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**COMPARATIVE KINETIC ANALYSIS OF FURFURAL PRODUCTION FROM  
XYLAN AND XYLOSE**

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*by*

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## Declaration

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## Abstract

Furfural is a valuable platform chemical with a wide range of industrial applications. The replacement of petrochemicals with alternative bio furfural will reduce the overall carbon footprint of crude oil based products. The current industrial furfural production method is a direct catalyzed conversion of lignocellulosic biomass in a continuous or batch reactor system. The mechanism of the reaction is primarily a two-step reaction process comprising xylan hydrolysis and xylose dehydration along with the simultaneous conversion of other components of the lignocellulose biomass material. Examining the kinetics of furfural production using xylan and xylose as starting material will provide insights and fundamental knowledge on the furfural production reaction with little effect of the inhibitory components present in whole lignocellulose biomass.

This study focuses on the kinetics of furfural formation from xylan and xylose at temperature ranges of 140 °C-170 °C, H<sub>2</sub>SO<sub>4</sub> concentration of 0.5wt%-2wt % and solids loading of 4-14wt %. The solids loading for xylan experiments were determined by standardizing the xylan reaction against the xylose reaction considering only the xylose composition of xylan (xylose-equivalent). The range of conditions were selected with reference to literature to obtain data that were relevant to industrial processes. Statistical analysis of the results showed that temperature and acid concentrations demonstrated significant effect on the reaction. However, it was found that the effect of solids loading on the reaction was insignificant.

Based on the results, it was determined that the xylan conversion process is described by a kinetic model consisting of a two-step first order reaction, whereas the conversion process for xylose consisted of a single step first order reaction model. The main difference in the models was found to be the xylan hydrolysis step that precedes xylose dehydration in the xylan conversion reaction. This hydrolysis step was found to be fast compared to the xylose dehydration resulting in xylose accumulation within 5minutes of the reaction. The dehydration reaction (in xylan conversion process) was found to be the rate determining step of the reaction relative to the fast hydrolysis step with 98kJ/mol and 55 kJ/mol activation energies, respectively. The xylose dehydration in both xylose and xylan conversion process can be described by a first order single step reaction without any side product formation and degradation reaction. Consequently, it was determined from the models that xylose condensation degradation reactions were negligible in the range of condition investigated in this study. The activation energies of xylose dehydration step for xylan and xylose feed were

98kJ/mol and 95kJ/mol, respectively. Comparing the xylan and xylose conversion to furfural processes, it was determined that the xylan conversion process was generally faster despite the two steps process. Finally, higher furfural yields were observed for xylan compared to xylose at all conditions investigated in this study.

## Abstrak

Furfuraal is 'n waardevolle platform chemikalie met 'n wye bestek van industriële toepassings. Die vervanging van petrochemikalieë met alternatiewe biofurfuraal sal die algehele koolstofspoor van produkte gebaseer op ru-olie, laat afneem. Die huidige industriële furfuraalproduksiemetode is 'n direkte gekataliseerde omsetting van lignosellulosiese biomassa in 'n kontinue of lotreaktor stelsel. Die meganisme van die reaksie is primêr 'n twee-stap reaksie proses wat bestaan uit xilaan hidrolise en xilose dehidrasie saam met die gelyktydige omsetting van ander komponente van die lignosellulose biomassa materiaal. Deur die kinetika van furfuraalproduksie te ondersoek deur xilaan en xilose te gebruik as begin materiaal, sal insig en fundamentele kennis verskaf oor furfuraalproduksie met min effekte van die inhiberende komponente teenwoordig in heel lignosellulose biomassa.

Hierdie studie fokus op die kinetika van furfuraal formasie van xilaan en xilose by 'n temperatuurbestek van 140–170 °C, H<sub>2</sub>SO<sub>4</sub>-konsentrasie van 0.5–2 wt.% en vastestoflading van 4–14 wt.%. Die vastestoflading vir xilaan eksperimente is vasgestel deur die standaardisering van xilaan reaksie teen xilose reaksie met in agneming van die xilose komposisie van xilaan (xilose-ekwivalent). Die bestek van toestande is gekies met verwysing na literatuur om data te verkry wat relevant is tot industriële prosesse. Die data verkry is verder gepas tot kinetiese modelle voorheen voorgestel in literatuur om vas te stel watter model elke omsettingsproses die beste beskryf. Statistiese analise van die resultate het gewys dat temperatuur en suurkonsentrasies 'n beduidende effek op die reaksie het. Dit is egter gevind dat die effek van vastestoflading op die reaksie onbeduidend was.

Gebaseer op hierdie resultate is dit vasgestel dat 'n kinetiese model wat uit 'n twee-stap eerste orde-reaksie bestaan (xilaan hidrolise en xilose dehidrasie) die xilaan omsettingsproses kan beskryf, waar die omsettingsproses vir xilose uit 'n enkel stap eerste orde-reaksie (xilose dehidrasie) model bestaan. Dis gevind dat die hoof verskil tussen die modelle die xilaan hidrolise stap is, wat die xilose dehidrasie stap voorgaan in die xilaan omsettingreaksie. Hierdie hidrolise-stap is bevind om vinniger te wees in vergelyking met die xilose dehidrasie wat xilose akkumulase binne vyf minute van die reaksie tot gevolg het. Die dehidrasie reaksie (in xilaan omsettingsproses) is bevind om die tempo-bepalende stap van die reaksie te wees relatief tot die vinnige hidrolise stap met 98 kJ/mol en 55 kJ/mol aktiveringsenergieë, onderskeidelik. Die xilose dehidrasie in beide xilose en xilaan omsettingsprosesse kan beskryf word deur 'n eerste orde enkel stap reaksie sonder enige newe- en afbrekingprodukt formasie. Gevolglik is dit vasgestel uit die modelle dat xilose kondensasie

afbrekingsreaksies weglaatbaar in die bestek van toestande ondersoek in hierdie studie is. Die aktiveringsenergieë van die xilose dehidrasie stap vir xilaan en xilose voer was 98 kJ/mol en 95 kJ/mol, onderskeidelik. Deur die xilaan en xilose omsetting met furfuraal prosesse te vergelyk, is dit vasgestel dat die xilaan omsettingsproses oor die algemeen vinniger was ten spyte van die twee-stap proses. Ten slotte, hoër furfuraalopbrengste is waargeneem vir xilaan in vergelyking met xilose by al die toestande in hierdie studie.

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## Nomenclature and Abbreviations

Bmim	1-Butyl-3 methylimidazolium
BRD	Batch reactive distillation
C5	Five carbon sugar
CPME	Cyclopentyl methyl ether
DC	Decomposition products
DMSO	Dimethyl sulfoxide
GVL	Gamma-valerolactone
HPLC	High performance liquid chromatography
HTLW	High temperature liquid water
MIBK	Methyl isobutyl ketone
RI	Refractive index
SLR	Solid liquid ratio
THF	Tetrahydrofuran
UV	Ultra violet

# Chapter 1

## Introduction

### 1.1. Background

Petrochemicals are an important component of our daily lives. However, due to diminishing crude oil and the overall carbon footprint of crude oil related activities, bio-alternatives to crude oil and its derivatives received increasing attention recently (Fatih Demirbas 2009). With the increased awareness of the energy crisis, recent studies have typically focused on systems that have sustainable operations with environmentally friendly alternatives to crude oil (Bozell & Petersen 2010; Geraili et al. 2014; Farzad et al. 2017). This search for alternative energy and chemical sources has culminated in the exploration and utilization of biomass as a substitute to fossil fuels (Mariscal & Ojeda 2016).

Lignocellulose biomass is a plant biomass mainly made up of cellulose, hemicellulose and lignin. The composition of each varies with respect to the source plant. Generally, hardwoods have more carbohydrates content than lignin, whereas the softwoods have more lignin compared to hardwoods. The average proportions of hemicellulose in hardwoods and softwoods are 35% and 28%, respectively (Fatih Demirbas 2009). Several biofuels and valuable chemicals such as furfural can be derived from the hemicellulosic component of lignocellulose biomass. The purpose of utilization determines the substrate selection, which makes pentose rich hardwoods favorable for furfural production (Cai et al. 2013).

Furfural is a platform chemical derived from the xylan rich hemicelluloses of hardwood and grasses. Furfural is produced commercially by direct conversion of whole lignocellulose material in a batch or continuous reactor (Cai et al. 2013). Corncob and sugar cane bagasse are the biomass materials most frequently used in industrial furfural production due to their relative high xylan composition. The xylan content of corn cob is estimated to be 37 wt.% (Eken-Saraçoğlu et al. 1998) and 22.4% in sugarcane bagasse (Girisuta et al. 2013).

The typical traditional process of furfural production utilizes whole lignocellulose biomass with mineral acid catalyst such as sulfuric acid within a temperature range of 158 °C -280°C (Cai et al. 2013; Zeitsch 2001). This method is referred to as the *direct method* of production.

However, furfural can also be produced via an *indirect method* that utilizes pretreated lignocellulose material to isolate a xylose-rich hemicellulose hydrolysate, containing xylan, xylose and oligomers. This hydrolysate is subsequently converted to furfural in a separate processing step (Mandalika & Runge 2012). Whereas the direct method is applied in industry (Cai et al. 2013), the indirect method has been proven to result in improved yields, due to the absence of inhibiting components present in the whole lignocellulose biomass (Mandalika & Runge 2012). Recent studies regarding improvements of furfural production have received attention primarily due to the extensive utilization potential of furfural (Luo et al. 2018).

Furfural is used as a solvent or as an additive for fuels and lubricating oils. It is also converted into precursor chemicals such as furfuryl alcohol and tetrahydrofuran (THF) to produce plastics, polyamides, resins and pharmaceuticals (Neill et al. 2009; Weingarten et al. 2010; Abad et al. 1997). Over the years, several authors have studied the process of furfural production to improve it (Oefner et al. 1992; Antal et al. 1991; Peleteiro et al. 2015; Le Guenic et al. 2016; Zhang et al. 2017). Key areas that have been investigated include yield improvement (Weingarten et al. 2010; Zhang et al. 2014), equipment and technology evolution (Yemiş & Mazza 2011; Weingarten et al. 2010; Zhang et al. 2010; Mandalika & Runge 2012), catalyst analysis (Yemiş & Mazza 2011; Zhang et al. 2010; Peleteiro et al. 2015; Zhang et al. 2017) and kinetics and mechanistic analysis (Danon et al. 2014; Antal et al. 1991).

The first industrial process of furfural formation was in the 1920's via the direct method (Mandalika & Runge 2012; Cai et al. 2013). Since then, different authors have investigated the mechanism and kinetics of furfural formation (Eken-Saraçoğlu et al. 1998; Dussan et al. 2013; Lavarack et al. 2002; Danon, Marcotullio, et al. 2014; Byul et al. 2011). These studies have been conducted with different feedstock (Chiang et al. 2008; Qi & Xiuyang 2007; Liu et al. 2014; Yang et al. 2006), catalyst (Lavarack et al. 2002; Ahola & Tanskanen 2012; Danon, Hongsiri, et al. 2014), solvents (Peleteiro et al. 2016; Zhang et al. 2014) and temperature ranges (Cai et al. 2013). The conversion processes have also been studied using the major compounds in the reaction process such as xylan and xylose (Yemiş & Mazza 2011; Yang et al. 2005). The use of different reaction feedstock and conditions of reaction have resulted in varying reaction mechanisms and kinetics models (Eken-Saraçoğlu et al. 1998; Garrote et al. 2001; Byul et al. 2011; Danon, Marcotullio, et al. 2014).



The kinetics of furfural formation from whole lignocellulose biomass is generally described as a simple two step reaction of xylan hydrolysis and xylose dehydration (Zeitsch 2001). Over the years, different models have been proposed. Lavarack et al.(2002) studied the kinetics of furfural formation from corncob and sugar cane and determined that the above simple two step reaction provided the best fit for the reaction. However, other authors have considered the existence of two reaction paths (fast and slow steps) for the first hydrolysis step (Eken-Saraçoğlu et al. 1998; Borrega et al. 2011). This model proposed in literature has however not been agreed upon entirely. Whereas, some reports have confirmed this reaction scheme (Borrega et al. 2011), others have suggested it is unnecessary and has no effect on the reaction process (Lavarack et al. 2002). Besides the two- steps hydrolysis reaction, the presence of reaction intermediates and by-products have also not had consensus agreements. Garrote et al. (2001) studied the kinetics of furfural formation and proposed a model that includes xylooligomers and the effect on the reaction. Other models proposed in literature have determined that xylooligomers are only relevant in non-catalyzed high temperature liquid water (HTLW) and weak acid catalyzed reactions below 130°C (Morinelly et al. 2009; Lau et al. 2014). Despite the studies conducted on the kinetics of lignocellulose biomass to furfural, recent studies have not conclusively arrived at a single mechanism or a model to describe the reaction. This is a consequence of different lignocellulose feed materials, catalyst, experimental conditions and the interactions of these factors of reaction with each other (Eken-Saraçoğlu et al. 1998).

Xylan hydrolysis and xylose dehydration are consecutive reactions leading up to furfural production, although the kinetics of xylan conversion to furfural has not been reported extensively in literature. The proposed reaction path suggested by Zeitsch (2001) closely mimics the conversion reaction of whole lignocellulose biomass (Lavarack et al. 2002). Monomeric xylose conversion reactions on the other hand have been studied extensively (Danon, Marcotullio, et al. 2014; Byul et al. 2011; Oefner et al. 1992). The conversion has been studied in non-catalyzed high temperature liquid water reactions (Qi & Xiuyang 2007; Aida et al. 2010; Byul et al. 2011) and in catalyzed mediums (Oefner et al. 1992; Dias et al. 2005; Ahola & Tanskanen 2012). Different catalyst including mineral acids (Hongsiri et al. 2014; Danon et al. 2014), organic acids (Ahola & Tanskanen 2012) and recently the use of solid catalyst and heterogeneous catalyst (Zhang, Yu & Wang 2013; Le Guenic et al. 2016) have

also been studied. However for the purpose of this research, reaction mechanisms and kinetics were focused on mineral acids catalyzed reaction of xylan and xylose.

The study of xylose conversion over the years have not culminated into a single universal model to describe the process of furfural formation just as in the direct method (Danon, et al. 2014). Previous studies have proposed different reaction models including a single step dehydration reaction (Oefner et al. 1992) and the presence of intermediates and side reactions (Lamminpää et al. 2015; Weingarten et al. 2010). The rate of xylose conversion have a positive proportions relationship with catalyst concentration (Zeitsch 2001; Ahola & Tanskanen 2012). Almost all reactions of xylose dehydration are assumed to be first order reactions with respect to catalyst concentrations (Ahola & Tanskanen 2012; Aida et al. 2010; Weingarten et al. 2010), with few authors suggesting different reactions orders besides the proposed first order reaction (Byul et al. 2011).

The main difference in the mechanism of xylan and xylose conversion to furfural is the preceding polymer hydrolysis to xylose dehydration in the xylan feed. In a study that could basically describe the kinetics of H<sub>2</sub>SO<sub>4</sub> catalyzed xylan conversion to furfural using whole lignocellulose biomass, they found that the activation energy for the hydrolysis step was lower at 82.2kJ/mol compared to the 119.8kJ/mol recorded for the dehydration step (Lavarack et al. 2002). A similar trend is observed when HCl was used as catalyst under the same conditions (Lavarack et al. 2002). This trend has been corroborated in other studies that reported activation energies for the hydrolysis and dehydration steps between 65-170 kJ/mol and 78-180 kJ/mol, respectively (Eken-Saraçoğlu et al. 1998; Lavarack et al. 2002; Chiang et al. 2008; Dussan et al. 2013). These results suggest that the dehydration step is the rate-determining step of the reaction (Eken-Saraçoğlu et al. 1998; Dussan et al. 2013; Aellig et al. 2015).

Although some research focused on kinetics of xylose conversion to furfural has been executed as part of the indirect method, the kinetics of furfural production from pre-extracted xylan has not yet received much attention. At most, there have been quantitative studies on its conversions (Yemiş & Mazza 2011; Zhang et al. 2014; Zhang et al. 2017; Luo et al. 2018). Most kinetics studies referring to xylan conversion (both hydrolysis and dehydration) have been performed using lignocellulose biomass substrate (Lavarack et al. 2002; Morinelly et al. 2009). Yang et al. (2006) studied the kinetics of xylan solubility by extracting xylan through a

pretreatment method where some furfural was formed. Their study was focused on xylan extraction whilst furfural production was stifled as it was considered a toxic by product of the extraction process. Therefore, the model developed did not consider the subsequent furfural formation process adequately and cannot describe sufficiently the xylan conversion to furfural process.

Given the limited research on the kinetics of furfural production in general, it is important to conduct more research in this area. Particularly, there is an absence of data on the kinetics of furfural production from polymeric xylan that has been pre-extracted from lignocellulose. This study aimed to select the most accurate kinetics models from literature that are capable of describing the kinetics of xylan and xylose conversion to furfural, respectively, by conducting experimental investigations of the conversion processes within a specified range of conditions. The selected models were compared to each other to demonstrate the differences of the polymer and monomer conversion process and to provide fundamental insight on the kinetics of pre-extracted xylan to furfural which till now has not been explored adequately in literature.

## 1.2. Research Scope

### 1.2.1. Aim and objectives

The main goal of this research was to investigate and compare the kinetics of xylan and xylose conversion to furfural at selected operating conditions. To achieve this aim, separate experiments of xylan and xylose conversion to furfural at different operating conditions have been examined. The operating conditions were specified based on previous studies and industrial experiences as temperature (140 °C-170 °C) (Cai et al. 2013; Danon et al. 2014; Marcotullio & Jong 2010; Yemiş & Mazza 2011), solids loading (4-14wt %) (Byul et al. 2011; Danon et al. 2014; Root et al. 1956) and H<sub>2</sub>SO<sub>4</sub> concentration (0.5-2 wt%). The effect of these operating conditions were examined and their significance determined. Kinetic models were obtained by fitting experimental data to models previously developed in literature.

Three models of xylose conversion to furfural recorded in literature (Ahola & Tanskanen 2012; Weingarten et al. 2010; Danon et al. 2014; Qi & Xiuyang 2007; Byul et al. 2011; Oefner et al. 1992) considering the presence or absence of side and degradation reactions of xylose were

investigated to select the best model that sufficiently describes the xylose conversion process. On the other hand, since there were no adequate models in literature describing pre-extracted xylan conversion to furfural, a basic model described in (Zeitsch 2001) for xylan conversion to furfural was investigated together with models derived from the direct method of furfural production (Lavarack et al. 2002; Dussan et al. 2013; Chiang et al. 2008) to select the model with the highest accuracy to the experimental data. Further, the kinetic models selected for xylan and xylose conversion to furfural were compared with each other to determine the differences and to provide new knowledge on the kinetics of xylan conversion to furfural.

### 1.2.2. Novelty

The process of furfural formation has been studied across a varying range of conditions (Danon et al. 2014; Cai et al. 2013; Lavarack et al. 2002; Zeitsch 2001; ). Different groups have studied the process using whole untreated lignocellulose material (direct method) and pretreated substrates such as hemicellulose hydrolysate, xylan and xylose (indirect method) (Zeitsch 2001; Mandalika & Runge 2012; Zhang, Yu, Wang, et al. 2013; Zhang et al. 2017). The direct method has been studied extensively with different lignocellulose biomass material including corncob and sugarcane bagasse (Zhang et al. 2014; Girisuta et al. 2013; Cai et al. 2013), whilst the indirect method has mostly been focused on the monomeric xylose molecules generated by pretreatment/hydrolysis processes (Gairola & Smirnova 2012; Byul et al. 2011; Danon et al. 2014; Kim et al. 2011). Hence, whereas there are several studies on xylose conversion to furfural, there are only few studies on pre- extracted xylan to furfural.

Xylan is the primary component of the hemicellulose that is hydrolyzed to xylose and further dehydrated to furfural. The conversion of xylan to furfural has been studied in a series of novel catalyst investigation by (Zhang et al. 2017; Zhang et al. 2014; Zhang, Yu & Wang 2013). These studies on xylan conversion were focused on the effectiveness of the new catalysts and solvents without considering the actual conversion processes of xylan to furfural. On the other hand, (Yemiş & Mazza 2011) studied the performance of xylose and xylan together over varying conditions of temperature (140 °C -190 °C), catalyst type (HCl and H<sub>2</sub>SO<sub>4</sub>), pH(2-0.13), and solids: liquid (1:5-1:200). To the author's knowledge, the above study is the only study that considers the conversion xylan and xylose together at relatively conventional and industrially relevant conditions (Yemiş & Mazza 2011). Although these studies have examined

the effect of various experimental conditions and relative furfural yields of xylan and xylose, none of the studies of xylan conversions considered the nature of its kinetics to provide fundamental understanding of the reaction process. Consequently, there are currently no models identified that sufficiently describe the kinetics of xylan conversion to furfural. For this study, xylan and xylose conversion at industrial relevant conditions were investigated to provide knowledge on the kinetics of xylan conversion to furfural and to investigate the effect of the operating condition (temperature, acid concentration and solid loading) on the conversion process.

## Chapter 2

### Literature Review

Optimization of the furfural production process is necessary to improve its economic viability. These processes have been explored over many years and have resulted in improved yields, energy consumption reduction, lower cost of production and a better understanding of the reaction processes. In this chapter, a review of the various discussions of furfural production will be covered with a focus on the fundamental kinetics of xylan and xylose conversion to furfural.

#### 2.1. Biomass and biorefinery

Increasing concern for fossil extinction, market prices of crude oil and the adverse effect on the environment has fueled the exploration and utilization of alternative sources of energy and chemicals. In recent years the world has turned its attention on biomass to obtain sustainable and renewable alternatives for fossil fuels and chemicals (Dussan et al. 2013). However, the utilization of biomass in industrial synthesis processes has raised the question of food security and sustenance, which has motivated considering non-edible, lignocellulosic biomass to eliminate the interference with the natural food chain (Danon et al. 2014; Steinbach 2017). About 170 billion tons of lignocellulosic biomass is produced annually worldwide making it a significant alternative to petroleum in making bio alternatives of petrochemicals (Steinbach 2017).

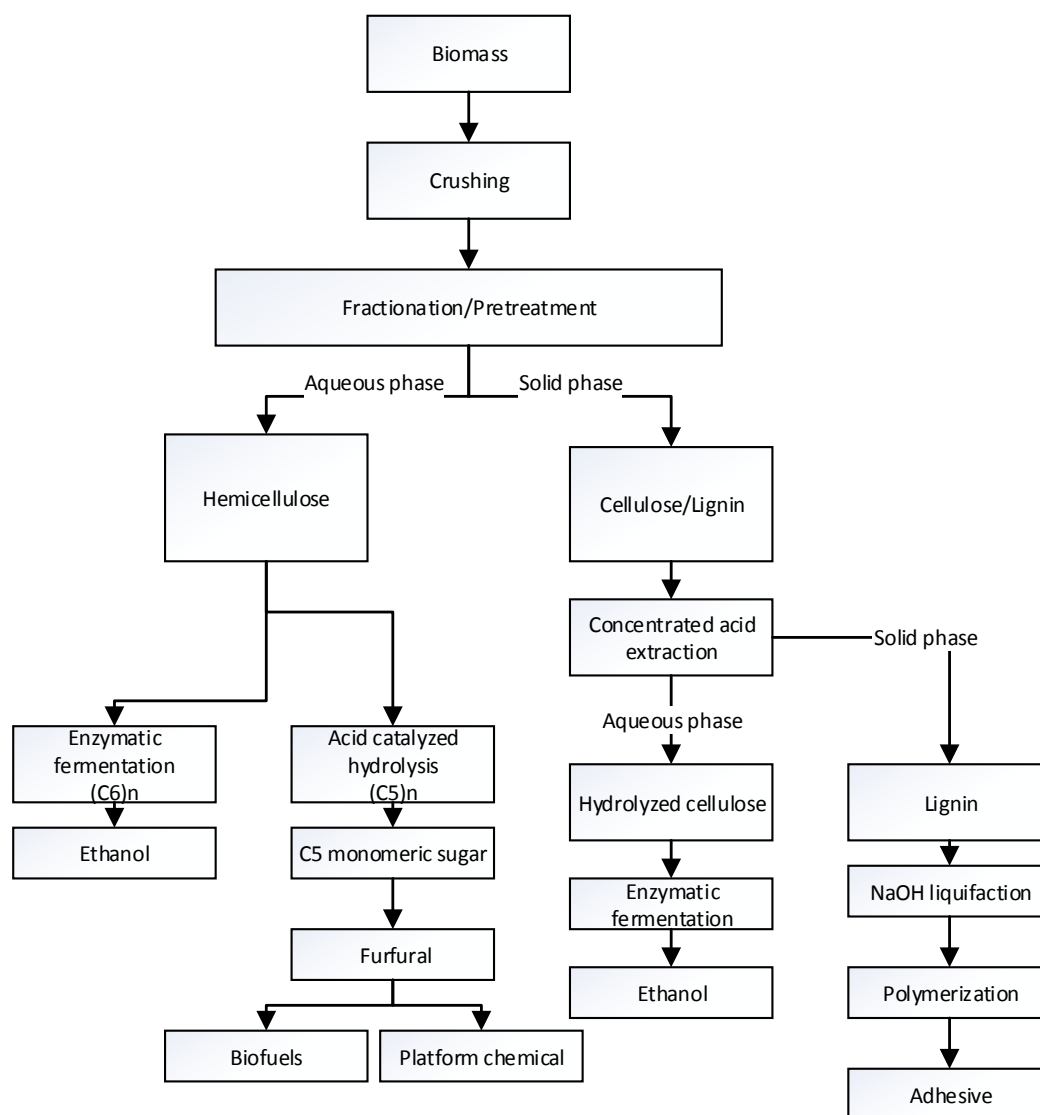
Lignocellulose biomass is made up of three major components including lignin, cellulose and hemicellulose (Eken-Saraçoğlu et al. 1998). Hemicelluloses are a heteropolysaccharide components of lignocellulose with a random, amorphous structure that makes it more susceptible to hydrolysis by dilute acid or base, compared to cellulose. They are the second largest composition of lignocellulose after cellulose and make up about 10-40% of its dry weight (Eken-Saraçoğlu et al. 1998). The hemicelluloses of hardwoods and grasses are mainly composed of xylan polymers, while other pentose or hexoses polymers (arabinan, glucan, mannan, galactan) can also be present in minor amounts. These components can occur by themselves or in a mixture (Abad et al. 1997; Cai et al. 2013). Xylan polymers are the primary

pentosan carbohydrate hydrolyzed in the process of furfural production. The incorporation of a biorefinery will enhance the process of furfural production to include production of other valuable chemicals and fuel components from all the components of lignocellulose biomass (Farzad et al. 2017). The concept of biorefinery development is aimed at optimizing the utilization of biomass through multiple products. The biorefinery can be designed to achieve simultaneous production of biofuel, bio-based chemicals, heat and energy from a low valued lignocellulose biomass to valuable products similar to petroleum refineries. This may result in cost efficiency, environmental protection and feedstock utilization (Fatih Demirbas 2009).

