CERTIFICATION OF APPROVAL

Bio-Oil Yield from Fast Pyrolysis of Malaysian Bamboo via Drop Type Pyrolyzer

by

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

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.

(MOLLY KUEH HUI PING)

ACKNOWLEDGEMENT

The author would like to take this opportunity to acknowledge with utmost appreciation towards the numerous valuable comments, suggestions, constructive criticisms, morale support and monetary support from all people, lecturers, family, friends and the highest authority, God. The preparation of this report would not be possible without the help from these people:

1) Supervisor, Professor Dr. Yoshimitsu Uemura
2) Co-supervisor, Dr. Noridah Binti Osman
3) Miss Norizan Ali
4) Mr Salman Naqvi
5) Miss Shazleen Shadoon
6) Miss Hafizah Binti Ahmad Afif
7) All CBBR students, staffs and part time assistants
8) Mechanical Department UTP staffs and lab technicians
9) Chemical Department UTP staffs and lab technicians
10) Block P technicians and staff
11) Friends in nearest circle of life.

Each of their contribution to the completion of this work is very valuable and it is an honor to do a project which can contribute greatly to the society’s future pathway.

ABSTRACT

The basis of this project was to explore the potential of Malaysian bamboo as a candidate of clean energy resource which can be produced renewably. The driving force towards this project was due to the limited information on bamboo pyrolysis in Malaysia even though bamboo pyrolysis was given considerable attention in other countries. Therefore, this led to the main purpose of this study which would be to investigate the yield of *Gigantochloa Scortechinii* focusing on bio-oil energy properties and conditions affecting the bio-oil yield. Due to time limitation, the scope of this study would be concentrated on the effect of temperature towards the yield of bio-oil and its properties. The bamboo, *Gigantochloa Scortechinii* was amassed from Tasik Banding Gerik with permission from Department of Forestry, Gerik, Perak. The experimental approach was divided into three steps. Firstly, sample preparation and characterization of bamboo. This included grinding the bamboo to desired fractional size of 250-500 μm as well as preliminary analyses of bamboo characteristics such as moisture content, ash content, elementary composition of C, H, N and S, and calorific value. Secondly, pyrolysis experiment would be carried out using fast pyrolysis technique via drop type pyrolyzer. Three types of products were to be obtained namely char, bio-oil, and gas with bio-oil as the main product under study. The experiment would be repeated with three different temperatures of 450^{o}C, 500^{o}C, and 550^{o}C respectively. Lastly, the bio-oil and other products would be analyzed qualitative and quantitatively. Ultimately, the results of this study would be treated as a comparative basis towards other similar studies in the future.

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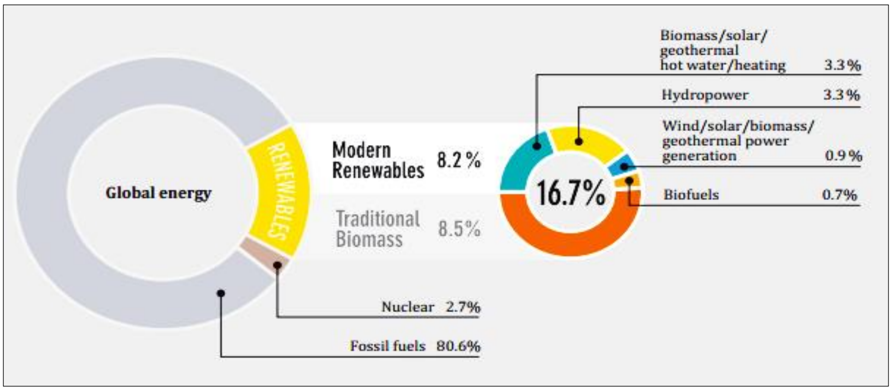
INTRODUCTION

1.1 Background of Study

1.1.1 An Overview of Energy Resources

Energy is an indispensable component of society. Our modern society depends on energy for almost everything ranging from home appliances, lighting, transportation, heating/cooling, communication, to industrial processes to supply commodities for our daily needs. From Renewables 2012 Global Status Report by REN21, the worldwide energy consumption of the human race was 16.7% coming from renewable resources and 80.6% coming from fossil fuels at 2010. Among the renewable resources, only less than 5% of total are generated from biomass.

Figure 1: Renewable energy share of global final energy consumption, 2010



At present status of renewable resources in Malaysia, according to NEBM report 2010 by Ministry of Energy, Green Techonology and Water (KeTTHA), the trend of final energy demand is increasing yearly except for economy crisis during 2009. For the complete trend from 1990 to 2010 of energy demand, see Appendix A. On 2010, the energy demand is 41,476ktoe which is 27% higher than at 1990 with 13,217ktoe consumption, and this present system relies mainly on fossil fuels, i.e. coal, natural gas, and oil which are consumed far more than the amount it is produced. However, the dependency towards petroleum products are impossible to last long as these resources are finite. According to the

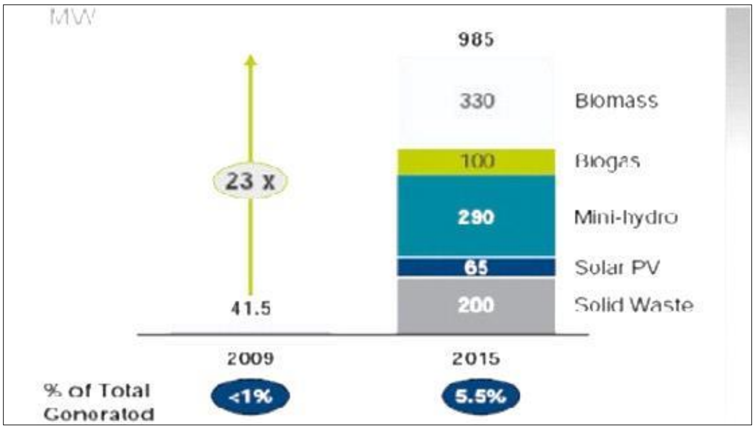
Hubbert Peak Theory (Hubbert peak theory, 2013), for any geographical area, the rate of fossil fuel production tends to follow a bell shaped curve because of resource depletion. One example is the forecast of total world production of crude oil, it is estimated that at the year 2100 (G. Haubrich & Meyer, 2007), crude oil production will face depletion. Also, the use of fossil fuels and other petroleum products as energy resources are creating numerous environmental effects towards mother earth. Decomposition of fossil fuels led to the disastrous effects such as air pollution and GHG emission. Dwindling reserves in the face of rapidly increasing energy consumption, combined with an increasing lack of energy security due to regional conflicts, and the environmental devastation that results from decomposition of fossil fuels, clearly suggest that we must act urgently and decisively to develop sustainable, clean, affordable, and renewable energy sources.

1.1.2 Development of Renewable Energy in Malaysia

Renewable energy (RE) derived from wind, solar, geothermal, tidal, hydropower and biomass all can contribute equally to our renewable energy portfolio. There are tremendous research and technology advancement efforts toward the development of sustainable energy. Effective policies and incentive on RE is critical to promote low carbon economy and society in the future. Even though the RE development was still at an early stage, there are more and more studies being conducted to support this mission to go green. A journal written about sustainable energy future status in Malaysia estimated that a 5 percent increment of renewable energy in the energy mix could save a total of RM5 billion over the period of 5 years (Hashim & Shin Ho, 2011).

In our country, RE was first introduced in the country's energy mix through the Fifth-Fuel Policy which was formulated under the 8th Malaysia Plan (8MP-2001-2005) to reduce dependency on fossil fuel and to address concern towards climate change. During the 8MP, BioGen project was launched however with total capacity of only 12MW. The progress of renewable energy is also slow during the 9th Malaysia Plan (9MP-2006-2010) with RE contribution towards the total energy mix through grid-connected power generation of 56.7MW. Due to this scenario, Malaysia aggressively continues its goal to promote and increase the share of RE in the country’s energy mix under the 10th Malaysia Plan (10MP - 2011-2015) which had begun in year 2011 with new target to achieve which is 985MW in 2015. According to 10MP, one of the progressive steps is the launching of National Renewable Energy Policy 2010 with a few notable measures such as the introduction of Feed in Tariff (FiT) and establishment of RE fund from FiT.

Figure 2: FiT latest target for short-term renewable energy capacity



1.1.3 Bamboo as Sustainable Biomass Feedstock for Pyrolysis

Biofuel/bioenergy derived from biomass (lignocellulose) has received considerable attention lately and is considered a leading candidate as a renewable energy generation. According to one of the world top five biomass power capacity producer, China, herbacous plants have very high potential in derivation of biofuel. Liberal studies have been carried out to study the potential of different crop feedstocks to produce biofuel (Sawin, et. al., 2013). Among all crops, bamboo has always been experimented due to the vast population and the high content of lignin in bamboo plant in China. Various researchers are eager to find the optimum conditions in order to generate the maximum liquid bio-oil of higher quality.

Malaysia is endowed with more than 50 species of bamboo, 25 of which are indigenous while the rest are exotics. There are however only 13 types of bamboo species which are commercially utilized (Nordahlia et. al., 2012). Nevertheless, according to a study conducted in Pahang National Park, Malaysia, the species *Gigantochloa Scortechinii* has the highest relative density of 58.8% compared to five other species in Kuala Keniam Forest (Asari & Suratman, 2011). Also *Gigantochloa*

Scortechinii possesses the biggest clump diameter of 6.5cm. In addition from other studies, this species of bamboo can grow up to more than 14cm in diameter size. Furthermore, the rate of growth of bamboo is especially fast compared to other types of herbaceous plants. From numerous study, the average maturity age of bamboo is 2-3 years. (Razak O. et. al., 2012) As for *Gigantochloa Scortechinii*, assumptions had been made to calculate its availability as biomass per year basis. Based on calculation, the total biomass supply of the culm part of *Gigantochloa Scortechinii* is 6.88 million metric tonnes per year.

1.2 Problem Statement

In Malaysia, information regarding bamboo conversion into energy resource is very limited. The amount of bamboo population is not stated in Malaysia Forestry Inventory even though it is one of the fastest growing crops among herbaceous plants. (Global Forest Resource Assessment, 2010) This is due to the fact that bamboo is not industrially popular. Also, there is no information on selectivity and optimal conditions of bamboo as biomass to get yield of bio-oil. In addition, the energy properties of bamboo in Malaysia are inadequate. However, bamboo is a very precious asset and the potential of it to become biomass resource should not be overlooked. The impact of finding the energy properties and capability of bamboo towards bio-oil production is beneficial to promote bamboo as one of the herbaceous plants biomass available in Malaysia. This possesses a great economical influence especially in the renewable energy sector with respect to fossil fuel demand and agriculture sector, as well as merits in environmental issues. For this project, the raw material used is bamboo viz *Gigantochloa Scortechinii* thermally decomposed via a reaction known as fast pyrolysis using drop type pyrolyzer. Other than that, the results obtained from this study also will be used as base to do comparative study on bamboo species selection for bio energy sector in the future. The project is significant in finding the energy properties of bamboo and its yield as well as to find the optimum conditions for bamboo to produce the highest yield of bio-oil.

1.3 Objective(s) of Study

The aim of the research is to discover the energy properties of *G. Scortechinii* in Malaysia. The detailed objectives of this study are as follows:

i. Feedstock preparation and characterisation of bamboo
ii. To analyze all products of pyrolysis
iii. To investigate the optimum temperature of maximum bio-oil yield

1.4 Scope of Study

In order to achieve the aim and objectives of the study, the scope of the study has been determined. For this project, the parameters used are:

i. Main feedstock: bamboo Gigantochloa Scortechinii
ii. Particle size of biomass: 250-500 µm
iii. Amount of biomass per run: 15.00gram
iv. Reactor operated: Drop type pyrolyzer
v. Temperature of reactor: 450^{o}C, 500^{o}C, and 550^{o}C

The types of analysis that will be carried out are:

i. Moisture content
ii. Ash content
iii. Calorific value
iv. CHNS analysis
v. Bulk density

vi. Volatile matter

vii. Fixed carbon

viii. Water content

ix. GC-MS analysis

x. GC-TCD analysis

1.5 Relevancy of Study

The project is closely-related and in-line with the syllabus of chemical engineering program of UTP which are structured based on oil and gas industry. Therefore, the application of thermodynamics, process heat transfer and chemical analysis are being utilized extensively in this project in studying the properties of the biomass. The knowledge of using the equipment in obtaining the necessary data is much related to the course Chemical Analysis which is taught during the final year. From another perspective, this project is relevant to the current scenario in Malaysia in which renewable resource is given high emphasis in the 10th Malaysian Plan (10MP-2011-2015). The outcome of this final year project can be used as reference for further related study in the area.

1.6 Feasibility of Project

The preparation part of the project has been completed during FYPI which is last semester, from January to May 2013. For FYPII, the experimental parts are expected to be accomplished this semester within 2 months which is from May to July 2013. It is sufficient to have the project done within the stipulated time considering the campus has adequate facilities to perform most of the preparation and analysis work. Starting from early August 2013, project dissertation should have started which includes the final analysis and conclusion. Objectives of the project shall be met prior to the accomplishment.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Biomass Pyrolysis Today

Biomass is the currently the world's only source of organic carbon (Pushkaraj, 2009). Biomass has gained particular importance in the subject of pyrolysis due to the growing interest in bio-oil conversion into fuel. The structure of biomass is chemically and biologically important as they will determine the behavior of decomposition during pyrolysis reaction (Fivga, 2011). In general, biomass consists of three organic polymers, namely hemicellulose, cellulose and lignin together with some impurities such alkali, alkali earth metal and so on (Zhang, 2012). During a pyrolysis process, the biomass will be thermally decomposed in the absence of oxygen. The decomposition of these organic components produces numerous chemicals which some of them contains valuable energy. The product that requires attention the most is the condensed vapour, known as bio-oil.

In addition, for simplicity, the general expression to illustrate the components in a biomass feedstock is $C_xH_yO_z$ (Jansen, 2011). This value x, y and z can be obtained by running CHNS analysis on the sample desired.

