

Utilization of Brønsted Acidic Ionic Liquids in the Hydrolysis and Dehydration Reactions of Saccharides

*Thesis Submitted to AcSIR For the Award of
the Degree of
DOCTOR OF PHILOSOPHY
In
Chemistry*



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March, 2016



हीरक जयन्ती वर्ष 2009-10

राष्ट्रीय रासायनिक प्रयोगशाला

(वैज्ञानिक तथा औद्योगिक अनुसंधान परिषद)

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This is to certify that the work incorporated in this Ph.D. thesis entitled "**Utilization of Brønsted acidic ionic liquids in the hydrolysis and dehydration reactions of saccharides**" submitted by **Mr. Babasaheb Mansub Matsagar** to Academy of Scientific and Innovative Research (AcSIR) in fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy in Chemistry**, embodies original research work under my supervision/guidance. I further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material obtained from other sources has been duly acknowledged in the thesis. Any text, illustration, table etc., used in the thesis from other sources, have been duly cited and acknowledged.

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I hereby declare that the thesis entitled "**Utilization of Brønsted acidic ionic liquids in the hydrolysis and dehydration reactions of saccharides**" submitted for the award of the Degree of **Doctor of Philosophy in Chemistry** to the **Academy of Scientific & Innovative Research (AcSIR)**, New Delhi, has been carried out by me at Catalysis & Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Pune-411008, India, under the supervision of Dr. Paresh L. Dhepe. The work is original and has not been submitted as a part or full by me for any degree or diploma to this or any other university.

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DEDICATED TO.....

MY PARENTS,

MY BROTHER &

MY WIFE

ACKNOWLEDGEMENTS

I find it very difficult to write something in short to acknowledge my research guide, Dr. Paresh L. Dhepe. His constant inspiration, invaluable guidance and constructive criticism helped me a lot to focus my views in proper perspective. Wholeheartedly, I am very much grateful to him for motivating me in the field of research. I sincerely thank for his care and affection that I have received from him in the entire period of my Ph.D. degree. I take this opportunity to express my intense respect towards him for guiding me in the right direction throughout the course of this work. My deepest personal regards are due for him forever.

I am highly indebted to Dr. D. Srinivas Head of Catalysis Division and Dr. A. P. Singh, Dr. Rajiv Kumar, former Heads of Catalysis Division, not only formally for allowing me to use all the available facilities in the division but also personally for many stimulating discussions and valuable guidance throughout the course of this investigation.

I owe my sincere gratitude to Dr. Nandini Devi for UV-Vis analysis, Dr. C. V. V. Satyanarayana for TGA analysis, Dr. S. Shubhangi for FTIR, Dr. P. R. Rajamohanan of NMR Division for solid and liquid state NMR analysis and discussions, Ms. V. Samuel for XRD, Microanalysis laboratory staffs for elemental analysis. My heartfelt thanks are due Dr. C. V. V. Satyanarayana, Dr. R. Nandini Devi, Dr. T. Raja, Dr. N. M. Gupta, Dr. A. K. Kingae Dr. Gopinath and all other scientific and non-scientific staff of the division for their valuable help and cooperation during my tenure as a research scholar. I also thank other divisional scientists Dr. Anil Kumar, Dr. Santosh Mhaske, Dr. Vincent Paul, Dr. B. L. V. Prasad, for constructive discussions and help throughout this course of study.

I would like to express my thanks to my DAC committee members Dr. M. S. Shashidhar, Dr. C. V. V. Satyanarayana, Dr. A. A. Kelkar and AcSIR coordinator Dr. C. G. Suresh for their valuable suggestions and guidance during my research work.

I would like to thank Mr. Purushottaman, Mr. Madhu, Dr. Tejas, Ms. Samuel Violet, I thank the staffs of Accounts & Finance, Bill, Administration, Engineering and Stores & Purchase sections for their help in a way or the other.

I would like to express my appreciation to my labmates, Dr. Deepa, Dr. Prasenjit, Dr. Anup, Manisha, Sandip, Richa, Himani, Neha, Nilesh for their presence

and making my comfortable atmosphere all the time in the lab. Also, I would like to acknowledge Dr. Ramakant, Dr. Atul for encouragement and support. I would like to express my gratefulness to colleagues in the NCL Dr. Deepak, Jijil, Dr. Rajesh, Dr. Soumya, Leena, Sourik, Devraj, Anjani, Anish, Dr. Sanjay, Dr. Priti, Atul, Dr. Nishita, Dr. Kanna, Dr. Hanmant, Dr. Pavan, Dr. Joby, Dr. Unni, Debdatta, for their constant support throughout my stay in NCL.

I take this golden opportunity to convey my earnest gratitude to my friends, Akbar, Sourav, Datta, Balwant, Prashant, Sandip Mahesh More and Mahesh Walle for the wonderful time I had with them. It will remain in my memories of life that I had wonderful time, fun and enjoyment at Pashan & NCL Colony during my research time. It gives me great pleasure to thank my old friends, Akbar and Prashant from whom I have received unfailing support and encouragement during many years of studies that they have shown to me in their own special way. I also take this golden opportunity to convey my earnest respect to my school teachers, college teachers and my M.Sc. teachers (Dr. S. N. Thore, Dr. Bhagat, Mr. Sonar and Mr. Pardeshi) for their extraordinary way of teaching that build up my research career in science. I further, thank Mr. Mahesh Shioorkar for constant support and encouragement.

*The thesis could not have been completed without the endless support and blessings from my family. **Akka** and **Nana**, I should not belittle you by thanking; you taught me how to dream, gave me the skills to chase after those dreams, and encouraged me to reach for the unreachable star. Due adoration to my brother Yogesh and his persistent faith in my capability has always spurred me to go ahead, especially in difficult times. I appreciate the supports and fun given by my nephews Om, Sai, Samrat and my daughter Srushti. I must acknowledge my wife Snehal without her love, care, trust, I would not have finished this thesis.*

Finally, my thanks to Council of Scientific and Industrial Research, Government of India, for awarding the Research Fellowship, and to Dr. Sourav Pal (former Director), Dr. Ashwini K. Nangia (Director), and Dr. Vivek. V. Ranade, (Deputy Director), CSIR-National Chemical Laboratory, to carry out my research work and extending all possible infrastructural facilities, and to submit this work in the form of a thesis for the award of the Ph.D. degree.

*..... **B.M. Matsagar***

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Chapter 5

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List of Abbreviations

BAIL	Brønsted acidic ionic liquid
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DOE	Department of energy
DP	Degree of polymerization
FAS	Ferrous ammonium sulfate
FDCA	2,5-furan dicarboxylic acid
FID	Flame ionization detector
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HMF	5-Hydroxymethylfurfural
HMOR	Mordenite (H-form)
HPLC	High pressure liquid chromatography
HUSY	Ultra stable zeolite Y (H-form)
H- β	Beta zeolite (H-form)
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
MIBK	Methyl isobutyl ketone
NMR	Nuclear magnetic resonance
OD	Oven dried
PTSA	<i>p</i> -Toluenesulfonic acid monohydrate
RID	Refractive index detector
TAPPI	Technical association of the pulp and paper industry

TGA	Thermogravimetric analysis
TPD	Temperature programmed desorption
USDA	United States Department of agriculture
UV-Vis	Ultra violet-visible
XRD	X-ray diffraction

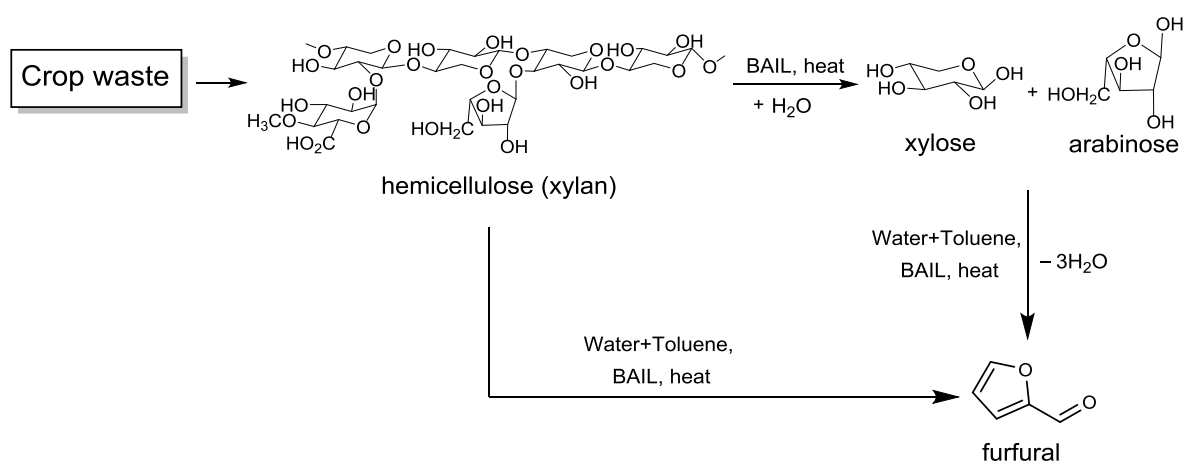
Abbreviations of ILs

[BMIM][Cl]	1-butyl-3-methyl imidazolium chloride
[C ₃ SO ₃ HBenzMIM][PTS]	1-methyl-3-(3-sulfopropyl)-benzimidazolium <i>p</i> -toluenesulfonate
[C ₃ SO ₃ HBezMIM][HSO ₄]	1-methyl-3-(3-sulfopropyl)-benzimidazolium hydrogen sulfate
[C ₃ SO ₃ HMIM][Cl]	1-methyl-3-(3-sulfopropyl)-imidazolium chloride
[C ₃ SO ₃ HMIM][HSO ₄]	1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate
[C ₃ SO ₃ HMIM][PTS]	1-methyl-3-(3-sulfopropyl)-imidazolium <i>p</i> -toluenesulfonate
[C ₃ SO ₃ HNEt ₃][HSO ₄]	N,N,N-triethyl-(3-sulfopropyl)-ammonium hydrogen sulfate
[C ₃ SO ₃ HNEt ₃][PTS]	N,N,N-triethyl-(3-sulfopropyl)-ammonium <i>p</i> -toluenesulfonate
[C ₃ SO ₃ HPPPh ₃][PTS]	triphenyl-(3-sulfopropyl)-phosphonium <i>p</i> -toluenesulfonate
[C ₃ SO ₃ HPy][PTS]	1-(3-sulfopropyl)-pyridinium <i>p</i> -toluenesulfonate
[C ₄ SO ₃ HMIM][HSO ₄]	1-methyl-3-(4-sulfobutyl)-imidazolium hydrogen sulfate
[C ₄ SO ₄ HMIM][PTS]	1-methyl-3-(4-sulfobutyl)-imidazolium <i>p</i> -toluenesulfonate

Abstract of thesis

Introduction

Biomass is an alternative for fossil feedstock to convert it into fuels, chemicals and energy. It has various advantages over fossil feedstock as it is renewable, sustainable, abundant, and inexpensive. Also, it can make the process carbon neutral. Use of biomass for the production of fuels and chemicals is challenging in the development of a sustainable process.^[1] Lignocellulosic biomass is a major component of the plant's cell wall and it is non-edible. It is made up of cellulose, hemicellulose and lignin. While cellulose is a polysaccharide made up of glucose units linked together by $\beta(1\rightarrow4)$ glycosidic bonds, hemicellulose is homo or heteropolysaccharide made up of pentoses (C5 sugars), hexoses (C6 sugars) and sugar acids linked together by $\beta(1\rightarrow4)$, $\beta(1\rightarrow3)$ and $\beta(1\rightarrow6)$ glycosidic linkages. The lignin is 3D aromatic polymer made up of different phenylpropanoid units.^[2] The use of non-edible biomass will not conflict with food demand, and hence, it is important to use this biomass as chemical precursors. Sugars obtained by hydrolysis of polysaccharides from non-edible biomass can be the first platform chemicals in the biorefinery.^[3] The dehydration of C5 and C6 sugars into furfural and 5-hydroxymethyl furfural (HMF) have various important industrial applications. Therefore, the hydrolysis of polysaccharides like isolated hemicellulose, hemicellulose from crop waste, and dehydration reactions of C5 and C6 sugars into furans were performed in my Ph.D. work (Scheme 1).



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

Statement of Problem

There is an extensive literature available on the conversion of xylose into furfural and very few reports on the direct conversion of hemicellulose into furfural.^[4] The reported methods show the use of mineral acids, solid acids and ionic liquids as catalysts for the hydrolysis and dehydration reactions of saccharides. The drawbacks of the known methods are as below.

- Use of mineral acid makes reaction system homogeneous and has a serious problem of recyclability of catalyst, lower selectivity, corrosiveness and environmental issues.^[5]
- 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.^[6-7]
- Higher quantity of ionic liquids (as a solvent) is used and in some reports, it is used along with metal halide or mineral acids.^[8-9]

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, ionic liquids reported in the literature can be replaced with the catalytic amount of Brønsted acidic ionic liquids (BAILs) and these catalysts can be used without metal halide and mineral acid.

Methodology used

- Various BAILs were synthesized and characterized using NMR, FTIR, TGA & CHNS characterization techniques.
- BAILs with various cations and anions were synthesized for understanding its effect in the hydrolysis and dehydration reactions of saccharides.
- All the BAILs are used for the hydrolysis of isolated hemicellulose and crop waste selectively into sugar monomers and further dehydration into furans in one pot method. Also, BAILs were used for dehydration reactions of C5 and C6 sugars into furfural and 5-hydroxymethyl furfural (HMF), respectively.
- Characterization of fresh and recovered BAILs from the reaction was performed to understand the stability and reusability of BAILs.
- The performance of BAILs was compared with solid acid and mineral acid catalysts in above mentioned reactions.

- Ion-dipole type of interaction between saccharide and BAILs were studied using NMR spectroscopy.

Sample results

Conversion of hemicellulose into C5 sugars and furfural:

BAILs were evaluated for the conversion of xylan type hemicellulose. The reactions were carried out at 160 °C for 1 h and showed >99% conversion of hemicellulose and 87% C5 sugar (xylose+arabinose) yield using 1-methyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate ([C₃SO₃HMIM][HSO₄]) catalyst (Fig. 1). The difference in activity of BAILs can be explained on the basis of acid strength calculated using Hammett acidity function (*H_o*). The acid strength of all these catalysts are in the order of HMOR > HUSY > H₂SO₄ > [C₃SO₃HMIM][HSO₄] > [C₃SO₃HMIM][PTS] > [C₃SO₃HMIM][Cl]. The [C₃SO₃HMIM][HSO₄] BAIL has highest acid strength compared to all other BAILs and hence it showed a higher yield of C5 sugars. 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) IL was synthesized and its activity is compared with BAILs. The IL without Brønsted acidity shows lower activity (59% C5 sugar yield) compared to BAILs (75-87% C5 sugar yield).

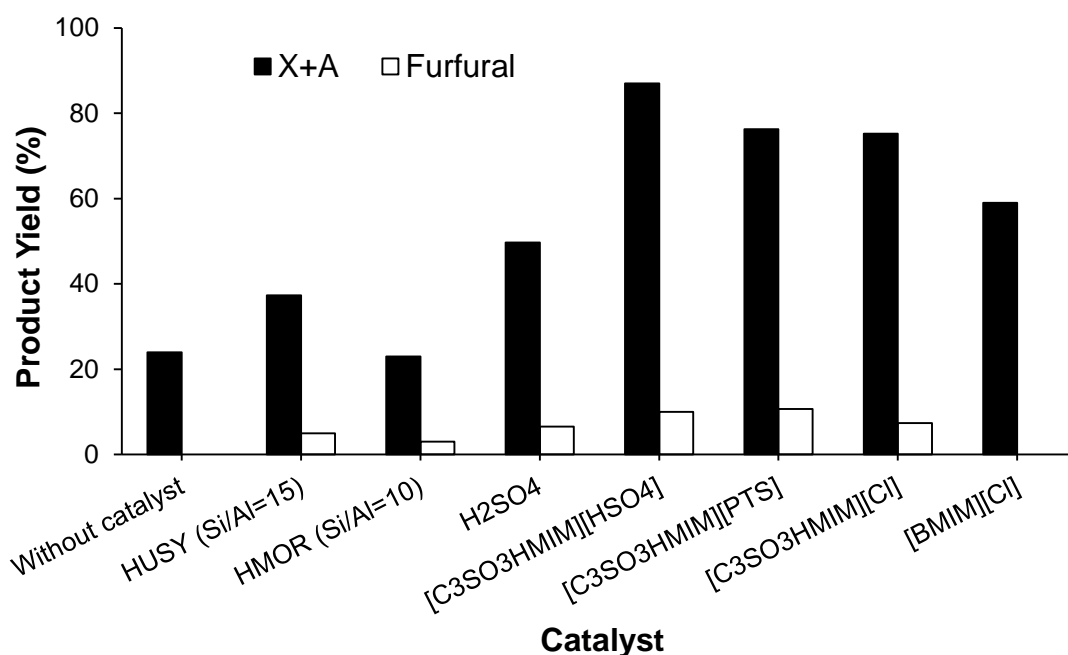


Figure 1. Catalyst evaluation study for the conversion of hemicellulose; Reaction condition. hemicellulose (birchwood) 0.6 g, catalyst 0.24 g, water 60 mL, 160 °C, 1 h.

The lower activity of solid acid catalysts is due to its heterogeneous nature and diffusion limitations because of which all the acid sites are not available for the

substrate molecules to react. Also, the BAILs shows higher activity (75-87% C5 sugar yield) compared to H₂SO₄ (50% C5 sugar yield) since BAILs are shown to have the ion-dipole type of interaction with hemicellulose.^[10] This interaction was understood from ¹H NMR study.

Conversion of hemicellulose into furfural was carried out using BAILs in biphasic solvent system like water+toluene 1:5 (v/v) at 170 °C for 4 h using 0.6 g hemicellulose and 0.125 g catalyst. Catalyst evaluation study again shows the best catalytic results (63% furfural yield) with [C₃SO₃HMIM][HSO₄] BAIL catalyst compared with solid acid (HUSY (Si/Al=15); HMOR (Si/Al=10), Amberlyst-15) and H₂SO₄. The highest furfural yield (85%) can be obtained by decreasing hemicellulose concentration from 0.6 g to 0.2 g.

Selective conversion of hemicellulose from crop waste into C5 sugars and furfural:

Various crop wastes (rice husk, bagasse, wheat straw, cotton stalk and corn cob etc.) used in this study were analyzed using TAPPI and ICP methods to understand their composition. For the conversion of crop waste, similar reaction condition is used as like used in the conversion of isolated hemicellulose into C5 sugars (Fig. 1). The [C₃SO₃HMIM][HSO₄] BAIL is an efficient catalyst and can convert almost all types of crop wastes into C5 sugars with very high yields (93-67%) (Fig. 2).

Next crop waste conversion into furfural was carried out using [C₃SO₃HMIM][HSO₄] BAIL in water+toluene 1:5 (v/v) solvent system and it was observed that BAILs performs better compared to solid acid and mineral acid catalysts. The reactions were carried with 0.6 g crop waste and 0.125 g BAIL at 170 °C (3 h). Different types of crop wastes were used and it is observed that using [C₃SO₃HMIM][HSO₄] BAIL almost all types of crop wastes could be efficiently converted into furfural in one pot method with very high yield (88-73%).

Dehydration of C5 & C6 sugars into furfural and HMF:

Dehydration of C5 sugar (xylose) into furfural was carried out at 170 °C (4 h) using 0.6 g xylose and 0.08 g BAIL in water+toluene 1:5 (v/v) biphasic solvent system. The highest yield of furfural (73%) was obtained with [C₃SO₃HMIM][HSO₄] BAIL. Further, decreasing the concentration of xylose from 6 wt% to 3 wt%, an increase in furfural yield was seen from 73% to 81%. The recycle experiment carried out for this reaction

with $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL shows that the catalyst is a recyclable and almost similar yield of furfural can be obtained in 4 recycle experiment.

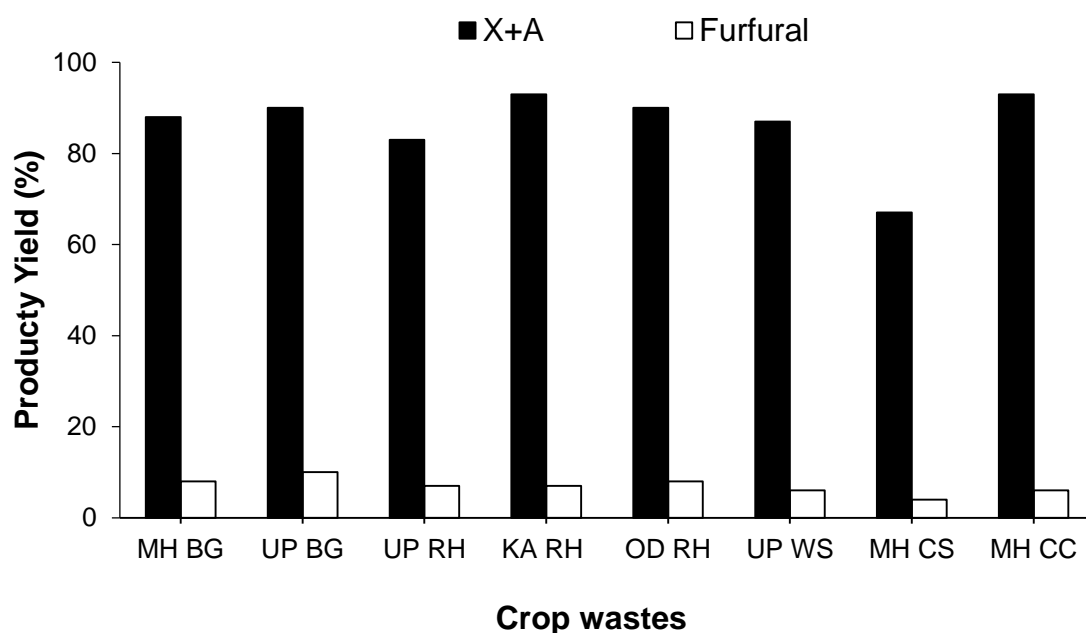


Figure 2. Effect of crop wastes for the selective conversion of hemicellulose from crop wastes into sugars; Reaction condition. crop waste 2 g, water 60 mL, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.24 g, 160, 1 h.

Fructose dehydration reactions were carried out at 150 °C, (30 min) using 0.5 g fructose and 0.025 g $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL in water+MIBK 1:5 (v/v) biphasic solvent system. The $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL showed highest HMF yield (73%). Further, to make the process economic compared to known processes, reactions were carried out with higher fructose concentration (10 wt% to 40 wt%). With 40 wt% fructose solution, similar HMF yield as like 10 wt% fructose solution can be obtained (Fig. 3). Recycle study carried out using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL shows that catalyst is showing an almost similar yield of HMF up to 6 recycle runs.^[11]

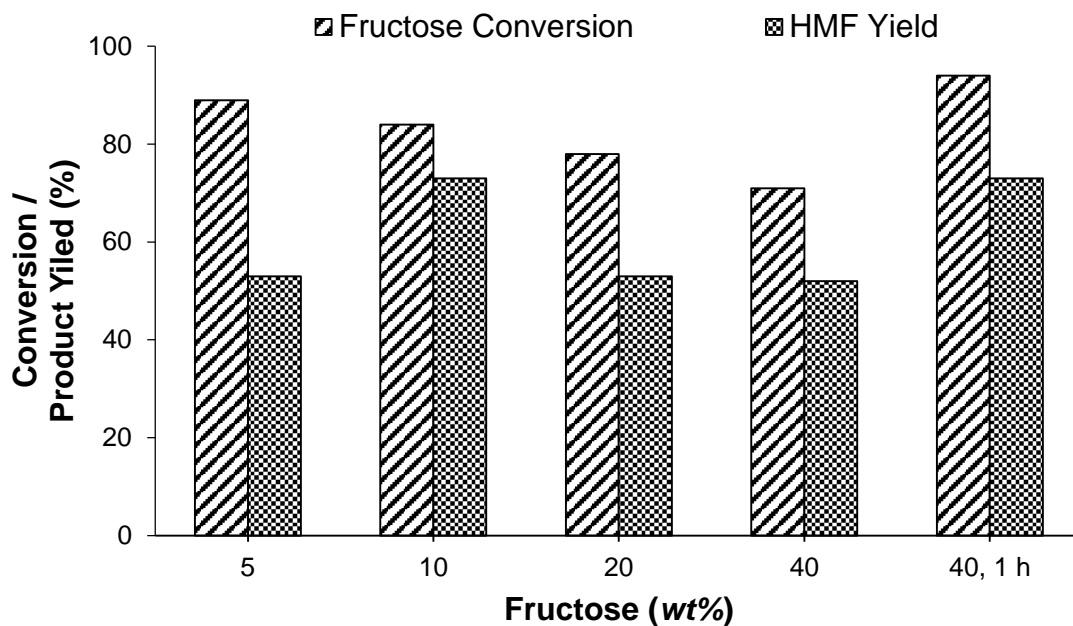


Figure 3. Effect of fructose concentration; Reaction condition. $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.025 g, Water+MIBK 30 mL (1:5 v/v), 150 °C, 30 min.

It is concluded that catalytic amount of BAILs without metal halide and mineral acid were successfully used for the hydrolysis and dehydration reactions of saccharides. Selective conversion of hemicellulose from various crop wastes into C5 sugars (93-67%) and furfural (88-73%) were carried out using the catalytic amount of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL. The catalyst is the stable, recyclable and ion-dipole type of interaction present between BAIL and hemicellulose plays an important role in achieving higher activity with BAILs. The imidazolium based BAILs showed higher activity compared to quaternary ammonium and triphenyl phosphonium based BAILs because of the presence of efficient interaction.

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Chapter 1

Introduction, Literature Survey & Inspiration of Work

1.1. Introduction

Fossil resources are used to provide a wide range of chemicals and satisfy our energy needs that enrich our lives.^[1] The fossil raw materials are crude oil, natural gas, and coal. The transportation sector is responsible for almost one third of the total energy consumed in the world. Also, an energy required (96%) for transportation sector is currently derived from fossil feedstock, crude oil.^[2] There are three important issues with large scale utilization of fossil feedstock; 1) Uneven geographical distribution of reserves, 2) Global warming and 3) Availability of fossil feedstock. The fossil feedstocks are finite because for their synthesis millions of years are required and also their current consumption rate is higher than their corresponding regeneration. However, the U.S. Department of Energy (USDOE) and the U.S. Department of Agriculture (USDA) have mandated that 5% of heat and power energy, 20% of liquid transportation fuel, and 25% of chemicals and materials should come from biomass by 2022.^[3] Various platform chemicals synthesized from biomass will show huge value addition and therefore, it is important to convert biomass into chemicals. Considering this, there is a need to develop various catalytic methods for the synthesis of chemicals from biomass.

It is acknowledged that biomass is the most attractive alternative source for fossil feedstock. Nature produces around 170 billion metric tons of biomass per year by way of photosynthesis and out of this ca. 75% is assigned to the class of carbohydrates.^[4] But, only 3-4% of these compounds are used by humans for food and non-food purposes. Hence, there is much scope for the development of efficient methods for the conversion of carbohydrates into chemicals.^[4] Utilization of biomass feedstock instead of fossil feedstock has various important advantages such as it can make process carbon neutral, it is widely available, inexpensive, renewable and sustainable.^[5-6] Therefore, it is highly desirable to convert renewable lignocellulosic biomass selectively into platform chemicals under mild reaction conditions, which can subsequently be used for the production of various chemicals. Extensive research and development programs have been initiated worldwide to convert lignocellulosic biomass, such as agricultural residues, forestry wastes, and energy crops, into valuable products, through a sugar platform. There are two types of sugars which are most common and those are hexoses (six-carbon sugars) and pentoses (five-carbon

sugars). Glucose is the most common sugar in hexoses and xylose is the most common sugar in pentoses type. There are two ways to transform these sugars into valuable bio-products: one is fermentation process, and the other one is the chemical transformation.

The list of 12 potential bio-based platform chemicals is presented in the U.S. DOE report.^[7] The 12 sugar based building blocks are 1,4-diacids (succinic, fumaric and malic), 2,5-furandicarboxylic acid, (FDCA) 3-hydroxypropanoic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutrolactone, glycerol, sorbitol, and xylitol/arabinitol.^[7] Other important chemicals synthesized from biomass are furfural, 5-hydroxymethylfurfural (HMF), xylose, and arabinose. This shows the potential of biomass for the synthesis of various important chemicals.

1.1.1. Utilization of biomass

There are two major problems with the utilization of lignocellulosic biomass; the first one is the recalcitrance nature of lignocellulosic biomass due to the rigid and compact structure of plant cell wall and the second one is higher oxygen content.^[8] Recalcitrance nature of lignocellulosic biomass constitute a barrier for enzymes/catalysts to access several linkages and therefore, it is a must that biomass should be at least partially deconstructed before the reaction by way of pretreatment.^[5] Another issue with lignocellulosic biomass is higher percentage of oxygen content in their molecular structure, which makes difficulty in biomass processing. Lignocellulosic biomass has a higher fraction of hydrogen (ca. 5-6%), oxygen (ca. 43%), and less carbon (48-50%) than coal. Typical element composition of Anthracite coal is 2-4% hydrogen, 2-5% oxygen, 91-94% carbon and in bituminous coal, it is 4-6% hydrogen, 3-8% oxygen, and 83-89% carbon. As a result, biomass tends to generate less energy (two-third on a mass basis) than coal.^[9] In addition, the differences in composition causes biomass to have a higher fraction of volatile matter, which causes to have more “flaming combustion” and less “char combustion”. To make the biomass a desirable feedstock, it is very important to decrease the oxygen content. There are three ways by which oxygen content of carbohydrate can be decreased.^[10]

- 1) Removal of small highly oxidized carbon molecules such as CO₂, formaldehyde, and formic acid. Example the fermentation of carbohydrate into ethanol, butanol, and CO₂.
- 2) Hydrogenolysis, which removes oxygen from the molecule by forming water at the expense of one molecule of hydrogen for each oxygen atom.
- 3) Dehydration of carbohydrates into a wide variety of interesting compounds. Example furans and levulinic acid.

1.2. Overview of biomass classification

The term biomass (bio+mass derived from Greek word bios meaning life and maza meaning mass) refers to non-fossilized and biodegradable organic material originating from plants, animals, and microorganisms derived from biological sources. Biomass includes products, by-products, residues and waste from agriculture, forestry and related industries, as well as the non-fossilized and biodegradable organic fractions of industrial and municipal solid wastes. Biomass also includes gasses and liquids recovered from the decomposition of non-fossilized and biodegradable organic materials.

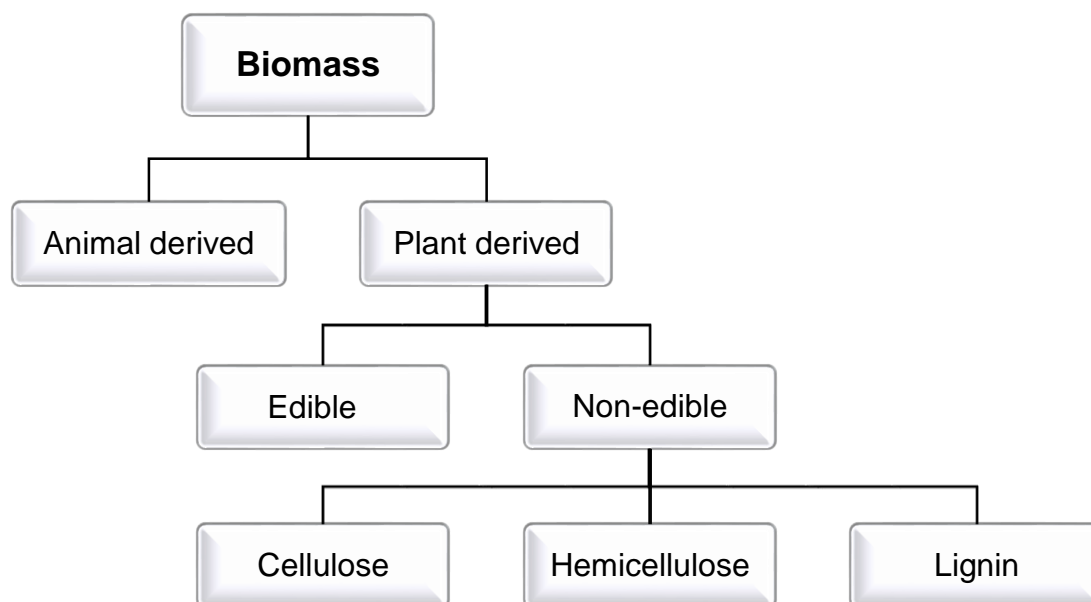


Figure 1.1. Classification of biomass.

Depending on the sources of biomass, it is classified as animal derived biomass and plant derived biomass (Fig. 1.1.). The animal derived biomass includes fishery resources and animal residues such as chitin. Chitin is a long chain polymer of N-

acetylglucosamine. It is a characteristic component of cell walls of fungi and the exoskeletons of arthropods (crabs, lobsters, and shrimps).

The examples of plant derived biomass are agricultural waste (crop waste), marine plants, wood, forestry, and residues obtained from the plant. Plant derived biomass is further classified as edible and non-edible biomass (Fig. 1.1.).

1.2.1. Edible biomass

The edible biomass is digestible to human beings and it is used as food. The example of edible biomass is wheat, bajra, rice, potato, cereals, corn etc. These food items typically contain carbohydrates like glucose, sucrose, fructose xylose, lactose, maltose, starch etc. (Fig. 1.2.).

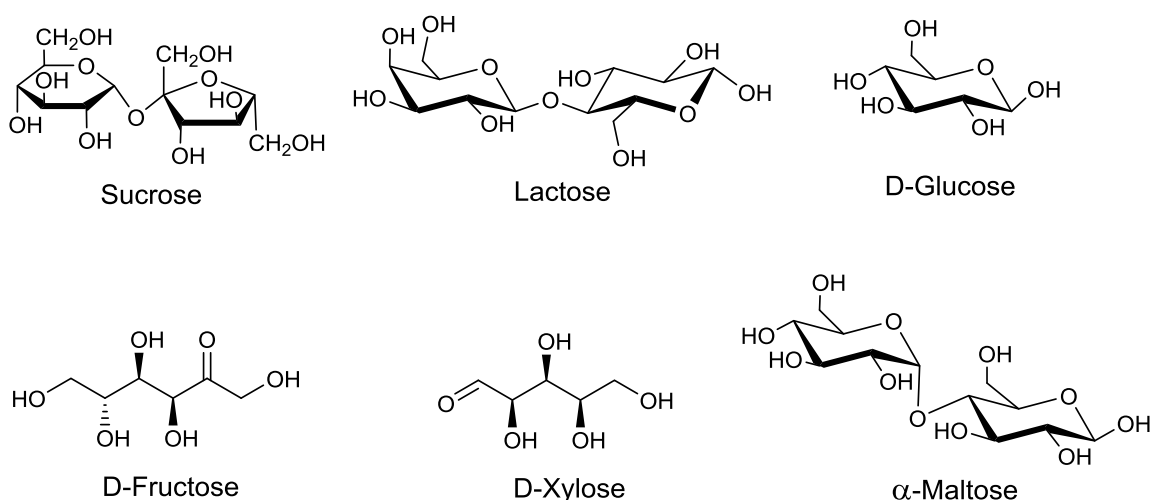


Figure 1.2. Structures of common edible sugars.

Starch is the most common carbohydrate in human diets and it is present in large amount in main food items such as wheat, rice, maize (corn), potatoes etc. Starch is made up of α -D-glucose units linked through α -1 \rightarrow 4 glycosidic linkage to form amylose, and if to the amylose, α -D-glucose is linked with α -1 \rightarrow 6 glycosidic linkages then it forms amylopectin part of a starch (Fig. 1.3.). Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin by weight.

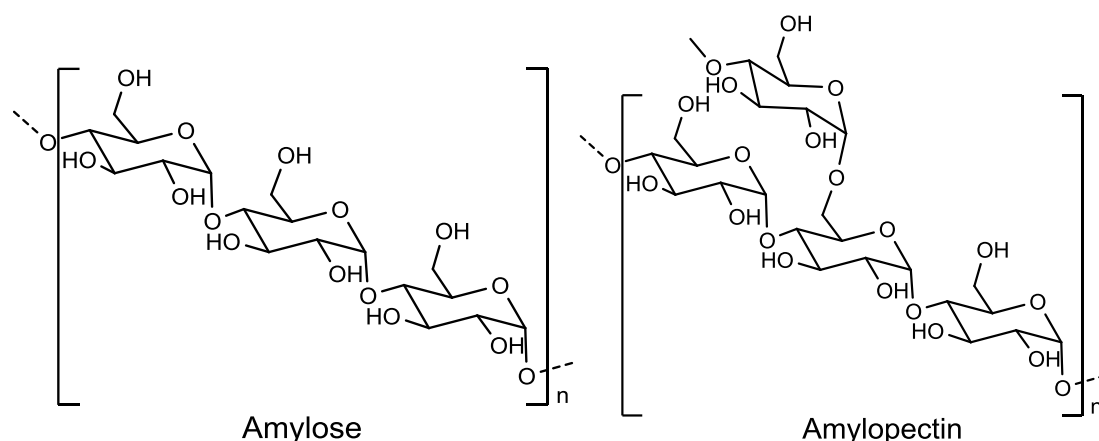


Figure 1.3. Structure of starch.

1.2.2. Non-edible biomass & components of lignocellulosic biomass

The non-edible biomass is not digestible to human beings. The example of non-edible biomass is disaccharides such as cellobiose and xylobiose; polysaccharides such as cellulose and hemicellulose. Cell walls of plants consists of mainly cellulose (40-50%), hemicellulose (20-30%) and lignin (18-28%) as organic compounds (Fig. 1.4.). These three compounds are also major components of natural lignocellulosic biomass as shown in Fig. 1.4. Cellulose molecules are arranged regularly, gather into bundles, and determine the framework of the cell wall. The fibers are filled with hemicellulose and lignin. The structure of the plant cell wall is compact and it is mainly consisting of cellulose, hemicellulose, and lignin in a ca. 4:3:3 ratio. This ratio varies from sources such as hardwood, softwood, and herbs. Besides these three components, lignocellulosic biomass contains a small amount of pectin, nutrients, and ash.

Utilization of non-edible biomass has various applications over fossil feedstock to convert it into various chemicals (section 1.1.). The edible biomass is being used as a food source and if it is converted into chemicals then it may create a problem of food crisis (issue of food versus chemicals). Lignocellulosic biomass is the major component found in plant and algae biomass, and the estimated annual production of lignocellulosic biomass is ca. 2×10^{11} metric tons.^[11-12] India produces annually approximately 20% major crops (sugarcane, rice paddy, wheat, etc.) with respect to the total worldwide production of these crops.^[13] This shows that in India huge amount of agriculture waste can be generated by utilizing the edible part of these crops. Thus, it is very important to develop an efficient process for the conversion of non-edible biomass (lignocellulosic biomass) into chemicals.

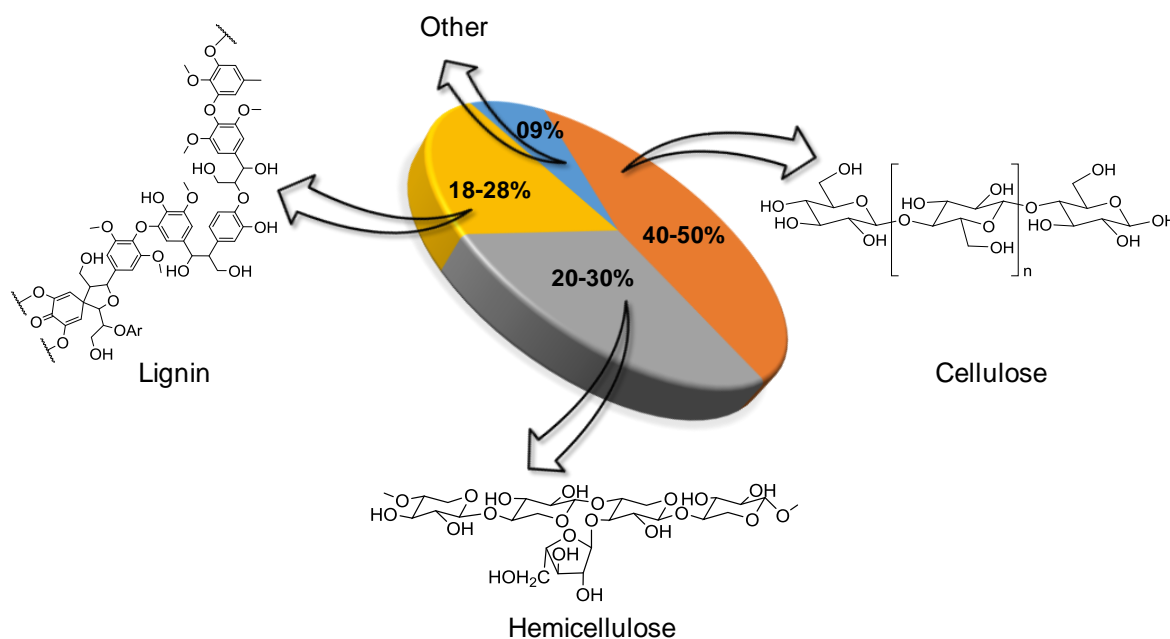


Figure 1.4. Components of lignocellulosic biomass.

1.2.2.1. Cellulose

Cellulose is a linear homopolysaccharide made up of β -D-glucose units. The anhydroglucose units are bonded to each other through $\beta(1\rightarrow4)$ glycosidic linkage and the bond is called as β -1,4-glycosidic bond. The number of repeating anhydroglucose units present in cellulose decides the degree of polymerization (DP) of cellulose. DP for α -cellulose derived from the wood fiber is typically 800-1100 and for raw cotton cellulose it is ca. 700.^[14] Natural cellulose shows crystalline and non-crystalline phases interlinked with each other. The non-crystalline phase assumes an amorphous state when tested using X-ray diffraction because most hydroxyl groups on glucose are amorphous. However, large amounts of hydroxyl groups in the crystalline phase form many hydrogen bonds, and these hydrogen bonds construct a huge network that directly contribute to the compact crystal structure.^[15] The hydrolysis of cellulose is difficult because of its robust crystal structure and high chemical stability. In cellulose, the β -1,4-glycosidic bond is tightly linked through intra and intermolecular hydrogen bonds, because of this extensive hydrogen bonding the access of catalyst to glycosidic bond is hindered and it also makes cellulose insoluble in the conventional solvents, which results in the low convertibility for the production of glucose.^[16-17]

1.2.2.2. Hemicellulose

Hemicellulose is one of the main component of plant fiber and it is defined as “homo or heteropolysaccharide made up of pentoses (C5 sugars), hexoses (C6 sugars) and sugar acids linked together by $\beta(1\rightarrow4)$, $\beta(1\rightarrow3)$ and $\beta(1\rightarrow6)$ glycosidic linkages”.

Hemicellulose is divided into four general classes of structurally different cell-wall polysaccharide types, i.e. mannans, xylans, xyloglucans and β -glucans with mixed linkages.^[18] The various types of sugars present in hemicellulose are shown in below Fig. 1.5.

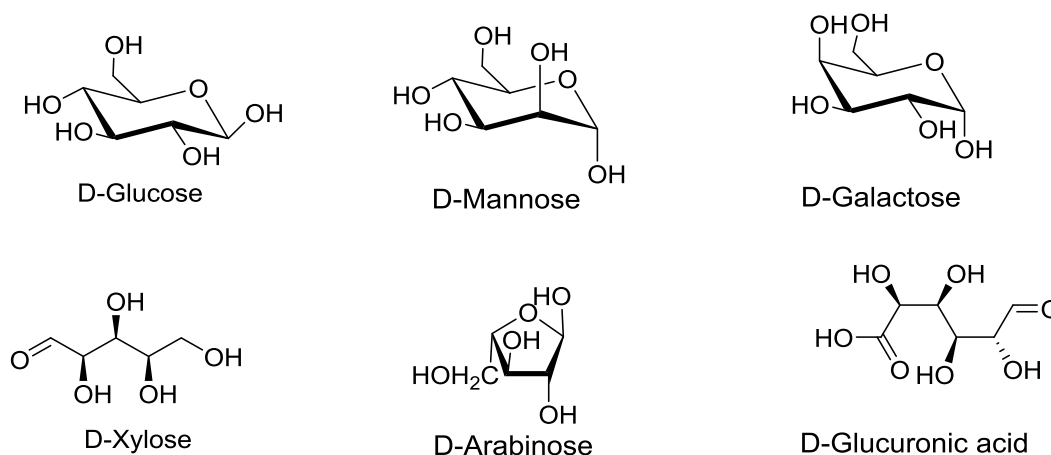


Figure 1.5. Sugars present in hemicellulose.

Chemical structures of different types of hemicellulose are classified as below:

- Mannans or Glucomannans (GM) or galactoglucomannans (GGM)
- Xylan or glucuronoxylans or arabinoxylans (AX) or glucuronoarabinoxylans (GAX)
- Xyloglucan (XG)
- Galactan or arabinogalactans (AGs)
- Arabinan

Mannan compounds include mannan, galactomannan (GaM), glucomannan (GM), glucuronic acid mannan etc. Mannans are made up of mannose sugars linked by $\beta(1\rightarrow4)$ linkage, and if it is linked to galactose residue by $\alpha(1\rightarrow6)$ bond then it is called as GaM.^[18] GM (Fig. 1.6.) backbone is acetylated; and also contains one galactose residue as a branched chain. Therefore, it is sometimes called as galactoglucomannan (GGM). Mannans are water insoluble and resembles with

cellulose in confirmation of the individual molecular chains, and occurs in cellulose microfibrils of the plant tissues.^[18]

Softwood contains the highest content of mannan hemicellulose; some hardwoods also have mannan hemicellulose. In hardwood hemicellulose, the main chain of mannan is composed of glucose and mannose in a 1.5-2:1 ratio and the average DP is 60-70. For the mannan hemicellulose of softwood, glucose and mannose are arranged in a ratio of 3:1 in a random fashion to form the main chain. The average DP is in the range of 60-100.^[19-20]

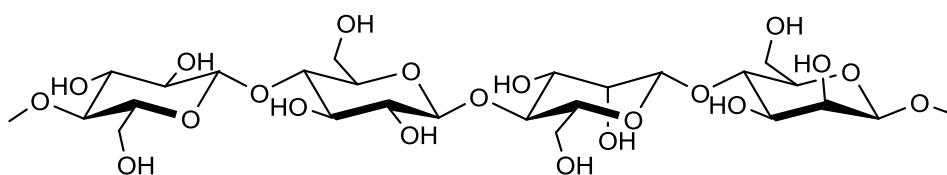


Figure 1.6. Primary structure of D-gluco-D-mannan (GM).

Xylans are a polysaccharide made up of $\beta(1\rightarrow4)$ linked xylose residues. Xylan type hemicellulose from hardwood is *O*-acetyl-L-4-*O*-methyl-glucuronic acid xylan while 4-*O*-methyl-glucuronic acid arabinose xylan with almost no acetyl is the most important hemicellulose from softwoods.^[19] A common modification of xylans is a substitution with $\alpha(1\rightarrow2)$ linked glucuronosyl and 4-*O*-methyl glucuronosyl residues. Xylan having this type of substitution are often called as glucuronoxylans. This structural type usually named as 4-*O*-methyl-D-glucurono-D-xylans (MGXs). MGXs were found in various dicotyls such as ground nut shells, sunflower hulls, flax fiber, jute, bark, and medicinal plants (Fig.1.7.).^[21] The xylans containing α -L-arabinofuranose residues attached at *O*-3 or *O*-2 or both to the xylose residue backbone are called as arabinoxylans (AX).^[18, 21-22] The AX has been identified in a variety of the main commercial cereals: rye, wheat, corn, oat, rice, barley, and sorghum as well as in other plants such as grass, and bamboo shoots.^[22-26] Xylans occur as neutral as well as slightly acidic polymers i.e. glucuronoarabinoxylans (GAXs).

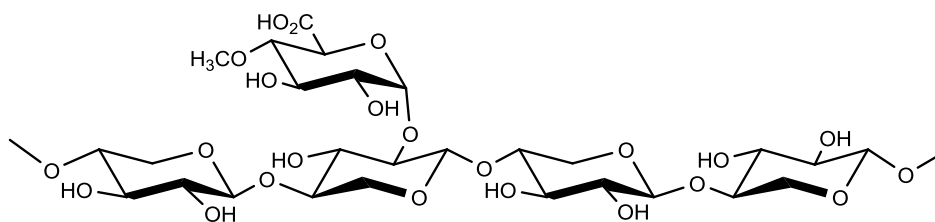


Figure 1.7. Primary structure of 4-*O*-methyl-D-glucurono-D-xylan (MGX).

Xyloglucan (XG) is a hemicellulose polysaccharide found in all higher plants and mainly contains glucose, xylose, and galactose, and its residual ratio is approximately 4:3:1. XG has cellulosic i.e., (1→4)-β-D-glucopyranan backbone (Fig. 1.8.). Most XG are tightly hydrogen bonded to the cellulose microfibrils.^[27] In XG, α-xylose residues are linked to the *O*-6 bond of the β-glucose residues. The terminal galactose is linked to the *O*-2 site of galactose residues with α bond. In some cases, arabinose also exists in xyloglucan, but the amount is small.^[20]

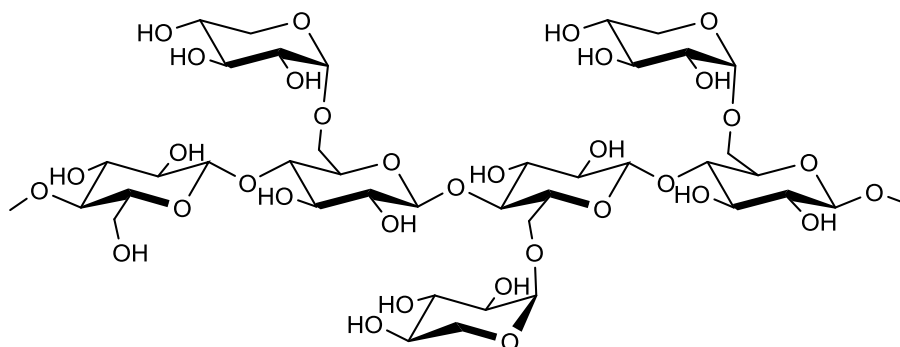


Figure 1.8. Primary structure of D-xylo-D-glucan (XG).

In galactan, galactose residues are connected by β(1→4) bonds to form the backbone of galactan. In galactan if the arabinofuranose residues are linked terminally then those are called as arabinogalactan (AG) as it is shown in Fig. 1.9.^[19-20] AGs are widely spread throughout the plant kingdom and it occurs in two structurally different forms described as type I and type II AG. Type I AG commonly found in potato, apple, and pectins from citrus and has a linear (1→4)-β-D-Galactopyranose backbone, bearing 20-40% of α-L-Arabinofuranosyl residues.^[18] AG type II is more widespread than AG I and it has a (1→3)-β-D-Galactopyranose backbone heavily substituted at position 6 by mono- and oligosaccharides composed

of arabinosyl and galactosyl units. AG type II occurs in cell walls of dicots and cereals and is often linked to proteins.^[18]

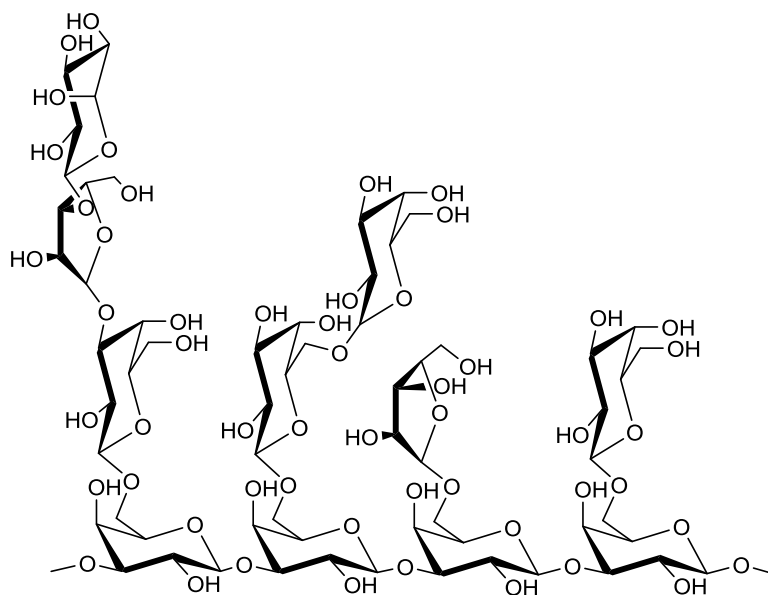


Figure 1.9. Structure of larch arabinogalactan.

Arabinan is entirely made of arabinose, and the α -L-arabinofuranosyl residues are linked with each other by α -1-5 linkage. In arabinan there are many branched chains; some are side chains of arabinofuranosyl linked at either O-2 or O-3 or at both of these positions.

1.2.2.3. Lignin

Lignin is the three-dimensional aromatic polymer made up of phenylpropanoid units. The phenylpropanoid derivatives are the basic units of the lignin. These units are combined by ether bonds or carbon-carbon bonds to form the high molecular weight organic compound. The lignin content in herbaceous plants is about 14-25% and in woody plants, it is about 27-32%.^[28] According to the physical characteristic, the lignin structure is rigid, which increases the hardness of the cell wall.

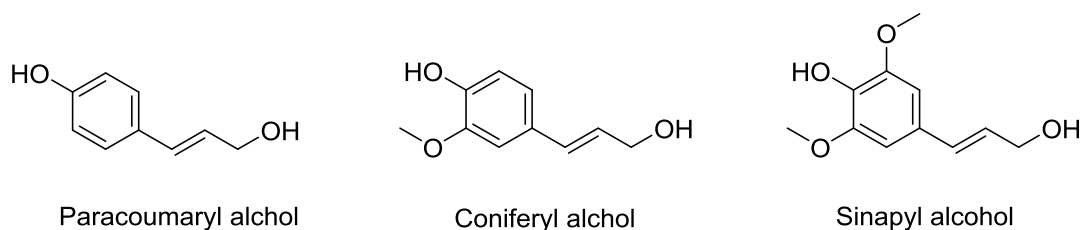


Figure 1.10. Basic structural units of lignin.

The depolymerization of lignin gives aromatic monomers such as paracoumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Fig.1.10.).

1.2.2.4. Additional components of lignocellulosic biomass

Besides cellulose, hemicellulose and lignin there are 10-15% other components present in the lignocellulosic biomass. In plants except carbon, hydrogen, and oxygen, few other basic elements are also present. These are nitrogen, phosphorous, silica, potassium, sulfur, calcium magnesium, iron, sodium, copper, zinc, manganese, chlorine etc. When the dried lignocellulosic biomass heated in high temperature furnace at 650 °C, elements such as carbon, hydrogen, oxygen, nitrogen, sulfur, etc. disappear in the form of gaseous compounds, and the residue obtained is ash which contains many types of mineral element in the form of oxides. Additionally, lignocellulosic biomass may contain a wide range of organic extractives, such as pectins, proteins fats waxes, alkaloids, and essential oils.^[19]

1.2.3. Biorefinery concept

The definition of biorefinery published by U.S. National Renewable Energy Laboratory (NREL) is, “A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass”. The biorefinery concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum. It is estimated that in 2025, up to 30% of raw materials for the chemical industry will be produced from renewable biomass (Fig. 1.11.). For achieving this goal, it is important to develop new biorefinery platform technologies.^[29] The various processes may be developed to get desirable output through biorefinery are listed below:

- Efficient pretreatment method.
- Improvement of thermal, chemical and mechanical processes.
- Use of non-edible biomass.
- Advancement of biological/catalytic method.
- Use of ionic liquids as a catalyst.
- Use of stable and recyclable catalyst.

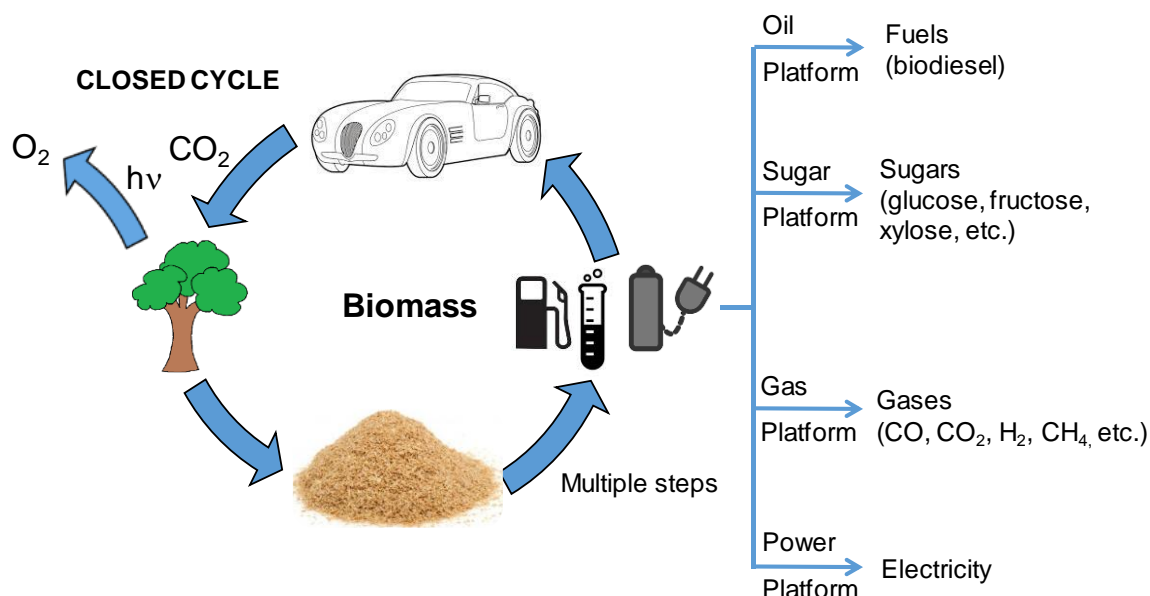


Figure 1.11. Biorefinery concept.

From biorefinery, it is understood that the process is cyclic, with the carbon liberated in the atmosphere in the form of carbon dioxide (CO_2) is utilized during the growth of plants. This shows that utilization of biomass can make the process carbon neutral. This is an advantage of biorefinery over petroleum refinery. In the case of petroleum refinery; the starting material, fossil feedstock requires millions of years for its synthesis and it is a finite source. Thus, the utilization of fossil feedstock will not make a process carbon neutral as like biomass.

1.2.4. Methods for biomass conversion

There are three common ways to use biomass such as, it can be burned to produce heat and electricity; changed to gas like fuels such as methane, hydrogen, and carbon monoxide; or converted to a liquid fuel (biofuel). There are two biomass based liquid transportation fuels that might replace petroleum. Bioethanol can replace gasoline and biodiesel can replace diesel. The conversion of biomass into gaseous and liquid fuels can be carried out using thermochemical processes as illustrated in Fig. 1.12.

Thermochemical conversion processes were studied in the 17th century, and Robert Gardner has received the first patent in 1788 for his work on gasification.^[30] Thermochemical biomass conversion includes a number of possible routes to produce useful fuels and chemicals from renewable biomass. Thermochemical

conversion processes include three main sub categories as it is shown in Fig. 1.12.; pyrolysis, gasification, and liquefaction.

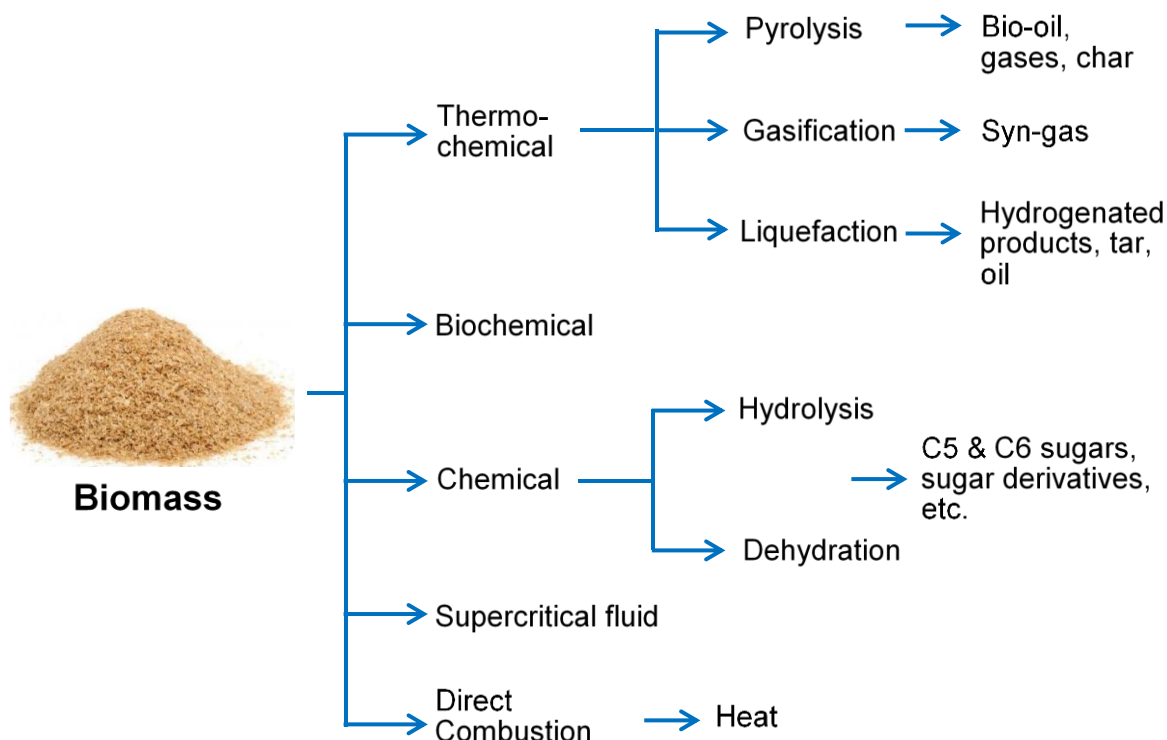


Figure 1.12. Illustration of biomass conversion processes.

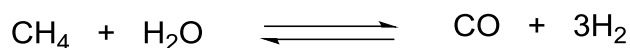
In pyrolysis thermochemical process, first moisture evaporated at 110 °C and then hemicellulose is decomposed at 200-260 °C temperature followed by cellulose at 240-340 °C and lignin at 280-500 °C. Once the temperature reaches 500 °C, the reactions of pyrolysis are almost finished.^[31] When pyrolysis is carried out using higher heating rate, it results in the most rapid generation of vapor products, the shorter residence time of vapor product in the reactor, increasing pressure, and higher liquid yield; called as fast pyrolysis or flash pyrolysis.^[32] In pyrolysis process liquid, gas and char are obtained. The liquid has the higher moisture content which results in lower viscosity and lowers heating value. The gas obtained in pyrolysis contains more CO₂, CO, H₂, and C1 to C5 hydrocarbon as combustible gases.

Gasification of biomass for use in internal combustion engines for power generation provides an important alternative renewable energy resource. Gasification is the partial combustion of biomass feedstock (raw material) to produce gasses, mainly CO₂. The process also generates some methane and other higher hydrocarbons depending on the design and operating conditions of the reactor. To

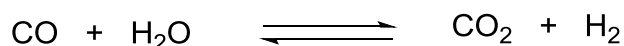
keep the reaction temperature at 800 °C and above for direct gasification, air, oxygen and steam are required as gasification agent.

