OPTIMIZATION OF BIO-CHEMICAL CONVERSION OF RICE STRAW TO 5-(HYDROXYMETHYL)FURFURAL

Poornima Nishadhi Wanninayake

198080N

Master of Philosophy

Chemical and Process Engineering
Faculty of Engineering

University of Moratuwa
Sri Lanka

February 2024

OPTIMIZATION OF BIO-CHEMICAL CONVERSION OF RICE STRAW TO 5-(HYDROXYMETHYL)FURFURAL

Poornima Nishadhi Wanninayake

198080N

Thesis submitted in partial fulfillment of the requirements for the degree
Master of Philosophy

Chemical and Process Engineering
Faculty of Engineering

University of Moratuwa
Sri Lanka

February 2024

DECLARATION

I declare that this is my own work and this Thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or Institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text. I retain the right to use this content in whole or part in future works (such as articles or books).

Signature: Date: 2024-02-08

The supervisors should certify the Thesis with the following declaration.

The above candidate has carried out research for the Master of Philosophy Thesis under our supervision. We confirm that the declaration made above by the student is true and correct.

Name of Supervisor: Prof. S. H. P. Gunawardena

Signature of the Supervisor: Date: 02-08-2024

Name of Supervisor: Dr. S. A. D. T. Subasinghe

Signature of the Supervisor: Date: **08-02-2024**

Name of Supervisor: Dr. H. H. M. P. Rathnayake

Signature of the Supervisor: Date: 08-02-2024

DEDICATION

This thesis is dedicated,

To my husband Thilina, for his understanding, love, and support which helped me a lot to overcome the barriers I have faced.

To my father and mother, the shadow of my success and for their unconditional love.

To all my teachers from University of Moratuwa, University of Peradeniya, and Eppawala Central College, for making me who I am today.

ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my supervisors, Prof. (Mrs.) Sanja H. P. Gunawardena, Dr. S.A.D.T. Subasinghe, and Dr. H.H.M.P. Rathnayake for their exceptional supervision and motivation expressed to me during the period of my research. Prof. Gunawardena has been a role model for me and guided me from the first day I met her even before starting my research to be a successful researcher. Dr. Subasinghe has been a great mentor and supported me in various ways to be a successful researcher. Dr. Rathnayake's inputs trained me to look at any problem from a different perspective and provided valuable feedback which made me confident enough to manage the research properly.

Next, I would like to express my sincere gratitude to Prof. (Mrs.) Chamari M. Hettiarachchi of Department of Chemistry, University of Colombo, for being the chair of the progress review committee. Prof. Hettiarachchis' feedback and guidance during the progress reviews were helpful to me to improve the research. I would also like to especially thank, Analytical Chemist of Department of Chemical and Process Engineering, for her guidance and great help during my research work. My next sincere gratitude goes to Prof. S. Walpalage, Head of the Department of Chemical and Process Engineering, for his guidance and great help during my research work. Furthermore, I would like to thank my colleagues and friends who helped me in various ways.

The last, but not least, I would like to express my deepest gratitude to my father, my mother and my husband Thilina for their endless support, trust on my focus, motivation extended towards me, and care.

ABSTRACT

Agricultural waste-based biorefinery merges waste and production sectors to develop a circular economy. One such biorefinery product, 5-(hydroxymethyl) furfural (5-HMF) has gained increasing interest as a versatile platform chemical to produce chemicals and fuels, and rice straw will be an ideal feedstock to produce 5-HMF. Limited studies on the direct conversion of rice straw to 5-HMF reveal the requirement of extensive research. This MPhil research study focuses to identify the most feasible conversion process to convert rice straw into 5-HMF, and optimize the required process parameters in laboratory-scale to be used in unit processes in scaled-up implementation. As the first objective, this thesis has proposed a roadmap, elucidating the existing methods for rice straw pretreatment to convert cellulose and cellulose conversion to 5-HMF processes. Then cellulose conversion to 5-HMF was evaluated, considering catalyst used, solvent system, process temperature, and process time. Eventually, an evaluation method, based on a generalized objective function with penalty scores, was developed and used its minimum value to find the optimal process configuration at the lowest cost for large-scale 5-HMF production. However, considering the feasibility of large-scale application of these processes in Sri Lankan context, combinatory acid/ alkaline pretreatment method and mineral acid-catalyzed cellulose to 5-HMF conversion process were selected for the optimization. The final objective was experimentally optimization of the process parameters of each, using an advanced optimization technique, response surface methodology. Central composite design-based experiments were used to develop statistical models for each process. Quantitative analyses were performed, using regression techniques, analysis of variance, and residual analysis, whereas qualitative analyses were carried out via Fourier Transform Infrared Spectroscopy. The pretreatment process was carried out to maximize the outcome of rice straw biorefinery. It included two steps: (1) dilute sulphuric acid treatment at reduced temperatures to optimize hemicellulose removal, and (11) dilute sodium hydroxide treatment at reduced temperatures to optimize lignin removal. The maximum hemicellulose removal ($15.78\,\%$) was observed at optimal conditions of $0.26\,\mathrm{mol\,dm^{-3}}$ acid concentration, $98.1\,°\mathrm{C}$ reaction temperature, and 30.48 min reaction time. The maximum removal of lignin ($20.98\,\%$) was obtained at $2.55\,\mathrm{mol\,dm^{-3}}$ sodium hydroxide concentration, $80.5\,°\mathrm{C}$ reaction temperature, 106.48 min reaction time. An optimized acid- catalyzed hydrothermal process for the in-situ production of 5-HMF from rice straw extracted cellulose was obtained, using a biphasic reaction system. The maximum yield of 5-HMF was $23.51\,\%$ at optimal conditions of $0.046\,\mathrm{mol\,dm^{-3}}$ dilute hydrochloric acid concentration, $180\,°\mathrm{C}$ process temperature, and 107 min process time. Finally, validation experiments were performed, and the observed optimum results showed close agreement with the predicted, confirming rice straw biorefinery process optimization.

Keywords: Rice straw, Biorefinery, 5-(hydroxymethyl) furfural, Pretreatment, Cellulose, Catalytic conversion, Optimization, Response surface methodology

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Abbreviated Terms

CCD	Central composite design
CMF	Cellulose microfibrill
DAP	Dilute acid pretreatment
DES	Deep eutectic solvent
DOE	Design of experiments
DSAP	Dilute sulphuric acid pretreatment
HTC	Hydrothermal carbonization
LCC	Lignin-carbohydrate complex
OFAT	One factor at one time
RSM	Response surface methodology

Chemical Substances

BMIMCl	1-butyl-3-methylimidazolium chloride
DMF	2,5–dimethylfuran
DMSO	Dimethyl sulfoxide
EL	ethyl levulinate
EMF	5-ethoxymethylfuran
EmimAc	1-ethyl-3-methylimidazolium acetate
FDCA	2,5–dicarboxylic acid
GVL	γ-Valero lactone
H2SO4	Sulphuric acid
HCl	Hydrochloric acid
HMF	5-hydroxymethylfurfural
ILs	Ionic liquids
MIBK	Methyl isobutyl ketone
NaOH	Sodium hydroxide
THF	Tetrahydrofuran

Other Symbols

α_i	Relative weightage to represent the significance of i^{th} parameter to the overall process
θ_k	Process temperature of the k^{th} process
C_k	Catalysts used of the k^{th} process
E	Energy required to reach and maintain the operating temperature
$E_{1,k}$	Energy needed to heat the reaction system comprised of cellulose, solvents, and catalyst
$E_{2,k}$	Energy required to maintain the temperature for process time t_k

P_k	Process considered
RS_k	Reaction system of the k^{th} process
t_k	Process time of the k^{th} process
y_k	Yield of the k^{th} process

CHAPTER 1

INTRODUCTION

This chapter contains background (Section 1.1) of the study of optimization of rice straw to 5-hydroxymethylfurfural conversion. The aim (1.2) and the contribution of the study (Section 1.3) are then explained. Finally, a brief outline of the chapters in the thesis is presented (Section 1.4).

1.1 Background

Industrial production of broad ranging fuels and chemicals depends on fossil resources. However, the rate of diminishing fossil resources along with their devastating environmental effects, such as global climate transtitions and unacceptable ways of waste disposal issues have become raised due to the huge consumption of petro-based materials and products. Despite of these issues, the demand for petro-based fuels and chemicals has been increasing continuously, especially from developing economies since these products are bound to provide a high quality of life for all human beings. Towards this end, immediate development of new technologies for the manufacturing of alternative chemicals and fuels based on sustainable energy sources has received higher attention than ever.

In this context, 5-(hydroxymethyl)furfural (5-HMF) is identified by the US Department of Energy, as a versatile intermediate platform chemical compound to connect chemical industry and renewable biomass resources. As a fundamental molecular building block, 5-HMF is converted into a series of high quality fuels, such as 2,5–dimethylfuran (DMF), 5-ethoxymethylfuran (EMF), ethyl levulinate (EL), and γ-Valero lactone (GVL), and high value chemical compounds, including 2,5–dicarboxylic acid (FDCA), 2,5 –diformylfuran (DFF), 2,5–bis(hydroxy-methyl)furan (BHMF), Levulinic(LA) etc. Hence, 5-HMF is generally accepted by the scientific community as the main building block to bridge the gap from fossil energy-based economy to sustainable biomass based one. As a result, this has led to producing more than 10, 000 scientific articles and patents in the fields of 5-HMF synthesis and chemistry over the past decade. Nonetheless, although there are many significant amount of research work, 5-HMF industrial production is still going in minor quantities as a specialty chemical compound for research and laboratory purposes.

The limitation of current industrial production of 5-HMF is associated with not only the factors typical to lagging bio-refinery development, but also relying on edible biomasses, especially fructose. Generally, 5-HMF yield is obtained up to $99\,\%$ by using fructose as the feedstock. However, it is not an ideal feedstock due to the high price and low abundance in nature. Nonetheless, most of the studies are focused on fructose to 5-HMF conversion. However, from the viewpoint of practical applications, there are strong economic and socio issues related to the utilization of edible biomasses. As a result, they do not appear as sustainable sources at commercial scale up to this point. In contrast, lignocellulosic biomass conversion to 5-HMF is more applicable due to the higher chances of improving the economics of 5-HMF production, using less expensive raw materials. In this context, rice straw (RS) will be an ideal feedstock as one of the most highly available agricultural waste.

Despite the potential of RS, the mass-scale 5-HMF manufacture using RS is not still facile from both economic and efficiency point of view thus far. The limited studies on the direct utilization of RS signify the inefficient production rate of 5-HMF, due to the recalcitrance nature of RS itself. Various catalysts, solvents, reaction systems with high energy and cost-intensive process conditions are applied to obtain high 5-HMF yield as per to the published studies in the literature. To this end, identification of economically feasible and scalable process to achieve high 5-HMF yield is an important challenge worthy to study.

1.2 Aim of thesis

The overall objective of the thesis is to identify the most feasible RS to 5-HMF conversion method and optimize the required process parameters to improve the final yield. To this end, specific aims are:

- To investigate the current developments in RS to 5-HMF conversion processes through a comprehensive literature survey.
- To evaluate the feasibility of RS to 5-HMF conversion processes via proposing an evaluation method and select the most feasible process.
- To optimize the selected conversion process by means of process parameters and 5-HMF yield for the developement of future biorefinery in Sri Lanka.

1.3 Contribution of thesis

The first major contribution of the thesis is proposal of a roadmap for the conversion of RS to 5-HMF. The proposed roadmap is comprehensively dicussed, reviewing RS to cellulose pretreatments processes and cellulose into 5-HMF catalytic conversion processes. The review highlights advantages and disadvantages of each method for mass-scale 5-HMF production. This work is presented in Wanninayake et. al [1].

The next major contribution is, proposing a process evaluation method in terms of energy-efficient and economical perspectives to select an optimal conversion process for future investigations. The applicability of this method is shown, using defined parameter weights and process conditions, obtained from the comprehensive literature survey. This work is also presentred in Wanninayake et. al [1].

Optimization of operating parameters of dilute acid pretreatment to extract hemicellulose from RS at reduced temperatures ($< 100\,^{\circ}\mathrm{C}$) is presented as the third contribution of this thesis. The process was optimized using response surface methodology with experimental design analysis, and outcomes are presented in Wanninayake et. al [2].

Then, hemicellulose extracted RS residue was subjected to alkaline pretreatment to recover lignin at reduced temperatures ($< 100\,^{\circ}\mathrm{C}$). The process parameters of alkaline pretreatment were optimized, applying the same optimization techniques as the fourth contribution.

For the convertion of pretreated RS to 5-HMF, a catalyitc conversion process, feasible to Sri Lankan context, is selected through the proposed evaluation method and optimized its' process parameters, using response surface methodology. The outcomes are presented as the final contribution of this thesis to be used in future RS biorefinery studies.

1.4 Organization of thesis

The chapter two presents related work. As per to the first objective of this study, comprehensive literature survey is carried out to investigate the current developments in RS to 5-HMF biorefinery. Accordingly, the chapter has presented a critical assessment of the progresses in RS to cellulose pretreatment and cellulose into 5-HMF catalytic conversion processes for 5-HMF production. The third chapter is focused to find out optimal process configuration to convert RS to 5-HMF. To accomplish this goal, the chapter has introduced a process evaluation method which is based on a generalized objective function with penalty scores. The fourth chapter explains the methodology adapted to optimize the selected RS into cellulose pretreatments and cellulose into 5-HMF conversion processes. The chapter has elaborated the advanced optimization technique, response surface methodology and the experimental designs for the quantitative analysis. The fifth and sixth chapters present the methods and results of experimentally optimization of RS into cellulose pretreatments and cellulose into 5-HMF conversion processes with a comprehensive central composite design-based analysis.

The final chapter concludes the thesis with possible future work, a general discussion, and a conclusion on overall research.

CHAPTER 2

COMPREHENSIVE LITERATURE SURVEY

2.1 Introduction

Gradual depletion of fossil resources has influenced to pursue sustainable alternative sources to fulfill the increasing demand of energy requirements. Despite many green energy sources, such as solar, hydro, tidal, and wind, the existence of chemical and fuel manufacture depends on biomass, which is the only green fixed, organic carbon reservoir on earth. In this context, biomass-based chemical manufacturing has gained rising interest during past decade and led to intensified research [4–7].

One such biomass derived 5-hydroxymethylfurfural (5-HMF) acts as a versatle platform chemical to produce broad range of value added fuels and chemicals [8]. Chemical structure of 5-HMF comprises aldehyde and alcohol gruops, as shown in Fig. 2.1. This has made 5-HMF to being simultaneously as an aromatic aldehyde, furan ring system, and aromatic alcohol [9]. Wang et al. [10] has reported several molecular attributes of 5-HMF for the sysnthesis of various chemicals and fuels. As a bifunctional molecule, 5-HMF has substituents in both 5 and 2 positions. Therefore, being a quite unsaturated chemical compound, 5-HMF can be subjected to hydrogenation to produce fuels. To synthesize various polymers, 5-HMF can be oxidized into diols and dicarboxylic acids due to its both aldehyde and alcohol functionalities. In addition, the heterocyclic structure of 5-HMF is also important in producing various biologically active molecules for pharmaceutical applications [10].

These uniquie properties makes 5-HMF as a fundamental molecular building block to produce a series of high-quality fuels, such as 2,5 – dimethylfuran (DMF), 5-ethoxymethylfuran (EMF), ethyl – levulinate (EL), and gamma – valerolactone (gvl), and high value platform chemicals, including 2,5 – dicarboxylic acid (FDCA), levulinic acid (LA), 2,5 – diformylfuran (DFF), 2,5 – bis(hydroxy-methyl)furan (BHMF) as depicted in Fig. 2.2. 5-HMF derived DMF posseses high energy density ($31.5\,\mathrm{MJ\,L^{-1}}$), and the value fairly similars to diesel ($36.9\,\mathrm{MJ\,L^{-1}}$) and gasoline ($34.6\,\mathrm{MJ\,L^{-1}}$). Unlike bioethanol, DMF is immiscible with water and also shows less volatility than

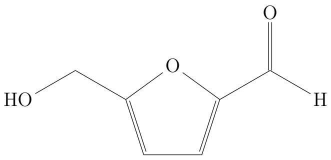


Fig. 2.1: 5-HMF chemical structure [3]

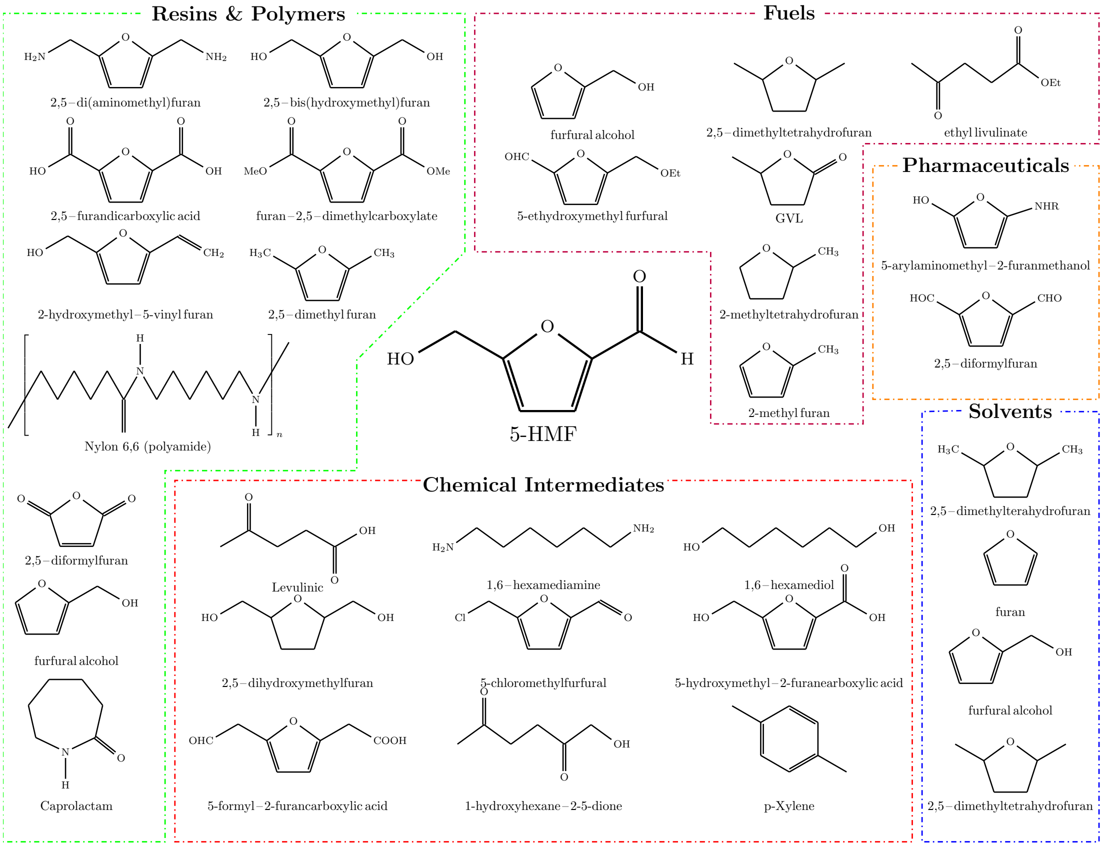


Fig. 2.2: 5-HMF derived value added chemicals, and fuels

ethanol (boiling point 351 K). Therefore, DMF is comparatively suitable to use as an optional biofuel in transportation sector [11, 12], as shown in Table 2.1. 5-HMF derived another valuable platform chemical LA can be used in fuel and chemical production, such as acrylic acid, 2-butanone, and diphenolic acid [13]. FDCA, another high value platform chemical that can be derived from 5-HMF is used as an alternative to terephthalic acid to produce polyethylene−furanoate (PEF) [5, 14]. 5-Arylaminomethyl-2-furanmethanol (AAMFM) which is also derived from 5-HMF is utilized as a natural photosensitizer precursor in photodynamic therapy in cancer treatments. As a viscosity controlling agent, 5-HMF derived 1,2,6−Hexanetriol is utilized in both cosmetics and drugs production, and it is also used as a humidity regulator. Moreover, 5-HMF is regarded as an antisickling agent, and without inhibition of plasma proteins and tissue, it shows the ability to bind intracellular sickle hemoglobin [15].

5-HMF is generally accepted by the scientific community as a main building block to bridge the gap from fossil energy-based economy to sustainable biomass-based one. As a result, this has led to producing more than 10, 000 scientific articles and patents in the field of 5-HMF synthesis and chemistry over the past 10 years. Eventhough, de-

TABLE 2.1: Fuels property comparison with DMF

Fuel property	Unit	Diesel oil	Biodiesel	Bioethanol	DMF
Cetane number	-	52	51	6	9
Lower heating value	MJ/Kg	42.5	37.5	28.4	33.7
Density	Kg/m^3	840	871	786	890
Latent heat of evaporation	KJ/Kg	250 - 290	300	840	320
Boiling point	C	210 - 235	300 350	79	92 - 94
Flash point	C	52 - 96	120 - 170	12	-1

spite the enormous research work, 5-HMF industrial scale production is still low, and its lower production is utilized as a special compound in research and laboratory work [16, 17]. This limitation is associated with relying on edible biomass feedstock, especially fructose. In general, 5-HMF can be synthesized via acid-catalyzed dehydration of C6 carbohydrates, including fructose, glucose, cellulose, starch, and lignocellulosic biomasses. Among these, fructose is the most appropriate model biomass feedstock to produce 5-HMF. Its' simple and regular molecular structure makes easier the catalytic conversion mechanism than other biomass feedstocks [18]. As a result, to date, most of ongoing research work are concentrated around fructose to 5-HMF conversion. There is a critical concern regarding the sustainability of 5-HMF production using fructose, which relies on corn and sugar crops. Using these crops for chemical production usually leads to consequences like food scarcity due to its competition with food production. Even if, fructose produces significant yield of 5-HMF at laboratory scale, the results for the same processes at mass scale manufacture are impractical due to high price of the feedstock.

Torres and his co-workers analyzed 5-HMF continuous production using fructose as the feedstock. Using a formulated optimization problem, they found the optimum operating conditions for the cost reduction. They obtained a minimum cost of production for 5-HMF which was higher than the cost of oil derived p-xylene, a compound that 5-HMF could theoretically replace. The dominant factor to increase cost of production of 5-HMF was the cost of fructose as the price of one mole of fructose was almost the same as that of p-xylene. Dumesic and coworkers performed a techno-economic study for the mass-scale fructose into 5-HMF conversion. 5-HMF minimum selling price was estimated, and they revealed that ratio of fructose into 5-HMF conversion was a significant parameter affecting its economy. In 2018, Carvalho et al. also studied fructose conversion to 5-HMF at mass scale. According to their sensitivity analysis the most significant factor affecting to 5-HMF price was process selectivity which was depended on solvent, catalyst, temperature and time. In addition to selectivity, fructose price was the second most important factor affecting 5-HMF price. Hence, all these studies emphasizes the importance of using a non edible, low cost feedstock instead of fructose is crucial to lower the 5-HMF production cost and thereby to promote its large scale manufacture.

As a viable solution, lignocellulosic biomass into 5-HMF direction conversion is highly demanded and more applicable due the utilization of low-cost materials improves the 5-HMF production process economics. In this context, RS will be an ideal feedstock as an abundant agricultural waste around world. Since, agricultural and forest residues represent as a highly available carbon-neutral regenerative material in green chemical/ fuel manufacture, RS has gained enormous attraction as a potential feedstock for industrial-scale bio-refinery processes [19–23]. Despite this potential, RS is not attractive from both efficiency and economic point of views thus far. Limited studies on the direct utilization of RS further signify the inefficient production rate of 5-HMF, due to the recalcitrance nature of it [23]. Various catalysts, solvents, reaction systems with high energy and cost-intensive process conditions have being applied to increase the 5-HMF yield. For this reason, an evaluation of existing processes from economic and energy efficiency perspective and selecting the best catalytic conversion processes are required and studies in this direction are still scarce.

2.2 Rice straw as sustainable feedstock

Among grain crops, the third most cultivated crop is rice apart from corn and wheat [24]. Approximately 780 million tonnes of rice production was generated in 2018 as per to the FAO statistics [25]. Generally, rice grain one kilogram harvested generates 1.0 to 1.5 kg of RS [20, 24], and hence approximated annual RS production is 1,170 million tonnes [26]. As shown in Table 2.2, Asia is the largest RS producer 90 % followed by the Americas(5 %), Africa (3 %), and Europe (1 %).

In general, RS major proportion is used as cattle feed and the rest as waste. The utilization of RS is not facile because of its inherent characteristics, such as its slow decomposition rate in the soil and harboring of several plant diseases. Therefore, field burning of RS has been popularized among farmers as a common practice. However, open field burning of RS leads to air pollution and consequently affects public health [20, 24]. Utilizing agro-industrial residues for energy applications has gained increas-

TABLE 2.2: Estimated 2018 global rice grain and straw production [26]

Area	**Rice Production** ($\times 10^6$ t)	**Rice Straw Production** ($\times 10^6$ t)
Asia	705.393	1058.089
Africa	33.174	49.761
Americas	38.763	58.145
Europe	4.023	6.035
Oceania	0.646	0.969

ing interest [20], thus for industrial-scale 5-HMF production, RS is deserved as an ideal feedstock.

Moreover, RS will be a promising alternative bio-resource, not only because of its abundant availability, but also its attractive composition. Generally, RS is mainly comprised of cellulose $42.19\,\% \pm 2.78$, lignin $20.83\,\% \pm 3.77$, and hemicellulose $24.26\,\% \pm 5.39$ on dry weight basis [21]. RS cellulose hydrolysis into sugars can be done for the production of 5-HMF due to the similarity between organic fraction of RS ($C_6H_{9.63}O_{4.57}N_{0.11}S_{0.02}$) and cellulose monomer ($C_6H_{10}O_5$), and hence identified as an ideal bio-resource to manufacture valuable chemicals and fuels for future requirements [24].

2.3 Limitations in rice straw direct utilization

RS can be theoritically hydrolysed into monomeric sugars for the ultimate conversion of 5-HMF. However, in reality the decomposition of RS is identified as an extremely slow process and a challenging task. This is mainly due to the plant cell wall complex architecture and molecular structure, which is called as recalcitrance nature. RS recalcitrance nature has evolved as a superior mechanism to prevent chemical or biological attacks on its structural sugars [27–29].

Cellulose, the main component of RS is a homopolymer of D–glucopyranose moieties, linked via β-(1,4) glycosidic bonds, and thus exists as linear chains [27]. Unlike other glucan polymers, the repeating unit of cellulose is cellobiose, a disaccharide unit of two glucose molecules. The degree of polymerization of cellulose can be ranged upto 10,000 to 15,000 of glycopyranose units. These linear cellulose chains are arranged as cellulose microfibrills (CMFs), in which 36 cellulose chains are compacted. These CMFs are laid separately in the swollen gel of hemicelluloses creating a nanoscale network to strengthen the plant cell wall. Cellulose is stabilized in its ultrastructure due to the presence of large-scale intermolecular and intramolecular hydrogen bonding network also with the Van der Waals forces [30, 31]. Crystallinity and paracrystallinity (amorphous) in cellulose is determined by hydrogen bonding. These crystalline and amorphous regions of cellulose are surrounded by hemicelluloses and finally associated with lignin to form lignin-carbohydrate complex (LCC) in RS [32, 33].

The next main component of RS is hemicellulose. Unlike cellulose, hemicelluloses is not chemically homogeneous and shows a random and amorphous structure. Different categories in heteropolymers including mainly xylan, xyloglucan, glucuronoxylan, arabinoxylan, glucomannan, and galactomannan are present in hemicellulose [5]. Heteropolymers are composed of different sugars such as hexoses (mannose, galactose, and glucose) and pentoses (arabinose, xylose) along with uronic acids (glucuronic and galacturonic acids). RS hemicellulose main constituent is xylan, and it is a heteropolymer of xylopyranose units with combination of ferulic and acetic acids [28]. Acting as strings, hemicellulose binds cellulose linear chains into CMFs, and then cross-links with lignin, forming a complex network [34].

The third most abundant polymer in RS is lignin, a three-dimentional polymer with non-repetitive order of different components and irregular linkages among them. The structure of lignin is formed by three types of phenylpropane building blocks, such as (ρ-coumaryl, sinapyl, and coniferyl) and the derivatives via oxidative coupling. Strucutre of lignin has become more complicated due to the existence of various linkages, including (β-β, β-5, β-1, 4-O−5, 5-5, β-O−4, and α-O−4) [33, 35]. Lignin connects with hemicellulose chains in the cellulose-hemicellulose matrix, and then functions as cellular glue to build lignin-carboh- ydrate complex in RS. Moreover, silica present in RS also influeces to more rigidify RS tissues [27–29]. Hence, this whole structure has provided comprehensive strength to RS to stiffen further and making the entire structure resistant to chemical or biological attacks [36, 37], eventually making RS direct conversion to 5-HMF more complicated [23].

2.4 Roadmap for convertin of rice straw into 5-HMF

Thermochemical processes to produce value added fuel and chemicals using biomass feedstocks include hydrolysis/alcoholysis, pyrolysis, gasification, carbonization, and hydrothermal liquefaction. From these processes, hydrothermal carbonization (HTC) and acid catalyzed hydrolysis are mainly used as conversion technologies for biomass to 5-HMF. In the conventional HTC process, biomass undergoes hydrolysis, dehydration, decarboxylation, and decarbonylation reactions: ultimately converting it into a carbon-densified product called hydrochar. A modified HTC process allows extracting 5-HMF, after dehydration of biomass prior to polymerization step into hydrochar. In spite of this process yields 5-HMF at high purity levels, it is not highly scalable and cost efficient at industrial scale, due to the dependence on edible biomass, fructose. Contradictory, acid-catalyzed hydrolysis processes which are generally conducted at a relatively mild temperature 100 to $250\,^{\circ}\mathrm{C}$ allow the conversion of both edible and non-edible lignocellulosic biomass to 5-HMF.

Since a precise method to convert RS to 5-HMF is almost non-existent, this study has proposed a roadmap as shown in Fig. 2.3. According to this proposed roadmap, RS to 5-HMF conversion is identified as a two step process. The first step is RS pretreatment, and the second step is cellulose catalytic conversion into 5-HMF.

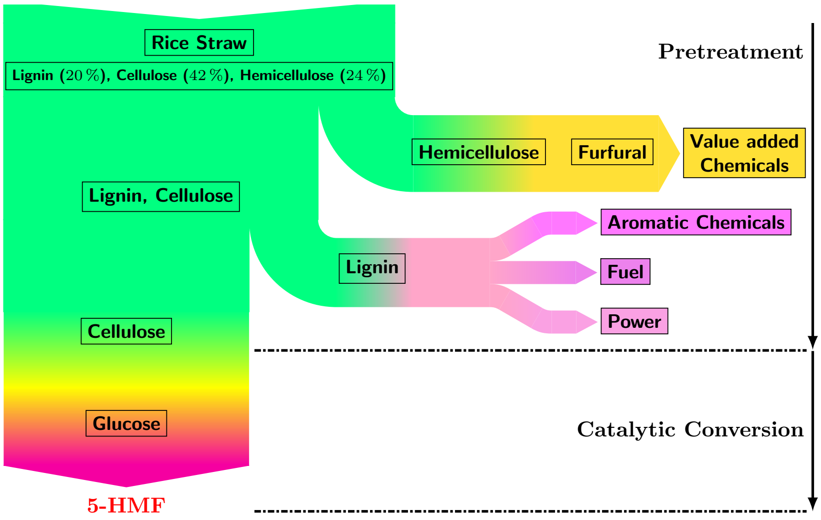


Fig. 2.3: Roadmap for conversion of rice straw to 5-HMF

Here, acid-catalyzed hydrolysis processes are mainly used as conversion technologies for biomass to 5-HMF [23]. However, pretreatment step preceding to the catalytic conversion is needed [38, 39] to break down the RS recalcitrace structure [35, 38]. Pretreatment methods alter the interactions among cellulose, hemicellulose, and lignin present in RS and eventually disrupting the lignin-carbohydrate structure. A compatible pretreatment method helpful in reducing cellulose crystallinity in order to improve its monomeric sugar availability for subsequent processes [40]. Moreover, pretreatment of RS not only directs 5-HMF production, but also helpful in recovering other valuable components, such as hemicellulose and lignin present in RS. Hemicellulose can be utilized for the production of another value added chemical furfural from RS other than 5-HMF. Furfural has being used in wide applications, including transportation fuel, agrochemical industries, pharmaceuticals, and plastic production [41–44]. On the other hand, lignin recovered from pretreatment can be used to produce liquid transportation fuels, such as cyclohexanol, cyclohexane, and cyclohexanone. And also, as a versatile biogenic polymer, lignin can be used to generate aromatic chemicals, including toluene, phenol, and benzene [45–47].

At the second step, cellulose recovered from RS pretreatment can be converted to 5-HMF by applying acid catalysts and reaction systems [12, 48]. However, 5-HMF rehydration into levulinic acid and repolymerization into humins like unwanted side reactions can be occured in acid-catalyzed reaction system. Hence, it is required to select an appropriate acid-catalyzed reaction system for future applications [49].

Amiri and co-workers studied the conversion of RS into 5-HMF [50]. Ball milled RS (size distribution between 295 to 833 µm) was subjected to hydrolysis using dilute sulfuric acid solution as the catalyst at high temperatures 120 to 180 °C, employing both biphasic and monophasic systems. Aqueous monophasic system, consisting of $0.5\,\%$ sulfuric acid solution yielded, 5-HMF $15.3\,\mathrm{g}$ from RS $1\,\mathrm{kg}$ at $180\,^{\circ}\mathrm{C}$ within 3 hours. Methyl isobutyl ketone (MIBK), 1-BuOH, 2-PrOH, acetone at $180\,^{\circ}\mathrm{C}$ for 3 hour and tetrahydrofuran (THF) at $150\,^{\circ}\mathrm{C}$ for 5 hour were examined as the extracting solvents in biphasic systems. Application of extracting solvents immensely influenced to obtain improved 5-HMF yield compared to single aqueous phase system. A significant 5-HMF yield, more than $59\,\mathrm{g}$ for $1\,\mathrm{kg}$ of RS, was resulted in the system consisting either 1-BuOH or 2-PrOH.

Nguyen et al. studied RS to 5-HMF efficient production process, using combinational diluted acid/base assisted pretreatment and following a subsequent catalytic conversion process [23]. $CrCl_3 \cdot 6\,H_2O$, $CrCl_2$, amberlyst$_{15}$, $H_3PW_{12}O_{40}$, and H_3BO_3 were applied as the catalysts and dimethyl sulfoxide (DMSO), EMIMCl, and 1-butyl-3-methylimidazolium chloride (BMIMCl) were used as the solvents. Significant yield of 5-HMF, $76\,\%$ was obtained from alkali pretreated RS with using $CrCl_3 \cdot 6\,H_2O$ as the catalyst and (BMIM)Cl as the solvent for 6 hours at $120\,^{\circ}\mathrm{C}$. Marginally reduced 5-HMF yield $67\,\%$ was generated through acid pretreated RS with the same catalytic system.

Zhang et al. investigated on a one step conversion process for lignocellulosic biomass into biofuel and platform chemicals [51]. They demonstrated RS to 5-HMF conversion in ionic liquid, C_4mimCl as solvent and $CrCl_3$ as the catalyst under microwave irradiation and yield $47\,\%$ of 5-HMF within 3 minutes. The authors stated that this process was rapid and did not require an additional pretreatment step of biomass, hence facilitated cost effective one pot transformation of RS to 5-HMF. Feng et al. studied a green pathway to convert RS into 5-HMF [52]. They developed green, sustainable betaine-based catalysts. Direct dehydration of glucose to 5-HMF was improved with the application of combined BX catalyst with metal chlorides, such as $CuCl_2 \cdot 2\,H_2O$, $FeCl_3 \cdot 6\,H_2O$, $MgCl_2 \cdot H_2O$, $SnCl_4 \cdot 5\,H_2O$, $AlCl_3 \cdot 6\,H_2O$. Satisfactory 5-HMF yield, $51\,\%$ was obtained from RS in water-MIBK classic biphasic reaction system within 30 minutes at $180\,^{\circ}\mathrm{C}$.

2.5 Rice straw pretreatment methods

Numerous pretreatment techniques to decompose RS for the production of chemicals and fuels have been studied in past decade [53, 54]. The highly studied pretreatment methods are physical, chemical, physico-chemical, and combinations of them [55]. However, these methods have been shown both advantages and disadvantages in practical conditions [56–58].

2.5.1 Physical pretreatments

Physical pretreatment refers to a process of mechanical fragmentation of RS structure. An ideal physical pretreatment method decreases crystallinity of cellulose and degree of polymerization then, allows continues heat and mass transfer at following process conditions [24, 35, 59]. Therefore, it is a prerequisite step for further RS processing. Mechanical crushing, microwave radiation, and ultrasonic treatment are the highly used physical pretreatment methods for RS decomposition [12, 13]. These methods cause less environmental pollution. Typically, physical techniques appear simple, they require high energy and power, thus increasing the total cost of the pretreatment process [40].

