Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

One-Step Lignocellulose Depolymerization and Saccharification to High Sugar Yield and Less Condensed Isolated Lignin

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Table S1. Yields of soluble products from soxhlet extracted poplar wood saccharification in $ZnBr_2$ AMSH.

Soluble products	Yield (%) based on theoretical glucose and xylose amounts in soxhlet extracted poplar wood				
	0.5	**1h**	**2h**	**3h**	**5h**
Glucose	11.5	30.2	75.7	86.6	85.4
Xylose	60.9	72.1	84.0	88.9	87.1
Levoglucosan	1.3	2.7	5.8	6.4	6.7
Acetic acid	8.1	9.4	14.9	17.1	17.4
HMF	0.7	0.7	0.8	1.1	0.8
FF	1.3	2.0	4.9	8.9	9.6
Oligosaccharides	26.3	44.9	7.4	0.7	0.6
Cellopentaose	1.9	5.7	0.0	0.0	0.0
Cellotetraose	6.8	8.4	1.0	0.0	0.0
Cellotriose	8.9	12.6	2.2	0.0	0.0
Cellobiose	8.7	18.3	4.2	0.7	0.6

Reaction conditions: 3.45 wt% soxhlet extracted poplar wood, 73 wt% $ZnBr_2$, water/salt molar ratio 4, 0.05 M H_2SO_4, 85°C.

Table S2. Composition of solids separated at different times during soxhlet extracted poplar wood saccharification.

Time (h)	Wt (%) of components		
	Glucan	**Xylan**	**Lignin**
0.5	29.4	12.4	58.1
1	0.9	0.2	98.9
2	0.4	0.1	99.5
3	0.4	0.1	99.5
5	0.2	0.1	99.7

Reaction conditions: 3.45 wt% soxhlet extracted poplar wood, 73 wt% $ZnBr_2$, water/salt molar ratio 4, 0.05 M H_2SO_4, 85°C.

Table S3. Yields of phenols obtained from the CoS_2 catalyzed depolymerization of MSH lignin. The structures of monomers A-H are given below in Figure S5.

Monomer	Yield (mmol%)
A	0.8
B	1.2
C	3.9
D	1.8
E	1.1
F	6.7
G	1.2
H	0.4

Reaction conditions: 50 mg lignin, 50 mg CoS_2, 20 mL THF (solvent), 50 bar H_2, 250 °C, 15 h.

Table S4. Results for the reductive catalytic fraction of raw poplar wood, MSH and AMSH lignin.

No	**Label**	**Yield (wt%)* based on lignin weight**		
		Poplar wood	**No acid lignin**	**Acid lignin**
1	Phenol	1.5	0.2	0.8
2	4-Ethyl phenol	0.6	0.8	1.4
3	4-Ethyl-3-methoxy phenol	0.7	2.2	2.4
4	2,5-dimethoxy phenol	1.7	3.9	-
5	4pG - OH	2.0	3.2	0.6
6	4pG	12.8	3.1	1.5
7	Phenyl acetic acid ester derivatives	3.5	1.8	1.3
8	4pS	18.0	3.7	0.5
9	3,5-Dimethoxy-4-hydroxy-phenyl ethanol	5.3	1.7	0.4
10	4pS - OH	3.3	-	-
11	Total monomer yield (%)	49.4	20.6	9.7

Reaction conditions: 100 mg lignin, 50 mg Ru/C, 10 ml methanol, 40 bar H_2, 250 °C and 15 hr.