The main thermochemical reactions include in gasification process are as follows:

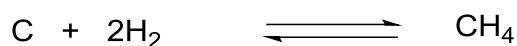
Steam and methane reaction (steam reforming reaction):



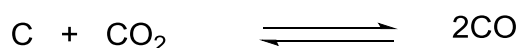
Water gas shift reaction:



Carbon char to methane formation (hydrogasification reaction):



Carbon char oxides formation (Boudouard reaction):



The above mentioned reactions can happen in a gasifier when air and/or steam is used as oxidizing agents.^[33] The process is efficient, achieving over 97% conversion of biomass carbon to useful syngas without producing troublesome tars, oils or contaminated effluents. The typical method uses a dry biomass feedstock with generally <10 wt% moisture. For efficient processing of biomass with higher moisture content, a different technology is required i.e. gasification in pressurized water environment called hydrothermal gasification. The process is robust in its ability to handle feedstocks with varying degrees of inherent moisture 10-85 wt %.^[34]

The liquefaction process was first developed for coal conversion. Liquefaction used for the biomass conversion is a medium temperature high-pressure thermochemical process which produces a liquid product called bio-oils.^[35] Liquefaction of biomass feedstock can be accomplished directly or indirectly. The direct liquefaction is also called as hydrothermal liquefaction. The hydrothermal liquefaction is the thermochemical conversion of biomass into liquid fuel by processing in a hot, pressurized water environment for sufficient time. The hydrothermal liquefaction is carried out at 150-420 °C of temperature and 1 to 240 bar of pressure.^[36]

Hydrothermal processing divided into three separate processes, depending on the temperature of the operating conditions.

- 1) Hydrothermal carbonization at below 247 °C temperature (hydro carbon formation).
- 2) Hydrothermal liquefaction at 300-550 °C temperature (liquid fuel known as biocrude).
- 3) Hydrothermal gasification at above 374 °C temperature (synthetic fuel gas).

The important application of hydrothermal gasification over liquefaction is the lower amount of organic carbon found in the water phase leading to high carbon efficiencies. The Indirect liquefaction involves the use of a catalyst to convert non-condensable, gaseous products of pyrolysis or gasification into liquid products.

Presently the major problem in commercializing the hydrothermal liquefaction process (HTL) or direct liquefaction for biomass conversion is that, it remains uneconomical when compared to the cost of diesel or gasoline production.

In biochemical process sugars produced from biomass can be converted into biofuels (ethanol, butanol, acetone, isobutanol, etc.) using microbial fermentation. This process can be performed in combination with enzymatic hydrolysis (simultaneous saccharification and fermentation), or separately from enzymatic hydrolysis (separate hydrolysis and fermentation).^[37] Lignocellulosic biomass can also be directly fermented to biofuels by various microbes.^[38-39] In enzymatic hydrolysis microorganisms secrete enzymes to degrade biomass for producing monomeric sugars for their own existence. For enzymatic hydrolysis different types of enzymes are needed to cleave different types of bonds during hydrolysis reaction of lignocellulosic biomass due to a complex network of cellulose and hemicellulose.^[40-42]

In the chemical method of biomass conversion into chemicals such as sugars and furans, the catalyst is employed. For the catalytic conversion of biomass the chemical routes reported in the literature are heterogeneous catalysis; homogeneous and enzymatic processes. In the next section (1.2.5. and 1.2.6.) the importance of sugars and furans are discussed and also the reported methods for the synthesis of sugars and furans using heterogeneous (solid acid) and homogeneous catalyst

(mineral acid) are explained. Furthermore, the drawbacks of the present method for the conversion of biomass into sugars and furans, and inspiration of work is described and finally the objective of the thesis is defined.

1.2.5. Applications of C5 sugars and furans

1.2.5.1. Applications of C5 sugars

As discussed in earlier section (section 1.2.2.) the lignocellulosic biomass is made up of cellulose, hemicellulose, and lignin. The hydrolysis of xylan type of hemicellulose can give C5 sugars (xylose+arabinose) since it is made up of xylose and arabinose as the main C5 sugar units. The overview of synthesis of various chemicals from C5 sugars and furfural is shown in Scheme 1.1. Xylose and arabinose upon hydrogenation will give xylitol and arabinitol as sugar alcohols which are used as a low calorie sweetener (Scheme. 1.1.).^[43] Xylitol is a five-carbon sugar alcohol and its sweetness capacity is higher than that of sucrose. As such, it is an excellent artificial sweetener that is now used extensively by the confectionary industry, being responsible for the cold, fresh sensation of certain chewing gums. Xylitol is used for the prevention of dental caries (tooth decay) and also used in pharmaceutical and cosmetic products such as toothpaste, fluoride tablets, and mouthwashes.^[44-46]

The oxidation of xylose will give xylonic acid which occurs naturally in some foodstuffs and is a five-carbon sugar acid. It is one of the high-value chemicals identified by USDOE.^[47] In industrial foods xylonic acid could be used as a replacement for gluconic acid, thus acting as a latent acid in bakery products, an acidulant in meat products, or as a milk coagulant in cheese curd formation. Xylonic acid is very good substituent for gluconic acid in cement formulations, the cement setting time containing xylonic acid is two times faster than that cement containing gluconic acid.^[48] Moreover, xylonic acid is used as a precursor for the synthesis of 1,2,4-butanetriol, and for the synthesis of polyamides.^[49] Arabinose is categorized as rare sugar that is only produced in small amount from hemicellulose, being used as a chemical for specialty applications and as a food ingredient.

1.2.5.2. Applications of furans

HMF and furfural can be obtained by dehydration reactions of C6 sugars (glucose, fructose) and C5 sugar (xylose). The synthesis of these furans using different catalytic chemical process is explained in next section. The furan derivatives, HMF, and

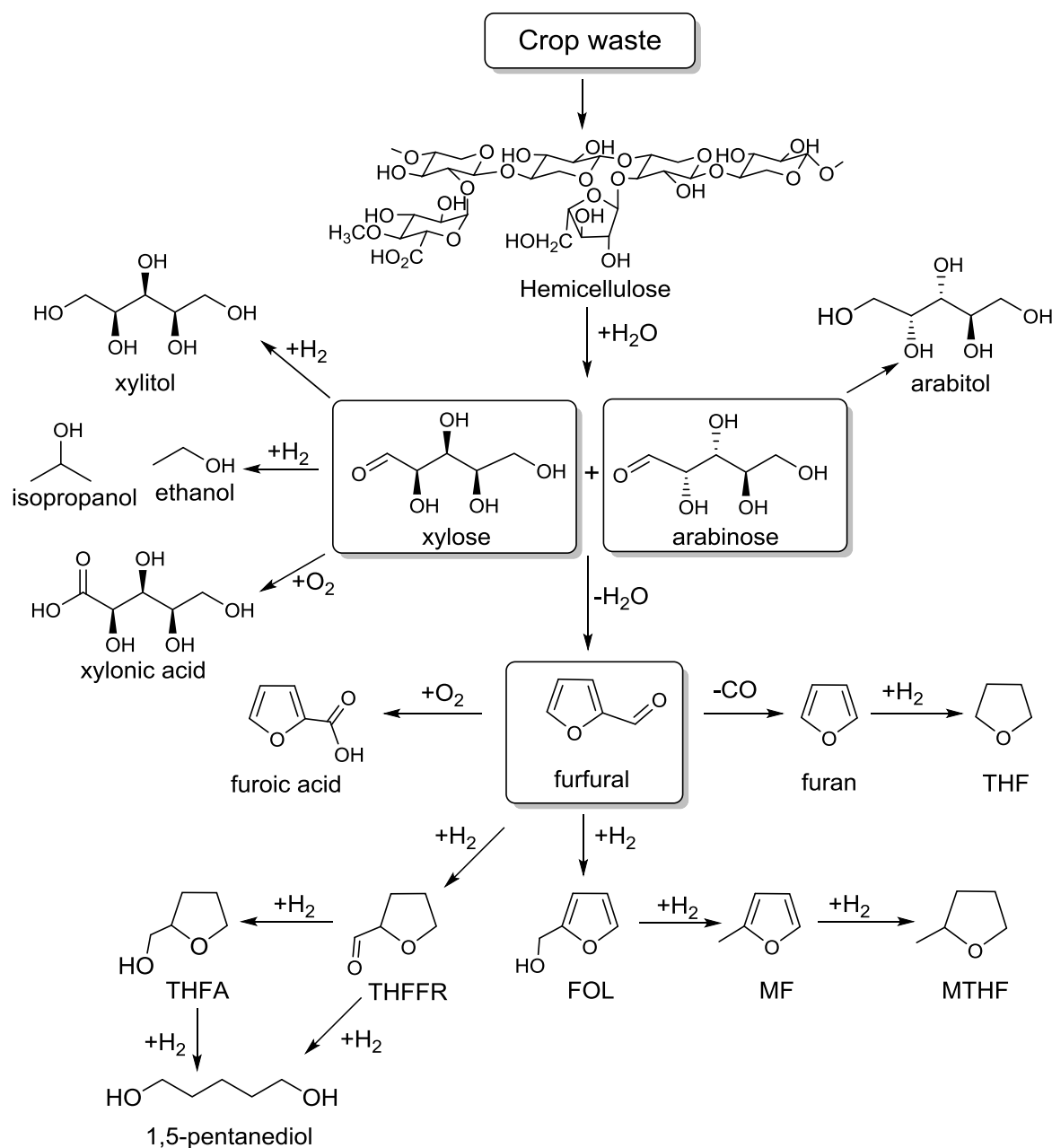
furfural are of great importance since those have many industrial applications and their further conversion can yield a range of industrially important chemicals.^[50-51] Furan molecules such as HMF, furfural and FDCA are mentioned in the USDOE list.^[52]

Applications of furfural

The furfural is obtained from xylose and it can also be obtained from xylan type hemicellulose in one-pot method. The furan derivatives obtained from furfural has many industrial applications and their further conversion can yield a range of industrially important chemicals, therefore, furfural has great importance. The hydrogenation of furfural gives furfuryl alcohol and tetrahydrofuran as products which are known as solvents and starting compounds in the synthesis of a variety of chemicals.^[4, 53] Furfural itself has applications in several industries like Lube oil refining, pharmaceuticals and in the manufacture of phenolic resins.^[54-55]

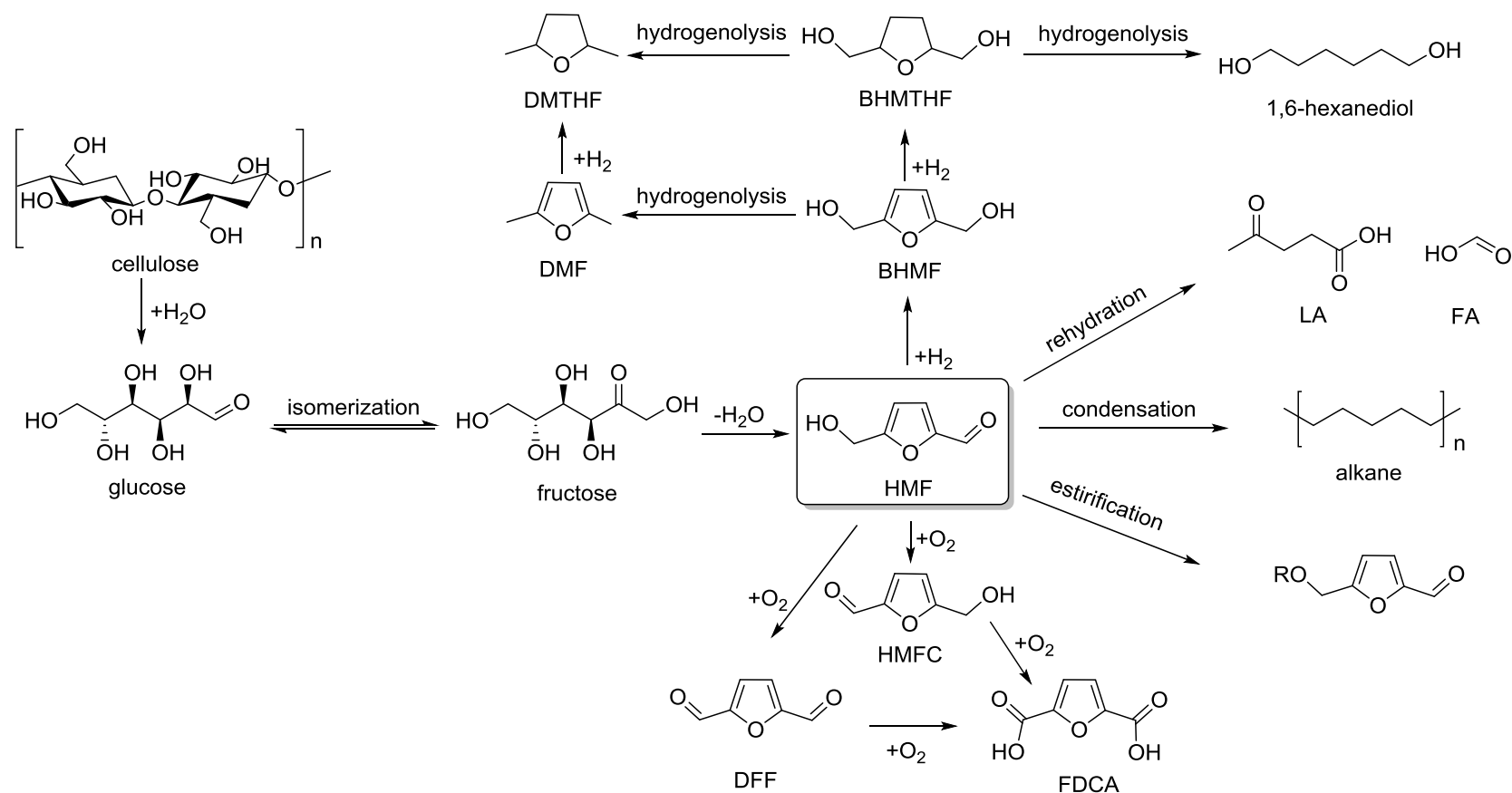
Applications of HMF

The various applications of HMF are shown in Scheme 1.2. HMF can be obtained from fructose. Glucose can also be converted into HMF via fructose, wherein the first step is the isomerization of glucose into fructose and in second step fructose is converted into HMF. It is known that HMF upon oxidation gives various chemicals as shown in Scheme 1.2. FDCA obtained by the oxidation reaction of HMF^[56-57] has a potential to replace a terephthalic acid in polymer synthesis.^[58-59] Ru-containing hydrotalcite as a catalyst is reported for hydrogenation of HMF to give DMF which has a potential application as a fuel.^[60] Moreover, HMF can also act as raw material to synthesize many significant chemicals such as levulinic acid, γ -valerolactone, alkyl levulinate etc.^[10-11, 61]



Scheme. 1.1. Synthesis of C5 sugars and furfural from crop waste and their applications for commercially relevant products.

Abbreviations: Tetrahydrofuran (THF); Tetrahydrofurfuryl alcohol (THFA); Tetrahydrofurfurylaldehyde (THFFR); Furfuryl alcohol (FOL); Methyl furan (MF); Methyltetrahydrofuran (MTHF).



Scheme 1.2. Synthesis of HMF and its application for the synthesis various important chemicals.

Abbreviation: Levulinic acid (LA); Formic acid (FA); 5-Hydroxymethyl-2-furancarboxaldehyde (HMFC); 2,5-Furandicarboxylicacid (FDCA); 2,5-Diformylfuran (DFF); 2,5-Bis(hydroxymethyl)furan (BHMf); 2,5-Bis(hydroxymethyl)tetrahydrofuran (BHMTHF); 2,5-Dimethylfuran (DMF); 2,5-Dimethyltetrahydrofuran (DMTHF).

1.2.6. Ionic liquids (ILs)

Recently Ionic liquids are used extensively for the conversion of biomass into value added chemicals. In biomass conversion reactions ILs are used for various purposes such as pretreatment, as a solvent, additives, as a catalyst, etc. because of its tunable properties. Apart from this, ILs have other applications such as phase-transfer reagent,^[62] surfactant,^[63] fungicides and biocides, etc.^[64] Considering these advantages of ILs, I propose to use those in my Ph.D. work. In this section, I will briefly discuss ILs and their properties.

Over the last fifteen years the use of ILs has dramatically increased (Fig. 1.13.) because of its interesting tunable properties. The database shows that use of ILs in various fields has increased, in 2014 to around 2500 publications worldwide, which is very high compared to publications in 2000 (59 publications) as shown in Fig. 1.13. This shows that the use of ILs are increasing.

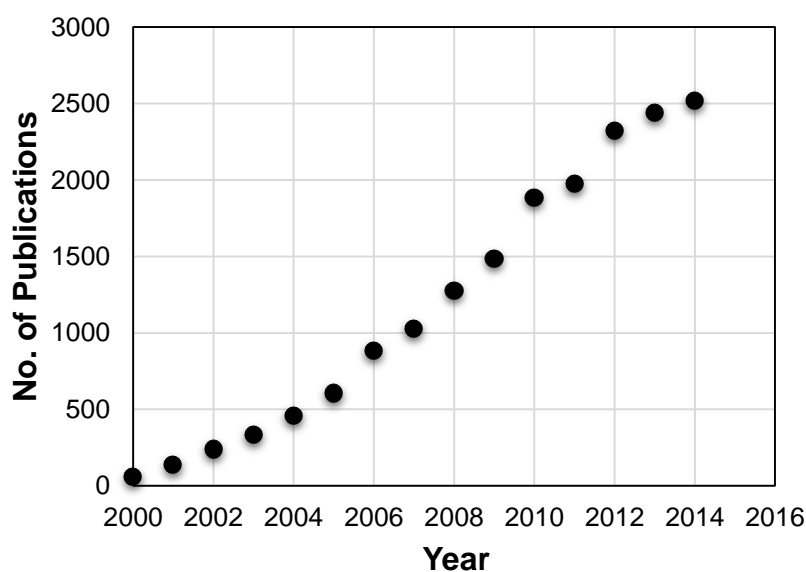
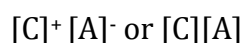


Figure 1.13. Publications per year dealing with ILs.*

*The rise in publications concerning ILs as a function of time was determined using SciFinder on 14 October 2015.

“Ionic liquids are defined as salts with melting temperature below the boiling point of water”. Practically, most of the ILs those are liquid at room temperature are called as room temperature ionic liquids. The ILs are represented by their cations and anion as shown below.



Where 'C' is cation and 'A' is anion part of the IL. Different ILs can be prepared by changing their cations and anions as shown in Fig. 1.14.

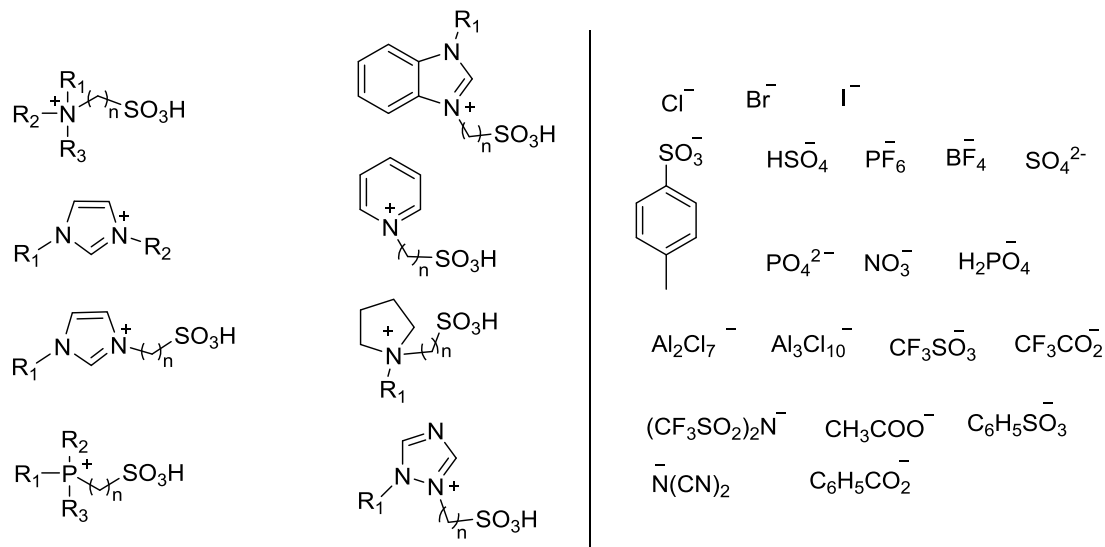


Figure 1.14. Typical cations and anions of ILs.

The R1/R2/R3 are the alkyl groups on the cations and those ranges from C1-C12 ($n = 1-12$), in some ILs substitutes like alkoxy, aryl, aryl alkyl, etc. are present.

Till today, most of the studies are performed using imidazolium based ionic liquids such as [BMIM][Cl], [EtMIM][AlCl₃], etc. Moreover, ionic liquids containing other classes of organic cations are also known. For e.g. quaternary ammonium, phosphonium, and pyridinium salts with a combination of a variety of anions (Fig. 1.14.).

ILs have interesting properties as mentioned below, those can be altered by a combination of different cations and anions. The [BMIM][Cl] IL is hydrophilic and [BMIM][PF₆] IL is hydrophobic; this shows that by changing Cl anion with PF₆ anion changes the solubility of IL. Similarly, the acidity of the IL can be changed by using a different combination of cations and anions. This explanation shows that the properties of ILs can be changed by altering cation and anion of IL. One of the important property of IL is the liquid crystalline structure of IL that means a material state which shows properties between those of conventional liquid and those of solid crystals. Because of this property, IL behaves very differently and shows good catalytic activity. Few of the properties of the ILs are;

Properties of ILs:

- Thermal stability
- Low vapor pressure
- Biphasic solvent systems possible
- Non-flammability
- High heat capacity
- Acidity
- Liquid crystalline structures

1.2.7. Overview of chemical processes for the synthesis of sugars and furans

Conventionally, homogeneous catalysts mainly mineral acids are known for the hydrolysis and dehydration reactions of saccharides.^[55, 57, 65-66] Hemicellulose hydrolysis into C5 sugars has been carried out using mineral acids such as H₂SO₄, HCl, H₃PO₄, etc.^[67-68] Xylose dehydration into furfural is reported using Lewis acid and a Brønsted acid catalyst like CrCl₃·6H₂O and HCl. These catalysts showed 39% furfural yield in aqueous medium and 76% furfural when biphasic solvent system is used.^[69] Some more reports on the hydrolysis and dehydration reactions of saccharides using homogeneous catalyst are summarized in Table 1.1. The results show that it is possible to achieve 61% C5 sugar yield from isolated hemicellulose using H₂SO₄ as a catalyst and 73% xylose yield can be obtained from wheat straw with HCl as a catalyst. These reactions were carried out at 122 °C and 120 °C for 1.4 and 2 h reaction time, respectively. Cellulose and cellobiose hydrolysis are also reported using H₂SO₄ as a catalyst and the result shows that 10% glucose yield from cellulose and 29% glucose yield from cellobiose (Table 1.1.) is possible to obtain. Later use of heteropoly acids such as H₃PW₁₂O₄₀ is evaluated for the hydrolysis of cellobiose and 51% glucose yield was obtained. Moreover, mineral acid like H₂SO₄ is reported for the dehydration of fructose in presence of [BMIM][Cl] IL as a solvent and shows very good yield of HMF (92%). The mineral acid shows a good yield of C5 sugars (hydrolysis reaction of hemicellulose) and furans (dehydration reaction of C5 and C6 sugars), nevertheless those are not preferred because of their several drawbacks such as recyclability, a corrosive reaction system, require a base for neutralization, risks of handling due to corrosive nature, etc.

Table 1.1. Reports on the biomass conversion using homogeneous catalyst.

Substrate	Catalyst	Solvent	t (h)	T (°C)	Conv. (%)	Yield (%)	Ref.
Hemi-cellulose	H ₂ SO ₄	H ₂ O	1.4	122	-	61 (X+A) 12 Fur	[70]
Wheat straw	HCl	H ₂ O	2	120	-	73 X	[71]
Cellulose	H ₂ SO ₄	H ₂ O	48	150	14	10 Glu	[72]
Cellobiose	H ₂ SO ₄	H ₂ O	48	120	34	29 Glu	[72]
Cellobiose	H ₃ PW ₁₂ O ₄₀	H ₂ O	48	120	53	51 Glu	[72]
Xylose	HCl	CrCl ₃ .6H ₂ O	0.83	195	90	39 Fur	[69]
Fructose	H ₂ SO ₄	[BMIM][Cl]	0.5	120	96	92 HMF	[30]

Time (t); Temperature (T); Conversion (Conv.); Reference (Ref.); Xylose (X); Arabinose (A); Glucose (Glu); Fructose (Fru).

To avoid above mentioned drawbacks of homogeneous catalysts, heterogeneous catalysts were employed for these reactions (Table 1.2.). Recently conversion of hemicellulose to sugars using solid acid catalysts such as zeolites (HUSY, H β , HMOR) and silicon-containing aluminophosphates (SAPOs) is shown.^[73-77] However, in these reactions, it was difficult to attain higher yields of sugars in a shorter time.^[73-74] The selective conversion of hemicellulose present in bagasse is also reported, and it is carried out in a biphasic solvent using HUSY catalyst to obtain 20% C5 sugars and 55% furfural.^[76] Enzymatic saccharification of hemicellulose was also reported and it is carried out using different enzymes, the structure of hemicellulose is more complex than cellulose and requires different enzymes with different specificities for complete hydrolysis.^[78]

A lot of works are reported on the dehydration of xylose into furfural using solid acid catalysts including sulfonic acid appended porous silicas,^[79] heteropolyacids.^[80-81] Amberlyst-15 and Nafion-117. They show good furfural yields (68% and 66%) in xylose dehydration reaction (Table 1.2.).^[79, 82] But these catalysts

are not stable under reaction condition. Moreover, the structured solid acid catalyst reported for the hydrolysis and dehydration reactions of saccharides show deformation of zeolite morphology under reaction condition.^[76] This, in turn, showed lower activity in recycling runs. Hemicellulose hydrolysis into C5 sugar is easier method compared to cellulose hydrolysis into glucose, but the products C5 sugars formed in the reaction are more reactive compared to glucose^[83] therefore it is difficult to have maximum selectivity for C5 sugars in the hemicellulose hydrolysis reaction.

Table 1.2. Reports on the biomass conversion into C5 sugars and furfural using heterogeneous catalyst.

Substrate	Catalyst	Solvent	t (h)	T (°C)	Conv. (%)	Yield (%)	Ref.
Hemicellulose (xylan)	HUSY	H ₂ O	3	170	>90	41 (X+A) 14 Fur	[73]*
Bagasse	HUSY	Water+ MIBK	6	170	-	20 (X+A) 55 Fur	[76]
Cellulose	Fe ₃ O ₄ -SBA- SO ₃ H	H ₂ O	3	150	-	26 Glu	[84]*
Xylose	Amberlyst-15	DMSO	4	140	87	68 Fur	[79]
Xylose	Nafion-117	DMSO	2	150	91	66 Fur	[82]*

Recycle study* Time (t); Temperature (T); Conversion (Conv.); Reference (Ref.); Xylose (X); Arabinose (A); Furfural (Fur); Glucose (Glu).

Since the properties of ILs are tunable^[66, 85] and those are considered as green solvents, their uses in the biomass related reactions are increasing in the last couple of years. In one of the latest studies, hydrolysis of hemicellulose in the presence of 1-ethyl-3-methylimidazolium chloride, ([EMIM][Cl]); IL and mineral acid, (H₂SO₄; 200 mM) is reported to achieve 47% yield of xylose. However, in this work large amount of IL (500 µl) was used compared to substrate (27 mg).^[47] Moreover, there are reports on the conversion of hemicellulose using ILs, and for

this reaction, ILs are used as solvent and additives and it is used along with HCl and CrCl₃ (Table 1.3.).

Table 1.3. Conversion of hemicellulose and cellulose using ILs.

Substrate	Catalyst	Solvent	Additives	t (h)	T (°C)	Yield (%)	Ref.
Bagasse	-	H ₂ O	[BMIM][Cl] HCl	0.5	130	-	[86]
Hemicellulose (birch Xylan)	CrCl ₂ , HCl	DMA	[EMIM][Cl]	4	140	15 Fur	[87]
Hemicellulose (oat Xylan)	CrCl ₂ , HCl	[EMIM][Cl]	-	2	140	25 Fur	[87]
Cellulose	[C ₃ SO ₃ HMI M][Cl]	[C ₃ SO ₃ HMI M][Cl]	-	1.5	70	14 Glu	[88]
Cellulose	[C ₃ SO ₃ HMI M][HSO ₄]	[BMIM][Cl]	-	1.5	100	90 TRS	[89]
Cellulose	CrCl ₃ .H ₂ O	[BMIM][Cl]	-	.033	MI	60 HMF	[90]

Recycle study* Time (t); Temperature (T); Conversion (Conv.); Reference (Ref.); Furfural (Fur); Glucose (Glu); Total reducing sugar (TRS); Microwave irradiation (MI).

Application of 1-ethyl-3-methylimidazolium hydrogen sulfate, ([EMIM][HSO₄]) IL; in the synthesis of furfural (29%) is also reported in the literature.^[87] In yet another report, synthesis of furfural from xylose using dimethylacetamide (DMA)-LiCl, CrCl₂ and IL, [EMIM][Cl] is described.^[91] Moreover, xylose dehydration using [BMIM][Cl] IL in the presence of mineral acid H₂SO₄ is reported.^[30] In recently reported methods, [BMIM][Cl] ILs are used as a solvent for the conversion of cellulose.^[89-90, 92] The ILs are also widely used in the dehydration reactions of C₆ sugars (glucose, fructose) to yield HMF.^[93-94] In one of the reports, researchers have used [BMIM][Cl] IL, as a solvent and metal chlorides as a catalyst to achieve 71% of HMF yield from glucose under microwave heating.^[95] Conversion

of fructose into HMF using choline chloride/citric acid based IL in the biphasic solvent system is also known.^[94] There are some more reports on the conversion of C5 and C6 sugars into furfural and HMF as listed in Table 1.4. A careful look at the literature reveals that in biomass conversion, ILs are used either as a solvent (with high concentrations) or used in combination with another catalyst (typically acidic catalysts like H₂SO₄, metal chlorides etc.). Besides this, use of ILs in the pretreatment of cellulose to loosen the crystalline structure and lignocellulosic materials to separate the components (cellulose, hemicellulose, and lignin) is well documented.^[96-98]

Table 1.4. Literature on xylose and fructose dehydration using ILs.

Substrate	Solvent	Catalyst	Additives	t (h)	T (°C)	Yield (%)	Ref.
Xylose	[EMIM][HSO ₄]	[EMIM] [HSO ₄]	Toluene	6	100	84 Fur	[99]
Xylose	DMA	CrCl ₂	[BMIM] [Br]	4	100	56 Fur	[100]
Fructose	MIBK	[EMIM] [HSO ₄]	-	0.5	100	88 HMF	[99]
Fructose	[EMIM] [BF ₄]	SnCl ₄	-	24	100	60 HMF	[101]
Fructose	DMSO	Amberlyst-15	[EMIM] [BF ₄]	25	80	75 HMF	[102]
Glucose	[EMIM] [BF ₄]	SnCl ₄	-	3	100	60 HMF	[101]

Time (t); Temperature (T); Reference (Ref.); Furfural (Fur).

1.2.8. Drawbacks of earlier methods and inspiration of work

In earlier reports, hemicellulose is used for obtaining C5 sugars and there are very few reports on the conversion of crop waste into sugars. In the majority of reactions, homogeneous catalysts (mineral acids) have showed good activity but those have various drawbacks such as corrosive reaction system, hazards of handling mineral

acids, higher environmental risks^[103] and it requires an extra base to neutralize the acid present in the reaction mixture.

To overcome these problems associated with mineral acids, use of solid acid catalysts are reported in the literature for the conversion of biomass. The solid acid catalysts such as Amberlyst-70, sulfonated silica, HUSY zeolite, H- β zeolite, etc. are known for these reactions. The Amberlyst-15, Nafion-117 are reported for xylose dehydration reaction (Table 1.2.), but the problem with these catalysts is that they are not stable under reaction condition. The HUSY catalyst can convert hemicellulose from crop waste into C5 sugars and furfural in one pot method.^[76] However, the problem with this catalyst is that under reaction condition it undergo structural deformation. Hence, a significant decrease in the yield of C5 sugar and furans is observed after first catalyst recycling.^[75, 77]

There is extensive literature available for the conversion of xylose into furfural and very few reports on direct conversion of hemicellulose into furfural is known.^[104] The drawback with these methods is that xylose was used for furfural synthesis, and it is synthesized from xylan type of hemicellulose. Therefore, it would be better to convert xylan type of hemicellulose directly into furfural in one-pot method.

There is a need to develop catalytic methods to overcome the drawbacks associated with reported conventional catalytic methods such as use of mineral acids, enzymes, solid acid catalysts and use of ionic liquids along with mineral acids or metal chloride, etc. for the conversion of biomass. Also, the non-edible biomass (crop waste) should be used as feedstock instead of edible biomass. Further, the catalyst used for the conversion of biomass should be stable, recyclable, and exploitable for hydrolysis and dehydration reactions of saccharides.

To overcome the drawbacks of the present catalytic methods used for biomass conversion, it would be desirable to use BAILs in a catalytic amount. If BAILs are used for biomass conversion, then there is no need to use an additional acid such as mineral acid or Lewis acid as it is reported in earlier works.^[87, 90-91, 101] It is important to note here that in earlier works the quantity of ILs used is very high and also those are used along with mineral acids or metal halides. Using ILs in higher quantity is not a good idea because ILs are expensive, hence, in the present

thesis, I am proposing to use BAILs in catalytic amount without any metal halide and mineral acid. In my Ph.D. work, I have used the BAILs for hydrolysis and dehydration reactions of saccharides.

1.2.9. Objective and scope of the thesis

The C5 sugars are used for the synthesis of various industrially important chemicals such as xylitol, xylonic acid, arabinitol, etc. (Section 1.5.1.). Therefore, it is very important to synthesize the C5 sugars from non-edible biomass. The use of conventional methods for the synthesis of C5 sugars has various drawbacks as discussed in earlier section 1.2.7. and 1.2.8. The objective of present work is to develop an efficient method for the synthesis of C5 sugars and/or furfural from isolated hemicellulose and hemicellulose from different types of crop wastes. Also, to develop an efficient method for the dehydration of C6 and C5 sugars into HMF and furfural.

Moreover, furans (furfural and HMF) obtained after dehydration reactions of C5 and C6 sugars also have wide range of applications as discussed in (section 1.5.2.). The problem with sugar dehydration reaction is that it is very difficult to achieve higher selectivity for furans because of several predominant side reactions. Hence, in the reported methods very low concentration of sugars are used for dehydration reaction. In the present work my objective is to use; 1) concentrated sugar solutions for the dehydration reaction and 2) catalytic amount of BAILs. Hence, for developing an efficient method for the synthesis of C5 sugars (hydrolysis of hemicellulose) and furans (dehydration of C5 and C6 sugars) BAILs can be used in catalytic amounts without mineral acid and metal halides. Following objectives were set for my Ph.D. work for developing an efficient method for the synthesis of C5 sugars and furans.

- To use BAILs in catalytic amount for the conversion of isolated hemicellulose and hemicellulose from crop waste into C5 sugars and/or furfural.
- It is reported in the literature that the C5 sugars obtained from hemicellulose have lower selectivity and yields, and the catalyst used for these reactions are mineral acids and solid acids. Ionic liquids are also used along with mineral acid and metal halides for these reactions. Hence, it is interesting to carry out the reaction using only acidic ionic

liquid as a catalyst without addition of mineral acid and/or solid acid catalyst.

- To carry out detailed analysis of various crop wastes, (bagasse, rice husk, wheat straw, corn cob, cotton stalk, etc.) Technical Association of the Pulp and Paper Industry (TAPPI) and Inductively coupled plasma optical emission spectrometry ICP-OES analysis methods was used.
- ❑ Conversion of crop waste into sugars and furans in one-pot method is important and economical compared to known methods where the reactions are carried out with isolated hemicellulose. Also, in some reports ILs are used for the pretreatment of biomass in the first step and in second step, the reaction was carried out using different catalysts such as mineral acid or metal halide. In the present thesis, the objective is to analyze different types of crop waste and to use BAILs for their conversion into sugars and furans in one-pot method. Before reaction, detailed analysis of all the crop wastes will be done by TAPPI method and elemental analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) method. It is important to carry out these analysis since this will give the information of pentosan (hemicellulose) percentage present in crop waste and then this data will be used to calculate the yields of the products. Moreover, analysis of metal nutrients present will give information on possible contamination of catalyst by these metals.
- To establish the catalyst property - activity correlation in the conversion of saccharides into sugars and furans.
 - ❑ To understand property - activity correlation of catalyst, various properties of BAILs will be determined using several characterization techniques such as ^1H NMR, ^{13}C NMR, FTIR, UV-Vis, CHNS analysis Hammett acidity function (H_0), etc. These characterization techniques will help in the determination of the structure of the catalyst and will also help in understanding which properties of catalyst plays important role for achieving varying activity.

- To study the dehydration reactions of C5 and C6 sugars using BAILs for higher selectivity and yields of furans (HMF and furfural).
 - Reported literature on sugar dehydration reaction shows the use of lower concentration of sugar solutions to get higher selectivity and yields of furans. In present work, my aim is to use concentrated sugar solutions and catalytic amount of BAILs for the dehydration reaction for getting higher selectivity and yields of furans. Because using higher concentration of sugar solutions and the catalytic amount of catalyst will make a process economically feasible.

1.2.10. Outline of the thesis

The thesis is divided into six chapters and the brief contents of each chapter are drawn below.

Chapter 1 provides the introduction of topic and overview of biomass, its classification and the available processes for the conversion of biomass. The detailed classification of hemicellulose is given because in present thesis most of the work is carried out with different types of hemicellulose. Also, the chemical methods are explained in detail for conversion of biomass into sugars and furans and the drawbacks of these methods are understood. For overcoming these drawbacks of conventional method alternative method (use of BAILs) for the conversion of biomass is discussed. Finally, objectives of the work are defined.

Chapter 2 deals with the catalyst synthesis and characterization. The rationalization behind catalyst synthesis is explained, and synthesis methods of various types of BAILs are presented. Along with BAILs other catalysts are also used in this study such as solid acid catalysts (HUSY (Si/Al=15), HMOR (Si/Al=10), H- β (Si/Al=19), Amberlyst-15, etc.), mineral acids (H₂SO₄, HCl), and organic acid (*p*-toluenesulfonic acid monohydrate). All these catalysts are characterized using several characterization techniques such as ¹H and ¹³C NMR, FTIR, CHNS analysis, XRD, UV-Vis, etc.

Chapter 3 is divided into two chapters, Chapter-3A and Chapter-3B. In Chapter-3A, the results on the conversion of hemicellulose into sugar monomers using BAILs are described. In Chapter-3B results on the conversion of hemicellulose

into furfural using BAILs in a one-pot method are explained. Moreover, detailed experimental procedures and methods for analysis of reaction mixture are discussed.

Chapter 4 describes the use of BAILs for the selective conversion of hemicellulose from crop waste into sugars and/or furfural. Detailed analysis of various crop wastes is presented using TAPPI method. Effect of various substrates is studied using BAILs for the synthesis of C5 sugars and furfural. Further, in this chapter catalyst recycle study for the selective conversion of hemicellulose from crop wastes into furfural is presented.

Chapter 5 provides information about dehydration of C6 and C5 sugars into HMF and furfural, respectively using BAILs. Various parameters are optimized for these reactions such as catalyst concentration, reaction time, temperature, solvent and substrate concentration, etc. Further, in this chapter also catalyst recycle study for both the reactions is carried out and the results are presented.

1.2.11. References

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Chapter 2
**Catalyst Synthesis &
Characterization**

2.1. Introduction

As discussed in Chapter-1, conversion of lignocellulosic biomass into sugars and furans such as 5-hydroxymethylfurfural (HMF) and furfural is very important (Chapter-1, section 1.5.2.), because of their wide range of applications.^[1-4] Moreover, there are reports available for the conversion of polysaccharides into sugars and their further dehydration into furans.^[5-8] The conventional catalytic methods used for the conversion of lignocellulosic biomass into C5 sugars and furans have various drawbacks such as lower yield, instability of catalysts, harsh reaction conditions, etc. Therefore, it is important to develop an efficient method for the conversion of lignocellulosic biomass into sugars and furans. As it is suggested in Chapter-1, Brønsted acidic ionic liquids (BAILs) can be used as catalyst for these reactions because of their acidic nature and tunable properties. Here the idea is to use BAILs in catalytic amount without using any mineral acid and metal halide. The important points are that small quantity of BAILs is being proposed to use (used as catalyst not solvent) and the acidic nature of BAIL will avoid the use of mineral acid and metal halide. Therefore, use of BAILs for the conversion of lignocellulosic biomass can make a process much economical compared to known methods reported in the literature.

ILs are the salts with melting temperature below the boiling point of water. In reality, most of ILs are liquid at room temperature and are called as room temperature ILs.

Ethanolammonium nitrate was the first IL reported in 1888 by S. Gabriel and J. Weiner.^[9] The first room temperature IL, ethylammonium nitrate (m.p. 12 °C) was synthesized in 1914 by Paul Walden.^[10] Much work was reported on imidazolium based ILs because in the case of imidazolium based ILs the properties such as viscosity, melting point, and acidity could be easily adjusted by changing the alkyl substituents on imidazole or in other way, properties of ILs can be changed by changing anions and cations of ILs. The synthesis of ILs can be carried out by two methods such as formation of cations and exchange of anion.

Typically, ILs are synthesized by two methods, which are listed below;

1) Formation of the desired cation.

The desired cation can be synthesized either by the protonation of the amine by an acid or through Quaternization reactions of the amine with haloalkanes.

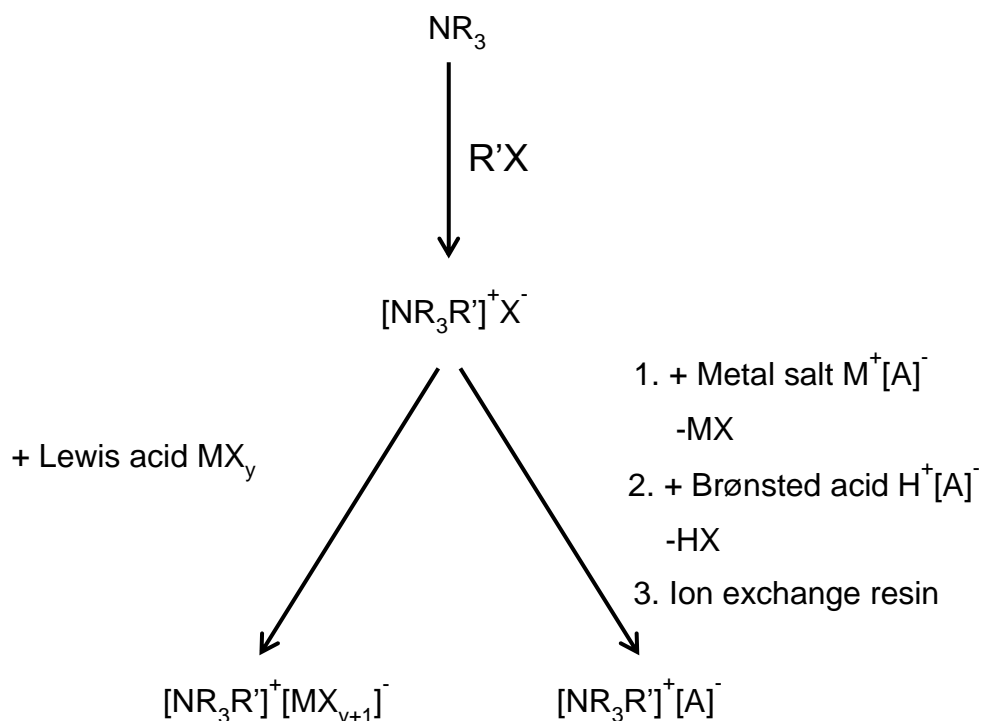
2) Anion exchange method.

Anion exchange reactions of IL is divided into two distinct types;

- a) Direct treatment of halide salt with Lewis acid to form Lewis-acid based ILs
- b) Formation of IL by anion metathesis.

Quaternization reactions: The formation of cation may be carried out by protonation with free acid, or by Quaternization of haloalkanes, phosphine or amine. For e.g. In the synthesis of ethylammonium nitrate, the ethylamine was reacted with H_2SO_4 .

In some cases, for the synthesis of IL only the first step is required (Quaternization reaction), as is the case with the formation of ethylammonium nitrate. The typical pathways for the synthesis of ILs are shown in Scheme 2.1.



Scheme 2.1. Typical synthesis pathways for the preparation of ILs.

In general term, the treatment of a quaternary halide salt Q^+X^- with a Lewis acid MX_n results in the formation of more than one species depending on the relative proportions of Q^+X^- and MX_n . The Lewis acids reported in the literature for the synthesis of ILs are $AlEtCl_2$,^[11] BCl_3 ,^[12] $CuCl$,^[13] and $InCl_3$.^[14] The water and air stable ILs based upon 1,3-dialkylimidazolium cation are synthesized by anion metathesis. Using various combination of anions and cations wide range of ILs can be synthesized. Because of the unique nature and interesting physical properties of ILs as explained in chapter-1 (section 1.2.6.), ILs find applications in many fields such as storage media for toxic gasses, catalyst, and/or solvents in organic synthesis, additives in pigments and matrices etc.^[15-17] Because of this wide range of applications and tunable properties (Chapter-1, section 1.26) of ILs, in present work I have decided to use BAILs in catalytic amount for the hydrolysis and dehydration reactions of saccharides. The use of BAIL can help to avoid the use of mineral acid and metal halides for the above titled reactions.

The brief outline of this chapter can be described as follows;

In this Chapter, detailed discussions on the synthesis of various IL catalysts and their characterization are made. Along with ILs other catalysts were also employed in this work such as solid acid catalysts (HUSY, (Si/Al=15); HMOR, (Si/Al=10); Amberlyst-15, H β (Si/Al=19) zeolite), mineral acids (H_2SO_4 , HCl), organic acid (*p*-toluenesulfonic acid monohydrate), etc. Furthermore, the rationalization behind catalyst synthesis (ILs) is also discussed. Subsequently, various properties of ILs such as solubility in different solvents, acid strengths, hydrothermal and thermal stabilities are explained. Next, the effect of different cations and anions of ILs was explored in the conversion of hemicellulose. Since, various ILs can be prepared with different types of cations and anions, the following rationalizations were used for the synthesis of ILs.

2.2. Synthesis of ionic liquids (ILs)

2.2.1. Materials & methods

For the synthesis of various ILs the precursors were procured from different sources. The details are given in Table no. 2.2.

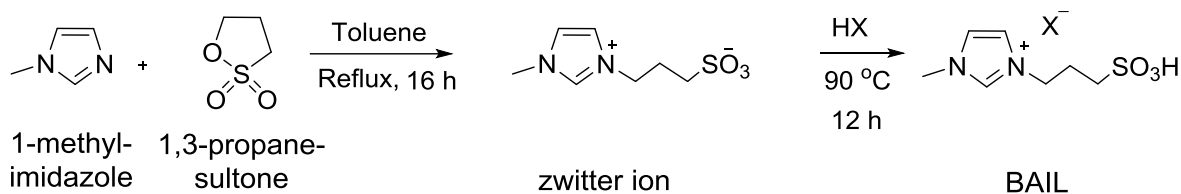
Table 2.1. Summary of materials used for the synthesis of ILs.

Chemical Name	CAS No.	Molecular Formula	Purity (%)	Supplier
1-methylimidazole	616-47-7	C ₄ H ₆ N ₂	99	Across Organics, USA
1-chlorobutane	109-69-3	C ₄ H ₉ Cl	99	Sigma-Aldrich, USA
1,3-propane sultone	1120-71-4	C ₃ H ₆ O ₃ S	99	Alfa Aesar, India
1,4-butane sultone	1633-83-6	C ₄ H ₈ O ₃	99	Alfa Aesar, India
1-methylbenzimidazole	1632-83-3	C ₈ H ₈ N ₂	99	Alfa Aesar, India
triethylamine	121-44-8	C ₆ H ₁₅ N	98	Alfa Aesar, India
<i>p</i> -toluenesulfonic acid monohydrate	6192-52-5	C ₇ H ₁₀ O ₄ S	98	Sigma-Aldrich, USA
triphenylphosphine	603-35-0	C ₁₈ H ₁₅ P	98	Loba Chemie, India
pyridine	110-86-1	C ₅ H ₅ N	98	s. d. Fine-Chem Limited, India

All the chemicals were used as received and all the solvents such as toluene, methyl isobutyl ketone (MIBK), *p*-xylene, ethyl acetate etc. used in present work were purchased from Loba Chemie (India) and Merck Chemicals (India). The solid acid catalyst (Zeolites) such as H β (Si/Al=19), HUSY (Si/Al=15), HMOR (Si/Al=10) were procured from Zeolyst International (USA). Prior to use, zeolites were calcined at 550 °C (temperature ramping 2 °C/min) for 16 h in an air flow (20 mL/min). Amberlyst-15 was purchased from Sigma-Aldrich Chemicals (USA) and before use was dried at 80 °C for 2 h.

2.2.2. Catalyst synthesis procedure

The typical method used for the synthesis of BAILs in present work is shown in Scheme 2.2. The rationalization behind catalyst synthesis is discussed in next section (section 2.2.3.) of this chapter.



Scheme 2.2. Synthesis method used for the synthesis of imidazolium based BAILs.

HX: HCl, H₂SO₄, PTSA, X: Cl⁻, HSO₄⁻, PTS.

2.2.2.1. Synthesis of 1-methyl-3-(3-sulfopropyl)-imidazolium *p*-toluenesulfonate ([C₃SO₃HMIM][PTS]) BAIL

For the synthesis of [C₃SO₃HMIM][PTS] BAIL, 1-methylimidazole, (7.625 mmol) and 1,3-propane sultone, (7.625 mmol) were dissolved in 10 mL toluene and refluxed for 16 h in an inert atmosphere in a round bottom flask under constant stirring. The product; zwitter ion was precipitated out as a white solid in quantitative yield. The white precipitate formed was isolated by filtration, and washed with toluene and then dried under high vacuum (-760 Torr) at 80 °C for 4 h and then used as such in the next step. Synthesis of IL was accomplished by mixing equimolar quantities of *p*-toluenesulfonic acid monohydrate (PTSA) and zwitter ion. The resulting mixture was stirred at 90 °C for 12 h. During this time the solids react, resulting in the formation of the [C₃SO₃HMIM][PTS] BAIL. The color of the IL was pale yellow.

2.2.2.2. Synthesis of 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([C₃SO₃HMIM][HSO₄]) BAIL

The synthesis procedure is same as mentioned in above section 2.2.2.1. However, in the second step of reaction, instead of *p*-toluenesulfonic acid monohydrate, sulphuric acid (H₂SO₄) was used and mixed with zwitter ion which was formed in the first step of reaction between 1-methylimidazole and 1,3-propane sultone (equimolar mixture) and stirred at 90 °C for 12 h to give [C₃SO₃HMIM][HSO₄] BAIL.

2.2.2.3. Synthesis of 1-methyl-3-(3-sulfopropyl)-imidazolium chloride ([C₃SO₃HMIM][Cl]) BAIL

For the synthesis of this IL also, similar procedure was used in the first step of reaction as explained in above section 2.2.2.1. In the second step of reaction, instead of *p*-toluenesulfonic acid monohydrate, HCl was used and it is reacted with zwitter ion which is obtained in the first step of reaction (reaction of 1-methylimidazole and 1,3-

propane sultone). The equimolar mixture of zwitter ion and HCl is stirred at 90 °C for 12 h. This will result in the formation of desired BAIL ([C₃SO₃HMIM][Cl]).

2.2.2.4. Synthesis of 1-methyl-3-(4-sulfobutyl)-imidazolium *p*-toluenesulfonate ([C₄SO₄HMIM][PTS]) IL and 1-methyl-3-(4-sulfobutyl)-imidazolium hydrogen sulfate ([C₄SO₃HMIM][HSO₄])

For the synthesis of these BAILs, the first step of the reaction was carried out using an equimolar mixture of 1-methylimidazole and 1,4-butane sultone instead of 1,3-propane sultone (as it was used in the first step of zwitter ions synthesis mentioned in section 2.2.2.1.). Next, the reaction mixture was refluxed in 10 mL toluene in the presence of nitrogen for 16 h to get respective zwitter ion (white solid). The zwitter ion formed was isolated and washed with toluene and then dried under high vacuum (-760 Torr) at 80 °C for 4 h. In the second step of the reaction, this zwitter ion was reacted with *p*-toluenesulfonic acid monohydrate and H₂SO₄ at 90 °C (12 h) on an equimolar basis to get [C₄SO₃HMIM][PTS] and [C₄SO₃HMIM][HSO₄] BAILs.

2.2.2.5. Synthesis of 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) IL

[BMIM][Cl] IL was prepared according to literature procedure.^[18] In a typical synthesis, a solution of 1-chlorobutane, (108 mmol) and 1-methylimidazole, (108 mmol) were taken in a round bottom flask fitted with a condenser. The mixture was refluxed in 60 mL acetonitrile for 48 h under vacuum. Then, the mixture was cooled to room temperature to observe two distinct layers. The upper layer containing unreacted starting material was decanted and the bottom layer was extracted with ethyl acetate. This procedure was repeated thrice to achieve efficient extraction of unreacted reactants still present in lower layer. The remaining solvent from ionic liquid was distilled off using rotary evaporator and the product was dried under high vacuum at 50 °C for 16 h. Dried [BMIM][Cl] IL showed slightly yellow appearance.

2.2.2.6. Synthesis of 1-methyl-3-(3-sulfopropyl)-benzimidazolium hydrogen sulfate ([C₃SO₃HBezMIM][HSO₄]) and 1-methyl-3-(3-sulfopropyl)-benzimidazolium *p*-toluenesulfonate ([C₃SO₃HBenzMIM][PTS])

Synthesis of these BAILs, were carried out using a two-step reaction. In the first step, an equimolar quantity of 1-methylbenzimidazole and 1,3-propane sultone was mixed and refluxed in 15 mL toluene for 16 h to obtain zwitter ion. Next, this zwitter ion was filtered out and washed with toluene to remove unreacted starting material. Then, it

is dried at 80 °C for 4 h and used in second step. In the second step, the zwitter ion was mixed with H₂SO₄ on an equimolar basis and stirred at 90 °C for 12 h to obtain [C₃SO₃HBenzMIM][HSO₄] BAIL. Similarly, for the synthesis of [C₃SO₃HBenzMIM][PTS] BAIL *p*-toluenesulfonic acid monohydrate was used instead of H₂SO₄ and it is mixed with zwitter ion (which is obtained in the first step) on equimolar basis and stirred at 90 °C for 12 h.

2.2.2.7. Synthesis of N,N,N-triethyl-(3-sulfopropyl)-ammonium hydrogen sulfate ([C₃SO₃HNEt₃][HSO₄]) and N,N,N-triethyl-(3-sulfopropyl)-ammonium *p*-toluenesulfonate ([C₃SO₃HNEt₃][PTS]) BAIL

[C₃SO₃HNEt₃][HSO₄] and [C₃SO₃HNEt₃][PTS] BAILs are quaternary ammonium based BAILs. The synthesis of these BAILs was also carried out using a two-step reaction. In the first step, equimolar mixture of triethylamine (7.5 mmol) and 1,3-propane sultone (7.5 mmol) were mixed in 10 mL toluene. The mixture was refluxed for 16 h to get zwitter ion. The zwitter ion obtained in the first step was isolated and washed with toluene and then dried under high vacuum (-760 Torr) at 80 °C for 4 h. In the second step, the formed zwitter ion was reacted with H₂SO₄ and *p*-toluenesulfonic acid monohydrate (equimolar mixture), respectively and stirred at 90 °C for 12 to get [C₃SO₃HNEt₃][HSO₄] and [C₃SO₃HNEt₃][PTS] BAILs.

2.2.2.8. Synthesis of triphenyl-(3-sulfopropyl)-phosphonium *p*-toluenesulfonate ([C₃SO₃HPPH₃][PTS]) and 1-(3-sulfopropyl)pyridinium *p*-toluenesulfonate ([C₃SO₃HPy][PTS]) BAIL

For the synthesis of these BAILs, triphenylphosphine and pyridine were mixed individually in 1,3-propane sultone on the equimolar basis in the presence of toluene as a solvent and refluxed for 16 h to get respective zwitter ions. In the second step, these zwitter ions were mixed with *p*-toluenesulfonic acid monohydrate (equimolar mixture) and stirred at 90 °C for 12 h to get [C₃SO₃HPPH₃][PTS] and [C₃SO₃HPy][PTS] BAILs.

For the above synthesized ILs the acidity (mmol/g) was measured using molecular *wt* of IL and moles of H⁺ present in IL were calculated; the data is summarized in Table no. 2.2.

Table 2.2. List of catalyst used in the present work their acidity in mmol/g.

Catalyst	Molecular formula	Mole wt.	Acidity (mmol/g)	H_o
[C ₃ SO ₃ HMIM][PTS]	C ₁₄ H ₂₀ N ₂ O ₇ S ₂	376	2.65	2.33
[C ₃ SO ₃ HMIM][HSO ₄]	C ₇ H ₁₄ N ₂ O ₇ S ₂	302	6.61	2.08
[C ₃ SO ₃ HMIM][Cl]	C ₇ H ₁₃ ClN ₂ O ₃ S	240	4.15	2.47
[C ₄ SO ₃ HMIM][PTS]	C ₁₅ H ₂₂ N ₂ O ₆ S ₂	390	2.56	2.34
[C ₄ SO ₃ HMIM][HSO ₄]	C ₈ H ₁₆ N ₂ O ₆ S ₂	316	6.32	2.10
[BMIM][Cl]	C ₈ H ₁₅ ClN ₂	174	-	-
[C ₃ SO ₃ HBenzMIM][HSO ₄]	C ₁₁ H ₁₆ N ₂ O ₇ S ₂	352	5.67	2.22
[C ₃ SO ₃ HBenzMIM][PTS]	C ₁₈ H ₂₂ N ₂ O ₆ S ₂	426	2.34	2.61
[C ₃ SO ₃ HNEt ₃][HSO ₄]	C ₉ H ₂₃ NO ₇ S ₂	321	6.22	2.19
[C ₃ SO ₃ HNEt ₃][PTS]	C ₁₆ H ₂₉ NO ₆ S ₂	395	2.52	2.57
[C ₃ SO ₃ HPPH ₃][PTS]	C ₂₈ H ₂₉ O ₆ PS ₂	556	1.80	2.39
[C ₃ SO ₃ HPy][PTS]	C ₁₅ H ₁₉ NO ₆ S ₂	373	2.67	2.38
HUSY (Si/Al=15)	Na _{0.4} H ₁₁ Al _{11.3} Si _{180.7} O ₃₈₄	-	0.55	0.97
HMOR (Si/Al)=10)	-	-	1.18	1.31
Amberlyst-15	C ₁₈ H ₁₈ O ₃ S	-	4.6	
Sulfuric acid	H ₂ SO ₄	98	20	1.67

Hammett acidity function (H_o) calculated with the help of UV-Vis spectrometer by using *p*-nitroaniline indicator, ILs 0.075 g dissolved in 50 mL indicator solution (10 mg *p*-nitroaniline in 1000 mL water). The acidity for BAILs in mmol/g was calculated based on molecular *wt* of BAILs while the acidity of solid acid in mmol/g was calculated using ammonia TPD.

2.3. Rationalization behind IL synthesis

It is important to note here that in earlier study the concentration of ILs used is very high and also those are used along with mineral acids or metal halides. Using ILs in higher quantity is not a good idea because ILs are expensive hence in present work the aim is to use ILs in catalytic amount for the conversion of biomass. If BAILs are used as catalyst (as it is acidic) for the biomass conversion, then there is no need to use an additional acid such as mineral acid or Lewis acid as it is reported in earlier works.^[8, 19-21] hence, in the present work, I am planning to use BAILs in catalytic amount without any metal halide and mineral acid. The details of rationalization used behind IL synthesis are explained as follows;

2.3.1. Synthesis of IL without Brønsted acidity

For understanding the effect of Brønsted acidity in the hydrolysis and dehydration reactions of saccharides, similar type of ILs were synthesized with or without Brønsted acidity ($[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ and $[\text{BMIM}][\text{Cl}]$).

The structures of $[\text{BMIM}][\text{Cl}]$ IL and $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ BAIL are shown in below Fig. 2.1. The $[\text{BMIM}][\text{Cl}]$ IL and $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ BAIL both are similar IL but the only difference between them is that one has Brønsted acidity ($[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$) and another one is not having any Brønsted acidity associated with it ($[\text{BMIM}][\text{Cl}]$). By using these ILs, the effect of Brønsted acidity present in ILs in the conversion of hemicellulose can be understood.

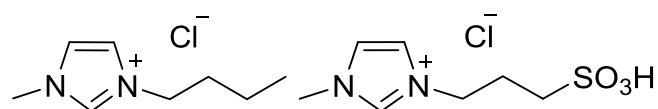


Figure 2.1. Structure of ILs without acidity and similar IL with Brønsted acidity.

2.3.2. Use of solid acid and mineral acid as a catalyst.

The solid acid catalysts which are best known for the conversion of hemicellulose and dehydration reactions of sugars such as HUSY (Si/Al=15), HMOR (Si/Al=10), H β (Si/Al=19) and Amberlyst-15,^[7, 22-23] are used in the present study for the comparison purpose. Furthermore, the use of mineral acid catalysts is also reported for the above mentioned reactions^[23-24] and hence, mineral acid catalyst such as H_2SO_4 , HCl and organic acid such as *p*-toluenesulfonic acid were used for the conversion of hemicellulose and the results of BAILs can be compared with these catalysts. With the

help of this study, the performance of IL can be compared with solid acid and mineral acid catalysts.

2.3.3. BAILs with different cations and anions

As the present thesis shows the use of BAILs for the hydrolysis and dehydration reactions of saccharides, it would be very important to study the effect of various types of cations and anions of the BAILs for these conversions. Because the properties of ILs (solubility, acidity viscosity, etc.) can be tuned by the change of cation or anion part of IL.

The acidity of BAILs are strongly depends on the anion of BAILs,^[25] similar fact can also be understood in present study for the BAILs. The $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL has highest acid strength ($H_o=2.08$) on the other hand, the $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ ($H_o=2.33$) and $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ ($H_o=2.37$) BAILs has lower acid strength compared to $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL. This implies that by changing the anion of BAILs the acidity of BAILs can be changed. The hydrolysis and dehydration reactions of saccharides are acid catalyzed reaction. Therefore, it is very interesting and also important to study the effect of BAILs with different acidity as the acidity of BAILs can be tuned or changed by changing anion of BAILs. Considering this, important role of cations and anions in BAILs, in the present work BAILs with various types of cations and anions were synthesized. The ILs synthesized with different cations and anion are presented in Fig. 2.2. and Fig. 2.3. Further, these ILs with different cations and anions were employed in the conversion of lignocellulosic biomass (hydrolysis and dehydration reactions of saccharides) to understand the effect of cations and anion.

2.3.3.1. Imidazolium based ILs

The Fig. 2.2. shows the synthesis of various ILs with imidazolium cations along with variety of anions such as *p*-toluenesulfonate, hydrogen sulfate, chloride etc. The ionic liquid without Brønsted acidity was also synthesized which is $[\text{BMIM}][\text{Cl}]$ IL, and its structure is very much similar to $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ BAIL.

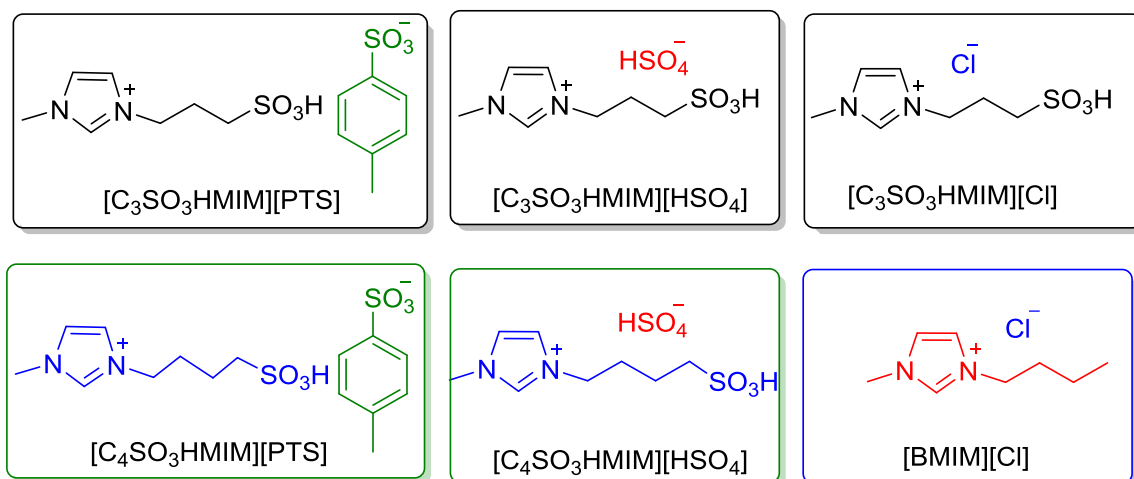


Figure 2.2. ILs with imidazolium cations.

