Synthesis and Characterization of 5-Hydroxymethylfufural from Microcrystalline Cellulose Using Biomass Based Solid Acid Catalyst

Mohammed Ali Mohammed

Thesis Paper Submitted to Chemical Engineering

School of Mechanical, Chemical and Material Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

October 2021

Adama, Ethiopia

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Advisors: Zelalem Tumsa (Ph.D)

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DECLARATION

I hereby declare that this Master Thesis entitled "Synthesis and Characterization of 5-Hydroxymethylfufural from Microcrystalline Cellulose Using Biomass Based Solid Acid Catalyst" is my original work. That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

Mohammed Ali Mohammed _____ _____

Name of the student Signature Date

RECOMMENDATION

We, the advisor(s) of this thesis, hereby certify that we have read the revised version of the thesis entitled “Synthesis and Characterization of 5-Hydroxymethylfufural from Microcrystalline Cellulose Using Biomass Based Solid Acid Catalyst” prepared under my/our guidance by Mohammed Ali Mohammed submitted in partial fulfillment of the requirements for the degree of Mater’s of Science in Chemical Engineering (Specialization Process Engineering). Therefore, I/we recommend the submission of revised version of the thesis to the department following the applicable procedures.

Zelalem Tumsa (Ph.D)	_____	_____
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Co-advisor	Signature	Date

APPROVAL PAGE

We, the advisors of the thesis entitled “Synthesis and Characterization of 5-Hydroxymethylfufural from Microcrystalline Cellulose Using Biomass Based Solid Acid Catalyst” and developed by Mohammed Ali Mohammed hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Zelalem Tumsa (Ph.D)	_____	_____
Major Advisor	Signature	Date
Melaku Tesfaye (Ph.D)	_____	_____
Co-advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by Mohammed Ali have read and evaluated the thesis entitled “Synthesis and Characterization of 5-Hydroxymethylfufural from Microcrystalline Cellulose Using Biomass Based Solid Acid Catalyst” and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical Engineering (Specialization in process engineering).

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Finally, approval and acceptance of the thesis is contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

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ACKNOWLEDGEMENT

First of all, I would like to gratitude and praise my **GOD** for the successful completion of my thesis research work.

I am thankful to my advisors Dr. Zelalem Tumsa and Dr. Melaku Tesfaye for their valuable support, giving intellectual freedom in my work, tireless advising, engaging me in new ideas and demanding a high quality of work, kindness, positive criticism, advising throughout the present research work, continuous encouragement and guidance.

Besides, my advisors, I am deeply indebted to all my teachers in School of Mechanical, Chemical and Materials Engineering at department of Chemical Engineering who had laid a critical foundation of knowledge that inspired me in many ways. I also extend my sincere thankfulness to the laboratory technicians of School of Mechanical, Chemical and Materials at department of Chemical engineering to Mr Adana Tilahun and Mr. Bundi Roba, from department of chemical Engineering and department of Biology Eticha Abdisa for their consistent and valuable help during my experimental work. Bahir Dar University and Addis Ababa university lab for their support to experimental works. I would also like to express my appreciation towards my family for their support and offered help to attain this thesis. My honest thankfulness also goes to my best friends especially Mr. Sisay Demisie, Mr.Mulukan Mannaye, Mr.Gamachu Shumi, Ms. Genet Bent and Mr.Abdu Ababaw for their encouragement, motivating in discussions and ideas throughout the research work.

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LIST OF ACRONYMS AND ABBREVIATION

RSM	Response Surface Methodology
BBD	Box-Behnken Design
BC	Biochar
COOH	Carboxyl Group
OH	Hydroxyl Group
SO_3H	Sulfonated Group
SCBC	Sulfonated Carbon-based Catalyst
SAC	Sulfonated Active Carbon
MCC	Microcrystalline Cellulose
AGU	Anhydroglucopyronos
HMF	Hydroxymethylfufural
MTHF	Methyl tetrahydrofuran
FDCA	Furan-2,5-Dicarboxylic Acid
BHMTF	2,5-Bis hydroxymethyltetra hydro furan
DMF	2,5-Dimethyl Furan
MF	2-Methylfuran
FF	Furfural
LA	Levulinic Acid
FA	Formic Acid
HMVF	2-Hydroxymethyl-5-Vinylfuran
MOFs	Metal−Organic Frameworks
DFT	Density Feature Theory

ABSTRACT

With growing concerns on environmental issues and energy crisis, biomass resources have attracted much attention as a renewable source of fuels, chemicals and carbon-based catalyst. Among the possible biomass-derived chemicals is 5-hydroxymethylfurfural (HMF). It was produced from hexose sugar content biomass by heating in acid catalyst and solvent system. Sulfonated carbon-based solid acid catalyst was produced from corn cob biomass for 5-HMF synthesis. A sulfonated carbon material was prepared by soaking 50g of corncob powder with 85%v/v of H_3PO_4 with desired ratio 1 and this activated corncob carbonize at 450^oC for 8hr in muffle furnace and followed by sulfonation with concentrations of 98%v/v of sulfuric acid. The sulfonation variables for the synthesis of sulfonated biochar-based catalysts were optimized using the Response Surface Method (RSM) within the Box Behnken design method. Also, in this study catalytic conversion of microcrystalline cellulose in to 5-HMF and the effect of reaction conditions temperature, time and catalyst loading on the concentration of 5-HMF were investigated. Microcrystalline cellulose (MCC) was converted into 5-hydroxymethylfurfural (HMF) using optimized sulfonated carbon-based catalyst in biphasic solvent system (2-Methyl tetrahydrofuran 2-MTHF/water at ratios of 1: 4 with NaCl(4wt%). The effects of three sulfonation variables were investigated, namely, temperature (80-200^oC), time (12-19hr) and the ratio of concentrated sulfuric acid to biochar (3: 1 - 25: 1 ml/ g). Of the three parameters examined, the relationship between sulfonation temperature and sulfonation time was found to be the most important parameter in the acid density of the sulfonic acid group because it has a low p-value. The optimal sulfonation conditions generated numerically by the RSM were 161.9^oC temperature, 16.78hr of time and a ratio of 13.03:1ml/g of concentrated sulfuric acid to biochar, which resulted in a density of sulfone groups of 1.27mmol /g. The optimal sulfonated biochar catalyst was characterized by acid group titration, thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) to determine its properties. Maximum conversion of microcrystalline cellulose and 5-HMF concentration was observed at 190^oC for 4hr catalyst load 0.3g. 5-HMF product was analyzed using UV-VIS, FT-IR and HPLC.

Key words: Activated corncob, Sulfonic group acid density, Sulfonated biochar-based catalyst, Optimization, microcrystalline cellulose and 5-hydroxymethyl furfural.

CHAPTER ONE

1.INTRODUCTION

1.1. Background

The most important source of functionalized carbon structures for the small chemical industry, as well as for the transport of heat and energy, is still based on the fossil deposit(Rosatella et al., 2011).However, due to the reduction of world fossil fuel reserve, the increasing of its price and negative environmental impact has pushed the world to look for alternative renewable fossil reserve and energy sources. Biofuels in comparison to fossil fuels should be relatively cheap and rich in energy, locally produced to saving foreign currency, have environmental benefits (low greenhouse gas emission), and be producible in large quantities without influence on food supplies. Transformation of biomass, especially Lignocellulosic biomass which is abundant and cheap renewable resource into fuels, chemicals, and materials precursors, has a great significance to reduce the excessive dependence on fossil resources, ease the energy crisis, decrease the environmental pollution, and promote the sustainable development of the whole human society(H. Li et al., 2014).

Lignocellulosic biomass is promising as both carbon-based energy source and sustainable feedstock for the chemical industry. One of the main challenges in converting lignocellulosic biomass is producing chemicals or fuels at high selectivity and yields at economical costs. This happens because of the recalcitrance of lignocellulosic, thus requiring both physical and chemical pretreatments, which is still one of the most expensive stages of biomass conversion strategy. Typically, two-step processing methods are employed to control the reactivity of lignocellulosic and improve product selectivity(Wettstein et al., 2012). These methods first fractionate the lignocellulosic into its main components, hemicellulose, cellulose, and lignin, which allows for processing each fraction at different conditions to achieve high yields of target products(Wettstein et al., 2012). Cellulose accounts for 30–50wt% of lignocellulosic biomass and is a linear homopolymer made up of anhydro-D-glucopyranose units linked via β-glycosidic bonds and C_6 sugars (such as glucose, galactose and mannose); the ratio of which depends on the type of biomass (Wyman et al., 2005). Hemicellulose accounts for 15–30wt% of lignocellulosic biomass and is an amorphous polymer consisting of C_5 (such as xylose and arabinose) (Cheng & Stomp, 2009).

Lignin is an amorphous polymer rich in aromatic monomers that accounts for 15–30wt% of the lignocellulosic biomass.(H. M. Wang et al., 2020)

Amongst the numerous routes of lignocellulosic biomass valorization, catalytic hydrolysis - dehydration of cellulose to produce 5-hydroxymethylfurfural (HMF) represents an attractive strategy(T. Wang et al., 2014). This is because of the versatility of using HMF as an important platform molecule to synthesize an array of intermediate chemicals, from which a diverse range of biofuels as well as commodity and fine chemicals can be generated for example, HMF can be selectively oxidized to furan-2,5-dicarboxylic acid (FDCA) which may be a replacement for terephthalic acid in the production of polyethylene terephthalate(Matsumura et al., 2008). Alternatively, HMF can be reduced to 2,5 bis (hydroxymethylfuran) and 2,5 bis (hydroxymethyl) tetrahydrofuran (BHMTF), both of which can serve as alcoholic components in the manufacture of polyesters and in combination with FDCA deliver polymers fully derived from biomass(Kamm, 2007). HMF may also be rehydrated to levulinic acid from which gamma valerol actone can be produced, which can be utilized as a solvent and fuel additives. Another important derivative of HMF is 2,5-dimethylfuran (DMF) and 2-methylfuran (2-MF), and both are potential liquid transportation fuels. Moreover, HMF can used as a precursor in the synthesis of liquid alkanes for use as diesel fuel(Zhong et al., 2010).

5HMF is synthesis by the acid catalyzed removal of three water molecules from hexoses. The reaction is accompanied by a number of other side reactions that lead to the formation of soluble and insoluble humins substances through the decomposition of sugars or reactions between 5HMF molecules and with sugar molecules, while organic acids, including acid Levulinic acid and formic acid are formed through rehydration Hydroxymethylfufural. Fructose is the most suitable substrate for the reaction in terms of reactivity and selectivity of the product, which is due to the coexistence of the cyclic furanose tautomer, the preferred form for the production of 5-HMF, with the pyranose form of sugar as opposed to the primary glucose. It goes back to the pyranose form. Since glucose is the preferred starting material due to its natural abundance as a component of the polysaccharides, cellulose, and starch, as well as the disaccharide sucrose, dehydration to 5HMF is often preceded or integrated by an isomerization of glucose to fructose(Sayed et al., 2020).

Biochar, a by-product from biomass pyrolysis process, is another potential carbon source to be used as a support for solid acid catalyst (Tagusagawa et al., 2010).Pyrolysis of agricultural waste (biomass) is one of the promising thermo-chemical methods to produce bio-oil, biochar and combustible gases numerous recent studies have focused on the utilization of these products, but biochar has received very little attention(Gaskin et al., 2008). The two technologies that have been successfully applied to produce biochar from biomass are pyrolytic carbonization of biomass (300–800^{o}C) in oxygen-limited atmosphere(Flores et al., 2019) and hydrolytic carbonization of biomass (water precipitation, 180–260^{o}C and pressures from 2 to10 MPa)(Ziyun Liu & Liu, 2020).In general, biochar's defining property is its high carbon content; similar to graphite, it is composed mainly of the aromatic carbon rings linked together; but unlike graphite, these rings are irregularly stacked and randomly arranged.

Recently, sulfonated carbon-based solid acid catalyst is developing rapidly and carbon material has become a hot research area because it can be applied as smart materials(Lathiya et al., 2018). Sulfonation of the biochar promotes activation and oxidation of carbon that led to the improvement in the surface area and pore structure. The carbon material prepared by sulfonation of the biochar is a novel solid Bronsted acid. Concentrated and fuming sulfuric acids are commonly used as the sulfonating agents to introduce the functional groups in the carbon chain which is responsible for the catalyst. Carbon-based solid acids, the amorphous carbons consisting of aromatic carbon sheets bearing active sites such as (-SO_3H), (-OH), and (-COOH) groups have attracted a great deal of attention due to their favorable characteristics such as low cost, metal free composition high acid densities, stability and recyclability(Shen et al., 2014). Sulfonated solid acid catalysts were synthesized sulfonation at a temperature of 150-180^{o}C for 10–15 hr with concentrated H_2SO_4 in the range of 10cm^3 per gram of catalyst(Clohessy & Kwapinski, 2020).

1.2. Statement of The Problem

The gradual running down of fossil resources, the increasing demand, its price and negative environmental impact for fossil fuels has pushed the world to look for alternative renewable energy chemical sources. In fact, with lessening and expensive of fossil resources, the development of new technologies to exploit adaptable and renewable biomasses as alternative feedstock for platform chemicals has received more attention than ever. Lignocellulose biomass was among the most promising sustainable sources for the production of environmentally friendly bio-fuels and bio-chemicals due to its abundance. Therefore, investigating alternatives to fossil fuels was great importance. One of the most promising alternatives is biomass-based platform chemical intermediate product is 5-HMF. Synthesis and Characterization of 5-Hydroxymethylfurfurals (HMF) from nonedible biomass-such as microcrystalline cellulose for provide a new step toward achieving renewable biomass -based chemicals and fuels platform.

In addition, due to corrosion and waste disposal problems of liquid acid-catalyst had significantly lower attraction. Therefore, producing green catalyst from lignocellulose biomass especially waste biomass (raw corncob) is preferable. Green catalyst is easy to produce, separate and environmentally friendly. It is also economically feasible to replace toxic catalysts. In recent years, the Response Surface Method (RSM) has been widely used to optimize chemical and biochemical processes. RSM is a combination of mathematical and statistical techniques that can be used to assess the importance of process variables and improve processes. Compared to CCD, another RMS-based method, the Box-Behnken design, has the advantage that the number of experiments is reduced and experiments are not performed under extreme conditions(Jiménez Toro et al., 2019).In this study Box-Behnken method was applied for sulfonated carbon catalyst. Therefore, the aims of this work were to hydrolysis and dehydration of microcrystalline cellulose into HMF and investigate the effect of reaction parameters such as reaction temperature, reaction time and catalyst loading on 5-HMF concentration by using corncob based sulfonated catalyst bearing SO_3H, COOH and OH groups as catalyst instead of enzymes or conventional homogeneous acid catalysts and 2-MTHF solvent as extractive with water as medium.

1.3. Objectives

1.3.1. General Objective

The General objective of this study is to synthesize 5-HMF using biomass based sulfonated solid catalyst and investigate the effect of reaction conditions on the concentration of 5-HMF.

1.3.2. Specific Objectives

The following are the specific objective of this study

- To synthesize, optimize and characterize of sulfonated solid carbon catalyst from corncob biomass
- To investigate the reaction conditions on 5-HMF concentration (reaction time, reaction temperature, catalyst load)
- To characterize 5-Hydroxymethylfurfurals (HMF)

1.4. Scope of The Study

The focused of this thesis works covers characterization of corncob biomass, synthesis and optimization of sulfonated biochar from corncob biomass by activation, carbonization and sulfonation steps. In optimization of sulfonated biochar catalyst based on acid -base titration was also conducted and one with highest acidic density was selected for further experimental works. Characterization of solid acid catalyst using FT-IR, TGA, XRD and SEM analyses were conducted. Synthesis of 5-Hydroxymethylfurfural (HMF) and investigation on the effect of reaction temperature, reaction time and catalyst loading on the cellulose conversion or product concentration were conducted in organic solvent 2-Methyltetrahydrofrun and water medium. Finally, the produced 5-Hydroxymethyl furfural (HMF) was characterized using UV-VIS, FT-IR and HPLC.

1.5. Significance of The Study

Significance of this study is to replace fossil-based fuels and chemicals with bio-based fuels and chemicals by conversion of nonedible microcrystalline cellulose to 5-hydroxymethylfufural (HMF). 5-Hydroxymethylfufural (HMF) holds a key position in the production of liquid biofuels and biomass-derived intermediates including a vast number of chemicals like in oil refining, agrochemical industry, pharmaceuticals, bioplastic and fuels.

Another importance of this work is to protect environmental pollution by developing safe and green catalyst from waste lignocellulose biomass agricultural residue such as corn cob instead of using toxic catalyst. This green catalyst haves their own unique properties: it can be easily synthesized, efficient, safe, environmentally friendly and economically feasible more than commercial solid catalyst.

Additional use of this study green solvent was used for extraction of 5-HMF.It was not toxic because already derived from biomass based and also, it was easily separable solvent within low boiling point to separate easily from the system of reaction in order to save environment and recycling it.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Introduction

(5hydroxymethyl-2furaldehyd,5hydroxymethyl-2furancarboxaldehyde), usually referred to as HMF, is an organic compound and a common product. It is formed when biomass and foods containing carbohydrates are heat-treated in the presence of amino acids (Maillard reaction). It is a natural ingredient in dried fruits, coffee, grains and baked goods. It has a molecular weight of 126.11 $gmol^{-1}$ and a boiling point of 114^{o}C (Abraham et al., 2011). HMF can be used as a flavoring agent or food additive in food. Its chemical structure (Figure 2.1) is a heterocyclic furan molecule with alcohol and aldehyde functional groups, which makes it very active(T. Wang et al., 2014):

a) HMF is an α bifunctional molecule with substituents at positions 2 and 5 at position.

b) HMF is a relatively unsaturated aromatic compound and

c) The heterocyclic structure of furan exists in many pharmaceutical products Applications in Bioactive Molecules.

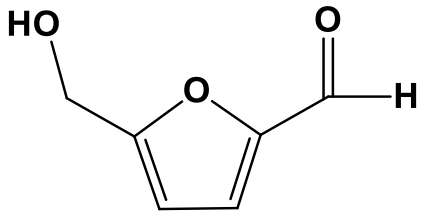

Figure 2.1. 5-Hydroxymethylfurfural (HMF) structure(T. Wang et al., 2014).

5HMF, which is derived from renewable material, retains the structure of the six carbon atoms present in the original starting material, and is a valuable bio-based key platform chemical. It is used to produce various substances. So far, these have been obtained from petrochemical raw materials-bulk and fine chemicals, such as monomers, drugs, agrochemicals, flavors and fragrances, as well as liquid fuels and precursors of mixture components. The use of bio-based 5HMF to produce various intermediate products, marketable products and energy is in line with the concept of bio economy and is an option to reduce dependence on depletable fossil. However, it is still a major challenge to find new technologically feasible, economically feasible and environmentally friendly methods to replace non-renewable with bio based (Design et al., 2020).

The exquisite sensible capacity of bioderived HMF and its derivatives showed in Figure 2.2. The entire spectrum of programs is starting from fuels and solvents to natural synthesis and training of biologically lively molecules for pharmaceutical programs. Oxidation of HMF to FDCA is the maximum very well studied vicinity of HMF chemistry, due to the fact FDCA is frequently provided as a precursor of biobased polymers. Reduction of HMF is any other crucial path of HMF chemistry, due to the fact the reduced products may be used as solvents, fuels and polymer precursors. Some of papers describing the manufacturing of FDCA-primarily based totally MOFs with beneficial optical residences had been published. The received 2-hydroxymethyl-5-vinylfuran (HMVF) became polymerized giving a polymer with excessive adhesiveness to steel, copper, aluminum, and glass. BHMF and DFF are crucial furan-containing chemical substances that may be received with the aid of using slight hydrogenation or oxidation of HMF, respectively. In current investigations, BHMF, DFF, and their derivatives had been used as precious intermediates for the synthesis of biofuels, polymers, drugs, and different products of great chemistry(Kucherov et al., 2018).

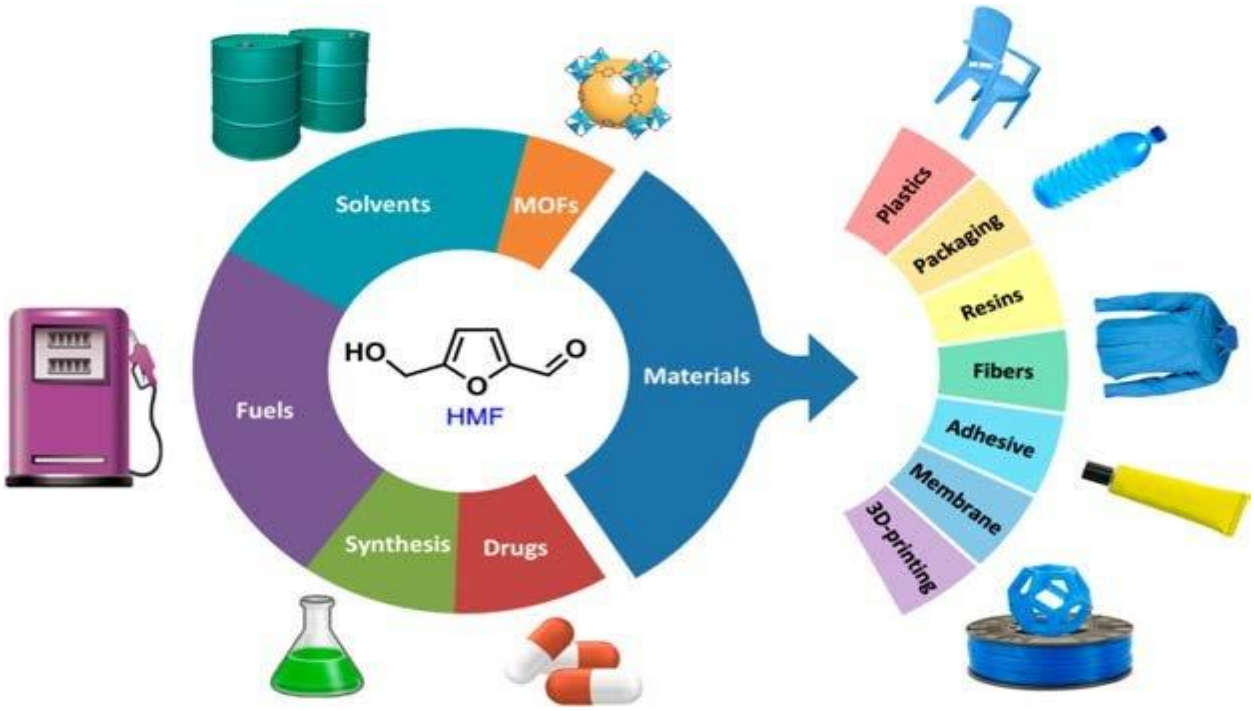

Figure 2.2. Application of 5-HMF and its derivatives(Kucherov et al., 2018).

5HMF is actively studying mass production wear and tear to meet the continuing challenges. For example, when the HMF yield is less than 50% of the cellulose content, biomass non-compliance limits one-step conversion(Mirzaei & Karimi, 2016). The method of converting lignocellulose-containing biomass into HMF includes three steps of cellulose hydrolysis, glucose isomerization and fructose dehydration. The by-product levulinic acid is easily formed by HMF rehydration. At present, the production of HMF still uses sugar syrup as raw material, which is extracted from energy crops in industrial production, causing a waste. Use biomass-based carbohydrates directly, as raw materials face the problem of low HMF yield, which shows that measures to improve HMF yield are indispensable (Shao et al., 2021). Since 5HMF is an intermediate molecule and the market for HMF itself is small, it is necessary not only to optimize its synthesis process, but also to develop an efficient separation/purification process for its subsequent upgrading reactions, especially organic phase reactions. 5HMF extraction stage makes the whole process economically feasible and can be used for large-scale production(Delidovich & Palkovits, 2016).

Critical selection of catalysts and solvents based on the requirements of high-performance conversion systems requires a comprehensive understanding of the success factors in advance. Discover catalyst properties, for example. active species, active sites, pore size, and surface area the catalytic activity and selectivity of the required intermediates and products. As far as solvents are concerned, characteristics such as partition coefficient, boiling point and thermal stability are indicators of performance and recyclability(Delidovich & Palkovits, 2016).

HMF is one of the most attractive biochemical substances obtained from plant cellulose. It is made from C_6 sugar through an acid-catalyzed dehydration process. Due to its specific functional groups, HMF can also derive a variety of valuable chemicals. Compared with reducing sugars, synthesis of HMF from cellulose is a difficult task(Rout et al., 2016). This study has mainly focus on the inedible cellulosic biomass or isolated cellulose for synthesis of HMF.

