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$SnCl_4$-Catalyzed Isomerization/Dehydration of Xylose and Glucose to Furanics in Water

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Abstract

A number of Lewis acid catalysts were screened for their effectiveness in converting both xylose and glucose in aqueous media to furfural and 5-HMF, respectively. While other catalysts were found to be more active, $SnCl_4$ was identified as the most selective Lewis acid. Hydrolysis of $SnCl_4$ was observed at various concentrations and temperatures resulting in the production of Brønsted acidic protons in a 3.5:1 ratio to Sn^{4+} at all $SnCl_4$ concentrations above 60 ºC. As a consequence, there was no need to add a Brønsted acid in order to promote the dehydration of either xylose or glucose. $SnCl_4$-promoted isomerization/dehydration of xylose and glucose at 140 ºC in water resulted in conversions of 55% and 33%, respectively, after 2 h of reaction, and furfural and 5-HMF selectivities of up to 58% and 27%, respectively. Significant conversion of sugars to humins was observed in both cases, and in the case of glucose, degradation of 5-HMF to levulinic and formic acids was also noted. The effects of secondary reactions could be greatly suppressed by extraction of the furanic product as it was produced. Using *n*-butanol as the extracting agent, xylose and glucose conversions of 90% and 75%, respectively, were observed after 5 h of reaction, and the selectivities to furfural and 5-HMF increased to 85% and 69%, respectively. Small additional increases in the furfural and 5-HMF selectivities were obtained by adding LiCl to the aqueous phase without much effect on the conversion of either sugar. In this case, the selectivities to furfural and 5-HMF were 88% and 72%, respectively, after 5 h of reaction at 140 ºC.

1. Introduction

Furfural and 5-hydroxymethyl furfural (5-HMF) are of great interest as platform molecules for the production of specialty chemicals and fuels.[1] Both products can be obtained from the carbohydrate portion of lignocellulosic biomass. Furfural is produced by dehydration of xylose, obtained by hydrolysis of hemicellulose, and 5-HMF is produced by dehydration of glucose, obtained by hydrolysis of cellulose. The primary reactions occurring during both dehydration processes are shown in Schemes 1 and 2,[2,3] with the pathways shown in black catalyzed by Brønsted acids and those shown in blue catalyzed by Lewis acids. The dehydration of xylose can occur directly to furfural catalyzed by a Brønsted acid. However, intermediates involved in this process can react with either xylose or furfural to condense and form humins, undesired soluble and insoluble degradation products. In the presence of a Lewis acid, xylose can epimerize to lyxose, and either carbohydrate can isomerize to xylulose. This aldose to ketose isomerization is thought to occur via enolization.[4] Xylulose can then dehydrate with the aid of a Brønsted acid to form furfural. Scheme 2 shows an analogous set of reaction pathways for the conversion of glucose to 5-HMF in the presence of Brønsted and Lewis acids. It should be noted that furfural and 5-HMF can both undergo Brønsted acid-catalyzed secondary reactions. In the case of furfural, self-condensation or resinification leads to humins, and in the case of 5-HMF, hydrolysis of the primary product leads to levulinic and formic acids.

While high yields of furfural and 5-HMF have been reported in organic solvents,[5-7] similar yields have not been achieved for dehydration occurring in water at moderate reaction temperatures. Higher conversions and yield of furanics can be achieved using a mixture of Brønsted and Lewis acids than is possible using only a Brønsted acid catalyst.[2,3,7] The higher conversion of xylose and glucose is a consequence of the lower apparent activation energy barrier for Brønsted acid-catalyzed dehydration of xylulose and fructose, and the higher selectivity to furanics is a consequence of the lower susceptibility of the furanose isomers to participate in degradation reactions compared to the corresponding pyranose isomers.[7] Additional improvements in the yields of furanics can be attained by *in situ* extraction of the product from the aqueous phase into an immiscible organic phase.[1,7-9]

In this work we investigate a number of Lewis acid catalysts and evaluate their ability to selectively dehydrate both xylose and glucose to their corresponding furanics, furfural and 5-HMF, in water at moderate temperatures. Screening studies revealed that the highest yields of furfural and 5-HMF could be achieved using $SnCl_4$ and hence all further work was carried out with this catalyst. Minimization of the effects of secondary reactions by means of *in situ* solvent extraction of the furanic product was also investigated.

2. Results and Discussion

2.1 Xylose and Glucose Isomerization/Dehydration in Water

A number of metal chlorides and triflates were screened in order to establish their effectiveness as Lewis acid catalysts in converting xylose and glucose to furfural and 5-HMF, respectively. The results are summarized in Tables 1 and 2. Glucose selectivity is tabulated to reflect 5-HMF and levulinic/formic acid production, as 5-HMF was found to hydrolyze to the acid products in all cases. For both sugars, all Lewis acids increased the rate of sugar conversion and the total product yield when compared to the results observed for Brønsted acid-catalyzed reactions. Of the metal triflates, $In(OTf)_3$ converted both sugars at the highest rate (in excess of 93% after 2 h), however, $Sn(OTf)_2$ was the most selective to dehydration products (41% for xylose and 70% for glucose). Chromium(II) and (III) chloride exhibited the highest activities for sugar conversion of all metal chlorides (in excess of 90% after 2 h); however, $SnCl_4$ was the most selective to dehydration products (58% for xylose and 70% for glucose). For this reason, $SnCl_4$ was used exclusively for the remainder of this study.

The temporal evolution of products for $SnCl_4$-catalyzed dehydration of xylose and glucose is shown in Figures 1 and 2, respectively. For both sugars, the isomeric products lyxose, xylulose, mannose, and fructose were either not observed or were present in negligible quantities. Figure 1 shows xylose conversion reaching 55% over 2 h, with furfural production increasing toward 32% over the same period. Any unaccounted mass is attributed to the formation of soluble degradation products and humins. Figure 2 shows that glucose is converted to 67% of its initial concentration in 2 h, while 5-HMF is produced in small quantities and goes through a maximum of 6% after 1 h of reaction. The low concentration of 5-HMF is due to its hydrolysis to levulinic and formic acids, shown to reach yields of 12% and 19%, respectively, after 2 h of reaction. Produced in a 1:1 molar ratio from 5-HMF, the two acid yields are not found in the expected stoichiometric ratio because levulinic acid undergoes cyclization to form α-angelica lactone (found to be present in <5%).[9] A proposed pathway for this side reaction is given in Scheme 3, wherein the cyclization is shown to be initiated via either carbonyl or hydroxyl group attack of the ketone carbon, followed by dehydration.

2.2 Lewis Acid Hydrolysis in Water

The production of any dehydration product from xylose and glucose is an indication of the presence of a Brønsted acid, as protons in solution are necessary for hydroxyl group removal during all dehydration steps leading to furfural and 5-HMF.[9] Furthermore, levulinic and formic acid formation from 5-HMF and α-angelica lactone formation from levulinic acid can also only occur in the presence of a Brønsted acid.[9] Therefore it is important to evaluate the extent to which $SnCl_4$ generates Brønsted acidity in water.

