Effect of Thermal Treatment on Composition of Malaysian Biomass

by

Syed Faiq Bin Syed Adnan

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
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Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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Approved by,

____
(Prof. Dr. Yoshimitsu Uemura)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2010

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.

SYED FAIQ BIN SYED ADNAN

ABSTRACT

This paper describes the effect of torrefaction on the basic characteristics of agricultural biomass waste in Malaysia, such as oil palm trunk as a potential source of solid fuel. Torrefaction is a mild pyrolysis process (usually up to 300 ^{o}C) that changes the chemical and physical properties of biomass. This process is a possible pre-treatment prior to further processes (transport, grinding, combustion, gasification, etc) to generate energy or biofuels. In this study two different sample size of Oil palm trunk (OPT) were subjected to different torrefaction temperatures at constant retention time to determine the alterations in their compositions for comparison. The overall mass loss is proposed as a relevant parameter to synthesize the effect of torrefaction conditions (temperature and duration). Accordingly, all results are presented by analytical expressions able to predict the energy properties as a function of the overall mass loss. These expressions are intended to be used in any optimization procedure, from production in the field to the final use in the future.

Keywords: torrefaction; biomass; oil palm trunk(OPT); mass lost

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First of all, I would like to say Alhamdulillah, for giving me the strength and health to do this project work until it’s done because by His willing, I have completed my Final Year Project.

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TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Project's Background

Renewable energy has become more important globally especially with the current fuel and economic crisis. In Malaysia, the government has encouraged the use of renewable energy through its Five Fuels Policy plan in 1999 with the estimation of 5% utilization of renewable energy in the energy mix for year 2008 and this usage will increase to 35% in 2030 [T.R. Zanzi, D.T. Ferro, A.Torres, P. B. Soler and E. Björnbom,2005]. Malaysia is well positioned amongst the ASEAN countries to promote the use of biomass as a renewable energy source in her national energy mix since she is a major agricultural commodity producer in the region. The main concern over global warming and greenhouse gas also put the biomass fuels as the forefront in reduction of the pollution as biomass is considered to be CO2 neutral [S. S. Idris, Norazah A. Rahman, K. Ismail, A.B. Alias, Z. A. Rashid, M.J.Aris, 2010]. Raw biomass, such as wood, straw, bagasse, peat and municipal solid waste are relatively low energy density, high moisture content and difficult to convert into small particles. As new technologies improvise, thermal treatment process known as torrefaction was introduced to encounter the problem faced on biomass fuel. [Mark J. Prins , K. J. Ptasinski, Frans J.J.G. Janssen, 2006]

The process comprises the heating of the raw biomass at the range of 225 – 300 ^{o}C, which aims to produce a fuel with increased energy density by decomposing the reactive hemicellulose fraction in biomass. In this process, the decomposition of reactive fraction in wood, cellulose, hemicellulose and lignin takes place to produce a quality product of fuels. The examples of the final product of the torrefaction process are barbeque fuels and firelighters [S. S. Idris, Norazah A. Rahman, K. Ismail, A.B. Alias, Z. A. Rashid, M.J.Aris, 2010].

The researches of the biomass decomposition mainly focus on the thermal treatment of biomass at the temperature range of 200 ^{o}C and above. No formal research on the decomposition of the raw biomass under 200 ^{o}C had been done, as many researchers simply neglect the effect of the decomposition of biomass at lower temperature. Based on the torrefaction process, the effect of the thermal treatment on composition of biomass will be studied at the temperature range of below 200 ^{o}C.

1.2 Problem Statement

Conventionally, the lowest temperature range of biomass treatment has been between 200 and 300 ^{o}C, which is called torrefaction. Recent experiment had discovered that oil palm waste such as EFB, mesocarp fiber and kernel shell are decomposed even at temperature of drying, 105 ^{o}C considerably. A few researches also notice the decomposition of wood below 200 ^{o}C but neglected them as it is insignificant. Since information available on the torrefaction of oil palm trunk is not widely available, this project will contribute to clarify the basic behavior of lignocellulosic biomass at the temperature, ranging 220 – 300 ^{o}C. To find the best torrefaction temperature of OPT is a challenge to many researcher.

1.2.1 Significant of the Project

This project may mark a new milestone in the study of torrefaction and Pyrolysis analysis in the future. The research done in this project has no direct reference, which indicates there is no research is done as the new finding is found. This experiment will investigate and experiment the possibility and feasibility of the problem arise in the future.

1.3 Objectives and Scope of Study

1.3.1 Objective

The objectives of this project are:

- To study the effect of drying and decomposition behavior of OPT at various torrefaction temperatures (220,250 & 300^{o}C) on the carbon content,ash content and calorific value (of OPT under air and nitrogen atmosphere).
- To find the optimum torrefaction temperature for OPT that will be used as green fuel in the future.

1.3.2 Scope of Study

The scope of study, as outlined in the above objective above, includes investigating the thermal treatment effect under temperature variation. To study the effect of thermal treatment, similar methodology as torrefaction will be used in the experiment, which using lab scale tubular reactor. During the experiment, two different samples of oil palm trunk 100-250μm & 250-500μm in particle size will be used at various temperatures from 220–300 ^{o}C by adjusting the heating temperature of reactor; retention time is constant at 30 minutes, under nitrogen environment. However, the heating rate during experiment will be kept constant for any torrefaction temperature. The experiment started at 30^{o}C and the temperature increased at 10^{o}C per minute until reaching the desired torrefaction temperature.

1.3.3 Relevancy of the Project

As there is lack of study had been done by other researchers regarding the topic, this project is relevant in investigating the effect of thermal treatment on oil palm trunk at the temperature of 220-300 ^{o}C, which may lead to new findings that can be extended in the future. This project will mark new milestone in torrefaction and pyrolysis analyses if the hypothesis of this project can be proven.

1.3.4 Feasibility of the Project

This project is feasible to be carried out in the time frame given. Based on the research and study of the equipment, the experiment can be done in the time frame of two months. Below is the Gantt chart for my planning of the experimentation on the project:

Week	JULY					AUGUST				
Activity	W1	W2	W3	W3	W4	W1	W2	W3	W3	W4
Sample Preparation	🟨	🟨	🟨	🟨	🟨	🟨				
• Drying	🟨									
• Grinding		🟨								
• Sieving		🟨								
• Composition Analysis			🟨							
Pyrolysis Experiment				🟨	🟨	🟨				
Tubular Reactor Exp							🟨	🟨	🟨	
• Sample Analysis										🟨

Table 1: Gantt Chart of Experimental Planner

CHAPTER 2

LITERATURE REVIEW

2.1 Structure and Composition of Biomass

For this research, the study on structure and composition of wood will be focused to indicate the general idea on the composition of the biomass. There are 3 distinguish zone that will be decomposed during the thermal treatment of wood. On microscopic scale, wood cells are composed of microfibrils, bundles of cellulose molecules coated with hemicellulose and lignin took place in between the microfibrils. These 3 layers of wood will decompose through heating period with different level of temperature. Hemicellulose, most reactive compounds decompose at 225 – 325 ^{o}C while cellulose and lignin decompose at 305 – 375 ^{o}C and 250 – 500 ^{o}C respectively. It was reported that the thermal treatment at 185 – 225 ^{o}C [M.J.Prins, Krzysztof J.Ptasinski, Frans J.J.G. Janssen,2006] will increase the durability, mechanical dimensional stability and water repellent characteristics of wood. The depolimerization, recondensation of hemicellulose and glass transition or softening process of lignin happens at 200 ^{o}C while no changes observed on cellulose at the same temperature. A slight decomposition of hemicellulose is observed, but no valid data that can be used to support the observation.

A study was carried out on the effect of densification on composition of wood showed that the amount of total lignin increased after desorption, but it was not significant. Generally, mature wood samples tend to lose 2 to 3.5 % of their hemicelluloses during desorption, with southern pine recording the highest losses. As a result of these hemicellulose losses, there was an increase in percent of lignin and cellulose content resulting from desorption.

Different types of biomass contain different composition of cellulose, hemicellulose and lignin. Based on the study [M.J. Prins, K.J. Ptasinski, F.J.J.G. Janssen,2006], the torrefaction on different type of the biomass will result in different scheme of decomposition of the active composition in wood. The study on bamboo, willow, coconut shell and wood exhibit different behavior of decomposition at certain temperature.