2.3.3.2. ILs without imidazolium cation

Some more ILs were synthesized without imidazolium cations such as benzimidazolium based BAIL, quaternary ammonium based BAIL, triphenylphosphonium based BAIL, and pyridinium based BAIL with *p*-toluenesulfonate anion Fig. 2.3. Few more BAILs were synthesized with benzimidazolium and quaternary ammonium based cations having hydrogen sulfate as an anion. These BAILs were synthesized to understand the effect of cations for the conversion of hemicellulose.

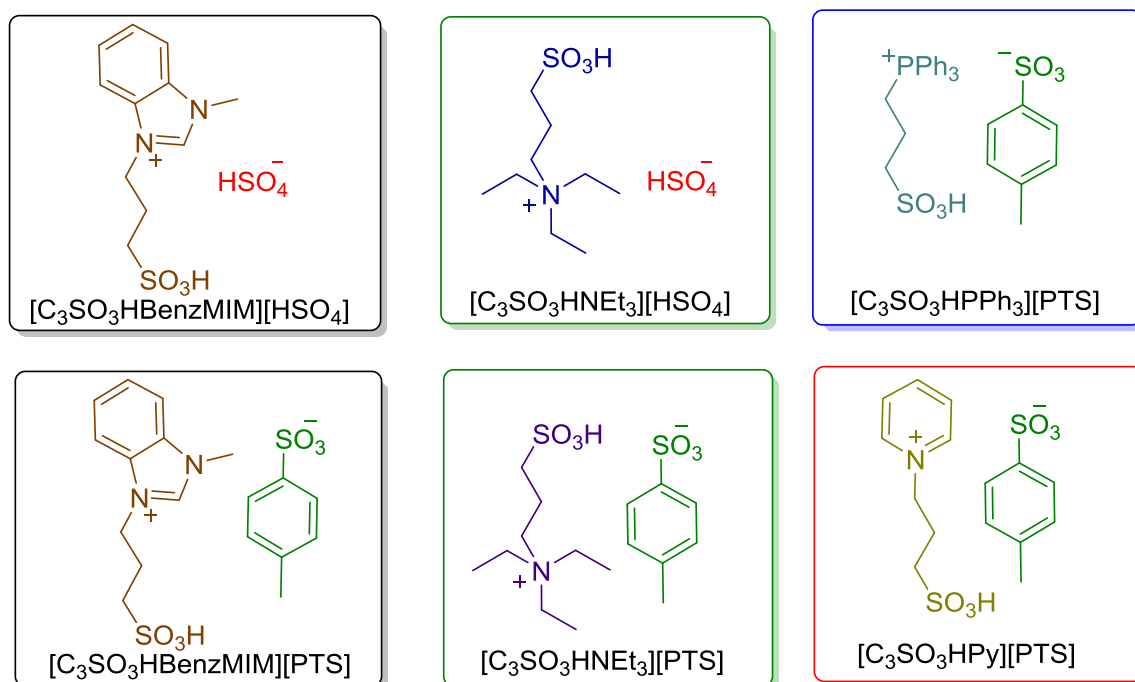


Figure 2.3. ILs without imidazolium cations

2.3.4. ILs with different solubility parameter

Typically, hemicellulose conversion reactions were carried out in water medium for obtaining sugars. When ILs are used as catalyst in the conversion of hemicellulose in water medium sugar monomers can be formed which are soluble in water. However, ILs are mostly polar in nature and hence which are also soluble in water. This may create a problem in separation of products (sugars) and catalyst (IL) from reaction mixture. To overcome this problem of separation of catalyst (IL) from reaction mixture solubility study of ILs was carried out.

Various ILs were synthesized as shown in Fig. 2.2. and 2.3. which have different combination of cations and anions and therefore, they may show the difference in the solubility in water and organic solvents. If the IL used for hemicellulose hydrolysis reaction is soluble in both organic and in water, then it can be separated using organic solvent. The following procedure can be used for the separation of IL from reaction; after completion of the reaction, solvent can be evaporated using rotary evaporator to obtain IL and sugars as a semi-viscous mass. Then by adding organic solvent to this mass, selectively IL will be dissolved, while the sugars formed in the reaction which are not soluble in organic solvent will remain undissolved. Therefore, the solubility of various ILs was studied in different types of solvents and the results are presented in Table 2.3.

The ILs are ionic in nature and shows very good solubility in water, methanol, and ethanol. The $[C_3SO_3HPy][PTS]$, $[C_3SO_3HPPPh_3][PTS]$, $[C_3SO_3HNEt_3][PTS]$, $[C_3SO_3HNEt_3][HSO_4]$, $[C_3SO_3HBenzMIM][HSO_4]$, and $[C_3SO_3HBenzMIM][PTS]$ BAILs are soluble in organic solvent but unfortunately these BAILs are less active for the hydrolysis and dehydration reactions of saccharides. Therefore, $[C_3S_3OHMIM][PTS]$, $[C_3S_3OHMIM][HSO_4]$, $[C_3S_3OHMIM][Cl]$ BAILs were preferred for the above titled reaction and these BAILs are soluble in polar solvents [water (10.2), methanol (5.1), ethanol (4.3)].

Table 2.3. The solubility of ILs in various solvents.*

Sr. No.	Ionic Liquids (ILs)	Solvents (Polarity index)							
		H ₂ O (10.2)	MeOH (5.1)	EtOH (4.3)	Acetone (5.1)	Toluene (2.4)	MIBK (4.2)	DCM (3.1)	DMSO (7.2)
1	[C ₃ S ₃ OHMIM][PTS]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.	Insol.
2	[C ₃ S ₃ OHMIM][HSO ₄]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.	Insol.
3	[C ₃ S ₃ OHMIM][Cl]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.	Insol.
4	[C ₄ S ₃ OHMIM][HSO ₄]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.	Insol.
5	[C ₄ S ₃ OHMIM][PTS]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.	Insol.
6	[BMIM][Cl]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Sol.	Sol.
7	[C ₃ SO ₃ HPy][PTS]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.	Insol.
8	[C ₃ SO ₃ HPh ₃][PTS]	Insol.	Insol.	Insol.	Insol.	Insol.	Insol.	Sol.	Sol.
9	[C ₃ SO ₃ HNEt ₃][PTS]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.	Sol.
10	[C ₃ SO ₃ HNEt ₃][HSO ₄]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.	Sol.
11	[C ₃ SO ₃ HBenzMIM][HSO ₄]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Sol.	Sol.
12	[C ₃ SO ₃ HBenzMIM][PTS]	Sol.	Sol.	Sol.	Insol.	Insol.	Insol.	Sol.	Sol.

MIBK=Methyl isobutyl ketone, DCM=Dichloromethane, DMSO=Dimethyl sulfoxide.

* solubility is checked by dispersing 10 mg of IL in 5 mL solvent.

2.4. Catalyst characterization techniques

2.4.1. Nuclear magnetic resonance spectroscopy (NMR)

The ^1H and ^{13}C NMR gives structural information of the molecule. From the ^1H NMR spectroscopy, the information about the behavior of protons of the molecule can be understood. The NMR technique has an ability to differentiate small differences in molecular configuration make it an ideal technique for identifying chemical compounds.

The Carbon-12 nucleus is not magnetically active because of it does not have nuclear spin. However, Carbon-13 has a presence of unpaired neutron and hence it is NMR active. The Carbon-13 nuclei make up approximately one percent of the carbon nuclei on the earth. Therefore, ^{13}C NMR spectroscopy is less sensitive than ^1H NMR spectroscopy. The ^{13}C NMR tells information about the carbon atoms present in the organic molecule. Moreover, ^{13}C NMR spectroscopy can be used to supplement the information of ^1H NMR spectroscopy.

NMR measurements were carried out on a Bruker AV 200 MHz NMR spectrometer equipped with a 4.7 Tesla superconducting magnet. Before the analysis the samples were dissolved in D_2O . The resonance frequency for ^1H and ^{13}C NMR was 200 MHz. The ^1H NMR spectra were taken with a standard one pulse experiment using a 30-degree flip angle and 1 sec relaxation delay. 32 to 64 scans and 32K data points were used for data collection. The raw data obtained were Fourier Transformed to get the frequency domain spectrum without the application of any window function. ^{13}C NMR spectra were obtained with a standard pulse sequence with continuous proton decoupling. A flip angle of ~ 30 degrees, the relaxation delay of 2 sec and 32K data points were used for data collection. The proton decoupling was achieved by a standard ZGPG30 pulse technique. A standard distortion less enhancement of polarization transfer (DEPT) pulse sequence with a sorting pulse of 135 degrees (DEPT-135) was employed for the ^{13}C spectral editing so that the CH_2 peaks appear as negative and CH and CH_3 as positive. The number of scans for the ^{13}C spectral data collection varied from a few hundred to a couple of thousand depending on the concentration. Prior to Fourier Transformation, the raw ^{13}C data (FIDs) were multiplied by an exponential window function with a line broadening (LB) of 2Hz for

sensitivity enhancement. The chemical shift for the solvent peak (HDO) was found at 4.72 ppm.

2.4.2. Elemental microanalysis

Here elemental analysis refers to CHNS analysis, it is the technique by which determination of the mass fraction of carbon, hydrogen, nitrogen and sulfur can be done. This technique will help to determine the structure of the compound and it will also help for the understanding the purity of a synthesized compound. Element percentage was calculated using CHNS analysis (elemental microanalysis was performed using a Thermo Finnigan Flash EA 1112 series instrument).

2.4.3. Hammett acidity function (H_o)

Hammett acidity functions (H_o) of the catalysts were determined by means of a UV-vis spectrophotometer (Jasco V-570 spectrophotometer, Jasco Corporation, Japan) using *p*-nitroaniline as a basic indicator.

Hammett acidity function (H_o) of various catalysts were determined by using UV-Vis spectrophotometer (V-570 Spectrophotometer, Jasco corporation, Japan), and *p*-nitroaniline as a basic indicator. The Hammett function, H_o was calculated using Equation 1.

$$H_o = pK(I)_{aq} + \log\left(\frac{[I]}{[IH^+]}\right) \dots\dots\dots(1)$$

Here, $pK(I)_{aq}$ is the pK_a value of the indicator (*p*-nitroaniline). The $[IH^+]$ & $[I]$ are the molar concentrations of the protonated and unprotonated forms of the indicator solution, respectively. The $[I]/[IH^+]$ ratio was determined from the difference in the measured absorbance after the addition of catalyst and before the addition of a catalyst to the indicator solution. The maximum absorbance for the unprotonated indicator in UV-Vis spectra was observed at 380 nm.

2.4.4. Thermogravimetric analysis (TGA)

TGA is a thermal analysis method in which the changes in physical and chemical properties of materials are measured as a function of increasing temperature and/or mass loss. This characterization was performed under the air atmosphere using Mettler Toledo Instrument TGA/SDTA851^e. Using this characterization technique, the mass loss in ILs can be understood with respect to temperature.

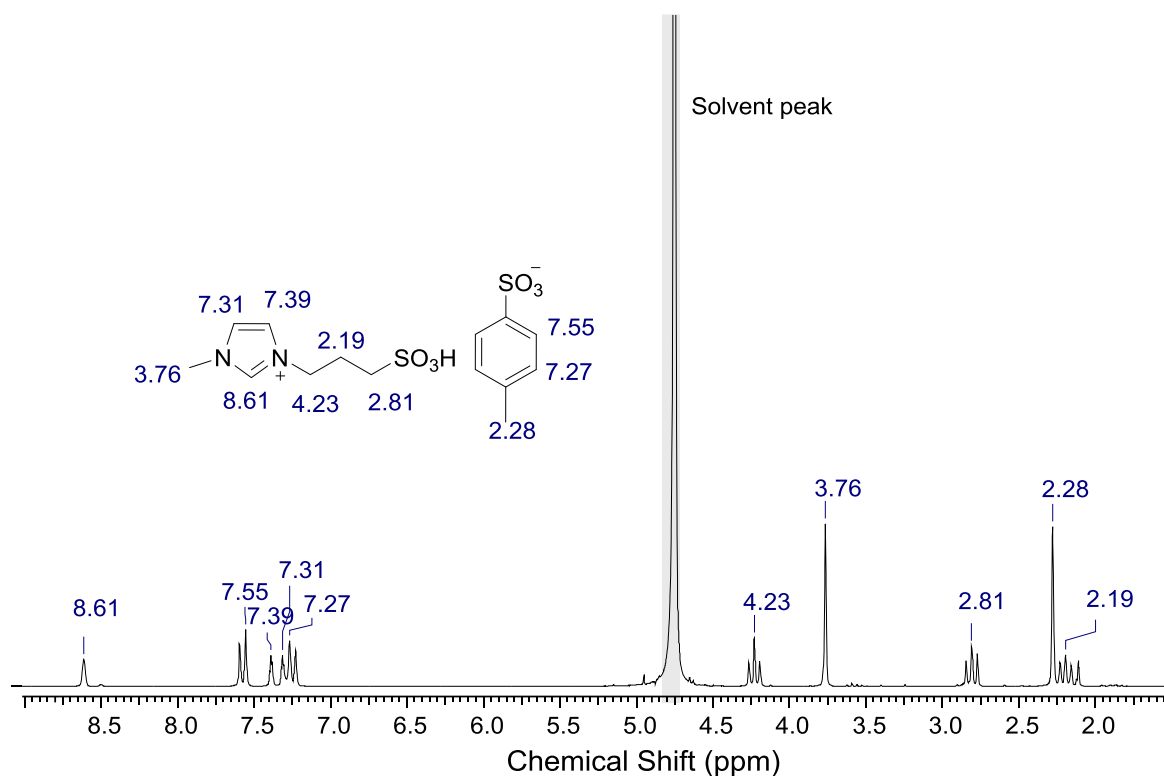
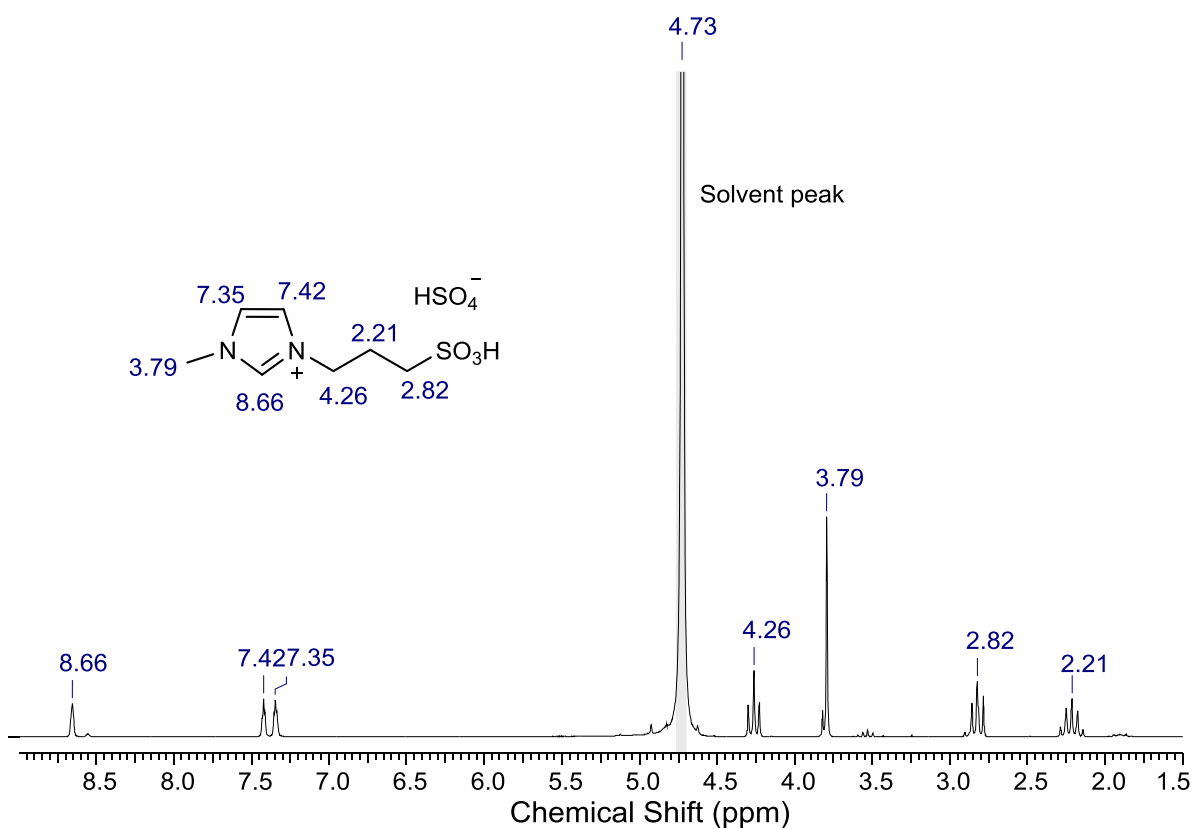
2.4.5. Fourier transform infrared spectroscopy (FTIR)

FTIR stands for Fourier Transformed Infrared, the preferred method of infrared spectroscopy. The FTIR spectroscopy is a highly diverse molecular spectroscopy technique and chemical analysis method. Using this method various functional groups present in the molecule can be identified. In general sample analysis, the process of instrument comprises of source, interferometer, sample detector and the computer. The FTIR instrument has various advantages over the dispersive technique such as faster speed of analysis, good sensitivity, mechanical simplicity and internal calibration. As these instruments are self-calibrating and never need to be calibrated by the user. The IR experiments were performed using Bruker Tensor 27 IR instrument

2.5. Results and discussion

2.5.1. NMR analysis

All the synthesized catalysts were characterized using ^1H NMR and ^{13}C NMR spectroscopy and the results are presented in Fig. 2.4. to 2.24. All the ^1H NMR and ^{13}C NMR characterization was carried out using D_2O solvent. The analysis of [BMIM][Cl] IL was performed using DMSO-d_6 solvent. The result showed that all the ILs synthesized are in pure form because in NMR there is no any extra peaks apart from IL. In case of imidazolium BAIL such as $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ BAIL the imidazolium C-H protons are coming at 7.39 and 7.31 δ ppm, the chemical shift value for proton flanked between two nitrogen atom is observed at 8.61 δ ppm. The methylene protons are observed at 2.81, 2.19 and 4.23 δ ppm. The methyl protons linked to nitrogen of imidazole ring is detected at 3.76 δ ppm chemical shift value. The aromatic protons of *p*-toluenesulfonate showed two doublets one at 7.55 δ ppm and another one at 7.27 δ ppm. Finally, the methyl protons of *p*-toluenesulfonate showed singlet at 2.28 δ ppm. Similarly, the NMR (^1H and ^{13}C) of all other synthesized ILs can be explained.

2.5.1.1. ^1H NMR of ILsFigure 2.4. ^1H NMR of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ BAIL.Figure 2.5. ^1H NMR of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL.

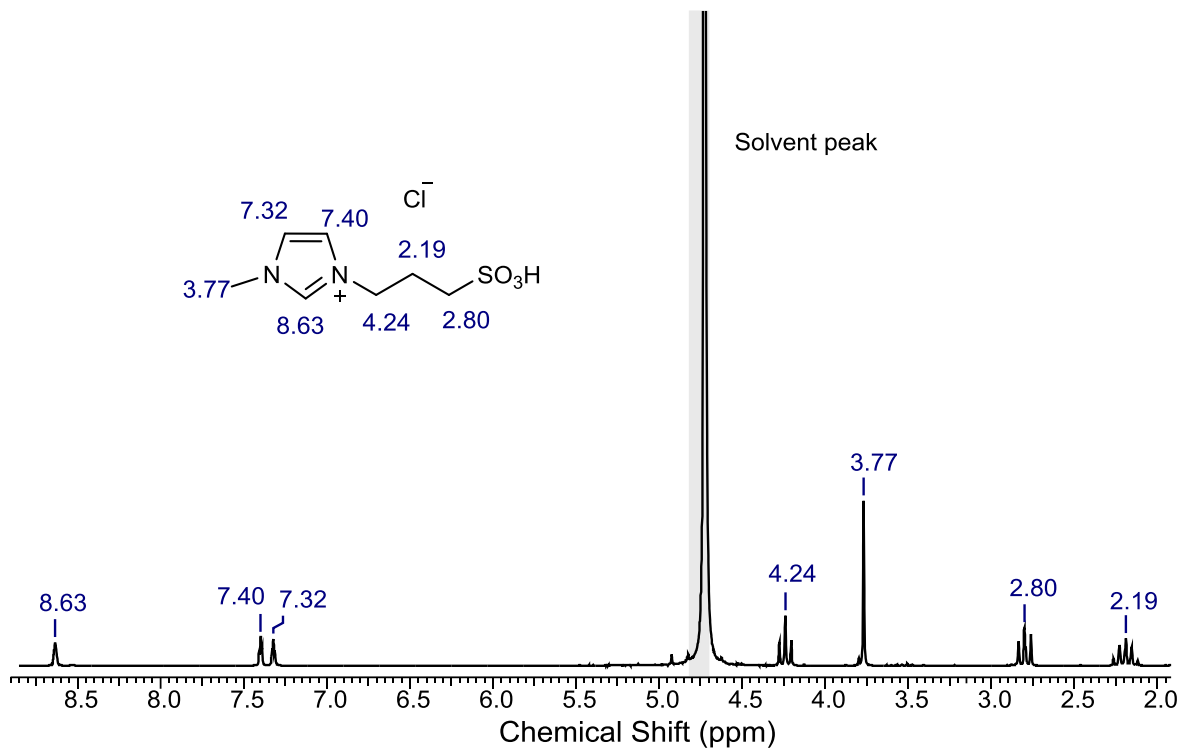


Figure 2.6. 1H NMR of $[C_3SO_3HMIM][Cl]$ BAIL.

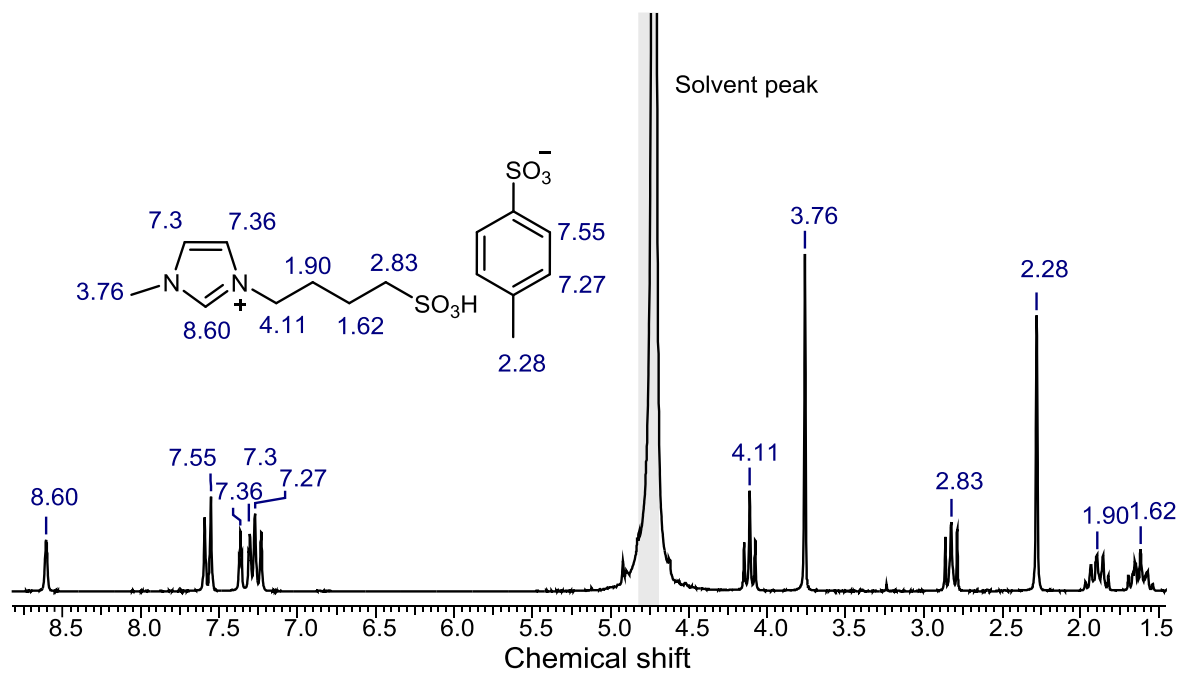


Figure 2.7. 1H NMR of $[C_4SO_3HMIM][PTS]$ BAIL.

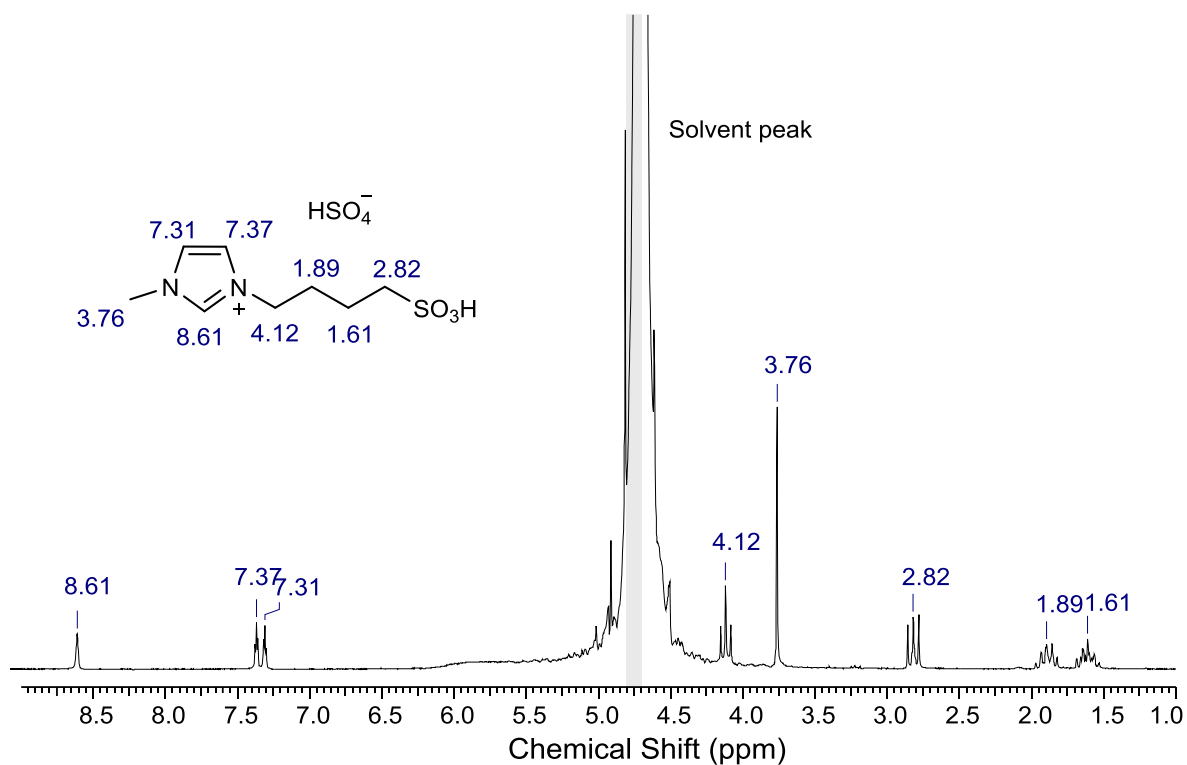


Figure 2.8. ^1H NMR of $[\text{C}_4\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL.

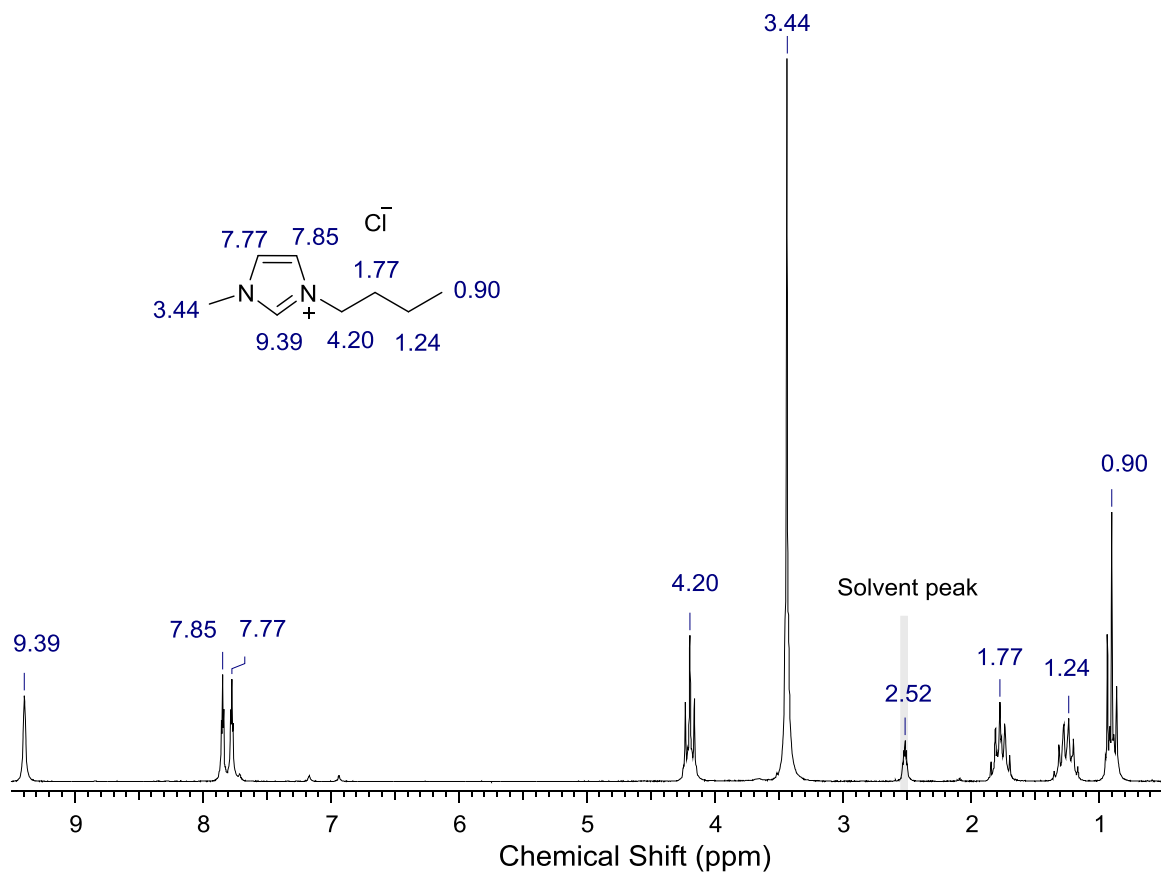


Figure 2.9. ^1H NMR of $[\text{BMIM}][\text{Cl}]$ IL in DMSO-d_6 .

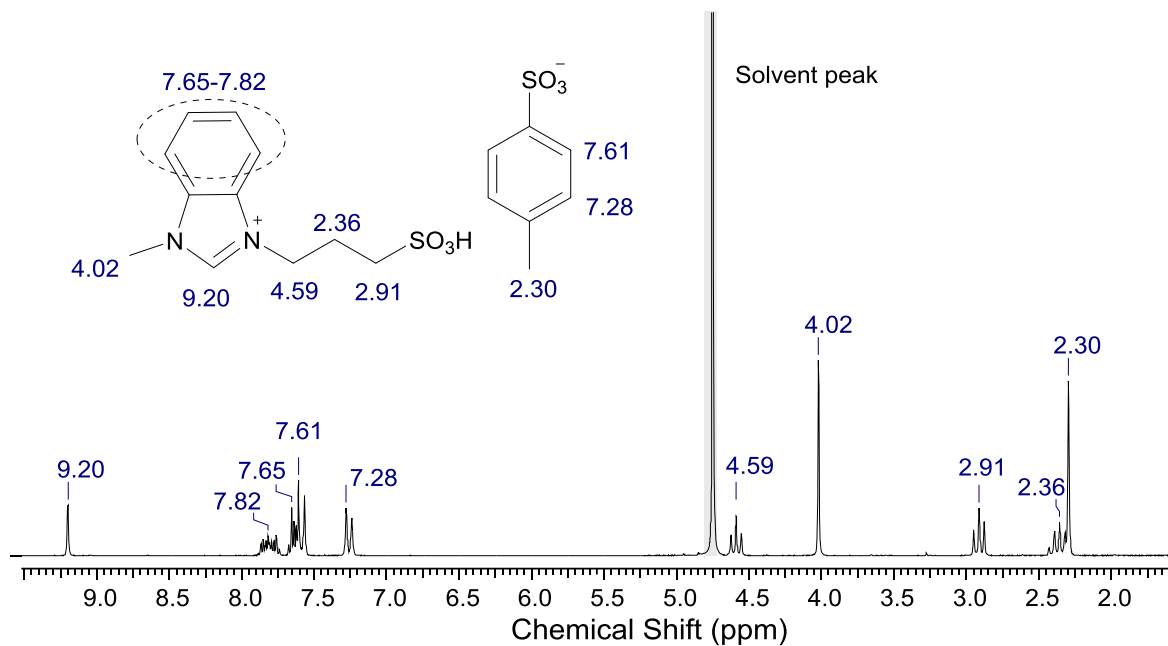


Figure 2.10. ¹H NMR of [C₃SO₃HBenzMIM][PTS] BAIL.

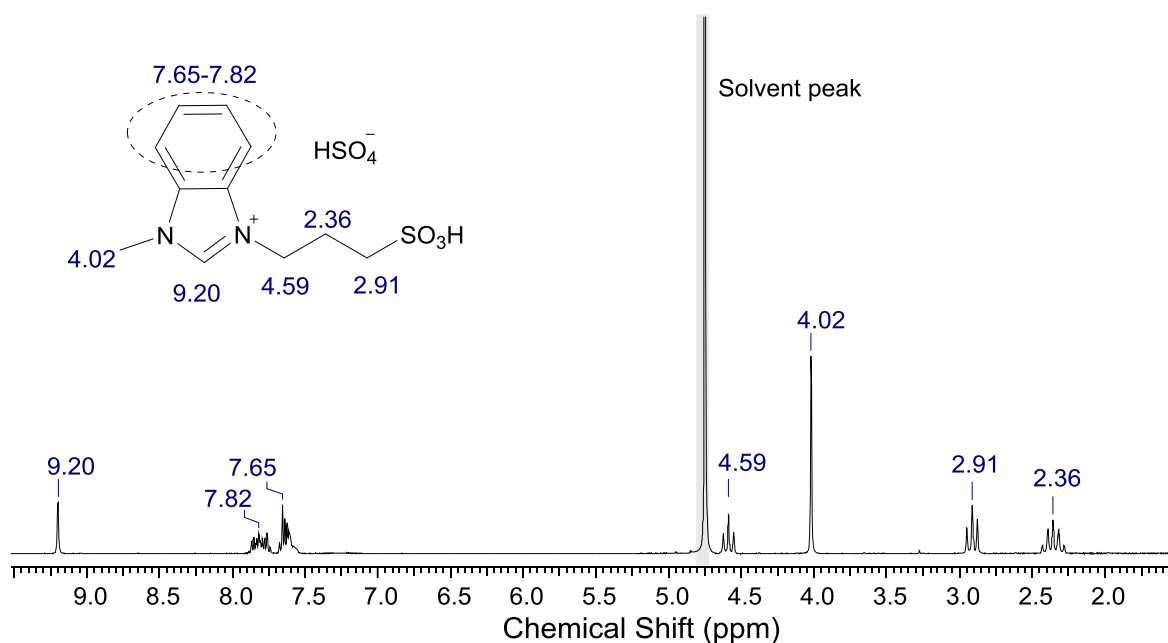


Figure 2.11 ¹H NMR of [C₃SO₃HBenzMIM][HSO₄].

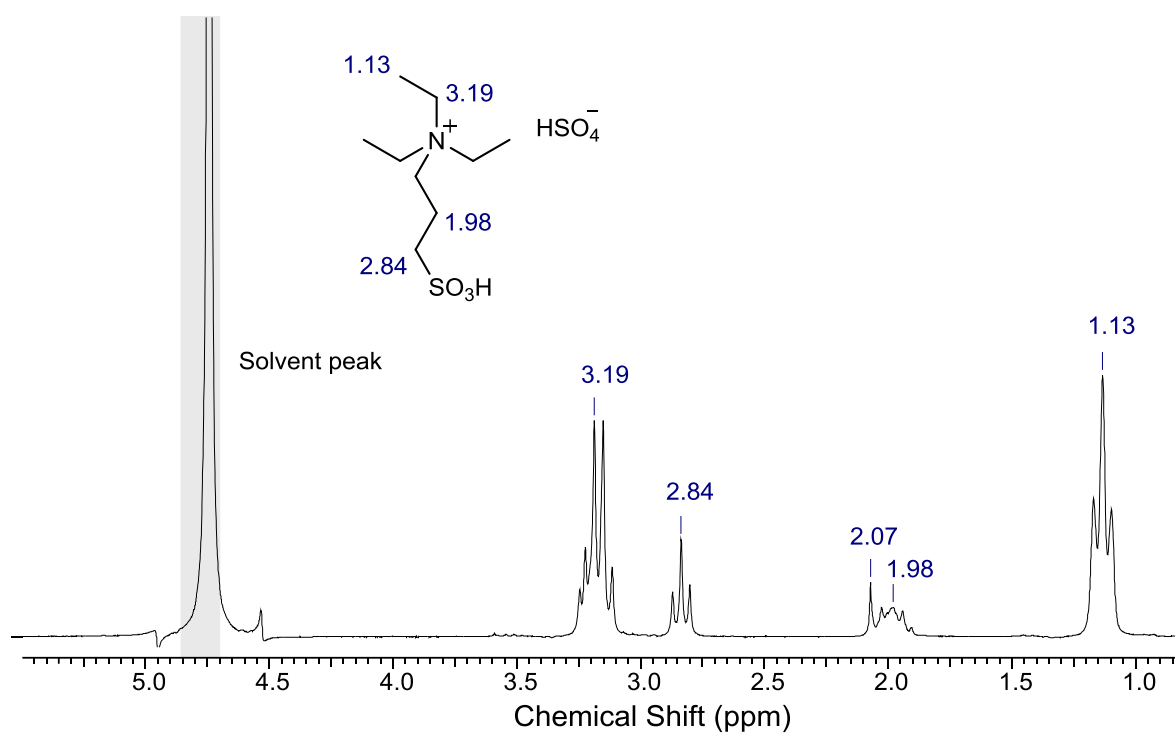


Figure 2.12. ^1H NMR of $[\text{C}_3\text{SO}_3\text{HNEt}_3][\text{HSO}_4]$ BAIL.

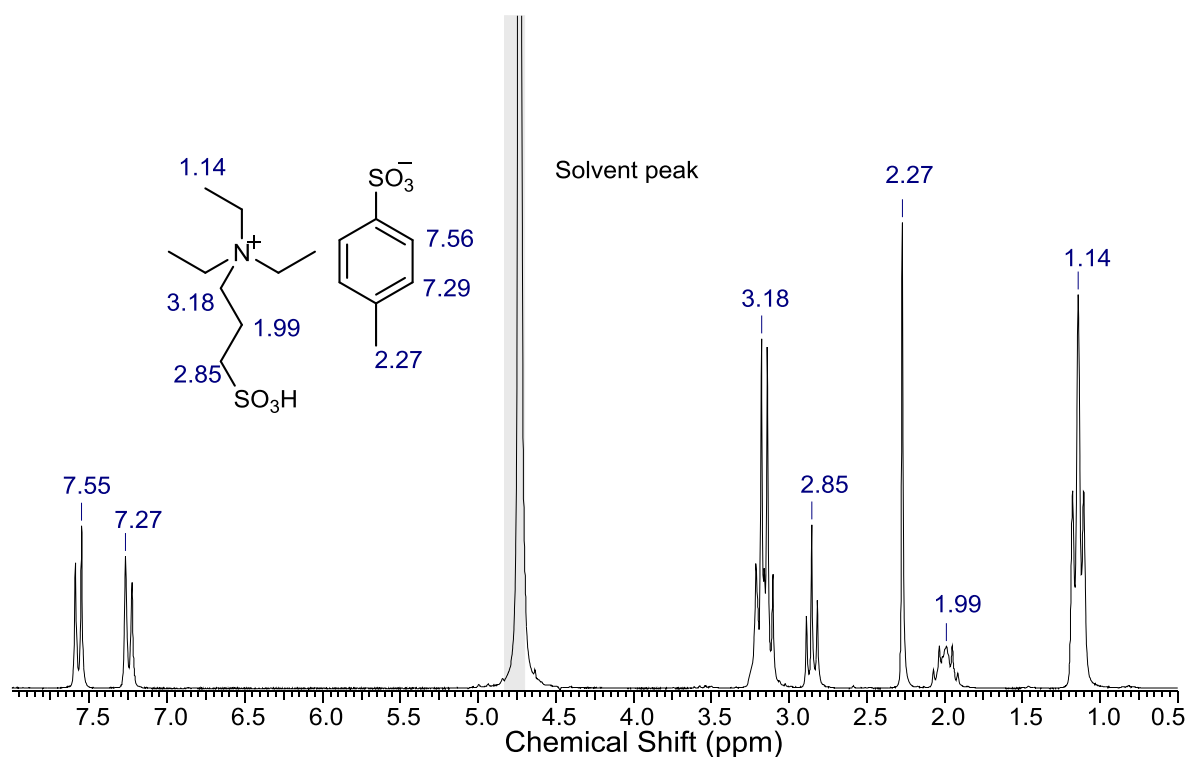


Figure 2.13. ^1H NMR of $[\text{C}_3\text{SO}_3\text{HNEt}_3][\text{PTS}]$ BAIL.

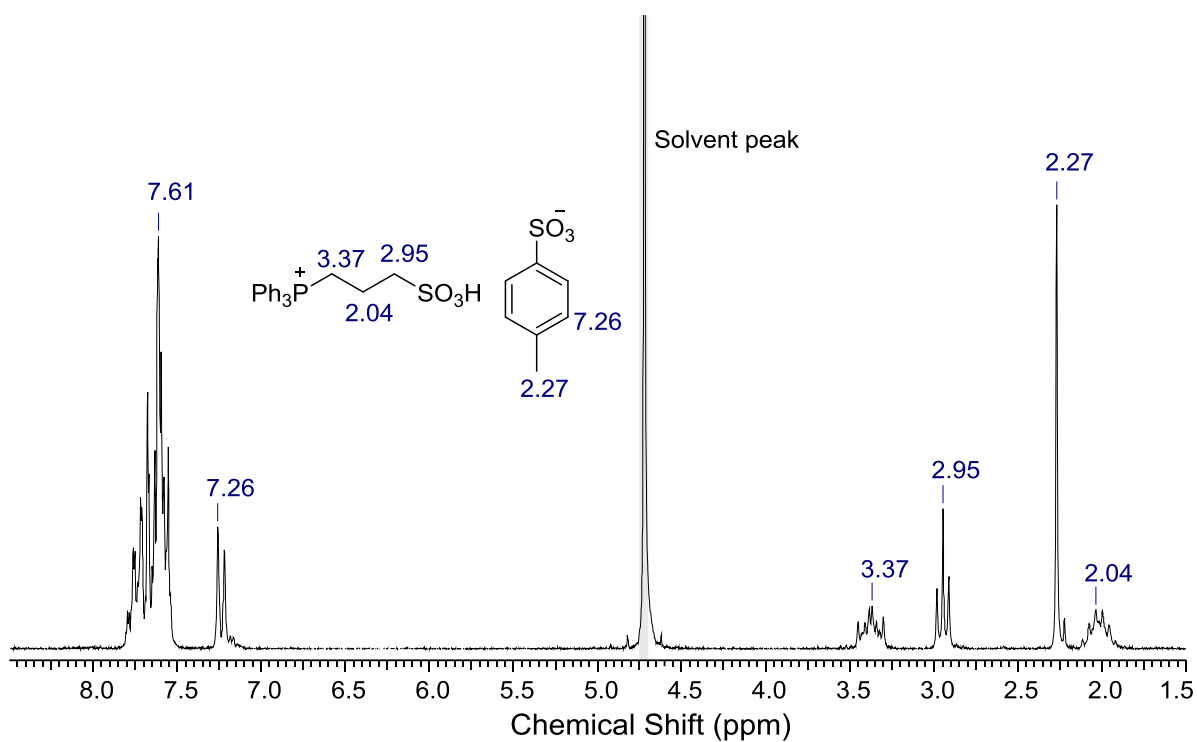


Figure 2.14. ^1H NMR of [C₃SO₃HPPH₃][PTS] BAIL.

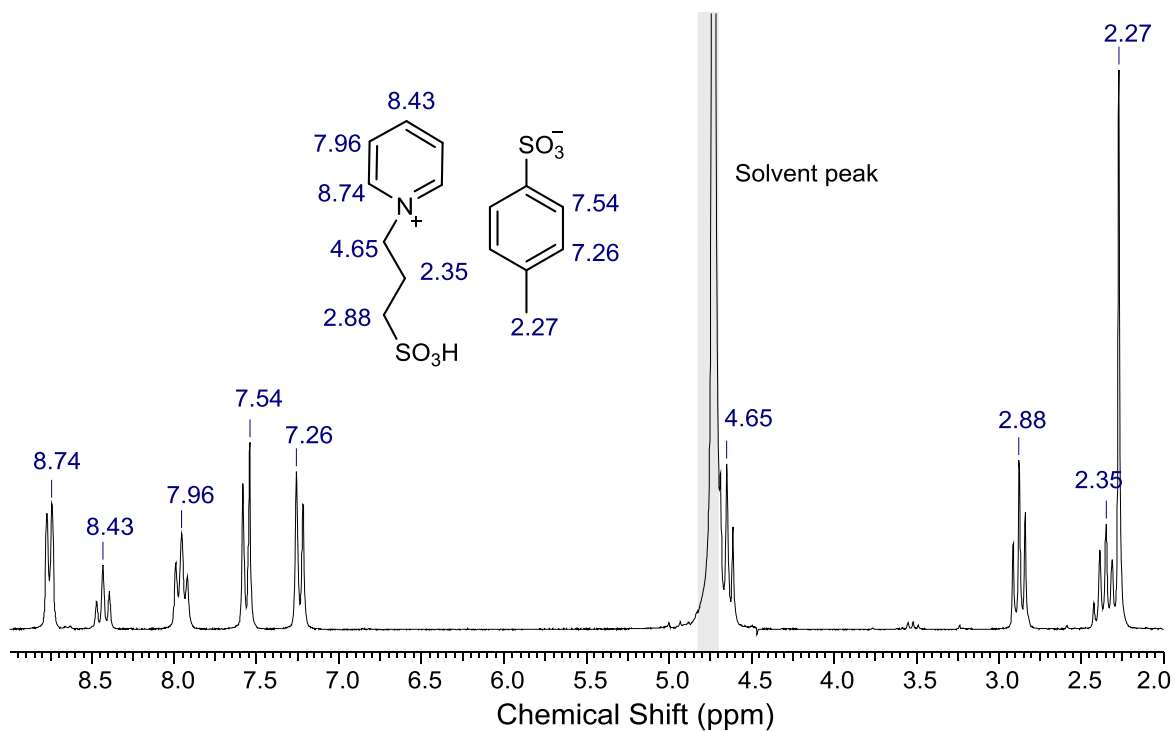
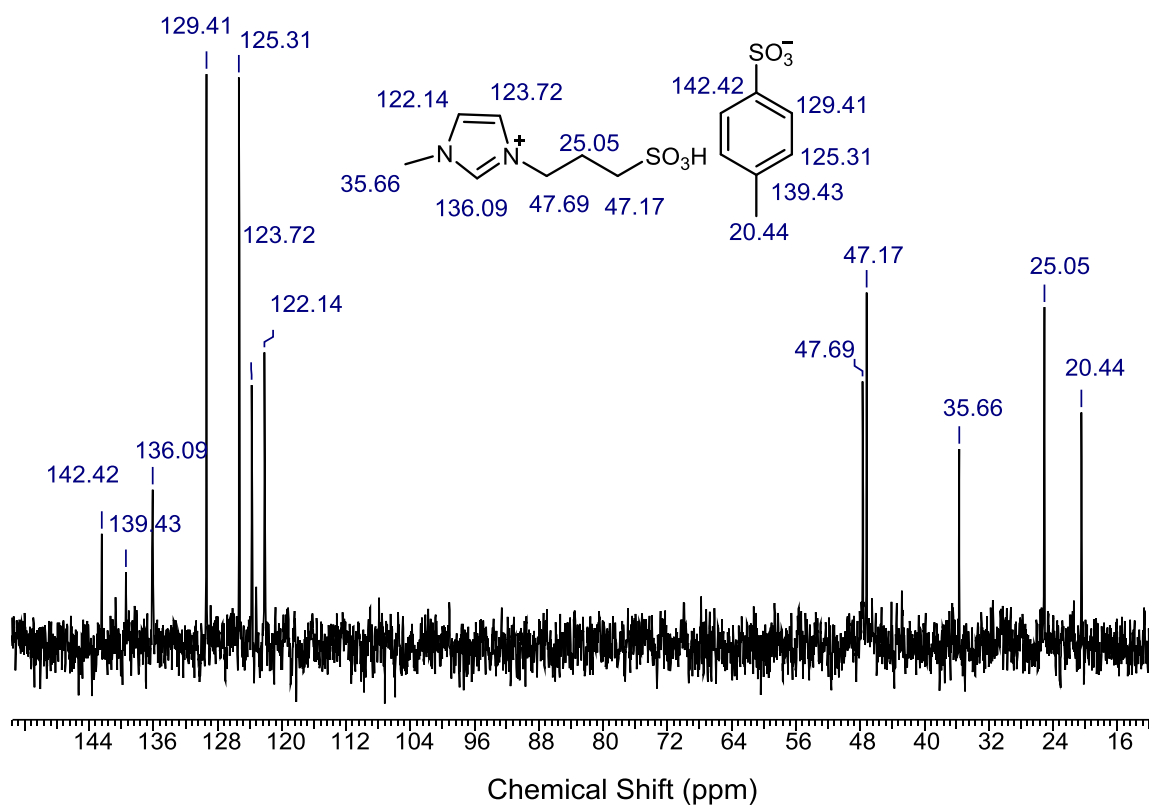
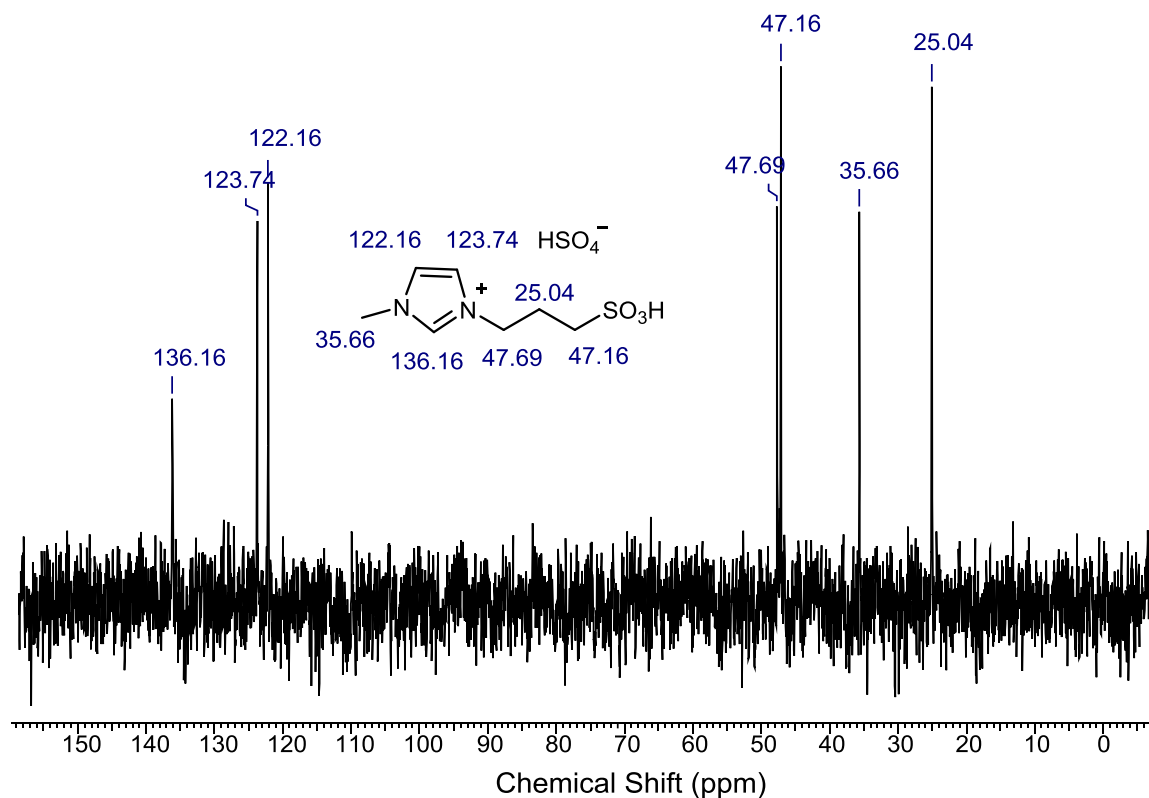


Figure 2.15. ^1H NMR of [C₃SO₃HPy][PTS] BAIL.

2.5.1.2. ^{13}C NMR of ILsFigure 2.16. ^{13}C NMR of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ BAIL.Figure 2.17. ^{13}C NMR of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL.

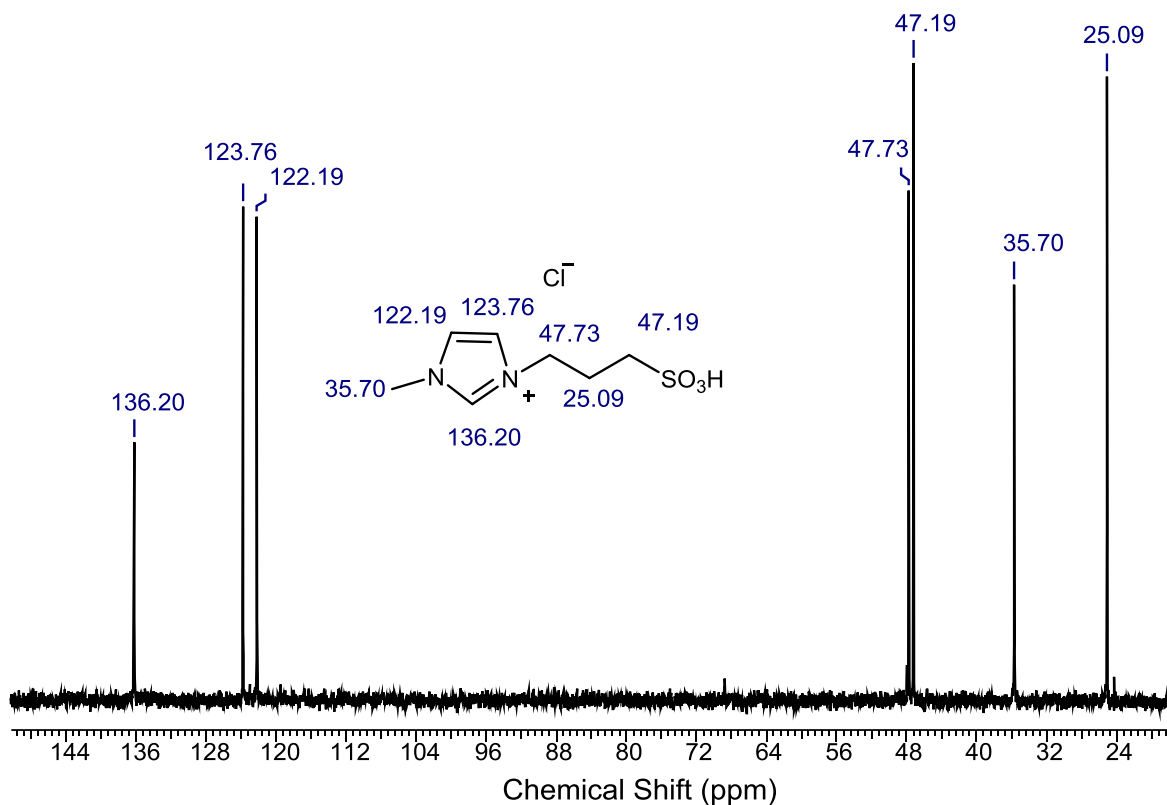


Figure 2.18. ^{13}C NMR of [C₃SO₃HMIM][Cl] BAIL.

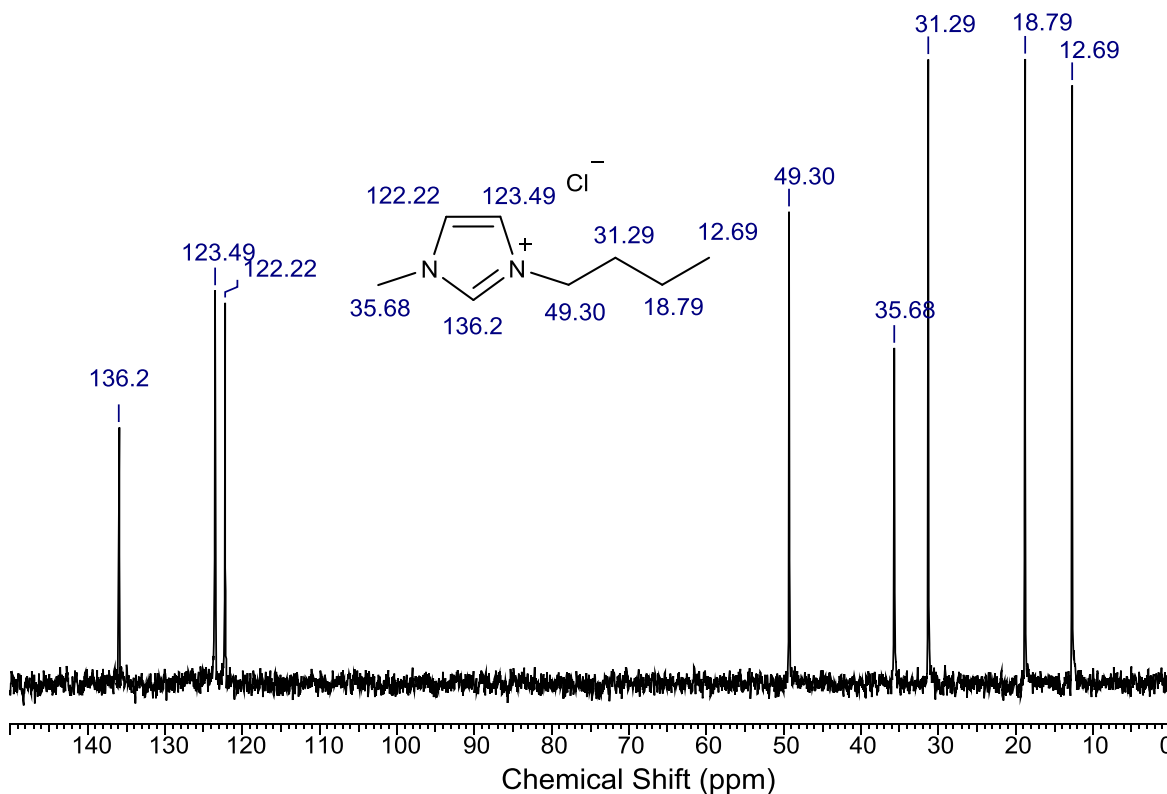
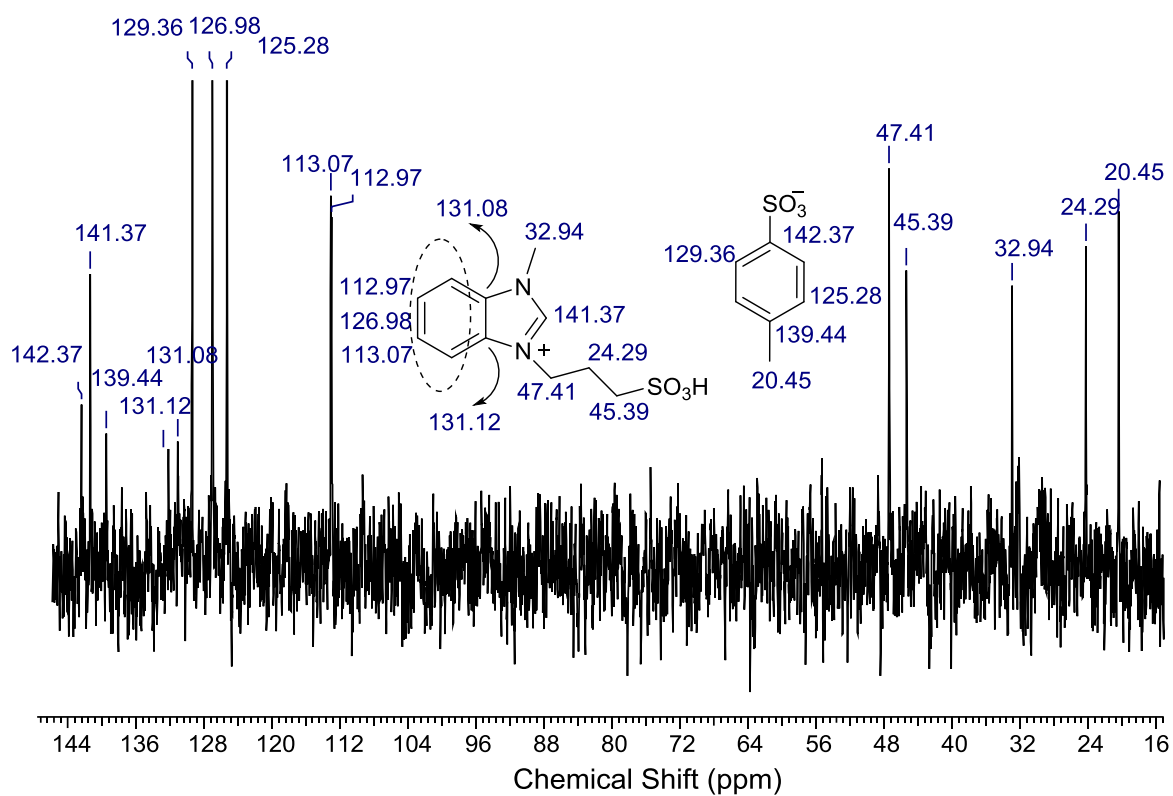
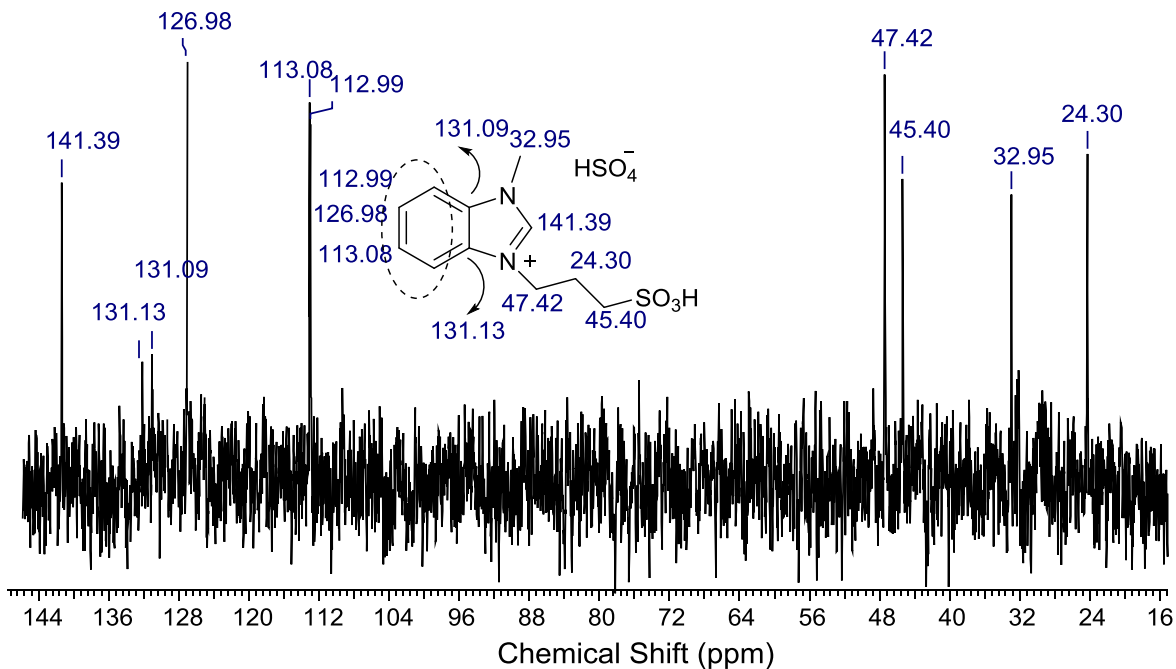
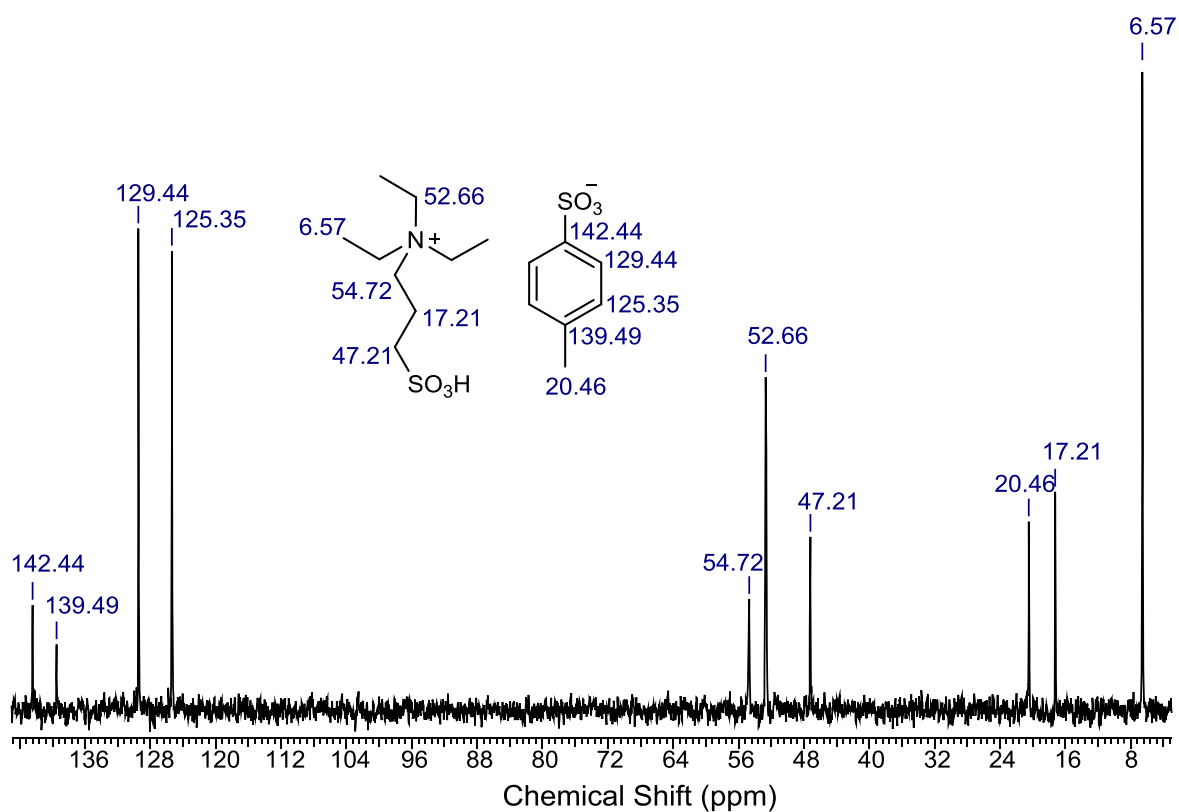
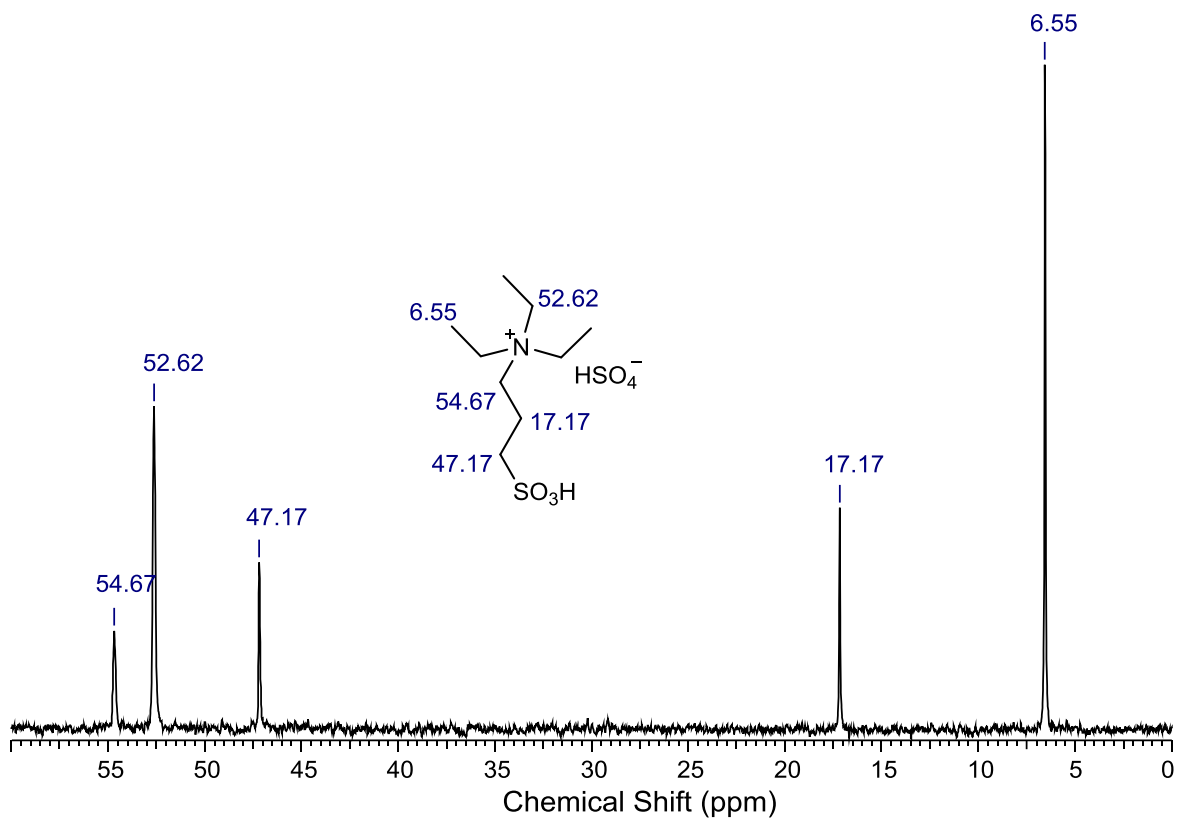


Figure 2.19. ^{13}C NMR of [BMIM][Cl] BAIL.

