# OPTIMIZATION OF THE PHYSICOCHEMICAL PARAMETERS OF SELECTED AGRICULTURAL WASTES TO INCREASE BIOSYNTHETIC GAS AND BIOCHAR YIELDS

**BY**

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# DECLARATION

I, John Chrysostom Opedun, declare that the work carried out and reported in this dissertation is my original work and has never been submitted elsewhere before for any academic award.

Sign: …………………………… Date: ……… / ………… /……….

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# APPROVAL

We confirm and approve the work done by the candidate under our supervision;

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# DEDICATION

To the Almighty God, and to my parents, who spent their lives building a good family and brightening my life with their love and affection.

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# ABSTRACT

Biosynthetic gas and biochar are gaseous and solid fuels, respectively, that can be produced from various lignocellulosic feedstocks via pyrolysis and are recognized as clean and attractive sources of renewable energy. They can be easily transported and used directly in boilers and modified turbines or upgraded for chemical production.

In this work, physicochemical characterization; moisture, ash, volatile matter, total solids, hemicellulose, lignin and cellulose contents were gravimetrically determined and subsequent pyrolysis of agricultural wastes namely; groundnut shells, coffee and rice husks to produce biosynthetic gas and biochar were conducted. The parameters; moisture, particle size and cellulose, that were used to improve the biosynthetic gas and biochar yields were optimized using Design-Expert® software Stat-Ease version 7.0.0 USA. Response Surface Methodology and Box-Behnken design were applied.

Results showed that rice husks had the highest amount of ash and total solids content at averages of 22.94 ± 0.75% w/w and 89.54 ± 0.18% w/w, respectively. Coffee husks had the least amount of ash with an average of 1.58% w/w, and total solids at 87.69 ± 0.51% w/w but with the highest amount of cellulose; 40.45 ± 1.58 % w/w, followed by groundnut shells at an average of 28.28 ± 4.45% w/w, and finally rice husk had the least amount of cellulose in the magnitude of 20.81 ± 3.61% w/w. Moisture content was essentially similar across all the biomass samples analyzed at averages of 10.46 ± 0.18% w/w, 12.31 ± 0.51% w/w and 12.49 ± 0.70% w/w for rice and coffee husks, and groundnut shells, respectively.

Basing on the overall interactive effect of particle size, moisture and cellulose content to maximize yields of biochar and biosynthetic gas, the most optimal interaction that yielded the highest quantity of biochar (1.54 g) was found to be at levels of 0.36 mm, 10.3% and 25.45% for particle size, moisture and cellulose content, respectively, whereas the most optimal interaction that yielded the highest quantity of biosynthetic gas (40.10 $cm^3$) was found to be at 2.86 mm, 0% and 32.52% for particle size, moisture and cellulose content, respectively. In both interactions, cellulose levels corresponded to groundnut shells as the best biomass material for producing biochar and biosynthetic gas. The study recommends the use of groundnut shells for pyrolysis to produce high yields of both biochar and biosynthetic gas.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background

A great fraction of energy carriers and material products worldwide come from fossil fuels. The use of fossil-based fuels as the principal energy source has declined in consideration because of the ever-increasing prices of fossil fuels; their unreliability and unsustainability coupled with negative environmental effects. Therefore, alternative sources of energy that can be used to mitigate climate change and reduce the consumption of fossil fuels are being promoted (Cherubini, 2010).

The probable alternatives to crude oil are bio-oils from pyrolysis of biomass as a raw material for fuel and chemical production and are an interesting option and driving force for the development of bio-fuel refinery complexes. In the bio-fuel refinery, almost all types of biomass feed stocks can be converted to different classes of biofuels and biochemicals through jointly applied conversion technologies (Cherubini, 2010).

According to Lim *et al*. (2012), biomass is one of the most promising alternative energy sources, because of its availability from multiple sources. Biomass can be thermochemically converted into solid and liquid fuels, gases such as methane, carbon monoxide, or hydrogen by pyrolysis and gasification. There are three main reasons why biomass can reduce the use of fossil-based energy sources: It is a clean and renewable energy source that could dramatically improve our environment, economy, and energy security; biomass energy generates far less toxic emissions than fossil fuels, reduces the amount of biomass waste sent to landfills, and decreases reliance on fossil based oil. Biomass energy can also create thousands of jobs and help revitalize rural communities (Gokcol *et al*., 2009).

The huge availability of biomass capable of yielding petroleum-like products presents a promising sustainable and renewable alternative resource to fossil fuels. Due to the limited availability of fossil feedstocks, the manufacture of high valued fuel products from low valued feedstock like heavy oil residues and biomass has received great interest of researchers and oil producers (Nigam, 2011).

Biomass material such as that obtained from agricultural waste products presents a good opportunity for conversion to useful energy products. Some of these agricultural wastes include groundnut shells, coffee and rice husks, and have huge potential for biochar and biosynthetic gas production.

The conversion technologies for utilizing biomass can be separated into four basic categories: direct combustion processes, thermochemical processes, biochemical processes and agrochemical processes. Thermochemical conversion processes can be subdivided into gasification, pyrolysis, supercritical fluid extraction and direct liquefaction (Balat, 2009). Pyrolysis is one of the thermochemical processes that converts biomass into liquid oils, biochar and non-condensable gases, acetic acid, acetone and methanol by heating the biomass to about 750 K in the absence of air (Demirbaş, 2001). Noteworthy, is that pyrolysis is attractive because solid biomass and wastes, which are difficult and costly to manage, can be readily converted to liquid products, bio-oils and gases, that have many advantages in transportation, storage, handling, combustion and flexibility in production and marketing (Phuong *et al*., 2014).

During biomass pyrolysis, an oil-like liquid called bio-oil or bio-liquid, a gas mixture containing mainly the oxides of carbon; some methane and higher hydrocarbon gases in minor quantities; and biochar are produced. Among them, bio-oil is the most interesting product, which is a complex mixture of organic compounds such as acetic acid, levoglucosan, furan, furfural, phenolics (guaiacol), aldehydes, and ketones which are all bio-based chemicals and fuels providing potential alternatives to petroleum-based chemicals and fuels (Lee *et al*., 2016). Furthermore, bio-oil can be used as a source of valuable chemicals such as phenols after separation. It is also considered as a potential biofuel since it can be easily transported using conventional methods and burned to produce energy.

Despite the importance of pyrolysis technologies, challenges still exist in ensuring an efficient and effective pre-pyrolysis treatment and selection of biomass required for higher yields and quality products and has warranted further studies to identify ways on how pyrolysis yields can be optimized.

Biomass such as groundnut shells are under-utilized as a domestic fuel and are mostly gotten rid of by garden disposal and open burning which have had a significant contribution to both soil and air pollution. In addition, studies on alternative use of renewable resources such as biomass for generation of eco-friendly biofuels and chemical feed stocks in place of depleting fossil fuel reserves have highlighted a great potential in boosting the worlds fuel and chemical needs.

## 1.2 Problem statement

Uganda is a developing nation with a high dependence on agriculture which consequently generates huge amounts of wastes such as groundnut shells, coffee and rice husks. The use of different agricultural biomass feed stocks in Uganda for fast pyrolytic conversion to useful products is still barely exploited, owing to limited knowledge of its potential. Studies have shown that agricultural residues can vary in composition based on regional cultivation patterns (Rossberg *et al*., 2015), and different varieties of groundnuts, coffee and rice are currently being cultivated. The rightful varieties and optimal compositional qualities of shells and husks for effective pyrolysis have not yet been established for high biofuel yields.

Fossil fuels are non-renewable, emit carbon dioxide and other harmful air pollutants when burned. These emissions lead to a wide range of negative public health and environmental effects that are borne at local, regional, national and global levels; of the many environmental and public health risks associated with burning fossil fuels, the most serious in terms of its universal and potentially irreversible consequences is global warming, and yet there is an abundance of agricultural wastes for an alternative source of renewable and green energy. Omulo *et al.*, 2018, optimized slow pyrolysis of banana peels wastes using response surface methodology, and focused on increasing the yield of banana peels vinegar, tar and biochar as bio-infrastructure products, the physicochemical characteristics of other available lignocellulosic biomass such as groundnut shells, coffee and rice husks have not yet been considered for optimization. The present study therefore sought to use groundnut shells, coffee and rice husks as feed stocks for intermediate pyrolysis to produce biosynthetic gas and biochar and to optimize the physico-chemical parameters that affect biosynthetic gas and biochar yields for maximum output.

### 1.3 Objectives of the study

The general objective of the study was to optimize the biosynthetic gas and biochar yields by varying the physico-chemical parameters of selected agricultural wastes. The Specific objectives were to;

1. Determine the content of moisture, ash, volatile matter, extractable matter, hemicellulose, lignin and cellulose in groundnut shells, coffee and rice husks.
2. Establish optimal pyrolysis physicochemical parameters of the selected agricultural wastes for high biochar and biosynthetic gas yields.

## 1.4 Research questions

1. What is the moisture, ash, volatile matter, extractable matter, hemicellulose, lignin and cellulose content of groundnut shells, rice and coffee husks?
2. What are the optimal particle sizes, moisture and cellulose contents of groundnut shell, rice and coffee husks that can produce high yields of biosynthetic gas and biochar?

## 1.5 Scope

The main focus of this study was to optimize biosynthetic gas and biochar yields by varying particle size, cellulose and moisture content using selected agricultural wastes.

Purposive samples of groundnut shells (*Igola 1*) were obtained from Ngora district in the Eastern region of Uganda; coordinates; 01 27 20N, 33 46 41E (Latitude: 1.4555; Longitude: 33.7780), upland rice and Arabica coffee husks were collected from Mbale District (01 04 50N, 34 10 30E). Determination of moisture, ash, volatile matter, extractable matter, hemicellulose, lignin and cellulose content of groundnut shells, rice and coffee husks was carried out, and then they were pyrolyzed to produce biosynthetic gas and biochar in the chemistry laboratory at Kyambogo University. Characterization of biomass lasted for about two and half months, and the subsequent pyrolysis experiments lasted for about three months.

## 1.6 Justification

The industrialized countries today are faced with a big challenge of increasing pollutant emissions as well as meeting the growing energy needs worldwide. The increasing demand for energy tied with the need to minimize the greenhouse gas emissions and the menace of reducing oil reserves has brought into focus the potential use of biomass as a renewable energy source. There is a marked abundance of agricultural waste such as groundnut shells, rice and coffee husks generated mostly from the rural areas of Uganda, and now even accumulating in urban centres owing to the transportation of agricultural produce to urban markets mostly in an unprocessed form.

All fossil fuels are not renewable and emit carbon dioxide, nitrogen dioxide, sulphur dioxide and other harmful air pollutants when burned. These emissions create a wide range of negative public health and environmental effects such as reducing visibility due to formation of fog. These effects are borne at local, regional, national and global levels; of the many environmental and public health risks associated with burning fossil fuels, the most serious in terms of its universal and potentially irreversible consequences is global warming, and yet there is an abundance of agricultural wastes for an alternative source of renewable and green energy.

These problems resulting from the combustion of fossil fuels have a possibility of being alleviated by alternative conversion of agricultural wastes to more useful and environmentally friendly fuels such as biosynthetic gas, biochar and bio-oil via green technologies such as pyrolysis. Consequently, this would greatly lower air and soil pollution loads caused by the careless disposal methods currently used in rural homesteads. Groundnut shells, coffee and rice husks have also generally been found to constitute very significant levels of cellulosic and lignocellulosic polymers that have a high potential of being depolymerized via pyrolysis to more useful lower molecular weight fractions such as biochar and biosynthetic gas which can be a source of biofuel and also chemical feed stocks.

## 1.7 Significance of the study

The findings of this study could be used to;

1. Provide the potential alternative uses of the abundant and locally available agricultural waste such as groundnut shells, coffee and rice husks as a feed stock for pyrolysis and subsequent production of biofuels and chemical feed stocks that could offer a cheaper and abundant supplement to Uganda’s fuel and chemical needs.

2. Provide base line data on some of the abundant under-utilized agricultural wastes.
3. Reduce Uganda's air pollution load as well as lower global emission of greenhouse gases due to combustion of fossil fuels.

### 1.8 Definition of terms

**Pyrolysis**: The thermal degradation of biomass at temperatures between 400℃ and 900℃ in the absence of oxygen or other reagents, which results in the production of biochar (solid), bio-oil (liquid), and biosynthetic gas products.

**Extractable matter**: Also known as extractives; a complex and non-uniform mixture of compounds such as non-structural sugars, amino acids, lipids, salts, waxes, terpenes, flavonoids, sterols, and chlorophyll, all with different chemical properties.

**Fast pyrolysis**: Is a high-temperature pyrolysis process in which biomass is rapidly heated in the absence of oxygen at 1000 - 10,000℃/s to a temperature around 650℃ - 1,000℃ depending on which products are desired and then the product gases are quickly removed and quenched ($t < 2$ s)

**Slow pyrolysis**: A pyrolysis process that utilizes low temperatures of around 400℃ over a long period of time to maximize biochar formation through carbonization.

**Volatile matter**: It is termed as the weight loss due to heating of 1 g of biomass at 925 ± 5℃ in a furnace for 7 minutes.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Fuel characterization of agricultural waste.

Agricultural wastes comprise of animal waste, food processing waste, crop waste (groundnut shells, coffee and rice husks, corn stalks, sugarcane bagasse, drops and culls from fruits and vegetables) and others. Many of these agricultural wastes are still largely under-utilized, and left to rot or openly burned in the field, especially in developing countries. In Kampala city alone, over 1000 megatons of these wastes accumulate daily and only about 30% are removed and dumped into dump fills like that at Kitezi in Kawempe division (Sabiiti, 2011).

The availability of large amounts of agricultural residues presents Uganda with a sustainable energy source that could contribute to solving the country's present energy needs. This in turn could impact positively on the country's economy, bringing about growth and development hence improving the quality of life (Okure *et al*., 2006).

Due to the diverse nature of biomass materials, their properties widely range and exhibit different behaviors in thermal processes. The most important properties that provide information about a fuel are calorific values, ash content, proximate (moisture, ash, volatile and fixed carbon content), and ultimate analysis (C, H, N, S and O composition) (Miranda *et al*., 2012).

### 2.1.1 Moisture content.

Maduako *et al*. (2005), reported a moisture content average of 11.3% from the shells of three different varieties of groundnut shells that were analyzed.

Normally, residual biomass has a high moisture content (over 100% on a dry basis), so it requires prior conditioning for subsequent energy purposes. The peanut shell has a very low moisture content (5.79%) wet basis, which is a great advantage since it is not necessary to dry it for energy purposes

(Perea-Moreno *et al*., 2018). Mbugua *et al*. (2014), reported moisture content for coffee husks at an average of 9.96%.

### 2.1.2 Ash content.

Ash content is the noncombustible residue left after fuel is burnt. It represents the bulk mineral matter after carbon, oxygen, sulphur and water have been driven off during combustion (Mbugua *et al*., 2014). The average ash content in the peanut shell was 4.26% dry basis (Perea-Moreno *et al*., 2018). On the other hand, Mbugua *et al*. (2014) reported an ash content for coffee husks of 5.47%.

### 2.1.3 Volatile matter

Mbugua *et al*. (2014) determined volatile matter in coffee husks by heating the samples out of contact with air in a furnace to 900°C ± 10°C for seven minutes. The percentage mass of volatile matter was calculated from the loss in mass of the sample after reducing the loss in mass due to moisture and it was at an average of 80.9%. Perea-Moreno *et al*. (2018), reported volatile matter content of pea nut shells at an average of 84.9% dry basis. Mansaray *et al*. (1997), reported that the volatile matter content in different rice husk varieties ranged from 63.00% to 70.20%.

Table 2.1: Physical-chemical characteristics of some biomass materials grown in Brazil

Ultimate Analysis

(wt.% on wet basis) Compositional Analysis

| **Biomass** | **Moisture (%)** | **Ash (%)** | **VM+FC (%)** |
|---|---|---|---|
| Coffee husk (Arabica) | 8.44 | 7.40 | 82.54 |
| Groundnut shell (IAC) | 7.98 | 12.80 | 79.10 |
| Rice husk (Low land-IR8) | 8.19 | 29.53 | 61.68 |

VM-Volatile matter, FC-Fixed carbon, AIC- Agronomic Institute of Campinas.

Source; (Braz *et al*., 2014)

Table 2.1 shows some of the compositions of different agricultural residues cultivated in brazil, the moisture content was essentially similar in all biomass analyzed, and ash content was very prominent in rice husk.

### 2.1.4 Extractives, lignin, cellulose and hemicellulose.

Biomass is a complex solid material constructed from oxygen-containing organic polymers produced by natural processes. The major structural chemical components with high molar masses are carbohydrate polymers and oligomers (65-75%) and lignin (18-35%). The major constituents are; cellulose (a polymer glucosan), hemicelluloses (which are also called polyose), lignin, organic extractives and inorganic minerals (Miranda *et al*., 2012). In a study by Sun *et al*. (2002), lignocellulose was found to be the main component of groundnut shells, with cellulose content ranging from 28 to 36%, hemicellulose ranging from 23 to 28% and lignin ranging from 12 to 16%.

#### 2.1.4.1 Extractives

It has long been known that removal of extractives prior to analysis improved the accuracy of the Klason lignin assay and structural carbohydrates. The technical report by National Renewable Energy Laboratory (USA) 2008, also recommended the use of extracted biomass for carbohydrates and lignin analysis. Omission of this extraction step resulted in a bias of structural carbohydrates and lignin levels (Kuchelmeister *et al*., 2015). This implies that biomass extraction is a necessary step in order to obtain accurate biomass compositional analysis data.

A standard analytical procedure for determination of extractives in biomass was developed by Sluiter *et al*. (2008b), where replicate tests for wheat straw gave a standard deviation of 0.2% and a percentage variation coefficient of 1.6% while Monterey pine gave a standard deviation of 0.2% and a percentage variation coefficient of 8.0%. It was further stated that prolonged heating of the extractive residue may bias the reported results to be low because of evaporation of semi-volatile constituents, while insufficient heating or use of inadequate vacuum may bias the results to be high due to incomplete removal of solvent.

The results obtained from a small-scale method for the extraction of a range of feedstock samples by Kuchelmeister *et al.* (2015), comprising herbaceous, hard, and soft wood, were in the range of 4.3 to 19.9% and were comparable to those obtained from a conventional method using accelerated solvent extraction (ASE), and the manual method was highly reproducible (0.1 – 1.6% relative standard deviation, n = 5).