Table 1: Typical compositions of organic polymers in biomass (Demirbas, 2009)

Biomass Type	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt%)
Apricot stone	22.4	20.8	51.4
Beech wood	44.2	33.5	21.8
Birchwood	40	25.7	15.7
Hazelnut shell	25.2	28.2	42.1
Legume straw	28.1	34.1	34
Orchard grass	32	40	4.3
Pine sawdust	43.8	25.2	26.4
Rice straw	34	27.2	14.2
Spruce wood	43	29.4	27.6
Tea waste	31.2	22.8	40.3
Tobacco stalk	21.3	32.9	30.2

2.2 Fast Pyrolysis Principles and Technologies

Pyrolysis is a thermochemical treatment of biomass whereby biomass is degraded and decomposed at high temperature in the absence of oxygen to produce a mixture of condensable liquids, gases, char and other products. This technology has gained extensive attention in recent years, as the condensable liquid, bio-oil is regarded as a promising candidate of petroleum fuels (Balat, 2011). There are a few different modes of pyrolysis which are fast, intermediate, carbonisation (slow), gasification, and torrefaction pyrolysis (Bridgwater, 2012). These modes are different mainly in terms of heating rates and maximum reaction temperatures (Brown, et al., 2011).

Fast pyrolysis refers to pyrolysis at temperature of about 500^{o}C and would entail a very high heating rate (>10^{3o}C/s) with short vapour residence time (Heo, et al., 2010) to produce highest yield of liquid products. It is currently of particular interest as liquid is convenient to be stored and transported, and used for energy, chemicals or as an energy carrier. In fast pyrolysis, biomass decomposes very quickly to generate mostly vapours and gas (Bridgwater, 2012). Upon pyrolysis, there will be three products formed, which are termed as bio-char, bio-oil, and bio gas. The approximate proportion of fast pyrolysis products can be illustrated from the equation below (Sadaka & Boateng, 2009):

$$100\text{lb of biomass} \xrightarrow[\text{No oxygen}]{450^{o}\text{C -}500^{o}\text{C}} 60\text{lb of bio-oil} + 20\text{lb of char} + 20\text{lb of gas}$$

These products can shift depending on the biomass composition such as ash content and operating conditions.

Only upon cooling and condensation, a dark brown homogenous mobile liquid (bio-oil) is formed which has a heating value about half that of conventional fuel oil. The essential features of a fast pyrolysis process for producing liquids are (Bridgwater, 2012):

i. Very high heating rates and very high heat transfer rates at particle reactive surface of biomass, however biomass needs to be finely ground of typically less than 3mm in response to this process as biomass has generally low thermal conductivity.

ii. Control of reaction temperature at around 500°C for maximization of bio-oil yield.

iii. Short vapour residence time of typically less than 2s in order to avoid secondary cracking.

iv. Removal of product char in the elementary stage of reaction to minimize cracking of vapour.

v. Rapid cooling of pyrolysis vapour to give the liquid bio-oil product.

2.3 Bamboo *Gigantochloa Scortechinii* Chemical Composition

In general, bamboo main constituents are cellulose, hemicellulose and lignin, similar with wood (Li, 2004). There are a few studies that had been conducted in Malaysia on *Gigantochloa Scortechinii* towards its chemical composition prior to its age, growing environment and so on. For example, a study took place in Kedah, Malaysia on "Effect of Oil Heat Treatment on Chemical Constituents of *Gigantochloa Scortechini*"(Salim & Wahab, 2008), with objective that the composition of three major components of bamboo, hemicellulose, cellulose and lignin will differ under different heating condition using oil heat treatment. The results from the study indirectly give an idea on the fraction of these components in *Gigantochloa Scortechinii*. In summary, the content of cellulose is the highest with approximately 53wt% followed by hemicellulose 27wt% and lignin 22wt%. There are also some other minor constituents of the bamboo such as resins, tannins, waxes and inorganic salt.

Table 2: Mass fraction of *G. scortechinii* culm due to heating with palm oil at different temperature

Heating Condition	Hemicellulose (wt%)	Cellulose (wt%)	Lignin (wt%)
Control	26.2	55.2	22.3
140°C/60	27.8	53.6	21.1
180°C/30	26.6	53.1	21.6
180°C/60	24.1	52.4	22

2.4 Current Study on Bamboo Pyrolysis

Recently, a number of researches have been carried out especially in China on the fast pyrolysis of herbaceous plants specifically on bamboo. The factors influencing the distributions of pyrolysates derived from herbaceous plant are experimented at Hunan Province, China (Lou et. al., 2013). By comparing two biomasses which are rice straw and bamboo, it is concluded that the higher cellulose and lower ash content in bamboo has led to production of more volatiles and higher conversion towards bio-oil. The attained bio-oil consists of phenols, furans, ketones (hemicellulose), and organic acids.

Next, another study is carried to investigate the pyrolysis characteristics of moso bamboo (Jiang et. Al., 2012). The aim of the study is to better design manufacturing processes of bio-energy, made from moso bamboo by thermal chemical conversion method which is pyrolysis. From the qualitative and quantitative analysis of pyrolysis products and residues of moso bamboo, 450K to 650K is the main decomposition temperature range and over 68.89% of mass was degraded. The degradation compositions are mainly hemicellulose, cellulose and partial lignin of moso bamboo.

Lastly there are a few studies carried out specifically on the lignin extracted from bamboo (Rui Lou, et al., 2010). The lignin is separated by means of enzymatic/mild acidolysis method (Rui Lou, et al., 2010) which is later employed for pyrolysis. The investigation is focused on the effect of conditions towards the product distribution upon pyrolysis. The factors under study are the pyrolysis temperature and the effect of catalyst, sodium chloride (NaCl). The obtained pyrolysis products composed of heterocycles, phenols, ester, and small amount of acetic acid. Other than that, the addition of catalyst inhibits the generation of coke and reduce production of 2,3 dihydrobenzofuran (DHBF) from 19.15% to 13.08%.

The table below will illustrate the comparison of results obtained from two recent journals with respect to temperature.

Table 3: Production yield from Bamboo[a] and Bamboo[b]

Temperature (°C)	Bamboo[a] (wt %)			Bamboo[b] (wt %)		
	Char	Gas	Bio-oil	Char	Gas*	Bio-oil*
400	30.41	14.6	54.99	61.83	19.085	19.085
450	22.29	18.13	59.58	-	-	-
500	18.2	19.39	62.41	-	-	-
550	19.13	26.75	54.12	-	-	-
600	19.81	21.35	58.84	38.24	30.88	30.88
700	18.19	29.21	52.6	-	-	-
800	15.12	31.62	53.26	28.26	35.87	35.87
900	15.47	37.36	47.17	-	-	-

[a] Results adapted from Lou et al. Fast Pyrolysis factors for grasses (2013)

[b] Results adapted from Lou et al. Effect of conditions of fast pyrolysis of bamboo lignin (2010)

*Calculation is by assumption based on literature from Sadaka S. & Boateng A. Pyrolysis and Bio-Oil (2009)

2.5 Main Product under Study: Bio-Oil

Bio-oil can be used as the substitute for the depleting fossil fuels. From research in Malaysia, petroleum will be spent in the year 2020, followed by natural gas in 2058 and coal around the year 2066 (Muda & Tey, 2012). Therefore our country are currently emphasizing on generating renewable sources of energy in the future.

Figure 3: Bio-Oil

Bio-oil is a dark-brown liquid fuel produced from the pyrolysis of biomass. It comprises of a complex mixture of water (15–35wt%), solid particles (0.01–3wt%) and hundreds of organic compounds that belong to acids, aldehydes, ketones, phenols, alcohols, ethers, esters, sugars, furans, nitrogen compounds as well as large molecular oligomers (Lu, et al., 2010). Bio-oil is not as stable as conventional fuels; it is a low-grade liquid fuel which can be upgraded by various chemical and physical methods, for example emulsification with diesel oil (Qiang, et al., 2012). The bio-oil produced from various biomass types can be greatly different in terms of chemical composition, physical, and chemical properties as these raw materials come from various sources and hence, they have different characteristics. Currently, bio-oil are mainly used in boilers and furnace, but hardly can be directly used as transportation fuel, diesel engines, and gas turbines mainly due to the nature of oil itself, which is inhomogeneity, high viscosity and high corrosiveness (Chiaramonti, et al., 2007). For example, based on a report in IEA, global production of biofuels has increases rapidly to 83 billion litres in 2008, however the share of transport fuel market is still small (IEA. Key World Energy Statistics, 2012).

What will be the future usage of bio-oil? Bio-oil is yet to become a high demand product in the market due to its high acidity, high viscosity, high water content and high inorganic content (Imam & Capareda, 2011). Bio-oil generation using pyrolysis has been ongoing to achieve a goal which is to utilize bio-oil as future transportation fuel. However, various research regarding reactor design, pyrolysis condition, characterization, quality improvement and production has yet to overcome the problematic conditions of bio-oil. The table below illustrates general CHNS content of different types of energy source (Imam & Capareda, 2011).

Table 4: General CHNS and Oxygen content of different energy sources

	Carbon (wt%)	**Hydrogen (wt%)**	**Nitrogen (wt%)**	**Sulphur (wt%)**	**Oxygena (wt%)**	**Total content (wt%)**
Boiler Fuel	71.06	10	0.13	0	18.81	81.19
Bio-Diesel	78.18	9.71	0.41	0	11.7	88.3
Raw Bio-Oil	36.17	7.84	0.03	0	55.96	44.04
Hydrocarbon	79	10.62	0	0	10.37	89.62

2.6 Proximate and Ultimate Analysis

A proximate analysis determines the moisture content, volatile matter content, ash content and fixed carbon content of a sample (Jansen, 2011). It is important in order to allow comparison before and after experiment and determine whether there are harmful substances in a certain sample. On the other hand, ultimate analysis focuses on the chemical composition and the heating value of a sample, by which the composition is done by carbon, hydrogen, nitrogen and sulphur (CHNS) analysis. It is important to determine the ultimate analysis of a feedstock as it can lead an insight towards the amount of energy content of sample. These analyses are normally carried out on feedstock sample before experiment.

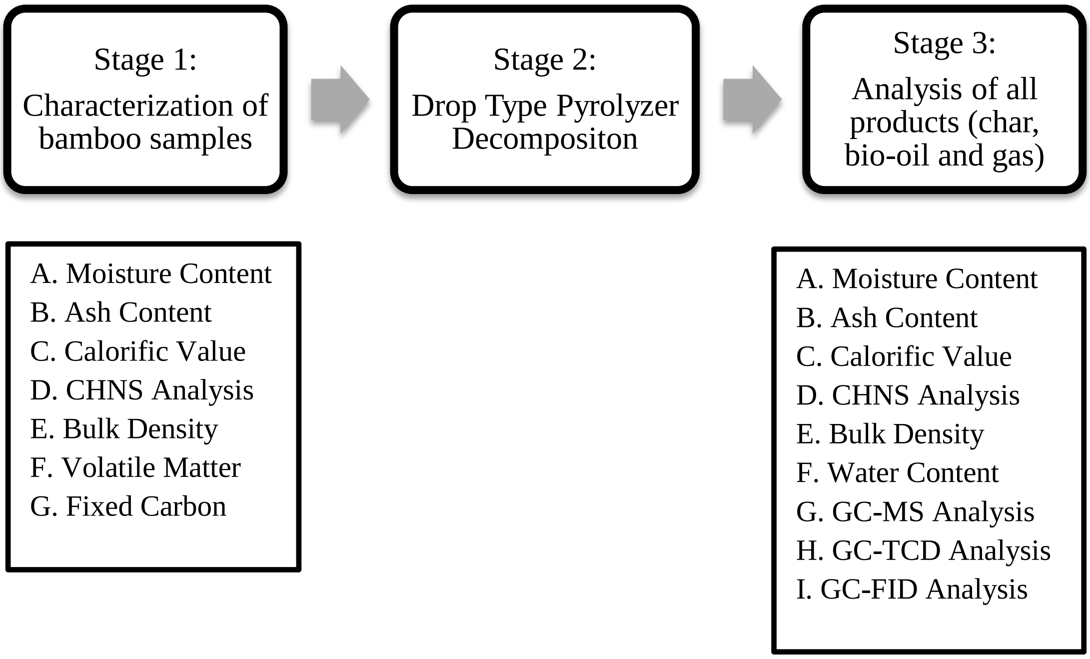
CHAPTER 3

RESEARCH METHODOLOGY

3.1 Research Methodology

For this project, there is a three-step process involved in order to achieve the objectives aforementioned. Stage 1 is the characterization of samples, stage 2 is the decomposition of feedstock with Drop Type Pyrolyzer and stage 3 is product analysis. There will be a total of 11 analyses that are going to be carried out. These include moisture content analysis, ash content analysis, calorific value, CHNS analysis, bulk density, volatile matter, fixed carbon, water content analysis, gas chromatography-mass spectrometry (GC-MS) analysis, gas chromatograph with Flame Ionization Detector (GC-FID) analysis and gas chromatography with Thermal Conductivity Detector analysis (GC-TCD). The three-step process is illustrated as the flow chart in Figure 4.

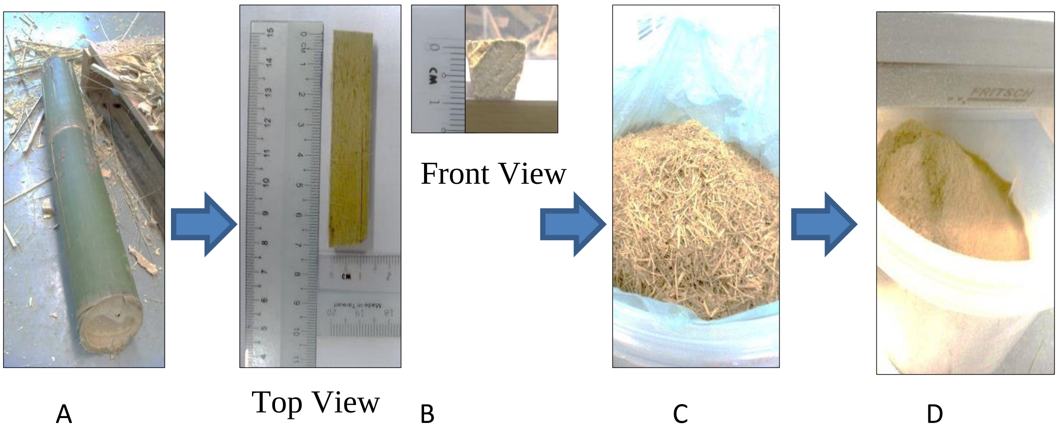
Figure 4: Three-stage process of experiment



3.2 Project Activities

3.2.1 Feedstock Preparation

Figure 5: Flow diagram of feedstock grinding process



A: 0.15m diameter, 0.8m height; B: 7cmx1cmx1cm; C: 4mm; D: 250μm

The samples that were used throughout the project had been obtained from Tasik Banding Gerik, Perak Darul Ridzuan. A bundle of bamboos had been taken with culm size of 0.15m diameter and 0.8 meter height each. The bamboos were cut by using a *parang knife* into smaller pieces of size approximately 7cm x 1cm x 1cm each. These small pieces were gathered and weighed a total of 30kg. After that, they were distributed evenly on top of a normal waterproof net as to avoid extra moisture from humid air to enter the bamboo. Extra humidity would cause the growth of fungus and mold as bamboo itself contained organic elements. After that, they were put into oven of temperature 105^{o}C for 24 hour to remove surface moisture content.

