A Thesis

Entitled

Catalytic Conversion of Sugar Mixtures into Furan Products in Ionic Liquid Media with Organic Solvent Extraction

By

Wenwen Zhang

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

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An Abstract of

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With the increasing demands and dwindling supplies of petroleum, more attention is diverted to an abundant, renewable, and carbon-neutral resource for fuels and chemicals —lignocellulosic biomass. Lignocellulosic biomass has a great potential to become an alternative for conventional crude-oil, due to its ample availability, renewability and, more importantly, its amenability for conversion to liquid fuels and products. An important class of products that could be made from the carbohydrates of lignocellulosic biomass is furan derivatives, which are commercially used as building blocks for fuel and material production. Furfural and 5-(Hydroxymethyl) furfural (5-HMF) are two value-added furan derivatives that have several industrial applications.

This work focuses on the catalytic dehydration of a mixture of xylose and glucose – sugars derived from hemicellulose and cellulose portions of biomass, respectively - to a mixture of furfural and 5-HMF in ionic liquid (IL) medium comprising 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl). Most previous studies focused on converting individual pentose or hexose sugars in IL. Often, it was observed that operating conditions suitable for one kind of sugar are significantly sub-optimal for the other. In this study, we identified conditions that promote conversion of both kinds of sugars simultaneously. Highest yields resulted when the furan products were extracted into an organic solvent immiscible with the reaction medium.

Acknowledgements

First and foremost, I want to thank my advisor Sasidhar Varanasi for the continuous support throughout my course-work and research. It has been an honor to be his M.S. student. His patience, motivation, enthusiasm and immense knowledge helped me in all the phases of research and writing this thesis. I appreciate all his contributions of time and ideas in making my masters experience productive and stimulating. I would also like to thank Dr. Sridhar Viamajala for his guidance in my research.

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Chapter 1

Introduction

Over two thirds of all energy produced in the United States comes from burning fossil fuels (see Figure 1-1), which includes oil, coal and natural gas. Burning these fuels results in global warming effects[1]. During last decade, there has been a trend of increasing demand for petroleum all over the world, and several reports indicate that oil production will peak in the next 15-30 years. Moreover, currently there are no commercially viable methods of sequestering the carbon dioxide and mitigating the greenhouse effect caused by fossil fuel combustion. Since fossil fuel resources are limited, non-renewable, being depleted rapidly, and major culprits for greenhouse effect, it is imperative that renewable and environmentally friendly energy sources to replace fossil fuels are developed urgently.

In this regard, biomass has attracted considerable attention, because it is renewable and abundant. Typical biomass includes dead trees, tree branches, crops, yard-clippings, left-over crop residues, wood chips, etc.[2]. Biomass-based energy is carbon-neutral[3], which offsets the increase in atmospheric carbon dioxide caused by petroleum combustion. It has been shown that biomass derived sugars can be converted to furan products, including hydroxymethylfurfural (HMF), dimethylfuran (DMF), furfural, etc. Some furans (such as HMF) serve as intermediates for the production of plastics and other chemicals that currently rely on petroleum[4]. Some other furans such as DMF and 2，5-dimethyltetrahydrofuran (DMTHF) can be used as “drop-in” fuels as they possess energy densities higher than ethanol and much closer to gasoline[5].Thus, biomass sugar-derived furans are a potential source of green liquid transportation fuels, with a great potential to replace gasoline.

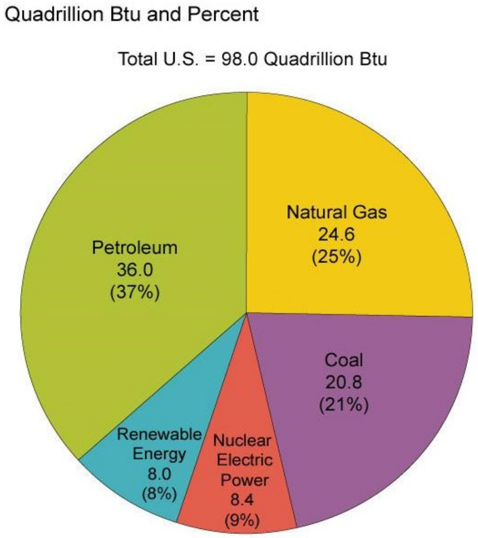


Figure 1-1: Distribution of power produced in 2010 in the USA amongst available resources (Source: U.S. Energy Information Administration, Annual Energy Review 2010)

Chapter 2

Literature review

2.1 Background

The principal structural components of biomass are cellulose, hemicellulose and lignin, see figure 2-1[6]. Of these, cellulose is the largest fraction and constitutes 40-80% of its weight-it is a crystalline glucose polymer. Hemicellulose, the other important component of biomass (15-30 wt. %), is a polymer made up of five and six carbon sugars, although xylan, the polymer derived from the monomeric sugar xylose, is its primary component. Lignin, a large polyaromatic compound, is the other major component of biomass. The first step of the biomass conversion is to "pretreat" the lignocellulosic biomass to open-up its dense structure and provide access to the enzymes that hydrolyze the carbohydrates (cellulose and hemicellulose). This pretreatment step is followed by enzymatic saccharification to release the soluble sugars obtained by depolymerizing cellulose and hemicellulose. Glucose and xylose are the main monomeric sugars produced following pretreatment and enzymatic saccharification (Figure 2-1). It has been shown that these two monosaccharaides can be used for the production of furans and furan additive through catalytic dehydration.

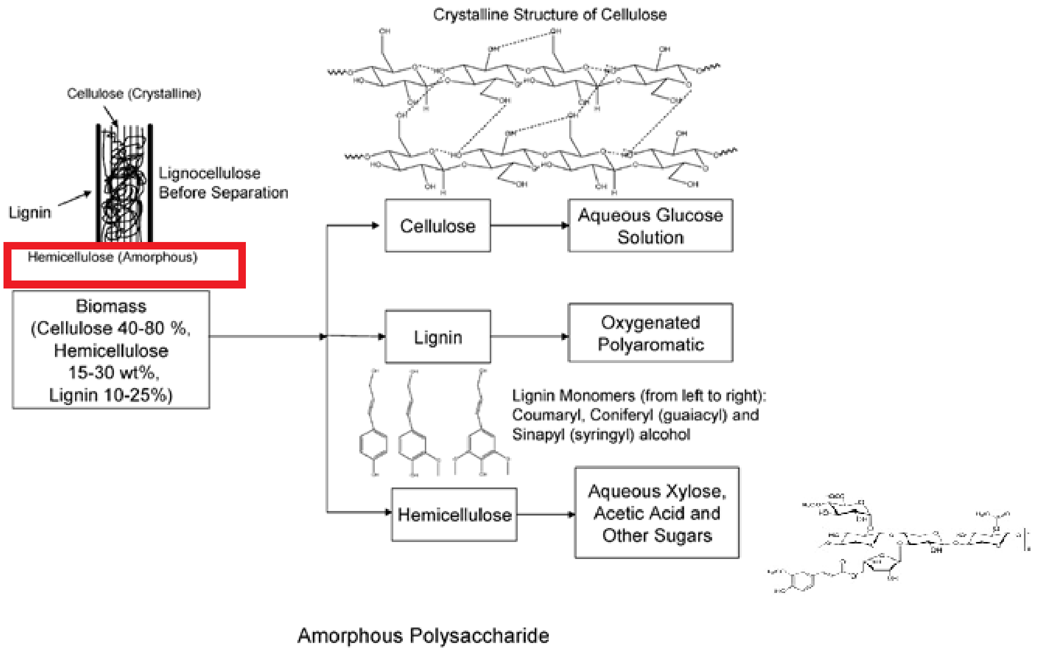


Figure 2-1: Structure of lignocellulose and of its principal fractions (cellulose, lignin and hemicellulose) before and after hydrolysis

Both homogeneous and heterogeneous catalytic processes have been attempted in the conversion of sugars to furans[7]. Problems inherent to homogenous catalysis are the recovery of the catalyst and the issue of disposal of waste streams. Hence, heterogeneous-catalytic processes are preferred for large scale implementation of catalyst-driven chemical conversions. Jean Lessard et al.[8] reported that protonated micro-porous -zeolites can be used as heterogeneous catalysts for xylose dehydration to furfural in a two-phase system comprised of water and toluene; here, toluene serves as an immiscible extraction solvent for furfural produced in the catalyst-containing aqueous medium. The authors reported that high yield of isolated furfural (~98%) was obtained when mordenite-13 (protonated with phosphoric acid) was used as catalyst. However, this system requires (1) demanding operating conditions of high temperature and pressure (260^0C and 55 atm) and (2) very high ratio of catalyst to sugar (2:1). Moreover, the activity of the regenerated catalyst was much lower compared to that of freshly-prepared ones. Ana S. Dias et al.[9] demonstrated that sulfonic acid-anchored MCM-41 could catalyze the xylose dehydration with high selectivity of over 90% in 24hours at 140^0C. A major concern with this approach is that the duration of the reaction is rather long, which could preclude its consideration as an option for industrial implementation. Masaru Watanabe et al.[10]reported a single-pot, two-step process for the production of 5-hydroxymethyl furfural (5-HMF) from glucose in hot (at 200 ^{0}C) pressurized aqueous media in presence of TiO_2 catalyst. The sequential reaction steps are isomerization of glucose to fructose, followed by dehydration of fructose to 5-HMF. Similarly, Goto and Sasaki [11] studied glucose dehydration in supercritical water at temperatures of over 250^0C. It is evident from these studies that sugar dehydration in aqueous media needs demanding operating conditions, namely high temperature, high pressure and/or long reaction times.

Of late, ionic liquids (ILs), which are molten salts at room temperatures with negligible vapor pressures, have been attracting considerable attention as desirable reaction media for catalytic conversions. ILs can be tuned for task-specific applications by varying the cation/anion combinations to achieve desired properties for miscibility, melting point, solubility, acidity, basicity etc.[12],[13]. ILs have attracted much attention as a novel and promising medium for biomass pretreatment[14],[15],[16],[17].

While direct catalytic conversion of the carbohydrates of biomass to furans (following dissolution of biomass in IL-containing solvent systems) has been attempted recently [18], the product yields were only modest. Moreover, the complex structure of biomass, its limited solubility in reaction medium, and issues associated with the recovery of products, catalysts and IL from the reaction system are problems in this approach that cannot be readily resolved. There have also been attempts in literature aimed at catalytic conversion of cellulose to HMF in IL media[19],[20],[21]. The observed HMF yields were in general well below 50%, although conversion of cellulose was high which suggests that a major portion of the cellulose carbon is diverted to undesirable products. While single-pot syntheses that covert biomass carbohydrate to products directly are appealing, the multi-step conversions involved make it difficult to gain a clear understanding of the rate-controlling steps and the nature and severity of the side-reactions associated with the individual steps. Hence, a thorough investigation of the dehydration of biomass sugars in IL media to furans and optimization of these conversions is a necessary first step towards developing IL-mediated catalytic conversion of biomass carbohydrates to furans. Accordingly, the focus of this study is the optimization of the dehydration of biomass sugars to furans in IL media. As already noted, unlike aqueous media, ILs provide a benign and facile reaction environment. Moreover, the non-volatile character of ionic liquid facilitates its recycle and product separation after the reaction.

Most investigations (dealing with dehydration of biomass sugars to furans in IL media) focused on the conversion of either glucose or xylose to the corresponding furan (HMF and furfural, respectively). However, depending on the pretreatment method used, the sugars harvested from biomass may reside in separate streams consisting predominantly of C6 sugar from cellulose and C5 sugar from hemi-cellulose or may be present as a single mixed C5 and C6 sugar stream. The ionic liquid pretreatment method developed by our group leads to a hydrolysate containing a mixture of C6 and C5 sugars[22]. To date there have not been any reports on converting both C6 and C5 sugars simultaneously in ionic liquid media. This work also addresses simultaneous catalytic dehydration of glucose and xylose sugar mixtures in ionic liquid media.

2.2 Furfural

2.2.1 Properties of furfural

Furfural is a heterocyclic aldehyde with a ring structure (See Figure 2-2). It is an organic compound, with an almond scent[23]. Its physical properties are listed in Table 2.1.

Figure 2-2: Structure of furfural

Table 2.1 Physical properties of furfural[24]

Molecular Weight	96.1g/mol
Appearance	Clear, colorless oil
Boiling point (°C)	161.7
Density at 20°C	1.16g/ml
Melting Point (°C)	-37
Viscosity at 20°C	1.5
Water solubility at 20°C	7.81g/100ml
Solvent solubility (g/L at 20 °C)	Alcohol(infinite) ,Ether (infinite) Miscible in octanol, xylene and methanol
Critical Temperature (°C)	397.4
Heat of Combustion at 20°C (kcal/gm. Mole)	-560.3
Heat of Formation (liquid at 20°C) (kcal/gm. Mole)	-49.2

2.2.2 Applications of furfural

Furfural has a wide variety of applications including the following[25],[26]

- As an extractant

Furfural possesses unique solubility characteristics and can dissolve compounds ranging from aromatics to some unsaturated olefins. Based on its solubility characteristics and its easy recovery by steam distillation, furfural is widely used in refining lubricating oils and as a decolorizing agent. Also, several industries employ furfural extraction for removing polar components and mercaptans from petroleum.

- Chemical feedstock for other furan derivate

Furfural is a main feedstock for the production of furfuryl alcohol, 2-methyltetrahydrofuran (MTHF) and other 5-membered oxygen-containing heterocyclic compounds such as methylfuran, acetylfuran and furoic acid.

- Reactive solvent and good wetting agent

Furfural is unusually effective as a solvent for phenolic resins. In the manufacture of abrasive wheels, fiberglass, some aircraft components, automotive brakes, and brake linings, furfural is widely used as a reactive solvent and excellent wetting agent.

2.2.3 Synthesis of furfural from hemicellulose

Furfural formation from hemicellulose portion of biomass consists of two steps: depolymerization of carbohydrates into monosaccharaides (saccharification) and dehydration of C5 sugar (See scheme 1). This study focused on the second step.

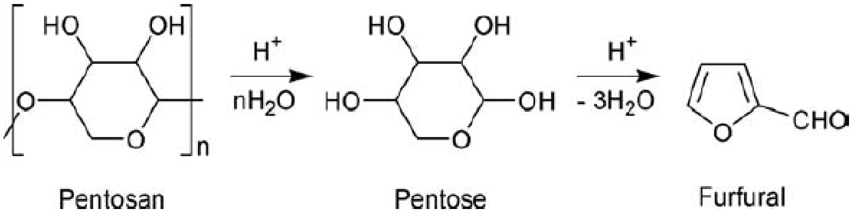


Figure 2-3: Simplified reaction mechanism of acidic degradation of pentosan to furfural.

As already noted, several existing investigations and industrial processes were reported on conducting this dehydration process in concentrated acid reaction media (viz., sulfuric acid, phosphoric acid and superphosphate). These acid environments are not only toxic and corrosive, but also pose problems with product separation from the homogeneous catalytic system and acid contamination of the product [26],[27] .

As already indicated, in this work we attempted to conduct the dehydration of xylose in ionic liquid media to take advantage of the advantages afforded by ILs. The properties of ionic liquids will be discussed in chapter 2.4.

2.3 5-(Hydroxymethyl) furfural

5-(Hydroxymethyl) furfural (5-HMF) is a yellow solid, with low melting point. It has a furan ring and contains both aldehyde and alcohol functional groups. (See Figure 2-4). Although 5-HMF is an organic compound, it is highly water-soluble. (See Table 2.2)

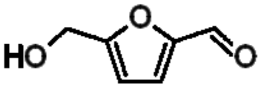


Figure 2-4: Structure of 5-HMF

Table 2.2 Properties of 5-HMF[28]

Formula	$C_6H_6O_3$
Molecular weight	126.11 g/mol
Density	1.243 g/mL at 25^{0}C
Boiling point	114-116^{0}C/1mm Hg
Melting point	28-34^{0}C
Solubility	Freely soluble in water, methanol, ethanol; Soluble in ether, benzene.

2.3.1 Applications of 5-HMF

5-HMF has extensive applications. It can be used as a major feedstock for conversions to 2,5-dimethylfuran(DMF), which is a liquid biofuel alternative[5]. It can be converted to 2,5-furandicarboxylic acid (FDA), which is a potential substitute of terephthalic acid in the manufacturing process of polyesters[29]. (See Figure 2-5)

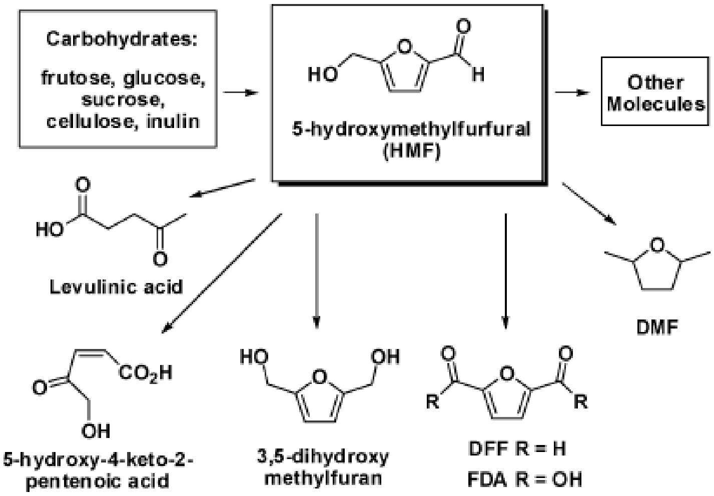


Figure 2-5: Synthetic applications of 5-HMF

2.3.2 Synthesis of 5-HMF

5-HMF is produced via dehydration of C6 sugars such as glucose or fructose (see figure 2-6)[30],[31]. Traditionally, dehydration of hexose was conducted in aqueous media with an heterogeneous Lewis or Bronsted acid catalysts or in mineral acid media[32]. The extant methods for synthesizing 5-HMF from glucose also require enzyme-catalyzed isomerization of glucose to fructose as a first step to achieve high yields of 5-HMF in the subsequent acid-catalyzed dehydration step. This study focused on an effective “one-pot” synthesis of 5-HMF from biomass-derived glucose using environmentally sustainable reaction media, namely Ionic liquids.

