GRADUATE PROGRAMS

Zr-BDC MOF AS A SUSTAINABLE CATALYST FOR EFFICIENT HYDROLYSIS OF LIGNOCELLULOSIC BIOMASS

BY

GETAHUN GETACHEW HABTEMARIAM

A THESIS PRESENTED TO THE GRADUATE PROGRAMS OF THE ADDIS ABABA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ENVIRONMENTAL SCIENCE

ADDIS ABABA UNIVERSITY

ADDIS ABABA, ETHIOPIA

DECEMBER 2023

ADDIS ABABA UNIVERSITY
GRADUATE PROGRAMS

Zr-BDC MOF as a Sustainable Catalyst for Efficient Hydrolysis of Lignocellulosic Biomass

By

Getahun Getachew Habtemariam

A Thesis Presented to the Graduate Programs of the Addis Ababa University in Partial Fulfillment of the Requirements for the Degree of Master of Science in Environmental Science

Approved by Examining Board:-

Name and Signature of Members of the Examining Board

Name	Signature	Date
1. Dr. Ahmed Hussen (Advisor)		Jan 15, 2024
2. Prof. Abi Tadesse (Advisor)		Jan 15, 2024
3. Dr. Jemal Mohammed (Examiner)		Jan 15, 2024
4. Dr. Yedilfana Setarge (Examiner)		Jan 15, 2024
5. Dr. Ahmed Hussen (Chairman)		Jan 15, 2024

December, 2023

Declaration

I thus declare that I am the only author of this thesis, that it has not been submitted for consideration for a degree at any university and all references used for the thesis have been duly acknowledged. I give Addis Ababa University permission to lend or distribute this thesis to other institutions or individuals for the purpose of research.

Getahun Getachew

Signature: _____

Zr-BDC MOF as a Sustainable Catalyst for Efficient Hydrolysis of Lignocellulosic Biomass

Abstract

Lignocellulosic biomass, such as plant matter and agricultural residues, is a major source of renewable organic carbon on our planet. Of this lignocellulose, 40–50% is composed of cellulose that serves as a valuable feedstock for the production of fuels, chemicals, and various industrial applications. Cellulose can be converted into glucose through a process called hydrolysis. The hydrolysis of cellulose using homogenous acids is known to have drawbacks due to the generation of a large amount of toxic and corrosive wastes, making the use of heterogeneous catalysts like metal organic frameworks (MOFs) crucial for eco-friendly cellulose conversion. In this study, Zr-BDC MOF was synthesized sustainably using water as the sole green solvent, at room temperature, and without modulation. The as-synthesized Zr-BDC MOF exhibited a semi-crystalline structure with desirable properties such as a specific surface area of 380.367 m^2/g, a pore volume of 0.55cm^3 and a pore radius of 13.24 Å. The evaluation of this MOF as a solid-acid catalyst for the hydrolysis of lignocellulosic biomasses, specially Sugarcane bagasse and Pineapple peels was conducted for the first time in this study. Under optimum conditions, a mixture of 4 g biomass (Sugarcane bagasse or Pineapple peels) and 0.8 g Zr-BDC MOF in 100 mL distilled water was hydrolyzed at 130 ^oC for 4 h. The hydrolysis process yielded 0.60 mg/mL and 2.044 mg/mL of total reducing sugar (TRS), mainly glucose, from the hydrolysis of Sugarcane bagasse and Pineapple peels, respectively. These promising results demonstrated the potential of Zr-BDC MOF as an alternative catalyst for the hydrolysis of lignocellulosic biomass, enabling the conversion of cellulose to glucose for bioethanol production. The use of Zr-BDC MOF offers economic feasibility and environmental friendliness, addressing the challenges associated with homogeneous acid hydrolysis. Furthermore, this study can serve as a benchmark for future research on catalytic application of MOFs in biomass conversion to glucose for bioethanol production.

Keywords: Metal Organic Frameworks (MOFs), Catalyst, Lignocellulosic biomass, Hydrolysis, Total Reducing Sugar (TRS), Bioethanol

Acknowledgements

First and foremost, I want to express my gratitude to my supervisors, Dr. Ahmed Hussen, Prof. Seyoum Leta, and Prof. Abi Tadesse, for the chance and all of their help throughout this work.

I want to express my gratitude to my family for their unwavering love and daily support. I also want to express my gratitude to my wife, Mieraf Gebrekidan, for her support, love, and assistance. Without you, my darling, I could not have done it.

Lastly, I would like to express my gratitude to Dr. Jemal Mohammed for his assistance, as well as to my friends Wuletw Adane and Memeheru Melkamu, as well as to all of my coworkers at the Addis Ababa Education Bureau's Curriculum Development and Implementation Directorate for their support during both the good and the bad times.

Table of Contents

List of figures

List of Tables

List of Acronyms

AFEX- Ammonia Fiber Explosion

AHP- Alkaline Hydrogen Peroxide

BDC- BenzenediCarboxylate

BET- Brunauer-Emmet-Teller

DDW- Double Distilled Water

DMF- DiMethylFormamide

DNS- 3, 5-dinitrosalicylic acid

EDX- Energy Dispersive X-ray spectroscopy

FTIR- Fourier Transform Infrared Spectroscopy

GHG- Greenhouse Gases

2G- Second Generation

HMF- Hydroxyl Methyl Furfural

LAG- Liquid-Assisted Grinding

LHW- Liquid Hot Water

MOFs- Metal-Organic Frameworks

OD- Optical Density

PP- Pineapple Peels

PXRD- Powder X-Ray Diffraction

SCB- Sugarcane Bagasse

SEM- Scanning Electron Microscopy

SSF- Simultaneous Saccharification and Fermentation

TCC- Total Carbohydrate Content

TGA- Thermogravimetric Analysis

TRS- Total Reducing Sugar

UiO-University of Oslo

Chapter One

Introduction

1.1 Background

Scientists have been interested in environmental issues related to climate change as well as global warming because of its paramount significance to human survival [1]. To balance the demand-supply chain and enhance the quality of life, it is now necessary to look for an alternative sustainable and clean fuel source due to an increasing levels of greenhouse gas, the depletion of oil reserves, and expanding demands of energy. Therefore, fully utilizing biomass has great capacity to reduce the use of fossil fuels, lower greenhouse gas (GHG) emissions, and promote the growth of the agricultural sector [1]. However, there is still more work to be done in developing productive and affordable technology for the processing and utilization of biomass, especially for the production of cellulosic ethanol.

Metal-Organic Frameworks (MOFs) are newly developed family of porous materials that are made up of organic linkers and metal ions or clusters [2]. MOFs have several advantageous properties over traditional porous materials like SiO_2, zeolites, activated carbon, and molecular sieves. These properties include a high specific surface areas and porosity, well-organized configuration, ordered and tunable pore structures, low crystal densities and easily functionalized surface chemical structures [3]. For this reason, MOFs have been used for a variety of applications, such as for sensing of chemicals [4], delivering drugs [5], storing gases [6], catalysis process [7], and pollutant separation [8]. Among these areas, currently there is much

interest in applying MOFs as solid catalysts for organic reactions in the liquid-phase, especially as heterogeneous catalyst for efficient catalytic organic transformations [9].

The utilization of biomass as a renewable substitute for fossil feedstocks in the production of chemicals and fuels is growing [10]. Lignocellulosic biomass is the most abundant feedstock for the production of bioethanol. Agricultural residues, the organic portion of municipal solid wastes, forest biomass and wastes, and energy crops are the primary sources of lignocellulose [11]. Using lignocellulose biomass for fuel has numerous benefits, such as lower environmental impact, financial gains, resolution of the fuel vs. food debate, and a desirable substitute for disposing of these residues. Lignocellulosic bioethanol can be obtained by two distinct steps: hydrolysis and fermentation, by running each step under its optimum operation conditions. Enzymatic hydrolysis of pretreated biomass can be achieved using cellulase, although the reaction may be constrained by activity loss, reaction conditions, and product inhibition [12].

Despite the great promise of MOFs, one of the primary obstacles to their widespread industrial application is typically their synthesis process. The majority of MOFs that have been documented thus far are typically made using organic solvents like dimethylformamide (DMF) or others, which can be hazardous or poisonous to work with. Furthermore, a lot of MOFs need for extended synthesis times (one week or more in certain circumstances), high synthesis temperatures (100–280 ^{o}C in many cases), and overpressures [13]. Therefore, it is obvious that new, more environmentally friendly, and easily scalable synthesis techniques of MOFs need to be developed to facilitate their transfer to industrial-scale manufacturing.

Catalysis is an environmentally friendly and economically appealing technology that can meet customer demands for ever-higher-quality goods and

services while still being environmentally conscious. It is anticipated that MOFs' three remarkable characteristics— well-defined pore size, high specific surface area, and unique coordination chemistry of main group elements and transition metals —will result in remarkable catalytic performances. These characteristics ought to make it possible to develop highly selective catalysts for atom and energy efficient processes. However, there is little work reported in literature on the catalytic role of MOFs for the hydrolysis of lignocellulosic biomass for bioethanol production. Therefore, in this work, we have synthesized a Zr-BDC MOF by using water as a sole solvent at room temperature and evaluated its catalytic potential for the hydrolysis of lignocellulosic biomasses (Sugarcane bagasse and Pineapple peels).

1.2 Statement of the Problem

Environmental degradation and public health issues have been significantly exacerbated by the overuse of non-renewable energy. Consequently, there is a need to find a renewable energy source. Therefore, with its ability to sufficiently replace gasoline as a transportation fuel, bioethanol—produced by fermenting plant biomass— is considered to be an environmentally friendly alternative to replace fossil fuels [14]. This bioethanol production mostly utilizes enzymatic catalysis of biomass. However, enzyme issues, such as high cost approximately 30% of cellulosic ethanol production [15], low stability, use of buffer solutions, and the need for high glucose purity, can considerably limit the process [16] of bioethanol production. Hence, searching for optional catalysts, namely MOFs is important.

Nevertheless, a number of MOFs, even those being researched for possible green application are still synthesized in, and washed with hazardous and high boiling point solvents such as N,N-dimethylformamide (DMF) are used in large amounts

[17]. Thus, risks are of twofold: the first is to the environment and the second is to human health, where prolonged exposure to DMF can cause cancer and reproductive problems [17].

The applications of MOFs as heterogeneous catalysts have been reported by different researchers. For example, Ahmed et al. [12] reported that UiO-66 MOF participated in enzymatic hydrolysis of planetree exfoliating bark as co-catalyst for production of bioethanol. Moreover, Zheng et al. [15] reported that adding Zr-based MOFs (UiO-66 and UiO-66-NH_2) decreased about 50% enzyme dosage in the enzymatic hydrolysis of corncob residues. However, there is a gap in fully replacing cellulase enzyme by MOF catalysts for hydrolysis of lignocellulosic biomasses for bioethanol production. Herein, we have synthesized a Zr-BDC MOFs using water as a solvent at room temperature and evaluated its catalytic potential in hydrolysis of Sugarcane bagasse and Pineapple peels for the first time.

1.3 Objectives of the Study

1.3.1 General objective

The major objective of this study was to evaluate catalytic potential of Zr-BDC MOF in the hydrolysis of lignocellulosic biomass for bioethanol production.

1.3.2 Specific objectives

- Synthesize a Zr-BDC MOF using water as a solvent at room temperature in an environmentally friendly condition.
- Characterize the physicochemical properties of Zr-BDC MOF
- To optimize different variables (Zr-BDC MOF load, biomass load, temperature, and time) for the hydrolysis of pretreated sugarcane bagasse and Pineapple peels.

- Evaluate catalytic potential of Zr-BDC MOF for the hydrolysis of cellulose into TRS (glucose) from lignocellulose biomass (Sugarcane bagasse, and Pineapple peels).
- To indicate catalytic potential of Zr-BDC MOF as an alternative catalyst for the hydrolysis of lignocellulosic biomasses for bioethanol production

1.4 Significance of the Study

Biomass is a sustainable and renewable source of energy and chemicals. Thus, synthesizing a Zr-BDC MOF and evaluating its catalytic potential for the hydrolysis of lignocellulosic biomass is very vital. Therefore, the significance of this study is to synthesize a Zr-BDC MOF using water as a sole solvent at room temperature and evaluate its catalytic potential for the hydrolysis of cellulose into TRS (glucose) for bioethanol production.

Chapter Two

Literature Review

2.1 Metal Organic Frameworks (MOFs)

Metal organic frameworks are types of hybrid inorganic-organic crystalline substances that consist metal ions and organic linkers [18]. Metal ions and organic linkers can be combined to made millions of unique metal organic frameworks [19]. Currently, more than 500,000 MOFs are predicted and more than 90,000 have been synthesized. [19]. MOFs have a high surface area and porosity, which makes them appealing for uses in drug delivery, gas storage and separation, and catalysis [20].

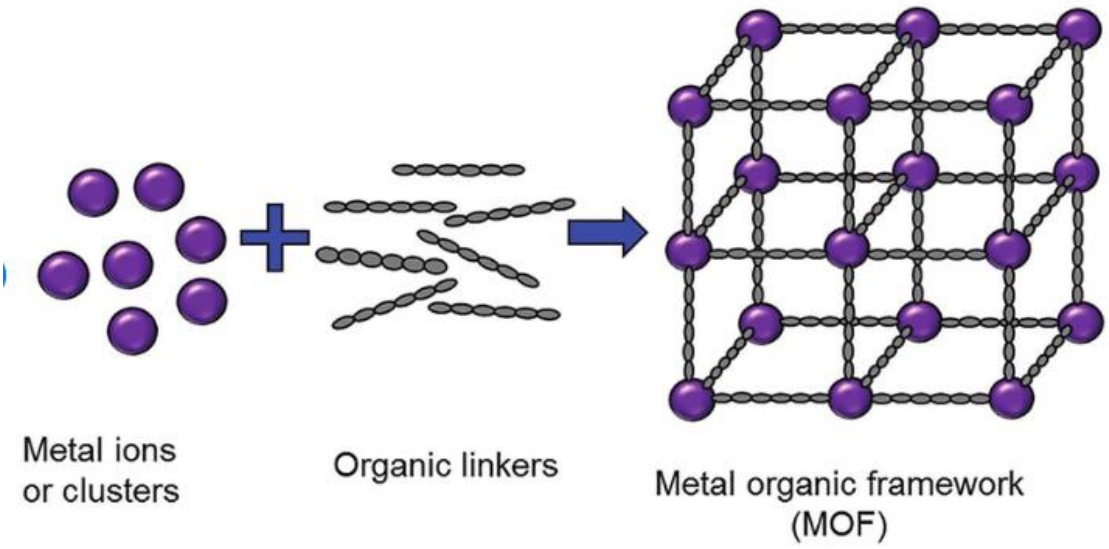


Fig. 1 MOF structure

2.2 Synthesis of MOFs

MOFs are often synthesized via a solvothermal method, which involves the solubilization of a metal precursor (often in the form of salt) and an organic ligand in a solvent [21]. As a result, the synthesis of MOFs is usually done in the liquid phase, either with a suitable solvent mixture or a pure solvent. Moreover, some MOFs are synthesized without solvent by mechanochemical method. The formation of crystalline framework takes place by self-assembly of the structural units by forming an ordered network of metal organic coordination bonds [22]. Typically, the synthetic method involves combining two solutions that comprise the metal and the organic component. This can be done at room temperature or under hydro-solvothermal conditions, and it can also involve the use of extra auxiliary molecules [22]. Moreover; as an alternative to conventional MOF syntheses, mechanochemistry, has been recently introduced. Mechanochemical techniques, like liquid-assisted grinding (LAG) enables the synthesis of MOFs without bulk solvents, corrosive reagents frequently applied in solution syntheses, and aggressive conditions [23].

MOFs are usually synthesized using formamide solvents such as N,N-dimethylformimide (DMF) which are dangerous to the environment and human health [24], even other impurity or formate ion byproduct exist in the final product due to the decomposition of DMF at high temperature. Therefore, safer and more environmentally friendly solvent alternatives like N,N-dimethyl-9-decenamide are employed for the synthesis of a variety of structurally varied MOFs in order to reduce the environmental impact of MOF synthesis in both academic and industrial settings [17]. Moreover, recent studies indicate that MOFs are synthesized in water at room temperature [25, 26]. Therefore, greener alternatives for the synthesis of MOFs

make it economically feasible and also environmentally friendly when compared to the synthesis of MOFs by using DMF solvent.

2.3 MOFs as Catalysts

A catalyst is a substance that speeds up a chemical reaction toward equilibrium without significantly being consumed. The word “catalysis” originate from Greek words “κατα” which means “down” and “λυσισ” which means “loosening” [27]. Catalysts are useful to modern society in many fields, such as environmental remediation, chemical manufacturing, and energy conversion, with a world catalyst market of billions of US dollars per year [28].

MOFs are appealing for catalytic applications since they can potentially bridge the gap between heterogeneous and homogeneous catalysis due to their ease of structural design, very large surface area, high porosities and capacity to significantly load the structure with active guest molecules that are accessible to the relevant reactants. [29]. Therefore, tens of thousands of MOFs have been synthesized in the last two decades and numerous structures had been studied in relation to catalysis. Some of the MOFs investigated in catalysis includes: ZIF-8 [30], MOF-5 [31], UiO-66 [32], MOF-808 and NU-1000 [33], and MIL-100 [34].

MOFs have demonstrated excellent catalytic activity in a variety of chemical processes like hydrogenation [35], oxidation [36], isomerization [37] and esterification [38]. This is explained by the many MOF structural components where active sites may be present or may be engrafted. It was thus found that the active sites might be included in: (i) the porous network by encapsulating active guest species [39], (ii) the organic linker functionalized with Brønsted basic groups [40] or acidic groups [41], (iii) the uncoordinated metal nodes functioning as Lewis acid [42].

The existence of structural defects in the framework of MOFs is another cause that raises their catalytic activity. As a result, several researchers have become curious about the defected MOFs and have attempted to purposefully introduce these defects into the framework. [43]. This is because defected MOFs clearly demonstrated an elevated level of porosity, surface area, and catalytic activity when compared to the ideal structure where the catalytic activity is inhibited by the fully-coordinated metal cluster [43, 44]. As a result., modulated synthesis was developed and first evaluated by Schaate et al. [45], which involves supplementing mono-dentate ligands (modulators) having the same chemical functionality with the linker. The modulator's role is to rival the linker by trying to either regulate the nucleation [45–47], morphology of MOFs, crystallinity, or to generate defects in the structure [48]. For example, di and tri-fluoroacetic acid [43], acetic acid [43], benzoic acid [45], and formic acid [47] have been employed as modulators to produce various MOFs. After removing these monocarboxylate ligands, new open active sites can be left behind for improved catalytic performance, which significantly enhances the levels of catalytic activity.

MOF catalysts exhibit the following unique characteristics: (i) suitable hydrophilic and hydrophobic pore characteristics to aid in the identification and transportation of reactant and product molecules; (ii) evenly distributed catalytic sites on the porous surface, that helps for selectivity; (iii) simple separation and recovery for long-term usage; and (iv) multipurpose microenvironment to achieve synergistic catalysis [49]. Metal coordination centers in MOF frameworks have the potential to stimulate a variety of organic reaction, especially those that are important for the conversion of biomass [50].