Next, almost all of the bamboos were put into oven again for 24 hour at 105^{o}C and labeled as dried bamboos, leaving only 1kg of bamboo labelled as raw bamboo. Uniform particle size of sample will ensure the uniform feeding rate when conducting pyrolysis experiment later. Therefore the dried bamboo was first being taken to block 17 for preliminary grinding. Here also, 1kg of dried bamboo was stored and kept away from grinding. At block 17, the SG-21P Series Low Speed Granulator equipped with staggered rotating blade and screen hole diameter of 4mm were operated. The grinded bamboo, at which the expected size would be less than 4mm were taken for further grinding at block P, using a Pulverisette 25 Cutting Mill.

This cutting mill was equipped with three fixed knives with low rotational speed to effectively reduce the size of grinding sample. The sieve cassette used was of size 250µm to produce grinded sample of approximately this size. Later, the grinded sample was sieved according to three different particle sizes which were:

i. 150 – 250 µm
ii. 250 – 500 µm
iii. 500 – 1000 µm

The desired size of sieving was 250-500 µm however three different sizes of sieves were used to eliminate other unwanted smaller or larger particles. After sieving, the samples were contained in plastic bags accordingly and stored in air tight containers to prevent moisture from being absorbed by the sieved dried bamboo. In the end, three different samples of feedstock were obtained, namely raw bamboo (BR), dried bamboo (BD) and sieved dried bamboo (BDS).

3.2.2 Moisture Content Analysis

Moisture content analysis is done for feedstock samples and product char to investigate the percentage of mass of water in a given biomass. The moisture content is determined by using the standard method ASTM E871-82 with slight modification. Approximately 15 grams of bamboo is weighed in petri dish. Then it is placed in oven of 105^{o}C for 24 hours. After 24 hours, the sample is weighed hourly till the decrease in weight become negligibly small. Each sample is repeated 3 times to get the average moisture content. The general equation for calculating percentage of moisture for dry basis is:

$$Moisture\ content, wt\% = \frac{Mass_{initial} - Mass_{after\ drying}}{Mass_{initial}}\ x\ 100\ \ ---\ (eq. 1)$$

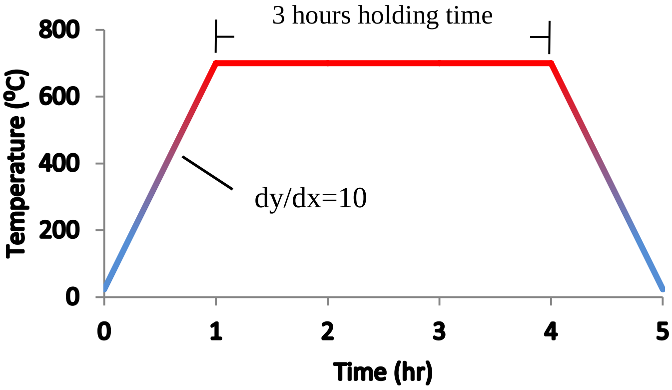
3.2.3 Ash Content Analysis

Ash content analysis is performed for feedstock samples and also products which are bio-oil and char, in order to investigate the amount of mineral residue after combustion. The analysis is done referring to ASTM E1755-95. An approximate 4g of sample is weighed on a ceramic crucible. It is then transferred into a muffle furnace and combustion will take place at 700^{o}C for 3 hours with reaction rate of

10^{o}C/min. This temperature is chosen to minimize any volatile material. After that, the furnace will be turned off and let to cool down to ambient temperature. The crucible containing the remaining ash will be weighed again. Each sample is repeated 3 times to get the average ash content. The general equation for calculating percentage of ash content is:

$$Ash\ content, wt\% = \frac{Mass_{ash}}{Mass_{sample}}\ x\ 100 - - - - - - - - -(eq. 2)$$

Figure 6: Time frame of ashing process



3.2.4 Calorific Content

The calorific value of a material is an expression of the energy content when burnt in air. The samples tested are feedstock samples and product, char and bio-oil. By following ASTM standard E711-87, a weighed sample is burned in a bomb calorimeter model C5003 series manufactured by IKA Werker. The calorific value is computed from temperature observations made before and after combustion, taking proper allowance for thermometer and thermochemical reactions Each sample is repeated 3 times to get the average calorific value. The obtained calorific value represents the high heating value (HHV) in unit MJ/kg, which includes the latent heat of the vapor released from the sample. However, for liquid sample, which will be bio-oil, if the water content of bio-oil is too high, methanol will be added to increase the combustibility of bio-oil. Therefore the energy content of bio-oil will be calculated with formula which involves the calorific value and mass of samples as shown below:

$$CV_{bio-oil} = \frac{(CV_{mix}\,x\,(m_{CH3OH} + m_{bio-oil})) - (CV_{CH3OH}\,x\,m_{CH3OH})}{m_{bio-oil}} \quad --(eq.3)$$

*CV_{mix} is the result obtained from decomposition of liquid sample with methanol.

3.2.5 CHNS Analysis

The elemental analysis of the mass fractions of carbon, hydrogen, nitrogen and sulphur of sample is carried out with Perkin Elmer CHNS/O Analyzer model 2400. The analyzer uses a combustion process to break down substances into simple compounds. Solvent is used to separate the inorganic carbon. Oxygen is calculated by difference (Wissam, et al., 2011). Each sample is repeated 3 times to get an average value.

3.2.6 Bulk Density

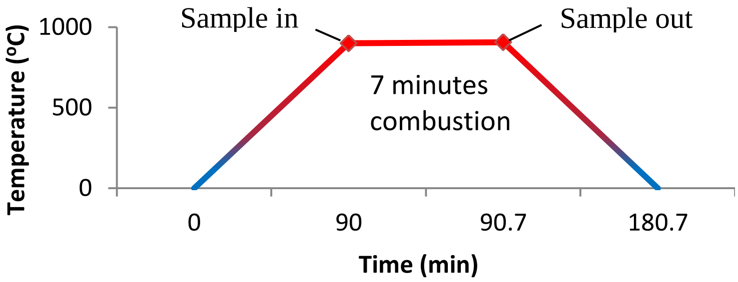
Density is the mass of a sample over volume. A cylinder's volume is to be determined within 16.39cm^3 as according to ASTM E873-82 and sample is filled in the cylinder. Each sample is repeated 3 times to get the average value. The calculation is to divide weighed sample by the volume of the cylinder, using this equation:

$$Bulk\ Density = \frac{Mass_{sample}}{Volume_{box}} ---------- (eq.4)$$

3.2.7 Volatile Matter

An approximate 2 gram of bamboo is weighed and put into crucible. Next the muffle furnace is heated until 900^{o}C which take 1.5 hours with reaction rate of 10^{o}C/min. The weighed sample is quickly put into the muffle furnace at this temperature and continues to be burned for 7 minutes. The sample is let to cool until ambient temperature and final weight of bamboo is obtained. Each sample is repeated 3 times to obtain the average value. This procedure follows standard EN 15148.

Figure 7: Time frame of volatile matter analysis in muffle furnace



$$Weight\ loss\ (\%) = \frac{M_{initial} - M_{final}}{M_{initial}} x100 - - - - - - - - - - (eq.5)$$

$$Volatile\ matter\ (\%) = Weight\ loss - Moisture\ Content (eq.6)$$

3.2.8 Fixed Carbon

The percentage of fixed carbon content is calculated as below:

$$Fixed\ carbon,\ FC(\%) = 100 - (Moisture + Ash + Volatile\ Matter (eq.7)\ .$$

This procedure follows standard ASTM D3172-89.

3.2.9 Water Content

Water content analysis is done on product bio-oil using Metrohm 870 KF Tritino Plus. The titration reagent and titration solvent used are HYDRANAL Composite 5 (Riedel-de Haen) and Methanol Rapid, respectively (Norizan, et al., 2012). The water content can be obtained directly from the equipment and the value is given in percentage.

3.2.10 GC-MS Analysis

Gas Chromatography-Mass Spectrometry (GC-MS) analysis is the qualitative analysis of product bio-oil. Bio-oil will be analyzed by GC-MS type Agilent Technology 7890A to identify the organic compounds. Bio-oil sample wil be injected into a HP5 fused silica (5% phenyl polysilphenylene-siloxane) capillary column BPX5 with 30m, 0.25mm, and 0.25μm of its length, internal diameter and film thickness, respectively. The oven is heated to temperature 35°C for 2 minutes before increasing to 250°C with the heating rate of 20°C/min and held for 20min. The temperature of injector and detector are set at 280°C while the flowrate of

99.999% of purified Helium as the carrier gas was set to 1.5ml/min. (Mohamad Azry, et al., 2009). The individual chemical compounds of the bio-oil are identified by matching their mass spectra with the NIST0.8L Mass Spectral Database. Sample preparation is done prior sending the samples to GC-MS at CAL Lab. Sample preparation is done by injecting bio-oil and methanol into a 2ml vial according to 1:9 ratio respectively.

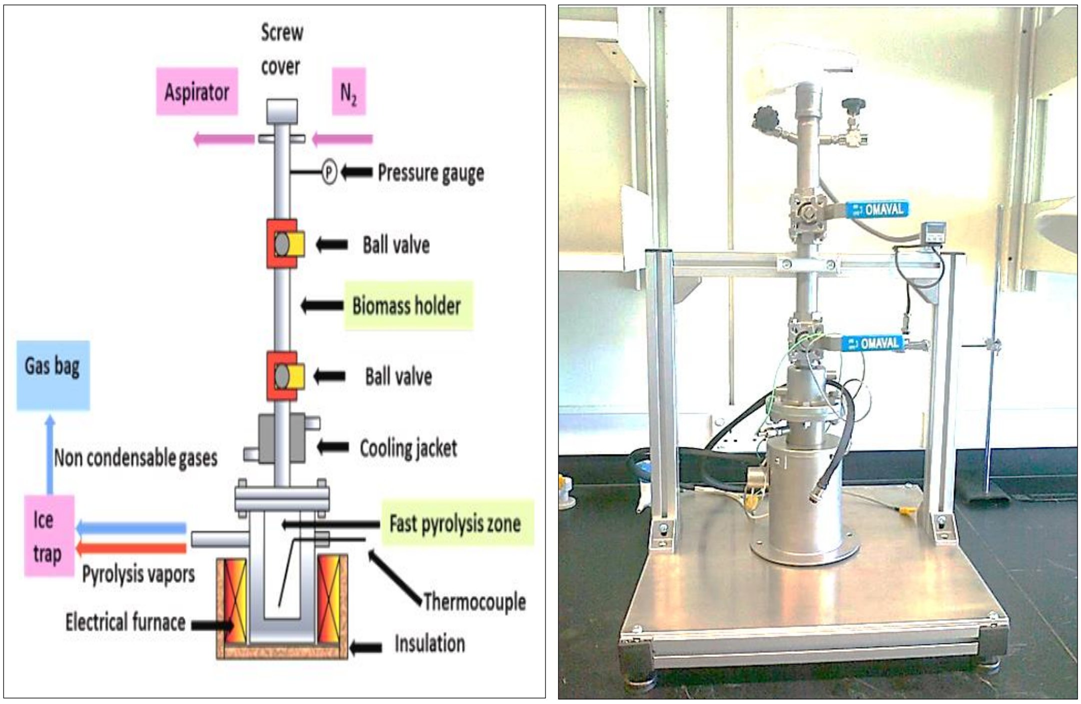
3.2.11 GC-TCD Analysis

Gas compositions from pyrolysis gas are analyzed by SHIMADZU GC-8A Gas Chromatography-Thermal Conductivity Detector (GC-TCD). 1 ml of gas sample is injected into the injector port. The carrier gas used is argon. Gas separation will be carried out by silica gel (60/80 mesh) packed column with 3mm internal diameter and 2m in length. The column temperature will be set at 80^{o}C while TCD detector is set at 90^{o}C. (Wissam, et al., 2011)

3.3 Equipment and Apparatus

A) Main Equipment: Drop Type Pyrolyzer

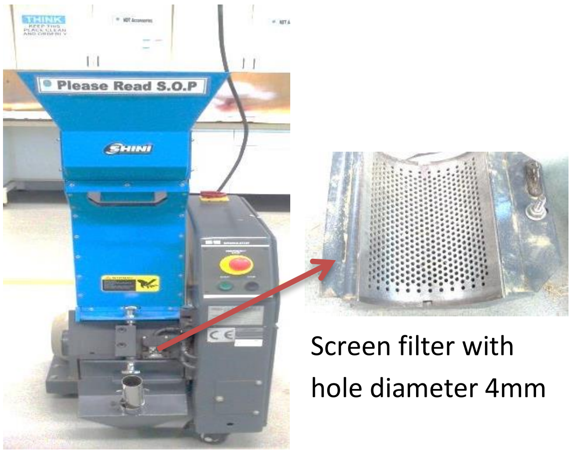
Figure 8: Left: Schematic Diagram of a drop type pyrolyzer obtained from CBBR of UTP; Right: Actual picture of drop type pyrolyzer

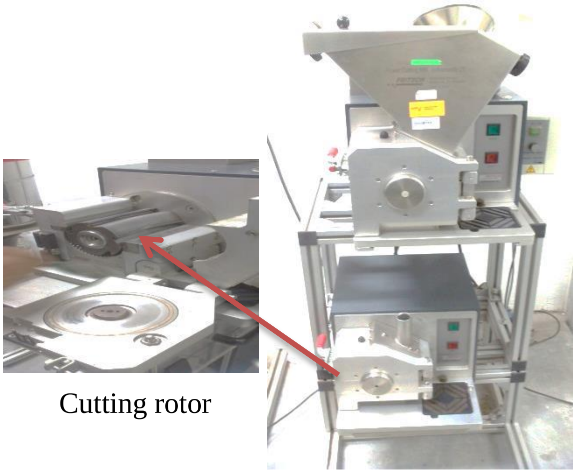
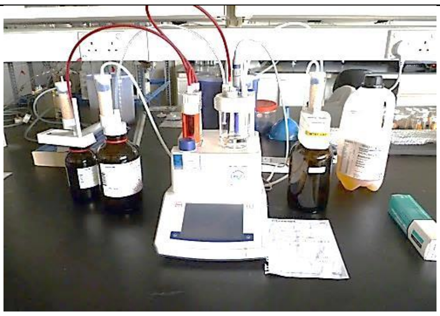


Setup and Specification

Fast pyrolysis of bamboo is conducted in a bench-scale drop type pyrolyzer. The Figure 8 above shows the schematic diagram (left) and actual picture (right) of the pyrolyzer. The drop type pyrolyzer is cylindrical in shape, 166mm in height, 53mm in internal diameter and is made of stainless steel. The reactor is located inside the electric heater and insulated as reaction may reach up to 600°C. The reactor is also equipped with biomass holder and purging is necessary by installing both nitrogen and vacuum lines at the reactor to replace air inside with nitrogen. The reactor is also equipped with a K-type thermocouple which is inserted inside the reactor to measure temperature rise. At the outlet from reactor, small tubes are connected to an ice trap immersed with ice-water bath to condense the pyrolysis vapors. Any remaining incondensable vapor will be collected in a Teflon gas sampling bag located at the outlet of ice trap. After the reaction, char and tar will be collected inside the reactor, bio-oil will be collected in ice traps and gas will be collected in gas bag.

