Synthesis and Optimization of Sugarcane Bagasse Derived Sulfonated Biochar Based Solid Acid Catalyst

By Nura Gintamo Osire

Thesis Paper Submitted to Chemical Engineering

School of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Maters of Science in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

March 2021

Adama, Ethiopia

Synthesis and Optimization of Sugarcane Bagasse Derived Sulfonated Biochar Based Solid Acid Catalyst

By Nura Gintamo Osire

Advisor: Mulugeta Yilma (Ph.D.)

Thesis Paper Submitted to Chemical Engineering

School of Mechanical, Chemical and Materials Engineering

Presented to Partial Fulfillment of the Requirement for the Degree of Masters of Science in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

March 2021

Adama, Ethiopia

APPROVAL SHEET OF EXAMINERS

A Thesis Submitted to School of Mechanical, Chemical and Materials Engineering, Adama Science and Technology University in Partial Fulfillment of the Requirements for the Award of the Degree of Master of Science in Chemical Engineering (Specialization in Process Engineering).

Signed by the Examining Board

Name	**Signature**	**Date**
Mulugeta Yilma (Ph.D.) *Advisor*	_____	_____
Zelalem Tumsa (Ph.D.) *Internal Examiner*	_____	_____
Elias Wagari (Ph.D.) *External Examiner*	_____	_____
Selvakumar Periyasamy (Ph.D.) *Chair Person*	_____	_____
Hunegnaw Baylie (M.Sc.) *Head of Department*	_____	_____
Tatek Temesgen (Ph.D.) *School Dean*	_____	_____
_____ *Post Graduate Dean*	_____	_____

DECLARATION

I declare that, this thesis work entitled "**Synthesis and Optimization of Sugarcane Bagasse Derived Sulfonated Biochar Based Solid Acid Catalyst**" for the partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering (Process Engineering Stream) at Adama Science and Technology University, hereby submitted by me, is my original work and has not been previously submitted for a degree at this university or any other university, and that all resources of materials used for this thesis have been duly acknowledged.

Name: Nura Gintamo

Signature: _____

Date of Submission: _____

This thesis has been submitted for the examination with the approval of my Advisor Mulugeta Yilma (Ph.D.), instructor in School of Mechanical, Chemical and Materials Engineering at Department of Chemical Engineering, ASTU.

Name: Mulugeta Yilma (Ph.D.)

Signature: _____

Data: _____

ACKNOWLEDGEMENT

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

I am heartily thankful to my advisor Dr. Mulugeta Yilma, for his 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 advisor, 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. Bundi Roba, at department of Material Engineering to Demeke Tesfaye, and department of Biology Eticha Abdisa for their consistent and valuable help during my experimental work. Bahir Dar University lab assistance staffs especially to Alebel for his support to experimental works. I would also like to express my appreciation towards my family for their support and offere help to attain this thesis. My honest thankfulness also goes to my best friends especially Mr. Adane Tilahun, Messay Teshome, Mr.Melkamu Girma, Mircheye and Tsegaye Assefa for their encouragement, motivating in discussions and ideas throughout the research work.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION AND ACRONYM

Word	Definition
ANOVA	Analysis of Variance
BC	Biochar
BHD	Box-Behnken Design
COOH	Carboxyl group
FTIR	Fourier Transform Infrared Spectroscopy
OH	Hydroxyl group
OSBBC	Optimized sulfonated biochar based catalyst
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
SO_3H	Sulfonic group acid group
TGA	Thermo gravimetric Analysis
XRD	X-ray Diffraction Spectroscopy

ABSTRACT

Sulfonated biochar based solid acid catalyst is an important biomass based catalyst. The synthesis of sulfonated biochar based catalyst from sugarcane bagasse for the biomass conversion is one of great practical significance for the comprehensive and efficient utilization of biomass. Sugarcane bagasse was found to be thermally stable based on TGA analysis, making it suitable as raw material for catalyst synthesis. The sulfonation variables for the synthesis of sulfonated biochar based catalyst were optimized using response surface methodology (RSM). Effects of three sulfonation variables namely, temperature (100 – 180℃), time (3-25 hr) and ratio of concentrated sulfuric acid to biochar (5:1- 25:1 ml/g) were investigated. Among three parameters studied, ratio of sulfuric acid to biochar was found to be the most significant parameter in the sulfonic group acid density since it shows low p-value (0.0001). The optimum sulfonation conditions generated numerically by the RSM were 135 ℃ of temperature, 13.3 hr of time, and 24:1mL/g ratio of concentrated sulfuric acid to biochar which gave 0.596 mmol/g amount of sulfonic group density. The optimum sulfonated biochar based catalyst was characterized by acid group titration, thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourier infrared (FTIR) spectroscopy and Scanning electron microscopy (SEM) to establish its properties.

Keywords: *Sugarcane bagasse, biochar, Sulfonated biochar based catalyst, sulfonic group acid density,*

CHAPTER ONE

1. INTRODUCTION

1.1. Background

Solid acid catalysts are a group of commonly used heterogeneous catalysts for several biomass conversion processes. Compared to conventional mineral acid/liquid inorganic catalysts, solid acid catalysts are environmentally benign, easy separation, non-corrosive and good recyclability [1]. The kinds of solid acid catalysts available comprise zeolites, metal oxides, phosphates and carbonaceous materials. In recent times, there has been great attention in the synthesis of solid acid catalysts using biochar materials derived from biomass as support. Up to now, the use of biomass as a raw materials to produce fine chemical products (e.g. catalytic materials) is becoming increasingly attractive for both academic research and practical purpose due to their numerous advantages [2]. A variety of biomass has been studied, including pelletized peanut hulls, pine pellets and pine chip char [3], rice husk [4], corn straw [5], corncob [6], cassava stillage [7], microalgae residue [8], oil palm trunk [9], biochar [10], carbohydrates (d-glucose, starch, sucrose and cellulose) [11], cocoa pod husk [12], *Musa paradisiacal* peel [13], *Musa balbisiana* Colla pells [14], camphor tree [15], rubber seed shell [16], coconut waste [17], *Lemna perpusilla* Torrey [18], tucuma peels [19], banana peels [20], bamboo and palm kernel shell [21], pine needles [22], coir fiber [23], coffee husk [24], lignin [25], lignin [26]and sugarcane bagasse [27]. Sugarcane bagasse has been used as the raw material for the preparation of solid acid catalysts and which are renewable and byproduct in the sugar process industries [28].

Biochar has received increasing attention due to its unique feature such as high carbon content, large specific surface area and stable structure [29]. Biochar refers to “a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment” according to the International biochar Initiative. Moreover, biochar is a biomass-derived char that mainly consists of 60–90% carbon with a highly porous structure. In the past decades, several studies have been performed with the heavy metal (loid)-rich biomass resulting from phytoremediation as a potential feedstock to produce valuable derivatives using thermochemical treatments, such as pyrolysis, gasification and liquefaction. Among all these, pyrolysis has been regarded as an efficient and promising biomass processing technology for production of solid residue (biochar) with different applications (i.e. soil amendment, contaminant adsorbent, catalyst support, solid fuel), a condensable liquid (bio-oil) and an un-condensable gaseous product that can be used for

energy applications [30]. Pyrolysis offers a potentially suitable solvent-free approach, which results in the breakdown of complex structures in lignocellulosic biomass by cleaving chemical bonds in the polymer chains using heat alone. Indeed, pyrolysis is the direct thermal decomposition of polymeric materials in the absence of oxygen to obtain solid, liquid, and gaseous products. Pyrolysis is the commonly used method to produce biochar from the biomass [31].

The two technologies have been successfully applied to produce biochar from biomass are pyrolytic carbonization of biomass (400–600 °C, oxygen-limited atmosphere) [32] and hydrolytic carbonization of biomass (water precipitation, 180–260 °C and pressures from 2 to10 MPa) [33]. Carbonization technologies and treatment parameters through the preparation process both play significant roles in the production of the precursors. With the treatment of hydrothermal carbonization, unstable carbon on hydrochar might be removed in aqueous reaction solution. Hereafter, the leachable carbon species reduction can improve its hydrothermal stability [34]. However, in pyrolytic carbonization a series of intense thermal reactions (i.e. e.g., decomposition, polymerization, condensation) of biomass materials induced under high temperatures, result in the generation of unstable branched and carbon side-chains of pyrochar [35].

Most of the biomass derived sulfonated solid acid catalysts are synthesized by a two-step method, e.g. a carbonization step followed by a sulfonation step. Carbonization is employed to bring formation of biochar to serve as support for the active sites [36]. Sulfonation using sulfonating reagents is then carried out to introduce the sulfonic acid ($-SO_3H$) functional groups into the biochar through covalent attachment by substitution of hydrogen in the C-H bonds of the catalyst structure [28]. An additional two-step method is the hydrothermal carbonization sulfonation method, which is demanded to be less energy intensive than the pyrolysis-sulfonation route. Hydrochars are prepared by hydrothermal carbonization of corncob at 120 -240℃ [6]. The hydrochars are reacted through concentrated sulfuric acid at 60 – 150 ℃ to gain sulfonated solid acid catalysts. For example, magnetic solid acid catalysts are prepared the alike way from banana peel feedstock [37]. Separately from the two-step method, one-step synthesis of solid acid catalysts from biomass were also reported in the literature. As suggested by Savaliya and Dholakiya [38] in which both carbonization and sulfonation are carried out in one single step. This method importantly reduces the preparation time as well as the energy requirements of the synthesis of solid acid catalysts from biomass. Sulfonated solid acid catalysts was synthesized by simultaneous

carbonization and sulfonation of sugarcane bagasse with sulfuric acid at a temperature of from 150 – 250℃ [27]. The gaps in the synthesis of sulfonated biochar based catalyst are using commercial /synthetic chemicals/ such as carbon nanotubes, microcrystalline cellulose as raw material for catalyst synthesis, preparation of active site support (biochar) from raw material without optimization of carbonization temperature, and effects of sulfonation temperature, sulfonation time, and ratio of sulfuric acid to biochar during sulfonation on sulfonic group acid density (key active site) were no studied. Biochar is a carbon-rich material which can be prepared from various organic waste feedstocks.

Recently, sulfonated carbon-based solid acid catalyst are developing rapidly and carbon material has become a hot research area because it can be applied as smart materials [39]. 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 Brønsted 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 catalytic activity. 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 [40].

Such as biomass derived solid acid catalysts is a moderately new research area. Consequently, there is limited information on the optimization of the synthesis process. In earlier days, the traditional one factor at a time method has been engaged for optimizing the process. On the other hand, it is time consuming, lengthy, and economically not viable since it includes an enormous number of experiments to assess the optimal points [33]. To overawed the above-said problems, response surface methodology (RSM) came into existence which is a multivariate statistical tool suitable for modeling the complex processes [41]. In this study, the sugarcane bagasse was used for the synthesis of sulfonated biochar based solid acid catalysts owing to its abundant availability and non-food source. A low cost non-corrosive sulfonated biochar based solid acid catalyst was synthesized by TGA suggested temperature carbonization technique and the Box-Behnken design was applied to optimize the sulfonation process variables and maximize the sulfonic group acid density of synthesized sulfonated biochar based solid acid catalysts. The numerically optimized

sulfonated biochar based solid acid catalyst with the highest sulfonic group acid density was characterized to establish its physical and chemical properties.

1.2. Statement of the Problem

Homogeneous acids, such as sulfuric acid and hydrochloric acid, are the most commonly used catalysts and proven to be highly efficient in many acid-catalyzed reactions. In spite of being cheap and efficient catalysts, homogeneous acids have the disadvantages concerning environmental issues including the production of a large volume of waste, corrosion of equipment, hazardous for operators, difficult to separate from the reaction mixture and environmental pollution [42]. Another method for chemical processes is enzymatic catalysts. Enzymatic catalysts has relatively better selectivity to chemical processes compared to acid solid acid catalysts; nevertheless, the difficulty of enzymes separation after chemical reactions, enzyme cost, and the necessity of a longer period of chemical processes it less attractive [43].

The limitations associated with the mineral acid and enzyme catalyzed industrial reactions stimulate research on the synthesis of easily reusable, environmentally benign solid catalysts. Also heterogeneous catalysts such as zeolites, cation exchange resin, niobic acid, heteropoly acids, niobium phosphate, sulfated zirconia and noble metal catalyst are commonly used in various acid-catalyzed reactions. However; these catalysts have several disadvantages including high cost, low catalytic activity, complex fabrication technology and poor stability [44]. From heterogeneous catalyst which is used in biomass transformation reactions carbon based sulfonated catalyst materials have lower production cost, renewable, abundant, and low-cost produced directly from biomass compared to other solid acid catalysts such as sulfated zirconia and niobium phosphate [45]. Among heterogeneous solid acids, carbon based sulfonated such as amorphous carbons consisting of aromatic carbon sheets bearing active sites (-SO_3H, -OH, and -COOH groups), have attracted a great deal of attention owing to their favorable characteristics such as contains different acidic and phenolic groups, high acid densities, good tolerance to water, low cost stability and reusability, which are commonly used in the acid catalyzed reactions [46]. In this study, sugarcane bagasse from Wonji/Shoa sugar factory with cane variety N14, L-188 and NCO334 is considered as a feedstock for synthesis of sulfonated biochar based solid acid catalyst, and to overcome problems related reactor corrosion in biomass conversion processes such as hydrolysis, esterification and transesterification and the establishment of more sustainable environment.

1.3. Objectives

1.3.1. General Objective

The general objective of this study is to synthesize and optimize sugarcane bagasse derived sulfonated biochar based solid acid catalyst.

1.3.2. Specific Objectives

The specific objectives of this study were:

- To synthesize sulfonated biochar based catalyst via a two-step process involving incomplete carbonization and sulfonation starting from sugarcane bagasse.
- To study the main and interaction effect of sulfonation parameters (temperature, time and ratio of sulfuric acid to biochar) on sulfonic group density of sulfonated biochar based catalyst using response surface methodology (RSM).
- To determine the optimum conditions such as temperature, time and ratio of sulfuric acid to biochar ratio that gives highest sulfonic ($-SO_3H$) group acid density.
- To characterize the synthesized catalyst using, acid group titration, TGA, XRD, FTIR and SEM.

1.4. Significance of the Study

The main significance of this research is to synthesize easily recyclable and environmentally benign sulfonated biochar based catalyst for the effective biomass conversion processes. The synthesizes of value added fine chemicals such as sulfonated biochar based catalysts from lignocellulose biomass for biomass transformation in an efficient, cost effective and environmentally friendly way. Synthesizes of sulfonated biochar based catalyst from lignocellulose biomass (i.e. sugarcane bagasse) is attractive which can substitute commercial or synthetic carbonaceous chemicals that are not economically sustainable. Sulfonated biochar based solid acid catalyst is one of the most important heterogeneous catalyst, and it can be used for a variety of industrial reactions for the biomass conversion processes. Sulfonated biochar based catalyst gets increased attention for biomass conversion processes since it is neither dissolved nor consumed in the reaction thereby makes the biomass conversion processes more efficient. Thus, shifting the biomass conversion processes trend from the conventional to the new approach of using sulfonated biochar based catalyst because it has many advantages including less pollution, low cost, easy catalyst separation from reaction mixture, reuse, metal free composition, and sustainability. Additionally, the source of the solid acid catalyst is abundantly available biomass that is a non-food source.

Therefore, this study will add some valuable knowledge on the existing facts of catalyst synthesis from the lignocellulosic biomass. In addition to this, the results of this work will indicate the potential of sugarcane bagasse to be used as a biochar source material for further catalyst development works and other applications.

1.5. Scope of the Study

In this study, characterization of feedstock (sugarcane bagasse) such as the proximate analysis, TGA analysis, and different sulfonated biochar based catalyst synthesis steps such as pretreatment of feed stock (sun drying, size reduction), carbonization of feed stock at TGA suggested temperature (i.e., 550℃) to produce biochar from feedstock (sugarcane bagasse), size reduction of biochar in mortar and pestle to get best particle size of biochar, investigations for the effects of operating variables on the sulfonation process to synthesize sulfonated biochar based catalyst, optimization of sulfonation operating variables, and characterization of optimized sulfonated biochar based catalyst and its initial biochar using acid group titration, TGA, XRD, FTIR and SEM were studied.

1.6. Organization of the Thesis

This thesis is organized into five chapters as shown below.

- Chapter one – Introduction,
- Chapter two – Literature review,
- Chapter three – Materials and methods,
- Chapter four – Results and discussion,
- Chapter five – Conclusion and recommendations.

CHAPTER TWO

2. LITERATURE REVIW

Sulfonated biochar based solid acid catalyst is one of the most important heterogeneous acid catalysts, which is used as a promising option in organic transformations into desirable chemicals [47]. Generally, the sulfonated biochar based solid acid catalysts would be equipped with functional groups of sulfonic acid groups ($-SO_3H$), hydroxyl group (-OH) and carboxyl group (-COOH) grafted on the surface by the sulfonation treatment [48].

Mainly, sulfonated biochar based catalysts was synthesized from commercial or synthetic carbonaceous chemicals. Synthesis of solid acid catalyst from commercial or synthetic carbonaceous chemicals are not economically sustainable [25]. Consequently, synthesis of sulfonated biochar based solid acid catalyst from lignocellulosic biomass such as sugarcane bagasse which can be obtained from by-products of sugarcane process industry is economically sustainable.

In general, synthesis of fine chemicals such as catalysts from lignocellulosic biomass is attractive, since abundant and cheaper compared to other catalysts support. Therefore, this study is concerned with the determination of sustainability of synthesizing a fine chemical which is called sulfonated biochar based solid acid catalyst from lignocellulosic biomass particularly sugarcane bagasse instead of commercial or synthetic carbonaceous chemicals. Furthermore, this could lead to the valorization of these waste materials while at the same time addressing waste management concerns [27].

