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Coupling metal halides with a co-solvent to produce furfural and 5-HMF at high yields directly from lignocellulosic biomass as an integrated biofuels strategy

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Abstract:

Metal halides are selective catalysts suitable for production of the fuel precursors furfural and 5-HMF from sugars derived from lignocellulosic biomass. However, they do not perform nearly as well when applied to biomass even in combination with immiscible extracting solvents or expensive ionic co-solvents. Here, we couple metal halides with a highly tunable co-solvent system employing renewable tetrahydrofuran (THF) to significantly enhance co-production of furfural and 5-HMF from biomass in a single phase reaction strategy capable of integrating biomass deconstruction with catalytic dehydration of sugars. Screening of several promising metal halide species at 170°C in pH-controlled reactions with sugar solutions and larger 1 L reactions with maple wood and corn stover revealed how the interplay between relative Brønsted and Lewis acidities was responsible for enhancing catalytic performance in THF co-solvent. Combining $FeCl_3$ with THF co-solvent was particularly effective, achieving one of the highest reported simultaneous yields of furfural (95%) and 5-HMF (51%) directly from biomass with minimal levulinic acid formation (6%). Furthermore, over 90% of the lignin from biomass was extracted by THF and recovered as a fine lignin powder. Tuning the volume ratio of THF to water from 4:1 to 1:1 preserved 10% to 31% of the reacted biomass as a glucan-rich solid suitable for further catalytic reaction, enzymatic digestion, or possible pulp and paper production.

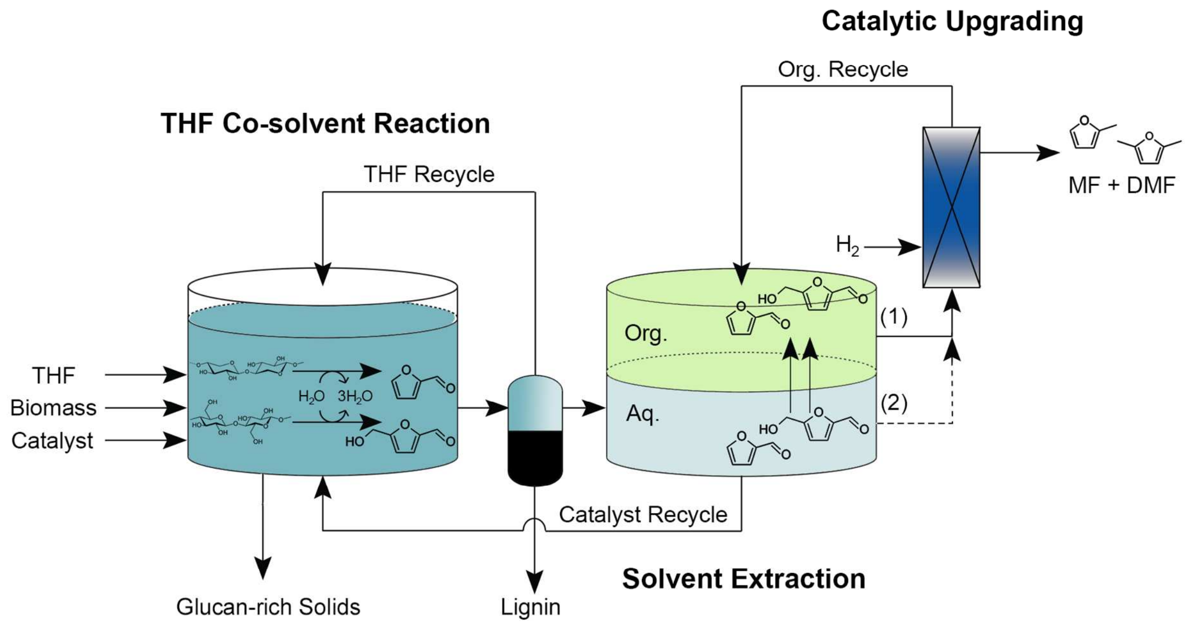

Table of Contents

3. Results and Discussion

1. Introduction

Lignocellulosic biomass in such forms as agricultural and forestry residues and herbaceous and woody energy crops is the only sufficiently prevalent sustainable resource for impactful conversion into renewable liquid transportation fuels[1, 2]. Furthermore, because lignocellulosic biomass sold at \$60/ton is theoretically equivalent in energy cost to oil at about \$20/barrel, it provides the most promising near-term option for achieving low enough costs to alleviate our dependence on fossil resources[3]. The conversion of cellulosics into compatible transportation fuels has enormous benefits for addressing global climate change, energy security, rural economic growth and employment, trade deficits, and global competitiveness issues[4, 5]. What we term as fuel precursors (FPs) must generally be derived as intermediate platform compounds[6] from lignocellulosic biomass before conversion to “drop-in” liquid transportation fuels and other fuel products is possible. However, the major challenge to realizing this pathway has been to produce primary fuel precursors, such as monomeric sugars, and secondary fuel precursors, such as furfural, 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA), directly from biomass at the high yields (>80% recovery of C5 and C6 products) essential to low unit costs (<\$5 gal^{-1})[7] without complicated processes, expensive catalysts, and/or high energy demand.

Figure 1 outlines a reaction network for the production of ethanol and promising gasoline, jet, and diesel range fuel products from primary and secondary fuel precursors. As shown, xylose from hemicellulose and glucose from cellulose can be fermented to ethanol or dehydrated with acid catalysts to produce the secondary FPs furfural and 5-HMF. Further 5-

HMF hydrolysis results in equimolar formation of more stable products LA and formic acid (not shown). LA can also be synthesized from furfural by a furfuryl alcohol intermediate. These secondary fuel precursors can be catalytically upgraded into potential fuel products by selective hydrogenation over metal-based solid catalysts[8]. As shown, catalytic hydrogenation of furfural and 5-HMF produces promising gasoline blending products 2-methylfuran (MF, 131 Research Octane Number RON)[9] and 2,5-dimethylfuran (DMF, 119 RON)[10], respectively. 2-methyltetrahydrofuran (MTHF, 86 RON)[11] can be produced from hydrogenation of LA or MF and ethanol can be produced from sugars by yeast and/or bacteria fermentation[12], both of which are primary components in P-series biofuels. Ethanolysis of LA produces ethyl levulinate [13], a diesel blendstock, whereas aldol-addition using acetone and hydrodeoxygenation of secondary fuel precursors with hydrogen can produce longer-chained hydrocarbon fuels of up to 16 carbon lengths for jet and diesel applications[8, 14].

