EFFECT OF STEAM EXPLOSION PRETREATMENT ON THE PYROLYSIS PROPERTIES OF PINEAPPLE (*Ananas comosus*) CROWN WASTE

By

Augustine Junior Sackey

(B.Sc. Natural Resources Management)

A Thesis Submitted to The Department of Agricultural and Biosystems Engineering, Kwame Nkrumah University of Science and Technology, Kumasi in partial fulfilment of the requirements for the award degree of

MASTER OF PHILOSOPHY IN AGROENVIRONMENTAL ENGINEERING

JANUARY, 2023

EFFECT OF STEAM EXPLOSION PRETREATMENT ON THE PYROLYSIS PROPERTIES OF PINEAPPLE (*Ananas comosus*) CROWN WASTE

By

Augustine Junior Sackey

(B.Sc. Natural Resources Management)

A Thesis Submitted to The Department of Agricultural and Biosystems Engineering, Kwame Nkrumah University of Science and Technology, Kumasi in partial fulfilment of the requirements for the award degree of

MASTER OF PHILOSOPHY IN AGROENVIRONMENTAL ENGINEERING

JANUARY, 2023

DECLARATION

I hereby declare that this submission is my work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma at Kwame Nkrumah University of Science and Technology, Kumasi or any other educational institution, except where due acknowledgement is made in the thesis.

Augustine Junior Sackey (PG5106520) ..………………………. ………………………

Name of Student and ID Signature Date

Certified by:

Prof. Francis Kemausuor ……………………… ..……………………

Name of Supervisor Signature Date

Certified by:

Prof. Francis Kemausuor ………………………. …..…………………

Head of Department Signature Date

ABSTRACT

The use of biomass as a substitute for fossil fuel has gained attention due to its renewability and availability. Biomass can be converted into fossil fuel equivalents through processes such as gasification, pyrolysis or hydrothermal liquefaction. However, before conversion into valuable fuel forms, several pre-treatment activities are carried out to make biomass amenable to the conversion process. One such pre-treatment approach is steam explosion where biomass components are broken down by high-pressure saturated steam. Pineapple crown waste is a typical biomass source that requires attention regarding disposal. During harvesting and processing activities, a lot of waste is generated from peels to crowns which may end up in landfills or burnt in the open. This can contribute to environmental problems and thus, exploitation of this waste's valuable uses is imperative. Therefore, this study seeks to determine the effect of steam explosion pre-treatment on thermal decomposition behaviour during the pyrolysis of pineapple crown waste. Three pre-treatment pressures of 6 bar, 8 bar and 10 bar were used for the process in a reactor. Each pre-treatment pressure had residence times varied at 5 min,10 min, and 15 min. Compositional analysis revealed the potential of pineapple crown waste biomass as a valuable resource for thermochemical applications. After the steam explosion pre-treatment, the pyrolysis study was done through thermogravimetric analysis (TGA) at a heating rate of 20 ˚C min^{-1}. TGA curves and derivative thermogravimetry (DTG) curves showed the decomposition pattern of the pineapple crown waste biomass components. Thermal degradation of the pineapple crown waste happened in four different stages. Moisture was released in the early stage, followed by the degradation of weak cellulose and hemicelluloses in the second stage. The third stage is where cellulose mainly decomposes and pyrolysis primarily occurs to produce bio-oil and gas. The final stage decomposed the remaining biomass components which were not degraded during the previous stages, forming char. Lignin is mostly degraded at this stage. Pronounced peaks were observed for each pre-treatment pressure at 15 min residence time. Calculation of kinetic parameters according to the Coats and Redfern model depicted an increase in frequency factor and a slight significant decrease in activation energy, especially for pre-treatment pressure at 10 bar. This shows that the thermal reactivity of the pineapple crown waste was improved with steam explosion pre-treatment. Also, higher pressure and increased residence time during pre-treatment contributed to the better decomposition of pineapple crown biomass during pyrolysis, and thus yield good products for biofuel utilization.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGEMENTS

To begin with, I thank the Lord Almighty for granting me the knowledge, wisdom, understanding, good health and sound mind to sail through graduate education and complete my project successfully.

I sincerely appreciate The Brew-Hammond Energy Centre for funding my graduate education under the project titled “Hybrid Waste to Energy as a Sustainable Solution for Ghana”. My earnest gratitude goes to my supervisor Prof. Francis Kemausuor for his constructive criticisms, propositions and counsel towards the success of my project. I am grateful to Dr Michael Commeh and Madam Gloria Sarfo for their guidance and coaching during the conduction of my experiments and for granting me access to the laboratory at all times.

Finally, I extend my gratitude to Mr Solomon Asare, Mr Samuel Amoah, Mr Ayelzoe Thomas Akalali, Mr Kingsley Sackey, Mr Anthony Sackey and all my friends, family and colleagues who contributed to the success of my project, God bless you.

CHAPTER ONE

INTRODUCTION

1.1 Background to the study

The rise of urbanization and industrialization has increased the demand for fossil fuels like coal and crude oil (Panpatte and Jhala, 2019). These fuels tend to be expensive due to the supply and demand dynamics of countries like Russia, Iran, Saudi Arabia, and the United States on their market price (Victor, 2009). The process of obtaining fossil fuels also affect the sustainability of the environment from land degradation to air pollution, where harmful gases are released, contributing to the presence of greenhouse gases in the atmosphere (Perera, 2017). The non-renewable nature of petroleum fuels is causing the rapid exhaustion of fossil fuel resources. This has necessitated the shift in focus to the utilization of environmentally friendly and renewable ways of supplying fuels and energy. Popularly adapted sources of renewable energy include solar, wind, water and biomass. Biomass can substitute fossil fuels since it can produce equivalents of petrochemical products. These equivalents can be achieved by converting biomass into gaseous or liquified forms via gasification, pyrolysis or hydrothermal liquefaction. Due to the application of biobased energy or biofuel (fuel from plant matter) as fuel and in other value-added chemicals, it has attracted great interest and gained major importance (Hu and Gholizadeh, 2019).

Geographically, biofuels are more prevalent than fossil fuels, and as such will be largely from domestic sources and guarantee the stability of supply (Hahn-Hägerdal *et al*., 2006). As compared to fossil fuels, biofuels have a lower sulfur and nitrogen content thus producing less sulfur and nitrogen oxides. This property contributes to the maintenance of the carbon balance in the environment, alongside minimizing the impact on the environment, primarily climate change (Pattanaik *et al*., 2019). The agricultural sector is an area where biomass can easily be obtained. Countries like the United Kingdom and Germany grow energy crops such as corn and sugarcane to be used as feedstock for biomass plants to produce heat and electricity (Szarka *et. al*, 2021). However, agricultural activities like harvesting food crops lead to the generation of waste which can serve as feedstock for biobased energy generation. The quest for a clean and sustainable environment has brought about research into the advantageous utilization of agricultural waste. Without re-utilization of agricultural wastes, they are dumped, left on the field, or incinerated, creating further environmental pollution such as methane emission. One such way of reutilizing agricultural waste is through pyrolysis, where biomass can easily be transformed into transportable and storable liquid fuel. This liquid fuel (bio-oil) can be used to produce chemicals, heat and power. Pyrolysis is thus, the thermochemical conversion of organic material by heating in an atmosphere lacking oxygen, into solid materials (biochar), liquid substances (bio-oil), and gases (syngas).

Moreover, before the conversion of biomass, certain pretreatment activities are carried out to make the biomass more amenable to the pyrolysis process. Pretreatment may involve the use of chemicals, biological agents, heat, and mechanical means which may alter the composition of the biomass. This altering of composition enhances the grade of biomass, improving the output of pyrolysis products and the efficiency of the pyrolysis process (Amenaghawon *et. al*, 2021). Therefore, biomass pretreatment is a necessary step in biofuel production.

1.2 Problem Statement

Conventionally, biofuels are produced through pyrolysis which is the thermal decomposition of biomass in an inert atmosphere. Reports on pre-treatment practices have proved to affect the quality of biofuel. Three varieties of shrub willow were pyrolyzed and evaluated for the effect of using hot water extraction to pretreat biomass by Tarves *et al*. (2017). They reported that hot water greatly affected bio-oil composition more than bio-oil yield. A study conducted by Zheng *et al*. (2016) asserted that hydrothermal pretreatment enhanced bio-oil yield but lowered aldehydes, ketones and organic acids contents which aid in improving biofuel quality. Therefore, hydrothermal pretreatment such as steam explosion could be adapted to determine its effect on the pyrolysis behaviour of common wastes from pineapple fruit harvesting and processing. Pineapple is widely enjoyed as a fruit and as such produces waste during consumption. Pineapple sellers generate a lot of waste from the peels to the crown. The crowns are mostly discarded which may end up in landfill or burnt openly which contributes to air pollution. The potential of pineapple crowns as a feedstock could be explored for the production of biofuel.

1.3 Aim and specific objectives

This study is designed to determine the effect of steam explosion pretreatment on thermal decomposition behaviour on the pyrolysis of pineapple crown waste.

The specific objectives are to:

- Assess the composition of pineapple crown feedstock through ultimate, proximate, and chemical analysis.

- Investigate the influence of varying the pressure (6, 8, and 10 bars) and residence time (5, 10, and 15 mins) on pineapple crown feedstock during steam explosion treatment.
- Evaluate the effect of steam explosion pre-treatment on the decomposition kinetics such as activation energy and mass loss of pineapple crown feedstock through thermogravimetric analysis.

1.4 Justification

Production of quality biofuel is of importance to biofuel producers. Biofuel producers and scientists are continually searching for prudent ways to achieve this goal. Pre-treating through the steam explosion of organic matter (biomass) before the pyrolysis procedure is one of the potential ways of enhancing the quality of biofuel (Zheng *et al*., 2016). Focus has now shifted to sustainable energy sources with biomass energy as a typical source due to the unsustainable nature of fossils, like crude oil and coal, thus substitute for fossil should be as quality as possible to perform it function of producing clean and sustainable energy (Perera, 2017). Also, through photosynthesis, plant sources capture almost the same quantity of carbon dioxide while maturing as it is released during burning, making biomass a carbon-neutral source of energy. The outcome of this study will help provide an understanding of the possibility of producing quality biofuel from pineapple crown waste.

CHAPTER TWO

LITERATURE REVIEW

2.1 Biomass

Biomass encompasses plants and animal materials that contain carbon in organic form and can be used for renewable energy generation. Developing countries make use of biomass for cooking and heating (Bensch *et al*., 2021). Exploration of fossil fuels causes the release of harmful gases into the atmosphere and as such wealthy nations are adopting biomass fuels for transportation and for electricity generation to avoid these harmful gas emissions (Hu and Gholizadeh, 2019). Biomass stores solar energy chemically which results from photosynthesis (van Bel *et al*. 2003). Biomass can be obtained from various sources as it is abundant in nature. Geographically, biomass is evenly distributed and as such it provides security of supply to a larger extent (Hahn-Hägerdal *et al*., 2006). Hence, using biomass as a source of energy generation is sustainable as it is readily available.

2.2 Sources of biomass energy

Biomass sources involve non-petrified and decomposable organic substances made by animals, plants and microorganisms (Garba, 2020). Sources of biomass are categorized into four major types with some listed examples below:

1. Agricultural residues – wheat straw, soybean stalk, rice straw, corn stover, etc.
2. Energy crops – sugarcane, switchgrass, duckweed, sweet sorghum, algae, and cattail.
3. Forestry residues - sawdust, woody plants, and chips.
4. Processing waste – wastes from the processing of crops, food, wood (sawdust), animal manure, paper (black liquor from pulp and paper mills), cotton as well as municipal solid waste.

2.3 Biomass conversion methods

Various methods can be used to convert biomass into heat, renewable liquid, and gaseous fuels (Garba, 2020). As biomass is made up of stored energy, utilizing the energy requires certain procedures to release the energy. These procedures alter the composition of biomass by breaking down the structural biomass components, to release the stored energy. Converting biomass is largely dependent on the characteristics of the biomass and the desired end product (Sansaniwal *et al*., 2017). Improving existing conversion methods and developing alternative conversion methods to utilize more biomass for energy is a growing concern for researchers

(Lee *et al*., 2019). Releasing stored energy in biomass is done through various processes, including:

- Thermochemical conversion
- Chemical conversion
- Biochemical conversion

2.3.1 Thermochemical Conversion

Thermochemical conversion involves the use of heat or thermal energy to decompose the chemical makeup of biomass. The thermochemical conversion techniques include combustion in ambient air, gasification in less air, pyrolysis in an inert atmosphere, and hydrothermal liquefaction.

2.3.1.1 Combustion

In combustion, biomass is directly burned while being exposed to air (oxygen) to produce heat. This technique is commonly used in converting biomass to useful energy. Biomass undergoes combustion to produce flammable vapours, which burn resulting in flames. This burning leaves behind charcoal as a by-product, which is burnt in a pressurized air supply to increase heat production (Jenkins *et al*., 2019). The hot combustion gases are transported via a heat exchanger to generate hot water, hot air, or steam. Occasionally the hot combustion gases are utilized directly to dry products. The various biomass classifications can be directly burnt to heat buildings and water, produce heat for industry, and generate electricity in steam turbines. Optimal oxygen contact with biomass fuel ensures the efficiency of combustion. Combustion leads to the evolution of water vapour and carbon dioxide alongside smoke, tars, and alkaline ash particles. Reduction of these emissions and efficient management of their probable effects are imperative in the construction of environmentally acceptable biomass combustion systems (Jenkins *et al*., 2019).

2.3.1.2 Gasification

Gasification is the process of heating organic materials with insufficient oxygen or steam at high temperatures and pressures to produce fuel known as synthetic gas or syngas (Molino *et al*., 2016). Temperatures for gasification are mostly from 750 –1100 ˚C. Syngas can be defined as a hydrogen-rich and carbon monoxide gas with the potential of being used for heating, for powering diesel engines, and generating electricity in gas-operated turbines (Speight, 2019). Syngas can also be refined into liquid fuels such as gasoline or ethanol.

Gasification takes place in a gasifier where the feedstock oxidizes to produce syngas alongside carbon dioxide, methane, water vapour, char, slag, and trace gases (depending on the composition of the feedstock) (Molino *et al.*, 2016). Trace metals and sulfur or acid gases are removed from the syngas through purification or cleaning. Before the waste is put in the gasifier, it is cut or ground to reduce its size and dried to minimize the usage of energy (Kataki *et al.*, 2015).

2.3.1.3 Pyrolysis

Pyrolysis is termed as the thermochemical conversion of organic material by heating in a system devoid of oxygen, into products such as biochar, bio-oil, and gases. The temperature for pyrolysis is usually from 400 – 600 ˚C (Adhikari *et al*., 2018). Historically, charcoal has been formed through pyrolysis. In indigenous societies of South America and Africa the organic material, usually, wood is carbonized in a mound of soil cover, to reduce the oxygen content around the organic material (Dutton, 2020). High carbon material remains which is commonly used as a source of heat for cooking with low volatility (Adhikari *et al*., 2018). This high-carbon material can also be used for soil amendment. This process of converting organic material to high-carbon material is also known as torrefaction or slow pyrolysis. Here, comparatively low temperatures (200-300 ˚**C**) are used in the pyrolysis process in the absence of oxygen (Dutton, 2020). Heating during torrefaction is done at a slow rate of less than 50 ˚C/min for intervals of hours to days; releasing volatiles and leaving behind a rigid carbon structure. Water, which can impede the calorific value of fuel is removed in the early stages of torrefaction, and subsequently a loss of H_2, CO, CO_2, and CH_4 in low quantities. This leads to the retention of nearly 70% of mass with 90% of the energy content. The carbonaceous material can be stored for a long period as it does not attract water.

2.3.1.4 Types of pyrolysis

There are three types of pyrolysis namely;

1. **Conventional/slow pyrolysis**: Thermal decomposition occurs in an oxygen-deficient atmosphere at moderate to high temperatures (400 -500 ˚C) with a low heating rate with a long residence time. This process yields gases, char, and bio-oil (tar). The main aim of slow pyrolysis is to produce char and as such little oil (tar) is produced (Amenaghawon *et al*., 2021).

2. **Fast pyrolysis**: This occurs in an oxygen-deficient atmosphere at moderate to high temperatures (400 – 650 ˚C). Fast pyrolysis yields condensates of liquid substances (30-60%); gaseous substances (H_2, CO, CH_4, CO_2, and light hydrocarbons)- 15-35% and solid char (10 – 15%) (Dickerson and Soria, 2013).
3. **Ultrafast pyrolysis/flash pyrolysis:** Here, thermal decomposition occurs at elevated heating rates varying mostly from 100-10,000 ˚C/s with a brief residence time. The products include liquid condensates - 6 ~10-20%; gases – 60-80%; and char (10-15%) (Dutton, 2020).

2.3.2 Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is a thermal altering process where biomass (wet) is converted into the oil with semblance to that of crude source referred to as bio-oil, using high pressure and medium temperature (Zhang and Chen, 2018). Crude-like oil from this conversion has energy density at a higher level and a heating value at lower levels of 33.8-36.9 MJ/kg and percentages of renewable chemicals and oxygen at 5-20 wt% (Tzanetis *et al*., 2017). The quality of products and yield is improved by involving homogenous and/or heterogeneous catalysts (Tzanetis *et al*., 2017). The hydrocarbons in organic substances namely; peat (lignite) and biomass are transformed thermochemically into low viscous and highly soluble hydrophobic compounds. The conditions of processing during hydrothermal liquefaction determine whether the resulting fuel can be used for heavy machinery operations, like in train and marine ship engines. The resulting fuel can also be upgraded for use as transportation fuels (gasoline, diesel or jet fuels). Hydrothermal liquefaction applications are mostly conducted within 250 – 550 °C temperatures and pressures of 5-25 MPa with catalysts for 20-60 minutes albeit in hydrothermal liquefaction applications, lower or higher temperature conditions can be used to optimize liquid or gas yields, respectively (Fang *et al*., 2022). Depending on the conditions of liquefaction, pressures and temperatures cause the subcritical or supercritical nature of water present in biomass, thus acting as a reactant, solvent, and catalyst to facilitate the reaction of biomass to bio-oil. Research has reported hydrothermal liquefaction as a means of converting any biomass into bio-oil since it does not require biomass to be free of water, there have been tests of the varying biomasses from agriculture and forestry residues, sewage sludges, food processing wastes, to new non-food biomass sources such as algae (Sahu *et al*., 2020). The standard and output of oil from the process are however influenced by the contents of hemicellulose, cellulose, protein, and lignin in the feedstock.

