Catalytic conversion of hemicellulosic sugars into furfural in ionic liquid media

Akinwale A. Shittu
The University of Toledo

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Catalytic Conversion of Hemicellulosic Sugars into Furfural in Ionic Liquid Media

By

Akinwale A. Shittu

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Master of Science Degree in Chemical Engineering

Dr Sasidhar Varanasi, Committee Chair

Dr Maria Coleman, Committee Member

Dr Sridhar Viamajala, Committee Member

Dr Patricia Komuniecki, Dean
College of Graduate Studies

The University of Toledo
December 2010
An Abstract of

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Over the last decade, there has been a growing interest in the potential of lignocellulosic biomass as an alternative for petroleum resources; this is because of its abundance as a feed stock and its carbon neutrality. Industrially, the conventional way lignocellulosic biomass is utilized results in its conversion to bioethanol, but in order to achieve full scale commercial profitability, it is imperative to generate other value added chemicals from lignocellulosic biomass. One compound that shows a lot of promise is furfural. Furfural is synthesized by the cyclodehydration of pentose sugars and it is a strategic chemical because of its numerous possible applications in oil refining, plastics and pharmaceuticals.

This work focuses on the catalytic dehydration of hemicellulose sugars that are present in lignocellulosic biomass to obtain furfural; this was done in ionic liquid media
and also in a DMA-LiCl reaction system. This work has been able to obtain the optimized processing conditions for the synthesis of furfural in the media used, a carbon balance was also obtained for the reaction and the kinetics of the reaction was better understood. In addition, the presence of side products in the reaction were identified, and it was also established that xylulose formation is an integral part of furfural synthesis from xylose.
This work is dedicated to God Almighty for he is a convenant keeping God. To my Mother, Mrs Abiodun Shittu for her unwaning love and support over the years
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Chapter 1

Introduction

As a result of the increase in global population and a surge in the automobile industry, the dependence on fossil fuels has increased rapidly. With declining petroleum resources, combined with political and environmental concerns, it is imperative to develop economical and energy-efficient processes for the sustainable production of fuels and chemicals\(^1\). In an effort to provide substitutes, a variety of alternative resources such as natural gas, coal and biomass have been used. Among all these, biomass is a key resource because it is CO\(_2\) neutral, generates lower greenhouse emissions, and can be produced in a sustainable manner.\(^3\) Lignocellulosic biomass is comprised of three major components (with varying composition according to the type of biomass): Cellulose (30-45%), hemicellulose (20-35%) and lignin (10-20%) (see Figure 1-1)

Indeed, biomass has the potential to be a renewable resource that can suitably replace crude oil in a biorefinery to produce energy and value added chemicals (e.g. alcohols, aldehydes, acids)\(^4\) (see Figure 1-2)
Figure 1-1  Typical biomass composition (NREL)

Biorefinery: Sugar = Ethanol + Other, Higher Value Chemicals

Figure 1-2  Value added chemicals from biomass$^4$
In plant cell walls, crystalline cellulose fibrils are surrounded by amorphous hemicellulose matrix that is, in turn, enveloped by hydrophobic lignin cladding. Cellulose is made up of straight chains of anhydro-glucose units that are connected by $\beta 1-4$ linkages, and is the most abundant polymer in nature. Hemicellulose, on the other hand has a branched structure and is an amorphous polymer consisting of xylose, arabinose, glucose, galactose and mannose. It is the second most abundant polysaccharide in nature after cellulose\(^{24}\), its composition also varies depending on plant species, but the major component is usually xylan. The structure of a typical hemicellulose polymer chain is shown below in Figure 1-3. Clearly, the main building block of hemicellulose is xylose. Xylose is classified as a monosaccharide of the aldopentose type, which means that it contains five carbon atoms and includes an aldehyde functional group.

![Figure 1-3 Stucture of Hemicellulose with xylan backbone](image)

Finally, the lignin component of plant biomass is a cross-linked network of phenyl proponoid units that are covalently attached to hemicellulose\(^{36}\). Lignin is
hydrophobic and has high calorific value, and is usually considered a fuel that can be directly subjected to combustion for power generation. However, with the development of new methods of deconstructing lignin, its constituent aromatic monomeric units could also serve as precursors for chemical and polymer production.

A variety of conversion pathways exist for transforming biomass into fuels or fuel and chemical precursors, including pyrolysis, gasification, transesterification, and hydrolysis and fermentation\(^5\). In processes based on saccharification of biomass carbohydrates, the monosaccharides resulting from cellulose and hemicellulose are used as basic, inexpensive raw material for the synthesis of a large number of chemicals for the chemical industry\(^4\).

For example, for producing fuel ethanol, these sugars are fermented using suitable microorganisms. The fermentation scheme involves the conversion of glucose and xylose by microorganisms according to the following equations:

\[
\begin{align*}
C_6H_{12}O_6 & \rightarrow 2C_2H_5OH + 2CO_2 \\
3C_5H_{10}O_5 & \rightarrow 5C_2H_5OH + 5CO_2
\end{align*}
\]

The issue with this process however, is that even assuming quantitative efficiency both in the derivation of glucose and xylose from cellulose and hemicellulose respectively, as well as the fermentation process, one third of the available carbon is expelled as carbon dioxide, 9.6 g of which is produced for every 10 g of ethanol \(^6\).
This challenge therefore necessitates a different route to biomass utilization that will make use of all the available carbon and does not necessarily involve fermentation.

An approach which has been used to utilize biomass sugars without involving fermentation is the dehydration of these sugars to furanic compounds such as furfural and HMF, these compounds can subsequently be converted into diesel fuel additives (by aldol condensation and aqueous phase dehydration-hydrogenation), industrial solvents (e.g., furan, tetrahydrofurfuryl alcohol, furfuryl alcohol), various bioderived polymers (by conversion of HMF into furan dicarboxylic acid (FDCA) and P-series fuel (by subsequent hydrogenolysis of furfural)\(^3\)

This work has focused on the conversion of hemicellulosic sugars into furfural. Furfural is one of the important chemical intermediates used widely in the petrochemical and fine-chemical industries and it is proposed as a top value-added chemical from biomass in a recent report by the United States Department of Energy (DOE)\(^8\). An important use of furfural is that it can be catalytically hydrogenated to 2-methyltetrahydrofuran (MTHF). MTHF is an oxygenated fuel additive with high oxygen content (20 wt.%), the same octane number as regular gasoline (87) and a lower heating value (32 MJ/kg) that is slightly higher than that of ethanol (26.7 MJ/kg)\(^1\). This set of properties allows it to be mixed with ethanol and natural gas liquids to create P-series fuel, which has been officially proposed as an additional substitute for gasoline\(^9\).

Chapter 2 of this thesis focuses on the background knowledge, properties of furfural, major factors affecting yield and the state of the art. In chapter 3, the dehydration of pure xylose dissolved in the ionic liquid, 1-Ethyl-3-methylimidazolium chloride (EMIMCl), was investigated in the presence of metal halides, CrCl\(_2\) and CuCl\(_2\), to optimize the
reaction conditions to achieve high yield and conversion of xylose. In chapter 4, the results of attempts to achieve a carbon mass balance closure on the dehydration reaction are presented. NMR analysis data was gathered to identify the presence of any-side products formed during the reaction. As the hemicellulose derived pentose sugars also contain arabinose in addition to xylose, in chapter 5 the reaction scheme of chapter 3 and 4 was implemented for the case of xylose-arabinose mixtures. The proportion of the individual sugars is varied from a 50:50 mixture to that corresponding to a typical lignocellulosic biomass case. Chapter 6 investigates the dehydration of C5 sugars in a more recently proposed reaction medium\textsuperscript{27}, namely, N,N-Dimethylacetamide (DMA)-LiCl, that was shown to provide better yields and conversions for the dehydration of C6 sugars when compared to IL-based reaction media, The thesis is concluded with a mention of the principal conclusions of this work and future directions (Chapter 7).
2.1 Background

As noted in the Introduction, one of the process alternatives for utilizing lignocellulosics as biorefinery feedstocks is saccharifying their carbohydrate fractions into monomeric sugars; these form the precursors for subsequent chemical/biochemical conversion to other platform chemicals.

Indeed, production of ethanol from lignocellulosic biomass is traditionally accomplished through a series of stages: the pretreatment stage which reduces the biomass recalcitrance and makes the biomass more amenable to hydrolysis, enzymatic hydrolysis which releases the sugars from pretreated biomass, and the fermentation of these sugars to ethanol.

Dehydration of biomass sugars by chemical means to furans has been suggested recently as a promising alternative strategy to produce “drop-in” fuels as well as platform chemicals suitable for the production of industrial solvents and materials\(^ {27,28,29}\). The early studies focused on production of hydroxymethylfurfural (HMF) from glucose and fructose dehydration reactions and its subsequent conversion to dimethylfurfural (DMF).
More recently, the techniques were modified and extended to achieve a single-pot conversion of cellulose directly to HMF\(^{30}\). Not much attention was however given in literature to the dehydration of the C5 sugars resulting from the hemicellulose portion of biomass (namely, xylose and arabinose). Unlike C6 sugars, dehydration of C5 sugars leads to the formation of furfural, which is also an important platform chemical.