2.1. Solid Acid Catalyst for Biomass conversion Process

Functionalized solid acid catalysts with large pore size and strong and strong acid strength such as metal oxides, sulfonated carbonaceous acids heteropoly acids and H-zeolite for biomass conversion processes aqueous medium is an effective approach thereby safeguarding the environmental sustainability, decreasing equipment corrosion, ease of separation and recyclability or reusability [49]. Between them, sulfonated carbonaceous solid acids which are prepared by sulfonation of carbonized raw material considered as a promising option in organic transformations into desirable chemicals [50]. In general, chemical reactions that were carried out privileged the use of heterogeneous catalysts not only because of environmental concerns, but also for technical and economic considerations. Altogether, the use of a renewable feedstock, production of biodegradable materials and incorporation of heterogeneous catalysis takes place this research within the concept of green

chemistry [51] and therefore, contribute to the sustainable development of our society. From those point of view carbon material has become a hot research area, and carbon-based sulfonated catalysts (CBSCs) are developing rapidly [2]. All of the CBSCs own the carbon skeleton and -SO3H group, and the carbon skeleton is stable and insoluble in most acidic/basic conditions as well as organic solvents. All of the CBSCs own the carbon skeleton and -SO3H group, and the carbon skeleton is stable and insoluble in most acidic/basic conditions as well as organic solvents.

2.2. Lignocellulosic Biomass

Lignocellulosic biomass is a long-term alternative carbon source to fossil, and it could be used as raw material to prepare liquid fuels and valuable chemicals [52]. Agricultural residues such as sugarcane bagasse, corn stover, corn cob, rice hulls, woody crops, coconut shell, oil palm trunk, corn straw, spent coffee grounds, corn straw, rice husk, citrus peel waste, sawdust, paper pulp, municipal solid waste, and paper mill sludge's and others are a great source of lignocellulosic biomass, in which they are renewable, useless, widespread, abundant non-edible and inexpensive [53]. Today, these biomasses are the most abundantly used renewable materials on the earth, and so far, they are the most suitable and favorable materials used as a feedstock for production of biochar, and other platform compounds (e.g. glucose, 5- hydroxymethylfurfural, and levulinic acid, and their derivatives) [54] which are being used in food, textile industries and biodiesel has greater environmental, economic and strategic significance [55]. Platform compounds are mainly produced via the decomposition of lignocellulose, which mainly consist of cellulose [56].

Lignocellulosic biomass is primarily composed of three main components such as cellulose, hemicellulose, and lignin [57]. These components in the lignocellulose materials have different functions and chemistries. And around 90 wt% of the dry matter in lignocellulosic biomass is made up of polymeric carbohydrates such as cellulose (20-60 wt%), hemicellulose (15-30 wt%) and lignin (10-25 wt%), and also (1-12 wt%) of extractives depends on the nature of the plant, and they occur in complex structure each other [58].

- **Hemicellulose**

Hemicellulose is an amorphous polymer, which composes of carbo pentaose and carbo hexose. Hemicellulose is another component of plant cell wall, and it is the most abundant heterogeneous group of polysaccharides next to cellulose. It is made up of pentose's (xylose, arabinose), hexoses (mannose, glucose, and galactose) and acetylated sugars. Hemicellulose

is an amorphous matrix material which binds the cellulose fibrils non-covalently through hydrogen bonding. In lignocellulose biomass, hemicellulose occurs with the composition of approximately 15-35% depends on the nature of the plant. In contrast to cellulose, hemicelluloses are differed by the composition of various sugar units, lower degree of polymerization (around 100-200), low strength and easy to hydrolysis, shorter and branched molecular chains and are lower crystalline than of celluloses.

- **Lignin**

Lignin is the third most abundant component of lignocellulosic biomass next to cellulose and hemicellulose and they are surrounded by cellulose and hemicellulose. Lignin is a structural skeleton in plant cell walls. The degree of lignification is involved with the compressive strength of stems and the dehydration of plant cell walls. Lignin is an amorphous aromatic network polymer which is made up of phenylpropane units through carbon-carbon and ether bonds. It is difficult for microbes to decompose the structure of this connection. The most inert component in the cell wall of plants is lignin. Also, lignin is considered as the "cement" of the cell wall that increases its structural rigidity and confers mechanical strength to the plant. Lignin is a composition of monomeric components such as; p-coumaryl, coniferyl or sinapyl alcohols, and these components are inter-linked in between lignin and hemicellulose as well as between lignin and cellulose. Due to strong inter-linkage between the components, such as ester, ether, or glycoside bonds, lignins are extremely resistant to biodegradation and they occur in the form of three-dimensional in the plant cell wall in nature.

- **Extractives**

Extractives are other components of lignocellulose biomass, which includes, the non-structural aromatic compounds, such as volatile oils, chlorophyll, fatty acids, waxes, resins, tannins, terpenes, sterols, inorganic compounds and so on, and they can be extracted with polar and non-polar solvents. These components can occur in the plant cell wall in small quantities, approximately 1-12% of the total lignocellulosic biomasses.

2.3. Sugarcane Bagasse as a Raw Material for Synthesis of Sulfonated Biochar Based Catalyst

Most of the biochar sources currently used for catalyst synthesis are expensive commercial or synthetic carbonaceous chemical feedstocks such as microcrystalline cellulose, glucose, graphene oxide, tannic acid, sucralose, and carbon nanotube [25]. Lignocellulosic biomass-derived feedstocks have been publicized as one of the most likely alternatives for the

synthesis of value added fine chemicals [59]. Consequently, the search for green and sustainable biochar sources is important for the synthesis of sulfonated biochar based catalyst. Sugarcane bagasse has the advantage of low cost, availability, and can be obtained from by-products of sugarcane process industry. Therefore, in this study, lignocellulose biomass, particularly sugarcane bagasse was used for the synthesis of fine chemicals particularly for synthesis of sulfonated biochar based catalyst. Sugarcane bagasse is obtained after the juice extraction in the sugar production industries, and approximately 540 million tons per year of sugarcane bagasse is produced in the world [60].

2.3.1. Pretreatment of Sugarcane Bagasse

Lignocellulose biomass such as sugarcane bagasse has a complex and inflexible structure. So, pretreatment is one of the most important process steps for synthesis of fine chemicals such as catalysts. The goal of pretreatment is to change or even destruct the lignocellulosic structure so that the carbonization effectiveness can be enhanced.

On the whole, lignocellulosic biomass pretreatment methods can be classified into four common categories [61]. These are, physical pretreatment, physicochemical pretreatment, and biological pretreatment. The most important lignocellulosic biomass pretreatment method used to enhance the effectiveness of carbonization is physical pretreatment. Physical pretreatment method includes size reduction by mechanical methods such as grinding /milling and drying. Reduction of particle size is required to make material handling easier, and to enhance uniform heat transfer during carbonization, and it can be done by grinding, milling and chipping. On the other hand, this method of pretreatment needs a tremendously high amount of energy to reduce the size of the feedstock from large size to a particle size of a millimeter and fine particles of micrometers, which is undesirable from the engineering perception [62]. From the physical treatment methods, grinding and milling methods are more operative at reducing the particle size. Drying is the easiest pretreatment process to reduce the moisture of feedstock to below 10%wt.

2.4. Proximate Analysis of Precursor

Proximate analysis is the most often used analysis for characterizing a material in connection with their utilization. The proximate analysis of a substance means of determining the distribution of products obtained when the char sample is heated under specified conditions. When analysis of biomass involves the determination of ash, moisture, volatile matter and fixed carbon, it is called proximate analysis [63].

2.5. Preparation of Biochar

Biochar is considered as a versatile carbon platform for developing functional materials with multidisciplinary applications. Activation, amination, oxidation, recombination and sulfonation are the principle functionalization processes with products used for energy storage, pollutant mitigation, biorefinery, soil remediation and solid acid catalysis[64]. Biochar is a carbon-rich material which can be prepared from various organic waste feedstocks, such as agricultural wastes and municipal sewage sludge under certain thermal combustion with limited oxygen [64]. In general, biochar produced at high temperature has higher surface area and carbon content, mainly due to the increase of micro-pore volume caused by the removal of volatile organic compounds at high temperature [65]. However, the biochar yields decreased with the increase of temperature [66]. Therefore, an optimal strategy is needed in terms of biochar yields. Biochar can be used directly as a soil conditioner, water purification, adsorption [67], energy storage and heterogeneous catalysis[68]. Recently, biochar is used for the synthesis of solid catalyst by functionalizing with different chemical [69]. The catalytic activity of biochar derived catalyst is highly correlated to its porosity, surface area and mineral content. In addition to this, biochar material has high contents of oxygen (27–34 wt. %) mostly in the form of acidic groups such as phenolic and carboxylic. Biochar with remarkable specific surface area and porous structure is more desirable for hydrophobic acid-catalyzed process, which provides the catalyst with more effective active sites to capture the amorphous part of cellulose [70]

Biochar is a promising green materials that have been utilized successfully to synthesize value added products such as sulfonated carbon catalysts. Biochar based solid acid (SO_3H), which could be easily synthesized by sulfonation of biochar, is widely used in variety of fields as proton donor, particularly hydrolysis of cellulose [36]. Firstly used biochar generated from glucose as the support for the synthesis of solid acid catalysts, and it exhibited high catalytic activity for the hydrolysis. Feedstock can be converted into char using the carbonization processes including pyrolysis, gasification and hydrothermal carbonization. The common carbonization processes for preparing of biochar is pyrolysis, while the char obtained by gasification and hydrothermal carbonization generally do not meet the definition of biochar. And also, compared to the conventional preparation methods of carbon materials such as graphene, biochar preparation by pyrolysis is facile and low-cost, which contributes to the environmental sustainability [71]. There are different pretreatment methods before carbonation of the biomass: physical, physiochemical,

chemical, biological, electrical, or a combination of the methods. Typical physical pretreatment methods include chipping, grinding, milling and thermal methods [72]. The pretreatment aims at improving productivity and profitability by reducing particle size, increasing pore size and removing inhibitors resulting in structure alternation. In general, biochar obtained from biomass has abundant functional groups (C−O, C=O –COOH, and –OH), which being highly modifiable act as a platform for the synthesis of various functionalized carbon materials [73]. Biochar that is functionalized with H_2SO_4 is novel, recoverable, and renewable solid acid catalyst for hydrolysis of cellulose and biodiesel production [74].

2.6. Synthesis of Biochar Based Sulfonated Catalyst

In recent years, the utilization of biochar as the starting material for synthesis of solid acid catalyst for biomass transformations has gained significant attention. In view of catalyst synthesis, sulfonated carbon catalysts synthesized via a two-step process involving carbonization of lignocellulosic biomass at a temperature of 350 ℃ − 700 ℃ for about 0.5 −4 h followed by sulfonation at a temperatures of 80 −210 ℃ for about 15 h [75] . Carbonization is employed to induce formation of small polycyclic aromatic carbon that will support active site [36]. Sulfonation using sulfuric acid is then carried out to introduce the sulfonic acid ($-SO_3H$) functional groups into the aromatic carbon of carbon rings of the amorphous carbon sheets [76]. It is one of the most efficient routes for biomass-upgrading, biofuel production, and carbon-based catalyst (e.g., solid acids) synthesis. Sulfonic acid group ($-SO_3H$) bearing solid acids synthesized via sulfonation process are one of the main avenues for solid acid catalyst production. Sulfonation of biochar increases the total acid density of sulfonated carbon based catalyst by forming $-SO_3H$ groups and additional weak carboxylic (−COOH) and phenolic (-OH) groups. Characterization of solid acids catalysts revealed that the carbon materials consist of uniformly functionalized graphene sheets, bearing $–SO_3H$, -COOH and phenolic groups that are different compared to conventional solid acids bearing a single functional group. The excellent performance of sulfonated carbon-based catalysts opens a broad range of opportunities for biomass transformation processes including hydrolysis for bioethanol production, esterification and transesterification for biodiesel production and dehydration for furfural production. The high performance of the sulfonated solid acid catalysts for cellulose hydrolysis is attributed to phenolic–OH and –COOH groups in the carbon material, which are capable of adsorbing cellulose and water molecules effectively. Afterward, the $–SO_3H$ groups bonded to the

carbon material decomposes the hydrogen bonds and hydrolyze the β-1,4-glycosidic bonds in the adsorbed cellulose molecules [77].

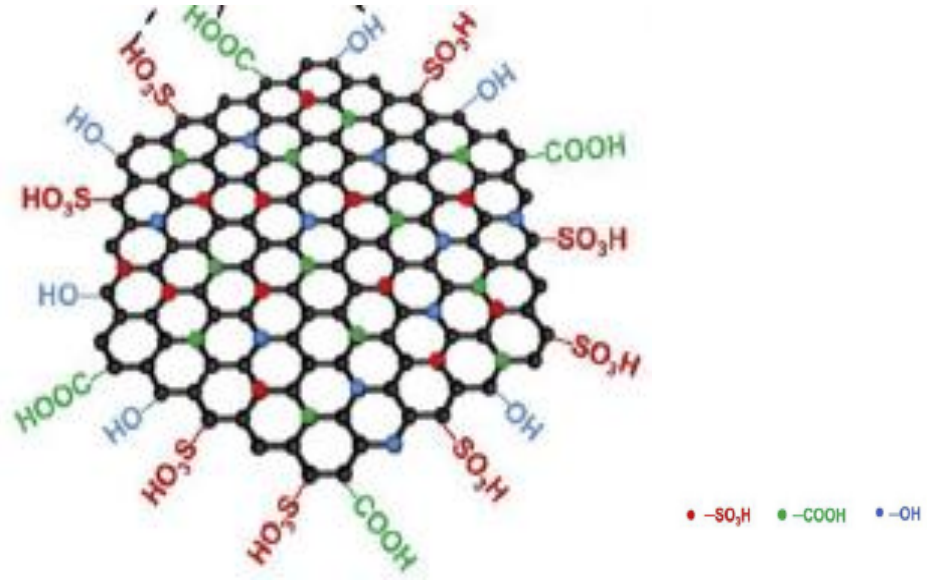


Figure 2.1 Structure of the sulfonated carbon catalyst [25]

2.6.1. Factors that Affect the Performance of Biochar Based Catalyst

2.6.1.1. Carbonization Temperature

The temperature at which the biochar produced has a significant effect on biochar based catalyst. When the carbonization runs at higher temperature (>650℃) it will create more rigid structure in carbon material that makes unfavorable for the sulfonic acid group introduction. To avoid such rigidity generally, the synthesis of biochar at a pyrolysis temperature (400 – 600°C) will result in the generation of soft aggregated, cross-linked polymer that is suitable for the introduction of the sulfonic group [78].

2.6.1.2. Sulfonation Reagents

For converting biomass or biochar to sulfonated solid acids, commonly used sulfonating reagents include concentrated sulfuric acid, oleum, sulfamic acid, and p-toluenesulfonic acid. The first three chemicals are widely used in sulfonation reagents in industry and the first two are more intensive than others. Concentrated sulfuric acid (H_2SO_4; 98% - 100%) is reactive towards numerous organic feedstocks, and the sulfonation reaction is usually mild with few side reactions and less by products [79].

Excessive quantity of concentrated sulfuric acid in bochar sulfonation is preferable due to the reason of excessive use of concentrated sulfuric acid can decrease the viscosity of the reaction solution, thus enhancing the heat transfer inside the solution[79].

2.6.1.3. Sulfonation Temperature

The sulfonation temperature affects greatly the concentration of $-SO_3H$ groups on the carbon-based catalysts. An increase in the sulfonation temperature could increase $-SO_3H$ group density on carbonaceous materials but the excessively high sulfonation temperature may trigger the degradation of some components and negatively affect the acid density [80].

2.6.1.4. Sulfonation Time

A suitable sulfonation time is essential for the linkage of $–SO_3H$ groups and carbon materials during the sulfonated carbon catalyst preparation process. Prolonging the sulfonation time increases the $–SO_3H$ density in sulfonated carbon catalyst. However, longer sulfonation time to functionalize the carbonized materials did not significant show effect on $–SO_3H$ density [81].

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Materials

The materials used during the experimental work were sugarcane bagasse, concentrated sulfuric acid 96% (H_2SO_4), Hydrochloric acid (HCl 37 %), Ethanol, Sodium chloride (NaCl), sodium hydroxide (NaOH) and phenolphthalein indicator. All above chemicals were analytical grade.

3.2. Equipment

The type of Equipment's used during the experimental work includes digital mass balance, grinder, sieves, Muffle furnace, centrifuge, oven, digital pH meter, hot plate, shaker, crusher, autoclave reactor, ball mill, grinder, vacuum pump, TGA, XRD, FTIR, and SEM.

3.3. Research Procedure

The overall procedure of this thesis work procedures is, as illustrated in Figure 3.1**.** Collection of sugarcane bagasse as raw material was done from Wonji/Shoa sugar production factory. Afterwards, preparation of sugarcane bagasse, proximate analysis of sugarcane bagasse, carbonization of sugarcane bagasse at TGA suggested temperature, soaking of biochar in HCl, washing, drying of biochar and sulfonation of the biochar and characterization of sulfonated biochar based catalyst such as, sulfonic group acid density and total acid density was done at School of Mechanical, Chemical and Materials Engineering at Chemical Engineering department Laboratory, ASTU. The characterization of the raw sugarcane bagasse, biochar and sulfonated biochar based catalyst such as TGA and FTIR analysis were done at School of Chemical Engineering at Bahir Dar University, BDU. XRD analysis of sulfonated biochar based catalyst and its initial biochar was done at School of Material, Chemical and Material Engineering at department of Materials Engineering, ASTU. SEM analysis of sulfonated biochar based catalyst, and biochar were done at School of Natural Science at department of Biology, ASTU.