2.3.2.1 Differences between Pyrolysis and HTL

Hydrothermal liquefaction is quite different from pyrolysis as it processes biomass of wet nature, producing an energy-dense bio-oil twice that of pyrolysis bio-oil. Although pyrolysis and HTL have similarities in operation, biomass is required to be dry to increase the yield (Hognon *et al*., 2015). Water content in pyrolysis leads to the vaporization of the heat of the organic material at a higher rate, increasing the energy needed to degrade the biomass. For a successful pyrolysis process, the moisture content should be below 40% to process biomass to bio-oil. Reducing the water content in biomass such as tropical grasses (water contents as high as 80-85%) will require a significant amount of pretreatment, and even further treatment for aquatic species, with water contents as high as 90% (Hognon *et al*., 2015). In HTL, carbon contents of the feedstock are maintained up to 80% in the resulting bio-oil in a single pass (Kumari *et al*., 2021). HTL bio-oil has a good chance of producing drop-in qualities such that it may be delivered directly through existing petroleum infrastructure (Dutton, 2020).

2.3.3 Properties of bio-oil

Bio-oils may have similar physical characteristics (dark and tar-like with an odour) as petroleum crude oils but they do not mix (Dutton, 2020). Bio-oils are denser than water with a heating value of 13-18 MJ/kg and a high-water content (20-30%). Also, the oxygen content of bio-oils is high (35-50%), which causes high acidity (Dutton, 2020). Bio-oils have substantial solid residues (up to 40%) and are viscous (20-1000 cp @ 40 °C) (Panwar and Paul, 2021). Bio-oils in storage can be oxidatively unstable as they can polymerize or agglomerate which can lead to viscosity increase and volatility.

2.3.4 Upgrading of bio-oil

Due to the instability of bio-oils as a result of their high-water content, high acid content, and high oxygen content, it is important to upgrade them to remove these issues. Upgrading of bio-oil takes place physically and chemically. Physically, bio-oils are treated through filtration to remove char and emulsification of hydrocarbons for stability (Yang *et al*., 2014). Chemically, bio-oils are treated through esterification to remove corrosive acids: where the bio-oil is reacted with an alcohol to form esters; through catalytic deoxygenation/hydrogenation; through thermal cracking; through physical extraction, and through gasification. A process known as hydrotreating is adapted to upgrade bio-oil from fast pyrolysis. In hydrotreating, hydrogen at raised conditions of temperature and pressure in the presence of a catalyst is used to produce renewable fuels (gasoline, diesel, and jet fuel) (Dutton, 2020).

2.4 Chemical conversion

Chemical agents are usually used in chemical conversion to change biomass to liquified fuels. A known chemical conversion process called transesterification is used to produce biodiesel. This chemical transformation process valorizes animal fats, vegetable oils, and greases into fatty acid methyl esters (FAME) which are transmuted into biodiesel (Zarli, 2019).

2.5 Biochemical conversion

Biochemical conversion employs bacteria, enzymes, and other microbes in the conversion of biomass to useful forms such as ethanol and methane. The major forms of biochemical conversion include fermentation and anaerobic digestion.

2.5.1 Fermentation

Fermentation is the process whereby organic waste is converted into alcohol or acid (ethanol or lactic acid) in the absence of oxygen (Kumari *et al*., 2021). Traditionally, fermentation is done to produce ethanol using sugar crops; however, organic materials such as starchy crops or lignocellulosic biomass can be used (Pascault *et al*., 2012). The process occurs in the presence of yeast like *Saccharomyces cerevisiae* at atmospheric pressure and ambient temperature (Yukesh Kannah *et al*., 2020). The ethanol produced is a clean source of fuel for transportation.

2.5.2 Anaerobic Digestion

Anaerobic digestion deals with organic matter decomposition in an oxygen-starved environment, through the action of various types of anaerobic microorganisms to produce renewable natural gas (Biogas) (Kumari *et al*., 2021). Anaerobic digestion is common in numerous natural environments namely peat bogs, marine water sediments, or stomachs of ruminants (Sikora, 2021). Biogas systems make use of the anaerobic digestion procedure resulting in the production of biogas and the digestate. Varying kinds of feedstock (substrate) (e.g., organic wastes and animal slurries from food and agriculture industries) are mostly mixed for the production of biogas, the process is known as co-digestion which is common in conventional biogas operations (Kumari *et al*., 2021). When biogas is properly treated, it has the same uses as natural gas from fossil fuels and can be directly applied in spark-ignition gas engines and gas turbines, and also for the production of chemicals through dry reforming (Damyanova and Beschkov, 2020).

2.6 Pretreatment of biomass

Conversion of biomass is not done without pretreatment activities to make the biomass more amenable to the conversion process. As biomass is made up of lignocellulosic components, they affect the converted product in numerous ways. For instance, the cellulose and hemicellulose components contribute to bio-oil formation and lignin is responsible for the formulation of char in pyrolysis (Amenaghawon *et al*., 2021). There are several pretreatment activities and they can be classified into five major groups namely;

1. Physical pretreatment
2. Biological pretreatment
3. Chemical pretreatment
4. Thermal pretreatment
5. Physicochemical pretreatment

2.6.1 Physical pretreatment

This involves activities like crushing, washing, densification, and extrusion performed on biomass to alter its original form. To produce a high oil yield during pyrolysis washing of biomass is necessary as most alkaline components that can be extracted as alkali easily dissolves in water (Scott *et al*., 2000). Biomass can be minimized into smaller sizes by crushing and sieving to get the desired particle sizes for the pyrolysis process. Crushed biomass causes an increase in surface area per unit mass which leads to proper heat and mass transfer (Wang *et al*., 2017). Also, in physical pretreatment biomass can be compacted to enhance storage, handling, and transportation (Wang *et al*., 2017). The compaction process is known as densification, where biomass materials such as straws, wood chippings, and sawdust are compacted into uniformly packed solids known as pellets or briquettes. Biomass for pyrolysis has been compacted using a briquette press, pellet mill, and screw extruder (Tumuluru *et al*., 2011).

2.6.2 Biological Pretreatment

Pretreatment by biological means is a slow, safe, and environmentally friendly process with low energy requirements used for the pretreatment of biomass. The widely used fungi include;

soft-rot fungi, brown-rot fungi, and white-rot fungi (Rahmati *et al.*, 2020). The fungi are responsible for degrading lignin and hemicellulose and cellulose. The by-products of degradation by fungi are water and carbon dioxide. Brown-rot degrades cellulose while soft and white-rot fungi target both cellulose and lignin (Kumar *et al.*, 2009). White-rot fungi have a high lignin-degrading ability because of the activity of lignin-degrading enzymes (laccase and peroxidases) (Kumar *et al.*, 2009). Also, the emission of $SO_{x,}$ an environmental pollutant is inhibited when rot fungi are used as a pretreatment measure (Nowakowski *et al.*, 2010). Rot fungi pretreatment causes the biomass to be compacted making it more susceptible to pyrolysis concerning energy-saving (Rahmati *et al.*, 2020).

2.6.3 Chemical pretreatment

Inorganic minerals in biomass can interfere with their conversion into useful forms. These inorganic minerals can be removed by chemical pretreatment techniques such as acidic, basic (alkaline), carbon dioxide treatment, ionic liquids, Organosolv, and ozonolysis. Chemical pretreatment involves the use of solvents or a combination of reagents to cause a change physically or chemically in the structure of biomass. The various forms of chemical pre-treatments are briefly described below;

2.6.3.1 Acid pretreatment

Dilute and concentrated acids are employed to carry out acid pretreatment. The procedure is performed by using either a blend of low temperature and concentrated acid (30-70% and 40 ˚C) or varied instances involving dilute acid and high temperature (e.g., 0.1% and 230 ˚C) (Hu and Gholizadeh, 2019). Due to the high crystalline nature of cellulose, extreme circumstances such as heat treatment or acid treatment, or a combination of both are required to break down cellulose to facilitate change into value-added products (Amenaghawon *et al*. 2014). Employing dilute acid in acid pretreatment does not require the acid to be recycled as the reaction process is usually fast, whereas acid recovery is required when concentrated acid is used as the process is slow owing to its toxic and corrosive nature (Amenaghawon *et al*. 2014). Inorganic (mineral acids) such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and nitric acid (HNO_3) as well as organic acids such as acetic acid (CH_3COOH), propionic acid (CH_3CH_2COOH), and formic acid (HCOOH) have been used for acid pretreatment (Kumar *et al.*, 2009; Den *et al.*, 2018).

2.6.3.2 Alkaline pretreatment

Alkaline solutions that have been diluted, such as calcium hydroxide, Ca $(OH)_2$, sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), etc. are used in alkaline pretreatment under working parameters of 60 ˚C – 90 ˚C temperature, 10 – 60 min. retention time, 1–3 MPa pressure, and a liquid-solid ratio of 1% – 2% w/w (Mohammed *et al*., 2017). During pretreatment, alkaline agents facilitate the formation of char. In the presence of the alkaline solution, acidic elements react to form a salt, serving as a catalyst for char formation and thus reducing the yield of bio-oil (Carrillo *et al*., 2005).

2.6.3.3 Carbon dioxide pretreatment

A subcritical fluid of carbon dioxide (CO_2) at relatively minimal temperatures and high pressures is used to pretreat biomass for several minutes. The CO_2 is introduced into the biomass at increased conditions of pressure to cause a hike in the digestibility of biomass (Behera *et al*., 2014). The high pressure causes the explosion of the biomass structural components and augments the surface area, increasing exposure to further processing (Kumar *et al*., 2009).

2.6.3.4 Ionic liquid pretreatment

Ionic liquids are liquids made up of positive and negative ions with distinctive properties such as non-flammability, low volatility, high thermal stability, efficient recyclability, and less toxicity. With the application of mild heat, they are used as green chemicals to pretreat biomass (Putro *et al*., 2016). Solvents used during ionic liquid pretreatment are highly recoverable as they possess low vapour pressure (Elgharbawy *et al*., 2016). Some notable ionic liquid examples include 1,3-dialkyl imidazolium, 1-ethyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium diethyl phosphate (Raj *et al*., 2018). Ionic liquor is the byproduct of ionic liquid pretreatment, which mostly consists of lignin, hemicellulose, and a solidified fraction enriched in cellulose (Financie *et al*., 2016).

2.6.3.5 Organosolv

Organosolv is a shortened term for organic solvent pretreatment which makes the extraction of biomass constituents to be employed as pre-extracted substances for the alteration into biofuels and the formulation of value-added chemicals (Putro *et al*., 2016). This pretreatment method is mainly targeted at extracting highly pure lignin-containing traces of aliphatic hydroxyl and phenolic compounds from biomass using acidic or alkaline catalysts (Macfarlane *et al*., 2014).

A mixture of an inorganic acid catalyst (HCl and H_2SO_4) and an organic or aqueous-organic solvent is used to delignify biomass during the organosolv pretreatment process, facilitating cellulose access (Mielenz, 2020). Some known organic solvents used in the Organosolv procedure include; ethanol, methanol, acetone, glycerol, and 1,4-dioxane (Liu and Abu-Omar, 2021). As a catalyst for the organosolv process, organic acids such as acetylsalicylic, oxalic, and salicylic acid were also synthesized. (Maurya *et al*., 2015).

2.6.3.6 Ozonolysis

Biomass is highly de-lignified during ozonolysis causing alterations in biomass structure to increase digestibility in subsequent processing (Travaini *et al*., 2015). In ozonolysis, biomass is exposed to ozone (O_3) which reacts with lignin leading to a removal of approximately 80% of the lignin present in biomass (Travaini *et al*., 2015). Ozone pretreatment possesses several advantages such as no production of inhibitory compounds, no use of required chemicals, mild operating conditions, and low effects on carbohydrates (Kumar and Sharma, 2017).

2.6.4 Thermal pretreatment

Most biomass contains various levels of moisture which will require a significant amount of energy to remove the moisture during conversion processes like pyrolysis (Amenaghawon *et al*., 2021). Drying the biomass before pyrolysis can help conserve energy and prevent the reactor from getting choked due to excess moisture in the substrate or feedstock as well as heightening the energy content of the formulated bio-oil (Cummer and Brown 2002). A typical thermal pretreatment approach before pyrolysis is known as torrefaction. Heat at temperature ranges of 200 ˚C–300 ˚C is applied to biomass in an oxygen-free environment. Energy is densified after torrefaction as 85% of the pervious energy value of biomass and 70% of biomass weight remains as torrefied biomass (Mamvura and Danha, 2020; Mukhtar *et al*., 2020). This torrefied biomass possesses benefits over raw biomass such as higher resistance to biological deterioration, high energy content, reduced size, and ease of feeding to the pyrolysis reactor (Gent *et al*., 2017).

2.6.5 Physicochemical pretreatment

Physicochemical pretreatment is a unified pretreatment approach which employs both physical and chemical pretreatment for efficient pretreatment of biomass. This technique has proven effective in breaking down biomass but may leave behind by-products including weak acids, furan derivatives, and inorganic and phenolic compounds that can impede the breakdown of sugar and fermentation (Rahmati *et al*., 2020). Physicochemical pre-treatments include wet oxidation, ammonia fibre explosion, solvolysis, and steam explosion. Briefly discussed below are the various physicochemical pretreatment methods;

2.6.5.1 Wet oxidation

In wet oxidation, air (oxygen) and water are used at high-temperature conditions (150-300 ˚C) and pressures (2-15 MPa) to influence the structure of biomass (cellulose, hemicellulose, and lignin). Free radicals are produced when oxygen is present as well as maximization of reaction rates (Rahmati *et al.*, 2020). Wet oxidation does not require dewatering of biomass before treatment making it advantageous over other alternatives.

2.6.5.2 Ammonia fibre explosion

Aqueous ammonia is used at elevated temperatures with an abrupt reduction of pressure. The reduction in pressure will disrupt the biomass structure. It is a well-suited pretreatment method for herbaceous and agricultural residues (Galbe *et al.*, 2011). Ammonia fibre explosion does not produce inhibitory compounds during pretreatment. Ammonia is highly volatile and this property makes it easily recoverable allowing enzymatic hydrolysis of the remaining dried biomass.

2.6.5.3 Plasma pretreatment

In plasma treatment, an ionized gas made up of electronically stimulated atoms and molecules, charged particles, radicals, and UV rays is used. The dry (gas phase) cycle incites both physical and chemical changes in the biomass structure. Using the plasma technique is characterized by the absence of pollutants, as plasma uses electrical energy to produce highly reactive ionized gas which can be used for numerous purposes (Benoit *et al.*, 2011).

2.6.5.4 Solvolysis

Solvolysis is also termed hydro thermolysis, aqueous fractionation, liquid hot water, and aquasolv. In solvolysis, pure water or deionized water is used at elevated temperatures for the hydrolysis of biomass (Ikegwu *et al.*, 2021). This brings about the penetration of the biomass cell wall to break down cellulose, and hemicellulose, and degrade lignin. Solvolysis can be considered environmentally benign as it does not involve the introduction of chemicals to break down biomass. Despite the advantage of not requiring the dewatering of biomass before solvolysis, it brings about an increase in energy consumption and processing cost (Ikegwu *et al.*, 2021).

2.6.5.5 Steam explosion pretreatment

Steam explosion pretreatment makes use of high-pressure saturated steam to react with biomass where the pressure is decreased at a point causing the biomass to explode as it decompresses. It is a commonly used biomass pretreatment method due to its low utilization of energy and less usage of chemicals (Amenaghawon *et al*., 2021). Biswas *et al*. (2011) conducted a study where the steam explosion was used to pretreat Salix wood chips at different pretreatment conditions. They concluded that both pyrolysis characteristics and biomass structure were altered because of the steam explosion pretreatment activity. Gu *et al*. (2014) investigated the change in poplar wood sawdust components after steam explosion pretreatment. They reported that pretreatment with steam explosion could make biomass into a mid-level feedstock with favourable thermochemical application compared to the untreated poplar wood sawdust. A review conducted by Chen *et al*. (2015) revealed that combining steam explosion pretreatment with other pretreatment approaches could affect biomass characteristics and modify the disposition of products during the subsequent pyrolysis or hydrolysis.

Factors like temperature, moisture content, residence time, and particle size play important roles in steam explosion pretreatment (Kulshreshtha, 2022). Steam explosion pretreatment does not require the involvement of an acid catalyst except on softwood and permits the use of bigger particle sizes, thus making it potentially applicable for industrial settings (Pielhop *et al*., 2016). A disadvantage of the steam explosion pretreatment, however, is that some degradation products created during the procedure can interfere with subsequent conversion activities (Baruah *et al*., 2018). Pressures used for steam explosion range from 0.69 - 4.83 MPa and higher temperatures of about 260 – 285 ˚C for short periods usually several seconds to a few minutes (Rahmati *et al*., 2020). Small cracks in biomass structure, to total defibrillation of the biomass fibres, can occur when temperature and residence time is varied (Hu and Gholizadeh, 2019). Partial breakdown of cell wall components can occur as acetic acid can be produced during the explosion process (Kumar *et al*., 2009).

2.7 Description of *Ananas comosus*

Pineapple (*Ananas comosus*) is a popular sweet fruit produced in tropical and subtropical regions. In the Amazon basin of South America, pineapple is an indigenous fruit of Brazil and Paraguay but is now grown in many warm counties (Hossain, 2016). Countries noted for the primary production of pineapple include; Brazil, Costa Rica, India, the Philippines, and Thailand (Firățoiu *et al*., 2021). Cultivation of pineapple in Ghana is mostly centered in the

Greater Accra, Volta, Eastern and Central regions of Ghana (Williams *et al*.,2017). Ghana produces approximately 120,000 to 150, 000 tons per year of pineapple (GSS, 2008). Varieties of pineapple grown in Ghana are the MD2, smooth cayenne and the sugar loaf (Ankrah, 2021). The pineapple plant is a short-lived stoloniferous perennial with waxy, succulent, swordlike leaves surrounding its short and thick stem, and it produces tiny, trimerous, red or purple flowers on top of the stem (Oyedoko *et al*., 2020). The fruit, which takes about 20 days to develop, is a single, cone-shaped, juicy, and seedless product of fused berries, varying in size, shape, weight, and colour from green to reddish or yellow, with flesh ranging from nearly white to yellow (Assumi *et al*., 2021). The plant produces both aerial and basal suckers, the latter of which can be used for ratooning but yield less (Oyedoko *et al*., 2020). The morphological structure of the pineapple plant is shown in figure 1.