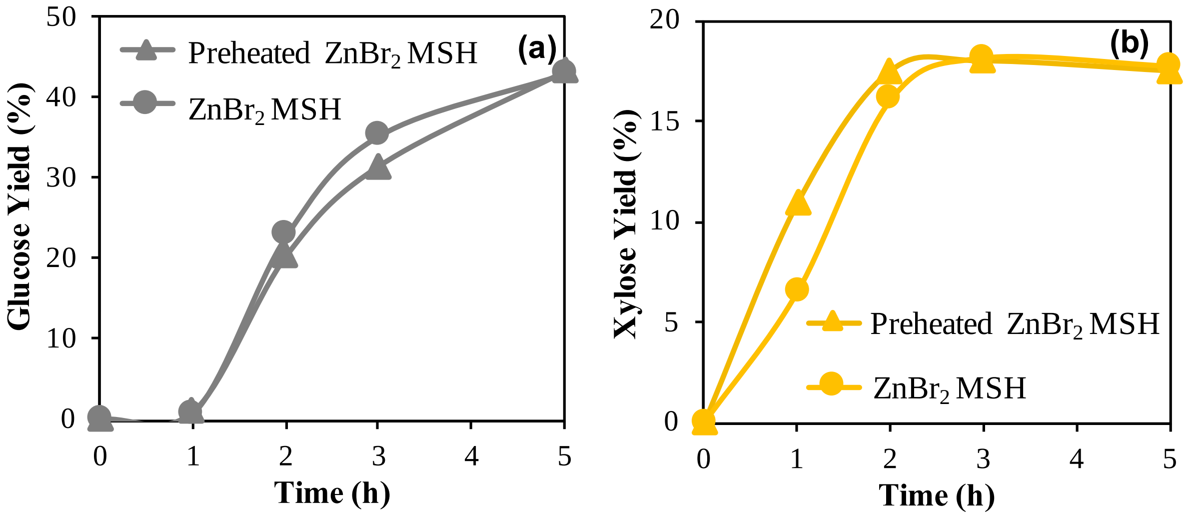

Figure S1. Comparison of (a) glucose and (b) xylose yields from one-step soxhlet extracted poplar wood depolymerization and saccharification in $ZnBr_2$ MSH and preheated $ZnBr_2$ MSH media, respectively. Soxhlet extracted poplar wood was added into the $ZnBr_2$ MSH medium preheated at 85 °C for 1 h to match the induction time. Reaction conditions: 3.45 wt% oxhlet extracted poplar wood, water/$ZnBr_2$ molar ratio 4 and 85 °C. The yields are calculated on the basis of dry weight of soxhlet extracted poplar wood.

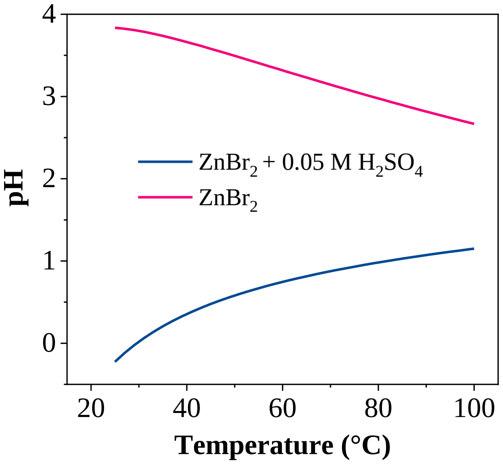

Figure S2. pH of ZnBr$_2$ MSH and ZnBr$_2$ AMSH (ZnBr$_2$ + 0.05 M H$_2$SO$_4$) vs. temperature calculated using OLI.