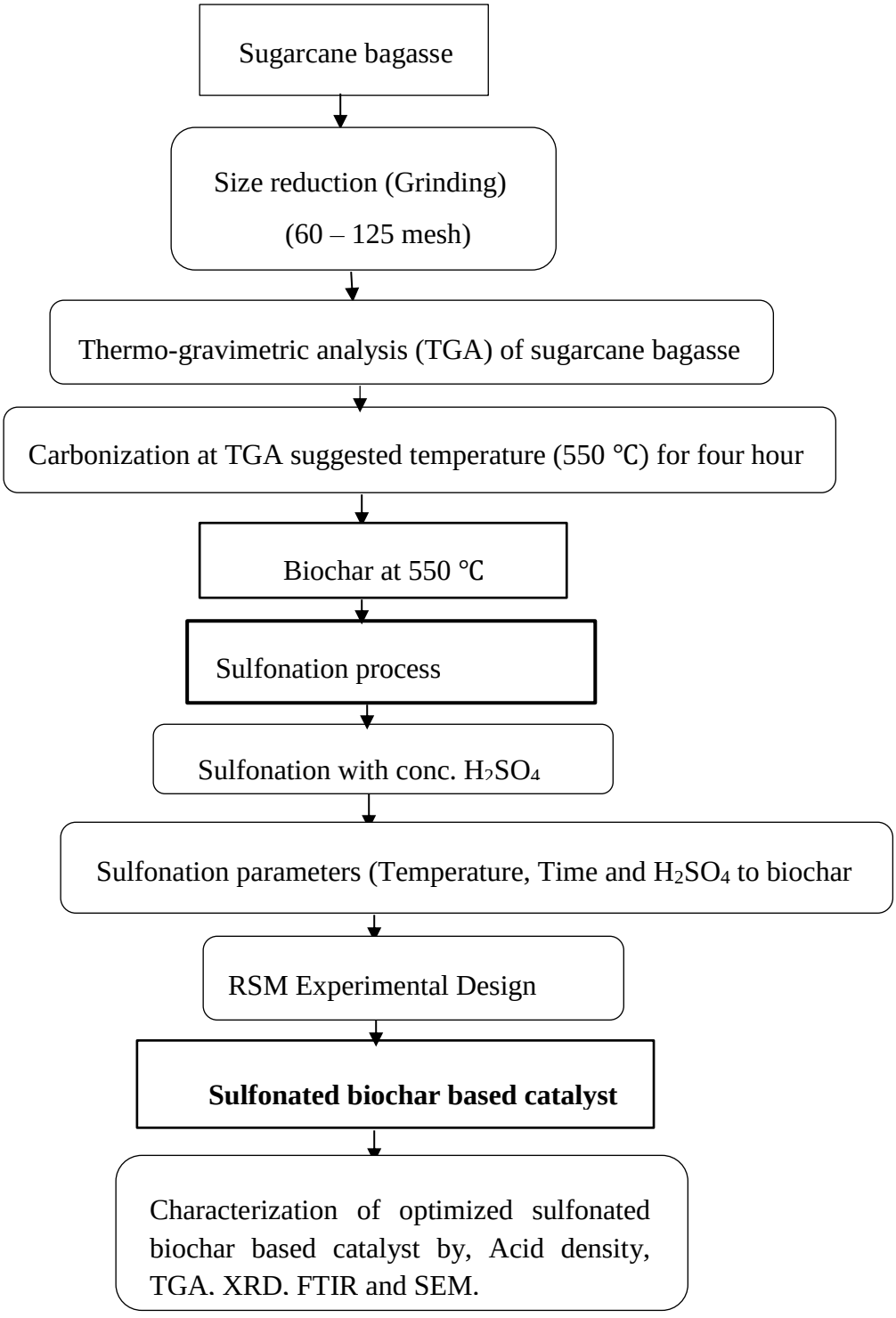


Figure 3.1 Over all thesis work procedure

3.4. Methodology

3.4.1. Sample Collection and Preparation

In this study, the raw material sugarcane bagasse (i.e. the feedstock) was collected from Wonji/Shoa Sugar factory. After the sample is collected it was sun dried for two days to reduce the moisture content and then after were oven dried at 105 ℃ for 24 hr until a moisture content of less than 10% w/w was achieved. After that, cut into small pieces with knife by hand (length less than 4 mm) and then subjected to a grinding process in a ball milling, followed grading by using sieves of 60 and 125 mesh and they were collected in plastic bags under dry condition prior to use for next experiments.

Figure 3.2 a) Sugarcane bagasse before size reduction; b) Size reduction of sugarcane bagasse using Ball mill at 150rpm; c) Sample after size reduction

3.4.2. Characterization of Feedstock (Sugarcane bagasse)

In this section, the proximate analysis of the lignocellulose biomass was calculated. The measured values of proximate analysis such as moisture content, volatile matter, ash content and fixed carbon of feedstock's are important factors to understand the nature and the properties of the feedstock.

In the synthesis of Sulfonated biochar based catalyst, an important consideration was the carbon content of the catalyst support. Among the proximate components, special interest was given to the fixed carbon content.

3.4.2.1. Proximate Analysis of Sugarcane Bagasse

Proximate analysis was used to determine moisture content, volatile matter, ash content, and fixed carbon of the sample. The procedure for proximate analysis of sugarcane bagasse was adopted from ASTM method D1762-84.

A). Determination of moisture content

The crushed sugarcane bagasse with desirable size was put into crucible. The crucible was weighed with and without the amount of sugarcane bagasse sample. The crucibles containing the samples were heated in an oven at 105 ℃ for 2 h, transferred to a desiccator and allowed to cool for an hour prior to weighing. This drying procedure was repeated until no change in weight is obtained. Finally, the weight was taken and compared with the initially recorded weight. The percentage weight of moisture in the sugarcane bagasse sample was calculated using the formula:

$$\%M\ (\frac{\%W}{W}) = \frac{W_1 - W_2}{W_1} \times 100\% \quad (3.\ 1)$$

Where, %M is the moisture content, W_1 is the original weight of the sample before drying and W_2 is the weight of the sample after drying.

B). Determination volatile matter

For the determination of volatile matter content, the crucibles were covered with crucible lids were pre-heated in a furnace at (950 ℃) for 5 minute. The crucible was then cooled in a desiccator and weighed. The weight of the sample between before heating and after heating was used to determine the amount of volatile matter present in the sample using the following equation.

$$\%VM\ (\%\frac{W}{W}) = \frac{M1 - M2}{M1} \times 100\% \quad (3.\ 2)$$

Where, VM is the volatile matter, M_1 is grams of sample before drying and M_2 is grams of the sample after heating at 950 ℃.

C). Determination Ash content

For the determination of ash content, the uncovered crucibles containing the samples used for the determination of volatile matter were placed in the furnace and heated at 750 ℃ for 6 h. After the required heating, the crucible was cooled in a desiccator and then weighed. The amount of residual substance is equal to the ash present in the sample.

$$\%Ac\ (\%\frac{W}{W}) = \frac{Md}{Mc} \times 100\% \quad (3.\ 3)$$

Where, A is ash content, M_d is grams of residue and Mc is gram of sample before drying

D). Determination of fixed carbon

The fixed carbon content is determined by subtracting the sum of volatile matter content and ash content form 100 by assuming the negligible content of other elements. The value obtained is the amount of fixed carbon present in the sample expressed in percentage. The percentage of fixed carbon content in the sample was calculated using the formula:

$$FC= (\%\frac{w}{w}) = 100\% - \%Vm - \%Ac \quad (3.4)$$

Where, FC is fixed carbon, VM is volatile matter and Ac is ash content

3.4.2.2. Thermo-gravimetric Analysis (TGA) of Sugarcane Bagasse

The optimal carbonization temperature of sugarcane bagasse was determined by using thermogravimetric analysis (TGA) following the method reported in the literature [82], which is useful in selecting the optimum temperature for carbonization of the sample. The raw sugarcane bagasse was first washed and dried in the oven at 105 ℃ for at least 24 hr prior to analysis. The TGA analysis was performed under operating conditions: heating rate of 20℃, temperature range of 30-800℃, and nitrogen purging at 20 ml/min rate of flow.

3.4.3. Preparation of Biochar

Sugarcane bagasse was used as a starting feedstock raw material for the preparation of the biochar by carbonation. The sugarcane bagasse was cleaned by water for removing dust particles as well as other impurities. Thereafter, they were subjected to additional cleaning by deionized water for removing residual ions, after which they were dried in a hot air oven; this removes the moisture. The sugarcane bagasse grains fraction with greater retention (> 60 mesh) were carbonized in a muffle furnace. The carbonization temperature was determined prior to the process by TGA of the raw sugarcane bagasse to determine the temperature at which the mass loss was negligible resulting in a steady residual mass. The obtained temperature used for carbonization. After carbonation, the sample is cooled by the running water. The carbonized biochar was then soaked in 0.1 M HCl and stirred for one hour to remove the ash contents that may clog the pores, followed by washing with distilled water several times until the pH of the washing solution was neutral. Then the biochar was dried at drying oven 105 ℃ for 12 h and then was pulverized using a mortar and pestle (i.e.in order to improve acidity by exposing more surface sites) and stored in airtight containers prior to sulfonation process.

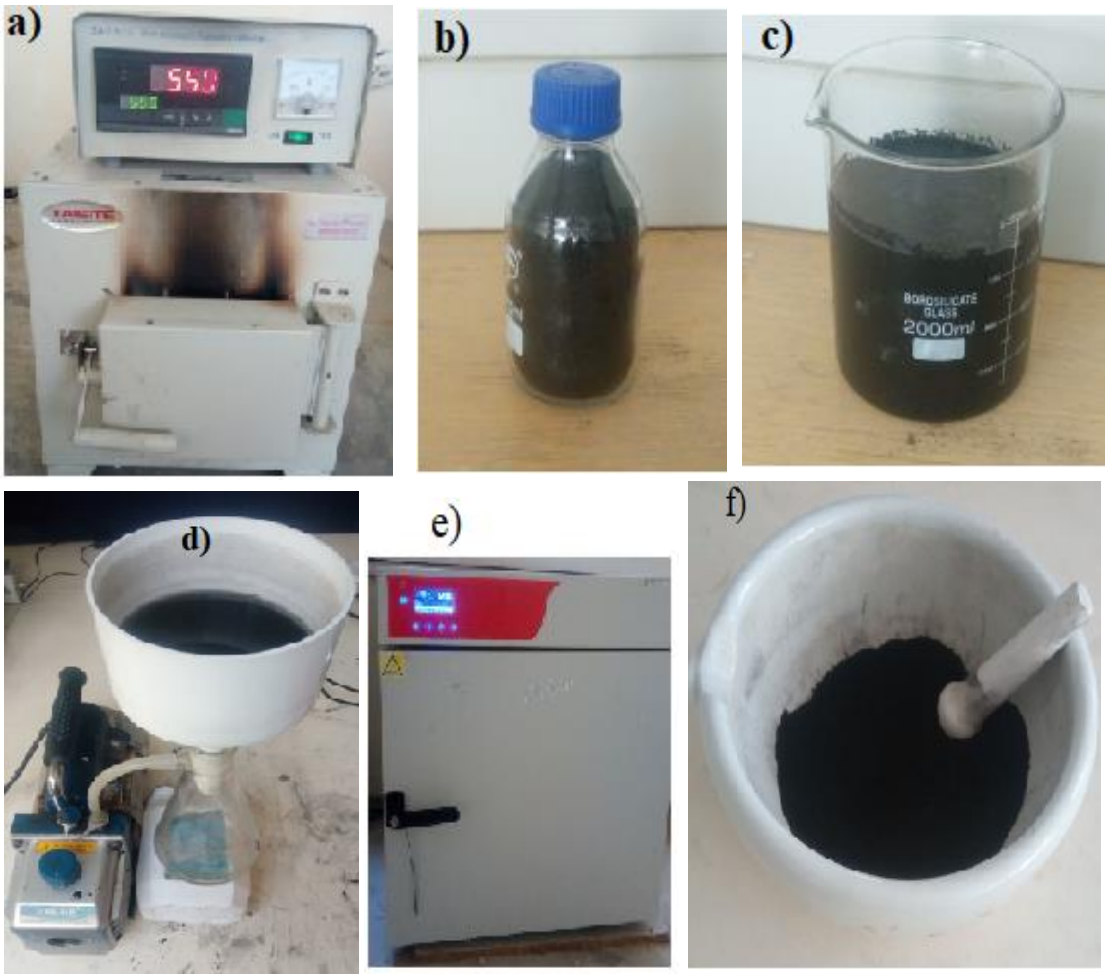


Figure 3.3 a) Sieved raw sugarcane bagasse and thermogravimetric ally analyzed (TGA) sugarcane bagasse Carbonization in Muffle furnace at 550℃ ; b) Sample of biochar after carbonization of sugarcane bagasse; c) Sample after soaking of biochar in 0.01 M HCl; d) Vacuum filtration to separate the liquid from the solid (biochar); e) Washed biochar drying set up at 90 ℃ for 24 hr; e) Biochar pulverization using mortar and pestle

3.4.4. Functionalization (Sulfonation) of Biochar

The biochar's prepared at Thermo-gravimetric analysis (TGA) suggested temperature was then functionalized with concentrated sulfuric acid (98% H_2SO_4) was used to introduce sulfonic groups onto the biochar support. For sulfonation processes, the ratio of sulfuric acid (H_2SO_4) to biochar were varied from (25:1 to 5:1) and sulfonation reaction took place in a Teflon autoclave reactor and used hot air oven for heating the desired sulfonation temperatures range of 100−180℃ and sulfonation time (5 to 23 hr). After the reaction, the samples were cooled down to room temperature and then slowly transferred to a beaker with

deionized water. The mixture was cooled down and separated by vacuum filtration. The solid residue was washed with hot (> 80°C) deionized water until pH of wash water was equal to that of the initial deionized water. The washed sample was then dried at 105°C for at least 24 h to obtain the sulfonated biochar based catalyst. The parameters, sulfonation temperature, sulfonation time and sulfuric acid to biochar ratio were investigated by RSM experimental design during the preparation process of the sulfonated biochar based catalyst.

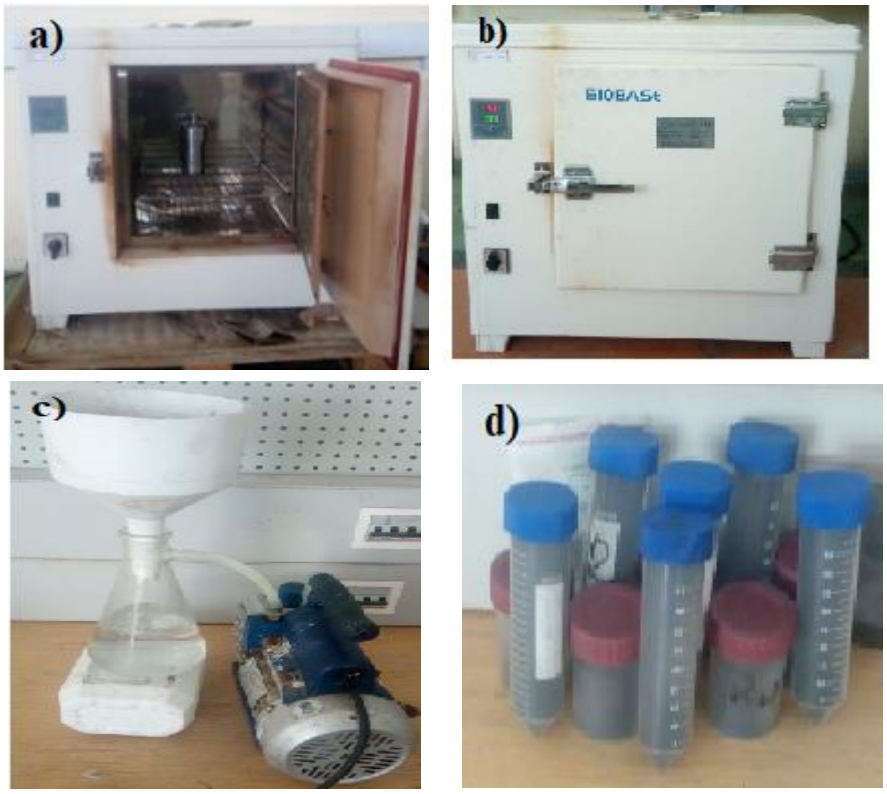


Figure 3.4 a) Teflon lined autoclave reactor set up; b) Biochar sulfonation process experimental set up in oven; c) Vacuum filtration to separate the liquid from sulfonated biochar based catalyst; d) Samples of sulfonated based catalyst after sulfonation.

3.4.5. Experimental Design for Sulfonated Biochar Based Catalyst Synthesis

In the synthesis process, there are several parameters that have an effect on the sulfonic group acid density. The conventional method of experimenting with one variable at a time is time consuming and labor intensive. Box-Behnken experimental design (BHD), one of the response surface methodologies, was used to find the optimum synthesis conditions to attain highest sulfonic group acid density. Box-Behnken experimental design (BHD), was preferred over the usual central composite design as it has the advantage to avoid treatment combinations that are extreme. The response surface methodology was applied to evaluate

the impacts of sulfonation parameters. Sulfonation temperature, sulfonation time and ratio of sulfuric acid to biochar have been selected as input parameters for sulfonation process as shown in Table 3.1. In order to find the optimum synthesis condition to achieve highest sulfonic group acid density (-SO_3H), a Box-Behnken experimental design (BHD) with three variables, three levels and fifteen experimental runs was applied as shown in Table 3.**2** and three center point runs as replicate which helps to reduce experimental error [83]. The number of experiments was determined according to:

$$N= k^2 + k + c \quad (3.5)$$

Where N is experimental runs, k is the variables number and c is the center point

Table 3.1 Range and levels of independent variables for sulfonation process. The lower and higher levels are chosen by considering the operating limits of sulfonation process conditions.

Table 3.1 Range and levels of independent variables for sulfonation process optimization

Independent variables	Units	Low	Middle	High
Temperature	℃	100	140	180
Time	hr	5	14	23
Ratio of sulfuric acid to biochar	mL/g	5:1	15:1	25:1

Table 3.2 Total number of Box-Behnken Design (BHD) experimental design matrix

Run	Factor 1	Factor 2	Factor 3
	A:Temperature (^oC)	B:Time (hr)	C:Ratio of sulfuric acid to biochar (ml/g)
1	140	14	15
2	140	14	15
3	100	14	5
4	140	5	5
5	140	14	15
6	100	23	15
7	180	5	15
8	100	5	15
9	180	14	25
10	140	23	5
11	180	23	15
12	140	23	25
13	100	14	25
14	180	14	5
15	140	5	25

3.4.6. Catalyst Characterization

Catalyst was characterization by titration method, TGA, XRD, FTIR, and SEM.