2.5.1.1 Mechanical Crushing Techniques

Mechanical crushing is the most conventional RS pretreatment method [38], which includes grinding, chipping, and milling techniques [40]. These techniques allow decreasing the cellulose crystallinity to improve the hydrolysis efficiency in the following reaction process. Biomass particle size is reduced up to 10 to $30\,\mathrm{mm}$ by applying chipping methods, whereas milling and grinding methods contribute to reduce up to $0.2\,\mathrm{mm}$ [60]. As a most investigated milling method, ball milling is effective in decreasing cellulose crystallinity through hydrogen bonding network splitting and exposing $\beta - 1$, 4-glycosidic bonds in cellulose [61–63]. Compared to ball milling, energy-saving wet disk milling is useful in RS pretreatment [38]. Hideno et al. studied the effects of wet disk milling and ball milling to pretreat RS. At the optimal condition of 60 min milling, $89.4\,\%$ and $78.5\,\%$ of glucose yield were obtained from balling milling and wet disk milling, respectively. Ball milling was found to be a better pretreatment method than wet disk milling as per to the comparative analysis on milling treatments of baggase and straw [64]. Moreover, compared to ball milling, more effective resluts are obtained from planetary and attrition milling [65]. However, combination of milling methods with chemical treatments, such as acidic or alkaline, has provided better results [38, 66]. Qu et al. has reported $86.14\,\%$ of lignin and $93.76\,\%$ of hemicellulose removal in RS, applying combined less severity NaOH treatment with ball milling [67]. Qi et al. investigated on weak-acid carbon catalysts added ball milling pretreatment for RS and reported improved hydrolysis of hemicellulose [66]. However, mechanical crushing methods require high energy supply. Therefore, these methods are regarded as not economical at industrial applications [40].

2.5.1.2 Ultrasound Radiation Treatment

Ultrasound treatment is a relatively new technique used in RS pretreatment. Here, ultrasound waves alter the physical and chemical morphology of RS structure. This occurs through the formation of small cavitation bubbles [38, 68]in the RS LCC, and then rupturing it to increase cellulose accessible parts [69, 70]. Generally, the effectiveness and efficiency of this method are decided by duration, freuency, solvent, and reactor used [71]. However, biomass characteristics also influence the this treatment [71]. Delignification and sugar release from RS is highly determined by the duration of this method [72]. Degradation of cellulose crystallinity requires the range of 10 to 100 kHz ultrasound frequency [73]. The heat energy dissipated from this treatment is useful to break cellulose crystallintiy [74]. However, high power in ultrasound adversely influences on pretreatment. Generally, high power generates bubbles near the tip of ultrasound transducer and thereby blocks energy transferring to the medium [73]. Also, it was found that to disintegrate biomass particles spatial arrangement, the energy of ultrasound vibration is not sufficient. Therefore, a compatible chemical method combined ultrasound treatment is considered as effective [12]. For instance, high amount of cellulose and lignin were generated by applying alkali added ultrasound treatment, and even at 230 °C, the both seperated components had shown high thermal stability [75]. When using NaOH as the alkali in combined treatment, NaOH has the ability to selectively remove lignin and hemicellulose present in RS without degrading cellulose and mainly because of NaOH influence to improve the surface area and porosity [74]. However, this method generates high cost at large-scale operations, and therefore it is still limited to laboratory-scale investigations [13].

2.5.1.3 Microwave Treatment

Microwave treatment is regarded as an effective green technology for RS pretreatment due to certain factors, including (1) degradation of crystallitniy of cellulose (2) easy operation (3) low energy requirement, and (4) high heating capacity at minimum duration of time [38, 76–79]. Since, the conventional acid or alkali pretreatment under high temperature and pressure, demands high energies, combining them with microwave treatment is preferred [80, 80–82]. Binod and co-workers studied the influence of microwave-alkali, microwave-alkali-acid, and microwave-acid pretreatment methods for baggase degredation, and revealed that sugar yield was improved by microwave-acid-alkali pretreatment while significant lignin removal was observed in microwave-alkali method [81]. Microwave-alkali pretreatment on switch grass has generated sugar yield approximately 70 to 90 %. As the most effective alkali, sodium hydroxide is common in microwave treatment on switch grass and coastal bermuda grass. Microwave-assisted ionic liquid pretreatment is investigated by Sorn et al., and they revealed that this combined method has improved delignification of RS [83]. However, this method must be performed at high temperatures (<160 °C) as almost no effect can be observed at temperature below 100 °C. Though, microwave irradiation is used as a successful method in biomass treatment, its application in mass-scale production is limited still due to high cost at equipment investment [12, 40].

2.5.2 Physico-chemical pretreatments

As physico-chemical methods, liquid hot water and steam explosion are commonly used in RS pretreatment [84–86].

2.5.2.1 Steam Explosion

As a thermo-chemical-mechano treatment, steam explosion is highly applicable to RS decomposition. In this method, 0.69 to $4.83\,\mathrm{MPa}$ pressurized saturated steam is employed to treat RS at 160 to $260\,°\mathrm{C}$ temperatures for few minutes. Then, through a rapid pressure reduction, RS is explosively decompressed [87, 88]. Compared to alkali/acid/ionic liquid treatments, this method does not require external catalysts, and thus relatively low cost [89]. In this method, RS pretreatment is occured through autohydrolysis, and the efficiency of the process is determined by the applied temperature, pressure, and steaming time. During steaming, a mild acidic condition is generated and this is helpful in hydrolyzing the α-ether linkages in lignin and β-1,4 – glycosidic bonds in hemicellulose. However, low cellulose yield can be generated at extreme streaming conditions due to the degradation of amorphous cellulose to some degree [88, 90]. A steam explosion system at pilot-scale for RS pretreatment generated cellulose-rich residue by employing high-pressure steam approximately 10 to $15\,\mathrm{bar}$ at 180 to $200\,°\mathrm{C}$ for 5 to $10\,\mathrm{min}$. Cellulose content of 53.7 to $63.0\,\%$ (w/w, on a dry basis) was observed when analyzing the steam exploded RS [91]. Steam explosion combined acid pretreatment has the ability to improve the dissolution of hemicellulose, compared to water-assisted steam explosion [92]. For instance, a recent study has compared both conventional water-assisted steam explosion and acid impregnated steam explosion, and revealed that hemicellulose dissoulution has being increased by, exploying acid impregnated steam explosion at $200\,°\mathrm{C}$. Further higher glucan conversion ($89.6\,\%$) was observed in acid impregnated steam explosion, compared to water-assisted steam explosion ($74.8\,\%$). More importantly, these results were achieved, subjecting $10\,\mathrm{mm}$ particle size RS for pretreatment. Hence it can be conluded that high energy demand for RS grinding and the high cost generated in large-scale processing can be reduced by applying acid-catalyzed steam explosion method [93]. Although hemicellulose dissolution is high when applying steam explosion treaments, studies has revealed that lignin removal is poor. To overcome poor lignin solubility, steam explosion method can be combined with orgainc solvents treatments, because organic solvents, including organic acids, alcohols, and ketones have shown high lignin dissolution at 100 to $220\,°\mathrm{C}$ temperatures. Matsakas et al. investigated on a novel steam explosion combined organic solvent treatment using ethanol. Improved lignin solubility was observed in their study, and they obtained high yield of cellulose for their next processing steps [94].

2.5.2.2 Liquid hot water pretreatment

As a green technique, liquid hot water pretreatment is highly used in RS decomposition. Compare to steam explosion method, liquid hot water treatment does not need rapid decompression of RS [95–97]. Generally, high temperatures 150 to $260\,^{\circ}\mathrm{C}$ [13, 98], and pressures higher than $5\,\mathrm{MPa}$ are required by this method to maintain liquid state of water [85]. However, the pretreatment effectiveness of liquid hot water treatment is determined by operating temperatures [99]. This is mainly due to the generation of hydrogen and hydroxide ions at high temperatures for the splitting of linkages among cellulose, lignin, and hemicellulose [12, 100]. In the study from Syaftika et al., they reported high glucose yield by applying high pretreatment temperatures, and at $180\,^{\circ}\mathrm{C}$, the highest glucose yield was observed [101]. In addition to high yield of glucose, elevated temperatures in liquid hot water pretreatment provide several other advantages, including no use/handling/ recovery of catalysts [13]. However, Alvira et al. have reported that although this method is capable to remove more than $80\,\%$ of hemicellulose present in RS, delignification is not occured completely due to partially depolymerized lignin has the tendency to recondensation [84]. To support lignin removal from RS, Sato et al. investigated on alkaline addition in liquid hot water pretreatment, and they reported efficient removal of both hemicellulsoe and lignin at the presence of NaOH [97]. Therefore, to improve liquid hot water treatment economics, it is required alkali addition to the method.

2.5.3 Chemical pretreatments

Chemical pretreatment methods are promising dissolve hemicellulose, remove lignin, and reduce cellulose crystallinity of RS [102]. The most widely studied RS chemical pretreatment methods are alkali, acidic, and ionic liquid treatments [12, 23, 38, 40, 103, 104].

2.5.3.1 Acidic pretreatment

Application of acidic treatments methods to pretreat RS has received increasing interest during past years. Compared to the application of concentrated acidic treatment, dilute acidic treatments are highly used for RS pretreatment. This is mainly due to requirement of high maintenance and operational facilities for concentrated acidic methods. The most commonly used dilute acids in this method include sulfuric, nitric, hydrochloric, and phosphoric [105]. Usually, $10\,\%$ or less acid concentrations at $>$ $180\,^{\circ}\mathrm{C}$ temperatures for short reaction times are used in this method [104]. In these conditions, acids generate hydronium ions to split β-1,4 – glycosidic linkages in both hemicellulose and cellulose. This is important to cleave the long hemicellulose and cellulose chains into their respective sugar monomers [90]. After the acidic pretreatment, digestible cellulose can be obtained as the pretreated RS residue and dissoloved hemicellulose as the liquid fraction [106]. Acid soluble lignin present in RS can be easily removed by applying dilute acidic treatments, and this is occured through the cleavage of ester bonds in LCC at elevated temperatures [107]. Kim et al. investigated the application of dilute sulfuric acid pretreatment for maximum recovery of hemicellulose from RS, and after optimization of treatment, they reported the optimal conditions as $1.2\,\%$ sulfuric concentration, $110\,°\mathrm{C}$ temperature, and $14.02\,\mathrm{min}$ reaction time for hemicellulose recovery [108]. A study on pilot-scale application of acidic pretreatment have provided $0.35\,\mathrm{wt\%}$ acid concentration, $162\,°\mathrm{C}$ temperature, and 10 minutes reaction time as the optimal process conditions [106]. However, after the acidic pretreatment, relatively higher quantity of acid-insoluble lignin can be present in pretreated RS, compared to untreated RS due to pseudolignin formation [109, 110]. This can be minimized by combining acidic pretreatments with alkali methods. For instance, Kim et al. investigated on ammonia treatment after the sulfuric acid pretreatment of RS, and the results showed that increased removal lignin from RS. And also, they obtained high quality cellulose redisue, which had the same crystallinity index of α cellulose [65]. Therefore, more investigations on combined acidic and alkaline treatment methods are required to develop efficient treatment techniques for industrial-scale applications [13]. However, the main disadvantages related to these methods are toxicity and corrosiveness to equipments. Therefore, application of acid corrosive-resistant equipments are required in these treatments.

2.5.3.2 Alkalic pretreatment

Alkali pretreatments show strong effects to dissolve lignin present in RS. Commonly used alkalic catalysts are NaOH, NH_4OH, KOH, and $Ca(OH)_2$. Among these alkalic catalysts, NaOH is the most used for RS pretreatment. Alkali solutions generate hydroxyl ions to saponify intermolecular ester linkages between lignin and hemicellulose, dissolving both components in RS pretreated slurry. Lignin and hemicellulose dissolution impacts gradually to expose crystalline cellulose, and assists to take place cellulose swelling via reducing its degree of polymerization and crystallinity [104]. Moreover, the hydroxyl ions present in alkali solutions helpful to increase the rate of glucose isomerization into fructose. This is helpful to improve the fructose yield which is required as intermediate step in 5-HMF production [111, 112]. Nguyen et al. studied 5-HMF production from NaOH pretreated RS, and obtained higher 5-HMF yield ($76\,\%$), compared to untreated RS [23]. Therefore, alkali pretreatment step is regarded as a more effective treatment method to remove both lignin and hemicellulose, and to expose cellulose for subsequent 5-HMF formation. However, alkali treatment methods generates high volume of waste water. This is mainly due to the requirement of considerable washing of pretreated RS residue to avoid neutralization reaction in following acid-catalyzed 5-HMF production process. Therefore, handling such huge volume of waste water has become challenging at large-scale applications [38, 104]. Further the recovery and recyclability of alkali catalysts are required to investigate. Considering these issues, Zhang et al. studied to develop a novel recyclable alkali for RS pretreatment by using less volume of water and adding an organic solvent, 2-phenoxyethanol. They revealed that NaOH pretreatment was compatible with the application of 2-phenoxyethanol, and the system showed improved delignification, using $6\,\mathrm{mL}$ of less water consumption for one gram of RS [113]. Moreover, urea added low concentrated NaOH pretreatment for RS showed high delignification at $-10\,^{\circ}\mathrm{C}$ temperatures [114, 115]. Mishra et al. investigated on complete removal of hemicelllulose and lignin from RS by applying organic acids, such as formic and acetic acids with alkaline pretreatments [116]. However, alkali treatment methods are well studied in the literature, it is still required to investigate on environmentally friendly and commercially feasible combined alkaline methods to avoid their regular drawbacks.

2.5.3.3 Ionic liquids (ILs) pretreatment

ILs are considered as effective and environmentally friendly solvents that can be applied in RS pretreatment [117]. Generally, ILs are salts which have low melting points. ILs generate high polarity system, consisting anions and cations. Therefore, these solvents have being using in RS pretreatment [118, 119]. Among these, ILs based on imidazolium, such as 1-butyl-3-methylimidazolium acetate ([BMIM][Ac]) and 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) are regarded as effective for RS pretreatment [120, 121]. Several advantages, such as low sugar degradation, high recyclability, and less toxicity, compared to alkali and acidic treatments have made ILs popularized in RS pretreatment [118, 119]. However cetain disadvantages, including low thermal stability and high cost have limited ILs application in commercial-scale pretreatment processes [120–123]. As a solution for these issues, synthesis of morpholinium-based ILs as a new solvent type for RS pretreatment has being investigated. These novel morpholinium-based ILs are less toxic and less expensive, compared to conventional ILs, and also they have being shown higher efficiency for the decomposition of RS [124]. Mohammadi et al. also studied on morpholinium-based ILs, and they reported higher cellulose crystallinity reduction, using 1-H-3-methylmorpholinium chloride ([HMMorph][Cl]) at mild reaction conditions [125]. Triethylammonium hydrogen sulfate [TEA][HSO_4], a inexpensive protic IL, has shown excellent removal of lignin ($82\,\%$) from RS via splitting β-O–4' aryl ether bonds present in lignin [126]. Suwannabun et al. studied on reducing the high cost associated with ILs, and they reported that addition of inorganic salts, such as KCl, NaCl, KNO_3, $NaNO_3$, $Mg(NO_3)_2$, and $MgCl_2$ has high impact to reduce the overall cost of the ILs usage. Also they revealed, combination of $71.856\,\%$ of EMIM-AC with $0.9\,\%$ of NaCl in $9\,\%$ of water was highly effective at RS pretreatment [127]. This is mainly due to the reduction of ILs viscosity by adding water, and hence facilitating to pretreat higher RS loading [128]. Here, water tolerance of ILs was highly improved by the addition of inorganic salts [129].

Combinations of ILs pretreatment with physical treatments, such as microwave irratdiation and ultrasound technique, have reported higher efficiency for RS [130]. In comparison with conventional heating, EMIM-AC pretreatment combined with microwave irradiation has shown higher effectiveness [131]. [BMIM]Cl added microwave pretreatment has shown higher efficiency to reduce to cellulose crystallinity, and it was also capable at removing $57.02\,\%$ of lignin present in RS [83]. A study on IL-hydrochloric-ultrasound pretreatment for RS has increased the degradation RS [132]. Generally, ILs pretreatment is partially effcient to remove lignin and hemicellulose of RS, compared to alkalic treatments [133]. As a solution, hemicellulose recovery can be enhanced by acidification of ILs pretreatment [128]. Also, addition of surfactants, such as biosurfactant, anionic-, nonionic-, and cationic- to the ILs pretreatment has shown higher delignification rate [133]. Further, alkali peroxide added ILs pretreatment has provided higher lignin removal, SI63.8% under mild conditions [134]. Hence, more studies to develop effective and low-cost ILs pretreatment methods for RS are required in mass-scale application.

As a summary, RS pretreatment methods are discussed and reported as independent approaches of chemical, physico-chemical, and physical methods. Among the chemical treatment methods dilute alkaline and dilute acid are in common use to generate pure cellulose to produce 5-HMF [23]. However, in this section, pretreatment methods targeted bioethanol and other biomass produce are not highly reviewed [135–137]. There is a growing interest for combinatory pretreatment methods to improve the process [67, 75, 83, 93, 116, 138]. Combinatory pretreatment methods reduce the disadvantages of their individual applications and provide the benefits of each [94]. Combinatory treatments like physical-alkaline [74], physical-acid [66], hydrothermal-acid [92, 94], acid-alkaline [65, 138], physical-ILs [131, 132], and hydrothermal-alkaline [97] were capable in removing RS lignin and hemicellulose, and reducing in cellulose crystallinity. From these work related to physical-alkaline [67, 75, 81], acid-alkaline [116, 138], and physical-acid [66, 93] are highlighted as common combinatory pretreatments. Suitable pretreatment method selection to develop combinatory methods depend low energy demand, easy recovery of hemicellulose, cellulose, and lignin, cost effectiveness of acid/ alkaline catalysts, and environmental friendliness as well [103].

Corrosive alkali/acid catalysts usage can be reduced by applying eco-friendly organic solvents [113] and ILs [120, 125, 126]. Eventhough, the feasibility of using these solvents at large-scale is still limited due to the high cost related to them [120–123]. Therefore, to replace high cost ILs, future studies are needed for the investigation of cost-effective choline-based ILs [103], morpholinium-based ILs [125], and choline chloride like deep eutectic solvents [139]. Moreover, using cost effective alkali/ acid catalysts with hydrothermal and physical pretreatment methods and optimization those processes can reduce the energy consumption and reaction time of them. Response surface methodology like advanced optimization technique can be used to investigate the reaction process and to build up mathematical models for the achievement of optimum operating points in pretreatment [108]. Table 2.3 summarizes the most widely used RS pretreatment methods, providing process conditions with pros and cons, targeting mass-scale application.

2.6 Cellulose conversion into 5-HMF

As shown in Fig. 2.4, catalytic conversion of cellulose into 5-HMF consists three major steps. Those are Bronsted acidic catalysts catalyzed cellulose to glucose hydrolysis, Lewis acidic catalysts catalyzed glucose to fructose isomerization, and fructose dehydration into 5-HMF mainly catalyzed, using Bronsted acidic catalysts [48, 140–142]. There are four main parameters, including solvents, catalysts, reaction systems, and reaction conditions have shown direct influence on this kind of conversion processes [12, 48]. Catalytic conversion processes which are carried out during past ten years are summerized in Table 2.4.

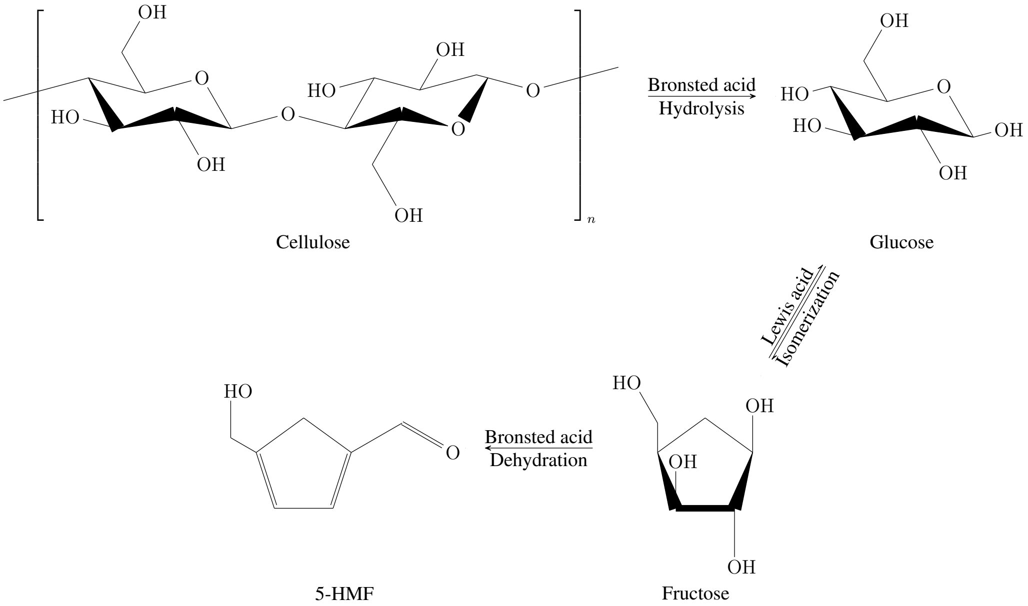


Fig. 2.4: General reaction scheme of cellulose to 5-HMF conversion [16]

TABLE 2.3: Methods for rice straw pretreatment with advantages and disadvantages

Method	**Operating conditions**	**Advantages**	**Disadvantages**	**Ref.**
Dry ball milling	60 min	Reduce crystallinity of cellulose with increasing milling time	Consume substantial energy	[143]
Wet disk milling	3 min, 10 repeated operations	Reduce cellulose crystallinity, low energy consumption	Compared to ball milling, low reduction in cellulose crystallinity	[143]
Hot compressed water treatment	100 to 200 °C	Energy-efficient green method to dissolve hemicellulose	High temperature effect on cellulose degradation	[97, 143]
Steam explosion	180 to 230 °C, 10 to 30 bar, and 10 to 20 min	Disrupt lignin-carbohydrate structure, green technique	High energy consumption	[88, 91, 144–147]
Dilute acid treatment (DAP)	0.25 to 1 % of acid concentration (H_2SO_4, HCl, HNO_3, H_3PO_4), 120 to 180 °C, 5 to 10 min	Low-cost method to increase removal of hemicellulose and cellulose	Low eco-friendliness and require equipments with acid corrosive-resistency	[23, 106, 148–158]
Combined steam explosion dilute acid pretreatment	DAP (2 % H_2SO_4, 165 °C, 2 min), Steam Explosion (20 min, 180 °C)	Maximized hemicellulose dissolution	High energy consumption, need corrosive-resistant equipment	[159]
Combined mechanochemical treatment with solid acid catalyst	100 mg ball milled rice straw, 10 mL of 0.015 wt% HCl, solid acid catalyst 50 mg, 60 min, 200 °C	High glucose yield, catalyst preparation from rice straw black liquor	Both cost and energy require process and difficulty in seperation of catalysts	[66]
Alkali pretreatment	0.25 to 4 % concentrations of alkalis (NaOH, KOH, $Ca(OH)_2$, NH_4OH, 55 to 140 °C or room temperature, 10 to 60 min or 24 h	Cost effective operation, high cellulose recovery, increased delignification rate	Need treated rice straw extensive washing prior to next production steps	[160–168]

Combined alkaline and dilute acid treatment	1 to 6 % of acid concentration, 2 to 6 % of alkali concentration, 60 min, 121 °C	High recovery of cellulose, hemicellulose and lignin	Less eco-friendly	[138]
Alkaline hydrothermal treatment	100 to 200 °C, 0 to 7 % NaOH	Increased delignification and hemicellulose dissolution	Need treated rice straw extensive washing prior to next production steps	[97]
Ultrasound assisted alkaline pretreatment	0.4 to 1 % concentration of NaOH, 22 kHz ultrasound waves	Remove lignin and hemicellulose selectively	Increaed energy consumption	[74]
Deep eutectic solvent (DES) treatment	50 to 100 % concentration of ChoCl, 60 to 150 °C, 30 to 1440 min,	Increased recovery of cellulose and removal of hemicellulose/ lignin, cost effective at mild treatment conditions	Cost intensive solvent recycling process	[139, 169–175]

TABLE 2.4: Cellulose catalytic conversion into 5-HMF processes

PID	**Quantity**	**Catalyst**	**Reaction System**	**Inorganic Salts**	**Reaction Conditions**	**HMF yield**	**Ref.**
1	Cellulose 25 mg	**Ho** HCl 0.1285 mol/dm^3	**R** H_2O 250 µL **E** MIBK 4.75 mL	none	177 °C & 60 min	43.27 %	[176]
2	Cellulose 4 wt%	**Ho** $CrCl_2$ 25 %, HCL 6 %	**M** DMA -LiCl 10 %, [EMIM]Cl 60 %	none	140 °C & 2 h	54.00 %	[177]
3	Cellulose 4 g	**Ho** $RuCl_3$ 0.125 mol/dm^3	**R** H_2O **E** C_4H_9OH	NaCl 35 %	220 °C & 30 min	83.30 %	[178]
4	Cellulose 1 g	**He** [Ni]n/CS 200 mg	**M** H_2O 45 mL	none	200 °C & 60 min	85.00 %	[179]
5	Cellulose 1 g	**Ho** HCl pH 3	**M** H_2O 30 mL	none	300 °C & 30 min	20.72 %	[180]
6	Cellulose 50 mg	**Ho** $CrCl_3 \cdot 3\,H_2O$ 15 mg	**M** [BMIM]Cl 1 g	none	150 °C & 10 min	54.00 %	[181]
7	Cellulose 10 g	**He** $P-TiO_2$ 1.25 g	**R** H_2O + NMP **E** THF	NaCl 4 g	180 °C & 105 min	86.20 %	[182]
8	Cellulose 50 mg	**Ho** $CuCl_2 + CrCl_2$	**M** [EMIM]Cl 0.5 g	none	120 °C & 8 h	60.00 %	[183]
9	Cellulose 0.1 g	**Ho** $CrCl_3 \cdot 6\,H_2O$ 10 mg	**M** Bu−DBUCl 1 g	none	130 °C & 2 h	41.00 %	[184]
10	Cellulose 0.1 g	**Ho** $CrCl_3 \cdot 6\,H_2O$ 10 mg	**M** Oc−DBUCl 1 g	none	130 °C & 2 h	42.00 %	[184]
11	Cellulose 0.1 g	**Ho** $CrCl_3 \cdot 6\,H_2O$ 10 mg	**M** HEOE−DBUCl 1 g	none	130 °C & 2 h	24.00 %	[184]
12	Cellulose 50 mg	**Ho** $CrCl_2 + RuCl_3$	**M** [EMIM]Cl 0.5 g	none	120 °C & 2 h	60.00 %	[185]
13	Cellulose 0.35 g	**Ho** $CuCl_2 + C_4SO_3$ 1.5 mL	**M** [EMIM]OAc 10 mL	none	160 °C & 3.5 h	69.70 %	[186]
14	Cellulose 0.35 g	**Ho** $CuCl_2 + HSO_4$ 1.5 mL	**M** [EMIM]OAc 10 mL	none	160 °C & 3.5 h	64.90 %	[186]
15	Cellulose 0.15 g	**Ho** $MnCl_2$ 3 mol% + [bi−C_3SO_3HMIM][HSO_4] 9 mol%	**M** [BMIM]OAc 3 mL	none	120 °C & 60 min	62.63 %	[187]

TABLE 2.4: (ctd.) Cellulose to 5-HMF conversion processes

PID	**Feedstock**	**Catalyst**	**Reaction System**	**Inorganic Salts**	**Reaction Conditions**	**HMF yield**	**Ref.**
16	Cellulose 0.1 g	**He** ATP – SO_3 H – Cr(III) 0.1 g	**M** [EMIM]Cl 2 mg	none	120 °C & 2 h	31.20 %	[188]
17	Cellulose 0.1 g	**He** Bronsted-acidic polymer nanotubes with hydrophobic surface wettability 30 mg	**M** [EMIM]Cl 2 mg	none	120 °C & 30 min	34.60 %	[189]
18	Cellulose 0.1 g	**He** H-form zeolite 20 wt%	**M** [EMIM]Cl 1 mg	LiCl 6 mol%	160 °C & 30 min	70.30 %	[190]
19	Cellulose 0.1 g	**He** H-form zeolite 20 wt%	**M** [EMIM]Cl 1 mg	NaCl – KCl 3 mol% + 3 mol%	160 °C & 2 h	58.20 %	[190]
20	Cellulose 21.6 mg	**Ho** H_2SO_4 0.88 wt%, 2-methoxycarbonylphenyl boronic acid 120 mol%)	**M** [EMIM]Cl 493.4 mg	$MgCl_2 \cdot {}_6H_2O$ 300 mol% + 3 mol%	105 °C & 1 h	41.00 %	[191]
21	Cellulose 0.1 g	**Ho** $Cr([PSMIM]HSO_4)_3$ 0.05 g	**M** [BMIM]Cl 2 g	none	120 °C & 5 h	53.00 %	[192]
22	Cellulose 0.5 g	**Ho** 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate (2 g), $CoSO_4$(0.2 mol/dm^3, 1 mL)	**R** H_2O 1 ml **E** MIBK 8 mL	none	150 °C & 5 h	24.00 %	[193]
23	Cellulose 1 g N_2 3 MPa	**Ho** $NaHSO_4$ 1.5 mol/dm^3, $ZnSO_4$ 2.3 mol/dm^3	**R** DI H_2O 4 ml **E** THF 40 mL	none	160 °C & 1 h	53.00 %	[194]
24	Cellulose 100 mg	**Ho** $AlCl_3$ 8.2 mg	**M** DMSO 4.5 g, [BMIM]Cl 0.5 g	none	150 °C & 9 h	54.90 %	[195]
25	Cellulose	**He** Sn – Mont 0.2 g	**R** H_2O 1 ml **E** THF 5 mL	NaCl 6 wt%	160 °C & 3 h	39.10 %	[196]

TABLE 2.4: (ctd.) Cellulose to 5-HMF conversion processes

PID	**Feedstock**	**Catalyst**	**Reaction System**	**Inorganic Salts**	**Reaction Conditions**	**HMF yield**	**Ref.**
26	Cellulose 100 mg	**Ho** $ZrCl_4$ 10 mol%	**M** [BMIM]Cl] 2 g	none	3.5 h	51.40 %	[197]
27	Cellulose 100 mg	**He** Cellulose derived Carbonaceous Catalyst 40 mg	**M** [BMIM]Cl] 1 g	none	160 °C & 15 min	40.50 %	[198]
28	Cellulose 50 mg	**Ho** $InCl_3$ 0.20 mmol, $[C_3SO_3Hmim][HSO_4]$ (1.5 g)	**M** DMSO 4.5 mL	none	160 °C & 5 h	45.30 %	[199]
29	Cellulose 0.1 g	**He** $HfO(PO_4)_x$ 0.03 g, 30 wt%	**R** H_2O 1 ml **E** THF 4 mL	NaCl 0.2 g	190 °C & 4 h	69.80 %	[200]
30	Cellulose 0.1 g	**He** Nb/C (0.1 g)	**R** H_2O 2 ml **E** THF 6 mL	NaCl	170 °C & 8 h	53.30 %	[201]
31	Cellulose 0.15 g	**Ho** $MnCl_2$ 3 mol% + $[bi-C_3SO_3HMIM][CH_3SO_3]$ 9 mol%	**M** [BMIM]OAc 3 mL	none	120 °C & 60 min	66.50 %	[187]
32	Cellulose 0.15 g	**Ho** $MnCl_2$ 3 mol% + $[C_3SO_3HMIM][HSO_4]$ 9 mol%	**M** [BMIM]OAc 3 mL	none	120 °C & 60 min	52.46 %	[187]
33	Cellulose 0.15 g	**Ho** $MnCl_2$ 3 mol% + $[C_3SO_3HMIM][CH_3SO_3]$ 9 mol%	**M** [BMIM]OAc 3 mL	none	120 °C & 60 min	54.51 %	[187]
34	Cellulose 0.1 g	**He** $HNTs-PSt-PDVB-SO_3H(I)$ 0.1 g	**M** [EMIM]Cl 2 mg	none	120 °C & 2 h	28.22 %	[188]
35	Cellulose 0.1 g	**He** $HNTs-PSt-PDVB-SO_3H(II)$ 0.05 g	**M** [EMIM]Cl 2 mg	none	120 °C & 2 h	32.86 %	[188]

TABLE 2.4: (ctd.) Cellulose to 5-HMF conversion processes

PID	**Feedstock**	**Catalyst**	**Reaction System**	**Inorganic Salts**	**Reaction Conditions**	**HMF yield**	**Ref.**
36	Cellulose 0.1 g	**He** Bronsted-acidic polymer nanotubes with hydrophobic surface wettability 30 mg	**M** [EMIM]Cl 2 mg	none	120 °C & 30 min	37.10 %	[189]

Ho	Homogeneous catalyst
He	Heterogeneous catalyst
M	Monophasic reaction system
R	Reaction phase of a biphasic reaction system
E	Extraction phase of a biphasic reaction system
PID	Process ID

2.6.1 Catalysts used in cellulose to 5-HMF conversion

This section presents a detailed description on the catalysts, involved to hydrolyze cellulose into glucose, isomerization of sugars, and dehydration of fructose.

2.6.1.1 Bronsted acidic catalysts

Both cellulose to glucose hydrolysis and fructose into 5-HMF dehydration catalysis can be performed, using Bronsted acidic catalysts. These catalysts mainly include mineral acids, solid acids, ionic liquids, and organic acids [12, 17]. Generally, cellulose hydrolysis catalyzed via Bronsted acids consists three steps: (I) cellulose glycosidic oxygen in C-O-C bonds protonation, (II) β-1,4 – glycosidic bonds scission , and (III) to form glucose monomers nucleophilic attack of water on broken cellulose chains as depicted in Fig. 2.5 [202]. Here, the rate determining step is cleavage of β-1,4 – glycosidic bonds of cellulose mainly due to the reduced accessibility of catalysts towards cellulose crystalline areas [203].

As low cost catalysts, in Bronsted acidic catalysts the most used ones are mineral acids, such as HCl, H_2SO_4, and HNO_3. These catalysts work as homogeneous proton catalysts for the penetration of heterogeneous matrix of cellulose [159]. HCl acts an important role in 5-HMF formation facilitation. Li and co-workers studied the influence of catalysis of H_2SO_4 and HCl, using hydrogen ions same quantity. They achieved

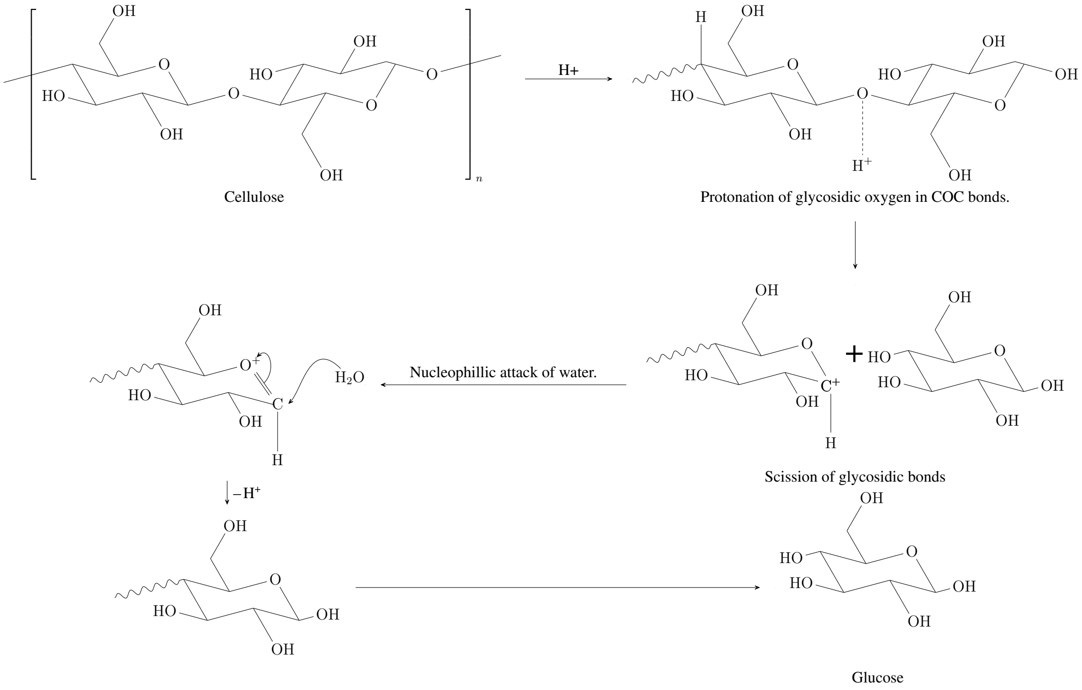


Fig. 2.5: Reaction mechanism of cellulose hydrolysis into glucose [48]

considerably greater amount of 5-HMF yield from HCl, compared to the yield generated from H_2SO_4. They studied on the influence of acid concentration and temperature at the same time. Usually, high reaction temperatures need low acid concentrations and vice versa. This is due to the combined effect of reaction temperature and acid concentration for the formation of 5-HMF [204]. In contrast, high temperatures ($> 300\,^{\circ}\mathrm{C}$), high acid loadings ($>$ 0.3 M), and extended reaction periods ($>$ 30 min) have negative influence on generating 5-HMF in the reaction medium. This is mainly due to the 5-HMF repolymerization and rehydration reactions into humins and levulinic acid in the reaction phase, respectively. Generally, these mineral acid catalysts are immensely employed in mass-scale 5-HMF produce, despite the disadvantages, including environmental pollution and reactor corrosion [12].

Due to the disadvantages of using mineral acid catalysts, nowadays researchers have tendency to investigate on heterogeneous solid acid catalysts, such as resins, metal oxides, immobilized ionic liquids, H-form zeolite, and heteropolyacids for the catalytic hydrolysis of cellulose [205]. Generally, acidic ion-exchange resins, which act as solid Bronsted acidic catalysts have showed super catalytic effect on 5-HMF formation. These catalysts include Amberlyst-38 (wet), Dowex-50, heteropolyacids, Amberlyst-15, and their derivatives [12]. Usually, ideal solid acidic catalysts, Zeolites with balanced Lewis and Bronsted acidic sites on its' surface, have exhibited satisfactory catalytic performance on cellulose hydrolysis, sugar isomerization, and dehydration of sugar into 5-HMF [17]. For an instance, an application of zeolites functionalized choline chloride (ChoCl) (HBeta, HZSM5, NaY, HY, and HMOR) for cellulose to 5-HMF conversion has generated $46.30\,\%$ yield of 5-HMF [206]. When these H-form zeolite catalyts are incorporated with metal alkali chlorides, such as LiCl, KCl, and NaCl catalytic performance can be improved. Studied revealed that catalyst combinations like Zeolite/NaCl and Zeolite/LiCl were effective in generating more than 5-HMF $70\,\%$ yield for 30 min at $160\,^{\circ}\mathrm{C}$ [190]. Despite these advantages of solid acidic catalysts, their synthesis operations are cost-intensive and hence, difficult at using for large-scale 5-HMF production.