Furfural is a bio-based platform chemical with extensive applications in industry (Peleteiro et al. 2015) and it is rated among the top 10 products of value and a competitive petrochemical substitute (Werpy & Petersen 2004; Steinbach 2017). Furfural is often considered an undesired sugar degradation product during the conversion of lignocellulose-carbohydrates to fermentable sugars, due to its inhibitory effect on the various biological steps in a typical enzymatic hydrolysis processes resulting in the generated furfural discarded as waste (Mandalika & Runge 2012; Lau et al. 2014). Furthermore, the cellulose-rich solids generated as residues from lignocelluloses in a stand-alone furfural production process, are often used as boiler fuel or discarded, whereas organic acids, ethanol or sugars could be derived from it (Steinbach 2017). The incorporation of a biorefinery unit in already existing plants will result in the development of other valuable chemicals beside furfural in a simultaneous production process.

The major steps in a typical biorefinery can include fractionation, liquefaction, pyrolysis and hydrolysis (Fig 1). Process selection depends on the substrate and the desired products to be recovered (Aristidou & Penttilä 2000; Fatih Demirbas 2009). Pretreatment and fractionation are the first steps in a bioconversion biorefinery process. Pretreatment makes the various components available through hydrolysis and fractionation separates the different components, allowing maximum utilization of the biomass. There are several methods of pretreatment applied in industry (Chiang et al. 2008). Hot water or alkaline-based solution is used to obtain a hemicellulose-rich liquid stream without degrading the lignin and cellulose portion of lignocellulose (Mandalika & Runge 2012; Luterbacher et al. 2014), see for example Fig 1. In this approach, the portions of lignin and cellulose can be recovered and utilized

efficiently, while the hemicellulose-rich stream can be used to produce valuable products such as furfural.



**Fig 1:** Example of a fractionation process of biomass (modified from Fatih Demirbas 2009)

## 2.2. Furfural Production

Furfural is a valuable chemical with extensive potential industrial applications (Zhang et al. 2017; Zeitsch 2001). It is also known as furan-2-aldehyde, 2-furanaldehyde and 2-furfural and is made of a heteroaromatic furan ring and an aldehyde functional group (Win 2005; Mariscal & Ojeda 2016). Furfural is a clear, colorless liquid with a characteristic ‘almond-benzaldehyde’ odor, which darkens when exposed to air (Win 2005). The production of furfural from xylan



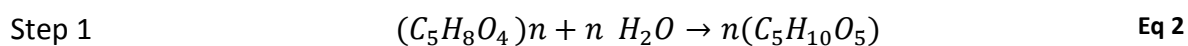
and xylose is a very carbon efficient process by retaining all five carbon in the pentose compound (Eq 1).

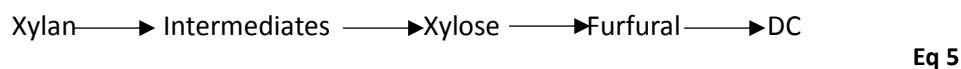
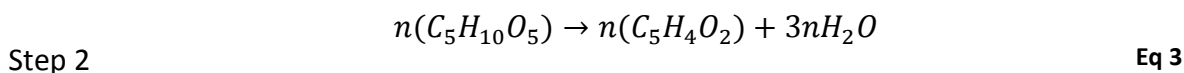


To improve the existing industrial methods of furfural production, several researchers have investigated the different aspects of the process of furfural formation including the direct and indirect methods of furfural production (Yemiş & Mazza 2011; Zhang, Yu, Wang, et al. 2013; Mandalika & Runge 2012; Yang et al. 2005).

### 2.2.1. Direct Furfural production

Direct furfural production is employed in most industrial processes, this is the production of furfural from whole, untreated lignocellulosic biomass. Corn cob and sugarcane bagasse are the feedstock used the most due to their xylan composition. The relative xylan composition were estimated to be 37 wt.% in corn cob and 19 wt.% in sunflower seed hulls (Eken-Saraçoğlu et al. 1998) and 22.4% in sugarcane bagasse (Girisuta et al. 2013). The amounts of xylan derived from these hemicelluloses varies with respect to the parent plant. Direct furfural production method involves a catalytic reaction of untreated lignocellulosic biomass and sulfuric acid at temperature ranges of 153°C-240 °C, which mostly have shown yields of about 50%. The low yields reported are due to the batch reactor systems operated in most industrial processes which promotes extensive degradation of furfural when they remain in the catalyzed aqueous phase of the reaction. (Cai et al. 2013). The reaction of furfural formation is basically a two-step reaction, including the hydrolysis of the xylan component of the lignocellulosic biomass to xylose and the subsequent xylose dehydration to furfural (Eq 2Eq 3). The combined reaction scheme is displayed in Eq 4. In some cases, xylose oligomers are formed with various degrees of polymerization before the monomers (Eq 5). DC describes the lump sum of decomposition products formed in reaction. Degradation reactions and their resulting products have an extensive influence on the overall production process. This will be discussed further in section 2.2.3.





The formation of xylooligomers from xylan is relevant at temperatures 120°C to 130 °C and acids concentrations 0.6 -1v/v% ((Lau et al. 2014)). Significant amounts of oligomers are recorded at conditions lower than 140°C and 1wt% acid concentration (Kamireddy et al. 2014; Morinelly et al. 2009). At temperatures above 140°C the oligomer conversions to monomers are so fast that the monomeric sugars become the focus of the formation reactions (Jin et al. 2011). The optimum temperature for furfural formation falls within the range of 153 °C -240 °C (Cai et al. 2013).

Besides the xylose monomers in reaction, other polymeric components like glucans, arabinan among others can also be hydrolyzed to form their corresponding monomeric sugars glucose and arabinose (Dussan et al. 2013; Lavarack et al. 2002). The several monosaccharides constituted in lignocellulosic biomass have effects on the reaction. Lavarack et al. (2002) studied the hydrolysis of sugarcane hemicellulose at a wide range of temperature ( 80-200°C) and reported the formation of xylose, arabinose and minor amounts of acid soluble lignin (ASL) at the same conditions. The mole ratio of xylose to arabinose was reported within the range of 0.019 to 0.247 (Lavarack et al. 2002). The arabinose together with the xylose dehydrates further to form furfural (Lavarack et al. 2002; Hongsiri et al. 2014). Contrarily, others suggested that the relative amounts of arabinans present in the hemicelluloses used for furfural production are far less than the amounts of xylan. A 1:9 ratio is reported in most cases and is therefore assumed to be negligible (Cai et al. 2013; Peleteiro et al. 2016; Zeitsch 2001). However, the influence of the arabinose present extends to enhanced furfural degradation (Hongsiri et al. 2014; Danon et al. 2014). Danon et al.(2014) investigated an acid catalyzed dehydration of xylose in the presence of arabinose and glucose and observed that presence of arabinose and glucose enhanced the degradation of furfural. Furthermore, the existence of side reactions that consume sugars and furfural is to be considered. For example, the presence of lignin promotes a reaction between furfural and some phenolic compounds found in lignin (Liu et al. 2014). The presence

and interactions of inhibitory components of the lignocellulosic biomass leading to enhanced furfural degradation is one of major challenges in furfural production.

## Evolution in industrial furfural production

The technology for traditional furfural production has only changed slightly since the first process in 1921 (Mandalika & Runge 2012; Cai et al. 2013). The same challenges that plagued the initial process are still present. The problems associated with the traditional furfural production method employed in literature include low yield, high energy consumption, prohibitive cost of neutralizing process residue, equipment corrosion and lack of co-product development (Lamminpää et al. 2015; Peleteiro et al. 2016). These challenges have brought about extensive research to maximize the efficiency of furfural production. The use of sulfuric acid as catalyst results in corrosion of equipment, decomposition reactions, difficult separation and recycling of process residue (Dias et al. 2005). To replace the use of harsh acids, several solid catalysts have been employed in research to increase yield and enable separation and recycling (Zhang, Yu & Wang 2013; Le et al. 2015). As stated earlier, there is a very low yield of furfural in industrial production. The current yield of direct industrial production methods are around 50%, compared to 80% yield recorded for an indirect biphasic system (Weingarten et al. 2010). Most industrial furfural processes adopted the batch reactor system similar to the method developed by Quaker oats (Cai et al. 2013). The monophasic process used in industry implies that the furfural produced remains in the aqueous phase, where it is in contact with catalytic active species to facilitate loss reactions.

Some companies have patents on improved industrial processes on the original Quaker oats process which delivers yields above 50%. The improvement studies in the direct furfural method has brought about processes like the Westpro, Biofine and Suprayield. The Westpro is a modification on the conventional batch process into a continuous process by Huaxia Furfural Company. This method similar to the Biofine incorporates a refining step; distillation and stripping to achieve yields between 50 to 70% (Cai et al. 2013; Win 2005). The Suprayield patented model is designed to overcome the inefficiencies that come with the industrial process. This model combines temperature and pressure controls to keep the reacting medium in constant boiling state resulting in instant removal of the furfural into a gaseous phase with yields about 70% of the theoretical (Arnold & Buzzard 2003.; Win 2005). These processes are

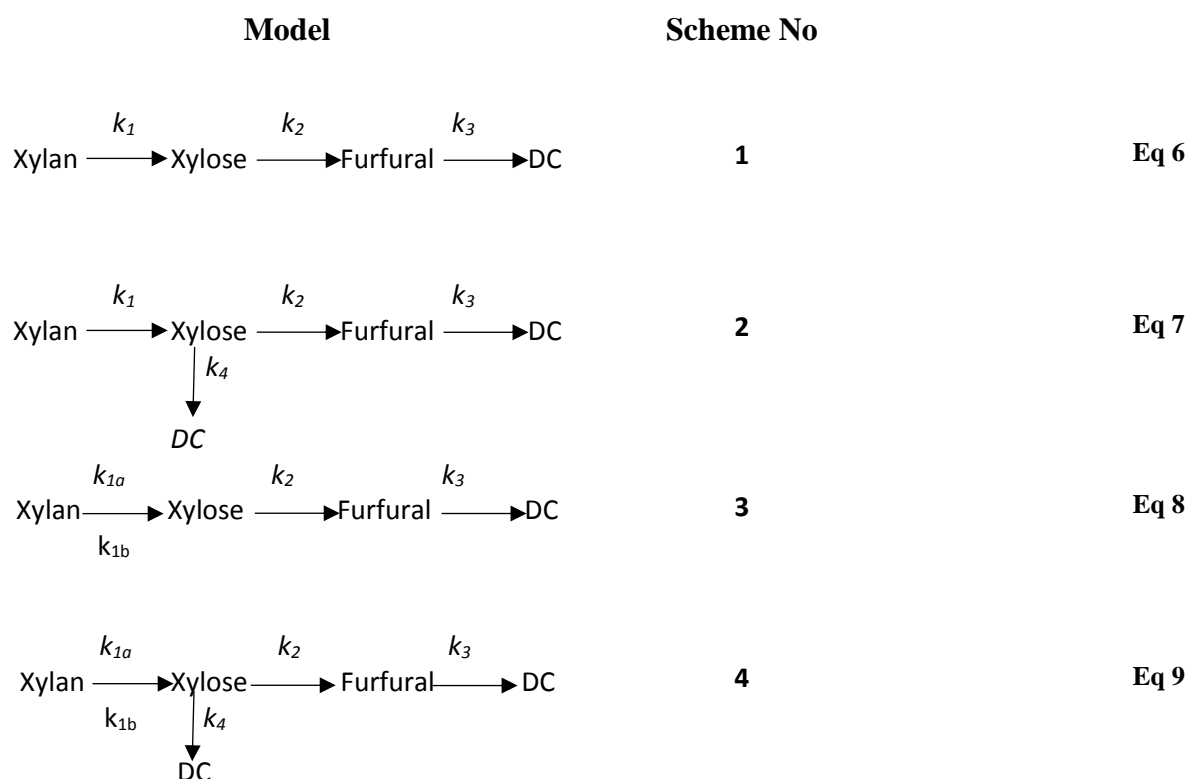
designed to achieve continual removal of furfural from the reacting system hence eliminating the chances of degradation (Arnold & Buzzard 2003). Other patents and their specific improvements to furfural production are discussed in (Zeitsch 2001; Cai et al. 2013). The general benefits associated with these novel methods and modifications are energy efficiency, product purity and increased yield.

Furfural yields are also influenced by the biomass material fed in the reaction. The biomass materials used in furfural formation have been investigated in literature (Chiang et al. 2008; Eken-Saraçoğlu et al. 1998). The use of a xylan/xylose rich feedstock will consequently improve furfural yields. The substrates used in industrial furfural production are xylose rich lignocellulose biomass. Oat hulls were used in the first industrial furfural production (Zeitsch 2001). In recent industry, corncobs and sugarcane bagasse are used (Cai et al. 2013). Other xylose rich lignocelluloses like cottonseed hull bran, almond husks, switch grass, *miscanthus giganteus* have been studied in literature (Chiang et al. 2008; Eken-Saraçoğlu et al. 1998; Dussan et al. 2013; Lavarack et al. 2002). The effect of biomass structure on reaction was investigated and found that different hemicelluloses structures of the biomass result in different kinetics properties and yields (Eken-Saraçoğlu et al. 1998). 90% yields of xylose were obtained in switch grass compared to 70% for balsam (Chiang et al. 2008). With the recent interest in biorefinery, the sugar industry have explored the use of sugarcane bagasse in an incorporated process to produce furfural. Also, the combination of different lignocellulosic biomass have been investigated to maximize feedstock utilization. It was suggested that different biomass species can be combined in a processing unit and still obtain good yields (Chiang et al. 2008). The disadvantages of the direct production include the resultant low yields, degrading of other components of the lignocellulosic biomass like cellulose which could otherwise start a process of pulp and ethanol production. Understanding the process of furfural formation could improve furfural yields.

### Mechanism of direct furfural formation

The direct furfural formation process is characterized by a two-step process as described, i.e. the hydrolysis of xylan and the dehydration of xylose (Eq 2 and Eq 3). Different researchers have reported the xylan hydrolysis to xylose differently. It has been shown to be 1) a single step reaction without any side decomposition reactions (Garrote et al. 2001; Chiang et al. 2008)

shown in Eq 6, 2) a single step with a side degradation term on xylose (Dussan et al. 2013) Eq 7, 3) a two-step reaction (Eken-Saraçoğlu et al. 1998; Borrega et al. 2011) demonstrated in Eq 8 and 4) a two-step hydrolysis plus a xylose degradation term described in Eq 9 (Lavarack et al. 2002). The inclusion of an intermediate xylo-oligosaccharide step have also been discussed (Morinelly et al. 2009; Garrote et al. 2001). The differences in the mentioned mechanisms have stemmed from various angles of argumentation and its relevance has seen contradictions.



Lavarack et al. (2002) checked the veracity of several models stipulated in literature by performing catalyzed hydrolysis on sugarcane bagasse. These models include a simplified one-step hydrolysis to xylose Eq 6) and a two-step hydrolysis to xylose (fast and slow steps) (Eq 8). It stated that the fast and slow parallel steps of xylan hydrolysis were for the ease of calculation and have no relevant effect on the reaction. This means that the hydrolysis step actually happens in one-step (fast step) while the effect of the slow step is kinetically ignored. They concluded that the simplified one-step reaction in Eq 6 was a better fit than the two-step xylan hydrolysis, which confirmed the initial assumption. Another author assumed a two-step mechanism (without justification), and concluded it was a suitable model to predict xylan conversion (Eken-Saraçoğlu et al. 1998). On the other hand, (Borrega et al. 2011) gave

references that explained the phenomenon of fast rate hydrolysis occurring up to 80% conversion and a progressively very slow hydrolysis step till a 100 % hydrolysis is obtained. They postulated that there exists a xylan-part that is susceptible to hydrolysis (forming the larger part of the xylan) and a xylan-part that hydrolyzes slowly. The distinction of these susceptibilities necessitated separate fast and slow reaction steps to compensate for over- and under-estimations. Nonetheless, other authors, e.g. (Abad et al. 1997), acknowledged the fast and slow hydrolysis steps, but still used a one-step hydrolysis mechanism to fit their experimental data and attributed the deviation as the omission of the slow hydrolysis stage. There is not a consistent nor agreed position on the relevance of the fast and slow hydrolysis step.

Garrote et al. (2001) expounded the xylan to xylose intermediate (xylooligomers) in an auto-hydrolysis system. The intermediates were composed of two levels, high molecular weight and low molecular weight xylooligomers. These intermediates were relevant in the high temperature liquid water (HTLW) systems and the amount of xylooligomers and xylose monomers recovered were significant. (Morinelly et al. 2009) also investigated the oligomers with a one-step xylooligomer product formation in dilute acid hydrolysis. This model had slight inconsistencies in fitting the experimental data, but was still described as a satisfactory model. The use of high temperature liquid water (HTLW) and weak acid catalysts results in a slow reaction and makes the characterization of intermediates possible and relevant whereas strong acids speed up the reactions, hence intermediate yield recoveries are low and less relevant (Garrote et al. 2001). It is concluded that the fast and slow hydrolysis steps and the intermediate xylooligomers steps are irrelevant in modelling for mineral acid catalyzed reactions (Garrote et al. 2001; Lavarack et al. 2002).

### Kinetics models of direct furfural formation from literature

The kinetics of furfural formation elaborate the rate of reaction and the influence of the operating conditions. It is generally described as pseudo-homogeneous, irreversible and a first-order reaction (Morinelly et al. 2009). The general rate equations are described with respect to the pentose concentration (Eq 10). The different kinetics models in literature are presented in (Eq 6 to Eq 9). The adapted Arrhenius equation in Eq 11 is used to estimate the kinetics parameters (Zeitsch 2001).

$$r_A = kC_A \quad \text{Eq 10}$$

$$k = Ae^{\frac{-E}{RT}}C_{H^+} \quad \text{Eq 11}$$

Where  $k$ , is the rate constant ( $s^{-1}$ ),  $A$  is the pre-exponential factor ( $m^3/mols$ ),  $E$  is the activation energy (kJ/mol),  $R$  is the universal gas constant (kJ/molK),  $T$  is the temperature (K),  $C_X$  is the concentration of species in reaction (M),  $C_{H^+}$  is the concentration of hydrogen ions in reaction (M) and  $r$  the measured rate of reaction ( $s^{-1}$ ).

The rate dependence on the reaction conditions (temperature, solids loading and acid concentration) is used to model the behavior of the reaction by kinetics. The parameters derived from several experiments in literature are reported in Table 1. The activation energy for xylan hydrolysis and xylose dehydration are estimated between (65-170) kJ/mol and (78-180) kJ/mol, respectively (Table 1) with reported  $R^2$  values greater than 0.75 (Lavarack et al. 2002; Chiang et al. 2008). The kinetics of xylose dehydration will be considered in details in section 2.2.2. Different substrates used in the xylan hydrolysis are listed in Table 1. The reaction parameters as stated in the table are dependent on the mechanism of reaction considered in modelling the kinetics. In all cases, there is an expected variation in the kinetics parameters, because the experiments are performed using different biomass, catalyst and varying experimental conditions. Also, the variation of the xylan structure and composition in the lignocellulosic biomass results in inconsistent data and mechanism models across literature (Eken-Saraçoğlu et al. 1998; Lavarack et al. 2002; Chiang et al. 2008).

**Table 1: Kinetics parameters of furfural production via the direct method**

Substrate	Temperature (°C)	Catalyst	Catalyst Concentration (wt%)	Solvent	Solids loading (wt%)	Scheme	E <sub>a</sub> (kJ/mol)				Refs <sup>1</sup>
							k1a	k1b	k2	k3	
Sunflower	98-130	H <sub>2</sub> SO <sub>4</sub>	1-3	H <sub>2</sub> O	3:1	3	92.31	78.35			1
Corn cob	98-130	H <sub>2</sub> SO <sub>4</sub>	1-5	H <sub>2</sub> O	4:1	3	80.34	85.67	133.7		1
Sugarcane bagasse	80-200	H <sub>2</sub> SO <sub>4</sub>	0.25-0.8	H <sub>2</sub> O	5:1-20:1	1	82.8		118.9		2
Sugarcane bagasse	80-200	HCl	0.25-0.8	H <sub>2</sub> O	5:1-20:1	1	74.5		114.8		2
Micanthus gingantus	150-200	H <sub>2</sub> SO <sub>4</sub>	1-5	H <sub>2</sub> O	9wt%	1	107.9		167.9	105.7	3
Timber variety	160-190	H <sub>2</sub> SO <sub>4</sub>	0.25-1	H <sub>2</sub> O	10:1	1	49-179		47-165		4

<sup>1</sup> 1=Eken-Saraçoğlu et al. 1998, 2=Lavarack et al. 2002, 3=Dussan et al. 2013, 4=Chiang et al. 2008



## 2.2.2. Indirect furfural production

The indirect furfural production method involves a pretreatment and fractionation of lignocellulose material to isolate a xylose-rich hemicellulose hydrolysate, polymeric xylan and monomeric xylose (Mandalika & Runge 2012). It is estimated to result in higher yields of furfural compared to the direct method (Zhang, Yu & Wang 2013). This could be attributed to the presence of enhanced side reaction and formation of inhibiting compounds with the direct process (Morinelly et al. 2009; Danon et al. 2014). Pretreatment of the lignocellulosic biomass and subsequent separation processes results in various pentose rich components such as hemicellulose hydrolysate, xylan and xylose. This process results in a reduction in the amounts of inhibitory components such as lignin that forms phenolic compounds with furfural (Lamminpää et al. 2015; Liu et al. 2014) and contributory components like arabinose which also dehydrates to form furfural (Lavarack et al. 2002; Dussan et al. 2013). Arabinose and glucose are also reported to increase the rate of furfural degradation due to the formation of acids such as levulinic acids during the hydrolysis stage (Danon et al. 2014). Similarly, a study on furfural formation from hemicellulose hydrolysate and xylose showed increased furfural yields in xylose compared to the hydrolysate (Mandalika & Runge 2012). The main components of hemicellulose hydrolysate converted in furfural formation are the polymeric compound xylan and the hydrolyzed monomer xylose.

### Xylan conversion to furfural

Xylan is the major fraction of hemicelluloses present in the lignocellulosic biomass that is suitable for furfural production (Garrote et al. 2001). The amount of xylan derived from these hemicelluloses varies with respect to the parent plant. Conversion of xylan to furfural have been studied in literature under different conditions (Zhang, Yu, Wang, et al. 2013; Aellig et al. 2015; Yemiş & Mazza 2011; Zhang et al. 2014(2)). A few authors in different studies investigated the hydrolysis of xylan to furfural using novel catalyst and solvents and recorded very high yields (Zhang, Yu, Wang, et al. 2013; Zhang et al. 2014; Aellig et al. 2015). Zhang & Zhao (2010) recorded a furfural yield of 63 mol% when they used pure xylan in ionic liquids whiles (Aellig et al. 2015) reported 69% for xylan in a biphasic system over solid catalyst. Even higher yields were recorded by (Zhang, Yu, Wang, et al. 2013) when they converted xylan to furfural with  $\text{AlCl}_3$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  as catalyst. They reported 84.8% and 93.7% for

AlCl<sub>3</sub> and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, respectively. Besides the applications of new catalyst and solvent, the conversion of xylan to furfural was investigated by (Yemiş & Mazza 2011). They obtained yields of 58% and 45% with HCl and H<sub>2</sub>SO<sub>4</sub> as catalysts, respectively. Table 2 summarizes the yields of furfural from xylan and the catalyst and solvents applied. Other authors have studied the extraction and solubility of xylan, but did not focus on the conversion of xylan to furfural (Yang et al. 2006; Mittal et al. 2009). Most authors focused on the quantitative conversions without investigating the kinetics of the process (Zhang, Yu, Wang, et al. 2013; Aellig et al. 2015; Yemiş & Mazza 2011; Zhang et al. 2014(2)). Knowledge of the mechanism and kinetics of furfural formation from xylan will provide a fundamental understating of the reactions leading up to furfural production.

