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ARTICLE

Effects of cations, anions and H^+ concentration of acidic ionic liquids in the valorization of polysaccharides into furfural

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Babasaheb M. Matsagar,[ab] Paresh L. Dhepe*[ab]

Valorization of hemicellulose to valuable chemicals such as C5 sugars and furfural in the one-pot fashion is crucial. In this work, acidic ionic liquids in presence of water showed high yields of C5 sugars (>80%) with >99% conversion of hemicelluloses at 160 °C. With water+toluene biphasic solvent system, within 4 h, 85% furfural yield was obtained directly from hemicellulose in a one-pot fashion using the catalytic amount of 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate. It is seen that BAILs perform better than solid acid [Faujasite and Mordenite zeolites; ion exchange resin, Amberlyst-15] and mineral catalysts [HCl and H_2SO_4]. The higher activity of BAILs compared to solid acids and mineral acid was correlated to Hammett acidity function (*Ho*) and ion-dipole type of interaction. The catalysts were characterized using NMR (^{1}H and ^{13}C), elemental analysis and TGA to confirm that those are stable under reaction conditions and thus were recyclable.

Introduction

Biomass is a renewable, sustainable, abundant, CO_2 neutral and inexpensive alternating feedstock to fossil feedstock for the synthesis of chemicals and fuels.[1] Lignocellulosic biomass, the main constituent of cell walls of plants is non-edible and is made up of cellulose (40-50%), hemicelluloses (20-30%) and lignin (15-25%). While cellulose is a polysaccharide made up of glucose units linked together via β(1→4) glycosidic bonds, hemicellulose is either homo- or hetero-polysaccharide made up of C5 sugars, C6 sugars and sugar acids linked together via β(1→4), β(1→3) and β(1→6) glycosidic linkages.[2] On the other hand, lignin is a 3-D polymer made up of different substituted aromatic units linked together via ether and C-C bonds.[3] Typically, hemicellulose is rich in C5 sugars[4] but, in certain types of hemicelluloses (mannans, galactan), C6 sugars are found to be major constituents.[5] In particular, C5 sugars based xylan type (with xylose backbone) hemicellulose is found in most of the plants. The complex structure of biomass makes it difficult to convert it into various chemicals and fuels in a very selective and effective way.[6, 7]

In the biorefinery concept sugars obtained upon hydrolysis of polysaccharides are considered as primary platform chemicals. In view of this, conventionally, hydrolysis of hemicelluloses is achieved using mineral acids and enzymes to obtain variety of sugars depending on the type of hemicelluloses used.[8, 9] Although, these methods are efficient but due to obvious drawbacks (handling, separation, neutralization waste, pH dependent etc.) related to the utilization of acids and enzymes, solid acid (Amberlyst-70, sulfonated silica gel, HUSY zeolite, etc.) catalyzed hydrolysis processes are developed.[10, 11] However, it is seen that under the reaction conditions employed, many of these solid acid catalysts undergo morphological changes and thus it becomes obligatory to propose a new catalytic system for the efficient valorization of hemicelluloses into sugars. Although, upon hydrolysis, it is easy to obtain xylose (C5 sugar) from xylan compared to formation of glucose from cellulose, but due to the high reactivity of C5 sugars many undesired products are formed and hence it is challenging to achieve better yields of C5 sugars.[12] To accomplish this, ionic liquids (ILs) with acidity were shown to hydrolyze xylan type hemicellulose to yield xylose with high yields (>80%).[13]

Xylose is formed by the hydrolysis of xylan, there has been much of an interest in its dehydration into furfural by various catalytic methods.[14-16] This is because furfural is used as a solvent, in the manufacturing of phenolic resins as starting compounds and for obtaining a variety of chemicals (furfuryl alcohol, cyclopentanone, methyl furan, pentane diols, furoic acid, aromatics etc.) in several industries.[15, 17] To obtain furfural from xylose, heterogeneous acid catalysts such as sulfonic acid decorated porous silicas,[18] heteropolyacids,[19] Lewis acid and Brønsted acid catalysts ($CrCl_3 \cdot 6H_2O$ and HCl) are known.[20] Use of ILs, such as [BMIM][Cl] like a solvent in presence of mineral acid (H_2SO_4) is also reported for obtaining furfural from xylose.[21] While this method is efficient but the use of IL in large quantity is detrimental in commercializing this method.

[a] Catalysis and Inorganic Chemistry Division CSIR-National Chemical Laboratory. Pune 411008, India, Email: pl.dhepe@ncl.res.in; Fax +91-2025902633; Tel: +91-2025902024
[b] Academy of Scientific and Innovative Research (AcSIR), New Delhi (India).

† Footnotes relating to the title and/or authors should appear here.
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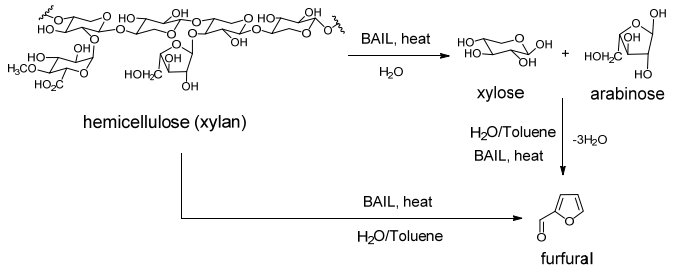
Although these two-pot reactions (xylan to xylose and xylose to furfural) to yield furfural are known but, it would be better to convert xylan type of hemicellulose directly into furfural in a one-pot fashion. In view of this, few efforts are put towards the direct valorization of hemicelluloses into furfural over solid acid catalysts.[10] Nonetheless, as mentioned above in many of these reactions, catalyst's stability is an issue.