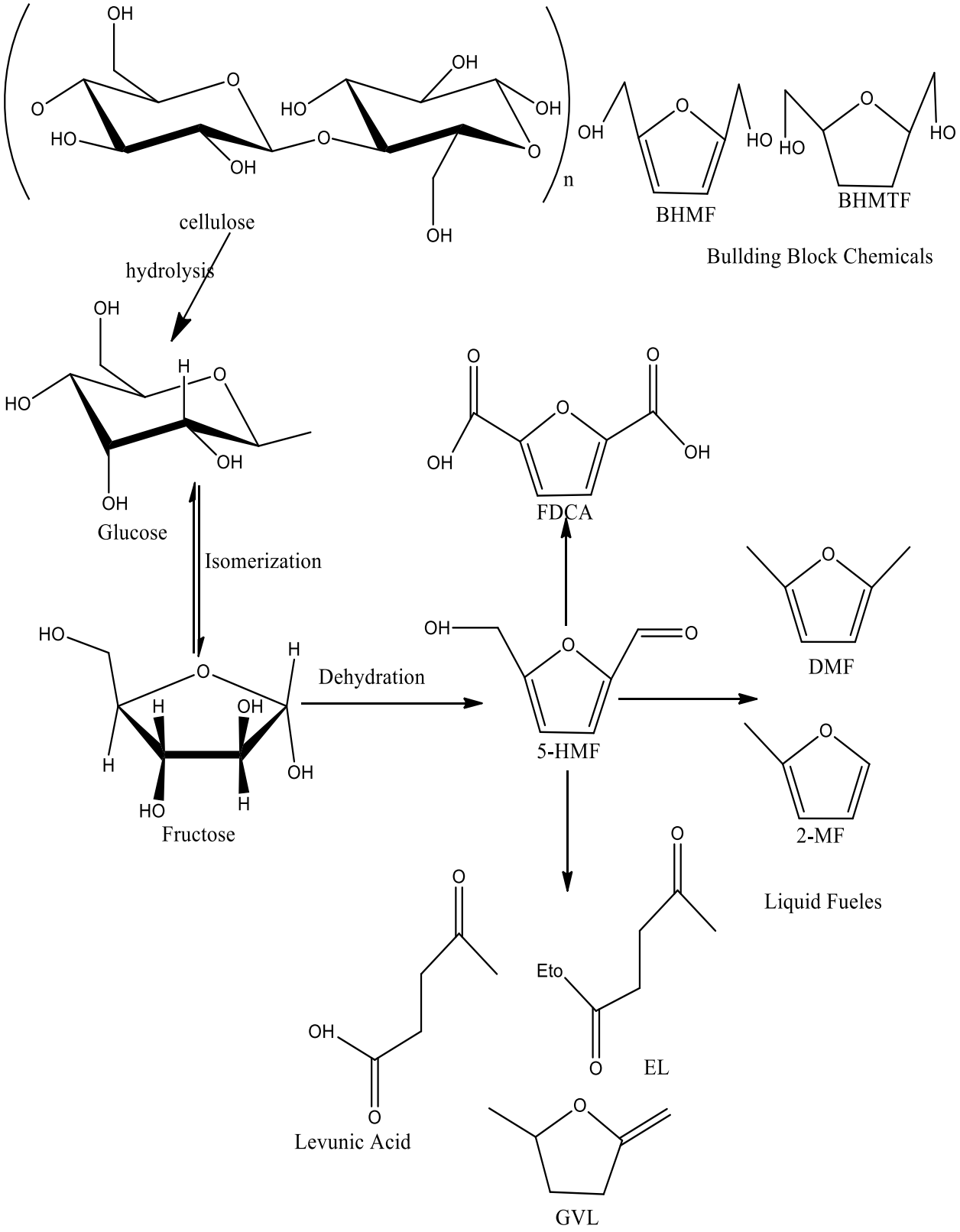

Figure 2.3.HMF production and its utilization routes for chemicals and fuels(Saha & Abu-Omar, 2014)

2.2. Lignocellulosic Biomass

Lignocellulosic biomass is a long-term alternative to fossil carbon and can be used as a raw material for the production of liquid fuels and valuable chemicals (Dai et al., 2017). Agricultural residues, such as bagasse, corn stalks, corn cobs, rice husks, wood fruits, coconut husks, oil palm stalks, corn stalks, coffee grounds, corn stalks, rice husks, citrus peel waste, sawdust, shredded paper, municipal solids waste and sludge from paper mills are important of wood-based organic pulp and other renewable, useless, widely distributed, inedible and low-cost (Hu et al., 2015). Today, these biomasses are the most widely used renewable materials on the planet, and are by far the most suitable and cheapest materials for the production of biochar and other platform compounds such as (glucose, 5-hydroxymethylfurfural and levulinum Acid) used Raw material for acid and its derivatives (Xu et al., 2018) in the food, textile, solvent, polymer and biodiesel industries, it has greater ecological, economic and strategic importance (X. L. Shi et al., 2018).

The platform compound is mainly made by decomposing lignocellulose, which is mainly composed of cellulose (Parveen et al., 2017). Lignocellulosic biomass is mainly composed of three main components: cellulose, hemicellulose and lignin. These components in lignocellulosic materials have different functions and chemical properties. About 90% of the dry matter of lignocellulose-containing biomass is composed of polymerized carbohydrates, such as cellulose (20-60% by weight), hemicellulose (15-30% by weight), lignin (10-25% by weight), and extracts (1-12% (weight)) depends on the nature of the plant, and they appear in a complex structure with each other(Varanasi et al., 2013).

2.1.1. Cellulose

Cellulose is the main material that constitutes the cell wall of plants, and most of it is composed of glucose residues. Cellulose is the most abundant component of biomass, accounting for 35-50% of lignocellulosic biomass(Rinaldi & Schüth, 2009). Cellulose mainly contains glucose units linked together by β1,4-glycosidic bonds. In contrast to starch, cellulose is a crystalline material with an extended, flat, double-helical conformation(F. Guo et al., 2012).

Hydrogen bonding helps maintain and strengthen the flat linear conformation of the chain. The top and bottom of the cellulose chain are essentially completely hydrophobic. The side of the cellulose

chain is hydrophilic and can form hydrogen bonds, because all aliphatic hydrogen atoms are in the axial position, and the polar hydroxyl groups are in the equatorial position.

The degree of polymerization of cellulose in wood or cotton is about 10,000 to 15,000 glucopyranose monomer units(Huang & Fu, 2013). Partial acid hydrolysis, cellulose breaks down into cellobiose (glucose dimer), cellotriose (glucose trimer) and cellotetraose (glucose tetramer), and complete acid hydrolysis is broken down into glucose unit (Pang et al., 2010).

2.1.1.1. Structure of Cellulose

In Figure 2.4 structure of cellulose is composed of many glucose mediators linked together in the form of βD-anhydroglucopyranose units (AGU). AGUs are connected to each other via glycoside bridges on the C_1 and C_4 carbon atoms. The number of repeated AGUs is defined as the degree of polymerization (DP) of the cellulose. Generally speaking, the DP of cellulose varies with the original type of material. For example, the typical DP range of wood pulp is about 300-1,700, while the typical DP range of cotton or other plant fibers is 800-10,000. Due to the connection of a large number of hydroxyl groups and β1,4 glycosidic bonds, it is easy to form intramolecular and intermolecular hydrogen bonds, which makes cellulose stable during chemical and biological treatment and is extremely difficult to dissolve in common solvents.(Huang & Fu, 2013).

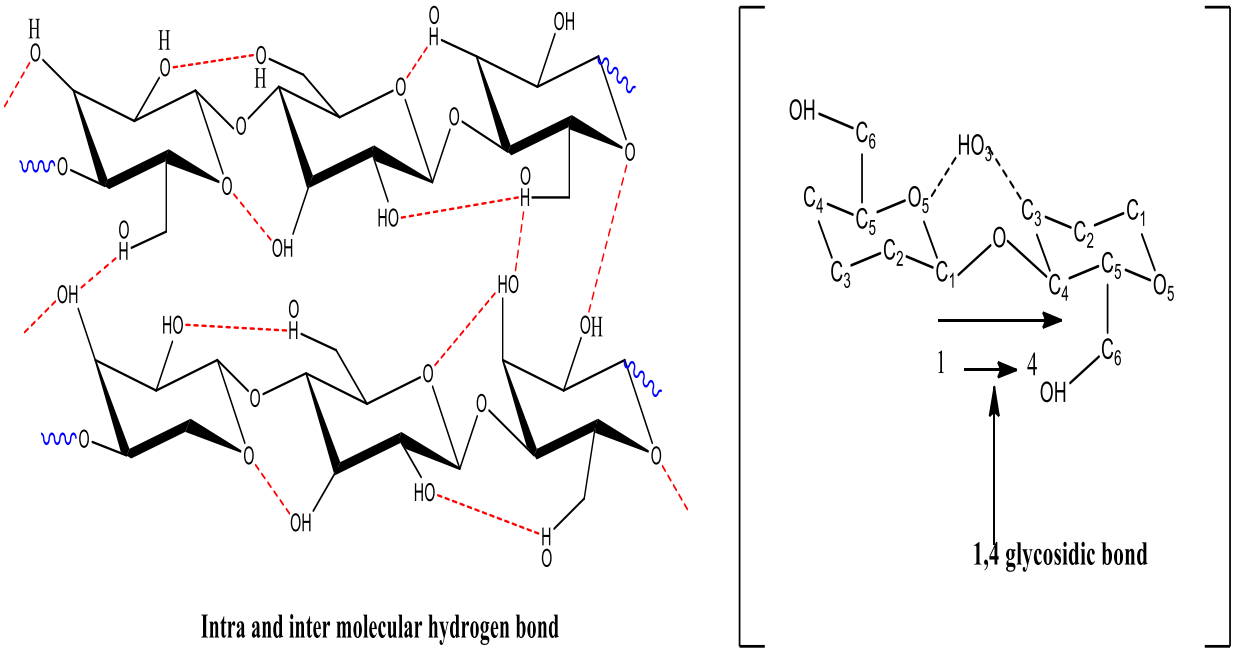

Figure 2.4.Chemical structure of Cellobiose With β-1,4-Glycosidic Bonds and Intra- and intermolecular Hydrogen Bonding(Shaghaleh et al., 2018).

2.1.1.2. Microcrystalline Cellulose

Microcrystalline cellulose (MCC) is a white, odorless, water-insoluble fine powder or granular material. Made from natural cellulose by acid hydrolysis, it has the characteristics of high crystallinity and small particle size. It is widely used in food, chemical, pharmaceutical and other industries(Jianjian Wang et al., 2011).

2.1.1.3. Degree of Crystallinity

The crystallinity of cellulose can be reduced by dissolving cellulose in protic solvents, ionic liquids, or reducing the size of cellulose by ball milling. The cellulose first dissolved in the ionic liquid and hydrolyzed with the solid acid catalyst releases more glucose than the cellulose insoluble in the ionic liquid(Rinaldi & Schüth, 2009).

2.1.2. Hemicellulose

Hemicellulose is an amorphous polymer composed of carbon penta saccharide and carbon hexose. Hemicellulose is another component of plant cell wall and, together with cellulose, is the most common heterogeneous group of polysaccharides. It is composed of pentose (xylose, arabinose), hexose (mannose, glucose and galactose) and acetylated sugars. Hemicellulose is an amorphous matrix material that binds cellulose fibrils non-covalently through hydrogen bonds. Lignocellulosic biomass contains approximately 15-35% hemicellulose, depending on the type of plant. Compared with cellulose, hemicellulose is different in the composition of different sugar units, lower degree of polymerization (about 100-200), low strength and good hydrolysis, shorter and branched molecular chains, and with fiber the crystallinity is lower than that of the cellulose.

2.1.3. Lignin

Like cellulose and hemicellulose, lignin is the third most common component of lignocellulose-containing biomass, surrounded by cellulose and hemicellulose. Lignin is the structural skeleton in plant cell walls. The degree of lignification is related to the compressive strength of the stem and the dehydration of the plant cell wall. Lignin is an amorphous aromatic network polymer composed of phenylpropane units through carbon-carbon and ether bonds. It is difficult for microorganisms to decompose the structure of this compound. The inert component of plant cell walls is lignin. Lignin is also considered to be the "cement" of the cell wall, which can increase its structural rigidity and give plants mechanical strength. Lignin monomers form complex

amorphous polymers through H-O-H, C-C bonds, C-O-C bonds, or intramolecular/intermolecular hydrogen bonds. Lignin usually accounts for 20-30% of wood (wt.)(K. Guo et al., 2019).

2.2. Mechanism of 5-HMF Production

At present, the mechanism of 5-hydroxymethylfurfural (HMF) is mainly considered to be lignocellulosic biomass. The conversion of lignocellulose to HMF generally includes three steps: (1) hydrolysis of cellulose to glucose, (2) isomerization of glucose to fructose, (3) dehydration of fructose to HMF and by-products such as humins and 2-hydroxyacetyl.(Antal et al., 1990). The conversion of C_6 sugar to HMF and the mechanism of acid-catalyzed production process were carefully studied (Binder et al., 2010).

2.2.1. Process Mechanism of Hydrolysis

Hydrolysis can selectively and energy-efficiently convert biomass into monomer units, which can then be selectively converted into fuel or chemicals. A large number of cellulosic materials are hydrolyzed through enzymatic and acid-catalyzed processes. However, the limitations of the enzyme system are obvious, because these processes are always inefficient and the cost of enzymes is high(Salvador et al., 2010).

There are two types of acidic hydrolysis processes that can be used to saccharify cellulosic materials. One is a high-temperature process using dilute acid, and the other is a low-temperature process using concentrated acid. In the two process categories, sulfuric acid and hydrochloric acid are the preferred acids(Okamura et al., 2006).

The hydrolysis reaction is the decomposition of water molecules into hydrogen cations (H^+) and hydroxide anions (^-OH). In (Figure 2.5) Schematic mechanism the presence of cellulose, (H^+) attacks the oxygen atom in the 1,4-glycosidic bond. Therefore, the 1,4'β-glycosidic bond is broken to form a cyclic carbocation having a stool shape. This step is considered a rate limiting step. Finally, glucose is formed by rapid ion transfer from (^-OH) separated from water molecules to glucose-based carbocations. According to the reaction conditions of the solid acid catalyst and the solvent, the reaction mechanism of water splitting is beneficial to the hydrolysis of cellulose. The splitting of water molecules into hydrogen cations (H^+) and hydroxide anions (^-OH) can be considered deprotonation. These results indicate that stronger Bronsted acidity is more conducive to the catalytic hydrolysis of cellulose. In addition, the increase in the amount of water has a

positive effect on the decomposition of 1,4-glycosidic bonds and intramolecular hydrogen bonds in insoluble cellulose, resulting in more hydrolysis products(C. H. Zhou et al., 2011).

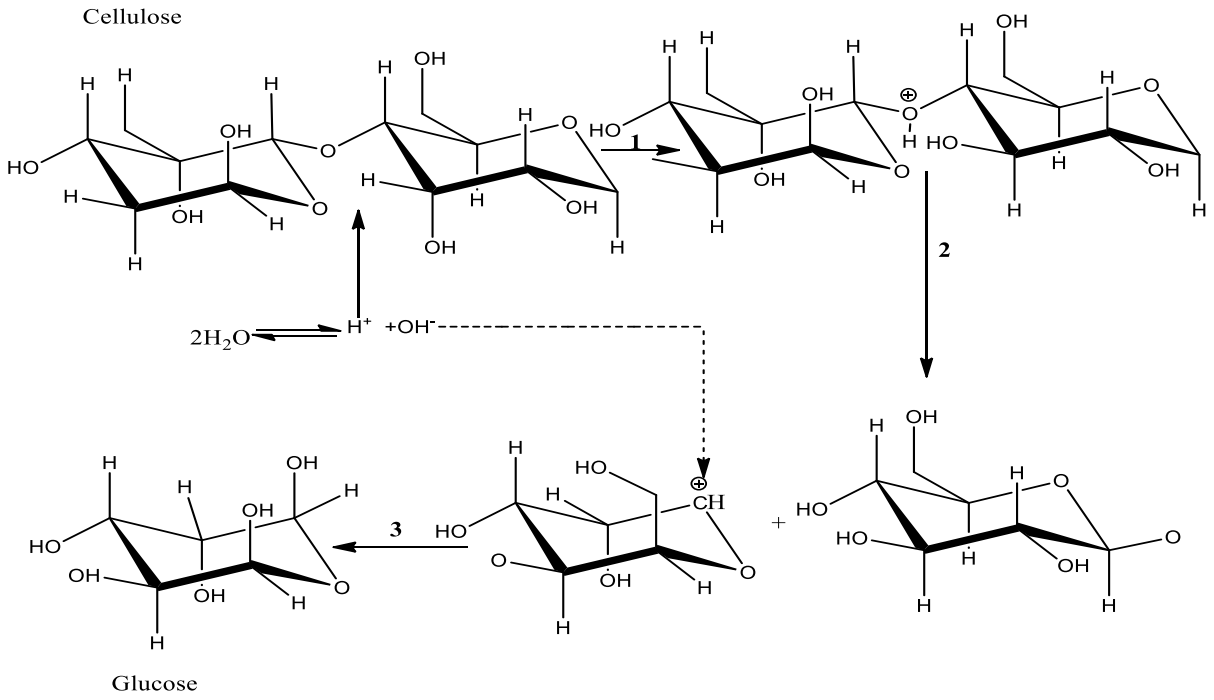

Figure 2.5. Schematic mechanism of breakage of 1, 4'-**β**-glycosidic bonds and formation of glucose in the hydrolysis of cellulose

It was also reported that the phenolic hydroxyl groups and carboxyl groups in the carbon material, which were capable of adsorbing cellulose and water molecules effectively, and the SO_3H groups bonded to the carbon material could decompose hydrogen bonds and hydrolyze the β-1,4-glycosidic bonds in the adsorbed cellulose molecules. Based on this report, it could be predicted that the main catalysis effects of phenolic hydroxyl groups and carboxyl groups in the synthesized carbon-based solid acids were absorbing hemicellulose and water molecules, and the SO_3H groups could decompose the bonds in the adsorbed hemicellulose molecules and released xylose or xylo-oligosaccharides(X. Li et al., 2018).

2.2.2. Process Mechanism of Isomerization and Dehydration

Isomerization is the process of converting molecules, ions, or molecular fragments into isomers. Explain the isomerization mechanism of glucose in aqueous system through isotope labeling and nuclear magnetic resonance spectroscopy (NMR) (Binder et al., 2010), molecular dynamics (Mushrif et al., 2014) and DFT (G. Li et al., 2016). In Figure 2.6 the catalytic process, Lewis's

acid promotes the ring opening of glucose, and then forms a complex with acyclic glucose at the hydroxyl oxygen of C_1 and C_2. This coordination allows the electron-deficient Lewis acid to polarize the carbonyl group (C_1 in glucose), thereby promoting the transfer of hydride from C_2 to C_1. This mechanism is applicable to many types of Lewis acid catalysts, including $CrCl_3$ (Mushrif et al., 2014) and $AlCl_3$(Dai et al., 2017).

During the acid-catalyzed hydrolysis of polysaccharides, protons weaken the glycoside C-O-C bond by attacking the oxygen atom of the bond. (L. Zhou et al., 2013). The dehydration of fructose illustrates a catalytic mechanism similar to that represented by the attachment of protons to the C_2 hydroxyl group of fructose to begin eliminating the first water molecule to produce carbocations intermediates. This intermediate is converted to enol, and then condenses into HMF by releasing more than two water molecules(Antal et al., 1990).

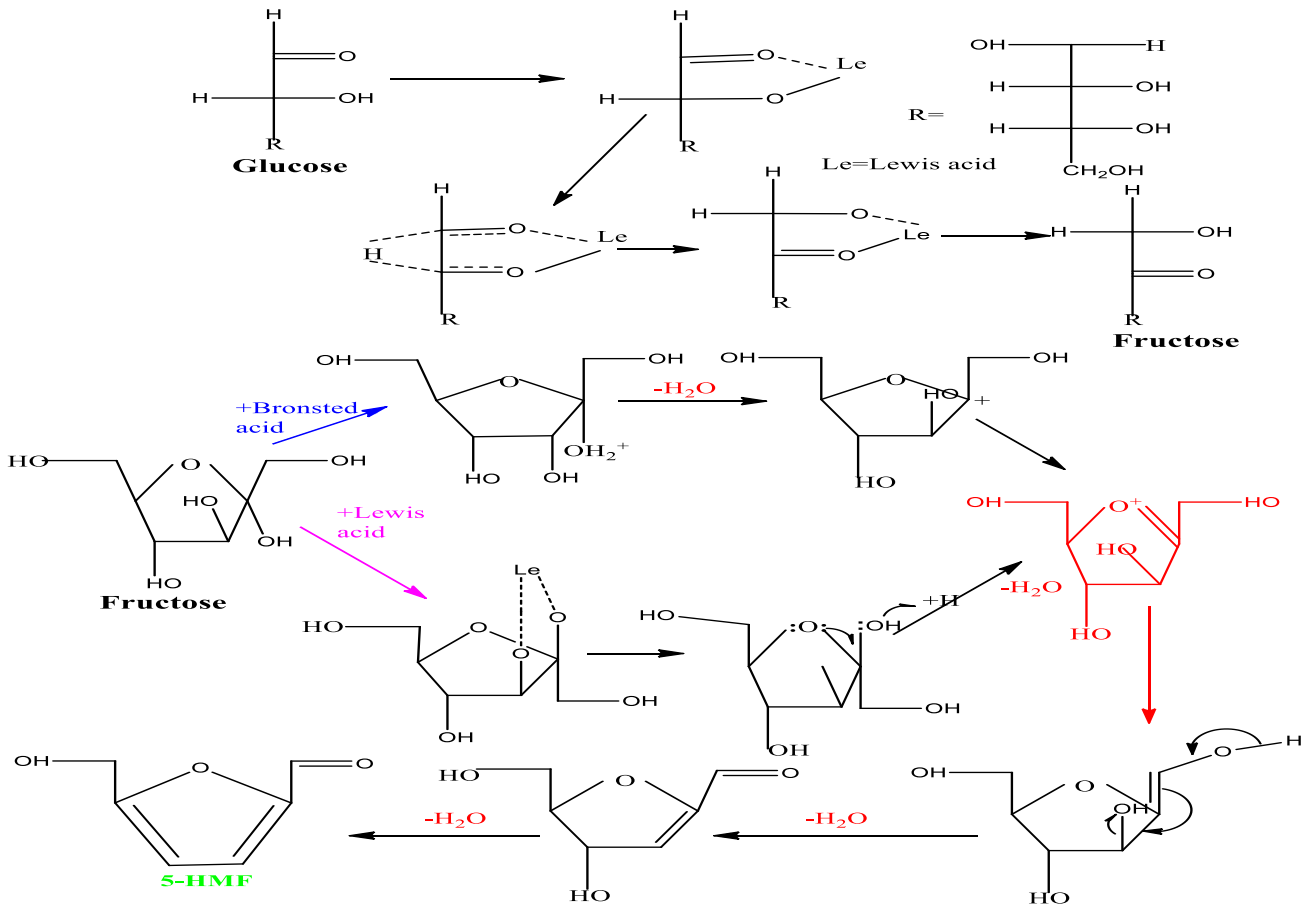

Figure 2.6.Reaction pathways of glucose to fructose and dehydrate fructose to 5-HMF using Lewis and Bronsted acid(Muranaka et al., 2020)

Recent studies have shown that the one-pot conversion of biomass into HMF with Bronsted acid can simultaneously promote the direct dehydration of glucose to HMF, bypassing the glucose-fructose isomerization(L. Yang et al., 2015). A cyclic mechanism for such opportunity course has been proposed the use of Car-Parrinello primarily based totally ab initio molecular dynamics and metadynamics simulation (Qian, 2012). A cyclic mechanism for such opportunity course has been proposed the use of Car-Parrinello primarily based totally ab initio molecular dynamics and metadynamics simulation (Qian, 2012) And microkinetic modelling primarily based totally on density feature theory (DFT)(L. Yang et al., 2015). The dehydration mechanism occurs through the sulfonated solid Bronsted acid catalyst, and the mechanism is through the jump of the glucose-fructose isomerization stage. The sulfuric acid group plays a key role in the catalytic reaction. It is not only providing hydrogen ions, but also assists the transfer of hydrogen ions as conjugate bases, thereby promoting the formation of 1,2-diol as shown in Figure 2.7. The conversion process begins with the protonation of the SO_3H sulfone group on the hydroxyl group of glucose C_2, resulting in the formation of a five-membered ring intermediate in preparation for dehydration (also known as condensation reaction) molecules or ions. The formation of HMF may follow the following mechanism, that is, the dehydration of glucose in the open-chain form at C_2 to form carbocations, which react with the hydroxyl group at C_5 to generate tetrahydro 3,4 dihydroxy 5 (hydroxymethyl) 2 furfurals, which is then further dehydrated in to HMF

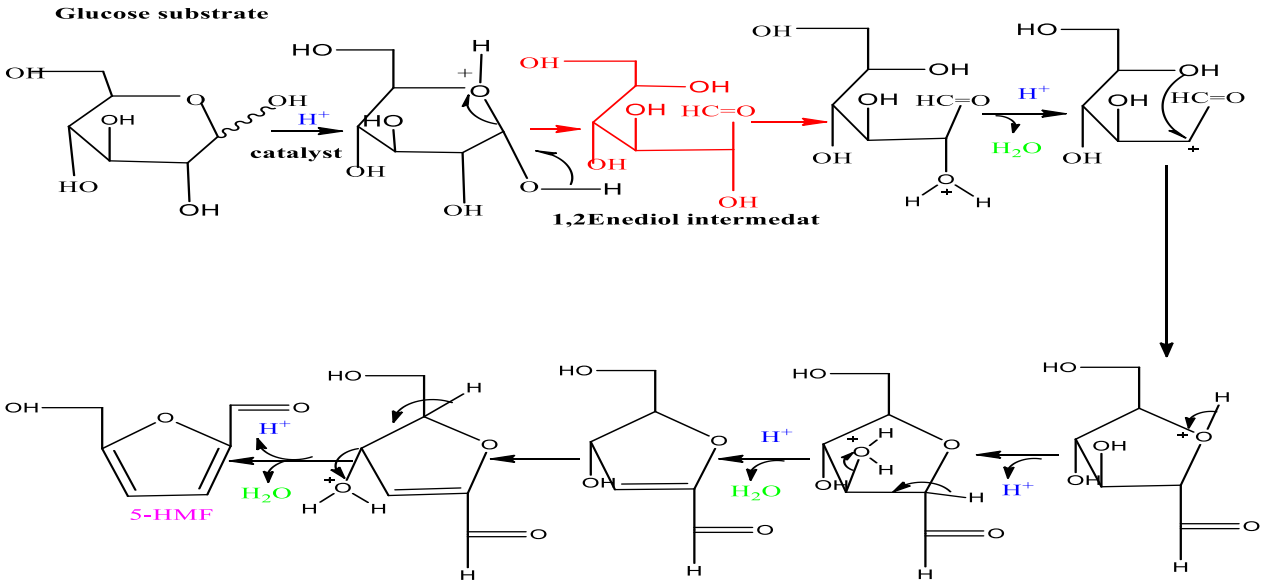

Figure 2.7. Dehydration mechanism for 5-HMF production

2.3. Factors That Affect 5-HMF Production

2.3.l. Reaction Temperature

During the HMF production process, the reaction temperature further increased, and the HMF yield decreased slightly. In the valorization process of carbohydrates, glucose or fructose is first dehydrated to form HMF, and then subsequent reactions are prone to produce LA, FA and FF (through rehydration) and humins (through polymerization). Too high temperature is conducive to the side reaction of HMF. The total output of LA + FA + FF is very low, and gradually increases as the temperature rises. The color of the reaction solution darkened as the reaction temperature increased, indicating that the main by-product of the side reaction was human. At lower temperatures, the direct dehydration of glucose to HMF is not complete in a short time. At higher temperatures, the side reactions of by-products (mainly humins) occur more intensely, resulting in a lower HMF yield(L. Zhang et al., 2017).

