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Evaluation of Pyrolysis on the Yield and Physicochemical Properties
of Corncob Biochar

by

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A Dissertation Submitted in Fulfilment of the Requirements for the Degree of

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In the

Faculty of Engineering and the Built Environment

University of Johannesburg

South Africa

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November 2019
Declaration of Authorship

I, AKINTOLA, Ayooluwa Tomiwa hereby declare that this dissertation, with the title: “Evaluation of Pyrolysis on the Yield and Physicochemical Properties of Corncob Biochar”, and the works in it are mine. It was done solely by me while in study for a master’s programme in chemical engineering at the University of Johannesburg South Africa. Where any section has been previously submitted for any qualification at this University or another, this was well stated in my references. Similarly, where I have consulted and quoted from another person’s work, this has also been clearly specified. Other than this, this dissertation is my work. The production and publication of this work by the University of Johannesburg will not at all infringe any third-party rights.

Signature:

Date: 28/11/2019
Acknowledgement

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Daddy Heritage (Late), I dedicate this work to you, you wanted me to be great. It pains me you are not around to see my graduation. I appreciate you, and to Dr. (Mrs.) Akintola and Heritage Akintola, thank you.
Research Output

Book Chapter

1 Biochar as an adsorbent: A short overview (Submitted and Accepted for publication by Springer Books). Authors: Akintola A.T., Akinlabi E.T., Masebinu S.O.

Journal Article

1 The potential of producing biochar from corncob in South Africa: A Review (Submitted and under Review): Authors: Akintola A.T., Akinlabi E.T., Masebinu S.O.
Abstract

Lately, biomass, because of its abundance and sustainability has recently gained rising attention to produce various useful bio-products such as biochar. Biochar is the solid product obtained when biomass undergoes different thermochemical conversion processes. Examples of such are thermal liquefaction, gasification, and pyrolysis. Pyrolysis has, however, been reported as the most efficient for producing biochar owing to its huge biochar throughput and easy operation. The ability to effectively control its process conditions in producing biochar with desired physicochemical properties has also made pyrolysis the choicest to produce biochar. Although different feedstock has been reportedly used in its production, corncob waste has not been utilized to produce biochar in South Africa. Furthermore, most reports on the study of biochar have reported only the effect of a single or two process parameters on biochar’s yield and physicochemical characteristics. In this study, slow pyrolysis was used to produce corncob biochar from corncob waste in South Africa under the influence of three process parameters that are temperature, residence time and particle size. The temperature was varied between 300-900 °C, residence time between 0.5-2 hrs, and particle size of 0.5-4.0 mm. The result fully validated the research hypothesis that temperature would have the most significant impact on corncob biochar’s yield and physicochemical properties. Also, the influence of residence time and particle size was better understood when varied with temperature. The observations from this study would assist further research into optimization of pyrolysis process on the yield and physicochemical characteristics of corncob biochar for specific applications in South Africa.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane gas</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetres</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius (unit of temperature)</td>
</tr>
<tr>
<td>hrs</td>
<td>Hours (unit of time)</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen element</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin (unit of temperature)</td>
</tr>
<tr>
<td>kg</td>
<td>Kilograms</td>
</tr>
<tr>
<td>kJ</td>
<td>Kilojoules</td>
</tr>
<tr>
<td>mm</td>
<td>Millimetres</td>
</tr>
<tr>
<td>mins</td>
<td>Minutes (unit of time)</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometres</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen element</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen element</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen gas</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Nitrogen oxide gases</td>
</tr>
<tr>
<td>S</td>
<td>Sulfur element</td>
</tr>
<tr>
<td>SO₂</td>
<td>Sulfur dioxide</td>
</tr>
<tr>
<td>wt.%</td>
<td>Weight percentage</td>
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</table>
List of Acronyms

AC:  Ash Content

ASTM: American Society for Testing and Materials

BBD: Box-Behnken Design

BFD: Block Flow Diagram

CCB: Corncob Biomass

CCBC: Corncob Biochar

CCD: Central Composite Design

CCS: Carbon (CO\textsubscript{2}) Capturing and Storage

CHNS: Carbon, Hydrogen, Nitrogen, Sulfur

DOE: Design of Experiment

FC: Fixed Carbon

GHGs: Greenhouse gases

MC: Moisture Content

OFAT: One Factor at Time

PEETS: Process, Energy and Environmental Technology Station

PSD: Particle Size Distribution (PSD)

RSM: Response Surface Methodology

VM: Volatile Matter
Glossary of Terminology

Amazon-Basin: A region around the southern area of America where biochar was first found.

Amelioration: The process of improving the initial condition of something. It is mostly used for soil improvement.

Aperture: It is an opening where solid particles pass through, it is related to sieves for sizing.

Bio-adsorbent: This is an adsorbent material; whose source is from biological origin.

Biochar: A black material obtained from heating biomass without oxygen.

Bio-chemicals: They are chemical substance obtained from the processing of bio-materials.

Biodegradable: It implies decomposable by the action of microbes.

Bio-oil: The main portion of the liquid obtained during the pyrolysis of biomass.

Catalyst: A substance that promotes the rate of a chemical reaction.

Charcoal: A black solid obtained by heating biomass within a restricted oxygen environment.

Characterisation: The process of determining the properties of a material.

Corncob: One of the residues from the harvest and processing of corn.

Decomposition: The breaking down of the initial components of a material by the action of heat, chemical or microorganisms.

Dehydration: The removal of water from a substance with the aid of heat.

Design of Experiment: The planning of an experimental run with the use of computer aided software.

Endothermic: A process that takes in heat from its surroundings.

Exothermic: A process that liberates heat to its surroundings.

Gasification: A thermochemical conversion in the presence of a little amount of oxygen and gasifying agents.

Greenhouse gases: These are gaseous substances that causes global warming. One major example is carbon dioxide.
Global Warming: The gradual depletion of some portion of the ozone layer. This is as a result of the continuous release of Greenhouse gases into the air.

HAZOP: A hazard and operability study used to mitigate the likelihood of accidents and to ensure safety in industrial operations.

Heterogenous: It implies non-uniform. This includes the mixture of different size or phase of a substance.

Hydrocarbon: An organic substance whose main components are carbon and hydrogen.

Infancy: At the beginning.

Inorganic: It denotes a mineral substance; whose origin is not organic.

Lignocellulosic: A material whose major components are lignin and cellulose; although with a portion of hemicellulose.

Moisture: The amount of water present in a material.

Optimise: To maximise or minimise the property of a substance.

Organic: It denotes a natural or biological source.

Physicochemical: It implies physical and chemical. It is mostly used to describe the physical and chemical characteristics of a material.

Pollutants: These are impurities that reduce the purity of a material.

Process parameters: These are operating conditions such as temperature, pressure, residence time, rate of heating and size of particle.

Properties: The characteristics of a substance.

Pyrolysis: A chemical reaction that breaks down materials (mostly biomass) without oxygen, with the aid of heat.

Reactor: A machine where chemical reaction takes place.

Reaction: A unit operation that involves the interaction between chemical substance to form new ones.
Renewable: It refers to being limitless and unending.

Sequestration: It means to seize or impound. It could also refer to lessening.

Synthesis: The formation or production of a material usually from others.

Terrestrial: It means land dwelling. It refers to organisms that take their abode on land.

Tons: A unit of mass measurement.

Traditional: This means the usual or conventional way of doing things.

Yield: The throughput of a material obtained from a chemical reaction or process. It is always expressed in percentage.
CHAPTER ONE

INTRODUCTION

1.1 Introduction
The background of study, problem declaration, aim and objectives, hypothesis statement, research question, scope of study, justification and an overview of the entire research are contained in chapter one.

1.2 Background of Study
One of the most copious resources accessible universally is biomass\(^1\). Its universal production has been estimated to be around \(10^{11}\) tons per year\(^2\), and is projected to increase in the nearest future owing to its abundance and renewability\(^3\). Not only is it a renewable resource, it is becoming a sustainable and attractive source for the production of products that assists in meeting the quest for a cleaner and more environmental friendly atmosphere\(^2\). This is connected to its carbon-neutral property and low sulfur content, presenting it as a stable resource for a green technology\(^4\). In utilizing its abundance and accessibility, the possibility of converting biomass into various valuable products have been reported\(^1\). Biomass can be transformed into energy, biochar, bio-oil, and other useful biochemicals. However, in recent time, research into the field of biochar production from biomass has increased extensively\(^5\), due to its multifaceted benefits, which keeps evolving.

Biochar is a solid substance with high carbon composition that is obtained when biomass is pyrolyzed within restricted oxygen environment\(^6\), it is charcoal-like and could be formed in soils naturally due to vegetation fires\(^7\). The history of biochar dates back to its discovery around the Amazon Basin in the South American region over 2500years, where it was reported to improve the productivity of toxic soils\(^7\). The persistency in research into the field of biochar is increasing and keeps unfolding the benefits associated with its usage.

It has been reported to possess good physicochemical properties that presents it as an effective bio-adsorbent for soils and water contaminated with heavy metals\(^8\). Its production has been reported to possess the potential of controlling global warming through the seizure of carbon for an extended time (about 1000 years)\(^9\). The amelioration of degraded soils with it has also proven to be beneficial, such that it improves soil structure, amending some of its degraded properties, and in reducing the leaching of heavy metals within it\(^9\).
In relation to other sustainable carbon-containing materials, biochar is reported to be less-costly and efficient for treating organic and inorganic pollutants in different applications like in bio-remediation and bio-adsorption. The storage of biochar within the soil has been signalled not only to present agricultural advantage, but also to be environmentally beneficial. Other benefits associated with its usage are: its ability to seize the activities of toxic substance and surplus nitrogen in groundwaters, lessening the need for mineral fertilizer, and in the control of climatic change. Biochar has also been reported to possess the potential of improving plant growth and the activity of microbes in soils. Furthermore, it works efficiently in the treatment of wastewater.

These potentials in diverse functions has been connected to its exceptional physical and chemical properties like huge surface area, increased pH, rich amount of carbon, and presence of functional groups that possess better affinity for different pollutants. However, if biochar will continue to be relevant, there should be a further research into understanding how its physicochemical properties are affected under different production conditions. Some of these conditions are temperature, time of residence, particle size, carrier gas flow rate, and pressure.

1.3 Problem Statement

There exists numerous biomass that can be used as precursor to produce biochar. Examples of this biomass are: straw, sugarcane bagasse, husk, roots, wood chips, sawdust, switchgrass, elephant grass, orange peel, pine wood, cotton wood, rice husk, oak bark, bagasse, and corncob. Nevertheless, in order to avoid food scarcity that might arise from the use of food-consuming biomass, there is a gradual shift into the utilization of waste biomass for the production of biochar. This has led to an increase in the number of studies into the field of waste biomass and their valorisation for the production of biochar.

Furthermore, as opposed to the other parts of the world, biochar research is in its early stage in Africa. However, to make biochar technology attractive in Africa, there is a need to make the choice of waste biomass feedstock for biochar production available and accessible, with a possible low or zero cost of acquisition. In South Africa, there exists numerous biomass waste, however, one of the most generated biowaste in the country is corncob waste, with a yearly generation of about 9 million metric tons (MMT) within the country. The reason to the colossal generation of corncob is due to the huge annual production of corn within the country. Corncob is the portion of the corn crop that is left after removing the
grains, and which is underutilized in a lot of countries. It is a lignin and cellulose containing biomass, presenting it as a suitable starting material for making biochar. It would therefore be of immense socio-economic benefit if corncob could be successfully used to produce biochar in South Africa. Not only that, the problem of corn residue management would be a thing of the past if used efficiently for this task, and the environmental challenges associated with the burning of corncobs will be lessened if it is rather utilised for biochar generation.

However, another challenge is the choice of thermochemical process to use for biochar production. There exists various thermochemical conversion techniques like gasification, liquefaction, fast pyrolysis, flash pyrolysis and slow pyrolysis that are used for producing biochar, nonetheless, slow pyrolysis is reported as the most efficient method for its production. This is because of its high throughput of biochar and syngas, when compared to biooil. Nonetheless, in the production of biochar with slow pyrolysis, most researchers have studied only the impact of one (like temperature, residence time, particle size, pressure, and reactor type) or the combination of only two process factors (like temperature and residence time, temperature and particle size, temperature and carrier gas flow rate) on the yield and physicochemical properties of biochar.

Owing to all the presented problem statements, would it not be necessary to explore the potential of producing biochar from corncob in South Africa? Furthermore, would it not be of immense benefit to recognise the influence of combinations of process parameters on the physicochemical characteristics of corncob biochar. Another thing to be studied is the yield of biochar, this is because the likelihood of biochar to be used on commercial scale rests not only on its physicochemical properties, but also on the quantity of biochar available. In lieu of these, this research study was birthed.

1.4 Purpose of Study

The aim of the study was at evaluating the effect of pyrolysis parameters (specifically temperature, residence time and biomass particle size) on corncob biochar’s yield and physicochemical properties.

1.5 Objectives of Study

The aim was attained through the following specific objectives:
To investigate the changes in the physicochemical properties of corncob derived biochar due to varying pyrolytic conditions.

To investigate the process parameter that had the highest impact on the yield and physicochemical characteristics of corncob biochar.

1.6 Hypothesis Statement

It is hypothesized that among various pyrolytic process parameters used to produce biochar from corncob, it is expected that temperature will have the highest impact on biochar yield and physicochemical properties.

1.7 Research Questions

Will temperature, residence time and biomass particle size impact the yield and physicochemical properties of corncob biochar?

Which of the pyrolysis process conditions (temperature, residence time, and corncob particle size) would have the weightiest effect on the physicochemical properties of corncob biochar?

1.8 Gap in the Literature

Limited research exists on the production of biochar from corncobs in South Africa. Some of the only reports on biochar in the country are those of Muvhiiwa et al. (2019), that produced biochar from wood pellets, Carrier et al. (2012), produced char from sugarcane bagasse and Uras et al. (2012), that made biochar from black wattle and vineyard biomass in South Africa. However, since there are existing report on the use of corncob for biochar production in other parts of the world, coupled with the huge amount of corncob waste in the country, there is an enormous potential of using corncob to produce biochar in South Africa.

Besides, past research has only focused on the impact of one or at most two pyrolytic parameters during corncob biochar production. Some of them are: Lateef et al. (2019), who varied only temperature between 300-400 °C during the production of corncob biochar, Shen et al. (2019), that synthesized biochar from corncob at a constant heating rate of 10 °C/min and temperature of 600 °C, and Li et al. (2018), that produced biochar from corncob at a temperature interval of 250-750 °C; albeit at a constant residence time of 2 hrs. Although they were able to present some findings on how the studied parameters
influenced the yield and some physicochemical properties of corncob biochar. However, to fully understand the potential of corncob biochar in numerous applications, different process parameters should be studied during pyrolysis. In this study, three process parameters (temperature, particle size and residence time) were considered. The result obtained would assist in possessing a wide understanding of the behaviour of corncob biomass under the influence of pyrolytic process parameters, and the potentials of corncob biochar for specific domestic and industrial applications in South Africa.

