PHYSICAL CHARACTERIZATION ON HYDROTHERMAL CARBONIZATION AND TORREFACTION PRODUCT FROM WOOD FIBER WASTE

NORFATIN SAHIRA BINTI SAIDI

UNIVERSITI MALAYSIA PAHANG

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NORFATIN SAHIRA BINTI SAIDI

Report submitted in partial fulfilment of the requirements for the award of the degree of Bachelor of Chemical Engineering

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature

Name of Supervisor: DR SAIDATUL SHIMA BINTI JAMARI

Position:

Date:

STUDENT'S DECLARATION

I hereby declare that the work in this project is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature

Name : NORFATIN SAHIRA BINTI SAIDI

ID Number : KA09146

Date :

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ABSTRACT

The world today is faced with serious global warming and environmental pollution. Besides that, the fossil fuel will become decrease in the near future and also increasing prices of fuel cause awareness to find alternative energy. Carbon is one of the most abundant elements found on earth. Nowadays carbon is really useful in the chemical industries and the demand of carbon used is high based on its applications towards the human needed. Carbonization is one of the possible thermo chemical conversions of biomass into energy, where a solid residue known as charcoal is produced through a slow process of partial thermal decomposition of in the absence or controlled presence of oxygen. (Bridgewater, 2003). There are three objectives that need to achieve at the end of this research. The objectives are; to develop and demonstrate the technology of hydrothermal carbonization process; to compare the carbon particles produce from HTC process and pyrolysis process; to study the effect of the wood fibre waste used towards the production of carbon. The HTC process occurs in the excess of water. About1 liter water was used for every experiment of hydrothermal carbonization process. The reaction is based on catalyst which is 50ml of citric acid was used for every experiment of hydrothermal carbonization process.the reaction occur in the supercritical unit for temperature about 200^{o}C. The product obtained then was drying to remove the water contain. Second process which is the pyrolysis was run in the furnace by using the same operation condition as the HTC process. The differences between the process is the pyrolysis is no including water during the process. The process is about heating the wood fiber waste with absence of oxygen. Then the products were undergoing the physical characteristic testing by using Field Emission Scanning Electron Microscopy (SEM) and Nuclear Magnetic Resonance (NMR). After analyzing the sample from both process through FESEM and NM) the comparison was made. Through the FESEM characterization, the diameter of the sample and the morphology effect was determined. The comparison was made and the best sample shown by the sample from HTC process using 150g of wood fiber waste. The diameter of the sample shown about 7.3μm and the highest rupture occur at the surface of the particles. Results from NMR proves that the carbon content inside the sample was changes after undergo the HTC and pyrolysis process. The comparison was made and it shows that after undergo the HTC process the carbon content for cellulose and lignin was increased and HTC sample shows the content of aromatic lignin. Differ with pyrolysis process which does not contain aromatic lignin but for other content still increase after undergo the pyrolysis process. The proximate analysis also was done and it was found that HTC 175g WF gives the highest value of moisture content, HTC 150g WF gives the highest values of ash content with15.07%. for volatile content the highest values was the sample from pyrolysis 175g WF with 91.89% and lastly for calorific value proves the pyrolysis with 175g of WF give the highest calorific value with 24.88 MJ/kg.

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LIST OF SYMBOLS

µm	Micrometres
M	Molar
Mg	Milligram
g	Gram
hr	Hour
L	Litre
m	Meter
cm	Centimetre
%	Percentage
MW	Molecular Weight

LIST OF ABREVIATIONS

HTC	Hydrothermal Carbonization
TF	Torrefaction
FESEM	Field Emission Scanning Electron Microscopy
NMR	Nuclear Magnetic Resonance

CHAPTER 1

INTRODUCTION

1.1 Research Background

Carbon is one of the most abundant elements found on earth. Nowadays carbon is really useful in the chemical industries and the demand of carbon uses is high based on its applications towards the human needed. Naturally carbon was founded from earth which is residue from the petroleum refinery also called as coal or charcoal. As limited number of petroleum founded from days to days, other alternative was found in order to produce carbon particle continuously. One of the best alternatives is by converting the biomass into the carbonaceous materials. Biomass is defined as the biological material derived from living or recently living organisms. In the other words, biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, nitrogen and also small quantities of other atoms like alkali, alkali earth and heavy metal.

Biomass can be divided into several types which are wood and agricultural products, solid waste, landfill gas and biogas and alcohol fuels. The main focus of this research is on the wood waste. Wood waste like logs, chips, bark and sawdust accounts for about 46 percent of biomass energy. A large proportion of wood fiber wastes produce by the agricultural activities and forest today become global issues in managing the waste to be reused or recycled compared just thrown away to the landfill. Knowing the carbon used to construct biomass is absorbed from the atmosphere as carbon dioxide (CO_2) by plant life using energy from the sun. If the plant is broken down or die it will release the carbon back to the atmosphere mainly as either carbon dioxide (CO_2) or methane (CH_4) depending on the conditions and processes involved. As the wood fiber waste is thrown away to the landfill it will contribute towards the releasing back the carbon dioxide to the atmosphere. Besides that it by thrown away to the landfill it will reduce the space of earth. The proper way in managing, reusing and recycling the wood fiber waste is important in order to reduce the wood fiber waste in landfill.

Direct combustion is the old method in converting biomass into energy but only in about 10 percent of energy produce. The conventional method was not environmental friendly process since during the combustion the present of oxygen during process will cause the large amount of carbon dioxide release to the atmosphere. Usually the common way in converting the biomass into the value added product is by using pyrolysis process. The process of pyrolysis is about heating the biomass in specific temperature in absence of oxygen. The absence of oxygen during the process will help to reduce the carbon dioxide release to the atmosphere beside maintain the quality of the carbon produce. Pyrolysis can be divided into two types which is slow pyrolysis and fast pyrolysis. The key words that represented the pyrolysis process are temperature. Slow pyrolysis will occur if the reaction temperature less than 450^{o}C while the fast pyrolysis will occur when the temperature applied greater than 800^{o}C. New alternative was founded in converting the biomass to the carbon which called as hydrothermal carbonization process (HTC).

Hydrothermal carbonization process will convert biomass into the valuable product which is carbon particle based on thermal processes. Biomass is biological material derived from living, or recently living organisms. In the context of biomass for energy this is often used to mean plant based material. Actually biomass can equally apply to both animal and vegetable derived material. Besides that, biomass is carbon based and is composed of a mixture organic molecules containing hydrogen and usually including atoms of oxygen, often nitrogen and also small quantities of other atoms like alkali, alkaline earth and heavy metals. These metals are often found in functional molecules such as the porphyrins which include chlorophyll that contains magnesium.

Dehydration is the main chemical reaction in the hydrothermal carbonization process. This is due to the high carbon content in the final product. In the other words, hydrothermal carbonization is an exothermal process that lowering both the oxygen and hydrogen content of the feed using mainly dehydration. Carbonization is one of the possible thermo chemical conversions of biomass into energy, where a solid residue known as charcoal is produced through a slow process of partial thermal decomposition of in the absence or controlled presence of oxygen. (Bridgewater, 2003). There are a few parameters that need to be considering during the process take place which are temperature and pressure, time of reaction, volume of water and concentration of catalyst. All of the parameters will strongly affect the carbon produce at the end of the process. The comparison can be made and the best carbon produce can be choosing easily through the series of testing with different parameters applied.

Characterization is also important in analyzing the result obtained. The properties of the carbon produce can be obtained fro the characterization for example the chemical and physical characteristic of the carbon produce. The chemical characteristic is about the composition of the carbon produce and the physical characteristic is about the shape, color, the diameter of the carbon produce and others. Besides that, the comparison between the carbon produce from the pyrolysis and hydrothermal carbonization process can be done. The characteristic involve in analyze the morphology of the product. Morphology defined as the study of the physical characteristic of the sample in terms of surface area, shape of molecule, molecule content, diameter of the particle and others. Further study on the process will cover in chapter 2.