The past few years have seen an increase in demand for pineapple fruits and products worldwide (Kleeman, 2016). As a result of this demand, a tremendous amount of waste is being produced from the harvesting, processing, and consumption of pineapple (Hamzah *et al*., 2021). Most of the parts of pineapple such as the peels, crown, leaves, core, and stems end up as waste during processing, transportation, and storage activities (Baidhe *et al*., 2021). The volume of waste from pineapple and disposal techniques are of great concern. Waste from pineapple contains sugar, high moisture, albumins, lipids, and vitamins that are susceptible to microbial decadence thus contributing to environmental problems. The abundance of these wastes depicts the level of non-exploitation and as such are mostly discarded in landfills or burnt in the open as a mitigation technique (Rabiu *et al*., 2018). Pineapple waste is a good source of carbon and as such wine, vinegar, dye adsorbent, biofuel, organic acid, and biogas can be produced from it. Common techniques that can be used to manage wastes from pineapple include; pyrolysis, gasification, composting, and anaerobic digestion (Rabiu *et al*., 2018). Therefore, exploiting waste from pineapple into useful commodities could be the most sustainable approach to managing these residues due to their valuable qualities and components (Hamzah *et al*., 2021).

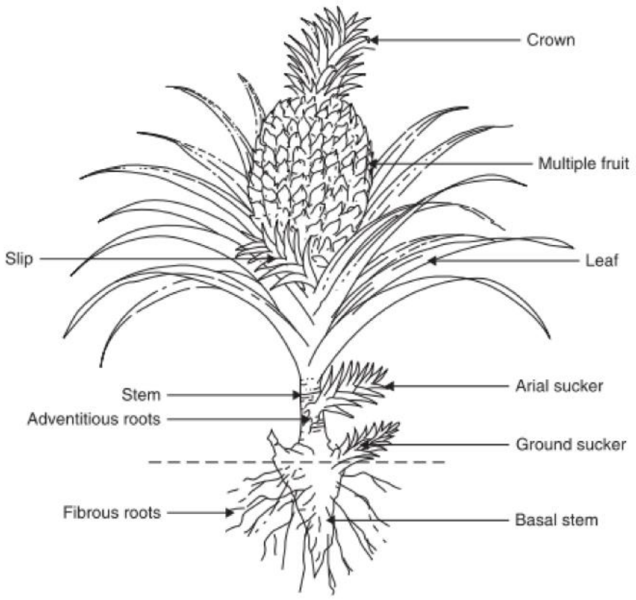


Figure 1.1: Morphology of Pineapple Plant
(Hamzah *et al*., 2021)

2.8 Kinetic study of biomass pyrolysis

The kinetic study of the biomass pyrolysis process is an important study to know the decomposition activities that occur during pyrolysis reactions and how the rate of reaction is related to the variables responsible for the pyrolysis process. In designing efficient reactors, knowing the pyrolysis kinetic parameters namely pre-exponential factor, activation energy, and reaction model is imperative. A thermogravimetric analyser (TGA) is mostly used to carry out kinetic studies. The TGA is used to carry out analysis by recording a sample's mass loss as a function of temperature under a monitored heating rate and gas condition. To assess the pyrolysis kinetics of biomass, differential thermogravimetric analysis (DTG) curves, which are produced from thermogravimetric analysis (TG) curves, have been used extensively (Kok and Ozgur, 2017). There are three major areas by which kinetic models can be grouped, they include; one-stage global decomposition models, which use a first-order irreversible reaction to represent the material's thermal degradation, single-step multiple reactions, and two-step models, which explain the primary and secondary reactions of the pyrolysis process. (Patwardhan, 2010). The kinetic models for biomass pyrolysis are usually obtained from model-fitting methods and model-free methods.

2.8.1 Model-fitting methods

Under model-fitting methods, various reaction models (differential or integral) are fitted into the general kinetic equation and regression analysis is used to estimate the pre-exponential factor (A) and activation energy (Ea). Curves generated from the equation fitted with different groups of kinetic parameters which closely fit experimental curves are taken into consideration as a potential remedy. A reaction model is mostly assumed in model-based procedures. The order of the reaction model is usually the first and nth-order. The classifications of model fitting methods are either the conventional (isothermal) technique or the non-isothermal approach. In the conventional method, the first determined best-fitting parameter is the rate constant (k), then subsequently activation energy (Ea) and frequency factor (A) which are computed from the Arrhenius equation. With regards to non-isothermal model-fitting methods, various methods such as; the direct differential method, Freeman-Carroll (difference-differential) method (Freeman and Carroll 1958), and the Coats-Redfern method (Coats and Redfern 1965) are adapted to establish the kinetic constants (activation energy, reaction model, and frequency factor).

2.8.2 Model-free methods

Model-free methods are also known as isoconversional methods and as such do not need any initial assumed model. The intercept of the linear equation slope bearing the reaction model's and frequency factor's parameters is used to evaluate the activation energy (Ea) of the reaction without the assumption of a model. However, it is also possible to estimate the frequency factor (A) from the intercept of the equation, although this estimation requires the presupposition of a model. As a result, model-free/isoconversional approaches usually solely provide activation energy numbers. Model-free techniques are derived from the isoconversional principle, according to which temperature is the primary determinant of reaction rate at fixed conversion. There exist two types of model-free categories: isothermal and non-isothermal. Isothermal incorporates both Friedman's and the conventional isoconversional procedures (Friedman 1964). Temperature integrals are used in non-isothermal techniques. These techniques include the modified Coats-Redfern approach, the Ozawa, Flynn, and Wall (OFW) method (Ozawa 1965; Flynn and Wall 1966); and the Vyazovkin (VYZ) (1999) method.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

This study was conducted at the General Chemical Laboratory of the Faculty of Renewable Natural Resources (FRNR), Kwame Nkrumah University of Science and Technology (KNUST), the Technology Consultancy Centre (TCC) - KNUST and the Department of Materials Science and Engineering Laboratory, University of Ghana, Legon. Freshly removed pineapple crown wastes of the sugar loaf variety were collected from a farm in Odumadze in the Ekumfi district, Mankessim Ghana. The pineapple crown wastes were obtained in march 2022.

3.2 Sampling and Processing of Materials

Pineapple crown wastes were air-dried and ground in a hammer mill and sieved through a 0.5 µm mesh. The moisture content of the milled samples was determined and the samples were stored in airtight vials until needed.

3.3 Compositional analysis

Ash, fixed carbon, and volatile matter proximate analysis was performed with a muffle furnace according to ASTM Standard D5142-02a (2002). The moisture content was determined according to ASTM E871-82 (2006). Ultimate analysis of carbon, hydrogen, sulphur and nitrogen content of pineapple crown waste was done using the wet-oxidation, titrimetric, turbidimetric and Kjeldahl methods respectively. Oxygen content was calculated by difference. Chemical analysis was done following the method described by Omoniyi and Olorunnisola (2014).

3.3.1 Moisture Content Determination

The moisture content in the pineapple crown waste was assessed using the oven-drying method. This was conducted at 105± 2 ˚C for 24 hours. Equation 1 was used to compute the moisture content;

$$\text{Moisture Content} = \frac{Wi-Wf}{Wi} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where:

Wi = original weight of the sample

Wf = final sample weight

3.3.2 Ash Content Determination

A mass of 5g of the sample was weighed into a pre-weighed crucible and placed inside a muffle furnace at 550 ˚C for 4 hours. The muffle furnace was maintained at a temperature below 200 ˚C for 20 min to allow for cooling. The hot crucible with the ash was removed from the furnace and deposited in a desiccator, cooled for an hour and weighed. Equation 2 was used to determine the ash content;

$$\% \text{ Ash} = \frac{Weight\ of\ ash}{weight\ of\ sample} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

3.3.3 Volatile Matter

Determination of volatile matter (VM) was done per ASTM D5832-98 (2014). 2g of the milled pineapple crown was put inside a crucible. The sample was then oven-dried at 105 ˚C and placed in a muffle furnace at 550 ˚C for 10 min, cooled in a desiccator and weighed afterwards. Equation 3 was used to calculate the volatile matter;

$$\text{Volatile matter (\%)} = \frac{Sample\ after\ drying\ at\ 105^{\circ}\text{C} - \text{Sample after drying at } 550^{\circ}\text{C}}{Sample\ after\ drying\ at\ 105^{\circ}\text{C}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

3.3.4 Fixed Carbon

The fixed carbon content was determined using the relationship below as described by Debdoudi *et al*. (2005);

Fixed Carbon = 100% - %Ash - %VM …………………… (4)

3.3.5 Carbon determination

A mass of 5g of milled sampled was weighed into an Erlenmeyer flask (500 ml). 10 ml of burette containing a solution of 1.0 N $K_2Cr_2O_7$ was tapped into the flask, and then an addition of 20 ml of concentrated H_2SO_4 was introduced. To ensure that the solution mixed well with all of the sample's particles, the mixture was swirled. The solution was given 30 minutes to cool. Then, 200 ml of distilled water and 10 ml of orthophosphoric acid were added. Additionally, 2.0ml of diphenylamine indicator was included. Thereafter, the mixture was titrated with 0.5 N ferrous sulphate solution until the colour transitioned to dark blue and finally to green. To account for the blank solution, the titre value was noted and adjusted to 10.5.

Equation 4, as described by Shaw (2006) was used for the determination of the percentage of carbon;

$$\% \text{ C} = \frac{M \times (V_{bl} - V_s) \times 0.003 \times 1.33 \times 100}{g} \text{ ………………………………………………... (5)}$$

Where;

M =Molarity of $FeSO_4$

V_{bl} = Volume of $FeSO_4$ blank titration

V_s = Volume of $FeSO_4$ sample titration

g = sample mass

0.003 = Carbon milli-equivalent weight (12/4000)

1.33 = Correction factor. This value was chosen as a result of the about 75% (100/75 = 1.33) efficiency of wet combustion of carbon to convert to the true carbon value.

3.3.6 Nitrogen Content determination

1g of milled sample was weighed into a long-necked Kjeldahl flask. 10 ml of distilled water was added and left to moisten for 10 min. 10 ml of conc. H_2SO_4 and one spatula of Kjeldahl catalyst was also added. Then after, digestion of the mixture was performed until it was clear, colourless, or light greenish. After letting the flask cool, the material was transferred into a 50 ml volumetric flask.

10 ml of the digest is pipetted into the Kjeldahl distillation apparatus, and 90 ml of distilled water is added. 40% NaOH (20 ml) was added. In a 250 ml conical flask, the distillate was collected over 10 ml of 4% boric acid and three (3) drops of mixed indicator. The distillate was then poured out into a 100 ml volumetric flask. The collected distillate (100 ml) was titrated with 0.1 N HCl till the blue colour changed to grey and then rapidly flashed to pink. The estimation of nitrogen content was done using Equation 5;

$$\textbf{\% N} = \frac{(a-b) \times 1.4 \times N \times V}{S \times t} \text{ …………………………………… (6)}$$

Where:

a = Volume of HCl for sample titration

b = Volume of HCl used in the blank titration

N = Normality of standard HCl

V = total volume of digest

S = mass of oven-dried sample taken for digestion

t = volume of aliquot taken for distillation (10ml)

3.3.7 Hydrogen determination

A sample of 3g was placed in a digestion flask. Acqua regia (10 ml) was added and then digested for 10 min. The content of the digest was then filtered into a volumetric flask (100 ml). 10 ml of the digest was measured into the Erlenmeyer flask and phenolphthalein indicator (5 drops) was administered. Titration to the pink endpoint of the digest was performed using 0.05 *N* NaOH. The volume of NaOH used was recorded. Hydrogen content was calculated according to Equation 6;

$$\textbf{\% H} = \frac{V \times 0.05 \times 100}{W} \text{ ……………………………………. (7)}$$

Where;

V = Titre volume of NaOH used (ml)

Normality of NaOH = 0.05 *N*

W= Sample weight

3.3.8 Sulphur Content

The turbidimetric method using a spectrophotometer was used to determine the total sulphur. Di-acid digestion was used to digest sulphur in the sample. 2ml of Serial standard prepared from pure sodium sulphate compound was pipetted into a labelled test tube. 0.5ml Gum acacia-acetic acid (GAAA) was measured in the test tube. The sample was incubated at room temperature for 30min and the turbidity intensity was read on the spectrophotometer at 420 nM.

3.3.9 Oxygen content determination

By deducting the percentages of carbon, hydrogen, nitrogen, and sulphur from 100%, the oxygen concentration was estimated.

3.3.10 Determination of Hemicellulose, Cellulose, and Lignin

To determine the chemical constituents (Cellulose, Hemicellulose and Lignin) of the raw sample, three major parameters were used namely Acid detergent Fibre (ADF), Neutral detergent Fibre (NDF), and Acid detergent Lignin (ADL).

3.3.10.1 Estimation of NDF

1g of the ground sample was introduced into a condensation flask alongside a cold neutral detergent solution (100 ml). 2ml of decahydronaphthalene and 0.5 g sodium sulphite was also added. The mixture was heated to boiling and refluxed for 60 min. The contents were then filtered and washed with hot water and washed twice with acetone. The leftover material was transferred to a crucible and dried at 100 ˚C overnight. The crucible with the content was cooled in a desiccator and weighed. Equation 7 was used to calculate NDF;

% NDF = $\frac{W}{S} \times 100$ ……………………………… (8)

Where;

W= Weight of the dried filtration residue

S = Weight of the sample

3.3.10.2 Estimation of ADF

100 ml of the acid detergent solution was added to a round-bottom flask along with 1 g of the ground sample. For 5 to 10 min, the mixture was brought to a boil. The heat was lowered to prevent foaming as boiling started. After the onset of boiling the mixture was refluxed for 1hr. The flask's contents were filtered and given two hot water rinses after being removed, swirled and cleaned. Acetone was then used to wash the filtrate to break lumps. The filtrate was repeatedly washed in acetone until it became colourless. The filtrate was then dried overnight at 100 ˚C and weighed after cooling in a desiccator. Equation 8 was used for the estimation of ADF;

% ADF = $\frac{W}{\boldsymbol{S}} \times 100$ ……………………………… (9)

Where;

W = Weight of fibre

S = Weight of sample

3.3.10.3 Estimation of ADL (Lignin content determination)

A 100 ml beaker was used to hold the ADF that was acquired from the preceding experiment. ADF obtained from the previous experiment was transferred to a 100 ml beaker. The content was covered with 72% H_2SO_4 and let to stand for 3 hours while being periodically stirred with a glass rod. Distilled water was used to dilute the acid, and a pre-weighed Whatman No. 1 filter paper was used for filtration. Thorough washing of the glass rod and the residue was done to remove the acid. The filter paper with the residue was dried at 100 ˚C and weighed after cooling in a desiccator. The filter paper was transferred to a pre-weighed crucible and incinerated in a muffle furnace at 500 ˚C for about 3 hours. The crucible was then cooled and weighed and ash content was determined. Equation 9 was used to estimate the ADL;

$$\textbf{\% ADL} = \frac{W1 - W2}{Original\ weight\ of\ ADF\ sample} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(10)}$$

Where:

W1 = Oven-dried weight of ADF sample after filtration with 72% H_2SO_4

W2 = Weight of ash

3.3.10.4 Percentage Cellulose and Hemicellulose Calculation

The percentages of cellulose and hemicellulose were calculated according to Omoniyi and Olorunnisola (2014);

% Hemicellulose = % NDF - % ADF ……………………………… (11)

% Cellulose = % ADF - % ADL …………………………. (12)

3.4 Steam explosion pretreatment

The steam explosion setup was made up of two main units: a steam generation unit and a reaction chamber. The steam generation unit was connected to the reaction chamber by hot water tubes fitted with valves. A discharge ball valve was situated at the base of the reaction chamber to release the steam exploded sample into a collector. 100 g of about 2-3cm cut pineapple crown waste was loaded into a reactor, the valve closed and steam was forced into the chamber at the required pressure. The steam-saturated pineapple crown waste was then discharged into a blow-down chamber after the desired residence time. This caused the macromolecules in the pineapple crown waste sample to undergo explosive breakdown as the pressure was reduced abruptly. Steam-exploded samples were then washed with water, airdried to get rid of the moisture and stored in airtight vials until needed. Three pre-treatment pressures were used: 6 bar, 8 bar and 10 bar. For each pre-treatment pressure residence, times of 5 min, 10 min and 15 min were used.

3.5 Thermogravimetric Pyrolysis Study-ASTM E1131, ISO 11358

Thermogravimetric analysis (TGA) was performed using a TA instruments SDT Q600 V20.9 Build 20 thermogravimetric analyser. 5mg of milled pineapple crown waste samples from steam explosion pretreatments and the untreated sample was placed in an alumina crucible. Samples were then calcinated at a temperature of about 1300 ˚C to reduce the effects of other impure constituents on the TGA curves. To ensure an inert atmosphere, nitrogen (99.99%) was passed at a flow rate of 50 $\text{mL}\cdot\text{min}^{-1}$ through the furnace. The furnace's initial setting was 30 ˚C. From 30 to 600 ˚C, the sample was heated linearly at a rate of 20 ˚C min^{-1}.

3.6 Calculation Method of TG kinetics

TGA data were analysed using the Coats and Redfern method. Computations were done using Origin pro software. The first-order rate equation for the reaction according to Coats and Redfern (1965) is;

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\frac{AR}{\beta E_a}\left[1-\frac{2RT}{E_a}\right]-\frac{E_a}{2.303RT} \text{ ------------------ } (13)$$

Where α is the fraction of sample decomposed at time t given by $\alpha = \frac{W_o - W_t}{W_o - W_f}$ .... (14)

W_o = Initial weight of sample at the start of decomposition

W_t = Weight of sample at any given temperature

W_f = Final weight of the sample after completion of the reaction

B = Linear heating rate

T = Absolute temperature

E_a = Activation energy

A = Frequency factor or Pre-exponential factor

R = Universal gas constant

From Equation (13) a graph is plotted between $\left[\frac{-\log(1-\alpha)}{T^2}\right]$ and $\frac{T}{1000}$ for the estimation of activation energy.

