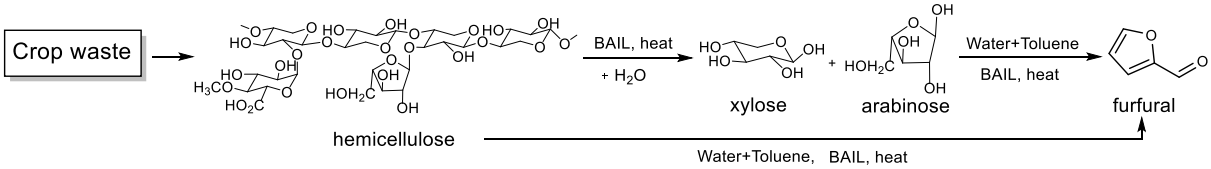
Novel method for the conversion of saccharides into sugars and furans using acidic ionic liquids

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Statement of the problem: Extensive literature available on the conversion of xylose into furfural and very few reports on the direct conversion of hemicellulose into furfural.[1] The reported methods show the use of mineral acid, solid acid catalyst and ionic liquids (ILs) as solvent for the hydrolysis and dehydration reactions of saccharides. The drawbacks with the known methods are 1) Use of mineral acid makes reaction system homogeneous and has a serious problem of recyclability of catalyst, lower selectivity, corrosiveness and environmental issues.[2] 2) Use of solid acid catalysts shows lower yields of desired products and the catalyst is not stable in most of the cases under reaction condition.[3-4] 3) Very high quantity of ILs (as a solvent) is used and in some reports, it is used along with metal halide or mineral acids.[5-6]

To avoid above mentioned drawbacks, it is very important to develop an efficient catalytic method for the synthesis of sugars and furans (furfural & HMF) from non-edible biomass. For this, ILs reported in literature can be replaced with catalytic amount of Brønsted acidic ionic liquids (BAILs) and these catalysts can be used without metal halide and mineral acid.



Scheme 1 Hydrolysis of hemicellulose into sugar monomers and further dehydration into furfural using BAILs

Methodology used: Various BAILs with various cations and anions were synthesized and characterized using NMR, FTIR, TGA & CHNS-analysis characterization techniques. Further these BAILs were used in the hydrolysis and dehydration reactions of saccharides for understanding the effect of cations and anions of BAILs in these reactions. Further, in the above-mentioned reactions the performance of BAILs was compared with of solid acid catalyst and mineral acid catalyst (H_2SO_4, HCl), respectively.

The hemicellulose conversion was carried out in water medium at 160 °C for 1 h and we achieved 87% yield for C5 sugars (xylose and arabinose) when 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate ([C_3SO_3HMIM] [HSO_4]) is used as a catalyst. Along with C5 sugars, 10% furfural yield was also obtained.[7] The ionic liquid without –SO_3H group like 1-butyl-3-methylimidazolium chloride ([BMIM] [Cl]) gives less activity (60% C5 sugar yield). This shows that Brønsted acid sites are responsible for the hemicellulose conversion. The results of BAILs are compared with mineral acid like H_2SO_4 and the solid acid catalysts [HUSY (Si/Al= 15), HMOR (Si/Al= 10)] and it was found that H_2SO_4 gives 50% C5 sugar yield while HUSY (Si/Al= 15) and HMOR (Si/Al=10) gives 37% and 23% C5 sugar yield, respectively. This shows that BAILs are better catalyst compared to mineral acid and solid acid catalyst for hemicellulose conversion into sugars.[7,8] After successful conversion of isolated hemicelluloses, crop wastes like rice husk, bagasse and wheat straw were also converted in to sugar monomers using the BAIL and obtained exceptionally high C5 sugar yields (70-85%). The higher activity for BAILs obtained because of presence of ion dipole type of interaction between BAIL and polysaccharide this is estimated using ^{1}H NMR spectroscopy.[7] The BAILs used for hemicellulose conversion into sugar monomers are stable under reaction condition which is confirmed by ^{1}H NMR spectroscopy.

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