When $SnCl_4$ is added to water, it dissociates into Sn^{4+} and Cl^-, followed immediately by the complexation of Sn^{4+} ions with 6 water molecules to form the octahedrally-coordinated aquachlorotin(IV), $[SnCl_x(H_2O)_{6-x}]^{(4-x)+}$, and hexaaquatin(IV), $[Sn(OH)_y(H_2O)_{6-y}]^{(4-y)+}$, complexes.[10-12] However, at $SnCl_4$ concentrations of 100 mM and lower, only a single peak is observed when such solutions are analyzed via ^{119}Sn NMR. This peak has been exclusively attributed to hexaaquatin(IV) ions, indicating that any chloride-containing complexes are completely dissociated at low $SnCl_4$ concentrations.[10] The $[Sn(OH)_y(H_2O)_{6-y}]^{(4-y)+}$ complex ions can undergo hydrolysis, releasing a proton for each stage of hydrolysis, for example:

$$[Sn(H_2O)_6]^{4+} + H_2O \leftrightarrows [Sn(OH)(H_2O)_5]^{3+} + H_3O^+ \qquad (1)$$

It has also been reported that $SnCl_4$ can hydrolyze to form water-insoluble SnO_2, releasing 4 protons per oxide formed.[11,13] Small quantities of white precipitate were observed after allowing aqueous $SnCl_4$ solutions of concentrations 10, 20, 40, and 60 mM to sit at room temperature over 24 h, which is likely an indication that the metal oxide forms under the conditions used in the present study.

The exact distribution of hexaaquatin(IV) complexes and SnO_2 existing in sub-100 mM $SnCl_4$ solutions is undefined and consequently an assessment of aggregate Lewis acidity cannot be made. However, the distinction does not appear to be important. A recent study has found that chitosan could be converted to 27.4% levulinic acid via 5-HMF when either $SnCl_4$ or the equivalent of SnO_2 and HCl were used, indicating either complete oxidation of tin in the first case or a relatively similar Lewis acidity exists for hexaaquatin(IV) cationic complexes and SnO_2 species.[14] In either case, we investigated the overall extent of hydrolysis by measuring solution pH as a function of $SnCl_4$ concentration in water. Figure 3 shows that proton concentration increases with both $SnCl_4$ concentration and temperature over the range of 20-80 ºC. For a given $SnCl_4$ concentration, increasing temperature appears to have a diminishing effect on proton concentration, such that at temperatures in excess of 80 ºC, the proton concentration varies little with increasing temperature. This conclusion is reinforced by the observation that at 140 ºC, a 25 mM $SnCl_4$ solution has a pH of 1.1 ($[H^+]$ = 80 mM). Figure 3 also shows that for all conditions tested, the H^+:Sn ratio is always less than 4, an indication that $SnCl_4$ does not hydrolyze completely to SnO_2 nor do $[Sn(OH)_y(H_2O)_{6-y}]^{(4-y)+}$ complexes hydrolyze to form neutral or negative charged Sn species.

We note that regardless of the exact distribution of Sn(IV) complexes in solution, $SnCl_4$ provides both Lewis- and Brønsted-acid centers for aqueous phase reactions. Previous work has shown that even with 200 mM of HCl, xylose conversion only reached

45% after 2 h using purely Brønsted-acid centers at 140 ºC.[15] When the isomerization/dehydration of xylose is carried out with 25 mM $SnCl_4$ in the absence of added Brønsted acid, 55% of the xylose was converted over 2 h even though tin hydrolysis results in less Brønsted acidity by comparison. Therefore, SnO_2 and $[Sn(OH)_y(H_2O)_{6-y}]^{(4-y)+}$ complexes evolved from $SnCl_4$ hydrolysis are active as Lewis acids and providers of Brønsted acidity.

Lastly, the fact that little to no xylulose and fructose were observed can be explained by the hydrolysis of the tin increasing the Brønsted acidity of our aqueous solutions such that the rate of ketose carbohydrate dehydration became competitive with the isomerization of xylose and glucose under these conditions.

2.3 Effect of Lewis Acid Concentration and Reaction Temperature on Selectivity

The initial rates of xylose/glucose conversion and furfural/5-HMF production were evaluated as a function of $SnCl_4$ initial concentration and temperature. The results are presented in Table 3. As the $SnCl_4$ concentration increases from 25 to 75 mM at either 140 ºC or 160 ºC, the rates of both xylose and glucose conversion increase, as do those of furfural and 5-HMF production. The selectivity toward furfural does not change with Lewis acid concentration, however, 5-HMF selectivity increases with $SnCl_4$ concentration. As previously noted, Sn^{4+} hydrolysis increases linearly with $SnCl_4$ concentration at temperatures above 40-60 ºC, such that proton concentration increases proportionally with the amount of metal cations dissolved (about 3.5 protons per Sn^{4+} cation). Since xylose selectivity to furfural is unaffected by $SnCl_4$ concentration, Brønsted acid- and Lewis acid-catalyzed reaction pathways shown in Scheme 1 must have the same rate-order dependencies on proton and Sn^{4+} concentrations, respectively.

With glucose selectivity toward 5-HMF increasing slightly with $SnCl_4$ concentrations, however, Lewis acid-catalyzed reaction pathways shown in Scheme 2 may have higher rate-order dependencies on Sn^{4+} concentration than the Brønsted acid-catalyzed reaction pathways have on proton concentration.

Comparing the results from 140 ºC and 160 ºC for a given catalyst concentration, the rates of carbohydrate conversion and furanic production increase with temperature, however, selectivities toward furanics decrease for both furfural and 5-HMF. This is due to differences in the activation energies for the direct sugar dehydration pathways versus the sugar isomerization-initiated pathways (see Schemes 1 and 2). For xylose, the activation energies for direct dehydration to furfural, isomerization to xylulose, and dehydration of xylulose to furfural are reported to be 32, 15.5, and 23.1 kcal/mol, respectively (where $CrCl_3$ was used for isomerization).[2] Similarly, the activation energies for direct dehydration of glucose to 5-HMF, isomerization to fructose, dehydration of fructose to 5-HMF, and hydrolysis of 5-HMF to levulinic and formic acids have been found to be 36.4, 20, 29.4, 23.1 kcal/mol, respectively.[7] Reactions with higher activation energy barriers are more sensitive to increases in temperature. For example, by taking the ratio of Arrhenius rate constants at two temperatures, one finds that the rate of the direct dehydration of xylose increases by 6.2-fold whereas the rate of xylose isomerization only increases by 2.4-fold when the temperature is adjusted from 140 ºC to 160 ºC (similarly, 7.8-fold compared to 3-fold for glucose). Therefore, the direct dehydration pathway for both sugars becomes increasingly competitive with the isomerization/dehydration pathway as the temperature increases. The overall selectivity to furanics decreases as a result of the increased production of highly reactive intermediates involved in the direct dehydration process, which are proposed to be the primary participants in degradation pathways leading to humins.[15] Maintaining lower reaction temperatures, therefore, results in a shift in the ratio of direct dehydration to isomerization pathways in favor of isomerization and higher furanic selectivity.