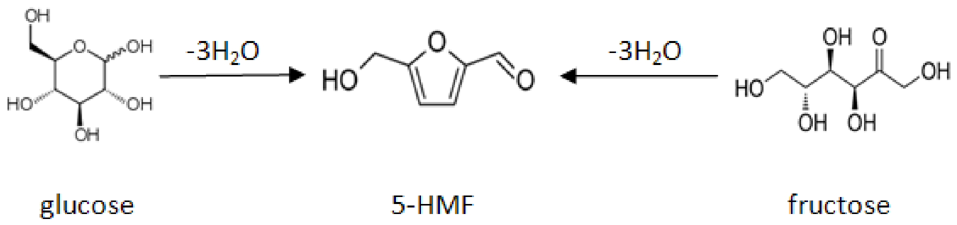


Figure 2-6: Reaction mechanism of glucose/fructose into 5-HMF

2.4 Ionic Liquid

Ionic liquids, as already alluded to, are salts in the liquid state at low temperature, typically composed of a huge organic cation and an inorganic anion. They have many unique characteristics (See Table 2.3), including low vapor pressure, excellent thermal stability, and water solubility.

Table 2.3 Properties of Ionic liquid

Freezing point	Preferably below 100ºC
Liquids stability	Usually high
Viscosity	Normally <100 cP, workable
Dielectric constant	Implied≤ 30
Polarity	Moderate
Specific conductivity	Usually <10 $mScm^{-1}$, Good
Molar conductivity	<10 $Scm^2\ mol^{-1}$
Solvent and/or catalyst	Excellent for many organic reactions
Vapor pressure	Usually negligible

In this study, 1-Ethyl-3-methylimidazolium chloride (EMIM Cl) (See Figure 2-7) was selected as a suitable reaction medium based on its distinctive physical and chemical properties which are as follows:

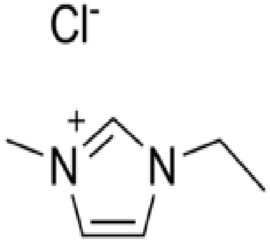


Figure 2-7: Structure of EMIM Cl

- Non volatility and thermal stability[33],[34] As is the case with many ILs, EMIM Cl also has negligible vapor pressure in the temperature range in which the sugar dehydration reactions are conducted, while the reaction products, namely furans and other additives (including extraction solvent) are volatile. These volatility differences between the IL and other components of the reaction mixture facilitate easy separation of the products and recycling of the IL after reaction. Since EMIM Cl remains liquid over a wide temperature range, precise thermal and kinetic control of the chemical processes becomes feasible in this IL medium. Thus, EMIM Cl provides a stable and convenient reaction medium for performing the reactions and isolating the products.

- Effective in biomass dissolution

Swatlowski et al., reported that many imidazolium based ILs, including EMIM CL, are capable of dissolving cellulose pulp and even biomass in appreciable amounts[35],[36]. Ability to dissolve biomass carbohydrates in ILs, opens interesting possibilities; indeed, several recent investigations[7],[37], have explored *in situ* saccharification of the dissolved carbohydrates into their monomeric sugars by controlled addition of water and acid (catalyst) to the IL, following biomass dissolution. Since this approach provides biomass-derived sugars directly in the IL-medium, it provides an opportunity to attempt one-pot synthesis of furans from biomass without the need to isolate sugars following biomass dissolution and carbohydrate saccharification. In this study, *dehydration of carbohydrates into furans* was attempted in EMIM Cl. Thus, this IL medium makes the deconstruction of lignocellulosics, de-polymerization of carbohydrates, and subsequent dehydration into furans feasible in “one-pot".

- Solubility and miscibility

EMIM Cl exhibits a broad range of solubility and miscibility characteristics. From the stand point of the present investigation, C5 and C6 sugars, the catalysts and furan products are *all* soluble in IL. At the same time, the immiscibility of IL in some organic extraction solvents (such as MIBK, Ethyl acetate, toluene) facilitates the reactive-extraction of furans into these solvents, thus facilitating higher conversions and yields.

Chapter 3

Optimization of the dehydration reaction from xylose to furfural

3.1 Introduction

Dehydration of xylose to furfural in aqueous acidic media has been explored by a number of groups[38],[39]. However, the high temperature and pressures required in this approach, will significantly contribute to the high cost of production on a commercial scale. As noted, ionic liquids can not only provide reaction media that facilitate benign operating conditions, but would also provide opportunities for "one-pot" synthesis due to their ability to dissolve lignocellulosic biomass[40],[41]. With ILs, it is possible to accomplish deconstruction of lignocellulosics, de-polymerization of carbohydrates and dehydration into furans all in one-pot. In this chapter, our efforts on optimizing the catalytic dehydration of xylose in ionic liquid media are described. Xylose is the major five carbon sugar obtained from the de-polymerization of the hemicellulosic fraction of biomass.

For initial reactions, mixture of 50 mg of xylose, 500 mg of EMIM Cl and a metal halide catalyst (20 mol.% of sugar) were reacted for 3.5 hours at an appropriate temperature. In order to optimize the dehydration reaction conditions to maximize the furfural yield, the use of different catalysts, different types and proportions of extraction solvents, different temperatures and reaction times were explored. The results of these efforts are described in the sections below.

3.2 Materials and Methods

1-Ethyl-3-methylimidazolium chloride (98% pure), $CrCl_3$ (99% pure), $ZnCl_2$ (99% pure), $FeCl_2$ (99% pure), $CuCl_2$ (99% pure) and $CrCl_2$ (99% pure) were supplied by Sigma-Aldrich. C_6H_5-B-Cl_2 (98%) was obtained from Fisher Scientific. Xylose (99%) was purchased from Acros. Acetonitrile (99%), toluene (99%), ethyl acetate (99%), methyl isobutyl ketone (MIBK, 99%), dimethyl sulfoxide (DMSO, 99%) and 1-butanol were supplied by Fisher Scientific.

Prior to each experiment, IL was thoroughly dried in a BUCHI Rotavapor (R-215), maintained at 80-85 ^{0}C and a vacuum of 39 mbar, for 4 to 5 hours so that the moisture content was less than 0.5 wt.%. The moisture content was measured by 756 KF Coulometer (BRINKMANN).

In a standard experiment, 500 mg EMIM Cl was loaded into 22 ml vials (15.5 mm x 50 mm). $CrCl_2$ (20 mol. % with respect to sugars) was added as a catalyst. IL and catalyst mixture was incubated at 150 °C for 20 min to make a homogeneous solution. 50mg of xylose was then added into the individual vials. In some experiments, an IL- immiscible organic solvent was added to the system. The reaction vial was sealed and heated to the pre-specified reaction temperature and maintained at that temperature for the specified reaction time with continuous stirring (at 700 rpm) with a magnetic stir-bar.

After the reaction, the vial was inserted into ice bath for 15min to arrest the reaction. In the experiments without organic phase, DI water was added to quench the reaction and dilute the sample to a total solution volume of 10ml. The liquid mixture samples were filtered by a syringe filter prior to analyzing for sugars and furan compounds. The analysis was carried out in an Agilent 1100 high performance liquid chromatograph (HPLC), with two Aminex HPX-87H Ion Exclusion columns (300mm x 7.8mm) connected in series using a refractive index detector (RID). For the experiments with organic phase, after cooling the reaction mixture in an ice bath, a phase separation was seen in the vial. The upper layer of organic phase was removed for analysis of furan products. Furans in the organic phase were analyzed using a Gas chromatograph (GC-2010 SHIMADZU), equipped with a Flame ionization detector (FID), and an Rtx-5 column (15m x0.25mmx 0.1μm). Then DI water was added to dilute the aqueous liquid mixture till the total volume was 10ml. The aqueous layer was filtered and collected for HPLC analysis. The result of conversion, yield and carbon balance was computed based on total measured substrate and product concentrations in both IL and organic phases.

3.3 Definitions of conversion, yield and carbon balance:

Xylose conversion: Conversion of xylose is defined as the mole ratio of xylose consumed to the initial xylose loading.

$$X = \left(\frac{mole of xylose\ consumed}{intial\ xylose\ moles\ in\ the\ loaded\ sample}\right) \times 100\% = \left(1 - \frac{xylose\ moles\ in\ product}{intial\ xylose\ moles\ in\ the\ loaded\ sample}\right) \times 100\%$$

Product yield: Yield is defined as the moles of carbon in the consumed xylose that appears in the furfural product.

$$Y = \left(\frac{moles\ of carbon\ in\ furfural\ product}{moles\ of\ carbon\ consumed\ in\ the\ xylose\ feed}\right) \times 100\%$$

Carbon balance: Carbon balance is defined as the ratio of moles of carbon in products and reactants and intermediates left to the mole of carbon in the initial reactants.

$$Z = \left(\frac{moles\ of carbon\ in\ the\ furfural\ product + xylose\ and\ xylulose\ left\ in\ the\ reaction\ mixture}{mole\ of\ carbon\ in\ the\ xylose\ feed}\right) \times 100\%$$

All the conversion and yield numbers reported in the thesis are based on the above definitions.

3.4 Analysis method

Xylose and xylulose are only soluble in the IL phase and not dissolved in the organic solvent[42], which means that the mass of xylose and xylulose measured in the IL phase accounts for their total amounts in the reaction vial. Since furfural is soluble in both organic and IL phases, the yield of furfural was determined from the sum of the amounts in the IL and organic phases. Carbon balance was computed based on all the carbon in the reaction system, which was also the sum from both phases.

3.4.1 IL (Aqueous) phase analysis

Since the IL phase samples are diluted with water prior to analysis using HPLC, we refer to this phase as the aqueous phase or IL phase. In all our experiments, the aqueous phase was analyzed by HPLC with two Aminex HPX-87H Ion Exclusion columns (300mm x 7.8mm) connected in series and refractive index detector (RID). In our specific HPLC system, the xylose and xylulose peaks appear at around 24 min and 25 min, while furfural peak appears at near 110 min. Though xylose and xylulose peaks are close to each other, they separate well when two 87H-columns are connected in series[37].

Before analyzing the actual reaction samples by HPLC, at least 7 standards, which had a range of different concentrations, were prepared. 4mg, 3mg, 2mg, 1mg, 0.5mg, 0.25mg and 0.125mg of xylose, xylulose and furfural were weighted and put into 7 vials (5ml, 12mm*96mm) individually. Then 1ml of DI water was added into each vial and the vial was shaken thoroughly to ensure complete dissolution of the sugar/furan. 70-80µL of each solution was put into the HPLC vial for generating a calibration curve. Calibration curves (See Figures 3-1, 3-2, 3-3) were developed for each compound to relate the concentration to the peak area. (X axis is concentration of each compound and Y axis is the peak area.)

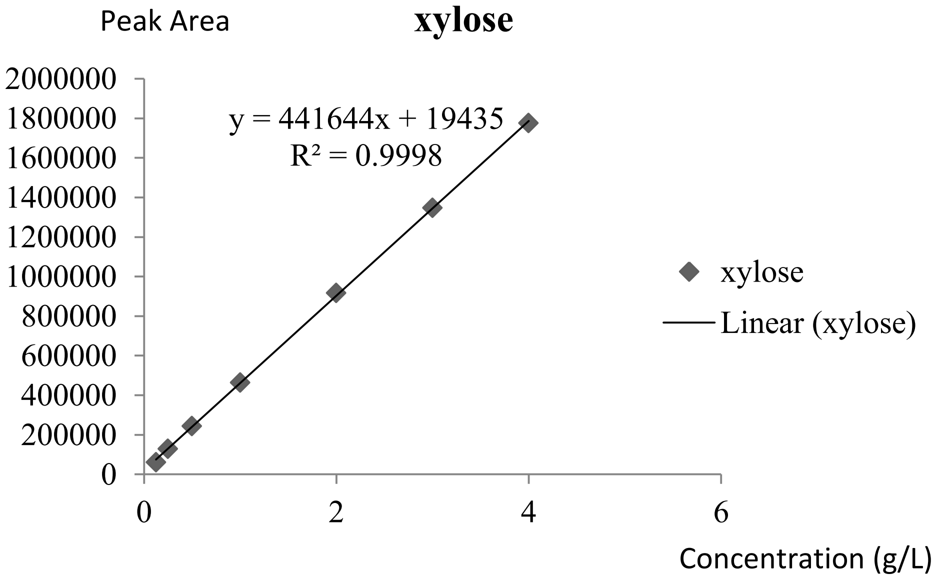


Figure 3-1: Calibration curve of xylose

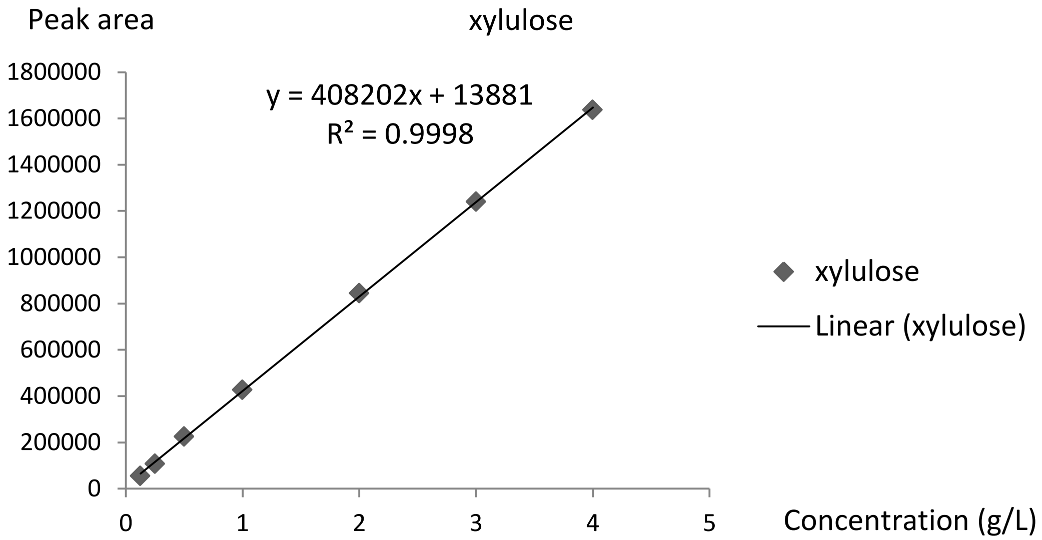


Figure 3-2: Calibration curve of xylulose

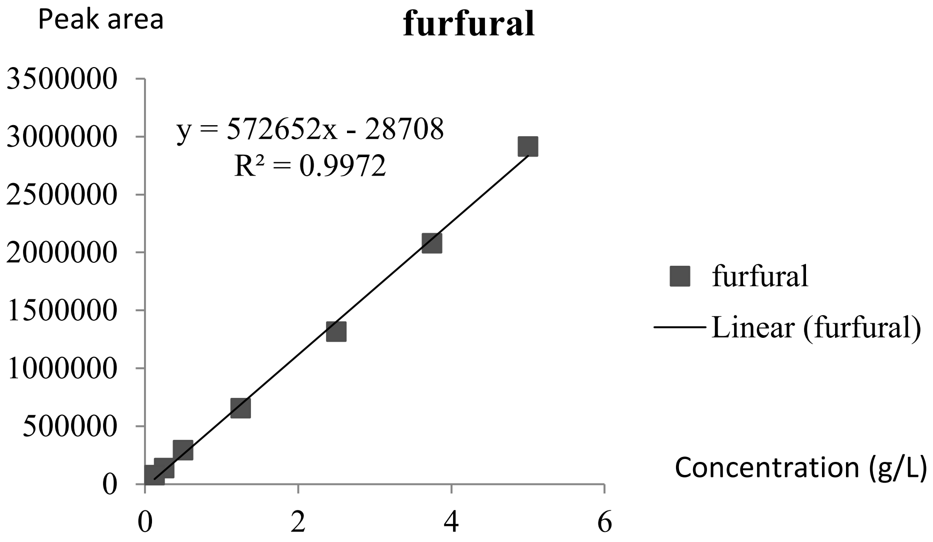


Figure 3-3: Calibration curve of furfural in HPLC

Using the equation of the calibration line, the concentration of the reaction sample could be calculated from its peak area. From HPLC results, the conversion of xylose can be computed using the definition for conversion provided above. A new calibration curve was generated every time analysis of a new set of experimental data was required.

3.4.2 Organic phase analysis

Some of the experiments had an organic phase immiscible with IL as an extraction-solvent for the furan. The organic phase was analyzed for furan by GC with a flame ionization detector (FID), using an Rtx-5 column (15m x0.25mmx 0.1μm).

Following a procedure similar to HPLC analysis, a standard calibration curve was generated for the GC analysis of furfural. Since other major species of the dehydration reaction, except furfural, were insoluble in the organic solvent, the calibration was done only for furfural. Seven different amounts of furfural were weighted into 5ml (12mm*96mm) vials: 7mg, 6mg, 5mg, 4mg, 3mg, 2mg, and 1mg. Then, 1ml of the organic solvent was added to these vials. After shaking the vial well, 100 -150 μL of solution was added into GC vials for analysis. A typical calibration curve shown below was made in the MIBK and 1-butanol mixture system (Figure 3-4). In our GC system, the peak for furfural was seen around 11min.