Scheme 1. Valorization of hemicellulose (xylan).

The conversion of xylan type of hemicellulose into furfural (63% yield) is also reported using $CrCl_3$ as a catalyst in presence of IL under microwave-assisted heating.[22] Yet, again the use of IL on large scale is a drawback of this method. Thus, in spite of few efforts, it is a challenge to develop a proficient method for obtaining furfural from hemicellulose.

Since acidic ILs are known to catalyze the hydrolysis of hemicelluloses to yield xylose,[13] it was believed that similar catalytic system can be employed for the production of furfural from xylan in a one-pot fashion after optimizing the reaction conditions (Scheme 1). By doing so, drawbacks associated with reported conventional catalytic methods like mineral acids, enzymes and use of huge amount of ILs along with mineral acids or metal chlorides, etc. for the valorization of hemicellulose into monosaccharides (C5 sugars) and their further dehydration into furfural can be avoided. Moreover, with the use of acidic ILs, the issue of stability of solid acids would be avoided.

Herein we report valorization of hemicellulose to furfural in a direct fashion using the catalytic amount of Brønsted acidic ILs (BAILs) as a catalyst in aqueous as well as biphasic solvent systems. Moreover, the effects of cations and anions on the catalytic performance are studied in detail. Additionally, to overcome the problems associated with dilute substrate systems typically employed in most of the literature reports, studies on the higher hemicellulose loading are performed (6 *wt%*).

Experimental

Catalytic Experiments

Reactions were performed in Parr autoclave (300 mL) having temperature and stirring controller unit. In a typical hemicellulose to sugar reaction, 0.6 g hemicellulose (birchwood) along with 0.24 g catalyst (substrate/catalyst 2.5 *wt/wt*) and 60 mL water were charged and then reaction temperature was set to desired value under stirring of 200 rpm. After reaching the set reaction temperature stirring speed was increased (800 rpm) and this time, is considered as starting time of a reaction. Once the reaction is finished, the reactor is cooled to room temperature and the reaction mixture was analyzed using high performance liquid chromatography (HPLC). For hemicellulose to furfural reaction also similar reactor is used as mentioned above. In this reaction, 0.6 g hemicellulose (beechwood) was charged along with catalyst 0.12 g (substrate/catalyst 5 *wt/wt*) and solvent water+MIBK (1:5 *v/v*). The charged reactor is then heated to the desired temperature and time. Here also before achieving desired temperature 200 rpm stirring speed was maintained and after achieving the desired temperature, stirring was increased to 800 rpm. Upon completion of the reaction, the biphasic reaction mixture (aqueous and organic) is separated using a separating funnel. The aqueous reaction mixture was analyzed using HPLC and the organic reaction mixture was analyzed using GC.

Analysis

The reaction mixture was analyzed using HPLC, GC, and GC-MS. The aqueous reaction mixture is analyzed using HPLC (Agilent 1200 series) equipped with Pb^{2+} column (Rezex RPM-Monosaccharide, 300 x 7.8 mm; particle size 8 μm). The analysis was carried out at 80 °C of oven temperature. Degassed HPLC grade water was used with 0.5 mL/min flow rate. A RID (G1362A 1260RID) with 40 °C cell temperature of was used for analysis. Prior to the analysis, the samples were filtered through 0.22 μm syringe filter and then 10 μL of the sample was injected for the analysis. Before analyzing the reaction mixture, a calibration curve of different standards like xylose, arabinose, furfural, were done.

The organic phase of the reaction was analyzed using GC (Agilent 7890B) instrument equipped with HP-5 capillary column (30 m x 0.23 μm ID) and flame ionization detector (FID) operated at 280 °C. The following oven program was used for the analysis: 100 °C → 7 °C min^{-1} → 250 °C (hold time: 3 min). The flow rates of H_2, air and N_2 were 30, 300 and 20 mL min^{-1}, respectively. For GC analysis all the samples were filtered through 0.22 μm syringe filter before analysis and 1 μL sample was injected.

RESULTS AND DISCUSSION

For carrying out reactions, several ILs were synthesized (Section 1, ESI) and characterized (Sections 2-4, ESI) for their purity, stability, and acidity.

Valorization of hemicellulose into sugars:

Evaluation of various catalysts

The results of catalysts evaluation study for the valorization of hardwood hemicellulose (xylan from birchwood) into monosaccharides such as C5 sugars (xylose+arabinose (X+A)) at 160 °C for 1 h are summarized in Fig. 1. As observed, the $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst could give the best yield of C5 sugars (87% yield). Under similar conditions, $[C_3SO_3HMIM][PTS]$ BAIL (76%), $[C_3SO_3HMIM][Cl]$ BAIL (75%), and $[C_3SO_3HBenzMIM][PTS]$ BAIL (73%) also showed better activity for C5 sugars (X+A). The $[C_3SO_3HNEt_3][PTS]$ (39%) and

$[C_3SO_3HPPh_3][PTS]$ (25%) BAILs showed lower activity towards C5 sugars formation compared to other BAIL catalysts used in this study.

