UNIVERSITI MALAYSIA KELANTAN

THERMOGRAVIMETRIC ANALYSIS OF BANANA PEELS VIA PYROLYSIS

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DECLARATION

I declare that this thesis entitled "Thermogravimetric Analysis of Banana peel via Pyrolysis" is the results of my own research except as cited in the references.

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ABSTRACT

Banana peels is outer covering of the banana fruit which rich in various organic matter. Banana peels as biomass waste that should disposal properly to reduce enviromental problems. It was potential become renewable energy such as bio-oil and biogas in pyrolysis. Unripe and ripe banana peel was used in pyrolysis. Study of characteristics biomass to determine the ability of biomass as a renewable energy source. Present research was conducted with thermogravimetric analysis to study the characteristic of ripe and unripe banana peel at different heating rates. The objectives of this research is investigate proximate and ultimate analysis of banana peel. Next, characterize banana peel by using SEM-EDX, FTIR, TGA and DSC for morphology structure, functional group and thermal stability of banana peels. Objectives also determine kinetic and thermodynamic of banana peel by using different isoconversional method via thermogravimetric analysis. TGA analyzer was used to analyze the weight loss of banana peel sample by increasing temperature over time with different heating rates of 10 °C/min, 20°C/min and 30°C/min. DSC method was run together within TG analysis to determine heat flow of sample as temperatre increase over time. Proximate analysis showed in content of volatile matter in banana peel, ultimate analysis showed elements hyrogen and oxygen were major elements. Averaged activation energy calculated from model-free isoconversional method Flynn-Wall-Ozawa(FWO), Friedman and Kissinger from 0.2-0.7 conversion were 48.82, 38.77 and 29.58 kJ/mol for unripe banana peel whereas 56.22, 59.86 and 31.55 kJ/mol for ripe banana peel. Pre-exponential factor obtained from FWO and Kissinger method was found to vary from 10^4 to 10^9 s^{-1}. Thermodynamic analysis for enthalpy, Gibss free energy and entropy in average 40.29, 1750.61, and -5.54 kJ/mol for unripe banana peel. For ripe banana peel it showed average in 64.13, 1774.95 and -5.19 kJ/mol. Unripe banana peel more efficient in pyrolysis due to activation energy was lower than ripe banana peel. In short both types of banana peel was potential to become biorenewable energy source such as biochar and bio-oil. Banana peel possess good thermal stability and characteristics which capable high temperature and convert to bioenergy to produce heat and energy.

ABSTRAK

Kulit pisang adalah kulit luar buah pisang yang kaya dengan pelbagai bahan organik. Kulit pisang sebagai sisa biojisim yang perlu dilupuskan dengan betul untuk mengurangkan masalah alam sekitar. Ia berpotensi menjadi tenaga boleh diperbaharui seperti bio-minyak dan biogas dalam pirolisis. Kulit pisang yang belum masak dan masak digunakan dalam pirolisis. Kajian ciri biojisim untuk menentukan keupayaan biojisim sebagai sumber tenaga boleh diperbaharui. Penyelidikan semasa telah dijalankan dengan analisis termogravimetrik untuk mengkaji ciri kulit pisang yang masak dan tidak masak pada kadar pemanasan yang berbeza. Objektif kajian ini adalah untuk mengkaji analisis proksimat dan muktamad kulit pisang. Seterusnya, mencirikan kulit pisang dengan menggunakan SEM-EDX, FTIR, TGA dan DSC untuk struktur morfologi, kumpulan berfungsi dan kestabilan terma kulit pisang. Objektif juga menentukan kinetik dan termodinamik kulit pisang dengan menggunakan kaedah isokonversi yang berbeza melalui analisis termogravimetrik. Penganalisis TGA digunakan untuk menganalisis penurunan berat sampel kulit pisang dengan meningkatkan suhu dari semasa ke semasa dengan kadar pemanasan berbeza 10 °C/min, 20°C/min dan 30°C/min. Kaedah DSC dijalankan bersama dalam analisis TG untuk menentukan aliran haba sampel apabila suhu meningkat dari semasa ke semasa. Analisis proksimat menunjukkan kandungan bahan meruap dalam kulit pisang, analisis muktamad menunjukkan unsur hirogen dan oksigen adalah unsur utama. Purata tenaga pengaktifan yang dikira daripada kaedah isokonversi bebas model Flynn-Wall-Ozawa(FWO), Friedman dan Kissinger daripada penukaran 0.2-0.7 ialah 48.82, 38.77 dan 29.58 kJ/mol untuk kulit pisang yang belum masak manakala 56.22 dan 59.86 untuk kulit pisang yang belum masak. kulit pisang masak. Faktor pra-eksponen yang diperoleh daripada kaedah FWO dan Kissinger didapati berbeza dari 104 hingga 109 s^{-1}. Analisis termodinamik untuk entalpi, tenaga bebas Gibss dan entropi dalam purata 40.29, 1750.61, dan -5.54 kJ/mol untuk kulit pisang yang belum masak. Bagi kulit pisang masak ia menunjukkan purata dalam 64.13, 1774.95 dan -5.19 kJ/mol. Kulit pisang yang belum masak lebih cekap dalam pirolisis kerana tenaga pengaktifan adalah lebih rendah daripada kulit pisang masak. Pendek kata kedua-dua jenis kulit pisang ini berpotensi untuk menjadi sumber tenaga boleh diperbaharui seperti biochar dan bio-minyak. Kulit pisang mempunyai kestabilan haba yang baik dan ciri-ciri yang mampu suhu tinggi, ia dapat bertukar jadi bahan mentah untuk menghasilkan haba dan tenaga.

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LIST OF ABBREVIATIONS

TGA	Thermogravimetric Analysis
DSC	Differential scanning calorimetry
TG	Thermogravimetric
E_a	Activation energy
FWO	Ozawa-Flynn–Wall
SEM-EDX	Scanning electron microscopy-Energy-Dispersive X-ray
FTIR	Fourier-Transform Infrared
K	Potassium
Cl	Chlorine
N	Nitrogen
C	Carbon
O	Oxygen
S	Sulphur
Ca	Calcium
Mg	Magnesium
OH	Hydroxyl group
CH	Methine group
Wt.	Weight

LIST OF SYMBOLS

°C	Degree celcius
T_m	Peak temperature
ß	Heating rates
ΔH	Enthalpy
ΔS	Entrophy
ΔG	Gibss free energy

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The utilization and disposal issue of biomass waste are a challenges in this era globalization. Technique and approaches to disposal the increasing generation of biomass waste was focused on by many countries. Increasing utilize of energy cause the unrenewable energy source decreasing. Utilization of biomass as a renewable energy source are focus to replace the non-alternative fossil fuels energy (Syaifuddin et al., 2022). Biomass residues was potential as sources and to generate bioenergy. Thermal heat energy produce in decomposition process of lignocellulosic compounds it was converted into renewable liquid and gaseous fuels as bioenergy resources as a fuel to generate energy. .

Pyrolysis burned a material without the presence of oxygen. Using this method, biomass can be converted into bioenergy resources such as bio-oil and biochar for use in other energy-generating processes. High temperature caused decomposition of sample and change the chemical structure to form products. Pyrolysis product is organic compounds that can be used as it as a fuel or heat generation such as biochar, bio-oil and biogas (Eveline et al., 2020). Thermogravimetric analysis is carry out to measure a material weight change when heating up material in temperature change over time. The data from TGA is use to calculate Model-free isoconversional methods from biomass pyrolysis kinetics. FWO, Friedman and Kissinger method applied TGA data to calculate the activation energy of a biomass, it was kinetics parameters of biomass that show the characteristic and behavior of biomass in energy production. A biomass that possess good properties were high in efficient in pyrolysis, the process can be done in high efficiency reaction and more product can be yield.

Malaysia is a country that produce many kinds of agriculture feedstock includes banana feedstock. Total of banana feedstock increase fom year to year shows that the development of feedstock in Malayisia. In banana cultivation in 2012, the banana produced is 335, 974 tones and total biomass produced results in 806 337.6 tonnes of potentially available banana biomass (Razak et al., 2021). Almost 60% of banana biomass is left and become waste after harvest. The amount of biomass waste is high in Malaysia, we should utilize the biomass wisely so that it can brings benefits to human and environment.

1.2 Problem Statement

Banana peels are eco-friendly biomass, it's able to solve environmental pollution problems and produce renewable energy as well. Compare to previous research that use wood and straw crop to produce renewable energy, banana peels can replace the demand of wood and straw in the approaches to produce renewable energy. This is because the agriculture crop need to supply for food and caused the limitation in production of renewable energy. Banana peels are biomass waste that does not exist futher useful compare to different biomass. Therefore, chosen of banana peels are potential as renewable energy production.

There are two types of banana peel was choosen which are unripe banana peel and ripe banana peel. Ripening process of banana changed composition of banana peel so two different peel was conducted to see how is the characterization. To prove that banana peels potential become renewable energy sources, the pyhsicochemical properties of banana peel should be investigated. Characterization of banana peel with different compounds composition was determined by Proximate & ultimate analysis. Through the analysis major component of banana peel can be investigated to understand the chemical characteristics as a renewable resource. Besides, various of chemical compounds that can be analyzed by technique SEM-EDX and FTIR. The morphological structure of biomass reveal in SEM analysis while element composition on surface can be identified with EDX analysis. FTIR are technique to investigate various of presence of certain functional groups in an organic molecule by infarred scanning. Characteristics of banana peel biomass can be identify through the chemical compounds.

Thermogravimetric analysis is necessary to determine the data of energy yield by biomass. The data such as weigh loss and heat rate can be obtained from TGA used to calculate the kinetic parameter, Model free isoconversional methods apply TG analysis data to calculate activation energy with FWO, Friedman and Kissinger methods. Value of activation energy determine kinetic characteristics of biomass as burning in high temperature. Lower Ea value indicates more efficient of biomass in the reaction process, it was predicting the dynamics and behavior of biomass. Calculated activation energy use apply to calculate thermodynamic which showed the Heat capacities and enthalpie of biomass. Pre-exponential factors calculated collision molecule biomass within pyrolysis, it determines frequency value of collosion biomass in various conversion.

Heat flow of biomass determine the heat trasfer of the biomass in pyrolysis with DSC method. Energy transfer of biomass is related with heat flow this characterize ability of heat transfer of biomass. Biomass wastes can be transformed into clean energy and/or fuels by a variety of technologies, ranging from conventional combustion process to state-of-the art thermal depolymerization technology. Besides recovery of substantial energy, these technologies can lead to a substantial reduction in the overall waste quantities requiring final disposal, which can be better managed for safe disposal in a controlled manner while meeting the pollution control standards.

1.3 Objectives

The objectives of this research are:

1. To investigate the proximate and ultimate analysis of unripe and ripe banana peel
2. To characterize banana peels by using SEM-EDX, FTIR, TGA and DSC for morphology structure, functional groups and thermal stability.
3. To determine kinetic and thermodynamic of banana peel by using different isoconversional method via thermogravimetric analysis.

1.4 Scope of Study

Banana peels are characterize through thermogravimetric analysis to determine it is able use as biomass in generating energy through pyrolysis. Ripening process of banana change composition of banana peel so two different peel unripe and ripe peel was conducted to see how is the characterization. Thermogravimetric analysis is a technique use to measure a material weight change when heating up material in temperature change over time. TGA data is use to determine the value of energy produce by banana peels and leaves biomass with increasing of temperature over time. With Thermogravimetric analysis, characteristics of kineric parameters, exponential factor and thermodynamic can be determine with application of model-free isoconversional methods. For investigate the characterization composition of banana peel, Proximate and ultimate, Scanning Electron Microscopy (SEM), Energy-dispersive X-ray (EDX) analysis and Fourier transform infrared spectroscopy (FTIR) conduct to analyze compounds within banana peel.

Initially, unripe and ripe banana peel collect from stall in Jeli, Kelantan. The banana spesies that use in research was Musa sp. (Pisang Nangka). Collected banana peel dry in oven for 24 hours the and then grind the sample to powder form with grinder. The powder keep in glass bottle and placed inside desiccator. Characterization of banana peel show in pysicochemical content. Proximate and ultimate analysis was analyzed using In-house Method No: STP/Chem/A05 based on AOAC 20th Edition: 923.03. The sample use in the analysis are 100 gram of powder form. SEM-EDX carry out with SEM equipment, several powder sample was paste at on the spesimen to run the test. For FTIR analysis, sample was placed on detector of equipment to scan samples and observe chemical properties by convert the data into computer.

TGA is carry out in the Thermogravimetric analyzer, it is furnace with a programmable control temperature. The thermal reaction is proceed under vacuum or high presure as heating up the sample (Xi Wen et al., 2022). The data will be analysis and convert into graph curve, y-axis shows percentage weight loss of mass while x-axis shows temperature or time for the process. After pyrolysis, the data will be convert in StarEvaluation software to extract data to create slope from various conversion. The isoconversional method apply mathematical model to calculate activation energy from TG curve data. The three methods in isoconversional methods are Ozawa-Flynn–Wall(FWO), Friedman and Kissinger are use to calculate kinetic parameter which is activation energy of biomass. The data from TG curve would apply in isoconversional method formula to determine the slope eventually calculate the activation energy. These data should be analysis to determine that the banana is potential as a renewable energy source (Mudassir et al., 2019). The kinetic parameter determine the characteristic of the sample, which it can produce more or less biosource. Comparison result in this studies compare to previous study. For thermodynamic, Enthalpy, entrophy and Gibss energy were calculated as heat capacity produce from biomass. Different heating rates that use to heat up the biomass and heat capacity are the parameter in the analysis. The parameters should be setting well so that the data of properties can be obtain properly. Actication energy obtained from isoconversional method was applied in equation of thermodynamic to calculate the parameters.