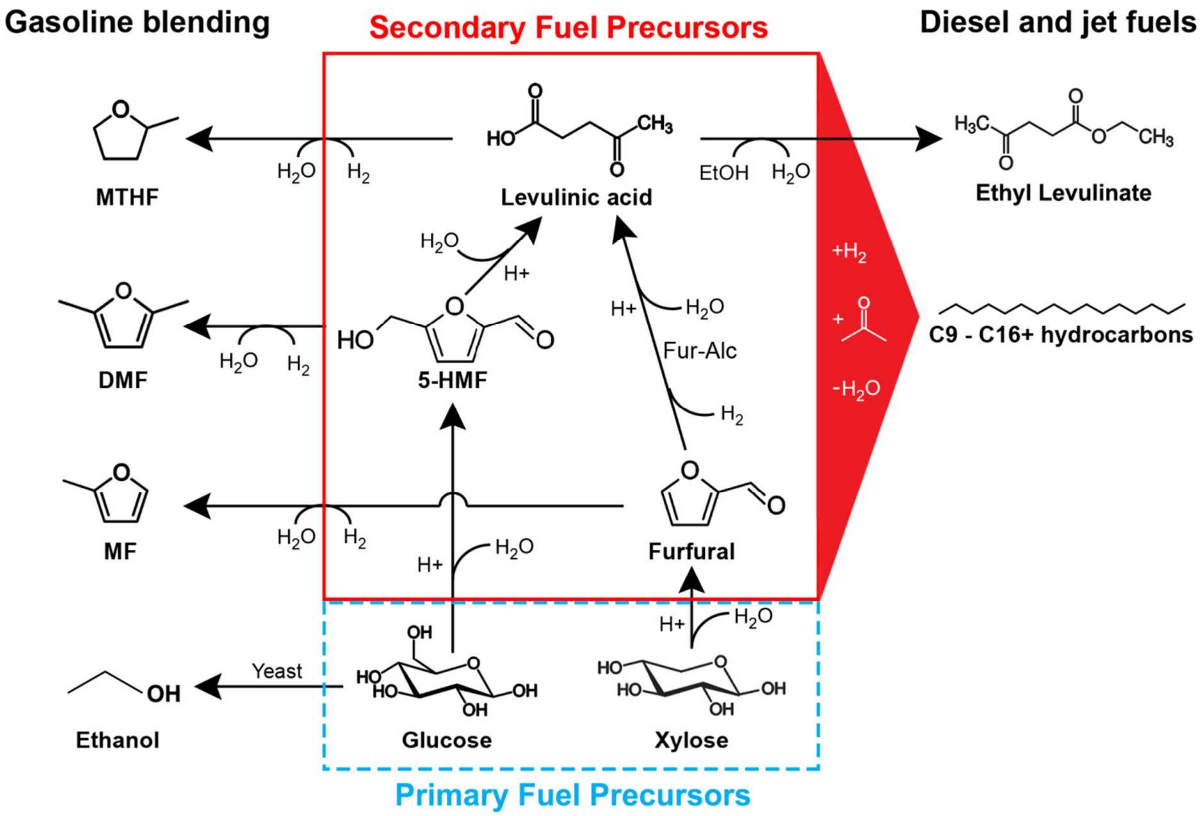

Figure 1. Reaction network illustrating primary and secondary fuel precursors for production of ethanol and gasoline, jet, and diesel range aromatic and hydrocarbon fuels. 5-HMF: 5-hydroxymethylfurfural; MF: 2-methylfuran; DMF: 2,5-dimethylfuran; MTHF: 2-methyltetrahydrofuran; Fur-Alc: furfuryl alcohol.

Ongoing advances in catalysis have improved the selective conversion of secondary fuel precursors to so-called drop-in fuel products that are compatible with the existing fuel infrastructure[15-18], but obtaining high overall fuel precursor yields directly from lignocellulosic biomass has been a long-standing barrier to achieving reasonable product costs of < \$5 gal^{-1} [19, 20]. Thus, there is a pressing need to develop effective strategies that integrate catalytic conversion with biomass deconstruction to co-produce FPs from both C5 and C6 sugars in order for biomass drop-in fuels to have impact[19, 20]. Achieving high overall product yields from the major biomass fractions hemicellulose, cellulose, and lignin in an integrated process has the highest potential to enable future biomass-to-fuel technologies[19]. Various acid catalyzed co-production schemes from biomass have been proposed including co-producing furfural with LA, furfural with 5-

HMF, furfural with cellulose, and LA from both furfural and 5-HMF, but many suffer from low yields due to the complex heterogeneous nature of biomass[9]. For example, furfural and 5-HMF produced early in biomass deconstruction are rapidly degraded before sufficient LA yields from C6 sugars can be achieved. Consequently, LA production and recovery would have to follow furfural removal, thereby necessitating multi-stage reactions with independent product recovery steps, expensive steam stripping to remove furfural, use of corrosive mineral acids, and/or biphasic reactions. Alternatively, co-production of furfural and 5-HMF would appear more desirable as both products could be recovered together by a suitable extracting solvent and simultaneously converted into “drop-in” fuels such as MF and DMF by a single catalyst[21].

Recently, we demonstrated that tetrahydrofuran (THF) is an exceptionally effective single phase co-solvent for integrated biomass reactions that enhance fuel precursor yields during biomass deconstruction, as well as delignification[22]. Using just dilute sulfuric acid in a miscible solution of THF and water, we achieved higher overall yields of furfural, 5-HMF, and LA from maple wood than previously reported in a single phase reaction[22]. However, because sulfuric acid favored furfural and LA production, it became apparent that tuning of this co-solvent system with different catalysts could improve yields for co-production of furfural and 5-HMF. Because aqueous monophasic reactions with dilute mineral acids typically suffer from low 5-HMF yields (<5%)[9, 22] as it readily hydrolyzes to form LA and formic acid, methyl isobutyl ketone (MIBK) was employed as an extracting solvent in a biphasic reaction[23], but solvent recovery was an issue and the high energy requirements for heating and stirring and limited effective solids loading of a biphasic reaction for large scale fuel production from solid biomass hinder its commercial appeal[22]. Thus, a single phase reaction is beneficial if a more selective acid catalyst could be used to improve selectivity of biomass glucan to 5-HMF instead of LA.

Metal halides are inexpensive acid catalysts that are well studied for selectively promoting alternate reaction mechanisms of xylose to furfural and glucose to 5-HMF compared to traditional mineral acids[24-26]. In analogous pathways, aldose-to-ketose isomerization of glucose to fructose and xylose to xylulose was observed in the presence of certain bi- and trivalent metal cations that can more easily undergo acid-catalyzed dehydration[26]. Metal cations such as Al^{3+}, Fe^{3+}, and Cr^{3+} also form oxides with water molecules that increase the acidity of the solution as a Brønsted acid[27]. When bound to halide anions such as I-, Br-, and Cl-, the Lewis acid/base pair can further catalyze production of furfural and 5-HMF from aldose sugars through consecutive dehydration reactions that first proceed by enolization to a 1,2-enediol intermediate[25]. However, evidence also suggests that the strong Lewis acid character of metal halides accelerates several competing loss reactions that could potentially decrease product yields. When used in biphasic[28] and expensive ionic-liquid (IL) co-solvent[29] systems, metal halides demonstrated good performance with sugar solutions but poor performance (19% to 26% 5-HMF, 51% to 66% furfural for biphasic, <30% for IL) on cellulose and biomass[30], necessitating additional biomass pretreatment.

In this paper, we demonstrate that metal halide acid catalysts in combination with THF is as a novel miscible co-solvent can significantly improve yields for co-production of both furfural and 5-HMF from lignocellulosic biomass such as maple wood and corn stover from that possible before. In this way, biomass pretreatment and catalytic dehydration of soluble sugars can be performed in a one-pot reaction. We first screened five promising metal salt acid catalysts $AlCl_3$, $CuCl_2$, $CrCl_3$, $FeCl_3$, and $ZrOCl_2$ for sugar conversion and selectivity for furfural, 5-HMF, and LA production by applying our co-solvent system to sugar solutions. We then optimized reaction severity and solvent loadings in 1 L scale biomass reactions with maple wood and corn stover catalyzed by these metal halides to achieve the highest furfural and 5-HMF yields reported from these feedstocks by a single phase reaction strategy. The results reveal how different Brønsted and Lewis activities of metal halide acid catalysts can play a key role in harmonizing the dehydration kinetics of both C5 and C6 sugars and degradation reactions of the final products to maximize overall yields of furanic products for a biorefinery process.