1.9 Scope of the Study
This study was narrowed down to using waste corncobs from Gauteng province of South Africa as feedstock to produce biochar through pyrolysis process. This is because of the ease of availability of corncob in the area. Although there are different pyrolysis techniques, however, only the impact of pyrolytic process parameters was studied on the yield and physicochemical characteristics of biochar. Slow pyrolysis, which favours the production of biochar over syngas and bio-oil was selected as the pyrolysis type, while D-optimal design was used for the hybrid design of the experimental runs. The pyrolysis reactor used was a fixed bed tube furnace pyrolyzer at the Process Energy Environmental and Technological Station (PEETS) laboratory, University of Johannesburg, South Africa. The specific pyrolysis parameters whose effects were studied on the yield and physicochemical characteristics of corncob biochar are temperature (300-900 °C), residence time (0.5-2.0 hrs.), and particle size (0.5-4 mm). The specific characterization carried out on corncob biomass and biochar are elemental, proximate, and pH analysis.

1.10 Justification of the Study
Instead of burning the huge amount of corncob waste produced annually in South Africa, the slow pyrolysis of this feedstock into useful biochar product would be of massive benefit. Biochar can be used in improving soil properties, controlling of climatic change, and in the synthesis of biomaterials. The evaluation of the influence of process parameters on the yield and physicochemical properties of corncob biochar in this study would assist in verifying their impact on the product, which if well understood, would assist in understanding and optimizing the yield and physicochemical property of corncob biochar needed for precise applications in future research.
1.11 Overview of Dissertation

This report is divided into five main chapters. They are:

Chapter One: The section introduced the entire research study, aim and objectives, and the motive of this study.

Chapter Two: This is the literature section that explained more about existing information on biomass, biochar production and the influence of pyrolysis parameters on biochar’s yield and physicochemical properties.

Chapter Three: This section explained the method used to achieve each of the objectives and the overall purpose of this research study.

Chapter Four: This section revealed the result of the study and explained the changes observed with respect to the varied process parameters.

Chapter Five: This section includes the conclusion and recommendation for this research study.

1.12 Conclusion

Having understood the problem that birthed this research, coupled with a clear view of the purpose and objectives of the study, literature review is presented in the next section.
CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction
Detailed information on biomass, biomass conversion techniques; with emphasis on pyrolysis, and the effect of its process conditions (temperature, residence time and biomass particle size) on biochar’s yield and physicochemical properties were reviewed. Furthermore, some of the existing characterization techniques were also revised. The overview of this chapter is presented in Figure 2.1.

Figure 2.1: Overview of the Literature Review
2.2 Biomass

Biomass encompasses all biological substance\textsuperscript{27,28}. It is any organic material that is limitlessly available, including vegetation plants, grasses, food or energy crops, agronomic wastes, wood wastes, bio wastes (food waste and animal waste) and organic portion of municipal solid wastes\textsuperscript{29–34}. Dhyani & Bhaskar (2018), together with Crown (2008), further described biomass as the general term for plant (phytomass) and animal (zoomass)\textsuperscript{35,36}, resulting from living, recently living or dead organic substance\textsuperscript{31,37–41}. Plant biomass is formed through photosynthesis, where water and carbon dioxide (CO\textsubscript{2}) are transformed into an organic substance with the aid of sunlight; hence makes plant biomass a product of the direct and indirect growth of plant matter\textsuperscript{27,28,32,40–42}. Furthermore, Houghton (2008), referred to plant biomass as the embodiment of plant tissues that are above and below the ground. This includes: “leaves, twigs, branches, stems, roots of trees and rhizomes of grasses”\textsuperscript{43}. More so, algae has been recently identified as being part of plant biomass\textsuperscript{44}. On the other hand, animal biomass comprises of small insects to huge animal wastes, such as cow dung, poultry litter, horse manure, and pig manure\textsuperscript{33,40,45–48}. From a biochemical viewpoint irrespective of being sourced from plant or animal, biomass is a complex heterogeneous organic substance that is mostly made up of cellulose, hemicellulose, lignin, and inorganic (ash) substance\textsuperscript{43,44,49}. Although the proportion of the organic and inorganic substance varies depending on the biomass type\textsuperscript{49}. This definition correlates with the view of Yaman (2004), who described biomass relatively to be a hydrocarbon matter with different compositions\textsuperscript{50}. Mohlala et al. (2016) also described biomass in relation to energy content as a non-fossil fuel, which is biodegradable and renewable\textsuperscript{16}. The United Nations Framework Convention on Climatic Change (UNFCCC) added that biomass comprises of gases and liquids derived from the disintegration of non-fossil and biodegradable carbon-based substance\textsuperscript{31}.

2.2.1 Sources of Biomass

Biomass source varies, this is because of their natural abundance. It includes: agricultural, forest, municipal, energy crops, and biological source\textsuperscript{40} (See Figure 2.2).

- Biomass from agricultural source includes: food grain, bagasse (squeezed sugarcane), corn stems, corn and wheat straw, corn stover, rice husks, soybean stalk, olive husk, tea waste, seed casing, nutshells, cattle manure, poultry manure, pig manure\textsuperscript{28,40,41,51}.
- Biomass from forest source includes: trees, waste from wood, wood or its bark, sawdust, wooden slits, chips from wood, and mill wastes\textsuperscript{40,41}.
• Biomass from municipal source comprises of only its solid portion. It includes: sewage sludge, discarded paper, refuse derived fuel (RDF), food leftover, and trimmed grass waste \(^{28,40,41}\).

• Biomass from energy crop’s source includes: poplars, willows, alfalfa, corn, soybean, canola, oils from plants, switch grass, sweet sorghum, sugar canes, miscanthus, algae, cattail, and duckweed \(^{28,40,41}\).

• Biomass from biological source comprises of animal waste (carcass), aquatic biomass, and biological related waste \(^{40}\).

\[
\text{Figure 2.2: Sources of Biomass (Information source:}^{40})
\]
2.2.2 Classification of Biomass

There are various school of thoughts on the classification of biomass; however, each of them has a connecting point, which is their source. Biomass has been classified as virgin and non-virgin, with the latter also being referred to as waste biomass. Virgin biomass are mostly food sources or feedstocks that are used in food processing. Basu (2010), mentioned that virgin biomass include terrestrial and aquatic biomass. Terrestrial consists of forest biomass, grasses, energy crops and cultivated crops, while aquatic biomass comprises of algae and water plant. However, the rise in food demand and the likely competition with food availability has resulted into virgin biomass being unattractive for energy and biochar production. Biomass has also been classified as modern or traditional. The modern biomass aims at large scale energy production to replace conventional energy sources. Examples of modern biomass include agricultural and wood remains, municipal wastes, and energy crops. On the other hand, traditional biomass comprises of wood fuel and charcoal, plant remains and wastes from animals. Tursi (2019), also mentioned that biomass can be classified based on its existing nature, in relation to environment and vegetation type. Based on this assumption, biomass classes are: Wood and woody biomass, herbaceous biomass, aquatic biomass, animal and human waste biomass, and biomass mixtures. However, in precise term, the classification of biomass can be reduced to only virgin or non-virgin biomass, and modern or traditional biomass (See Table 2.1).
<table>
<thead>
<tr>
<th>S/N</th>
<th>Classes of Biomass</th>
<th>Sub-class</th>
<th>Examples</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Virgin Biomass</td>
<td>Terrestrial</td>
<td>forest biomass, grasses, energy crops and cultivated crops</td>
<td>16,40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aquatic Biomass</td>
<td>algae and water plant</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Non-Virgin/Waste Biomass</td>
<td>Municipal Waste</td>
<td>the solid portion of municipal wastes, sewage, and landfill wastes</td>
<td>16,40,58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Agricultural Solid Waste</td>
<td>human and animal waste, and residues of agricultural crops</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Forestry Residues</td>
<td>bark, leaves and floor remain of forest trees</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Industrial Waste</td>
<td>sawdust, oil or fat waste</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Modern Biomass</td>
<td></td>
<td>agricultural and wood remains, municipal wastes, and energy crops</td>
<td>54,55</td>
</tr>
<tr>
<td>4</td>
<td>Traditional Biomass</td>
<td></td>
<td>wood fuel and charcoal, plant remains and wastes from animals</td>
<td>54,55</td>
</tr>
</tbody>
</table>

2.2.3 Properties of Biomass

Biomass properties are mainly related to their physical, chemical and mechanical characteristics. However, the mechanical characteristic of biomass is most times connected to its physical attribute; hence, only its physical and chemical properties are discussed below.

2.2.3.1 Biomass Physical Property

The physical property of biomass comprises of its shape and size, particle size distribution, density and porosity. These properties are fundamental to understanding the effectiveness of biomass in various environmental applications.

2.2.3.1.1 Biomass Particle Shape and Size

The particles of biomass consist of diverse shapes and sizes. They could be flake shape, cylindrical shape, and almost spherical shape (See Figure 2.3); although of different sizes, which could vary from μm, mm, to cm. The shape and size of biomass have a large impact on
its behaviour during mixing and fluidization, heat and mass transfer, internal friction angle, and flow properties \(^{28,60}\).

![Image of biomass particle shapes](image-source:61–63)

**Figure 2.3:** Different shapes of biomass particles *(Image source: 61–63)*

### 2.2.3.1.2 Biomass Particle Size Distribution (PSD)

The distribution of biomass particle size can be obtained by utilizing set of sieves that have varying aperture. Generally, the size of the aperture reduces from the top to the bottom. Crushed or grinded biomass is added from the topmost sieve, and the sieves are loaded onto a shaker. The sieves are then agitated, such that each sieve section holds a fraction of the initially fed biomass particle. Practically, the larger ones remains on the topmost sieve, while the smaller particles flows to the base of the sieve set \(^{28}\). The size of biomass particles influences its physical properties and kinetic behaviour during chemical reaction \(^{64}\). However, the PSD of various biomass differs, and depends on the range of sieve sizes that are utilized (See Table 2.2).

**Table 2.2: Particle Size Distribution of Corn Residues (Information source: 65)**

<table>
<thead>
<tr>
<th>Size range (mm)</th>
<th>Weight percentage (%) (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corncobs</td>
</tr>
<tr>
<td>0.0-0.212</td>
<td>18.23</td>
</tr>
<tr>
<td>0.212-0.300</td>
<td>9.19</td>
</tr>
<tr>
<td>0.300-0.355</td>
<td>6.15</td>
</tr>
<tr>
<td>0.355-0.425</td>
<td>5.30</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>6.90</td>
</tr>
<tr>
<td>0.500-0.710</td>
<td>10.98</td>
</tr>
<tr>
<td>0.710-0.850</td>
<td>17.99</td>
</tr>
<tr>
<td>&gt;0.850</td>
<td>25.26</td>
</tr>
</tbody>
</table>

\(^{a}\)Average of three replicates.
2.2.3.1.3 **Biomass Density**

The density of biomass is the proportion of its mass to its volume. Biomass density can be classified into three, they are: solid, particle, and bulk density. The solid density of a biomass is specifically the ratio of the biomass mass to its volume, without taking into consideration the internal pores that are being occupied by air. It is usually the same as the bulk density if the internal pore volume of the biomass materials are insignificant. On the other hand, the particle density is in relation to the mass per unit volume of a single biomass particle, when its internal pores are being considered. The summation of the particle density of each of the biomass particle will make up the solid density of the entire biomass sample. For the bulk density, it considers the proportion of the mass of huge biomass particle to its total volume, and puts into consideration the pore spaces between the biomass particles. Furthermore, bulk density shows the gross extent of the size and distribution of biomass particle that impacts its flow steadiness and packaging size. The bulk density of coarse biomass materials will however depend on the way they are being handled. For instance, the bulk density of free flowing biomass particle is lesser than the compacted ones. Typical bulk densities of some biomass materials are shown in Table 2.3.

### Table 2.3: Typical Size and Bulk Density of Some Biomass Particle

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Bulk density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corncobs</td>
<td>282.38</td>
</tr>
<tr>
<td>Corn Leaves</td>
<td>81.61</td>
</tr>
<tr>
<td>Corn Stalks</td>
<td>127.32</td>
</tr>
</tbody>
</table>

2.2.3.1.4 **Porosity**

Porosity of a biomass particle is the fraction of its total volume that is being occupied by air. The voidage within these particles will permit the flow of fluid and support the formation of larger pores for adsorption purpose. It is mathematically expressed by Equation 2.1. The porosity of some biomass samples is presented in Table 2.4.

\[
\text{Porosity} (\%) = \frac{\text{Total volume} - \text{Particle volume}}{\text{Particle volume}} \times 100\% \quad (2.1)
\]
2.2.3.2 Biomass Chemical Property

The chemical characteristics of a biomass material consist of its moisture content, fixed carbon, volatile matter, ash content, and elemental composition \(^{28}\).

2.2.3.2.1 Moisture Content (MC)

The amount of moisture within a biomass material is a good measure of its fuel property. Biomass that would make a good fuel contains less moisture. Those with a high amount of moisture would not burn easily, and its valuable heat per unit mass is little, as more of the energy within the biomass will be utilized to heat up the water it contains. The amount of moisture within biomass could be calculated via two methods. It is either through wet or dry calculations. For wet, moisture content is similar to the mass of water present in the biomass divided by the entire mass of the biomass (See Equation 2.2). On the other hand, the dry calculation involves dividing the mass of water present in the biomass by the mass of the dry biomass (See Equation 2.3) \(^{41}\). Table 2.5 shows the MC of some biomass samples.

\[
\text{Moisture Content for Wet Calculation} = \frac{M_W}{M_T} \times 100 \quad (2.2)
\]

\(M_W\) is the mass of water, and \(M_T\), the entire biomass.

\[
\text{Moisture Content for Dry Calculation} = \frac{M_W}{M_D} \times 100 \quad (2.3)
\]

\(M_W\) is the mass of water, and \(M_D\), mass of dry biomass.

---

Table 2.4: Porosity of Corn Residues

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corncobs</td>
<td>67.93</td>
</tr>
<tr>
<td>Corn Leaves</td>
<td>86.06</td>
</tr>
<tr>
<td>Corn Stalks</td>
<td>58.51</td>
</tr>
</tbody>
</table>

---
Table 2.5: Moisture Content of Some Biomass Samples

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Moisture Content (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn cobs</td>
<td>6.38&lt;sub&gt;db&lt;/sub&gt;</td>
<td>65</td>
</tr>
<tr>
<td>Corn leaves</td>
<td>7.92&lt;sub&gt;db&lt;/sub&gt;</td>
<td>65</td>
</tr>
<tr>
<td>Corn stalks</td>
<td>6.4&lt;sub&gt;db&lt;/sub&gt;</td>
<td>65</td>
</tr>
<tr>
<td>Saw dust</td>
<td>13.8&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Groundnut shell</td>
<td>10.1&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Bamboo leaves</td>
<td>7.7&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Cotton stalk</td>
<td>7.5&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Prosopis</td>
<td>7.7&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Coconut husk</td>
<td>13.4&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Jatropha cake</td>
<td>7.3&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Rice husk</td>
<td>7.2&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Sugarcane Bagasse</td>
<td>4.5&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Elephant grass</td>
<td>11.5&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Typha</td>
<td>8.2&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Castor stalk</td>
<td>20.5&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Ipomea</td>
<td>11.7&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Sunhemp</td>
<td>17.1&lt;sub&gt;bns&lt;/sub&gt;</td>
<td>67</td>
</tr>
</tbody>
</table>

<sub>db: dry basis, bns: basis not stated</sub>

2.2.3.2.2 Fixed Carbon (FC)

Fixed carbon can also be referred to as uncombine carbon, and is the portion left after volatile matter has been totally taken out (exclusive of ash and moistures) of biomass<sup>68</sup>. It dictates the stability of a biomass material. Fixed carbon content of some biomass materials is presented in Table 2.6.