2.4 Combination of $SnCl_4$ and a Brønsted Acid

The use of $SnCl_4$ produces very little quantifiable xylulose or fructose since the hydrolysis of the Lewis acid catalyst provides ample Brønsted acidity to catalyze the dehydration of the ketose carbohydrates at a rate equal to or superior than the isomerization of the aldose carbohydrates. Thus, the further addition of a Brønsted acid would only accelerate the competing direct carbohydrate dehydration and furanic degradation reactions. However, a comparison of the $SnCl_4$-catalyzed isomerization/dehydration of either xylose or glucose with and without the addition of a small amount of HCl (50 mM) shows that Brønsted acid addition has little impact on the chemistry (Figure S1 in Supplemental Information). This is so because when low concentrations are added to solutions of $SnCl_4$ under 100 mM, hydrolytic exchange occurs between the positive H_3O^+ and the anionic Sn-OH species, evidenced by a broadening of the ^{119}Sn NMR peak attributed to $[Sn(OH)_y(H_2O)_{6-y}]^{(4-y)+}$.[10] This exchange shifts the equilibrium from hydrolyzed variants of Sn^{4+} toward $[Sn(H_2O)_6]^{4+}$ while the solution pH remains approximately the same. As a consequence, the extent to which this hydrolysis occurs is governed by the solution pH, such that for pH values <2, solvated Sn^{4+} exists primarily as cationic hexaaquatin(IV) species.[12]

2.5 Xylose and Glucose Isomerization/Dehydration in a Biphasic System

The dehydration of xylose and glucose in the presence of Brønsted acidity, whether added extrinsically or derived via Lewis acid cation hydrolysis, is necessary for furanic production but also detrimental because it promotes furanic-consuming side reactions that lead to the formation of humins. Furanic consumption can be avoided by removing furfural and 5-HMF immediately as they are produced. One way to accomplish this is through the employment of a biphasic system that utilizes an appropriate solvent capable of extracting furfural and 5-HMF from the reactive aqueous phase *in situ*. Such systems have been observed to be successful in curtailing degradation and improving overall furanics yields.[8] However, identifying a solvent that is serviceable for the removal of both furfural and 5-HMF is complicated due to the structural differences in the two molecules affecting solvation. Instead of performing an exhaustive screening of organic solvent candidates by physically performing biphasic extraction experiments, we used the UNIFAC (**UNI**versal quasichemical **F**unctional-group **A**ctivity **C**oefficients) method to rapidly determine activity coefficients for both furfural and 5-HMF in water and various organic solvents.[16,17] This method has been found to accurately predict activity coefficients for small molecule solvents and solutes at temperatures below 200 ºC.[17] After acquiring these activity coefficients, we calculated the partition coefficient for each solute between water and a given organic solvent as:

$$\log(K) = -\log\left(\frac{\gamma_{organic}^{solute}}{\gamma_{water}^{solute}}\right) \tag{2}$$

where K is the partition coefficient and γ is the activity coefficient of the solute in either the water or organic phase. Partition coefficient values >1 calculated in such a fashion indicated a preference for the organic phase. After qualitative comparison of solvent K values, *n*-butanol was found to strike the best balance of partition coefficients for both furanics of interest. The UNIFAC results for both furfural and 5-HMF in some optimal biphasic systems at 140 ºC are shown in Figure S2 in the Supplemental Information. For the low mole fractions of furanics expected under the typical reaction conditions (<0.02), the partition coefficients for furfural and 5-HMF between *n*-butanol and water were found to be $\geq$ 11.3 and $\geq$ 3.8, respectively.

Using *n*-butanol as an extracting agent, we performed the $SnCl_4$-catalyzed isomerization/dehydration of xylose and glucose, separately, in a biphasic system consisting of a 1:2 ratio of water:butanol (by volume). The results for this experiment are shown in Figures 4A and 4B for xylose and glucose, respectively. Xylose conversion proceeds at a rate similar to that observed for its reaction in water alone, reaching a conversion of 90% after 5 h. The furfural selectivity for the biphasic system was nearly constant at 85% throughout the reaction, resulting in a yield of 77% after 5 h of reaction. The initial conversion of glucose in the biphasic system was lower than in the single-phase system, but reached a conversion of 75% after 5 h. The selectivity of 5-HMF tracked the conversion of its glucose and remained nearly constant at 69%, resulting in a 5-HMF yield of 52% after 5 h. Furthermore, formic acid (10%) and levulinic acid (5%) production was reduced in the biphasic system after 5 h, indicating less 5-HMF degradation to these products as compared to the reaction in water alone (19% and 12%, respectively, after only 2 h). Including formic acid yields with those of 5-HMF, selectivity to desirable products from glucose increases to 83% in a biphasic system. Levulinic acid degradation was also lower in the two-phase system, with only 5% degradation products (mainly angelica lactone) produced when *n*-butanol was used compared to 7% after 2 h with water alone.

Despite the employment of a biphasic system, selectivities to furfural and 5-HMF never reach 100%, consistent with previous observation.[7] A review of Schemes 1 and 2 reveals that reaction pathways to degradation products not involving furanics exist, which can consume carbohydrates in the aqueous phase regardless of the extraction of furfural/5-HMF and result in the reduction of apparent product selectivity. These reactions can be mitigated by controlling the Brønsted acidity of the aqueous phase, though, this can be difficult to accomplish when using hydrolyzable Lewis acid catalysts as in this study. Also, while *n*-butanol is a good extracting agent, the partitioning of either furanic does not reach 100%, resulting in an observable amount of furanics remaining within the aqueous phase capable of participating in Brønsted acid-catalyzed side reactions. The latter issue can be moderated through the use of aqueous phase modifiers, which is addressed in the next section.

2.6 Effect of LiCl on Xylose and Glucose Isomerization/Dehydration in a Biphasic System

The addition of metal halides to aqueous solutions has been observed to improve the thermodynamics of solute extraction from aqueous phases into organic phases, with higher metal halide concentrations found to be more effective.[18,19] However, previous work has also shown that, while the addition of metal halides to the Brønsted acid-catalyzed dehydration of xylose increases the rate of xylose consumption and furfural production, product selectivity decreases with increasing salt concentrations because the metal halide can also promote the undesired formation of humins.[15] Therefore, it is important to select an appropriate metal halide concentration such that additives can improve the partitioning efficacy of a biphasic system by reducing water activity and increasing the activity coefficients of furanics in water without interfering in the dehydration chemistry. The concentration at which the metal halide activity coefficient in water is also the point it is at its lowest chemical potential and least likely to interact with other solutes, namely carbohydrates. LiCl was selected based on earlier work showing this salt to be an optimal additive for the dehydration of xylose in a biphasic system.[19] The activity coefficient minimum in water was found to be 0.734 with a water activity of 0.983 for a concentration of 500 mM LiCl.[20]

The biphasic experiment described previously was repeated with the addition of 500 mM LiCl to the aqueous phase. These results are presented in Figure 5. Xylose and glucose conversion rates increased slightly, such that 95% of the xylose and 81% of the glucose was consumed after 5 h. Similarly, the furfural yield reached 84% and the 5-HMF yield reached 58%, raising the furanic selectivities to 88% for furfural and to 72% for 5-HMF. The slight increase in carbohydrate conversion is likely due to dissolved LiCl assisting in the dehydrations of xylulose and fructose, while selectivity increases toward furanics can be attributed to a minor enhancement in partitioning from the reactive aqueous phase to the *n*-butanol phase. A similar enhancement in the selectivity to furanics has been reported by Abu-Omar, et al. who observed that the addition of NaCl to the $AlCl_3$-catalyzed dehydration of glucose in a H_2O/THF biphasic system improved the selectivity of HMF from 52% to 61%.[8a]

The present observations of glucose dehydration in a biphasic system catalyzed by $SnCl_4$ in the aqueous phase are similar to those found for glucose dehydration in a water/THF biphasic system catalyzed by Sn-BEA zeolite and HCl.[6] However, the biphasic Lewis acid-catalyzed xylose conversion results exceed those typically reported in aqueous media (for example, selectivities of ~80% were found when $CrCl_3$ was used as catalyst).[2]

3. Conclusion

$SnCl_4$ was investigated as a selective Lewis acid catalyst for the production of both furfural and 5-HMF from xylose and glucose, respectively, in aqueous media. At moderate concentrations and reaction temperature, $SnCl_4$ provides the Lewis acidity necessary for isomerization of both xylose to xylulose and glucose to fructose, as well as the Brønsted acidity necessary to dehydrate both xylulose to furfural and fructose to 5-HMF. The significant Brønsted acidity resulting from hydrolysis of $SnCl_4$ also catalyzes secondary reactions that consume furfural and 5-HMF to produce humins and hydrolyze 5-HMF to produce levulinic and formic acid, both processes limiting the selectivities to the desired furanic product. *n*-Butanol was found to be an appropriate solvent for removing both furanics from water. Working in a 1:1 water:butanol biphasic system with $SnCl_4$ in the aqueous phase, conversions of both carbohydrates in excess of 75% with selectivities of 85% toward furfural and 69% toward 5-HMF could be achieved at 140 ºC in 5 h. The addition of LiCl to the aqueous phase increased the conversion of xylose to 95% and that of glucose to 81%, and increased the selectivity to furfural to 88% and that to 5-HMF to 72%.