From a catalytic perspective, MOFs are advantageous for applications in the liquid phase since they have the catalytic site characteristics of homogeneous catalysts and the benefits of simple separation and recycling. The nano-spherical cavities inside the MOF networks function as reaction chambers. The chemical environment and the void volumes of the interior of MOFs can be modified or designed as required for the use in catalysis. In general, MOF catalysts' active sites can be (i) the sites inherent in the framework (ii) unsaturated coordination environment in metal centers, and (iii) additional catalytic species contained within the pores [9].

2.4 Biomass

According to EU Directive 2003/30/EC, "biomass" refers to the biodegradable portion of wastes, products, and residues from forestry, agriculture (including substances derived from animals and vegetables), and related industries. It also includes the biodegradable portion of wastes from municipal and industries [51].

2.4.1 Lignocellulosic Biomass

"Lignocellulosic" refers to any variety of plant molecules or biomass that contains cellulose, with differing amounts of lignin, chain lengths, and degree of polymerization [52]. An abundant natural resource, lignocellulosic biomass consists of three major components in its cell walls: lignin (15–25% w/w), a phenolic polymer; hemicellulose (20–40% w/w), a heteropolymer made of several sugars, including galactose, arabinose, and xylose; and cellulose (30–50% w/w), a homopolymer made of glucoses [53, 54]. The composition of lignocellulosic biomass also contains trace amounts of ash, including sulfur and oxide components. [55], and proteins, starch, pectin, waxes, aromatics, minerals and lipids [56, 57].

Lignocellulosic biomass is very resistant to biological and chemical attack because of its characteristics such as the complicated structure of the cell wall [58], the level of cellulose crystallinity [59], the crossed-bonds among the components [60], and the amount of lignin [58].

2.4.2 Structure of lignocellulosic biomass

Lignocellulose contains lignin, hemicelluloses and cellulose. These polymers are closely related to form the structural framework of the plant cell wall. The species, age, and growth circumstances of plants all affect the lignocellulose composition. Plant species have a significant impact on the distribution of cellulose, hemicelluloses, and lignin as well as the varying sugar contents of hemicelluloses [61].

a. Cellulose- It covers the majority of the plant cell wall with a degree of polymerization up to 10,000 or more. It is a homopolysaccharide made completely of D-glucose units connected by β-1, 4-glucosidic linkages. Because of the cellulose chain's linear structure, hydrogen bonds can form between and within molecules, causing the chains to aggregate into simple crystalline fibrils made up of 36 chains of cellulose.

The structure of the elementary fibrils, together with the intermolecular hydrogen bonds, makes cellulose insoluble in most solvents, gives it high tensile strength, and is partially contributes for the resistance of cellulose against microbial breakdown [62]. Enzyme and degradation product diffusion along the cellulose surface may be slowed by the dense layer of water that forms due to the hydrophobic surface of cellulose. [63].

b. Hemicelluloses - They consist of the monomeric residues D-galactose, D-glucose, D-xylose, D-mannose, L-arabinose, D-glucoronic acid, and 4-O-methyl-D-glucoronic acid. They are complex heterogeneous polysaccharides. They have a degree of polymerization under 200, side chains and are acetylable. They are categorized based on the primary sugar present in the polymer's backbone, such as mannan (β-1, 4-linked mannose) or xylan (β-1, 4-linked xylose) [64].

c. Lignin- It is the most prevalent non-polysaccharide fraction in lignocellulose and is a complex network formed by the polymerization of phenyl propane molecules. P-coumary alcohol, conifer alcohol, and sinapyl alcohol are the three monomers that make up lignin. They are joined by ether linkages of the alkyl-aryl, alkyl-alkyl, and aryl-aryl types. Since lignin embeds the cellulose, it provides protection against chemical and microbial breakdown. Furthermore, lignin can form covalent bonds with certain hemicelluloses, such as benzyl ester bonds with xylan's 4-O-metthyl-D-glucoronic acid carboxyl group. In xylans and mannans, lignin can form more stable ether bonds, or lignin carbohydrate complexes, with arabinose or galactose side groups. [65]. The lignocellulose's structure is described in Fig. 2.

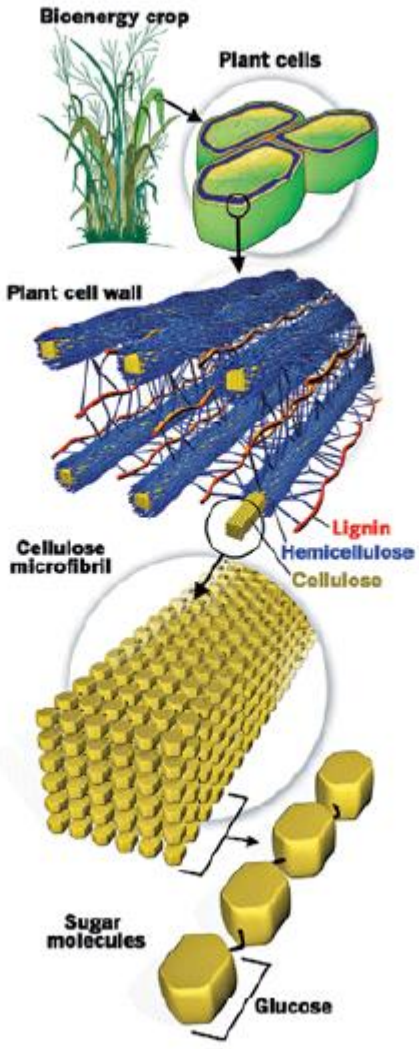


Fig.2. lignocellulose structure [66].

2.5 Lignocellulosic Bioethanol

Lignocellulosic bioethanol is a 2nd generation (2G) bioethanol that is produced from lignocellulosic materials mainly by biochemical method. The main steps in the biochemical process are pretreatment, hydrolysis (saccharification), fermentation and distillation [67].

2.5.1 Lignocellulosic Biomass Pretreatment

In order to facilitate the hydrolysis of cellulose by acids or enzymes, it is necessary to pretreat lignocellulosic biomass in order to break down the structures of

lignin and hemicellulose, disrupt the crystalline structure, and enhance porosity [52]. Depending on the type of pretreatment method used., lignocellulosic biomass pretreatment methods are primarily categorized into biological and Non-biological methods [68]. There are three primary categories of non-biological pretreatment methods: chemical, physical, and physico-chemical. These methods do not involve any microbial treatments [68].

2.5.1.1 Physical pretreatment

Mechanical comminution

This method enables the comminution of biomass using a variety of techniques including irradiation, extrusion, chipping, grinding, shredding, and milling. The size and crystallinity of the biomass are successfully reduced by milling and grinding. Reducing heat and limiting mass transmission is the primary objective of chipping. According to studies, chipping reduces biomass size to 10–30 mm, whereas milling and grinding reduce it to 0.2-2 mm [69]. Nevertheless, research indicates that reducing biomass particles below 0.4 mm does not significantly impact the rate and yield of hydrolysis [70].

2.5.1.2 Chemical pretreatment

Lignocellulosic biomass pretreatment with chemical includes methods such as acid, alkaline, oxidative, ozone, ionic liquids, and organosolv pretreatment [51].

a) **Acid**: In this technique, the biomass is dried and ground. After that, it is presoaked in water and left to sit in an acidic solution at a particular temperature for a while. The purpose of the acid pretreatment is to increase the cellulose's accessibility to enzymes by solubilizing the hemicellulosic part of the biomass. For this method, both diluted and concentrated acids can be utilized; however, employing concentrated acids is not recommended as they tend to produce compounds that

hinder the formation of ethanol. Acids such as HCl, H_2SO_4, HNO_3, and H_3PO_4 are some of the commonly used acids in this method [68].

b) Alkaline: With this method, the biomass is soaked in the alkaline solution and mixed for a predetermined amount of time at the necessary temperature. When compared to acid treatment, alkaline pretreatment results in less degradation of sugar and is carried out at lower pressure and temperature [71]. It helps to remove lignin by breaking down the ester and glycosidic side chains and increases the digestibility of cellulose and partially solvates hemicellulose. Additionally, it eliminates uronic acid substitutions on hemicellulose and acetyl. It involves the use of chemicals like ammonia, potassium, sodium, and calcium hydroxides that are non-corrosive and non-polluting.

c) Organosolv: With this technique, aqueous organic solvents like acetone, methanol, ethylene glycol, ethanol, etc. are added to the biomass under specific conditions of pressure and temperature [72, 73]. This pretreatment increases the conversion of biomass by increasing the accessibility of the cellulose fibers for enzymatic hydrolysis due to the removal of lignin from the biomass [74].

d) Oxidative: this process involves treating lignocellulosic biomass with oxidizing agents such air, hydrogen peroxide, ozone, or oxygen [75]. Several chemical reactions including side chain displacement, oxidative cleavage and electrophilic substitution of aromatic ring ether linkages may occur during this pretreatment. This process led to delignification through the conversion of lignin into acids, which may have inhibitory effects. As a result, these acids must be eliminated [76]. Hydrogen peroxide is the most frequently used oxidizing agent. It has been discovered that the hydrolysis of hydrogen peroxide produces hydroxyl radicals, which are in charge of breaking down lignin and produce low molecular weight compounds. When lignin is removed from

lignocellulose, cellulose and hemicellulose are exposed, which promotes enzymatic hydrolysis [77]. In comparison to the absence of alkali, Saha and Cotta's (2007) [78] study found that applying NaOH to an alkaline peroxide pretreatment enhanced the production of reducing sugars, resulting in a cellulose conversion of over 96%.

2.5.1.3 Physicochemical pretreatment

Ammonia fiber explosion (AFEX), CO_2 explosion, hydrothermal treatment, liquid hot water, and steam explosion are methods used in the physicochemical pretreatment of lignocellulosic biomass [51].

a) **Steam explosion**: It is the physicochemical pretreatment technique for lignocellulosic biomass that is most frequently utilized. Due to the notion that the biomass needs to be explosively altered in order to make it ready for hydrolysis, this method was formerly known as steam explosion [74]. It is also called 'autohydrolysis' because of the changes that occur during the process. Usually, steam pretreatment combines chemical actions (autohydrolysis of hemicellulose's acetyl groups) with mechanical forces (pressure drop). This technique hydrolyzes and releases hemicellulose by subjecting biomass to high pressure (0.7–4.8 MPa) saturated steam at elevated temperatures (between 160 and 260 ^{o}C) for a few seconds to minutes.

b) **Ammonia fiber explosion**: Using this approach, lignocellulosic biomass is heated in a closed container at 60–90 ^{o}C and pressure over 3 MPa for 30–60 minutes in a 1:1 ratio with liquid ammonia. Once the container has maintained the appropriate temperature for five minutes, the valve is opened, causing the pressure to explode and the ammonia to evaporate, causing the system's temperature to drop [79]. This technique is comparable to steam explosion, however instead of using water, ammonia is employed [80]. After being treated with ammonia at high pressure and temperature, lignocellulosic biomass undergoes swelling and a phase change in its

cellulose crystallinity, which increases the reactivity of the remaining carbohydrates. Modifications to the lignin structure lead to an increase in digestibility and water-holding capacity.

c) **CO_2 explosion:** This method uses supercritical CO_2 to pretreat biomass, which causes the gas to behave like a solvent. A high pressure vessel containing the biomass is subjected to the supercritical CO_2 [81]. After being heated to the necessary temperature, the vessel is maintained at a high temperature for a few minutes [82]. When CO_2 is introduced into biomass under high pressure, it transforms into carbonic acid, which hydrolyzes hemicellulose. When the pressured gas is released, it causes the biomass structure to be disrupted, increasing the surface area that is accessible [83].

d) **Liquid hot water**: it is a method used to pretreat a biomass with water at high pressure and temperature. This method is also called hydrothermal pretreatment, hydrothermolysis, aqueous fractionation, aquasolv or solvolysis [84]. Solvolysis with hot compressed water interacts with biomass for up to 15 min at 200–230 °C. During the process, 40–60% of the total biomass dissolves, and all of the hemicellulose, 35–60% of the lignin, and 4–22% of the cellulose are removed. When the resultant liquid was hydrolyzed with acid, more than 90% of the hemicellulose was recovered as monomeric sugars. Moreover, acetic acid is produced during the process and facilitates the hydrolysis of polysaccharides. As a result, monomeric sugars are formed, which have the potential to further break down into furfural, an inhibitor of fermentation. The biomass type with significant lignin solubilization preventing recovery of hemicellulose sugars was linked to variation in the results [85].

2.5.1.4 Biological pretreatment

Microorganisms like white, brown, and soft rot fungi are used in this class of pretreatments to break down lignin and hemicellulose. Biological pretreatments provide the advantages of gentle operating conditions and low energy requirements. However, biological hydrolysis often occurs at a relatively slow rate, so this pretreatment method needs long residence times [86–88].

2.5.1.5 Difficulties in applying the various pretreatment methods

a) Acid Pretreatments

This method is among the effective method that is less expensive and simpler to use. Even if it is economical, it has certain shortcomings such as formation of inhibitory by-products, high reactor expenses for their usage, and production of gypsum during neutralization following the pretreatment. In acid pretreatment, the primary inhibitors formed are furfural, hydroxyl methyl furfural (HMF) and product by-products like aliphatic carboxylic acids and phenylic compounds [89].

b) Alkali Pretreatments

In this method, the high expense of alkali is a major problem. In comparison to acid pretreatments, less inhibitory chemicals are formed. They produce hydroxyl acids, Small amounts of furan aldehydes and acetic acid [89].

c) Solvent based Pretreatments

In this method, ionic liquids and organic solvents are used to eliminate lignin. The major problem of this method is the left out of little solvents and ionic liquids found in the biomass which is hazardous to microorganisms and enzymes [89].

d) Hydrothermal Pretreatments

The disadvantage of this technique is that only very less amount of lignin is eliminated during the pretreatment of lignocellulosic biomass.

2.5.1.6 The role of AHP in the refining of biomass

Hydrogen peroxide is an extremely reactive and a powerful oxidizing agent, and also miscible in all ratios with water. It is mostly found in aqueous solution in concentrations varying from 20 to 60% (w/v). As it is strongly oxidizing, it can be applied to enhance the enzymatic digestibility of agricultural secondary and primary residues. AHP is one of the best pretreatments for delignification of various lignocellulosic agricultural residues such as residues such as rapeseed straw [90], cashew apple bagasse [91], sweet sorghum bagasse [92], rice husks [93], wheat straw [94], and sugarcane bagasse [95]. AHP has an oxidative effect on the cell wall of biomass and that ruptures ester bonds in them with increased digestibility and lower sugar degradation. During the AHP pretreatment, very little or no secondary product formation takes place [96]. Therefore, higher lignin removal can be achieved during the pretreatment of lignocellulosic biomass by efficiently using AHP pretreatment.

2.5.1.7 Mechanism of AHP treatment

Hydrogen peroxide needs alkaline pH to produce oxidizing radicals to breakdown lignin. The best appropriate pH of this pretreatment is 11.5 and decreasing or increasing pH below or above the range of 10-12.5 will lead to improper delignification or degradation of the sugar molecules. Therefore, the appropriate pH for this pretreatment method is adjusted by adding NaOH.

Hydrogen peroxide is used for pretreating lignocellulosic biomasses due to the chemical reactions it has with the alkaline liquid media. Its dissociation produces the hydroperoxide anion (HOO^-) through Eq. (1) [97].

$$H_2O_2 + H_2O \leftrightarrow HOO^- + H_3O^+ \quad (1)$$

As stated in Eq. (2), the hydroperoxide anion can react with H_2O_2 in an alkaline media to produce hydroxyl and superoxide radicals.

$$H_2O_2 + HOO^- \leftrightarrow OH^{\cdot} + O_2^{-\cdot} + H_2O \quad (2)$$

Since these radicals are the strongest oxidizers, delignification occurs when α-O-4 and β-O-4 bonds rupture, generating new compounds that are then eliminated by oxidation of phenolic groups into aldehydes and carbonyl compounds [98].

2.5.2 Hydrolysis (Saccharification) of lignocellulosic biomass

After pretreatment step, the biomass undergoes hydrolysis in order to produce bioethanol. This can be done using either enzymatic hydrolysis or acid hydrolysis. For acid hydrolysis, pretreatment and hydrolysis can be carried out in a single step, however both enzymatic hydrolysis and acid hydrolysis require pretreatment to increase the susceptibility of the cellulose materials [99].

Acid Hydrolysis

Acid hydrolysis may be done either with concentrated or dilute acid. For dilute acids, the operating temperatures are around 200-240 ^oC and acid concentration of approximately 1.5% are needed to hydrolyze cellulose. Under these conditions, hydroxymethyl furfural (HMF) and other compounds that are inhibitory to fermentation might be produced as a result of glucose degradation. Xylose is also broken down into furfural and other compounds under this conditions [69].

The dilute acid process can have a time of reaction within a few seconds or minutes, so a continuous process is available although batch mode is also possible [100]. Additionally, this dilute acid hydrolysis can occur in two steps in order to hydrolyze both the hemicellulose and cellulose at their respective optimal conditions. In this setup, the initial stage is done under a low temperature, maximizing yield from hemicellulose, while the second step is performed at a higher temperature

to hydrolyze the cellulose [101]. Yields of glucose in the range of 50% were reported for this two –stage system [102].

Higher yields can be obtained using concentrated acids, such as 30-70% H_2SO_4. This system has a higher glucose yield of 90%, and takes approximately 10-12 h [103]. Due to the low operating pressure and temperature; concentrated acid processes produce few degradation products [103]. However, costly acid recycling must be employed to maintain the profitability of the process.

Enzymatic Hydrolysis

Enzymatic hydrolysis is performed by cellulase enzyme. A proposed mechanism of cellulolytic hydrolysis is given in Fig.3. A common cellulase cocktail used to break down cellulose and hemicellulose contains mixture of β-glucosidases, exoglucanases and endoglucanases [99]. In the cellulose hydrolysis, endoglucanases breaks down cellulose chains randomly, which makes free ends, enabling increased degradation with exoglucanases [104]. The β-glucosidases catalyze the hydrolysis of cellobiose to glucose. Additionally, hemicellulases can be used to hydrolyze the hemicellulose polymer into its component sugars.

Enzymatic hydrolysis can be performed either separately from the fermentation step, or simultaneously in the presence of microorganisms for fermentation. The later, simultaneous saccharification and fermentation (SSF), implies the use of genetically modified microorganisms which can ferment glucose and xylose in similar broth as the hydrolysis of cellulose (into glucose) and hemicellulose (into xylose, arabinose and other minor sugars such as mannose, galactose and ribose) [84]. SSF minimizes product inhibition of cellulolytic enzymes and therefore enables higher saccharification rates and higher yield of sugars and therefore ethanol [105].

Compared to chemical hydrolysis, enzymatic hydrolysis produces less byproducts that are inhibitory to the fermentation step [106], operate under milder process conditions and therefore allow the use of less expensive materials for equipment, and consumes less energy in the process [107]. However, it was still reported to be less economical than chemical hydrolysis [108] due primarily to the very high cost of the enzymes [102, 109].