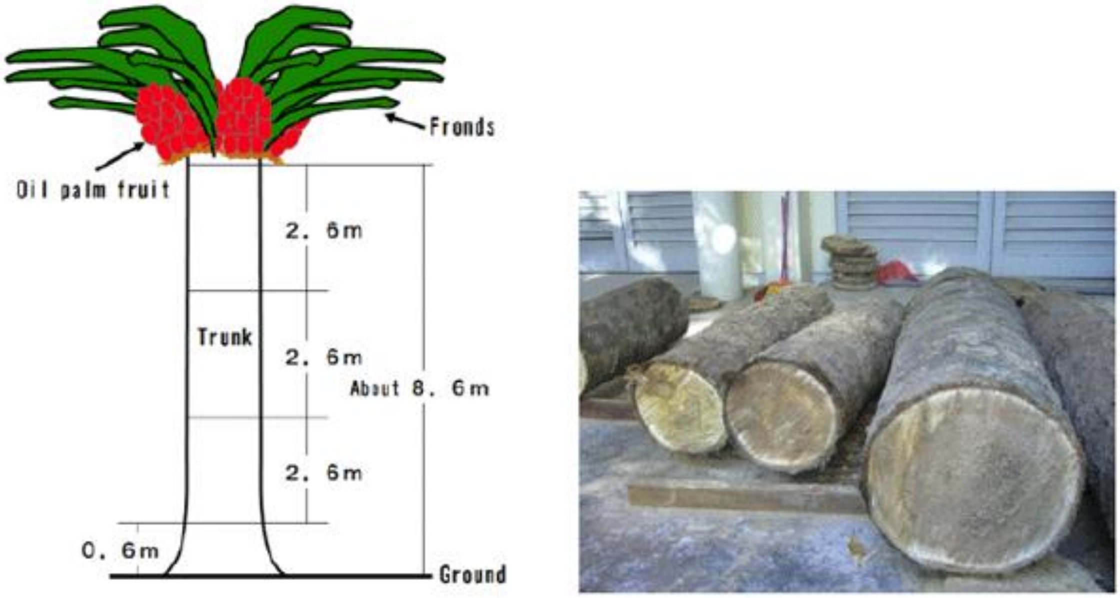


Figure 1: Raw Feedstock of Oil Palm Trunk

2.2 Lab Scale Tubular Reactor

For the experiment, lab scale tubular is designed and built in order to do the thermal treatment for the biomass at lower temperature with small scale. This reactor is significant to observe and record the effect of the treatment on the sample. The reactor consists of nitrogen gas supply, a tubular reactor, ice traps for tar and water, and a gas sampling point.

A stainless steel pipe with the diameter of one inch is used as the heating medium for the reactor and being heat up by the heater that controlled by thermocouple inserted through the reactor to measure the wall temperature of the tube during the experiment. Ice trap is placed at the outlet of the reactor to capture the tar and water vaporized due to the thermal treatment. This is vital to test on the tar generated through the experiment to indicate the decomposition of the samples.

Nitrogen acts as the inert gas for the experiment to ensure there is no oxygen during the experiment. Before the experiment, air in the reactor was replaced by nitrogen gas, which was allowed to flow into the reactor until the concentration of oxygen at the exit was less than 1% [R.H.V. Corley and P.B. Tinker, 2003].

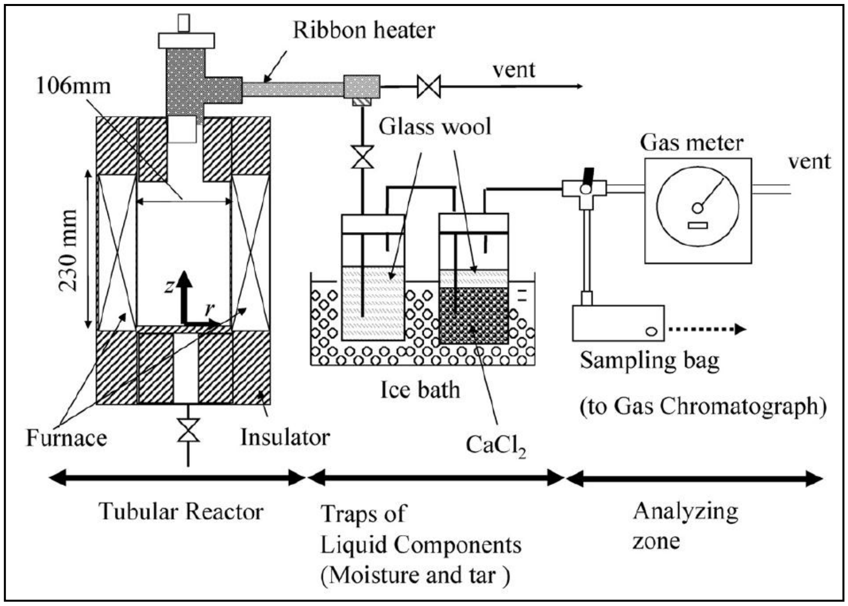


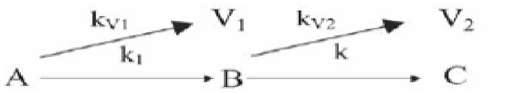
Figure 2: Lab Scale Tubular Reactor

2.3 Torrefaction Process

In this experiment, torrefaction will be used as the reference experiment, where the method of torrefaction experiment will be applied to study the weight loss of the sample. Torrefaction is a thermal treatment step in the temperature range of 225 – 300 ^{o}C, which aims to produce a fuel with increased energy density by decomposing the reactive hemicellulose fraction [C.D.Blasi, 2008]. This experiment is carried out using many different devices; however, tubular reactor is seen as the most effective equipment. The process is being carried out under nitrogen environment.

Torrefaction can be carried out under different gaseous atmospheres. Nitrogen or hot gases released during the thermal treatment are employed most of time. It avoids exothermic reactions that are likely to occur in presence of oxygen. When exothermic reactions take place, a fast and uncontrolled increase in temperature of the material occurs. However, chemical reactions involved during torrefaction as well as final properties of the material depend strongly on the temperature of the wood [M.J.Prins , Krzysztof J. tasinski, Frans J.J.G. Janssen,2006].

Torrefaction is involving the multi - step reaction in order to decompose active component in biomass, which are hemicellulose, cellulose and lignin. The process occurs with the intermediate process during the torrefaction where biomass is converted into intermediate reaction product before yielding char as the final product. The first reaction is substantially faster than the second reaction and the reaction is expected to occur in continuous manner [Mark J. Prins, Krzysztof J. Ptasinski, Frans J.J.G. Janssen, 2006].



The solid yields are given by:

$$y_1 = \frac{k_1}{k_1 + k_{V_1}}$$

$$y_2 = \frac{k_2}{k_2 + k_{V_2}}$$

The most recent modification is discussed proposed that torrefaction is involving tar cracking in the multi – step mechanism in torrefaction. The literature suggested that the decomposition of cellulose will produce intermediate reaction product of active – cellulose and being decompose to char, tar and gas as below;

Torrefied biomass has several advantages in different markets, which makes it a competitive option compared to conventional biomass (wood) pellets. The torrefied biomass contains higher energy density; 18 - 20 GJ/m3 compared to 10 - 11 GJ/m3 driving a 40 - 50% reduction in transportation costs [M.J. Prins, K.J. Ptasinski, F.J.J.G. Janssen, 2006]. Torrefied biomass also can be produced from a wide variety of raw biomass feedstock while yielding similar product properties. The main reason for this is that almost all biomass contains lignocellulose. All biological activity is eliminated reducing the risk of fire and stopping biological decomposition.

2.4 Pyrolysis

Pyrolysis is a chemical decomposition of condensed substances by heating that occurs spontaneously at high temperatures .The word is coined from the Greek-derived elements pyro "fire" and lysys "decomposition".

Pyrolysis is a special case of thermolysis, and is commonly used for organic materials, being then one of the processes involved in charring. The pyrolysis of wood, which starts at 200–300 °C (390–570 °F), occurs for example in fires or when vegetation comes into contact with lava in volcanic eruptions. In general, pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization.

This chemical process is heavily used in the chemical industry, for example, to produce charcoal, activated carbon, methanol and other chemicals from wood, to convert ethylene dichloride into vinyl chloride to make PVC, to produce coke from coal, to convert biomass into syngas, to turn waste into safely disposable substances, and for transforming medium-weight hydrocarbons from oil into lighter ones like gasoline. These specialized uses of pyrolysis may be called various names, such as dry distillation, destructive distillation, or cracking.

Pyrolysis also plays an important role in several cooking procedures, such as baking, frying, grilling, and caramelizing. And it is a tool of chemical analysis, for example in mass spectrometry and in carbon-14 dating. Indeed, many important chemical substances, such as phosphorus and sulfuric acid, were first obtained by this process. Pyrolysis has been assumed to take place during catagenesis, the conversion of buried organic matter to fossil fuels. It is also the basis of pyrography.

Pyrolysis differs from other high-temperature processes like combustion and hydrolysis in that it does not involve reactions with oxygen, water, or any other reagents. However, the term has also been applied to the decompositon of organic material in the presence of superheated water or steam (hydrous pyrolysis), for example in the steam cracking of oil.