**Figure 2.20.** ^{13}C NMR of $[\text{C}_3\text{SO}_3\text{HBenzMIM}][\text{PTS}]$ BAIL.**Figure 2.21.** ^{13}C NMR of $[\text{C}_3\text{SO}_3\text{HBenzMIM}][\text{HSO}_4]$ BAIL.



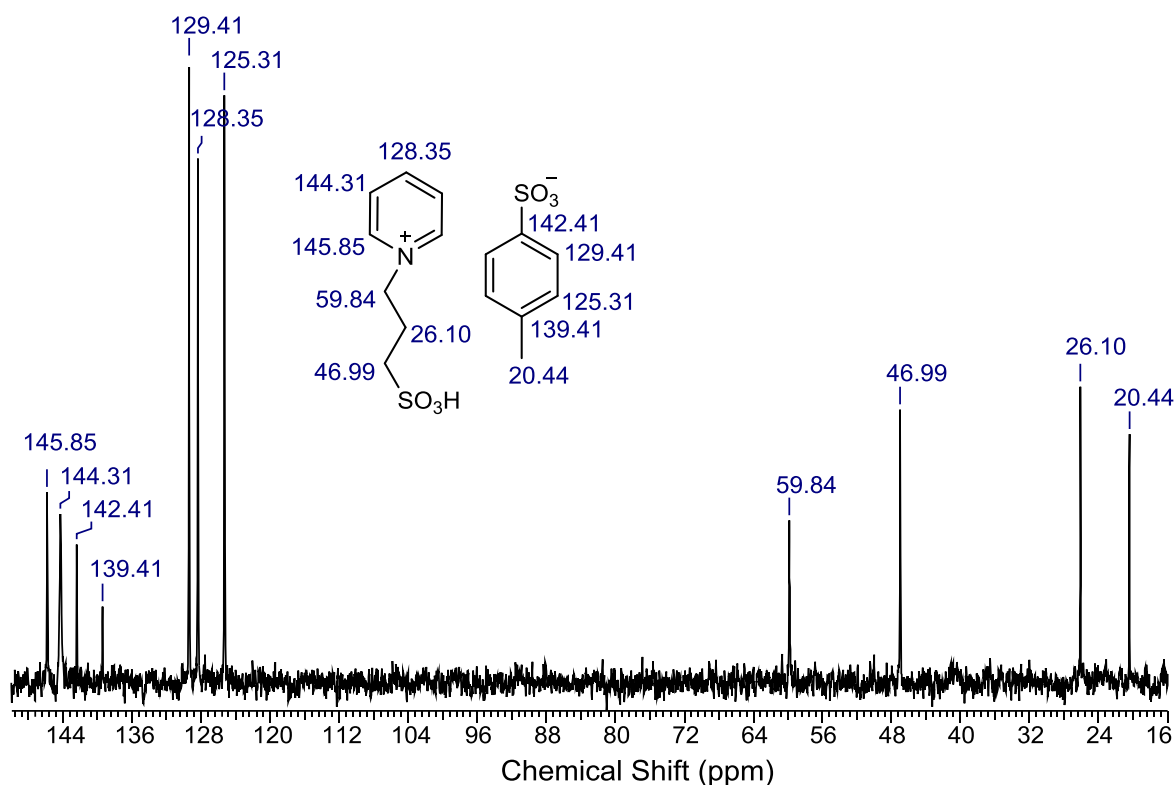


Figure 2.24. ^{13}C NMR of $[\text{C}_3\text{SO}_3\text{HPy}][\text{PTS}]$ BAIL.

The ^{13}C NMR characterization additionally support for the structure of BAIL. For ^{13}C NMR also the D_2O solvent was used for all the IL except $[\text{BMIM}][\text{Cl}]$. $\text{DMSO-}d_6$ solvent was used for $[\text{BMIM}][\text{Cl}]$ IL. The presence of primary, secondary and tertiary carbon atoms were understood from Distortionless enhancement by polarization transfer (DEPT) NMR method and then these values are assigned in main ^{13}C NMR spectra.

^1H NMR and ^{13}C NMR characterization clearly showed that the synthesized ILs are pure in nature. After confirming the structure of all the ILs using this NMR spectroscopic method it is used in the hemicellulose conversion reactions.

2.5.2. Elemental analysis for the determination of C, H, N and S elements

The determined percentages of C, H, N, and S calculated using CHNS analysis are presented in Table 2.4. The results of elemental analysis obtained for ILs showed that the synthesized ILs are pure in nature and also the molecular formula of ILs can be drawn with the help of values obtained from elemental analysis. Also, this analysis method helps for calculating the acid amount present in the catalyst, this can be calculated with the help of available percentage of sulfur.

Table 2.4. Elemental analysis of ILs.

No.	Catalyst	C (%)	H (%)	N (%)	S (%)
1	[C ₃ SO ₃ HMIM][PTS]	44.2	7.1	7.7	16.6
2	[C ₃ SO ₃ HMIM][HSO ₄]	27.5	4.8	9.0	21
3	[C ₃ SO ₃ HMIM][Cl]	34.7	5.2	11.5	12.6
4	[C ₄ SO ₃ HMIM][PTS]	46.2	5.7	7	16.4
5	[C ₄ SO ₃ HMIM][HSO ₄]	30.3	5.1	8.8	20.3
6	[BMIM][Cl]	55	8.6	16	0
7	[C ₃ SO ₃ HBenzMIM][PTS]	50.7	5.3	6.6	15.0
8	[C ₃ SO ₃ HBenzMIM][HSO ₄]	37.5	4.6	8	18.1
9	[C ₃ SO ₃ HNEt ₃][PTS]	48.6	7.4	3.5	16.3
10	[C ₃ SO ₃ HNEt ₃][HSO ₄]	33.6	7.2	4.4	20
11	[C ₃ SO ₃ HPPPh ₃][PTS]	60.4	5.2	0	11.5
12	[C ₃ SO ₃ HPy][PTS]	48.3	5.1	3.7	17.2

All the above values obtained for element analysis are very much closer to theoretical values with $\pm 0.2\%$ difference. This implies that all the ILs synthesized are pure and does not contains any impurity.

2.5.3. Hammett acidity function (*H_o*) for calculating the acid strength of BAILs, solid acid and mineral acid catalyst

The Hammett acidity of all the BAILs, solid acid and mineral acid catalysts were calculated and the values are shown in Table no. 2.5. the formula used for *H_o* analysis and method is explained in section 2.4.3.

Table 2.5. Hammett acidity function (H_o) data for various catalysts.

Catalyst	Amax	[I]%	[IH ⁺]%	H_o
Blank	0.94	100	0.0	-
HUSY (Si/Al=15)	0.46	48.9	51.1	0.97
HMOR (Si/Al=10)	0.64	68.0	32.0	1.31
H ₂ SO ₄	0.78	82.9	17.1	1.67
[C ₃ SO ₃ HMIM][HSO ₄]	0.87	92.5	7.5	2.08
[C ₃ SO ₃ HMIM][PTS]	0.90	95.7	4.3	2.33
[C ₃ SO ₃ HMIM][Cl]	0.91	96.8	3.2	2.47
[C ₄ SO ₃ HMIM][PTS]	0.901	95.9	4.1	2.34
[C ₄ SO ₃ HMIM][HSO ₄]	0.874	93.0	7.0	2.10
[C ₃ SO ₃ HBenzMIM][HSO ₄]	0.888	94.5	5.5	2.22
[C ₃ SO ₃ HBenzMIM][PTS]	0.917	97.6	2.4	2.61
[C ₃ SO ₃ HNEt ₃][HSO ₄]	0.883	93.9	6.1	2.19
[C ₃ SO ₃ HNEt ₃][PTS]	0.916	97.5	2.5	2.57
[C ₃ SO ₃ HPPPh ₃][PTS]	0.904	96.2	3.8	2.39
[C ₃ SO ₃ HPy][PTS]	0.903	96.1	3.9	2.38
[BMIM][Cl]	0.94	100	-	-

0.075 g of catalyst is added in 50 mL of water solution of *p*-nitroaniline (10 mg *p*-nitroaniline in 1000 mL H₂O, pK_a of *p*-nitroaniline = 0.99).

The trend of acid strength detected for all the BAILs are observed as follows. [C₃SO₃HMIM][HSO₄] > [C₄SO₃HMIM][HSO₄] > [C₃SO₃HNEt₃][HSO₄] > [C₃SO₃HBenzMIM][HSO₄] > [C₃SO₃HMIM][PTS] > [C₄SO₃HMIM][PTS] > [C₃SO₃HPy][PTS] > [C₃SO₃HPPPh₃][PTS] > [C₃SO₃HMIM][Cl] > [C₃SO₃HNEt₃][PTS] > [C₃SO₃HBenzMIM][PTS]. From this results it can be understood that [C₃SO₃HMIM][HSO₄] BAIL has higher acid strength compared

to all other ILs synthesized for the conversion of hemicellulose. This implies that $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ can give better performance in the above tilted reaction.

2.5.4. Thermogravimetric analysis

The TGA study of the synthesized ILs was studied, and the result shows that there is no any mass loss because of IL up to 250 °C. This implies that ILs can be used up to 250 °C for the conversion of biomass. The TGA analysis was performed under the air atmosphere, and the heating rate used for the analysis was 10 °C/min. TGA of ILs is presented in Fig. 2.25. The initial loss in mass is observed because of loss of water from ILs. The hydrothermal stability of all BAILs was checked at 170 °C for 5 h and it was found that these ILs are hydrothermally stable. For hydrothermal stability 0.24 g BAILs was taken in 60 mL water and stirred at 170 °C for 5 h, after 5 h the reactor was cooled to RT and the aqueous layer was analyzed using HPLC.

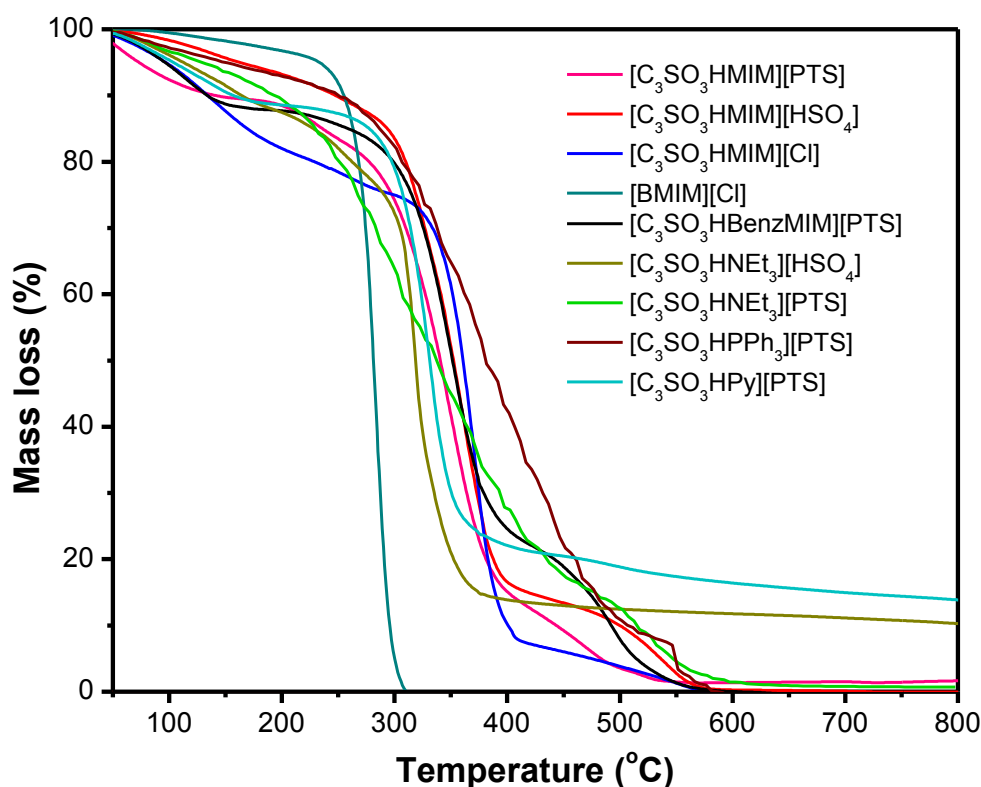


Figure 2.25. TGA of ILs

#TGA of $[\text{C}_3\text{SO}_3\text{HBenzMIM}][\text{PTS}]$, $[\text{C}_3\text{SO}_3\text{HNEt}_3][\text{HSO}_4]$ and $[\text{C}_3\text{SO}_3\text{HPy}][\text{PTS}]$ were performed in presence of N_2 atmosphere.

2.5.5. Fourier transform infrared spectroscopy for the determination of functional groups present in ILs

The FT-IR of all the synthesized ILs is presented in below Fig. 2.26.

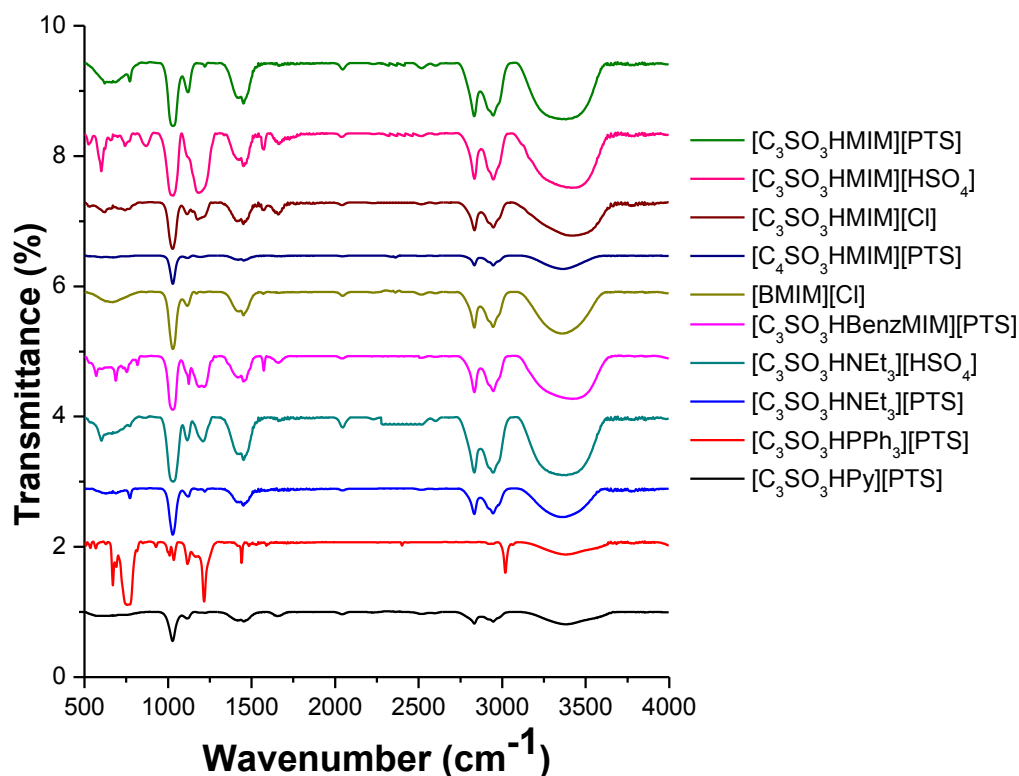


Figure 2.26. FTIR spectra of ILs.

In the spectra, the SO₂ asymmetric stretching was observed at 1390-1290 cm⁻¹, while SO₂ symmetric stretching was observed at 1190-1120 cm⁻¹. The S=O stretching was seen at 1060-1020 cm⁻¹. Furthermore, the C=C and C=N of imidazole ring stretching were seen at 1610 and 1578 cm⁻¹ in the spectrum (Fig. 2.26.). Singly substituted aromatic for [C₃SO₃HPPPh₃][PTS] BAIL can be seen at 765 cm⁻¹. The peak for S-O-H, of the HSO₄ anion for [C₃SO₃HMIM][HSO₄] and [C₃SO₃HEt₃N][HSO₄] BAILs at 1200-1220 cm⁻¹ can be seen in the spectrum. Also, the -OH stretching of the HSO₄ can be seen at 3410-3500 cm⁻¹. For S=O a weak peak at 1050 cm⁻¹ can be observed. On the other hand, the C-N stretching of imidazolium cation can be seen at 1028 cm⁻¹ (medium peak). Because of this it is difficult to distinguish peak for S=O and C-N stretching. The small peak for S=O can be seen in [C₃SO₃HPPPh₃] PTS IL. However in case of [C₃SO₃HPPPh₃][PTS] no C-N stretching is possible so peak is not seen for this in the FTIR.

The FTIR characterization showed the information of various function groups (S=O, C=N, C=C, aromatic, -OH, HSO₄, etc.) present in ILs. The anion present in the ILs can also be confirmed with the help of this technique. Moreover, from this characterization it is seen that there are no any additional peaks for undesired functional group.

2.5.6. Conclusion

Various BAILs (catalyst) were synthesized for the conversion of lignocellulosic biomass (hydrolysis and dehydration reactions of saccharides). To discover the effect various types of cations and anions in the entitled reaction, the ILs with different types of cations and anions were synthesized. Various types of ILs synthesized with the different cations such as imidazolium, benzimidazolium, pyridinium, quaternary ammonium, triphenylphosphonium, etc. These ILs with difference in their cations will have the difference in their properties and structure of cations. Some cations are having the planar structure such as imidazolium, benzimidazolium, and pyridinium and some are not having the planar structure such as quaternary ammonium and triphenylphosphonium. Moreover, the solubility of these ILs are different such as the triphenylphosphonium based IL is hydrophobic, while other ILs are hydrophilic. Hence because of this difference in properties a difference in activity were expected in the above titled reaction.

To understand the effect of Brønsted acidity of the BAILs in the above titled reaction, similar IL with and without Brønsted acidity were synthesized. The IL without Brønsted acidity was synthesized is [BMIM][Cl] IL and its activity compared with [C₃SO₃HMIM][Cl] BAIL (both are similar type of IL with similar anion (Cl) only difference is Brønsted acidity) for understanding the contribution of Brønsted acidity in the reaction. Further mineral acid (H₂SO₄, HCl) and solid acid catalyst (HMOR, HUSY, H β) were used in the same reactions and the activity of BAILs can be compared with these catalysts for understanding the advantages of BAILs over the solid acid and mineral acid catalysts.

All the synthesized catalysts were characterized using various characterization techniques such as NMR (¹H NMR and ¹³C NMR), Elemental analysis (CHNS analysis), Hammett acidity (*H₀*), and FTIR. Thermogravimetric analysis technique was used for understanding the mass loss of catalyst with respect to temperature. Using all these

characterization techniques, it was confirmed that the catalysts (ILs) were synthesized in pure form.

2.5.7. References

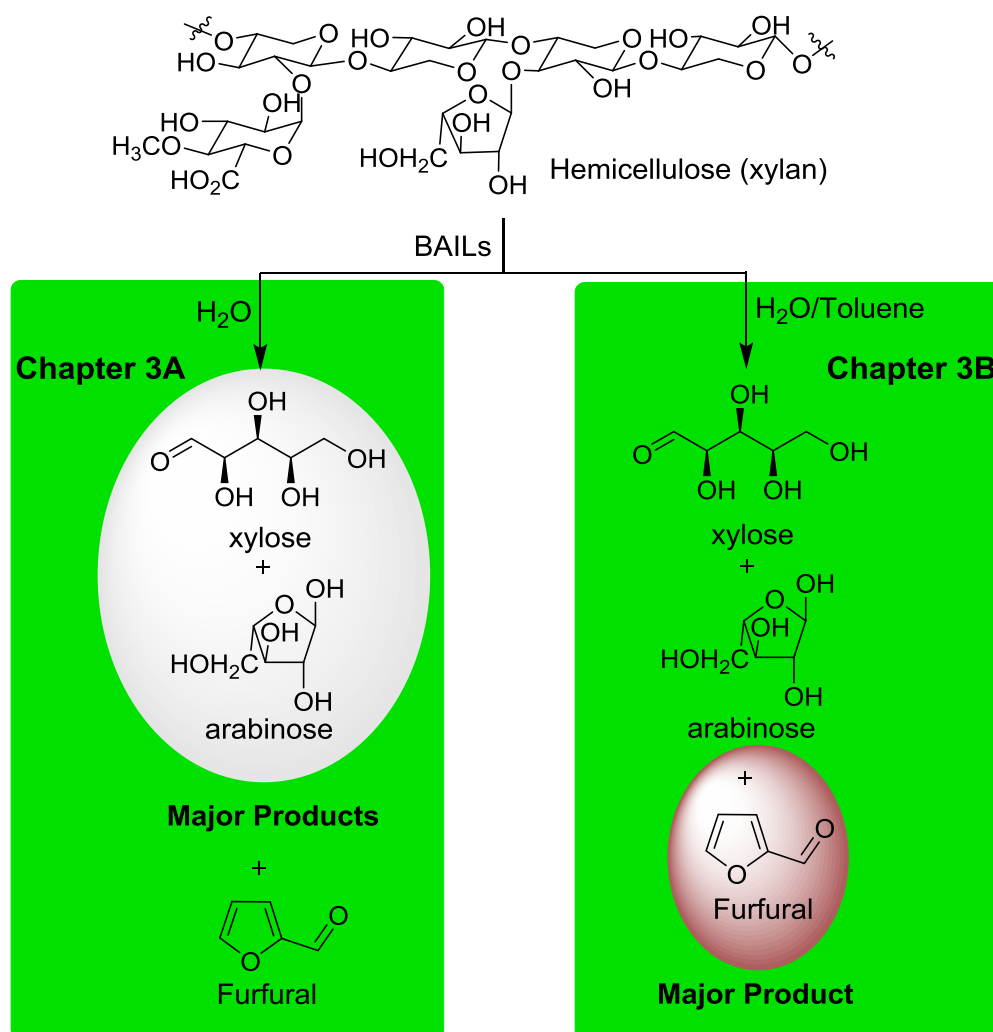
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Chapter 3

Conversion of Hemicellulose using Brønsted Acidic Ionic Liquids

The conversion of hemicellulose into furfural is a two-step reaction, in the first step of reaction the hemicellulose is hydrolyzed into C5 sugars i.e. xylose+arabiose (X+A) and in second step of reaction the C5 sugars upon dehydration gives furfural. Both of these reactions can be carried out using acidic catalyst (Scheme 3.1.). Hence Brønsted acidic ionic liquid (BAIL) can convert hemicellulose selectively into C5 sugars and also hemicellulose can be converted into furfural in a one-pot method. However, the optimized reaction conditions required for the conversion of hemicellulose into C5 sugars is different than the required for the conversion of hemicellulose into furfural. Hence the present chapter is divided into two sub chapters, Chapter-3A and Chapter-3B. In Chapter 3A the discussions are made on the conversion of hemicellulose into C5 sugars using BAILs. On the other hand, in Chapter 3B the discussions are made on the conversion of hemicellulose into furfural using BAILs in the one-pot fashion.



Scheme. 3.1. Reaction for the conversion of hemicellulose (xylan) into C5 sugars (X+A) & furfural using BAIL .

Chapter 3A

Conversion of Hemicellulose into Sugars

3A.1. Introduction

Efficient production of chemicals such as C5 sugars and furans from alternative renewable resources, such as biomass, is a major challenge.^[1-4] Hemicellulose is the second largest component (20–35%) of plant-derived lignocellulosic biomass. It is usually known as a complex polysaccharide, made up of pentoses (xylose, arabinose) and hexoses (glucose, galactose, mannose) along with minor quantities of sugar acids.^[5-6] Depending on the composition, the hemicellulose can be named as xylan (xylose, arabinose), arabinogalactan (arabinose, galactose), glucomannan (glucose, mannose) etc. as it is shown in Chapter-1 (section 1.2.2.2.). However, amongst all these hemicelluloses; xylans, which are usually present in hardwood, are available in large amounts. Generally, the degree of polymerization (DP) for hardwood hemicellulose ranges from 100 to 250 and for softwood hemicellulose from 70 to 130.^[7] Even though hemicellulose is available in an enormous quantity from paper and pulp industries, it is still considered as one of the most under-utilized substrates to produce chemicals.

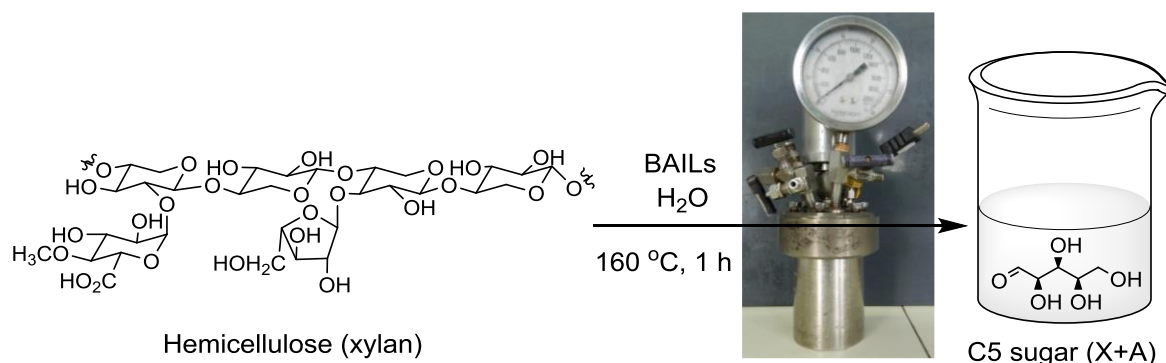
The selective conversion of hemicellulose into sugar monomers is very important reaction because the C5 sugars are capable of producing several industrially important chemicals, such as sugar alcohols (low-calorie sweeteners),^[8] furans (furfural and methylfuran) as well as acids (xylonic, levulinic, formic, etc.).^[9] Additionally, their conversion into other value-added chemicals is well documented.^[10-12] Thus, it is vital to synthesize sugars from hemicellulose with high efficiencies. The possibility of hemicellulose undergoing hydrolysis reactions to produce sugar monomers is known from the literature.^[1-3, 5, 10, 13] Conventionally, mineral acid and enzyme-catalyzed methods for the hydrolysis of hemicellulose into sugars are known.^[13-15] Moreover, conversion of hemicellulose into sugars using solid acid catalysts, such as HUSY (Si/Al=15), HMOR (Si/Al=10), H- β (Si/Al=19) and silicoaluminophosphates (SAPOs) has been shown.^[16-20] These methods reported for the conversion of hemicellulose have various drawbacks such as non-recyclability of the catalyst, stability of catalyst, lower selectivity for sugar monomers and lower loading of the substrate.

Moreover, there are some reports where ILs are used as a catalyst for the conversion of hemicellulose into C5 sugars. Nonetheless, those catalysts are used in

very large quantities. Also, these ILs are used along with mineral acid or metal halides. This shows that using ILs in larger quantities is not a better idea because the ILs are expensive.^[21] Therefore, to overcome all these drawbacks associated with present methods for the selective conversion of hemicellulose into sugars, the BAILs were synthesized (Chapter-2) and exploited in the entitled conversion. Here it is important to note that the BAILs were used in catalytic amounts and in addition to this, the BAILs were used without the addition of any extra Lewis or Brønsted acid catalysts and metal halide because BAILs are having their own Brønsted acidity. This will help in reducing the use of ILs in large quantities as well as in avoiding the use of mineral acids and metal halides in the reaction.

This chapter deals with the utilization of BAILs for the conversion of hemicellulose selectively into sugars monomers. Also, the comparison study of the BAILs was performed with various catalysts such as, mineral acids (HCl, H₂SO₄) and solid acid catalysts (HUSY, HMOR) for the above titled reaction. Moreover, the effect of acid strength of the BAILs over the conversion of hemicellulose was discussed. In addition to this, the catalytic activity of BAILs was compared with the IL which does not have any Brønsted acidity associated with it ([BMIM][Cl]). Similarly, the effect of various parameters such as reaction time, temperature, catalyst concentration, substrate quantity was studied for the conversion of hemicellulose selectively into sugar monomers using catalytic amount of BAILs.

The reaction scheme for the conversion of hemicellulose into sugar monomers using BAILs is shown in Scheme 3A.1.



Scheme 3A.1. Conversion of hemicellulose (xylan) into C5 sugars (X+A) using BAILs.

3A.2. Experimental

3A.2.1. Materials and methods

Four different hemicellulose substrates were used in present study and those are: softwood hemicellulose [xylan from oat spelt (Aldrich Chemicals, USA, product no. X0627) has a composition $\geq 70\%$ xylose, 10% arabinose and 15% glucose], hardwood hemicellulose [xylan from birchwood (Sigma Chemicals, USA, product no. X0502) has a composition $\geq 90\%$ xylose], and beechwood hemicellulose (TCI Chemicals, Japan, product no. X0064 composed of 90% C5 sugars), larch wood arabinogalactan (TCI Chemicals, Japan, product no. A1328; composed of 15% arabinose and 85% galactose). These substrates were used without any further treatment. Xylose, arabinose, glucose, furfural, etc. were procured from Loba Chemie, India and Aldrich Chemicals, USA. To quantify the oligosaccharides, a xylooligosaccharide standard was purchased from Cascade Analytical Reagents and Biochemicals, USA (product no. XYLOO). Solvents such as toluene, methyl isobutyl ketone (MIBK), *p*-xylene were procured from Loba Chemie, India.

3A.2.2. Catalyst synthesis

Various types of BAILs were used as a catalyst for the conversion of hemicelluloses and the synthesis procedures and materials are discussed in Chapter-2 (section 2.2.). BAILs were characterized using different characterization techniques to confirm their purity (Chapter-2, section 2.5.). The solid acid catalysts [HUSY (Si/Al=15) and HMOR (Si/Al=10)] were obtained from Zeolyst International, USA. Prior to use, all of these solid acid catalysts were evacuated under vacuum at 150 °C for 2 h for the removal of any adsorbed moisture.

3A.2.3. Reaction set-up and catalytic methods

All of the catalytic reactions were performed in high pressure and high temperature batch mode reactor (Parr autoclaves, USA) equipped with temperature controller unit. In a typical reaction, 0.6 g (4.54 mmol) of solid hemicellulose was charged in the reactor and then 60 mL of water along with 0.24 g of catalyst were added to it (substrate/catalyst=2.5 (wt/wt)). The reactions were performed at the desired temperature for a definite time. During the heating, 200 rpm stirring speed was used and after attaining the desired reaction temperature the stirring speed was increased to 800 rpm. After the completion of reaction, the stirring speed was decreased to 200

rpm and the reactor was cooled to room temperature and the reaction mixture was then analyzed using High performance liquid chromatography (HPLC).

3A.2.4. Analysis

3A.2.4.1. Analysis using HPLC

The reaction mixture analysis was performed using an HPLC instrument (Agilent Infinity 1200 series) equipped with a Pb^{2+} column (Rezex RPM-Monosaccharide; dimensions 300 x 7.8 mm; particle size 8 μm) maintained at 80 °C. Millipore water was used as an eluent with a flow rate of 0.6 mL/min. The refractive index detector (RID) with a cell temperature of 40 °C was used to detect the products. Additionally, the reaction mixture was also analyzed using an HPLC instrument (Shimadzu, Japan) equipped with an H^+ column and an RID (40 °C). 0.1% aqueous solution of orthophosphoric acid was used as the mobile phase with a flow rate 0.6 mL/min. The calibration curve was drawn with the standard compounds. In the case of [BMIM][Cl], [C₃SO₃HMIM][HSO₄] and H₂SO₄ catalyzed reactions, the peaks of oligomers in HPLC overlapped with the peak due to the catalysts, hence quantification of the oligomers was not possible.

3A.2.5. Calculations

For hemicellulose conversion reaction, the considered molecular weight of hemicellulose is 132 g/mol since hemicellulose is mostly made up of C5 sugars such as xylose and arabinose (the molecular weight of xylose and arabinose is 150 g/mol). When forming hemicellulose from C5 sugars, loss of water molecules takes place (molecular weight of H₂O=18 g/mol). The C6 sugars glucose and galactose are present in very small amounts and therefore, for simplicity of calculations, the molecular weight of hemicellulose is considered as 132 g/mol.

% yield calculation for xylose + arabinose (C5 sugars)

From 132 g of hemicellulose, 150 g of C5 sugars can be formed (considering 100% conversion and selectivity).

Hemicellulose conversion (%) = [(weight of hemicellulose charged in the reactor – weight of hemicellulose recovered after the reaction)/(weight of initial hemicellulose charged in the reactor)] × 100

Xylose + Arabinose (X + A) yield (%)

$$= \frac{\text{moles of xylose + arabinose formed (HPLC)}}{\text{therotical moles of xylose + arabinose expected from 100\% conversion}} \times 100$$

Furfural yield (%)

$$= \frac{\text{moles of furfural formed (HPLC)}}{\text{therotical moles of furfural expected from 100\% conversion}} \times 100$$

3A.3. Results and Discussion

3A.3.1. Evaluation of catalytic activities for the conversion of hemicellulose

The Fig. 3A.1. shows the results of catalyst evaluation study for the conversion of hardwood hemicellulose (xylan from birchwood) into C5 sugars. The reactions were conducted in the presence of water as a solvent at 160 °C for 1 h using various catalysts. The [C₃SO₃HMIM][HSO₄] BAIL catalyst was very selective in forming C5 sugars (X+A) with 87% yield within 1 h of reaction time. Similarly, other BAILs evaluated in this study, such as [C₃SO₃HMIM][PTS] BAIL (76%), [C₃SO₃HMIM][Cl] BAIL (75%), and [C₃SO₃HBenzMIM][PTS] BAIL (73%) also showed good activity for C5 sugars formation. The [C₃SO₃HNEt₃][PTS] BAIL and [C₃SO₃HPPPh₃][PTS] BAIL showed lower activity towards C5 sugars (39% and 25% C5 sugar yield). The reason for lower activity with these catalysts is explained in section 3A.3.3.

The [BMIM][Cl] IL used for the conversion of hemicellulose showed only 59% of C5 sugar yield. On the other hand, a similar type of BAIL ([C₃SO₃HMIM][Cl]) having Brønsted acidity showed 75% C5 sugar yield. This suggests that the Brønsted acidity of BAIL is important for obtaining higher C5 sugars yield. In the case of [BMIM][Cl] IL, the yield of oligomer is not shown because the peaks for [BMIM][Cl] IL and oligomers were overlapping. Further, the catalytic activity of BAILs was compared with solid acid catalysts such as HUSY (Si/Al=15) and HMOR (Si/Al=10) and the result shows lower C5 sugar yield (37% and 22%) compared to BAILs (Fig. 3A.1.). The lower yield of C5 sugars with the solid acid catalysts is because of their heterogeneous nature and diffusion limitations because of which all the acid sites are not available for the reaction. Additionally, the activity of BAILs was also compared with mineral acid (H₂SO₄) under similar reaction condition and the result shows that with H₂SO₄ catalyst only 50% yield of C5 sugars was possible, which is lower compared to

[C₃SO₃HMIM][HSO₄] BAIL (87%). This shows that [C₃SO₃HMIM][HSO₄] BAIL is the best catalyst amongst all the catalysts shown in Fig. 3A.1.

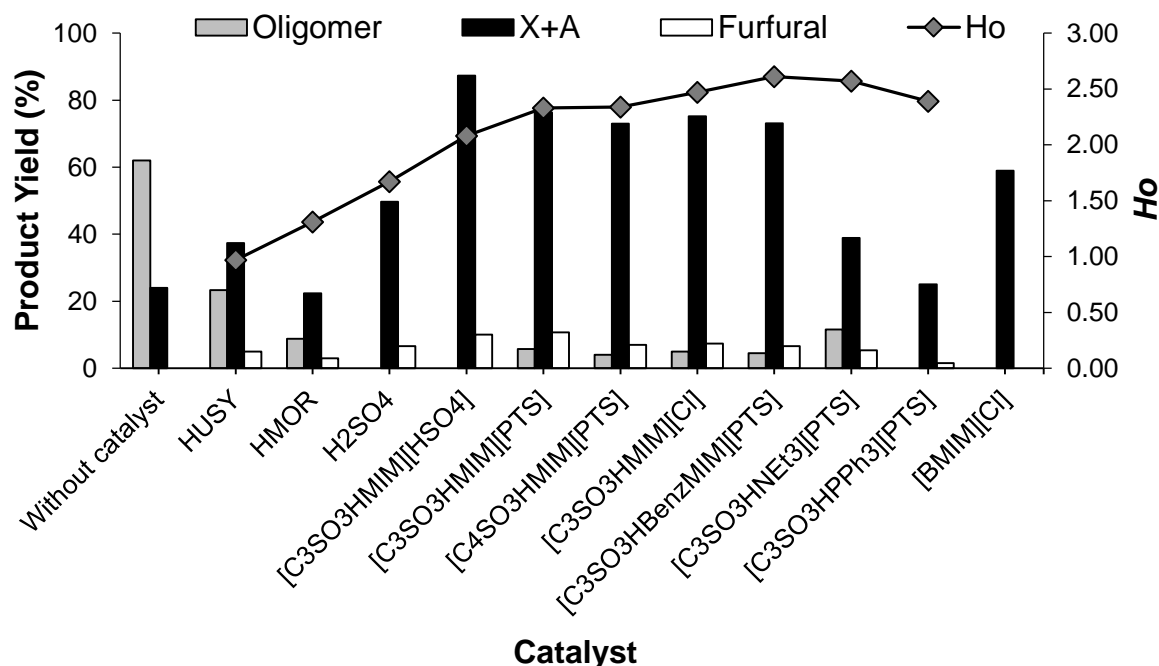


Figure. 3A.1. Catalyst evaluation study for the conversion of hemicellulose; Reaction condition. hemicellulose (birchwood) 0.6 g, catalyst 0.24 g, water 60 mL, 160 °C, 1 h.

3A.3.2. Effect of acid strength on the catalytic activity of catalyst

The acid strength of all the catalysts was calculated using Hammett acidity function (H_o). The results of Hammett acidity (H_o) are shown in Chapter-2, section 2.5.3. From the data of Hammett acidity function (H_o) the order of acid strength was found as HUSY (Si/Al=15; (0.97)) > HMOR (Si/Al=10; (1.31)) > H₂SO₄ (1.67) > [C₃SO₃HMIM][HSO₄] (2.08) > [C₃SO₃HMIM][PTS] (2.33) > [C₃SO₃HMIM][Cl] (2.47).

It is understood from the literature that as the H_o value decreases, the acid strength increases. Among the BAILS evaluated in this study, [C₃SO₃HMIM][HSO₄] BAIL has a H_o of 2.08, which is lower than all other BAILS, [C₃SO₃HMIM][PTS] (2.33) and [C₃SO₃HMIM][Cl] BAIL (2.47). This is reflected in the activity of the catalyst, as [C₃SO₃HMIM][HSO₄] BAIL showed the maximum yield (87%), and [C₃SO₃HMIM][PTS], [C₃SO₃HMIM][Cl] BAILS showed lower (76 and 75%) C5 sugars yields. The [BMIM][Cl] IL does not exhibit Brønsted acidity, and hence, its activity is the lowest (59% C5 sugar yield) amongst all of the ILs evaluated in this study. Moreover, mineral acid (H₂SO₄) is observed to have a lower H_o (H_o =1.67) than the BAILS; however, there

is a clear difference in the activity of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ and H_2SO_4 . The H_2SO_4 showed lower yield of C5 sugar (50%) compared to $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL (87% C5 sugar yield). This implies that even if BAIL has lower acid strength than H_2SO_4 catalyst it has showed higher activity for C5 sugars formation. The higher activity of BAILS can be understood from the ion-dipole type of interaction of BAILS with the substrate molecules (section 3A.3.10.). It is evident that HUSY (Si/Al=15) ($H_o=0.97$) has a higher acid strength than HMOR (Si/Al=10) ($H_o=1.31$), thus, it showed enhanced activity (Fig. 3A.1.). Although solid acids have higher acid strength compared to BAILS, their catalytic activity is lower than those of BAILS because they form a heterogeneous phase in reaction solution.

3A.3.3. Effect of cations of BAILS

To understand the effect of cations of BAILS on the conversion of hemicellulose reaction, BAILS with different types of cations were used by keeping similar anion *p*-toluenesulfonate (PTS) in all the BAILS. The reactions were carried out at optimized reaction condition (1 h, 160 °C) in the water medium. The results are presented in Fig. 3A.2., which shows that BAILS with imidazolium based cations showed 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 higher yield of C5 sugars with BAILS having imidazolium based cations can be explained on the basis of the structure of cations. The structure of all the cations used in this study are shown in Fig. 3A.3. The ILs with imidazolium based cation shows the ion-dipole type of interaction with polysaccharide (hemicellulose) the more discussions on this are made in section 3A.3.10.^[22] Furthermore, the structure of imidazolium cation is planar which can help for this interaction. While, in case of BAIL with quaternary ammonium based cation, the structure of cation is not planar hence, there will not be sufficient interaction between the IL and substrate molecule (hemicellulose) and hence showed lower C5 sugar yield (38%). The BAIL with triphenylphosphonium based cation has bulky phenyl groups and also the structure of cations is not planar because of which there will not be a good interaction between BAIL and polysaccharide. Hence, triphenylphosphonium based BAIL also shows the lower yield of C5 sugars (25%).

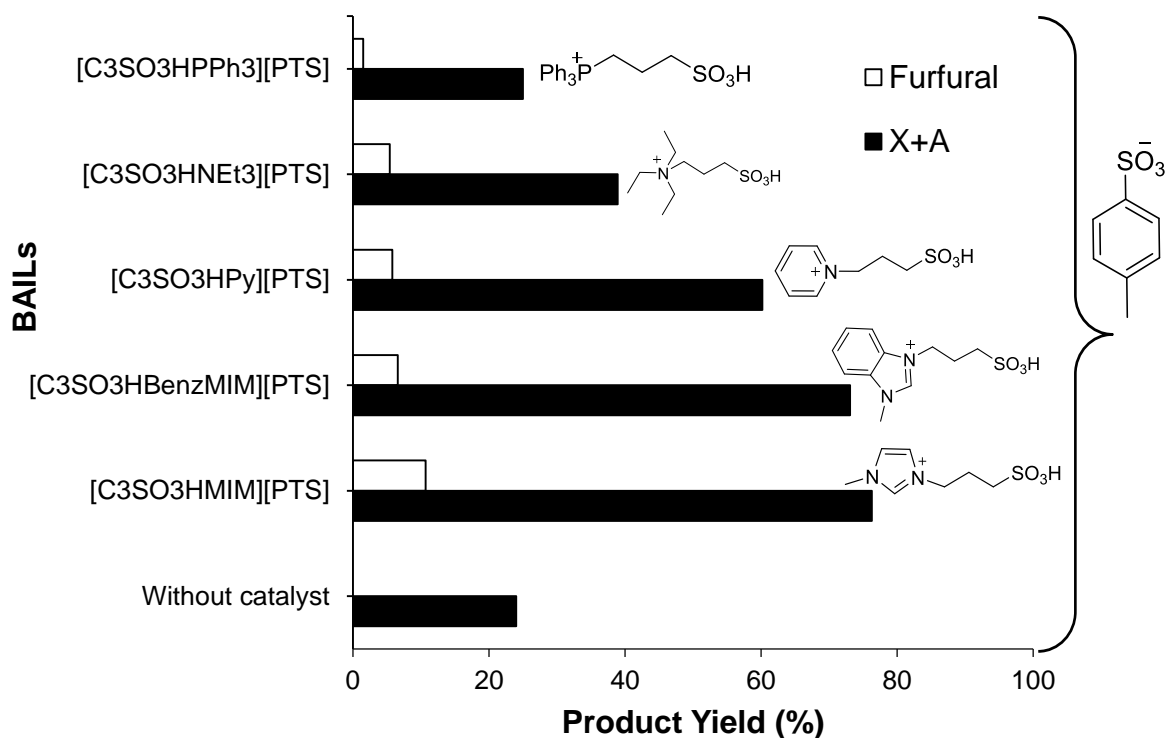


Figure 3A.2. Effect of cations of BAILs on the conversion of hemicellulose; Reaction condition. hemicellulose 0.6 g, catalyst 0.24 g, water 60 mL, 160 °C, 1 h.

To understand the structural difference in cations of BAILs all the structures of cations of BAILs were drawn using ChemBioDraw Ultra 14.0 software. After drawing all the structures in ball and stick model minimization of energy job was done. In the 3D structure (Fig. 3A.3.) gray ball denotes carbon atom, while the blue and pink ball denotes nitrogen and phosphorous atoms, respectively. The yellow and red balls denote sulfur and oxygen atoms, respectively. In all the structures it can be seen that the imidazolium and pyridinium based cations are planar while the quaternary ammonium and triphenylphosphonium based cations are not planar. This gives an idea that BAILs with imidazolium and pyridium cation can have significant interaction with polysaccharide because of their planar nature.

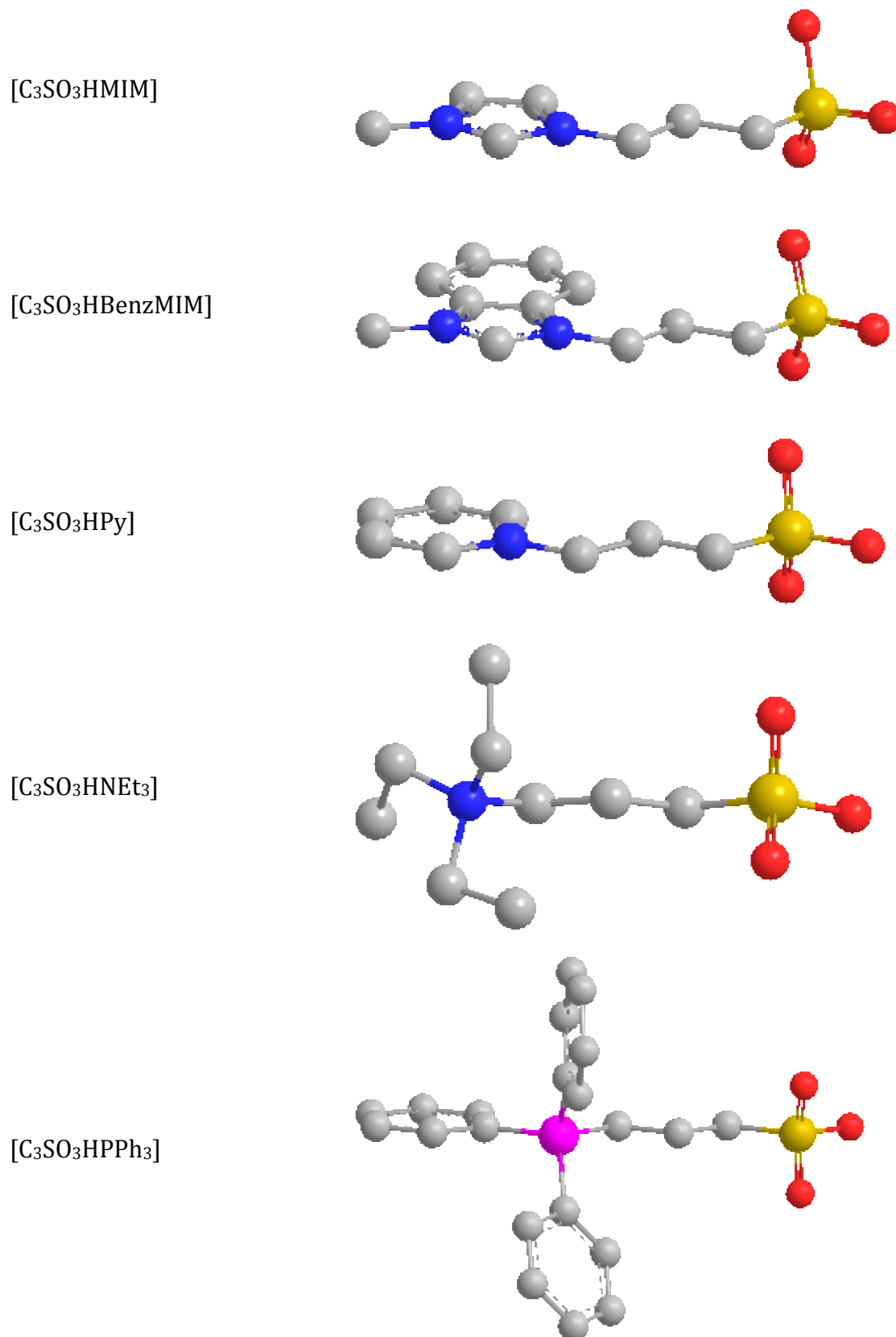


Figure 3A.3. 3D-Structures of various cations of BAILs.

3A.3.4. Effect of reaction time on the conversion of hemicellulose

To improve the C5 sugar yield obtained using BAILs, the reactions were carried out for a longer time using $[C_3SO_3HMIM][PTS]$ BAIL catalyst at 160 °C. As observed from Fig. 3A.4., when the reaction was conducted for 1 h, 76% yield of C5 sugars was obtained. Further, with the increase in reaction time, catalyst did not show any improvement in the C5 sugar yield compared to the result of 1 h of reaction time (76%). Because with an increase in reaction time the concentration of furfural increases in the reaction solution and subsequently concentration of C5 sugar decreases. This is because, in the presence of an acid catalyst, xylose is known to undergo dehydration reactions to form furfural. The sharp decrease in the C5 sugar yield (76-50%) and a decrease in carbon balance was observed when the reactions were done for a longer time (Fig. 3A.4.). This shows that by increasing the reaction time, the formation of degradation products increases which could not be detected by HPLC analysis (since degradation products are not completely soluble in the reaction mixture).

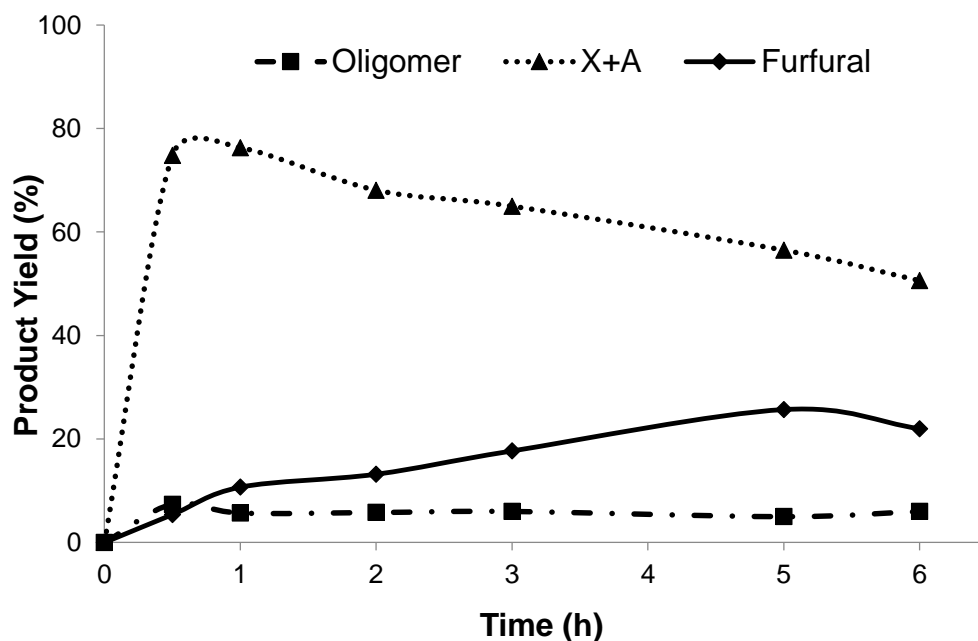


Figure 3A.4. Effect of reaction time on the conversion of hemicellulose; Reaction condition. hemicellulose (birchwood) 0.6 g, $[C_3SO_3HMIM][PTS]$ 0.24 g, water 60 mL, 160 °C.

In case of $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst, the result shows a similar trend of decrease in C5 sugar yield with increasing time beyond 1 h (4 h: 21% furfural yield and 25% C5 sugars yield). With $[C_3SO_3HMIM][PTS]$ BAIL catalyst, the reaction was

performed for 30 min since, at 1 h, 76% yield of C5 sugars was observed; hence, there is a possibility that the optimum reaction time might be shorter. Yet, within a 30 min of reaction time under similar reaction conditions (160 °C), 74% C5 sugar yield was obtained. This showed that the 1 h is the optimum reaction time for achieving highest possible C5 sugars yield using [C₃SO₃HMIM][PTS] BAIL.

3A.3.5. Influence of reaction temperature on the conversion of hemicellulose

To check the effect of reaction temperature on the conversion of hemicellulose into C5 sugars, the reactions were performed for 1 h using birchwood hemicellulose and the [C₃SO₃HMIM][HSO₄] BAIL as a catalyst and the results are presented in Fig. 3A.5. When the reaction was performed at 150 °C, 33% C5 sugar yield was achieved. By increasing the temperature to 170 °C, enhancement in the C5 sugar yield (48%) was observed. Although the best result was obtained when the reaction was performed at 160 °C (87% C5 sugar yield). Temperature studies were also carried out with the [C₃SO₃HMIM][PTS] BAIL catalyst for 1 h reaction time. Using this catalyst, 20% C5 sugar yield was observed at 150 °C temperature. By increasing the reaction temperature to 170 °C, 28% yield for C5 sugars was obtained. Moreover, best result was obtained for reaction carried out at 160 °C temperature. The reason for 160 °C as the best reaction temperature can be explained by considering the results obtained with [C₃SO₃HMIM][HSO₄] BAIL at various temperatures. When the reaction was carried out at 170 °C, 100% conversion with lower mass balance (63%) was observed, which means that products are undergoing further transformations. Further, if the reaction was carried out at 150 °C only 51% hemicellulose conversion can be obtained. However, when reaction was performed at 160 °C >99% hemicellulose conversion and 98% mass balance was observed. This shows that 160 °C reaction temperature is necessary to obtain higher C5 sugar yield.

To check the possibility of whether at lower temperatures and longer reaction time higher yields for C5 sugars can be obtained, the reaction was performed at 130 °C for 6 h using [C₃SO₃HMIM][PTS] BAIL catalyst and 77% C5 sugar yield was obtained. This shows that the efficient conversion of hemicellulose can be carried out at a lower temperature but the time required for the reaction increases.

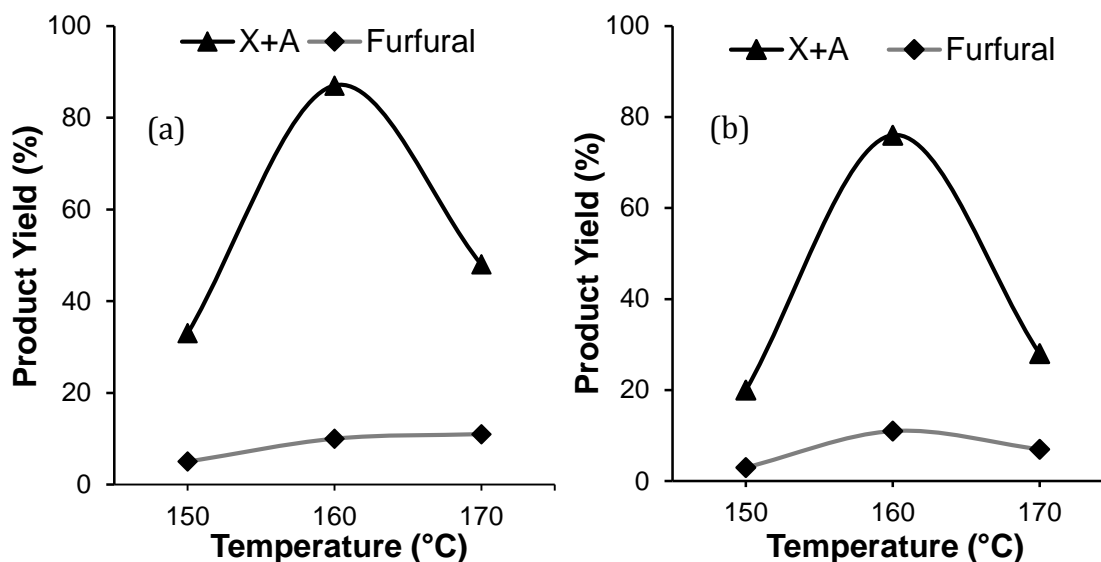


Figure 3A.5. Effect of reaction temperature on the conversion of hemicellulose; Reaction condition. hemicellulose (birchwood hemicellulose) 0.6 g, catalyst 0.24 g, water 60 mL, 1 h. (a) using [C₃SO₃HMIM][HSO₄] catalyst and (b) using [C₃SO₃HMIM][PTS] catalyst.

3A.3.6. Comparison of BAILs with mineral acid and solid acid catalysts

To compare the results of BAILs with those of a conventional mineral acid catalyst, reaction with H₂SO₄ was carried out. When 0.24 g of H₂SO₄ was used (4.9 mmol of H⁺) in the reaction, only 50% yield of C5 sugars (X+A) was achieved (Table 3A.1.). The lower yield of C5 sugars is attributed to the formation of insoluble degradation products (obtained dark color reaction mixture), which could not have been detected by HPLC. The formation of degradation products in this reaction was predominant because when 0.24 g of H₂SO₄ was used, very high concentration of H⁺ ions (4.9 mmol) were present, which may initiate many side reactions. Compared to this, when 0.24 g of [C₃SO₃HMIM][PTS] BAIL was used in the reaction solution, very low concentrations of H⁺ (0.64 mmol) ions are present. To nullify the effect of the higher concentration of H⁺ in H₂SO₄ on the product formation, the reaction was carried out with H₂SO₄ using the same H⁺ concentration (0.64 mmol) in the solution as that when [C₃SO₃HMIM][PTS] BAIL was used as a catalyst. In this reaction, 65% yield of C5 sugars was observed, which is still lower than the yield of the [C₃SO₃HMIM][PTS] BAIL catalyst (76%).

