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CATALYTIC CONVERSION OF SUGARCANE BAGASSE INTO FURFURAL

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Doctor of Philosophy

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Declaration

I declare, to the best of my knowledge, the work presented in this dissertation is original and was not presented for any other awards. Every effort is made to clearly identify this with proper reference to literature and the recognition of joint research and discussions, wherever contributions from other parties are involved. Part of the research work in the thesis was published and a list of research publications was provided.

Signature:

Date:

Certification

This is to certify that the dissertation entitled: "**Catalytic conversion of sugarcane bagasse into furfural**" submitted in fulfillment of the requirements for the degree of **Doctor of Philosophy in Chemical Engineering (Process Engineering Stream)** complies with the regulations of the university and meets the accepted standards concerning originality and quality.

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Publications

Journal Articles

N. W. Dulie, B. Woldeyes, H. D. Demsash, and A. S. Jabasingh, “An Insight into the Valorization of Hemicellulose Fraction of Biomass into Furfural: Catalytic Conversion and Product Separation,” *Waste and Biomass Valorization*, vol. 12, no. 2, pp. 531–552, 2020, doi: 10.1007/s12649-020-00946-1.

N. W. Dulie, B. Woldeyes, and H. D. Demsash, “Synthesis of lignin-carbohydrate complex-based catalyst from Eragrostis tef straw and its catalytic performance in xylose dehydration to furfural,” *Int. J. Biol. Macromol.*, vol. 171, pp. 10–16, 2021, doi: 10.1016/j.ijbiomac.2020.12.213.

N. W. Dulie, B. Woldeyes, and H. D. Demsash, “Xylose Release from Sugarcane Bagasse via Acid-Catalyzed Hydrothermal Reaction and Its Conversion into Furfural Using Teff (Eragrostis tef) Straw-Based Catalyst” ‘*Waste and Biomass Valorization*, 2021, 1-11

Abstract

The production of furfural, high-value-added platform chemicals, is hampered by the typical drawbacks of homogeneous acid catalysts, such as difficulty in separating the catalyst from the reaction mixture. As a result, developing a heterogeneous catalyst to overcome the limitations of current commercial processes is highly desirable. The carbon-based catalysts were synthesized by carbonizing and functionalizing teff-straw as a carbon precursor in concentrated sulfuric acid simultaneously and showed the ability to dehydrate xylan/xylose to generate furfural. As shown by FTIR, the catalyst comprises functional groups such as $–SO_3H$, –COOH, and –OH, which are extremely beneficial to catalytic performance. The elemental analysis of the samples also confirmed the successful attachment of sulfur to the carbon structure and XRD results, the diffraction peak at 2θ from 15 to 30^o, depicted the amorphous nature of the catalyst prepared. Experimental runs, catalytic and thermal, were carried out over the prepared catalyst to investigate catalytic activities such as overall conversion, selectivity, and catalyst stability. Conversion of xylose to furfural was investigated using a Teff straw-based sulfonated catalyst (TSSC) in water/toluene as an extraction medium. A maximum furfural yield of 62.50% was obtained at 190°C for 20 min with 0.2g solid acid.

Besides, hydrolysis of sugarcane bagasse to xylose using a dilute sulfuric acid catalyst was investigated. An optimum xylose yield of roughly 0.18g/g of dry bagasse was obtained in 32 minutes with 0.77% sulfuric acid at 143 °C. Model-Based Calibration Toolbox in MATLAB software was used for the design of experiments, statistical modeling, and optimization. Although the combined effect of temperature, acid concentration, and time was positive towards the formation of glucose and furfural, harsher treatment conditions showed negative effects on the yield of xylose.

The experimental data were analyzed to create a kinetic model for lignocellulosic biomass conversion to furfural using the synthesized catalyst. The kinetic model for the dehydration of xylose to furfural was developed using experimental data obtained based on the Central composite design. The well-evaluated kinetic model matched well with the experimental data and kinetic parameters. The thermodynamic analysis suggested that the presence of toluene, in the reaction system, as a solvent for instantaneous extraction of furfural enhanced furfural production while decreasing degradation rate as compared to water-only system.

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Notations

Symbol	*Defintion*
n_{ij}	Number of moles of component *i* in *j*
μ_{ij}	Chemical potential of component *i* in *j*
P	Number of phases
C	Number of components
$\mu_i^{\theta}(T)$	Chemical potential of pure component *i* at temperature T
$\widehat{f_\iota}$	Fugacity of component *i*
$\mu_i^{*}(T,P)$	Chemical potential of pure liquid component *i*
$\widehat{a_\iota}$	Activity of component *i*
γ_i	Activity coefficient of liquid component *i*
V_{NaOH}	Volume of NaOH
V_{HCl}	Volume of HCl
m_{Cat}	Mass of catalyst
Y_C	Catalyst yield
w_{cat}	Weight of catalyst in grams
w_{tef}	Weight of teff straw

x_i	Coded values of independent variables
X_i	Actual values of independent variables
X_o	Actual value of the independent variable at the center point
ΔX_i	Step-change in actual value of independent variable
R_o	Severity factor
R'	Combined severity factor
T	Temperature
t	Time
k_1 and k_2	Rate constants
A	Frequency factor
E_i	Apparent activation energy
m_i	Reaction order.

1. INTRODUCTION

1.1. Background

The unstable price of crude oil and the environmental impact of fossil-based products has driven the focus of researchers toward the use of biomass as a greener and renewable alternative source of carbon for the production of energy and chemicals [1]. Furfural is one of the biomass-based platform chemicals which can be further converted into various useful products applicable in pharmaceuticals, fine chemical, oil refining, agrochemical, biofuels, and polymer industries.

Furfural is produced from the acid-catalyzed dehydration of D-xylose, a pentose sugar. D-xylose occurs as a significant member of hemicellulose, a polymer that forms part of plant cell walls in association with cellulose and lignin. The lignocellulosic biomass can be used as a source of pentoses and hexoses which can be used to produce furfural. Hemicellulose exists predominantly in the structural components of plants e.g.; the hulls of sunflower seeds and oat husks and it also exist in sugarcane bagasse which remains after the sugar has been extracted.

Furfural was originally produced in a high temperature, high-pressure process, using high concentrations of sulphuric acid. Due to the corrosive effects of the sulphuric acid and the high pressures and temperatures that had to be maintained, these circumstances led to a significant cost of furfural production, both capital and operating. This process had low yields of the order of 53%, was also detrimental to the environment, and was also a batch process, thus it is not a suitable method for producing furfural.

Carbon-based catalysts have shown promising results in the conversion of biomass to furfural. They can suppress the formation of humins and attribute hydrophobic nature which prevents the leaching of the active site into the reaction medium [2]. Several catalyst preparation methods have been adopted to prepare solid carbon-based catalysts with a desired characteristic. Carbon precursors are used through carbonization and sulfonation for various applications like dehydration of xylose to furfural. Catalysts prepared from sucrose by sulfonation using 4-benzenediazoniumsulfonate and resorcinol-formaldehyde resin carbon sulfonated with sulfanilic acid [3] were effective in the conversion of xylose and biomass into furfural in a biomass-based solvent, the γ-valerolactone. Gómez et al. tested Starbon®450-SO_3H for its activity and stability in the conversion of xylose to furfural in water/cyclopentyl methyl ether and come up with a conclusion that it is efficient with significant stability [4].

The biomass-based carbon sources such as rice husk, corncob, sugarcane bagasse, and sawdust are low-cost, abundant, and sustainable. Several studies are focusing on the use of these agricultural wastes as carbon sources for solid acid catalyst preparation. Teff straw is a lignocellulosic waste generated after harvesting a cereal crop known as teff which is widely cultivated in the horn of Africa, Ethiopia, and Eritrea. Teff is grown on over 3 million hectares of land and more than 15 million tons of teff straw is generated each year in Ethiopia [5] and part of it is disposed of through burning causing environmental pollution [6]. This abundantly available resource is an alternative source of carbon which can be used for furfural synthesis.

As lignocellulosic biomass, teff straw contains cellulose, hemicellulose, and lignin which could be used as a raw material for fuel, chemicals, and biomaterials production. Both cellulose and lignin were reported as sources of carbon in the synthesis of catalysts. These biopolymers exist as lignin-carbohydrate matrix giving a variety of physical and chemical properties to lignocellulosic biomasses. Lignin acts as a binding element between hemicellulose and cellulose in the matrix. During carbonization, the lignin showed the tendency to maintain the natural macrostructure of the original biomass [7]. Cellulose has amorphous and crystalline structures formed by the glycosidic bonds between the D-glucopyranose units and hydrogen bonds between the chains [8].

1.2. Problem Overview

Lignocellulosic biomasses are quickly replacing petroleum in the manufacture of value-added chemicals, reducing the negative environmental and economic consequences of global warming and avoiding reliance on a single source. In this regard, low-volume, high-value products such as furfural are commercially generated through biomass feedstock conversion. Furfural is a major green platform chemical for the production of other chemicals and biofuels, and it is one of the top value-added chemicals derived from biomass. Low furfural yields and energy efficiency and a high operation cost are the major drawbacks associated with the existing technology that led the batch process to its closure [9]. Increasing process conversion efficiencies, using and valorizing wastes, and reducing energy input are all inherent solutions to problems of the existing systems. A competitive economic advantage can be gained by combining the use of agroindustrial wastes like sugarcane bagasse with high-performance catalysts to produce furfural. Furthermore, optimizing operating factors such as residence time, reaction temperature, and catalyst concentration can improve furfural yields and production rates.

Sugarcane bagasse is a cheap and abundant source for the production of furfural; it does not compete with food resources. It is used as fuel in sugar factory boilers to produce process steam and electricity for the factory, with 33-45 percent of the bagasse surplus remaining after meeting the needs of steam/electricity requirements[10]. Yearly, roughly 1900 million tons of sugarcane are processed globally, yielding over 150 million tons of surplus bagasse. Bagasse from sugar industries is a raw material with a high hemicellulose content that can be obtained centrally in large quantities in Ethiopia. In recent years, the Ethiopian government has paid special attention to increasing the country's capacity to produce sugar. With an estimated production capacity of

4.2 million tons, Ethiopian Sugar Corporation works to become one of the biggest sugar manufacturers in 2023. In Ethiopia, therefore, large amounts of lignocellulosic (sugarcane bagasse) residue would be made available from different sugar industries that may be used as a feedstock in the production of furfural.

The acid-base homogeneous catalysis is a basis for most organic conversions in the chemical process industries. However, these catalysts are corrosive and have to be treated carefully. Using homogenous acid catalysts needs more steps to separate after reaction, resulting in additional costs. The production of furfural is one of the chemical processes involving the use of such a toxic, hazardous, and corrosive kind of catalyst. In addition, these catalysts cannot be reused and retrieved from the reaction mixture, because they form a complex product molecule, or are highly soluble in the mixture leading to hazardous waste effluent[11]. Therefore, separation and recycling of the used acid is the challenge of using mineral acid as catalysts in such a liquid phase conversion process. This also contributes to the formation of by-products of harmful inorganic acids that have a significant impact on the environment. Today, the impact of these processes on the environment is a major global problem. Greener, efficient, and recyclable heterogeneous catalysts have been explored recently for the conversion of biomass to solve the problems associated with homogeneous catalysts.

Researchers have attempted to reduce chemical emissions through the use of heterogeneous acid catalysts in several ways. Heterogeneous solid acids have advantages over traditional acid catalysts, such as ease of handling, and reduced reactor and plant corrosion issues, which can be recovered and reused many times without any performance loss.

Over time, the world has moved its focus to environmentally sustainable, renewable resource items, and reusable catalysts. In this regard, carbon-based sources are appealing candidates for catalysis in furfural production. There have been few studies on actual feed employing such a heterogeneous catalyst, and data from Ethiopia's sugarcane processing sector on real feed such as bagasse are particularly scarce. Besides, little in-depth analysis of furfural production from lignocellulosic biomass was carried out for kinetic and thermodynamic analysis. Therefore, kinetic and thermodynamic models are required to dehydrate the pentoses in furfural, with higher catalytic activity, greater selectivity, and greater stability.

1.3. Objective

1.3.1. General Objective

The primary objective is to study the conversion of locally available sugarcane bagasse to furfural over teff straw-based acid catalyst.

1.3.2. Specific Objective

Specific research objectives include:

i. To synthesize, characterize and test the performance and stability of teff straw-based solid acid catalysts for the production of furfural.

ii. To investigate the acid-catalyzed hydrothermal extraction of xylose from sugarcane bagasse.

iii. To perform a kinetic study and examine the effects of the various reaction conditions on the conversion of sugarcane bagasse hydrolysate to furfural.

iv. To perform the thermodynamic analysis of the isolation of furfural from the reaction mixture.

1.4. Significance of the research

Incorporeal knowledge about the use of biomass has been added in the study on furfural derived from sugarcane bagasse: The research outcome is published in Reputable journals of Waste and Biomass Valorization and International Journal of Biological Macromolecules.

The followings are the major significance of the research.

- A critical review of the valorization of hemicellulose fraction of biomass into furfural: the catalytic conversion process of sugarcane bagasse and product separation from the reaction mixture to enhance the furfural yield. Establishment of the reaction mechanisms, pretreatment methods to enhance furfural yield, and assessment of the various catalysts which can be applied for biomass valorization processes.
- The Synthesis of lignin-carbohydrate complex-based catalyst from *Eragrostis tef* straw as suitable catalysts for the conversion of furfural and assessment of its catalytic performance in dehydration of the xylose-rich liquor from hydrolysis of sugarcane bagasse.
- The effects of the preparation conditions, the carbonization and sulfonation time, and temperature, on the functionalization of the carbon structure.
- Acid-catalyzed hydrothermal extraction of xylose from sugarcane bagasse and its conversion into furfural using teff (*Eragrostis Tef*) straw-based catalyst.
- The thermodynamic and kinetic analysis of the furfural production process.

1.5. Scope and Limitations

Based on the defined research gap, this study is divided into four principal areas with a focus on synthesizing a novel catalyst and developing renewable resource-based and environmentally sustainable valorization of sugarcane bagasse and teff straw. The four research scopes in this study are summarized as follows:

i. The synthesis of biomass-based solid acid catalyst from abundantly available agricultural waste, the teff straw.

   In this scope, the study proposes a novel method for the synthesis of carbon-based catalysts through simultaneous carbonization and functionalization of teff-straw as a carbon precursor. The new catalyst can solve the problems like recyclability and efficiency that traditional catalysts can't do. The suitability of teff straw as a carbon source in the synthesis of sulfonated acid catalysts for use in the production of furfural is the subject of this research. The effects of the preparation conditions, the carbonization and sulfonation time and temperature, on the functionalization of the carbon structure were also investigated. The catalytic performance of the prepared teff straw-based catalyst was evaluated and the catalyst was efficient and stable to convert xylose to furfural in toluene/ water biphasic systems. Furthermore, the furfural yields are considerable. Additionally, the study tests the reusability of the catalyst and shows it has a great performance.

ii. The catalytic activity test on the sugarcane bagasse hydrolysate conversion into the furfural.

   This scope further discusses and expands the catalytic performance test on the more complex raw material proposed in the previous scope of the study. The catalytic efficiency test in the previous scope was confined to the analytic grade reagents as a representative raw material. However, here the hydrolysate of sugarcane bagasse was used to study the more complex reaction scheme. Optimal process conditions based on different optimization objectives must be established to generate furfural effectively (e.g., maximum yield of the xylose, lowest environmental effect, etc.). In the course of addressing this issue, experimental data obtained based on the central composite design was produced for the hydrolysis of sugarcane bagasse to xylose.

iii. The study on the dehydration of the C-5 sugar in sugarcane bagasse to produce furfural.

To obtain a high furfural yield and decrease undesired products by degradation, it will be important to understand the kinetics of the conversion of xylose in bagasse to furfural and the effects of various reaction parameters on the conversion of xylose in bagasse to furfural. The kinetics of the dehydration of xylose and the effects of temperature, time, and catalyst loading on the dehydration of xylose in sugarcane bagasse to furfural using sulfonated catalyst was studied. Careful optimization of operating conditions is necessary to achieve high recovery of furfural. Based on the research, an equation to predict the furfural yield at a certain temperature and acid concentration is proposed.

iv. The thermodynamic analysis of the isolation of furfural from the reaction mixture.

Thermodynamic equilibrium study is used to analyze the thermodynamic restriction, the conditions that are favored by a certain reaction, and the conditions that support furfural formation, by analyzing complex reaction networks. In this scope, the thermodynamic parameters of furfural extraction into the organic phase were investigated. The Gibbs free energy change in a process shows the spontaneity of the isolation process. The Gibbs free energy changes of mixing of the water, furfural, and toluene to extract furfural into the organic phase were calculated to know the spontaneity of the process.

This thesis did not address the hydrolysis of sugarcane bagasse using the prepared catalyst. It also did not consider the parameters like solid to liquid ratio, water to toluene ratio, and the effect of using different types of solvents besides toluene.

1.6. Organizational Structure of the Thesis

The thesis is organized into five chapters to discuss the above objectives:

Chapter 2: The "Literature Review" provides the latest insight on the bagasse treatment methods, the mechanisms of furfural formation and degradation, the various catalysts used, and product extraction methods for improving the yield.

This chapter also explores the potential of sugarcane bagasse for producing furfural and the challenges encountered in processing the raw material upto product purification.

Chapter 3: The “Materials and methods” of the work, including extraction procedures and conditions, characterization methods and apparatus, and statistics and calculations for data analysis, are described in the experimental methodology.

Chapter 4: “Result and Discussion”. In chapter 4, the suitability of teff straw-based catalyst for use in the production of furfural is explored. The effects of the preparation conditions, the carbonization and sulfonation time and temperature, on the functionalization of the carbon structure and the catalytic performance of the prepared teff straw-based catalyst was evaluated. The optimization studies of hydrolysis reactions were also discussed in chapter 4. An empirical equation is provided based on the optimization study to predict the xylose production at a given temperature and acid content. The acid-catalyzed hydrolysis of sugarcane bagasse for the extraction of xylose from the lignocellulosic matrix, an intermediate in the production of furfural, was the focus of this chapter. The catalytic activity of a solid acid catalyst with a $-SO_3H$ functional group as an active site in a biphasic water toluene system is investigated. The catalytic dehydration of sugarcane bagasse hydrolysate to furfural was studied using temperature and reaction time. This chapter also discusses the thermodynamic aspects of furfural production in a biphasic system.

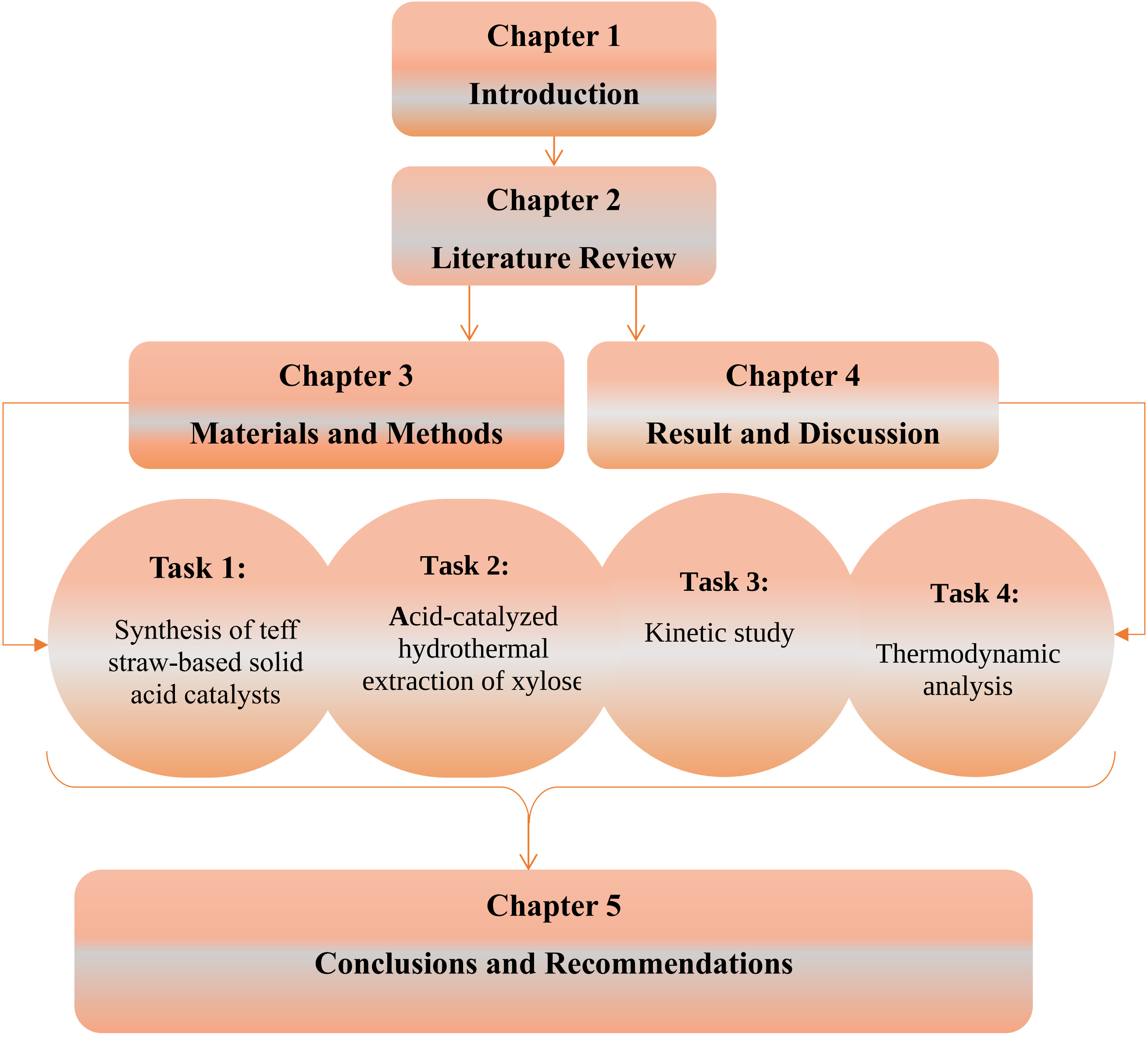


Figure 1. 1: Organizational structure of the thesis.

Chapter 5: Conclusion and Recommendations in this dissertation provide the summary of the tasks in the study and give a short-, medium- and long-term outlook for upcoming work related to the subject area.

2. LITERATURE REVIEW

2.1. Recent research outlook

The conversion of biomass into sustainable energy and various chemicals is recently becoming an attractive alternative to resolve the problems of mankind. Lignocellulosic biomass contains cellulosic, hemicellulosic, and lignin components which can be transformed into various platform chemicals such as furfural. Furfural can be produced from xylan, a five-carbon saccharide, undergoing a hydrolysis reaction followed by dehydration upon the release of the three water molecules. Most organic conversions in chemical process industries are based on acid-base homogeneous catalysis. Mineral acids are used in industrial furfural productions and sulphuric acid is the most widely used catalyst in the production of furfural [12]. Hydrochloric acid, nitric acid, and phosphoric acid are also among the reported homogeneous catalysts used to catalyze the conversions. These catalysts, however, are corrosive to the reaction system and careful handling of them is required. The use of homogeneous acid catalysts requires extra separation steps after reaction which may lead to additional costs. The production of furfural is one of the chemical processes that involve the use of these catalysts which may be toxic, hazardous, and corrosive. Besides, these catalysts are not reusable and recoverable from the reaction mixture, as either, they may form a complex molecule with the product or they are highly soluble in the reaction mixture resulting in hazardous waste effluents [11]. This also leads to the formation of hazardous inorganic acids as by-products. Hence, the environment is soaringly affected by these chemical processes. Various attempts have been carried out by the researchers to mitigate the chemical pollution occurring due to the use of acid homogeneous catalysts. Heterogeneous solid acids have advantages over conventional homogeneous acid catalysts, for instance, the simplicity in handling, decreased reactor problems, and plant corrosion problems, and they can be easily recovered and reused several times without considerable loss of their efficiency. The current research outlooks on the valorization of lignocellulosic wastes into furfural, which include biomass pretreatment, a relevant reaction mechanism in furfural synthesis, furfural separation, and the different utilized catalysts, are described in depth in the following sections.

2.2. Lignocellulosic biomass as a source of carbohydrate furfural production

Furfural is produced mainly from the lignocellulosic biomass with high hemicellulose content. Lignocellulosic biomass, the raw materials for furfural production, differ in composition and structure based on the species of the biomass and environmental growth conditions. The most common sources to produce furfural are sugarcane bagasse and corncobs. Lignocellulosic biomass contains three main components based on their mass contributions. These are cellulose, hemicellulose, and lignin which are mainly linked together by the hydrogen bond. Cellulose is a polymer composed of six carbon glucose linked to each other with β- glycosidic bonds. Cellobiose is the repeating unit and hydrogen bonds are responsible for the high water insolubility and flexibility of cellulose crystalline structure [13]. The elementary fibrils formed by the adjacent chains contain amorphous and crystalline regions, the amorphous region is subjected to hydrolysis first. Hemicellulose is a mixed polymer of both five and six-carbon monosaccharide molecules. It consists of polymers of glucose, galactose, mannose, xylose, arabinose, and other five and six-carbon monosaccharides. Xylan, mannans, and galactans are the main amorphous polymer groups in hemicellulose. The polymer xylan is the major component of sugarcane bagasse hemicellulose which is composed of thousands of the monomers xylose linked to each other by the β-(1,4)-glycosidic bonds [14]. Its backbone contains xylose of more than 80% [15].

Lignin, one of the major components of lignocellulosic biomass, is a highly cross-linked hydrophobic polymer that binds the hemicellulose to cellulose [16]. It is an amorphous three-dimensional aromatic biomolecule consisting of tyrosine and phenylalanine as building blocks. The three monomer units, p-hydroxyphenylpropane (H), guaiacylpropane (G), and syringylpropane (S), synthesized from coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol respectively, polymerize by dehydrogenation to form lignin having different structures and relatively high recalcitrant property from cellulosic polysaccharides. The cellulose, hemicellulose, and lignin are linked to each other by hydrogen bonds. Besides these, the lignin is linked to hemicellulose with the covalent feruloyl ester-ether chemical bonds[17]. The presence of non-hydrolyzable C-O-C and C-C bonds in its structure and heterogeneity of the ether & C-C bonds hamper the degradation of lignin. During the acid hydrolysis for the fractionation of the lignocellulosic biomass into cellulose, hemicellulose, and lignin, the formation of the complex products due to the possible formation of acid-soluble lignin-based components in the reaction, may occur [18]. Lignin tends to neutralize the acidity and inhibit the formation of furfural by dehydration of the xylose in an acidic reaction medium [19]. Lamminpää et al., 2015 studied the effect of the presence of lignin along with the hemicellulose on the yield of furfural and confirmed that it has a negative effect on both the conversion of xylose and the yield of furfural [19]. Daorattanacha et al., 2013 reported a 24% decrease in xylose conversion and an 11% decrease in the yield of furfural upon the addition of 50 wt. % lignin loading [20]. On the other hand, the presence of lignin assists the isomerization of glucose to fructose and the subsequent conversion, provided no low catalyst loading conditions, to hydroxymethylfurfural. Several methods, for example, alkaline and alkaline peroxide pretreatment, organic solvent extraction, ultrasonication, and twin-screw extrusion

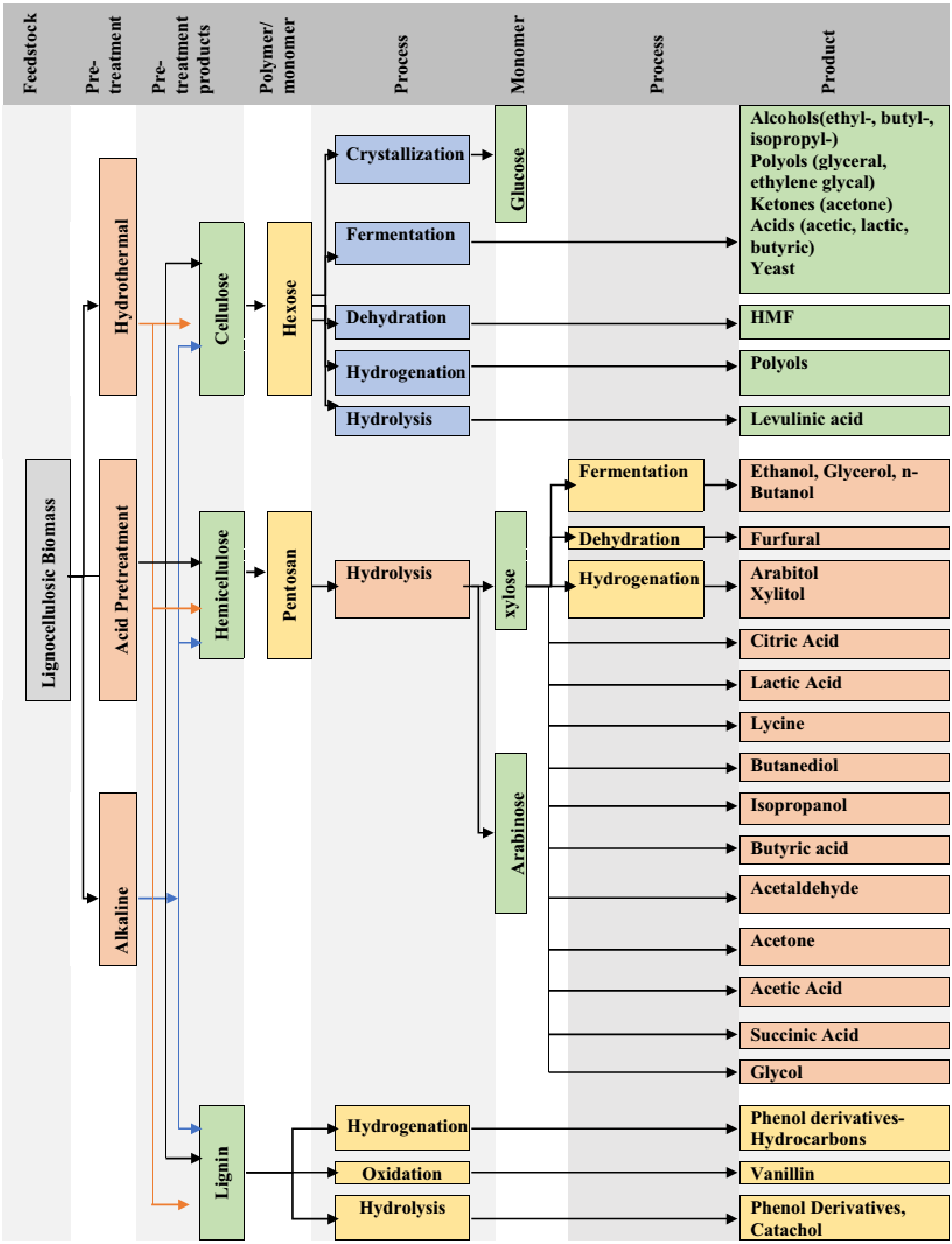


Figure 2. 1: Major polymeric and monomeric sugar intermediates and products of lignocellulosic biomass processing

treatments, and microwave treatment have been used to remove lignin. In alkaline treatment, the most widely used delignification method [21], a soda solution is used to solubilize and remove the lignin after the biomass is exposed to mechanical and hot water pretreatment at around 100 °C and above for about or more than an hour [22]. In the acid pretreatment, dilute sulfuric acid is used to isolate hemicellulose from lignin and cellulose. The combination of the two methods appears to be promising because their advantages could be coupled and minimize their disadvantages. Acid pretreatment followed by alkaline improves the removal of lignin through solubilization by breaking the ether bonds and deprotonation of ionizable groups. Luo et al., 2017 fractionated pubescens into 87 wt % cellulose, 93.6 wt % hemicellulose, and 80.2 wt % lignin derivatives in 25% GVL/water system at 160°C within 4 h [23].