**Table 2: Furfural yields (mol%) from xylan conversions at different conditions**

Substrate	Initial Concentration (wt%)	Catalyst	Solvent	Time (min)	Temperature (°C)	Yield	Ref <sup>2</sup>
Xylan	0.5	HCl	H <sub>2</sub> O	20	180	58	1
Xylan	0.5	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	20	180	45	1
Xylan	N/A	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	[Bmim]Cl	10	160	93.7	2
Xylan	N/A	AlCl <sub>3</sub>	[Bmim]Cl	0.17	170	84.8	3
Xylan	2.4	FeCl <sub>3</sub>	GVL	100	184	68.6	4
Xylan	2.5	GaUSY Amberlyst- 36	CPME <sup>3</sup>	13.6	140	69	5
Xylan	N/A	NR50/NaCl		60	190	55	6

<sup>2</sup> 1=Yemiş & Mazza 2011, 2= Zhang, Yu & Wang et al. 2013, 3= Zhang, Yu, Wang, et al. 2013, 4= Zhang et al. 2014, 5= Aellig et al. 2015 6=Le Guenic et al. 2016

<sup>3</sup> CPME=Water-cyclopentyl methyl ether (CPME), GVL= Gamma-valerolactone, Bmim=1-Butyl-3-methylimidazolium

## Mechanism and kinetics of xylan conversion to furfural

Xylan is a polymer characterized by a (1-4)-linked beta-D-xylopyranosyl backbone substituted by other polymers including arabinosyl, uronic acid, acetyl acids and glucopyranosyl (Peleteiro et al. 2016; Kabel et al. 2002). The hydrolysis of xylan is simply illustrated as the breaking of the glycosidic bonds in the polysaccharide to form the monomeric sugars (Zhang & Zhao 2010) and a subsequent xylose dehydration step to be discussed in the next section.

Kinetics studies of xylan conversions to furfural are few, with the majority of kinetics studies referring to xylan performed using lignocellulose biomass as substrate and the direct furfural production method (Lavarack et al. 2002; Morinelly et al. 2009). The kinetic values and yields of lignocellulose biomass hydrolysis cannot be related to xylan hydrolysis directly, due to interference of the other constituents of the biomass. Yang et al. (2006). investigated the kinetics of xylan solubility by extracting xylan from corncob in a steam pretreatment process they recorded high activation energies for the xylan hydrolysis stage (166-109 kJ/mol) Because the process was focused on xylan extraction and solubility, conditions were selected to restrict xylose and furfural formation. Their experimental data did not fit well to first order and second order models for furfural formation. The model presented was not sufficient to describe the kinetics of xylan conversion to furfural. There are currently no papers identified that sufficiently describes the kinetics of xylan conversion to furfural this far.

## Xylose Conversion to furfural

Xylose ( $C_5H_{10}O_5$ ), a  $C_5$  monosaccharide that is formed by hydrolysis of the xylan present in some types of hemicelluloses, is the major pentose sugar found in such hemicelluloses, with varying compositions based on the substrate plant (Aristidou & Penttilä 2000; Ahola & Tanskanen 2012). Pure xylose is a white crystalline powder with extensive industrial and domestic applications. These include the production of xylitol, a functional sweetener with low caloric value for diabetic patients (Herrera et al. 2003), ethanol production (Aristidou & Penttilä 2000) and furfural production (Qi & Xiuyang 2007; Antal et al. 1991).

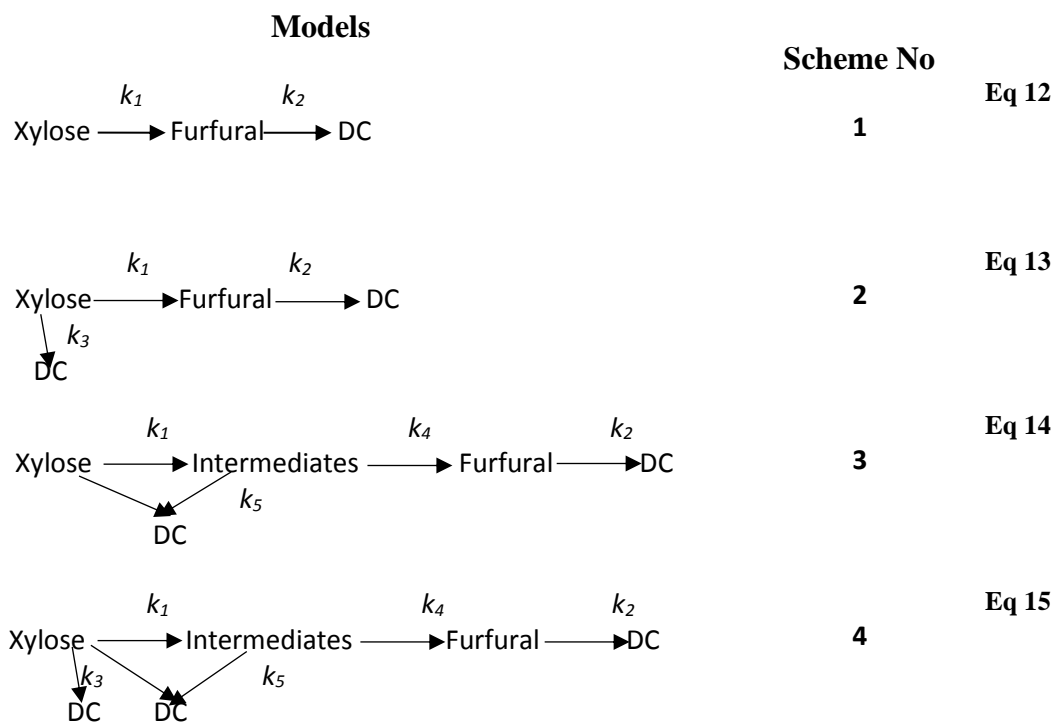
## Mechanism and kinetics of xylose conversion to furfural

There is no agreement on a mechanism in literature to describe furfural formation from xylose. Different authors have postulated different mechanisms and reaction schemes of xylose

dehydration to furfural (Weingarten et al. 2010; Byul et al. 2011; Oefner et al. 1992). (Antal et al. (1991) described two routes leading to furfural production, made up of a succession of reactions that occur via open chain intermediates and an acid catalysed sequence through a 2, 5 –anhydride shift. Experimental analysis on catalyzed and non-catalyzed dehydration confirmed the 2, 5 anhydrides intermediate. This author also postulated the three forms of xylose (xylopyranose, xylofuranose and acyclic xylose) and the progressive formation of furfural from the pyranose form.

More recent studies have suggested more than two routes of production (Mandalika & Runge 2012; Danon et al. 2014; Rasmussen et al. 2015). (Mandalika & Runge 2012) referred to three schemes of xylose conversion (dehydration) to furfural. In their study, two other routes that involved direct rearrangement of the pyranose structure challenged the acyclic intermediate route. Furthermore, ( Danon et al. 2014) observed the same contradictions of acyclic pentose (1,2 enediol intermediate), straight 2,3 unsaturated aldehyde and Pyranose formation route. (Rasmussen et al. 2015) stated that both mechanisms postulated via the aromatic and aliphatic routes are possible and that it is even possible to produce furfural without going through the debated intermediates. The above postulated mechanisms are simply described as single step dehydration of xylose to furfural and the dehydration of xylose intermediates to furfural shown in Eq 12 and Eq 15. The decomposition of xylose to side products and decomposition products of resinification and condensation are incorporated in the mechanism of furfural production (Ahola & Tanskanen 2012; Weingarten et al. 2010; Qi & Xiuyang 2007; Oefner et al. 1992) .

The effect of the intermediate is considered insignificant, due to the minimal effect it has on the process of a mineral acid catalyzed dehydration (Antal et al. 1991; Qi & Xiuyang 2007; Hongsiri et al. 2014).



Kinetics parameters of some xylose dehydration reactions in literature are reported in Table 3. The activation energy reported is widely dependent on the catalyst and temperature of reactions. In the previous section, the mechanism of furfural production from xylose was postulated as a direct xylose to furfural reaction due to the minimal effect of the intermediates on acid catalyzed systems. To further elucidate this, three models were investigated by Ahola & Tanskanen (2012) see Eq 13 to Eq 15. These models were fitted with experimental data from formic acid catalyzed reactions. The first model can be explained as a simplified direct dehydration of xylose to furfural together with a xylose decomposition path, the second is described by a xylose through an intermediate to form furfural with an intermediate furfural interaction path and the third model was a combination the first two. It was observed that  $k_1$  (xylose dehydration) and  $k_3$  (xylose decomposition) values for all three models were nearly the same, the  $k_4$  value that describes the intermediate to furfural path was found to be negligible and postulated to have very little effect in the reaction kinetics. Amongst the three models, scheme 1 and 3 gave better fits of the data than scheme 2. It was concluded that the intermediate step was negligible. This validated the initial assumption that, the intermediates have insignificant effect on the acid catalyzed reaction

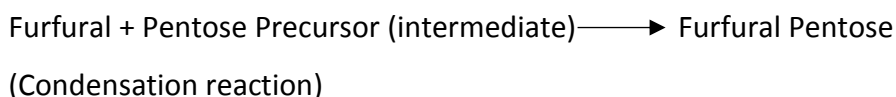
**Table 3:** Kinetics parameters of xylose conversion to furfural

Substrate	Temperature	Catalyst	Catalyst Concentration (wt)	Solvent	Solids loading (wt%)	Scheme	E <sub>a</sub> (kJ/mol)			Refs <sup>4</sup>
	(°C)						k1	k2	k3	
		formic acid					152	75.5	161	
Xylose	130-200	acid	7-30	H <sub>2</sub> O	0-0.2	2				1
Xylose	160-200	HCl/NaCl	0.5 /2.9	H <sub>2</sub> O	0.05	2	133	102.1	125.8	2
Xylose	180-220	None		H <sub>2</sub> O	0.072	2	111.5	58.8	143	3
Xylose	140-240	None		H <sub>2</sub> O	0.02-1	2	76.6	24.2	58.8	4
							130-			
Xylose	180-200	H <sub>2</sub> SO <sub>4</sub>	0.1-1	H <sub>2</sub> O	0.07	1	120			5
Xylose	180-200	None		H <sub>2</sub> O	0.07	1	119			5
Xylose	160-280	H <sub>2</sub> SO <sub>4</sub>	0.031-4	H <sub>2</sub> O	0.02 -1	1	140			6

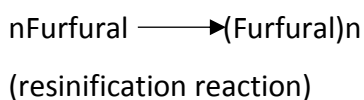
<sup>4</sup> 1=Ahola & Tanskanen 2012, 2=Hongisiri et al. 2014, 3=Qi & Xiuyang 2007, 4=Byul et al. 2011, 5=Oefner et al. 1992, 6= Root et al. 1956

### 2.2.3. Furfural Degradation

Furfural degradation results in the formation of unwanted products from furfural. These furfural consumption reactions occur simultaneously with the furfural formation reactions, and thus under the same reaction conditions. The simultaneous formation and decomposition of furfural in typical industrial reactors will result in lower overall process yields (Root et al. 1956). The furfural degradation reactions include resinification, condensation and fragmentation (Peleteiro et al. 2016; Cai et al. 2013; Zeitsch 2001). Resinification is the reaction of furfural with itself to form polymeric resins and humins, and is also called self-coupling polymerization (Eq 16). Condensation, also called cross-polymerization, is a reaction of furfural with xylose and/or xylose intermediates to form decomposition products including humins and other unidentified products (Eq 17) (Zhang, Yu, Wang, et al. 2013). Humins have been described as an undesirable black solid and its characteristics have so far not been clearly defined (Le Guenic et al. 2016). The magnitude of condensation decomposition exceeds that of resinification (Zeitsch 2001). Hence, the effective way to eliminate or reduce degradation is to avoid contact between xylose and furfural in the solution. This degradation reaction can be avoided when the furfural is separated in situ from the liquid phase containing the catalytic species, by phase separation (Weingarten et al. 2010) or continuous distillation and stripping of the furfural from reaction (Mandalika & Runge 2012). Fragmentation is the decomposition of furfural to form smaller compounds, such as formic acid, formaldehyde, acetaldehyde, pyruvaldehyde, lactic acid, glyceraldehyde and glycoaldehyde (Antal et al. 1991). Since furfural degradation is promoted by inhibiting components of the feed, elimination and reduction of these components in a pretreatment step will reduce the rate and magnitude of furfural degradation (Danon et al. 2014). Condensation degradation reaction occurs when furfural reacts with xylose and xylose intermediates in a catalyzed reaction. Therefore, degradation is enhanced by high concentrations of monomeric and oligomeric xylose in reaction (Yemiş & Mazza 2011).



**Eq 16**



Eq 17

Generally, hydrothermal reactions of xylan to furfural yields lots of oligomers compared to monomers and an acid catalyzed reactions yield copious amounts of xylose monomers to form furfural. Temperatures above 140°C combined with mineral acid catalyst produces rather sparse amounts of oligomers (Zhang & Wyman 2013; Morinelly et al. 2009). This implies that different conditions of reactions will result in each of the above condensation reactions or a combination of both, leading to loss in yields of furfural. Consequently, the extent of degradation depends on the concentration of oligomers and monomers existing in reaction with furfural in a catalytic aqueous.

Despite the frequent and unavoidable occurrence of furfural degradation, there are factors that increase or decrease the rate of condensation, resinification and fragmentation. The degradation reactions are facilitated by high xylose loading, high acid concentrations and elevated temperatures when occurring together (Ahola & Tanskanen 2012). There is therefore a need to find a reasonable synergy with the conditions of reaction. The rate of furfural decomposition by resinification and condensation is much lower than the rate of xylose dehydration, hence the condensation reactions will cease once the xylose is exhausted from the reaction (Qi & Xiuyang 2007), but resinification will continue till all the furfural is degraded at high temperatures.

### 2.3. Comparison of xylan and xylose conversion to furfural

Xylan and xylose conversion to furfural have been studied together at varying reaction conditions (Zhang, Yu, Wang, et al. 2013; Aellig et al. 2015; Yemiş & Mazza 2011; Zhang et al. 2014(b)). Although furfural production from xylan and xylose are classified as indirect method of furfural formation (Morinelly et al. 2009; Mittal et al. 2009; Marcotullio et al. 2011), the kinetics of xylan conversion will need some clarification. In the process of xylan conversion described in section 2.2.2, xylan conversion is seen to be similar to the process of direct method of furfural production (Lavarack et al. 2002). More importantly, some authors have used the term xylan conversion to loosely describe direct furfural production (Garrote et al. 2001;



Dussan et al. 2013; Luo et al. 2018). This is however inaccurate since xylan is a pretreated compound separated from lignocellulose material with different compositions (Yang et al. 2005; Evangelina et al. 2015). In this study, pretreated xylan and xylose will be studied as indirect method of furfural formation, even though the kinetics of the xylan conversion to furfural will be realized to describe a process similar to the direct method of furfural production.

Xylan and xylose conversion reactions have been conducted with new catalyst and solvents to improve yields (Zhang, Yu, Wang, et al. 2013; Zhang et al. 2014; Aellig et al. 2015). The studies with new catalyst and solvents provide valuable insights into optimization processes. However, the use of specific and new catalyst and solvents that are not applied in industry makes these results limited and incomparable to industrial processes.

In furfural formation, the difference between the xylan and xylose process is the breaking of the glycosidic bonds in the polymer to form a monomer (Zhang & Zhao 2010), together with the formation/presence of minor quantities of non-xylose products of xylan hydrolysis such as reactions involving lignin, cellulose and acetyl acids compounds present in xylan (Mittal et al. 2009). Xylan hydrolysis and xylose dehydration are successive steps in furfural production. Xylan is basically the polymeric form of the xylose monomer, with a number of side groups attached.

In the kinetics of furfural production at the same process conditions, the xylan would have to go through both an initial hydrolysis stage and a subsequent dehydration of xylose to form furfural, whereas xylose monomer conversion involves a direct dehydration. This xylan hydrolysis step utilizes the same catalyst as the dehydration reaction, and is likely to result in slight deficiency in catalyst availability for the subsequent dehydration (Yemiş & Mazza 2011). Xylose dehydration is the rate determining step in the furfural production based on the average reported activation energies for hydrolysis (49-107) kJ/mol, and xylose dehydration (114-170) kJ/mol (Table 1 and Table 3).

(Yemiş & Mazza 2011) observed significant differences in the yields of furfural from xylan and xylose substrates. They performed a series of experiments at varying temperatures, reaction times, catalyst, pH and solid loading. They observed a significantly higher furfural yield for xylose compared to xylan in all the cases. They attributed it to the extra hydrolysis step, the

autocatalytic dehydration of xylose into furfural, purity of raw materials and loss reactions such as direct decomposition of feed to char and humins formation. Although extensive studies were done on xylose and xylan conversion at arguably industrial relevant conditions, the study was purely quantitative and hence the kinetics of the reactions were not considered.

## 2.4. Effects of operating conditions on reactions

Furfural production is highly dependent on reaction conditions, as discussed in the previous sections. Important parameters to be considered include the temperature and the properties of the chemicals used in the reaction. The effects of operating condition on the furfural yield have been investigated by different researches as described in the following sections.

### 2.4.1. Solid loading

The concentrations of xylose and xylan have been expressed to affect the yields and degradation significantly (Yemiş & Mazza 2011). This makes solids concentration an important parameter of reaction. Concentration range of 0.02M to 1M is usually used for xylose dehydration in literature, see Table 3. On the contrary, there is limited data for xylan reactions. Most xylan reactions studied in literature, investigated xylose at similar concentrations (Zhang, Yu, Wang, et al. 2013; Zhang et al. 2014; Le Guenic et al. 2016). Therefore, solids concentrations will be discussed with reference to xylose reactions. High solid loading for xylose has been reported to promote decomposition reactions (Yemiş & Mazza 2011; Mandalika & Runge 2012; Byul et al. 2011). (Yemiş & Mazza 2011) performed experiments to investigate the effect of loading on furfural yields. It was observed that increasing xylose concentration resulted in decreasing furfural yields. It was also observed that the amount of char formed was approximately equal to the amount of furfural lost. In their experiment, the optimum loading reported was 1:200 solid to liquid mass ratio (SLR) for SLR range of 1:200 to 1:5. This implies that minimum loading gave the best yield, nonetheless this is an extremely low concentrated feed and not industrially viable. Accordingly, most literature focused on xylose concentrations of about 0.02M-0.2M to attain high yields (Ahola & Tanskanen 2012; Qi & Xiuyang 2007; Danon et al. 2014). However, with low concentrated feed, proportional amounts of yield are achieved. Therefore there is a need to explore xylose concentrations above 0.2M to observe their effects on the mechanism of the reaction.

## 2.4.2. Catalyst

The kinetic rate constant is highly dependent on catalyst concentration (Zeitsch 2001). The mineral acids currently used in industry are the major causes of corrosion, some decomposition reactions and high cost of downstream residue processing (Zhang et al. 2017). This has led to extensive research into alternative catalysts. Literature has explored the use of no catalyst at all, organic acids, mineral acids (Ahola & Tanskanen 2012; Qi & Xiuyang 2007; Honghiri et al. 2014) and also solid catalyst and heterogeneous catalyst (Zhang et al. 2013) which have been shown to result in higher furfural yields (Peleteiro et al. 2016; Zhang et al. 2017). (Ahola & Tanskanen 2012) studied the dehydration of xylose in formic acid without stating its effect on the experiment, although the development of co-product from experiment and less strenuous processes for downstream separation were indicated as advantages. Other weak acids like phosphoric acid and acetic acid have been studied as catalyst for furfural production (Zeitsch 2001; Yemiş & Mazza 2011; Abad et al. 1997) and they are known to result in lower yield than mineral acids at the same experimental conditions (Yemiş & Mazza 2011).

Weak acids obtained by biomass hydrolysis and ionized water can result in autohydrolysis (dehydration of substrate in the absence of an added catalyst). Esters attached to the xylan backbone can be hydrolyzed to form organic acids. The formed acetyl and formyl acids, then act as catalyst for furfural production in high temperature water (HTW). Autohydrolysis has been studied in systems at temperatures of 200°C and higher (Antal et al. 1991; Qi & Xiuyang 2007; Aida et al. 2010).. The benefits of auto-catalyzed reactions include its minimal effect on the environment and the low cost of treating residue (Qi & Xiuyang 2007); on the other hand, it requires expensive costs in energy and results in low yields. The yields recorded for autohydrolysis are generally lower than acid-catalyzed reactions (Byul et al. 2011), apart from (Oefner et al. 1992) who reported that the differences in yields between low concentrations of mineral acid and HTLW are insignificant.

In the presence of a strong mineral acid such as  $H_2SO_4$  and  $HCl$ , the effect of weak acids may become negligible. This has been described by Zeitsch (2001) as the specific acid catalysis and general acid catalysis effect. The general acid effect is the total effect of the dominant catalytic species ( $H_2SO_4$  or  $HCl$ ) and the secondary catalytic species (weak acids and ionized  $H_2O$ ). While the specific acid effect is the effect of the dominant catalyst without the secondary.

They determined that whereas the “specific” can be an accurate approximation for the “general”, this is only true for high concentrations of the dominant catalyst such as H<sub>2</sub>SO<sub>4</sub> and HCl.

The use of HCl and H<sub>2</sub>SO<sub>4</sub> as catalyst have been debated across literature (Danon et al. 2014; Zeitsch 2001; Lavarack et al. 2002). HCl was found to result in higher yields and was comparatively a better catalyst compared to H<sub>2</sub>SO<sub>4</sub> that has been determined to promote furfural degradation (Danon et al. 2014; Zeitsch 2001; Marcotullio & Jong 2010). However, some other study determined H<sub>2</sub>SO<sub>4</sub> to be the better catalyst (Lavarack et al. 2002). Nevertheless, H<sub>2</sub>SO<sub>4</sub> has a distinct industrial advantage over HCl, almost all industrial plants in the world use H<sub>2</sub>SO<sub>4</sub> as catalyst. It is also the less corrosive alternative of the two. (Hongsiri et al. 2014; Marcotullio & Jong 2010) performed extensive works combining salts with mineral acid to improve yields of furfural. The use of different catalyst with different feedstock generates a complexity, which makes results incomparable.

### 2.4.3. Temperature

Temperature influences the actions of acids in reactions and in determining the rate of reaction in general (Antal et al. 1991). In selecting the temperature, it is imperative that a temperature range is selected that will enable us to achieve total or maximum conversion of the substrate, maximum yield of product and minimum loss reactions. High temperatures favor furfural production (Borrega et al. 2011), whereas low temperatures have been reported to result in deviated reactions and outlier results (Danon et al. 2014). (Antal et al. 1991) pegged the optimum temperature range for furfural production at 160-280°C. Industrial production of furfural applies a temperature range of 153-240°C (Zeitsch 2001; Cai et al. 2013). (Yemiş & Mazza 2011) investigated the influence of temperature on furfural production. Temperatures of 140, 160, 170, 180 and 190°C were studied with a maximum yield obtained at 190°C. It was also observed that char formation increased with increasing temperature, though this was attributed to the possibility of substrate insolubility and improper mixing within the reactor. Similar work was done by (Marcotullio & Jong 2010; Yang et al. 2013) by conventional heating and in a biphasic system, respectively; maximum yield in this case was recorded around the upper limit temperature 190°C. Temperature range used in literature has been consistent within the ranges of 130-280°C as demonstrated in Table 1 and Table 3.

#### 2.4.4. Reaction time

Reaction time is dependent on the temperature of reaction and the severity of catalyst concentration. At low temperatures and catalyst conditions, a short reaction time will result in intermediate products of reactions (Danon et al. 2014). The yield of the reaction has been known to increase with longer reaction times (Antal et al. 1991; Yemiş & Mazza 2011; Borrega et al. 2011b). In selecting a reaction time, a main factor to consider is the lifetime of the experiment to achieve the desired results. For example, yields increase with longer reaction time until a maximum yield is recorded. At too short reaction times, complete conversion is not achieved and reactions would be incomplete. (Borrega et al. 2011) performed experiments in HTLW and reported that once furfural reaches its maximum yield any increase in reaction time will have very little effect on it. However, an increase in char formation is observed when reaction time is prolonged beyond the optimum time period (Yemiş & Mazza 2011).