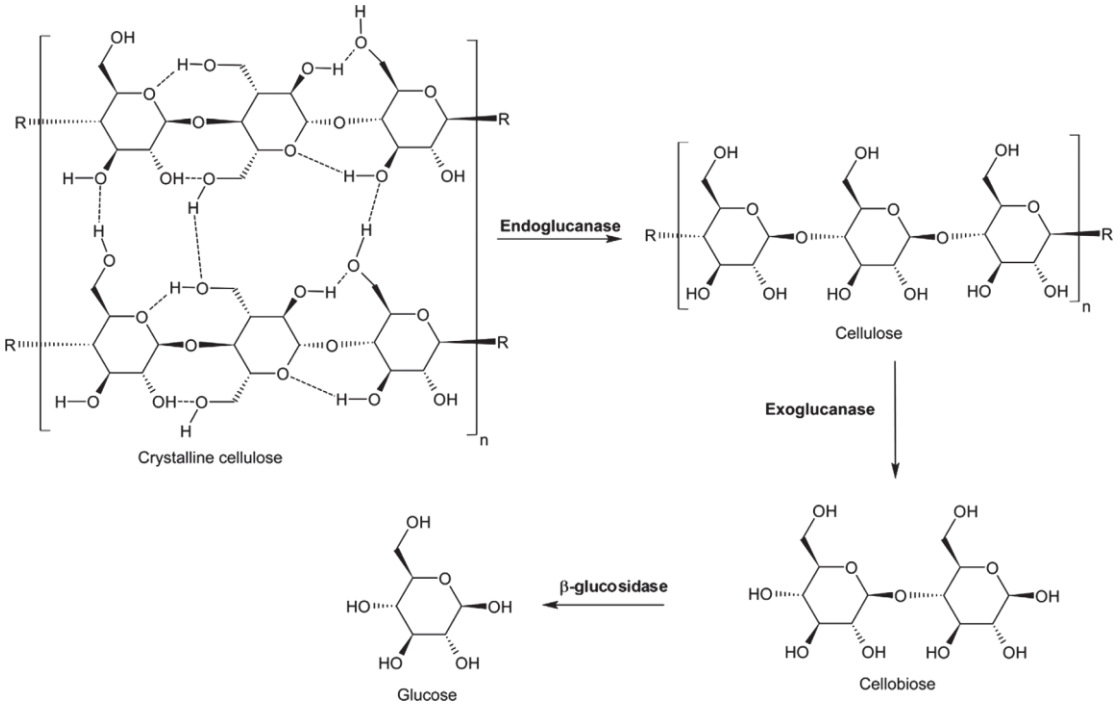


Fig.3. Enzymatic hydrolysis mechanism of cellulose [110].

Hydrolysis by using MOF Catalysts

In this type of hydrolysis, MOF catalysts fully replace liquid acids and cellulase enzymes for the hydrolysis of cellulose. The 1st attempt of cellulose hydrolysis by MOF catalyst was reported by Akiyama et al. [111]. In brief, the hydrolysis of cellulose by MIL-101(Cr)-SO_3H MOF was performed at 120 ^{o}C for 3 h and obtained 1.2, 1.4, and 2.6 % yields of cellobiose, glucose, and xylose respectively.

Additionally, Ahmed et al. [12] also reported the hydrolysis of cellulose by UiO-66 MOF at 120 ^{o}C for 1 h. However, they reported that the participation of the UiO-66 MOF for the hydrolysis of cellulose was very low at the studied conditions.

2.5.3 Fermentation of lignocellulosic hydrolysate to bioethanol

Fermentation of lignocellulosic hydrolysate is a biological process that converts the monomeric units of sugars obtained from the hydrolysis step into gases, acids and ethanol using fungi, yeast, or bacteria [112]. The widely used microorganism is yeast; Saccharomyces cerevisiae due to high tolerance limits and high yield of ethanol. Saccharomyces cerevisiae converts xylan from the hydrolysis of hemicellulose can be converted to xylose while glucose, fructose or mannose which can be obtained from the hydrolysis of cellulose to ethanol [112].

Three types of fermentation—fed-batch, batch, or continuous—can be used to produce bioethanol [113]. In fed-batch fermentation, one or more constituents are added to the container as fermentation is happening whereas in batch fermentation, feedstock is added to the fermentation vessel along with nutrients, microorganism, and other constituents at the start of fermentation of whole batch followed by recovery of ethanol [103]. The kinetics of the microorganisms being utilized and the type of feedstocks are the primary determinants in the choice of the most appropriate fermentation mode. Constant ingredient addition and output removal from the fermentation tank are necessary for continuous fermentation. Batch fermentation is the simplest fermentation technique since it requires less control, is less expensive, easier to sterilize, handle feedstocks, and employs unskilled labor. Fed-batch mode is widely used in industrial production because it combines the advantages of continuous and batch processes [114]. This fermentation method has some benefits over traditional batch processing, including the ability to maintain the highest

concentration of viable cells, produce more, prolong the life of the cell, and control a number of crucial parameters like pH, temperature, and dissolved oxygen at a particular level through feedback activities [115]. There are two primary reactor types that can be used for continuous fermentation: plug flow reactors and continuous stirrer tank reactors. These reactor types have certain advantages over batch fermentation. This fermentation process increases production while lowering costs because it requires less downtime for cleaning and filling the vessel [116].

2.5.3.1 Factors affecting bioethanol production

The following factors impact the generation of bioethanol: pH, temperature, time of fermentation, sugar concentration, size of inoculum, and rate of agitation [113]. Elevated temperatures may denature the enzyme and decrease its activity. The best temperature range for biomass fermentation is 20–35 ^{o}C [117]. The highest possible yield of bioethanol production might be obtained using a concentration of 150 g/L [113]. The broth's pH also has an impact on the production of bioethanol due to its effects on yeast growth, bacterial contamination, by-product formation, and fermentation rate [112].Fermentation of biomass using Saccharomyces cerevisiae requires a pH range of 4.0–5.0 [112]. A longer incubation time is needed at pH values below 4.0, whereas the concentration of ethanol is greatly decreased at pH values above 5.0. Another factor to be considered in bioethanol production is the agitation rate. The amount of ethanol produced increases with increasing agitation rate. The standard agitation rate for fermentation using yeast cell is 150–200 rpm. However, excessive agitation rate may restrict a cell's ability to perform metabolic processes [113].

2.5.4 Distillation

Most of the time, the fermentation of monomeric sugars is followed by the recovery of ethanol from the fermentation broth. Anhydrous ethanol with a minimum of 99.5% by volume can be formed when the broth's water content is typically lowered to about 0.5% by volume [112]. This process, which can be implemented using the distillation principle, is constrained by the azeotropic nature of the ethanol-water solution. The azeotropic solution's drawback is addressed by employing a separating agent that modifies the primary component's relative volatility. Pure ethanol is recovered from the fermentation broth using membrane, azeotropic, extractive, adsorption, diffusion, vacuum distillation, and chemical dehydration techniques [112]. Conventional methods encompass extractive and azeotropic distillation as well as liquid-liquid extraction [118]. The predominantly utilized technique for large scale production of ethanol is extractive distillation. Other methods are becoming more and more popular for use in the future because they utilize less energy. These are salt distillation and pervaporation [119].

Chapter Three

Materials and Methods

3.1 Materials

Analytical grade chemicals such as zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$, 98%, Avra Synthesis Pvt.Ltd., India), Terephthalic acid (H_2BDC, 98%, Sigma Aldrich, USA), sodium hydroxide pellets (NaOH, Rankem Laboratory Reagent, India), ethanol (C_2H_5OH, absolute, Carlo Erba Reagents, France), sulfuric acid (H_2SO_4, 98%, Carlo Erba Reagents, France), 3,5-dinitrosalicylic acid (DNS, Abron Chemicals, India), sodium potassium tartrate ($C_4H_4O_6KNa.4H_2O$, T.Gerrard & Co.Ltd. Biological Laboratories, UK), hydrogen peroxide (H_2O_2, 30%, Dallul Pharmaceuticals, Ethiopia), acetone (UNI-CHEM chemical reagents, UK), and D-glucose (GuangZhou Jinhuada chemical Reagent Co.Ltd., China) were used.

Lignocellulosic biomasses such as sugarcane bagasse (SCB) and Pineapple peels (PP) were also used. Moreover; apparatuses/instruments such as drying oven (GX-65B, China), hot plate (MSH-300i, England), UV-vis spectrophotometer (Jeneway 6850, UK), pH-meter (Jenway 3510, UK), shaker (Model no. SHO-2D, Korea), autoclave (DIXONS Surgical instruments Ltd, UK), Centrifuge (Model no. 80-2A), electronic balance (Model no. JD210-4, UK), Muffle furnace(SX-2.5/10, China), Desiccator, Water bath, Filtering crucibles, Erlenmeyer flasks, Filter paper, Sieve of mesh size 0.5 mm (Model no.SSIC-90, SISCO, India) and grinder (Model no. GCG684, Geepas, UAE) were used in this study.

3.2 Methods

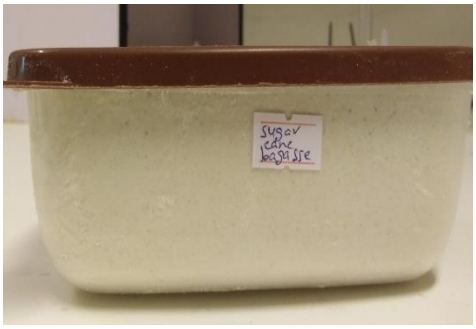
3.2.1 Sample collection and preparation

Two lignocellulosic biomasses sugarcane bagasse (SCB) and pineapple peels (PP) were collected from juice houses found in Addis Ababa city. The collected samples were air dried. The air dried samples were chopped into pieces, ground, and milled by a grinder and sieved by using 0.5 mm mesh. 1.5 Kg of each of the sugarcane bagasse and Pineapple peels powder were measured and kept inside different vessels. The sample preparation processes are shown below in Fig.4.

a. Sugarcane bagasse

b. Pineapple peels

c. grinding the air dried sample



d. Sugarcane bagasse powder e. Pineapple peels powder

Fig.4. Sample preparation processes

3.2.2 Composition analysis of the raw and pretreated SCB and PP

The composition of the raw and pretreated biomass (SCB, PP) material was determined using the gravimetric method [120].

Extractives: Dried raw biomass (SCB, PP) weighing 2.5 g was loaded into a cellulose thimble. Moreover, 150 mL of acetone that was used as a solvent for extraction was transferred into a round-bottom flask. Then, after the Soxhlet extractor was configured, residence times for the boiling and rising stages was carefully adjusted to 70 ^{o}C and 25 min respectively on the heating mantle for 4 h. Following extraction, the sample was air dried for few minutes at room temperature. The extracted material was then dried in an oven at 105 ^{o}C until a constant weight was achieved. The % (w/w) of the extractives content was calculated by dividing the weight of the extractives by the weight of the dried raw biomass and multiplying by 100 [121–123].

Hemicellulose: A dried extracted/pretreated biomass (1 g of SCB, PP) was weighed and transferred into a 250 mL Erlenmeyer flask. Then, 150 mL solution of 0.5mol/L NaOH was added to the flask containing the biomass. The mixture was boiled for 3.5 h with distilled water. After boiling, the mixture was allowed to cool, filtered through vacuum filtration and washed repeatedly with distilled water until it reaches a neutral pH. The residue was dried in an oven at 105 ^{o}C until it reaches a constant weight. The

hemicellulose content (%w/w) was calculated by dividing the weight of hemicellulose that was extracted during the process by the initial biomass weight and multiplying it by 100 [121–124].

Lignin: Dried extracted raw/pretreated biomass (300 mg of SCB, PP) was weighed and transferred in to a glass test tube. Then, 3 mL of 72% H_2SO_4 was added to the biomass in the test tube. The sample was kept at room temperature for 2 h with carefully shaking at 30 min intervals to ensure complete hydrolysis. After the initial hydrolysis, 84 mL of distilled water was added to the test tube to dilute the mixture. The diluted mixture was transferred to an autoclave and subjected to hydrolysis for 1 h at 121 ^{o}C. After the hydrolysis in the autoclave, the slurry was cooled to room temperature. The hydrolyzates were separated from the solid residue by vacuum filtration using a filtering crucible. The residues remaining on the filtering crucible were washed with distilled water. Then, they were transferred to weight filters and dried in an oven at 105 ^{o}C until constant mass was achieved. The dried residues were incinerated at 575 ^{o}C in a muffle furnace to determine the ash content. The percentage of insoluble lignin was calculated relative to the dry sample mass using Equation 1. The acid soluble lignin fraction was determined by measuring the absorbance of the acid hydrolyzed samples at 320 nm. The lignin content was calculated as the summation of acid insoluble lignin and acid soluble lignin [125].

$$\%L_{Ki} = \frac{Mk - Mc}{MA} \text{x } 100 \quad (1)$$

Where L_{Ki} is Lignin Klason insoluble; M_k is mass of dry insoluble lignin; M_c is ash mass of the insoluble lignin; M_A is the dry sample mass.

Ash: in order to determine the total ash, 1 g of dried extracted raw/pretreated biomass (SCB, PP) was weighed and transferred into a previously weighed porcelain crucible.

Then, the sample was incinerated at 575 ^{o}C in a muffle furnace for 2 h. By mass difference, the ash content was determined using Equation 2.

$$\% \text{ ash} = \frac{Mc}{Ma} \text{x } 100 \quad (2)$$

Where % ash is percentage by mass of ash; M_c is ash mass (difference between the mass of the crucible with ash and the mass of the empty crucible); M_a is mass of the dried raw biomass sample.

Cellulose: The cellulose content (%w/w) was determined by difference, assuming that cellulose, hemicellulose, lignin, extractives and ash are the only components present in the lignocellulosic biomass [121–123].

3.2.3 Pretreatment of SCB and PP

In this study, SCB and PP were pretreated by alkaline hydrogen peroxide pretreatment method previously used by Rabelo et al. [95]. The pretreatment was performed under optimal conditions of 7.35% (w/v) of peroxide at 25 ^{o}C for 1 h. In brief, the pretreatment solution of alkaline peroxide was prepared by adding 24.5 mL of 30% H_2O_2 in 75.5 mL distilled water and the pH was adjusted to 11.5 with sodium hydroxide.

In each pretreatment run, 4 g of each biomass (SCB, PP) were treated at 25 ^{o}C for 1 h with 100 mL of 7.35% hydrogen peroxide in 500 mL flasks by stirring it with a shaker agitated at 150 rpm. Following the pretreatment step, the liquors were separated from the solid fraction by filtration. The solids fraction was washed many times to remove the water-soluble solids, dried at room temperature and its mass was weighted to determine the pretreatment yield and chemical composition [125, 126]. Then, 1M H_2SO_4 was added to the pretreatment liquor that was obtained above until

pH 2 to precipitate lignin. After the lignin was washed with distilled water and dried at room temperature, its mass was weighted.

3.2.4 Synthesis of Zr-BDC MOF

The methodology previously used by Yassin et al. [26] was followed in the synthesis of Zr-BDC MOF. In brief, 1.95 g of $ZrOCl_2.8H_2O$ was dissolved in 28 mL of distilled water (solution 1) and in separate beakers; 1.03 g of H_2BDC was suspended in 22 mL of distilled water. Subsequently, 13 mL of 1.0 M NaOH solution was gradually added to the linker suspension as deprotonating agent, and the resultant mixture was then stirred for 30 min until reaching clear solution (solution 2). Next, solution 1 was transferred dropwise into solution 2 or vice versa, resulting in an instantaneous precipitation of a white solid. The sample was left under stirring at 300 rpm with a magnetic stirrer for 24 h at room temperature. The formed solid was centrifuged and washed with distilled water (three times) and with ethanol (two times). The sample was then dried at 80 ^oC in an oven.

3.2.5 Characterization of the Zr-BDC MOF

The synthesized Zr-BDC MOF was characterized using various advanced techniques. To determine the crystalline structure and phase purity of the as-synthesized material, Powder X-ray diffraction (PXRD) patterns were recorded using a Philips X'PERT diffractometer equipped with an X'Celerator detector and employing Cu Kα radiation with a wavelength of 1.5418 Å. The diffraction patterns were registered in the 2θ range from 4 to 90^o. N_2 sorption properties were measured at -196 ^oC (77 K) using a Micrometrics instrument ASAP 2420 device. Approximately 100 mg of each sample was prepared and subjected to outgassing at 120-150 ^oC under high vacuum for 16 h before the measurements of any isotherms. The Brunauer-Emmet-Teller (BET) method was used to estimate the surface area of the material.

The t-plot approach was used to determine the material's micropore and external surface areas. The total pore volume and average pore radius were estimated from the relative pressure close to unity (p/p_o = 0.98). The morphology of the Zr-BDC MOF was examined using a high-resolution Philips XL 30 SEM device.

3.2.6 Hydrolysis of the pretreated SCB and PP using Zr-BDC MOF

The hydrolysis was carried out on the pretreated lignocellulosic biomass (SCB, PP) by optimizing the amount of Zr-BDC MOF, biomass (SCB, PP) load, temperature and hydrolysis time using one factor at a time method [127] that is adjusting one variable at a time while maintaining the same value for the others. Following is an outline of the process for each parameter.

3.2.6.1 Optimization of Zr-BDC MOF Mass

About 4 g of each pretreated biomass (SCB, PP) was taken and placed in a round bottom flask. Then, different amounts of the Zr-BDC MOF catalyst (0.4, 0.6, 0.8, 1.0 and 1.2 g) were added to each biomass sample. Finally, 100 mL of distilled water was added to each sample in a round bottom flask. The flask containing the mixture was fitted with a condenser to prevent solvent loss through evaporation, and placed on a hot plate with magnetic stirrer. Then, the mixture was heated at 130 ^{o}C for 4 h independently with continuous stirring at 300 rpm. A control sample reaction without the Zr-BDC MOF catalyst was also carried out under the same conditions. At the end of the reaction, each flask was removed from the hot plate and rapidly cooled to room temperature. The mixture was then centrifuged at 2058 x g for 5 min to separate the solids. The clear hydrolysate obtained after centrifugation was used for the determination of total reducing sugars.

The total reducing sugar (TRS) of the hydrolysate was determined by dinitrosalicylic acid (DNS) method. Thus, 1 mL of the clear hydrolysate was placed into a 25 mL test tube and then 3 mL of dinitrosalicilic acid (DNS) reagent was added to the test tube. The reaction mixture was heated in boiling water for 5 min, resulting in the development of a red color, indicating the presence of reducing sugars. After cooling the mixture, the absorbance was measured using a UV-vis spectrophotometer at a wavelength of 540 nm. The TRS concentration was calculated by employing a standard calibration curve prepared using a glucose solution [128, 129]. The TRS concentration was calculated using equation 3:

$$\text{TRS concentration} = \frac{(\text{absorbance of the hydrolysate}) - (\text{y-intercept})}{\text{slope}} \quad \text{.....3}$$

3.2.6.2 Optimization of Biomass (SCB, PP) Load

About 3, 3.5, 4, 4.5 and 5 g of each pretreated biomass (SCB, PP) were taken along with the optimized Zr-BDC MOF catalyst concentration and placed in a round bottom flask. Then, 100 mL of distilled water was added to each sample in a round bottom flask. The mixture was heated at 130 ^{o}C for 4 h independently with continuous stirring at 300 rpm. The hydrolysis procedure and TRS determination were carried out in the same way as described previously for the Zr-BDC MOF catalyst concentration.

3.2.6.3 Optimization of Hydrolysis Time

The hydrolysis time was optimized by varying the time from 1 to 5 h while keeping the biomass load and Zr-BDC MOF catalyst concentration at the optimized values and temperature at 130 ^{o}C. The hydrolysis procedure and TRS determination were carried out in the same way as described previously for the Zr-BDC MOF catalyst concentration.