2.3. Biomass pre-treatment for isolation of hemicellulose

Quaker Oats Technology, the oldest commercial way of producing furfural conceived in 1921, or its modified versions are used to produce furfural. In the Quaker Oats Technology, biomass is treated with sulfuric acid at 153 °C for 5 h to hydrolyze the pentosan content and generate pentoses. In this process, the raw 100 kg biomass is mixed with 2.246 kg sulfuric acid without any pretreatment step and fed to the reactor. Steam stripping is applied to recover furfural after it is formed by the dehydration of the pentoses in the subsequent stage. Low yield of around 50%, high steam requirement, disposal problems due to extremely acidic waste discharge, and high operating cost are the major challenges in this process [24]. Various studies have been undertaken to improve furfural production technology to achieve higher yield and lower cost and to make it environmentally friendly. In this regard, scholars have been searching for low-cost catalysts, better product separation technology, and a suitable solvent. To facilitate, the heat and mass transfer, the biomass should undergo size reduction, and then the isolation of the components is carried out [25]. Separation of the hemicellulose component, to reduce the recalcitrant nature of the biomass or the biomass pretreatment is an important step. Pretreatment has an impact on the furfural yield by reducing the amount of lignin, which polymerizes with other compounds in acidic conditions [26]. It may also reduce operating costs if the recycling of catalysts is considered.

Isolation of hemicellulose can be done through several pretreatment ways using chemical, biochemical, physical, or physicochemical methods. This step can be performed by steam explosion, organic solvents, acids such as dilute sulfuric acid or phosphoric acid, alkali treatment using alkaline agents such as sodium hydroxide, ammonia, or lime, and autohydrolysis [27]. Fig.2.1 illustrates the various pretreatment methods along with the possible intermediate and final products obtained from the biomass. The applications and purpose of the extraction products, mainly containing the hemicellulose, are the main considerations that should be incorporated in determining the extraction method. The degree of polymerization, reactivity, purity, and solubility are among the important characteristics of the extracted hemicellulose which can be affected by the method of isolation used.

2.3.1. Dilute acid pretreatment

Acid pretreatment selectively extracts hemicellulose from the cellulose, hemicellulose and lignin complex because hemicellulose is more readily separated under acidic conditions due to its amorphous nature. It is often done using dilute acids to reduce the problems associated with the use of concentrated acids like the corrosion of the reactors, other equipment, and energy requirement for acid recovery. H_2SO_4, HCl, and H_3PO_4 are commonly used to cleave the glucosidic linkage thereby solubilizing the hemicellulose component predominantly to pentose and at some extent to insoluble cellulose and lignin fractions. In this isolation method, furfural is also formed in a small amount [28]. The concentration of 0.5 to 1.5% of sulfuric acid at a temperature above 121-160 °C was reported for the hydrolysis of hemicellulose [29]. About 75 to 95% recovery of sugar can be achieved using the dilute acid treatment.

2.3.2. Hydrothermal pretreatment

Hydrothermal pretreatment is used to preferentially extract the hemicellulose from the cellulose, hemicellulose, and lignin complex. Hemicellulose can be extracted in hot water at a lower temperature than cellulose and lignin [30]. Hot, compressed water depolymerize and solubilize the hemicellulose into pentoses and di- and poly-saccharides of pentoses. Autohydrolysis and steam explosion are the hydrothermal pretreatment methods.

i. Autohydrolysis

Autohydrolysis uses hot, compressed water usually at temperatures between 150-230 °C. Like dilute acid pretreatment, this isolation method uses hydronium ions to catalyze the hemicellulose extraction process [31]. O-glycosidic linkages and acetyl groups break, resulting in partial depolymerization when hydronium ion is released because of an increase in temperature. The acetate group cleaves to some extent and the pH decreases resulting in the formation of additional acetic acid. Autohydrolysis is a green process as it uses only aqueous media without the addition of chemicals [27]. The liquor resulting from the hot water pretreatment includes oligosaccharides and polysaccharides. 55 to 84% of hemicellulose was obtained through autohydrolysis [29]. The solids remaining after the pretreatment contain, mainly cellulose and lignin which can be further converted to useful chemicals.

ii. Steam explosion

Steam explosion is another physical pretreatment method that helps to separate the hemicellulose from the lignocellulosic material by solubilizing the soluble components. In this method, the chipped biomass is exposed to saturated steam under high pressure and then the pressure is suddenly reduced to help the biomass undergo explosive decomposition [32]. The sudden compression and expansion depolymerize the fiber and the soluble products of the pretreatment should be removed from the reactor to reduce destruction reactions. Full recovery of hemicellulose can be achieved in the presence of sulfuric acid or sulfur dioxide [32]. Steam explosion is the less expensive and less energy-consuming process when compared to acid pretreatment because it uses no external catalyst and requires less amount of water (around 3 to 7 times less) to pretreat the same amount of biomass [33]. Even though it is an inexpensive pretreatment method, the steam explosion has limitations like the destruction of some portion of the pentosan.

2.3.3. Alkaline pretreatment

Organic solvents and alkaline agents remove lignin together with hemicellulose as they do not selectively remove hemicellulose from the complex matrix [34]. Alkaline pretreatment can be categorized into two, i.e. alkaline/alkaline earth metals and ammonia-based, depending on the type of catalyst involved in fractionating the lignocellulosic components [29]. Using Na_2CO_3, up to 82% xylan extraction from sugarcane bagasse was achieved, and low formation of furan aldehyde was observed. Alkaline pretreatment under microwave radiation with improved recovery was also studied [35]. Biomass pretreatment should achieve optimized isolation of the hemicellulose component with lower recalcitrance to facilitate the successive conversion to value-added chemicals such as furfural. To mitigate issues related to disposal, environmentally benign chemicals are required to be used during the pretreatment. Suitable, energy-efficient, and inexpensive pretreatment methods are also required [36].

2.3.4. Microwave-assisted pretreatment

Electromagnetic waves with frequencies ranging from 0.3-300 GHz are useful to heat up dielectric substances with a high potential to absorb microwaves. Aqueous systems are very suitable for the application of microwaves because water is a highly polar substance.

Furthermore, microwave heating has advantages like energy efficiency, faster reaction time, and lower reaction temperature when compared to conventional heating. It directly provides energy to substances by molecular interaction with electromagnetic fields. It also saves costs by reducing the amount of chemical/solvents used to fractionate the biomass components, minimizing the by-product formation, and increasing the yield. The extent of biomass fractionation depends on the microwave intensity and irradiation time. Several studies have been carried out on the extraction of the hemicellulosic components from various lignocellulosic biomass like spruce wood, tobacco biomass, aspen wood, and sugarcane trash. Up to 66.1 and 5.3%, xylan and xylose were obtained respectively from aspen wood at 195 ℃ in 20 minutes and up to 50% (w/w) xylan and 6% (w/w) xylose from sugarcane trash at temperatures above 170 ℃. Gulbrandsen et al., 2014 also reported up to about 70 wt % hemicellulose from sugarcane bagasse at 185 ℃ in 20 minutes and 77% from softwood sawmill shavings at 190 ℃ in 10 minutes.

2.4. Furfural

Furfural is a promising chemical platform aldehyde with the empirical formula $C_5H_4O_2$. It is a colorless liquid with a characteristic 'almond-benzaldehyde' odor [37]. It was first isolated in 1821 by a German scientist, Dobereiner [38]. These days, furfural is considered as one of the top value-added chemicals with a huge potential to be produced from the lignocellulosic biomass [39]. Furfural can be produced from agro-industrial residues, including corncob, wood wastes, and sugarcane bagasse. Sugarcane bagasse and corncob are the main raw materials used for commercial production. It can also be produced from fossil-based raw materials like 1,3-dienes, but this is not economical as compared to the lignocellulosic biomass-based sources [40]. As shown in Fig.2.2, furfural can be subjected to other different reactions to produce various other useful chemicals.

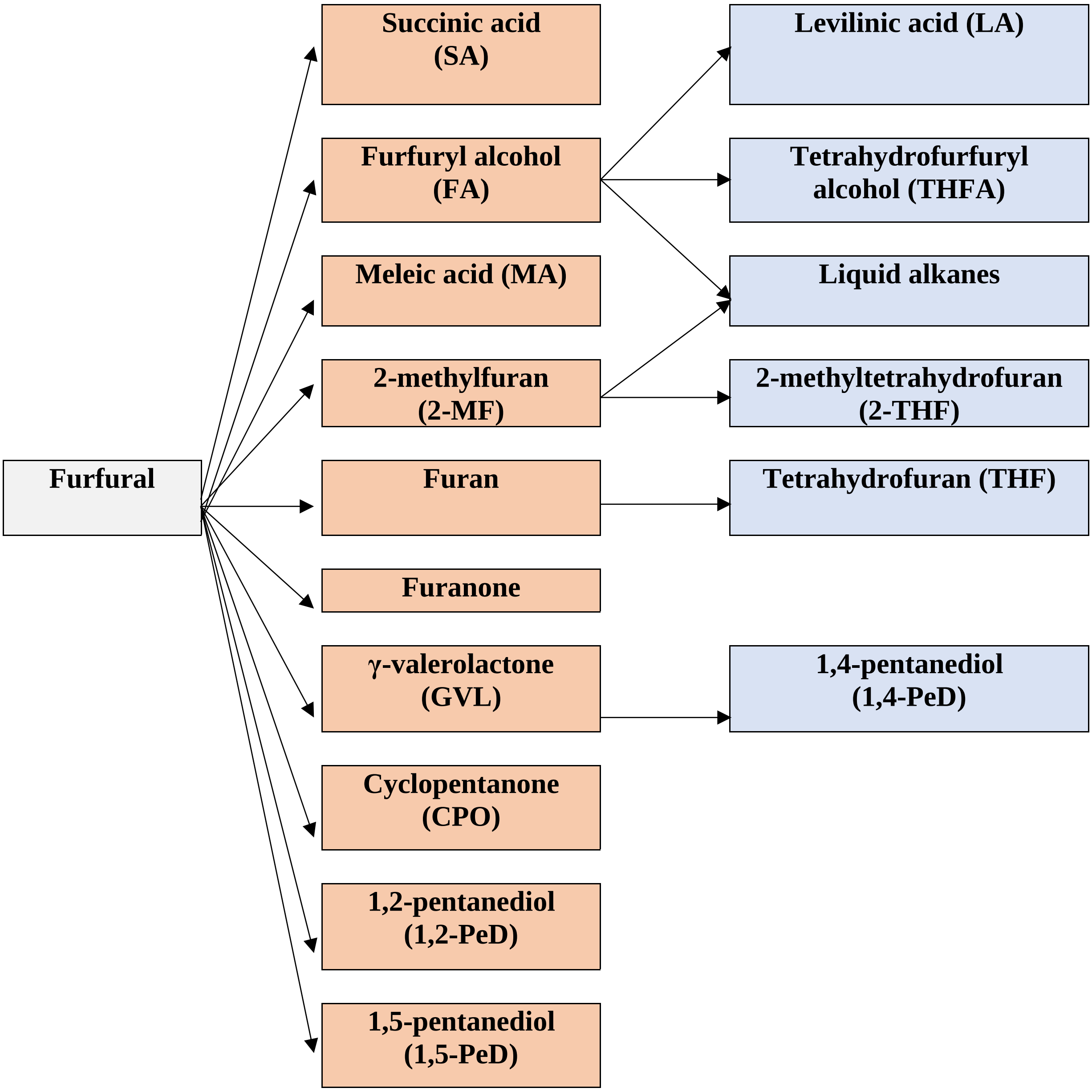


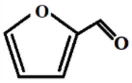
Figure 2. 2: Possible chemicals that can be produced from furfural

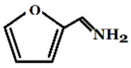
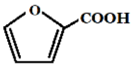
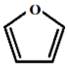
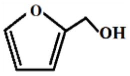
2.4.1. Applications of furfural

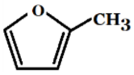
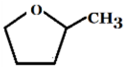
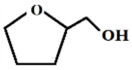
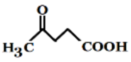
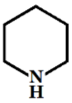
Furfural is a platform chemical having various industrial applications. It has an excellent property for dissolving the components selectively. It can be used to extract unsaturated compounds from oil which can be used to make drying oils and remove aromatic compounds from diesel fuel and lubrication oil to improve their properties and hence produce high-quality motor oil. It can also be used as a very effective fungicide with better effect and faster action as compared to formaldehyde, even if applied at low concentrations. It kills wheat smut in 3 h while formaldehyde does in 6 h at a 0.5% concentration dose. The advantage of using furfural as a fungicide is, that its effect on the seed germination power is insignificant whereas formaldehyde completely damages this power at a concentration of 0.5% if wheat seed is soaked for 6 h [41].

Furfural can be converted to other useful compounds such as furfuryl alcohol, methyl tetrahydrofuran, furoic acid, tetrahydrofurfuryl alcohol, α-Methylfurfuryl alcohol, levulinic acid, pyrrole, furfurylamine, tetrahydro furfuryl amine, piperidine furoic esters, and tetrahydrofuroic acid. Furfuryl alcohol (FA) is used to make furan resins, cement, composites, and corrosion-resistant fiber-reinforced plastics. FA acts as viscosity reducing agent and reactive solvent in the production of epoxy resins and phenolic resins respectively. Tetrahydrofuryl alcohol is a specialty solvent and chemical intermediate produced through further conversion of FA.

Table 2. 1: Applications of furfural and its derivatives

Name of compound	**Chemical Structure**	**Applications**
Furfural		• used as anematocide, fungicide and preservative • Solvent: Extractant for aromatics from lubricating oils, Purification solvent for hydrocarbons, reactive solvent and wetting agent • Platform for many chemicals such as • Furfurylamine, furoic acid, furan, α-(Methyl)-furfuryl alcohol, furfuryl alcohol, 2-methylfuran, furoic esters, levulinic acid, 2-methyltetrahydrofuran,

		tetrahydrofurfurylamine, tetrahydrofuroic acid, tetrahydrofurfuryl alcohol, α-Acetylfuran and Piperidine
Furfurylamine		• a platform to produce diuretic furosemide for the removal of excess water and salt from human body. • synthesis of herbicides, pesticides, pharmaceuticals, and piperidine derivatives.
Furoic acid		• used to produce furoyl chloride, which is used in medication and insecticide manufacturing • is precursor for synthesis of perfumes, cardiovascular and cancer drugs, antibiotic, alpha blockers, and corticosteroid intermediates.
Furan		• Preparation of specialty chemicals such as *a*-acetylfuran, 2,5-dimethoxy-2,5-dihydrofuran, 2,2-difurylpropane, 2,2-di(tetrahydrofurfuryl)propane, and pyrrole derivatives.
Furfuryl alcohol		• production of foundry sand binders, wood protection, corrosion-resistant fiber-reinforced plastics, cements and mortars, • used as reactive solvent for phenolic resins in the refractory industry, as paint stripper, cleaning compound formulation, lubricants, dispersing agents, viscosity reducer for epoxy resins, • chemical building block for drug synthesis, synthetic fibers, rubbers, lysine and vitamin C

2-Methylfuran		• used for antimalarial drug production • used as an octane number improver
2-Methyltetra-hydrofuran		• gasoline additives and higher boiling substitute for tetrahydrofuran as specialty solvent. • used in the electrolyte formulation for secondary lithium electrodes and as a component of alternative fuels
Tetrahydro-furfuryl alcohol		• high-boiling solvent for dyes, printing inks, pesticides and herbicides, paint-stripping agent, industrial cleaner, • reactive diluent for epoxy resins. • preparation of disinfectants and antimetabolite drugs.
Levulinic acid		• Production of succinic acid and δ-aminolevulinic acid
Piperidine		• Piperidine is used as a solvent and building block in the pharmaceutical industry

2.4.2. Chemistry of furfural formation

The conversion of hemicellulose to furfural takes place through two steps. The first step is the hydrolysis of polysaccharide into simple sugar. In this step, xylan is broken into the monomer xylose. Xylose is then converted to furfural in the second step through dehydration by the removal of three molecules of water [38] .

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 \ + \ 3H_2O \qquad (2.\ 1)$$

i. Mechanism for the Hydrolysis of Pentosan

Pentosan consists predominantly of rings linked by oxygen bridges (ether bridges). As shown in Fig.2.3, protonation of oxygen link is the first step of hydrolysis of pentosan and carbon-oxygen bond cleavage follows resulting in the formation of the hydroxyl group on one side oxygen bridge and carbonium ion is formed during the reaction on the other side. The addition of water molecule onto carbocation forms H_2O^+ group and then H_2O^+ group liberates hydrogen ion leaving a hydroxyl group behind. These steps of hydrolysis continue until all oxygen bridge disappear.

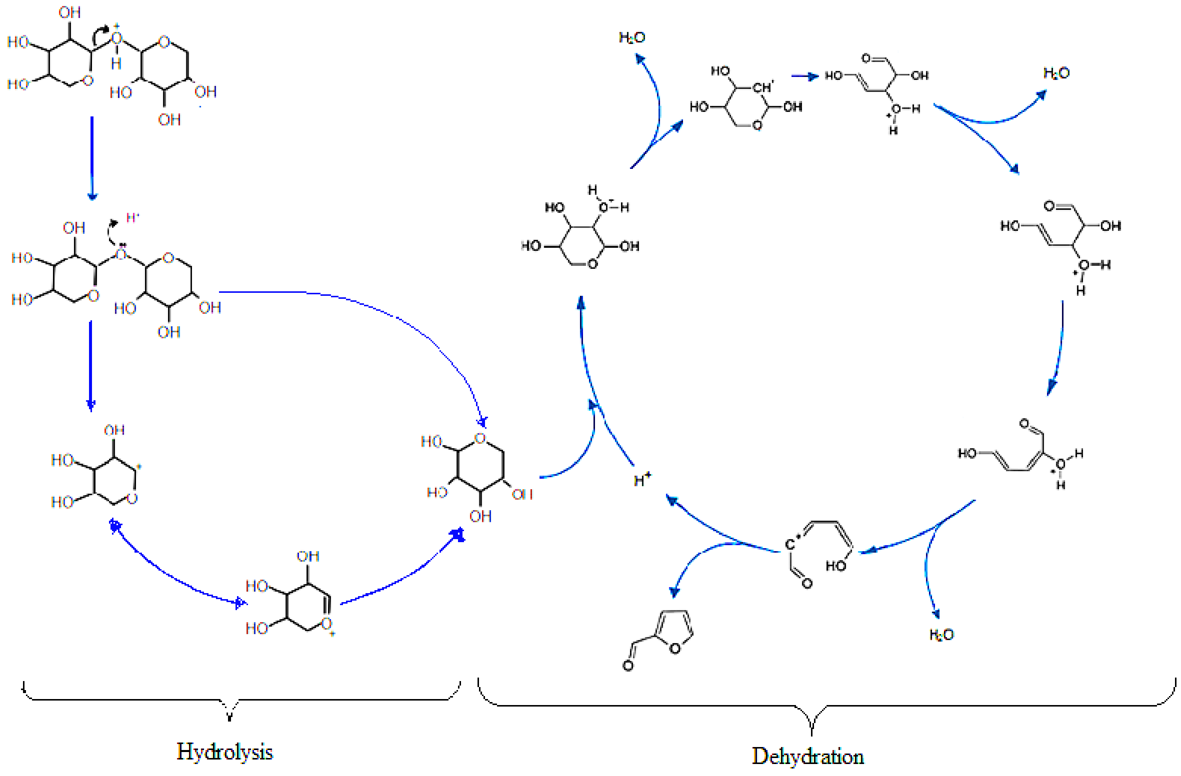


Figure 2. 3: The Mechanism for the Hydrolysis of Pentosan and the dehydration of Pentose

ii. The Mechanism for the dehydration of Pentose

Various mechanisms for the transformation of xylose to furfural have been proposed but, most studies focus on the cyclodehydration mechanism removing three molecules of water using heterogeneous catalysts. Fig 2.3 shows the mechanism for removal of three molecules of water from xylose to form furfural. First, protonation of the free electron pair on hydroxyl group results in trivalent positively charged oxygen and the positive charge moves to the adjacent carbon atom to arrange itself to more stable conformation before C-O bond breaks and a water molecule is released. Then, the two electrons from the neighboring C-O bond are attracted to the C-C bond. This causes the formation of the double bond and the C-O bond breaks liberate another hydrogen ion. This hydrogen ion then attacks electron pair on the oxygen of another hydroxyl group to liberate another water molecule. The attacked site splits to another carbocation and water molecule. The resulting hydrogen ion migrates and attacks another non-bonded pair of electrons on another hydroxyl groups and other two water molecules are released upon dissociation. In the end, ring formation takes place by 1,4-elimination. Other reaction mechanisms such as xylose dehydration via enolization and β-elimination were also proposed as shown in Fig. 2.4.

Xylose dehydration to furfural through lyxose and xylulose formation by functional group rearrangement or by reconfiguration around C1 and C2 carbon atoms were also reported as it can be seen in Fig 2. 4. With Brønsted acids, furfural can be formed directly from xylose while Lewis acids lead to furfural through the intermediate xylulose. Choudhary et al., 2011 reported that the zeolite produces xylulose from xylose and the intermediated xylulose can be quickly transferred into furfural in the presence of Brønsted-acid catalysts such as HCl and Amberlyst-15 [42]. Binder and coworkers also proposed isomerization by enolization and hydride shift mechanisms for the transformation of xylose to furfural using chromium as a catalyst [43]. First, xylose isomerizes to xylulose by 1,2-hydride shift and the resulting xylulose then dehydrates over chromium catalyst to form furfural. Xylose also isomerizes to xylulose by enolization over chromium and enediol is formed.

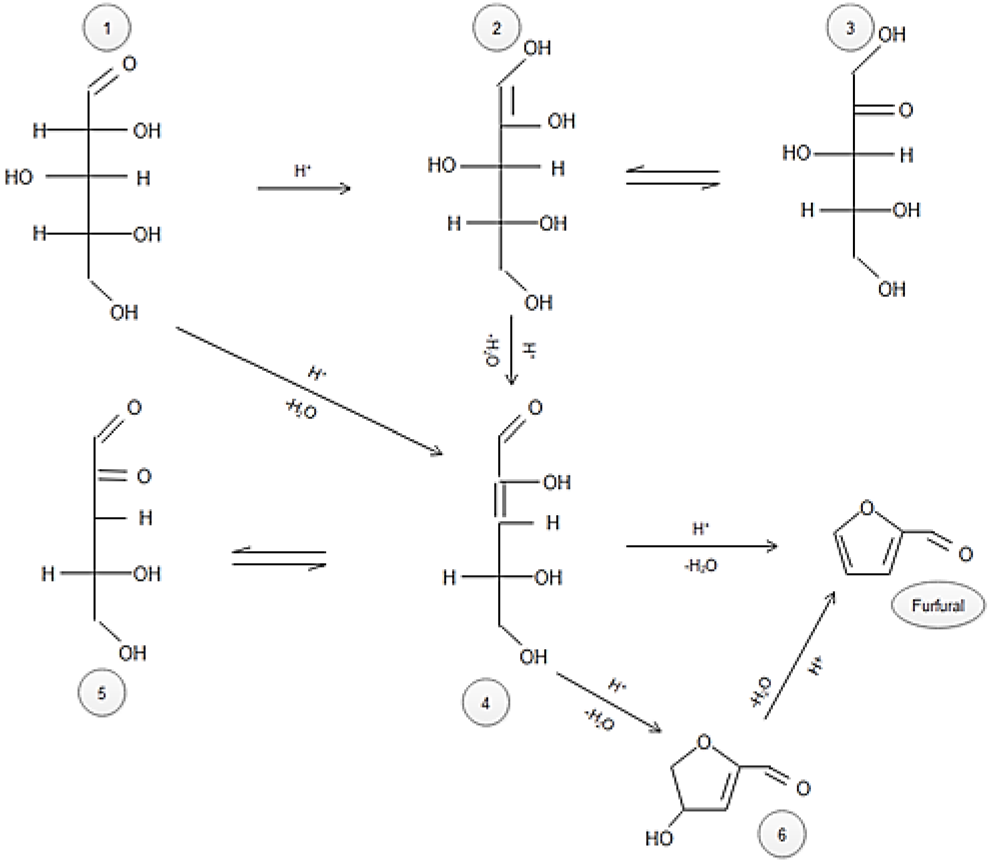


Figure 2. 4: Xylose dehydration mechanism via enolization andβ-elimination.

2.5. Catalysts used to produce furfural from pentoses

Different studies have been made by many researchers to increase furfural yield. Pentosan content of the feed, catalysts loading, time and temperature of hydrolysis, and residence time of furfural in the reaction medium are among the determinant factors that should be considered to optimize the yield in the production of furfural [44].

2.5.1. Homogeneous catalysts

In the last decades, extensive studies on the conversion of reagent grade xylose and xylan into furfural have been performed instead of raw biomass for simplification of analysis. Homogeneous catalysts, mineral acids, and metal chlorides have been investigated for furfural production. Among the mineral acids, sulfuric acid and hydrochloric acid are the most widely used catalysts for the commercial production of furfural. Using sulfuric acid as a catalyst, Quaker Oats produce furfural with around 50% yield at 150℃ in 5 hours and similar yields have been reported for most industrial processes [45]. Undesired polymerization reactions are the causes for the formation of solid humins which are in turn responsible for the moderate yield of furfural. Yemis and Mazza [46] studied and compared the catalytic activities of sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, acetic acid, and formic acid-targeting the yield of furfural. The highest yield of furfural from xylose using hydrochloric acid was about 65% at 170 ℃ [47]. $AlCl_3$ gave 84.8 % furfural yield from xylan at 170℃ in a reaction time of 10 seconds [48].

Marcotullio and De Jong have shown the effect of Cl^- ions on the dehydration rate of xylose to furfural in aqueous acidic solutions. The presence of Cl^- ions has shown improvement in the yield of furfural and selectivity using conventional heating [49]. On the other hand Xiouras et al, using microwave heating [50] investigated the effect of sodium chloride on the dehydration rate of xylose to furfural and achieved 76% furfural yield at 200 ℃ in less than 8 minutes. However, mineral acids are extremely corrosive to the equipment, recovery of the catalysts from the reaction mixtures is difficult, and we cannot reuse the catalysts. Various attempts have been carried out by researchers to mitigate the chemical pollution occurring because of the use of acid homogeneous catalysts.

