Electronic Supporting Information

Unlocking biomass energy: continuous high-yield production of 5-hydroxymethylfurfural in water

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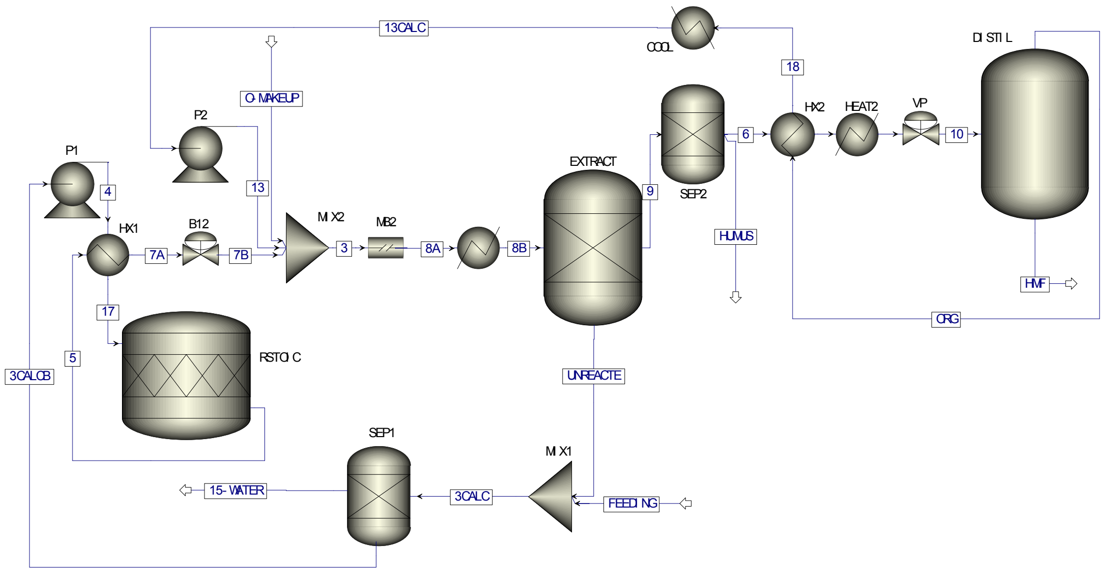

Figure S1. Process flow diagram generated by using Aspen Plus Process Simulator for HMF production with fructose or glucose as feedstock.

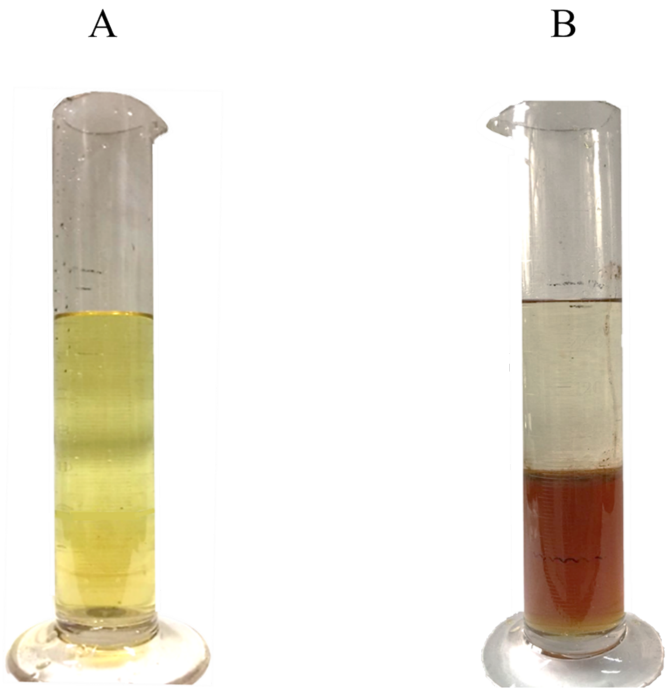

Figure S2. Aqueous and organic phases of H_2O/EAC system after reaction. (A) without addition of NaCl in the aqueous phase; (B) with saturated NaCl solution in the aqueous phase.