$-\frac{E_a}{2.303R} = -slope$ ----------------- (15), R = 8.314 J/mol. K

Ea = 2.303×R×slope

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Compositional Analysis

A compositional analysis is performed on biomass to assess the potential of biomass for biofuel applications. Analysis carried out on biomass to assess the potential includes proximate, ultimate, and chemical analysis. The proximate analysis (Table 4.1) lay out percentages of biomass that burn in solid (fixed carbon) and gaseous (volatile matter) states alongside the percentage of inorganic substances (waste material) known as ash (Nunes *et al*., 2018). The 10% moisture content (Table 4.1) recorded depicted the suitability of the pineapple crown waste biomass for pyrolytic and combustion processes (Laougé and Merdun, 2020). The volatile matter was found to be high (93.72%) in pineapple crown waste and ash content at 5.8%. Ignition of fuel is high when ash content is low and volatile matter is high (Patidar *et al*., 2022). On the other hand, higher ash contents increase the cost of processing, reduce the conversion of energy, delay the process of combustion, and cause disposal issues (Arenas *et al*., 2019). According to Patidar *et al*. (2022), fixed carbon content promotes the formation of heat during combustion, and as such fixed carbon content should be high enough to perform its function of formation of heat. This formation of heat relates to the production of char in the thermochemical conversion process (Islam, 2021). In other words, high fixed carbon signifies the potential of producing a high yield of char. Fixed carbon content recorded for pineapple crown waste was at a low content and as such may not help in the adequate formation of heat during combustion to yield char as a product.

The ultimate analysis (Table 4.1) shows that as the pineapple crown waste is undergoing volatilization during pyrolysis the material that remains is enriched in carbon and the lower content of sulphur and nitrogen recorded signifies less production of sulphur and nitrogen oxides. This property contributes to the generation of low net emissions of greenhouse gases in the atmosphere, thus reducing impacts on the environment, especially on climate change, and maintaining carbon balance in the environment. Carbon content was high for pineapple crown waste biomass, making it a suitable feedstock for bioenergy production. The formation of free radicals is inhibited due to the presence of hydrogen which reduces the proportion of hydrocarbons that are unsaturated leading to an increase in the quality of bio-oil that may be produced from pineapple crown waste (Dhyani and Bhaskar, 2017). The higher oxygen content

(50.67%) is mainly a result of the highly oxygenated content in biomass viz hemicellulose, cellulose, and lignin (Liu *et al*.,2021).

Chemical analysis of the pineapple crown biomass revealed the biomass percentage of these oxygenated constituents. Cellulose content was the highest and the least was lignin (Table 4.1). Cellulose content determines the yield of maximum liquid by-products. Selective pyrolysis occurs when cellulose is high in quantity resulting in the formulation of chemically rich bio-oil. (Amenaghawon *et al*., 2021). Gaseous product from biomass is mostly due to the presence of hemicellulose. Additionally, Hemicellulose produces less tar during combustion compared to cellulose (Basu, 2018). Lignin determines the yield of char and has a complex structure which is considered an impediment to the thermochemical conversion process (Emiola-Sadiq *et al*., 2021). This implies that, for a successful thermochemical conversion, the content of lignin in biomass should be in small quantities. Lignin content is low in pineapple crown waste; thus, a small amount of char may be produced compared to the amount of bio-oil and gas. The high cellulose content in pineapple crown waste signifies the potential of producing bio-oil of good quality. The above properties make pineapple crown waste biomass a suitable and valuable source for thermochemical applications.

Table 4.1: Compositional analysis of pineapple crown waste

Composition	Percentage (%)
Proximate Analysis	
Moisture	10.00
Volatile Matter	93.72
Fixed Carbon	0.48
Ash	5.80
Ultimate Analysis	
Carbon (C)	35.51
Hydrogen (H)	12.19
Nitrogen (N)	1.60
Sulphur (S)	0.03
Oxygen (O)	50.67
Chemical Analysis	
Cellulose	32.00
Hemicellulose	22.00
Lignin	13.00

4.2 Thermogravimetric Analysis of Untreated Pineapple Crown Waste

Estimation of the percentage loss in weight of a sample heated at a uniform rate in a suitable environment is done through thermogravimetric analysis (TGA). The composition of the sample as well as indications of thermal stability is depicted by the weight loss over specific temperature ranges (El-Sayed and Mostafa, 2014). Three basic components make up biomass: cellulose, hemicellulose, and lignin (Biswas *et al*., 2011). These components can be characterized using derivative thermogravimetry (DTG) (Zhai *et al*., 2016). That is, the location and intensity of these components can be easily identified in DTG due to the intrinsic structural difference of biomass components. Thermal degradation of hemicellulose, cellulose, and lignin occurs in the ranges of 225 to 350 ˚C, 325 to 375 ˚C, and 250 to 500 ˚C respectively (Zhai *et al*., 2016). This shows that the degradation of biomass constituents does not occur uniformly. The operating conditions during thermochemical conversion determine the rate and degree of deterioration. Decomposition occurs in the order of hemicellulose, cellulose, and lignin which deteriorates under a wide scope of temperatures (Amenaghawon *et al*., 2021).

The decomposition pattern of untreated pineapple crown waste is shown in Figure 4.1. According to Gu *et al*. (2014), the initial loss in weight of most biomass is a result of the release of moisture which occurs below 200 ˚C. From the DTG graph, it can be observed that decomposition occurred in four distinct stages (Figure 4.2). The first stage shows a small peak near 100 ˚C which relates to the evaporation of moisture and the escape of some light gases from air-dried pineapple crown waste. Similar outcomes were observed by other researchers on the pyrolysis of biomass (Lui *et al*., 2015; Zhai *et al*., 2016; Ren *et al*., 2020). The pyrolysis of hemicellulose and unstable cellulose occurred in the second stage from around 108 – 200 ˚C. The third stage lasted from around 200 ˚C to 400 ˚C. In this stage, the maximum rate of pyrolysis was achieved at around 325 ˚C. The highest peak around 325 ˚C corresponds to cellulose decomposition. The peak however appeared unsymmetrical. Hemicellulose content in pineapple crown waste is lower than cellulose (Table 1). Hemicellulose decomposition merges with cellulose decomposition as a result of the low amount, explaining the unsymmetrical shape in that region (Biswas *et al*., 2011). The emission of carbon dioxide, carbon monoxide, methane, etc. alongside heat occurs throughout the thermal breakdown of cellulose, hemicellulose, and lignin (Liu *et al*., 2015). After 325 ˚C, shoulders broadened at different temperatures, progressing into the fourth and final pyrolysis stage, occurring between 400 and 600 ˚C. Pyrolysis of lignin and charring of cellulose happens in the fourth stage. Shoulders in that range represent lignin degradation. In summary, DTG revealed the decomposition of pineapple crown waste at different zones instead of decomposing uniformly over temperature, hence supporting the idea of determining lignocellulosic structural changes and pyrolysis characteristics qualitatively (Biswas *et al*., 2011).

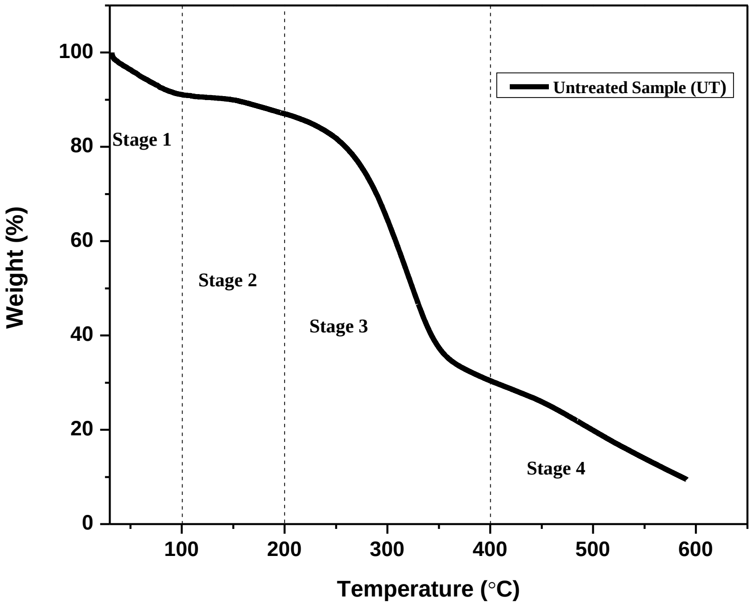


Figure 4.1: TGA Curve for Untreated Pineapple Crown Waste

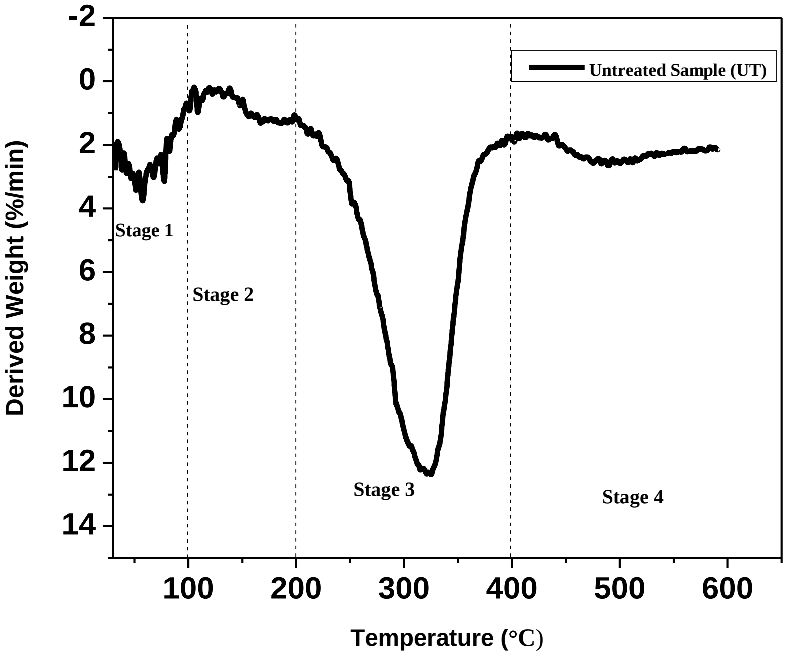


Figure 4.2: DTG curve for Untreated Pineapple Crown Waste

4.3 Thermogravimetric Analysis of Steam-Exploded Pineapple Crown Waste

TGA and DTG dispersion versus temperature for steam-exploded biomass at 6 bars compared to that of raw (untreated) biomass are shown in Figure 4.3 and Figure 4.4 respectively. Times for pre-treatment were 5, 10, and 15min. In each instance, the highest peak was identified at around 348 ˚C. The peak portrays the cellulose decomposition (Figure 4.4). Steam-exploded samples depicted a relatively broad region before the cellulose peak compared with untreated biomass where there was a peak of hemicellulose (Figure 4.4). That broadened region shows the decomposition of transformed hemicelluloses. Hemicellulose decomposition is known to undergo rapid thermal decomposition at temperatures inferior to that of lignin or cellulose as it contains combined moisture and a low point of weakness than lignin (Basu, 2018). As a result, hemicellulose reaches its exothermic peak at lower temperatures compared to cellulose or lignin. This is evident in the pyrolysis of the untreated pineapple crown waste where the hemicellulose peak appeared at around 170 ˚C (Figure 4.2). Pre-treatment by the steam explosion has been reported to cause hydrolysis of hemicelluloses (Martin-Sampedro *et al*., 2011; Gu *et al*., 2014; Simangunsong *et al*., 2018; Yu *et al*., 2022). This means that hemicelluloses present in pineapple crown waste biomass may have been removed during the steam explosion process, which explains the loss in hemicellulose peak in all the steam exploded samples as compared with the untreated sample. Steam explosion pre-treatments at 5 and 10 min are characterised by little to no peaks with uniform decomposition before the cellulose peak. Increasing the pre-treatment time to 15 min ensured a more uniform decomposition during pyrolysis.

TG and DTG curves of steam explosion pre-treatment at 8 bars under residence times of 5, 10, and 15 min compared with untreated material (Figure 4.5 and Figure 4.6) have similar decomposition patterns as described above. When pre-treatment pressure was increased to 10 bar, cellulose decomposition was more pronounced in the pre-treated sample at 15min (Figure 4.8). The intensity of decomposition was higher in all zones before cellulose decomposition compared to untreated biomass. Also, the region for steam-exploded biomass moved to higher temperature zones than that of the untreated. The shift to high-temperature zones is a result of high heating rates (Olatunji *et al*.,2018; Flores *et al*., 2020). In the study of pineapple crown waste biomass, the heating rate was at 20 ˚C /min causing samples to decompose at higher temperatures, leading to the shift to higher temperature zones. The weight loss rate of untreated pineapple crown and steam-exploded pineapple crown waste is shown in Table 4.2 where the total loss rate in weight of untreated pineapple crown is at a higher level than steam-exploded pineapple crown waste. This means that volatiles escaped more readily when pyrolyzing raw biomass, which may be because chemicals that create volatiles were hydrolysed into aqueous chemicals during steam explosion pre-treatment (Gu *et al*., 2014).

It could also be observed that in all steam-exploded pineapple crown wastes, the lignin peak flattened compared with the raw pineapple crown waste biomass (Figure 4.4, Figure 4.6 and Figure 4.8). In thermochemical conversion, condensation and re-polymerization reactions occur between the degradation product of hemicellulose and lignin explaining the flattened peak of lignin (Biswas *et al*., 2011). The reactivity of biomass can be reduced by high lignin contents during thermochemical conversion as a result of softening, melting and carbonization of lignin (Biswas *et al*., 2011). Pineapple crown waste biomass, however, has a low lignin content (Table 4.1) and hence contributing to its increased reactivity during pyrolysis. Kinetic parameters were calculated using the Coats and Redfern model. Untreated pineapple crown waste yielded a pyrolysis frequency factor of $4.59 \times 10^{-5} \text{min}^{-1}$ (Table 4.2) and an activation energy of 30.23 kJ/mol (Table 4.2) at a heating rate of 20min^{-1}. The steam exploded samples depicted an increase in the frequency factor and a slight significant decrease in the activation energy, typically that of the 10-bar pressure. The correlation coefficient for raw and steam-exploded biomass was greater than 0.97 (Table 4.2), which depicts the reliability of the activation energy calculations (Liu *et al*., 2021). The frequency factor describes the rate of collisions between reacting molecules that leads to products (Ren *et al*., 2020). Generally, activation energy in pyrolysis is the minimum energy required for the thermal decomposition of the sample to generate pyrolytic products (Ren *et al*., 2020). Hence with regards to activation energy data, steam explosion improved the thermal reactivity of pineapple crown waste biomass.

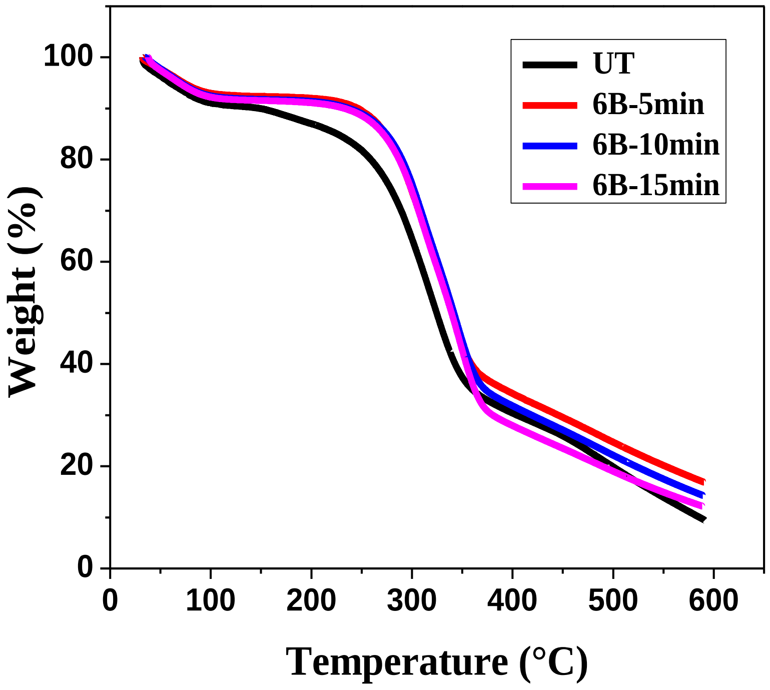


Figure 4.3: TGA curves at 6 bar pressure and varied residence times compared with untreated sample curve

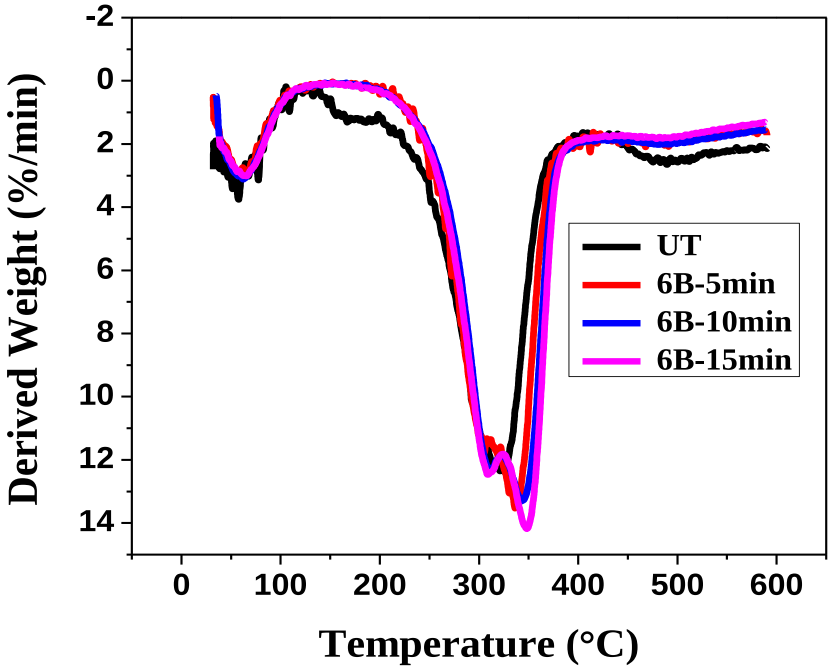


Figure 4.4: DTG curves at 6 bar pressure and varied residence times compared with untreated sample curve

