Analysis of Pyrolysis Behaviors of Biomass Residues

by

Fatin Mardiyah binti Mahadi

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the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

____

(Assoc. Prof. Dr. Ye Lwin)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
August 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

FATIN MARDIYAH BINTI MAHADI

ABSTRACT

This project focusing on the pyrolysis behaviors on different biomass residues samples using two different approaches, Py-GCMS and TGA machine. In this project the author also discussed the kinetic study of each biomass during the pyrolysis process. Pyrolysis is one of the processes that took part during the thermochemical conversion of biomass into useful energy. Even though there are a lot of studies and experiment still ongoing to fully understand this process, pyrolysis gain a lot of attention from the experts since the process directly convert biomass and yields 3 major products at once; an array of solid, liquid and gaseous products only by undergo thermal decomposition with the absence of oxygen. Therefore, to achieve the objectives, the study first emphasize on total understanding regarding the biomass and its conversion process. The draft of the experiment methodology will be prepared once the basic information regarding the process is understood. The data obtain after the experiment commencement is analyzed and comparison between all biomass residues samples will be jot down for further discussion. Based on the above comparison, the pyrolysis behavior of each sample is elaborated and then determined biomass with the highest energy conversion rate. The kinetic parameters of each biomass samples are calculated to help in better understanding of the pyrolysis process.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

The global usage of energy has been growing faster, proportional with the growth of world population. Up until today, most of the country depends on the coal and oil; both consider as fossil fuel as their country main energy sources. With the amount of energy consumption today, experts from The American Petroleum Institute predicted based on year 2004 energy consumption, the world's oil supply would be depleted by the year 2057 [1]. In order to overcome this prediction, the attention is being given to new and renewable energy sources such as solar, wind, thermal, hydroelectric, biomass, etc. Besides, the environmental pollution causes by the fossil fuel increased the concern most environmentalist regarding the usage of these sources as the main source of energy. With increasing energy demand, renewable energy expected to take an increasing role in world energy main sources for future energy consumption, besides the reduction of environmental concerns and impacts with regard to air, water, global warming, etc.

One of the most common renewable energy sources that are being used widely nowadays is biomass. It has been the third largest primary energy resources worldwide. Due to high demand towards this source, analysis and studies of the energy conversion of biomass never reaches an end. Thermochemical conversion is the most important process of energy converted from biomass. This includes several major process; combustion, pyrolysis, liquefaction and gasification. One of the most crucial processes that have been through a lot of study to maximize the efficiency of the conversion process is pyrolysis. Even though this process is still under developing and being experimented, it has received special attention by the scientist since can convert biomass directly into solid, liquid and gaseous products just by the thermal decomposition with the absence of oxygen. Thus, the behavior of pyrolysis on different biomass will be further analyzed in this project.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

As one of the major renewable energy, biomass is known as the third largest primary energy resources in the world, next after coal and oil, which also known as fossil fuels. Due to high demand of fossil fuels, this phenomenon causing increment in the fossil fuels oil as well as the environmental concerns regarding the emission caused by this energy source. In some developing country, agricultural residues have been used to the extent of almost 50% of total gross energy consumption [2]. Even though biomass has a low energy density, its thermochemical conversion processes; combustion, pyrolysis, liquefaction and gasification can produce fuel gas of higher density, yet reduce the demand of fossil fuels an environmental impacts caused by fossil fuels. By analyzing and study the mechanism of thermochemical conversion, it can help us to further understand how the conversion process affects the production energy from biomass residues and the evolved gases, chemically and physically.

1.2.2 Significant of the Project

This project significant to the industry as the analysis and deep understanding regarding the pyrolysis process, the behavior on different species of biomass and the kinetic behavior can help to further improve the thermochemical conversion process of biomass. It will also aid in further understand the mechanism involved in the process in order to reach optimization of the conversion.

1.3 PROJECT'S OBJECTIVES

Towards completing the project, a few objectives need to be achieved:-

a) To analyze the pyrolysis behavior of different species of biomass residues.
b) To study and understand the kinetic behavior of pyrolysis process.
c) To investigate the kinetics of thermal decomposition of different kind biomass.

1.4 SCOPE OF STUDY

This project will probe the relationship between the polymer and the elemental compositions together with their pyrolysis behavior of different variety of biomass residues. In this project, six samples will be used; four in solid forms and remaining two in liquid form. The experiment will be conducted using the Pyrolysis – Gas Chromatography-Mass Spectrometry (Py-GCMS) instrument located in Centralized Analytical Laboratory (CAL) in Block P. The composition of each material will be determined using the CHNS analyzer. The pyrolysis process will be analyzed using the Py-GCMS and Thermogravimetric analyzer (TGA). The results from the conversion process among the different biomass residues will be compared and the pyrolysis behavior will be further discussed.

CHAPTER 2

LITERATURE REVIEW/THEORY

2.1 BIOMASS AS ENERGY RESOURCES

Biomass can be defined as any hydrocarbon materials that consists mainly carbon, hydrogen, oxygen and nitrogen [3]. Sometimes, sulfur can also exist in a small proportion. It also can be define as non-fossil, energy-containing forms of carbon including all land- and water-based vegetation. Since 1800s, biomass being used and supplied majority of the world's energy and fuels needs [4]. Due to First Oil Shock in the mid 1970s, the existence of biomass as the source of the energy then realized by the government and policy makers to be domestic energy resources and has the potential of reducing the usage of the fossil fuels. Since then, biomass is recognized as one of the main renewable energy resources for mitigating the shortage of fossil fuel.

Nowadays, biomass is known as the third most important energy resources, next after coal and oil, where both can be considered as fossil fuel [5]. Current energy consumption of biomass brings up to 14% of total world energy consumption. The need for energy recovery from renewable sources along with the necessity for emission reduction and greenhouse effect has increased the attention towards the biomass research and technology. Numerous studies have dealt with pyrolysis of biomass to get a deeper insight of the kinetics and mechanism of the thermal decomposition. In this way, it can help to aid the development of biomass utilization processes.

2.1.1 Biomass Sources.

There are many sources of biomass that can be used as energy resources and it can be categorized into five major groups of sources [6].

- Virgin wood

  Consists of wood and other product of wood, such as sawdust and wood chips that is not being contaminated by chemicals. It may range in moisture content from dry oven to fresh green wood which contain 60% or higher moisture content.

- Energy crops

  It is grown specifically to use as fuel and offer high output with low inputs per hectare. This includes coppice and wheat.

- Agricultural residues

  It has a wide variety of types, including dry basis residues (such as straw and corn cobs) and wet basis residues (such as animal slurry and grass silage).

- Food waste

  Residues and waste that is produced at all points of food supply chain, starting at the initial production up until post-consumers waste from hotel, restaurant and houses.

- Industrial waste and co-product

  Residues, wastes and co-products from industrial processes and manufacturing operations that has potential to be converted into biomass. These wastes can be categorized into woody and non-woody materials.

2.1.2 Major Component of Biomass.

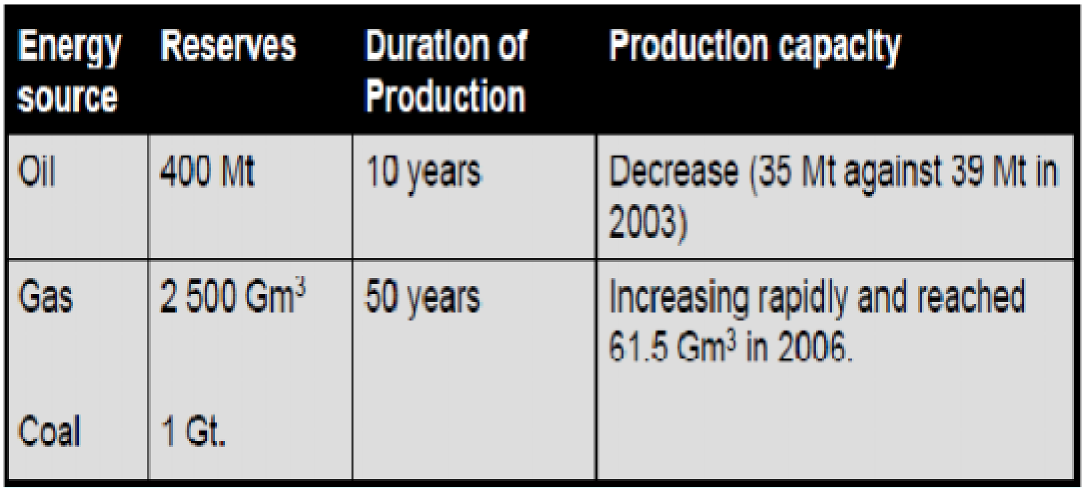
Chemical structure of each biomass is important in the development of processes of producing the derived fuels and chemicals. Major component biomass can be categorized into three major groups; cellulose, hemicelluloses and lignin. Alpha cellulose is a polysaccharide that having the general formula of $(C_6H_{10}O_5)_n$ with average molecular weight 300,000 to 500,000. Cotton is considered almost pure alpha cellulose. Most cellulose is insoluble in water [4].

Second major group component of biomass is hemicelluloses. They are complex polysaccharides which, together with the cellulose create the cell wall. Unlike cellulose, hemicelluloses soluble in dilute alkali and having the general formula of $(C_5H_8O_4)_n$. the most liberal hemicelluloses is xylan [4].

The third and last major component of biomass is lignin, which are highly branch mononuclear aromatic polymers located in the cell walls of certain biomass. Lignin alone is quite resistant to the conversion by microbial systems. However, by treatment with strong acid, which lignins are insoluble, the complex can be broken. Lignin contents on a dry basis biomass in various herbaceous species, such a bagasse, rice hulls and straws [4].

2.1.3 Biomass Demand in Malaysia.

Energy sources in Malaysia mostly depend on the fossil fuel, which is oil. From Table 1 and Figure 1, we can conclude that almost 90% of Malaysia energy sources depend on the non-renewable energy [7]. Only a small part of hydroelectric, one of the famous renewable energy potential is exploited in this country. Malaysia has a high potential in practicing renewable energy sources from which it is mainly resulting from palm oil and wood waste.



Energy source	Reserves	Duration of Production	Production capacity
Oil	400 Mt	10 years	Decrease (35 Mt against 39 Mt in 2003)
Gas	2 500 Gm^3	50 years	Increasing rapidly and reached 61.5 Gm^3 in 2006.
Coal	1 Gt.		

Table 2.1: Energy sources in Malaysia

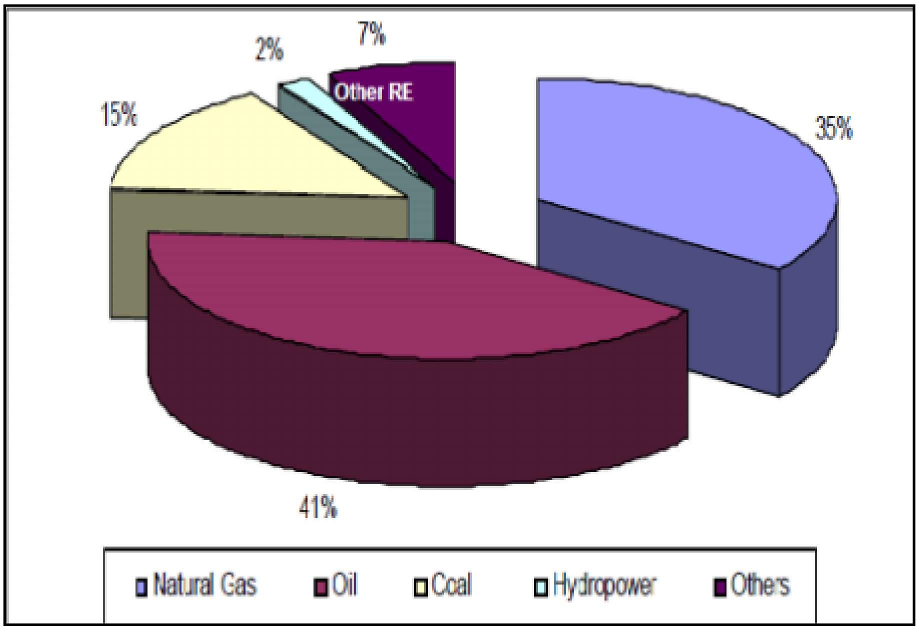


Figure 2.1: Statistic of energy consumption in Malaysia (2008)

Due to rapid industrialization towards achieving Wawasan 2020, prediction has been made regarding energy resources in Malaysia where country will be exhaust the national fossil fuel reserves in period of 30 to 40 years and will totally depends on the imported fuel from other country. Therefore, a lot of studies regarding renewable energy especially biomass has been conduct in order to overcome the predicted problem.