1.2 Problem Statement

Nowadays, a large proportion of the woody waste generated which consists of used particleboard, sawdust and others from the industrial activities becoming the global issue in terms of managing the wood fiber waste to be recycled compare to thrown-away to the landfill. Edward Madigan (2012) state that since the turn of this century, world has been dubbed by some “the throw-away society”, and it generates 50 percent of the world’s solid and industrial waste. “The throw-away society” is the society that just simply thrown away the rubbish to the landfill. Almost half the municipal solid waste that goes into landfills consists of paper and wood fiber.

Based on the above facts, concern about the global warming and environmentally friendly processes for converting the wood fiber waste to the value added product is raised. Also the need for research that aims to develop clean technology or in the other words new process that reduces waste and pollutants is mentioned. From this problem, the new and environmentally sustainable process of carbon was developed through aqueous media. This process called as the hydrothermal carbonization process (HTC). Hydrothermal carbonization process is the process that converting biomass into value added product with less environment pollution effect due to no carbon dioxide release during the process. The process is about to lower the oxygen and hydrogen content of the feed using mainly dehydration process. The process is exothermic process which occurs at high temperature in range 180^{o}C – 300^{o}C and under pressure.

1.3 Research Objectives

There are three objectives that need to be achieving at the end of this research. The objectives are:

1. To develop and demonstrate the technology of hydrothermal carbonization process.
2. To make a comparison of carbon produce from the hydrothermal carbonization process and pyrolysis process.
3. To study the effect weight of biomass used on morphology characteristic.

Hydrothermal carbonization is the method in producing carbon particles with wood fiber waste as the raw material.This process is one of the alternatives on converting the biomass into the value added product. The process of hydrothermal carbonization occur subcritical condition in which at high temperature and pressure. The detail of the hydrothermal carbonization process will be discussed in section 2. Since the old method of converting the biomass is pyrolysis process, the comparison of the carbon produce from the HTC process and the pyrolysis was made. The comparison was made in terms of physical characteristics. The characteristic of the product will be investigated through Field Emission Scanning Electron Microscopy (FESEM) and Nuclear Magnetic Resonance (NMR) and the result obtained from the characterization will be used to make the comparison. The further characterization process will be discussed on chapter 3.

1.4 Significance of Proposed Study

The study is about the production of the carbon from the process of hydrothermal carbonization process by using wood fiber waste as the biomass. Hydrothermal carbonization process is the most environmental friendly process as the carbon dioxide (CO_2) release through the process is less compare to the combustion. This is because the process is dehydration process which is only oxygen and hydrogen will release as the carbon need to be in solid form. Besides that this process will reduce the waste of wood by converting the waste to value added product which is carbon. As the result, the wood fiber waste generated will be recycled and it will reduce the waste and pollution to the landfill.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The main resource for the literature search was the research journal with title “The Production of Carbon Materials by Hydrothermal Carbonization of Cellulose”. This source was really fulfilled with the title of the research which is “Morphology Studies on Hydrothermal Carbonization Product from Wood Fiber Waste”. Combinations of the following keywords were used to identify relevant material; carbon particles, wood fiber waste, hydrothermal carbonization process and others.

A limited number of studies were found that carbon particles give many applications in the chemical industries. Kim (2011) states in his article titled “Electrochemical Uses of Carbon” that the carbon is the one of the most abundant elements found on earth. According to Titirici et al (2009), carbon particles are synthesized under hydrothermal conditions using different biomass (glucose, xylose) and biomass derivatives (s-hydroxymethyl-furfural-1-aldehyde and furfural) as a carbon sources. The emergent themes may be divided into five broad areas; history and background of carbon particles; properties of carbon particles; application of carbon particles; wood fiber waste; and hydrothermal carbonization process.

2.2 Wood Fiber Waste as Biomass

According to Jay (2012), biomass is defined as any organic material that comes from plants or animals. The others research from Libra et al (2011) stated that biomass has been assigned many roles to play in strategies for sustainable consumption. In addition, other than being a food source and renewable raw material, it can be used for energy production, carbon sequestration and finally, as an essential element to increase soil fertility. Biomass energy resources are plentiful. Anything that will decompose and burn can be used as biomass energy. Grass clippings, animal waste, corn stalks, acorns, tree limbs, meal scraps and others can all be used for biomass energy. The utilization of woody biomass for a variety of products, including energy, has increase in recent years. Based on DeAnna (2011), due to the growing interest in climate change, the environment, and energy security, woody biomass is receiving more attention as a renewable energy source. Woody biomass has become the topic of intense regarding its sustainability, cost effectiveness and greenhouse gas impact.

Recycling today constitutes that most environmentally friendly method of managing wood waste. A large proportion of the wood generated consists of used furniture and other constructed wooden items, which are composed mainly of particleboard, a material which can be potentially be reused. (Charalampos et al, 2007). Similarly, the other research from Todd et al (2007), woody biomass holds a great potential as a renewable source for bio-based materials, feed stock and energy. Besides that the use of renewable energy has been widely discussed as an alternative to fossil fuels. The biomass, consisting mainly of agricultural and forestry waste can be regarded as a renewable energy source with potential to supply the global energy demands. Moreover the use of biomass contributes to reduce the greenhouse effect. (Marcela et al, 2011). The information gain from U.S Energy Information website (2008), biomass energy is derived from three distinct energy sources: wood, waste, and alcohol fuels. Wood energy is derived both from direct use of harvested wood as a fuel and from wood waste streams. The largest source of energy from wood is pulping liquor or “black liquor,” a waste product from processes of the pulp, paper and paperboard industry.

Besides that Robert (1993) state that we are facing a serious challenge in the United States in dealing with municipal waste landfills that are near or at capacity. Wood waste including wastepaper, construction waste, demolition waste, and tree trimmings make up a significant portion of this municipal waste.

2.3 Effect of Wood Fiber Waste on Environment

As the demand for biomass has grown, so has the number of criticisms and misconceptions about it. One of the major effects of biomass towards the environment is that the burning of biomass as fuels releases carbon dioxide (CO_2) and other greenhouse gases which are contributing to global warming. In reality, woody biomass is a carbon neutral energy source. According to DeAnna (2011), trees are part of an atmospheric cycle. As they grow, they absorb carbon from the atmosphere temporarily storing it. When a tree dies, the same amount of carbon that it absorbed during its lifetime is released back into the atmosphere as it decomposes, adding no new carbon to the atmosphere. When woody biomass is burned to produce to produce energy, it released that same amount of carbon that would have naturally been released if the tree had been left to decompose on the forest floor.

Other research from Roger *et al* (2010), wood material is composed of about 50% carbon by dry weight, this carbon having been drawn from the CO_2 removed from the atmosphere by the growing tree. In other words, wood products provide a physical storage of carbon that was previously in the atmosphere as a greenhouse.