2.2.3.2.3 Volatile Matter (VM)

The number of volatiles present in a biomass is a measure of the portion of its mass that turns to vapor very easily, when heated to a high temperature. The higher the volatility of biomass sample, the lower the energy input to devolatise the biomass<sup>41</sup>. Volatile matter content of some lignocellulosic biomass is shown in Table 2.6.

2.2.3.2.4 Ash Content (AC)

The ash within a biomass is the portion of its mass that is made up of incombustible minerals. It is majorly made up of silica (SiO), Alumina (Al<sub>2</sub>O<sub>3</sub>), Calcium oxide (CaO), Iron oxides (FeO, Fe<sub>2</sub>O<sub>3</sub>), and Magnesium oxide (MgO). Generally, biomass materials that are sourced
from energy, agricultural crops or their remains possesses a huge ash content than those from woody source\textsuperscript{41,67,69}. The amount of ash in some lignocellulosic biomass is presented in Table 2.6.

\begin{table}[h!]
\centering
\caption{FC, VM and AC of some Lignocellulosic Biomass}
\begin{tabular}{lllll}
\hline
\textbf{Biomass} & \textbf{FC} & \textbf{VM} & \textbf{AC} & \textbf{Reference} \\
\hline
Rice husk & 16.95 & 61.81 & 21.24 & 70 \\
Sal seed husk & 28.06 & 62.54 & 9.40 & 70 \\
Olive husk & 26.10 & 70.30 & 3.60 & 70 \\
Peanut hull & 21.09 & 73.02 & 5.89 & 70 \\
Hazel nutshell & 28.30 & 69.30 & 1.40 & 70 \\
Brazil nutshell & 22.20 & 76.10 & 1.70 & 70 \\
Akhrot shell & 18.78 & 79.98 & 1.20 & 70 \\
Coconut shell & 22.10 & 77.19 & 0.71 & 70 \\
Pistachio shell & 16.84 & 82.03 & 1.13 & 70 \\
Groundnut shell & 21.60 & 72.70 & 5.70 & 70 \\
Chaparral wood & 18.68 & 75.19 & 6.13 & 70 \\
Spruce wood & 29.30 & 70.20 & 1.50 & 70 \\
Ailanthus wood & 24.80 & 73.50 & 1.70 & 70 \\
Beech wood & 24.60 & 74.00 & 0.40 & 70 \\
Bamboo wood & 11.24 & 86.80 & 1.95 & 70 \\
\hline
\end{tabular}
\end{table}

\subsection*{2.2.3.2.5 Elemental Composition}
This is the amount of C, H, O, and N present within a biomass. However, it sometimes comprises a little amount of sulfur (S). To know the elements present in a particular biomass, an analysis called elemental or ultimate analysis is carried out on the biomass sample in the laboratory\textsuperscript{28}. The elemental composition of some biomass is presented in Table 2.7.
Table 2.7: Elemental Composition of Some Lignocellulosic Biomass

<table>
<thead>
<tr>
<th>Biomass(^{db})</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat Straw</td>
<td>45.93-47.00</td>
<td>5.86-6.10</td>
<td>41.00-41.87</td>
<td>0.64-0.70</td>
<td>0.13</td>
<td>71,72</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>47.97</td>
<td>5.92</td>
<td>43.54</td>
<td>0.28</td>
<td>0.03</td>
<td>71</td>
</tr>
<tr>
<td>Bark (Spruce)</td>
<td>49.66</td>
<td>5.63</td>
<td>39.36</td>
<td>0.34</td>
<td>0.03</td>
<td>71</td>
</tr>
<tr>
<td>Sugarcane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bagasse</td>
<td>45.00</td>
<td>5.80</td>
<td>37.00</td>
<td>0.50</td>
<td>0.004</td>
<td>72</td>
</tr>
<tr>
<td>Corn stover</td>
<td>45.00</td>
<td>5.70</td>
<td>38.00</td>
<td>1.60</td>
<td>0.009</td>
<td>72</td>
</tr>
<tr>
<td>Palm oil empty fruit bunches</td>
<td>48.00</td>
<td>6.10</td>
<td>38.00</td>
<td>0.90</td>
<td>0.05</td>
<td>72</td>
</tr>
<tr>
<td>Poplar</td>
<td>49.00</td>
<td>6.10</td>
<td>42.00</td>
<td>0.40</td>
<td>0.004</td>
<td>72</td>
</tr>
<tr>
<td>Rice husk</td>
<td>38.50</td>
<td>5.20</td>
<td>34.61</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Sal seed husk</td>
<td>48.12</td>
<td>6.55</td>
<td>35.93</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Olive husk</td>
<td>50.00</td>
<td>6.20</td>
<td>42.20</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Wood Chips(Beech)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood Chips(Spruce)</td>
<td>48.88</td>
<td>6.23</td>
<td>44.54</td>
<td>0.02</td>
<td>0.004</td>
<td>71</td>
</tr>
<tr>
<td>Wood Chips(Pine)</td>
<td>48.50</td>
<td>6.05</td>
<td>44.74</td>
<td>0.06</td>
<td>0.009</td>
<td>71</td>
</tr>
<tr>
<td>Peanut hull</td>
<td>45.77</td>
<td>5.46</td>
<td>39.56</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Hazel nutshell</td>
<td>52.90</td>
<td>5.60</td>
<td>42.70</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Brazil nutshell</td>
<td>49.15</td>
<td>5.70</td>
<td>42.80</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Akhrot shell</td>
<td>49.81</td>
<td>5.64</td>
<td>42.94</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>50.22</td>
<td>5.70</td>
<td>43.37</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Pistachio shell</td>
<td>48.79</td>
<td>5.91</td>
<td>43.41</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Groundnut shell</td>
<td>48.59</td>
<td>5.64</td>
<td>39.49</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Chaparral wood</td>
<td>46.90</td>
<td>5.08</td>
<td>40.17</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Spruce wood</td>
<td>51.90</td>
<td>6.10</td>
<td>40.90</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Ailanthus wood</td>
<td>49.50</td>
<td>6.20</td>
<td>41.00</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>Beech wood</td>
<td>49.50</td>
<td>6.20</td>
<td>41.20</td>
<td>-</td>
<td>-</td>
<td>70</td>
</tr>
</tbody>
</table>

\(^{db}\): dry basis
2.2.4 Biomass Composition

The main composition of biomass material are cellulose, hemicellulose and lignin, and a little amount of extractives and ash (See Figure 2.4). Nonetheless, the exact amount of each of the component depends on the type of biomass.

![Figure 2.4: Biomass General Composition (Information source: 39-41,74)](image)

2.2.4.1 Cellulose

This is the most prevalent organic substance on earth, which has been reported to be the basic component of the cell wall of any biomass. It is always located in the innermost section of a biomass material, enclosed by interlinked hemicellulose and lignin components. It is vulnerable to attack by enzymes and it breaks down easily. Its chemical structure comprises of tens of thousands of β-D-glucose monomeric units; also known as hexose sugars that are binded via glucosidic linkages (See Figure 2.5). The empirical formula of cellulose is written as \((C_6H_{10}O_5)_n\), with \(n\) representing the number of β-D-glucose units. Cellulose is a polymer with a long chain that has a high extent of polymerization (<10,000 units), together with a huge molecular weight (<500,000 units), and is reported to be the most copious polymer from bio-substance in the universe. Its configurations are known to be crystal-like, and are recognised to support biomass resistance to hydrolysis reaction. Furthermore, cellulose has a high carbon content when compared with the other major components (hemicellulose and lignin) of biomass. Furthermore, it is reported to be responsible for the substantial amount of energy within biomass materials.
2.2.4.2 Hemicellulose

Hemicellulose comprises of various molecules. Asides cellulose, hemicellulose is another main source of carbon within biomass materials, whose molecules are mostly hydrocarbons with a branched structure that is made up of pentose (C$_5$) sugars, hexose (C$_6$) sugars (L-arabinose, D-xylose, D-glucose, D-mannose, D-glucuronic acid, D-mannose and D-galactose (See Figure 2.5), which are five and six carbon sugars respectively. The extent of polymerization within hemicellulose is however low (~100–200 units), and could be denoted by the general empirical formula (C$_5$H$_8$O$_4$)$_{40}$. Unlike cellulose, it is comparatively easy to hydrolyse back into simple sugars, even though the simple sugars within it are difficult to ferment. It is also made up of an unsymmetrical amorphous-like configuration, with little strength. This however makes its components disintegrate easily when subjected to heat treatment.

2.2.4.3 Lignin

Lignin is a complex polymer containing several numbers of branched phenyl propane and aromatic rings connected by various bonds (C–O–C, ethers and C–C) (See Figure 2.5). The central monomer in its polymeric structure are benzene rings. One major function of lignin in a biomass is its ability to act as a binding element for the cellulose and hemicellulose component. It is a vital portion of plant’s secondary cell wall, and one of the most plenteous organic polymers on earth; only second to cellulose. Furthermore, it is the third most vital portion of plant’s cell wall, after cellulose and hemicellulose respectively. The most stable component is lignin and is difficult to break down. The difficulty in breaking it, makes it resistant to biochemical conversions unless treated at a very high temperature.

![Figure 2.5: Biomass General Composition (Information source: 39–41,74)](image-url)
2.3 Biomass Conversion Process

Biomass can be converted into bioenergy, chemicals and several other useful products (such as syngas, biooil and biochar) through different conversion pathways. However, the two major paths for biomass conversion are biochemical and thermochemical conversion processes (See Figure 2.6).

Figure 2.6: Biomass Conversion Processes (Information Source: 32,40,73,78,80; drawn by me)

2.3.1 Biochemical Conversion

Sometimes, biochemical conversion process is also referred to as biological conversion process. It comprises of fermentation, digestion (aerobic and anaerobic), and transesterification processes (See Figure 2.7), which utilizes the assistance of enzymes and microorganisms for biomass conversion into biofuels and useful chemicals. An example of the mechanism involved in the utilization of one of the biochemical conversion pathways (anaerobic digestion) in the production of biofuels is shown in Figure 2.7.

Figure 2.7: Anaerobic Digestion Process for Converting Biomass into Valued Products (Image source: 82)
Dhyani and Bhaskar (2018) highlighted some important differences that make thermochemical conversion the choicest conversion process in the production of biochar, biooil and some other useful chemicals. They are: (i) Unlike biochemical conversion process that is slow, extending into days, thermochemical conversion takes place at a faster rate; from a few seconds to hours. (ii) Also, biochemical process finds it difficult to breakdown, hence, producing lignin as a by-product, whose pentose sugars (C₅) are difficult to ferment, while thermochemical conversion process uses the entire feedstock in the production of useful hydrocarbons; hence, greater conversion and yield. (iii) Furthermore, thermochemical conversions are not restricted to a type of feedstock, they can utilize any feedstock, or even a combination of feedstocks.

2.3.2 Thermochemical Conversion

Thermochemical conversion of biomass majorly utilizes heat, and sometimes with catalyst to convert biomass into biofuels like syngas, biooil and biochar, and some other valued chemicals. The thermochemical conversion of biomass includes torrefaction, thermal liquefaction, gasification, combustion and pyrolysis. Nonetheless, the choice depends on the preferred product. As stated earlier, the major driving force in a thermochemical conversion process is heat. As shown in Figure 2.8, this could be generated from an electrical or chemical source.

![Figure 2.8: A Pictorial Representation of Heat](image)

2.3.2.1 Torrefaction

Another name for torrefaction is mild pyrolysis. It includes the moderate heating at temperature intervals of 200-320 °C, within an inert atmosphere. It is mainly classified as an efficient method of increasing the fuel potential of biomass materials. This is aided via the removal of moisture within the biomass material to upsurge its combustion properties. Although the major product of torrefaction process is the solid torrefied biomass, which could also be regarded as biochar, nonetheless, the mild reaction that occurs during the process makes the biochar unfit to be used in biochar applications, perhaps as a precursor for energy purpose. A simple torrefaction process set-up is shown in Figure 2.9.
2.3.2.2 Thermal Liquefaction

The thermal liquefaction of biomass is analogous to fast pyrolysis. This is because the main target is the liquid fraction of the product, although the thermal liquefaction of biomass takes place within a liquid medium and under pressurized conditions, thereby handling biomass with a high moisture content. This technique can further be classified as: hydrothermal liquefaction, solvent enhanced liquefaction, and catalysed-solvent enhanced liquefaction (See Figure 2.10). Biomass conversion via thermal liquefaction process still faces the challenges of complicated operation due to the need for high pressure, solvents and catalysts. Similarly, since this process majorly fits the large production of liquids, with a little amount of biochar; it was not considered for the thermochemical conversion process used to produce biochar in this research work.

Figure 2.10: Classes of Thermal Liquefaction Process
2.3.2.3 Biomass Gasification

Biomass gasification involves the thermochemical transformation of biomass mainly into gases (producer, combustible, or synthesis gases). This comprises carbon monoxide (CO), methane (CH\(_4\)), hydrogen (H\(_2\)), carbon dioxide (CO\(_2\)) and other side products; including char, and some other heavy hydrocarbons like tar with the aid of a gasifying agent. This could be air, oxygen (O\(_2\)), H\(_2\)O (steam) and CO\(_2\) or any of their combinations. During gasification, the choice of gasifying agent influences the reaction. For instance, O\(_2\) as a gasifying agent results in an exothermic reaction. Conversely, when steam is utilized, the entire reaction involved is endothermic, therefore, an external heat source is required. Generally, the gases produced can be utilized in electricity generation, chemical production and as one of the precursors for producing fertilizer. The temperature at which gasification takes place is mostly between 500-1400 °C.\(^{32,33,39,49,77,80,84}\) Even though gasification is an effective thermochemical transformation route of biomass into combustible gases, nevertheless, the development and utilization of a clean and effective cleaning technology for the gas generated is still challenging. Also, large scale gasification plants will require a huge amount of biomass feedstock, which will subsequently result into a rise in the cost of collecting, transporting and storing biomass.\(^{39}\) Furthermore, the amount of biochar being produced is so small when compared with the quantity of gas being generated. Gasification was therefore not considered in this research work to produce biochar. A typical gasification setup is shown in Figure 2.11.

*Figure 2.11: Gasification Process of a Typical Biomass (Image source: \(^{91}\)*)
2.3.2.4 Combustion

It is possibly the earliest thermochemical process used for biomass conversion. It has been used for cooking and keeping people warm. This is the method of producing heat and energy from biomass through open flame burning. The three requirements for combustion to take place are air (oxygen), fuel (biomass), and a source of ignition (See Figure 2.12). Combustion is mostly used in generating heat and not in the production of carbonated solids. Therefore, combustion was not considered to produce biochar in this research work.