Reaction time selection is also dependent on severity of other factors of reaction like temperature and acid concentrations. At low severity conditions, the reaction progresses slowly whereas the opposite happens in high severity experiments. The reaction time reported in literature vary over a wide range (1-2000min) due to variation of equipment, catalyst and solid loading (Yemiş & Mazza 2011; Lavarack et al. 2002; Mandalika & Runge 2012; Dussan et al. 2013; Zhang, Yu & Wang 2013). (Dussan et al. 2013) recorded a range of 60 to 90 min in the H<sub>2</sub>SO<sub>4</sub> catalyzed batch reaction to form furfural. (Mandalika & Runge 2012) also recorded reaction times of 20 to 60 min in their BRD system. Different reaction system, equipment and conditions severity will determine the right reaction time to be employed.

#### 2.4.5. Solvents

The use of solvents in furfural production is very relevant. The recent incorporation of alternative solvents such as DMSO, GVL and [bmim]H<sub>2</sub>SO<sub>4</sub>/MIBK has resulted in improved furfural yields compared to water (Peleteiro et al. 2016; Hu et al. 2014). These novel solvents are more expensive but are known to give higher yields of furfural up to 70%. Most industrial processes nonetheless use water as solvent. This is because of the relative cheaper cost of water compared to other organic solvents applied. Water also has less effect on the environment and requires no downstream purification process. In spite of the suitability of water as solvents,

furfural yields recovered from water solvent reactions are low compared to some organic solvents and ionic liquids applied in recent literature (Hu et al. 2014). (Hu et al. 2014) demonstrated in their work, “acid catalyzed conversion of xylose in 20 solvents”, the efficiency of organic solvents compared to water. Yields as high as 80% were obtained for DMSO compared to just 17% for water at the same conditions. This is a representation of a vast improvement from water. Biphasic systems have been used to separate the furfural from the active catalytic species by ensuring phase separation. An organic co-solvent is employed as the extractive phase and the reaction media is in the aqueous phase (Weingarten et al. 2010; Zhang, Yu & Wang 2013). MIBK and THF among other organic solvents have been studied in literature (Zhang, Yu, Wang, et al. 2013; Weingarten et al. 2010). Other studies explored the use of ionic liquids (Peleteiro et al. 2016) and gamma-valerolactone (GVL) (Zhang et al. 2014) as solvents. Solvents such as [bmim]H<sub>2</sub>SO<sub>4</sub>/MIBK and GVL gave a yield of 90% and 80%, respectively (Zhang et al. 2017; Zhang et al. 2014). Although improved yields are recorded, these solvents are expensive, require additional downstream recovery and could be hazardous (Mandalika & Runge 2012).

#### 2.4.6. Reactor

There has been several modifications and novel methods since the first furfural production. The first reactor equipment used in producing furfural were iron pressure cookers that were initially meant for cereal production. These iron pressure cookers were later lined with acid resistant material to prevent the corrosion effect of the catalyst (Zeitsch 2001). In recent years, several means have been employed for the hydrolysis process. Conventional reactors (Hongsiri et al. 2014; Chiang et al. 2008; Abad et al. 1997; Danon et al. 2014) and microwave reactors (Yemiş & Mazza 2011; Weingarten et al. 2010; Le Guenic et al. 2016; Zhang, Yu & Wang 2013) are some of the equipment used. Process modifications like Suprayield (Arnold & Buzzard n.d.), Westpro among others have also been developed to increase the yield of furfural production. The constant removal of furfural from the overhead vapor phase with the batch reactive distillation (BRD) process resulted in higher yields compared to the ordinary batch process (Mandalika & Runge 2012). A similar mechanism of constant furfural separation in the vapor phase is employed by the Suprayield to obtain improved yields. (Yemiş & Mazza 2011; Weingarten et al. 2010) employed microwave energy in hydrolysis and dehydration

processes. Microwave assisted reactors work by concentrating the energy directly on substrates which results in rapid heat up such as observed in continuous industrial reactors where cold feed is fed into a hot reactor. It was determined that temperature was a significant factor in the process just like in conventional heating. (Weingarten et al. 2010) reported of equal performance of microwave compared to conventional heating apart from short heat up and reaction times recorded for microwave heating. This happens to be the major advantage of microwave heating. Consequently, a conventional reactor is selected.

## 2.5. Research Questions from Literature

As discussed above, the kinetic of xylan conversion to furfural was not investigated thoroughly in literature. Furthermore, it was observed that very few studies have considered the mineral acid catalyzed conversion of xylan and xylose to furfural. Comparison of xylan and xylose conversion to furfural at similar operating condition will provide fundamental knowledge about furfural production. These observations led to the following research considerations:

1. Although the kinetics of mineral acid catalyzed conversion of xylose to furfural have been investigated in some studies (Oefner et al. 1992; Weingarten et al. 2010; Bart Danon, Marcotullio & de Jong 2014; Hongsiri et al. 2014; Ahola & Tanskanen 2012) there are currently no relevant kinetics studies of xylan conversion to furfural. Yang et al. (2006) studied kinetics of xylan solubility and degradation but did not obtain a model that sufficiently describe the kinetics of xylan conversion to furfural. Consequently this work aims to select a model that describes the kinetics of xylan conversion to furfural.
2. Furthermore, previous research has studied the conversion of xylan and xylose together at varying conditions of temperature, acid concentrations and solids loading (Yemiş & Mazza 2011; Zhang et al. 2014; Le Guenic et al. 2016). However, these investigations did not consider the kinetics of the conversion processes. No study on xylan and xylose conversion kinetics is available to the author's knowledge that clarifies their similarities and differences.
3. Xylan and xylose have been studied together with different kinds of new catalysts and solvents (Zhang et al. 2014; Le Guenic et al. 2016; Luo et al. 2018). However, the use of specific and new catalyst and solvents that are not applied in industry makes these results limited and incomparable to real industrial processes. Only one study available

in literature investigated xylan and xylose conversion together under arguably conventional and industrial relevant catalyst (HCl and H<sub>2</sub>SO<sub>4</sub>) (Yemiş & Mazza 2011). The present project aims to investigate furfural production at industrially relevant condition and evaluate the effects of operating parameters on the conversion process. The result will enable the kinetics comparison of xylan and xylose conversion to furfural at industrially relevant conditions for the first time.



## Chapter 3

### Methodology

One of the aims of this study is to select a kinetic model that can be implemented for improving industrial furfural reactors. The model will comprise of a xylan and xylose conversion plus furfural degradation part. This project is focused on the kinetics of the pentose sugar conversion whilst the kinetics of furfural degradation is currently being studied by a different student within the project team (Steiner 2018). The experimental data and kinetic model from the furfural degradation project will be incorporated with the sugars conversion models in this study to produce a complete model that is sufficient to describe the process of furfural formation within a specified range of conditions. Therefore, there is a need to attain compatibility in experimental conditions with the furfural degradation project. To effectively achieve this, experiments must be designed to obtain sufficient data for kinetics modelling that are also relevant to industrial processes. This chapter will describe the various materials, chemical and methods used in the study.

#### 3.1. Chemical and Materials

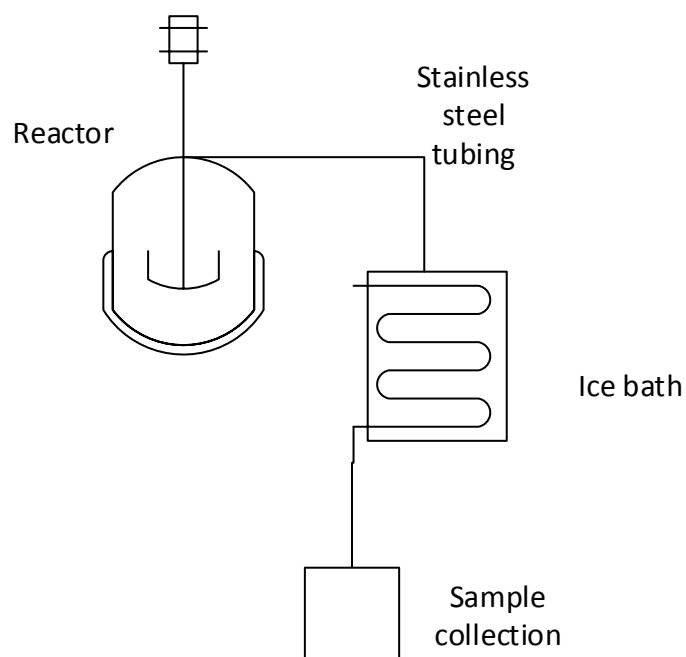
The major chemicals required in this study are xylose, xylan and sulfuric acid. Xylan and xylose are derived from the hemicellulose components of the lignocellulose biomass. All chemicals and materials were sourced from commercial suppliers. A complete list of the chemicals and materials used are listed in Table A- 1.

##### 3.1.1. Chemicals

Xylose (5kg, D-(+)-Xylose,  $\geq 99\%$ ) and sulfuric acid (ACS reagent 95.0-97.0%) were obtained from Sigma-Aldrich and used without further purification. Xylan (10kg,  $\geq 65\%$ ) was obtained from Xi'an Leader Biochemical Engineering Co. Ltd, China. Further details of the procured xylan is discussed in section 3.2.3. Demineralized water was sourced from the department reverse osmosis purification plant.

### 3.1.2. Equipment and Materials

A rotary sample splitter (model: Eries Magnetics 10 way) was used in the splitting and mixing batches of xylan. A 2L Büchiglasuster Polyclave type pressure reactor with reinforced anti corrosion material, Hastelloy C-22 alloy was used for all catalyzed reactions using xylan and xylose. The reactor is fitted with a Büchiglasuster automatic stirrer and temperature control device. A schematic diagram of the experimental set up is shown in Fig 2



**Fig 2: A Schematic diagram of the reactor set-up**

### 3.2. Experimental Conditions.

Temperature, catalyst type, catalyst concentration, solid loading and reaction times are amongst the most important parameters to be considered when designing furfural production experiment. Specifically, corrosion abilities should be considered to avoid damage to the equipment and fouling of solutions, volume of the reactor should be selected such that it is not too big to result in material wastage or excessive heat losses, nor too small to give sufficient samples as required for analysis and modelling (Morinelly et al. 2009).

Effectively, experiments should be designed to obtain sufficient data for modelling which is the main goal of this project. There are three experimental parameters at three levels of severity

(low, medium and high) which brings the number of runs to 27 per saccharide feed and 54 in total. Factoring in 30% duplicate to check repeatability and loss experiments, total number of required runs is 72 runs (Table 4). Selection of the operating conditions to achieve the best possible outcome of experiments is discussed below.

Table 5 gives a summary of the experimental conditions in this study.

The experimental data to model the degradation reactions will not be covered within the scope of this experiment. Extensive furfural degradation experiments have been performed and data collected in a parallel work. In order to obtain a complete model, experimental conditions will be selected to ensure compatibility for both formation and degradation studies.

**Table 4: Experimental design**

Experiment set/Runs	Core	X1.3 (Duplicate and losses)
Xylose	27	36
Xylan	27	36
Total	54	<b>72</b>

**Table 5 Summary of experimental conditions**

Condition	Range		
	Low	Medium	High
Temperature (°C)	140	155	170
Acid concentration (wt %)	0.5	1	2
Pentose concentration (wt %)	4	8	14
Feed stock	Xylan and Xylose		

### 3.2.1. Temperature

Temperature is the most important parameter in a thermochemical reaction. The temperatures employed in literature spans a wide range (100°C- 280°C) (Table 1 and Table 3). For this study temperatures of 140°C to 170°C was selected as a good range that was consistent with literature. This selected range is compatible with the furfural degradation experiment and will satisfy the conditions of compatibility between this work and the furfural degradation experiments previously undertaken.

### 3.2.2. Acid catalyst

The catalyst used in the catalyzed furfural production determines the general rate of reaction to a large extent. Sulfuric acid is used in this study. Since almost all commercial furfural plants use H<sub>2</sub>SO<sub>4</sub> as catalyst, the use of sulfuric acid will provide results that are closely relatable to industry. This is in spite of the fact that it is not the most effective acid catalyst. Other types of catalysts studied in literature have been shown to be more effective with less environmental burdens, but much more expensive to use even if recoverable for this lab experiment (Dias et al. 2005; Zhang, Yu & Wang 2013; Zhang et al. 2014; Zhang et al. 2017). The use of mineral acids such as sulfuric acid and hydrochloric acid are the most relevant catalyst for this experiment. Sulfuric acid is selected because of its industrial relevance compared to hydrochloric acids (Zeitsch 2001; Cai et al. 2013; Lavarack et al. 2002). Sulfuric acid concentrations between 0.031wt% and 5wt% have been studied in literature (Table 1 and Table 3). For this study sulfuric acid concentrations between 0.5-2wt% were selected as a good range well within literature values as well as to satisfy compatibility with the furfural degradation study. Initial experimental analysis showed good results.

The sulfuric acid concentration was selected based on previous studies in literature (Table 1 and 3) considering previous studies

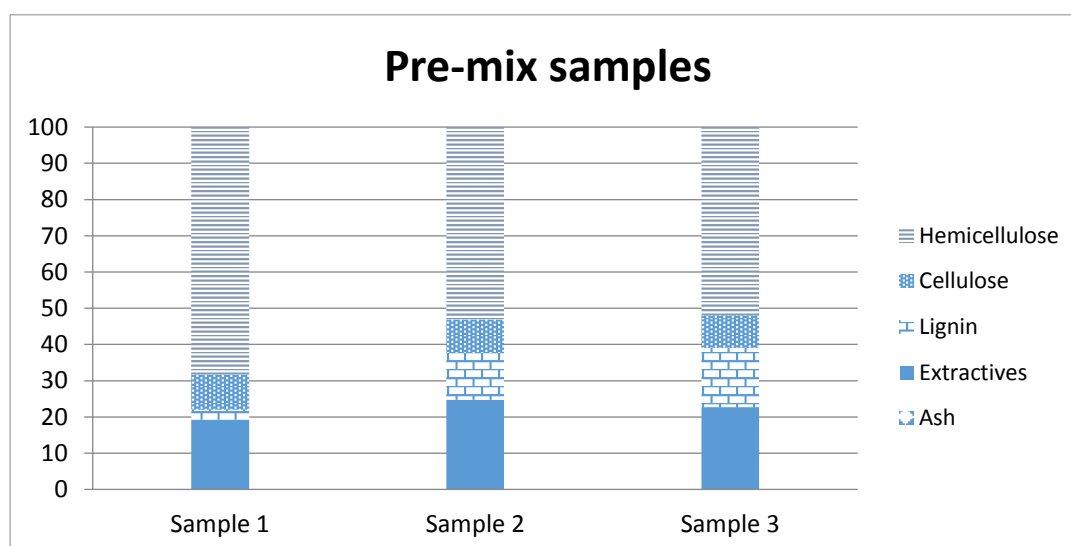
### 3.2.3. Solid loading

The effect of solids loading on furfural production has been studied in literature (Yemiş & Mazza 2011; Qi & Xiuyang 2007). Most studies suggest that lower solids loading in the range of 0.4 to 4wt% are optimum for furfural production (Oefner et al. 1992; Qi & Xiuyang 2007;

Danon et al. 2014). In order to compare the effect of solids loading on xylan and xylose on furfural formation, a concentration had to be selected that will be reasonably applicable to both saccharides. For industrial relevance, high xylose loading is more beneficial. From the feed concentrations presented in Table 1 and Table 3, it was observed that most studies were carried out at concentrations lower than 4wt%. To investigate the effect of increased xylose concentrations on the reactions, xylose concentrations above the optimum range was selected. Choosing feed concentration in the range of 4-14wt%, will enable us to explore an area of work that has not been done often and will facilitate analysis of the effect of high solid loadings on both xylan and xylose in solution.

### Feed preparation

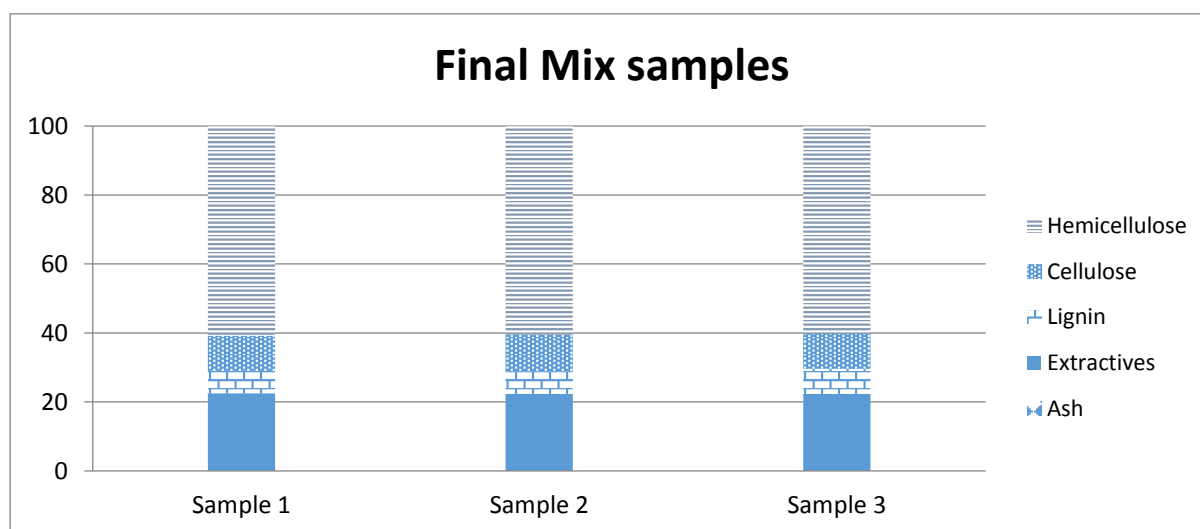
The xylose obtained was used without any further treatment or preparation. The stock was received in a powdery form with particle sizes sufficient to ensure effective mass and heat transfer during the reaction process. However, 10kg of xylan obtained from vendors were packed in smaller packets of 1kg each. Each sample pack was checked for the relative compositions. The preliminary method of characterization was performed by total sugar content analysis (by mild hydrolysis) according to the NREL laboratory analytical procedures (LAP 2012). The analytical results revealed inconsistent relative compositions of the different packets. The results from three such packets are shown in Fig 3. Therefore, the packets were mixed and sampled using the batch sampling method described in the next section.



**Fig 3: Inconsistent composition ratios of randomly sampled packets of xylan**

## Mixing and Batch Sampling Procedure

5kg of the xylan packets were mixed evenly using an Eries Magnetics 10 way rotary splitter. The equipment operates to divide each stock to 10 equal parts. The 10 representative samples were then mixed again and the operation repeated in the rotary splitter. The process was repeated for the next 5kg. Two samples from each badge was tested for relative compositions according to the NREL Laboratory analytical procedures (LAP 2012) and results showed even mixing with average standard deviations of 0.5 (Fig 4). The new sample after mixing contained 66g of xylose in every 100g of sample.



**Fig 4: Representative composition of xylan after mixing**

## Xylan feed estimation

To achieve the aim of this study, approximately equal amounts of xylose in polymeric (xylan) and monomeric forms were selected to make the two reactions comparable. Xylose concentrations of 4wt%, 8wt% and 14wt% were fed to the reactor. To obtain approximately equal concentrations of xylose in the polymeric form (xylan), xylan amounts containing the corresponding desired xylose was fed. The method for estimation is shown in Eq 18 using a basis of 66g of xylose per 100g of xylan.

$$Xylan\ feed = \frac{Corresponding\ xylose\ feed}{66} \times 100 \quad \text{Eq 18}$$

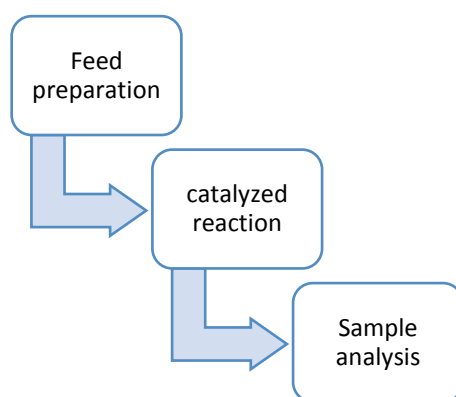
For the ease of comparison, solid loadings for xylan feed are reported with respect to the xylose concentration. For example, 60g of xylan contains 40g of xylose and will be referred to as the same loading percentage of the corresponding monomeric xylose component. The relative amounts of xylan required to make up the corresponding amounts of xylose is demonstrated in Table 6.

**Table 6: Relative feed concentrations of xylose and xylan**

Xylose feed (g)	Xylan feed (g)
40g	60g
80g	120g
140g	210g

### 3.3. Experimental Procedure

This section describes the experimental process. An overview of the experimental procedure is displayed in Fig 5.



**Fig 5: Schematic representation of experimental procedure.**

The samples are weighed using an Ohaus adventurer electronic balance with an accuracy of +/- 2g in a pre- weighed dry beaker. The amount in grams of sample is recorded and the beaker is

topped up with demineralized water to 900g. The mixture of xylose/xylan and water is stirred to dissolve the xylose and an initial sample is collected. The mixture is poured into the pre-prepped reactor, stirred at 500rpm, and heated to the set temperature. Meanwhile a dilute acid solution is prepared by weighing the required grams of H<sub>2</sub>SO<sub>4</sub> which is topped up to 100g with demineralized water. The acid bomb is filled with the dilute acid solution and screwed shut. The bomb is fitted to the reactor carefully with the right personal protection equipment.

At the set temperature (time =0 min), the dilute acid solution is dosed into the reactor under pressure by opening the bomb valves bringing the total weight of reactants to 1000g. A nitrogen gas tank is used to provide counter pressure during bombing. The reactor temperature is controlled to +/-5°C of the desired temperature until the end of the experiment.

The total time of reaction is 90mins starting from the time set temperature is arrived at (t=0). Twelve samples (2ml each) are collected during the process and sampling time is selected to allow the fast reactions to be observed and recorded. Samples are collected at time 0min, 5min, 10mins, 20mins, 30mins, 40mins, 60mins, 80mins and 90mins. The effluent line was flushed with the reaction fluid before all samples were taken to eliminate errors and ensure reproducibility. The volume of fluid per flush was calculated based on the volume of the effluent line. 13ml of reaction fluid was used per flush, with a total of 130ml loss in flushing per experiment.

#### Analytical methods

The samples are analyzed in the HPLC to determine and quantify furfural, unreacted sugars and by products in the liquid effluent including formic acids and acetate acids. The effluent samples obtained from the reactor were prepared for HPLC analysis by a simple two steps process described below

1. 0.2ml of sample is taken and diluted with 4ml of water to bring the pH to a range of (1.8-3)
2. Diluted sample is filtered through a 0.22um syringe filter into the HPLC vial and capped.



The diluted samples were analyzed in the HPLC to quantify furfural, unreacted sugars and by products, including formic acids and acetate acids. The diluted sample was analyzed with high performance liquid chromatography (HPLC). The Thermo Separations Product (TSP) HPLC was fitted with a HPX-87H Biorad column with guard cartridge, Shodex 101 RI (refractive index) detector as well as UV (Ultra violet) detector with 210nm wavelength. The column was operated at a temperature of 65°C with a mobile phase of 5mM sulfuric acid at a flow rate of 0.6ml/min. The UV detector was employed to monitor the furfural content, while the RI detector was used in measuring the sugars in solution.

### 3.4. Yield and conversion calculations

The results as obtained from the HPLC were in g/L. The concentrations obtained are corrected to compensate for the dilution factor of 0.2 ml. To adequately use this values in the modelling equation, the values were corrected to mol/L using the molecular weights (Xylose= 150.13g/mol, furfural= 96.08g/mol). The conversion of xylose and yield of furfural from xylose were estimated with the formulas in Eq 19 and Eq 19 for xylan using Eq 21 and Eq 21.

$$\text{Xylose conversion} = \frac{\text{Xylose in} - \text{Xylose out}}{\text{Xylose in}} \quad \text{Eq 19}$$

$$\text{Furfural yield from xylose} = \frac{\text{Furfural produced}}{\text{Xylose in}} \quad \text{Eq 20}$$

$$\text{Xylose yield from xylan} = \frac{\text{Xylose out}}{\text{Xylan in}} \quad \text{Eq 21}$$

$$\text{Furfural yield from xylan} = \frac{\text{Furfural produced}}{\text{Xylan in}} \quad \text{Eq 22}$$

### 3.5. Kinetics modelling

The experimental data is fitted to different kinetics models in literature to determine which one best describes the xylan and xylose conversion processes. The kinetics modelling was performed using python 3.6 with Spyder interface. The major packages utilized include NumPy, matplotlib and SciPy from the Python libraries. The reaction rate is dependent on

temperature, catalyst concentrations and feed concentrations as shown in Eq 10 and Eq 11. These reaction conditions are the major parameters in modelling the reaction.