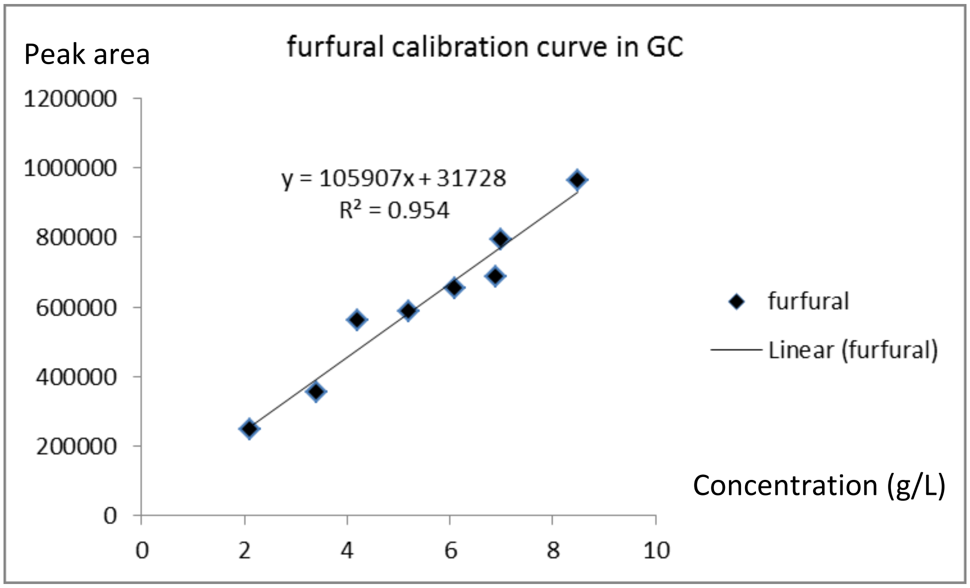


Figure 3-4: Calibration curve of furfural dissolved in MIBK-butanol solvent mixture from GC

3.5 Results and discussion

3.5.1 Effect of different catalysts

Recent studies have shown that metal halides can catalyze the dehydration of xylose in EMIM Cl media at $80^0C^{[19]}$. In order to properly analyze the effects of different halide catalysts, a group of catalysts were screened in this section, including $CrCl_3$, $ZnCl_2$, $FeCl_2$, $CuCl_2$, $CrCl_2$ and C_6H_5-B-Cl_2. In all cases the molar ratio of catalyst to xylose was 0.2. While these catalysts are solids initially, they could be dissolved completely in EMIM Cl when heated to 150°C for 20 min.

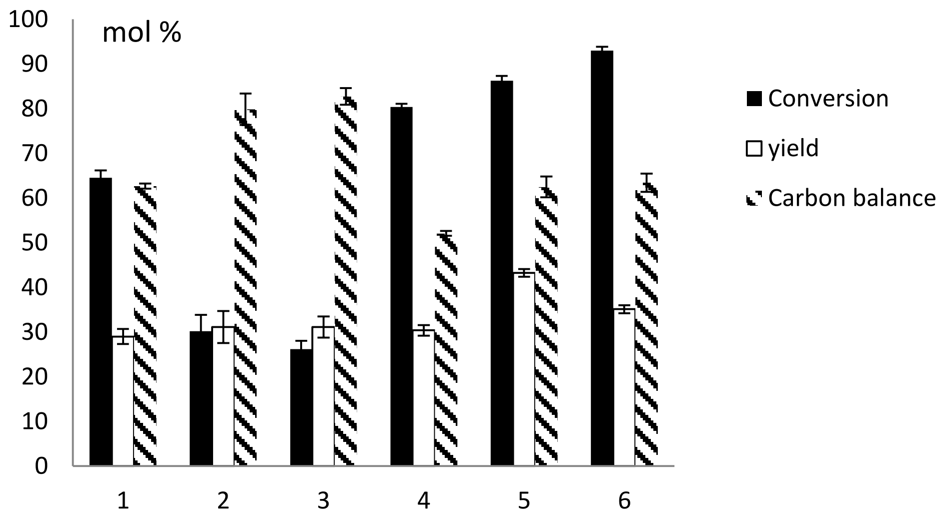


Figure 3-5: Xylose conversions, furfural yields and carbon balance following reaction in EMIM Cl at 80^{0}C for 3.5 hours in presence of different catalysts.

Table 3.1 Catalysts used for dehydration of xylose to furfural in Figure 3-5

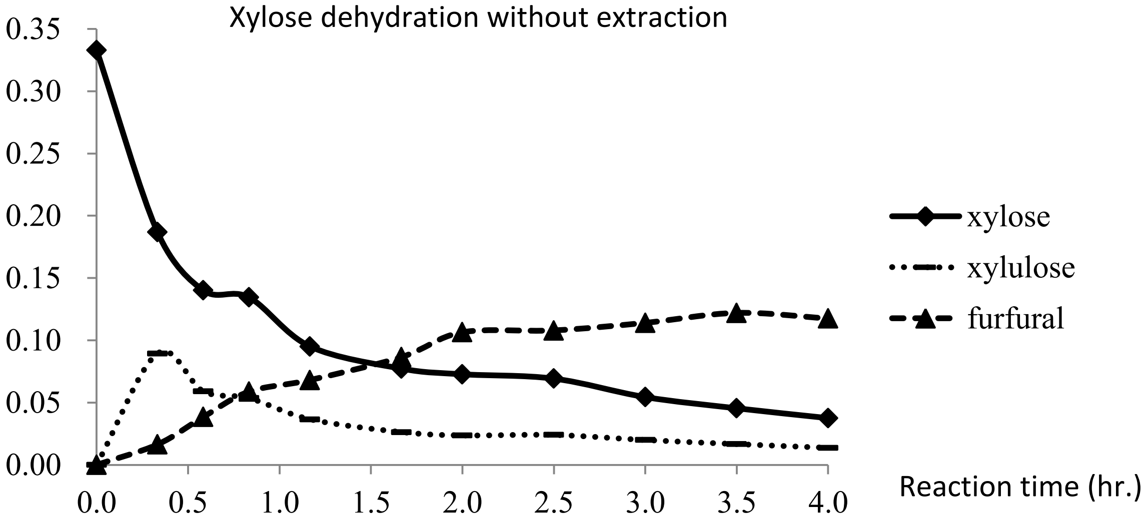
Entry	Catalyst	
1	$CrCl_3$	Chromium(III) chloride
2	$ZnCl_2$	Zinc chloride
3	$FeCl_2$	Iron(II) chloride
4	$CuCl_2$	Copper(II) chloride
5	$CrCl_2$	Chromium(II) chloride
6	C_6H_5-B-Cl_2	Dichloro(phenyl)borane

Figure 3-5 shows that most of the six catalysts are reasonably effective for xylose dehydration. $CrCl_3$, $CuCl_2$, $CrCl_2$ and C_6H_5-B-Cl_2 can lead to xylose conversions over 60% within 3.5 hrs. $CrCl_2$ was selected for further investigation, since this catalyst produced a good conversion of xylose, 86.6% and a high yield to furfural, 43.2%. Experiments were next conducted to study the effect of adding extraction solvents with $CrCl_2$ as a catalyst.

3.5.2 Use of extraction solvents

In the dehydration reaction, xylose was converted to xylulose first (Figure 3-6 step1) and then undergoes dehydration to furfural (Figure 3-6 step 2)[43]. From HPLC analysis, accumulation of xylulose can be detected during and after the reaction (see Figure 3-7), which means that both steps appear to proceed at comparable rates and are reversible. Removal of furfural as it is formed during the reaction will drive the second-step forward, which, in turn will hasten the first-step. Thus, in order to accelerate the rate of both the steps, an extraction solvent immiscible with the IL and capable of selectively extracting furfural was added to the reaction system. There is evidence from previous investigations, dealing with conversion of glucose to HMF, that biphasic systems can facilitate the dehydration reactions in favor of producing more products. As expected, in-situ extraction of furfural, using MIBK and 1-Butanol mixture as extracting solvent (V_{MIBK}: $V_{1\text{-butanol}}=7:3$, $M_{\text{organic solvent}}$: $M_{IL}=3:1$), drove the dehydration reaction forward leading to higher furan yields. With this organic extraction, the yield of furfural can be improved to over 53.6%; while in the absence of organic solvent, the yield is around 40%.

Figure 3-6: Proposed mechanism of xylose dehydration reaction



(Reaction is catalyzed by $CrCl_2$ in EMIM Cl medium at 100 ^0C)

Figure 3-7: Moles of xylose, xylulose and furfural in the reaction mixture as a function of time.

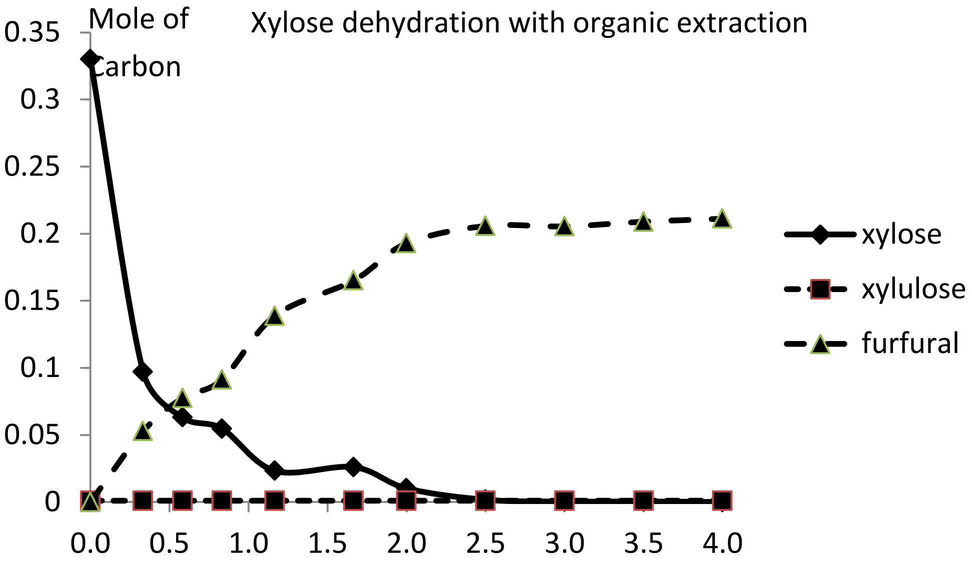


Figure 3-8: Moles of xylose, xylulose and furfural in the reaction mixture as a function of time. (Reaction is catalyzed by $CrCl_2$ in EMIM Cl medium at 100 ^{0}and MIBK –butanol mixture was used to extract furfural from the reaction medium as it is formed.(V_{MIBK}:$V_{1\text{-butanol}}$=7:3, $M_{\text{organic solvent}}$: M_{IL} =3:1)

Figure 3-8 shows the reaction kinetic data in presence of the organic phase, MIBK and 1-butanol mixture. Clearly, rate of step 2 in Figure 3-6 appears to have become faster relative to step 1 since the furfural is extracted into the organic phase as it is formed. No xylulose accumulation in the IL medium is seen in Figure 3-8. Rapid utilization of xylulose will also minimize the possibility of sugar loss to undesirable side reactions. Similarly, elimination of furfural from the IL medium will also prevent its subsequent degradation and/or participation in side reactions that could contribute to reduced yield. The organic solvent is likely to provide a more stable environment compared to the acidic conditions in the IL medium, and prevent furfural from further degradation or transformation.

3.5.3 Effect of different extraction solvents

The previous sub-section has demonstrated the effectiveness of an extraction solvent in controlling the kinetics and improving the reaction yields. Accordingly, in this section we attempted to identify the most effective extraction solvent from numerous choices. We investigated some pure organic solvents and organic solvent mixtures to build an optimal biphasic system with IL[44] for the furfural production reaction.

Chidambaram and Bell [33]reported that the dehydration of glucose into 5-HMF would be accelerated in the EMIM Cl system, when acetonitrile was added to the reaction mixture; acetonitrile is *miscible* with EMIM Cl. Jean Lessard[8] observed that the dehydration of xylose into furfural in aqueous media was benefitted by in-situ extraction of furfural with toluene. Similarly, Yuriy Roman-Leshkov and Dumisec[44] developed an efficient process of fructose dehydration into 5-HMF in aqueous media, by extracting 5-HMF with a mixture of MIBK and 1-butanol.

Guided by these earlier studies, acetonitrile, toluene, (MIBK and 1-butanol) mixture along with ethyl acetate, and dimethylsulfoxide (DMSO) were selected as the organic phase candidates in our studies.

For each experiment, the extraction solvent was added to the vial following the addition of the catalyst, IL and xylose. $CrCl_2$ was chosen as the catalyst. And the mass ratio of organic solvent to sugar was selected as 3:1.

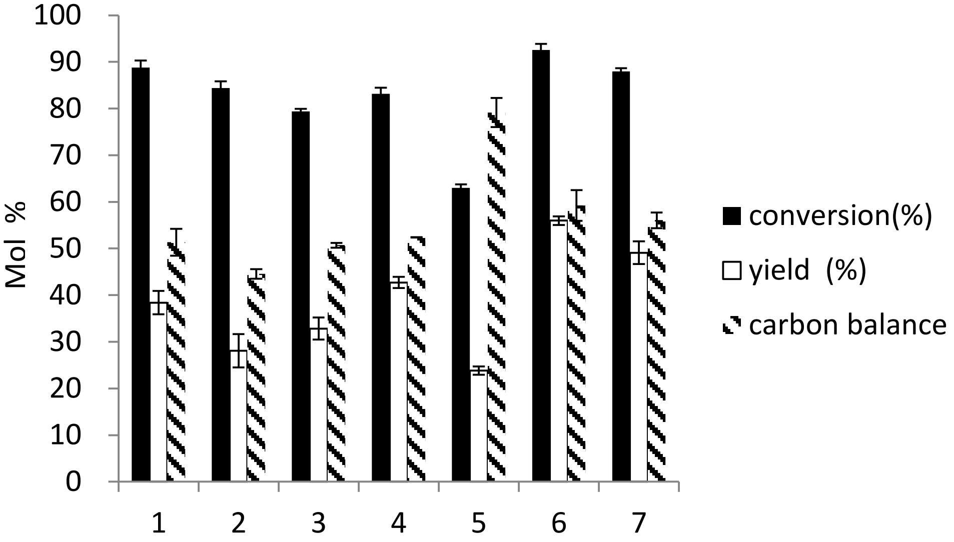


Figure 3-9: Xylose conversions, furfural yields and carbon balance for the system in EMIM Cl, with $CrCl_2$ as a catalyst and with different extraction solvents at 80^0C for a total reaction time of 2 hours. ($M_{\text{organic solvent}}$: $M_{\text{ionic liquid}}$= 3:1)

Table 3.2 Extraction solvents **used in xylose dehydration**

Entry	Extraction solvents	
1	CH_3CN	Acetonitrile
2	$C_6H_5CH_3$	Toluene
3	$CH_3COOCH_2CH_3$	Ethyl Acetate
4	$(CH_3)_2CHCH_2COCH_3$	Methyl Isobutyl Ketone (MIBK)

5	$(CH_3)_2SO$	Dimethyl Sulfoxide (DMSO)
6	$(CH_3)_2CHCH_2COCH_3$ and $CH_3(CH_2)_3OH$	MIBK and 1-butanol mixture (7:3, v:v)
7	$C_6H_5CH_3$ and CH_3CN	Toluene and acetonitrile mixture (1:1,v:v)

Figure 3-9 shows that, while xylose conversions are well over 60% in the presence of most of the extraction solvents, the highest furfural yield (55.98%) is attained only with MIBK and 1-butanol mixture as the extraction solvent. Hence, MIBK and 1-butanol mixture was selected as the extraction phase for further investigations in the following chapters.

3.5.4 Determination of extraction solvent loading

After establishing that MIBK and 1-butanol mixture is the most effective extraction solvent for the conversion of xylose into furfural, we attempted to determine the optimal ratio of organic solvent to ionic liquid. A wide range of ratios of organic liquid to ionic liquid from 2:1 to 5:1 were tested for this purpose.

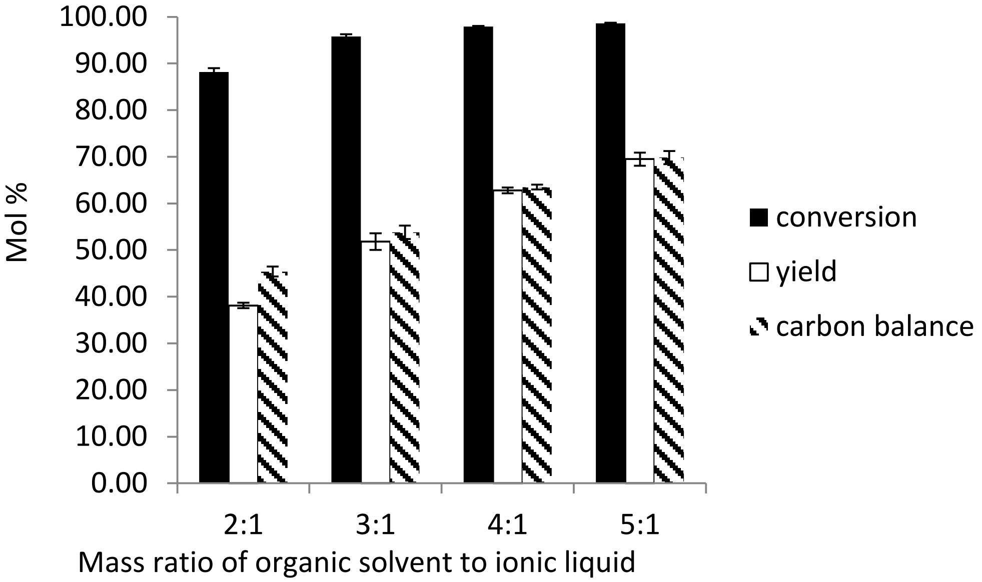


Figure 3-10: Results of $CrCl_2$- catalyzed dehydration of xylose in EMIM Cl media. Runs were carried out at 100^{0}C for 2 hours with MIBK and 1-Butanol mixture as an extraction solvent. (V_{MIBK}: $V_{1\text{-butanol}}$ =7:3). Mass ratios of organic solvent to ionic liquid tested were: 2:1, 3:1, 4:1 and 5:1.