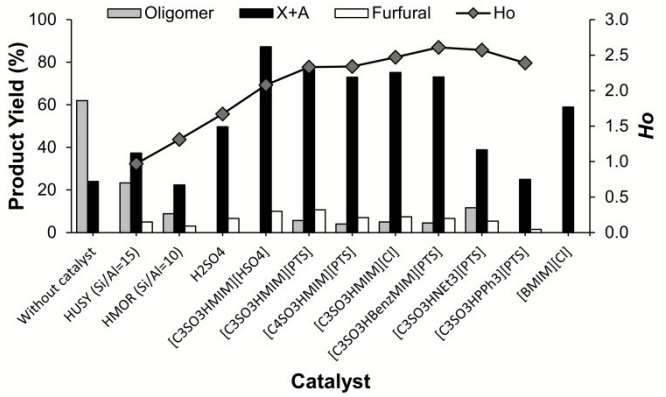


Figure 1. Catalyst evaluation studies for the valorization of hemicellulose into sugars. Reaction condition: substrate 0.6 g, catalyst 0.24 g, water 60 mL, 160 °C, 1 h.

The [BMIM][Cl] IL which does not have any acidity under similar reaction conditions showed only 59% of C5 sugars (X+A) yield. On the other hand, a similar type of BAIL ($[C_3SO_3HMIM][Cl]$) having Brønsted acidity showed 75% of C5 sugars yield. This suggests that the Brønsted acidity of BAIL is important for obtaining higher C5 sugars yield. Further, the catalytic performance of BAILs was evaluated against solid acid catalysts such as Faujasite and Mordenite zeolites. The results show lower C5 sugars yield with these solid acid catalysts (37% and 22%) compared to BAILs (Fig. 1). Additionally, with mineral acid (H_2SO_4) only 50% yield of C5 sugars was possible, compared to $[C_3SO_3HMIM][HSO_4]$ BAIL (87%). Thus it is implied that $[C_3SO_3HMIM][HSO_4]$ BAIL is the best performing catalyst in this reaction.

To understand the differences in the activities between all these catalysts, the strength of the acid in all the catalysts was measured using Hammett acidity function (*Ho*). From the data of Hammett acidity function (Section 4, ESI) the order of acid strength was found as,

HUSY (Si/Al=15; (0.97)) > HMOR (Si/Al=10; (1.31)) > H_2SO_4 (1.67) > $[C_3SO_3HMIM][HSO_4]$ (2.08) > $[C_3SO_3HMIM][PTS]$ (2.33) > $[C_3SO_3HMIM][Cl]$ (2.47).

The acid strength is higher for the catalyst if its *Ho* value is lower. Among all the BAILs evaluated for hemicellulose valorization, $[C_3SO_3HMIM][HSO_4]$ BAIL has a *Ho* of 2.08, which is lowest than all other BAILs ($[C_3SO_3HMIM][PTS]$ (2.33) and $[C_3SO_3HMIM][Cl]$ (2.47)). This trend is in line with the *Ho*, as $[C_3SO_3HMIM][HSO_4]$ BAIL showed the maximum C5 sugars yield (87%), and $[C_3SO_3HMIM][PTS]$, $[C_3SO_3HMIM][Cl]$ BAILs showed lower (76 and 75%) C5 sugars yields. The [BMIM][Cl] IL is neutral and hence, its activity is the lowest (59% C5 sugar yield) compared to all other ILs evaluated present work. Moreover, mineral acid (H_2SO_4) has a lower *Ho* (*Ho*=1.67) than the BAILs; yet, the activity of $[C_3SO_3HMIM][HSO_4]$ is higher than H_2SO_4. This implies that even if BAIL has lower acid strength than H_2SO_4 catalyst, it has shown higher activity for C5 sugars formation. The higher activity of BAILs is due to the interaction of BAILs with the hemicellulose (ion-dipole type interaction) and its homogenous nature.[13] It is evident that compared to HMOR (Si/Al=10) (*Ho*=1.31), HUSY (Si/Al=15) (*Ho*=0.97) has higher strength and therefore, it showed better activity (Fig. 1). The solid acid catalysts form the heterogeneous phase in reaction solutions and hence showed lower activity compared to BAILs catalyst.

Effect of H^+ concentration

The effect of H^+ concentration in acidic ILs and mineral acid catalyzed reactions was studied at optimized reaction condition (160 °C, 1 h). Fig. 1 shows that 50% C5 sugars (X+A) yield can be obtained if 0.24 g of H_2SO_4 is used (4.9 mmol of H^+) for the reaction (Fig. 1; Section 5, Table S3, ESI). The inferior yield of C5 sugars is because when 0.24 g of H_2SO_4 was used, very high concentration of H^+ (4.9 mmol) was present in the reaction solution. This high concentration of H^+ may eventually initiate many side reactions, which otherwise would not occur when lower concentrations of H^+ are available in reaction. The higher concentration of H^+ (4.9 mmol) present when H_2SO_4 is used, compared to when 0.24 g of $[C_3SO_3HMIM][PTS]$ BAIL (0.64 mmol H^+) was used in the reaction solution may thus hamper the activity. To cancel the effect of the H^+ concentration in H_2SO_4 on the formation of products, the reaction was performed with H_2SO_4 using the similar H^+ concentration (0.64 mmol) for the reaction as that observed with $[C_3SO_3HMIM][PTS]$ catalyst. In this reaction, a slight improvement in the yield (65%) was observed, but still, this yield was lower than the yield obtained with $[C_3SO_3HMIM][PTS]$ catalyst (76%). The effect of H^+ concentration was studied in detail by charging varying quantity of H_2SO_4 (Table S3, ESI) in the reaction. The best yield of C5 sugars (76%) was achieved when 2.4 mmol of H^+ concentration is used when the effect of H^+ concentration was studied in detail with H_2SO_4. Further by decreasing the H^+ concentration of H_2SO_4 (1.26 mmol) lower yield of C5 sugar was seen (66%).

