1 Supplementary Information:

2 Tetrahydrofuran (THF) is a versatile chemical that has commercial application as a solvent for the manufacture of plastics and is closely related to 1,4-butanediol (BDO) and γ -butyrolactone 3 (GBL).²⁶ Since THF polymers (PolyTHF and PTMEG) are also major commercial products, 4 further investigation into the application of these products will be of great interest, particularly 5 6 for the potential production of THF from furfural in this co-solvent strategy. THF owes its excellent solvent properties to the polar oxygen in its ring and dispersive character from the four 7 methylene groups. In a binary mixture with water, the dispersive character of THF increases with 8 increasing THF content in the aqueous phase. THF is also an excellent extracting solvent for 9 furfural and 5-hydroxymethylfurfural (HMF), and its affinity for these aldehydes may play a key 10 role in its ability to improve their yields in our single-phase system. THF can also be used to 11 12 solubilize extracted lignin products from organosoly or ionic-liquid pretreatment strategies or directly used to fractionate raw biomass as with our single-phase process. 13

Furfural is typically synthesized by acid-catalyzed dehydration of C5 sugars (arabinose 14 and xylose) whereas levulinic acid (LA) can be derived from either C5²⁹ or C6 sugars¹ (glucose, 15 galactose, and mannose). Water-soluble Brønsted acids such as HCl and H₂SO₄ have typically 16 been used to catalyze such dehydration reactions.²³ but homogeneous and heterogeneous solid 17 acid catalysts have also been applied successfully. Furfural is targeted in this paper as one of the 18 only natural precursors to furan-based chemicals. However, its low commercial yields (~50% of 19 theoretical) from xylan-rich lignocellulosic residues²³ hinder its economic potential, and new 20 approaches are needed to make it economically viable as a fuel precursor. HMF is an important 21 platform chemical that can be produced from the acid-catalyzed dehydration of hexoses. HMF 22 will readily hydrolyze to form equimolar amounts of LA and formic acid (FA)¹ in the presence of 23

a strong acid. Since LA is more stable than HMF in an aqueous environment,¹ higher final yields
of LA were observed in single phase reactions with sulfuric acid.

Room temperature liquid densities after the 40 min reactions (0.989 kg L^{-1} with 1:1 THF 3 and 1.015 kg L⁻¹ without THF at 21 °C) accounted for a 3% difference in the maximum furfural 4 yield. For both solvent and non-solvent reactions in Table 1, the highest furfural yield was 5 6 achieved much sooner (40 min) than the highest LA yield (120 min). Due to the more acid labile amorphous structure of hemicellulose, the rate of hydrolysis of xylan from hemicellulose was 7 much greater than that of glucan from crystalline cellulose.³⁰ By increasing the ratio of THF to 8 3:1 (density: 0.935 kg L⁻¹), co-production yields of furfural, HMF, and LA improved with 9 increased solubilisation of biomass without significant furfural losses. 10

11



Fig. S1 (A) Image showing the 1:1 THF co-solvent solution (left) next to water solution without solvent added (right) before reaction. (B) Precipitated lignin and degradation tars accumulated on the glass bottle after recovery of THF and removal of remaining liquids. (C) Isolated lignin powder from co-solvent reaction.

17

12

Figure S1(A) shows bottles of maple wood and acid solution with and without addition ofTHF co-solvent. Aside from the additional pigmentation in the solvent mixture, the two appear

nearly identical. These mixtures were subjected to batch reactions in order to obtain fuel
precursor yields reported in the main article. As shown in Fig. S1(B), removal of THF from the
post-reaction liquid by room temperature vacuum distillation allowed lignin to precipitate as a
solid residue. Further washing of the solid residue with diethyl ether produced a brown powdered

5 lignin product largely free of sugars, proteins, and ash, as shown in Fig. S1(C).