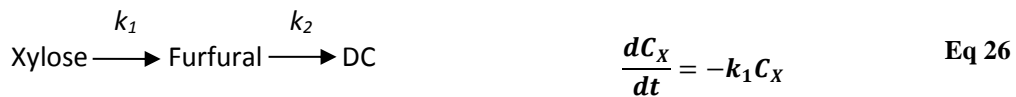
The concentration profile of xylose and furfural in reaction were simulated with the Python differential and integral solver Odeint using the initial concentrations of xylose, furfural and sulfuric acid. The rate parameters of the reaction is then determined by minimization of the Sum of squared errors using the Nelder-Mead method from SciPy. The reaction parameters were solved by iteration using initial conditions from literature. The conditions were adjusted until optimization was complete. This method have been proven to result in accurate estimations also used by (Danon et al. 2014). The simulated model is selected by the measurement of the minimum error between the model and the corresponding experimental component. The coefficient of determination ( $R^2$ ) equation is used determine the level of agreement of the simulated model and experimental data. Different rate equations were simulated and the mechanism with the best fit and  $R^2$  was selected. The calculation of the coefficient of determination is demonstrated in Eq 23 to Eq 25. The reaction mechanism and the corresponding rate equations for xylose conversion and furfural formation considered in the modelling are shown in Eq 26 to Eq 28.

$$R^2 = 1 - \frac{\text{Sum of squared error residual (SSE}_{res})}{\text{Sum of squared error total (SSE}_{tot})} \quad \text{Eq 23}$$

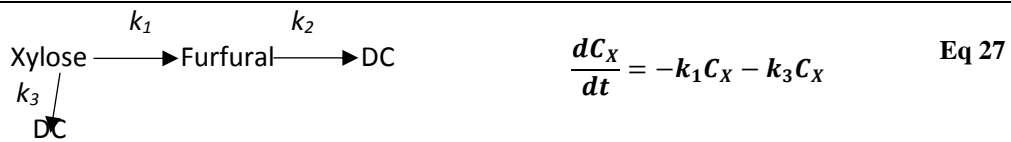
$$SSE_{res} = \sum_i (y_i - f_i)^2 \quad \text{Eq 24}$$

$$SSE_{tot} = \sum_i (y_i - \bar{y})^2 \quad \text{Eq 25}$$

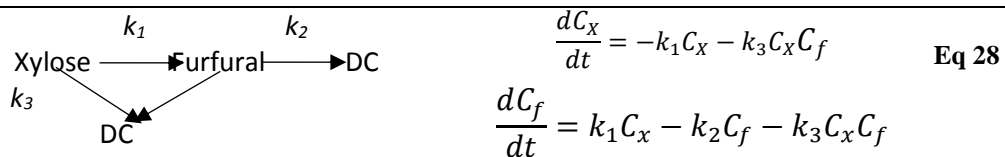
Where  $y_i$  is a term of the experimental data,  $f_i$  is the corresponding model data of  $y_i$  and  $\bar{y}$  is the mean of experimental data.



$$\frac{dC_f}{dt} = k_1 C_x - k_2 C_f$$



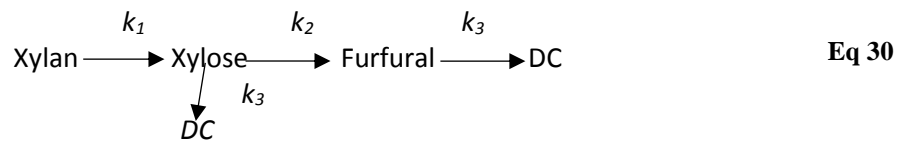
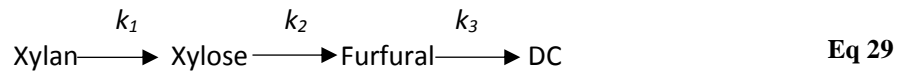
$$\frac{dC_f}{dt} = k_1 C_x - k_2 C_f$$



$$\frac{dC_f}{dt} = k_1 C_x - k_2 C_f - k_3 C_x C_f$$

The models described above were selected from literature as relevant reaction models for xylose conversion reactions. From literature, the effect of intermediates on the reaction were considered negligible at high severity conditions such as the one applied in this study (temperature (140 °C-170 °C), solids loading (4-14wt %) and H<sub>2</sub>SO<sub>4</sub> concentration (0.5wt%-2wt %)) (Antal et al. 1991; Ahola & Tanskanen 2012). Eq 26 is described by a first order xylose dehydration to furfural in which side reactions are considered non-existent or negligible. This mechanism was based on a similar work done by Root et al. (1956). The model described in Eq 26 is the simplest model recorded in literature suggesting a 100% xylose conversion to furfural. Hence, all degradation reactions are assumed to be as a result of furfural resinification degradation reaction since no reactions besides xylose dehydration to furfural can be accounted for in this model. On the other hand, Eq 27Eq 28 are described by reactions that include a direct xylose degradation to side products (Ahola & Tanskanen 2012; Byul et al. 2011; Danon et al. 2014; Qi & Xiuyang 2007; Liu et al. 2014) and a condensation degradation reaction that involves xylose and furfural reactions to form degradation products, respectively (Weingarten et al. 2010). The selection of equation Eq 27 and Eq 28 will confirm the presence of degradation reactions as proposed in the studies above. The selection of the best fit model was based on R<sup>2</sup> measurement for best fit as described in Eq 23.

The kinetics modelling of xylan conversion to furfural was conducted in a manner similar to the previously described xylose conversion modelling. In as much as there were no adequate models found in literature to describe specifically the conversion of pre-extracted xylan to furfural, basic models (Eq 29 and Eq 30) derived from the direct method of furfural production (Lavarack et al. 2002; Chiang et al. 2008; Dussan et al. 2013) were investigated to select the model that best describes the conversion process. Initial consideration of the fast and slow xylan conversion showed poor model-data agreement as reported by other authors (Lavarack et al. 2002). The quality of the models were monitored by testing duplicate experiments, plotting figures of parameter progression, plotting figures as a function of each parameter and performing statistical analysis on the experimental data.



## Chapter 4 Results and discussions

The aim of this study was to provide a better fundamental understanding of the kinetics of xylan and xylose conversion to furfural. Experiments were carried out at different operating conditions to obtain kinetics data that were fitted to mechanism models presented in literature. This was to determine the model that best describes the conversion of xylan and xylose to furfural and consequently determine the differences between the two conversion processes. Further, the interactions between the important process variables will be investigated to determine the significant parameters of reaction and their effect on the reaction. In this section, kinetics models and parameters of the xylose and xylan conversion processes are investigated separately, and the two models are compared to show the differences.

To effectively determine the kinetics of furfural formation, 27 experiments were performed for xylan and xylose substrates each. Experimental results at 90minutes are summarized in Table 7, while the complete experimental data is presented in appendix B.

### 4.1. Effect of operating condition on reaction

Statistical analysis of these results were carried out to ascertain the significance of the experimental variables on the results. The p-values are measured for each response variable and the results are reported in Table 8. The recorded p-value evaluates the probability of the selected reaction variable having a significant effect on the reaction. The p-value less than 0.05 ( $p < 0.05$ ) is the threshold of significance of measurement and ( $p < 0.05$ ) suggests that the effect of the selected variable on the reaction is significant. From the analysis, it was determined that solids loading had no significant effect on the reaction.

**Table 7:** Experimental conditions and the resulting xylose conversion and furfural yields obtained at 90minutes reaction time

Number	Experimental variables			Response variables			
	Temperature (°C)	Solids concentration (wt %)	Acid concentration (wt%)	Xylose feed(g/g)		Xylan feed(g/g)	
				Xylose Conversion	Furfural Yield	Xylose conversion	Furfural yield
1	140	4.00	0.50	0.40	0.10	0.53	0.21
2	140	4.00	1.00	0.47	0.14	0.71	0.22
3	140	4.00	2.00	0.66	0.12	0.72	0.34
4	140	8.00	0.50	0.34	0.07	0.33	0.12
5	140	8.00	1.00	0.59	0.06	0.51	0.20
6	140	8.00	2.00	0.68	0.06	1.00	0.18
7	140	14.00	0.50	0.42	0.04	0.20	0.16
8	140	14.00	1.00	0.45	0.10	0.30	0.21
9	140	14.00	2.00	0.65	0.15	0.70	0.47
10	155	4.00	0.50	0.59	0.10	0.64	0.30
11	155	4.00	1.00	0.81	0.22	0.93	0.37
12	155	4.00	2.00	1.00	0.24	0.95	0.30
13	155	8.00	0.50	0.62	0.14	0.43	0.31
14	155	8.00	1.00	0.85	0.16	0.76	0.78
15	155	8.00	2.00	0.96	0.19	0.93	0.59
16	155	14.00	0.50	0.68	0.07	0.68	0.41
17	155	14.00	1.00	0.95	0.23	0.84	0.53
18	155	14.00	2.00	0.98	0.14	0.97	0.38
19	170	4.00	0.50	0.92	0.24	1.00	0.40

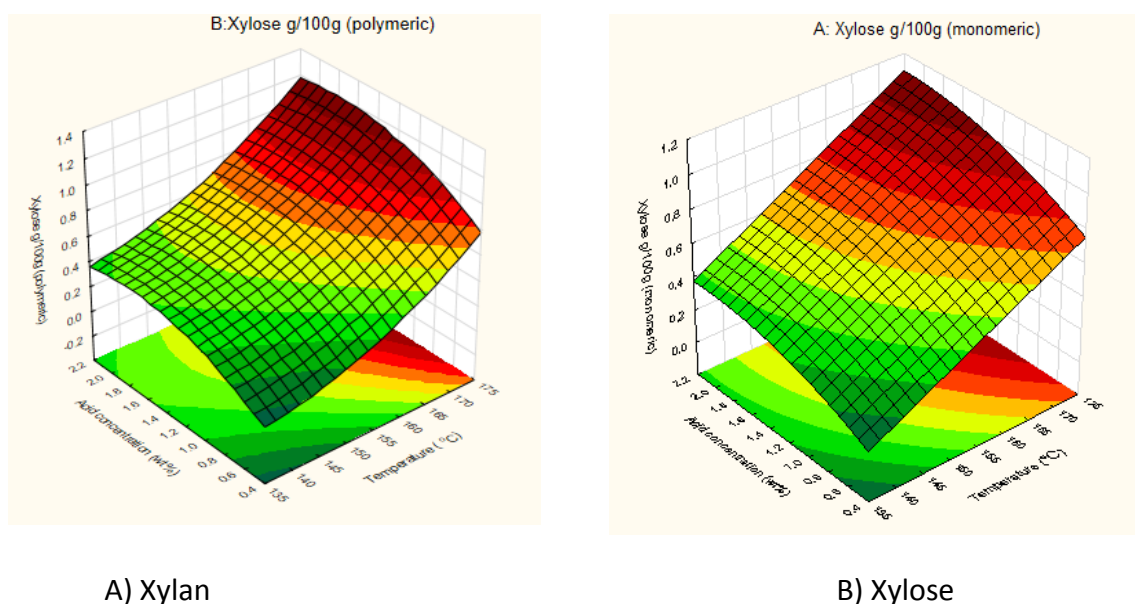
**Table 7:** Experimental conditions and the resulting xylose conversion and furfural yields obtained at 30minutes reaction time (continued)

Number	Experimental variables			Response variables			
	Temperature (°C)	Solids concentration (wt %)	Acid concentration (wt%)	Xylose feed(g/g)		Xylan feed(g/g)	
				Xylose Conversion	Furfural yield	Xylose conversion	Furfural yield
20	170	4.00	1.00	1.00	0.22	1.00	0.23
21	170	4.00	2.00	1.00	0.10	1.00	0.19
22	170	8.00	0.50	0.94	0.19	0.79	0.74
23	170	8.00	1.00	0.98	0.19	1.00	0.48
24	170	8.00	2.00	1.00	0.10	1.00	0.23
25	170	14.00	0.50	0.94	0.15	1.00	0.15
26	170	14.00	1.00	0.99	0.05	1.00	0.41
27	170	14.00	2.00	1.00	0.10	1.00	0.15

**Table 8:** P-values for xylose conversion and furfural yields in the process of converting xylan and xylose to furfural

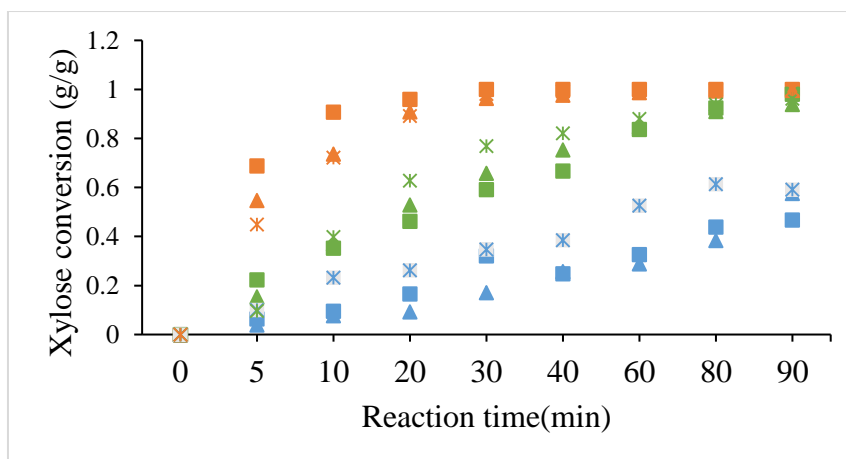
Variables	p-values			
	Xylose feed (g/100g)		Xylan feed (g/100g)	
	Xylose g/100g	Furfural g/100g	Xylose g/100g	Furfural g/100g
Temperature (T) (°C)	0.0000	0.0000	0.0000	0.0000
Solids concentration (S) wt%	0.5200	0.0400	0.4100	0.0660
Acid concentration (A) (wt%)	0.0000	0.0005	0.0000	0.0180
TXS	0.6000	0.0800	0.2400	0.6600
TXA	0.4770	0.1780	0.6500	0.0580
SXA	0.4800	0.6700	0.1900	0.1800

As can be seen from Table 8, temperature had a significant effect on the reaction ( $p < 0.05$ ). The effect of temperature on xylose dehydration was measured for both xylan and xylose and the surface plot diagram is presented in Fig 6. As can be seen the maximum conversion occurred at 170 °C for both xylan (Fig 6a) and xylose (Fig 6b) reactions. To demonstrate the effect of temperature on the reaction further, The change in xylose concentration with change in temperature (140 °C -170 °C) and solids loading (4wt% - 14wt%) at 5wt% acid concentration is shown in Fig 7, for xylose substrate. As demonstrated in Fig 7, the highest conversion achieved at 140°C was 62% compared to the 100% conversion achieved at 170°C. At lower temperatures, maximum xylose conversion is not achieved, leaving most of the xylose unreacted. As temperature increased from 140 °C to 170 °C the reaction conversion is increased until a 100% conversion is achieved at 170 °C. Similarly, furfural yields from both xylan and xylose are positively influenced by temperature. Fig 8 shows a relation of furfural formation in xylan compared to xylose with increase in temperature. These observations are in line with literature as generally high temperatures have resulted in higher rates of xylose conversion and high furfural yields (Borrega et al. 2011; Yemiş & Mazza 2011; Yang et al. 2006).



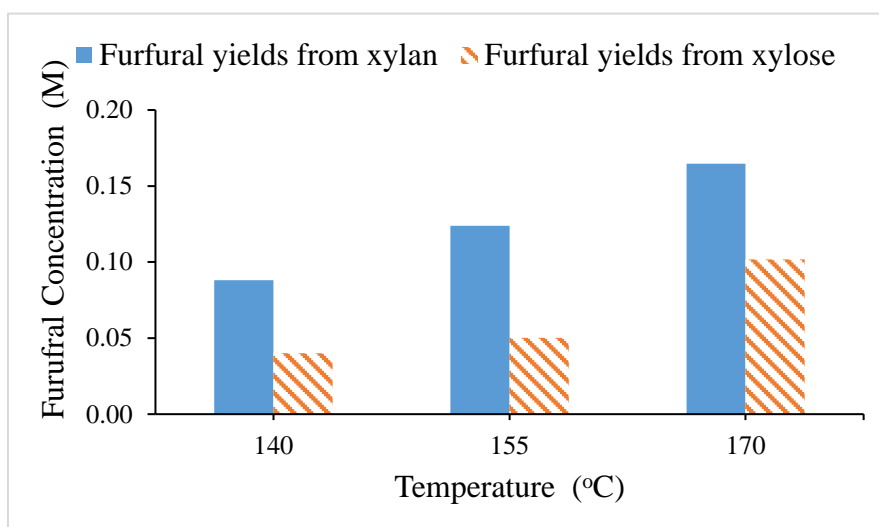
**Fig 6:** Surface plot diagram of A) xylose conversion to furfural, B) xylan conversion to furfural (xylose-equivalent) as a function of Temperature and acid loadings





**Fig 7:** Xylose conversion with change in temperature and solid loading (Xylose feed) at 0.5wt%

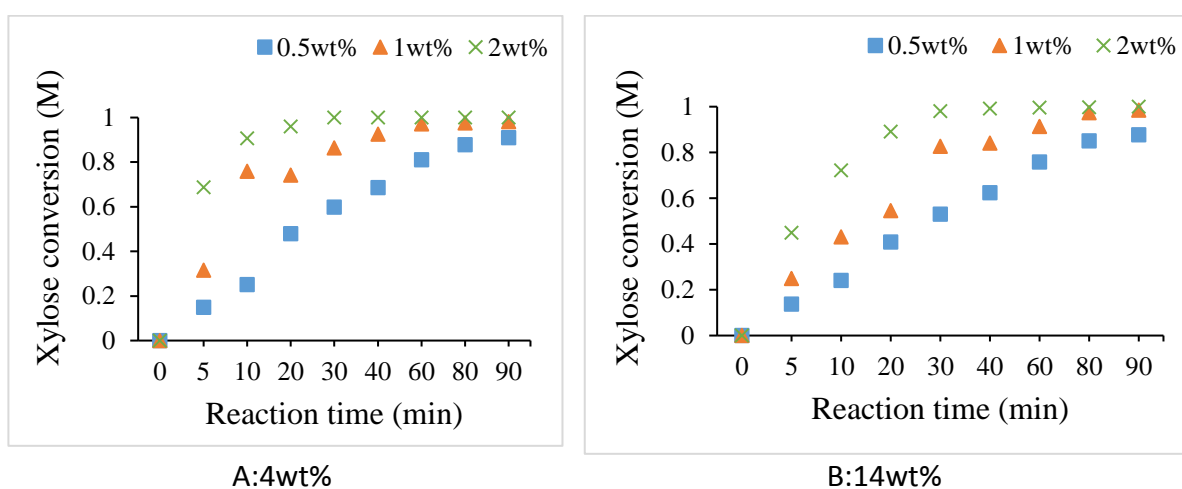
(●:140 °C; ●: 155°C, ●:170°C, ■:4wt%; ▲: 80wt%;\*140wt%)



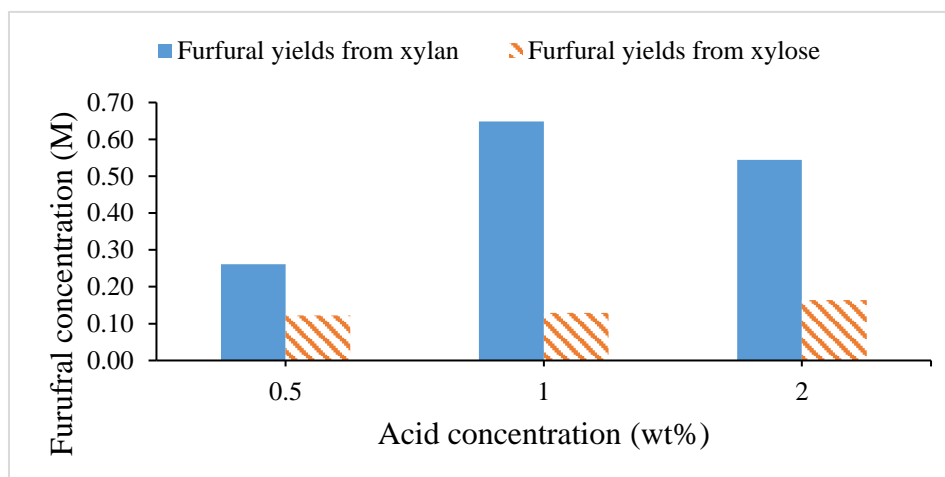
**Fig 8:** Relative furfural yields from xylan and xylose with change in temperature at 0.5wt% acid concentration, 4wt% solids loading and 30minutes reaction time.

Acid concentrations also demonstrates a significant effect on the reaction process involving the two substrates, as presented in Table 8. The effect of acid concentration on the reaction is further demonstrated in Fig 9 and Fig 10 for xylose conversion and furfural yields, respectively. An increase in acid concentration resulted in increased conversion of xylose to furfural at all other conditions. At the severest of conditions (170°C, and 14 wt% xylose concentration), xylose conversion increased progressively until 100% conversion was achieved within 80minutes for 1 wt% of acid concentration. When the acid concentration was increased to

2wt%, 100% conversion is observed earlier at 30mins as can be seen in Fig 9b. A semi-linear relationship between acid concentration and xylose conversion was suggested by (Chiang et al. 2008). However, the effect of acid concentration on furfural formation cannot be described as linear. This is due to the presence of degradation reactions in furfural that is highly dependent on acid concentration. The increase in acid concentrations increases furfural formation to some extent, whereas further increase in acid concentration will result in lower yield due to increased furfural degradation. A follow up kinetics studies of furfural degradation can be found in Steiner (2018).



**Fig 9:** Xylose conversion with change in acid concentrations and solids loading at 170°C



**Fig 10:** Relative furfural yields from xylan and xylose with change in acid concentration at temperature 170°C, 4wt% solids loading and 30mins reaction time

## 4.2. Kinetics of xylan and xylose conversion to furfural

The experimental data obtained from the catalyzed dehydration of xylose were fitted to different reaction schemes presented in literature. The rate equations obtained from the reaction schemes were used to estimate the kinetics parameters of the reaction. Several reaction schemes were considered and the reaction scheme which best described the process was selected. The whole range of experimental data (27 runs) for each experimental set (xylan and xylose) were modelled together to enable the selection of kinetic models that can predict the reaction over a wider range of conditions.

### 4.2.1. Monomeric xylose conversion to furfural

Three different mechanisms of a first order kinetic model (Eq 26 to Eq 28) described in the methodology were investigated for xylose conversion to furfural and the best fitting model was selected based on the  $R^2$ . The reaction was assumed to be first order with respect to the pentose and acid concentrations. Model- Experimental data fit were conducted for the schemes presented in Eq 26 to Eq 28. Eq 26 showed a fit with  $R^2$  of 0.81 showing a good agreement with a first order dependency on the pentose concentration and also the acid concentration terms. Eq 27 showed wide deviations demonstrating non agreement with the first order reaction scheme assumed with  $R^2$  values of 0.62. Model-data fit for Eq 28 even showed greater deviations with very low  $R^2$  values of 0.57. Previous literature unanimously agrees that xylose conversion to furfural are fundamentally a pseudo first order reaction (Danon et al. 2014). A combined first order and second order reaction was only suggested by (Byul et al. 2011) for the xylose degradation to side reaction term, whilst maintaining a first order reaction for the xylose conversion to furfural. The first order reaction assumption is maintained in this study for the purpose of selecting the reaction scheme from literature that best describes the reaction processes. For this reason, a first order reaction scheme, Eq 26 demonstrated as Scheme 1 was found to be the best fit reaction model within the scope.

Fig 11 and Fig 12 displays the experimental data for xylose conversion together with their corresponding predicted kinetics curves for the best model (Scheme 1) at different temperatures, acids concentrations and xylose concentrations. Fig 11a-c shows the experimental data and model (Scheme 1) for xylose conversion at 4wt%, 8wt% and 14wt%,

respectively. As can be seen the model which suggests a complete xylose conversion to furfural, fits quite well to the experimental data with  $R^2$  above 0.80 at 140 °C. This agreement demonstrates a good model-data fit of the initial assumption of a first order model. However, as demonstrated in Fig 12a-c at higher temperature (170 °C) the model showed deviations from the experimental data. This deviations in the model suggests that at different temperatures, the reaction could be explained by a reaction order the first order reaction initially assumed. Antal et al. (1991) determined that the mechanism of xylose dehydration could be different at higher severity conditions, such as the high temperature in this study.