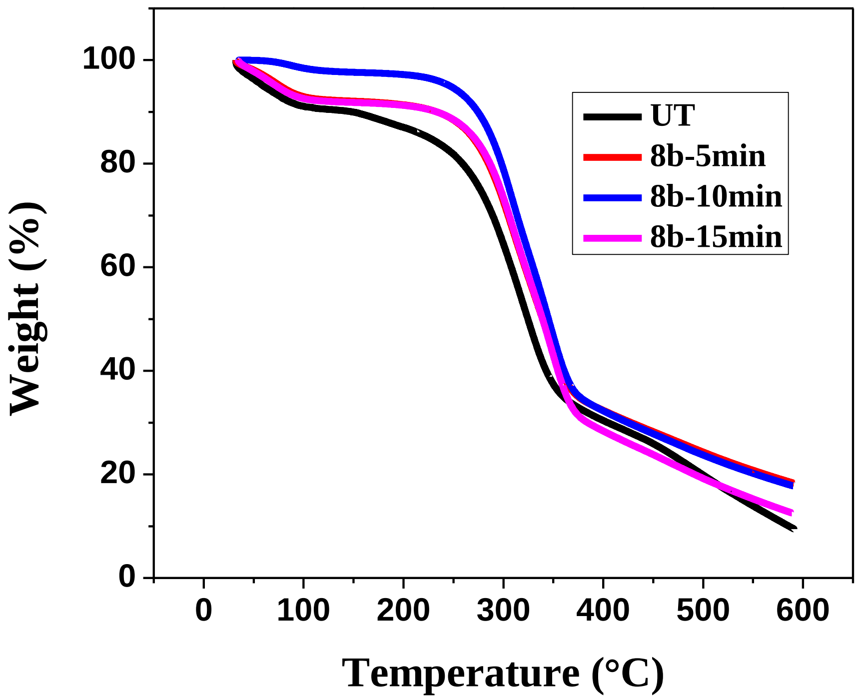


Figure 4.5: TGA curves at 8 bar pressure and varied residence times compared with untreated sample curve

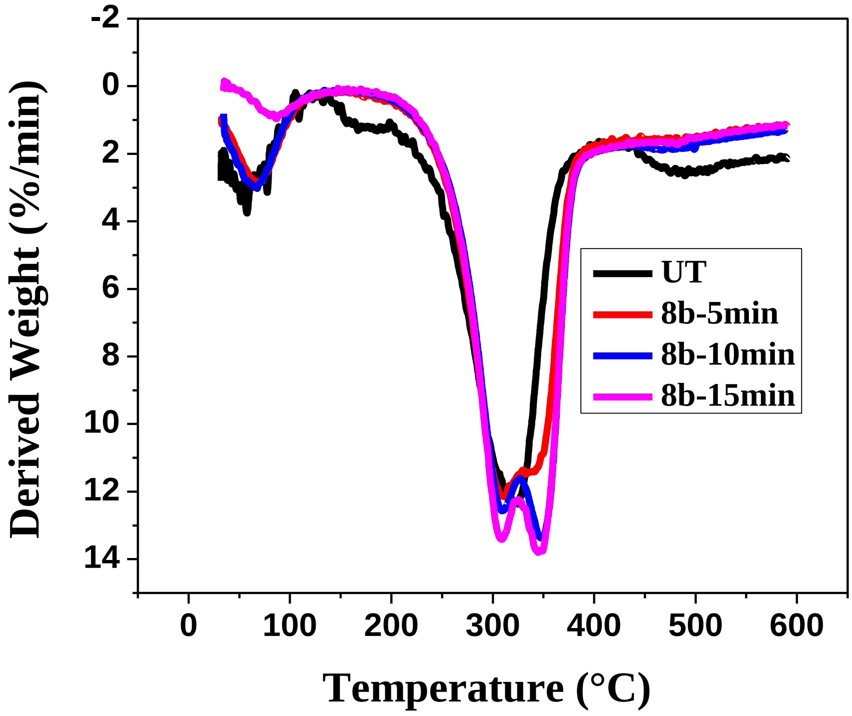


Figure 4.6: DTG curves at 8 bar pressure and varied residence times compared with untreated sample curve

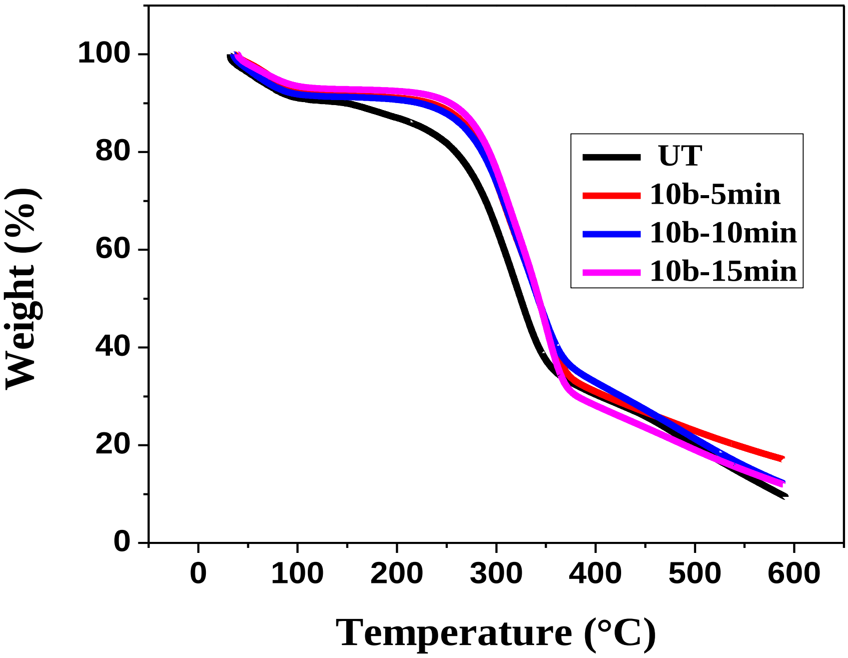


Figure 4.7: TGA curves at 10 bar pressure and varied residence times compared with untreated sample curve

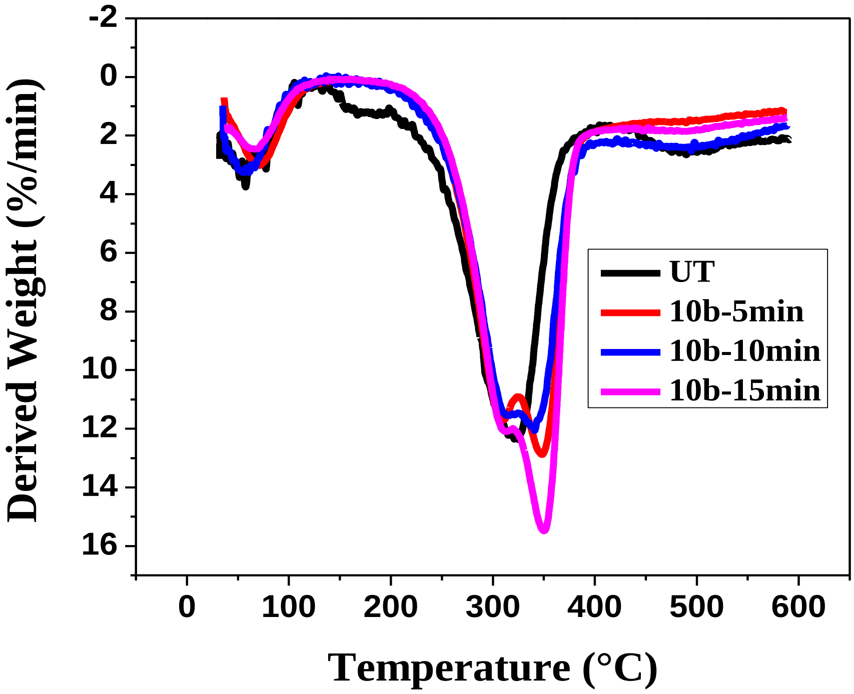


Figure 4.8: DTG curves at 10 bar pressure and varied residence times compared with untreated sample curve

Table 4.2: Kinetic parameters of raw and steam-exploded pineapple crown waste at varying pressures and residence times

Sample	Maximum Temp (˚C)	Maximum DTG (%/min)	Residue (%)	Weight loss rate (%)	Ea (kJ/mol)	A (min^{-1})	R^2
Untreated	325.30	12.37	9.45	90.23	30.23	4.59×10^{-5}	0.982
6b-5min	336.37	13.54	16.86	83.01	30.22	4.03×10^{-4}	0.982
6b-10min	342.59	13.31	14.30	85.75	30.13	4.02×10^{-4}	0.982
6b-15min	348.32	14.18	12.20	87.86	30.05	4.03×10^{-4}	0.983
8b-5min	310.99	12.15	18.30	81.56	30.20	4.03×10^{-4}	0.982
8b-10min	348.63	13.37	17.77	82.30	30.17	4.03×10^{-4}	0.982
8b-15min	344.80	13.80	12.57	87.59	30.13	4.03×10^{-4}	0.982
10b-5min	348.11	12.06	17.15	82.77	30.12	4.03×10^{-4}	0.982
10b-10min	340.70	12.88	12.22	87.86	30.13	4.03×10^{-4}	0.983
10b-15min	349.93	15.48	12.01	88.13	30.00	4.02×10^{-4}	0.983

Maximum Temp = Temperature at which the highest DTG value is recorded on each occasion

Maximum DTG = Corresponding percentage per minute of the major decomposition zone in the DTG curve.

Ea = Activation energy

A= Pre-exponential factor or Frequency factor

R^2 = Correlation coefficient

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The present research investigated the effect of steam explosion pre-treatment using three different pressures of 6 bar, 8 bar, and 10 bar at residence times of 5 min, 10 min, and 15 min for each pressure level, on the pyrolysis characteristics of pineapple crown waste. The conclusions from the work are as follows;

Compositional analysis of the raw pineapple crown waste biomass indicated the presence of high volatile matter, carbon content, and cellulose content which are required to produce biofuels such as bio-oil, syngas, and biochar that may result from pyrolysis.

The decomposition of pineapple crown waste biomass occurred in four main stages. The first stage is the evaporation of water, followed by the decomposition of unstable cellulose and hemicelluloses in the second stage. The third stage depicted the decomposition of cellulose which is the primary pyrolysis stage, at this point most of the components in pineapple crown biomass have been decomposed. This stage is also where thermal decomposition occurs to produce bio-oil and gas. The last stage portrays the charring stage where the remaining biomass components which were not able to decompose at the initial stages are decomposed to form char. Lignin is mainly decomposed at the final stage.

The peaks in TG curves for the 6 bar-15 min, 8 bar-15 min, and 10 bar-15 min are more pronounced than those for the other times (5 min and 10 min). The Steam explosion pre-treatment at 10 bar produced a better decomposition compared to pressures of 6 bar and 8 bar. Thus, increasing pressure and residence time during steam explosion pre-treatment improved decomposition during pyrolysis and thus will yield good biofuel uses.

Kinetic parameters were determined according to Coats and Redfern method. The activation energies of the steam-exploded samples differed significantly compared to the untreated sample, which shows that steam explosion has an advantageous effect as a procedure for pre-treating pineapple crown waste for the synthesis of biofuel. Steam explosion pre-treatment enhanced thermal reactivity and significantly lowered the energy barrier of the pineapple crown waste biomass.

5.2 Recommendations

It is recommended that:

- The impact of higher pressures on pineapple crown waste biomass will likely yield different results. Conducting studies on the effect of higher pressures on pineapple crown waste will help provide valuable insights for steam explosion pretreatment for implementation in biorefinery concepts.
- The emergence of gases from the pineapple crown waste biomass could be studied by combining thermogravimetric analysis with Fourier-transformed infrared spectroscopy (TG-FTIR). This will help in the efficient design of a reactor for the pyrolysis of pineapple crown feedstock considering environmental impacts.

REFERENCES

Adhikari, S., Nam, H. and Chakraborty, J.P. (2018). Conversion of Solid Wastes to Fuels and Chemicals Through Pyrolysis. *Waste Biorefinery*, pp 239–263.

Amenaghawon, A. N., Anyalewechi, C. L., Okieimen, C. O., Kusuma, H. S. (2021). 'Biomass pyrolysis technologies for value-added products: a state-of-the-art review.' *Environment, Development, and Sustainability*, 23(10), pp 14324–14378.

Amenaghawon, N.A., Okieimen, C.O., Ogbeide, S.E. (2014). 'Modelling and Statistical Optimization of Dilute Acid Hydrolysis of Eucalyptus Wood Chips using Response Surface Methodology'. *The Pacific Journal of Science and Technology*, 15(1), pp 245-256.

American Standard for Testing Materials - ASTM D5142-02a (2002). 'Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures, ASTM International, West Conshohocken, PA, www.astm.org

American Standard for Testing Materials - ASTM D5832-98 (2014). 'Standard Test Method for Volatile Matter Content of Activated Carbon Samples.' ASTM International, West Conshohocken.

American Standard for Testing Materials - ASTM E871-82 (2006). 'Standard Test Method for Moisture Analysis of Particulate Wood Fuels' ASTM International, West Conshohocken.

Ankrah, D. A. (2022) Ghana's pineapple innovation history: An account from stakeholders in Nsawam Adoagyiri Municipal Assembly, *African Journal of Science, Technology, Innovation and Development*, 14(7), pp 1916-1932.

Arenas, C.N., Navarro, M.V., and Martínez, J.D. (2019). 'Pyrolysis kinetics of biomass wastes using isoconversional methods and the distributed activation energy model.' *Bioresource Technology*, 288, pp 1-34.

Assumi, S.R., Singh, P.T. and Jha, A.K. (2021). 'Pineapple (*Ananas comosus L. Merr.*).' In Ghosh, S.N., and Sharma, R.R. (Eds.). Tropical Fruit Crops: Theory to Practical. Jaya Publishing House, New Delhi, pp 487-541.

Baidhe, E., Kigozi, J., Mukisa, I., Muyanja, C., Namubiru, L. and Kitarikawe, B. (2021). 'Unearthing the potential of solid waste generated along the pineapple drying process line in Uganda: A review.' *Environmental Challenges*, 2, pp 1-11.

Baruah, J., Nath, B. K., Sharma, R., Kumar, S., Deka, R. C., Baruah, D. C., and Kalita, E. (2018). ‘Recent Trends in the Pretreatment of Lignocellulosic Biomass for Value-Added Products.’ *Frontiers in Energy Research*, 6, pp 1-19.

Basu, P. (2018). ‘Pyrolysis’ Chapter 5 In Biomass Gasification, Pyrolysis and Torrefaction pp 155–187.

Behera, S., Arora, R., Nandhagopal, N. and Kumar, S. (2014). ‘Importance of chemical pretreatment for bioconversion of lignocellulosic biomass,’ *Renewable and Sustainable Energy Reviews, Elsevier*, 36(C), pp 91-106.

Benoit, M., Rodrigues, A., Zhang, Q., Fourré, E., Vigier, K. D. O., Tatibouët, J.-M. and Jérôme, F. (2011). ‘Depolymerization of Cellulose Assisted by a Nonthermal Atmospheric Plasma.’ *Angewandte Chemie International Edition*, 50 (38), pp 8964-8967.

Bensch, G., Jeuland, M. and Peters, J. (2021). ‘Efficient biomass cooking in Africa for climate change mitigation and development’ *One Earth* 4(6), pp 879-890.

Biswas, A.K., Umeki, K., Yang, W. and Blasiak, W. (2011). ‘Change of pyrolysis characteristics and structure of woody biomass due to steam explosion pretreatment.’ *Fuel Processing Technology*, 92(10), pp 1849–1854.

Carrillo, F., Lis, M.J., Colom, X., Lopez-Mesas, M., Valldeperas, J. (2005). ‘Effect of alkali pretreatment on cellulase hydrolysis of wheat straw: Kinetic study’. *Process Biochemistry*, 40(10), pp 3360-3364.

Chen, H. Z., and Liu, Z. H. (2015). Steam explosion and its combinatorial pretreatment refining technology of plant biomass to bio-based products. *Biotechnol. J.* 10, 866–885. doi: 10.1002/biot.201400705

Coats, A. W., Redfern, J. P. (1965). Kinetic parameters from thermogravimetric data. II. *J. Polym. Sci. Part C*: Polym. Lett., 3(11), pp 917–920

Cummer, K. R., and Brown, R. C. (2002). ‘Ancillary equipment for biomass gasification.’ *Biomass and Bioenergy*, 23, pp 113–128.

Damyanova, S. and Beschkov, V. (2020). ‘Biogas as a Source of Energy and Chemicals’, In Beschkov, V. (ed.), *Biorefinery Concepts, Energy and Products*, Intech Open, London.

Den, W., Sharma, V.K., Lee, M., Nadadur, G. and Varma, R.S. (2018). ‘Lignocellulosic Biomass Transformations via Greener Oxidative Pretreatment Processes: Access to Energy and Value-Added Chemicals’. *Frontiers in Chemistry*, 6, pp 1-23.

Dhyani, V. and Bhaskar, T. (2017). ‘A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renewable Energy*, pp 1-45.

Dickerson, T. and Soria, J. (2013). ‘Catalytic Fast Pyrolysis: A Review.’ *Energies*, 6(1), pp 514-538

Dutton (2020). ‘Biomass pyrolysis’. Pennsylvania State University College of Earth and Mineral Sciences. Available at: https://www.e-education.psu.edu/egee439/node/537

Elgharbawy, A.A., Alam, M. Z., Moniruzzaman, M., and Goto, M. (2016). ‘Ionic liquid pretreatment as emerging approaches for enhanced enzymatic hydrolysis of lignocellulosic biomass.’ *Biochemical Engineering Journal*, 109, pp 252–267.

