5-hydroxymethylfurfural (HMF) synthesis in a deep eutectic solvent-based biphasic system: closing the loop of solvent reuse, product isolation and green metrics

Nico Thanheuser[a], Leonie Schlichter[a], Walter Leitner[a,d] , Jesús Esteban[b,c], Andreas J. Vorholt[a*]*

[a] *Max-Planck-Institute for Chemical Energy Conversion, Stiftstraße 34, 45470 Mülheim an der Ruhr, Germany*

[b] *Department of Chemical Engineering and Materials, Faculty of Chemical Sciences, Complutense University of Madrid. Avda. Complutense s/n, Madrid 28040, Spain*

[c] *Department of Chemical Engineering, School of Engineering, The University of Manchester, Manchester M13 9PL, United Kingdom*

[d] *Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany*

Supporting Information

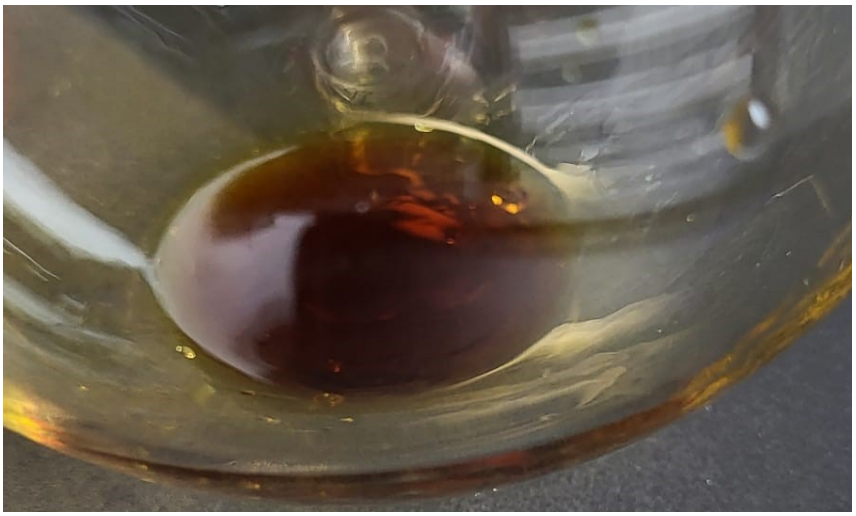

Figure S1. Bottom product containing HMF after MeCN separation with a rotary evaporator