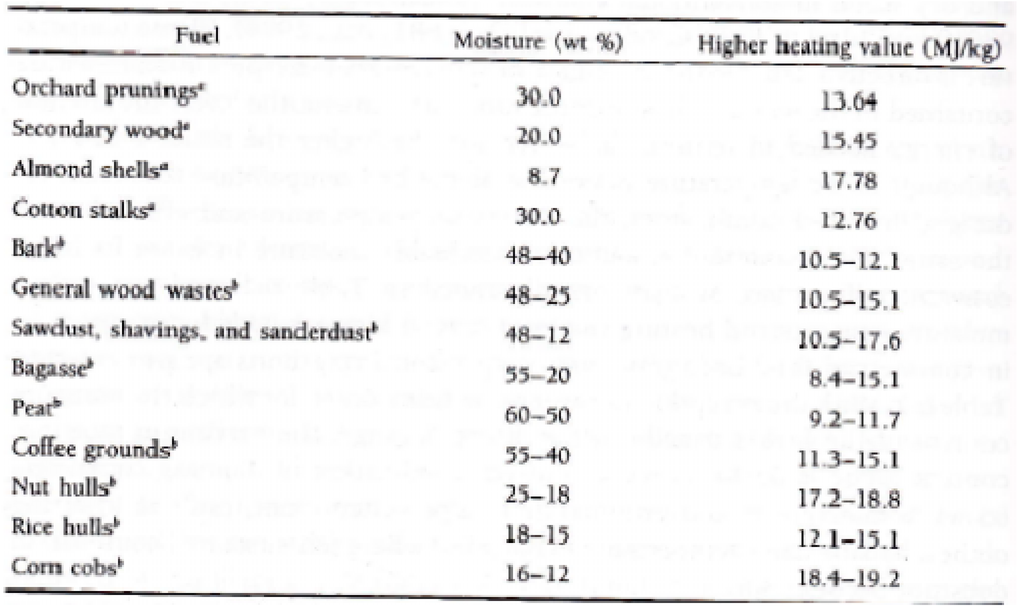
2.2 BIOMASS CONVERSION PROCESS

There are numbers of approaches that is available to put in operation wide variety of biomass as an important renewable energy source [8]. Conversion technologies that help releasing the energy directly from the biomass have evolved every single day. Years ago, direct combustion on biomass is used to take advantage of its heating value. The method is not favorable anymore since the biomass contains too high moisture content and not suitable to perform a stable combustion

[9]. Thus, scientist, engineers and technologist have come out with three major conversion of biomass that can help enhance the energy produce from the biomass.

2.2.1 Physical Conversion

There are numerous aquatic and terrestrial virgin biomasses that can be used as the potential feedstock of energy conversion. Removal of moisture content is important for the conversion process. Dry biomass burns at high temperature and help increased the boiler/thermal efficiency [10]. With low moisture content, the amount of energy needed to remove the moisture during the thermal conversion process also reduces. Table 2 shows the acceptable moisture content of several biomasses that are usually being used as the feedstock [11].



Fuel	Moisture (wt %)	Higher heating value (MJ/kg)
Orchard prunings[a]	30.0	13.64
Secondary wood[a]	20.0	15.45
Almond shells[a]	8.7	17.78
Cotton stalks[a]	30.0	12.76
Bark[b]	48–40	10.5–12.1
General wood wastes[b]	48–25	10.5–15.1
Sawdust, shavings, and sanderdust[b]	48–12	10.5–17.6
Bagasse[b]	55–20	8.4–15.1
Peat[b]	60–50	9.2–11.7
Coffee grounds[b]	55–40	11.3–15.1
Nut hulls[b]	25–18	17.2–18.8
Rice hulls[b]	18–15	12.1–15.1
Corn cobs[b]	16–12	18.4–19.2

Table 2.2: Typical Moisture Contents & Heating Values of Waste Biomass

Due to its high moisture content, they are not suitable to be used for thermochemical conversion because they do not support self-sustained combustion under conventional conditions unless the moisture is being removed [4]. Therefore, there are few physical conversion that can be applied to the biomass before proceed with the thermal conversion in order to maintain the efficiencies.

a) Dewatering

Dewatering is a process of removal all moisture from the biomass in liquid form. This method is the combination of shearing devices and the mechanical pressing. Dewatering method is suitable for most of the high water content virgin or waste biomass. One of the major drawbacks of this method is that the direct physical separation is not feasible unless the biomass is subjected to physical process that disrupts the cell walls.

b) Drying

Unlike dewatering process, drying process removes the moisture content from the biomass as vapor. The most popular method is the open-air solar drying method which has been used for hundreds years. Instead of low cost as its advantage, this method consumes a lot time since it is a slow process and depends on the local climates. Nowadays, the conventional method is only being used in the rural area while for the industries and large scale drying application, a faster and efficient dryer is being used. Spray dryers, drum dryers and convection ovens are usually used as industrial dryers while for a large-scale drying application, kiln drying including forced-air furnace and hot stack gases drying systems is introduced. The used of superheated steam for drying may allow further improvements in efficiency [12]. This is to make sure that the moisture content is being reduced to 25 wt % or less before proceed to the thermal conversion process.

c) Size reduction

Reduction of the biomass size is required before it is being used as the fuel or feedstock. Even though it is not as important as the moisture content of the biomass, particle size does influence the rate of conversion, operating condition and also product yield. Smaller size of the particles reduces the volume of storage volumes. Size reduction become the most critical part when it come to drying process since the drying time and method is determined by the exposed surface area of the particle. There are some common method that is being used in reducing the sample size such as dry shredders, chipping and granulation [4].

2.2.2 Thermochemical Conversion

Thermochemical conversion processes involved combustion, liquefaction, pyrolysis and gasification. This process is based on two basic approaches. The first approach is the gasification of the biomass and its conversion into hydrocarbon while the second approach is the liquefaction of biomass directly by high-temperature pyrolysis and high-pressure liquefaction [13]. Both processes are important as they convert the waste biomass into energy rich useful products. The choice of the conversion method is depends on the type and quantity of the biomass feedstock as well as the desired form of energy.

a) Combustion

The simplest way to obtain heat, sometimes light by burning the biomass is known as one of the oldest biomass conversion in the history. Complete combustion of biomass involving oxygen consist rapid chemical reaction [4]. During the process, the bond of carbon and hydrogen is oxidized, producing carbon dioxide and water vapor in excess air. Incomplete combustion can cause the emission of particulate matter where some might be toxic to mankind. One of the drawbacks of this process is that not all biomass arises naturally in form of burning. Most cases it requires pre-treatment like physical conversion that may cost more energy and financially.

b) Pyrolysis

Pyrolysis can be described as decomposition of organic material at elevated temperature in the absence of oxygen, where most cases are using nitrogen as the substituted of oxygen [14]. This process begins at temperature of 350°C and goes up until it reaches 700°C. Even though this process is still under developing and being experimented, it has received special attention by the scientist since can convert biomass directly into solid, liquid and gaseous products just by the thermal decomposition with the absence of oxygen [13]. So far, this method has been used for commercial production of wide range of fuels, chemicals, solvents and other products based from biomass feedstock.

c) Liquefaction

Liquefaction process is where liquid is obtained using a catalyst in the presence of hydrogen during the thermochemical conversion at low temperature and high pressure. More studies are done on direct and indirect thermal liquefaction of biomass and wastes [15]. This process is not so favorable since it is a very costly process. Besides, liquefaction process yields a tarry lump product, which is very difficult to handle [16].

d) Gasification

Gasification process is generally designed for the purpose of producing low to medium energy fuel gases or hydrogen [4]. This process converted biomass into combustible gas mixture by partial oxidation of biomass in high-temperature between the ranges of 800°C to 900°C [17]. Under ideal conditions, the primary products of biomass gasification are carbon dioxide and hydrogen. But under certain conditions, methane and light hydrocarbon might be formed too.

2.2.3 Biochemical Conversion

Biochemical conversion of biomass plays the major role in production of bio-fuels such as bio-ethanol, bio-diesel and wide variety of bio-products [18]. The development of this process still under close observation so that the production of ethanol and co-product in an environmental-friendly condition can be implemented in order to provide energy security and environmental sustainability.

The biochemical conversion involves the broke down of biomass into its sugar components which then can be split (fermented) into valuable chemicals and fuels. This process make used of enzymes, bacteria and micro organism to help break down the biomass [19].

2.3 PYROLYSIS OF BIOMASS

Pyrolysis of biomass can be describe as direct thermal decomposition of organic compound in biomass in the absence of oxygen in order to produce a variety of useful product – mostly consist of char (solid), pyrolysis oil (liquid), and syn-gas (gas) [4]. Figure 2 shows the composition changes during the pyrolysis process.

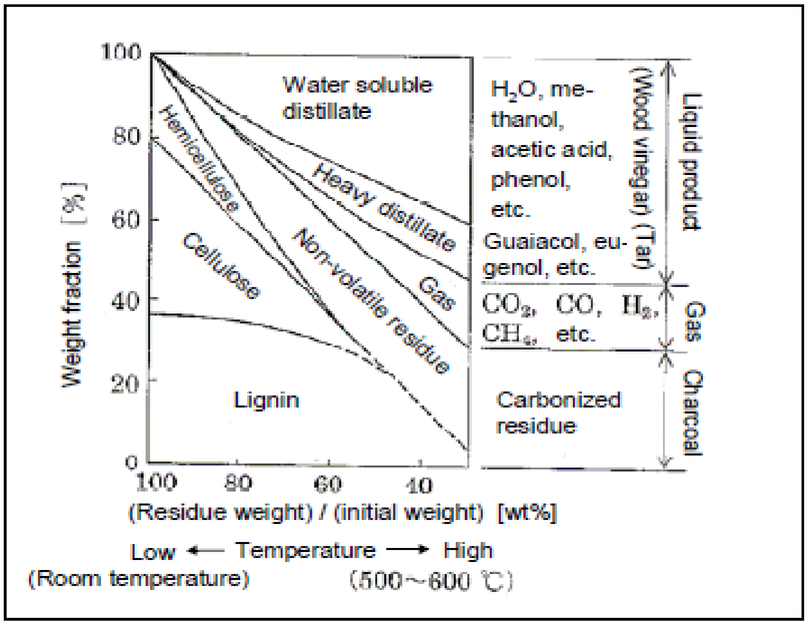


Figure 2.2: Composition Changes during Pyrolysis

Depending in the pyrolysis temperature, char fraction which contains inorganic material might varies. Different condition of pyrolysis process might lead to the formation of products in different proportion.

2.3.1 Slow/Conventional Pyrolysis

Conventional pyrolysis involves slow, irreversible thermal decomposition of organic component in biomass. This method has been used for ages for production of charcoal. In conventional pyrolysis, chars, gases, light and heavy liquids, and water are formed in varying amounts. The yields are particularly depending on the composition and dimension of the feedstock, temperature, heating rate and reaction time [4]. By using this method, the selectivity and the yields of the solid, liquid and gaseous product can be control by manipulating the pyrolysis temperature and heating rate. Higher temperature together with longer residence time produce more gaseous production, while higher production of chars are obtained at lower temperature and slower heating rate.

2.3.2 Fast Pyrolysis

Fast pyrolysis produce higher yields of desirable liquid product compare to conventional pyrolysis which produce more char due to slow heating rate. This process involves rapid heating biomass but not as fast as flash pyrolysis. Normally, for fast pyrolysis, the heating rate does not exceed or somewhere around 300°C/min using the fluidized bed reactors as it offers high heating rate, easily to control and to obtain the product [20]. With this process condition, a high grade of bio-oil can be obtained.

2.3.3 Flash Pyrolysis

Flash pyrolysis is the process where the systems continuously operated at temperature range from 400°C to 650°C with residence times of a few seconds to a fraction of a second. Since the heating rate is very high, it requires special reactor configuration in which the biomass' residence times are only for a few seconds [13]. There are two appropriate reactor designs for this process; entrained flow reactor and fluidized bed reactor. Since flash pyrolysis requires rapid heating, therefore the particle size should be small enough to be fully pyrolized in just a few seconds, approximately around 105µm to 250µm [21].

2.3.4 Catalytic Biomass Pyrolysis

Based on the literature, it is shown that the liquids that is obtained from slow, fast and flash pyrolysis cannot be used straight away as the transportation fuels [13]. It is found that the pyrolysis oils contain high oxygen and water content, less miscible and less stable to be used directly. Therefore, catalytic biomass pyrolysis is proposed in order to improve the quality of the oil obtained from the pyrolysis process. This process helps in reducing the cost of preupgrading procedure which includes condensation and re-evaporation. There is wide variety of catalyst that is being used together with the biomass feedstock for example, zeolite and aluminas [22].