#### 2.1.4.2 Hemicellulose, cellulose and lignin composition in biomass.

Numerous works deal with the use of thermogravimetric analysis (TGA) of plant biomass for determining thermal decomposition mechanisms. The use of TGA can be coupled to a spectrometer for improving the understanding of the thermal decomposition mechanisms and to estimate the amounts of biosynthetic gas produced during the pyrolytic process. Thermogravimetric analysis can quantitatively resolve complex mixtures because of the characteristic thermal decomposition temperature of each component. It is well established for instance that the pyrolytic decomposition of woody plant tissues in inert atmospheres occurs at mild temperatures for hemicelluloses (250℃ - 300℃) followed by cellulose (300℃ - 350℃) and finally lignin (300℃ - 500℃). Moreover, the combination of TGA and differential thermogravimetric analyses (DTG) allows obtaining the lignin content and particularly its influence during the combustion process. Finally, cellulose and lignin contents of pulp and paper have been determined by TGA especially in the description of the biomass pyrolysis leading to high errors on hemicelluloses contents. In view of these studies, TGA turns out to be a powerful tool for these analytical purposes (Carrier *et al*., 2011). Gouvea *et al*. (2009) reported an average cellulose content of 43% in coffee husks analyzed using TGA.

## 2.2 Conversion of biomass into energy and higher value products

Thermochemical conversion techniques have been demonstrated to be a feasible method for conversion of biomass to liquid fuels, including via pyrolysis of biomass in an induction heater. Operating parameters for pyrolysis, a process performed at atmospheric pressure that yields a liquid fuel directly (as opposed to gasification), range from 300 to 700°C and residence times of less than two seconds. The major advantage over gasification and hydrothermal liquefaction is the direct production of liquid fuels and the lack of costly high-pressure system, respectively, thus simplifying the reactor design.

Aguilar *et al*. (2015) studied the conversion of Chinese tallow tree and energy cane of different particle sizes to bio-oil via pyrolysis at different particle sizes. The results indicated that the range from 0.5 – 1.4 mm is a better range for optimizing bio-oil production while keeping water content low, thus when combined with proper upgrading and refining techniques, pyrolytic bio-oil has the potential to partially alleviate current petroleum oil and energy demands.

There are several routes of biomass conversion focusing on the generation of electrical/heat energy, transport fuel and chemical feedstock. To select a specific conversion process, several factors should be taken into consideration and the chemical and physical characteristics of the fuel are an important aspect because they can influence the performance of a specific fuel in a process. For example, ash content and composition is an important parameter in thermal conversion, because it can impact the operational system leading to the formation of slag, reducing the efficiency of the process, and influencing the economic aspects as a whole (McKendry, 2002).

Biomass can be converted into useful biofuels and biochemicals via biomass upgrading and biorefinery technologies. There are several thermo-chemical routes for biomass-based energy production, such as direct combustion, liquefaction, pyrolysis, supercritical water extraction, gasification, air–steam gasification and so on. The lignocellulosic biomass occurs naturally and includes materials such as grasses, forest cover, bushes, trees, industrial and domestic waste such as sewage sludge. These materials are cheap and highly abundant in tropical countries like Uganda. Pyrolysis of biomass materials has the advantage of low capital investment costs. The agricultural wastes usually take the form of crop residues (residual stalks, straw, leaves, roots, husks, shells and many others) and animal waste (manures) and are widely available, renewable and virtually free; hence they can be an important resource. They can be converted into heat, steam, charcoal, methanol, ethanol, bio diesel as well as raw materials (animal feed, composting, energy and biogas construction). However, many of the agricultural wastes are still largely under-utilized, and are left to rot or openly burned in the field, especially in developing countries (Sabiiti, 2011).

### 2.2.1 Pyrolysis of biomass

Pyrolysis, an efficient and eco-friendly process, is a feasible alternative for the production of fuels, chemicals, and hydrogen from biomasses and waste polymers. Pyrolysis methods can be divided into slow and fast pyrolysis. Slow pyrolysis involves slow heating rates of 0.1 – 1℃/s, a residence time varying from minutes to hours and a temperature range of 400 – 600℃. Slow pyrolysis has been used to produce methanol, but also results in the formation of large amounts of side products such as char, gas, and low-quality liquid. In contrast, fast pyrolysis rapidly heats samples to temperatures ranging from around 600℃ to 1000℃ with a heating rate of 10 – 1000℃/s in a non-oxidizing environment during a short residence time. Low temperatures, together with long vapor residence times support charcoal yields. High temperatures and long residence times favor biomass conversion to gas, whereas moderate temperatures and short vapor residence time are favorable for producing liquids. The yield is usually three products, but the quantities can be varied over a wide range by adjusting the parameters of the process (Zhang *et al*., 2018).

Table 2.2 shows product distribution obtained from different modes of pyrolysis, showing the considerable flexibility achievable by changing process conditions.

Table 2.2: Product distributions from different pyrolysis modes.

| Mode | Conditions | Liquid | Solid | Gas |
|---|---|---|---|---|
| Fast | 500°C, hot vapour residence time of 1 s | 75% | 12% char | 13% |
| Intermediate | 500°C, hot vapour residence time 10 - 30 s | 50% in 2 phases | 25% char | 25% |
| Carbonisation (slow) | 400°C, vapour residence for hours/days | 30% | 35% char | 35% |
| Gasification | 750 - 900°C temperature. | 5% | 10% char | 85% |
| Torrefaction (slow) | 290°C, solids residence time between 10 to 60 minutes | 0% except if condensed, then up to 5% | 80% solid | 20% |

Modified Table from Bridgwater (2007).

#### 2.2.1.1 Slow pyrolysis

Slow pyrolysis yields good quality charcoal using low temperature and low heating rates. The vapor residence time can be around 5 – 30 minutes in this process. The volatile organic fractions present in vapor phase continue to react with each other to yield char and some liquid fractions. The quality of bio-oil produced in this process is very low. Longer residence time initiates further cracking hence reducing the yield of bio-oil. The process suffers from low heat transfer values with long retention time leading to enhancement of the expenditure by high input of energy (Zaman *et al.*, 2017).

Biomass pyrolysis products are a complex combination of the products from the individual pyrolysis of cellulose, hemicellulose, lignin and extractives; each component has its own kinetic characteristics. In addition, secondary reaction products result from cross-reactions of primary pyrolysis products and reactions between pyrolysis products and the original feedstock molecules (Mohan *et al.*, 2006).

### 2.2.1.2 Fast pyrolysis

A study by Mohan *et al.* (2006) on fast pyrolysis of wood produced 60 - 75 wt % of liquid bio-oil, 15 - 25 wt % of solid char, and 10-20 wt % of non-condensable gases. It was further stated that depending on the feedstock used, no waste was generated, because the bio-oil and solid char were each used as fuel and the gas too could be recycled into the process. The process used much faster heating rates than traditional pyrolysis of about 10℃/second, and was carefully controlled to give high liquid yields.

### 2.2.2 Effect of particle size, moisture and cellulose content of feedstock on yields

The effects of important parameters such as biomass particle size, shape, composition, heating rate, and residence time on the kinetics of devolatilization and bio-oil composition need to be understood thoroughly in order to successfully scale up the process (Suriapparao *et al*., 2018).

Septien *et al*. (2012) worked on the effect of particle size and temperature on fast pyrolysis and results showed that a high tar yield occurred at a low temperature of 500°C. Particle size ranging from 0.35 mm to 0.80 mm had no effect on the products at high temperatures greater than 1000℃, but low temperatures affected tar yields by up to 75 wt.% of the initial biomass. However, at a high temperature, gas yield increased to the detriment of the tar yield, but in all cases, the char yield remained very low.

A study by Aguilar *et al*. (2015), quantified the product yields on weight basis of initial biomass weight. For the energy cane biomass, liquid yield slightly increased as the particle size increased from the range 0 – 0.5 mm to a range of 0.5 – 1.4 mm with a corresponding decrease in gas and char yields. Further increase in the particle size did not significantly change the liquid yield. The highest yield achieved was 48% for particle size range of 0.5 – 1.4 mm.

This observation could be linked to the possibility that at smaller particle sizes (< 0.5 mm); the heat transfer rate is high causing high overall temperatures. This may result in a more thorough breakdown of biomass and localized superheating of biomass causing fractionation of biomass to form non-condensable gases such as CO and $CO_2$ and decreasing liquid yield. As the particle size increases, the heat transfer rate decreases, hence reducing the effect of local superheating and increases the oil yield. However, particle sizes that are too large may also result in temperature gradient within the particle which may cause increased char yield and lower liquid yield.

Presence of water in pyrolysis reaction results from two main reaction mechanisms; dehydration of biomass structure and inter- or intra- particle secondary cracking of biomass. The dehydration of biomass has been determined to be independent of the reaction temperature and particle size as it can also occur at temperatures as low as 350℃ throughout the particle size ranges. However, secondary cracking reactions can occur for smaller particle sizes (< 0.5 mm) (Aguilar *et al*., 2015). In the study by Gani *et al*. (2007), it was concluded that for the biomass with high cellulose content, the pyrolysis rate became fast. While, the biomass with high lignin content gave slow pyrolysis rates. The cellulose and lignin content in the biomasses were some of the important parameters to evaluate the pyrolysis characteristics. The combustion characteristics for the actual biomass depends on the char morphology produced.

Pyrolysis of mixed wood sawdust of eight different particle sizes (26.5 – 925 µm) was conducted at nine different heating rates (0.5 – 100°C minute$^{-1}$) in a thermogravimetric analyzer, and at fast heating rates (~10,000°C s$^{-1}$) in an analytical pyrolyzer coupled with gas chromatograph/mass spectrometer by Suriapparao *et al*. (2018) and the apparent activation energies ($E_\alpha$) evaluated by iso-conversional Friedman method in the very slow (0.5 – 3°C min$^{-1}$), slow (5 – 20°C min$^{-1}$) and medium heating rate regimes (50 – 100°C min$^{-1}$) were 153 – 203, 174 – 251 and 286 – 380 kJ mol$^{-1}$, respectively. The yield of phenolics and linear hydrocarbons decreased, while the production of gases like CO and $CO_2$ increased with particle size during fast pyrolysis. High yield of aromatics was obtained with medium sized particles (362.5, 512.5 μm). This study demonstrated that $E_\alpha$ decreases and increases with particle size in the very slow and slow heating regimes, respectively, which is attributed to the effect of particle shape that induces mass transfer limitations in the transport of volatiles, and intraparticle thermal gradients that induce tar decomposition reactions.

A study by Demirbas (2004), on the effects of temperature and particle sizes of 0.5 – 2.2mm on biochar yield from pyrolysis of agricultural residues reported that the biochar yield increased with increasing particle size of the sample. A high temperature and small particle size increase the heating rate resulting in a decreased biochar yield.

### 2.3 Improvement of pyrolysis products

Many approaches have been devised to improve the quality of fast pyrolysis products. Among which is the pre-treatment methods to reduce the undesirable components of biomass before eventual pyrolysis and these include; hydro-processing, demineralization and torrefaction, hydro-treatment has been found to increase yield but the major problems are catalyst fouling and pugging (Elliott *et al*., 2015).

A study by Yang *et al*. (2014) on steam in the catalytic fast pyrolysis of cellulose showed that steam caused de-alumination; loss of total acidity; increased zeolite crystal size; and agglomeration of particles. This resulted in low yields for aromatics, biochar and coke; and high yield of methane and other unidentified products. In addition, steam co-feeding was also found to lower aromatic yields; biochar; increased yields of carbon monoxide and methane; but no change in overall yields of carbon monoxide and olefins.

The pyrolysis temperature has an important impact on the yield and composition of bio-oil, biochar, and biosynthetic gas. Biomass particle size has a significant effect on the water content of bio-oil. It is interesting to note that the temperature for maximum bio-oil yield, between 450 and 470°C, resulted in an oil with the highest content of oligomers and, consequently, with the highest viscosity. Such observations suggest that the conventional viewpoint of pyrolyzing biomass at temperatures over 400°C to maximize bio-oil yield needs to be re-evaluated considering the final use of the produced bio-oil. The increase in bio-oil yield with increasing temperature from 350 to 500°C was mainly due to the increase in the production of lignin-derived oligomers insoluble in water but soluble in $CH_2Cl_2$ (Garcia-Perez *et al*., 2008).

It is possible to have some influence on the bio-oil and biochar produced from pyrolysis reactions by manipulation of the particle size of feedstock biomasses in pyrolysis reactions. These manipulations can be useful in optimizing the pyrolysis process for larger or commercial grade pyrolysis for bio-oil and biochar production, especially when used in unison with temperature optimization and upgrading techniques to reduce cost, simplifying processing, and create high value products (Aguilar *et al*., 2015).

### 2.3.1 Preparation of biomass for pyrolysis

It is reported that pre-treatment of biomass before pyrolysis will produce high quality products (Isahak *et al.*, 2012). Hydrolysis is carried out under acidic, basic or sequential acid/base treatments at 25℃ or 122℃ at ambient pressure for 1 hour. The oxygen content is slightly reduced and influenced by oxygen-rich compounds removal during acid treatment method. The presence of inorganic species in bio-oil also greatly influences the subsequent use of bio-oil. For example, the alkali and alkaline earth metallic (AAEM) species are also associated with the accelerated ageing of bio-oil. Thus, contributing to modifications of the physical properties of bio-oil during storage. The pretreatment via water-washing can also remove more than 70% of AAEM species from the biomass substrate. However, it will change water content in the bio-oil product. On the other hand, the removal of remaining 25% of AAEM species by acid washing resulted is almost 5% reduction in the water content of bio-oil. The formation of water during biomass pyrolysis remains a topic of debate.

Particle size of biomass feedstock has a major influence on the heating rate of solid fuel, making it an important parameter controlling the rates of drying and primary pyrolysis and the extent to which these processes overlap during fuel decomposition. In fact, lower yields of liquids were reported when pyrolyzing large feedstock particles (Isahak *et al*., 2012).

A study by Aguilar *et al*. (2015) on the effect of biomass particle size showed a range of 0.5 to 1.4 mm to be better for optimizing bio-oil production while keeping water content low. Some studies had accounted for particle size as a variable in optimizing bio-oil production while others had used particle size as a way to isolate other variables, such as pellet compression effectiveness before pyrolysis.

### 2.4 Characterization and quantification of pyrolysis products

Pyrolysis oils are composed of differently sized molecules, which are derived primarily from the de-polymerization and de-fragmentation reactions of the components of the original biomass, mainly cellulose, hemicellulose and lignin (Mohan *et al*., 2006).

The process of pyrolysis of organic matter is very complex and consists of both simultaneous and successive reactions when organic material is heated in a non-reactive atmosphere. In this process; thermal decomposition of organic components in biomass starts at 350°C – 550°C and goes up to 700°C – 800°C in the absence of oxygen. The long chains of carbon, hydrogen and oxygen compounds in biomass break down into a variety of smaller molecules in the form of gases, aldehydes, ketones, carboxylic acids, furans, phenols, tars and solid charcoal under pyrolysis conditions. The rate and extent of decomposition of each of these components depends on the process parameters of the reactor such as temperature, biomass heating rate, pressure, reactor configuration, feedstock and others (Jahirul *et al*., 2012).

Pyrolysis products have been analyzed in detail using a gas chromatograph equipped with a mass spectrometer (GC–MS) for analysis of tars, and a gas chromatograph equipped with a thermal conductivity detector (GC-TCD) for analysis of light and non-condensable gases. Differences between yields of light gas species were small between plant species. Composition of tar included aromatic compounds of 1 to 5 rings with very few attachments. The pyrolysis products observed at this temperature and heating rate appeared to have experienced secondary pyrolysis. The tar composition showed some large changes with plant species.

A study by Amini *et al*. (2019) compared the products from pyrolysis of fresh living vegetation and dried vegetation of the same plant species and showed differences in tar, biosynthetic gas, and biochar yields, but no major changes in the types of chemical compounds observed. This shows that moisture content affects gaseous and solid yields.

The quantification of acetic acid, the highest yielding condensable volatile product, can be used as an indicator of the number of acetyl groups in biomass (Nsaful *et al*., 2015).

Biochar properties are easiest to describe if char is treated as having two fractions: the carbon fraction and the inorganic ash fraction. The carbon fraction includes hydrogen, oxygen and other elements bonded to carbon and is the fraction most affected by reaction conditions. Reaction time, temperature and heating rate convert to some degree the mostly carbohydrate and organic components into the condensed aromatic structures characteristic of biochar. The inorganic ash fraction is the fraction most affected by feedstock properties. The reaction conditions have some effect on the ash properties and ash-to-carbon ratio of the biochar. However, overall mineral constituents in the biomass become concentrated in the ash (Brewer, 2012).

The second most common analysis and one that is critical to further characterizations is the measurement of carbon, hydrogen and nitrogen content, also known as elemental or CHN analysis. In this technique, a sample is combusted at very high temperatures with excess oxygen and the produced carbon, hydrogen and nitrogen species ($CO_2$, $H_2O$ and NO; respectively) are trapped and quantified. Results from this analysis are typically reported in terms of percent weight of a dry sample (Brewer, 2012).

A thermogravimetric analysis technique coupled to analysis of evolved gases was applied by Nsaful *et al*. (2015) in the measurement of biosynthetic gas, the chemical composition of condensable volatiles was correlated statistically with the original lignocellulose composition, using principal component analysis (PCA), a total of 15 to 19 wt% (dry weight) of biomass pyrolysis products were quantified by the method, with an average relative standard deviation of 6.4% on the high concentration of condensable volatiles yield.

A simple, low-cost, and robust method for determining gas volumes was also described by Brack *et al*. (2016) where the hydrogen generated from the reaction of solids with aqueous solutions was measured by channeling it through tubing into a water-filled inverted measuring cylinder, the water displaced from the measuring cylinder by the incoming gas was diverted to a beaker on a balance. In this study, it was adopted and modified to suit the pyrolysis process by using a graduated cylindrical tube that directly reads the volumes of water displaced instead of taking weights of brine water displaced. Salt was added in the displacement water to limit dissolution of the produced biosynthetic gas.

## 2.5 Optimization of fast pyrolysis yields

Studies have been conducted on the optimization of pyrolysis yields using operating conditions of temperature, pressure, heating rate and residence time for efficient pyrolysis of lignocellulose (Dhyani, 2018) and others have focused on thermal decomposition properties and conversion pathways of the various biomass components (Nsaful *et al*., 2015). No approach has been done that combines the use of moisture, particle size, and cellulose content to optimize biochar and biosynthetic gas yields.

A study conducted by Hodgson *et al*. (2016), identified that optimum process conditions in terms of both biochar yield and zinc adsorption performance were achieved from slow-pyrolysis at 300°C for 2 hours using a feedstock with average particle size of less than 1 mm. This implies that optimization is possible even at low temperatures of 300°C.