4. Experimental

4.1 Materials

D-xylose (99%, Sigma-Aldrich), D-glucose (≥99.5%, Sigma), D-xylulose (≥98%, Santa Cruz Biotechnology), D-fructose (≥99% Sigma), D-lyxose (99%, Sigma-Aldrich), D-mannose (≥99% Sigma), 2-furaldehyde (furfural, 99%, Sigma-Aldrich), 5-hydroxymethylfurfural (5-HMF, 98%, Acros Organics), levulinic acid (≥97%, Aldrich), formic acid (≥99.5%, Fisher Chemical), and α-angelica lactone (98%, Sigma-Aldrich) were used as reagents and standards (for quantification).

Aluminum chloride hexahydrate ($AlCl_3$ x $6H_2O$, 99.0%, crystalline), cerium(III) chloride heptahydrate ($CeCl_3$ x $7H_2O$, 99.999%, trace metals basis), chromium(II) chloride ($CrCl_2$, 95%, water soluble), chromium(III) chloride hexahydrate ($CrCl_3$ x $6H_2O$, 98%), iron(II) chloride tetrahydrate ($FeCl_2$ x $4H_2O$, 99.0%), iron(III) chloride hexahydrate ($FeCl_3$ x $6H_2O$, ACS reagent, 98.0-102%, crystalline), indium(III) trifluoromethanesulfonate ($In(OTf)_3$, 99%), lithium chloride (LiCl, BioXtra, ≥99.0% (titration)), scandium(III) triflate ($Sc(OTf)_3$, 99%), tin(II) chloride dihydrate ($SnCl_2$ x $2H_2O$, 99.995%, trace metals basis), tin(IV) chloride pentahydrate ($SnCl_4$ x $5H_2O$, 98%), tin(II) trifluoromethanesulfonate ($Sn(OTf)_2$, 98%), and ytterbium(III) trifluoromethanesulfonate ($Yb(OTf)_3$, 99.99%) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 37% v/v, Fisher Scientific) was used as the Brønsted acid catalyst. *n*-Butanol (ACS Reagent, ≥99%, Fluka) was used as the organic extracting agent in biphasic experiments. All materials were used as purchased, without further purification or modification.

4.2 Experimental Approach

All experiments were performed in 10 ml glass vials (from Sigma-Aldrich via supplier Supelco) sealed with 20 mm aluminum-crimped PTFE septa and heated using a silicon oil bath to maintain constant reaction temperature and stirring rate. In a representative glucose dehydration experiment, glucose was dissolved in nanopure water, to which $SnCl_4$ and HCl were added to create a solution (750 mM glucose, 25 mM $SnCl_4$, 50 mM H^+). A 4 ml aliquot of this solution was sealed into a 10 ml glass vial. The vial was then placed in a silicone oil bath heated to 140 ºC and stirred at 600 rpm. Upon completion of the reaction, the sample was removed and quenched in an ice bath. An internal standard (1 ml of 75 mg/ml 1,6-hexanediol in water) was added and the sample centrifuged to remove all water insoluble particulates. A portion of the reaction mixture (500 µl) was diluted in a 1:1 ratio with nanopure water and taken for HPLC analysis. For reactions involving an additional organic phase, the aqueous phase volume was reduced to 1 ml and butanol (4 ml) was added prior to sealing the reaction vial. At reaction end, the organic phase was separated via centrifuging. The aqueous phase was treated as above and analyzed via HPLC while a different internal standard (1 ml of 5 mg/ml guaiacol in toluene) was added to the organic phase prior to GC/MS analysis.

4.3 Product Analysis

A Shimadzu HPLC equipped with a Phenomenex Rezex RFQ-Fast Acid H+ column (100 x 7.8 mm; 0.01 N H_2SO_4; 1.0 ml/min; 55 ºC) and a refractive index detector (RID) was used to analyze all aqueous samples. Product quantities were determined by converting integrated HPLC peak areas into concentrations using a 7-point calibration curve generated from purchased standards: xylose, glucose, xylulose, fructose, lyxose, and mannose.

A Varian CP-3800 Gas Chromatograph equipped with a FactorFour Capillary Column (UF-5ms 30 m, 0.25 mm, 0.25 µm, P/N CP8944) connected to a Varian quadrupole-mass spectrometer (MS) and flame ionization detector (FID) was used to analyze all organic phase samples. After product identification by mass spectrometer, product concentrations were determined from integrated FID peak areas using a 6-point calibration curve generated from purchased standards.

Reagent and product yields are reported as molar percentages relative to initial molar concentrations of carbohydrate (i.e. furfural yields = moles furfural/initial moles xylose). All reported yields were typically reproducible to within a +/- 5% relative error (based upon the calculation of one standard deviation).

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6. References

1. a) Climent, M. J.; Corma, A.; Iborra, S. *Green Chem.,* **2011**, *13*, 520-540.; b) Tompsett, G. A.; Li, N.; Huber, G. W. Catalytic Conversions of Sugars to Fuels. In *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power*; Brown, R. C., Ed; John Wiley & Sons: Chichester, 2011; pp 223-279.; c) Chheda, J. N.; Huber, G. W.; Dumesic, J. A. *Angew. Chem. Int. Ed.*, **2007**, *46*(38), 7164-7183.; d)

Werpy, T.; Petersen, G.; Aden, A.; Bozell, J.; Holladay, J.; White, J. Manheim, A. Report No. NREL/TP-510– 35523. *Top Value Added Chemicals from Biomass: Vol. 1—Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; National Renewable Energy Laboratory: Golden, CO, 2004; pp 1-77.; e) Zeitsch, K. J. *Sugar Ser.*, **2000**, *13*, 1-353.

2. a) Choudhary, V.; Sandler, S.; Vlachos, D. *ACS Catal.*, **2012**, *2*(9), 2022-2028.; b) Choudhary, V.; Caratzoulas, S.; Vlachos, D. *Carbohydr. Res.,* **2013**, *368*, 89-95.

3. Choudhary, V.; Mushrif, S. H.; Ho, C.; Anderko, A.; Nikolakis, V.; Marinkovic, N. S.; Frenkel, A. I.; Sandler, S. I.; Vlachos, D. G. *J. Am. Chem. Soc.*, **2013**, *135*, 3997-4006.

4. Binder, J. B.; Blank, J. J.; Cefali, A. V.; Raines, R. T. *ChemSusChem*, **2010**, *3*(11), 1268-1272.

5. a) Weingarten, R.; Rodriguez-Beuerman, A.; Cao, F.; Luterbacher, J. S.; Alonso, D. M.; Dumesic, J. A.; Huber, G. W. *ChemCatChem*, **2014**, *6*(8), 2229-2234.; b) Gürbüz, E. I.; Gallo, J. M. R.; Alonso, D. M.; Wettstein, S. G.; Lim, W. Y.; Dumesic, J. A. *Angew. Chem. Int. Ed.*, **2012**, *52*(4), 1270-1274.