2.6.1.2 Lewis acidic catalysts

For the facilitation of 5-HMF formation, glucose to fructose isomerization is required. This is mainly due to the higher dehydration capacity in fructose conversion into 5-HMF, compared to glucose conversion. The reason lies within the stable pyronoide structure of glucose and hence, lowering the direct dehydration capacity of glucose to 5-HMF. Therefore, sugar isomerization is regarded as the most critical step when determining 5-HMF formation rate [198, 207, 208]. Generally, Lewis acidic catalysts include metal salts, enzymes, and bases [48, 209, 210]. Metal chlorides are the most commonly used Lewis acidic catalysts beacuse of their stability at strong Bronsted acidic environments, compared to enzymes and bases [48]. The most widely used Lewis acidic metal chlorides are $CrCl_3$, $CrCl_2$, $AlCl_3$, $FeCl_3$, $FeCl_2$, $ZnCl_2$, $RuCl_3$, and $CuCl_2$ [12, 211]. As shown in Fig. 2.6, metal chlorides catalytic performance is occured through transformation in glucose open form into fructose, using intermolecular hydride shift [212].

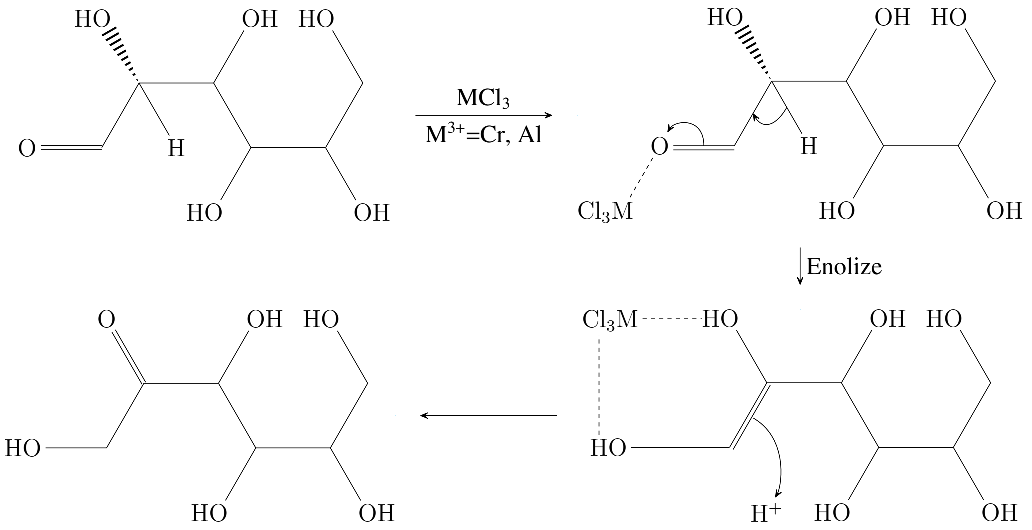


Fig. 2.6: Reaction mechanism of metal chlorides catalyzed isomerization of glucose to fructose [213]

Based on the hydrolysis constant, metal chlorides, as water sensitive catalysts produce both Bronsted and Lewis acidity [214]. For an example, Cr_3^+ and Al_3^+ like Lewis acid metal ions generate both Bronsted and Lewis acidity in aqueous solutions according to this equation (2.1), where trivalent Lewis acid metal ion is denoted as “M_3^+” [215].

$$xM^{3+} + yH_2O = M_x(OH)_y^{(3x-y)+} + yH^+ \tag{2.1}$$

2.6.1.3 Bifunctional catalysts

Bifucntional catalysts are composed of both Lewis and Bronsted acid sites on its' surface. Therefore, these catalysts are capanle in facilitating one-pot conversion of cellulose to 5-HMF [48]. It is required a balanced Lewis and Bronsted acid sites ratio in bifunctional catalysts to fasten the kinetics of cellulose hydrolysis, glucosse to fructose isomerization, and fructose dehydration to 5-HMF [216]. Organic salts like bifunctional organocatalysts are capable in generating more than $52\,\%$ 5-HMF yield in a completely metal free reaction system [217]. Currently, using agricultural waste to develop Bronsted and Lewis acid functionalized carbonaceous catalysts has gained increasing interest due to several advantages, such as cost effectiveness, environmentally friendliness, and sustainability. In this regard, carbonaceous catalysts [198] generated from cellulose and Niobia/carbon(Nb/C) composites generated from glucose [201] are proved in improving sugars dehydration into 5-HMF and hydrolysis of cellulose with yields of $53.3\,\%$ and $40.50\,\%$, respectively. The shape, particle size, and surface area of these catalysts provide superior performance in increasing the selectivity of 5-HMF. However, catalysts synthesis processes are extremely difficult and it has limited these catalysts usage at mass-scale production of 5-HMF [17].

As a conclusion, in the reaction system, controlling Lewis and Bronsted acidity is important for the promotion of faster kinetics of dehydration, hydrolysis, and isomerization. Therefore, Table 2.5 has presented a brief description on mass-scale applicability of 5-HMF synthesis catalysts with pros/cons.

2.6.2 Solvents used in conversion of cellulose to 5-HMF

Solvents are required in 5-HMF synthesis, mainly to create the medium reaction by dissolving biomass and catalysts. Solvents also act as catalysts to improve reaction kinetics. These solvents can be categorized into five types as polar aprotic solvents, polar protic solvents, biomass-derived solvents, deep eutectic solvents, and ionic liquids [13, 208].

2.6.2.1 Polar protic solvents

Among polar protic solvents, the most commonly used type is subcritical water [208]. As the reaction medium, subcritical water creates around pH 3.5 acidic nature helping autocatalysis of dehydration of sugars into 5-HMF [218]. Saito investigated cellulose conversion to 5-HMF in hot pressurized water at 200 to $240\,^{\circ}\mathrm{C}$ and 15 to $20\,\mathrm{MPa}$ and gained high yield of 5-HMF [219]. However, 5-HMF decomposition to humin in water at high temperatures for extended times is avoidable, and thus 5-HMF selectivity can be reduced [180, 218].

2.6.2.2 Polar aprotic solvents

Higher applicability is shown by polar aprotic solvents in the conversion of biomass to 5-HMF, compared to polar protic solvents [208]. These solvents include tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), N,N-Dimethylacetamide (DMA), and methyl isobutyl ketone (MIBK). As one of the most widely used solvent, DMSO exhibits strong effect on dehydration of fructose into 5-HMF [220–222]. Ionic liquid and DMSO system has improved hydrolysis of cellulose withincreased sugar concentration for the dehydration. Application of ionic liquid/ceInCl3/DMSO catalytic/solvent system has provided considerable amount of 5-HMF yield $(45.3\,\%)$ [199]. However,

TABLE 2.5: Catalysts utilized in cellulose to 5-HMF conversion with pros and cons

Type of catalyst	Examples	Pros	Cons	Ref.
Bronsted homogeneous acids	**Inorganic acids** Hydrochloric acid (HCl), Sulfuric acid (H_2SO_4), Nitric acid (HNO_3), Phosphoric acid (H_3PO_4)	Inexpensive and easy accessible method with robust handling practices, moderate 5-HMF yield.	Less 5-HMF selectivity, costly acid recovery processes, and corrosive nature.	[17, 48, 176, 180, 204, 208]
	Organic acids Formic acid, Lactic acid, Maleic acid, Acetic acid.	less toxic and safe method, in high acid concentrations 5-HMF with low to moderate yields.	In comparison to mineral acids less efficient in hydrolysis of cellulose, Occuring of side reactions at high acid loadings, and less recoverability of catalysts at mass-scale operations.	[208]
Homogeneous Lewis acids	**Metal salts and minerals** $CrCl_2$, $CrCl_3$, $AlCl_3$, $FeCl_3$, $ZnCl_2$, $ZrCl_4$, $CuCl_2$, $MnCl_2$	Moderate to high 5-HMF yields by aluminium and chromium salts in an appropriate solvent system (mostly in ionic liquids and solvents with polar aprotic nature), catalyst recoverability is satisfactory, and less corrosive to equipments.	Less efficient in cellulose hydrolysis, limited application at mass-scale operations due to high cost, and toxic nature in chromium salts catalyzed processes.	[17, 48, 178, 186, 208, 211, 223]

TABLE 2.5: (ctd.) Catalysts utilized in cellulose to 5-HMF conversion with pros and cons

Type of catalyst	**Examples**	**Pros**	**Cons**	**Ref.**
Heterogeneous solid acids	**Bronsted and Lewis mixed acidic catalysts - Zeolites** $\mathrm{Sn}-\beta$, $\mathrm{HY}-\mathrm{Zeolite}$, $\mathrm{HZSM}-5$, $\mathrm{H}-\mathrm{modernite}$, **Ion-exchange resins** $\mathrm{Dowex}-50\,\mathrm{wx}_8-100$, $\mathrm{Amberlyst}-15$, **Heteropoly acids** 12-CsTPA, 12-AgTPA, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, 12-TSA	Increased yield of 5-HMF in suitable solvents like ionic liquids and when using microwave irradiation like heating mechanisms, moderate to high yield of 5-HMF, acidic sites improve the catalyst efficiency.	Costly catalyst synthesis methods, low efficiency in hydrolysis of raw biomass, requirement of high catalyst dosage, and separation difficulties from solid acid catalysts and unreacted cellulose.	[12, 17, 182, 200, 206, 208, 224]

DMSO usage has being limited to laboratory experiments due to its' toxicity and cost-intensive recovery processes [17]. In contrast to DMSO, MIBK is considered as a less toxic solvent. Adding MIBK to water acidified phase, it creates water-immiscible extracting phase for 5-HMF continuous extraction, and thus has caused to immprove the selectivity of 5-HMF [176]. Therefore, CHEM21 guide has recommended to use MIBK to produce 5-HMF even at mass-scale production [212]. Another favourable solvent, THF widely applies in cellulose to 5-HMF conversion due to its' improved reaction kinetics [42, 182, 200, 201]. Generally, THF creates water-miscible reaction system. However, salt addition transforms it into water-immiscible reaction system and supports to increase 5-HMF selecvity [194].

2.6.2.3 Ionic liquids

Ionic liquids (ILs) is used aqueous phase replacement in reaction system of 5-HMF producion. Generally, ILs is capable to function as catalysts and solvents at the same time to convert cellulose to 5-HMF [223, 225]. ILs, like [BMIM]Cl, [AMIM]Cl, and [EMIM]Cl exhibit satisfactory performance to yield 5-HMF [187, 188, 190, 225]. The main reason to this is their acidic functional group (HSO_4^- or Cl^- anion). These acidic functional groups have the ability to facilitate both hydrolysis of cellulose and dehydration of fructose into 5-HMF [226]. Shi and co-workers have investigated cellulose transformation into 5-HMF with [BMIM]Cl application. They have reported a high 5-HMF yield $66.5\,\%$ [187]. However, high cost of synthesis processes, toxicity, and difficult recycling have restricted ILs usage in mass-scale operations [17, 225].

2.6.2.4 Biomass-derived solvents

Biomass-derived gamma valerolactone (GVL) has gained increasing interest recently to produce 5-HMF like value-added chemicals [227–229]. This is mainly due to the revealation of recent studies that higher 5-HMF production in water/GVL systems, compared to conventional aqueous systems [204, 227, 230, 231]. Generally, water/GVL systems fasten the hydrolysis of cellulose via disrupting crystallinity of cellulose and avoiding reprecipitation of lignin on cellulose [232]. Water/GVL systems are also important for the efficient sugar isomerization and dehydration of 5-HMF [173]. This is mainly due to the influence of GVL to facilitate acid-catalyzed isomerization and dehydration by stabilizing the acidic portion [233, 234]. As another valuable solvent, methyltetrahydrofuran (MTHF), is applied in the conversion of cellulose into 5-HMF. High stability of MTHF in water has created an efficient MTHF/water biphasic reaction system to produce 5-HMF in higher yields [235]. As a summary, Table 2.6 shows commonly used 5-HMF synthesis solvents used with advantages/disadvantages.

TABLE 2.6: 5-HMF synthesis solvents with pros and cons

Type of Solvent	Description	Pros	Cons	Ref
Polar protic solvent - Subcritical water	Pressurized liquid water in between the temperatures of its critical temperature (374 °C) and normal boiling point (100 °C)	low cost and green reaction medium, via offering hydroxyl ions and protons catalyze dehydration and hydrolysis reactions, autocatalytic nature	Less efficiency in hydrolysis of cellulose, lower yield and selectivity of 5-HMF, rapid rehydration of 5-HMF into formic acid and levulinic acid	[17, 180, 208, 218]
Polar aprotic solvents – Dimethylsulfoxide (DMSO)	DMSO neucleophilic action promotes dehydration of sugar into 5-HMF.	Stabilize 5-HMF via lowering the occuring of undesirable side reactions, compatibility with various types of catalysts, and higher effectivity compared to aqueous systems.	High energy required 5-HMF separation process due to DMSO high boiling point.	[17, 195, 208, 236]
Tetrahydrofuran (THF)	miscible solvent with water	Higher yield of 5-HMF	High temperatures ($> 180\,^{\circ}$C) cause to 5-HMF degradation.	[208, 237, 238]
Methyl isobutyl ketone (MIBK)	Serve as an extraction phase	Higher yield of 5-HMF. Higher extraction efficiency of 5-HMF into MIBK	Expensive	[176, 208, 239]
Ionic liquids (ILs) $[\mathrm{BMIM}^+][\mathrm{Cl}-]$, $[\mathrm{EMIM}^+][\mathrm{Cl}-]$	Liquid salts at low temperatures.	High concentration of ILs favours cellulose dissolution at mild temperatures for the production of 5-HMF.	High cost synthesis processes, difficulty in product separation, and low reusability.	[17, 181, 190, 208, 211]
Biomass derived solvents	Biomass derived gamma valerolactone (GVL) and methyltetrahydrofuran (MTHF) are highly used.	Green solvents, 5-HMF in moderate to high yields, and breakdown of crystaline cellulose.	Costly synthesis operations.	[208]

2.6.3 Reaction systems used in cellulose to 5-HMF conversion

The reaction systems can be categorized as biphasic and monophasic systems. In monophasic system there is one solvent or miscible two solvents. In biphasic systems consist two immisible solvents as reaction phase and extracting phase [12, 208]. The aqueous monophasic system produces comparable 5-HMF yield from glucose and fructose like model carbohydrates [208]. Biphasic systems have a strong effect on improving both yield and purity of 5-HMF by increasing its partition coefficient into the extracting phase. Organic solvents are highly used as the extracting phase due to the effective 5–HMF extraction. The continues development of biphasic systems is important to minimize secondary reactions mainly, 5-HMF rehydration into formic acid and levulinic acid and repolymerization into humins. This is required to increase 5-HMF selectivity and yield [180, 187, 195, 212, 240].

2.6.4 Reaction conditions influences on conversion of cellulose to 5-HMF

Operating parameters, such as reaction temperature and time show high influence on 5-HMF production. In general, to prduce satisfactory yield of 5-HMF, reaction temperature varies between 80 to $240\,^{\circ}\mathrm{C}$, and variation of reaction time around seconds to hours. The literature reveals that an application of high temperatures for short reaction time is important in producing high 5-HMF yield [241, 242]. In contrast, $> 60\,\mathrm{min}$ long reaction times at elevated temperatures ($> 140\,^{\circ}\mathrm{C}$) has shown negative effect on yield 5-HMF because of 5-HMF decompostion into humin and rehydration into levulinic acid [204].

CHAPTER 3

COMPARATIVE EVALUATION OF CELLULOSE TO 5-HMF

The literature on the catalytic conversion of cellulose into 5-HMF processes reveals four unique process parameters that can be used to characterize a process. These process parameters includes process temperature (θ_k), process time (t_k), reaction system used (RS_k), and catalysts used (C_k), where k denotes the k^{th} process considered. When application of these parameters for a process P_k, y_k yield can be resulted. Consequently, as given in eq (3.1), P_k process can be represented, using these parameters as inputs θ_k, t_k, RS_k, and C_k providing y_k yield.

$$y_k = P_k \left(t_k, \theta_k, C_k, RS_k \right) \tag{3.1}$$

Even so, 5-HMF production processes provides the values of 5-HMF yield and above mentioned parameters, they are not adequate to infer optimality of each process. Therefore, in this study, an objective function, f_c is proposed to find out a optimal process to produce 5-HMF [243, 244]. Optimal process conditions are corresponded to the $f_c(u_k)$ minimum value and (3.2) gives the u_k. Then, prior to defining of objective function, the contribution of each parameter to it is presented.

$$u_k = \{\theta_k, t_k, C_k, y_k, RS_k\} \tag{3.2}$$

1. **Process time (t_k) and process temperature (θ_k)**

   Considering a cellulose to 5-HMF conversion process, energy $E_{1,k}$ is needed for the heating of system of reaction comprising cellulose, solvents, and catalyst(θ_k). The required energy $E_{1,k}$ is shown as in eq (3.3), where cellulose, catalyst, and solvent specific heat capacities and masses are $m_{c,k}$, m_o, C_o, $m_{s,k}$, $C_{s,k}$, and $C_{c,k}$, respectively.

   $$E_{1,k} = \left(m_o C_o + m_{s,k} C_{s,k} + m_{c,k} C_{c,k} \right) \left(\theta_k - \theta_o \right) \tag{3.3}$$

   Generally, as stated in Newton's cooling law, $(\theta_k - \theta_o)$ proportional, $Pw_{2,k}$ power will be drived away to the ambient when the process continues. Therefore, it is required to provide $Pw_{2,k}$ power to the system for the maintaining of process temperature. For process time t_k, it is required to maintain the temperature, and the required energy $E_{2,k}$ can be given as in eq (3.4), where K is shown as a parameter specific to the reactor.

   $$E_{2,k} = Pw_{2,k} t, \text{ and as } Pw_{2,k} \propto \left(\theta_k - \theta_o \right) \Rightarrow E_{2,k} = K \left(\theta_k - \theta_o \right) t_k \tag{3.4}$$

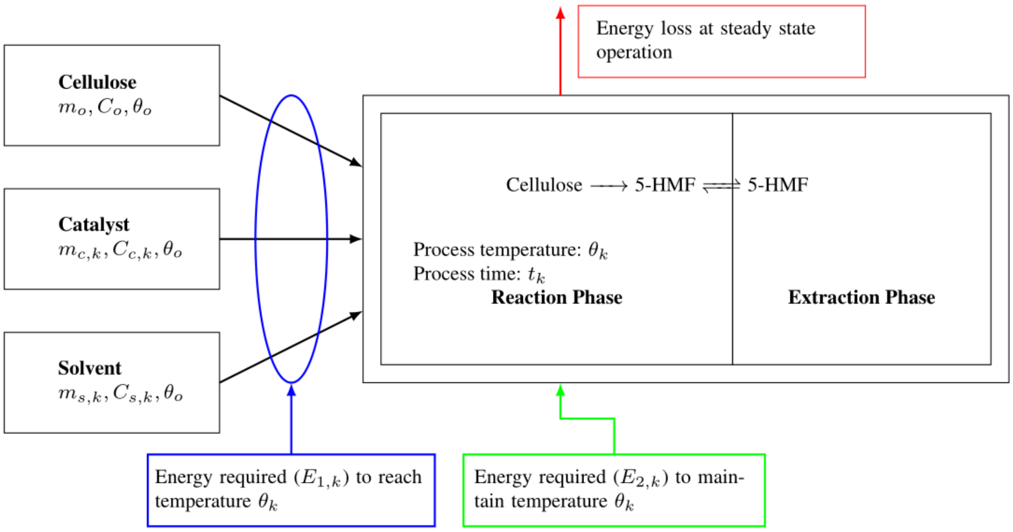


Fig. 3.1: Biphasic system of conversion of cellulose into 5-HMF. Characterization of inputs (cellulose, catalyst, and solvent) via specific heat capacities C_o, $C_{s,k}$, $C_{c,k}$ and masses m_o, $m_{s,k}$, $m_{c,k}$, respectively. System starting temperature is θ_o

Accodingly, the required (E) total energy to reach and maintain the operating reaction temperature can be expressed as given in eq (3.5) based on results generated from eq (3.3) and (3.4).

$$E_k = E_{1,k} + E_{2,k} = (m_o C_o + m_{s,k} C_{s,k} + m_{c,k} C_{c,k} + K t_k)\,(\theta_k \;-\; \theta_o) \tag{3.5}$$

2. **Catalysts used** (C_k)

   Catalyst contribution evaluated considering its price, amount required, toxicity, and non-recoverability. Formation of the parameters discussed in section 3.1.

3. **Reaction system** (RS_k)

   The evalutation parameter RS_k is formulated similar to the formation of C_k, based on certain subparameters: price, non-recoverability, and toxicity. In section 3.2, reaction system parameter formualtion is discussed.

4. **Yield % (Y) of 5-HMF**

   According to above proposed objective function, better process is represented by low parameter values. Therefore, to maintain the consistency, eq (3.6) defines $\bar{Y}$ yield loss %, not considering directly the yield of 5-HMF as a input parameter.

$$\bar{Y_k} = 1 - Y_k \tag{3.6}$$

Finally eq (3.7) defines the objective function, based on the above parameters. Reffering [243, 244], coefficients α_1,α_2,α_3, and α_4 are used as relative weightages to the above process to represent the significance of parameters.

$$f_{c,k} = f_c(u_k) = \bar{Y}_k^{\alpha_1} E_k^{\alpha_2} C_k^{\alpha_3} RS_k^{\alpha_4} \tag{3.7}$$

This equation (3.7) is comprised of powers of individual parameters. Therefore, eq (3.8) is shown the $\log$ value of the objective function, for the reduction of computational complexity.

$$\bar{f}_{c,k} = \alpha_1 \log \bar{Y}_k + \alpha_2 \log E_k + \alpha_3 \log C_k + \alpha_4 \log RS_k \tag{3.8}$$

Although yield loss relative weightage α_1, is general to the 5-HMF production plant location, α_2 to α_4 relative weightages are influenced by locations' human resource availability, technology availability, and environmental regulations. Considering parameters contribution: yield, operating temperature, and operation time are connected to the objective function directly. Although, there are certain parameters which are not easily mapping such as, catalyst used and reaction system used.

3.1 Catalyst contribution (C_k)

Considering three factors, the contribution of catalyst is determined.

1. **Catalysts price ($P_{C,k}$)**

   Catalyst price is taken as $1\,\mathrm{g}$ of pure catalyst price. Employing (3.9) and (3.10), solid and liquid catalysts prices are calculated. In equations, material purity is indicated as $\frac{w}{W}\%$ ratio.

   $$P_{C,k} = \frac{price}{quantity \times \frac{w}{W}\% \times density} \tag{3.9}$$

   $$P_{C,k} = \frac{price}{mass \times \frac{w}{W}\%} \tag{3.10}$$

2. **Catalysts non-recoverability ($nRe_{C,k}$)**

   Here, higher recoverability of catalysts is obtained, using less soluble catalysts in the reaction medium. However, sufficient data for the catalyst recoverability is not available in the literature and hence, catalyst solubility in grams in water $100\,\mathrm{mL}$ between temperature range 20 to $25\,^\circ\mathrm{C}$ is used to define the non-recoverability of catalyst ($nRe_{C,k}$) [245].

3. **Catalysts toxicity ($Tx_{C,k}$)**

   relative measure are used to define catalyst toxicities here, because of the non-availability in comparison of catalysts used [245]. For the evaluation of catalsyts toxicities, 1 - 10 spanning relative scale is presented. In this relative scale 1 is regarded as the lightest and 10 is regarded as the toughest.

In the contribution function eq. (3.11), catalysts contribution is shown as (C_k), defined like in eq (3.8) objective function. In the contribution function C_1, C_2, and C_3 represent each factor weightages.

$$C_k = \frac{1}{C_1 + C_2 + C_3} \left(C_1 \log P_{C,k} + C_2 \log \mathrm{nRe}_{C,k} + C_1 \log \mathrm{Tx}_{C,k} \right) \tag{3.11}$$

3.2 Contribution of reaction system (RS_k)

Four factors are considered to determine contribution of the reaction system (RS_k). These factors can be listed as,

1. Solvents price ($P_{RS,k}$)
2. Solvents toxicity ($Tx_{RS,k}$)
3. Solvents quantity ($W_{RS,k}$)
4. Solvents non-recoverability ($nRe_{RS,k}$)

As there is limited data availability for each above mentioned factor, "very low" to "very high" spaning a relative measure is used for comparison of factors in different processes. Therefore, a relative value is assigned considering severity in each factors in various processes. Eventually, as in eq. (3.12), monophasic system contribution function is presented. m_1, m_2, m_3, and m_4 represent the monophasic system factor weightages.

$$RS_{mono,k} = \frac{\beta}{m_1 + m_2 + m_3 + m_4} \left(m_1 \log P_{RS,k} + m_2 \log Tx_{RS,k} + m_3 \log W_{RS,k} + m_4 \log nRe_{RS,k} \right) \tag{3.12}$$

However, due to the low production stability of 5-HMF in a monophasic system, for the contribution function eq (3.12), β monophasic penalty is included.

Similarly, for the biphasic system, to gain the contribution for ($RS_{(reaction)}$) reaction phase and ($RS_{(extraction)}$) extraction phase, two sub-equations are set according to (3.13). Here also, r_1 to r_4 and e_1 to e_4 represent factor weightages related to respective reaction phase and extraction phase.

$$\begin{aligned} RS_{(reaction,k)} &= \frac{r_1 \log P_{RS,k} + r_2 \log Tx_{RS,k} + r_3 \log W_{RS,k} + r_4 \log nRe_{RS,k}}{(r_1 + r_2 + r_3 + r_4)} \\ RS_{(extraction,k)} &= \frac{e_1 \log P_{RS,k} + e_2 \log Tx_{RS,k} + e_3 \log W_{RS,k} + e_4 \log nRe_{RS,k}}{(e1 + e2 + e3 + e4)} \end{aligned} \tag{3.13}$$

Finally, as in eq (3.14), defining of biphasic reaction system contribution function is completed, and β_1 and β_2 parameters are utilized here for the merging of extraction phase contribution with reaction phase contribution as $RS_{(reaction)}$ and $RS_{(extraction)}$ aggregation.

$$RS_{(Bi,k)} = \beta_1 RS_{(reaction,k)} + \beta_2 RS_{(extraction,k)} \tag{3.14}$$

3.3 Process Evaluation

Before demonstrating the proposed evaluation method, a set of assumptions were used. The basis of setting the assumptions was to simplify and generalize the proposed process evaluation method as far as possible. Assigning values to each and every relative weightage and other co-factors was totally subjective to the financial capacity, technology availability, and environmental regulations of the area considered to establish 5-HMF plant. Here, calculation of cost of energy was done using the energy needed for the convertion of cellulose into $1\,\mathrm{g}$ of 5-HMF.

1. The value of α_1, α_2, α_3, and α_4 relative weightages were taken as unity. Based on that, eq (3.15) shows the simplified objective function.
$$\bar{f_{c,k}} = \log \bar{Y_k} + \log E_k + \log C_k + \log RS_k \tag{3.15}$$
2. In all processes, the reactor energy loss constant (K) and the reactor heat capacity (γ), were considered common and taken as unity.
3. The required energy for the heating of catalyst was assumed insignificant.
4. C_1, C_2, and C_3 contributor weightages in catalyst contribution were taken as unity.
5. m_1, m_2, m_3, and m_4 contributor weightages in monophasic system and β monophasic penalty were taken as unity.
6. r_1 to r_4 contributing weightages in reaction phase and e_1 to e_4 contributing weightages in extraction phase in biphasic system were taken as unity.
7. In a biphasic system, as merging values, β_1 reaction phase and β_2 extraction phases were taken as 0.5 value for the system.

As the first step of evaluation, analysis of catalyst contribution is carried out. To simplify the price represention of this comparative evaluation, priceses of catalysts were obtained from a recognized database, Sigma-Aldrich, 2020 [246]. Tables 3.1 and 3.2 show the catalysts contributions, weightages and each categorys' scores.

TABLE 3.1: Evaluation of contribution of catalysts to objective function part (I)

		Homogeneous - Lewis						
	Weightage	**Metal Salts**						
		$AlCl_3$	**$CrCl_3$**	**$RuCl_3$**	**$CuCl_2$**	**Na_2SO_4**	**$ZrCl_4$**	**$InCl_3$**
Price ($)		23.5	115	144	33.8	26.9	35.4	10
Pack Amount		100 g	5 g	2 g	25 g	500 g	4 g	10 g
$\frac{w}{W}\%$		98	95	50	99	99	100	98
Unit cost (P_C)	1	239.8	24210.53	144000	1365.66	54.34	8850	13367.35
Non-recoverability (nRe_C)	1	45.8	58.5	70	75.7	20	55	195
Toxicity (Tx_C)	1	3	10	8	6	4	5	7
Contribution (C)		1.505	2.383	3.635	1.930	1.212	2.128	2.4204

TABLE 3.2: Evaluation of contribution of catalysts to objective function part (II)

		Homogeneous - Bronsted			**Heterogeneous**	
	Weightage	**Mineral Acids**				
		HCl	**H_2SO_4**	**ILs**	**Solid Acid**	**Biomass**
Price ($)		85.8	131	55.9	98.1	
Pack Amount		500 mL	100 mL	5 g	100 g	
$\frac{w}{W}\%$		37	99.99	98	100	
Unit cost (P_C)	1	463.78	1310.13	11408.16	981	20000
Non-recoverability (nRe_C)	1	72	72	50	1	1
Toxicity (Tx_C)	1	3	3	9	2	1
Contribution (C)		1.666	1.8172	2.236	1.097	1.433

TABLE 3.3: Scores used in evaluation of reaction systems

Condition	*Very Low*	*Low*	*Medium*	*High*	*Very High*
Score	1	2	3	4	5

Finally the results show that $RuCl_3$, $CrCl_3$, $InCl_3$, and ILs have shown high costs because of their toxicities and high unit prices. In contrast, solid acid catalysts, Na_2SO_4, and $AlCl_3$ have shown reduced costs because of low toxicities and low unit prices in comparison with other catalysts.

In reaction systems evaluation, evaluation weightages, which are listed Table 3.3 were used for the assigning of each factor score in both biphasic/ monophasic reaction systems.

The monophasic reaction systems evluation results are depicted in Table 3.4. Based on the results, water has exhibited the lowest contribution among other monophasic reaction systmes because of reduced toxicity and price . On the other hand, ILs and organic solvents have showned costs elecated because of their requirement of large amount and elevated unit prices.

Table 3.5 has shown a similar evaluation for biphasic reaction system. By applying the same method for the evaluation, water has emerged as as the best reaction phase, because of its lowest contribution. On the other hand, the highest contribution is made by DMSO, because of its high unit price. As the best extraction phase, THF has obtained the lowest cost mainly due to its high recoverability.

Finally, cellulose into 5-HMF conversion methods were evaluated by using the eq (3.15) and applying the intermediate results listed in Tables 3.1, 3.2, 3.4, and 3.5. The summarized results are shown in Table 3.6, also showing the contribution of different process parameters in each process.

According to the results, considering 18 processes which are out of 36 processes, the optimal process is process No. 4 and here, because of inadequaate data availability the rest of 18 processes were not taken into account. Considering process No. 4, it has applied a clean and novel biomass-based carbon catalyst which is Ni-doped (Ni_n/CS). The process has used a cost effect monophasic system which is water-based at $200\,^{\circ}\mathrm{C}$ for $60\,\mathrm{min}$. Ultimately, the process has generated $(85\,\%)$ 5-HMF yield from cellulose [179].

TABLE 3.4: Evaluation of contribution of monophasic reaction systems to objective function

	Weightage	**Mono-Solvent**			**Multi-Solvent**
		Water	**ILs**	**DMSO**	**Org + ILs**
Cost	1	“Low”	“High”	“Medium”	“Very High”
Non-recoverability	1	“Very High”	“Medium”	“Low”	“High”
Toxicity	1	“Very Low”	“High”	“Low”	“Medium”
Amount	1	“Low”	“Very High”	“Medium”	“High”
Contribution ($RS_{(mono)}$)		2.5	4.0	2.5	4.0

TABLE 3.5: Evaluation of contribution of biphasic reaction systems to objective function

	Weightage	**Reaction Phase**			**Extraction Phase**		
		Water	**NMA**	**DMSO**	**MIBK**	**THF**	**Butanol**
Cost	1	“Very Low”	“Medium”	“High”	“Low”	“Medium”	“High”
Non-recoverability	1	“High”	“Medium”	“Medium”	“Medium”	“Low”	“High”
Toxicity	1	“Very Low”	“Low”	“Low”	“High”	“Medium”	“Low”
Amount	1	“Low”	“Low”	“Medium”	“High”	“Medium”	“Low”
		$RS_{(reaction)}$			$RS_{(extraction)}$		
Contribution ($RS_{(bi)}$)		2.0	2.5	3.0	3.25	2.75	3.0

TABLE 3.6: Evaluation of objective function of 5-HMF production processes

	Energy	**Catalyst**	**Reaction System**	**Yield**	
Weightage	1	1	1	1	
Process ID	**Effect Distribution Among Parameters**				**Total Effect**
1	5.3328	1.6669	2.3750	0.5673	**1.0783**
4	11.7200	1.0976	2.5000	0.1500	**0.6834**
5	10.4350	1.6669	2.5000	0.7928	**1.5375**
6	5.3937	2.3837	4.0000	0.4600	**1.3739**
8	30.6880	2.3837	4.0000	0.4000	**2.0683**
9	9.2867	2.3837	4.0000	0.5900	**1.7180**
10	9.2867	2.3837	4.0000	0.5800	**1.7106**
11	9.2867	2.3837	4.0000	0.7600	**1.8280**
12	9.0880	2.3837	4.0000	0.4000	**1.5398**
20	7.0879	1.8173	4.0000	0.5900	**1.4829**
21	21.6430	2.2368	4.0000	0.4700	**1.9591**
22	18.4250	2.2368	2.6250	0.7600	**1.9150**
23	3.9240	1.2127	2.3750	0.4700	**0.7252**
24	44.8655	1.5059	2.5000	0.4510	**1.8818**
26	19.3108	2.1288	4.0000	0.4860	**1.9026**
27	3.5829	1.4337	4.0000	0.5950	**1.0873**
29	16.2810	1.0976	2.3750	0.3020	**1.1078**
30	32.9030	1.0976	2.3750	0.4670	**1.5893**

Therefore, satisfactory catalytic performance is exhibited by this novel biomass-based carbon catalyst, because of carbon support with Ni metal interactions and its both active Lewis acid and Bronsted sites. Although this process has used hydrothermal conditions at (200 °C) high temperature for 60 min, the conditions make easier the process of dissolving cellulose through energy barrier of the reaction minimization. Then considering the cost of entire process based on the reaction system, water consisting monophasic reaction system in this process has lowered the cost of entire process, creating an eco-friendly path for the production of 5-HMF. As a conclusion, process No. 4 which produces high yield of 5-HMF in comparison to other processes in a cost effective way is selected in this evaluation as the most economical process configuration to be developed and optimized further in future studies.

CHAPTER 4

EXPERIMENTAL DESIGN AND ANALYSIS PROCEDURE

4.1 General procedure for rice straw to 5-HMF conversion

The major components of RS are $42.19\,\% \pm 2.78\,\%$ cellulose, $24.26\,\% \pm 5.39\,\%$ hemicellulose, and $20.83\,\% \pm 3.77\,\%$ lignin on dry weight basis [21]. Low volume high value compounds production, such as cellulose derived 5-HMF, hemicellulose derived furfural, and aromatic chemicals from lignin adds value to RS biorefinery other than bioethanol production [20]. However, the recalcitrance nature of RS itself has direct impact on the recovery process of cellulose, hemicellulose, and lignin, making the pretreatment process extremely slow and cost intensive. Numerous pretreatment procedures including, mechanical (dry ball milling and wet disk milling), acidic, alkaline, stream explosion, liquid hot water, ultrasound, microwave irradiation, organic solvents, ionic liquids, and deep eutectic solvents methods have been investigated well in the literature to slacken the solid structure of RS [1].

As shown in Fig. 4.1, acidic pretreatment methods are highly effective in selective dissolution of hemicellulose present in RS, compared to hydrothermal and alkaline methods. In acidic pretreatment, hydronium ions cause splitting β-1,4-glycosidic bonds inside hemicellulose chains and provide liquid portion mainly consisting solubilized hemicellulose and cellulose/lignin rich residue for further reactions. The most popular acidic pretreatment method to recover hemicellulose is dilute sulphuric acid pretreatment. This is mainly due to its' economic feasibility at large-scale production [106]. However, high temperatures (more than $100\,^{\circ}\mathrm{C}$) used in acidic pretreatment for prolonged time, have degraded certain part of amorphous cellulose which will be required in subsequent 5-HMF conversion. Moreover, high acid loadings, high reaction temperatures, and prolonged reaction time have influenced in escalating the overall cost of the pretreatment process.