2. Materials and Methods

2.1 Experimental Materials

Reagent-grade THF (>99% purity, Fisher Scientific, Pittsburgh, PA) was used in all THF co-solvent reactions. The THF co-solvent solution was prepared on a volume basis of increasing the amount of THF additions to realize 1:1 (THF 50 % v/v) to 7:1 (THF 87.5 % v/v) THF-to-water ratios. Hydrated metal halide catalysts and ≥99% pure xylose and glucose sugars were purchased from Sigma Aldrich (St. Louis, MO, US). Due to the high purity of the purchased sugars from Sigma, we use the term pure sugars to designate solutions prepared using these sugars. The hydrate form of each metal halide catalyst ($AlCl_3{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $CrCl_3{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, and $ZrOCl_2{\cdot}8H_2O$) was used but were loaded based on their equivalent anhydrous mass to achieve 0.1M or 1 wt% catalyst loading. Concentrated sulfuric acid (72 wt% H_2SO_4) was purchased from Ricca Chemical Company (Arlington, TX) and used to make dilute sulfuric acid solutions.

Maple wood chips obtained in upper New York State were provided by Mascoma Corporation (Lebanon, NH), and air-dried Kramer corn stover was provided by the National Renewable Energy Laboratory (NREL, Golden, CO, Lot #33A14). The relatively dry biomass (10-15% moisture) was knife milled to pass through a 1 mm particle size interior sieve using a laboratory mill (Model 4, Arthur H. Thomas Company, Philadelphia, PA). Biomass composition was determined according to the established National Renewable Energy Laboratory procedure (TP-510-42618, ver. 8-03-2012) in triplicates with a resulting composition of 40.9 ± 0.3 wt.% glucan, 15.5 ± 0.2% xylan, 2.1 ± 0.1% mannan, 24.4 ± 0.3% K-lignin, and 17.1% other material for maple wood and 32.7 ± 0.4 wt.% glucan, 20.7 ± 0.2% xylan, 2.6 ± 0.1% arabinan, 16.0 ± 0.1% K-lignin, and 28.0% other material for corn stover. Other materials needed for the biomass composition to total 100% were not characterized in this study but were expected to include minor saccharides, ash, sugar acids, acetate, and protein[31]. Because arabinan, galactan, and mannan were not present in significant quantities and specific quantification of these minor sugars was difficult via HPLC, we elected to treat all quantified biomass pentosans as xylan and all hexosans as glucan.

2.2 THF Co-Solvent Sugar Reactions

Sugar solutions were prepared in 1:1 THF:water co-solvent mixture containing 20 g/L glucose or 10 g/L xylose and 0.1M (anhydrous) loading of the metal halide catalyst based on total liquid volume. Due to the different acidities of each catalyst, all solutions were normalized to 1.6 pH by titrating with 72 wt% concentrated sulfuric acid. An acidity of 1.6 pH was selected because it was close to the Brønsted acidity of the most acidic 0.1M $ZrOCl_2$-containing mixture (Table 1). Pure sugar solutions containing only sulfuric acid were also prepared and titrated to 1.6 pH to directly compare with metal halide acid catalysts as an acid control.

The reactions were carried out in non-stirred 14.3 mL Hastelloy tube reactors (Hastelloy C-276, O.D. of 0.0127 m or 0.5 in.) with a wall thickness of 0.0008890 m (0.035 in.) and length of 0.1524 m (6 in.) to give a working reaction liquid volume of 10 mL. The tube reactors were loaded into a heavy-duty custom steam chamber made of readily available steam rated (to 1 MPa steam pressure) 316 stainless steel 0.102 m (4 in.) internal diameter fittings (McMaster, Santa Fe

Springs, CA). A high-pressure steam boiler (FB-075-L, Fulton Companies, Pulaski, NY) provided steam for rapid and stable heating of triplicate tube reactors. Temperature was monitored by both in-line pressure gauges and two K-type thermoprobes (Omega Engineering Co., Stamford, CT) and controlled by a PID controller via steam pressure. Due to the lengthwise construction of the tube reactors and the application of steam for heating and cold water for quenching, heat transfer was relatively rapid (<30 sec) even for shorter reaction times (<10 min)[32]. Initial time was defined when a reaction temperature of 170 °C was reached. At the end of the reaction, the steam supply was shut off and the steam chamber was flooded with tap water to stop the reaction.

The liquid content of each reaction tube was transferred into 2 mL glass vials. These samples were centrifuged (2500 rpms for 20 min) and the supernatant was transferred into glass HPLC vials for HPLC analysis by an Agilent 1200 system equipped with a Bio-Rad Aminex® HPX-87H column and RI detector with an eluent (5 mM sulfuric acid) flow rate of 0.6 ml/min. The calculations for conversion of sugars and selectivity of secondary fuel precursor products are shown below where Ω is the molar equivalence ratio from the starting sugar:

$$\text{(1)} \quad \text{\% Conversion} = \left[1-\frac{\text{Sugar concentration}_{final}(\text{g/L})}{\text{Sugar concentration}_{initial}(\text{g/L})}\right]*100\%$$

$$\text{(2)} \quad \text{\% Selectivity} = \text{FP concentration}_{final}(\text{g/L}) * \Omega \,/\, \text{\% Conversion}$$

$$\text{(3)} \quad \Omega_{\text{furfural}} = \frac{1.563}{\text{Concentration of xylose}_{\text{initial}}}$$

$$\text{(4)} \quad \Omega_{\text{LA}} = \frac{1.552}{\text{Concentration of glucose}_{\text{initial}}}$$

$$\text{(5)} \quad \Omega_{\text{5-HMF}} = \frac{1.428}{\text{Concentration of glucose}_{\text{initial}}}$$

2.3 THF Co-Solvent Maple Wood and Corn Stover Biomass Reactions

Corn stover or maple wood solids loadings were calculated based on the total mass of the reaction (800 g) so that each reaction contained 5 wt% solids (40 g dry basis) and 1 wt% acid (7.6 g by anhydrous weight) based on THF:water mixture weight (760 g). Biomass mixtures were then allowed to pre-soak overnight at 4°C to insure an even distribution of acid catalyst within the biomass pores. Contents were then left in the laboratory for an hour for the temperature to reach about room temperature prior to reaction.

The whole biomass slurry was then transferred to a high-pressure continuously stirred 1 L Parr reactor (Parr Instrument Company, Moline, IL) heated by a 4 kW fluidized sand bath (Model SBL-2D, Techne, Princeton, NJ). Mixing was performed by twin 6-blade impellers operating at 200 rpm by a top mounted electric motor, and the reactor temperature was directly measured by an in-line thermocouple (Omega, K-type). At the conclusion of a run, the reactor was cooled by quickly lowering it into a large room temperature water bath. All liquid containing receptacles were made of glass to prevent the loss of furfural and THF that was observed when plastics were used. The solids were then separated from the reaction liquor by vacuum filtration at room temperature through glass fiber filter paper (Fisher Scientific, Pittsburgh, PA). Mass and density of the liquid fraction were measured to complete accurate yield calculations. Due to the difference in density between the co-solvent mixtures and pure water, final densities were determined by weighing 25 mL of the reacted liquid in a volumetric flask after each reaction.