3.4.6.1. Acid Group Titration

The titration method employed here to determine the amount of SO_3H group density and total acidity group density existed in sugarcane bagasse biochar as well as in sulfonated sugarcane biochar based catalyst was established according to a previous work [84]. Typically, 0.1 g of catalyst was added into a sodium chloride aqueous solution (10 mL, 0.05 mol/L), and followed by 1 h ultrasonic treatment at room temperature. After filtration, the supernatant was titrated with an aqueous solution of sodium hydroxide (0.05 mol/L) using phenolphthalein as indicator and the titration was continued until the equivalent point colorless to pink is recognized. The SO_3H content was the moles of sodium hydroxide used in titration. 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:

$$SO_3H \text{ density (mmol/g)} = \frac{Volume\ of\ NaOH\ used\ in\ titration \times Normality\ of\ NaaOH}{mass\ of\ catalyst} \quad (3.6)$$

The total acid density was determined using back titration method. A mass of 0.1 g of catalyst was added into a sodium hydroxide aqueous solution (10 mL of 0.05 M NaOH) and the mixture was sonicated for hour at room temperature. The analyte (NaOH solution) was titrated against the titrant (0.05 M HCl) using the phenolphthalein as an indicator and the titration was continued until the equivalent point pink to colorless is renowned. 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 TA) was calculated using the following formula:

$$TA \text{ (mmol/g)} = \frac{Volume\ of\ NaOH \times Normality\ of\ NaOH - Volume\ of\ HCl \times Normality\ of\ HCL}{Mass_{\ catalyst}} \quad (3.7)$$

Figure 3.5 a) Samples before ultrasonic treatment; b) Ultrasonic treatment of catalyst using ultrasonic cleaner at room temperature for 1 hr.

3.4.6.2. Thermogravimetric Analysis (TGA)

The thermal stability of the sulfonated biochar based catalyst was done 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 thermoxidative degradation.

3.4.6.3. The X-Ray Diffraction (XRD)

X-ray diffraction was involved to represent structural information of the sulfonated biochar based catalyst and biochar 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 $4°min^{-1}$.

3.4.6.4. Fourier Transform Infrared (FTIR) Analysis

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

3.4.6.5. Scanning Electron Microscopy (SEM)

The surface morphology, of selected sulfonated biochar catalyst and its initial biochar were analyzed using JEOL scanning electron microscope.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

This chapter includes the results of all the laboratory activities such as characterization of the feed stock (e.g. proximate analysis, which includes: the percentage of moisture content, volatile matter content, ash content as well as fixed carbon content of the sample, and the thermo-gravimetric analysis (TGA) of the sample). And also, it includes different analysis and studies with the most operational parameters, in catalyst synthesis which affects the sulfonation of biochar using Design expert®11.0 software. Furthermore, it includes the characterization results of optimized sulfonated biochar based catalyst and its initial biochar using acid group titration, TGA, XRD, FTIR and SEM.

4.1. Characterization of Sugarcane Bagasse

4.1.1. Proximate Analysis of the Raw Sugarcane Bagasse

Figure 4.1 shows the proximate analysis of the raw sugarcane bagasse.

Sugarcane bagasse used in this study was determined of its proximate constituents and was found to have the following composition from the triplicate analysis: 8.97 moisture content, 77.9 volatile matter, 4.12 ash content and 17.96 fixed carbon in % w/w based on dry basis. Based on the dry basis the percentage of fixed carbon content was estimated by difference as follows: FC (%) =100 %-(%Vm+%Ac) [85]. These results are within values reported in literature (73.78−78.6% volatile matter, 3.3−11.27% ash content, 14.95−18.1% fixed carbon) [86]. The sugarcane bagasse delivered had a moisture content of about 8.97%, which is well accepted value for production of biochar. The moisture content influences the heat transfer during carbonization process by posing significant effect on product distribution and also, its increase increases the pyrolysis reaction temperature. From the literature, an increase in moisture content increased liquid product yield whereas the biochar and gas yields decreased [87]. This is because the moisture present in the biomass produce large quantities of condensate water in liquid phase. Mostly, moisture content less than 10% is appropriate to achieve high yield of biochar. Therefore, in this study the moisture content of physically pretreated sugarcane bagasse was 8.97% that is lower than 10% and reasonably appropriate for high biochar yield. As shown in Figure 4.1, sugarcane samples has a volatile matter of content of 77.9% and this value was viewed as a higher value in other previous works by [88]. The high amount of volatile content require higher time during carbonization process to remove them for effective carbonization product quality. However, the biomass with higher volatile matter gives many porous which was used for the grafting of sulfonic group

during sulfonation step. Moreover, as volatile matter increased then fixed carbon and ash content is decreased. The fixed carbon content of sugarcane bagasse obtained in this study was relatively higher than some other biomass [89]. In the synthesis of solid acid catalyst from biomass, an important consideration is the fixed carbon (FC) content of the catalyst. The fixed carbon content of the sugar cane bagasse used in study (i.e.17.96%) was within the range of values (9.53 -35.2%) of fixed carbon contents of the other biomass residues that were studied as raw material for the synthesis of solid acid catalysts [90]. The proximate analysis result of sugar cane bagasse, which reveal a significant amount fixed carbon content (17.96%) when compared by other biomass residues, which is enough for developing a carbonaceous support, providing the chosen precursor material suitable for attachment of sulfonate group during sulfonation.

Biomass ash content is classified as low (<5%), medium (5−10%) and high (< 10%) [88]. Based on this classification, the sugarcane bagasse considered in this study has low ash content (4.14) which would result in minimal effect of inorganic impurities during carbonization. The ash content in biomass also contains of mainly minerals such as silica, alumina, iron, magnesium, calcium and mineral salts. These mineral salts are considered as impurities that clog the pores and part of concentrated sulfuric acid was consumed owing to reactions between inorganic salts and concentrated sulfuric acid and the decreased concentration of concentrated sulfuric acid is not beneficial to the secondary sulfonation of aromatics [91]. Therefore, this proximate analysis results of the sugarcane bagasse was considered as fit for the synthesis of solid catalyst in this work.

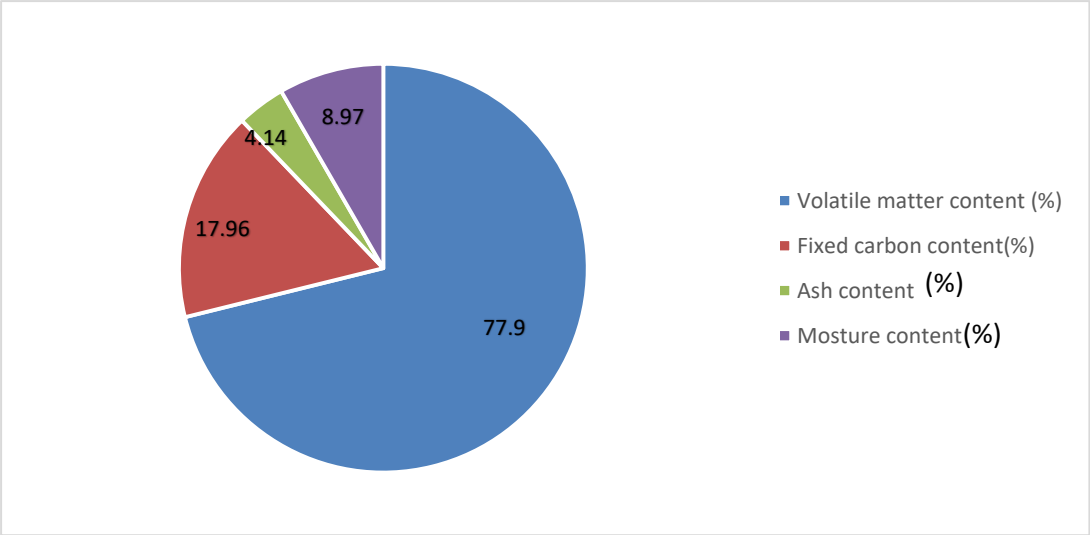


Figure 4.1 Proximate analysis result of raw sugarcane bagasse

4.1.2. Thermogravimetric Analysis of Raw Sugarcane Bagasse

The TGA curves for the raw sugarcane bagasse is shown in Figure 4.2. Thermal stability of the raw sugarcane bagasse was determined using thermos-gravimetric analysis. According to the TGA reports obtained as can be seen from Figure 4.2, it is clear that all volatile matter is lost when temperature is rise up to 550 ℃. Further rise in temperature till 800 ℃ does not affect the mass loss considerably, and residual mass is constant at round 32%. Thus the carbonization temperature is set at 550 ℃. In general, in the TGA curve the weight loss in temperature range between 30-550 ℃, is due to loss of water molecules, physically adsorbed moistures and volatile organic components. In the temperature range between 30 –250 ℃ , evaporationof free waters, small amounts of volatile matters are removed and a temperature range of 250 -550 ℃ , here loss of high amount of volatile matter occurs and maximum mass loss is achieved. From the literature, similar finding with this study, weight loss in the TGA curve of sugarcane bagasse in the temperature range between 350-550 ℃, which is accribed to organic matter [92]. Moreover, the TGA curve of sugarcane bagasse analyzed in study was similar with TGA curves of sugarcane bagasse reorted in the literature [93].

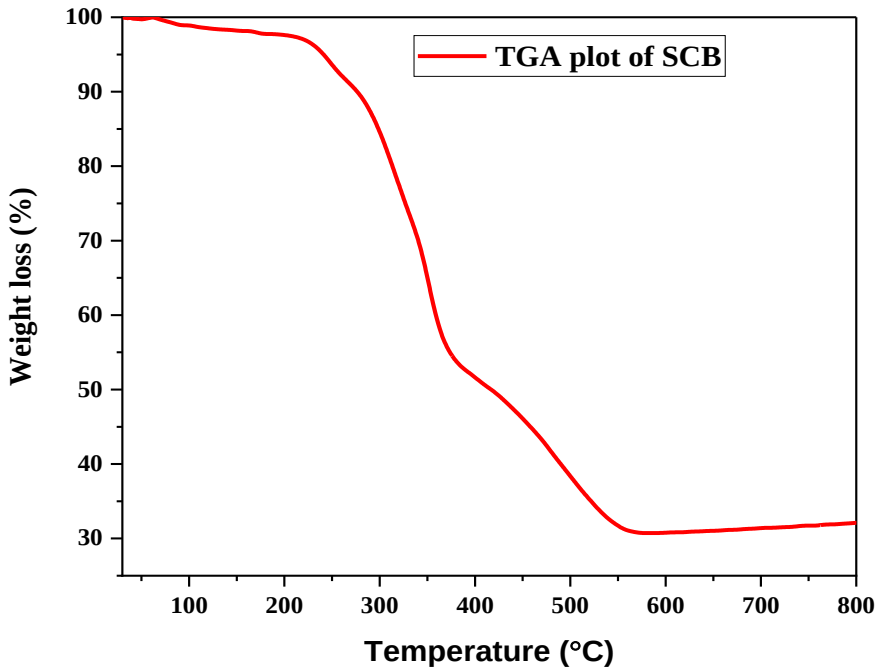


Figure 4.2 Thermogravimetric analysis (TGA) of raw sugarcane bagasse

4.2. Statistical Analysis on Variables that Affects Sulfonation Process

Experimental design technique (i.e. Design expert 11) was used to analyze and investigate the process parameters that affect the sulfonation process. The experimental design selected for variables that affect sulfonation process was Box-Behnken Design (BHD). Box-Behnken Design are commonly used experimental design models for three-level three factor experiments. In sulfonation process, we have three main operating parameters mostly affects the sulfonation process, such as sulfonation temperature, sulfonation time and ratio of concentrated sulfuric acid to biochar and the response variable was sulfonic group acid density. So, the design expert tool is used to analyze and investigate all parameter effects on the response as shown below in Table 4.1. The actual sulfonic group acid density of sulfonated biochar based catalyst synthesized at different process parameters is determined by using titration method.

Table 4.1 Box-Behnken design matrix for catalyst synthesis Experimental and Predicted value

Run	Factor 1	Factor 2	Factor 3	Response 1	
	A:Temperature (℃)	B:Time (hr)	C:Ratio of sulfuric acid to biochar (mL/g)	Experimental Sulfonic group density (mmol/g)	Predicted Sulfonic group density (mmol/g)
1	140	14	15	0.579	0.5870
2	140	14	15	0.59	0.5870
3	100	14	5	0.486	0.4924
4	140	5	5	0.466	0.4629
5	140	14	15	0.592	0.5870
6	100	23	15	0.526	0.5210
7	180	5	15	0.486	0.4950
8	100	5	15	0.524	0.5188
9	180	14	25	0.531	0.5246
10	140	23	5	0.521	0.5216
11	180	23	15	0.496	0.4972
12	140	23	25	0.518	0.5211
13	100	14	25	0.598	0.6019
14	180	14	5	0.526	0.5221
15	140	5	25	0.576	0.5754

Table 4.1 shows that the maximum amount of sulfonic group density was 0.598 mmol/g at process conditions of 100 ℃ sulfonation temperature, 14 hr sulfonation time, and 25:1 mL/g ratio of sulfuric acid to biochar while the minimum amount of sulfonic group density was 0.466 mmol/g at process conditions of 140 ℃ sulfonation temperature, 5 hr sulfonation time, and 5:1mL/g ratio of sulfuric acid to biochar. More precisely, it can be observed that the experimental value of sulfonic group density varied from 0.466 mmol/g to 0.598 mmol/g.

The second order polynomial equation that correlates the response (i.e. sulfonic group density) to the independent sulfonation process parameters in terms of actual value, when the insignificant items are excluded, was given below. The predicted second order polynomial equation in terms of the coded factors is illustrated in equation (4.1).

$$\textbf{Sulfonic group acid density (mmol/g)} = 0.5870 - 0.0119A + 0.0011B + 0.0280C - 0.0267\,AC - 0.0282BC - 0.0320A^2 - 0.0470B^2 - 0.0198C^2 \quad (4.1)$$

Where A = Sulfonation temperature

B= Sulfonation time

C= Ratio of sulfuric acid to biochar

4.2.1 Checking Model Adequacy for Sulfonated Biochar Based Catalyst Synthesis

The model was tasted for adequacy by analysis of variance (ANOVA). Normally, three types of tests namely, significant of terms, regression model and lack of fit (Table 4.2) are used to evaluate the significance and reliability of the model.

Table 4.2 ANOVA analysis results for response surface quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0254	8	0.0032	52.14	< 0.0001	significant
A-Temperature	0.0011	1	0.0011	18.56	0.0050	
B-Time	0.0000	1	0.0000	0.1666	0.6974	
C-Ratio of sulfuric acid to biochar	0.0063	1	0.0063	103.17	< 0.0001	
AC	0.0029	1	0.0029	47.08	0.0005	
BC	0.0032	1	0.0032	52.51	0.0004	
A^2	0.0038	1	0.0038	62.19	0.0002	
B^2	0.0082	1	0.0082	134.17	< 0.0001	
C^2	0.0014	1	0.0014	23.69	0.0028	
Residual	0.0004	6	0.0001			
Lack of Fit	0.0003	4	0.0001	1.36	0.4652	not significant
Pure Error	0.0001	2	0.0000			
Cor Total	0.0257	14				

The ANOVA analysis results in the Table 4.2 was 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 of the quadratic model. The model was significant and is confirmed by the p-value of less than 0.0001 and higher F-value of 52.14.

In this study, for the response as shown in the Table above 4 the values of P-value less than 0.05 indicates model terms are significant. In this case, A, C, AC, BC, A^2, B^2, and C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. This shows that the reaction temperature, ratio of sulfuric acid to biochar, interaction between reaction temperature and ratio of sulfuric acid to biochar, interaction between reaction time and ratio of sulfuric acid to biochar, square of reaction temperature, square of reaction time and square ratio of sulfuric acid to biochar affects the sulfonic group

acid density in sulfonated biochar based catalyst significantly. The model F-value of 52.14 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 indicates stronger influence of parameters on response. The individual sulfonating parameters that has influenced the sulfonic group acid density of sulfonated biochar catalyst were in the order ratio of sulfuric acid to biochar (ml/g) > Temperature(℃) > time (h).

Table 4.3 Model adequacy measures for sulfonic group acid density

R^2	0.9858
Adjusted R^2	0.9669
Predicted R^2	0.8885
Adeq Precision	23.0153

From the above Table 4.3 the values of R-squared, adjusted R squared and predicted R squared and Adeq precision have a value of 0.9858, 0.9669, 0.8885 and 23.0153 respectively.

The predicted R square of 0.8885 is in reasonable agreement with the adjusted R square of 0.9669; i.e. the difference is less than 0.2. The difference between R square and predicted R square is 0.0784 (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 0.9858, this indicates 98.58% 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 23.0153 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 4.3. The results in in Figure 4.3 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 prefect fit. This result indicates that it was successful in capturing the correlation between the three independent sulfonation process variables (i.e. sulfonation temperature, sulfonation time and ratio of sulfuric acid to biochar) to the response (sulfonic group acid density).