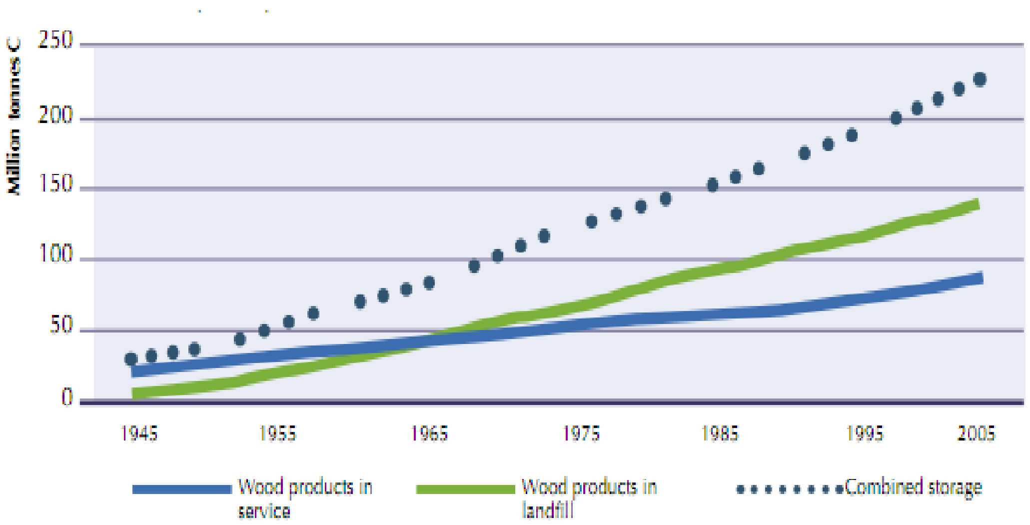


Figure 2.1 Net carbon storage in wood and paper product and landfills in Australia. (Source: Australian Greenhouse Office Wood Products Model)

The figure 2.1 shows that the carbon storage in the wood product and landfills in Australia is increase every year. It proves that the wood fiber is the best carbon removal from the atmosphere which is contributing in decreasing the effect of greenhouse. However, burning biomass for energy provision increase the amount of carbon in the air just like burning coal, oil or gas if harvesting the biomass decreases the amount of carbon stored in plants and soils or reduces carbon sequestration.(Helmut et la, 2012). Based on Aaron (2012), the rate at which trees release that CO_2 depends on how they are managed by human. If the tree is allowed to die and rot, its carbon is released into the soil. If the tree burns up in the forest fire it will release its carbon into the atmosphere instantly. The high rate of carbon storage can be maintained by transforming the trees into lumber. By storing the carbon in the form of lumber, the carbon released into the air can be offset by others means.

2.4 Hydrothermal Carbonization Process

There are many methods to produce advanced materials. One of them is hydrothermal processing. This technique enables the production of complex materials with interesting physicochemical properties. A wide range of materials such as metals, oxides, hydroxides, silicates, carbonates, phosphate and sulphates are being produces by this technique as nanostructure particles. (Guiotoku et al, 2011). Carbonization is one of the possible thermo chemical conversions of biomass into energy, where a solid residue known as charcoal is produced through a slow process of partial thermal decomposition of wood in the absence or controlled presence of oxygen. (Bridgwater, 2003). Same goes to Langner (2008), the HTC is an promising process to produce coal from biomass. Imitating the natural way of coalification in a chemical process, it has several advantages. One of them is the fact that no undesired byproducts produces. Particularly there will be no CO_2 as byproduct. This is a big difference to most of the other biomass energy processes. So by storing away the carbon for example as a newly-developed carbon-based insulating material, the process is able to reduce the CO_2 in the atmosphere. From the above statement it confidently prove that this process is more green and environmental friendly.

According to Yoshimura and Byrappa (2008), a hydrothermal process can be defined as any homogenous or heterogeneous chemical reaction in the present of solvent (whether aqueous or non-aqueous) above room temperature and at pressure greater than 1 atm in a closed system. Basically, the method consists of heating the biomass in the presence of a catalyst in a closed vessel under pressure, at temperature ranging from

180^oC to 300^oC, with reaction times between 1 and 48 hours. Thus, the hydrothermal carbonization allows the use of stored energy in biomass more efficiently. Theoretically, in anaerobic conversion, about 18% of energy is lost and 50% of carbon is released as carbon dioxide. In the HTC process, the carbon efficiency is very close to 100 which means the almost the carbon from biomass is converted into carbonized material, without generating CO and CO_2. (Titirici, 2007)

Some studies from Ramke *et al* (2009), hydrothermal carbonization (HTC) is a chemical process which emulates the natural coalification of biomass. First experiments were carried out by Bergius (1913), who described the hydrothermal conversion of cellulose into coal-like materials, and systematic investigations were performed in the nineteen-thirties. The process was rediscovered some years ago at the Max-Planck Institute of Colloids and Interfaces in Golm/Potsdam (MPI), where comprehensive state-of-the-art experiments helped to understand the process much more in detail. In co-operation with the MPI the University of Applied Sciences Ostwestfalen-Lippe started the first feasibility study on the HTC process using organic waste, funded by the DBU (Deutsche Bundesstiftung Umwelt), in 2007. Within the scope of this project more than 100 carbonizations were performed in a 25-litre pressure vessel. For hydrothermal carbonization to take place, plant-based products such as leaves, straw, grass, wood chippings or fir cones are placed in a pressure vessel together with water and a suitable catalyst. The reactor is then closed, and under air-exclusion is heated under pressure. The HTC process generally takes place at temperatures between 180°C and 220°C over a 4 to 12 hour period, after which, the mixture is cooled down and the vessel is opened: It now contains a black watery fluid comprised of finely dispersed spherical carbon particles (colloids). Carbon which was formerly bound in the organic material now lies in front of us in particle form as small, porous brown-coal spherules.

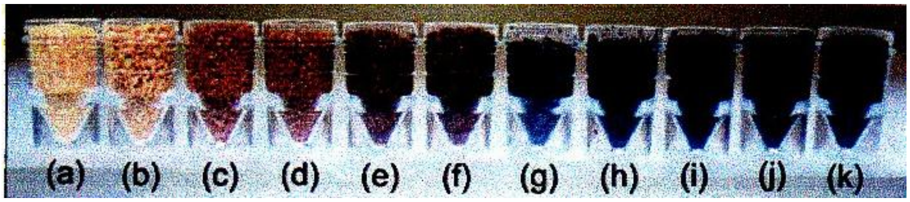


Figure 2.2 Hydrothermally carbonized of pine sawdust with different catalyst concentration. (Sevilla,2009)

The conventional methods of converting biomass into renewable energy are based on thermal, biochemical or physical processes. The raw materials of the pine dust will undergo the hydrothermal carbonization in the reaction vessel with some amount of water and in the present of catalyst. Based on the figure above, it proves that with different concentration of catalyst will produce different quality of the carbon. The sample labeled (a) with no catalyst added show no changes and no carbon produce. For sample (k) use the highest concentration of the catalyst. The result show the best quality of carbon produce and it can be say the highest conversion of sawdust to the carbon.

Figure 2.3 Equipment Used for Hydrothermal Carbonization Process (Remke *et al*,200)

2.5 Reaction Mechanism

Based on Nicole *et la* (2011), hydrothermal carbonization was first experimentally explored as a means to produce coal from cellulose in 1913 by Bergius. Hydrothermal carbonization is a process which already has a long history and one of the possible processes that will help in reducing the CO_2 release from the wood fiber waste. In the ongoing discussion about global warming one remarkable aspect has until now largely escaped consideration which is the huge CO_2 and methane emissions produced by unused biomass. This means that the everyday decomposition of dead plant material results in the production of innumerable tons of CO_2 which is continuously making its way into the atmosphere.

Titrici et al, Sevilla and Fuertes, and Funke and Zeigler report that char formation results from a seris of hydrolysis, condensation, decarboxylation and dehydration reactions. Referring on Nicole et al (2011), water is a necessary and key ingredient of hydrothermal carbonization. As temperature increase, the physical and chemical properties of water change significantly, mimicking that of organic solvents.

In hydrothermal processes, the solid material is surrounded by water during the reaction, which is kept in a liquid state by allowing the pressure to rise with the steam pressure in high-pressure reactors. Knowing that water is easily evaporate at the certain condition, in order to get the pure of carbon the product need to be drying about several hour to make sure there is no more water contain.