Table 3A.1. Comparison study of BAILs with mineral acid and solid acid catalysts for the conversion of hemicellulose.*

Catalyst	H ⁺ (mmol)#	X+A yield (%)	Furfural yield (%)
H ₂ SO ₄	0.32	33	0
H ₂ SO ₄	0.64	65	4
H ₂ SO ₄	1.26	68	5
H ₂ SO ₄	2.4	76	7
H ₂ SO ₄	4.9	50	6
HCl	0.64	39	5
[C ₃ SO ₃ HMIM][PTS]	0.64	76	11
[C ₃ SO ₃ HMIM][HSO ₄]	1.58	87	10
HUSY (Si/Al = 15)	0.13	37	5
HMOR (Si/Al = 10)	0.28	22	3
HUSY (Si/Al = 15)	0.64	61	8
HMOR (Si/Al = 10)	0.64	48	6
PTSA	0.64	44	5

*All reactions were carried out using constant hemicellulose loading (0.6 g) at 160 °C for 1 h. #The acidity of solid acid catalysts was calculated using ammonia TPD. PTSA; *p*-toluenesulfonic acid monohydrate.

Reactions were also performed with varying molar concentrations of H⁺ by charging different concentrations of H₂SO₄ and the results for C5 sugar formation (yield) are summarized in Table 3A.1. The following trend was observed for the C5 sugar yields;

0.32 mmol of H⁺ (33% yield) < 0.64 mmol of H⁺(65%) < 1.26 mmol of H⁺(68%) < 2.4 mmol of H⁺(76%) < 4.9 mmol of H⁺(50%)

As seen, there is an optimum concentration of H₂SO₄ (1.2 mmol, 2.4 mmol of H⁺) at which the highest yield (76%) is observed. However, compared to

[C₃SO₃HMIM][PTS] BAIL having 0.64 mmol of H⁺, higher concentration of H₂SO₄ is required to achieve an almost similar activity to that observed with the BAIL. This difference in the activity can be explained on the basis of the ion-dipole type of interaction (for more details, please refer to section 3A.3.10.).

The results obtained for BAILs are also compared with the solid acid catalysts such as HUSY (Si/Al=15) and HMOR (Si/Al=10) using similar catalyst loading (0.24 g). The results (Table 3A.1.) indicate the formation of 37% and 22% of C5 sugars. Moreover, reactions with the solid acid catalysts were also carried out by maintaining similar H⁺ concentrations (0.64 mmol, same as when the BAIL [C₃SO₃HMIM][PTS] was used in the reaction). To achieve this, the catalyst loading was altered in the reaction [HUSY, 1.16 g (total acidity 0.55 mmol/g); HMOR, 0.53 g (total acidity 1.20 mmol/g), Table 3A.1.]. In these reactions, 61% yield of C5 sugar was observed for HUSY and 48% yield for HMOR. This shows that even when very high (weight basis, 1.16 g, and 0.53 g) loading of solid acid catalysts was used compared to those of BAILs (0.24 g) to maintain the same H⁺ concentration in the solution, lower yields were obtained with solid acid catalysts. The reason for the difference in the activity between BAILs and solid acid catalysts is due to the difference in the catalytic system, as BAILs are soluble in water (BAIL homogeneous with reaction solution), whereas solid acid catalysts are not (heterogeneous with reaction solution). This gives rise to a difference in the interaction between the catalyst and the substrate. Also, in case of solid acid catalyst there is problem of diffusion limitation.

Reactions with hardwood hemicellulose (birchwood hemicellulose) were also carried out using HCl and organic acid such as *p*-toluenesulfonic acid mono-hydrate (PTSA) catalysts by maintaining the similar H⁺ concentration (similar to that of the [C₃SO₃HMIM][PTS] BAIL catalyst (0.64 mmol of H⁺)). In these reactions at 160 °C within 1 h of reaction time, 44% and 39% yield of C5 sugars with PTSA and HCl catalysts were observed, respectively (Table 3A.1.). Compared to the [C₃SO₃HMIM][PTS] BAIL catalyst (76% yield of C5 sugars), PTSA and HCl showed lower yields, which again confirmed the fact that BAILs are better catalysts than mineral acids and organic acid.

3A.3.7. Conversion of different types of hemicellulose into C5 sugars using BAILs

To generalize the catalytic system, hemicellulose isolated from four different sources, such as hardwood hemicellulose (xylan obtained from birchwood), softwood hemicellulose (xylan obtained from oat spelt and beechwood), and arabinogalactan (softwood hemicellulose) made up of arabinose and galactose sugars were subjected to hydrolysis reactions using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ BAIL catalyst (Fig. 3A.6.). It was observed that when the reactions were performed using the $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ BAIL catalyst at 160 °C for 1 h, oat spelt-derived hemicellulose gave 86% C5 sugar yield while beechwood-derived hemicellulose gave 83% yield. Compared to these, with birchwood hemicellulose 76% C5 sugar yield was observed. Along with C5 sugars, very low yields of furfural (8-11%) were also obtained in these reactions. The arabinogalactan type of hemicellulose shows 78% yield of arabinose and galactose.

The higher C5 sugar yield achieved for softwood derived hemicellulose [(beechwood hemicellulose (83%), oat spelt hemicellulose (86%), birchwood hemicellulose (76%)] was because of lower DP (70-130) compared to that of hardwood derived hemicellulose (100–250) as known from the literature.^[20] Nevertheless, the results demonstrate the capability of BAILs to convert all types of hemicellulose into C5 sugars with very good yield.

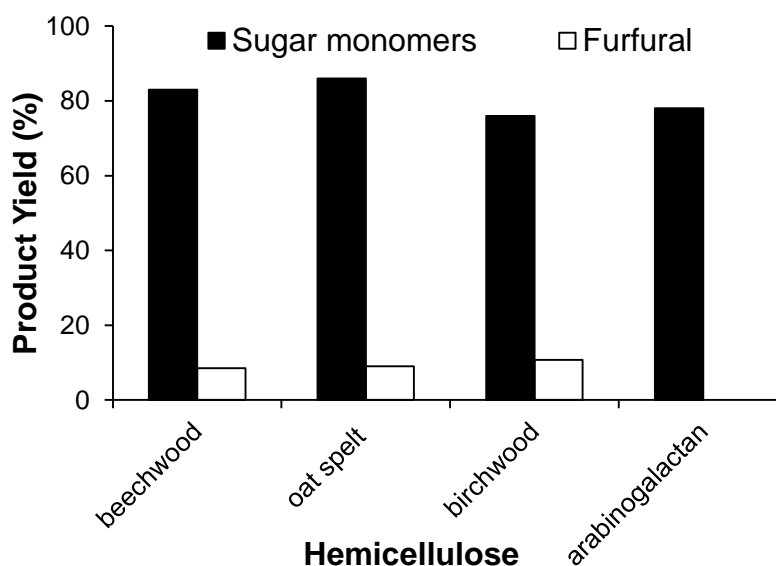


Figure. 3A.6. Effect of hemicellulose types on the conversion of hemicellulose; Reaction condition. hemicellulose 0.6 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ 0.24 g, water 60 mL, 160 °C, 1 h.

3A.3.8. Influence of hemicellulose concentration

It is always desirable to use higher hemicellulose loadings (with respect to solvent) and hence the effect of hemicellulose concentrations and catalyst activity to get the highest yield of C5 sugars was checked. The reaction was performed at 160 °C by charging 3 times more hardwood hemicellulose (birchwood hemicellulose 1.8 g, 3 wt%) in the reactor by maintaining similar loadings of catalyst ([C₃SO₃HMIM][PTS], 0.24 g) and water 60 mL as presented in Fig. 3A.7. and the result showed 60% yield of C5 sugars. This reveals that a marginal decrease in yield is possible within 1 h of reaction time, however, with the increase in reaction time to 1.5 h similar C5 sugars yields (73%) as was observed with lower hemicellulose loading (1 wt%, 76%) was seen. Because by increasing hemicellulose concentration from 0.6 g to 1.8 g and carrying out reaction for 1 h showed 74% hemicellulose conversion. Therefore, the reaction was performed for 1.5 h to convert all the hemicellulose so that higher C5 sugars can be obtained. The above results are apparent since, when the reaction was performed with higher hemicellulose concentration; Substrate/Catalyst (S/C) ratio was increased by 3 times compared to standard reaction conditions (from 2.5 to 7.5 wt/wt).

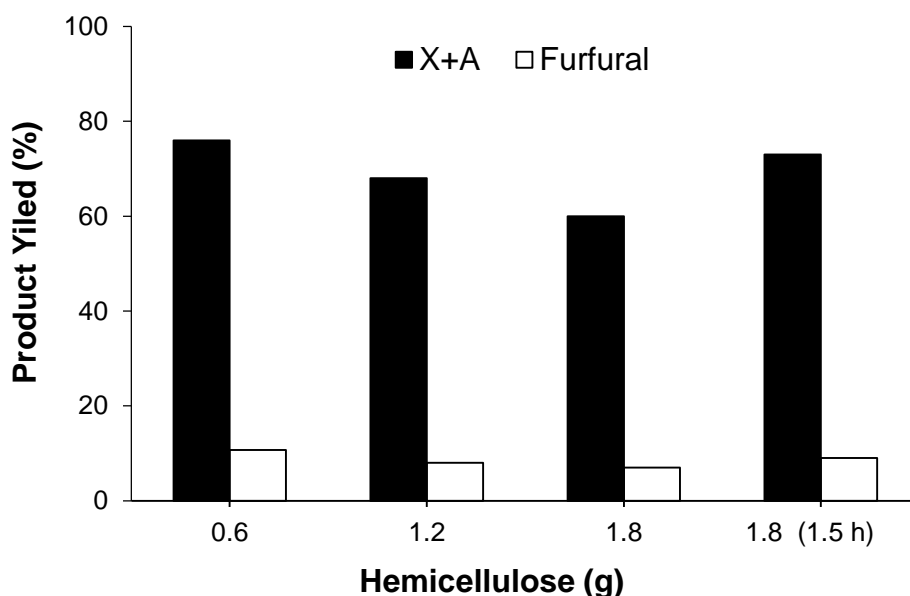


Figure 3A.7. Effect of substrate concentration on the conversion of hemicellulose; Reaction condition. [C₃SO₃HMIM][PTS] 0.24 g, water 60 mL, 160 °C, 1 h.

3A.3.9. Influence of catalyst concentration in the conversion of hemicellulose

Reactions were also performed using $[C_3SO_3HMIM][PTS]$ BAIL at 160 °C for 1 h by varying the catalyst loading but charging similar hardwood hemicellulose (birchwood hemicellulose, 0.6 g) and water (60 mL) in the reactor and the results are presented in Fig. 3A.8. It was seen that with the increase in S/C molar ratio from 7 to 14, the C5 sugars yield was decreased from 76% to 62%. Further increase in S/C ratio to 21 (60%) and 28 (40%) showed decrease in the yields. Hence, the optimum substrate to catalyst molar ratio for hemicellulose conversion is 7. The yield of C5 sugar decreases with increasing S/C ratio because the concentration of catalyst decreases with increasing S/C ratio which means there is not sufficient catalyst available to convert all the hemicellulose into C5 sugars (75% hemicellulose conversion when 21 molar S/C ratio was used) within 1 h reaction time. This can be understood from the data on hemicellulose conversion i.e. when reaction was carried out with 7 molar ratio, >99% hemicellulose conversion was seen and when reaction was carried out with 21 molar ratio, 75% hemicellulose conversion was seen. This clearly shows that with a decrease in catalyst quantity, the hemicellulose conversion decreases.

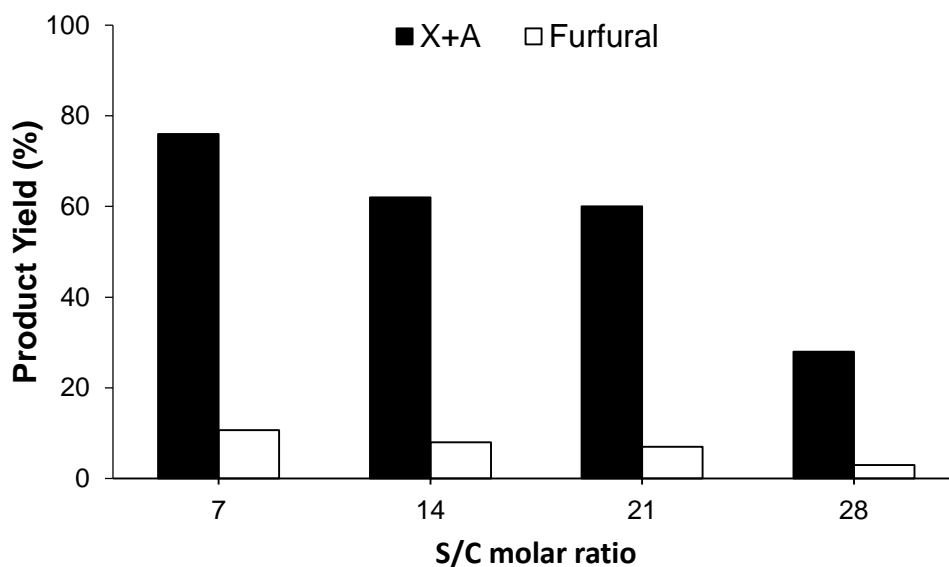


Figure 3A.8. Effect of catalyst concentration on the conversion of hemicellulose; Reaction condition. hemicellulose 0.6 g, catalyst $[C_3SO_3HMIM][PTS]$, water 60 mL, 160 °C, 1 h.

3A.3.10. Interaction and mechanistic studies for the conversion of hemicellulose into sugars

Based on the above results it is clear that the BAILs perform very well in the conversion of hemicellulose into C5 sugars and in particular, better than the mineral acids (H_2SO_4 , HCl) and solid acid catalysts. This phenomenon may arise from the interaction of BAIL with the substrate as illustrated in Fig. 3A.9. It is suggested that the imidazolium ring (the cation) $[\text{C}_3\text{SO}_3\text{HMIM}]$ interacts with the oxygen of hydroxyl groups present on carbohydrate (hemicellulose, oligomers, monomers) and thus in a way, IL is attached to the substrate. At the same time, anion, $[\text{HSO}_4^-]$ will also interact with the hydrogen of the hydroxyl group and ensures that IL is attached to the substrate. This ion-dipole type of interaction may force the BAIL catalyst to float along with hemicellulose molecule in the reaction medium and make easy availability of H^+ from the ionic liquid (attached $-\text{SO}_3\text{H}$ group on cation) in the periphery of the hemicellulose molecule to undergo hydrolysis reaction.^[22-23] The interaction is also capable of breaking inter and intramolecular hydrogen bonding present in the substrate molecule that will loosen the structure and can help to achieve better activity for hydrolysis reaction.

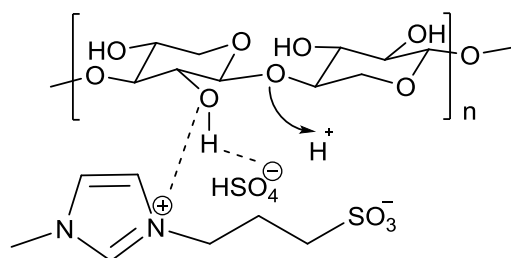


Figure 3A.9. Ion-dipole type of interaction present between BAIL and polysaccharide.

To suggest this interaction, ^1H NMR (200 MHz) study of cellobiose, and a mixture of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4^-]$ BAIL catalyst (having acid functionality) and cellobiose in DMSO-d_6 solvent was performed. The cellobiose is chosen for this study in place of hemicellulose because cellobiose is soluble in DMSO-d_6 while hemicellulose is not. Moreover, the DMSO-d_6 was used as a solvent in this study because with other solvents, H-D exchange of $-\text{OH}$ protons is possible and that can hamper the purpose of this study. Since hydrogen bonding influences the chemical shifts,³⁴ and if there is an interaction between BAIL and polysaccharide then the

change in the chemical shift can be seen in the ^1H NMR spectrum and hence, this study will help in proposing ion-dipole type interaction.

The ^1H NMR spectrum for cellobiose presented in Fig. 3A.10. shows peaks for methylene and methine 'H' until 4.5 ppm and hydroxyl (-OH) protons from 4.5 ppm onwards. This data matches well with the earlier reported work on cellobiose.^[23] Further, to check the ion-dipole type of interaction, the recorded ^1H NMR spectrum for cellobiose + $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL is presented in Fig. 3A.10., c. As seen from the spectrum, peaks for hydroxyl proton (>4.5 ppm) are missing and only one single broad peak is observed at 5.12 ppm. On the contrary, peaks due to methylene and methine protons are still observed in the spectrum. It is suggested that the absence of peaks is because of fast exchange of -OH protons with $-\text{SO}_3\text{H}$ protons of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL. It is reported that in presence of acid, rate of -OH proton exchange is fast and hence it becomes almost impossible to detect the peaks due to -OH protons in the ^1H NMR.³⁵ Similar observations is also made in the spectrum (Fig. 3A.10., d) obtained when mineral acid is used along with cellobiose for ^1H NMR study. This phenomenon can also be corroborated by the fact that peak for $\alpha\text{-H-1'}$ in cellobiose (Fig. 3A.10., a) appearing at 4.90 ppm shows no change in the chemical shift when BAIL (Fig. 3A.10., c) or H_2SO_4 (Fig. 3A.10., d) are added to cellobiose. The extra peaks appearing in Fig. 3A.10., c are due to $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL. While under acidic environment it was not possible to show the interaction, subsequently $[\text{BMIM}][\text{Cl}]$ IL was used which does not have $-\text{SO}_3\text{H}$ functionality to check the interaction between IL and cellobiose. Since, $[\text{BMIM}][\text{Cl}]$ is also an imidazolium based IL, the results obtained with this IL can be extrapolated for BAILs used in this study.

The ^1H NMR spectrum recorded for $[\text{BMIM}][\text{Cl}]$ and cellobiose mixture in $\text{DMSO-}d_6$ is presented in Fig. 3A.10., b. The spectrum clearly showed the peaks for hydroxyl protons from 4.5 ppm onwards. However, a careful look at both the spectra recorded for cellobiose (Fig. 3A.10., a) and cellobiose + $[\text{BMIM}][\text{Cl}]$ (Fig. 3A.10., 5) showed a difference in the peak positions and broadening of peaks of -OH protons. The protons of hydroxyl group showed a slight downfield shift in the mixture of cellobiose and $[\text{BMIM}][\text{Cl}]$ compared to cellobiose. The. the peak for $\beta\text{-OH-3',6'}$ shifts from 4.61 to 4.67 ppm and peak for $\beta\text{-OH-1'}$ shifts from 6.64 to 6.76 ppm. To verify that these chemical shifts are not misinterpreted, peak present for $\alpha\text{-H-1'}$ (cellobiose)

at 4.90 ppm is observed at the same chemical shift value in both the ^1H NMR spectra. This implies that the only peaks due to hydroxyl protons are shifted when cellobiose is mixed with IL. The study reveals that the IL has an interaction with the substrate molecule and hence BAIL could achieve higher catalytic activity. It is indicated that the broadening of peaks (Fig. 3A.10., b) is due to slow exchange of protons due to mild acidity in [BMIM][Cl] IL (presence of hydrogen atom attached to carbon flanked between two nitrogen atoms). The ^1H NMR of pure [BMIM][Cl] is presented in Chapter-2 (section 2.5.1.1., Fig. 2.9.). The similar interaction must be present when BAILs are used, however, as shown above, due to the fast exchange of protons it was not possible to validate it.

The ion-dipole type of interaction between catalyst and substrate is not possible with the mineral acids and therefore, BAILs perform better than the H_2SO_4 . Moreover, in earlier study also the IL is used along with H_2SO_4 ,^[24] and in that work also though not reported, but still it is possible for IL to interact with substrate by way of ion-dipole type of interaction. But lack of presence of acidic group ($-\text{SO}_3\text{H}$) on IL and separate presence of H_2SO_4 is not sufficient to show higher activity as observed in this work. The same explanation can also be extended to [BMIM][Cl] catalyst, as with this IL there is a presence of an ion-dipole type of interaction (by NMR study) but still it shows the lower catalytic activity (50%) compared to BAILs. This information clearly suggests that presence of $-\text{SO}_3\text{H}$ group on IL helps in achieving higher activity.

In case of [BMIM][Cl] IL there is ion-dipole type of interaction and at higher temperature there may be possibility that proton flanked between two nitrogen atom can act as acid therefore with this catalyst 59% C5 sugar yield was obtained which higher compared to non-catalytic reaction (24% C5 sugar yield). This shows that because of ion-dipole type of interaction the [BMIM][Cl] BAIL or imidazolium based catalysts are better than other catalyst (IL)

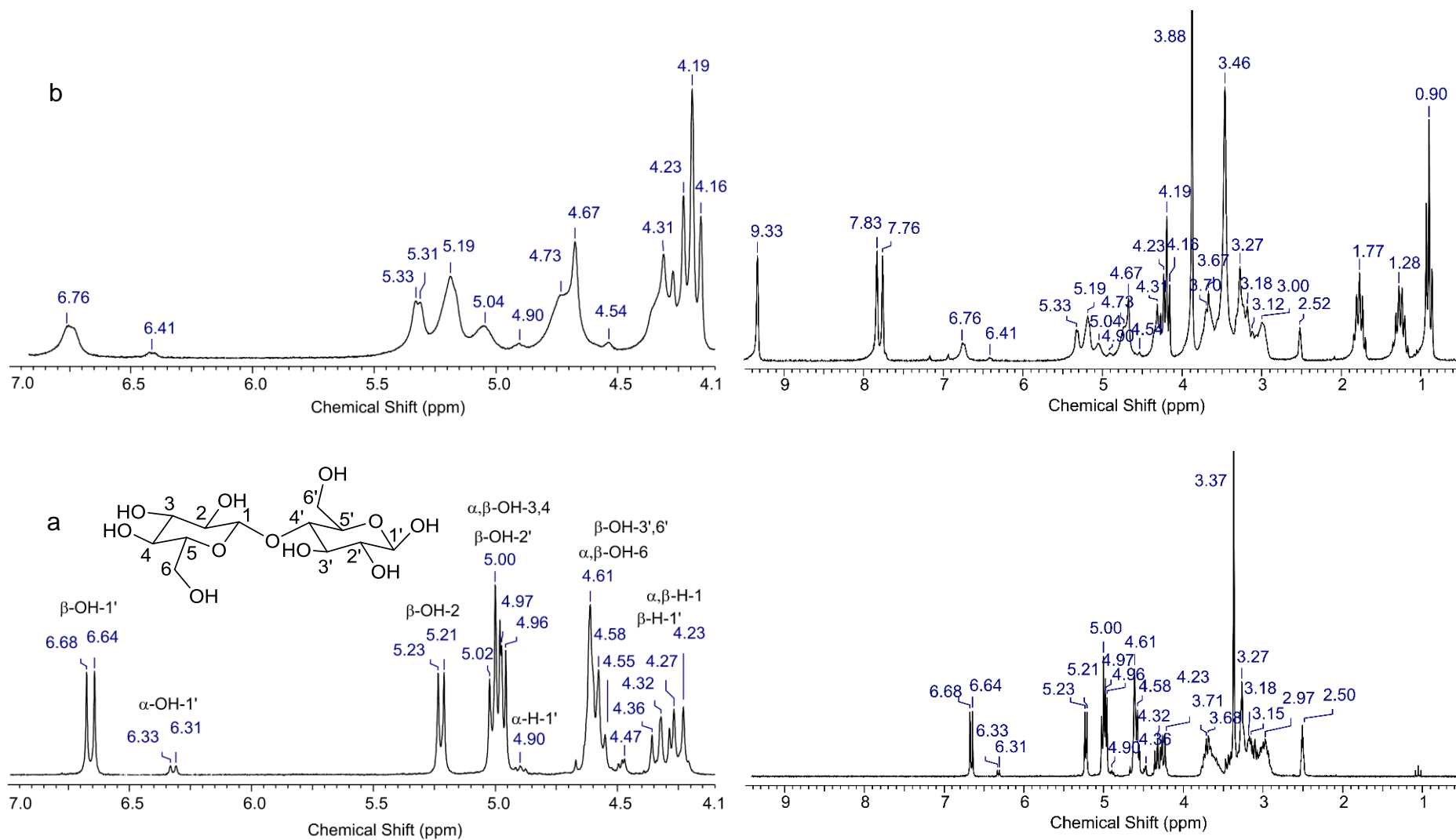
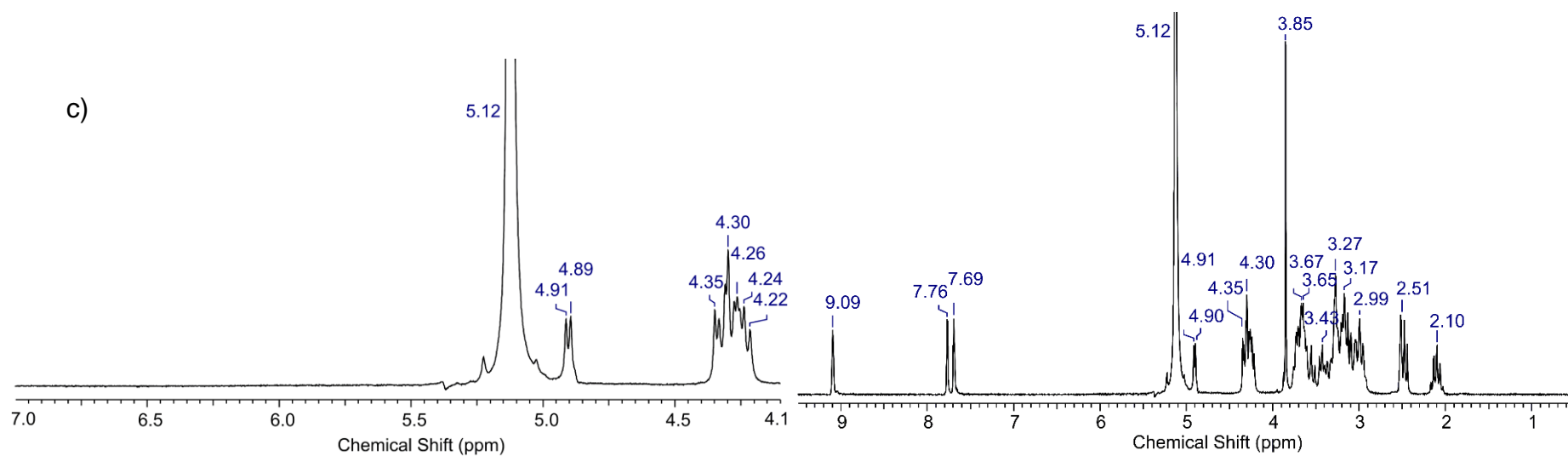
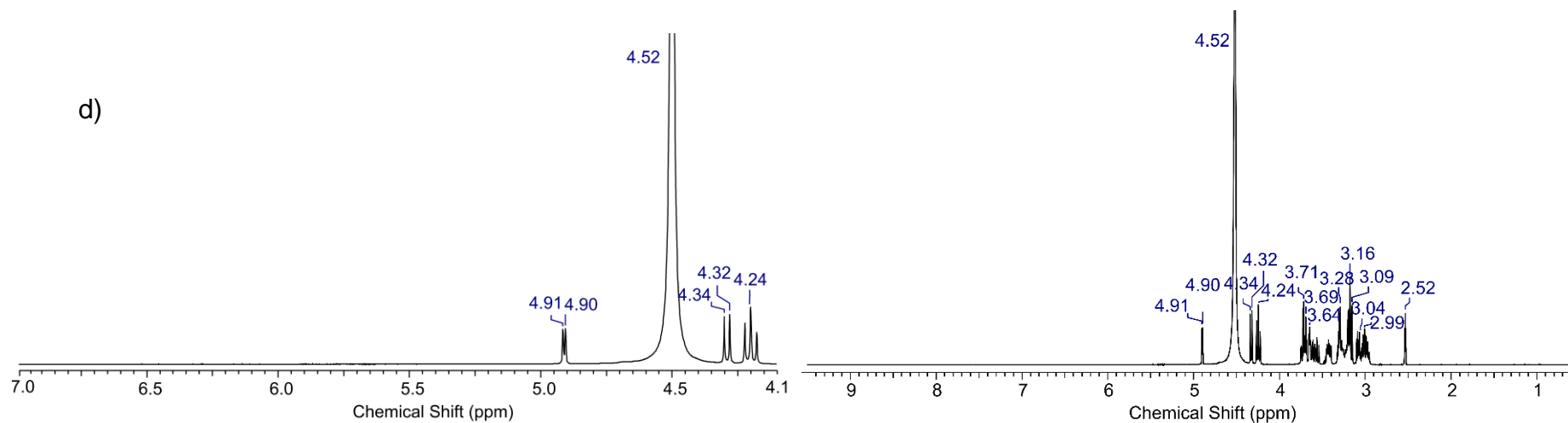


Figure 3A.10. ^1H NMR studies to understand the interaction of IL with cellobiose. a) cellobiose, b) mixture of cellobiose and [BMIM][Cl].



Continued.... c) mixture of cellobiose and $[C_3SO_3HMIM][HSO_4]$ BAIL and d) mixture of cellobiose and H_2SO_4 . All of these 1H NMR spectra were recorded in a $DMSO-d_6$ solvent.

Based on the above discussion on the interaction between BAIL and cellobiose, the proposed mechanism of hemicellulose hydrolysis using BAIL can be shown as follows (Fig. 3A.11.);

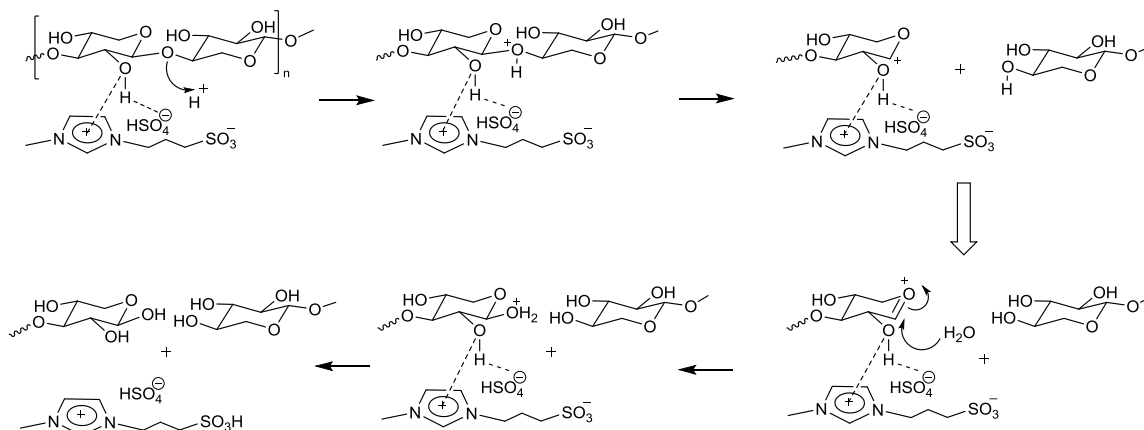


Figure 3A.11. Mechanism for hemicellulose hydrolysis into C5 sugars using BAIL.

3A.3.11. Recycle study

The results of recycle study for the conversion of hemicellulose selectively into C5 sugars are presented in Fig. 3A.12. Recycle study carried out with $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ BAIL catalyst showed slight decrease in the activity after each reaction (1st run: 76%; 2nd run: 61%; 3rd run: 49%). This is because only ca. 65% BAIL was recovered after each run. But in the reactor same amount of substrate was charged (0.6 g) for the reaction. The change of S/C ratio from 2.5 to 3.75 (wt/wt) might be responsible for lower yields. For the recycle experiment, the procedure used for the separation of catalyst is as follows; After completion of a reaction, water is removed by rotavap and after that 2 mL of distilled water was added to it and then slowly acetone (30 mL) was added to give light white color solution. Up on addition of excess of acetone, light white color disappears. The solution was kept under static condition for 1 h. Afterwards, the acetone layer is decanted leaving viscous liquid at the bottom of a container. This liquid contains ionic liquid which was used in recycle study.

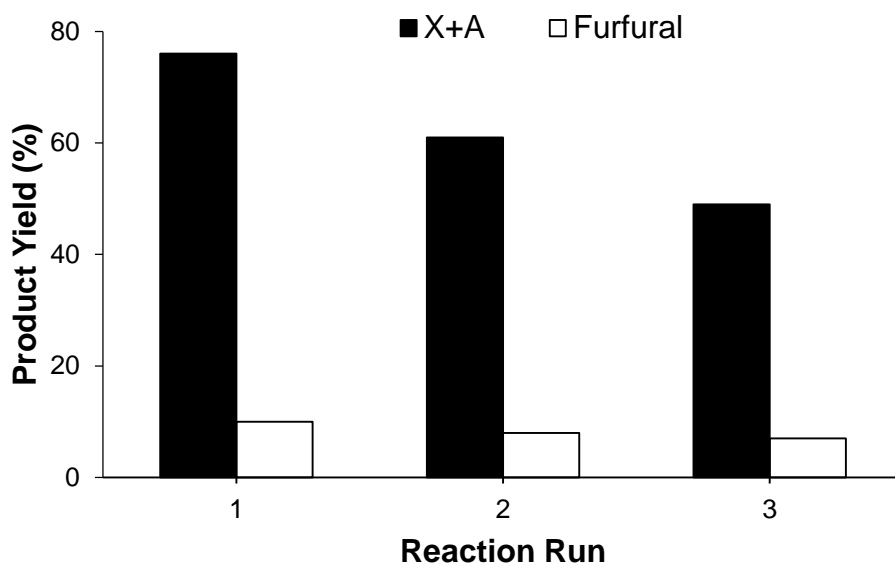


Fig. 3A.12. Recycle study for the conversion of hemicellulose into C5 sugars; Reaction condition. hemicellulose 0.6 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ 0.24 g in first reaction, water 60 mL, 160 °C, 1 h.

3A.3.12. Conclusion

In summary, it is shown that the $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL could efficiently convert hemicellulose derived from hardwood (birchwood) selectively into C5 sugars (X+A) in exceptionally high yields (87%) when reaction was carried out at 160 °C for 1 h. The BAILS are shown to have an ion-dipole type interaction with the substrate molecules, as proposed by ^1H NMR spectroscopy, which helps in achieving higher yields compared to mineral acid catalysts. The Hammett acidity function (H_0) for the BAILS observed is in the order of, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ (2.47) > $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ (2.33) > $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ (2.08) and the correlation of catalytic activity with H_0 was clearly visible. It is shown that all BAILS shows better catalytic activity compared to solid acid catalysts such as HUSY (Si/Al=15) and HMOR (Si/Al=10). These BAILS thus can be used in many other acid catalyzed reactions to improve the yields.

The imidazolium based BAILS shows better activity compared to BAILS having quaternary ammonium and triphenylphosphonium based cations because in the case BAIL having quaternary ammonium based cation the structure of cation is not planar so there may not be efficient interaction of BAIL with hemicellulose and hence these BAILS shows lower C5 sugar yield. On the other hand, in case of BAIL having triphenylphosphonium based cation again the structure of cation is not planar and it

has three bulky phenyl groups which can hinder the interaction between hemicellulose and BAIL.

The BAILS are capable of converting various types of hemicelluloses selectively into sugars e.g. [C₃SO₃HMIM][PTS] BAIL shows 83, 86, 76, and 78% yield of sugar monomer when reactions were carried out with beechwood, oat spelt, birchwood and arabinogalactan type hemicellulose at 160 °C for 1 h.

3A.3.13. References

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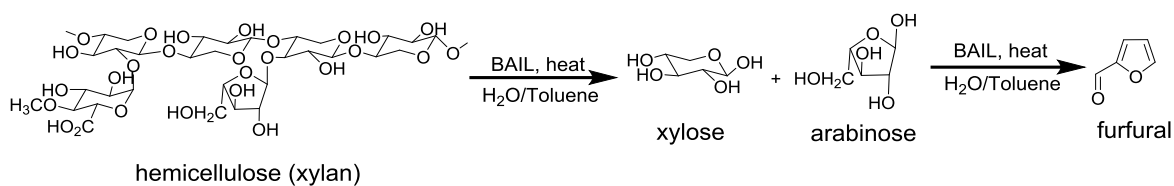
Chapter 3B

Conversion of Hemicellulose into Furfural in One-pot Method

3B.1. Introduction

In chapter-3A the discussions on the efficient method for the conversion of hemicellulose into C5 sugars using BAILs were made. In this chapter, the conversion of hemicellulose into furfural in the one-pot method using BAILs is discussed. Furfural is a promising renewable platform chemical used for the production of biochemicals and biofuels from low cost and abundant lignocellulosic biomass. Various industrially important chemicals can be obtained from furfural such as methylfuran,^[1-3] furfuryl alcohol, tetrahydrofuran,^[4-6] methyltetrahydrofuran,^[2, 5] dihydropyran^[2, 7] and furoic acid.^[2, 8] Methylfuran (MF) has a boiling point (63 °C) and octane value (103) similar to gasoline and thus it is suitable as a gasoline (97) blendstock.^[5, 9] There are several processes reported for the conversion of biomass into furfural but those are associated with some drawbacks such as recyclability of catalyst, lower selectivity for furfural, harsh reaction conditions, use of a homogeneous catalyst, and use of ionic liquids in large quantity along with mineral acid or metal halides (Chapter-1; section 1.2.7.).

To overcome the drawbacks of conventionally reported methods, various Brønsted acidic ionic liquids (BAILs) were synthesized (for synthesis of ILs please refer Chapter-2, section 2.2.) and evaluated for the conversion of hemicellulose into furfural in a one-pot fashion. The BAILs were used for this reaction in catalytic amount without addition of any mineral acid and metal halide. The furfural can be obtained from hemicellulose in two consecutive reactions; 1) hydrolysis of hemicellulose into C5 sugars and 2) dehydration reaction of C5 sugars into furfural. Both of these reactions are acid catalysed and hence, BAILs can convert hemicellulose into furfural. Industrially furfural is produced using H₂SO₄ as a catalyst which has several drawbacks^[10-12] such as recyclability, the corrosive reaction mixture, degradation reaction to give side products, etc. Moreover, in many reported methods, the furfural synthesis was discussed using xylose as a starting material. However, xylose can be obtained from xylan type of hemicellulose using hydrolysis reaction. Hence, it may be beneficial if this hemicellulose is directly converted into furfural in a one-pot fashion. Therefore, in present chapter the conversion of hemicellulose into furfural was attempted using BAILs in one-pot fashion as shown in Scheme 3B.1.



Scheme 3B.1. Conversion of hemicellulose into furfural using BAILs in a one-pot method.

The catalytic results of BAILs were compared with mineral acid (H₂SO₄) and solid acid catalysts such as HUSY (Si/Al=15) and Amberlyst-15. Effect of reaction time, temperature and catalyst quantity were studied using [C₃SO₃HMIM][HSO₄] BAIL. The reactions were carried out in only water as a solvent system and biphasic solvent system such as water+toluene, water+MIBK and water+*p*-xylene. The water+toluene biphasic solvent system was found to perform better for the above titled reaction, the reason can be discussed with the help of partition coefficient of furfural in the different solvent system (organic/water) and the solubility of the organic solvent in the aqueous phase. Further, the results of recycling study of BAILs were discussed for the above entitled reaction and the recycled catalyst was characterised using ¹H NMR spectroscopy to check the stability of the catalyst.

3B.2. Results and discussion

The results for the conversion of hemicellulose into furfural using BAILs are presented in this section. In this section, various reaction optimization parameters are discussed such as catalyst evaluation, influence of reaction time and temperature, effect of catalyst concentration, effect solvent concentration, effect of substrate concentration, etc.

3B.2.1. Catalyst evaluation studies for the conversion of hemicellulose into furfural

The catalyst evaluation study for the conversion of hemicellulose into furfural is presented in Fig. 3B.1. The reactions were carried out in water+toluene biphasic solvent system and the temperature and time used for the reaction was 170 °C and 4 h, respectively. The non-catalytic reaction carried out under this reaction condition showed 22% furfural yield and 8% xylose+arabinose (X+A) yield. The solid acid catalyst such as HUSY (Si/Al=15) and Amberlyst-15 showed 34% and 42% furfural yield, respectively. The best result was obtained with [C₃SO₃HMIM][HSO₄] BAIL

which showed 62% furfural yield along with 14% X+A yield. The $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL showed the highest yield of furfural compared with all other catalysts used in this reaction. The other BAILs such as $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ and $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ BAILs showed 44% and 41% furfural yield along with 4 and 13% X+A yield. In case of all the BAILs, the furfural yield obtained is in the order of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4] > [\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}] > [\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$. This trend can be explained on the basis of Hammett acidity (H_0). The H_0 value of BAILs obtained in the order of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ (2.08) < $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ (2.33) < $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ (2.47). The trend shows that $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL has a highest acid strength (lower the value of H_0 , higher will be the acid strength) and hence it is showing higher activity (62% furfural yield) compared to all other BAILs.

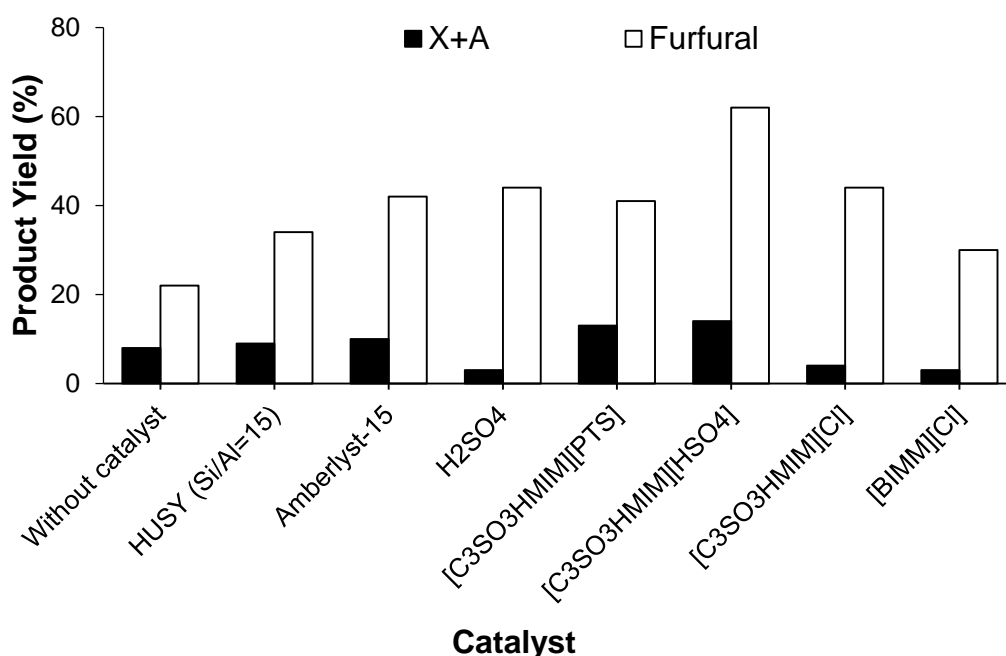


Figure 3B.1. Catalyst evaluation studies for the conversion of hemicellulose into furfural; Reaction condition. hemicellulose 0.6 g, catalyst 0.12 g, Water+Toluene 60 mL (1:5 v/v), 170 °C, 4 h.

The $[\text{BMIM}][\text{Cl}]$ IL used for the conversion of hemicellulose showed only 30% furfural yield along with 3% X+A yield. The lower yield of furfural was observed because the $[\text{BMIM}][\text{Cl}]$ IL is not having any Brønsted acidity associated with it. On the other hand, with $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ BAIL (similar type of IL having Brønsted acidity), 44% furfural yield was achieved along with 4% X+A yield. The comparison of the catalytic activity of $[\text{BMIM}][\text{Cl}]$ IL and $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ BAIL showed that Brønsted acidity is important for achieving higher furfural yield.

It is reported in the literature that the solid acid catalysts such as HUSY (Si/Al=15) and Amberlyst-15 used for this reactions are not stable and undergo morphological changes during the course of reaction.^[13] Nevertheless, BAILs are stable under reaction condition which was confirmed with the help of ¹H NMR study (section 3B.2.7.). More importantly, the [C₃SO₃HMIM][HSO₄] BAIL showed higher furfural yield compared to HUSY (Si/Al=15) and Amberlyst-15. The higher yield of furfural with [C₃SO₃HMIM][HSO₄] BAILs compared with solid acid catalyst can be explained as; the BAILs are soluble in reaction solvent but solid acid catalysts are not. Moreover, solid acid catalysts with higher acid strength compared to BAILs are still showing lower activity because it forms heterogeneous phase with substrate and additionally, the active sites are not accessible to substrates in solid acid catalysts because of defined pore diameter and porosity.^[14] It is very important to note that the concentrated hemicellulose solution (6 wt%; with respect to water) was used for the reaction and achieved 62% furfural yield in one-pot method. However, in previous work on hemicellulose conversion into furfural, 1wt% hemicellulose solutions were used.^[15]

3B.2.2. Effect of solvent system and the ratio of biphasic solvent system for the conversion of hemicellulose

3B.2.2.1. Effect of solvent system

This study was carried out to find out the best solvent system to achieve highest furfural yield in the conversion of hemicellulose. The polar aprotic solvents were reported in the literature for the production of furfural. Takagaki et al.^[16] Showed that the furfural yield of 37% was obtained from xylose in N,N-dimethylformamide (DMF) using Amberlyst-15 with the addition of hydrotalcite (HT) as a catalyst. When the dehydration of xylose was performed in DMSO by the use of Nafion 117, 60% furfural yield was achieved. Although polar aprotic solvents inhibit the formation of side-products to some extent, they also suffer from the drawback of the poor solubility of carbohydrates and problem such as high boiling points, which are unfavourable to the production and separation of furfural.^[17-18] Moreover, biphasic solvents like water+toluene and water+MIBK in the presence of H-faujasites and mordenite were found to be effective for the conversion of xylose into furfural.^[19]

Hence, the different biphasic solvent system was studied instead of polar aprotic solvent to improve the furfural yield.

The reactions were carried out with beechwood hemicellulose as substrate and $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL as the catalyst and the results are presented in Fig. 3B.2. The reactions were performed at 170 °C for 4 h. The various biphasic solvent systems were used such as water+toluene, water+*p*-xylene and water+MIBK. The water+toluene solvent system showed 62% furfural yield, whereas water+*p*-xylene and water+MIBK showed 49 and 52% furfural yields, respectively. When the conversion of hemicellulose into furfural was carried out using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL under similar reaction condition with only water as solvent, it showed a lower yield of furfural (21%) (Fig. 3B.2.). The effect of solvent study on the conversion of hemicellulose into furfural shows that to achieve maximum furfural yield water+toluene biphasic solvent system is best.

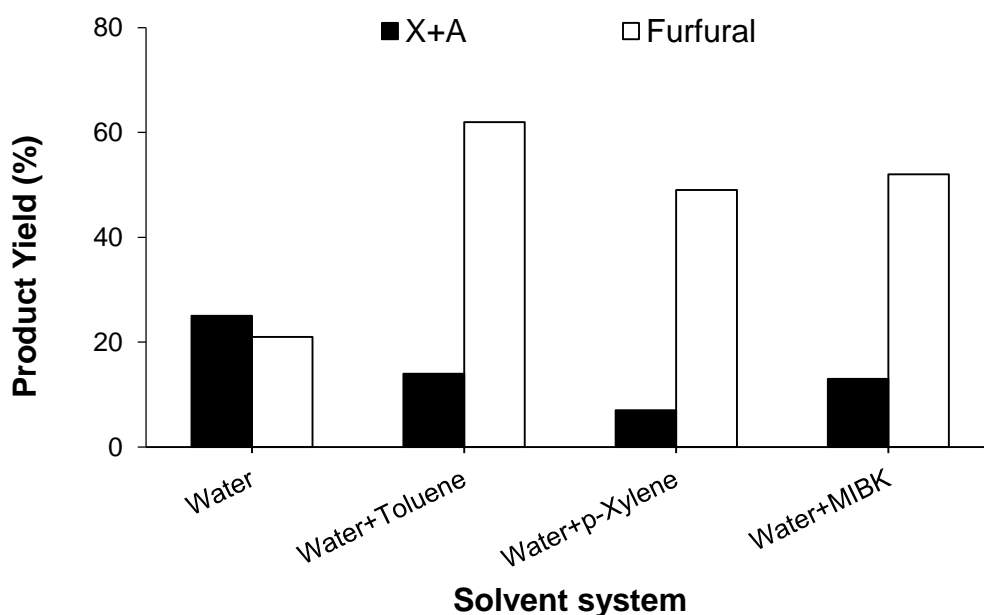


Figure 3B.2. Effect of the solvent system for the conversion hemicellulose into furfural; Reaction condition. hemicellulose 0.6 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.125 g, solvent 60 mL (biphasic solvent 1:5 v/v), 170 °C, 4 h.

The observance of maximum furfural yield in water+toluene solvent system can be explained on the basis of furfural partition coefficient (Fig. 3B.3. and Table 3B.1.). From the partition coefficient study, it was observed that furfural has a maximum solubility in toluene layer compared to *p*-xylene and therefore in water+toluene biphasic solvent system higher quantity of furfural can be extracted in

toluene during the course of reaction compared to *p*-xylene in water+*p*-xylene system. Likewise, furfural has 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 3B.1. and Fig. 3B.3.). Hence, water+MIBK biphasic solvent system should show higher furfural yield, but practically water+toluene solvent system showed better furfural yield. This can be explained on the basis of solubility of MIBK and toluene in water. The MIBK has higher solubility in water layer (19 g/L at 20 °C) compared to the solubility of toluene in water layer (0.52 g/L at 20 °C).^[13] Because of the solubility difference, in the case of water+MIBK biphasic solvent system, there is a possibility that furfural can come in water layer from MIBK layer and undergo further side reactions, as the catalyst (BAIL) is soluble in the water layer. This phenomenon is less prominent in the case of water+toluene biphasic solvent system.

Calculation of partition coefficient of furfural in different organic solvents:

Table 3B.1. Partition coefficient of furfural in organic/water solvent system.*

Solvent system	Distribution of furfural		Partition Coefficient
	Organic Phase (g)	Aqueous Phase (g)	
Water/Toluene	0.192	0.009	1.32
Water/ <i>p</i> -Xylene	0.185	0.016	1.06
Water/MIBK	0.193	0.008	1.38

*The error for distribution of furfural in organic phase was ± 2 mg.

For the calculation of partition coefficient, 0.2010 g furfural was added in the water+organic biphasic solvent system 30 mL (1:5 v/v). The solution was stirred for 2 h at RT, after 2 h the water and organic phases were separated using a separating funnel and analysed using HPLC and GC instrument. The aqueous layer was analysed using HPLC and the organic phase was analysed using GC. The furfural concentration present in aqueous and the organic phase was calculated with the help of slope of calibration curve obtained with furfural standard.

Partition coefficient, ($\log P$) organic/water = $\log_{10} ([\text{furfural}]_{\text{organic}} / [\text{furfural}]_{\text{water}})$

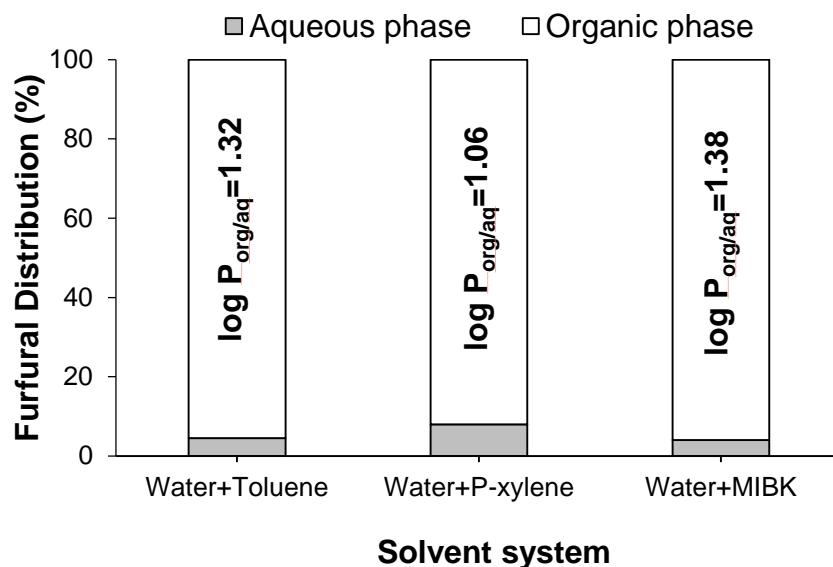


Figure 3B.3. Partition coefficient of furfural in organic/water solvent system; Reaction condition. furfural 0.2 g, Water+Organic biphasic solvent 30 mL (1:5 v/v), RT, 2 h stirring.

3B.2.2.2. Effect of ratio of biphasic solvent system

After successfully choosing the best biphasic solvent system, water+toluene for the conversion of hemicellulose into furfural, the effect of the ratio of biphasic solvent system was studied. The reaction was carried out with beechwood hemicellulose using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL at 170 °C for 4 h and the results are presented in Fig. 3B.4. The reaction was carried out with various water/toluene ratio such as 1:1 v/v, 1:3 v/v, 1:5 v/v and 1:7 v/v. When 1:1 v/v, 1:3 v/v, water/toluene biphasic solvent was used 45 and 47% furfural yield was seen. The best result (62% furfural yield) was obtained with water+toluene biphasic solvent system having 1:5 v/v ratio. Further, increase in toluene concentration in water+toluene biphasic solvent system (1:7 v/v) showed decrease in the yield of desired products (60% furfural yield along with 10% X+A yield). This can be explained as with increasing toluene concentration the aqueous layer becomes more concentrated with respect to catalyst and substrate, which causes side reactions to happen and in turn shows decrease in mass balance (for water+toluene (1:5 v/v) 81% mass balance and for water+toluene (1:7 v/v) 73% mass balance).

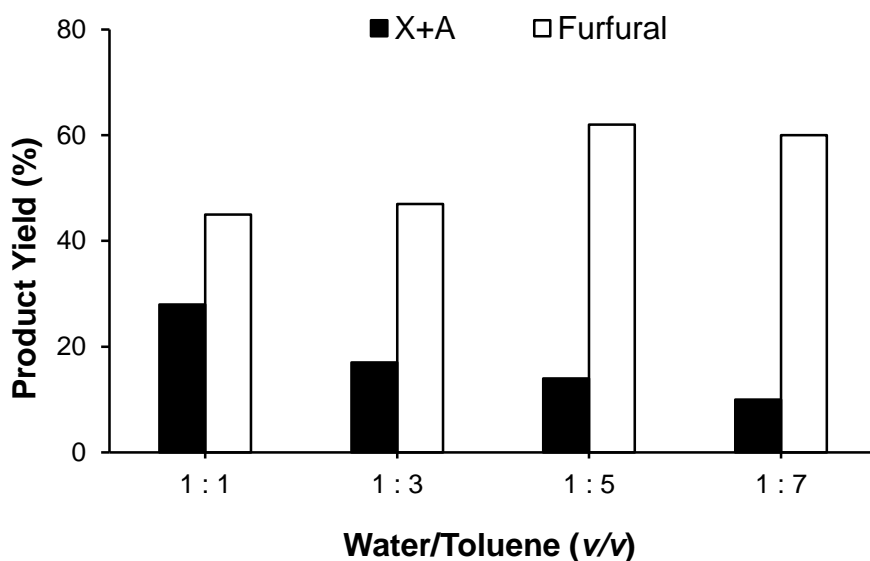


Figure 3B.4. Effect of the ratio of biphasic solvent for the conversion of hemicellulose into furfural; Reaction condition. hemicellulose 0.6 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.125 g, Water+Toluene 60 mL, 170 °C, 4 h.

3B.2.3. Influence of reaction time on the conversion of hemicellulose into furfural

In Chapter-3A (section 3A.3.1.) it was understood that when hemicellulose conversion is carried out using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL at 160 °C for 1 h in only water as a solvent, 10% furfural yield along with 87% X+A yield could be obtained. Hence, the time of reaction was increased to enhance the furfural yield, and after increasing the reaction time up to 4 h, maximum furfural yields i.e. 21% was achieved (Chapter-3A, section 3A.3.4.). However, with further increase in reaction time to 6 h showed decrease in furfural yield (17%). No much improvement in the furfural yield was observed when reaction was carried out for the longer reaction time in water medium because in water medium undesired side reactions are prominent that decreases the furfural yield.^[14] 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.^[18] To avoid this, further reactions were carried out using water+toluene biphasic solvent system.

The influence of reaction time on the conversion of hemicellulose into furfural was checked and the results are presented in Fig. 3B.5. When the reactions were carried out using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL at 170 °C for 4 and 5 h in water+toluene

(1:5 v/v) biphasic solvent system, similar yield of furfural (62%) can be obtained after 4 h and 5 h of reaction time. However, higher X+A yield was obtained in 4 h (14%) reaction compared to 5 h (7 %). The mass balance calculations show that when reaction is carried out for 4 h, higher mass balance is possible (81%) compared with 5 h reaction (73%). This is again because, if reaction is carried out for longer time, degradation reactions become predominant. For the reaction carried out for 1 h showed only 27% furfural yield and 58% X+A yield. Moreover, the reaction carried out for the longer time such as 8 h showed the decrease in furfural yield (57%) compared to the reaction carried out for 4 h and 5 h (62% furfural yield). This shows that the 4 h is the optimum reaction time for achieving better furfural yield along with higher mass balance using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL at 170 °C.

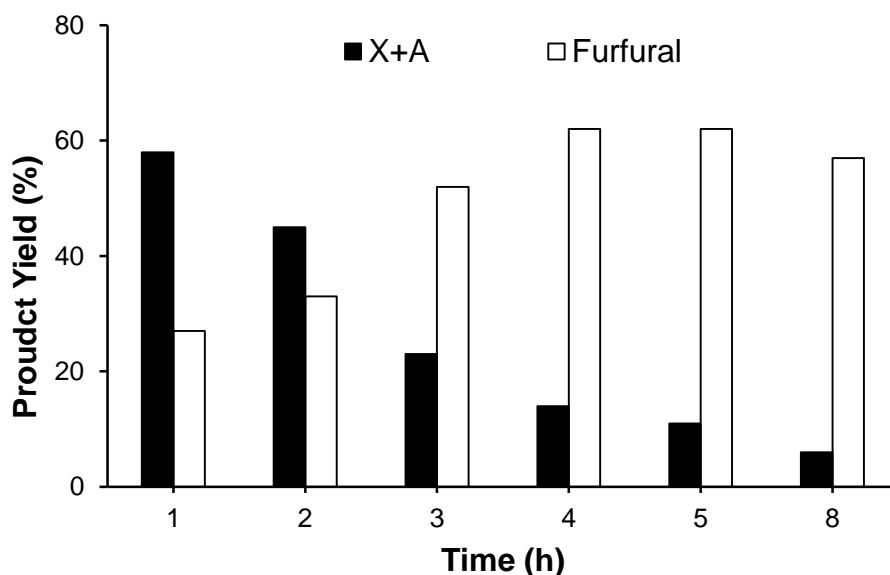


Figure 3B.5. Effect of reaction time on the conversion of hemicellulose into furfural; Reaction condition. hemicellulose 0.6 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.12 g, Water+Toluene 60 mL (1:5 v/v), 170 °C.

The hemicellulose conversion carried out using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL for shorter reaction time (1 h) showed the better yield of C5 sugars (58%). On the other hand, by increasing reaction time, the furfural yield increases up to 62% for 4 h reaction. Simultaneously the selectivity for desired products decreases (X+A and furfural) with increasing reaction time because of increasing side reactions such as humin formation and condensation reactions (formation of dark brown colour reaction mixture and insoluble solid mass was seen). Hence, the conversion of hemicellulose into furfural cannot be carried out for longer time at 170 °C.

3B.2.4. Optimization of reaction temperature for the conversion of hemicellulose into furfural

Similar to the effect of reaction time, optimization of reaction temperature was carried out for the above titled reaction and the results are shown in Fig. 3B.6. The reactions were carried out for 4 h, using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst, because as seen from the earlier section, best possible yield of furfural (62%) was seen after 4 h reaction carried out at 170 °C. When the reactions were carried out at 160 °C and 180 °C, 35 and 64% furfural yield along with 41 (160 °C) and 5% (180°C) X+A yield was seen. This shows that the reactions carried out at 170 °C and 180 °C gives almost similar furfural yield (62% and 64%). The reaction carried out at 180 °C shows lower X+A yield (5%) compared to the reaction carried out at 170 °C (14%) for similar time (4 h). These results suggest that at 170 °C, 81% mass balance could be achieved while at 180 °C, 72% mass balance could be obtained. Again, here it can be said that with increase in reaction temperature, side reactions are favourable and hence it is better to carry out reactions at 170 °C than 180 °C.

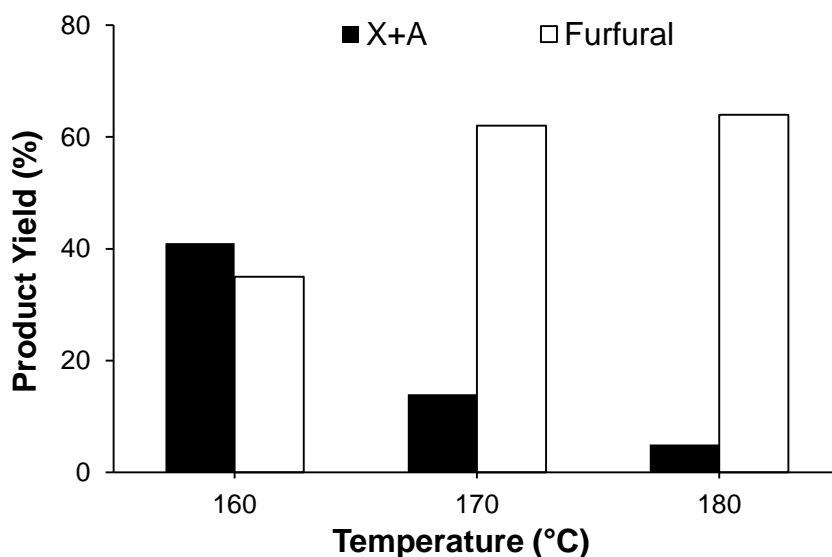


Figure 3B.6. Influence of reaction temperature on the conversion of hemicellulose into furfural; Reaction condition. hemicellulose 0.6 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.12 g, Water+Toluene 60 mL (1:5 v/v), 4 h.

In the conversion of hemicellulose reaction, lower yield and selectivity of furfural was observed; this can be explained with the help of two reasons first one is the stability of furfural in the reaction mixture and the second reason is the side reactions of furfural with C5 sugars and reactions between C5 sugars. Therefore, to

check the furfural stability under optimized reaction condition is necessary. Hence, for furfural stability study the reaction was carried out under optimized reaction condition (water+toluene 60 mL (1:5 v/v), 170 °C) for 5 h with and without BAIL catalyst ([C₃SO₃HMIM][HSO₄]). This study was performed with 0.436 g furfural because the hemicellulose conversion reactions were carried out with 0.6 g hemicellulose which can give 0.436 g furfural (at 100% yield). After the completion of the reaction, the water and toluene layers were separated using a separating funnel. 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. 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 this implies that the conversion of furfural is very small in water+toluene solvent system at 170 °C for 5 h. Hence, this might not be the reason for the drop in furfural yield and selectivity in the above titled reactions. Furthermore, to validate 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 [C₃SO₃HMIM][HSO₄] BAIL and the result shows that black colored solid formation with 70% furfural yield (0.268 g) and 10% xylose (0.03 g xylose) was found to be unconverted. This shows that in the conversion of hemicellulose into furfural, the mass loss is observed because of side reactions between C5 sugars and also the side reactions between furfural and C5 sugar.