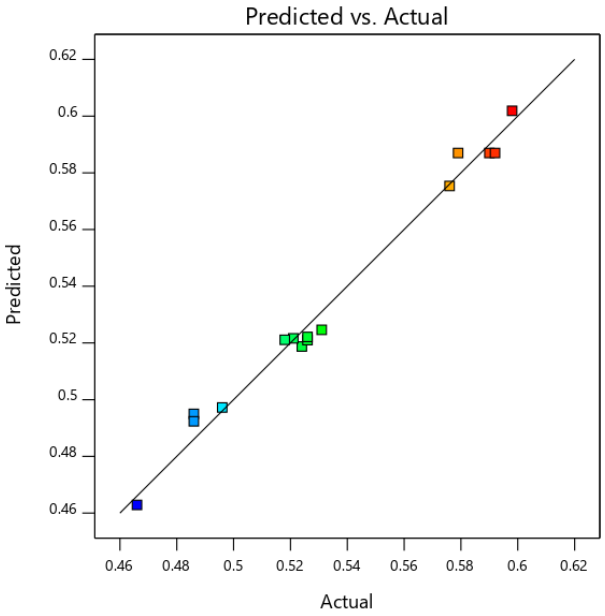


Figure 4.3 The predicted versus actual sulfonic group acidity on sulfonated biochar based catalyst synthesis

4.2.2. Effects of Experimental Variables on Sulfonated Group Acid Density

Based on the analysis of variance, sulfonic group acid density was significantly affected by various interaction between the sulfonation process variables. In addition to interaction effect, significant individual experimental variables that affect sulfonic group acid density are sulfonation temperature, A and ratio of sulfuric acid to biochar, C.

4.2.2.1. Effect of Individual Sulfonation Variables

Figure 4.4, shows that the highest amount of sulfonic (-SO_3H) acid density were obtained at sulfonation temperatures of between low level (100 ℃) and middle point (140 ℃) as compared to high sulfonation temperature i.e. high level (180 ℃). This accused that sulfonation temperature had a distinctive effect on the sulfonic group acid density of the synthesized catalyst. Low sulfonation temperature favored the attachment of sulfonic acid groups on to the biochar, resulting in higher sulfonic group acid density. This was in agreement with other sulfonation process performed by other similar research studies under the temperature range of 100 to 200 ℃ [94]. However, sulfonation temperature lower than 100 ℃ was found to be insufficient to facilitate the formation of chemical linkage (interaction) between the sulfonating reagent and biochar, resulting in a reduced rate of sulfonation and therefore the amount of sulfonic group acid density on the prepared

sulfonated biochar based catalyst was in-adequate. An increase in the sulfonation temperature could facilitate the mass transfer between the sulfonating agent and the biochar and favored the attachment of sulfonic acid groups on to the biochar, resulting in higher sulfonic group acid density, but the high sulfonation temperature may trigger the degradation of some compounds and negatively affects the sulfonic group acid density. Further increment of sulfonation temperature over 140 ℃ had a negative impact on the sulfonic (-SO_3H) group acid density of sulfonated biochar based catalyst. This was associated with the destruction of porous structures of biochar's and domination of side reactions such as condensation, oxidation or dehydrogenation under the high temperature sulfonation conditions [95].

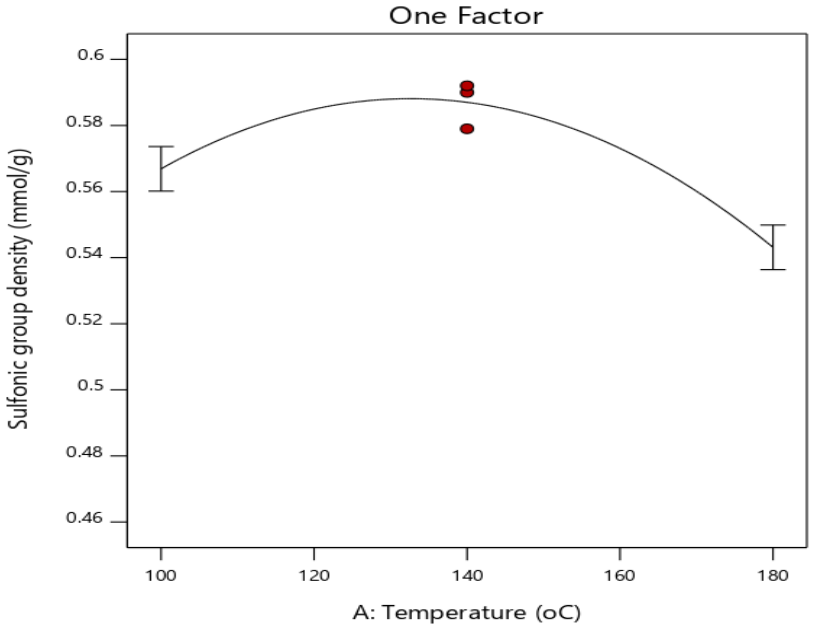


Figure 4.4 Sulfonic group acid density versus sulfonation temperature

Figure 4.5 shows that the effect of ratio of sulfuric acid to biochar on the sulfonic group acid density. Increasing the amount of ratio of sulfuric acid to biochar increases the sulfonic group acid density significantly. As reported in literature, increasing the amount of concentrated sulfuric acid can decrease the viscosity of the reaction solution, thus enhancing the heat transfer inside the solution due to this reason the sulfonic group acid density increases as the amount of concentrated sulfuric acid increases [79]. However, as seen in Figure 4.5, the further increase the ratio of concentrated sulfuric acid to biochar ratio beyond 22.3:1 ml/g, the amount of sulfonic group acid density starts to slow decrease may be due to the gradual degradation of the biochar with concentrated sulfuric acid [96]. Moreover, a large amount of concentrated sulfuric acid would make no distinct change in increasing the amount of sulfonic group acid density if the carbonaceous material surface occupied by the –SO_3H

group approaches a saturated state. Therefore, 22.3 ml concentrated sulfuric acid was enough to synthesis sulfonated biochar based catalyst with 1 g of biochar.

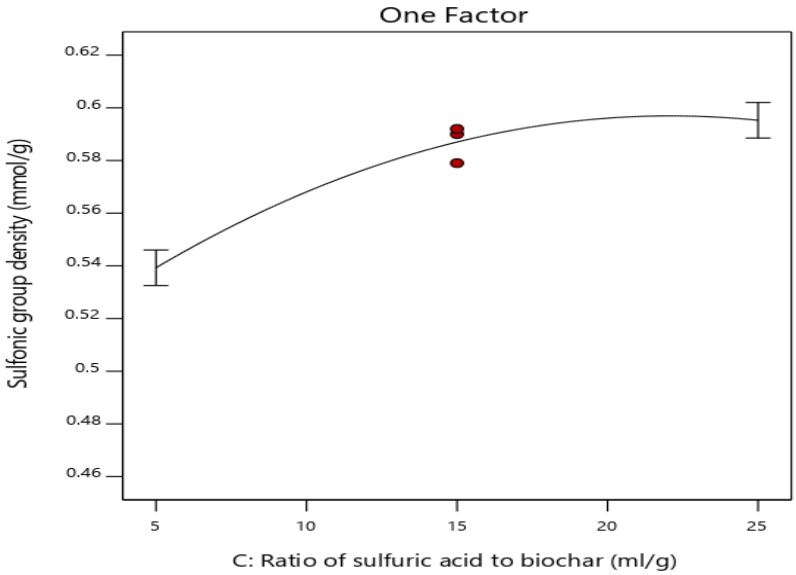


Figure 4.5 Sulfonic group acid density versus ratio of sulfuric acid to biochar

4.2.2.2. Effect of Interaction between Sulfonation Process Parameters

The most common method to summarize the results of interaction effect between process variables in a design experiment is in the form of a response surface plot and via response contours plot.

The sulfonation parameters were found to have significant interaction effect except sulfonation temperature with sulfonation time. Figure 4.6 and Figure 4.7 shows the 3D surface plot interaction between reaction temperature and ratio of sulfuric acid to biochar, and reaction time and ratio of sulfuric acid to biochar on the sulfonic group acid density respectively. From the three interaction effects shown in the figures and contours it can be seen that:

- at round high level of ratio of sulfuric acid to biochar, sulfonation temperature round center point and sulfonation time at the center point, resulted in the higher amount of sulfonic group acid density than when using lower or middle level ratio of sulfuric acid to biochar, lower or higher sulfonation temperature and lower or higher reaction time. The above interpretations can be easily explained at higher amount of ratio of sulfuric acid to biochar and medium sulfonation temperature will enhance heat transfer inside the reaction solution and the medium sulfonation time will ensure high sulfonic group acid density grafting on biochar which results in high amount of sulfonic group density in sulfonic group acid density.

Another notable interpretations is:

- at higher range of ratio of sulfuric acid to biochar, the interpretations showed that using a combination of higher ratio of sulfuric acid to biochar, longer (higher) sulfonation time, and higher sulfonation time is not valuable in increasing the amount of sulfonic group acid density. This is because at this sulfonation process conditions, higher amount of ratio of sulfuric acid to biochar is already sufficient to decreasing viscosity of the reaction solution, thus enhancing the heat transfer in the solution. This phenomena is further supported by the fact that ratio of sulfuric acid to biochar is the most significant sulfonation process variable that affect the sulfonic group acid density as indicated by F-value and P-value in the analysis of variance (ANOVA) as shown in Table 4.2.

The response surface methodology was used to optimize sulfonic group acid density and to understand the interaction of sulfonation parameters affecting sulfonic group acid density.

Figure 4.6 and Figure 4.7 shows the surface plot between the sulfonation process variables and dependent variable (sulfonic group acid density) for fixed parameters.

Figure 4.7 shows the interaction of sulfonation time and ratio of sulfuric acid to biochar on the sulfonic group acid density. A relatively lower amount of sulfonic group acid density at a high level sulfonation time could also be due to consequent degradation of the carbonized material (biochar) which destroys the porous structure of biochar which reduces sulfonating reagent grafting on the biochar surface.

From Figure 4.6 the amount of sulfonic group acid density increased with increasing sulfonation temperature up to a center point, at a near high level of ratio of sulfuric acid to biochar ratio. Furthermore, from Figure 4.7 the amount of sulfonic group acid density becomes higher at near the middle level (optimal) condition of sulfonation time and higher (near close to high level) of a ratio of sulfuric acid to biochar ratio.

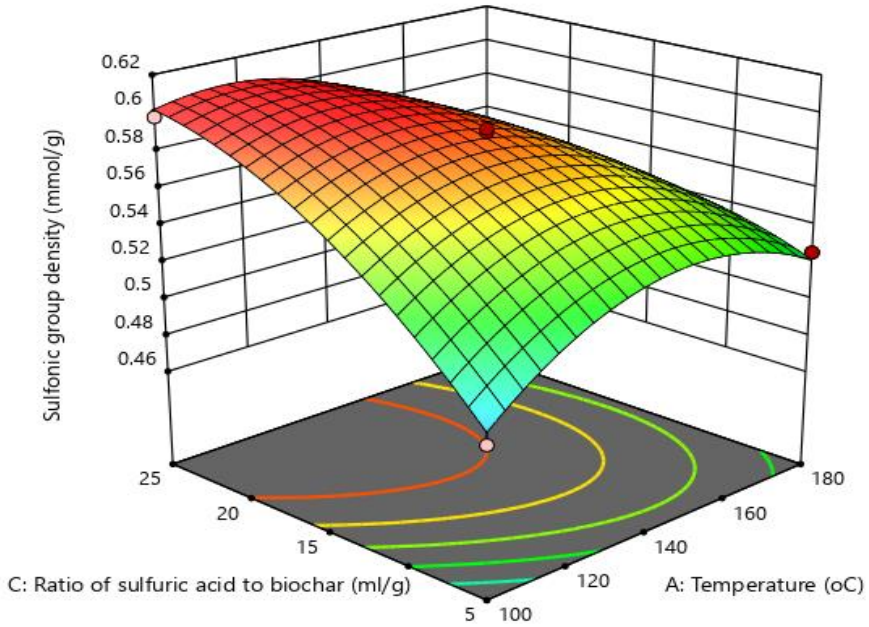


Figure 4.6 Surface plot of the interaction of sulfonation temperature and ratio of sulfuric acid to biochar versus sulfonic group acid density

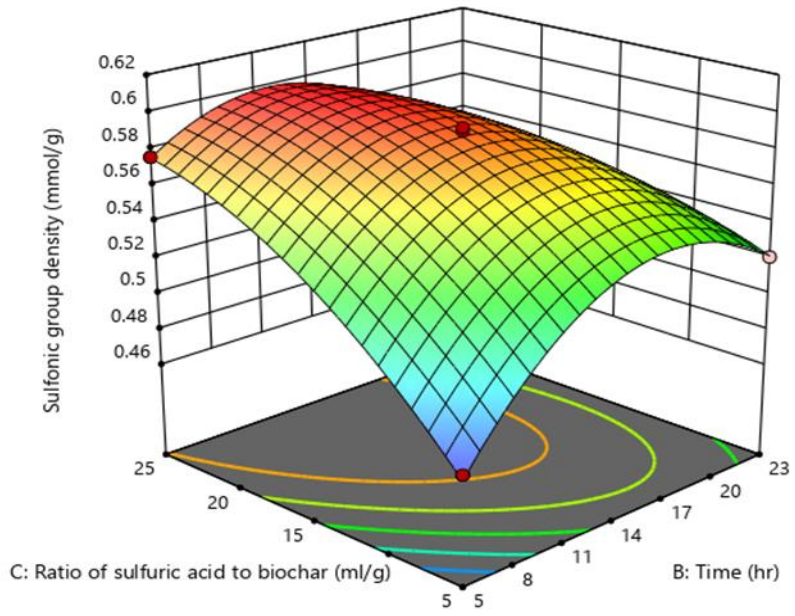


Figure 4.7 Surface plot of interaction effect of sulfonation time and ratio of sulfuric acid to biochar ratio versus sulfonic group acid density

Figure 4.8 and Figure 4.9 shows contour plot degree of significance of the interaction between sulfonation process parameters and dependent variable (sulfonic group acid density) for fixed parameters. The degree of significance of the interaction between pair of process variables can be expressed in terms of degree of ellipticity of the contour plot. A rounder contour plot indicates that the effect of interaction on the response value is less significant. As shown in Figures 4.8 and 4.9, the contour plots of the interactions between the two factors were elliptical, indicating that the interaction between the two factors was significant. However, Figure 4.9 shows elliptical contour plots than ones in Figure 4.8 were the contour plots where less elliptical. This statement was consistent with the p-values for BC interaction and AC interaction obtained in ANOVA Table 4.2.

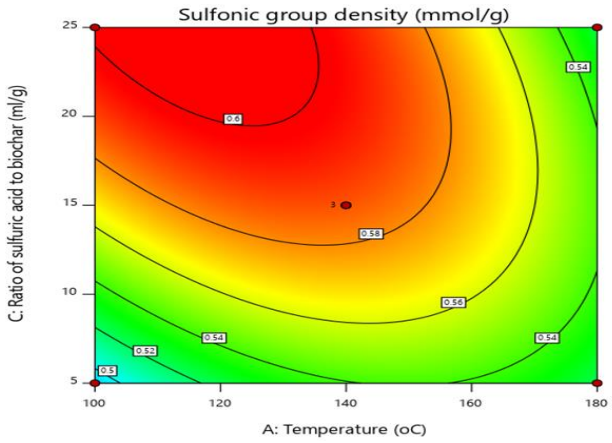


Figure 4.8 Contour plot of the interaction effect of sulfonation temperature and ratio of sulfuric acid to biochar versus sulfonic group acid density.

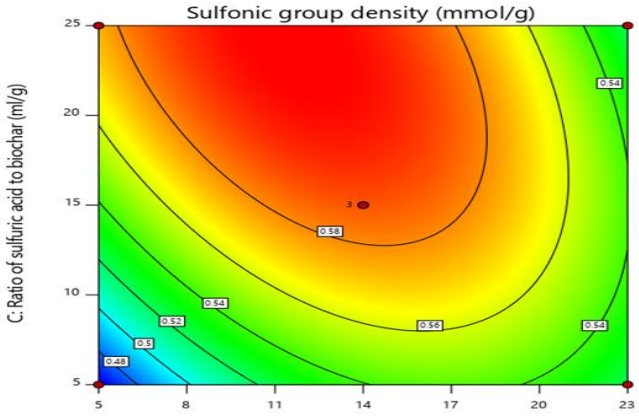


Figure 4.9 Contour plot of interaction effect of sulfonation time and ratio of sulfuric acid t biochar versus sulfonic group acid density

4.2.3. Optimization of Sulfonation Process Variables

The above results demonstrates that the three sulfonation parameters and the interaction between the independent process variables affect the sulfonic (-SO_3H) group density. The optimal condition chosen was based on the maximum amount of sulfonic (-SO_3H) group density obtained. Consequently, in order to maximize the amount of sulfonic group acid density, the predicted combination of sulfonation process parameters was as follows: sulfonation temperature of 135℃, sulfonation time of 13.3 hr and ratio of sulfuric acid to biochar of 24:1. Under this condition the predicted amount of sulfonic group acid density was 0.602 mmol/g. To confirm the optimum process conditions, triplicate experiments were conducted using the optimized sulfonation process conditions and with average value of 0.596 mmol/g was obtained and the results are closely with the software predicted.

4.3. Characterization of Optimized Sulfonated Biochar Based Catalyst

4.3.1. Acid Group Titration of Catalyst

The acid density analysis was determined by direct and back titration method for evaluating the sulfonic (–SO_3H) and total acidity group and the results are shown in the Table 4.4. As can seen in Table 4.4, sulfonic group acid density was nil in biochar before sulfonation. However, after sulfonation, the sulfonic group acid density was found to be 0.596 mmol/g. This result indicates that the sulfonation (functionalization) process was successful to chemically graft sulfonic group (-SO_3H) acid density into the biochar. This finding was also supported by Fourier transform infrared (FTIR) analysis obtained in this study.

Table 4.4 Sulfonic and total acidity of BC and OSBBC

Sample Name	Total acid density (mmol/g)	Sulfonic group acid density (mmol/g)
Biochar	1.94	–
Optimized sulfonated biochar based catalyst	4.12	0.596

Also, as shown in Table 4.4 the total acid density of biochar and optimized biochar based catalyst was reported to be 1.94 mmol/g and 4.12 mmol/g respectively. Obviously, the acid titration results approves the presence of high surface total acidity on the optimized sulfonated biochar based catalyst than its biochar. It was due to the sulfonation process has induced additional acidic group probably by formation of additional new functional groups or explosion of the existing inaccessible site to the surface such as carboxylic (-COOH)

groups. The acidic density accounted for lately formed acid species was found to be 1.584 mmol/g. This was calculated ultimately by subtracting of optimized sulfonated biochar based catalyst sulfonic group density (0.596 mmol/g) and biochar total acidity (1.94 mmol/g) from optimized sulfonated biochar based catalyst total acid density (4.12 mmol/g). The hydroxyl and carboxyl groups makes the sulfonated biochar based catalyst to have a special attribute of adsorbing reactants and then after, accessing reactants to the sulfonic group acid density. However, the catalytic efficiency of the sulfonated biochar based catalyst is credited to the sulfonic (-SO_3H) groups, thus its density is closely related to catalytic activity [70].