2.5.2. Heterogeneous catalysts

Solid acid catalysts could be regenerated and reused in catalytic processes with comparable efficiencies. Sulfonic acid-functionalized mesoporous SBA-15 materials, modified zeolites such as HUSY, H-Beta zeolite, H-mordenite, and MCM-41 are among heterogeneous solid catalysts that were developed for furfural production to solve the problems associated with the use of homogeneous catalysts. Arenesulfonic SBA-15 catalysts were prepared via co-condensation for the dehydration of d-xylose to furfural [51]. These selective and hydrothermally stable catalysts incorporate high arenesulfonic-site and posse hexagonal pore arrangement. The activities of sulfonic acid functionalized mesoporous SBA-15 materials were studied with emphasis on the stability of the catalyst. At 160°C with 99% selectivity, they obtained 82% furfural yield from D-xylose in water/toluene. Even though the solvent (toluene) used in the study for extraction of furfural from water medium is not a green chemical, arenesulfonic functionalized SBA-15 supports aged at higher temperatures show higher stability and recyclability [51]. The most studied solid catalysts are zeolites, which are thermally and chemically stable, have tunable acidities and shapes. Furfural yield of mostly lower than 40% was achieved in studies using a variety of H-zeolites (e.g., HY-faujasite, H-mordenite, and H-ferrierite) in water, water/ methyl isobutyl ketone (MIBK), water/toluene and dimethyl sulfoxide (DMSO) in a batch reactor at 140~170 °C [52].

A sulfated tin ion-exchanged montmorillonite (SO_4^{2-}/Sn-MMT) in 2-Methyltetrahydrofuran (2-MTHF)/NaCl-water showed high activity and reusability with a furfural yield of 79.64% from xylose at 160°C[53]. The presence of NaCl showed a decrease in the yield of furfural from xylan. Silico-aluminophosphate (SAPO) based catalysts have shown up to 65% yield of furfural from hemicellulose in bi-phasic systems at 170 °C in 8 hours [54]. Bhaumik and Dhepe (2013) showed in their work that the SAPO-44 can be washed with water and reused eight times without loss of efficiency. This catalyst contains both the Lewis and

Bronsted acid sites where isomerization and dehydration reactions take place. Bhaumik and Dhepe (2014) have also shown in other work that hydrothermally stable SAPO-44 can achieve up to 93% furfural yield from the raw lignocellulosic material such as bagasse, rice husk, and wheat straw [55].

Sulfonated metal oxides and ion-exchange resins were also used for dehydration of xylose to produce furfural. 40-70% yield was achieved by using ion-exchange resins [56]. Metal oxides, sulfonated with H_2SO_4, such as TiO_2, ZrO_2, SnO_2, and Al_2O_3 were also studied and proved that SnO_2 gives the highest xylose conversion and furfural yield [57]. $SO_4^{2-}/ZrO_2\text{-}TiO_2$ gave a higher yield than the selected zeolite catalysts [58]. TiO2 coupled nanocellulose was proved to enhance the conversion of cellulose to glucose [59]. Neill et al., 2009 studied the conversion of furfural over ZSM-5 zeolite in H^+ form at 140-220 °Cin a batch reactor and proposed a kinetic model for the reaction as the first order with the activation energy of 32.1kcal/mol. The catalyst achieved a yield of 46% furfural from xylose at the optimum temperature of 200℃. The effects of parameters like the catalyst pore size, time, and temperature were investigated and found to be highly influential in product distribution [60].

Carbon materials are becoming very attractive in recent years for their versatile use as catalysts, catalyst supports, a sorbent for air and water purification, supercapacitors, and fuel cells. Solid acid catalysts with different functional groups have been tested for the production of the furfural, a top 12 versatile platform chemical obtained from biomass [61]. For catalytic processes, solid acid catalysts based on carbon sources are getting attention due to their recyclability, low cost, unique structure, environment-friendly properties, and easy preparation methods.

Among the desired characteristics of these catalysts are high specific surface area, adjustable porous structure, hydrothermal stability, and easy functionalization [2]. The thermochemical conversions could take place in concentrated sulfuric acid for simultaneous carbonization and sulfonation. H_3PO_4 was also reported as an activating agent in the preparation of activated carbons from hemp, alcell kraft lignin, and olive stone. Activated carbon monoliths, the catalysts with well-defined axial channels, produced by the impregnation of H_3PO_4 and extrusion of lignin showed good mass transfer, low-pressure drop, good mechanical strength, and thermal stability [62].

Carbon-based solid acids have suitable catalytic properties to produce furfural by dehydration of xylose. The accessibility to xylose is good as the specific surface area and porosity of these solid acids are high. Besides, these types of catalysts have excellent electron conductivity and have relatively high chemical and thermal stability[63]. Carbon materials can be prepared from cheap and abundant biomass residue to be used as catalysts and catalyst support for various biomass transformations. Carbon black and activated carbon are prepared via different techniques. Pyrolysis of polymers or hydrocarbon at about 1500℃ can produce an amorphous carbon black with a randomly cross-linked structure and roughly planar layers of sp^2 hybridization carbons [64]. Activated carbon is an amorphous solid with high porosity and surface area. It is prepared by the carbonization of carbon materials in the absence of oxygen if physical activation is required. Steam or oxygen is used as physical activation at 600-1200 ^{o}C [65]. The carbon material is carbonized after impregnated with an acid, a strong base, or a salt in chemical activation.

Carbon materials exhibit acid-base character with different oxygen functionality. Biomass-based amorphous carbon has been studied for biomass conversion by bearing SO_3H, COOH, and OH groups. The catalyst can be easily prepared from biomass resources by incomplete carbonization and subsequent sulfonation at a high temperature greater than 160 ℃ with a large amount of fuming sulfuric acid (15 wt% SO_3) or concentrated sulfuric acid (98%) for the introduction of

SO_3H groups into the amorphous carbon surface. Lignin can be used to produce activated carbon and acidic sulfonated carbon for hydrolysis/dehydration of polysaccharides and polyols.

Porous carbon materials are becoming very attractive in recent years for their versatile use as catalysts, catalyst supports, a sorbent for air and water purification, supercapacitors, and fuel cells. For catalytic processes, solid acid catalysts based on carbon sources are getting attention due to their recyclability, low cost, unique structure, environment-friendly properties, and easy preparation methods. They can be obtained from carbon precursors through carbonization and sulfonation for various applications like dehydration of xylose to furfural. Hydrothermal, ionothermal, and molten salt carbonization are among the various techniques adopted to synthesize porous structured carbon materials reported in some literature. Thermochemical conversions take place in water for the case of hydrothermal carbonization and in ionic liquids and molten salt for ionothermal and molten salt carbonization respectively. Hydrothermal carbonization is an inexpensive, mild, and green process involving the thermal decomposition of carbon precursors in an aqueous solution in the presence of heat.

Lam et al., 2014 [66] reported that the water-tolerant carbon catalyst sulfonated graphene oxide (SGO) with 2% loading converted xylose to furfural with a selectivity of about 75% and yield of 62% in 35 minutes at 200 °C. At these same conditions, i.e., catalyst loading, time of reaction, and temperature; graphene, graphene oxide, and, sulfonated graphene achieved a relatively lower yield of 51,53 and 55% as compared to SGO. SGO exhibits a large surface area ($680m^2/g$), contains aryl sulfonic acid group which are active sites responsible for the dehydration process and remains active after repeated reactions.

Properties of carbon-based solid catalysts that affect the catalytic performance include acidic property, specific surface area and pore size[67]. The acidity of the catalyst is among the properties of a catalyst that can significantly affect the performance of a catalyst. The strength and distribution of acid sites on the solid surfaces in addition to their nature are determinant catalytic properties of a solid acid catalyst that affect the conversion and selectivity of a reaction. A Brønsted acid donates protons while Lewis acids accept electrons. Lewis acid sites promote the xylose-xylulose-furfural route instead of xylose to furfural direct conversion and Brønsted acid sites catalyze the conversion of xylulose to furfural [68]. Agirrezabal-Telleria et al., 2014 used partially hydroxylated MgF_2 catalysts by varying the Lewis/Brønsted acid ratio to produce furfural in water/toluene [69]. Lewis acidity is due to Mg^{2+} ions and hydroxyl groups are responsible for the Brønsted acid property of the catalyst. A combination of Sn-beta zeolite as a Lewis acid and Amberlyst-15 as a Brønsted acid can be used to convert xylose to xylulose and then to furfural in an aqueous medium [70]. The Lewis/Brønsted acid site ratio is, therefore, one of the factors that affect the rate of dehydration reaction and furfural yield. The optimum Lewis/ Brønsted loading is required to achieve the optimized conversion and yield[69]. Carbonaceous by-products will be formed at a higher L/B ratio and a lower L/B ratio leads to an undesired polymerization reaction. The rate of reaction increases with an increase in acid content and strength, but too strong acidity accelerates undesired reactions. The variation of acidity of zeolite catalysts is mainly due to the preparation conditions and Si/Al ratio [68]. Carbon-based catalysts possess Brønsted acid sites like $-SO_3H$ and –COOH. Phenolic –OH group are also present in these types of catalysts [71].

IUPAC defines pore sizes less than 2nm as micropores, 2-50 nm as mesopores and greater than 50 nm as macropores. The pore size of the catalyst should match the molecular size of xylose and furfural to facilitate the diffusion of reactants into the catalyst and the removal of products in the furfural production processes. Small pore size than xylose and furfural results in diffusional resistance problem by inhibiting the diffusion rate and larger sizes may be suitable for furfural rearrangement into large molecules because of the longer residence time of the product inside the porous structure [68]. Catalyst screening by Iglesias et al., 2016 showed that

H-ZSM5 containing narrow pore size was unable to promote the desired transformation, and probably transformations may occur on the active sites located at the outer surface of the catalyst [72]. The size of xylose and furfural were approximate to be 0.68 and 0.57 nm, respectively based on literature. Neill et al., 2009 concluded in their work that zeolite with a pore size(0.8 nm) close to the size of xylose and furfural would be effective for xylose conversion to furfural [60].

The specific surface area of the catalysts is another factor that affects the catalytic performance. A higher specific surface area promotes the performance of a catalyst by increasing the accessibility of the active sites to xylose [68]. Lima et al., 2008 experimented with delaminated Nu-6 zeolite with a greater surface area in about seven-folds than standard Nu-6 zeolite and increased rate of reaction in two folds with furfural yield of about 50% at 453K [54]. Table 2.2. shows the summary of the reaction conditions and the yield of furfural with various catalysts.

Table 2. 2: Catalysts used for furfural production

Substrate	Catalyst	Solvent	Characterization BET Surface Area (m^2/g) Acid density	Temperature (°C)	Time	Yield in %	References.
Bagasse	Silicoaluminophosphate	Toluene/Water	-	170	8 h	93	[73]
Camellia oleifera shell	sulfonated swelling mesoporous polydivinylbenzene (PDVB–SO_3H)	γ–Butyrolactone/ Water	BET 676.18 m^2/g 2.6 mmol/g	170	30 min	61.3	[74]
Cassava waste	Sulfonated Carbon-Based Catalyst	Acetone/DMSO/Water	BET 1.1 m^2/g 1.46 mmol/g	250	1 min	2.1	[75]
Corn stover	SC-CaCt-700	γ-valerolactone	BET 921 m^2/g 2.62mmol/g	200	100 sec	93	[76]
Corncob	SO_4^{2-}/SnO_2-MMT/NaCl	Toluene	BET 93 m^2/g	190	20 min	66.1	[77]
Corncob	SO_4^{2-} /TiO_2 -ZrO_2/La^{3+})	Water	-	180	2h	(6.18 g/100 g	[78]

Corncob hydrolysate	SO_4^{2-}/SnO2-MMT	Toluene	BET 93 m^2/g	190	15 min	81.69	[77]
D-xylose	Acid-functionalized multi-wall carbon nanotubes (MWCNTs)	Water	BET 131 m^2/g 0.31 mmol/g 3.3 nm	170	3h	57	[67]
Hydrolysates from corncob	Tin- loaded montmorillonite	SBP/Nacl-DMSO	-	190	10 min	57.8	[79]
Isolated Hemicellulose	Silicoaluminophosphate	Toluene/Water	-	170	10 h	82	[73]
Maple wood	Sulfuric acid	Methyl Isobutyl Ketone/Water	-	170	50 min	85.3	
Soft- Wood Hemicellulose	SAPO-5	H_2O/Toluene	BET 309 m^2/g 0.8 mmol/g	170	8 h	65	[80]
Soft- Wood Hemicellulose	SAPO-11	H_2O/Toluene	BET 42 m^2/g 0.3 mmol/g	170	8 h	58	[80]
Soft- Wood Hemicellulose	SAPO-44	H_2O/Toluene	BET 369 m^2/g 1.2 mmol/g 0.45 nm	170	8h	63	[80]

Xylan	SO_4^{2-}/Sn-MMT	2-MTHF/water	BET 153.52 m^2/g 0.58 mmol/g	160	1.5 h	77.35	[53]
Xylose	$CrCl_2$, LiBr	N,N-dimethylacetamide	-	100	4 h	56	[43]
Xylose	PSZ-MCM-41	Toluene/Water	-	160	4 h	42.8	[81]
Xylose	Dealumin. HNu-6 (2)	Toluene/Water	-	170	4 h	47	[82]
Xylose	H-mordenite 13	Toluene/Water	-	260	0.05 h	98	[83]
Xylose	Arenesulfonic SBA-15	Toluene/Water	BET 568 m^2/g 0.94 mmol/g 2.3 nm	160	20 h	86	[51]
Xylose	SO_4^{2-}/Sn-MMT	2-MTHF/water-NaCl	BET 153.52 m^2/g 0.58 mmol/g	160	2 h	79.64	[53]
Xylose	HY-faujasite (15)	H_2O/MIBK	7.4x7.4 Å	170	50 min	29.7	[84]

Xylose	HY-faujasite (15)	H_2O/toluene	7.4x7.4 Å	170	50 min	41.82	[84]
Xylose	H-mordenite (12)	H_2O/MIBK	6.5 x7 Å	170	50 min	20.16	[84]
Xylose	H-mordenite (12)	H_2O/toluene	6.5x7 Å	170	50 min	33.62	[84]
Xylose	HY-ferrierite (20)	H_2O/toluene	BET 389.9 m^2/g 4.2x5.4 Å	140	4h	35	[85]
Xylose	HY-ferrierite (20)	H_2O	BET 389.9 m^2/g 4.2 x 5.4 Å	140	4h	13	[85]
Xylose	HY-ferrierite (20)	DMSO	BET 389.9 m^2/g 4.2x5.4 Å	140	4h	23	[85]
Xylose	H-ZSM-5	H_2O	0.16 mmol/g 1.2nm	200	30 min	46	[60]
Xylose	Sn-Beta+HCl	H_2O	BET 100 m^2/g	110	3h	14.3	[42]
Xylose	Sn-Beta+Amberlyst	H_2O	-	110	3h	9.5	[42]
Xylose	MCM-41	H_2O/Butanol	BET 800 m^2/g 3 nm	170	3 h	44	[86]
Xylose	MCM-41-SO_3H	H_2O/MIBK	BET 438 m^2/g	140	24h	51	[52]
Xylose	MCM-41-SO_3H	H_2O/toluene	BET 438 m^2/g	140	24 h	76	[52]
Xylose	MCM-41-SO_3H	DMSO	BET 438 m^2/g	140	24 h	75	[52]

Xylose	H-MCM-22 (24)	H_2O	BET 333 m^2/g 0.204 mmol/g	170	16 h	52	[87]
Xylose	H-MCM-22 (24)	H_2O/Toluene	BET 333 m^2/g 0.204 mmol/g	170	16 h	70	[87]
Xylose	ITQ-2 (24)	H_2O	BET 623 m^2/g 0.198 mmol/g	170	16 h	54	[87]
Xylose	ITQ-2 (24)	H_2O/Toluene	BET 623 m^2/g 0.198 mmol/g	170	16 h	66	[87]
Xylose	Nu-6(2)	H_2O/Toluene	-	170		23	
Xylose	ITQ-18	H_2O/Toluene	-	170		43	[54]
Xylose	SBA-15-SO_3H	H_2O/Toluene	-	160	4h	69	
Xylose	SO_4^{2-}/ZrO2–Al2O3/ SBA-15	H_2O/Toluene	BET 271 m^2/g 0.91 mmol/g 6.59 nm	160	4h	52.8	[88]
Xylose	Nafion 117	DMSO	-	150	2h	60	[66]
Xylose	Amberlyst-15 / Hydrotalcite	N,N-dimethylformamide (N,N-DMF)	-	10	1h	37	[89]

Xylose	Sulphonated Graphene oxide SGO	Water	BET 680 m^2/g	200	35 min	62	[66]
Xylose	Graphene oxide	Water	BET 318 m^2/g	200	35 min	53	[66]
Xylose	Sulphonated Graphene	Water	BET 634 m^2/g	200	35 min	55	[66]
xylose	Glu-TsOH-Ti	Methyltetrahydrofuran/ Water	BET 42.5 m^2/g 1.03 mmol/g 4.5	180	30 min	51	[90]
Xylose	PTSA-POM	γ-valerolactone	2.2-2.4 mmol/g	170	10 min	80.4	[91]
Xylose	Nb50-MCM-41	Water/ Toluene	BET 1040 m^2/g 4 nm	160	6h	38.6	[81]
Xylose	H-AM-11	Water/ Toluene	BET 328 m^2/g 0.17 cm^3 g^{-1}	160	6h	49.8	[81]
Xylose	Na,H-AM-11	Water/ Toluene	BET 489 m^2/g 0.22 cm^3 g^{-1}	160	6h	50	[81]
Xylose	magnetic porous carbon- based solid acids prepared from sawdust	DMSO	-	150	6h	61	[92]

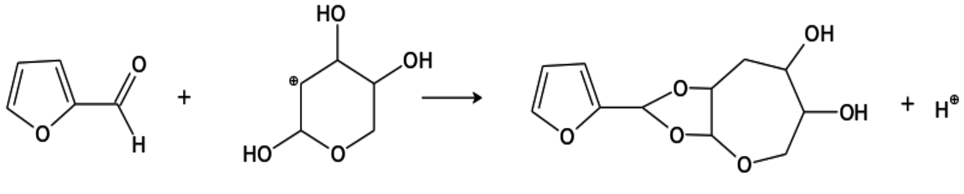
Xylose	sulfonated carbon prepared from D-glucose	γ-valerolactone	-	175	20 min	70	[92]
Xylose	WH-PTSA-220	γ-valerolactone	-	170	2h	60	[92]
Xylose	Al-TUD-1(21)	Water/ Toluene	BET 757 m^2/g 0.197 mmol/g	170	6 h	60	[93]

2.6. Conversion of hexoses to furfural

Most of the investigations towards furfural focus on the conversion of hemicellulose component of biomass, but there are also several published works that confirm the possibility of converting cellulose component into furfural. Jin et al., 2011 illustrated two possible mechanisms of furfural formation from hexoses. The first pathway is the conversion of hexose to HMF and then to furfural, while the second is hexose to pentose and then to furfural [94]. In the conversion of glucose to HMF, glucose isomerizes in the rate-limiting step to fructose and fructose then dehydrates to form HMF [20]. The formed HMF then loses –CH_2O by decarboxylation to form furfural [95]. The formation of pentose via retro-aldol reaction from ketose is the other plausible pathway to produce furfural from C6 sugars [96]. Aida et al., 2007 investigated the effect of temperature, residence time, and pressure on the yield of furfural from D-glucose in water and the yield was 12.2 % at 400 °C [97]. Some literature reported the higher yield of furfural from raw biomass when compared to pure xylose, where the possible reason could be the co-conversion of five- and six-carbon sugar in the polymer matrix. Looking for simultaneous utilization of cellulose and hemicellulose component derived sugars, 51.1 and 40.9 % yield of furfural on molar basis were achieved from corncob and sugarcane bagasse respectively in γ-valerolactone at 185 °C within 85 minutes [98]. A maximum yield of 22.3 % furfural on the molar basis was obtained from cellulose at 175 °C in 100 minutes using Fe-beta zeolite as a catalyst γ-valerolactone [98]. In one pot processing of corn stalk, a furfural yield of 83.8 % (at 170 °C, 100 min), 84.5% (at 180 °C, 80 min) and 86.3 % (at optimal conditions of 190°C, 40 min) were obtained while a maximum yield of 80.4 % was obtained from xylose (at 170 °C, 10 min) using PTSA-POM catalyst in GVL/water system [91].

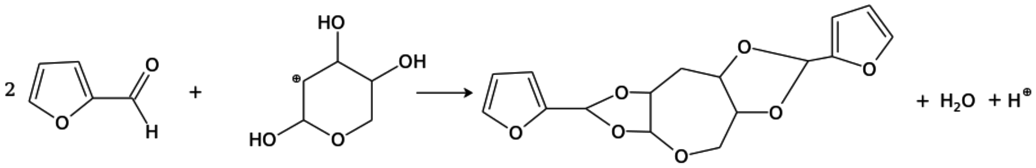
2.7. Reduction of yield loss through isolation of furfural from the reaction mixture

Since furfural is very reactive, in the acidic medium it undergoes various reactions such as polymerization which lead to lower furfural yield. Resinification and condensation reactions are the causes for the decrease in the yield of furfural [41]. These reactions occur when the furfural formed during the reaction stays dissolved in the liquid phase. Resinification reactions take place when furfural reacts with another furfural molecule and condensation reactions take place when furfural combines with an intermediate.



(2. 2)

Difurfural xylose is also formed as a degradation product if an additional furfural molecule reacts with an intermediate [41]. These furfural degradation reactions are possible only when furfural is present as a dissolved product in the liquid phase, whereas impossible in the vapor phase where the catalytically active components are absent [24].Table 2.3 shows the summary of various furfural separation approaches.



(2. 3)

In industrial processing of biomass for the production of furfural, steam is injected into the reaction chamber to supply heat for the reaction to take place and also to preferentially remove furfural from the liquid phase. This selective removal of furfural from the liquid phase into vapor phase help the process to achieve higher furfural yield by preventing the product loss due to resinification and condensation reactions. In the analytical method, the amount of furfural produced can be escalated to 100% yield because the presence of HCl saturated with NaCl raises the boiling point and result in the superheating of vapor [24].

Continuous removal of furfural product from the acidic medium is required to stop the polymerization and condensation reactions which reduce yields. This can be done by steam stripping, reactive distillation, water/organic biphasic systems, use of supercritical fluids (CO_2),d and gaseous acid catalysis (using superheated steam and HCl vapor) [99].

2.7.1. Steam stripping

Steam stripping is a separation process that uses steam to preferentially extract components from a liquid stream. Commercially furfural is produced from biomass using H_2SO_4 and recovered from the aqueous solution by steam stripping to stop the further transformation of furfural to larger molecules and purification is done by double distillation [40]. The energy consumption by this method of product recovery has been reported to be very high as it uses 25 to 35 tons of steam to produce a ton of furfural [49]. In the Rosenlew process 30 to 1 ratio of steam to furfural is used to achieve 59.5% yield of furfural at 180 ℃. Gandarias and Arias [100] suggested in their work that a high amount of utilities are required when fresh steam is used and cooling of vapors are required. Further purification also requires high energy input if the concentration of furfural in the steam is too low [100]. The volume of steam used for stripping can affect the yield of furfural. Too low amount of steam is not sufficient for fast isolation of the furfural formed during the reaction. The furfural remaining in the acidic medium will be lost due to resinification and condensation reactions. Too high steam input hinders the catalytic activity towards the formation of furfural by reducing the acidity of the medium [41]. Therefore, an optimum amount of steam is required to produce a higher amount of furfural as both too much and too low volume of steam reduce the product output. Costs of steam stripping appear to be high because of high steam usage to extract the furfural from the reaction medium and the high cooling requirement for stripping vapor and the high energy requirement for boilers in the distillation process for the dilute furfural-water stream separation [41].

2.7.2. Nitrogen-stripping

Nitrogen is another stripping agent for producing furfural from biomass at higher yields. It is inert, easily separable, and recyclable gas. Agirrezabal-Telleria et al., 2012 achieved 67%, a higher yield of furfural as compared to that obtained using steam stripping [101]. Agirrezabal-Telleria et al., 2014 studied partially hydroxylated MgF_2 catalysts by varying the Lewis/Brønsted acid ratio and simultaneous stripping with nitrogen achieved 87% furfural selectivity at 160 ℃ in water/toluene [69]. The introduction of the nitrogen stripping current commercial process reduces the energy requirements and allows the recycling of the stripping agent and reduces the cost up to 60%. But, high recompression is required to recycle if the reduction of the use of fresh nitrogen is to be applied [100]. High product purity, high furfural yield, lower product dilution, easy separation of catalyst and stripping agent recycling are among the advantages of nitrogen stripping [56]. Nitrogen stripping showed better industrial feasibility as compared to biphasic water/organic solvent systems. 39% furfural yield was reported in water toluene system using ion-exchange sulfonic resin (A70) as a catalyst, which is less than that obtained using nitrogen as an extracting agent at the same temperature of 175 °C [56]. Nitrogen stripping has also the advantage of reducing the cost of final product separation challenging the commercial production processes of furfural. Considering the stripping agent recycling and product dilution, nitrogen stripping has a cost advantage over steam stripping.

2.7.3. Water/organic biphasic systems

Furfural can be produced in biphasic systems consisting of water and organic mixture [100]. In this system, furfural produced in the aqueous phase will be immediately transferred to the organic phase. The spontaneous transfer of furfural into organic phase protects it from undergoing further transformation to a larger molecule. The purpose of a biphasic reaction is to increase furfural yield by reducing the side reactions and to simplify the separation process by avoiding the azeotropic point of the furfural-water mixture. The organic phase includes solvents like toluene, butanol, methyl isobutyl ketone (MIBK), MIBK-2-butanol mixture, tetrahydrofuran (THF), or dichloromethane (DCM), which have a great affinity for absorbing furfural. Furfural resinification reactions appear to be negligible in the organic phase of toluene/water system. The yield of furfural was 70, 66 and 35 in water/ toluene byphasic system and 52, 54 and 13 in water only in the presence of H-MMC-22(24), ITQ-2(24) and HY-ferrierite(20) respectively [85]. Deng et al., 2016 reported higher yield of furfural in water/dichloromethane than in water only [102]. The addition of NaCl into the water/dichloromethane further improved the yield of furfural.

With the aim to produce furfural using green process and develop an appropriate kinetic model for conversion of xylose to furfural, Hua et al., 2016 achieved improved furfural yield under optimal conditions [103]. They used high-temperature water as a catalyst to dehydrate xylose to furfural and ethyl butyrate, butyl acetate, n-butanol, n-butyl ether, and toluene solvents to extract the product. Ethyl butyrate showed the highest extraction efficiency. Selection of an appropriate solvent along with a proper catalyst can give high furfural yields. Zeolites, sulfated and tungstated zirconia catalysts, and sulfonic acid materials, which have different textural, surface, and acid properties in methanol, ethanol, and 2-propanol were tested. β-zeolite achieved best results as it exhibits best Brønsted and Lewis acid site combinations among the tested catalysts and 2-propanol was found to be the best medium to hinder side reactions that may occur in aqueous media and to give higher furfural yield than methanol and ethanol [72]. 68.3% furfural yield was achieved in H_2O/toluene over SBA-15-SO_3H [104]. The MCM-41 resulted in a furfural yield of about 44% in DMSO [52] and less than 40% in H_2O/1-butanol [86], while 51% in water/MIBK and 76% yield achieved in water/toluene by MCM-41-SO_3H [52], [104]. With $H_3PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$ supported on MCM-41, the yields in H_2O/toluene were 48% and 33%, respectively, and increased to 52% and 45% in DMSO, respectively[68].

The presence of biomass particles in water also reduce the furfural yield loss by preventing the movement of furfural molecules and catalytically active components towards each other [56]. Environmental issues, solvent recovery, and process complexity are the major problems associated with biphasic systems [9]. For large scale processing, separation of the product furfural from the organic solvents consumes a substantial amount of energy and vigorous mixing of water and solvent for efficient extraction of furfural is a problem. The use of solvents with a low boiling point is another challenge in biphasic systems as heat treatment develops high pressure in the reaction vessel which in turn leads to additional capital cost. In water/ organic biphasic systems the use of organic solvents in commercial processes could add economic burdens because of the consumption of solvents, costs extra separation steps and waste management to protect the environment from pollution. Cleaning the water effluents from these systems is difficult as high energy is required to remove the solvents and recovery of solvents is also a must to make the process economical [105].