Thus, it can be suggested that the lower selectivity and yield of furfural was observed because of undesired side reactions of furfural with sugars or the sugars degrade directly into other undesired products.

3B.2.5. Effect of catalyst concentration

The study on the effect of catalyst concentration was carried out and the results are presented in Fig. 3B.7. The reaction was carried out with beechwood hemicellulose at 170 °C for 4 h in water+toluene (60 mL (1:5 v/v)) solvent system. The study shows that very less quantity (0.12 g BAIL for 0.6 g hemicellulose, S/C=5 wt/wt) of [C₃SO₃HMIM][HSO₄] BAIL was required to achieve 62% furfural yield along with 14% X+A yield (Fig. 3B.7.). In this reaction >96% hemicellulose conversion was observed

with 81% mass balance, this might be due to undesired side products formation which were not detected by 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% X+A with 90% hemicellulose conversion while rest of the products formed are oligomers and some side products that which are not soluble in reaction solvent hence, cannot be identified using HPLC and GC. 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% X+A yield was observed. In this reaction >99% hemicellulose conversion was seen with 71% mass balance. This implies that with 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 X+A yield (14%) was achieved when S/C=5 was used compared to S/C=2.5. This shows that S/C=5 wt/wt is optimized S/C ratio for the conversion of hemicellulose into furfural.

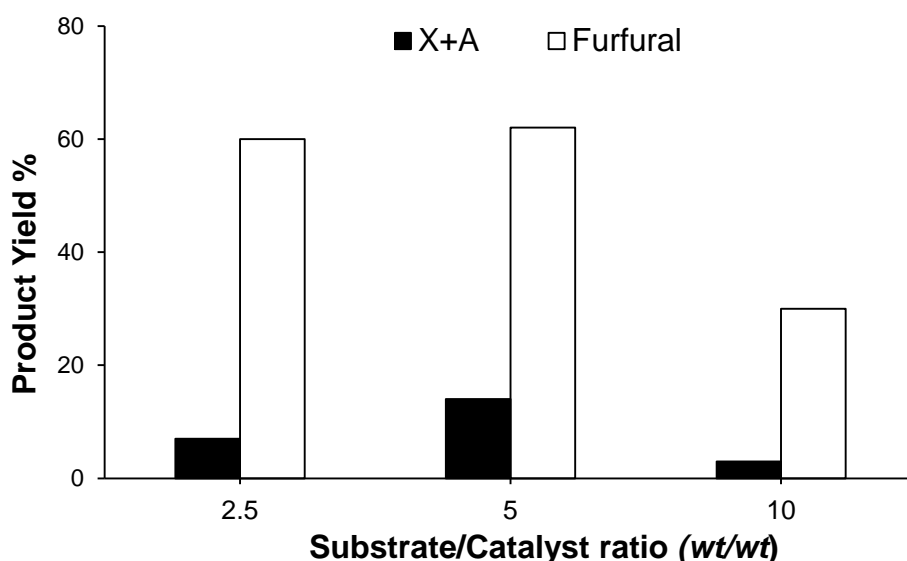


Figure 3B.7. Optimization of catalyst concentration for the conversion of hemicellulose into furfural; Reaction condition. hemicellulose 0.6 g, Catalyst $[C_3SO_3HMIM][HSO_4]$, Water+Toluene 60 mL (1:5 v/v), 170 °C, 4 h.

3B.2.6. Effect of substrate concentration

It is very important to test the developed catalytic method with the concentrated substrate to minimize the cost of the experiment. Considering this, effect of substrate concentration was studied. The reactions were carried out using $[C_3SO_3HMIM][HSO_4]$ BAIL as catalyst and beechwood hemicellulose as the substrate and water+toluene

(60 mL (1:5 v/v) as a biphasic solvent system (Fig. 3B.8.). Substrate concentration study was carried for various concentrations at 170 °C and 4 h reaction time by keeping BAIL and solvent quantity constant. 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 (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) hemicellulose showed 70 and 62% furfural yield. The effect of substrate concentration study for the conversion of hemicellulose into furfural reaction suggests that lower hemicellulose concentration (0.2 g hemicellulose in 60 mL water+toluene (1:5 v/v)) is better which gave 85% furfural yield. The lower furfural yield obtained with higher substrate concentration can be explained as; with the increase in hemicellulose concentration side reaction will increase which lead to the decrease in selectivity of desired products. A similar trend was also observed for xylose dehydration reaction, with increasing xylose concentration the furfural yield is dramatically decreased (Chapter 5, section 5.3.3.5.)

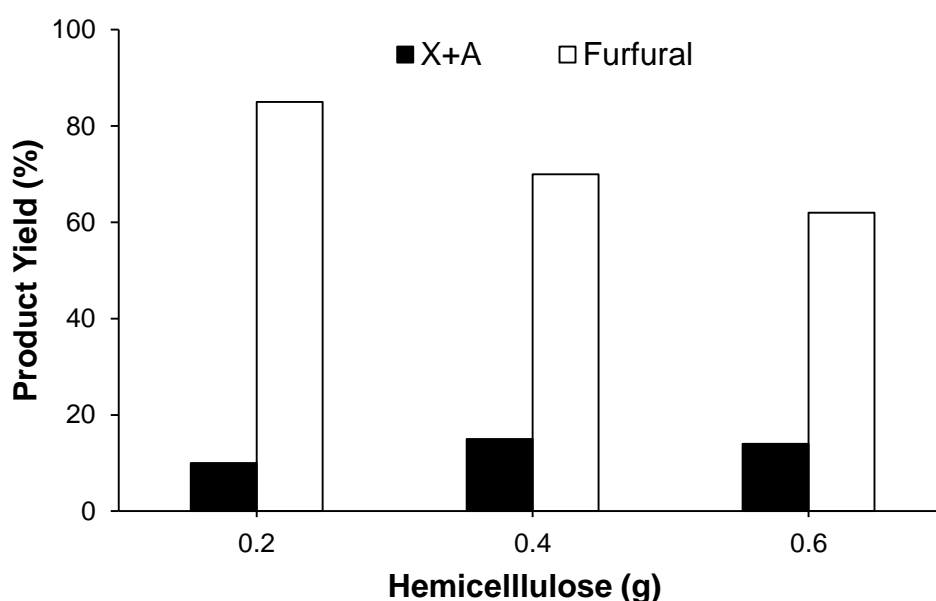


Figure 3B.8. Effect of hemicellulose concentration for its conversion into furfural; Reaction condition. $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.12 g, Water+Toluene 60 mL (1:5 v/v), 170 °C, 4 h.

3B.2.7. Recycling and stability of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL

For the recycle study the separation of aqueous layer containing $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL layer was carried out as follows; After the completion of the reaction, the

aqueous and organic phases were separated using a separating funnel. The separated aqueous layer contains $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst because the $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL is soluble in water and not in toluene solvent. Next, the aqueous layer was washed three times with fresh toluene solvent for the extraction of furfural which was soluble in the water layer. Then this aqueous layer obtained after furfural extraction by toluene was used for next reaction which contains $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst and small amount of sugars. In this aqueous layer, hemicellulose was added along with toluene and the reaction was performed. After the completion of reaction again the water and the toluene layers were separated using separating funnel and the reaction mixture was analysed using HPLC and GC. The result showed 62% furfural yield along with 11% X+A yield.

For understanding the stability of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL under reactions condition the ^1H NMR study was carried out. The recycling of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL for the ^1H NMR study was carried out as follows; after completion of reaction the aqueous and toluene layer was separated using separating funnel. The aqueous layer contains BAIL catalyst, furfural and small amount of sugars, for removing furfural the aqueous layer was washed three times with toluene solvent. Next, after extraction of furfural the aqueous layer was subjected to rotavap for the removal of water and to obtain BAIL and sugars. After rotavap, the viscous liquid was obtained which contains BAIL and sugars, for removing sugars from BAIL the procedure used as follows; In this viscous liquid (BAIL+C5 sugars) 2 mL of water was added and then slowly acetone (30 mL) was added to give light white color solution. Up on excess addition of acetone, light white color disappears. The solution was kept under static condition for a while. Afterwards, the acetone layer is decanted (contains sugars) leaving viscous liquid at the bottom of a container. Next, the viscous liquid was dried at 80 °C for 4 h under vacuum. This dried viscous liquid (BAIL) was then dissolved in D_2O and used for ^1H NMR spectroscopy (Fig. 3B.9.). From the ^1H NMR study it was found that there is no change in the structure of recovered $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst both the ^1H NMR of fresh and recovered BAIL are similar, this shows that the catalyst is stable under reaction condition. Very few peaks can be seen in the ^1H NMR of recovered BAIL those are because of impurity from reaction mixture and rest of all other peaks are retained for the recovered BAIL as like fresh BAIL. The TGA study of BAILs shows that there is no mass loss up to 250 °C from BAILs (Chapter-2, section

2.5.4.). This shows that the $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL used for the conversion of hemicellulose into furfural reaction is a stable catalyst.

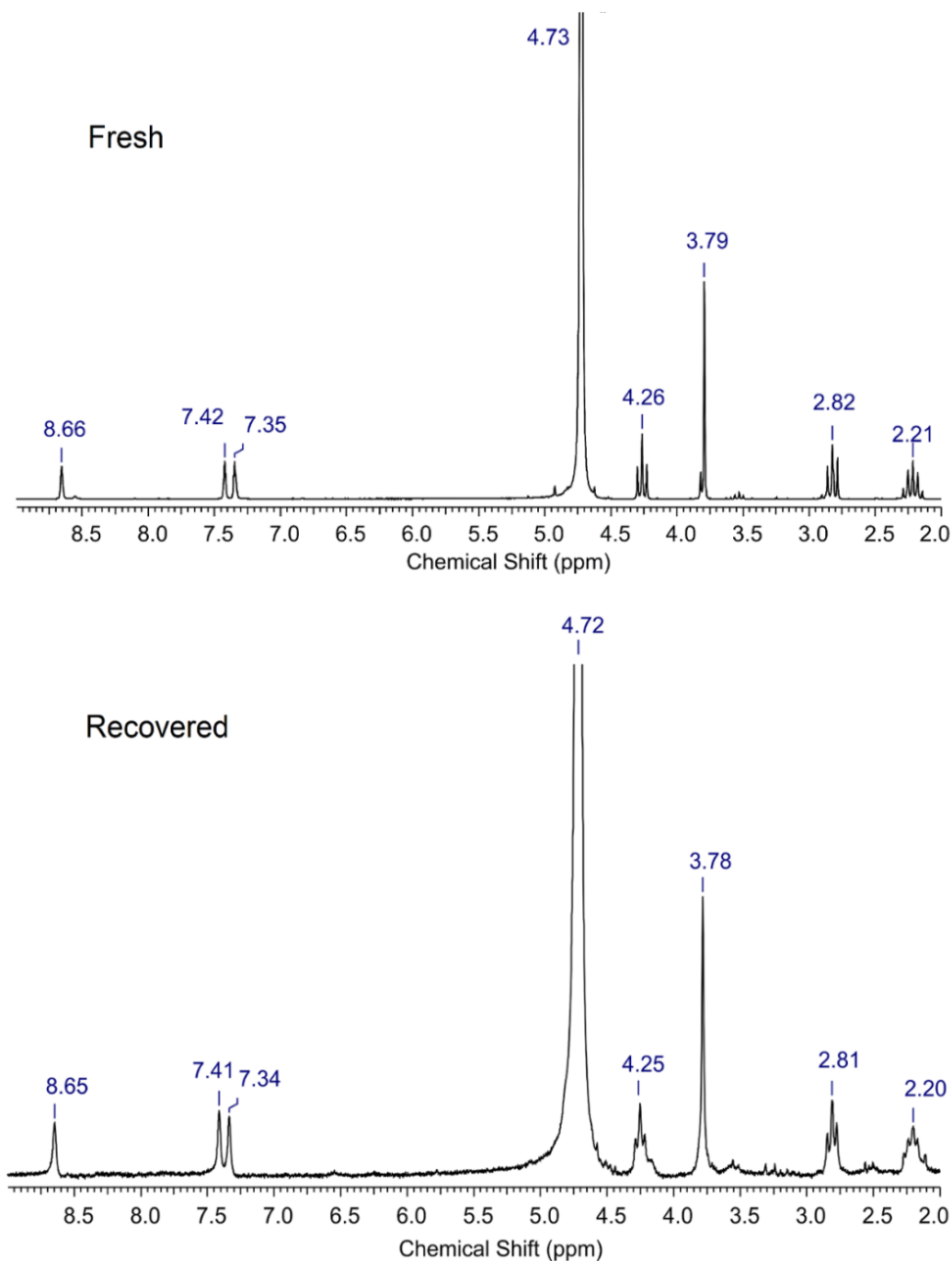


Figure 3B.9. ^1H NMR spectra of fresh and recovered $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL from the reaction of hemicellulose conversion into furfural.

3B.2.8. Conclusion

The catalytic amount of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL (0.12 g) can convert hemicellulose (0.2 g) into furfural in the one-pot method with a very high yield of furfural i.e. 82% under optimized reaction conditions (170 $^\circ\text{C}$, 4 h, water+toluene 60 mL (1:5 v/v)).

The reaction carried out with concentrated hemicellulose (0.6 g) under similar conditions showed 62% furfural yield. The result shows that with increasing hemicellulose concentration side reactions increases and hence furfural yield and selectivity decreases. Similarly, with increasing the reaction time more than 4 h at 170 °C and temperature above 170 °C (4 h) shows that furfural yield decreases and degradation reactions were favoured. For achieving 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 [C₃SO₃HMIM][HSO₄] BAIL catalyst used for the conversion of hemicellulose into furfural performs better compared to solid acid and mineral acid catalysts such as HUSY (Si/Al=15), Amberlyst-15 and H₂SO₄.

The hemicellulose could be efficiently converted into C5 sugars (Chapter-3A) and also it could be converted into furfural in one-pot fashion using catalytic amount of [C₃SO₃HMIM][HSO₄] BAILs (0.12 g) without using any metal halide and mineral acids. The [C₃SO₃HMIM][HSO₄] BAIL recovered from the reaction mixture is a stable and recyclable catalyst which was confirmed by ¹H NMR study.

3B.2.9. References

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Chapter 4

**Selective Conversion of
Hemicellulose from Crop Wastes
into Sugars & Furfural using
Brønsted Acidic Ionic Liquids**

4.1. Introduction

After converting hemicellulose into C5 sugars (xylose+arabinose; X+A) and furfural using BAILs successfully, efforts were made to obtain sugars and furfural from crop waste in a one-pot method. In earlier chapters, 3A and 3B, the BAIL showed very good catalytic activity compared to mineral acid and solid acid catalysts for the conversion of hemicellulose into C5 sugars and/or furfural. Considering this, BAILs were preferred for the selective conversion of hemicellulose from crop waste into sugars and/or furfural in a one-pot method.

The present literature available for the furfural synthesis shows the use of xylose or xylan (hemicellulose) as the substrate.^[1-4] If the furfural synthesis is carried out using xylan rich crop waste in a one-pot method, then it is possible to develop an economic method. This is because for the synthesis of furfural, separation step of hemicelluloses from crop waste will be avoided. There are some reports where conversion of crop waste into C5 sugars (73% yield using HCl) and furfural (62 and 42% yield using H β and HMOR; 55% yield using H₂SO₄) is shown using mineral acid and solid acid catalysts.^[5-7] But the problem with these methods is that the reactions were carried out in more than one pot. It is understood that for the conversion of crop waste into sugars and furfural, it is necessary to pretreat the crop waste for breaking structural framework of polysaccharides present in lignocellulosic biomass and/or for deconstructing hemicellulose and cellulose from lignocellulosic biomass. Hence for converting crop wastes into sugar and furfural the pretreatment is given to the lignocellulosic biomass,^[8] and further hemicellulose is isolated from crop waste which is then converted into sugars and furfural. In Chapter-1 (section 1.2.7.) a one-pot conversion of bagasse is discussed using HUSY (Si/Al=15) catalyst to yield 20% X+A and 55% furfural.^[9] This solid acid catalyst gave lower yields and it is also reported that the catalyst is not stable under reaction condition.^[9] The mineral acid catalysts reported for the conversion of crop waste into sugars and furfural have various drawbacks such as; they are not recyclable and also acids can make the reaction system more corrosive, which increases the capital cost.^[7, 10] To overcome the drawbacks associated with the solid acid and mineral acid catalysts, Brønsted acidic ionic liquids (BAILs) were employed in this work. Hence, the present chapter is dedicated to the selective conversion of hemicellulose from crop waste into sugars and/or furfural using BAILs.

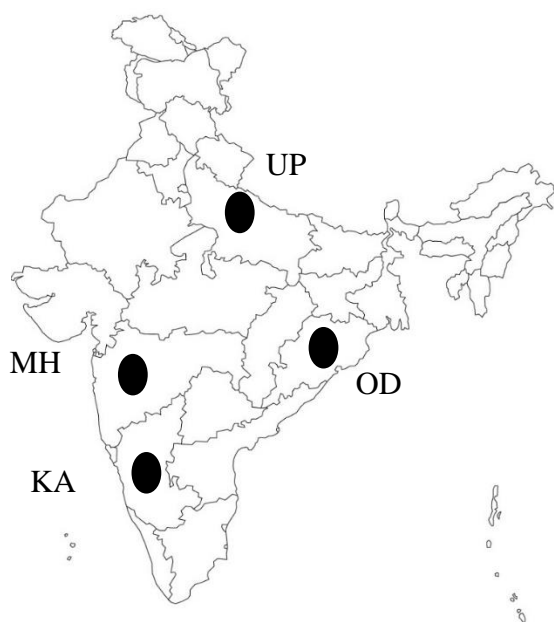
India is one of the largest producers of major crops such as sugarcane, rice and wheat. If the annual production of these crops is compared with world's annual production, then it can be seen that India produces 17 to 21% crops with respect to world's total crop production (Table 4.1.). Moreover, the annual production of other crops such as maize (2.36×10^7 MT) and cotton (8.77×10^6 MT) is also very huge.^[11] After utilizing the edible part of all these crops, huge quantity of crop waste is produced. This inspired me to use the wastes generated from these crops as a substrate for chemical synthesis (sugars and furfural).

Table 4.1. Production of crops (India and world scenario).^[11]

Source	Region/ country	2010 (MT)	2011 (MT)	2012 (MT)	2013 (MT)	2014 (MT)
Sugarcane	World	1.69×10^9	1.80×10^9	1.87×10^9	1.91×10^9	1.89×10^9
Sugarcane	India	2.92×10^8 (17% w.r.t. world)	3.42×10^8 (19% w.r.t. world)	3.51×10^8 (19% w.r.t. world)	3.41×10^8 (18% w.r.t. world)	3.52×10^8 (19% w.r.t. world)
Rice (paddy)	World	7.01×10^8	7.23×10^8	7.37×10^8	7.40×10^8	7.40×10^8
Rice (paddy)	India	1.44×10^8 (21% w.r.t. world)	1.58×10^8 (22% w.r.t. world)	1.58×10^8 (21% w.r.t. world)	1.59×10^8 (21% w.r.t. world)	1.57×10^8 (21% w.r.t. world)
Wheat	World	6.52×10^8	7.01×10^8	6.93×10^8	7.15×10^8	7.28×10^8
Wheat	India	8.08×10^7 (12% w.r.t. world)	8.69×10^7 (12% w.r.t. world)	9.41×10^7 (13% w.r.t. world)	9.31×10^7 (13% w.r.t. world)	9.44×10^7 (13% w.r.t. world)

The different types of crop wastes were collected for this study from various parts of India (Maharashtra, Uttar Pradesh, Karnataka, and Odisha) as it is shown in Fig. 4.1. The composition of crop waste was determined using known method i.e. Technical Association of the Pulp and Paper Industry (TAPPI) method^[12] and the nutrients present in crop wastes were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). Further, the reaction conditions were

optimized for the above titled reactions using BAILs as a catalyst. The catalytic results obtained with BAILs were compared with solid acid and mineral acid catalysts.



Sources of crop waste

Odisha Rice Husk (OD RH)
Karnataka Rice Husk (KA RH)
Uttar Pradesh Rice Husk (UP RH)
Uttar Pradesh Wheat Straw (UP WS)
Maharashtra Bagasse (MH BG)
Uttar Pradesh Bagasse (UP BG)
Maharashtra Cotton Stalk (MH CS)
Maharashtra Corn Cob (MH CC)

Figure 4.1. Sources of crop wastes.

4.2. Experimental

4.2.1. Materials and methods

Materials

For the reactions, various types of crop wastes are used such as rice husk, wheat straw, bagasse, cotton stalk and corn cob, which were collected from agricultural fields located in different parts of India as is shown in Fig. 4.1. Before experiments, all these crop wastes were grinded using a mixer and sieved to obtain ca. 2 mm size particles. Then the bagasse crop waste was washed (for removing residual sugars) with water at room temperature and dried in an oven at 60 °C for 16 h. On the other hand, all the other crop wastes were oven dried at 60 °C for 16 h. Further, these were vacuum dried (-700 Torr) at 80 °C for 16 h. Afterwards these crop wastes were used in the reaction for the selective conversion of hemicellulose into sugars and furfural.

Catalyst

After efficiently converting isolated hemicellulose into C5 sugars and/or furfural (Chapter 3A and 3B) the BAILs are used for the selective conversion of hemicellulose

present in crop wastes into sugars and furfural. The detailed synthesis procedure of BAILs is discussed in Chapter 2 (section 2.2.2.).

4.2.2. Reaction set-up and catalytic methods

All the reactions were carried out in high pressure and high temperature batch mode autoclave (Parr autoclave; 300 mL capacity) equipped with temperature controller unit. In a typical reaction, for the selective conversion of hemicellulose from crop waste into C5 sugars, 2 g of crop waste was charged in the reactor and then 60 mL of solvent (water) along with 0.24 g catalyst (BAIL) was added to the reactor. For the reaction of selective conversion of hemicellulose from crop wastes into furfural, 0.6 g of crop waste was charged in the reactor and then water+toluene biphasic solvent was added (60 mL; 1;5 v/v) along with 0.12 g catalyst (BAIL). Reactions were performed at desired reaction temperature for definite reaction time under mechanical stirring (800 rpm).

4.2.3. Analysis

Analysis using HPLC

The analysis of reaction mixture was performed using HPLC instrument (Agilent Infinity 1200 series) equipped with a Pb²⁺ column (Rezex RPM-Monosaccharide, dimensions 300 x 7.8 mm; particle size 8 μm) maintained at 80 °C. Millipore water was used as an eluent with a flow rate of 0.6 mL/min. The refractive index detector (RID) with a cell temperature of 40 °C was used to detect the products. Before analysis, the samples were filtered through 0.22 μm syringe filter, and then 10 μL sample was injected for the analysis. The calibration curve was drawn with the standard compounds.

Analysis using GC

The organic phase of the reaction mixture was analyzed using Agilent 7890B GC system, equipped with HP-5 column (50 m × 0.22 μm ID) and flame ionization detector (FID) operated at 280 °C. The oven program used for the analysis has 100 °C temperature at the start of the analysis, which is then increased by a rate of 7 °C/min up to 250 °C and finally, it was held for 3 min at 250 °C. The flow rates of H₂, air and N₂ were 30, 300, and 20 mL/min, respectively. For GC analysis also, all the samples were filtered through 0.22 μm syringe filter before analysis and 1 μL sample was

injected. For the calculation of furfural yields, the calibration curve was drawn with the furfural standard.

4.2.4. Calculations

The yield of sugars obtained by selective conversion of hemicellulose from crop waste was calculated based on the concentration of pentosan present in the particular crop waste. TAPPI method was used for the determination of pentosan concentration in all the crop wastes used in the current work and the detail procedure and analysis results of pentosan are explained in section in 4.3.2.

Calculation of C5 sugar (X+A) and furfural yield for the selective conversion of hemicellulose from crop wastes into C5 sugars is done as follows,

$$\text{Xylose + Arabinose yield (\%)} = \frac{\text{moles of xylose + arabinose (HPLC)}}{\text{theoretical moles of xylose + arabinose}} \times 100$$

$$\text{Furfural yield (\%)} = \frac{\text{moles of furfural (HPLC)}}{\text{theoretical moles of furfural}} \times 100$$

Calculation of furfural yield for the conversion of hemicellulose from crop wastes into furfural reaction.

$$\text{Furfural yield (\%)} = \frac{\text{moles of furfural (HPLC + GC)}}{\text{theoretical moles of furfural}} \times 100$$

4.3. Compositional analysis of crop wastes

TAPPI method was used to understand the composition of crop wastes (holocellulose, pentosan, lignin, ash, etc.). As crops use various metal nutrients for its growth, there is a possibility of the presence of various metal nutrients in the crop wastes. The metal nutrients present in crop wastes were determined by ICP-OES analysis.

4.3.1. Determination of ash and moisture content

Oven dried (O.D.) sample (100 °C for 12 h under vacuum) was taken for the analysis of ash content. 5 g of O.D. sample was taken in silica crucible (W1). The crucible was placed in a muffle furnace at 650 °C for 4 h in the presence of air. Afterwards the sample was cooled to 70 °C and then placed in a desiccator containing indicating-grade anhydrous alumina. After cooling the sample to room temperature, the weight of ash content with crucible is determined (W2).

$$\text{Ash content (\%)} = \frac{W1 - W2}{\text{O. D. weight of the sample}} \times 100$$

For the determination of moisture present in crop wastes, the crop wastes were dried in an oven at 100 °C for 12 h under vacuum. The amount of moisture was calculated using the difference in the weight of the sample before and after drying.

$$\text{Moisture content (\%)} = \frac{\text{Initial weight} - \text{Oven dry weight}}{\text{Initial weight}} \times 100$$

4.3.2. Determination of pentosan in crop waste

Biomass such as crop waste and wood contains a 20-30% hemicellulose. The xylan type of hemicellulose is mainly made up of C5 sugars but on the other hand, hemicellulose derived from softwood consists of both pentosan and hexosans. The hardwood hemicellulose consists mainly of pentosan.

The pentosan is a polysaccharide yielding only pentoses (C5 sugars) on hydrolysis. The distillation apparatus used for the determination of pentosan is shown in Fig. 4.2. 3.85 N HCl (13.5%) reagent was used for the determination of pentosan (the 315 mL of HCl was taken in 1000 mL volumetric flask and diluted with distilled water to 1000 mL).

The stepwise procedure used for pentosan determination is explained below.

Procedure:

- 3 g oven dried crop waste was placed in boiling flask and 100 mL 3.85 N HCl was added along with boiling stones.
- The flask is connected to the distillation apparatus and marked the acid level in the flask.
- Then heating is started using a heater with controlling unit and 250 mL of 3.85 N HCl was added dropwise using dropping funnel, as it is shown in Fig. 4.3.
- During the distillation process, the volume of the flask is maintained constant (100 mL) by adding HCl dropwise from separating funnel. The distillation was performed till the 220 mL of distillate is collected in the volumetric flask.
- The collected 220 mL of distillate is placed in 500 mL volumetric flask and diluted with water to 500 mL.
- The absorbance of the distillate at 280 nm is measured using UV-spectrophotometer and the pentosan % was calculated using the below formula.

$$\text{Pentosan (\%)} = \frac{\text{Absorbance at 280 nm} \times \text{Dilution} \times 1.563 \times 0.5 \times 100}{151 \times \text{O. D. weight of sample}}$$

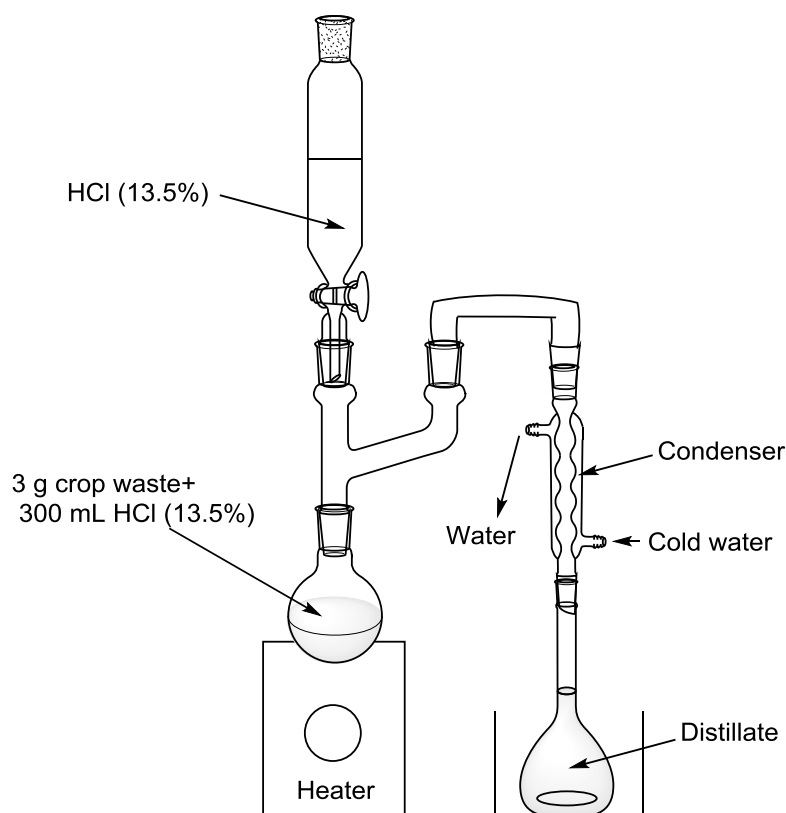


Figure 4.2. Distillation apparatus used for pentosan determination.

4.3.3. Determination of holocellulose

The holocellulose is nothing but the total carbohydrate content of the raw biomass material. The holocellulose comprises of cellulose hemicellulose part of lignocellulosic biomass. The holocellulose content can be calculated using delignification method which uses sodium chlorite (NaClO_2) and acetic acid (CH_3COOH) reagents.

4.3.3.1. Delignification of lignocellulosic biomass

For delignification 3 g O.D. sample was taken in 250 mL conical flask. 150 mL distilled water was added to it along with 1.5 g of sodium chlorite (NaClO_2) and 0.5 mL of acetic acid (CH_3COOH). Then the flask was placed in a water bath and heated at 70 °C temperature. While heating the conical flask was closed with a small flask in an inverted position. The heating is continued up to 1 h. After cooling, the supernatant transferred to a tared crucible. The lignin is soluble in solution and lignin free

(holocellulose) pulp can be obtained after filtration. Nevertheless, some lignin is associated with holocellulose even after this treatment. Hence, the treatment sodium chlorite and acetic acid were repeated at least three times for complete delignification. Next, the content of conical flask filtered through tared crucible, and the obtained residue was then washed with acetone. Further, the residue was dried in oven at 100 °C for 2 h and the weight of filtering crucible with contents was recorded.

The difference in weight of O.D. crop waste and holocellulose pulp will give the amount of lignin. The holocellulose obtained in this treatment contains ash therefore for determination of the exact amount of holocellulose, the weight of ash was subtracted from holocellulose (ash correction) as explained in section 4.3.1.

4.3.4. Determination of acid insoluble lignin in pulp

For the analysis of lignin concentration present in crop waste, this method was used.

Procedure:

- For the analysis of lignin, 1 g of biomass was taken in a beaker and to it, 15 mL 72% H₂SO₄ was added.
- Then the mixture was stirred at 30 °C for 2 h. Next, in 1000 mL RB flask 150 mL water was taken after this the material from the beaker was transferred to the RB flask.
- The leftover digested H₂SO₄ in the beaker was washed with 195 mL water and it is then added to 1000 mL RB flask (H₂SO₄ concentration becomes 3%).
- The solution was then boiled for 4 h, maintaining constant volume by using reflux condenser.
- Next, the RB flask was cooled to room temperature for overnight to settle down the insoluble material (lignin).
- The insoluble material was then filtered through G2 crucible, all the quantity of solid mass (lignin) was transferred to the filter.
- To make acid free lignin it was washed with hot water.
- Finally, the crucible with lignin was dried at 60 °C for 16 h and then it is further dried in an oven at 105 °C for 1 h.
- Finally, the crucible with lignin was cooled in a desiccator and then the weight was taken down.
- The lignin obtained was called as uncorrected lignin.

- The uncorrected lignin was transferred to quartz boat and next, it was heated at 650 °C for 4 h in the presence of air for ash correction.

wt of uncorrected lignin (g) = [wt of (crucible + solid) – wt of empty crucible]

$$\text{Ash corrected lignin (\%)} = \frac{[\text{wt of uncorrected lignin} - \text{wt of ash}]}{\text{O. D. weight of sample}} \times 100$$

4.3.5. Determination of α -cellulose, β -cellulose and γ -cellulose

The separation of α -cellulose, β -cellulose and γ -cellulose, is originally invented by Cross and Bevan and it is determined volumetrically by oxidation with potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) while the α -cellulose is an insoluble fraction and it is derived by the difference.

Generally, the α -cellulose indicates undegraded, higher-molecular weight cellulose content in pulp; the β -cellulose indicates that of degraded cellulose, and the γ -cellulose consists mainly of hemicellulose. The α -cellulose is the pulp fraction resistant to 17.5% and 9.45% NaOH solution under reaction condition. β -cellulose is the soluble fraction which is re-precipitated on acidification of the solution, and lastly γ -cellulose is the fraction remaining in the solution.

Procedure:

- For the analysis of α -cellulose, β -cellulose and γ -cellulose, the delignified pulp of crop waste was dried at 100 °C for 12 h under vacuum.
- 1.5 g dry pulp was placed in 500 mL conical flask and 75 mL of 17.5% NaOH reagent was added to it and the time is noted at which the reagent was added.
- The temperature is adjusted to 25 °C and the pulp was stirred with apparatus until it is completely dispersed. During stirring the drawing air into the pulp suspension was avoided.
- When the pulp is dispersed, the stirrer was taken out and it is rinsed with 25 mL of 17.5% NaOH reagent, added this into conical flask so that exactly 100 mL of 15.7% NaOH have been added to the pulp.
- After the period of 30 min from the first addition of 100 mL NaOH reagent, 100 mL distilled water was added at 25 °C to the pulp.

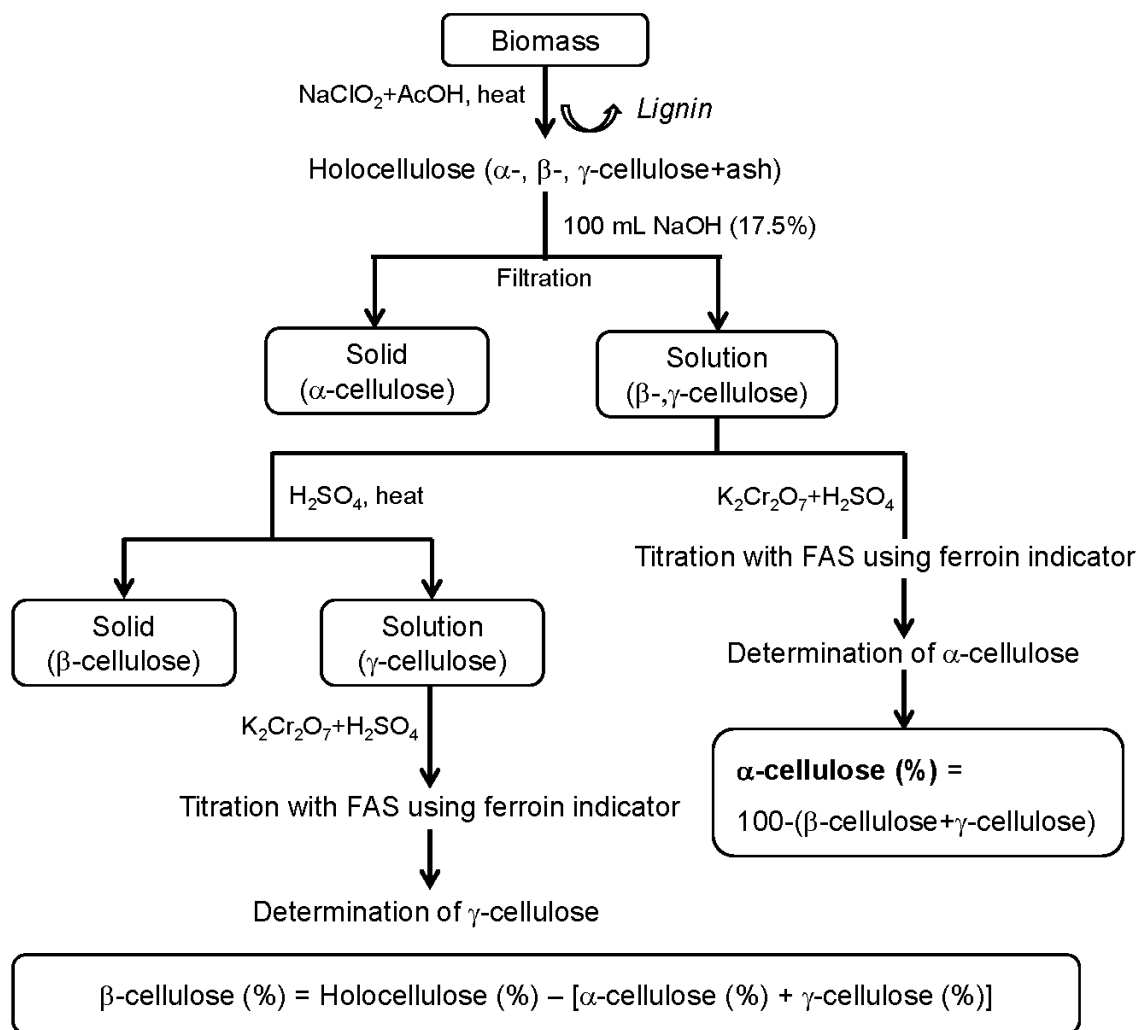
- The conical flask was kept for another 30 min (total extraction time 60 min).
- Finally, after 60 min period, the pulp suspension was stirred with a glassrod and transferred to filtering funnel.
- First 10 to 20 mL of filtrate was discarded and 100 mL of the filtrate was collected in a clean dry filtration flask.

4.3.5.1. α -cellulose determination

25 mL of the filtrate (F1) and 10 mL of 0.5 N potassium dichromate ($K_2Cr_2O_7$) solution pipetted out in the conical flask (250 mL). Then 50 mL of concentrated H_2SO_4 solution was added slowly with caution. The solution was kept for 15 min, then 50 mL water was added and cooled to room temperature. Next, 2 to 3 drops of Ferroin indicator was added and titrated with 0.1 N ferrous ammonium sulfate solution (FAS). The end point of the titration is a purple color. The volume of FAS required for the titration was recorded (V_1) and the blank titration was performed by substituting pulp filtrate with 12.5 mL of 17.5% NaOH and 12.5 mL of water. The volume required for blank titration was also recorded (V_2).

4.3.5.2. β - and γ -cellulose determination

50 mL of filtrate was pipetted out into 100 mL graduated cylinder having a ground glass stopper. Then 50 mL 3 N H_2SO_4 was added and the solution was mixed thoroughly by inverting. Next the solution was heated at 70-90 °C for 10-20 min to coagulate the β -cellulose. Finally, the precipitate was settled down (mainly β -cellulose) in overnight, then the solution is decanted to obtain a clear solution. For titration, 50 mL of clear solution (F2) and 10 mL of 0.5 N $K_2Cr_2O_7$ solution was pipetted out into 300 mL flask, then 90 mL of concentrated H_2SO_4 was added with caution. The solution was kept for 15 min and 2 to 3 drops of Ferroin indicator was added and the solution titrated against 0.1 N FAS. The end point of titration was the purple color at which volume of 0.1 N FAS recorded (V_3). The blank titration was performed by substituting filtrate with 12.5 mL of 17.5% NaOH, 12.5 mL of water and 25 mL of 3 N H_2SO_4 . In this case also, the volume of 0.1 N FAS recorded at the end point when color changes to purple (V_4). The general procedure for the determination of α -, β - and γ -cellulose can be represented as shown in Scheme 4.1.



Scheme 4.1. Schematic for the determination of α -, β - and γ -cellulose.

Calculations:

Calculation of α -cellulose content:

$$\alpha\text{-cellulose (\%)} = 100 - [(6.85 (V_2 - V_1) \times N \times 20) / A \times W]$$

where:

V_1 = titration of the pulp filtrate, mL

V_2 = blank titration, mL

N = exact normality of the FAS solution

A = volume of the pulp filtrate used in the oxidation, mL

W = oven-dry weight of pulp g

Calculation of γ -cellulose content:

$$\gamma\text{-cellulose (\%)} = [6.85 (V_4 - V_3) \times N \times 20] / [25 \times W]$$

where:

V_3 = titration of the solution after precipitation of β -cellulose, mL

V_4 = blank titration, mL

Calculation of β -cellulose:

$$\beta\text{-cellulose (\%)} = 100 - (\alpha\text{-cellulose \%} + \gamma\text{-cellulose \%})$$

Table 4.2. Summary on the composition of crop wastes.

Content*	Crop wastes							
	OD	KA	UP	UP	MH	UP	MH	MH
	RH	RH	RH	WS	BG	BG	CS	CC
Ash	15.6	17.1	18.6	12.3	2.8	3.3	2.5	1.4
Pentosan	15.8	11.2	12.4	21.4	24.2	21.6	15.4	27.9
Lignin	24.1	21.7	22.6	17.7	20.4	21.6	26	15.2
Hollocellulose	60.5	52.5	52.5	63.2	71.1	68.3	64	73.2
α -Cellulose	37.1	28.5	34.2	36.7	41.2	39.8	36	n.d.
β -Cellulose	9.8	11.7	6.8	17.1	15.2	15.3	n.d.	n.d.
γ -Cellulose	13.5	12.2	11.4	9.4	14.6	12.1	n.d.	n.d.

*Various content present in crop wastes were determined using TAPPI method. n.d. stands for not done.

4.3.6. Determination of nutrients present in crop wastes

The nutrients (metal components) present in various crop wastes were determined using ICP-OES analysis. For the ICP-OES analysis, the samples were prepared as follows; 3 g of oven dried crop waste was taken in a quartz boat and heated in a muffle furnace at 650 °C for 4 h in the presence of air to remove carbon in the form of CO₂. After 4 h the sample (ash) was cooled to RT. Next, the silica present in the sample was removed with the help of hydrofluoric acid (HF) treatment, because silica reacts with HF to form a hexafluorosilicic acid (H₂SiF₆) which is miscible with water and can be evaporated. After HF treatment, the solution formed (hexafluorosilicic acid) was evaporated and the left over residue was dissolved in freshly prepared aqua regia (HNO₃+3HCl, molar). Next, the solutions were diluted using Millipore water and

analyzed using ICP-OES technique to quantify the metal nutrients present in various crop waste.

Table 4.3. Concentration of various metal nutrients (mmol/g) present in crop wastes.

Nutrients* (mmol/g)	OD	KA	UP	UP	MH	MH	MH
	RH	RH	RH	WS	BG	CS	CC
Na	0	0	0	0	0	0	0
K	0.07	0.07	0.05	0.45	0.03	0.01	0.04
Ca	0.03	0.02	0.01	0.06	0.03	0.01	0.01
Mg	0.04	0.01	0.04	0.07	0.02	0.01	0.01
Al	0.02	0.01	0.01	0.02	0.01	0.04	0.03
P	0.05	0.01	0.05	n.d.	0.01	n.d.	n.d.

*Determined using ICP-OES analysis. The calculations were done based on 1 g of crop waste. n.d. stands for not done.

The crop wastes analyzed using ICP-OES method showed that there are various metals present in crop waste in different concentrations (Table 4.3.).

4.4. Results and discussion

4.4.1. Evaluation of catalytic activities for the selective conversion of hemicellulose from crop waste into C5 sugars.

The catalytic activity for the selective conversion of hemicellulose from crop waste was studied with various catalysts as shown in Fig. 4.3. The reactions were performed in a water medium (60 mL) at 160 °C for 1 h. Similar reaction conditions were used for the conversion of hemicellulose present in crop waste as like the reaction conditions which were used for the conversion of isolated hemicellulose into C5 sugars (Chapter 3A, section 3A.1.1.). However, for the selective conversion of hemicellulose from crop waste such as Maharashtra Bagasse (MH BG) into C5 sugars, 2 g of the substrate was used (Fig. 4.3.). The imidazolium-based BAILs such as [C₃SO₃HMIM][HSO₄], [C₃SO₃HMIM][PTS], and [C₃SO₃HMIM]Cl showed 88, 81 and 75% of C5 sugar yields which are higher compared to the C5 sugar yields obtained with mineral acid like H₂SO₄; (58%) and solid acid catalyst like HUSY (Si/Al=15)

(20%).^[13] The non-catalytic reaction showed only 10% C5 sugar yield under similar reaction conditions. The reaction carried out using quaternary ammonium cation based BAILs ($[\text{C}_3\text{SO}_3\text{HNEt}_3][\text{HSO}_4]$ and $[\text{C}_3\text{SO}_3\text{HNEt}_3][\text{PTS}]$) showed lower C5 sugar yields (40 and 42%, respectively). This indicates that to achieve better C5 sugar yield imidazolium BAILs are better catalysts. The presence of imidazolium cation in the BAIL can have the ion-dipole type of interaction with polysaccharide (Chapter 3A, section 3A.3.10.) because of which easy availability of H^+ for the hydrolysis of pentosan present in crop waste is possible. On the other hand, in the case of quaternary ammonium based BAILs ($[\text{C}_3\text{SO}_3\text{HNEt}_3][\text{HSO}_4]$ and $[\text{C}_3\text{SO}_3\text{HNEt}_3][\text{PTS}]$) the structure of cations are not planar and hence there may not be an efficient interaction between BAIL and polysaccharide.

The reaction was carried out using $[\text{BMIM}][\text{Cl}]$ IL which is not a BAIL to understand the contribution of Brønsted acidity in the selective conversion of hemicellulose from crop waste (MH BG). The result showed only 21% C5 sugar yield, which confirms that the higher C5 sugar yield was obtained using BAILs is because of Brønsted acidity of BAIL.

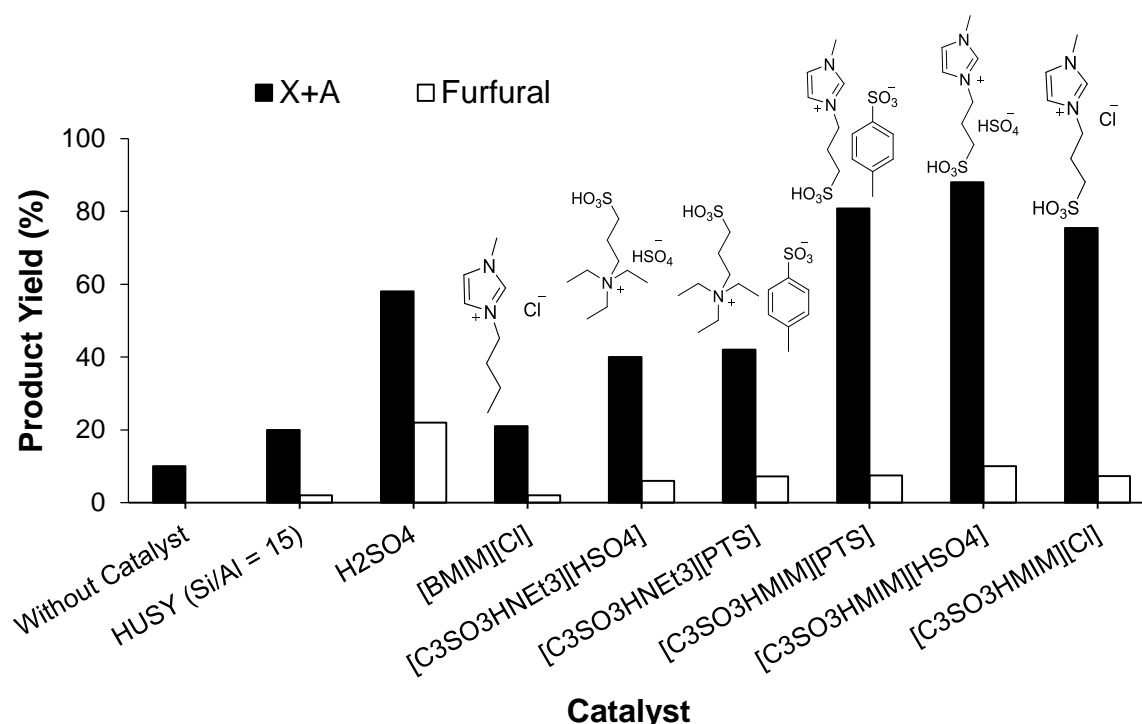


Figure 4.3. Catalyst evaluation study for the selective conversion hemicellulose from MH BG crop waste into C5 sugars; Reaction condition. hemicellulose 2 g, catalyst 0.24 g, water 60 mL, 160 °C, 1 h.

The catalyst evaluation study carried out for MH BG crop waste showed that [C₃SO₃HMIM][HSO₄] BAIL performs better compared to all other BAILs. The reason for this is explained in Chapter-3A (section 3A.3.2.). Also, the [C₃SO₃HMIM][HSO₄] BAIL showed higher C5 sugar yield compared with HUSY (Si/Al=15) solid acid and H₂SO₄ mineral acid catalyst.

Apart from C5 sugars formation, C6 sugar (glucose and fructose, 3-4%), furfural (6-10%) and HMF (2-3%) yields were seen. However, no any aromatic products derived from lignin was observed which indicates that selectively pentosan part of crop waste was converted into C5 sugars.

4.4.2. Effect of crop waste on the selective conversion of hemicellulose from crop waste into C5 sugars

After obtaining an exceptionally high yield of C5 sugars (88%) from MH BG crop waste using [C₃SO₃HMIM][HSO₄] BAIL, reactions were attempted with a wide range of crop wastes as shown in Fig. 4.4. The reactions were carried out using [C₃SO₃HMIM][HSO₄] BAIL as a catalyst because this catalyst was the best catalyst understood from the catalyst evaluation study (section 4.4.1.). All these reactions were carried out at 160 °C for 1 h in a water medium (60 mL). The result showed that almost all types of crop wastes could be efficiently converted into C5 sugars. The yields of C5 sugars were calculated based on pentosan present in crop waste (Table 4.2.). All the experiments were repeated 3 times and the error in the yields of C5 sugars was ±3%.

The method used for converting crop wastes such as bagasse, rice husk, wheat straw, corn cob, cotton stalk into C5 sugars is important because the catalytic amount of [C₃SO₃HMIM][HSO₄] BAIL (0.24 g) was used for reaction without addition of any mineral acid and metal halide. Furthermore, the hemicellulose present in crop waste was converted into C5 sugars, and the lignin present in crop waste was not undergoing any change. This developed method can have scope for the synthesis of C5 sugars in very high yield from pentosan rich crop waste.

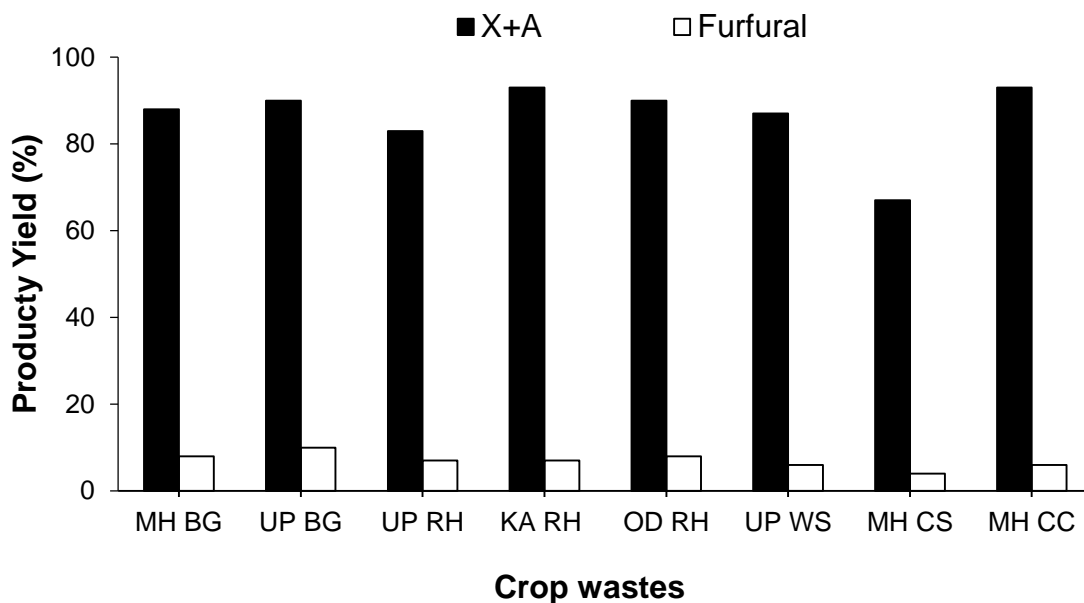


Figure 4.4. Effect of crop wastes on the selective conversion of hemicellulose from crop wastes into C5 sugars; Reaction condition. crop waste 2 g, water 60 mL, $[C_3SO_3HMIM][HSO_4]$ 0.24 g, 160, 1 h.

Abbreviation; Maharashtra Bagasse (MH BG); Uttar Pradesh Bagasse (UP BG); Uttar Pradesh Rice Husk (UP RH); Karnataka Rice Husk (KA RH); Odisha Rice Husk (OD RH) Uttar Pradesh Wheat Straw (UP WS); Maharashtra Cotton Stalk (MH CS); Maharashtra Corn Cob (MH CC).

4.4.3. Effect of substrate on the selective conversion of hemicellulose from crop waste into furfural

After selectively converting hemicellulose from crop wastes into C5 sugars using $[C_3SO_3HMIM][HSO_4]$ BAIL successfully, the $[C_3SO_3HMIM][HSO_4]$ BAIL was exploited for the selective conversion of hemicellulose from crop waste into furfural. Dilute substrate systems were used for this reaction as it is learnt from Chapter-3B section 3B.2.6. that for achieving better yield of furfural dilute hemicellulose substrate concentration is required. The reactions were carried out with 0.6 g crop wastes and 0.12 g $[C_3SO_3HMIM][HSO_4]$ BAIL in water+toluene biphasic solvent system as is presented in Fig. 4.5. The reactions were carried out with various crop wastes at 170 °C, for 3 h and the result shows that almost all types of crop wastes were successfully converted into furfural with very high yield (73-88%). Rice husk collected from different places of India such as Karnataka, Uttar Pradesh, and Odisha showed >80% furfural yield while the bagasse collected from Maharashtra and Uttar Pradesh

showed 73 and 76% furfural yield along with 22 and 15% C5 sugar yield, respectively. Finally, the wheat straw collected from Uttar Pradesh showed 78% furfural yield along with 20% C5 sugar yield.

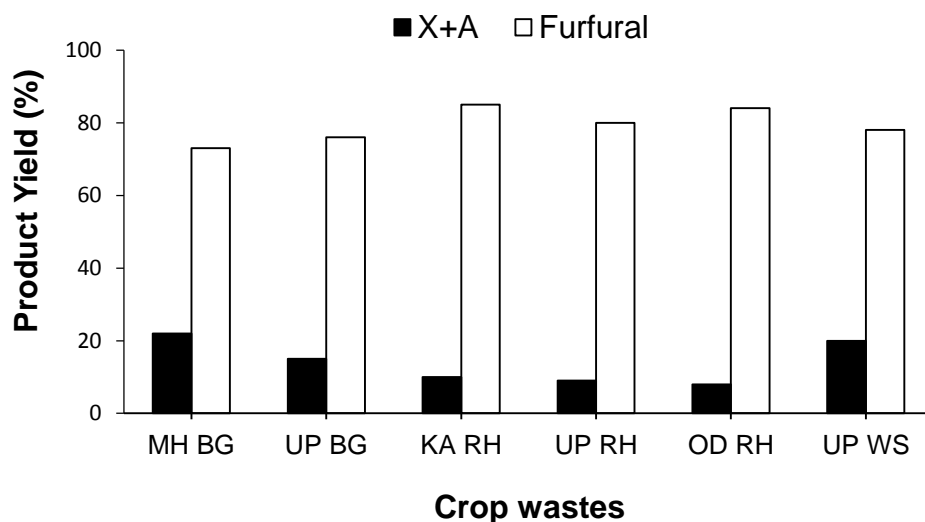


Figure 4.5. Influence of crop wastes on the selective conversion of hemicellulose from crop wastes into furfural; Reaction condition. crop waste 0.6 g, $[C_3SO_3HMIM][HSO_4]$ 0.12 g, Water+Toluene 60 mL (1:5 v/v), 170 °C, 3 h.

Abbreviation: Maharashtra Bagasse (MH BG); Uttar Pradesh Bagasse (UP BG); Karnataka Rice Husk (KA RH); Uttar Pradesh Rice Husk (UP RH); Odisha Rice Husk (OD RH); and Uttar Pradesh Wheat Straw (UP WS).

In the selective conversion of hemicellulose from MH BG crop waste into furfural reaction >99% conversion of pentosan was obtained. 73% furfural yield along with 22% C5 sugars was seen. On the other hand, cellulose and lignin are intact because no any products derived from cellulose and lignin were found in substantial amount. This showed that selectively hemicellulose was converting into furfural and sugars. In these reactions, >98% mass balance was obtained as is understood from the mass of solid recovered after reaction. 0.6 g MH BG (which contains 0.145 g pentosan) was used for the reaction and after reaction 0.451 g of solid was recovered this shows that only pentosan was converting and all other part such as cellulose and lignin is remain intact in presence of $[C_3SO_3HMIM][HSO_4]$ BAIL.

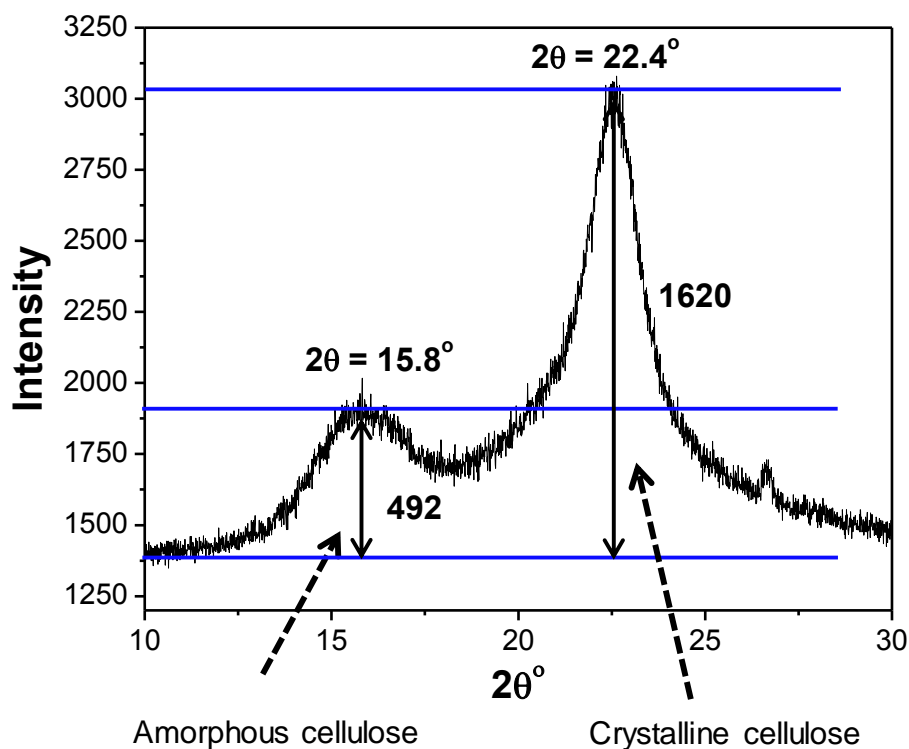
The $[C_3SO_3HMIM][HSO_4]$ BAIL could convert hemicellulose selectively into C5 sugars and/or furfural from crop wastes in a one-pot method and showed a very good yield of both C5 sugars and/or furfural. The catalytic amount of BAIL was used without any

additional mineral acid and metal halide for the conversion of hemicellulose present in crop waste.

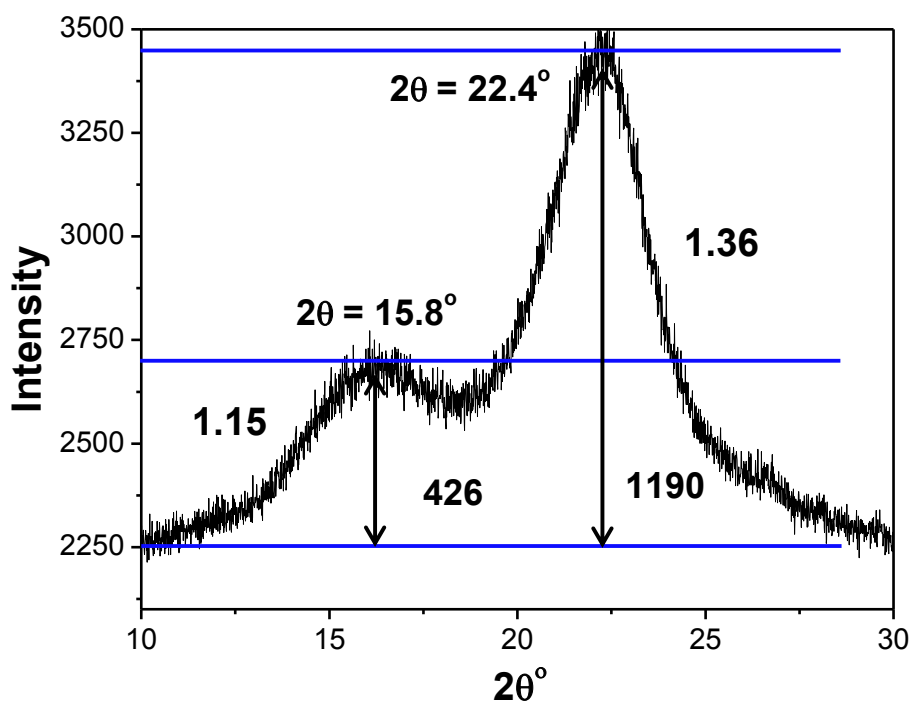
4.4.4. Selective conversion of pentosan and pretreatment of cellulose

The pentosan present in crop waste was completely converted into C5 sugars and furfural using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAILs. Along with C5 sugars and furfural, 4-6% yield of C6 sugars (glucose and fructose), was also seen when reaction temperature and time increased to 170 °C and 3 h. This shows that cellulose was converting into sugars when reaction temperature and time is increased. To understand how much is exactly the cellulose conversion from crop waste the reaction of pure microcrystalline cellulose (Aldrich, USA) was performed under similar reaction condition (170 °C, 3 h) using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL, and the result showed 10% cellulose conversion with 7% product yield (glucose, fructose and HMF).