B) **Table 5:** Other Equipment

No	Equipment and Description	Picture
1.	SG-21P Series Low Speed Granulator Equipped with staggered rotating blade and screen hole diameter of 4mm to grind bamboo. Location: Block 17	 Screen filter with hole diameter 4mm

2.	Power Cutting Mill Pulverisette 25 Equipped with steel cutting rotor of speed 360rpm. Sieve cassette used is 250 µm to grind bamboo to powder form. Location: Block P	
3.	Bomb calorimeter C5003 IKA Werker Measure the heat of combustion of a particular reaction. Designed to withstand large pressure within calorimeter. While heating, air ignites copper tube which heat water outside tube. Temperature of water is used to calculate calorie content in unit J/g. Location: Block 4	
4.	CHNS Analyzer Perkin Elmer 2400 Analyze four primary elements which are Carbon, Hydrogen, Nitrogen and Sulphur content in sample. The analyser uses combustion process to break down substances to simple compounds. Location: Block 14	
5.	Water Content Analyzer Metrohm 870 KF Titrino Plus It is a type of titrator for volumetric water determination. It is used to calculate the water content in bio-oil. Location: Block 4	

6.	GC-MS Agilent Technology 7890A It is a type of analyzer to qualitatively identify the organic compounds in bio-oil. Location: Block 4	
7.	GC-TCD Shimadzu GC-8A Determine the gas composition of pyrolysis gas by identifying analytes (gas composition) from peaks and determining the concentration of gas composition by area under a peak. Location: Block 5	
8.	Muffle Furnace brand WiseTherm Able to withstand very high temperature up to 700°C, used for ash content analysis and volatile matter analysis. Equipped with Type K thermocouple. Location: Block 5	
9.	Sieve Shaker RP200 type Sieving analysis. Capacity: Up to 8 sieves per run Maximum amplitude vibration: 2.5mm Location: Block	
10.	Oven Memmert brand For drying purpose, has been set to 105°C. Location: Block 4	

C) Apparatus

1. Airtight glass sample bottle
2. Gas sampling syringe
3. Gas bag
4. Beaker
5. Petri Dish
6. Porcelain crucible
7. Large airtight containers
8. Face masks
9. Gloves

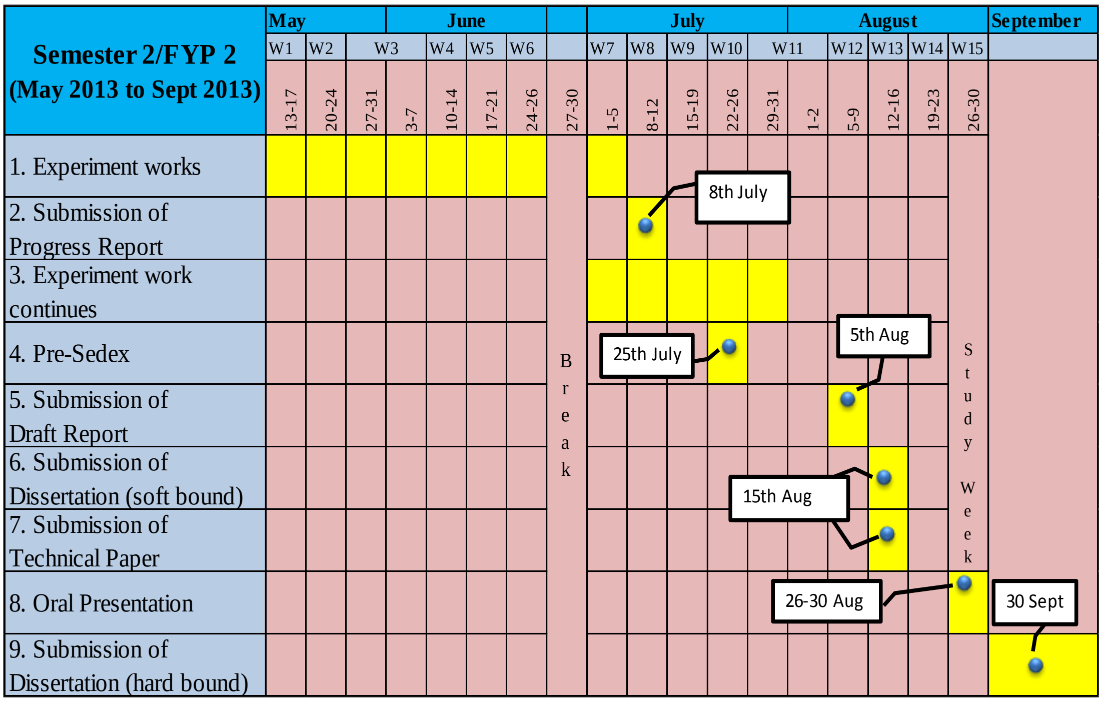
3.4 Key Milestones

The table below shows the key milestones of this research project for the semester which has been achieved up to week 8 so far.

Table 6: List of key milestones for FYP2

Week	Activities	Involved Party
1	Lecture 1 Talk from Central Analytical Lab, CAL Talk about HSE	Student and coordinator
2	Lecture 2 Talk on how to write your thesis paper	Student and coordinator
3	Meeting with supervisor	Student and supervisor
5	-IEE visit -Meeting with supervisor	Student and external panel Student and supervisor
6	Lecture 3 Educational Talk on Plagiarism	Student and UTM professor
8	-Submission of Progress Report -Meeting with supervisor	Student Student and supervisor
9	Submission of Dissertation	Student, coordinator, supervisor

3.5 Gantt Chart/Study Plan



Semester 2/FYP 2 (May 2013 to Sept 2013)	May			June					July					August					September
	W1	W2	W3		W4	W5	W6		W7	W8	W9	W10	W11		W12	W13	W14	W15	
	13-17	20-24	27-31	3-7	10-14	17-21	24-26	27-30	1-5	8-12	15-19	22-26	29-31	1-2	5-9	12-16	19-23	26-30	
1. Experiment works	■	■	■	■	■	■	■	Break	■									Study Week	
2. Submission of Progress Report										■ 8th July									
3. Experiment work continues									■	■	■	■	■						
4. Pre-Sedex												■ 25th July							
5. Submission of Draft Report															■ 5th Aug				
6. Submission of Dissertation (soft bound)																■ 15th Aug			
7. Submission of Technical Paper																■ 15th Aug			
8. Oral Presentation																		■ 26-30 Aug	
9. Submission of Dissertation (hard bound)																			■ 30 Sept

Important points to note on the Gantt Chart:

1. All the dates written in Gantt Chart are of year 2013.

2. Student is expected to finish all experimental works by week 11, which is at the end of July 2013.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Results for characterization of bamboo

Table 7: Characteristics of bamboo G.S. as per average dry basis

Main Characteristics of G.S. (dry basis, average value)			
Proximate Analysis	Value (wt%)	Ultimate Analysis	Value (wt%)
Moisture	7.33	C	46.34
Volatile Matter	72.83	H	7.00
Fixed Carbon	18.60	N	0.55
Ash	1.24	S	0.14
		O[a]	37.40
Calorific Value, HHV (MJ/kg)			16.86
Bulk Density, (g/ml)			0.2964

[a] by difference, using C, H, N, S, ash and moisture content

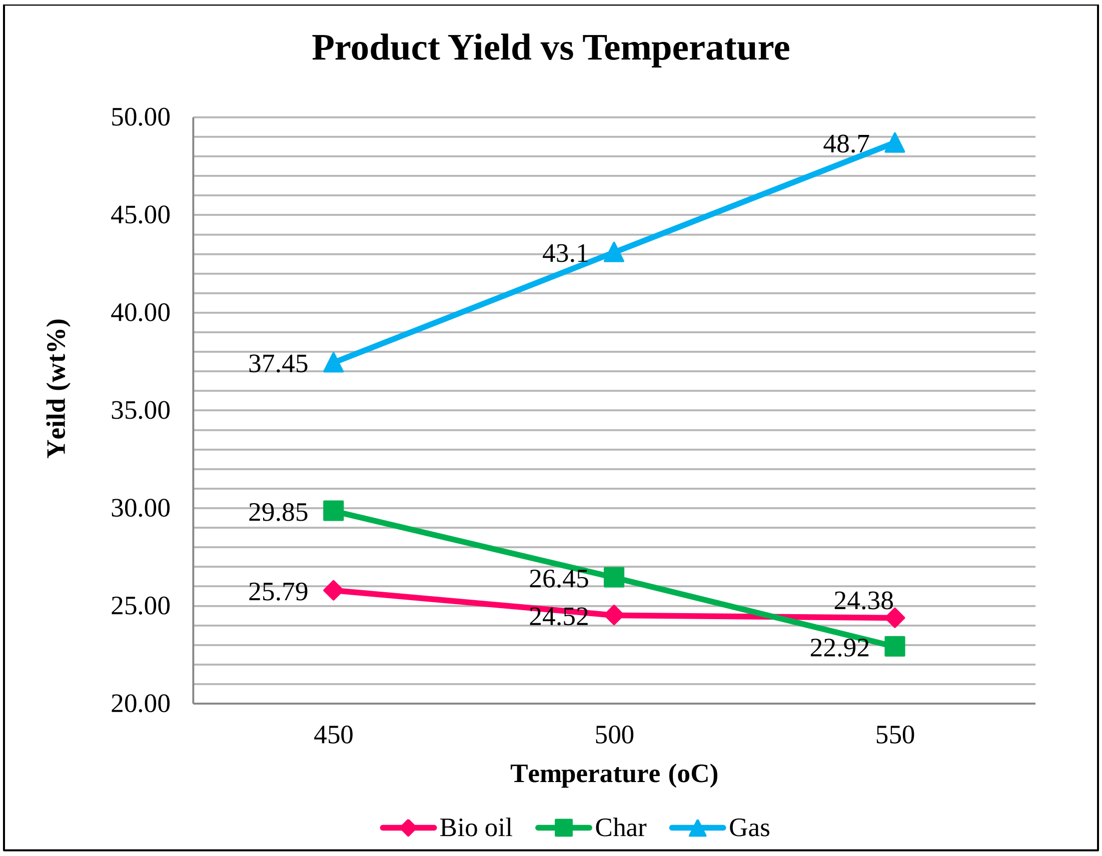
Table 8: Proximate and Ultimate analyses of bamboo **(Gang, et al., 2007)**

Properties of bamboo dry basis			
Proximate Analysis	Value (wt%)	Ultimate Analysis	Value (wt%)
Moisture	9.15	C	45.88
Volatile Matter	73.92	H	5.36
Fixed Carbon	15.30	N	0.32
Ash	1.63	S	0.26
		O	37.40
Calorific Value, HHV (MJ/kg)			17.82
Bulk Density, (g/ml)			-

4.2 Results for product analysis

4.2.1 Product Yield vs. Temperature

Figure 9: A graph of product yield vs. temperature from pyrolysis experiment



4.2.2 Moisture/Water and Ash Content comparison

Table 9: Moisture and Ash content before and after pyrolysis experiment

Before Experiment		**After Experiment**				
Bamboo		Temperature (^{o}C)	Bio Oil		Char	
Moisture (wt%)	Ash (wt%)		Water (wt%)	Ash (wt%)	Moisture (wt%)	Ash (wt%)
7.33	1.24	450	64.15	0	2.32	4.76
		500	62.08	0	3.44	6.37
		550	69.29	0	2.17	5.63

4.2.3 Characteristics of bio-oil derived from pyrolysis

Figure 10: Bio-Oil derived for each temperature

Figure 11: Phase separation of bio-oil

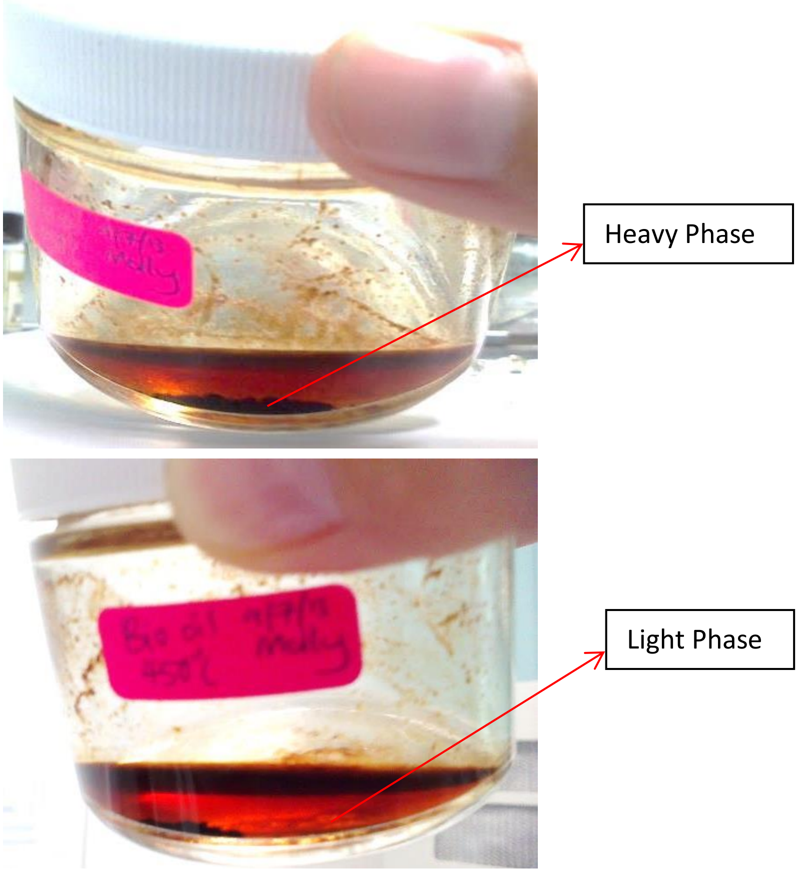


Figure 12: A graph of CV, CHO and water content vs. temperature of heavy phase bio-oil