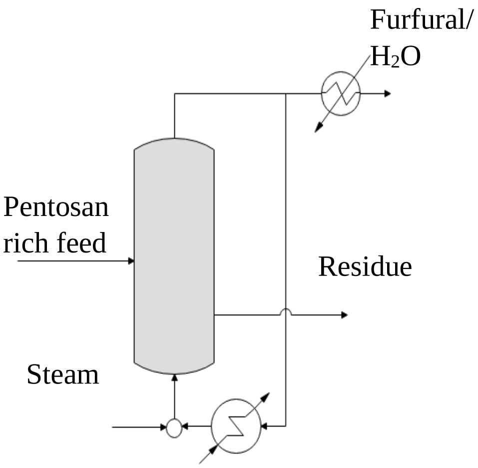
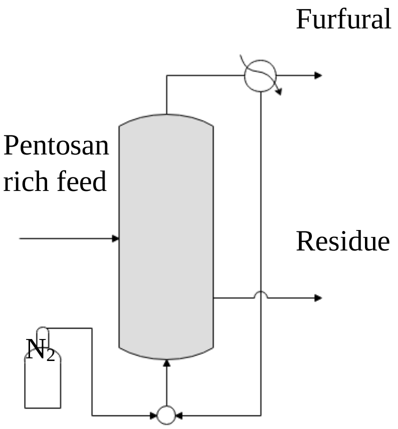
2.7.4. Monophasic systems

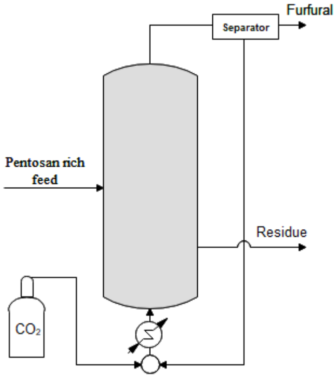
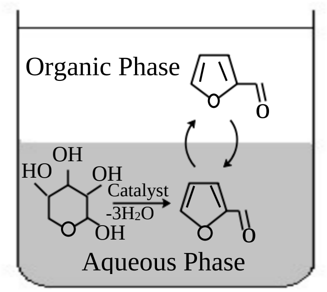
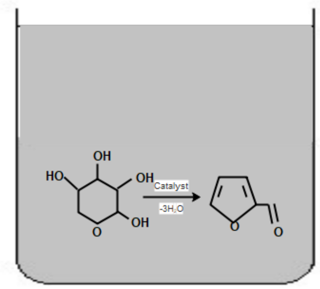
Gürbüz et al., 2013 [96] reported the use of a γ-valerolactone solvent as a monophasic system for conversion of xylose into furfural using a solid acid catalyst. γ-valerolactone has the advantage that it is a green solvent that can be produced from biomass. But, multi-step processing for γ-valerolactone production, its high boiling point, and miscibility with water makes it feasible only for laboratory[106]. Use of γ-valerolactone as a solvent has advantages like the promotion of xylose conversion rate and inhibition of the furfural degradation rate and the separation of furfural from the solvent is simple due to the difference in their volatility. There is no further step needed for liquid-liquid separation as in the case of biphasic systems to recover organic solvents from aqueous/organic phases.

2.7.5. Supercritical carbon dioxide

Supercritical carbon dioxide was also reported for the extraction of furfural from the reaction solution. In this extraction type liquified CO_2 is introduced into a reactor containing the solution and transferred to a container with a cooling system. Supercritical CO_2 is easily recoverable, green, and also tends to acidify the reaction system. Hydrothermal conversion of sugar under the pressure up to 12 MPa achieved 68% furfural yield [107]. Sako et al., 1992 evaluated the conversion of different concentrations of xylose to furfural to investigate the effect of supercritical CO_2 on the selectivity and the yield of furfural at 150 ℃. From the experimental data they reported, it is clear that the yield obtained without the use of supercritical CO_2 is less than the yield obtained in the presence of supercritical CO_2 for the same xylose conversion and they obtained an improved maximum yield of 70%[108]. Sangarunlert et al., 2007 reported a maximum yield of furfural approaching 90% from rice husk using supercritical CO_2 for extraction of the product [109]. Diffusivity, surface tension, and solubility are highly desirable properties for supercritical CO_2 extraction. High diffusivity enhances the mass transfer, reduced surface tension is required for easy penetration and wetting of pore of biomass materials and solubility is important for selective extraction. The compression of CO_2 takes a major part of the energy requirement for supercritical extraction. This method of extraction is at the experimental level due to the high capital and operating costs.

Table 2. 3: The summary of furfural separation approaches

Process	**Advantages/ Disadvantages**
Steam stripping 	• Very high energy consumption: high amount of steam is required to produce furfural • Azeotropic separation of furfural/water mixture required • High cooling requirements for the stripping vapors
Nitrogen-stripping 	• Inert, easily separable and recyclable gas is used • Require lower energy than steam stripping • high product purity, lower product dilution, easy catalyst separation • better industrial feasibility than water/organic biphasic systems • recompression of stripping agent and significantly larger vacuum unit required: thus, increasing the investment.
Supercritical carbon dioxide	• Supercritical CO_2 is chemically inert, non-flammable, can be easily recycled and easily separated from the product • Has also the capability of acidifying the reaction system

	• The dissolving efficiency and selectively can be controlled by the selection of suitable pressure/temperature combination • Enable extraction of furfural at a low temperature < 50 ºC.
Water/organic biphasic systems 	• avoid azeotropic separation process of furfural/water mixture • ease of catalyst and product separation • higher yield than in the aqueous phase alone
Monophasic systems 	• Green solvent γ-valerolactone (GVL) • Feasible for laboratory scale due to multistep processing for GVL production, high boiling point, and miscibility with water • No additional step for liquid-liquid separation to recover solvent

2.8. Challenge in furfural production

Solvent recycling, catalyst reuse, and product purification are very crucial factors to be considered for the economical industrial conversion of the various feedstocks to furfural. Currently, azeotropic distillation is in use for the purification of furfural as the product streams contain up to 6% furfural and over 90% water in pentoses conversion processes. But it requires a large investment and high energy. In producing furfural, various technologies have been developed at the experimental level. For instance, the supercritical CO_2 extraction technology is one of the methods applied to separate furfural from the reaction mixture in view of getting a higher yield by suppressing reactions leading to furfural loss. But this technology is being applied only at the laboratory stage due to its high operating and material cost requirements to be applied on an industrial scale.

To reuse a catalyst for the next catalytic runs, separating it from the reaction mixture and regeneration may be required. But catalyst reuse is still a challenge for industrial applications due to reduced activity and deactivation of catalysts upon regeneration. In catalytic valorization of biomass, difficulty in the separation of solid catalysts from the solid residue remaining in the reaction mixture is often observed [95], [110]. Washing the used catalyst with water and organic solvent to separate it from corn stover residue and the drying is a difficult task [95] and it incurs additional costs of solvents for washing and energy for drying. Up to 5%, furfural yield reduction was observed in the first run after regeneration and calcination deactivated the Al-beta [98]. In the MSPFR catalyzed conversion of xylose to furfural, the yield was 77.3% when the catalyst was used for the first time, but on the 5th run, 62.5 % was obtained [95]. Besides the loss of active sites due to leaching, accumulation of by-products and corn stover residue were the main reasons for the reduced performance of the catalyst. CrPO4 catalyst was tasted for furfural production by washing and drying after each use and achieved a yield of 47% from xylose on the 4th run with a significant difference of 41% from the first run and this reduced activity can be due to the partial dissolution of the catalyst [47]. The activity of H-SAPO-34 zeolite in producing furfural from eucalyptus sawdust was about 88%, but it reduced to 57.24 % in the 5th run and it couldn’t be recovered by calcination [111].

Solvent recycling is one of the important processes in chemical industries for economical operations because it reduces the costs associated with waste stream management and chemical consumption [112]. Environmental pollution is a problem of high priority these days. Solvent released in waste streams from industries needs to be reduced to protect the environment. And, also to keep consistent operating conditions throughout the process in furfural production, the solvent used should be fully recovered and reused or makeup solvent is required. Generally, to reduce the amount of solvent required and to minimize the negative environmental impact associated with the disposal of solvents in waste streams, recovery and reuse of solvents is required. Recovery processes might be possible at a laboratory scale, but it would be tough for commercialization [9].

2.9. Research Gaps

The worldwide push to develop alternative fuels and value-added chemicals to decrease greenhouse gas emissions is putting a lot of pressure on companies to diversify and valorize waste. This also seeks to valorize agro-industrial by-products by turning them into furfural. The goal of this review is to identify the gaps in efficiently producing furfural from biomass.

A thorough investigation of research advances particularly, the pretreatment of biomass, a pertinent reaction mechanism in furfural production, separation of furfural, and the various used catalysts was explored in the current review. The biomass, which contains fiber, lignin, pentosans, and pith, can be converted into furfural by the application of suitable chemical, biochemical and microbial methods.

Dilute acid, alkali, and hydrothermal pretreatment methods for hemicellulose separation from the biomass matrix were discussed in detail. The use of sulfuric acids to remove hemicellulose components and expose cellulose for subsequent conversion has been widely researched. However, there hasn't been enough research into using hydrolysis to isolate hemicellulose for further use. To address this gap, acid-catalyzed hydrolysis of locally accessible sugarcane bagasse for the extraction of xylose from the lignocellulosic matrix, a key step in the synthesis of furfural, should be investigated. As a result, it's critical to develop a general model for the acid-catalyzed hydrolysis of sugarcane bagasse to xylose and determine the optimal reaction conditions for extracting it.

Studies on the creation of a reliable and effective catalyst to overcome the limitations of present commercial methods were also examined. To prepare solid carbon-based catalysts with the necessary characteristics, several catalyst production techniques have been used. Catalysts synthesized from carbon precursors are utilized in a variety of applications, such as the dehydration of xylose to furfural, and are obtained by carbonization and sulfonation. To the best of our knowledge, no research has been published that looks at the usefulness of teff straw as a carbon source in the manufacture of sulfonated acid catalysts for use in the manufacturing of furfural.

The strategies including steam stripping, nitrogen stripping, supercritical carbon dioxide extraction, and mono- and biphasic solvent extractions were discussed in this chapter, as a way forward towards the removal of furfural from the reaction medium, thereby assisting in the avoidance of the product degradation. The extraction of furfural into the organic phase to prevent them from degrading into other products has been studied in depth by various scholars. The thermodynamics of product extraction into the organic phase, which indicates spontaneity, has not, however, been thoroughly investigated.

2.10. Conclusions

Significant studies have been carried out in the last several decades on the catalytic transformation of lignocellulosic biomass to furfural. This review provided an overview of the catalytic valorization process of biomass to a valuable platform product, the furfural. Various catalysts were employed by the researchers to achieve high catalytic activity and selectivity in converting the carbohydrate fractions of various biomass, but economical scale-up is still a challenge due to the difficulties in solvent recycling, catalyst reuse, and product purification. Isolation of hemicellulose is required to reduce the recalcitrant nature of biomass and to allow the use of the other lignocellulosic fractions, like cellulose, to obtain diversified products through integration of processes with furfural production. Extracting hemicellulose with a desired characteristic such as the degree of polymerization, reactivity, purity, and solubility remains still a challenge. Researchers have also pioneered the furfural stripping methods from the reaction medium for suppressing product degradation. Resinification and condensation reactions, which cause the degradation of furfural, could be minimized by removing the furfural formed in the liquid phase and transferring the same into the vapor or organic phases, which are devoid of the catalytically active components.

3. MATERIALS AND METHODS

3.1. Task 1: Synthesis of teff straw-based solid acid catalysts for the production of furfural

3.1.1. Materials

The teff straw was collected from the areas around Gubrye town in the Gurage zone, Ethiopia. D-xylose powder (99%), furfural (99%), toluene 99%, and sulphuric acid 99% were from local suppliers in Addis Ababa, Ethiopia, and used in the experiments without further purification.

3.1.2. Catalyst synthesis

The catalyst was prepared by simultaneous carbonization and sulfonation of biomass. The previously oven-dried teff straw at 60 °C for 48 hours was ground to the size of 0.8mm and stored in plastic bags. The 3g of ground straw was oxidized in 50ml concentrated sulfuric acid at 150-250 ^{o}C for 4 - 8 hours in a glass reactor. The resulting black solid was then washed with excess distilled water until no sulfate ion was detected in the washing water and oven-dried at 105 ^{o}C for 24 hours. The catalyst obtained from teff straw by simultaneous carbonization and sulfonation was denoted as CST.

3.1.3. Chemical composition of teff straw before pretreatments

Humidity and ash content were determined using muffle furnace (Nüve, Turkey) and analytical balance (Mettler, USA) by using ASTM 3173-87, and ASTM 3174-04 methods [113], respectively in triplicate. The raw teff straw had its extractive content determined by Soxhlet extraction.

3.1.4. Catalyst characterization

The various characterization techniques were applied to understand the interaction and the effect of the prepared catalyst on the catalytic conversion of xylose into furfural. The acidity, chemical composition, and crystallinity of the catalyst are the main properties that were considered in catalyst characterization.

The total acidity achieved by bearing $–SO_3H$, –COOH, and –OH was measured by acid-base back titration of NaOH with HCl. Both NaOH and HCl were prepared in a molar concentration of 0.01 and 20 ml of the prepared NaOH was mixed with 0.05g catalyst and kept for 1 hour under stirring to accelerate the reaction. The mixture was then filtered and the obtained filtrate was titrated by the previously prepared 0.01M HCl. The total acidity was estimated from the amount of HCl consumed by titration. The acidity due to $–SO_3H$ functional group was determined by treating 0.05g catalyst in 15 ml 2M NaCl aqueous solution and titrating with 0.05 M NaOH solution [114]. Here, phenolphthalein is used as an indicator and the amount of NaOH consumed infers the acid density.

The concentration was calculated as follows and presented in Fig 4.3.

$$[\mathrm{H}^+] = \frac{\mathrm{V}_{\mathrm{NaOH}} * [\mathrm{NaOH}] - \mathrm{V}_{\mathrm{HCl}} * [\mathrm{HCl}]}{\mathrm{m}_{\mathrm{Cat}}} \tag{3.1}$$

The $-SO_3H$ density in the produced catalyst was determined by treating with NaCl and titrating it with NaOH.

$$[-\mathrm{SO_3H}] = \frac{\mathrm{V_{NaOH}} * [\mathrm{NaOH}]}{\mathrm{m_{cat}}} \tag{3.2}$$

Where $[\mathrm{H^+}]$, [NaOH], [HCl] and $[-\mathrm{SO_3H}]$ are the concentrations of $\mathrm{H^+}$, NaOH, HCl, and $-\mathrm{SO_3H}$ respectively, $\mathrm{V_{NaOH}}$ and $\mathrm{V_{HCl}}$ are volumes of NaOH and HCl, and $\mathrm{m_{Cat}}$ is the mass of the catalyst.

Catalyst yield was calculated using Equation 3.3

$$\mathrm{Y_C} = \frac{\mathrm{w_{cat}}}{\mathrm{w_{tef}}} * 100\% \tag{3.3}$$

Where $\mathrm{Y_C}$ is the catalyst yield, $\mathrm{w_{cat}}$ is the weight of the catalyst in grams and $\mathrm{w_{tef}}$ is the weight of the teff straw used in the carbonization and sulfonation.

Elemental analyses (CHNS) were performed using EA 1112 Flash CHNS/O- analyzer operating under conditions; carrier gas flow rate of 120 ml/min, reference flow rate 100 ml/min, oxygen flow rate 250 ml/min; furnace temperature of 900 °C and oven temperature of 75 °C. 7 calibration points for every component. The sample was run in duplicate and the average values were taken.

Proximate analysis of lignin-carbohydrate complex-based catalyst was performed according to ASTM D3172-89 (2002). The fixed carbon was calculated by subtracting the sum of the moisture content, volatile matter, and ash content from 100%. The bulk density was determined following the procedure in ASTM D6683-14, 2014. The gas pycnometer (Quantachromepentatype 5200e, USA) was used to determine the particle density using helium and the result obtained is shown in Table 2.2.

X-ray diffraction is a non-destructive method for structure analysis. This analysis was performed to understand the morphology of the catalyst prepared. The data were recorded at room temperature on miniflex 300/600, Japan at 40 kV and a current of 15 mA with Cu k*a* radiation (1.54059-1.54441). Interferogram was determined experimentally in FTIR spectroscopy, with the Spectrum 65 FT-IR(PerkinElmer) in the range 4000-400 cm-1 using KBr pellets and the corresponding spectrum frequency against intensity plot was computed.

3.1.5. Catalytic test for conversion of xylose into furfural

0.4 g of xylose (AR), 0.2 g of the prepared carbon catalyst, and 25 ml of water/toluene mixture with water to solvent ratio of 1:4 were loaded into a 250ml glass reactor. The mixture was then heated in an oil bath for up to 60 minutes over the range of temperatures. Finally, the reaction was stopped by quenching in an ice bath and the sample was analyzed for the determination of the conversion of xylose and the amount of furfural produced.

3.1.6. Quantification of products

The concentrations furfural was quantified using the HPLC system equipped with Jasco-As-2050 autosampler and Jasco UV-2075 detector at 280nm using Kinetex C18-XB 150 × 4.6 mm column (Phenomenex). The samples were analyzed after diluted with known amounts of water and centrifuged. Methanol/water (2:3 by volume ratio) was pumped as mobile phases for furfural determination. Xylose content in the sample was determined using the Dionex HPLC coupled with Bio-Rad Aminex HPX-87H column (300 x 7.8mm) and RI 2000 detector. The mobile phase was H2SO4 (0.005 M) with a flow rate of 0.6ml/min at 60 °C.

The moles of xylose and furfural were calculated from HPLC peak integration and used in the equations 3.4 and 3.5.

$$\mathrm{X} = \frac{\mathrm{n_i}}{n_o} * 100\% \tag{3.4}$$

$$\mathrm{Y} = \frac{n_{fur}}{\mathrm{n_o}} * 100\% \tag{3.5}$$

Where X represents xylose conversion, n_i and n_o are moles of xylose reacted and starting xylose respectively. Y is furfural yield and $n_{fur}$is moles of furfural produced.

3.2. Task 2: Hydrothermal extraction of xylose from sugarcane bagasse

3.2.1. Raw materials, chemicals, and reagents

Sugarcane bagasse was obtained from the WonjiShoa sugar factory, Wonji, Ethiopia. D-Xylose powder (99%, Sigma Aldrich), glucose (99%), furfural (99%, SigmaAldrich), wereused in the experiments without further purification. Distilled water was prepared using CHINCAN ZLSC-5 Stainless Steel Double Steam Distillation Water Distiller in our laboratory.

3.2.2. Experimental procedure

The hydrolysis reaction experiments were carried out in a 50-mL autoclave with a magnetic stirrer. Typically, 0.5 g sugarcane bagasse was mixed with 20ml of dilute sulfuric acid. The concentrations of the acid were 0.5 to 1.5 % and the temperatures were set to 130-170℃. The reaction times of all experiments were recorded starting from the point when the target temperatures reached. Finally, the reactions were stopped and the filtrate was collected using filter paper for the next analysis.

3.2.3. Raw material characterization

Cellulose and hemicellulose were estimated according to the method in Basu et al., 2018 [115], [116]. The lignin contents were estimated using TAPPI T222 om-98 and TAPPI UM 250. Extractive-free sugarcane bagasse was prepared following TAPPI T 264. Sugarcane bagasse (0.2 g) was mixed with 2ml of 72% H_2SO_4 and placed in a water bath at 30 ^oC with continuous string. The mixture is then diluted with 56 ml of water in an Erlenmeyer flask and autoclaved at 120 ^oC for 1hr. The resulting solid residue was filtered, washed thoroughly, dried at 105 ^oC, and finally weighed as lignin content. The acid-soluble lignin was determined from the absorbance of the hydrolysate at 250 nm using a UV visible spectrophotometer.

Hot distilled water (80 ml), acetic acid (0.5ml), and sodium chlorite (1g) were added to 2.5g of extractive free bagasse sample and heated in a water bath at 70 ^{o}C for 1 hr. Then, the mixture was heated for another 1 hr after the same dose of acetic acid (0.5 ml) and $NaClO_2$ (1g) was added. After repeatedly treated with acetic acid and $NaClO_2$ for 6 to 8 hours, the mixture was then filtered after 24h. The solid was washed with acetone and dried at 105 ^{o}C for 24 h and the weight was recorded as holocellulose.

The holocellulose obtained was used for the determination of cellulose and hemicellulose content. 0.2 g of dried holocellulose was treated with 1.25 ml of 17.5% NaOH in a water bath at 20 ^{o}C. Additional doses of 0.6 ml of 17.5 % NaOH were added in 5 min for 3 times. After 30 min, dilute the sample with 6.6 ml water, filter and wash it with 12.5 ml of 8.3% NaOH, and then soaked in 1.9ml 10% acetic acid for 5 min. Finally, the solid residue was washed, dried, and weighed as cellulose. The difference between the holocellulose and cellulose was recorded as a hemicellulose content.

3.2.4. Quantification of products

Xylose and glucose concentrations in the sample were determined using the Dionex HPLC coupled with Bio-Rad Aminex HPX-87H column (300 x 7.8mm) and RI 2000 detector. The concentrations furfural was quantified using the HPLC system equipped with Jasco UV-2075 detector at 280nm using Kinetex C18-XB 150 ×4.6 mm column (Phenomenex). The samples were analyzed after diluted with known amounts of water and centrifuged. H_2SO_4 (0.005 M) and methanol/water (2:3 by volume ratio) were the mobile phases used with a flow rate of 0.6ml/min at 60 °C.

The grams of xylose, glucose, and furfural were calculated as in equation 3.6.

$$\mathrm{X_i} = \frac{\mathrm{m_i}}{m_o} * 100\% \qquad (3.6)$$

Where X_i represents the yield of xylose, glucose, or furfural conversion, m_i is the mass of xylose, glucose, or furfural in the hydrolysate. m_o represents the mass of sugarcane bagasse initially used in the hydrolysis.

3.2.5. Optimization of the hydrolysis process

Central composite design, a response surface methodology, was used to compare the effects of various parameters and select the highest xylose yield. The parameters include temperatures and time for hydrolysis and the concentration of sulfuric acid used for hydrolysis. The central composite design and graphical presentations were made using a model-based calibration tool in MATLAB software.

Table 3. 1: Experimental coded and actual values

Independent Variables	**Symbols**	**Coded and Actual Levels**		
		-1	0	1
Hydrolysis Temperature (℃)	X_1	130	150	170
Hydrolysis Time (min)	X_2	20	40	60
Acid concentration (%)	X_3	0.5	1	1.5

Equation 3.7 is used as a model

$$\mathrm{Y_i} = \mathrm{b_o} + \sum \mathrm{b_i X_i} + \sum \mathrm{b_{ij} X_i X_j} + \sum \mathrm{b_{ii} X_i^2} + \mathrm{e_i} \qquad (3.7)$$

$$x_{\mathrm{i}} = \frac{\mathrm{X_i} - \mathrm{X_o}}{\Delta \mathrm{X_i}} \tag{3.8}$$

Where x_i and X_i are coded and the actual values of the independent variables. X_o is the actual value of the independent variable at the center point and ΔX_i is the step-change in the actual value of the independent variable.

3.2.6. Severity factor calculation

The combined severity factor was used to predict the results and to compare efficiencies of the release of hemicellulose from lignocellulosic biomass under the diverse test conditions. The combined severity factor (equation 3.10) is the extension of the severity factor (equation 3.9). It incorporates the effect of the sulfuric acid and therefore is expressed in terms of temperature, time, and pH using Arrhenius Law.

$$R_o = \int_0^t \exp^{\left[\frac{\mathrm{T}-100}{14.75}\right]} dt \tag{3.9}$$

$$R' = \log_{10}\left[t * \exp\left(\frac{T - 100}{14.75}\right)\right] - pH \tag{3.10}$$

3.3. Task 3: The effects of reaction conditions on the conversion of sugarcane bagasse hydrolysate to furfural

3.3.1. Raw Material

The sugarcane bagasse was obtained from the local sugar industry (Wonji/Shoa Sugar Factory, Ethiopia). Sugarcane bagasse was dried in the oven, ground down to 0.8 mm in size, and stored in plastic bags until the experiment.

3.3.2. Catalytic test for conversion of sugarcane bagasse hydrolysate into furfural

Dehydration reactions of sugarcane bagasse hydrolysate were carried out in a 100-ml batch reactor. The reactor was heated to the required temperature after 10 ml of xylose-rich liquor were placed in the reactor and 20 ml of toluene were added as a medium of reaction and furfural extracting solvent respectively. Then, the products in both the aqueous and organic phases were cooled to room temperature and quantified when the target reaction time was reached.

3.3.3. Quantification of products

The analysis of xylose and furfural were done using HPLC equipped with a refractive index and UV detectors respectively and quantified according to the equations 3.11 and 3.12.

$$\mathrm{X} = \frac{\mathrm{n}}{n_0} * \ 100\% \tag{3.11}$$

$$\mathrm{Y} = \frac{\mathrm{n_f}}{n_0} * \ 100\% \tag{3.12}$$

Where X and Y are xylose conversion and furfural yield; n, n_0 and n_f are moles of xylose reacted, moles of starting xylose and moles of furfural produced respectively.

3.3.4. Analytical Methods.

The composition of the liquid phase was analyzed for furfural using an HPLC system (LabAlliance) with a BioRadAminex HPX-87H column at 65°C and 5 mM aqueous sulfuric acid as the mobile phase flowing at 0.6 mL/min. Furfural concentrations were analyzed by Bio-Rad high-performance liquid chromatography using a UV detector at a wavelength of 254 nm.

3.3.5. Experimental design

Table 3. 2: Experimental design for sugarcane bagasse hydrolysate conversion to furfural

Temperature in ℃	Catalyst loading in %	Time in minutes
150	0.1	30
150	0.1	60
150	0.1	90
170	0.1	30
170	0.1	60
170	0.1	90
190	0.1	90
190	0.1	30
190	0.1	60
150	0.25	90
150	0.25	30
150	0.25	60
170	0.25	30
170	0.25	60
170	0.25	90
190	0.25	60
190	0.25	90
190	0.25	30
150	0.4	60
150	0.4	90
150	0.4	30
170	0.4	90
170	0.4	30
170	0.4	60
190	0.4	30
190	0.4	60
190	0.4	90

3.3.6. Kinetic Models.

This study considered the simplified model for consecutive reactions which include the conversion of xylose to furfural and further degradation of furfural through condensation and resinification. The intermediates formed during the dehydration processes are all ignored in the simplification and the simplified model is presented as follows.

$$\mathrm{xylose} \overset{k_1}{\rightarrow} \mathrm{furfural} \overset{k_2}{\rightarrow} \mathrm{degradation\ product} \tag{3.13}$$

The respective rate equations for xylose, furfural, and degradation product are;

$$\frac{dC_{xylose}}{dt} = -k_1 C_{xylose} \tag{3.14}$$

$$\frac{dC_{furfural}}{dt} = k_1 C_{xylose} - k_2 C_{furfural} \tag{3.15}$$

$$\frac{dC_{degradation}}{dt} = k_2 C_{furfural} \tag{3.16}$$

where C_{xylose} , $C_{furfural,}$ and $C_{degradation}$ are the concentrations of xylose, furfural and degradation products respectively in g/L. k_1 and k_2 are rate constants.

The linear differential method was used to solve the reaction rate equation as follows:

$$C_f = \frac{k_1 C_{x_0}}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{3.17}$$

A modified Arrhenius equation, eq 3.18, was applied to calculate the activation energy and evaluate the effect of catalyst concentration and temperature on the rate constants in eq 3.17:

$$k_i = Ae^{\left(-\frac{E_i}{RT}\right)} C_{catalyst}^{m_i} \tag{3.18}$$

Where R is the universal gas constant and is equal to 8.314 $\times 10^{-3}$ kJ/(mol·K). A corresponds to the frequency factor (min^{-1}), E_i is the apparent activation energy (kJ/mol), and m_i is the reaction order.

The activation energy was computed from the plot of $\ln k_i$ vs 1/T using eq. 3.19. The slope represents the activation energy and pre-exponential factors were obtained from the intercept of the plot.

$$lnk_i = lnA_{0i} + lnC_{catalyst}^{mi} - \frac{E_i}{R}\frac{1}{T} \tag{3.19}$$

The dsolver function in MATLAB was used to solve the above differential equations and lsqcurvefit function to find the kinetic parameters in the conversion of xylose in bagasse to furfural.

Applying $dF/dt\ = 0$ to eq 3.17, the time $t_{\max}$ to reach the maximum furfural yield in toluene solvents (at a fixed temperature and catalyst loading) is found to be

$$t_{max} = \frac{\ln k_2 - \ln k_1}{k_2 - k_1} \tag{3.20}$$

3.4. Task 4: Thermodynamic analysis of the dehydration of xylose to furfural

3.4.1. Process simulation

Aspen Plus V.10 was used to simulate and predict the dehydration of xylose to furfural under diverse operating conditions.

3.4.2. Thermodynamic analysis

The Gibbs free energy minimization technique was employed for the thermodynamic analysis of the production of furfural.

$$G = \sum_{i=1}^{c}\sum_{j=1}^{p} n_{ij}\mu_{ij} \qquad (3.21)$$

For gases

$$\mu_i = \mu_i^{\theta}(T) + RTln\widehat{f_\iota} \qquad (3.22)$$

$$\widehat{f_\iota} = y_i P \qquad (3.23)$$

For liquids

$$\mu_i = \mu_i^{*}(T, P) + RTln\widehat{a_\iota} \qquad (3.24)$$

$$\widehat{a_\iota} = \gamma_i x_i \qquad (3.25)$$

where

$n_{ij}$and μ_{ij} are respectively the number of moles and chemical potential of component i in j phase

p and c are the number of phases and number of components respectively.