The highest C5 sugar yield (76%) was obtained when 2.4 mmol of H^+ concentration of H_2SO_4 was used. By maintaining similar H^+ concentration (0.64 mmol of H^+) HCl (39%) and organic acid (*p*-toluenesulfonic acid monohydrate (PTSA) 44%) were also used in the reactions; however, those showed lower activity (Table S3, ESI) than BAIL. This phenomenon of BAIL showing higher yields than conventional acids is because of the ion-dipole type of interaction as shown in earlier work.[13]

The solid acid catalysts showed 37% (Faujasite) and 22% (Mordenite) of C5 sugars yield when 0.24 g catalyst loading was used (Section 5, Table S3, ESI). When reactions were carried using similar H^+ concentration (0.64 mmol, similar like BAIL $[C_3SO_3HMIM][PTS]$ by altering the catalyst loading (Table S3, ESI), with HUSY catalyst, 61% yield and with HMOR catalyst 48% C5 sugars yield was observed. It is anticipated that due to diffusivity problem in solid acids, their activity is lower than BAILs.

The reactions were performed with different substrates using $[C_3SO_3HMIM][PTS]$ BAIL catalyst and it was seen that all other substrates could also give higher yields of C5 sugars (Fig. S18,

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ESI). This conveys that the catalyst is capable of valorizing almost all types hemicellulose substrates.

Role of cations on activity

To comprehend the effect of cations of BAILs on the valorization of hemicellulose, BAILs with different types of cations were used by keeping similar anion *p*-toluenesulfonate (PTS) in all the BAILs. Additionally, in all the catalysts propyl sulfonic acid group attached to cation was kept constant which actually is responsible for giving acidity. The reactions were carried out at optimized reaction condition (1 h, 160 °C) in the water medium. The results presented in Fig. 2, shows that BAILs with imidazolium-based cations shows the best catalytic activity (76% C5 sugar yield) compared to BAILs with quaternary ammonium (39% C5 sugar yield) and triphenylphosphonium (25% C5 sugar yield) based cations.

The discrepancy in the C5 sugars yield among all the catalysts is believed to be due to the structure of cations because as mentioned above anion part was kept similar in all the BAILs. It is understood that the BAILs with imidazolium based cation shows the better interaction (ion-dipole type) with the substrate.[13] While, the structure of imidazolium cation is planar which can help for this type of interaction, in the case of BAIL with quaternary ammonium based cation, the structure of cation is not planar and hence there might not be sufficient interaction between the IL and substrate molecule (Section 6, Table S4, ESI). This effect eventually would show lower C5 sugar yield (38%). The possibility of varying H^+ concentration on the yields was nullified by considering that quaternary ammonium based IL has almost similar H^+ concentration (0.6 mmol g^{-1}) in reaction system compared with imidazolium based BAIL, [C_3SO_3HMIM][PTS] (0.64 mmol g^{-1}). The BAIL with triphenylphosphonium based cation has bulky phenyl groups attached to the phosphorus atom and also the structure of cations is non-planar and hence it is suggested that this factor is responsible for achieving poor interaction between BAIL and polysaccharide. Therefore, triphenylphosphonium based BAIL also shows a lower yield of C5 sugars (25%). On the contrary, since benzimidazolium and pyridinium cations have planar structures those showed nearly same activity as that was observed for imidazolium-based BAIL. It is particularly interesting because, in the case of benzimidazolium based IL, slightly lower H^+ concentration (0.56 mmol g^{-1}) is present compared with imidazolium based BAIL (0.64 mmol g^{-1}).

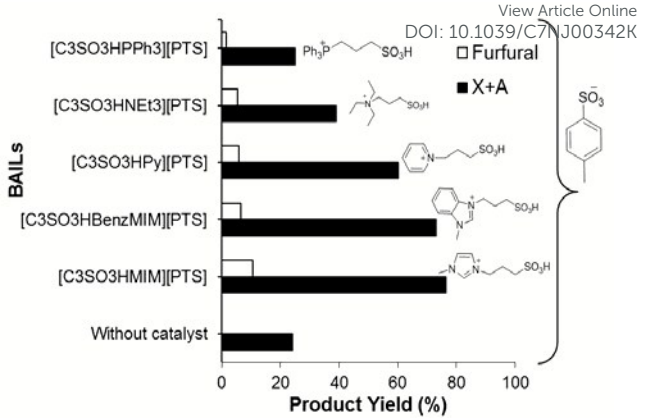

Figure 2. Effect of cations of BAILs on the valorization of hemicelluloses. Reaction condition: substrate 0.6 g, catalyst 0.24 g, water 60 mL, 160 °C, 1 h