The following section provides an overview of the dehydration of C5 sugars into furfural, the existing processes for furfural production, the major inhibitors for the dehydration reaction and the state of the art.

### 2.2 Furfural

#### 2.2.1 Properties of furfural

Furfural is an almond-scented, oily, colorless liquid that turns yellow to dark brown when exposed to air. The physical properties of furfural are listed in Table 2.1 below. Furfural is used as a solvent for refining lubricating oils, and in the production of tetrahydrofuran, an important industrial solvent.

![Structure of furfural](image)

**Figure 2-1 Structure of furfural**

In addition, furfural along with its sister molecule HMF, can serve as a building block for other potential transportation fuels including dimethylfuran and ethyl levulinate\(^{10}\)
Table 2.1  General Properties of Furfural \textsuperscript{25}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>96.1</td>
</tr>
<tr>
<td>Freezing Point (\degree C)</td>
<td>-36.5</td>
</tr>
<tr>
<td>Boiling Point (\degree C)</td>
<td>161.7</td>
</tr>
<tr>
<td>Density at 25\degree C</td>
<td>1.16</td>
</tr>
<tr>
<td>Viscosity at 25\degree C</td>
<td>1.5</td>
</tr>
<tr>
<td>Critical Pressure (psi)</td>
<td>798.2</td>
</tr>
<tr>
<td>Critical Temperature (\degree C)</td>
<td>397.4</td>
</tr>
<tr>
<td>Heat of Combustion at 25\degree C (kcal/gm.mole)</td>
<td>-560.3</td>
</tr>
<tr>
<td>Heat of Formation (liquid at 25\degree C) (kcal/gm.mole)</td>
<td>-49.2</td>
</tr>
<tr>
<td>Heat of Fusion (kcal/gm.mole)</td>
<td>3.43</td>
</tr>
<tr>
<td>Heat of Vaporization at 433.8\degree K (kcal/gm.mole)</td>
<td>9.22</td>
</tr>
</tbody>
</table>

About 74\% of the world’s furfural production capacity is located in China, as of January 1, 2008. Other important countries with furfural production include the Dominican Republic and South Africa. Together, these three countries account for about 90\% of worldwide installed furfural production capacity\textsuperscript{11} (see Figure 2-2). However, recently there is an increasing awareness in the United States towards producing furfural and other furanic compounds from biomass as a result of an increase in oil prices and the potential of these compounds to produce value added chemicals.
2.2.2 Mechanism of xylose dehydration to furfural (in an acidic media)

Furfural is produced by dehydrating five-carbon sugars such as xylose and arabinose which can be obtained from the hemicellulose fraction of lignocellulosic biomass (see Figure 2-3)
During cyclodehydration of xylose to furfural, hydrogen ions protonate with hydroxyl group attached to carbon atom thus resulting in transition state with a trivalent, positively charged oxygen atom \(^\text{10}\) (first step in Figure 2-3). Because oxygen is more electronegative when compared with carbon, the positive charge (electron deficiency) delocalizes to form a positively charged fragment of carbon atom and to the dissociation of the C-O bond with the liberation of a water molecule (second step in Figure 2-3). Subsequently, the two electrons from a neighboring C-O bond are used to form a double bond between two carbon atoms (third step in Figure 2-3) This causes fission of C-O bond from which
electrons are taken, thus freeing a hydrogen atom for migration within the molecule (fourth step), this hydrogen ion protonates another lone (non-bonding) electron pair of hydroxyl oxygen to trigger the liberation of another water molecule\(^4\) (fifth and sixth steps). Finally, the trivalent carbon atom leads to the formation of a ring structure rather than a double bond; this is due to the fact that the carbon atoms participating in double bond form a planar structure which is characterized by bond angles of 120º. The 1, 4 elimination of H\(^+\) completes the process of furfural molecule formation\(^4\) (seventh Step). The conversion of pentose sugars to furfural, thus, has been shown to be based on the fact that the hydrogen ions transform the hydroxyl group from the pentose to H\(_2\)O\(^+\), which is the prerequisite for the liberation of water.\(^{10}\)

**2.3 Traditional Processes for Furfural Production**

All the traditional processes are based on the Quaker Oats Technology which uses aqueous sulfuric acid to digest the biomass and subsequently cyclodehydrate the sugars obtained. This reaction occurs at a temperature of about 170ºC-185ºC with a residence time of 3 hours, and provides furfural yield of 40-50%\(^{10}\). There have been several modifications to this technology such as Westpro Modified Huaxia technology\(^{13}\), Suprayield\(^{14}\), and Vedernikov’s single-step furfural process\(^{12}\). The aim of these modifications is to improve the yield, selectivity, furfural recovery and product purity; these methods utilize different reactors and different methods such as fixed bed reactors\(^{13}\) and a single step furfural process from pentosan which uses a continous process to extract furfural from the product stream\(^{14}\). Nevertheless, they still make use of the conventional acid catalyst which leads to substantial amount of solid residues (humins) and also results
in undesired side reactions. Another major drawback of this traditional soluble acid technology is the extremely slow rate at which pentosan sugars are converted to furfural; the saccharification of lignocellulosic biomass is 50 times faster than the subsequent conversion of sugars to furfural, thus making the dehydration reaction the limiting factor\textsuperscript{12}. Hence, there is a need for approaches that do not rely on soluble acid catalyst and produce better yield of furfural without resulting in formation of large quantities of humins.

2.4 Major Factors Affecting Furfural Yield

Yield-loss reactions occur while the furfural is in the liquid phase, by polymerization and by reaction with the precursor pentose, leading to low final furfural yield\textsuperscript{15}. Condensation reactions between furfural and intermediates of the xylose-to-furfural conversion give rise to species such as furfural pentose and difurfural xylose\textsuperscript{16}. Concomitantly, resinification, which is the combination of multiple furfural molecules to give intermediates, could also take place (see, Figure 2-4). It was shown by Zeich et al\textsuperscript{10} that, when condensation and resinification reactions occur simultaneously:

1. The loss by condensation is much greater than the loss by resinification, and
2. The loss of furfural via both these processes diminishes strongly with increasing temperature due to the so-called “entropy effect”: increasing temperature creates an environment that propagates the disintegration of molecules, which in turn inhibits the build up of larger molecules.
2.5 State of The Art (Approaches for furfural production)

Various attempts have been reported in the literature on the dehydration of hemicellulosic sugars into furfural\textsuperscript{5,13,17,32}. These aim at both improving the yield of furfural by suppressing the side reactions and also facilitating easy recovery of the catalysts. Dias et al\textsuperscript{32} have investigated the conversion of xylose into furfural using solid acid catalysts which have large surface areas and narrow pore size distributions, called sulfonic acid-functionalized mesoporous silicas (SAMS), these catalysts have displayed a high furfural selectivity of about 82\% but the process requires long reaction time (more than 25 hours) and that eventually results in catalyst deactivation because of interaction between reaction products and acid sites as a result of the long residence time. Moreau et al\textsuperscript{33} have also attempted to convert xylose to furfural using the zeolites; faujasite and mordenite, these catalysts have a porous structure that can accommodate a wide variety
of cations which are then rather loosely held and can readily be exchanged for others in a contact solution, they both delivered high selectivity of 90-95% at conversions of less than 30%, and delivered reduced selectivity at higher conversions, thereby not providing an optimum dehydration condition. Potapov et al.\textsuperscript{31} studied the dehydration of sugars by attaching catalytically active centers (Cr and Ti-porphyrin complexes) to cross-linked polymers that are swellable in the reaction medium (polyacrylamide gel) with an addition of anhydrous acetic acid, this approach allowed for xylose dehydration at lower temperatures with a relatively higher selectivity, but it results in the formation of a large amount of solid residues (humins) (10wt%). As an improvement to these processes, the work on this thesis seeks to catalytically convert C5 sugars to furfural in relatively shorter reaction times without the use of strong mineral acids, it also aims to reduce the formation of solid residues (humins) while identifying the ideal reaction conditions, and optimizing furfural yield. The objective of this work also extends to understanding the kinetics of the reaction, obtaining a carbon mass balance closure and identifying the reasons for the observed yield loss.
Chapter 3

Conversion of Xylose to Furfural in EMIMCl-CrCl₂-CuCl₂ Media: Optimization of the reaction conditions

3.1 Introduction

Lignocellulosic biomass sugars, primarily C₆ sugars, have been dehydrated and converted to value-added chemicals e.g 5-Hydroxymethylfurfural, using different methods such as sulfated zirconia, acid hydrolysis, ionic liquids, and DMSO/dichloromethane mixture. Worthy of note are the results obtained by Zhang et al. in which they dehydrated glucose into HMF. The novelty of their work is that they showed, for the first time, that an ionic liquid medium containing catalytic amounts of metal halides allows glucose to be directly dehydrated to the furan, HMF in high yields. Prior to their work, it was deemed essential to isomerize glucose to fructose and convert fructose via acid catalysis to HMF to achieve acceptable yields. Also, ionic liquids possess several unique properties that would make them desirable reaction media. Most important among them are their non-volatility, thermal stability, ability of their constituent ions to catalyze specific reactions.