Additionally, high temperature treatments require special reactors due to the evaporation of acid solution at $100\,^{\circ}\mathrm{C}$ and atmospheric pressure. Hence, it is required to investigate further on dilute sulphuric acid pretreatment at reduced temperatures for the efficient recovery of hemicellulose with minimum degradation of cellulose. Dilute sulphuric acid pretreatment is not capable to dissolve majority of lignin content except the acid soluble part present in RS [164]. Therefore, after removing hemicellulose, further pretreatment step is required to improve crystalline cellulose accessibility. This can be performed through breaking down lignin sheath which lies on cellulose as shown in Fig. 4.1. Alkaline pretreatments including, NaOH, $Ca(OH)_2$, KOH, and

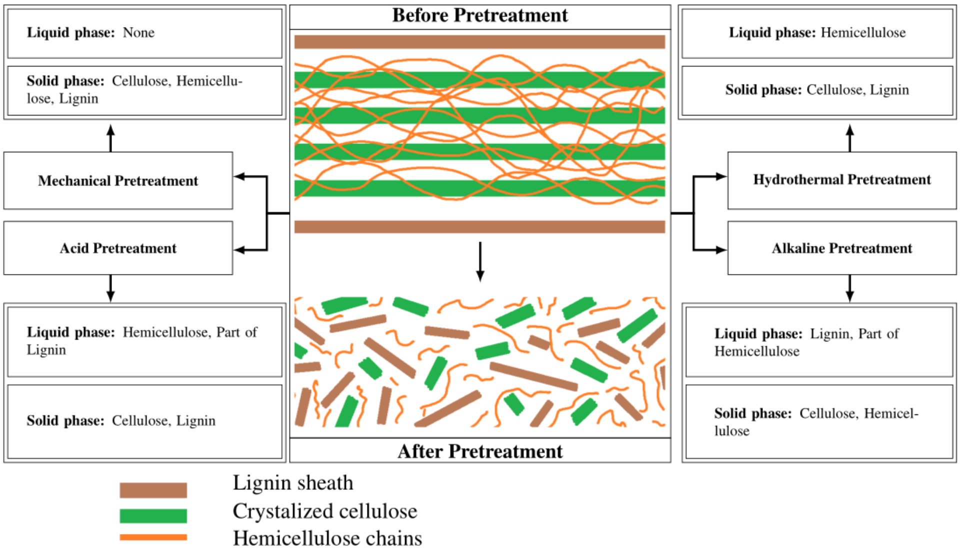


Fig. 4.1: Schematic representation of rice straw pretreatment

ammonia are the most promising methods to dissolve lignin. Among these methods, NaOH pretreatment is the most popular method in perspectives of effectiveness, cost, and large-scale applicability [1]. Application of NaOH saponifies the ester linkages present in lignin and provide liquid portion consisting dissolved lignin and cellulose rich residue for next reaction [164]. However, concentrated NaOH loadings, high reaction temperatures for prolonged time periods have caused to increase the degradation of cellulose and cost of the process. Hence, it is required to investigate further on dilute NaOH pretreatment at reduced temperatures to recover lignin from RS and obtain high amount of cellulose residue for the subsequent 5-HMF conversion process.

After performing pretreatment reactions, the recovered cellulose conversion into 5-HMF is carried out. The most appropriate method to convert cellulose to 5-HMF is selected via the proposed evaluation scheme, considering certain input parameters, including 5-HMF yield, process temperature, process time, reaction system used, and catalyst used. Accordingly, process number 04, 23, and 01 as shown in Table 4.1, were selected as the most feasible processes to produce 5-HMF.

TABLE 4.1: Most feasible cellulose to 5-HMF conversion processes

Parameters	**Process 04**	**Process 23**	**Process 01**
Catalyst used	Biomass based carbon catalyst	$NaHSO_4$ and $ZnSO_4$	HCL
Reaction system used	Aqueous monophasic system	Water/THF Biphasic system	Water/MIBK Biphasic system
Process temperature	200 °C	160 °C	177 °C
Process time	60 min	60 min	60 min
5-HMF yield	85 %	53 %	43 %

However, considering the financial capacity, technology availability, environmental regulations, and human resource availability, feasibility of these processes are subjective to a country, establishing the 5-HMF production plant [1]. Pertaining to Sri Lankan context, lack of financial capacity and technology availability always hinder the 5-HMF production at large-scale. A feasible process should be selected for the optimization at local conditions. Therefore, it is required an evaluation of these three processes considering local conditions.

The evaluation of process number 04, 23, and 01 based on catalyst cost, reaction system cost, and energy cost is shown in Fig. 4.2. Process 04 is the most feasible process which is capable at yielding high amount of 5-HMF ($85\,\%$), using Ni-doped biomass-based carbon catalyst (Nin/CS). However, considering catalyst cost, process 04 is having the highest cost due to its cost intensive catalyst synthesis methods. Process 23 also shows a higher cost compared to process 01, because it consumes high amount of catalysts ($NaHSO_4$ and $ZnSO_4$ ($2.3\,\mathrm{mol\,dm^{-3}}$)) in the conversion process. Process 01 shows the lowest catalyst cost due to the usage of dilute hydrochloric acid solution (0.1285mol/dm-3). Dilute hydrochloric acid is less environmentally friendly, and it produces moderate 5-HMF yield. However, its low price, robust handling practices, and easy accessibility have made it as the most feasible catalyst at Sri Lankan conditions. Based on reaction system cost, process 04 represents the lowest cost due to the application of cost-effective water based monophasic system, which is also considered as a green method at large-scale operations. However, a sole aqueous medium can be inefficient to produce high 5-HMF yields because of 5-HMF repolymerization and rehydration reactions. Process 23 shows the highest cost due to its water/ tetrahydrofuran (THF) biphasic system. Even though THF is effective at increasing 5-HMF yield, its higher price than methyl isobutyl ketone (MIBK) in process 01, has made it difficult in using 5-HMF production at Sri Lankan context. MIBK is also efficient at

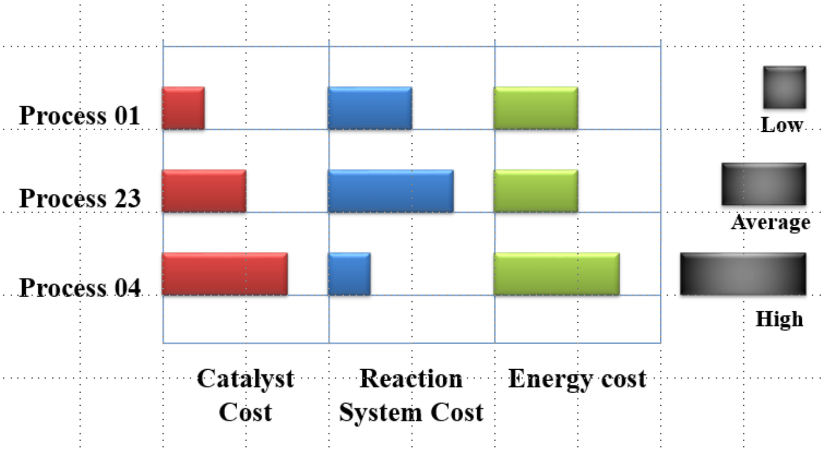


Fig. 4.2: Evaluation of most feasible processes to select locally feasible process

5-HMF extraction, and hence it can be considered as a good alternative to develop a locally feasible 5-HMF production process. Both reaction time and temperature shows a strong effect on determining energy cost of these processes. According to the energy cost analysis of process 04, 23, and 01, the highest cost is showed by process 04 as it operates at 200 °C for 60 min. Process 23 and 01 have shown average costs compared to process 04, because the temperatures are within 160-177 °C for 60 min. Eventually, considering all three parameters (catalyst, reaction system, and energy costs), process number 01 has shown low catalyst cost, low reaction system cost, and average energy cost at Sri Lankan context. Therefore, process 01 can be selected as the most feasible process to be optimized at local conditions. Finally, the proposed general procedure to convert RS into 5-HMF is presented in Fig. 4.3.

4.2 Experimental design using response surface methodology

Optimization of the conversion of RS to 5-HMF is performed, applying response surface methodology (RSM), instead of time consuming and conventional optimization methods, like one factor at one time approach. As advanced design of experiments (DOE) techniques, response surface designs are helpful in superior understanding and optimizing the responses. Response surface equations model the effects of changes (linear, quadratic, and interactions) in independent variables to a certain response variable of interest. Moreover, compared to factorial designs, response surface designs facilitate to detect the levels of each independent variable that optimize the response, performing few experimental runs.

The general methodology of RSM is presented in Fig. 4.4 which is adapted from “response surface methodology. in: Design and Analysis of Experiments (2017). Springer Texts in Statistics for the optimization”. As per to the methodology, literature-based screening test is performed to find out effective factors that highly and directly influence the process cost in pretreatments and catalytic conversion of cellulose into 5-HMF

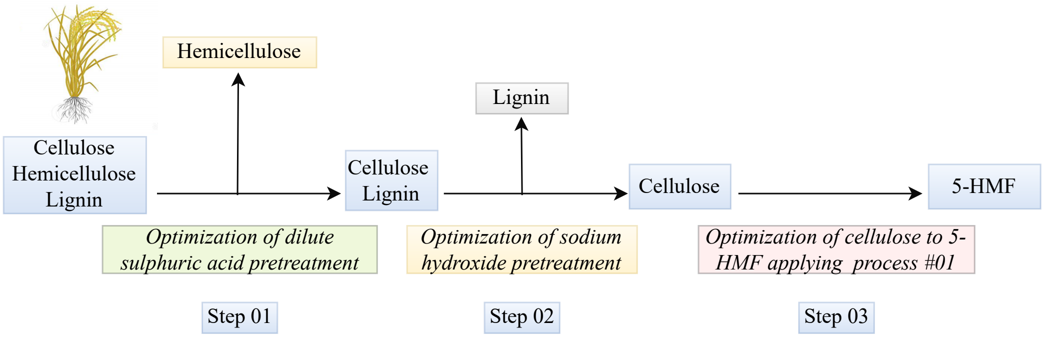


Fig. 4.3: General procedure for conversion of RS to 5-HMF

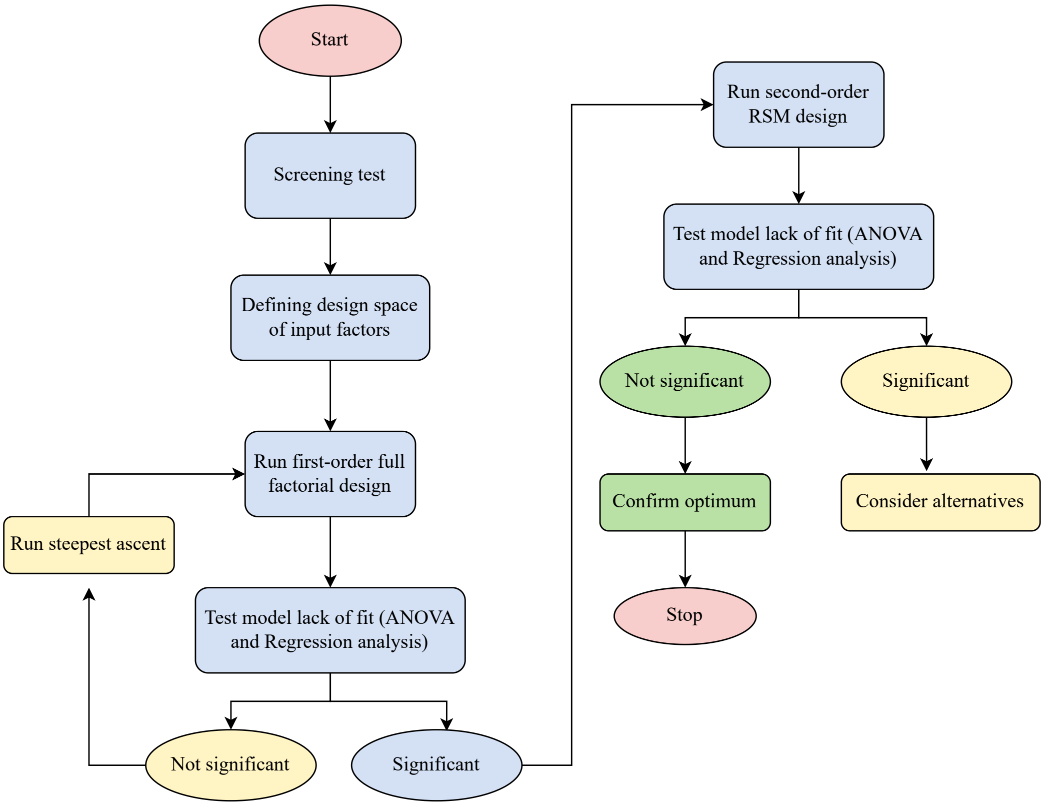


Fig. 4.4: Adapted response surface methodology for optimization

process. The design space of input factors is determined via literature-based analysis. Then, using a first order polynomial model and a full factorial design the vicinity of the optimum region is found out. After testing the model lack of fit via ANOVA and regression analysis, if the model was not significant steepest ascent method is used to find out the optimum region. If the model lack of fit is significant, a response surface methodology design employed for the finding of optimal conditions of the input factors.

There are two main types of classical response surface designs in RSM as central composite designs and Box-Behnken design. Moreover, central composite designs consist of three types designs as central composite circumscribed, central composite inscribed, and central composite face centered. The desirable properties of these designs include:

1. Rotatability or constant distribution of prediction variance at all points across the experimental region
2. Minimized residuals via as much as possibly close fitted values to observed values

TABLE 4.2: Comparison of structural differences in classical response surface designs for three factor experiments.

CCC (CCI)				**CCF**				**Box-Behnken**			
1	-1	-1	-1	1	-1	-1	-1	1	-1	-1	0
1	+1	-1	-1	1	+1	-1	-1	1	+1	-1	0
1	-1	+1	-1	1	-1	+1	-1	1	-1	+1	0
1	+1	+1	-1	1	+1	+1	-1	1	+1	+1	0
1	-1	-1	+1	1	-1	-1	+1	1	-1	0	-1
1	+1	-1	+1	1	+1	-1	+1	1	+1	0	-1
1	-1	+1	+1	1	-1	+1	+1	1	-1	0	+1
1	+1	+1	+1	1	+1	+1	+1	1	+1	0	+1
1	-1.682	0	0	1	-1	0	0	1	0	-1	-1
1	1.682	0	0	1	+1	0	0	1	0	-1	-1
1	0	-1.682	0	1	0	-1	0	1	0	+1	+1
1	0	1.682	0	1	0	+1	0	1	0	+1	+1
1	0	0	-1.682	1	0	0	-1	3	0	0	0
1	0	0	1.682	1	0	0	+1				
6	0	0	0	6	0	0	0				
Total runs = 20				**Total runs = 20**				**Total runs = 15**			

3. Fewer experimental runs
4. Checking of constant variance
5. Internal estimate of error
6. Estimation of transformation
7. Superior detection in lack of fit
8. Building stepwise designs, from simpler designs to higher order designs
9. Superior graphical analysis using simple data patterns

Table 4.2. elaborates the structure of each response surface design, considering three factor optimization experiment. As identical designs, CCC and CCI are shown in combined mode.

Selection of an appropriate response surface design is performed, considering the properties of each response surface design as shown in Table 4.3.

Considering the properties of each design, CCC is selected as the appropriate response surface design type as it explores the largest process space, providing high-quality prediction. Schematic representation of the CCC for three factor experiment is shown in Fig. 4.5.

TABLE 4.3: Comparison of structural differences in classical response surface designs for three factor experiments.

Response surface design type	**Description**
Central composite circumscribed design (CCC)	• Delivers superior prediction on the whole design space • Considering factorial part, it needs factor settings outside the range of factors, thus establishing new extremes (axial/star points) for high and low settings of all the factors • The desired properties and design factors number determine star points distance from center point of the design • Required 5 levels for each factor
Central composite inscribed design (CCI)	• Compared to CCC, factor settings are utilized in CCI for star points and within the originally specified factor ranges, it is used to create factorial or fractional factorial design • Therefore, non-delivery of superior prediction for the whole design space • Require 5 levels for each factor
Central composite face centered (CCF)	• Provides comparatively superior prediction for the whole design space • In the outside of original factor settings, there are no need of star points • Require 3 levels for each factor
Box-Behnken design	• Shows a small number of design points, compared to central composite designs, and hence a cost-effective design for same number of factors • Efficient estimation of linear and quadratic coefficients • Does not include runs of factors in their extreme settings, thus containing regions of poor prediction quality similar to CCI designs • Require 3 levels for each factor

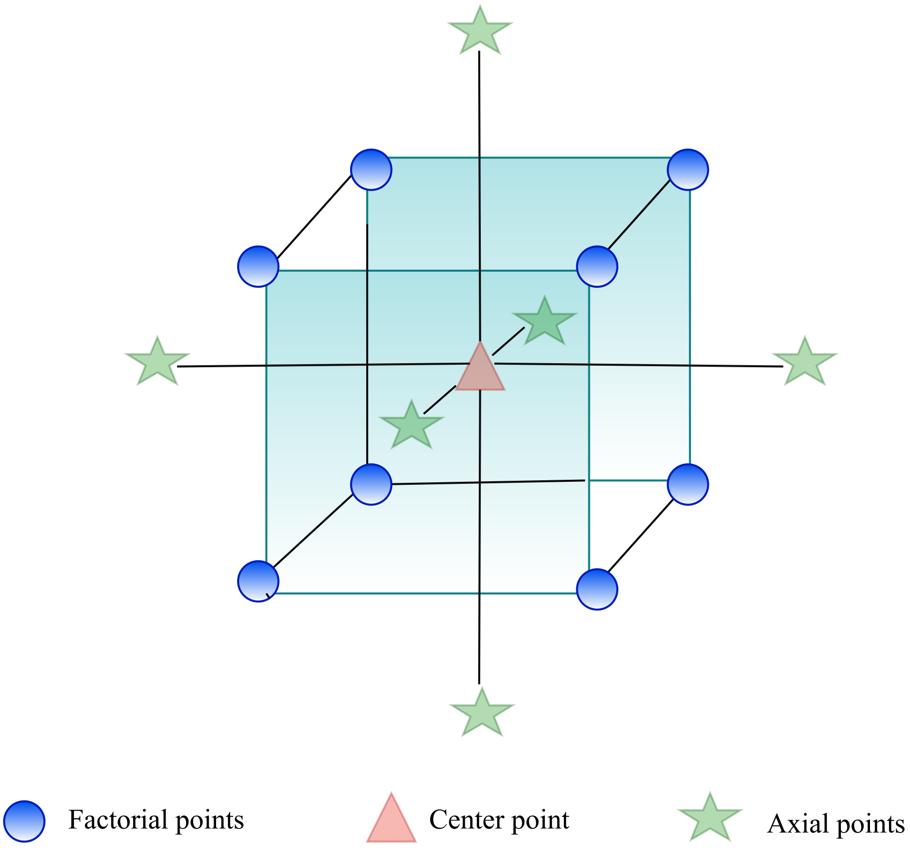


Fig. 4.5: Schematic representation of three factor central composite design

The distance of a star point from center point is based on CCC factorial potions' units of experimental runs as indicated in equation (4.1).

$$\alpha = (2^k)^{(1/4)} \tag{4.1}$$

Where, α and 2^k denote a star point distance from the center point and number of full factorial runs, respectively. The CCC designs used in pretreatment of RS and conversion of cellulose into 5-HMF have followed the above-mentioned equation to maintain the rotatability of all designs.

4.3 Statistical analysis procedure

The second order polynomial regression model is employed in statistical analysis to characterize relationships in terms of linear, quadratic, and interactions among the independent variables and the response variable. The proposed model for each pretreatment and cellulose to 5-HMF conversion process is given in equation (4.2).

$$Y_i = \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j + \epsilon \tag{4.2}$$

where Y_i represents the predicted response variable; X_i and X_j are the independent variables that influence the response variable Y_i; β_0 is the interception coefficient; β_i, β_{ii}, and β_{ij} are the partial regression coefficients of independent variables in terms of linear, quadratic, and interactions. ϵ is the random error.

MATLAB software simulations are used to conduct regression analysis of experimental data to estimate main effects and interaction effects of each independent variable. Statistical significance of partial regression coefficients is determined by performing Student's t-test (t-test). Software based analysis of variance (ANOVA) is performed for the identification of source of each component variation and test for their statistical significance at 0.05, a specified α level. Adequacy of the proposed model is expressed using determination coefficient (R^2), and Fischer's test (F-test) is used to determine its' statistical significance. Residual analyses are performed to validate assumption on error terms. Finally, parameters require to be included in the models are selected based on their statistical significance, using F-test.

CHAPTER 5

OPTIMIZATION OF RS TO CELLULOSE CONVERSION

5.1 Dilute Acid Pretreatment

The dilute sulfuric acid pretreatment is optimized, employing low operating temperatures ($< 100\,^{\circ}\mathrm{C}$), low acid concentrations ($< 0.3\,\mathrm{mol\,dm^{-3}}$), and moderate reaction time (<45 min) to recover hemicellulose from RS. Here, RSM based central composite experimental design is applied to optimize dilute sulfuric acid pretreatment. The effect of each pretreatment parameter is investigated, performing a comprehensive statistical analysis. Qualitative analysis of recovered hemicellulose is carried out to verify the results of statistical analysis. Additional experiments have also been carried out to validate optimization conditions as determined by RSM.

5.1.1 Materials

Unprocessed RS was obtained from local farmers in Anuradhapura area. The raw material was cut into pieces and washed thoroughly using tap water to remove impurities, such as dirt and sand. Seven days in ambient temperature, was used to air dry the washed RS. Dried RS was ground as shown in Fig. 5.1, and it was sieved through a mesh 0.18mm for homogeneity maintenance. At temperature $105\,^{\circ}\mathrm{C}$ for 24 hours, was used to dry RS powder and then stored in a desiccator until used for pretreatment. Sigma-Aldrich ACS grade reagents were taken and utilized as receipt.

5.1.2 Design of experiments

The literature-based screening of parameters was carried out to identify the most significant factors in dilute sulfuric acid pretreatment. Sulfuric acid concentration, reaction temperature, reaction time, and ratio of RS to acid solution loading are the main

Fig. 5.1: Dried rice staw.

parameters, affecting hemicellulose yield. However, in this study, sulfuric acid concentration, reaction temperature, and reaction time have been selected as the critical factors based on their direct influence on both hemicellulose yield and pretreatment process cost. Ratio of RS to pretreatment solution loading (1:20, w/v) was maintained constant in all experiments.

Design of experiments was conducted through two stages. At the first stage, the design space of each input factor was decided, applying one factor at a time approach (OFAT) and results obtained from previous studies. In the second stage, the levels of each input factor were optimized, using central composite design (CCD) method in RSM. CCDs are capable to establish high quality prediction over the entire design space, providing independent variables estimations and for the response variable, fitting a quadratic polynomial regression model. However, in the factorial part, CCDs require, computing appropriate outside factor settings from factors boundaries. Therefore, an experimental design was developed, setting the distance of the axial points from center points (α value) equals to $(2^{n^{\frac{1}{4}}})$ without using software simulations. In the resulted CCD, there were 20 experimental runs, including factorial runs 1 to 8 , axial point runs 9 to 14, and center point runs 15 to 20. Adding 5 center points runs were essential to estimate pure error squares sum in the design of experimental. Independent variables and the corresponding coded values for the response surface analysis are shown in Table 5.1. There, X_1,X_2, and X_3 in accord with sulfuric acid concentration, reaction temperature, and reaction time, respectively. These variables were coded, using equation (5.1), where, the coded value of the dimensionless independent variable X_i is denoted by x_i. X_0 is the actual value of X_i at the center point and ΔX_i is the step change value of X_i.

$$x_i = \frac{1}{\Delta X_i}\left(X_i - X_o\right), \quad i = 1, 2, 3. \tag{5.1}$$

5.1.3 Rice straw pretreatment

RS pretreatment was carried out in a water bath (J.P. SELECTA, 3001373), and utilizing falcon tubes $50\,\mathrm{mL}$. Oven dried $1\,\mathrm{g}$ of RS was subjected to pretreatment, adding $20\,\mathrm{mL}$ of dilute sulfuric acid solution, and employing the conditions indicated in Table 5.1. High temperature ($> 100\,°\mathrm{C}$) experiments were conducted in an oven (memmert, UF 110). After allowing the reaction to happen for specified times, samples were kept

TABLE 5.1: Actual and coded values of independent variables in acid pretreatment

Factor	**Variable**	**-1.682**	**-1**	**0**	**1**	**1.682**
Acid concentration ($\mathrm{mol\,dm^{-3}}$)	X_1	0.03	0.10	0.20	0.30	0.37
Reaction temperature ($°\mathrm{C}$)	X_2	46.36	60	80	100	113.64
Reaction time (min)	X_3	4.77	15	30	45	55.23

in a cool bath to prevent further reaction.

5.1.4 Hemicellulose recovery and characterization

Hemicellulose rich filtrate as shown in Fig. 5.2, was separated after the pretreatment via Buchner filtration and reduced its' volume under vacuum. Then, ethanol tenfold volume (absolute, 99.8 %) was put in and remained for 24 hours at 4 °C to precipitate hemicellulose, and precipitated hemicellulose is shown in Fig. 5.3.

Finally, hemicellulose precipitates were recovered 3500 g, 10 min centrifugation. After vacuum drying the hemicellulose precipitate was obtained and it is shown in Fig. 5.4. The schematic representation of the dilute sulphuric acid pretreatment is illustrated in Fig. 5.5.

Fig. 5.2: Hemicellulose rich rice straw pretreated filtrate

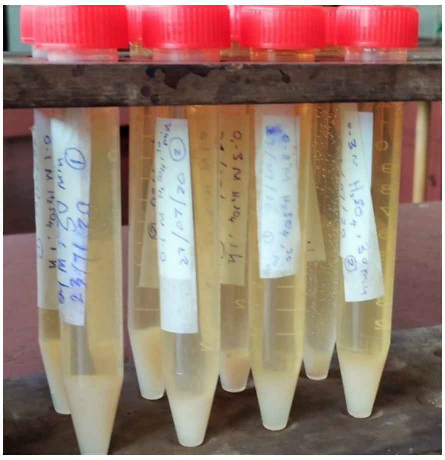


Fig. 5.3: Precipitated hemicellulose after keeping at 4 °C for 24 hours

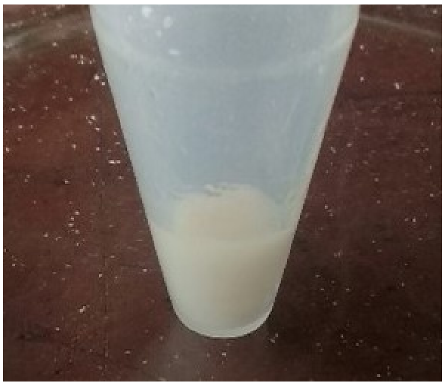


Fig. 5.4: Recovered hemicellulose from rice straw

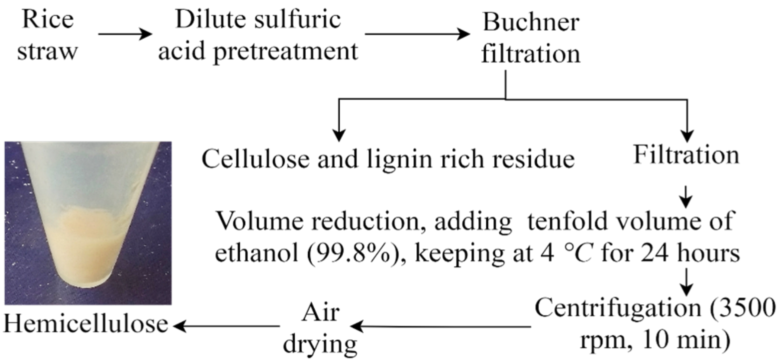


Fig. 5.5: Schematic representation of dilute acid pretreatment process

Hemicellulose yield was measured using a gravimetric method [247] and the yield was expressed as a percentage of hemicellulose dry weight per $1\,\mathrm{g}$ of dried RS. Characterization of the recovered hemicellulose was carried out using Fourier Transform Infrared Spectroscopy (FTIR) analysis. Bruker ALPHA spectrometer (Bruker Corporation, Billerica, MA) with a resolution of $1\,\mathrm{cm}^{-1}$ was used to obtain the FTIR spectra and recorded in the range of 600 to $4000\,\mathrm{cm}^{-1}$.

5.1.5 Results and discussion

FTIR study is a facile procedure for qualitative and quantitative determination of RS components in IR region of the spectrum. Therefore, FTIR analysis results were used for the recovered solid residue identification which was hemicellulose. The FTIR spectrum, showing the peak positions related to different functional groups in hemicellulose is presented in Fig. 5.6. The results are characteristic of hemicellulose. The region of absorption band at 850 to $1200\,\mathrm{cm}^{-1}$ is unique for hemicellulose. $877.14\,\mathrm{cm}^{-1}$ absorption band has indicated β-1,4 glycosidic linkages (C–O–C) between sugar units in hemicellulose.

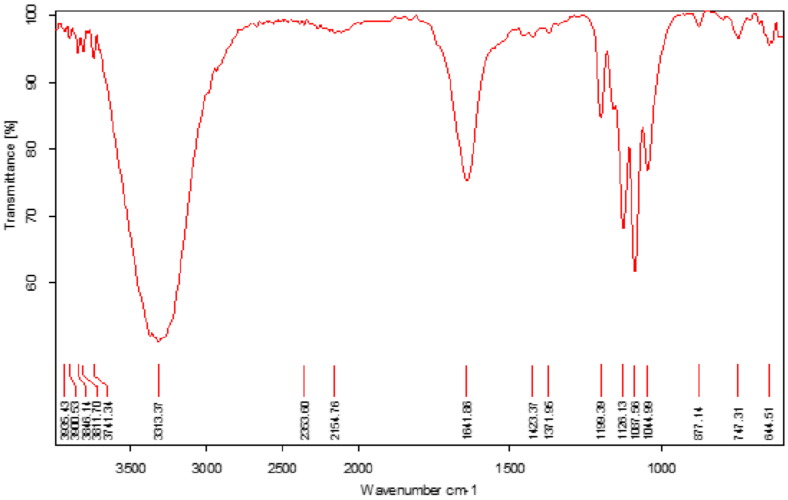


Fig. 5.6: FTIR spectrum of recovered hemicellulose

The strongest absorption bands at $1044.99\,\mathrm{cm}^{-1}$, $1087.56\,\mathrm{cm}^{-1}$, and $1126.13\,\mathrm{cm}^{-1}$ are attributed to C–O, C-OH bending, and C–C stretching in xylan and galactan side chains present in hemicellulose, respectively. Absorption band at $1199.39\,\mathrm{cm}^{-1}$ is typical to C-O stretching vibrations. Since hemicellulose has strong affinity with water, bending mode of water is indicated at band intensity of $1641.86\,\mathrm{cm}^{-1}$. $3313.37\,\mathrm{cm}^{-1}$, the strongest absorption band has shown the O-H stretching vibrations between sugar units [148, 248–250].

Hemicellulose yield obtained for all treatments by applying CCD experimental design are presented in Table 5.2.

Developed second order polynomial regression model for hemicellulose recovery in terms of coded variables is given in equation (5.2), where X_1,X_2, and X_3 represent the applied sulfuric acid concentration, reaction temperature, and reaction time, respectively. For the developed model, predicted responses are obtained by applying X_1, X_2, and X_3 actual values. A close agreement has been observed between the predicted and experimental responses.

$$Y = 14.11 + 1.56X_1 + 2.67X_2 + 0.59X_3 - 1.28X_1^2 - 1.46X_2^2 - 2.31X_3^2 \qquad (5.2)$$

Regression analysis is performed for the determination of relationship between independent variables and the response variable. Regression coefficients of each independent variable, standard errors, results of t-test, and p-values are shown in Table 5.3. The p-values are used for the determination of the significance of each independent variable for the response in terms of first order, interaction, and quadratic effects.

TABLE 5.2: Coded and actual values of independent variables

Exp[1]	**Coded variables**			**Hemicellulose yield %**		**Error**
	X_1	X_2	X_3	**Observed**[2]	**Predicted**	
1	-1	-1	-1	3.5	3.6745	-0.17450
2	1	-1	-1	5.8	7.0417	-1.24167
3	-1	1	-1	9.7	9.9608	-0.26081
4	1	1	-1	13.6	13.1780	0.42203
5	-1	-1	1	4.4	5.9127	-1.51270
6	1	-1	1	8.1	8.9299	-0.82985
7	-1	1	1	10.6	10.4490	0.15100
8	1	1	1	12.4	13.3161	-0.91614
9	-1.682	0	0	8.4	7.8574	0.54255
10	1.682	0	0	14.1	13.1005	0.99950
11	0	-.1.682	0	7.2	5.4911	1.70885
12	0	1.682	0	14.3	14.4668	-0.16678
13	0	0	-1.682	6.8	6.5797	0.22028
14	0	0	1.682	9.9	8.5782	1.32178
15	0	0	0	14.2	14.1106	0.08942
16	0	0	0	14.5	14.1106	0.38942
17	0	0	0	13.8	14.1106	-0.31058
18	0	0	0	14.3	14.1106	0.18942
19	0	0	0	13.5	14.1106	-0.61058
20	0	0	0	14.1	14.1106	-0.01058

Small p-values (< 0.05) and large t-test values reveal the significance of corresponding regression coefficient term. It is observed that positive first order effects of sulfuric acid concentration and temperature, negative quadratic effects of sulfuric acid concentration, temperature, and time are statistically significant on hemicellulose recovery. However, main effect of time and interaction effects of each independent variable combination are not statistically significant on the response. Similar results have been shown by Kim et al. However, according to their study, when the experiments were

---

[1] Experiment number

[2] Mean of triplicate determination.

[3] Acid concentration

[4] Temperature

TABLE 5.3: Regression analysis of proposed model for hemicellulose recovery from rice straw

Term	**Estimate**	**Standard error**	**t-stat**	**p-value**
(Intercept)	14.1106	0.4534	31.1204	2.7554×10^{-11}
Conc[3]	1.5586	0.3008	5.1812	4.1238×10^{-4}
Temp[4]	2.6681	0.3008	8.8697	4.7168×10^{-6}
Time	0.5941	0.3008	1.9749	7.6515×10^{-2}
Conc×Temp	-0.0375	0.3930	-0.0954	9.2588×10^{-1}
Conc×Time	-0.0875	0.3930	-0.2226	8.2832×10^{-1}
Temp×Time	-0.4375	0.3930	-1.1131	2.9171×10^{-1}
$Conc^2$	-1.2836	0.2927	-4.3841	1.3686×10^{-3}
$Temp^2$	-1.4604	0.2927	-4.9877	5.4716×10^{-4}
$Time^2$	-2.3087	0.2927	-7.8850	1.3364×10^{-5}

conducted at high temperature range (90 to 190 °C), positive main effect of time was significant on hemicellulose recovery [108]. Similarly, Roberto and co-workers have indicated a significant main effect of time at 121 °C on xylose recovery from RS [251].

Lack of fit was not detected in the model developed, which has indicated a high R^2-value of 0.953. Generally, high R^2-values show high reliability between predicted and observed data. However, adjusted R^2 statistic (R^2_{adj}) is also estimated to obtain an accurate measurement of the amount of reduction in variability of the response by using these independent variables. Similitude between R^2 (0.953) and R^2_{adj} (0.910) has implied that the regression model developed is adequate to explain the variability in the response. The results obtained from ANOVA analysis are presented in Table 5.4. ANOVA is required to partition the total variation observed in responses into various components and test the developed model adequacy. Here, the variability is given by sum of squares (SS) of components. However, more realistic measure of variability is given by mean square (MS) values, which are the results of SS corrected for number of observations. According to the developed model, the total observed variability can be partitioned into SS due to model and SS due to experimental error. Testing the ratio of MSmodel and MSerror against unity (F-test) is needed for the model adequacy checking. There, 22.4, F-test value, indicates that the proposed regression model can explains the observed variation in hemicellulose yield in this study. Very low p-value ($p < 0.05$) associated with F-test statistic confirms further that the model is significant at 95 % of confidence level. In addition, Table 5.4 shows p-values for the F-test statistics related to each component variation. These test statistics confirms further the results obtained from the regression analysis.

---

[5] Acid concentration

[6] Temperature

TABLE 5.4: Analysis of variance for hemicellulose recovery from rice straw

Source of Variation	Sum of Squares	DOFc	Mean Squares	F-stat	p-value
Conc[5]	33.1780	1	33.1780	26.8445	4.1238×10^{-4}
Temp[6]	97.2331	1	97.2331	78.6718	4.7168×10^{-6}
Time	4.8205	1	4.8205	3.9003	7.6515×10^{-2}
Conc:Temp	0.0112	1	0.0112	0.0091	9.2588×10^{-1}
Conc:Time	0.0612	1	0.0612	0.0495	8.2832×10^{-1}
Temp:Time	1.5312	1	1.5312	1.2389	2.9171×10^{-1}
$Conc^2$	23.7551	1	23.7551	19.2204	1.3686×10^{-3}
$Temp^2$	30.7467	1	30.7467	24.8773	5.4716×10^{-4}
$Time^2$	76.8422	1	76.8422	62.1735	1.3364×10^{-5}
Error	12.3593	10	1.2359	1	5.0000×10^{-1}

Three-dimensional (3D) response surface mesh graphs are helpful in: (I) visualizing the relationships among response variable and each independent variable experimental levels, (II) interactions identification, and (III) determining approximate optimal point of each variable required to obtain maximum response. The response surfaces of sulfuric acid concentration, reaction temperature, reaction time, and the hemicellulose yield are illustrated in Fig. 5.7, Fig. 5.8, and Fig. 5.9. Here, keeping the third coded variable at zero, each response surface has shown two independent variables.

Fig. 5.7 clearly shows the significant first order and quadratic effects of both acid concentration and reaction temperature on hemicellulose recovery. A significant interaction between reaction temperature and acid concentration is not visible in that region. Quadratic relationship of acid concentration and reaction time are depicted in Fig. 5.8, where significant interaction is not present. According to Fig. 5.7 and Fig. 5.8, quadratic terms of reaction temperature and reaction time show more impact on hemicellulose dissolution than that of acid concentration. As observed in Fig. 5.9, reaction time has a more prominent quadratic effect, compared to the quadratic effect of reaction temperature.