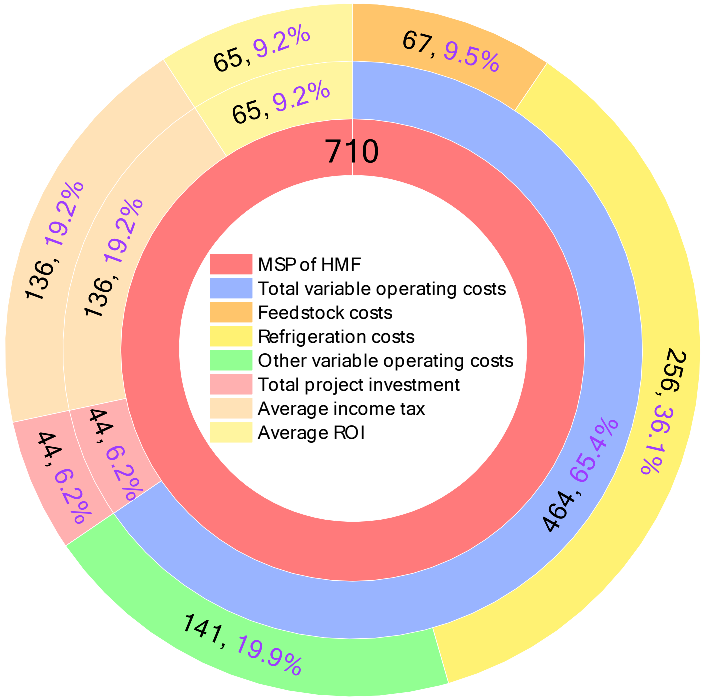

Figure S3. Techno-economic analysis for the production of HMF from glucose. The flow rate of MIBK was 10 mL/min. The black font represents the costs of the components, unit is $/ton. The purple font represents relative contribution of the components of the HMF's MSP. ROI, return on investment.

Table S1. Process operating data (data of feedstock dehydration at high temperature per pass).

	Fructose feedstock	Glucose feedstock
Parameters		
Conversion (mol%)	40.0	32.6
Selectivity (mol%)	87.5	40.2
Organic phase	2-MeTHF	MIBK
The flow rate of organic phase (mL/min)	10	20
Temperature (°C)	150	140

Table S2. Energy requirements for the HMF production (with the use of heat exchanger).

	Energy required		
Fructose feedstock	Heating, kW	Refrigerating, kW	Electricity, kW
Fructose to HMF reactor unit	446	/	/
The circulated aqueous phase system	1445	/	30.6
The circulated organic phase system	12104	-13115	4.7
Total, fructose to HMF	13995	-13115	36
Glucose feedstock			
Glucose to HMF reactor unit	568	/	/
The circulated aqueous phase system	7061	/	39.5
The circulated organic phase system	21911	-23612	9.2
Total, glucose to HMF	29540	-23612	49

Table S3. Project investment and operating costs.

	Fructose feedstock	Glucose feedstock
Process section	*Units (MM$)*	
HMF Production system	5.910	7.520
OSBL[a]	2.370	3.010
Total project investment [b]	8.280	10.530
Raw material		
Feedstock	7.240	0.703
Refrigeration	2.980	5.362
Solvent makeup	0.680	0.286
Steam	1.110	2.294
Catalyst	~0	~0
Cooling water	~0	~0
Electricity	0.061	0.023
Wastewater disposal	0.003	0.006
Total variable operating costs	12.074	8.674
HMF production		
Production (ton/yr)	10128	10560
Purity (wt%) & recovery (%)	98.6 & >99.9	98.0 & >99.9

[a] OSBL (outside battery limits of the plant) includes infrastructure costs for waste disposal, on-site storage, and utilities.

[b] the total project investment including the total installed cost.

The minimum selling price of HMF is obtained as follows[S1, S2]:

HMF sales = Total variable operating costs + Total project investment/20 + Average income tax + Average ROI (1)

Fructose feeding HMF sales ($/ton HMF) = 12074000/10128 + 8280000/10128/20 + (1192 + 41) × 0.21 / (1 - 0.21) + (1192 + 41 + 328) × 0.10

= 1192 + 41 + 328 + 156

= 1716

Glucose feeding HMF sales ($/ton HMF) = 8674000/10560 + 10530000/10560/20 + (822 + 50) × 0.21/ (1 - 0.21) + (822 + 50 + 232) × 0.10

= 822 + 50 + 232 + 111

= 1215

Table S4. List of economic parameters and assumptions for the HMF production (with the use of heat exchanger).