Since pyrolysis is endothermic [R.H.V. Corley and P.B. Tinker, 2003], various methods have been proposed to provide heat to the reacting biomass particles:

- Partial combustion of the biomass products through air injection. This results in poor-quality products.
- Direct heat transfer with a hot gas, ideally product gas that is reheated and recycled. The problem is to provide enough heat with reasonable gas flow-rates.
- Indirect heat transfer with exchange surfaces (wall, tubes). It is difficult to achieve good heat transfer on both sides of the heat exchange surface.
- Direct heat transfer with circulating solids: Solids transfer heat between a burner and a pyrolysis reactor. This is an effective but complex technology.

2.5 Yields of Torrefied Products

The thermal decomposition of the agricultural residues under torrefaction temperatures produces mainly three products: a solid product which retains 30–66% of the energy content of the feedstock, a condensable liquid including most of moisture, acetic acid and other oxygenates and non-condensable gases (mainly carbon dioxide, carbon monoxide and small amounts of methane).

The last two products can be represented by volatiles. The total yield of volatiles increases with both raising reaction temperature and higher volatile content. As the temperature increases, the yield of solid product decreases, whereas the yield of liquid and gas increases accordingly. That is a result of the competition between charring and devolatilization reactions which are more reactive at higher temperature. The bio-char yield of the rice straw decreases roughly by 23 wt% when the torrefaction temperature increases from 200 ºC to 300 ºC and a larger decrease of 38 wt% is observed for the rape stalk. The particles tended to shrink in all directions and the fiber linking between particles disappeared. [A. Uslu, A.P.C. Faaij, P.C.A. Bergman, 2008] Thus the biomass particles became more spherical which can improve the poor flow properties of the biomass. Furthermore, the reduced size led to a greater bulk density. The color of the residues during torrefaction changed from brown at a lower temperature to black at a higher temperature. The condensed fraction was brownish liquid mixing water with tar. Generally, the hemicellulose breaks down firstly at the temperatures ranging from 200 ºC to 250 ºC, and then does cellulose at the temperatures ranging from 240 ºC to 350 ºC, with lignin being the last component to decompose at temperatures between 280 ºC and 500 ºC. Water is a major product released in two different mechanisms, firstly during drying when moisture evaporates and secondly during dehydration reactions between organic molecules.

2.6 Measurements

For the OPT (wet) used in this study, the moisture content and the calorific value were measured. For the dried biomass wastes and the torrefied samples, the calorific value, elementary (CHNS) composition and ash content were measured.

The calorific value was measured using a bomb calorimeter, IKA-WERKE supplied by GMBH & CO KG. The calorific value from a bomb calorimeter is the high heat value (HHV), which includes the latent heat of the vapor emitted from the specimen. Values of HHV obtained by the measurement were converted to those of the low heat value (LHV) using equation (1) [Asano, 1999]. LHV is more realistic than HHV, because LHV does not contain any contribution from the latent heat of the vapor.

$$LHV = HHV - (21.987w_H + 2.443w_W) \quad (1)$$

Where LHV and HHV are in MJ/kg; w_H is the hydrogen mass fraction of the specimen; w_W the free water fraction. Elementary (CHNS) analysis was carried out using CHNS-932 supplied by LECO Corporation. The small difference of analyzed data between this study and the literatures can be acceptable because those properties vary depending on surrounding conditions and harvesting season [L. Núñez-Regueira, J.A. Rodríguez-Añon, J. Proupín-Castiñeiras, A. Vilanova-Diz, N. Montero-Santoveña, 2001].

CHAPTER 3
PROJECT METHODOLOGY

3.1 Project Methodology

Basically, below is the general experiment flow how the experiment conducted:

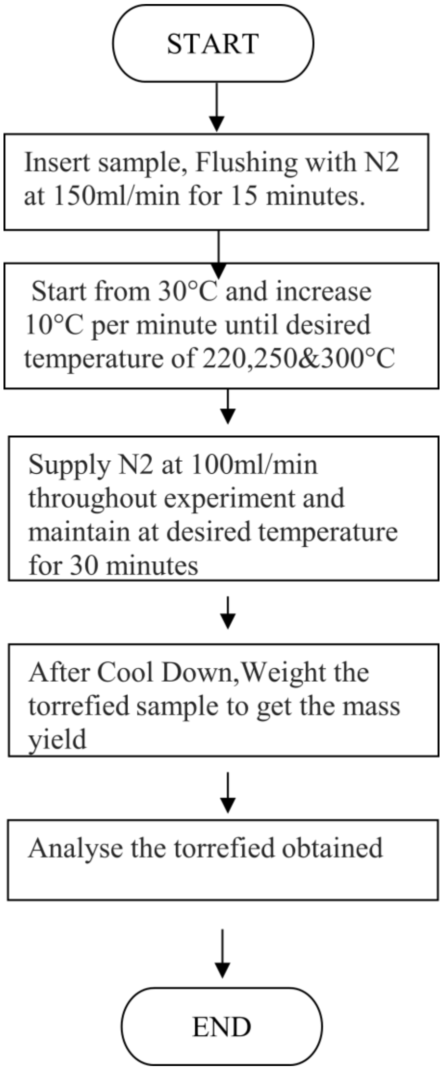


Figure 3: General Experimental Flow

For this experiment, the procedure is divided into three major steps; (1) Biomass samples preparation, (2) Designing and assembly of tubular reactor and (3) Experiment using lab – scale tubular type reactor.