It was observed from Fig. 3-10 that an increase of organic solvent/IL ratio appears to result in higher conversions, yields and carbon balances, reaching a maximum conversion of 98.42%, yield of 69.12% and carbon balance of 72.18% at mass ratio of 5:1 in 2 hours. It is also worthy of mention that even though the best results are seen at the ratio of 5:1, the conversion and yield have already reached over 90% and 55% when the ratio is 3:1.

Isolation of furfural from the extraction solvent after the reaction requires distillation. The energy consumption associated with this step will be lower if less solvent were used during the extraction step. Hence, although the best results for the reactive-extraction process were seen at an organic to IL ratio of 5:1, the ratio of 3:1 was selected as a viable option for further studies in light of the costs associated with the subsequent furfural purification step.

3.5.5 Effect of temperature

The kinetics as well as the equilibrium of the reactions involved is strongly affected by the temperature at which the reaction is carried out. The temperature will affect the conversion of xylose and the yield of furfural from this dehydration reaction. This section focuses on the temperature effect on the conversion, yield of the product and the total carbon balance of the system.

As our previous experiments have shown that the best catalyst and extraction solvent for the system are $CrCl_2$ and (MIBK and 1-butanol) mixture, respectively, our investigations on optimal temperature conditions were performed with this combination of catalyst and extraction solvent. In all experiments, an extraction-solvent to IL ratio of 3:1 was employed. The temperature range studied was from 80^0C to 120^0C.

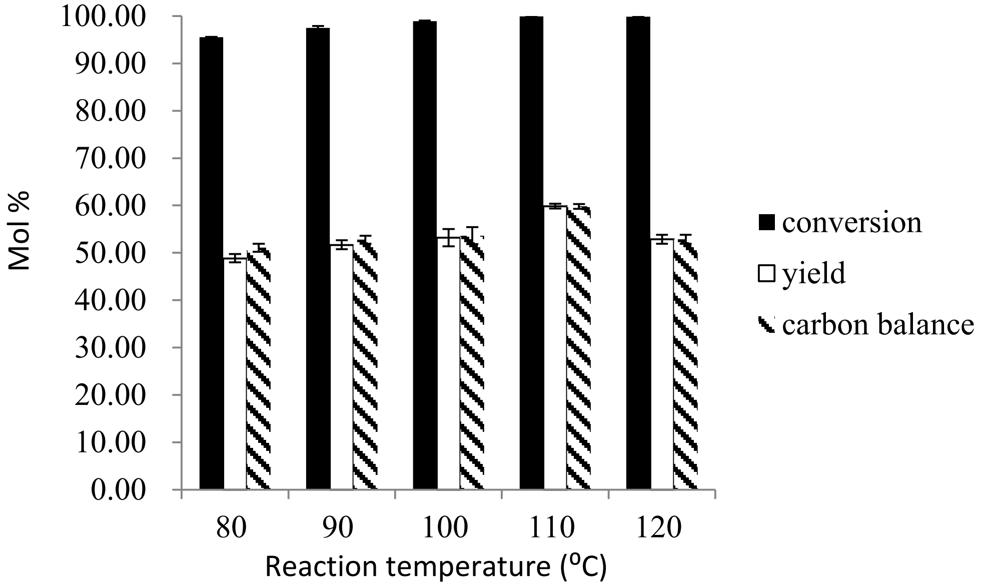


Figure 3-11: Effect of reaction temperature on xylose conversion, furfural yield and total carbon balance. All experiments were carried out in EMIM Cl medium, with $CrCl_2$ as catalyst and (MIBK and 1-butanol) mixture as the extraction solvent for 2 hours.

A moderate improvement in yield is seen as the temperature was raised from 80^0C to 110^0C (Figure 3-11). Xylose conversions were consistently over 95%, and yield of furfural increased from 52.41% to 60.89% at the temperature range of 80^0C to 110^0C. When temperature was raised from 110 to 120^0C, the yield and carbon balance decreased. It was concluded that reaction temperature between 100^0C and 110^oC was adequate to achieve a good conversion and yield.

3.5.6 Kinetics of the dehydration reaction

Base on the above parametric investigation, the following conditions were adjudged as suitable conditions for carrying out the dehydration of xylose in EMIM Cl ionic liquid:

Reaction temperature: 100°C

Catalyst: $CrCl_2$ (at a sugar to catalyst mole ratio of 5:1)

Biphasic furfural extraction Medium: (MIBK + 1-Butanol) mixture (at a V_{MIBK} to $V_{1-butonal}$ proportion of 7:3)

Mass ratio of extraction phase to IL phase: 3:1

We studied the kinetics of the dehydration reaction at these optimized conditions, following the experimental protocols described at the beginning of this chapter. For this kinetic study, ten reaction vials were loaded with the same amounts of initial reaction mixtures, and the reactions were allowed to proceed for times of 20min, 35min, 50min, 70min, 100min, 120min, 150min, 180min, 210min and 240min, respectively. The conversion, yield and carbon balances reached at each of these times were shown in Figure 3-12.

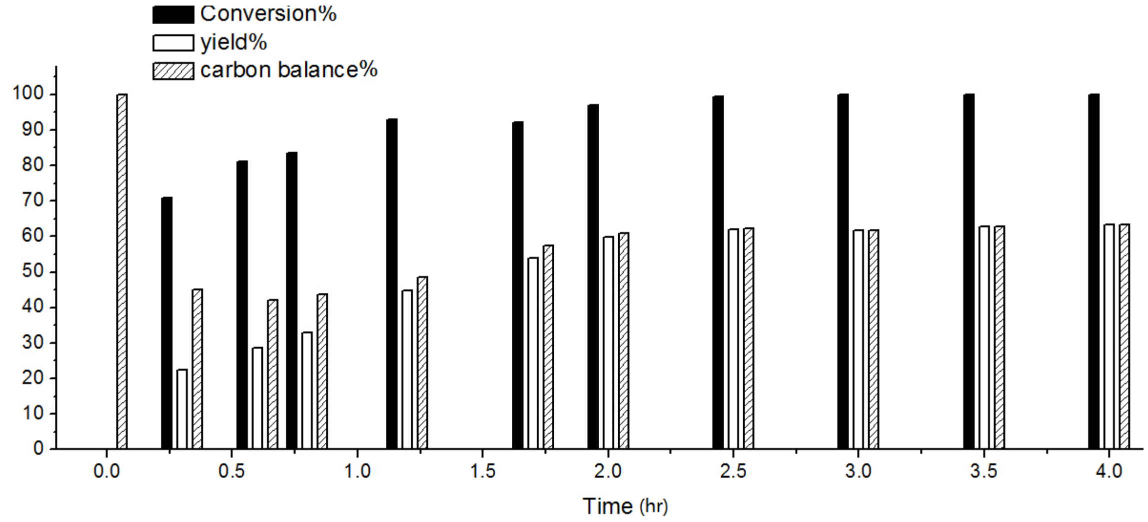


Figure 3-12: Xylose conversions and furfural fields in EMIM Cl, $CrCl_2$ and MIBK and 1-butanol at 100⁰C for 20min, 35min, 50min, 70min, 100min, 120min, 150min, 180min, 210min and 240min.

The conversion and yield increase steadily to reach their peak values at a reaction time of about 150minutes. These values are a conversion of 99.7% and yield of 62.1%. After 150minutes, the loss of furfural yield seen might be caused by side reactions or furfural degradation in the IL phase.

3.6 Conclusions

In this chapter, the optimal conditions for dehydration of xylose to furfural were established. $CrCl_2$ was determined as the most effective catalyst. Also, MIBK and 1-butanol mixture was identified as a valid extraction solvent with the loading of 3:1 ($M_{organic\ solvent}$: M_{IL}). A reaction temperature of 100 ⁰C and a reaction time of 120 minutes were selected as optimal to achieve the maximum yield of furfural. Under these conditions, best results of xylose dehydration reaction obtained were conversion of 99.70%, yield of 62.1% and carbon balance of 62.24%.

Chapter 4

Optimization of the dehydration reaction from glucose to 5-HMF

4.1 Introduction

As noted in the Introduction, glucose and xylose give rise to different furans upon dehydration. While xylose produces furfural, glucose leads to 5-hydroxymethyl furfural (5-HMF). Hydrogenation products of 5-HMF, such as dimethyl furan and tetrahydrofuran form viable candidates for "drop-in" fuels due to their high energy densities which are very close to that of gasoline. Several investigations reported on the dehydration of glucose into 5-HMF in *aqueous or acid media*[45],[46]. As noted in Chapter 2, aqueous-phase dehydration requires high temperature and pressures. Moreover, in this type of approach, loss of 5-HMF due to its hydrolysis to form levulinic and formic acid is an issue, and its isolation from aqueous media can be very energy-intensive.

In this chapter, we extend our investigation of xylose dehydration in IL media in the presence of Lewis acid catalysts, to glucose dehydration. While there were some previous reports dealing with glucose conversion to 5-HMF in IL media in presence of Lewis and Bronsted acid catalysts[47], to the best of our knowledge there is no systematic investigation of simultaneous conversion of mixtures of xylose and glucose to their corresponding furans in the same IL reaction medium. Since, most biomass pretreatment methods give rise to a mixture of C6 and C5 sugars, it is of great interest to understand the furan formation from a mixture of glucose and xylose sugars. However, before studying sugar mixtures, we explored in this chapter the conditions that are optimal for 5-HMF formation from glucose in the same system that was investigated in Chapter 3 for Xylose dehydration. The goal is to compare the experimental conditions suitable for each of the sugars in order to identify conditions that are optimal (if any) for a sugar mixture. Accordingly, in this chapter a parametric study is presented for the reaction of 5-HMF formation from glucose in EMIM Cl IL with $CrCl_2$ catalyst.

In a typical reaction, 60mg of glucose (which provides the same number of moles as 50 mg of xylose) was added to 500 mg EMIM Cl, which has previously been incubated with $CrCl_2$ catalyst at 150^0C for 20 min in a vial. 1500mg of MIBK and 1-butanol mixture was then added into the vial. The vial with sugar, IL, catalyst and extraction solvent was heated and maintained at a pre-specified reaction temperature, under continuous stirring, for a specified length of time, at which point the contents were analyzed to determine the extent of conversion and yield. Through this approach, the optimum conditions of temperature and reaction time for glucose dehydration were established.

4.2 Materials and Methods

Glucose (99% pure) and 5- HMF (98% pure) were purchased from Sigma-Aldrich. Prior to each experiment, IL was thoroughly dried in a BUCHI Rotavapor (R-215), maintained at 80-85 ^{0}C and a vacuum of 39 mbar, for 4 to 5 hours so that the moisture content was less than 0.5 wt.%. The moisture content was measured by 756 KF Coulometer (BRINKMANN supply). In a standard experiment, 500 mg EMIM Cl was loaded into 22 ml vials (15.5 mm x 50 mm). $CrCl_2$ (20 mol. % with respect to sugars) was added as a catalyst. IL and catalyst mixture was incubated at 150 °C for 20 min to make a homogeneous solution. 60mg of glucose was then added into the individual vials. In some experiments, an IL- immiscible organic solvent was added to the system. The reaction vial was sealed and heated to individual the pre-specified reaction temperature and maintained at that temperature for the specified reaction time with a continuous stirring (at 700 rpm) with a magnetic stir-bar.

After the reaction, the vial was inserted into ice bath for 15min to arrest the reaction. In the experiments without organic phase, DI water was added to quench the reaction and dilute the sample to a total solution volume of 10ml. The liquid mixture samples were filtered by a syringe filter prior to analyzing for sugars and furan compounds. The analysis was carried out in an Agilent 1100 high performance liquid chromatograph (HPLC), with two Aminex HPX-87H Ion Exclusion columns (300mm x 7.8mm) connected in series using a refractive index detector (RID). For the experiments with organic phase, after cooling the reaction mixture in an ice bath, a phase separation was seen in the vial. The upper layer of organic phase was removed for analysis of furan products. Furans in the organic phase were analyzed using a Gas chromatograph (GC-2010 SHIMADZU), equipped with a Flame ionization detector (FID), and an Rtx-5 column (15m x0.25mmx 0.1μm). Then DI water was added to dilute the aqueous liquid mixture till the total volume was 10ml. The aqueous layer was filtered and collected for HPLC analysis. The result of conversion, yield and carbon balance was computed based on total measured substrate and product concentrations in both IL and organic phases.

4.3Analysis method

Glucose is only soluble in the IL phase and do not dissolve in the organic solvent, which means that the mass of glucose measured in the IL phase accounts for their total amounts in the reaction vial. Since 5-HMF is soluble is both organic and IL phases, the yield of 5+HMF was determined from the sum of the amounts in the IL and organic phases. Carbon balance was computed based on all the carbon in the reaction system, which was also the sum from both the phases.

4.3.1 Aqueous (IL) phase analysis

Since the IL phase samples are diluted with water prior to analysis using HPLC, we refer to this phase as the aqueous phase or IL phase. In all our experiments, the aqueous phase was analyzed by HPLC with two Aminex HPX-87H Ion Exclusion columns (300mm x 7.8mm) connected in series and refractive index detector (RID). Technically, in our equipment, the glucose peak appears at around 23min, while 5-HMF peak appears near 70 min.

Before analyzing the actual reaction samples by HPLC, at least 7 standards, which had a range of different concentrations, were prepared. 4mg, 3mg, 2mg, 1mg, 0.5mg, 0.25mg and 0.125mg of glucose and 5-HMF were weighted and put into 7 vials (5ml, 12mm*96mm) individually. Then 1ml of DI water was added into each vial and the vial was shaken thoroughly to ensure complete dissolution of the sugar/furan. 70-80µL of each solution was put into the HPLC vial for generating a calibration curve. Calibration curves (See Figures 4-1, 4-2) developed for each compound to relate the concentration to the peak area. (X axis is concentration of each compound and Y axis is the peak area.)

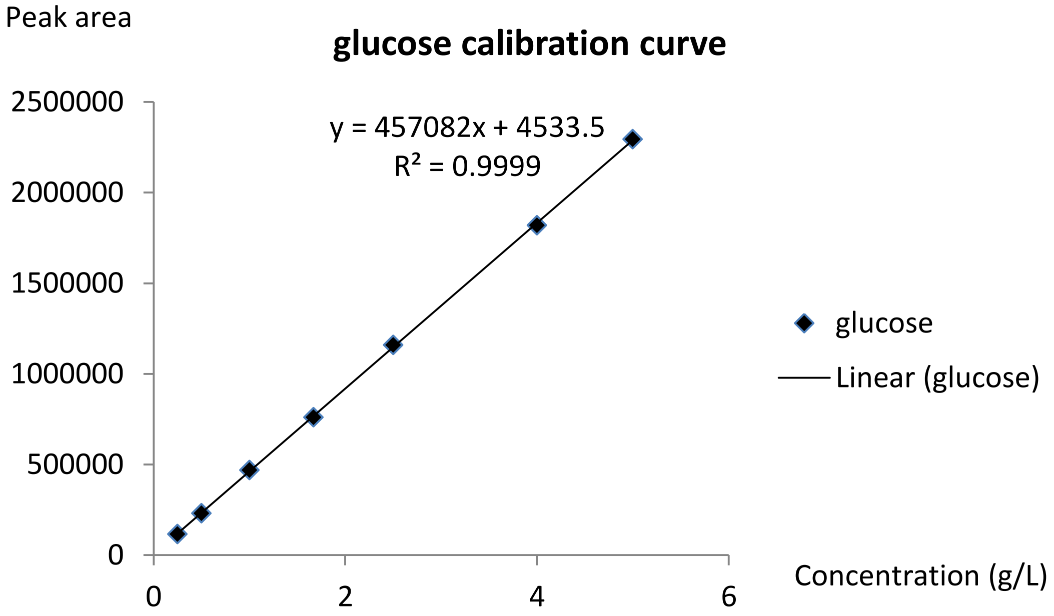


Figure 4-1: Calibration curve of glucose

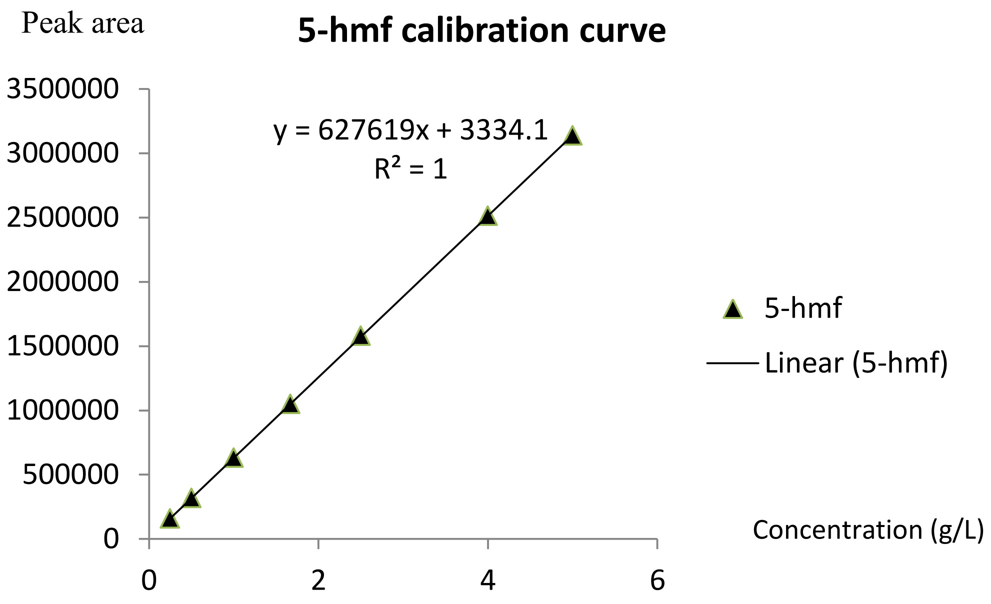


Figure 4-2: Calibration curve of 5-HMF in HPLC

Using the equation of the calibration line, the concentration of the reaction sample could be calculated from its peak area. From HPLC results, the conversion of glucose can be computed using the definition for conversion provided above. A new calibration curve was generated every time analysis of a new set of experimental data was required.