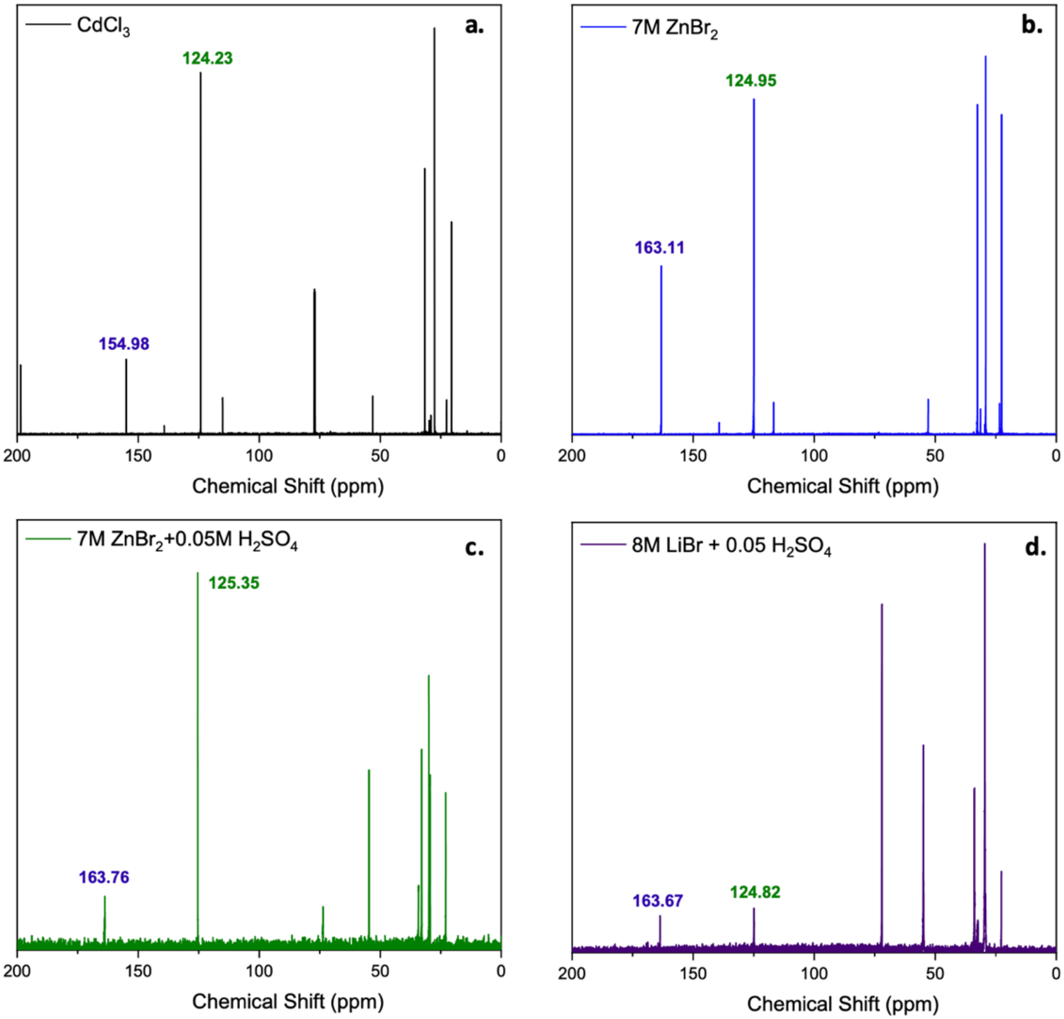

Figure S3. ^{13}C-NMR spectra for mesityl oxide (MO) in a) deuterated chloroform, b) 7 M ZnBr$_2$ (MSH), c) 7 M ZnBr$_2$ in 0.05 M sulfuric acid (AMSH), and d) 8 M LiBr in 0.05 M sulfuric acid (LiBr AMSH). Chemical shift of alpha and beta carbons in MO shown in purple and green color font, respectively.

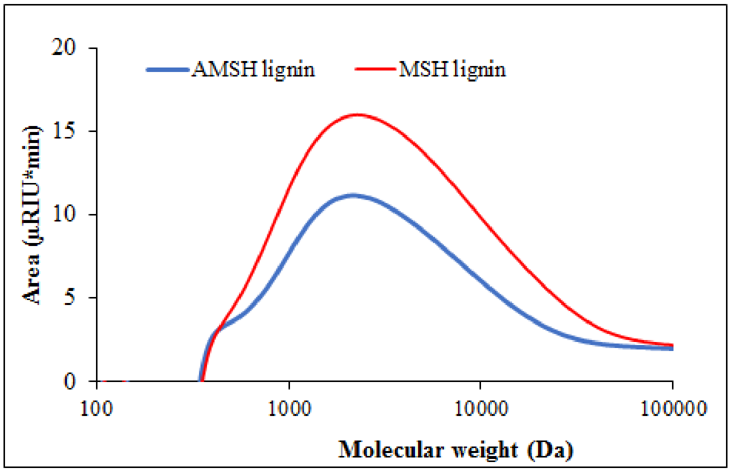

Figure S4. GPC molecular weight distribution of lignin recovered from $ZnBr_2$ AMSH and lignin recovered from $ZnBr_2$ MSH.