3.2 Biomass Sample Preparation

To prepare the OPT of 100-250µm and 250-500 µm in particle size,

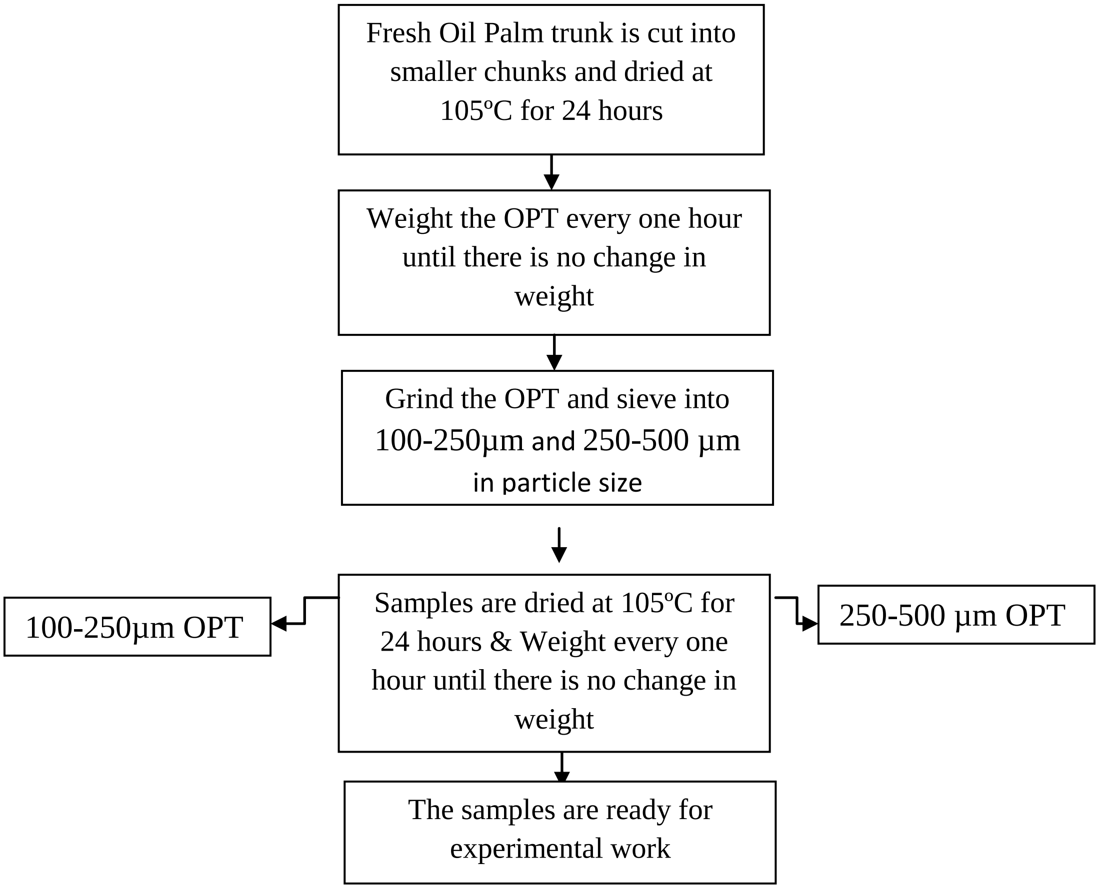


Figure 4: Sample preparation methods

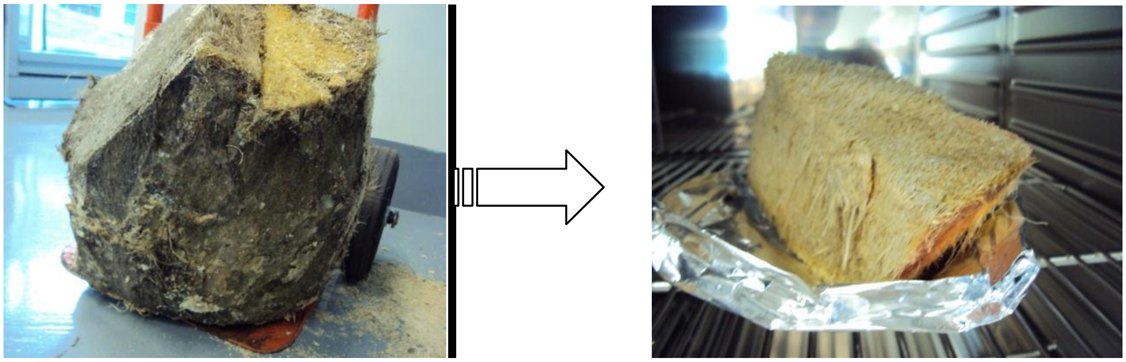


Figure 5: Fresh Oil Palm Trunk and OPT chunk

The moisture content of the samples is measured as follows. Fresh oil palm trunk is cut into different sizes and weighed to take the initial weight and dried separately in the electric oven for 24 hours at temperature of 105 ^{o}C. After 24 hours, the sample is weighed every one hour till the decrease in weight became negligibly small, indicating no moisture is present in the samples. The dried samples are then being ground using grinding machine to a particle size of 0.5 mm. After grinding, the samples are sieved using sieve shaker equipment to a particle size of **100-250µm & 250-500µm**. A prescribed amount of sample (3 g) was weighed in a crucible, and moisture elimination steps are repeated. The prepared samples are then being analyzed using Bomb Calorimeter, Ash Content Analyzer and CHNS equipment to take initial composition of the samples.

3.3 Designing and Assembly of Tubular Reactor

A lab scale tubular type reactor is designed and assembled to run the experiment for the prepared samples. The reactor consists of nitrogen gas supply, a tubular reactor, ice traps for tar and water, and a gas sampling point [K-I Tanoe, T. Hinauchi, T. Oo, T.Nishimura, M. Taniguchi and K-I Sasauchi, 2007]. A stainless steel pipe with the diameter of one inch is used as the heating medium for the reactor and being heated up by the heater that controlled by thermocouple inserted through the reactor to measure the wall temperature of the tube during the experiment. Ice trap is placed at the outlet of the reactor to capture the tar and water vaporized due to the thermal treatment.

Figure 6:Experimental Setup

3.4 Experiment Using Lab – Scale Tubular Reactor

The reactor is operated fully under nitrogen atmosphere. The prepared sample, which being analyzed is weighed to 1 gram each and placed in a sample boat with a long rod holder is prepared. The sample is placed at the center of the reactor to ensure an efficient heat transfer during the experiment. The flow rate of the nitrogen into the reactor is set to 150 ml/min to for 15 minutes to flush all oxygen in the reactor. After 15 minutes, the nitrogen flow rate is decreased to 100 ml/min at the operating condition of the experiment. The flow rate remains constant throughout the experiment. The heater is first being set to 30 ^{o}C for 15 minutes and the heating rate for the heater is 10 ^{o}C for every one minute up to desired temperature for each run. During the experiment, the residence time is constant at 30 minutes. The experiment will be carried out using 2 different sample particle sizes; 100 – 250 μm and 250 – 500 μm, under three various temperatures; 220 ^{o}C, 250 ^{o}C and 300^{o}C.

After 30 minutes of residence time is reached, the heater temperature is then being cooled to 30 ^{o}C for the reactor to cool off. When the reactor temperature reached, 40 ^{o}C, the sample is taken out to be weighed and analyzed using Bomb Calorimeter, Ash Content Analyzer and CHNS equipment.

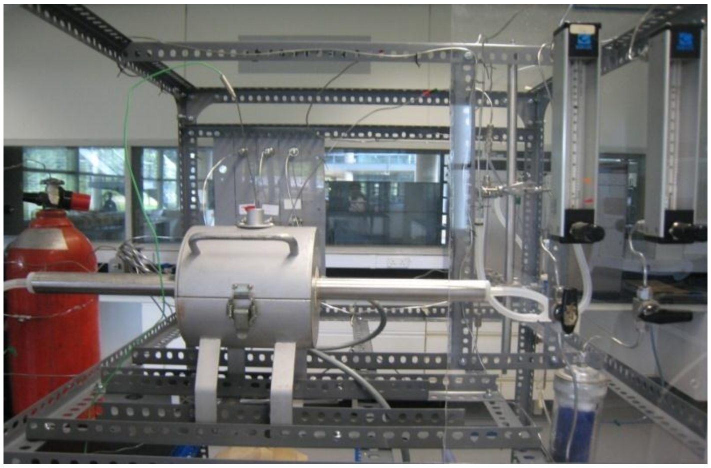


Figure 7: Lab Scale Tubular Reactor

Below are some pictures of equipments used for samples analysis:

Figure 8: Perkin Elmer CHNS analyser

Figure 9: Torrefied samples in the furnace at 700°C for 3 hours

Figure 10: Bomb Calorimeter

3.5 Research Process

The research process starts with stating the hypothesis after choosing the problem. Then, the author has to formulate the research design which is mainly related to laboratory experiment in the synthesis period. After the synthesis period, the product will proceed to be characterized under specific parameters. After that, available data and information are collected from reliable sources, followed by analysis and interpretation of result obtained from the characterization. A systematic documentation is important in order to produce a good report.

3.5.1 Project Planning

The remaining steps of this project are to do the experiment of thermal treatment on the biomass and the analysis of the treated samples. The experiment is to be conducted as soon as possible and the analysis of the treated samples will be done continuously from time to time.

In overall, there are 6 runs required to complete this project, and each run will take an average of three hours. This step is feasible as the project is still in line with the initial planning and continuous runs will ensure that the experiment will be completed within time.

The analysis of the treated samples will be done as soon as the experiment is carried out for each run. This can be done during the experiment or after series of samples had completed. The analyses of treated samples are Bomb Calorimeter, Ash Content and CHNS analysis.

3.6 Materials

For this experiment, oil palm trunk is to be tested for the purpose of the experiment, which sample is being prepared with different particle sizes for the experiment. The experiment will use a lab – scale tubular reactor, under various temperatures and inert atmosphere.

List of samples and equipments in this project:

- OPT 100-250 & 250-500 µm

List of the samples

>Lab Scale Tubular Reactor
>Perkin-Elmer CHNS analyser
>Bomb Calorimeter
>Furnace

List of lab equipments

3.7 Project Activities Flow:

In this project, activities flow is divided into FYP 1 and FYP 2 flow.