Error terms are tested for normality performing a residual analysis as shown in Fig. 5.10. The residual plot shows a systematic pattern of residuals, lying around zero and within a fixed band. Therefore, any major violation of underlying assumption on error term and proposed model lack of adequacy are not observed.

The response surfaces in Fig. 5.7, Fig. 5.8, and Fig. 5.9 indicate the existence of a maxima within the domain of interest. Therefore, the partial derivatives of the developed model in equation (5.3) are used to identify the operating point of maximum yield. The system, which defined the maximum point of yield using partial derivatives of each variable, can be represented in matrix form as given in equation (5.3), where C, θ, and t are acid concentration, reaction temperature, and reaction time coded values, relevantly. The non-zero determinant of coefficient matrix validates the existence of maxima for the system defined in equation (5.3).

$$\begin{bmatrix} -2.5673 & -0.0375 & -0.0875 \\ -0.0375 & -2.9208 & -0.4375 \\ -0.0875 & -0.4375 & -4.6174 \end{bmatrix} \begin{bmatrix} C \\ \theta \\ t \end{bmatrix} = \begin{bmatrix} -1.5586 \\ -2.6681 \\ -0.5941 \end{bmatrix} \tag{5.3}$$

The solution of equation (5.3) is decoded to extract the actual temperature, using the step size and the center point of each variable as listed in Table 5.5. Accordingly, the maximum hemicellulose yield ($15.78\,\%$) is observed at optimal pretreatment condition. Further experiments carried out to validate the results gave hemicellulose yield of $14.8\,\%$ at optimal conditions and is in close agreement with the predicted result, thus

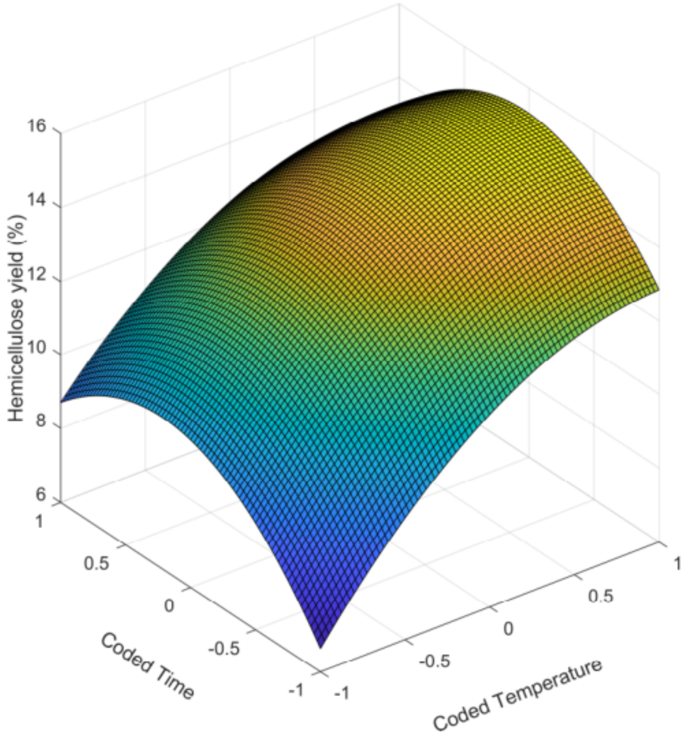


Fig. 5.7: Response surface analysis of coded time and temperature vs yield confirming the pretreatment process optimization, carried out using Sri Lankan RS.

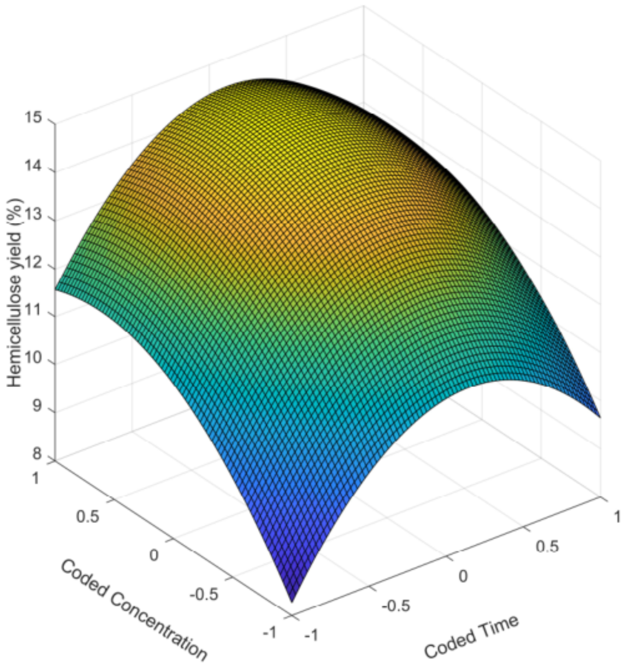


Fig. 5.8: Response surface analysis of coded concentration and time vs yield

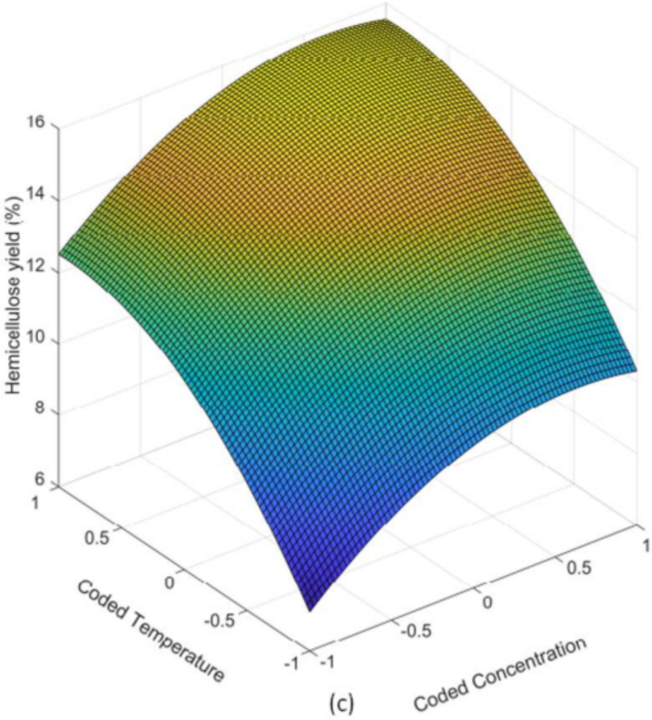


Fig. 5.9: Response surface analysis of coded temperature and concentration vs yield

Table 5.6 has shown the optimization results of similar acid pretreatments, conducted in different countries in the world. In most studies, they have expressed the hemicellulose yield as the percentage of solubilized xylose (the major sugar constituent in hemicellulose) and have not clearly indicated the extracted amount of hemicellulose

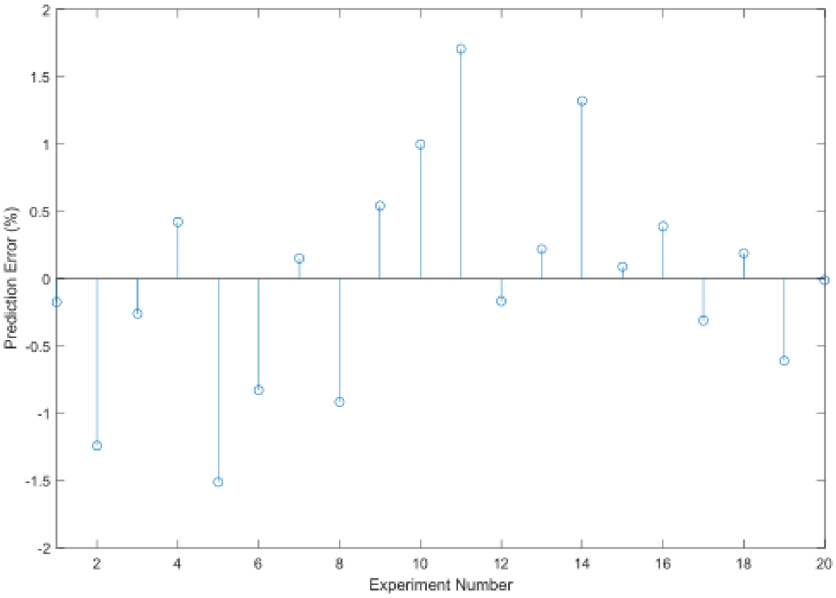


Fig. 5.10: Analysis of predicted error vs experiment number

TABLE 5.5: Optimum operating conditions for maximum hemicellulose yield

Optimal Condition	**Coded Value**	**Actual Value**
Acid concentration	0.5928	0.2593 $\mathrm{mol\,dm^{-3}}$
Reaction temperature	0.9011	98.0129 °C
Reaction time	0.0320	30.4807 min

TABLE 5.6: Comparison of rice straw acid pretreatments carried out in different countries

Country	**Solubilized xylose**	**Acid concentration**	**Temperature**	**Time**	**Ref**
Korea	76.31%	12%	110 °C	14.02 min	[108]
Brazil	77%	1 %	121 °C	27 min	[251]
India	31.9 $\mathrm{g\,L^{-1}}$	035%	162 °C	10 min	[106]
China	83.2%	10%	100 °C	120 min	[252]
Iran	80.8%	05%	201 °C	10 min	[253]

from RS in dry weight basis. According to these results, high temperatures ($>$180 °C) and short reaction times ($<$ 10 min) dissolve high amount of xylose. Conversely, 30-90 min longer reaction times need around 120 °C for high amount xylose dissolution [1, 108]. These optimal conditions are successful to dissolve RS xylose more than 90 %. However, by analyzing the hemicellulose rich hydrolysate, it can be identified around 50 % of dissolved xylose as xylose . The reason is xylose degradation and formation of pseudolignin [106]. Contrastly, the proposed low-cost dilute acid pretreatment has provided high quality hemicellulose. Here, the hemicellulose recovery can be enhanced when dilute acid pretreatment is combined with physical methods, such as ultrasound treatment and microwave irradiation [1]. Therefore, future studies are needed to develop combined dilute acid pretreatment to increase hemicellulose recovery from RS at reduced temperatures.

5.2 NaOH Pretreatment

Sodium hydroxide pretreatment is optimized, employing low operating temperatures ($<$ 100 °C), low NaOH concentrations ($<$ 0.5 $\mathrm{mol\,dm^{-3}}$), and moderate reaction time ($<$ 180 min) to recover lignin from RS. Here also the response surface methodology is applied to find out optimal pretreatment conditions to recover the maximum amount of lignin. RSM based central composite experimental design is used to optimize the pretreatment. The effect of each pretreatment parameter is investigated, performing a comprehensive statistical analysis. Finally, additional experiments have also been carried out to validate optimization conditions as determined by RSM.

5.2.1 Materials

Hemicellulose extracted RS residue was washed using distilled water. Then at $105\,^{\circ}\mathrm{C}$, the residue was subjected to dry for 24 hours and stored in desiccator until used for experiments. Sigma-Aldrich ACS grade reagents were taken and utilized as receipt.

5.2.2 Design of experiments

The literature-based screening of parameters was carried out to identify the most significant factors in NaOH pretreatment. NaOH concentration, reaction temperature, reaction time, and ratio of RS to alkaline solution loading are the main parameters, affecting lignin yield. However, in this study, NaOH concentration, reaction temperature, and reaction time have been selected as the critical factors based on their direct influence on both lignin yield and pretreatment process cost. Ratio of RS to pretreatment solution loading (1:20, w/v) was maintained constant in all experiments. Similar to the acid pretreatment process, design of experiments was conducted through two stages. At the first stage, the design space of each input factor was decided, applying one factor at a time approach (OFAT) and results obtained from previous studies. In the second stage, the levels of each input factor were optimized, using central composite design (CCD) method in RSM. Independent variables and the corresponding coded values for the response surface analysis are shown in Table 5.7. There, X_1,X_2, and X_3 correspond to NaOH concentration, reaction temperature, and reaction time, respectively. These variables were coded, using previously mentioned standard equation (5.1).

5.2.3 Rice straw pretreatment

Pretreatment was carried out in a water bath (J.P. SELECTA, 3001373), utilizing falcon tubes $50\,\mathrm{mL}$. As shown in Fig. 5.11, oven dried RS residue $1\,\mathrm{g}$ was subjected to pretreatment, adding $20\,\mathrm{mL}$ of NaOH solution, and employing the conditions indicated in Table 5.7. High temperature (greater than $100\,^{\circ}\mathrm{C}$) experiments were conducted in an oven (memmert, UF 110). After allowing the reaction to happen for specified times, samples were kept in a cool bath to prevent further reaction.

TABLE 5.7: Actual and coded values of independent variables in NaOH pretreatment

Factor	**Variable**	**-1.682**	**-1**	**0**	**1**	**1.682**
NaOH concentration ($\mathrm{mol\,dm^{-3}}$)	X_1	0.35	0.5	1.75	3.0	3.85
Reaction temperature ($^{\circ}\mathrm{C}$)	X_2	46.36	60	80	100	113.64
Reaction time (min)	X_3	19.08	60	120	180	220.92

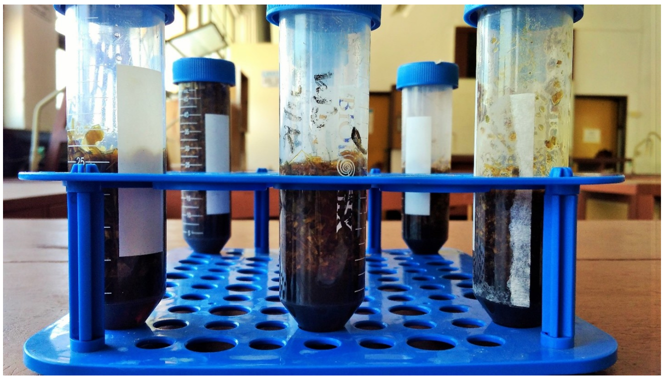


Fig. 5.11: Sodium hydroxide pretreated rice straw

5.2.4 Lignin recovery

Lignin rich filtrate (black liquor) as shown in Fig. 5.12, was separated after the pretreatment via Buchner filtration. The filtrate was acidified with $6\,\mathrm{mol\,dm^{-3}}$ HCl until pH 1 was reached. It was kept for 24 hours to allow the precipitation of lignin as shown in Fig. 5.13. Finally, the precipitated lignin as shown in Fig. 5.14, was collected through $3500\,\mathrm{g}$ centrifugation for 10 min, and then air dried.

Lignin yield was measured using the same gravimetric method [247], and the yield was expressed as a percentage of lignin dry weight per $1\,\mathrm{g}$ of dried RS residue. The schematic representation of dilute sodium hydroxide pretreatment is illustrated in Fig. 5.15

5.2.5 Results and discussion

Lignin yield obtained for all treatments by applying CCD experimental design are presented in Table 5.8. Developed second order polynomial regression model for lignin

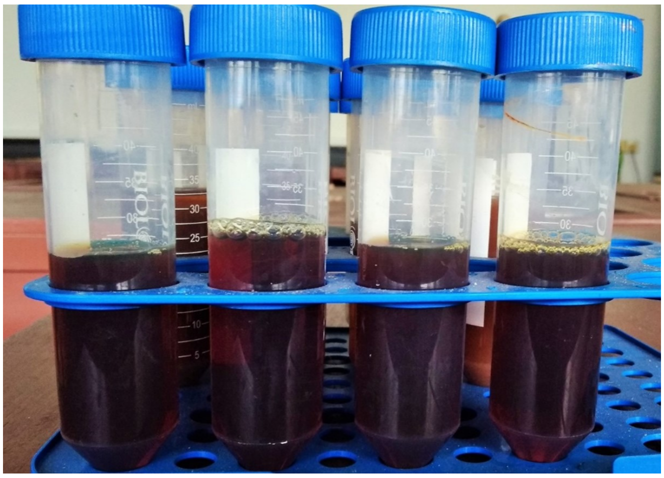


Fig. 5.12: Lignin rich rice straw filtrate

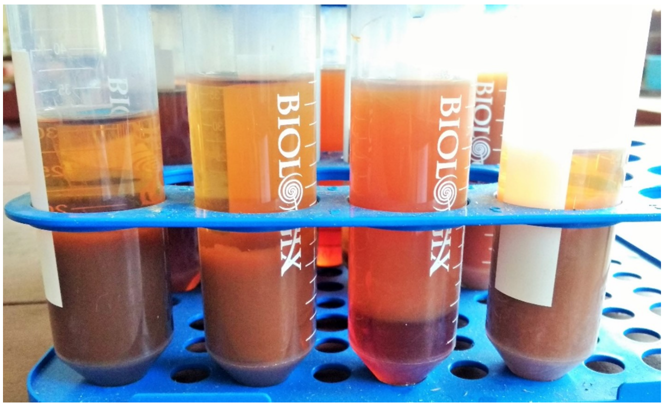


Fig. 5.13: Precipitation of lignin at pH 1

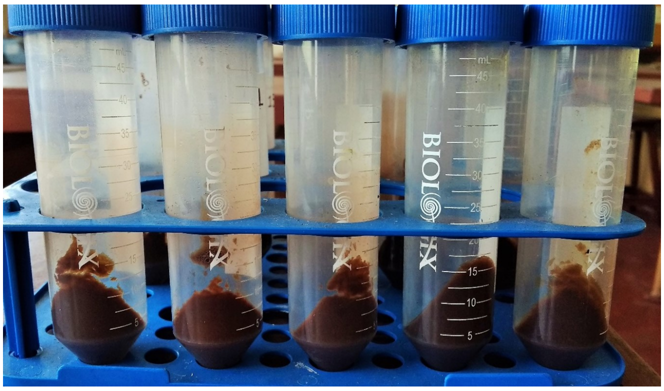


Fig. 5.14: Recovered lignin

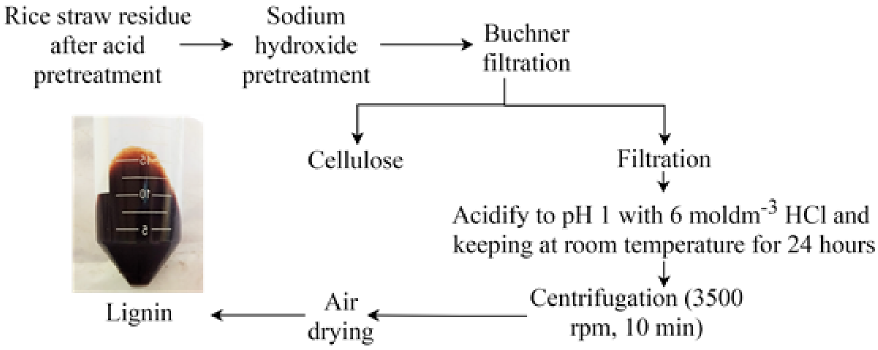


Fig. 5.15: Schematic representation of sodium hydroxide pretreatment process

recovery in terms of coded variables is given in (5.4), where NaOH concentration, reaction temperature, and reaction time are represented by X_1, X_2, and X_3, respectively. Predicted responses are obtained for the developed model by applying X_1, X_2, and X_3 actual values. A close agreement has been observed among experimental and predicted responses. Regression coefficients of each independent variable, standard

TABLE 5.8: Coded and actual values of independent variables NaOH pretreatment

Exp[7]	**Coded variables**			**Lignin yield %**		**Error**
	X_1	X_2	X_3	**Observed**[8]	**Predicted**	
1	-1	-1	-1	8.1	8.7332	-0.63323
2	1	-1	-1	19.2	18.607	0.59287
3	-1	1	-1	11.5	12.093	-0.59295
4	-1	1	-1	11.5	12.093	-0.59295
5	-1	-1	1	9.7	11.085	-1.3851
6	1	-1	1	16.2	16.309	-0.10901
7	-1	1	1	13.3	14.595	-1.2948
8	1	1	1	15.8	15.869	-0.068732
9	-1.682	0	0	10.7	8.7161	1.9839
10	1.682	0	0	17.1	18.091	-0.9914
11	0	-.1.682	0	14.4	13.826	0.57387
12	0	1.682	0	16.7	16.281	0.41862
13	0	0	-1.682	15.3	15.668	-0.36807
14	0	0	1.682	17.2	15.839	1.3606
15	0	0	0	20.3	20.095	0.20507
16	0	0	0	20.2	20.095	0.10507
17	0	0	0	19.8	20.095	-0.29493
18	0	0	0	20.1	20.095	0.005068
19	0	0	0	20.2	20.095	0.10507
20	0	0	0	19.8	20.095	-0.29493

errors, results of t-test, and p-values are shown in Table 5.9.

$$Y = 20.09 + 2.78X_1 + 0.73X_2 + 0.05X_3 - 2.36X_1^2 - 1.78X_2^2 - 1.53X_3^2 \qquad (5.4)$$

Small p-values (< 0.05) and large t-test values reveal the significance of corresponding regression coefficient term. It is observed that positive first order effects of NaOH concentration and temperature, negative quadratic effects of NaOH concentration, temperature, and time are statistically significant for the lignin recovery. However, main effect of time is not statistically significant on the response. Considering the interaction effects of independent variable combinations, NaOH concentration/ reaction temperature and NaOH concentration/ reaction time showed significant effects on lignin recovery. However, combination of reaction temperature and time has not significant

---

[7] Experiment number

[8] Mean of triplicate determination.

[9] NaOH concentration

[10] Temperature

TABLE 5.9: Regression analysis of proposed model for lignin recovery from rice straw

Term	Estimate	Standard error	t-stat	p-value
(Intercept)	120.095	0.46198	43.497	9.908×10^{-13}
Conc[9]	2.7869	0.3065	9.0929	3.7726×10^{-6}
Temp[10]	0.72986	0.3065	2.3813	0.038527
Time	0.05094	0.3065	0.16621	0.8713
Conc×Temp	-0.9875	0.40048	-2.4658	0.033343
Conc×Time	-1.1625	0.40048	-2.9028	0.015758
Temp×Time	0.0375	0.40048	0.093638	0.92725
$Conc^2$	-2.3651	0.29833	-7.9279	1.2745×10^{-5}
$Temp^2$	-1.7819	0.29833	-5.973	0.00013697
$Time^2$	-1.5345	0.29833	-5.1436	0.0004355

effect on pretreatment process.

The model has indicated a high R^2 value of 0.954. Adjusted R^2 statistic (R^2_{adj}) is also estimated to obtain an accurate measurement of the amount of reduction in variability of the response by using these independent variables. Similarity between R^2 (0.954) and R^2_{adj} (0.913) has implied that the regression model developed is adequate to explain the variability in the response. Therefore, lack of fit of the model is not detected for this developed model.

Then, ANOVA analysis is conducted to partition the total variation observed in responses into various components and for the testing of the developed model adequacy. The results obtained from ANOVA analysis are presented in Table 5.10. The total observed variability can be partitioned into SS due to model and SS due to experimental error. Testing the ratio of MSmodel and MSerror against unity (F-test) is needed for the checking of model adequacy. 23.1, F-test value, indicates that the proposed regression model explains the lignin yield variation for the study. Very low p-value ($p < 0.05$) associated with F-test statistic confirms further that the model is significant at 95 % of confidence level. Table 5.10 also shows p-values for the F-test statistics related to each component variation. Therefore, these test statistics have confirmed further the results obtained from the regression analysis.

The response surfaces of NaOH concentration, reaction temperature, reaction time, and the lignin yield are illustrated in Fig. 5.16, Fig. 5.17, and Fig. 5.18. Here also, each response surface has shown two independent variables, maintaining at zero the

---

[11] NaOH concentration

[12] Temperature

TABLE 5.10: Analysis of variance for lignin recovery from rice straw

Source of Variation	**Sum of Squares**	**DOFc**	**Mean Squares**	**F-stat**	**p-value**
Conc[11]	106.08	1	106.8	82.681	3.7726×10^{-6}
Temp[12]	7.2757	1	7.2757	5.6706	0.038527
Time	0.035447	1	0.035447	0.027627	0.8713
Conc:Temp	7.8012	1	7.8012	6.0802	0.033343
Conc:Time	10.811	1	10.811	8.4262	0.015758
Temp:Time	0.01125	1	0.01125	0.0087682	0.92725
$Conc^2$	80.642	1	80.642	62.852	1.2745×10^{-5}
$Temp^2$	45.774	1	45.774	35.676	0.00013697
$Time^2$	33.945	1	33.945	26.456	0.0004355
Error	12.831	10	1.2831		5.0000×10^{-1}

third coded variable.

Fig. 5.16 clearly shows the significant positive first order and negative quadratic influences of both NaOH concentration and reaction temperature for the lignin recovery. Significant interaction between reaction temperature and NaOH concentration is visible in the plot. The highest yield of lignin is visible in the upper right corner of the plot, and it is corresponded to high value of NaOH concentration and moderate value of reaction temperature. Quadratic relationship of NaOH concentration and reaction time is depicted in Fig. 5.17, where significant interaction is not present. A high lignin recovery can be observed at left right corner of the plot and it is corresponded to both high values of NaOH concentration and reaction time. As observed in Fig. 5.18, both reaction temperature and reaction time showed more prominent quadratic effects on lignin recovery. However, a significant interaction can not be observed between reaction temperature and time in the plot. The lignin recovery has improved with increasing the reaction temperature and time. The highest lignin yield is observed when applying a high value of reaction time and a moderate value of reaction temperature.

Error terms are tested for normality performing a residual analysis as shown in Fig. 5.19. The residual plot shows a systematic pattern of residuals, lying around zero and within a fixed band. Therefore, any major violation of underlying assumption on error term and lack of adequacy of the proposed model are not observed.

The response surfaces in Fig. 5.16, Fig. 5.17, and Fig. 5.18 indicate the existence of a maxima within the domain of interest. Therefore, the partial derivatives of the developed model in (5.5) are used to identify the operating point of maximum yield. The system, which defined the maximum point of yield using partial derivatives of each

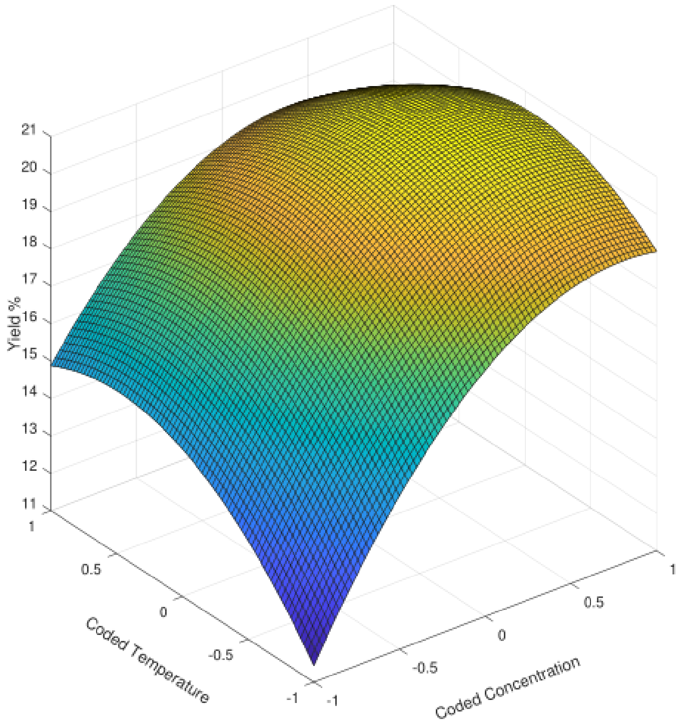


Fig. 5.16: Response surface analysis of coded concentration and temperature vs yield

variable, can be represented in matrix form as given in (5.5), where C, θ, and t are the coded values of NaOH concentration, reaction temperature, and reaction time, re-

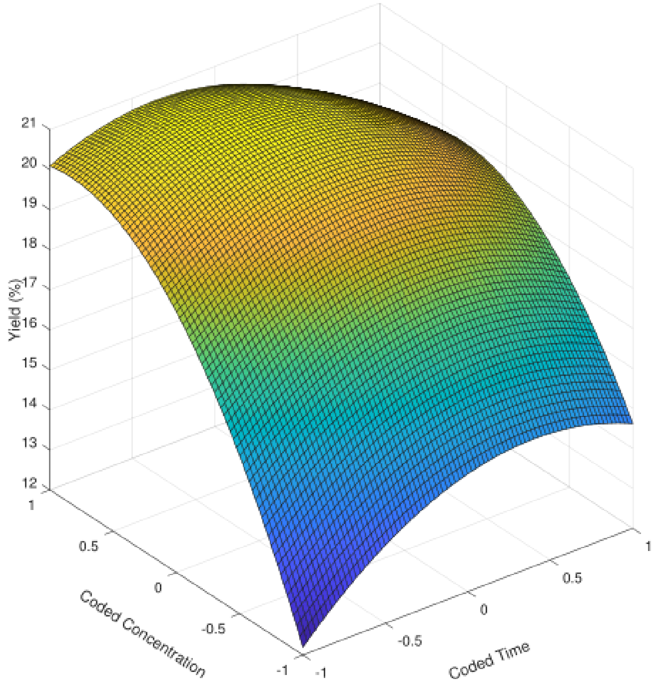


Fig. 5.17: Response surface analysis of coded concentration and time vs yield

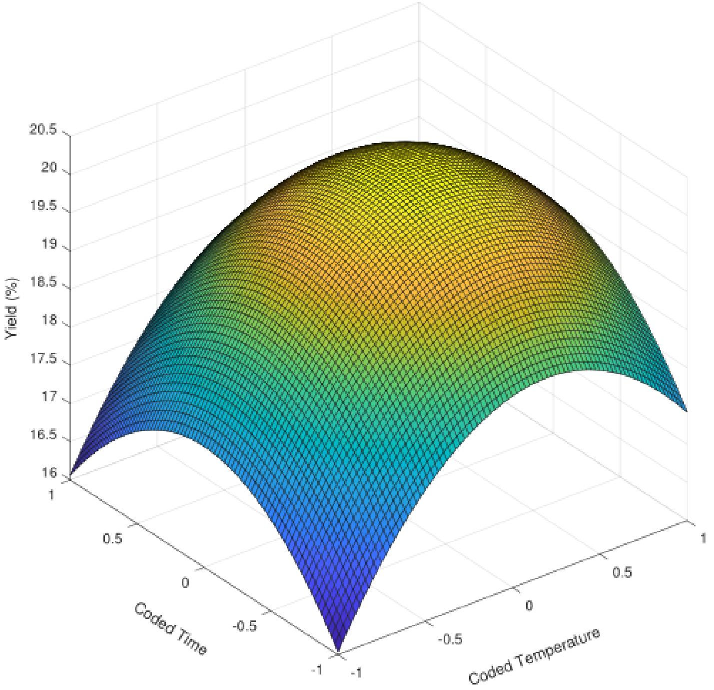


Fig. 5.18: Response surface analysis of coded temperature and time vs yield

spectively. The non-zero determinant of coefficient matrix validates the existence of maxima for the system defined in (5.5).

$$\begin{bmatrix} -4.7302 & -0.9875 & -1.1625 \\ -0.9875 & -3.5638 & 0.0375 \\ -1.1625 & 0.0375 & -3.0689 \end{bmatrix} \begin{bmatrix} C \\ \theta \\ t \end{bmatrix} = \begin{bmatrix} -2.7869 \\ -0.7299 \\ -0.0509 \end{bmatrix} \tag{5.5}$$

The solution of (5.5) is decoded to extract the actual temperature, using the step size and the center point of each variable as listed in Table 5.11. Accordingly, the maximum lignin yield ($20.98\,\%$) is observed at optimal pretreatment condition.

Finally, experiments were extended to validate the optimal conditions obtained for NaOH concentration, reaction temperature, and reaction time. Validation results pro-

TABLE 5.11: Optimum operating conditions for maximum lignin yield

Optimal Condition	**Coded Value**	**Actual Value**
NaOH concentration	0.6393	$2.55\ \mathrm{mol\,dm^{-3}}$
Reaction temperature	0.0253	$80.50\ ^\circ\mathrm{C}$
Reaction time	-0.2252	106.48 min

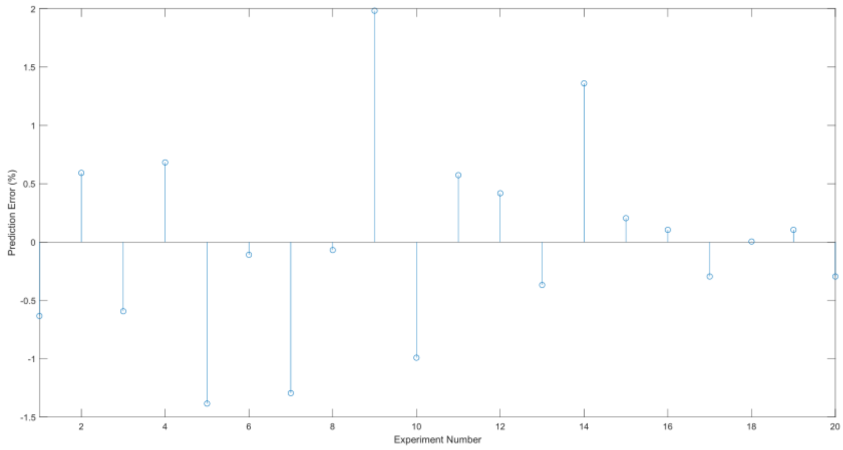


Fig. 5.19: Analysis of predicted error vs experiment number in NaOH pretreatment

vided 20.91 % of lignin yield at optimal conditions, confirming the predicted results.

Table 5.12 shows a comparison of the results, obtained in this study with other NaOH pretreatment processes carried out using RS. Compared to these pretreatment conditions, optimal conditions of this study has provided a satisfactory yield of lignin.

5.3 Cellulose Recovery from Rice Straw

After completing the whole pretreatmnet process, the residue was used as cellulose. To obtain white fibrous cellulose as shown in Fig. 5.20, RS pretreated residue was washed thoroughly until it becomes neutral, using deionized water. Then washed RS residue was subjected to drying at 105 °C for 24 hours and stored in a desiccator until used for 5-HMF conversion process.

TABLE 5.12: Comparison of resulted optimal conditions with other NaOH pretreatment processes

Reference	**NaOH concentration**	**Reaction temperature**	**Reaction time**	**Lignin yield %**
[164]	12 wt%	55 °C	60 minutes	19.32 %
[75]	2 mol dm^{-3}	90 °C	150 minutes	13.84 %
[254]	4 wt%	55 °C	180 minutes	13.30 %
[97]	1 mol dm^{-3}	121 °C	15 minutes	14.30 %
Present study	2.55 mol dm^{-3}	80 °C	106 minutes	20.91 %

Fig. 5.20: Recovered cellulose after pretreatment process

CHAPTER 6

OPTIMIZATION OF CELLOLOSE TO 5-HMF CONVERSION

6.1 Introduction

The conversion of recovered cellulose into 5-HMF is carried out after completing pretreatment process. The selection of the most appropriate method to convert cellulose to 5-HMF is done based on the proposed evaluation scheme proposed in this thesis. Eventually, considering 18 processes, process number 01 (HCL catalyzed microwave assisted 5-HMF synthesis process in a water/MIBKbiphasicreactionsystem) was selected as the most feasible process to be optimized at local conditions. Fig. 6.1 has shown a continuous production system to convert RS recovered cellulose into 5-HMF. It is consisted with a biphasic reactor, solvent separation unit, catalysts recovery unit, and HMF recovery unit. However, the research objective is limited to the experimentation on optimization of cellulose to 5-HMF conversion. Therefore, the entire experiments were performed, focusing to the biphasic reactor.

The research targeted to investigate the feasibility of industry scalable 5-HMF synthesis process. In scalable perspective, a hydrothermal reactor based biphasic system is more feasible, compared to a microwave reactor. Therefore, eventhough microwave reactor based process was selected as the benchmark process for the optimization, hydrothermal reactor was used in this research to function as the biphasic reaction system. As a result, this thesis has proposed and investigated an optimized acid catalyzed hydrothermal process for the in-situ production of 5-HMF from rice straw recovered cellulose.

6.2 Materials

The experiment was carried out using rice straw extracted cellulose. To obtain white fibrous cellulose, deionized water was used to wash thoroughly RS pretreated residue until all the washings were become neutral. Then washed RS residue was dried for 24 hours at $105\,^{\circ}\mathrm{C}$, and a desiccator was used to store until it was used in 5-HMF conversion process. The required catalyst, HCl and the organic phase of the reaction system, MIBK were purchased from Sigma-Aldrich. Deionized water was used as the aqueous phase of the biphasic reaction system.

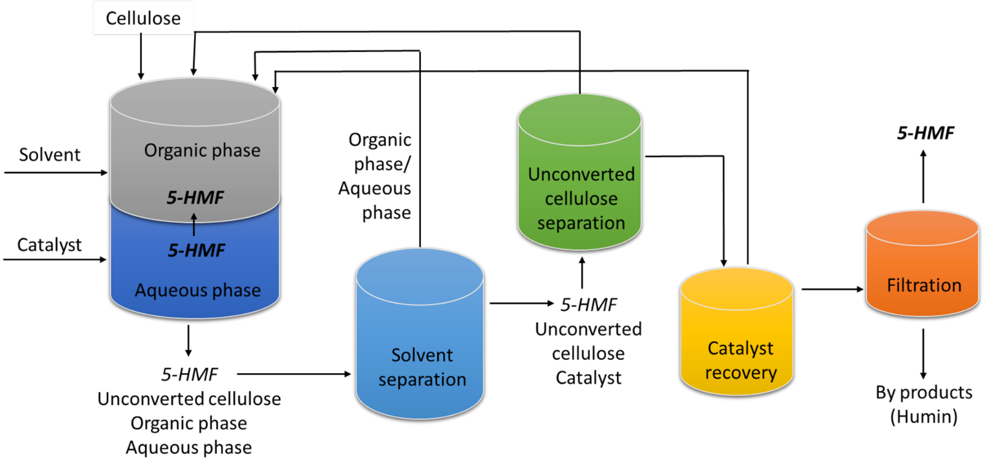


Fig. 6.1: Continuous production system to convert rice straw recovered cellulose to 5-HMF

6.3 Design of experiments

Screening test of the most significant parameters in cellulose to 5-HMF conversion process, was performed based on published studies. Accordingly, catalyst concentration, reaction temperature, and reaction time were selected as these parameters have shown direct influence on 5-HMF yield and process cost [176]. Ratio of aqueous phase to organic phase in the biphasic system was kept at constant (1:19, v/v) in all experimental runs as per to the literature. All experiments were carried out using a hydrothermal autoclave synthesis reactor with Teflon lining ($100\,\mathrm{mL}$). The reactor vessel and its structural parts are shown in Fig. 6.2 and 6.3, respectively. The reactor specifications are listed in Table 6.1.