![Figure 2.12: Requirements for Combustion Process (Image source:)](image)

2.3.2.5 Pyrolysis

This involves the thermal breakdown of organic materials without oxygen. Pyrolysis process usually takes place at temperatures of 300-900 °C. The products of the process are solid fraction known as char, vapor fraction that is later condensed into bio-oil (known as pyrolysis oil) and incondensable gas (known as syngas). The major reactions that results in the formation of pyrolysis products have been grouped into three. They are: moisture-removing reaction (dehydration), primary and secondary decomposition reaction, and product-formation reaction. The research interest in the use of pyrolysis for the conversion of biomass has been linked to the numerous benefits associated with it. Chen et al. (2018), described pyrolysis as an effective technique for transforming biomass into different products that can be used in meeting various energy demands. Furthermore, it has been mentioned as one of the major methods for the production of bio-chemicals and transportation fuels. Similarly, pyrolysis has been reported as the appropriate substitute for different traditional conversion methods like aerobic digestion, fermentation, and combustion, in the effective conversion of biomass into extensive number of valued products. When compared to combustion and incineration processes, the negative environmental impact of pyrolysis has been observed to be lesser. Besides, its operation is viewed by many to be simple. Equally, it is highly perceived as the most appealing and eco-friendly
approach of breaking down biomass \cite{79,99}. Hence, it is reported by many researchers as the choicest thermochemical method for producing biochar from biomass \cite{81}. A typical pyrolysis process is shown in *Figure 2.13*.

![Biomass Pyrolysis Process Plant](image)

*Figure 2.13: Biomass Pyrolysis Process Plant (Image source: \cite{100})*

### 2.3.2.6 Classification of Pyrolysis Process

The classification of pyrolysis rests on the range of the process parameters. Some of the parameters are temperature range, rate of heating, particle size, carrier gas flow rate, residence time, pressure and the reactor type during the process \cite{12,101,102} (See *Figure 2.14*). Based on this, it can be mainly grouped into three. They are: fast, flash and slow pyrolysis \cite{12,39,85,87,103}.

![Examples of Process Parameters Varied During Pyrolysis](image)

*Figure 2.14: Examples of Process Parameters Varied During Pyrolysis*
2.3.2.6.1 Fast Pyrolysis
It is an example of thermochemical conversion process that transforms biomass into liquids. The main content of the liquid is bio-oil and is the mostly desired product, with little char and syngas as by-products. The common process conditions for fast pyrolysis are presented in Table 2.8.

2.3.2.6.2 Flash Pyrolysis
Flash pyrolysis also occurs at modest temperatures, usually at a temperature range of 400–1300 °C, and a rate of heating rate greater than 200 °C/s. Its residence time is also lesser than 1s. Like fast pyrolysis process, flash pyrolysis also favours the production of liquids, although the amount of liquid produced is not as high as that from fast pyrolysis.

2.3.2.6.3 Slow Pyrolysis
Its other name is conventional pyrolysis. For slow pyrolysis, the temperature range is usually from 300-900 °C, with a slow rate of heating, usually between 0.1–1 °C/s. Furthermore, the residence time ranges from 30 mins to some hours (1-24 hrs). Other process conditions of slow pyrolysis process are shown in Table 2.8. Slow pyrolysis mainly favours the production of biochar and syngas. It was therefore considered in this research work to produce biochar.

Table 2.8: Process Conditions of Major Pyrolysis Process

<table>
<thead>
<tr>
<th>Pyrolysis Process</th>
<th>Heating Rate (°C s⁻¹)</th>
<th>Temperature (°C)</th>
<th>Residence Time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>1-100</td>
<td>500-1250</td>
<td>0.5-20s</td>
<td>96,102,103,106–108,110</td>
</tr>
<tr>
<td>Flash</td>
<td>&gt;200</td>
<td>400-1300</td>
<td>&lt;1s</td>
<td>101,103,106,107,110</td>
</tr>
<tr>
<td>Slow</td>
<td>0.1-1</td>
<td>≥ 300</td>
<td>≥ 30 mins</td>
<td>80,102,106–110</td>
</tr>
</tbody>
</table>

2.3.2.7 Pyrolysis Reaction Mechanism
There are two main reactions during the pyrolysis of biomass. They are primary and secondary. During the primary, the initial compacted functional groups within biomass are disintegrated by heat into carboxyl, carbonyl and hydroxyl groups. The primary reaction is further classified as dehydration, decarboxylation and dehydrogenation of organic molecules within biomass material. During the disintegration reaction, hemicellulose decomposes first into acetic acid, sugars, and furans, then cellulose into levoglucosan and other anhydrocelluloses, while lignin finally breaks down into oligomers and monomers of...
polysubstituted phenols $^{32,51,112}$. In the secondary reaction, long chain hydrocarbons are thermally broken down into shorter ones to support the formation of the desired product. Generally, pyrolysis reaction occurs endothermically to the magnitude of 100 kJkg$^{-1}$.$^{110,113}$ A typical equation of reaction during the pyrolysis of biomass is presented in Equation 2.4.$^{40}$

\[
\text{Organic + energy (heat) + (free O}_2\text{ atmosphere)} \rightarrow (H_2 + CO + CH_4 + \cdots + C_5H_{12}) + (H_2O + CH_3OH + CH_3COOH + \cdots) + C\ (\text{Solid product called biochar})
\]

(2.4)

where:

- $(H_2 + CO + CH_4 + \cdots + C_5H_{12})$ → Gaseous Products
- $(H_2O + CH_3OH + CH_3COOH + \cdots)$ → Liquid Products
- $C$ → Solid Product

### 2.3.3 Design of Pyrolysis Experiment

To completely study and understand the effect of more than one experimental process parameter on biochar’s yield and physicochemical properties, it is imperative to properly design the experimental runs using a suitable design of experiment method. Experimental design is a numerical tool, which is broadly used to effectively combine a set of given process parameters, whose impacts would be studied on various responses after an experiment.$^{114}$ There are different experimental design techniques based on the number of process parameter(s), process level(s), design response(s), and the desired number of experimental runs. Examples of experimental design techniques are: Factorial, Taguchi, Response Surface, and D-Optimal Design.$^{114}$ A practical concept to the design of experiment is shown in Figure 2.15.

![Figure 2.15: Typical Design of Experimentation Concept](image-url)
2.3.3.1 Factorial Experimental Design
Unlike the traditional one factor at a time (OFAT) design, it is one of the techniques used in the design of experimental runs that allows the experimenter to investigate the effect of the possible parameter combination of interdependent variables on the desired response(s). It could be referred to as a full factorial design or a fully crossed design and is effective in generating a moderate number of experimental runs; thereby lessening the overall cost of the experiment. Although it is an effective tool for the design of experimental parameters, however, each of them can only be studied at two or three levels \(^{114-116}\). Hence; it was not considered for the design of experiment in this research work.

2.3.3.2 Response Surface Experimental Design
This experimental design technique was presented by George Box and Wilson in the year 1951. Response surface methodology (RSM) as it is fondly called, describes and explores the connection between different process parameters and response(s) \(^{117}\). The concept behind RSM is the use of a series of planned experimental runs to attain an optimum response \(^{117}\). This technique is advanced and can be used to refine experimental design models \(^{118}\). Basically, there are two classifications of RSM. They are: Central Composite Design and Box-Behnken Design \(^{118}\).

2.3.3.2.1 Central Composite Design (CCD)
CCD is the mostly used RSM design method. It is either a full or partial factorial design that has centre points, which is improved by a collection of axial points (sometimes referred to as star points). It can be effectively used to evaluate first, then second order of an experimental design and in modelling the response of an experiment by adding both centre and axial points \(^{118}\).

2.3.3.2.2 Box-Behnken Design (BBD)
Unlike CCD, BBD does not take a fixed or fractional factorial design into consideration. Rather, it effectively estimates the coefficients of first and second order models. Nonetheless, this design does not have axial points and cannot analyse factors that are all set at their highest levels \(^{118}\).

Although RSM is an efficient method for optimizing the impact of process parameters on responses, however, neither CCD nor BBD can be used to study experimental parameters at a level higher than three. Thus, RSM was not used for the design of experiment in this research work.
2.3.3.3 D-Optimal Design

D-optimal design is preferred above other experimental designs. It is able to reduce the area of poise regions and generates experimental runs in a moderately easy manner. Another benefit of the D-optimal design is that it does better at predicting values at extreme conditions (multiple levels of process parameters), such that it produces the best parameter combination. When compared with factorial and RSM designs, experimental parameters can be studied on more than three levels. Hence, D-optimal design was used for the design of pyrolysis experimental runs in the production of biochar in this research work.

2.3.4 Choice of Biomass Feedstock in Biochar Production

It has been argued that the choice of biomass is one of the major determinants of the yield and physicochemical properties of biochar; thus, a need to be careful in the selection of biomass feedstock for its production. Besides, the disintegration and conversion pattern within biomass varies during pyrolysis. In respect to this, various observations have been noted by different researchers in recent years. Chen et al. (2014), reported that the calorific value of biochar produced from woody biomass was higher than herbaceous biomass, linking the result to the presence of a higher amount of carbon and lower amount of ash within the woody biomass. Ahmad et al. (2014), also reported that biochar made from animal manure displayed a smaller specific surface area, unlike that obtained from the remains of crops and wood. These observations confirm that biomass choice affects the yield and physicochemical behaviour of biochar.

Various biomass has been reportedly used by different researchers in the production of biochar. Nonetheless, lignocellulosic biomass remains the most considered as the renewable and viable biomass feedstock for the production of biochar, owing to its affordability and accessibility. Examples and composition of some lignocellulosic biomass is presented in Table 2.9.

In South Africa, one of the most cultivated lignocellulosic biomasses is corn (also known as maize). Several reports have confirmed that in Africa, South Africa is one of the major producer and exporter of corn. This presents corn as a potential feedstock to produce biochar in the country. However, since corn is mostly used as human food and animal feed in the country, it is not safe to be considered as the choicest biomass to produce biochar. In order to fully utilize the corn growing and harvesting potential of South Africa, corncob (See Figure 2.16); one of the residues from corn cultivation, has been reported as a suitable
precursor for biochar production. Although it could be argued that the cobs could be utilized directly through burning as a source of fuel for rural area dwellers, however, the environmental impact is detrimental to their health. The direct combustion of corncob releases Greenhouse gases like CO$_2$, and some other toxic gases like NOx and CO, which are poisonous and could result in acidic rain\textsuperscript{132}. The utilization of corncob for biochar production would however be beneficial to the health, environment and economy of South Africa. This is because the biochar produced can be utilized to enhance soil fertility and crop productions in rural areas, it can also be used to mitigate the activities of some environmental contaminants like heavy metals and some toxic chemicals like phenylaniline produced from industrial activities\textsuperscript{9}. Furthermore, other side products of corncob biochar pyrolysis such as bio-oil and syngas can be utilized directly or indirectly as fuel or fuel carriers. Corncob is therefore a choice material to produce biochar in South Africa and was used to produce biochar in this research work.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure216.png}
\caption{A Typical Corncob (Image source:\textsuperscript{133})}
\end{figure}
<table>
<thead>
<tr>
<th>Lignocellulosic Biomass</th>
<th>Lignin (%)</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corncobs</td>
<td>6.1-15.9</td>
<td>33.7-45</td>
<td>31.9-36</td>
<td>134–137</td>
</tr>
<tr>
<td>Poplar</td>
<td>16</td>
<td>52</td>
<td>27</td>
<td>134,136</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td>21</td>
<td>54</td>
<td>18</td>
<td>134,136</td>
</tr>
<tr>
<td>Oak</td>
<td>24</td>
<td>40</td>
<td>36</td>
<td>134,136</td>
</tr>
<tr>
<td>Sweet Sorghum</td>
<td>21</td>
<td>45</td>
<td>27</td>
<td>134</td>
</tr>
<tr>
<td>Rice straw</td>
<td>5.5-19</td>
<td>29.2-34.7</td>
<td>23-25.9</td>
<td>134–137</td>
</tr>
<tr>
<td>Newspaper</td>
<td>18-30</td>
<td>40-55</td>
<td>25-40</td>
<td>134,135,137</td>
</tr>
<tr>
<td>Nut shells</td>
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<td>25-30</td>
<td>25-30</td>
<td>134,137</td>
</tr>
<tr>
<td>Fresh Bagasse</td>
<td>18.9</td>
<td>33.4</td>
<td>30</td>
<td>134,135</td>
</tr>
<tr>
<td>Barley Hull</td>
<td>13.8-19</td>
<td>34</td>
<td>36</td>
<td>134,136</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>12-20</td>
<td>33-40</td>
<td>20-30</td>
<td>134,136,137</td>
</tr>
<tr>
<td>Corn stover</td>
<td>7-18</td>
<td>35-40</td>
<td>17-35</td>
<td>134,139</td>
</tr>
<tr>
<td>Pine</td>
<td>20</td>
<td>42-52</td>
<td>24-27</td>
<td>136</td>
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<tr>
<td>Douglas fir</td>
<td>27</td>
<td>44</td>
<td>11</td>
<td>136</td>
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<td>Spruce</td>
<td>27.9</td>
<td>45.5</td>
<td>22.9</td>
<td>136</td>
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<tr>
<td>Barley Straw</td>
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<td>36-43</td>
<td>24-33</td>
<td>136</td>
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<tr>
<td>Rice Husks</td>
<td>15.4-20</td>
<td>28.7-35.6</td>
<td>12-29.3</td>
<td>136</td>
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<tr>
<td>Oat Straw</td>
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<td>31-35</td>
<td>20-26</td>
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<tr>
<td>Ray Straw</td>
<td>9.9-24</td>
<td>36.2-47</td>
<td>19-24.5</td>
<td>136</td>
</tr>
<tr>
<td>Corn Stalks</td>
<td>7-18.4</td>
<td>35-39.6</td>
<td>16.8-35</td>
<td>136</td>
</tr>
<tr>
<td>Sorghum Straw</td>
<td>15-21</td>
<td>32-35</td>
<td>24-27</td>
<td>136</td>
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</table>
2.4 Biochar

Biochar is not only considered as a carbon-surplus product, it is also a black material obtained through the thermal disintegration of biomass materials \(^{109,140}\), within a restricted oxygen environment \(^{141,142}\). It is also a porous material with a recalcitrant property \(^12\). It has been reported as being multifunctional and effective in different applications. However, in order to recognise the best application that will suit a specific biochar material, it is crucial to understand the influence of process parameters during pyrolysis on its yield and some of its physicochemical properties. As stated in the scope of this study, the physicochemical properties of biochar studied are pH, elemental properties, and proximate properties, while the process parameters varied are temperature, time of residence, and particle size. The effect of these parameters on the yield and proposed physicochemical characteristics of biochar are reviewed in the sections below.

2.4.1 Effect of Process Parameters on Biochar’s Yield

Various observations have been reported on the impact of pyrolysis conditions on the yield of biochar. The existing reports on the effect of temperature, residence time and particle size on biochar’s yield are presented below.