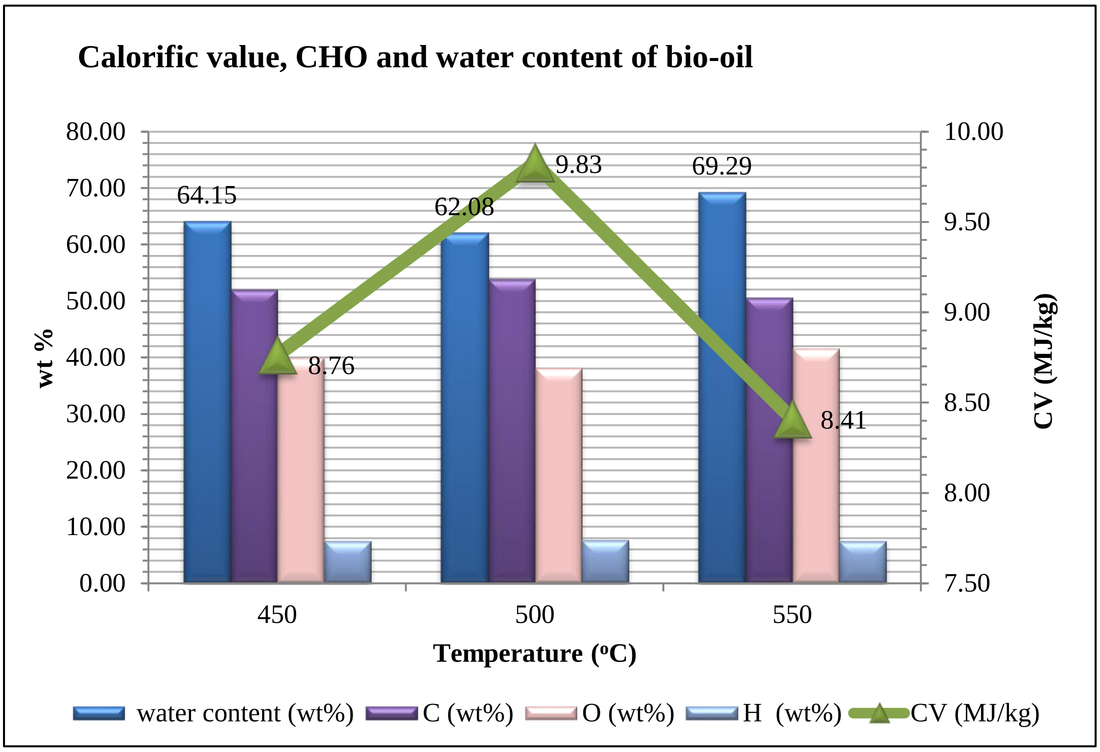
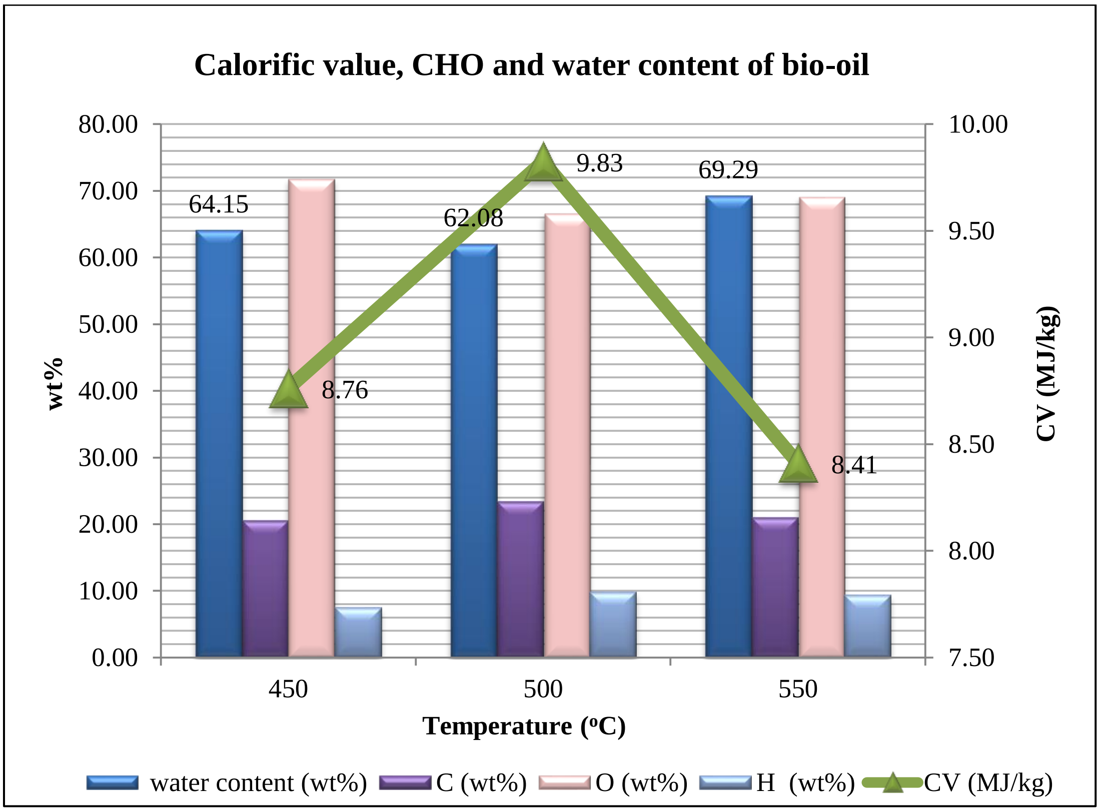


Figure 13: A graph of CV, CHO and water content vs. temperature of light phase bio-oil



4.2.4 GC-MS Analysis of Bio-Oil Components

Table 10: Concentration of major components in bio-oil

	Compound	**Area %**				
		Mix			**Light Phase**	**Heavy Phase**
Class		**450^{o}C**	**500^{o}C**	**550^{o}C**	**450^{o}C**	**450^{o}C**
Furan	2-Furanmethanol	0.75	0.73	0.52	0.77	0.82
Acid	Acetic acid	6.05	5.22	4.77	6	5.61
	acetic acid, methyl esther	-	0.3	0.27	0.25	0.23
	Propanoic acid	0.6	0.32	0.32	0.62	0.61
Ketones	Hydroxy-2-butanone	0.52	0.57	-	0.53	0.51
	2-Cyclopenten-1-one, 2-hydroxy-	0.37	0.48	-	0.44	0.45
	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	0.57	0.61	-	0.6	-
	2-Cyclopenten-1-one, 3-methyl-	0.12	0.14	-	0.12	0.15
	2-Propanone, 1-hydroxy-		2.09	2.09	1.85	1.58
Phenols	Benzaldehyde, 3-hydroxy-4-methoxy-	-	-	-	0.08	0.13
	Phenol	0.44	0.59	0.6	0.45	0.59
	Phenol, 2,6-dimethoxy-	0.59	0.7	-	0.68	0.83
	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.02	-	-	0.06	0.14
	Phenol, 2-methoxy-	0.45	0.57	0.26	0.46	0.64
	Phenol, 2-methoxy-4-methyl-	0.12	0.19	0.07	0.12	0.2
	Phenol, 4-ethyl-	0.43	0.7	0.52	0.41	0.81
	Phenol, 4-ethyl-2-methoxy-	0.34	0.33	-	-	0.49
	Phenol, 4-methyl-	-	0.36	0.39	0.22	0.34
	1,2-Benzenediol	0.24	0.79	0.72	0.21	0.8
	1,2-Benzenediol, 4-methyl-	0.09	0.12	0.14	0.08	0.13

Figure 14: A chart of bio-oil major components distribution from bamboo pyrolysis under different temperature

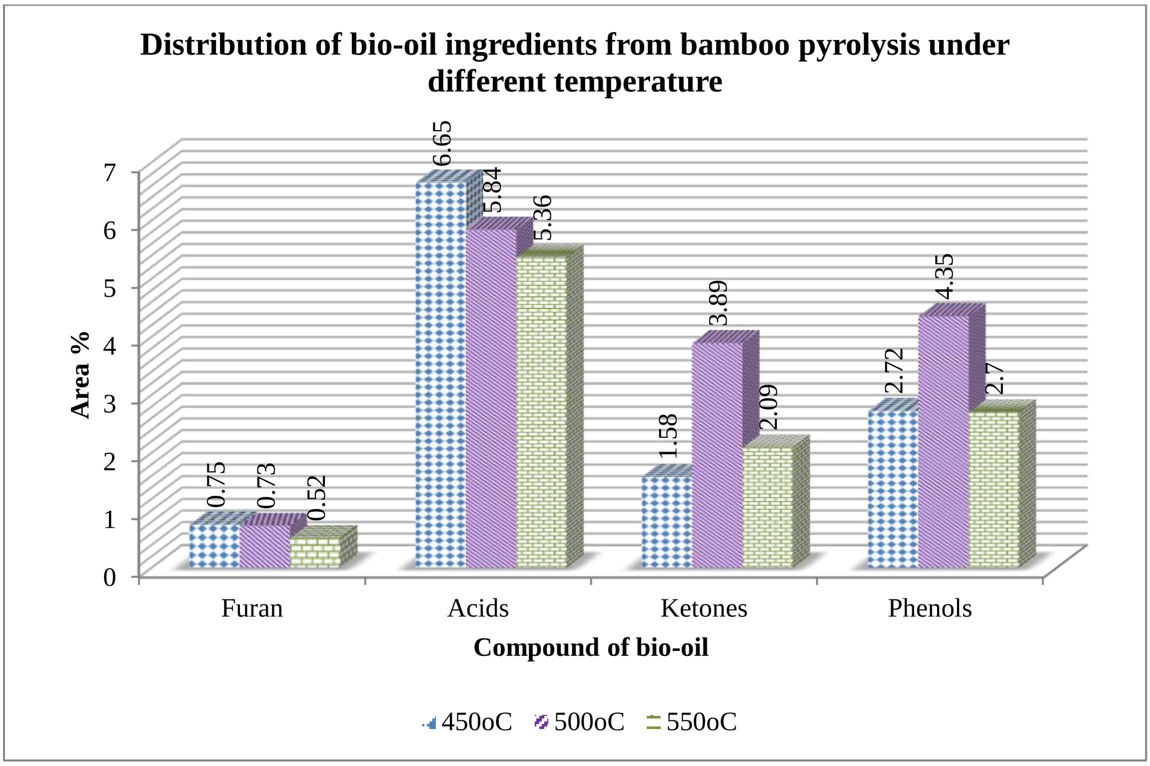
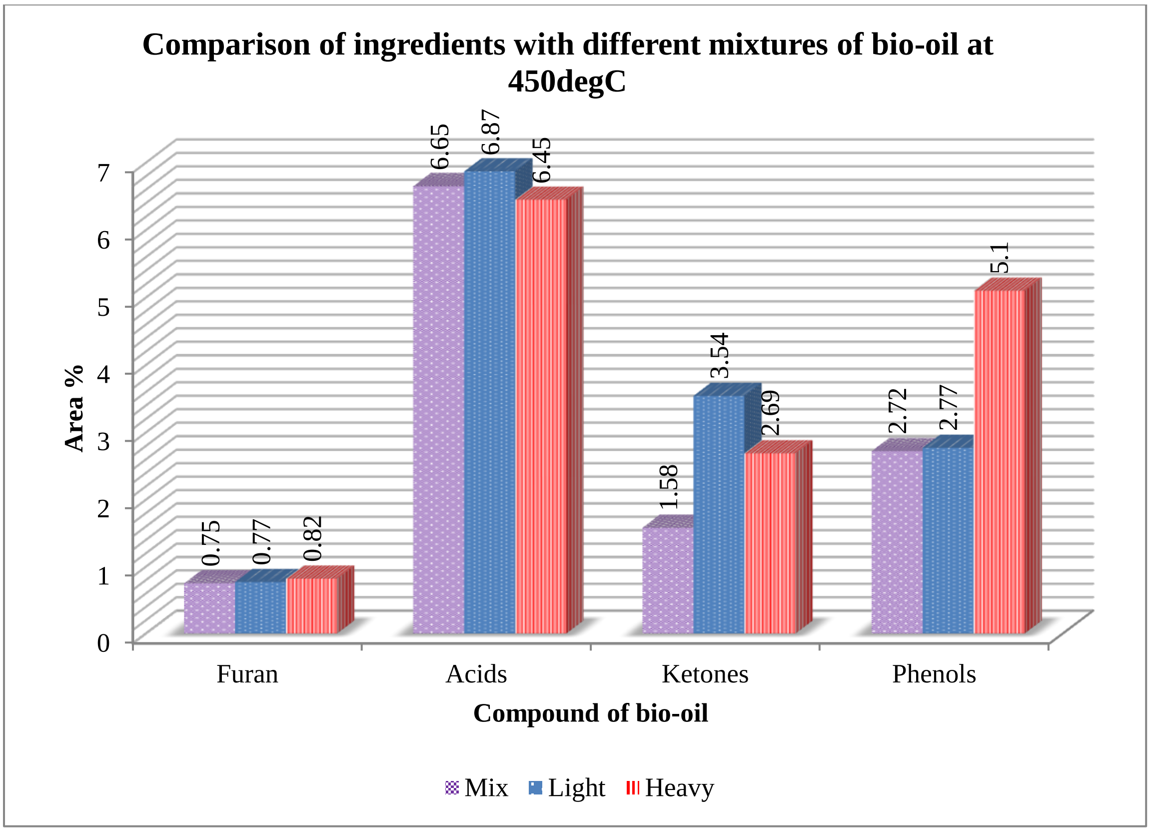