As in dry pyrolysis, reaction temperature and pressure determines the product distribution. With process temperatures of up to 220°C and corresponding pressures up to approximately 20 bar, very little gas (1–5%) is generated, and most organics remain as or are transformed into solids. At higher temperatures, up to approximately 400°C, and with the use of catalysts, more liquid hydrocarbons are formed and more gas is produced. This so called ‘hydrothermal liquefaction’ has drawn some interest, although most liquefaction work is performed using organic solvents instead of water. If the temperature and pressure are increased further, the supercritical state for water is reached and the primary product is gaseous (hydrothermal gasification). Depending on the process conditions, either more methane or more hydrogen is generated; char is not yielded in noticeable amounts.(Libra et la,2011)

Table 2.1 Differences between process (Libra *et al*, 2011)

Process	**Reaction conditions (temperature oC): vapor residence time)**	**Product distribution (weight %)**		
		Char	**Liquid**	**Gas**
Pyrolysis :slow	~400:h-week	35	30	35
Pyrolisis : intermediate	~500: ~10-20s	20	50	30
Pyrolisis : fast	~500:s	12	75	13
Gasification	~800: ~10-20s	10	5	85
HTC	~180-250:no vapor residence time, ~1-12h processing time	50 – 80	5 -20 (dissolved in process water, TOC)	2-5

2.6 Exothermic Process

Hydrothermal carbonization (HTC) is a relatively simple exothermic process involving the application of moderate heat and pressure to biomass feed stock to create a carbon or coal. The process lowers both the oxygen and hydrogen content of the feedstock by dehydration and decarboxylation, while maintaining carbon efficiency. Exothermic process is the process that generates energy or heat during the hydrothermal carbonization process occurs. Even in an exothermic reaction in which the change in enthalpy between the products and the reactants is negative, there must be an input of energy to start the reaction.

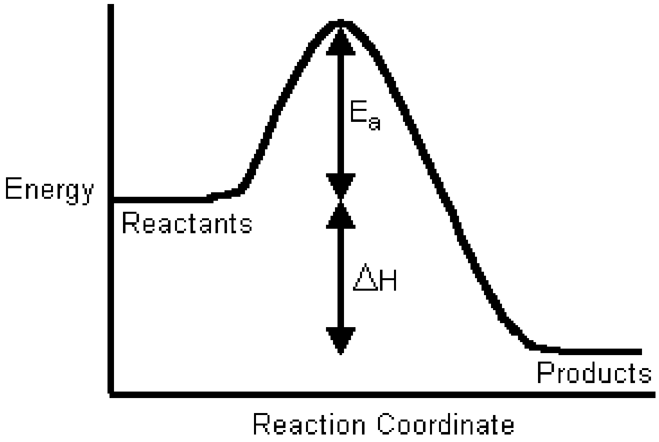


Figure 2.4 Exothermic Process

Hydrothermal carbonization is an exothermic process due to high energy require for dehydration to occur which means that the high temperature require for the sufficient energy for the process to occur. Besides that, during the process occur heat will be release to avoid the over pressure inside the reactor.

2.7 Process Parameters

The series of test will be performed to identify which parameters will effect the conversion of the carbon. Based on theory of hydrothermal carbonization process, the HTC process generally takes place at temperatures between 180°C and 220°C over a 4 to 12 hour period, after which, the mixture is cooled down and the vessel is opened. (Remke *et al*,2009). From theory it prove that there are about 4 parameters that need to consider during the process. The first one is temperature and pressure, volume of water, time of reaction and concentration of catalyst. All of the parameters will strongly affect the product obtained at end of the experiment.

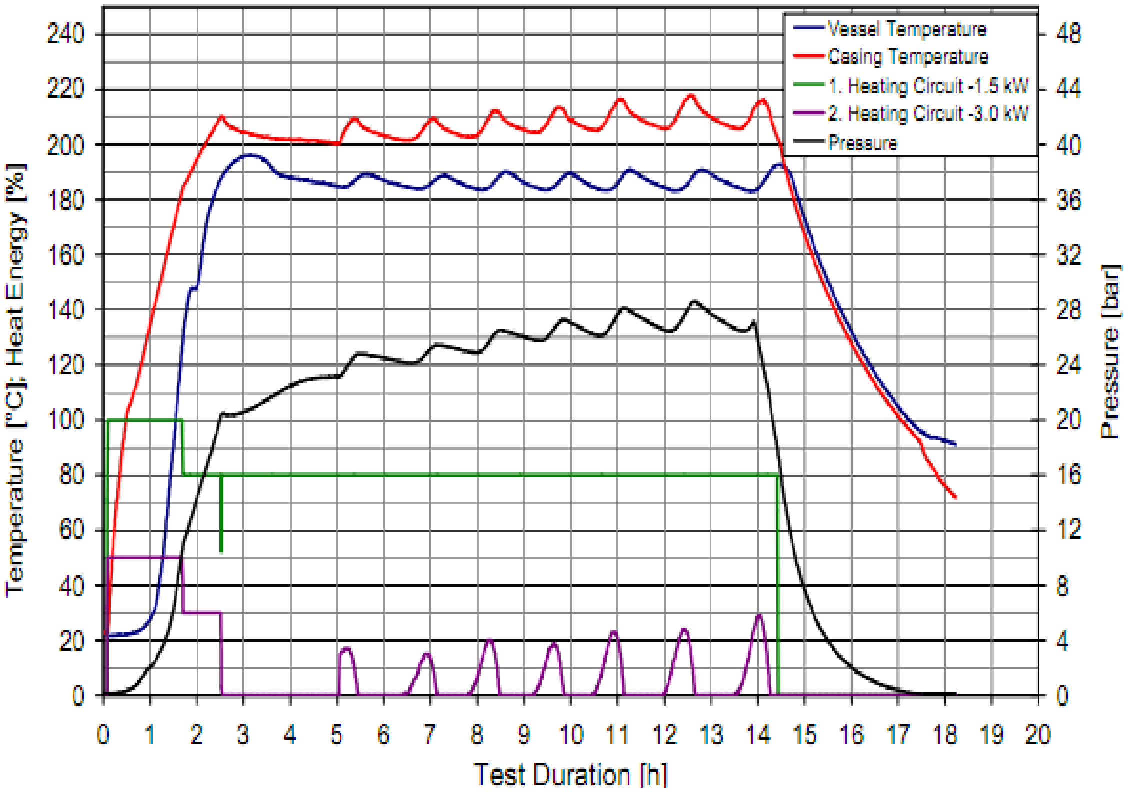


Figure 2.5 Process Parameters of Typical HTC Process (Remke *et al*, 2009)

Referring to Remke *et al* (2009), in pursuit of optimizing the process conditions, the temperatures of the reaction have been varied. In particular, the temporal adaptation of the reaction temperatures to the carbonization process led to a marked intensification of the processes and to a significant reduction of the reaction time. The process-linked temperature regulation subsequently led to an improvement to the properties of the HTC-Biochar. Precisely, the fuel qualities (C-content, calorific value) of the HTC-Biochar can be positively influenced. Furthermore, it has ascertained that, in the catalyzing effect of additives there is a significant potential available for the intensification and steering of hydrothermal reactions.

The other research Sevilla(2009) prove that the concentration of catalyst used during the process is strongly effect the properties of the carbon produce. The figure below shows the increasing concentration catalyst used at different test. As the concentration of the catalyst used increase, the properties of the carbon produce become better.