6

Fig. S2 FT-IR absorbance spectra of isolated lignin product from THF co-solvent reaction and
K-lignin residue from concentrated sulphuric acid extraction

9

Figure S2 shows the FT-IR absorbance spectra in the fingerprint region of lignin product
extracted by THF overlaid against that of the K-lignin residue from concentrated sulphuric acid
extraction of maple wood. Baseline correction and scaling were applied by Resolutions Pro
(Agilent Technologies) to better compare the relative peak heights. Differences in the relative

1 peaks shown indicate potential changes in the lignin chemistry by the two extraction methods. The stronger absorbance seen at 1710 cm-1 represents carbonyl stretching of unconjugated β -2 ketones and conjugated acid/esters and indicates a greater oxidation of the lignin structure 3 4 extracted by THF. The triple peak in the 1400 to 1500 cm-1 range of these samples matched closely and is characteristic of the phenolic hydroxyl groups, C-H deformation, and aromatic 5 skeletal vibrations in hardwood lignin. Peaks between 1100 cm-1 and 1330 cm-1 represent the 6 C-H and C-O bonds of the guaiacyl and syringyl rings. Peaks present in the 1000 cm-1 range 7 represent C-O bonds in the secondary alcohols or potential carbohydrate carry-over residues. 8



9

Fig. S3 Concentration profiles of (A) glucose, (B) xylose + mannose + galactose, (C) LA, and
(D) furfural over 60 min of reaction time (■ with THF, ▲ without THF). THF dissolved over

Electronic Supplementary Material (ESI) for Green Chemistry This journal is © The Royal Society of Chemistry 2013

90% (by wt.) of the lignin and degradation tars that otherwise accumulated in the non-solvent
 case. Reaction conditions: 5 wt% maple wood and 1 wt% H₂SO₄ in batch reactions at 170 °C.
 The THF co-solvent solution contained a 1:1 ratio of THF and water.

4

Figure S3(A-D) compares the concentration profiles of the fuel precursors produced from 5 maple wood with and without THF. As shown, the higher initial concentration of glucose with 6 THF suggested that THF enhanced the hydrolysis of cellulose to glucose compared to the non-7 solvent case (as confirmed by Fig. 1 in the paper). Disappearance of glucose and production of 8 LA were also enhanced by the solvent (Fig. S3(A) and Fig. S3(C) respectively). As for xylose, 9 the HPLC column (Aminex HPX-87H) we used first could not differentiate retention times for 10 xylose, mannose, and galactose monomers present in maple wood, resulting in a lumped 11 concentration profile. Due to the much slower decomposition rate of mannose vs. xylose³⁰, we 12 were unable to determine the exact concentration profile of xylose. Instead, we measured xylose 13 concentrations from neutralized reaction samples separately (Aminex HPX-87P) and found that 14 xylose was completely consumed by 40 min with THF and by 60 min for no THF. These results 15 indicated that THF had a catalytic effect on destruction of both glucose and xylose. A more 16 detailed kinetic study is in progress to quantify the improvements in reaction rates. 17



1

Fig. S4 Material balance of total products recovered from the hexosan, pentosan, and lignin
fractions of raw maple wood after THF co-solvent reaction with yields as percent of the
maximum theoretical for the initial biomass composition in parenthesis. Reaction conditions: 5
wt% maple wood and 1 wt% H₂SO₄ in batch reactions at 170 °C. The THF co-solvent solution
contained a 1:1 ratio of THF and DI water.

7

Figure S4 shows a material balance of a 1:1 THF co-solvent reaction with maple wood at
conditions that were found to be optimal for furfural production (40 min at 170 °C), the least
stable fuel precursor. Product masses of both solid and liquid streams were independently
quantified for each compound and then combined to calculate the total percent of product
recovered from each major lignocellulose fraction (87% for C5, 92% for C6, and 91% for
lignin).

14

15 **References:**

16 1. G. Dautzenberg, M. Gerhardt and B. Kamm, *Holzforschung*, 2011, **65**, 439-451.