2.4.1.1 Effect of Temperature on Biochar’s Yield

The temperature of pyrolysis influences the yield of biochar from different biomass feedstock. Several revisions have been carried out on the effect of temperature on biochar’s yield. Manya et al. (2013), reported that the yield from olive mill decreased with rise in pyrolysis temperature (400–550 °C) \(^{143}\). This observation is like Xu et al. (2019) findings. They stated that biochar’s yield obtained from the pyrolysis of plant wastes reduced substantially with increase in temperature; basically from 300-700 °C \(^{144}\). Similarly, Yang et al. (2020), observed that the yield of biochar reduced as the temperature of pyrolysis increased from 300-500°C \(^{21}\). Sato et al. (2019) \(^{145}\), and Luo et al. (2015) \(^{146}\), observed a similar reduction in biochar’s yield with increase in pyrolysis temperature from 300-700 °C and 200–700 °C respectively. The reported decrease in the yield of biochar with increase in the temperature of pyrolysis was linked to a colossal extent of biomass decomposition, devolatilization, and disintegration with temperature increase \(^{110,147}\). The relationship between the yield of biochar and pyrolysis temperature can be mathematically represented by Equation 2.5. Although the reduction in the yield of biochar has been reported by some other researchers to reduce mildly at higher temperatures above 600 °C \(^{21,148}\). In overall, the
relationship between the yield of biochar and temperature remains a negatively correlated one, although with a significant impact.

\[ y \propto \frac{1}{T} \quad (2.5) \]

2.4.1.2 Effect of Residence Time on Biochar’s Yield

Although some researchers reported that the influence of residence time on the yield of biochar is significant, however, others have contrasting view. On biochar’s reduction with increase in residence time, Kim et al. (2012), observed a significant reduction in biochar made from Saccharina japonica. It reduced from 86.6% to 59.1% as the residence time rose from 1-5 mins, at a pyrolysis temperature of 380 °C. Similarly, Sato et al. (2019), noted a decrease in the yield of biochar with rise in residence time, and Luo et al. (2015), confirmed the observation of a parallel trend with increase in residence time (1-8 hrs). Conversely, Zhao et al. (2018), observed that residence time of 10-100 mins had only a trifling effect on the yield of biochar from rapeseed stem, while Wystalska et al. (2018), observed a slight reduction in the yield of biochar with increasing residence time from 60-100 mins. Some other studies have revealed that the differing influence of residence time on biochar’s yield is temperature dependent. On this basis, Sun et al. (2017), mentioned that the yield of biochar reduced with increasing residence time, at a constant temperature of 300 °C, but also disclosed that the yield became stable after 8 hrs, and that the residence time had a trifling effect at a high temperature of 600 °C. In essence, research studies have conflicting views on the influence of residence time on biochar’s yield, with some reporting that the impact of residence time on biochar’s yield is momentous, while some argued otherwise. The conflicting observations on the impact of residence time on biochar’s yield might be due to disparity in the type of biomass material used by the researchers. Furthermore, the study of the influence of residence time might be observed together with pyrolysis temperature; owing to the significance of temperature on biochar’s yield. This is because the study of the influence of residence time alone might not give the true interpretation to its effect on biochar’s yield. Hence, a need to combine residence time with temperature when observing its impact on the yield obtained during pyrolysis.

2.4.1.3 Effect of Biomass Particle Size on Biochar’s Yield

Particle size is an imperative parameter that affects the extent to which heat is being transferred within biomass samples during pyrolysis. For biomass with bigger particle size, it has been reported that there is a possibility of the biomass sample to be recalcitrant to
thermal treatment, and hence, might result in an incomplete thermochemical conversion process with high biochar yield. This was confirmed by Demirbas (2004), who reported that the yield of corncob and olive husk biochar increased with increasing size of biomass particle. Specifically, the pyrolysis of corncob with rise in the particle size (precisely from 0.5-2.2 mm), at a temperature of 677 °C, resulted in a rise in the yield of biochar (from 5.7-16.6 wt.%); interpreting to a rise of about 65.7%. Similarly, the yield of olive husk biochar increased specifically from 19.4-35.6 wt.% with similar increase in the particle size. In essence, all the observations correspond to larger particle size favouring the production of more biochar’s yield, because of their resistance to thorough heating, while smaller size of biomass particle did not, as there was little resistance to the flow of heat resulting to the formation of more volatiles.

2.4.2 Effect of Process Parameters on Biochar’s Elemental Composition

Although there are several elements (like magnesium (Mg), sodium (Na), calcium (Ca), carbon (C), hydrogen (H), oxygen (O), and nitrogen (N)) that might be found within biomass, and subsequently in biochars. However, for this research study, the elemental composition of biochar would be limited to: C, H, N, and O. The effect of pyrolysis temperature, residence time and biomass size on these elements as reported by past studies on biochar are presented in this section.

2.4.2.1 Effect of Pyrolysis Temperature on Biochar’s Elemental Composition

Zhao et al. (2017) stated that carbon content within apple tree branches biochar increased from 62.20-80.01% as the temperature increased from 300-600 °C. A contrasting observation was reported for the contents of H and O, whose values reduced from 5.18%-2.72% and 24.21%-6.59% respectively within the same temperature range. Wei et al. (2019), also confirmed that the content of C within biochar increased with temperature rise from 300-700 °C. For H and O contents, Budai et al. (2014) and Wei et al. (2019), observed that the amount of H and O within biochar reduced within a temperature of 300-700 °C. However, for C, Xu et al. (2019), observed a rise in the amount of C present in biochar obtained from rice straw, phragmites communis, and sawdust. The C content increased from 36.4%, 37.4% and 55.9% to 54.1%, 59.2% and 71.7% respectively, as the temperature increased from 300-700 °C. Nonetheless, the amount of H, N, and O present within these biochars were reportedly reduced within the same temperature range. Analogous to the trend observed to the C content, the content of N within biochar obtained from corn stalk,
peanut hull, rice hull, and tobacco stalk was observed by Cao et al. (2018), to increase with rising pyrolysis temperature. Based on these observations, it can be deduced that a rise in pyrolysis temperature would mostly favour the rise in C and sometimes N content (depending on biomass type), while the other elemental components would reduce.

2.4.2.2 Effect of Residence Time on Biochar’s Elemental Composition

There are only a few reports on the influence of residence time on the elemental composition of biochar. Wang et al. (2019), reported from the co-pyrolysis of sewage sludge and cotton stalks that the amount of C within the biochar produced reduced with increase in residence time. Similarly, the amount of H, N and O were observed to also display parallel trend with increasing residence time. The reduction in biochar’s C, H and O contents have been linked to the huge loss of C-bond, together with atoms of O and H as a result of extended residence time favouring decomposition of -C, -O, and -H bonds. Wystalska et al. (2018), also observed that varying the residence time had no impact on N content within biochar.

2.4.2.3 Effect of Biomass Particle Size on Biochar’s Elemental Composition

No information was found on the effect of particle size on biochar’s CHNS content. However, with larger particle size inhibiting heat transfer, there might be mild effect of temperature on larger biomass particle size, and would probably lead to the production of biochar with low amount of carbon, low N content and high O, N and S content. While for biomass with small particle size, the observation might be vice versa.

2.4.3 Effect of Process Parameters on Biochar’s Proximate Properties

The proximate properties of biochar include its moisture, volatile, ash and fixed carbon content. The effect of temperature, time of residence and particle size on these properties as reported by previous studies are presented in the sections below.

2.4.3.1 Effect of Pyrolysis Temperature on Biochar’s Proximate Properties

The moisture in corncob derived biochar was observed by Liu et al. (2014), to reduce from 2.4-1.7% with temperature rise from 300-600 °C. This was confirmed by Sun et al. (2017), with a parallel observation on the reduction in the moisture of biochar with rising pyrolysis temperature. For the volatile matter, Liu et al. (2014), reported that the amount of volatile matter in corncob biochar reduced substantially from 43.6-7.2%, with increase in pyrolysis temperature from 300-600 °C. Similarly, Sato et al. (2019) observed that the percentage of volatile within Acai agroindustry waste biochar reduced with temperature rise, meaning that a rise in pyrolysis temperature results in the release of more volatile matter and thereby
produces less volatile matter content within biochar materials. As regards ash content, Xu et al. (2019) noticed that the ash content within biochar from plant waste increased meaningfully from 19.14-39.04% as the pyrolysis temperature rose from 300-700 °C. Guilhen et al. (2019) also reported that the percentage of ash in biochar increased with rising temperature. Relatively, Wei et al. (2019), mentioned that the amount of ash within biochar augmented with subsequent rise in temperature, and was also confirmed by Zhao et al. (2018), Liu et al. (2014), and Sato et al. (2019). This implies that ash content within biochar has a positive correlation with rising pyrolysis temperature. For the amount of fixed carbon, an increase in temperature during pyrolysis has been stated to result in an increase in the amount of fixed carbon, more notable between the temperature interval of 300-500 °C. Liu et al. (2014), also noted that the amount of fixed carbon in corn cob biochar increased from 49.1-82.4%, as the pyrolysis temperature increased.

2.4.3.2 Effect of Residence Time on Biochar’s Proximate Properties

There exist only a few numbers of studies on the impact of residence time on biochar’s proximate properties. For ash content, Wang et al. (2019), observed a rise in the amount of ash present within biochar with extended residence time and was confirmed by Sato et al. (2019). They reported that the ash content within biochar increased with surge in residence time. For fixed carbon content, Yang et al. (2020) noticed that the amount of fixed carbon within biochar was correlated negatively with increasing residence time. In actual term, they reported that an increase in the residence time from 60-120 mins, led to a gradual increase in the amount of fixed carbon within prune apple tree biochar, from a value of 78.37-79.38%. This progression was also observed with a rise in the residence time from 120-360 mins, as the fixed carbon content increased from 79.38-80.36%. The rise in the amount of fixed carbon within biochar with increasing residence time is reported to be probably due to the completion of pyrolysis reaction and biomass carbonization. As the residence time rose, the percentage of volatile matter in biochars from different biomass feedstock was also reported to reduce significantly. Although, most report on the impact of process parameters on biochar’s moisture content were silent on residence time’s influence, however, a similar trend would be observed for moisture content, as an increase in the time of residence will amount to an increase in the amount of heat being transferred into the biomass, resulting in dehydration reaction that would remove moisture within the biomass. Thus, a likely drastic reduction in the moisture content within biochar, with increase in residence time. However, if a significant amount of moisture is found in biochar, this might be associated to the ambient
humidity and the affinity of biochar for moisture, due to the presence of pores that would present it as a hygroscopic material.

**2.4.3.3 Effect of Particle Size on Biochar’s Proximate Properties**

For the influence of particle size on biochar’s proximate properties, only a few reports exist. They are: the release of volatile matter within biomass particle reduces with a rise in particle size during pyrolysis, meaning that biochar produced from a large biomass particle will have a high amount of volatile and vice versa. On fixed carbon content, biomass with huge particle size is found to consist of low amount of fixed carbon. This is because the size of the particle interfered with the thermochemical reaction process. Hence, an incomplete pyrolysis reaction. For moisture content, since the behaviour of moisture under thermochemical conversion is similar with that of volatile matter, the amount of moisture present in a biochar produced from biomass with huge particle size would probably be higher as compared to that in biochar obtained from biomass with small particle size. For ash content, since the percentage of ash within biochar is directly proportional to the extent of pyrolysis reaction within a biomass sample. The amount of ash within biochar from biomass with huge particle size would probably be lower than that from biomass with smaller particle size.

**2.4.4 Effect of Process Parameters on Biochar’s pH**

The pH of biochar plays a momentous role in its potential for various applications like soil amendment and water treatment. There is a need to fully understand the impact of temperature, residence time, and particle size on the pH of biochar produced from the pyrolysis of biomass. Existing reports on the influence of these conditions on biochar’s pH are presented below.

**2.4.4.1 Effect of Temperature on Biochar’s pH**

The temperature of pyrolysis has been stated to affect the pH of biochar. Xu et al. (2019), observed that the pH of biochar from plant waste increased from acidic to alkaline range as the temperature rose from 300 to 700 °C. Cao et al. (2018), also confirmed that the pH of biochar made from corn stalk, rice hull, tobacco stalk and peanut hull increased from 8.07-11.54 with a rise in pyrolysis temperature. Furthermore, Budai et al. (2014), Zhao et al. (2018), and Wei et al. (2019), also observed that the pH of biochar increased with a simultaneous increase in pyrolysis temperature. In some situations, biochar produced at low pyrolysis temperatures (usually between 200-300 °C) sometimes possess a number of carboxylic and phenolic functional groups that makes them acidic. Luo et al.
confirmed this, when they reported that the pH of biochar made at a pyrolysis temperature of 250 °C was acidic. In summary, the impact of pyrolysis temperature on the pH of biochar could be in two ways. One, an increase in the temperature of pyrolysis could increase the amount of ash within biochar and result in an increase in pH, due to the presence of minerals that are alkaline within the ash component. Secondly, biochars made at lower temperatures could possess increased densities of functional groups that are acidic, such as phenolic and carboxylic groups, which could reduce the pH of such.

2.4.4.2 Effect of Residence Time on Biochar’s pH

The influence of residence time on the pH of biochar has not really been studied. Only a few information exists. Wang et al. (2019), noted an increase in the pH of biochar with extended residence time. On the other hand, Zhao et al. (2018), reported that residence time had no significant correlation with the pH of biochar. Furthermore, the influence of residence time on the pH of biochar has been reported to depend on the temperature of pyrolysis. At a temperature of 300 °C, Sun et al. (2017), presented that the biochar obtained from forest litter had a pH of 7.2 at a residence time of 0.5 hr and became stable with a pH of 11.05 at a residence time of 4 hrs. However, increasing residence time was observed not to have a significant effect on the pH at a temperature of 600 °C. Cao et al. (2018), observed an analogous trend and mentioned that the pH of biochar increased with residence time at moderate temperatures (200-500 °C), while they observed that there was no substantial change in the pH as the residence time increased, but only at high temperatures (≥500 °C).

The reported observations above present that possibly, the nature of biomass might play a significant part on the pH of biochar formed, and the influence of residence time, together with the temperature of pyrolysis would play a cogent part in understanding the influence of residence time on biochar’s pH.

2.4.4.3 Effect of Particle Size on Biochar’s pH

To the best of our understanding, and series of literature search on the effect of biomass particle size on the pH of biochar, there has not been any documented report on that. However, the behavioural pattern of various sizes of biomass particle under the influence of heat might be used to recognise the effect of particle size on biochar’s pH. Generally, biomass with larger particle size has been observed to resist the flow of heat. Owing to this, the acidic functional groups that gets broken down under high temperature might possibly remain within the biochar sample, hence, producing biochars with acidic properties and vice-
versa. This implies that larger biomass size would likely support the acidity of biochar and vice-versa.

2.5 Summary

2.5.1 Choice of Biomass
Due to the abundance of corncob in South Africa, it was chosen as the preferred lignocellulosic biomass to produce biochar in this study.

2.5.2 Pyrolysis Type
Owing to the ability of slow pyrolysis to aid the production of biochar, compared to biooil, slow pyrolysis was considered for the production of biochar in this study.

2.5.3 Pyrolysis Parameters
There are different pyrolysis parameters, however, based on the most studied parameters of temperature residence time, pyrolysis parameters of temperature, residence time and particle size were considered to be studied in this study (particle size was studied due to the few numbers of research on its impact on biochar).