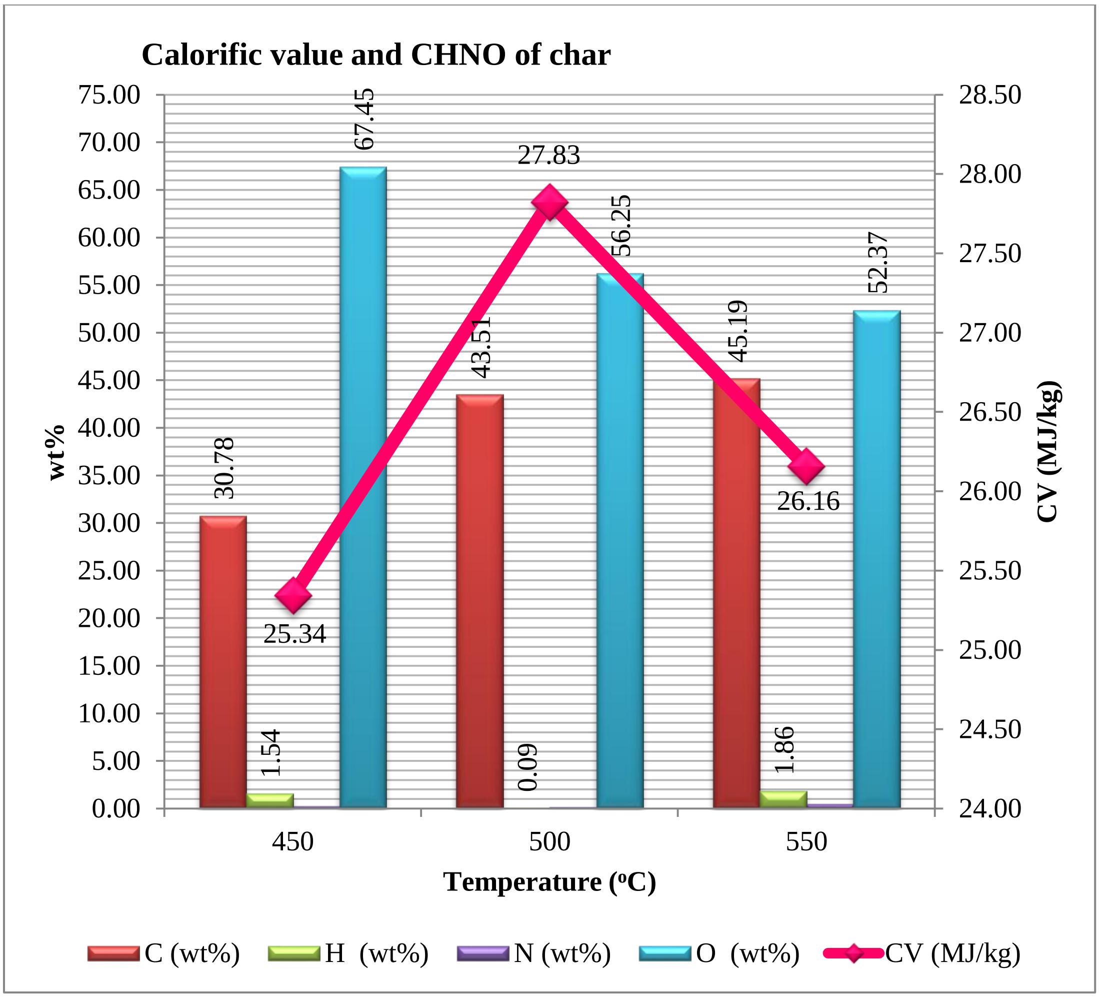
Figure 15: Comparison of ingredients with different mixtures of bio-oil at 450°C.



4.2.5 Characteristics of char derived from pyrolysis

Figure 16: Char produced from pyrolysis

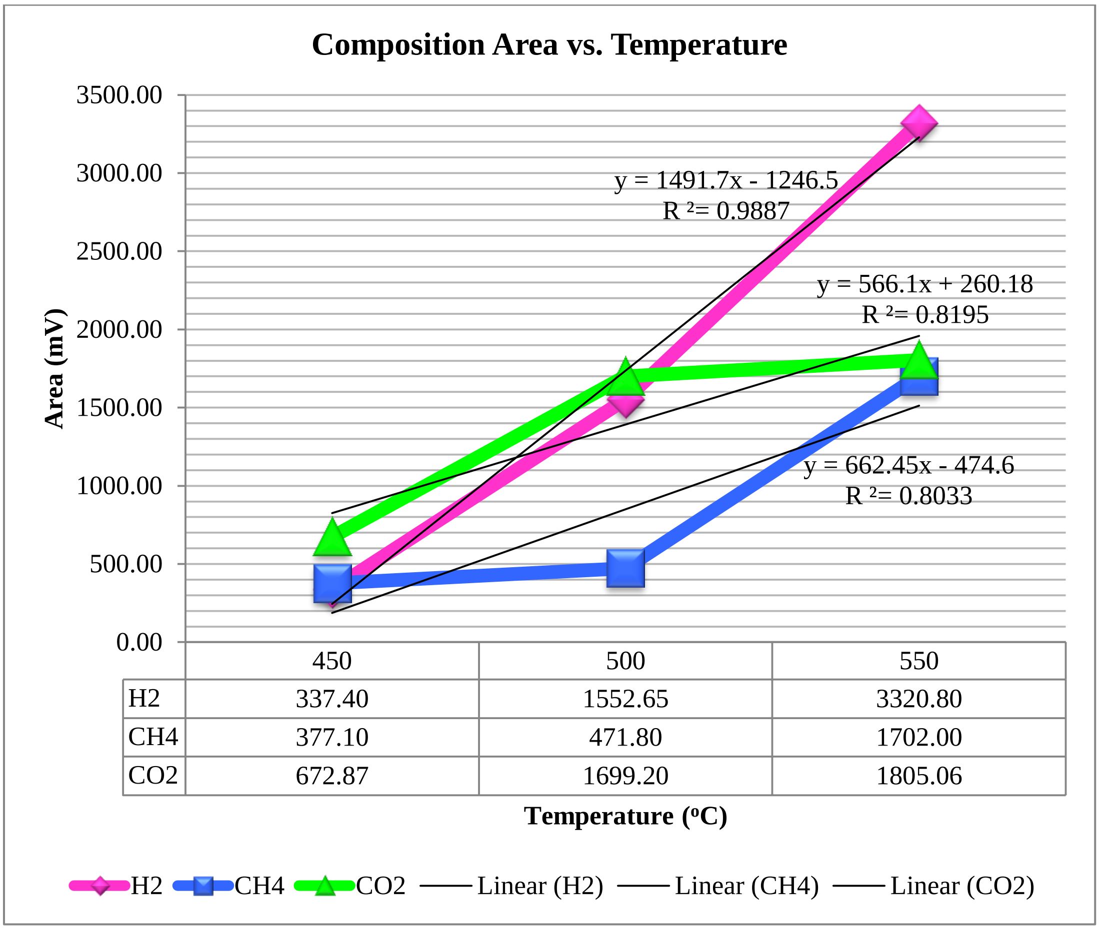
Figure 17: A graph of calorific value and CHNO vs. temperature of char



4.2.6 Gas composition area vs. temperature

Figure 18: Gas sample collected during pyrolysis

Figure 19: A graph of composition area vs. temperature of pyrolysis gas



	450	500	550
H2	337.40	1552.65	3320.80
CH4	377.10	471.80	1702.00
CO2	672.87	1699.20	1805.06

4.3 Discussion and Recommendation

4.3.1 Characterization of bamboo

In order to determine the validity and accuracy of the results, all the analyses are replicated. The tables of results obtained for all the analyses are shown in Appendix. Also, the results obtained in table 6 are compared with a selected literature presented in table 7. The details of the results obtained are discussed thoroughly below:

a) Moisture content

Moisture content influences the heat transfer in pyrolysis， it has been observed that higher moisture content results in increased bio-oil production (Minkova V. et. Al., 2001). However, moisture content cannot be too high or else the calorific value of the bio-oil will reduce, and it cannot be too low as the extraction of water-soluble components from gaseous phase might be incomplete (Dasappa S. et. al., 2004). Low moisture content results in adverse effect on the bio-oil quality such as acidity, pH, corrosiveness, and so on (I Jahirul et. al., 2012). Therefore the most suitable moisture content of biomass should be in the range of 5-15 wt % (Siemons R.V., 2012) The moisture content can be obtained by wet basis and dry basis, whereby the difference is wet basis uses the bamboo before drying process and dry basis is bamboo after drying treatment. The moisture content of raw bamboo is higher than dried bamboo, which is 41.0wt3% to 7.33wt%. This is due to the drying process of bamboo in oven which terminates the water content of the bamboo. Compared to literature review, there is not much difference with the moisture content of dry bamboo with the other bamboo. The moisture content is also below 10 wt % which is suitable for pyrolysis process.

b) Ash content

Ash is produced during the pyrolysis process which is actually the residue of the non-biodegradable carbon material of bamboo. Ash is an unfavoured product because the amount of ash can cause several damages, such as slag and fouling in a plant system. Therefore studies have been carried out by researchers to reduce the mineral content in biomass before experiment, such as pretreatment of biomass with catalyst. Also, lower mineral content which means the ash residue will favor bio-oil yield (Friedl et. al., 2005). From the results obtained, the ash content of raw bamboo compared to dry bamboo is higher which is 2.03wt% and 1.24wt% respectively. The difference is not significant. From literature, biomasses such as switchgrass and sugarcane baggage have 4.5-5.8 and 1.5-4.5 wt % of ash respectively (Yaman. S., 2004). Therefore, it is observed that ash content can be obtained at a range of 1-3 wt %. Ideally, after drying of biomass, the ash content should be lower due to the evaporation of volatile minerals. However, the result indicates the other way around. There might be some impurities present during the combustion process which cause the ash content of wet basis bamboo to be higher. In order to get more accurate result, it is recommended to repeat the experiment for a few more times. Nevertheless, the amount of ash in dried bamboo is comparatively lower than the one in literature review, which indicates that the mineral in bamboo is lower.

c) Volatile matter

Volatile matter is the amount of volatile compounds present in the biomass after thermal degradation which does not include moisture content. High volatile matter generally gives higher bio-oil production. (I Jahirul et al., 2012) The volatile matter of raw bamboo is lower than of dried bamboo, which is 42.56wt% and 72.83wt% respectively. Due to only 7 minutes available for degradation of biomass in furnace, this is logical because the moisture content may inhibit the complete decomposition of biomass, whereby some volatile gas could not reach its boiling point due to presence of water. Comparing with literature review, the volatile matter of bamboo under study is slightly lower than others. This indicates that the chance of high bio-oil yield might be lower.

d) CHNS analysis

CHNS analysis is important to characterize the elements present inside the bamboo. The red values are omitted due to inaccuracy. From result, raw bamboo has lowest carbon content, followed by dried bamboo, and sieved dried bamboo has highest carbon content, which are 44.15wt%, 46.34wt% and 46.86wt%

respectively. This indicates that dried and sieved bamboo is better for pyrolysis to obtain more desired product. Besides that, CHNS analysis is also used to find the oxygen content of biomass. The oxygen content of dried sieved bamboo is the lowest, which is 37.41wt%. Compared to literature review, the oxygen content of bamboo is higher which indicates that the bamboo is not very suitable for bio-oil production.

e) Fixed carbon

In general, the amount of fixed carbon indicates the amount of solid products. High fixed carbon biomass generates higher Fixed carbon can be related to the heating value of biomass. It is the solid combustible residue that remains heating whereby the volatile matter is also expelled. The amount of fixed carbon for dried bamboo is higher than raw bamboo, which is 18.60wt%. Compared to literature review, it is lower.

f) Bulk density

Bulk density is important to determine the capacity of solid biomass in a container. It will be an important parameter in the future, for example, the shipping cost of transporting bamboo can be estimated based on the bulk density. From the result, the bulk density of dried sieved bamboo is the smallest, indicating that the porosity of it is smaller than other two samples.

g) Calorific Content

The calorific content of a material is an expression of the energy content, or heat released when burnt in air. It is one of the key of pyrolysis sample analysis. Calorific content shows the amount of energy which is useful as combustion material in a biomass, usually expressed in MJ/kg for solids, MJ/l for liquids, or MJ/Nm_3 for gases. The calorific content can be influenced by the presence of moisture in bamboo. Therefore, the lower the moisture content, the higher the calorific value of bamboo. This theory is depicted in the results. Compared to raw bamboo, the dried bamboo has higher calorific content, which is 16863J/g. The moisture content of dried bamboo is subsequently lower than raw bamboo, which acclaim that's the moisture content indeed will influence the energy present in bamboo. However, compared to literature, the calorific value is slightly lower.

In overall, the bamboo under study had a calorific value of about 16 MJ/kg (on dry basis) and a moisture content of 7.33%. The fixed carbon and the volatile matter contents are typically about 18.60% and 72.83% respectively. The sulphur content in the fuel is non-traceable and therefore poses no problem. The above classifies bamboo as a good fuel for energy conversion and comparable to any other wood. This is particularly so when the percentages of ash are below 5% as is the case here (Ganesh, 2003).