Fructose price ($/ton)	450 [a]
Glucose price ($/ton)	300 [a]
HCl price ($/ton)	17 [b]
$AlCl_3 \cdot 6H_2O$ price ($/ton)	186 [a]
MIBK price ($/ton)	1000 [a]
2-MeTHF price ($/ton)	5000 [a]
Wastewater treatment cost ($/ton)	0.570 [c]
Low pressure steam cost ($/ton)	6.737 [c]
-29°C refrigerant ($/ton)	1.300 [c]
Electricity price ($/kWh)	0.0572 [c]
Cooling water ($/ton)	9.85×10^{-3} [c]
Operating mode	Continuous
Plant life (years)	20 [d]
Plant operating hours per year (hours)	8000 [d]
Discount rate (%)	10 [d]
General plant recovery period (years)	7 [d]
Corporate income rate (%)	21 [d]
Equity financing (%)	40 [d]
Loan terms	10-years loan at 8% APR [d]
Working capital	5% of fixed capital investment [d]
Length of start-up period (weeks)	20 [d]
Revenues during start-up (%)	50 [d]
Fixed costs during start-up (%)	100 [d]

[a] The price standards used refer to China's chemical market price level in 2018.

[b] Taken from refence prices by *P. Desir et al.*[S3]

[c] Taken from refence prices by *A. H. Motagamwala et al*. [S4]

[d] Data were taken from a study by NREL. [S5]

Table S5. Results of HMF extraction ratio in biphasic system. Conditions: 0.5 g HMF; aqueous phase: 4 g H_2O, 1 g DMSO, 5mg HCl; 5 ml MIBK; T = 25°C; t = 1 h, triplicate.

Entry	HMF_{aq} (g/ml)	HMF_{org} (g/ml)	R	Average of R
1	0.052	0.048	0.90	
2	0.049	0.051	1.04	0.97
3	0.050	0.049	0.98	

Table S6. Space-time yields for different extraction models. Reaction condition: 5 wt% fructose, 28 mM HCl, 150°C, t = 210 min, 60 g aqueous phase (H_2O/DMSO = 8/2, w/w) and 80 g MIBK were added to the extraction device, the rates of aqueous and cyclic continuous flow of organic phase were set at a flow rate of 7 and 10 mL/min, respectively.

Extraction models	Fructose conversion (mol %)	HMF selectivity (mol %)	HMF yield (mol %)	Space-time yield [g/g(cat)/min]
Static extraction	91.5	42.8	39.1	6.5×10^{-2}
Intermittent replacement extraction	95.8	65.3	62.5	1.0×10^{-1}
Cyclic continuous extraction	90.7	83.4	75.6	1.3×10^{-1}

Table S7. Results of dehydration of fructose in H_2O/MIBK circulating system. Reaction condition: 5 wt% fructose catalyzed by different kinds of acids; T = 150°C; the flow rate of aqueous phase and organic phase were 7 and 20 mL/min, respectively.

Entry	Catalyst	Conversion (mol%)	Selectivity (mol%)	Yield (mol%)	t (min)
1	28 mM HCl	99.3	87.9	87.3	360
2	28 mM H_2SO_4	64.5	56.7	36.6	300
3	28 mM H_3PO_4	47.2	77.8	36.7	300

Table S8. Rate constants (*k*) of acid-catalyzed dehydration of fructose in H_2O/MIBK circulating system were calculated by Berkeley Madonna software.

Parameters		k (min^{-1})
HCl dosage (mM)	0	0.00090
	14	0.00417
	28	0.01211
	42	0.01737
Temperature (°C)	140	0.00771
	150	0.01311
	160	0.03701
	170	0.11125

Table S9. Results of acid-catalyzed dehydration of fructose in H_2O/EAC circulating system. Reaction condition: 5 wt% fructose; 28 mM HCl; T = 150°C; the flow rate of aqueous phase and organic phase were 7 and 20 mL/min, respectively.

t (min)	Conversion (mol%)	Selectivity (mol%)	Yield (mol%)
60	62.4	84.9	53.0
120	87.8	92.9	81.6

Table S10. Comparison with other reaction systems.

Type	Feedstock	Solvent	Catalyst	T (°C)	Yield (mol%)	Ref.
Biphasic circulating system	5 wt% fructose	H_2O/2-MeTHF	28 mM HCl	150	94.3	This work
Stirred tank	30 wt% fructose	H_2O/MIBK	250 mM HCl	180	54.6	28 (S6)
Continuous reactor	2 wt% fructose	(4:1 w/w) THF/H_2O	500 mg λ-Al_2O_3-SO_3H	90	69.4	27 (S7)
Biphasic continuous flow	10 wt% fructose	H_2O/MIBK	250 mM HCl	140	75.0	22 (S8)
Biphasic circulating system	5 wt% glucose	H_2O/MIBK	70 mM $AlCl_3 \cdot 6H_2O$ and 22 mM HCl	140	69.6	This work
Biphasic slug flow capillary microreactor	2 wt% glucose	H_2O/MIBK	40 mM $AlCl_3 \cdot 6H_2O$ and 40 mM HCl	160	53.0	36 (S9)

Supplemental references

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