2.4 THERMOGRAVIMETRIC ANALYSIS & KINETIC STUDIES

Thermogravimetric analysis (TGA) is one of the methods that can be used in order to determine the pyrolysis kinetic. By using this method, weight loss of the sample will be recorded against temperature under controlled heating rate to obtain the differential thermogravimetric analysis (DTG) curves [23]. The DTG curve that is obtained from the pyrolysis process can be described as independent parallel reactions. Thus, the thermal behavior of each sample can be concluded as the sum of the behavior of its individual component [24].

2.4.1 Estimation of Kinetic Parameters

From journal of L. Guo & A.C. Lua [25], the kinetic parameters of pyrolysis can be described as:-

$$\frac{da}{dt} = F(T, a) \qquad (1)$$

Where the rate of decomposition is function of temperature and the conversion. The conversion, of mass loss of the biomass during the pyrolysis process can be calculated by using formula below:

$$a = \frac{(m_0 - m)}{(m_0 - m_f)} \qquad (2)$$

Where,

m_o = initial weight

m = actual weight

m_f = final weight

Function of temperature can be elaborate more by using the Arrhenius equation

$$k(T) = A\,exp\left(\frac{-E}{RT}\right) \tag{3}$$

In order to determine the kinetic parameter of the process, the integral method is applied to the equation where constant heating rate, β, is introduced.

$$\beta = \frac{dT}{d\tau} \tag{4}$$

Substituting Eq. (4) into Eq. (3), the new equation can be defined as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT}(1-\alpha)^n \tag{5}$$

Rearranging and integrated both Eq. (5) for constant heating rate, *B*, we get,

$$\frac{1-(1-a)^{1-n}}{1-n} = \frac{ART^2}{BE}\left(1-\frac{2RT}{E}\right) exp\left(\frac{-E}{RT}\right) \tag{6}$$

Expressing Eq. (6) into logarithm form, we get

$$ln\left[\frac{1-(1-a)^{1-n}}{T^2(1-n)}\right| = ln\left(\frac{AR}{BE}\right) - \frac{E}{RT} \qquad , for\, n \neq 1$$

$$ln\left[\frac{ln(1-a)}{T^2}\right| = ln\left(\frac{AR}{BE}\right) - \frac{E}{RT} \qquad , for\, n = 1$$

The activation energy, *E*, can be calculated by plotting graph $ln\left[\frac{ln(1-a)}{T^2}\right|$ vs $\frac{1}{T}$. There are basic assumptions involved in this estimation:-

- The reaction is assumed to be purely kinetic controlled
- The pyrolysis process followed first-order reaction

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 PROJECT FLOW

The project's flow has been determined and has been commenced for two semesters. The flow of this particular study can be defined as below:-

a) Goal settings

The objectives are set up according to the study needs and should be completed within the specified time frame.

b) Development of appropriate course of action

Each process should be parallel to the objectives stated at the beginning of the project. Process that is developed should be logical and can be done without interfering with the purpose of the study.

c) Data collection

Data is gathered from any established journals and articles that is related to the project title to further understand the basic of the project and provide the flow of experiment that will be conducted.

d) Data analysis

Data is interpreted from the results of the experiment that has been conducted. The pyrolysis behavior of each biomass is analyzed and the kinetic of the pyrolysis is being studied.

3.2 PROJECT PLANNING

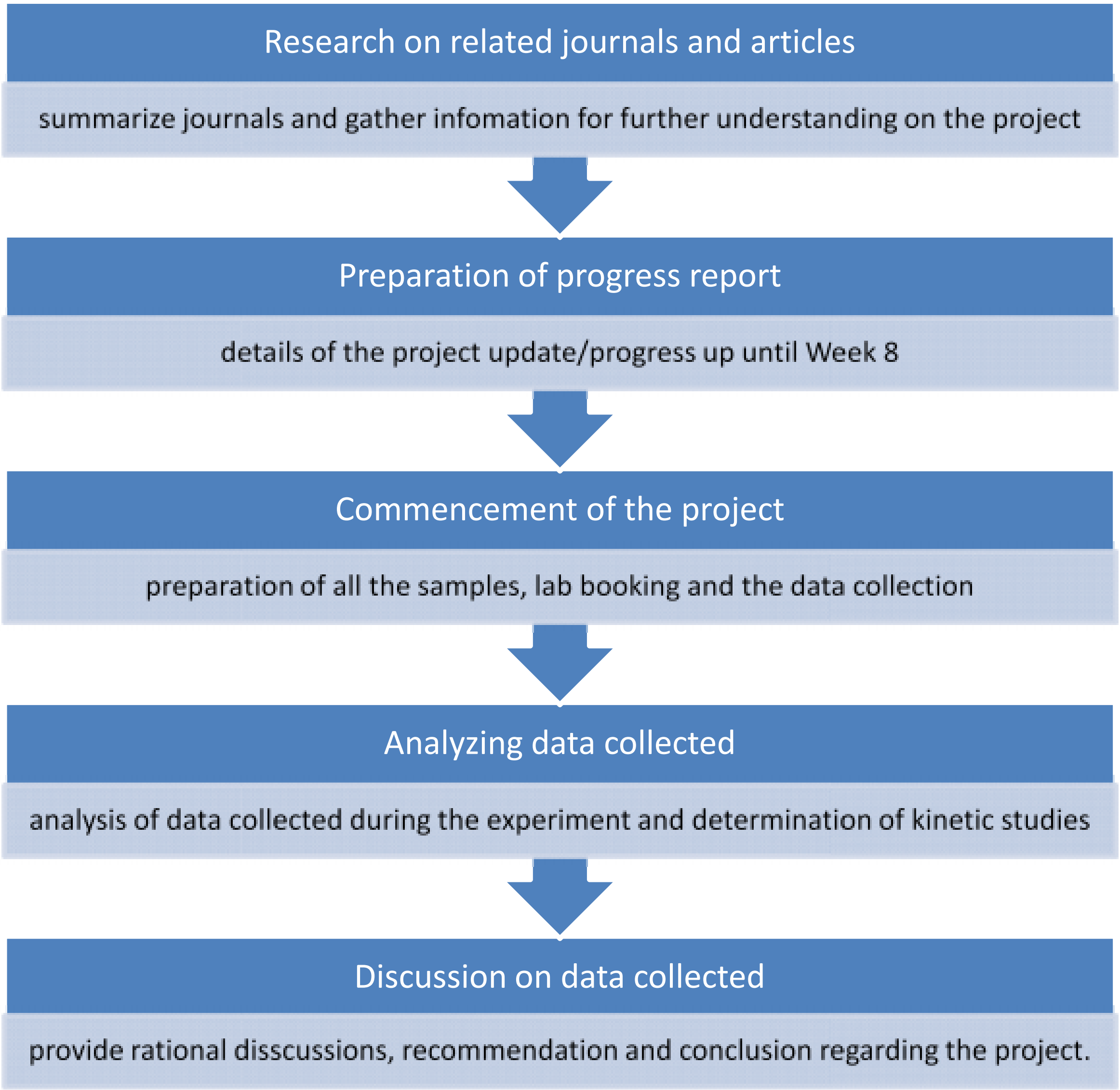
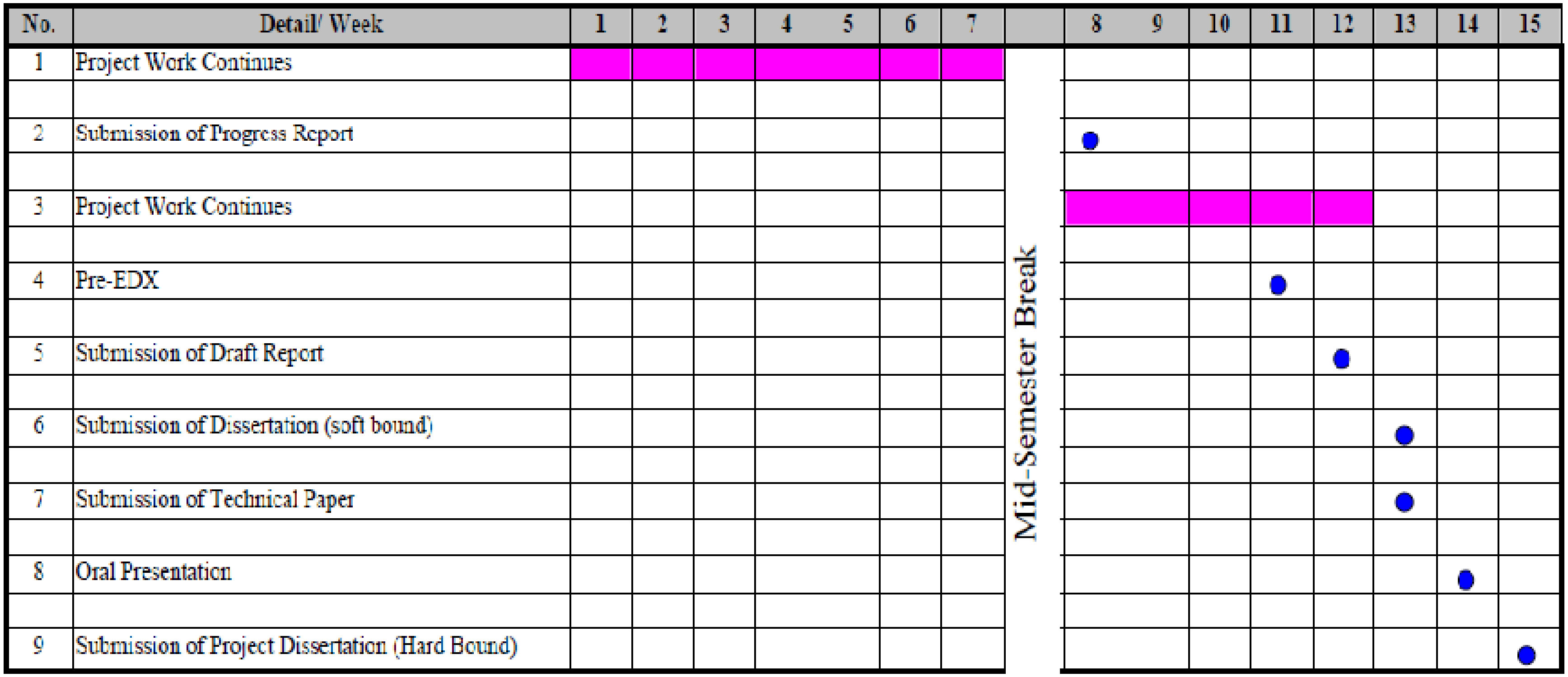