1.5 Significance of Study

TGA shows the properties data of materials that we want to use in an experiment or process to produce a product. The materials will be react well in the process with others materials so the desire result and product can be produce properly. TGA brings benefits to renewable energy production, the biomass materials properties and thermal characteristic can be evaluated, a good materials can be chosen to produce the energy. Characteristic of a biomass based on thermal staibility can be evaluated, the data from TGA can be used further to determine more parameter for characterization of biomass. Potential of a biomass can be determined to become a renewable energy source. Therefore, biodiesel and biogas can be produce to generate energy for electricity and vehicle. Futhermore, the disposal of biomass waste is important and should concern to reduce the waste in environment. Using of biomass waste to produce bionergy is an efficient and friendly environmental way of biomass treatment (Zdenka Kwoczynski & Jiří Čmelík, 2021). The sustainbility of energy can continue as renewable energy replace petroleum energy. The utilization of biomass energy decrease demand of fossil in energy generation, the sustainbility of energy can be keep going in future generation.

CHAPTER 2

LITERATURE REVIEW

In this research, banana leaves and peels use as biomass waste to determine the characteristic. The biomass can be use to produce renewable energy by pyrolysis. In fact, Thermogravimetric analysis use to analytze the properties of the biomass. We can calculated the kinetic parameters of banana biomass to determine the energy yield in pyrolysis. TGA contribute the data in this research so that we are able to use the data and apply in mathematical modelling to calculate energy. The banana biomass can be prove as renewable energy producer with the calculation of energy kinetic parameter and thermodynamic. Knowledge of biomass pyrolysis and TGA is important to learn in the research. We should elaborate out and clear information about the title so that the research can be proceed well and no mistaken occur during research. The information related to title is elaborate out which refer journal that will helps for the research.

2.1 Banana peel

Banana peels is the outer layer of banana fruits and use to protect banana fruits. Banana peels composition by starch, fiber, protein and lipids. The most composition of banana peels is starch which occupies 59% of compounds compare to others. Banana peels provides many benefits to us when we remove it from banana. However, banana peels mostly act as biomass waste when we used it. For example, banana peels used as ingredient in cooking, water purification, bioproduct and inorganic waste production. (Waafaa et al., 2022). There are two types of banana peel which are unripe and ripe banana peel. Disposal of biomass waste is nessacary to avoid environment pollution problems. Banana peels waste can use as catalytic pyrolysis to yield renewable energy for sustainable useful such as biodiesel and electric. Previous studies indicated that using banana peels waste for the production of biochar may reduce environmental losses. The banana peels as biomass able convert to bioenergy source for replacement of unrenewale energy. (Mudassir et al., 2019) investigated as a potential material for biofuel production via pyrolysis. These findings suggested that banana peel pyrolysis would be a workable procedure for producing bioenergy. As short with proper disposal of banana waste it able to bring benefits to environment and humans.

Figure 2. 1: Banana peel as biomass

(Source: Melis, 2022)

2.2 Pyrolysis

Organic materials can be decompose through high temperature. Pyrolysis is decomposition of organic material process in high temperature with the absence of oxygen. The burning of the materials is carry out in high temperature (above 500°C) so that the polymer of the materials can be deconstruct. In this research the biomass from banana taken as sample to decompose. The kinetic parameters of biomass showed as the thermal decomposition proceed such as activation energy and reaction rate which overlapping with components of biomass (Xin Wang et al., 2019). Pyrolysis produces char, liquid and gas products, the char and gaseous products can be combusted to provide energy for heat and power generation as example in figure 2.3. The fundamental information such as kinetics and thermodynamic characteristic of biomass in the pyrolysis process can be determined, it is essential for designing and scaling up of industrial equipments and modelling in mathematical enginering pathway (Asma Ben Abdallah et al., 2023). In this research, data pyrolysis of banana is obtain from thermo-gravimetric analysis (TGA). In the pyrolysis process, the sample produce activation energy and heat while it was decompose.

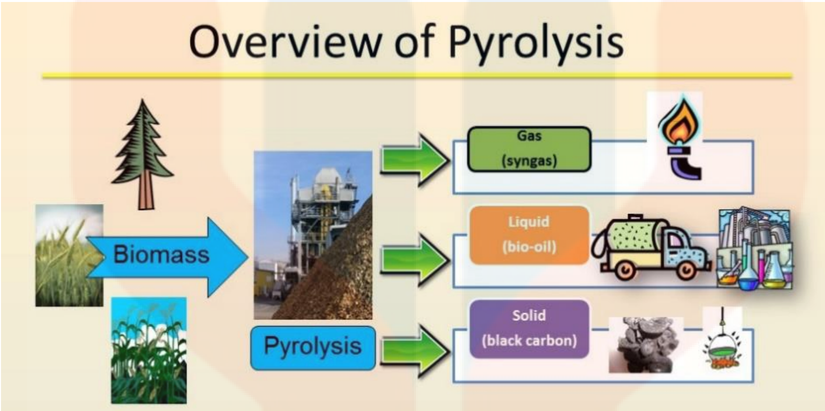


Figure 2. 2: *Pyrolysis of biomass to form biochar, bio-oil and bio gas*

(Source: Spokes, 2018)

2.3 Biomass catalytic pyrolysis

The components of banana peels and leaves biomass are cellulose, hemicellulose and lignin. These components are carbohydrat which capable yield biochar, gas, and bio-oil production which serve as bioenergy for renewable source. During process pyrolysis, large hydrocarbon molecules of biomass are decompose into small ones with reactions such as depolymerization and dehydration. Cellulose pyrolysis includes depolymerization and dehydration in 500°C of temperature formed bio-oil from dehydration of cellulose. Cellulose pyrolysis proceeds depolymerization reaction to form furan ring and covert to form HAA, propionic acid, acetaldehyde and oligosaccharide (DengYu et al., 2022). For hemicellulose pyrolysis, xylan compounds dehydrated producing didehydrated pentose, multi-step dehydration caused the forming of char in futher dehyration.

2.4 Biomass forming bio-energy

Decomposition of biomass yield biochar, biogas and bioliquid which can be converted to produce renewable energy such as biodiesel and methane gas. The energy that is obtained from fossil fuels cannot be renewable agian and also give negative impact on ecosystem due to to high emission of carbon dioxide. Thus, developing of bioenergy is focusing to minimize the utilization of fossil fuels increasing the production of renewable energy from available sources (Arawind Kumar et al., 2023) . The energy can be use as fuel vehicle and electricity generation for human use to instead of petroleum fuel to generate power.

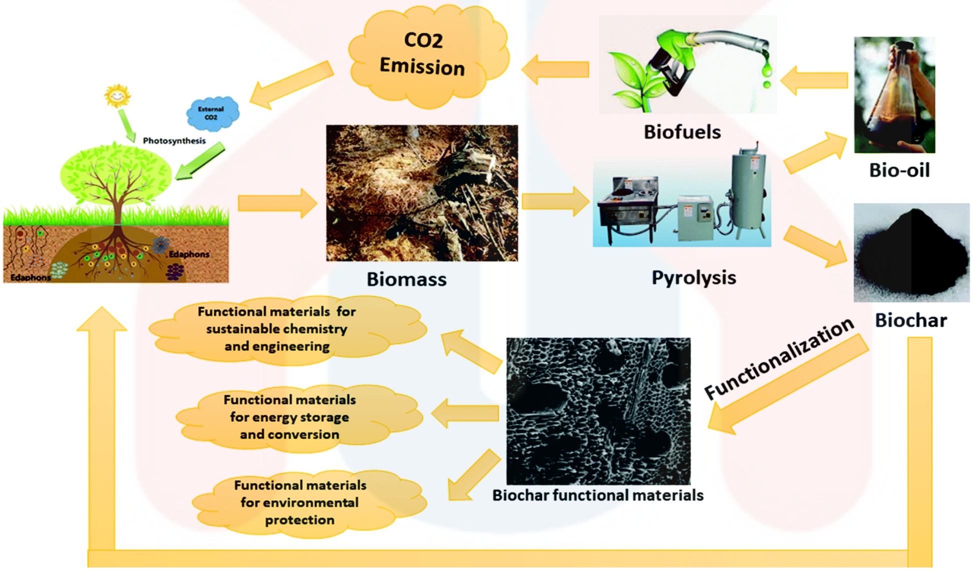


Figure 2. 3: Bioenergy produce from biomass with application

(Sources: Osman, 2023)

2.5 Trends of biomass waste

Increasing of human population nowadays produce large amount of biomass waste through activities human. Disposal of biomass waste is important to avoid the lead of environmental pollution, recycling of biomass waste is more focus to value-added applications such as converted into a variety of useful sources of bioenergy (Chufan & Yixiang ., 2020). Most of the literature is focus on wood biomass and agricultural rice straw waste as development of this biomass. Instead, food processing and domestic biomass waste is consider as biomass waste which capable produce high bioenergy such as banana leaves and peels. In this literature, the banana leaves and peels is study to prove that it's potential to generate bioenergy due to it possess high component of lignocellulosic compounds. Besides, from previous literature of banana leaves and peels analysis, this research brings more information of energy production in various calculation. Most of literature not calculated Pre-exponential factor and reaction rate. These data can be prove as characteristic of biomass as well, more data obtained and it can more to approve the potential of banana as renewable energy production source.

2.6 Effect of heating rate in renewable energy production

Heating rate is rate of heat transfer in a reaction, which heat energy is transfer per unit of time. In TG analysis, different of heating rates will effect the amount of energy production for various sample. Some sample produce higher activation energy in low heating rate and instead some sample produce low activation energy. This is because the decomposition characteristic of various sample is not same, the characteristic is effect by chemical compounds content of sample such as functional group and volatile compounds. For example, final conversion of biomass to volatiles increase as higher heating rate increase. This reduce the repolymerization of volatiles to form char (Jordan et al., 2018). Thus, it shows that increasing of temperature in short time caused the sample more volatile, the activation energy obtained is lower than lower heating rate.

2.7 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is use to anaylze a material weight change as heating the material in different temperature over time. The components of sample will volatilize as time taken and heating up, the weight loss and temperatire are recorded to determine the properties of the material. Properties of sample such as thermal stability, moisture content, volatile matter, fixed carbon and ash content of can be determine trough TGA. In this research, TGA use to determine the kinetic parameters of the banana leaves and peels biomass. Due to its efficiency, TGA has been used widely for kinetic analysis involving decomposition different types materials. This technique provides the heat capacity and decomposition of materials as a function of temperature over a yime and carry in controlled temperature. (Emiola et al. 2021)

2.7.1 Thermogravimetric Curve

Thermogravimetric curve shows data in % weight loss of sample against temperature after measuring the mass of a sample during heating. The data shows in ploting graph, which y-axis represent weight loss % and X-axis represent temperature change. TG curve is the basic principle of TGA that shows the result of weight change sample againts temperature changes.

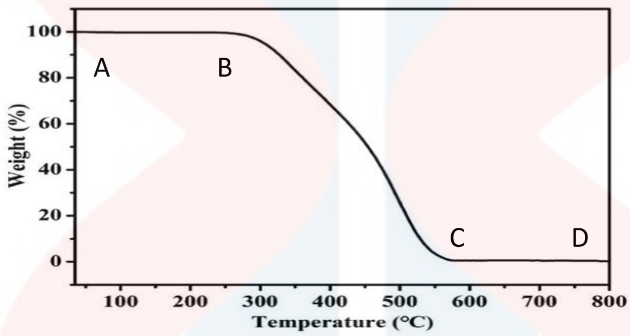


Figure 2. 4: Example of TG curve

(Source: WeiDong, 2019)

For example analysis of TGA curve in figure 3.3, AB is horizontal portion and indicates that no weight change of material and remain constant. Next, BC portion shows that changes of weight (weight loss) and decomposition is started. The material thermally stable up to a temperature of 450°C. The weight loss stopped at portion CD and remain constant leaving.

2.8 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a technique to determine heat flow of a materials and sample which is measured in temperature or time changed. As the sample is heating, the heat will flow in and out for the sample, endothermic and exothermic reaction of the sample can be determined which the sample is produce or absorb heat. The data heat flow is use to calculate the thermodynamic of the sample so that the heat capacity can be determined (Karimi et al., 2022). A sample that posses high heat capacity which have high ability to absorb and store thermal energy. Therefore, more renewable energy such as biodiesel and biogas can be produce in the pyrolysis. Thermal analyisis and properties materials can be determine with this technique.

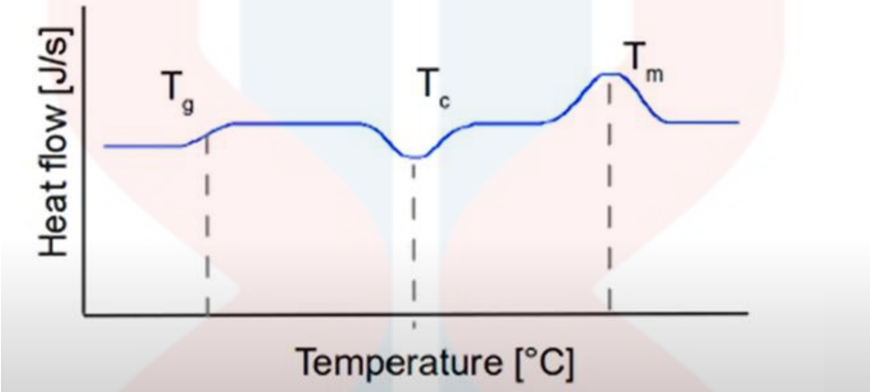


Figure 2. 5: Differential Scanning Calorimetry (DSC) Curve

(Source: Saija, 2021)

DSC curve shows the change of heat flow at different heating rates in pyrolysis process. The direction of heat flow is effected by changes of temperature during pyrolysis. Temperature and heating rate as a function to determine the heat flow. DSC curves were plotted based on heat flux versus temperature or time. Exothermic and endothermic reaction showed in the curve. For example in figure 3.4, the glass transition temperature phase shows that no physical change of material, as the heat flow increasing, the mechanical properties of materials start changes. For Tc, the materials undergo crystalization and exothermic occur and heat released. Until Tm, it was melting temperature and endothermic process, heat abdorb by meterial to change the state.