There has been no work reported to date in the literature on converting hemicellulose sugars to furanic compounds using metal chlorides in ionic liquid media, while the techniques developed for C₆ sugars were recently implemented directly on
cellulose. This chapter contains a description of the efforts to catalytically dehydrate xylose which is a hemicellulose sugar, in the ionic liquid, ethyl imidazolium chloride (EMIMCl), containing catalytic amounts of CrCl$_2$ and CuCl$_2$. Several combinations of reaction conditions have been employed to improve the yields of furfural in product. For initial reactions, conditions same as those used for glucose and fructose dehydration by Zhang et al were employed for xylose dehydration as well with reasonably good yields. These conditions used were: 50mg of sugar was added to 500mg of EMIMCl which has been previously heated to 150°C with metal halide and this mixture was reacted for 3 hours. In order to optimize the sugar dehydration process and to maximize furfural yield, it is important to study this dehydration reaction with different (a) catalyst loadings, (b) reaction times, (c) catalysts, (d) ionic liquids, (e) reaction temperatures, (f) catalyst combinations, and (g) xylose to ionic liquid ratios. The results of these investigations are presented and discussed in this chapter.

3.2 Materials and Methods

Xylose (99%) was obtained from Acros. CuCl$_2$ and CrCl$_2$, Sulfuric acid (concentrated, ACS reagent grade), 1-Ethyl-3-methylimidazolium chloride (EMIMCl, 98% pure), 1-Butyl-3-methylimidazolium chloride (BMIMCl, 98% pure), 1- Ethyl-3-methylimidazolium acetate([EMIM]Ac, 98% pure), 1-Butyl-3-methylimidazolium trifluoromethansulfonate (98% pure), and 1-3-dimethylimidazolium methanesulfonate were purchased from Sigma-Aldrich. 1-Butyl-3-methylimidazolium trifluorophosphate (96% pure), 1-Hexyl-3-methylimidazolium trifluoromethansulfonate (95% pure), 1-
Ethyl-3-methylimidazolium thiocyanate, Benzyldimethyltetradecylammonium chloride, and 1-3-dimethylimidazolium methylsulfate were obtained from Fluka,

Batch catalytic experiments were carried out in 22 ml vials heated in a temperature controlled oil bath placed on top of a magnetic stirrer. The temperature in the oil bath was measured by a K type thermocouple (Omega) and controlled using a series 16A temperature controller (Dwyer Instruments) coupled with a 150W heating cartridge.

In a typical experiment, 500 mg of EMIMCl was loaded into vials (15.5mm x 50mm). CrCl$_2$ and/or CuCl$_2$ (approximately 6 mol% with respect to sugars) with a total metal chloride loading of 37µmol/g of EMIMCl were added individually to each vial. The vials are sealed and heated on the oil bath at 150 ºC and 700 rpm for 20 minutes. After the reactor was cooled to room temperature, 50 mg of xylose was added to each vial and the vials were subsequently heated on the oil bath at 80 ºC and 700rpm. After 3 hours of reaction, the vials were rapidly cooled to room temperature and 2mL of water was added to each vial to end the reaction. Figure 3-1 is a photograph which shows the typical change in appearance of the IL media at various stages of the reaction process. For EMIMCl, it is shown in Figure 3-1 (A, B, C) that the reaction mixture changes from golden yellow (IL) to green (IL and CrCl$_2$) and finally dark brown (IL, CrCl$_2$ and xylose). On the other hand, Figure 3-1 (D, E, F) shows the change in appearance for a BMIMCl media from near colorless ( IL) to green (IL and CrCl$_2$) and finally dark brown (IL, CrCl$_2$ and xylose).
Figure 3-1  Change in physical appearance of reaction medium. (A) EMIMCl (B) EMIMCl with CrCl2 catalyst after heating at 150°C for 20 minutes (C) EMIMCl, CrCl2 and xylose mixture that has been converted to furfural after 3 hours of reaction at 80°C (D) BMIMCl (E) BMIMCl with CrCl2 catalyst after heating at 150°C for 20 minutes (F) BMIMCl, CrCl2 and xylose mixture that has been converted to furfural after 3 hours of reaction at 80°C

The vials were placed in the centrifuge and centrifuged at 2000 rpm for 15 minutes. Upon centrifugation, the liquid layer obtained was filtered using a syringe filter and the clear liquid analyzed for xylose and furanic compounds in a Dionex high performance liquid chromatograph (HPLC), equipped with a refractive index detector, using a HPX-87 H column (Bio-Rad Laboratories Inc, Hercules, CA) at 65 °C. The mobile phase was 5mM H2SO4 solution with a flow rate of 0.6mL/minute. Several standards with different concentrations of xylose ranging from 0.0625mg/mL to 4mg/mL and furfural ranging from 0.145mg/ mL to 9.28mg/ml were analyzed in order to generate a calibration curve. A linear correlation between the signal of the HPLC and concentration of xylose and furfural was established as shown in Figure 3-2 below;
3.3 Definitions of conversion and yield:

Xylose conversion: Conversion of sugar is defined as the percent of the initially loaded sugar that is consumed during the course of the reaction.

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Product yield: Yield is defined as the grams of carbon in the consumed xylose that appear in the furfural product

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All the conversion and yield numbers reported in the thesis are based on the above definitions. From the conversion and yield percentages, one could determine the mass of furfural obtained from a given initial mass of xylose by the formula:

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3.4 Results and Discussions

3.4.1 Effect of mixing speed on xylose conversion and furfural yield

Since IL media are significantly more viscous than aqueous systems, to establish the minimal stirring speed required for achieving uniform instantaneous concentrations of the reactants and products in the batch catalytic reaction system, yields and conversions were measured over a range of stirring speeds. All the catalytic reactions were performed batch-wise using magnetically stirred glass micro-reactors, at constant reaction temperature of 80°C and reaction time of 3 hours. The catalyst, xylose and ionic liquid loading were also kept constant at 6 mol%, (relative to sugar), 50mg and 500mg respectively. It was observed that at mixing speeds higher than 500 rpm, the conversion and the yields were unchanged indicating that mixing speeds greater than 500 rpm are sufficient to achieve good-mixing and eliminate any mass transfer limitations. All the experiments reported below were run at a magnetic stirrer speed of 700 rpm.

![Conversion and yield graph](image)

**Figure 3-2** Xylose conversions and furfural yields at different mixing speeds between 400 and 800rpm at 80°C for 3 hours
3.4.2 Use of different ionic liquids

Recent studies have demonstrated the potential of hydrophilic ionic liquids for the conversion of C6 sugars into HMF \(^{18,19}\). In these studies, a range of imidazolium ionic liquids with different anions have been studied. However, there are no data on the effect of these different ionic liquid media in the catalyzed dehydration of hemicellulosic sugars into furfural. This sub-section discusses the impact of ionic liquid structure on xylose conversion and furfural yield. For these experiments, the amount of the different ionic liquids was kept constant at 500mg, likewise the amount of xylose which was kept constant at 50mg, the reaction conditions were also kept constant at 80°C and 3 hours. Figure 3-3 shows that amongst all the ionic liquids used, the highest yield and conversion were displayed by EMIMCl and BMIMCl with conversions between 84% to 86%, and yields from 47% to 49%.

![Figure 3-3 Xylose conversions and furfural yields in different ionic liquid solvents reacted at 80°C for 3 hours](image-url)
Table 3.1 Ionic liquids used for catalytic dehydration of xylose to furfural

<table>
<thead>
<tr>
<th>Label</th>
<th>Ionic Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1-Ethyl-3-Methylimidazolium Acetate (EMIMAc)</td>
</tr>
<tr>
<td>B</td>
<td>1-Butyl-3-Methylimidazolium Hexafluorophosphate (BMIMHFP)</td>
</tr>
<tr>
<td>C</td>
<td>1-Butyl-3-Methylimidazolium trifluoromethansulfonate (BMIMTMS)</td>
</tr>
<tr>
<td>D</td>
<td>1-Hexyl-3-Methylimidazolium trifluoromethansulfonate (HMIMTFS)</td>
</tr>
<tr>
<td>E</td>
<td>1-Ethyl-3-Methyl Imidazoliumthiocyanate (EMIMTC)</td>
</tr>
<tr>
<td>F</td>
<td>1,3-Dimethylimidazolium methanesulfonate (DMIMMS)</td>
</tr>
<tr>
<td>G</td>
<td>1,3-Dimethylimidazolium methanesulfate (DMIMMSA)</td>
</tr>
<tr>
<td>H</td>
<td>Benzyldimethyltetracylcammonium chloride (BMMTACl)</td>
</tr>
<tr>
<td>I</td>
<td>1-Ethyl-3-Methylimidazolium chloride (EMIMCl)</td>
</tr>
<tr>
<td>J</td>
<td>1-Butyl-3-Methylimidazolium chloride (BMIMCl)</td>
</tr>
</tbody>
</table>

Some other ionic liquids like 1, 3-Dimethylimidazolium methanesulfonate exhibited a comparable yield of 46% but had a lower conversion of 62%, while 1-Butyl-3-methylimidazolium trifluoromethansulfonate had a conversion of 72% and yield of 30%, this shows the effectiveness of the sulfonate anion. Other anions which were used but did not deliver good yields are the acetate anion, phosphate anion and thiocyanate anion as shown by the 92% conversion but 5% yield by 1-Ethyl-3-Methyl Imidazolium Acetate (EMIMAc), 17% conversion and 8% yield by 1-Butyl-3-Methylimidazolium Hexafluorophosphate (BMIMHFP) and the 7% conversion and 3% yield delivered by 1-Ethyl-3-Methyl Imidazoliumthiocyanate (EMIMTC) respectively.