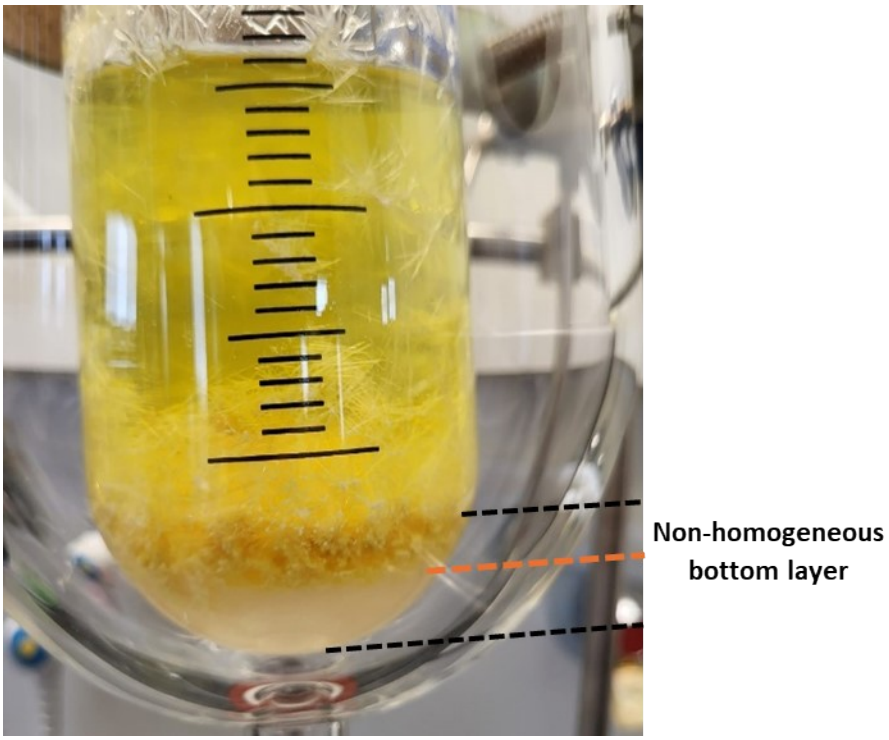

Figure S2. Formation of multiple phases instead of two phases due to insufficient mixing for the dehydration of Fru to HMF. Reaction Conditions: 18 g ChCl, 4,5 g Fru, ChCl:Fru (5:1), $V_{solvent}$= 150 mL, T= 80 °C, t= 15 min, ω= 400 rpm, $c_{H_4SiW_{12}O_{40}}$= 0.87 $mol\%_{Fru}$