3.7.1 FYP 1 Flow:

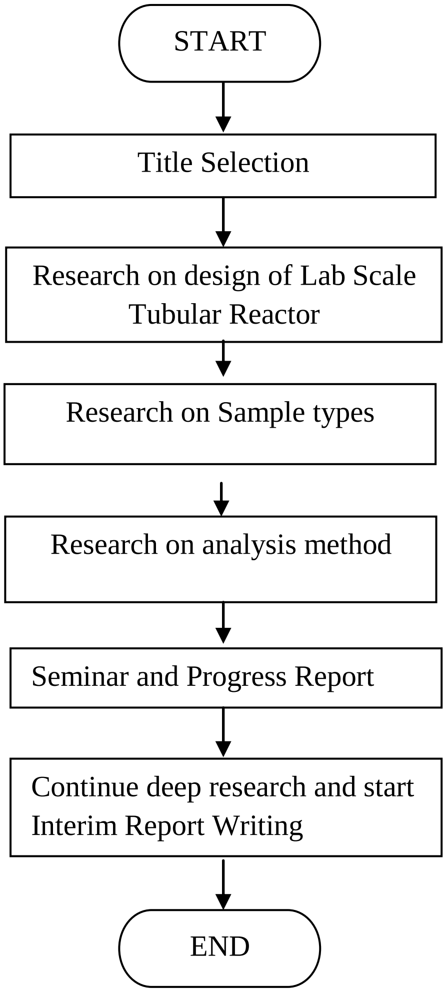


Figure 11: Project Activities Flow for FYP1

3.7.2 FYP 2 Flow:

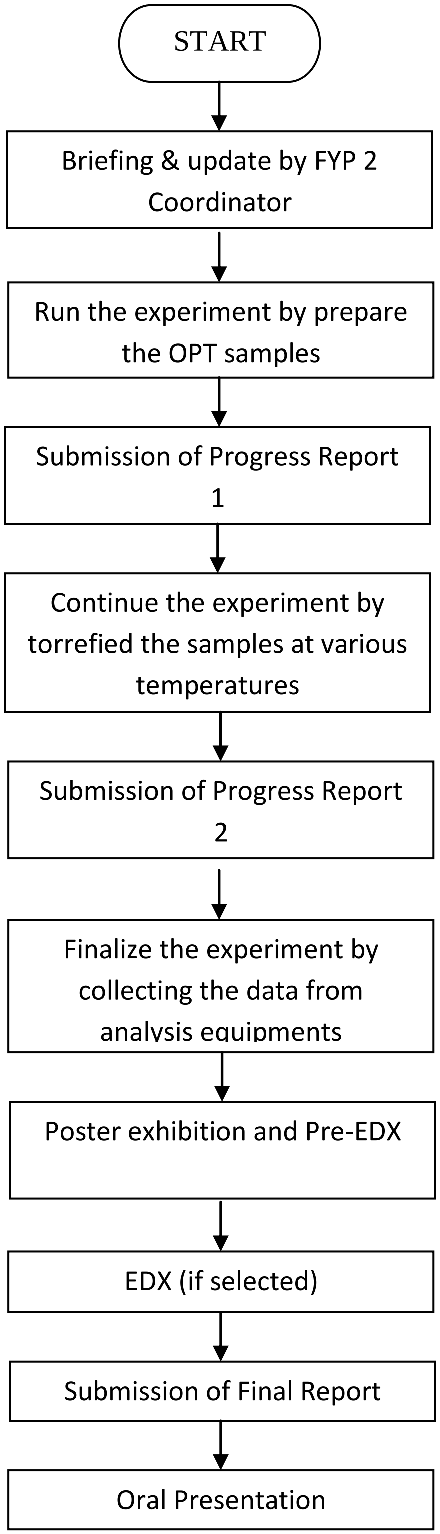


Figure 12: Project Activities Flow for FYP 2

3.8 Project Gantt Chart:

Table 2: Project Gantt Chart for FYP 2

No.	Detail/ Week	1	2	3	4	5		6	7	8	9	10	11	12	13	14	15
1	Briefing & update by FYP 2 Coordinator	🟪					Semester Break										
2	Run the experiment		🟪	🟪	🟪												
3	Submission of Progress Report 1					●											
4	Continue the experiment							🟪	🟪	🟪	🟪	🟪					
5	Submission of Progress Report 2												●				
5	Finalize the experiment												🟪	🟪	🟪		
8	Poster exhibition and Pre-EDX												●				
9	Submission of Final Report															●	
10	Oral Presentation																●

*Legend - 🟪 : Milestone Process

CHAPTER 4
RESULTS & DISCUSSION

4.1 Moisture Content of Oil Palm Trunk(OPT)

Table 3 shows the moisture content of fresh oil palm trunk chunk. Table 4 shows the moisture content of Dry OPT and torrefied samples measured 8 days after torrefaction experiment just before analysis as the equipments for analysis need to be booked and wait prior approval. All samples need to be free from moisture in order to avoid any error during analysis.

Conditions	Oil Palm Trunk
Empty Vessel(g)	52.7245
Vessel + OPTChunk (g)	65.6273
OPT Chunk Weight (g)	12.9028
OPT Chunk Weight (g) After Drying	7.9845
Moisture Content	**38.12%**

Table 3: Moisture Content of Fresh Oil Palm Trunk Chunk

Sample	Moisture Content(%)
100-250µm Dry OPT	2.93%
250-500µm Dry OPT	3.56%
100-250µm at 220°C	4.44%
250-500µm at 220°C	2.90%

100-250µm at 250°C	3.62%
250-500µm at 250°C	2.75%
100-250µm at 300°C	4.55%
250-500µm at 300°C	3.92%

Table4 : Moisture Content of Dry and Torrefied OPT

4.2. Appearance of Torrefied Samples

In this study, oil palm trunk was torrefied. In Fig. 13, photos of all the samples including raw materials and torrefied samples are exhibited. The color of OPT becomes darker as the torrefaction temperature increases. Particularly, OPT torrefied at 300ºC exhibits almost black in color. A similar tendency was observed for a woody biomass in a previous paper [M.J.Prins , K.J. Ptasinski, Frans J.J.G. Janssen,2006].

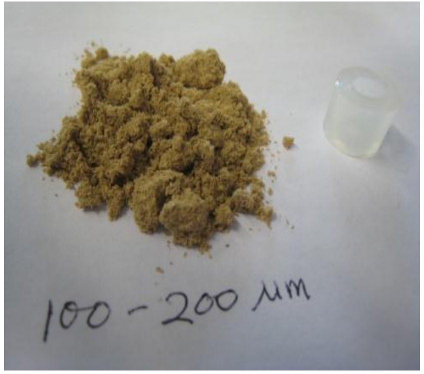
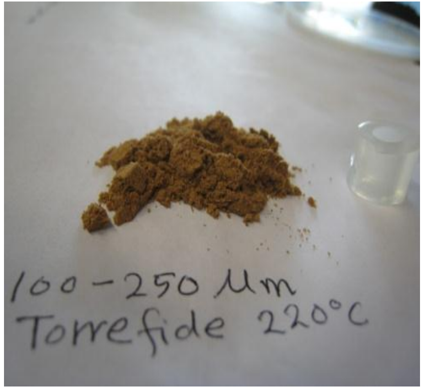
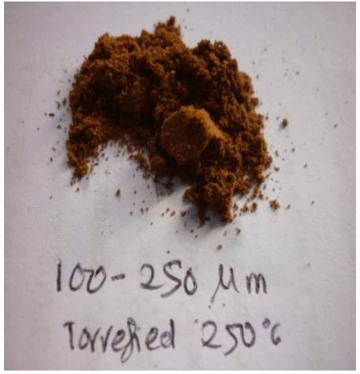
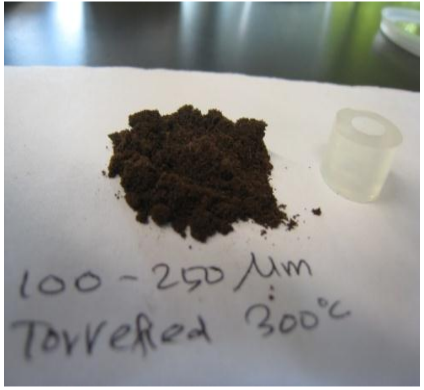
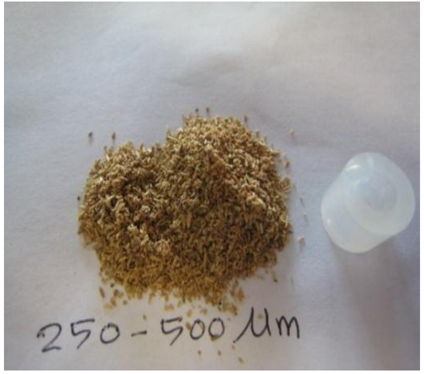
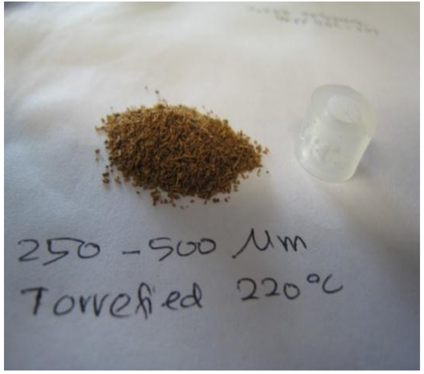
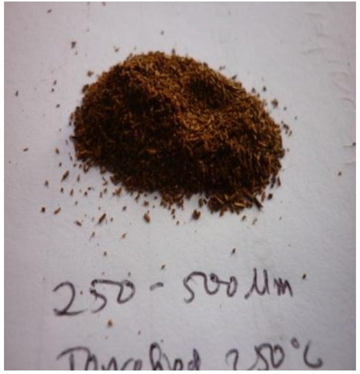
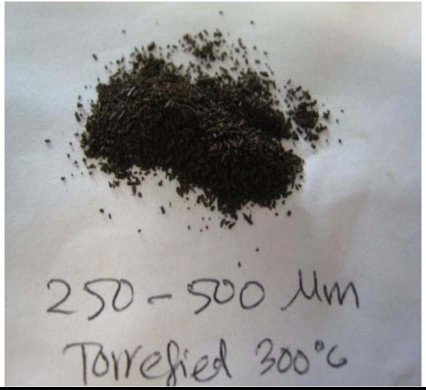
Sample Size(µm)	Dry OPT	Torrefied at 220°C	Torrefied at 250°C	Torrefied at 300°C
100-250µm				
250-500 µm				

Figure 13: Physical Appearance of Samples

4.3 CHN and Calorific Value Analysis

The results of CHN, calorimetry analyses for the dried and torrefied samples are listed in Table 5 and 6. In general, for all the two type of OPT samples; torrefaction resulted in a higher calorific value and a higher carbon content. The CHN analysis in the table shows the comparison of carbon content in untreated sample and torrefied sample at temperature of 220ºC, 250 ºC and 300 ºC. As expected, an increase in carbon (hence a decrease involatiles) with increased duration and temperature of torrefaction was observed for oil palm trunk. An increase in carbon is highly suitable for use in energy production. From the data obtained, the carbon content in torrefied sample increased quite significantly.