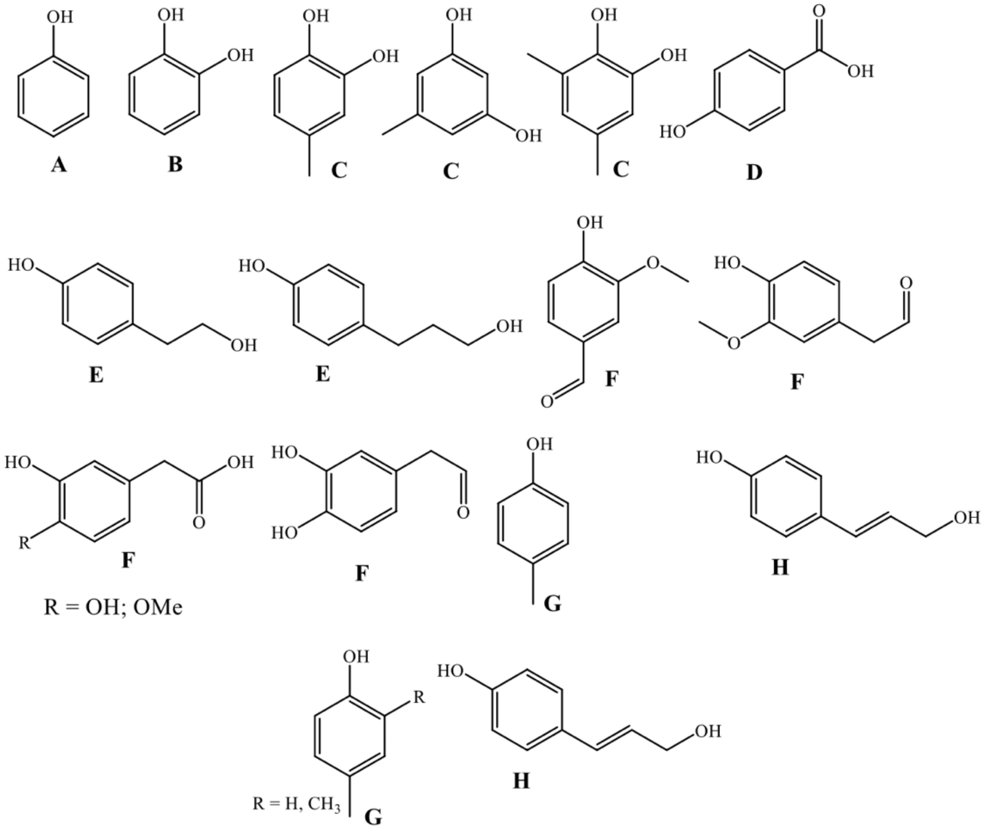

Figure S5. Chemical structures of monomeric phenols formed in the CoS_2 catalyzed depolymerization of MSH-derived lignin. Reaction conditions: 50 mg lignin, 50 mg CoS_2, 20 mL THF (solvent), 50 bar H_2, 250 °C, 15 h.