6. Nikolla, E.; Roman-Leshkov, Y.; Moliner, M.; Davis, M. E. *ACS Catal.*, **2011**, *1*(4), 408-410.

7. a) van Putten, R.; van der Waal, J. C.; de Jong, E.; Rasrendra, C. B.; Heeres, H. J.; de Vries, J. G. *Chem. Rev.*, **2013**, *113*, 1499-1597.; b) Gallezot, P. *Chem. Soc. Rev.*, **2012**, *41*, 1538-1558.

8. a) Yang, Y.; Hu, C.; Abu-Omar, M. *Green Chem.*, **2012**, *14*(2), 509-513.; b) Pagan-Torres, Y. J.; Wang, T.; Gallo, J. M. R.; Shanks, B. H.; Dumesic, J.A. *ACS Catal.*, **2012**, *2*(6), 930-934.; c) Roman-Leshkov, Y.; Dumesic, J. A. *Top. Catal.*, **2009**, *52*, 297-303.

9. Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.*, **2006**, *106*(9), 4044-4098.

10. Taylor, M. J.; Coddington, J. M. *Polyhedron*, **1992**, *11*(12), 1531-1544.

11. Jensen, K. M. O.; Christensen, M.; Juhas, P.; Tyrsted, C.; Bojesen, E. D.; Lock, N.; Billinge, S. J. L.; Iversen, B. B. *J. Am. Chem. Soc.*, **2012**, *134*, 6785-6792.

12. Fringuelli, F.; Pizzo, F.; Vaccaro, L. *J. Org. Chem.*, **2001**, *66*, 4719-4722.

13. a) Wiberg, N.; Holleman, A. F. *Inorganic Chemistry*, 34th ed; Academic Press: San Diego, CA, 2001.; b) Jarzevski, Z. M.; Marton, J. P. *J. Electrochem. Soc.*, **1976**, *123*(7), 199-205.; c) Nagasawa, M.; Shionoya, S.; Makishima, S. *Jpn. J. Appl. Phys.*, **1965**, *4*(3), 195-202.

14. Omari, K. W.; Besaw, J. E.; Kerton, F. M. *Green Chem.*, **2012**, *14*, 1490-1487.

15. Enslow, K. R.; Bell, A. T. *ChemCatChem*, **2015**, *7*(3), 479-489.

16. a) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.*, **1975**, *21*, 1086-1099.; b) Magnussen, T.; Rasmussen, T.; Fredenslund, A. *Ind. Eng. Chem. Process Des. Dev.*, **1980**, *20*, 1269-1277.

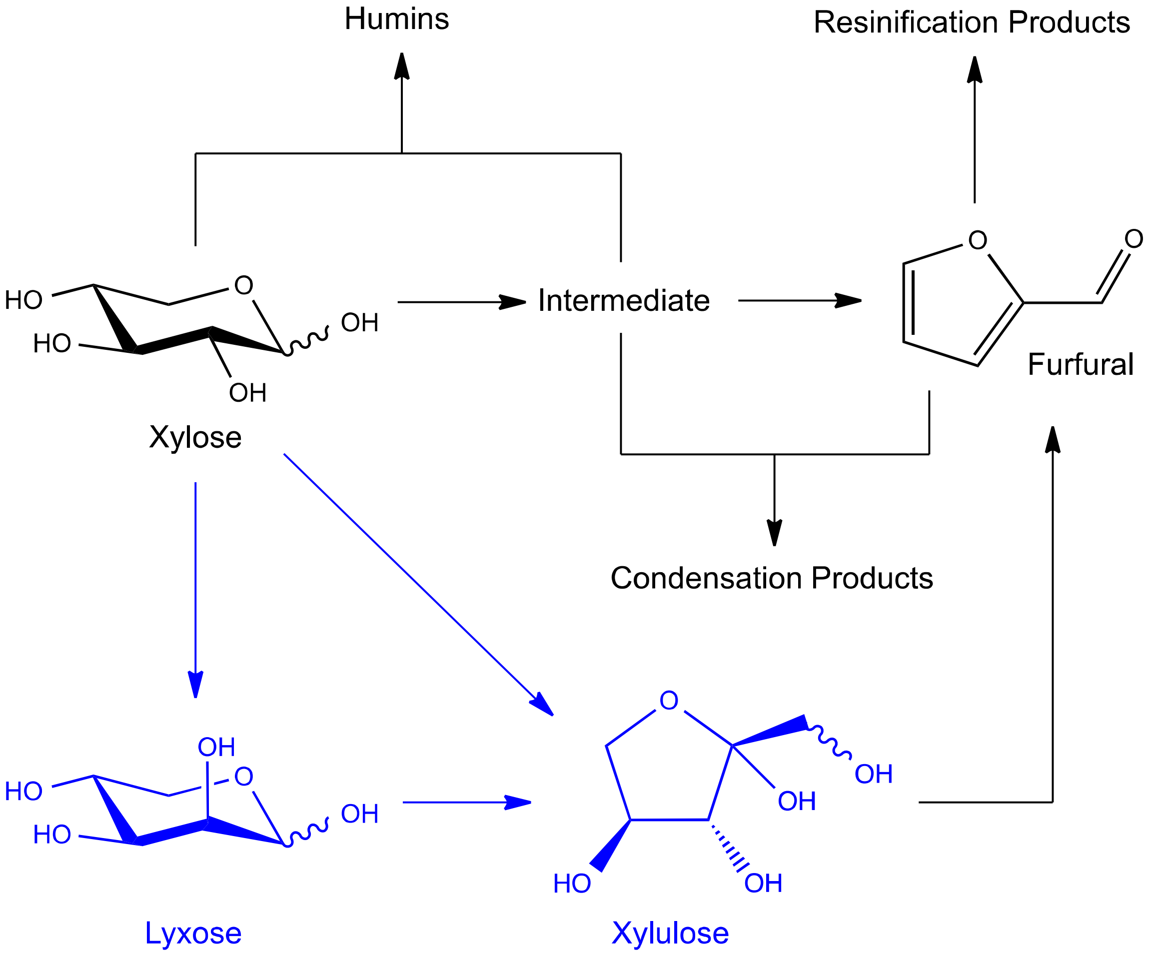
17. Wittig, R.; Lohmann, J.; Gmehling, J. *Ind. Eng. Chem. Res.*, **2003**, *42*, 183-188.

18. a) Pitzer, K.; Kim, J. *J. Am. Chem. Soc.*, **1974**, *96*(18), 5701-5707.; b) Long, F. A.; McDevit, W. F. *Chem. Rev.*, **1952**, *51*(1), 119-169.; c) Curtis, R. G.; Hatt, H. H. *Aust. J. Chem.*, **1948**, *1*(2), 213-235.; d) Hofmeister, F. *Arch. Exp. Pathol, Pharmacol.*, **1888**, *24*, 247-260.