2.9 Chemical kinetic

Chemical reaction proccess involved reactant reaction to form a product. Chemical kinetic is a study of the rates of chemical reactions, the rates for conversion of chemical compounds from reactant to become products (Mokhtar et al., 2020). This provide a quantitative or qualitative measurement of the rate of reactions and provide dependence of these rates on variables such as concentration, temperature, pressure and the presence of catalysts. These interactions variables is controlling the reaction for a successful outcome. In the pyrolysis process, the sample decomposition process produce activation energy and heat while it was burned and product produce from reactant (reactant to product). Energy release. In this research, the kinetic rate is calculated in kinetic parameter which is Ea produce by biomass through pyrolysis process. From the reaction kinetic rates, activation energys and other kinetic parameters can be determined in a reaction. Measuring the progress of a reaction as a function of time yields the reaction rates is important to enhance the reaction (Bispo, F. J. S., Kartnaller, V., & Cajaiba, J. 2019). Measuring the progress of a reaction as a function of time yields the reaction rates, and from this data rate constants and activation energies can be determined. The biomass which has higher kinetic reaction required low Ea and more able to produce high value of energy as heating it with increasing temperature. Reaction kinetics provide a measurement of reaction rates, factors that affect the speed of a chemical reaction and insight into reaction mechanisms. Pyrolysis is mainly induced by effective collision of reactant molecules with sufficient kinetic energy. Consequently, the chemical bonds were cleaved and reformed, thereby yielding various pyrolytic product. Therefore, a reactant that had high sufficient kinetic energy, lower Ea required for biomass pyrolysis (Mudassir, 2019). Previous literature calculate average activation energy from pyrolysis of banana leaves, the value was found to be 92.12 and 70.75 kJ/mol compare to banana peel from 108.42 kJ/mol. Lower Ea obtained indicates that the biomass was more energy efficient as burning in high temperature.

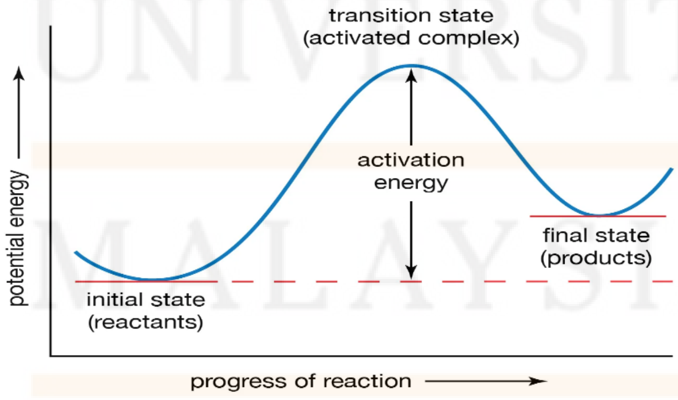


Figure 2.5: Activation energy as kinetic of reaction

(Source: Liubov, 2015)

2.10 Thermodynamic

Thermodynamic determine the relationship of heat and work in the changes of chemical reaction. Chemical reactions release energy in heat capacity and occur energy changes in the reaction process. Thermodynamic shows that the thermal energy converts to other types of energy and how this affects the properties of reactant in the reaction. For example in this researh, the reaction of pyrolysis biomass release energy in the reaction when heating it. The energy that release are kinetic energy which enable the formed of the bioenergy product. The thermodynamic in this research is represented by entalphy ΔH, entrophy ΔS and Gibbs free energy ΔG. Thermodynamic shows that the thermal energy converts to other types of energy and how this affects the properties of reactant in the reaction. Low ΔSα values indicate pyrolysis of biomass experiences small physical and chemical changes.

Changes value of thermodynamic parameters showed how is the reaction molecule of biomass within pyrolysis. Literature investigated that the variation of Enthalphy, Entrophy and Gibbs Free Energy. In the research the thermodynamic parameters was found to increase as temperature increasing in pyrolysis. This indicates that endothermicity of biomass pyrolysis increase, heat energy transfer in high frequency that the reaction rate fast as temperature increase.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Two types of banana peel-Unripe and ripe banana peel collect in fried banana stall at Jeli, Kelantan, the spesies of banana peel is ‘Pisang Nangka’ (*Musa.sp*.).

3.2 Method

3.2.1 Preparation of banana peel powders

Oven was used to dry banan peel at 70 °C for 24 hours. Next, the samples was grind with grinding machine to become powder formed size (250 μm) and kept in tiny bottle glass, the glass store within desiccator to avoid moisture.

3.2.2 Proximate & Ultimate analysis.

Proximate analysis determine the composition of the biomass such as moisture content, volatile matters, ash content, and fixed carbon. Ultimate analysis analyze the elemental composition Carbon, Hydrogen, Nitrogen and Oxygen within biomass. The analysis carried our with In-house Method No: STP/Chem/A05 based on AOAC 20th Edition: 923.03 with 100 gram of sample.

3.2.3 Banana peel characterization

Scanning Electron Microscopy (SEM) is a techniques that scans a sample with an electron beam to produce a magnified image to observe surface morphology of materials. Energy-dispersive X-ray (EDX) analysis an X-ray technique that is used to determine the elemental composition or chemical characterization of material. Sample powder of banana peel was paste on the spesimen and proceed analyze with SEM-EDX detector. The result showed in connected computer. The spot can be choose on the surface of sample to determine element composition on sample.

Technique Fourier-transform Infrared Spectroscopy FTIR spectroscopy used to identify the functional group compounds that content in the banana peel, it showed pyhsicalchemical properties of the biomass. The working of FTIR is sending infrared radiotion in specific wavelenth to the sample, the sample molecules absorb radiation of specific wavelengths, different types of compounds posses specific wavelength and the data will output through computer analysis. In the experiments 5 g of banana peels powder was placed on detector to test the compounds. Instrument transfer the data to computer, data with organic matter present in Omnic software. Composition of organic matter, absorbance value and other parameter showed in the software with wavenumber 4000cm^{-1} to 300 cm^{-1}.

The TGA and DSC is carry out with thermogravimetric analyzer by the same time. Instrument use in the analysis are Simultaneous Thermogravimetry & Differential Scanning Calorimetry. The analysis of the samples (unripe and ripe) was conducted at different value of heating rate which are 10°C/min, 20 and 30 °C/min. Heating of TG is under nitrogen atmosphere, nitrogen is non-reacting inert gas, the gas volumetric flow rate is 20 mL / min. The furnace was pre-treated with with nitrogen at 383 K for 1 hour. 2.4mg of sample weight was loaded in the crucible, total 6 sample which unripe and ripe banana peel for 10°C/min, 20 and 30 °C/min heating rates. Heat flux sensor tested the heat flow of the sample within pyrolysis. The analyzer heating conducted at a heating rate of 10 °C/min over a temperature range of 25°C to 900 °C for 2 hours (Rajnish Kumar Singh et al., 2020). The analyzer transfer the weight loss and temperature change data into computer. The TG and DSC data and blank for TG curve create in StarEvaluation software, extract the data into Excel to calculate kinetic parameter and thermodynamic parameter.

3.3 Kinetic parameters, Model-free isoconversional method

Model-free isoconversional method used to calculate the activation energy from TG data by plotting the logarithm of heating rate as a function of the inverse of the temperature, at different conversions. The three methods used were FWO (Ozawa, 1965), Friedman (Friedman,1964) and Kissingerr (Kissinger, 1956) method. FWO (Ozawa, 1965) method was proposed by Ozawa using Doyle's approximations provides the Flynn-Wall-Ozawa (FWO) method. Friedman method proposed based on comparison of various experiment, different linear rates of heating performed in the research. Homer E. Kissinger deliver peak temperature in various heating rates with kenetic. Kinetic constant obtained from peak temperature to calculate E_a in the reaction.

3.3.1 Flynn-Wall-Ozawa (FWO) method

FWO method calculating activation energy from β, different constant heating rates equation as:

$$\text{In}\ (\beta) = \text{In}\left[\frac{\text{AE}_\text{a}}{RG_{(\alpha)}}\right] - 5.331 - 1.052\left(\frac{\text{E}_\text{a}}{\text{RT}}\right) \qquad \text{Equation 3.1}$$

Where, A is pre-exponential factor, R is gas constant 8.314 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, g (α) is integral form of conversion 1-α.

Conversion for weight loss and temperature from 10, 20 and 30 heating rates was calculated with w_0-w_t / w_0-w_f. Value of 1000/T was calculated from initial to final temperature for 10, 20 and 30 heating rates. ß refer to heating rates which are In (10),In (20) and In (30). Value of conversion that near 0.2-0.7 was choosed to plot graph by plotting In(β) vs 1000/T for 10, 20 and 30 heating rates together. The slope obtained from plotting graph, was equal to −1.052 Ea/R. Activation energy can be evaluated from slope −1.052 E_a /R.

Pre-exponential factor was calculated by insert Ea into $\text{In}\left[\frac{\text{AE}_\text{a}}{RG_{(\alpha)}}\right]$ equal to C, y-intercept from plotting graph In(β) vs 1000/T.

β	α	C	1000/T	ln β	m	R2	Ea kj/mol
10			2.1875	2.3026	-7.9588	0.94	62.8987
20	0.2		2.1315	2.9957			
30			2.0528	3.4012			
10			2.0305	2.3026			
20	0.3	13.884	2.0155	2.9957	-9.561	0.8908	75.561
30			1.8792	3.4012			
10			1.8634	2.3026			
20	0.4	14.818	1.8479	2.9957	-6.5677	0.7133	51.9048
30			1.7327	3.4012			
10			1.7757	2.3026			
20	0.5	15.374	1.7601	2.9957	-7.2091	0.7229	56.9738
30			1.6552	3.4012			
10			1.6709	2.3026			
20	0.6	8.8456	1.6802	2.9957	-3.6929	0.5703	29.1851
30			1.479	3.4012			

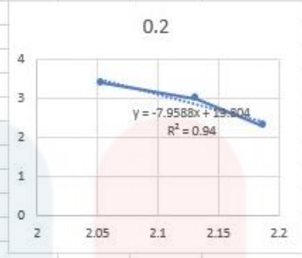


Figure 3.1: Activation energy, Ea calculated by FWO

Pre-exponential factor								
Heating r	Conversion	Ea	C	ga	C+5.311	ex	A	Average
10				0.24827			14110362532	2.17 x 10^9
20	0.2	62.8987	19.804	0.242103	25.115	80780383942	13759863311	
30				0.266504			15146652918	
10				0.42762			55421462.16	8.57 x 10^6
20	0.3	75.561	13.884	0.409165	19.215	221293404.2	53029565.88	
30				0.422193			54718037.87	
10				0.656252			315073247.9	6.05 x 10^7
20	0.4	51.9048	14.818	0.664812	20.149	563118137.6	319182844.3	
30				0.693144			332785392.5	
10				0.945426			721055089.2	1.39 x 10^8
20	0.5	56.9738	15.374	0.981991	20.705	981899972.4	748942236.2	
30				0.99113			755912335.7	
10				1.512994			3291876.478	6.30 x 10^6
20	0.6	29.1851	8.8456	1.598141	14.177	1434891.795	3477133.794	
30				1.516824			3300209.997	
10				2.391169			304102.5874	5.60 x 10^5
20	0.7	12.667	5.1714	2.37295	10.502	36402.76455	301785.5836	
30				2.322264			295339.4227	

Figure 3.2: Exponential factor, A calculated from Ea

3.3.2 Friedman method

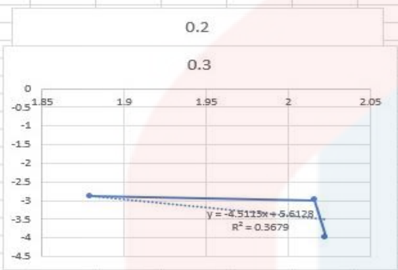
Friedman method used to calculate activation energy with apply of temperature and heating rates from TGA data. The equation of Friedman method is:

$$\text{In}\left(\frac{\text{da}}{\text{dt}}\right) = \text{In}\,[\text{f(a)}A_a] - \frac{E_a}{RT_a} \qquad \text{Equation 3.2}$$

Where, A is exponential factor, R is gas constant 8.314 J·K−1·mol−1, f (α) is is function of conversion.

Conversion for weight loss and temperature from 10, 20 and 30 heating rates was calculated with w_0-w_t / w_0-w_f. Value of 1000/T was calculated from initial to final temperature for 10, 20 and 30 heating rates. In $\left(\frac{\mathrm{da}}{\mathrm{dt}}\right)$ calculated derivative of conversion and time for 60 seconds which In derevative of conversion divide derivative time by 60 for 10, 20 and 30 heating rates. Value of conversion that near 0.2-0.7 was choosed to plot graph by plotting In $\left(\frac{\mathrm{da}}{\mathrm{dt}}\right)$ vs 1000/T for 10, 20 and 30 heating rates together. The slope, m obtained from plotting graph, was equal to −1.052 Ea/R. Activation energy can be evaluated from slope −1.052 E_a /R. Activiation energy is calculated by plot $In\left(\frac{da}{dt}\right)$ againts 1000/T gives a slope - $\frac{E_a}{R}$

Pre-exponential factor was calculated by insert Ea into $\mathrm{In}\ [\mathrm{f(a)}A_a]$ equal to C, y-intercept from plotting graph In $\left(\frac{\mathrm{da}}{\mathrm{dt}}\right)$ vs 1000/T.