In general, EMIMCl and BMIMCl proved to be the most efficient ionic liquid media for xylose dehydration among all the ionic liquids were evaluated. This effectiveness may be due to the fact that the chloride counterions in both ionic liquids form only weak ion pairs which favors the isomerization of sugars from the aldose form to the ketose form.
and the subsequent dehydration of the ketose form to the furfural. As a result of the weak coordination of the ionic liquid structures\(^{35}\), they do not compete with sugar for the binding of metal chlorides; therefore it is more likely that a sugar-metal coordination will be formed. In this case, the chloride counterions may aid the isomerization of xylose to xylulose as shown by HPLC analysis (see Appendix) and the subsequent dehydration of the xylulose obtained to furfural.

Figure 3-4 Chemical structure of xylulose

3.4.3 Nature of Ionic Liquid (EMIMCl and BMIMCl) and their effectiveness as dehydration solvents

In the section 3.3.1, EMIMCl and BMIMCl have been shown to be the most effective amongst all the ionic liquids used, and there seems to be a disparity in the capability of these different ionic liquids to dehydrate xylose into furfural. The goal of this experiment was to identify the ideal reaction conditions (temperature and time) for each of these two ionic liquids, whose structures are shown in Figure 3-5 below;

Figure 3-5 Chemical structures of (a) 1-Butyl-3-methylimidazolium chloride (BMIMCl) and (b) 1-Ethyl-3-methylimidazolium chloride (EMIMCl) \(^{37}\)
A constant catalyst loading of 6 mol% (with respect to the sugars) was dissolved in 500mg of the ionic liquids to obtain a homogenous solution at 150°C for 20 minutes, 50mg of xylose was subsequently added and the reaction occurred at temperatures 80°C, 100°C and 120°C for times 1hour, 2hours, 3hours and 4 hours. All experiments were repeated three times with a standard deviation less than 10%.

BMIMCl demonstrated an increased percent conversion at 80°C with increased reaction times and it seems to stabilize at 100°C regardless of the reaction time as shown by Figure 3-6-3.8, the yield increases steadily with increased reaction times at 80°C reaching a maximum 55% at 3 hours. However at 100°C and 120°C, increased reaction time appeared to have an adverse effect on furfural yield as the yield reduced with higher residence times. The yield loss experienced may be due to furfural loss from resinification and condensation as a result of long residence time in the liquid phase.

Figure 3-6 Xylose conversion and furfural yields in BMIMCl and CrCl₂ at 80°C for 1 hour, 2 hours, 3 hours and 4 hours
Figure 3-7 Xylose conversion and furfural yields in BMIMCl and CrCl$_2$ at 100°C for 1 hour, 2 hours, 3 hours and 4 hours

Figure 3-8 Xylose conversion and furfural yields in BMIMCl and CrCl$_2$ at 120°C for 1 hour, 2 hours, 3 hours and 4 hours

Figure 3-9-3.11 below shows the effect of time and temperature on xylose conversion and furfural yield when EMIMCl is used as the solvent, it is observed that at 80°C, the yield
appears to increase with longer reaction times with a maximum conversion of 82% and yield of 53%. In general, there seems to be a steady increase in furfural yield with an increase in reaction times for mild conditions (for example 80°C). Whereas at temperatures as high as 120°C, there seems to be no change in furfural yield with increasing reaction times, this may be due to yield loss as a result of furfural degradation and it might also be that higher temperatures are much more favorable for the major side reactions that occur in furfural synthesis. When they are compared side by side based on the results of the experiments, EMIMCl and BMIMCl have delivered relatively good yields and therefore either one of them is a good solvent for xylose dehydration to furfural. In the course of this work, EMIMCl was used as the choice solvent.

Figure 3-9 Xylose conversion and furfural yields in EMIMCl and CrCl₂ at 80°C for 1 hour, 2 hours, 3 hours and 4 hours
Figure 3-10 Xylose conversion and furfural yields in EMIMCl and CrCl$_2$ at 100°C for 1 hour, 2 hours, 3 hours and 4 hours

Figure 3-11 Xylose conversion and furfural yields in EMIMCl and CrCl$_2$ at 120°C for 1 hour, 2 hours, 3 hours and 4 hours
3.4.4 Effect of Xylose to Ionic liquid ratio

It is imperative to investigate the optimum xylose to ionic liquid ratio in order to avoid deposition of solid residues, prevent side reactions and reduce yield-loss due to resinification. The dependence of the reaction performance on the ionic liquid content of the whole system was established by studying the conversion and yield under xylose/ionic liquid ratios ranging from 5%-15%.

In these experiments, a constant catalyst (CrCl$_2$) loading of 6mol% (with respect to the sugars) was added to 500 mg of EMIMCl and BMIMCl each, this mixture was heated to 150°C for 20 minutes. Different amounts of xylose corresponding to a xylose to IL ratio of 5%, 10% and 15% was added, and the resulting mixture was heated in the vials for time periods of 1 hours, 2hours, 3hours, and 4hours at 80°C.

![Conversion graph](attachment:image.png)  

Figure 3-12 Xylose conversion in EMIMCl and CrCl$_2$ using different xylose/IL ratio of 5%, 10% and 15% at 80°C for 1hr, 2hr, 3hr and 4hr
It is observed from Figure 3-12 and Figure 3-13 that an increase in the xylose/IL ratio appears to result in lower conversions and on the other hand higher yields, reaching a maximum conversion of 97% at 5% xylose /IL ratio in 4 hours, and a maximum yield of 48% at 15% xylose/IL ratio in 3 hours. It appears that, while low xylose-to-IL proportions lead to high conversions relatively quickly, the yield of furfural is unacceptably low under these conditions. Also, the yield tends to reach an optimum around 3 hrs, and carrying the reaction beyond three hours seems to lead to a drop in the yield indicating that furfural formed may get consumed via condensation and resinification side-reactions at longer times.
3.4.5 Effect of catalyst loading

The catalyst loading used may also affect the conversion and yield of the dehydration product. To investigate this, catalytic dehydration experiments were performed at a constant reaction temperature of 80°C and reaction time of 3 hours, the amount of catalyst used in these reactions were varied such that they corresponded to 6 mol%, 15 mol%, 20 mol% and 40 mol% with respect to xylose concentration, for each of these catalyst loading, 500mg of IL and subsequently, 50mg of xylose were added.

Figure 3-14 shows the effect of the variation of catalyst loading with respect to the amount of xylose present in the feed (50mg).

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Figure 3-14 Xylose conversions and furfural yields in EMIMCl and CrCl2 for different catalyst loading of 6 mol%, 15 mol%, 20 mol% and 40 mol% (with respect to xylose) at 80°C for 3 hours.
It was observed that the optimum catalyst loading is 20 mol% with respect to the sugars, at this catalyst loading, a maximum 93% conversion and 42% yield was obtained, an increase in the catalyst loading beyond this results in an increase in the conversion and a decrease in the yield, this points to the fact that more xylose is being dehydrated but there is more yield-loss due to side reactions.

### 3.4.6 Effect of Catalyst combination

Previous experiments were performed which shows that Chromium (II) chloride and Copper (II) chloride are the two most effective catalysts in the cyclodehydration of sugars to furans\(^{28}\). These two different catalysts were postulated to have different impacts on the mechanism of dehydration of six carbon sugars\(^{19}\): Copper (II) chloride was proposed to affect the mutarotation of glucose anomers while Chromium (II) chloride was postulated to play a key role in the isomerization of glucose to fructose through an intermediate and the subsequent dehydration of fructose to HMF\(^{19}\). This section discusses the effect of a catalyst combination of these two metal halide catalysts at different mole fractions on xylose conversion and furfural yield.

The total metal chloride loading was maintained at 37 \(\mu\text{mol/g}\) of EMIMCl solvent, which corresponds to 6 mol% with respect to the xylose molar concentration. The metal chlorides were dissolved in the ionic liquid at 150°C (as used in previous
experiments) and sugar was added to the homogenous solvent, followed by reaction at 80°C for 3 hours.

Figure 3-15 shows that xylose conversion and furfural yield increases slightly with a rise in the amount of CrCl₂ until a mole fraction of CuCl₂ : CrCl₂ = 0.4 : 0.6 is reached where a maximum conversion of 90% and a maximum yield of 49% was achieved, after which the xylose conversion and furfural yield decrease gradually with increasing amount of CrCl₂.