3.2.6.4 Optimization of Hydrolysis Temperature

The hydrolysis of optimized biomass (SCB, PP) was performed in a round bottom flask at different temperatures of 50, 90 and 130 ^{o}C. The Zr-BDC MOF catalyst concentration and hydrolysis time were kept at the previously optimized values. The hydrolysis procedure and TRS determination were carried out following same steps as described for the Zr-BDC MOF catalyst concentration.

Finally, TRS (mg/mL) obtained during hydrolysis was taken into consideration to calculate the hydrolysis yield. It was calculated as follow [130]:

$$\text{Hydrolysis (\%)} = \frac{\text{TRS concentration obtained x total volume of hydrolysate}}{\text{mass of sample used}} \text{ x } 100$$

The hydrolysis processes are shown in Fig.5.

Fig.5. Hydrolysis process

Chapter Four

Results and Discussion

4.1 Chemical Compositions of Raw SCB and PP

The compositional analysis of the raw SCB and PP was determined using gravimetric method. Biomass compositions can vary depending on whether they are classified as woody or non-woody biomass, methods developed for analysis, geographical locations of materials, differences in solvents used, biomass variety and the different parts of plants used in the compositional analysis [120].

The compositions of the two lignocellulosic materials are as shown in Table 1. Each experiment was done in triplicate; reported results indicate the average mean values of the triplicated experiments. Therefore, the chemical composition of raw SCB was 48.36±0.44% cellulose, 24.0±0.46% hemicellulose, 20.66±0.49% lignin, 4.19±0.04% ash, and 2.37±0.03% extractives. Moreover; the chemical composition of raw PP was 42.83±0.39% cellulose, 21.37±0.67% hemicellulose, 10.24±0.24% lignin, 9.2±0.26% ash, and 15.2±0.4% extractives.

Table 1 Chemical composition of raw SCB and PP (% w/w)

Materials	Component (% w/w)				
	Cellulose	Hemicellulose	Total lignin	Ash	Extractives
SCB	48.36±0.44	24.0±0.46	20.66±0.49	4.19±0.04	2.37±0.03
PP	42.83±0.39	21.37±0.67	10.24±0.24	9.2±0.26	15.2±0.4

Results in this study are comparable to other reported values in the literature [127, 131]. For example; Paturau et al. [132] reported 26-47% cellulose, 19-33% hemicellulose, 14-23% lignin and 1-5% ash content for SCB. Moreover,

Sherif et al. [127] reported 41.54±2.31% cellulose, 21.97±0.81% hemicellulose, 10.37±0.46% lignin, 8.80±0.04% ash and 15.49±0.13% extractives content for PP. The content of cellulose in SCB and PP were 48.36±0.44% and 42.83±0.39%, respectively, showing that SCB and PP were a good substrate for fermentable sugars production.

4.2 Effect of Alkaline Hydrogen Peroxide Pretreatment on SCB and PP

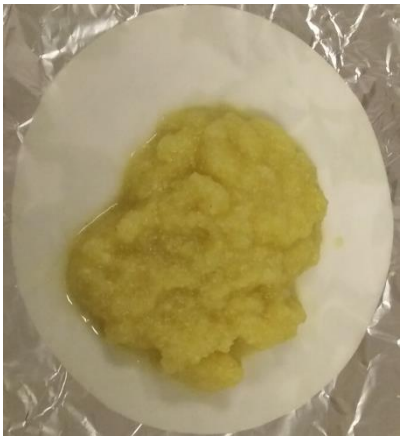
Pretreatment is considered as an essential step in a biorefinery in reducing the recalcitrance of the biomass. In this study, pretreatment was performed using alkaline hydrogen peroxide. Alkaline hydrogen peroxide treatment has been shown to have an oxidative action on the cell wall of biomass, resulting in the breaking of ester linkages within the cell wall matrix. This oxidative action promotes the disruption of lignin-carbohydrate complexes and the removal of lignin from the biomass, thereby increasing the digestibility of the biomass [98]. In the presence of NaOH, the intramolecular ester bonds between lignin and hemicellulose can undergo saponification, resulting in the extraction of lignin from the lignin-hemicellulose complex [133]. Thus, AHP pretreatment is used to achieve higher lignin removal during the biomass (SCB and PP) pretreatment process [98].

Table 2 Chemical composition of pretreated SCB and PP by AHP (% w/w)

Materials	Component (% w/w)			
	Cellulose	Hemicellulose	Total lignin	Ash
Pretreated SCB	79.12±0.69	11.03±0.25	8.13±0.21	1.46±0.06
Pretreated PP	81.49±1.49	12.19±0.35	2.51±0.03	2.02±0.02

In this study, the white color of the raw SCB was changed into a light yellow color (Fig.6a), while the dark brown color of the PP was changed into a light yellow color (Fig.6b) after the biomasses were pretreated with AHP. The change in color of the raw SCB and PP after treatment with AHP indicates the changes in chemical composition (Table 2), with the removal of non-cellulosic materials such as ashes, extractives, hemicellulose, lignin, and oils.

a. Pretreated SCB



b. Pretreated PP

Fig.6 Pretreated SCB and PP

The content of cellulose was increased to 79.12±0.69 %, while hemicellulose (11.03±0.25%), lignin (8.13±0.21 %), and ash (1.46±0.06%) were decreased (Table 2) when SCB was pretreated with AHP. Similarly, the content of cellulose was increased to 81.49±1.49%, while hemicellulose (12.19±0.35%), lignin (2.51±0.03%), and ash (2.02±0.02%) were decreased (Table 2) as expected when PP was pretreated with AHP, indicating the effectiveness of AHP treatment to remove recalcitrant lignin and make cellulose more accessible to Zr-BDC MOF for hydrolysis.

4.3 Characteristics of the Zr-BDC MOF

a) Synthesis of Zr-BDC MOF

Zr-BDC was prepared by instantaneous precipitation at room temperature in aqueous solution (in the presence of NaOH) containing equimolar ratio of zirconyl(IV) chloride and linker H_2BDC. The white precipitate formed was then centrifuged, whashed with distilled water three times and with ethanol two times , and dried in an oven at 80 ^{o}C. Finally, as shown in Fig. 7, a white solid Zr-BDC was obtained.

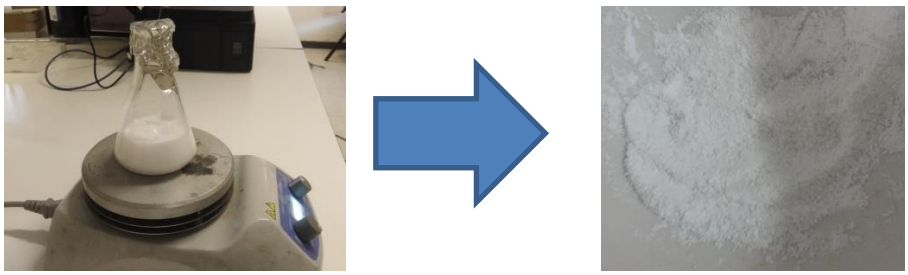


Fig. 7 Zr-BDC MOF synthesis

b) XRD pattern of Zr-BDC MOF

Figure 8 shows the XRD pattern of the as-synthesized Zr-BDC MOF prepared under sustainable conditions, water as a solvent and under room temperature, unlike the conventional approach which uses DMF as a solvent and relatively high temperature i.e. 120 ^{o}C. The major peak exhibited arround 2 thetha of 8^{o} typically evidences the formation of Zr-BDC MOF. Although the peak shows in the range from 30 to 40 degrees make this MOF similar to UiO-66, the peak apparent around 2 thetha of 15^{o} could be associated to the linker, terephthalic acid remained as a residue due to insufficient washing. The presence of such linkers could be justified by the relatively lower specific surface area of the as-synthesized MOF compared with previous similar report by Yassin et al. [26]. It appears that the MOF has a semi-crystalline

structure since a broadened reflections are observed. Yassin et al. [26] also reported that Zr-BDC MOF has a semi-crystalline structure.

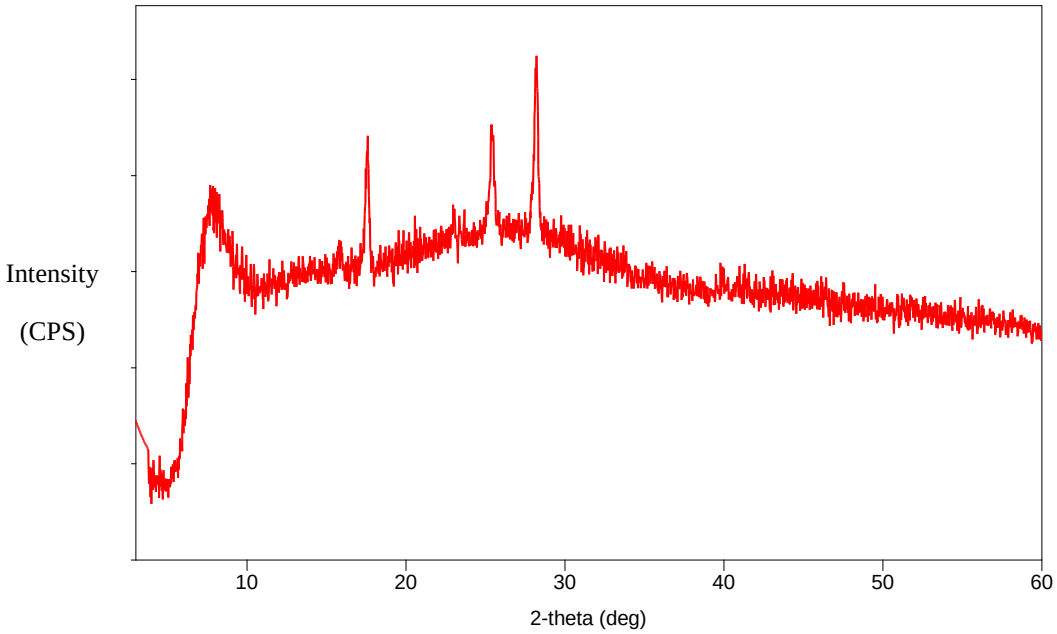


Fig. 8 PXRD pattern of Zr-BDC MOF

c) Textural Properties of Zr-BDC MOF

The Nitrogen adsorption-desorption isotherms at 77 K for Zr-BDC MOF is depicted in Fig.9. The material exhibited a significant uptake of nitrogen at lower relative pressure values ($P/P_o < 0.1$),which suggests the presence of micropores within the material. Moreover, the BET results indicate that the Zr-BDC MOF has a specific surface area of 380.367 m^2/g, a pore volume of 0.55 cm^3, and a pore radius of 13.24 Å. The relatively lower specific surface area (380 m^2/g) compared with similar MOF prepared by Yassin et al. [26] ,(450 m^2/g) could be due residual linker not removed by washing.

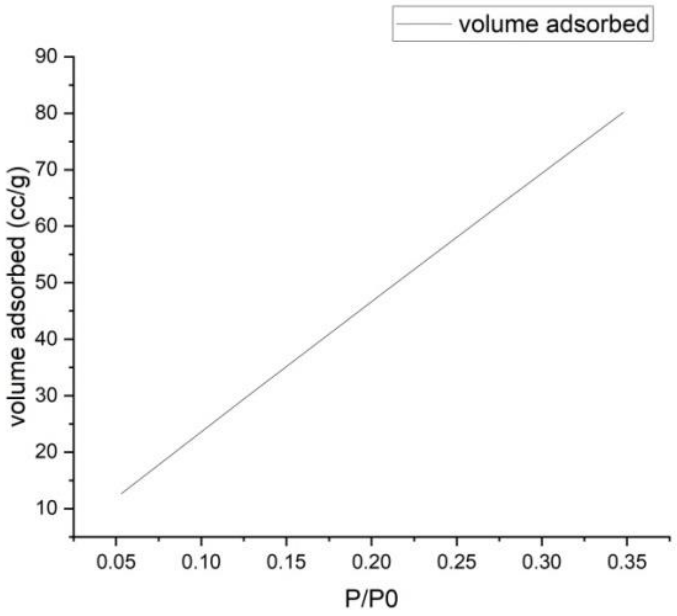
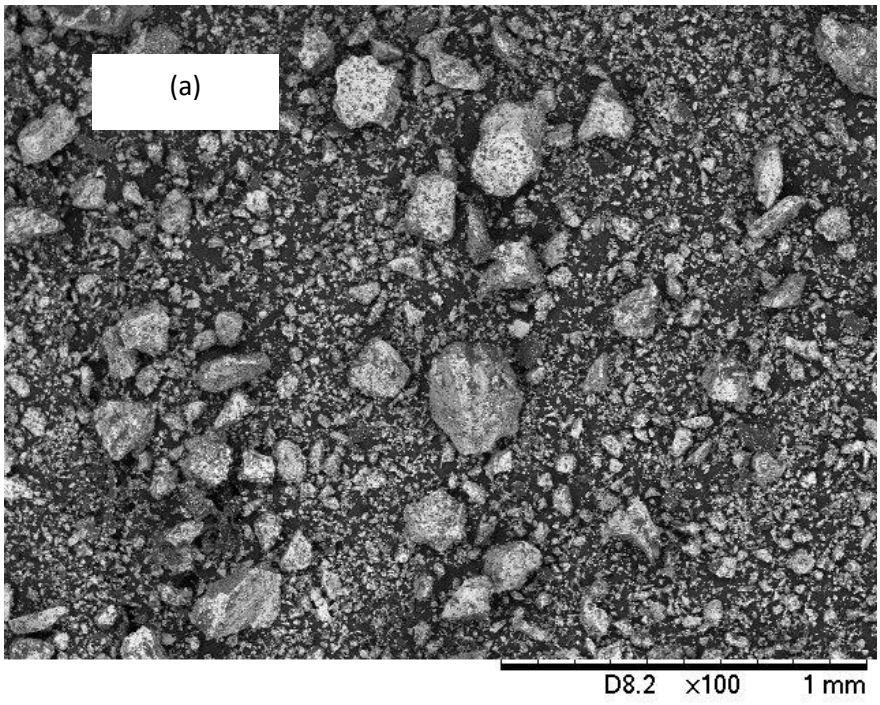
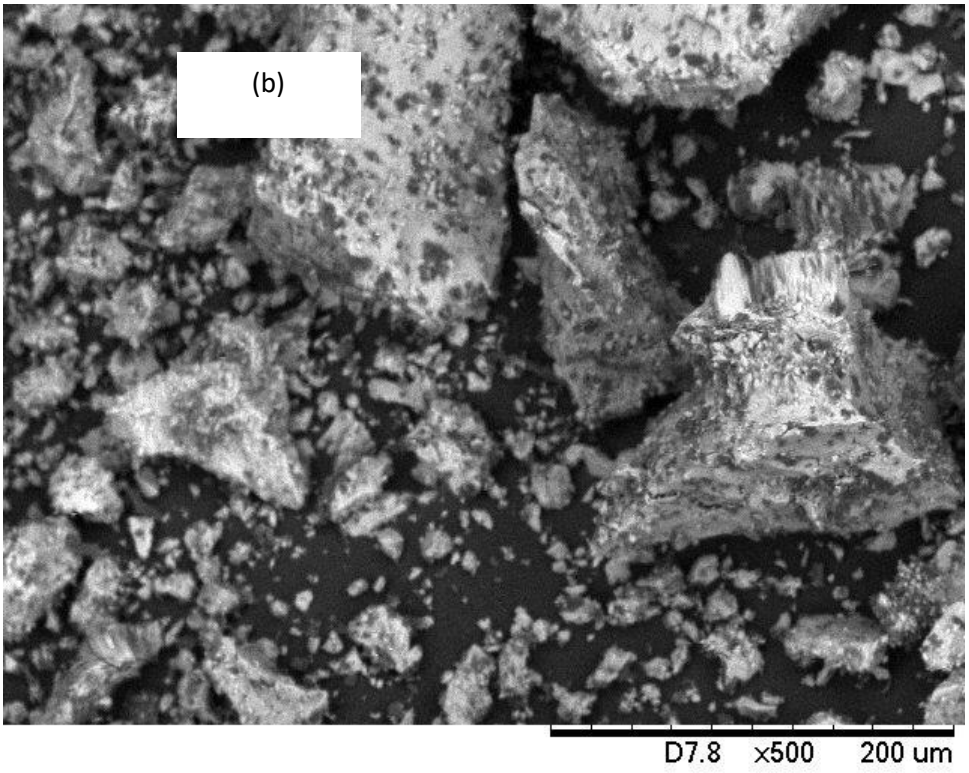


Fig. 9 Nitrogen adsorption-desorption isotherm for Zr-BDC MOF

d) Morphological Properties of Zr-BDC MOF

The SEM images of the Zr-BDC MOF show different sized irregular-shaped particles (Fig. 10a-b). A closer look at the SEM micrograph of this MOF (Fig. c) however reveals the porous nature of this material.





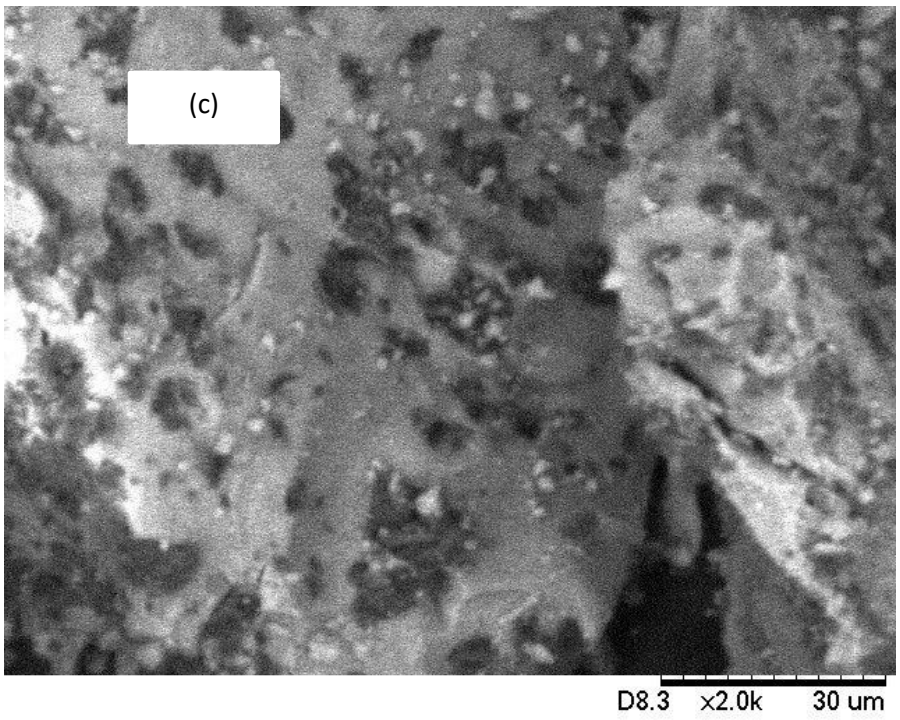


Fig. 10 SEM images of Zr-BDC MOF

4.4 Optimum Parameters for the Hydrolysis of Pretreated SCB and PP

The hydrolysis of pretreated SCB and PP was optimized with respect to Zr-BDC mass, SCB and PP load, reaction temperature and time by using one factor at a time approach. In the literature, different researchers use different ranges of the parameters (temperature, time, and amount of catalyst) for the hydrolysis of biomass. For example Sherif et al. [127] have used temperature ranges of 90, 110, 130 and 150 ^{o}C in the time range of 1to 4 h and catalyst concentrations of 0.05, 0.1 and 1M for the hydrolysis of multi substrate biomass. Besides, Ahmed et al. [12] have used temperature ranges of 50, 80,100 and 120 ^{o}C for the hydrolysis of 50 mg cellulose at 120 ^{o}C for 1 h. Additionally, Rekha et al. [134] have used 3 g biomass, 0.1 to 0.3 g of catalyst at temperature ranges of 30, 45 and 60 ^{o}C for 1 h for the hydrolysis of corncob. Thus, this indicates that different ranges of parameters were used in the literature. Therefore, in our study we have used a Zr-BDC MOF catalyst mass in the range of 0.4 to 1.2 g, a pretreated SCB and PP mass in the range of 3 to 5 g at a temperature range of 50, 90 and 130 ^{o}C in a time range of 1 to 5 h for optimizing the parameters for the hydrolysis of pretreated SCB and PP.