4.3.2 Product Analysis

The pyrolysis experiment is conducted for three different temperatures. The average value of amount obtained from each product is shown in figure 9. The overall data can be obtained at Appendix.

a) Product yield vs. temperature

Yield of liquid product can be generally maximized by low temperature, high heating rate, short gas residence time process and suitable water content of biomass (Arni S.A. et. al., 2010). From the observation of figure 9, there are a few justifications that can be made. Firstly, bio-oil and char content decreases with the increase in temperature from 450^oC to 550^oC. Secondly, the when the bio-oil and char is decreasing, the gas composition will increase. This is due to mass balance of the product compositions. Lastly, the yield of bio-oil is highest at temperature 450^oC (25.79 wt %). By comparing with literature, the bio-oil generated by bamboo is 62.41 wt % at 500^oC (Lou et. al., 2013). This indicates that the bamboo under study has the potential to generate highest amount of bio-oil at low temperature of 450^oC, however modifications could be done to increase the potential bio-oil yield such as minimization of heat loss during condensation of pyrolysis gas.

b) Moisture/Water and Ash Content comparison

From table 9 under section 4.2.2, the moisture content and ash content for bamboo before pyrolysis, bio-oil and char are analyzed. There are a few justifications to be made. The moisture and ash content of bamboo before experiment have been justified previously. In addition, based on literature review, water content of bio-oil may be coming from two sources: the moisture in the biomass and water produced as a result of dehydration reaction occurring during pyrolysis. Also, the concentration of water is usually miscible with the oligo-cellulosic derived components due to the solubilizing effect of other polar hydrophilic compounds which are the decomposition of carbohydrates (Yu, et al., 2007) Water content vary with different temperature but lay in the range of 60-70 wt %. However, a good bio-oil water content amount should be kept within 15-20 wt % (C. Brown, 2007). Due to the type of reaction which is fast pyrolysis, the water content is high (Kwon Park et. al., 2004). Although the water content (hydrophilic) lowers NOx, and improves bio-oil's flow characteristics, it also means that bio-oil is immiscible in petroleum fuels (hydrophobic), and lowers the heating value of the fuel. Next, the ash content of char is higher than ash content in bamboo. From literature review, a "non-slagging" reactor operated at high temperature (750-900^{o}C) will generate high-ash char (~10 wt %) and some tar (Brewer, 2012). The amount of ash from char is lower than 10 wt % which indicates the reactor is quite slagging.

c) Characteristics of bio-oil derived from pyrolysis

Based on observation from figure 11, the bio-oil derived from the pyrolysis experiment is observed to contain two visible phases during normal state. The heavy phase of bio-oil will settle down the bottom part of the container while the lighter liquid will float above the heavy phase. Theoretically, in thermo effect, bio-oil components are either polymerized to char or separated into heavy organics and light organics, which is observed in the bio-oil derived from this study (Gopakumar, 2012). There are some justifications that are observed. Firstly, when the water content and oxygen content of bio-oil is decreasing, the HHV and carbon content of bio-oil will increase. The highest HHV is achieved at 500°C (9.83 MJ/kg) with water content at its lowest, 62.08 wt %. This indicates that water content and oxygen content are one of few factors that reduce the energy content of bio-oil. In addition, the HHV content is lower as compared to literature, at which the HHV is 14.4 MJ/kg for bamboo (Su-Hwa et. al., 2008). Even though energy content can be increased by decreasing the moisture content of biomass to below 5 wt% (Siemons, 2010), however this increases the risk of bio-oil with low quality such as low pH and high viscosity. Secondly, HHV and carbon content are observed to achieve their highest peak at temperature 500°C. This shows that the bio-oil is more combustible at temperature 500°C with lowest amount of water and oxygen level. Thirdly, from figure 12 and figure 13, there is a significant difference between heavy phase and light phase in terms of carbon content and oxygen content. The carbon content is higher in heavy phase bio-oil with lower oxygen level compared to light phase bio-oil. Light phase normally consists of organic compounds such as esters, ketones, alcohols, ethers, and phenols (Gopakumar, 2012). However, light phase contains more aqueous component than heavy phase which decreases the amount of carbon content in light phase.

d) GC-MS Analysis of bio-oil components

The compounds present from the bamboo are verified and tabulated in table 10 (Ganesh, 2003). There are a few types of components found in the bio-oil from bamboo. In general, hemicellulose would be the easiest one to be pyrolyzed, next would be cellulose, while lignin is the most difficult one. However, it is evident plant with higher lignin content contribute to more bio-oil yield due to the different physio-chemical characteristics of cellulose, hemicellulose and lignin (I Jahirul, et. al., 2012). GC-MS analysis indicated that the bio-oil contained a series of important and useful chemical compounds like phenols, aliphatic hydrocarbons, aromatic hydrocarbons, and furan derivatives. (Dutta, 2010). From previous chapter, it is known that bamboo G.S. contains hemicellulose (27 wt %), cellulose (53 wt %) and lignin (22 wt %) respectively. Hemicellulose and cellulose will produce furans, ketones and acid, and lignin will mainly produce phenols, furans, aromatic compounds and acid alcohol (Rui et. al., 2010). Based on figure 14, the total number of acid and furan decrease with decreasing temperature. Hydrocarbon products reach the peak at 500^{o}C. The most abundant acid component is acetic acid which decreases with increasing temperature. The most abundant phenols derivatives are phenols, phenol 2.6-dimethoxy, phenol, 2-methoxy-, phenol, 4-ethyl-, phenol and 4-ethyl-2-methoxy-. These components exhibit the same trend which the amount of phenols increases with increasing temperature. Lastly, there is only one furan derivative detected in bio-oil which is 2-Furanmethanol, which depicts a decreasing trend with decreasing temperature. In total, the amount of acid concentration is the highest among all other bio-oil components. This agrees with literature review that the fast pyrolysis process will produce bio-oil with high acid concentration. Pretreatment of biomass with catalyst is one of the alternatives to decrease the acidic concentration. Next, based on figure 15, which is a chart of comparison of ingredients in bio-oil with different mixtures at 450^{o}C. 450^{o}C is the temperature chosen because the yield of bio-oil is highest at this temperature, therefore a deeper research is carried out. Phase separation occurs due to chemical composition whereby the larger molecular weight of components will sink to the bottom of the bio-oil. The bottom phase is a large molecule oily mixture characterized by high viscosity and water insolubles, and is named as heavy oil, meanwhile the light phase contains By comparison, most acids and ketones falls under the light phase bio-oil while the primary compounds of heavy phase bio-oil consists of furans and phenols. Therefore, light phase or the aqueous phase is acidic due to the presence of H^{+} ions which agrees to literature review. The non-aqueous phase contains more furans and phenols from lignin decomposition. This indicates that carbon content of this phase is high, which agrees with the CHNS analysis indicating that at light phase the carbon content is 20.62 while at heavy phase the carbon content is 62.03.

e) Characteristics of char derived from pyrolysis

It can be seen that the calorific value of char is highest at 500^{o}C (27.83 MJ/kg). In addition, it can be observed that the trend for carbon versus oxygen content is similar to bio-oil trend. When the carbon content is increasing, the oxygen content will decrease. There are a few justifications that can be made. Firstly, carbon content increases with temperature increment. Secondly, the char still has a high amount of HHV, which indicates that improvement needs to be done to improve the yield of bio-oil with higher HHV.

f) Gas composition area vs. temperature

From figure 18, it is seen that when CO_2, H_2 and CH_4 increases with increasing temperature. This is due to mass balance of the products, as the yield of bio-oil is decreasing with increasing temperature, therefore the gas increment with increasing temperature is valid.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Green technology is the key to sustainable development. One of the green technologies being highlighted is the exploration into bio-oil development, which can bring huge impact towards future generation especially in the transportation industry. The project brings about the potential and ability that bamboo G.S. possesses in order to produce bio-oil yield. The determination of the biomass' characteristics is exceptionally important as it will affect both the conditions during experiment and pyrolysates produced. From the characterization observed, the low water and ash content of bamboo makes it an excellent choice as biomass for fast pyrolysis. By carrying out the fast pyrolysis experiment using bench-scale drop type pyrolyzer, the optimum temperature for the highest yield of bio-oil is obtained, which is at 450°C. Each of the products is also analyzed to determine the quantity and quality of bio-oil, char and gas. The objectives of this project which are

i. Feedstock preparation and characterization of bamboo
ii. To investigate the optimum temperature of maximum bio-oil yield.
iii. To analyze all products of pyrolysis

have been successfully achieved within two semesters.

There are still rooms of improvement for this project, a few recommendations that can be implemented in the future are:

i. Fast pyrolysis with addition of catalyst
ii. Fast pyrolysis with different size of biomass
iii. Fast pyrolysis with different types of reactor

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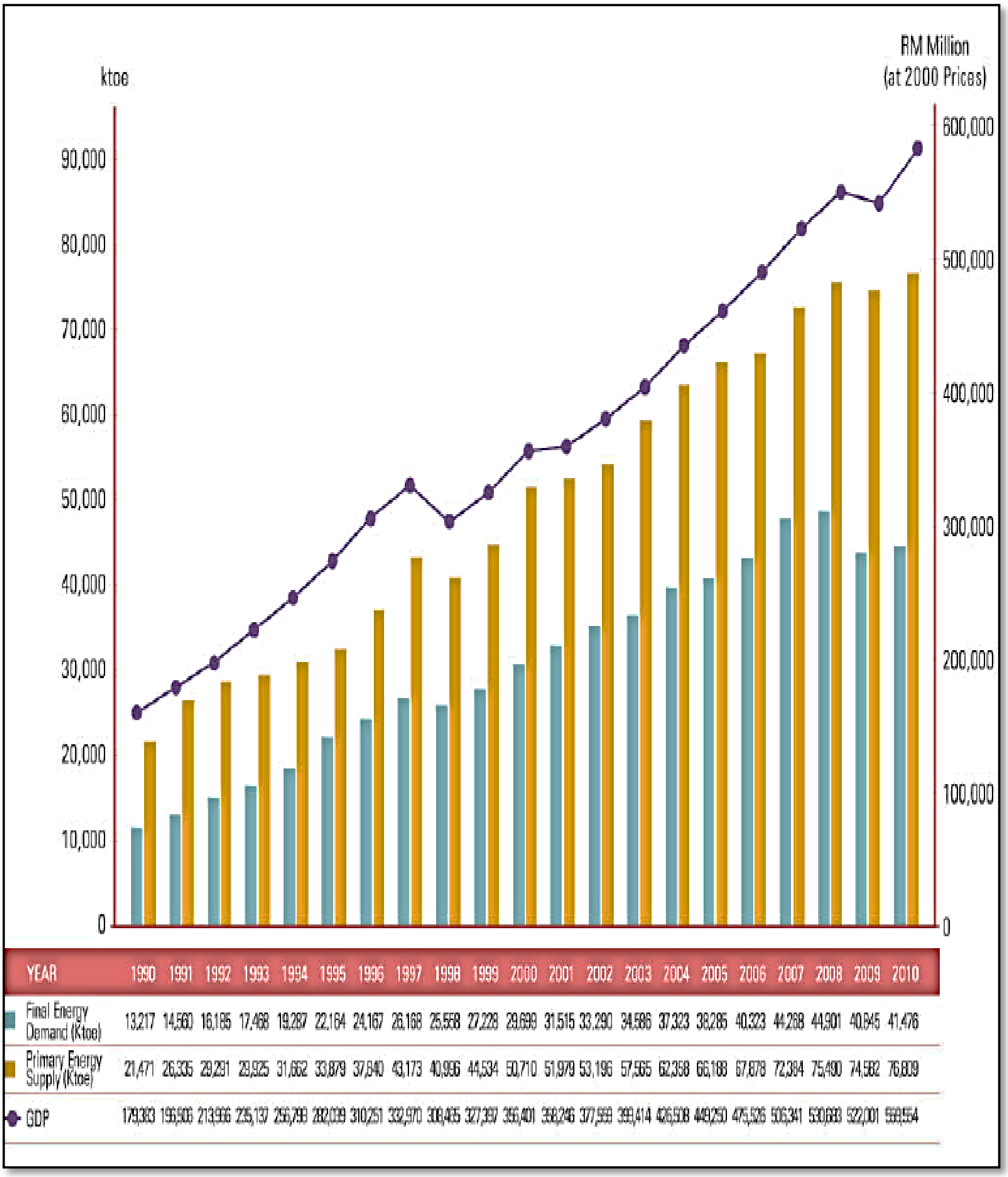
APPENDICES

Appendix A: A graph of Fuel Energy Demand, Primary Energy Supply and GDP from year 1990 to 2010.



YEAR	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
▨ Final Energy Demand (Ktoe)	13,217	14,560	16,185	17,468	19,287	22,164	24,167	26,168	25,558	27,228	29,699
▨ Primary Energy Supply (Ktoe)	21,471	26,335	29,291	29,925	31,662	33,879	37,840	43,173	40,996	44,534	50,710
● GDP	179,383	196,906	213,966	235,137	256,798	282,039	310,251	332,970	308,485	327,397	356,401

YEAR	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
▨ Final Energy Demand (Ktoe)	31,515	33,290	34,586	37,323	38,285	40,323	44,268	44,901	40,845	41,476
▨ Primary Energy Supply (Ktoe)	51,979	53,196	57,565	62,358	66,168	67,878	72,384	75,480	74,582	76,809
● GDP	358,246	377,559	399,414	426,508	449,250	475,526	506,341	530,683	522,001	559,554

Appendix B: A table of Malaysia Key Emphasis on Energy Development from 7th MP to 10th MP.

Malaysia Plan	Key Emphasis on Energy Development
Seventh Malaysia Plan (1996-2000)	Emphasis on sustainable development and of depleted resources and the diversification of energy resources. Ensuring adequacy of generating efficiency as well as expanding and upgrading the transmission and distribution infrastructures. Encourage the use of new and alternative resources as well as efficient utilisation of energy.
Eighth Malaysia Plan (2001-2005)	Emphasis on the sustainable development of energy resources, both depletable and renewable. The energy mix includes five fuels: oil, gas, coal, hydro, and RE. Intensive efforts on ensuring adequacy, quality and security of energy supply. Greater emphasis on energy efficiency (EE); encourage efficient utilisation of gas and RE as well as provide adequate electricity generating capacity. Supports the developments of industries in production of energy-related products and services. Highlights in promoting RE and EE: Incentives for EE. Incentives for the use of RE resouces. Incentives to maintain quality of power supply.
Ninth Malaysia Plan (2005-2010)	Emphasis on strengthening initiatives for EE especially in transport, commercial and industrial sectors, and in government buildings. Encourage better utilisation of RE through diversity of fuel sources. Intensify efforts to further reduce the dependency on petroleum provides for more to integrate alternative fuels. Incentives in promoting RE and EE are further enhanced.

Tenth Malaysia Plan (2011-2015)	Short term goals vested in National Green Technology Policy. Increased public awareness and commitment for the adoption and application of green technology through programmes. Widespread availability and recognition of green technology in terms of products, appliances, equipment, a system in the loca market through standards, rating, and labeling programmes. Increased foreign and domestic direct investment in green technology manufacturing and services sector. Expansion of local research institutes and institutions of higher learning to expand research, development and innovation activities on green technology towards commercialization through appropriate mechanisms. New RE act and FiT mechanism to be launched.

Appendix C: Comparison between bamboo species *Gigantochloa Scortechinii* and *Bambusa Vulgaris* on biomass production as per year basis in Malaysia

Table 1: The table shows the calculation of amount of bamboo portrayed in hectare of selected bamboo species at every state in Peninsular Malaysia Forest. (Lockman, 1994)

Bamboo / **State**	***G. Scortechinii***		***B. Vulgaris***	
	No. of culms (overal)	**Size (ha)**	**No. of culms (overal)**	**Size (ha)**
Johor	4881600	31820.76	-	-
Kedah	6405900	20902.55	-	-
Kelantan	31035750	90747	-	-
Melaka	249750	563.37	-	-
Negeri Sembilan	7415460	24284.22	-	-
Pahang	23480760	120367.63	2288130	5342.29
Perak	20174160	67680.49	17293410	56019.75
Pulau Pinang	1096950	2739	-	-
Selangor	12397410	39641.36	4833900	27448
Terengganu	3446400	22976	-	-
Total	110584140	**421722.38**	24415440	**88810.04**

Table 2: The table shows the data collected from a study which compares the amount of culm dry weight availability between two different bamboo species per year basis. (Azmy & Abd., 2002)

No	Data	*G. scortechinii*	*B. vulgaris*
1	**Avr DBH (m)**	0.09	0.11
2	**Avr Height (m)**	13.50	120
3	**Avr Dry Weight (kg/culm)**		
	Culm Branch Leave Total Dry Weight	5.10 1.00 1.10 7.20	3.82 2.14 0.44 6.40
4	**Estimated no. of culms per ha**	3200	3600
5	**No. of culms per metric tonne**	196	261
6	**Culm dry weight metric tonnes per ha**	**16.32**	**13.75**

Avr =Average; DBH=Diameter at breast height; ha=hectare; culm dry weight=biomass content of culm part of bamboo

Table 3: A summary of calculation for determining the total culm dry weight a.k.a the biomass content of both species of bamboo per year basis in Malaysia.