To understand the change in crystallinity (under reaction condition) of cellulose present in crop waste such as bagasse, XRD study was carried out for fresh MH BG and solid recovered after reaction of MH BG. The XRD of fresh MH BG shows peaks for amorphous and crystalline cellulose at 15.8° and 22.4° (Fig. 4.6., a). Similarly, the XRD of solid obtained after reaction (conversion of MH BG at 170 °C, 3h using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL) was taken and again the result showed peaks for amorphous and crystalline cellulose but in this case, the intensity of both the peaks was decreased. In the XRD of pure bagasse, the intensity of peaks due to amorphous and crystalline cellulose are 492 ($2\theta=15.8^\circ$) and 1620 ($2\theta=22.4^\circ$) on the other hand the intensity of these peaks for solid obtained from bagasse reaction was 426 ($2\theta=15.8^\circ$) and 1190 ($2\theta=22.4^\circ$). Further, the ratio of decrease in intensity of amorphous and crystalline peaks was calculated and it is shown in Fig. 4.6., b. The intensity of crystalline peak decreases much higher (1.36) compared to the intensity of peak due to amorphous peak (1.15). This shows that the crystallinity of cellulose decreases under reaction condition in the presence of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL. The process used for the recovery of solid for XRD analysis is explained as; the 0.6 g MH BG crop waste was used for the reaction, after reaction solid was separated using filtration. The solid (0.44 g) recovered from reaction mixture was then dried at 60 °C for 16 h. Next, the solid was vacuum dried at 100 °C for 12 h and then it was used for XRD analysis.



a) XRD of Fresh MH BG



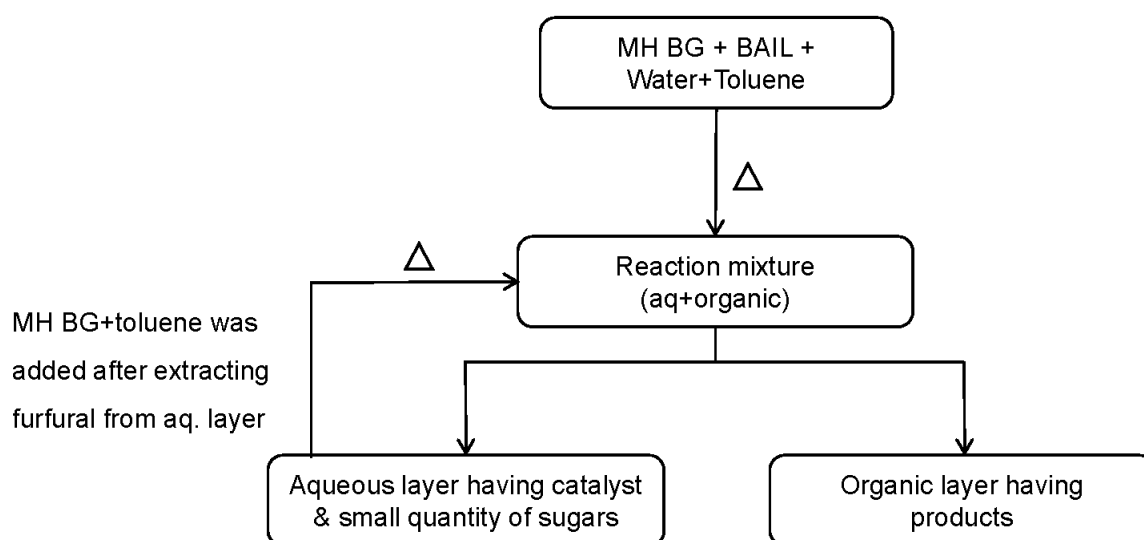
b) XRD of Recovered MH BG

Figure 4.6. XRD of Fresh and recovered MH BG from the reaction of selective conversion of hemicellulose; Reaction condition. Maharashtra Bagasse (MH BG) 2 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.24 g, water 60 mL, 170 °C, 3 h.

The ionic liquids were used for the pretreatment of cellulose to decrease crystallinity of cellulose. The [BMIM][Cl] IL (2 g) is used for the pretreatment of cellulose (0.1 g) at 100 °C, which decreases the crystallinity of cellulose.^[14-15] By carrying out pretreatment of cellulose using ionic liquid its solubility in reaction solution can be increased and hence cellulose was hydrolyzed in presence of an acid catalyst. However, for the pretreatment of cellulose very large catalyst quantity (IL) was reported in the literature (2 g IL for 0.1 g isolated cellulose). In present work it can be understood that catalytic amount of BAIL such as [C₃SO₃HMIM][HSO₄] can decrease the crystallinity of cellulose present in crop waste.

4.4.5. Recycle study for [C₃SO₃HMIM][HSO₄] BAIL

The procedure used for the recycling of the catalyst and the recycle run is shown in Scheme 4.2. and it is discussed below.



Scheme 4.2. Process for recycling study for the selective conversion of hemicellulose from MH BG into furfural.

Catalyst recycle studies were performed with [C₃SO₃HMIM][HSO₄] BAIL as a catalyst. After the 1st reaction, the solid present in reaction mixture was separated using filtration and then the toluene and water layers were separated using a separating funnel. The furfural is soluble in toluene while, the [C₃SO₃HMIM][HSO₄] BAIL is not soluble in toluene. Small amount of furfural which is soluble in aqueous layer was extracted using fresh toluene solvent (3 times extraction). The aqueous

layer then left contains soluble IL and small amount of sugars. This water containing IL was then used for the next reaction. Subsequent reactions were carried out by decreasing the substrate and solvent quantity (for keeping S/C ratio and S/solvent ratio constant). As the quantity of aqueous layer decreases in every subsequent reaction, accordingly the substrate and solvent quantity were changed. The C5 sugars present in aqueous layer was considered for calculating furfural yield.

The recycle study was carried out for the selective conversion of hemicellulose from crop waste into furfural from Maharashtra bagasse using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst and the results are presented in Fig. 4.7. The reactions were carried out at 170 °C for 3 h in water+toluene bi-phasic solvent system. For all the reactions the substrate to catalyst ratio was kept constant. The recycle run showed an almost similar yield of furfural in 4 reaction runs. In the 1st recycle run (reaction run 2) 69% furfural yield was obtained and in second and third recycle runs (reaction runs 3 and 4) 70 and 67% furfural yield were obtained, respectively. In all reactions 18-22% C5 sugar yield was obtained.

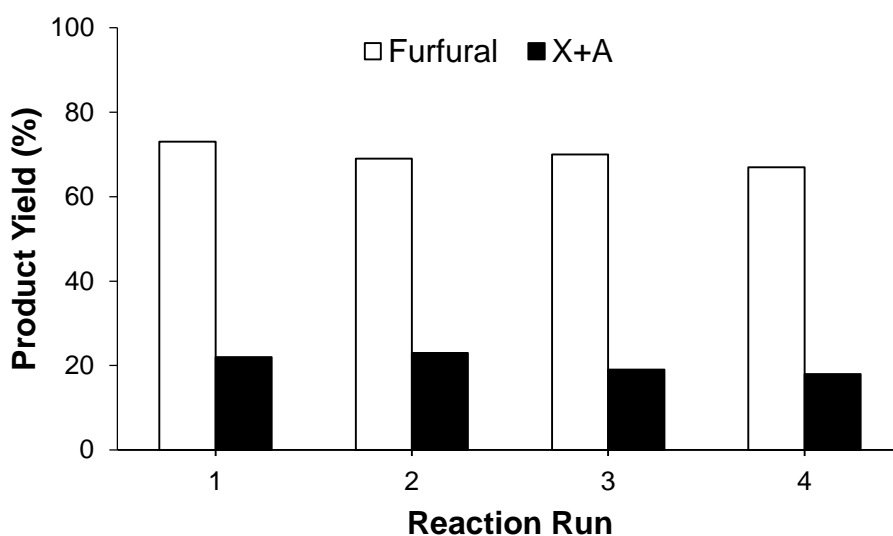


Figure 4.7. Recycle study for $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL on the selective conversion of hemicellulose from MH BG into furfural; Reaction condition; MH BG/ $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 4.8 wt/wt, Water+Toluene 1:5 v/v, 170 °C, 3 h.

4.4.6. Metal exchange study

As the BAILs used in the current study are acidic in nature because of presence of $-\text{SO}_3\text{H}$ group, there may be a possibility that H^+ of BAILs can be exchanged with the metals which are present in the crop waste. This exchange can destroy the acid sites

of BAIL and hence, to understand whether any exchange of H⁺ of BAILs is possible by metal ion, the reaction mixture (selective conversion of hemicellulose from MHBG into furfural using [C₃SO₃HMIM][HSO₄] BAIL) and the solid obtained after reaction were analyzed using ICP-OES technique. The results for this analysis are presented in Table 4.4. The result showed that there are some metal nutrients which are present in the reaction solution such as 0.01 mmol/g of K and Ca. The solid obtained after reaction was analyzed using ICP-OES and showed the presence of remaining metal nutrients (Table 4.4.).

The total quantity of metal nutrients present in MH BG is very small (0.06 mmol for 0.6 g MH BG) compared to the quantity of BAIL (0.4 mmol) used in the reaction. ICP-OES results showed that K and Ca were found in reaction solution but their quantity is very less (0.01 mmol/g for K and 0.01 for Ca (0.012 mmol K Ca for 0.6 g MH BG)) compared to [C₃SO₃HMIM][HSO₄] BAIL (0.4 mmol). This implies that there is a very less possibility for the considerable exchange of metals with the H⁺ of BAILs and hence BAILs can be recycled and used for the selective conversion of hemicellulose present in crop wastes.

Table 4.4. ICP-OES results for metal exchange study.

Nutrients (mmol/g)	Fresh MH BG	MH BG Rm	MH BG Solid recovered from Rm
Na	0	0	0
K	0.03	0.01	0.02
Ca	0.03	0.01	0.02
Mg	0.02	0	0.02
Al	0.01	0	0.01
P	0.01	0	0.01

ICP-OES analysis; calculations were done based on 1 g of MH BG. MH-BG, Maharashtra bagasse; Rm, reaction mixture.

4.4.7. Conclusion

In Chapter-3A and Chapter-3B, conversion of hemicellulose into C5 sugars and furfural is performed using BAILs. In present chapter the study is extended for the selective conversion of hemicellulose present in crop wastes into C5 sugars and/or furfural using BAILs. The [C₃SO₃HMIM][HSO₄] BAIL showed the best results

compared to all other ILs used for the selective conversion of hemicellulose from crop waste into C5 sugars and/or furfural. In the selective conversion of hemicellulose from MH BG crop waste into C5 sugars using [C₃SO₃HMIM][HSO₄] BAIL, 88% C5 sugar yield was obtained at 160 °C within 1 h. On the other hand, HUSY (Si/Al=15) solid acid and H₂SO₄ showed 20 and 58% C5 sugar yields, respectively. This shows that [C₃SO₃HMIM][HSO₄] BAIL is better catalyst compared to HUSY (Si/Al=15) solid acid and H₂SO₄ mineral acid. Moreover, a wide range of substrates were used in this study and the results showed that almost all types of crop wastes were efficiently converted into C5 sugars with an exceptionally high yield (67-93%).

The [C₃SO₃HMIM][HSO₄] BAIL was also used in the selective conversion of hemicellulose from crop wastes into furfural. A wide range of crop wastes were used for the reaction and very high yields of furfural (73-85%) were obtained. The novelty of this study is that the hemicellulose present in crop wastes were efficiently converted into C5 sugars and/or furfural using the catalytic amount of BAIL without using any mineral acid and metal halides. The [C₃SO₃HMIM][HSO₄] BAIL used for the conversion of hemicellulose from crop wastes into furfural showed good recyclability up to three recycle runs.

4.4.8. References

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Chapter 5

**Dehydration of C6 & C5 Sugars into
HMF & Furfural using Brønsted
Acidic Ionic Liquids**

5.1. Introduction

The furan derivatives, 5-hydroxymethylfurfural (HMF) and furfural are of great importance since those have many industrial applications and their further conversion can yield a range of industrially important chemicals.^[1-2] It is known that HMF upon oxidation yields 2,5-furandicarboxylic acid (FDCA),^[3-4] which has a potential to replace terephthalic acid in polymer synthesis.^[5-6] Hydrogenation of HMF to yield 2,5-dimethyl furan which has a potential application as a fuel is also known.^[7] Moreover, HMF can also act as raw material to synthesize many significant chemicals such as levulinic acid, γ -valerolactone, alkyl levulinate etc.^[8-10] The hydrogenation of furfural gives furfuryl alcohol and tetrahydrofuran as products which are known as solvents and starting compounds in the synthesis of a variety of chemicals.^[11-12] Furfural itself has applications in several industries like Lube oil refining, pharmaceuticals and in the manufacture of phenolic resins.^[13-14]

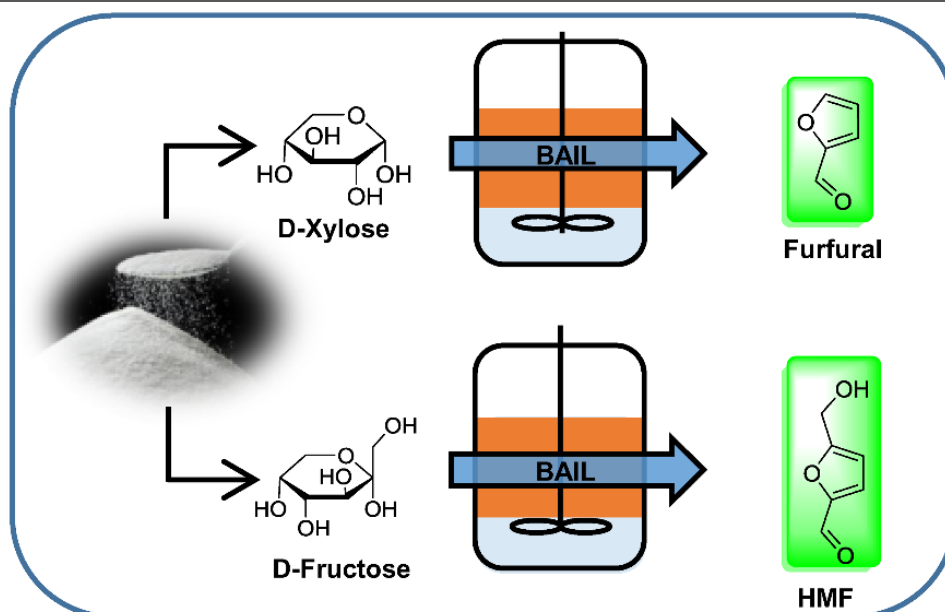
In view of this importance of furans, acid catalyzed methods are being developed for their synthesis from C5 and C6 sugars.^[15-19] The use of several solid acid catalysts such as, acidic resins (Dowex 50wx8-100, acetone/DMSO; Amberlyst-15, DMF),^[20-21] heteropolyacids (Keggin-type heteropolyacids ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$), DMSO),^[22-23] zeolites (del-Nu-6(1), water/toluene),^[24] sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$, acetone/water),^[25] etc. are investigated for the synthesis of HMF. Synthesis of furfural from xylose using few of the above mentioned catalysts is also known.^[24, 26-27] However, it is difficult to achieve higher furan yields since furans are prone to undergo polymerization and degradation reactions to yield humins, levulinic, and formic acid etc.^[16] Few of the studies use aprotic high boiling solvents such as DMSO and DMF to achieve higher yields of furans but the separation of products from these high boiling solvents is very difficult.^[21] To overcome the problem associated with high boiling solvents and to improve the yields of furans, use of bi-phasic solvent systems is reported in the literature.^[28-30]

Recently, use of ionic liquids (ILs) as a solvent and/or catalyst is increasing due to their unique tunable properties such as low vapor pressure, stability, polarity, recyclability etc. The conversion of cellulose, starch and inulin to yield glucose, HMF and furfural is reported using ILs (as solvents) such as, [EMIM][BF₄], [BMIM][Cl], [EMIM][Cl] and [EMIM][HSO₄].^[31-36] In the synthesis of HMF from either fructose or

glucose, use of several catalysts such as, CrCl_3 ,^[31, 37-40] SnCl_4 ,^[33] HCl ,^[41] PTSA,^[42] Amberlyst-15,^[42] WCl_6 ,^[43] lanthanide chlorides,^[44] boric acid^[45] along with ILs as solvent is reported. Since the main purpose of using ILs in these reactions is to dissolve the substrate, it has been used in very high quantities (1-5 times to that of substrate). Use of ILs along with mineral acid (HCl) to yield dehydration products is also known.^[46] Additionally, use of homogeneous organic acids (citric, malonic and oxalic) or insoluble organic acid resins (Amberlyst-15) together with ILs [EMIM][HSO_4] as a solvent in fructose dehydration reaction into HMF is also reported.^[47] In yet another report, use of [BMIM][HSO_4] for fructose conversion into HMF in the presence of metal chloride as a catalyst is shown.^[48] Few more reports also show the possibility of use of imidazolium based ionic liquids for the synthesis of HMF from fructose or glucose under varying reaction conditions.^[49-50]

Though, use of ILs in these reactions (primarily as solvent) is shown to be beneficial, but due to their high cost and high viscosity (limited interaction between catalyst and substrate), those cannot be used on higher scales. To overcome these disadvantages, it would be desirable to use ILs in small quantities dissolved in water or water-organic solvent systems. Moreover, it is advantageous if the use of metal salts is avoided. Considering these points, it was anticipated that ILs with acidic characteristics might prove to be standalone catalysts (without an addition of extra catalyst) to catalyze dehydration reactions in the bi-phasic solvent system. Further, most of the earlier studies have been carried out using low substrate concentrations (2-3.5 wt%) since at higher concentrations, the formation of undesired products is seen.^[51] However, industry demands use of concentrated substrate systems to make the overall process economical and hence efforts should be taken to develop methods with high substrate concentrations.

After understanding the various aspects mentioned above, in this chapter, the method for the dehydration of fructose and xylose into HMF and furfural is described using standalone (without using any additional catalysts) Brønsted acidic ionic liquids (BAILs). The dehydration of C5 and C6 sugar is shown in Scheme 5.1.



Scheme 5.1. Dehydration of D-xylose and D-fructose into furfural and HMF using BAILs.

5.2. Experimental

5.2.1. Material and methods

The ILs used for the sugar dehydration reactions were synthesized and characterized with the help of various characterization techniques (chapter 2, section 2.4.). The chemicals required for the synthesis of ionic liquids were procured from various sources as it is mentioned in Chapter 2 (section 2.2.). While solvents such as toluene and MIBK were purchased from Spectrochem (India) and Loba Chemie (India), D-fructose (AR grade; purity 99%), D-glucose (AR grade; purity 99%), D-xylose (AR grade; purity 99%), and furfural (AR grade; purity 99%) were also purchased from Loba Chemie (India). *p*-nitroaniline (AR grade; purity 99.5%) was purchased from Thomas Baker (India), and HMF (>99% purity) was purchased from Aldrich Chemicals (USA). All the chemicals were used as received. Zeolites, H β (Si/Al=19), HUSY (Si/Al=15), HMOR (Si/Al=10) were procured from Zeolyst International (USA). Prior to use, zeolites were calcined at 550 °C for 16 h in an air flow. Amberlyst-15 was purchased from Aldrich Chemicals (USA) and before use was dried at 80 °C for 2 h.

5.2.2. Catalytic runs and analysis of reaction mixture

Catalytic and non-catalytic fructose dehydration reactions were carried out in batch mode autoclave (Parr reactor; 50 mL). For performing reactions; fructose (0.5 g), solvent (water+MIBK; 1:5 v/v; 30 mL) and catalyst were charged in the batch mode

autoclave and reactions were carried out at various temperatures (140 to 160 °C) and various time intervals (20 min to 1 h). For all the reactions 100 rpm stirring speed was used before attaining the desired reaction temperature, and after attaining the desired temperature, stirring speed was increased to 800 rpm. After completion of the reaction, the reactor was allowed to cool and finally the reaction mixture was analyzed using high pressure liquid chromatography (HPLC) and gas chromatography (GC) instruments.

Similarly, for performing xylose dehydration reactions, 300 mL batch mode autoclave (Parr reactor) was used. The reactor was charged with substrate (xylose, 0.6 g), solvent (water+toluene; 1:5 v/v; 60 mL) and catalyst, and then the reaction mixture was heated to the desired temperature under stirring (100 rpm). After attaining the desired reaction temperature, stirring was increased to 800 rpm. After completion of the reaction, the reactor was cooled to room temperature and the reaction mixture was analyzed using HPLC and GC instruments.

5.2.3. Analysis of reaction mixture

The analysis of aqueous phase of both the reactions (fructose and xylose dehydration reactions) was done using high pressure liquid chromatography (HPLC) instrument. HPLC (Agilent Technology 1260 infinity) was equipped with Pb²⁺ column (Rezex RPM-Monosaccharide, dimensions 300 x 7.8 mm; particle size 8 µm) having 80 °C column temperature and refractive index detector (RID) maintained at 40 °C. The Millipore water was used as an eluent with a flow rate of 0.5 mL/min. The sample used for analysis was filtered through 0.22 µm syringe filter and 10 µl sample was injected for each analysis.

The organic phase of the reaction mixture was analyzed using Agilent 7890B Gas Chromatography (GC) system, equipped with HP-5 column (50 m × 0.22 µm ID) and flame ionization detector (FID; 280 °C). The oven program used for analysis has 100 °C temperature at the start of analysis which is increased with a ramping of 7 °C/min up to 250 °C and finally this temperature was hold for 3 min. The flow rates of H₂, Air and N₂ were 30 mL/min, 300 mL/min and 20 mL/min respectively. All samples were filtered through 0.22 µm syringe filter before analysis.

5.2.4. Calculation

For the calculation of conversion and product yield, calibration curves were drawn using commercially procured compounds. From calibration curve, the slope was calculated and it was used for the calculation of conversion and yield.

$$\text{Conversion of substrate (\%)} = \frac{[\text{Initial substrate, mol}] - [\text{Final substrate, mol}]}{[\text{Initial substrate, mole}]} \times 100$$

$$\text{Product yield (\%)} = \frac{[\text{Product formed, mole}]_{(\text{GC}[\text{Org}] + \text{HPLC}[\text{water}])}}{[\text{Theoretical moles of product}]} \times 100$$

5.3. Results and discussion

5.3.1. Dehydration of Fructose into HMF

5.3.1.1. Catalyst evaluation for the dehydration of fructose into HMF

Fructose dehydration reactions (0.5 g fructose in 5 mL water; 10 wt% solutions) were carried out with different BAILs at 150 °C for 30 min using water+MIBK (1:5 v/v) solvent system and the catalytic results are presented in Fig. 5.1. As seen from the Fig. 5.1, with [C₃SO₃HMIM][HSO₄] BAIL as a catalyst, maximum HMF yield of 73% was obtained with 87% selectivity. The other BAILs used in the reaction also showed good HMF yields ([C₃SO₃HMIM][PTS], 55% yield with 65% selectivity; [C₃SO₃HMIM][Cl], 50% yield with 66% selectivity).

The [BMIM][Cl] IL catalyst was used in this reaction for understanding the contribution of Brønsted acidity of IL. The [BMIM][Cl] IL used was not having any Brønsted acidity and shows only 3% HMF yield while a similar type of IL having Brønsted acidity such as [C₃SO₃HMIM][Cl] BAIL catalyst shows 50% HMF yield. This shows that Brønsted acidity is playing an important role in the fructose dehydration reaction. Under similar reaction conditions, in the absence of a catalyst, 9% conversion was seen, and no HMF formation was observed, which means that fructose is yielding some side products which were not detected by GC and HPLC.

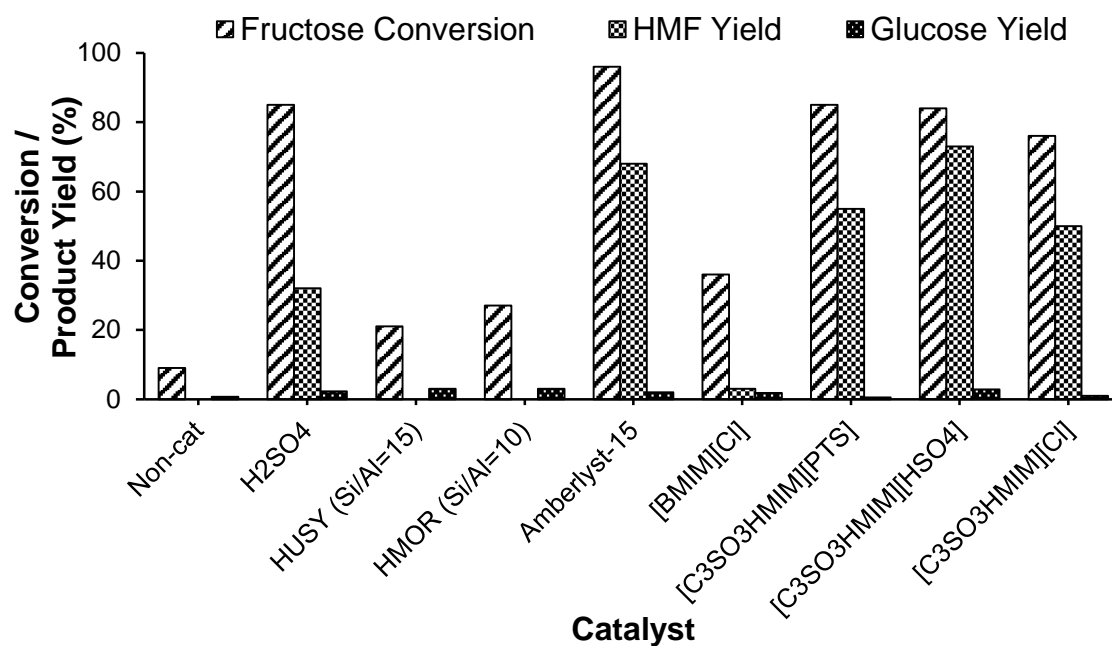


Figure 5.1. Catalyst evaluation studies on the dehydration of fructose into HMF; Reaction condition. fructose 0.5 g, catalyst 0.025 g, Water+MIBK 30 mL (1:5 v/v), 150 °C, 30 min.

A careful look at the data (Fig. 5.1.) suggests that although with all the catalysts, except with [BMIM][Cl], 80 ± 5% conversion of fructose was observed, the difference in the HMF yields is notable. This implies that for achieving higher selectivity for HMF, [C₃SO₃HMIM][HSO₄] BAIL was the best catalyst. This phenomenon can be explained based on the difference in the acid amount ([C₃SO₃HMIM][PTS], 2.65 mmol/g; [C₃SO₃HMIM][HSO₄], 6.61 mmol/g of H⁺; [C₃SO₃HMIM][Cl], 4.15 mmol/g of H⁺) as same quantity (0.025 g) of ILs is charged. To substantiate this possibility, reactions with [C₃SO₃HMIM][PTS] and [C₃SO₃HMIM][Cl] BAILs were carried out using 0.05 g of catalyst (S/C=10 wt/wt) instead of 0.025 g (S/C=20 wt/wt) at 150 °C for 30 min. The increase in HMF yield to 72% with [C₃SO₃HMIM][PTS] (76% selectivity) and 73% with [C₃SO₃HMIM][Cl] (77% selectivity) along with slight improvement in selectivity was seen. Since with [C₃SO₃HMIM][PTS] and [C₃SO₃HMIM][Cl] catalysts, an increase in HMF yields was seen when reactions were carried out for higher catalyst loading (S/C=10 wt/wt). Then [C₃SO₃HMIM][HSO₄] catalyst was also evaluated under the similar reaction condition (S/C=10 wt/wt). Nevertheless, the result with [C₃SO₃HMIM][HSO₄] shows lower HMF yield (61%) after 30 min due to the formation of side products (dark color solution with char formation). These results imply that though yields can be

increased by maintaining an almost same concentration of H⁺ (0.1 to 0.2 mmol) in all the ILs, but to achieve the highest selectivity, [C₃SO₃HMIM][HSO₄] is necessary. Also, It is observed that [C₃SO₃HMIM][HSO₄] (*Ho*, 2.08) has higher acid strength than [C₃SO₃HMIM][PTS] (*Ho*, 2.33) and [C₃SO₃HMIM][Cl] (*Ho*, 2.47) (Chapter 2, Table 2.5.) and this may be helping to achieve higher yield/selectivity.

Furthermore, reactions carried out with mineral acid (H₂SO₄) and solid acid catalysts such as zeolites (HUSY (Si/Al=15), HMOR (Si/Al=10)) and ion exchange resin (Amberlyst-15) showed lower HMF yield compared to BAILs. The detailed discussions on the comparison of BAIL with solid acid catalysts and mineral acid catalyst are made in section 5.3.2.

5.3.1.2. Effect of solvent

Since [C₃SO₃HMIM][HSO₄] BAIL catalyst showed best yields (73%) with high selectivity (87%), the influence of solvent system on the HMF synthesis was studied with water, water+MIBK (1:5 v/v) and water+toluene (1:5 v/v) solvent system. The reactions were carried out at 150 °C for 30 min and it was observed that the maximum HMF yield (73%) was obtained with the water+MIBK solvent system. While, with the water+toluene solvent system, 39% HMF yield, and with only water as a solvent, 17% HMF yield (60% selectivity) was observed (Fig. 5.2). The calculated ratio of presence of HMF in MIBK and water layers was, 4.21 (HMF yield in MIBK 59% and in water 14%) while it was 0.45 (HMF yield in toluene 12% and in water 27%) in the case of toluene and water. This suggests that MIBK solvent is efficient in extracting HMF from water than toluene solvent and hence higher HMF yield was obtained with the water+MIBK solvent system.

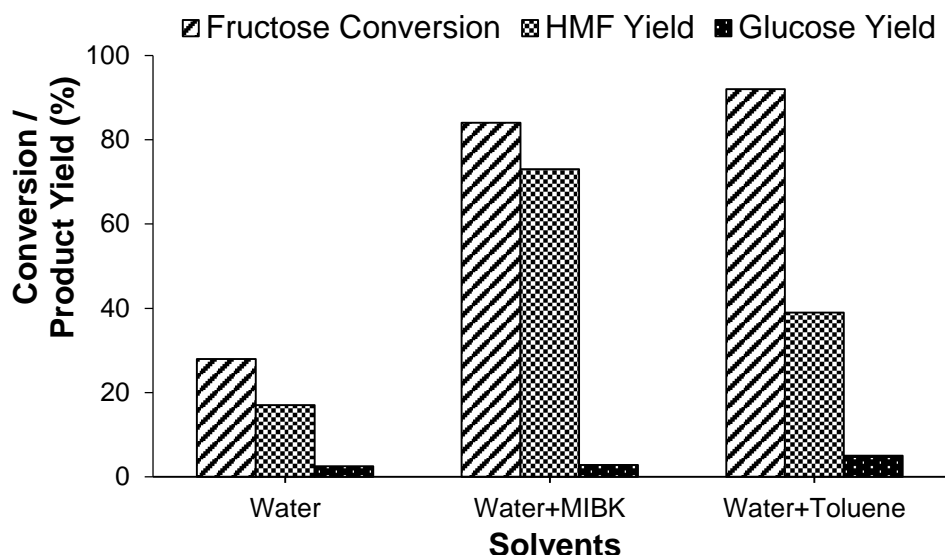


Figure 5.2. Effect of solvent system on the dehydration of fructose using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst; Reaction condition. fructose 0.5 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.025 g, solvent 30 mL (for bi-phasic solvent, water:organic solvent; 1:5 v/v) 150 °C, 30 min.

Subsequently, effect of water+MIBK solvent ratio was studied using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL and it was seen that with increase in MIBK solvent in water, enhancement in the HMF yields is possible (water+MIBK (v/v) = 1:1, 12%; 1:2, 24%; 1:3, 40%; 1:5, 73%). However, further increase in ratio to 1:7 (v/v) did not show any increase in HMF yield (71%). With an increase in the water+MIBK solvent ratio above 1:7 and by keeping similar catalyst loading (0.025 g), increased the catalyst ($[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$) concentration in water, which might enhance the possibility of degradation reactions and this can cause a decrease in HMF yield.

5.3.1.3. Effect of catalyst and substrate concentration

Typically reactions were carried out with S/C ratio of 20 (wt/wt) (fructose 0.5 g; IL 0.025 g). In order to study the effect of catalyst concentration, reactions were carried out with S/C (wt/wt) = 10, 20 and 40 after keeping solvent (30 mL) and substrate (0.5 g) quantity constant in all reactions. The results are presented in Fig. 5.3. When S/C ratio was maintained at 10 (wt/wt) ($[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$, 0.05 g), $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ catalyst gave 61% HMF yield (67% selectivity) after 30 min. However, when S/C ratio was maintained at 20 (wt/wt), an increase in HMF yield to 73% (87% selectivity) was seen. Further increase in S/C ratio to 40 (wt/wt) ($[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$, 0.0125 g), yielded 50% HMF (70% selectivity). The decrease in

yield at higher S/C ratio of 40 (wt/wt) is due to the insufficient catalyst in the system. On the other hand, the decrease in HMF yield (61%) at S/C ratio of 10 (wt/wt) was observed because of higher catalyst concentration in the reaction system which can increase the possibility of degradation reaction and thus can show decrease in HMF selectivity (67%).

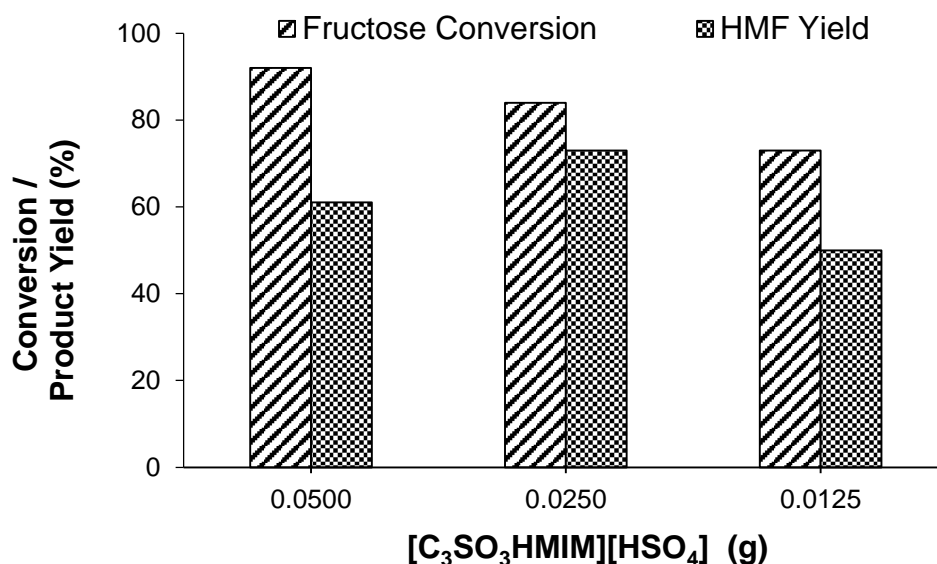


Figure 5.3. Effect of [C₃SO₃HMIM][HSO₄] BAIL catalyst concentration on the dehydration of fructose; Reaction condition. fructose 0.5 g, catalyst [C₃SO₃HMIM][HSO₄], Water+MIBK 30 mL (1:5 v/v), 150 °C, 30 min.

Next, reactions were done at 150 °C for 30 min by varying fructose concentration and keeping the catalyst (0.025 g) and solvent (water+MIBK=30 mL) quantity constant. When the reaction was done using 5 wt% of fructose solution (0.25 g), 53% yield (60% selectivity) for HMF was observed. On the contrary, when 10 wt% fructose solution (0.5 g) was used, 73% yield (87% selectivity) was seen (Fig. 5.4.). But with the increase in fructose concentration to 20 wt% (1 g fructose), a decrease in HMF yield (53% yield and 68% selectivity) was observed. Further increase in fructose concentration to 40 wt% (2 g fructose) showed almost similar HMF yield (52% yield and 74% selectivity). When with 40 wt% solution, the reaction was continued for long er time (1 h), 93% conversion with almost similar yield (73%) with 78% selectivity for HMF was seen. This shows that [C₃SO₃HMIM][HSO₄] BAIL can efficiently convert concentrated sugars solution into HMF. Concentrated sugar solution (40 wt%) was efficiently converted into HMF using catalytic amount of BAIL as a catalyst without any metal halide and mineral acid, which shows the economic

importance of developed method compared to reported methods where lower substrate concentrations were used. Similar to S/C ratio study, in case of substrate concentration study also optimum substrate concentration (10 wt%) is required to achieve highest HMF yield (73%) with better selectivity (87%) in shorter reaction time (30 min). With 5 wt% fructose solution, lower selectivity was seen due to the possibility of side reactions catalyzed by excess catalyst (same catalyst quantity is used (0.025 g) in all runs).

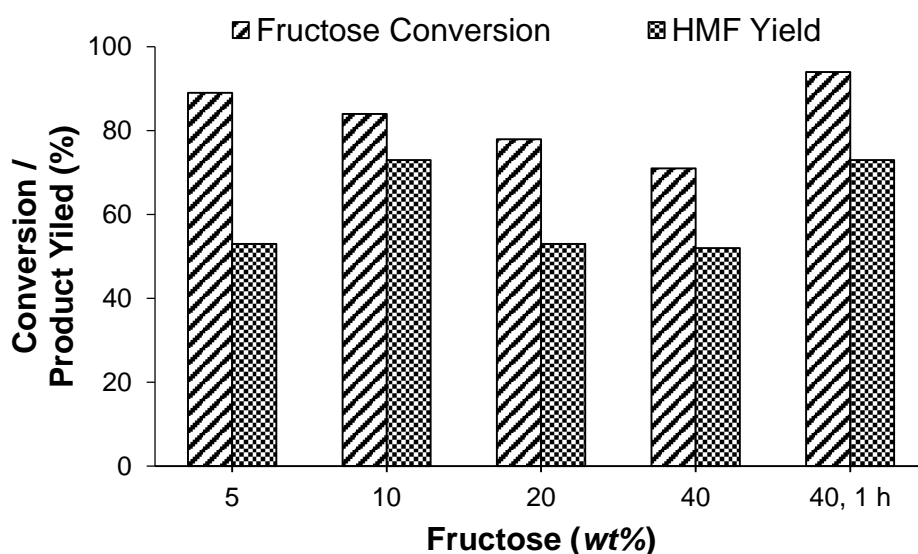


Figure 5.4. Effect of fructose concentration; Reaction condition. $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.025 g, Water+MIBK 30 mL (1:5 v/v), 150 °C, 30 min.

5.3.2. Comparison studies of catalytic activities for the Dehydration of fructose

Comparative studies on the catalytic activities of BAILs with solid acid catalysts $[\text{H}\beta$ (Si/Al=19), HMOR (Si/Al=10) and HUSY (Si/Al=15)] in the fructose dehydration reactions were done, and most of the solid acid catalysts showed no HMF yield compared with BAILs. The higher HMF yield (68%) obtained with Amberlyst-15 catalyst was either due to leaching of $-\text{SO}_3\text{H}$ groups in the solution during the reaction or due to the very high acid amount (4.65 mmol/g) compared with other catalysts (Table 5.1.). However, during recycling study with Amberlyst-15, a decrease in HMF yield (59%) was seen, which suggests that during the first reaction, $-\text{SO}_3\text{H}$ groups were leached in the solution. The other solid acid catalysts used have lower acidity (HMOR, 0.06 mmol H^+ /0.05 g; HUSY, 0.027 mmol H^+ /0.05 g) compared to $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ (0.165 mmol H^+ /0.025 g) and hence no activity was expected. To

overcome this, reactions were carried out with HMOR catalyst by maintaining similar H⁺ concentration (0.165 mmol H⁺, 0.14 g) as like H⁺ concentration of [C₃SO₃HMIM][HSO₄] BAIL and in this reaction 6% HMF yield with 36% fructose conversion was observed after 30 min reaction. To boost the yield, the reaction was carried out at 160 °C instead of 150 °C and 13% HMF yield with 44% fructose conversion was achieved (Table 5.1.). However, the results obtained with [C₃SO₃HMIM][HSO₄] BAIL (73%) are better than HMOR having similar H⁺ concentration. The inferior performance of HMOR than [C₃SO₃HMIM][HSO₄] BAIL is due to potential diffusion constraints in the mono-dimensional pore network of MOR (6.7 x 7 Å), which may restrict access of substrate to acid sites.

Table 5.1. Comparison study for BAILs with solid acid and mineral acid catalysts for the dehydration of fructose.

Sr. No.	Catalyst	Acid amount [mmol/g] ^[a]	HMF yield [%] ^[b]
1	H β (Si/Al= 19)	0.94	0
2	HUSY (Si/Al=15)	0.55	0
3	HMOR (Si/Al=10)	1.2	0
4	HMOR (Si/Al=10)	1.2	6 ^[c]
5	HMOR (Si/Al=10)	1.2	13 ^[d]
6	Amberlyst-15	4.65 ^[e]	68
7	H ₂ SO ₄	20.0 ^[f]	59 ^[g]
8	H ₂ SO ₄	20.0 ^[f]	33
9	H ₂ SO ₄	20.0 ^[f]	47 ^[h]
10	[C ₃ SO ₃ HMIM][HSO ₄]	6.61 ^[f]	73 ^[g]
11	[C ₃ SO ₃ HMIM][PTS]	2.65 ^[f]	72

[a] Acid amount measured by TPD-NH₃.

[b] Fructose 0.5 g, catalyst 0.05 g, 150 °C, 30 min.

[c] Fructose 0.5 g, catalyst 0.140 g, 150 °C, 30 min.

[d] Fructose 0.5 g, catalyst 0.140 g, 160 °C, 30 min.

[e] Acid amount was determined by back titration with 0.01 M NaOH.

[f] Acid amount calculated by considering molecular weight.

[g] Reaction condition; fructose 0.5 g, catalyst 0.025 g, 150 °C, 30 min.

[h] Reaction condition; fructose 0.5 g, catalyst 0.0082 g, 150 °C, 30 min.

As presented in Table 5.1, H₂SO₄ with varying quantities (varying H⁺ concentrations) was used to carry out the dehydration reactions of fructose. With 0.05 g of H₂SO₄ (1.02 mmol H⁺) very low yield of HMF (33%) was seen compared with [C₃SO₃HMIM][HSO₄] BAIL catalyst (73%, 0.165 mmol H⁺). This may be due to a higher concentration of H⁺ in H₂SO₄ reaction, the formation of degradation products would be predominant and thus lower yield was obtained. Hence, reactions were carried out using 0.510 (59%) and 0.165 (47%) mmol of H⁺ to improve the yields of HMF. Still, the [C₃SO₃HMIM][HSO₄] BAIL (73%) showed a better yield of HMF compared with H₂SO₄ (47%) when similar H⁺ concentrations are used.

5.3.2.1. Catalyst recycles study

Catalyst recycle studies were performed with [C₃SO₃HMIM][HSO₄] BAIL as a catalyst. After the 1st reaction, MIBK and water layers were separated using a separating funnel. The HMF is soluble in MIBK while, the BAIL is not soluble in MIBK. HMF which is soluble in aqueous layer was extracted using fresh MIBK solvent (3 times extraction). The aqueous layer left contains soluble ionic liquid and some degradation products formed during the reaction. Next, this aqueous layer was passed through activated carbon to adsorb any degraded products as shown in Fig. 5.5. This water (containing IL) was then used for the next reaction. Three times extraction of HMF from the aqueous layer and after passing this aqueous layer through activated carbon showed 50% decrease in volume. Subsequent reactions were carried out by decreasing the quantity of substrate and solvent (by keeping S/C ratio and S/solvent ratio constant). As the quantity of aqueous layer decreases by 50% accordingly the substrate and solvent quantity were changed.

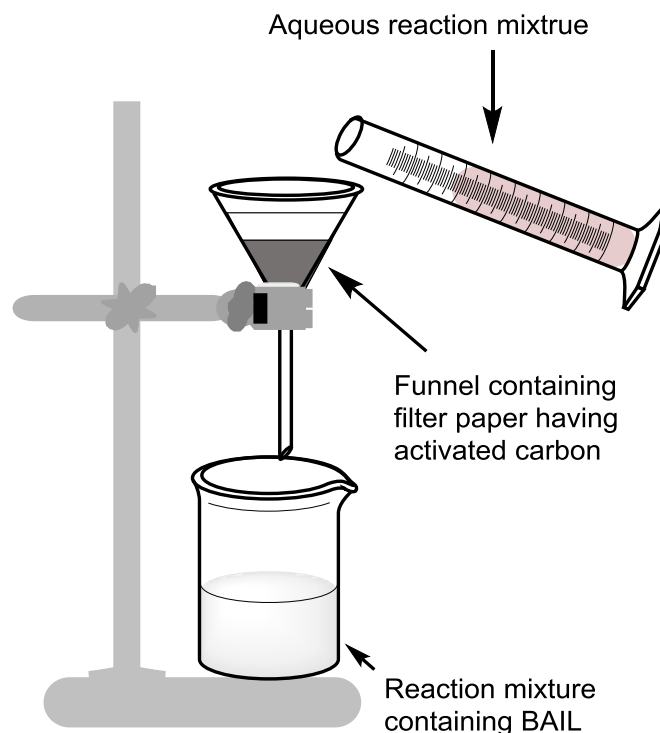


Figure 5.5. Treatment of activated carbon to the aqueous layer of reaction mixture containing catalyst.

To confirm the stability and reusability of the BAILs, recycle study of the $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst was performed in fructose dehydration reaction. The result showed HMF yield of 73-66% [73% (1st run), 73% (2nd run), 70% (3rd run), 68% (4th run), 66 (5th run) and 66 (6th run)] was achieved (Fig. 5.6.). This shows that the catalyst is recyclable, with a small decrease in activity. The small decrease in HMF yield was observed because these reactions were carried out for different volumes. Also, there are some degradation products which were increased in subsequent reactions, because of this in aqueous layer there is an increase in degradation products, which might favour some side reactions and shows a decrease in activity.

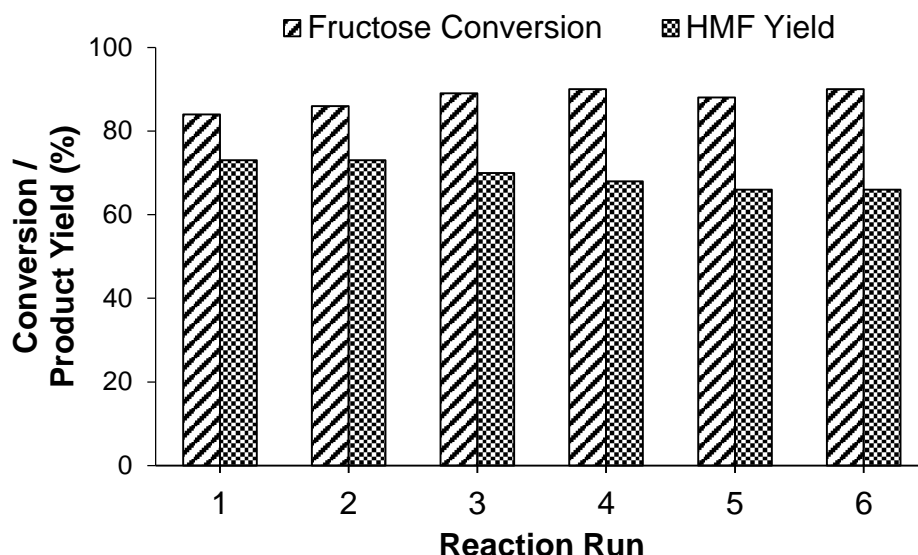


Figure 5.6. Recycle studies for [C₃SO₃HMIM][HSO₄] BAIL for the dehydration of fructose; Reaction condition. fructose/catalyst 20 wt/wt, catalyst [C₃SO₃HMIM][HSO₄], Water+MIBK (1:5 v/v), 150 °C, 30 min.

The efficiency of BAILs in recycling experiment and use of concentrated sugar solutions (40 wt% fructose) can make this process economical compared to known methods,^[51] which either do not show reproducible activity or use lower substrate concentrations.

5.3.3. Dehydration of xylose into furfural

The dehydration of xylose into furfural is also an important reaction. The applications of furfural are explained in the Chapter 1 (section 1.2.5.2.). Furthermore, the discussions on available literature for xylose dehydration reactions are also made in the introduction section of this chapter. In this section, detailed discussions are made on the dehydration of xylose into furfural using BAILs. The optimization of various reaction parameters is performed such as reaction time, temperature, catalyst quantity, substrate concentration and recycle study. Also, the comparison studies of BAILs with solid acid and mineral acid catalyst etc. are shown.

5.3.3.1. Catalyst evaluation studies for the dehydration of xylose

The BAILs, solid acid and mineral acid catalysts were evaluated for the dehydration of xylose into furfural using water+toluene (1:5 v/v) bi-phasic solvent system. The results are presented in Fig. 5.7. When reactions were done at 170 °C for 4 h with [C₃SO₃HMIM][HSO₄] as a catalyst, 73% yield (selectivity, 76%) of furfural was

obtained. While with $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ BAIL as a catalyst, 70% yield (selectivity, 74%) of furfural was seen and with $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ BAIL catalyst 63% (selectivity, 69%) furfural yield was obtained. The furfural yield for a non-catalytic reaction was only 36% under similar reaction conditions. The furfural yield for a non-catalytic reaction was only 36% under similar reaction conditions. The $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL shows better yield compared with $[\text{C}_3\text{SO}_3\text{HMIM}][\text{PTS}]$ and $[\text{C}_3\text{SO}_3\text{HMIM}][\text{Cl}]$ BAILs. Xylose dehydration reaction was also carried out with $[\text{BMIM}][\text{Cl}]$ IL, which is imidazolium based IL having no Brønsted acidity. This reaction was performed to see the effect of Brønsted acidity in BAILs and the result shows only 12% furfural yield with $[\text{BMIM}][\text{Cl}]$ IL (Fig. 5.7.). This implies that the higher yield of BAIL was achieved because of Brønsted acidity of the catalyst.

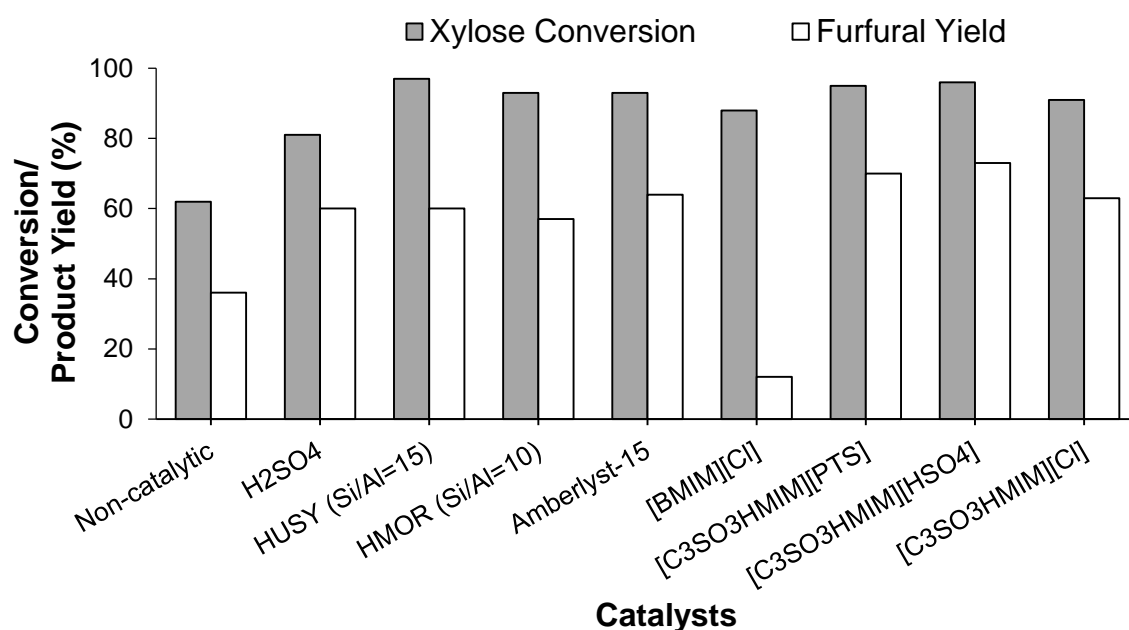


Figure 5.7. Catalyst evaluation study for the dehydration of xylose into furfural; Reaction condition. xylose 0.6 g, catalyst 0.08 g, Water+Toluene 60 mL (1:5 v/v), 170 °C, 4 h.

Furthermore, the reactions were carried out with mineral acid (H_2SO_4) and solid acid catalysts such as HUSY (Si/Al=15), HMOR (Si/Al=10) and ion exchange resin, Amberlyst-15. The mineral acid catalyst (H_2SO_4) showed 60% furfural yield with 81% xylose conversion. While, with solid acid catalysts, HUSY (Si/Al=15) and HMOR (Si/Al=10) 60 and 57% furfural yields with 97 and 93% xylose conversions, respectively were observed. The reaction carried out with Amberlyst-15 as a catalyst showed 64% furfural yield with 97% xylose conversion (Fig. 5.7.). These reactions were carried out for comparing the activity of BAILs with a mineral acid and solid

acid catalyst and the result shows that BAILs giving better furfural yield. Also, the solid acid catalyst used in this type of reactions are not stable as they undergo structural changes during the reaction.^[52]

5.3.3.2. Effect of solvent on xylose dehydration

Since water+MIBK solvent system proved to be better in the case of fructose dehydration reaction (section 5.3.1.2.), xylose dehydration reactions were also carried out using the same solvent system at 170 °C for 4 h with [C₃SO₃HMIM][HSO₄] BAIL catalyst and the result showed 54% furfural yield and 90% xylose conversion. But for the conversion of hemicellulose into furfural (Chapter 3B) it was observed that water+toluene solvent system was the best solvent system,²³ and therefore, this reaction was also carried out using water+toluene bi-phasic solvent system under similar reaction condition and showed 73% furfural yield with 95% xylose conversion (Fig. 5.8.). Further, xylose dehydration reaction was carried out using only water as a solvent system and 37% furfural yield with 80% xylose conversion was achieved. The lower yield with water is because in water medium more side reactions are happening and hence lower furfural yield with low selectivity was obtained. This shows that for xylose dehydration reaction, water+toluene solvent system is better compared to only water and water+MIBK solvent system.

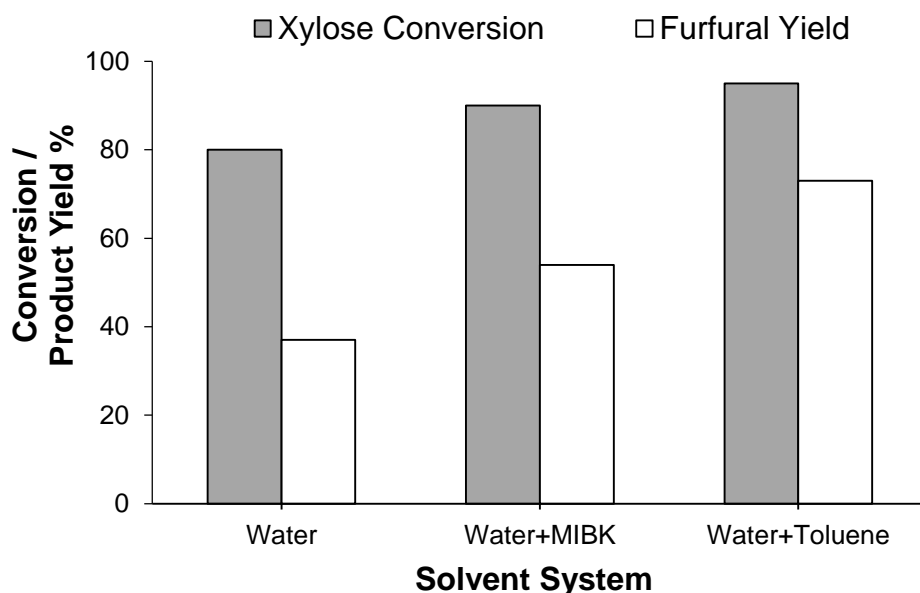


Figure 5.8. Effect of solvent system on the dehydration of xylose using [C₃SO₃HMIM][HSO₄] BAIL catalyst; Reaction condition. xylose 0.6 g, [C₃SO₃HMIM][HSO₄] 0.08 g, solvent 60 mL (bi-phasic solvent 1:5 v/v), 170 °C, 4 h.

The difference in yield with water+MIBK and water+toluene solvent system might be due to following reasons. Since HMF and furfural are extracted in organic phase and as MIBK has higher miscibility in water (19.1 g/L at 20-25 °C) than miscibility of toluene in water (0.47 g/L at 20-25 °C), it is possible for furans to again come in contact with water and catalyst when MIBK is used. This phenomenon can also be understood from a simple experiment in which similar quantity of water was taken in two NMR tubes (Fig. 5.9., a) and to it similar quantity of toluene in one NMR tube and MIBK in another NMR tube was added (Fig. 5.9., b). The outcome of this experiment shows the decrease in interface level in case of water+MIBK solvent system (Fig. 5.9., b). This again experimentally confirms that MIBK has higher solubility compared to toluene in water. Because of this solubility difference it is possible for furans to again come in contact with water and catalyst when MIBK is used. This phenomenon is more predominant in the case of furfural than HMF since reaction time for furfural (4 h) is longer than HMF (0.5 h). However, few reports suggest that for furfural synthesis, the water+MIBK solvent system is better.^[53] The reason for a discrepancy in presented results and earlier work is that in present method batch mode reaction system was used whereas, in earlier work, reactions were carried out in a continuous flow mode. As explained above, compared to a batch mode in continuous mode, contact time is very less so the effect of solvent (miscibility) would be different.

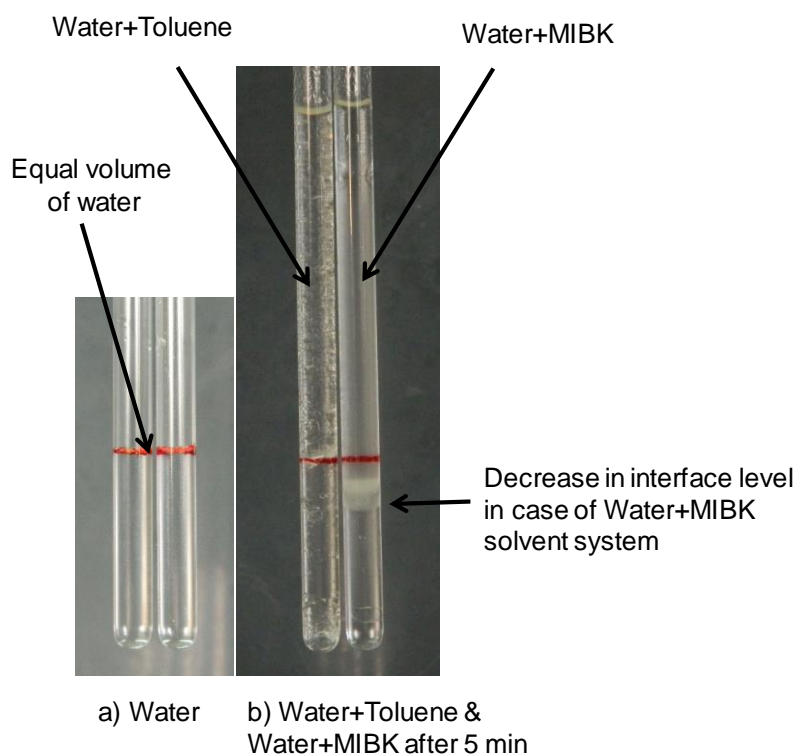


Figure 5.9. Solubility difference for water+toluene and water+MIBK solvent system.

5.3.3.3. Effect of reaction time

The result of the effect of reaction time on the conversion of xylose into furfural is presented in Fig. 5.10. Since for xylose dehydration reaction, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst showed better yields among all the catalysts, to boost the yields of furfural further, reaction with $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL was done for longer time (5 h) at 170 °C. However, almost similar furfural yield (74%, 76% selectivity) was seen as was obtained after 4 h reaction time (73%). For 1 h and 3 h reaction, 56 and 62% furfural yields were obtained, and for 7 h reaction time, a slight decrease in furfural yield (71%) was seen. This shows that for achieving better furfural yield (73%) at 170 °C, 4 h reaction time is optimum reaction time.

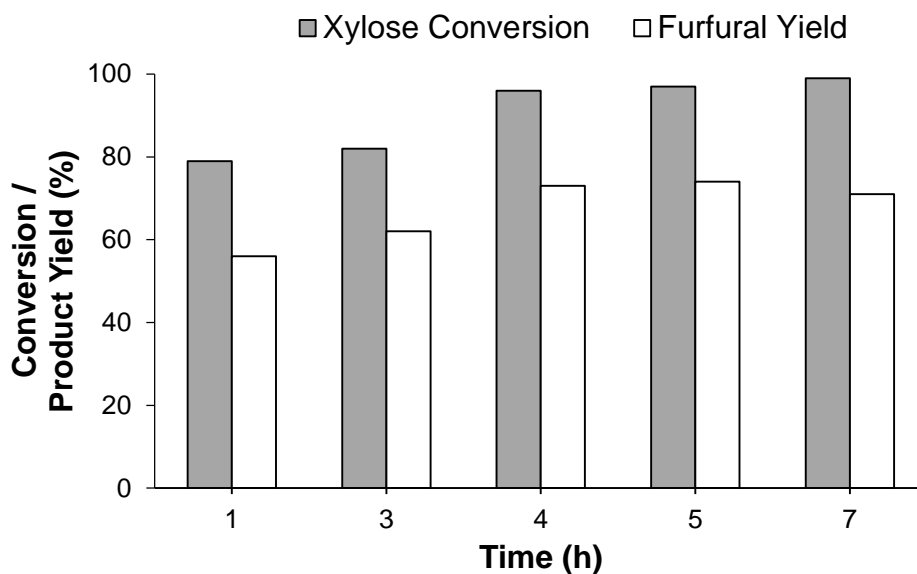


Figure 5.10. Effect of reaction time on the dehydration of xylose in the presence of $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst; Reaction condition. xylose 0.6 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.08 g, Water+Toluene 60 mL (1:5 v/v), 170 °C.

The furfural stability study was performed in water+toluene solvent system with and without $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst (Chapter-3B, section 3B.2.4.) and the results showed that furfural is stable under reaction conditions. The lower selectivity of furfural was seen in xylose dehydration reaction is because of side reactions between the unreacted xylose and furfural during the course of the reaction.

5.3.3.4. Effect of reaction temperature

The effect of temperature on xylose dehydration reaction was studied using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst, for 4 h reaction time and the results are shown in Fig. 5.11. With the decrease in reaction temperature from 170 °C to 160 °C, it was expected that furfural yield may improve because of suppression of the side reactions, but lower yield (66%) was observed with 90% conversion. For the xylose dehydration, reaction carried out at 180 °C further lower yield of furfural was observed (65% yield) compared with 170 °C reaction (73%). The reaction carried out at 170 °C showed the highest yield of furfural (73% furfural yield) with better furfural selectivity (76 %). The reaction carried out at 160 °C temperature showed lower furfural yield (66%) because at this temperature the conversion is lower (90%). On the other hand, when reaction was performed at 180 °C lower furfural yield (64%) was seen because at higher temperature degradation reactions were preferred which

decreases furfural selectivity (xylose conversion 100% furfural selectivity 64%) and hence lower furfural yield was obtained.

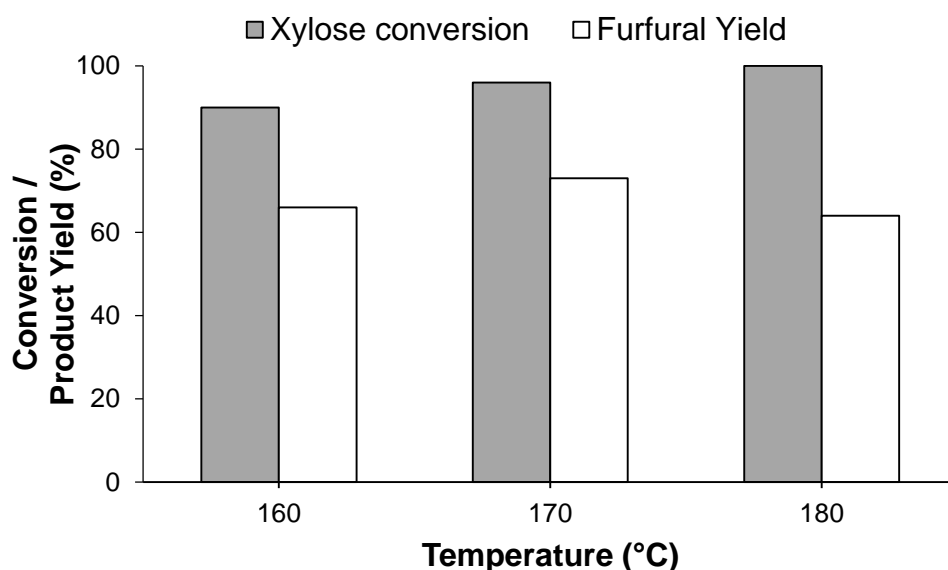


Figure 5.11. Influence of reaction temperature on the xylose dehydration reaction in the presence of $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst; Reaction condition. xylose 0.6 g, $[C_3SO_3HMIM][HSO_4]$ 0.08 g, Water+Toluene 60 mL (1:5 v/v), 4 h.

5.3.3.5. Effect of substrate concentration

Subsequently, for xylose dehydration reaction, effect of substrate concentration was studied, and the results are shown in Fig. 5.12. It is very important to test the developed catalytic system for the conversion of concentrated substrate solutions to minimize the cost of the experiment. In this context, reactions were carried out under optimized reaction condition with various substrate loadings and by keeping the constant catalyst loading (0.08 g $[C_3SO_3HMIM][HSO_4]$ BAIL) and solvent quantity (Fig. 5.12.). In the case of xylose dehydration reaction with lower xylose concentration (0.3 g xylose in 10 mL water; 3 wt%), better furfural yield was obtained (81%). But with further increase in the xylose concentration to 0.45 g (4.5 wt%) and 0.6 g (6 wt%), slight decrease in furfural yield (76 and 73%) was seen. This shows that for xylose dehydration reaction, lower substrate concentration is required to get better furfural yield. Similar results were obtained in the conversion of hemicellulose into furfural (Chaper-3B; section 3B.2.6.).