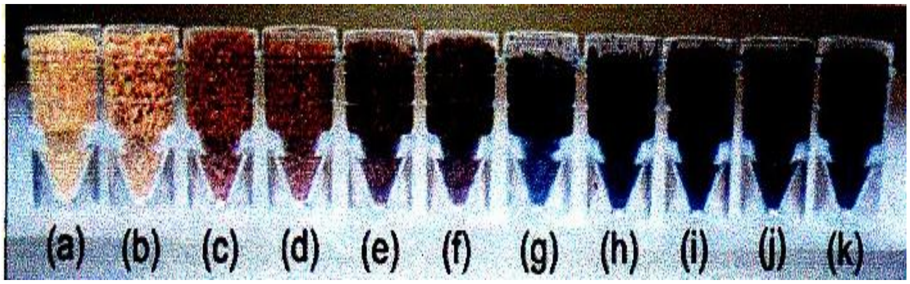


Figure 2.6 Hydrothermally carbonized of pine sawdust with different catalyst concentration. (Sevilla,2009)

2.8 Dewatering and Drying Properties of Carbon Produces

The advantages of HTC for energetic use of organic wastes with high moisture contents can only be assessed if the complete process chain of conditioning and utilization is considered. It is necessary to drying the mixture in order to get high purity of the carbon particle. Some studies from Remke *et al* (2009), special test equipment has been developed for this purpose. Dewatering tests are oriented on the usual techniques for sewage sludge dewatering. By using a press, normally used for testing building material, a cylinder filled with wet HTC-Biochar is put under a constant pressure of 15 bars. The discharge of water is passed over a filter plate and caught in electronic scales. Figure 2 illustrates the progress of discharge of water against time (curves of total volume related to the original mass of water).

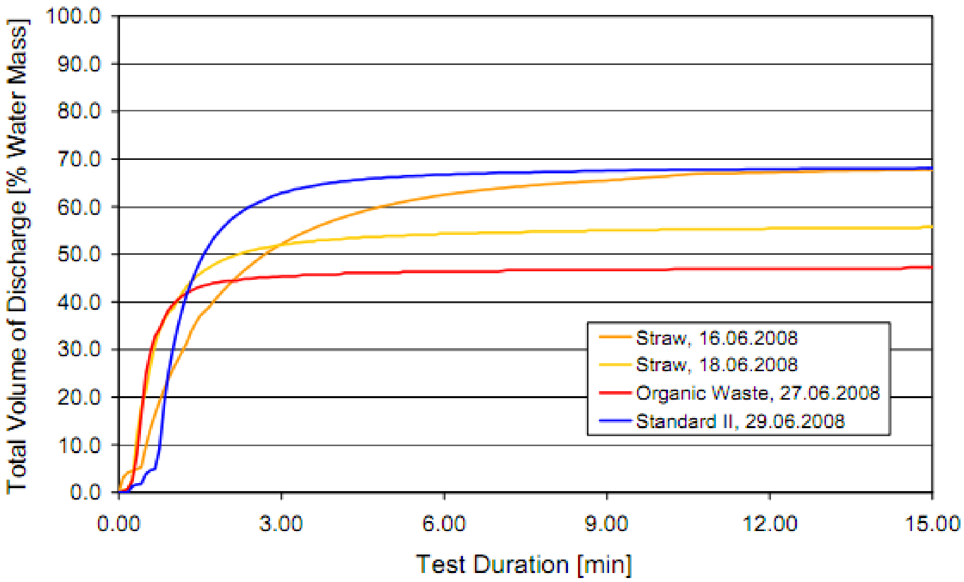


Figure 2.7 Examples of development of discharge in dewatering tests with various substrates (Remke *et al*,2009)

Comparison of the curves of discharge enables an assessment of the dewatering properties of the different materials at start and after hydrothermal carbonization under varying process conditions. Analogies with sewage sludge indicate that dewatering properties of sewage sludge after carbonization are actually much better than that of non-carbonized sewage sludge. This leads one to expect that this also applies to other wastes with high moisture contents.

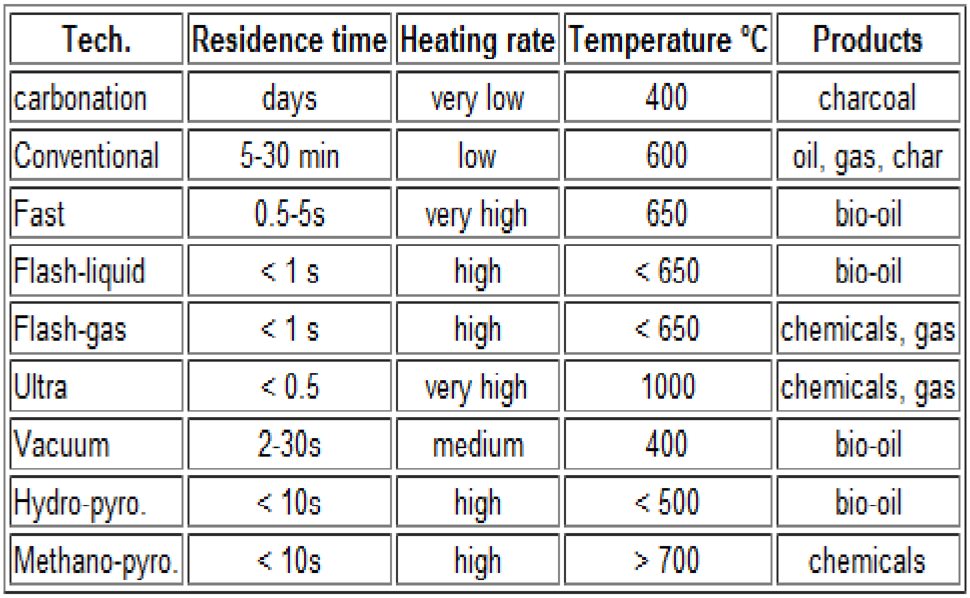
After water was separated with carbon product, the sample need to be dry to eliminate the water contain inside the carbon particles. From that dry carbon in form of powder can be obtained. Normally drying process occurs in the closed oven to make sure the water content is fully evaporate. Besides that if the less water content inside the carbon particles, the sample can be dry by let it in the room temperature about several hours. This is because water molecule is easy to evaporate in a little amount. Based on Remke *et al* (2009), the drying tests are performed in an enclosed test cell, in which warmed air is passed over a 30 by 30 cm test sample. For the determination of evaporation once again electronic scales are used, upon which the test sample lies. By comparing the evaporation behavior of different HTC-Biochars, it possible to make relative conclusions about the drying properties. In the course of further testwork, the measurements will be calibrated against those from natural brown coal.

2.9 Pyrolysis Process

Direct combustion is the old way of using biomass. The biomass is completely transformed into heat, but the efficiency is just about 10 percent. Besides that by direct burning the biomass, the CO_2 release from the process will cause the environment effect which contributing towards the greenhouse effect. Pyrolysis is the other method or in the other words as the pre treatment of the biomass before converting to the energy. Pyrolysis is a thermo-chemical decomposition process process in which organic material is converted into a carbon rich solid and volatile matter by heating in the absence of oxygen.(Demirbas and Arin,2002). The solid termed variously as char, biochar, charcoal or coke, is generally of high carbon content and may contain around half the total carbon of the original organic material. Based on Salman (2009), depending on the thermal environment and final temperature, pyrolysis will yield mainly biochar at low temperatures which is less than 450 ^{o}C and mainly gas at high temperature which is greater than 800^{o}C with rapid heating rates.

The temperature profile is the most important aspects of operational control for pyrolysis process. For fast pyrolysis a rapid heating rate and rapid rate for cooling primary vapors are required to minimize the extent of secondary reactions. These reaction not only reduce the liquid yield but also tend to reduce its quality which is giving more complex mixture.(Bridgwater and Peacocke, 2000). Conversely, in slow pyrolysis there is some evidence that slow heating leads to higher char yield, but this is nor consistent.(Antal and Gronli,2003). Slow pyrolysis can be divided into traditional charcoal making and more modern processes. It is characterized by slower heating rates, relatively long solid and vapor residence times and usually a lower temperature than fast pyrolysis, typically 400oC. The target product is often the char, but it always be accompanied by liquid and gas products although these are not always recovered.