2.5.3.1 Temperature
The review presents that the impact of temperature on biochar’s yield and physical properties have been well studied, especially when other process parameters are constant, or at most one other parameter varied. Even though temperature was reported to have an important influence on the yield, elemental compositions, proximate properties and pH of biochars, however, the influence of temperature when other process parameters are varied needs to be studied extensively. This is to understand the degree to which temperature would influence the yield and physicochemical characteristics of biochar under different process parameter combinations.

2.5.3.2 Residence Time
The report of the influence of residence time on the yield of biochar and its physicochemical properties has been conflicting with no steady progression. While some mentioned that residence time had a meaningful impact on the yield, elemental composition, proximate properties and pH of biochar, some others have a contrasting opinion. Furthermore, the impacts were not well understood until one other parameter; like temperature was co-studied. Besides, only a few have reportedly produced and studied the influence of residence time on
cornocob biochar. There is therefore a need to comprehend the effect of residence time, together with its relationship with other process conditions on the yield and physiochemical characteristics of corncob biochar.

2.5.3.3 Particle Size
Limited report exists on the influence of particle size on biochar’s physicochemical properties. Although there are some mentions of its influence on biochar’s yield, nevertheless, not in relation with other process conditions. There is therefore a reason to study and understand the influence of particle size, together with other process parameters on the yield and physicochemical characteristics of biochar; importantly corncob biochar. This is due to no report of its impact on biochars produced from corncob.

2.6 Conclusion
In this research, the influence of process parameters of pyrolysis temperature, residence time and particle size were studied on corncob biochar’s yield and physicochemical properties. The methods used to produce and study the impact of these process parameters are presented in the next section.
CHAPTER THREE

METHODOLOGY

3.1 Introduction

This chapter presents a comprehensive explanation of the experimental procedures that were carried out to realise the objectives and the overall purpose of this study. Summary of each of the basic tasks are shown in Figure 3.1.

![Figure 3.1: Summary of the Research Methodology](image)

3.2 Feedstock Selection and Source

Corncob waste was chosen as the feedstock to produce biochar. The motivation behind choosing it has been earlier highlighted in section of the literature review. The corncob biomass used in this research work was obtained from MTN Bree market, Johannesburg city.
South Africa. Although the cobs were initially intended for disposal, but it was obtained and used for biochar production in this research study. Some of the cobs collected are presented in Figure 3.2.

![Figure 3.2: Collected Corncob Waste](image)

### 3.3 Feedstock Preparation

The feedstock (corncob) was prepared prior to slow pyrolysis using the following techniques: drying, crushing, and sieve-sizing, as shown in Figure 3.3. The essence of this was to ensure that the feedstock was in the best condition before being subjected to the process of pyrolysis.

![Figure 3.3: Corncob Preparation Steps](image)

#### 3.3.1 Drying

The corncob feedstock was dried to lessen the moisture content (MC) within it. The MC for biomass feedstocks to be subjected to pyrolysis process should be less than 30%, for an optimum yield of biochar.\(^{30}\) Corncob was therefore dried using an electrical oven at the
Process, Energy, Environmental, and Technological Station (PEETS) laboratory, located at the University of Johannesburg, South Africa. The samples were placed on the trays inside the drying oven and left inside the oven at a temperature of 105 °C, for 24hrs (See Figure 3.4). After 24hrs, they were permitted to cool down inside the oven to room temperature (25°C) and kept tight in a plastic container prior to size reduction. The cooling inside the oven was to avoid the likelihood of the dried corncob absorbing moisture if allowed to cool outside.

Figure 3.4: Corncob Biomass during Drying

3.3.2 Biomass Size Reduction

The dried corncob biomass was reduced into smaller sizes using a roller and cone crushing machine at the metallurgy laboratory of the University of Johannesburg South Africa. A roller crusher (See Figure 3.5) was initially utilized to break down the extended size of the corncob into smaller sizes of about 5-10 mm, before it was fed into a cone crusher (See Figure 3.5) for further size reduction into 0.5-4 mm. During size reduction, corncob biomass was fed into the crushers gradually to ensure free flow and safe operation. The base of the crushers was covered with a clean transparent plastic (See Figure 3.5), in order to ensure that the reduced biomass samples were kept clean.
3.3.3 Biomass Sieve Sizing

To properly classify the reduced size of corncob biomass into different size range: precisely 0.5 mm, 1.0 mm, 1.5 mm, 2.0 mm and 4.0 mm, different sieve sizes were used. In the sieve arrangement, the size reduced downwardly such that the sieves with large opening sizes stayed at the top of the sieve arrangement before being placed inside an automatic sieve shaker (See Figure 3.6). The topmost sieve was covered with a lid and the base sieve was placed on an enclosed container. This is to ensure that the particle size lower than the smallest sieve size does not waste off. The sieve shaker was timed at 20 minutes to ensure that there was proper shaking to induce the separation of the crushed corncob biomass particles into different sizes. After the sieve sizing operation, corncob particle sizes of 0.5 mm, 1.0 mm, 1.5 mm, 2.0 mm and 4.0 mm were obtained (See Figure 3.6).
3.4 Biomass and Biochar Characterization

The prepared corncob biomass feedstock was analysed to understand its conditions prior to pyrolysis, while the produced biochar was characterized to understand the transformations that took place during pyrolysis. The characterizations in this research work are: elemental, proximate, and pH analysis. The steps involved in the characterization of fresh biomass and biochar are similar and are explained below.

3.4.1 Elemental Analysis

The elemental composition (CHNS) of the corncob and biochar produced were obtained using a CHNS elemental analyser at the Physical and Applied Chemistry Laboratory of the University of Johannesburg, Auckland Campus, while the amount of oxygen present was calculated by percentage difference, where the sum of C, H, N, and S content only was subtracted from 100. About 1.75 to 1.85g of the sample was weighed into a universal soft tin cup, then the cup was folded using tweezers to a barrel shape and placed into an auto sampler. Using a Flash 2000 CHNS Elemental analyser from Thermofisher Scientific, the folded sample one at a time was pushed into a Quartz reactor in the instrument furnace at 950°C for flash combustion with the aid of oxygen. The gaseous combustion products N₂, NOₓ, H₂O, SO₂, O₂ and CO₂ are carried by the helium as carrier gas through a column filled with copper oxide and from there to a Cu-column where nitrogen oxides are reduced to elementary nitrogen, and O₂ to CuO, while water was absorbed in another column. The remaining gasses were introduced into a Temperature Programmed Desorption (TPD) column where N₂ went right through it and the other gases were bound to the column. With a programmed temperature increase in the column, the gases were released distinctly. They flowed along a thermal conductivity detector (TCD) that generates an electrical signal proportional to the concentration of nitrogen, carbon, hydrogen and sulfur. The mathematical expression for the estimation of the oxygen content is presented in Equation 3.1.

\[
\%O = 100 - (C + H + N + S) \quad (3.1)
\]

3.4.2 Proximate Analysis

Proximate analysis was utilised to determine the amount moisture, volatile matter, ash and fixed carbon present within the sample. It was carried out using the American Society of Testing and Materials (ASTM) D5142 as described by Zhao et al. (2017). The scale resolution for the proximate analysis from the mass measurement was around ± 0.01g. The analysis was done in duplicates, with the average reported. In practice, 0.50g of the sample
was measured into a white ceramic crucible, whose empty mass had been initially measured (See Figure 3.7). To determine the percentage of moisture, a furnace (See Figure 3.8) was heated up to a temperature of 105 °C, and an uncovered crucible that contains the sample was placed and left in the furnace for 24 hrs. The percentage weight loss after 24hrs was the amount of moisture. For the volatile matter, the furnace was heated up to 950 °C, and the crucible containing the initial sample after moisture analysis was placed in the furnace at 950 °C for 7 mins; although covered at this time. For the ash content and fixed carbon analysis, the sample after heating at 950 °C in a covered crucible, was heated up in an open crucible for 6 hrs at 750 °C. The percentage weight difference was calculated by subtracting the amount of volatiles, together with ash from 100%\(^{148}\). (See Equation 3.2)

\[
\text{Fixed carbon} \% = 100\% - (\text{Ash} \% + \text{Volatile matter} \%)
\]  

(3.2)

Figure 3.7: Mass of the Crucible Plus Corncob Biomass

Figure 3.8: Proximate Analysis Furnace
3.4.3 pH Analysis

The pH of the biomass sample was carried out to determine the acidity or alkalinity of the biomass. As reported by Zhao et al. (2018), a 1:20 (wt.: vol.) of the sample (biomass/biochar) to deionized water was measured into a conical flask. The resulting solution was placed on a magnetic stirrer and stirred at 1200 rpm, temperature of 25 °C, for 1.5 hrs. The mixture obtained after stirring was placed into a test-tube and left there for 20 mins. After this, a calibrated pH meter (See Figure 3.9) was placed into the mixture, with the pH electrode touching the base of the mixture, the electrode was left inside the mixture for another 20 mins to ensure a stable reading was recorded. This was done out in duplicate, with the average reported. A pictorial view of the process set-up is displayed in Figure 3.9.

![Figure 3.9: pH Analysis Set-up at the Chemical Engineering Laboratory University of Johannesburg South Africa](image)

3.5 Experimental Design

In this research work, experimental design was utilised in the effective combination of process conditions (temperature of pyrolysis, residence time and particle size) that were varied. D-optimal design on Stat Ease design of experimentation software (design expert) was used in this research work for the design and combination of the selected independent process parameters. The independent variables were represented by x. For the temperature, the range was from 300-900 °C, with a step size of 100 °C, i.e. (300: n: 900; n=100). For
residence time, the range was from 0.5-2.0 hrs, with a step size of 0.5 hr, i.e. (0.5: n: 2.0; n=0.5). For particle size, the range was from 0.5-4 mm, but with an irregular step increment, this was due to the shortage of ordered set of sieves during the experiment. The actual sieve sizes used are: 0.5 mm, 1 mm, 2 mm, and 4 mm. The experimental design user interface is presented in Table 3.1.

**Table 3.1: Initial Step in the Design of Experimental Runs**

<table>
<thead>
<tr>
<th>Independent Parameters (x)</th>
<th>Level1</th>
<th>Level2</th>
<th>Level3</th>
<th>Level4</th>
<th>Level5</th>
<th>Level6</th>
<th>Level7</th>
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</thead>
<tbody>
<tr>
<td>Temperature (℃)</td>
<td>300</td>
<td>400</td>
<td>500</td>
<td>600</td>
<td>700</td>
<td>800</td>
<td>900</td>
</tr>
<tr>
<td>Biomass Size (cm)</td>
<td>0.5</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residence Time (hrs.)</td>
<td>0.5</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The yield and the physicochemical properties that were studied after the production of biochar are the response y. In specific terms, the responses are biochar’s yield, elemental compositions (%C,%H,%N,%O), proximate properties (MC,VM, AC and FC), and pH. The D-optimal design assisted in screening out the excessive number of runs and limited it to a feasible number of optimal runs. The experimental runs in this work were reduced to 9 (See Table 3.2).

**Table 3.2: Final (9) Experimental Runs**

<table>
<thead>
<tr>
<th>Runs</th>
<th>Designation</th>
<th>Temperature (oC)</th>
<th>Time (hrs)</th>
<th>Particle Size (mm)</th>
<th>Yield</th>
<th>Elemental composition</th>
<th>Proximate properties</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CCBC1</td>
<td>300</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CCBC2</td>
<td>300</td>
<td>0.5</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CCBC3</td>
<td>400</td>
<td>2</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>CCBC4</td>
<td>500</td>
<td>2</td>
<td>2</td>
<td></td>
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<tr>
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<tr>
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<td>CCBC9</td>
<td>900</td>
<td>1.5</td>
<td>4</td>
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</tbody>
</table>

Where CCBC denotes CornCob BioChar, and 1-9 stands for each number of the experimental runs in a chronological order.
3.6 Pyrolysis (Experimental Process)

Parallel to the method used by Lateef et al. (2019), in the synthesis of corncob biochar, slow pyrolysis of corncob biomass was carried out using a tube furnace reactor (See Figure 3.10), located at PEETS laboratory, University of Johannesburg. The schematic illustration of the tube furnace setup is shown in Figure 3.11. In each of the experiment, a fixed mass (0.53g) of corncob biomass (with varied particle size, depending on the experimental run) was fed into a crucible. The crucible was placed into the heating zone of the tube furnace reactor at the specified temperature of each experimental run. Before pyrolyzing the corncob biomass, nitrogen gas was allowed to flow continuously inside the tube furnace at a fixed flow rate of 230 ml/min. A gas metering device was fixed along the nitrogen line for proper metering of the nitrogen gas flow (See Figure 3.12). The furnace was heated to specified pyrolysis temperatures (300, 400, 500, 600, 700, 800 and 900 °C), at a fixed heating rate of about 11 °C/min. The feed inside the crucible was left in the reactor for different periods, depending on the specific residence time (0.5, 1.0, 1.5, and 2.0 hrs) of each experimental run. After each of the design specification was met, biochar was formed and the crucible containing the formed biochar was allowed to cool down and weighed. This was done to account for the loss in mass during the conversion process (See Figure 3.12). The biochar formed was later poured and kept inside a plastic container prior to characterization (See Figure 3.12). The condensable and incondensable gases formed during the process were passed into an extractive fume. This is because the scope of this research study was basically towards biochar production. The experiment was carried out in triplicates to ascertain the yield of the products being formed, and the average value was reported.
Figure 3.11: Schematic Diagram of the Corncob Pyrolysis Process Set-up


Figure 3.12: Mass Measurement and Gas Measuring During Pyrolysis Process
3.7 Biochar’s Yield
As reported by Gupta et al. (2017)\textsuperscript{158}, and Sato et al. (2015)\textsuperscript{145}, the yield of corncob biochar was calculated using the mathematical relationship represented by Equation 3.3.

\[ Yield = \frac{M_{bc}}{M_b} \times 100\% \quad (3.3) \]

Where $M_{bc}$ is biochar’s mass, and $M_b$ is the mass of the initial corncob biomass feedstock fed into the tube furnace pyrolysis reactor.

3.8 Conclusion
Corncob biochar was successfully produced from corncob obtained from the Gauteng province of South Africa. Physicochemical characterisation (elemental, proximate and pH) of the biomass and biochar were also carried out. The result and discussion of the result are presented in the next session.
CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Introduction
This section presents the outcome of the experimental procedure and the characteristics of corncob biochar with variations in the process parameters (temperature, residence time and particle size). The results and discussion provide answers to the questions raised in this research.

4.2 Biochar Yield
The yield of corncob biochar describes the amount of biochar obtained from the initial corncob biomass. Impact of each of the process parameter on corncob biochar’s yield is presented below.

4.2.1 Temperature
As shown in Figure 4.1, the yield of corncob biochar reduced from 61.32% to 8.49% with temperature increase from 300-900 °C. This result shows similar trend with what has been reported in literature, where the yield of biochar was reported to decrease with rise in pyrolysis temperature \(^{110,148}\). The reduction in biochar’s yield with rising temperature has been connected to a great extent of biomass decomposition, devolatilization, and disintegration of biochars as temperature rises \(^{110,147}\). The high yield of biochar at lower temperature has also been linked to the partial disintegration of biomass components at lower temperatures of pyrolysis \(^{113}\).