No	Data	*G. scortechinii*	*B. vulgaris*
1	Estimated no of culms (per ha year)	3200	3600
2	No of hectares	421722	88810
3	No of culms per year	1349511616	319716144
4	No of culms per tonne	196	261
5	Culm dry weight(metric tonnes per ha)	16.32	13.75
6	**Total culm dry weight (metric tonnes)**	**6.88 million**	**1.22 million**

Appendix D: Moisture Content Analysis

Date of Experiment: 15 and 16 March 2013

Table 11: Reading for moisture content analysis

	Reading 1	MC (wt%)	Reading 2	MC (wt%)	Reading 3	MC (wt%)
BR						
Wp (g)	56.9099		56.3032		54.7010	
Wbamboo (g)	15.0435		14.9431		15.0174	
W24 (g)	66.0263	39.3997	65.1554	40.7606	63.3432	42.452089
W25 (g)	66.0265	39.3984	65.0663	41.3569	63.3442	42.44543
W26 (g)	66.0262	39.4004	65.0957	41.1601	63.3376	42.489379
W27 (g)	66.0224	39.4257	65.0944	41.1688	63.3376	42.489379
W28 (g)	66.0225	39.4250	65.0952	41.1635	63.3374	42.490711
MC wt%=	39.43		41.16		42.49	
Avg MC wt%=	**41.03**					
BD						
Wp (g)	56.9835		46.5084		45.9478	
Wbamboo (g)	9.8841		9.1684		9.1752	
W24 (g)	66.1432	7.3289	55.0020	7.3601	54.4499	7.3361
W25 (g)	66.1436	7.3249	55.0032	7.3466	54.4501	7.3339
W26 (g)	66.1441	7.3198	55.0040	7.3382	54.4510	7.3241
W27 (g)	66.1441	7.3196	55.0040	7.3380	54.4510	7.3240
MC wt%=	7.3196		7.3380		7.3240	
Avg MC wt%=	**7.33**					

*p=petri dish

Appendix E: Ash Content Analysis

Date of Experiment: 16 and 17 March 2013

Table 12: Reading for ash content analysis

	Wc (g)	Wb (g)	Wf (g)	Ash Content (wt%)	Avr Ash Content (wt%)
BR					
Reading 1	79.6467	7.6090	79.8003	2.0187	**2.03**
Reading 2	82.0646	7.2077	82.2121	2.0464	
Reading 3	91.5029	7.7748	91.6601	2.0219	
BD					
Reading 1	86.7405	4.1515	86.7912	1.2212	**1.24**
Reading 2	79.8054	4.2011	79.8579	1.2497	
Reading 3	80.1478	4.1061	80.1991	1.2494	

c=crucible; b=bamboo; f=final; Avr=average

Appendix F: Calorific Content

Date of Experiment: 30 May 2013

Table 13: Reading for calorific content

	Mass sample (g)	CV(J/g)	CV total (J/g)
BR			
Reading 1	0.4999	15861	15862.00
Reading 2	0.4999	15913	
Reading 3	0.4999	15812	
BD			
Reading 1	0.5001	16884	16863.00
Reading 3	0.5000	16872	
Reading 4	0.5000	16833	
BDS			
Reading 1	0.5000	17019	17046.335
Reading 2	0.5001	17097	
Reading 3	0.5001	17023	

Appendix G: Bulk Density

Date of Experiment: 31 May 2013

Table 14: Bulk density measurement

	Cylinder size (ml)	Mass sample (g)	Bulk Density (g/m^3)	Avr Bulk Density (g/m^3)
BR(7cmx1cmx1cm)				
Reading 1	200	66.4000	0.3320	0.3332
Reading 2	200	66.6800	0.3334	
Reading 3	200	66.8600	0.3343	
BD(7cmx1cmx1cm)				
Reading 1	200	55.5800	0.2779	0.2777
Reading 2	200	55.4600	0.2773	
Reading 3	200	55.5600	0.2778	
BDS (250-500µm) freely settled				
Reading 1	10	1.9627	0.1963	0.1963
Reading 2	10	1.9617	0.1962	
Reading 3	10	1.9637	0.1964	

Avr=average

Appendix H: CHNS Analysis

Date of Experiment: 30 April 2013

Table 15: Reading for CHNS analysis

Sample	Carbon C, (wt%)	Hydrogen H, (wt%)	Nitrogen N, (wt%)	Sulphur S, (wt%)	Oxygen[a] (wt%)
Standard					
Run 1	51.82	4.546	17.48	11.86	-
Run 2	52.60	5.382	21.79	11.50	
Run 2	50.92	5.282	21.13	11.14	
BR					
Reading 1	43.32	7.691	0.713	0.411	4.26
Reading 2	44.47	7.427	0.709	0.239	
Reading 3	44.66	7.113	0.615	0.292	
Average	44.15	7.56	0.71	0.27	
BD					
Reading 1	26.3	3.788	0.4	0.099	37.41
Reading 2	46.27	6.935	1.129	0.324	
Reading 3	46.40	7.062	0.697	0.185	
Average	46.34	7.00	0.55	0.14	
BDS					
Reading 1	46.88	7.193	0.458	0.095	45.51
Reading 2	46.66	7.123	0.384	0.091	
Reading 3	47.04	6.894	0.366	0.085	
Average	46.86	7.07	0.40	0.09	

a= by difference, using C, H, N and S content; red colour values are invalid

Appendix I: Volatile Matter

Date of Experiment: 9 April 2013

Table 16: Volatile matter data obtained

Sample	Mc + Lid (g)	Mb (g)	Mf (g)	Mb,f (g)	Weight loss (wt%)	Volatile matter (wt%)	Avr Volatile matter (wt%)
BR							
Reading 1	36.2089	2.0070	36.5373	0.3284	83.6373	42.6109	42.56
Reading 2	37.3651	2.0010	37.6908	0.3257	83.7231	42.6967	
Reading 3	36.1541	2.0007	36.4862	0.3321	83.4008	42.3744	
BD							
Reading 1	14.4452	2.0011	14.8421	0.3969	80.1659	72.8387	72.83
Reading 2	36.5478	2.0012	36.9404	0.3926	80.3818	73.0546	
Reading 3	56.7692	2.0014	57.1708	0.4016	79.9340	72.6068	

Appendix J: Water Content of bio-oil

Date of Experiment: 20 July 2013

Table 17: Water content of bio-oil

Sample	Weight (g)	Water content (mg/g)	Water content (wt %)	Mean Value (wt%)
450°C				
Reading 1	0.0672	646.95	64.695	64.15
Reading 2	0.0267	666.78	66.678	
Reading 3	0.0820	664.600	66.460	
500°C				
Reading 2	0.0587	602.91	60.291	62.08
Reading 3	0.0820	615.81	61.581	
Reading 4	0.0788	625.78	62.578	
550°C				
Reading 2	0.0147	696.80	69.68	69.30
Reading 5	0.0108	695.59	69.559	
Reading 7	0.0690	686.34	68.634	

Appendix K: Ash content of char

Date of Experiment: 22 July 2013

Table 18: Ash content of char

Weight	Wc (g)	Wb (g)	Wf (g)	Ash Content wt%	Avr Ash Content wt%
450°C					
Reading 1	24.7190	0.5080	24.7448	5.0787	4.76
Reading 2	24.7084	0.5074	24.7341	5.0650	
Reading 3	30.8985	0.5021	30.9193	4.1426	
500°C					
Reading 1	15.7734	0.5088	15.8061	6.4269	6.37
Reading 2	26.0118	0.5021	26.0428	6.1741	
Reading 3	31.8695	0.5002	31.9020	6.4974	
550°C					
Reading 1	80.3865	0.4508	80.4142	6.1446	5.63
Reading 2	86.1079	0.4518	86.1261	4.0283	
Reading 3	29.2606	0.4517	29.2909	6.7080	

Appendix L: Moisture content of char

Date of Experiment: 19 July 2013

Table 19: Moisture content of char

Weight	Reading 1	MC (wt%)	Reading 2	MC (wt%)	Reading 3	MC (wt%)
450°C						
Wv (g)	6.5870		6.5341		6.6584	
Wchar (g)	0.1071		0.1038		0.1036	
W24 (g)	6.6918	2.1475	6.6360	1.8304	6.7607	1.2548
W25 (g)	6.6912	2.7077	6.6352	2.6012	6.7595	2.4131
W26 (g)	6.6915	2.4276	6.6355	2.3121	6.7595	2.4131
W27 (g)	6.6916	2.3343	6.6355	2.3121	6.7596	2.3166
MC wt%=		2.3343		2.3121		2.3166
Avg MC wt%=						2.32
500°C						
Wv (g)	6.5327		6.5982		6.6197	
Wchar (g)	0.1012		0.1022		0.1023	
W24 (g)	6.6316	2.2727	6.6974	2.9354	6.7194	2.5415
W25 (g)	6.6306	3.2609	6.6967	3.6204	6.7183	3.6168
W26 (g)	6.6307	3.1621	6.6966	3.7182	6.7186	3.3236
W27 (g)	6.6304	3.4585	6.6968	3.5225	6.7185	3.4213
MC wt%=		3.4585		3.5225		3.4213
Avg MC wt%=						3.44
550°C						
Wv (g)	6.5080		6.5921		6.5526	
Wchar (g)	0.1041		0.1080		0.1063	
W24 (g)	6.6092	2.7858	6.6978	2.1296	6.6567	2.0696
W25 (g)	6.6097	2.3055	6.6979	2.0370	6.6568	1.9755
W26 (g)	6.6098	2.2094	6.6977	2.2222	6.6564	2.3518
W27 (g)	6.6098	2.2094	6.6978	2.1296	6.6566	2.1637
MC wt%=		2.2094		2.1296		2.1637
Avg MC wt%=						2.17

Appendix M: Calorific content of char and bio-oil

Date of Experiment: 5 August 2013

Table 20: Calorific value of char and bio-oil at different temperature

Sample	Mass sample (g)	Mass methanol (g)	CV (J/g)	Cvmethanol (J/g)	CVoil (J/g)
Char					
450^{o}C	0.3553	-	25344	-	-
500^{o}C	0.3512	-	27825	-	-
550^{o}C	0.3546	-	26158	-	-
Bio Oil					
450^{o}C	0.3109	0.4025	15474.00	20658	8762.65
500^{o}C	0.3075	0.4075	15999.00	20658	9824.88
550^{o}C	0.3050	0.4004	15363.00	20658	8411.79

Appendix N: Product CHNS content

Product CHNS content			
Product	Bio Oil (light)	Bio Oil (heavy)	Char
C (wt %)			
450^{o}C	20.62	62.03	30.78
500^{o}C	23.42	53.92	43.51
550^{o}C	21.05	60.56	45.19
H (wt%)			
450^{o}C	7.54	7.52	1.54
500^{o}C	9.93	7.61	0.0900
550^{o}C	9.44	7.52	1.8600
N (wt%)			
450^{o}C	0.00	0.32	0.24
500^{o}C	0.00	0.14	0.15
550^{o}C	0.04	0.23	0.47
S (wt%)			
450^{o}C	0.01	0.30	0
500^{o}C	0.00	0.25	0.00
550^{o}C	0.37	0.24	0.11
O^{a} (wt%)			
450^{o}C	71.83	29.90	67.45
500^{o}C	66.65	38.09	56.25
550^{o}C	69.10	31.45	52.36

Appendix O: Pyrolysis Experiment for three temperature

Experiment	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
Date	25.06.13	26.06.13	09.07.13	10.07.13	10.07.13	19.07.13	19.07.14
Time	9.30am	9.30am	10.00am	10.00am	3.00pm	10.00am	3.30pm
Temperature	500^{o}C	550^{o}C	450^{o}C	450^{o}C	450^{o}C	550	500
Inert gas	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Nitrogen
Reaction time (min)	10	10	10	10	10	10	10
Biomass							
Size	250-500µm	250-500µm	250-500µm	250-500µm	250-500µm	250-500µm	250-500µm
Type	Dried bamboo	Dried bamboo	Dried bamboo	Dried bamboo	Dried bamboo	Dried bamboo	Dried bamboo
Weight (g)	15.00	15.00	15.00	15.01	15.01	15.01	15.01
Before Experiment							
Reactor weight (g)	1524.50	1524.41	1524.39	1524.37	1524.38	1524.56	1524.37
1st condenser weight (g)	112.91	110.37	120.87	120.87	120.87	120.86	120.86
2nd condenser weight (g)	113.16	115.37	112.99	112.99	112.99	112.97	112.97
1st pipe weight (g)	26.42	26.43	23.68	23.68	23.76	23.67	23.73
2nd pipe weight (g)	9.51	8.81	7.62	7.61	7.62	7.60	7.63
After Experiment							
Reactor weight (g)	1525.25	1525.36	1525.33	1525.37	1525.24	1525.16	1525.26
1st condenser weight (g)	116.20	113.7	124.25	124.14	123.91	124.11	124.11
2nd condenser weight (g)	113.57	115.53	113.33	113.45	113.49	113.18	113.18
1st pipe weight (g)	26.69	26.64	23.87	23.85	23.94	23.84	23.95
2nd pipe weight (g)	9.53	8.83	7.63	7.63	7.67	7.63	7.63

Products							
Char (g)	4.28	4.79	4.47	4.52	4.45	3.44	3.97
Bio Oil (g)	3.99	3.72	3.92	3.92	3.77	3.66	3.68
Tar (g)	0.75	0.95	0.94	1.00	0.86	0.60	0.89
Percent Yield							
Char (wt%)	28.53	31.93	29.80	30.11	29.65	22.92	26.45
Bio Oil (wt%)	26.60	24.80	26.13	26.12	25.12	24.38	24.52
Tar (wt%)	5.00	6.33	6.27	6.66	5.73	4.00	5.93
Bio Gas[a] (wt%)	39.87	36.93	37.80	37.11	39.51	48.70	43.10

a= by difference, using percent yield of char, bio-oil and tar