

Supplementary Material (ESI) for Green Chemistry  
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**Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-  
derived mono- and poly- saccharides**

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## Supplementary Online Material

### Energy Efficiency Analysis

Basis: We process 30 kg/hr of fructose as feedstock to make 5-hydroxymethylfurfural (HMF) as a 30 wt% feed solution using the following three processing scenarios:

1. 30 wt% fructose solution is reacted in a biphasic reactor system using 5:5 (w/w) W:DMSO as aqueous layer and twice the amount (by mass) of 7:3 (w/w) MIBK:2-butanol as extracting solvent at 443 K. We assume the reaction achieves 90% selectivity at 100% conversion. The organic layer which contains the HMF and 5 wt% DMSO carry-over from the aqueous phase is available for HMF separation (Stream 1, Table S1).
2. 30 wt% fructose solution is reacted in a biphasic reactor with 3:7 (w/w) W:DMSO as aqueous layer and equal amounts (by mass) of dichloromethane (DCM) as an extracting solvent at 413 K. We assume the reaction achieves 78% selectivity at 100% conversion. The organic layer, which contains the HMF and 20 wt% DMSO carry-over from the aqueous phase is available for HMF separation (Stream 2, Table S1).
3. 30 wt% fructose solution is reacted in pure DMSO solvent at 363 K.<sup>1</sup> We assume the reaction achieves 90% selectivity at 100% conversion, leading to a reaction mixture stream with DMSO as a solvent for HMF separation (Stream 3, Table S1).

**Table S1.** Composition and condition of the streams from the reactor outlet along with normal boiling points of various components.

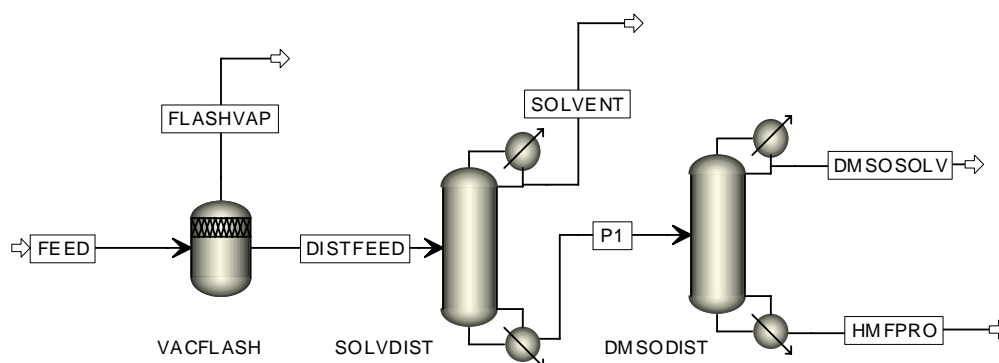
<b>Components / mass flow (kg/hr)</b>	<b>Stream 1</b>	<b>Stream 2</b>	<b>Stream 3</b>	<b>Normal Boiling Point (K)</b>
HMF	14.2	11.7	19	523+
DMSO	10.5	20	70	463
MIBK	140	-	-	390
2-Butanol	60		-	372.5
DCM	-	100	-	312.8
Water	-	-	11	373
<b>Total (kg/hr)</b>	224.7	131.7	100	
<b>Temperature K</b>	443	413	363	
<b>Pressure (atm)</b>	10	12.5	1	

To separate HMF in pure form the solvent must be evaporated or distilled. Because HMF in its pure state is unstable at high temperatures,<sup>2</sup> above 423 K, it sets a constraint on the operating temperature of the reboiler at the bottom of the distillation column. This limitation necessitates vacuum operation to isolate the product from the solvent.<sup>3-5</sup>

A separation scheme for the first and second stream is presented in Figure S1. For the first case (Stream 1), the strategy is first to evaporate as much as possible of the relatively volatile solvent (7:3 MIBK-2-butanol) using a flash drum under adiabatic conditions and a vacuum of 10 Torr created by condensing vapors. The liquid stream containing HMF is subsequently fed to a distillation column at 10 Torr to remove the remaining fraction of the volatile solvent. Finally the DMSO-HMF rich stream from the bottom of this column is fed to a second distillation column to obtain pure HMF product. The distillation operation can also be performed in a single column to separate DMSO and volatile solvent, but it requires a condenser temperature of 253 K to condense the low

fractions of volatile solvent, thereby requiring additional refrigeration system cost. Thus, the net energy required (summation of flash heat duty and reboiler duties) per kg of HMF produced is found to be 394 kcal/kg (Table S2).

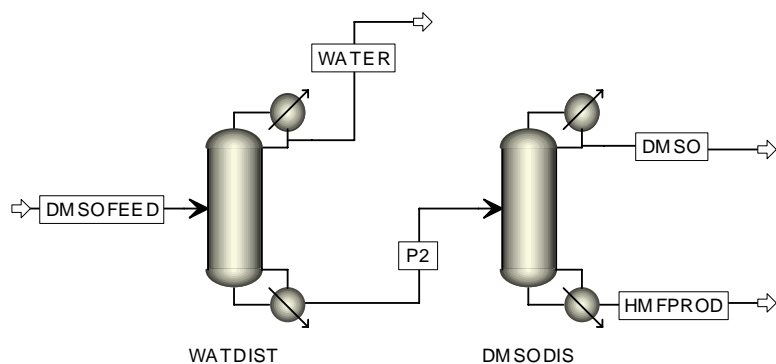
A similar strategy is adopted for separation of an organic layer having DCM as a solvent (Stream 2). However, because DCM is very volatile, the flash drum and first column are operated at a higher vacuum pressure (175 Torr) to maintain the condenser temperature within the limit of 277 to 313 K. The DMSO-rich stream is then separated in the final column to obtain the energy requirement of 608 kcal/kg of HMF produced (Table S3).