Figure 3.1: Project planning

3.3 PROJECT MILESTONE (GANTT CHART)

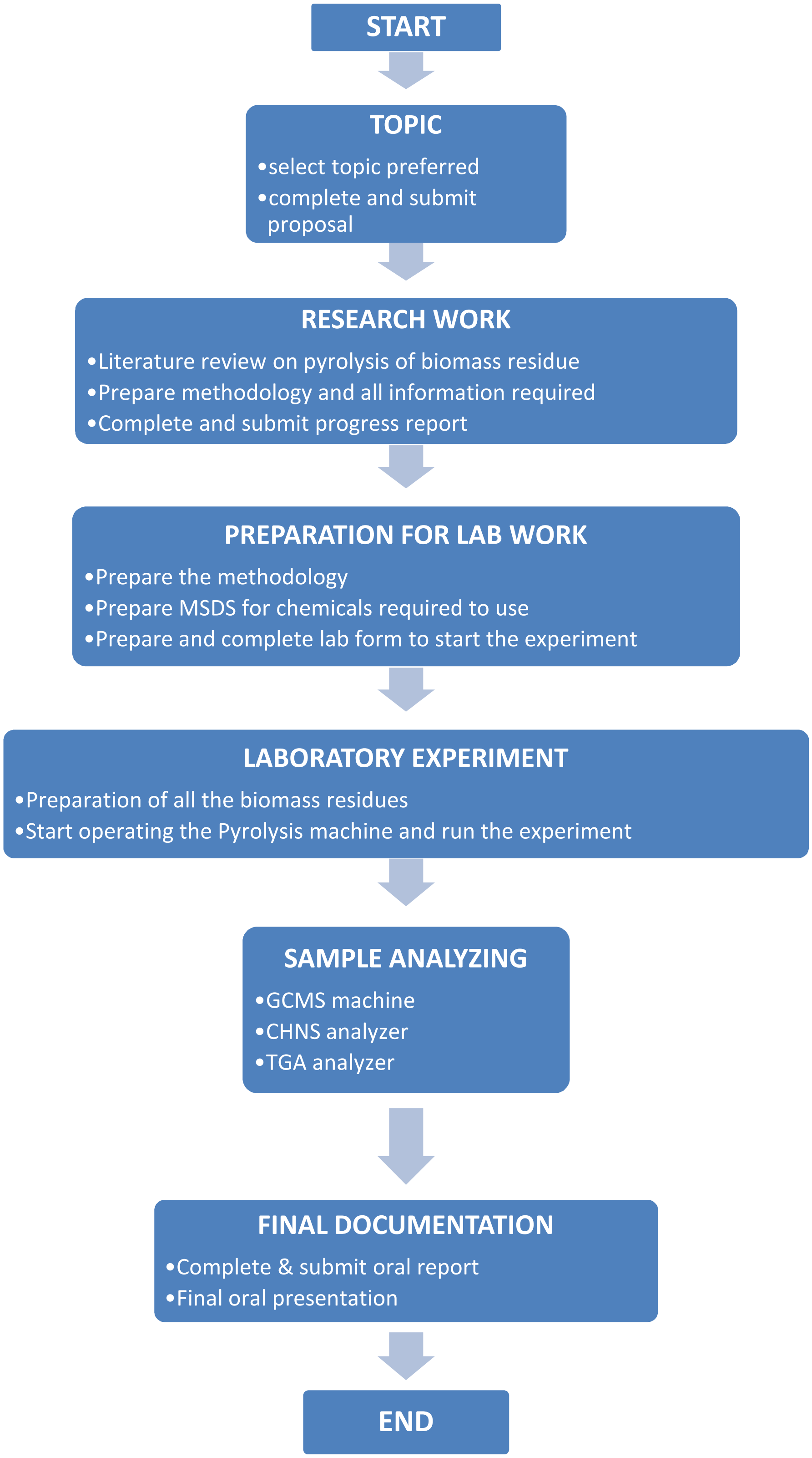


Timelines for FYP 2

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	▨	▨	▨	▨	▨	▨	▨	Mid-Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									▨	▨	▨	▨	▨			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

Figure 3.2: Project milestone/ Gantt chart

3.4 RESEARCH METHODOLOGY



3.5 SAMPLES PREPARATION.

3.5.1 Chemicals/ samples

There are four solid samples that should be prepared before proceed with the experimental methodology. All samples can be found nearby Universiti Teknologi PETRONAS (UTP) area without any difficulties.

a) Sugarcane bagasse
b) Rice husks
c) Corn cobs
d) Wood sawdust

3.5.2 Tools/ Machines

This project involved five different kind of machine, each has specification and contribution in data gathering process:-

a) Pyrolyzer – Gas Chromatography-Mass Spectrometry Machine (Py-GCMS) Agilent GC:7890A MS: 5975C attached to Pyrolizer PY2020iD
b) Thermogravimetric Analyzer (TGA)
c) CHNS Analyzer
d) Granulator
e) Furnace oven

The experiment is done following the standard listed below:

i) ASTM E1131 : Standard Test Method For Compositional Analysis By Thermogravimetry
ii) ASTM E1641 : Standard Test Method For Decomposition Kinetics By Thermogravimetry
iii) ASTM D3452 : Standard Practice For Rubber - Identification By Pyrolysis-Gas Chromotography

iv) ASTM D7544 : Standard Specification For Pyrolysis Liquid Biofuel

3.6 EXPERIMENTAL METHODOLOGY

3.6.1 Physical Conversion of Biomass

Assumption being made that the experiment is began with bulk feedstock.

i) The bulk feedstocks are brought to Building 21 (Fabrication Lab) and the size of the samples are reduced to a smaller size that can be fit into the oven. (Estimation of 1-inch overall dimension).
ii) Samples are then dried in a furnace oven in Building 4 (Physical Chemistry Lab) at temperature of 71°C and are left for one whole day to make sure 80 wt % of moisture content is removed.
iii) After the samples are confirmed to be dry, they are then brought to Building 17 (Mechanical Department) and granulated using the granulator to further reduce the bulk samples into granules/particles size.
iv) The samples are then transferred into sample bottles and labeled before hand to the technician to precede the next procedure.

S1 : sugarcane bagasse
S2 : rice husks
S3 : corn cobs
S4 : wood sawdust

3.6.2 Thermochemical Conversion of Biomass – Pyrolysis process

<u>Thermochemical conversion by Py-GCMS machine.</u>

i) A weighed amount of biomass sample (2-3 mg) was introduced into the quartz tube.
ii) The tube is then placed inside platinum filament coil on the probe inside the pyrolyzer.

iii) Sample is then being heated until it reach 600°C and is left at that temperature for few second.
iv) The outlet of the sample is then analyzed by GC-MS machine.
v) Step i to iv is repeated for each biomass samples and the results are collected.

<u>Thermochemical conversion by TGA machine.</u>

i) Sample is weighed around 0.8 g and is loaded into the sample pan in the heating zone of TGA machine.
ii) The sample is heated up to 600°C with heating rate of 20°C/min and was conducted in Nitrogen environment.
iii) The sample is left for 5 minutes when it reached 600°C for it to stabilize.
iv) The entire steps above are repeated for each biomass sample. The remaining of the sample is analyzed and the results are collected.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 ANALYSIS BY PY-GCMS

All the four samples have successful being analyzed by the GCMS machine directly after the pyrolysis process. The results obtain for each sample is shown in Figure 4.1, 4.2, 4.3 and 4.4 below.

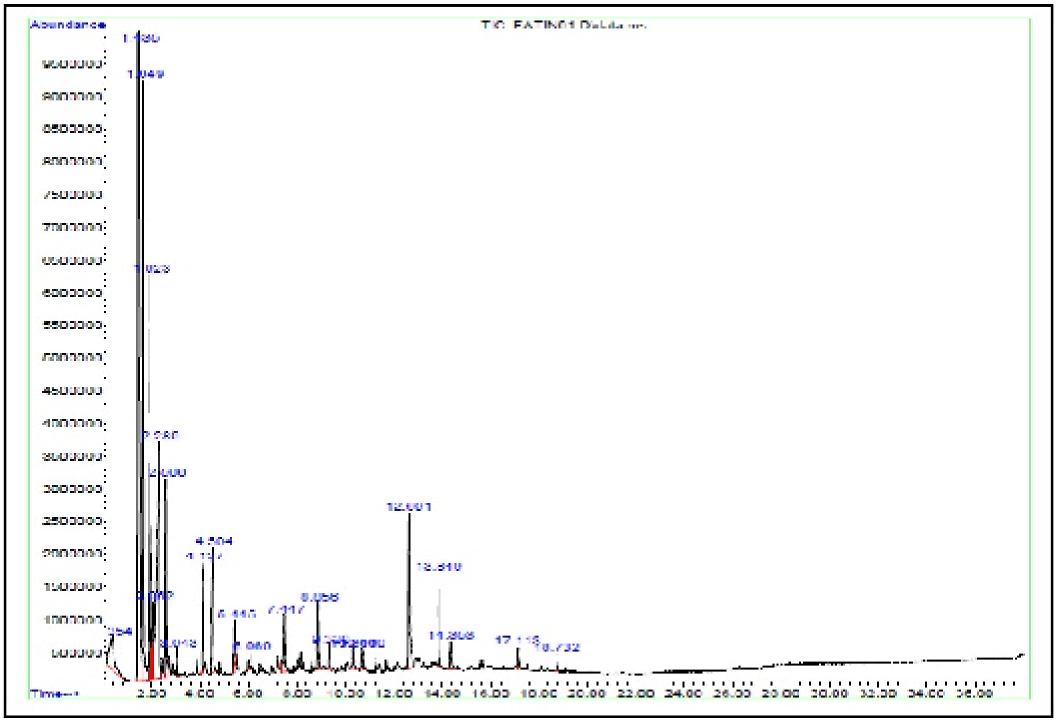


Figure 4.1: Result for sugarcane bagasse

As shown in the graph obtain from the GCMS, the highest peak detected in sugarcane bagasse is carbon dioxide. There are total of 22 peaks detected in the biomass containing different kind of chemical species.

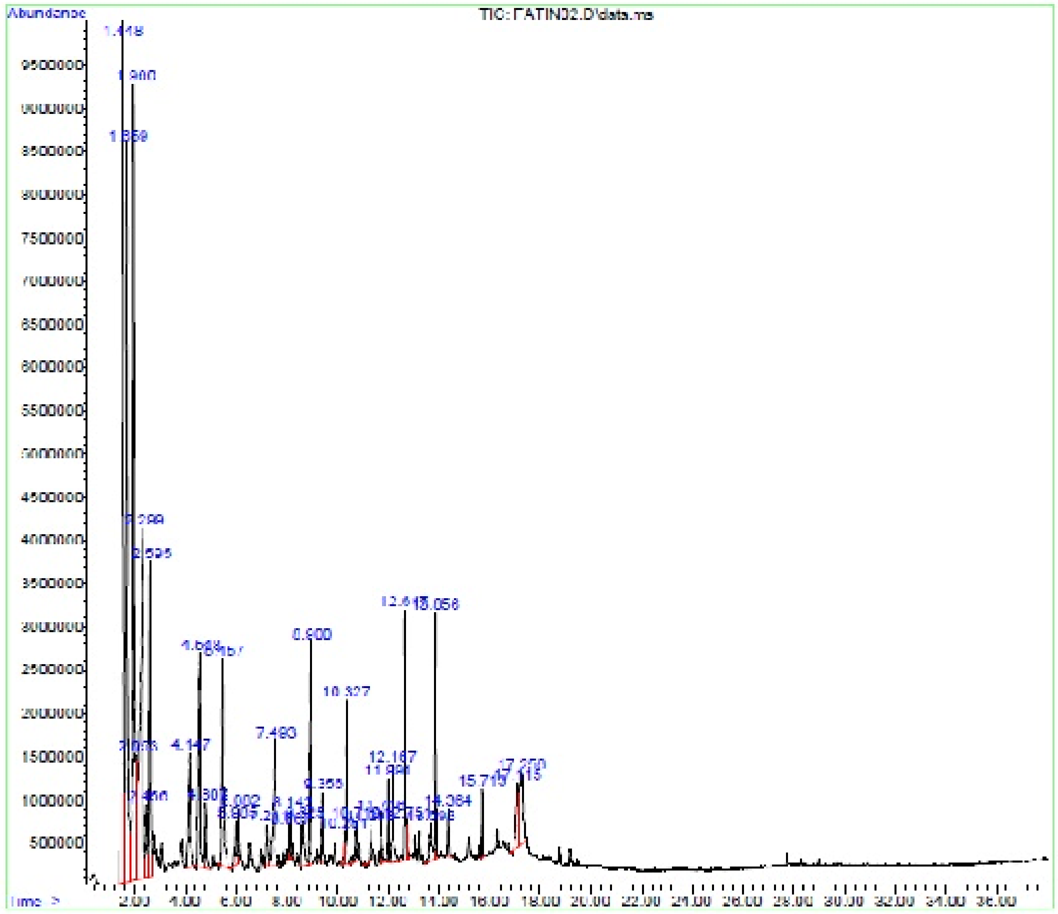


Figure 4.2: Result for rice husks.

Figure above shows the result obtained from the GCMS for rice husks sample. The highest peak detected from this biomass after the pyrolysis process is similar to the highest peak obtained from sugarcane bagasse, carbon dioxide. The GCMS able to distinguish35 peaks from the sample containing different chemical elements.