β	α	1000/T	In da/dt	m	R2	Ea
10		2.1786	-3.3295	7.3818	0.7332	61.3723
20	0.2	2.1322	-2.4625			
30		2.0534	-2.322			
10		2.0229	-3.9787	4.5113	0.3679	37.5069
20	0.3	2.0161	-2.9934			
30		1.8797	-2.8902			
10		1.857	-3.6118			
20	0.4	1.8484	-2.8632	7.6057	0.7207	63.2338
30		1.7331	-2.3647			
10		1.7699	-3.2589			
20	0.5	1.7606	-2.5168	3.3567	0.2669	27.9076
30		1.6556	-2.5617			
10		1.6657	-3.7561			
20	0.6	1.6807	-2.6261	1.4965	0.1099	12.4419
30		1.4479	-3.4729			
10		1.5306	-4.2052			
20	0.7	1.5848	-3.0579	3.6334	0.7789	30.2081
30		1.1325	-5.0856			
AVERAGE						38.7784

Figure 3.3 : Activation energy calculated by Friedman method for conversion 0.2-0.7

		Average	C	1-a	Pre-exponential A
0.2	0.80111	0.79853	12.955	0.20147	2.0933 × 10^6
	0.80509				
	0.7894				
0.3	0.70047	0.70442	5.6128	0.29558	9.2 X10^3
	0.70964				
	0.70314				
0.4	0.60377				
	0.60067	0.59835	10.841	0.40165	1.2 × 10^5
	0.59062				
0.5	0.51403				
	0.50454	0.50693	3.0755	0.49307	4.3 X 10^4
	0.50223				
0.6	0.39793		5.6766		
	0.38489	0.41202		0.58798	2.9 X 10^4
	0.45324				
0.7	0.29488		9.261		
	0.29648	0.31306		0.68694	1.5 X 10^3
	0.34782				

Figure 3.4: Pre-exponential factor calculated for Friedman method

3.3.3 Kissinger method

Kissinger method calculated overall activation energy at different heating rates with maximum peak temperature, T_m, the equation is following:

$$In\left(\frac{\beta}{T^2{}_m}\right) = -\frac{E}{RT_m} + \ln\left(\frac{AR}{E_a}\right) \qquad \text{Equation 3.3}$$

Where, A is exponential factor, R is gas constant 8.314 J·K−1·mol−1

Peak temperature for 10, 20 and 30 heating rates was determined by highest derivative value which are changes of weight loss divide changes of time. The value was change to Kelvin, K and calculated in $In\left(\frac{\beta}{T^2{}_m}\right)$ for 10, 20 and 30 heating rates. Plot graph for $In\left(\frac{\beta}{T^2{}_m}\right)$ vs 1000/T for 10, 20 and 30 heating rates respectively to obtain average value of slope, m. The activation energy obtained by slope $-\frac{E}{RT_m}$

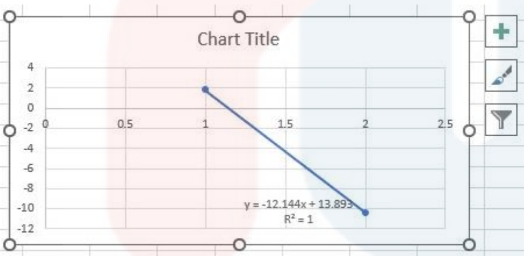


Chart Area

β	Tp (K)	Tp2 (K2)	β/Tp2	1/Tp	LN(β/TP2	1000/Tp	Average Tr	m	R	RTm	Ea (J/mol)	Ea(kJ/mol)
10	571.833	326993	3E-05	0.00175	-10.3951	1.74876		12.144	8.314	2484.4976	30171.7	30.171
20	586	343396	6E-05	0.00171	-9.75091	1.70648	924.833	11.457		2602.282	29814.3	29.814
30	586	343396	9E-05	0.00171	-9.34544	1.70648		11.052		2602.282	28760.4	28.76
								11.551				29.5817

Figure 3.5: Calculation of Kissinger method

The activation energy calculation obtained from FWO methods can apply in Kissenger method to calculate pre-exponential factor at each conversion (Dhyani et al.,2017), the equation is represented by following:

$$A = \frac{\beta E_a \exp(\frac{Ea}{RT_m})}{RT^2{}_m} \qquad \text{Equation 3.4}$$

Pre-exponential factor analyzed the decomposition of the biomass in collision of molecule. High Pre-exponential factor indicates that high collision in the reaction of molecules, high activation energy released to form product for pyrolysis of biomass.

3.4 Thermodynamic analysis

Pyrolysis of biomass occur heat transfer and heat reaction. The heat release as energy from the reactant (materials) and represented by entalphy ΔH, entrophy ΔS and Gibbs free energy ΔG. Total heat that release from the decomposition can be obtain and show that which biomass release most energy. The formula for entalphy ΔH, entrophy ΔS and Gibbs free energy ΔG was presented by equation:

Enthalpy change: $\Delta H = E_a - RT$ Equation 3.5

Entrophy: $\Delta S = \Delta H - \Delta G / T_m$ Equation 3.6

Gibbs free energy $\Delta G = E_a\ RT_m\ (\ \ln \frac{K_b \times T_m}{hA})$ Equation 3.7

where, K_b is Boltzman constant (1.38×10^{-23} m^2 kgs^{-2} K^{-1}), h is Planck constant (6.626×10^{-34} $m^2 kg\ s^{-1}$) for Gibbs free energy. Activation energy from FWO method in 10, 20, and 30 °C/min heating rate is taken to calculate the enthalpy, entropy and Gibbs free energy.

	A	B	C	D	E	F	G
1	ACTIVATION ENERGY FROM FWO						
2							
3							
4	Enthalpy (ΔH)= Ea- RT kj/mol						
5	Conversi	Ea	m	Ea*1.052	m*1.052	RT=	(ΔH)
6	0.2	62.8987	-7.9588	-66.1695	-8.37266	7.90304	54.9957
7	0.25	67.1585	-8.4978	-70.6507	-8.93969	7.90304	59.2554
8	0.3	75.561	-9.561	-79.4902	-10.0582	7.90304	67.6579
9	0.35	48.6448	-6.1552	-51.1743	-6.47527	7.90304	40.7418
10	0.4	51.9048	-6.5677	-54.6039	-6.90922	7.90304	44.0018
11	0.45	72.1674	-9.1316	-75.9201	-9.60644	7.90304	64.2644
12	0.5	56.9738	-7.2091	-59.9365	-7.58397	7.90304	49.0708
13	0.55	39.2481	-4.9662	-41.289	-5.22444	7.90304	31.345
14	0.6	29.1851	-3.6929	-30.7028	-3.88493	7.90304	21.2821
15	0.65	20.5851	-2.6047	-21.6555	-2.74014	7.90304	12.682
16	0.7	12.667	-1.6028	-13.3257	-1.68615	7.90304	4.76395
17							
18							

	I	J	K	L	M	N	O	P	Q	R	S	T	U	V
1		0		298.988										
2				313										
3				313										
4	Gibbs free energy (ΔG)										0			
5	Kb=	1.38*10^-23		h=	6.626*10^-34									
6	β	α	Tm	Ea	RTm	Tm	A	Ea*RTm	Kb*Tm	hA	Kb*Tm/hA	LN (Kb*Tı	Gibbs (J/	Gibss (kJ/mol)
7	10	0.2		62.8987	2563.02	308.278	8.6E+08	161210.734	4.2542E-21	5.679E-25	7491.2826	8.9215	1438241	1438.24
8	20	0.3		75.561	2563.02	308.278	1610125	193664.35	4.2542E-21	1.067E-27	3987585.6	15.1987	2943446	2973.45
9	30	0.4		51.9048	2563.02	308.278	1106037	133033.087	4.2542E-21	7.329E-28	5804970.6	15.5742	2071887	2071.89
10		0.5		56.9738	2563.02	308.278	1214052	146025.067	4.2542E-21	8.044E-28	5288497.3	15.481	2260621	2260.62
11		0.6		29.1851	2563.02	308.278	621905	74802.1208	4.2542E-21	4.121E-28	10323947	16.15	1208053	1208.05
12		0.7		12.667	2563.02	308.278	269920	32465.7692	4.2542E-21	1.788E-28	23786689	16.9846	551419	551.419
13														1750.61

Figure 3.6: Calculation of thermodynamic

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Banana peel properties were ascertained using a variety of ways. The results obtained presented with graphs and tables as the outcome of TGA/DSC, Proximate analysis, SEM-EDX, and FTIR. Banana peels were pyrolyzed at a high temperature to measure weight loss at three different rates of heating for thermogravimetric analysis. The information was used to determine thermodynamics and kinetic in order to study the characterization of banana peels. Proximate, ultimate, SEM-EDX and FTIR were used to characterize physicochemical properties of unripe and ripe banana peel.

The ash content, volatile matter, moisture contents of banana peels were determined using proximate analysis, which provided information on their physicochemical characteristics. While FTIR was used to identify the chemical hydrocarbon components included in banana peels, SEM-EDX examination revealed the morphological image and element percentage in banana peels. The characteristics of ripe and unripe banana peels from this study were compared to those of other studies for identified problems from the experiments. Hypothesis made in discussion to clarify the issues gives this study significance.

4.2 Proximate & Ultimate analysis

The physicochemical characteristics of banana peel, as determined by proximate and ultimate analysis, results were summarised in Table 4.1 for comparison with previous research. Table 4.1 showed the composition of the banana peel includes types of composition such as moisture content, ash content, volatile matter and fixed carbon. The elements that make up the ultimate analysis are carbon, hydrogen, nitrogen, and sulphur. Moisture content recorded

25.5% which occupied high amount in banana peel. Water content used by fruits peels for proliferation of microorganisms and degradation of chemical reaction in rioening process thus it necessary towards fruits (Silva et al., 2020). The value of this studies was higher than previous studies as the spesies of banana that used was different in the research. The spesies of Musa sp. in this study contained more amount of water content than other studies (Xia et al., 2012). Volatie matter undergo vaporized rapidly as burned due to its volatile properties such as cellulose, hemicellulose and lignin. These were major componrnt in banana peel to the formation of pyrolytic product in pyrolysis which showed high susceptibility to thermal degradation status potential of the banana peel. Comparison of this studies value to (Mudassir Hussain et al., 2019) showed the volatile matter was nearly but (Kabenge et al., 2018) recorded that volatile matter in high as the possibility of a high organic load. Besides, ash content showed low amount in the banana peel. Ash content was inorganic noncombustible material and it may affected heat transfer in pyrolysis. Minerals such as Ca and K composed in ash content which used by fruits for metabolism process. There were low value of ash content recorded in this studies compare to previous studies indicates that effective of this studies as more bioenergy product can be yield which ash content was low in pyrolysis. Fixed carbon is a measure of the amount of non-volatile carbon remaining after volatile matter is burned and left residue. The amount of fixed carbon was low indicates that more volatie compounds had volatile thus showing the biomass was potential to yield more bio-gas. High value of fixed carbon by (Mudassir Hussain et al., 2019) indicated that the higher the char production as the properties in (Mudassir Hussain et al., 2019) was better than this studies and previous studies.

Ultimate analysis of banana peel analyzed carbon, hydrogen, nitrogen sulphur and oxygen that elements formed the banana peel. The major element were carbon (43.28%), hydrogen (3.79%) and oxygen (50.83%) constituents of cellulose and hemicellulose content of banana peel (Nimmanterdwong et al., 2021) . These content as volatile matter as burning to form biogas, carbon rich content formed biochar and bio-oil as solid content. Nitrogen and sulphur content occupied less amount that form in ash content of the biomass. Ash content contribute forming of biochar and bio-oil product by lignin in the pyrolysis.

Table4. 1: Proximate & ultimate analysis of this study compare with previous literature

Proximate analysis (Wt%)	This study	(Mudassir Hussain et al., 2019)	(Kabenge et al., 2018)
Moisture content	25.5	8.53	11.56
Volatile matter	61.5	66.79	88.02
Ash	0.5	4.13	2.70
Fixed carbon	5.2	20.55	9.28
Ultimate analysis (wt %)			
Carbon, C	43.28	35.65	45.53
Hydrogen, H	3.79	6.19	5.67
Nitrogen, N	1.3	1.94	2.31
Sulphur, S	0.8	9.55	0.35
Oxygen, O	50.83	45.94	36.40

4.3 SEM-EDX

The morphological structure of banana peel was examined using SEM. Morphology of banana peel stripes in the composition. The SEM image revealed that appear of irregular stripes on the surface of unripe and ripe banana peel in figure 4.1. The stripes were cellulose and hemicellulose compounds which carbohydrates with long polymer compounds. Besides, banana peel have a rough and uneven external surface with a lump composed of fiber content. The crater-like pores makes the structure easily to trap mineral ions for plants metabolism (Udochukwu, 2022).

EDX used to quantify the elemental composition and chemically characterise both banana peel. Result showed that oxygen and potassium occupy high percentage of composition compare to another element for both banana peels in Table 4.2. Potassium is a mineral which rich in the banana peel, it used by plant to grow bloom, development of plants cell for growth and metabolism (Xu et al., 2020). Composition potassium in ripe and upripe not difference more which are 35.29% and 39.78 % respectively. The percentage showed that potassium were rich in banana peel which exist in the biomass cell (Kamsonlian et al., 2011).

Ripe banana peel had high percetage due to more potassium participates increase of soluble sugar accumulate and the acid metabolism pathway during the ripening of fruit, thus more potassium transport through phloem assimilates in ripening of fruits. Oxygen was element that formed carbohydrates such as cellusose, hemicelulose and starch in banana peels so it occupy high composition from another elements. Carbon element in ripe and unripe banana peels showed lower percentage which were 0.01%. Carbon contamination occur in the sample cause sample surface migration and then its reaction with the electron beam, often induces background carbon signal (Säckl et al., 2022).

Fruit ripening process caused accumulated starch degraded and increase in soluble sugars, the solid sugar content formed and the content carbohydrate decrease, the composition of element decreased (Gao et al., 2016). Besides, composition of oxygen in unripe peels is 51.58% had decrease to 43.34 % in ripening stages due to ethylene production in banana tissue (Mohd Zaini et al., 2022). The process used oxygen in respiratory of banna peels tissue to produce ethylene acids. For the mineral elements, the ripe banana peels contained 0.54 % of sulphur and 5.23 % of chlorine, had lower percentage of composition compare to unripe which 0.16% sulphur and 2.49 % of chlorine. Conversion of pigments such as converting chlorophyll to carotenoids in ripening process caused the minerals released from the fruits peels (Kraithong & Issara, 2021).

Characteristics of ripe and unripe banana peels on biomass pyrolysis can be analyzed through EDX analysis. To achieve a potential biomass that is suitable for renewable energy, unripe banana peel become more potential due to the element for combustion such as oxygen and carbon were more in the unripe stage. Composition elements of fiber content such as cellulose and hemicellulose were high so this induces more char can be produce during pyrolysis combustion. Mineral content may decrease the pyrolysis temperature, increase the char yields, and catalyse the pyrolysis of cellulose and hemicelluloses. (Hong-xiang et al., 2013).