$\mu_i^{\theta}(T)$ is the chemical potential of pure component i at temperature T

$\widehat{f_i}$ is fugacity of component i

$\mu_i^{*}(T, P)$ is the chemical potential of pure liquid component i

$\widehat{a_i}$is the activity of component i

γ_i is the activity coefficient of liquid component i

The chemical potentials of the pure components were from the literature.

$$\text{Conversion of xylose} = \frac{\text{moles of xylose consumed}}{\text{moles of xylose fed}} = \frac{F_{Ao} - F_A}{F_{Ao}} \tag{3.26}$$

Where F_{A0} is moles of xylose fed and F_A is moles of xylose remaining in the reaction mixiture.

The Aspen Plus process simulator was used to perform thermodynamic modeling of xylose conversion to furfural. The RGibbs reactor was used in the simulation flowsheet. The estimates were completed by minimizing the Gibbs free energy to achieve dehydration equilibrium compositions.

4. RESULTS AND DISCUSSIONS

4.1. Task 1: Synthesis of teff straw-based solid acid catalysts for the production of furfural

As shown in Table 4.1, the teff straw contains 29.8 % hemicellulose, 35.6 % cellulose, 12.2 % lignin,19.9 extractives and 1 % ash.

Table 4. 1: Chemical composition of Teff straw (on dry basis).

Components	Composition [%, w/w]
Cellulose	35.6 ± 1.3
Hemicellulose	29.8 ± 0.7
Lignin	12.2 ± 0.9
Extractives (Water)	17.7 ± 0.5
Extractives (EtOH)	2.2 ± 0.3
Ash	1.0 ± 0.1
Moisture	7.3 ± 0.5
Crude protein	2.8 ± 0.3

The FTIR spectra of the raw teff straw and the prepared catalyst were recorded at wavelengths in the range 4000 to 400 cm^{-1} to determine the functional groups available. The FTIR spectra results were shown in Fig 4.1. The wavenumbers 3429 and 798 cm^{-1} respectively represent O-H vibrations in hydroxyl groups and aromatic substitution. 2923 and 2853 cm^{-1} are for C-H vibrations, 1709, and 1616 correspond to C=O stretching and C=C [117], [118]. SO_3H is represented by 1102 cm^{-1}. Therefore, the FTIR result has clearly shown the successful attachment of the -SO_3H functional group onto the polymer matrix. The acidity of the catalyst as observed in the FTIR is due to the functional groups -COOH, -OH, and -SO_3H.

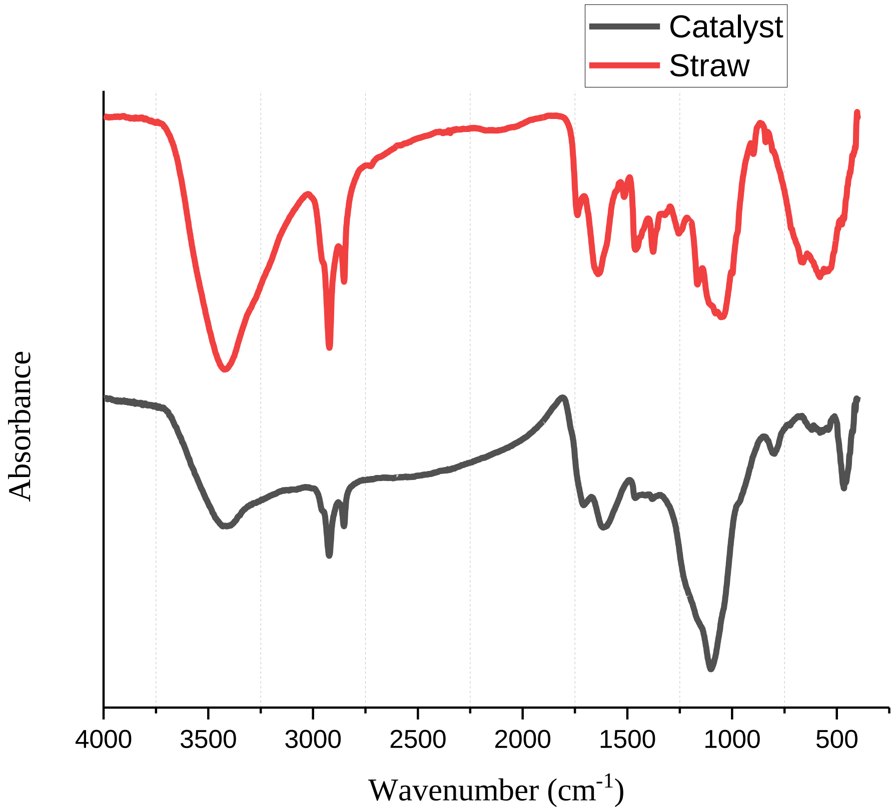


Figure 4.1: FTIR Spectra of the raw and the carbonized and sulfonated Teff straw Samples.

From the elemental analysis of the catalyst prepared through carbonization, it can be concluded that the sulfur has been successfully introduced into the carbon structure. In Table 4.2 the result shows 2.81 wt% of the catalyst is sulfur. The yield of the catalyst obtained after the carbonization and sulfonation of 3 grams of teff straw was 54.5%.

Table 4.2: Elemental and proximate analysis of the synthesized lignin-carbohydrate complex-based catalyst

Elemental analysis (wt%)	
Carbon	53.82± 1.32
Hydrogen	3.28±0.19
Oxygen	40.08±0.86
Sulfur	2.81±0.23
Proximate (wt%)	
Moisture	6.33±0.36
Volatile mater	43.27±0.63
Fixed carbon	41.19±1.02
Ash	9.21±0.26

The XRD result shown in Fig 4.2 reveals the amorphous nature of the catalyst prepared. The diffraction peak 2θ = 15 to 30^o is for a characteristic peak attributed to the amorphous carbon structure. The change of sharper diffraction peaks in between 2θ =20 and 30 in the teff straw to broader peaks in the prepared catalyst confirm the distraction of the crystalline structure of cellulose under the thermal treatment in sulfuric acid and the formation of amorphous structure [119].

Table 4. 3: Summary of bulk density and particle density of the lignin-carbohydrate complex-based catalyst

	Value
Bulk density (g cm^{-3})	0.43
Particle density (g cm^{-3})	0.63
Porosity	0.31

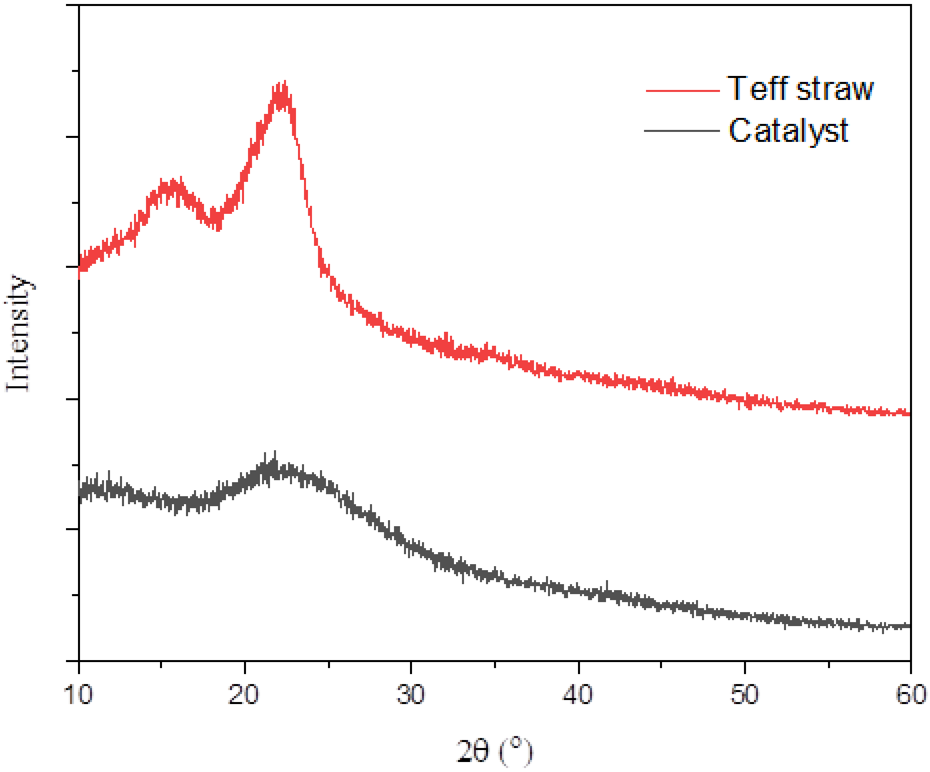


Figure 4.2: XRD Patterns for raw teff straw and, carbonated and sulfonated teff straw.

4.1.1. Effect of the rising temperature of carbonization and sulfonation on the acid density

The activities of carbon-based catalysts in furfural production depend on the preparation conditions like carbonization and sulfonation reaction temperatures and times. Carbonization is important to facilitate the formation of the biomass carbon structure in the favor of -SO_3H loading by sulfonation reaction, the process of grafting -SO_3H active functional groups into the carbon skeleton[120], [121]. Polycyclic aromatic hydrocarbon sheets are formed when the volatile and weak acid functional groups are removed by carbonization [122]. The FTIR result (Fig 4.1) showed the shortened peaks at 3429 and 1709 cm^{-1} which respectively represent O-H vibrations in hydroxyl groups and C=O bending vibration of –COOH, and a peak appeared at 798 cm^{-1} is attributed to aromatic substitutions.

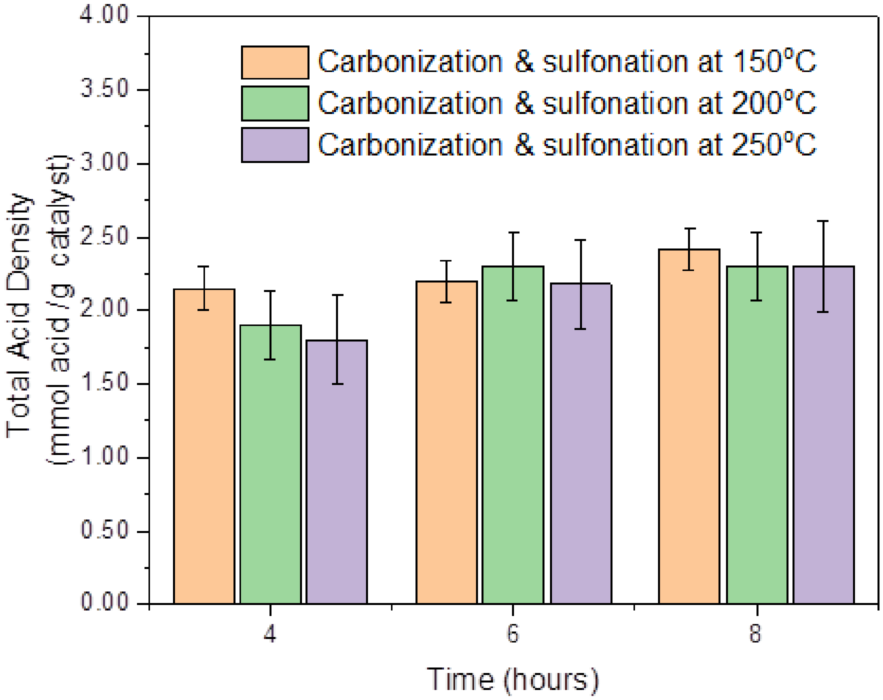


Figure 4.3: The total acid density of teff straw-based catalyst

To study the effect of combined carbonization and sulfonation temperature on the property of the catalyst, teff straw was treated over the temperatures 150, 200, and 250 ℃. The catalytic activity tests were then performed at 170 ℃. As can be seen in Fig 4.3., during the carbonization and sulfonation over 4- and 8-hour treatments the total acid density decreased as the temperature increased from 150 to 250℃. But, for the 6 h treatments, it increased with the temperature and then decreased after reaching maximum may be due to saturation of the active site adsorption and gradual distraction of the carbon structure by excessive carbonization and sulfonation.

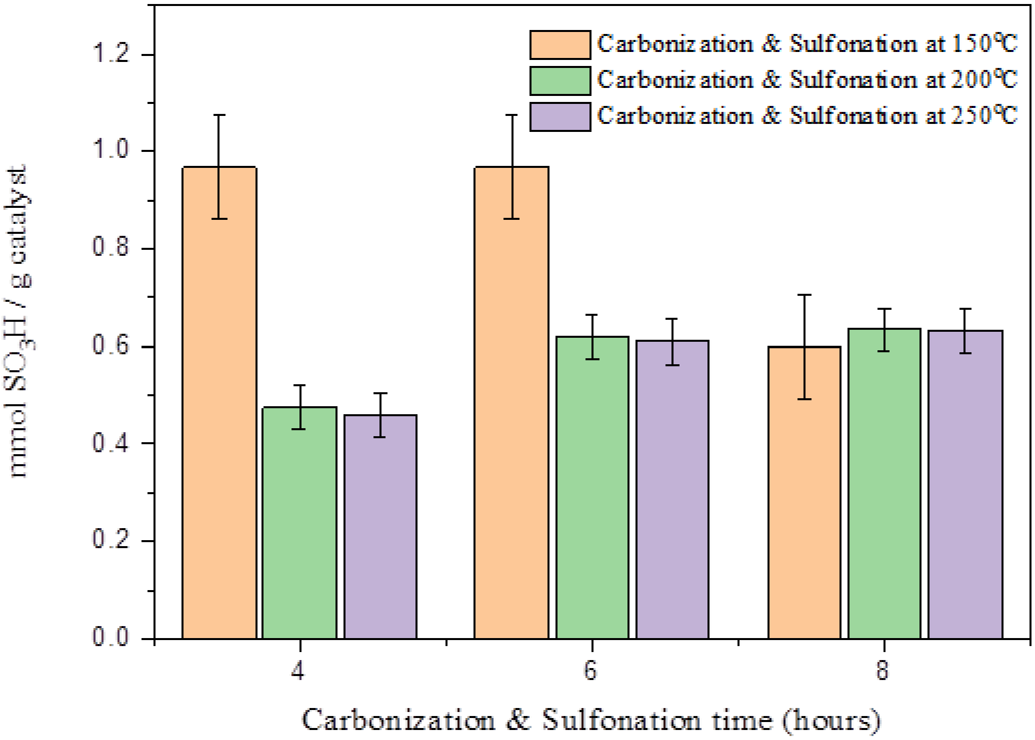


Figure 4.4: Sulfonic acid density of teff straw-based catalyst

Initially, in the 4-hours treatment, the $-SO_3H$ density was higher but it appears to be lower at higher temperatures with slight differences between the treatments at 200 and 250 ℃. But, at prolonged carbonization and sulfonation time, i.e., the 8-hours treatment, the strong acid density changed slightly with temperature change. These show that the highest sulfonic acid density can be obtained at relatively lower temperatures and shorter carbonization and sulfonation time. Low sulfonic acid loading at high carbonization and sulfonation temperature is probably due to the collapse of carbon structure [123] and the formation of a rigid structure. Adsorption-desorption equilibrium of -SO_3H groups onto the carbon surface could also affect the -SO_3H loading by reducing the rate of sulfonation reaction [124].

4.1.2. Effect of time of carbonization and sulfonation on acid density

The total acid density achieved when the samples were treated for longer times is higher, but the sulfonic acid density decreased. It can be seen from Fig 4.4. that the sulfonic acid density sharply decreased after the treatment for 6 hours duration, but the same and high for 4- and 6-hour treatments. Bureros et al., 2019 and Fonseca et al. 2020 also observed the same decreasing phenomena at a prolonged time of sulfonation [121][125]. High total acid density can be achieved upon treatment for a longer time but comparable results were obtained with shorter time and lower temperatures. The fine particle size of the catalyst, which is not easily manageable during washing, was also observed at high temperatures and prolonged carbonization and sulfonation time.The appearance of small broken pieces is due to the damage of the structure of the catalyst by high carbonization temperature [126].

4.1.3. Catalytic performance of the carbon-based catalyst

The sulfonated lignin-carbohydrate complex-based catalyst contains -SO_3H, -COOH, and -OH functional groups. The total impact of these functional groups endows the catalysts with better catalytic performance. Lewis acid sites favor the xylose-xylulose-furfural route instead of xylose to furfural direct conversion and Brønsted acid sites catalyze the conversion of xylulose to furfural [68]. The -SO_3H and -COOH act as Brønsted acid in the formation of furfural. The -SO_3H group protonates the hydroxyl group on xylose to form furfural via cyclodehydration upon release of water molecules. The hydrophilic nature of -OH and -COOH groups favor the accessibility of the active site of the catalyst by facilitating the adsorption of the reactant [127], [128]. Functionalization of the carbon structure with -COOH and -OH groups provide a hydrophilic nature to the hydrophobic carbon surfaces.

In the view of the dehydration of xylose to produce furfural, the prepared catalyst was tested in the presence of toluene and water as a medium of reaction. As a control experiment, 0.4 g xylose was allowed to react in the hydrothermal glass reactor without the addition of catalyst in 25 ml water at 170℃ for 30 minutes, and the conversion of xylose was 3.6 % and no furfural was obtained. In the rest of the experiments, 0.4 g xylose was mixed with 0.2 g catalyst and introduced into the reactor. 20 ml toluene and 5 ml water were added into the mixture and heated at the desired temperature for 30 minutes. Xylose conversion to furfural via dehydration in aqueous medium leads to furfural loss. In the biphasic system, 20 ml toluene, and 5 ml water the maximum yield was 62.4 %. All the catalytic performance tests were performed in triplicates.

4.1.4. Effect of time and temperature on furfural yield

The effects of time and temperature on the yield of furfural from xylose were investigated in the presence of the prepared catalysts. The investigations were performed in the temperature range 160-180 ℃ and time up to 60 minutes using 0.2 g catalyst, 0.4 g xylose, and 25 ml water/toluene systems (5 ml water and 20 ml toluene). The performance of CST was tested at different dehydration temperatures for xylose conversion to furfural. As shown in Fig.4.5 the yield increased with the increase in reaction temperature up to 170 ℃. However, for temperatures exceeding 170 ℃, the activity decreased and lower furfural yields were obtained. The lower yields might be due to the degradation of products and the formation of byproducts. Furfural formed is converted to the by-products, mainly to humins, when exposed to higher temperatures [129][130]. The humin, in turn, affects the performance of solid acid catalysts, when deposited on the active sites, by preventing the reactants from accessing the active site [131]. Ershova et al., 2015, performed experimental tests to study the behavior of furfural concerning its degradation at varied temperatures above 180 ℃ and found decreasing amounts of furfural in both the reactions with and without catalyst [132]. Various works by different researchers also revealed the same diminishing trend in furfural yield at higher temperatures after reaching maximum [133], [134].

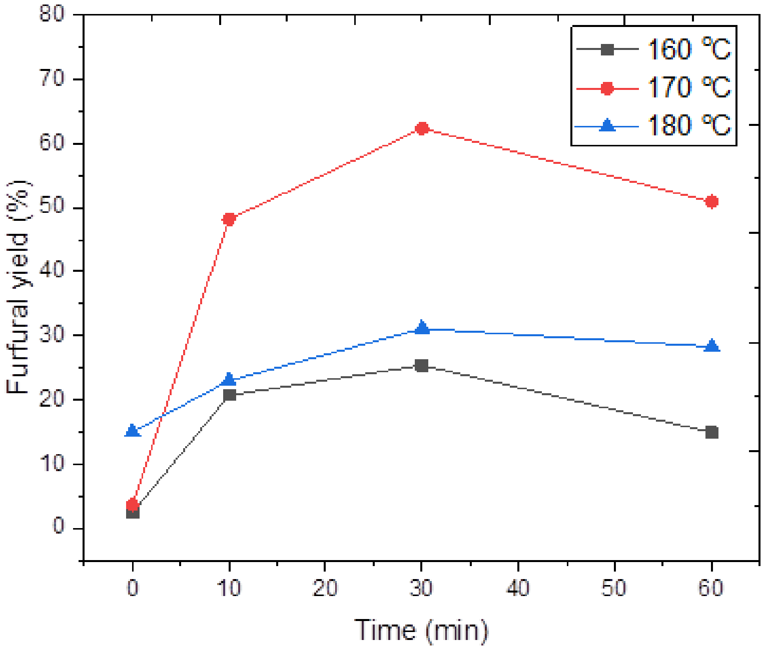


Figure 4.5: Effect of reaction time and temperature on furfural yield (0.4g xylose, 0.2 g CST, 25 ml water/ toluene biphasic system)

The decreasing yield of furfural could also occur when xylose undergoes retro aldol fragmentation into acids, aldehydes, and ketones [135]. For the first 30 minutes, the degree of dehydration increases, and hence the yield of the product increased. But the yield decreased for the reaction time greater than 30 minutes as illustrated in Fig 4.5, which may also be due to degradation of furfural upon further treatment beyond 30 minutes. A better yield of furfural from xylose was obtained using teff-straw based catalyst than other catalysts like PSZ-MCM-41 [81], Dealumin HNu-6 (2) [82], HY-faujasite (15), H-mordenite (12)[84] and HY-ferrierite (20) [85] in water toluene system in shorter reaction time.

4.1.5. Effect of catalyst loading on furfural

The catalyst loading was one of the major parameters that affect the yield of furfural. As shown in Fig 4. 6, this effect was studied by using 0, 0.1,0.2,0.3, and 0.4 grams of catalyst in a water toluene biphasic system to convert xylose at 170 ℃ for 30 minutes. Very low furfural yield was recorded for conversion test without catalyst and increased yields were observed with the increase in the amount of catalyst up to 0.2 g. At higher catalyst loadings in between 0.3-0.4g, almost similar yields were observed. Amounts of catalyst loading up to some extent increase the yield of furfural from xylose. As the amount of the catalyst added in the reaction system increased, sufficient catalytically active sites will be available for xylose dehydration to furfural, and therefore the yield of furfural increases. However, the overloading of the catalysts would lead to side reactions such as fragmentation, condensation, and resinification, which limits the final yield of products[136]. The fragmentation of furfural results in the formation of lactic and formic acids and the various aldehydes such as glyceraldehyde, formaldehyde, pyruvaldehyde, glycolaldehyde, and acetaldehyde [137]. The adsorption of furfural is also possible [138] as a strong hydrogen bond may probably be formed between the -OH and -COOH functional groups on the catalyst and the aldehyde group of furfural [127]. These phenomena include both reversible and irreversible adsorption [138]. Zhang et al., 2018 obtained decreased furfural yield from corncob when using a high amount of bifunctional solid acid catalyst [136]. Mittal et al., 2017 also reported similar observations in the dehydration of pentose-rich hydrolyzate to furfural in a biphasic system using solid acid catalyst [139].

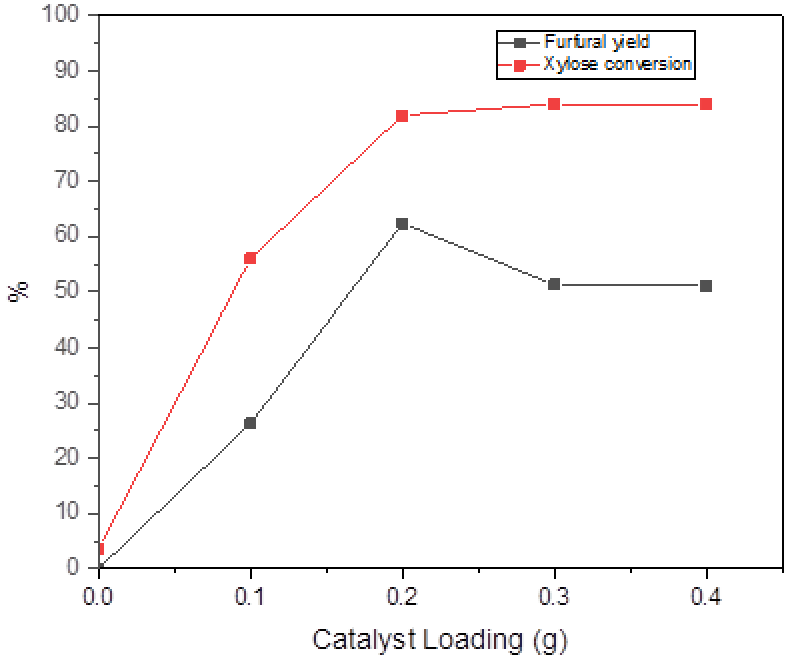


Figure 4.6: Effect of catalyst loading on the conversion of xylose and yield of furfural from xylose in water toluene biphasic system (5 ml water to 20ml toluene), 0.40 g xylose at 170 ℃ for 30 min.

4.1.6. Catalyst recycling

The catalyst was checked for its recyclability by filtering and washing after used in each catalytic run. The spent catalysts were filtered and washed repeatedly with ethanol and water several times until no furfural detection in the washing liqueur was confirmed using a UV vis spectrophotometer (MateshUV-M90). The recovered catalysts were then dried overnight in an oven at 80 ^{o}C and applied for the next catalytic test. The performance of the catalyst was almost similar for 4 consecutive runs. On the fourth run, the yield was found to be 56.8 % at 170 ℃ and 30 minutes reaction time.

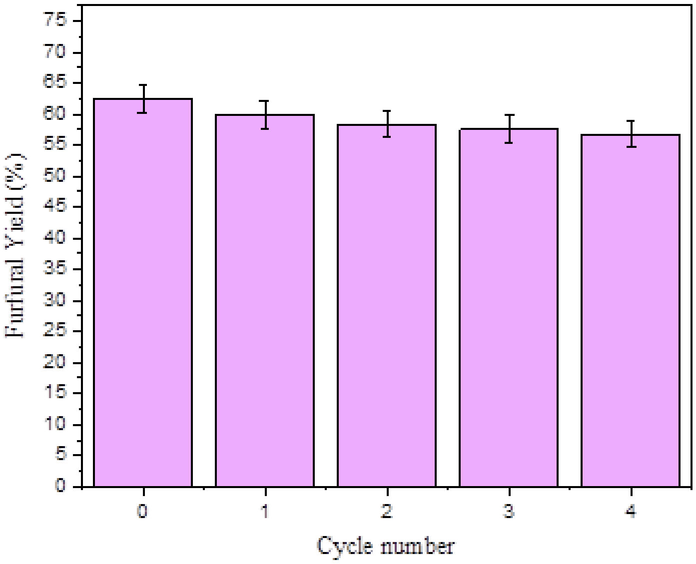


Figure 4.7: Recyclability test of the catalyst at 170 ℃ and 30 minutes reaction time.

4.1.7. Conclusion

This study gives an important reference for a more profound understanding of the utilization of abundantly available agricultural and industrial biomass waste for the production of furfural. The catalyst was successfully prepared and showed good catalytic performance in the dehydration of sugars to a platform chemical. The preparation conditions such as carbonization and sulfonation time and temperature can highly affect the functional properties of the catalysts. The lower carbonization and sulfonation temperature and time were beneficial to get higher SO_3H density. Too high temperature above 200 ℃ showed insignificant change in the attachment of the sulfonic acid functional group. The catalyst preparation method was energy and time saving as compared to other methods employed to prepare the carbon-based catalyst. The FTIR results confirmed the introduction of $-SO_3H$ group into the porous polymer matrix. The teff straw showed promising potential as a carbon precursor for the preparation of low-cost heterogeneous catalysts that can be used in the dehydration reactions.

4.2. Task 2: Hydrothermal extraction of xylose from sugarcane bagasse

4.2.1. Raw material Characterization

Cellulose content and the hemicellulose contents were estimated according to the methods in Basu et al. 2018[115]. The percentages of cellulose, hemicellulose, and lignin present in the bagasse are 36 ± 1.05, 29 ± 0.8, and 21±1.16 respectively. These results show that the cellulose and hemicellulose content of the sugarcane bagasse is high. Therefore, the biomass has a high potential to be used to produce monomeric sugars and sugar-derived chemical products.

4.2.2. Variables and response surface optimization

From the results obtained in the experiments, temperature, time, and concentration of the acid influence the yield of xylose. When the hydrolysis temperature, time, and acid concentration are raised to above a certain level the yield of the product starts to decrease. To maximize the yield, an optimum combination of the factors is required, and therefore, the response surface method was employed as a statistical tool for the determination of model coefficients and optimization. Table 2 summarizes the hydrolysis reaction experimental and predicted results for sugarcane bagasse.

In Table A1, ANOVA showed significant differences ($p<0.0001$) between experimental data and predicted model and lack of fit ($p<0.001$). P-values <0.05 and F-values >1 are acceptable and show the significance of the coefficients.

Table 4. 4: Central composite design runs with actual values for the three independent variables and the experimental and model-fitted responses

Hydrolysis Temperature in °C	Hydrolysis Time in min.	Acid Concentration in %	Glucose released	Furfural yield in g/100 g bagasse	Xylose yield in g/100 g bagasse	
					Experimental	Model-fitted
116	40	1	0.77	0	8.15	12.33
130	20	0.5	0.28	0.02	6.45	14.33
		1.5	0.97	0.07	14.91	15.66
	60	0.5	0.94	0.08	7.99	16.59
		1.5	1.22	0.09	18.12	17.92
150	6.36	1	0.84	0	11.61	12.59
	40	0.16	0.85	0.04	12.93	12.57
		1	1.57	0.043	21.32	22.22
		1.84	2.52	0.31	20.94	20.98
	73.6	1	1.92	0.23	15.9	16.4
170	20	0.5	1.17	0.02	12.6	13.75
		1.5	1.76	0.13	12.35	10.97
	60	0.5	1.8	0.19	13.05	16.01
		1.5	2.6	0.47	15.42	13.23
183	40	1	2.18	0.07	10.63	7.89

The coefficients X_1, X_2, X_3, X_1^2, X_2^2, X_3^2, and X_1X_3 are significant, therefore reaction temperature, reaction time and catalyst concentration have all significant effects on the yield of xylose.