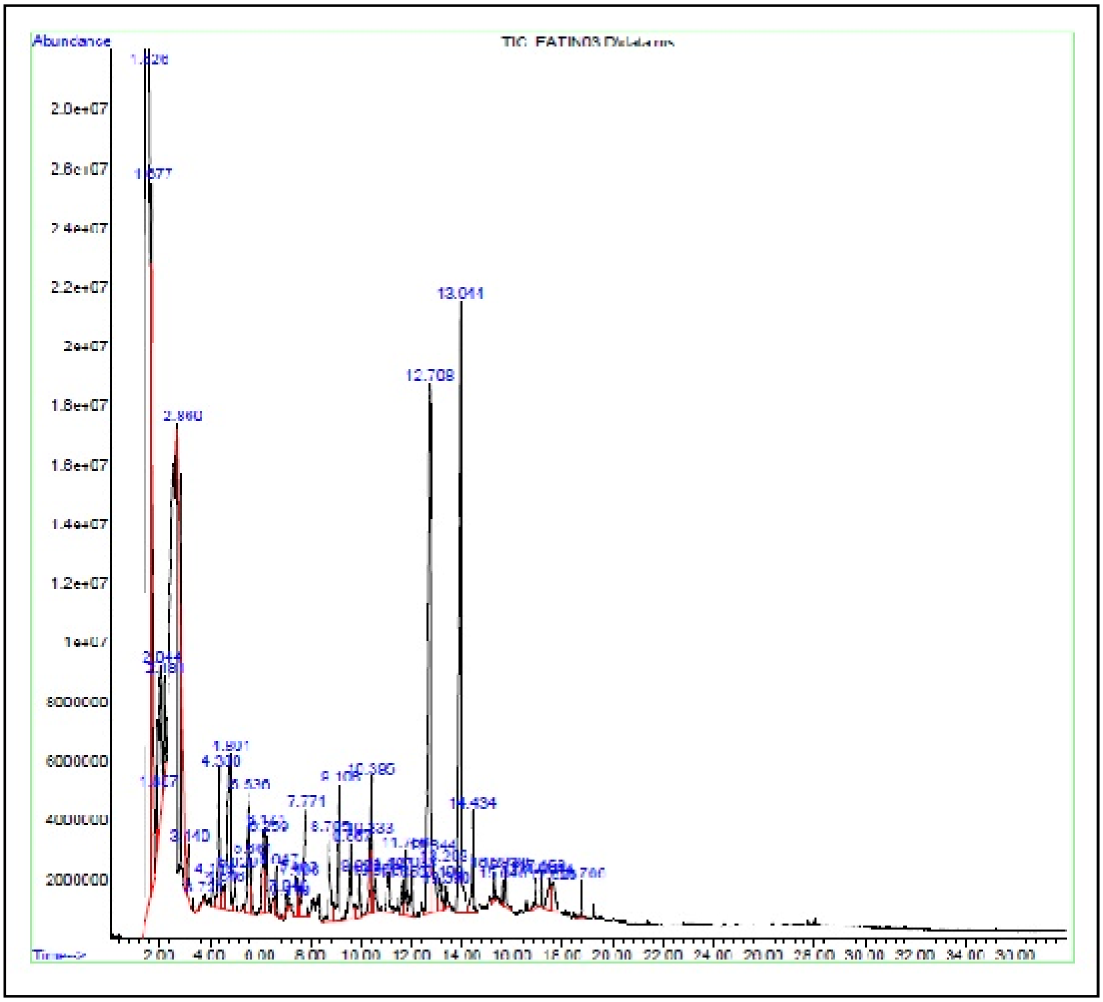


Figure 4.3: Result for corn cob

Figure 4.3 show graph obtain from the pyrolysis of corn cob. The highest peak in this graph detected by GCMS is dimethylamine. A total of 51 peaks have been distinguished and analyzed by the machine from the yields produce during the pyrolysis process.

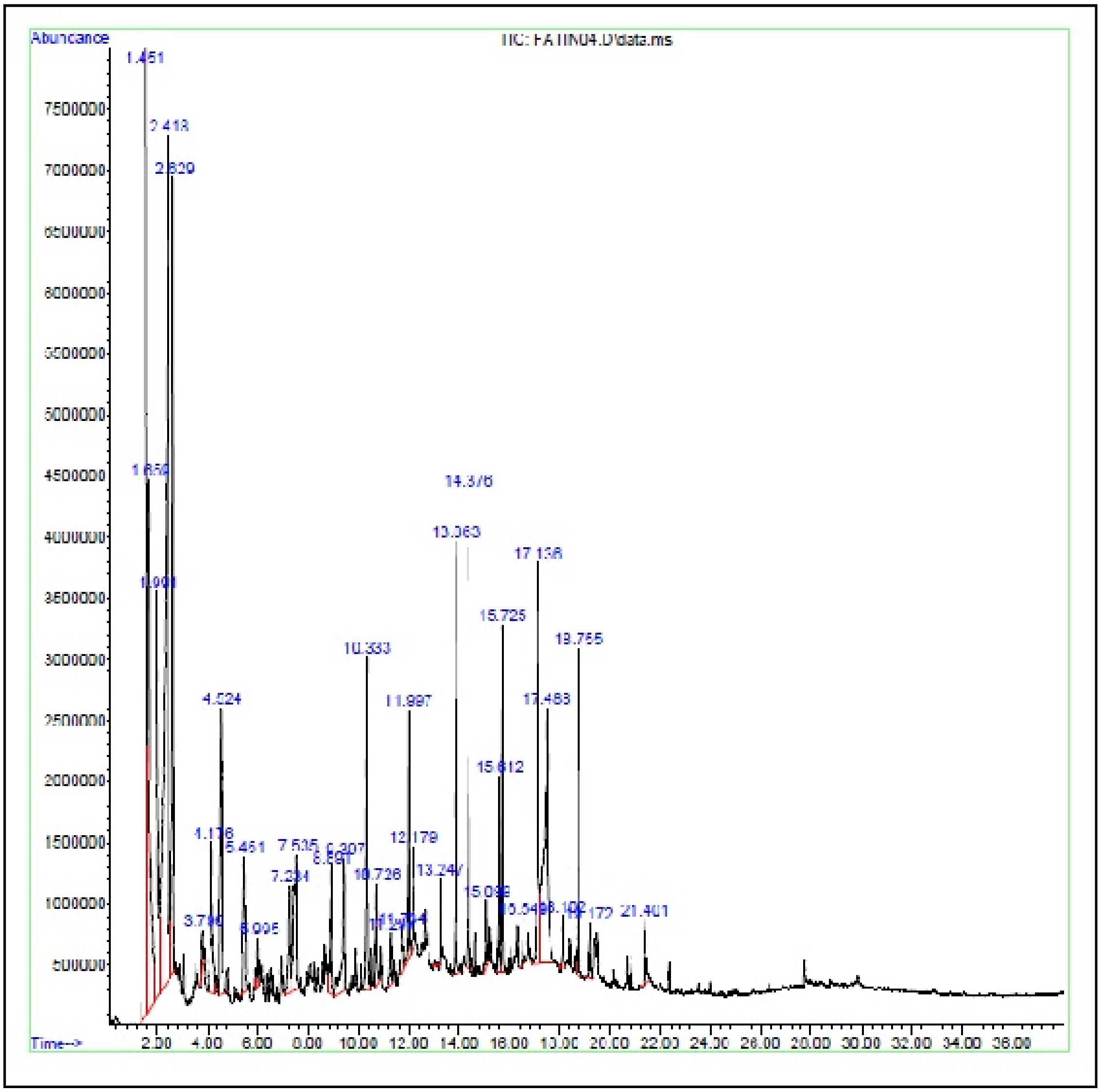


Figure 4.4: Result from wood dusts

Last but not least, figure 4.4 shows the total peak analyzed by the GCMS machine. The highest peak detected by the machine and read by the library search report as alanine. 33 peaks is detected and plotted on the graph and shows in this figure.

4.2 ANALYSIS BY TGA

4.2.1 Sugarcane bagasse

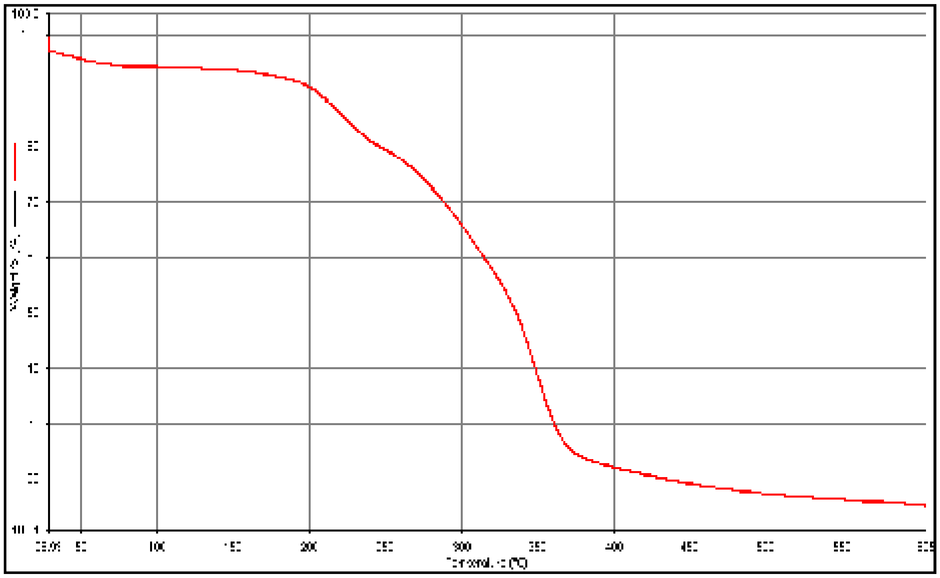


Figure 4.5: Graph of weight percentage vs Temperature for sugarcane bagasse

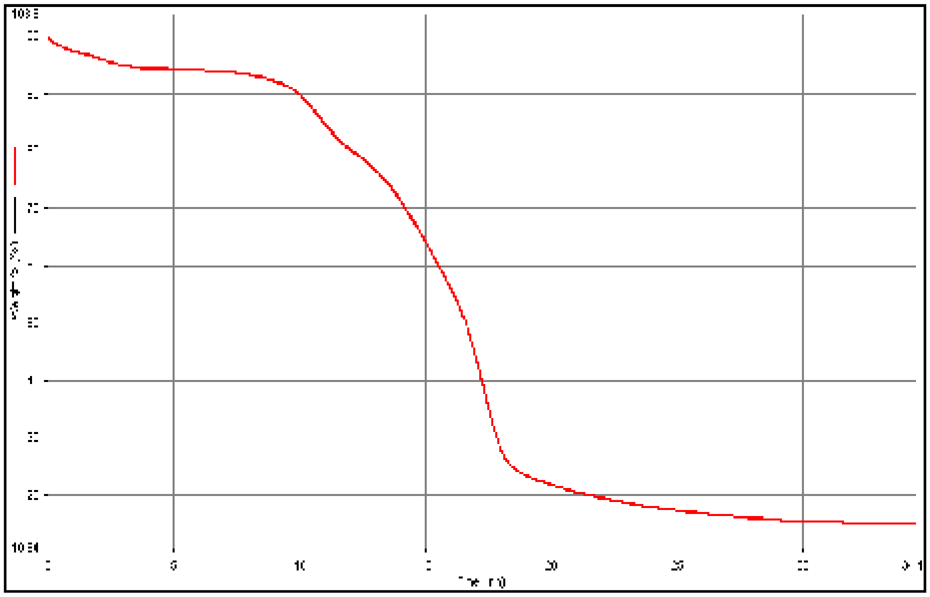


Figure 4.6: Graph of weight percentage vs Time for sugarcane bagasse

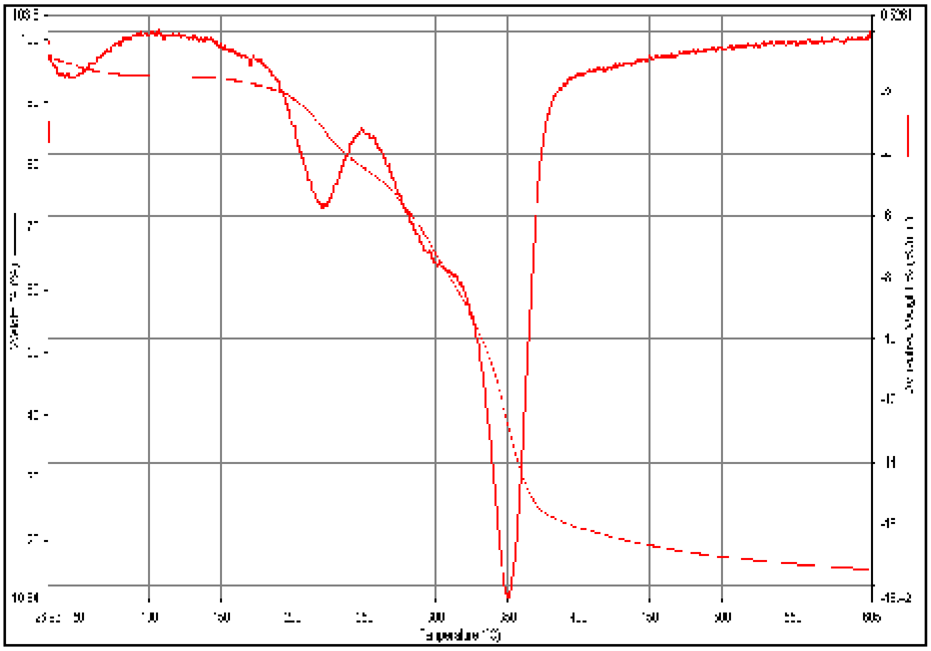


Figure 4.7: Graph of derivative weight percentage vs temperature for sugarcane bagasse