4.4.1 Optimum Parameters for the Hydrolysis of Pretreated SCB

a. Zr-BDC MOF Mass

Hydrolysis of 4 g pretreated SCB was carried out with varying amounts of Zr-BDC MOF (0.4, 0.6, 0.8, 1 and 1.2 g) at 130 ^{o}C for 4 h to optimize the mass of the catalyst. Therefore, different MOF masses i.e. 0.4, 0.6, 0.8, 1 and 1.2 g resulted into a TRS yield of 0.56, 0.58, 0.60, 0.60 and 0.59 mg/mL respectively (Fig.11). An increase in mass of Zr-BDC MOF from 0.4 to 0.8 g resulted in an increase of TRS yield (from 0.56 to 0.60 mg/mL), but slightly decreased beyond 1 g of Zr-BDC MOF. The decrease in TRS content with further increase in Zr-BDC MOF mass may be due

to further decomposition of sugars into other by-products. Hence, 0.8 g Zr-BDC MOF was observed for maximum TRS yield (0.60 mg/mL) and was employed for hydrolysis of pretreated SCB in subsequent optimization studies.

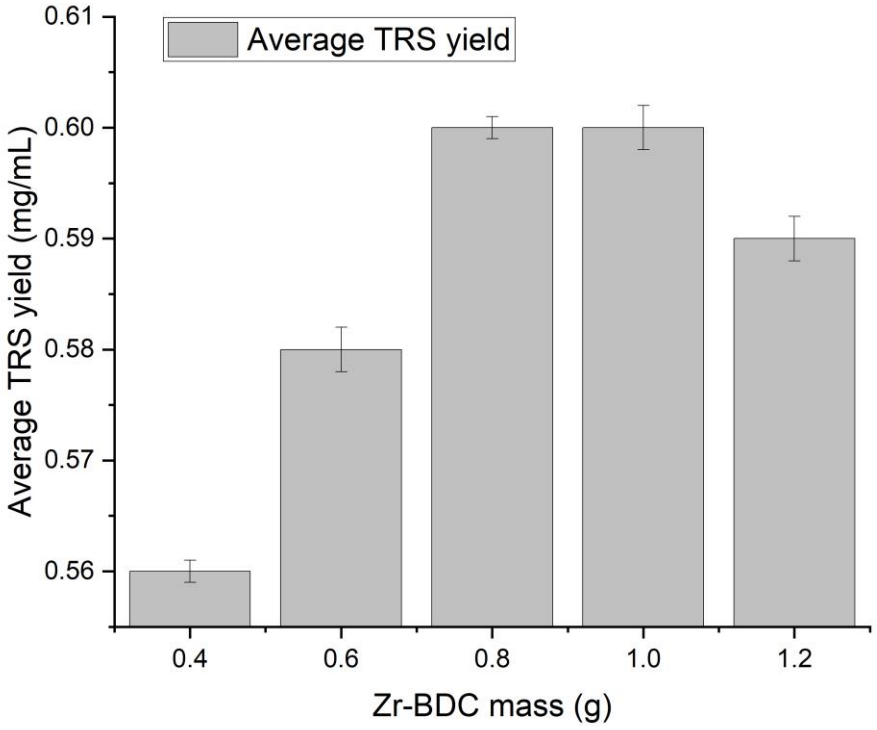


Fig.11. Zr-BDC mass optimization for the hydrolysis of SCB

b. SCB Load

To get the optimum load of SCB for hydrolysis, the reaction was carried out using the optimum amount of Zr-BDC MOF (0.8 g) at 130 ^{o}C for 4 h with varying amounts (3, 3.5, 4, 4.5 and 5 g) of SCB. As depicted in Fig.12, the maximum TRS yield of 0.60 mg/mL was obtained at 4 g of SCB. There is a slight reduction in reducing sugar yield beyond 4 g of SCB. The decrease in TRS content may be due to the decrease in the adsorption capacity of the Zr-BDC MOF catalyst as a result of high substrate loading that slows down mass transfer phenomena. Thus, the results

suggest that 4 g is the optimum amount of SCB for the hydrolysis reaction at the given reaction conditions.

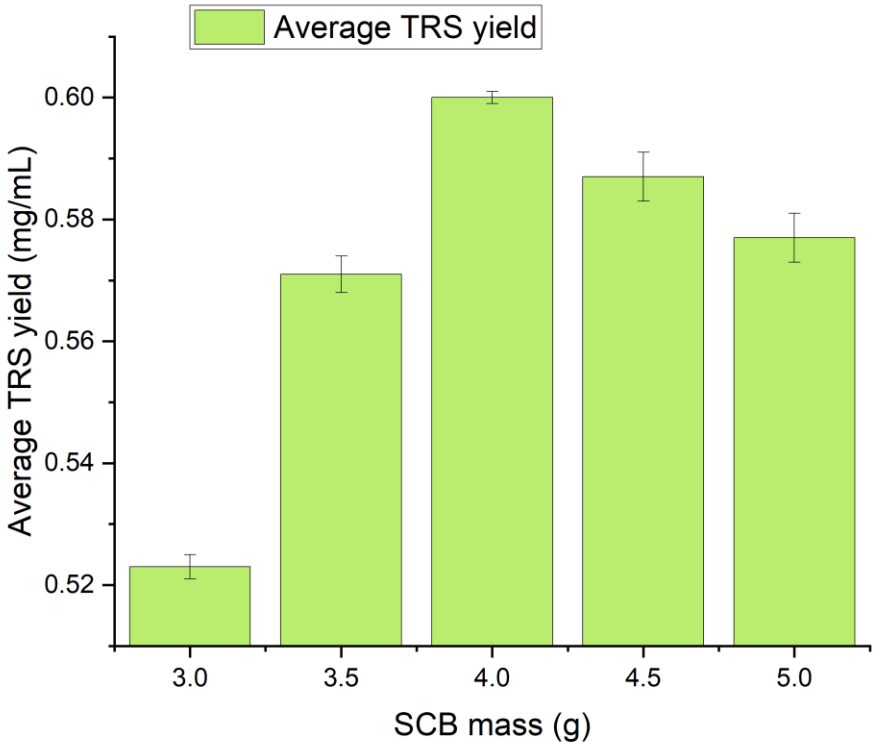


Fig.12. SCB mass optimization for the hydrolysis of SCB

c. Time

Hydrolysis time is one of the most critical factors among different physical factors affecting the yield of sugar during the hydrolysis of lignocellulosic biomass. To optimize time, the hydrolysis was carried out using 4 g SCB, 0.8 g Zr-BDC MOF at 130 ^{o}C by varying time from 1 to 5 h. As shown in Fig.13, there is a gradual increase of TRS yield from 0.244 to 0.289 mg/mL for the reaction period of 1 to 2 h. Besides, the reducing sugar yield increases linearly for the reaction period of 3 to 4 h reaching at a maximum TRS yield of 0.60 mg/mL at 4 h. Beyond 4 h, the TRS concentration is almost similar with the TRS concentration obtained at 4 h, but the volume of TRS hydrolysate was decreased due to the loss of more water through

evaporation. Hence, 4 h is found to be the optimum hydrolysis time, which led to the production of 0.60 mg/mL of TRS.

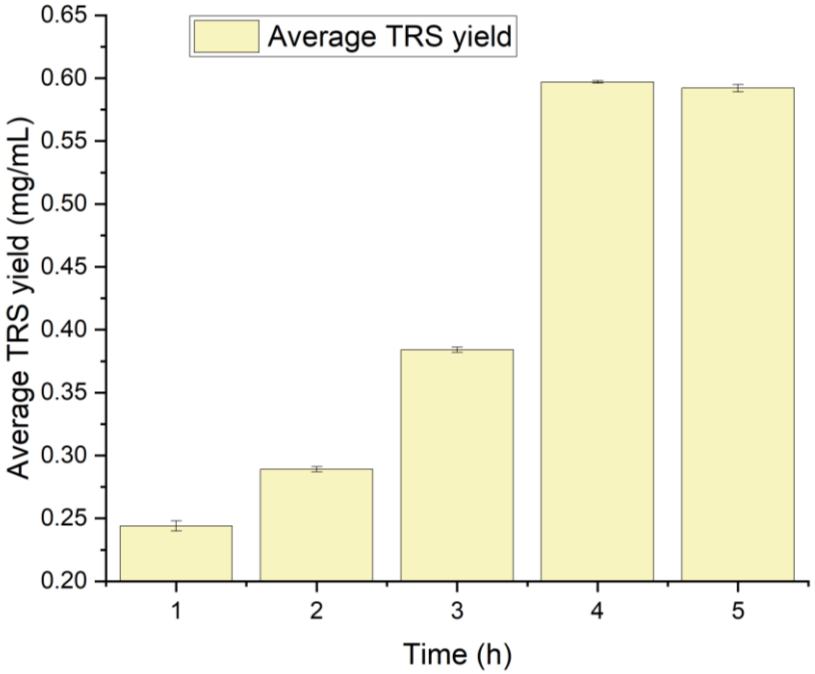


Fig. 13 Time optimization for the hydrolysis of SCB

d. Temperature

The reaction temperature is a critical criterion in hydrolysis processes and can significantly impact the sugar yield obtained from biomass. To study the effect of temperature on the hydrolysis process, experiments were conducted at three different temperature ranges: 50, 90, and 130 ^{o}C by keeping Zr-BDC MOF mass, SCB mass and time at the optimum values. As shown in Fig.14, the TRS yield at 50 and 90 ^{o}C is very low (i.e. 0.053 and 0.056 mg/mL respectively) when compared to the yield at 130 ^{o}C, which is 0.60 mg/mL. This indicates that the catalytic effect of the Zr-BDC MOF below 100 ^{o}C is very low. Hence, the optimum temperature of the hydrolysis using the Zr-BDC MOF catalyst at the given reaction condition is 130 ^{o}C which gave 0.60 mg/mL of TRS. Moreover, we have tried the hydrolysis reaction beyond 130 ^{o}C.

However, the slurry solidified quickly during the hydrolysis due to significant water loss through evaporation before the reaction reach to completion.

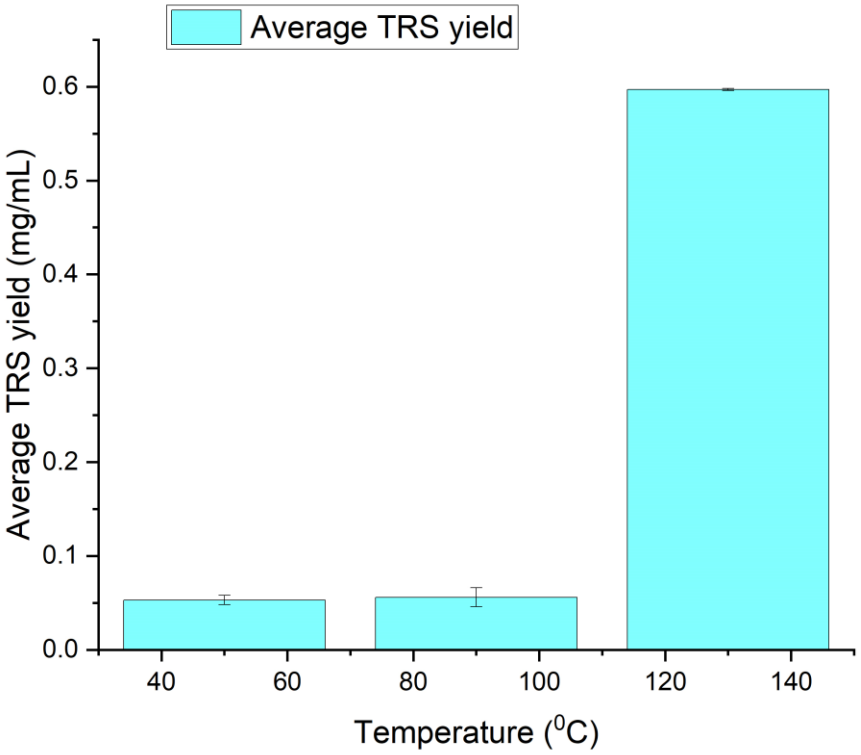


Fig.14 Temperature optimization for the hydrolysis of SCB

Therefore, by employing the optimum values (0.8 g Zr-BDC MOF, 4 g SCB, 4 h and 130 ^{o}C) of the four parameters together, we have evaluated the catalytic potential of Zr-BDC MOF for the hydrolysis of SCB and obtained TRS yield of 0.60 mg/mL.

4.4.2 Optimum Parameters for the Hydrolysis of Pretreated PP

a. Zr-BDC MOF mass

About 4 g pretreated PP was hydrolyzed with varying amounts of Zr-BDC MOF (0.4, 0.6, 0.8, 1 and 1.2 g) at 130 ^{o}C for 4 h to optimize the amount of the catalyst. As shown in Fig.15, increasing the amount of Zr-BDC MOF from 0.4 to

0.8 g resulted in an increase in TRS yield from 0.878 to 2.044 mg/mL. However, a slight decline in TRS yield was observed when Zr-BDC MOF amount exceeded 0.8 g, reaching 1.915 mg/mL. This decrease in TRS content with further increase in Zr-BDC MOF mass might be attributed to additional factors such as the saturation of active sites on the MOF surface or the occurrence of side reactions. It is possible that beyond a certain point, further increase in Zr-BDC MOF mass might lead to the decomposition of sugars into other by-products, resulting in a reduced TRS yield. Therefore, the optimum amount of Zr-BDC MOF for maximizing the TRS yield was found to be 0.8 g.

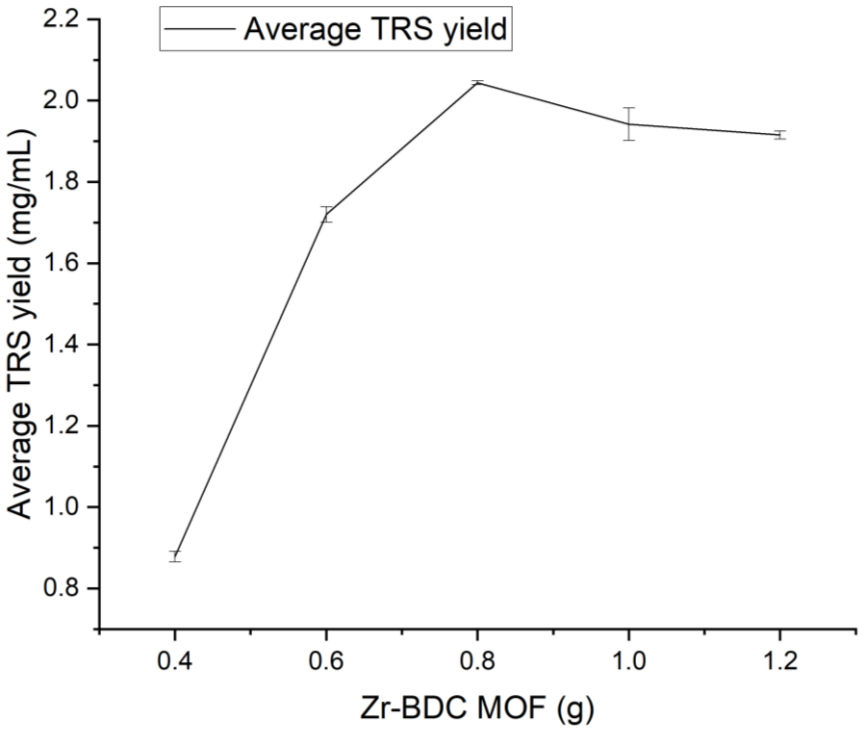


Fig.15 Zr-BDC MOF optimization for the hydrolysis of PP

b. PP Load

To get the optimum load of PP for hydrolysis, the reaction was carried out using the optimum amount of Zr-BDC MOF (0.8 g) at 130 ^{o}C for 4 h with varying amounts (3, 3.5, 4, 4.5 and 5 g) of PP. As depicted in Fig.16, the maximum TRS yield

of 2.044 mg/mL was obtained at 4 g of PP. A decrease in reducing sugar yield was observed beyond 4 g of PP. The decrease in TRS content may be due to the decrease in the adsorption capacity of the Zr-BDC MOF catalyst as a result of high substrate loading that slows down mass transfer phenomena. Thus, the results suggest that 4 g is the optimum amount of PP for the hydrolysis reaction at the given reaction conditions.

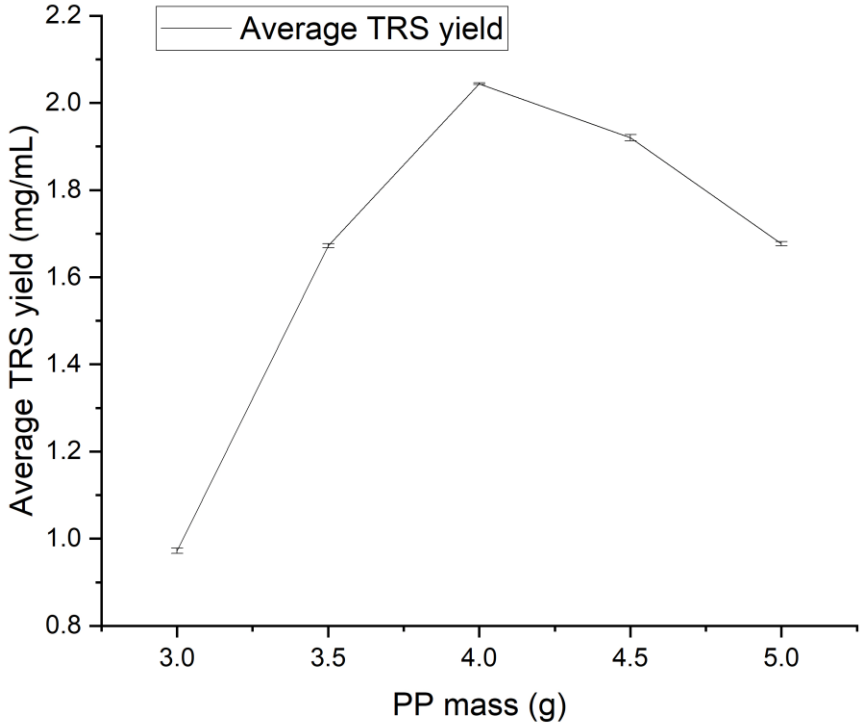


Fig.16 PP mass optimization for the hydrolysis of PP

c. Time

To optimize time, hydrolysis was carried out using 4 g PP and 0.8 g Zr-BDC MOF at 130 ^{o}C by varying time from 1 to 5 h. As shown in Fig.17, there is a gradual increase in TRS yield from 0.419 to 0.805 mg/mL for the reaction period of 1 to 2 h. Beyond 2 h, the reducing sugar yield increases linearly reaching at a maximum TRS yield of 2.044 mg/mL at 4 h. Beyond 4 h, the TRS concentration is almost similar

with the TRS concentration obtained at 4 h, but the volume of TRS hydrolysate was decreased due to the loss of more water through evaporation. Thus, 4 h is found to be the optimum hydrolysis time, which led to the production of 2.044 mg/mL of TRS.