![Figure 3-15 Conversion of xylose and yield of furfural at 80°C and 3 hrs in EMIMCl containing a catalytic mixture of CuCl₂ and CrCl₂. The total amount of metal halide was kept constant at 6 mole % of xylose. The x-axis refers to the molar proportion of CrCl₂ relative to CuCl₂ in the metal halide mixture.](image.png)
The additional yield observed by a combination of these two catalysts at a CrCl$_2$ mole fraction may be due to the fact that CuCl$_2$ aids the mutarotation of xylose anomers and CrCl$_2$ plays a key role in the isomerization of the aldopentose sugar (xylose) to its keto-isomer form (xylulose), and in addition aids the subsequent dehydration of xylulose to furfural.

### 3.4.7 Effect of addition of mineral acids

The dehydration of cellulosic sugars such as glucose and fructose in ionic liquid in the presence of sulfuric acid resulted in substantial HMF yields. An 80% HMF yield was achieved when 18 mol % H$_2$SO$_4$ (relative to fructose) was used. While a lower acid loading (1.8 mol %) gave 75% yield. Accordingly, in this sub-section, the effect of adding sulfuric acid to the IL-media on the furfural yield was investigated. In these experiments, 25mg of CrCl$_2$ was added to 500 mg of EMIMCl and BMIMCl separately, and each mixture was heated to 150°C for 30 minutes. Subsequently, 50mg of xylose and 18mol% H$_2$SO$_4$ (relative to xylose) was added, and the resulting mixture was heated in the vials at 80°C for time periods of 30 minutes, 1 hours, 2hours, 3hours, 4hours, and 5 hours.

Figure 3-16 shows the effect of sulfuric acid on the furfural yield, it is observed that sulfuric acid does not have the desired effect of yield improvement on xylose dehydration as it does with fructose dehydration, the addition of sulfuric acid results in a reduction of furfural yield both in EMIMCl and BMIMCl media.
Although sulfuric acid is used industrially to dehydrate xylose to furfural, this reaction is carried out at temperatures greater than 150°C \(^{10}\). As shown by previous experiments, in IL media, milder conditions were relatively more effective for rapid xylose conversion and high furfural yield (see sub-section 3.4.3). Accordingly, additional mineral acids were not included in subsequent investigations.

### 3.4.8 Determination of the effect of furfural side reactions on yield loss

As was already noted, several side reactions may contribute to the loss of furfural. These side reactions include condensation reactions between furfural and intermediates of the
xylose-to-furfural conversion to give fufural pentose and difurfural xylose \(^{23}\). A close examination of the HPLC chromatographs obtained from the dehydration reaction mixtures does not reveal any additional peaks to indicate that other compounds are present. This is likely due to the fact that the products of these side reactions are much heavier and cannot be resolved by the HPX-87 H column used in the HPLC analysis.

To assess the role of the purported condensation reactions between fufural and the reaction intermediates, the effect of deliberate addition of fufural to the reaction mixture on the dehydration of xylose to fufural was studied.

In this experiment, 25mg of CrCl\(_2\) was added to 500 mg of EMIMCl, and this mixture was heated to 150°C for 30 minutes and cooled to room temperature. Subsequently, 5mg, 10mg and 20mg each of fufural was added to 50mg of xylose, and the resulting mixture was heated in the vials at 80°C for 3 hours. Figure 3-17 below shows the effect of the addition of fufural to the xylose feed on the amount of end products. For computing fufural yields, the fufural formed by the dehydration of xylose was determined after subtracting the amount of fufural initially added from the final fufural measured by HPLC in order to account for the fufural added to reaction media. The addition of higher amounts of fufural appears to increase xylose conversion, with a maximum conversion of 89% obtained in this experiment for the addition of 20 mg of fufural.
On the other hand, furfural yield seems to diminish with the addition of higher amounts of furfural to the feed, with the addition of 20 mg of furfural reducing yield by about 15% when compared with one without furfural. From the results obtained, the effect of yield-loss from side reactions is pronounced. This might be due to loss from condensation or resinification, and an investigation into the type of reaction requires additional analytical measurements to determine the other compound(s) formed during the dehydration reaction. In the next chapter, experiments in which HPLC and NMR analysis were used to identify the presence and nature of the other side products are described.
3.5 Conclusions

The most effective ILs and the optimum reaction conditions for the dehydration of xylose into furfural were identified in this chapter. EMIMCl and BMIMCl were adjudged as the most effective dehydration solvents amongst the IL’s used with conversions as high as 84% and yields as high as 48%. The metal halide catalyst loading of 20 mol% with respect to xylose gave optimum conversion and yield amongst the different catalyst loadings used. For a catalyst combination of CrCl\textsubscript{2} and CuCl\textsubscript{2}, the optimum mole fraction of the mixture was 0.4:0.6 (CuCl\textsubscript{2}:CrCl\textsubscript{2}) resulting in a maximum conversion of 90% and yield of 49%. The variation of xylose/IL ratio indicates that xylose/IL ratio of 15% leads to a maximum conversion of 76% and furfural yield of 48%, which translates to 0.242 g of furfural/g of xylose fed to the reactor.

An investigation of the effect of reaction time and temperature on the two most effective IL’s showed that; xylose conversion in BMIMCl reaches an optimum of 98% conversion and yield of 55% at 80°C for a reaction time of 3 hours. The addition of mineral acids had an adverse effect on furfural yield and it resulted in lower conversions when compared with reactions without the acid catalysts.
Chapter 4

Investigation of the possible side products and the kinetics of furfural formation from xylose in IL media

4.1 Introduction

Chapter 3 dealt with obtaining the optimum conditions for furfural synthesis from xylose in ionic liquid media in the presence of metal halide catalysts. It was observed that at optimal reaction conditions, while xylose conversion can reach very high values (> 90%), the yield of furfural was at best 50 to 55%, indicating that some of the reacted xylose goes to form side products. However, the HPLC chromatographs obtained from the dehydration reaction mixtures do not reveal any additional peaks to indicate that other compounds are present. It is very likely that the products of these side reactions cannot be resolved by the HPX-87 H column and the Refractive Index Detection (RID) method used in the HPLC analysis. Accordingly, $^{13}$C NMR analysis was attempted, the results of which are discussed in this chapter. In addition, a detailed carbon balance was performed on the reaction to assess the amount of xylose carbon that is shuttled towards the formation of side products, as the reaction progresses. For this purpose, batch kinetics studies were done by performing HPLC and $^{13}$C NMR analyses of the reaction mixture at frequent time intervals. These additional efforts were helpful in gaining more insight into the nature of the side products.
4.2 Materials and methods

All the batch kinetic studies were done in 1-Ethyl-3-methylimidazolium chloride (EMIMCl) following a procedure identical to that described in sub section 3.4. In order to obtain batch kinetic data, a series of vials, all of which initially were loaded with identical reaction mixtures, were set-up. The reactions in the individual vials were quenched at different times by adding water to these vials, and the reaction mixture was analyzed by HPLC and/or $^{13}$C NMR. Through this procedure kinetic data was obtained at 20 minute time intervals over a period of four hours. For these experiments, 500 mg of EMIMCl was loaded into the vials (15.5mm x 50mm). CrCl$_2$ (approximately 6 mol% with respect to xylose) with a total metal chloride loading of 37µmol/g of EMIMCl was added individually to each vial. The vials were sealed and heated on the oil bath at 150 ºC and 700 rpm for 20 minutes. After the reactor was cooled to room temperature, 50 mg of xylose was added to each vial and the vials are subsequently heated again in the oil bath at 80 ºC and 700rpm. The reaction in any given vial was arrested by adding 2 ml of water at the appropriate time and cooling it down to room temperature. The vials were then placed in the centrifuge and centrifuged at 2000 rpm for 15 minutes. Upon centrifugation, the liquid layer obtained was filtered using a syringe filter and the clear liquid analyzed for sugars and furfural compounds in Dionex high performance liquid chromatograph (HPLC), equipped with a refractive index detector, using a HPX-87 H column (Bio-Rad Laboratories Inc, Hercules, CA) at 65 ºC. The mobile phase was 5mM H$_2$SO$_4$ solution with a flow rate of 0.6mL/minute. All experiments were repeated with a % standard deviation less than 10%.
Several standards with different concentrations of xylose ranging from 0.0625mg/mL to 4mg/mL and furfural ranging from 0.145mg/mL to 9.28mg/ml were analyzed in order to generate a calibration curve. A linear correlation between the signal of the HPLC and concentration of xylose and furfural was established. 

\(^{13}\)C NMR analysis was conducted with samples reacted for 1-hour, 3-hour, 5-hour and 7-hours. 0.5mL of deuterated DMSO was added to each reaction mixture and subsequently transferred to 5mm NMR tubes. \(^{13}\)C NMR spectra were collected at room temperature on a Varian 400MHz spectrophotometer. A total of 33 repetitions were collected with an acquisition time of 3 seconds and relaxation delay \((d_1)\) of 2 seconds. The spectra were referenced against the internal NMR-solvent standard (DMSO) and chemical shifts were reported in ppm.