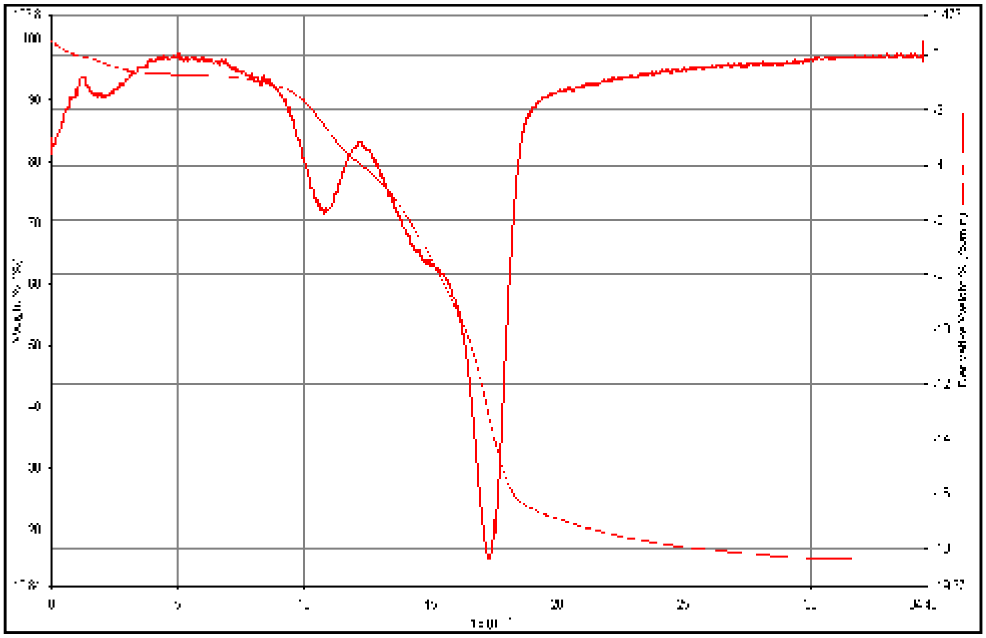


Figure 4.8: Graph of derivative weight percentage vs Time for sugarcane bagasse

4.2.2 Rice Husks

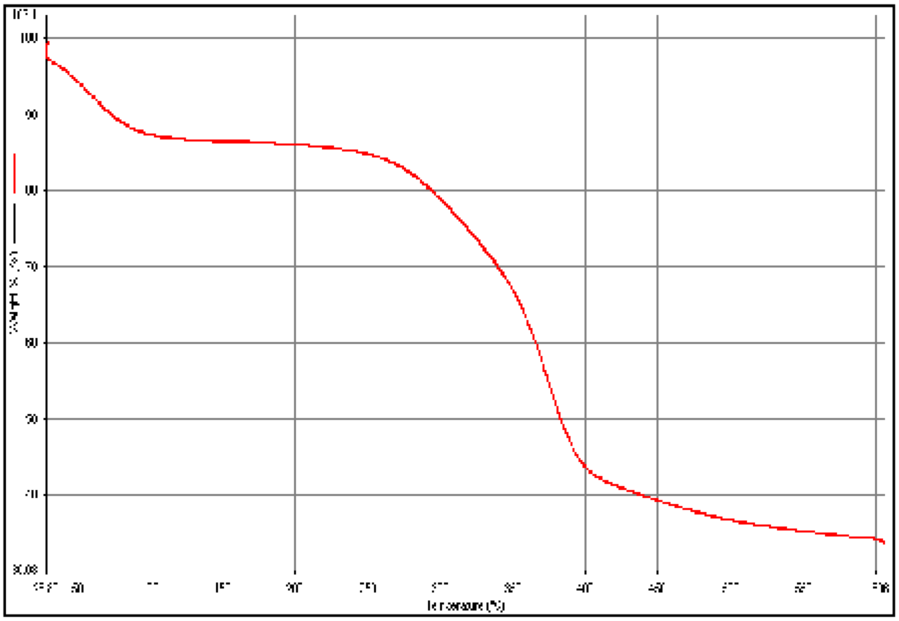


Figure 4.9: Graph of weight percentage vs Temperature for rice husks

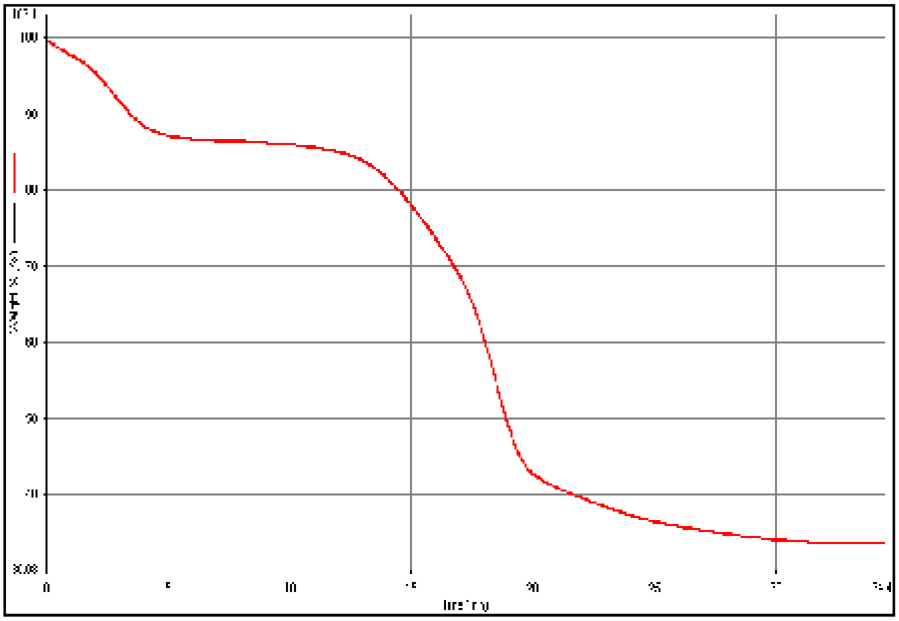


Figure 4.10: Graph of weight percentage vs Time for rice husks

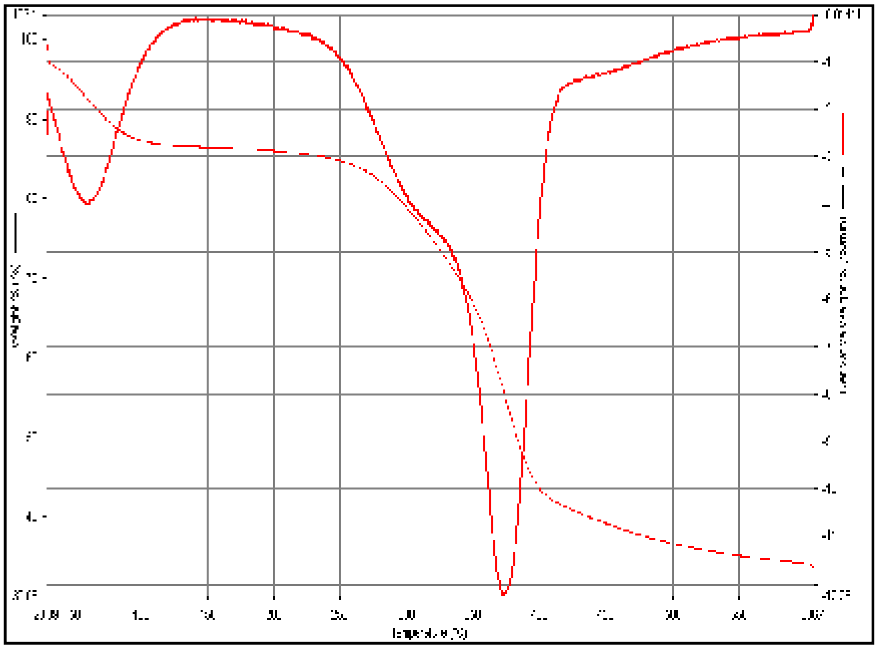


Figure 4.11: Graph of derivative weight percentage vs temperature for rice husks

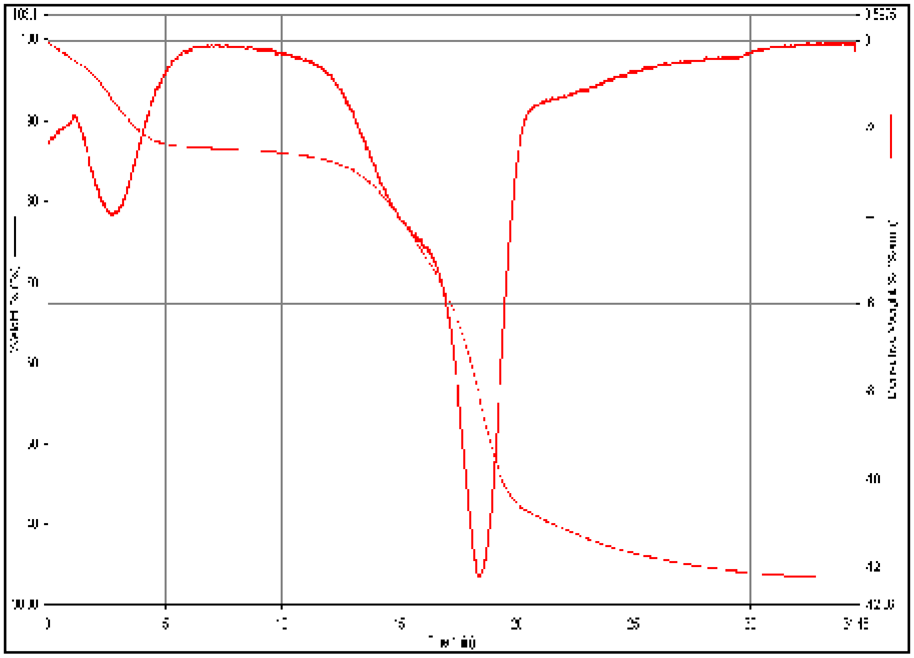


Figure 4.12: Graph of derivative weight percentage vs Time for rice husks

4.2.3 Corn Cob

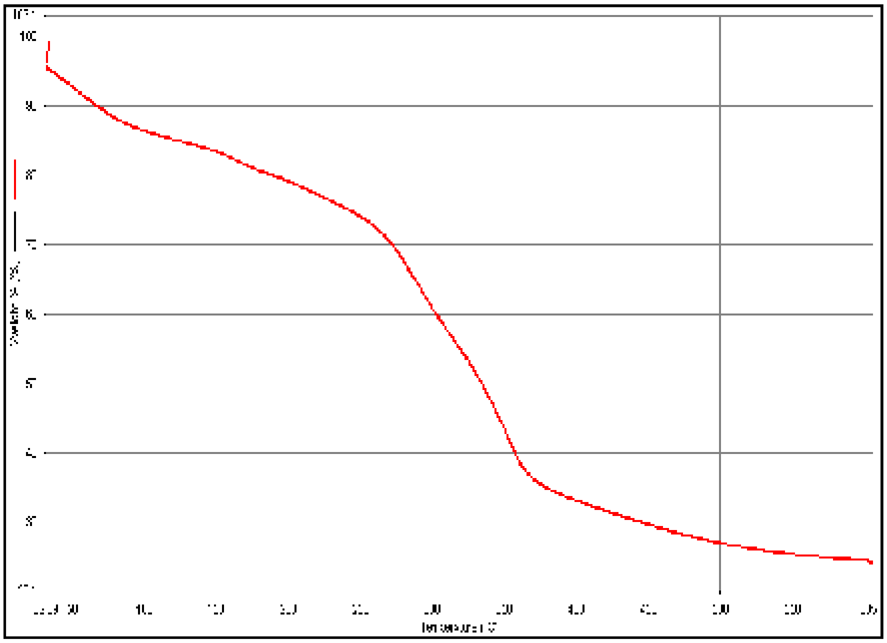


Figure 4.13: Graph of weight percentage vs Temperature for corn cob

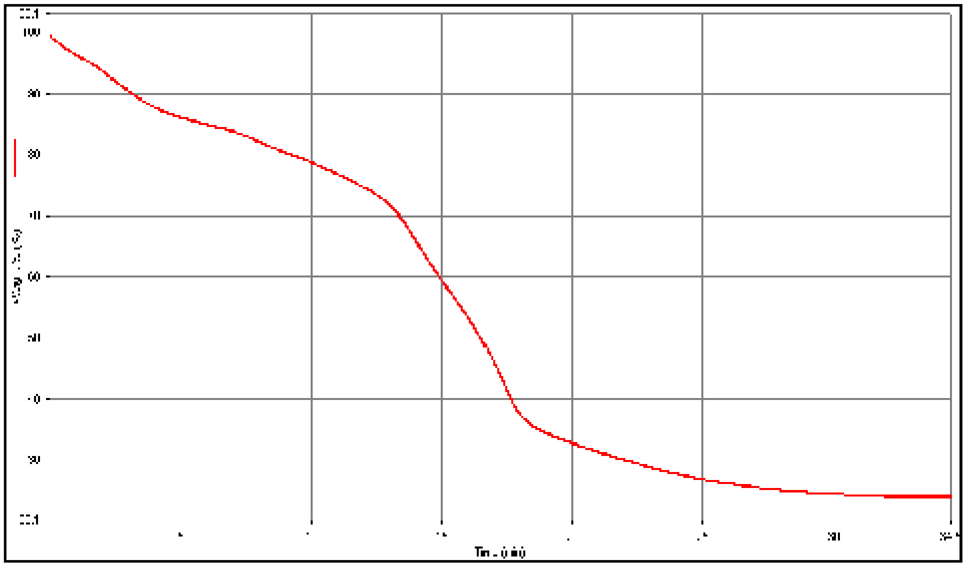


Figure 4.14: Graph of weight percentage vs Time for corn cob

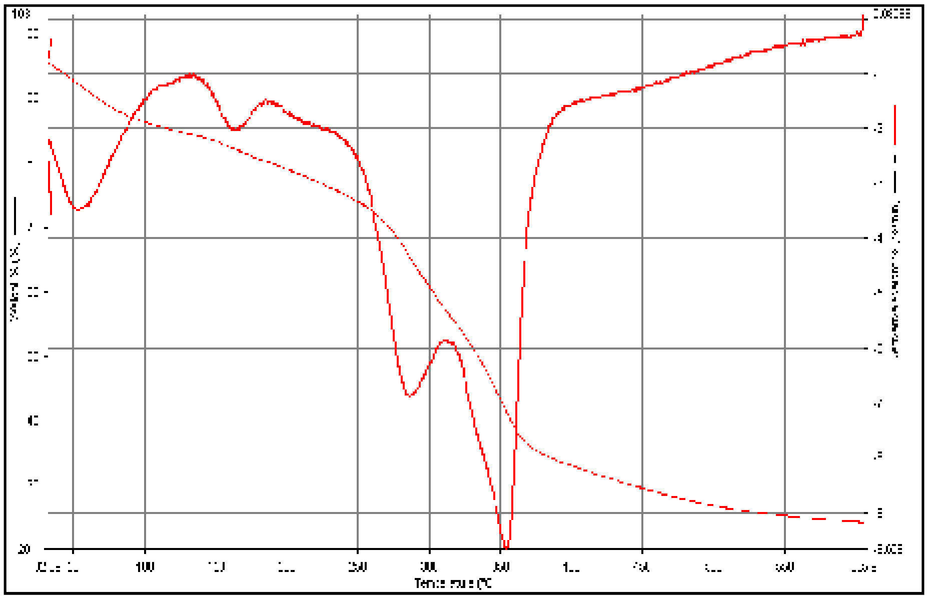


Figure 4.15: Graph of derivative weight percentage vs temperature for corn cob