$R^2 = 0.98$ indicates the predicted model can sufficiently represent the yield of xylose. The Model F-value of 56.58 suggests the model is significant. There is just a 0.01% possibility that an F-value this large could happen because of noise.

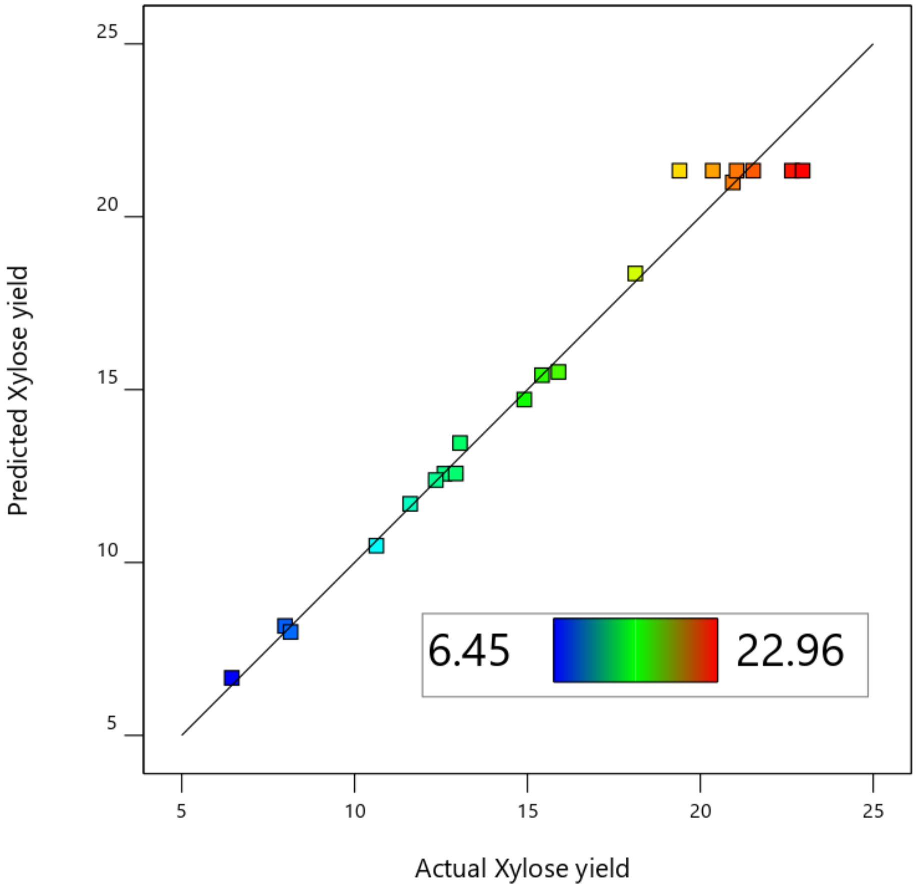


Figure 4.8: Plot of Predicted vs Actual responses

X_1X_2 and X_2X_3 are not significant terms because the F-values greater than 0.1000 show the model terms are not significant. The Lack of Fit F-value of 0.07 isn't significant relative to the pure error. There is a 99.38% possibility that a Lack of Fit F-value this large could happen because of noise. Adeq Precision of 20.9 shows signal to noise ratio was in the desirable range (greater than 4).

According to Fig.4.8., the model has a positive impact compared to the null model. The points are near to the fitting line, with small confidence bands. This ensures a successful fit to the experimental data.

4.2.3. Dilute acid hydrolysis optimization

Dilute acid hydrolysis efficiencies to produce xylose at specified reaction conditions including temperature, time, and acid concentration are presented in Fig.4.9., Fig 4.10., and Fig 4.11. The experimental runs were performed according to the Central composite design and the results of all the 20 runs are shown in Table 2. The final model equation obtained in terms of coded factors is

$$Y = 21.33 + 0.74X_1 + 1.13X_2 + 2.50X_3 - 4.28X_1^2 - 2.73X_2^2 - 1.61X_3^2 - 2.06X_1X_3 \qquad 4.1$$

4.2.4. Effect of acids concentration on the extraction of xylose

Sulfuric acid has been accounted for to be viable for acid hydrolysis, which fractionates the sugar contents of biomass and thus is utilized in this investigation. The impacts of the acid concentration on the fractionation of sugarcane bagasse into the significant segments were analyzed, aiming at developing an economical process by minimizing the acid consumption and maximizing the yield of hemicellulose. Diluted acid pretreatment of lignocellulosic biomass is usually carried out at 120-215 ^{o}C with 0.5-5 percent acid [140]. It allows virtually full hydrolysis of hemicellulose, disruption of lignin and structural alteration, and partial solubilization of cellulose under these circumstances. The severe process conditions induce rapid sugar breakdown, resulting in low hydrolytic efficiency. Therefore, preliminary experimental tests were carried out based on the information obtained from the literature [141], [142], and suitable operating conditions were set out. The pretreatment temperatures of 130-170 ^{o}C, the residence time of 20 to 60 minutes, and acid concentrations of 0.5 to 1.5 percent with central points 150 ^{o}C, 40 min, and 1% were selected.

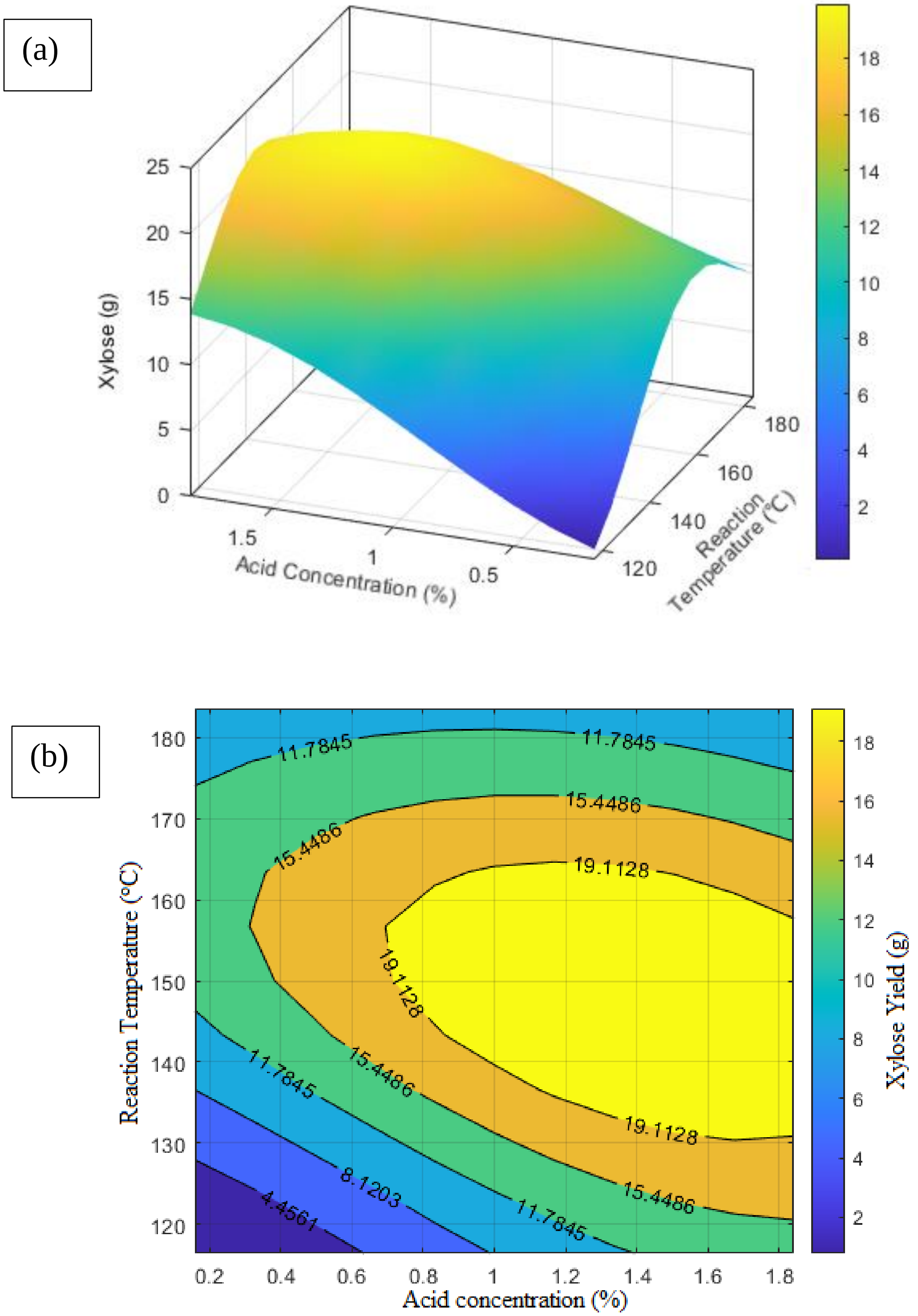


Figure 4.9: Effect of hydrolysis temperature and acid concentration on xylose yield represented as surface (a) and contour (b) plots

Hydrolysis reaction experiments were performed using 0.5, 1.0, and 1.5 % sulfuric acid in a reactor over a range of temperatures and time. The surface and contour plots of the hydrolysis reaction in Fig. 4.9. outline the relationships between the concentration of the acid, time and reaction temperature. The maximum yield of xylose was obtained at the acid concentration of 1 % in 40 minutes at a temperature of 150 ^{o}C. Roughly, 0.7% was the least acid concentration that potentially achieved a yield of xylose higher than 0.19g from 1g of bagasse. Increasing the concentration above 0.7% slightly increased the xylose yield as shown by the contour plot of acid concentration vs temperature in Fig. 4.9. Compared to other carbohydrates, hemicellulose is easily hydrolyzed in acidic media because of its amorphous structure [143], [144]. Stronger acid conditions are not favorable for xylose generation because of the further conversions of monomeric sugars to degradation products [145].

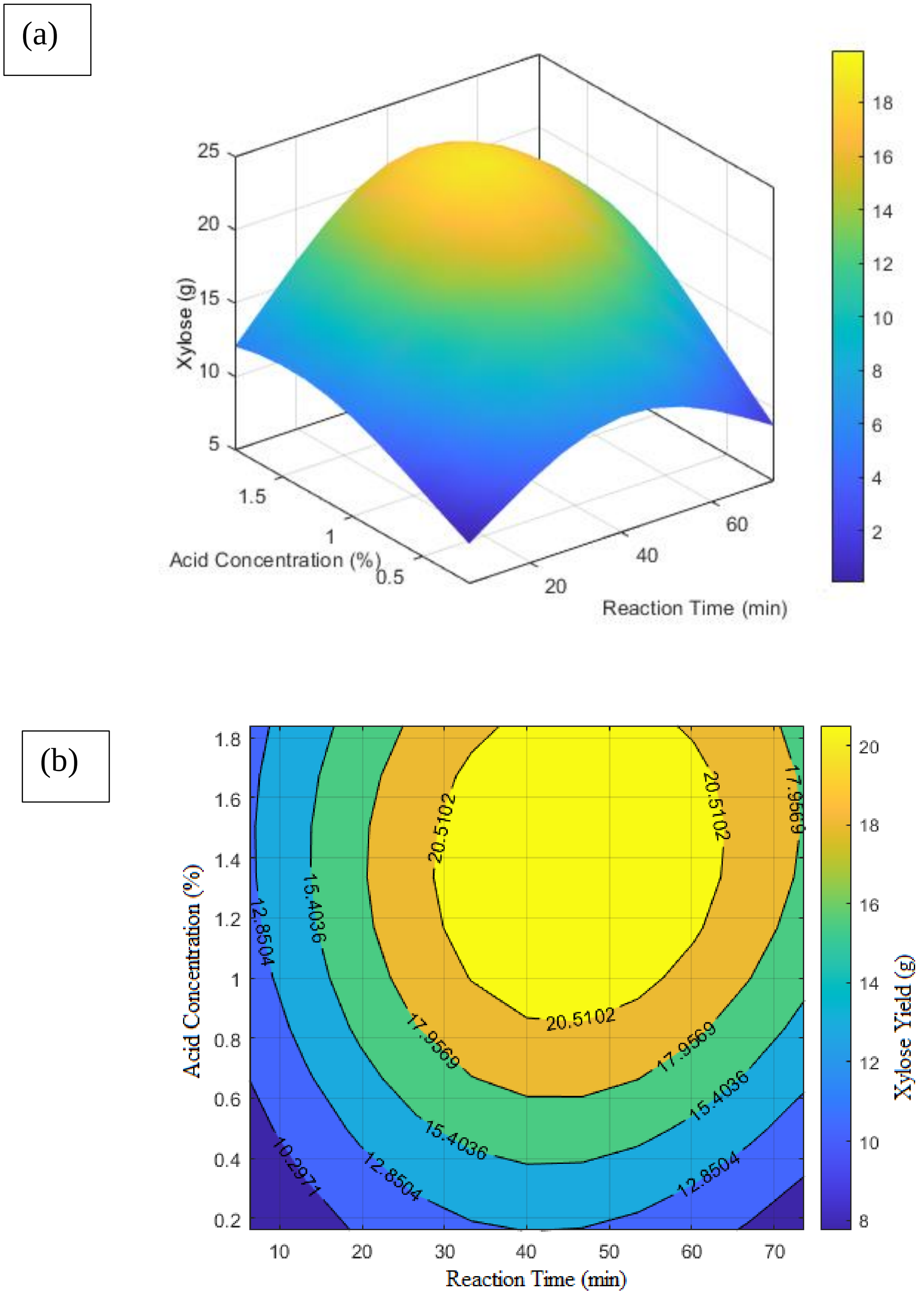


Figure 4.10: Effect of hydrolysis time and acid concentration on xylose yield represented as surface (a) and contour (b) plots

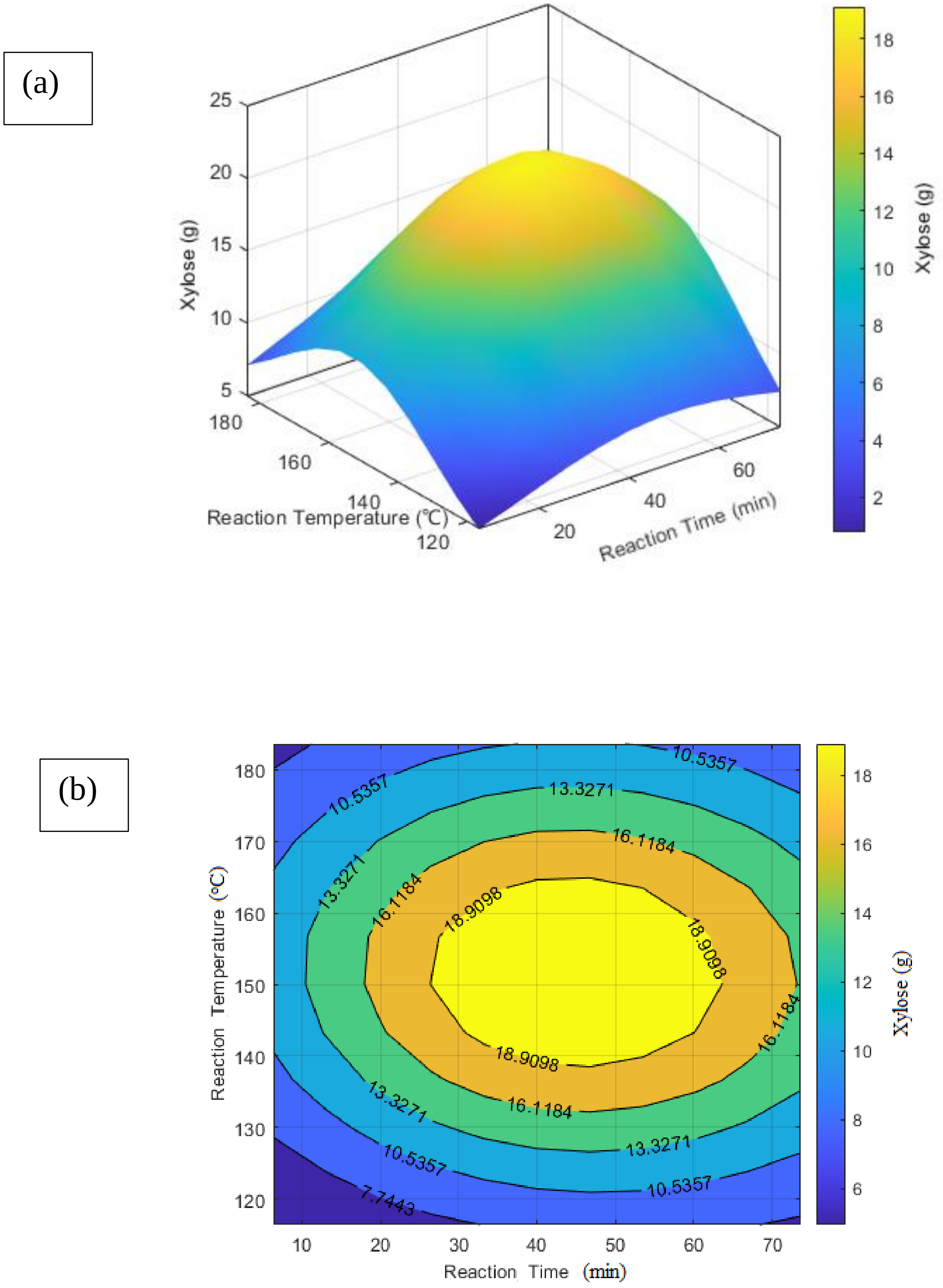


Figure 4.11: Effect of hydrolysis time and temperature on xylose yield represented as surface (a) and contour (b) plots

4.2.5. The effect of the reaction temperature and retention time on the extraction of xylose

The nature of the biomass and mechanical pretreatment conditions like size reduction affect the optimum time required for hydrolysis [146]. Smaller particles require less reaction time than the coarser ones, because of their high surface area for mass and heat transfer but more prone to further degradation to byproducts [147]. Elevated temperatures generally increase the release of xylose from the lignocellulosic matrix but the released xylose is often unstable in acidic conditions. Optimum temperature is required to increase the yield of xylose in industrially acceptable reaction time. The effect of temperature was investigated over the range of 130-170℃ in time of up to 60 minutes. The simple glycosidic bonds in hemicellulose and cellulose can be easily broken into the corresponding monomeric sugars under acidic conditions. Initially, a rapid rate of hydrolysis of hemicellulose was observed as measured by the formation of xylose. But the degree of this rapid hydrolysis is restricted, the rate slowed down after some period of residence time, and indeed the yield of xylose reduced upon prolongation of the reaction time as shown in Fig.4.9. The diminishing yield of xylose could be because of the further conversion of xylose to furfural and other degradation byproducts.

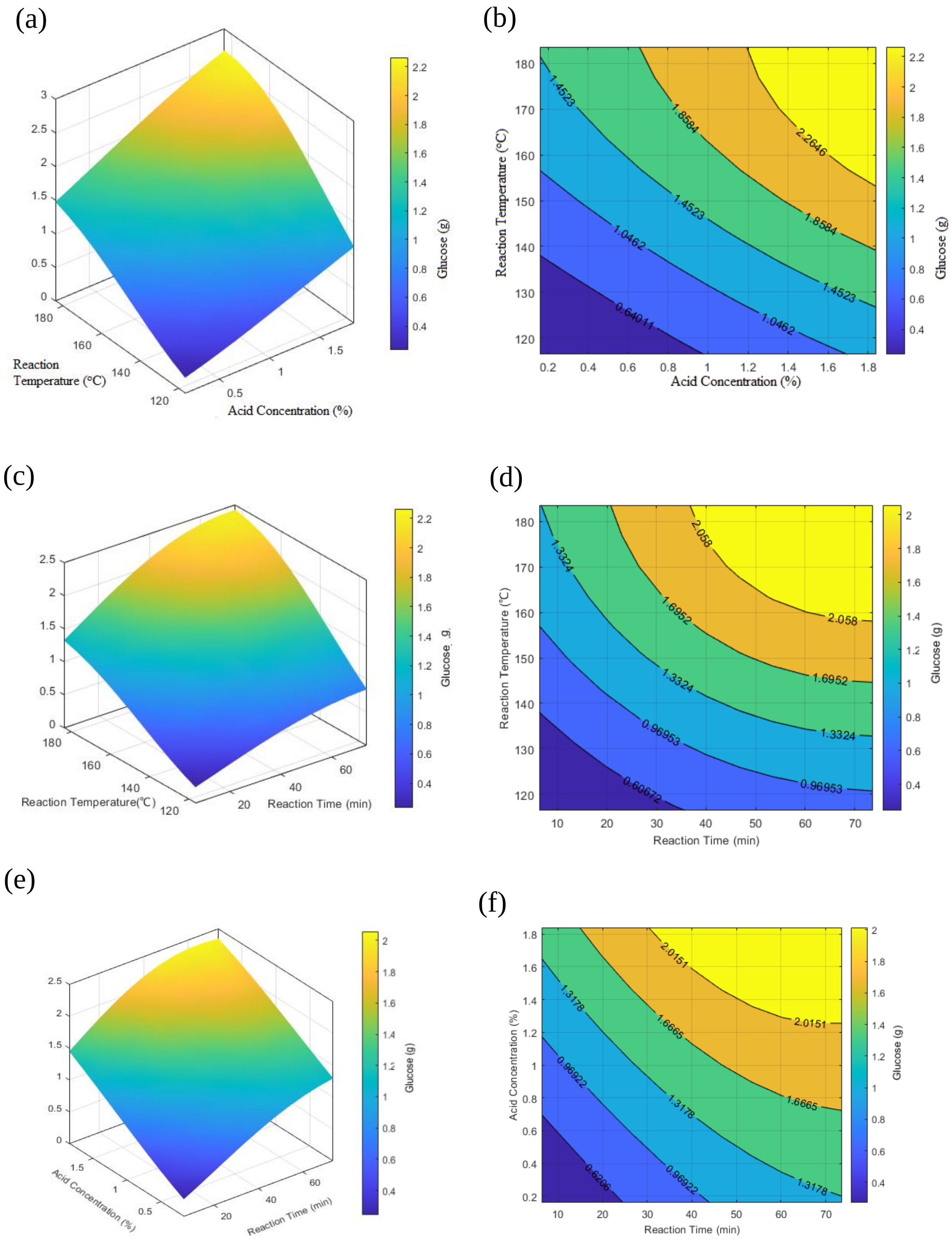


Figure 4.12: Effect of acid concentration, hydrolysis time, and temperature and on glucose yield represented as surface (a),(c) and (e) and contour (b), (d), and (f) plots

The impact of a lower reaction temperature on the yield of glucose is low (Fig.4.12 and A1), but higher temperatures debase glucose to furfural and different results. The extent of glucose formation is dependent on the degree of the crystallinity of cellulose which is the result of the beta configuration of glycosidic bonds. The amorphous cellulose structures are readily hydrolyzed along with the hemicellulose at the lower temperature ranges under acidic conditions. The yield of furfural increased as the temperature and acid concentration increased. From Fig. 4.13 and A2, it can be concluded that there was very low conversion of bagasse to furfural as initially observed at 130 °C but kept increasing with temperature, and acid concentration. At a temperature of 130 °C, the xylose yield, which is 0.181g/g bagasse in the acid with a concentration of 1.5% is the highest compared to other concentrations. Therefore, the amount of xylose obtained could additionally be improved by increasing the concentration of catalysts, but the cost of catalysts would have an impact on the general financial aspects.

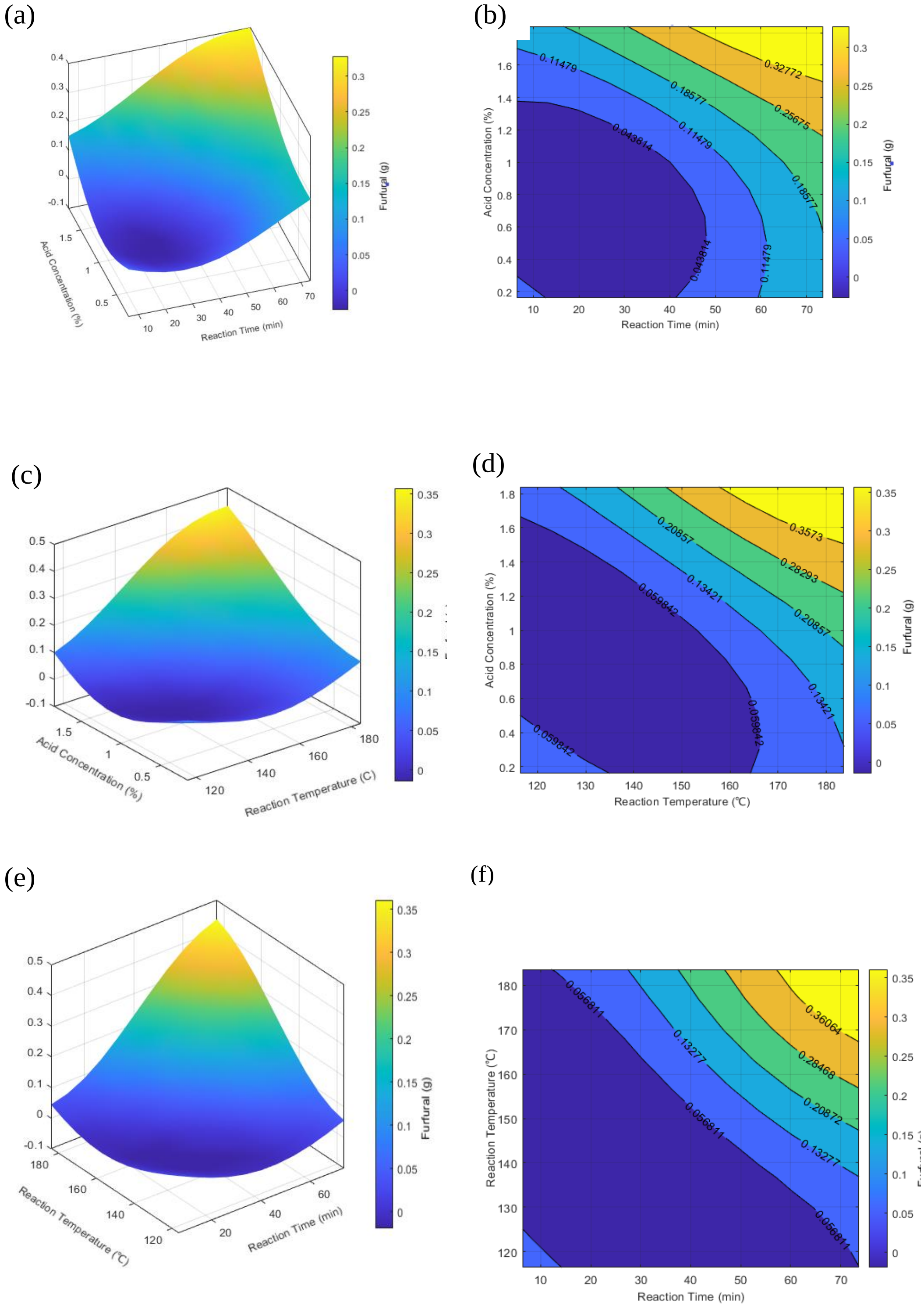


Figure 4.13: Effect of acid concentration, hydrolysis time, and temperature and on furfural yield represented as surface (a),(c) and (e) and contour (b), (d), and (f) plots

The yield of glucose and furfural increased as the severity increased, but xylose yield showed an increasing trend with the increase in severity of treatment and then decreased after reaching maximum, Fig. 4.14. Although the combined effect of temperature, acid concentration, and time was positive towards the formation of glucose and furfural, harsher conditions have negative effects on the yield of xylose. The decrease in xylose yield at the high severity of treatment may be because of its conversion to form furfural and the various degradation products.