Different research of banana peel from other studies was compared with this study, result of analysis were different from other studies compared to this study. Potassium was high percentage in study (Shrivastava. et al., 2023) which was 74.21 % compare to this study about 35.29 and 39.78%. Disposal of banana peel method is quite different in this studies, tap water used to clean sample and dried for losing weight of 80–90 %, this lead to potassium element become active and more accumulated on surface of the peels (Hussain et al., 2022). Carbon and oxygen not detected in (Shrivastava. et al., 2023) study because the composition was less, carbohydrates content of this study was higher than previous literature. This showed that banana peel for this study had more potential than (Shrivastava. et al., 2023) study.

For (Hussain. et al., 2023) study, banana peel in the study was mix with date stones to form activated carbon. mineral that detected in the study was less compare to this study due to the minerals elements was treated by activated carbon. Carbon and oxygen content absorb by activated carbon caused the composition of these elements was higher than this study (Rajan & C.I, 2022). High Carbon and oxygen content leads to more char formed, but for potential biorenewable resource we need to look for overall characteristics of the resources. It does not mean that the study of banana peel is more potential than this study.

In the investigation conducted by Kamsonlian et al. (2011), various minerals were identified, revealing calcium at 0.32%, magnesium at 2.33%, and potassium at 15.60%. However, it is noteworthy that the mineral composition reported in our study appears to be lower. This divergence can be attributed to the distinct cultivar of banana peel utilized in each research endeavor, as highlighted by Segura-Badilla et al. (2022). It is well-established that different banana cultivars exhibit varying mineral compositions.

Despite the disparities in mineral content, the carbon and oxygen composition in our study, at 30.12% and 41.81% respectively, exhibited negligible differences compared to the findings reported. This suggests that the banana peel examined in our research is notably rich in cellulose and hemicellulose compositions.

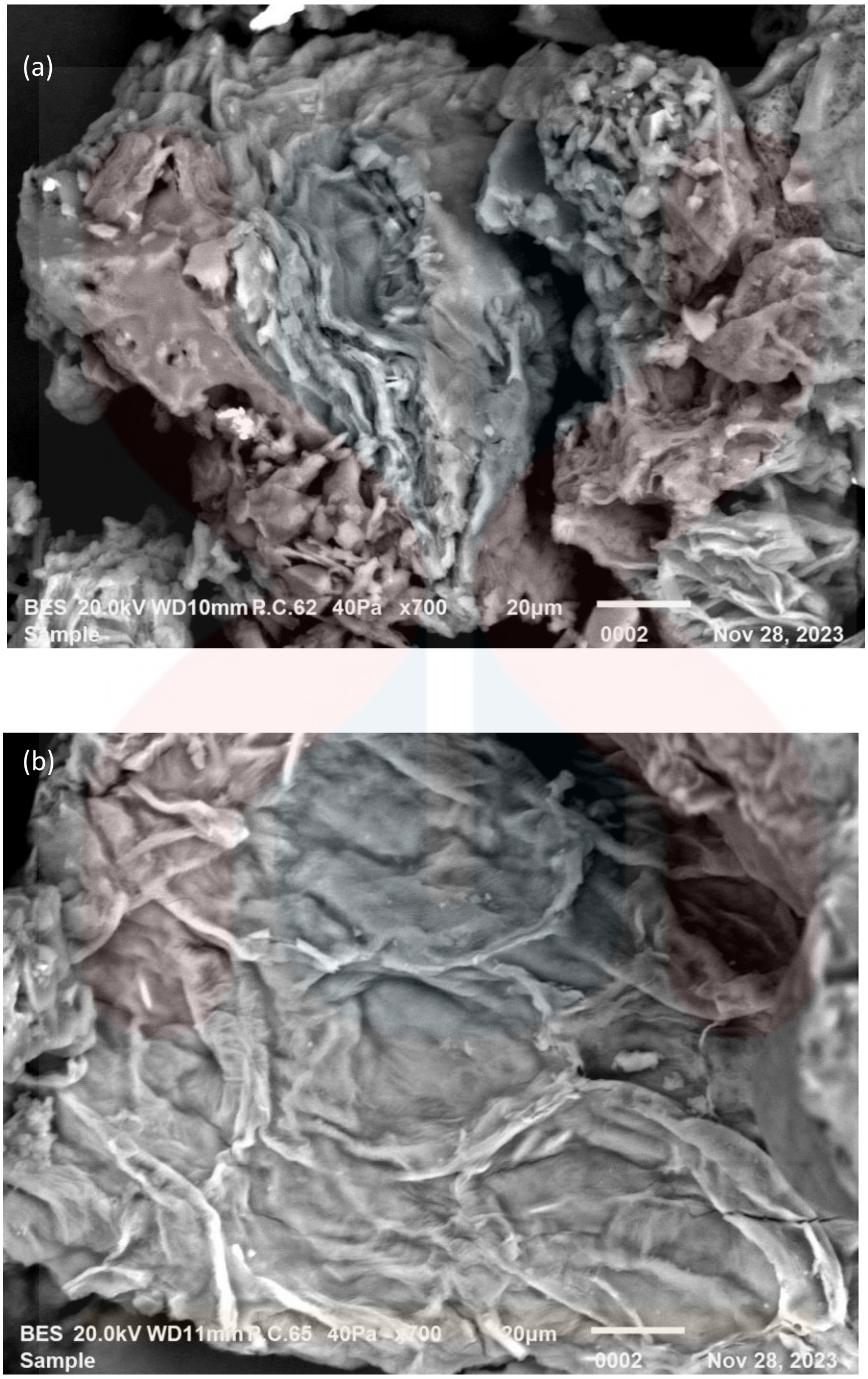


Figure 4. 1(a)&(b): SEM image of unripe (a) and ripe (b) banana peel with 700X magnification

Table4. 2: EDX analysis of unripe and ripe banana peel compared to previous study

Element	This study		Literature study (Shrivastava. et al., 2023)	Literature study (Hussain. et al., 2023)	Literature study (Kamsonlian. et al., 2011)
	Unripe (%)	Ripe (%)			
K	35.29	39.78	74.21	1.28	15.60
N	0.01	0.02	-	-	-
C	0.01	0.01	-	23	30.12
O	51.58	43.34	-	62	41.81
S	0.54	0.16	-	12.73	-
Ca	2.22	-	3.86	-	0.32
Mg	-	8.83	-	-	2.33
Cl	5.23	2.49	21.82	-	-

4.4 FTIR analysis

FTIR spectroscopy proceeded to identify functional group compounds that content in the banana peel. This analysis showed pyhsicalchemical properties of the biomass by chaaracterize of various chemical compounds. As shown in figure 4.2, the chemical compounds of ripe and unripe banana peel was rich in high amount of primary aliphatic alcohols, it coverages from 1000 cm-1 to 3600 cm-1 wavelength with the band 3280.01 for unripe and 3277.40 for ripe banana peel. This compounds formed by hydroxyl group (OH) which carbon atom attached to alkyl group in one single ways. Banana peel were riched in cellulose and hemicellulose, primary alcohol was compounds found in one on the branch being in the compounds (Galebach et al., 2018). Second rich compounds of composition in banana peel was inorganic phosphates which found from 2600 cm-1 to 3400 cm- and the band were 2917.47 and 2849.69 for ripe and unripe banana peel respectively. Phosphates compounds formed phenolic compounds, the compounds used in fruits peels for growth of fruits thus the amount should be higher in peels. Unripe banana peel showed 2918.07 with band while ripe banana peel showed 2917.47 cm-1 band covered from 2600 to 3450 wavelength. Aliphatic hydrocarbon was are hydrocarbons based on chains of C atom such as alkanes and alkenes. Hydrocarbon are major component of volatile matter in the fruits peels. Weak wavelength with band 1027.33 cm-1 and 1027.30 cm-1 that identified aliphatic primary amines in ripe and unripe banana peel respectively. Alkyl groups in amine compounds serve as nitrogen's bonding partner to generate amino acids, which are known as aliphatic amines. Pectin which lignocellulose of compoudns was formed by amine compounds to support cell of fruits peel (Chandel et al., 2022).

Comparison of major component of unripe and ripe banana peel showed that hydrocarbon and aliphatic alcohol in unripe banana peel was higher than ripe banana peel is due to CH stretching vibrations of CH, CH2, and CH3 groups (Tahir., 2018). The volatile matter such as cellulose and hemicellulose more comprised in unripe banana peel. Pyrolysis process able to yield more product as composition of volatile matter high in biomass.

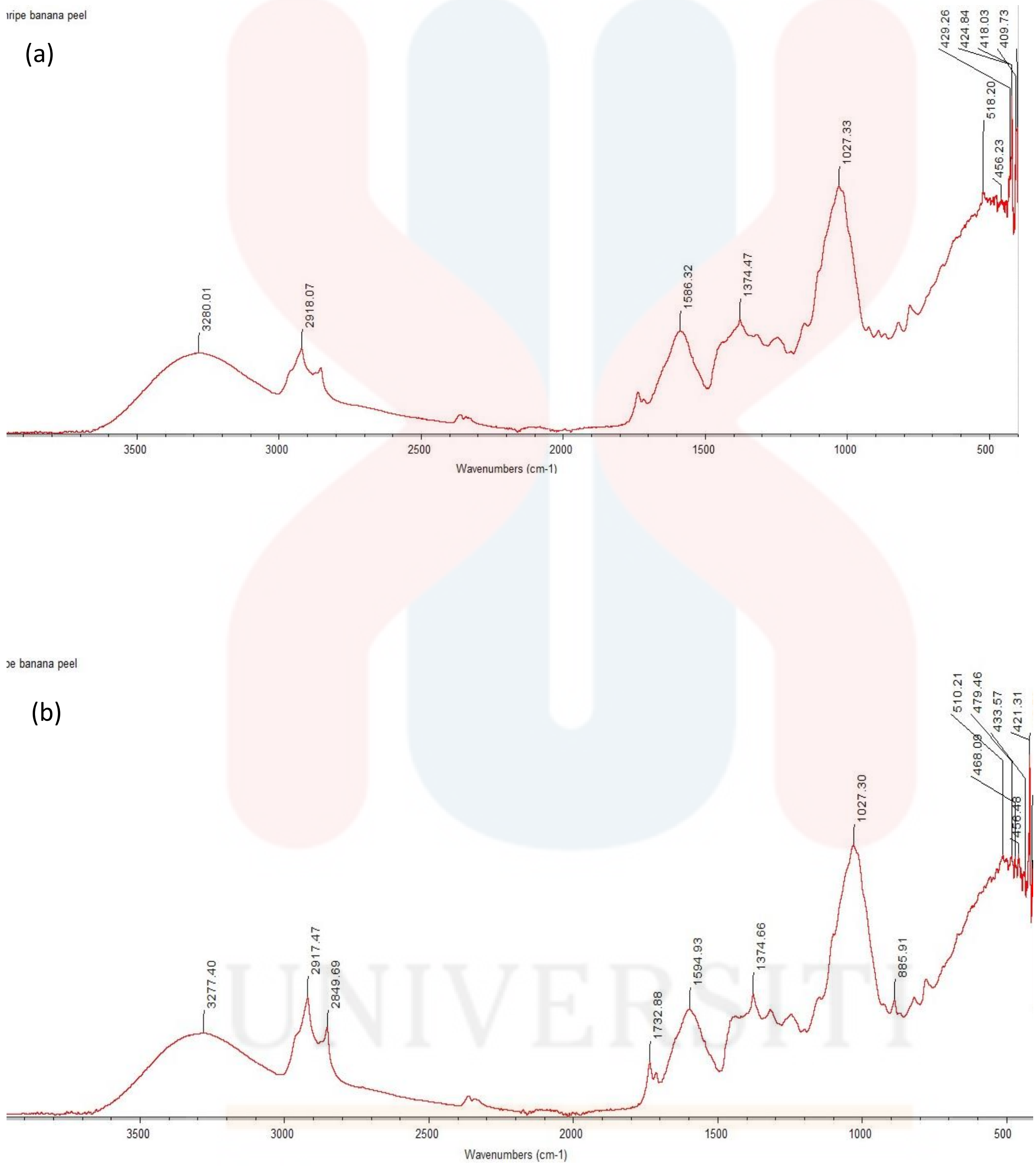


Figure 4. 2(a) & (b): FTIR analysis of unripe (a) and ripe (b) banana peel with peak wavelength of organic content 3600 cm-1 to 400 cm-1

4.5 TGA-DSC analysis

Pyrolysis of banana peels occurs in the decomposition process in thermogravimetric analysis, through TG analysis the characterization of banana peel can be studied. Banana peel was burned at three different heating rates such as 10, 20, and 30 °C/min in nitrogen gas environment, the weight loss of both banana peel as temperature increases were present by TG curve (figure 4.3 & 4.5) which demonstrates thermal properties (Gomes et al., 2018). DTG is differential thermogravimetry which was first derivative of the TG curve (figure 4.4 & 4.6). DTG represents temperature change with changes rate mass, thus DTG is used to determine the process that material undergoes in specific temperature with help of peak temperature. (Yao et al., 2023).

Thermal decomposition of unripe and ripe banana peel biomass was studied from TG curve. Through the TG curve characteristics of banana peel in pyrolysis analyzed that the thermal properties of banana peel. Firstly, decomposition of banana peel can be separated into three phases or region which occur different chemical process of the content of peels. TG curve which distributed into three phased shown as Figure 4.3 for unripe banana peel while figure 4.5 for ripe banana peel. Initially the pyrolysis occur dehydration of content banana peel in first phases. For unripe banana peel, the dehydration process (Rasool & Kumar, 2020) occur from 30°C to 170 °C while ripe banana peel dehyrdration temperature was occurred from 30°C to 170 °C . There are removal of moisture content such as water content and caused 15% of weight are lost from 100%.