2.3.2. Reaction Time

The yield of HMF increased rapidly at the initial stage and then decreased, indicating that the newly formed HMF was converted into other unwanted by-products after a longer reaction time. The decrease in HMF yield after a period of time may be related to the decomposition of HMF into LA + FA + FF and the self-polymerization/cross-polymerization at high temperature or longer time (M. Li et al., 2017).

3.2.3. Catalyst Loading

The yield of glucose and HMF increased steadily with the increase of the catalyst loading, but gradually decreased after the catalyst loading increased. The yield of HMF decomposition by-products such as levulinic acid (LA), formic acid (FA) and furfural (FF) under different catalyst loadings. Considering the efficiency of catalyst loading and the suppression of by-product formation, SBC loading> 0.5 g has not been studied. This is consistent with the characteristics of Bronsted acid in carbohydrate utilization, that is, cellulose is hydrolyzed to monosaccharides, and monosaccharides are directly dehydrated to HMF(V. et al., 2017).

2.4. Carbon as Catalyst

Approximately 90% of industrial chemicals are produced through heterogeneous catalysts using various petroleum feedstocks as raw materials (precursors). However, this does not apply to biomass-based products, because industrial-level biomass processing is still based on homogeneous catalysis routes, which have low selectivity and generate large amounts of waste. This will eventually lead to higher production costs and reduce the competitiveness of biomass-based products in the market. Therefore, in recent years, research on biomass conversion catalysts has mainly focused on heterogeneous catalysis. As mentioned earlier, the researched catalysts mainly include traditional and chemically synthesized, such as zeolite, silica and metal-supported (Pt, Pd, Au, Ni) zeolite and silica. However, the important of these traditional catalytic systems in biomass conversion has disadvantages such as low catalytic activity, poor reusability, and high material costs using expensive precious metals and carrier materials, and so forth, thus making them less attractive for industrial scale applications .Therefore, there is a special need to develop an active, robust and inexpensive catalytic system that can transform complex biomass molecules(Konwar et al., 2014).

In recent years, with the emergence of the concept of green chemistry, the use of cheaper green materials for chemical conversion has recently attracted considerable attention, and some research groups have tried to develop a catalyst that uses cheap precursors (such as biomass and waste). Among them, sulfonated carbon or -SO_3H functionalized carbon catalysts have received great attention as promising solid acid catalysts. These materials are similar to H_2SO_4 in terms of acidity and catalytic activity, and also provide high operational stability (> 240^oC and reusability), making them multifunctional acid catalysts for acid-catalyzed biomass conversion reactions(Xiong et al., 2018).

Functionalized carbon catalysts have proven to be one of the most active and economically attractive catalysts for biofuel and other chemical production. They are structurally equivalent to activated carbon, and like activated carbon, they can also be made from any carbon source. And their texture properties can be easily changed by changing the carbonization/activation conditions. Therefore, sulfonated carbon is much cheaper than traditional solids such as amberlyst, zeolite,

and sulfated zirconia. In addition, this kind of activated carbon made from cheap precursors can be a universal carrier for making cheap catalysts(Okamura et al., 2006).

2.5. Corncob Biomass as Raw Material for Synthesis of Solid Catalyst

Using natural resources to process materials in the long run, waste is potentially renewable and has no negative impact on the environment. Ethiopia has natural resources that can be used and developed in a balanced, sustainable and social manner. This process is the embodiment of the green technology concept, and it provides a clear direction for how the synthesis process can become more sustainable and reduce the impact on the environment. Corncob is an agricultural waste containing lignocellulose, which is abundant in Ethiopia. Corncob contains approximately 36.4% cellulose, 34.9% hemicellulose and 14.8% lignin(Nata et al., 2017).

Recently, there has been a tendency for some people to use only corn cob scraps as animal feed, fuel, or waste. To overcome this problem, it is necessary to develop the use of corncob, for example as a carbon material and a resource for catalysts and good properties such as activated carbon, production of cellulose gel, conversion of cellulose to glucose and then to 5HMF, synthesis for biodiesel, production of formic and acetic acid.(Konwar et al., 2016).

Figure 2.8. The waste corncob

Homogeneous acids such as sulfuric acid and hydrochloric acid are the most commonly used catalysts and have been found to be very effective in many acid-catalyzed reactions. Although homogeneous acid is a cheap and efficient catalyst, it has disadvantages in terms of environmental problems, including generating a large amount of waste, corroding equipment, difficult to separate from the reaction mixture, and polluting the environment(Zeng et al., 2016).

Heterogeneous catalysis is one of the most economical and efficient materials in the field of catalysts. Conventional solid acid catalysts such as zeolite, cation exchange resin and niobic acid are commonly used in various acid-catalyzed reactions, but these catalysts have the disadvantages of high cost, poor catalytic activity, and poor stability, Compared with other catalyst supports, like carbonaceous materials have the advantages of easy manufacture, abundant resources and low price(Liang et al., 2010).In carbohydrate conversion, it is necessary to create cheaper, more environmentally friendly and more effective catalysts. In the past, homogeneous liquid inorganic acids (H_2SO_4, HCl, $HClO_4$, etc.) were widely used in catalytic reactions, despite their corrosive effects in the reactor system, poor recyclability, and the formation of large amounts of waste. Alternatively, heterogeneous solid acid catalysts such as zeolites, metal oxides, ion exchange resins, supported heteropoly acids, and carbonaceous materials are more preferred because they are easy to recycle; they can be stable at higher temperatures and surface acidity to improve product selectivity. In particular, the heterogeneous cheap carbonaceous solid acid catalyst has received more and more attention in biomass conversion. It can be used in various types of reaction media (water, organic solvents or ionic liquids), and can be used in model biomass compounds or incomplete carbonization and sulfonation of real biomass at low temperatures(Kaya et al., 2019).

2.5.1. Proximate Analysis of Precursor

Proximity analysis is the information needed for moisture, volatiles and ash, and fixed carbon. The proximate analysis of a substance means of determining the distribution of products obtained when the char sample is heated under specified conditions. These properties are related to the heat conversion of biomass materials into energy(Parikh et al., 2007).

2.5.2. Physical and Chemical Activation for Biomass

Before the carbonation of biomass, there are various pretreatment processes: physical, physio chemical, chemical, biological, electrical, or a combination of these processes. Typical physical pretreatment processes include machining, grinding, milling and heat treatment(F. Guo et al., 2012).

The activation process plays an important role in increasing the pore volume, increasing the pore diameter and improving the pore formation of carbon materials. On the other hand, activation can also increase the specific surface area of the formed carbon material by 4 to 50 times, thereby providing more surface area. The activation process can be performed by chemical activation using

a chemical activator or by physical activation using a gaseous activator. The choice of activation method and the choice of activator are important because they affect the properties of the activated carbon formed. In chemical activation, biomass is first treated with a chemical activator and then carbonized at high temperature to form activated carbon(Härmas et al., 2016).

Compared with physical activation, chemical activation can produce activated carbon with higher pore density, higher carbon content and shorter carbonization time. The most commonly used activators are phosphoric acid (H_3PO_4), potassium hydroxide (KOH), sodium hydroxide (NaOH), zinc chloride ($ZnCl_2$) and iron chloride ($FeCl_3$)(Somasundaram et al., 2013). H_3PO_4, $ZnCl_2$ and KOH are several examples of the commonly used chemical activating agents as they are able to effectively enhance the pore development with higher surface area(Sun et al., 2016).

Compared to chemical activation, physical activation is cheaper due to cheaper activators. However, the activated carbon produced by it has a narrow pore size distribution and is mainly composed of micropores. In addition, it was found that compared with chemical activation, the specific surface area of physical activated carbon increased less. On the other hand, chemical activation can produce activated carbon with a wider pore size distribution ranging from micropores to mesopores, and greatly increase the specific surface area of carbon materials(Yacob et al., 2014).

2.6. Preparation of Bio char

The type of carbonaceous material extracted from biomass residues is called biochar, which is produced by the incomplete carbonization process of the starting material. Biochar has a high oxygen content (27-34% by mass), mainly in the form of phenols and carboxylic acid groups, and contains trace amounts of nitrogen and sulfur. Biochar with significant specific surface area and porous structure is suitable for hydrophobic acid catalysis process, which makes the catalyst have more effective active centers to capture the amorphous part of cellulose(Okamura et al., 2006).

Biochar is a kind of carbon-rich material, which can be prepared by thermal combustion of various organic waste materials such as agricultural waste and urban sewage sludge under certain oxygen conditions(Jianlong Wang & Wang, 2019). Biochar can be used directly as a soil conditioner, water purification, adsorption(Chen et al., 2018) ,energy storage and heterogeneous catalysis(Fraile et al., 2015). The technical, economic and climatic aspects of biochar production

technology and its application in soil remediation(Šumić et al., 2016). Recently, biochar is used for the synthesis of solid catalyst by functionalizing with different chemical(O. L. Li et al., 2017).

Biochar is a promising green material and has been successfully used to synthesize value-added products such as sulfonated carbon catalysts. Biochar-based solid acid (SO_3H) can be easily synthesized by the sulfonation of biochar and used as a proton donor in many fields, especially in the hydrolysis and dehydration of cellulose(Lu & Love, 2005).

It also distinguishes biochar from activated carbon (two typical amorphous carbon materials). From a structural point of view, there is no fundamental difference between biochar and activated carbon because both are amorphous charcoal with high porosity. Activated carbon obtained from biomass can also be regarded as a certain type of activated carbon. However, compared with activated carbon, biochar usually has abundant surface functional groups (C-O, C = O, C=C, COOH, OH, etc.). These functional groups are highly modifiable and can be used as a platform for the synthesis of various functionalized carbon materials. In general, biochar obtained from biomass has abundant functional groups Aromatic C=C/C=O, O—H, COOH, C−O, and C—H(Ramanayaka et al., 2020). There are several ways to synthesize carbon materials(biochar) from biomass. Basically, carbon materials can be synthesized by two main methods, including hydrothermal carbonization (HTC) and direct carbonization (pyrolysis).

Hydrothermal carbonization (HTC) is a thermochemical process, usually in the presence of water and a highly porous carbon product called Hydro char. Direct carbonation (pyrolysis): This method is simple and straightforward. However, unlike HTC, which uses water, the direct carbonation method does not require any additional materials. Generally, it is through direct heat treatment of biomass to remove and decompose volatile substances and oxygen, hydrogen, nitrogen and other non-carbon elements on biomass to form rigid skeleton carbon with aromatic carbon structure, thereby forming biochar. Pyrolysis is widely used to produce porous carbon from natural biomass. In the direct pyrolysis process, the dry biomass is heated to a high temperature in the range of 300-1000^0C in an inert atmosphere (such as nitrogen, argon) or an environment with low oxygen content. The conversion of biomass to porous carbon involves several aspects. Dehydration, condensation, cross-linking depolymerization, cracking, isomerization and other reactions(Szczęśniak et al., 2020).

Biomass carbon sulfonic acid ($BCSO_3H$) is a new, recyclable and renewable solid acid. This study investigated the effectiveness of sulfonated biochar as a catalyst for the hydrolysis and dehydration of microcrystalline cellulose to 5HMF. Corncobs were supplied from Adama agricultural land and ground with a Boal mill. The powder was collected and dried at 105^{o}C for 12 hr to avoid moisture. Then, the dried corn cob was activated with phosphoric acid, and the activated corn cob was carbonized in a muffle furnace at different temperature such as 400^{o}C, 450^{o}C, and 500^{o}C for 8 hr.

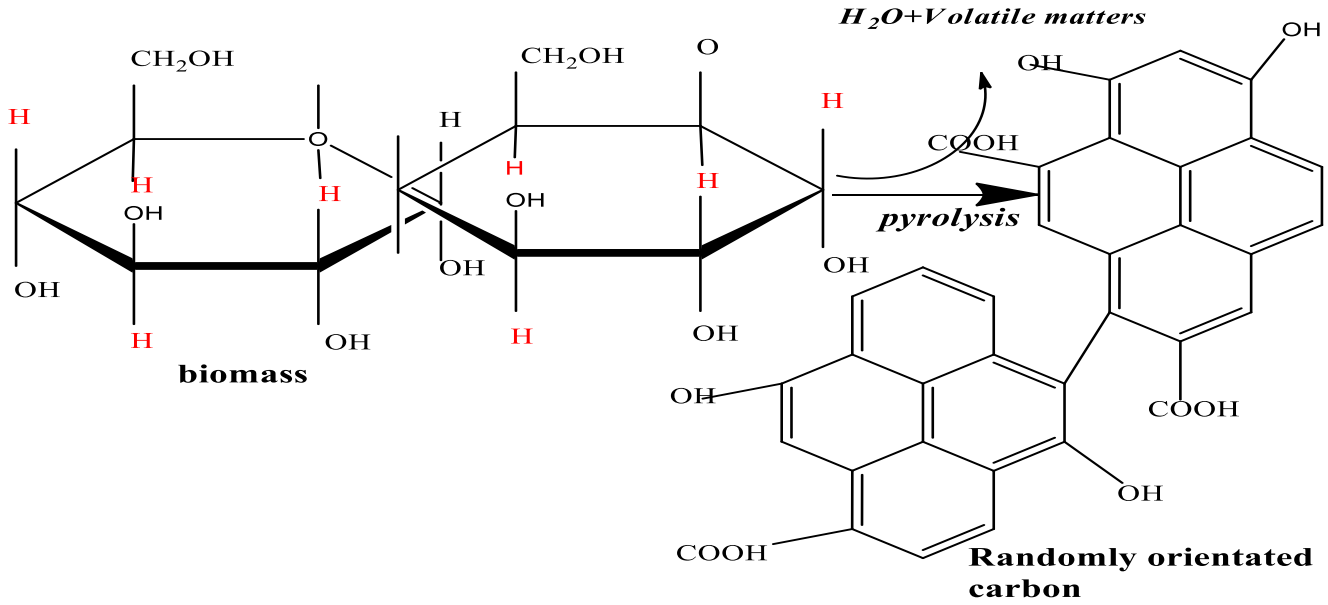

Figure 2.9.Structure of biochar from biomass(Zo Ee Tang, 2019)

2.6. Sulfonation Methods

Sulfonation is an electrophilic aromatic substitution reaction in which the hydrogen atoms in aromatic hydrocarbons are replaced by functional sulfonic acid groups. The carbon material (biochar) produced by carbonization has been functionalized by sulfonation to form a carbon-based acid catalyst. The sulfonation process of carbon is usually carried out by direct acid sulfonation and heat treatment or arylation reaction. The most common sulfonation method is direct sulfonation using H_2SO_4 at high temperature. The sulfonation of carbon can be carried out using different types of sulfonating agents such as H_2SO_4, p-toluenesulfonic acid (PTSA), oleum and 4-benzenediazonium sulfonate (4BDS). The functionalization of carbon by direct sulfonation is usually done by directly grafting the -SO_3H functional group to the carbon structure, and thermally treating the activator and the carbon. Most research on the synthesis of carbonic acid catalysts has focused on direct sulfonation using H_2SO_4(Zo Ee Tang, 2019).

Sulfonated carbon-based catalysts (SCBC) are produced by a two-step process, including pyrolysis or hydrothermal carbonization at a temperature of 350-700^{o}C for about 5-15 hr, and then sulfonation at a temperature of 80-210^{o}C. It is about 4 -24hr (Mateo et al., 2020). Regarding catalyst synthesis, SCBC is usually synthesized by a two-step method, including partial carbonization of crushed at a temperature of 300-800^{o}C for about 0.5-20hr, and then sulfonation at a temperature of 120-200^{o}C for 3-20 hr. Partial carbonization is used to induce the formation of a small polycyclic aromatic ring, which serves as a skeleton or support for the active site(Flores et al., 2019).

2.7. Factors That Affect the Performance of Biochar -Based Catalyst

2.7.1. Effect of Carbonization Factors

Due to either decreasing or increasing the carbonization temperature. the degree of graphitization of the carbonized product and the loading of SO_3H groups are also weakened. Small polycyclic aromatic carbon layers are preferably used for loading sulfonic acid groups, but their formation is limited at low temperatures. Therefore, the derived solid acid catalyst has poor catalytic ability due to insufficient acid sites. Conversely, too high a smoldering temperature will make the situation worse also (X. Tang & Niu, 2019).

2.7.2. Effect of Sulfonation Factors

2.7.2.1. Sulfonation Temperature

During the sulfonation process, a reversible exothermic electrophilic substitution reaction occurs, and the position of the sulfonic acid group in the aromatic compound is affected by the sulfonation temperature. The low sulfonation temperature is not conducive to the formation of chemical bonds between the -SO_3H group and the carbonaceous material, so the number of acidic sites on the sulfonated carbon catalyst is insufficient. Likewise, the catalytic capacity of the produced sulfonated carbon catalyst was as low as expected because it lacks acidic sites. Increasing the sulfonation temperature can accelerate the mass transfer between the -SO_3H group donor and the carbonaceous material to enhance the sulfonation process, but an excessively high sulfonation temperature will cause some components to decompose and negatively affect the acid density(Zaizhi Liu et al., 2019). The equal become pronounced that growing the sulfonation temperature reduced the entire acid density of the SCBC because of sulfone aspect reactions that inhibit attachment of sulfonic companies to the carbon sheet (Bureros et al., 2019).

2.7.2.2. Sulfonation Time

In the manufacturing process of the sulfonated carbon catalyst, the proper sulfonation time is very important for grafting the SO_3H group and the carbon material. Of course, in order to complete the sulfonation process, it takes some time to form a chemical bond so that the active sites of the SO_3H group are fully charged on the carbon material carrier. In contrast, the continuous consumption of concentrated sulfuric acid to reduce the reversible sulfonation reaction and the chemical equilibrium gradually reaches. Increasing the sulfonation time significantly enhanced the catalytic ability of the produced carbon-based solid acid catalyst and confirming the strong sulfonation. However, further extension of the sulfonation time has little effect on the catalytic ability. Therefore, it is meaningless to extend the sulfonation time, and the optimal sulfonation time is required(Flores et al., 2019)

2.7.2.3. Solid-Acid (w/v in g of biochar per mL of concentrated H_2SO_4)

It is observed that the ratio in g of biochar per ml of concentrated sulfuric acid, the increase of sulfuric acid influences the biochar sulfonation, since there is a decrease in the acid density values followed by gradual degradation of the biochar Therefore, it can be assumed that this point is close to the saturated state of the functionalization. So the most common in biochar is 1:10-1:30 (w/v)(da Luz Corrêa et al., 2020).

In this regard, heterogeneous acid-based catalysts those are easy to manufacture, inexpensive, non-toxic and reusable without disadvantages are cheaper. Many researchers have used different types of biomass to synthesize carbon-based catalysts, such as bamboo, coffee grounds, de-oiled waste cake, glucose, microalgae pomace, oil palm tree trunks, and bagasse, and have shown their use in biofuels and different chemicals broad prospects in production(Z. E. Tang et al., 2018). Corncob was chosen as the raw material for this study because it is abundantly produced and easily available in Ethiopia. In this study, the sulfonated activated carbon (SAC) catalyst was prepared in three steps, such as Activation, Carbonization and Sulfonation. Phosphoric acid used as activates the corncob, the carbonization of activated corncob and finally, sulfonated with concentrated sulfuric acid. The purpose of this study is the effects of sulfonation temperature, time and the ratio of biochar to sulfuric acid on the density and yield of the SO_3H group on the SAC catalyst were investigated. Numerical optimization was used to determine the optimal conditions for sulfonation

to obtain the highest SO_3H density and yield. The optimal sulfonation catalyst was also used in the synthesis of 5HMF.

2.8. Sulfonation Mechanism of Bio char

Sulfonation is an electrophilic aromatic substitution reaction in which the hydrogen atoms in aromatic hydrocarbons are replaced by functional sulfonic acid groups. It is understood that the process of sulfuric acid sulfonated biochar is shown in the Figure 2.10. below. In the first step, the active ingredient is sulfuric anhydride (SO_3), which acts as an electrophile and is formed by the reversible reaction of H_2SO_4 decomposition. The second step is an intramolecular reaction, in which the carbon structure is a deproteinization process. It is speculated that the chemical bonding of sulfonate to the carbon material can occur through the interaction of SO_3 and the C (sp^2) site on the carbon material, which leads to the formation of C-SO_3H species(H. Shi, 2017).

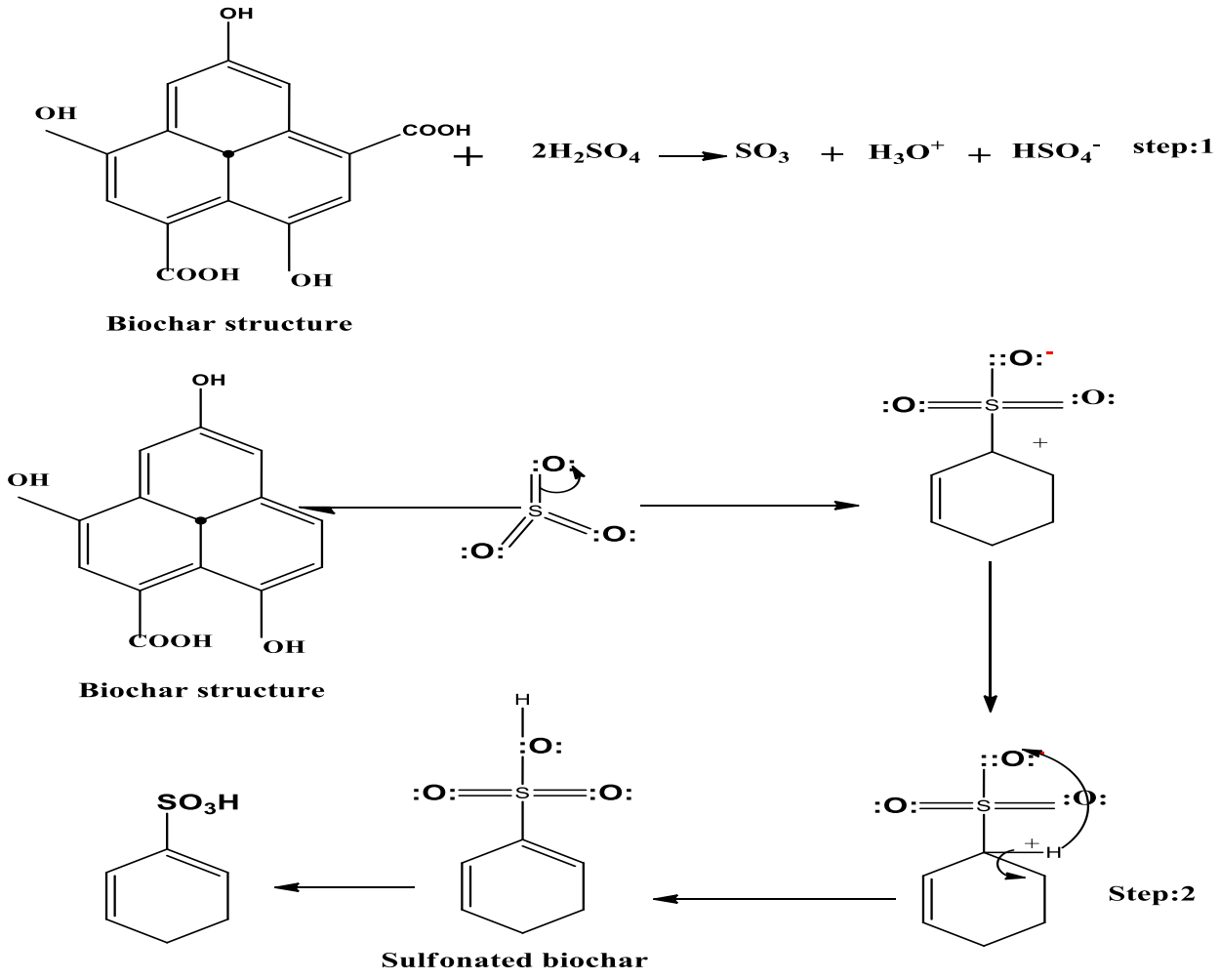

Figure 2.10.Reaction mechanism of sulfonation process(H. Shi, 2017).