4.3.2. Thermogravimetric Analysis

The results of the thermal analysis of the optimized sulfonated biochar based catalyst and its biochar under nitrogen flow are shown in Figure 4.10 which illustrated three main stages of weight loss shown below.

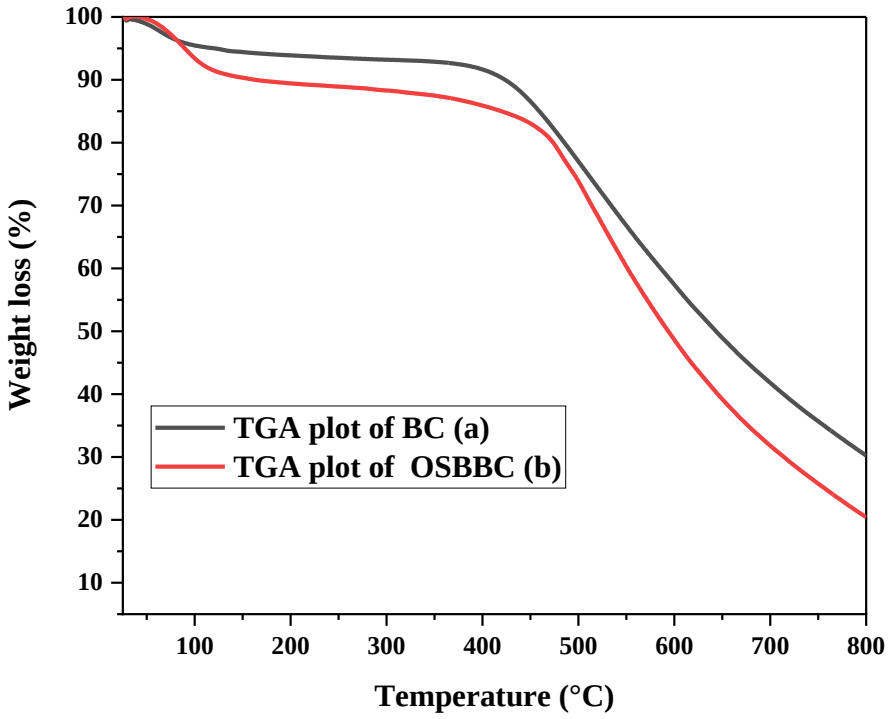


Figure 4.10 TGA curve of biochar, (a) and optimized biochar based catalyst, (b)

From the temperature between 25 and 120 ℃ free water molecules, physically adsorbed moisture and low volatile matter are removed from both samples. Then, a reduction in weight loss approximately 15.36% was caused by thermal degradation of the oxygen containing groups such as hydroxyl (-OH) and carboxyl (-COOH) groups in the temperature range of

250-500 ℃. In addition to this, for the optimized sulfonated biochar based catalyst in this temperature range, removal of sulfonic acid group from the catalysts framework structure is also observed. This fact was conformed with finding from the literature, for the carbonaceous materials as well as the sulfonated catalyst the degradation starts at round 240 ℃ and also, the mass loss are in the forms of CO_2 attributed to the degradation of the carbon material, and loss for sulfonic groups from the catalyst in the form of SO_2 [97] . The final weight loss observed between 500 and 750 is may be due to removal of hydrogen of which is leading to the formation of aromatized residue [98] . The total weight loss for sample biochar is around 64% while for optimized sulfonated biochar based catalyst, it is around 75% (see in Figure 4.10) showing an increment in the functionalization of the optimized sulfonated biochar based catalyst. The weight loss associated with optimized sulfonated biochar based catalyst indicates an important increase in the sulfonation of surface contributing further to the degradation of the biochar.

Furthermore, the small difference in mass loss for the biochar and the optimized sulfonated biochar based catalyst near 200 ℃ can be ascribed to the sulfonation process weakening the biochar structure [99].

4.3.3. XRD Analysis

Figure 4.11, shows the XRD patterns of biochar (a) and the optimized sulfonated biochar based catalyst (b).

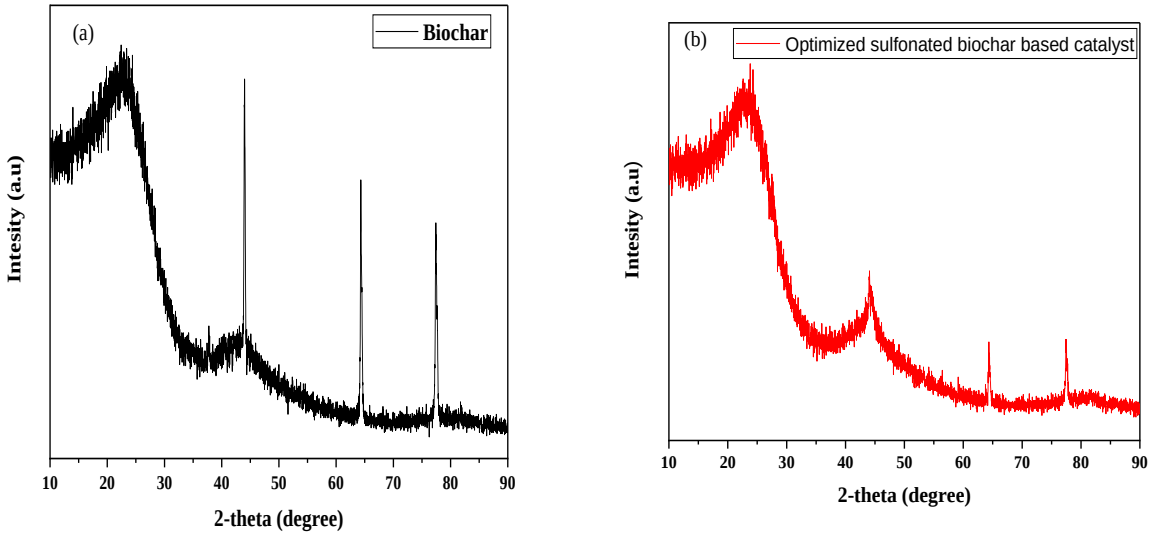


Figure 4.11 XRD pattern of biochar (a) and optimized sulfonated biochar based catalyst (b)

Both of them exhibited broad range diffraction peak within 2θ angle of 10-30° assigned to amorphous carbon and was interpreted as the reflection of aromatic carbon composed of aromatic carbon sheets oriented considerably in a random [7]. Furthermore, XRD pattern of optimized sulfonated biochar based catalyst in Figure 4.11 (b) shows higher intensity of the peaks and as compared to biochar in Figure 4.11 (a) which may be due to the biochar precursor under goes further carbonization during the sulfonation, resulting in the growth of the size of aromatic carbon sheets [100]. The significance of amorphous structure in the catalytic process was concluded by Mertinez et al and additionally Okamura et al suggested that there was marked that difference in catalytic activity due the accessibility of reactants to sulfonic ($-SO_3H$) groups in the amorphous carbon structure than crystalline ones [101]. In addition, sharp peaks round 44°, 64° and 76° are probably due some inorganic substances. Other studies regarding carbon based catalysts presents similar behavior of sharp peaks [102].

4.3.4. FTIR Analysis

The FTIR spectrum of the biochar (a) and optimized sulfonated biochar based catalyst (b) are shown in Figure 4.12.

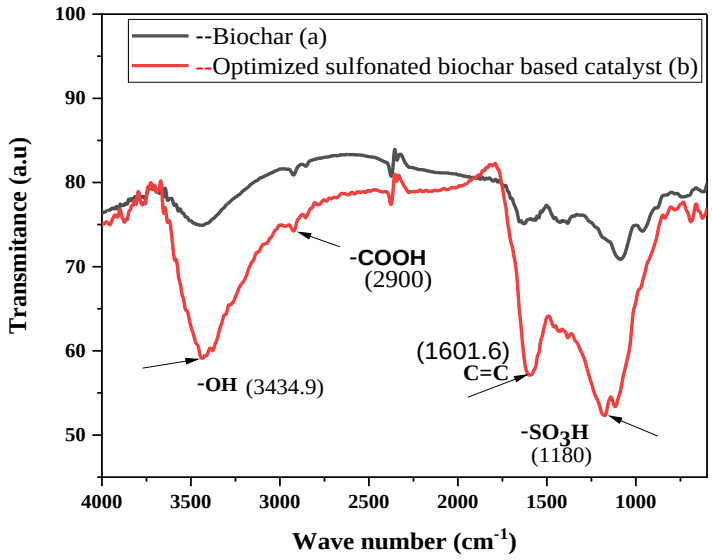


Figure 4.12 FTIR spectra of biochar (a) and optimized sulfonated biochar based catalyst (b)

Both the spectra of biochar and optimized sulfonated biochar catalyst show the presence of OH stretching at a wave number of 3454.26 cm^{-1}, which is credited to intermolecular hydrogen bonding and a small shift to a lower wave number after sulfonation to 3434.88 cm^{-1} showing the reduced concentration of OH^- due to acid attaching during sulfonation [103]. A characteristic band at 1634 cm^{-1} cm is detected in Figure 4.12 for the biochar (a), which is due to C=C vibration. Instead, for the optimized sulfonated biochar based catalyst spectrum in Figure 4.12 (b), bands are observed at 1601.55 cm^{-1} which is assigned to C=C vibration, which were formed as a consequence of the carbonization processes [104]. The bands shown in Figure 4.12 in both samples at 2900 cm^{-1} and round 2848 cm^{-1} may represent vibrations of –COOH group [105]. Also, the new band at 1180 cm^{-1} for the $–SO_3H$ group and band at 1110 cm^{-1} for the S=O group [106] demonstrates the successful introduction of sulfur containing groups during sulfonation for the catalyst preparation. In addition, the peak of C-S at round 690 cm^{-1} also confirm that $–HSO_3$ groups were successfully introduced on the carbonaceous materials [107]. Therefore, the sulfonation treatment successfully grafted the $–SO_3H$ group into the biochar, resulting in sulfonated biochar based solid acid catalyst. Overall, the FTIR analysis was showed that the synthesized catalyst sample contains $–SO_3H$, -COOH, and -OH groups which is agreement with [108] and suggested successful functionalization of these functional groups on the biochar.

4.3.5. Scanning Electron Microscope (SEM)

Figure 4.13 a, b represents SEM images of biochar and optimized sulfonated biochar based catalyst respectively.

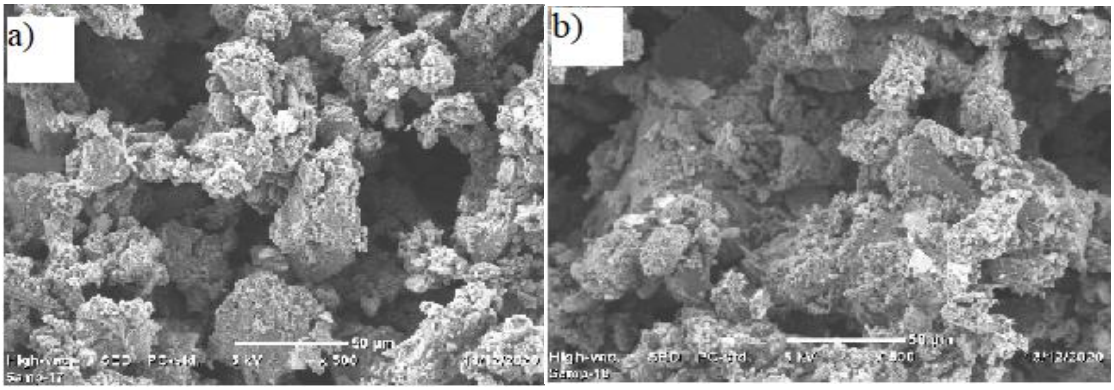


Figure 4.13 SEM image of biochar (a) and optimized sulfonated biochar based catalyst (b)

SEM analysis reveals that the surface of biochar were smooth with many cavities. On the other hand, compared to biochar the SEM image of optimized biochar based catalyst was composed of rough with a markedly decrease in cavity. The roughness and decreases in cavity in the optimized sulfonated biochar based catalyst was probably due to the process of functionalization with concentrated sulfuric acid which is a strong sulfonating agent [94].

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

Lignocellulosic biomass have a great potential to synthesize value added products such as paper, biochar, solid acid catalysts and others by economically viable ways. Consequently, this study has been focused on the synthesis of sulfonated biochar based solid catalyst. TGA suggested temperature (i.e. 550℃) carbonized sugarcane bagasse was prepared and sulfonated (functionalized) with concentrated sulfuric acid to synthesis sulfonated biochar based catalyst. The experiment were conducted using design expert®11.0 software used for study of sulfonation process. 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. In case of sulfonation process parameters, based on the analysis of the experimental result (ANOVA), sulfonation temperature, ratio of sulfuric acid to biochar, interaction effect of sulfonation temperature and ratio of sulfuric acid to biochar, interaction effect of sulfonation time and ratio of sulfuric acid to biochar are significant effect on sulfonic group acid density. During the experiment was studied that as the sulfonation temperature increases from 100 ℃ to 180 ℃ the amount of sulfonic group acid density was increased until it reaches 140 ℃ and tend to decrease as the sulfonation temperature is above 140℃. In this, initially the amount of sulfonic group acid density was increased from 0.57 mmol/g to 0.59 mmol/g, and as the sulfonation temperature is increased above 140℃, the amount of sulfonic group acid density was decreased to 0.54 mmol/g.

And also, as the ratio of sulfuric acid to biochar was increased from 5:1 to 25:1 mL/g, the amount of sulfonic group acid density was increased until it reaches 23.3 mL/g and slowly decreases as the ratio of sulfuric acid to biochar is 23.3 mL/g. Herein, initially the amount of sulfonic group acid density was increased from 0.538 mmol/g to 0.597 mmol/g and as the ratio of sulfuric acid to biochar is increased above 22.3 mL/g, the amount of sulfonic group acid density small decreased to 0.59 mmol/g. 0.596. Furthermore, at a sulfonation temperature of 135 ℃, sulfonation time of 13.3 hr, and ratio of sulfuric acid to biochar 24:1 mL/g results an optimal amount of 0.596 mmol/g sulfonic group acid density. The results of FTIR analysis indicated that the sulfonic group was successfully attached onto the surface of the biochar, and the catalyst has good thermal stability based on the performed thermogravimetric analysis.

5.2. Recommendations

Based on the results of present study the following recommendations are forwarded;

In this thesis, the selection of raw material were based on the availability and non-food source but selection of raw material based on high amount of fixed carbon content, maturity, low ash content and microporous structure in selection of raw material are important points not covered in this thesis work which needs further study.

Sugarcane bagasse biochar was used as the starting materials for sulfonation with concentrated sulfuric acid, however the effects of precursor characteristics on acidic properties of the product not investigated in this thesis work which needs further study.

In the present study the carbonization of sugarcane bagasse was carried out by using muffle furnace without nitrogen purging system and heating rate adjusting system and the absence of these components affects the raw biochar characteristics. Therefore, it was required to use tubular carbonite furnace and microwave reactors for future thesis work.

For more research work on the synthesis of sulfonated biochar based catalyst, using ambient sulfonation temperature functionalizing reagents, such as chlorosulfonic acid ($ClSO_3H$) is suggested.

REFFERANCES

[1] T. Okuhara, 'Water-tolerant solid acid catalysts', *Chem. Rev.*, vol. 102, no. 10, pp. 3641–3666, 2002, doi: 10.1021/cr0103569.

[2] Z. Liu, Y. Qi, M. Gui, C. Feng, X. Wang, and Y. Lei, 'Sulfonated carbon derived from the residue obtained after recovery of essential oil from the leaves of Cinnamomum longepaniculatum using Brønsted acid ionic liquid , and its use in the', pp. 5142–5150, 2019, doi: 10.1039/c8ra08685k.

[3] J. R. Kastner, J. Miller, D. P. Geller, J. Locklin, L. H. Keith, and T. Johnson, 'Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon', *Catal. Today*, vol. 190, no. 1, pp. 122–132, 2012, doi: 10.1016/j.cattod.2012.02.006.

[4] M. Li, D. Chen, and X. Zhu, 'Preparation of solid acid catalyst from rice husk char and its catalytic performance in esterification', *Cuihua Xuebao/Chinese J. Catal.*, vol. 34, no. 9, pp. 1674–1682, 2013, doi: 10.1016/s1872-2067(12)60634-2.

[5] T. Liu, Z. Li, W. Li, C. Shi, and Y. Wang, 'Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol', *Bioresour. Technol.*, vol. 133, pp. 618–621, 2013, doi: 10.1016/j.biortech.2013.01.163.

[6] H. Ma *et al.*, 'Hydrothermal preparation and characterization of novel corncob-derived solid acid catalysts', *J. Agric. Food Chem.*, vol. 62, no. 23, pp. 5345–5353, 2014, doi: 10.1021/jf500490m.

[7] L. Wang, X. Dong, H. Jiang, G. Li, and M. Zhang, 'Preparation of a novel carbon-based solid acid from cassava stillage residue and its use for the esterification of free fatty acids in waste cooking oil', *Bioresour. Technol.*, vol. 158, pp. 392–395, 2014, doi: 10.1016/j.biortech.2014.02.132.

[8] X. Fu *et al.*, 'A microalgae residue based carbon solid acid catalyst for biodiesel production', *Bioresour. Technol.*, vol. 146, pp. 767–770, 2013, doi: 10.1016/j.biortech.2013.07.117.