The Increase of temperature from 170°C to 580°C was the second phase of the pyrolysis of banana peel was devolatilization process of banana peel. There were decomposition of volatile matter content including the hemicellulose, cellulose and little content of lignin in second phase. Referring to the DTG curve with figure, the rate of weight loss in second phase is higher than the first phase, illustrating that more changes of reaction in the content, and achieved peak temperature in this phase (Kabenge et al., 2018) . This content was major in the peel, decomposition of these content was rapid due to it being volatile matter and reaction changes fast at high temperature, this caused dramatic weight loss in this phase which was about 40% weight loss of total weight. The peak temperature for ripe and unripe banana peels are similar, from 298 °C for heating rates 10°C to 376 °C for 30°C heating rates. Peak temperature showed that highest weight loss rate in the decomposition of the hemicellulose and cellulose. Different changes of value in this phase formed three peak temperature in pyrolysis for both banana peel in different heating rates. This is because there were different compounds decomposed in every different peak temperature area. Based on study (Gao et al., 2019), hemicelluloses underwent major weight loss between 180 and 315 °C and the peak temperature is 260 °C while cellulose decompose at temperature 315 and 390 ◦C with a maximum rate at 310 ◦C. Others studied (Waters et al., 2017) explain that hemicellulose decomposes initially in lower temperature with range 200–315 °C than cellulose (300–400 °C). Thus, the second peak temperature is decompose of cellulose content, ripe banana peel had three peaks and the third peak was decomposition of lignin.

The third phase of pyrolysis process of unripe & ripe banana peel was occur from 580°C to 890°C. From TG curve the process can be determine was lignin decomposition process which cellulose and hemicellulose was decompose completely (Lu & Gu, 2022) . From DTG curve in figure we observed that the changes of weight is in low value due to lignin decompose slow in pyrolysis. After the pyrolysis the char residues left after decomposition of hydrocarbon and water compound in the banana peels left approximately 10% from total weight.

Characterization on thermal behavior of unripe and ripe banana peel, phase 2 temperature range showed the highest weight loss percentage in the pyrolysis. After phase 3 there were residue char left showed that the banana peel can be burned in high temperature to produce renewable source at least not all the content of banana peel was decomposed. It demonstrated that banana peels have the ability potential to be a renewable energy source. Besides ripening process influenced chemical compounds of banana peel. Ripe banana peel composed simple sugar and acid content and degraded at ripening process. Thus it decompose quickly as the degraded sugar bonding not too strong, less product formed within pyrolysis.

The total weight loss for unripe banana peel exhibited varying percentages at three different heating rates, registering values of 73.27%, 61.65%, and 46.24% shown in Table 4.5. In contrast, the weight loss for ripe banana peel was observed to be 69.99%, 74.91%, and 83.05%, as detailed in the accompanying Table. This indicates that thermal stability of unripe banana peel was better than ripe banana peel because weight loss decreased as heating rates increased, less composition loss in the pyrolysis and it form more product. The yield product was higher and showed that unripe banana peel more potential as renewable energy resources. Research on the bioenergy potential of banana peel pyrolysis (Mudassir H. et al., 2019) found weight reductions of 4.14%, 5.41%, and 6.50% at increasing heating rates. These findings indicated that banana peel pyrolysis was a workable methodology for producing bioenergy. Therefore, present research obtained weight loss of banana peel higher than studies (Mudassir et al., 2019) indicates that both banana peel by this research was potential as well as renewable energy souce.

Heat flow of banana peel in DSC analysis showed the graphs in Figure 4.7 and Figure 4.8 studied as a function used to determine temperature change and heating rate. DSC curve showing the linear increased of heating rates as temperature increased for all heating rates. Increasing of heat flow during pyrolysis indicates that absorption of heat in decomposition which undergoes endothermic process, heat transfer in the reaction with high rate detect increasing of heat flow (Jinbo et al., 2023). Heat flow for both banana peel increased gradually after 600°C due to high temperature and decomposition of lignin content needed heat transfer to decompose the content. For unripe banana peel, 20°C/min of heating rates recorded highest heat flow at 900°C. Besides, ripe banana peel showed 10°C/min of heating rates was highest value of heat flow. This characterized that banana peel properties in this two heating rates made high capacity of heat transfer in the pyrolysis. Heat energy transfer more caused the reaction rate fast and efficient.

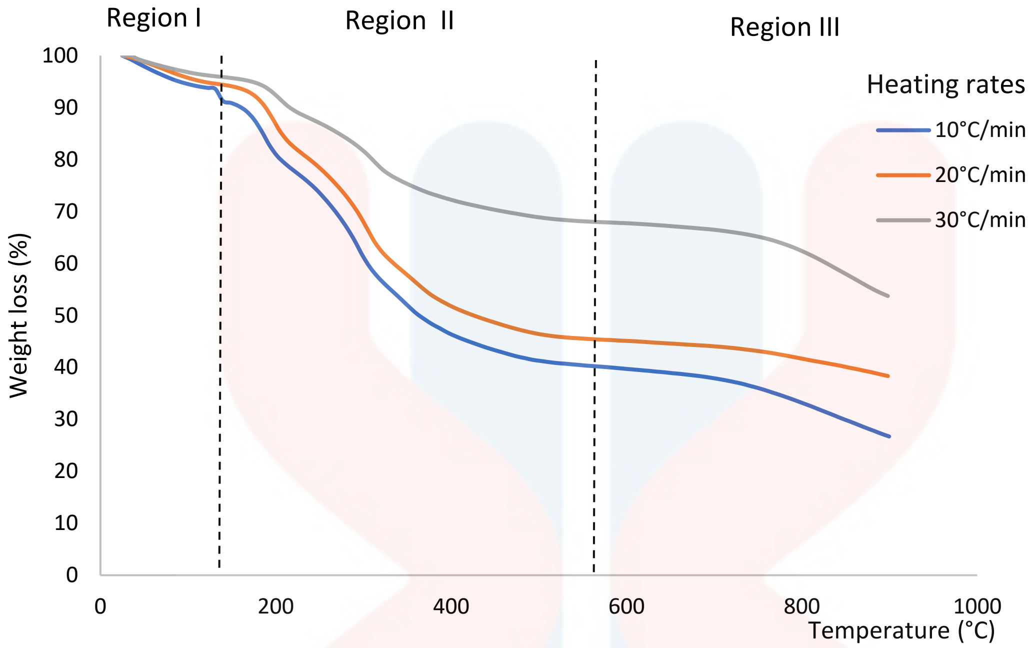


Figure 4. 3: Unripe banana peel TG curve with distributed phase at 10, 20 & 30 °C/min

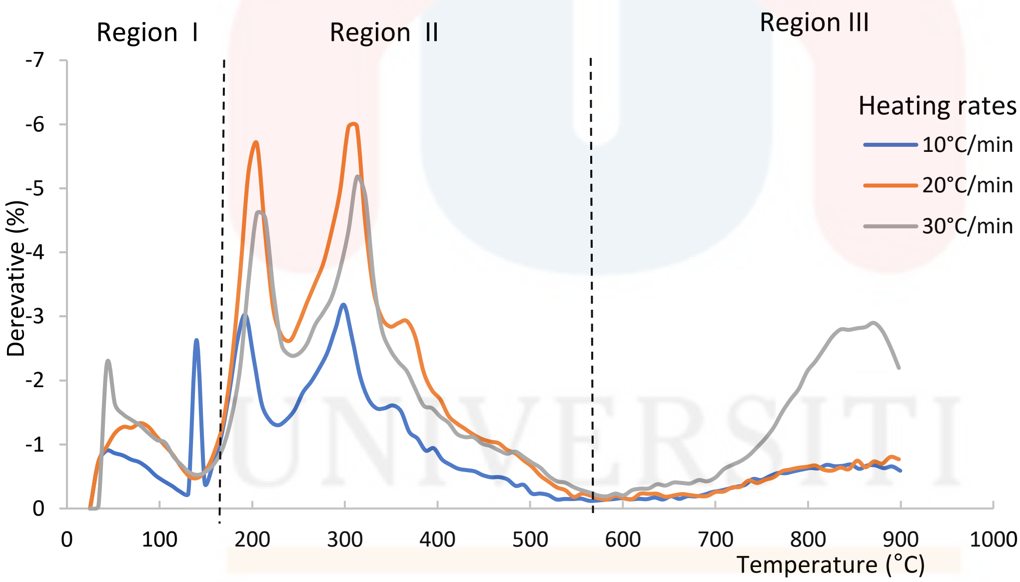


Figure 4. 4: Unripe banana peel derivative curve distrivuted phase at 10, 20 & 30 °C/min

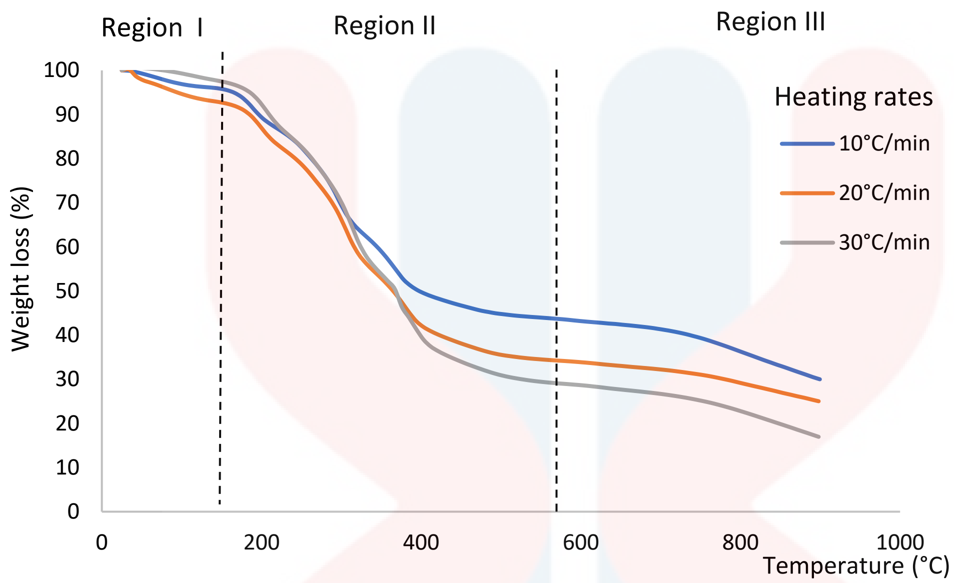


Figure 4. 5: Ripe banana peel TG curve distributed phase at 10, 20 & 30 °C/min

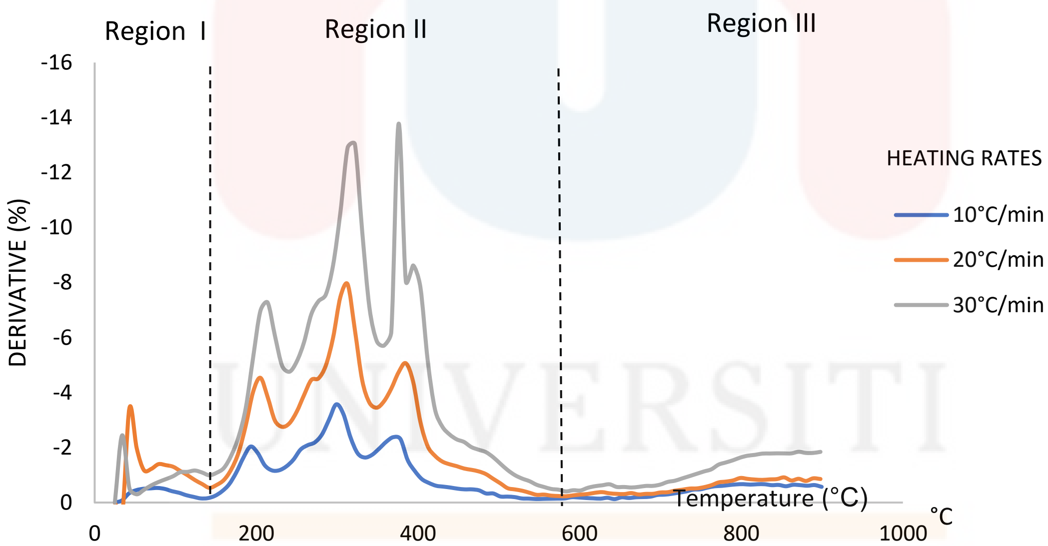


Figure 4. 6: Ripe banana peel derivative curve distributed phase at 10, 20 & 30 °C/min

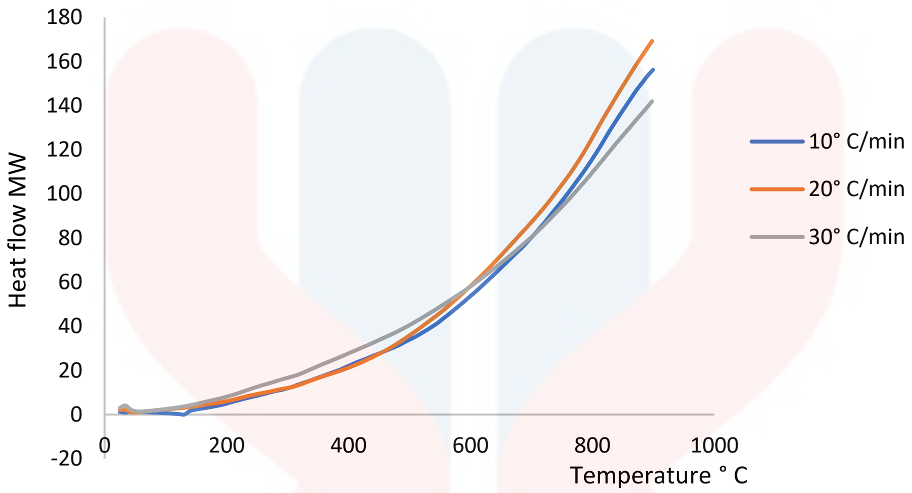


Figure 4. 7: Unripe banana peel DSC curve

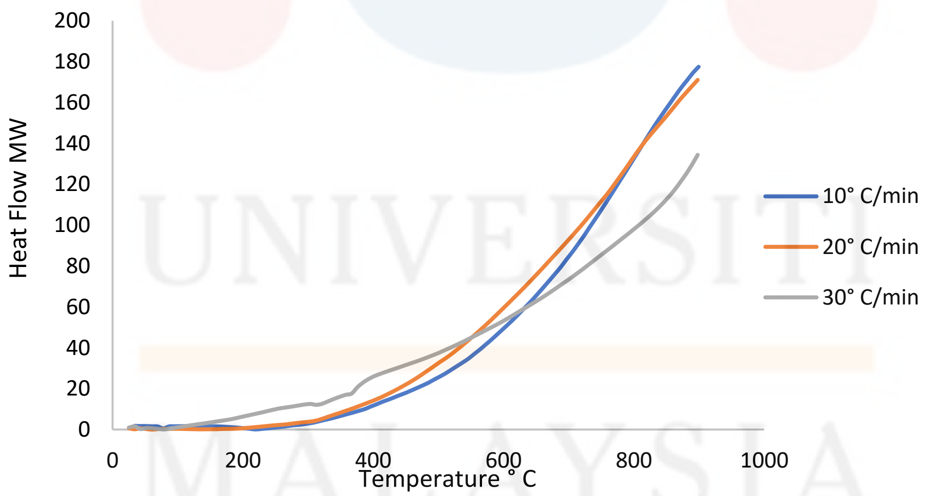


Figure 4. 8: Ripe banana peel DSC curve

Table 4. 3: Decomposition weight loss percentage of banana Unripe banana peel based on phase on TG curve in 10, 20 & 30 °C/min