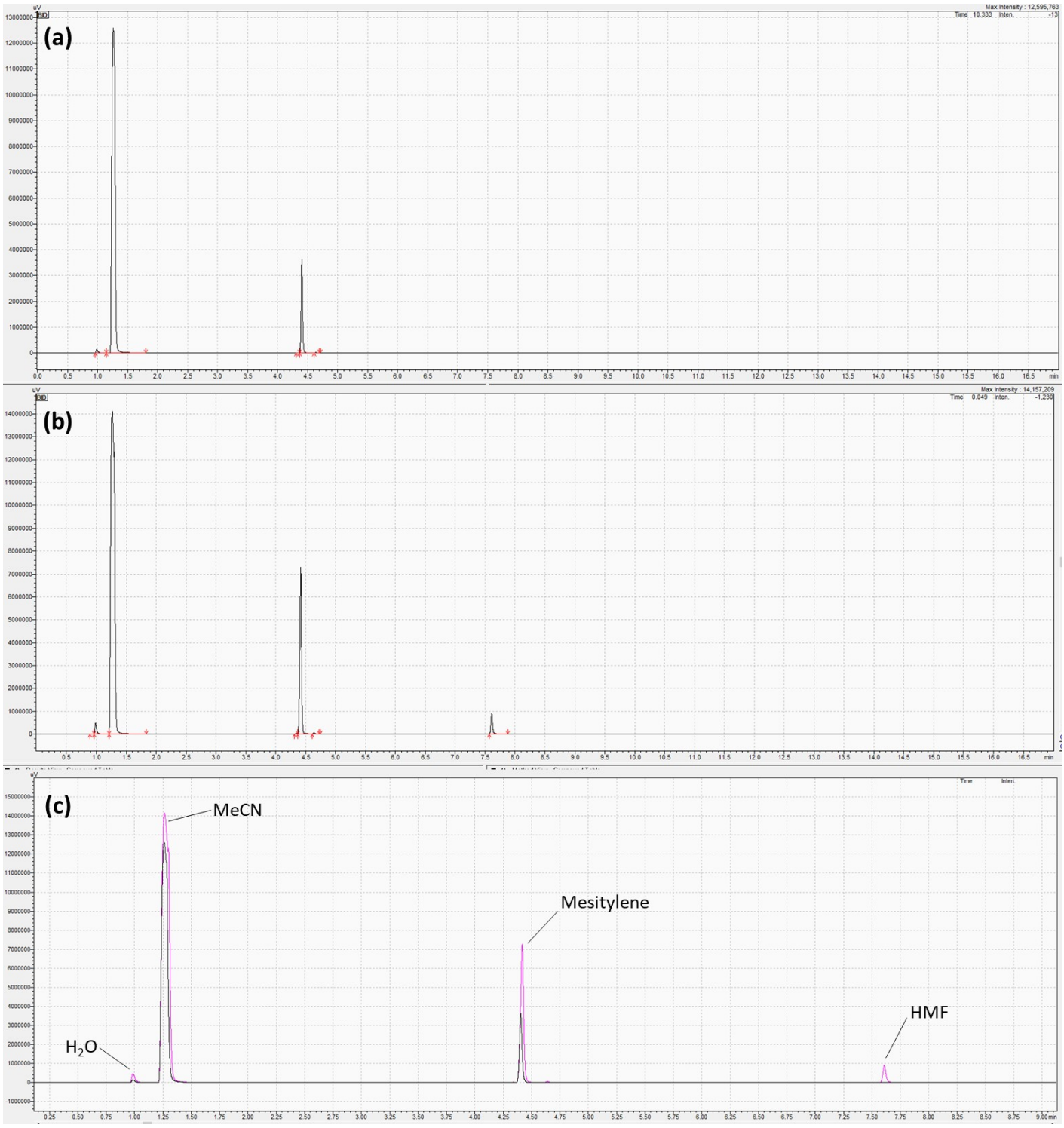

Figure S3. GC-BID chromatograms for 2 typical reaction mixtures for the dehydration of Fru to HMF a) t = 55 s, b) t = 571 s c) stacked and zoomed a) and b) and assigned peaks. Mesitylene was used as internal standard. Reaction Conditions: 18 g ChCl, 4,5 g Fru, ChCl:Fru (5:1), $V_{solvent}$= 150 mL, T= 80 °C, t= 15 min, ω= 400 rpm, $c_{H_4SiW_{12}O_{40}}$= 0.87 $mol\%_{Fru}$