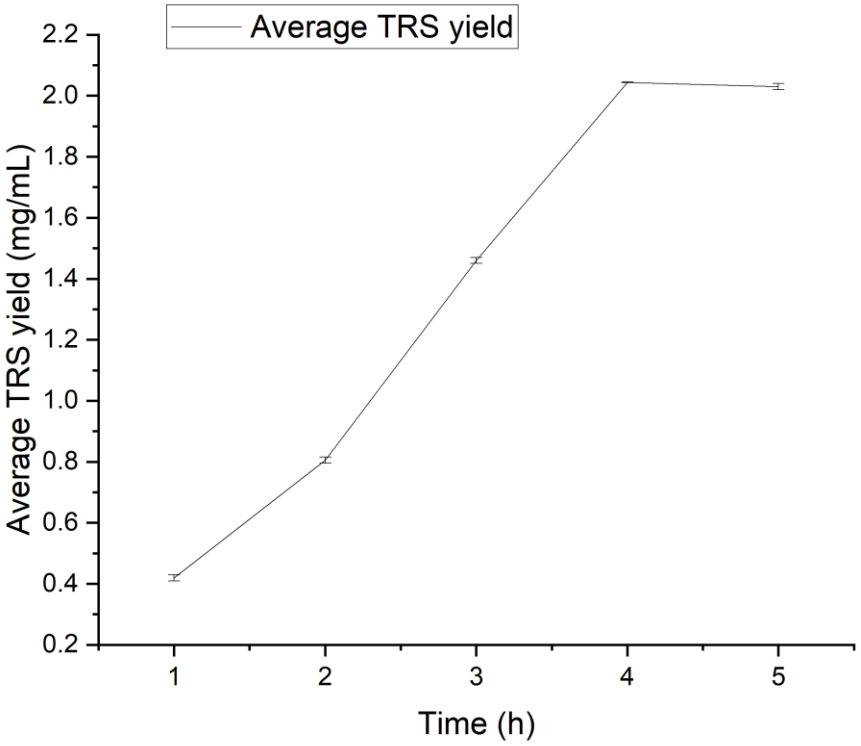


Fig.17 Time optimization for the hydrolysis of PP

d. Temperature

Different temperatures (50, 90 and 130 ^{o}C) were used for optimization with one factor at a time approach. So, the hydrolysis was carried out at temperatures of 50, 90, and 130 ^{o}C by keeping Zr-BDC MOF mass, PP mass and time at the optimum values. As indicated in Fig.18, the TRS yield at 50 and 90 ^{o}C was significantly lower (0.117 and 0.189 mg/mL, respectively) compared to the TRS yield at 130 ^{o}C (2.044 mg/mL). This suggests that the catalytic effect of the Zr-BDC MOF is relatively low at temperatures below 100 ^{o}C. However, as the temperature increased beyond 100 ^{o}C, the TRS yield showed a linear increase, reaching a maximum value of 2.044 mg/mL

at 130 ^{o}C. This indicates that Zr-BDC MOF exhibits improved catalytic activity for hydrolysis at higher temperatures. Based on the results, 130 ^{o}C was identified as the optimum temperature for the hydrolysis under the given conditions. At this temperature, the catalytic effect of Zr-BDC MOF was maximized, resulting in the highest TRS yield. It was observed that attempting to carry out the hydrolysis reaction beyond 130 ^{o}C led to the slurry solidifying within a short period of time due to excessive water loss through evaporation before the hydrolysis reaction reach to completion.

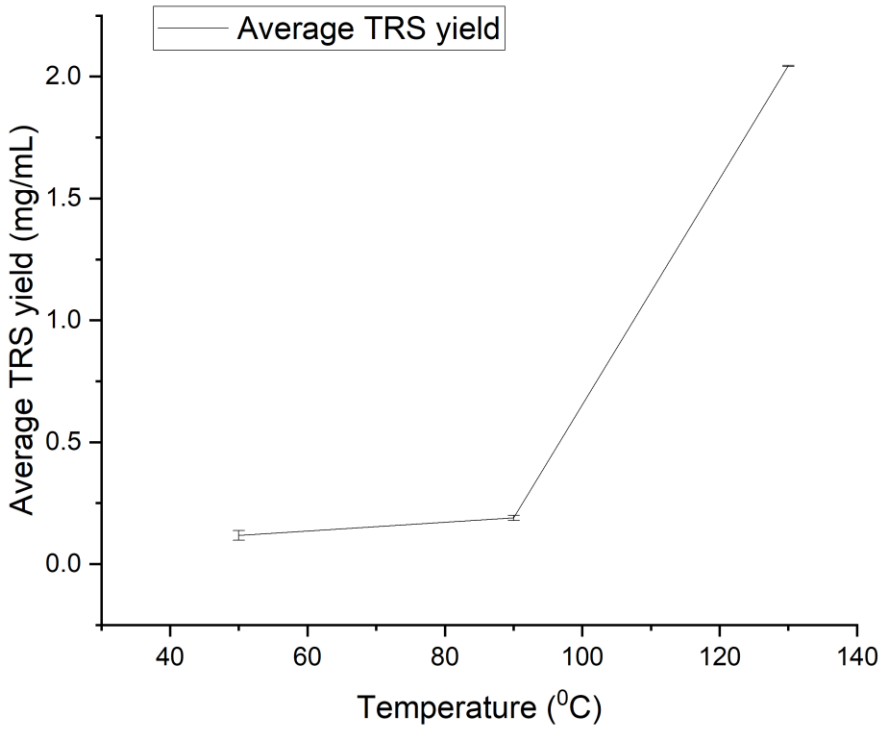


Fig.18 Temperature optimization for the hydrolysis of PP

Therefore, by using these optimized values (0.8 g Zr-BDC MOF, 4 g PP, 4 h and 130 ^{o}C) for all four parameters together, the catalytic potential of Zr-BDC MOF for the hydrolysis of PP was evaluated, resulting in a total reducing sugar (TRS) yield of 2.044 mg/mL.

4.5 Control Sample Hydrolysis of SCB and PP

When the hydrolysate for both SCB and PP obtained at the end of the control sample reaction was tested for the presence of TRS by DNS method, there is no color change observed. This implies that TRS was not present in the hydrolysate indicating that the pretreated SCB and PP was not depolymerized to glucose in the absence of the catalyst. The control sample reaction for both SCB and PP is shown at Fig.19:

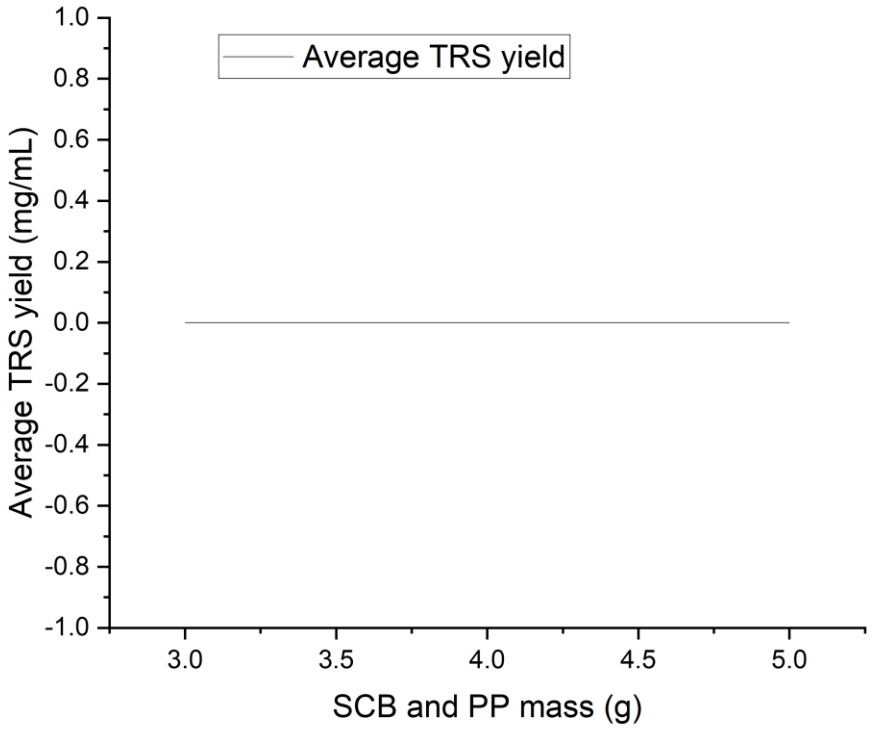


Fig.19 hydrolysis of varying amounts of pretreated SCB and PP without Zr-BDC MOF at 130 ^{o}C for 4 h

Interestingly, the experimental results indicate that PP conversion to TRS using Zr-BDC MOF catalyst is higher as compared to SCB conversion (Fig.20). This might be due to the presence of less amount of lignin (2.51 %) in the pretreated PP when compared to the lignin (8.12 %) found in the pretreated SCB. Moreover, it might be due to the diffusion of more cellulose of PP than the cellulose of SCB through the

porous system of the Zr-BDC MOF to reach the acid site (open metal site) of the MOF that could function as Lewis acid site for catalytic activity [50, 135]. The observed catalytic activity of Zr-BDC MOF for the hydrolysis of SCB and PP was due to the coordinatively unsaturated open metal site (Zr^{4+} ion) of the framework that can exhibit Lewis acid activity.

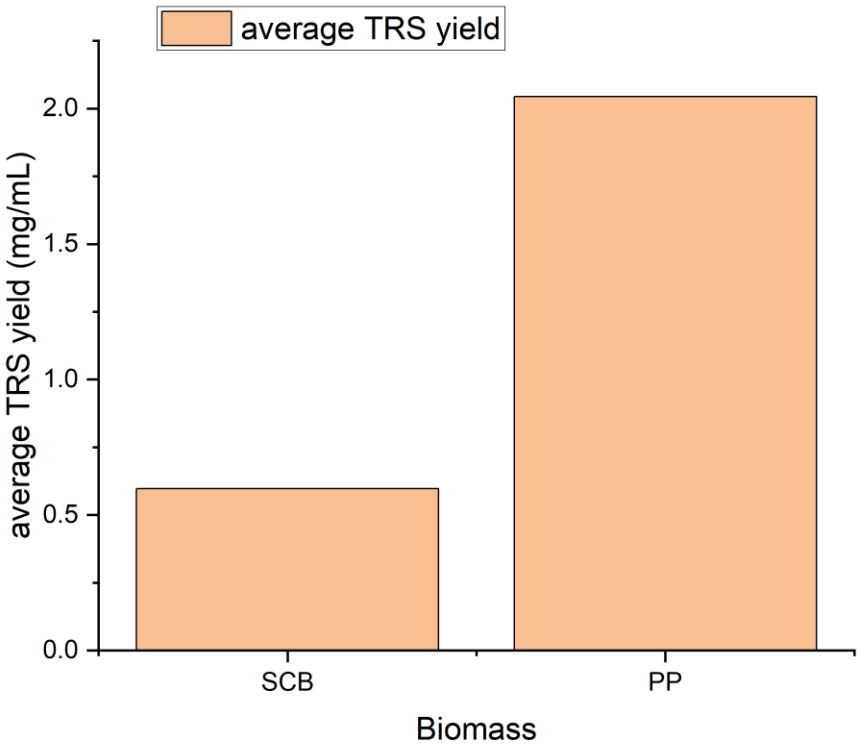


Fig.20 hydrolysis yield of SCB and PP

Chapter Five

Conclusion and Recommendation

5.1 Conclusions

The evaluation of Zr-BDC MOF as an acid heterogeneous catalyst for the hydrolysis of lignocellulosic biomasses, such as sugarcane bagasse (SCB) and pineapple peels (PP) has shown promising results. The remarkable ability of Zr-BDC MOF to function as a catalyst for cellulose hydrolysis can be attributed to the contribution of Lewis acid sites provided by the unsaturated zirconium centers present in the MOF framework, especially under the optimized reaction conditions.

In the case of SCB hydrolysis, 4 g of SCB were subjected to hydrolysis using 0.8 g Zr-BDC MOF as catalyst. The reaction was carried out at 130 ^{o}C for 4 h, resulting in a total reducing sugar (TRS) yield of 0.60 mg/mL. This indicates that Zr-BDC MOF demonstrated catalytic activity in breaking down the cellulose present in SCB and releasing reducing sugars.

Similarly, when 4 g of PP were hydrolyzed using 0.8 g of Zr-BDC MOF as catalyst at 130 ^{o}C for 4 h, a higher TRS yield of 2.044 mg/mL TRS was obtained. This further confirms the ability of Zr-BDC MOF to catalyze the hydrolysis of cellulose in lignocellulosic biomasses, leading to the production of significant amounts of reducing sugars.

The results indicate that Zr-BDC MOF holds promise as a catalyst for cellulose hydrolysis in both SCB and PP, highlighting its potential for biomass conversion and the production of valuable products such as reducing sugars.

In 2011 Akiyama et al. [111] tested the catalytic activity of MIL-101Cr-SO_3 MOF in cellulose hydrolysis and obtained a very poor yield of 1.4% glucose. A large

amount of MIL "catalyst" relative to substrate used (200 mg catalyst vs. 25 mg cellulose) makes the process economically not feasible. Moreover, the catalyst was synthesized at high temperature (180 ^{o}C) that takes long period of time (6 days) using a hazardous solvent such as DMF.

In 2019 Ahmed et al. [12] also evaluated the catalytic potential of UiO-66 MOF for the hydrolysis of carboxyl methyl cellulose (CMC) at 120 ^{o}C for 1 h. However, the contribution of the MOF in the hydrolysis of polymeric CMC was insignificant at the studied temperature.

Therefore, the usage of water as the sole solvent, lower energy requirement (room temperature), shorter synthesis time (1 day) for the preparation of Zr-BDC MOF, and efficient catalyst-to-substrate ratio have made the findings of this study economically feasible and environmentally friendly for the hydrolysis of real lignocellulosic biomasses, such as sugarcane bagasse (SCB) and pineapple peels(PP).

5.2 Recommendations

Other researchers in the MOF world can use the findings of this study as a bench mark for the greener synthesis of MOF catalysts at room temperature for the hydrolysis of lignocellulosic biomasses for bioethanol production. Therefore, they may increase the catalytic potential of Zr-BDC MOF for hydrolysis by improving its textural properties (pore size, pore volume, surface area, and crystallinity nature); increase the number of accessible Lewis-acid sites in the MOF and attach acidic functional groups on the organic linker of the MOF by post-synthetic modification or other methods.

References

[1] J. W. A. Langeveld, J. Dixon, and J. F. Jaworski, “Development perspectives of the biobased economy: a review,” *Crop Sci.*, vol. 50, p. S--142, 2010.

[2] Y. Qin, J. Guo, and M. Zhao, “Metal--organic framework-based solid acid materials for biomass upgrade,” *Trans. Tianjin Univ.*, vol. 27, no. 6, pp. 434–449, 2021.

[3] X. Liu, B. Tang, J. Long, W. Zhang, X. Liu, and Z. Mirza, “The development of MOFs-based nanomaterials in heterogeneous organocatalysis,” *Sci. Bull.*, vol. 63, no. 8, pp. 502–524, 2018.

[4] R. J. . Allendorf, M.D., Bauer, C.A., Bhakta, R.K. and Houk, “Luminescent metal–organic frameworks,” *Chem. Soc. Rev.*, vol. 38, pp. 1330–1352, 2009.

[5] J. . Horcajada, P., Chalati, T., Serre, C., Gillet, B., Sebrie, C., Baati, T., Eubank, J.F., Heurtaux, D., Clayette, P., Kreuz, C. and Chang, “Porous metal–organic-framework nanoscale carriers as a potential platform for drug delivery and imaging,” *Nat. Mater.*, vol. 9, 2010.

[6] L. J. Murray, M. Dinc\ua, and J. R. Long, “Hydrogen storage in metal--organic frameworks,” *Chem. Soc. Rev.*, vol. 38, no. 5, pp. 1294–1314, 2009.

[7] J. . Lee, J., Farha, O.K., Roberts, J., Scheidt, K.A., Nguyen, S.T. and Hupp, “Metal–organic framework materials as catalysts,” *Chem. Soc. Rev.*, vol. 38, pp. 1450–1459, 2009.

[8] N. A. Khan, B. K. Jung, Z. Hasan, and S. H. Jhung, “Adsorption and removal of phthalic acid and diethyl phthalate from water with zeolitic imidazolate and

metal--organic frameworks," *J. Hazard. Mater.*, vol. 282, pp. 194–200, 2015.

[9] A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov, and F. Verpoort, "Metal--organic frameworks: versatile heterogeneous catalysts for efficient catalytic organic transformations," *Chem. Soc. Rev.*, vol. 44, no. 19, pp. 6804–6849, 2015.

[10] R. Fang, A. Dhakshinamoorthy, Y. Li, and H. Garcia, "Metal organic frameworks for biomass conversion," *Chem. Soc. Rev.*, vol. 49, no. 11, pp. 3638–3687, 2020.

[11] M. Balat, "Production of bioethanol from lignocellulosic materials via the biochemical pathway: a review," *Energy Convers. Manag.*, vol. 52, no. 2, pp. 858–875, 2011.

[12] I. N. Ahmed *et al.*, "Zirconium based metal-organic framework in-situ assisted hydrothermal pretreatment and enzymatic hydrolysis of Platanus X acerifolia exfoliating bark for bioethanol production," *Bioresour. Technol.*, vol. 280, pp. 213–221, 2019.

[13] J. Chen *et al.*, "Metal-Organic Framework@ Metal Oxide Heterostructures Induced by Electron-Beam Radiation," *Angew. Chemie*, vol. 134, no. 47, p. e202212532, 2022.

[14] O. Oiwoh, B. V Ayodele, N. A. Amenaghawon, and C. O. Okieimen, "Optimization of bioethanol production from simultaneous saccharification and fermentation of pineapple peels using Saccharomyces cerevisiae," *J. Appl. Sci. Environ. Manag.*, vol. 21, no. 7, pp. 1256–1261, 2017.

[15] X. Zheng *et al.*, "Efficient short-time hydrothermal depolymerization of

sugarcane bagasse in one-pot for cellulosic ethanol production without solid-liquid separation, water washing, and detoxification," *Bioresour. Technol.*, vol. 339, p. 125575, 2021.

[16] I. Delidovich and R. Palkovits, "Catalytic isomerization of biomass-derived aldoses: A review," *ChemSusChem*, vol. 9, no. 6, pp. 547–561, 2016.

[17] P. Marino, P. R. Donnarumma, H. A. Bicalho, V. Quezada-Novoa, H. M. Titi, and A. J. Howarth, "A Step toward Change: A Green Alternative for the Synthesis of Metal--Organic Frameworks," *ACS Sustain. Chem. \& Eng.*, vol. 9, no. 48, pp. 16356–16362, 2021.