The effects of pyrolysis temperature, heating rate, particle size, holding time, and gas flow rates were investigated to optimize bio-oil yield from rice husk pyrolysis. Thermogravimetric analysis showed thermal degradation of hemicellulose, cellulose and lignin, and indicated faster decomposition of cellulose compared to lignin. The optimization process was carried out using central composite design (CCD) in response surface methodology (RSM) with Design Expert StatEase version 7.5.1 (USA). A two-level fractional factorial was initially carried out and followed by RSM. By utilizing response surface method, the four combined factors were investigated, analyzed and optimal conditions were obtained at pyrolysis temperature of 473.37℃, heating rate of 100℃/minute, particle size of 0.6 mm and holding time of 1 minute. Confirmation tests gave 48.30% and 47.80% of bio-oil yield compared to 48.10% of predicted value (Isa *et al*., 2011). These results showed that optimization of pyrolysis yields using rice husks is indeed a feasible process.

Another research by Flores *et al*. (2017), demonstrated the optimization and production of biochar from barley husk, corn cob, and century plant leaves via pyrolysis in a muffle furnace using Taguchi experimental design (L9) to conduct the experiments at different levels by altering four operating parameters; carbonization temperature (300 – 500°C), carbonization time (30 - 90 minutes), precursor mass (2 - 5 g) and $N_2$ flow rate (100 - 200 $cm^3$/minute). Results showed that the optimum conditions for maximum biochar yield are; carbonization temperature of 400°C, carbonization time of 30 minutes, precursor mass of 2 g, and $N_2$ flow rate of 150 $cm^3$/minute. The biochar samples produced under optimum conditions were characterized physically and chemically. Biochar yields of 19.75% for corn cob, 32.88% for barley husk, and 31.14% for agave leaves were reported. This implies that optimization of biochar yields from pyrolysis using other parameters is possible.

In conclusion, there are multiple factors that affect the yield of bio-oil, biochar and biosynthetic gas in the production process namely; biomass type, particle size of biomass, pyrolysis temperature, reactor efficiency, chemical composition of the biomass and initial moisture content. While some of these factors have been studied extensively for different biomass types, the effects of particle size, moisture content, lignin and cellulose content for groundnut shells, coffee and rice husks from Uganda have not been studied.

# CHAPTER THREE

# MATERIALS AND METHODS

This chapter considers analytical methods and equipment that were used in characterization, preparation of biomass samples for pyrolysis, the methods for pyrolysis, quantification of biosynthetic gas and biochar, and optimization of biosynthetic gas and biochar yields.

## 3.1 Materials

### 3.1.1 Reagents and solvents

Distilled water, NaOH pellets 95% assay $H_2SO_4$ acid 98% assay, Anhydrous $HNO_3$ acid 99.9% assay, HCl acid 35-38% assay, all of analytical grade, Organic solvents; Petroleum ether AR, Acetone AR, Absolute Ethanol AR and Methanol AR, all analytical grade reagents purchased from Labx Chemical Suppliers Uganda limited.

### 3.1.2 Equipment

Equipment that were used included a hot air oven DNO-30; Muffle furnace FHP-03; Electronic balance ML204 /01; Genesis UV visible spectrophotometer; Xinkyo Batch pyrolizer SK2-2-12TPA2, Oil, char and gas sample containers, ceramic crucibles and sealable Ziplock plastic bags; water bath HH-S8, Heating plate, PS-80 grinder, International standard test sieves; 3.35 mm, 2.36 mm, 0.71 mm, 1 mm, 0.3 mm and 0.425 mm mesh sizes, U-tube manometer(modified), rotary vane vacuum pump VP-125.

## 3.2 Methods

About 10 kg of groundnut shells *Igola 1* variety (Okello, 2010), were purposively sampled from several selected homesteads in Ngora district, as well as 5 kg of both upland rice and arabica coffee husks obtained from coffee and rice mills in Mbale district in September 2017 and were transported to Kyambogo University Chemistry laboratory and stored under ambient conditions. The sampled biomass was each subjected to preliminary analyses, which included; ultimate analysis, proximate and biochemical analyses summarized in the Table 3.1.

Table 3.1: Selected characterization parameters for biomass.

| **Parameter** | **Method** |
|---|---|
| Moisture Content/Total dry matter | NREL/TP-510-42621 and ASTM E871 |
| Ash Content | ASTM D1102 |
| Volatile Matter | ASTM E872 |
| Extractives | NREL/TP-510-42619 |
| Hemicellulose | Modified from Ayeni *et al*. (2015) |
| Lignin (Acid soluble and insoluble) | Modified from Ayeni *et al*. (2015) |
| Cellulose | By difference (Ayeni *et al*. (2015)) |

### 3.2.1 Analytical methods

Most of the methods adopted in this work for characterization of biomass were those recommended by the Association of Official Analytical Chemists (AOAC 1980) and National Renewable Energy Laboratory (NREL) standard methods of analysis (2008).

### 3.2.2 Determination of moisture content and total solids

In oven drying methods, which are direct methods, each sample was heated under specified conditions, and the loss of weight was used to calculate the moisture content of the sample. The amount of moisture determined was highly dependent on the type of oven used, conditions within the oven, and the time and temperature of drying. The procedures describe the methods used to determine the quantity of solids and moisture present in a solid and slurry biomass sample.

In the present study, a convection oven drying procedure was applied and also intended for determination of the quantity of total solids remaining after 105℃ drying of a biomass sample. All analyses were performed in accordance with an appropriate laboratory specific Quality Assurance Plan (QAP) as follows;

Five clean ceramic crucibles were placed in an oven set at 105 ± 3℃ for four hours. They were then removed and cooled in a desiccator. Using gloves to handle the pre-dried crucibles, they were each weighed to the nearest 0.1 mg. Groundnut shells *(Igola-1)* were then thoroughly mixed and 2 g weighed to the nearest 0.1 mg, into each of the five crucibles separately to allow for replicate analysis. The samples were then placed into a Convection oven at 105 ± 3℃ for 4 hours, removed and then allowed to cool at room temperature in a desiccator. They were each re-weighed to the nearest 0.1 mg. After, they were placed back into the oven at 105 ± 3℃ and dried to a constant weight. The moisture content and total solids were then calculated using the following formulas;

$$\text{percent total solids} = \frac{(Weight\ of\ dry\ crucible + dry\ sample) - (Weight\ of\ dry\ crucible)}{Weight\ of\ sample\ as\ recieved} \times 100)$$

$$\text{percent moisture} = \left[100 - \left( \frac{(Weight\ of\ dry\ crucible + dry\ sample) - (Weight\ of\ dry\ crucible)}{Weight\ of\ sample\ as\ recieved} \times 100\right)\right]$$

Similar and replicate moisture analyses were carried out for coffee and rice husks and both moisture and total solids computed as weight percent, dry basis (Sluiter *et al*., 2008a).

### 3.2.3 Determination of ash content

The oven-dried samples each of 2 g biomass in five replicates were accurately weighed and placed in pre-dried crucibles of known weight. These were then ignited in a Muffle furnace and ashed for 6 hours at 600 ± 25°C. The crucibles containing ash were then removed, cooled in a desiccator; weighed and the ash determined in terms of oven-dry weight of the sample using the formula;

$$\text{percent ash} = \frac{(Weight\ of\ the\ crucible + Ash) - Weight\ of\ crucible}{ODW\ of\ the\ sample} \times 100$$

where ODW = Oven Dry Weight

$$\text{ODW} = \frac{Weight\ of\ air\ dry\ sample \times \%Total\ solids}{100}$$

The procedure for ash determination is substantially similar to ASTM standard method number E1755-01 “Standard Method for the Determination of Ash in Biomass”. This test method covers the determination of ash, expressed as the percentage of residue remaining after dry oxidation at 550 to 600℃.

### 3.2.4 Volatile matter

A 2 g sample was oven-dried and five replicates were heated at 600 ± 25℃ for six minutes and then at 900 ± 25℃ for another six minutes in pre-weighed open ceramic crucibles in a Muffle furnace. The amount of weight loss in the sample gave the volatile matter of each of the biomass samples, calculated as follows;

percent volatile matter = $[\frac{\text{Oven dry weight of sample} - \text{weight of residue}}{Oven\ dry\ weight\ of\ sample} \times 100]$.

### 3.2.5 Biochemical composition analysis.

The extractives; cellulose; hemicellulose and lignin content were determined using a method reported by Ayeni *et al*. (2015). Each of the three samples of pre-dried biomass was separately ground to a uniform particle size for the subsequent analyses.

### 3.2.6 Extractives

Methods for determination of extractives were based on a standard method (TAPPI T 264 cm-07) developed by the pulp and paper industry. Standard methods describing the preparation of extractive-free wood have been validated by the American Society for Testing and Materials (ASTM). One standard procedure (“ASTM D1105-96: preparation of extractive-free wood”) describes a 4-hour Soxhlet extraction with an ethanol-toluene mixture followed by a 4-hour ethanol extraction and a subsequent hot water extraction of the previously extracted and air-dried material for another 3 hours. A second standard method (“ASTM E1690-08: determination of ethanol extractives in biomass”) is a gravimetric determination of ethanol extractives in biomass after a 24-

hour exhaustive Soxhlet extraction. This procedure is suitable for agricultural residues like corn stover, wheat straw, and bagasse and many others (Kuchelmeister *et al*., 2015), and was applied with some modifications in the present study as follows;

Dried raw biomass (2.5 g) was placed onto pre-dried and weighed filter paper and loaded into the extraction thimble of the Soxhlet extractor. With this set up, 150 ml of acetone was used as solvent for extraction, it was chosen after conducting a series of comparative tests on a number of potential solvents such as petroleum ether, ethanol, acetone and petroleum spirit. The temperature and residence time for the boiling and rising stage was carefully adjusted to 70℃ and 25 minutes respectively, on the heating mantle for a 4-hour run period. After extraction, the sample was air dried at room temperature for a few minutes. Constant weight of the extracted material was achieved in a convection oven at 105℃. The percentage weight of the extractives content was evaluated as the difference in weight between the raw extractive-laden biomass and extractive-free biomass (Adeeyo *et al*., 2015). This was replicated five times for groundnut shells, rice and coffee husks separately, and calculated as;

$$\text{percent extractives} = \frac{Weight\ of\ the\ raw\ biomass - weight\ of\ extracted\ biomass}{Weight\ of\ raw\ biomass} \times 100$$

### 3.2.7 Hemicellulose

Using a method by Ayeni *et al*. (2015), extracted and dried biomass of 1 g was placed in a 250 ml conical flask and 150 ml of 0.5M NaOH was added. The mixture was boiled at about 100℃ for 3.5 hours while adding some distilled water to keep up the volume. It was filtered after cooling through vacuum filtration and washed to a neutral pH using distilled water. The residue was dried to a constant weight at 105℃ in a convection oven. The difference between the sample weight before and after was the hemicellulose content (%w/w) of dry biomass (Adeeyo *et al.,* 2015). This was replicated five times for the groundnut shells, rice and coffee husks.

percent hemicellulose = $\frac{Weight\ of\ extracted\ dried\ biomass - weight\ of\ treated\ biomass}{Weight\ of\ extracted\ dried\ biomass} \times 100$

### 3.2.8 Lignin

A method from Ayeni *et al*. (2015) was used, dried and extracted raw biomass of 0.3 g was weighed into glass boiling tubes and 3 ml of 72% $H_2SO_4$ acid was added to it. The sample was subjected to room temperature for 2 hours while carefully agitating at 30-minute intervals to enable complete hydrolysis. After initial hydrolysis, 84 ml of distilled water was added. The second step of hydrolysis was done in an autoclave for 1 hour at 121℃. The slurry was then cooled at room temperature. Hydrolysates were filtered through vacuum using a filtering crucible. The acid insoluble lignin was established by drying the residues at 105℃ and compensating for ash by incinerating the hydrolyzed samples at 575℃ in a Muffle furnace. The acid soluble lignin was determined by measuring absorbance of the acid hydrolyzed samples at 320 nm wavelength with a UV visible spectrophotometer (Genesis 10S). The lignin content was calculated as the sum of acid insoluble lignin and acid soluble lignin.

percent acid soluble lignin = $\frac{\text{Absorbance}}{\text{Molar absorptivity of acid soluble lignin}} \times 100$

percent acid insoluble lignin = $(\text{Weight of dry hydrolyzed residues after digestion} - \text{weight of ash}) \times 100$

### 3.2.9 Cellulose

The cellulose content (%w/w) was calculated by difference, taking extractives, hemicellulose, lignin, ash, and cellulose as the only components of the entire biomass (Adeeyo *et al*., 2015).

percent cellulose = $100 - \%\ lignin - \%\ hemicellulose - \%\ ash - \%\ extractives.$

### 3.3 Preparation of groundnut shells, coffee and rice husks for pyrolysis

Basing on the three optimization variables chosen for each of the three selected feedstocks, each material was separately ground and screened to three selected levels of particle size in the ranges of 3.35 mm – 2.36 mm; 2.36 mm – 1 mm; and 0.300 mm – 0.425 mm using three sets of two different standard sieves with the aim of obtaining average particle sizes of 2.855 mm, 1.68 mm and 0.3625 mm as high, mid and low, respectively. Cellulose content previously established for each kind of biomass was used as a basis for variation in each feedstock namely; the groundnut shells *(Igola 1* variety*)*, arabica coffee and upland rice husks. The moisture content was varied by conditioning each of the respective samples to three different levels of moisture composition chosen for optimization (high, mid and low), that is for the normal fresh samples, then subjected to half drying treatment and the bone-dry samples, respectively as shown in Table 3.2. Each sample of biomass was then crushed to three different categories of particle sizes using a grinder and subsequently screened with each of the three pairs of standard test sieves. Thus, all the samples subjected to pyrolysis had various compositions used as a means of obtaining optimum quantities of pyrolysis yields. This is shown in Tables 3.3 and 3.4. The time used for complete drying was halved in order to condition the moisture content, assuming uniformity in moisture loss during the drying process inside the convection oven.

Table 3.2: Design levels for moisture content.

| **Experimental Level** | **High** | **Mid** | **Low** |
|---|---|---|---|
| **Actual value/wt.%** | 11.75 | 5.88 | 0 |
| **Coded value** | 1.00 | 0.00 | - 1.00 |

Table 3.3: Design levels for particle size.

| Experimental Level | High | Mid | Low |
|---|---|---|---|
| **Mean particle size/mm** | 2.86 | 1.68 | 0.36 |
| **Coded value** | 1.00 | 0.00 | - 1.00 |

Table 3.4: Design levels for cellulose content

| Experimental Level | High | Mid | Low |
|---|---|---|---|
| **Average /wt.%** | 40.45 | 28.28 | 20.81 |
| **Coded value** | 1.00 | 0.00 | -1.00 |

Using Design Expert® Stat Ease software version 7.0.0, Response Surface Method (RSM)-Box Behnken design was chosen so as to determine the ideal process settings and to achieve optimal performance for the selected design parameters. Box Behnken design was chosen because it created designs with desirable statistical properties, and most importantly, it generated only a fraction of experimental runs required for its alternative 3-level factorial design, enabling to fit well within the time constraints of the entire data analysis process in the present study. All the factors used for RSM were quantitative and continuous variables. Within the goal of optimizing the process, the objective was to find a desirable surface in the design space, Box-Behnken initial designs were used to fit three levels of the chosen factors as low, mid and high, respectively, coded as -1, 0, and +1. Because there are only three levels, the quadratic model was deemed appropriate and satisfactory for the initial design. Considering biochar and biosynthetic gas as responses, and the mean values of all variables selected, a total number of 17 experimental runs were generated to fit the optimization as shown in the Tables 3.5 and 3.6.

Table 3.5: Design parameters.

| Factor | Name | Unit | Type | Low Actual | Mid Actual | High Actual | Low Coded | Mid Coded | High Coded |
|---|---|---|---|---|---|---|---|---|---|
| A | PS | mm | Numeric | 0.36 | 1.68 | 2.86 | -1.00 | 0.00 | 1.00 |
| B | MC | w% | Numeric | 0.00 | 5.88 | 11.75 | -1.00 | 0.00 | 1.00 |
| C | Cellulose | w% | Numeric | 20.81 | 28.28 | 40.45 | -1 | 0 | 1 |

PS-Particle size, MC-Moisture content.

Table 3.6: Experimental run sheet for actual factors.

| Std | Run | Particle size /mm | Moisture content /% | Cellulose content /% |
|---|---|---|---|---|
| 4 | 1 | 2.86 | 12.49 | 28.28 |
| 6 | 2 | 2.86 | 5.23 | 20.81 |
| 1 | 3 | 0.36 | 0.00 | 28.28 |
| 14 | 4 | 1.68 | 6.24 | 28.28 |
| 15 | 5 | 1.68 | 6.24 | 28.28 |
| 7 | 6 | 0.36 | 6.16 | 40.45 |
| 16 | 7 | 1.68 | 6.24 | 28.28 |
| 5 | 8 | 0.36 | 5.23 | 20.81 |
| 17 | 9 | 1.68 | 6.24 | 28.28 |
| 2 | 10 | 2.86 | 6.24 | 28.28 |
| 8 | 11 | 2.86 | 6.16 | 40.45 |
| 9 | 12 | 1.68 | 0.00 | 20.81 |
| 12 | 13 | 1.68 | 12.31 | 40.45 |
| 13 | 14 | 1.68 | 6.24 | 28.28 |
| 11 | 15 | 1.68 | 0.00 | 40.45 |
| 10 | 16 | 1.68 | 10.46 | 20.81 |
| 3 | 17 | 0.36 | 12.49 | 28.28 |

### 3.4 Pyrolysis

The method used for carrying out the pyrolysis was developed from the equipment operation manual for the tubular furnace pyrolizer used in this study with some minor modifications.

Each of the experimental runs were conducted by feeding 4 g of the conditioned sample into the tubular furnace of the pyrolizer, and the air within the glass tubular furnace pumped out using a rotary vane vacuum pump before completely closing the furnace taps to ensure no further infiltration of atmospheric air occurs. The conditions that were kept constant throughout the pyrolysis were; an average heating temperature rise of 1.5℃ per second, with average residence time of about 2.5 seconds for biosynthetic gas and 1 hour for biochar. The heating program was set to heat from around room temperature to 500℃ and automatically stopping the heating, for all samples. The outlet tap was opened to allow the gaseous vapors produced to pass through an airtight water cooled condenser with circulation temperatures of about 15℃ so as to trap mostly heavier condensable vapors consisting of components like organic acids, phenolics and furans and directly connected to the U-tube manometer so as to measure the total volume of the non-condensable gases produced such as CO, $CH_4$, $CO_2$, $H_2$ and light hydrocarbons by volume displacement. After the furnace being subsequently cooled, all the biochar remaining was then weighed; the non-condensable gases were quantified at room temperature by the displacement method using a U-tube manometer. All the responses were determined by taking direct measurements of volume and weight for non-condensable gas and biochar, respectively.