Heating rates °C/min	Region 1 / Phase 1			Region 2 / Phase 2			Region 3 / phase 3		
	T_i (°C)	T_f (°C)	Wt. loss %	T_i (°C)	T_f (°C)	Wt.loss (%)	T_i (°C)	T_f (°C)	Wt.loss (%)
10	RT	162.99	10.66	162.99	580.27	49.32	580.27	893.84	13.15
20	RT	173.45	8	173.45	582.61	46.72	582.61	891.73	6.92
30	RT	171.93	5.26	171.93	582.53	26.83	582.53	891.76	14.13

Table 4. 4: Decomposition weight loss percentage of banana ripe banana peel based on phase on TG curve in 10, 20 & 30 °C/min

Heating rates (°C/min)	Region 1 / Phase 1			Region 2 / Phase 2			Region 3 / phase 3		
	T_i (°C)	T_f (°C)	Wt. loss (%)	T_i (°C)	T_f (°C)	Wt.loss (%)	T_i (°C)	T_f (°C)	Wt.loss (%)
10	RT	175.16	6.05	175.16	581.5	50.4	581.5	899.5	13.53
20	RT	178	9.02	178	583	56.84	583	898	9.08
30	RT	178	4.16	178	583	66.92	583	898	11.96

Table 4. 5: Total weight loss of unripe banana peel in pyrolysis

Heating rates (°C/min)	Initial		Final		Total weight loss (%)
	Weigh loss (%)	Mass (mg)	Weigh loss (%)	Mass (mg)	
10	99.97	2.39	26.70	0.64	73.27
20	99.98	2.39	38.33	0.91	61.65
30	99.97	2.49	53.73	1.34	46.24

Table 4. 6: Total weight loss of unripe banana peel in pyrolysis

Heating rates (°C/min)	Initial		Final		Total weight loss (%)
	Weigh loss (%)	Mass (mg)	Weigh loss (%)	Mass (mg)	
10	99.99	2.69	30.00	0.81	69.99
20	99.91	2.59	25.05	0.65	74.91
30	100.01	2.50	16.96	0.42	83.05

4.6 Model-free isoconversional methods

Activation energy from iso-conversional method able to determine the kinetic reaction of banana peel at particular conversion, as how is kinetic of content as temperature increased in pyrolysis process. In the studies the calculation of activation energy was combine with three heating rates 10, 20 & 30 °C/min so that the thermal behavior of biomass be seen from overall of heating rates. Thus value of average Ea was used as standard kinetic charactirization of biomass in three different heating rates. Variation of activation energy was calculated in unripe and ripe banana peel from FWO, Friedman and Kissinger method. Activation energies for FWO and Friedman method was calculated by slope (-Ea/RT), plotting data In (β) vs. (1000/T) for FWO and Friedman In (da/dt) vs. (1000/T) combine in three heating rates at particular conversion. Tables 4.7 and 4.8 showed the computed variation in activation energy with conversion for model-free isoconversional methods. Average activation energies for unripe banana peel recorded 48.82, 38.77.03 and 29.58 kJ/mol respectively. For ripe banana peel, average activation energy for FWO, Friedman and Kissinger method were 56.11, 59.86 and 31.55 kJ/mol respectively.

Trending of activation energy calculated for both banana peel showed increasing of E_a conversion range from 0.2 to 0.5, this indicates that endothermic of reaction occur in pyrolysis process at that temperature (El-Sayed et al., 2023). Decomposition of biomass content absorb heat to cleave the bond in the content. Thus, the decomposition of hemicellulose and cellulose was high kinetic energy, the molecule collide intense which show high activation energy. From studied (Piskulich et al., 2019) explained theory as temperature increases, heat transfer in pyrolysis process also increased caused molecules gain energy and collide faster so the molecules carry more kinetic energy. Thus, the proportion of collisions that can overcome the activation energy for the reaction increases with temperature. Exothermic reaction occur after 0.4 conversion for unripe and 0.5 for ripe banana peel due to it releasing energy as the bonds in the original compound are broken and biochar products are formed in new bonding (Rasool & Kumar, 2020). When the bonds in the products are formed, more energy is released than when the bonds in the reactants are broken. Explanation from studied (Lu & Gu, 2022), due to aromatic side chains and rigid structure of lignin, the decomposition reaction are slow so kinetic energy is low and yield low activation energy at decomposition of lignin.

Both unripe and ripe banana peel showed similar trending of activation energy value which from conversion 0.2 to 0.7 for every method. Based on Table 4.6, unripe banana peel recorded activation energy for FWO and Friedman showed variant of value which increased and decreased repeatly no linearly increased from 0.2 to 0.5 and after 0.5 the activation energy decreased at conversion 0.7. This is because the chemical structure of cellulose and hemicellulose was similar in unripe banana peel, the reaction of decomposition pyrolysis did not require more energy to degrade the content.

The activation energies for unripe banana peel at initial conversion 0.2, showed high value because the decomposition of volatile matter such as hemicellulose at that temperature range occur in high collision and more heat transfer, more energy needed to degreade the composition. This showed that the properties content of unripe banana peel which high energy needed, the peel content was not easily to decompse. Besides, the structure of unripe banana peels are affected by the ripening process of the peel. Ripe banana peel composed in strong inter-molecular hydrogen bonding as the sugar content formed at ripening process (Pongprasert et al., 2013). Thus, more activation energy is needed to achieve the decomposition reaction. Activation energy obtained in 0.2 to 0.5 conversion of unripe banana peel showed different value of Ea, the value increased and decreased repeatly which did not linearly increase. This is because the chemical structure of cellulose and hemicellulose was similar in unripe banana peel, the reaction of decomposition pyrolysis did not require more energy to degrade the content. Decomposition of lignin content occur in slow rate due to the complexity of its bonds and cross-linkages. The kinetic energy in the reaction is low thus little of energy required to overcome chemical reaction so that the activation energy calculated was in low value.

Through kinetic analysis, characterization of unripe and ripe banana peel can be determined based on activation energies obtained from pyrolysis. Comparison for both banana peel based on kinetic analysis was able to determine that which is better as potential renewable energy. Activation energy average in conversion from FWO, Friedman and Kissinger method based on table 4.7 and table 4.8, unripe banana peel was lower than ripe banana peel. This indicates that unripe banana peel is more energy efficient than ripe banana peel due to the value of activation energy being lower than ripe banana peel (Kumar R. et al., 2020). If using unripe banana peel as pyrolysis, better properties of biomass let the reaction complete faster, more time can be saved as decomposition rate was fast. Saving of time was used to decompose another content thus more content can be decomposed to yield product at short time, more product can be yield in pyrolysis.

. Based on kinetic theory, activation energy is the minimum amount of energy by reactant to form a product in the reaction. Low activation energy indicates that low energy will be required for the reactant to proceed collision in the reaction such as kinetic and heat energy. Thus the reaction requires a smaller energy input to occur, reaction rate becomes fast and more product yield. Therefore, pyrolysis of unripe banana peels becomes faster, more biochar or bio-oil yield compare to ripe banana peel (Bhattarai et al., 2023). For aspect thermal behavior, the characterization for unripe banana peel showed that the Ea started decreased first (at 0.4 conversion) compare to ripe banana peel (at 0.5 conversion). This showed that thermal properties composition of unripe banana peel required a low amount of energy compared to ripe banana peel, the kinetic of the molecule colliding easily as temperature increased to complete the reaction.

Comparison of this studies to other studies was made to prove that banana peel was biomass that has potential as a renewable energy source which shown in Table 4.9. Studies (Pravin Kumar et al., 2022) were similar research that proceed characterization of banana peel, recorded average activation energy as 108.42 kj/mol, 157.42 kj/mol and 181.27 kj/mol for Kissinger, FWO and Friedman method. Average in activation energy from 0.2-0.7 conversion in this research for both banana peel were about 30-48 kj/mol while ripe banana peel recorded 31-59 kj/mol for Kissinger Flynn–Wall–Ozawa and Friedman method. As compared to the value of average activation energy, biomass in this research are more efficient in pyrolysis compared to study due to reaction rate become fast and more product yield in lower activation energy.

Similar biomass for banana leaves recorded in study (Singh et al., 2020) that average activation energy ranges between 70.75 and 92.12 kJ/mol calculated by isoconversional model-free methods. Ea calculated in this study were lower than Ea for banana leaves. Characterization of feedstock biomass-rice straw and rice husk which was recorded from research (Chen et al., 2021) showed average activation energy calculated was 149.79 and 161.76 kJ mol −1 in pyrolysis. Compared to other types of biomass, banana peel biomass also represents a high efficiency of kinetic pyrolysis. In short, through the activation energy was lower than other studies unripe and ripe banana peel was potential as a biorenewable energy resources. Thermal properties of banana peel reveals that it was able burned in high temperature, bioenergy product able to form after pyrolysis process and potential become renewable energy source.

Pre-exponential factors calculated from isoconversional method are shown in Table 4.10 & 4.11, the value was found in FWO and Friedman methods from 0.2 to 0.7 conversion. Kissinger method used equation at 0.2-0.7 conversion. Ranges of pre-exponential factor ranges for FWO,Friedman and Kissinger method was ranges between 10^4 to 10^9 for both banana peel. Pre-exponential factors determined the frequency collision of molecules in the pyrolysis process. The trending of pre-exponential factors was similar to activation energy at each conversion. Pyrolysis of banana peel undergo complex reaction which more than one step elementary with whole mechanism. Ranges of pre-exponential factor showed that collison of molecule, undergo decomposition to form bio-product. In the initial conversion shows that only surface reaction was reacted in decomposition so the collision not to strong for ranges 10^4 to 10^7. However for unripe banana peel the value at initial conversion was high due to the properties content of unripe banana peel more energy needed to degreade the composition. For higher expenoentaial factor in 10^8 - 10^9 showed that high collision in decomposition of cellulose and hemicellulose (Kumar R. et al., 2020). As conversion forward the collision of molecule decreased as decomposition of lignin which is slow process in pyrolysis.

Table 4. 7: Activation energy for pyrolysis of unripe banana peels using different iso-conversional model-free methods from TG data in 10, 20, and 30°C heating rates.

Conversion	Flynn-Wall-Ozawa(FWO)method	Friedman	Kissinger
	E_a(kJ/mol)	E_a(kJ/mol)	E_a(kJ/mol)
0.20	62.89	61.37	-
0.30	75.56	37.51	-
0.40	51.91	63.23	-
0.50	56.97	27.91	-
0.60	29.19	12.44	-
0.70	12.67	30.21	-
Average	48.82	38.77	29.58

Table 4. 8: Activation energy for pyrolysis of ripe banana peels using different iso-conversional model-free methods from TG data in 10, 20, and 30°C heating rates.

Conversion	Flynn-Wall-Ozawa(FWO)method	Friedman method	Kissinger method
	E_a(kJ/mol)	E_a(kJ/mol)	E_a(kJ/mol)
0.20	28.33	18.31	-
0.30	34.6	48.048	-
0.40	67.69	102.97	-
0.50	106.05	82.40	-
0.60	53.38	55.65	-
0.70	47.26	51.78	-
Average	56.22	59.86	31.552

Table 4. 9: Comparison of average activation energy from particular conversion to other studies

Studies research	Type of research	Calculated average Ea from FWO (kJ/mol)	Calculated average Ea From Friedman (kJ/mol)	Calculated average Ea From Kissinger (kJ/mol)
This research	Banana peel	48.82/59.95	40.03/73.32	29.58/31.52
(Pavin Kumar et al., 2022)	Banana peel	157.42	181.27	108.42
(Singth. et al.,2020)	Banana leaves	84.02	73.89	70.75
(Chen. et al., 2021)	Rice straw	149.79 to 161.76		

Table 4. 10: Pre-exponential factor for pyrolysis of unripe banana peels, calculated from activation energy obtained from different iso-conversional model-free methods.

Conversion	Friedman method Pre-exponential factor,A(s^{-1})	Flynn-Wall-Ozawa(FWO)method Pre-exponential factor, A(s^{-1})	Kissinger Pre-exponential factor, A(s^{-1})
0.2	2.09×10^6	2.17×10^9	8.57×10^9
0.3	9.2×10^3	8.57×10^6	1.03×10^7
0.4	1.2×10^5	6.05×10^7	7.07×10^8
0.5	4.3×10^4	1.39×10^8	7.77×10^8
0.6	2.9×10^4	6.30×10^5	3.98×10^5
0.7	1.5×10^3	5.60×10^4	1.73×10^4

Table 4. 11: Pre-exponential factor of ripe banana peels, calculated from activation energy obtained from different iso-conversional model-free methods.