**Figure S1.** Separation scheme for organic stream from biphasic reactor system (Stream 1 and 2) using 7:3 MIBK-2-butanol and DCM as extracting solvents.

Figure S2 shows the separation system for the 3<sup>rd</sup> process using pure DMSO as a solvent. The flash drum, as used in earlier cases, serves no useful purpose because it leads to loss of product due to the narrow difference in relative volatility between DMSO and HMF. Thus the required separation can be performed using 2 distillation columns to remove the water and subsequently DMSO to obtain the pure HMF product. The energy requirement with this arrangement lead to 880 kcal/kg of HMF produced (Table S4). Thus, it can be seen that our process with 7:3 MIBK-2-butanol and DCM achieves 55%

and 30% higher energy efficiencies, respectively, when compared to the conventional case of producing HMF in DMSO.



**Figure S2.** Separation scheme using pure DMSO as reaction solvent (Stream 3).

### References

- 1 H. H. Szmant and D. D. Chundury, *J. Chem. Technol. and Biotechnol.* 1981, **31**, 135.
- 2 D. W. Brown, R. G. Kinsman and Y. Roshan-Ali, *J. Chem. Technol. Biotechnol.* 1982, **32**, 920.
- 3 R. E. Jones, H. B. Lange, *US Pat.*, 2,994,645 1958.
- 4 R. H. Hunter, *US Pat.*, 3,201,331 1965.
- 5 J. Harris, J. Saeman, L. Zoch, *Forest Products Journal* 1960, **10**, 125.

**Table S2:** Composition, conditions and heat duty of various operating units for producing pure HMF using 7:3 (w/w) MIBK:2-butanol as extracting solvent.

Component mass flow (kg/hr)	Reactor Output (kg/hr)	Adiabatic Flash			Solvent Distillation			DMSO Distillation		
		Feed	Vapor	Liquid	Feed	Distillate	Bottoms	Feed	Distillate	Bottoms
HMF	14.2	14.2	0.0	14.2	14.2	0.0	14.2	14.2	0.0	14.2
DMSO	10.5	10.5	2.9	7.6	7.6	1.0	6.6	6.6	6.6	0.0
2-Butanol	60	60.0	47.8	12.2	12.2	12.0	0.2	0.2	0.2	0.0
MIBK	140	140.0	124.8	15.2	15.2	15.2	0.0	0.0	0.0	0.0
Total (kg/hr)	224.7	224.7	175.5	49.2	49.2	28.2	21.0	21.0	6.8	14.2
Temperature K	443	443	299	299	299	285	360	360	298	400
Pressure (Torr)	7600	7600	10	10	10	10	10	10	1	1
Heat Duty (kcal/hr)		<b>0</b>			<b>4389</b>			<b>1211</b>		

Net Heat Duty = 5600 kcal/hr, HMF yield = 14.2 kg/hr, Energy required per kg of product = 394 kcal/kg.

**Table S3:** Composition, conditions and heat duty of various operating units for producing pure HMF using DCM as extracting solvent.

Component mass flow (kg/hr)	Reactor Output (kg/hr)	Adiabatic Flash			Solvent Distillation			DMSO Distillation		
		Feed	Vapor	Liquid	Feed	Distillate	Bottoms	Feed	Distillate	Bottoms
HMF	11.7	11.7	0.0	11.7	11.7	0.0	11.7	11.7	0.0	11.7
DMSO	20	20.0	0.1	19.9	19.9	0.7	19.2	19.2	19.2	0.0
DCM	100	100.0	64.8	35.2	35.2	35.2	0.0	0.0	0.0	0.0
Total (kg/hr)	131.7	131.7	64.9	66.8	66.8	35.9	30.9	30.9	19.2	11.7
Temperature K	413	413	295	295	295	277	424	424	305	397
Pressure (Torr)	9500	9500	175	175	175	175	175	175	1	1
Heat Duty (kcal/hr)		<b>0</b>			<b>5151</b>			<b>1967</b>		

Net Heat Duty = 7118 kcal/hr, HMF yield = 11.7 kg/hr, Energy required per kg of product = 608 kcal/kg.

**Table S4:** Composition, conditions and heat duty of various operating units for producing pure HMF using DMSO as reaction solvent.

Component mass flow (kg/hr)	Reactor Output (kg/hr)	Water Distillation			DMSO Distillation		
		Feed	Distillate	Bottoms	Feed	Distillate	Bottoms
HMF	19	19	0.0	19.0	19.0	0.0	19.0
Water	11	11	10.8	0.2	0.2	0.2	0.0
DMSO	70	70	9.2	60.8	60.8	60.8	0.0
Total (kg/hr)	100	100.0	20.0	80.0	80.0	61.0	19.0
Temperature K	363	363	307	370	370	304	402
Pressure (Torr)	760	760	30	30	30	1	1
Heat Duty (kcal/hr)		<b>8156</b>			<b>8559</b>		

Net Heat Duty = 16715 kcal/hr, HMF yield = 19 kg/hr, Energy required per kg of product = 880 kcal/kg.