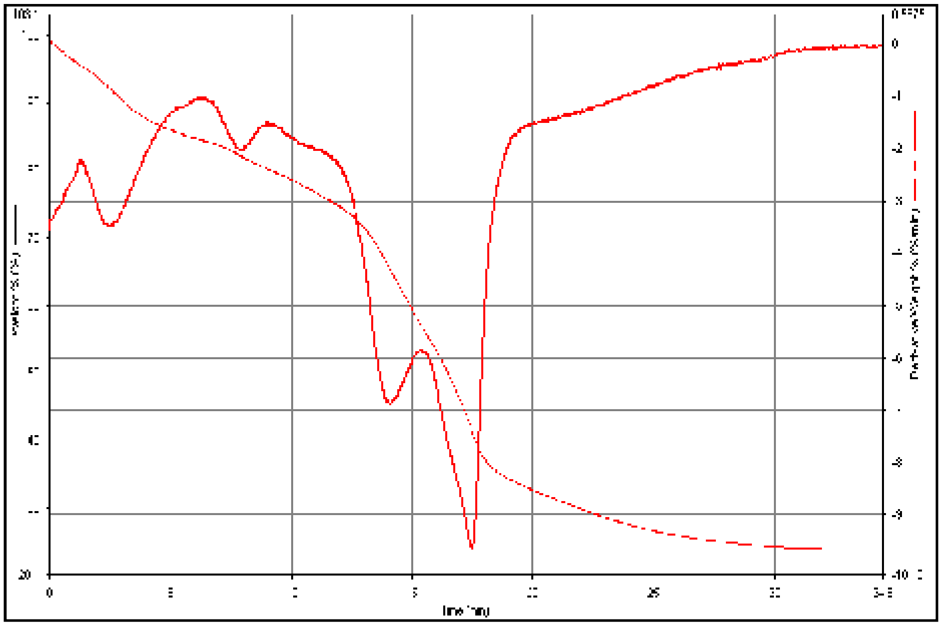


Figure 4.16: Graph of derivative weight percentage vs Time for corn cob

4.2.4 Wood Dusts

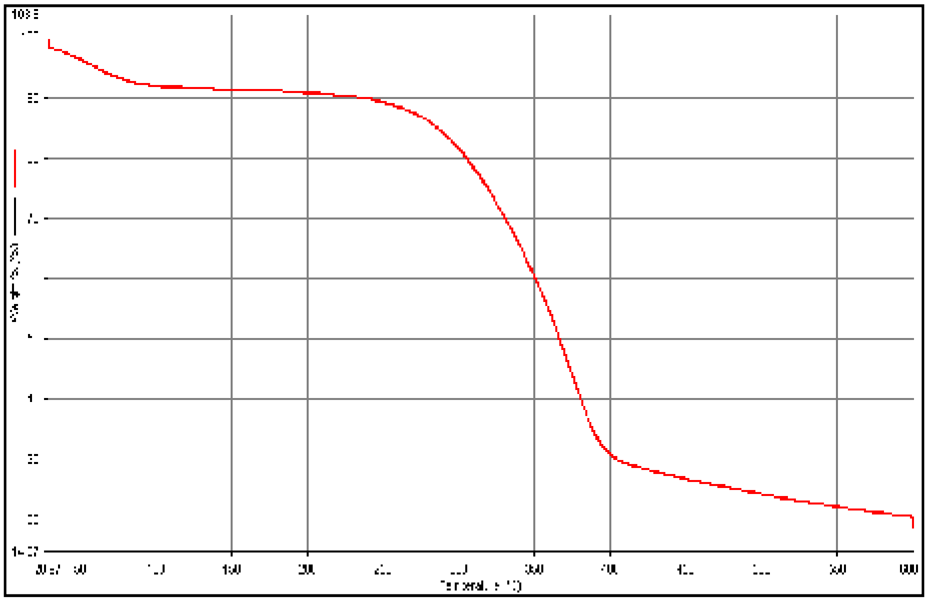


Figure 4.17: Graph of weight percentage vs Temperature for wood dusts

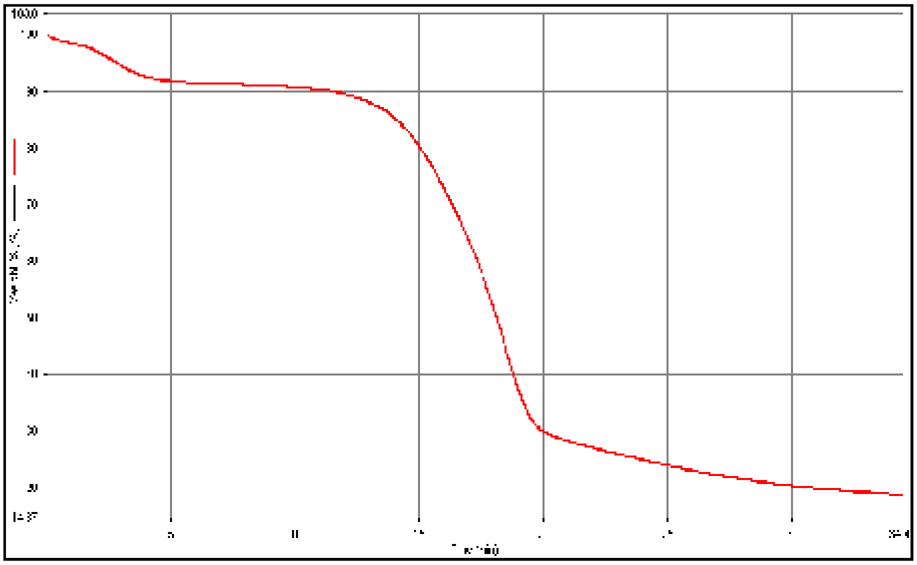


Figure 4.18: Graph of weight percentage vs Time for wood dusts

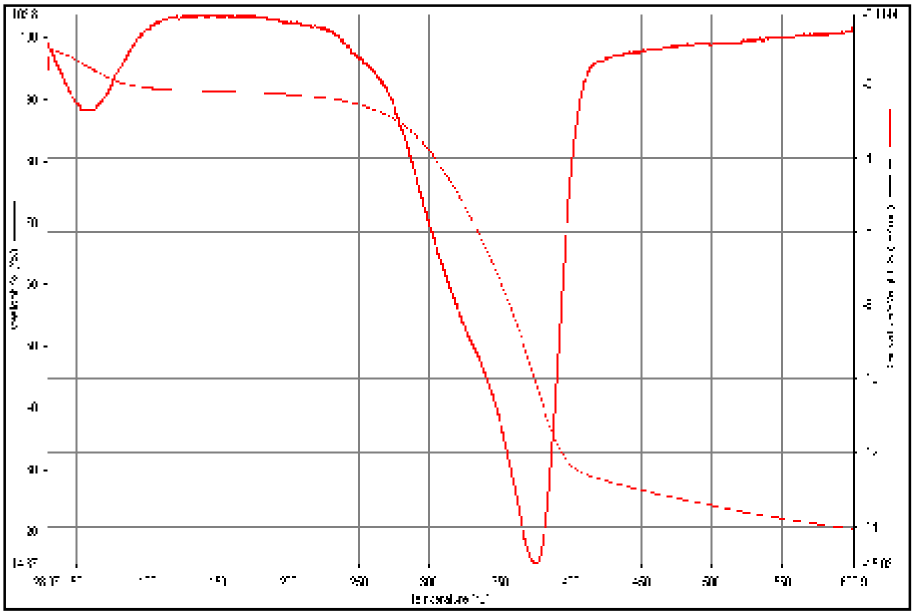


Figure 4.19: Graph of derivative weight percentage vs temperature for wood dusts

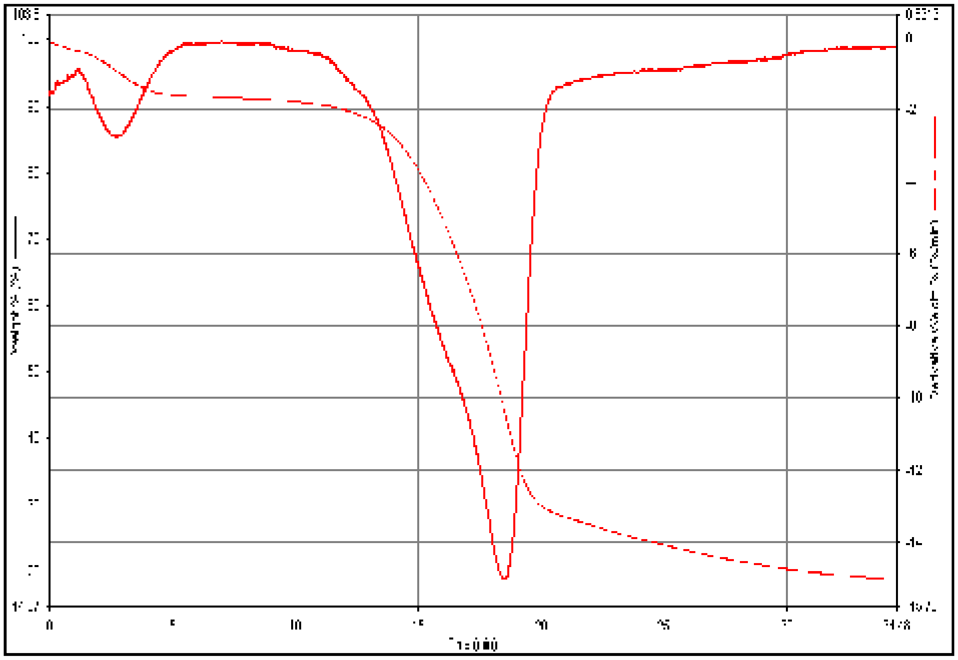


Figure 4.20: Graph of derivative weight percentage vs Time for wood dusts

4.3 DISCUSSIONS

Pyrolysis process can be analyze using two approaches; one using the known method, thermogravimetric analyzer while the other approach is quite new in the study, Py-GCMS machine. Since there are two analyses being done on the same time, we would go through one by one.