Valorization of hemicellulose into furfural:

Effect of solvent system and the ratio of biphasic solvent system

From the above studies it is understood that when hemicellulose conversion is carried out using [C_3SO_3HMIM][HSO_4] BAIL at 160 °C for 1 h in only water as a solvent, 10% furfural yield along with 87% C5 sugars (X+A) yield could be obtained (Fig. 1). To improve the yield of furfural which is a dehydration product of C5 sugars (X+A), the time of reaction was increased, and maximum furfural yield i.e. 21% was achieved after 4 h (Fig. 3). Subsequently, to improve the furfural yield, the reaction was performed for 6 h, but a decrease in furfural yield (17%) was seen. This is because in water many undesired side reactions are prominent which decreases the furfural yield when reactions are carried out for a longer time. Since sugars, furfural and BAILs are soluble in water, it is possible that sugars and furfural may react together in water to yield some undesired products in presence of catalyst, which may hamper the yield of furfural.[23] From the earlier studies it is evident that with the introduction of water immiscible organic solvent (biphasic system), improvement in furfural yield is possible.

The employment of polar aprotic solvents is reported in the literature for obtaining furfural.[24] It is reported that the furfural yield of 37% can be achieved from xylose in N, N-dimethylformamide (DMF) solvent in presence of Amberlyst-15 along with hydrotalcite (HT) as a catalyst. When the reaction was performed in DMSO over Nafion 117, furfural yield of 60% was obtained. While these solvents could yield furfural in good quantity but their high boiling points are detrimental in using them on a larger scale and in the separation of products from them.[23, 25] To surmount the problems related to earlier systems, use of the biphasic solvent system was proposed. It is successfully shown that with water either addition of toluene or MIBK in the presence of zeolitic catalysts (HY, HMOR) can efficiently conversion of xylose into furfural.[26, 27] Considering this, in this work, various biphasic solvent systems were studied to improve the furfural yield.

As seen from Fig. 3, along with only water, 3 biphasic solvent systems were evaluated for their effect on improvement in

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furfural yield using $[C_3SO_3HMIM][HSO_4]$ BAIL as a catalyst at 170 °C for 4 h. While carrying out this study, reactions were done at 170 °C for 4 h instead of at 160 °C because with an increase in temperature improvement in yield was observed. As seen, with water+toluene solvent system maximum furfural yield (62%) was achieved compared to water+*p*-xylene (49%) and water+MIBK (52%). When the hemicellulose valorization into furfural was carried out using $[C_3SO_3HMIM][HSO_4]$ BAIL under similar reaction condition with only water as a solvent, it showed a lower yield of furfural (21%) (Fig. 3). The effect of solvent study on the valorization of hemicellulose into furfural shows that to achieve maximum furfural yield, the addition of toluene to water is beneficial.

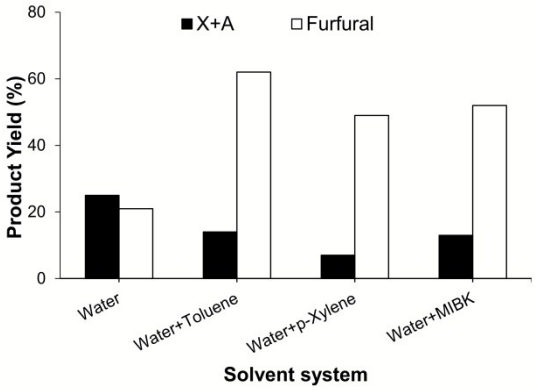

Figure 3. Valorization of hemicellulose to furfural in different solvents. Reaction condition: substrate 0.6 g, $[C_3SO_3HMIM][HSO_4]$ 0.12 g, water+organic solvent 60 mL (1:5 *v/v*), 170 °C, 4 h

The observance of maximum furfural yield with water+toluene solvent system can be explained on the basis of the partition coefficient (Table S5, and Fig. S19, ESI). It was observed that furfural has a maximum solubility in toluene compared to *p*-xylene and therefore in the water+toluene biphasic solvent system effective extraction of furfural is possible in toluene during the course of reaction compared to *p*-xylene in the water+*p*-xylene system. Likewise, furfural has a slightly higher solubility in MIBK compared to toluene, this can be understood from the partition coefficient of furfural in MIBK/water (1.38) and toluene/water (1.32) solvent system (Table S5, and Fig. S19, ESI). Hence, the water+MIBK biphasic solvent system should have shown higher furfural yield, but experimentally water+toluene solvent system showed better furfural yield. This is because MIBK has higher solubility in water (19.1 g L^{-1} at 20 °C) compared to the solubility of toluene in water (0.52 g L^{-1} at 20 °C).[10] Because of higher miscibility of MIBK in water, furfural extracted in MIBK can again come in contact with water and eventually with catalyst and thus it can undergo further side reactions. This phenomenon is less prominent in the case of water+toluene biphasic solvent system and thus the maximum yield of furfural was obtained with this solvent system.