[18] H. G. T. Ly, G. Fu, A. Kondinski, B. Bueken, D. De Vos, and T. N. Parac-Vogt, "Superactivity of MOF-808 toward peptide bond hydrolysis," *J. Am. Chem. Soc.*, vol. 140, no. 20, pp. 6325–6335, 2018.

[19] S. M. Moosavi *et al.*, "Understanding the diversity of the metal-organic framework ecosystem," *Nat. Commun.*, vol. 11, no. 1, pp. 1–10, 2020.

[20] D. . áDu Bois, "N, N-Diethyl-3-methylbenzamide (DEET) acts as a metal–organic framework synthesis solvent with phase-directing capabilities," *Chem. Commun.*, vol. 56(69), pp. 9966–9969, 2020.

[21] S. Qiu and G. Zhu, "Molecular engineering for synthesizing novel structures of metal--organic frameworks with multifunctional properties," *Coord. Chem. Rev.*, vol. 253, no. 23–24, pp. 2891–2911, 2009.

[22] A. Corma, H. I. Garcia, and F. X. i Xamena, "Engineering metal organic frameworks for heterogeneous catalysis," *Chem. Rev.*, vol. 110, no. 8, pp. 4606–4655, 2010.

[23] K. Užarević *et al.*, “Mechanochemical and solvent-free assembly of zirconium-based metal--organic frameworks,” *Chem. Commun.*, vol. 52, no. 10, pp. 2133–2136, 2016.

[24] D. . Middleton, “Request for assistance in preventing adverse health effects from exposure to dimethylformamide (DMF).,” 1990.

[25] B. Yeskendir *et al.*, “Water-Based Synthesis of Zr6-Based Metal--Organic Framework Nanocrystals with Sulfonate Functions: Structural Features and Application to Fructose Dehydration,” *ACS Appl. Nano Mater.*, vol. 5, no. 10, pp. 14561–14571, 2022.

[26] J. M. Yassin, A. M. Taddesse, and M. Sánchez-Sánchez, “Sustainable synthesis of semicrystalline Zr-BDC MOF and heterostructural Ag3PO4/Zr-BDC/g-C3N4 composite for photocatalytic dye degradation,” *Catal. Today*, vol. 390, pp. 162–175, 2022.

[27] J. Bavykina, A., Kolobov, N., Khan, I.S., Bau, J.A., Ramirez, A. and Gascon, “Metal–organic frameworks in heterogeneous catalysis: recent progress, new trends, and future perspectives,” *Chem. Rev.*, vol. 120(16), pp. 8468–8535, 2020.

[28] Y. Zhang, W., Wang, Z., Huang, J. and Jiang, “Zirconia-based solid acid catalysts for biomass Conversion,” *Energy & Fuels*, 2021.

[29] B. Jrad, A., Ahmad, M., Hmadeh, M. and Abu Tarbush, “Materials engineering of Zr-metal-organic frameworks catalysts for the optimized production of biofuel additives,” 2021.

[30] J. . Karagiaridi, O., Lalonde, M.B., Bury, W., Sarjeant, A.A., Farha, O.K. and

Hupp, “Opening ZIF-8: a catalytically active zeolitic imidazolate framework of sodalite topology with unsubstituted linkers,” *J. Am. Chem. Soc.*, vol. 134(45), pp. 18790–18796, 2012.

[31] M. Stubbs, A.W., Braglia, L., Borfecchia, E., Meyer, R.J., Román-Leshkov, Y., Lamberti, C. and Dincă, “Selective catalytic olefin epoxidation with MnII-exchanged MOF-5,” *ACS Catal.*, vol. 8(1), pp. 596–601, 2018.

[32] S. Chavan, S., Vitillo, J.G., Gianolio, D., Zavorotynska, O., Civalleri, B., Jakobsen, S., Nilsen, M.H., Valenzano, L., Lamberti, C., Lillerud, K.P. and Bordiga, “H 2 storage in isostructural UiO-67 and UiO-66 MOFs.,” *Phys. Chem. Chem. Phys.*, vol. 14(5), pp. 1614–1626, 2012.

[33] N. Lammert, M., Glißmann, C. and Stock, “Tuning the stability of bimetallic Ce (IV)/Zr (IV)-based MOFs with UiO-66 and MOF-808 structures,” *Dalt. Trans.*, vol. 46(8), pp. 2425–2429, 2017.

[34] H. Dhakshinamoorthy, A., Alvaro, M., Horcajada, P., Gibson, E., Vishnuvarthan, M., Vimont, A., Grenèche, J.M., Serre, C., Daturi, M. and Garcia, “Comparison of porous iron trimesates basolite F300 and MIL-100 (Fe) as heterogeneous catalysts for lewis acid and oxidation reactions: roles of structural defects and stability,” *Acs Catal.*, vol. 2(10), pp. 2060–2065, 2012.

[35] S. B. Bakuru, V.R. and Kalidindi, “Synergistic hydrogenation over palladium through the assembly of MIL-101 (Fe) MOF over palladium nanocubes,” *Chem. Eur. J.*, vol. 23(65), pp. 16456–16459, 2017.

[36] H. Dhakshinamoorthy, A., Alvaro, M. and Garcia, “Metal–organic frameworks as heterogeneous catalysts for oxidation reactions,” *Catal. Sci. Technol.*, vol.

1(6), pp. 856–867, 2011.

[37] M. Guo, Q., Ren, L., Kumar, P., Cybulskis, V.J., Mkhoyan, K.A., Davis, M.E. and Tsapatsis, “A Chromium Hydroxide/MIL-101 (Cr) MOF Composite Catalyst and Its Use for the Selective Isomerization of Glucose to Fructose,” *Angew. Chemie*, vol. 130(18), pp. 5020–5024, 2018.

[38] S. . Hasan, Z., Jun, J.W. and Jhung, “Sulfonic acid-functionalized MIL-101 (Cr): An efficient catalyst for esterification of oleic acid and vapor-phase dehydration of butanol,” *Chem. Eng. J.*, vol. 278, pp. 265–271, 2015.

[39] J. Wang, B., Liu, W., Zhang, W. and Liu, “Nanoparticles@ nanoscale metal-organic framework composites as highly efficient heterogeneous catalysts for size-and shape-selective reactions,” *Nano Res.*, vol. 10(11), pp. 3826–3835, 2017.

[40] L. . Zhu, L., Liu, X.Q., Jiang, H.L. and Sun, “Metal–organic frameworks for heterogeneous basic catalysi,” *Chem. Rev.*, vol. 117(12), pp. 8129–8176, 2017.

[41] S. . Bakuru, V.R., Churipard, S.R., Maradur, S.P. and Kalidindi, “Exploring the Brønsted acidity of UiO-66 (Zr, Ce, Hf) metal–organic frameworks for efficient solketal synthesis from glycerol acetalization,” *Dalt. Trans.*, vol. 48(3), pp. 843–847, 2019.

[42] K. Fujita, M., Kwon, Y.J., Washizu, S. and Ogura, “Preparation, clathration ability, and catalysis of a two-dimensional square network material composed of cadmium (II) and 4, 4’-bipyridine,” *J. Am. Chem. Soc.*, vol. 116(3), pp. 1151–1152, 1994.

[43] K. . Shearer, G.C., Chavan, S., Bordiga, S., Svelle, S., Olsbye, U. and Lillerud,

"Defect engineering: tuning the porosity and composition of the metal–organic framework UiO-66 via modulated synthesis," *Chem. Mater.*, vol. 28(11), pp. 3749–3761, 2016.

[44] Y. Xu, C., Fang, R., Luque, R., Chen, L. and Li, "Functional metal–organic frameworks for catalytic applications," *Coord. Chem. Rev.*, vol. 388, pp. 268–292, 2019.

[45] P. Schaate, A., Roy, P., Godt, A., Lippke, J., Waltz, F., Wiebcke, M. and Behrens, "Modulated synthesis of Zr-based metal-organic frameworks: from nano to single crystals," *Chemistry (Easton).*, vol. 17(24)., 2011.

[46] P. Zahn, G., Zerner, P., Lippke, J., Kempf, F.L., Lilienthal, S., Schröder, C.A., Schneider, A.M. and Behrens, "Insight into the mechanism of modulated syntheses: in situ synchrotron diffraction studies on the formation of Zr-fumarate MOF," *CrystEngComm*, vol. 16(39), pp. 9198–9207, 2014.

[47] P. Wißmann, G., Schaate, A., Lilienthal, S., Bremer, I., Schneider, A.M. and Behrens, "Modulated synthesis of Zr-fumarate MOF," *Microporous mesoporous Mater.*, vol. 152, pp. 64–70, 2012.

[48] C. Vermoortele, F., Bueken, B., Le Bars, G., Van de Voorde, B., Vandichel, M., Houthoofd, K., Vimont, A., Daturi, M., Waroquier, M., Van Speybroeck, V. and Kirschhock, "Synthesis modulation as a tool to increase the catalytic activity of metal–organic frameworks: the unique case of UiO-66 (Zr)," *J. Am. Chem. Soc.*, 2013.

[49] H. Dhakshinamoorthy, A., Asiri, A.M. and Garcia, "Tuneable nature of metal organic frameworks as heterogeneous solid catalysts for alcohol oxidation,"

Chem. Commun., vol. 53(79), pp. 10851–10869, 2017.

[50] L. M. Isaeva, V.I., Nefedov, O.M. and Kustov, "Metal–organic frameworks-based catalysts for biomass processing," *Catalysts*, vol. 8(9), p. 368, 2018.

[51] K. . Nitsos, C.K., Matis, K.A. and Triantafyllidis, "Optimization of hydrothermal pretreatment of lignocellulosic biomass in the bioethanol production process," *ChemSusChem*, vol. 6(1), pp. 110–122, 2013.

[52] K. Periyasamy, "Bioethanol production from lignocellulosic biomass using immobilized cellulolytic enzymes," 2018.

[53] F. Cherubini, "The biorefinery concept: using biomass instead of oil for producing energy and chemicals," *Energy Convers. Manag.*, vol. 51(7, pp. 1412–1421, 2010.

[54] M. Menon, V. and Rao, "Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept.," *Prog. energy Combust. Sci.*, vol. 38(4), pp. 522–550, 2012.

[55] W. Lewandowski, I., Clifton-Brown, J.C., Scurlock, J.M.O. and Huisman, "Miscanthus: European experience with a novel energy crop," *Biomass and Bioenergy*, vol. 19(4), pp. 209–227, 2000.

[56] K. Pauly, M. and Keegstra, "Cell-wall carbohydrates and their modification as a resource for biofuels," *Plant J.*, vol. 54(4), pp. 559–568, 2008.

[57] T. . Vassilev, S.V., Baxter, D., Andersen, L.K., Vassileva, C.G. and Morgan, "An overview of the organic and inorganic phase composition of biomass," *Fuel*, vol. 94, pp. 1–33, 2012.

[58] T. D. Himmel, M.E., Ding, S.Y., Johnson, D.K., Adney, W.S., Nimlos, M.R., Brady, J.W. and Foust, "Biomass recalcitrance: engineering plants and enzymes for biofuels production," *Science (80-.).*, vol. 315(5813), pp. 804–807, 2007.

[59] P. Kumar, P., Barrett, D.M., Delwiche, M.J. and Stroeve, "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production," *Ind. Eng. Chem. Res.*, vol. 48(8), pp. 3713–3729, 2009.

[60] R. Harmsen, P.F., Huijgen, W., Bermudez, L. and Bakker, "Literature review of physical and chemical pretreatment processes for lignocellulosic biomass," *Wageningen UR-Food Biobased Res.*, 2010.

[61] M. Carpita, N., Tierney, M. and Campbell, "Molecular biology of the plant cell wall: searching for the genes that define structure, architecture and dynamics," *Springer Netherlands*, pp. 1–5, 2001.

[62] K. Ward, O.P., Moo-Young, M. and Venkat, "Enzymatic degradation of cell wall and related plant polysaccharides," *Crit. Rev. Biotechnol.*, vol. 8(4), pp. 237–274, 1989.

[63] J. . Matthews, J.F., Skopec, C.E., Mason, P.E., Zuccato, P., Torget, R.W., Sugiyama, J., Himmel, M.E. and Brady, "Computer simulation studies of microcrystalline cellulose Iβ," *Carbohydr. Res.*, vol. 341(1), pp. 138–152, 2006.

[64] N. . Carpita, "Structure and biogenesis of the cell walls of grasses," *Annu. Rev. Plant Biol.*, vol. 47(1), pp. 445–476, 1996.

[65] K. E. . Kuhad, R.C., Singh, A. and Eriksson, "Microorganisms and enzymes

involved in the degradation of plant fiber cell walls," *Biotechnol. pulp Pap. Ind.*, pp. 45–125, 2006.

[66] G. Santi, "Second generation bioethanol production from orange peel waste," 2012.

[67] D. Hodzic, A. and Karlsson, "From Waste to Bioethanol-A Feasibility Study on Animal Bedding," 2017.

[68] S. Kumar, A.K. and Sharma, "Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review," *Bioresour. Bioprocess.*, vol. 4(1), pp. 1–19, 2017.

[69] J. Sun, Y. and Cheng, "Hydrolysis of lignocellulosic materials for ethanol production: a review.," *Bioresour. Technol.*, vol. 83(1), pp. 1–11, 2002.

[70] M. . Chang, V.S., Burr, B. and Holtzapple, "Lime pretreatment of switchgrass. In biotechnology for fuels and chemicals: proceedings of the eighteenth symposium on biotechnology for fuels and chemicals," *Humana Press*, pp. 3–19, 1997.

[71] P. Kumar, P., Barrett, D.M., Delwiche, M.J. and Stroeve, "Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production," *Ind. Eng. Chem. Res.*, vol. 48(8), pp. 3713–3729, 2009.

[72] J. Alriols, M.G., Tejado, A., Blanco, M.A., Mondragon, I. and Labidi, "Agricultural palm oil tree residues as raw material for cellulose, lignin and hemicelluloses production by ethylene glycol pulping process," *Chem. Eng. J.*, vol. 148(1), pp. 106–114, 2009.

[73] T. . Ichwan, M. and Son, “Study on organosolv pulping methods of oil palm biomass,” *Int. Semin. Chem.*, pp. 364–370, 2011.

[74] D. . Agbor, V.B., Cicek, N., Sparling, R., Berlin, A. and Levin, “Biomass pretreatment: fundamentals toward application,” *Biotechnol. Adv.*, vol. 29(6), pp. 675–685, 2011.

[75] F. Nakamura, Y., Daidai, M. and Kobayashi, “Ozonolysis mechanism of lignin model compounds and microbial treatment of organic acids produced,” *Water Sci. Technol.*, vol. 50(3), pp. 167–172, 2004.

[76] M. . Alvira, P., Tomás-Pejó, E., Ballesteros, M. and Negro, “Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review,” *Bioresour. Technol.*, vol. 101(13), pp. 4851–4861, 2010.

[77] Z. C. Hammel, K.E., Kapich, A.N., Jensen Jr, K.A. and Ryan, “Reactive oxygen species as agents of wood decay by fungi,” *Enzyme Microb. Technol.*, vol. 30(4), pp. 445–453, 2002.

[78] M. . Saha, B.C. and Cotta, “Enzymatic saccharification and fermentation of alkaline peroxide pretreated rice hulls to ethanol,” *Enzyme Microb. Technol.*, vol. 41(4), pp. 528–532, 2007.

[79] B. . Alizadeh, H., Teymouri, F., Gilbert, T.I. and Dale, “Pretreatment of switchgrass by ammonia fiber explosion (AFEX).,” *Appl. Biochem. Biotechnol.*, vol. 124, pp. 1133–1141, 2005.

[80] S. Rabemanolontsoa, H. and Saka, “Various pretreatments of lignocellulosics.,” *Bioresour. Technol.*, vol. 199, pp. 83–91, 2016.

[81] J. Kim, K.H. and Hong, “Supercritical CO2 pretreatment of lignocellulose enhances enzymatic cellulose hydrolysis,” *Bioresour. Technol.*, vol. 77(2), pp. 139–144, 2001.

[82] G. Hendriks, A.T.W.M. and Zeeman, “Pretreatments to enhance the digestibility of lignocellulosic biomass,” *Bioresour. Technol.*, vol. 100(1), pp. 10–18, 2009.

[83] G. . Zheng, Y., Lin, H.M., Wen, J., Cao, N., Yu, X. and Tsao, “Supercritical carbon dioxide explosion as a pretreatment for cellulose hydrolysis,” *Biotechnol. Lett.*, vol. 17, pp. 845–850, 1995.

[84] M. Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M. and Ladisch, “Features of promising technologies for pretreatment of lignocellulosic biomass,” *Bioresour. Technol.*, vol. 96(6), pp. 673–686, 2005.

[85] M. . Mok, W.S.L. and Antal Jr, “Uncatalyzed solvolysis of whole biomass hemicellulose by hot compressed liquid water,” *Ind. Eng. Chem. Res.*, vol. 31(4), pp. 1157–1161, 1992.

[86] Ó. . Cardona, C.A. and Sánchez, “Fuel ethanol production: process design trends and integration opportunities,” *Bioresour. Technol.*, vol. 98(12), pp. 2415–2457, 2007.

[87] H. Sun, F. and Chen, “Evaluation of enzymatic hydrolysis of wheat straw pretreated by atmospheric glycerol autocatalysis,” *J. Chem. Technol. Biotechnol. Int. Res. Process. Environ. Clean Technol.*, vol. 82(11), pp. 1039–1044, 2007.

[88] G. Tengerdy, R.P. and Szakacs, “Bioconversion of lignocellulose in solid

substrate fermentation," *Biochem. Eng. J.*, vol. 13(2–3), pp. 169–179, 2003.

[89] C. Jönsson, L.J. and Martín, "Pretreatment of lignocellulose: formation of inhibitory by-products and strategies for minimizing their effects," *Bioresour. Technol.*, vol. 199, pp. 103–112, 2016.

[90] I. Karagöz, P., Rocha, I.V., Özkan, M. and Angelidaki, "Alkaline peroxide pretreatment of rapeseed straw for enhancing bioethanol production by same vessel saccharification and co-fermentation," *Bioresour. Technol.*, vol. 104, pp. 349–357, 2012.

[91] M. V. . da Costa Correia, J.A., Júnior, J.E.M., Gonçalves, L.R.B. and Rocha, "Alkaline hydrogen peroxide pretreatment of cashew apple bagasse for ethanol production: study of parameters," *Bioresour. Technol.*, vol. 139, pp. 249–256, 2013.

[92] L. Cao, W., Sun, C., Qiu, J., Li, X., Liu, R. and Zhang, "Pretreatment of sweet sorghum bagasse by alkaline hydrogen peroxide for enhancing ethanol production," *Korean J. Chem. Eng.*, vol. 33, pp. 873–879, 2016.

[93] A. A. Ayeni, A.O., Daramola, M.O., Sekoai, P.T., Adeeyo, O., Garba, M.J. and Awosusi, "Statistical modelling and optimization of alkaline peroxide oxidation pretreatment process on rice husk cellulosic biomass to enhance enzymatic convertibility and fermentation to ethanol," *Cellulose*, vol. 25, pp. 2487–2504, 2018.

[94] Y. Qiu, J., Ma, L., Shen, F., Yang, G., Zhang, Y., Deng, S., Zhang, J., Zeng, Y. and Hu, "Pretreating wheat straw by phosphoric acid plus hydrogen peroxide for enzymatic saccharification and ethanol production at high solid loading,"

Bioresour. Technol., vol. 238, pp. 174–181, 2017.