Liquid samples were analyzed by an Agilent 1200 HPLC system equipped with a Bio-Rad Aminex® HPX-87H column and RI detector with an eluent (5 mM sulfuric acid) flow rate of 0.6 ml/min. Since the HPX-87H column cannot distinguish between xylose, mannose, and galactose sugar peaks, we also equipped our HPLC with an Aminex® HPX-87P column to differentiate xylose from the other C6 sugars for yield calculations. Since the HPX-87P column is incompatible with acids, we elected not to use this column for fuel precursor analysis. Calculation of the fuel precursor yields is given by Equation (6) where the molar equivalent number (θ) of furfural (Eq. 7), LA (Eq. 8), and 5-HMF (Eq. 9) are individually calculated and divided by the fraction of the total glucan or xylan in the raw material.

$$(6) \quad \%\ \text{FP yield} = \theta_{FP} * \frac{\text{FP}_{\text{final}}(\text{g/L}) * \text{mass of liquor}_{\text{final}}(\text{g})}{\text{total biomass}_{\text{initial}}\ (\text{g}) * \text{density of liquor}_{\text{final}}(\text{g/L})} * 100\%$$

$$(7) \quad \theta_{\text{furfural}} = \frac{1.375}{\text{fraction of total xylan}_{\text{initial}}}$$

$$(8) \quad \theta_{\text{LA}} = \frac{1.396}{\text{fraction of total glucan}_{\text{initial}}}$$

$$(9) \quad \theta_{\text{5-HMF}} = \frac{1.286}{\text{fraction of total glucan}_{\text{initial}}}$$

For the recovery of extracted lignin, the reaction liquor was transferred to a glass bottle with a screw-on cap that was tapped with a 0.25 in. metal hose barb fitting. The fitting was connected by a flexible hose to a vacuum pump to perform vacuum distillation of THF. The liquor was agitated by a magnetic stir bar on a stir plate as THF was boiled off at room temperature under vacuum. Once the THF was removed from the aqueous liquor, the extracted lignin precipitates from solution as a black resinous solid. The solid lignin residue was then separated from the liquor and crushed to a fine powder by a ceramic mortar and pestle. The powder was then rinsed with water, air-dried, and then rinsed with diethyl ether. The resulting fine lignin powder product is shown in Figure 6.

3. Results and Discussion

3.1 Assessment of Catalyst Performance in Sugar Reactions

Little is currently known about the application of THF as a water-miscible co-solvent to enhance the production of FPs from biomass sugars. Although strong mineral acids such as sulfuric acid have been used successfully to improve FP yields with THF co-solvent[22], metal halide acid catalysts are promising alternatives that are less corrosive, recyclable, and more selective than strong mineral acids[33]. Table 1 shows the measured pH for the sugar co-solvent solutions containing 0.1M of each metal halide before titration to 1.6 pH. It is known that metal oxide species form when the metal halides are hydrolyzed by water at elevated temperatures and the formation of OH ligands (as electron pair donors) during hydrolysis of the metal cations increases their acidity[34]. The resulting pH of the solution is related to the first hydrolysis constant of the cationic species[34], where we found Zr and Fe cations to be the strongest. Metal chlorides are also known to form stable adducts with THF which can influence their ionizability and catalytic activity. As Brønsted acidity typically dominates sugar dehydration kinetics, we elected to normalize the pH of all the sugar solutions to 1.6 using sulfuric acid (close to that of the most acidic metal halide) prior to each reaction. Doing so allowed us to better understand how the relative Lewis strength of each catalyst influenced their selectivity to secondary fuel precursors, the propensity for degradation of final products, and the tunability of the catalysts for optimizing co-production of furfural and 5-HMF from biomass.

Table 1. pH of metal halide catalysts in co-solvent solution containing 1:1 THF:water[a]

Catalyst	pH
$CrCl_3{\cdot}6H_2O$	3.13 ± .01
$AlCl_3{\cdot}6H_2O$	2.88 ± .02
$CuCl_2{\cdot}2H_2O$	2.78 ± .01
$FeCl_3{\cdot}6H_2O$	1.90 ± .01
$ZrOCl_2{\cdot}8H_2O$	1.65 ± .01

[a] 0.1M catalyst loading based on each catalyst's anhydrous mass.

In order to characterize catalyst performance with this co-solvent system, we reacted pure glucose and xylose in 1:1 (v:v) THF:water solutions using different metal halides to compare sugar conversion and selectivity toward furfural, 5-HMF, and LA. Metal halides $AlCl_3{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $CrCl_3{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, and $ZrOCl_2{\cdot}8H_2O$ were selected for this comparison as they have demonstrated high selectivity towards furfural and 5-HMF in previous literature reports[24, 26, 33, 35, 36]. The sugar co-solvent solutions contained either 20 g L^{-1} glucose or 10 g L^{-1} xylose to simulate likely sugar concentrations from real biomass reactions at 5 wt% solids loading. Each metal halide was added based on their anhydrous catalyst mass to a concentration of 0.1M for each reaction. The sugar solutions were then loaded into Hastelloy tube reactors (10 mL working volume) and heated to 170°C by a custom designed stainless steel steam chamber. The reaction proceeded until the steam was turned off and the chamber was flooded with cold tap water to quench the reaction. As shown in Figure 2A and 2B, the conversion of both xylose and glucose was significantly improved by all metal acid catalysts beyond what was possible for sulfuric acid alone in the THF co-solvent system. The relative performances of the metal halides were also very consistent for glucose and xylose. The most active metals were Cr, Zr, and Al due to their high Lewis acid strength, achieving nearly complete conversion of xylose by 5 min and glucose by 10 min. Cu- and Fe- based catalysts were notably slower in sugar conversion, but still achieved near complete conversion after 20 min.