After identifying the best biphasic solvent system, water+toluene for the valorization of hemicellulose into furfural, the effect of the ratio of the biphasic solvent system was studied since depending on the ratio of solvent, concentration of substrate in water and extraction possibility of furfural in toluene will increase which may affect the furfural yield. The reactions were carried out with various water+toluene ratios such as 1:1 *v/v*, 1:3 *v/v*, 1:5 *v/v* and 1:7 *v/v* using beechwood hemicellulose and $[C_3SO_3HMIM][HSO_4]$ BAIL. As observed from Fig. S20 (ESI), when 1:1 *v/v* and 1:3 *v/v* ratios were used, 45 and 47% furfural yields were observed, respectively. The best result (62% furfural yield) was obtained with a water+toluene biphasic solvent system having 1:5 *v/v* ratio. Further, increase in toluene concentration in the water+toluene biphasic solvent system (1:7 *v/v*) showed a decrease in the yield of desired products (60% furfural yield along with 10% C5 sugars yield). This is due to the fact that with a decrease in water in the system, the solution becomes very concentrated with respect to catalyst and substrate and this enhances the probability of occurrence of side reactions (almost similar phenomenon observed with higher H^+ concentration of H_2SO_4). The decreased yield of furfural with 1:7 *v/v* ratio, in turn, showed a poor mass balance (for water+toluene (1:5 *v/v*) 81% mass balance and for water+toluene (1:7 *v/v*) 73% mass balance was observed).

Effect of reaction temperature & time

As it was believed that with alteration of reaction temperature, improvement in furfural yield is possible using $[C_3SO_3HMIM][HSO_4]$ catalyst and water+toluene biphasic solvent system. When reactions were carried out at 160 °C, 170 °C and 180 °C, 35, 62 and 64% furfural yield along with 41% (160 °C), 14% (170 °C) and 5% (180 °C) C5 sugars (X+A) yield was seen (Fig. S21, ESI). Although, similar furfural yield was achieved at 170 and 180 °C, but after the reaction was carried out at 180 °C lower C5 sugars yield (5%) compared to the reaction performed at 170 °C (14%) for a similar time (4 h) was obtained. These results suggest that at 170 °C, 81% mass balance could be achieved while at 180 °C, 72% mass balance could be obtained. Considering this, evaluation of other catalysts was done at 170 °C for 4 h in presence of water+toluene (1:5 *v/v*).

The influence of reaction time on the valorization of hemicellulose into furfural was also checked and the results are presented in Fig. S22 (ESI). When the reactions were carried out using $[C_3SO_3HMIM][HSO_4]$ BAIL at 170 °C for 4 and 5 h in water+toluene (1:5 *v/v*) biphasic solvent system, the similar yield of furfural (62%) could be obtained. However, higher C5 sugars (X+A) yield was obtained in 4 h (14%) compared to 5 h (11 %). The mass balance calculations show that when the reaction is carried out for 4 h, higher mass balance is possible (81%) compared with 5 h reaction (73%). This is obvious since, with longer reaction time, degradation reactions become predominant.

Evaluation of catalysts

Conversion of hemicellulose into furfural is much challenging compared to the conversion of xylose into furfural. This is because in the conversion of hemicellulose into furfural two reactions are happening i.e. hydrolysis of hemicellulose into sugars and further dehydration of these sugars into furfural. While converting the hemicellulose into furfural the catalyst

should first convert hemicellulose into sugars in a short reaction time compared to the conversion of xylose into furfural. Because if catalyst and furfural along with sugar are present in the solution for a longer time then it becomes difficult to obtain higher selectivity for furfural due to the formation of humins through side reactions. As BAIL ($[C_3SO_3HMIM][HSO_4]$) is observed to convert hemicellulose into sugars in a very short time (< 1 h) compared to many other solid acid catalysts. Therefore it is anticipated that $[C_3SO_3HMIM][HSO_4]$ BAIL can covert hemicellulose into furfural efficiently.[13]

Since with $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst, maximum C5 sugars (X+A) yield (87 %) was achieved in hemicellulose hydrolysis reaction, the same catalyst was also employed in earlier discussed works on furfural synthesis. After optimizing the reaction parameters (*t, T*, solvent ratio etc.) with this catalyst, subsequently, all other catalysts were evaluated for their performance in yielding furfural under optimized reaction conditions. Fig. 4 illustrates that the solid acid catalysts like HUSY (Si/Al=15) and Amberlyst-15 could yield 34 and 42% of furfural, respectively. Although as seen from results, solid acid catalysts showed comparable results as that observed with a mineral acid and BAILs but due to their lower thermal stability those could not be reused. It is reported in the literature that the solid acid catalysts often undergo morphological changes during the course of reaction[10] and similar results were also observed in this work (data not shown). In case of all the BAILs, following trend of activity was observed,

$[C_3SO_3HMIM][HSO_4]$ (62%) > $[C_3SO_3HMIM][Cl]$ (44%) > $[C_3SO_3HMIM][PTS]$ (41%).

This trend can be explained on the basis of Hammett acidity (*Ho*) as explained above and in ESI (Section 4, Table S2).