*Figure 4.1: Bar Graph of Biochar Yield vs. Temperature*
There was a sharp reduction in the yield from 50.94%-16.98%, at a temperature interval of 300-600 °C, and this might be possibly due to the breaking down of cellulose component into a more stable compound named anhydrocelluloses that supports the increase in the yield of biochar at initial pyrolysis temperatures. Furthermore, an early sharp reduction in the yield of biochar has been linked to the reduction in volatile matter with temperature increase, while some attributed the rapid decline to the early dehydration reactions, that takes off most of moisture within the biomass, at temperature intervals. Some others attributed the initial sharp decrease in biochar’s yield to the release of volatile matter with low boiling point, and some other non-condensable gases like CO₂, H₂, CH₄ and CO. As the temperature increased above 600 °C, the yield began reducing slightly; from 15.09%-8.49%. Similar result was reported by Zhao et al. (2017). The mild reduction in yield at higher pyrolysis temperature was related to the idea of most volatiles already being taken out at lower pyrolysis temperature (300-600 °C). The reports that temperature is negatively correlated with the yield of biochar, was confirmed in this study as shown in Figure 4.2. Furthermore, the coefficient of regression for the relationship between the yield of biochar and temperature is substantial (R²=0.7796) with p<0.05, which reveals that temperature has a strong influence on the yield of corncob biochar, as mentioned by Sato e al. (2019).

![Figure 4.2: Line Graph of Biochar’s Yield Vs. Temperature](image)

**Figure 4.2: Line Graph of Biochar’s Yield Vs. Temperature**

### 4.2.2 Residence Time

The influence of residence time on the yield of corncob biochar was not significant (p>0.05). This is shown by the linear regression graph in Figure 4.3, which presents the coefficient of regression (R³) to be 0.0424. Although this observation relates with that of Zhao et al. (2017)
They reported that residence time had trifling effect on the yield of biochar. However, one of the possible reasons why the yield was not significant is owing to variations in the particle size of the biomass (from 0.5-4 mm), during pyrolysis. Most studies on the impact of residence time on biochar’s yield used a uniform particle size. The effects of residence time alone as shown was not well understood; hence, the influence of residence time was studied together with variations in the pyrolysis temperature. Similar study was reported by Tripathi et al. (2016).
As represented in Figure 4.4, with an increase in the residence time, and a subsequent rise in the temperature of pyrolysis, the yield of corncob biochar reduced, although the reduction was mild at temperature intervals of 300-600 °C, and residence time of 0.5-1.5 hrs. This might possibly be due to the disintegration of more volatile matter that remains in the biochar, favouring the formation of gaseous product to solid biochar. The reduction in the yield of biochar became more obvious at a temperature interval of 600-800 °C, and a subsequent rise in residence time from 1.5-2.0 hrs. This implies that pyrolysis reaction was not complete, inhibiting the formation of biochar, while supporting the formation of more volatiles. At a residence time of 2 hrs and temperature of 800 °C, there was a steady decrease in biochar’s yield from about 35-20%. The reduction in the yield was stable since most of the volatile components have been removed, with no significant let-off of volatiles that would have significantly lessened biochar’s yield. At a higher temperature of 800 °C and lower residence time of 0.5 hrs, the yield of biochar reduced drastically to about 18%. This might be attributed to the ability of heat to flow through the small particle size, leading into more disintegration reaction favouring the formation of more gaseous product, as opposed to biochar. Although at moderate temperature of 400-600 °C, and moderate residence time of 1-1.5 hrs. The influence of residence time was not significant, as the yield was around 9.5%. The observations in this research work correlates with that of Wystaliska et al. (2018), who mentioned that the yield of biochar obtained during pyrolysis is a function of the temperature during pyrolysis, and not on the retention time. The p value for the impact of residence time on the yield of biochar was not significant in this research work (p>0.05).

4.2.3 Particle Size

The influence of particle size on corncob biochar’s yield was more pronounced than that of the residence time. The correlation coefficient (R²) of regression between the particle size of corncob biomass and the yield of biochar is 0.3003 (See Figure 4.5), unlike that of residence time with 0.0424. Nevertheless, the impact of particle size alone on the yield of biochar was not well understood. For instance, a particle size of 0.5 mm showed a yield of 61.32 and 29.25%. Similar trend was observed for a particle size of 2.0 mm with yields of 50.94, 16.98 and 8.49%. This implies the influence of particle size on the yield of corncob biochar did not have a direct interpretation and was confirmed by its p value (p>0.05). Thus, the influence of particle size was studied together with pyrolysis temperature. As shown in Figure 4.6, the relationship between the particle size and the amount of biochar obtained was better understood with variation in temperature. At a lower temperature of 300 °C, biochar produced
from corncob biomass with a particle size of 0.5 mm had a higher yield of 61.32%, while that from a particle size of 2.0 mm had a lower yield of 50.94%. This, however contradicts previous observations that reported that an increase in particle size leads to the production of more yield of biochar. The reason behind this could however be linked to an extension in residence time from 0.5-1.5 hrs that probably favoured recondensation of vapor to increase the yield of biochar. The corncob biomass sample with a particle size of 0.5 mm, at a short residence time of 0.5 hrs produced more biochar than the one formed at the same temperature, with a larger particle size of 2.0 mm, and at an extended residence time of 1.5 hrs. This implies that not only does the particle size affects the yield of biochar at low temperature, but residence time also plays a part on the influence of particle size on biochar’s yield. Furthermore, the reduction in the yield of corncob biochar at a temperature of 300 °C, particle size of 0.5 mm and 300 °C, particle size of 2 mm was mild; from a yield of 61.32% to 50.94%, unlike the significant reduction in the yield of biochar from 61.32% to 29.25%, at process conditions of 300 °C, 0.5 mm and 400 °C, 0.5 mm respectively. This translates to a decrease in the yield of biochar produced from biomass samples with uniform particle size as the temperature of pyrolysis increases. As the temperature rose from 400 °C to 500 °C, and particle size of 0.5 mm and 4.0 mm respectively; although at uniform residence time (2 hrs), the yield of corncob biochar decreased from 29.25% to 18.87%, with a difference of 10.38%. This could however be as a result of an increase in the resistance to heat treatment for the 4.0 mm particle size as reported by Demirbas (2004). Nevertheless, the negative relationship between pyrolysis temperature and the yield of biochar was still obvious. At operating conditions of 600 °C; 2 mm, 700 °C; 1 mm and 800 °C; 4 mm, the yield was 16.98, 15.09, and 10.38% respectively. The mild difference (1.89%) between the yield at 600 °C; 2 mm, and 700 °C; 1 mm, might be attributed to the diminutive difference in the particle size from 2 mm to 1 mm; meaning that, particle size played a significant role in ensuring that the impact of temperature was trifling. However, at temperature of 800 °C, and particle size of 4 mm, the difference in the yield was more pronounced, with a difference of 6.60%; translating to particle size does not have a significant effect on the yield of biochar at a very high temperature, while temperature does. At a temperature and particle size of 900 °C; 2 mm and 900 °C; 4 mm, the yield was 8.49 and 9.43% respectively. At this temperature, the claim that higher particle size favours more yield was justified and confirmed. However, the inference from our observation is that at higher and uniform temperatures (≈900°C), larger biomass particle size would favour the yield of biochar, while the effect of particle size would be well
understood together with variation in temperature and residence time at other temperatures (≈300-800°C).

**Figure 4.5: Linear Graph of Biochar Yield Vs. Particle Size**

**Figure 4.6: Graph of Residence Time and Temperature Relationship with Biochar Yield**
4.3. Elemental Analysis

The elemental analysis revealed the amount in percentage of C, H, N, and O (by difference) present in corncob biomass (See Figure 4.7) and biochar (See Figure 4.8).

**Figure 4.7: Elemental Composition of Corncob Biomass (d: determined by difference)**

**Figure 4.8: Elemental Composition of Corncob Biochar**

CCBC1: 300°C,0.5hr,0.5mm. CCBC2: 300°C,1.5hrs,2mm. CCBC3: 400°C,2.0hrs,0.5mm. CCBC3: 400°C,2hrs,0.5mm. CCBC4: 500°C,2hrs,4mm. CCBC5: 600°C,0.5hr, 2mm. CCBC6: 700°C,2.0hrs,1mm. CCBC7: 800°C,1hr,4mm. CCBC8: 900°C,1hr,2mm. CCBC9:900°C,1.5hrs,4mm.
4.3.1 Temperature

4.3.1.1 C content

The elemental carbon within corncob biochar formed at a temperature of 300 °C was almost the same; 66.42 and 68.19%, although with a mild difference of 1.67%. The content of carbon increased with rise in pyrolysis temperature (400-500 °C), from 72.51-77.98%. This is logical, as an increase in temperature increases carbonization reaction and leads to the formation of more carbon. However, the carbon content reduced from 77.98-76.03% as the temperature increased from 500-600 °C. This is possibly due to a reduction in the residence time from 2-0.5 hrs; hence the reaction was more complete at the former residence time. The carbon content later increased from 76.03-78.40% with temperature rise from 600-800 °C. This increase was not dependent on the residence time nor particle size. This implies that the rise in the content of carbon within this temperature interval was mainly related to temperature increase. Furthermore, the rise in C-content might possibly be due to the removal of OH-groups during dehydration and disintegration reactions with temperature rise 158. However, at the pyrolysis temperature of 900 °C, the carbon content increased from 75.26-76.52%; although at different residence time of 1 and 1.5 hrs respectively. The slight increase of 1.26% in the carbon content might be due to the extended residence time that favoured carbonization reaction of unvaporized volatiles within the sample. The temperature of pyrolysis had a significant impact on the amount of C during the pyrolysis of corncob biochar with a R² of 0.5666 (See Figure 4.9).

4.3.1.2 H content

The impact of pyrolysis temperature on the amount of H in corncob biochar was significant, with a R² value of 0.965 (See Figure 4.9), although with a negative correlation. Generally, the H content within corncob biochar reduced gradually from 4.29%-0.00% as the temperature increased from 300-900 °C. The negligible H content within corncob biochar as temperature increases was due to the volatilisation of some H-containing functional groups within corncob biochar, with increase in pyrolysis temperature 148.
4.3.1.3 N Content
The influence of temperature on the N content within corncob biochar was not significant with a p value >0.05; although the $R^2 = 0.5656$ (See Figure 4.10). The nitrogen content reduced from 1.40-0.70% as the temperature increased from 300-900 $^\circ$C. The fluctuating rise and decrease in N content was mostly attributed to the particle size. Furthermore, this might be related to the breaking down of the nitrile groups present on corncob biomass as the temperature increased, and the possibility of NO$_X$ and NH$_3$ removal with temperature rise during pyrolysis. Corncob biochars with smaller particle size had more N content compared with those with larger particle size in spite the pyrolysis temperature. This might be due to the formation of N-containing groups, as smaller particle size favours more pyrolysis reaction, and possibly the formation of new N-rich compounds.

4.3.1.4 O Content
The impact of temperature on the O content of corncob biochar was not significant. The $R^2$ value was very low ($R^2 = 0.2262$) (See Figure 4.10). Initially, the O content reduced from 27.89-18.98% with increase in the pyrolysis temperature from 300-500 $^\circ$C. This might possibly due to the breakdown of O-containing functional groups as the pyrolysis reaction attained completion. However, the O-content later increased in a staggering manner from 20.92-22.79% from a temperature of 600-900 $^\circ$C. This might be due to the condensation of O-
functional group that were initially turned into vapor onto the surface of corncob biochar during the pyrolysis reaction.

![Graph of Temperature’s Impact on O and N content of Corncob Biochar](image)

**Figure 4.10: Graph of Temperature’s Impact on O and N content of Corncob Biochar**

### 4.3.2 Residence Time

#### 4.3.2.1 C content

The impact of residence time on the content of C within corncob biochar was significant at constant temperature, with observations that corncob biochar produced at a temperature of 300 °C (See Figure 4.11), but at different residence time of 0.5 and 1.5hrs respectively having a C content of 66.42 and 68.19 respectively. This might be attributed to the increase in pyrolysis reaction with temperature rise, resulting in more carbonization and in the formation of more C-contents. However, at a temperature of 400 and 500 °C, with constant residence time, temperature was the major parameter that induced a rise in the content of C, specifically from 72.51-77.98%. This is logical, as high temperature favours the formation of more C content in biochar. As the temperature increased form 600-700 °C, and at a residence time of 0.5 and 2 hrs respectively, the C-content increased. This is both due to the increase in the temperature of pyrolysis and also due to the increase in the residence time, as an extended residence time would also favour more disintegration and possible condensation of some C-functional groups on the surface of biochar. The effect of residence time was also a bit significant at peak temperatures of 900 °C. The biochar produced at residence time of 1 and 1.5 hrs have a C-content of 75.26 and 76.52% respectively, meaning that residence time plays a significant role on the C-content present within biochar at elevated temperatures.
4.3.2.2 H Content

The H-content within the produced corncob biochar did not have a significant correlation with the residence time during pyrolysis, irrespective of the residence time of each of the runs (See Figure 4.12). This could possibly mean that study of the effect of residence time on the amount of H within corncob biochar might not be necessary.
4.3.2.3 N Content
At lower temperature, the residence time had a mild effect on the N-content within corncob biochar. The N-content within corncob biochar at the temperature interval of 300-400 °C and a residence interval of 1.5-3 hrs resulted in an increase in N-content, basically from 0.98-1.14% (See Figure 4.8). This might probably be due to the mild formation of N-containing compounds with an increase in both temperature and residence time. A similar trend was observed for a pyrolysis temperature of 600-700 °C (See Figure 4.8), at residence time of 0.5-2 hrs. The N-content increased from 0.87-1.04% respectively. At a pyrolysis temperature of 900 °C, an increase in the residence time from 1-1.5 hrs resulted in a mild decrease in the N-content from 0.79-0.70%. This could probably be related to the breaking down of unstable nitrogen compounds into other stable compounds\textsuperscript{155}.

4.3.2.4 O Content
The O-content within corn cob biochar reduced from 27.89-23.36% as the residence increased from 0.5-2 hrs, with a subsequent rise in the temperature of pyrolysis from 300-400 °C (See Figure 4.8). This is could be due to the support of reactions that favoured the removal of oxygen containing functional groups at initial temperatures, with extended residence time. For the rest of the process, temperature had the major impact on the presence of O-content on the surface of corncob biochar.

4.3.3 Particle Size
The particle size of corn cob biomass did not have a considerable effect on the elemental composition of corncob biochar. Ideally, the extent of pyrolysis reaction should be higher in biochar obtained from lower particle sizes, however, this was not the case, and makes the influence of particle size on CHNS a bit difficult to decipher. The graph of the particle size against the elemental composition of corncob biochar is presented in Figure 4.13.
Figure 4.13: Graph of Elemental Compositions of Corncob Biochar Vs. Particle Size

4.4 Proximate Analysis

The proximate property of corncob biomass and corncob biochar(s) is presented in Figure 4.14 and Figure 4.15 respectively.