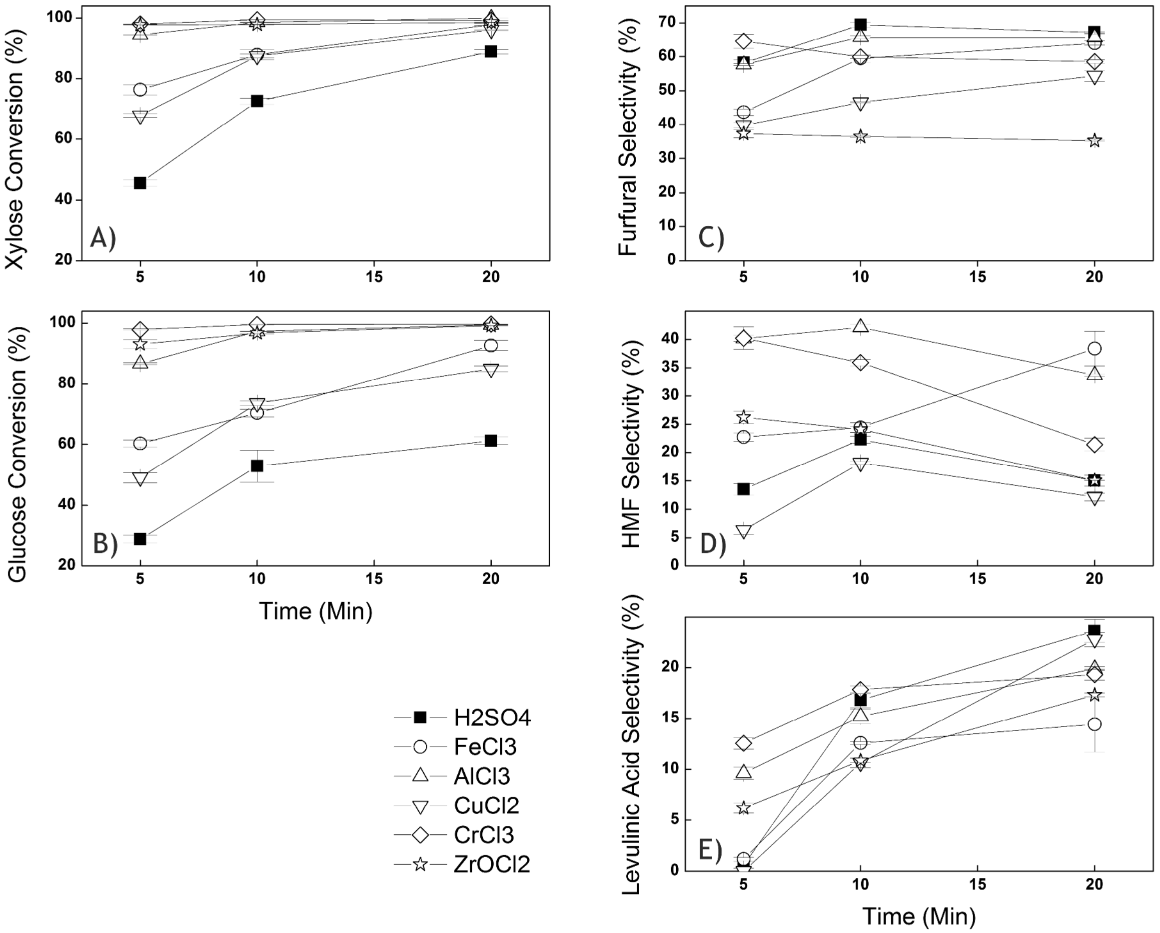

Figure 2. Conversions and selectivities for pure sugar reactions with metal halide acid catalysts in THF co-solvent mixture plotted against reaction time. A) xylose and B) glucose conversions and C) furfural selectivity from xylose and D) 5-HMF and E) LA selectivity from glucose. Reaction conditions: 170°C, 20 g L^{-1} glucose or 10 g L^{-1} xylose, 1:1 THF: water ratio, 0.1M catalyst loading, and normalization of all solutions to pH 1.6 using 72% sulfuric acid. Black squares represent sulfuric acid control also titrated to 1.6 pH. Error bars represent one standard deviation.

In all of the THF co-solvent sugar reactions, we observed accumulation of secondary sugar species whose retention times on the HPLC matched that of fructose and xylulose. Their concentrations also tracked that of glucose and xylose disappearance over the course of the reaction suggesting that aldose-to-ketose isomerization occurred at a faster rate than sugar dehydration (Concentrations shown in Supplementary Information Figure S1 and Figure S2).

Although it is known that metal halides catalyze an open-chain reaction mechanism that produces ketose sugars with a lower energy barrier for dehydration[26], we also found ketose sugars in the sulfuric acid reactions suggesting that THF co-solvent promotes a similar mechanism involving sugar isomerization. This observation supports our earlier findings that THF appeared to co-catalyze C5 and C6 sugar dehydration[22] by promoting the more kinetically favorable open-chain dehydration pathway.

Selectivity to the secondary FPs was then calculated based on their concentrations after each reaction. In terms of furfural selectivity from xylose (Fig. 2C), sulfuric acid achieved a maximum of about 70% selectivity at 10 min that bested all other metal salt catalysts. This result suggested that although the Lewis acid character of the metal halides accelerated destruction of sugars, it also promoted competing loss reactions that diminished furfural accumulation in solution attributed to condensation reactions between intermediate sugar species and furanic products to form humins[26]. Due to rapid sugar conversion, the Cr catalyst achieved the highest furfural selectivity of about 65% earliest at 5 min, whereas $FeCl_3$ required 20 min to reach a maximum furfural selectivity of also about 65%. $ZrOCl_2$ had the lowest selectivity to furfural despite its ability to rapidly degrade xylose, likely due to the high formation of loss products.

In the case of 5-HMF selectivity from glucose (Fig. 2D), all metal salts except $CuCl_2$ achieved higher selectivities (~40%) than sulfuric acid (~22%) in the co-solvent system, with Al, Cr, and Fe metals performing best. Again, the Fe- based catalyst required the longest reaction time and continually increased 5-HMF selectivity over the entire time, with it reaching 38% after 20 min. Interestingly, for all catalysts except $CuCl_2$, the maximum selectivity for both furfural and 5-HMF occurred at approximately the same time with the best co-production of the furfurals demonstrated by Al, Cr, and Fe metals. Overall, however, 5-HMF selectivity was significantly lower than furfural selectivity owing to significant loss reactions to both condensation products and LA[37]. This was apparent by the more drastic drop in 5-HMF selectivity than observed with furfural over the course of the reaction for all the metal halides except $FeCl_3$.

In the case of LA selectivity from glucose (Fig. 2E), all metal halides demonstrated lower selectivity to LA formation than sulfuric acid, in line with the goal of this study. As LA is produced from the hydrolysis of 5-HMF in this system, $CuCl_2$ and sulfuric acid achieved the highest LA selectivity as their selectivity towards 5-HMF was lowest. By extrapolation of the increasing trend of LA selectivity over longer reaction times, we believe furfural and LA are not compatible co-products on a basis of their formation kinetics. Instead, furfural and 5-HMF can be produced together, whereas LA production would be most effectively targeted in a reaction independent of furfural. The more rapid sugar conversions observed with Cr-, Zr-, and Al- based halides compared to the slower Fe- and Cu- based halides are important differences among these catalysts that can help explain their performance in reacting actual biomass reported in the next section. Quantifiable parameters in the sugar reactions such as sugar conversion, fuel precursor selectivity, and acidity of these metal halide catalysts will impact biomass conversion to achieve high combined furfural and 5-HMF yields.

3.2 Co-Production of Furfural and 5-HMF from Maple Wood and Corn Stover

The primary fractions of lignocellulosic biomass of interest for catalytic conversion to platform chemicals are cellulose, hemicellulose, and lignin. Xylan contained within amorphous hemicellulose presents the most readily available source of sugars as it can be completely hydrolyzed at mild to moderate severity reaction[38]. Cellulose, on the other hand, is composed of crystalline polymeric glucose chains that are a primary source of C6 but remains the most recalcitrant sugar fraction to acid hydrolysis and is usually treated with cellulase enzymes after pretreatment to achieve high yields of glucose monomers in solution[39]. Because the hemicellulose fraction of lignocellulosic biomass is far more acid-labile than crystalline cellulose, furfural is produced much sooner than 5-HMF and LA[9]. Thus, an integrated conversion strategy to co-produce furfural and 5-HMF directly from biomass must be tunable to minimize competing side reactions of the least stable products to maximize product yields. For this reason, optimization for high furfural yields is a primary concern as the glucan remaining in the slower solubilizing cellulose fraction can be recovered as a solid product for further biological conversion into glucose or thermochemical conversion into glucose, 5-HMF, and/or LA if not all of it was converted into 5-HMF or LA.

In addition to manipulation of the temperature, time, and acid loadings (combined reaction severity) to optimize yields from a biomass reaction, the THF co-solvent strategy allowed additional tuning by increasing THF concentrations in water to achieve greater selectivity to 5-HMF and increased biomass solubilization[22]. In this study, we compared the performance of the metal halide catalysts against sulfuric acid in 1 L THF co-solvent reactions with 5 wt% loading of maple wood or corn stover. Table 2 lists the secondary FP yields achieved at the reaction conditions found to maximize production of both furfural and 5-HMF for each catalyst.. The THF:water ratio was also varied from 1:1 to 7:1 (by volume) to determine the extent of improved product yields and the limit of the single phase regime. The catalysts were loaded on a mass basis similar to commercial operation at a dilute 1 wt% in terms of the total liquid mass contained within the reaction. The heating temperature profile of the reactor shown in the supplementary information (Figure S3) demonstrated that total heating time to a stable 170 °C reaction temperature could be achieved in about 5 min.