[95] A. . Rabelo, S.C., Andrade, R.R., Maciel Filho, R. and Costa, "Alkaline hydrogen peroxide pretreatment, enzymatic hydrolysis and fermentation of sugarcane bagasse to ethanol," *Fuel*, vol. 136, pp. 349–357, 2014.

[96] R. S. C. Dutra, E.D., Santos, F.A., Alencar, B.R.A., Reis, A.L.S., de Souza, R.D.F.R., Aquino, K.A.D.S., Morais Jr, M.A. and Menezes, "Alkaline hydrogen peroxide pretreatment of lignocellulosic biomass: status and perspectives," *Biomass Convers. Biorefinery*, vol. 8, pp. 225–234, 2018.

[97] J. M. Gould, "Studies on the mechanism of alkaline peroxide delignification of agricultural residues," *Biotechnol. Bioeng.*, vol. 27(3), pp. 225–231, 985.

[98] M. Niju, S. and Swathika, "Delignification of sugarcane bagasse using pretreatment strategies for bioethanol production," *Biocatal. Agric. Biotechnol.*, vol. 20, p. 101263, 2019.

[99] D. M. Gollapalli, L.E., Dale, B.E. and Rivers, "Predicting digestibility of ammonia fiber explosion (AFEX)-treated rice straw.," *Appl. Biochem. Biotechnol.*, vol. 98, pp. 23–35, 2002.

[100] O. A. Ojumu, T.V. and Ogunkunle, "Production of glucose from lignocellulosic under extremely low acid and high temperature in batch process, auto-hydrolysis approach.," *J. Appl. Sci.*, vol. 5(1), pp. 15–17, 2005.

[101] A. G. Farooqi, R. and Sam, "Ethanol as a transportation fuel," *Cent. Appl. Bus. Res. Energy Environ. Clim. Chang. Initiat. Univ. Alberta, Canada.*, 2004.

[102] A. . Hamelinck, C.N., Van Hooijdonk, G. and Faaij, "Ethanol from

lignocellulosic biomass: techno-economic performance in short-, middle-and long-term.," *Biomass and bioenergy*, vol. 28(4), pp. 384–410, 2005.

[103] P. Chandel, A.K., Chan, E.S., Rudravaram, R., Narasu, M.L., Rao, L.V. and Ravindra, "Economics and environmental impact of bioethanol production technologies: an appraisal," *Biotechnol Mol Biol Rev*, vol. 2(1), pp. 14–32, 2007.

[104] C. G. Oyekola, O.O., Pletschke, B.I. and Whiteley, "Isolation and characterization of endoclucanase from sewage sludge under biosulphidogenic conditions of sewage hydrolysis.," 2004.

[105] L. Zhao, J. and Xia, "Simultaneous saccharification and fermentation of alkaline-pretreated corn stover to ethanol using a recombinant yeast strain," *Fuel Process. Technol.*, vol. 90(10), pp. 1193–1197, 2009.

[106] D. . Kumar, S., Singh, S.P., Mishra, I.M. and Adhikari, "Recent advances in production of bioethanol from lignocellulosic biomass.," *Chem. Eng. Technol. Ind. Chem. Equipment-Process Eng.*, vol. 32(4), pp. 517–526, 2009.

[107] P. . Badger, "Ethanol from cellulose: a general review," *Trends new Crop. new uses*, vol. 14, no. 17–21, 2002.

[108] G. Galbe, M. and Zacchi, "A review of the production of ethanol from softwood," *Appl. Microbiol. Biotechnol.*, vol. 59, pp. 618–628, 2002.

[109] A. Singhania, R.R., Sukumaran, R.K. and Pandey, "Improved cellulase production by Trichoderma reesei RUT C30 under SSF through process optimization.," *Appl. Biochem. Biotechnol.*, vol. 142, pp. 60–70, 2007.

[110] Z. Gamage, J., Lam, H. and Zhang, “Bioethanol production from lignocellulosic biomass, a review.,” *J. Biobased Mater. Bioenergy*, vol. 4(1), pp. 3–11, 2010.

[111] S. Akiyama, G., Matsuda, R., Sato, H., Takata, M. and Kitagawa, “Cellulose hydrolysis by a new porous coordination polymer decorated with sulfonic acid functional groups.,” *Adv. Mater.*, vol. 23(29), pp. 3294–3297, 2011.

[112] I. Edeh, “Bioethanol production: An overview,” *Bioethanol Technol. F. Ina. (Ed.), Pietermaritzburg, Sudáfrica Univ. KwaZulu-Natal*, pp. 1–22, 2021.

[113] A. Zabed, H., Faruq, G., Sahu, J.N., Azirun, M.S., Hashim, R. and Nasrulhaq Boyce, “Bioethanol production from fermentable sugar juice,” *Sci. world J.*, 2014.

[114] E. Saarela, U., Leiviskä, K. and Juuso, “Modelling of a fed-batch fermentation process,” *Univ. Oulu*, pp. 1–21, 2003.

[115] C. H. Wang, F.S. and Shyu, “Optimal feed policy for fed-batch fermentation of ethanol production by Zymomous mobilis,” *Bioprocess Eng.*, vol. 17, pp. 63–68, 1997.

[116] C. . Brethauer, S. and Wyman, “Continuous hydrolysis and fermentation for cellulosic ethanol production,” . *Bioresour. Technol.*, vol. 101(13), pp. 4862–4874, 2010.

[117] F. Liu, R. and Shen, “Impacts of main factors on bioethanol fermentation from stalk juice of sweet sorghum by immobilized Saccharomyces cerevisiae,” *Bioresour. Technol.*, vol. 99(4), pp. 847–854, 2008.

[118] R. Nitsche, M., Gbadamosi, R., Nitsche, M. and Gbadamosi, “Extractive and azeotropic distillation.,” *Pract. column Des. Guid.*, pp. 153–164, 2017.

[119] P. Nagy, E., Mizsey, P., Hancsók, J., Boldyryev, S. and Varbanov, “Analysis of energy saving by combination of distillation and pervaporation for biofuel production,” *Chem. Eng. Process. Process Intensif.*, vol. 98, pp. 86–94, 2015.

[120] T. E. Ayeni, A.O., Adeeyo, O.A., Oresegun, O.M. and Oladimeji, “Compositional analysis of lignocellulosic materials: Evaluation of an economically viable method suitable for woody and non-woody biomass,” *Am. J. Eng. Res.*, vol. 4(4), pp. 14–19, 2015.

[121] G. Di Blasi, C., Signorelli, G., Di Russo, C. and Rea, “Product distribution from pyrolysis of wood and agricultural residues,” *Ind. Eng. Chem. Res.*, vol. 38(6), pp. 2216–2224, 1999.

[122] Q. Li, S., Xu, S., Liu, S., Yang, C. and Lu, “Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas,” *Fuel Process. Technol.*, vol. 85(8–10), pp. 1201–1211, 2004.

[123] Y. L. and W. J. L. Lin, R. Yan, “In-depth investigation of enzymatic hydrolysis of biomass wastes based on three major components: cellulose, hemicellulose, and lignin,” *Bioresour. Technol.*, vol. 101(21), pp. 8217–8223, 2010.

[124] R. A. Ayeni, A.O., Hymore, F.K., Mudliar, S.N., Deshmukh, S.C., Satpute, D.B., Omoleye, J.A. and Pandey, “Hydrogen peroxide and lime based oxidative pretreatment of wood waste to enhance enzymatic hydrolysis for a biorefinery: Process parameters optimization using response surface methodology,” *Fuel*, vol. 106, pp. 187–194, 2013.

[125] D. L. A. . Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D. and Crocker, “Determination of structural carbohydrates and lignin in biomass.,” *Lab. Anal. Proced.*, 2010.

[126] D. Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J. and Templeton, “Determination of sugars, byproducts, and degradation products in liquid fraction process samples,” *Golden Natl. Renew. Energy Lab.*, vol. 11, pp. 65–71, 2006.

[127] D. Sherif, A., Hussen, A. and Firemichael, “Hydolysis of multi substrate biomass using para-toluenesulphonic acid for bioethanol production: A promising option over the sulfuric acid treatment.,” . *Biomass Bioenergy*, vol. 144, p. 105922, 2021.

[128] J. N. Breuil, C. and Saddler, “Comparison of the 3, 5-dinitrosalicylic acid and Nelson-Somogyi methods of assaying for reducing sugars and determining cellulase activity,” *Enzyme Microb. Technol.*, vol. 7(7), pp. 327–332, 1985.

[129] G. L. Miller, “Use of dinitrosalicylic acid reagent for determination of reducing sugar,” *Anal. Chem.*, vol. 31(3), pp. 426–428, 1959.

[130] S. . Jiménez, I.M., Chandel, A.K., Marcelino, P.R., Anjos, V., Costa, C.B., Bell, M.J.V., Pereira, B. and da Silva, “Comparative data on effects of alkaline pretreatments and enzymatic hydrolysis on bioemulsifier production from sugarcane straw by Cutaneotrichosporon mucoides,” *Bioresour. Technol.*, vol. 301, p. 122706, 2020.

[131] M. L. Maurice, “Factors effecting ethanol fermentation via simultaneous saccharification and fermentation,” *Worcester Polytech. Inst.*, 2011.

[132] J. M. Paturau, “By-products of the cane sugar industry. An introduction to their industrial utilization.,” *Elsevier Sci. Publ. BV*, 1989.

[133] T. H. Kim, J.S., Lee, Y.Y. and Kim, “A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass,” *Bioresour. Technol.*, vol. 199, pp. 42–48, 2016.

[134] R. Rekha, B. and Saravanathamizhan, “Catalytic conversion of corncob biomass into bioethanol,” *Int. J. Energy Res.*, vol. 45(3), pp. 4508–4518, 2021.

[135] C. Herbst, A. and Janiak, “MOF catalysts in biomass upgrading towards value-added fine chemicals,” *CrystEngComm*, vol. 19(29), pp. 4092–4117, 2017.

Appendix

Table 3 Zr-BDC MOF optimization for the hydrolysis of SCB

Run no.	Zr-BDC (g)	SCB (g)	Temperature (^{o}C)	Time (h)	Absorbance	Yield of TRS after hydrolysis (mg/mL)	Average TRS yield (mg/mL)	SD
1	0.4	4	130	4	0.780	0.561	0.56	0.001
					0.777	0.559		
					0.779	0.560		
2	0.6	4	130	4	0.812	0.582	0.580	0.002
					0.810	0.581		
					0.806	0.578		
3	0.8	4	130	4	0.836	0.598	0.60	0.001
					0.834	0.597		
					0.833	0.596		
4	1.0	4	130	4	0.833	0.596	0.60	0.002
					0.831	0.595		
					0.828	0.593		
5	1.2	4	130	4	0.83	0.594	0.59	0.002
					0.828	0.593		
					0.825	0.591		

Table 4 optimization of SCB mass for the hydrolysis of SCB

Run no.	Zr-BDC (g)	SCB (g)	Temperature (^{o}C)	Time (h)	Absorbance	Yield of TRS after hydrolysis (mg/mL)	Average TRS yield (mg/mL)	SD
1	0.8	3	130	4	0.727	0.525	0.523	0.002
					0.724	0.523		
					0.722	0.522		
2	0.8	3.5	130	4	0.78	0.574	0.571	0.003
					0.795	0.571		
					0.792	0.569		
3	0.8	4	130	4	0.836	0.598	0.60	0.001
					0.834	0.597		
					0.833	0.596		
4	0.8	4.5	130	4	0.825	0.591	0.587	0.004
					0.819	0.587		
					0.813	0.583		
5	0.8	5	130	4	0.81	0.581	0.577	0.004
					0.803	0.576		
					0.801	0.575		

Table 5 Optimization of time for hydrolysis of SCB

Run no.	Zr-BDC (g)	SCB (g)	Temperature (^{o}C)	Time (h)	Absorbance	Yield of TRS after hydrolysis (mg/mL)	Average TRS yield (mg/mL)	SD
1	0.8	4	130	1	0.312	0.248	0.244	0.004
					0.305	0.243		
					0.302	0.241		
2	0.8	4	130	2	0.376	0.291	0.289	0.002
					0.372	0.288		
					0.37	0.287		
3	0.8	4	130	3	0.519	0.386	0.384	0.002
					0.517	0.385		
					0.513	0.382		
4	0.8	4	130	4	0.836	0.598	0.60	0.001
					0.834	0.597		
					0.833	0.596		
5	0.8	4	130	5	0.831	0.595	0.592	0.003
					0.827	0.592		
					0.822	0.589		

Table 6 Optimization of temperature for the hydrolysis of SCB

Run no.	Zr-BDC (g)	SCB (g)	Temperature (^{o}C)	Time (h)	Absorbance	Yield of TRS after hydrolysis (mg/mL)	Average TRS yield (mg/mL)	SD
1	0.8	4	50	4	0.028	0.058	0.053	0.005
					0.017	0.051		
					0.014	0.049		
2	0.8	4	90	4	0.034	0.062	0.056	0.01
					0.029	0.059		
					0.013	0.048		
3	0.8	4	130	4	0.836	0.598	0.60	0.001
					0.834	0.597		
					0.833	0.596		

Table 7 Zr-BDC MOF optimization for the hydrolysis of PP

Run no.	Zr-BDC (g)	PP (g)	Temperature (^{o}C)	Time (h)	Absorbance	Yield of TRS after hydrolysis (mg/mL)	Average TRS yield (mg/mL)	SD
1	0.4	4	130	4	1.277	0.893	0.878	0.013
					1.246	0.872		
					1.241	0.869		
2	0.6	4	130	4	2.531	1.731	1.720	0.019
					2.529	1.73		
					2.482	1.698		
3	0.8	4	130	4	3.01	2.048	2.044	0.005
					3	2.045		
					2.992	2.039		
4	1	4	130	4	2.914	1.987	1.942	0.04
					2.829	1.93		
					2.799	1.91		
5	1.2	4	130	4	2.821	1.925	1.15	0.01
					2.805	1.914		
					2.793	1.906		

Table 8 optimization of PP mass for the hydrolysis of PP

Run no.	Zr-BDC (g)	PP (g)	Temperature (^{o}C)	Time (h)	Absorbance	Yield of TRS after hydrolysis(mg/mL)	Average TRS yield (mg/mL)	SD
1	0.8	3	130	4	1.404	0.978	0.972	0.006
					1.394	0.971		
					1.388	0.967		
2	0.8	3.5	130	4	2.452	1.678	1.672	0.005
					2.441	1.671		
					2.437	1.668		
3	0.8	4	130	4	3.0	2.045	2.044	0.002
					2.999	2.044		
					2.996	2.042		
4	0.8	4.5	130	4	2.826	1.928	1.920	0.007
					2.811	1.918		
					2.806	1.915		
5	0.8	5	130	4	2.458	1.682	1.677	0.005
					2.45	1.677		
					2.444	1.673		

Table 9 Optimization of time for hydrolysis of PP

Run no.	Zr-BDC (g)	PP (g)	Temperature (^{o}C)	Time (h)	Absorbance	Yield of TRS after hydrolysis (mg/mL)	Average TRS yield (mg/mL)	SD
1	0.8	4	130	1	0.578	0.426	0.419	0.01
					0.568	0.419		
					0.559	0.413		
2	0.8	4	130	2	1.156	0.812	0.805	0.01
					1.147	0.806		
					1.135	0.798		
3	0.8	4	130	3	2.136	1.467	1.460	0.01
					2.127	1.461		
					2.112	1.451		
4	0.8	4	130	4	3.0	2.045	2.044	0.002
					2.999	2.044		
					2.996	2.042		
5	0.8	4	130	5	2.99	2.038	2.030	0.01
					2.975	2.028		
					2.968	2.023		

Table 10 Optimization of temperature for the hydrolysis of PP

Run no.	Zr-BDC (g)	PP (g)	Temperature (^{o}C)	Time (h)	Absorbance	Yield of TRS after hydrolysis (mg/mL)	Average TRS yield (mg/mL)	SD
1	0.8	4	50	4	0.151	0.14	0.117	0.02
					0.106	0.11		
					0.091	0.1		
2	0.8	4	90	4	0.234	0.196	0.189	0.01
					0.224	0.189		
					0.212	0.181		
3	0.8	4	130	4	3.0	2.045	2.044	0.002
					2.999	2.044		
					2.996	2.042		

Table 11 glucose standard concentration vs. absorbance for DNS method

D-glucose standard concentration(mg/mL)	absorbance
0	0
0.1	0.099
0.2	0.212
0.3	0.361
0.4	0.485
0.5	0.683
0.6	0.847
0.7	1.032
0.8	1.072
0.9	1.381
1	1.409

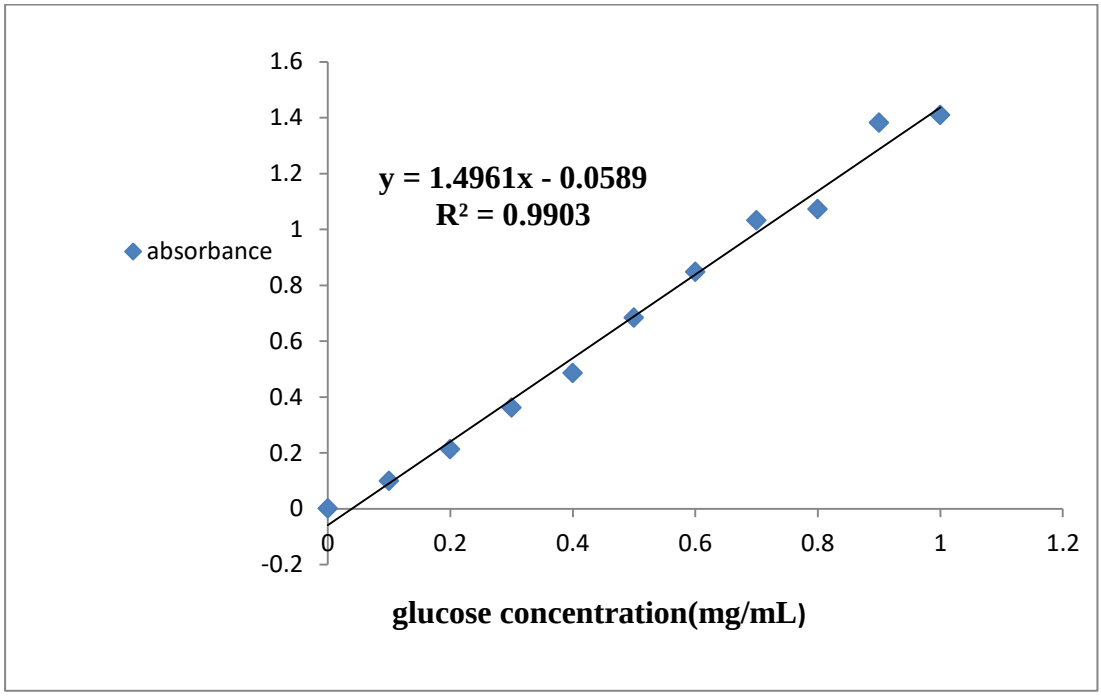


Fig. 21 glucose standard curve

Best fit Equation of the standard curve

Y = 1.4961x – 0.0589

Where "x" is concentration of glucose; "y "is the corresponding absorbance value at 540 nm