### 3.5 Data analysis

The results obtained under specific objective 1 were analyzed using Microsoft Excel 2016 software, and the entire design of experiments and optimization under specific objective 2 was done using Design-Expert® Stat Ease version 7.0.0 software.

# CHAPTER FOUR

# RESULTS AND DISCUSSION

This chapter contains all results obtained in the study for objectives one and two, with their discussions.

## 4.1 Results of proximate analysis

All the proximate analysis results obtained for groundnut shells, coffee and rice husks are as shown in Table 4.1.

Table 4.1: Total solids, moisture, ash and extractives for groundnut shell, rice and coffee husks

| **Dry basis (Mean value)** | **Total solids %** | **Moisture %** | **Ash %** | **Extractives %** | **Volatile matter %** |
|---|---|---|---|---|---|
| Groundnut shells | 87.51 ± 0.70 | 12.49 ± 0.70 | 3.64 ± 0.22 | 2.24 ± 0.35 | 96.53 ± 0.31 |
| Rice husk | 89.54 ± 0.18 | 10.46 ± 0.18 | 22.94 ± 0.75 | 3.44 ± 0.37 | 76.51 ± 0.88 |
| Coffee husks | 87.69 ± 0.51 | 12.31 ± 0.51 | 1.58 ± 0.43 | 1.22 ± 0.47 | 98.98 ± 1.45 |

Rice husks had the highest amount of ash content for all the biomass analyzed at 22.94 ± 0.75%, and consequently the lowest quantity of volatile matter, the high ash content can be attributed to the minerals present in the husk. Moisture and ash content are slightly comparable with those reported by Braz *et al*. (2014). The amount of moisture determined in this study was significant enough to support the optimization studies as the presence of moisture has been reported to greatly affect the yields of both biochar and biosynthetic gas. High moisture content lowers biomass ignition temperature (Demirbas, 2004), significantly resulting into more biochar yields and less biosynthetic gas. The extractives content was lowest in all the three materials analyzed as compared to other physicochemical characteristics, however the quantities of extractives was prominent in rice husk. The composition of extractives in mainly high molecular weight compounds that mainly constitute the condensable components of the pyrolysis yield, exclusive of secondary cracking reactions that take place in the pyrolysis reactor.

Coffee husks had the highest amount of volatile matter at 98.98 ± 1.45% compared to both rice husks and groundnut shells. The ash content of the coffee husks was the least amongst all the biomass samples analyzed. The moisture content in coffee husks was close to that observed for rice husks and groundnut shells in this study. The average ash content was lower than that determined by Mbugua *et al*. (2014) and Braz *et al*. (2014) in coffee husks, although the moisture content determined is comparable to that reported by Mbugua *et al*. (2014) also in coffee husk. The average levels of ash and moisture content were below the mean values reported by Perea-Moreno *et al*. (2018) and Maduako *et al*. (2005), although volatile matter content was higher than that reported by Perea-Moreno *et al*. (2018).

Therefore, on a comparative basis for the three different biomass materials analyzed, the average levels of volatile matter, moisture and total solids were found to be fairly equal. Rice husks gave the highest amount of extractable matter and ash content than all the three, followed by groundnut shells and finally coffee husks had the least. This trend is in agreement with that reported by Braz *et al*. (2014), Perea-Moreno *et al*. (2018) and Maduako *et al*. (2005) for rice husks, coffee husks and groundnut shells respectively. The comparison of three types of biomass analyzed is shown in the Figure 4.1;

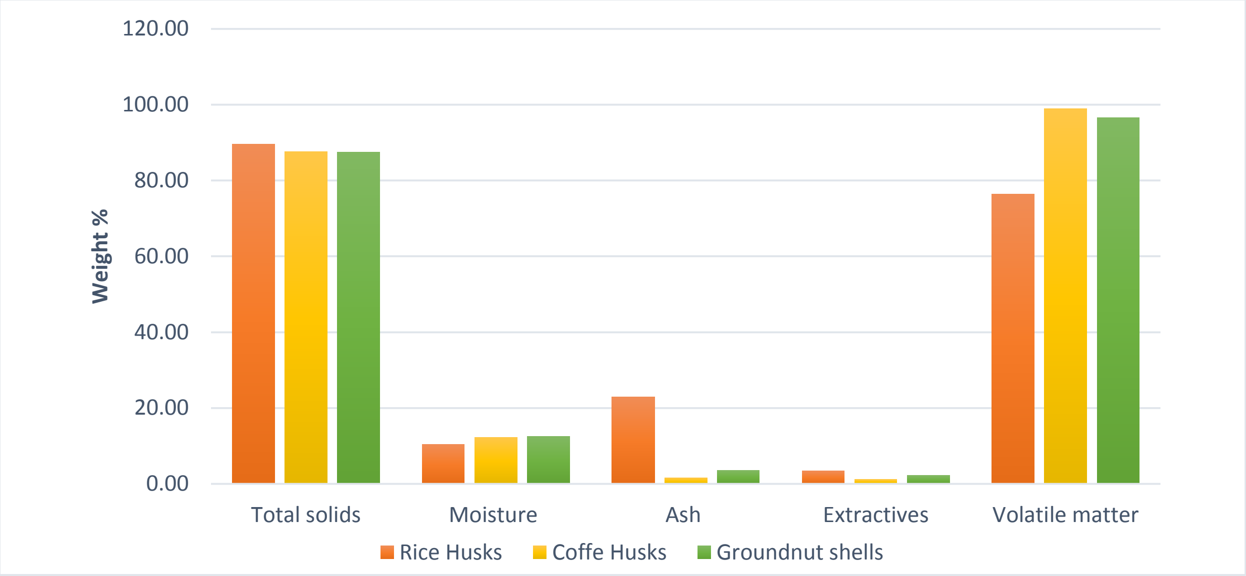

Figure 4.1: Mean values of total solids, moisture, ash, extractives and volatile matter.

### 4.2 Results of biochemical analysis of groundnut shells, coffee and rice husks

The biomass was subjected to analysis of lignin, hemicellulose and cellulose content and the results are presented in the Table 4.2.

Table 4.2: Mean values of hemicellulose, lignin and cellulose for groundnut shells, coffee and rice husks.

| | Rice Husk | Coffee Husk | Groundnut shell |
|---|---|---|---|
| Hemicellulose/w% | 57.49 ± 2.15 | 20.62 ± 2.02 | 23.35 ± 2.05 |
| Lignin/w% | 36.93 ± 2.89 | 36.13 ± 2.27 | 42.49 ± 4.03 |
| Cellulose/w% | 20.81 ± 3.61 | 40.45 ± 1.58 | 28.28 ± 4.45 |

The highest amount of hemicellulose was found in rice husks, followed by groundnut shell, and then least in coffee husk. The composition of hemicellulose and cellulose was in agreement with that reported in literature by Collazo-Bigliardi *et al*. (2018) and Gouvea *et al*. (2009). The amount of hemicellulose and cellulose in groundnut shell was below that reported by Gajula *et al*. (2011).

The composition of lignin was found to be almost equal for both rice and coffee husks, while the amount of lignin was highest in groundnut shell compared to rice and coffee husks. The lignin content for coffee husk was below that established by Veiga *et al*. (2017). A comparison for three types of biomass analyzed is shown in Figure 4.2

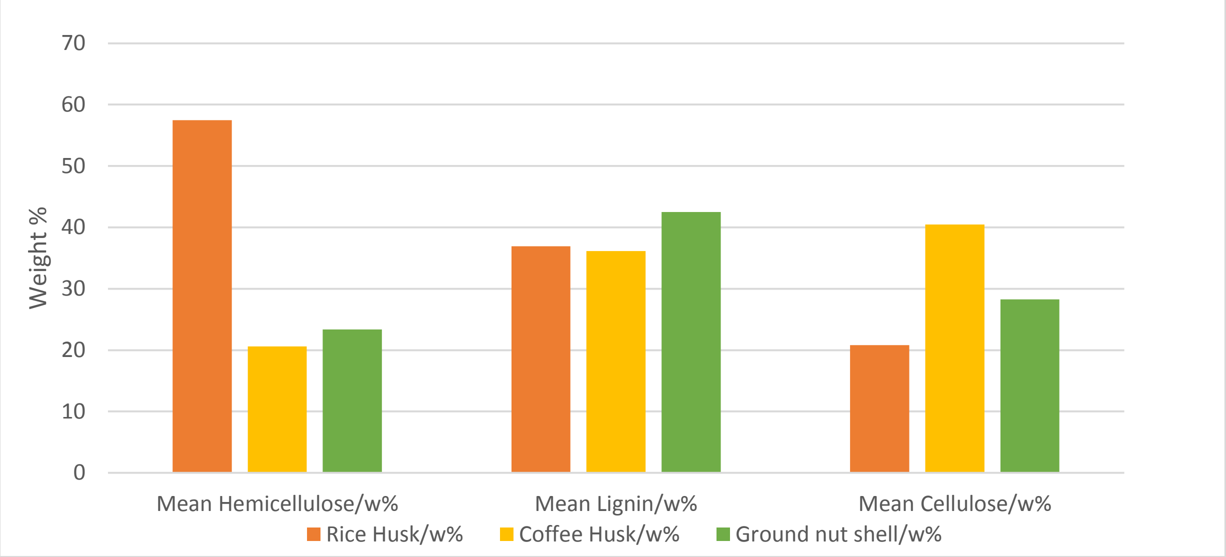

Figure 4.2: Mean values of hemicellulose, lignin and cellulose.

### 4.3 Results for pyrolysis of groundnut shells, coffee and rice husks

The experimental results for 17 runs conducted are shown in Table 4.3

Table 4.3: Actual design variables and the yields of biochar and biosynthetic gas.

|  |  | Factor 1 | Factor 2 | Factor 3 | Response 1 | Response 2 |
|---|---|---|---|---|---|---|
| **Expt.** | **Run** | **A: Particle size** | **B: Moisture content** | **C: Cellulose** | **Biochar** | **Biosynthetic gas** |
|  |  | mm | w% | w% | g | cm$^3$ |
| 1 | 3 | 0.36 | 0.00 | 28.28 | 1.44 | 40.10 |
| 2 | 10 | 2.86 | 6.24 | 28.28 | 1.37 | 40.10 |
| 3 | 17 | 0.36 | 12.49 | 28.28 | 1.38 | 17.40 |
| 4 | 1 | 2.86 | 12.49 | 28.28 | 1.28 | 17.70 |
| 5 | 8 | 0.36 | 5.23 | 20.81 | 0.19 | 2.70 |
| 6 | 2 | 2.86 | 5.23 | 20.81 | 1.54 | 3.50 |
| 7 | 6 | 0.36 | 6.16 | 40.45 | 0.82 | 10.50 |
| 8 | 11 | 2.86 | 6.16 | 40.45 | 1.07 | 10.50 |
| 9 | 12 | 1.68 | 0.00 | 20.81 | 0.54 | 3.50 |
| 10 | 16 | 1.68 | 10.46 | 20.81 | 1.27 | 2.60 |
| 11 | 15 | 1.68 | 0.00 | 40.45 | 1.11 | 13.30 |
| 12 | 13 | 1.68 | 12.31 | 40.45 | 0.83 | 2.80 |
| 13 | 14 | 1.68 | 6.24 | 28.28 | 1.35 | 21.60 |
| 14 | 4 | 1.68 | 6.24 | 28.28 | 1.37 | 29.20 |
| 15 | 5 | 1.68 | 6.24 | 28.28 | 1.33 | 16.40 |
| 16 | 7 | 1.68 | 6.24 | 28.28 | 1.32 | 30.70 |
| 17 | 9 | 1.68 | 6.24 | 28.28 | 1.32 | 22.30 |

The highest biochar yield from experiment 6, run 2 as shown in Table 4.3 may be attributed to high composition of ash in the rice husk reported in Table 4.2, since ash is not easily volatilized at the pyrolysis temperature used. The largest amount of biosynthetic gas was obtained from the pyrolysis of groundnut shells at particle sizes of 0.36 mm and 2.86 mm for both the least and medium moisture contents of the feed stock, respectively.

### 4.4 Statistical analysis of pyrolysis results

The two responses were analyzed using Design Expert StatEase software. The fit summaries for both biochar and biosynthetic gas are as shown in Tables 4.4 to 4.5 and 4.6 to 4.7, respectively.

Table 4.4: Model fit summary for biochar.

**Response 1: Biochar Transform: None**

**Sequential Model Sum of Squares [Type I]**

| Source | Sum of Squares | df | Mean Square | F Value | p-value Prob > F | |
|---|---|---|---|---|---|---|
| Mean vs Total | 22.40 | 1 | 22.40 | | | Suggested |
| Linear vs Mean | 0.29 | 3 | 0.10 | 0.71 | 0.5638 | |
| 2FI vs Linear | 0.48 | 3 | 0.16 | 1.23 | 0.3498 | |
| Quadratic vs 2FI | 0.69 | 3 | 0.23 | 2.69 | 0.1266 | Suggested |
| Cubic vs Quadratic | 0.60 | 4 | 0.15 | 284.43 | 0.0003 | Aliased |
| Residual | 0.00 | 3 | 0.00 | | | |
| Total | 24.46 | 17 | 1.44 | | | |
| | Std. Dev. | R-Squared | Adjusted R-Squared | Predicted R-Squared | PRESS | |
| Linear | 0.37 | 0.14 | - 0.06 | - 0.73 | 3.56 | |
| 2FI | 0.36 | 0.37 | 0.00 | - 2.47 | 7.16 | |
| Quadratic | 0.29 | 0.71 | 0.33 | 8.03 | 18.59 | Suggested |
| Cubic | 0.02 | 1.00 | 1.00 | | + | |

df – Degrees of freedom

From the sequential model sum of squares [Type I] in Table 4.4, the highest order polynomial was selected where the additional terms were significant and the model was not aliased. Focus was given on the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared" which favored both the quadratic and cubic models for preliminary tests on biochar data. From the lack of fit tests, the quadratic model had an insignificant lack-of-fit as shown in Table 4.5

Table 4.5: Lack of fit tests for biochar

| Source | Sum of Squares | df | Mean Square | F Value | p-value Prob > F | |
|---|---|---|---|---|---|---|
| Linear | 1.77 | 10 | 0.18 | 335.96 | 0.0002 | |
| 2FI | 1.29 | 7 | 0.18 | 350.57 | 0.0002 | |
| Quadratic | 0.60 | 4 | 0.15 | 284.43 | 0.0003 | Suggested |
| Cubic | 0.00 | 0 | | | | |
| Pure Error | 0.00 | 3 | 0.00 | | | |

Both the sequential model sum of squares [Type I] and the lack of fit tests for biosynthetic gas suggested the quadratic model as the best for analysis of its data as shown in Table 4.6 and 4.7

Table 4.6: Model fit summary for biosynthetic gas

| **Response 2: Biosynthetic gas** | **Transform: Natural log** | | **Constant:0** | | | |
|---|---|---|---|---|---|---|
| Sequential Model Sum of Squares [Type I] | | | | | | |
| Source | Sum of Squares | df | Mean Square | F Value | p-value Prob > F | |
| Mean vs Total | 102.08 | 1 | 102.08 | | | |
| Linear vs Mean | 0.94 | 3 | 0.31 | 0.28 | 0.8374 | |
| 2FI vs Linear | 1.46 | 3 | 0.49 | 0.37 | 0.7742 | |
| Quadratic vs 2FI | 12.62 | 3 | 4.21 | 70.04 | < 0.0001 | Suggested |
| Cubic vs Quadratic | 0.18 | 4 | 0.04 | 0.55 | 0.7147 | Aliased |
| Residual | 0.24 | 3 | 0.08 | | | |
| Total | 117.53 | 17 | 6.91 | | | |
| Model Summary Statistics | | | | | | |
| Source | Std. Dev. | R-Squared | Adjusted R-Squared | Predicted R-Squared | PRESS | |
| Linear | 1.06 | 0.06 | -0.16 | -0.73 | 26.73 | |
| 2FI | 1.14 | 0.16 | -0.35 | -2.36 | 51.83 | |
| Quadratic | 0.25 | 0.97 | 0.94 | 0.79 | 3.28 | Suggested |
| Cubic | 0.28 | 0.98 | 0.92 | | + | Aliased |

Table 4.7: Lack of fit tests for biosynthetic gas

| **Lack of Fit Tests** | | | | | | |
|---|---|---|---|---|---|---|
| Source | Sum of Squares | df | Mean Square | F Value | p-value Prob > F | |
| Linear | 14.26 | 10 | 1.43 | 17.68 | 0.0187 | |
| 2FI | 12.80 | 7 | 1.83 | 22.67 | 0.0134 | |
| Quadratic | 0.18 | 4 | 0.04 | 0.55 | 0.7147 | Suggested |
| Cubic | 0 | 0 | | | | Aliased |
| Pure Error | 0.24 | 3 | 0.08 | | | |

### 4.4.1 Analysis of variance (ANOVA) for biochar

There was no statistical transformation required for biochar shown in Table 4.4. This is because all the responses for biochar ranged from 0.19 g to 1.54 g and thus the ratio of maximum to minimum was found to be 8.25, for which being less than 10 usually does not require a transformation, and given the fact that power transformations also have a little effect for ratios of less than 3 magnitude.

A cubic model was used that yielded different combinations of terms as shown in the final model equations (1) and (2) for the biochar response in terms of the design variables used, the coefficients are shown in Table 4.8.

Table 4.8: Coefficient estimates for the design terms selected for biochar

| Factor | Coefficient Estimate | Standard Error | 95% CI Low | 95% CI High | VIF |
|---|---|---|---|---|---|
| Intercept | 8.78 | 7.80 | -16.05 | 33.60 | |
| A-Particle size | -96.86 | 101.72 | -420.59 | 226.86 | 157520647.00 |
| B-Moisture | 26.00 | 27.18 | -60.50 | 112.50 | 9797980.87 |
| C-Cellulose | -10.46 | 11.04 | -45.58 | 24.67 | 1840693.02 |
| AB | -98.89 | 104.86 | -432.59 | 234.82 | 69381708.00 |
| AC | 64.40 | 67.70 | -151.06 | 279.86 | 34893643.00 |
| BC | -93.81 | 97.83 | -405.15 | 217.53 | 67912832.00 |
| $A^2$ | 134.58 | 141.28 | -315.03 | 584.20 | 1.60E+08 |
| $B^2$ | 148.95 | 156.32 | -348.54 | 646.44 | 2.02E+08 |
| $C^2$ | -159.86 | 167.37 | -692.50 | 372.78 | 2.05E+08 |
| ABC | 1168.00 | 1220.04 | -2714.73 | 5050.73 | 3.91E+08 |
| $A^2B$ | -323.74 | 339.59 | -1404.46 | 756.99 | 7.26E+08 |
| $A^2C$ | 50.84 | 53.35 | -118.94 | 220.61 | 21532487.00 |
| $AB^2$ | 369.30 | 387.78 | -864.79 | 1603.39 | 1.06E+09 |

Final Equation in terms of coded factors was as follows;

$$\text{Bio char} = 8.78 - 96.86A + 26.00B - 10.46C - 98.89AB + 64.40AC - 93.81BC + 134.58A^2 + 148.95B^2 - 159.86C^2 + 1168.00ABC - 323.73A^2B + 50.84A^2C + 369.30AB^2 \quad \text{.....................(1)}$$

Where; A - Particle size, B - Moisture content, C - Cellulose.