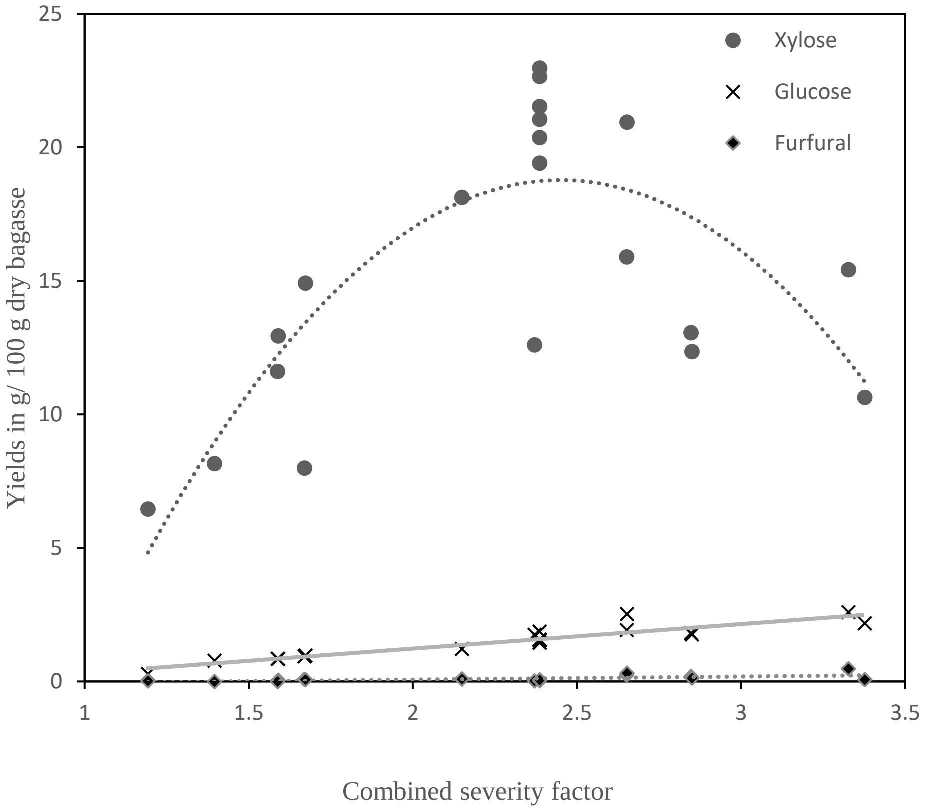


Figure 4.14: The yield of xylose, glucose, and furfural as a function of the combined severity factor for the treatment of Sugarcane bagasse

4.2.6. Conversion of sugarcane bagasse hydrolysate to furfural using TSSC

The transformation of raw biomass with solid catalysts requires a very low amount of solid raw material charging which produces a highly diluted product. The main challenge here is concentrating the product on energy-intensive processes [148]. The use of extracted hemicellulose is less complex in certain respects instead of directly using the raw biomass for the production of furfural. The suitability of the hemicellulose extracted was checked for furfural production using TSSC and the results are shown in Fig.4.15. The dehydration reactions were detected as predicted when TSSC was used in the biphasic water toluene system, and furfural induced from hemicellulose were observed. Indeed, the quantity of generated furfural is yet evidence of a higher catalytic effect of TSSC in the hemicellulose transformations, considering the more complex existence of the sugarcane bagasse hydrolysate than the monomer.

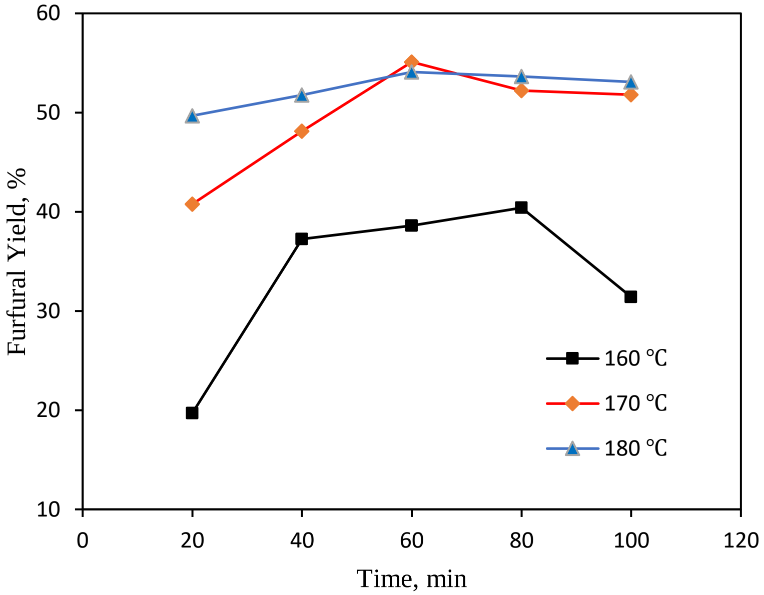


Figure 4.15: Yields of furfural from sugarcane bagasse hydrolysate (10 ml hydrolysate, 0.2 g TSSC,20 ml toluene) at various times and reaction temperatures.

A maximum yield of 54.09 % furfural was obtained from the sugarcane bagasse hydrolysate. This result is lower than the yield obtained from xylose in a previously published work [149]. More interactions between reactants, intermediate reactions, and the formed furfural could take place when hydrolysates are employed instead of xylose alone. Probably more humins and other byproducts were thus produced, which resulted in lower furfural yields.

The yield of furfural increased with an increase in time and temperature of the reaction. Faster generation of furfural with higher reaction temperatures than 160 ℃ was observed. This means that, at longer times and higher temperatures, hemicellulose and catalysts may be interacting more efficiently. For reaction temperatures above 170 ℃ in longer times, the final furfural outputs were roughly the same.

The hemicellulose and cellulose contents in the thoroughly washed residue left after the reaction were determined to verify the extent of hydrolysis. As seen in Table 4.5 the cellulose and lignin contents were not significantly affected indicating a preferential hydrolyzing of the hemicellulose portion.

The catalytic stability of the TSSC in hemicellulose conversion to furfural was investigated in a five-cycle experiment. The spent catalysts were filtered and re-washed repeatedly using ethanol and water and then dried overnight at 80°C before the next catalytic test. On the 5th round at 170 °C and 30 minutes, an insignificantly reduced yield of 45.9 % was obtained as shown in Fig 4.16.

Table 4. 5: The compositional analysis of the residue of sugarcane bagasse after hydrolysis at various severity factors

Treatment Severity	Amount of xylose in hydrolysate	Hemicellulose in g/g residue	Cellulose in g/g residue	%Cellulose in residue	%Hemicellulose in residue	%Lignin in residue
1.19	0.06	0.20	0.36	46.84	25.77	27.39
1.59	0.13	0.14	0.36	50.72	19.48	29.80
2.15	0.18	0.09	0.35	54.48	13.42	32.10
2.39	0.23	0.05	0.36	58.13	7.52	34.35

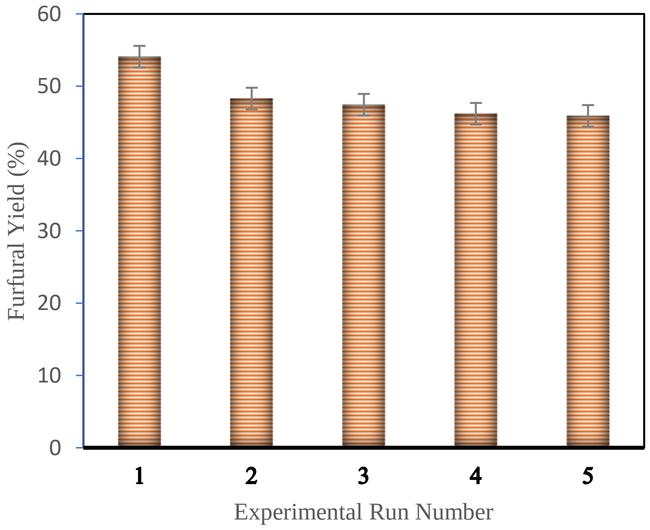


Figure 4.16: Results of the catalyst TSSC recycling study. Reaction conditions: 10 ml Sugarcane bagasse hydrolysate, 0.2 g TSSC, 20 ml toluene, 170˚C, 30 min.

4.2.7. Conclusion

Owing to the high hemicellulose content of the sugarcane bagasse, acid hydrolysis primarily produces xylose during the first phase of the process. The process conditions like time and temperature of the reaction and acid concentration have a significant effect on the performance of the acid hydrolysis. The acid concentration increased the yield of xylose at lower concentrations below 0.8%, but higher concentrations did not significantly increase the yield. A yield of more than 0.21 g/g of bagasse could be obtained at 150 ℃ using 1 % sulfuric acid. Increasing the temperature increased furfural and glucose content at the end of acid hydrolysis. An increase in a yield of furfural up to 0.0047g/g of bagasse is probably because of the increasing rate of decomposition of xylose at higher temperatures and acid concentrations. With a maximum yield of 54.09%, the TSSC was stable and successful in converting the hemicellulose-rich liquor into furfural.

4.3. Task 3: The effects of reaction conditions on the conversion of sugarcane bagasse hydrolysate to furfural

4.3.1. Effect of TSSC loading and reaction temperature on reaction rate constants

The rates of conversion of xylose in the hydrolysate to furfural can be greatly affected by the catalyst loading. In general, the conversion rate increased with increasing catalyst loading, and the results are shown in Fig. 4.17. The impacts of reaction temperature and time on furfural generation from sugarcane bagasse were researched and the outcomes are also introduced in Fig.4.18. The temperature indicated a colossal impact on the response in connection to the furfural yielding.

The rate constants of furfural formation and degradation, k_1 and k_2 respectively, that were calculated from the experimental data are listed in Table A2.

Table 4. 6: Rate Constant Changes with Temperature According to Arrhenius Expression:

r_i	A_i (min)	E_i (kJ/mol)	m_i
r_1	1.26×10^{16}	110.2	1.52
r_2	1.54×10^{12}	129.3	0.12

In Table 4.6, the higher activation energy E2 (129.3 kJ/mol), than E1 (110.2 kJ/mol), shows the difficulty of furfural degradation in the reaction temperature range, 150-190℃, used in the experiments. The model closely matched the experimental results and kinetic parameters. It also suggested the presence of toluene increased furfural yield thus slowing down degradation as compared to water.

At 0.1g catalyst loading, an increase in reaction temperature increased furfural formation rates, but the rate eventually declines after 60 min of reaction time at 190℃. The values of k1 were substantially higher than those of k2, indicating that the furfural production reaction was the primary reaction. At 150℃ reaction temperature, the values of k1 and the frequency factor (A1) increased with an increase in catalyst loading leading to an increase in the rate of formation (r1) of furfural.

To match kinetic parameters in the conversion of sugarcane bagasse hydrolysate to furfural, a modified Arrhenius equation was used. Activation energy, frequency factor, and reaction order are 110.2 kJ/mol, $1.26x10^{16,}$ and 1.52 respectively. The activation energy of furfural degradation over TSSC in water/toluene obtained was greater when compared to the values of activation energy in water only using H-ZSM-5 [60]. The water/ toluene system was an efficient medium for the conversion of hemicellulose compared to H_2O only. It has led to significant improvements in reaction rate and improved product yield as an extraction medium. The result also confirmed that the use of toluene as a solvent changes the activation energy of the reaction, i.e., hydrolysate dehydration to furfural. The presence of toluene has a positive impact on the prevention of the active sites from deactivating by acting as a shield that prevents the deposition of the humins on the catalyst surface [150].

4.3.2. Effect of reaction time on furfural yield

Apparently, sufficient time is required to achieve high yields. The short interaction time between the catalyst and the solution is inadequate, resulting in low output performance. When low catalyst loading is employed at 150 ℃, the yield of furfural gradually increases and takes a long time to reach a high yield. The prolonged duration of reaction could result in the decline of the yield of furfural as shown in Fig. 4.17 B at 190 ℃ and Fig. 4.17 C at 170 and 190 ℃.

4.3.3. Effect of temperature on furfural yield

The effects of reaction temperature and time on furfural production from sugarcane bagasse were investigated and the results are presented in Fig.4.17.

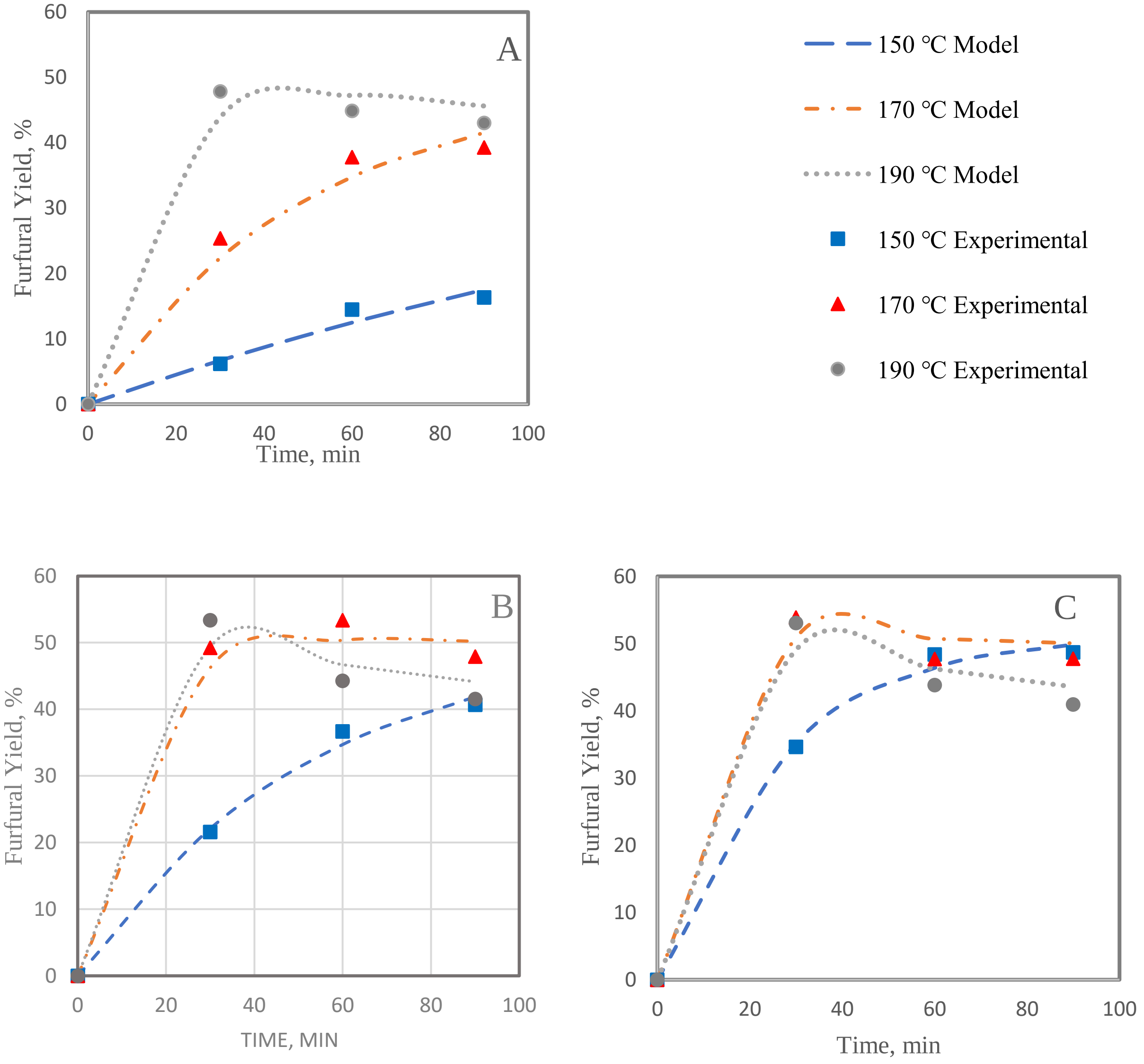


Figure 4.17: Effect of temperature and residence time on the yield of furfural at various catalyst loading (A) 0.1g, (B) 0.25g, and (C) 0.4g

The temperature showed a considerable effect on the reaction in association with the furfural yielding. The effect of temperature and time on the yield of furfural from xylose was studied at 150-190 ℃ in 90 minutes using carbon-based solid acid catalysts. The yield of furfural increased with the time at a temperature of 150 ℃. But it increased with time initially and decreased after 40 minutes of treatment time at a higher temperature of 170 ℃ and 190℃ if a catalyst loading of 0.4g is applied. This phenomenon, the decrease in the yield of furfural at higher temperatures and time, maybe due to the further conversion of furfural to degradation products by resignification and condensation reactions [151].

As the temperature of the reaction increases the slope of the curve of time against the yield of furfural gets more flattened after the reaction time of 60 minutes, implying that the rate of furfural formation is decreasing or the rate of furfural degradation is increasing. At initial times the rate is increasing with some sort of increase in slope upon the increase of the reaction temperature. In the range of 30 minutes to 60 minutes, at catalyst loading, the yield increased by 59.7 and 32.2 %, for the temperatures 150 and 170 respectively, and decreased by 10.65% at 190℃ clearly showing the flattening and then declining of the curve with increasing temperatures. For specific reaction times, the yield increased with increasing temperatures. Increasing the temperature above 190 ℃ may further improve the yield but too high temperatures favor the furfural degradation reactions. The highest yield achieved in our case was 54.68 % at 170 ℃ in a reaction time of 30 minutes, 0.4 g catalyst loading.

4.3.4. Effect of TSSC dosage on furfural yield

The effect of the catalyst amount was studied by the xylose dehydration experimental test using 0.1, 0.25, and 0.4 g of catalyst and xylose-rich liqueur in 20 ml toluene. The yield of furfural initially increased upon the increase of catalyst loading but at higher loading above 0.25g the trend is reversed, i.e., the yield decreased. This may occur because of the excess active site provided by the excess catalyst which may, in turn, affect the conversion process by promoting the undesired reactions [151].

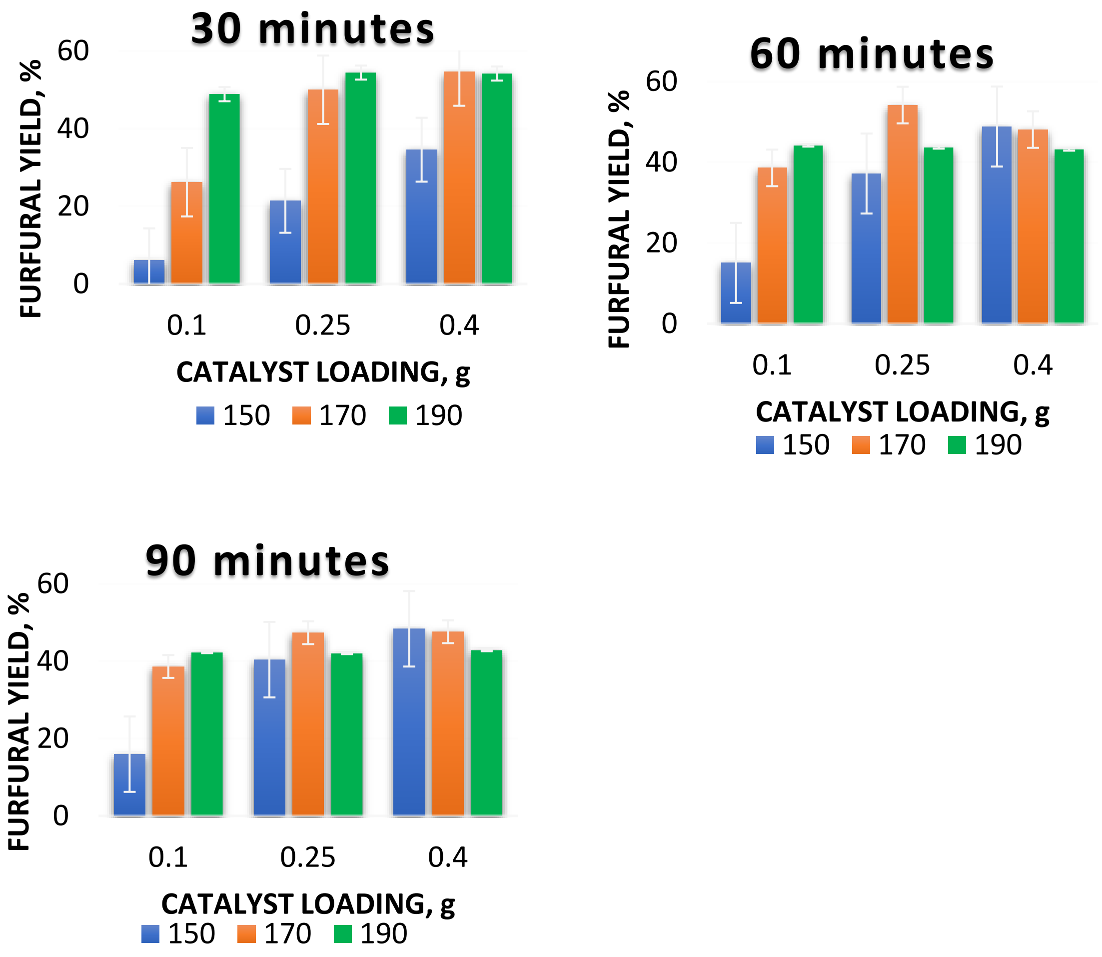


Figure 4.18: Effect of catalyst loading on the yield of furfural with a residence time of (A) 30, (B) 60, and (C) 90 min over various reaction temperature

4.3.5. Conclusion

In this kinetic analysis, the concentration of catalyst and temperature, and time of hydrolysis are key factors affecting furfural production. The furfural yield increases with the reaction time in the early stages of the reaction and then declines. A kinetic model based on a chemical pathway that involves the dehydration of xylose to furfural and the degradation of furfural was developed. The kinetic model sufficiently represented the amount of furfural generated in various conditions of reactions.

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4.4. Task 4: Thermodynamic analysis of production of furfural

4.4.1. Effect of Temperature on xylose conversion and furfural yield

The molar flow profile of xylose and its conversion and furfural selectivity at various reaction temperatures are shown in Fig. 4.19 and Fig. 4.20 respectively. In all of the temperature ranges investigated, xylose is completely consumed at equilibrium. The conversion of xylose is very complete due to its low stability at high temperatures.

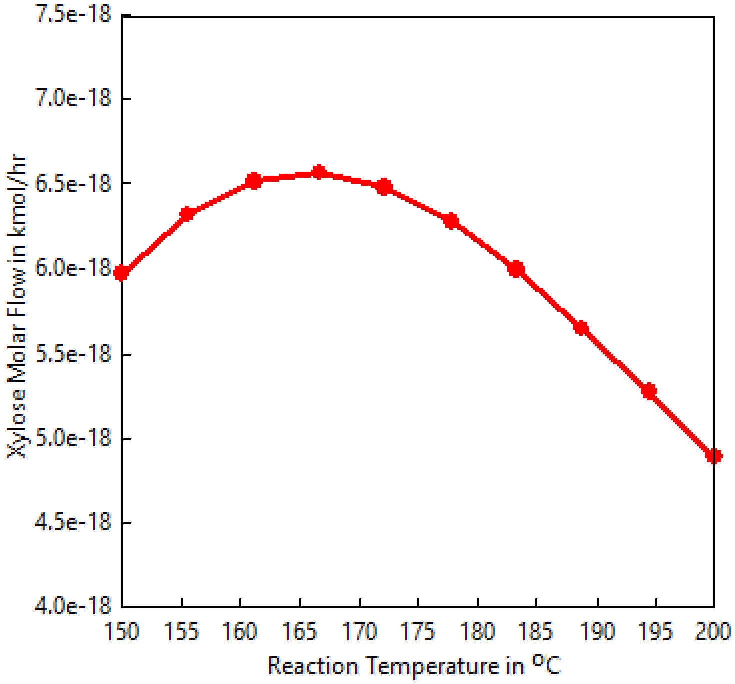

Figure 4.19: Molar flow profile of xylose at various reaction temperatures

Raising the operating temperature raises the molar fraction as well as the molar flow of the furfural. Fig. 4.21 shows a rise in furfural concentration during high-temperature operation. This is related to the high temperatures, which favor the xylose dehydration process. Increased reaction temperatures have the advantage of achieving high furfural concentrations, which would improve furfural yield; however, too high operating temperatures will cause a decrease in the yield. Temperatures that are too high have a proclivity for degrading furfural.

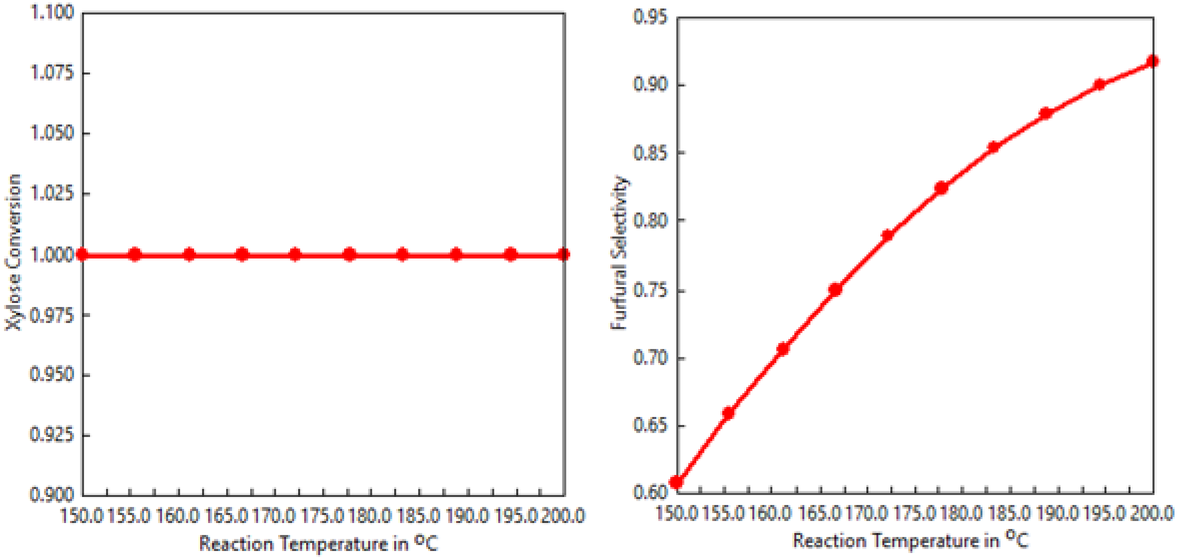

Figure 4.20: The effect of temperature on equilibrium xylose conversions and furfural selectivity

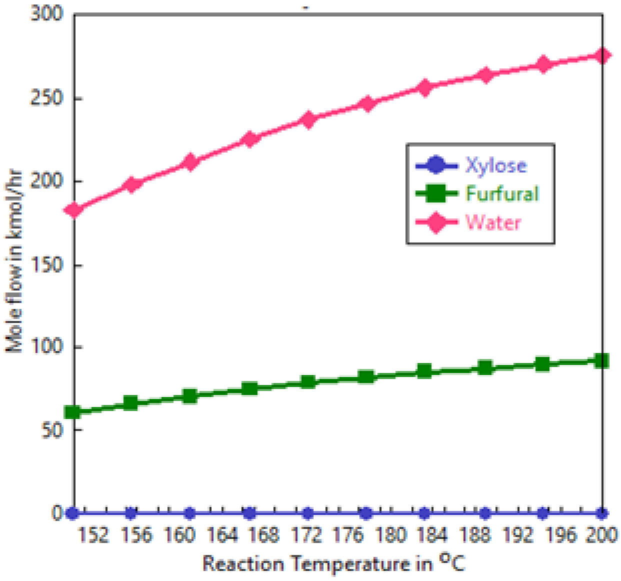

Figure 4.21: Mole flow of components in the product stream

4.4.2. Effect of Temperature on ΔG of xylose conversion reaction.

A reaction is thermodynamically conceivable under given working conditions if $\Delta G < 0$, whereas zero change in free energy, $\Delta G = 0$, corresponds to the chemical equilibrium state [152].

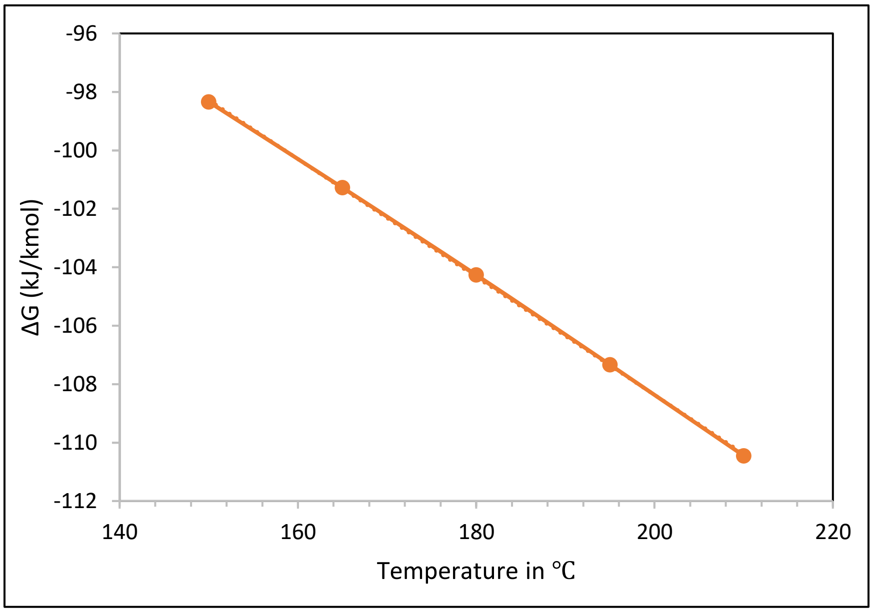

Figure 4.22: The effect of temperature on the change in Gibbs free energy for xylose dehydration reaction

The negative sign of change in Gibbs free energy, shown in Fig 4.22, implies that the xylose dehydration reaction is spontaneous. Therefore, the reaction is thermodynamically favorable in the temperature range investigated, and the process is irreversible in terms of entropy change.