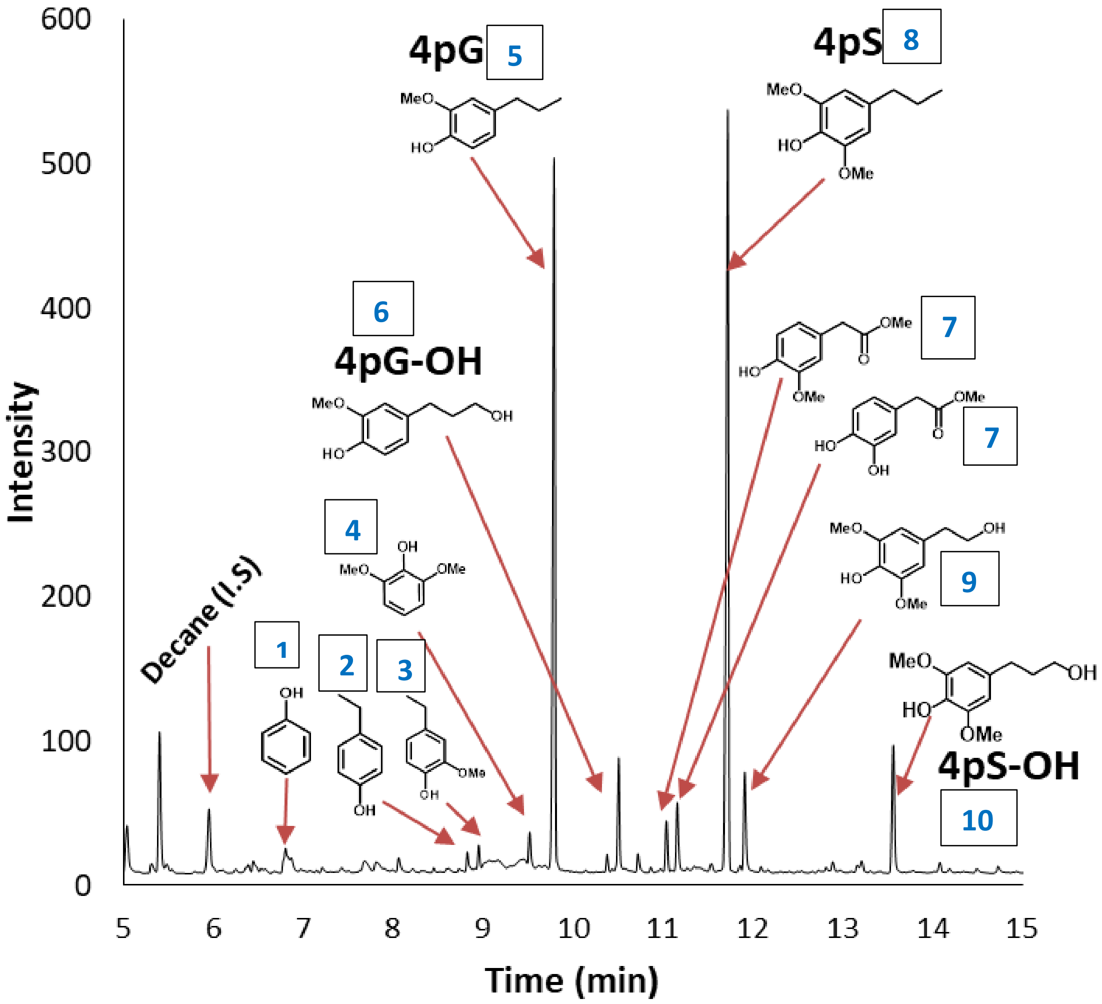

Figure S6. GC chromatogram for the whole poplar wood after reductive catalytic fractionation over Ru/C catalyst. Reaction conditions: 100 mg lignin, 50 mg Ru/C, 10 ml methanol, 40 bar H_2, 250 °C, and 15 hr.

Process Simulation and Economics

Process flowsheets including different hydrolysis processes and the production of HMF from lignocellulose have been developed and are shown in Figures S9-S10. The simulation is performed using Aspen Plus V8.8. The NRTL thermodynamic package is utilized to predict the liquid–liquid and liquid–vapor behavior.[1] All components are modeled using the Aspen database except those not included in the database (i.e., lignin, hemi-cellulose etc.), whose structures and properties taken are taken from NREL.[2]. For humins and molten salt hydrate, surrogates are used. All the missing parameters are estimated by the molecular structures using the Unifac

Model and Thermo Data Engine (TDE). TDE is a thermodynamic data correlation, evaluation, and prediction tool developed by the collaboration of Aspen plus and the National Institute of Standard and Technology.

The information on operating conditions is taken from literature as well as from experimental data. The following assumptions are made:

1. The composition of biomass is taken to be 40% cellulose, 30% hemi-cellulose and 30% lignin. Generally, hardwoods and softwoods contain around 40-50% cellulose, 25-30% hemicellulose, 18-25% lignin and <1% ash. For the base scenario, the assumption is satisfactory.
2. The biomass loading is taken as 10 wt%.
3. All the filtration processes are assumed to have 99.5% separation efficiency for lowering operational costs.
4. In the biphasic reactor, it is assumed that 90% of the furans (HMF and furfural) are extracted by the organic solvent. No solvent is dissolved in the aqueous phase.

The Aspen Economic analyzer V8.8 is used to assess the production cost of HMF. The production cost of HMF is used to determine the minimum cost, which is defined as the selling price of the product when the net present value (NPV) is zero[3]. Some additional assumptions are necessary to perform the economic analysis:

1. All the equipment and operating costs estimated by the Aspen Economic Analyzer V8.8 are based on the price of the first quarter in 2014.
2. The plant capacity is assumed as 50 metric tons per hour of biomass feedstock.
3. The plant operates in a continuous mode for 8000 h per year. The economic life of the project is assumed to be 20 years. The internal rate of return (ROR) on investment is assumed as 15%. 35% corporate tax is applied to the profits. The simplest depreciation method -- the straight-line method is applied as the salvage value is 10% of the original capital cost after 20 years. Recovery period is considered as 10 years.
4. The cost of biomass is averaged to $60 per ton as per data of NREL[4].
5. The market price of ethyl acetate as well as aluminium chloride is estimated as $910/metric ton and $600/metric ton based on the prices reported at www.alibaba.com[5] - a worldwide e-commerce market site. The price of chemicals may vary with many factors, such as season, location, producer, policy, etc.
6. Other costs include raw materials, solvents and acids: cost of Zinc Bromide is $1000/metric ton and hydrogen is priced at $653/metric ton. The market price of sulfuric acid is $250/metric ton.[5]
7. In the base scenario, the value of byproducts is not considered.
8. Utilities and wastewater treatment plants are not modeled explicitly; rather it is assumed instead that utilities are purchased, and wastewater is treated by a third party at a fixed price per unit volume.[6]

The capacity of the process for the production of HMF is 400,000 metric ton of biomass per year. The AMSH process produces 103,478 metric ton/year of HMF, 67,803 metric ton of furfural and 134,074 metric ton of lignin whereas the MSH Process produces 95,038 metric ton/year 64,038 metric ton of furfural and 152,671 metric ton of lignin. The purity of HMF and furfural for both the process is 99%. The purity of lignin for AMSH process is 85% and for MSH process is 77%. For the base case, we produce electricity for either process by burning lignin.