Final equation in terms of actual factors was as follows;

$$\text{Bio char} = -5800.63 + 2321.04P + 845.73M + 255.18C - 468.83PM - 99.08PC - 26.69MC + 196.9P^2 - 9.1M^2 - 1.6C^2 + 15.62PMC - 34.74P^2M + 3.27P^2C + 8.23PM^2 \quad \text{.......................(2)}$$

Where P – Particle size, M – Moisture content, C – Cellulose.

ANOVA for biochar was conducted and results are as shown in Table 4.8;

Table 4.9: ANOVA for Response Surface Cubic Model - Biochar

| **Response**1 | | **Biochar** | | | |
|---|---|---|---|---|---|
| Source | Sum of Squares | Mean Square | F Value | p-value Prob > F | |
| **Model** | **2.06** | **0.16** | **300.73** | **0.0003** | **significant** |
| Pure Error | 0.0015792 | 0.000526 | | | |
| Cor. Total | 2.06 | | | | |
| **R – Squared** | **0.9992** | | | | |
| **Adeq. Precision** | **64.98** | | | | |

The numerator for lack of fit was found to be artificially small for the cubic model and hence decisions concerning the usage of the model had to be made basing on other statistical properties as indicated in Table 4.9. The Model F-value of 300.73 implied that the model was significant. There is only a 0.03% chance that a "Model F-Value" this large could occur due to noise. The value of R-squared signified a high correlation within the selected model terms.

"Adeq. Precision" in Table 4.8 measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 64.98 indicates an adequate signal. This model was therefore used to navigate the design space.

### 4.4.2 Model graphs for biochar

Single factor effects on biochar are presented in Figures 4.3, 4.4 and 4.5;

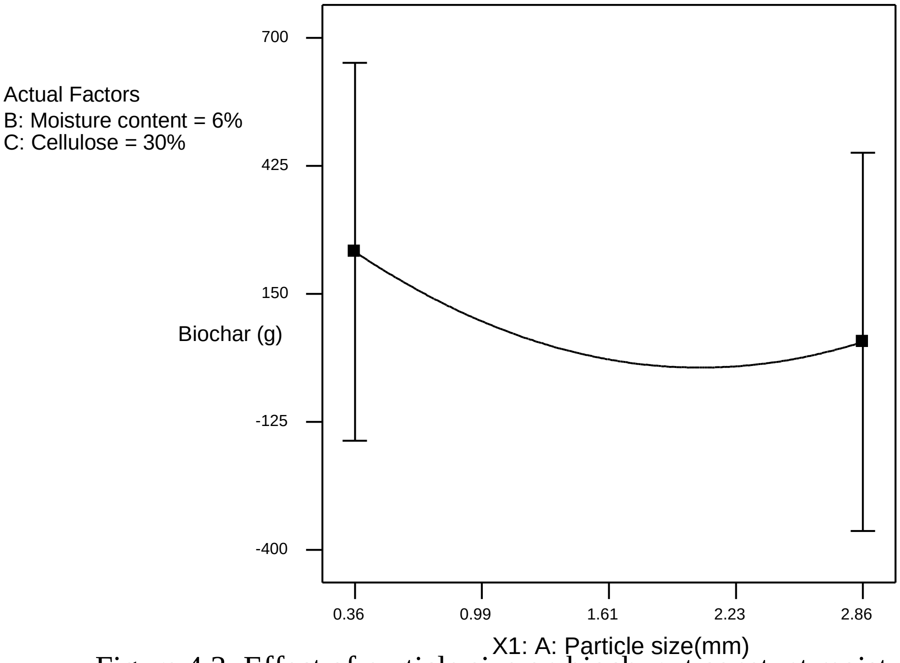

Figure 4.3: Effect of particle size on biochar at constant moisture and cellulose.

Initially as particle size increases, the yield of biochar is observed to reduce up to the midpoint, then it starts to increase up to a particle size of 2.86 mm, the later observation is in agreement with that reported by Demirbas (2004). The increase in biochar yields beyond 2.23 mm particle size is also in agreement with the study by Zaman *et al*. (2017). This could be attributed to larger particles that restrict the rate of disintegration, resulting in the increased scope of secondary biochar forming reactions (Antal *et al*., 2003). However, both small and large particle sizes are good for obtaining more biochar yields, the maximum yield of biochar was obtained at 0.36 mm particle size as shown in Figure 4.3. It is also noteworthy that all the three factors were involved in the interaction that yields biochar, in which case single factor effects alone may not be enough to conclude on the yields.

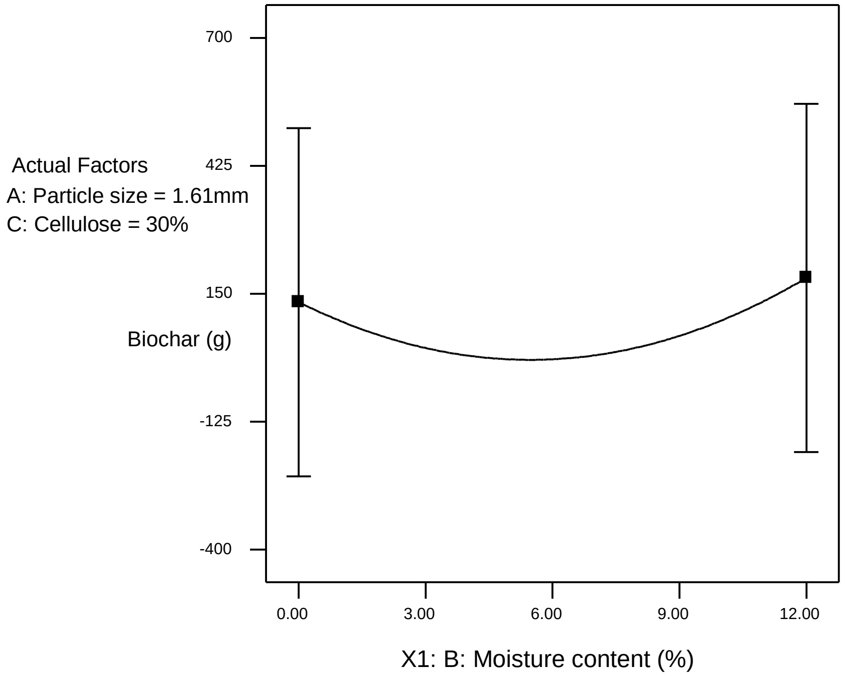

Figure 4.4: Effect of moisture content on biochar yields at constant particle size and cellulose

The data in Figure 4.4 shows single factor effect of moisture content on biochar yield at constant particle size of 1.61mm and cellulose of 30%. Increasing moisture content from 6% to 12% is seen to favor the generation of biochar at the pyrolysis conditions applied in the present study, thus high moisture content favors high yields of biochar.

Moisture lowers biomass ignition temperature as energy is dissipated via the latent heat of vaporization of water, thus restricting biosynthetic gas formation due to a lesser degree of depolymerization with increasing moisture.

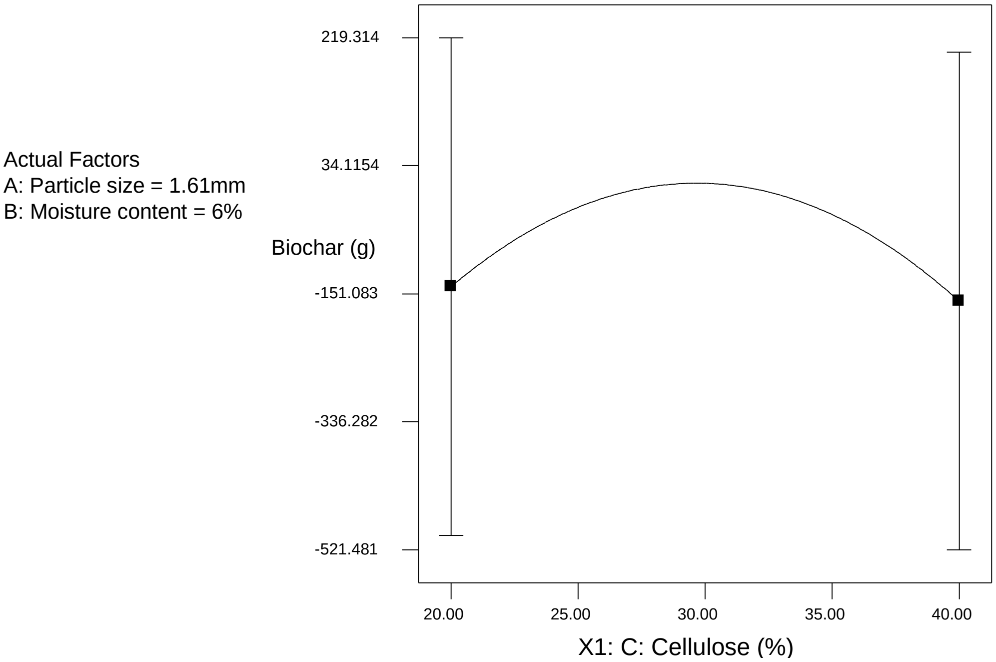

Figure 4.5: Effect of cellulose content on biochar yields at constant particle size and moisture.

Figure 4.5 shows the effect of cellulose on biochar yield at constant particle size of 1.61 mm and moisture of 6%. The yields of biochar in relation to the cellulose content of biomass feed stock are highest at mid-level quantities of cellulose, high and low cellulose contents both do not favor the production of biochar, as a result of interaction with particle size and moisture content. Response surface plots were generated for interactive effects between the variables on biochar and biosynthetic gas.

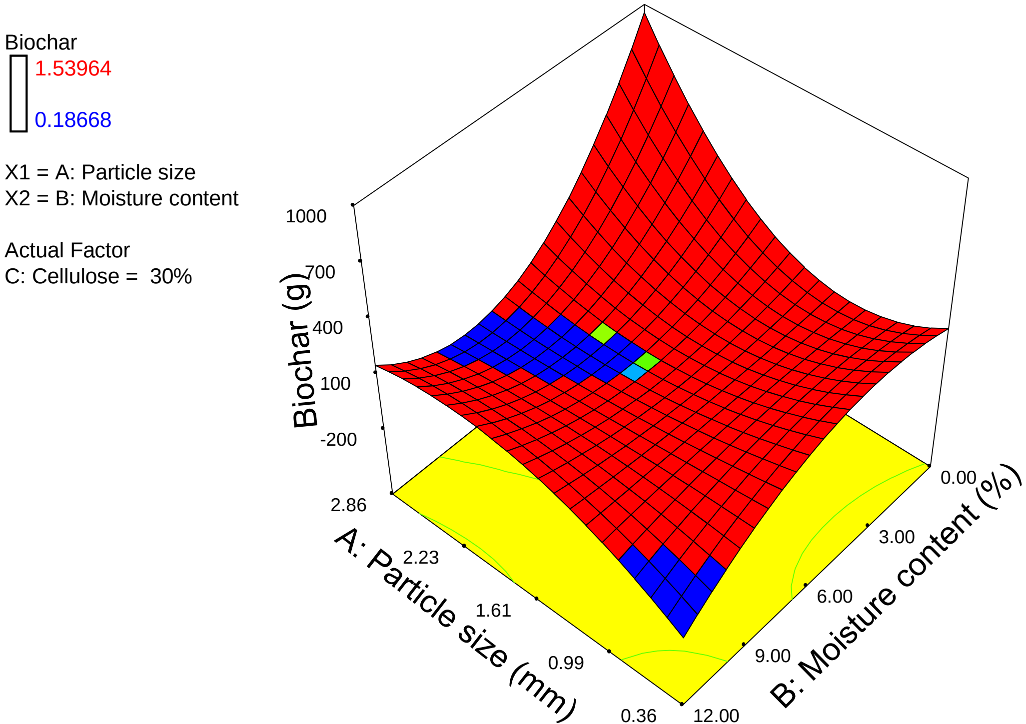

Figure 4.6: Response surface showing the influence of moisture content and particle size on biochar yield.

Figure 4.6 shows the interactive effect of moisture content and particle size on biochar yield. The data in the plot shows that the quantity of biochar produced at low particle size and high moisture content is low. However, it increases as particle size increases and with decreasing moisture content. The peak yield for biochar is realized at a low level of moisture content and a high level of particle size that lies between 2.23 mm to 2.86 mm as shown in Figure 4.6.

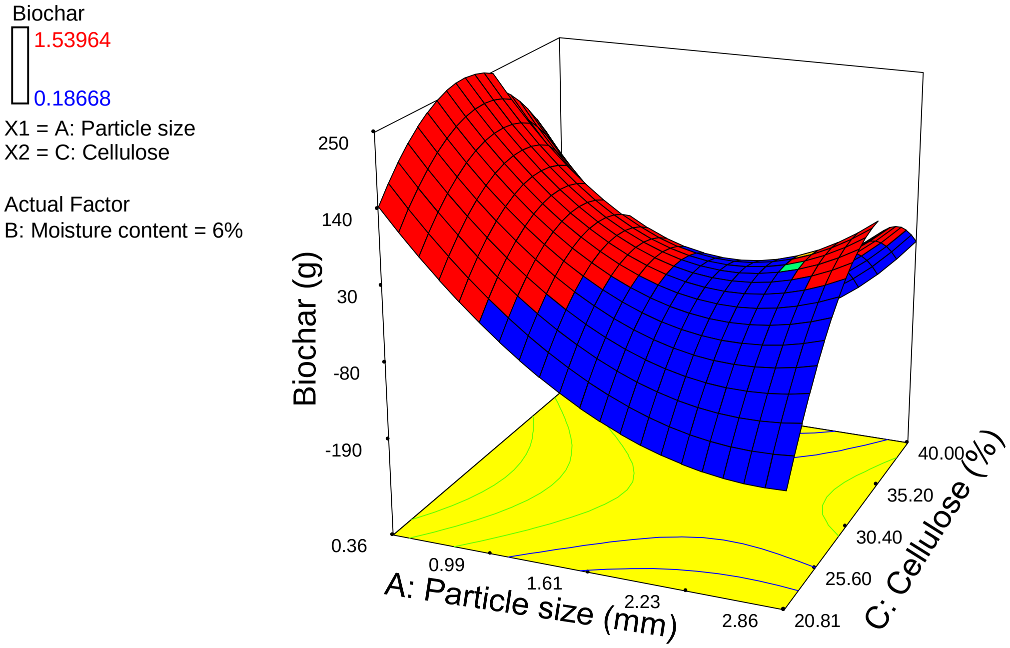

Figure 4.7: Response surface showing the influence of cellulose and particle size on biochar yields

Figure 4.7 Shows the interactive effect between cellulose content and particle size on biochar yield. The data shows that the yield of biochar increases with increase in cellulose content and decrease in particle size, attaining a maximum at particle size in the range of 0.99 mm to 0.36 mm and cellulose content at 30.40%. This shows that high biochar yields are favored by increase in cellulose content and decrease in particle size on an interactive basis.

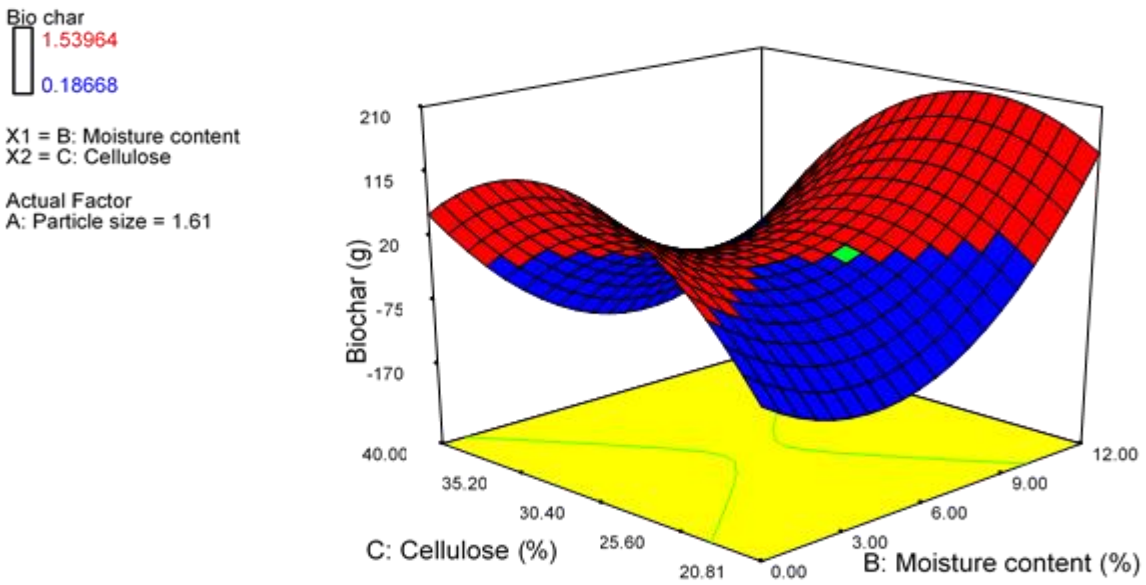

Figure 4.8: Response surface showing the influence of cellulose and moisture content on biochar yields.

Figure 4.8 shows the interactive effect between cellulose and moisture content on biochar yield. The yield of biochar is observed to increase with increase in cellulose content up to 30.4% and increase in moisture content from 6% to 12%, resulting in a maximum output at cellulose contents in the range of 30.4% to 25.6% against high moisture content in the range 9% to 12%. This implies that biochar yield is more favored by increasing moisture content at a medium level of cellulose.

### 4.4.3 Statistical results for biosynthetic gas

A natural log transform was used for the analysis of data for biosynthetic gas. This is because all the responses for biosynthetic gas ranged from 2.6 cm$^3$ - 40.1 cm$^3$ and thus the ratio of maximum to minimum was found to be 15.42, for which ratios greater than 10 require a transformation, and power transformations have a little effect for ratios less than 3 magnitude.

A quadratic model was used that yielded 10 different combinations of terms as shown in the final model equations (3) and (4) for biosynthetic gas within the ranges of the design variables used.