4.3 Results and discussion

4.3.1 Kinetics Data

As noted, kinetic data was collected at 20 minute intervals for a period of 300 minutes. Figure 4-1 below shows how the xylose conversion and furfural yield progress over this time period. Initially, there was a steady increase in xylose conversion with increased reaction time until near complete conversion was achieved at 240 minutes. There also appears to be a consistent and gradual increase in furfural yield until a reaction time of 140 minutes where the yield seems to stabilize at a maximum 48% over the next 60 minutes, and subsequently decreases to a minimum yield of 30% at 260 minutes.
In Figure 4-1, there is a time period over which xylose conversion is high while furfural yield is still low. This period, perhaps, corresponds to the time where the intermediate steps in the reaction mechanism of xylose dehydration to furfural are in progress; some of the xylose that has disappeared could be in the form of one or the other of the intermediate compounds, such as xylulose, involved in the eventual formation of furfural. Indeed, conversion of aldose sugars to their keto-isomer form was suggested as a necessary intermediate step in the conversion of sugars to furans.\textsuperscript{28} As time progressed, furfural builds up in the reaction mixture through the conversion of these intermediates into furfural. The fact that the HPLC technique does not provide a signature for these intermediates is not surprising as HPLC methods are not sensitive in resolving isomers of sugars.

This observed decrease in furfural yield beyond 240 minutes is probably due to the susceptibility of furfural to undergo side reactions when present in the reaction media for long periods. These side reactions can include condensation reactions with intermediate compounds in the xylose-furfural reaction mechanism or degradation reactions. Indeed, as discussed later the NMR analysis show the presence of at least one other major compound in the reaction mixture.
Figure 4.1 Batch kinetics of xylose conversion and furfural yields in EMIMCl and CrCl$_2$ at 80°C

4.3.2 Carbon balance closure

From the results shown in Figure 4.1, it is clear that not all the xylose converted is going toward furfural formation and some side products are also produced. It is imperative to obtain a carbon balance of the reaction in order to identify the amount of carbon that directly results in furfural formation and that which results in other side products of the dehydration reaction scheme. Accordingly, a carbon balance is attempted based on the compounds that could be measured using the HPLC method, namely xylose, xylulose and furfural. Carbon that could not be accounted for are identified as carbon deficit. The calculations below illustrate the approach used and a sample carbon balance for the reaction performed at the end of 180 minutes.
\[
\begin{align*}
C_5H_{10}O_5 & \quad \rightarrow \quad C_5H_4O_2 \quad + \quad 3H_2O \\
\text{Atomic mass of carbon} &= 12.01\text{g} \\
\text{Molecular mass of xylose} &= 150.13\text{g} \\
\text{Molecular mass of furfural} &= 96.08\text{g} \\
\text{Volume of reaction product} &= 2.5\text{mL} \\
\textbf{Carbon IN} \\
\text{Mass of xylose} &= 50\text{mg} \\
\text{Mass of carbon present} &= (60/150.13) \times 50 = 19.98 \text{mg} = 0.01998\text{g} \\
\text{Moles of carbon} &= (0.01998/12) = \text{1.665 X 10^{-3} mols} \\
\text{Moles of carbon present in feed} &= \text{1.665 X 10^{-3} mols} \\
\textbf{Carbon OUT} \\
\textit{Xylose} \\
\text{Concentration of xylose in product} &= 3.1 \text{mg/mL} \\
\text{Mass of xylose in product} &= 3.1 \text{mg/mL} \times 2.5\text{mL} = 7.75\text{mg} \\
\text{Mass of carbon present in product} &= (60/150.13) \times 7.75 = 3.097\text{mg} = 3.097 \times 10^{-3}\text{g} \\
\text{Moles of carbon present in xylose from product} &= (3.097 \times 10^{-3}/12) = \text{2.581X 10^{-4} mols} \\
\textit{Xylulose} \\
\text{Concentration of xylulose in product} &= 3.9\text{mg/mL} \\
\text{Mass of xylulose in product} &= 3.9 \text{mg/mL} \times 2.5\text{mL} = 9.75\text{mg} \\
\text{Mass of carbon present in product} &= (60/150.13) \times 9.75 = 3.897\text{mg} = 3.897 \times 10^{-3}\text{g} \\
\text{Moles of carbon present in xylulose from product} &= (3.897 \times 10^{-3}/12) = \text{3.247 X 10^{-4} mols} \\
\textit{Furfural} \\
\end{align*}
\]
Concentration of furfural in product = 5.61mg/mL

Mass of furfural in product = 5.61mg/mL * 2.5mL = 14.025mg

Mass of carbon present in furfural = (60/96.08) * 14.025 = 8.758mg = 8.758 X 10⁻³ g

Moles of carbon present in furfural from product = (8.758 X 10⁻³ / 12) = 7.299 X 10⁻⁴ mols

Total moles of carbon analyzed in product = (2.581 X 10⁻⁴) mols + (3.247 X 10⁻⁴) mols + (7.299 X 10⁻⁴) mols

Total moles of carbon analyzed in product = 1.3127 X 10⁻³ mols

Carbon Deficit

Deficit in carbon balance = (1.665 – 1.3127) X 10⁻³ = 3.523X 10⁻⁴ mols

Deficit in carbon balance = 21% of the carbon in feed

### 4.3.3 ¹³C NMR analysis

Based on the calculations in the previous section, it was determined that some amount of the carbon input into the reaction is converted to side products apart from furfural, this necessitates an experiment which would substantiate the presence of side products and the relationship between these side products and furfural. For this experiment, sample reactions with 500mg IL, 50mg xylose and CrCl₂ corresponding to 6mol% of sugars were reacted at 80°C for 3 hours and ¹³C NMR spectra were run on this sample to reconcile the ppm values of the carbon atom shifts obtained to those expected from the library. Xylose, ionic liquid and furfural peaks obtained from the library are distinguishable in the ¹³C NMR spectra with characteristic chemical shifts. (see Figures 4.3 – 4.5)
Figure 4-3 Predicted NMR spectra for xylose showing the characteristic peaks at different ppm values

Figure 4-3 above shows five peaks which correspond to the resonance of the carbon atoms present in xylose, these peaks are present at 69.00, 71.79, 72.03, and 95.32 ppm.
Figure 4-4 Predicted NMR spectra for furfural showing the characteristic peaks at different ppm values

Figure 4-4 above shows five peaks which correspond to the resonance of the carbon atoms present in furfural, these peaks are present at 112.85, 121.45, 148.49, 153.47, and 178.03 ppm.
Figure 4-5 Predicted NMR spectra for IL (BMIMCl) showing the characteristic peaks at different ppm values

Figure 4-5 above shows eight peaks which correspond to the resonance of the carbon atoms present in BMIMCl, these peaks are present at 13.27, 18.16, 30.06, 36.00, 50.12, 122.42, 123.91, 131.23 ppm.
Figure 4-6 NMR spectra for a sample reaction with 500mg IL, 50mg xylose and CrCl$_2$ corresponding to 6mol% of sugars were reacted at 80°C for 3 hours.

Table 4.1 below shows the different peaks for all the compounds being overlapped, and they are individually identified with corresponding alphabets (a) to (r).
Table 4.1 Chemical shifts corresponding to xylose, furfural and IL

<table>
<thead>
<tr>
<th>xylose</th>
<th>furfural</th>
<th>IL</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.41 (i)</td>
<td>112.85 (n)</td>
<td>13.27 (a)</td>
</tr>
<tr>
<td>69.00 (j)</td>
<td>121.45 (o)</td>
<td>18.16 (b)</td>
</tr>
<tr>
<td>71.79 (k)</td>
<td>148.49 (p)</td>
<td>30.06 (c.)</td>
</tr>
<tr>
<td>72.03 (l)</td>
<td>153.47 (q)</td>
<td>36.00 (d)</td>
</tr>
<tr>
<td>95.32 (m)</td>
<td>178.03 (r)</td>
<td>50.12 (e)</td>
</tr>
</tbody>
</table>

A closer look at the NMR spectrum obtained for a 3hour sample reaction in Figure 4-6 reveals that there are some peaks which have resonances at chemical shift values not characteristic to the identifiable compounds (i.e xylose, furfural, IL), on expanding different regions of this spectra as shown in Figure 4-7-4.8, it becomes clearer that there are some unidentified peaks which might be due to the side products formed.
Figure 4-7 Expanded NMR spectra between 150-180ppm for a sample reaction with 500mg IL, 50mg xylose and CrCl$_2$ corresponding to 6mol% of sugars were reacted at 80°C for 3 hours.

Figure 4-8 Expanded NMR spectra between 50-115ppm for a sample reaction with 500mg IL, 50mg xylose and CrCl$_2$ corresponding to 6mol% of sugars were reacted at 80°C for 3 hours.
From Figure 4-7, there are four peaks at chemical shift values which correspond to a carbon environment of O=C-X (where X is an alkyl group). Also, From Figure 4-8 above, one compound which can be identified from this expanded region based on its characteristic chemical shifts is xylulose, as shown below in Figure 4-9, xylulose has characteristic chemical shifts at 66.8, 72.85, 76.1, 212.9 ppm.

Figure 4-9 Predicted NMR spectra for xylulose showing the characteristic peaks at different ppm values.

The presence of characteristic chemical shifts for xylulose in the NMR spectra and the amount shown by the HPLC signifies that xylulose is a key intermediate in the conversion of xylose to furfural,
Figure 4-10 Expanded NMR spectra between 175-210ppm for a sample reaction with 500mg IL, 50mg xylose and CrCl$_2$ corresponding to 6mol% of sugars were reacted at 80°C for 3 hours.