In order to discuss more specifically, the CHN contents, the calorific value, and the ash content (the change against the dried sample) are plotted against the torrefied temperature in Figs. 14 to 18, respectively. From Fig. 18, it is found that the tendency of calorific value against torrefaction temperature is similar quantitatively between the two types of samples used in this study. The calorific value of the biomass is an important value as a solid fuel. The calorific value of all the samples increases with temperature. This tendency is consistent with the previous works [B. Arias, C. Pevida, J. Fermoso, M.G. Plaza, F. Rubiera, J.J. Pis,2008], and is mainly due to the carbon content increase (Fig. 14) and the oxygen content decrease. The hydrogen content decreases as torrefaction temperature increases except for one exception (Fig. 15). This decrease in hydrogen and oxygen is due to dehydration and de-carbon dioxide from the biomass during the torrefaction [M.J. Prins, K.J. Ptasinski, F.J.J.G. Janssen, 2006]. It is obvious that either CO_2 or H_2O emission will result in decrease in H and O contents of the OPT.

From Fig. 17, it is found that in general the ash content increases as torrefaction proceeds, except at temperature of 220°C. If ash is not emitted from the biomass during torrefaction, the ash content must increase in the torrefied samples. The result in Fig. 17 implies two possibilities. The first is that a major component in the OPT ash was lost (vaporized itself or accompanied with the tar sol) during the torrefaction. The second is that a major component in the OPT ash was converted into a higher-volatile form, and then was lost during the ash measurement at 700ºC.

Temperature (°C)	Carbon	Hydrogen	Nitrogen	Carbon	Hydrogen	Nitrogen
	100-250µm			250-500µm		
Dry OPT	44.35%	6.01%	1.12%	41.77%	6.01%	0.91%
220	43.20%	5.58%	1.09%	41.69%	5.75%	0.85%
250	44.62%	5.71%	1.16%	43.35%	5.89%	0.97%
300	45.36%	5.49%	1.23%	44.89%	5.11%	1.09%

Table 5: CHN Analysis of Dry and Torrefied OPT

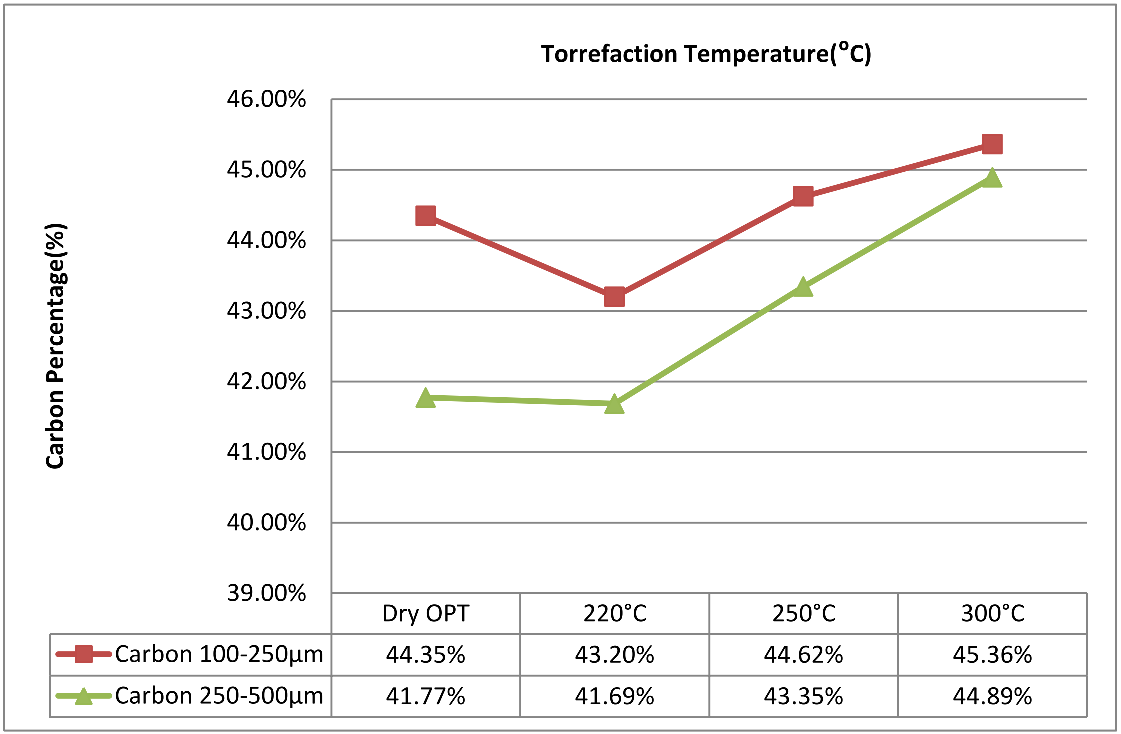
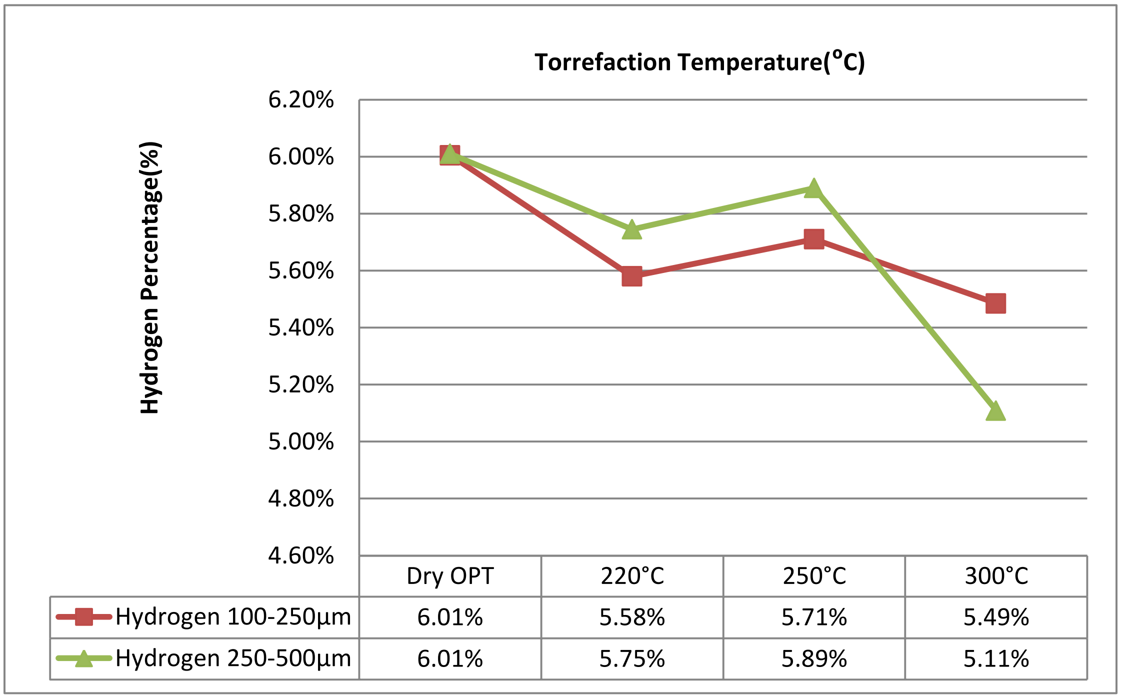
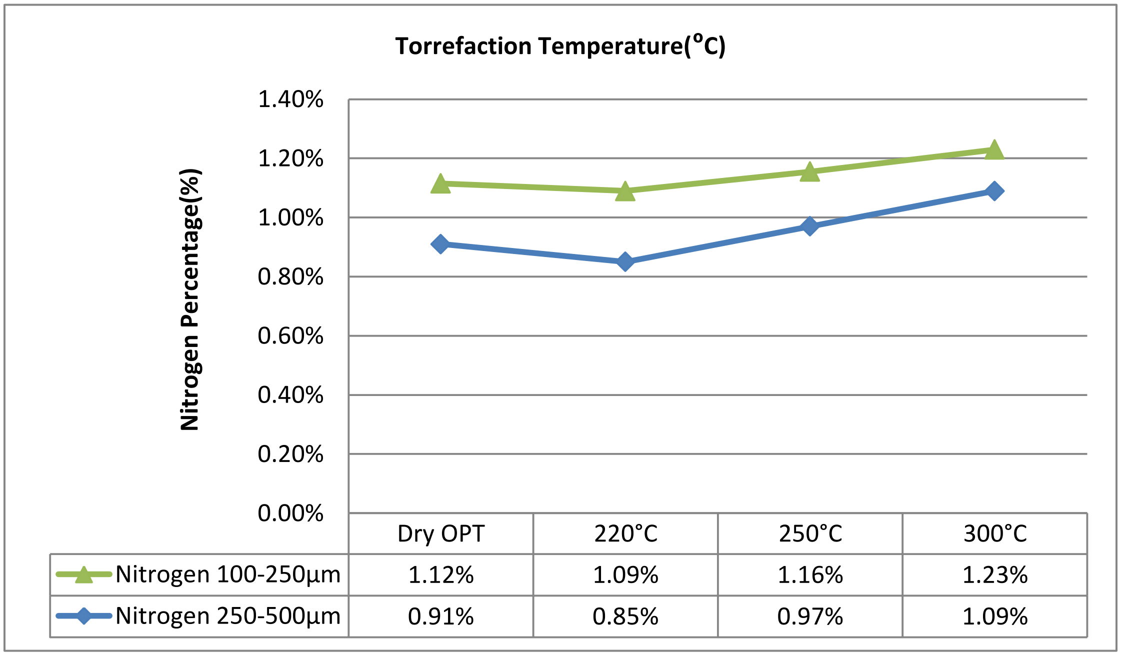