2.9. Catalysts and Solvents Used to Synthesize 5-HMF Using Cellulose Substrate

2.9.1. Catalysts

It has been reported that the use of homogeneous mineral acids, Bronsted acids, Lewis's acid metal halides, bifunctional catalysts and recoverable heterogeneous catalysts from monosaccharides and polysaccharides (including pretreated biomass) in pure organic or aqueous solvents has been reported.

2.9.1.1. Brønsted Acid

Brønsted acid an acid that can release protons (hydrogen ions) and promote the hydrolysis of glucan and the dehydration of fructose and glucose, depending on the strength of the acid

2.9.1.1.2. Sulfonated Solid Acids Catalysts

A solid acid catalyst is a type of catalyst that supports acid ions on a solid and transfers proton or accepts electrons in the reaction. They can be roughly divided into the following categories: immobilized liquid acids, oxides and metal salts, natural clay minerals, zeolites, heteropoly acids, cation exchange resins, solid super acids and sulfonated biochar. Among them, bio-based sulfonated acids have many advantages such as easy manufacture, high selectivity, high activity, easy separation, and easy recovery, and are considered to have potential practical value. According to reports, corn stover can be used not only for the synthesis of catalysts, but also as a starting material for one-step conversion to HMF. Through hydrothermal carbonization of corn stalks and then sulfonation with concentrated sulfuric acid, carbonaceous solid acids with SO_3H, COOH, and OH groups were synthesized. This catalyst is used in the production of HMF in ([BMIM] [Cl]). At 150^{o}C, an HMF yield of 44% was reached within 30 minutes. The authors confirmed that the good catalytic activity can be attributed to the OH or COOH groups, which adsorb cellulose molecules, and then the grafted SO_3H groups can hydrolyze the cellulose into glucose. In addition, the OH group facilitates the isomerization of glucose to fructose, which can be further converted to HMF under the catalysis of COOH and SO_3H groups. A possible mechanism for this process has been suggested(Menegazzo et al., 2018).

Other similar alternatives might be sulfonated carbon as a catalyst 40.5 mol% HMF from cellulose in ionic liquid(Hu et al., 2013) and SO_3Hpolymer, e.g., poly-divinylbenzene–SO_3H (PDVB) 34.6–37.1% HMF from cellulose in ionic liquid(Y. Zhang et al., 2015).

2.9.2. Solvents

In addition to the effectiveness of catalysts for high yield and high selectivity in HMF production, solvents also play an important role in increasing the yield of HMF; the purity and ease of separation of make the process economically and ecologically competitive. Solvents can play a variety of roles in the biomass conversion process:

(I) Dissolve substrates and catalysts to carry out the desired reaction;

(II) Stabilize substrates, intermediates and products to improve thermodynamic balance to increase product yield; And

(III) Act as a catalyst to improve reaction kinetics. The performance of commonly used solvents is in summarize below.

2.9.2.1. Polar Aprotic Solvents

This category of solvents has moderate polarity but no acidic hydrogen.

2.9.2.2.1. Biomass-Derived Solvents

Biomass-derived 2-**Methyl tetrahydrofuran (MTHF)** is an emerging green solvent. It is generally synthesized with the aid of using catalytic hydrogenation of furfural. Although its chemical structure is a bit like THF, MTHF has unique physical properties similar to toluene, such as, low solubility in water, high stability, and high boiling point. Conversion of cellulose and glucose to HMF yield was 555–1570 mg /l in biphasic using MTHF/water system with levulinic acid as the catalyst (Seemala et al., 2016).

Gamma-valerolactone (GVL) is another promising candidate from biomass as green solvent. It is made from levulinic acid, that is received from hexoses. Using corn cobs in GVL to prepare 27.1% satisfactory HMF on the acidic polymer catalyst in the pot (L. Zhang et al., 2017) .A two-step conversion protocol could reach a higher yield of 60% HMF from corn stover (Luterbacher et al., 2014).

2.10. Advantages of Biphasic Solvents

Due to the use of high-boiling organic solvents, ionic liquids, or pure water in single-phase solvent systems becomes difficult to separate and purify HMF. So, the current research work on HMF production has targeted the use of two-phase reaction systems in batch or continuous two-phase reactors. The aqueous solution or modified aqueous solution is used as the reaction phase for the catalytic conversion of the starting substrate acid into HMF. The organic layer of the two-phase system is used as the extraction phase for continuous accumulation in the organic phase immediately after HMF is formed in the reaction phase. Therefore, the lower HMF concentration in the water phase limits the rate of side reactions, thereby increasing the yield of HMF. This process allows the reactive aqueous phase containing the used homogeneous or heterogeneous catalyst to be easily separated and reused. The partition coefficient (R) is the ratio of HMF in the organic phase to HMF in the aqueous phase, and is an important parameter that determines the overall effectiveness of the two-phase medium. The higher distribution of HMF in the organic layer improves the effective extraction, thereby increasing the HMF selectivity. In addition to determining the nature of the organic solvent for effective extraction, the presence of inorganic salts, such as NaCl, plays an important role in improving the partition coefficient of HMF in the aqueous phase(Saha & Abu-Omar, 2014). Due to the various advantages of the two-phase reaction system, namely

(I). High HMF yield and selectivity are obtained by preventing unwanted side reactions,

(II). The reaction phase containing the spent catalyst is easy to separate and reusable, and

(III). Inexpensive to separate the desired product from the low boiling point

2.11. Catalyst/Solvent Recycling and HMF Separation

The solid catalyst can be filtered and washed with water and organic solvents such as ethanol, and then dried before use (Morales et al., 2014). In contrast, after the HMF is separated from the system, the soluble catalyst and solvent can be reused directly and catalyst was used up to five runs. After removing HMF with ether as a non-polar solvent, the homogeneous single-phase glucose conversion system water containing $ZrOCl_2$ was repeatedly used to maintain a good HMF yield > 35% (Saha et al., 2013).

The further separation and purification of HMF from the solvent depends on its boiling point and its affinity for HMF. Diethyl ether (35^{o}C), THF (66^{o}C) , 2-MeTHF (80.2^{o}C) and other low boiling point solvents can be vacuum distillation and flash separation at room temperature(Cai et al., 2013) However, medium to high boiling point solvents, including MIBK (118^{o}C) and DMSO (189^{o}C), require more energy-intensive processes (Mushrif et al., 2014).

Various methods including extraction, column/HPLC and activated carbon absorbents have been used to separate and purify HMF. The extraction process usually requires several cycles, which not only consumes a large amount of solvent, but also introduces a large number of impurities was into the organic phase. An isopropanol system for the production of HMF from fructose was recently reported. By reusing the distillation solvent, HMF can be easily separated from the reaction system. It was found that complete removal of the solvent from the original HMF solution is the key to obtaining high-quality HMF. This is done by first using a rotary evaporator to evaporate the isopropanol from the original HMF solution to completely remove the solvent. After the isopropanol evaporates, a thick black liquid is obtained. Then add water to this viscous liquid in the vial. HMF dissolves in water and forms a clear yellow solution. Most contaminants are insoluble and remain at the bottom as black solids(Yi et al., 2014).

CHAPTER THREE

3. METHODOLOGY

3.1. Overall Research Framework

This research was carried out to synthesizes corncob derived heterogeneous acid catalyst for 5-Hydroxymethylfufural (HMF) production. The research methodology of the whole study was summarized as shown in Figure 3.1.

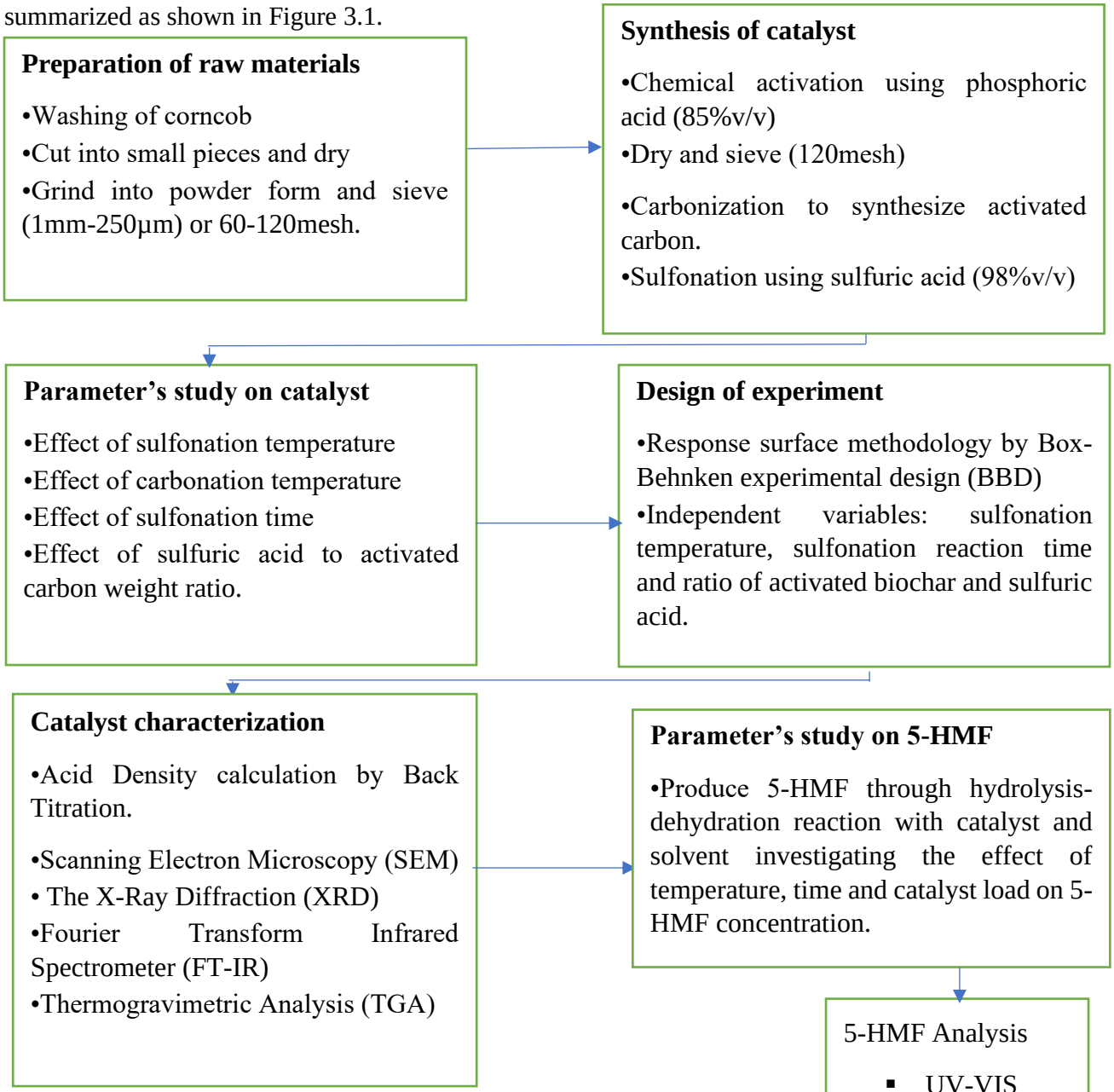

Figure 3.1.Overall flow of research Framework

3.2. Materials and Equipments

3.2.1. Materials and Chemicals

Various types of raw materials, equipment's and chemicals were used so that the experiments can be carried out efficiently. Corncob and microcrystalline cellulose were selected as the raw materials in this study for the synthesis of heterogeneous acid catalyst and 5-HMF respectively.

Materials	Function of Materials
Different size beaker	Were used to contain different volume of distilled water
Analytical balance	Was used to measured different sample weight
Stirring rod	Was used to mix sample
Different sieve	Were used to separate corncob powder in different size
Desiccator	Was used to cool heated sample in muffle furnace
Muffle furnace	Was used to carbonize a given sample of activated corncob
Digital pH meter	Was used to measure a pH of sample
Crucibles	Were used to put a sample for carbonization process
Round bottom flask	Was used to condenser setup in order to chemical reaction takes place
Hotplate magnetic stirrer	Was used to heat distilled water in order to adjust a pH of sample
Autoclave hydrothermal reactor	Sulfonation, hydrolysis and dehydration reaction were proceeded
Rotary evaporator	Was used to separate organic phase and 5-HMF

Chemicals	Function of chemicals
H_2SO_4(98%v/v)	Was used as sulfonating agents
H_3PO_4(85%v/v)	Was used as activating agents
NaOH(99%w/w)	Was used to titration of sulfonic acid density
Phenolphthalein	Was used as indicator for titration of sulfonic acid density
Ethanol(96%v/v)	Was used to wash solid catalyst for recycling
NaCl(99%w/w)	Was used to titration of sulfonic acid density
$NaHCO_3$(99%w/w)	Was used to titration of carboxyl group acid density
2-MTHF	Was used as extractive solvent for 5-HMF production
HCl(37%v/v)	Was used to remove metals and impurities that may block pores and back titration for total acid density.

3.3. Synthesis of Catalyst

3.3.1. Sample Collection and Preparation

Corncob preparation: The corncob was supplied from a local farm around Adama town. The corncob was washed with deionized water 3 times to remove surface contaminants, and dried in the sun for 48 hr to reduce moisture content. Then it was cut into 1cm:1cm and other sizes using knife to facilitate the reduction of the size by ball mill at 350rpm for 30 minutes, and sieving to obtain a powder with a size of about > 60 mesh sieve, and the powder was dried in an oven at 105^{o}C for 12hr until it reaches a moisture content of less than 10% w/w. Finally, in a dry condition the prepared sample was Collected in a plastic bag and used for the next experiment.

Figure 3.2. Row corncob preparation: (A) the raw corncob before size reduction;(B) the cute corncob;(C) the size reduction using ball mill at 350rpm for 30min, (D) the corncob after size reduction below the 60mesh sieved and (E) drying corncob using oven at 105^{o}C for 12hr.

3.3.1.1. Characterization of Feedstock (corncob)

In this section, a proximate analysis of lignocellulosic biomass was determined. The measurement of the moisture content, volatile content, ash content and fixed carbon of raw materials by adjacent analysis is an important factor to understand the properties and characteristics of raw materials. The carbon content of the catalyst support is an important factor in the synthesis of sulfonated biochar-based catalysts.

I. Moisture Content:

Corncob sample was measured and taken in a petri dish. It was dispersed nicely on the petri dish. It was heated at 105^{o}C ± 5for 2hr interval was measured until it becomes constant value. The petri-dish was left open during the heating process. After heating, the petri-dish was cooled in desiccator and measured. Finally, the amount of moisture content present in the sample was calculated using equation 3.1 (ASTM: E 871 – 82).

$$\textbf{Moisture Content}(\%) = \frac{\mathbf{W1-W2}}{\mathbf{M}} * \mathbf{100} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{3.1}$$

Where: W_1; weight of sample and petri dish before drying (gram), W_2; weight of sample and petri dish after drying (gram) and M; weight of sample.

II. Ash Content:

The ash content is an approximate measure of the mineral content and other inorganic matter in biomass. The corncob sample was measured and loaded into a crucible. The sample was heated to 650^{o}C for 4hr in muffle furnace. During this test, the crucible was left open. After the required heating, the crucible was cooled in a desiccator and measured. In this test, the amount of residual

substance was equal to the ash present in the sample and it was calculated as shown in equation 3.2. (ASTM :D 3174 – 02).

$$\textbf{Ash content}\ (\%) = \frac{\mathbf{W2}}{\mathbf{W1}} * \mathbf{100} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \mathbf{3.2}$$

Where: W_1; weight of initial sample before heating (g), W_2; weight of Ash(g).

III. Volatile Matter

The sample was measured and placed in a closed crucible. The temperature of sample was raised slowly up to 600°C in 6 min. After this preliminary heating the sample was heated for exactly 6 min at 950°C. The crucible was cooled in a desiccator and measured. The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample and it was calculated using equation 3.3. and 3.4. (ASTM: D3175 – 07).

$$\boldsymbol{Weight\ loss}(\%) = \frac{\mathbf{W1-W2}}{\mathbf{M}} * \mathbf{100} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{3.3}$$

$$\textbf{Volatile Matter}\ (\%) = \textbf{Weight loss}(\%) - \textbf{Moisture Content}(\%) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. \mathbf{3.4}$$

Where: W_1; weight of dry sample and closed crucible before heating (g), W_2; weight of dry sample and closed crucible after heating (g) and M; weight of sample(g).

IV. Fixed Carbon Content

The fixed carbon content was determined by subtracting the sum of volatile matter content and ash content from 100% by assuming the negligible content of other elements. The value obtained was the amount of fixed carbon present in the sample in percent. The percentage of fixed carbon content in the sample was calculated using equation 3.5 the.

$$\textbf{Fixed Carbon Content}(\%) = \mathbf{100}\% - (\mathbf{Vm}\% - \mathbf{Ac}\%) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{3.5}$$

Where, FC is fixed carbon, Vm (%) was volatile matter and Ac (%) was ash content.

3.3.2. Preparation of Activated Biochar

Accurately weighed 50g of corncob sample was soaked in 85% v/v concentrated phosphoric acid, by the desired impregnation ratio (IR) 1:1(mass of dried H_3PO_4/mass of crushed corncobs) (g/g). 150ml of distilled water was added to the corncob/acid slurry until the corncob is completely covered to ensure complete contact between the acid and the corncob. The mixing was kept at room temperature, and the soaking time is around 5 hr. The sample was covered with aluminum

foil. Finally, the resulting mixture was dried using a hot oven dryer at 120^{o}C for 12 hr. Activated corncob was used as a raw material for the production of biochar through carbonization. The active corn cob with higher retention rate (> 60 mesh sieve) was carbonized further in the muffle furnace. The carbonization temperature was selected by carbonizing the sample at different temperature such as 400^{o}C,450^{o}C and 500^{o}C for a fixed time of 8hr.The best carbonization temperature was selected by evaluating acid density after sulfonation. The carbonized sample was soaked in 200 ml of 0.1 M HCl and boiled at 80^{o}C, and stirred continuously for at least 1 hour in a magnetic stirrer to remove metals and impurities that may block pores. The tar formed during the carbonization process was also separated. The AC sample was further washed with hot deionized water at (80^{o}C) until it reached a neutral pH of 6-7. Finally, the sample was dried in an oven at 110^{o}C for 1 hr.

Figure 3.3. Activation of corncob: (A) powder of corncob soaked by 85%v/v of phosphoric acid before oven dry;(B) oven drying at 120^{o}C for 12hr and (C) the soaked corncob powder after oven dry.

Figure 3.4.Activated corncob carbonization: (A) Activated corncob before carbonization;(B) Carbonization at 450^{o}C for 8hr;(C) Rinsing process for removal of some impurity and clog at 80^{o}C for 1hr;(D) Vacuum pump for filtration solid from liquid ;(E) Oven dry at 110^{o}C for 1hr moisture removal from biochar and (F) Biochar valorization using mortar and pestle below.

3.3.3. Functionalization of Activated Biochar Using Sulfuric Acid

Concentrated sulfuric acid (98%v/v) H_2SO_4 was used to functionalize the produced activated biochar which implies a sulfonic acid group was introduced into the bio char carrier. For the sulfonation process, the ratio of sulfuric acid (H_2SO_4) to biochar varies from (25:1 to 3:1ml/g). The sulfonation reaction was carried out in a polytetrafluoroethylene autoclave reactor and a hot oven system to heat the required the sulfonation temperature range is 80-200^{o}C and sulfonation time (12-19 hr.). After the reaction, the sample was cooled to room temperature, and then slowly transferred to a beaker containing 1 liter of deionized water. The mixture was cooled and separated by vacuum filtration. The solid residue is washed with hot (>80^{o}C) deionized water until the pH of the wash water is equal to the pH of the initial deionized water. The washed sample was dried at 110^{o}C for 1 hr to obtain a sulfonated carbon-based catalyst.

Figure 3.5.Sulfonation of carbonized bio char. (A) Sulfonation reaction takes place in the autoclave ;(B) The vacuum pump filtration for separation of reaction mixture(solid-liquid) ;(C) Drying oven at 110^{o}C for 1hr for removal of moisture from sulfonated biochar and (D) Final product of sulfonated biochar.

3.3.4. Experimental Design for Sulfonated Biochar Synthesis

During the synthesis process, there are several parameters that affect the sulfonic acid density. The conventional method of testing one variable at a time is time consuming and laborious. Box

Behnken Experimental Design (BBD) is one of the reactive surface methods used to find the best synthesis conditions to achieve the highest density of sulfonic acid groups. The Box Behnken Experimental Design (BBD) is superior to the usual central composite design because it has the advantage of avoiding extreme processing combinations. Response surface methods are used to evaluate the impact of sulfonation parameters. According to Table 3.1, the sulfonation temperature, sulfonation time and the ratio of sulfuric acid to biochar were selected as the main factors affecting the sulfonation process. In order to achieve the best synthesis conditions for the highest sulfonic acid density (SO_3H), the Box Behnken experimental design (BBD) was applied, which contain three variables, three levels and 17 experimental runs with 5 replication of center point, as shown in Table 3.2.(Rashid et al., 2011). The number of experiments was determined according to equation 3.6:

$$N=K^2+K+C \quad \text{.....3.6}$$

Where N is experimental runs, K is the variables number and C is the center point.

Table:3.1. Experimental domain with natural and coded values of independent variables used in Box-Behnken design (BBD).

Factors	Symbol	Coded variable level		
		Level 1	Level 2	Level 3
		-1	0	+1
Temperature(^oC)	A	80	140	200
Time(hr.)	B	12	15.5	19
Ratio of biochar with acid(ml/g)	C	3	14	25

Table:3.2.Experimental Run sheet for Box-Behnken design.

Parameter	Run 1	Run 2	Run 10
Temperature(^oC)	140	200	140
Time(hr)	15.5	15.5	15.5
Ratio(ml/g)	14	3	14
SO_3H and Nt			
	Run 4	Run 8	Run 9
Temperature	140	140	200
Time	19	19	19
Ratio	25	3	14
SO_3H and Nt			
	Run 12	Run 6	Run 11
Temperature	80	80	80
Time	19	15.5	15.5
Ratio	14	25	3
SO_3H and Nt			
	Run 13	Run 14	Run 17
Temperature	140	140	140
Time	15.5	15.5	15.5
Ratio	14	14	14
SO_3H and Nt			
	Run 16	Run 5	Run 7
Temperature	200	140	200
Time	15.5	12	12
Ratio	25	3	14
SO_3H and Nt			
	Run 15	Run 3	
Temperature	80	140	
Time	12	12	
Ratio	14	25	

3.3.5. Catalyst Characterization

The prepared catalyst was characterized by titration method, TGA, XRD, FTIR, and SEM.

3.3.5.1. Acid Group Titration Analysis

The titration method used to determine the SO_3H group density and total acid group density. In the sulfonated corncob biochar catalyst was developed based on earlier work to select the best catalyst from the sulfonation step.

The **density of SO_3H groups** was determined by sonicating a mixture of 0.1g catalyst in 15ml NaCl solution (0.05M) in an ultrasonic bath at room temperature for 1hr. After sonication, a centrifuge at 5000rpm was used to separate the solids. The solids were then separated using Whatman filter paper from supernatant. The supernatant was mixed and titrated with 0.05N NaOH solution using phenolphthalein as the indicator and the titration was continued until the equivalent point colorless to pink is renowned. Every sulfonic group acid density (SO_3H) was the average value of three parallel titration experiments. The SO_3H group density amount in mmol/g was calculated using formula:

$$\mathbf{SO3H}\left(\frac{\mathbf{mmol}}{\mathbf{g}}\right) = \frac{\mathbf{volume\ of NaOH\ used\ for\ the\ titration} * \mathbf{Normality\ of\ NaOH}}{\mathbf{Mass\ of\ catalyst}} \ldots\ldots\ldots\ldots\ldots\ldots \mathbf{3.7}$$

For total acid group density, 0.1g of catalyst dissolved in 15ml of 0.05M NaOH solution was added in an ultrasonic bath at room temperature for 1hr. After sonication, the solids were separated using a centrifuge at 5000rpm. The solids were then separated using Whatman filter paper. After mixing the separated supernatant, using phenolphthalein as an indicator, back titration with 0.05M HCl solution until the equivalent point pink to colorless is recognized. The samples were tested in triplicate and the mean values were taken. This analysis combines all the acid groups carboxylic (-COOH), hydroxyl (-OH) and the sulfonic (-SO_3H) groups the total acid density in mmol/g (denoted as Nt) was calculated using the following formula:

$$\mathbf{Nt}\left(\frac{\mathbf{mmol}}{\mathbf{g}}\right) = \frac{(\mathbf{volume\ NaOH} * \mathbf{Normality\ of\ NaOH} - \mathbf{volume\ of\ HCl} * \mathbf{Normality\ of\ HCl})}{\mathbf{Mass\ of\ the\ catalyst}} \ldots\ldots\ldots\ldots \mathbf{3.8}$$

3.3.5.2. Thermogravimetric Analysis (TGA) Analysis

The thermal stability of the raw corncob, activated biochar and sulfonated biochar -based catalyst was analyzed using thermogravimetric analyzer (TGA) equipped with detector (DTG-60H) at a constant heating rate of 20℃/m within the temperature range of 30 to 830℃ under the nitrogen atmosphere to remove all the corrosive gas and avoid thermal oxidative degradation.

3.3.5.3. X-Ray Diffraction (XRD) Analysis

X-ray diffraction was used to represent crystallinity information of raw corncob, biochar and the sulfonated biochar-based catalyst using X-ray diffraction (XRD) analysis of Shimadzu, Japan diffractometer model XRD-7000 with scanning range of theta from 5° to 90° at scanning range of 4°/min.