4.3.2 Organic phase analysis

Some of the experiments had an organic phase immiscible with IL as an extraction-solvent for the furan. The organic phase was analyzed for furan by GC with a flame ionization detector (FID), using an Rtx-5 column (15m x0.25mmx 0.1µm).

Following a procedure similar to HPLC analysis, a standard calibration curve was generated for the GC analysis of 5-HMF. Since other major species of the dehydration reaction, except 5-HMF, were insoluble in the organic solvent, the calibration was done only for 5-HMF. Seven different amounts of 5-HMF were weighted into 5ml (12mm*96mm) vials: 7mg, 6mg, 5mg, 4mg, 3mg, 2mg, and 1mg. Then, 1ml of the organic solvent was added to these vials. After shaking the vial well, 100 -150 μL of solution was added into GC vials for analysis. A typical calibration curve (Figure4-3) shown below was made in the MIBK and 1-butanol mixture system. In our GC system, 5-HMF peak was seen around 9min.

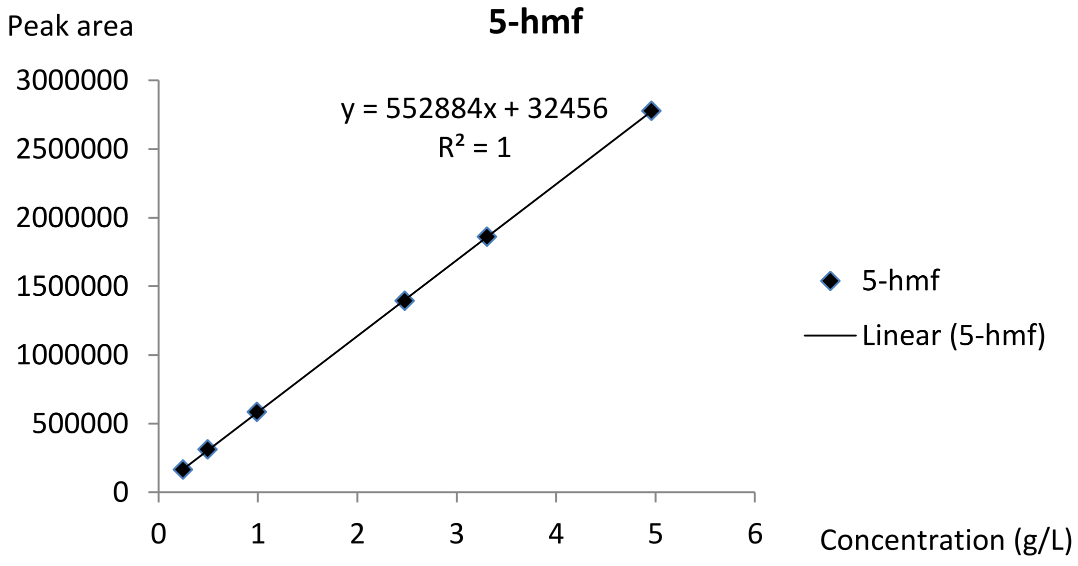


Figure 4-3: Calibration curve of 5-HMF in GC

4.4 Results and discussion

4.4.1Temperature effect

In this subsection, the effect of reaction temperature on glucose conversion and 5-HMF yield was investigated. The reaction was performed at temperatures of 80^{0}C, 90^{0}C, 100^{0}C, 110^{0}C and 120^{0}C. In all the experiments, $CrCl_2$ (at a loading of 20 % of the total number of moles of sugar) was used as the catalyst and MIBK and 1-butanol mixture was used as the extraction solvent (Mass organic solvent: Mass of IL = 3:1).

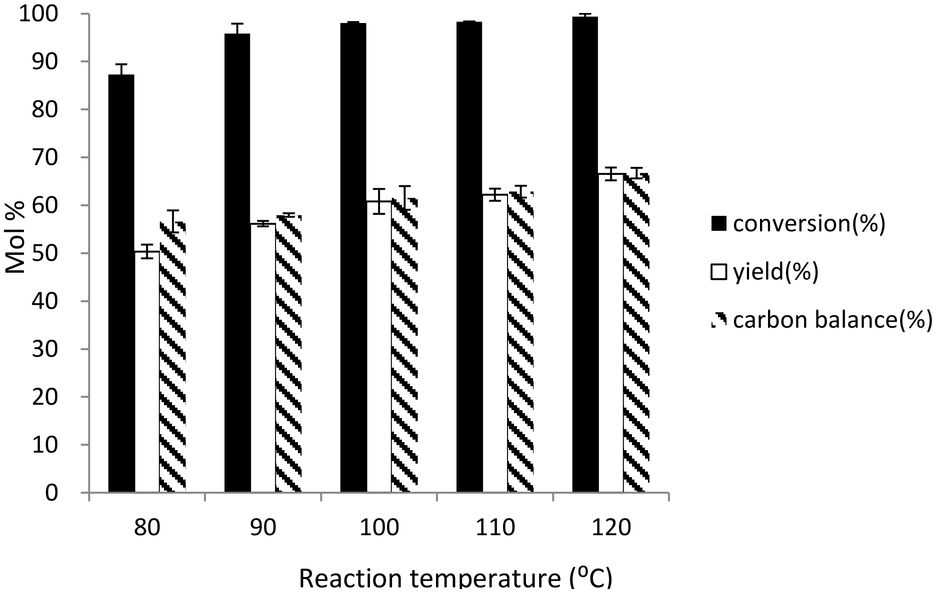


Figure 4-4: Effect of reaction temperature on conversion of glucose and yield of 5-HMF. In all experiments MIBK and 1-butanol (volume ratio of MIBK to 1-butanol =7:3) mixture was used as extraction medium to remove 5-HMF from the IL phase, as it is formed. All reactions were carried out for two hours.

As can be noted from Figure 4-4, the yield increased steadily as the reaction temperature was raised from 80^0C to 120^0C. Also, the conversion of glucose reached essentially 100% for all temperatures higher than 100 ^{o} C. From this data, it can be concluded that 120^0C or higher temperature would be a suitable reaction temperature for glucose dehydration reaction to obtain the highest yield and conversion.

In Chapter 3.5.5, 110^0C was determined as the optimal reaction temperature for xylose dehydration. However, for glucose dehydration reaction, temperatures higher than 110^0C might be needed to achieve the maximum yield. The operating conditions suitable for xylose dehydration were sub-optimal for glucose dehydration.

4.4. 2 Effect of extraction solvent

In attempting glucose dehydration in presence of MIBK and 1-butanol mixture (as an extraction medium for 5-HMF), we were guided by the effectiveness of this organic phase in extracting furfural from IL during xylose dehydration. (Section 3.5.3) To verify if this extraction phase is actually improving the 5-HMF yield or not, we compared the results of glucose dehydration with and without this extraction phase in Figure 4-5.

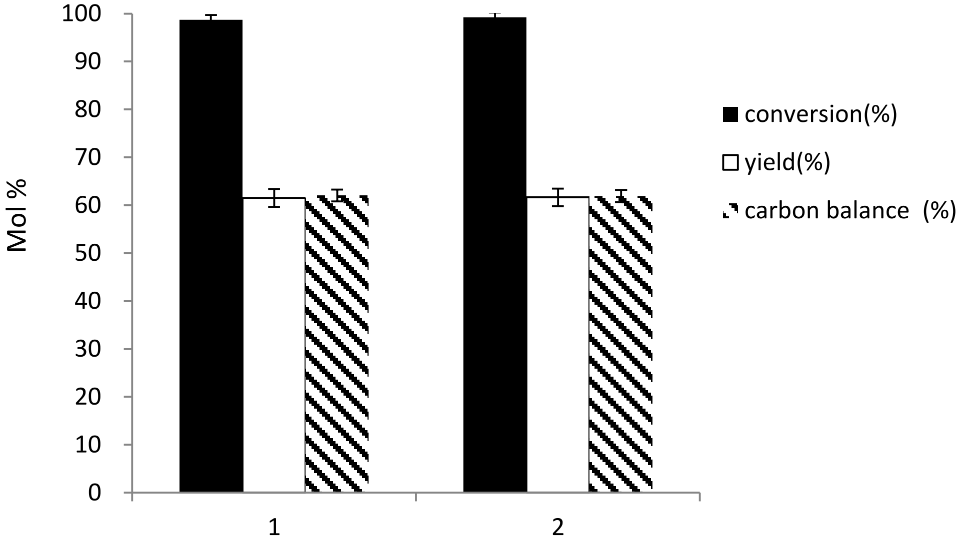


Figure 4-5: Glucose was subjected to dehydration reaction in EMIM Cl with $CrCl_2$ catalyst at 100^0C for 2 hours with and without the extraction phase of MIBK and 1-butanol Mixture. In experiment 2, MIBK and 1-butanol mixture was added as an extraction phase, while there was no organic phase in experiment 1.

MIBK and 1-butanol mixture was added in exp. 1, while there was no extraction solvent in exp. 2. Figure 4-5 shows that there was no significant difference between experiments 1 and 2. Also, the HPLC and GC analysis of the IL and organic phases revealed that over two thirds of HMF formed was in the aqueous phase at the end of the reaction. Clearly, 5-HMF preferentially partitions into the IL phase over the (MIBK+ 1-butanol) mixture phase. Hence, the organic phase does not contribute to the removal of the reaction product to the same extent of the xylose dehydration reaction.

4.5 Conclusions

For glucose dehydration, conversion, yield and carbon balance increased as the temperature went up from 80^{0}C to 120^{0}C. Yield of 5-HMF steadily increased from 46.79% to 72.13%, as the temperature was raised. The conversion of glucose was higher than 90% at all temperatures, indicating that a higher portion of the consumed glucose goes towards HMF formation at higher temperatures. Adding organic solvent did not improve the results significantly, due to the preferential solubility of 5-HMF in IL phase over the MIBK+1-butanol mixture phase.

Chapter 5

Optimization of the dehydration reaction of sugar mixture into furan products

5.1 Introduction

Following pretreatment and de-polymerization of lignocellulosic biomass, the major sugars released from cellulose and hemicellulose portions are glucose and xylose, respectively. In many pretreatment methods, these sugars are released as a mixture than as separate streams. Thus the ability to process the sugar mixtures to furans in a single-pot simultaneously is of interest both from process intensification and economic stand points. Most existing literature on furan production has focused on processing either xylose or glucose[27], and to the best of our knowledge, there were no previous studies dealing with production of furans from sugar mixtures. This chapter describes the results of our efforts to carry out dehydration of both C5 and C6 sugars in ionic liquid media in presence of *in situ* extraction solvents.

For these studies on sugar mixtures, mass ratio of glucose to xylose was selected as 2:1, which is relevant to the ratio the sugars are found in lignocellulosic biomass hydrolysates[48].

5.2 Materials and Method

In a standard experiment, 1500mg EMIM Cl was loaded into 22ml vials (15.5mm x 50m). $CrCl_2$ (20 mol. % with respect to sugars) was added as a catalyst. IL and catalyst mixture was incubated at 150 °C for 20 minutes under stirring at 700 rpm to make a homogeneous solution. 50mg of xylose and 100mg of glucose were then added into the vials. The reaction vial was sealed and heated to a pre-specified reaction temperature and maintained at that temperature for a pre-determined length of reaction time under stirring at 700 rpm.

After the reaction, the vial was inserted into ice bath for 15min to arrest the reactions. Upon cooling, a phase separation was seen in the vial. The upper layer of organic phase was removed for analysis of furan products by Gas chromatography (GC-2010 SHIMADZU), with a Flame ionization detector (FID), using an Rtx-5 (15m x 0.25mm x 0.1μm). Then 5ml of DI water was added to dilute the IL liquid mixture. The aqueous (IL) liquid layer was then filtered and kept for HPLC analysis of the sugars. The conversion, yield and carbon balance for both sugars were computed based on total measured substrate and product concentrations in both IL and organic phases.

5.3Definitions of conversion, yield and carbon balance:

Xylose conversion: Conversion of xylose is defined as the mole ratio of xylose consumed to the initial xylose loading.

$$X\ xylose\ = \left(\frac{moleofxylose\ consumed}{intial\ xylose\ moles\ in\ the\ loaded\ sample}\right) \times 100\%$$
$$= \left(1 - \frac{xylose\ moles\ in\ product}{intial\ xylose\ moles\ in\ the\ loaded\ sample}\right) \times 100\%$$

Glucose conversion: Conversion of glucose is defined as the mole ratio of glucose consumed to the initial glucose loading.

$$X\ glucose = \left(\frac{moleofglucose\ consumed}{intial\ glucose\ moles\ in\ the\ loaded\ sample}\right) \times 100\%$$
$$= \left(1 - \frac{glucose\ moles\ in\ product}{intial\ glucose\ moles\ in\ the\ loaded\ sample}\right) \times 100\%$$

Furfural yield: Yield is defined as the moles of carbon in the consumed xylose that appears in the furfural product.

$$Y\ furfural = \left(\frac{moles\ of carbon\ in\ furfural\ product}{moles\ of\ carbon\ consumed\ in\ the\ xylose\ feed}\right) \times 100\%$$

5-HMF yield: Yield is defined as the moles of carbon in the consumed glucose that appears in the 5-HMF product.

$$Y\,5-HMF = \left(\frac{moles\ of carbon\ in\ 5-HMF\ product}{moles\ of\ carbon\ consumed\ in\ the\ glucose\ feed}\right) \times 100\%$$

Carbon balance: Carbon balance is defined as the ratio of moles of carbon in products and reactants and intermediates left to the mole of carbon in the initial reactants.

$$Z = \left(\frac{\begin{array}{c} moles\ of carbon\ in\ the\ furfural\ and\ 5-HMF\ product\ + \\ xylose\ and\ xylulose\ and\ glucose\ left\ in\ the \\ reaction\ mixture \end{array}}{mole\ of\ carbon\ in\ the\ xylose\ and\ glucose\ feed}\right) \times 100\%$$

All the conversion and yield numbers reported in the thesis are based on the above definitions.

5.4 Results and discussion

5.4.1Temperature effect

A summary of results on temperature effect on furan yield observed for the individual sugars, xylose and glucose (from Figure 3-11 and 4-1), was re-plotted in Figure 5-1. The results in this figure are the yields of furfural and 5-HMF from pure sugar reactions. It is clear that 120^0C, which is suitable reaction temperature for glucose dehydration, is significantly sub-optimal for the xylose dehydration. Similarly, 100^0C, which is optimal reaction temperature for xylose dehydration, is not high enough to achieve a good yield of glucose dehydration. With the aim to identify conditions that promote conversion of both kinds of sugars simultaneously, 100^0C, 105^0C and 110^0C were tested, and the results of these experiments are shown in Figure 5-2.