At the first stage of conducting design of experiments, design space of each parameter was decided based on results obtained from OFAT and previous published studies [[176]]. Then at the second stage levels of each input parameter were optimized applying CCD in RSM. As there were three input variables, the CCD of the experiment was consisted with 20 experimental runs (1 to 8 factorials, 9 to 14 axial point runs, and 15 to 20 center point runs). Table 6.2 shows the independent variables, their design space, and corresponding coded values for the analysis of response surface. Here, X_1, X_2, and X_3 represent catalyst concentration, reaction temperature, and reaction time, respectively. Coding of each independent variable was performed using equation (5.1).

6.4 Experimental procedure

In an experiment, $100\,\mathrm{mL}$ hydrothermal synthesis reactor vessel was filled with $250\,\mathrm{mg}$ cellulose recovered from RS, $2.5\,\mathrm{mL}$ HCl acidified deionized water as the aqueous phase and $47.5\,\mathrm{mL}$ MIBK as the organic phase. The reactor was placed in a standard laboratory oven ((memmert, UF 110) to take place the catalytic conversion of cellulose to 5-HMF. Each experimental run was carried out employing the conditions indicated

Fig. 6.2: Hydrothermal autoclave synthesis reactor used for experimentation

Fig. 6.3: Structural parts of hydrothermal synthesis reactor

TABLE 6.1: Hydrothermal reactor specifications

Specification	**BJ-T-100 Series**
Material	304 stainless steel & PTFE
Size/ Volume	100 ml
Max Temperature	240 ^{o}C
Max Pressure	6 Mpa
Heating Rate	5 ^{o}C/min
Liner	PTFE
Acid & Alkali Resistance	✓/✗
Explosion Proof	✓
Suggested Heater	Heater with programmed heating

TABLE 6.2: Actual and coded values of independent variables in cellulose to 5-HMF conversion

Factor	**Variable**	**-1.682**	**-1**	**0**	**1**	**1.682**
HCl concentration ($\mathrm{mol\,dm^{-3}}$)	X_1	0.02	0.06	0.12	0.18	0.22
Reaction temperature ($^\circ\mathrm{C}$)	X_2	143.36	157	177	197	210.64
Reaction time (min)	X_3	26.36	40	60	80	93.64

in Table 6.2. After happening the reaction at specified temperatures and times, the reactor vessel was cooled down rapidly to room temperature by placing it in an ice bath to halt further reaction. Finally, the organic phase of the reaction mixture was filtered through a $0.45\,\mu\mathrm{m}$ polytetrafluoroethylene (PTFE) syringe filter and proceeded to 5-HMF analysis. Schematic and pictorial representation of the hydrothermal assisted catalytic conversion process is presented in Fig. 6.4. To confirm the repeatability, all experimental runs and analyses were carried out for three times.

6.5 Analysis of 5-HMF

Quantitative analysis of 5-HMF was performed using a UV-Visible spectrophotometer. Concentration of 5-HMF in each sample was calculated based on a standard calibration curve which was generated using reference 5-HMF. Absorbance detection of the samples was conducted at $284\,\mathrm{nm}$. Calibration curve of 5-HMF concentration with absorbency at $284\,\mathrm{nm}$ is shown in Fig. 6.5, and regression statistics are shown in Table 6.3. The yield of 5-HMF was expressed using cellulose weight as a basis and calculated, applying equation (6.1). Where, YHMF, mHMF, and mCellulose represent the

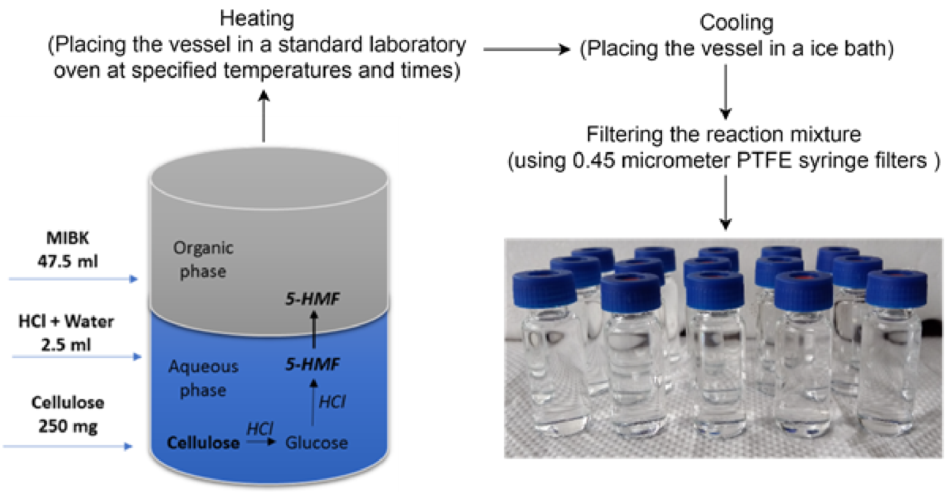


Fig. 6.4: Schematic and pictorial representation of hydrothermal catalytic conversion process followed

TABLE 6.3: Regression statistics of calibration curve data

Regression term	**Value**
R Square	0.9997
Adjusted R Square	0.9996
Standard Error	0.0036
Intercept	0.028

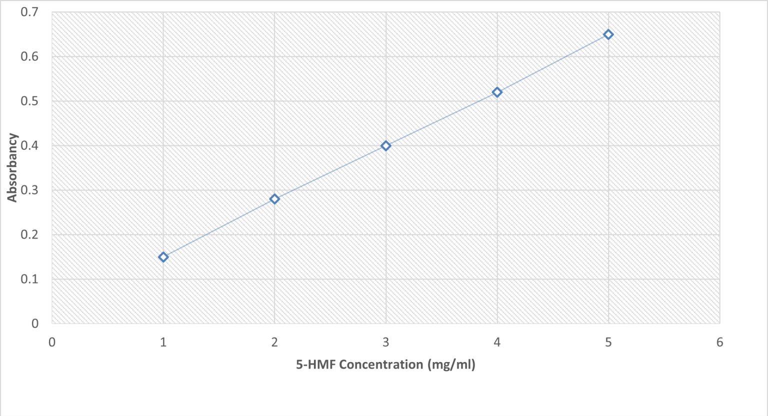


Fig. 6.5: Calibration curve of 5-HMF concentration with absorbency at 284 nm

yield percentage of 5-HMF, mass of generated 5-HMF, and mass of cellulose applied, respectively.

$$YHMF\% = \frac{mHMF}{mCellulose} \times 100\% \tag{6.1}$$

6.6 Statistical analysis procedure

After performing the hydrothermal catalytic conversion processes, a second-order polynomial regression model was introduced to characterize relationships among each independent variables (catalyst concentration, reaction time, and reaction temperature) and the response variable (5-HMF yield percentage), in terms of linear, quadratic, and interactions. Using MATLAB simulations, regression analysis and ANOVA of experimental data were conducted. To validate the assumptions on error terms, residual analysis was also carried out.

6.7 Results and discussion

5-HMF yield obtained for all treatments by applying CCD experimental design are presented in Table 6.4.

---

[1] Experiment number

[2] Mean of triplicate determination.

TABLE 6.4: Coded and actual values of independent variables in 5-HMF synthesis process

Exp[1]	**Coded variables**			**5-HMF yield %**		**Error**
	X_1	X_2	X_3	**Observed**[2]	**Predicted**	
1	-1	-1	-1	0.1	-0.1143	0.24435
2	1	-1	-1	16.6	16.586	0.03364
3	-1	1	-1	17.5	17.501	0.01935
4	-1	1	-1	9.8	9.7614	0.07864
5	-1	-1	1	12.7	12.707	-0.01675
6	1	-1	1	19.7	19.637	0.04254
7	-1	1	1	20.3	20.312	0.02824
8	1	1	1	2.6	2.8025	-0.1824
9	-1.682	0	0	14.4	14.504	-0.1337
10	1.682	0	0	13.9	13.824	0.04626
11	0	-.1.682	0	4.6	4.7308	-0.15077
12	0	1.682	0	5.4	5.3867	0.063258
13	0	0	-1.682	17.0	17.164	-0.1937
14	0	0	1.682	22.2	22.094	0.10619
15	0	0	0	21.5	21.079	-0.55917
16	0	0	0	22.2	22.079	0.14083
17	0	0	0	21.9	22.079	-0.15917
18	0	0	0	22.4	22.079	0.36083
19	0	0	0	21.8	22.079	-0.27917
20	0	0	0	22.6	22.079	0.51083

Developed second order polynomial regression model for 5-HMF synthesis in terms of coded variables is given in (6.2), where X_1, X_2, and X_3 represent HCl concentration, reaction temperature, and reaction time, respectively. Predicted responses are obtained by applying X_1, X_2, and X_3 actual values into the developed model. Close agreement has been observed between the predicted and experimental responses. Each independent variable regression coefficients, standard errors, results of t-test, and p-values are shown in Table 6.5.

$$Y = 22.09 - 0.20X_1 + 0.19X_2 + 1.46X_3 - 2.80X_1^2 - 6.02X_2^2 - 0.87X_3^2 - 0.61X_1X_2 - 2.44X_1X_3 - 2.50X_2X_3 \quad (6.2)$$

Small p-values (< 0.05) and large t-test values reveal the significance of corresponding regression coefficient term. It is observed that statistically significant positive first order effects of reaction temperature and reaction time, negative first order effect of HCl concentration, negative quadratic effects of all three factors on 5-HMF synthesis. Considering the interaction effects of independent variable combinations, interaction

---

[3] HCl concentration

[4] Temperature

TABLE 6.5: Regression analysis of proposed model for 5-HMF synthesis process

Term	Estimate	Standard error	t-stat	p-value
(Intercept)	22.079	0.13064	169	1.2926×10^{-18}
Conc[3]	-0.20215	0.086674	-2.3323	0.041886
Temp[4]	0.195	0.086674	2.2498	0.048196
Time	1.4656	0.086674	16.909	1.1003×10^{-8}
Conc×Temp	-6.11	0.11325	-53.951	1.1595×10^{-13}
Conc×Time	-2.4425	0.11325	-21.567	1.0252×10^{-9}
Temp×Time	-2.5025	0.11325	-22.097	8.0799×10^{-10}
$Conc^2$	-2.7978	0.084363	-33.164	1.4669×10^{-11}
$Temp^2$	-6.0161	0.084363	-71.312	7.1705×10^{-15}
$Time^2$	-0.86614	0.084363	-10.267	1.2481×10^{-6}

effects of all three variables are significant on 5-HMF synthesis. However, all the interaction terms are showed as negative effects.

The model has indicated a high R^2 value of 0.999. Adjusted R^2 statistic (R^2_{adj}) is also estimated to obtain an accurate measurement of the amount of reduction in variability of the response by using these independent variables. Similarity between R^2(0.999) and R^2_{adj} (0.998) implies the adequacy of the developed regression model to explain the variability in the response. Therefore, lack of fit is not visible in the developed model. Then, ANOVA analysis is conducted to partition the total variation observed in responses into various components and test the adequacy of the developed model. Table 6.6 presents the results obtained from ANOVA analysis. Here, 1161.25, F-test value, indicates that the proposed regression model can explain the variation in 5-HMF yield obtained in this study.

TABLE 6.6: Analysis of variance for 5-HMF synthesis process

Source of Variation	Sum of Squares	DOFc	Mean Squares	F-stat	p-value
Conc[5]	0.55813	1	0.55813	5.4396	0.041886
Temp[6]	0.51935	1	0.51935	5.0616	0.048196
Time	29.336	1	29.336	285.91	1.1003×10^{-8}
Conc:Temp	298.66	1	298.66	2910.7	1.2745×10^{-5}
Conc:Time	47.726	1	47.726	465.14	1.0252×10^{-9}
Temp:Time	50.1	1	50.1	488.28	8.0799×10^{-10}
$Conc^2$	112.85	1	112.85	1099.9	1.4669×10^{-11}
$Temp^2$	521.79	1	521.79	5085.4	7.1705×10^{-15}
$Time^2$	10.815	1	10.815	105.41	1.2481×10^{-6}
Error	1.0261	10	0.1026	1.0261	

Table 6.6 also shows p-values for the F-test statistics related to each component variation. Therefore, these test statistics have confirmed further the results obtained from the regression analysis. The response surfaces of 5-HMF yield, HCl concentration, reaction time, and reaction temperature are illustrated in Fig. 6.6, Fig. 6.7, and Fig. 6.8. Here, also keeping the third coded variable at zero, each response surface has shown two independent variables.

Fig. 6.6 clearly shows the significant first order and quadratic effects of HCl concentration and reaction temperature on 5-HMF synthesis. A significant negative interaction between reaction temperature and HCl concentration is visible in the plot. Significant first order and second order effects of HCl concentration and reaction time are depicted in Fig. 6.7, where significant interaction is also present. The highest 5-HMF yield can be observed at upper right corner in plot which is corresponded to both high values of HCl concentration and reaction time. As observed in Fig. 6.8, reaction temperature has showed more prominent quadratic effects on 5-HMF synthesis than the reaction time. Clear first order effect of time is visible in the plot. A significant interaction can also be observed between reaction temperature and time in the plot. The highest 5-HMF yield is observed at the upper left corner of the plot, corresponding to short reaction

---

[5] HCL concentration

[6] Temperature

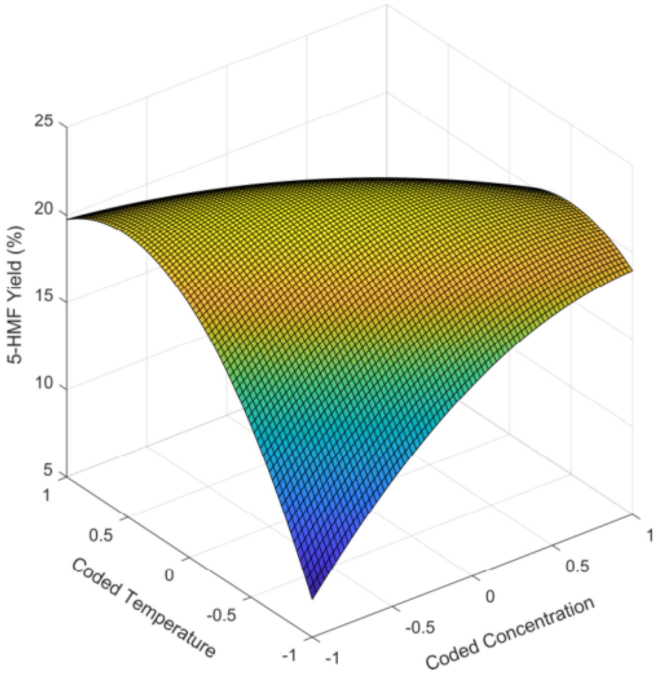


Fig. 6.6: Response surface analysis of coded HCl concentration and reaction temperature vs 5-HMF yield

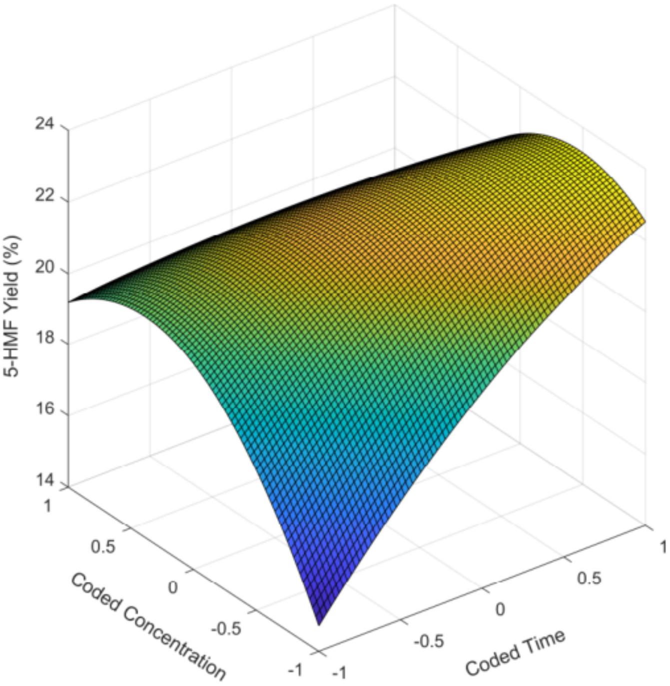


Fig. 6.7: Response surface analysis of coded HCl concentration and reaction time vs 5-HMF yield

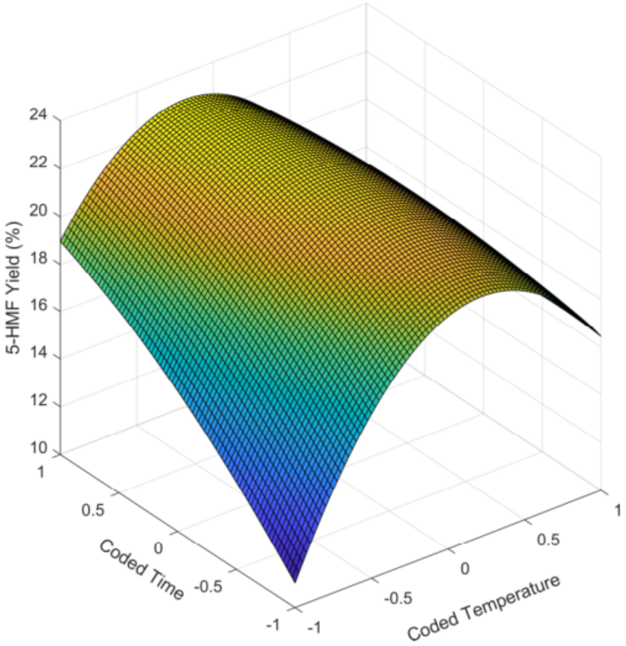


Fig. 6.8: Response surface analysis of coded reaction temperature and time vs 5-HMF yield

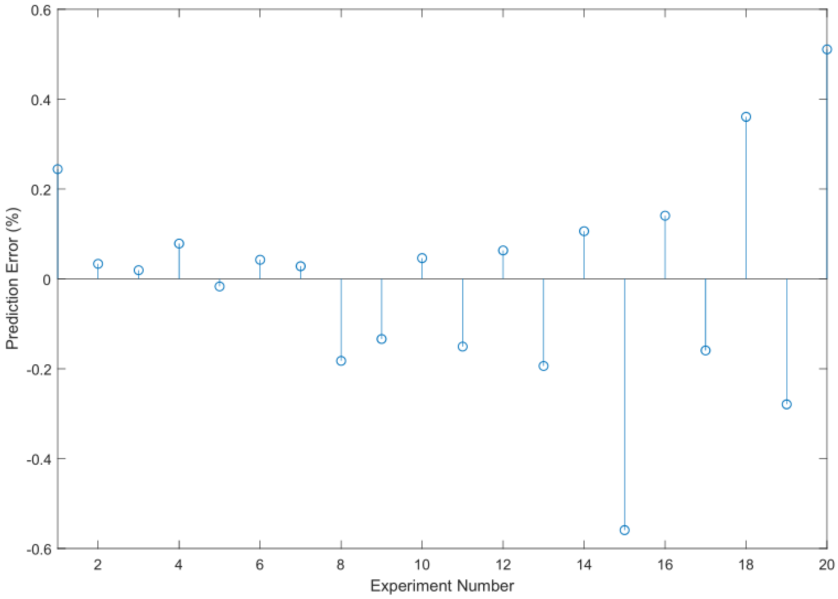


Fig. 6.9: Analysis of predicted error vs experiment number in 5-HMF synthesis process

times and high reaction temperatures. Error terms are tested for normality performing a residual analysis as shown in Fig. 6.9. The residual plot shows a systematic pattern of residuals, lying around zero and within a fixed band. Therefore, any major violation of underlying assumption on error term and the proposed model lack of adequacy are not observed.

The response surfaces in Fig. 6.6, Fig. 6.7, and Fig. 6.8 indicate the existence of a maxima within the domain of interest. Therefore, the partial derivatives of the developed model in (6.3) are used to identify the operating point of maximum yield. The system, which defined the maximum point of yield using partial derivatives of each variable, can be shown in matrix form as presented in (6.3), where C, θ, and t are the coded values of HCl concentration, reaction temperature, and reaction time, respectively. The non-zero determinant of coefficient matrix validates the existence of maxima for the system defined in (6.3).

$$\begin{bmatrix} -5.5957 & -6.1100 & -2.4425 \\ -6.110 & -12.0323 & -2.5025 \\ -2.4425 & -2.5025 & -1.7323 \end{bmatrix} \begin{bmatrix} C \\ \theta \\ t \end{bmatrix} = \begin{bmatrix} 0.2021 \\ -0.1950 \\ -1.4656 \end{bmatrix} \tag{6.3}$$

The solution of equation (4.10) is decoded to extract the actual temperature, using the step size and the center point of each variable as listed in Table 6.7. Accordingly, the maximum predicted 5-HMF yield ($23.95\ \%$) is obtained at optimal treatment condition.

TABLE 6.7: Optimum operating conditions for maximum 5-HMF yield

Optimal Condition	**Coded Value**	**Actual Value**
HCL concentration	-1.2346	$0.046\,\mathrm{mol\,dm^{-3}}$
Reaction temperature	0.1503	180 °C
Reaction time	2.3697	107.4 min

Finally, to confirm the predicted maximum 5-HMF yield, validation experiments were carried out. The resulted 5-HMF yield ($23.5\,\%$) at optimum reaction conditions was close agreement with the predicted yield. However, as shown in Table 6.8, the resulted maximum 5-HMF yield at optimal operating conditions in this study have considerably deviated from the benchmark process 01 (microwave-assisted process for 5-HMF in-situ production).

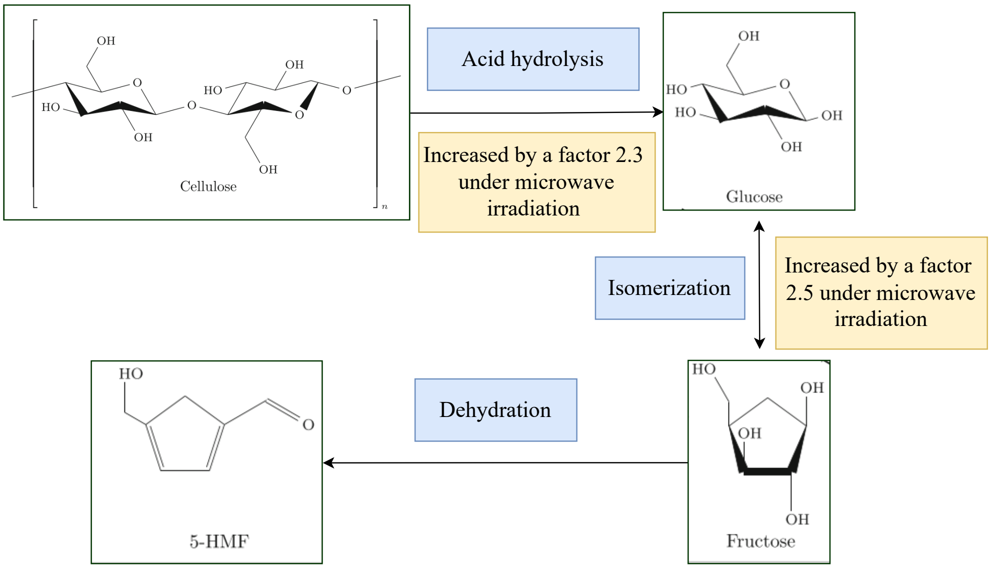
Based on the study of Sweygers et al. [176], the main reason for the yield difference between process 01 and the present study, lies within the application of microwave irradiation. According to the process 01, direct application of microwave energy as an internal heating mechanism on the molecules of reaction mixture has caused rapid rise in reaction temperature, due to dipole rotation and ionic conduction [176].Therefore, 5-HMF production was increased and the rate of 5-HMF transfering from the organic phase to the extraction phase was also improved. However, in this study, application of conventional hydrothermal heating which comprises combination of conductive and convective heat transfer, has resulted in lower heating rate and also non-uniform heating mechanism in the system. Therefore, it has led the system overheating and decomposition of HMF eventually [255].

Moreover, based on the significant effect of microwave irradiation on each reaction step in process 01 as shown in Fig. 6.10, it was identified that acid hydrolysis of cellulose to glucose was increased by 2.3 folds faster, and glucose to fructose isomerization was increased in 2.5 folds faster in the presence of microwaves. However, in an economic perspective, for the transformation of 5-HMF production into an industry scalable process, a tradeoff needs to be made [1]. In such scenario, tradeoff requires for moderate conditions with high energy demand or harsh conditions with low energy demand.

Hence, as the future directions of this study, necessary steps should be taken to improve the hydrothermal synthesis of 5-HMF. As presented in Fig. 6.11, increasing aqueous

TABLE 6.8: Comparison of process 01 and present study

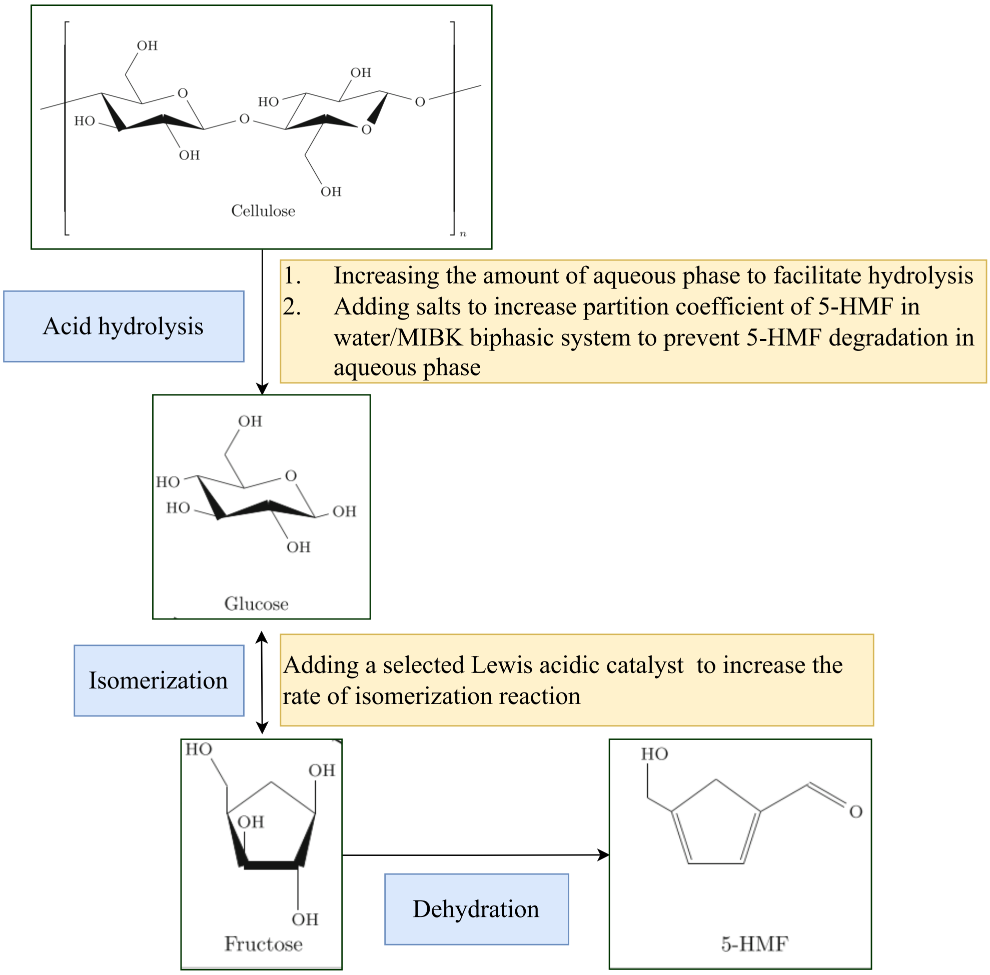
Process	**Reactor system**	**HCl concentration**	**Reaction temperature**	**Reaction time**	**5-HMF yield %**
Process 01	Microwave	$0.12\,\mathrm{mol\,dm^{-3}}$	177 °C	60 min	$43.27\,\%$
Present study	Hydrothermal	$0.04\,\mathrm{mol\,dm^{-3}}$	180 °C	107 min	$23.9\,\%$



Increased by a factor 2.3 under microwave irradiation

Increased by a factor 2.5 under microwave irradiation

Fig. 6.10: Effect of microwave irradiation on reaction steps in process 01



1. Increasing the amount of aqueous phase to facilitate hydrolysis
2. Adding salts to increase partition coefficient of 5-HMF in water/MIBK biphasic system to prevent 5-HMF degradation in aqueous phase

Adding a selected Lewis acidic catalyst to increase the rate of isomerization reaction

Fig. 6.11: Necessary steps to improve proposed hydrothermal process

phase amount in the reaction system is required to improve cellulose conversion into glucose acid hydrolysis. It is also required, increasing 5-HMF partition coefficient in water/MIBK system via adding salts at the same time to prevent the degradation 5-HMF in water phase at high temperatures. Moreover, addition of selected Lewis acidic catalysts is needed to improve mainly glucose to fructose isomerization and parallely fructose to HMF dehydration.

CHAPTER 7

CONCLUSIONS AND FUTURE DIRECTIONS

This thesis has proposed hydrothermal synthesis process to produce 5-HMF from RS and presented experimental optimization results for the conversion process. The drawn conclusions of the research are as follows.

The chapter 3, "Comparative process evaluation of cellulose to 5-HMF", presents penalty scores based generalized objective function-based method to evaluate and identify an optimal process configuration to convert cellulose into 5-HMF where the minimum value is used to discover the optimal process. The analysis procedure and the evaluation results are independently discussed in the same chapter, and followings are the conclusions drawn.

1. To stipulated conditions, the lowest value is exhibited by process 04, which has generated 85.00% 5-HMF yield in a water monophasic system with Ni-doped biomass-based carbon catalyst (Nin/CS) at 200 °C for 60 min.
2. The proposed evaluation method can easily be applied to shortlist a set of optimal processes from a large set of processes with insufficient data for deep financial analysis.

The chapter 5, "Optimization of rice straw to cellulose conversion" and chapter 6, "Optimization of cellulose to 5-HMF conversion" present experimental procedures related to RS pretreatment methods and cellulose to 5-HMF conversion process. Results and discussion sections are separately included in both chapters to facilitate clear understanding of the experimental results, and followings are the conclusions drawn from those sections.

The conclusions for the developed dilute sulphuric acid and dilute sodium hydroxide pretreatments at reduced temperatures to optimize hemicellulose removal and lignin removal from RS to recover cellulose and maximize the outcome of RS biorefinery,

1. The maximum hemicellulose removal (15.78%) is observed at optimal conditions of 0.26 M sulphuric acid concentration, 98 °C reaction temperature, and 30 min reaction time.
2. The maximum lignin removal (20.98%) was obtained at 2.55 M sodium hydroxide concentration, 80 °C reaction temperature, 106 min reaction time.
3. The proposed quadratic regression models were adequate to explain the variability observed in both pretreatments.

The conclusions for the developed an optimized acid-catalyzed hydrothermal process for the in-situ production of 5-HMF from RS extracted cellulose, using water/MIBK biphasic reaction system.

1. The maximum yield of 5-HMF is 23.51% at optimal conditions of 0.046 M HCl acid concentration, 180 °C process temperature, and 107 min process time.
2. Quadratic effect of reaction temperature has shown the highest influence on the variation in 5-HMF yield. Interaction effect of HCl concentration and reaction temperature has shown the highest influence on the 5-HMF yield, compared to other interaction effects.
3. The proposed second-order polynomial regression model to characterize the relationships among process parameters was adequate and exhibited high adjusted determination coefficient (0.998) and Fischer's test value (1161.25).

7.1 Future directions

This thesis has proposed hydrothermal synthesis process to produce 5-HMF from RS and presented experimental optimization results for the conversion process. However, the maximum 5-HMF yield generated from this study is low, compared to the yield in benchmark process. Therefore, future studies should be conducted to improve the hydrothermal synthesis process to generate high 5-HMF yield. Based on the reaction process, the immediate necessary steps to improve the process can be listed as,

- Increasing the amount of aqueous phase in the reaction system to improve the acid hydrolysis of cellulose to glucose.
- Increasing 5-HMF partition coefficient in water/MIBK system via adding salts.
- Adding selected Lewis acidic catalysts to improve glucose to fructose isomerization and fructose to 5-HMF dehydration.

After addressing above mentioned immediate necessary steps, future investigations should be directed towards developing practical implementation of mass-scale 5-HMF production. However, mass-scale RS to 5-HMF conversion is extremely difficult, compared to the laboratory-scale conversion and it can be generated advance scale-up effects as well. Therefore, future studies are requried to conduct comprehensive techno-economic analysis on the developed process and then pilot-scale studies prior to the mass-scale RS biorefinery to produce 5-HMF.

REFERENCES

[1] P. Wanninayake, M. Rathnayake, D. Thushara, and S. Gunawardena, “Conversion of rice straw into 5-hydroxymethylfurfural: review and comparative process evaluation,” *J Biomass Conv. Bioref.*, 2021. [Online]. Available: https://link.springer.com/article/10.1007/s13399-021-01351-x

[2] P. Wanninayake, M. Rathnayake, D. Thushara, and S. Gunawardena, “Optimization of hemicellulose recovery from rice straw for biorefinery: Dilute acid pretreatment at reduced temperatures,” in *2021 Moratuwa Engineering Research Conference (MERCon)*, 2021, pp. 315–320.

[3] L. Atanda, “Catalytic conversion of biorenewable-carbohydrate sources to 5-hydroxymethylfurfural: a platform molecule for future chemical and energy,” Ph.D. dissertation, Australian Institute for Bioengineering & Nanotechnology, The University of Queensland, Australia, 7 2016. [Online]. Available: https://espace.library.uq.edu.au/view/UQ:395187

[4] IEA, “Key world energy statistics 2019,” 2019. [Online]. Available: https://www.iea.org/reports/key-world-energy-statistics-2019

[5] F. Isikgor and R. Becer, “Lignocellulosic biomass: A sustainable platform for production of bio-based chemicals and polymers,” *Polym. Chem.*, vol. 6, 05 2015.