El-Sayed, S.A. and Mostafa, M.E. (2014). Pyrolysis characteristics and kinetic parameters determination of biomass fuel powders by differential thermal gravimetric analysis (TGA/DTG). *Energy Conversion and Management*, 85, pp 165–172.

Emiola-Sadiq, T., Zhang, L. and Dalai, A. K. (2021). Thermal and Kinetic Studies on Biomass Degradation via Thermogravimetric Analysis: A Combination of Model-Fitting and Model-Free Approach. ACS Omega, 6, pp 22233-22247.

Fang, Y., Li, W. and You, S. (2022). Techno-economic analysis of biomass thermochemical conversion to biofuels. *Value-Chain of Biofuels*, pp 379-394.

Financie, R., Moniruzzaman, M., and Uemura, Y. (2016). ‘Enhanced enzymatic delignification of oil palm biomass with ionic liquid pretreatment.’ *Biochemical Engineering Journal*, 110, pp 1–7.

Firățoiu, A. R., Chiurciu, I. A., Marcuta, L. and Chereji, A. I., Soare, E., Voicu, V. and Marcuta, A. (2021). ‘Study on The Production and Marketing of Pineapples Worldwide.’ Proceedings of the 37th International Business Information Management Association (IBIMA), pp 4973 – 4985.

Flores, J.J.A., Quiñones, J.G.R., Rodríguez, M.L.A., Vera, J.V.A., Valencia, J.E., Martínez, S.J.G., Montesino, F.M. and Rosas, A.A. (2020). Thermal Degradation Kinetics and FT-IR

Analysis on the Pyrolysis of Pinus pseudostrobus, Pinus leiophylla and Pinus montezumae as Forest Waste in Western Mexico. *Energies*,13, pp 1-25.

Flynn, J., and Wall, L. (1966). A quick, direct method for the determination of activation energy from thermogravimetric data. Journal of Polymer Science, Part B, 4(5), 323–328.

Friedman, H. (1964). Kinetics of thermal degradation of char-forming plastics from thermogravimetry application to a phenolic resin. Journal of Polymer Science Part C Polymer Letters, 6, 183–195.

Galbe, M., Wallberg, O. and Zacchi, G. (2011). 'Techno-Economic Aspects of Ethanol Production from Lignocellulosic Agricultural Crops and Residues.' *Comprehensive Biotechnology*, 6, pp 615-628.

Garba, A. (2020). 'Biomass Conversion Technologies for Bioenergy Generation: An Introduction.' In Basso, T. P., Basso, T. O., Basso, L. C. (eds.), Biotechnological Applications of Biomass, Intech Open, London. 10.5772/intechopen.93669.

Gent, S., Twedt, M., Gerometta, C. and Almberg, E. (2017). 'Introduction to Thermochemical Conversion Processes.' *Theoretical and Applied Aspects of Biomass Torrefaction*, pp 1–16.

Ghana Living Standards Survey Fifth Round (GLSS 5). Ghana Statistical Service; 2008.

Gu, X., Liu, C., Jiang, X., Ma, X., Li, L., Cheng, K., and Li, Z. (2014). 'Thermal behaviour and kinetics of the pyrolysis of the raw/steam-exploded poplar wood sawdust.' *Journal of Analytical and Applied Pyrolysis*, 106, pp 177–186.

Hahn-Hägerdal, B., Galbe, M., Gorwa-Grauslund, M.F., Lidén, G. and Zacch, G. (2006). 'Bio-ethanol – the fuel of tomorrow from the residues of today' *Trends in Biotechnology* 24(12), pp 549-556.

Hamzah, A.F.A., Hamzah, M.H., Man, H.C., Jamali, N.S., Siajam, S.I. and Ismail, M.H. (2021). 'Recent Updates on the Conversion of Pineapple Waste (Ananas comosus) to Value-Added Products, Future Perspectives, and Challenges.' *Agronomy*, 11, pp 1-27.

Hognon, C., Delrue, F., Texier, J., Grateau, M., Thiery, S., Miller, H. and Roubaud, A. (2015). Comparison of pyrolysis and hydrothermal liquefaction of Chlamydomonas reinhardtii. Growth studies on the recovered hydrothermal aqueous phase. *Biomass and Bioenergy*, 73, pp 23–31.

Hossain, M. F. (2016). ‘World pineapple production: an overview.’ *African Journal of Food, Agriculture, Nutrition, and Development*, 16 (4), pp 11443 – 11456.

Hu, X. and Gholizadeh, M. (2019). ‘Biomass pyrolysis: A review of the process development and challenges from initial research up to the commercialisation stage.’ *Journal of Energy Chemistry*, 39, pp 109-143.

Ikegwu, U. M., Ozonoh, M., Okoro, N-J.M., and Daramola, M.O. (2021). ‘Effect and Optimization of Process Conditions during Solvolysis and Torrefaction of Pine Sawdust Using the Desirability Function and Genetic Algorithm.’ *ACS Omega*, 6(31), pp 20112-20129.

Islam, Md. (2021). Re: What is the role of fixed carbon? Retrieved from: https://www.researchgate.net/post/What-is-the-role-of fixedcarbon/60a38c680270c22880379b44/citation/download.

Jenkins, B.M., Baxter, L.L. and Koppejan, J. (2019). ‘Biomass Combustion’ In Brown, R.C. (ed). *Thermochemical Processing of Biomass (Conversion into Fuels, Chemicals, and Power), Biomass Combustion.*, pp 49–83.

Kataki, R., Chutia, R.S., Mishra, M., Bordoloi, N., Saika, R. and Bhaskar, T. (2015). Feedstock Suitability for Thermochemical Processes. *Recent Advances in Thermo-Chemical Conversion of Biomass*, pp 31–74.

Kleemann, L. (2016). Organic Pineapple Farming in Ghana a Good Choice For Smallholders? *The Journal of Developing Areas*, *50*(3), 109–130. http://www.jstor.org/stable/24737422

Kok, M. V., & Ozgur, E. (2017). Characterization of lignocelluloses biomass and model compounds by thermogravimetry. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *39*(2), pp 134–139.

Kulshreshtha, A. (2022). ‘Sustainable energy generation from municipal solid waste.’ In Hussain, C.M., Singh, S., Goswami, L. (eds.), *Waste-to-Energy Approaches Towards Zero Waste, Elsevier*, pp 315-342.

Kumar, A.K., and Sharma, S. (2017). ‘Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review.’ *Bioresources and bioprocessing*, 4(1), pp 1-19.

Kumar, P., Barrett, D. M., Delwiche, M. J., and Stroeve, P. (2009). ‘Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production’. *Industrial and Engineering Chemistry Research*, 48(8), pp 3713–3729.

Kumari, K., Singh, A., Marathe, D. and Pariyar, P. (2021). Agricultural biomass as value chain developers in different sectors. *Biological processes*, 1, pp 467-509.

Laougé, Z. B. and Merdun, H. (2020). Pyrolysis and combustion kinetics of Sida cordifolia L. using thermogravimetric analysis. *Bioresour. Technol.*, 299, 122602, pp 1-7

Lee, S.Y., Sankaran, R., Chew, K.W., Tan, C.H., Krishnamoorthy, R., Chu, D. and Show, P. (2019). Waste to bioenergy: a review on the recent conversion technologies. *BMC Energy*, 1(4), pp 1-22.

Liu, B. and Abu-Omar, M.M. (2021). 'Lignin extraction and valorization using heterogeneous transition metal catalysts.' *Advances in Inorganic Chemistry*, 77, pp 137-174.

Liu, J., Jiang, X., Cai, H. and Gao, F. (2021). 'Study of Combustion Characteristics and Kinetics of Agriculture Briquette Using Thermogravimetric Analysis.' *ACS Omega*, 6, pp 15827-15833.

Liu, Z., Qi, N., Luan, Y., and Sun, X. (2015). 'Thermogravimetry-Infrared Spectroscopy Analysis of the Pyrolysis of Willow Leaves, Stems, and Branches.' *Advances in Materials Science and Engineering*, pp 1-8.

Macfarlane, A., Mai, M.R., and Kadla, J.F. (2014). 'Bio-based chemicals from biorefining: lignin conversion and utilisation.' *Advances in Biorefineries*, pp 659–692.

Mamvura, T.A. and Danha, G. (2020). 'Biomass torrefaction as an emerging technology to aid in energy production.' *Heliyon*, 6(3), pp 1-17.

Martin-Sampedro, R., Capanema, E.A., Hoeger, I., Villar, J.C. and Rojas, O.J. (2011). 'Lignin changes after steam explosion and laccase-mediator treatment of eucalyptus wood chips, *Journal of Agricultural and Food Chemistry*, 59, pp 8761–8769.

Maurya, D.P., Singla, A. and Negi, S. (2015). 'An overview of key pretreatment processes for biological conversion of lignocellulosic biomass to bioethanol.' *3 Biotech*, 5, pp 597–609.

Mielenz, J. R. (2020). 'Small-scale approaches for evaluating biomass bioconversion for fuels and chemicals.' *Bioenergy*, pp 545–571.

Molino, A., Chianese, S. and Musmarra, D. (2016). 'Biomass gasification technology: The state-of-the-art overview. *Journal of Energy Chemistry*, 25(1), pp 10-25.

Mukhtar, H., Feroze, N., Munir, H.M.S., Javed, F. and Kazmi, M. (2020). ‘Torrefaction process optimization of agriwaste for energy densification.’ *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 42(20), pp 2526-2544.

Nowakowski, D.J., Bridgwater, A.V., Elliott, D.C., Meier, D., and de Wild, P. (2010). ‘Lignin fast pyrolysis: Results from an international collaboration’. *Journal of Analytical and Applied Pyrolysis*, 88(1), pp 53–72.

Nunes, L. J. R., Matias, J. C. O., and Catalão, J. P. S. (2018). ‘Chapter 1-Introduction’ In Nunes, L. J. R., Matias, J. C. O., and Catalão, J. P. S. (Eds.). Torrefaction Of Biomass for Energy Applications: From Fundamentals to Industrial Scale. Academic Press, pp 1- 43.

Olatunji, O.O., Akinlabi, S.A., Mashinini, M.P., Fatoba, S.O., and Ajayi, O.O. (2018). Thermo-gravimetric characterization of biomass properties: A review. *Materials Science and Engineering*,423, pp 1-15.

Omoniyi, T.E., and Olorunnisola, A.O. Experimental Characterisation of Bagasse Biomass Material for Energy Production.’ *International Journal of Engineering and Technology*,4(10), pp 582-589.

Oyedoko, K. F., Agbetan, G.O. and Akinyemi, O.P. (2020). ‘Synthesis of Scale Inhibitors from Pineapple Leaf Fiber Extract (Ananas Comosus).’ *Engineering & Technology Research Journal*, 5(1), pp 32 – 40.

Ozawa, T. (1965). A new method of analyzing thermogravimetric data. Bulletin of the chemical society of Japan, 38, 1881–1886.

Panpatte D.G., and Jhala Y.K. (2019). ‘Agricultural Waste: A Suitable Source for Biofuel Production. In: Rastegari A., Yadav A., Gupta A. (eds) Prospects of Renewable Bioprocessing in Future Energy Systems. *Biofuel and Biorefinery Technologies*, 10, pp 337-355.

Panwar, N. L. and Paul, A. S. (2021). ‘An Overview of recent development in bio-oil upgrading and separation techniques.’ *Environmental Engineering Research*, 26(5), pp 1-17.

Pascault, J.-P., Höfer, R. and Fuertes, P. (2012). Mono-, Di-, and Oligosaccharides as Precursors for Polymer Synthesis. *Polymer Science: A Comprehensive Reference*, 10, pp 59–82.

Patidar, K., Singathia, A., Vashishtha, M., Sangal, V.K. and Upadhyaya, S. (2022). ‘Investigation of kinetic and thermodynamic parameters approaches to non-isothermal pyrolysis of mustard stalk using model-free and master plots methods.’ *Materials Science for Energy Technologies* 5, pp 6–14.

Pattanaik, L., Pattnaik, F., Saxena, D. and Naik, S. (2019). ‘Biofuels from agricultural wastes.’ In: Second and Third Generation of Feedstocks, pp.103-142.

Patwardhan, PR 2010: Understanding the product distribution from biomass fast pyrolysis. PhD Thesis, Iowa State University

Perera, F.P. (2017). ‘Multiple Threats to Child Health from Fossil Fuel Combustion: Impacts of Air Pollution and Climate Change *Environmental health perspectives* 125(2), pp 141- 148.

Pielhop, T., Amgarten, J., von Rohr, P. R., and Studer, M. H. (2016). ‘Steam explosion pretreatment of softwood: the effect of the explosive decompression on enzymatic digestibility.’ *Biotechnology for Biofuels*, 9(1), 152, pp 1-13.

Putro, J.N., Soetaredjo, F.E., Lin, S. Y., Ju, Y.H., and Ismadji, S. (2016). ‘Pretreatment and conversion of lignocellulose biomass into valuable chemicals.’ *RSC Advance*, 6(52), pp 1-60.

Rabiu, Z., Maigari, F., Lawan, U. and Mukhtar Z.G. (2018). ‘Pineapple Waste Utilization as a Sustainable Means of Waste Management.’ In Zakaria, Z. A. (ed), *Sustainable Technologies for the Management of Agricultural Wastes*, pp 143–154.

Rahmati, S., Doherty, W., Dubal, D., Atanda, L., Moghaddam, L., Sonar, P., Hessel, V. and Ostrikov, K. (2020). ‘Pretreatment and Fermentation of Lignocellulosic Biomass: Reaction Mechanisms and Process Engineering’. *Reaction Chemistry & Engineering*, pp 1-33.

Raj, T., Gaur, R., Lamba, B.Y., Singh, N., Gupta, R.P., Kumar, R., and Ramakumar, S.S.V. (2018). ‘Characterization of ionic liquid pre-treated plant cell wall for improved enzymatic digestibility.’*Bioresources Technology*, 249, pp 139–145.

Ren, X., Cuo, J., Li, S., and Chang, J. (2020). Thermogravimetric Analysis−Fourier Transform Infrared Spectroscopy Study on the Effect of Extraction Pretreatment on the Pyrolysis Properties of Eucalyptus Wood Waste.’ *ACS omega*, 5, pp 23364-23371.

Sahu, S. N., Sahoo, N. K., Naik, S. N., and Mahapatra, D. M. (2020). Advancements in hydrothermal liquefaction reactors: overview and prospects. *Bioreactors*, pp 195–213.

Sansaniwal, S.K., Pal, K., Rosen, M.A. and Tyagi, S.K. (2017). ‘Recent advances in the development of biomass gasification technology: A comprehensive review,’ *Renewable and Sustainable Energy Reviews*, Elsevier, 72(C), pp 363-384.

Scott, D. S., Paterson, L., Piskorz, J., and Radlein, D. (2000). ‘Pretreatment of poplar wood for fast pyrolysis of cation removal’. *Journal of Analytical and Applied Pyrolysis*, 57, pp 169–176.

Shaw, K. (2006). ‘Determination of organic carbon in soil and plant material.’ *European Journal of Soil Science*, 10(2) pp 316- 326.

Sikora, A.(ed.). (2021). ‘Anaerobic Digestion in Built Environments.’ Intech Open, London, United Kingdom, [cited 2022 May 09]. 130p. Available from: https://www.intechopen.com/books/10491 doi: 10.5772/intechopen.92507.

Simangunsong, E.; Ziegler-Devin, I.; Chrusciel, L.; Girods, P.; Wistara, N. J.; Brosse, N. (2018). Steam Explosion of Beech Wood: Effect of the Particle Size on the Xylans Recovery. *Waste and Biomass Valorization*, 11, pp 625-633.

Speight, J.G. (2019). ‘Unconventional gas.’ In Natural Gas (2nd ed), Gulf Professional Publishing, Boston, pp 59–98.

Szarka, N., Haufe, H., Lange, N., Schier, F., Weimar, H., Banse, M., Sturm, V., Dammer, L., Piotrowski, S., and Thrän, D. (2021). ‘Biomass flow in bioeconomy: Overview for Germany’ *Renewable and Sustainable Energy Reviews*, 150, pp 1-14.

Tarves, P.C., Serapiglia, M.J., Mullen, C.A., Boateng, A.A. and Volk, T.A. (2017). ‘Effects of hot water extraction pretreatment on pyrolysis of shrub willow’ *Biomass and Bioenergy*, 107, pp 299-304.

Travaini R, Martín-Juárez J, Lorenzo-Hernando A, Bolado-Rodríguez S. (2015). ‘Ozonolysis: An advantageous pretreatment for lignocellulosic biomass revisited.’ *Bioresource Technology*, pp 1-41.

Tumuluru, J.S., Wright, C.T., Hess, J. R., and Kenney, K. L. (2011). ‘A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application’. *Biofuels, Bioproducts and Biorefining*, 5(6), pp 683-707.

Tzanetis, K.F., Posada, J.A and Ramirez, A. (2017). Analysis of biomass hydrothermal liquefaction and biocrude-oil upgrading for renewable jet fuel production: The impact of reaction conditions on production costs and GHG emissions performance. *Renewable Energy*, 113, pp 1388–1398.

van Bel, A.J.E., Offler, C.E. and Patrick, J.W. (2003). 'PHOTOSYNTHESIS AND PARTITIONING, Sources and Sinks'. In Thomas, B. (ed), Encyclopaedia of Applied Plant Sciences, Elsevier, pp 724-734.

Victor, D.G. (2009). 'The Politics of Fossil-Fuel Subsidies' Available at SSRN: https://ssrn.com/abstract=1520984 or http://dx.doi.org/10.2139/ssrn.1520984 (Accessed 26th July 2020)

Vyazovkin, S., & Wight, C. A. (1999). Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermochimica acta, 340, 53–68.

Wang, W., Dai, G., Yang, H., and Luo, Z. (2017). 'Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review'. *Progress in Energy and Combustion Science*, 62, pp 33–86.

Williams, P.A., Crespo, O., Atkinson, C.J., and Essegbey, G.O. (2017). Impact of climate variability on pineapple production in Ghana. *Agric & Food Secur* **6**, (26), pp 1-14.