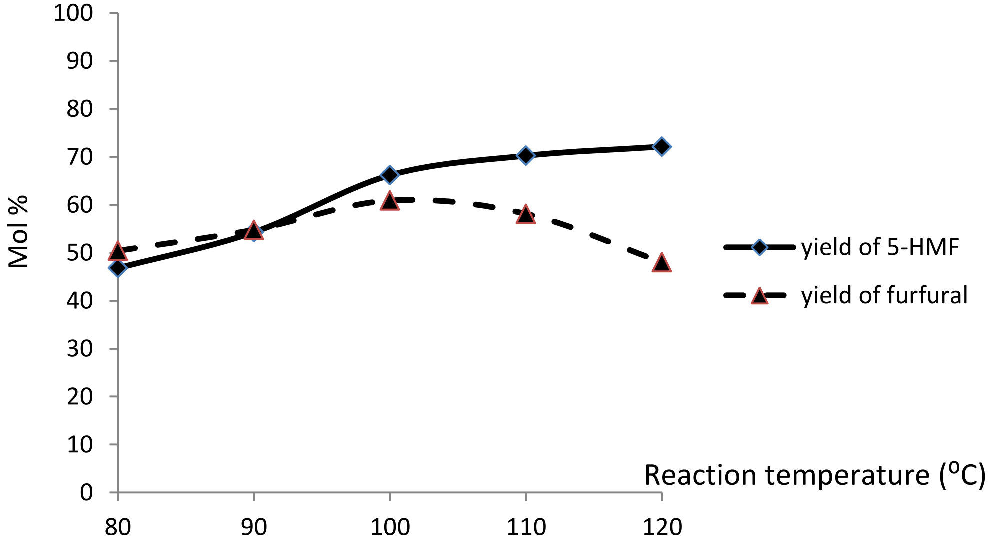


Figure 5-1: Yield of 5-HMF and furfural in pure sugar dehydration

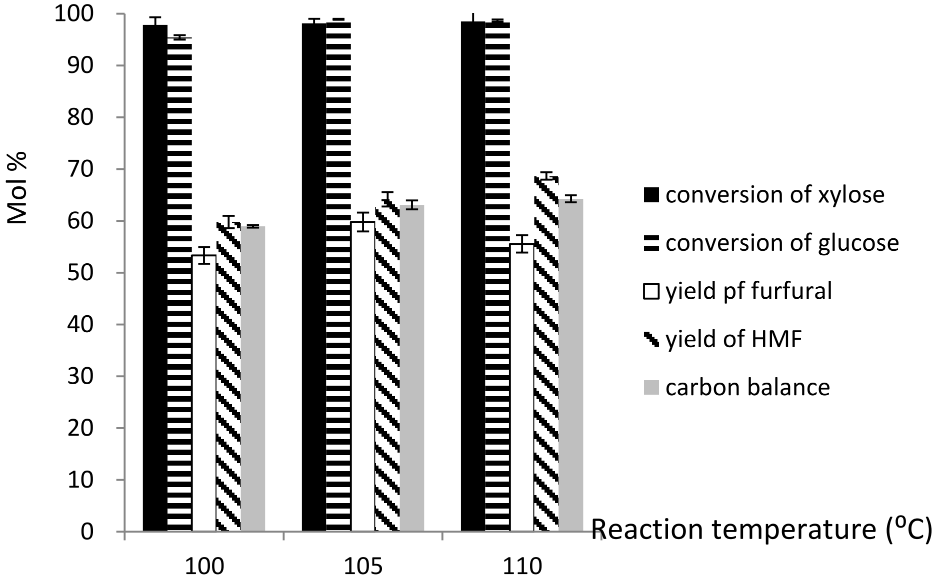


Figure 5-2: Conversion, yield and carbon balance of sugar mixture dehydration reaction. The experiment was carried out for 2 hours. (Mass $_{\text{organic solvent}}$: M $_{IL}$=3:1, V $_{MIBK}$: V$_{1\text{-butanol}}$= 7:3)

From Figure 5-2, it can be seen that from 100°C to 105°C, furfural yield improved from 53.3% to 59.7%, meanwhile 5-HMF yield also increased from 59.8% to 68.6%. Increasing the temperature above 105°C resulted in a decline in furfural yield to 55.6 %, although 5-HMF still kept increasing to 68.6%. In an effort to identify operating conditions suitable for both sugars; 105°C was finally chosen as the optimal reaction temperature for the mixture.

5.4.2 Kinetics of mixture sugar dehydration reaction

Experiments were carried out using the optimal conditions stated in the previous section for the reaction time of 0.5 hr., 0.75 hr., 1 hr., 1.5 hr., 2 hr. and 2.5 hr.

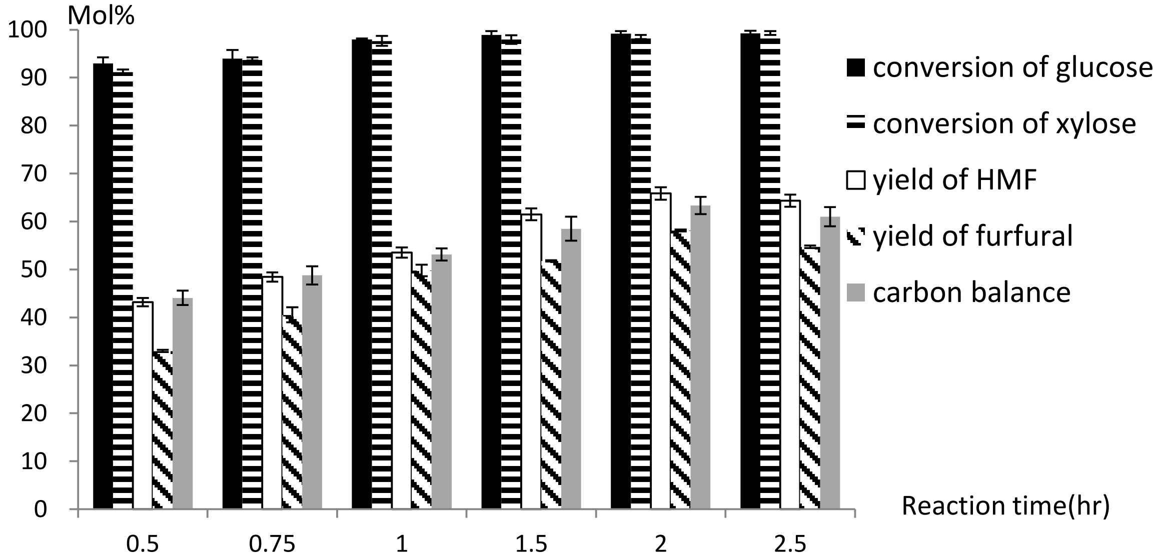


Figure 5-3: Kinetics of sugar mixture dehydration reaction: conversion, yield and carbon balance results of the sugar mixture dehydration reaction. The reaction was conducted in EMIM Cl with $CrCl_2$ as catalyst and MIBK and 1-butanol as the extraction solvent at 105^0C for different lengths of reaction time. Mass ratio of organic solvent to ionic liquid was 3:1.

From Figure 5-3, it was evident that conversion and yield increased steadily with the reaction time. For glucose dehydration part, 2 hour was enough to achieve the highest results. At the end of 2 hours of reaction time, 99.8% of glucose conversion and 65.8% of 5- HMF yield were seen. And for xylose dehydration part, 2 hours was the optimal reaction time. Yield of furfural achieved 58.4%, with almost 100% conversion. Also during the period of 1.5 hours to 2 hours, glucose dehydration results did not decline appreciably. Hence, in order to optimize the dehydration reaction of both sugars, 2 hours was identified as the most suitable reaction time.

5.5 Conclusions

For dehydration of 2:1 a mixture of glucose and xylose, the effect of reaction temperature and time were studied. It was observed that xylose dehydration and glucose dehydration have different characters. Xylose dehydration is favored by reaction temperatures below 110^0C, while 120^0C was the suitable temperature to achieve the maximum yield of 5-HMF from glucose dehydration. 1.5 hour was enough for glucose to be converted completely, while xylose dehydration needed 2 hours to acquire the best results. With the aim of identifying one optimal operating condition for both sugars simultaneously, 105^0C and 2 hours were chosen as the reaction temperature and time for the mixture. With $CrCl_2$ as catalyst and MIBK and 1-butanol as extraction solvent(Mass of organic solvent/ Mass of ionic liquid=3:1), xylose and glucose mixture (in 1:2 proportion) was dehydrated in EMIM Cl medium at 105^0C for 2 hours, giving the maximum results of nearly complete conversion of both sugars, and 67.3% yield of 5-HMF, 60.8%yield of furfural.

Chapter 6

Synthesis of furfural and 5-HMF from sugar mixtures in EMIM HSO4 media

6.1Introduction

Recent studies have demonstrated that the dehydration reaction of monosaccharaides into furan products can be selectively accelerated in Bronsted or Lewis acid catalyst media[47]. In previous chapters, results of studies on dehydration of biomass sugars in an imidazolium chloride ionic liquid medium in presence of the Lewis acid catalyst, $CrCl_2$, were presented. In this chapter, another imidazolium IL whose anion can serve as a Bronsted acid catalyst, namely:1-ethyl-3-methylimidazolium hydrogen sulfate (EMIM HSO_4) was investigated. The goal is to verify if this IL can lead to high yield of furans in the absence of an additional catalyst as the anion itself is capable of serving as an acid catalyst.

It has been recently reported that EMIMHSO4 is a good solvent for xylan and it can promote hydrolysis of xylan to xylose followed by its dehydration to furfural in a "one-pot" process, very efficiently. [49]. However, the performance of this IL on a mixture of xylose and glucose has not been reported. In this chapter, our goal is to study the dehydration of C6 and C5 sugar mixtures in EMIMHSO4, and compare the results to those obtained in EMIM Cl in presence of the Lewis acid catalyst, $CrCl_2$. The principal advantage of the EMIM HSO_4 system is it does not require a separate catalyst as its anion serves as a Bronsted acid catalyst that can facilitate the hydrolysis of polysaccharides and dehydration of the resulting sugars. Recycling of the IL will be relatively easier with this latter system as no external catalyst is added to the reaction medium.

6.2 Materials and Methods

1-ethyl-3-methylimidazolium hydrogen sulphate (EMIM HSO4) was obtained from Sigma-Aldrich and was used without any additional purification, except removal of dissolved water through drying in a ROTOVAP.

In each single experiment, 50 mg xylose, 100 mg glucose and 1680 mg EMIM HSO4 were added to a 22ml vial. The vial was heated in an oil bath to the reaction temperature, and the reaction was allowed to proceed for the specified length of time under magnetic stirring of the contents. After the reaction, the vial was rapidly cooled by immersing in ice water for 15minutes to arrest the reaction. 10 ml of DI water was then added to the contents of the vial. The diluted reaction mixture was filtered by a syringe filter and analyzed by HPLC equipped with two of 87-H columns connected in series. The conversion, yield and carbon balance were calculated with respect to total measured substrate and product concentrations.

6.3 Results and discussion

6.3.1 Kinetics of the reaction

For this section, the standard experiment was run over reaction time of 0.5hr., 1 hr., 2hr., 3hr. and 4 hr.

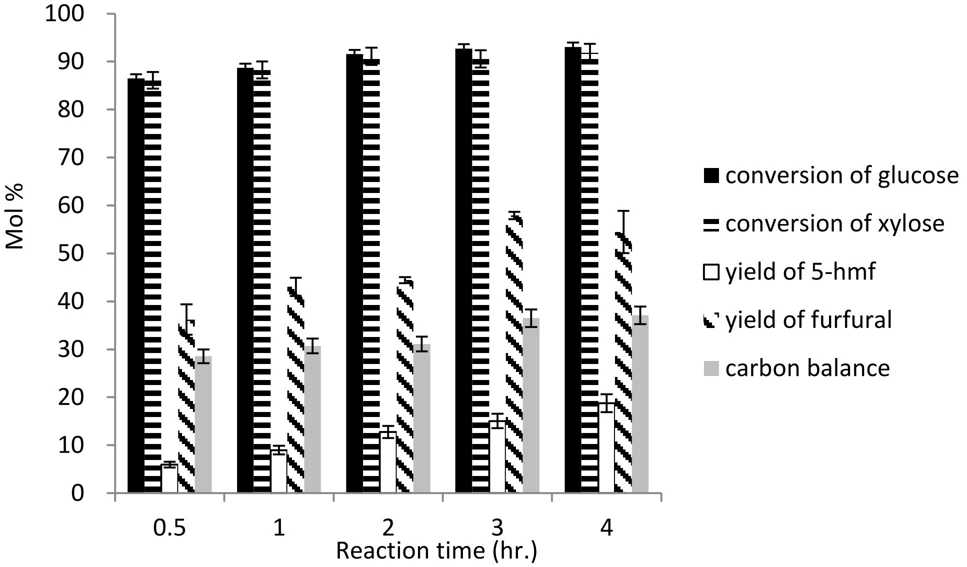
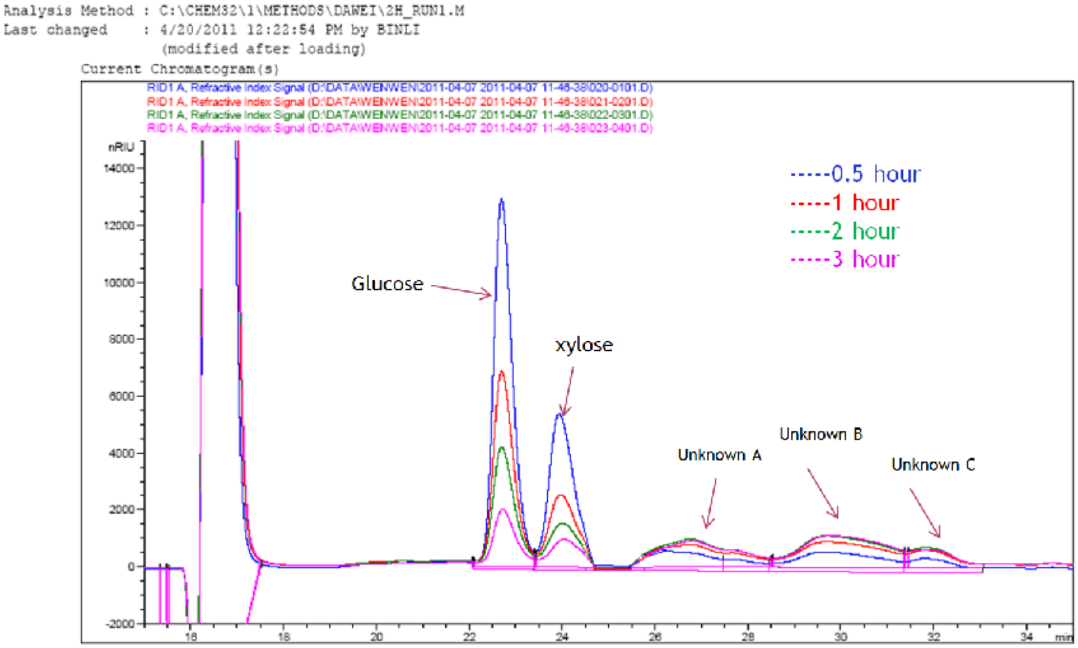


Figure 6-1: Conversion of glucose, conversion of xylose, yield of HMF, yield of furfural and total carbon balance. Experiment was carried out at the temperature of 100^0 C.

Figure 6-1 shows the conversion of glucose and xylose, yield of HMF and furfural and total carbon balance for various reaction times. Although the conversions of both he sugars was over 90%, the highest obtained yield of furfural was round 60% (at 3 hrs.) and yield of HMF was less than 20% after 4 hours of reaction time. Also the carbon balances indicate large percentages of unaccounted carbon. In our carbon balance computations only the carbon that is associated with the furans and sugars was included. Hence any carbon that forms volatile products and/or solid humins cannot be accounted for. To substantiate whether there is appreciable formation of other soluble byproducts during the dehydration reaction, HPLC chromatograms obtained for different reaction times were shown in Figure 6-2. This chromatogram reveals some unknown peaks of intermediate or by-product formed during the reaction. (The peaks for furfural and 5-HMF were not shown in the HPLC data as these compounds elute after a very long time relative to the sugar peaks). Further investigation of these unknown compounds was not carried out as the yields of 5-HMF for this system were very low and this IL medium was adjudged not viable for simultaneous conversion of glucose and xylose.



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                  (modified after loading)
          Current Chromatogram(s)
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Figure 6-2: HPLC result of xylose, glucose and some unknown compound from the reaction system.

6.4 Conclusions

Using EMIM HSO4 as a reaction medium for the dehydration of sugars is appealing as in this IL, there is no need to add any other separate catalyst. The anion of EMIM HSO4, itself, could catalyze the dehydration reactions. Though EMIM HSO_4 was suitable to achieve xylose dehydration in high yields, it gave poor results with respect to glucose dehydration. Formation of undesirable intermediates is seen and a major portion of the carbon in the reactants is diverted to these compounds. Hence, this IL medium, while promising for xylose dehydration, is adjudged not viable for simultaneous conversion of glucose and xylose.

Chapter 7

Conclusions and future work

In this work, it was demonstrated that furfural and 5-HMF synthesis from xylose and glucose mixture in an IL and metal halide media is feasible. This thesis investigated the optimal operating parameters needed for simultaneous xylose and glucose conversion to furans. The optimized reaction conditions, including catalyst and its loading, reaction temperature, extraction solvent and its loading, reaction time, were obtained for the xylose and glucose mixture dehydration process in an ionic liquid media.

Future work should be done to recycle the reaction media of IL and separate the products from other compounds. Because furan products exist in both organic phase and aqueous phase, it is important to devise suitable separation methods to isolate the products from both phases. Also reuse of IL is another essential step in the biomass conversion, if this process were to be scaled up into industrial practice.