As shown in Table 2 (Runs 1-9), with the exception of $CrCl_3$ and $ZrOCl_2$, metal halide catalysts demonstrated very consistent performance on both maple wood and corn stover, achieving maximum furfural yields close to that of sulfuric acid for a 1:1 THF:water mixture. 5-HMF yields were more comparable among catalysts, but metal halides produced lower LA yields compared to sulfuric acid owing to their increased selectivity to 5-HMF as found for the sugar reactions. Surprisingly, the high furfural (65%) and 5-HMF (40%) selectivities achieved by $CrCl_3$ from the model sugar solutions were not translated to better furfural yields (43%) from biomass. The results of the sugar reactions shed some light on the poor performance $CrCl_3$ and $ZrOCl_2$ with biomass. In solution, the lower acidity of $CrCl_3$ (pH 3.13) compared to the other metal halides (Table 1) may have limited its ability to hydrolyze sugar polymers effectively, particularly without the help of sulfuric acid. Consequently, the excellent xylose conversion performance of $CrCl_3$ (100% in 5 min, Figure 2A) may have negatively impacted furfural yields from biomass as furfural losses quickly exceeded furfural production due to much slower release of xylose from biomass. As seen by the rapid drop in furfural selectivity for xylose reactions with $CrCl_3$ (Figure 2C), the potential for high furfural yields from biomass suffered from the longer reaction times needed by the biomass reactions. We also suspect that the strong Lewis acid character of $CrCl_3$ was responsible for significant furfural losses. For $ZrOCl_2$, poor furfural selectivity from xylose (37%) resulted in low furfural yields (44%) despite having the highest Brønsted acidity (pH 1.65) of the group. Conversely, $FeCl_3$ was the best performer due to its higher Brønsted acidity, slower xylose conversion rates, and higher furfural selectivity at longer reaction times. $AlCl_3$ and $CuCl_2$ were middle performers owing to their more moderate Brønsted character, with trade-offs between higher 5-HMF yields or high furfural yields, respectively, consistent with their selectivity with the sugar reactions.

Table 2 Acid-catalyzed co-production of furfural, 5-HMF, and LA from maple wood and corn stover in batch reactions with THF co-solvent[a]

Run #	THF:Water[c]	Substrate[b]	Acid catalyst[d]	Time (min)	Solids remaining (%)	Yields (of theoretical)[f] Furfural (%)	5-HMF (%)	LA (%)
1[e]	1:1	Maple wood	H_2SO_4	40	21	87	13	11
2	1:1	Maple wood	$FeCl_3$	40	25	85	16	4.7
3	1:1	Maple wood	$CuCl_2$	30	29	83	14	6.3
4	1:1	Maple wood	$AlCl_3$	40	30	58	18	9.3
5	1:1	Maple wood	$CrCl_3$	40	30	43	15	5.9
6	1:1	Maple wood	$ZrOCl_2$	40	39	44	14	11
7	1:1	Corn stover	H_2SO_4	40	19	84	16	11
8	1:1	Corn stover	$FeCl_3$	40	31	85	12	4.0
9	1:1	Corn stover	$ZrOCl_2$	40	43	38	14	12
10[e]	3:1	Maple wood	H_2SO_4	60	1	86	21	40
11	3:1	Maple wood	$FeCl_3$	60	11	97	41	13
12	3:1	Maple wood	$CuCl_2$	60	16	81	22	21
13	3:1	Maple wood	$AlCl_3$	60	16	75	33	8.8
14	3:1	Corn stover	$FeCl_3$	80	14	97	42	12
15	3:1	Corn stover	$CuCl_2$	60	20	89	22	14
16	3:1	Corn stover	$AlCl_3$	60	22	76	36	17
17	4:1	Maple wood	$FeCl_3$	60	10	**95**	**51**	**6**
18	4:1	Corn stover	$FeCl_3$	80	15	**95**	**45**	**7**
19	7:1	Maple wood	$FeCl_3$	60	21	83	43	3

[a] All reactions were performed using a 1L Parr reactor at 170 C reaction temperature. [b] 5 wt% total solids loading. [c] By volume ratio. [d] All catalysts were loaded at 1 wt% anhydrous content. [e] Data from these runs are reported previously.[22] [f] Furfural yield calculated from raw xylan content, 5-HMF and LA yield calculated from raw glucan content.

In order to investigate the extent of biomass solubilization for each catalyst, maple wood was reacted for 30 min in an 1:1 THF co-solvent mixture and 5 wt% initial biomass loading and 0.1M equivalent catalyst loading in the 1 L Parr reactor. Figure 3 shows the composition of raw maple wood solids and the distribution of the major components in the solids remaining after reaction on the mass basis of 100 g of raw maple wood feed. As shown, biomass solubilization with metal halides was reduced compared to sulfuric acid. Also shown, over 90% of the maple wood K-lignin was removed during all metal halide reactions, except with $ZrOCl_2$, leaving behind a substantial amount of glucan-rich solids that contain no hemicellulose and minute amounts of other components. In the 1:1 THF reactions, maximizing lignin free glucan rich solids recovery from the co-solvent reaction is crucial to enhance the economics of this process as the cleanly fractionated solids are suitable as a direct feed to produce fermentable glucose or used to make additional 5-HMF or LA. In the case of $ZrOCl_2$, reduced delignification and the presence of a large non-sugar fraction (labeled 'Other' in Figure 3) provide an interesting opportunity for future study to help explain why its performance for producing FPs from real biomass was significantly poorer than by other catalysts. The non-sugar fraction may have resulted from accumulation of polymeric degradation products on the solids as the actual glucan remaining in the solids was much lower than from sulfuric acid catalyzed reactions. Composition of this non-sugar fraction still needs to be determined.

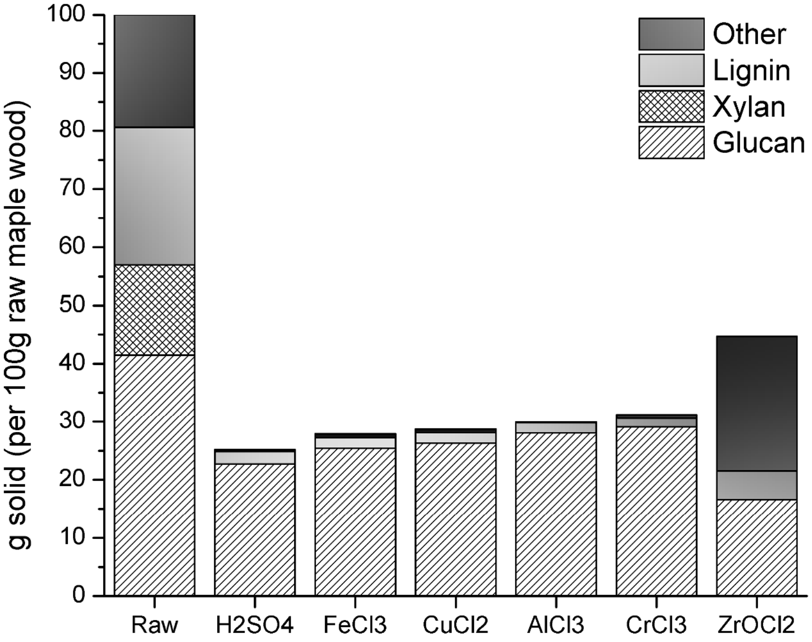

Figure 3. Composition of raw maple wood and distribution of major components to the solids remaining after reaction with 1:1 THF co-solvent and various acid catalysts based on 100 g of initial maple wood fed to the systems. Metal halides improved upon sulfuric acid performance by delivering greater amounts of glucan-rich solids for enzymatic conversion to glucose or thermochemical reaction to glucose, 5-HMF, and/or LA. Reaction conditions: 5 wt% maple wood, 0.1M acid catalyst concentration, 1:1 THF:water, 170°C, 30 min batch reactions. Numerical data and calculated standard deviations are shown in Table S1.