Final Equation in Terms of Coded Factors:

(Natural log) Biosynthetic gas = $+3.38 + 0.084A - 0.48B + 0.78C - 0.059AB - 0.072AC - 0.27BC + 0.2A^2 - 0.086B^2 - 2.00C^2$………….……………………………………………..………. (3)

Where A, B and C represent Particle size, Moisture content and Cellulose respectively.

Final Equation in terms of Actual Factors:

(Natural log) Biosynthetic gas = $-17.41 - 0.28P + 0.1M + 1.32C - 7.95\times10^{-3}PM - 5.74195\times10^{-3}PC - 4.58\times10^{-3}MC + 0.18P^2 - 2.4\times10^{3}M^2 -0.02\times C^2$…………………………...…………..………. (4)

Where; P – Particle size, M – Moisture content, C – Cellulose.

Table 4.10: Coefficient estimates for all significant design variables for biosynthetic gas

| **Factor** | **Coefficient Estimate** | **Standard Error** | **95% CI Low** | **95% CI High** | **VIF** |
|---|---|---|---|---|---|
| Intercept | 3.38 | 0.11 | 3.12 | 3.65 | |
| A-Particle size | 0.08 | 0.09 | - 0.14 | 0.31 | 1.17 |
| B-Moisture content | - 0.48 | 0.10 | - 0.72 | - 0.24 | 1.22 |
| C-Cellulose | 0.78 | 0.09 | 0.55 | 1.00 | 1.17 |
| AB | - 0.06 | 0.15 | - 0.42 | 0.30 | 1.26 |
| AC | - 0.07 | 0.12 | - 0.36 | 0.22 | 1.01 |
| BC | - 0.27 | 0.13 | - 0.58 | 0.03 | 1.03 |
| $A^2$ | 0.27 | 0.12 | -0.02 | 0.56 | 1.07 |
| $B^2$ | -0.09 | 0.13 | -0.38 | 0.21 | 1.15 |
| $C^2$ | -2.00 | 0.14 | -2.34 | -1.67 | 1.28 |

### 4.4.4 ANOVA for biosynthetic gas

ANOVA for biosynthetic gas was conducted and results are as shown in Table 4.11;

Table 4.11: ANOVA from Response Surface Quadratic Model-Biosynthetic gas

| Source | Sum of Squares | Mean Square | F Value | p-value Prob > F | |
|---|---|---|---|---|---|
| **Model** | **15.02** | **1.67** | **27.80** | **0.0001** | **significant** |
| A-Particle size | 0.05 | 0.05 | 0.81 | 0.3983 | |
| B-Moisture content | 1.33 | 1.33 | 22.17 | 0.0022 | |
| C-Cellulose | 4.11 | 4.11 | 68.41 | < 0.0001 | |
| AB | 0.01 | 0.01 | 0.16 | 0.7049 | |
| AC | 0.02 | 0.02 | 0.34 | 0.5792 | |
| BC | 0.27 | 0.27 | 4.55 | 0.0705 | |
| **Lack of Fit** | **0.18** | **0.04** | **0.55** | **0.71** | **not significant** |
| Pure Error | 0.24 | 0.08 | | | |
| Cor Total | 15.45 | | | | |

The Model F-value of 27.80 implies the model was significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, for the present study; B, C and $C^2$ are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The "Lack of Fit F-value" of 0.55 implies the Lack of Fit is not significant relative to the pure error. There is a 71.47% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good because we want the model to fit.

Table 4.12: Major statistical terms used for biosynthetic gas

| **Std. Dev.** | **0.25** | **R-Squared** | **0.97** |
|---|---|---|---|
| Mean | 2.45 | Adj R-Squared | 0.94 |
| C.V. % | 10.00 | Pred. R-Squared | 0.79 |
| PRESS | 3.28 | Adeq. Precision | 15.37 |

The "Pred. R-Squared" of 0.79 in Table 4.11 is in reasonable agreement with the "Adj R-Squared" of 0.94. "Adeq. Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 15.37 as obtained in the present study indicates an adequate signal. This model was therefore used to navigate the design space.

### 4.4.5 Model graphs for biosynthetic gas

Graphical illustrations of single factor effects of each variable on biosynthetic gas yield are shown in Figures 4.9, 4.10 and 4.11.

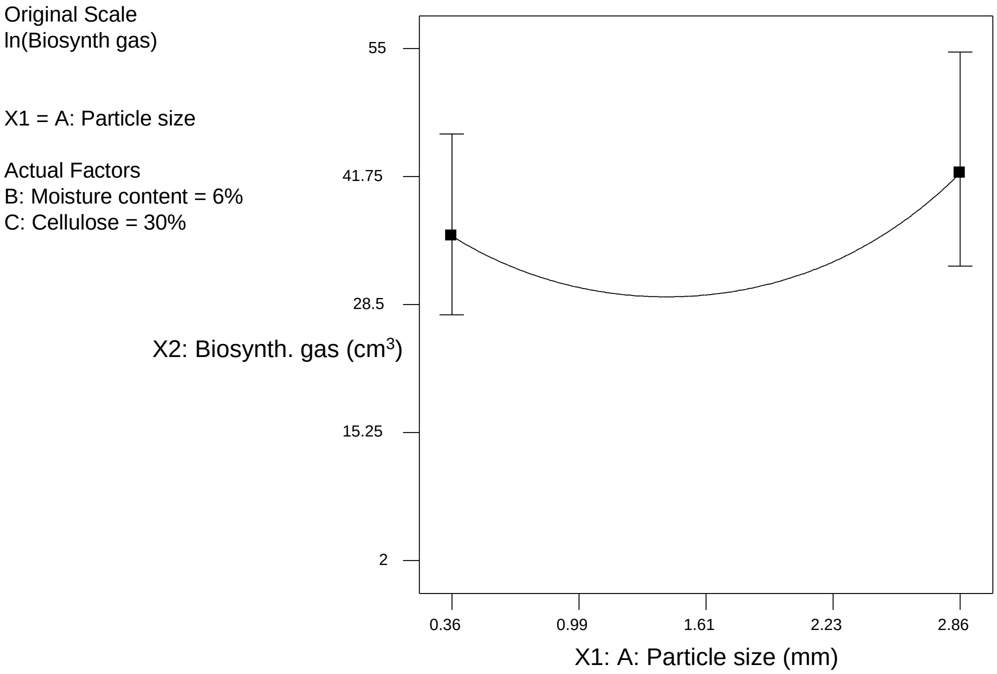

Figure 4.9: Effect of particle size on biosynthetic gas at constant moisture and cellulose.

For the smaller particle sizes in the range of 0.36 to about 1.0 mm, the biosynthetic gas yield decreases with increase in particle size, while the biosynthetic gas yield increases with particle size in the ranges above 1 mm as shown in Figure 4.9. The study showed that high particle sizes favor high biosynthetic gas yields, which is in agreement with that reported by Kabakcı *et al*. (2017). This could be explained by the fact that large biomass particles increase the residence time of volatile matter, favoring secondary cracking reactions of tar, thus increasing the gas yield.

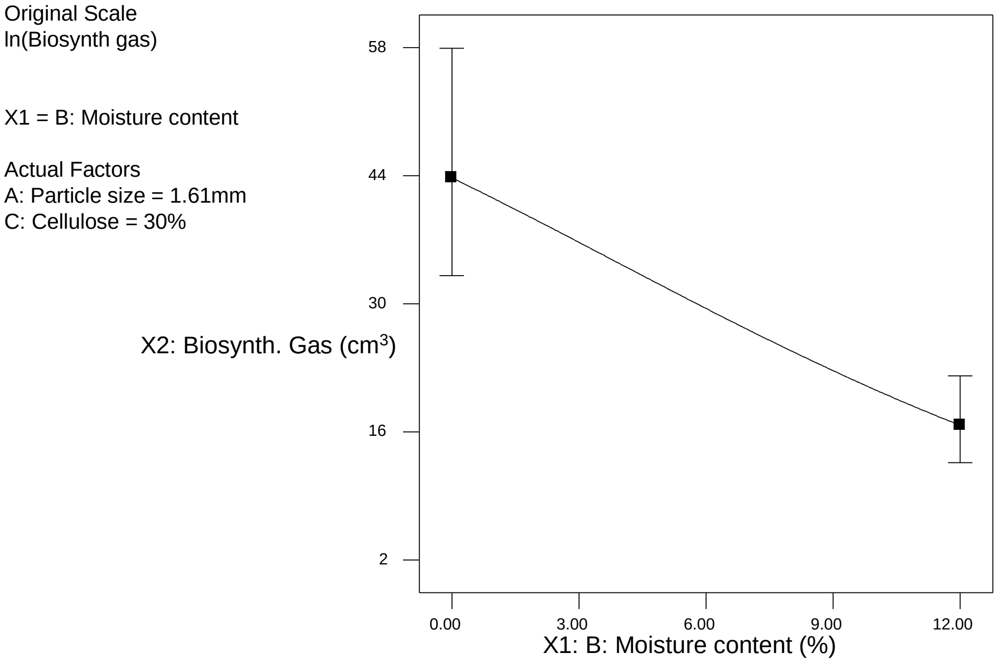

Figure 4.10: Effect of moisture on biosynthetic gas at constant particle size and cellulose.

The yield of biosynthetic gas decreases with increase in moisture content from 0% to 12% as shown in Figure 4.10. This is in agreement with a study by Zaman *et al*. (2017). This shows that biosynthetic gas yield increases with decrease in moisture content.

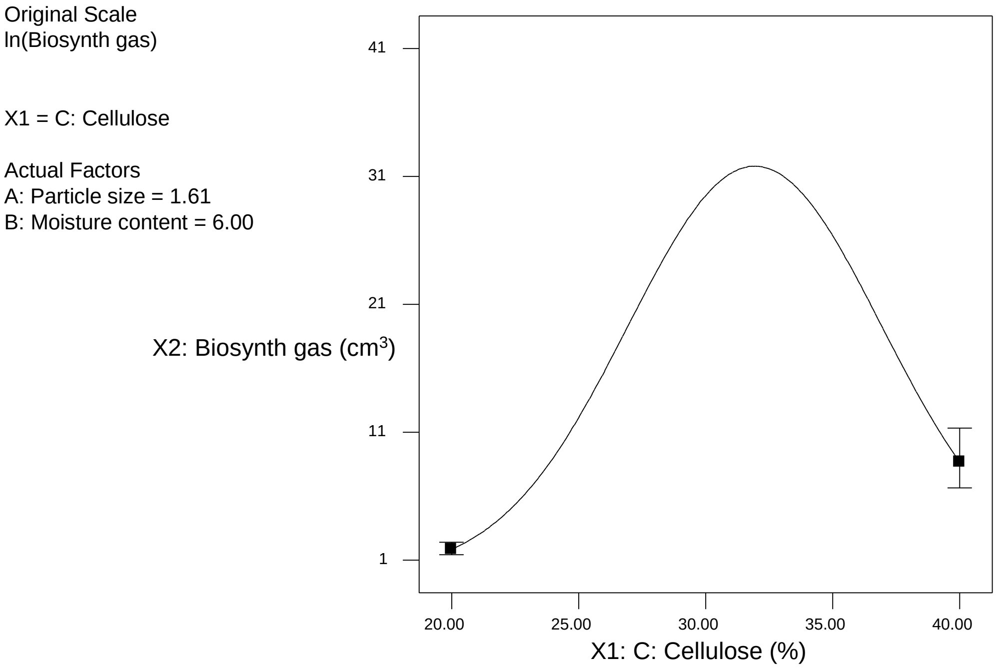

Figure 4.11: Effect of cellulose on biosynthetic gas at constant particle size and moisture.

Biosynthetic gas yield increases with increase in cellulose content of biomass upto mid-level cellulose content. This is due to the fact that rapid cellulose decomposition is highly favored by the temperatures used in pyrolysis during this study, since an increasing cellulose content at this temperature from 20% to 30% implied more biosynthetic gas yield. It however declines beyond the mid-level, which may be due to interactive impact of other factors on the yield.

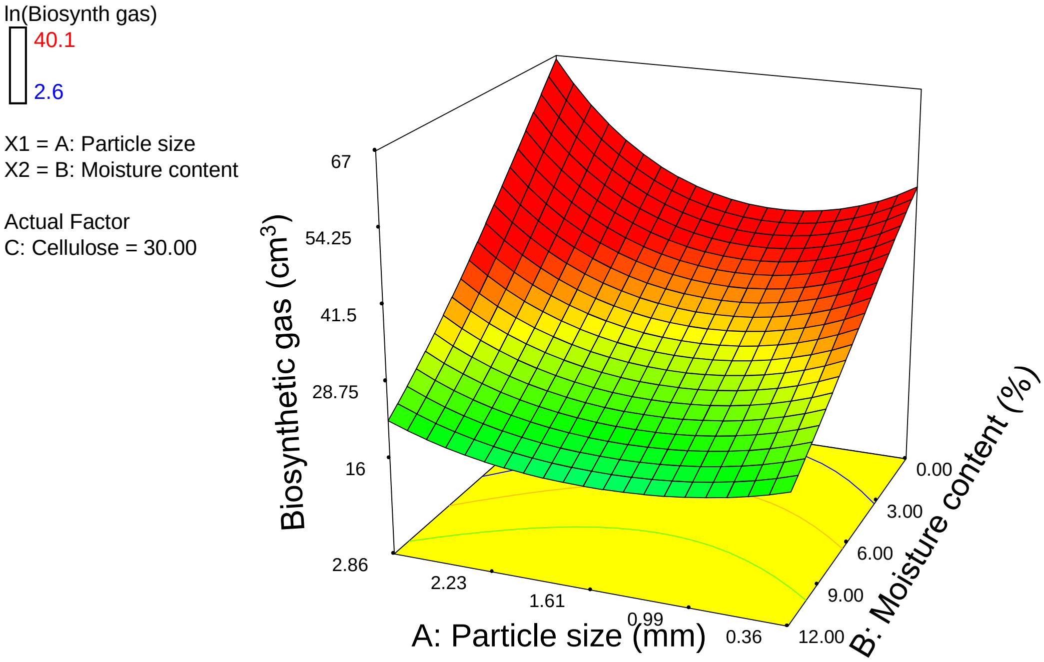

Figure 4.12: Response surface showing the effect of particle size and moisture on biosynthetic gas.

Figure 4.12 shows results for the interactive effect of particle size and moisture on biosynthetic gas yield. The yield of biosynthetic gas increases with increase in particle size as the moisture content decreases, with a peak output at around zero percent levels of moisture but at a high particle size almost at around the maximum (2.86 mm) used in this study.

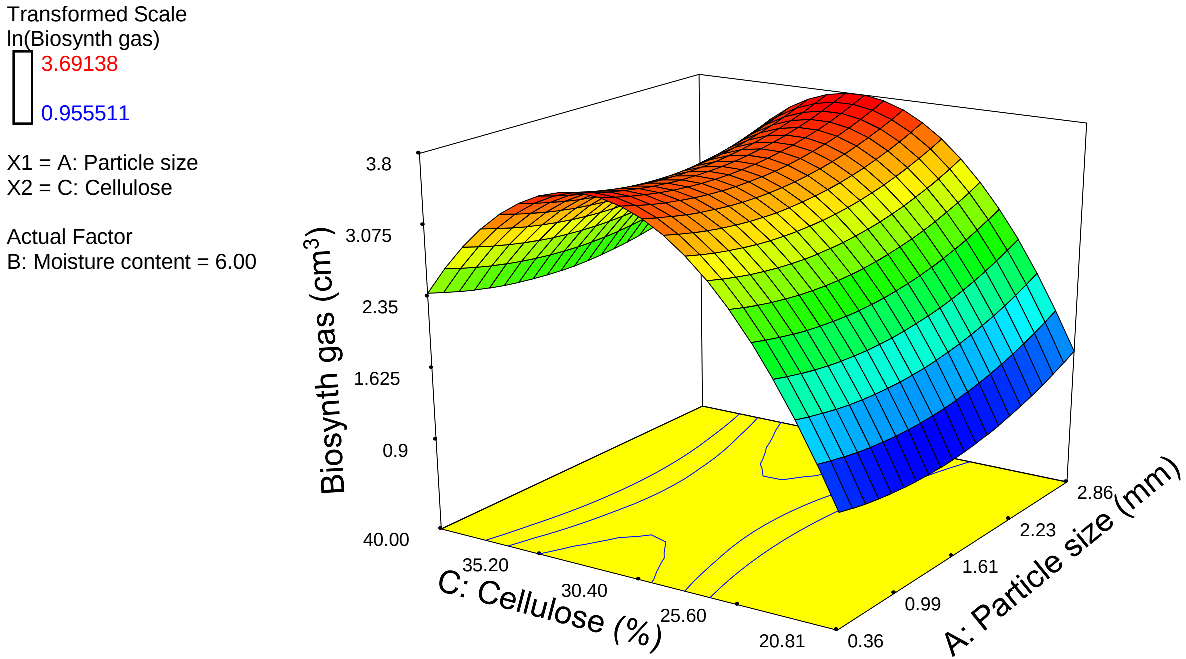

Figure 4.13: Response surface showing the influence of cellulose and particle size on biosynthetic gas.

The data in figure 4.13 shows that the yield of biosynthetic gas is high at both extremes of high and low particle size while cellulose content is around the mid-level of about 30.4% for the same quantity of feed stock.

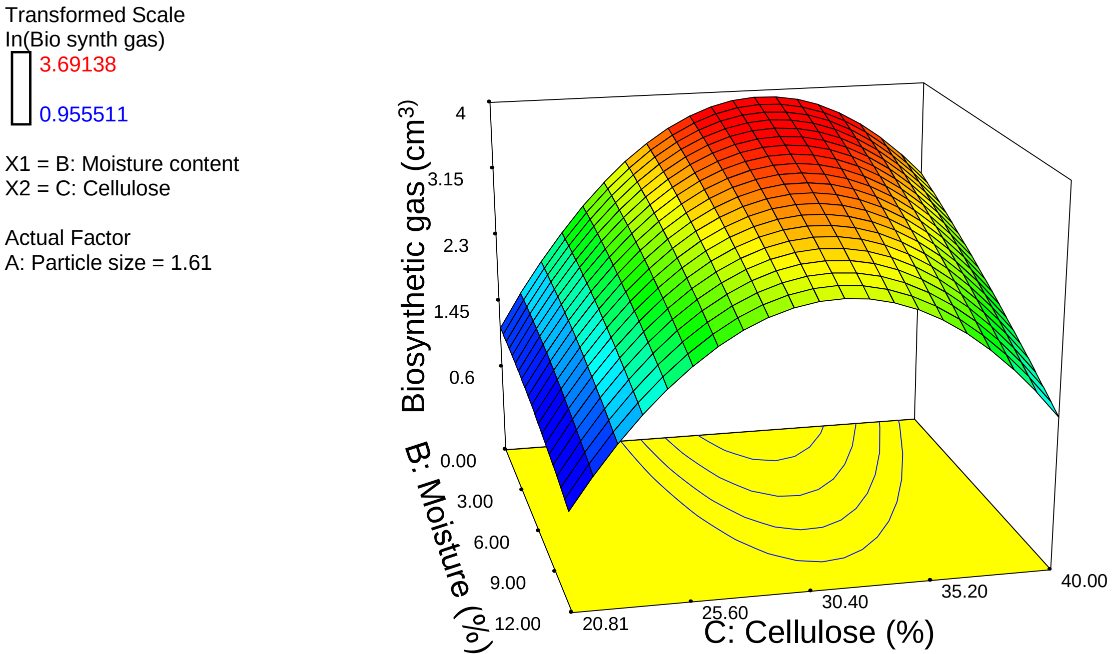

Figure 4.14: Response surface showing the influence of cellulose and moisture content on biosynthetic gas.