3.3.5.4. Fourier Transform Infrared (FTIR) Analysis

In order to investigate the presence of functional groups in the raw corncob, activated biochar and optimized sulfonated biochar-based catalyst, the Fourier Transform Infrared (FTIR) in the range of 4000-400 cm^{-1} was used.

3.3.5.5. Scanning Electron Microscopy (SEM) Analysis

The surface morphology of selected raw corncob, activated biochar and sulfonated biochar catalyst were analyzed using JEOL scanning electron microscope.

3.4. Synthesis, Separation, and Characterization of 5-HMF

3.4.1. Synthesis of 5-HMF

The catalytic microcrystalline cellulose hydrolysis-dehydration experiment was carried out batch wise in the autoclave batch reactor in the heating oven system. In a typical experiment, 1.0 g of microcrystalline cellulose, NaCl (4wt%) and 2-MTHF / H_2O (4:1v/v) are loaded into the reactor. The detailed reaction conditions carried out in the following reaction condition: the reaction temperature was 160-200^oC, the residence time was 1 to 5hr and the catalyst loading ranges from 0-0.4g. After the reaction was completed, the reactor was quenched to room temperature and the reaction mixture showed two phases: the upper layer was a 2-MTHF layer containing HMF and the lower layer was unreacted cellulose and catalyst. The catalyst is separated from the reaction mixture by filtration. Liquid samples containing aqueous and organic phases were collected for analysis. Sample product was centrifuge, filtered and measured the concentration of 5-HMF in the liquid product by UV-Vs technology. In particular, the UV-Vs of the sample solution showed clear peaks at 284nm and 276nm for 5-hydroxymethylfurfural (HMF) and furfural (FF) respectively. The absorbance of the solution is directly proportional to the concentration of 5-HMF. Therefore, UV-VIS spectrophotometry was chosen to study the appropriate conditions, such as the influence of temperature, time and catalyst loading on the formation of HMF.

Figure 3.6.Autoclave reactor in oven heating system for 5-HMF synthesis.

$$\textbf{Microcrystalline cellulose conversion}(\%) = \frac{\mathbf{M1-M2}}{\mathbf{M1}} * \mathbf{100} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{3.9}$$

Where M_1(g); the initial mass of microcrystalline cellulose and catalyst

M_2(g); the left over the reaction complete.

A correlation between HMF mass ratio and the maximum absorption wavelength was formulated as follows.

$$\mathbf{W} = \frac{\boldsymbol{\lambda} - \mathbf{276.65}}{\mathbf{7.48602}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{3.10}$$

Where λ was the absorption wavelength.

The total concentration of the mixture can be determined by following equation.

$$\mathbf{C} = \frac{\mathbf{A-C}}{\mathbf{K}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{3.11}$$

The individual HMF concentrations can be calculated as mg/l by following equations.

$$\mathbf{C} = \mathbf{WDC} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{3.12}$$

Where C was the concentration, W was the mass ratio of 5-HMF and D was dilution factor. Total concentration (C) equation 3.11 was calibrated from previous work(Paper, 2017).

Table:3.3. Effect of operating condition for 5-HMF synthesis.

Parameters	Run 1	Run 2	Run 3
Temperature(^{o}C)	160	170	180
Time(hr.)	3	3	3
Catalyst load(g)	0.2	0.2	0.2
Cellulose conversion&5-HMF concentration			
	Run 4	Run 5	Run 6

Temperature	190	200	190
Time	3	3	1
Catalyst load	0.2	0.2	0.2
Cellulose conversion&5-HMF concentration			
	Run 7	Run 8	Run 9
Temperature	190	190	190
Time	2	3	4
Catalyst load	0.2	0.2	0.2
Cellulose conversion&5-HMF concentration			
	Run 10	Run 11	Run 12
Temperature	190	190	190
Time	5	4	4
Catalyst load	0.2	0	0.1
Cellulose conversion&5-HMF concentration			
	Run 13	Run 14	Run 15
Temperature	190	190	190
Time	4	4	4
Catalyst load	0.2	0.3	0.4
Cellulose conversion5-HMF concentration			

3.4.2. Separation of 5-Hydroxymethylfurfural (HMF)

Solid residue such as solid acid catalyst, unreacted cellulose and other remain was separated by using vacuum pump using Whatman filter paper from 5-HMF solution. Finally, the aqueous and organic phase such as 2-MeTHF and water that contain 5-HMF solution was separated using rotary evaporator with the boiling point difference at 90^{o}C for 1hour.

Figure 3.7. 5-HMF layers separated by using a rotary evaporator.

3.4.3. Analytical Techniques of 5 HMF

3.4.3.1. UV -VIS Spectroscopic Analysis

In this work, a UV-VIS spectroscopic method was used for determination of HMF concentration. The present method was simple, rapid, and accurate. The absorption spectrum for each solution was measured at wavelength of 284 nm.

3.4.3.2. Fourier Transform Infrared (FT-IR)

In order to investigate the presence of functional groups in the 5-hydroxymethylfufural (HMF), the Fourier Transform Infrared (FTIR) was used in the range of 4000-400 cm^{-1} was used

3.4.3.3. High Performance Liquid Chromatography (HPLC)

The standards and samples of 5-HMF were analyzed by HPLC with column length (4.6mmx150mm,5µm) and it was used UV detector with wave length of 285nm. The mobile phase was a mixture of water-methanol (90:10 v/v) and stationary phase was zorbax SB CAT. Finally, filtered through a 0.4µm filter and delivered at a flow rate of 0.5ml/min, running time and temperature were 30min and 25^{o}C respectively.

CHAPTER FOUR

4.RESULTS AND DISCUSSIONS

This chapter contains the results of all laboratory activities, such as characterization of raw corn cob (proximate analysis, sample moisture percentage, volatile component content, ash content and fixed carbon content, as well as catalyst synthesis in different carbonization temperature). It also includes various analyses and studies on the optimization of the operating parameters in the synthesis of catalysts that affect the sulfonation of biochar using Design Expert®11.0 software. The characterization results of the optimized sulfonated biochar catalyst were also discussed in this section. This optimized sulfonated biochar catalyst characterized using TGA, XRD, FTIR and SEM. In addition, various analyses and studies on the important operating parameters that affect the concentration of 5HMF were presented. The characterization of product sample(5HMF) using of UV-VIS, FTIR and HPLC were discussed in this section.

4.1. Characterization of Raw Corncob

4.1.1. Proximate Analysis of The Raw Corncob

The raw corncob used in this study was brought from the nearby area and had the following composition from three repeated analyses: 5.67% moisture content, 83.3% volatile matter, 4.63% ash content, and 12.37% solids carbon% w/w (dry weight) basis. On a dry basis, the percentage of fixed carbon content is estimated by the difference as follows: FC (%) = 100%- (% Vm + %Ac)(Bureros et al., 2019). The raw corncob delivered had a moisture content of about 5.67%, which is well accepted value for production of biochar(Anukam et al., 2017). The moisture content affects the heat transfer during the carbonation process by having a significant impact on the product distribution. In addition, an increase in the moisture content increases the pyrolysis reaction temperature. The literature showed that when the moisture content increased the yield of liquid product also increased, while the yield of biochar and gas reduced. In most cases, a moisture content of less than 10% is suitable for achieving high yields of biochar. Therefore, the moisture content of the physically pretreated raw corn cob in this study is 5.67%, which is reasonable for biochar yield (Jahirul et al., 2012).

The volatile content of the corn cob sample is 83.3%, which is in agreement with the previous studies(Anukam et al., 2017). The higher the content of volatiles implies the longer devolatilization time and ensure effective carbonation product quality. However, biomass with higher volatile content produces many porous materials that are used to graft sulfonate groups during the sulfonation step. In addition, the fixed carbon and ash content decreases with an increase of volatile content.

The fixed carbon content of raw corncob obtained in this study was12.37% relatively higher than some other biomasses used in the previous study(Shariff et al., 2016). In the synthesis of solid acid catalysts from biomass, the fixed carbon (FC) content of the catalyst is taken an important factor. The fixed carbon content of other biomass residues studied as the raw material for the synthesis of solid acid catalysts (9.53-35.2%). The obvious analysis results of corncob, compared with other biomass residues, have carbon content (12.37%), which is sufficient to develop a carbonaceous carrier and provide a selection of precursor materials, which are added in the process for sulfonate group and Sulfonation is suitable for attachment of sulfonate group during sulfonation(Hirano et al., 1998).

Biomass ash content is classified as low ($<5\%$), medium ($5-10\%$) and high ($>10\%$)(Stella Mary et al., 2016). Based on this classification, the raw corncob considered in this study has a low ash content (4.63%) in contrast with other earlier study which is in the high range (Várhegyi et al., 2006). This could minimize the impact of inorganic impurities in the carbonation process. The ash content of biomass mainly contains minerals such as silica, alumina, iron, magnesium, calcium and mineral salts. These mineral salts are considered as impurities that block pores. Part of the concentrated sulfuric acid is consumed due to the reaction of inorganic salts with concentrated sulfuric acid. This reduction of concentrated sulfuric acid concentration is not conducive to the secondary sulfonation of aromatics. Therefore, based on the above analysis the proximate analysis results of corncobs imply corncob as a suitable biomass for the synthesis of solid catalysts in this work.

4.1.2. The Effect of Carbonization Temperature on the Biochar-Based Catalyst

4.1.2.1. Acid Group Titration of Catalyst Analysis

Acid density analysis was determined by direct titration and back titration. The sulfonic acid (-SO_3H) and total acid groups were affected by different carbonization temperatures such as 400^oC, 450℃ and 500℃.The carbonized biochar were evaluated under fixed time and sulfonation parameters(Jiang et al., 2020). 8hr was selected for carbonization time due to better yield of acid density from previous works (Hussain & Kumar, 2018) and also from proximate analysis data corncob showed high volatile matter so it requires long time to devolatilize the corncob. It can be seen from Table 4.1 that the acid density values of sulfonic acid groups are different at different carbonization temperatures. However, after sulfonation, the sulfonic acid and total acid density were founded to be 1.93 mmol/g and 4.64 mmol/g total acid density, respectively at temperature of 450^oC. This result showed that the effective sulfonation (chemically grafted the sulfonic acid group (SO_3H) and the total acid density of biochar was observed at 450^oC as compared to other temperature range.

Table 4.1.Acid values of solid acid catalyst at different carbonization temperatures.

Carbonization temperature(^oC)	Total acid density (Nt)(mmol/g)	Sulfonic group acid density (SO_3H) (mmol/g)
400	4.553	0.576
450	4.64	1.93
500	4.029	1.035

4.2. Statistical Analysis on Variables that Affects Sulfonation Process

Table 4.2.Box-Behnken design matrix for catalyst synthesis experimental and predicted value.

Run	Factor 1 Temperature(°C)	Factor 2 Time (hr.)	Factor 3 Ratio (ml/g)	Response 1 (Experimental value)	Response (Prediction value)
1	140	15.5	14	1.14	1.23
2	200	19	14	1.17	1.15
3	200	15.5	25	1.12	1.12
4	80	15.5	25	0.76	0.7647
5	140	15.5	14	1.17	1.23
6	140	15.5	14	1.26	1.23
7	140	12	3	0.7	0.6785
8	200	12	14	0.875	0.9012
9	80	15.5	3	1	0.9998
10	80	19	14	1.03	1.00
11	140	15.5	14	1.24	1.23
12	140	19	3	1.11	1.14
13	200	15.5	3	1	0.9952
14	80	12	14	0.673	0.6947
15	140	12	25	0.83	0.8035
16	140	15.5	14	1.34	1.23
17	140	19	25	0.88	0.9015

As shown from Table 4.2. the maximum sulfonic acid group density is 1.34 mmol/g at the sulfonation temperature of 140℃, sulfonation time 15.5 hr and the ratio of sulfuric acid to biochar are 14:1ml/g, whereas the minimum sulfonic group density 0.673mmol/g was observed at the sulfonation temperature of 80°C, sulfonation time 12 hr and sulfuric acid to biochar ratio14:1ml/g. More specifically, it was observed that the experimental value of the sulfonic acid group density changes from 0.673mmol/g to 1.34 mmol/g. The second order polynomial equation that correlates the response (i.e., sulfonic group density) to the independent sulfonation process parameters. The predicted second order polynomial equation in terms of the coded factors is illustrated in equation (4.1).

Sulfonic group acid density (mmol/g) = $1.23 + 0.0878A + 0.1390B + 0.09AC – 0.09BC – 0.0935A^2 - 0.1835B^2 – 0.1505C^2$ ……... ……(4.1)

Where A; Sulfonation temperature

B; Sulfonation time and C; Ratio of sulfuric acid to biochar

4.2.1 Model Adequacy for Sulfonated Biochar -Based Catalyst Synthesis

For adequacy analysis model was tasted by variance (ANOVA). Normally, three types of tests namely, significant of terms, regression model and lack of fit (Table 4.3.) were used to evaluate the significance and reliability of the model.

Table 4.3.ANOVA Analysis results for response surface quadratic model

Source	Sum of squares	DF	Mean square	F-value	p-value	
Model	0.6243	9	0.0694	16.46	0.0006	significant
A-temperature	0.0616	1	0.0616	14.62	0.0065	
B-time	0.1546	1	0.1546	36.68	0.0005	
C-ratio	0.0060	1	0.0060	1.44	0.2698	
AB	0.0010	1	0.0010	0.2280	0.6475	
AC	0.0324	1	0.0324	7.69	0.0276	
BC	0.0324	1	0.0324	7.69	0.0276	
A^2	0.0434	1	0.0368	10.29	0.0149	
B^2	0.1544	1	0.1544	36.64	0.0005	
C^2	0.1058	1	0.1058	25.10	0.00015	
Residual	0.0295	7	0.0042			
Lack of fit	0.0047	3	0.0016	0.2526	0.8563	Not significant
Pure error	0.0248	4	0.0062			
Cor total	0.6538	16				

The analysis results of ANOVA presented in Table 4.3 were used to study the effect of individual and interaction of the sulfonating parameters on response variable (sulfonic group acid density) as well as the significance and fitness by quadratic model. The model was significant and confirmed by the p-value of less than 0.0006 and higher F-value of 16.46.

The sulfonation condition in this study are shown in Table 4.3 a value of P value less than 0.05 indicates that the model term is significant. In this case, A, B, AC, BC, A^2, B^2, and C^2 are important model items. Values higher than 0.1000 indicate that the model term is not significant. This showed the reaction temperature, the reaction time, the interaction between the reaction temperature and the ratio of sulfuric acid to biochar, the interaction between the reaction time and the ratio of sulfuric acid to biochar, the square of the reaction temperature, the square of the reaction time and square ratio of square sulfuric acid on biochar affects sulfonic acid groups.

The model F-value of was 16.46 implies the model is significant. There is only 0.01% chance that an F-value this large could occur due to noise. The high F-value was indicated stronger influence of parameters on response. The individual sulfonating parameters that have influenced the sulfonic group acid density of sulfonated biochar catalyst were in the order of > Temperature(℃) > time (h) > ratio of sulfuric acid to biochar (ml/g).

Table 4.4. Model adequacy measures for sulfonic group acid density

R^2	0.9549
Adjusted R^2	0.8969
Predicted R^2	0.8258
Adeq precision	11.0769

As it was shown from the above Table 4.4 the values of R-square, adjusted R square, predicted R squared and Adeq precision have a value of 0.9549, 0.8969, 0.8258and 11.0769 respectively.

The predicted R square of 0.8258 is in reasonable agreement with the adjusted R square of 0.8969; i.e., the difference is < 0.2. The difference between adjusted R square and predicted R square is 0.0711(i.e., they are close to each other) and this indicates the close fit of the model to the actual response data. In addition to this, the value of R-squared for the developed correlation is 0.9549; this indicates 95.49% of the total variation in the sulfonic group acid density is the success to the experimental studies. Adeq Precision measures the signal to noise ratio, and when the ratio is greater than 4, it is desirable. Therefore, in this study, the ratio of 11.0769 indicates an adequate signal and this model can be used to navigate the design space.

The graph of the predicted values obtained using the developed correlation versus actual values is shown in the Figure 4.1. The results in in Figure 4.1 demonstrated that the regression model equation provided by accurate description of the experimental studies, in which all the points are very near to the line of the perfect fit. This result indicates that it was successful in capturing the correlation between the three independent sulfonation process variables (sulfonation temperature, sulfonation time and ratio of sulfuric acid to biochar) to the response.

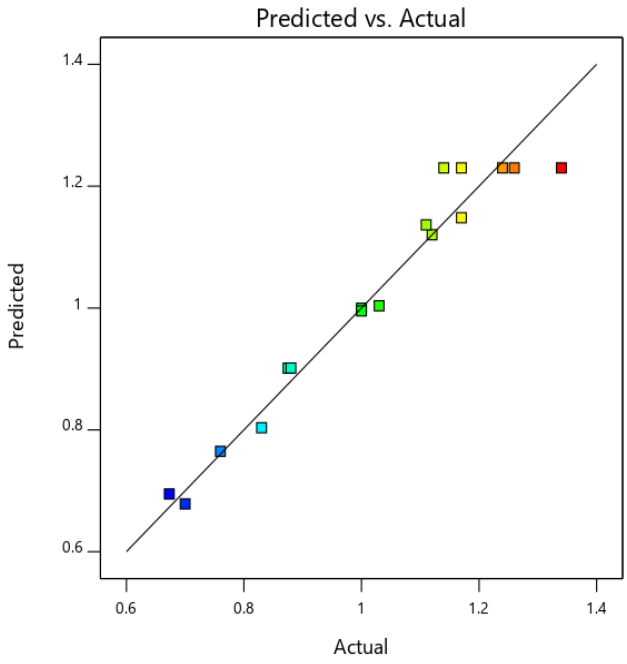

Figure 4.1.The predicted versus actual sulfonic group acidity on sulfonated biochar-based catalyst synthesis

4.2.2. Effects of Experimental Variables on Sulfonated Group Acid Density

Based on the analysis of variance, the sulfonic acid density is significantly affected by various interactions between the sulfonation process variables. In addition to the interaction effect, sulfonation temperature A and reaction time B are important individual experimental variables that affect the SO_3H group.

4.2.2.1. Effect of Individual Sulfonation Variables

Figure 4.2. showed that compared with high sulfonation temperature, the highest sulfonic acid density (SO_3H) is obtained between high (200^oC) and medium (140℃) sulfonation temperature. This implies that the sulfonation temperature has a characteristic effect on the sulfonic acid density of the synthesis catalyst. The lower sulfonation temperature promotes the addition of sulfonic acid groups to the biochar, resulting in a higher density of sulfonic acid groups. However, it has been found that the sulfonation temperature below 100^oC is not sufficient to promote the formation of chemical bonds (interactions) between the sulfonating agent and the biochar, resulting in a decrease in the sulfonation rate, so the amount of sulfonic acid groups produced (SO_3H) catalyst is insufficient. An increase of the sulfonation temperature can promote the mass transfer between the sulfonating agent and the biochar, and promote the addition of sulfonic acid groups to the biochar, resulting in higher sulfonic acid density, but further increment of sulfonation temperature decompose some compounds and negatively affects sulfonic acid. Further increase of the sulfonation temperature in Figure 4.2. above 140^oC has a negative effect on the acid density of the sulfonic acid (SO_3H) of the sulfonated plant carbon-based catalyst. This is related to the destruction of the porous structure of biochar and side reactions such as condensation, oxidation or dehydration under high-temperature sulfonation conditions. This is consistent with other sulfonation processes used in other similar studies in the 80-200^oC temperature range(Xiao & Hill, 2020)

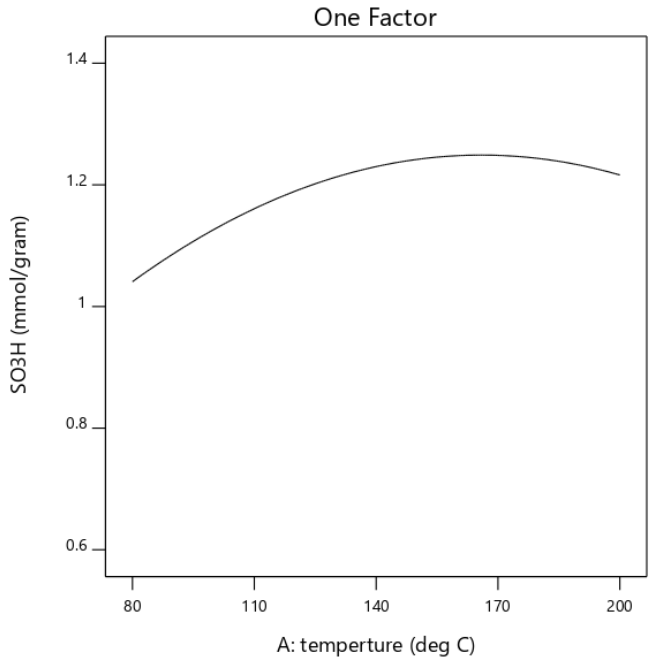

Figure 4.2. Effect of sulfonation temperature on the sulfonic acid group.

Figure 4.3. showed that the reaction time affects the density of sulfonic acid. The proper sulfonation time is very important for connecting the -SO_3H group and the carbon material during synthesis of the sulfonated carbon catalyst. Of course, in order to complete the sulfonation process, it takes some time to form the chemical bond (the active site of the SO_3H group is fully charged on the carbon material carrier). In contrast, the continuous consumption of concentrated sulfuric acid reduces the reversible sulfonation reaction and the chemical equilibrium gradually reached. However, due to the reversible reaction of the sulfonation process, in Figure 4.3. the density of SO_3H decreases as the reaction time was further extended beyond 15.5hr because of the aforementioned side reactions such as poly sulfonation and sulfone formation are likely to occur, thus reducing the incorporation amount of the sulfonic acid groups(N. Li et al., 2019).

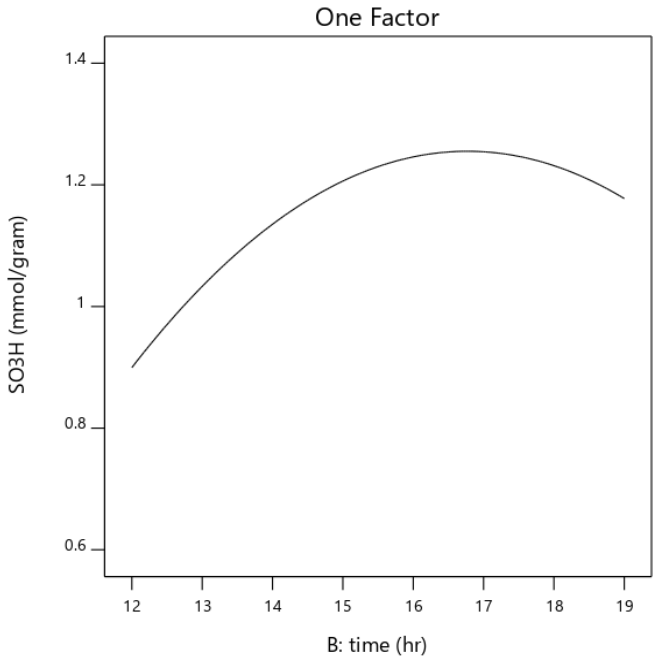

Figure 4.3. Effect of reaction time on the sulfonic group acid density

4.2.2.2. Effect of Interaction Between Sulfonation Process Parameters

The most common way to summarize the results of interactions between process variables in design experiments is to use the response surface plots and response contour plots. It was found that the sulfonation parameters have a significant interaction, except for sulfonation temperature and sulfonation time. Figure 4.4. and Figure 4.5. showed the 3D surface plot interaction of reaction temperature and ratio of sulfuric acid to biochar and reaction time and ratio of sulfuric acid to biochar respectively. The response surface method is used to optimize the sulfonic acid density and understand the interaction of sulfonation parameters that affect the sulfonic acid density. Figure 4.4. and Figure 4.5. showed the surface plots between the sulfonation process variable and the fixed parameter dependent variable (sulfonic acid density).

It can be seen from Figure 4.4. that the amount of sulfonic acid density increases with the increase of sulfonation temperature until it reaches the optimal point, which is almost the middle level of the ratio of sulfuric acid to biochar after this midpoint the sulfonation group decrease.

Figure 4.5. also showed the interaction effect of sulfonation time and the ratio of sulfuric acid to biochar on the density of sulfonic acid groups. Relatively low density of the sulfonic acid was observed due to longer sulfonation time and below the midpoint ratio of sulfuric acid to bio char.

This may be due to the subsequent degradation of the carbonized material, destroying the porous structure of the biochar, thereby reducing the grafting of the sulfonating agent on the surface of the bio char.

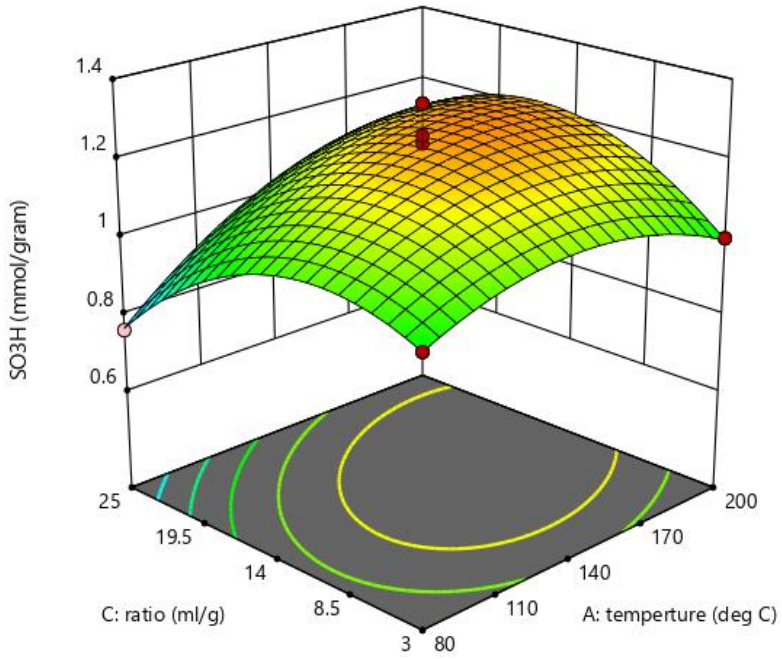

Figure 4.4. Response surface plot of the interaction of sulfonation temperature and ratio of sulfuric acid to biochar versus sulfonic group acid density.