Greater biomass solubilization at the higher solvent ratio of 3:1 (as shown in Table 2, runs 10-16) can support a reaction strategy that is more focused on furfural and 5-HMF production with less recoverable solids. At a 3:1 THF-to-water volume ratio, the top three performing (Al, Cu, Fe) metal halide catalysts greatly enhanced co-production of furfural and 5-HMF from maple wood and corn stover compared to sulfuric acid. In these reactions, $FeCl_3$ outperformed $CuCl_2$ and $AlCl_3$ in both furfural (97% yield for maple wood and corn stover) and 5-HMF (41% yield for maple wood and 42% for corn stover) production and biomass solubilization (11% solids remaining). $CuCl_2$ was unable to solubilize biomass as quickly as $FeCl_3$, and its lower 5-HMF yields from both maple wood and corn stover reactions could be explained by its lower 5-HMF selectivity (Figure 2D) from glucose in the sugar reactions. For $AlCl_3$, tuning the reaction to achieve high furfural and 5-HMF co-production was difficult as the optimal reaction time for furfural was 20 min shorter than for 5-HMF. Thus, higher furfural yields (81%) were achieved with $CuCl_2$ at the expense of greater 5-HMF losses (22% yield) at 60 min and higher 5-HMF yields (36%) were achieved with $AlCl_3$ at the expense of lower furfural yields (76%) at 60 min. Overall, the consistency in performance between corn stover and maple wood in all reactions indicated that the THF co-solvent system may be largely feedstock agnostic and capable of achieving high yields in heterogeneous or mixed feedstock streams, appealing to commercial feasibility.

At a 4:1 solvent ratio (Table 2, runs 17-18), $FeCl_3$ significantly outperformed sulfuric acid and the other metal halides and achieved the highest reported co-production yields of furfural (95% for both maple wood and corn stover) and 5-HMF (51% for maple wood and 45% for corn stover) from lignocellulosic biomass by a one-pot single phase reaction. The higher solvent ratio was also beneficial to further reducing yields of LA (6-7% at 4:1 ratio), the most difficult product to recover due to its high boiling point (245 °C). Thus, $FeCl_3$ proved to be the best metal halide for catalyzing co-production of furfural and 5-HMF in a biomass process using THF as a miscible co-solvent. Its strong acid strength allowed for reasonably fast deconstruction of both maple wood and corn stover, and the close reaction time for optimal furfural and 5-HMF production was beneficial to achieving good yields of both in one pot reaction. As shown in Figure 4, the 10% solids remaining after 4:1 co-solvent reaction of maple wood were very rich in glucan and could be recovered for efficient conversion to glucose by enzymes or further thermochemical reaction to 5-HMF and/or LA. A mass balance is shown for this run in the Supplementary Information (Figure S4) insuring accountability for 80% of the C6 products and 95% of the C5 products in the soluble and insoluble products after reaction.

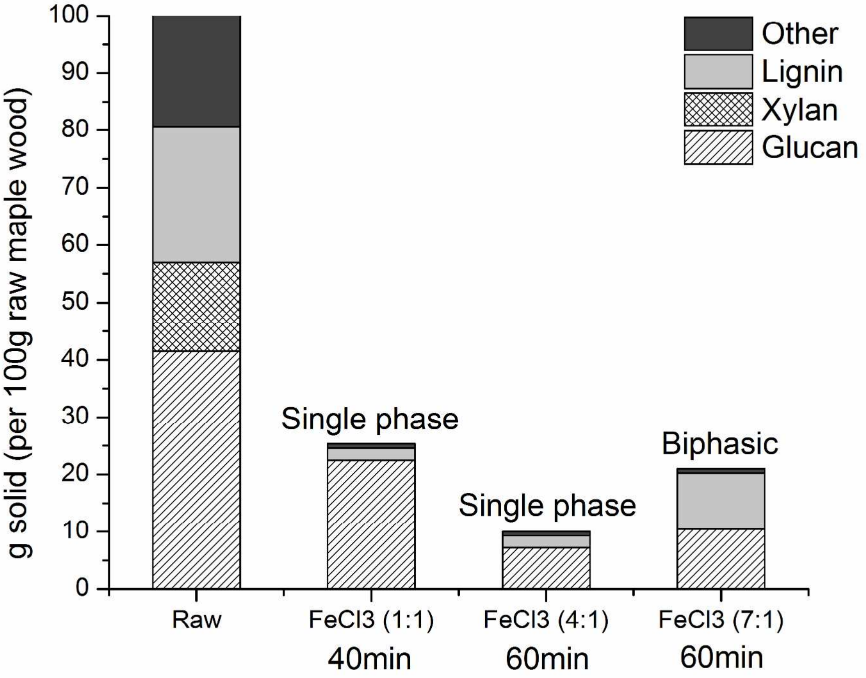

Figure 4. Composition of raw maple wood and distribution of major components of the solids remaining after reaction with THF co-solvent with $FeCl_3{\cdot}6H_2O$ at 1:1, 4:1, and 7:1 THF:water volume ratios. Solid mass is based on 100 g of initial maple wood fed to the systems. Suspected phase separation at 7:1 ratio is evident by larger lignin fraction, decreased solids solubilization, and increased remaining glucan fraction after 60 min reaction compared to the 4:1 ratio case. Reaction conditions: 5 wt% maple wood, 1 wt% $FeCl_3{\cdot}6H_2O$ based on anhydrous mass, 170°C. Numerical data and calculated standard deviations are shown in Table S1.

We found that at a 7:1 THF-to-solvent ratio (Table 2, run 19) or beyond, the behavior of the reaction suddenly shifted to resemble a two-phase regime. Although we were unable to qualitatively determine this yet (such as by a sight glass in the reactor), the reaction kinetics and composition of the resulting solid material strongly suggested that the system could have become biphasic at such high THF ratios over the course of the reaction. In such a biphasic reaction, the dehydration kinetics of the aqueous phase are largely unaffected by the presence of the extracting solvent[40]. Thus, THF would no longer be able to accelerate biomass solubilization as evident by the much higher solids fraction that remained after reaction (21% for Run 19 vs. 10% for Run 17 in Table 2). As shown in Figure 4, compositional analysis of this solid fraction also revealed that a larger glucan portion remained unsolubilized and more of the lignin was still intact and not extracted as would be expected at lower concentrations of THF. Reaction pressures increased from 225 psig to 265 psig and was the highest observed and close to the sum of the saturated vapor pressures of water and THF. Nevertheless, high yields of both furfural (83%) and 5-HMF (43%) were achieved with very little LA production (3%), but yields were slightly lower than the 4:1 case. In addition, because biomass often has moisture contents of up to 50% by weight for woods, elevated solvent ratios, such as 7:1 or higher would likely hurt biomass processing economics by requiring larger reactor sizing and consume more heat. The impressive co-production yields achieved by the THF co-solvent system without needing high solvent concentrations (such as >9:1 using GVL) is an important consideration when comparing other recently developed co-solvent systems[41].