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Appendix A

A.1Raw data in Figure 3.5

A.1Raw data in Figure 3.5

Reaction conditions for Table A1.1 and A1.2:

Loading: 50mg xylose+500mg EMIM Cl+ catalyst (20mol% of sugar)

Reaction temperature: 80ºC

Reaction time: 3.5hours

Table A.1.1 Data of calibration curves used in HPLC result progression

Concentration(g/L)	Xylose	Xylulose	Furfural
4	1810820.9	1663689.9	1936912.7
2.5	1358308.7	1240337.5	1182765.5
1.25	936122.1	850740.3	559946.4
0.5	477736	429092.3	215085.4
0.25	254885.5	225836.8	99107.2
0.125	122947.3	110956.3	50276.1
	y=425473x+215186	y=392215+189633	y=390368x-27427

Table A.1.2All experiments we ran for Figure 3.5

Catalyst	xylose	Mole of Carbon in the xylose	Mole of Carbon in consumed xylose	Conversion	xylulose	Mole of Carbon in xylulose	furfural	Mole of carbon in furfural	conversion	yield	Carbon balance
CrCl3	933867.80	0.11	0.22	66.22	208414.50	0.003	229071.00	0.07	66.22	31.01	55.27
	1004683.10	0.12	0.21	62.89	22457.30	0.000	184512.30	0.06	62.89	26.98	54.08
ZnCl2	1778394.60	0.24	0.09	26.52	39251.10	0.000	86403.10	0.03	26.52	34.36	82.59
	1622154.14	0.22	0.11	33.86	40215.20	0.000	90431.80	0.03	33.86	27.86	75.57
FeCl2	1825900.40	0.25	0.08	24.29	23762.80	0.000	73501.60	0.03	24.29	33.27	83.79
	1745341.20	0.24	0.09	28.07	26431.50	0.000	74125.70	0.03	28.07	28.96	80.06
CuCl2	617600.30	0.06	0.27	81.08	131211.50	0.000	293258.40	0.09	81.08	31.66	44.59
	648641.10	0.07	0.27	79.62	121021.70	0.000	262157.10	0.08	79.62	29.11	43.56
CrCl2	484321.10	0.04	0.29	87.35	298365.10	0.018	454647.10	0.13	87.35	44.18	56.79
	531546.10	0.05	0.28	85.13	215435.40	0.004	421642.80	0.12	85.13	42.23	52.14
C6H5-B-Cl2	382154.90	0.03	0.31	92.15	465613.20	0.047	365489.10	0.10	92.15	34.13	53.38
	346598.10	0.02	0.31	93.82	532143.10	0.058	395431.10	0.11	93.82	36.08	57.49

A.2 Raw data in Figure 3.7

Reaction conditions of data listed in this table were as followings:

Loading: 50mg xylose +500mg EMIM Cl+$CrCl_2$(20mol% of sugar)

Reaction temperature: 100ºC

Reaction time: 20min, 35min,50min,70min, 100min,

120min,150min,180min,210min,240min

Table A.2.1 Data of xylose, xylulose and furfural calibration curve

Concentration(g/L)	xylose	xylulose	Concentration(g/L)	furfural
0.125	142185.4	122184.5	0.125	51358.9
0.25	253712.5	221481.3	0.25	142122.7
0.5	473126.2	422545.5	0.5	267965.1
1.5	931116.7	842259.1	1.25	544427.2
3	1372903.4	1253964	2.5	1756776
5	1814190.1	1662291	4	2065323
	y=336964x	y=310905	6.9	3056154
	+248539	x+216515	y=458522x+109368	

Table A.2.2 Data of xylose from HPLC

Time(hr)	peak area of xylose	Mole of carbon in unreacted xylose	Mole of carbon in consumed xylose	Peak area of xylulose	Mole of carbon in xylulose	Furfural's peak area	Mole of carbon in furfural
0.0	1933359	0.33	0.00	0	0.000	0	0.000
0.3	1193430.3	0.19	0.15	634120.3	0.089	181742	0.016
0.6	957473.7	0.14	0.19	492238.1	0.059	279025.1	0.039
0.8	928825.1	0.13	0.20	466736.9	0.054	368434.5	0.059
1.2	729672.7	0.10	0.24	387416.2	0.037	409592.3	0.068
1.7	639513.3	0.08	0.26	339427.1	0.026	490693.7	0.087
2.0	616587.7	0.07	0.26	326936.5	0.024	578432.1	0.106
2.5	598900.9	0.07	0.26	328753.1	0.024	585027.4	0.108
3.0	523756.8	0.05	0.28	309721.1	0.020	611789.3	0.114
3.5	478392.3	0.05	0.29	294408.1	0.017	646921.5	0.122
4.0	438404	0.04	0.30	280406.9	0.014	627277.6	0.118

A3 Raw data of Figure 3.9

Reaction conditions of data listed in this table were as followings:

50mgxylose + 500mg EMIM Cl+$CrCl_2$(20mol% of sugar)+1500mg organic solvent

Reaction temperature: 80ºC

Reaction time: 2 hour

Xylose and xylulose data were collected in aqueous phase and analyzed by HPLC. Furfural data were collected both in aqueous and organic phase and analyzed by HPLC and GC individually. The computed furfural results were the sum of both HPLC and GC data.

Table A3.1 Raw data of calibration curve from GC results (All of the peak areas listed in this table are furfural peaks.)

Acetonitrile		Toluene		MIBK	
Concentration(g/L)	Peak area	Concentration(g/L)	Peak area	Concentration(g/L)	Peak area
14.3	1735463	10	1250711.4	2.1	246474.5
12.4	1667194	7.5	927410.3	3.4	354930.2
10.8	1268588	5	592930.8	4.2	562492.4
5	601258.6	1.25	129126.6	6.1	654246.3
2.5	289382.8	0.5	100593.4	7	794131.9
1.25	144724.3			8.5	965373.2
y=126373x-26846		y=124610x-10200		y=110428x+19186	

EA		mibk+butanol		dmso		Acetonitril+toluene	
Concentration(g/L)	Peak area	Concentration(g/L)	Peak area	Concentration(g/L)	Peak area	Concentration(g/L)	Peak area
12	1476164.3	0.8	202457.3	2	196858.6	7.1	1307667.2
9	1150401.1	1.92	313361.4	4.5	340667.9	5.68	1083416.9
6	811043.9	4.63333333	767063.4	6	546738.2	4.73333333	980650.7
3	344063.6	9.6	1474904.3	9.6	980511.1	2.36666667	419841
1.5	168029	13.9	2767557.9	12	1124262.9	1.42	273804.3
						0.8875	212622
y=126909x-13021		y=189789x-47653		y=100277x-39213		y=185570x+24651	

Table A3.2 Raw data of calibration curve used in HPLC

Concentration(g/L)	xylose	Concentration(g/L)	xylulose	Concentration(g/L)	furfural
4	1776147	4	1636741.5	5	2913265.3
3	1347255	3	1240746	3.75	2078031.6
2	916621.9	2	843913.8	2.5	1313691.1
1	464229.2	1	427486.4	1.25	652280.1
0.5	243379.8	0.5	225523.8	0.5	290291.4
0.25	129437.1	0.25	107461.4	0.25	135725.6
0.125	61861.1	0.125	54489.6	0.125	74971.8
y=441644x+19435		y=408202x+13881		y=572652x-28708	

Table A3.3 Calculation of conversion, yield and carbon balance in Figure 3.9

	xylose peak	Mole of Carbon in unreacted xylose	Mole of carbon in consumed xylose	xylulose peak	Mole of carbon in xylulose	furfural peak from HPLC	Mole of carbon in furfural from aqueous phase	furfural peak from GC	Mole of carbon in furfural from organic phase	total carbon in furfural	Conversion%	yield%	carbon balance%
1	276083.6	0.043	0.290	121297	0.019	329071	0.095	124516.2	0.024	0.119	87.22	40.90	54.20
2	303813.7	0.047	0.286	104362.8	0.016	96403.1	0.033	324562.1	0.048	0.081	85.83	28.51	43.48
3	444753.4	0.071	0.262	95791.6	0.014	83501.6	0.030	335654.1	0.056	0.085	78.81	32.52	50.98
4	330949.6	0.052	0.281	0	0.000	393258.4	0.112	122661.4	0.011	0.123	84.48	43.68	52.38
5	778525.8	0.126	0.207	543062.4	0.086	146285.8	0.046	14562.1	0.007	0.053	62.19	25.68	79.64
6	142178.1	0.020	0.313	0	0.000	405489.1	0.115	763071.6	0.069	0.185	93.89	59.03	61.49
7	276083.6	0.043	0.290	61297	0.008	337139.1	0.097	321546.2	0.038	0.136	87.22	46.69	55.78

Table A3.4 Data of all the experiments run for Figure3.9

	xylose	Mole of Carbon in the unreacted xylose	Mole of Carbon in consumed xylose	xylulose	Mole of Carbon in xylulose	furfural peak from HPLC	Mole of carbon in furfural from HPLC	furfual peak from GC	Mole of carbon in furfural from GC	Total mole of carbon in furfural	conversion(%)	yield (%)	Carbon balance
1	276083.6	0.043	0.290	121297.0	0.019	329071.00	0.10	124516.2	0.024	0.119	87.22	40.90	54.24
1’	213546.1	0.032	0.301	131564.1	0.021	284512.30	0.08	131547.3	0.025	0.108	90.33	35.91	48.45
2	303813.7	0.047	0.286	104362.8	0.016	96403.10	0.03	324562.1	0.048	0.081	85.83	28.51	43.51
2’	362154.7	0.057	0.276	117821.2	0.019	100431.80	0.03	281245.2	0.042	0.076	82.93	27.63	45.58
3	444753.4	0.071	0.262	95791.6	0.015	83501.60	0.03	335654.1	0.056	0.085	78.81	32.52	51.23
3’	421654.4	0.067	0.266	81237.5	0.012	84125.70	0.03	351245.7	0.059	0.088	79.96	33.14	50.17
4	330949.6	0.052	0.281	0.0	0.000	393258.40	0.11	122661.4	0.011	0.123	84.48	43.68	52.42
4’	384635.1	0.061	0.272	0.0	0.000	362157.10	0.10	108947.3	0.010	0.114	81.81	41.75	52.35
5	778525.8	0.126	0.207	543062.4	0.095	146285.80	0.05	14562.1	0.007	0.053	62.19	25.68	82.30
5’	746532.1	0.121	0.212	492131.1	0.086	121642.80	0.04	15012.8	0.007	0.047	63.78	21.97	76.01
6	142178.1	0.020	0.313	0.0	0.000	405489.10	0.12	563071.6	0.050	0.166	93.89	53.04	55.91
6’	196123.3	0.029	0.304	0.0	0.000	395431.10	0.11	731275.1	0.066	0.179	91.20	58.91	62.53
7	276083.6	0.043	0.290	61297.0	0.009	337139.1	0.10	321546.2	0.038	0.136	87.22	46.69	56.06
7’	246465.8	0.038	0.295	59124.2	0.008	392158.9	0.11	337814.20	0.040	0.152	88.69	51.51	59.43

A4 Raw data of Figure 3.10

Reaction conditions of data listed in this table were as followings:

Loading: 50mg xylose+ 500mg EMIM Cl+ $CrCl_2$(20mol% of sugar)+organic solvent(with mass ratio of organic solvent to IL from 2:1, 3:1, 4:1, to 5:1)

Reaction temperature: 100°C

Reaction time: 2 hours

Table A4.1 Data of calibration curve from HPLC result

Concentration(g/L)	xylose	Concentration(g/L)	xylulose	Concentration(g/L	furfural
4	1822210.1	4	1669470	4	2899224
3	1362792.4	3	1247423	3	1890430
2	923655.5	2	844620.1	2	1485401
1	472544	1	430503.5	1	628223.1
0.5	240904.9	0.5	214485.9	0.5	222880.7
0.25	127377	0.25	106697	0.25	142214.4
0.125	66518.5	0.125	54765.8	0.125	61176.5
Y=451496X+15140		Y=415691X+6760.4		Y=717252X-67224	

Table A4.2 Data of calibration curve from GC result

Concentration(g/L)	Furfural in GC result
23.4	2257706.5
19.23	1702839.4
15.5	1376775.4
12.8	916985.8
9.645	700728.4
4.8225	310927.2
Y=105707X-293526	

Table A4.3 Calculation of conversion, yield and carbon balance in Figure 3.10

Mass ratio of organic phase to IL	xylose peak	Mole of Carbon in unreacted xylose	Mole of carbon in consumed xylose	furfural peak from HPLC	Mole of carbon in furfural from aqueous phase	furfural peak from GC	Mole of carbon in furfural from organic phase	total carbon in furfural	Conversion%	yield%	carbon balance%
2:1	262636.7	0.037	0.297	243456.8	0.045	244174	0.066	0.111	89.04	37.52	44.34
3:1	98520.3	0.012	0.321	198144.8	0.039	480744.8	0.133	0.172	96.31	53.61	55.27
4:1	58605.6	0.006	0.327	101884.1	0.025	495007.2	0.182	0.207	98.07	63.38	64.03
5:1	47650.3	0.005	0.328	146285.8	0.031	389079.7	0.202	0.233	98.56	70.87	71.23

Table A4.4 All of experiments run for Figure 3.10

Mass ratio of organic phase to IL	xylose peak	Mole of Carbon in unreacted xylose	Mole of carbon in consumed xylose	furfural peak from HPLC	Mole of carbon in furfural from aqueous phase	furfural peak from GC	Mole of carbon in furfural from organic phase	total carbon in furfural	Conversion%	yield%	carbon balance %
2:1	262636.7	0.037	0.297	243457	0.045	244174	0.066	0.111	89.04	37.52	44.34
3:1	98520.3	0.012	0.321	198145	0.039	480745	0.133	0.172	96.31	53.61	55.27
4:1	58605.6	0.006	0.327	101884	0.025	495007	0.182	0.207	98.07	63.38	64.03
5:1	47650.3	0.005	0.328	146286	0.031	389080	0.202	0.233	98.56	70.87	71.23
2:1	301547.1	0.042	0.291	201534	0.039	304562	0.074	0.113	87.31	38.73	46.46
3:1	122487.9	0.016	0.317	175133	0.035	423230	0.124	0.159	95.24	50.03	52.36
4:1	64771.3	0.007	0.326	93255.6	0.023	481218	0.179	0.203	97.80	62.19	62.97
5:1	44124.9	0.004	0.329	124774	0.028	370005	0.196	0.224	98.72	68.10	68.45

A5 Raw data of Figure 3.11

Reaction conditions of data listed in this section were as following:

Loading: 50mg xylose+500mg EMIM Cl+$CrCl_2$ (20mol% of sugar)+ 1500mg organic solvent

Reaction temperature: 80^{O}C, 90^{O}C,100^{O}C,110^{O}C,120^{O}C

Reaction time: 2 hours

Table A5.1 Raw data of furfural calibration curve used in Figure3.11

This curve is computed from the solution of furfural dissolved in MIBK and 1-butanol mixture. Concentration is defined as mass of furfural divided by the volume of MIBK and1-butanol mixture solvent. Results were collected from GC.

Concentration(g/L)	furfural peak area
2.1	246474.5
3.4	354930.2
4.2	562492.4
5.2	587259.4
6.1	654246.3
6.9	685288.5
7	794131.9
8.5	965373.2
y=105907x+31728	

Table A5.2 Raw data of xylose, xylulose and furfural calibration curve

Concentration(g/L)	xylose	Concentration(g/L)	xylulose	furfural
0.5	91220.2	0.50	80657.9	150110.4
1	302314.1	1.00	256104.6	360537.4
1.27	570540.8	1.28	481155.8	499819.7
2.5	984355.1	2.50	829274.7	952475.1
3.29	1307459	3.30	1102146	1108870.5
5	1726813	5.00	1446942	1732655.6
y=364482x+5841.7		y=324448x+9387.1		y=34316x+24374

Table A5.3 Calculation of conversion, yield and carbon balance in Figure 3.11

Temperature (°C)	xylose peak	Mole of Carbon in unreacted xylose	Mole of carbon in consumed xylose	furfural peak from HPLC	Mole of carbon in furfural from aqueous phase	furfural peak from GC	Mole of carbon in furfural from organic phase	total carbon in furfural	Conversion%	yield%	carbon balance %
80	889871	0.015	0.318	103023.2	0.022	268965.5	0.130	0.152	95.42	47.90	50.24
90	553699	0.009	0.324	118429.3	0.027	282280.2	0.137	0.164	97.16	50.59	51.94
100	228633	0.004	0.329	98313.6	0.021	302875.3	0.148	0.169	98.85	51.31	51.82
110	22896	0.000	0.333	163394.4	0.040	327981.7	0.161	0.201	99.91	60.34	60.32
120	28380	0.000	0.333	125133.9	0.029	307444	0.150	0.179	99.88	53.80	53.81

Table A5.4 All experiments run for Figure 3.11

Temperature (°C)	xylose peak	Mole of Carbon in unreacted xylose	Mole of carbon in consumed xylose	furfural peak from HPLC	Mole of carbon in furfural from aqueous phase	furfural peak from GC	Mole of carbon in furfural from organic phase	total carbon in furfural	Conversion%	yield%	carbon balance %
80	889871	0.015	0.318	103023.2	0.022	268965.5	0.130	0.152	95.42	47.90	50.24
90	553699	0.009	0.324	118429.3	0.027	282280.2	0.137	0.164	97.16	50.59	51.94
100	228633	0.004	0.329	98313.6	0.021	302875.3	0.148	0.169	98.85	51.31	51.82
110	22896	0.000	0.333	163394.4	0.040	327981.7	0.161	0.201	99.91	60.34	60.32
120	28380	0.000	0.333	125133.9	0.029	307444	0.150	0.179	99.88	53.80	53.81
80	851114	0.015	0.318	110074	0.024	277004	0.134	0.159	95.63	49.78	51.93
90	412546	0.007	0.326	107598.1	0.024	303229.9	0.148	0.172	97.90	52.67	53.62
100	194648	0.003	0.330	89774.2	0.019	331217.5	0.163	0.182	99.02	55.04	55.43
110	19454	0.000	0.333	149982.1	0.036	329004.6	0.162	0.198	99.93	59.34	59.32
120	22025	0.000	0.333	114687	0.026	301354.2	0.147	0.173	99.92	51.92	51.91