Figure 14: Carbon Percentage(%) of Dry and Torrefied OPT



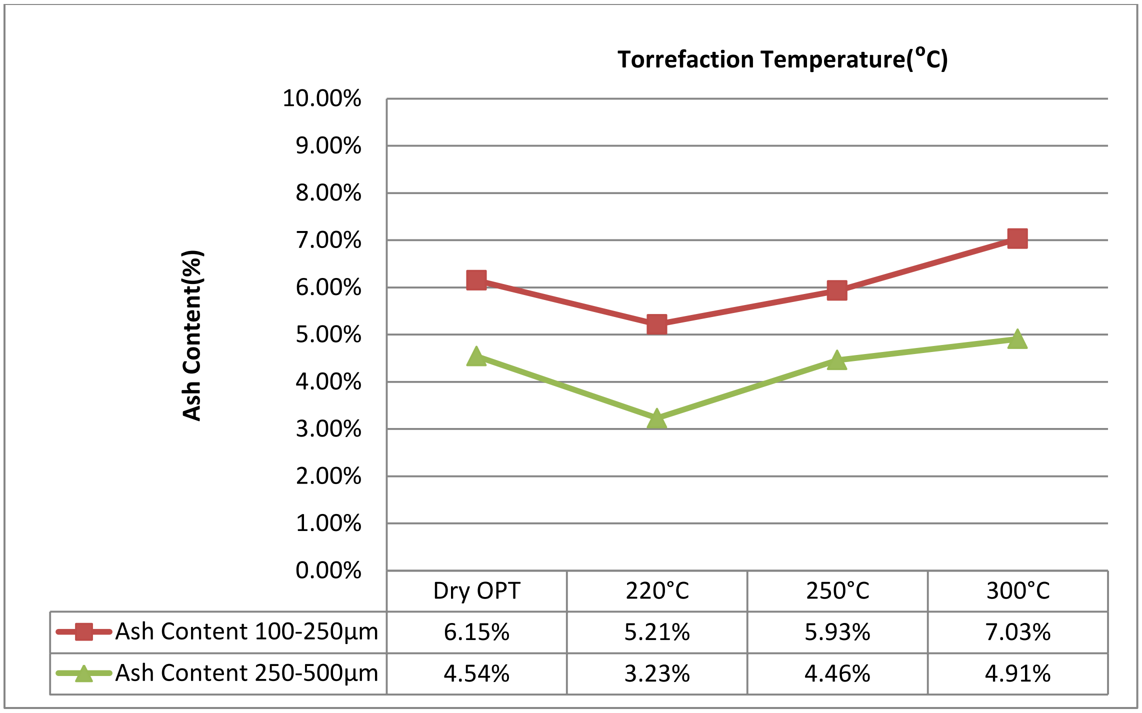
	Dry OPT	220°C	250°C	300°C
Hydrogen 100-250µm	6.01%	5.58%	5.71%	5.49%
Hydrogen 250-500µm	6.01%	5.75%	5.89%	5.11%

Figure 15: Hydrogen Percentage(%) of Dry and Torrefied OPT



	Dry OPT	220°C	250°C	300°C
Nitrogen 100-250µm	1.12%	1.09%	1.16%	1.23%
Nitrogen 250-500µm	0.91%	0.85%	0.97%	1.09%

Figure 16 :Nitrogen Percentage(%) of Dry and Torrefied OPT



	Dry OPT	220°C	250°C	300°C
■ Ash Content 100-250µm	6.15%	5.21%	5.93%	7.03%
▲ Ash Content 250-500µm	4.54%	3.23%	4.46%	4.91%

Figure 17: Ash Content as a function of Torrefaction Temperatures

Temperature (°C)	Calorific Value (MJ/kg)			
	Dry OPT	220°C	250°C	300°C
100-250µm	15.987	18.165	19.121	21.305
250-500µm	16.902	19.08	20.036	22.22

Table 6: Calorific Value(MJ/kg)

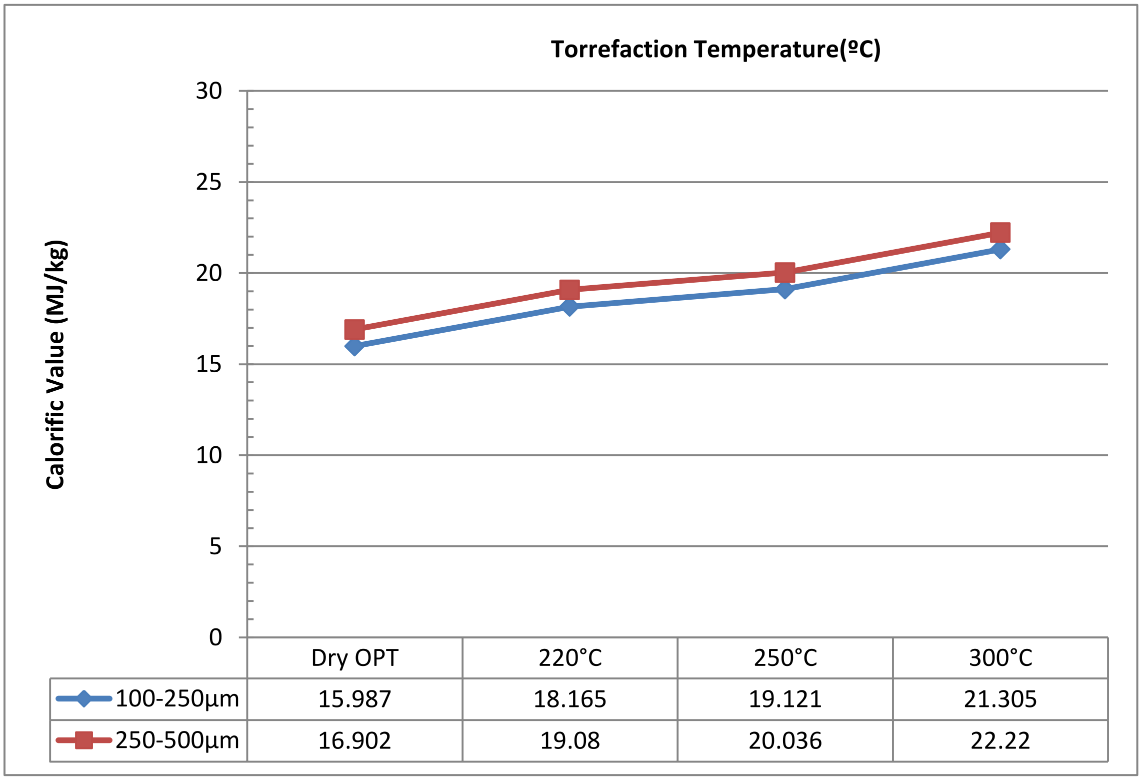


Figure 18: Calorific Value as a function of Torrefaction Temperatures

4.4 Effect of Torrefaction Temperatures on Mass Yield

The results of mass yield due to torrefaction according to biomass type, and torrefaction temperature, are presented in Fig. 19 . Mass yield is a very effective indicator of the severity of the torrefaction process. It is caused by degradation of the chemical components of oil palm trunk, especially hemicelluloses which are the components most sensitive to thermal degradation, and produces volatiles. The lower thermal stability of hemicelluloses compared to cellulose is usually explained by the lack of crystallinity of hemicelluloses.