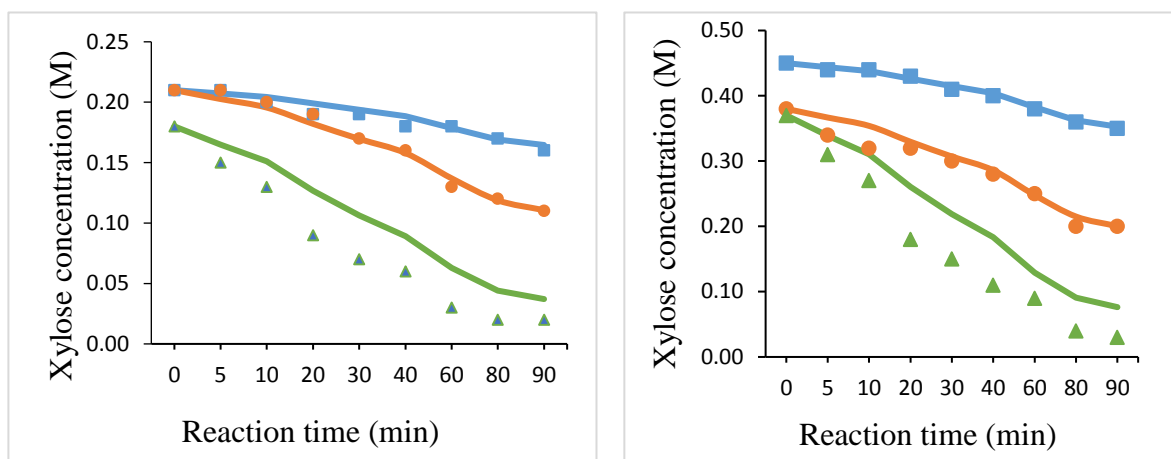
However, Scheme 1 was the best fit reaction scheme from literature that describes the kinetics conversion of xylose to furfural for the specified range of conditions investigated in this study. The scope of this study was to select a single model from literature that best describe the conversion process over the range of conditions investigated in this study. Scheme 1 was demonstrated by Root et al. (1956) and Oefner et al. (1992) for sulfuric acid catalyzed conversion of xylose to furfural.



Where  $k_1$  and  $k_2$  are first order reaction rates constants for xylose and furfural decomposition, respectively and DC the lump sum of degradation products formed in reaction.

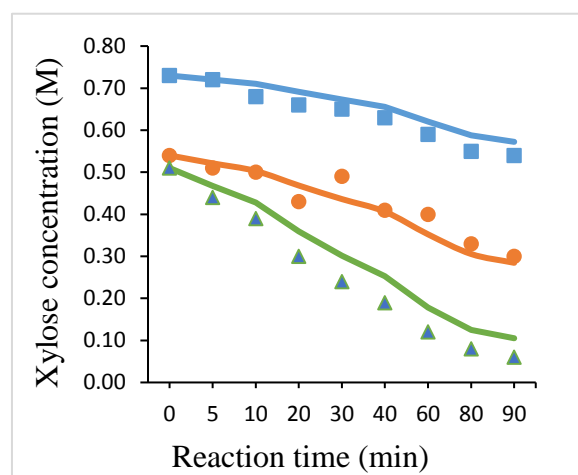
The reaction parameters for the reaction were determined with respect to Scheme 1 and were found to be within the range of literature values (Byul et al. 2011; Qi & Xiuyang 2007; Ahola & Tanskanen 2012). The activation energy (95 kJ/mol) recorded in this study is within the range (78 -180) kJ/mol reported in literature for different models and reaction conditions (Byul et al. 2011; Qi & Xiuyang 2007; Ahola & Tanskanen 2012). The pre-exponential factor (A) was found to be  $4.64 \times 10^{10}$  m<sup>3</sup>/mols. A summary of the values for activation energy found in this work compared to literature, considering Scheme 1 is presented in Table 9. Comparison of these studies indicates that increase in temperature results in increased energies of the reaction molecules and consequently the activation energies, as also reported by (Yemiş & Mazza 2011). It can be seen that the activation energy recorded for this study is lower compared to the value recorded by (Root et al. 1956 & Oefner et al. 1992). Root et al.(1956) reported a higher upper temperature limit with the highest value of activation energy (280°C, 140kJ/mol)

followed by Oefner et al (1992) (200°C, 130kJ/mol) with the present study recording the lowest upper limit temperature and corresponding activation energy (170°C, 95kJ/mol).



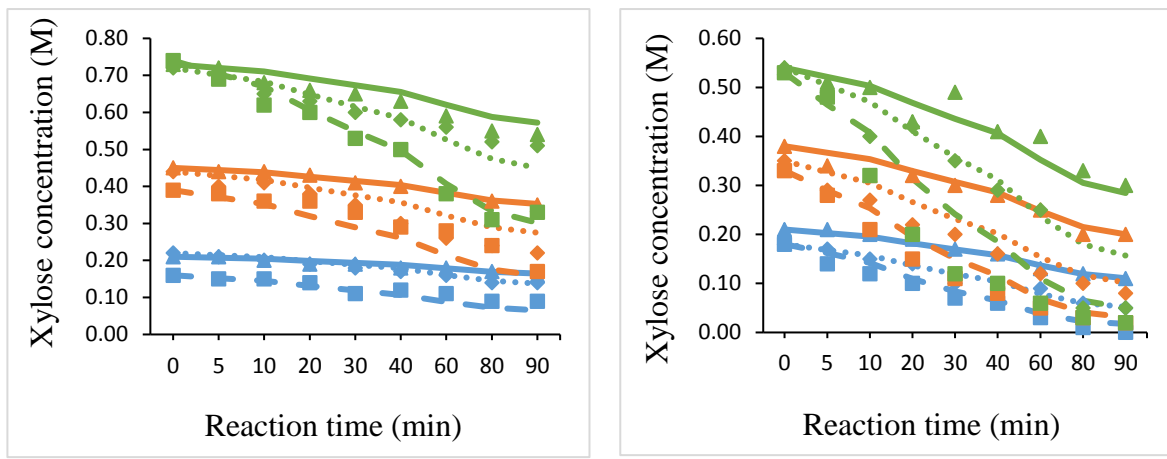
A) 4wt% xylose concentration

B) 8wt% xylose concentration



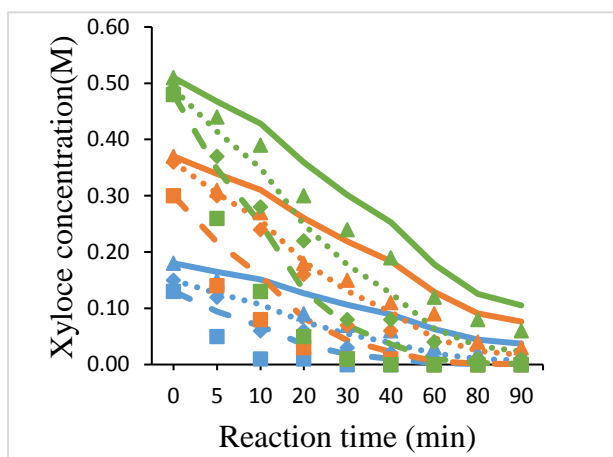
C) 14wt% xylose concentration

**Fig 11:** Experimental and predicted xylose conversion (scheme 1) with varying temperatures (■140°C; ●155°C, ▲.170°C) and xylose concentration (A: 4wt.%; B: 8wt.%; C: 14 wt.%) at 0.5wt% acid concentration.



A) 140°C

B) 155°C



C) 170°C

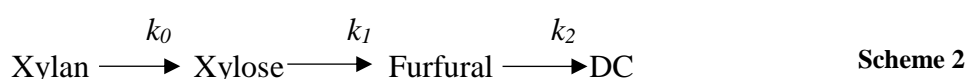
**Fig 12:** Experimental and predicted xylose dehydration with varying solids loading (● 4 wt% ● 8 wt%, ● 14 wt%), acid concentration (Δ 0.5 wt%, ◇ 1 wt% and □ 2 wt%) and temperature (A: 140°C; B: 155°C.; C: 170°C)

**Table 9: Reaction parameters and experimental conditions comparison**

References	Substrate	Reaction mechanisms	Temperature (°C)	Catalyst	Activation energy(kJ/mol)
This study	Xylose	1	140-170	H <sub>2</sub> SO <sub>4</sub>	95
Oefner et al. 1992	Xylose	1	180-200	H <sub>2</sub> SO <sub>4</sub>	130
Root et al. 1956	Xylose	1	160-280	H <sub>2</sub> SO <sub>4</sub>	140

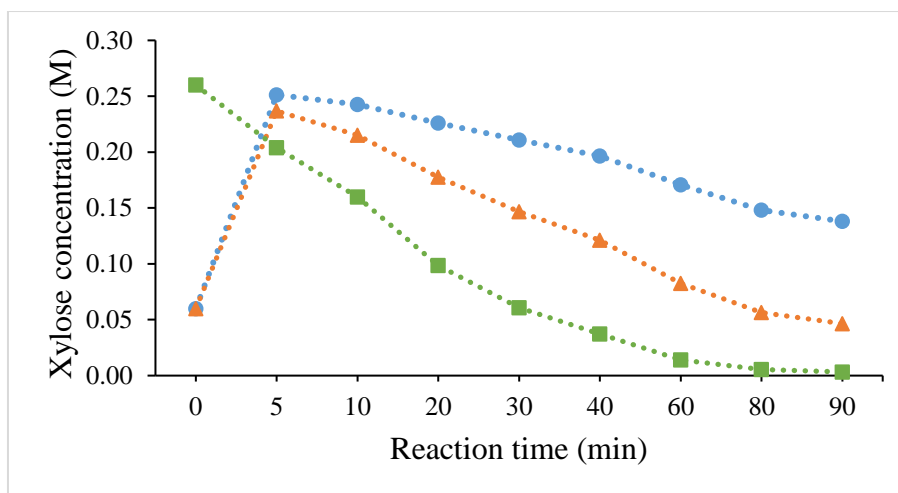
#### 4.2.2. Polymeric xylan conversion to furfural

Scheme 2, a two-step first order reaction model developed for xylan conversion by (Zeitsch 2001) was found to describe the reaction sufficiently with R<sup>2</sup> of 0.78 compared to the alternate model obtained from (Dussan et al. 2013) with R<sup>2</sup> value below 0.5 . It is worth mentioning that the reaction was monitored based on the xylose concentration observed relative to the xylose concentration fed in the reaction. The hydrolysis of xylan to xylose and dehydration of xylose to furfural is demonstrated at temperatures (140°C to 170°C) and solid loadings at 4wt% in Fig 13.



Where  $k_0$ ,  $k_1$  and  $k_2$  are first order reaction rate constants for xylose formation and xylose degradation and furfural degradation, respectively.

As can be seen from the Fig 13, hydrolysis reaction is faster than dehydration of xylose, as accumulation of xylose is observed within the first 5 minutes of the reaction. Most experiments at 140°C and 155°C reached the highest xylose concentration in 5minutes, whereas the conversion at 170 °C and 4 wt. % resulted in maximum xylose formation before the 5 minutes reaction time. Xylose formation, dehydration and furfural degradation are all simultaneous reaction processes. Although there is no literature for xylan conversion to furfural demonstrating similar observations, the previous study of furfural production from direct method demonstrates similar fast xylan hydrolysis prior to the xylose conversion reaction (Eken-Saraçoğlu et al. 1998; Lavarack et al. 2002; Dussan et al. 2013).

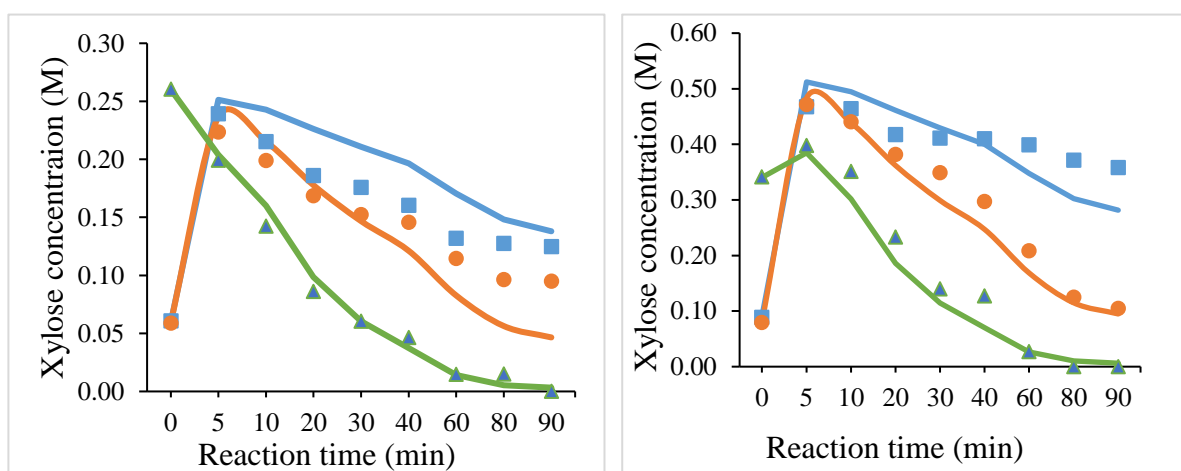


**Fig 13:** Xylose formation pattern at different temperatures at 4wt.% xylose concentration and 0.5wt% acid concentration  
 (●.140°C, ▲.155°C, ■.170°C)

From Fig 14 and Fig 15, Scheme 2 suggests that the hydrolysis step of the reaction is fast occurring in the first 5 minutes of reaction accompanied by a simultaneous xylose dehydration to furfural. Xylose dehydration to furfural happens without the direct formation of side and by products from xylose. Other studies have suggested similar mechanism for xylan conversion in the direct method (Lavarack et al. 2002). Although the model agrees well with the experimental data at 170 °C ( $R^2$  above 0.9), it failed to predict the experimental results at lower temperature as can be seen in Fig 14. Fig 14 showed the most deviation from the results at 140 °C and 0.5 % acid concentration. Whereas the deviation due to temperature was attributed to a shift in mechanism due to the range of temperature considered in this study (Antal et al. 1991), the deviation of the experimental data from the model at lower acid concentrations (0.5wt% -1wt%) was attributed to the assumption of “specific acid catalysis” rather than “general acid catalysis” in the rate equation as described by (Zeitsch 2001). The general acid catalysis effect is defined as the effect of the total catalytic species of the reaction in this case mineral acids ( $H_2SO_4$ ) and weak organic acids (acetyl acids). Whereas specific acid effect is the consideration of the dominant catalyst specie ( $H_2SO_4$ ) whilst the weaker acids component are considered negligible. This assumption is only adequately correct at high concentrations of strong mineral acid catalyst such as  $H_2SO_4$ . In this study, this assumption only holds true at 2wt% where the effect of the weak organic acids could be considered negligible, hence the catalytic effect applied in the model and experimental design become equals whereas, at acid

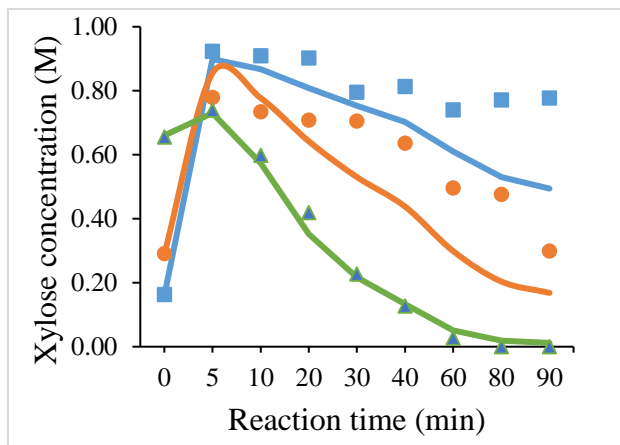


concentrations less than 2wt% the catalytic effect of the experimental data is higher (general) than that of the model (specific) resulting in model under prediction. As seen in Fig 15 at 2wt% H<sub>2</sub>SO<sub>4</sub>, the catalytic effect of the weak acids becomes insignificant equating the general acid effect (experimental data) to the specific acid effect (predicted model) hence a good model data agreement as observed. The reaction parameters obtained for this study were  $7.75 \times 10^8 \text{ m}^3/\text{mols}$  and 55 kJ/mol for the pre exponential factor (A) and activation energy ( $E_a$ ), respectively for xylan hydrolysis to xylose and  $2.96 \times 10^{11} \text{ m}^3/\text{mols}$  (A) and 98 kJ/mol ( $E_a$ ) for xylose dehydration to furfural. Since there were no relevant kinetics model in literature to compare, a thorough kinetic investigation should be done to enable development of a detailed mechanism at lower temperature. The complete set of experimental and model concentration profiles from the suggested models Scheme 1 and Scheme 2 are presented in Appendix C with their corresponding coefficient of determination values.



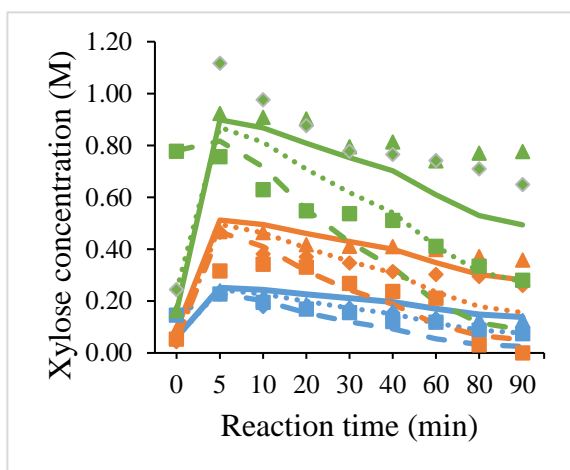
A) 4wt% xylose concentration

B) 8wt% xylose concentration

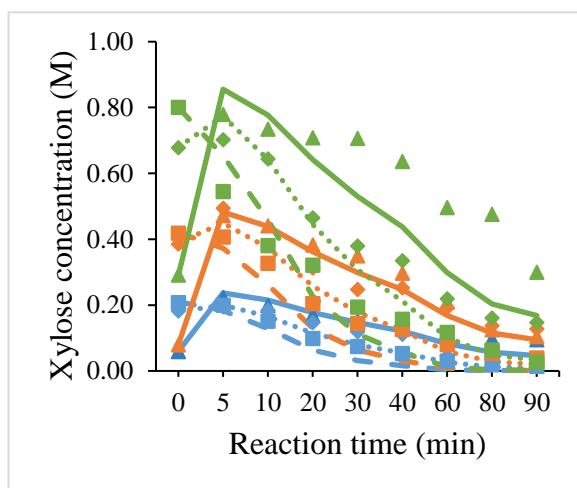


C) 14wt% xylose concentration

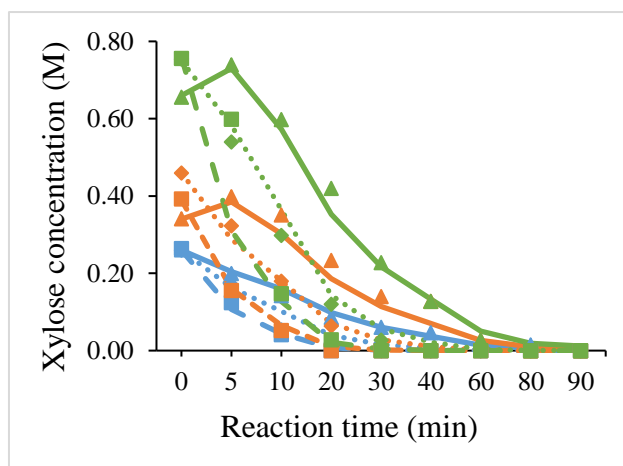
**Fig 14:** Experimental and predicted values for xylan conversion to furfural (xylose-equivalent) with varying temperatures (■ 140°C; ● 155°C, ▲ 170°C) and solids loading (A: 4wt.%; B: 8wt.%; C: 14 wt.%) at 0.5wt% acid concentration,



A 140°C



B 155°C



C 170°C

**Fig 15:** Experimental and predicted values for xylan conversion (xylose-equivalent) with varying solids loading (● 4 wt% ● 8 wt%, ● 14 wt%), acid concentration (Δ 0.5 wt%, ◇ 1 wt% and □ 2 wt%) and temperature (A: 140°C; B: 155°C.; C: 170°C)

#### 4.2.3. Comparison of the kinetics of xylan and xylose conversion to furfural

As discussed in the model generation section, xylose dehydration in both xylose and xylan conversion process can be described by a first order single step reaction without any intermediate formation and side reaction (Scheme 1 and Scheme 2, respectively). As discussed, it was generally determined that the selected reaction schemes were the best kinetics models in the literature to describe xylan and xylose conversion within the specified range of conditions. However, the kinetic models demonstrated deviation from experimental results at 170 °C for xylose conversion and 140 °C for xylan conversion model. These deviations were attributed to the wide range of experimental data and the possibility of a shift in reaction mechanism with change in reaction conditions (Antal et al. 1991). Although this was observed, the aim of the study was to choose a kinetic model valid for a wide range of operating conditions and therefore different kinetic models for different operating conditions were not investigated.

Furthermore, it was found that hydrolysis step (in xylan conversion process) was very fast compared to xylose dehydration reaction. The low  $E_a$  (55 kJ/mol) obtained for the xylan

hydrolysis step relative to the  $E_a$  (98 kJ/mol) for the dehydration step indicated the dehydration step as the rate determining step. The overall conversion reaction is more dependent on the xylose dehydration reaction that has activation energies of 98 kJ/mol. The reaction parameters for xylan and xylose conversion to furfural are summarized in Table 10. There are currently no investigative studies on the kinetics of xylan and xylose conversions together. However, rapid hydrolysis of xylan and xylose accumulation in xylan conversion process using whole lignocellulose biomass have been suggested by (Lavarack et al. 2002; Chiang et al. 2008).

**Table 10: Summary of reaction parameters for xylan and xylose conversion to furfural (A=m<sup>3</sup>/mols, E=kJ/mol)**

Feed	$k_0$		$k_1$		$k_2$	
	A	E <sub>a</sub>	A	E <sub>a</sub>	A	E <sub>a</sub>
Xylan	$7.75 \times 10^8$	55	$2.96 \times 10^{11}$	98	$1.20 \times 10^{11}$	120
Xylose	-	-	$4.64 \times 10^{10}$	95	$3.77 \times 10^2$	28

As discussed in sections 4.1.1 and 4.1.2, xylose degradation and condensation degradation reactions were found to be negligible in the range of condition investigated in this study. The suggested kinetics of xylose dehydration for both xylose and xylan includes a simple xylose dehydration model without side or degradation products formation (Scheme 1 and Scheme 2, respectively). This is in agreement with the previous literature where the rate of xylose disappearance was not affected by loss reactions including condensation degradation reactions (Zeitsch 2001; Rushin & Natal 1992; Oefner et al. 1992). (Rushin & Natal 1992) suggested a 100% xylose conversion to furfural with a conclusion that all degradation formed in the reaction are a resultant of furfural degradation and not from xylose decomposition. Danon et al. (2014) also stated that the rates and kinetics of xylose conversion is not affected by other components of the reaction including carbohydrates and furfural hence the condensation reaction is negligible.

In addition, the results showed higher yields of furfural from xylan compared to xylose over all investigated conditions as presented in Table 7. This observation was attributed to the loss

of feed material at the heating up phase of the reaction and the degradation of the furfural once produced, which will be discussed in the following sections.

The loss of feed material during the heating up period of the reaction is believed to affect the furfural yields obtained in this study. The batch reactor system used required an average of 30min, 45mins and 60min to heat up to 140°C, 155°C and 170°C, respectively. This heat up period resulted in loss of xylose in both feed substrates. However, higher losses were observed in xylose conversion relative to the xylan conversion process. The losses observed in the xylose feed reaction could be responsible for the low yields recorded in this study. The average amount of xylose loss (calculated from nine measurements) in xylose converting experiments is summarized in Table 11. It is worth mentioning that the xylose concentrations at the temperature set point in the xylan converting experiments could not be measured accurately after the heat up phase of the reaction due to the possibility of oligomer formation that are not easy to measure. However, the measurements obtained demonstrated higher losses in the xylose compared to xylan. A previous study of furfural yields from xylan and xylose with H<sub>2</sub>SO<sub>4</sub> showed higher furfural yields from xylose compared to xylan for all conditions experimented (Yemiş & Mazza 2011). The study attributed the lower furfural yields obtained from xylan to the insolubility of the birchwood xylan used in their study, which they suggested could have resulted in direct charring of some xylan without forming furfural. However, the xylan used in this study was soluble, eliminating the possibility of direct charring. The loss of xylose in this study on the other hand can be attributed to auto conversion of xylose in high temperature liquid water (HTW) as previously reported in literature (Qi & Xiuyang 2007; Byul et al. 2011) (Rushin & Natal 1992; Yemiş & Mazza 2011).