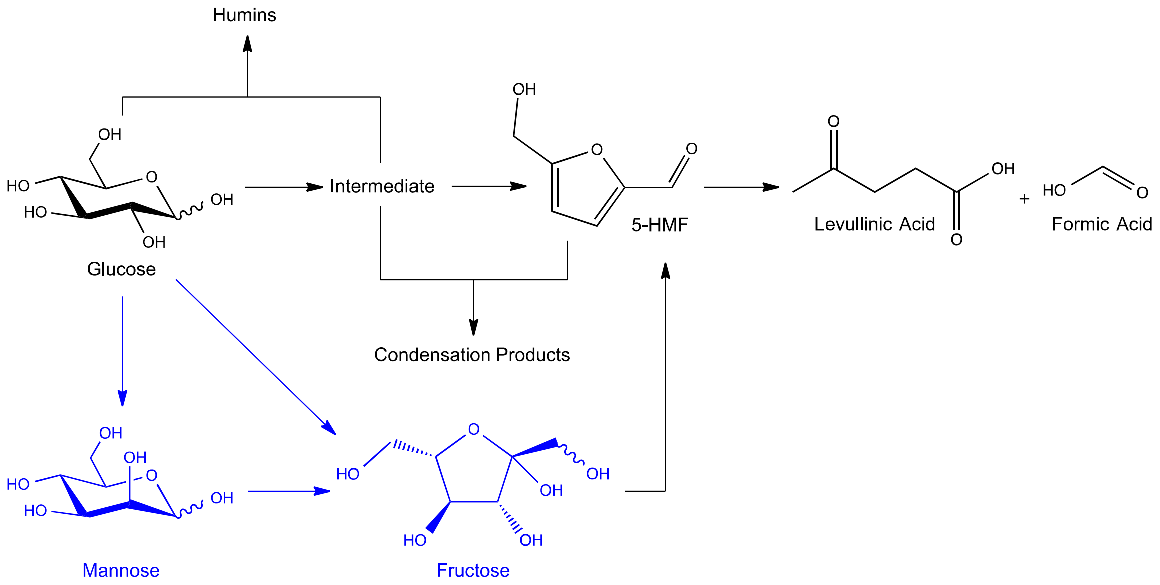
19. Eisen, E. O.; Joffe, J. *J. Chem. Eng. Data,* **1966**, *11*(4), 480-484.

20. Hamer, W. J.; Wu, Y. C. *J. Phys. Chem. Ref. Data*, **1972**, *1*, 1047-1100.

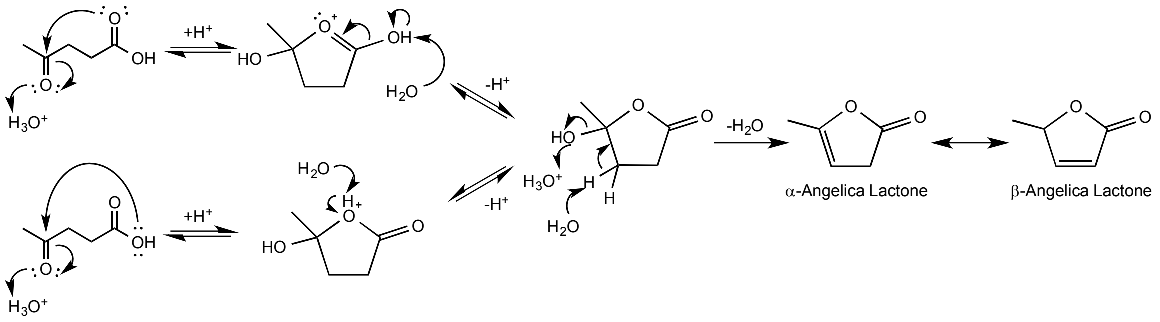
Schemes/Figures/Tables



Scheme 1. The reaction network for xylose dehydration catalyzed by a Brønsted acid (shown in black) and a Lewis acid (shown in blue).



Scheme 2. The reaction network for glucose catalyzed by a Brønsted acid (shown in black) and a Lewis acid (shown in blue).



Scheme 3. A proposed reaction scheme for the Brønsted acid-catalyzed cyclization of levulinic acid to an equilibrium mixture of α- and β-angelica lactone.

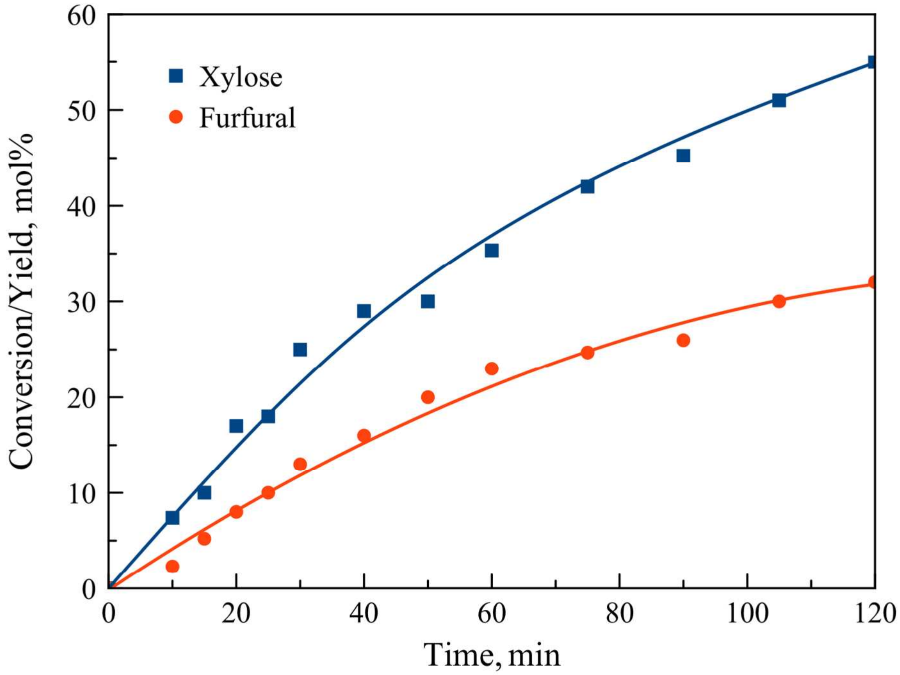


Figure 1. The conversion of xylose (750 mM) and the yield of furfural at 140 ºC catalyzed by 25 mM $SnCl_4$ in a single aqueous phase.

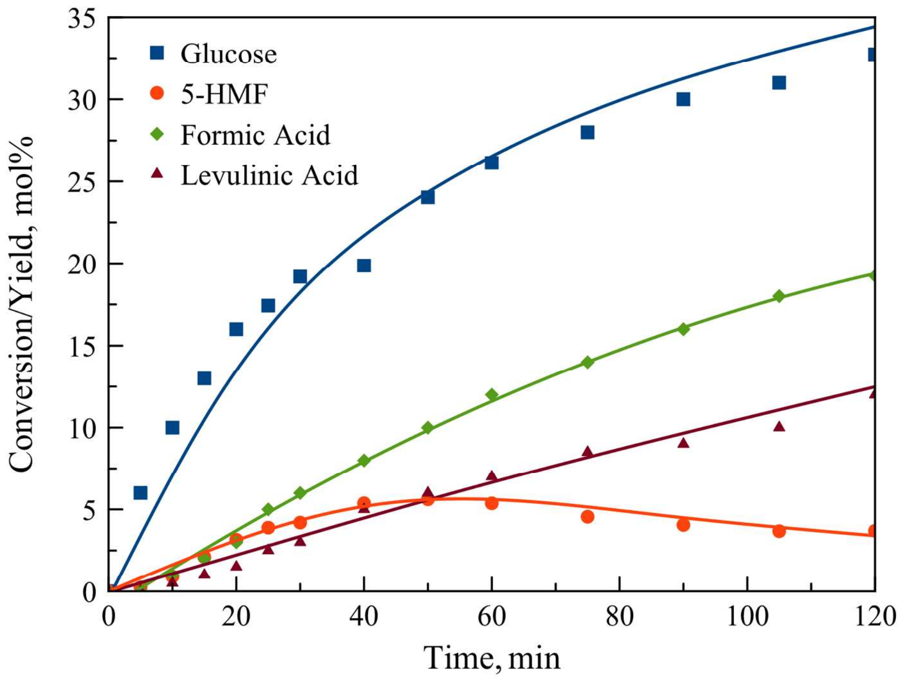


Figure 2. The conversion of glucose (750 mM) and the yields of 5-HMF, levulinic acid, and formic acid at 140 ºC catalyzed by 25 mM $SnCl_4$ in a single aqueous phase.