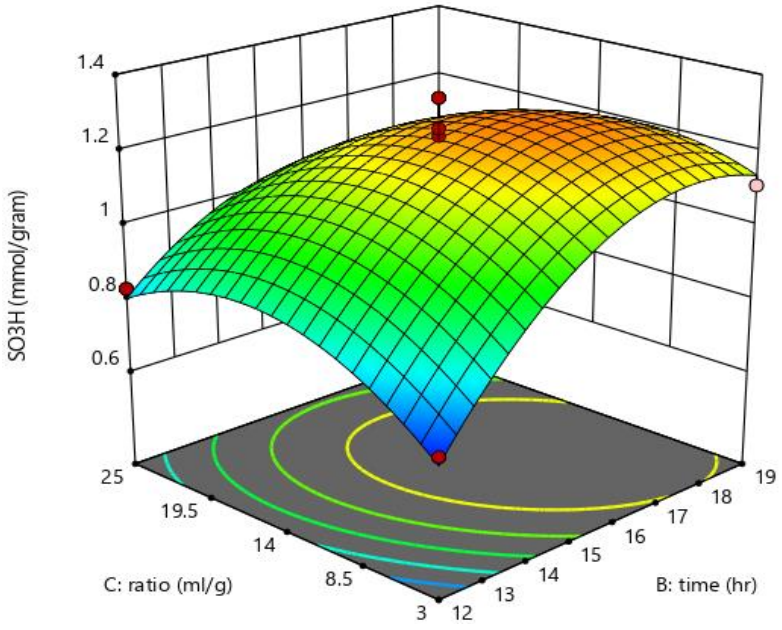

Figure 4.5. Response surface plot of interaction effect of sulfonation time and ratio of sulfuric acid to biochar ratio versus sulfonic group acid density.

It was shown in below both figure the significant degree of interaction between the fixed parameter sulfonation process parameters and the dependent variable (sulfonic acid density) in the contour plot. The significance of the interaction between the pair of process variables can be expressed as the ellipticity of the contour map. The rounded contour plot shows that the interaction has less effect. As shown in Figure 4.6. and Figure 4.7. the contour plot of the interaction of the two factors is elliptical, indicating that the interaction of the two factors is significant. It showed an elliptical contour map, while the contour map in Figure 4.7 has a smaller ellipticity. This statement is consistent with the p-values of BC-interaction and AC-interaction obtained in Table 4.3. of Analysis of Variance

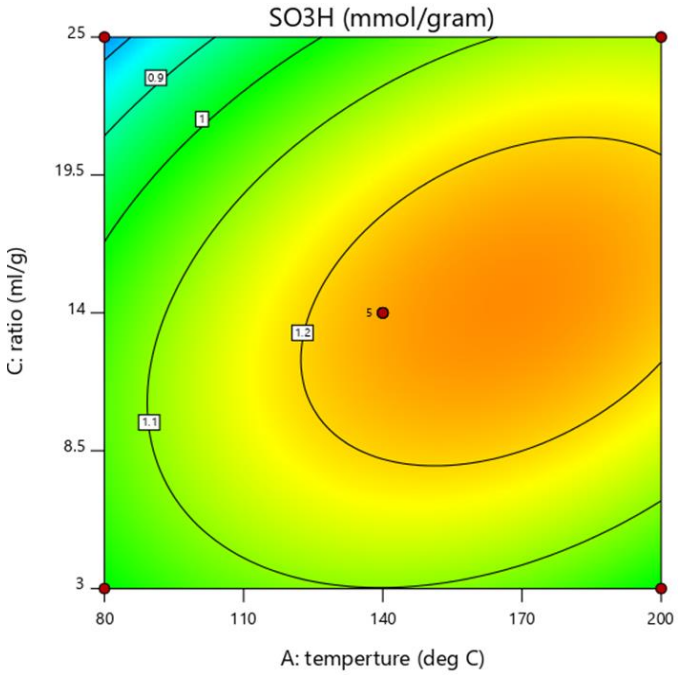

Figure 4.6. Contour plot of sulfonation temperature and ratio of sulfuric acid to biochar versus sulfonic group acid density.

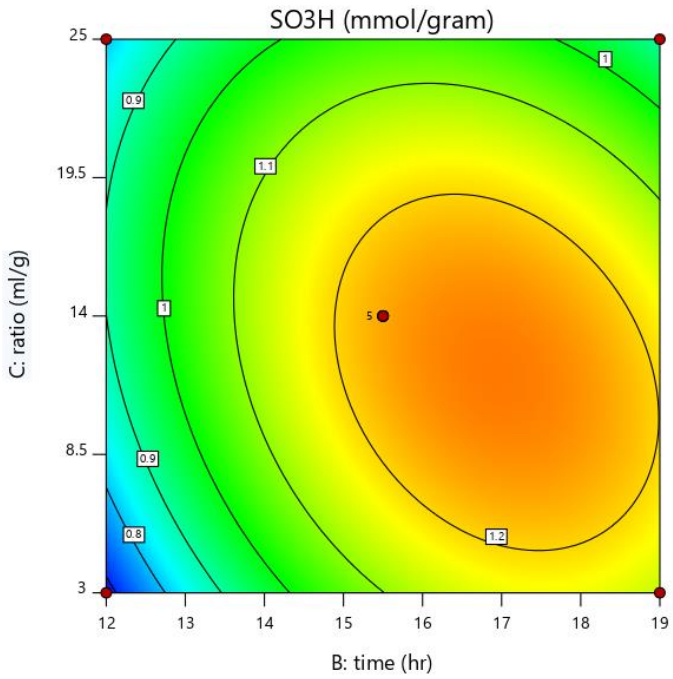

Figure 4.7. Contour plot of sulfonation time and ratio of sulfuric acid to biochar versus sulfonic group acid density.

4.2.3. Optimization of Sulfonation Process Variables

The above results indicate that the interaction between the three sulfonation parameters and independent process variables affects the sulfonic acid (SO_3H) group density. The optimal conditions selected are based on the maximum sulfonic acid (SO_3H) group density obtained. Therefore, the predicted combination of sulfonation process parameters to maximize the acid density of sulfonic acid groups was: sulfonation temperature 161.9^oC, sulfonation time 16.78 hr, and the ratio of sulfuric acid to biochar 13.03:1. Under this condition the predicted amount of sulfonic group acid density was 1.27mmol/g. In order to validate the optimum condition predicted by the model, triplicate experiments were conducted and the average value of 1.267mmol/g was obtained, which was in good agreement with the software prediction.

4.3. Characterization of Optimized Sulfonated Biochar Based Catalyst

4.3.1. Acid Group Titration of Catalyst

Acid density analysis was measured by direct titration and back titration to evaluate the sulfonic acid (-SO_3H) and the maximum sulfonic acid and total acid group densities obtained from experiment were 1.3367 mmol/g and 4.4 mmol/g, respectively. This result indicates that the sulfonation (functionalization) of the sulfonic acid group (SO_3H) into the biochar successfully. The Fourier Transform Infrared (FTIR) analysis obtained in this study also supports this finding.

4.3.2. Fourier Transform Infrared (FTIR) Analysis

The FTIR spectrum of the raw corncob, biochar and optimized sulfonated biochar-based catalyst are shown in Figure 4.8.

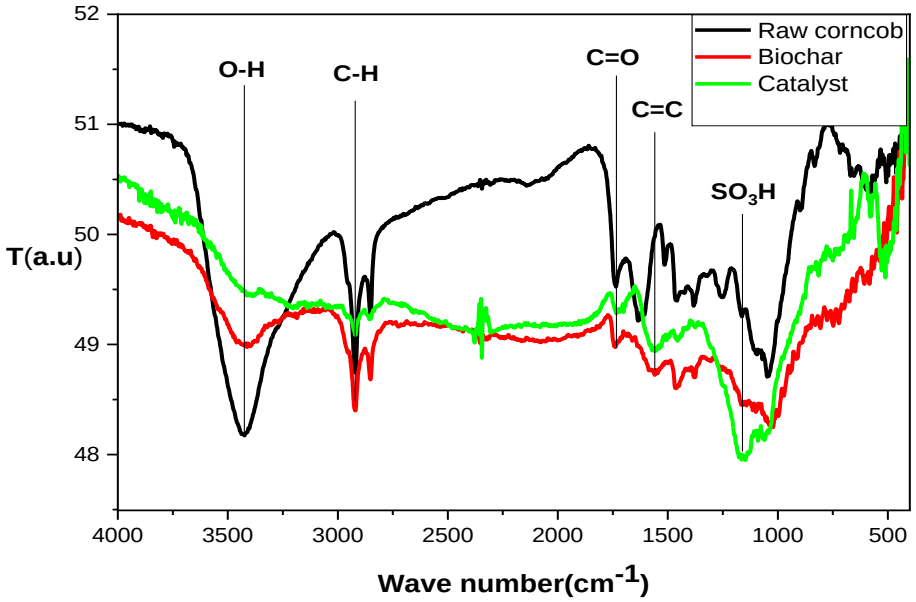

Figure 4.8. FT-IR analysis of raw corncob, activated biochar and sulfonated

For all the spectra of raw corncob, activated biochar and sulfonated biochar catalyst shown in Figure 4.8. the presence of O-H stretching, which is related to intermolecular hydrogen bonding and the C–H vibration band were observed at a wave number of 3427.07 and at 2924 cm^{-1} respectively. From the spectra of FT-IR results show that O-H and C-H spectra were reduced in case of Sulfonated solid acid catalysts which indicate dehydration effect during the activation and sulfonation process(Mateo et al., 2020).

For activated biochar and sulfonated catalyst showed absorption bands at 1581 and1597cm^{-1} which were attributed to aromatic ring C=C stretching variations of polyaromatic carbon. Also absorption bands at 1732 and 1722 cm^{-1} could be assigned to the C=O stretching mode of -COOH groups, which indicate the presence of acidic groups(Ibrahim et al., 2020).

The presence of the new peak for sulfonated bio char catalyst shows from Figure 4.8 which is SO_3H group covalently bonded to the polyaromatic carbon structure of sulfonated catalyst was confirmed by strong vibration bands at ($-SO_3^-$)1168 cm^{-1} and (O=S=O)1046 cm^{-1}, which are respectively associated with asymmetric and symmetric stretching modes of C-O-SO_3H. Therefore, the sulfonation treatment successfully grafted the –SO_3H group into the biochar, resulting in sulfonated biochar based solid acid catalyst(Hussain & Kumar, 2018). Overall, the FTIR analysis was showed that the synthesized catalyst sample contains –SO_3H, -COOH, and -OH groups which is agreement with other studies and implied successful functionalization of these functional groups on the biochar.

4.3.3. Thermogravimetric Analysis (TGA) Analysis

The results of the thermal analysis of the raw corncob, activated biochar and optimized sulfonated biochar-based catalyst under nitrogen flow are shown in Figure 4.9

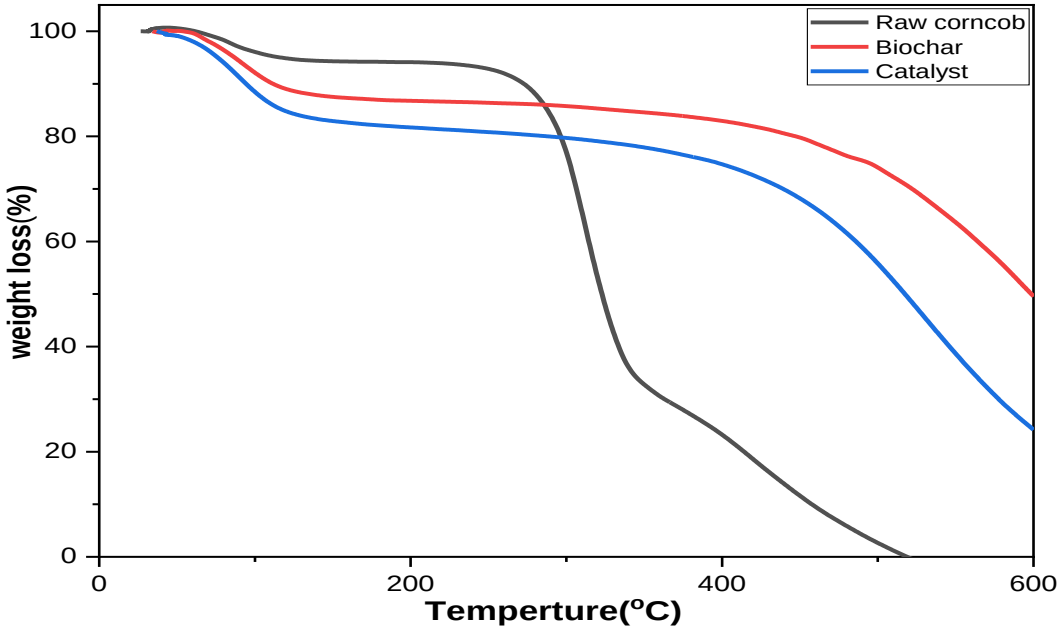

Figure 4.9.Thermogravimetric analysis for raw corncob, activated biochar and sulfonated biochar.

The thermal decomposition of raw corncob carbon structure from the above Figure 4.9. can be divided into three stages the first one is the removal of some adsorbed moisture for corncob carbon from 29 to 121^{o}C temperature range and the weight loss around 4.683% was observed. In the second stage in the temperature range from 250 to 320^{o}C the rapid change and the huge weight loss around 62.99% was observed which represent the decomposition of hemicellulose and cellulose structure of raw corncob carbon and finally from the temperature range from 320 to 520^{o}C slow change and the weight loss around 32.327% was observed due to the decomposition of lignin in the corncob and the carbon material formed in the heating processes (S. Wang et al., 2020).

The thermal behavior of activated biochar and sulfonated catalysts functional group were also determined by TGA from the above TGA plots. Both the biochar and sulfonated catalyst showed weight loss by increasing the temperature under N_2 atmosphere at a heating rate of 20^{o}C.The thermal decomposition behavior for biochar and sulfonated catalyst attributes to a marginal weight loss 12.13% and 16.23% were observed in temperature range 29-123^{o}C respectively, this is probably due to the thermo-desorption of the physical adsorb material, basically the moisture contents depicted to the loss of water molecules present in the catalyst which is being absorbed from the environment due to the hydrophilic properties of bio material.

Meanwhile, as it can be seen from Figure.4.9. for both sulfonated carbon catalyst and biochar are stable temperature range from 127-400^{o}C and 132-500^{o}C respectively. Based on the above Figure, the sulfonated catalyst shows thermal stability as the main decomposition of -SO_3H started at higher temperature which starts at 400^{o}C compared to other catalyst that started at 250^{o}C that indicates stronger -SO_3H bonding. Theoretically, the stronger bond of SO_3H to the bio char increases the reusability of the catalyst(Sangar et al., 2019).

Rapid weight loss was observed after 400^{o}C, which normally represents the decomposition of SO_3H for sulfonated carbon. This fact was confirmed by the literature findings that for both carbonaceous materials and sulfonated catalyst, degradation begins at> 240^{o}C and mass loss was also in the form of CO_2, which is due to degradation of carbon and the loss of sulfonic acid groups from the catalyst in the form of sulfur dioxide($SO_{2)}$(Xiong et al., 2018). TGA analysis shows that the sulfonated carbon material was relatively stable compared to the other sulfonated carbon catalysts(Jamil et al., 2020).

4.3.4. The X-Ray Diffraction (XRD) Analysis

Figure 4.10, shows the XRD patterns of raw corncob, biochar and the optimized sulfonated biochar-based catalyst.

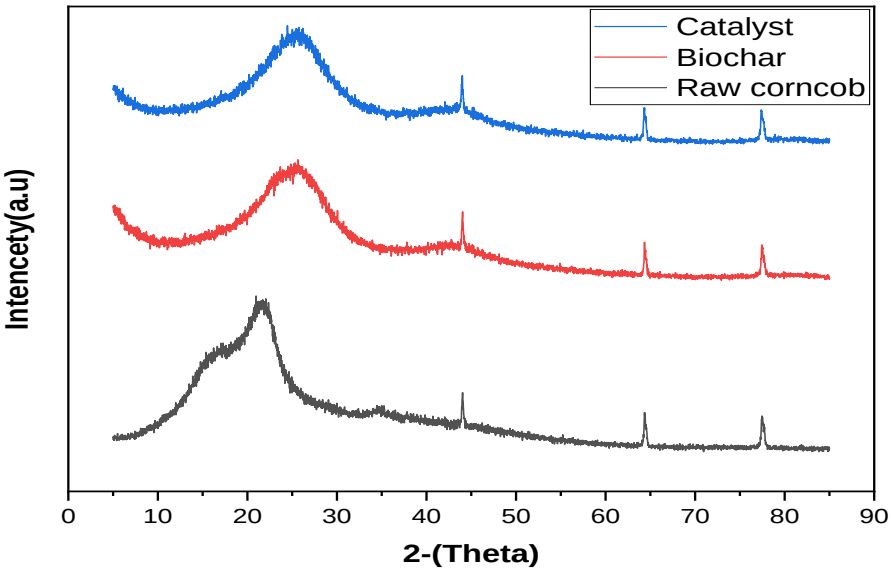

Figure 4.10.XRD analysis for raw corncob, activated biochar and sulfonated catalyst.

Figure 4.10. It was observed that the raw corncob has two broad peaks at 21^{o} and 16^{o} and other small peaks at 44^{o}, 65^{o} and 78^{o}, suggested the presence of crystalline cellulose in corncob and other impurities(S. Wang et al., 2020). Activated biochar and sulfonation biochar sample had diffractogram patterns. For both biochar and sulfonated biochar some slight differences were noted among the samples, shifting and broad peak on C-SO_3H at diffraction peak (2Θ = 10^{o}-30^{o}) the amorphous structure of carbon was observed(Nata et al., 2017).

Furthermore, XRD pattern of optimized sulfonated biochar-based catalyst in Figure 4.10. showed broadness, more rigid and amorphous than activated biochar which could be due to the biochar precursor under goes sulfonation. Loading of sulfonation group resulting in the growth of the size of aromatic carbon materials(Shen et al., 2013). In addition, sharp peaks round 44^{o},65^{o} and 78^{o} are probably due to some inorganic substances. Other studies regarding carbon-based catalysts presented similar behavior of sharp peaks(Wong et al., 2020).

4.3.5. Scanning Electron Microscopy (SEM) Analysis

Figure 4.11 A, B, and C represents SEM images of raw corncob, biochar and optimized sulfonated biochar-based catalyst respectively.

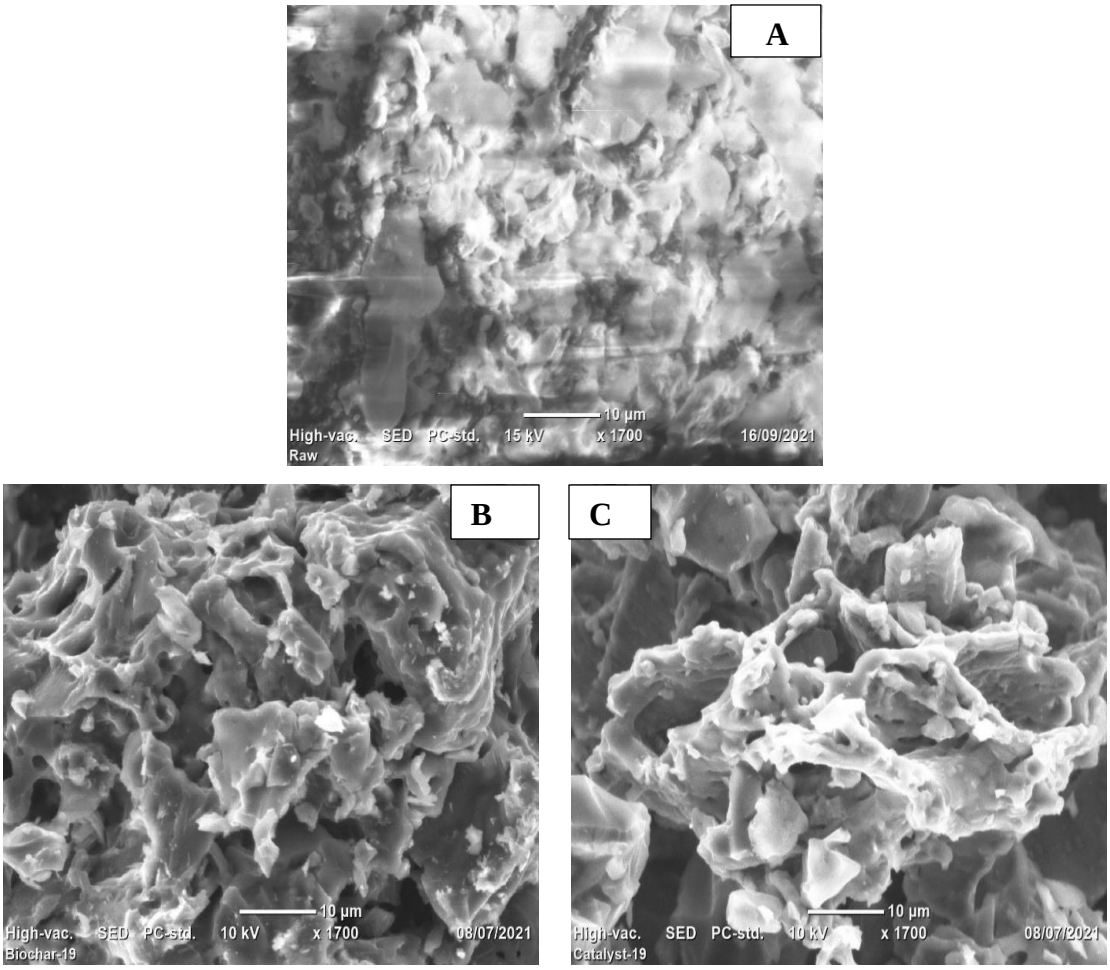

Figure 4.11.SEM analysis for raw corncob(A), activated biochar(B) and sulfonated catalyst(C)

The surface morphologies of raw corncob, activated biochar and sulfonated biochar were characterized using SEM analysis. From the above Figure 4.11.a. SEM images revealed that original structure of the cob is a rough surface that contains lignin, hemicelluloses and cellulose(Nata et al., 2017). Figure 4.11.b. showed that SEM images of Activated biochar revealed that the carbonization of phosphoric acid activated corncob. A porous structure was developed because of activation and carbonization process and another component which staked on the surface of corn cob were also removed. Figure 4.11.c. showed that during sulfonation reaction biochar cavity can decrease due to the attachment of sulfonation group and additionally crosslink was observed from the result which indicates SO_3H had correctly attached to the carbon layer due to sulfonation reaction and the catalyst is acidic in nature(Bastos et al., 2020).

4.4. Synthesis of 5-Hydroxymethylfufural (HMF)

The performance of biomass-based catalyst with functional group SO_3H, COOH and OH as an acid catalyst has been tested for the conversion of microcrystalline cellulose to HMF. In this work, the sufficient conversion of cellulose and HMF concentration 69.3% and 307.93mg/l were achieved respectively using sulfonated catalyst in 2-MeTHF/H_2O two-phase reaction medium. But in the absence of sulfonated catalyst minimum conversion and concentration of HMF 10% and 35.77mg/l were observed in Table 4.5 respectively. This indicates the sulfonated catalyst was crucial for cellulose hydrolysis and dehydration due to its low activation energy and high reaction selectivity. The strong immiscibility of 2-MeTHF with water was observed to remove 5-HMF from the reaction system as an extract, thereby preventing side reactions due to the presence of water and 2-MeTHF solvent molecules. In addition, due to the dynamic interaction of the reaction molecules, the chemical reaction is affected by time and temperature as well as the catalyst loading. Therefore, the effects of these parameters on the crystallite cellulose and glucose conversion rate and HMF concentration were studied, and the results are presented in the figures below.

Table 4.5. Effects of variable on 5-HMF Synthesis.