The data in figure 4.14 shows that the amount of biosynthetic gas produced increased with increase in cellulose content, but with decreasing moisture content, although it declined at maximum levels of moisture content even when the cellulose content is high. This could be because pyrolytic depolymerization is inhibited at high moisture levels of the biomass (Gray, 1985).

### 4.5 Optimization of process variables to maximize biochar and biosynthetic gas yields

Basing on the single factor effects of cellulose, moisture and particle size on biochar and biosynthetic gas, biochar yield was set to be maximized at limits of 0.19 g to 1.54 g with a weight of 10 and the following goals; for numerical optimization of both cellulose and moisture, they were set to be within the ranges of 25% to 35% and 10% to 12.5%, respectively; particle size was set to be minimized from 0.99 mm to 0.36 mm at a weight of 10 to give more emphasis to the goal and to allow for the use of experimentally feasible quantities.

Biosynthetic gas yield was set to be maximized at limits of 2.6 $cm^3$ to 40.1 $cm^3$ at the same lower weight as biochar, with the following goals; to maximize particle size within the limits of 2.23 mm to 2.86 mm, to minimize moisture in the limits of 0% to 3%, and to keep cellulose in the range of 30% to 35%. Both moisture and particle size were assigned weights of 10. High weights of 10 were assigned in order to focus on generating only solutions that meet all the goals. A summary of constraints for biochar and biosynthetic gas is shown in Tables 4.11 and 4.12, respectively. A maximum importance was accorded to all responses and variables.

Table 4.13: Optimization constraints for biochar

| **Name** | **Goal** | **Lower limit** | **Upper limit** | **Lower weight** | **Upper weight** |
|---|---|---|---|---|---|
| Particle size (mm) | minimize | 0.36 | 0.99 | 1 | 10 |
| Moisture (%) | is in range | 10 | 12.5 | 10 | 10 |
| Cellulose (%) | in range | 25 | 35 | 1 | 1 |
| Biochar (g) | maximize | 0.19 | 1.54 | 10 | 10 |

Table 4.14: Optimization constraints for biosynthetic gas

| **Name** | **Goal** | **Lower limit** | **Upper limit** | **Lower weight** | **Upper weight** |
|---|---|---|---|---|---|
| Particle size (mm) | maximize | 2.23 | 2.86 | 10 | 10 |
| Moisture content (%) | minimize | 0 | 3 | 10 | 10 |
| Cellulose (%) | is in range | 30 | 35 | 1 | 1 |
| Biosynthetic gas ($cm^3$) | maximize | 2.6 | 40.1 | 10 | 1 |

### 4.5.1 Optimal solutions generated

Table 4.15: Optimal solutions generated for biochar yield.

| Number | Particle size (mm) | Moisture content (%) | Cellulose (%) | Biochar (g) | Desirability |
|---|---|---|---|---|---|
| 1 | 0.36 | 12.08 | 25.94 | 314.42 | 1.00 |
| 2 | 0.36 | 10.36 | 27.38 | 215.27 | 1.00 |
| 3 | 0.36 | 10.69 | 25.87 | 340.63 | 1.00 |
| 4 | 0.36 | 10.21 | 26.91 | 257.86 | 1.00 |
| 5 | 0.36 | 12.01 | 28.08 | 61.01 | 1.00 |
| 6 | 0.36 | 10.97 | 28.11 | 119.77 | 1.00 |
| 7 | 0.36 | 11.70 | 28.24 | 62.24 | 1.00 |
| 8 | 0.36 | 11.41 | 27.54 | 157.32 | 1.00 |
| 9 | 0.36 | 10.45 | 29.02 | 63.67 | 1.00 |
| 10 | 0.36 | 10.33 | 26.10 | 321.97 | 1.00 |
| 11 | 0.36 | 10.96 | 28.49 | 82.09 | 1.00 |
| 12 | 0.36 | 10.11 | 27.67 | 198.81 | 1.00 |
| 13 | 0.36 | 12.31 | 28.33 | 7.89 | 1.00 |
| 14 | 0.36 | 11.85 | 25.93 | 320.47 | 1.00 |
| 15 | 0.36 | 10.66 | 28.40 | 108.78 | 1.00 |
| 16 | 0.36 | 10.28 | 28.51 | 120.02 | 1.00 |
| 17 | 0.36 | 10.89 | 27.65 | 170.31 | 1.00 |
| 18 | 0.36 | 10.60 | 28.82 | 73.11 | 1.00 |
| 19 | 0.36 | 12.18 | 27.75 | 90.43 | 1.00 |
| 20 | 0.36 | 11.85 | 26.89 | 211.12 | 1.00 |
| 21 | 0.36 | 10.15 | 29.71 | 22.77 | 1.00 |
| **22** | **0.36** | **10.30** | **25.45** | **374.29** | **1.00** |
| 23 | 0.36 | 11.03 | 28.30 | 97.94 | 1.00 |
| 24 | 0.36 | 12.29 | 28.02 | 49.95 | 1.00 |
| 25 | 0.36 | 10.87 | 28.86 | 50.83 | 1.00 |
| 26 | 0.99 | 11.35 | 29.59 | 83.27 | 0.00 |
| 27 | 0.99 | 10.67 | 29.50 | 92.63 | 0.00 |

From Table 4.15, a total of 27 solutions were generated for maximizing biochar, and optimization solution 22 was selected with the most optimal set of conditions that gave the highest biochar yield and satisfies all the goals set for biochar.

Table 4.16: Optimal solutions generated for biosynthetic gas at 0% moisture

| **Number** | **Particle size (mm)** | **Cellulose (%)** | **Biosynthetic gas (cm3)** | **Desirability** |
|---|---|---|---|---|
| 1 | 2.86 | 30.87 | 71.37 | 1.00 |
| 2 | 2.86 | 30.07 | 66.98 | 1.00 |
| 3 | 2.86 | 33.27 | 74.01 | 1.00 |
| 4 | 2.86 | 33.74 | 72.56 | 1.00 |
| 5 | 2.86 | 32.07 | 74.81 | 1.00 |
| 6 | 2.86 | 34.51 | 68.88 | 1.00 |
| 7 | 2.86 | 32.84 | 74.79 | 1.00 |
| 8 | 2.86 | 31.17 | 72.63 | 1.00 |
| **9** | **2.86** | **32.52** | **75.02** | **1.00** |
| 10 | 2.86 | 31.77 | 74.34 | 1.00 |
| 11 | 2.86 | 34.13 | 70.91 | 1.00 |
| 12 | 2.62 | 30.00 | 58.95 | 0.21 |

From Table 4.16, a total of 12 solutions were generated that maximize biosynthetic gas, and optimization solution 9 was selected with the most optimal set of conditions that gave the highest biosynthetic gas yield and also meets all the goals set for biosynthetic gas.

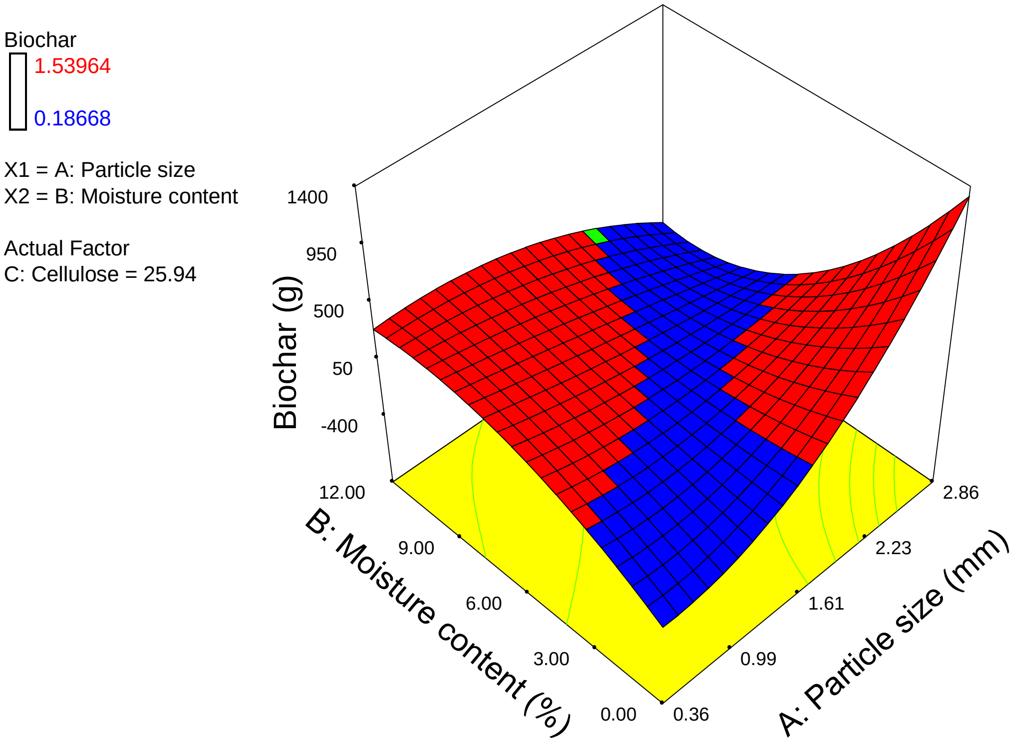

Figure 4.15: Response surface simulation of the influence of particle size and moisture on biochar.

Figure 4.15 shows the optimal interactive effect of particle size and moisture content on the yield of biochar. The most optimal effect between moisture content and particle size on the yield of biochar was found be at particle size of 2.86 mm at a 0 % moisture content resulting into the highest yield of biochar.

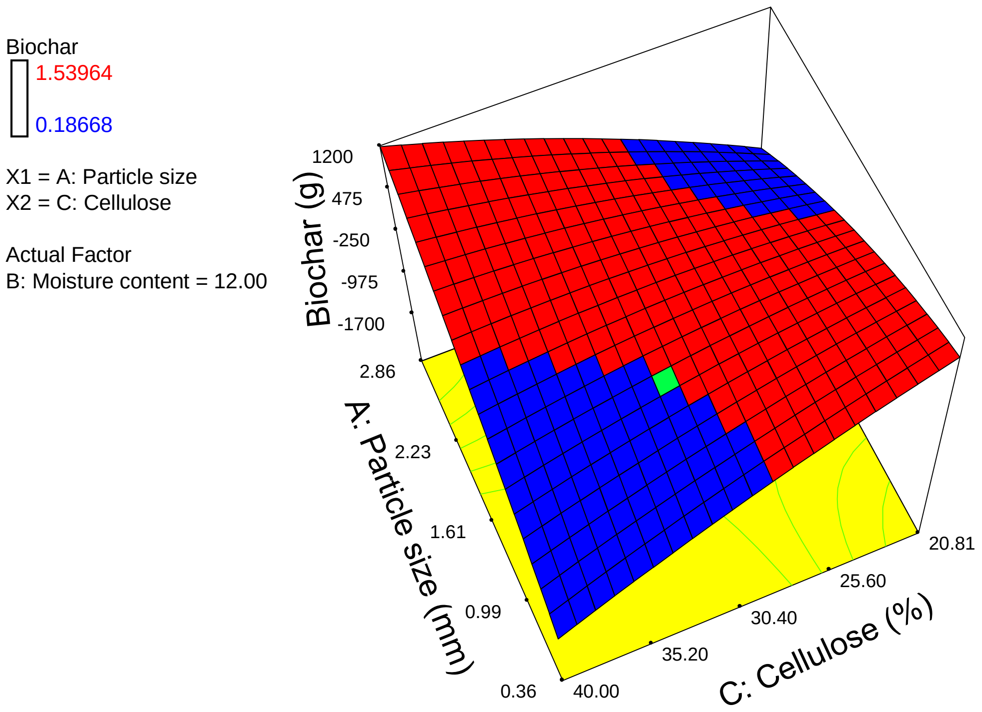

Figure 4.16: Response surface simulation showing the influence of cellulose and particle size on biochar.

Figure 4.16 shows the interactive effect of cellulose and particle size on biochar. The most optimal interactive effect between cellulose content and particle size that yielded the highest quantities of biochar was at 40% and 2.86 mm, respectively. Cellulose had been set to maximize the limits.

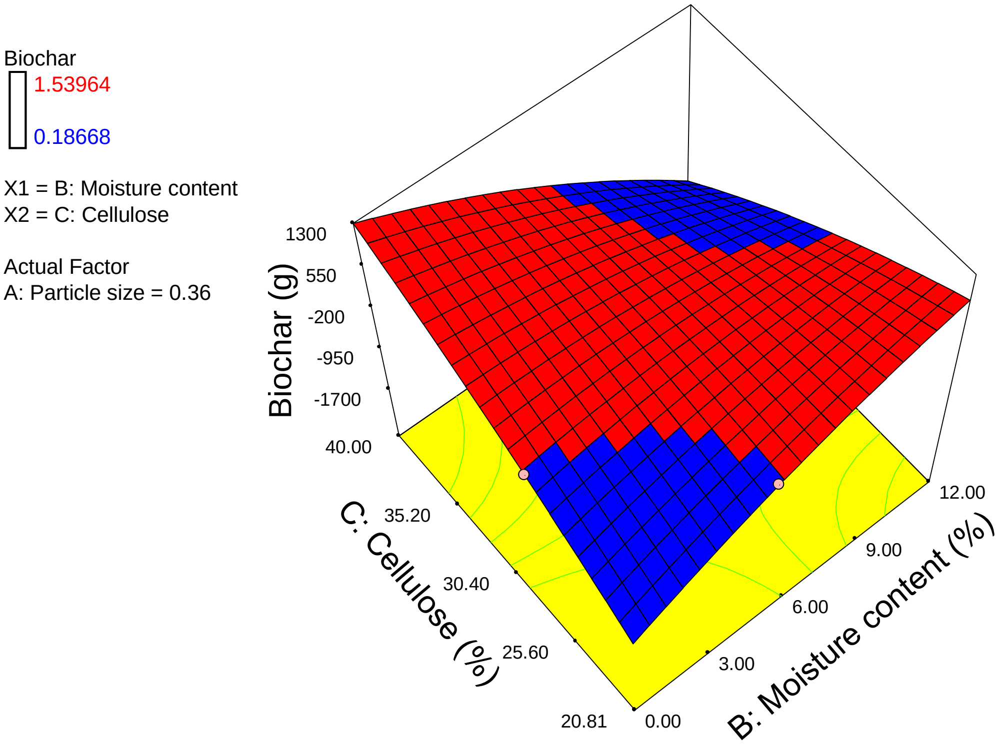

Figure 4.17: Response surface simulation of the effect of cellulose and moisture content on biochar.

Figure 4.17 shows a simulated interactive effect of cellulose and moisture content on biochar yield; the highest quantity of biochar was produced at a cellulose content of 40% and moisture content of 0%.

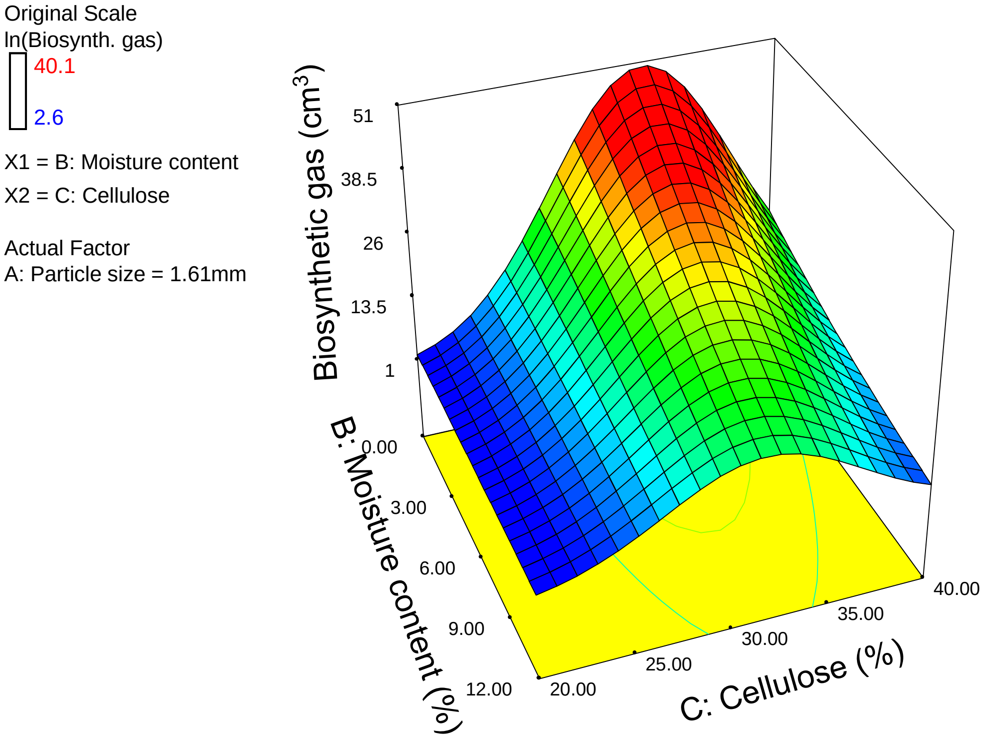

Figure 4.18: Response surface simulation showing the effect of moisture and cellulose on biosynthetic gas.

Figure 4.18 shows a simulated interactive effect of moisture and cellulose content on the yield of biosynthetic gas. The most optimal yield for biosynthetic gas was at a cellulose content of 30% and 0% moisture.