Py-GCMS machine applied flash pyrolysis in the process flow. Since the pyrolysis would only take a few seconds using this machine, kinetic parameter cannot be estimated. It only capable to provide preliminary information on chemical composition as well as the potential compound that can be derived from the bio-oil. Table 4.1 below shows the major chemical composition that can be derived from the biomass during the pyrolysis process together with the area in the graph.

Table 4.1 shows the chemical composition that can be derived from each sample of biomass. Based on the calculation, the main compound quantify by the Py-GCMS is acetic acid with total area percentage of 6.9075% compare to other chemical composition. During the pyrolysis process, three yields are being produced. Pyrolysis gas mainly contained carbon monoxide, carbon dioxide, methane or any hydrocarbon in gaseous form while the pyrolysis oil mostly contain organic and inorganic species. From the analysis using GCMS, sugarcane bagasse yields the highest amount of pyrolysis oil, thus proving the theory that said the longer the carbon chain (quantity of carbon), the higher the amount bio-oil produce during the pyrolysis process.

Chemical Composition	Area percentage (%)			
	Sugarcane bagasse	Rice husks	Corn cob	Wood dusts
Acetic Acid	11.26	6.73	-	9.64
Furfural	0.63	2.25	2.64	1.01
2-propanone, 1-hydroxy-	3.79	2.80	-	3.06
6-oxabicyclo[3.1.0]hexan-2-one	1.45	1.63	-	1.56
1,2-cyclopentanedione, 3-methyl-	0.45	0.52	1.34	1.00
Phenol, 2-methoxy-	0.49	1.05	1.05	1.49
Benzofuran, 2,3-dihydro-	4.33	2.32	9.50	-
2-methoxy-4-vinylphenol	1.30	-	8.01	1.61
Phenol, 2,6-dimethoxy	0.67	0.34	1.06	1.63
Phenol, 2-methoxy-4-methyl	-	0.38	0.59	0.79
Phenol, 2-methoxy-4-(1-propenyl)-	-	0.32	0.33	1.36
2-propanone, 1-(acetyloxy)-	0.23	0.52	0.82	-
-D-Glucopyranose, 1,6-anhydro-	-	2.71	1.48	3.87

Table 4.1: Chemical composition derived from Py-GCMS

Thermogravimetric analysis is used as the second approach in this project. TGA can be used to investigate the kinetics behaviors happened during the pyrolysis process. The advantage of using TGA instead of Py-GCMS is that, we can specify the heating rate of the process. This will give us the full authority of controlling the pyrolysis process. In this project, heating rate of 20°C/min is being used as this is the optimum heating rate that is used during thermal decomposition of biomass [25]. From the graphs shown in the previous section, the shape of the graph of each biomass during thermal decomposition is almost the same. Figure 4.21 below shows the comparison between all the biomass samples based on weight percentage.

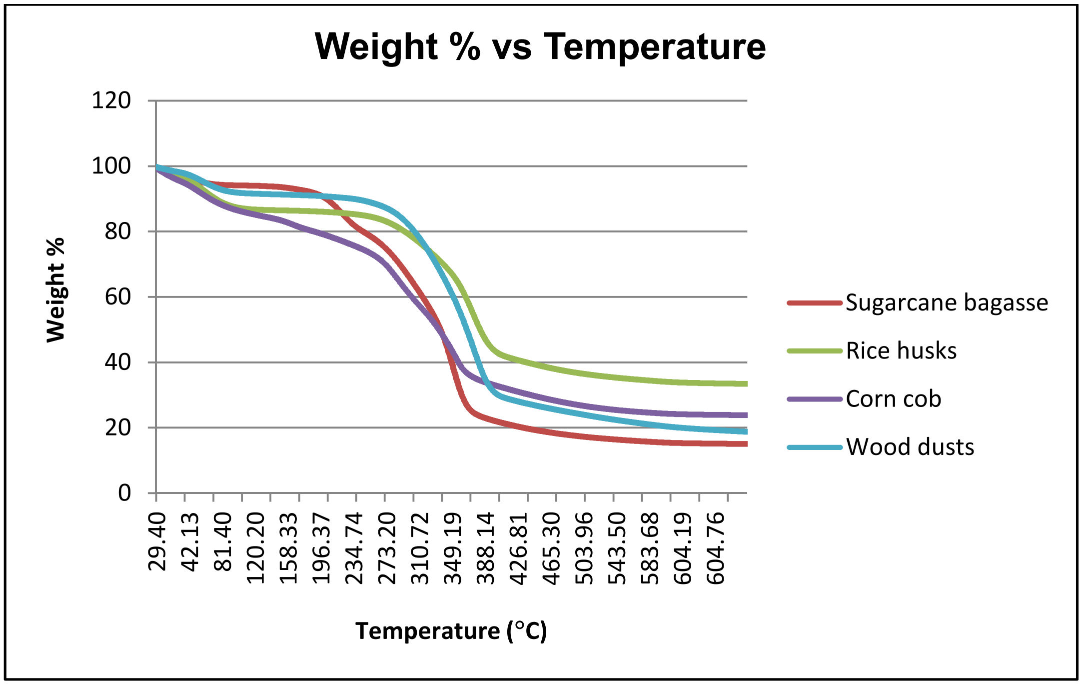


Figure 4.21: Graph of weight percentage vs Temperature for all biomass samples

Based on the graph showed above, sugarcane bagasse undergoes rapid weight loss during the devolatilization process. From the graph, the first slope shows that during that time, the moisture removal process happened. This is where moisture will first leave the sample until it completely dry. After that, the thermal decomposition process take place where the structure of the sample is started to pyrolize at rate of 20°C/min. Thermal degradation is plotted and examined using the TGA and DTG curves. From the graph, we can divide the plotted area into two prominent curves. By divide into two prominent curves, we can determine the initial degradation temperature for each biomass sample. From the experiment and data collected, the initial degradation temperature for all the samples was found around 196.37°C to 291.96°C [3].

4.4 KINETICS ANALYSIS

From set of data collected during thermal decomposition using TGA machine, the conversion, or mass loss of each biomass sample can be calculated using Eq. (2). By knowing the mass loss of the samples, the activation energy can be determined and the rate of decomposition can be calculated. Table 4.2 shows the mass loss for each biomass sample.

Biomass sample	Sample weight (gram)			Mass loss, α
	Initial	Actual	Final	
Sugarcane bagasse	0.724136	0.8	0.120520	-0.125680
Rice husks	0.698472	0.8	0.267192	-0.235411
Corn cob	0.564568	0.8	0.190992	-0.630212
Wood dusts	0.713408	0.8	0.149768	-0.153630

Table 4.2: Samples mass loss

To determine the kinetics parameters of the pyrolysis process, Eq. (6) is being used where the Arrhenius equation is applied. Since the experiment is done with constant heating rate, thus the value of β is fixed where$\beta = dT/dt$. By plotting the $ln\left[\frac{ln(1-\alpha)}{T^2}\right]$ versus $1/T$ graph, the activation energy, *E*, and the pre-exponential factor, *A*, can be calculated. In this experiment, the reaction is assumed to be first-order reaction, thus n=1. Graph 4.18 shows the relationship between the temperature and mass loss of pyrolysis process and from the graph, the value of *E* and *A* is calculated.

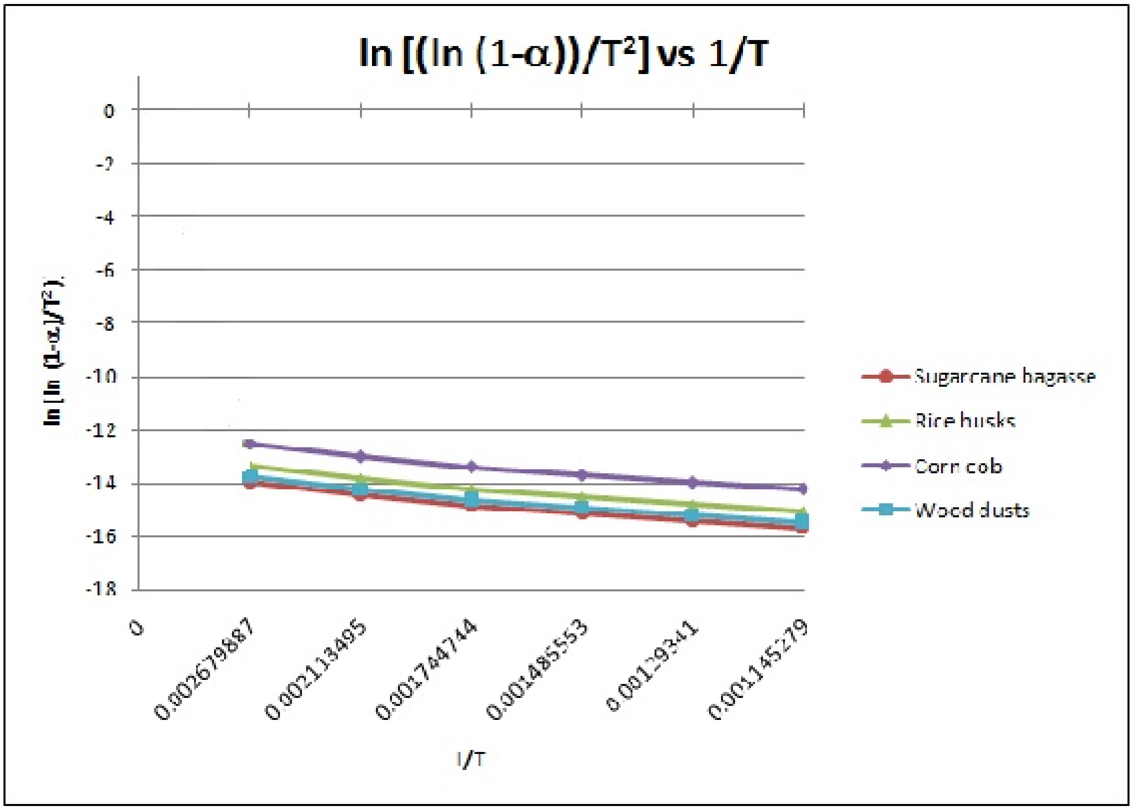


Figure 4.22: Graph of $ln\left[\frac{ln(1-\alpha)}{T^2}\right]$ versus $^1/_T$

From the graph, the value of the slope is determined as 1039.917. Thus, the *E* and *A* value is also calculated. Table 4.3 summarizes the value of the kinetic parameters of pyrolysis process for each biomass sample.

Biomass samples	Heating rate, β	Order of Reaction, n	Activation Energy, *E*	Frequency factors, *A*	Correlation Coefficient
Sugarcane bagasse	20°C/min	1	10.231 kJ/mol	8.459e-03	0.996
Rice husks				2.893e-02	
Corn cob				1.251e-02	
Wood dusts				7.008e-03	

Table 4.3: Kinetics parameters for pyrolysis process

From the table, we can conclude that activation energy will remain relatively constant. The frequency factor, *A* varies depending on the type or biomass and also the heating rate. The correlation coefficient that being used is quite high, where it is above value 0.98. From the parameter shows above, this suggested that the frequency factor depends on the biomass samples and also the heating rate. These parameters can be used to determine the time-conversion profile for the pyrolysis process of different heating rate and different biomass samples.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

From the experiment, it is showed that different biomass would yield same product but different in chemical composition. In this project also shows that different approach of analyzing the pyrolysis process resulting different analysis involvement. Py-GCMS is quite a new approach to be used to study the behavior of pyrolysis process on different biomass residues. This machine involving simple yet fast pyrolysis process and capable to provide the preliminary analysis on chemical composition as well as compound derived from pyrolysis oil. With this approach, it enables rapid comparison on pyrolysis behaviors of different biomass species.

Thermogravimetric analyzer has been used for past few years or might be decades in improving and better understanding regarding thermal decomposition of biomass. TGA can be utilized to investigate pyrolytic behaviors on biomass, kinetics parameters and kinetics behaviors depending on the heating rate since it provides rapid quantitative methods. The study of the kinetics behaviors might give us better understanding on thermochemical conversion of biomass thus improvised and optimized the process so that this energy sources can be used to replace fossil fuels demand, one day.

This project does meet the objectives at the beginning of the process work where the kinetics behaviors of pyrolysis process able to be investigated. This project proves that different kind of biomass does produce different kind of yields containing multi-component of chemical composition. The project and experiment that had been done give basic knowledge and ideas of the process, helps in order to reach the optimization of the process.

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APPENDICES