[9] F. Ezebor, M. Khairuddean, A. Z. Abdullah, and P. L. Boey, 'Esterification of oily-FFA and transesterification of high FFA waste oils using novel palm trunk and bagasse-derived catalysts', *Energy Convers. Manag.*, vol. 88, pp. 1143–1150, 2014, doi: 10.1016/j.enconman.2014.04.062.

[10] L. J. Konwar *et al.*, 'Biodiesel production from acid oils using sulfonated carbon catalyst derived from oil-cake waste', *J. Mol. Catal. A Chem.*, vol. 388–389, pp. 167–176, 2014, doi: 10.1016/j.molcata.2013.09.031.

[11] E. M. Santos *et al.*, 'New heterogeneous catalyst for the esterification of fatty acid produced by surface aromatization/sulfonation of oilseed cake', *Fuel*, vol. 150, no. February, pp. 408–414, 2015, doi: 10.1016/j.fuel.2015.02.027.

[12] I. Chakraborty *et al.*, 'Massive electrical conductivity enhancement of multilayer graphene/polystyrene composites using a nonconductive filler', *ACS Appl. Mater. Interfaces*, vol. 6, no. 19, pp. 16472–16475, 2014, doi: 10.1021/am5044592.

[13] E. Betiku and S. O. Ajala, 'Modeling and optimization of Thevetia peruviana (yellow oleander) oil biodiesel synthesis via Musa paradisiacal (plantain) peels as heterogeneous base catalyst: A case of artificial neural network vs. response surface

methodology', *Ind. Crops Prod.*, vol. 53, pp. 314–322, 2014, doi: 10.1016/j.indcrop.2013.12.046.

[14] M. Gohain, A. Devi, and D. Deka, 'Musa balbisiana Colla peel as highly effective renewable heterogeneous base catalyst for biodiesel production', *Ind. Crops Prod.*, vol. 109, no. May, pp. 8–18, 2017, doi: 10.1016/j.indcrop.2017.08.006.

[15] C. Li, X. Hu, W. Feng, B. Wu, and K. Wu, 'A supported solid base catalyst synthesized from green biomass ash for biodiesel production', *Energy Sources, Part A Recover. Util. Environ. Eff.*, vol. 40, no. 2, pp. 142–147, 2018, doi: 10.1080/15567036.2017.1405121.

[16] S. E. Onoji, S. E. Iyuke, A. I. Igbafe, and M. O. Daramola, 'Transesterification of Rubber Seed Oil to Biodiesel over a Calcined Waste Rubber Seed Shell Catalyst: Modeling and Optimization of Process Variables', *Energy and Fuels*, vol. 31, no. 6, pp. 6109–6119, 2017, doi: 10.1021/acs.energyfuels.7b00331.

[17] S. Sulaiman and N. I. F. Ruslan, 'A heterogeneous catalyst from a mixture of coconut waste and eggshells for biodiesel production', *Energy Sources, Part A Recover. Util. Environ. Eff.*, vol. 39, no. 2, pp. 154–159, 2017, doi: 10.1080/15567036.2016.1205683.

[18] A. P. S. Chouhan and A. K. Sarma, 'Biodiesel production from Jatropha curcas L. oil using Lemna perpusilla Torrey ash as heterogeneous catalyst', *Biomass and Bioenergy*, vol. 55, pp. 386–389, 2013, doi: 10.1016/j.biombioe.2013.02.009.

[19] I. M. Mendonça *et al.*, 'New heterogeneous catalyst for biodiesel production from waste tucumã peels (Astrocaryum aculeatum Meyer): Parameters optimization study', *Renew. Energy*, vol. 130, pp. 103–110, 2019, doi: 10.1016/j.renene.2018.06.059.

[20] V. O. Odude *et al.*, 'Application of Agricultural Waste-Based Catalysts to Transesterification of Esterified Palm Kernel Oil into Biodiesel: A Case of Banana Fruit Peel Versus Cocoa Pod Husk', *Waste and Biomass Valorization*, vol. 10, no. 4, pp. 877–888, 2019, doi: 10.1007/s12649-017-0152-2.

[21] M. S. A. Farabi, M. L. Ibrahim, U. Rashid, and Y. Hin, 'Esteri fi cation of palm fatty acid distillate using sulfonated carbon-based catalyst derived from palm kernel shell and bamboo', vol. 181, no. September 2018, pp. 562–570, 2019, doi: 10.1016/j.enconman.2018.12.033.

[22] W. Lu, A. Alam, C. Wu, Z. Wang, and H. Wei, 'Chemical Engineering & Processing : Process Intensi fi cation Enhanced deacidi fi cation of acidic oil catalyzed by sulfonated granular activated carbon using microwave irradiation for biodiesel production', vol. 135, no. July 2018, pp. 168–174, 2019, doi: 10.1016/j.cep.2018.10.019.

[23] M. Fauziyah, W. Widiyastuti, and H. Setyawan, 'Sulfonated carbon aerogel derived from coir fiber as high performance solid acid catalyst for esterification q', *Adv. Powder Technol.*, no. xxxx, pp. 1–8, 2020, doi: 10.1016/j.apt.2020.01.022.

[24] K. Ngaosuwan, J. G. Goodwin, and P. Prasertdham, 'A green sulfonated carbon-based catalyst derived from coffee residue for esterification A green sulfonated carbon-based catalyst derived from coffee residue for esteri fi cation', *Renew. Energy*, vol. 86, no. February, pp. 262–269, 2016, doi: 10.1016/j.renene.2015.08.010.

[25] S. Zhu *et al.*, 'Catalytic transformation of cellulose into short rod-like cellulose nanofibers and platform chemicals over lignin-based solid acid', *Appl. Catal. B*

Environ., vol. 268, no. November 2019, p. 118732, 2020, doi: 10.1016/j.apcatb.2020.118732.

[26] S. Wang, G. Sima, Y. Cui, L. Chang, and L. Gan, 'Efficient hydrolysis of cellulose to glucose catalyzed by lignin-derived mesoporous carbon solid acid in water', *Chinese J. Chem. Eng.*, vol. 28, no. 7, pp. 1866–1874, 2020, doi: 10.1016/j.cjche.2020.03.012.

[27] K. P. Flores *et al.*, 'Simultaneously carbonized and sulfonated sugarcane bagasse as solid acid catalyst for the esteri fi cation of oleic acid with methanol', *Renew. Energy*, vol. 130, pp. 510–523, 2019, doi: 10.1016/j.renene.2018.06.093.

[28] W. Y. Lou, Q. Guo, W. J. Chen, M. H. Zong, H. Wu, and T. J. Smith, 'A highly active bagasse-derived solid acid catalyst with properties suitable for production of biodiesel', *ChemSusChem*, vol. 5, no. 8, pp. 1533–1541, 2012, doi: 10.1002/cssc.201100811.

[29] X. Yang, S. Zhang, and M. Ju, 'applied sciences Preparation and Modification of Biochar Materials and their Application in Soil Remediation', 2019, doi: 10.3390/app9071365.

[30] J. He *et al.*, 'Pyrolysis of heavy metal contaminated Avicennia marina biomass from phytoremediation : Characterisation of biomass and pyrolysis products', *J. Clean. Prod.*, vol. 234, pp. 1235–1245, 2019, doi: 10.1016/j.jclepro.2019.06.285.

[31] Y. Wei, C. Shen, J. Xie, and Q. Bu, 'Science of the Total Environment Study on reaction mechanism of superior bamboo biochar catalyst production by molten alkali carbonates pyrolysis and its application for cellulose hydrolysis', *Sci. Total Environ.*, vol. 712, p. 136435, 2020, doi: 10.1016/j.scitotenv.2019.136435.

[32] C. Areeprasert and C. Khaobang, 'Pyrolysis and catalytic reforming of ABS/PC and PCB using biochar and e-waste char as alternative green catalysts for oil and metal recovery', *Fuel Process. Technol.*, vol. 182, no. May, pp. 26–36, 2018, doi: 10.1016/j.fuproc.2018.10.006.

[33] L. Axelsson, M. Franzén, M. Ostwald, G. Berndes, G. Lakshmi, and N. H. Ravindranath, 'Perspective: Jatropha cultivation in southern India: Assessing farmers' experiences', *Biofuels, Bioprod. Biorefining*, vol. 6, no. 3, pp. 246–256, 2012, doi: 10.1002/bbb.

[34] G. Chen, X. Wang, Y. Jiang, X. Mu, and H. Liu, 'Insights into deactivation mechanism of sulfonated carbonaceous solid acids probed by cellulose hydrolysis', *Catal. Today*, vol. 319, no. 2010, pp. 25–30, 2019, doi: 10.1016/j.cattod.2018.03.069.

[35] S. Wang, Z. Li, X. Bai, W. Yi, and P. Fu, 'Influence of inherent hierarchical porous char with alkali and alkaline earth metallic species on lignin pyrolysis', *Bioresour. Technol.*, vol. 268, pp. 323–331, 2018, doi: 10.1016/j.biortech.2018.07.117.

[36] E. T. Lu and S. G. Love, 'Gravitational tractor for towing asteroids', *Nature*, vol. 438, no. 7065, pp. 177–178, 2005, doi: 10.1038/438177a.

[37] R. L. Liu, X. Y. Gao, L. An, J. Ma, J. F. Zhang, and Z. Q. Zhang, 'Fabrication of magnetic carbonaceous solid acids from banana peel for the esterification of oleic acid', *RSC Adv.*, vol. 5, no. 114, pp. 93858–93866, 2015, doi: 10.1039/c5ra15767f.

[38] M. L. Savaliya and B. Z. Dholakiya, 'A simpler and highly efficient protocol for the preparation of biodiesel from soap stock oil using a BBSA catalyst', *RSC Adv.*, vol. 5, no. 91, pp. 74416–74424, 2015, doi: 10.1039/c5ra13422f.

[39] D. R. Lathiya, D. V Bhatt, and K. C. Maheria, 'Bioresource Technology Reports Synthesis of sulfonated carbon catalyst from waste orange peel for cost effective biodiesel production', *Bioresour. Technol. Reports*, vol. 2, pp. 69–76, 2018, doi: 10.1016/j.biteb.2018.04.007.

[40] S. Shen, B. Cai, C. Wang, H. Li, G. Dai, and H. Qin, 'Applied Catalysis A : General Preparation of a novel carbon-based solid acid from cocarbonized starch and polyvinyl chloride for cellulose hydrolysis', *"Applied Catal. A, Gen.*, vol. 473, pp. 70–74, 2014, doi: 10.1016/j.apcata.2013.12.037.

[41] M. Mäkelä, 'Experimental design and response surface methodology in energy applications : A tutorial review', *Energy Convers. Manag.*, vol. 151, no. May, pp. 630–640, 2017, doi: 10.1016/j.enconman.2017.09.021.

[42] M. Galbe and G. Zacchi, 'A review of the production of ethanol from softwood', *Appl. Microbiol. Biotechnol.*, vol. 59, no. 6, pp. 618–628, 2002, doi: 10.1007/s00253-002-1058-9.

[43] S. Ramakrishnan, J. Collier, R. Oyetunji, B. Stutts, and R. Burnett, 'Enzymatic hydrolysis of cellulose dissolved in N-methyl morpholine oxide/water solutions', *Bioresour. Technol.*, vol. 101, no. 13, pp. 4965–4970, 2010, doi: 10.1016/j.biortech.2009.09.002.

[44] J. Alcañiz-Monge, B. El Bakkali, G. Trautwein, and S. Reinoso, 'Zirconia-supported tungstophosphoric heteropolyacid as heterogeneous acid catalyst for biodiesel production', *Appl. Catal. B Environ.*, vol. 224, no. August 2017, pp. 194–203, 2018, doi: 10.1016/j.apcatb.2017.10.066.

[45] W. Mateo *et al.*, 'Bioresource Technology Synthesis and characterization of sulfonated activated carbon as a catalyst for bio-jet fuel production from biomass and waste plastics', *Bioresour. Technol.*, vol. 297, no. September 2019, p. 122411, 2020, doi: 10.1016/j.biortech.2019.122411.

[46] M. Zhang, M. Wu, Q. Liu, X. Wang, T. Lv, and L. Jia, 'Graphene oxide mediated cellulose-derived carbon as a highly selective catalyst for the hydrolysis of cellulose to glucose', *Appl. Catal. A Gen.*, vol. 543, no. June, pp. 218–224, 2017, doi: 10.1016/j.apcata.2017.06.033.

[47] H. Tondro, H. Zilouei, K. Zargoosh, and M. Bazarganipour, 'Bioresource Technology Investigation of heterogeneous sulfonated graphene oxide to hydrolyze cellulose and produce dark fermentative biohydrogen using Enterobacter aerogenes', *Bioresour. Technol.*, vol. 306, no. February, p. 123124, 2020, doi: 10.1016/j.biortech.2020.123124.

[48] Q. Lusha, S. Lee, and O. L. Li, 'Fast and Soft Functionalization of Carbon Nanotube with – SO 3 H , -COOH , -OH Groups for Catalytic Hydrolysis of Cellulose to Glucose', vol. 53, no. 3, pp. 87–94, 2020.

[49] J. Wei, X. Zhang, X. Zhang, Y. Zhao, and R. Li, 'Facile Synthesis of Hybrid Core – Shell Nanospheres for the Asymmetric Transfer Hydrogenation of Aromatic Ketones', pp. 1368–1374, 2014, doi: 10.1002/cctc.201301011.

[50] H. Naeimi and M. Golestanzadeh, 'Highly sulfonated graphene and graphene oxide nanosheets as heterogeneous nanocatalysts in green synthesis of bisphenolic antioxidants under solvent free conditions', *RSC Adv.*, vol. 4, no. 99, pp. 56475–56488, 2014, doi: 10.1039/c4ra10177d.

[51] F. Shen, T. Guo, C. Bai, M. Qiu, and X. Qi, 'Hydrolysis of cellulose with one-pot synthesized sulfonated carbonaceous solid acid', *Fuel Process. Technol.*, vol. 169, no. October 2017, pp. 244–247, 2018, doi: 10.1016/j.fuproc.2017.10.015.

[52] J. Dai *et al.*, 'Sulfonated polyaniline as a solid organocatalyst for dehydration of fructose into 5-hydroxymethylfurfural', *Green Chem.*, vol. 19, no. 8, pp. 1932–1939, 2017, doi: 10.1039/c6gc03604j.

[53] L. Hu, L. Lin, Z. Wu, S. Zhou, and S. Liu, 'Applied Catalysis B : Environmental Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts', *"Applied Catal. B, Environ.*, vol. 174–175, pp. 225–243, 2015, doi: 10.1016/j.apcatb.2015.03.003.

[54] S. Xu *et al.*, 'Direct conversion of biomass-derived carbohydrates to 5-hydroxymethylfurfural using an efficient and inexpensive manganese phosphate catalyst', *Fuel Process. Technol.*, vol. 181, no. April, pp. 199–206, 2018, doi: 10.1016/j.fuproc.2018.09.027.

[55] X. L. Shi, Q. Hu, Y. Chen, F. Wang, and P. Duan, 'Conversion of biomass components to methyl levulinate over an ultra-high performance fiber catalyst in impellers of the agitation system', *J. Ind. Eng. Chem.*, vol. 65, pp. 264–271, 2018, doi: 10.1016/j.jiec.2018.04.037.

[56] F. Parveen, K. Gupta, and S. Upadhyayula, 'Synergistic effect of chloro and sulphonic acid groups on the hydrolysis of microcrystalline cellulose under benign conditions', *Carbohydr. Polym.*, vol. 159, pp. 146–151, 2017, doi: 10.1016/j.carbpol.2016.12.021.

[57] P. Varanasi, P. Singh, M. Auer, P. D. Adams, B. A. Simmons, and S. Singh, 'Survey of renewable chemicals produced from lignocellulosic biomass during ionic liquid pretreatment', pp. 1–9, 2013.

[58] W. Sn, 'SUGARCANE BAGASSE : HOW EASY IS IT TO MEASURE ITS CONSTITUENTS ?', pp. 266–273, 2008.

[59] G. Kumar *et al.*, 'Biomass based hydrogen production by dark fermentation — recent trends and opportunities for greener processes', *Curr. Opin. Biotechnol.*, vol. 50, pp. 136–145, 2018, doi: 10.1016/j.copbio.2017.12.024.

[60] G. J. Vargas Betancur and N. Pereira, 'Sugar cane bagasse as feedstock for second generation ethanol production. Part I: Diluted acid pretreatment optimization', *Electron. J. Biotechnol.*, vol. 13, no. 3, pp. 1–9, 2010, doi: 10.2225/vol13-issue3-fulltext-3.

[61] M. S. Singhvi, S. Chaudhari, and D. V. Gokhale, 'Lignocellulose processing: A current challenge', *RSC Adv.*, vol. 4, no. 16, pp. 8271–8277, 2014, doi: 10.1039/c3ra46112b.

[62] V. S. Aigbodion, S. B. Hassan, T. Ause, and G. B. Nyior, 'Potential Utilization of Solid Waste (Bagasse Ash)', *J. Miner. Mater. Charact. Eng.*, vol. 09, no. 01, pp. 67–77, 2010, doi: 10.4236/jmmce.2010.91006.

[63] J. Parikh, S. A. Channiwala, and G. K. Ghosal, 'A correlation for calculating elemental composition from proximate analysis of biomass materials', *Fuel*, vol. 86, no. 12–13, pp. 1710–1719, 2007, doi: 10.1016/j.fuel.2006.12.029.

[64] J. Wang and S. Wang, 'Preparation , modi fi cation and environmental application of biochar : A review', *J. Clean. Prod.*, vol. 227, pp. 1002–1022, 2019, doi: 10.1016/j.jclepro.2019.04.282.

[65] B. Chen, D. Zhou, and L. Zhu, 'Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures', *Environ. Sci. Technol.*, vol. 42, no. 14, pp. 5137–5143, 2008, doi: 10.1021/es8002684.

[66] G. Xu, X. Yang, and L. Spinosa, 'Development of sludge-based adsorbents: Preparation, characterization, utilization and its feasibility assessment', *J. Environ. Manage.*, vol. 151, pp. 221–232, 2015, doi: 10.1016/j.jenvman.2014.08.001.