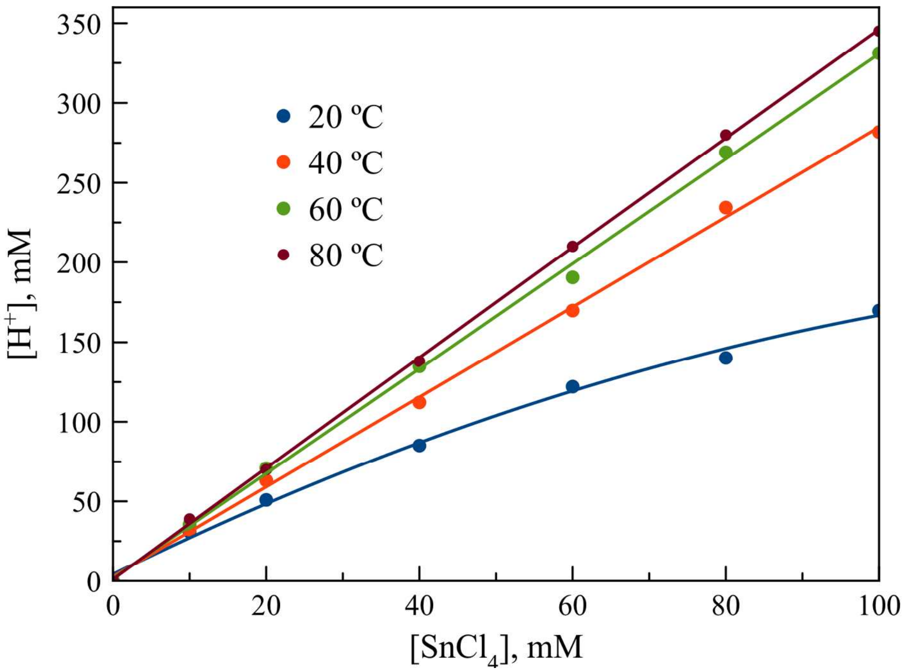


Figure 3. The effect of $SnCl_4$ concentration on H^+ concentration observed for temperatures between 20 ºC and 80 ºC. Measurements were taken after solutions were allowed to equilibrate for 12 h.

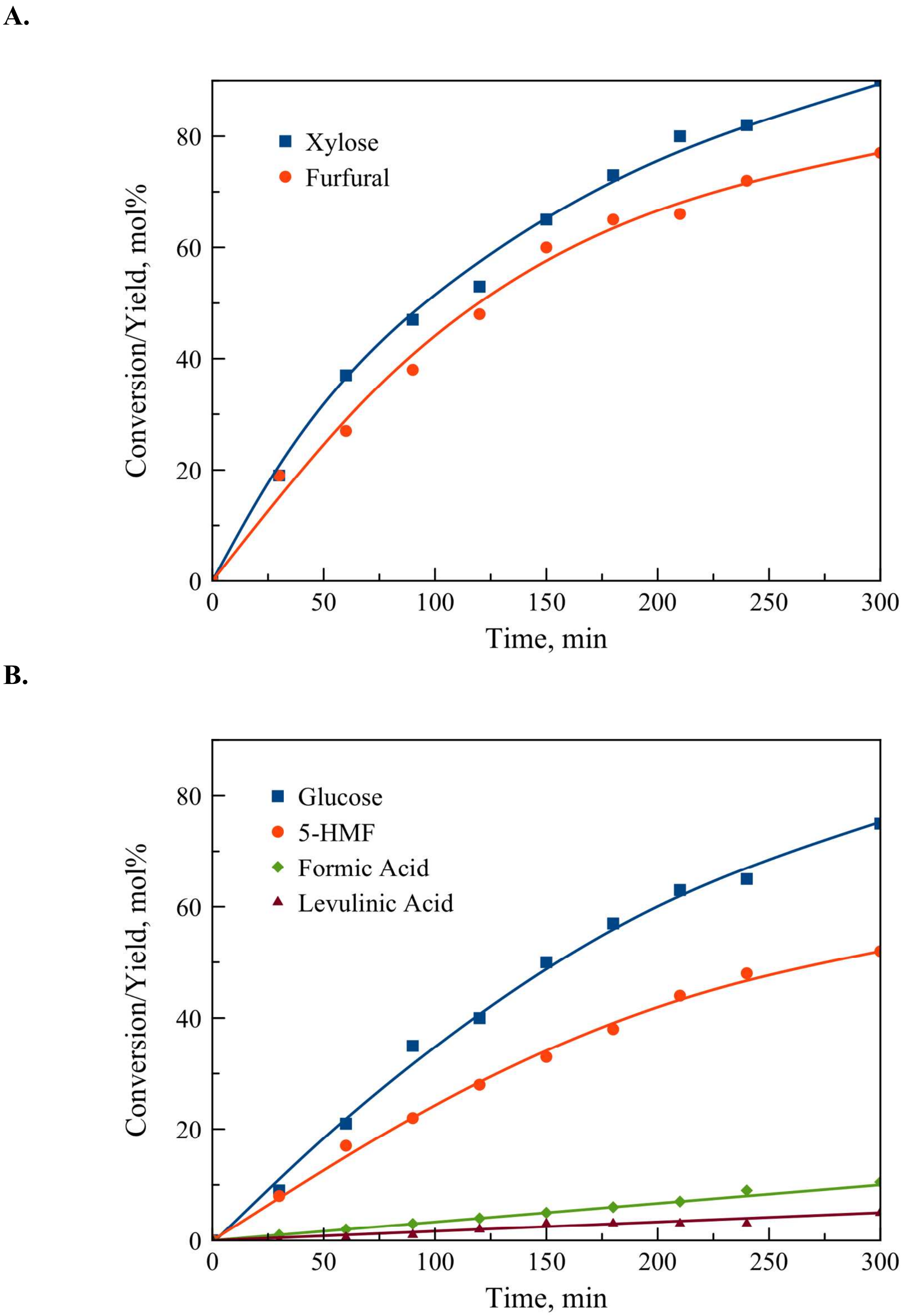


Figure 4. The $SnCl_4$-catalyzed conversion of **A)** xylose and **B)** glucose in a 1:2 water:butanol (v/v) biphasic system. Conditions: 750 mM initial sugar concentration, 25 mM $SnCl_4$, 140 ºC. All concentrations based upon the aqueous phase.