Parameters	Run 1	Run 2	Run 3
Temperature(^oC)	160	170	180
Time(hr.)	3	3	3
Catalyst load(g)	0.2	0.2g	0.2
Cellulose conversion (%) & HMF concentration(ml/g)	33.3and 61.91	35.8and 171	45and 269
	Run 4	Run 5	Run 6
Temperature	190	200	190
Time	3	3	1
Catalyst load	0.2	0.2	0.2

Cellulose conversion& HMF concentration	65and 303.76	62.5and 260	20and 59.05
	Run 7	Run 8	Run 9
Temperature	190	190	190
Time	2	3	4
Catalyst load	0.2	0.2	0.2
Cellulose conversion& HMF concentration	22.5and 85.67	33.3and 209	66.7and 277.85
	Run 10	Run 11	Run 12
Temperature	190	190	190
Time	5	4	4
Catalyst load	0.2	0	0.1
Cellulose conversion& HMF concentration	54.16and 107.88	10and 35.77	45.5and 133.04
	Run 13	Run 14	Run 15
Temperature	190	190	190
Time	4	4	4
Catalyst load	0.2	0.3	0.4
Cellulose conversion HMF concentration	54.16and 239	69.23and 307.93	50and 143.71

4.4.1. Factors Affecting 5-Hydroxymethylfurfural (HMF) Synthesis

4.4.1.1. Effect of Reaction Temperature in 5-HMF Synthesis

Figure 4.12. (A), (B) and Figure 4.13 showed that the sulfonated biochar catalyst with a two-phase solvent system is active in the production of HMF from microcrystalline cellulose in a wide temperature range of 160 to 200^{o}C. At the reaction condition of 160^{o}C,3hr and 0.2g catalyst loading of the conversion of microcrystalline cellulose and the HMF concentration were only 33.3% and 61.91mg/l respectively. As the temperature increases, cellulose conversion and HMF concentration also increases up to 190^{o}C.An increase the conversion of cellulose and HMF concentration was, due to the simple transfer of activation energy and solubility of microcrystalline of cellulose at high temperature, within the same reaction time and catalyst loading. As the reaction temperature further increased beyond 190^{o}C, the HMF concentration decreased slightly. In the valorization process of carbohydrates, glucose or fructose is first dehydrated to form HMF, and then subsequent reactions easily occur to produce LA, FA and FF (through rehydration) and humins (through polymerization). Too high temperature favored to the side reaction of HMF. In the current work, the output of LA + FA + FF is very low and gradually increases with increasing temperature as shown in Figure 4.12. (B). As shown Figure 4.12. (A). the color of the reaction solution darkened as the reaction temperature increased, indicating that the main by-product of the side reaction was humins. In the lower temperature range, the direct dehydration of glucose to HMF is incomplete for the specified reaction time (3hr). At higher temperatures (200^{o}C), side reactions of by-products (mainly humus) occur more intensely, resulting in reduction of HMF concentration(Cao et al., 2018).

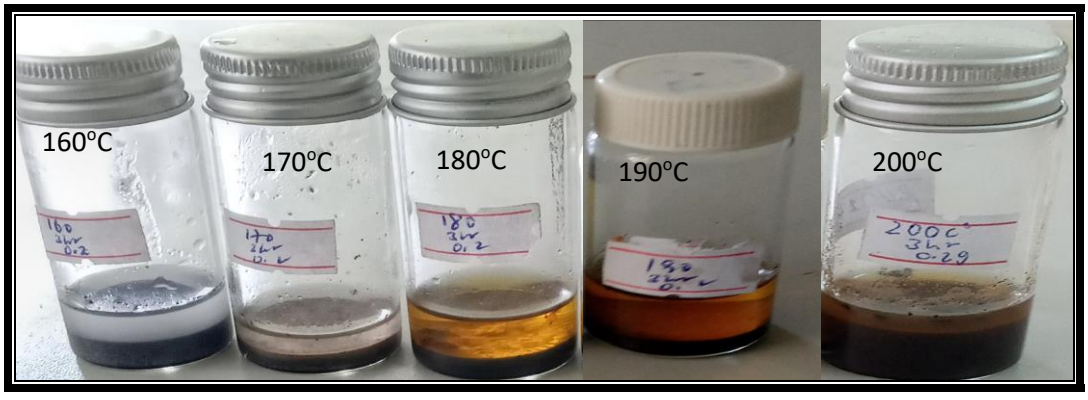

Figure 4.12 (A). The effects of temperature on the formation of 5-HMF

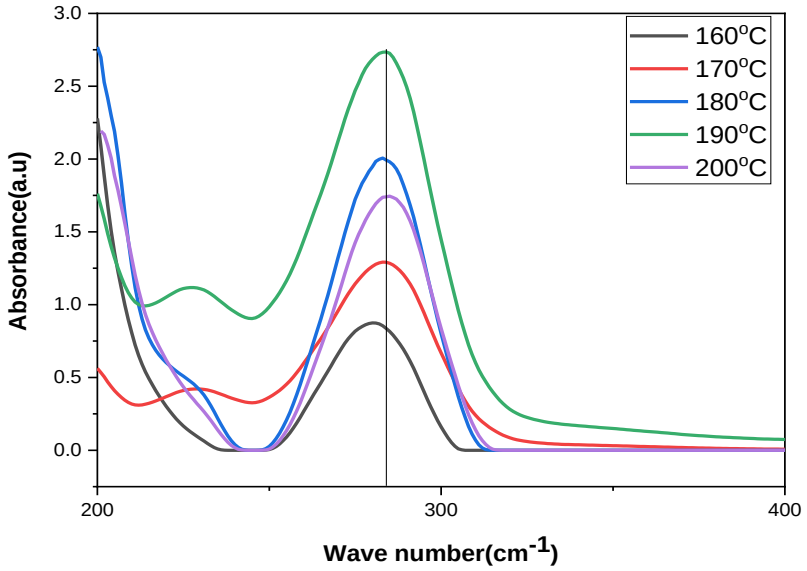

Figure 4.12. (B). Effects of reaction temperature on 5-HMF concentration result using UV-VIS.

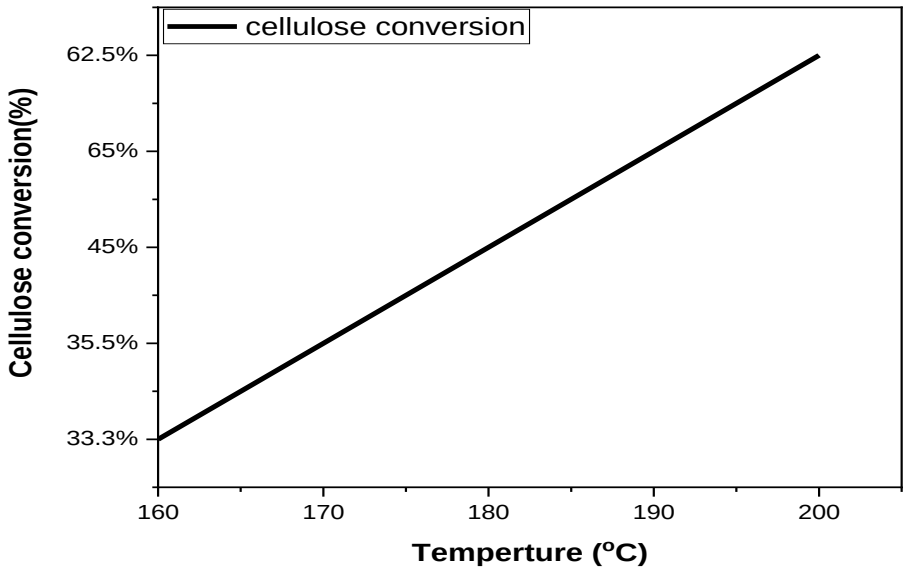

Figure 4.13. The effects of temperature on cellulose conversion.

4.4.1.2. Effect of Reaction Time

From Figure 4.14. (A), (B) and Figure 15. It can be observed that the reaction time has a significant effect on the crystallite conversion of cellulose and 5HMF concentration. The reaction time

investigation carried out from 1hr up to 5hr. Around 20% cellulose conversion and 59.05mg/l HMF concentration was observed after reaction time of 1hr.

When the reaction time increased to 4 hr, the conversion of microcrystalline cellulose and the concentration of HMF increased to 66.7% and 277.85mg/L, respectively. In addition, the HMF concentration initially increased with time but it decreased when the reaction time exceeds beyond 4hr. The concentration of 5HMF gradually decreased or remains constant, that is, what strikingly indicates the new formed 5HMF has been converted into other undesirable product or polymerization products, when the reaction time exceeds 4hr(Kaya et al., 2019).

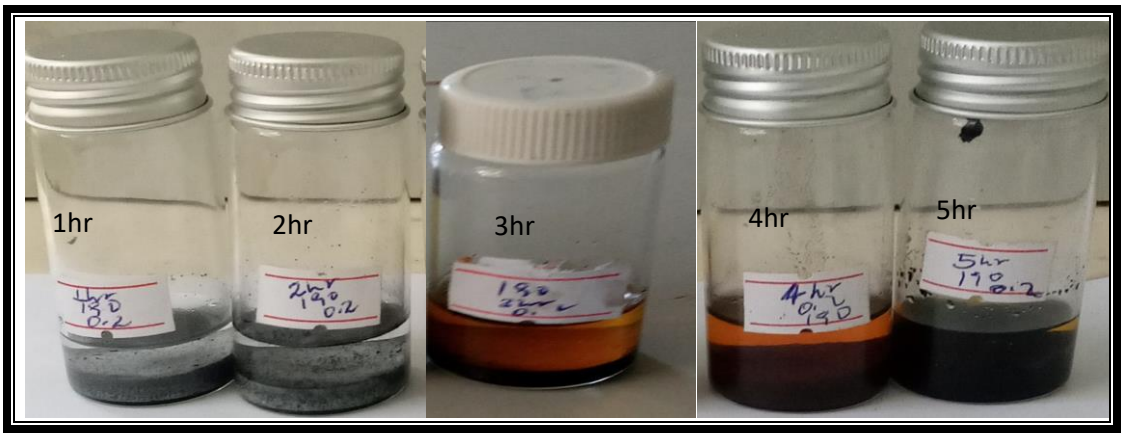

Figure 4.14. (A). The effects of reaction time on 5-HMF formation

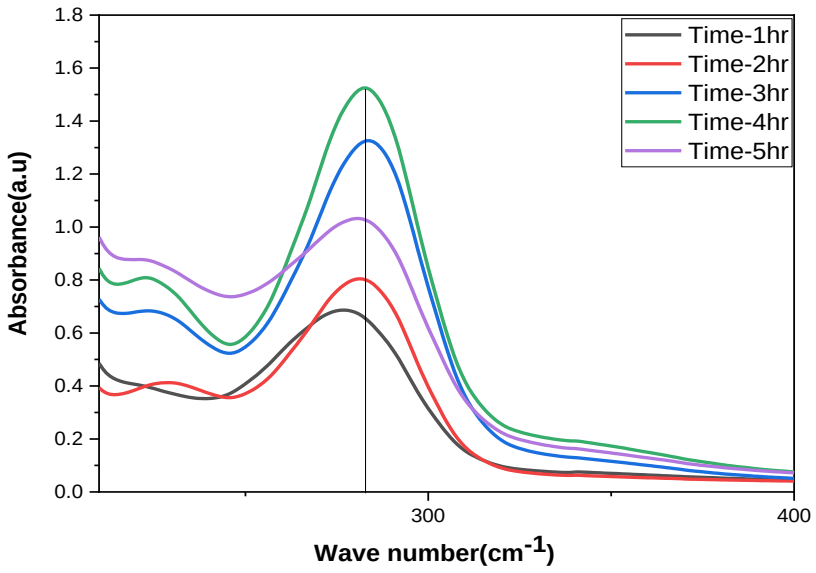

Figure 4.14. (B). Effects of reaction time on 5-HMF concentration using UV-VIS result.

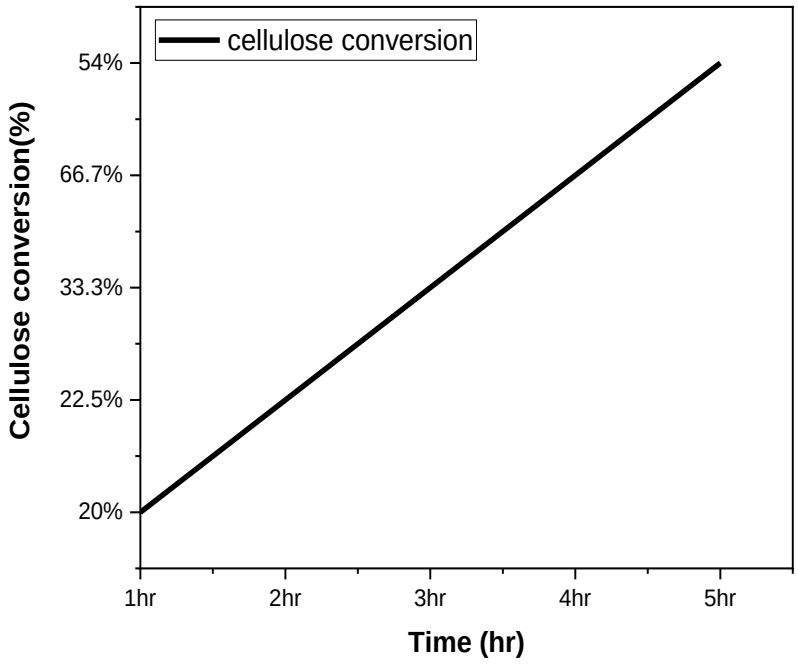

Figure 4.15. The effects of reaction time on cellulose conversion.

4.4.1.3. Effect of Catalyst Loading

Subsequently, the effect of catalyst loading on the conversion of microcrystalline cellulose into HMF was studied from 0-0.4g, and the results were observed from the Figure 4.16.(A), (B) and Figure 17. It can be seen that microcrystalline cellulose conversion and HMF concentration were only 10% and 35.77mg/l respectively when no catalysts were used, which indicate that the microcrystalline cellulose at high temperature can be soluble and converted into glucose and 5-HMF with the absence of catalyst. Increasing the amount of biochar carbon catalyst from 0.1g to 0.3g resulted in a re- markable increment in cellulose conversion from 10% to 69.7%and HMF concentration to 307.93mg/l. When the amount of biochar carbon catalyst was further increased to 0.4g, the conversion of microcrystalline cellulose was correspondingly reduced to 66.1%, however, the concentration of HMF was also sharply decreased to 143.71mg/l. This could be ascribed to that much more available acid sites derived from excessive biochar carbon catalyst probably facilitated the decomposition of HMF or the polymerization of HMF and glucose(Hu et al., 2013). Thus, the best effective catalyst loading of 0.3g was observed at,4hr and 190^{o}C in this work.

Figure 4.16 (A). Effects of catalyst load on 5-HMF formation

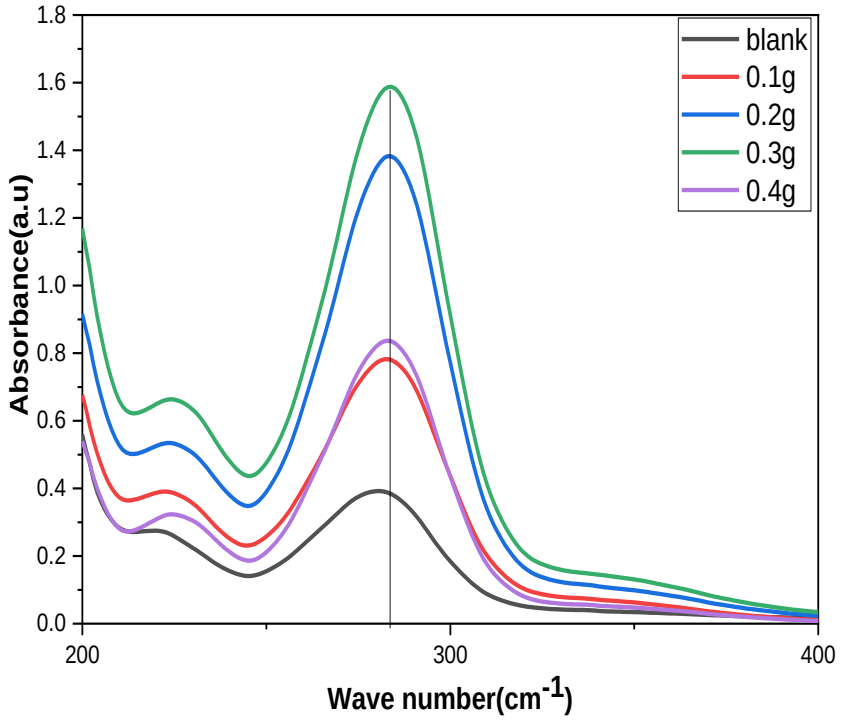

Figure 4.16. (B). Effects of catalyst load on 5-HMF concentration using UV-VIS results.

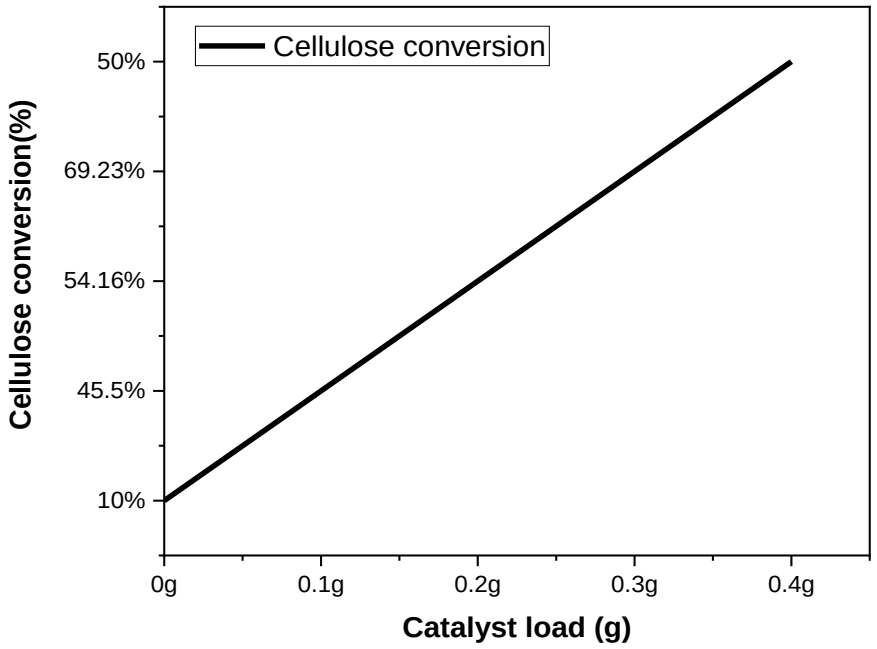

Figure 4.17. The effects of catalyst load on microcrystalline cellulose conversion.

4.4.2. Separation of 5-Hydroxymethylfufural (HMF)

In this study HMF can easily separate from the reaction system by rotary evaporator. Further investigation found that the dark humins impurities are highly soluble in 2-MeTHF, but insoluble in water. Since HMF is soluble in both water and 2-MeTHF solvent. In Figure 4.18. (A), the original HMF solution after the process of dehydration of Glucose in biphasic system was dark brown in color, whereas pure HMF solution is pale yellow. Apparently, the dark brown color came from the impurities, which are mainly humins. After evaporation of 2-MeTHF, a viscous black liquid was obtained in Figure 4.18. (B). 5ml of distilled Water was then added into the vial to this viscous liquid. HMF was dissolved in water, and formed a transparent yellow color solution. Most of the impurities were insoluble and remained at the bottom as black solid as shown in Figure4.18.C.

Figure 4.18. Separation and purification 5-HMF:(A) Sample containing 5-HMF and solvent, (B) Separated black viscous liquid and (C) Purified 5-HMF using 5ml distilled water.

4.4.3. Characterizations of 5-Hydroxymethylfufural

4.4.3.1. Fourier Transform Infrared (FTIR) Analysis

The FTIR spectrum of the 5-hydroxymethylfufural are shown in Figure 4.19.

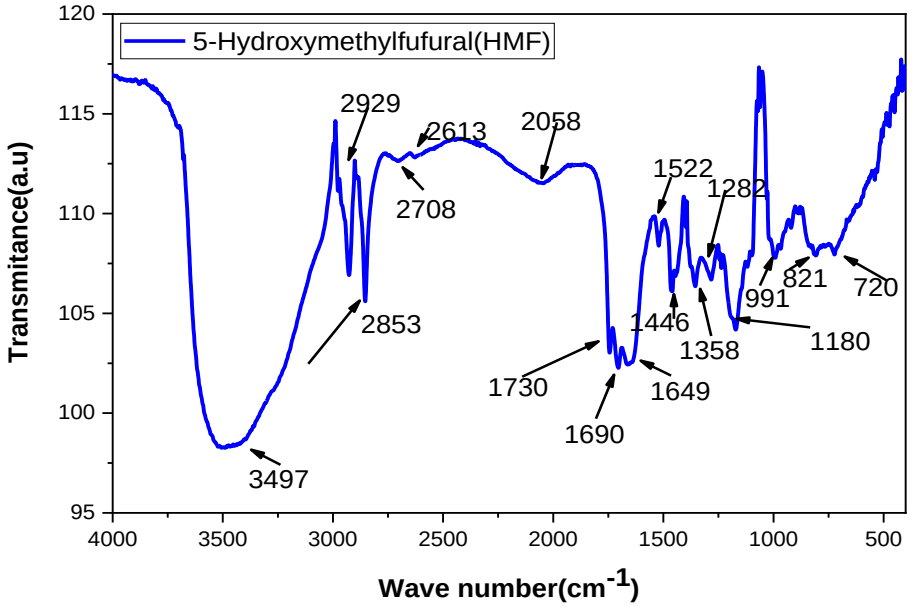

Figure 4.19. FT-IR analysis of 5-hydroxymethylfufural (HMF)

To demonstrate the formation of 5–HMF during the reaction, analyzed by FTIR and According to results shown in Figure 4.19. FT-IR analysis O–H group band at 3497 cm^{-1} due to stretching vibrations of these groups, which can be explained by the stretching vibrations of the O–H bond indicate present of alcohol group in the molecule 5–HMF. Also from IR analysis at 2929 and 2853 cm^{-1} the presence of two characteristic peaks of 5-HMF, due to the vibrations of C–H asymmetric stretching, it is noted that the presence of week aldehyde(Morales-Leal et al., 2019). It can be observed from IR analysis between 1740 and 1500 cm^{-1}, in order to observe more detail as the 1730, 1690 and 1649 cm^{-1} band from CH=O vibrations stretching show that presence of aldehyde group in the 5–HMF and the five-member heteroaromatic ring with double bond, and the band at 1522 cm^{-1}, due to C=C stretching vibrations 5–HMF for furan ring in molecule(Nishimura et al., 2019). The band at 1446,1358 and 1282$cm^{-1}$are the characteristic band stretches of the five-member heteroaromatic ring and the bands at 821 cm^{-1} to 720 cm^{-1} may be assigned to strong hydrogen wag absorption of the five-membered(M. Zhang et al., 2012). Also, the stretching vibration between1400 and 900 cm^{-1} indicates the C-C-H, C-O-H, and O-C-H of the furan ring

4.4.3.2. High Performance Liquid Chromatography (HPLC)

The HPLC chromatography of the 5-hydroxymethylfufural are shown in Figure 4.20.

HMF was analyzed qualitatively in order to know the selectivity of HMF and byproduct in organic solution. In Figure 4.20. HMF was formed at the retention time of 17.112min, width 0.2852, area 3754.7983 and height 191.9771. The solvent was observed at around 13.819min retention time with long peak. This HPLC results clearly confirms that high (89.4%) selectivity towards HMF. The presence of other by products were very low as it can be represented by very small peaks at different retention time. This small peak may be unconverted hexose sugar or by product formed during the reaction other than HMF.

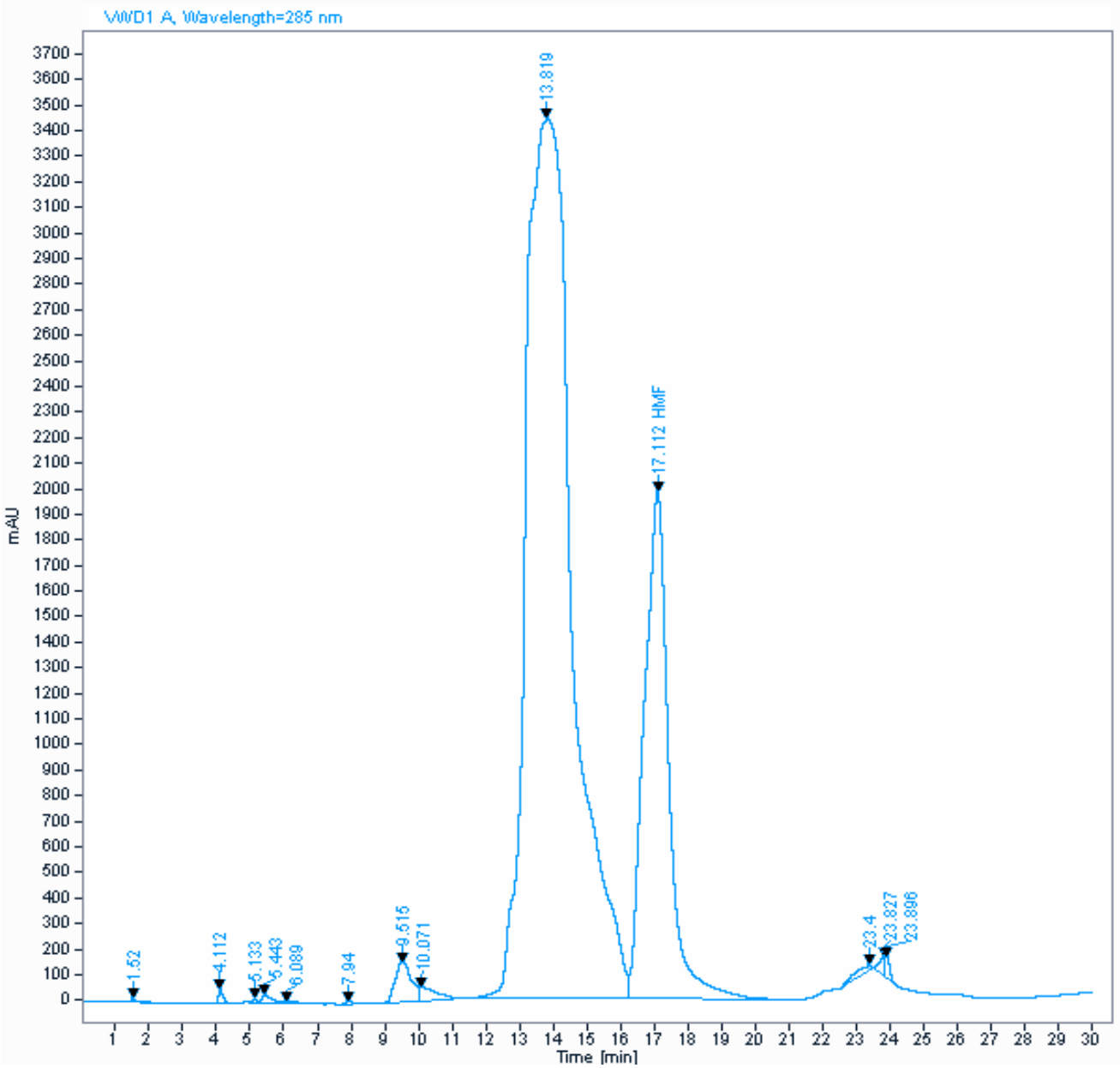

Figure 4.20. HPLC analysis of 5-hydroxymethylfufural (HMF).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

Conclusion

In this study, corncob based sulfonated solid acid catalyst was used as an efficient, green, cheap and recyclable heterogenous catalysts for 5-HMF synthesis. It has been prepared through three steps such as activation, carbonization and sulfonation step. Box-Behnken experimental Design was used to study the effect of process parameters such as sulfonation temperature, sulfonation time and ratio of concentrated sulfuric acid to biochar on the amount of sulfonic group acid density in the synthesis of biochar-based catalyst. Optimum sulfonic acid density (SO_3H) (1.273 mmol/g) was achieved at the optimum sulfonation conditions (sulfonation temperature 161.9^oC, sulfonation time 16.78 hr, and the ratio of sulfuric acid to biochar 13.03:1). The results of FTIR analysis indicated that the sulfonic group was successfully attached into the surface of the biochar and the catalyst showed good thermal stability up to 400^oC based on the thermo gravimetric analysis.