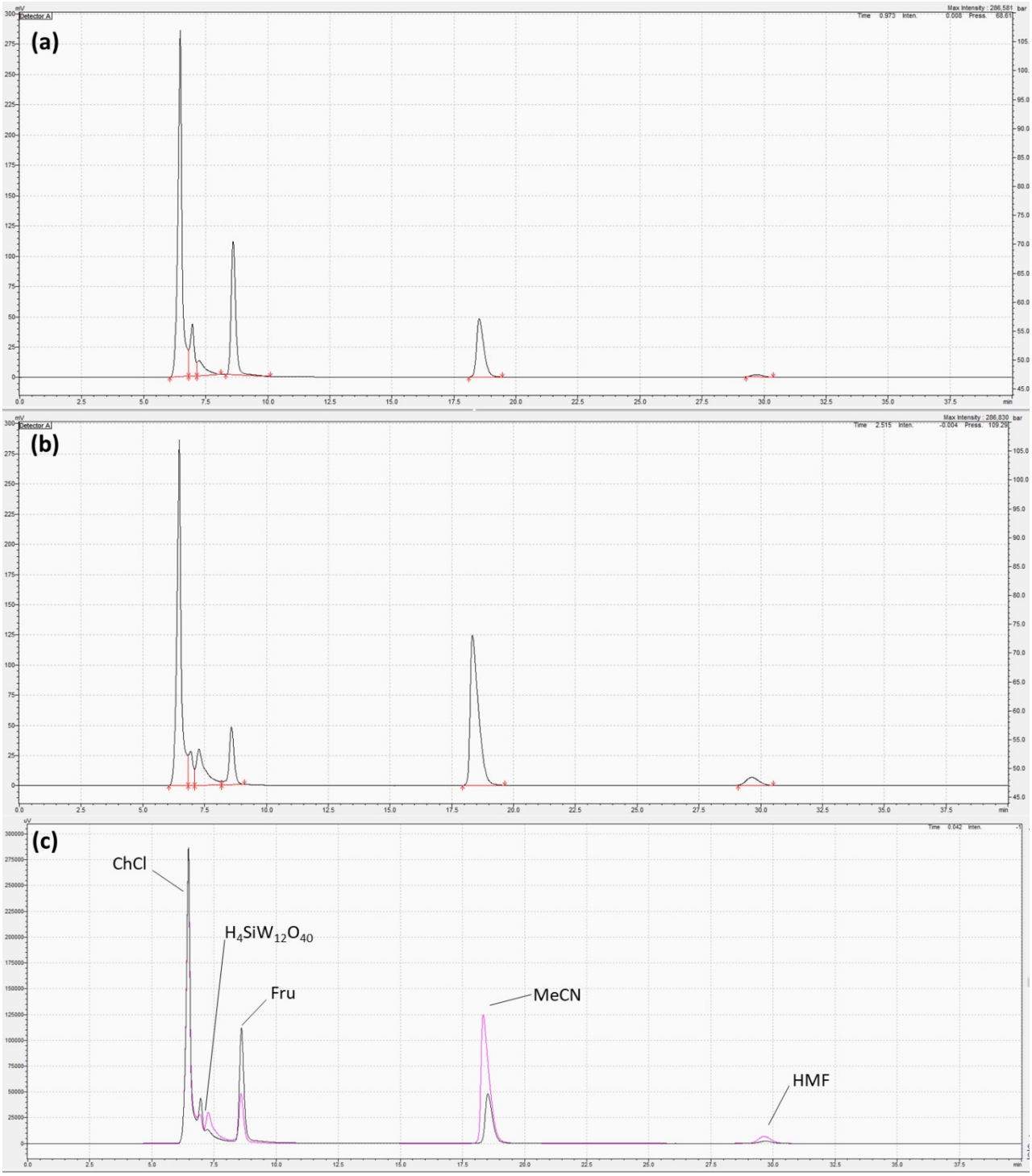

Figure S4. HPLC chromatograms for 2 typical reaction mixtures for the dehydration of Fru to HMF a) t = 55 s, b) t = 571 s c) stacked and zoomed a) and b) and assigned peaks. Reaction Conditions: 18 g ChCl, 4,5 g Fru, ChCl:Fru (5:1), $V_{solvent}$= 150 mL, T= 80 °C, t= 15 min, ω= 400 rpm, $c_{H_4SiW_{12}O_{40}}$= 0.87 $mol\%_{Fru}$