**Table 11: Estimated amounts (g) of xylose lost during heat up period**

Temperature/Initial loading	40g	80g	140g
140 <sup>0</sup> C	4	5	27
155 <sup>0</sup> C	6	11	56
170 <sup>0</sup> C	7	19	59

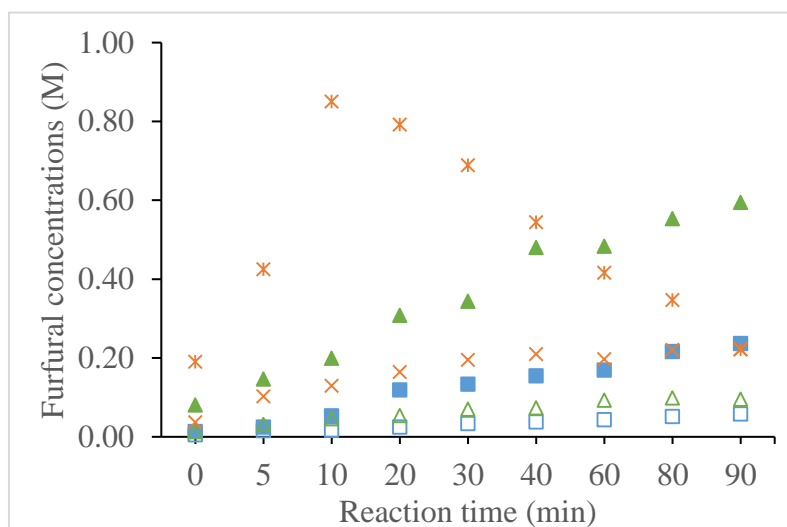
In order to further compare the furfural yields of the conversion processes, the kinetic models were extended considering a first order reaction to account for furfural degradation and the kinetic parameters of the models. The degradation products measured include solid humins,

formic acids and acetic acids. Although the conversion reaction schemes (Scheme 1 and Scheme 2) accounted for furfural degradation, low  $R^2$  values were observed showing poor data-model agreement. Gairola & Smirnova (2012) suggested that, it will require separate modelling of the conversion process and degradation process in order to obtain optimum kinetic models for the complete conversion processes. Similarly, the furfural formation and degradation processes were considered separately by Danon et al. (2014). In anticipation of these results, the kinetics of furfural degradation was studied separately to provide accurate models in Steiner (2018).

Nonetheless, the activation energies recorded indicated that higher rate of resinification degradation occurred for xylose conversion compared to xylan conversion. As presented in the Table 10. Ideally, the kinetic parameters ( $A$ ,  $E_a$ ) of the conversion processes for each conversion step  $k_1$  and  $k_2$  would be the same due to the kinetic models of the two conversion processes. This is evident in the  $k_1$  parameters of reaction that showed close relation with deviations that can be explained by random experimental errors and approximation of values. This observation was however different for the  $k_2$  values that showed deviations as shown in Table 10. The activation energies of furfural degradation reaction was found to be 120 kJ/mol and 28 kJ/mol for xylan and xylose conversion processes, respectively. Comparison of the activation energies for furfural degradation (120 kJ/mol) and furfural production (98 kJ/mol) suggests that in xylan conversion process furfural accumulation occurred as the latter had lower activation energy. However, xylose conversion process performed differently as degradation of furfural was faster than its production (activation energy of 28 kJ/mol vs. 95 kJ/mol) which resulted in faster furfural degradation and consequently lower furfural yield. The lower activation energies for furfural degradation in xylose conversion processes is observed by some authors and is believed to be responsible for the low yields recovered over time (Ahola & Tanskanen 2012; Byul et al. 2011; Hongsiri et al. 2014). However, there are no relevant kinetics parameters to be compared to the xylan conversion.

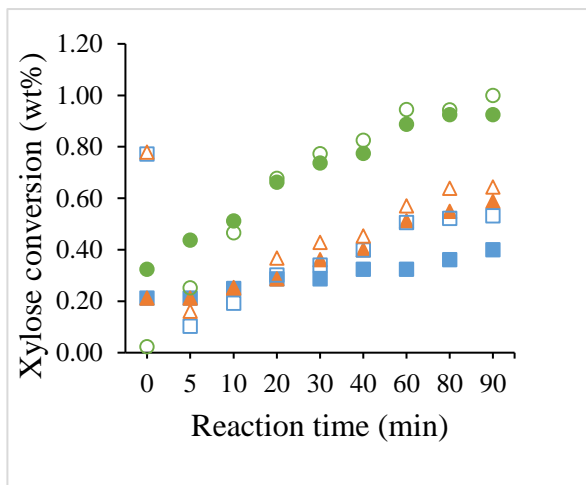
Further, relative furfural yields from xylan and xylose are shown in Fig 17, which indicates that xylan conversion is faster than xylose at most of the operating conditions. The xylan and xyloses conversion at different temperature (140°C-170°C) and acid concentration (0.5wt%-2wt %) are also shown in Fig 17. At low acid concentrations of 0.5 to 1 wt. % xylan was found to convert to furfural faster than xylose conversion to furfural resulting in higher concentrations

of furfural for xylan conversions compared to xylose at all conditions (Fig 16). However, the rate of xylan conversion at acids concentrations of 2wt% was the same as xylose conversion to furfural. For instance, 100% conversion of xylan to furfural was observed at 30minutes whereas it took 80minutes for xylose at the same reactions conditions of (170°C, 14wt% and 1wt %) (Fig 17b). This can be attributed to the formation of weak organic acids like acetyl acids in the process of xylan conversion to furfural. That is because xylan is made up of acetyl compounds that are hydrolyzed into acetic acids. The experimental results showed that higher concentrations of acetic acids occurred in the xylan reaction compared to xylose at all conditions. The weak acids formed increases the acid concentration of the reaction (lower pH) compared to the xylose and consequently a faster conversion of xylan to furfural compared to the xylose conversion process. The effect of weak acid on the reaction was also observed by (Yemiş & Mazza 2011).

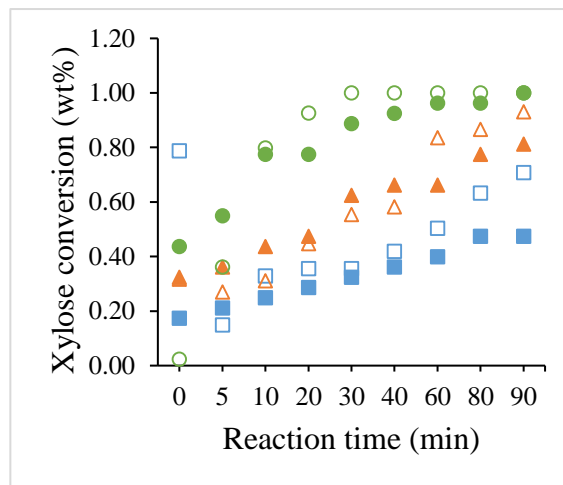


**Fig 16:** Furfural yields from xylose and xylan at 14wt% solids loading, 5 wt% and temperatures 140°C- 170°C.

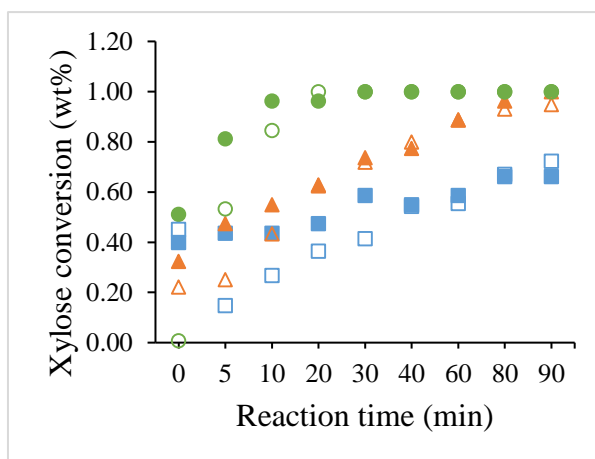
(Xylan ■140°C; ▲ 155°C; \* 170°C, Xylose □140°C; △155°C; x170°C)



A) 0.5wt%



B) 1wt%



C) 2wt%

**Fig 17:** Comparison of xylan and xylose conversion to furfural at different temperatures (140°C, 155°C; 170°C) and acid concentration (A: 0.5wt%; B: 1wt%; C: 2wt %) at 4wt% xylose concentration, where the opened and filled symbols represent xylan and xylose, respectively.



## Chapter 5

### Conclusions and Recommendations

The main goal of this research was to investigate and compare the kinetics of xylan and xylose conversion to furfural at specified operating conditions, and to determine the effects of these conditions on the reaction. Such systematic knowledge about the reaction process leading up to furfural production is important in order to improve the current industrial process.

In this study, furfural production from xylan and xylose at variable operating condition were investigated. Temperature in the range of 140°C-170 °C, acid concentrations at 0.5-2wt% and xylose concentration of 4-14wt% were applied in a 2L autoclave reactor. The experimental data were modelled in Python.3.6 with Spyder UI. The mechanism models were selected by fitting the experimental data to previous models available in literature to find one model that describes each of the reactions adequately. Statistical analysis of the experimental results showed that temperature and acid loading demonstrated significant effects on both conversion process whilst solids loading was found to be insignificant.

Based on the results, the xylan conversion process can be described by a kinetic model consisting of two-step first order reactions; 1) xylan hydrolysis and 2) xylose dehydration reactions without any side product formation. Over all the selected model was found to describe the reaction sufficiently, with the best data-model fit at 170 °C and 2 wt% with  $R^2$  value of 0.99. However, model-data deviations were observed at low temperature and acid concentrations, i.e. 140 °C and 0.5wt% acid concentration.

The hydrolysis step of the xylan conversion process was found to be faster than xylose dehydration, since xylose accumulation was observed at the start of the process (less than 5 min) with a simultaneous xylose dehydration reaction. The activation energies recorded for xylan hydrolysis and xylose dehydration in the xylan conversion process are 55 kJ/mol and 98kJ/mol, respectively. Based on these results, it was determined that the xylose dehydration reaction (in xylan conversion process) was the rate determining step of the reaction relative to the fast hydrolysis step.

The selected model for xylose conversion to furfural was the simple one-step xylose dehydration to furfural without the formation of side products. The selected model deviated from the experimental data at high temperatures of 170°C. Despite the deviation, the model was able to describe the reaction sufficiently well.

Comparing the selected models, the main differences in the reactions kinetics was the xylan hydrolysis step that precedes xylose dehydration in the xylan conversion process. Essentially, a first order single step dehydration reaction without any side product formation can describe xylose conversion in both xylose and xylan processes. The deviations observed in the data – model relation was attributed to the wide range of conditions investigated in this study. From the selected models, it was determined that xylose condensation degradation reactions were negligible in the range of condition investigated in this study for the two conversion processes. Hence all resulting degradation reactions were determined to be as a result of resinification degradation reaction. It was also concluded that the xylan conversion process was generally faster than the xylose conversion process despite the two steps process. This observation was attributed to the higher acid concentration observed in xylan conversion process compared to xylose. Generally temperature and acid loading were found to have a positive influence on the reaction with increase in temperature and acids loading resulting in higher rate of conversion in both xylan and xylose. Finally, higher furfural yields were observed for xylan compared to xylose at all conditions investigated in this study due to 1) the long heat up periods resulting in xylose loss and 2) extensive furfural resinification degradation. Although these observations were observed for both substrates (xylan and xylose), higher feed loss was observed in the xylose conversion process compared to xylan whilst the kinetics parameters obtained (activation energy) suggested higher rate of furfural degradation in xylose (28 kJ/mol) compared to xylan (120 kJ/mol).

## Implications of this study and recommendations

This study introduced a necessary study of the kinetics of furfural formation from xylan together with the subsequent xylose dehydration to give an insight into the kinetics leading up to furfural formation.

In carrying out these experiments, two major problems were encountered.

1. Significant amounts of xylose were lost at high temperature operations (170°C), due to the length of the heat up periods required. This losses did not affect the quality of the results because all modeling and calculations were done with concentrations measured at the start of reaction. The consistency and repeatability in the concentrations measured at each temperature and solids loading together with the duplicate experiments showed that the performance of the reactor was consistent for each selected condition. To minimize such losses in future studies, It is recommended that experiments be performed with revised feeding method or reactor type to eliminate long heating up period which results in xylose losses.
2. Although degradation reactions were expected in this study, it had two major implications on the study.
  - 2.1. Humins, char and degradation solids formed blocked the reactor filters many times which resulted in losing reaction days, failed experiments and loss of reaction feedstock. This problem can still be solved with revised reactor design that will accommodate extensive solids formation.
  - 2.2. The formation of furfural degradation could not be adequately fitted to a kinetic model due to the absence of data on the simultaneous degradation reactions. To resolve this, studies on the kinetics of furfural degradation was conducted by another student in the same research group. Care was taken to conduct both experiments at similar conditions to make the results obtained compatible for future works. The combination of conversion reaction and the degradation reaction will provide a complete understanding of the process of furfural production from xylan and xylose.
3. It is also recommended that the study should be extended to xylan from other plant sources such as sugarcane bagasse or a mixture from different lignocellulosic biomass to ascertain the effectiveness of using hydrolyzed xylan in furfural production.

## References

- Abad, S., Alonso, J.L., Santos, V. and Parajó, J.C., 1997. Furfural from wood in catalyzed acetic acid media: A mathematical assessment. *Bioresource Technology*, 62(3), pp.115-122.
- Aellig, C., Scholz, D., Dapsens, P.Y., Mondelli, C. and Pérez-Ramírez, J., 2015. When catalyst meets reactor: continuous biphasic processing of xylan to furfural over GaUSY/Amberlyst-36. *Catalysis Science & Technology*, 5(1), pp.142-149.
- Ahola, J. & Tanskanen, J., 2012. Kinetics of Xylose Dehydration into Furfural in Formic Acid. Kaisa Lamminpa a. *Industrial & Engineering Chemistry Research*, 51(18), pp.6297–6303.
- Aida, T.M., Shiraishi, N., Kubo, M., Watanabe, M. and Smith Jr, R.L., 2010. Reaction kinetics of d-xylose in sub-and supercritical water. *The Journal of Supercritical Fluids*, 55(1), pp.208-216.
- Antal Jr, M.J., Leesomboon, T., Mok, W.S. and Richards, G.N., 1991. Mechanism of formation of 2-furaldehyde from D-xylose. *Carbohydrate Research*, 217, pp.71-85.
- Aristidou, A. & Penttilä, M., 2000. Metabolic engineering applications to renewable resource utilization. *Current Opinion in Biotechnology*, 11(2), pp.187–198.
- Arnold, D.R. and Buzzard, J.L., 2003, September. A novel process for furfural production. In *Proceedings of South African Chemical Engineering Congress* (pp. 3-5).
- Borrega, M., Nieminen, K. & Sixta, H., 2011. Degradation kinetics of the main carbohydrates in birch wood during hot water extraction in a batch reactor at elevated temperatures. *Bioresource Technology*, 102(22), pp.10724–10732.
- Bozell, J.J. & Petersen, G.R., 2010. Cutting-edge research for a greener sustainable future technology development for the production of biobased products from biorefinery carbohydrates — the US Department of Energy ’ s “ Top 10 ” revisited. , 12(4).
- Cai, C.M., Zhang, T., Kumar, R. and Wyman, C.E., 2014. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. *Journal of Chemical Technology & Biotechnology*, 89(1), pp.2-10.
- Danon, B., Hongsiri, W., Van der Aa, L. and de Jong, W., 2014. Kinetic study on homogeneously catalyzed xylose dehydration to furfural in the presence of arabinose and glucose. *Biomass and Bioenergy*, 66, pp.364-370.

- Danon, B., Marcotullio, G. and de Jong, W., 2014. Mechanistic and kinetic aspects of pentose dehydration towards furfural in aqueous media employing homogeneous catalysis. *Green Chemistry*, 16(1), pp.39-54.
- Demirbas, M.F., 2009. Biorefineries for biofuel upgrading: a critical review. *Applied Energy*, 86, pp.S151-S161.
- Dias, A.S., Pillinger, M. & Valente, A.A., 2005. Dehydration of xylose into furfural over micro-mesoporous sulfonic acid catalysts. *Journal of Catalysis*, 229(2), pp.414–423.
- Dussan, K., Girisuta, B., Haverty, D., Leahy, J.J. and Hayes, M.H.B., 2013. Kinetics of levulinic acid and furfural production from *Miscanthus × giganteus*. *Bioresource technology*, 149, pp.216-224.
- Eken-Saraçoğlu, N., Mutlu, S.F., Dilmaç, G. and Çavuşoğlu, H., 1998. A comparative kinetic study of acidic hemicellulose hydrolysis in corn cob and sunflower seed hull. *Bioresource technology*, 65(1-2), pp.29-33.
- Farzad, S., Mandegari, M.A., Guo, M., Haigh, K.F., Shah, N. and Görgens, J.F., 2017. Multi-product biorefineries from lignocelluloses: a pathway to revitalisation of the sugar industry? *Biotechnology for biofuels*, 10(1), p.87.
- Gairola, K. and Smirnova, I., 2012. Hydrothermal pentose to furfural conversion and simultaneous extraction with SC-CO<sub>2</sub>–Kinetics and application to biomass hydrolysates. *Bioresource technology*, 123, pp.592-598.
- Garrote, G., Domínguez, H. & Parajó, J.C., 2001. Kinetic modelling of corncob autohydrolysis. *Process Biochemistry*, 36(6), pp.571–578.
- Geraili, A., Sharma, P. & Romagnoli, J.A., 2014. A modeling framework for design of nonlinear renewable energy systems through integrated simulation modeling and metaheuristic optimization : Applications to biorefineries. *Computers and Chemical Engineering*, 61, pp.102–117.
- Herrera, A., Téllez-Luis, S.J., Ramirez, J.A. and Vázquez, M., 2003. Production of xylose from sorghum straw using hydrochloric acid. *Journal of Cereal Science*, 37(3), pp.267-274.
- Hongsiri, W., Danon, B. & Jong, W. de, 2014. Kinetic Study on the Dilute Acidic Dehydration of Pentoses toward Furfural in Seawater. *Industrial & Engineering Chemistry Research*, 53(13), pp.5455–5463.

- Hu, X., Westerhof, R.J., Dong, D., Wu, L. and Li, C.Z., 2014. Acid-catalyzed conversion of xylose in 20 solvents: insight into interactions of the solvents with xylose, furfural, and the acid catalyst. *ACS sustainable chemistry & engineering*, 2(11), pp.2562-2575.
- Jin, Q., Zhang, H., Yan, L., Qu, L. and Huang, H., 2011. Kinetic characterization for hemicellulose hydrolysis of corn stover in a dilute acid cycle spray flow-through reactor at moderate conditions. *Biomass and Bioenergy*, 35(10), pp.4158-4164.
- Kabel, M.A., Carvalheiro, F., Garrote, G., Avgerinos, E., Koukios, E., Parajó, J.C., Girio, F.M., Schols, H.A. and Voragen, A.G.J., 2002. Hydrothermally treated xylan rich by-products yield different classes of xylo-oligosaccharides. *Carbohydrate Polymers*, 50(1), pp.47-56.
- Kamireddy, S.R., Kozliak, E.I., Tucker, M. and Ji, Y., 2014. Kinetic features of xylan depolymerization in production of xylose monomer and furfural during acid pretreatment for kenaf, forage sorghums and sunn hemp feedstocks. *International Journal of Agricultural and Biological Engineering*, 7(4), pp.86-98.
- Kim, S.B., Lee, M.R., Park, E.D., Lee, S.M., Lee, H., Park, K.H. and Park, M.J., 2011. Kinetic study of the dehydration of d-xylose in high temperature water. *Reaction Kinetics, Mechanisms and Catalysis*, 103(2), pp.267-277.
- Kim, S.B., You, S.J., Kim, Y.T., Lee, S., Lee, H., Park, K. and Park, E.D., 2011. Dehydration of D-xylose into furfural over H-zeolites. *Korean Journal of Chemical Engineering*, 28(3), pp.710-716.
- Lamminpää, K., Ahola, J. & Tanskanen, J., 2015. Acid-catalysed xylose dehydration into furfural in the presence of kraft lignin. *Bioresource Technology*, 177, pp.94–101.
- Lau, C.S., Thoma, G.J., Clausen, E.C. and Carrier, D.J., 2014. Kinetic modeling of xylose oligomer degradation during pretreatment in dilute acid or in water. *Industrial & Engineering Chemistry Research*, 53(6), pp.2219-2228.
- Lavarack, B.P., Griffin, G.J. & Rodman, D., 2002. The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products. *Biomass and Bioenergy*, 23(5), pp.367–380.
- Le Guenic, S., Delbecq, F., Ceballos, C. and Len, C., 2015. Microwave-assisted dehydration of D-xylose into furfural by diluted inexpensive inorganic salts solution in a biphasic system. *Journal of Molecular Catalysis A: Chemical*, 410, pp.1-7.

- Le Guenic, S., Gergela, D., Ceballos, C., Delbecq, F. and Len, C., 2016. Furfural production from D-xylose and xylan by using stable Nafion NR50 and NaCl in a microwave-assisted biphasic reaction. *Molecules*, 21(8), p.1102.
- Li, J.Q., 2001. The Chemistry and Technology of Furfural and its Many By-products-Karl J. Zeitsch; Elsevier, 2000, 358 pp, US \$235.00 (hardback), ISBN: 0-444-50351-X. *Chemical Engineering Journal*, 1(81), pp.338-339.
- Liu, H., Hu, H., Baktash, M.M., Jahan, M.S., Ahsan, L. and Ni, Y., 2014. Kinetics of furfural production from pre-hydrolysis liquor (PHL) of a kraft-based hardwood dissolving pulp production process *biomass and bioenergy*, 66, pp.320-327.
- Luo, Y., Li, Z., Li, X., Liu, X., Fan, J., Clark, J.H. and Hu, C., 2019. The production of furfural directly from hemicellulose in lignocellulosic biomass: A review. *Catalysis Today*, 319, pp.14-24.
- Luterbacher, J.S., Martin Alonso, D. & Dumesic, J.A., 2014. Targeted chemical upgrading of lignocellulosic biomass to platform molecules. *Green Chemistry*, 16(12), pp.4816–4838.
- Mandalika, A. and Runge, T., 2012. Enabling integrated biorefineries through high-yield conversion of fractionated pentosans into furfural. *Green Chemistry*, 14(11), pp.3175-3184.
- Marcotullio, G., Krisanti, E., Giuntoli, J. and De Jong, W., 2011. Selective production of hemicellulose-derived carbohydrates from wheat straw using dilute HCl or FeCl<sub>3</sub> solutions under mild conditions. X-ray and thermo-gravimetric analysis of the solid residues. *Bioresource technology*, 102(10), pp.5917-5923.
- Marcotullio, G. & Jong, W. De, 2010. Chloride ions enhance furfural formation from D -xylose in dilute aqueous acidic solutions. , pp.1739–1746.
- Mariscal, R. & Ojeda, M., 2016. Environmental Science molecule for the synthesis of chemicals and fuels. *Energy & Environmental Science*, 9, pp.1144–1189.
- Mittal, A., Chatterjee, S.G., Scott, G.M. and Amidon, T.E., 2009. Modeling xylan solubilization during autohydrolysis of sugar maple and aspen wood chips: Reaction kinetics and mass transfer. *Chemical Engineering Science*, 64(13), pp.3031-3041.
- Morinelly, J.E., Jensen, J.R., Browne, M., Co, T.B. and Shonnard, D.R., 2009. Kinetic characterization of xylose monomer and oligomer concentrations during dilute acid pretreatment of lignocellulosic biomass from forests and switchgrass. *Industrial & engineering chemistry research*, 48(22), pp.9877-9884.

- O'Neill, R., Ahmad, M.N., Vanoye, L. and Aiouache, F., 2009. Kinetics of aqueous phase dehydration of xylose into furfural catalyzed by ZSM-5 zeolite. *Industrial & engineering chemistry research*, 48(9), pp.4300-4306.
- Oefner, P.J., Lanziner, A.H., Bonn, G. and Bobleter, O., 1992. Quantitative studies on furfural and organic acid formation during hydrothermal, acidic and alkaline degradation of D-xylose. *Monatshefte für Chemie/Chemical Monthly*, 123(6-7), pp.547-556.
- Peleteiro, S., Rivas, S., Alonso, J.L., Santos, V. and Parajó, J.C., 2016. Furfural production using ionic liquids: A review. *Bioresource technology*, 202, pp.181-191.
- Peleteiro, S., da Costa Lopes, A.M., Garrote, G., Parajó, J.C. and Bogel-Lukasik, R., 2015. Simple and efficient furfural production from xylose in media containing 1-butyl-3-methylimidazolium hydrogen sulfate. *Industrial & Engineering Chemistry Research*, 54(33), pp.8368-8373.
- Qi, J. and Xiuyang, L.Ü., 2007. Kinetics of non-catalyzed decomposition of D-xylose in high temperature liquid water. *Chinese Journal of Chemical Engineering*, 15(5), pp.666-669.
- Rushin, M.S. & Natal, Mathematical modelling and optimization of a three phase auto hydrolysis reactor, B.S.E., 1992.
- Root, D.F., Saeman, J.F. & Neil W.K. 1956. Kinetics of acid catalyzed conversion of xylose to furfural. *Forest products Journal*. 9:158-165
- Steinbach, D., 2017. Pretreatment technologies of lignocellulosic biomass in water in view of furfural and 5-hydroxymethylfurfural production- A review.
- Steiner ACDP 2019, Mechanistic and kinetics aspects of furfural degradation in dilute acid media, MEng thesis, Stellenbosch University, South Africa
- Vallejos, M.E., Felissia, F.E., Kruyeniski, J. and Area, M.C., 2015. Kinetic study of the extraction of hemicellulosic carbohydrates from sugarcane bagasse by hot water treatment. *Industrial Crops and Products*, 67, pp.1-6.
- Weingarten, R., Cho, J., Conner Jr, W.C. and Huber, G.W., 2010. Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating. *Green Chemistry*, 12(8), pp.1423-1429.
- Werpy, T. & Petersen, G., 2004. Top Value Added Chemicals from Biomass: Volume I -- Results of Screening for Potential Candidates from Sugars and Synthesis Gas. Office of Scientific and Technical Information (OSTI). *Office of Scientific and Technical Information*, p.69.