The number of the (-SO_3H), (-COOH) and (-OH) groups on the optimized biochar sulfonated solid catalysts are responsible for the higher activity during hydrolysis and dehydration of microcrystalline cellulose into 5-HMF. An efficient catalytic conversion of cellulose to HMF was achieved using optimized biochar sulfonated solid catalyst. The reaction was intensified with water-2-MeTHF a biphasic solvent by addition of NaCl in the reaction medium for the purpose of creating an interface between the organic and water phases. Microcrystalline cellulose conversion and HMF concentration were affected by sulfonated biochar catalyst loading, temperature and reaction time. As the reaction temperature and time increases, cellulose conversion and HMF concentration also increases up to 190^oC and 4 hr respectively and increasing the amount of catalyst load up to 0.3g resulted in a re- markable increment in cellulose conversion and 5-HMF. Therefore, maximum cellulose conversion and 5-HMF concentration of 69.5% and 307.93mg/l were achieved respectively at the reaction temperature of 190^oC, reaction time of 4hr and 0.3g of catalyst loading in 2-MeTHF/DIW solvent. From FT-IR analysis, the presence of 5-HMF was confirmed by existence of alcohol (OH)and aldehyde group (CH=O). UV-VIS results also showed that the broad peak at 284nm wave number which indicates presence and concentration of 5-HMF product in the organic solution. In addition, HPLC result confirmed high (89.4%) selectivity of 5-HMF in the organic solution.

Recommendation

In the present study, the carbonization of activated corncob was carried out by using muffle furnace without nitrogen purging system and controlled heating rate system. Hence, the absence of these components affects the raw biochar characteristics such as porosity and surface area which helps to hold sufficient concentration of sulfonic acid group (SO_3H). Therefore, it was recommended to conduct the carbonization under inert atmosphere.

Bifunctional catalysts containing bronsted and lewis acid are desirable for promoting the one-pot conversion of glucose and polymerized carbohydrates, such as ,starch and cellulose in to 5HMF. Since, hydrolysis and dehydration are catalyzed by bronsted acid and isomerization is catalyzed by Lewis acid, synthsis of bifunctional hetrogenous catalyst for 5-HMF synthsis is recommended in future works.

In this study ,the effects of reaction temperture,reaction time and catalyst load were studied and thire effect was shown based on uv-vis results for 5-HMF concentartion. Therefore, it is recommended to apply optimization technic in order to obtain an optimum condition for 5-HMF synthsis in future works.

Research Fund Acknowledgment

This research project is funded by Adama Science and Technology University under the grant number ASTU/SM-R/349/21 Adama, Ethiopia.

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APPENDIX

Appendix A Proximate Analysis Calculation

1. Moisture content of corncob (<250µm)

Sample I

A. Wt. of empty crucible: 40.21g
B. Wt. of sample:1g
C. Wt. of crucible +wt. of sample:41.21g
D. Wt. of sample after drying:41.17g

$$\textbf{Moisture content}(\%)\ \frac{\textbf{W1}-\textbf{W2}}{\textbf{M1}}*\textbf{100}$$

$$=\frac{41.21g-41.17g}{1g}*100$$

=4%

Sample II

A. Wt. of empty crucible: 35.66g
B. Wt. of sample:1g
C. Wt. of crucible +wt. of sample:36.66g
D. Wt. of sample after drying:36.60g

$$\textbf{Moisture content}(\%)=\frac{\textbf{W1}-\textbf{W2}}{\textbf{M1}}*\textbf{100}$$

$$=\frac{36.66g-36.60g}{1g}*100$$

=6%

Sample III

A. Wt. of empty crucible: 37.78g
B. Wt. of sample:1g
C. Wt. of crucible +wt. of sample:38.78g
D. Wt. of sample after drying:38.71g

$$\textbf{Moisture content}(\%)=\frac{\textbf{W1}-\textbf{W2}}{\textbf{M1}}*\textbf{100}$$

$$=\frac{38.78g-38.71g}{1g}*100$$

=7%

Therefore, for overall moisture content of three sample take average value.

$$\textbf{Moisture content}(\%) = \textbf{sample I} + \textbf{sample II} + \textbf{sample III}$$

$$\textbf{Moisture content}(\%) = \frac{\textbf{4\%+6\%+7\%}}{\textbf{3}}$$

=5.677%

2. Volatility matter (corncob)
Sample I.
A: wt. of crucible: 40.21g
B: wt. of sample g: 1g
C: wt. of crucible + sample before heating g:41.21g
D: wt. of de-volatized sample g: 40.38g

$$\textbf{weight loss}(\%) = \frac{\textbf{C-D}}{\textbf{C-A}} * \textbf{100}$$

$$= \frac{41.21g - 40.38}{41.21 - 40.21} * 100$$

=83%

$$\textbf{Volatile mater}(\%) = \textbf{weight loss} - \textbf{moisture content}$$

=83%-4%

=79%

Sample II.
A: wt. of crucible: 35.65g
B: wt. of sample g: 1g
C: wt. of crucible + sample before heating g:36.65g
D: wt. of de-volatized sample g: 35.68g

$$\textbf{weight loss}(\%) = \frac{\textbf{C-D}}{\textbf{C-A}} * \textbf{100}$$

$$= \frac{36.65g - 35.68g}{36.65g - 35.65g} * 100$$

=97%

$$\textbf{Volatile mater}(\%) = \textbf{weight loss} - \textbf{moisture content}$$

=97%-6%

=91%

Sample III.
A: wt. of crucible: 37.76g
B: wt. of sample g: 1g
C: wt. of crucible + sample before heating g:38.76g
D: wt. of de-volatized sample g: 37.89g

$$\textbf{weight loss} = \frac{\mathbf{C-D}}{\mathbf{C-A}} * \mathbf{100}$$

$$= \frac{38.76g - 37.89g}{38.76g - 37.76g} * 100$$

$$= 87\%$$

$$\textbf{Volatile mater}(\%) = \textbf{weight loss} - \textbf{moisture content}$$

$$= 87\% - 7\%$$

$$= 80\%$$

Therefore, for overall moisture content of three sample take average value.

$$\textbf{Volatile mater}(\%) = \frac{\textbf{sample I} + \textbf{sample II} + \textbf{sample III}}{}$$

$$\textbf{Volatile mater}(\%) = \frac{\mathbf{79\% + 80\% + 91\%}}{\mathbf{3}}$$

$$= 83.3\%$$

3. Ash content of Corncob
Sample I
A. Mass of crucible before burning: 57.60g
B. Mass of sample: 1.g
C. Mass of sample + Crucible after burning: 57.66g

$$\textbf{Ash content}(\%) = \frac{\mathbf{C-A}}{\mathbf{B}} \mathbf{* 100\%}$$

$$= \frac{57.66g - 57.60g}{1g} * 100$$

$$= 6\%$$

Sample II

A. Mass of crucible before burning: 60.00g

B. Mass of sample: 1.g

C. Mass of sample + Crucible after burning: 60.049g

$$\textbf{Ash content}(\%) = \frac{\mathbf{C-A}}{\mathbf{B}}\mathbf{*100\%}$$

$$= \frac{60.049g - 60.00g}{1g} * 100$$

$$=4.9\%$$

Sample III

A. Mass of crucible before burning: 57.62g

B. Mass of sample: 1.g

C. Mass of sample + Crucible after burning: 57.65g

$$\textbf{Ash content}(\%) = \frac{\mathbf{C-A}}{\mathbf{B}}\mathbf{*100\%}$$

$$= \frac{57.65g - 57.62g}{1g} * 100$$

$$=3\%$$

Therefore, for overall moisture content of three sample take average value.

$$\textbf{Ash content}(\%) = \textbf{sample I} + \textbf{sample II} + \textbf{sample III}$$

$$\boldsymbol{Ash\ content}(\%) = \frac{\mathbf{6\%+4.9\%+3\%}}{\mathbf{3}}$$

$$=4.63\%$$

4.fixd carbon(corncob)

$$\textbf{Fıxed carbon}(\%) = \mathbf{100} - (\textbf{Volatıle matter} + \textbf{Ash content})$$

=100-(83+4.63)

12.37%

Appendix B Determination of Acid density of the catalyst

I. Sample calculation of SO_3H acid density for biochar sulfonated (-SO_3H)

The volume of 0.05 M NaOH (titrant) (data obtained from the titrate analysis): 2.675ml
SO_3H acidity per gram of the catalyst.

$$SO3H = \frac{(\text{volume ofNaOH used for the titration} * \text{Normality of NaOH})}{\text{Mass of catalyst}}$$

$$SO_3H = \frac{2.675\text{ml} * 0.05\text{M}}{0.1\text{g}}$$

$$= 1.3375\text{mmol/gram.}$$

Similarly, for other runs of experiment for calculation of -SO_3H. The measurement was repeated three times, with the average reported as the SO_3H acidity.

II. Determination of total acid density for biochar sulfonated acid.

Sample calculation for the determination of total acidity
Number of moles of 15 mL 0.05 M NaOH (titrate).

$$= 0.05\frac{mol}{L} \times 15\text{ml} \times \frac{1\ L}{1000\ ml} = 0.00075 \text{ moles of Sodium hydroxide}$$

Number of moles of 6.2 mL (from burette reading) 0.05 M HCl (titrant) (data obtained from the titrator analysis).

$$= 0.05\frac{mol}{L} \times 6.2\text{ ml} \times \frac{1L}{1000ml} = 0.00031 \text{ moles of Hydrochloric acid.}$$

$$\text{Total acid} = \frac{\text{Volume of NaOH} \times \text{Normality of NaOH} - \text{Volume of HCl} \times \text{Normality of HCl}}{\text{Mass of catalyst}}$$

$$= \frac{0.00075mol - 0.00031mol}{0.1g}$$

$$= 0.0044\text{mol/gram}$$

$$= 4.4\text{mmol/gram}$$

The measurement was repeated three times, and the average reported as total acid density of the catalyst

Table: Appendix C Simplified Infrared Correlation Chart

	Type of vibration	Frequency(cm^{-1})	intensity
C-H	Alkanes (stretch)	3000-2850	strong
	$-CH_3$ (bend)	1450 and 1375	medium
	$-CH_2$ bend	1465	medium
	Alkenes stretch	3100-3000	medium
	Out of plane bend	1000-650	strong
	Aromatics (stretch)	3150-3050	strong
	Out of plane bend	900-690	strong
	Alkyne stretch	3300	strong
	Aldehyde	2900-2800	week
		2800-2700	week
C-C	Alkane not interpretatively useful		
C=C	Alkene	1680-1600	medium
	aromatic	1600 and 1475	week
C≡C	Alkyne	2250-2100	medium
C=O	aldehyde	1740-1720	strong
	Ketone	1725-1705	strong
	Carboxylic acid	1725-1700	strong
	Ester	1750-1730	strong
	Amide	1670-1640	strong
	anhydride	1810 and 1760	strong
	Acid chloride	1800	strong
C-O	Alcoholes,ethers,esters,carboxylic acid,anhydries	1300-1000	strong
O-H	Alcholes,phenol		
	stretch	3500-3100	Medium
	bend	1640-1550	strong
C-N	Amines	13500-1000	Medium
C=N	Imines and oximes	1690-1640	weak
C≡N	Nitriles	2260-2240	medium
X=C=Y	Allenes,ketenes,isocyanates	2270-1950	strong
N=O	Nitro(R-NO2)	1550 And1350	Strong
S-H	Mercaptanes	2550	week
S=O	Sulfoxides	1050	strong
	Sulfones,sulfonyl chlorides,sulfates,sulfonamides	1375-1300 1200-1140	strong

(Source: http://en.wikipedia.org/wiki/Infrared_spectroscopy_correlation_table**)**

Appendix D Determine of microcrystalline cellulose conversion and 5-HMF concentration

I. Determine the microcrystalline cellulose conversion.

A. Mass of initial microcrystalline cellulose and catalyst M_1 (g): 1.3g

B. Mass of the left over the reaction complete M_2 (g): 0.4g

$$\textbf{Microcrystalline cellulose convartion} = \frac{\textbf{M1}-\textbf{M2}}{\textbf{M1}} * \textbf{100}$$

$$= \frac{1.3g - 0.4g}{1.3g} * 100$$

$$= 69.23\%$$

Table: APPENDIX D Determine of microcrystalline cellulose conversion

No run	Temperature	Time	Catalyst load	MCC after reaction	Conversion of MCC(g)
1.	160^{o}C	3hr	0.2g	0.8g	33.3%
2.	170^{o}C	3hr	0.2g	0.77g	35%
3.	180^{o}C	3hr	0.2g	0.66g	45%
4.	190^{o}C	3hr	0.2g	0.41g	65.8%
5.	200^{o}C	3hr	0.2g	0.45g	62.5%
6.	190^{o}C	1hr	0.2g	0.96g	20%
7.	190^{o}C	2hr	0.2g	0.93g	22.5%
8.	190^{o}C	3hr	0.2g	0.8g	33.3%
9.	190^{o}C	4hr	0.2g	0.40g	66.7%
10.	190^{o}C	5hr	0.2g	0.55g	54.1%
11.	190^{o}C	4hr	0g	0.9g	10%
12.	190^{o}C	4hr	0.1g	0.6g	45.5%
13.	190^{o}C	4hr	0.2g	0.55g	54%
14.	190^{o}C	4hr	0.3g	0.4g	69.2%
15.	190^{o}C	4hr	0.4g	0.7g	50%

II Determine the concentration of 5-HMF

At a given parameter of 190°C,4hr and 0.3g catalyst load can get this below information. λ=284nm, A=absorbance from UV-vis result 1.5, D=dilution factor 27ml, B=intercept -0.00478 and K=Coefficient derived from liner regression 0.1333

a correlation between HMF mass ratio and the maximum absorption wavelength was formulated as follows.

$$W = \frac{\lambda - 276.65}{7.48602}$$
$$= \frac{284 - 276.65}{7.48602}$$
$$= 0.982$$

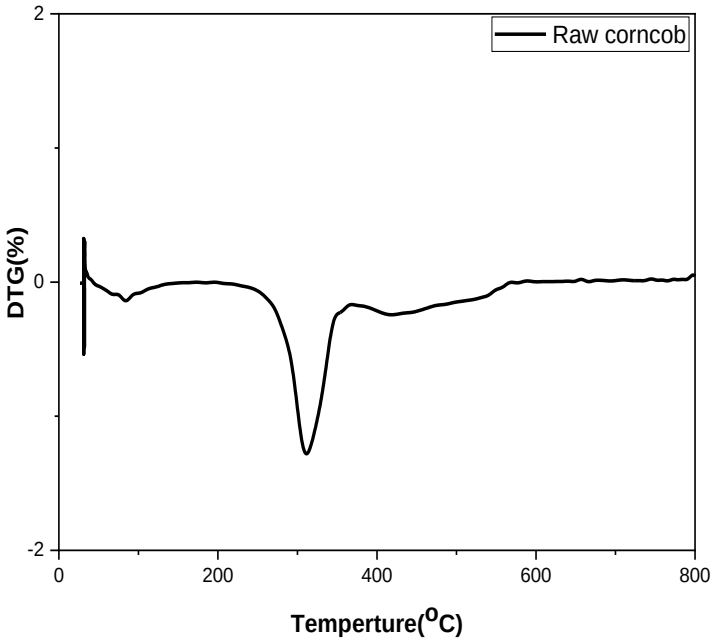
the total concentration of the mixture can be determined by following equation

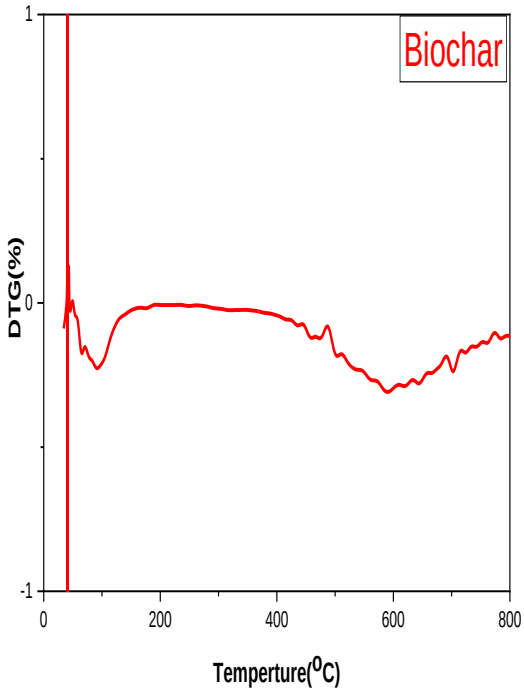
$$C = \frac{A - B}{K}$$
$$C = \frac{1.5 + 0.0478}{0.1333}$$
$$C = 11.62 \text{mg/l}$$

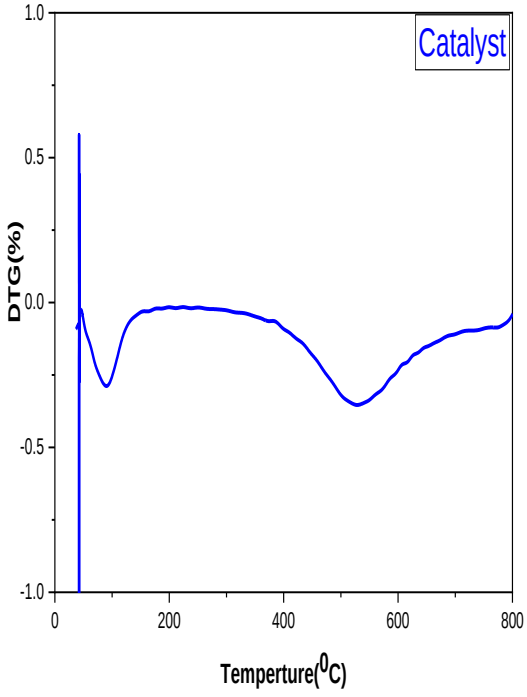
the individual HMF concentrations can be calculated as mg/L by following equations

$$CHMF = CWD$$
$$= \frac{11.62mg}{l} * 0.98 * 27$$
$$= 307.46 \text{mg/l}$$

Appendix E DTG Result of Raw corncob, biochar and Sulfonated biochar







Appendix F HPLC Result of 5-HMF

Area Percent Report

Agilent Technologies

Sample name: J-0085-0410-21

Sample amount: 1.000

Instrument: JATSL 1220 Location: 1

Acq. method: HMF 04-11-17.M Injection volume: 10.000

Analysis method: HMF 04-11-17.M Acq. operator: SYSTEM

Signal: VWD1 A, Wavelength=285 nm

RT [min]	Width [min]	Area	Height	Area%	Name
1.520	0.1453	192.9550	17.8258	0.0435	
4.112	0.1304	525.1137	58.6678	0.1184	
5.133	0.1071	126.2359	17.7300	0.0285	
5.443	0.2688	659.8599	35.0269	0.1487	
6.089	0.4364	277.1288	8.3666	0.0625	
7.940	0.2033	110.7762	8.2185	0.0250	
9.515	0.4762	5234.4087	154.1170	1.1799	
10.071	0.4251	1815.7142	53.0804	0.4093	
13.819	1.1382	331798.4063	3440.4041	74.7888	
17.112	0.7025	100391.7578	1986.7311	22.6287	HMF
23.400	0.5545	1039.2164	22.7237	0.2342	
23.827	0.1389	692.7543	71.6091	0.1561	
23.896	0.1574	782.9584	78.4963	0.1765	
	Sum	443647.2856			

Area Percent Report

Agilent Technologies

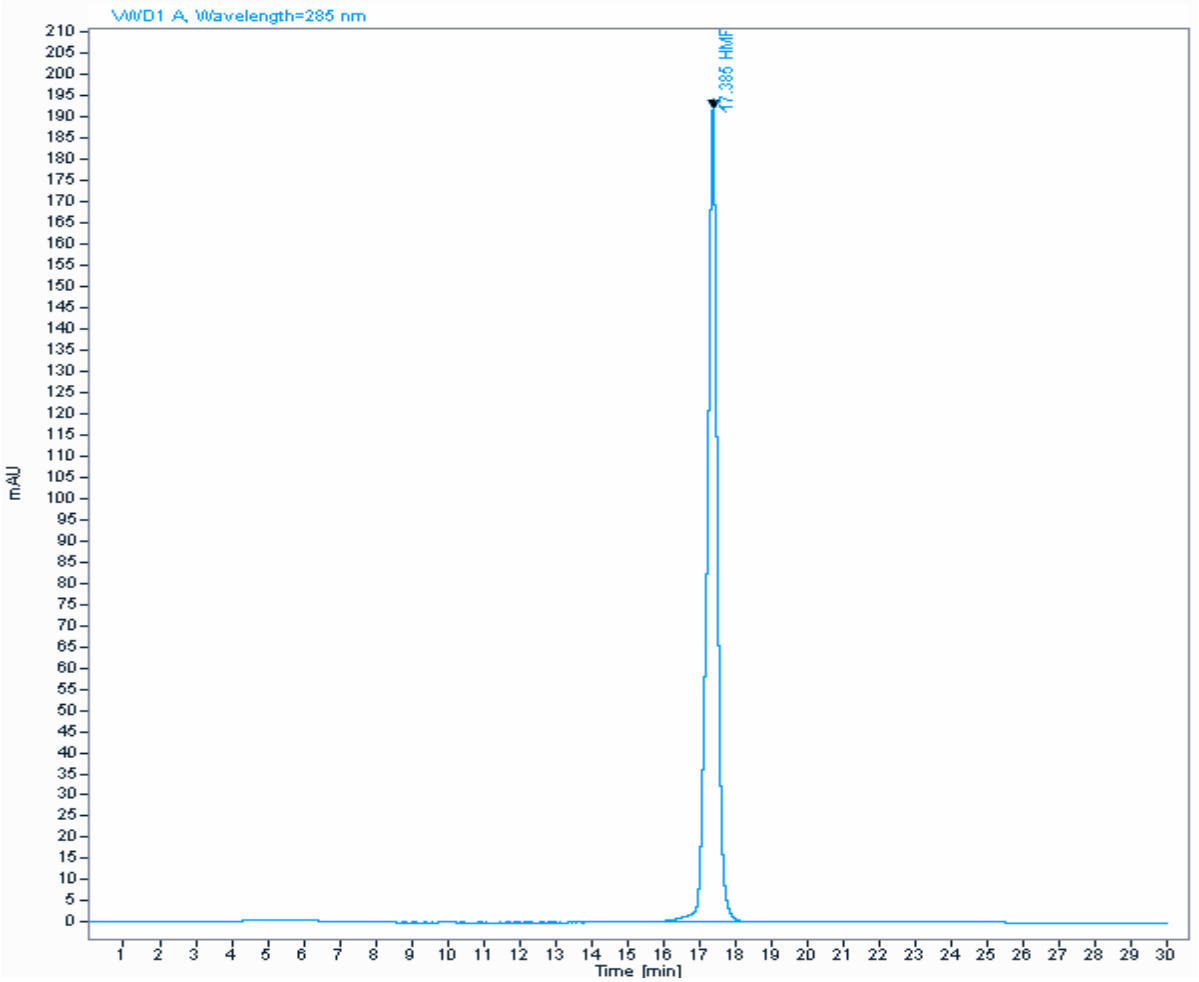
Sample name: 30 ppm HMF

Sample amount: 0.000

Instrument: 1220 Location: 24

Acq. method: HMF 04-11-17.M Injection volume: 10.000

Analysis method: HMF 04-11-17.M Acq. operator: SYSTEM



Selectivity calculation from the HPLC result

From HPLC result the area of solvent and HMF are 74.7 and 22.6287 respectively

So over all by product =100-(74.7888+22.6287)

=2.673%

Total HMF=HMF +By product

=22.627% + 2.673%

= 25.3%

Therefore, HMF selectivity=$\frac{\textbf{Area of HMF}}{\textbf{Total area of HMF}}$

$=\frac{22.627\ \%}{25.3\ \%}$

=89.4%