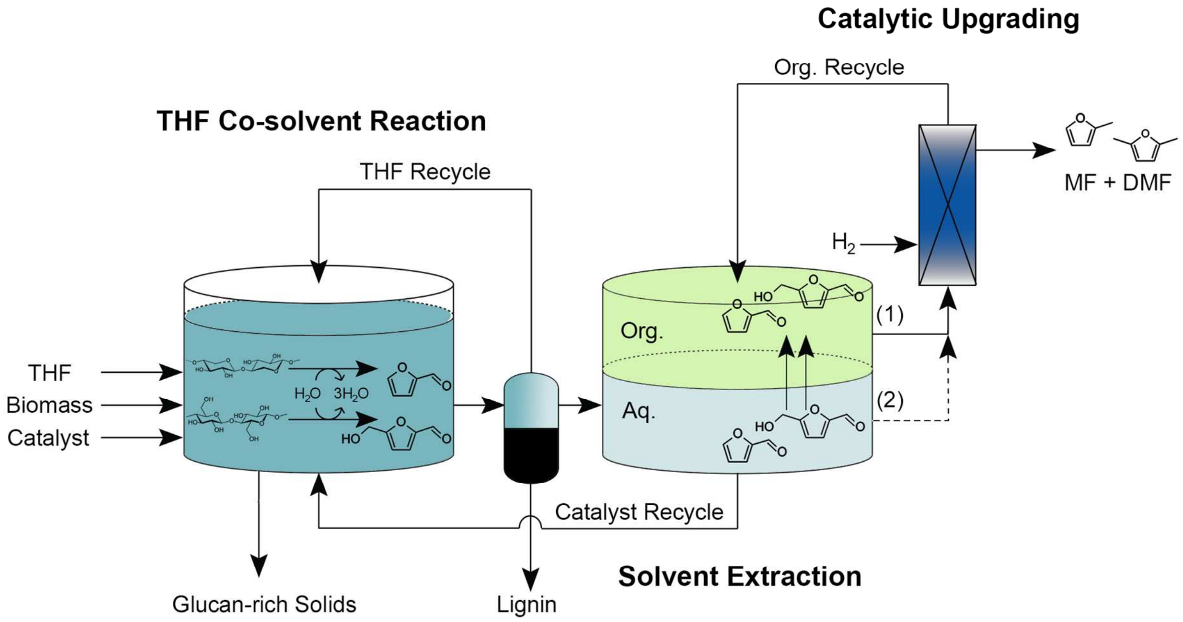

Figure 5. Simplified process diagram of the proposed THF co-solvent strategy for direct conversion of lignocellulosic biomass to co-produce furfural and 5-HMF for catalytic upgrading to aromatic fuel products. Furfural and 5-HMF will be extracted by an organic solvent and hydrogenated (blue box, right) to produce aromatic fuels such as MF and DMF. Lignin is precipitated upon recovery of THF. (1) Organic stream containing furfural and 5-HMF (2) Aqueous stream containing metal halide catalyst, furfural and 5-HMF.

Figure 5 outlines a proposed integrated THF co-solvent strategy for application of metal halide catalysts to enhance direct conversion of biomass into furfural and 5-HMF followed by two possibilities for their hydrogenation to MF and DMF, respectively. The experimental work in this study was focused on producing high FP yields to be most compatible with leading downstream catalytic upgrading operations. In the process concept pictured in Figure 5, raw biomass and acid catalyst are loaded into a reactor along with THF co-solvent solution, as shown in Figure 6A. Following reaction, high yields of both furfural and 5-HMF are achieved, and the reacted slurry is then collected and filtered to separate the solid residues. As THF is a low boiling solvent (66°C) and forms a 95.4% azeotrope with water, it could be easily flashed off in a biorefinery to be recovered and recycled[42]. In fact, we found that room temperature vacuum distillation was sufficient to recover THF from the water phase[22].

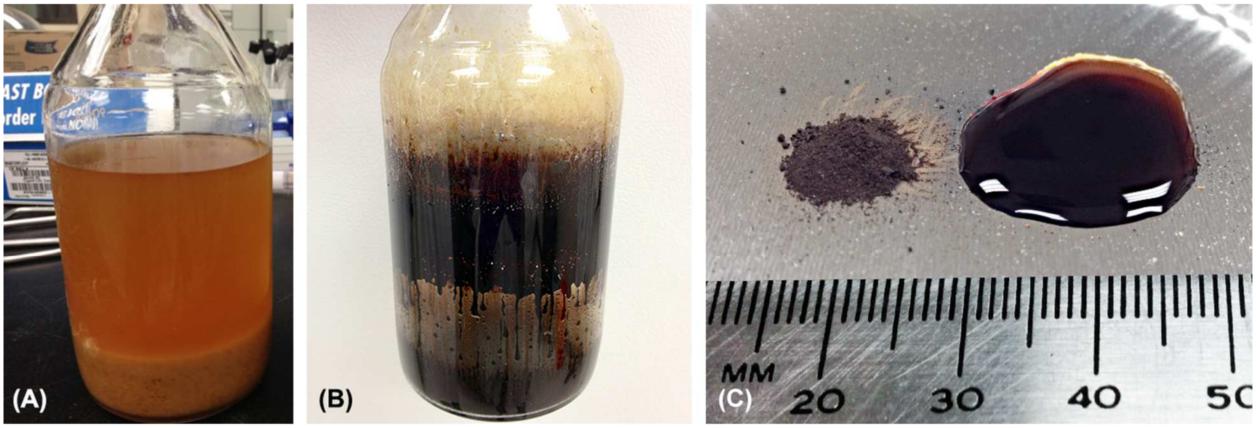

Figure 6. (A) 1 L THF co-solvent solution containing 5 wt% maple wood. (B) Precipitated lignin residue after co-solvent reaction, recovery of THF, and water removal. (C) Left, precipitated lignin powder from maple wood after co-solvent reaction with $FeCl_3$ catalyst. Right, same lignin powder shown dissolved in a large droplet of dimethylsulfoxide (DMSO). Metric ruler is shown for reference.

The removal of THF also precipitates extracted biomass lignin as a solid (Figure 6B) that can be recovered and rinsed with diethyl ether to produce a very pure lignin powder as shown in Figure 6C (left). This powder can in turn be re-dissolved in THF or DMSO (Figure 6C, right) and is suitable for catalytic upgrading to valuable chemicals[43]. Afterwards, an appropriate organic solvent (Figure 5, Stream (1)), such as MTHF, can be used as an immiscible solvent to extract and concentrate furfural and 5-HMF into the organic layer, leaving most of the trace sugars and contaminants in the aqueous layer. Alternatively, the aqueous stream resulting from THF removal could be fed directly to a catalytic reactor (Figure 5, Stream (2)) if desired, depending on the catalyst system chosen for upgrading furfural and 5-HMF. The aqueous stream containing the catalyst could be recycled as $FeCl_3$-containing aqueous streams have been shown to remain effective over several reactions in other systems[44]. In future studies, we will develop and optimize a high performance catalyst system to achieve high selectivity to final fuel products, such as MF and DMF, from the product stream of the THF co-solvent reaction.

4. Conclusions

Metal halides are non-corrosive and highly selective acid catalysts suitable for co-production of furfural and 5-HMF directly from lignocellulosic biomass without a separate pretreatment step. We presented here coupling metal halides with THF as a novel green co-solvent in a highly effective single phase conversion strategy that achieved one of the highest reported co-production yields of furfural and 5-HMF directly from biomass, producing a clean product stream suitable for catalytic hydrogenation to final fuel products. pH-controlled reactions with pure sugar and larger 1L scale reactions with maple wood and corn stover demonstrated that key differences in the catalytic nature of these metal halides affected conversion of lignocellulosic biomass. Screening of several promising metal halides $AlCl_3 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CrCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, and $ZrOCl_2 \cdot 8H_2O$ on the basis of sugar conversion and selectivity to secondary fuel precursors showed $FeCl_3$ to perform best in the THF co-solvent system owing to its high Brønsted acidity and moderate sugar conversion rate. Surprisingly, $CrCl_3$ did not produce high furfural yields, despite having demonstrated high sugar conversion and selectivity, due to its weaker Brønsted acidity and high Lewis acidity that caused xylose to be rapidly dehydrated and degraded.

At an optimum 4:1 THF:water ratio and 1 wt% $FeCl_3$, the co-solvent reaction achieved 95% yield of furfural and 51% yield of 5-HMF directly from maple wood and similar yields from corn stover after 60 min reaction at 170°C. Depending on the concentration of THF in the reaction, we could tune biomass solubilization to preserve a glucan-rich solid residue that is suitable for further catalytic reaction, enzymatic digestion, or a potential pulp and paper product.

During the co-solvent reaction, THF extracted over 90% of the lignin from biomass that could be recovered as a fine powder. Due to its low boiling point, THF was recovered by room temperature vacuum distillation. Furfural and 5-HMF can be concentrated by an immiscible extracting solvent and the catalyst can be recycled in the aqueous stream. Future study will confirm the recyclability of the catalyst in the aqueous phase and integration with the catalytic conversion of FPs to fuel products.

5. Acknowledgments

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