

Electronic Supplementary Information

Title:

Enhanced furfural production from biomass and its derived carbohydrates in renewable
butanone–water solvent system

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Distribution of Liquid-phase Product

The liquid-phase products were analyzed by DSQ II gas chromatography–mass spectrometry (GC-MS) system (Thermo Scientific, USA) equipped with a DB-wax capillary column (30 m × 0.25 mm × 0.25 mm). Helium (99.999%) at a flow rate of 1 mL/min was used as carrier gas. The GC oven temperature was programmed to increase from 40 °C (1 min) to 240 °C (20 min) at 8 °C/min heating rate. The MS detector was operated in electron ionization (EI) mode (70 eV) with a scan range of m/z 35–450 and an ion source temperature set to 200 °C. All detected chemicals were identified by comparison with the NIST (National Institute of Standards) MS library. The detection limit was set to 1%. The Product distribution is shown in Table S1.

Table S1 Typical products of the xylose conversion identified by GC-MS

Reaction Condition: 30 mg/mL xylose, 0.1 M catalyst, 140 °C, 180 min

	Product	Formula	Peak Area Intensity (×10 ⁹)
	Furans		
(1)	furfural	C ₅ H ₄ O ₂	3.90326646
(2)	3-(2-furanyl)-3-penten-2-one	C ₉ H ₁₀ O ₂	0.116723767
(3)	5-Hydroxy-4,5-dimethyl-2,5-dihydrofuran-2-one	C ₆ H ₈ O ₃	0.070361311
(4)	2(5H)-Furanone, 5-methyl-	C ₅ H ₆ O ₂	0.05438385
	Oxygenate aliphatics		
(5)	4-hydroxy-4-methyl-2-pentanone	C ₆ H ₁₂ O ₂	0.192212159
	Cyclohexenones		
(6)	2-hydroxy-3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one	C ₁₀ H ₁₆ O ₂	0.10199351
(7)	cis-4-Hydroxy-2-methyl-5-(1-hydroxy-1-isopropyl)-2-cyclohexen-1-one	C ₁₀ H ₁₆ O ₃	0.104109394

The soluble products from xylose conversion were divided into three main categories, namely oxygenated aliphatics, furans and cyclohexenones. Furfural (1) was a primary compound in the liquid-phase products, and it made up 94% of the furans. (2) could come from the aldol condensation reaction between (1) and pentanone intermediates from retroaldolization of xylose.[1] Furanone (3) and (4) might be the hydration products of hydroxyl-rich acids from the ring opening of xylose.[2] C6 ketone (5) was likely to be formed by the aldol condensation reactions between small molecules from the retroaldolization of xylose.[3-5] The origin of cyclohexenones might be from the cyclization of the chain intermediates.[6]

Table S2 Optimum furfural yield obtained within the time range of 0–240 min from xylose dehydration in various organic solvents

Organic Solvent	Reaction Time (min)	Xylose Conversion (%)	Furfural Yield (%)
butanone	90	99	56
acetone	240	85	39
ethyl acetate	180	71	21
tetrahydrofuran	180	77	44
γ -valerolactone	240	59	40
isobutyl acetate	180	97	36
isoamyl acetate	180	98	40
dimethyl carbonate	240	90	27
Reaction condition: 30 mg/mL xylose, organic solvent–water ratio = 4:1, 0.1 M catalyst, 140 °C All the solvents were commonly considered to be green and they were suggested to be used by <i>Green Chemistry</i> . [7]			

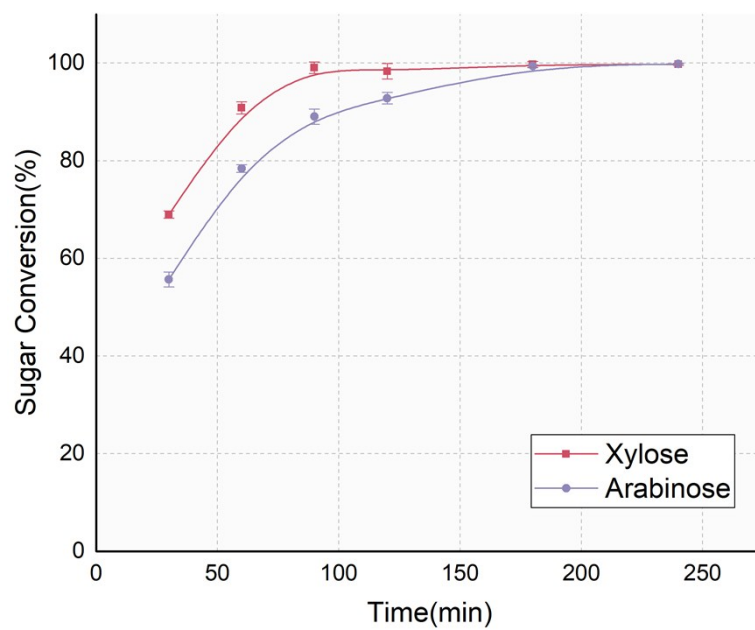


Figure S1 Sugar conversion vs. time on stream for xylose and arabinose (30 mg/mL sugar, butanone–water (4:1), 0.1 M catalyst, 140 °C)

References

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