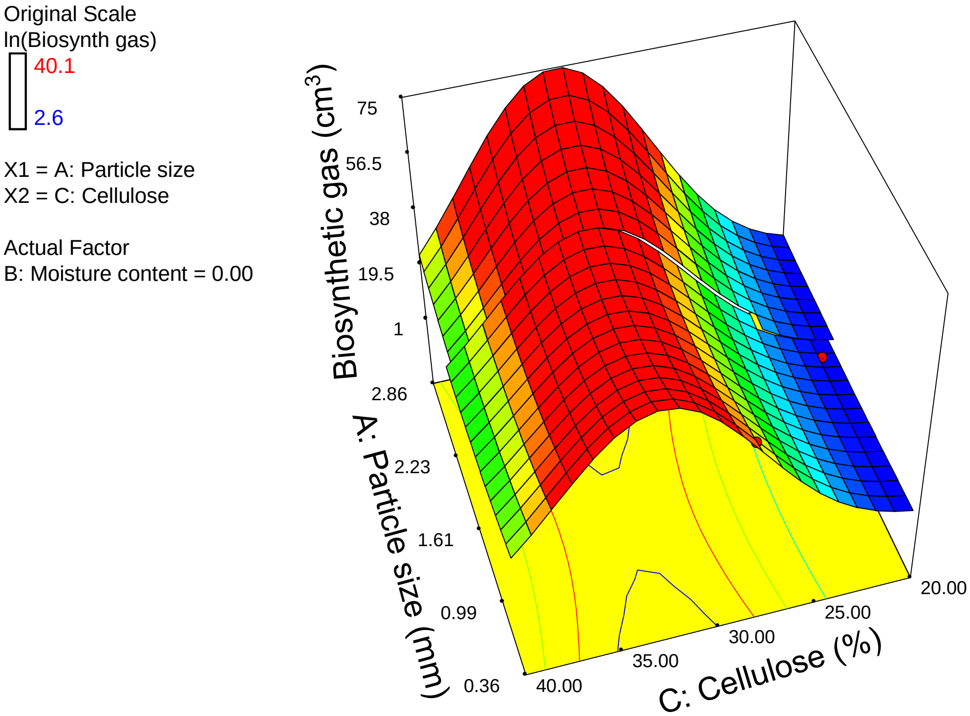

Figure 4.19: Response surface simulation showing effect of particle size and cellulose on biosynthetic gas.

Figure 4.19 shows a simulation of the interactive effect of particle size and cellulose content on the yield of biosynthetic gas. The results show that the highest output of biosynthetic gas is obtained at a cellulose content in the range of 30% to 35%, and 2.86-mm particle size.

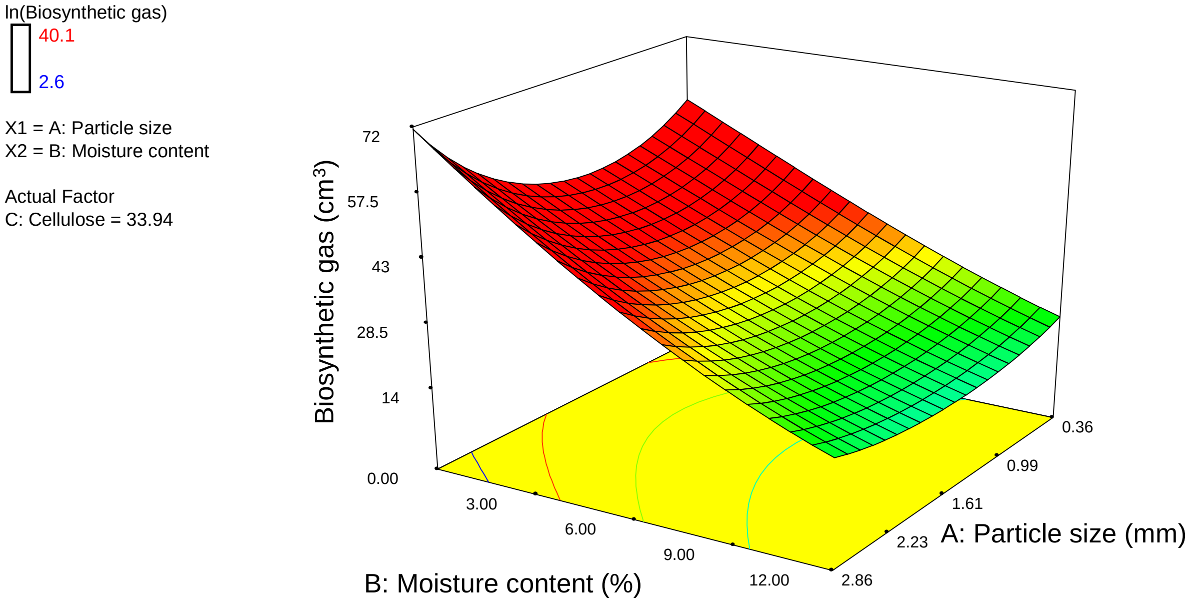

Figure 4.20: Response surface of moisture and particle size effect on biosynthetic gas.

Figure 4.20 shows a simulation of the interactive effect of moisture content and particle size variation on the yield of biosynthetic gas. As moisture content and particle size reduce, the yield of biosynthetic gas is observed to increase.

# CHAPTER FIVE

# CONCLUSION AND RECOMMENDATIONS

## 5.1 Conclusion

This study investigated optimization of biomass parameters, including particle size, moisture and cellulose content, on the yield of biochar and biosynthetic gas by pyrolysis of groundnut shells, coffee and rice husks. Basing on the results, the optimal conditions for maximum biosynthetic gas and biochar yields by pyrolysis of groundnut shells, coffee and rice husks were successfully identified and there is evident potential for the generation of biochar and biosynthetic gas from these materials. Under objective one of this study, it can be concluded that from the biomass analyzed, rice husks have the highest composition of ash and are best suited for optimization studies that seek to improve on the yields of biochar via pyrolysis. Basing on the overall interactive effect of particle size, moisture and cellulose content to maximize the yields of biochar and biosynthetic gas, the most optimal interaction that would yield the highest quantities of biochar was found to be at levels of 0.36 mm, 10.3% and 25.45% for particle size, moisture and cellulose content, respectively, while the most optimal interaction that yields the highest biosynthetic gas was found to be at 2.86 mm, 0% and 32.52% for particle size, moisture and cellulose content respectively. In both interactions, cellulose levels corresponded to groundnut shells as the best biomass material for producing biochar and biosynthetic gas.

## 5.2 Recommendations

It is recommended that pyrolysis of groundnut shells, coffee and rice husks at optimal conditions be adopted for biochar and biosynthetic gas production. Further studies should be conducted on optimizing the yields of bio oil from pyrolysis using similar factors used in the present study, however its collection needs first to be addressed for the instrument present in the laboratory before optimization can be considered.

Studies can also be conducted in order to find out the impact of the internal configuration of the tubular glass furnace on pyrolysis of biomass compared to other conventional and custom-designed reactor configurations such as fluidized bed pyrolysis reactors, the length of the furnace tube increased the retention time of biosynthetic gas.

Other than cellulose content, other intrinsic characteristics of biomass such as bulk density and fixed carbon content can be investigated for their collective impact on the yields of biochar, biosynthetic gas and bio oil, as well as how they can be suitably optimized so as to ease the scaling up of the pyrolysis process for commercial production of chemical feed stocks and biofuels.

### 5.3 Limitations.

The design of the pyrolysis reactor could not allow collection of the liquid products. This was a big challenge in the determination of the yields of the liquid products given the constraints in the design of the glass tubular furnace which prevented liquid product recovery and hence quantification of bio-oil produced. Optimization was therefore only conducted for biochar and biosynthetic gas. However, the adapter at the collecting end of the tubular furnace can be considered for reconfiguration to include a trap for retaining liquid products.

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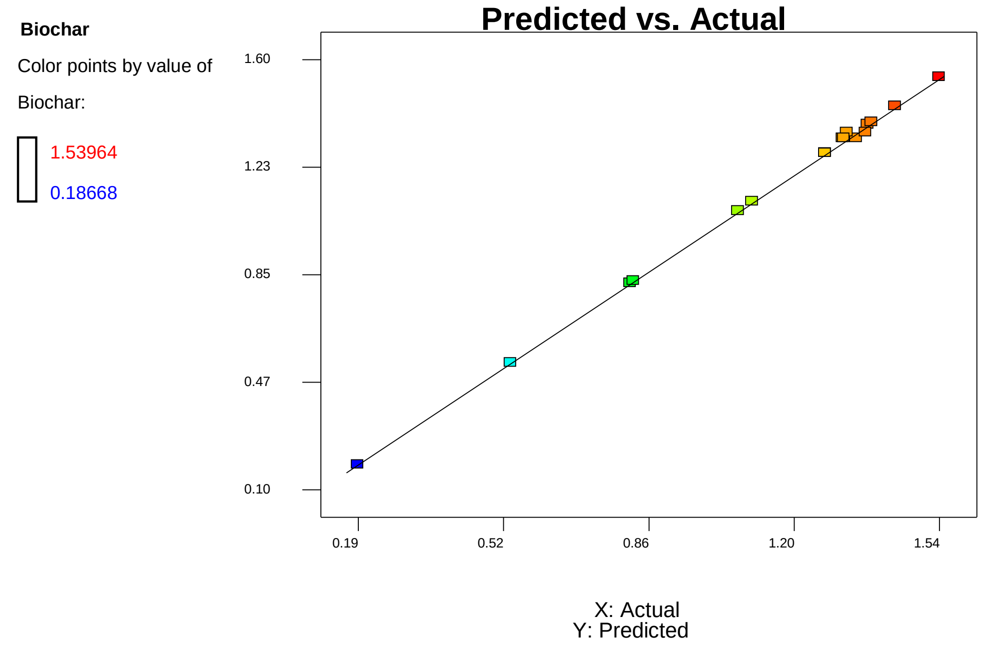
# Appendix 1: Raw data from analysis of groundnut shell, coffee and rice husk

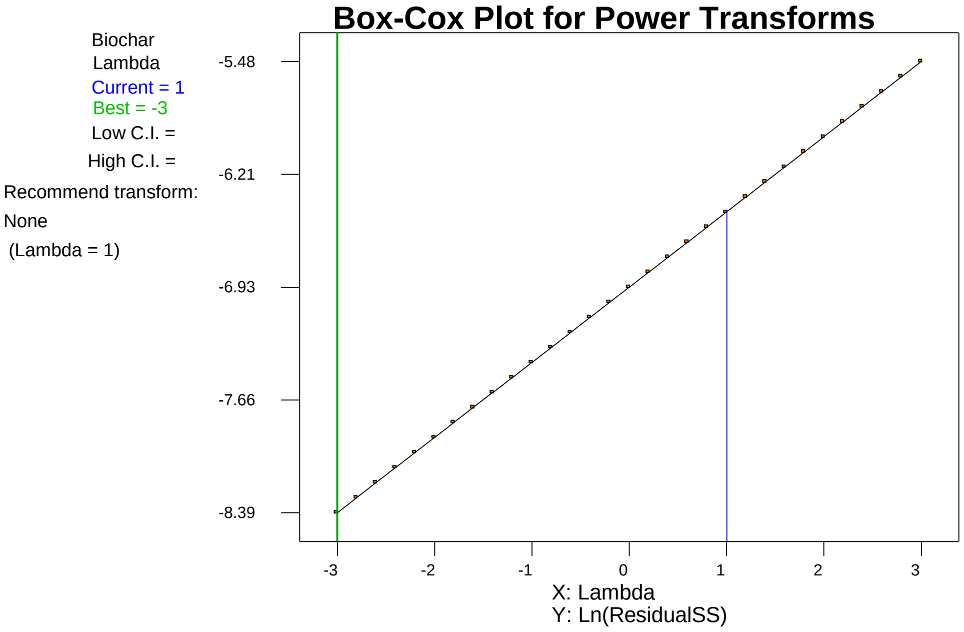
| Dry basis | Total solids % | Moisture % | Ash % | Extractives % | Volatile matter % |
|---|---|---|---|---|---|
| GH1(Groundnut shell) | 88.1032 | 11.8968 | 3.7780 | 1.9296 | 96.9185 |
| GH2(Groundnut shell) | 86.3076 | 13.6924 | 3.5593 | 2.5578 | 96.3453 |
| GH3(Groundnut shell) | 87.8361 | 12.1639 | 3.9344 | 1.8748 | 96.7209 |
| GH4(Groundnut shell) | 87.5828 | 12.4172 | 3.4963 | 2.2078 | 96.5533 |
| GH5(Groundnut shell) | 87.7379 | 12.2621 | 3.4071 | 2.6383 | 96.1254 |
| RH1(Rice husk) | 89.6241 | 10.3759 | 21.8201 | 3.6772 | 77.2423 |
| RH2(Rice husk) | 89.6510 | 10.3490 | 23.3114 | 3.4576 | 76.0491 |
| RH3(Rice husk) | 89.4394 | 10.5606 | 23.3427 | 3.8991 | 75.5371 |
| RH4(Rice husk) | 89.2867 | 10.7133 | 23.6771 | 3.1896 | 76.1092 |
| RH5(Rice husk) | 89.7120 | 10.2880 | 22.5661 | 2.9716 | 77.6270 |
| CH1(Coffee husk) | 88.2888 | 11.7112 | 2.0397 | 1.1220 | 97.4139 |
| CH2(Coffee husk) | 87.7794 | 12.2206 | 1.2409 | 2.0401 | 98.8042 |
| CH3(Coffee husk) | 87.7727 | 12.2273 | 1.8920 | 1.0044 | 98.5754 |
| CH4(Coffee husk) | 86.8799 | 13.1201 | 1.7046 | 1.0609 | 101.3627 |
| CH5(Coffee husk) | 87.7198 | 12.2802 | 1.0339 | 0.8695 | 98.7401 |

# Appendix 2: Raw data from analysis of hemicellulose, lignin and cellulose

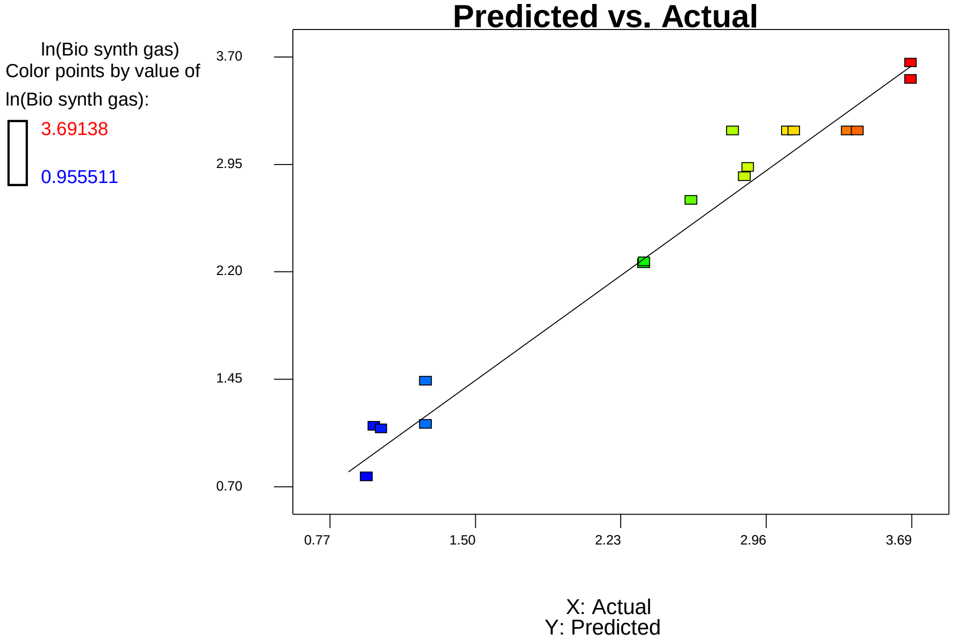
| **Hemicellulose** | | | |
|---|---|---|---|
| Run number | Rice Husk/w% | Coffee Husk/w% | Groundnut shell/w% |
| 1 | 57.7583 | 20.0519 | 24.4048 |
| 2 | 56.5347 | 19.1187 | 20.3356 |
| 3 | 54.4472 | 23.2507 | 22.6766 |
| 4 | 58.5666 | 18.5064 | 25.8337 |
| 5 | 60.1452 | 22.1580 | 23.4868 |
| **Lignin** | | | |
| 1 | 33.6366 | 35.0529 | 49.4384 |
| 2 | 41.0298 | 37.0887 | 42.0500 |
| 3 | 35.6305 | 35.2654 | 41.3580 |
| 4 | 35.7877 | 39.5517 | 39.1184 |
| 5 | 38.5812 | 33.6782 | 40.5010 |
| **Cellulose** | | | |
| 1 | 16.8922 | 41.7335 | 20.4493 |
| 2 | 24.3335 | 40.5117 | 31.4973 |
| 3 | 17.3195 | 38.5876 | 30.1562 |
| 4 | 21.2209 | 39.1763 | 29.3437 |
| 5 | 24.2640 | 42.2604 | 29.9668 |

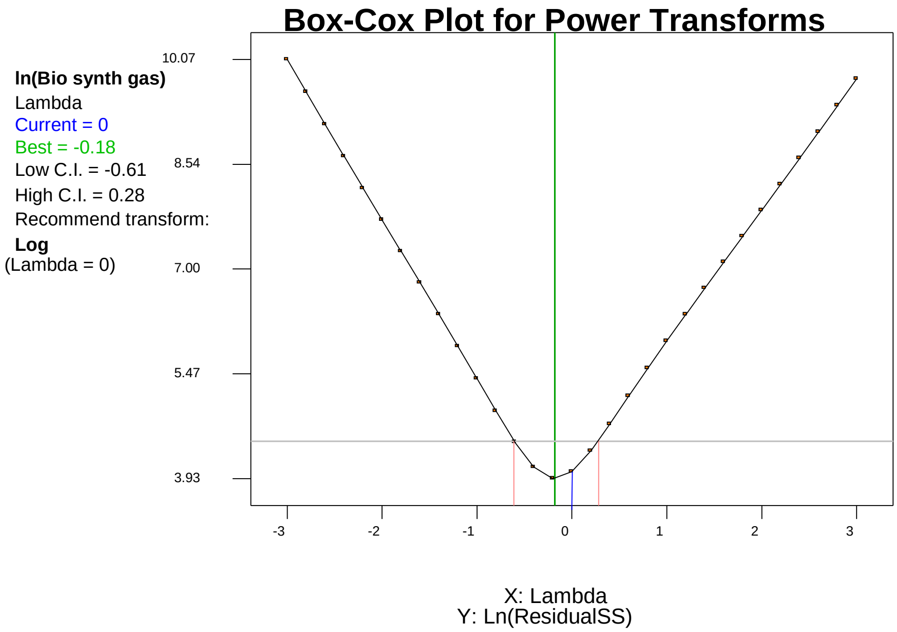
# Appendix 3: Statistical diagnostic plots for biochar





# Appendix 4: Statistical diagnostic plots for biosynthetic gas





# Appendix 5: Some of the photos taken during the research.

a) Standard test sieves used for Particle size screening

b) Particle size screening.

c) The tubular furnace pyrolizer (center), the vacuum pump (Right) and the U-tube manometer (left).

d) Sample of Biochar produced.