A6 Raw data of Figure 3.8 and Figure 3.12

Table A6.1Raw data of calibration curve used for HPLC data progression

Concentration(g/L)	xylose	Concentration(g/L)	xylulose	Concentration(g/L)	furfural
4	2330961	4	2180243	6	3238286
3.2	1873126	3.2	1751202	4.8	2609698
2	1172289	2	1103478	3	1615649
1.3	792294.9	1.3	758837.1	2	1086931
0.8	471547.5	0.8	456889.9	1.2	656544.4
0.4	246450	0.4	239911.3	0.6	328683.5
0.2	128033.4	0.2	132879.6	0.3	173849.2
y=580284x+12853		y=538602x+28018		y=539307x+8005.7	

Table A6.2 Raw data of calibration curve used for GC data progression

Concentration(g/L)	furfural
8	2060583
5.3	1378521
1.6	1135251
2	550781
1.6	365459.5
0.8	190298.1
y=230951x+204824	

Table A6.3Raw data of Figure 3.8 and Figure 3.12

Time(hr)	xylose peak	Mole of Carbon in unreacted xylose	Mole of carbon in consumed xylose	furfural peak from HPLC	Mole of carbon in furfural from aqueous phase	furfural peak from GC	Mole of carbon in furfural from organic phase	total carbon in furfural	Conversion%	yield%	carbon balance%
0.0									0.00	0.00	100.00
0.3	858457	0.097	0.236	150447.1	0.027	544744.2	0.025	0.053	70.86	22.37	44.95
0.6	562432.1	0.063	0.270	251878.9	0.047	614181.1	0.030	0.078	81.06	28.72	42.18
0.8	488607.8	0.055	0.278	287203.6	0.054	707773.8	0.037	0.091	83.60	32.79	43.77
1.2	215107.1	0.023	0.310	343172.6	0.065	1200661.0	0.074	0.139	93.03	44.79	48.60
1.7	239731.6	0.026	0.307	411608.9	0.078	1378278.0	0.087	0.165	92.18	53.81	57.37
2.0	102145.5	0.010	0.323	483064.1	0.092	1563732.0	0.101	0.193	96.92	59.72	60.91
2.5	27677.9	0.002	0.331	511668.7	0.097	1663909.0	0.109	0.206	99.49	62.10	62.24
3.0	15113.1	0.000	0.333	516319.1	0.098	1647447.0	0.107	0.205	99.92	61.73	61.71
3.5	17512.9	0.001	0.333	534891.9	0.102	1646336.0	0.107	0.209	99.84	62.83	62.84
4.0	0	0.000	0.333	545723.2	0.104	1648494.0	0.107	0.211	100.00	63.41	63.35

Table A7 Raw data for Figure4.1 and Figure 4.2

Concentration(g/L)	glucose	5-hmf
0.25	116727	158063.2
0.5	230374.2	317005.7
1	469000.5	630524.3
1.67	760634.3	1048879.7
2.5	1158872.7	1580542.9
4	1820306.3	2514666.3
5	2295476.7	3137735
y=457082x+4533.5		y=627619x+3334.1

A8 Raw data for Figure 4.4

Reaction conditions of data listed in this section were as followings:

Loading: 60mg glucose+500mg EMIM Cl+ $CrCl_2$ (20mol% of sugar)

Reaction temperature: 80^{O}C, 90^{O}C, 100^{O}C, 110^{O}C, 120^{O}C

Reaction time: 3.5hours

Table A8.1 Data of calibration curve used in HPLC data progression

Concentration(g/L)	glucose	5-hmf
0.25	116727	158063.2
0.5	230374.2	317005.7
1	469000.5	630524.3
1.67	760634.3	1048879.7
2.5	1158872.7	1580542.9
4	1820306.3	2514666.3
5	2295476.7	3137735
y=457082x+4533.5		y=627619x+3334.1

Table A8.2 All of the experiments run for Figure 4.4

Temperature(℃)	glucose peak area	mole of carbon in unreacted glucose	mole of carbon in consumed glucose	5-hmf peak area	Mole of carbon in 5-hmf	conversion(%)	yield(%)	carbon balance(%)
80	294995.9	0.035	0.298	1155738.4	0.146	89.41	48.90	54.30
90	61702.7	0.007	0.326	1467011.9	0.185	97.92	56.71	57.60
100	52770.6	0.006	0.327	1645134.3	0.207	98.24	63.40	64.03
110	48553.9	0.005	0.328	1649679.9	0.208	98.39	63.48	64.05
120	37918.4	0.004	0.329	1700744.5	0.214	98.78	65.19	65.60
80	116901.9	0.049	0.284	1580681.9	0.147	85.14	51.81	58.94
90	50768.0	0.021	0.312	1869249.9	0.174	93.78	55.58	58.32
100	19647.5	0.007	0.326	2043259.4	0.190	97.84	58.21	59.09
110	16825.9	0.006	0.327	2147781.2	0.199	98.21	60.95	61.62
120	3334.1	0.000	0.333	2434651.2	0.226	99.97	67.85	67.83

A9 Raw data for Figure 4.5

Reaction conditions of data listed in the section were as followings:

Loading: Exp. 1&1’ 60mg glucose+500mg EMIM Cl +CrCl2 (20mol% of sugar)

Exp. 2&2’ 60mg glucose+500mg EMIM Cl+ CrCl2 (20mol% of sugar)+1500mg organic solvent

Reaction temperature: 100^{O}C

Reaction time: 2hours

Table A9.1 Raw data of calibration curve used in HPLC data progression

Concentration(g/L)	glucose	5-hmf
5	2330960.5	3238286.3
4	1873126	2609698.3
2.5	1172288.6	1615649.4
1.67	792294.9	1086931.4
1	471547.5	656544.4
0.5	246450	328683.5
0.25	128033.4	173849.2
y=464265x+12552		y=647220+7588.9

Table A9.2 Raw data of calibration curve used in GC data progression

Concentration(g/L)	5-hmf
4.7	2060582.6
3.1	1378521.2
2.35	1135250.6
1.2	550781
0.8	365459.5
0.47	190298.1
y=440695x+19887	

Table A9.3 All the experiments ran for Figure 4.5

	glucose peak area	mole of carbon in unreacted glucose	mole of carbon in consumed glucose	5-hmf peak from HPLC data	mole of carbon from 5-hmf in aqueous phase	5-hmf peak from GC data	mole of carbon in 5-hmf from aqueous phase	total mole of carbon in 5-hmf	conversion (%)	yield(%)	carbon balance (%)
1	82056.2	0.008	0.325	1620996.4	0.198	0	0.000	0.198	97.50	60.86	61.84
1’	16226.2	0.000	0.333	1696508.2	0.207	0	0.000	0.207	99.87	62.20	62.25
2	44832.2	0.004	0.329	500571.2	0.060	4836498.1	0.143	0.203	98.84	61.78	62.22
2’	22325.9	0.001	0.332	511012.1	0.062	4819243.2	0.142	0.204	99.65	61.51	61.65

A10 Raw data of Figure 5.2

Reaction conditions of data listed below were as followings:

Loading: 50mg xylose+100mg glucose+ 1500mgIL+$CrCl_2$(20mol% of sugars)+4500ml organic solvent

Reaction temperature: 100°C, 105°C, 110°C

Reaction time: 2hours

Table A10.1 Raw data of calibration curve used in HPLC data progression

Concentration(g/L)	glucose	Concentration(g/L)	5-hmf	Concentration(g/L)	xylose	Concentration(g/L)	xylulose	Concentration(g/L)	furfural
0.2475	116822.5	0.248	165339.2	0.2	107391.8	0.2	91162	0.28	102863.6
0.495	232860.3	0.496	312048.7	0.4	217060.6	0.4	184054.6	0.56	231366
0.99	450731.8	0.992	585466.4	0.8	522130.1	0.8	440325.2	1.12	416882.3
2.475	1120754	2.48	1394792.9	1.333333	805598.2	1.333333	678937.7	3.733333	1451762
3.3	1515241	3.306667	1860544	2.666667	1464867	2.666667	1240751	4.48	1563735
4.95	2232670	4.96	2778010.5	4	2202094	4	1864133	5.6	2316320
Y=451359X+7712		Y=552884X+32456		y=543663x+34785		y=460413x+28581		y=392621x-18335	

Table A10.2Raw data of calibration curve used in GC data progression

Concentration(g/L)	HMF	Concentration(g/L)	furfural
8.6	1259717	7	1364977
5.733333	936735.2	4.666667	1023101
4.3	612573.9	3.5	675323.3
2.866667	465486.7	2.333333	450863
1.72	266796.6	1.4	269924.3
0.86	158164.6	0.7	165568.8
y=145836x+31290		y=198405x+10171	

Table A10.3 ALL of the experiments for Figure 5.2

				HPLC data				
Temperature(℃)	glucose peak area	mole of carbon in consumed glucose	xylose peak area	mole of carbon in consumed xylose	furfural peak area	mole of carbon in furfural from aqueous phase	5-hmf peak area	mole of carbon in 5-hmf from aqueous phase
100	236009.7	0.52708	138898.2	0.321	184457.4	0.054	1293113	0.181
105	61112.8	0.548588	64436	0.330	193005.4	0.056	1501726	0.211
110	77794.6	0.546536	148655.8	0.319	233352.4	0.067	1702636	0.240
100	194687.8	0.532161	55967.9	0.331	203866.5	0.059	1020197	0.142
105	54770.4	0.549368	113628.9	0.324	217524.9	0.063	1256449	0.176
110	59196.5	0.548823	9361.6	0.336	207416.5	0.060	1438491	0.202

	GC data										
Temperature(^{O}C)	furfural peak area	mole of carbon in furfural from organic phase	5-hmf peak area	mole of carbon in 5-hmf from organic phase	total mole of carbon in furfrual	total mole of carbon in HMF	conversion of xylose	conversion of glucose	yield pf furfural	yield of HMF	carbon balance
100	1504509	0.129	162053.5	0.154	0.183	0.335	96.26	94.94	57.12	63.51	62.88
105	1783808.7	0.154	167044.8	0.160	0.210	0.371	99.00	98.82	63.56	67.54	66.44
110	1429533.1	0.123	169608.5	0.163	0.190	0.402	95.90	98.45	59.36	73.62	69.17
100	1488303.3	0.128	208898.7	0.209	0.187	0.351	99.31	95.86	56.49	65.91	63.39
105	1640670.6	0.141	210363.2	0.211	0.204	0.386	97.19	98.96	62.92	70.33	68.15
110	1599978.1	0.138	201265.2	0.200	0.197	0.402	101.02	98.86	58.69	73.20	67.81

A11 Raw data of Figure 5.3

Reaction conditions of data listed in this section were as followings:

Loading: 50mg xylose+100mg glucose+ 1500 mg EMIM Cl+CrCl2(20mol% of sugar) +4500 organic solvent

Reaction temperature: 105^{O}C

Reaction time: 0.5hr, 0.75hr, 1hr,,1.5hr,2hr,2.5hr

Table A11.1 Calibration curve used in HPLC data progression

Concentration(g/L)	glucose	Concentration(g/L)	HMF	Concentration(g/L)	xylose	Concentration(g/L)	furfual
0.3	152078.1	0.2345	145689.2	0.25	122424	0.25	179315.8
0.6	294256.4	0.469	273691.8	0.5	228945	0.5	280070.5
2.1	936196.8	1.563333	855818.7	1	441987	1	481580
3.2	1398625	2.345	1288572	2.5	1081113	2	884599
4.2	1865539	3.126667	1700758	3	1294155	3	1287618
6.4	2790271	4.69	2546401	5	2146323	5	2093656
y=436445x+13519		y=538710x+19263		y=426084x+15903		y=403019x+78561	

Table A11.2 Calibration curve used in GC data progression

Concentration(g/L)	furfural	Concentration(g/L)	5-hmf
0.5	62297.3	0.5	56042.7
1.2	129704.9	1.2	113053.5
2	219579.7	2	188746.7
3	330135.8	3	280074.2
4	441625.5	4	348164.5
6	666146.5	5	556064
y=110449x+831.1		y=89970x+6608.5	

Table A11.3 All of the experiments ran for Figure 5.3

	HPLC							
Reaction time(hr)	glucose	mole of carbon in unreacted glucose	xylose	mole of carbon in unreacted xylose	5-hmf	Mole of carbon in 5-hmf from aqueous phase	furfural	mole of carbon in furfural from aqueous phase
0.5	380229	0.047	192492.6	0.028	889923.8	0.128	95515.1	0.004
0.75	355950.2	0.044	153445.7	0.022	999462.6	0.144	127218.2	0.013
1	93548.1	0.010	43967.2	0.004	1008109	0.146	182928.3	0.027
1.5	27162.5	0.002	40473.5	0.004	1095596	0.158	199828.4	0.031
2	27354.3	0.002	38826.5	0.004	1123576	0.163	219287.1	0.036
2.5	24743.3	0.001	39561.7	0.004	1095901	0.158	211878.2	0.034
0.5	206546	0.032	132452	0.031	805622.1	0.116	102431.2	0.005
0.75	155712	0.023	90798.6	0.019	1000462	0.144	117643.5	0.008
1	89456	0.013	63967.5	0.011	1001189	0.145	193346.2	0.024
1.5	77013	0.010	59172.4	0.010	1177532	0.170	201755.1	0.025
2	60121	0.008	48001.2	0.007	1282934	0.186	229798.4	0.031
2.5	54438	0.007	29447	0.001	1270920	0.184	215634.2	0.028

Continue

GC										
5-hmf peak from GC	mole of carbon in 5-hmf from organic phase	furfural peak area	mole of carbon in furfural from organic phase	total mole of carbon in 5-hmf	total mole of carbon in furfural	conversion of glucose	conversion of xylose	yield of HMF	yield of furfural	carbon balance
701711.2	0.101	625308.1	0.097	0.229	0.101	91.60	91.71	45.08	33.22	45.59
759869.7	0.110	763896	0.119	0.254	0.131	92.15	93.54	49.61	42.12	50.67
976185.4	0.141	853937	0.133	0.287	0.160	98.17	98.68	52.58	48.56	51.87
1127466	0.163	893814	0.139	0.321	0.170	99.69	98.85	58.08	51.69	55.98
1299376	0.188	995099.6	0.155	0.351	0.191	99.68	98.92	63.35	57.95	61.57
1251240	0.181	933045.1	0.145	0.339	0.179	99.74	98.89	61.31	54.46	58.99
695462.1	0.100	605301.2	0.094	0.216	0.099	94.26	90.57	41.26	32.79	42.57
742135.9	0.107	735466.2	0.114	0.251	0.122	95.77	94.26	47.28	38.96	46.87
1043379	0.151	903291.2	0.140	0.295	0.164	97.74	96.63	54.42	50.98	54.39
1265482	0.183	916546.7	0.142	0.354	0.168	98.11	97.06	64.91	51.93	60.99
1300002	0.188	1024399	0.159	0.374	0.190	98.61	98.05	68.33	58.32	65.16
1280488	0.185	992134.1	0.154	0.369	0.182	98.78	99.69	67.38	54.97	63.02

A12 Raw data for Figure 6.1

Reaction conditions of the data listed in this table were as followings:

Loading: 100mg glucose+ 50mg xylose+ 1680mg EMIM HSO4

Reaction temperature: 100^{O}C

Reaction time:0.5hour, 1hour,2hour, 3hour, 4hour

Table A12.1 Calibration curve used in HPLC data progression

concentration(g/L)	xylose	concentration(g/L)	furfural	concentration(g/L)	glucose	concentration(g/L)	5-hmf
0.22	116594.6	0.258	180022.2	0.318	181245.5	0.2345	193040.1
0.44	218804.8	0.516	335425	0.636	302185.7	0.469	280659.7
1.466667	642499.6	1.72	890540.7	2.12	929025.2	1.563333	854359.6
2.2	931160.9	2.58	1335722.9	3.18	1394512	2.345	1296818
2.933333	1231456	3.44	1874633.3	4.24	1843373	3.126667	1689362
4.4	2030548	5.16	2571717.3	6.36	1894233	4.69	1820226
y=447461x-7721.5		y=494940x+70043		y=425629x+36759		y=524917x+50434	

Table A12.2 All of the experiments ran for Figure 6.1

Reaction time(hr)	glucose	mole of carbon in the unreacted glucose	xylose	mole of carbon in the unreacted xylose	5-hmf	mole of carbon in 5-hmf	furfrual	mole of carbon in furfural	conversion of glucose	conversion of xylose	yield of 5-hmf	yield of furfural	carbon balance
0.5	623354.7	0.077	293693	0.045	234431.8	0.028	523278	0.095	86.23	86.54	5.80	33.04	27.50
1	523570.6	0.063	260661	0.040	337974.8	0.043	644048.3	0.121	88.57	88.01	8.83	41.14	30.10
2	394430.1	0.047	193876.2	0.030	472080.4	0.064	701470.1	0.133	91.60	91.00	12.52	43.78	30.73
3	356420.2	0.042	203354.9	0.031	567746.8	0.078	890247.9	0.172	92.50	90.57	15.21	57.13	36.42
4	347212.8	0.040	162566.8	0.025	701215.9	0.098	803329.4	0.154	92.71	92.40	19.09	50.07	35.81
0.5	600013.9	0.073	314592.1	0.048	245942.3	0.030	604471	0.112	86.78	85.61	6.13	39.38	29.63
1	514988.1	0.062	250779.2	0.038	347797.6	0.045	700023	0.132	88.77	88.46	9.11	44.93	31.30
2	400012.5	0.047	189766.4	0.029	488296.3	0.066	721388	0.137	91.47	91.18	13.02	45.07	31.49
3	341161.2	0.040	203434.9	0.031	557863.2	0.077	912435.2	0.177	92.85	90.57	14.86	58.68	36.56
4	322157.3	0.037	187242.2	0.029	682877.4	0.096	921653.3	0.179	93.30	91.29	18.43	58.85	38.35