Conversion	Flynn-Wall-Ozawa(FWO)method Pre-exponential factor A(s^{-1})	Friedman method Pre-exponential factor A(s^{-1})	Kissinger Pre-exponential factor A(s^{-1})
0.2	3.5×10^5	4.73×10^4	3.08×10^7
0.3	1.26×10^6	5.34×10^5	3.76×10^8
0.4	5.124×10^6	1.11×10^9	7.36×10^8
0.5	9.915×10^9	6.62×10^6	1.10×10^9
0.6	205150	9.3×10^4	5.80×10^7
0.7	66026	3.6×10^3	5.14×10^7

4.7 Thermodynamic analysis

From the result highest value of enthalpy was recorded at 67.65 kj/mol conversion 0.3 and 113.95 kj/mol at conversion 0.5 for unripe and ripe banana peel respectively in Table 4.12&4.13. Increased of value showed that endothermic process occur in pyrolysis as temperature increased. The heat of enthalphy decreased in conversion 0.4 and 0.5 for both banana peel. Decreased of enthalphy caused by heat flow decreased in the composition, the biochar forming as new form bonds to make the product and its released energy. Trend of Gibbs free energy was similar to enthalphy which recorded increasing to highest value at 2973.44 kj/mol at conversion 0.3 for unripe, 3191.63 kj/mol at 0.5 conversion was recorded for ripe banana peel. Gibbs free energy consider combine entropy and enthalpy reaction of a system into one value which showed energy work done in a reaction (Reichle, 2023). Entropy measured thermal energy that's not proceed to do work. Loss of energy consider as disorder in a system showed negative value in entropy. Conversion 0.2 for unripe and 0.5 for ripe recorded least energy which are -9.43 and -9.35 respectively. This means that energy loss in large amount to form bioproduct after the decomposition of volatile matter (Kuo et al., 2022). Energy was used to form bonding of biochar or bio-oil.

Thermodynamic behaviors of biomass is crucial that determine thermal properties of biomass towards heat transfer of composition in pyrolysis. Thermal properties indicates that heat conductivity of composition of biomass in pyrolysis, good properties showed that heat capacity of biomass capable to heat transfer. Comparison on both banana peel based on thermodynamic behavior reveals which biomass possess better heat capacity properties as temperature increases. From the result in table 4.12 and table 4.13 , unripe banana peel recorded average thermodynamic parameters in 40.29 kj/mol, 1750.611 and -5.54 for enthalpy, Gibbs free energy and entropy respectively. Whereas ripe banana peel showed 64.13 kj/mol, 1774.95 and -5.19 for enthalpy, Gibbs free energy and entropy respectively. Comparison of both banana peel is made based on the overall value of thermodynamic parameters at all conversions. Average heat energy for unripe banana peel was lower than ripe banana peel. Unripe banana peel was more potential and more efficient in pyrolysis based on thermodynamic analysis obtained. Refer studied (Patil et al., 2023) understanding that low energy was required for unripe banana peel compare to ripe banana peel in cleaving the bond in pyrolysis, thus the reaction become faster and more efficient.

Table 4.12: Thermodynamic parameters for pyrolysis of unripe banana peels using activation energy calculated from iso-conversional model-free methods in 10, 20, and 30°C heating rates.

Conversion	Enthalpy (ΔH) (kJ/mol)	Gibbs free energy (ΔG) (kJ/mol)	Entropy (ΔS) (kJ/mol)
0.2	54.99	1438.24	-4.48
0.3	67.65	2973.44	-9.42
0.4	44.00	2071.88	-6.57
0.5	49.07	2260.62	-7.17
0.6	21.28	1208.05	-3.84
0.7	4.76	551.41	-1.77
Average	40.29	1750.61	-5.54

Table 4.13: Thermodynamic parameters for pyrolysis of ripe banana peels using activation energy calculated from iso-conversional model-free methods in 10, 20, and 30°C heating rates.

Conversion	Enthalpy (ΔH) (kJ/mol)	Gibbs free energy (ΔG) (kJ/mol)	entropy (ΔS) (kJ/mol)
0.2	36.25	955.175	-2.79
0.3	42.55	1148.89	-3.36
0.4	75.59	2120.36	-6.21
0.5	113.95	3191.63	-9.35
0.6	61.28	1706.9	-4.99
0.7	55.16	1526.8	-4.47
Average	64.13	1774.95	-5.19

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

In conclusion, Thermogravimetric analysis determined that different process occur within pyrolysis which were dehydration, volatization and lignin decomposition process. Major weight loss was occur at volatization process which were about 49% and 66% for unripe and ripe banana peel, the left product was converted into renewable source. Average activation energy obtained from FWO, Friedman, and Kissinger was found to be in the range of 29– 48kJ/mol for unripe and 31-73.24 kJ/mol in conversion 0.2-0.7. Kinetic parameter anlaysis investigate that unripe banana peel more efficient in pyrolysis compare to ripe banana peel due to lower activation energy by unripe banana peel. Two types of banana peel was potential as renewable source become bioenergy as thermal properties are well in pyrolysis, there were product formed after pyrolysis.

5.2 Recommendation

Characterization of biomass via Thermogravimetric analysis able to show the properties of the biomass within pyrolysis. Recommendations are need to propose for improvement and optimization of biomass pyrolysis. In this research the characterization of banana peel biomass was Pisang Nangka Musa sp. x Paradisiaca sp. which the fruit peels that involved in pyrolysis were raw and not mixed with other substances. Thus the activation energy that yield in the pyrolysis was optimum as potential renewable energy.

To increase the efficiency buring reactant in pyrolysis in optimization, we recommend adding bio-catalysts to increase the reaction rate in pyrolysis. Benefits of biocatalysts are higher specificity and high reaction rate in the pyrolysis. Same as properties of chemical catalysts, it can lower activation energy by lower the barrier in the reaction to increase the reaction rate. For example, coconut chaff bifunctional catalysts add in the pyrolysis to accelerate the reaction. Thus reaction can proceed more quickly and efficiently. In addition bio catalysts are eco friendly as it made from biomass which is more sustainable alternative compare to chemical catalysts.

Error occur within the analysis characterization influenced the accuracy of the data, precautions during analysis should be taken to prevent error for persistent accurate data. Crucible geometry is able to influence decomposition rate of materials. Different sizes of the crucible showed different results of weight loss of materials. This is because exchange of gases to sample will be restricted by the crucible size, inert gas flow was not accurate thus the weight loss are not the same. To prevent this problem, the ratio of surface to sample mass was calculated to obtain a proper ratio of sample and crucible so that the air flow was not affected. To prevent sample material spilling out of the crucible, the crucible lid was applied in the analysis.

Mathematical model can be improvement to reduce uncertainty and error in the parameter value. The errors will appear in the present mathematical model that use to calculate parameter in the analysis. For example, error basically occur at uncertainty of activation energy as the uncertainty of slope in the plot of log β versus 1/T, this caused the calculated Ea was quite accurate. Studies (Fregoso-Israel et al., 2023) had proposed that alternative method to correct the error with reducing the working interval. The alternative method can be implemented by a new liner that substitutes x with a third-degree polynomia. As a result uncertainty for calculation can be reduced and the data become more accurate in analysis.

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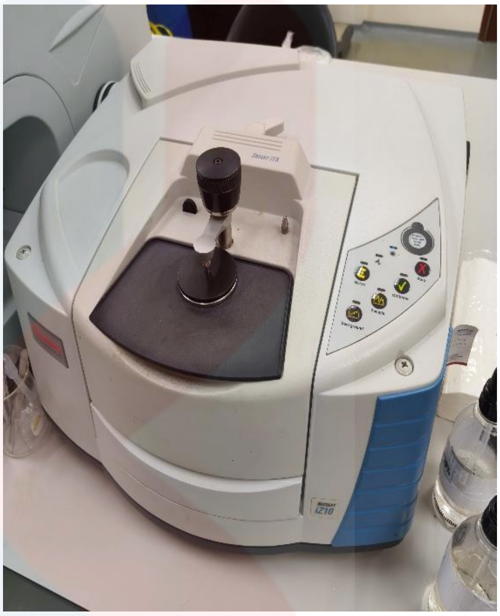
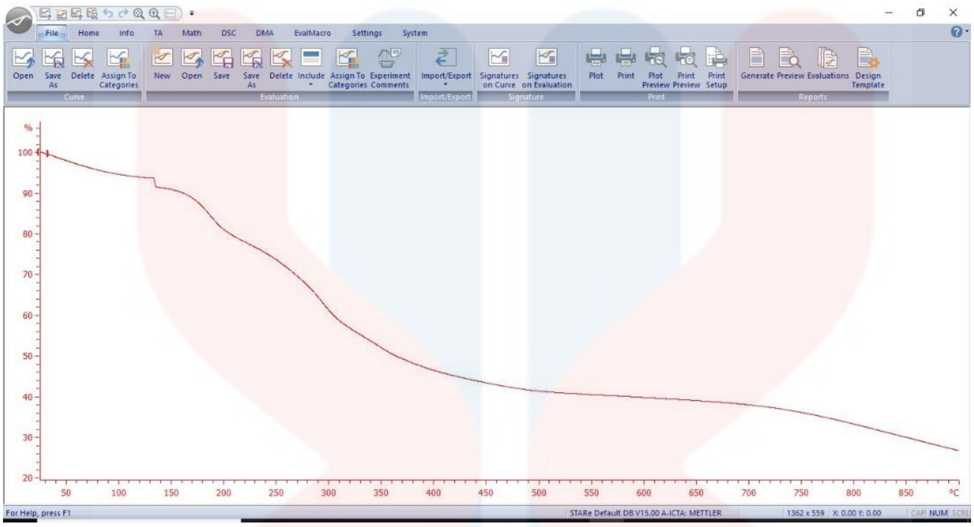
APPENDIX A

APPENDIX B



APPENDIX C


%
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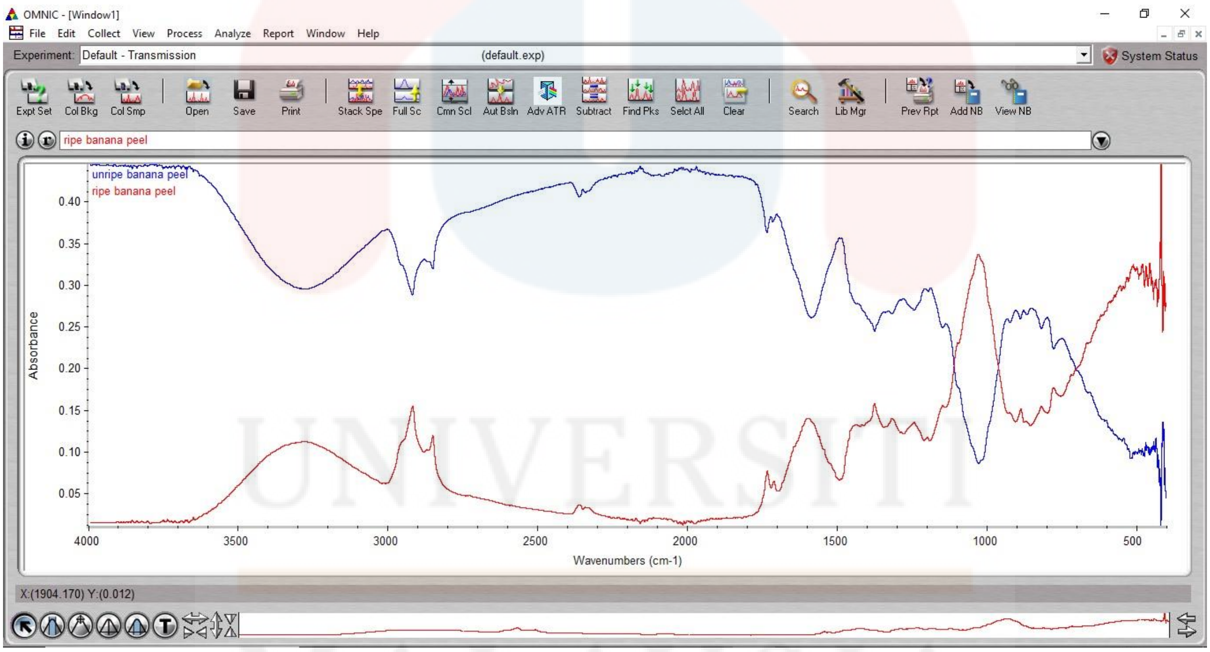
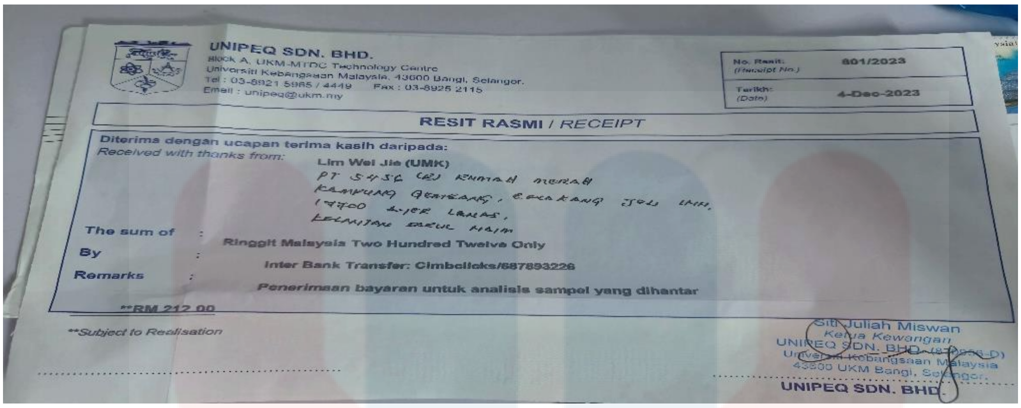

OMNIC - [Window1]
ripe banana peel
unripe banana peel
ripe banana peel
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
X:(1904.170) Y:(0.012)



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By : **Inter Bank Transfer: Cimbclicks/687893226**
Remarks : **Penerimaan bayaran untuk analisis sampel yang dihantar**

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