Table 2.2 The variant of pyrolysis process. (Brownsort,2009)



Tech.	Residence time	Heating rate	Temperature °C	Products
carbonation	days	very low	400	charcoal
Conventional	5-30 min	low	600	oil, gas, char
Fast	0.5-5s	very high	650	bio-oil
Flash-liquid	< 1 s	high	< 650	bio-oil
Flash-gas	< 1 s	high	< 650	chemicals, gas
Ultra	< 0.5	very high	1000	chemicals, gas
Vacuum	2-30s	medium	400	bio-oil
Hydro-pyro.	< 10s	high	< 500	bio-oil
Methano-pyro.	< 10s	high	> 700	chemicals

A wide range of biomass feedstocks can be used in pyrolysis processes. The pyrolysis process is very dependent on the moisture content of the feedstock, which should be around 10%. At higher moisture contents, high levels of water are produced and at lower levels there is a risk that the process only produces dust instead of oil. High moisture waste streams, such as sludge and meat processing wastes, require dring before subjecting to pyrolysis. (Salman,2009)

2.10 Characterization Process Using FESEM and NMR

Characterization is an important part during the experimental work. This is because characterization helps the result from the experimental work to be more valuable and more detailed. Through the characterization data, result can be analyzed easily based on properties shown during the characterization. SEM and NMR are the example of characterization equipment used to scan the physical characteristic of the sample.

2.10.1 Field Emission Scanning Electron Microscope (FESEM)

The field emission scanning electron microscope is an electron microscope that images the sample surface by scanning it with a high energy beam electrons. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image while the scanning electron microscope creates the magnified images by using electrons instead of light waves.(Joshi *et al*,2008)

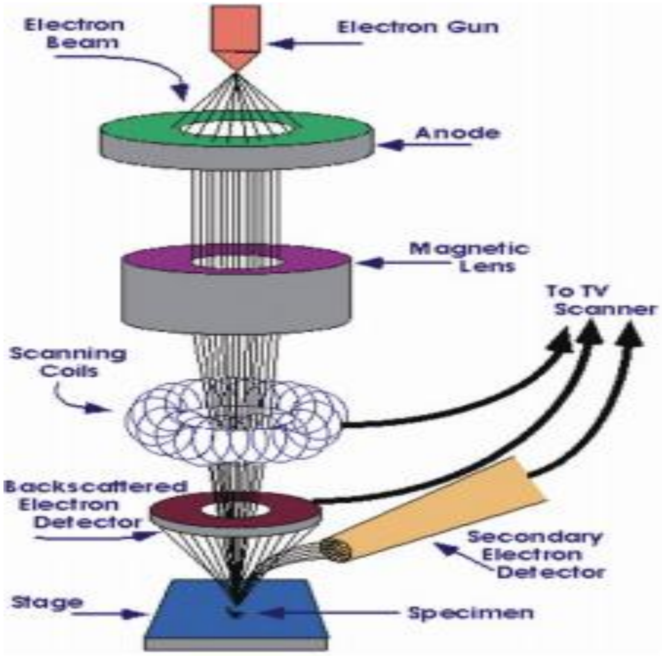


Figure 2.8 Schematic Diagram of FESEM (Joshi *et al*, 2008)

The FESEM produces clearer, less electro statically distorted images withspatial resolution down to 1 ½ nm, which is 3 to 6 times better than conventional SEM. Besides that the smaller area contamination spots can be examined at electron accelerating voltages compatible with Energy Dispersive X-ray Spectroscopy.

2.10.2 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance can be used to study the structure of molecules, the interaction of various molecules, kinetics or dynamics of molecules and the composition of mixtures or composites. It is a research technique that exploits the magnetic properties of certain atomic nuclei to determine physical and chemical properties of atoms. The NMR can provide detailed information about the structure, dynamics, and reaction rate and chemical environment of molecules.

2.11 Historical and Background of Carbon Particles

The English name of carbon comes from Latin carbo means coal and charcoal. Besides it also comes from French charbon, meaning charcoal. Carbon was discovered in prehistory and was known in the form of charcoal and soot. Rene' (1722) demonstrated that iron was transformed in steel through the absorption of some substance, now known to be carbon. Besides that Antoine (1772) showed that diamonds are a form of carbon when the samples of charcoal and diamond was burned and found neither produced any water and that both released the same amount CO_2/gram. In 1985, amore exotic form of carbon is called 'buckyball' was discovered. Kim (2011) stated in his article that the carbon form has a structure similar to a soccer ball. This discovery led to the 1996 Noble Prize in Chemistry to H.W.Kroto, R.F.Curl and R.E.Smalley.

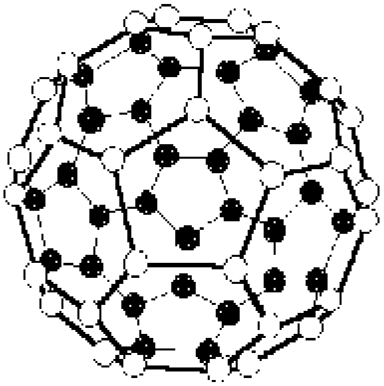


Figure 2.9 'Buckyball' formed of carbon

Referring to the figure 2.1 above, Kim (2011) stated that the structure of buckyball contains 60 carbon atoms in a spherical structure consisting 20 hexagons and a 12 pentagons arranged on the surface. The more scientific name for this form of carbon is fullerence, based on the name of person that developed the architectural structure known as the geodesic dome, Buckminster (1983).

2.12 Carbon Particles from HTC Process

Many types of biomass including different organic wastes from households and industries were successfully carbonised. At the end of the process the solid phase, the "HTC-Biochar", can easily be separated from the water. Approximately 75 - 80 % of the carbon input is found in the solid phase; about 15 – 20 % is dissolved in the liquid phase, and the remaining 5 % are converted to gas (mainly carbon dioxide). The liquid phase is highly loaded with organic components, which are easily degradable.(Ramke et al, 2009). Unlike traditional bioenergy processes, such as combustion or gasification, the HTC process allows the use of a biomass feed stock with inherently high water content such as those typical of pulp and paper and municipal waste streams. This characteristic removes the need for the energy-intensive and costly drying pre-treatment which is common in other bioenergy processes. The resulting product of the HTC process is a Bio-Coalwater-slurry. The Bio-Coal fraction can easily be separated and processed into a powder, pellet or briquette form, each with outstanding storage and transport characteristics.

2.13 Application of Carbon Particles.

Based on the properties of each type of carbon particles, there are wide applications of carbon particles in the industry. According to International Carbon Black Association (2006), carbon blacks is very useful in production of tires, rubber and plastic products, printing ink and coating is related to properties of specific surface area, particle size and structure, conductivity and color. In addition, carbon black is also in the top 50 industrial chemicals manufactured worldwide, based on annual tonnage.

Some information from online article also agreed that carbon black finds practical use in rubber products and it is used extensively with rubber tires. With rubber tires, carbon black is used as a pigment and reinforcing shield that helps to divert heat away from the tread and belt area, thereby reducing thermal damage and extending considerably the average life of tire. Nevertheless, it is used in all rubber applications where tensile strength and abrasion wear properties are essential. (Carrboncycle.biz, 2007-2011).

Some studies have examined the application of carbon particles towards chemical industry. Kim (2011) agreed that carbon has played a major role in the industrial electrochemical production of many chemical materials such as chlorine and caustic, aluminum metal and organic chemicals. Carbon is formed into solid structure that serves as the electrode sites where electrochemical reactions occur and products are formed.