Figure 4-10 is an expansion of the NMR spectra between 175-210ppm showing a peak which exclusively corresponds to xylulose (204ppm) amongst all known reactants and products, thereby establishing the presence of xylulose in the reaction mixture, the disparity between the expected value of the chemical shift (210ppm) and the obtained value (204ppm) is due to the expansion of the spectra beyond the range of the NMR. It can be proposed that the dehydration of xylose to furfural goes through two major steps; (i) isomerization of the aldopentose sugar (xylose) to its keto-isomer form (xylulose), and (ii) the subsequent dehydration of xylulose to furfural.

Finally, from figures 4.7 and 4.8 above, there is a clear identification of peaks on the NMR spectra which does not correspond to any of the reacting materials or the
identifiable end products, this peaks have chemical shifts between 90-100ppm and 160-177ppm which corresponds to a carbon environment with double bond carbon chain (C=C), and O=C-X (where X is an alkyl group) indicating that there are some side reactions occurring which affects the carbon balance by virtue of the formation of side products. In order to corroborate the possibility of xylulose presence in this reaction media, samples of the reaction media are run through a combination of 2 shodex columns in series on the HPLC, this method is specifically used to obtain a clear separation of these two compounds because they are not clearly separated by other methods, Figure 4-11 shows a chromatograph where xylose and xylulose are clearly separated at different retention times, these retention times are confirmed with xylose and xylulose standards.

Figure 4-11 HPLC Chromatograph showing a clear separation of xylose and xylulose peaks for a sample reaction with 500mg IL, 50mg xylose and CrCl\textsubscript{2} corresponding to 6mol\% of sugars were reacted at 80°C for 3 hours
There are a couple of possible side reactions that might arise during furfural synthesis; one possibility is that one molecule of furfural reacts with the intermediate of xylose-to-furfural conversion, to give furfural xylose\(^{(10)}\) and another is the reaction of two furfural molecules to give difurfural xylose.

### 4.4 Conclusion

An experiment to understand the kinetics of the reaction showed a steady increase in xylose conversion until a reaction time of 240 minutes where near complete conversion is achieved. On the other hand, there appears to be an increase in furfural yield until 140 minutes where a maximum 48\% was achieved followed by a gradual reduction in yield over time. In addition, an attempt to achieve a carbon balance closure revealed a deficit of 21\% of the carbon that could not be apportioned to the compounds measured by the HPLC technique.

Finally, a \(^{13}\text{C}\) NMR spectrum analysis reveals the presence of an unidentified peaks with chemical shifts corresponding to a carbon environment of double bond carbon (C=C), and O=C-X (where X is an alkyl group), this may be due to the side-products formed during furfural synthesis such as difurfural xylose or furfural pentose which are products that have been postulated by other researchers, a combination of two shodex H columns also gave a clear separation of xylose and xylulose thereby confirming the presence of xylulose and demonstrating that xylulose formation is an integral part of furfural synthesis from xylose.
Chapter 5

Catalytic dehydration of arabinose: xylose mixtures in ionic liquid media

5.1 Introduction

Even though a large part of hemicellulose is primarily xylose, there are other pentose sugars present in hemicellulose which if their potential is harnessed, will increase the efficiency of hemicellulose conversion to furfural. The most abundant hemicellulosic sugars are xylose and arabinose (24), and their amount in the hemicellulose portion varies according to the feedstock, but one of the abundant pentose sugars is arabinose.

Table 5.1 Hemicellulose composition of some biomass feedstock (24)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Xylose</th>
<th>Arabinose</th>
<th>Other sugars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice bran neutral xylan</td>
<td>46%</td>
<td>44.90%</td>
<td>9.10%</td>
</tr>
<tr>
<td>Wheat arabinoxylan</td>
<td>65.80%</td>
<td>33.50%</td>
<td>0.70%</td>
</tr>
<tr>
<td>Birch wood Xylan</td>
<td>89.30%</td>
<td>1%</td>
<td>9.70%</td>
</tr>
</tbody>
</table>

Based on the results from the previous chapter about the effectiveness of the ionic liquids and metal halides in the dehydration of xylose which is a pentose sugar, and also the
similarity in the chemical structure and physical properties of xylose and arabinose, the reaction conditions for this chapter are similar to those from the previous chapter.

5.2 Materials and Methods
Arabinose (99%) was obtained from Acros, Xylose (99%) was obtained from Acros CrCl₂ were purchased from Sigma-Aldrich. 1-Ethyl-3-methylimidazolium chloride (EMIMCl, 98%) was supplied by Sigma-Aldrich. Experimental conditions were similar to that used in the previous chapter.

5.3 Results and Discussion

5.3.1 Dehydration of arabinose to furfural
In this experiment, 25mg of CrCl₂ was added to 500 mg of EMIMCl, and this mixture was heated to 150°C for 30 minutes. Subsequently, 50mg of arabinose was added, and the resulting mixture was heated in the vials at 80°C for 1 hour, 2 hours, 3 hours and 4 hours. Figure 5-1 illustrates what appears to be a constant decrease in arabinose conversion and a rise in furfural yield with increased reaction time.
In this experiment, the reaction proceeds to near completion in 1 hour with arabinose conversion at a maximum 95% while the maximum furfural yield of 43% was gotten in 2 hours. Exceptions to this trend were observed for the 4 hour reaction where a high conversion and a low yield were obtained. This may be due to the reaction of the furfural obtained with the remaining xylose thereby leading the reaction to near completion and reducing the furfural yield.
5.3.2 Combination of xylose and arabinose in equal amounts

As explained in the chapter introduction, xylose and arabinose are the two major pentose sugars present in hemicellulose; this experiment aims to study what the effect of a combination of the hemicellulosic sugars in different amounts will be on furfural yield. In this experiment, 25mg of CrCl\textsubscript{2} was added to 500 mg of EMIMCl, and this mixture was heated to 150°C for 30 minutes. Subsequently, 50mg of xylose and 50mg of arabinose were added, and the resulting mixture was heated in the vials at 80°C and 100°C for 3 hours. Figure 5-2 shows that at a reaction temperature of 80°C which is more favorable for xylose dehydration as shown in the results of experiments in previous chapters, there appears to be more xylose conversion than arabinose conversion with xylose producing a 94% conversion and arabinose 76%.

![Figure 5-2 Dehydration of a mixture of arabinose and xylose (equal amounts) in EMIMCl and CrCl\textsubscript{2} at 80°C and 100°C for 3 hours](image-url)
It is also observed that regardless of the increase in reaction temperature from 80°C to 100°C, furfural yield did not increase significantly as expected by virtue of the presence of xylose.

5.3.3 Combination of glucose, xylose and arabinose based on biomass composition

As shown in Table 5.1, the composition of hemicellulose for most feed stock is not equally divided into xylose, arabinose and other sugars, this section aims to combine arabinose and xylose in mole fractions similar to what is obtainable in some lignocellulosic biomass feed stocks. 25mg of CrCl$_2$ was added to 500 mg of EMIMCl, and this mixture was heated to 150°C for 30 minutes. Subsequently, 35mg of xylose and 15mg of arabinose were added, and the resulting mixture was heated in the vials at 80°C and 100°C for 3 hours.

Figure 5-3 shows the effect of the combination as the xylose conversion is constantly higher than arabinose conversion even when the reaction temperature was increased from 80°C to 100°C, with a maximum arabinose conversion of 90% and maximum xylose conversion of 94%, this may be due to the fact that the isomerization of the xylose from its aldopentose form to xylulose which is the ketopentose form, and the subsequent dehydration of xylulose to furfural occurs more rapidly than the mechanism for the dehydration of arabinose to furfural. In addition, it was noticed that furfural yield reduced from 50% to 47%, this reduction is probably due to the fact that there is a greater amount of xylose present in the sugar mixture and an increase of the reaction temperature from 80°C to 100°C does not favor the cyclodehydration of xylose molecules to furfural.

Generally, the sugar mixture with xylose and arabinose composition similar to biomass
feedstock produced better yields when compared with the sugar mixture with equal amounts of xylose and arabinose.

![Figure 5-3 Dehydration of a mixture of arabinose and xylose (similar to biomass composition) in EMIMCl and CrCl2 at 80°C and 100°C for 3 hours](image)

5.4 Conclusions

For the dehydration of arabinose to furfural, a maximum conversion of 95% was obtained in 1 hour and a maximum yield of 43% was obtained in 2 hours. A combination of xylose and arabinose in equal amounts yields a maximum arabinose conversion of 76%, a maximum xylose conversion of 94% and a highest furfural yield of 49%. However, a combination of xylose and arabinose in compositions similar to what is obtainable in biomass feed stock results in a maximum arabinose conversion of 90%, a maximum xylose conversion of 99%. In conclusion, the results of the experiments performed in this
chapter provides an insight to the potential for dehydration of hemicellulosic sugars into furfural, where the bulk of the hemicellulose portion obtained from the pretreatment and enzymatic hydrolysis can be directly converted to furfural.
Chapter 6

Synthesis of furfural from hemicellulosic sugars in N,N-dimethylacetamide (DMA)-LiCl media

6.1 Introduction

In an attempt to explore different solvents with the aim of improving furfural yield from the cyclodehydration of pentose sugars, one of the solvents used for this reaction is a N,N-dimethylacetamide (DMA) and LiCl mixture. This reaction media has produced interesting results when combined with different catalytic compounds for the synthesis of 5-Hydroxymethylfurfural from hexose sugars, with yields as high as 80% obtained from glucose\textsuperscript{27}. It has also been reported that the DMA-LiCl solution is a good solvent for hemicellulose dissolution\textsuperscript{26}. As part of the efforts to make the furfural synthesis process more economically feasible, it is essential to reduce the cost of dehydration solvents, so an approach that utilizes different solvents to dehydrate hemicellulosic sugars is one that would be of interest; this approach aims to abate the use of ionic liquids which will consequently lessen the cost of furfural synthesis.