- Win, D.T., 2005. Furfural – Gold from Garbage. *Assumption University Journal of Technology*, 8(4), pp.185–190.
- Yat, S.C., Berger, A. and Shonnard, D.R., 2008. Kinetic characterization for dilute sulfuric acid hydrolysis of timber varieties and switchgrass. *Bioresource technology*, 99(9), pp.3855-3863.
- Yang, R., Xu, S., Wang, Z. and Yang, W., 2005. Aqueous extraction of corncob xylan and production of xylooligosaccharides. *LWT-Food Science and Technology*, 38(6), pp.677-682.
- Yang, R., Zhang, C., Feng, H. and Yang, W., 2006. A kinetic study of xylan solubility and degradation during corncob steaming. *Biosystems engineering*, 93(4), pp.375-382.
- Yang, W., Li, P., Bo, D., Chang, H., Wang, X. and Zhu, T., 2013. Optimization of furfural production from D-xylose with formic acid as catalyst in a reactive extraction system. *Bioresource technology*, 133, pp.361-369.
- Yemiş, O. & Mazza, G., 2011. Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction. *Bioresource Technology*, 102(15), pp.7371–7378.
- Zhang, J., Zhuang, J., Lin, L., Liu, S. and Zhang, Z., 2012. Conversion of D-xylose into furfural with mesoporous molecular sieve MCM-41 as catalyst and butanol as the extraction phase. *Biomass and Bioenergy*, 39, pp.73-77.
- Zhang, L., Yu, H., Wang, P., Dong, H. and Peng, X., 2013. Conversion of xylan, d-xylose and lignocellulosic biomass into furfural using AlCl<sub>3</sub> as catalyst in ionic liquid. *Bioresource technology*, 130, pp.110-116.
- Zhang, L., Xi, G., Yu, K., Yu, H. and Wang, X., 2017. Furfural production from biomass-derived carbohydrates and lignocellulosic residues via heterogeneous acid catalysts. *Industrial crops and products*, 98, pp.68-75.
- Zhang, L., Yu, H., Wang, P. and Li, Y., 2014. Production of furfural from xylose, xylan and corncob in gamma-valerolactone using FeCl<sub>3</sub>· 6H<sub>2</sub>O as catalyst. *Bioresource technology*, 151, pp.355-360.
- Zhang, L., Yu, H. & Wang, P., 2013. Biore source Technology Solid acids as catalysts for the conversion of D -xylose , xylan and lignocellulosics into furfural in ionic liquid. *Bioresource Technology*, 136, pp.515–521.

Zhang T., Kumar R., Wyamn C.E. Enhanced yields of furfural and other products by simultaneous solvent extraction during thermochemical treatment of cellulosic biomass. *RSC Advances* 3(25), 9809-9819

Zhang, Z. & Zhao, Z.K., 2010. Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid. *Bioresource Technology*, 101(3), pp.1111–1114.

## Appendices

### Appendix A

Table A1 contains the list of chemicals and materials used in the reaction process. Xylose (5kg, D-(+)-Xylose,  $\geq 99\%$ ) and sulfuric acid (ACS reagent 95.0-97.0%) were acquired from Sigma-Aldrich, Xylan (10kg,  $\geq 65\%$ ) was obtained from Xi'an Leader Biochemical Engineering Co. Ltd. All other consumable materials were sourced from ScienceWorld Company Limited

**Table A- 1: List of chemicals and material used in the process of furfural formation**

<b>Item</b>	<b>Quantity</b>
Xylose	4kg
Xylan	4 kg
Sulfuric Acid	2 kg
HPLC Vials & Caps	
Syringes & filters	
Sample Tubes	
Filters	

## Appendix B

**Table B 1 Naming index of reaction conditions**

INDEX			
<b>Factor/Severity</b>	Low	Medium	High
Temperature	L	D	M
Solid Loading	A( $\alpha$ )	B( $\beta$ )	G( $\gamma$ )
Acid concentrations	1	2	3

Table B 2: Monomeric xylose experimental data

Xylose concentration (Experimental)																											
Time	LA1	LA2	LA3	LB1	LB2	LB3	LG1	LG2	LG3	MA1	MA2	MA3	MB1	MB2	MB3	MG1	MG2	MG3	HA1	HA2	HA3	HB1	HB2	HB3	HG1	HG2	HG3
0	0.21	0.22	0.16	0.45	0.44	0.39	0.73	0.72	0.74	0.21	0.18	0.18	0.38	0.35	0.33	0.54	0.54	0.53	0.18	0.15	0.13	0.37	0.36	0.30	0.51	0.49	0.48
5	0.21	0.21	0.15	0.44	0.40	0.38	0.72	0.71	0.69	0.21	0.17	0.14	0.34	0.29	0.28	0.51	0.49	0.48	0.15	0.12	0.05	0.31	0.30	0.14	0.44	0.37	0.26
10	0.20	0.20	0.15	0.44	0.41	0.36	0.68	0.65	0.62	0.20	0.15	0.12	0.32	0.27	0.21	0.50	0.40	0.32	0.13	0.06	0.01	0.27	0.24	0.08	0.39	0.28	0.13
20	0.19	0.19	0.14	0.43	0.38	0.36	0.66	0.63	0.60	0.19	0.14	0.10	0.32	0.22	0.15	0.43	0.42	0.20	0.09	0.06	0.01	0.18	0.16	0.03	0.30	0.22	0.05
30	0.19	0.18	0.11	0.41	0.35	0.33	0.65	0.60	0.53	0.17	0.10	0.07	0.30	0.20	0.11	0.49	0.35	0.12	0.07	0.03	0.00	0.15	0.07	0.01	0.24	0.08	0.01
40	0.18	0.17	0.12	0.40	0.30	0.29	0.63	0.58	0.50	0.16	0.09	0.06	0.28	0.16	0.08	0.41	0.29	0.10	0.06	0.02	0.00	0.11	0.06	0.01	0.19	0.08	0.00
60	0.18	0.16	0.11	0.38	0.26	0.28	0.59	0.56	0.38	0.13	0.09	0.03	0.25	0.12	0.05	0.40	0.25	0.06	0.03	0.01	0.00	0.09	0.04	0.00	0.12	0.04	0.00
80	0.17	0.14	0.09	0.36	0.24	0.24	0.55	0.52	0.31	0.12	0.06	0.01	0.20	0.10	0.03	0.33	0.05	0.03	0.02	0.01	0.00	0.04	0.01	0.00	0.08	0.01	0.00
90	0.16	0.14	0.09	0.35	0.22	0.17	0.54	0.51	0.33	0.11	0.05	0.00	0.20	0.08	0.02	0.30	0.05	0.02	0.02	0.00	0.00	0.03	0.01	0.00	0.06	0.01	0.00

Xylose concentration (Model)																											
Time	LA1	LA2	LA3	LB1	LB2	LB3	LG1	LG2	LG3	MA1	MA2	MA3	MB1	MB2	MB3	MG1	MG2	MG3	HA1	HA2	HA3	HB1	HB2	HB3	HG1	HG2	HG3
0	0.21	0.22	0.16	0.45	0.44	0.39	0.73	0.72	0.74	0.21	0.18	0.18	0.38	0.35	0.33	0.54	0.54	0.53	0.18	0.15	0.13	0.37	0.36	0.30	0.51	0.49	0.48
5	0.21	0.21	0.15	0.44	0.43	0.37	0.72	0.70	0.70	0.20	0.17	0.16	0.37	0.33	0.29	0.52	0.50	0.46	0.16	0.13	0.09	0.34	0.30	0.22	0.47	0.41	0.35
10	0.20	0.21	0.14	0.44	0.42	0.35	0.71	0.68	0.67	0.20	0.16	0.14	0.35	0.31	0.25	0.50	0.47	0.41	0.15	0.11	0.07	0.31	0.26	0.16	0.43	0.35	0.25
20	0.20	0.20	0.13	0.43	0.40	0.32	0.69	0.65	0.61	0.18	0.14	0.11	0.33	0.27	0.20	0.47	0.41	0.31	0.13	0.08	0.04	0.26	0.18	0.08	0.36	0.25	0.13
30	0.19	0.19	0.12	0.41	0.38	0.29	0.67	0.62	0.55	0.17	0.12	0.08	0.31	0.23	0.15	0.44	0.36	0.24	0.11	0.05	0.02	0.22	0.13	0.04	0.30	0.18	0.07
40	0.19	0.18	0.11	0.40	0.36	0.26	0.66	0.58	0.50	0.16	0.10	0.06	0.29	0.20	0.12	0.41	0.31	0.19	0.09	0.04	0.01	0.18	0.09	0.02	0.25	0.13	0.04
60	0.18	0.16	0.09	0.38	0.32	0.21	0.62	0.53	0.41	0.14	0.08	0.04	0.25	0.15	0.07	0.35	0.24	0.11	0.06	0.02	0.00	0.13	0.05	0.01	0.18	0.06	0.01
80	0.17	0.14	0.07	0.36	0.29	0.18	0.59	0.47	0.33	0.12	0.06	0.02	0.22	0.12	0.04	0.31	0.18	0.07	0.04	0.01	0.00	0.09	0.02	0.00	0.13	0.03	0.00
90	0.16	0.14	0.07	0.35	0.28	0.16	0.57	0.45	0.30	0.11	0.05	0.02	0.20	0.10	0.03	0.28	0.16	0.05	0.04	0.01	0.00	0.08	0.02	0.00	0.11	0.02	0.00

Table 2: Monomeric xylose experimental data (continued)

Furfural concentration (Experimental)																											
Time	LA1	LA2	LA3	LB1	LB2	LB3	LG1	LG2	LG3	MA1	MA2	MA3	MB1	MB2	MB3	MG1	MG2	MG3	HA1	HA2	HA3	HB1	HB2	HB3	HG1	HG2	HG3
0	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.01	0.00	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.03	0.01	0.01	0.02	0.03	0.05	0.03	0.04	0.06	0.05
5	0.01	0.01	0.02	0.01	0.02	0.05	0.02	0.03	0.02	0.01	0.04	0.04	0.03	0.05	0.07	0.03	0.08	0.14	0.04	0.06	0.09	0.08	0.12	0.13	0.10	0.15	0.11
10	0.01	0.02	0.02	0.01	0.05	0.06	0.02	0.05	0.05	0.01	0.06	0.05	0.04	0.07	0.09	0.05	0.11	0.19	0.06	0.04	0.09	0.10	0.15	0.13	0.13	0.20	0.16
20	0.02	0.03	0.03	0.02	0.05	0.07	0.02	0.08	0.12	0.02	0.07	0.09	0.05	0.08	0.12	0.05	0.16	0.22	0.07	0.11	0.09	0.12	0.19	0.14	0.16	0.23	0.19
30	0.02	0.03	0.03	0.03	0.07	0.08	0.03	0.10	0.14	0.02	0.05	0.09	0.07	0.11	0.13	0.07	0.16	0.20	0.08	0.11	0.08	0.16	0.21	0.15	0.19	0.22	0.26
40	0.03	0.04	0.04	0.03	0.05	0.08	0.04	0.11	0.16	0.03	0.07	0.09	0.09	0.11	0.14	0.07	0.18	0.23	0.08	0.11	0.07	0.16	0.19	0.13	0.21	0.17	0.23
60	0.03	0.04	0.04	0.04	0.09	0.09	0.04	0.13	0.17	0.03	0.08	0.10	0.10	0.11	0.14	0.09	0.28	0.27	0.09	0.10	0.06	0.16	0.19	0.09	0.20	0.15	0.22
80	0.04	0.05	0.05	0.06	0.05	0.06	0.05	0.13	0.18	0.04	0.08	0.10	0.11	0.12	0.15	0.10	0.33	0.26	0.10	0.09	0.05	0.17	0.17	0.09	0.22	0.12	0.17
90	0.04	0.06	0.05	0.06	0.05	0.05	0.06	0.15	0.22	0.04	0.09	0.10	0.12	0.13	0.16	0.10	0.33	0.21	0.10	0.09	0.04	0.16	0.16	0.08	0.22	0.07	0.15
Furfural concentration (Model)																											
Time	LA1	LA2	LA3	LB1	LB2	LB3	LG1	LG2	LG3	MA1	MA2	MA3	MB1	MB2	MB3	MG1	MG2	MG3	HA1	HA2	HA3	HB1	HB2	HB3	HG1	HG2	HG3
0	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.01	0.00	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.03	0.01	0.01	0.02	0.03	0.05	0.03	0.04	0.06	0.05
5	0.00	0.01	0.01	0.01	0.02	0.03	0.02	0.04	0.04	0.01	0.02	0.03	0.03	0.04	0.05	0.03	0.05	0.09	0.02	0.03	0.05	0.06	0.10	0.10	0.08	0.13	0.16
10	0.01	0.01	0.01	0.01	0.03	0.04	0.03	0.05	0.07	0.01	0.03	0.04	0.04	0.06	0.07	0.05	0.08	0.13	0.04	0.05	0.07	0.08	0.14	0.14	0.11	0.18	0.22
20	0.01	0.02	0.02	0.02	0.05	0.06	0.05	0.08	0.12	0.03	0.05	0.06	0.06	0.09	0.11	0.08	0.13	0.18	0.06	0.07	0.07	0.12	0.18	0.16	0.17	0.24	0.26
30	0.02	0.03	0.03	0.03	0.06	0.08	0.06	0.10	0.15	0.04	0.06	0.07	0.08	0.11	0.12	0.10	0.16	0.20	0.07	0.08	0.07	0.15	0.20	0.15	0.21	0.26	0.23
40	0.02	0.03	0.04	0.04	0.07	0.09	0.08	0.12	0.17	0.04	0.06	0.07	0.10	0.12	0.12	0.12	0.18	0.20	0.08	0.08	0.05	0.17	0.20	0.12	0.24	0.27	0.19
60	0.03	0.04	0.04	0.06	0.09	0.10	0.10	0.15	0.19	0.06	0.07	0.06	0.12	0.13	0.11	0.16	0.20	0.18	0.09	0.07	0.03	0.19	0.18	0.07	0.26	0.24	0.11
80	0.03	0.05	0.04	0.07	0.10	0.10	0.12	0.17	0.19	0.07	0.07	0.05	0.13	0.13	0.09	0.18	0.20	0.14	0.09	0.06	0.02	0.19	0.14	0.04	0.27	0.19	0.06
90	0.04	0.05	0.04	0.08	0.11	0.10	0.13	0.18	0.18	0.07	0.07	0.04	0.14	0.13	0.07	0.19	0.20	0.12	0.09	0.05	0.01	0.19	0.12	0.03	0.26	0.17	0.04

Table B 3: Polymeric xylan experimental data

Xylose concentration (Experimental)																												
Time	LA1	LA2	LA3	LB1	LB2	LB3	LG1	LG2	LG3	MA1	MA2	MA3	MB1	MB2	MB3	MG1	MG2	MG3	HA1	HA2	HA3	HB1	HB2	HB3	HG1	HG2	HG3	
0	0.06	0.06	0.15	0.09	0.04	0.05	0.16	0.24	0.78	0.06	0.18	0.21	0.08	0.39	0.42	0.29	0.68	0.80	0.26	0.26	0.26	0.34	0.46	0.39	0.66	0.75	0.76	
5	0.24	0.23	0.23	0.47	0.47	0.32	0.92	1.12	0.76	0.22	0.19	0.20	0.47	0.49	0.41	0.78	0.70	0.55	0.20	0.17	0.12	0.40	0.32	0.16	0.74	0.54	0.60	
10	0.22	0.18	0.20	0.46	0.38	0.34	0.91	0.98	0.63	0.20	0.18	0.15	0.44	0.38	0.33	0.73	0.64	0.38	0.14	0.05	0.04	0.35	0.18	0.05	0.60	0.30	0.15	
20	0.19	0.17	0.17	0.42	0.37	0.33	0.90	0.88	0.55	0.17	0.15	0.10	0.38	0.31	0.20	0.71	0.46	0.32	0.09	0.02	0.00	0.23	0.06	0.00	0.42	0.12	0.03	
30	0.18	0.17	0.16	0.41	0.35	0.27	0.79	0.78	0.54	0.15	0.12	0.07	0.35	0.25	0.14	0.71	0.38	0.19	0.06	0.00	0.00	0.14	0.00	0.00	0.23	0.03	0.00	
40	0.16	0.15	0.12	0.41	0.31	0.24	0.81	0.77	0.51	0.15	0.11	0.05	0.30	0.25	0.13	0.64	0.33	0.16	0.05	0.00	0.00	0.13	0.00	0.00	0.13	0.00	0.00	
60	0.13	0.13	0.12	0.40	0.30	0.21	0.74	0.74	0.41	0.11	0.04	0.03	0.21	0.19	0.08	0.50	0.22	0.12	0.01	0.00	0.00	0.03	0.00	0.00	0.03	0.00	0.00	
80	0.13	0.10	0.09	0.37	0.30	0.03	0.77	0.71	0.33	0.10	0.04	0.02	0.12	0.14	0.05	0.48	0.16	0.06	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90	0.12	0.08	0.07	0.36	0.26	0.00	0.78	0.65	0.28	0.09	0.02	0.01	0.10	0.13	0.04	0.30	0.15	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Xylose concentration (Model)																											
Time	LA1	LA2	LA3	LB1	LB2	LB3	LG1	LG2	LG3	MA1	MA2	MA3	MB1	MB2	MB3	MG1	MG2	MG3	HA1	HA2	HA3	HB1	HB2	HB3	HG1	HG2	HG3
0	0.06	0.06	0.15	0.09	0.04	0.05	0.16	0.24	0.78	0.06	0.18	0.21	0.08	0.39	0.42	0.29	0.68	0.80	0.26	0.26	0.26	0.34	0.46	0.39	0.66	0.75	0.76
5	0.25	0.24	0.23	0.51	0.50	0.47	0.90	0.87	0.82	0.24	0.20	0.18	0.48	0.45	0.37	0.86	0.77	0.65	0.20	0.16	0.11	0.38	0.29	0.16	0.73	0.58	0.31
10	0.24	0.23	0.20	0.49	0.46	0.41	0.87	0.81	0.72	0.22	0.17	0.13	0.44	0.37	0.26	0.78	0.64	0.46	0.16	0.10	0.04	0.30	0.18	0.07	0.57	0.36	0.13
20	0.23	0.20	0.15	0.46	0.40	0.32	0.81	0.71	0.55	0.18	0.11	0.06	0.36	0.26	0.13	0.64	0.44	0.23	0.10	0.04	0.01	0.19	0.07	0.01	0.35	0.14	0.02
30	0.21	0.17	0.12	0.43	0.35	0.24	0.75	0.62	0.43	0.15	0.08	0.03	0.30	0.18	0.06	0.53	0.31	0.11	0.06	0.02	0.00	0.11	0.03	0.00	0.22	0.06	0.00
40	0.20	0.15	0.09	0.40	0.31	0.19	0.70	0.54	0.33	0.12	0.05	0.02	0.25	0.12	0.03	0.44	0.21	0.06	0.04	0.01	0.00	0.07	0.01	0.00	0.13	0.02	0.00
60	0.17	0.12	0.05	0.35	0.23	0.11	0.61	0.41	0.20	0.08	0.03	0.00	0.17	0.06	0.01	0.30	0.10	0.01	0.01	0.00	0.00	0.03	0.00	0.00	0.05	0.00	0.00
80	0.15	0.09	0.03	0.30	0.18	0.07	0.53	0.31	0.12	0.06	0.01	0.00	0.11	0.03	0.00	0.20	0.05	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.00
90	0.14	0.08	0.03	0.28	0.16	0.05	0.49	0.27	0.09	0.05	0.01	0.00	0.09	0.02	0.00	0.17	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00

Table B 3: Polymeric xylan experimental data (continued)

Furfural concentration (Experimental)																											
Time	LA1	LA2	LA3	LB1	LB2	LB3	LG1	LG2	LG3	MA1	MA2	MA3	MB1	MB2	MB3	MG1	MG2	MG3	HA1	HA2	HA3	HB1	HB2	HB3	HG1	HG2	HG3
0	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.01	0.00	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.03	0.01	0.01	0.02	0.03	0.05	0.03	0.04	0.06	0.05
5	0.01	0.01	0.02	0.01	0.02	0.05	0.02	0.03	0.02	0.01	0.04	0.04	0.03	0.05	0.07	0.03	0.08	0.14	0.04	0.06	0.09	0.08	0.12	0.13	0.10	0.15	0.11
10	0.01	0.02	0.02	0.01	0.05	0.06	0.02	0.05	0.05	0.01	0.06	0.05	0.04	0.07	0.09	0.05	0.11	0.19	0.06	0.04	0.09	0.10	0.15	0.13	0.13	0.20	0.16
20	0.02	0.03	0.03	0.02	0.05	0.07	0.02	0.08	0.12	0.02	0.07	0.09	0.05	0.08	0.12	0.05	0.16	0.22	0.07	0.11	0.09	0.12	0.19	0.14	0.16	0.23	0.19
30	0.02	0.03	0.03	0.03	0.07	0.08	0.03	0.10	0.14	0.02	0.05	0.09	0.07	0.11	0.13	0.07	0.16	0.20	0.08	0.11	0.08	0.16	0.21	0.15	0.19	0.22	0.26
40	0.03	0.04	0.04	0.03	0.05	0.08	0.04	0.11	0.16	0.03	0.07	0.09	0.09	0.11	0.14	0.07	0.18	0.23	0.08	0.11	0.07	0.16	0.19	0.13	0.21	0.17	0.23
60	0.03	0.04	0.04	0.04	0.09	0.09	0.04	0.13	0.17	0.03	0.08	0.10	0.10	0.11	0.14	0.09	0.28	0.27	0.09	0.10	0.06	0.16	0.19	0.09	0.20	0.15	0.22
80	0.04	0.05	0.05	0.06	0.05	0.06	0.05	0.13	0.18	0.04	0.08	0.10	0.11	0.12	0.15	0.10	0.33	0.26	0.10	0.09	0.05	0.17	0.17	0.09	0.22	0.12	0.17
90	0.04	0.06	0.05	0.06	0.05	0.05	0.06	0.15	0.22	0.04	0.09	0.10	0.12	0.13	0.16	0.10	0.33	0.21	0.10	0.09	0.04	0.16	0.16	0.08	0.22	0.07	0.15
Furfural concentration (Model)																											
Time	LA1	LA2	LA3	LB1	LB2	LB3	LG1	LG2	LG3	MA1	MA2	MA3	MB1	MB2	MB3	MG1	MG2	MG3	HA1	HA2	HA3	HB1	HB2	HB3	HG1	HG2	HG3
0	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.01	0.00	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.03	0.01	0.01	0.02	0.03	0.05	0.03	0.04	0.06	0.05
5	0.00	0.01	0.01	0.01	0.02	0.03	0.02	0.04	0.04	0.01	0.02	0.03	0.03	0.04	0.05	0.03	0.05	0.09	0.02	0.03	0.05	0.06	0.10	0.10	0.08	0.13	0.16
10	0.01	0.01	0.01	0.01	0.03	0.04	0.03	0.05	0.07	0.01	0.03	0.04	0.04	0.06	0.07	0.05	0.08	0.13	0.04	0.05	0.07	0.08	0.14	0.14	0.11	0.18	0.22
20	0.01	0.02	0.02	0.02	0.05	0.06	0.05	0.08	0.12	0.03	0.05	0.06	0.06	0.09	0.11	0.08	0.13	0.18	0.06	0.07	0.07	0.12	0.18	0.16	0.17	0.24	0.26
30	0.02	0.03	0.03	0.03	0.06	0.08	0.06	0.10	0.15	0.04	0.06	0.07	0.08	0.11	0.12	0.10	0.16	0.20	0.07	0.08	0.07	0.15	0.20	0.15	0.21	0.26	0.23
40	0.02	0.03	0.04	0.04	0.07	0.09	0.08	0.12	0.17	0.04	0.06	0.07	0.10	0.12	0.12	0.12	0.18	0.20	0.08	0.08	0.05	0.17	0.20	0.12	0.24	0.27	0.19
60	0.03	0.04	0.04	0.06	0.09	0.10	0.10	0.15	0.19	0.06	0.07	0.06	0.12	0.13	0.11	0.16	0.20	0.18	0.09	0.07	0.03	0.19	0.18	0.07	0.26	0.24	0.11
80	0.03	0.05	0.04	0.07	0.10	0.10	0.12	0.17	0.19	0.07	0.07	0.05	0.13	0.13	0.09	0.18	0.20	0.14	0.09	0.06	0.02	0.19	0.14	0.04	0.27	0.19	0.06
90	0.04	0.05	0.04	0.08	0.11	0.10	0.13	0.18	0.18	0.07	0.07	0.04	0.14	0.13	0.07	0.19	0.20	0.12	0.09	0.05	0.01	0.19	0.12	0.03	0.26	0.17	0.04



## Appendix C

A complete set of models at all conditions are compiled in appendix C. Table B1 describes the naming index of the different conditions of experiment. X=Xylose F=Furfural