The capital cost of AMSH process is estimated at $176 million and the operating cost is estimated at $51.5 million. The capital cost of MSH process is estimated at $182 million and the operating cost is estimated at $53 million. The residence time required and hence the capital cost for MSH process is higher than those of the AMSH process. The operating cost for both the process is almost the same.

In the base case scenario, where no byproducts value are considered and where lignin is used to generate electricity, the minimum price of HMF, is $774 per metric ton for AMSH process and $863 per metric ton for MSH process. When furfural is valued at $1,000 per metric ton, the minimum price of HMF decreases to $119 per metric ton for AMSH process and $190 per metric ton for MSH process. If lignin for MSH process is valued at $100 per metric ton and no electricity is produced, the minimum price of HMF from MSH process further decreases to $59 per metric ton. The breakdown cost is given in Table S4-S5 and Figure S8. The breakdown of raw material is shown in Figure S9. From our previous research, we also compare the prices of HMF for different hydrolysis processes, such as dilute acid hydrolysis and concentrated acid hydrolysis, as well as those of $ZnBr_2$ AMSH and $ZnBr_2$ MSH processes (Figure 8).

Table S5. Summary of the capital and operating cost of the AMSH process.

Item	**Cost (Million $)**	**Item**	**Cost per year (Million $)**
Purchased Equipment	132	Total Raw Materials Cost	41.6
Other	13	Total Utilities Cost	1.9
General and Administrative Overheads	4	Operating Labor Cost	0.8
Contract Fee	4	Maintenance Cost	1.9
Contingencies	14.5	Operating Charges	0.3
Working Capital	8.4	Plant Overhead	1.3
Total Capital Cost	**176**	General and Administrative Cost	3.8
		Total Operating Cost	**51.6**

Table S6. Summary of the capital and operating cost of the MSH process.

Item	**Cost (Million $)**	**Item**	**Cost per year (Million $)**
Purchased Equipment	136	Total Raw Materials Cost	41.5
Other	14	Total Utilities Cost	2.5

General and Administrative Overheads	4	Operating Labor Cost	0.8
Contract Fee	4.5	Maintenance Cost	2.2
Contingencies	15	Operating Charges	0.3
Working Capital	8.6	Plant Overhead	1.5
Total Capital Cost	**182**	General and Administrative Cost	3.9
		Total Operating Cost	**53**

Process Description

Hydrolysis using Molten Salt Hydrate (MSH): Hydrolysis of biomass using MSH is based on the laboratory-scale process. It is a single stage hydrolysis process. Biomass, sulfuric acid (for the MSH process sulfuric acid is not needed), water and MSH (stream 1) is fed to reactor (R1). The molten salt hydrate is Zinc Bromide ($ZnBr_2$). Biomass loading is assumed as 10 wt% with 65 wt% $ZnBr_2$. The strength of acid is 0.15 wt%. Reactor (R1) operates at 85 ^{0}C. The yield of glucose and xylose is 90% and 98% respectively for the AMSH process for a residence time of 3 hrs and 88% and 98% respectively for the MSH process for a residence time of 5 hrs. The product stream 2 is fed to a filter (FIL 1) where lignin is separated from the sugar mixture. As it is difficult to separate out the sugars from the molten salt hydrate mixture, we convert the sugars into furans and then an organic solvent is used to separate the furan and the molten salt hydrate.

HMF Production: HMF production is based on the laboratory-scale biphasic reaction for the conversion of sugars to HMF and furfural in water using ethyl acetate as the organic solvent and aluminum chloride ($AlCl_3$) as the catalyst.[7] Sugar from the hydrolysis process is mixed with ethyl acetate and aluminum chloride and fed to biphasic reactor (R1). Solvent is introduced in the second extraction phase. The organic phase streams 3 and 5 containing solvent, HMF and furfural for both stages are combined and fed to a distillation column (C1), where solvent and furfural are separated. Solvent stream 7 is recycled. Furfural stream 8 is purified (C2) and HMF is taken as the product. The aqueous phase stream 6 is fed to a filter (FIL 1) to remove humins. The outlet stream 9 from the filter is introduced into an evaporator (V1) where excess water is separated. The outlet stream containing unreacted raw materials and catalyst is recycled.