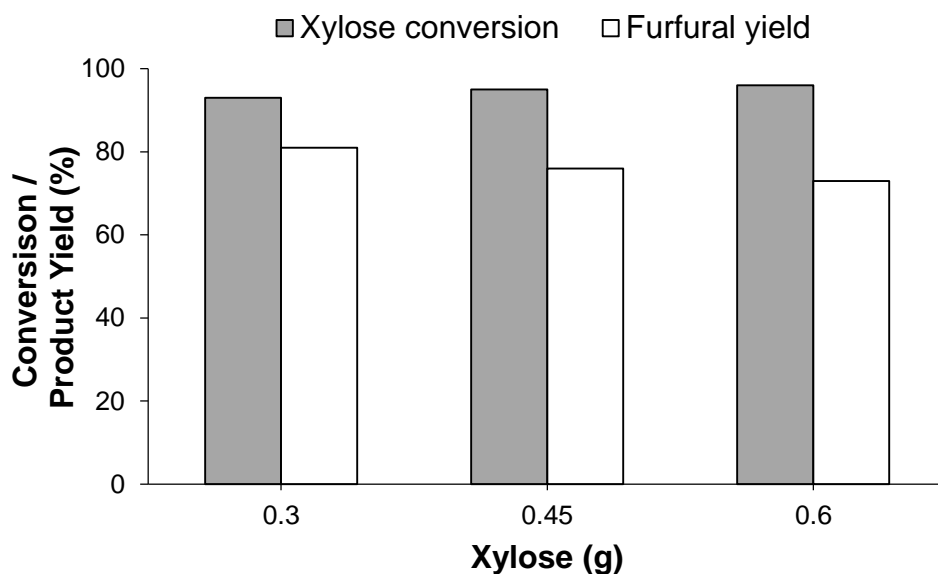
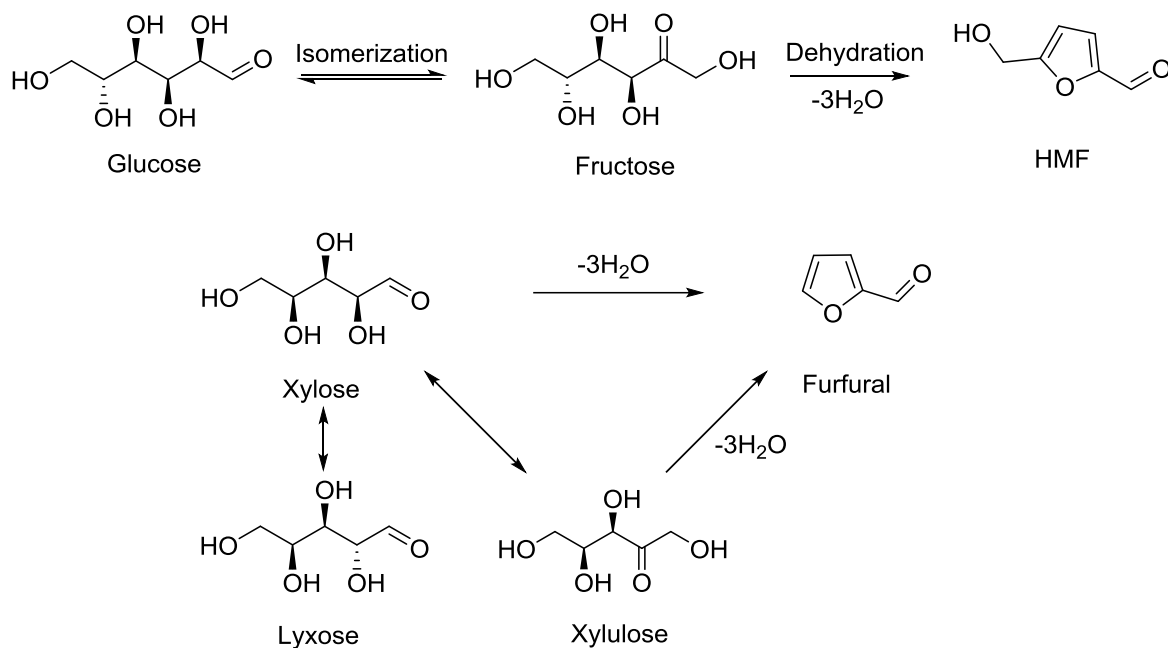


Figure 5.12. Effect of xylose concentration on the xylose dehydration reaction; Reaction condition. $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.08 g, Water+Toluene 60 mL (1:5 v/v), 170 °C, 4 h.

The lower furfural yield for concentrated xylose solution can be explained as follows; As seen from the results, with 40 wt% fructose solution, 73% HMF yield (78% selectivity) was obtained, which is similar (73%, 87% selectivity) with 10 wt% fructose solution (section 5.3.1.3.).^[54] However, the lower yield of furfural (73%) with 6 wt% xylose solution was seen compared to 81% obtained with 3wt% solution. It is suggested that difference in reaction time (30 min and 4 h) and temperature (150 °C and 170 °C) may play a role in deciding the course of the reaction and thus selectivity for furans formation. Another reason behind this phenomenon might be that fructose resembles xylulose and xylose resembles glucose as a substrate (Scheme 5.2.). In the case of glucose, it takes a longer time to achieve good yields of HMF compared to fructose since the first step; isomerization of glucose to fructose is difficult. Similarly, the first step of xylose to xylulose might be difficult to proceed over Brønsted acid catalysts. Nevertheless, the apparent activation energies calculated for mineral acid catalyzed fructose and xylose dehydration reactions are almost similar (140 kJ/mol).^[55] It is also mentioned in the literature that the apparent activation energy of degradation reactions of xylose is lower compared to dehydration reaction.^[56] These factors might be responsible for deciding the selectivity for furfural and HMF.



Scheme 5.2. General reaction pathways for the dehydration of C6 and C5 sugars in presence of acid catalyst.

5.3.3.6. Effect of catalyst concentration

This study was performed using [C₃SO₃HMIM][HSO₄] BAIL. The reactions were carried out using varying quantities of [C₃SO₃HMIM][HSO₄] BAIL catalyst and the results are shown in Fig. 5.13. All the reactions were performed in 60 mL water+toluene bi-phasic solvent system (1:5 v/v) using 0.6 g xylose. The obtained result shows that for xylose dehydration reaction, small quantity of [C₃SO₃HMIM][HSO₄] BAIL (0.041 g) can give a very good yield of furfural (71%). Further with increasing the catalyst quantity from 0.041 g to 0.08 g and 0.125 g 73% and 59% furfural yields were observed. The decrease in furfural yield for 0.125 g BAIL was because of increase in side reactions as the higher quantity of BAIL catalyst is present.

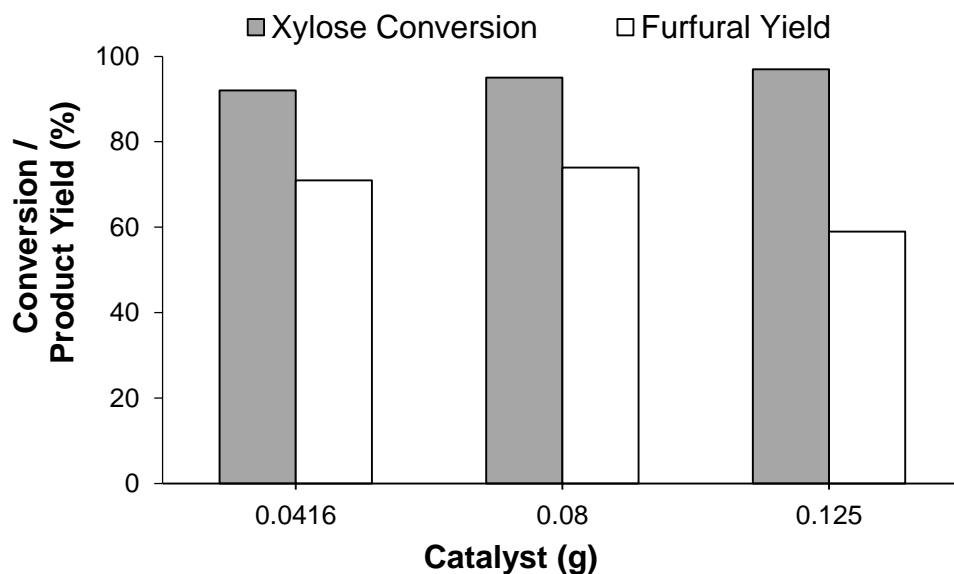


Figure 5.13. Effect of catalyst ($[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$) concentration on the xylose dehydration reaction; Reaction condition. xylose 0.6 g, catalyst $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$, Water+Toluene 60 mL (1:5 v/v), 170 °C, 4 h.

5.3.3.7. Recycle study of BAIL in xylose dehydration reaction

The similar procedures were used for catalyst recycle as explained in fructose dehydration reaction (section 5.3.2.1.) in this chapter. The $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ catalyst was recycled in the xylose dehydration reaction to yield furfural. The reactions were carried out under optimized reaction condition and for each reaction the S/C ratio (7.5 wt/wt) was kept constant. The reactions were carried out at 170 °C for 4 h (Fig. 5.14.). In the first and second run of reaction almost similar furfural yield was obtained (73-72%). But, in 3rd to 6th runs small decrease in furfural yield (69-64%) was seen. This shows that the BAIL catalyst is the almost recyclable catalyst. The small decrease in furfural yield may be due the reactions were performed with different reaction volumes however, similar S/C and S/solvent ratios were used.

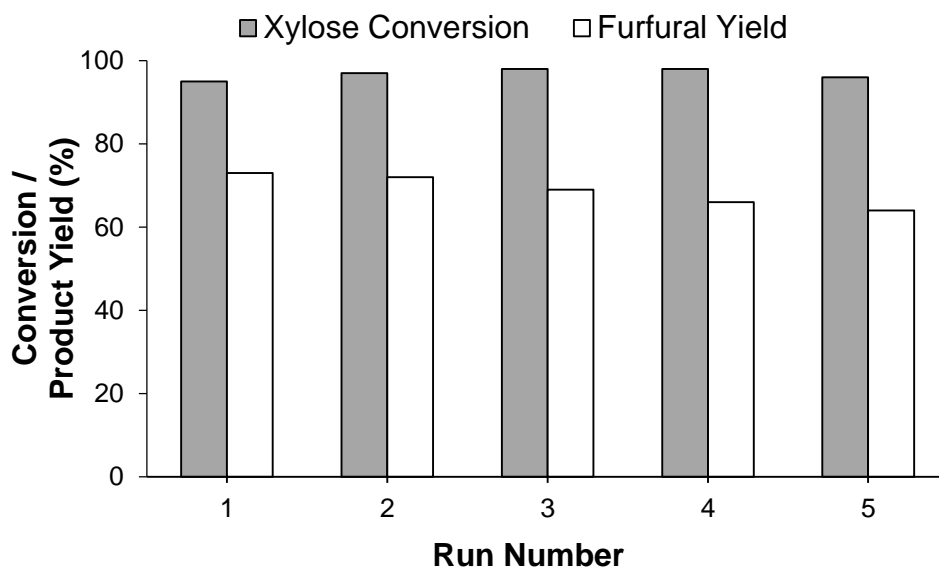


Figure 5.14. Recycle study for $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL catalyst on the dehydration of xylose; Reaction condition. xylose/catalyst 7.5 wt/wt, catalyst $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$, Water+Toluene (1:5 v/v), 170 °C, 4 h, similar substrate/solvent ratio was used in all reactions.

5.3.3.8. Isolation of furfural

Isolation of furfural was done from the reaction mixture and the details are given below. The optimum reaction condition for achieving better furfural yield is xylose 0.6 g, $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL as a catalyst, 0.08 g; water+toluene solvent system (60 mL, 1:5 v/v); 170 °C and 4 h. In this reaction, 73% furfural yield was obtained (64% from toluene layer and 09% from water layer). After the reaction, toluene layer was separated from the water layer using a separating funnel. Again, toluene was added to the water layer and furfural was extracted from the water layer. This toluene layer after separation from water layer was added to earlier toluene layer. This extraction procedure was repeated for total 3 times to make sure that the maximum furfural is extracted in toluene layer from the water layer. This was also checked by the color change of the water and toluene layers. Afterwards, toluene was evaporated using rotary evaporator and remaining mass was considered as furfural. To confirm the obtained mass is pure furfural, it is subjected to ^1H NMR analysis, for which the obtained mass was dried and dissolved in CDCl_3 and the ^1H NMR spectrum was recorded (Fig. 5.15.). From the ^1H NMR spectrum, it can be understood that the furfural obtained in the reaction was in pure form.

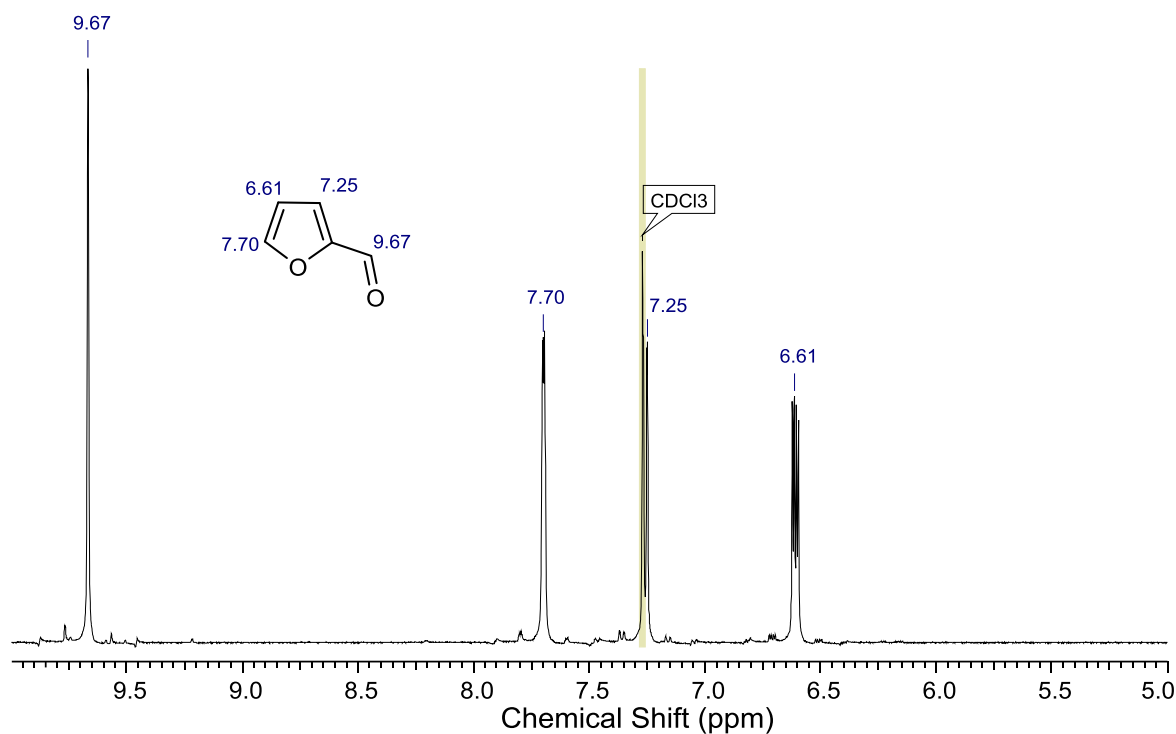


Figure 5.15. ¹H NMR of isolated furfural in CDCl₃ solvent.

5.3.4. Conclusion

In summary, this Chapter discusses the possibility of the use of standalone BAILs in the synthesis of furans from concentrated fructose and xylose solutions. It is noteworthy that the BAILs are used in the catalytic amount to achieve high yields (73% HMF, 87% selectivity and 73% furfural, 76% selectivity) with [C₃SO₃HMIM][HSO₄] BAIL catalyst. Even with 40 wt% solution of fructose, high yield of HMF (73%) was seen. The detailed studies on S/C ratio, substrate concentration reveal that both, acid strength and acid amount play an important role. Moreover, easy recyclability of the catalyst (6 runs) with almost similar yields for furans suggests good stability of [C₃SO₃HMIM][HSO₄] BAIL catalyst.

The better yields obtained with BAIL compared to H₂SO₄ can be attributed to the possibility of ion-dipole type of interaction between ions of ionic liquids and hydroxyl groups of substrate (cation of IL interacting with 'O' of -OH group and anion of IL interacting with 'H' of -OH group) as is reported earlier in hemicelluloses reactions (Chapeter-3A, section 3A.3.10).^[57-58] The similar type of interaction is not possible between mineral acid and hydroxyl groups of the substrate, which may decrease the probability of interaction between the substrate and catalyst. It is

suggested that the lower yields observed with solid acid catalysts compared with BAILs are due to the diffusion limitations (difficulty in accessing all the active sites present on the catalyst for substrate molecules to interact with) faced with solid acids.

5.3.5. References

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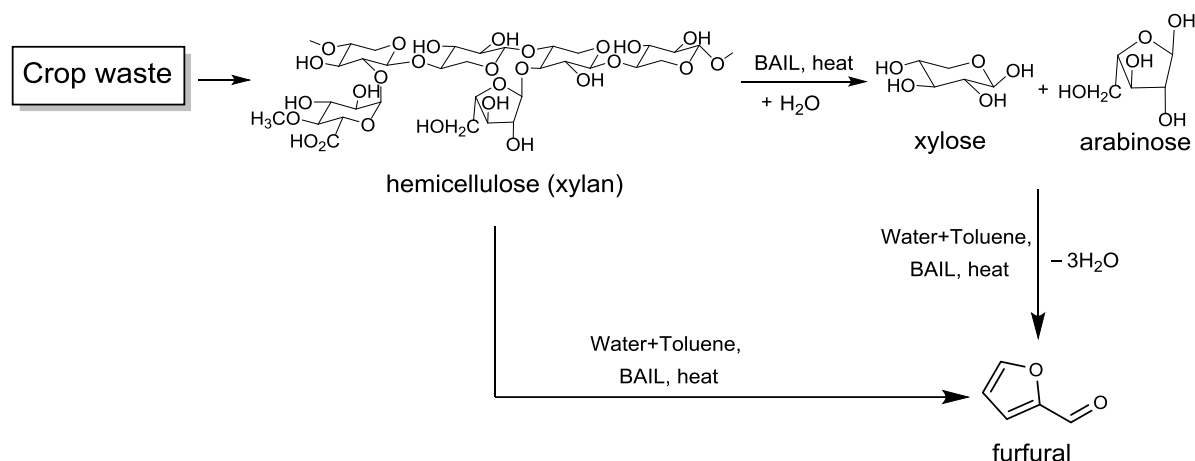
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Chapter 6
Summary & Conclusions

Summary and conclusions

Biomass is one of the important alternative source for fossil feedstock to convert it into fuels, chemicals, and energy. Nature produces 170 billion metric tons of biomass per year by the way of photosynthesis, this shows that the worlds production of biomass is huge. The utilization of biomass has various advantages over fossil feedstock such as it is widely available, renewable, inexpensive, sustainable and the use of it can make a process carbon neutral. Hence, it is highly desirable to use this renewable lignocellulosic biomass as an alternative to fossil feedstock to convert it into chemicals. Various important chemicals can be obtained from lignocellulosic biomass for e. g. hydrolysis of hemicellulose (mainly made of C5 sugars) can give xylose and arabinose (X+A as a C5 sugars) and their further dehydration can give furfural. The cellulose upon hydrolysis will give glucose which on dehydration reaction yields 5-hydroxymethylfurfural (HMF). Finally, lignin upon depolymerization reaction can give aromatic monomers such as *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol.

In the present thesis, I have worked on the hydrolysis and dehydration reactions of saccharides using Brønsted acidic ionic liquids (BAILs) for the synthesis of sugars and furans (Scheme 1) because of its wide range of important applications. Xylose and arabinose upon hydrogenation will give xylitol and arabinitol as sugar alcohols which are used as a low-calorie sweetener. Xylitol is used for the prevention of dental caries (tooth decay) and also used in pharmaceutical and cosmetic products such as toothpaste, fluoride tablets, and mouthwashes. The furan derivatives have many industrial applications such as HMF upon oxidation yields 2,5-furandicarboxylic acid (FDCA) which has the potential to replace terephthalic acid. Hydrogenation of HMF can give 2,5-dimethylfuran (DMF) which has a potential application as a fuel additive. Furthermore, many important chemicals such as levulinic acid, γ -valerolactone, alkyl levulinate etc. can be synthesized using HMF. Similarly, furfural has many applications such hydrogenation of furfural gives furfuryl alcohol and tetrahydrofuran as products which are known as solvents and starting compounds in the synthesis of a variety of chemicals.



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

The thesis is divided into 6 chapters, and the important results and conclusions are summarized as;

Chapter 1

In this chapter, the overview of work is described and the advantages of utilization of biomass over fossil feedstock for chemical synthesis are discussed. The discussion on the biomass classification based on plant and animal derived and more specifically, plant derived edible and non-edible biomass are done. Furthermore, the details of the chemical structure of different types of hemicelluloses are mentioned to understand the difference between various hemicelluloses. It is well known that C5 sugars and furans (furfural and HMF) are very important chemicals and thus in this chapter, their applications in various fields are summarized. The summary of chemical processes for the synthesis of C5 sugars and furans are discussed. The solid acid (HUSY, HMOR, H β , Amberlyst-15, etc.) and mineral acid (H₂SO₄, HCl, etc.) catalysts reported for the synthesis of C5 sugars and furans which have drawbacks such as lower product yield/selectivity, the heterogeneous solid acid catalysts used are not stable catalysts under reaction condition. The mineral acid catalysts used for these reactions have problems like recovery of the catalysts, formation of degradation products, requirement of an extra step for neutralization, toxicity and corrosiveness. Recently ILs are used for the hydrolysis and dehydration reactions of saccharides however, the ILs are used as solvents in major reactions. Since ILs are costly, using it as a solvent for the synthesis of chemicals from biomass is not a good method. Moreover, the use of ILs along with mineral acid (H₂SO₄ and HCl) and metal halide (Cr₂Cl₃.H₂O) catalysts

is known however, use of IL along with mineral acid and metal halide is not attractive because of the drawbacks associated with mineral acids and metal halides. To overcome the drawbacks associated with present methods for the synthesis of C5 sugars and furans, I have developed method for the hydrolysis and dehydration reaction of saccharides to synthesize C5 sugars and furans using catalytic amount of BAILs without any mineral acid and metal halides as a catalyst.

The objective and novelty of my work are given below,

- Use of catalytic amount of BAILs without any mineral acid and metal halide used for the conversion of hemicellulose into C5 sugars in water medium.
- Use of Catalytic amount of BAILs for the conversion of hemicellulose into furfural in water+organic biphasic solvent system to improve the yields/selectivity.
- To find out the interaction of BAILs with polysaccharides, because the BAILs are ionic in nature and polysaccharides are having plenty of -OH groups hence there is possibility of ion-dipole type of interaction.
- Selective conversion of hemicellulose from crop wastes into C5 sugars and/or furfural using catalytic amount of BAILs.
- Dehydration reactions of C6 and C5 sugars into HMF and furfural using catalytic amount of BAIL.
- Conversion of concentrated fructose solution into HMF using catalytic amount of BAILs.

Chapter 2

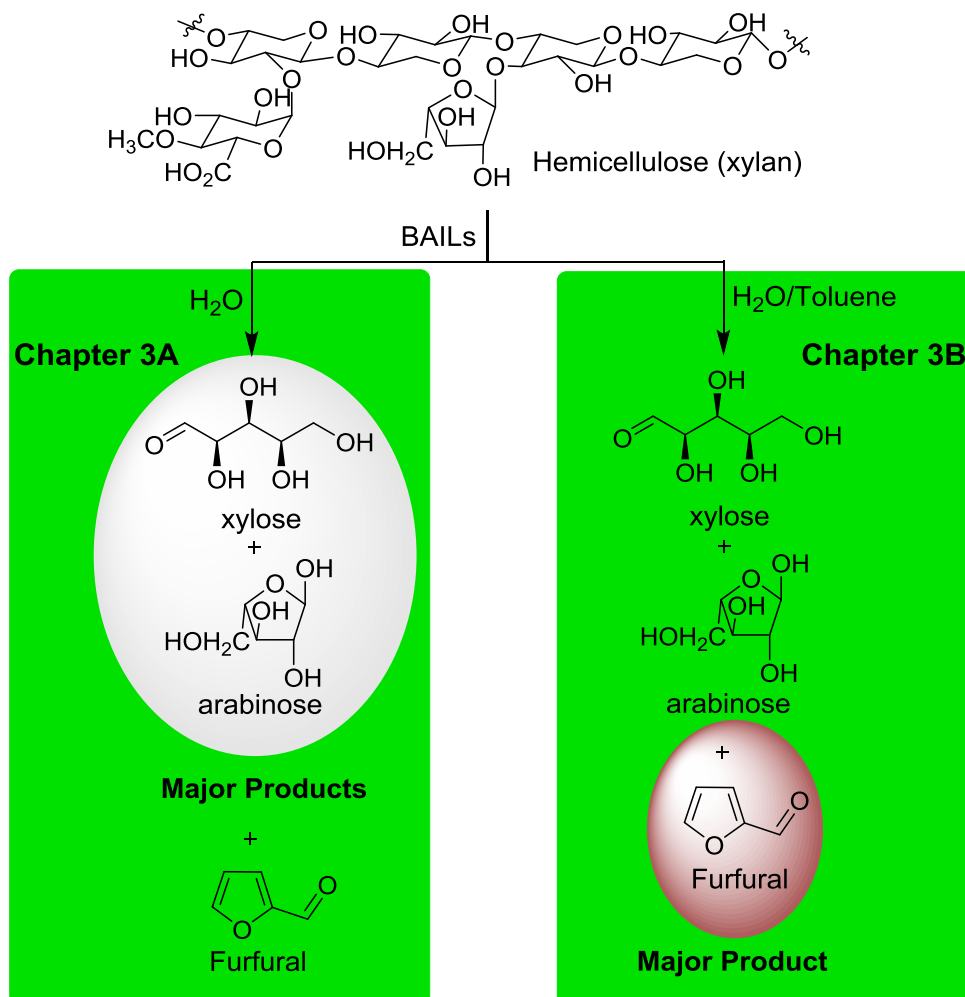
In this chapter, the information on the synthesis of various types of BAILs and the details on their characterization for structure determination are given. The important conclusions of this chapter are summarized below.

- Various imidazolium based ILs were synthesized with Brønsted acidity and the rationalization behind IL synthesis is explained in detail. Similar type of Brønsted acidic IL ($[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$) and IL ($[\text{BMIM}][\text{Cl}]$) without Brønsted acidity were synthesized to understand the effect of Brønsted acidity in the hydrolysis and dehydration reactions of saccharides.

- The properties of BAIL can be changed by changing combination of cations and anions of the BAILS. Hence ILs with various cations (imidazolium, benzimidazolium, quaternary ammonium, pyridinium and triphenylphosphonium) and anions (hydrogen sulfate, *p*-toluenesulfonate, chloride) were synthesized.
- The solubility parameters of all the synthesized ILs in various solvents (water, MeOH, EtOH, MIBK, toluene, DMSO, etc.) is studied to develop a methodology based on solubility difference to separate ILs from reaction mixture.
- All the synthesized ILs were characterized using various characterization techniques such as NMR (^1H and ^{13}C), elemental analysis (CHNS analysis), FTIR, and TGA. The acid strength of BAILS was calculated using Hammett acidity function (H_0).
- The NMR (^1H and ^{13}C) spectroscopic study showed that the synthesized ILs are in pure form.
- The presence of C, H, N and S elements in ILs were determined using elemental analysis (CHNS analysis), and the observed values match well with the theoretical values.
- The various functional groups present in ILs were determined using FTIR spectroscopy. The SO_2 asymmetric stretching ($1390\text{-}1290\text{cm}^{-1}$), SO_2 symmetric stretching ($1190\text{-}1120\text{ cm}^{-1}$), the S=O stretching ($1060\text{-}1020\text{ cm}^{-1}$), C=C and C=N of imidazole ring stretching (1610 and 1578 cm^{-1}) of ILs were understood from FTIR spectroscopy. Furthermore, the peak for S-O-H, of the HSO_4 anion for $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ and $[\text{C}_3\text{SO}_3\text{HEt}_3\text{N}][\text{HSO}_4]$ BAILS at $1200\text{-}1220\text{ cm}^{-1}$ can be seen in the spectrum.
- From TGA study it was understood that the ILs are thermally stable up to $250\text{ }^\circ\text{C}$. Also, hydrothermal stability of all BAILS was checked at $180\text{ }^\circ\text{C}$ for 5 h and it was found that these ILs are hydrothermally stable. The acid strength calculated using Hammett acidity function showed that the $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL has highest acid strength ($H_0=2.08$) when all the catalysts are used on similar weight basis.

Chapter 3

This chapter is divided into two sub chapters, Chapter-3A and Chapter-3B. In Chapter 3A, the discussions are made on the conversion of hemicellulose into C5 sugars using BAILs. On the other hand, in Chapter 3B the discussions are made on the conversion of hemicellulose into furfural using BAILs in the one-pot fashion (Scheme 3.1.).



Scheme. 3.1. Reaction for the conversion of hemicellulose (xylan) into C5 sugars (X+A) & furfural using BAIL.

Chapter 3A

The Chapter-3A describes the synthesis of C5 sugars such as xylose and arabinose (X+A) from hemicellulose using BAILs in water medium. The important outcomes of the work are summarized below.

- In this chapter the details on the catalytic reactions of hemicelluloses conversion, the analysis of reaction mixture and calculations of product yield (C5 sugars and furfural) and conversion of hemicellulose are given.
- The catalyst evaluation study carried out for the conversion of hemicellulose into C5 sugars showed that the BAILs are efficient catalyst compared to solid acid (HUSY and HMOR), mineral acid (H₂SO₄ and HCl) and organic acid (*p*-toluenesulfonic acid) catalysts even though the catalysts are used with similar H⁺ mmol basis. Furthermore, the effect acid strength on the conversion of hemicellulose into C5 sugars is explained for all the catalysts which showed that [C₃SO₃HMIM][HSO₄] BAIL has higher acid strength and hence higher C5 sugar yield was achieved (87%) with this catalyst. The Hammett acidity function (*H₀*) for the BAILs observed is in the order of, [C₃SO₃HMIM][Cl] > [C₃SO₃HMIM][PTS] > [C₃SO₃HMIM][HSO₄] and the correlation of catalytic activity with *H₀* was clearly possible (Fig. 3A.2.). The higher yield of C5 sugars (87%) using [C₃SO₃HMIM][HSO₄] BAIL compared with H₂SO₄ (50%) catalyst can be explained with the help of ion-dipole type of interaction of BAILs with hemicellulose which makes easy availability of H⁺ from the IL in the periphery of the hemicellulose molecule to undergo hydrolysis reaction (Fig. 3A.9.).

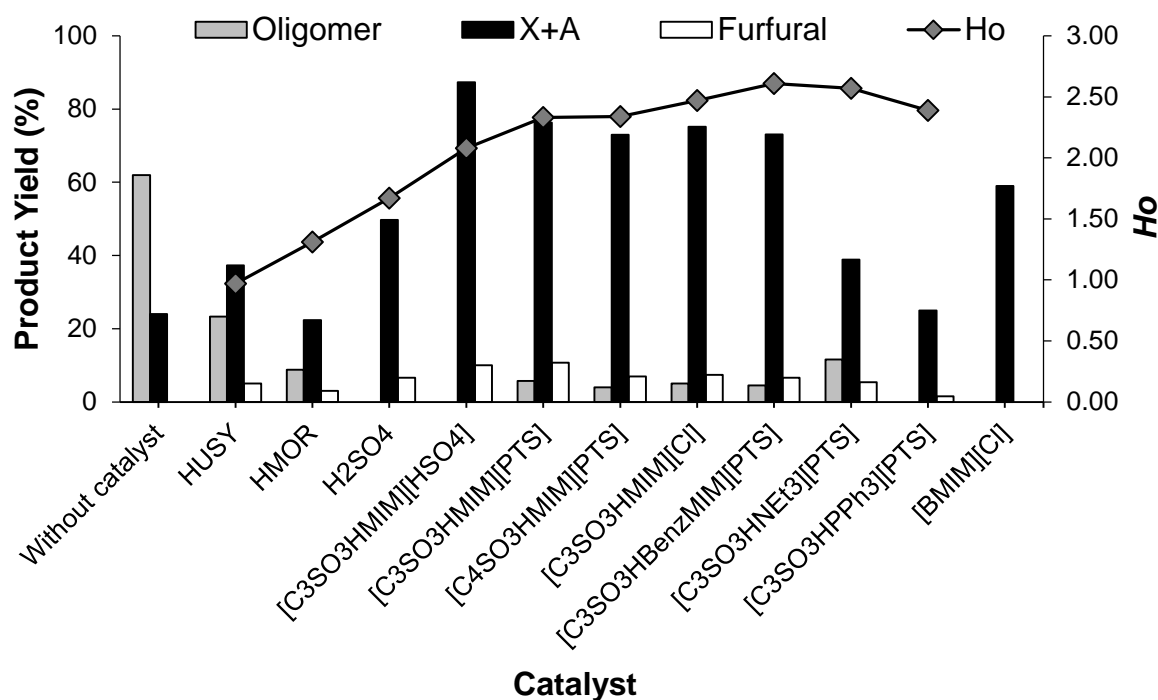


Figure. 3A.1. Catalyst evaluation study for the conversion of hemicellulose; Reaction condition. hemicellulose (birchwood) 0.6 g, catalyst 0.24 g, water 60 mL, 160 °C, 1 h.

- The effect of cations of BAILs was studied by keeping similar type of anion (*p*-toluenesulfonate) in all BAILs and the results showed that BAILs with imidazolium based cation ([C₃SO₃HMIM][PTS]) shows higher C5 sugar yield (76%) compared to benzimidazolium, quaternary ammonium, pyridinium and triphenylphosphonium based cations.
- Various types of hemicellulose such as hemicellulose derived from birchwood, beechwood, oat spelt and arabinogalactan type of hemicellulose are efficiently converted into C5 sugars using [C₃SO₃HMIM][PTS] BAIL.
- It is always desirable to use higher hemicellulose loadings (with respect to solvent) and hence the effect of hemicellulose concentrations and catalyst activity to get the highest yield of C5 sugars was checked. The reaction was performed at 160 °C by charging 3 times more hardwood hemicellulose (birchwood hemicellulose 1.8 g, 3 wt%) and 73% C5 sugar yield was obtained in presence of [C₃SO₃HMIM][PTS] BAIL if reaction was performed for 1.5 h. With 0.6 g hemicellulose substrate, 76% C5 sugar yield was obtained when reactions was performed for 1 h using [C₃SO₃HMIM][PTS] BAIL. This showed that concentrated hemicellulose solutions (3 wt%) can be efficiently converted into C5 sugars using BAILs.

- The BAILs perform better compared to mineral acid catalyst even though catalysts were used on similar H^+ mmol basis, because the BAILs used for the conversion of hemicellulose showed ion-dipole type of interaction with polysaccharide (Fig. 3A.9.). The ion-dipole type of interaction shown in Fig. 3A.9. is confirmed with the help of 1H NMR spectroscopic study.

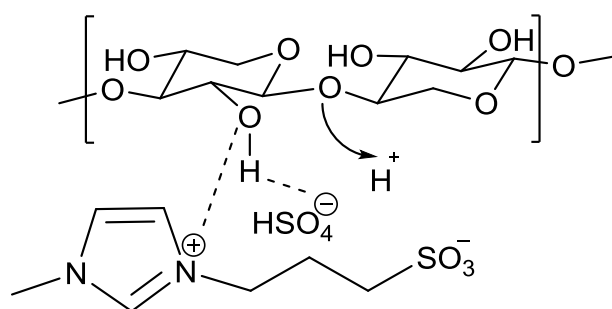


Figure 3A.9. Ion-dipole type of interaction present between BAIL and polysaccharide.

Chapter 3B

In this chapter, the details on the conversion of hemicellulose into furfural using BAILs is explained. The important outcomes of this chapter are summarized below,

- To obtain furfural from hemicellulose in a one-pot fashion the reaction conditions were optimized using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL because this BAIL showed better yield of C5 sugar (87%).
- For obtaining furfural reactions were performed in water+toluene biphasic solvent system (1:5 v/v) at 170 °C for 3 h using $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL (Figure 3B.1). The catalytic evaluation study showed that the $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL showed higher furfural yield (62%) and performs better compared to solid acid catalyst such as HUSY (Si/Al=15) (34% furfural yield) and Amberlyst-15 (42% furfural yield) and mineral acid catalyst like H_2SO_4 (42% furfural yield).

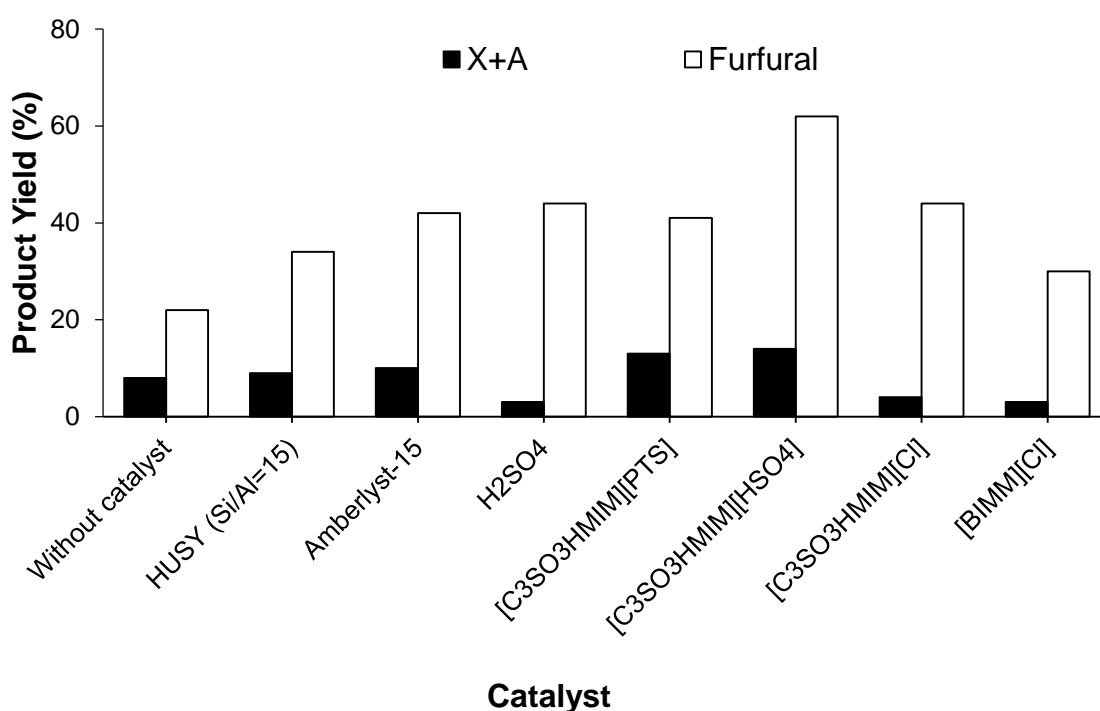


Figure 3B.1. Catalyst evaluation study on the conversion of hemicellulose into furfural; Reaction condition. hemicellulose 0.6 g, catalyst 0.12 g, Water+Toluene 60 mL (1:5 v/v), 170 °C, 4 h.

- Optimization of reaction temperature and time showed that 170 °C reaction temperature and 4 h of reaction time showed better furfural yield (62%) using [C₃SO₃HMIM][HSO₄] BAIL as a catalyst.
- Effect of catalyst concentration study reveals that 0.12 g [C₃SO₃HMIM][HSO₄] BAIL (S/C = 5 wt/wt) is required to get better furfural yield at 170 °C within 4 h. Furthermore, the effect of substrate concentration was studied at similar reaction conditions using [C₃SO₃HMIM][HSO₄] BAIL catalyst. The result showed exceptionally high furfural yield (82%) when lower hemicellulose concentration (0.2 g) was used.
- Hemicellulose conversion were carried out using various solvent system such as water, water+toluene, water+MIBK, and water+p-xylene. The water+toluene biphasic solvent system is required to get better yield of furfural using [C₃SO₃HMIM][HSO₄] BAIL. The reason for higher yield of furfural in water+toluene solvent system can be explained with the help of partition coefficient of furfural in organic/water bi-phasic solvent system and the solubility of organic solvent in water.
- [C₃SO₃HMIM][HSO₄] BAIL was recycled after hemicellulose conversion reaction and characterized using ¹H NMR spectroscopy for understanding the stability of catalyst under reaction condition. The ¹H NMR of fresh and recycled [C₃SO₃HMIM][HSO₄] BAIL is similar, which confirms that the BAIL used in the reaction is stable under reaction condition (Fig. 3B.9.).

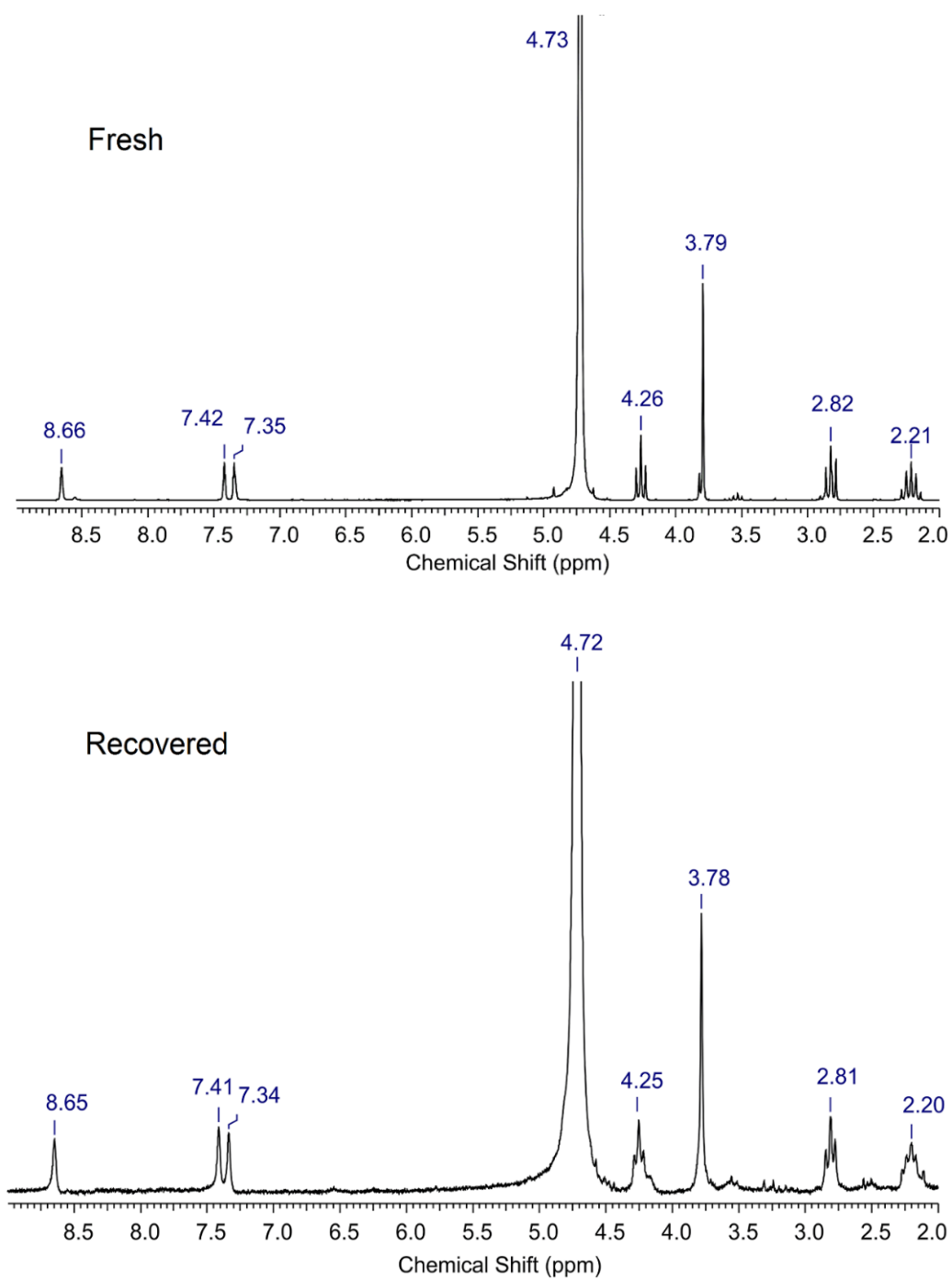


Figure 3B.9. ¹H NMR spectra of fresh and recovered [C₃SO₃HMIM][HSO₄] BAIL from the reaction of hemicellulose conversion into furfural.

Chapter 4

This chapter deals with the selective conversion of hemicellulose present in crop waste into C5 sugars and furfural using BAILs.

- India produces 17 to 21% of crops with respect to world's total crop production. This implies that in India huge crops are produced, and after utilizing the edible part of all these crops will generate huge amount of crop wastes. Hence utilization of this crop wastes for chemicals synthesis is very important.
- Various crop wastes were collected from different parts of India and analyzed using Technical Association of the Pulp and Paper Industry (TAPPI) method for understanding the composition of crop wastes. The metal nutrients present in crop wastes were analyzed using ICP-OES method.
- The reaction set up used for the reaction, catalytic methods, analysis of reaction mixture and calculations for the C5 sugar yield and furfural yield are explained. The C5 sugar and furfural yield were calculated based on pentosan present in crop waste.
- Similar reaction conditions were used for the selective conversion of hemicellulose from crop waste into C5 sugars, which was used for the conversion of hemicellulose in C5 sugars. The catalyst evaluation study carried out for Maharashtra bagasse (MH BG) crop waste and the results showed that $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL performs better and gives very high yield of C5 sugars (88%) compared to HUSY (Si/Al=15) (20%) solid acid catalyst and H_2SO_4 (58%) mineral acid (Fig. 4.3.).

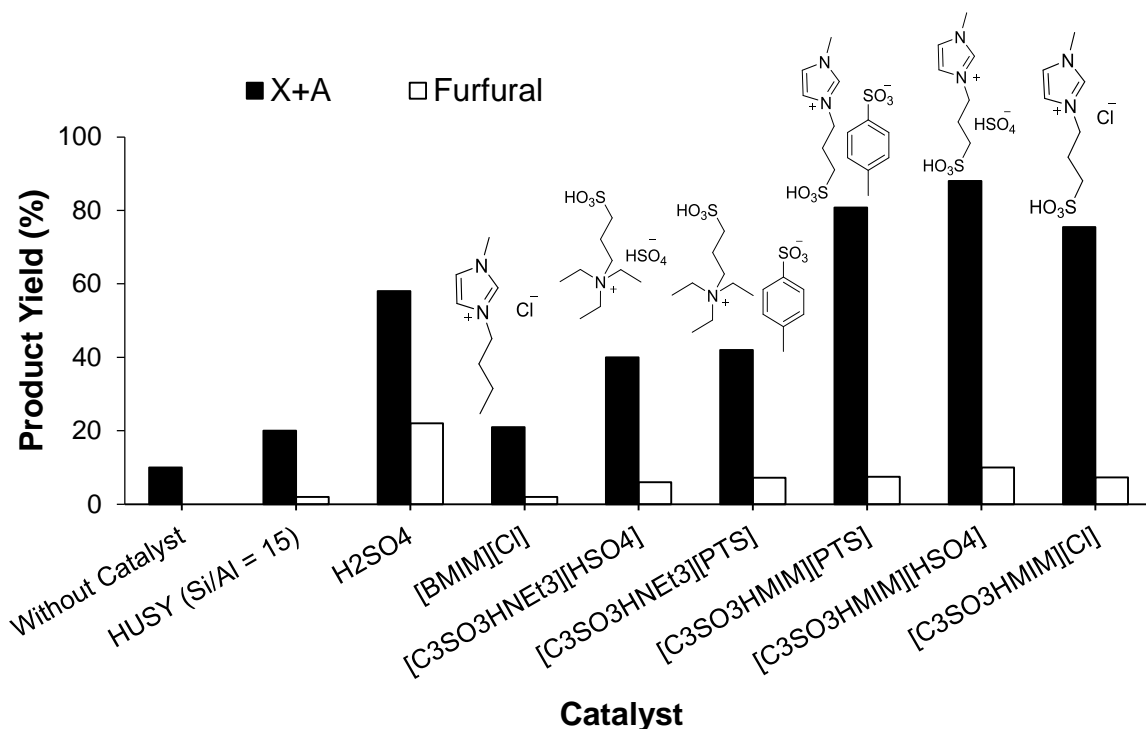


Figure 4.3. Catalyst evaluation study for the selective conversion hemicellulose from MH BG crop waste into C5 sugars; Reaction condition. hemicellulose 2 g, catalyst 0.24 g, water 60 mL, 160 °C, 1 h.

- The effect of crop wastes for the selective conversion of hemicellulose from crop wastes into C5 sugars was studied using [C₃SO₃HMIM][HSO₄] BAIL. Various types of crop wastes were used for this study such as bagasse from Uttar Pradesh and Maharashtra; rice husk from Karnataka, Odisha and Uttar Pradesh; wheat straw from Uttar Pradesh; cotton stalk and corn cob from Maharashtra. The [C₃SO₃HMIM][HSO₄] BAIL can convert selectively hemicellulose present in various types of crop wastes into C5 sugars.
- Similarly, the [C₃SO₃HMIM][HSO₄] BAIL can convert selectively hemicellulose from wide range of crop wastes into furfural in the one-pot fashion, with exceptionally high yield of furfural (73 to 85%) in water+toluene solvent system when reactions are carried out at 170 °C for 4h (Fig. 4.5.).

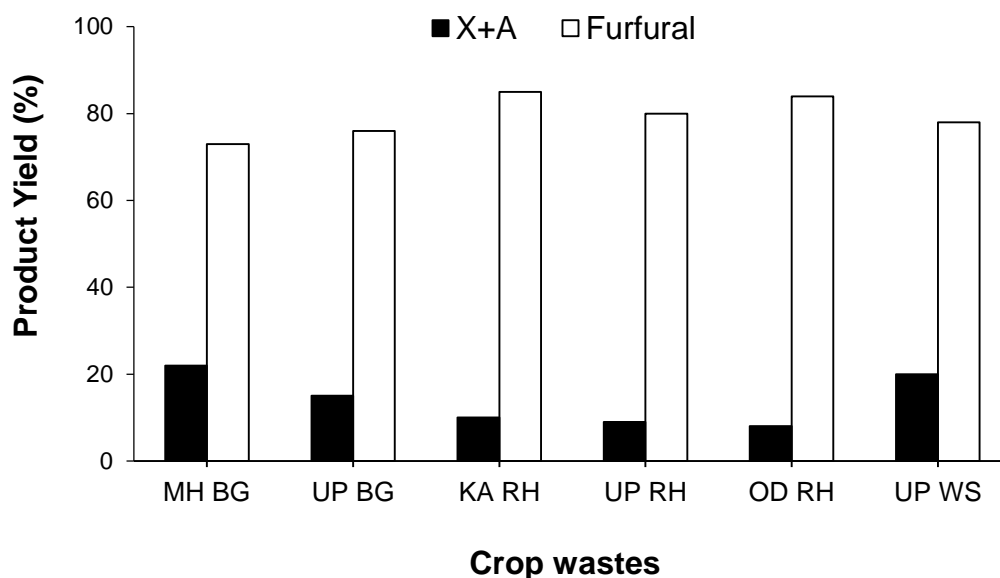


Figure 4.5. Influence of crop wastes for the selective conversion of hemicellulose from these crop wastes into furfural; Reaction condition; crop waste 0.6 g, $[C_3SO_3HMIM][HSO_4]$ 0.12 g, Water+Toluene 60 mL (1:5 v/v), 170 °C, 3 h.

Abbreviation: Maharashtra Bagasse (MH BG), Uttar Pradesh Bagasse (UP BG), Karnataka Rice Husk (KA RH), Uttar Pradesh Rice Husk (UP RH), Odisha Rice Husk, and Uttar Pradesh Wheat Straw (UP WS).

Chapter 5

This chapter deals with the dehydration reactions of C6 (fructose) and C5 (xylose) sugars into HMF and furfural using BAIL.

- Reaction set up, catalytic run, analytical methods and calculations for product yield and conversions are described. The fructose dehydration reactions were performed in water+MIBK biphasic solvent system using $[C_3SO_3HMIM][HSO_4]$ BAIL and obtained 73% HMF yield at 150 °C within 30 min.
- Various solvent systems were tried for fructose dehydration reaction such as water, water+toluene, water+MIBK biphasic solvent system. The water+MIBK solvent system showed better HMF yield (73%) using $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst.
- Effect of catalyst concentration and substrate concentration studies were carried out using $[C_3SO_3HMIM][HSO_4]$ BAIL catalyst. The fructose dehydration reactions were carried out using various catalyst concentrations such as 0.05 g, 0.025 g, and 0.0125 g for 0.5 g fructose in 30 mL water+MIBK biphasic solvent system

(1:5 v/v). The better yield of HMF (73%) was achieved when 0.025g of BAIL is used.

- For substrate concentration study, various fructose concentrations were used (5, 10, 20, and 40, wt% fructose with respect to water) by keeping constant catalyst loading (0.025 g) and solvent quantity (water+MIBK 30 mL; 1:5 v/v). The $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL showed 73% HMF yield with 40 wt% fructose solution when reaction was performed at 150 °C for 1 h (Fig. 5.4.). This is very important result because very high concentrated fructose solution is converted into HMF.

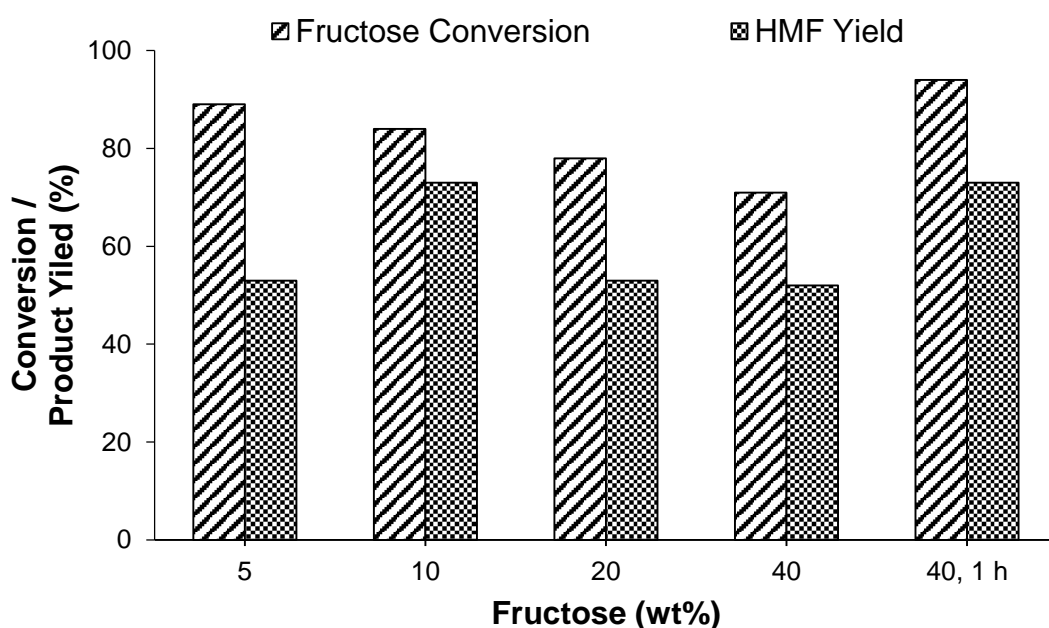


Figure 5.4. Effect of fructose concentration; Reaction condition. $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ 0.025 g, Water+MIBK 30 mL (1:5 v/v), 150 °C, 30 min.

- The comparison of catalytic activities for fructose dehydration reaction was studied using wide range of catalysts and the outcome of this study showed that BAILs perform better compared all the other catalysts used in the study. With solid acid catalyst such as H- β (Si/Al=19), HMOR (Si/Al=10) and HUSY (Si/Al=15) no HMF formation was observed. On the other hand the mineral acid catalyst like H_2SO_4 showed 59% HMF but this catalyst is not recyclable. With Amberlyst-15 catalyst very good yield of HMF (68%) was obtained because of either due to leaching of $-\text{SO}_3\text{H}$ groups in the solution during the reaction or due to the very high acid amount (4.65 mmol/g) compared with other catalysts

(Chapter 5, Table 5.1.). However, during recycling study with Amberlyst-15, a decrease in HMF yield (59%) was seen, which suggests that during the first reaction, $-SO_3H$ groups were leached in the solution.

- The catalyst recycle study suggest that the catalyst is recyclable and showed almost similar HMF yield up to 6th run.
- Dehydration of xylose into furfural was performed at 170 °C for 4 h using BAILS. The comparison of catalyst activities study showed that the BAIL perform better compared to solid acid and mineral acid catalysts. HUSY (Si/Al=15), HMOR (Si/Al=10) and Amberlyst-15 showed 60, 57 and 64% furfural yield, respectively. Moreover, with mineral acid catalyst like H_2SO_4 , 60% furfural was obtained, while $[C_3SO_3HMIM][HSO_4]$ BAIL showed 73% furfural yield (Fig. 5.7).

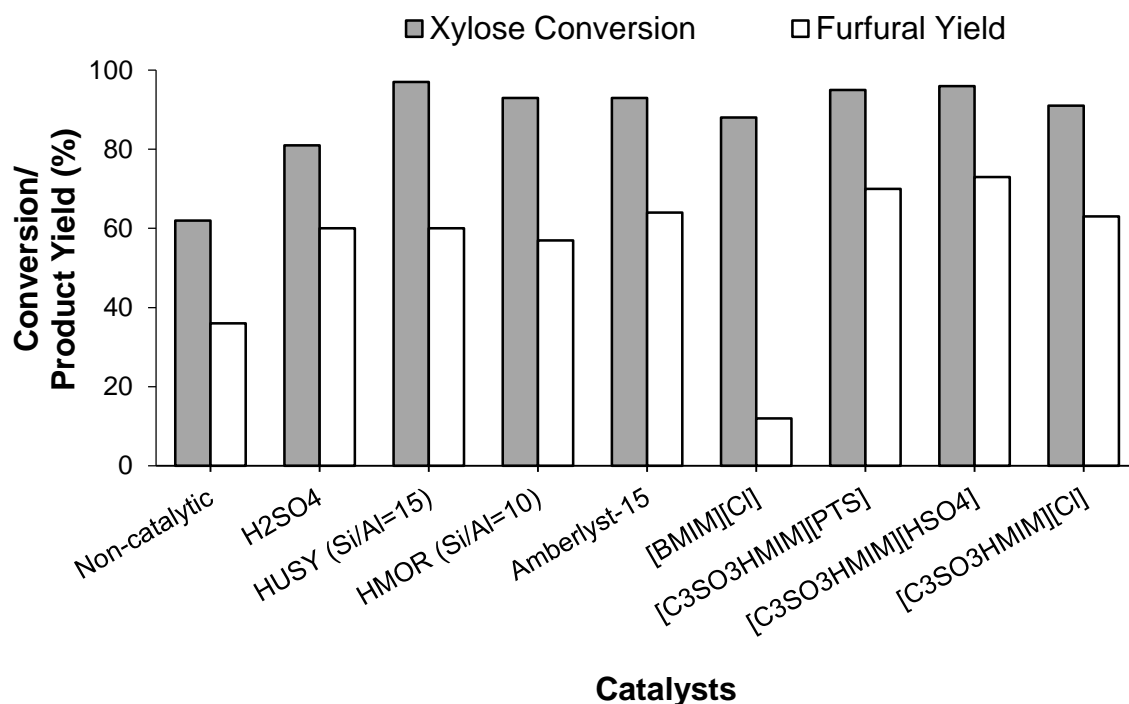


Figure 5.7. Catalyst evaluation study for the dehydration of xylose into furfural; Reaction condition. xylose 0.6 g, catalyst 0.08 g, Water+Toluene 60 mL (1:5 v/v), 170 °C, 4 h.

- For xylose dehydration reaction water+toluene biphasic solvent system was found to be the best while for fructose dehydration reaction water+MIBK biphasic solvent system was found to be the best.
- Effect of reaction time and temperature was studied using $[C_3SO_3HMIM][HSO_4]$ BAIL in water+toluene biphasic solvent system and the optimized reaction time

and temperature is 4 h and 170 °C,. Under these reaction conditions the effect of catalyst and substrate concentration was studied. The optimum catalyst quantity is 0.08 g for 0.6 g xylose to observe better furfural yield (73%). Furthermore, reactions were carried out with various xylose concentrations (0.3 g, 0.45 g and 0.6 g) by keeping constant catalyst quantity (0.08 g). The result showed that with increase in xylose concentration, furfural yield decreases. 81% furfural yield was obtained when 0.3 g xylose was used and 73% furfural yield was obtained when 0.6 g xylose was used.

- [C₃SO₃HMIM][HSO₄] BAIL used for xylose dehydration reaction is recyclable catalyst and showed almost similar furfural yield up to 6th run. Furthermore, the isolation of furfural was carried out from reaction mixture and it was characterized using ¹H NMR spectroscopy. The NMR result showed that furfural obtained from reaction mixture is in pure form.

Finally, it can be concluded that in all the above chapters; 3A, 3B, 4 and 5 the BAILs are used in catalytic amount without any extra catalyst such as mineral acid and metal halide for the hydrolysis and dehydration reactions of saccharides to obtain C5 sugars and furans (HMF and furfural). Very high concentrated fructose solution (40 wt%) can be efficiently converted into HMF. In all the above reactions, BAIL performs better compared to solid acid (HUSY, HMOR, H-β, and Amberlyst-15) and mineral acid (H₂SO₄ and HCl) catalysts because of its Brønsted acidity, homogeneous nature and ion-dipole type of interaction.

List of Publications and Patents

- ◆ Brønsted acidic ionic liquids-catalyzed conversion of hemicellulose into sugars.
Babasaheb M. Matsagar and Paresh L. Dhepe, *Catal. Sci. Technol.* **2015**, 5, 531-539.
- ◆ Conversion of concentrated sugar solutions into 5-hydroxymethyl furfural and furfural using Brønsted acidic ionic liquids.
Babasaheb M. Matsagar, Mudassir K. Munshi, Ashutosh A. Kelkar, Paresh L. Dhepe, *Catal. Sci. Technol.* **2015**, 5, 5086-5090.
- ◆ Efficient method for the selective conversion of hemicellulose from crop wastes into furfural using Brønsted acidic ionic liquids.
Babasaheb M. Matsagar and Paresh L. Dhepe, Manuscript communicated.
- ◆ Synthesis of furfural from hemicellulose in one-pot method using Brønsted acidic ionic liquids.
Babasaheb M. Matsagar and Paresh L. Dhepe, Manuscript communicated.
- ◆ Patent: Novel Process for the conversion of hemicellulose into C5 sugars using ionic liquids.
Babasaheb M. Matsagar and Paresh L. Dhepe, PCT/IN2015/050007.
- ◆ Patent: Acidic ionic liquids catalyzed depolymerization of lignin.
Babasaheb M. Matsagar, Sandip K. Shing, Paresh L. Dhepe and Ashutosh A. Kelkar, 1387/DEL/2013.

Contribution to National/International Symposia and Conferences

- ◆ Best poster award in the 22nd National symposium on catalysis held at CSIR-CSMCRI Bhavnagar, India during 7th to 9th Jan 2015.
- ◆ Presented poster in International Conference on Structural and Inorganic Chemistry held at CSIR-NCL Pune, India during 4th to 5th Dec 2014.
- ◆ Presented poster in the “21st National Symposium on catalysis for sustainable development” held at IICT Hyderabad, India during 11th to 13th Feb 2013.
- ◆ Presented poster in the International Conference on Technological Innovations for All Inclusive Growth held at Hotel ITC Maurya, New Delhi, India during 8th to 9th Nov 2012.

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