CHAPTER 3

METHODOLOGY

3.1 Research Design

The research is design in order to study the comparison of the physical properties of the carbon produce from the two different methods which are hydrothermal carbonization process and the pyrolysis process. Hydrothermal carbonization process was run in supercritical unit at specific condition. The HTC process generally takes place at temperatures between 180°C and 220°C over a 4 to 12 hour period, after which, the mixture is cooled down and the vessel is opened. Then the pyrolysis was run with same amount of wood fiber waste as hydrothermal carbonization process. Pyrolysis was run under temperature400^{o}C in the furnace. The process is about heating the wood fiber waste in the absence of oxygen, since the oxygen will cause the combustion. The product produce from both processes was then analyzed by using field emission scanning electron microscope (FESEM) and nuclear magnetic resonance (NMR).

3.2 Raw Materials and Equipment

3.2.1 Raw Materials

Wood fiber waste was used as the raw material in this study. The wood fiber waste was directly used as it is supply from Laboratory of Chemical Engineering and Natural Resources. The wood fiber waste was weight about 150 g and 175g. Figure 3.1 illustrate the sample before processing. The process occurs in the excess of water. About1.5 liter water was used for every experiment of hydrothermal carbonization process. The reaction is based on catalyst which is 50ml of citric acid was used for every experiment of hydrothermal carbonization process. For pyrolysis process no need to include water and catalyst as the process is only heating the wood fiber waste in the absence of oxygen.

Figure 3.1 The sample before processing

3.2.2 Citric Acid Preparation

Citric acid was acted as the catalyst for hydrothermal carbonization process which it helps in increasing the rate of reaction without effect the product produces. Citric aced was prepared by making a dilution of the citric acid powder. About 50ml of citric acid with 0.5M was prepared for every sample. The dilution was made by using the above equation:

$$M_1V_1 = M_2V_2$$

M_1 = initial molarity (8.66601M)

M_2 = final molarity (0.5M)

V_1 = initial volume

V_2 = final volume (50mL)

By using above equation, the required V1 was determined and it was multiply with density of the citric acid to determine the mass of citric acid required for dilution. After make a calculation, about 4.7g of citric acid powder was required for preparing 50mL of citric acid. Then, 4.7g of citric acid was added into 50mL of distilled water and it was stirred to make sure well mixed. About 4 set of 50mL citric acid was prepared for HTC process.

3.3 Hydrothermal Treatment of Wood Fiber Waste.

The hydrothermal carbonization process was conducted through the supercritical unit Buchiglauster model shown in figure 3.2. The unit and the monitor were switched on. The reactor was lift down so that the sample can be put in the reactor. About 150g of wood fiber waste was put in the reactor with 1 liter of water. The mixture was stirred to make sure it mixed well. Citric acid catalyst was pouring in the mixture. After the mixture was mixed well, the reactor was lifted up and the tied with screw. This is to make sure during the process no pressure release since the process in under pressure. As the reactor was tied up, the temperature was set at 200^{o}C and the stirrer was on at 50 rpm. The over temperature was set as 300^{o}C as the unit only can withstand at 350^{o}C. Then the power is switched on and the process profile was display at the monitor. The reaction was run about 4 hours and after that the cooling process will occur about one night. After the cooling process, the stirrer and the motor was switched off. The screw was opened and the reactor was lift down to collect the sample. As the first reaction was complete, the process was repeated by using 175g of wood fiber waste.

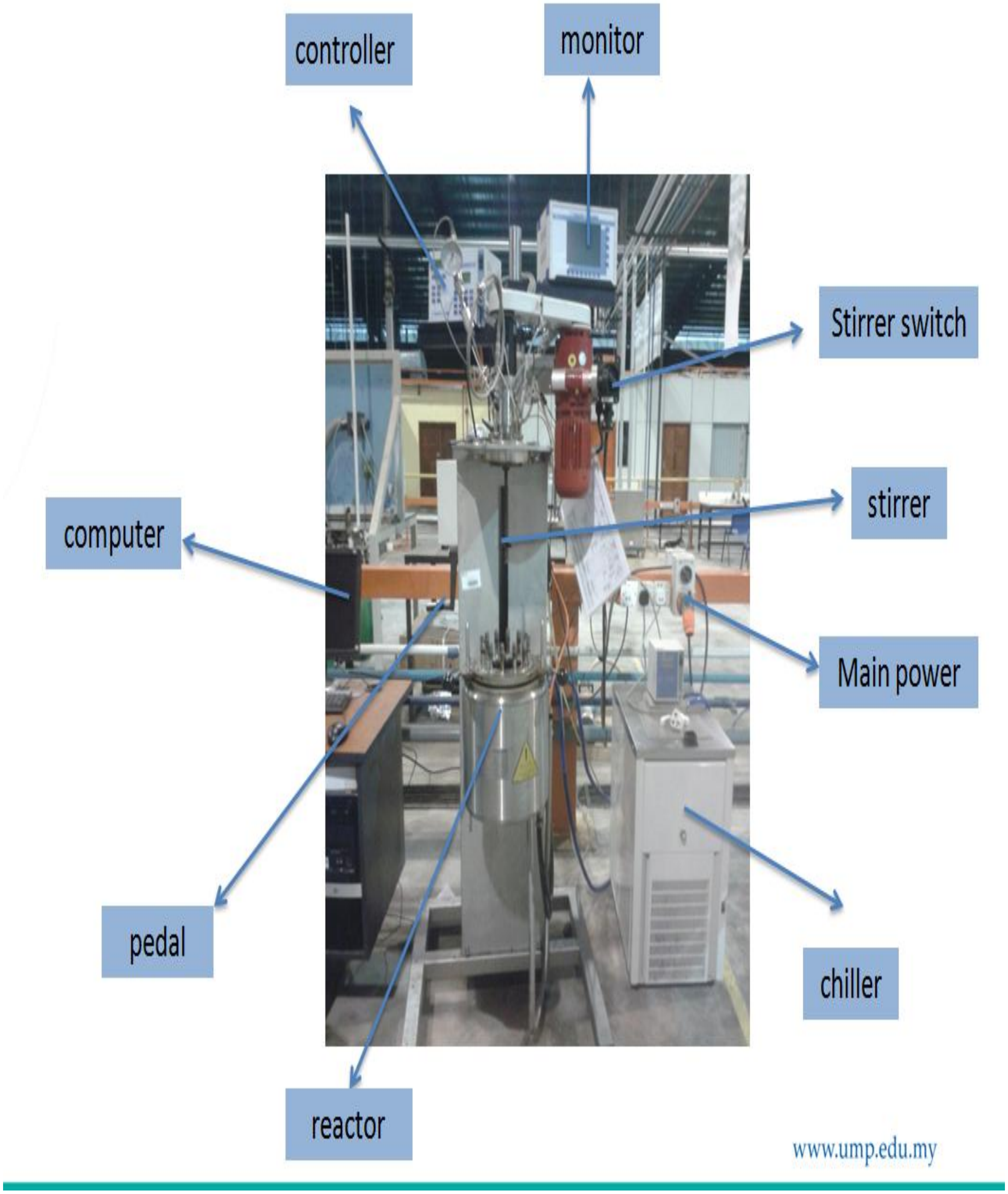


Figure 3.2 Supercritical unit Buchiglauster model.