[67] S. Chen *et al.*, 'Simultaneous and efficient removal of Cr(VI) and methyl orange on LDHs decorated porous carbons', *Chem. Eng. J.*, vol. 352, no. Vi, pp. 306–315, 2018, doi: 10.1016/j.cej.2018.07.012.

[68] J. M. Fraile, E. García-Bordejé, E. Pires, and L. Roldán, 'Catalytic performance and deactivation of sulfonated hydrothermal carbon in the esterification of fatty acids: Comparison with sulfonic solids of different nature', *J. Catal.*, vol. 324, pp. 107–118, 2015, doi: 10.1016/j.jcat.2014.12.032.

[69] O. L. Li, R. Ikura, and T. Ishizaki, 'catalysts sulfonated via a plasma process in', pp. 4774–4777, 2017, doi: 10.1039/c7gc02143g.

[70] M. Okamura *et al.*, 'Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon', *Chem. Mater.*, vol. 18, no. 13, pp. 3039–3045, 2006, doi: 10.1021/cm0605623.

[71] M. Hara, 'Biomass conversion by a solid acid catalyst', pp. 601–607, 2010, doi: 10.1039/b922917e.

[72] F. Guo, Z. Fang, C. C. Xu, and R. L. Smith, 'Solid acid mediated hydrolysis of biomass for producing biofuels', *Prog. Energy Combust. Sci.*, vol. 38, no. 5, pp. 672–690, 2012, doi: 10.1016/j.pecs.2012.04.001.

[73] B. K. H. Mariam, 'Synthesis and Characterization of Sulfonated Carbon Catalyst for Hydrolysis of Microcrystalline Cellulose', 2017.

[74] T. Dong *et al.*, 'Two-step microalgal biodiesel production using acidic catalyst generated from pyrolysis-derived bio-char', *Energy Convers. Manag.*, vol. 105, pp. 1389–1396, 2015, doi: 10.1016/j.enconman.2015.06.072.

[75] X. Xiong *et al.*, 'Sulfonated biochar as acid catalyst for sugar hydrolysis and dehydration', *Catal. Today*, vol. 314, no. February, pp. 52–61, 2018, doi: 10.1016/j.cattod.2018.02.034.

[76] A. Takagaki *et al.*, 'Esterification of higher fatty acids by a novel strong solid acid', *Catal. Today*, vol. 116, no. 2 SPEC. ISS., pp. 157–161, 2006, doi: 10.1016/j.cattod.2006.01.037.

[77] H. Guo, X. Qi, L. Li, and R. L. Smith, 'Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid', *Bioresour. Technol.*, vol. 116, pp. 355–359, 2012, doi: 10.1016/j.biortech.2012.03.098.

[78] S. H. Y. S. Abdullah *et al.*, 'A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production', *Renew. Sustain. Energy Rev.*, vol. 70, no. July, pp. 1040–1051, 2017, doi: 10.1016/j.rser.2016.12.008.

[79] Q. Xie, X. Yang, K. Xu, Z. Chen, B. Sarkar, and X. Dou, 'Conversion of biochar to sulfonated solid acid catalysts for spiramycin hydrolysis : Insights into the sulfonation process', *Environ. Res.*, vol. 188, no. March, p. 109887, 2020, doi:

10.1016/j.envres.2020.109887.

[80] Y. Xiao and J. M. Hill, ‘Chemosphere Solid acid catalysts produced by sulfonation of petroleum coke : Dominant role of aromatic hydrogen’, *Chemosphere*, vol. 248, p. 125981, 2020, doi: 10.1016/j.chemosphere.2020.125981.

[81] C. M. Mendaros *et al.*, ‘Direct sulfonation of cacao shell to synthesize a solid acid catalyst for the esteri fi cation of oleic acid with methanol’, *Renew. Energy*, vol. 152, pp. 320–330, 2020, doi: 10.1016/j.renene.2020.01.066.

[82] B. Karmakar, S. Samanta, and G. Halder, ‘Delonix regia heterogeneous catalyzed two-step biodiesel production from Pongamia pinnata oil using methanol and 2-propanol’, *J. Clean. Prod.*, vol. 255, p. 120313, 2020, doi: 10.1016/j.jclepro.2020.120313.

[83] U. Rashid, F. Anwar, M. Ashraf, M. Saleem, and S. Yusup, ‘Application of response surface methodology for optimizing transesterification of Moringa oleifera oil: Biodiesel production’, *Energy Convers. Manag.*, vol. 52, no. 8–9, pp. 3034–3042, 2011, doi: 10.1016/j.enconman.2011.04.018.

[84] Y. Wu *et al.*, ‘Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids’, *Green Chem.*, vol. 12, no. 4, pp. 696–70, 2010, doi: 10.1039/b917807d.

[85] G. Mae *et al.*, ‘Cacao shell-derived solid acid catalyst for esteri fi cation of oleic acid with methanol’, *Renew. Energy*, vol. 138, pp. 489–501, 2019, doi: 10.1016/j.renene.2019.01.082.

[86] F. Engineering and T. City, ‘Relationship Between of Selected Heating Agricultural Value and and Chemical Composition materials for fuel has been given attention in for biomass fuel conversion , the thermochem-’, vol. 38, no. 1, pp. 1–7, 1994.

[87] M. I. Jahirul, M. G. Rasul, A. A. Chowdhury, and N. Ashwath, ‘Biofuels production through biomass pyrolysis- A technological review’, *Energies*, vol. 5, no. 12, pp. 4952–5001, 2012, doi: 10.3390/en5124952.

[88] G. Stella Mary, P. Sugumaran, S. Niveditha, B. Ramalakshmi, P. Ravichandran, and S. Seshadri, ‘Production, characterization and evaluation of biochar from pod (Pisum sativum), leaf (Brassica oleracea) and peel (Citrus sinensis) wastes’, *Int. J. Recycl. Org. Waste Agric.*, vol. 5, no. 1, pp. 43–53, 2016, doi: 10.1007/s40093-016-0116-8.

[89] Z. Liu and G. Han, ‘Production of solid fuel biochar from waste biomass by low temperature pyrolysis’, *Fuel*, vol. 158, pp. 159–165, 2015, doi: 10.1016/j.fuel.2015.05.032.

[90] A. Hirano, K. Hon-Nami, S. Kunito, M. Hada, and Y. Ogushi, ‘Temperature effect on continuous gasification of microalgal biomass: Theoretical yield of methanol production and its energy balance’, *Catal. Today*, vol. 45, no. 1–4, pp. 399–404, 1998, doi: 10.1016/S0920-5861(98)00275-2.

[91] X. Yue, D. Chen, J. Luo, Q. Xin, and Z. Huang, ‘Upgrading of reed pyrolysis oil by using its biochar-based catalytic esterification and the influence of reed sources’, *Appl. Energy*, vol. 268, no. April, p. 114970, 2020, doi: 10.1016/j.apenergy.2020.114970.

[92] A. Pereira *et al.*, ‘Mechanical and durability properties of alkali-activated mortar based on sugarcane bagasse ash and blast furnace slag’, *Ceram. Int.*, vol. 41, no. 10, pp. 13012–13024, 2015, doi: 10.1016/j.ceramint.2015.07.001.

[93] A. K. Varma and P. Mondal, 'Physicochemical Characterization and Pyrolysis Kinetic Study of Sugarcane Bagasse Using Thermogravimetric Analysis', *J. Energy Resour. Technol. Trans. ASME*, vol. 138, no. 5, 2016, doi: 10.1115/1.4032729.

[94] A. Endut *et al.*, 'Optimization of biodiesel production by solid acid catalyst derived from coconut shell via response surface methodology', *Int. Biodeterior. Biodegrad.*, vol. 124, pp. 250–257, 2017, doi: 10.1016/j.ibiod.2017.06.008.

[95] K. Malins, J. Brinks, V. Kampars, and I. Malina, 'Esterification of rapeseed oil fatty acids using a carbon-based heterogeneous acid catalyst derived from cellulose', *Appl. Catal. A Gen.*, vol. 519, pp. 99–106, 2016, doi: 10.1016/j.apcata.2016.03.020.

[96] A. P. da Luz Corrêa, R. R. C. Bastos, G. N. da Rocha Filho, J. R. Zamian, and L. R. V. da Conceição, 'Preparation of sulfonated carbon-based catalysts from murumuru kernel shell and their performance in the esterification reaction', *RSC Adv.*, vol. 10, no. 34, pp. 20245–20256, 2020, doi: 10.1039/d0ra03217d.

[97] X. Xiong *et al.*, 'Sulfonated biochar as acid catalyst for sugar hydrolysis and dehydration', *Catal. Today*, vol. 314, no. February, pp. 52–61, 2018, doi: 10.1016/j.cattod.2018.02.034.

[98] L. Zhao *et al.*, 'Carbon dioxide capture on amine-rich carbonaceous materials derived from glucose', *ChemSusChem*, vol. 3, no. 7, pp. 840–845, 2010, doi: 10.1002/cssc.201000044.

[99] G. P. Perez and M. Dumont, 'Production of HMF in high yield using a low cost and recyclable carbonaceous catalyst', *Chem. Eng. J.*, vol. 382, no. August 2019, p. 122766, 2020, doi: 10.1016/j.cej.2019.122766.

[100] S. Shen *et al.*, 'Heterogeneous hydrolysis of cellulose into glucose over phenolic residue-derived solid acid', *Fuel*, vol. 113, pp. 644–649, 2013, doi: 10.1016/j.fuel.2013.06.021.

[101] L. Jiang, A. Zheng, Z. Zhao, F. He, H. Li, and N. Wu, 'The comparison of obtaining fermentable sugars from cellulose by enzymatic hydrolysis and fast pyrolysis', *Bioresour. Technol.*, vol. 200, pp. 8–13, 2016, doi: 10.1016/j.biortech.2015.09.096.

[102] W. Wong, S. Lim, Y. Pang, and S. Shuit, 'Science of the Total Environment Synthesis of renewable heterogeneous acid catalyst from oil palm empty fruit bunch for glycerol-free biodiesel production', *Sci. Total Environ.*, vol. 727, p. 138534, 2020, doi: 10.1016/j.scitotenv.2020.138534.

[103] S. Y. Oh *et al.*, 'Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy', *Carbohydr. Res.*, vol. 340, no. 15, pp. 2376–2391, 2005, doi: 10.1016/j.carres.2005.08.007.

[104] M. Toufiq Reza, J. Nover, B. Wirth, and C. J Coronella, 'Hydrothermal carbonization of glucose in saline solution: sequestration of nutrients on carbonaceous materials', *AIMS Energy*, vol. 4, no. 1, pp. 173–189, 2016, doi: 10.3934/energy.2016.1.173.

[105] C. M. Marques Cardoso, D. G. Zavarize, and G. E. Gama Vieira, 'Transesterification of Pequi (Caryocar brasiliensis Camb.) bio-oil via heterogeneous acid catalysis: Catalyst preparation, process optimization and kinetics', *Ind. Crops Prod.*, vol. 139, no. June, p. 111485, 2019, doi: 10.1016/j.indcrop.2019.111485.

[106] S. Niu *et al.*, 'Synthesis of 4-aminobenzenesulfonic acid functionalized carbon catalyst through diazonium salt reduction for biodiesel production', *Energy Convers.*

Manag., vol. 173, no. August, pp. 753–762, 2018, doi: 10.1016/j.enconman.2018.08.004.

[107] M. Gonçalves, F. C. Soler, N. Isoda, W. A. Carvalho, D. Mandelli, and J. Sepúlveda, 'Glycerol conversion into value-added products in presence of a green recyclable catalyst: Acid black carbon obtained from coffee ground wastes', *J. Taiwan Inst. Chem. Eng.*, vol. 60, pp. 294–301, 2016, doi: 10.1016/j.jtice.2015.10.016.

[108] E. Sinin, S. Abang, and J. Janaun, 'Synthesis and characterization of carbon-based bifunctional catalyst', *J. Eng. Sci. Technol.*, vol. 10, no. Spec.issue5, pp. 1–9, 2015.

APPENDICES

Appendix−A: Experimental results

A: Proximate Analysis of Sugarcane bagasse

- **Moisture content**

M: Moisture content
W_1: Original weight of the sample before drying
W_2: Weight of sample after drying

Moisture content (%) = $(\frac{w_1-w_2}{w_2}) \times 100\%$

Table A-1: Moisture content of Sugarcane bagasse

Run	Sample weight in grams (g)			Moisture content (%)	Average of triplicate Moisture Content (%)= $(\frac{R1+R2+R3}{3})$
	W_1	W_2	W_1-W_2		
1	2	1.7938	0.2062	9.48	8.97%
2	2	1.8834	0.1166	9.31	
3	2	1.8866	0.1134	8.13	

- **Volatile matter**

Vm: Volatile matter
M_1: Grams of the sample before drying
M_2: Grams of sample after heating
Volatile matter (%) = $\frac{m_1-m_2}{m_1} \times 100\%$

Table A-2: Volatile matter of Sugarcane bagasse

Run	Sample weight in grams (g)			Volatile matter (%)	Average of triplicate volatile matter (%)= $(\frac{R1+R2+R3}{3})$
	m_1	m_2	$m_1 - m_2$		
1	2.006	1.86905	0.1369	76.2	77.9%
2	2	1.8611	0.1389	79.3	
3	2.0038	1.862	0.1418	78.2	

- **Ash content**

Ac: Ash content

Md: Grams of residue

Mc: Grams of sample before drying

$$\text{Ac (\%)} = \frac{M_d}{M_c} \times 100\%$$

Table A-3: Ash content of Sugarcane bagasse

Run	Sample weight in grams (g)		Ash content (%)	Average of triplicate volatile matter (%)= $(\frac{R1+R2+R3}{3})$
	Mc	Md		
1	0.0225	2.009	1.12	4.14%
2	0.083	2.007	4.12	
3	0.159	2.009	7.2	

- **Fixed carbon content**

Fc: Fixed carbon content

Vc: Volatile matter content

Ac: Ash content

Fixed carbon content (%) = 100% - Vc (%)-Ac (%)

Fc (%) = 100% - 77.9% -4.14%

= 17.96%

A-4: Determination of Acid density of the catalysts

- **Determination of sulfonic group acid density**

The sulfonic group acid density was determined by titration method. In a typical analysis, a 0.1 g of catalyst was added into a sodium chloride aqueous solution (10 ml, 0.05 mol/L), and followed by 1 h ultrasonic treatment at room temperature. After filtration, the supernatant was titrated with an aqueous solution of sodium hydroxide (0.05 mol/L.

Volume of 0.05 M NaOH (titrant) (data obtained from the titrator analysis): 1.062 ml

SO_3H (mmol/g) = $\frac{Volume\ of\ NaOH\ used\ in\ titration \times Normality\ of\ NaaOH}{mass\ of\ catalyst}$

SO_3H (mmol/g) = $\frac{1.062 \times 0.05}{0.1_g}$ = 0.531mmol/g,

The measurement was repeated three times, and the average reported as the sulfonic (-SO_3H) group acid density.

- **Determination of total acid density**

In a typical analysis, 0.1g of catalyst was added into sodium hydroxide aqueous solution (10 ml, 0.05 mol/L), and followed by 1 h ultrasonic treatment at room temperature. The sodium hydroxide solution (containing the sample) as the analyte was then titrated using 0.05 M HCl as the titrant.

Sample calculation for the determination of total acidity

Number of moles of 10 mL 0.05 M NaOH (titrator)

$$= 0.05\frac{mol}{L} \times 10ml \times \frac{1\ L}{1000\ ml} = 0.0005 \text{ moles of Sodium hydroxide}$$

Number of moles of 1.82 mL (from burette reading) 0.05 M HCl (titrant) (data obtained from the titrator analysis).

$$= 0.05\frac{mol}{L} \times 1.82 \text{ ml} \times \frac{1L}{1000ml} = 0.000091 \text{ moles of Hydrochloric acid}$$

$$\text{TA(mmol/g)} = \frac{\boldsymbol{Volume\ of\ NaOH \times Normality\ of\ NaOH - Volume\ of\ HCl \times Normality\ of\ HCL}}{\boldsymbol{Mass}_{\boldsymbol{catalyst}}}$$

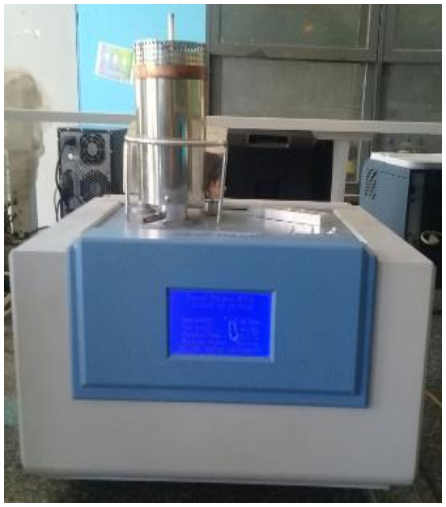
$$\text{TA(mmol/g)} = \frac{\mathbf{0.0005\ mol - 0.000091\ mol}}{\mathbf{0.1_g}} = \frac{\mathbf{0.000409\ mol}}{\mathbf{0.1_g}} = 0.00409\text{mol/g} = 4.09\text{mmol/g}$$

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

Table A-5: The amount of sulfonic group acid density data in the sulfonation process using Box-Behnken experimental design (BBD)

Run	A:Temperature ℃	B:Time (hr)	C:Ratio of sulfuric acid to biochar (ml/g)	Ultrasonic treatment condition	
				Time (min)	Room temp (25℃)
1	140	14	15	60	25
2	140	14	15	60	25
3	100	14	5	60	25
4	140	5	5	60	25
5	140	14	15	60	25
6	100	23	15	60	25
7	180	5	15	60	25
8	100	5	15	60	25
9	180	14	25	60	25
10	140	23	5	60	25
11	180	23	15	60	25
12	140	23	25	60	25
13	100	14	25	60	25
14	180	14	5	60	25
15	140	5	25	60	25

Appendix-B: Laboratory Equipment's Photo



B1. TGA instrument

B2. SEM instrument

B3. FTIR instrument