1	2.	L. R. Lynd, M. S. Laser, D. Bransby, B. E. Dale, B. Davison, R. Hamilton, M. Himmel,
2		M. Keller, J. D. McMillan, J. Sheehan and C. E. Wyman, Nat Biotech, 2008, 26, 169-172.
3	3.	C. E. Wyman, Trends Biotechnol, 2007, 25, 153-157.
4	4.	T. Werpy and G. Peterson, Top Value Added Chemicals From Biomass Volume I: Results
5		of Screening for Potential Candidates from Sugars and Synthesis Gas, EERE, PNNL,
6		NREL, US DOE, 2004.
7	5.	J. J. Bozell and G. R. Petersen, Green Chemistry, 2010, 12, 539-554.
8	6.	O. W. Cass, Industrial & Engineering Chemistry, 1948, 40, 216-219.
9	7.	G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, Science, 2005, 308, 1446-
10		1450.
11	8.	Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, Nature, 2007, 447, 982-
12		985.
13	9.	J. J. Bozell, Science, 2010, 329 , 522-523.
14	10.	E. Nikolla, Y. Roman-Leshkov, M. Moliner and M. Davis, Acs Catalysis, 2011, 408-410.
15	11.	H. Olcay, A. V. Subrahmanyam, R. Xing, J. Lajoie, J. A. Dumesic and G. W. Huber,
16		Energy & Environmental Science, 2013, 6, 205-216.
17	12.	L. R. Lynd, C. E. Wyman and T. U. Gerngross, Biotechnology Progress, 1999, 15, 777-
18		793.
19	13.	D. M. Alonso, S. G. Wettstein, M. A. Mellmer, E. I. Gurbuz and J. A. Dumesic, Energy
20		& Environmental Science, 2013.
21	14.	J. Binder, J. Blank, A. Cefali and R. Raines, ChemSusChem, 2010, 1268-1272.
22	15.	H. Amiri, K. Karimi and S. Roodpeyma, Carbohydrate Research, 2010, 345, 2133-2138.
23	16.	R. Xing, W. Qi and G. W. Huber, Energy & Environmental Science, 2011, 4, 2193-2205.

1	17.	G. Henriksson, J. Li, L. Zhang and M. E. Lindström, in Thermochemical Conversion of
2		Biomass to Liquid Fuels and Chemicals, The Royal Society of Chemistry, 2010, ch. 9,
3		рр. 222-262.
4	18.	I. M. Smallwood, Solvent Recovery Handbook, Blackwell Science Ltd., Oxford, UK,
5		2002.
6	19.	C. E. Wyman, S. R. Decker, M. E. Himmel, J. W. Brady, C. E. Skopec and L. Viikari, in
7		Polysaccharides: Structural Diversity and Functional Versatility, ed. S. Dumitriu, Marcel
8		Dekker, Inc, New York, Second edn., 2005, ch. 43, pp. 995-1033.
9	20.	JP. Lange, E. van der Heide, J. van Buijtenen and R. Price, ChemSusChem, 2012, 5,
10		150-166.
11	21.	B. Yang and C. E. Wyman, <i>Biotechnol Bioeng</i> , 2004, 86, 88-95.
12	22.	T. Zhang, R. Kumar and C. E. Wyman, RSC Advances, 2013.
13	23.	K. J. Zeitsch, The chemistry and technology of furfural and its many by-products,
14		Elsevier Science B.V., Amsterdam, The Netherlands, 2000.
15	24.	A. P. Dunlop, Industrial & Engineering Chemistry, 1948, 40, 204-209.
16	25.	D. L. Williams and A. P. Dunlop, Industrial & Engineering Chemistry, 1948, 40, 239-
17		241.
18	26.	A. Corma, S. Iborra and A. Velty, Chemical Reviews, 2007, 107, 2411-2502.
19	27.	B. H. Wojcik, Industrial & Engineering Chemistry, 1948, 40, 210-216.
20	28.	R. Xing, A. V. Subrahmanyam, H. Olcay, W. Qi, G. P. van Walsum, H. Pendse and G.
21		W. Huber, Green Chemistry, 2010, 12, 1933-1946.
22	29.	E. I. Gürbüz, S. G. Wettstein and J. A. Dumesic, ChemSusChem, 2012, 5, 383-387.
23	30.	J. F. Saeman, Industrial & Engineering Chemistry, 1945, 37, 43-52.