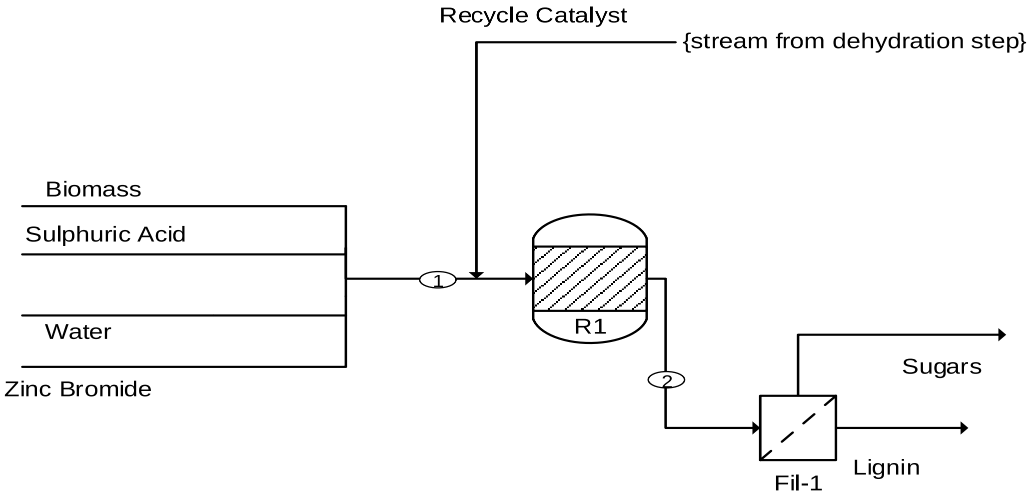

Figure S7. Process diagram for lignocellulose hydrolysis using MSH.