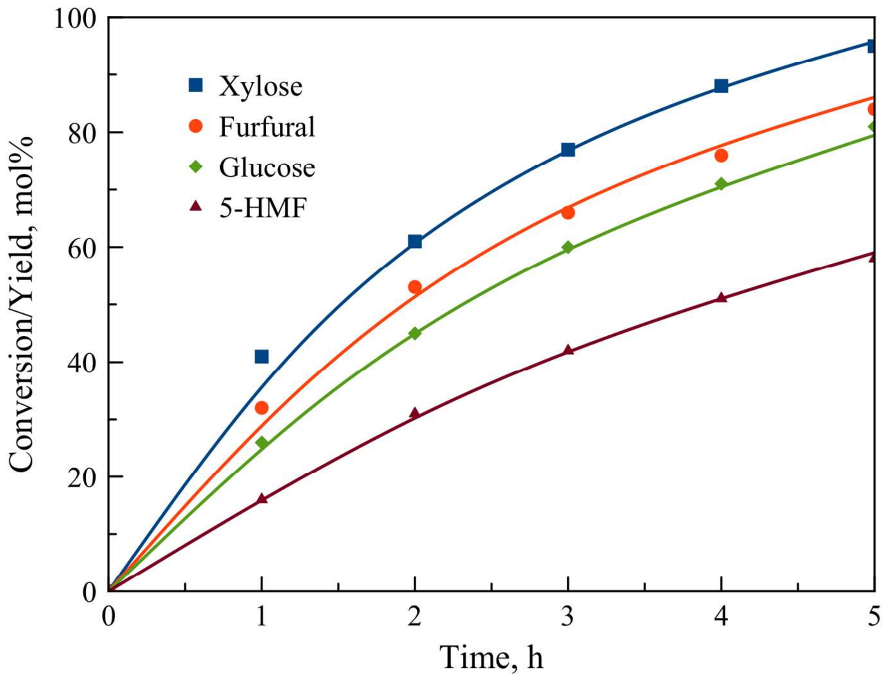


Figure 5. The effects of 500 mM LiCl added to the aqueous phase on the $SnCl_4$-catalyzed conversion of xylose and glucose in a 1:2 water:butanol (v/v) biphasic system. Conditions: 750 mM initial sugar concentration, 25 mM $SnCl_4$, 140 ºC.

Catalyst	Time (h)	Xylose Conversion, mol%	Furfural Yield, mol%	Selectivity, mol%
HCl	1	4	1.3	32
	2	8	2.4	30
$AlCl_3$ x $6H_2O$	1	75	31	41
	2	91	29	32
$CeCl_3$ x $7H_2O$	1	28	4	14
	2	35	7	20
$CrCl_2$	1	75	25	33
	2	92	28	30
$CrCl_3$ x $6H_2O$	1	70	32	46
	2	92	36	39
$FeCl_2$ x $4H_2O$	1	18	5	27
	2	30	8	25
$FeCl_3$ x $6H_2O$	1	24	7	30
	2	40	12	31
$SnCl_2$ x $2H_2O$	1	29	14	48
	2	42	20	48
$SnCl_4$ x $5H_2O$	**1**	**35**	**23**	**65**
	2	**55**	**32**	**58**
$In(OTf)_3$	1	89	22	25
	2	96	24	25
$Sc(OTf)_3$	1	48	14	29
	2	64	16	25
$Sn(OTf)_2$	1	32	11	35
	2	39	16	41
$Yb(OTf)_3$	1	32	9	30
	2	45	14	31

Table 1. The conversion of xylose (750 mM) and the yield of furfural at 140 ºC catalyzed by various Lewis acidic metal chlorides and triflates (25 mM) in a single aqueous phase measured after at 1 and 2 h of reaction. Data for the HCl-catalyzed (25 mM) dehydration under the same conditions is shown for comparison.

Catalyst	Time (h)	Glucose Conversion, mol%	5-HMF Yield, mol%	LA/FA Yield, mol%	Product Selectivity, mol%
HCl	1	2	-	-	-
	2	3	0.6	-	20
$AlCl_3$ x $6H_2O$	1	68	10	4	21
	2	80	18	10	35
$CeCl_3$ x $7H_2O$	1	21	3	2	24
	2	25	4	2	24
$CrCl_2$	1	70	9	7	23
	2	89	10	10	22
$CrCl_3$ x $6H_2O$	1	68	11	5	24
	2	90	13	10	26
$FeCl_2$ x $4H_2O$	1	9	2	0	22
	2	15	3	1	27
$FeCl_3$ x $6H_2O$	1	11	4	0	36
	2	18	6	1	39
$SnCl_2$ x $2H_2O$	1	22	4	9	60
	2	26	5	11	63
$SnCl_4$ x $5H_2O$	**1**	**26**	**5**	**13**	**69**
	2	**33**	**4**	**19**	**70**
$In(OTf)_3$	1	87	11	39	57
	2	93	9	46	59
$Sc(OTf)_3$	1	59	5	22	46
	2	66	5	25	45
$Sn(OTf)_2$	1	49	12	20	65
	2	58	17	24	70
$Yb(OTf)_3$	1	21	4	9	61
	2	31	7	12	61

Table 2. The conversion of glucose (750 mM) and the yields of 5-HMF, levulinic acid (LA), and formic acid (FA) at 140 ºC catalyzed by various Lewis acidic metal chlorides and triflates (25 mM) in a single aqueous phase measured after 1 and 2 h of reaction. Data for HCl-catalyzed (25 mM) dehydration of glucose under the same conditions are shown for comparison. Product selectivity is the sum of glucose selectivity toward 5-HMF and formic acid.

A.

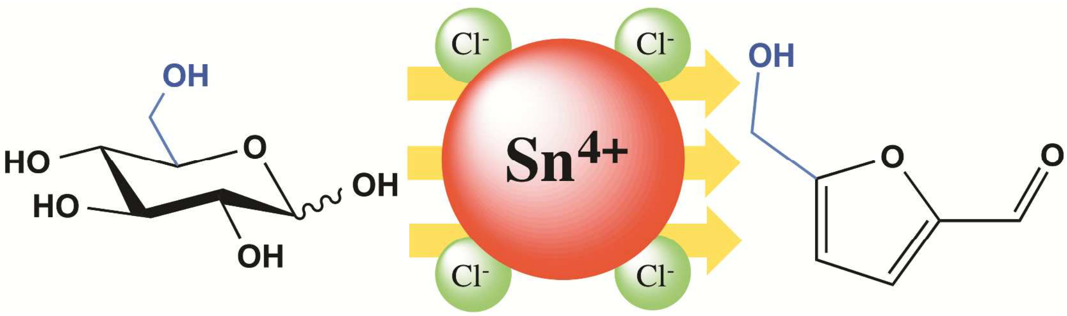
Temperature, °C	[$SnCl_4$], mM	Xylose Initial Rate of Reaction, µmol-L^{-1}-s^{-1}	Furfural Initial Rate of Formation, µmol-L^{-1}-s^{-1}	Furfural Selectivity, mol%
140	25	94	56	60
	50	182	108	59
	75	279	170	61
160	25	197	83	42
	50	385	159	41
	75	585	257	44

B.

Temperature, °C	[$SnCl_4$], mM	Glucose Initial Rate of Reaction, µmol-L^{-1}-s^{-1}	5-HMF Initial Rate of Formation, µmol-L^{-1}-s^{-1}	5-HMF Selectivity, mol%
140	25	87	18	20
	50	95	28	30
	75	103	32	31
160	25	199	38	19
	50	215	55	26
	75	230	61	27

Table 3. The initial rates of reaction of **A)** xylose (750 mM) and **B)** glucose (750 mM) and the initial rates of furfural and 5-HMF formation for different $SnCl_4$ concentrations (25-75 mM) and temperatures of 140 and 160 ºC. Selectivities toward furanic products are also included. Measurements were taken within the first 10 min of reaction.

Table of Contents Entry



Graphic Text

$SnCl_4$ was found to isomerize and dehydrate xylose and glucose effectively to furanics in water, with selectivities of 85% and 69%, respectively.