In this section, the aim is to investigate the effectiveness of this reaction media on the synthesis of furfural from arabinose, and a combination of hemicellulosic sugars.
6.2 Materials and Methods

N,N-dimethylacetamide (99%+) was obtained from Fischer Scientific, 1-Ethyl-3-methyltrimethylammonium chloride ([EMIM]Cl, 98%) was supplied by Sigma-Aldrich, Xylose (99%) was obtained from Acros, Arabinose (99%) was supplied by Sigma-Aldrich, CrCl2 were purchased from Sigma-Aldrich. In a typical experiment for the DMA-LiCl media, Arabinose and LiCl were mixed in DMA and the reaction mixture was stirred at 100 °C for 4 hours. At 1 hour intervals, aliquots of the reaction mixture were removed for HPLC analysis. For reactions that involved [EMIM]Cl, chromium (II) chloride was mixed with a portion of the ionic liquid at 150°C for 20 minutes before addition to the reaction mixture. The experiments were replicated with standard deviation less than 10%

All reaction products were analyzed by HPLC and quantified with calibration curves generated from arabinose, xylose and furfural standards. Following a typical reaction, the product mixture was diluted with a known mass of deionized water, centrifuged to sediment insoluble products, and analyzed. The concentrations of products were calculated from HPLC-peak integrations and used to calculate molar yields. HPLC analysis was performed with Dionex high performance liquid chromatograph, equipped with a refractive index detector, using a HPX-87 H column (Bio-Rad Laboratories Inc, Hercules, CA) at 65°C. The mobile phase was 5mM H2SO4 solution with a flow rate of 0.6 ml/minute.

6.3 Results and Discussion

6.3.1 Synthesis of furfural in N,N-dimethylacetamide-LiCl media

Figure 6-1 below shows the effect of using a DMA-LiCl mixture for the furfural synthesis process at 100°C for 3 hours.
Figure 6-1 Arabinose conversion and furfural yield in (a) DMA-LiCl media alone (b) DMA-LiCl media, CrCl₂ (c) DMA-LiCl media, CrCl₂, and EMIMCl (10 wt% of total mixture) (d) DMA-LiCl media, CrCl₂, and EMIMCl (20 wt% of total mixture)

The DMA-LiCl mixture proved to be an efficient solvent for pentose sugar conversion by virtue of the fact that about 100% conversion was achieved without any addition of catalyst and the subsequent addition of catalyst did not seem to increase or decrease the conversion of arabinose to furfural. On the other hand, this mixture alone delivered furfural yield of 7%. The addition of a metal halide (CrCl₂) increases the yield to 16% but it did not seem to have any effect on arabinose conversion. In order to increase the yield, a small amount of EMIMCl which corresponds to 10 wt% of the total mixture was added, this addition had a minute effect by increasing the yield to 18%, this prompted an increase in the amount of EMIMCl added, when the amount of EMIMCl was increased to 20 wt% of the total mixture, there was a dramatic rise in furfural yield to 40%, which is...
comparable to what was obtainable in other dehydration solvents. The performance of the DMA–LiCl media is probably due to the association of lithium ions with DMA to form DMA·Li\(^+\) macrocations, this combination may result in a high concentration of weakly ion-paired chloride ions which have been shown by Zhang et al to increase the yield of 5-Hydroxymethylfurfural.

![Proposed combination of DMA and LiCl to generate chloride ions](image)

Figure 6-2 Proposed combination of DMA and LiCl to generate chloride ions

### 6.3.2 Synthesis of furfural from a combination of hemicellulosic sugars in N, N-dimethylacetamide-LiCl media

In this experiment, 450mg of DMA was mixed with 50mg of LiCl and a combination of pentose sugars (arabinose and xylose) in equal amounts, EMIMCl corresponding to 20wt% of the total mixture and CrCl\(_2\) (corresponding to 6 mol%) were added. Figure 6-3 below shows that even though the amount of ionic liquid used in combination with the DMA-LiCl mixture is just 20% of that which was used for dehydration in ionic liquid media, the DMA-LiCl performed generally better than the IL media.
Figure 6-3 Conversion of a combination of pentose sugars into furfural (a) arabinose conversion (b) xylose conversion, for the DMA-LiCl media, equal amounts (50mg) of xylose and arabinose were mixed with 450mg of DMA, 50mg of LiCl, CrCl$_2$ (corresponding to 6 mol% of sugars), and EMIMCl corresponding to 20wt% of the total mixture.

Figure 6-4 Furfural yield from a combination of pentose sugars into furfural for the DMA-LiCl media, equal amounts (50mg) of xylose and arabinose were mixed with 450mg of DMA, 50mg of LiCl, CrCl$_2$ (corresponding to 6 mol% of sugars), and EMIMCl corresponding to 20wt% of the total mixture.
Although, the DMA-LiCl media gave an arabinose conversion of 53% that was much lower than that obtained by the ionic liquid media which was 78%, In terms of xylose conversion, as shown in Figure 6-3 (a), the DMA-LiCl outperformed the ionic liquid media under similar reaction conditions by delivering a xylose conversion of 99% compared with 93% given by the ionic liquid media. Finally, the DMA-LiCl media delivered better results in terms of furfural yield by giving 53% which is higher than the 49% obtained by the ionic liquid media under similar reaction conditions, this is illustrated in Figure 6-4.

5.4 Conclusions
For the DMA-LiCl media alone, a conversion of 99.1% and a yield of 7% was obtained, the addition of CrCl$_2$ (corresponding to 6 mol%) to this mixture delivers a conversion of 99.5% and yield of 16%. Similarly, a combination of DMA-LiCl mixture, CrCl$_2$ (corresponding to 6mol%) and EMIMCl (corresponding to 10wt% of the total mixture) gave conversions of 99.7% and yield of 18%. Finally, a combination of DMA-LiCl mixture, CrCl$_2$ (corresponding to 6mol%) and EMIMCl (corresponding to 20wt% of the total mixture) gave an arabinose conversion of 99.7% and furfural yield of 40% which were comparable to the results obtained in the ionic liquid media at similar reaction conditions. For the dehydration of a mixture of pentose sugars (arabinose and xylose) in equal amounts, an arabinose conversion of 53% was obtained, a xylose conversion of 99% was gotten and a furfural yield of 53% was obtained, these results mostly performed
better than those obtained in the ionic liquid media despite the relatively lower amount of ionic liquid used.

Based on the results obtained in this chapter, the dehydration of pentose sugars in DMA-LiCl media appears to be a viable, more economical alternative approach to furfural synthesis when compared to using an ionic liquid media.
Chapter 7

Conclusions and Future Work

Current methods that are used to utilize lignocellulosic biomass involve the conversion of the sugars obtained to obtain bioethanol, other applications include converting the hexose sugars obtained to obtain other value added chemicals. The focus of this thesis is to investigate methods with which the pentose sugars obtained from lignocellulosic biomass can be converted to furfural using different reaction media, the pentose sugars (xylose, arabinose, and a combination of both) were dehydrated into furfural using different reaction systems.

In this work, the optimized reaction conditions (catalyst loading, xylose/IL ratio, catalyst combination and mixing speed) were obtained for the xylose dehydration process in an ionic liquid media, and the effect of a combination of pentose sugars on furfural yield was also demonstrated both in equal amounts and according to biomass composition. A DMA-LiCl reaction system was also investigated for the dehydration of arabinose and a combination of pentose sugars to furfural, this reaction system proved to be a viable one by delivering better conversions and yields when compared with the ionic liquid and metal halide reaction system, even though only a relatively smaller fraction of ionic liquid was used. Further analysis which was done to identify the reason behind the
relatively lower furfural yield indicated the presence of side products which might be due
to the interaction of the furfural generated with the intermediate of xylose-to-furfural
conversion.

Future work should be done on the development of a method that reduces the residence
time of furfural generated in the aqueous phase; this is a limiting factor that has affected furfural yield due to side reactions that are favored because of its presence in the aqueous phase, an extraction into the vapor phase will be beneficial due to the absence of catalytically active species, thereby making furfural incapable of undergoing loss reactions. The value of this investigation can be increased by work on the recovery and isolation of the furfural produced as this will be an important step when the process is eventually scaled up for industrial application. In addition, because the ionic liquids are very expensive, techniques should be developed for effective purification, recovery and reuse.
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