[6] J. M. Howard, “Catalytic conversion of sugar manufacturing by-products to 5-(chloromethyl) furfural and 5-(hydroxymethyl) furural,” Ph.D. dissertation, Queensland University of Technology, 2017. [Online]. Available: 10.5204/thesis.eprints.107143

[7] J. K. Saini, R. Gupta, Hemansi, A. Verma, P. Gaur, R. Saini, R. Shukla, and R. C. Kuhad, *Integrated Lignocellulosic Biorefinery for Sustainable Bio-Based Economy*. Cham: Springer International Publishing, 2019, pp. 25–46. [Online]. Available: https://doi.org/10.1007/978-3-319-94797-6-2

[8] K. I. Galkin and V. P. Ananikov, “When will 5-hydroxymethylfurfural, the “sleeping giant” of sustainable chemistry, awaken?” *ChemSusChem*, vol. 12, no. 13, pp. 2976–2982, 2019. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/cssc.201900592

[9] A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, and C. A. M. Afonso, “5-hydroxymethylfurfural (hmf) as a building block platform: Biological

properties, synthesis and synthetic applications," *Green Chem.*, vol. 13, pp. 754–793, 2011. [Online]. Available: http://dx.doi.org/10.1039/C0GC00401D

[10] T. Wang, M. W. Nolte, and B. H. Shanks, "Catalytic dehydration of c6 carbohydrates for the production of hydroxymethylfurfural (hmf) as a versatile platform chemical," *Green Chem.*, vol. 16, pp. 548–572, 2014. [Online]. Available: http://dx.doi.org/10.1039/C3GC41365A

[11] M. J. Climent, A. Corma, and S. Iborra, "Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels," *Green Chem.*, vol. 16, pp. 516–547, 2014. [Online]. Available: http://dx.doi.org/10.1039/C3GC41492B

[12] H. Wang, C. Zhu, D. Li, Q. Liu, J. Tan, C. Wang, C. Cai, and L. Ma, "Recent advances in catalytic conversion of biomass to 5-hydroxymethylfurfural and 2, 5-dimethylfuran," *Renewable and Sustainable Energy Reviews*, vol. 103, pp. 227 – 247, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1364032118308050

[13] X. Li, R. Xu, J. Yang, S. Nie, D. Liu, Y. Liu, and C. Si, "Production of 5-hydroxymethylfurfural and levulinic acid from lignocellulosic biomass and catalytic upgradation," *Industrial Crops and Products*, vol. 130, pp. 184 – 197, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669018311440

[14] J. Artz and R. Palkovits, "Cellulose-based platform chemical: The path to application," *Current Opinion in Green and Sustainable Chemistry*, vol. 14, pp. 14 – 18, 2018, bioresources and Biochemicals / Biofuels and Bioenergy. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S2452223618300439

[15] O. Abdulmalik, M. K. Safo, Q. Chen, J. Yang, C. Brugnara, K. Ohene-Frempong, D. J. Abraham, and T. Asakura, "5-hydroxymethyl-2-furfural modifies intracellular sickle haemoglobin and inhibits sickling of red blood cells†,‡," *British Journal of Haematology*, vol. 128, no. 4, pp. 552–561, 2005. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1111/j.1365-2141.2004.05332.x

[16] F. Menegazzo, E. Ghedini, and M. Signoretto, "5-hydroxymethylfurfural (hmf) production from real biomasses," *Molecules*, vol. 23, no. 9, 2018. [Online]. Available: https://www.mdpi.com/1420-3049/23/9/2201

[17] G. P. Perez, A. Mukherjee, and M.-J. Dumont, "Insights into hmf catalysis," *Journal of Industrial and Engineering Chemistry*, vol. 70, pp. 1 – 34,

2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1226086X18308773

[18] A. H. Motagamwala, K. Huang, C. T. Maravelias, and J. A. Dumesic, “Solvent system for effective near-term production of hydroxymethylfurfural (hmf) with potential for long-term process improvement,” *Energy Environ. Sci.*, vol. 12, pp. 2212–2222, 2019. [Online]. Available: http://dx.doi.org/10.1039/C9EE00447E

[19] A. Ray, “Straw Based Biorefinery,” *Archive of organic and inorganic chemical sciences*, vol. 2, no. 5, pp. 249–255, 4 2018. [Online]. Available: https://ideas.repec.org/a/abr/oaoics/v2y2018i5p249-255.html

[20] A. Abraham, A. K. Mathew, R. Sindhu, A. Pandey, and P. Binod, “Potential of rice straw for bio-refining: An overview,” *Bioresource Technology*, vol. 215, pp. 29 – 36, 2016, waste Biorefinery - Advocating Circular Economy. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852416304837

[21] Y.-F. Huang and S.-L. Lo, “19 - utilization of rice hull and straw,” in *Rice (Fourth Edition)*, fourth edition ed., J. Bao, Ed. AACC International Press, 2019, pp. 627 – 661. [Online]. Available: http://www.sciencedirect.com/science/article/pii/B9780128115084000198

[22] M. Rathnayake, T. Chaireongsirikul, A. Svangariyaskul, L. Lawtrakul, and P. Toochinda, “Process simulation based life cycle assessment for bioethanol production from cassava, cane molasses, and rice straw,” *Journal of Cleaner Production*, vol. 190, pp. 24 – 35, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S095965261831179X

[23] C. V. Nguyen, D. Lewis, W.-H. Chen, H.-W. Huang, Z. A. ALOthman, Y. Yamauchi, and K. C.-W. Wu, “Combined treatments for producing 5-hydroxymethylfurfural (hmf) from lignocellulosic biomass,” *Catalysis Today*, vol. 278, pp. 344 – 349, 2016, novel materials for catalysis. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0920586116301912

[24] P. Binod, R. Sindhu, R. R. Singhania, S. Vikram, L. Devi, S. Nagalakshmi, N. Kurien, R. K. Sukumaran, and A. Pandey, “Bioethanol production from rice straw: An overview,” *Bioresource Technology*, vol. 101, no. 13, pp. 4767 – 4774, 2010, special Issue on Lignocellulosic Bioethanol: Current Status and Perspectives. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852409014862

[25] Food and A. O. of the United Nations (FAO STAT), “Paddy (rice) production in 2017,” 2017, data retrieved from FAO STAT, http://www.fao.org/faostat/en/#data/QC, Filters: Regions Total, Production Quantity, Rice, and 2017.

[26] Food and A. O. of the United Nations (FAO STAT), “Paddy (rice) production in 2018,” 2018, data retrieved from FAO STAT, http://www.fao.org/faostat/en/#data/QC, Filters: Regions Total, Production Quantity, Rice, and 2018.

[27] A. Barakat, H. de Vries, and X. Rouau, “Dry fractionation process as an important step in current and future lignocellulose biorefineries: A review,” *Bioresource Technology*, vol. 134, pp. 362 – 373, 2013. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852413002010

[28] V. B. Agbor, N. Cicek, R. Sparling, A. Berlin, and D. B. Levin, “Biomass pretreatment: Fundamentals toward application,” *Biotechnology Advances*, vol. 29, no. 6, pp. 675 – 685, 2011. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0734975011000607

[29] S. Morais, E. Morag, Y. Barak, D. Goldman, Y. Hadar, R. Lamed, Y. Shoham, D. B. Wilson, and E. A. Bayer, “Deconstruction of lignocellulose into soluble sugars by native and designer cellulosomes,” *mBio*, vol. 3, no. 6, 2012.

[30] M. C. Chang, “Harnessing energy from plant biomass,” *Current Opinion in Chemical Biology*, vol. 11, no. 6, pp. 677 – 684, 2007, model systems/Biopolymers. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1367593107001202

[31] Y.-H. P. Zhang and L. R. Lynd, “Toward an aggregated understanding of enzymatic hydrolysis of cellulose: Noncomplexed cellulase systems,” *Biotechnology and Bioengineering*, vol. 88, no. 7, pp. 797–824, 2004. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/bit.20282

[32] J. Houghton, S. Weatherwax, and J. Ferrell, “Breaking the biological barriers to cellulosic ethanol: A joint research agenda,” 6 2006.

[33] A. A. Modenbach and S. E. Nokes, “Effects of sodium hydroxide pretreatment on structural components of biomass,” *Transactions of the ASABE*, vol. 57, no. 4, pp. 1187–1198, 2014. [Online]. Available: https://elibrary.asabe.org/abstract.asp?aid=45059

[34] H. V. Scheller and P. Ulvskov, “Hemicelluloses,” *Annual Review of Plant Biology*, vol. 61, no. 1, pp. 263–289, 2010, pMID: 20192742. [Online]. Available: https://doi.org/10.1146/annurev-arplant-042809-112315

[35] X. Zhao, L. Zhang, and D. Liu, “Biomass recalcitrance. part i: the chemical compositions and physical structures affecting the enzymatic hydrolysis of lignocellulose,” *Biofuels, Bioproducts and Biorefining*, vol. 6, no. 4, pp. 465–482, 2012. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/bbb.1331

[36] A. U. Buranov and G. Mazza, “Lignin in straw of herbaceous crops,” *Industrial Crops and Products*, vol. 28, no. 3, pp. 237 – 259, 2008. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669008000630

[37] E. M. Rubin, “Genomics of cellulosic biofuels,” *Nature Reviews*, vol. 454, p. 841–845, 2008. [Online]. Available: https://www.nature.com/articles/nature07190

[38] A. Kiran Kumar and S. Sharma, “Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review,” *Bioresources and Bioprocessing*, vol. 4, 12 2017.

[39] E. C. Bensah and M. Mensah, “Chemical pretreatment methods for the production of cellulosic ethanol: Technologies and innovations,” *International Journal of Chemical Engineering*, vol. 2013, 2013. [Online]. Available: https://doi.org/10.1155/2013/719607

[40] H. Chen, J. Liu, X. Chang, D. Chen, Y. Xue, P. Liu, H. Lin, and S. Han, “A review on the pretreatment of lignocellulose for high-value chemicals,” *Fuel Processing Technology*, vol. 160, pp. 196 – 206, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0378382016311766

[41] E. E. Anthonia and H. S. Philip, “An overview of the applications of furfural and its derivatives,” *International Journal of Advanced Chemistry*, vol. 3, no. 2, pp. 42–47, 2015. [Online]. Available: https://sciencepubcocom.ipage.com/sciencepubco/index.php/IJAC/article/view/5048

[42] C. M. Cai, T. Zhang, R. Kumar, and C. E. Wyman, “Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass,” *Journal of Chemical Technology & Biotechnology*, vol. 89, no. 1, pp. 2–10, 2014. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/jctb.4168

[43] G. Machado, S. Leon, F. Santos, R. Lourega, J. Dullius, M. Mollmann, and P. Eichler, “Literature review on furfural production from lignocellulosic biomass,” *Natural Resources*, vol. 07, pp. 115–129, 01 2016.

[44] A. S. Mamman, J.-M. Lee, Y.-C. Kim, I. T. Hwang, N.-J. Park, Y. K. Hwang, J.-S. Chang, and J.-S. Hwang, "Furfural: Hemicellulose/xylosederived biochemical," *Biofuels, Bioproducts and Biorefining*, vol. 2, no. 5, pp. 438–454, 2008. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/bbb.95

[45] S. Elumalai, B. Arumugam, P. Kundu, and S. Kumar, "Chapter 18 - phenol derivatives of lignin monomers for aromatic compounds and cycloalkane fuels," in *Biomass, Biofuels, Biochemicals*, ser. Biomass, Biofuels, Biochemicals, S. Saravanamurugan, A. Pandey, H. Li, and A. Riisager, Eds. Elsevier, 2020, pp. 459 – 483. [Online]. Available: http://www.sciencedirect.com/science/article/pii/B9780444643070000184

[46] M. S. Karunarathna and R. C. Smith, "Valorization of lignin as a sustainable component of structural materials and composites: Advances from 2011 to 2019," *Sustainability*, vol. 12, no. 2, 2020. [Online]. Available: https://www.mdpi.com/2071-1050/12/2/734

[47] M. A. Helle and C. L. Cheung, "Methods of making and using lignin derivatives," patentus. [Online]. Available: https://patents.google.com/patent/US10533031B2/en

[48] S. Kang, J. Fu, and G. Zhang, "From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis," *Renewable and Sustainable Energy Reviews*, vol. 94, pp. 340 – 362, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1364032118304520

[49] I. K. Yu, D. C. Tsang, A. C. Yip, S. S. Chen, L. Wang, Y. S. Ok, and C. S. Poon, "Catalytic valorization of starch-rich food waste into hydroxymethylfurfural (hmf): Controlling relative kinetics for high productivity," *Bioresource Technology*, vol. 237, pp. 222 – 230, 2017, 1st International Conference on Bioresource Technology for Bioenergy, Bioproducts & Environmental Sustainability (BIORESTEC). [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852417300378

[50] H. Amiri, K. Karimi, and S. Roodpeyma, "Production of furans from rice straw by single-phase and biphasic systems," *Carbohydrate Research*, vol. 345, no. 15, pp. 2133 – 2138, 2010. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0008621510003174

[51] Z. Zhang and Z. K. Zhao, "Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid," *Bioresource Technology*, vol. 101, no. 3,

pp. 1111 – 1114, 2010. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S096085240901178X

[52] Y. Feng, M. Li, Z. Gao, X. Zhang, X. Zeng, Y. Sun, X. Tang, T. Lei, and L. Lin, "Development of betaine-based sustainable catalysts for green conversion of carbohydrates and biomass into 5-hydroxymethylfurfural," *ChemSusChem*, vol. 12, no. 2, pp. 495–502, 2019. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/cssc.201802342

[53] A. Abo-Hamad, M. Hayyan, M. A. AlSaadi, and M. A. Hashim, "Potential applications of deep eutectic solvents in nanotechnology," *Chemical Engineering Journal*, vol. 273, pp. 551 – 567, 2015. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1385894715004076

[54] R. Agrawal, R. Gaur, A. Mathur, R. Kumar, R. P. Gupta, D. K. Tuli, and A. Satlewal, "Improved saccharification of pilot-scale acid pretreated wheat straw by exploiting the synergistic behavior of lignocellulose degrading enzymes," *RSC Adv.*, vol. 5, pp. 71 462–71 471, 2015. [Online]. Available: http://dx.doi.org/10.1039/C5RA13360B

[55] S. Singh, G. Cheng, N. Sathitsuksanoh, D. Wu, P. Varanasi, A. George, V. Balan, X. Gao, R. Kumar, B. E. Dale, C. E. Wyman, and B. A. Simmons, "Comparison of different biomass pretreatment techniques and their impact on chemistry and structure," *Frontiers in Energy Research*, vol. 2, p. 62, 2015. [Online]. Available: https://www.frontiersin.org/article/10.3389/fenrg.2014.00062

[56] L. Capolupo and V. Faraco, "Green methods of lignocellulose pretreatment for biorefinery development," *Applied Microbiology and Biotechnology*, vol. 100, no. 22, pp. 9451–9467, 11 2016. [Online]. Available: https://doi.org/10.1007/s00253-016-7884-y

[57] W. Den, V. K. Sharma, M. Lee, G. Nadadur, and R. S. Varma, "Lignocellulosic biomass transformations via greener oxidative pretreatment processes: Access to energy and value-added chemicals," *Frontiers in Chemistry*, vol. 6, p. 141, 2018. [Online]. Available: https://www.frontiersin.org/article/10.3389/fchem.2018.00141

[58] P. R. Seidl and A. K. Goulart, "Pretreatment processes for lignocellulosic biomass conversion to biofuels and bioproducts," *Current Opinion in Green and Sustainable Chemistry*, vol. 2, pp. 48 – 53, 2016, bioresources, Biomass, Bio-fuels and Bioenergies 2016. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S2452223616300232

[59] D. Steinbach, A. Kruse, and J. Sauer, "Pretreatment technologies of lignocellulosic biomass in water in view of furfural and 5-hydroxymethylfurfural production- a review," *Biomass Conversion and Biorefinery*, vol. 7, no. 2, pp. 247–274, 6 2017. [Online]. Available: https://doi.org/10.1007/s13399-017-0243-0

[60] V. S. Chang, M. Nagwani, and M. T. Holtzapple, "Lime pretreatment of crop residues bagasse and wheat straw," *Applied Biochemistry and Biotechnology*, vol. 74, no. 3, pp. 135–159, 9 1998. [Online]. Available: https://doi.org/10.1007/BF02825962

[61] Y. Liao, Q. Liu, T. Wang, J. Long, L. Ma, and Q. Zhang, "Zirconium phosphate combined with ru/c as a highly efficient catalyst for the direct transformation of cellulose to c6 alditols," *Green Chem.*, vol. 16, pp. 3305–3312, 2014. [Online]. Available: http://dx.doi.org/10.1039/C3GC42444H

[62] F. Boissou, N. Sayoud, K. De Oliveira Vigier, A. Barakat, S. Marinkovic, B. Estrine, and F. Jerome, "Acid-assisted ball milling of cellulose as an efficient pretreatment process for the production of butyl glycosides," *ChemSusChem*, vol. 8, no. 19, pp. 3263–3269, 2015. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/cssc.201500700

[63] S. Nemoto, T. Ueno, A. Watthanaphanit, J. Hieda, and N. Saito, "Crystallinity and surface state of cellulose in wet ball-milling process," *Journal of Applied Polymer Science*, vol. 134, no. 22, 2017. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/app.44903

[64] A. S. da Silva, H. Inoue, T. Endo, S. Yano, and E. P. Bon, "Milling pretreatment of sugarcane bagasse and straw for enzymatic hydrolysis and ethanol fermentation," *Bioresource Technology*, vol. 101, no. 19, pp. 7402 – 7409, 2010. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852410008199

[65] H. Kim, J. Chang, B.-Y. Jeong, and J. Lee, "Comparison of milling modes as a pretreatment method for cellulosic biofuel production," *Journal of Clean Energy Technologies*, vol. 1, pp. 45–48, 01 2013.

[66] X. Qi, L. Yan, F. Shen, and M. Qiu, "Mechanochemical-assisted hydrolysis of pretreated rice straw into glucose and xylose in water by weakly acidic solid catalyst," *Bioresource Technology*, vol. 273, pp. 687 – 691, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852418315311

[67] T. Qu, X. Zhang, X. Gu, L. Han, G. Ji, X. Chen, and W. Xiao, "Ball milling for biomass fractionation and pretreatment with aqueous hydroxide solutions," *ACS Sustainable Chemistry & Engineering*, vol. 5, no. 9, pp. 7733–7742, 2017. [Online]. Available: https://doi.org/10.1021/acssuschemeng.7b01186

[68] S. S. Hassan, G. A. Williams, and A. K. Jaiswal, "Emerging technologies for the pretreatment of lignocellulosic biomass," *Bioresource Technology*, vol. 262, pp. 310 – 318, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852418306229

[69] Z.-Y. Xiong, Y.-H. Qin, J.-Y. Ma, L. Yang, Z.-K. Wu, T.-L. Wang, W.-G. Wang, and C.-W. Wang, "Pretreatment of rice straw by ultrasound-assisted fenton process," *Bioresource Technology*, vol. 227, pp. 408 – 411, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852416317837

[70] E. Shirkavand, S. Baroutian, D. J. Gapes, and B. R. Young, "Combination of fungal and physicochemical processes for lignocellulosic biomass pretreatment – a review," *Renewable and Sustainable Energy Reviews*, vol. 54, pp. 217 – 234, 2016. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1364032115010783

[71] M. Bussemaker and D. Zhang, "Effect of ultrasound on lignocellulosic biomass as a pretreatment for biorefinery and biofuel applications," *INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH*, vol. 52, no. 10, p. 3563–3580, 2013.

[72] M. Saif Ur Rehman, I. Kim, Y. Chisti, and J.-I. Han, "Use of ultrasound in the production of bioethanol from lignocellulosic biomass," *Energy, Education, Science and Technology*, vol. 30, pp. 1391–1410, 01 2013.

[73] P. R. Gogate, V. S. Sutkar, and A. B. Pandit, "Sonochemical reactors: Important design and scale up considerations with a special emphasis on heterogeneous systems," *Chemical Engineering Journal*, vol. 166, no. 3, pp. 1066 – 1082, 2011. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1385894710011654

[74] H. Wu, X. Dai, S.-L. Zhou, Y.-Y. Gan, Z.-Y. Xiong, Y.-H. Qin, J. Ma, L. Yang, Z.-K. Wu, T.-L. Wang, W.-G. Wang, and C.-W. Wang, "Ultrasound-assisted alkaline pretreatment for enhancing the enzymatic hydrolysis of rice straw by using the heat energy dissipated from ultrasonication," *Bioresource Technology*, vol. 241, pp. 70 – 74, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852417307459

[75] N. Dinh Vu, H. Thi Tran, N. D. Bui, C. Duc Vu, and H. Viet Nguyen, “Lignin and cellulose extraction from vietnam’s rice straw using ultrasound-assisted alkaline treatment method,” *International Journal of Polymer Science*, vol. 2017, p. 1063695, 2017. [Online]. Available: https://doi.org/10.1155/2017/1063695

[76] A. A. Issa, Y. S. Al-Degs, K. Mashal, and R. Z. A. Bakain, “Fast activation of natural biomasses by microwave heating,” *Journal of Industrial and Engineering Chemistry*, vol. 21, pp. 230 – 238, 2015. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1226086X14001142

[77] L. Dai, C. He, Y. Wang, Y. Liu, Z. Yu, Y. Zhou, L. Fan, D. Duan, and R. Ruan, “Comparative study on microwave and conventional hydrothermal pretreatment of bamboo sawdust: Hydrochar properties and its pyrolysis behaviors,” *Energy Conversion and Management*, vol. 146, pp. 1 – 7, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0196890417304363

[78] S. Irmak, B. Meryemoglu, A. Sandip, J. Subbiah, R. B. Mitchell, and G. Sarath, “Microwave pretreatment effects on switchgrass and miscanthus solubilization in subcritical water and hydrolysate utilization for hydrogen production,” *Biomass and Bioenergy*, vol. 108, pp. 48 – 54, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0961953417303550

[79] S. Mafuleka and E. G. Kana, “Modelling and optimization of xylose and glucose production from napier grass using hybrid pre-treatment techniques,” *Biomass and Bioenergy*, vol. 77, pp. 200 – 208, 2015. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0961953415001208

[80] Z. Hu and Z. Wen, “Enhancing enzymatic digestibility of switchgrass by microwave-assisted alkali pretreatment,” *Biochemical Engineering Journal*, vol. 38, no. 3, pp. 369 – 378, 2008. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1369703X07002756

[81] P. Binod, K. Satyanagalakshmi, R. Sindhu, K. U. Janu, R. K. Sukumaran, and A. Pandey, “Short duration microwave assisted pretreatment enhances the enzymatic saccharification and fermentable sugar yield from sugarcane bagasse,” *Renewable Energy*, vol. 37, no. 1, pp. 109 – 116, 2012. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960148111002990

[82] D. R. Keshwani and J. J. Cheng, “Microwave-based alkali pretreatment of switchgrass and coastal bermudagrass for bioethanol production,” *Biotechnology Progress*, vol. 26, no. 3, pp. 644–652, 2010. [Online]. Available: https://aiche.onlinelibrary.wiley.com/doi/abs/10.1002/btpr.371

[83] V. Sorn, K.-L. Chang, P. Phitsuwan, K. Ratanakhanokchai, and C.-D. Dong, "Effect of microwave-assisted ionic liquid/acidic ionic liquid pretreatment on the morphology, structure, and enhanced delignification of rice straw," *Bioresource Technology*, vol. 293, p. 121929, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852419311599

[84] P. Alvira, E. Tomás-Pejó, M. Ballesteros, and M. Negro, "Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review," *Bioresource Technology*, vol. 101, no. 13, pp. 4851 – 4861, 2010, special Issue on Lignocellulosic Bioethanol: Current Status and Perspectives. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852409015983

[85] E. Ximenes, C. S. Farinas, Y. Kim, and M. R. Ladisch, *Hydrothermal Pretreatment of Lignocellulosic Biomass for Bioethanol Production*. Cham: Springer International Publishing, 2017, pp. 181–205. [Online]. Available: https://doi.org/10.1007/978-3-319-56457-9_7

[86] Y. W. Bandara, P. Gamage, and D. S. Gunarathne, "Hot water washing of rice husk for ash removal: The effect of washing temperature, washing time and particle size," *Renewable Energy*, vol. 153, pp. 646 – 652, 2020. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S096014812030224X

[87] D. G. Mulat, S. G. Huerta, D. Kalyani, and S. J. Horn, "Enhancing methane production from lignocellulosic biomass by combined steam-explosion pretreatment and bioaugmentation with cellulolytic bacterium caldicellulosiruptor bescii," *Biotechnology for Biofuels*, vol. 11, no. 1, p. 19, 2018. [Online]. Available: https://doi.org/10.1186/s13068-018-1025-z

[88] M. Moniruzzaman, "Effect of steam explosion on the physicochemical properties and enzymatic saccharification of rice straw," *Applied Biochemistry and Biotechnology*, vol. 59, no. 3, pp. 283–297, 6 1996. [Online]. Available: https://doi.org/10.1007/BF02783570

[89] W. Schwald, C. Breuil, H. H. Brownell, M. Chan, and J. M. Saddler, "Assessment of pretreatment conditions to obtain fast complete hydrolysis on high substrate concentrations," *Applied Biochemistry and Biotechnology*, vol. 20, no. 1, p. 29, 1 1989. [Online]. Available: https://doi.org/10.1007/BF02936471

[90] X. Zhao, L. Zhang, and D. Liu, "Biomass recalcitrance. part ii: Fundamentals of different pre-treatments to increase the enzymatic digestibility of

lignocellulose," *Biofuels, Bioproducts and Biorefining*, vol. 6, no. 5, pp. 561–579, 2012. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/bbb.1350

[91] S. Sharma, R. Kumar, R. Gaur, R. Agrawal, R. P. Gupta, D. K. Tuli, and B. Das, "Pilot scale study on steam explosion and mass balance for higher sugar recovery from rice straw," *Bioresource Technology*, vol. 175, pp. 350 – 357, 2015. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852414015442

[92] W.-H. Chen, C.-C. Tsai, C.-F. Lin, P.-Y. Tsai, and W.-S. Hwang, "Pilot-scale study on the acid-catalyzed steam explosion of rice straw using a continuous pretreatment system," *Bioresource Technology*, vol. 128, pp. 297 – 304, 2013. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852412016203

[93] S. Semwal, T. Raj, R. Kumar, J. Christopher, R. P. Gupta, S. K. Puri, R. Kumar, and S. Ramakumar, "Process optimization and mass balance studies of pilot scale steam explosion pretreatment of rice straw for higher sugar release," *Biomass and Bioenergy*, vol. 130, p. 105390, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0961953419303393

[94] L. Matsakas, O. Sarkar, S. Jansson, U. Rova, and P. Christakopoulos, "A novel hybrid organosolv-steam explosion pretreatment and fractionation method delivers solids with superior thermophilic digestibility to methane," *Bioresource Technology*, vol. 316, p. 123973, 2020. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852420312451

[95] F. S. Asghari and H. Yoshida, "Dehydration of fructose to 5-hydroxymethylfurfural in sub-critical water over heterogeneous zirconium phosphate catalysts," *Carbohydrate Research*, vol. 341, no. 14, pp. 2379 – 2387, 2006. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0008621506003363

[96] Z. Wang, M.-Q. Zhu, M.-F. Li, J.-Q. Wang, Q. Wei, and R.-C. Sun, "Comprehensive evaluation of the liquid fraction during the hydrothermal treatment of rapeseed straw," *Biotechnology for Biofuels*, vol. 9, 12 2016.

[97] A. Sato, S. Soeprijanto, and A. Widjaja, "Influence of alkaline hydrothermal pretreatment of rice straw on biomass composition," *International Energy Journal*, vol. 19, pp. 115–124, 6 2019.

[98] L. M. Schmidt, L. D. Mthembu, P. Reddy, N. Deenadayalu, M. Kaltschmitt, and I. Smirnova, "Levulinic acid production integrated into a sugarcane

bagasse based biorefinery using thermal-enzymatic pretreatment," *Industrial Crops and Products*, vol. 99, pp. 172 – 178, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669017301000

[99] S. Imman, J. Arnthong, V. Burapatana, V. Champreda, and N. Laosiripojana, "Influence of alkaline catalyst addition on compressed liquid hot water pretreatment of rice straw," *Chemical Engineering Journal*, vol. 278, pp. 85 – 91, 2015, tailoring Sustainability through Chemical Reaction Engineering. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1385894714016428

[100] T. Oomori, S. H. Khajavi, Y. Kimura, S. Adachi, and R. Matsuno, "Hydrolysis of disaccharides containing glucose residue in subcritical water," *Biochemical Engineering Journal*, vol. 18, no. 2, pp. 143 – 147, 2004. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1369703X03002018

[101] N. Syaftika and Y. Matsumura, "Comparative study of hydrothermal pretreatment for rice straw and its corresponding mixture of cellulose, xylan, and lignin," *Bioresource Technology*, vol. 255, pp. 1 – 6, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852418300993

[102] S. Behera, R. Arora, N. Nandhagopal, and S. Kumar, "Importance of chemical pretreatment for bioconversion of lignocellulosic biomass," *Renewable and Sustainable Energy Reviews*, vol. 36, pp. 91 – 106, 2014. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1364032114002743

[103] S. Arora, N. Gupta, and V. Singh, "Choline based basic ionic liquid (bil)/acidic des mediated cellulose rich fractionation of agricultural waste biomass and valorization to 5-hmf," *Waste and Biomass Valorization*, 4 2019. [Online]. Available: https://doi.org/10.1007/s12649-019-00603-2

[104] A. Moreno, E. Tomás-Pejó, M. Ballesteros, and M. Negro, "Chapter 16 - pretreatment technologies for lignocellulosic biomass deconstruction within a biorefinery perspective," in *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels (Second Edition)*, second edition ed., ser. Biomass, Biofuels, Biochemicals, A. Pandey, C. Larroche, C.-G. Dussap, E. Gnansounou, S. K. Khanal, and S. Ricke, Eds. Academic Press, 2019, pp. 379 – 399. [Online]. Available: http://www.sciencedirect.com/science/article/pii/B9780128168561000166

[105] L. M. L. Laurens, N. Nagle, R. Davis, N. Sweeney, S. Van Wychen, A. Lowell, and P. T. Pienkos, "Acid-catalyzed algal biomass pretreatment for integrated

lipid and carbohydrate-based biofuels production," *Green Chem.*, vol. 17, pp. 1145–1158, 2015. [Online]. Available: http://dx.doi.org/10.1039/C4GC01612B

[106] M. Kapoor, S. Soam, R. Agrawal, R. P. Gupta, D. K. Tuli, and R. Kumar, "Pilot scale dilute acid pretreatment of rice straw and fermentable sugar recovery at high solid loadings," *Bioresource Technology*, vol. 224, pp. 688 – 693, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852416315371

[107] S. Singh, D. Kaur, S. K. Yadav, and M. Krishania, "Process scale-up of an efficient acid-catalyzed steam pretreatment of rice straw for xylitol production by c. tropicalis mtcc 6192," *Bioresource Technology*, vol. 320, p. 124422, 2021. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852420316965

[108] S. B. Kim, S. J. Lee, E. J. Jang, S. O. Han, C. Park, and S. W. Kim, "Sugar recovery from rice straw by dilute acid pretreatment," *Journal of Industrial and Engineering Chemistry*, vol. 18, no. 1, pp. 183 – 187, 2012. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1226086X11002012

[109] Z. Chen, A. Ragauskas, and C. Wan, "Lignin extraction and upgrading using deep eutectic solvents," *Industrial Crops and Products*, vol. 147, p. 112241, 2020. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669020301576

[110] F. Hu, S. Jung, and A. Ragauskas, "Pseudo-lignin formation and its impact on enzymatic hydrolysis," *Bioresource Technology*, vol. 117, pp. 7 – 12, 2012. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852412006426

[111] S. Souzanchi, L. Nazari, K. T. V. Rao, Z. Yuan, Z. Tan, and C. C. Xu, "Catalytic isomerization of glucose to fructose using heterogeneous solid base catalysts in a continuous-flow tubular reactor: Catalyst screening study," *Catalysis Today*, vol. 319, pp. 76 – 83, 2019, sI: Biomass Valorization. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0920586118303250

[112] R. O. Souza, D. P. Fabiano, C. Feche, F. Rataboul, D. Cardoso, and N. Essayem, "Glucose-fructose isomerisation promoted by basic hybrid catalysts," *Catalysis Today*, vol. 195, no. 1, pp. 114 – 119, 2012, catalysis for Biorefineries. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0920586112004129

[113] Q. Zhang, Y. Deng, X. Tan, W. Wang, Q. Yu, X. Chen, C. Miao, Y. Guo, Y. Zhang, X. Zhuang, and Z. Yuan, "Biphasic fractionation of

rice straw under mild condition in acidified 2-phenoxyethanol/water system," *Industrial Crops and Products*, vol. 145, p. 112091, 2020. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669020300078

[114] L. Dong, X. Wu, Q. Wang, G. Cao, J. Wu, C. Zhou, and N. Ren, "Evaluation of a novel pretreatment of naoh/urea at outdoor cold-winter conditions for enhanced enzymatic conversion and hythane production from rice straw," *Science of The Total Environment*, vol. 744, p. 140900, 2020. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0048969720344296

[115] J. Wu, L. Dong, B. Liu, D. Xing, C. Zhou, Q. Wang, X. Wu, L. Feng, and G. Cao, "A novel integrated process to convert cellulose and hemicellulose in rice straw to biobutanol," *Environmental Research*, vol. 186, p. 109580, 2020. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0013935120304734

[116] S. De, S. Mishra, E. Poonguzhali, M. Rajesh, and K. Tamilarasan, "Fractionation and characterization of lignin from waste rice straw: Biomass surface chemical composition analysis," *International Journal of Biological Macromolecules*, vol. 145, pp. 795 – 803, 2020. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0141813019372253

[117] N. Poornejad, K. Karimi, and T. Behzad, "Improvement of saccharification and ethanol production from rice straw by nmmo and [bmim][oac] pretreatments," *Industrial Crops and Products*, vol. 41, pp. 408 – 413, 2013. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669012002658

[118] O. A. El Seoud, A. Koschella, L. C. Fidale, S. Dorn, and T. Heinze, "Applications of ionic liquids in carbohydrate chemistry: A window of opportunities," *Biomacromolecules*, vol. 8, no. 9, pp. 2629–2647, 2007. [Online]. Available: https://doi.org/10.1021/bm070062i

[119] J. Luo, M. Cai, and T. Gu, *Pretreatment of Lignocellulosic Biomass Using Green Ionic Liquids*. Dordrecht: Springer Netherlands, 2013, pp. 127–153. [Online]. Available: https://doi.org/10.1007/978-94-007-6052-3_6

[120] E. M. Aung, T. Endo, S. Fujii, K. Kuroda, K. Ninomiya, and K. Takahashi, "Efficient pretreatment of bagasse at high loading in an ionic liquid," *Industrial Crops and Products*, vol. 119, pp. 243 – 248, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669018303078

[121] S. Wang, J. Chen, G. Yang, W. Gao, and K. Chen, "Efficient conversion of hubrid pennisetum to glucose by oxygen-aqueous alkaline ionic liquid media

pretreatment under benign conditions," *Bioresource Technology*, vol. 243, pp. 335 – 338, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852417310386

[122] A. George, A. Brandt, K. Tran, S. M. S. N. S. Zahari, D. Klein-Marcuschamer, N. Sun, N. Sathitsuksanoh, J. Shi, V. Stavila, R. Parthasarathi, S. Singh, B. M. Holmes, T. Welton, B. A. Simmons, and J. P. Hallett, "Design of low-cost ionic liquids for lignocellulosic biomass pretreatment," *Green Chem.*, vol. 17, pp. 1728–1734, 2015. [Online]. Available: http://dx.doi.org/10.1039/C4GC01208A

[123] B. Karimi and H. M. Mirzaei, "The influence of hydrophobic/hydrophilic balance of the mesoporous solid acid catalysts in the selective dehydration of fructose into hmf," *RSC Adv.*, vol. 3, pp. 20 655–20 661, 2013. [Online]. Available: http://dx.doi.org/10.1039/C3RA44214D

[124] S. Kahani, M. Shafiei, A. Abdolmaleki, and K. Karimi, "Enhancement of ethanol production by novel morpholinium ionic liquids," *Journal of Cleaner Production*, vol. 168, pp. 952 – 962, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0959652617319959

[125] M. Mohammadi, M. Shafiei, A. Abdolmaleki, K. Karimi, J.-P. Mikkola, and C. Larsson, "A morpholinium ionic liquid for rice straw pretreatment to enhance ethanol production," *Industrial Crops and Products*, vol. 139, p. 111494, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669019305060

[126] C. L. Chambon, M. Chen, P. S. Fennell, and J. P. Hallett, "Efficient fractionation of lignin- and ash-rich agricultural residues following treatment with a low-cost protic ionic liquid," *Frontiers in Chemistry*, vol. 7, p. 246, 2019. [Online]. Available: https://www.frontiersin.org/article/10.3389/fchem.2019.00246

[127] P. Suwannabun, K. Cheenkachorn, M. Prongjit, A. Tawai, and M. Sriariyanun, "Pretreatment of rice straw by inorganic salts and 1-ethyl-3-methylimdazolium acetate for biofuel production," in *2019 2nd Asia Conference on Energy and Environment Engineering (ACEEE)*, 2019, pp. 12–15.

[128] L. T. P. Trinh, Y.-J. Lee, C. S. Park, and H.-J. Bae, "Aqueous acidified ionic liquid pretreatment for bioethanol production and concentration of produced ethanol by pervaporation," *Journal of Industrial and Engineering Chemistry*, vol. 69, pp. 57 – 65, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1226086X18306270

[129] J. Gao, S. Xin, L. Wang, Y. Lei, H. Ji, and S. Liu, "Effect of ionic liquid/inorganic salt/water pretreatment on the composition, structure and

enzymatic hydrolysis of rice straw," *Bioresource Technology Reports*, vol. 5, pp. 355 – 358, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S2589014X18300392

[130] C.-Y. Yang and T. J. Fang, "Combination of ultrasonic irradiation with ionic liquid pretreatment for enzymatic hydrolysis of rice straw," *Bioresource Technology*, vol. 164, pp. 198 – 202, 2014. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852414006634

[131] A. Boonsombuti, O. Trisinsub, and A. Luengnaruemitchai, "Comparative study of three chemical pretreatments and their effects on the structural changes of rice straw and butanol production," *Waste and Biomass Valorization*, vol. 11, pp. 2771–2781, 2020. [Online]. Available: https://doi.org/10.1007/s12649-019-00622-z

[132] W. Zhang, J. Liu, Y. Wang, J. Sun, P. Huang, and K. Chang, "Effect of ultrasound on ionic liquid-hydrochloric acid pretreatment with rice straw," *Biomass Conversion and Biorefinery*, 2020. [Online]. Available: https://doi.org/10.1007/s13399-019-00595-y

[133] K.-L. Chang, X.-M. Chen, X.-Q. Wang, Y.-J. Han, L. Potprommanee, J. yong Liu, Y.-L. Liao, X. an Ning, S. yu Sun, and Q. Huang, "Impact of surfactant type for ionic liquid pretreatment on enhancing delignification of rice straw," *Bioresource Technology*, vol. 227, pp. 388 – 392, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852416316066

[134] Y.-Y. Hong, Y.-T. Wang, S.-M. Zhu, X.-C. Luo, S. Li, M. Zhuo, T. Zhou, and M.-J. Zhu, "Improved enzymatic hydrolysis and ethanol production by combined alkaline peroxide and ionic liquid-water mixtures pretreatment of rice straw," *Journal of Chemical Technology & Biotechnology*, vol. 94, no. 5, pp. 1451–1459, 2019. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/jctb.5895

[135] N. Akhtar, K. Gupta, D. Goyal, and A. Goyal, "Recent advances in pretreatment technologies for efficient hydrolysis of lignocellulosic biomass," *Environmental Progress & Sustainable Energy*, vol. 35, no. 2, pp. 489–511, 2016. [Online]. Available: https://aiche.onlinelibrary.wiley.com/doi/abs/10.1002/ep.12257

[136] Q. Yu, R. Liu, K. Li, and R. Ma, "A review of crop straw pretreatment methods for biogas production by anaerobic digestion in china," *Renewable and Sustainable Energy Reviews*, vol. 107, pp. 51 – 58, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1364032119301133

[137] Anu, A. Kumar, K. K. Jain, and B. Singh, "Process optimization for chemical pretreatment of rice straw for bioethanol production," *Renewable Energy*, vol. 156, pp. 1233 – 1243, 2020. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S096014812030584X

[138] A. Kaur and R. C. Kuhad, "Valorization of rice straw for ethanol production and lignin recovery using combined acid-alkali pre-treatment," *BioEnergy Research*, vol. 12, no. 3, pp. 570–582, 9 2019. [Online]. Available: https://doi.org/10.1007/s12155-019-09988-3

[139] M. Pan, G. Zhao, C. Ding, B. Wu, Z. Lian, and H. Lian, "Physicochemical transformation of rice straw after pretreatment with a deep eutectic solvent of choline chloride/urea," *Carbohydrate Polymers*, vol. 176, pp. 307 – 314, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0144861717309645

[140] X. Ge, C. Chang, L. Zhang, S. Cui, X. Luo, S. Hu, Y. Qin, and Y. Li, "Chapter five - conversion of lignocellulosic biomass into platform chemicals for biobased polyurethane application," in *Advances in Bioenergy*, ser. Advances in Bioenergy, Y. Li and X. Ge, Eds. Elsevier, 2018, vol. 3, pp. 161 – 213. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S2468012518300051

[141] L. T. Mika, E. Csefalvay, and A. Nemeth, "Catalytic conversion of carbohydrates to initial platform chemicals: Chemistry and sustainability," *Chemical Reviews*, vol. 118, no. 2, pp. 505–613, 2018, pMID: 29155579. [Online]. Available: https://doi.org/10.1021/acs.chemrev.7b00395

[142] A. Rusanen, R. Lahti, K. Lappalainen, J. Kärkkäinen, T. Hu, H. Romar, and U. Lassi, "Catalytic conversion of glucose to 5-hydroxymethylfurfural over biomass-based activated carbon catalyst," *Catalysis Today*, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0920586118313245

[143] A. Hideno, H. Inoue, K. Tsukahara, S. Fujimoto, T. Minowa, S. Inoue, T. Endo, and S. Sawayama, "Wet disk milling pretreatment without sulfuric acid for enzymatic hydrolysis of rice straw," *Bioresource Technology*, vol. 100, no. 10, pp. 2706 – 2711, 2009. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852408011371

[144] J. Zhou, B. H. Yan, Y. Wang, X. Y. Yong, Z. H. Yang, H. H. Jia, M. Jiang, and P. Wei, "Effect of steam explosion pretreatment on the anaerobic digestion

of rice straw," *RSC Adv.*, vol. 6, pp. 88 417–88 425, 2016. [Online]. Available: http://dx.doi.org/10.1039/C6RA15330E

[145] I. Wood, C. Giang, L. Tran, N. Cook, P. Ryden, D. Wilson, G. Moates, S. Collins, A. Elliston, and K. Waldron, "Comparison of saccharification and fermentation of steam exploded rice straw and rice husk," *Biotechnology for Biofuels*, vol. 9, 12 2016.