Figure 4.14: Proximate Property of Corncob Biomass
4.4.1 Temperature

4.4.1.1 Moisture

The impact of temperature on the moisture content of corncob biochar was not steady, with a low coefficient of regression $R^2=0.4783$ (See Figure 4.16). Normally, the presence of moisture content reduces with a rise in the temperature of pyrolysis $^6$, however, this was not the case for our study. The possible reason for this is because of the difference in the particle size of the initial corncob biomass, increasing the recalcitrant property of the biochars to the vaporization of moisture, another possible reason might be due to condensations of volatiles onto the surface of biochars produced at high temperatures. Nevertheless at initial temperature of 300-400 °C, the moisture content reduced from 6-3%, following the reported trend $^6$. This might be due to the initial breakdown of the hemicellulose and cellulose component of corncob biomass giving out moitures.
4.4.1.2 Volatile Matter

The effect of temperature on volatile matter was significant, with a $R^2$ of 0.736, and a significant p value ($p<0.05$). This supports the claim that the content of volatile matter is majorly influenced by the temperature of pyrolysis, and that it reduces with increase in pyrolysis temperature $^{78,145}$. In this research study, at temperatures of 300-900 °C, the volatile matter within corncob biochar reduced significantly from 47-8% (See Figure 4.17).

Figure 4.17: Graph of Volatile Matter Vs. Temperature
4.4.1.3 Ash Content

The variations in other process parameters of residence time and particle size made the influence of temperature on ash content of corncob biochar to be less significant. As opposed to existing observations that the amount of ash within biochar increases with increase in the temperature of pyrolysis \(^78\), our observation was not similar. Although it was relative at the temperature of 500-700 °C, such that the ash content increased from 4-10% (See Figure 4.18). This might be due to increase in the amount of minerals and the simultaneous disintegration of the lignin and cellulose structure of the initial biomass as the temperature increased \(^69\). However, it later reduced at 800 °C, before it increased to 13% at 900 °C. The unstable and irregular observation is likely due to the variation of other parameters of residence time and particle size during the pyrolysis of corncob biomass. This implies that the study of the impact of temperature on corncob biochar might be well understood if temperature is varied, while other parameters are held constant.

![Figure 4.18: Graph of Ash Content Vs. Temperature](image)

4.4.1.4 Fixed Carbon

The impact of temperature on fixed carbon content within corncob biochar was slightly significant \((R^2=0.564)\) (See Figure 4.19). Existing reports claim that fixed carbon content increases with rise in pyrolysis temperature \(^78,122\), and this was observed at initial temperature increase from 300-600 °C, such that the fixed carbon increased from 46-73%. This can be
attributed to increasing temperature supporting carbonization reaction in spite of the other process parameters of residence time and particle size, and probably because volatile matters that vaporised under the influence of heat left behind more stabilized residual carbon component \(^{21}\). At a temperature greater than 600 °C, the fixed carbon reduced, and later increased, before reducing. This might probably be related to the release of the remains of volatiles that recondensed onto the surface of biochar at high temperatures (>600 °C). In summary, the significant impact of temperature on the fixed carbon content of corncob biochar was only evident at a temperature interval of 300-600 °C.

![Graph of Fixed Carbon Vs. Temperature](image)

**Figure 4.19: Graph of Fixed Carbon Vs. Temperature**

### 4.4.2 Residence Time

The influence of residence time of pyrolysis reaction on the moisture content was insignificant (p>0.05), and there was no regular progression that could properly explain the relationship between residence time and moisture content. Similar trend was observed for the effect of residence time on ash content of corncob biochar. However, it had a mild effect on its volatile matter and fixed carbon. This is possibly due to the relationship between volatile matter and fixed carbon content, such that a decrease in volatile matter content would favour the formation of more fixed carbon. For better understanding of the effect of residence time on the proximate properties of corncob biochar, the residence time alone should be varied.
4.4.3 Particle Size

The variation in the particle size also did not have a significant effect on the moisture content, volatile matter, and fixed carbon content. Although, it had a significant p value (p<0.05) on the ash content. This is possibly due to the variation of inorganic minerals within different size of corncob biomass. Corncob biochar produced from biomass with particle size of 2 mm at 900 °C had the highest amount of ash (13%), and this is logical with the possibility of biomass with huge particle size to retain some of its inorganic minerals and alkali and alkali-earth metals. However, there are some unsteady variations between ash content and biomass particle size. Inspite of this, particle size still had better influence on the proximate properties of corncob biochar compared to other parameters.

4.5 pH Analysis

The pH of corncob biomass was 5.05 and that of the produced biochars; which represents the degree of acidity or alkalinity of the biochar samples are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Pyrolysis Temperature (°C)</th>
<th>Residence Time (hrs)</th>
<th>Particle Size (mm)</th>
<th>pH Value</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.5</td>
<td>4.18</td>
</tr>
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<td>300</td>
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<td>2</td>
<td>6.02</td>
</tr>
<tr>
<td>400</td>
<td>2</td>
<td>0.5</td>
<td>8.59</td>
</tr>
<tr>
<td>500</td>
<td>2</td>
<td>4</td>
<td>8.19</td>
</tr>
<tr>
<td>600</td>
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<td>8.25</td>
</tr>
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<td>1</td>
<td>8.53</td>
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</tr>
<tr>
<td>900</td>
<td>1.5</td>
<td>4</td>
<td>8.49</td>
</tr>
</tbody>
</table>
4.5.1 Temperature

The influence of temperature on the pH of biochar was slightly significant ($R^2=0.472$) (See Figure 4.20). This is probably because of the impact of residence time and particle size. It is also important to state that unlike most report where biochars are initially grounded to a uniform particle size before being tested for their pH value, the size of the produced corncob biochars were maintained even during the pH analysis, this was to test if the particle size would play a significant role on the pH of corncob biochar. The observation by previous researchers that the pH of biochar could be acidic at low pyrolysis temperature $^6,^{144}$ was noted for the pH of corncob biochar at 300 °C. The pH value was 4.18 and 6.02. This is probably due to incomplete pyrolysis reaction resulting in the condensation of acidic functional groups on the surface of corncob biochar $^{147}$. The pH later increased with temperature rise, however, not with a regular pattern. The increase in the pH of corncob biochar with rising temperature might perhaps be due to the reduction in the presence of organic functional groups (-COOH and -OH), and a subsequent increase in the formation of alkali-metals compounds (Na and K) on the surface of biochar $^{19,153}$.

![Figure 4.20: Graph of pH Vs. Temperature](image)

\[ \gamma = 0.0044x + 5.0346 \]
\[ R^2 = 0.472 \]
4.5.2 Residence Time

In general, the impact of residence time on the pH of corncob biochar was very mild \((R^2=0.192)\) (See Figure 4.21). At low pyrolysis temperature of 300-400 °C, increase in the residence time favoured the rise in the pH of corncob biochar. This is possibly due to an increased extent of pyrolysis reaction with extended period of pyrolysis time, as extended residence time was reported by Cao et al. (2018) to favour complete pyrolysis reaction, supporting the increase in the pH of biochar \(^{153}\), while Wang et al. (2019) also presented that this might be due to the decomposition of a higher amount of alkali and alkaline earth elements like Ca, Mg and K and the formation of their oxides \(^{155}\). However, the pattern was not regular, and might be linked to the non-uniformity of the particle size when analysing the pH of corncob biochar.

![Figure 4.21: Graph of pH Vs. Residence Time](image)

4.5.3 Particle Size

The influence of particle size was not significant \((R^2=0.1547)\) (See Figure 4.22), however, there is a possibility that the irregular variation in the pattern of increase in the pH value of corncob biochar could be linked to the variation in the particle size (0.5-4 mm). Nevertheless, there were still some noticeably effect of particle size on the pH of corncob biochar. The pH at 400 °C, 0.5 mm was greater than the pH of at 500 °C, 4 mm (8.59 and 8.19 respectively). The same observation was noted for the pH of corncob biochar at 900 °C, 2 mm, and 900 °C,
4 mm (8.50 and 8.49 respectively). This is possibly due to the small particle size that supported the leaching out of the alkaline component within the produced biochar as opposed to that of biochars with huge particle size.

![Graph of pH Vs. Particle Size](image)

**Figure 4.22: Graph of pH Vs. Particle Size**

### 4.6 Conclusion

The effect of each of the process parameters on the yield and physicochemical properties of corncob biochar has been discussed in this chapter. The conclusion and recommendation for future study is presented in the next chapter.
CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Introduction
Haven evaluated the impact of pyrolysis (specifically pyrolysis process parameters) on the yield and physicochemical properties of corncob biochar, conclusion and recommendation are highlighted below.

5.2 Conclusion
The effect of process parameters of temperature, residence time and particle size have been studied on corncob biochar produced from the slow pyrolysis of corncob biomass in South Africa. From overall observation in this study, the research hypothesis of temperature having the most significant effect on the yield and physicochemical properties (elemental composition, proximate properties and pH) of corncob biochar was validated. The temperature of pyrolysis had a measurable effect on all the studied properties. Residence time’s effect was not significant for all the physicochemical properties of corncob biochar, and similar observation was noted for the particle size. Temperature having the major impact on almost all the studied properties agrees with most existing report that claims the temperature of pyrolysis has the highest influence on the yield and physicochemical properties of biochar. With this observation, future research can use the result obtained from this study as a basis to delve more into understanding better the influence of pyrolysis parameters on corncob yield and physicochemical properties. Hence, the recommendations below are made.

5.3 Recommendation
This study has proven the importance of the effect of process parameters on the yield and physicochemical properties of corncob biochar which has an integral component in the production of adsorbent for adsorption of heavy metals, biocatalyst production and carbon sequestration applications. Nonetheless, in order to maximize these excellent potentials of biochar, the following are recommended:

✓ Investigation of the impact of temperature, residence time and particles size on the yield, elemental composition, proximate properties and pH of corncob biochar over an
extended period of runs (15-20) for proper evaluation of the process parameters on the yield and physicochemical properties of biochar.

✓ Commencement of study on the effect of two process parameters (temperature and particles size; or temperature and residence time) on the yield and physicochemical properties prior to studying the effect of three process parameters on the yield and physicochemical properties of corncob biochar. This will provide a thorough insight on the impact of the parameter combinations on the yield and physicochemical properties of corncob biochar.

✓ Optimization of the effect of each of the process parameters on the yield, elemental composition, proximate properties and pH of biochar. This will ease the application of any research discovery for different industrial applications in South Africa.
References


155. Wang, Z. et al. Effects of residence time on characteristics of biochars prepared via co-

156. Cheng, F. & Li, X. Preparation and application of biochar-based catalysts for biofuel

157. Zhao, B. et al. Effect of pyrolysis temperature, heating rate, and residence time on

158. Gupta, G. K., Ram, M., Bala, R., Kapur, M. & Mondal, M. K. Pyrolysis of chemically
treated corncob for biochar production and its application in Cr(VI) removal. Environ.
Appendices

Appendix 1

The Yield of Corncob Biochar

<table>
<thead>
<tr>
<th>Runs</th>
<th>Temp (°C)</th>
<th>Time (hrs.)</th>
<th>Particle Size (mm)</th>
<th>Biochar's Yield (%)</th>
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<tbody>
<tr>
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<td>0.5</td>
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<tr>
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<td>0.5</td>
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<tr>
<td>4</td>
<td>500</td>
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<td>4.0</td>
<td>18.87</td>
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<tr>
<td>5</td>
<td>600</td>
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<td>2.0</td>
<td>16.98</td>
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Elemental Composition Data

Elemental Composition of Corncob Biomass

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<tr>
<td>H</td>
<td>5.58</td>
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<tr>
<td>N</td>
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<td>O(^d)</td>
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\(d\): determined by difference

Elemental Composition of Corncob Biochar

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<th>Residence Time(hrs.)</th>
<th>Particle Size (mm)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O(^d) (%)</th>
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<th>H/C</th>
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Appendix 2
Proximate Analysis Data

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<td>Ash (%)</td>
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<tr>
<td>VM (%)</td>
<td>78±0.01</td>
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<tr>
<td>Fixed Carbon (%)</td>
<td>14±0.01</td>
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</table>

<table>
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<th>Ash (%)</th>
<th>VM (%)</th>
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<td>11</td>
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</table>
Appendix 3
Other Graphs

![Graph 1](image1)

**Pyrolysis Temperature (°C)**

**O/C**

**H/C**

![Graph 2](image2)

**Pyrolysis Temperature (°C)**

**O/C**

**H/C**

R² = 0.3208

R² = 0.957
Appendix 4
Statistical Analysis

In order to evaluate the impact of each of the parameter and their combination on the yield and physicochemical properties of corncob biochar, Regression analysis was used on Microsoft EXCEL suite. The impact of the process parameters was evaluated individually, before being analysed when combined. The result of the statistical analysis using the regression tool on EXCEL is presented below.

Analysis of Process Parameters on Biochar Yield

The result of using regression analysis for the evaluation of the impact of the process parameters on the yield of biochar is presented below. The significance of a parameter on the yield of biochar is valid if its p value is greater than 0.05 (p<0.05).

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<th>Parameters</th>
<th>p value</th>
<th>significant (p&lt;0.05)</th>
<th>R Square</th>
<th>Adjusted R Square</th>
</tr>
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<td>0.779622019</td>
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<td><strong>Impact of Particle Size Alone on Biochar's Yield</strong></td>
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<tr>
<td>Particle Size</td>
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<td>0.300267144</td>
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<tr>
<td>Time</td>
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### Analysis of Process Parameters on Elemental Analysis

**Impact of Three Parameter Combination on %H**

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**Impact of Three Parameter Combination on %N**

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<th>Adjusted R Square</th>
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<td>Temperature</td>
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**Impact of Three Parameter Combination on %O**

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**Impact of Three Parameter Combination on %C**

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### Analysis of Process Parameters on Proximate Analysis

**Impact of Three Parameter Combination on Moisture Content**

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**Impact of Three Parameter Combination on Volatile Matter**

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</table>

**Impact of Three Parameter Combination on Ash Content**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>p value</th>
<th>significant p&lt;0.05</th>
<th>R Square</th>
<th>Adjusted R Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>0.045614992</td>
<td>Significant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residence Time</td>
<td>0.969523928</td>
<td>Insignificant</td>
<td>0.717478586</td>
<td>0.547965738</td>
</tr>
<tr>
<td>Particle Size</td>
<td>0.019807883</td>
<td>Significant</td>
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</table>
### Impact of Three Parameter Combination on Fixed Carbon

<table>
<thead>
<tr>
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<th>R Square</th>
<th>Adjusted R Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>0.101436711</td>
<td>Insignificant</td>
<td></td>
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</tr>
<tr>
<td>Residence Time</td>
<td>0.535432995</td>
<td>Insignificant</td>
<td>0.66554604</td>
<td>0.464873664</td>
</tr>
<tr>
<td>Particle Size</td>
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### Analysis of Process Parameters on pH

<table>
<thead>
<tr>
<th>Parameters</th>
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<th>R Square</th>
<th>Adjusted R Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>0.05797681</td>
<td>Insignificant</td>
<td></td>
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<tr>
<td>Residence Time</td>
<td>0.119429848</td>
<td>Insignificant</td>
<td>0.69133</td>
<td>0.5061249</td>
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<tr>
<td>Particle Size</td>
<td>0.960861728</td>
<td>Insignificant</td>
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<td></td>
</tr>
</tbody>
</table>