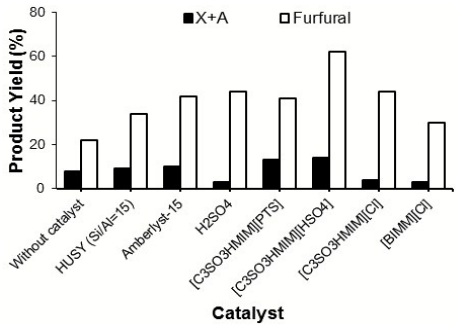

Figure 4. Catalyst evaluation for the valorization of hemicellulose into furfural. Reaction conditions: substrate 0.6 g, catalyst 0.12 g, water+toluene 60 mL (1:5 *v/v*), 170 °C, 4 h

The [BMIM][Cl] IL used for the valorization of hemicellulose showed only 30% furfural yield along with 3% C5 sugars (X+A) yield. When the reaction was performed in absence of a catalyst, 22% furfural yield along with 8% C5 sugars (X+A) yield was obtained. Even if almost half the furfural yield obtained in this reaction in comparison to catalytic reactions, but the poor mass balance (30%) emphasizes the fact that dehydration reactions are needed to be carried out with the catalyst. More importantly, the $[C_3SO_3HMIM][HSO_4]$ BAIL showed higher furfural yield compared to HUSY (Si/Al=15) and Amberlyst-15. The higher yield of furfural with $[C_3SO_3HMIM][HSO_4]$ BAILs compared with solid acid catalyst can be explained as; the BAILs homogeneous reaction phase but solid acid catalysts do not. It is very important to note that the concentrated hemicellulose solution (6 *wt%*; with respect to water) was used for the reaction and 62% yield of furfural could be achieved. However, in previous work on hemicellulose conversion into furfural, 1*wt%* hemicellulose solutions were used.[28]

It is expected that the catalyst with Brønsted acidity is active for hydrolysis of hemicellulose to yield xylose and for dehydration of this xylose to yield furfural. Considering this then H_2SO_4 should show better furfural yield from hemicellulose compared to BAIL because as shown in our earlier work in a two-pot reaction, it can efficiently convert hemicellulose into sugars (76% C5 sugar yield; 0.117 g H_2SO_4) and sugars into furfural (60% furfural yield; 0.08 g H_2SO_4).[13,15] But in reality, when direct one-pot conversion of hemicelluloses is performed (this work), BAIL performs better compared to H_2SO_4 ($[C_3SO_3HMIM][HSO_4]$ 62% furfural and 14% C5 sugar yield; H_2SO_4 44% furfural and 3% C5 sugar yield from hemicellulose). It is also reported in the literature that the catalytic system which is efficient in the conversion of xylose into furfural is not efficient for the conversion of xylan (hemicellulose) into furfural.[29] The $CrCl_3$ catalyst in a DMA-LiCl solvent and [EMIM][Cl] IL as additive showed 40% furfural yield from xylose while the same catalyst showed very less furfural yield (3%) from xylan. This shows that conversion of hemicellulose into furfural is much difficult compared to the conversion of xylose into furfural. The catalyst investigated in the present study is capable of converting hemicellulose into furfural successfully in the one-pot fashion.

Stability of furfural

Careful optimization of reaction parameters was performed to advance the furfural yield. It was seen that maximum possible yield of furfural was only 62%. This might be due to two reasons; first, due to the stability of furfural in the reaction mixture and the second, possible side reactions of furfural with C5 sugars and reactions between C5 sugars. To check the first possibility, furfural stability under optimized reaction condition was carried out (water+toluene (1:5 *v/v*) at 170 °C for 5 h with and without BAIL catalyst ($[C_3SO_3HMIM][HSO_4]$). Since in a typical reaction, 0.436 g of furfural can be obtained from 0.6 g of hemicelluloses charged anticipating 100% yield is achieved, this quantity of furfural was charged in the reactor. After the completion of a reaction, the water layer was analyzed using HPLC while the toluene layer was analyzed using GC. The result shows that there is no any extra peak apart from furfural (furfural and BAIL in the case of reaction carried out with BAIL) in both the layers in GC and HPLC. The furfural stability study carried out with BAIL catalyst showed 7% furfural conversion and the reaction carried out without BAIL catalyst showed 4% furfural conversion, which means that furfural is stable under reaction conditions. Furthermore, to validate the second possibility of side reactions between C5 sugars and furfural, the reactions were carried out under optimized reaction condition [water+toluene 60 mL (1:5 *v/v*), 170 °C] for 5 h with 0.3 g xylose and 0.16 g furfural using 0.12 g $[C_3SO_3HMIM][HSO_4]$ BAIL. After the reaction, the formation of

black colored solid along with 70% furfural yield (0.25 g) was seen. It was also observed that almost 90% xylose was converted during the course of the reaction. By considering this, it was expected to achieve 94% (0.33 g) yield of furfural, however, only 70% (0.25) yield was seen. This shows that in the hemicellulose valorization into furfural, the mass loss is observed because of side reactions between furfural and C5 sugars.