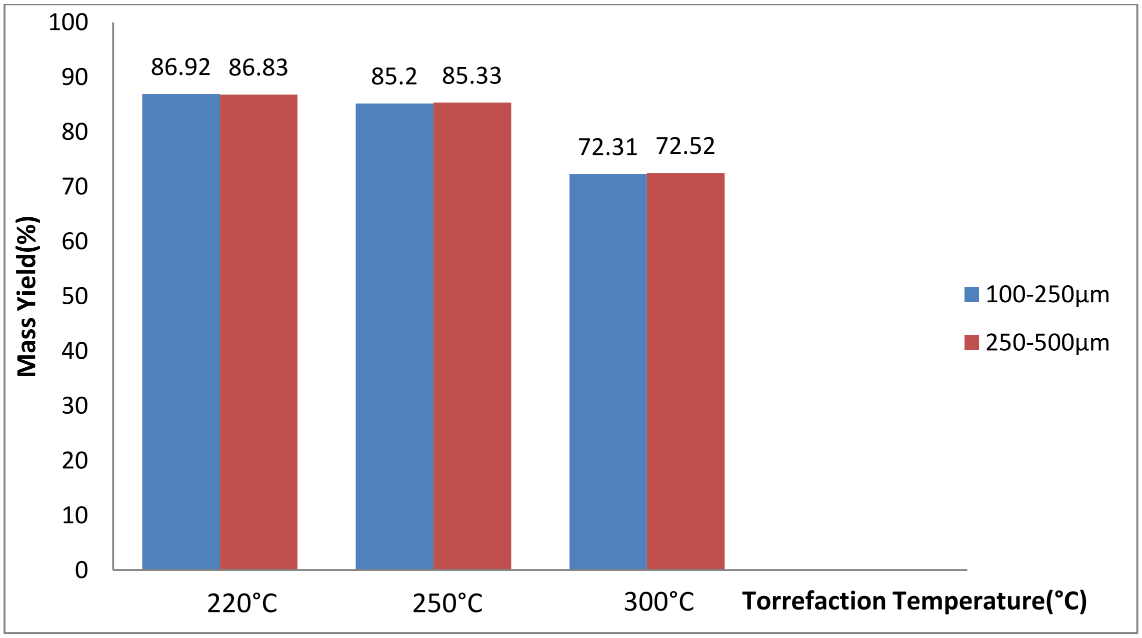


Figure 19: Mass Yield caused by different torrefaction conditions

The mass and energy yields of the dried and torrefied samples were calculated, based on equations used by Bridgeman et al. [T.G. Bridgeman, J.M. Jones, I. Shield, P.T. Williams,2008]. The mass and energy yields (Y_{mass} and Y_{ene}) are defined by equations (2) and (3), respectively.

Y_{mass} = 100 x (mass after drying or torrefaction /mass of wet sample before the treatment) (2)

Y_{ene} = Y_{mass} x (LHV after treatment / LHV before treatment)
(3)

Fig. 19 shows the mass yields under different conditions for OPT respectively. As shown in Fig. 19, for both two samples, the mass yield is less than 100%, i. e., the mass of torrefied samples was smaller than the corresponding wet raw material. Among them, the mass of torrefied samples treated at 220ºC, the lowest temperature, showed almost the same decrease in mass as that of dried at 105ºC. This indicates that the extent of torrefaction for the samples treated at 220ºC was negligible compared with those at 250ºC and 300ºC from the viewpoint of change in mass. As the torrefaction temperature increases, the mass yield decrease steadily, whereas the decreasing ratio is depending on the OPT particle size; 100-250µm has the highest decreasing ratio and 250-500µm has the lowest. OPT with particle size of 250-500µm has higher mass yield than OPT with particle size of 100-250µm at both 220ºC and 300ºC. To emphasize the data, Fig. 19 shows the comparison of mass yield for OPT with particle size 100-250µm and 250-500µm at three torrefacton temperatures which at 220ºC,250 ºC and 300ºC at 30 min retention time respectively.

There are two main causes for the decrease in mass of the dried or torrefied samples. One is moisture loss, another thermal decomposition to form volatile or gaseous products such as H_2O, CO, CO_2, acetic acid and other organics. The decrease in mass for the dried and 220ºC torrefied samples is thought to be mainly caused by the loss of moisture. For torrefaction at higher temperatures (250ºC and 300ºC), the decrease is attributed to the thermal decomposition of the hemicellulose part of the biomass [M.J. Prins, K.J. Ptasinski, F.J.J.G. Janssen, 2006].

When the mass yield of for both particle size of OPT is compared, it is obvious that OPT 100-250µm shows the lower mass yield. This means that OPT 100-250µm decomposed more than OPT 250-500µm during the torrefaction. Abdullah and Gerhauser reported that the ash in empty fruit bunch (EFB) enhanced the decomposition of the EFB [N. Abdullah and H. Gerhauser, 2008]. In our study, the OPT 100-250µm has higher ash content OPT 250-500µm. This high ash content in our OPT 100-250µm might have caused the lower mass yield.

4.5 Comparison With other Types of lignocellulosic biomass

Some torrefaction studies for woody and grass biomass have been reported recently [Mark J. Prins , Krzysztof J. Ptasinski, Frans J.J.G. Janssen,2006]. It is reasonable to mention that major ash components are different between woody biomass and oil palm, and this may result in a different decomposition rate. The ash content especially the potassium content in the oil palm trunk could enhance the biomass decomposition. Therefore, we should be careful about the high potassium content in the ash and its effect on the torrefaction kinetics.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this work, we measured the energy properties of oil palm trunk(OPT) before and after various torrefaction conditions. Our results prove that the torrefaction parameters (temperature levels and durations) can be tune to obtain various products, ranging from native biomass to charcoal. In this study, torrefaction of oil palm trunk (OPT), which is typical agricultural waste in Malaysia, was experimentally conducted. The effect of torrefaction temperatures on the composition of the samples of different particle sizes was investigated for those two types of OPT at different torrefaction temperatures. 250µm-500µm OPT sample showed higher calorific value than 100µm-250µm for overall experimental run. 250µm-500µm OPT sample also gave quite reasonable mass yield values of 85.33% and 72.52% which is slightly higher than mass yield of 100µm-250µm OPT sample.

Therefore, all results are summarized by analytical expressions able to predict the energy properties as a function of the overall mass loss. These expressions are intended to be used in any decision-making process, including the overall optimization of the transformation chain, from production in the field to the final need.

1) Torrefaction parameters (Temperature levels and durations) can be tuned to obtain various products, ranging from native biomass to charcoal.
2) Mass loss is an excellent indicator of the treatment intensity and from the mass loss; the composition and energy properties of the sample can be predicted.
3) Different Particle size of samples will definitely affect the composition(CHN,Calorific Values and Ash Content) which will directly affect the mass and energy yields respectively.

5.2 Recommendations

- All equipments to be used for analysis of the samples need a proper maintenance.
- Better comparison and justification can be obtained if more samples can be torrefied at the same time, so a major modification needs to be done on the tubular reactor.

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APPENDICES

Appendix 1

EXPERIMENT CHECKLIST

1. SAMPLE: **Oil Palm Trunk**

   a. Temperature: **220 ^oC, 250^oC, 300 ^oC**

Torrefaction temperature(^oC) SIZE (µm)	**220 ^oC**	**250^oC**	**300 ^oC**
100 µm – 250 µm			
250 µm – 500 µm			

Experiment Summary:

- Sample
  - Oil Palm Trunk
- Retention Time (RT)
  - 30 min
- Sample Size
  - 100 µm – 250 µm
  - 250 µm – 500 µm
- Operating Temperature
  - 220 ^oC
  - 250 ^oC
  - 300 ^oC
- Nitrogen flow rate: 100ml/min

CHNS Analysis

Temperature (°C)	Carbon	Hydrogen	Nitrogen	Carbon	Hydrogen	Nitrogen
	100-250µm			250-500µm		
Untreated	44.35%	6.01%	1.12%	41.77%	6.01%	0.91%
220	43.20%	5.58%	1.09%	41.69%	5.75%	0.85%
250	44.62%	5.71%	1.16%	43.35%	5.89%	0.97%
300	45.36%	5.49%	1.23%	44.89%	5.11%	1.09%

Bomb Calorimeter(Calorific Values)

Temperature (°C)	Calorific Value(MJ/kg)			
	Dry OPT	220°C	250°C	300°C
100-250µm	15.987	18.165	19.121	21.305
250-500µm	16.902	19.08	20.036	22.22

Ash Content Analysis:

Sample	Ash Content	Ash Content
	100-250µm	250-500µm
Dry OPT	6.15%	4.54%
220°C	5.21%	3.23%
250°C	5.93%	4.46%
300°C	7.03%	4.91%