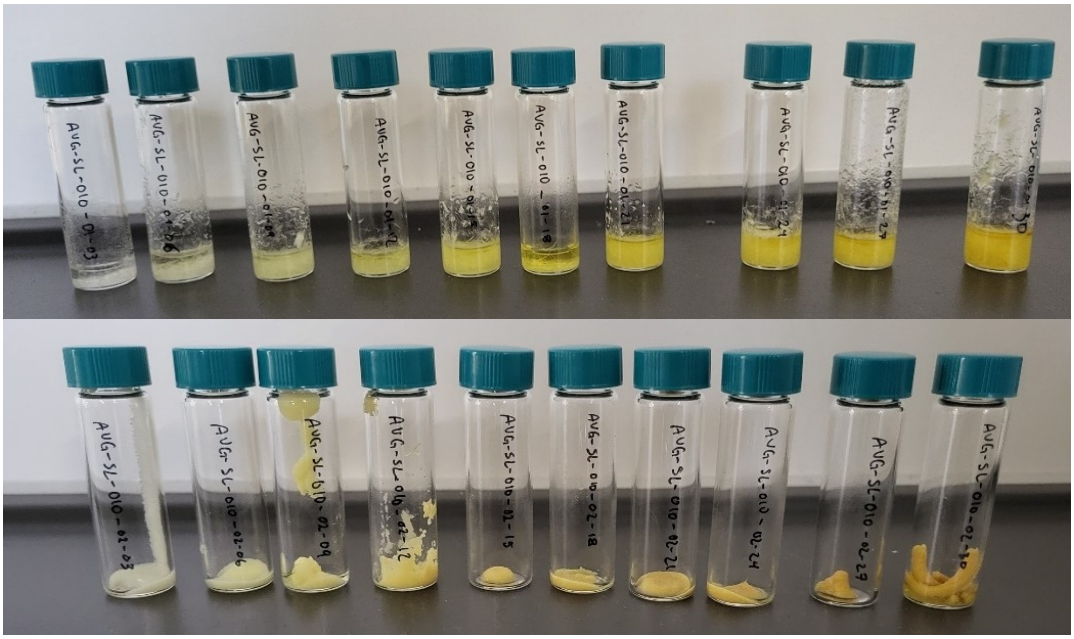

Figure S5. Samples of the extraction phase (top) and reaction phase (bottom) after: 3, 6, 9, 12, 15, 18, 21, 24, 27, 30 min. Reaction Conditions: 18 g ChCl, 4,5 g Fru, ChCl:Fru (5:1), $V_{solvent}$= 150 mL, T= 80 °C, t= 15 min, ω= 400 rpm, $c_{H_4SiW_{12}O_{40}}$= 0.87 mol%$_{Fru}$

Table S1. Formulae and definitions for the calculations of green metrics

E-factor: $E = \frac{Total\ mass\ of\ waste}{Mass\ of\ product}$	(S1)
Process mass intensity: $PMI = \frac{Total\ mass\ in\ process\ (incl.\ H_2O)}{Mass\ of\ product}$	(S2)
Solvent intensity: $SI = \frac{Mass\ of\ solvents}{Mass\ of\ product}$	(S3)
Reaction mass efficiency: $RME\% = \frac{Mass\ of\ product}{Total\ mass\ of\ reactants}100$	(S4)
Mass Productivity: $MP\% = \frac{Mass\ of\ product}{Total\ mass\ of\ reactants\ (incl.\ solvents)}100$	(S5)

Table S2. Values used to calculate the green metrics in Table 1

Case	RP	EP	Σm (RP) [g]	Σm (EP) [g]	Σm (Fru) [g]	Catalyst	Σm Catalyst [g]	Σ Yield HMF [g]	Ref
1.1	[Bmim][Cl] WCl6	THF	0.50	177.80	0.5	WCl_6	0.0110	0.2660	[40]
1.2	[Bmim][Cl] WCl6	THF	100.00	4445.00	70	WCl_6	2.2000	26.700	[40]
2	TEAC : fructose (1 : 0.92)[a d]	THF	2.00	71.10	5	$NaHSO_4 \bullet H_2O$	0.0766	1.7709	[41]
3	ChCl : fructose (1 : 0.2)[a]	MeCN	3.60	141.48	5.4	HCl	0.0354	3.2318	[15]
4	ChCl : citric acid (1 : 2.33)[a]	EtOAc	2.00	20	0.02	Citric Acid	0.7400	0.0129	[42]
5	ChCl : fructose (5 : 1)[a b]	MeCN	18.00	117.9	4.5	$H_4SiW_{12}O_{40}$	0.6230	2.4000	
6	ChCl : fructose (5 : 1)[a b c]	MeCN	18.00	117.9	22.5	$H_4SiW_{12}O_{40}$	0.6230	8.2000	

[a] for DESs. the ratio in brackets corresponds to the molar ratio of HBA : HBD.

[b] this work

[c] this work with recycled extraction phase according to Figure 6 (only considering HMF in the extraction Phase)

[d] 5 g H-Y Zeolite were added at the beginning of the reaction.

Table S3. Recovered volume of extraction phase from the reactor and volume of MeCN after the distillation step.

Recycling Run	V before distillation [mL]	V after distillation [mL]	loss [%]
0	139	135	2.9%
1	140	136	2.9%
2	138	133	3.6%
3	139	134	3.6%
4	140	137	2.1%
5	138	136	1.4%