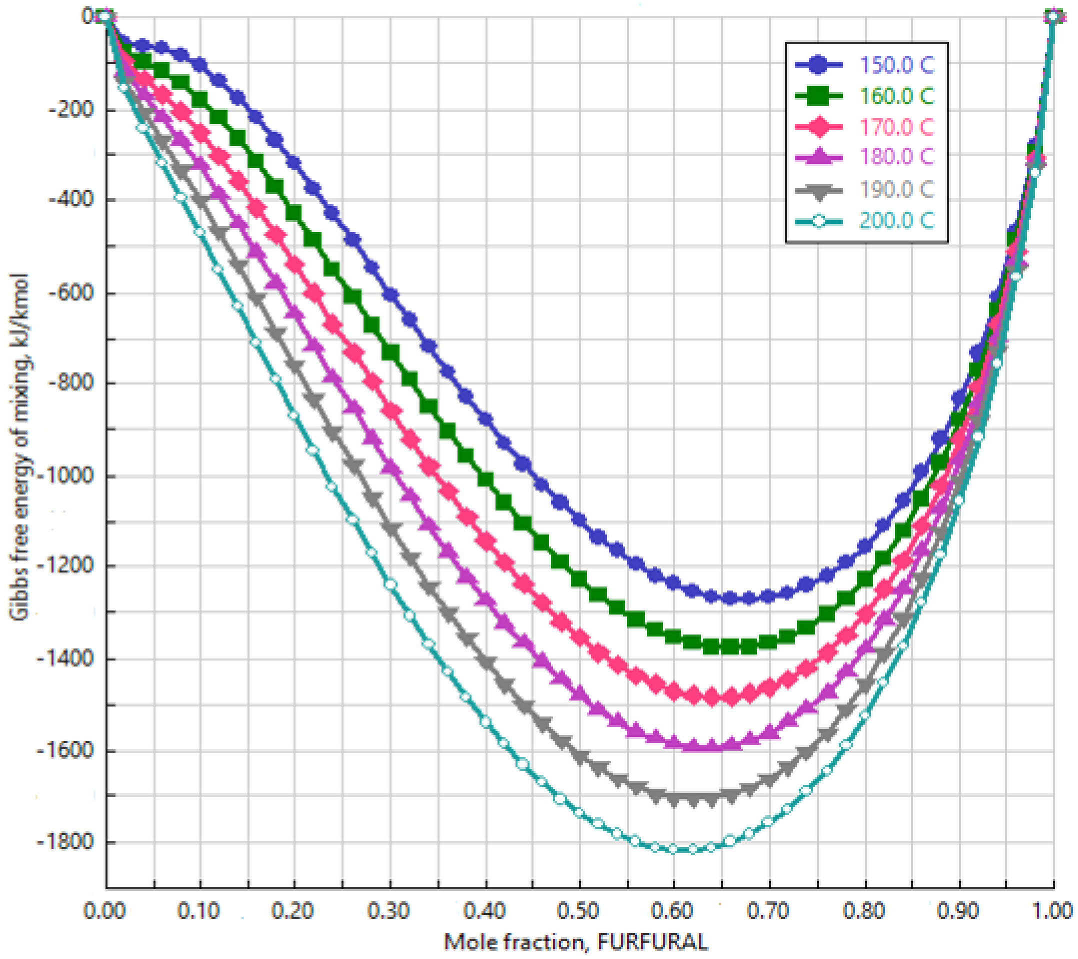

Figure 4. 23 A: Gibbs free energy of mixing for furfural/water systems at various mole fractions of furfural and temperatures

The Gibbs free energy of mixing at various temperatures has been presented in Fig. 4.23 A, 4.23 B, and 4.23 C. The Gibbs free energy mixing determines whether mixing is a spontaneous process at a particular temperature and pressure. When the Gibbs free energy of two liquid phases is lower than that of one liquid phase, two liquid phases arise. From Fig. 4.23 A, 4.23 B, and 4.23 C, it can be seen that the Gibbs free energy of mixing for furfural/water is higher than that of furfural/toluene mixture, but less than water/toluene system. This implies furfural solubility is higher in toluene than in water, and water and toluene are more likely immiscible.

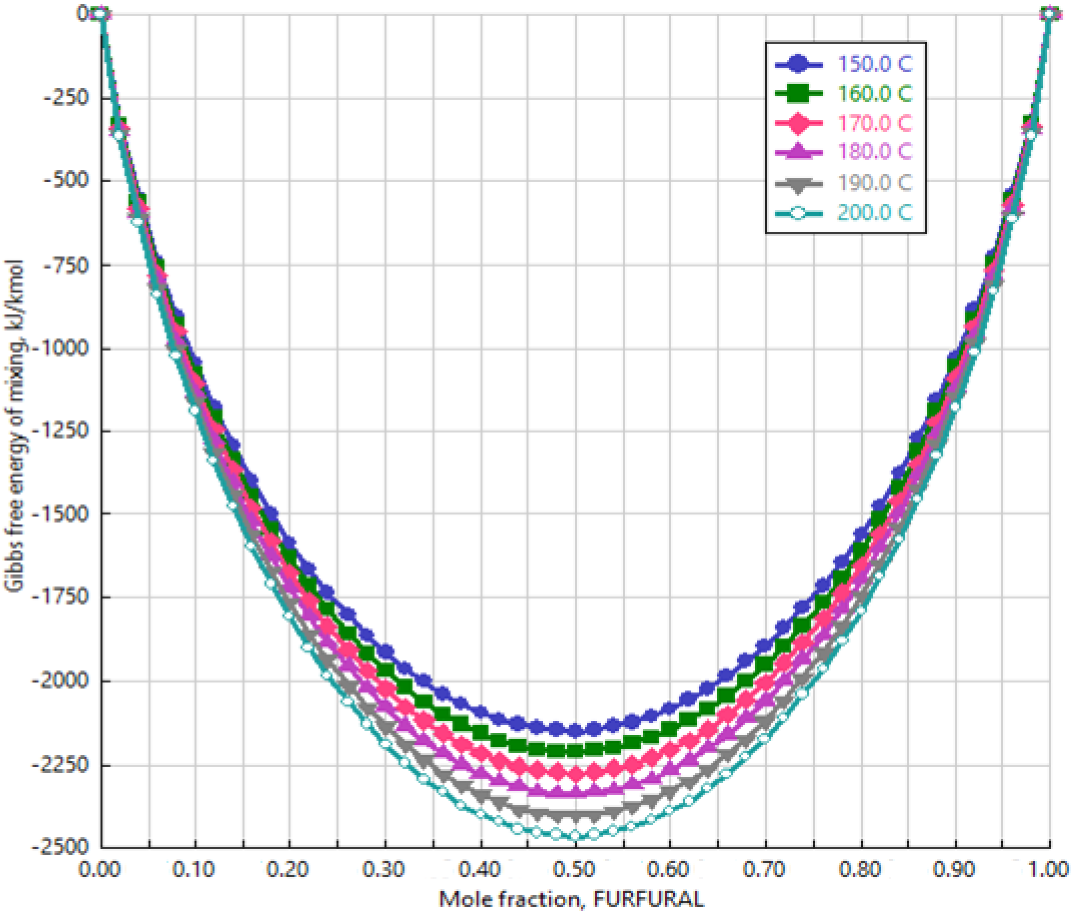

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Figure 4. 24 B: Gibbs free energy of mixing for furfural/toluene systems at various mole fractions of furfural and temperatures

The theoretical thermodynamic analysis agreed with the experimental study on xylose dehydration reaction in the water+ toluene system carried out at 170 °C using 0.1, 0.2, and 0.4 g catalyst.

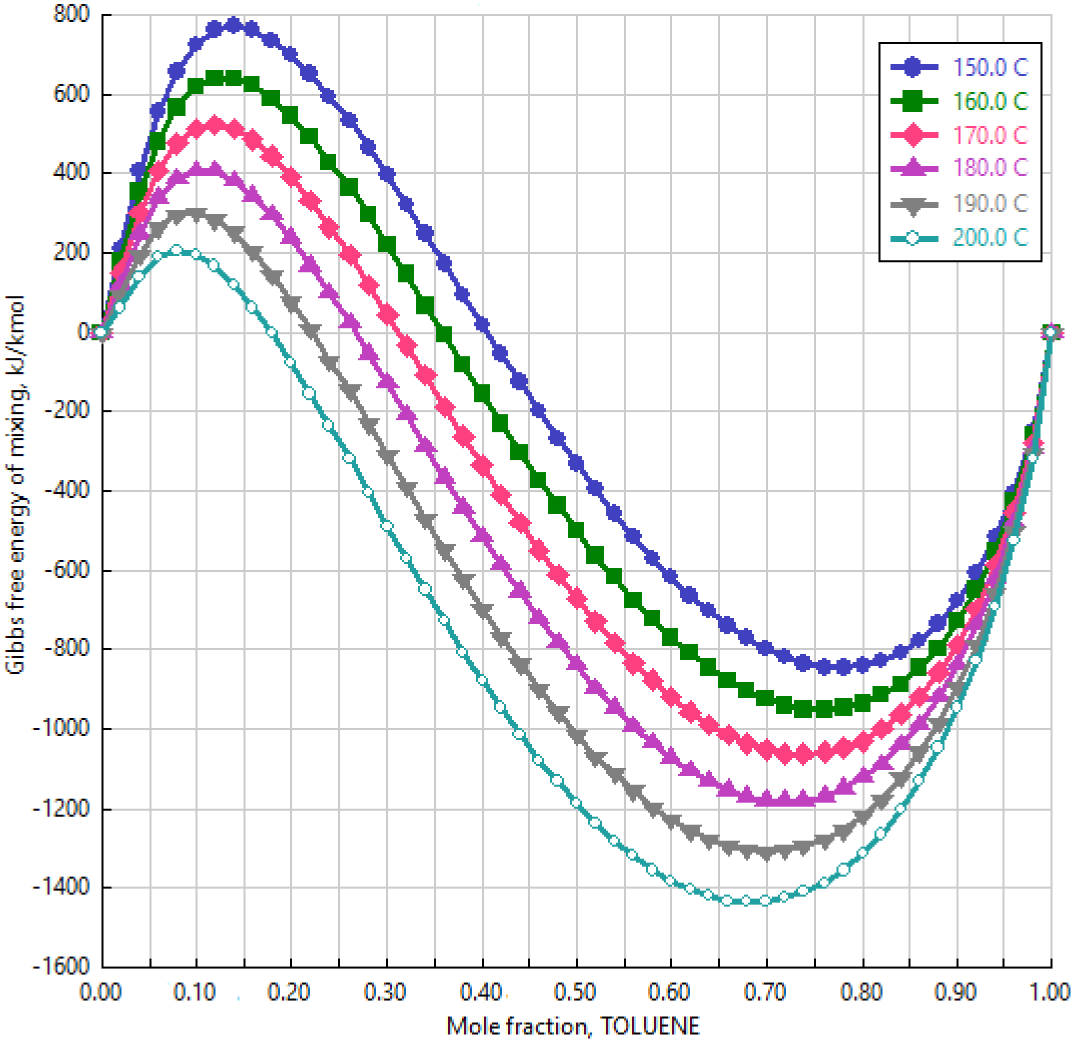

Figure 4. 25 C: Gibbs free energy of mixing for water/toluene system at various mole fractions of toluene and temperatures

Toluene showed excellent activities in the removal of furfural from water. The water-toluene-furfural system undergoes a spontaneous phase split into two phases, the toluene-rich phase containing more furfural and the water phase containing less furfural at the end of the reaction. The toluene-rich phase contains up to 1g of furfural, while the water phase contains a negligible fraction of it. As the amount of furfural produced by the reaction increases the fraction in the organic phase also increases with time.

The major reaction product of the conversion of xylose over noble-solid acid catalysts is furfural, according to experimental data. Furfural has been proven to be much more soluble in toluene than it is in water. Because all of the partition coefficients, or the ratio of mole fractions of furfural in toluene to those in water, were more than one, the solvent could extract furfural from an aqueous solution. A better separation is achieved if the partition coefficients are greater. The partition coefficients (also known as distribution coefficients) tended to rise when the concentration of furfural was increased.

The partition coefficient was calculated from experimental data and used as a benchmark for evaluating separation efficiency. The limitation is the effect of temperature on the partition coefficient was not considered because the mole fractions were calculated from the data obtained during the quantification of product in the sample at room temperature.

4.4.3. Conclusion

The thermodynamic analysis demonstrated a negative change in Gibbs free energy, which is the most prevalent condition that confirms the spontaneity of xylose to furfural conversion over the temperature range investigated. Furfural is more soluble in toluene than water, which is a favorable condition for furfural extraction into the organic phase to prevent the possible degradation of furfural in the water phase. The experimental results also confirmed the successful extraction of furfural into the toluene-rich phase.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

This thesis investigates the synthesis, characterization, and activity of a novel catalyst prepared from teff straw via simultaneous carbonization and sulfonation for the application in xylose dehydration reaction into furfural. The literature review in Chapter 2 on sugarcane bagasse valorization with a focus on catalytic conversion and product separation revealed that carbon-based catalyst has a significant potential to be applied in industrial processes for producing furfural.

The study of the TSSC materials revealed that they possessed a variety of features. The following findings can be obtained from the physicochemical analysis of the prepared catalyst:

The successful synthesis of the required teff straw-based catalyst containing -SO_3H as an active site was validated by XRD examination of newly synthesized materials. The transition from sharper diffraction peaks in the teff straw to broader peaks in the produced catalyst confirms the dissolution of cellulose's crystalline structure and the creation of a desirable amorphous structure during thermal treatment in sulfuric acid.

The produced catalyst had absorption bands that were typical of TSSC in their FTIR spectra. FTIR analysis revealed the presence of -SO_3H species along with -COOH and -OH in the catalyst prepared by carbonization and sulfonation. The elemental analysis confirmed the intended compositions i.e., sulfur has been successfully introduced into the carbon structure of TSSC. The new catalyst has a bulk density of 0.43 g cm-3, a particle density of 0.63 g cm-3, and a porosity of 0.31.

Tests were carried out in a variety of conditions to ensure that catalysts made from teff straw could be used effectively in the necessary catalytic process. Teff straw has shown promise as a carbon precursor for making low-cost heterogeneous catalysts for dehydration processes. The synthesized teff straw-based catalyst was tested for its ability to convert xylose to furfural in toluene/water biphasic systems, and the catalyst was found to be efficient and stable.

The impact of the carbonization and sulfonation times and temperatures, as well as the preparation conditions, on the functionalization of the carbon structure was studied. The results reveal that at lower temperatures and shorter carbonization and sulfonation times, the maximum sulfonic acid density can be achieved. Low sulfonic acid loading was achieved at high carbonization and sulfonation temperatures because of the collapse of the carbon structure and the formation of a rigid structure. Although a higher total acid density can be attained by treating for a longer period, comparable results can be obtained by treating for a shorter period and at lower temperatures. Too high temperatures and long carbonization and sulfonation periods are unfavorable because the catalyst structure is destroyed, resulting in extremely small particles that are difficult to control during washing.

Various outcomes were identified during the catalytic performance test of the carbon-based catalyst. Furfural yield increased as the reaction temperature was raised to 170 °C. However, at temperatures above 170 °C, the activity diminished, resulting in lesser yields. When furfural is subjected to higher temperatures, it is transformed into by-products, primarily humins. When humin is deposited on active sites, it inhibits the efficiency of solid acid catalysts by preventing reactants from entering the active site.

The conversion test without catalyst yielded very low furfural yields, but when the amount of catalyst was increased up to 0.25 g, the yields increased. The more catalyst supplied to the reaction solution, the more catalytically active sites are available for xylose dehydration to furfural, and therefore the yield of furfural grows. Overloading the catalysts, on the other hand, would cause side reactions such as fragmentation, condensation, and resinification, reducing the final product yield. After four successive runs, the catalyst was determined to be stable, with almost similar performance. The yield on the fourth run was 56.8% at 170°C and 30 minutes response time.

The optimal reaction conditions for extracting xylose from sugarcane bagasse were established using a generally applicable model developed for acid-catalyzed hydrolysis of sugarcane bagasse to xylose. The reaction temperature was varied between 130 and 170 °C, and the sulphuric acid content was varied between 0.5 and 1.5 percent in systematic studies. An empirical equation was developed based on optimization research to estimate the xylose production at a given temperature and acid content.

- The proposed model agreed well with experimental data obtained from the hydrolysis of sugarcane bagasse to xylose. The points predicted by the model are near the fitting line with narrow confidence bands, ensuring an excellent match to the experimental data.
- The highest yield of xylose was produced in 40 minutes at a temperature of 150 ^{o}C with an acid concentration of 1%, and around 0.7 percent was the lowest acid concentration that might theoretically provide a yield of xylose higher than 0.19g from 1g of bagasse. The harsh process conditions caused rapid sugar breakdown, resulting in low hydrolytic

efficiency. Although higher temperatures enhance xylose release from the lignocellulosic matrix, the liberated xylose is typically unstable under acidic circumstances. Initially, fast hemicellulose hydrolysis was detected, as evidenced by the amount of xylose produced. However, the extent of this fast hydrolysis is limited; the rate slowed after a period of residence time, and the yield of xylose decreased as the reaction time was extended.

- The yields of glucose and furfural grew as the severity of the sugarcane bagasse treatment increased, whereas the yield of xylose increased with the severity of the treatment and subsequently dropped after it reached its maximum because of its conversion to furfural and the various degradation products.

In the kinetic analysis, the concentration of catalyst, temperature, and time of hydrolysis are all important components in the formation of furfural. In the early phases of the reaction, the furfural yield rises with reaction time and eventually falls. The difficulty of furfural degradation in the reaction temperature range of 150-190°C is demonstrated by the higher activation energy E2 (129.3 kJ/mol) than E1 (110.2 kJ/mol). In comparison to water alone, the water/toluene system proved a more effective medium for hemicellulose conversion. The kinetic model successfully predicted the amount of furfural produced under varied reaction conditions. The short interaction time between the catalyst and the solution is inadequate, resulting in low output performance. The longer the reaction lasts, the lower the furfural yield will be. When using a low catalyst loading at 150 °C, the yield of furfural grows slowly and takes a long time to obtain a high yield.

5.2. Recommendations

The research effort in this dissertation met its objectives, however further work may be required to develop and evaluate the utilization of the teff-straw based catalyst for various applications. The synthesis of a catalyst utilizing indigenous biomass presented herein offers up a range of new opportunities for future research. Unused biomass residues rich in cellulose and lignin can be transformed into various products for economic gain during furfural production. The use of these wastes might lead to the development of a biorefinery concept, which could help with the industrialization of furfural technology. Because the process integration was not addressed in this thesis, it is beneficial to work on the cellulose and lignin valorization along with furfural production. Recent advances in the manufacture of furfural in combination with the co-generation of other biomass-based products such as methyl alcohol, acetone, acetic acid, levulinic acid etc. have been researched. These choices for integration must be investigated utilizing the newly synthesized catalyst.

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Appendix

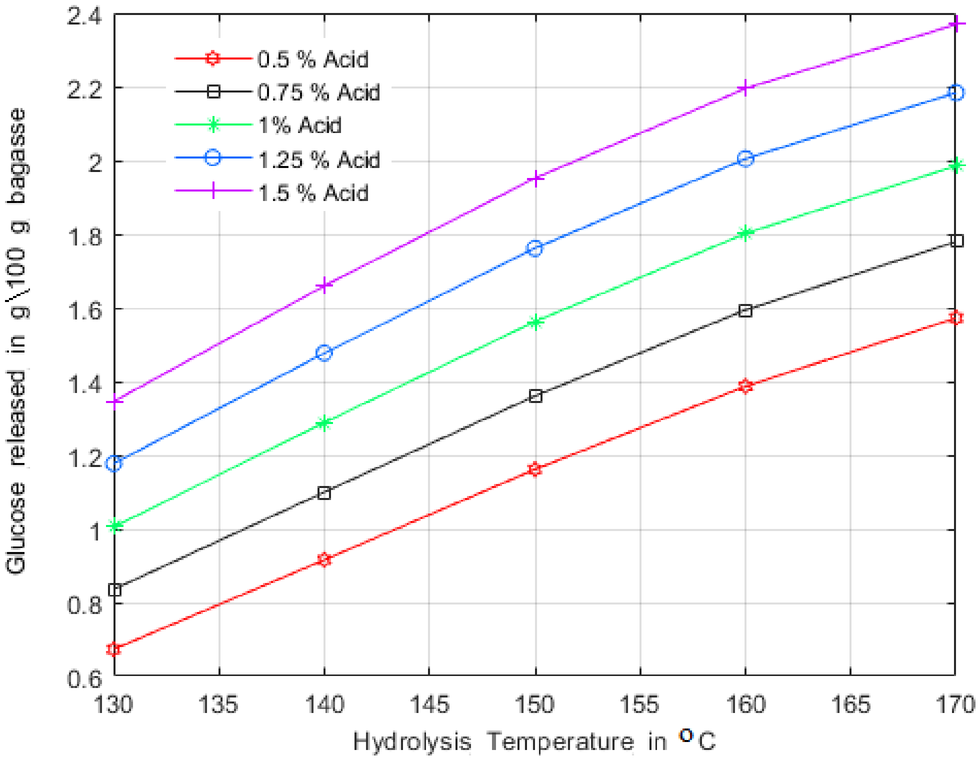

Figure A 1: Effect of acid concentration and hydrolysis temperature and on glucose yield

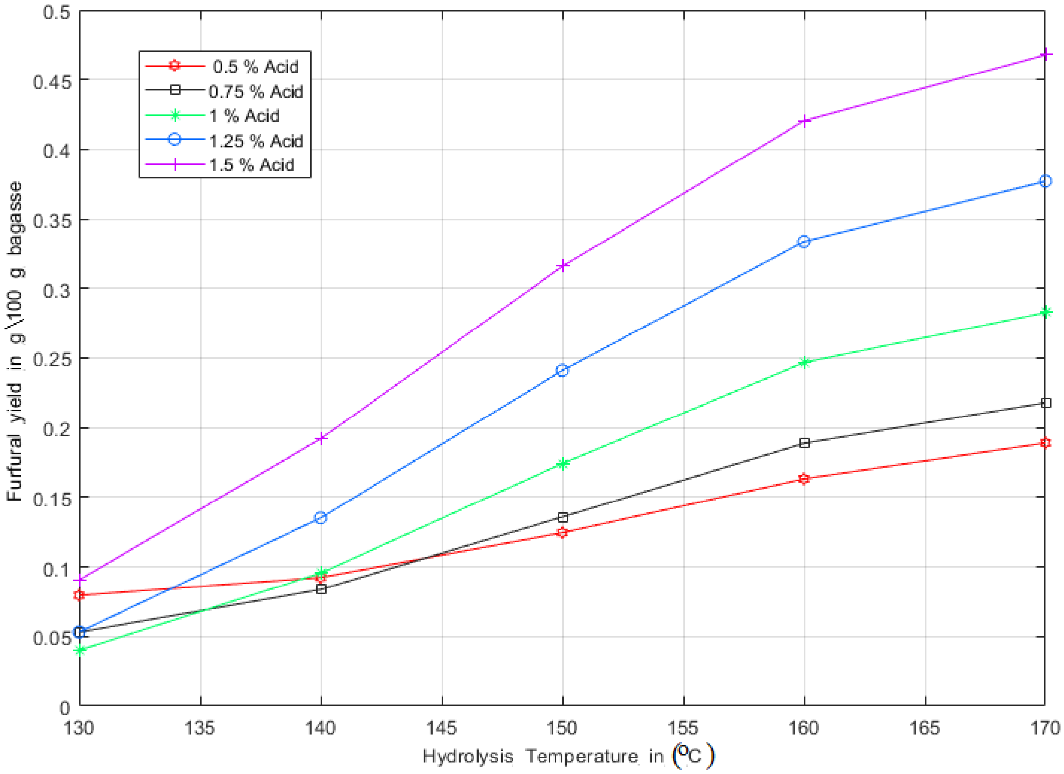

Figure A 2: Effect of acid concentration and hydrolysis temperature on furfural yield

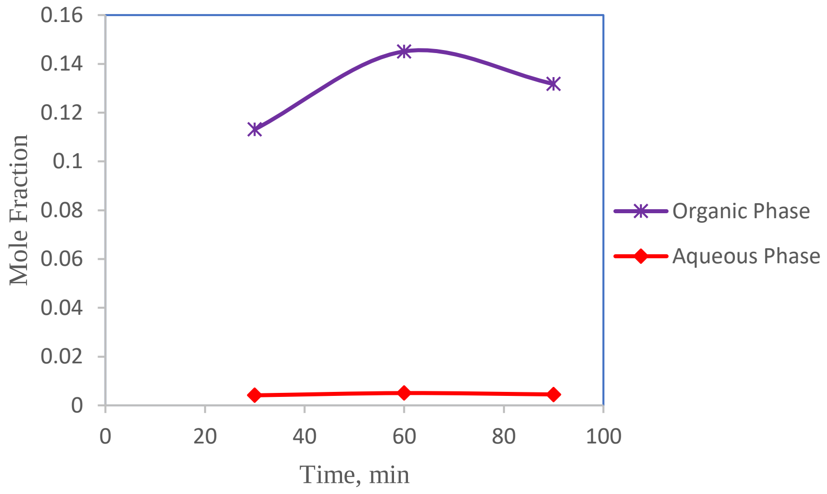

Figure A 3: Mole fractions of furfural in organic and aqueous phases (Furfural produced at 170℃, over 0.1 g catalyst)

Table A 1: ANOVA for Response Surface Reduced Quadratic Model [Sum of squares is Type III - Partial]

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	501.95	9	55.77	56.58	< 0.0001	significant
X_1-Temperature	7.50	1	7.50	7.61	0.0202	
X_2-Time	17.56	1	17.56	17.81	0.0018	
X_3-Concentration	85.55	1	85.55	86.79	< 0.0001	
X_1X_2	0.1891	1	0.1891	0.1918	0.6707	
X_1X_3	33.91	1	33.91	34.40	0.0002	
X_2X_3	2.30	1	2.30	2.33	0.1576	
X_1^2	263.46	1	263.46	267.27	< 0.0001	
X_2^2	107.60	1	107.60	109.15	< 0.0001	
X_3^2	37.27	1	37.27	37.81	0.0001	
Residual	9.86	10	0.9858			
Lack of Fit	0.6743	5	0.1349	0.0734	0.9938	not significant
Pure Error	9.18	5	1.84			
Cor Total	511.80	19				

Table A 2: The kinetic constants and tmax for the conversion of xylose to furfural

Temperature In ℃	Catalyst loading in gm	Time	Yield	Yield calculated	k1	k2	tmax
150	0.1	30	6.07	7.59	0.005789	0.004853	188.4215
150	0.1	60	15.06	13.03			
150	0.1	90	15.95	16.71			
150	0.25	30	21.39	23.04	0.019858	0.000802	168.4117
150	0.25	60	37.21	35.06			
150	0.25	90	40.38	41.26			
150	0.4	30	34.56	35.69	0.039124	0.000245	130.4877
150	0.4	60	48.86	46.45			
150	0.4	90	48.35	49.49			
170	0.1	30	26.20	27.09	0.026521	0.002966	93.00457
170	0.1	60	38.60	36.96			
170	0.1	90	38.61	39.36			
170	0.25	30	50	50.12	0.126786	0.000532	43.35397
170	0.25	60	54.17	50.38			
170	0.25	90	47.34	49.62			
170	0.4	30	54.68	50.63	0.281891	0.000878	20.53866

170	0.4	60	48.10	49.36			
170	0.4	90	47.59	48.10			
190	0.1	30	48.86	48.48	0.406658	0.002451	12.64569
190	0.1	60	44.17	45.06			
190	0.1	90	42.28	41.89			
190	0.25	30	54.43	48.86	0.241338	0.00229	19.48415
190	0.25	60	43.67	45.69			
190	0.25	90	42.02	42.65			
190	0.4	30	54.17	48.98	0.245945	0.002241	19.27825
190	0.4	60	43.16	45.82			
190	0.4	90	42.78	42.78			

Table A 3: Model components properties.

	Xylose	**Furfural**	**Water**
Molecular formula	$C_5H_{10}O_5$	$C_5H_4O_2$	H_2O
Molar mass (g/mol)	150.13	96.085	18.015
Density @ 20 °C (g/cm³)	1.52	1.1601	0.998
Boiling point (°C)	415.5	162	100
Melting point (°C)	144 to 145	-37	0

Table A 4: Distribution coefficient of furfural in water/toluene biphasic system (For furfural produced at 170℃)

Catalyst Loading	Reaction Time	Mole fraction of furfural in Organic Phase	Mole fraction of furfural in Aqueous Phase	Distribution Coefficient
0.1	30	0.113	0.004	27.46
0.1	60	0.145	0.005	28.72
0.1	90	0.132	0.0045	29.32
0.25	30	0.184	0.006	28.94
0.25	60	0.185	0.006	29.09
0.25	90	0.163	0.0056	29.10
0.4	30	0.186	0.0064	29.21
0.4	60	0.160	0.0054	29.48
0.4	90	0.159	0.0054	29.24