Yang, H., Yao, J., Chen, G., Ma, W., Yan, B. and Qi, Y. (2014). Overview of upgrading of pyrolysis oil of biomass. *Energy Procedia*, 61, pp 1306 – 1309.

Yu, Y., Wu, J., Ren, X., Lau, A., Rezaei, H., Takada, M., Bi, X., and Sokhansanj, S. (2022). Steam explosion of lignocellulosic biomass for multiple advanced bioenergy processes: A review. *Renewable and Sustainable Energy Reviews*, 154, pp 1-19.

Yukesh Kannah, R., Sivashanmugham, P., Kavitha, S., and Rajesh Banu, J. (2020). Valorization of food waste for bioethanol and biobutanol production. *Food Waste to Valuable Resources*, 39–73.

Zarli, A. (2019). Oleochemicals: all time players of green chemistry. In Basile A., Centi, G, De Falco, M. and Laquaniello (eds.), *[Studies in Surface Science and Catalysis] Catalysis, Green Chemistry and Sustainable Energy*, Elsevier, 179, pp 77–95.

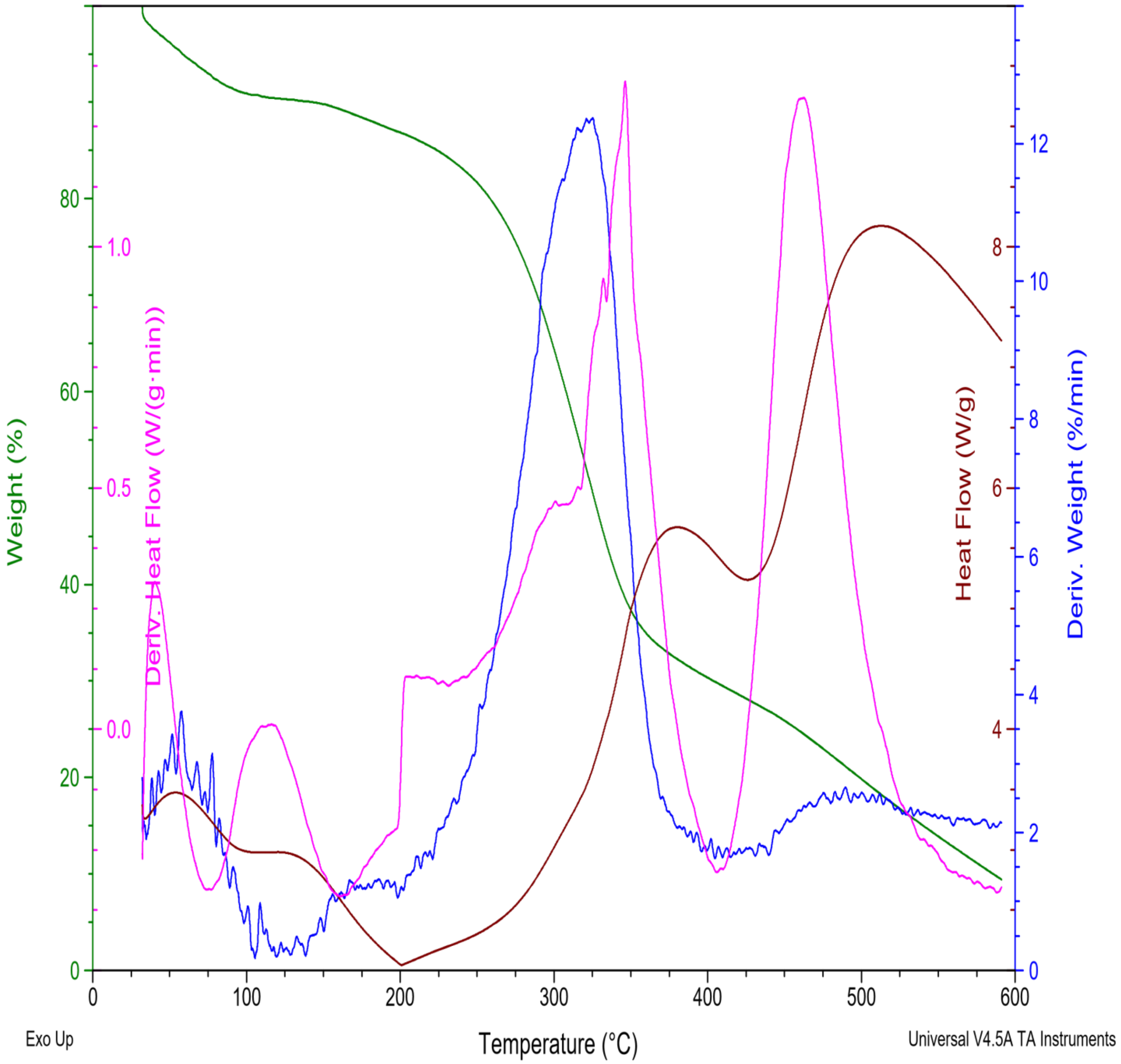
Zhang, Y. and Chen, W.T. (2018). Hydrothermal liquefaction of protein-containing feedstocks. *Direct Thermochemical Liquefaction for Energy Applications*, pp 127–168.

Zheng, A., Jiang, L., Zhao, Z., Chang, S., Huang, Z., Zhao, K., He, F., and Li, H. (2016). ‘Effect of Hydrothermal Treatment on Chemical Structure and Pyrolysis Behavior of Eucalyptus Wood’ *Energy Fuels* 30(4), pp 3057–3065.