[146] T. Pielhop, J. Amgarten, P. R. von Rohr, and M. H.-P. Studer, "Steam explosion pretreatment of softwood: the effect of the explosive decompression on enzymatic digestibility," in *Biotechnology for Biofuels*, 2016.

[147] Y. Bin and C. Hongzhang, "Effect of the ash on enzymatic hydrolysis of steam-exploded rice straw," *Bioresource Technology*, vol. 101, no. 23, pp. 9114 – 9119, 2010. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S096085241001223X

[148] T.-C. Hsu, G.-L. Guo, W.-H. Chen, and W.-S. Hwang, "Effect of dilute acid pretreatment of rice straw on structural properties and enzymatic hydrolysis," *Bioresource Technology*, vol. 101, no. 13, pp. 4907 – 4913, 2010, special Issue on Lignocellulosic Bioethanol: Current Status and Perspectives. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852409013510

[149] H. Teramura, K. Sasaki, T. Oshima, S. Aikawa, F. Matsuda, M. Okamoto, T. Shirai, H. Kawaguchi, C. Ogino, M. Yamasaki, J. Kikuchi, and A. Kondo, "Changes in lignin and polysaccharide components in 13 cultivars of rice straw following dilute acid pretreatment as studied by solution-state 2d 1h-13c nmr," *PloS one*, vol. 10, p. e0128417, 06 2015.

[150] S. Sun, W. Chen, J. Tang, B. Wang, X. Cao, S. Sun, and R.-C. Sun, "Synergetic effect of dilute acid and alkali treatments on fractional application of rice straw," *Biotechnology for Biofuels*, vol. 9, no. 1, pp. 1–13, 10 2016, electronic supplementary material The online version of this article (doi: 10.1186/s13068-016-0632-9) contains supplementary material, which is available to authorized users.

[151] S. Kshirsagar, P. Waghmare, P. Chandrakant Loni, S. Patil, and S. Govindwar, "Dilute acid pretreatment of rice straw, structural characterization and optimization of enzymatic hydrolysis conditions by response surface methodology," *RSC Advances*, vol. 5, no. 58, pp. 46 525–46 533, 1 2015.

[152] X. Meng and A. J. Ragauskas, "Recent advances in understanding the role of cellulose accessibility in enzymatic hydrolysis of lignocellulosic

substrates," *Current Opinion in Biotechnology*, vol. 27, pp. 150 – 158, 2014, energy biotechnology • Environmental biotechnology. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0958166914000275

[153] D. Chen, Y. Wang, Y. Liu, K. Cen, X. Cao, Z. Ma, and Y. Li, "Comparative study on the pyrolysis behaviors of rice straw under different washing pretreatments of water, acid solution, and aqueous phase bio-oil by using tg-ftir and py-gc/ms," *Fuel*, vol. 252, pp. 1 – 9, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0016236119306489

[154] M. Chownk, R. S. Sangwan, and S. K. Yadav, "A novel approach to produce glucose from the supernatant obtained upon the dilute acid pre-treatment of rice straw and synergistic action of hydrolytic enzymes producing microbes," *Brazilian Journal of Microbiology*, vol. 50, no. 2, pp. 395–404, 4 2019.

[155] S. Soam, M. Kapoor, R. Kumar, R. P. Gupta, S. K. Puri, and S. Ramakumar, "Life cycle assessment and life cycle costing of conventional and modified dilute acid pretreatment for fuel ethanol production from rice straw in india," *Journal of Cleaner Production*, vol. 197, pp. 732 – 741, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0959652618318547

[156] J. Peng, A. E.-F. Abomohra, M. Elsayed, X. Zhang, Q. Fan, and P. Ai, "Compositional changes of rice straw fibers after pretreatment with diluted acetic acid: Towards enhanced biomethane production," *Journal of Cleaner Production*, vol. 230, pp. 775 – 782, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0959652619316816

[157] S. Ukaew, J. Schoenborn, B. Klemetsrud, and D. R. Shonnard, "Effects of torrefaction temperature and acid pretreatment on the yield and quality of fast pyrolysis bio-oil from rice straw," *Journal of Analytical and Applied Pyrolysis*, vol. 129, pp. 112 – 122, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S016523701730668X

[158] T. Chiranjeevi, A. J. Mattam, K. K. Vishwakarma, A. Uma, V. C. R. Peddy, S. Gandham, and H. Ravindra Velankar, "Assisted single-step acid pretreatment process for enhanced delignification of rice straw for bioethanol production," *ACS Sustainable Chemistry & Engineering*, vol. 6, no. 7, pp. 8762–8774, 2018. [Online]. Available: https://doi.org/10.1021/acssuschemeng.8b01113

[159] W.-H. Chen, B.-L. Pen, C.-T. Yu, and W.-S. Hwang, "Pretreatment efficiency and structural characterization of rice straw by an integrated process of dilute-acid and steam explosion for bioethanol production," *Bioresource*

Technology, vol. 102, no. 3, pp. 2916 – 2924, 2011. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852410018547

[160] C. HARADA, Y. SAITO, Y. NAKAMURA, and H. MINATO, “The effect of sodium hydroxide treatment of rice straw on in situ disappearance of hemicellulose and lignin in its cell wall,” *Nihon Chikusan Gakkaiho*, vol. 72, no. 1, pp. 19–25, 2001.

[161] Y.-S. Cheng, Y. Zheng, C. W. Yu, T. M. Dooley, B. M. Jenkins, and J. S. VanderGheynst, “Evaluation of high solids alkaline pretreatment of rice straw,” *Applied Biochemistry and Biotechnology*, vol. 162, no. 6, pp. 1768–1784, 11 2010. [Online]. Available: https://doi.org/10.1007/s12010-010-8958-4

[162] I. Kim and J.-I. Han, “Optimization of alkaline pretreatment conditions for enhancing glucose yield of rice straw by response surface methodology,” *Biomass and Bioenergy*, vol. 46, pp. 210 – 217, 2012, international Conference on Lignocellulosic ethanol. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0961953412003388

[163] R. C. de Assis Castro, B. G. Fonseca, H. T. L. dos Santos, I. S. Ferreira, S. I. Mussatto, and I. C. Roberto, “Alkaline deacetylation as a strategy to improve sugars recovery and ethanol production from rice straw hemicellulose and cellulose,” *Industrial Crops and Products*, vol. 106, pp. 65 – 73, 2017, challenges in Building a Sustainable Biobased Economy. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669016305787

[164] S. Harun and S. Geok, “Effect of sodium hydroxide pretreatment on rice straw composition,” *Indian Journal of Science and Technology*, vol. 9, no. 21, 2016.

[165] J. Du, Y. Qian, Y. Xi, and X. Lü, “Hydrothermal and alkaline thermal pretreatment at mild temperature in solid state for physicochemical properties and biogas production from anaerobic digestion of rice straw,” *Renewable Energy*, vol. 139, pp. 261 – 267, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960148119301107

[166] G. Mancini, S. Papirio, G. Riccardelli, P. N. Lens, and G. Esposito, “Trace elements dosing and alkaline pretreatment in the anaerobic digestion of rice straw,” *Bioresource Technology*, vol. 247, pp. 897 – 903, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852417317807

[167] L. Dong, G. Cao, L. Zhao, B. Liu, and N. Ren, “Alkali/urea pretreatment of rice straw at low temperature for enhanced biological hydrogen production,”

Bioresource Technology, vol. 267, pp. 71 – 76, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852418307156

[168] D. J. Shetty, P. Kshirsagar, S. Tapadia-Maheshwari, V. Lanjekar, S. K. Singh, and P. K. Dhakephalkar, "Alkali pretreatment at ambient temperature: A promising method to enhance biomethanation of rice straw," *Bioresource Technology*, vol. 226, pp. 80 – 88, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852416316546

[169] W. Xing, G. Xu, J. Dong, R. Han, and Y. Ni, "Novel dihydrogen-bonding deep eutectic solvents: Pretreatment of rice straw for butanol fermentation featuring enzyme recycling and high solvent yield," *Chemical Engineering Journal*, vol. 333, pp. 712 – 720, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1385894717316832

[170] D. Liu, X. Yan, S. Zhuo, M. Si, M. Liu, S. Wang, L. Ren, L. Chai, and Y. Shi, "Pandoraea sp. b-6 assists the deep eutectic solvent pretreatment of rice straw via promoting lignin depolymerization," *Bioresource Technology*, vol. 257, pp. 62 – 68, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852418302037

[171] X.-D. Hou, A.-L. Li, K.-P. Lin, Y.-Y. Wang, Z.-Y. Kuang, and S.-L. Cao, "Insight into the structure-function relationships of deep eutectic solvents during rice straw pretreatment," *Bioresource Technology*, vol. 249, pp. 261 – 267, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852417318369

[172] X.-D. Hou, G.-J. Feng, M. Ye, C.-M. Huang, and Y. Zhang, "Significantly enhanced enzymatic hydrolysis of rice straw via a high-performance two-stage deep eutectic solvents synergistic pretreatment," *Bioresource Technology*, vol. 238, pp. 139 – 146, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852417305084

[173] C.-W. Zhang, S.-Q. Xia, and P.-S. Ma, "Facile pretreatment of lignocellulosic biomass using deep eutectic solvents," *Bioresource Technology*, vol. 219, pp. 1 – 5, 2016. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852416309907

[174] C. Florindo, M. M. Oliveira, L. C. Branco, and I. M. Marrucho, "Carbohydrates-based deep eutectic solvents: Thermophysical properties and rice straw dissolution," *Journal of Molecular Liquids*, vol. 247, pp. 441 – 447, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0167732217330581

[175] A. K. Kumar, B. S. Parikh, and M. Pravakar, "Natural deep eutectic solvent mediated pretreatment of rice straw: bioanalytical characterization of lignin extract and enzymatic hydrolysis of pretreated biomass residue," *Environmental Science and Pollution Research*, vol. 23, no. 10, pp. 9265–9275, 5 2016. [Online]. Available: https://doi.org/10.1007/s11356-015-4780-4

[176] N. Sweygers, J. Harrer, R. Dewil, and L. Appels, "A microwave-assisted process for the in-situ production of 5-hydroxymethylfurfural and furfural from lignocellulosic polysaccharides in a biphasic reaction system," *Journal of Cleaner Production*, vol. 187, pp. 1014 – 1024, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0959652618308758

[177] J. Binder and R. Raines, "Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals," *Journal of the American Chemical Society*, vol. 131, pp. 1979–85, 02 2009.

[178] L. Yan, R. Ma, H. Wei, L. Li, B. Zou, and Y. Xu, "Ruthenium trichloride catalyzed conversion of cellulose into 5-hydroxymethylfurfural in biphasic system," *Bioresource Technology*, vol. 279, pp. 84 – 91, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852419301531

[179] Q. Wu, G. Zhang, M. Gao, S. Cao, L. Li, S. Liu, C. Xie, L. Huang, S. Yu, and A. J. Ragauskas, "Clean production of 5-hydroxymethylfurfural from cellulose using a hydrothermal/biomass-based carbon catalyst," *Journal of Cleaner Production*, vol. 213, pp. 1096 – 1102, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0959652618340034

[180] S. Yin, Y. Pan, and Z. Tan, "Hydrothermal conversion of cellulose to 5-hydroxymethyl furfural," *International Journal of Green Energy*, vol. 8, no. 2, pp. 234–247, 2011. [Online]. Available: https://doi.org/10.1080/15435075.2010.548888

[181] X. Qi, M. Watanabe, T. M. Aida, and R. L. Smith Jr, "Fast transformation of glucose and di-/polysaccharides into 5-hydroxymethylfurfural by microwave heating in an ionic liquid/catalyst system," *ChemSusChem*, vol. 3, no. 9, pp. 1071–1077, 2010. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/cssc.201000124

[182] L. Atanda, A. Shrotri, S. Mukundan, Q. Ma, M. Konarova, and J. Beltramini, "Direct production of 5-hydroxymethylfurfural via catalytic conversion of simple and complex sugars over phosphated tio2," *ChemSusChem*,

vol. 8, no. 17, pp. 2907–2916, 2015. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/cssc.201500395

[183] Y. Su, H. M. Brown, X. Huang, X. dong Zhou, J. E. Amonette, and Z. C. Zhang, "Single-step conversion of cellulose to 5-hydroxymethylfurfural (hmf), a versatile platform chemical," *Applied Catalysis A: General*, vol. 361, no. 1, pp. 117 – 122, 2009. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926860X09002579

[184] J. Song, B. Zhang, J. Shi, H. Fan, J. Ma, Y. Yang, and B. Han, "Efficient conversion of glucose and cellulose to 5-hydroxymethylfurfural in dbu-based ionic liquids," *RSC Adv.*, vol. 3, pp. 20 085–20 090, 2013. [Online]. Available: http://dx.doi.org/10.1039/C3RA43934H

[185] B. Kim, J. Jeong, D. Lee, S. Kim, H.-J. Yoon, Y.-S. Lee, and J. K. Cho, "Direct transformation of cellulose into 5-hydroxymethyl-2-furfural using a combination of metal chlorides in imidazolium ionic liquid," *Green Chem.*, vol. 13, pp. 1503–1506, 2011. [Online]. Available: http://dx.doi.org/10.1039/C1GC15152E

[186] Z.-D. Ding, J.-C. Shi, J.-J. Xiao, W.-X. Gu, C.-G. Zheng, and H.-J. Wang, "Catalytic conversion of cellulose to 5-hydroxymethyl furfural using acidic ionic liquids and co-catalyst," *Carbohydrate Polymers*, vol. 90, no. 2, pp. 792 – 798, 2012. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0144861712005425

[187] J. Shi, H. Gao, Y. Xia, W. Li, H. Wang, and C. Zheng, "Efficient process for the direct transformation of cellulose and carbohydrates to 5-(hydroxymenthyl)furfural with dual-core sulfonic acid ionic liquids and co-catalysts," *RSC Adv.*, vol. 3, pp. 7782–7790, 2013. [Online]. Available: http://dx.doi.org/10.1039/C3RA41062E

[188] Y. Zhang, J. Pan, M. Gan, H. Ou, Y. Yan, W. Shi, and L. Yu, "Acid–chromic chloride functionalized natural clay-particles for enhanced conversion of one-pot cellulose to 5-hydroxymethylfurfural in ionic liquids," *RSC Advances*, vol. 4, p. 11664, 01 2014.

[189] Y. Zhang, J. Pan, Y. Shen, W. Shi, C. Liu, and L. Yu, "Brønsted acidic polymer nanotubes with tunable wettability toward efficient conversion of one-pot cellulose to 5-hydroxymethylfurfural," *ACS Sustainable Chemistry & Engineering*, vol. 3, pp. 871–879, 05 2015.

[190] H. Abou-Yousef and E. B. Hassan, "A novel approach to enhance the activity of h-form zeolite catalyst for production of hydroxymethylfurfural from

cellulose," *Journal of Industrial and Engineering Chemistry*, vol. 20, no. 4, pp. 1952 – 1957, 2014. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1226086X1300436X

[191] C. Benjamin R., P. Michael J., and R. Ronald T., "Organocatalytic conversion of cellulose into a platform chemical," *Chemical Science*, vol. 4, no. 1, 1 2012.

[192] L. Zhou, R. Liang, Z. Ma, T. Wu, and Y. Wu, "Conversion of cellulose to hmf in ionic liquid catalyzed by bifunctional ionic liquids," *Bioresource Technology*, vol. 129, pp. 450 – 455, 2013. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852412016884

[193] F. Tao, H. Song, and L. Chou, "Catalytic conversion of cellulose to chemicals in ionic liquid," *Carbohydrate Research*, vol. 346, no. 1, pp. 58 – 63, 2011. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0008621510004672

[194] N. Shi, Q. Liu, Q. Zhang, T. Wang, and L. Ma, "High yield production of 5-hydroxymethylfurfural from cellulose by high concentration of sulfates in biphasic system," *Green Chem.*, vol. 15, pp. 1967–1974, 2013. [Online]. Available: http://dx.doi.org/10.1039/C3GC40667A

[195] S. Xiao, B. Liu, Y. Wang, Z. Fang, and Z. Zhang, "Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide–ionic liquid mixtures," *Bioresource Technology*, vol. 151, pp. 361 – 366, 2014. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852413016829

[196] J. Wang, J. Ren, X. Liu, J. Xi, Q. Xia, Y. Zu, G. Lu, and Y. Wang, "Direct conversion of carbohydrates to 5-hydroxymethylfurfural using sn-mont catalyst," *Green Chem.*, vol. 14, pp. 2506–2512, 2012. [Online]. Available: http://dx.doi.org/10.1039/C2GC35699F

[197] B. Liu, Z. Zhang, and Z. K. Zhao, "Microwave-assisted catalytic conversion of cellulose into 5-hydroxymethylfurfural in ionic liquids," *Chemical Engineering Journal*, vol. 215-216, pp. 517 – 521, 2013. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1385894712014179

[198] L. Hu, G. Zhao, X. Tang, Z. Wu, J. Xu, L. Lin, and S. Liu, "Catalytic conversion of carbohydrates into 5-hydroxymethylfurfural over cellulose-derived carbonaceous catalyst in ionic liquid," *Bioresource Technology*, vol. 148, pp. 501 – 507, 2013. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852413014399

[199] H. Li, Q. Zhang, X. Liu, F. Chang, D. Hu, Y. Zhang, W. Xue, and S. Yang, "Incl3-ionic liquid catalytic system for efficient and selective conversion of cellulose into 5-hydroxymethylfurfural," *RSC Adv.*, vol. 3, pp. 3648–3654, 2013. [Online]. Available: http://dx.doi.org/10.1039/C3RA23387A

[200] Z. Cao, Z. Fan, Y. Chen, M. Li, T. Shen, C. Zhu, and H. Ying, "Efficient preparation of 5-hydroxymethylfurfural from cellulose in a biphasic system over hafnyl phosphates," *Applied Catalysis B: Environmental*, vol. 244, pp. 170 – 177, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926337318310695

[201] X. Li, K. Peng, Q. Xia, X. Liu, and Y. Wang, "Efficient conversion of cellulose into 5-hydroxymethylfurfural over niobia/carbon composites," *Chemical Engineering Journal*, vol. 332, pp. 528 – 536, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1385894717310562

[202] R. Rinaldi and F. Schuth, "Acid hydrolysis of cellulose as the entry point into biorefinery schemes," *ChemSusChem*, vol. 2, no. 12, pp. 1096–1107, 2009. [Online]. Available: https://chemistry-europe.onlinelibrary.wiley.com/doi/abs/10.1002/cssc.200900188

[203] S. Van de Vyver, J. Thomas, J. Geboers, S. Keyzer, M. Smet, W. Dehaen, P. A. Jacobs, and B. F. Sels, "Catalytic production of levulinic acid from cellulose and other biomass-derived carbohydrates with sulfonated hyperbranched poly(arylene oxindole)s," *Energy Environ. Sci.*, vol. 4, pp. 3601–3610, 2011. [Online]. Available: http://dx.doi.org/10.1039/C1EE01418H

[204] M. Li, W. Li, Y. Lu, H. Jameel, H.-m. Chang, and L. Ma, "High conversion of glucose to 5-hydroxymethylfurfural using hydrochloric acid as a catalyst and sodium chloride as a promoter in a water/gamma-valerolactone system," *RSC Adv.*, vol. 7, pp. 14 330–14 336, 03 2017.

[205] M. A. Kougioumtzis, A. Marianou, K. Atsonios, C. Michailof, N. Nikolopoulos, N. Koukouzas, K. Triantafyllidis, A. Lappas, and E. Kakaras, "Production of 5-hmf from cellulosic biomass: Experimental results and integrated process simulation," *Waste and Biomass Valorization*, vol. 9, no. 12, pp. 2433–2445, 12 2018. [Online]. Available: https://doi.org/10.1007/s12649-018-0267-0

[206] N. R. Peela, S. K. Yedla, B. Velaga, A. Kumar, and A. K. Golder, "Choline chloride functionalized zeolites for the conversion of biomass derivatives to 5-hydroxymethylfurfural," *Applied Catalysis A: General*, vol. 580, pp. 59 – 70, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926860X19301991

[207] J. M. Carraher, C. N. Fleitman, and J.-P. Tessonnier, “Kinetic and mechanistic study of glucose isomerization using homogeneous organic brønsted base catalysts in water,” *ACS Catalysis*, vol. 5, no. 6, 6 2015. [Online]. Available: http://par.nsf.gov/biblio/10048582

[208] I. K. Yu and D. C. Tsang, “Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms,” *Bioresource Technology*, vol. 238, pp. 716 – 732, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852417305072

[209] K. Buchholz and J. Seibel, “Industrial carbohydrate biotransformations,” *Carbohydrate Research*, vol. 343, no. 12, pp. 1966 – 1979, 2008, selected papers from the 14th European Carbohydrate Symposium, Lübeck, Germany, Sept. 2007. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S000862150800075X

[210] V. J. Jensen and S. Rugh, “[33] industrial-scale production and application of immobilized glucose isomerase,” in *Immobilized Enzymes and Cells, Part C*, ser. Methods in Enzymology. Academic Press, 1987, vol. 136, pp. 356 – 370. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0076687987360355

[211] H. Zhao, J. E. Holladay, H. Brown, and Z. C. Zhang, “Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural,” *Science*, vol. 316, no. 5831, pp. 1597–1600, 2007. [Online]. Available: https://science.sciencemag.org/content/316/5831/1597

[212] B. Saha and M. M. Abu-Omar, “Advances in 5-hydroxymethylfurfural production from biomass in biphasic solvents,” *Green Chem.*, vol. 16, pp. 24–38, 2014. [Online]. Available: http://dx.doi.org/10.1039/C3GC41324A

[213] X. Yu, X. Gao, R. Tao, and L. Peng, “Insights into the metal salt catalyzed 5-ethoxymethylfurfural synthesis from carbohydrates.” 2017. [Online]. Available: https://www.mdpi.com/2071-1050/12/2/734

[214] A. T. Pedersen, R. Ringborg, T. Grotkjer, S. Pedersen, and J. M. Woodley, “Synthesis of 5-hydroxymethylfurfural (hmf) by acid catalyzed dehydration of glucose-fructose mixtures,” *Chemical Engineering Journal*, vol. 273, pp. 455 – 464, 2015. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1385894715004106

[215] T. Wang, J. A. Glasper, and B. H. Shanks, “Kinetics of glucose dehydration catalyzed by homogeneous lewis acidic metal salts in water,” *Applied*

Catalysis A: General, vol. 498, pp. 214 – 221, 2015. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926860X15002239

[216] I. K. Yu, D. C. Tsang, A. C. Yip, S. S. Chen, Y. S. Ok, and C. S. Poon, "Valorization of food waste into hydroxymethylfurfural: Dual role of metal ions in successive conversion steps," *Bioresource Technology*, vol. 219, pp. 338 – 347, 2016. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852416311233

[217] H. M. Mirzaei and B. Karimi, "Sulphanilic acid as a recyclable bifunctional organocatalyst in the selective conversion of lignocellulosic biomass to 5-hmf," *Green Chem.*, vol. 18, pp. 2282–2286, 2016. [Online]. Available: http://dx.doi.org/10.1039/C5GC02440D

[218] F. S. Asghari and H. Yoshida, "Conversion of japanese red pine wood (pinus densiflora) into valuable chemicals under subcritical water conditions," *Carbohydrate Research*, vol. 345, no. 1, pp. 124 – 131, 2010. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0008621509004923

[219] T. Saito, M. Sasaki, H. Kawanabe, Y. Yoshino, and M. Goto, "Subcritical water reaction behavior of d-glucose as a model compound for biomass using two different continuous-flow reactor configurations," *Chemical Engineering & Technology*, vol. 32, no. 4, pp. 527–533, 2009. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/ceat.200800537

[220] S. H. Mushrif, S. Caratzoulas, and D. G. Vlachos, "Understanding solvent effects in the selective conversion of fructose to 5-hydroxymethyl-furfural: a molecular dynamics investigation," *Phys. Chem. Chem. Phys.*, vol. 14, pp. 2637–2644, 2012. [Online]. Available: http://dx.doi.org/10.1039/C2CP22694D

[221] S. Jia, Z. Xu, and Z. Zhang, "Catalytic conversion of glucose in dimethylsulfoxide/water binary mix with chromium trichloride: Role of water on the product distribution," *Chemical Engineering Journal*, vol. 254, pp. 333 – 339, 2014. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1385894714007050

[222] J. Wang, W. Xu, J. Ren, X. Liu, G. Lu, and Y. Wang, "Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon-based solid acid," *Green Chem.*, vol. 13, pp. 2678–2681, 2011. [Online]. Available: http://dx.doi.org/10.1039/C1GC15306D

[223] C. Li, Z. Zhang, and Z. K. Zhao, "Direct conversion of glucose and cellulose to 5-hydroxymethylfurfural in ionic liquid under microwave irradiation,"

Tetrahedron Letters, vol. 50, no. 38, pp. 5403 – 5405, 2009. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0040403909014014

[224] P. K. Rout, A. D. Nannaware, O. Prakash, A. Kalra, and R. Rajasekharan, "Synthesis of hydroxymethylfurfural from cellulose using green processes: A promising biochemical and biofuel feedstock," *Chemical Engineering Science*, vol. 142, pp. 318 – 346, 2016. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0009250915007794

[225] A. S. Khan, Z. Man, A. Nasrullah, Z. Ullah, N. Muhammad, A. Rahim, A. Bustam, A. Idris, and M. Uroos, "Chapter 1 - conversion of biomass to chemicals using ionic liquids," in *Green Sustainable Process for Chemical and Environmental Engineering and Science*, Inamuddin, A. M. Asiri, and S. Kanchi, Eds. Elsevier, 2020, pp. 1 – 30. [Online]. Available: http://www.sciencedirect.com/science/article/pii/B9780128173862000019

[226] F. Jiang, Q. Zhu, D. Ma, X. Liu, and X. Han, "Direct conversion and nmr observation of cellulose to glucose and 5-hydroxymethylfurfural (hmf) catalyzed by the acidic ionic liquids," *Journal of Molecular Catalysis A: Chemical*, vol. 334, no. 1, pp. 8 – 12, 2011. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1381116910004164

[227] W. Li, T. Yang, M. Su, and Y. Liu, "Catalytic conversion of glucose to 5-hydroxymethylfurfural and furfural by a phosphate-doped sno2 catalyst in γ-valerolactone-water system," *Catalysis Lette*, vol. 150, pp. 3304 – 3313, 2020. [Online]. Available: https://doi.org/10.1007/s10562-020-03227-7

[228] B. Song, Y. Yu, and H. Wu, "Solvent effect of gamma-valerolactone (gvl) on cellulose and biomass hydrolysis in hot-compressed gvl/water mixtures," *Fuel*, vol. 232, pp. 317 – 322, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0016236118309992

[229] L. Zhang, G. Xi, J. Zhang, H. Yu, and X. Wang, "Efficient catalytic system for the direct transformation of lignocellulosic biomass to furfural and 5-hydroxymethylfurfural," *Bioresource Technology*, vol. 224, pp. 656 – 661, 2017. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0960852416316182

[230] Y. Han, L. Ye, X. Gu, P. Zhu, and X. Lu, "Lignin-based solid acid catalyst for the conversion of cellulose to levulinic acid using γ-valerolactone as solvent," *Industrial Crops and Products*, vol. 127, pp. 88 – 93, 2019. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0926669018309312

[231] S. M. Bruce, Z. Zong, A. Chatzidimitriou, L. E. Avci, J. Q. Bond, M. A. Carreon, and S. G. Wettstein, "Small pore zeolite catalysts for furfural synthesis from xylose and switchgrass in a γ-valerolactone/water solvent," *Journal of Molecular Catalysis A: Chemical*, vol. 422, pp. 18 – 22, 2016, contributions of Homogeneous and Heterogeneous Catalysis in Biorefining: Special Issue in Honor of Prof. Ulf Schuchardt. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1381116916300590

[232] J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger, and J. A. Dumesic, "Nonenzymatic sugar production from biomass using biomass-derived γ-valerolactone," *Science*, vol. 343, no. 6168, pp. 277–280, 2014. [Online]. Available: https://science.sciencemag.org/content/343/6168/277

[233] J. M. R. Gallo, D. M. Alonso, M. A. Mellmer, and J. A. Dumesic, "Production and upgrading of 5-hydroxymethylfurfural using heterogeneous catalysts and biomass-derived solvents," *Green Chem.*, vol. 15, pp. 85–90, 2013. [Online]. Available: http://dx.doi.org/10.1039/C2GC36536G

[234] X. Tian, B. Qi, S. Zhang, J. Luo, and Y. Wan, "Catalytic production of 5-hydroxymethylfurfural from sucrose and molasses by aluminum chloride in green aqueous γ-valerolactone system," *Biomass Conversion and Biorefinery*, 2020. [Online]. Available: https://doi.org/10.1007/s13399-020-00603-6

[235] B. Seemala, V. Haritos, and A. Tanksale, "Levulinic acid as a catalyst for the production of 5-hydroxymethylfurfural and furfural from lignocellulose biomass," *ChemCatChem*, vol. 8, no. 3, pp. 640–647, 2016. [Online]. Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/cctc.201501105

[236] J. B. Binder, A. V. Cefali, J. J. Blank, and R. T. Raines, "Mechanistic insights on the conversion of sugars into 5-hydroxymethylfurfural," *Energy Environ. Sci.*, vol. 3, pp. 765–771, 2010. [Online]. Available: http://dx.doi.org/10.1039/B923961H

[237] S. Xu, D. Pan, W. Li, P. Shen, Y. Wu, X. Song, Y. Zhu, N. Xu, L. Gao, and G. Xiao, "Direct conversion of biomass-derived carbohydrates to 5-hydroxymethylfurfural using an efficient and inexpensive manganese phosphate catalyst," *Fuel Processing Technology*, vol. 181, pp. 199 – 206, 2018. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0378382018307859

[238] Y. Yang, C.-w. Hu, and M. M. Abu-Omar, "Conversion of carbohydrates and lignocellulosic biomass into 5-hydroxymethylfurfural using alcl3·6h2o catalyst

in a biphasic solvent system," *Green Chem.*, vol. 14, pp. 509–513, 2012. [Online]. Available: http://dx.doi.org/10.1039/C1GC15972K

[239] H. Ma, F. Wang, Y. Yu, L. Wang, and X. Li, "Autocatalytic production of 5-hydroxymethylfurfural from fructose-based carbohydrates in a biphasic system and its purification," *Industrial & Engineering Chemistry Research*, vol. 54, pp. 2657–2666, 03 2015.

[240] C. Moreau, A. Finiels, and L. Vanoye, "Dehydration of fructose and sucrose into 5-hydroxymethylfurfural in the presence of 1-h-3-methyl imidazolium chloride acting both as solvent and catalyst," *Journal of Molecular Catalysis A: Chemical*, vol. 253, no. 1, pp. 165 – 169, 2006. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S1381116906006753

[241] R. Weingarten, J. Cho, R. Xing, W. C. Conner Jr, and G. W. Huber, "Kinetics and reaction engineering of levulinic acid production from aqueous glucose solutions," *ChemSusChem*, vol. 5, no. 7, pp. 1280–1290, 2012. [Online]. Available: https://chemistry-europe.onlinelibrary.wiley.com/doi/abs/10.1002/cssc.201100717

[242] T. M. Aida, Y. Sato, M. Watanabe, K. Tajima, T. Nonaka, H. Hattori, and K. Arai, "Dehydration of d-glucose in high temperature water at pressures up to 80mpa," *The Journal of Supercritical Fluids*, vol. 40, no. 3, pp. 381 – 388, 2007. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0896844606002117

[243] C. C. Stowers, E. M. Ferguson, and R. D. Tanner, "Development of activity-based cost functions for cellulase, invertase, and other enzymes," in *Biotechnology for Fuels and Chemicals*, W. S. Adney, J. D. McMillan, J. Mielenz, and K. T. Klasson, Eds. Totowa, NJ: Humana Press, 2008, pp. 475–485.

[244] J. Cherry, S. Ko, R. Grainger, A. Prokop, and R. D. Tanner, "Developing an objective function to characterize the tradeoffs in salting out and the foam and droplet fractionation processes," *Brazilian Journal of Chemical Engineering*, vol. 17, pp. 233–238, 06 2000. [Online]. Available: http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322000000200011&nrm=iso

[245] N. C. for Biotechnology Information USA, "Pubchem," 2020. [Online]. Available: https://pubchem.ncbi.nlm.nih.gov/

[246] G. Merck KGaA, Darmstadt, "India sigma-aldrich," 2020. [Online]. Available: https://www.sigmaaldrich.com/india.html

[247] D. Barana, A. Salanti, M. Orlandi, D. S. Ali, and L. Zoia, “Biorefinery process for the simultaneous recovery of lignin, hemicelluloses, cellulose nanocrystals and silica from rice husk and arundo donax,” *Industrial Crops and Products*, vol. 86, pp. 31–39, 2016. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0926669016301753

[248] Z. Tian, J. Chen, X. Ji, Q. Wang, G. Yang, and P. Fatehi, “Dilute sulfuric acid hydrolysis of pennisetum (sp.) hemicellulose,” *BioResources*, vol. 12, no. 2, 2017. [Online]. Available: https://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_12_2_2609_Tian_Dilute_Sulfuric_Acid_Hydrolysis

[249] B. Xiao, X. Sun, and R. Sun, “Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw,” *Polymer Degradation and Stability*, vol. 74, no. 2, pp. 307–319, 2001. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S014139100100163X

[250] R. Sun, J. Tomkinson, P. Ma, and S. Liang, “Comparative study of hemicelluloses from rice straw by alkali and hydrogen peroxide treatments,” *Carbohydrate Polymers*, vol. 42, no. 2, pp. 111–122, 2000. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0144861799001368

[251] R. C. R. Ines C Roberto, Solange I Mussatto, “Dilute-acid hydrolysis for optimization of xylose recovery from rice straw in a semi-pilot reactor,” *Industrial Crops and Products*, vol. 17, pp. 171–176, 2003. [Online]. Available: https://www.sciencedirect.com/science/article/abs/pii/S092666900200095X

[252] S. Zhu, W. Huang, W. Huang, K. Wang, Q. Chen, and Y. Wu, “Pretreatment of rice straw for ethanol production by a two-step process using dilute sulfuric acid and sulfomethylation reagent,” *Applied Energy*, vol. 154, pp. 190–196, 2015. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0306261915006017

[253] K. Karimi, S. Kheradmandinia, and M. J. Taherzadeh, “Conversion of rice straw to sugars by dilute-acid hydrolysis,” *Biomass and Bioenergy*, vol. 30, no. 3, pp. 247–253, 2006. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0961953405001996

[254] Y.-S. Cheng, Y. Zheng, C. W. Yu, T. M. Dooley, B. M. Jenkins, and J. S. VanderGheynst, “Evaluation of high solids alkaline pretreatment of rice straw,” *Applied Biochemistry and Biotechnology*, vol. 162, p. 1768–1784, 2010. [Online]. Available: https://link.springer.com/article/10.1007/s12010-010-8958-4#citeas

[255] G. Yang and S.-J. Park, “Conventional and microwave hydrothermal synthesis and application of functional materials: A review,” *Materials*, vol. 12, no. 7, 2019. [Online]. Available: https://www.mdpi.com/1996-1944/12/7/1177