Effect of catalyst & substrate concentration

As it is always desired to obtain higher product yields with optimum quantity of catalyst, the study on the effect of catalyst concentration was carried out and the results are illustrated in Fig. S23 (ESI). The reactions were performed at 170 °C in water+toluene (1:5 *v/v*; 60 mL) solvent system for 4 h. The results indicate that a very less quantity (0.12 g BAIL for 0.6 g hemicellulose, S/C=5 *wt/wt*) of $[C_3SO_3HMIM][HSO_4]$ BAIL was required to achieve 62% furfural yield along with 14% C5 sugars (X+A) yield (Fig. S23, ESI). In this reaction, >96% hemicellulose conversion was observed with 81% mass balance, which might be due to the fact that some of the products were not detected in HPLC and GC. The reaction carried out with S/C=10 *wt/wt* (0.06 g BAIL for 0.6 g hemicellulose) gave 30% furfural yield and 3% C5 sugars with 90% hemicellulose conversion. In this reaction, besides furfural and C5 sugars formation, oligomers and some side products which were not soluble in reaction solvent were observed. With higher loading of $[C_3SO_3HMIM][HSO_4]$ catalyst, S/C=2.5 *wt/wt* (0.24 g BAIL for 0.6 g hemicellulose), 60% furfural yield and 7% C5 sugars yield was achieved. In the reaction, >99% hemicellulose conversion was seen with 71% mass balance. This implies that by increasing the catalyst quantity from 0.12 g to 0.24 g the mass balance decreases because of increase in side reactions. The reaction carried out with S/C=5 *wt/wt* and S/C=2.5 *wt/wt* showed almost similar furfural yield (60 and 62%) however, higher C5 sugars yield (14%) was achieved when S/C=5 was used compared to S/C=2.5. This indicates that S/C=5 *wt/wt* is optimized S/C ratio for the valorization of hemicellulose. The higher catalyst quantity (0.12 g) is required for converting hemicellulose into furfural in one-pot fashion compared to the conversion xylose into furfural (0.08 g).

It is vital to test the developed catalytic method with the concentrated substrate solutions to make the system economical. Considering this, the effect of substrate concentration was studied. The reactions were carried out using $[C_3SO_3HMIM][HSO_4]$ BAIL as a catalyst with water+toluene (1:5 *v/v*; 60 mL) as a biphasic solvent system at 170 °C by maintaining BAIL and solvent quantity constant (Fig. S24, ESI). The reaction carried out with 0.2 g hemicellulose (2 *wt%* hemicellulose solution with respect to water; S/C=1.6 *wt/wt*) showed 85% furfural yield, while the reaction carried out with 0.4 g (4 *wt%* hemicellulose solution with respect to water; S/C=3.3 *wt/wt*) and 0.6 g (6 *wt%* hemicellulose solution with respect to water; S/C=5 *wt/wt*) of hemicellulose showed 70 and 62% furfural yield. These results suggest that lower hemicellulose concentration (0.2 g hemicellulose in 60 mL water+toluene (1:5 *v/v*)) is beneficial to achieve higher (85%) furfural yield. To the best of our knowledge, these are the highest possible furfural yields obtained from hemicellulose in a one-pot method.

Recycling and stability of $[C_3SO_3HMIM][HSO_4]$ BAIL

For the recycling study of a catalyst, after the first reaction, the catalyst was recovered (Section 15, ESI) and was used in the next reaction. In the first run, 62% furfural yield along with 14% C5 sugars yield was achieved. In a 1st recycle run, similar furfural yield (62%) as that obtained with fresh catalyst was seen. However, the yield of C5 sugars (X+A) was marginally decreased in this reaction (11%). Again in 2nd (59%) and 3rd (57%) recycle runs almost similar yields were obtained. This suggests that the catalyst is recyclable.

For understanding the stability of $[C_3SO_3HMIM][HSO_4]$ BAIL under reaction conditions, recovered catalyst was characterized by ^{1}H NMR technique (Section 14, Fig. S25, ESI). The ^{1}H NMR spectrum of the recovered catalyst is similar to the fresh catalyst and thus it is believed that the catalyst does not undergo any transformation during reactions. The TGA study of recovered BAILs shows that there is no mass loss up to 250 °C (Section 3, Fig. S17, ESI), which again emphasizes that the $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst which showed the best performance in the valorization of hemicellulose into furfural reaction is a stable catalyst.

CONCLUSION

We demonstrated herein that BAILs are a selective and efficient catalyst for the valorization of hemicellulose into furfural in a one-pot fashion. Different types of hemicellulose employed in the study and observed that BAILs can efficiently convert a wide range of hemicellulose into sugar monomers. The catalytic amount (0.12 g) of $[C_3SO_3HMIM][HSO_4]$ BAIL (without addition of any extra catalyst like mineral acids or metal halides) efficiently converted hemicellulose into furfural in a one-pot fashion with a very high yield of furfural i.e. 85% under optimized reaction conditions (170 °C, 4 h, water+toluene 60 mL (1:5 *v/v*)). The reaction carried out with concentrated hemicellulose under similar conditions showed 62% furfural yield. The result shows that with increasing hemicellulose concentration side reactions were increased and hence furfural yield and selectivity was decreased. Similarly, with increasing the reaction time more than 4 h at 170 °C and temperature above 170 °C (4 h) favours degradation reactions. For achieving a better yield of furfural, water+toluene solvent system is necessary; this was explained with the help of partition coefficient of furfural in organic/water biphasic solvent system and the solubility of the organic phase in water. The $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst used for the valorization of hemicellulose into furfural performs better compared to solid acid and mineral acid catalysts such as HUSY (Si/Al=15), Amberlyst-15 and H_2SO_4. The $[C_3SO_3HMIM][HSO_4]$ BAIL recovered from the reaction mixture is a stable and recyclable catalyst which was confirmed by ^{1}H NMR study.

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