APPENDICES

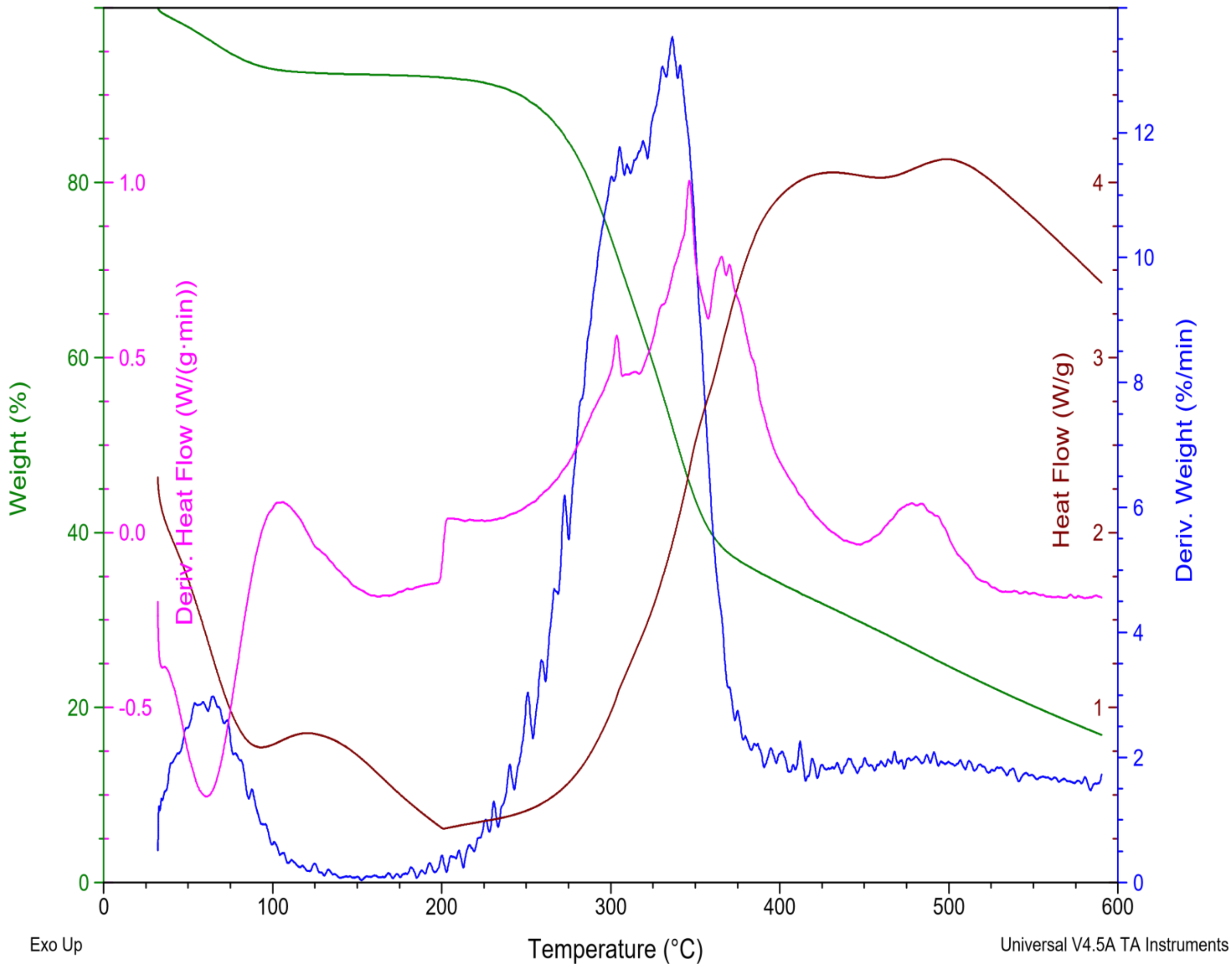
Appendix 1

Untreated Pineapple Crown Waste TGA Output



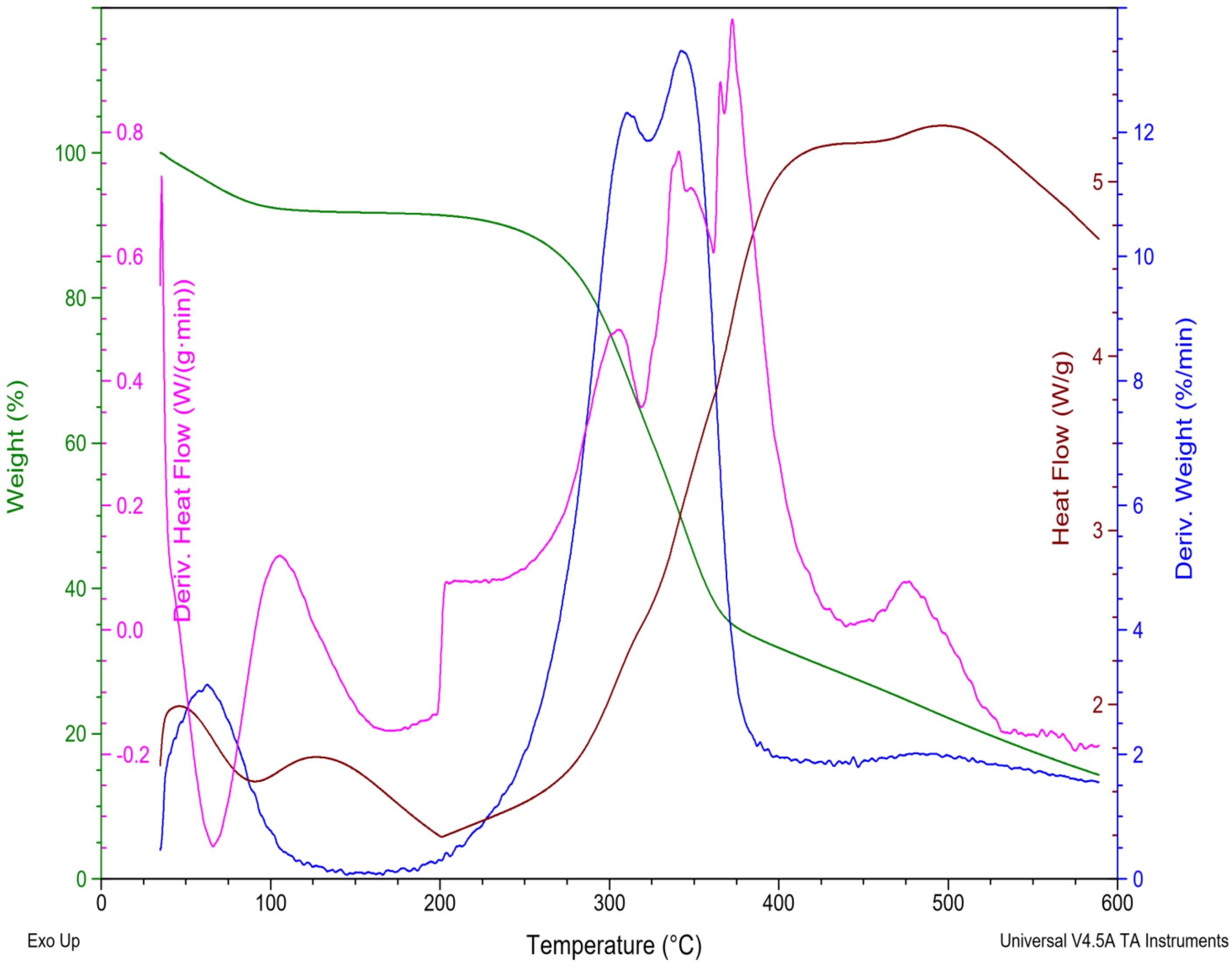
Appendix 2

TGA Output for 6 bars-5 min Steam-Exploded Sample



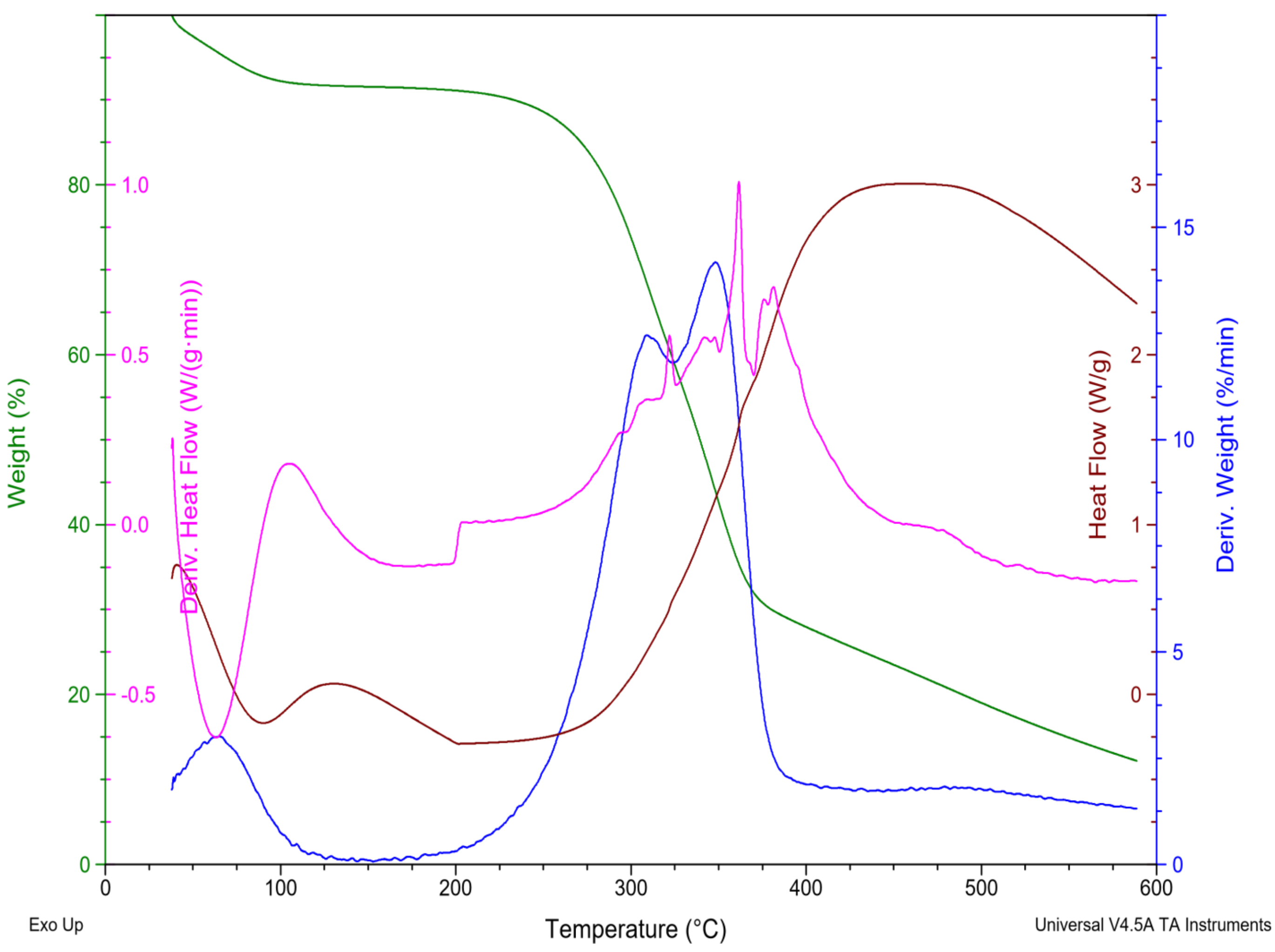
Appendix 3

TGA Output for 6 bars-10 min Steam-Exploded Sample



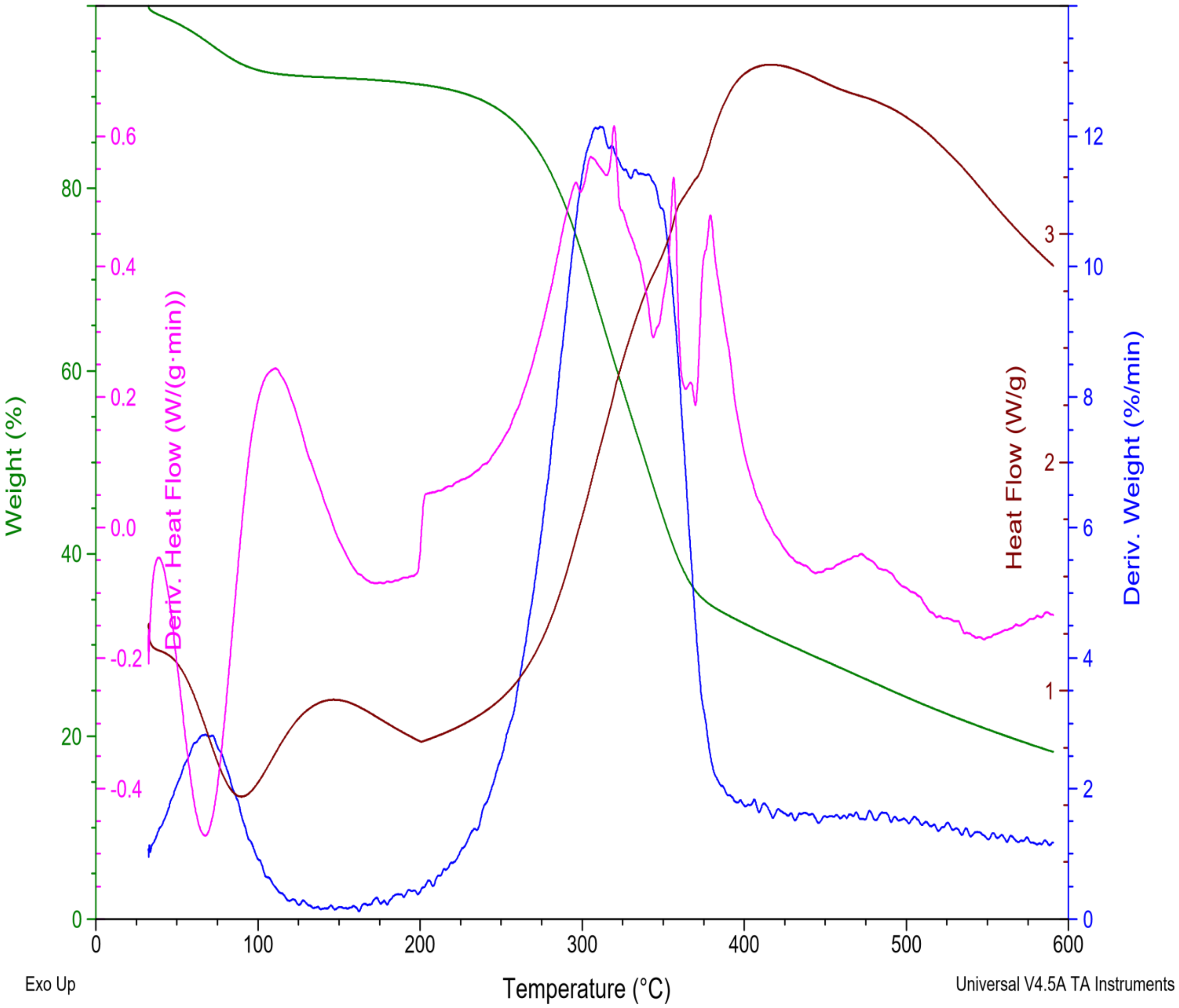
Appendix 4

TGA Output for 6 bars-15 min Steam-Exploded Sample



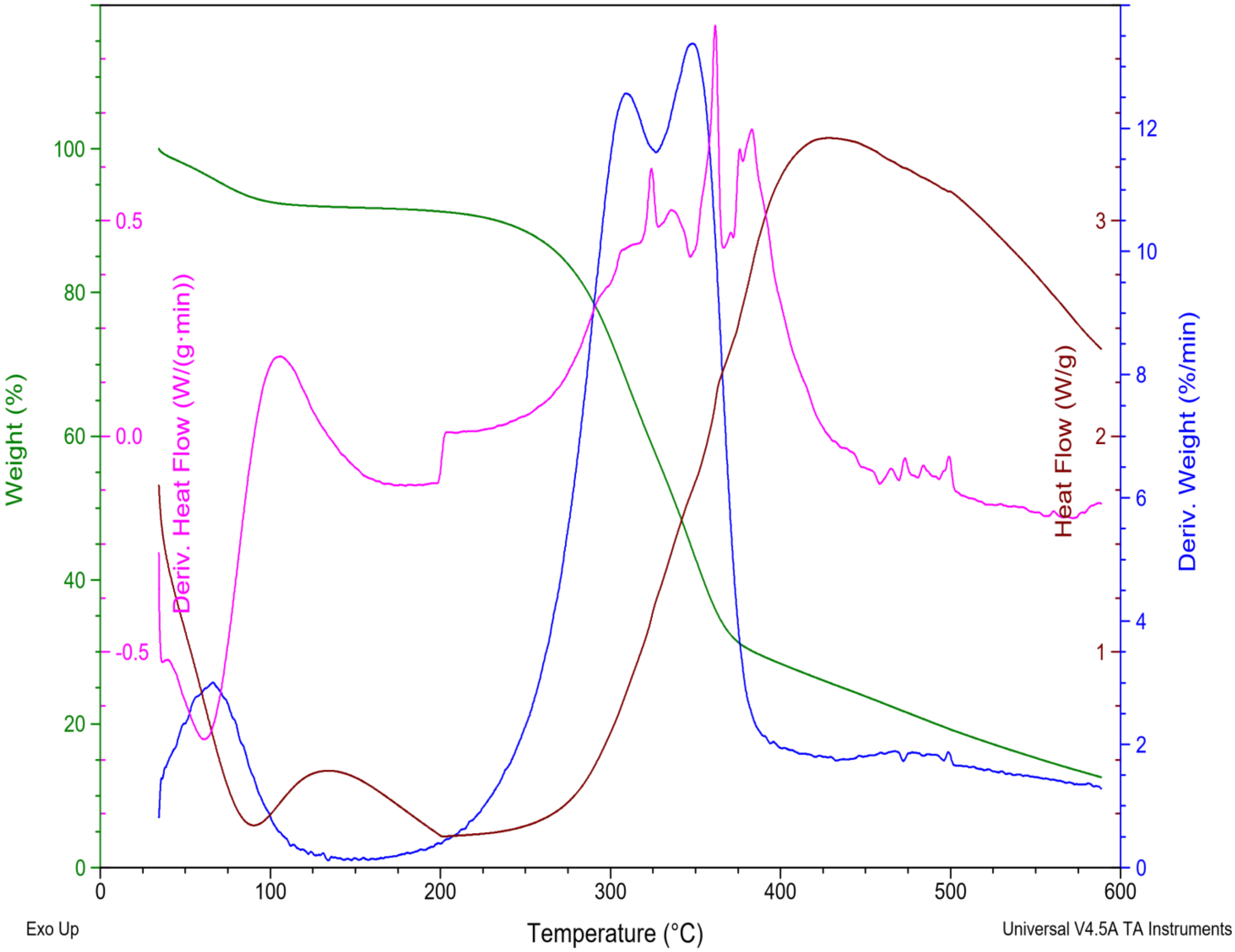
Appendix 5

TGA Output for 8 bars-5 min Steam-Exploded Sample



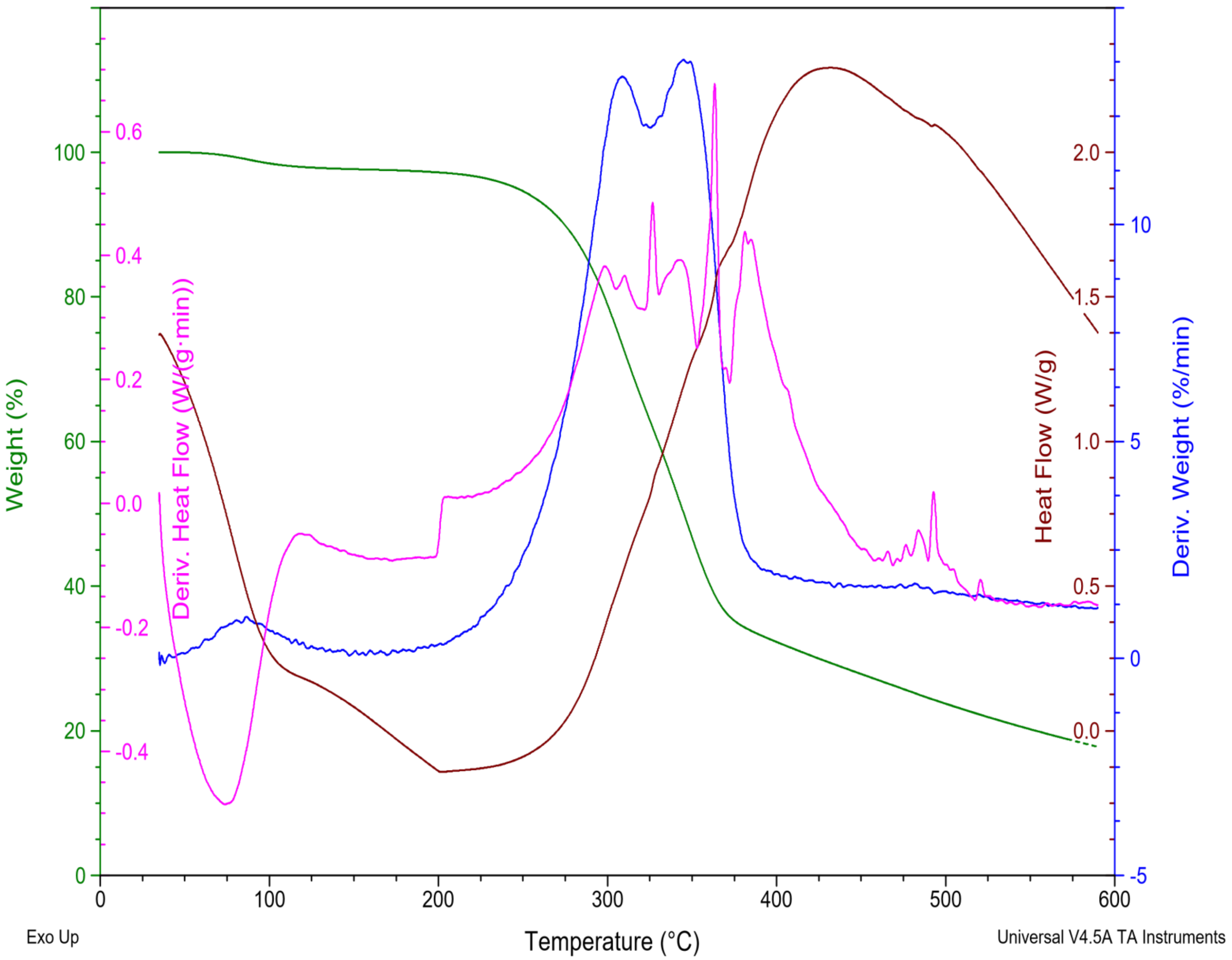
Appendix 6

TGA Output for 8 bars-10 min Steam-Exploded Sample



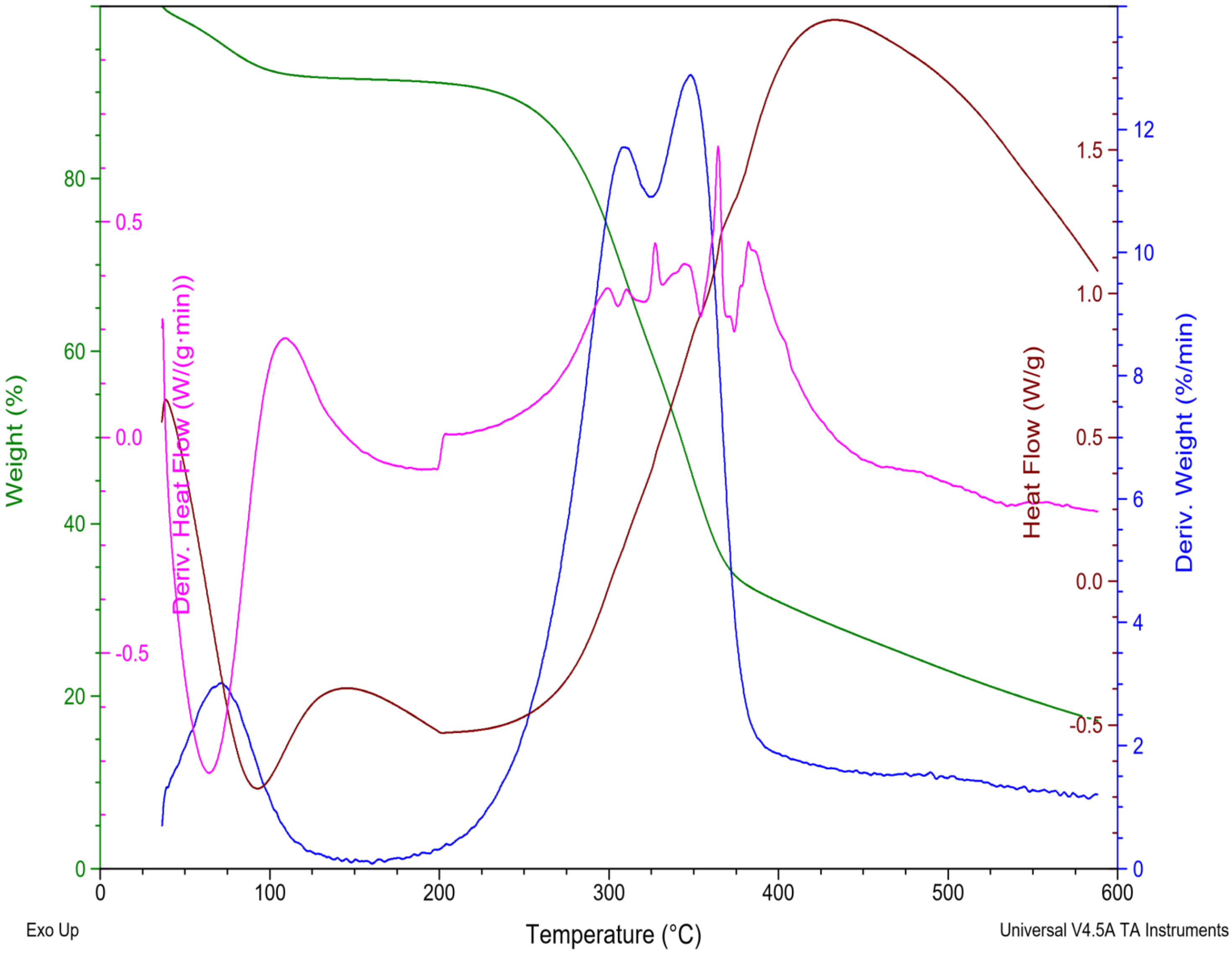
Appendix 7

TGA Output for 8 bars-15 min Steam-Exploded Sample



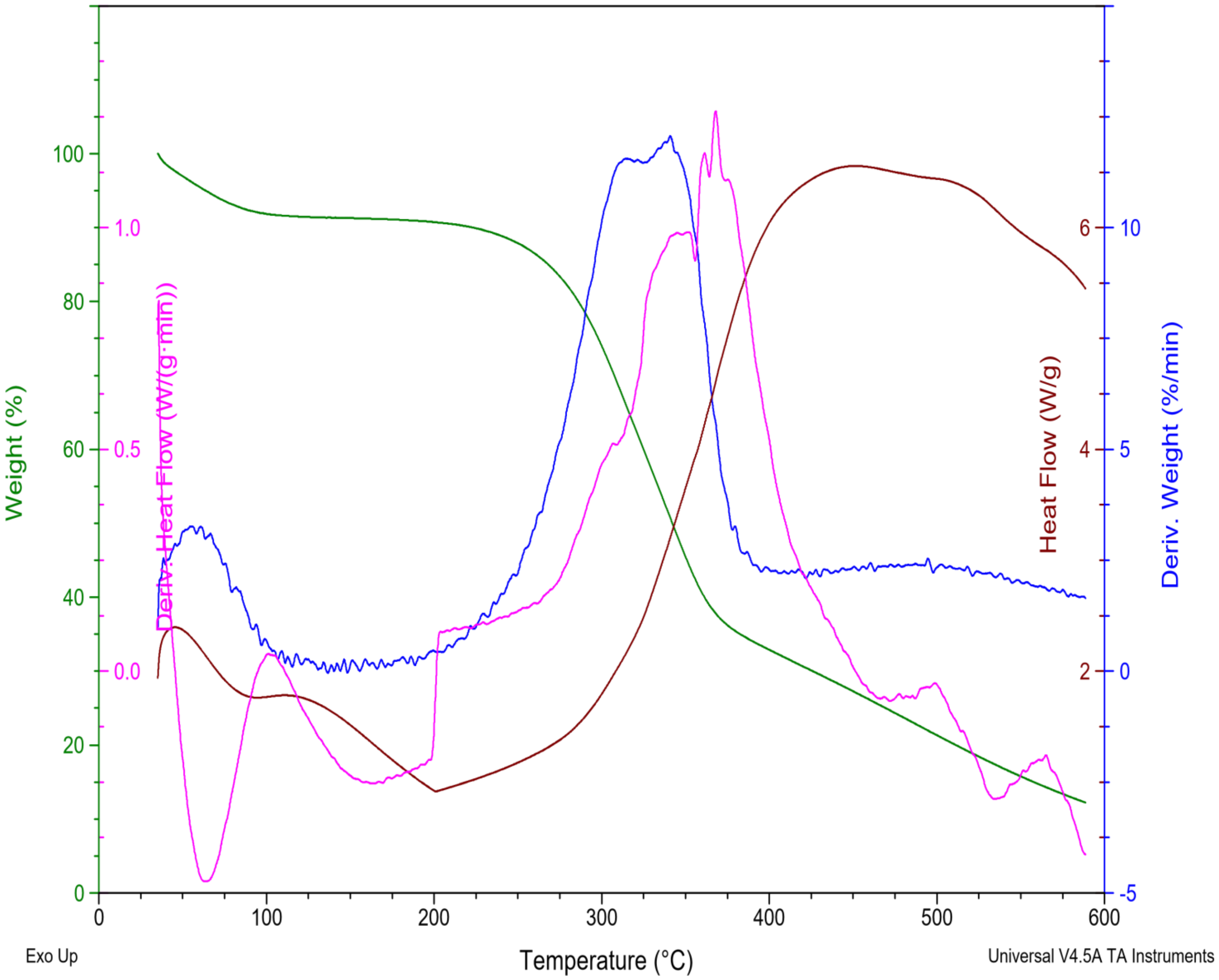
Appendix 8

TGA Output for 10 bars-5 min Steam-Exploded Sample



Appendix 9

TGA Output for 10 bars-10 min Steam-Exploded Sample



Appendix 10

TGA Output for 10 bars-15 min Steam-Exploded Sample