

Supplementary Information for:

Production and upgrading of 5-hydroxymethylfurfural using heterogeneous catalysts and biomass-derived solvents

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1. Experimental

1.1 Catalysts

Sn-SBA-15 with molar ratio Si:Sn of 40 was synthesized as described elsewhere.¹ Amb-70 was obtained from The Dow Chemical Company. Sn- β with molar ratio Si:Sn of 400 was provided by Haldor Topsøe A/S, Denmark. Hydrotalcite was purchased from Aldrich.

1.2 Biphasic reactors using γ -lactones as extracting layer and homogeneous catalysts

Biphasic dehydration reactions were carried out in 10 mL thick-walled glass reactors heated in an oil bath at 170 °C. Preparation of the aqueous layer consisted of using solutions containing 5 mmol L⁻¹ AlCl₃ and adjusting their pH to 2.5 with HCl. The pH-adjusted solutions were saturated with NaCl, and monosaccharide was added to obtain a 5 wt% aqueous feed. In a typical experiment, 1.5 g of the aqueous feed and 3.0 g of γ -lactone were added to the reactor. The reactor was placed in the oil bath at 170 °C and stirred at 1000 rpm. Reactors were removed from the oil bath at specific reaction times and cooled in an ice-water bath. Aqueous layers were directly titrated with a 0.01 mol L⁻¹ sodium hydroxide solution using phenolphthalein as indicator. Organic layers were contacted with water to extract the HCl before titration.

1.3 Monophasic reactors using γ -lactones or tetrahydrofuran with 10 wt% water and homogeneous catalysts

In 10 mL thick-walled glass reactors, 0.294 g of a 25 mmol L⁻¹ AlCl₃ aqueous solution with pH adjusted to 1.8 with HCl, 1.176 g of organic solvents and 0.03 g of monosaccharide was added to the reactor. The final concentrations were 2 wt% of monosaccharide, 5 mmol L⁻¹ of AlCl₃ and 3.17 mmol L⁻¹ of HCl. The reactor was placed in an oil bath at 170 °C and stirred at 700 rpm.

Reactors were removed from the oil bath at specific reaction times and cooled in an ice-water bath.

1.4 Monophasic reactors using γ -lactones or tetrahydrofurans with 10 wt% water and heterogeneous catalysts

In 10 mL thick-walled glass reactors, 0.03 g of monosaccharide, 0.147 g of water, 1.323 g of organic solvent and the appropriate amount of solid catalyst were added to the reactor. The final solution contained 2 wt% of monosaccharide and a weight ratio organic:water solvent of (9:1). The reactor was placed in the oil bath at 130 °C and stirred at 700 rpm. Reactors were removed from the oil bath at specific reaction times and cooled in an ice-water bath.

1.5 Hydrogenolysis of HMF in presence of lactone.

In a 50 mL Parr reactor, 0.5 g of SnRu/C, 20 mL of GVL and 2 wt% HMF were added. The reaction was carried out at 200 °C for 4 h.

1.6 Oxidation of HMF in presence of lactones

HMF was oxidized in a 50 mL Parr reactor. An aqueous solution containing 0.1 mol L⁻¹ HMF and 2 mol L⁻¹ NaOH was reacted at 22 °C for 22 h under 2000 kPa of oxygen using 1 wt% Au/TiO₂ (HMF: Au = 100). To study the effect of γ -lactones on the HMF oxidation, different γ -lactones were added to the aqueous solution.

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2. Effect of water content in glucose conversion to HMF.

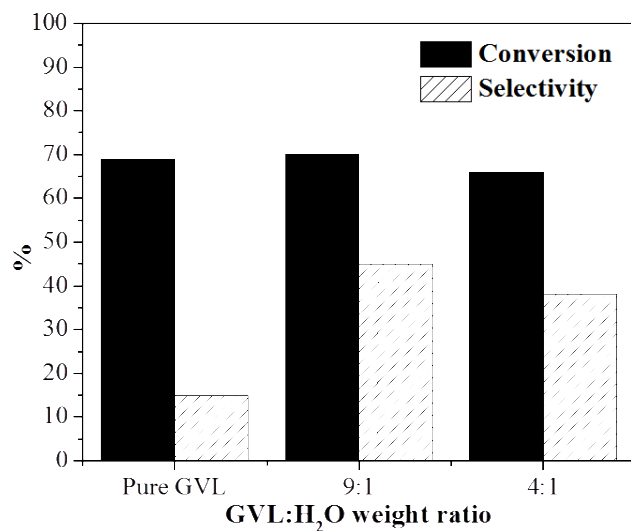


Fig. S1 Effect of water content in glucose conversion to HMF.

3. Effect of Amb-70/Sn- β weight ratio on the HMF yield using glucose and GVL:H₂O (9:1) as solvent.

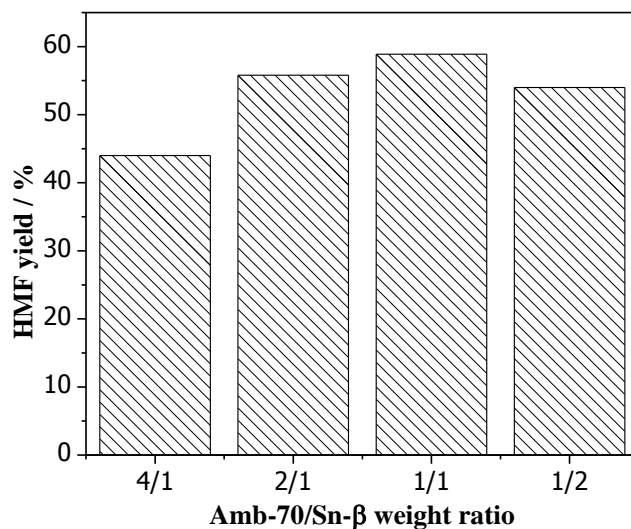


Fig. S2 Effect of Amb-70/Sn- β weight ratio on the HMF yield at 90 % conversion of glucose using GVL:H₂O (9:1) as solvent.

4. Extraction of HMF from GVL and GHL to water using CP.

Table S1. Extraction of HMF from GVL and GHL to water using CP.

Lactone	Extraction	CP / g	% HMF in water	% Lactone in water.
GVL	1 ^a	20	90	43
	2	20	80 ^b	5.00
	3	20	97 ^b	1.80
	4	20	99 ^b	0.5
GHL	1 ^a	16	80	5.00
	2	6	100 ^b	1.30
	3	6	100 ^b	0.35
	2	12	100 ^b	0.80

^a For the first extraction, one part of a HMF solution in lactone was contacted with one part of water and the amount of CP specified in the table. The aqueous phase was separated from the biphasic mixture for subsequent extractions with CP.

^b Based on the HMF remained in the aqueous layer on the previous extraction.

5. References

- (1) Shah, P.; Ramaswamy, A. V.; Lazar, K.; Ramaswamy, V. *Micropor Mesopor Mat* **2007**, 100, 210.