	3569.39	29.26	0.0002	
C^2	1169.00	1	1169.00	9.58	0.0093	
Residual	1463.72	12	121.98			
Total	18023.08	19				

Table S2 Analysis of Variance (ANOVA) for BMF production from cellulose

The predicted maximum product yield and suggested reaction conditions from the model were as follows: 94.2% of BMF yield at 0.181 mL of HBr loading, 125°C of reaction temperature, and 126 min of reaction time. Confirmation runs were also conducted under the suggested optimum conditions (Table S3).

Table S3 BMF	yields	from	cellulose	under	optimum	conditions
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Run #	BMF yield ^a (%)
1	88.91
2	93.17
3	88.84

^aBMF yield is molar %.



Fig. S6 Optimization of the conversion of cellulose to BMF in molten lithium bromide hydrate – $LiBr\cdot 3H_2O$ (BMF yield, molar % based on starting glucose in cellulose; reaction temperature, °C; reaction time, min; and HBr loading, mL).

Species	Glucan [wt %]	Xylan [wt %]	Galactan [wt %]	Arabinan [wt %]	Mannan [wt %]	Lignin [wt %]	Ash [wt %]
Corn stover	36.5±0.21	22.6±0.07	0.7±0.03	2.1 ± 0.01	0.0 ± 0.00	19.9±0.13	5.0±0.11
Switchgrass	33.5 ± 0.14	17.5 ± 0.05	1.1 ± 0.04	$2.6 {\pm} 0.07$	$0.0 \!\pm\! 0.00$	21.9 ± 0.17	4.2 ± 0.21
Poplar	43.5 ± 0.15	13.4 ± 0.04	0.5 ± 0.02	0.3 ± 0.02	2.3 ± 0.05	19.4 ± 0.08	0.7 ± 0.03
Aspen	43.5 ± 0.45	13.8 ± 0.02	0.6 ± 0.00	0.4 ± 0.02	1.3 ± 0.02	27.8 ± 0.09	0.8 ± 0.04
Douglas Fir	40.7 ± 0.17	5.2 ± 0.02	7.5 ± 0.09	2.0 ± 0.03	8.1 ± 0.24	28.9 ± 0.19	0.4 ± 0.02

Table S4 Chemical composition of different biomass

Note: % is based on dry biomass; The analysis was conducted according to the NREL procedure.¹

Table S5 Chemical composition of residual solids collected between two phases after reaction

Carl strate	Carbohydrates	Lignin	Ash
Substrate	[wt %]	[wt %]	[wt %]
Residual solid from poplar	ND	98.4	0.2
Residual solid from switchgrass	0.1	97.8	1.7
Residual solid from Douglas fir	ND	98.5	0.3

Note: ND – not detected; The analysis was conducted according to the NREL procedure.¹

References

1. A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, NREL/TP-510-42618, 2011.