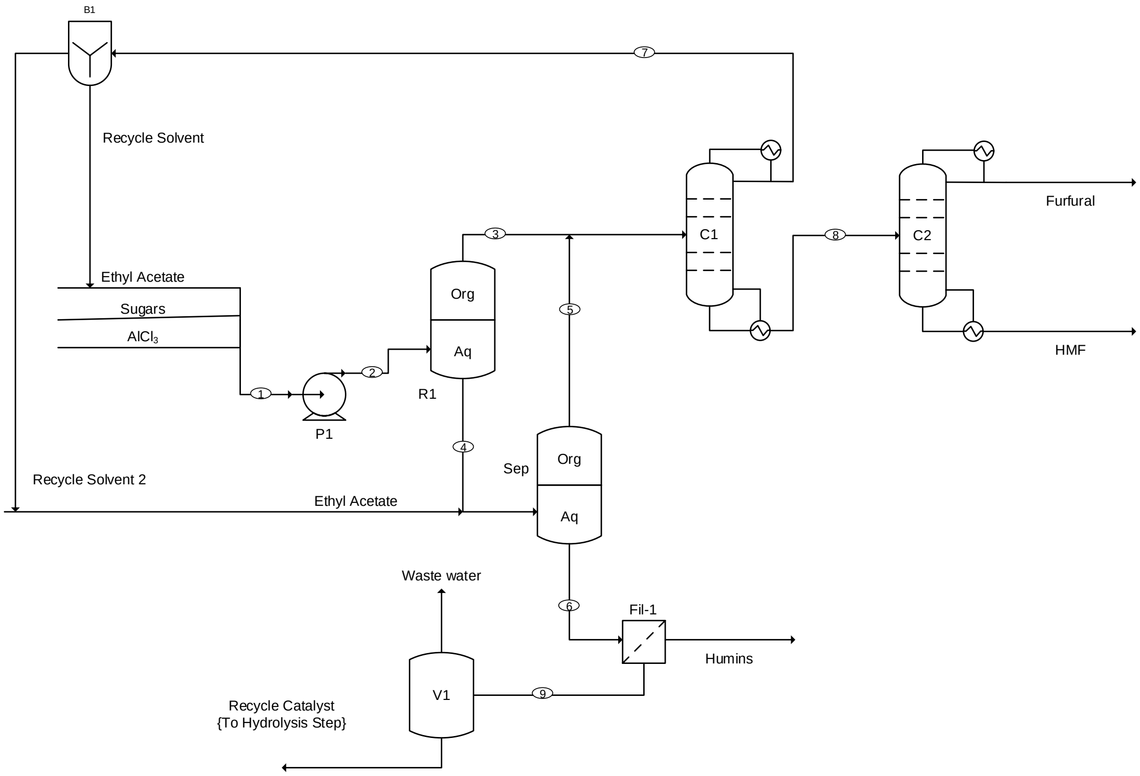

Figure S8. Process diagram for HMF production.

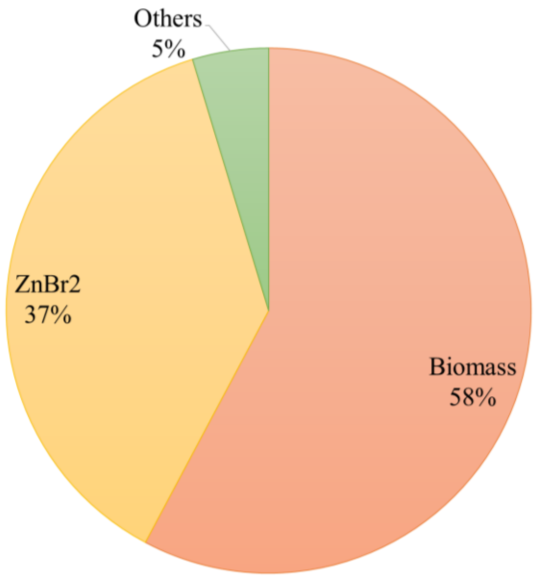

Figure S9. Contributions of raw materials on selling price of HMF.

Table S7. Mass balances for the MSH process.

Hydrolysis Section

Kg/hr	Glucose	Xylose	H_2SO_4	LiBr	$AlCl_3$	Water	HMF	Furfural	Humins	Biomass
Biomass	0	0	0	0	0	0	0	0	0	50,000
Sulphuric Acid	0	0	4	0	0	0	0	0	0	0
Water	0	0	0	0	0	90	0	0	0	0
$ZnBr_2$	0	0	0	1,948	0	0	0	0	0	0
1	0	0	735	325,000	14,373	125,000	678	407	28	50,000
Recycle Catalyst	0	0	731	323,052	14,373	124,910	678	407	28	1
2	21,778	15,341	735	325,000	14,373	120,981	678	407	28	16,900
Sugars	21,756	15,326	734	324,675	14,358	120,860	677	407	0	169
Lignin	22	15	1	325	14	121	1	0	28	16,732

Dehydration Section

Kg/hr.	Glucose	Xylose	H_2SO_4	LiBr	$AlCl_3$	Ethyl	Water	HMF	Furfural	Biomass	Humins
Ethyl Acetate	0	0	0	0	0	81	0	0	0	0	0

Ethyl Acetate 1	0	0	0	0	0	81	0	0	0	0	0
Sugars	21,756	15,326	734	324,675	14,358	0	120,860	677	407	160	0
$AlCl_3$	0	0	0	0	176	0	0	0	0	0	0
1/2	21,756	15,326	734	324,675	14,534	809,785	120,860	678	407	160	0
3	0	0	0	0	0	809,785	0	6,811	4,372	0	0
5	0	0	0	0	0	809,785	0	6,131	3,935	0	0
7	0	0	0	0	0	1,619,410	0	1	0	0	0
8	0	0	0	0	0	162	0	12,941	8,306	0	0
Recycle Solvent	0	0	0	0	0	809,704	0	0	0	0	0
Recycle solvent 2	0	0	0	0	0	809,704	0	1	0	0	0
Furfural	0	0	0	0	0	162	0	0	8,306	0	0
HMF	0	0	0	0	0	0	0	12,941	1	0	0
4	0	0	734	324,675	14,534	0	131,098	6,811	4,372	160	5,563
6	0	0	734	324,675	14,534	0	131,098	681	437	160	5,563
Humins	0	0	4	1,623	73	0	656	3	2	160	5,535
9	0	0	731	323,052	14,461	0	130,442	678	435	1	28
Waste water	0	0	0	0	89	0	5,532	0	28	0	0
Recycle catalyst	0	0	731	323,052	14,373	0	124,910	678	407	1	28

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