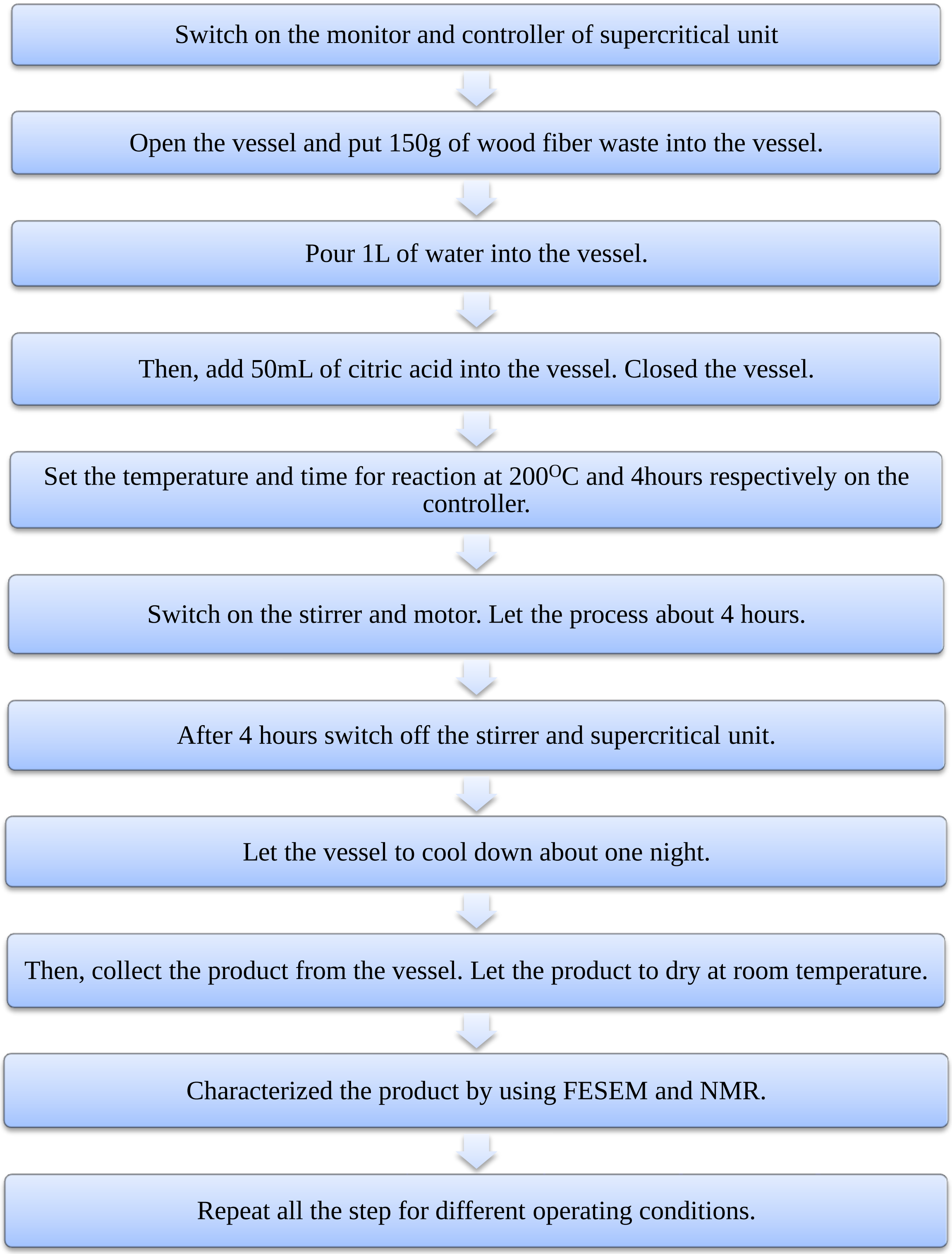


Figure 3.3 Flowchart for the hydrothermal carbonization process.

3.4 Pyrolysis Process

Pyrolysis process was conducted in the furnace at temperature 200^{o}C. About 150g of wood fiber waste was weighted by using analytical weight. Then the weighted wood fiber waste was put in the clay plate to make sure the plate can withstand the high temperature in the furnace. Then the plate clay was wrapped with aluminum coil to make sure there is absence of oxygen during the heating process. The sample was then placed in the furnace. The temperature of the furnace was set at 200 ^{o}C for about 6 hours. After the heating process the cooling process will take place. Then repeat the experiment with 175g of wood fiber waste.

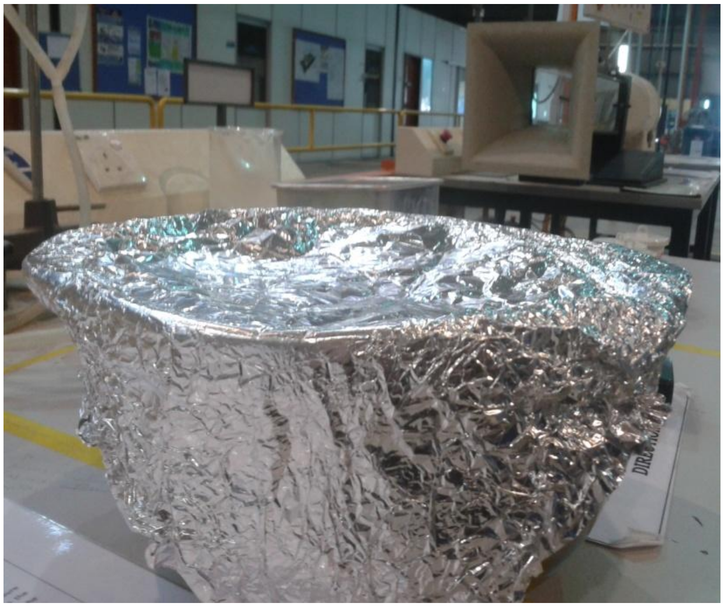


Figure 3.4 Sample wrapped with aluminium coil

3.5 Carbon Characterization

The carbon characterization is important to determine the characteristics of the carbon produced and thus determine the structure properties of the carbon produced. The property of carbon produced is analyzed based on morphology characteristics which is the diameter size of particles, the shape of the particles and the surface area of the particle. This can be done through Field Emission Scanning Electron Microscopy (FESEM) microscope and Nuclear Magnetic Resonance (NMR).

3.5.1 Field Emission Scanning Electron Microscopy (FESEM)

Since the Field Emission Scanning Electron Microscopy (FESEM) was not provided at Laboratory of Chemical Engineering and Natural Resources, the characterization was done at the central Laboratory of University Malaysia Pahang. The procedure of FESEM was dividing into three parts which are inserting the sample, obtaining an image and taking out the sample. For inserting the sample, the chamber door was opened gently when chamber is vented. The Vent button found on the Start-up or Work Page was clicked. During vented, the specimen chamber was opened and by using lint-free gloves, the specimens was placed into the specimen holder. The specimen was secured with appropriate hexkey unless a multi sample holder has been used. Once the sample was properly placed, the chamber door was closed. In the vacuum module found on the Start-up or Work page, the Pump button was clicked.

After inserting the sample, operation pre-check was done in order to make sure all the setting was set before vacuuming the system. The next part of the procedure is obtaining the image. On the Start-up or Work page, the HV button found in the electron column module was clicked in order to ramp up the voltage. After several seconds, an image was appear in the active Quad. The contrast and brightness was corrected with the adjuster in the Detectors module or by clicking on the Auto Contrast Brightness (ACB) icon (F9) in the tool bar. Then the specimen was moved to a desired area with X and Y stage controls. The selected area was zoom up or down to the desired magnification. The image was focused at 2x to 3x of the desired magnification. Then, after return to the desired magnification, the contrast and brightness was adjusted. The Snapshot button on the tool bar was clicked. When the image freezing, the Save As in the File menu was clicked.

After obtaining the image, the sample need to take out from the chamber. If HV button is on, the HV button was clicked to switch off the high voltage. The Vent button was clicked in the Vacuum module. When vented, the specimen chamber was opened and by using lint-free gloves the specimen was taken out from the specimen holder. The chamber was closed and Pump button was clicked in the vacuum module. During waiting for the system to reach vacuum status, the Home Stage in the Stage menu was clicked. Then the procedure was repeated with another sample.

Figure 3.5 FESEM used in Central Laboratory University Malaysia Pahang.

3.5.2 Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance was provides by Central Laboratory of University Malaysia Pahang. The aim of the NMR characterization is to study the physical structure of the carbon sample. The procedure for analyzing using NMR was divided into 6 steps. Firstly is starting Topspin to make sure the TopSpin window will appear. Then the process proceeds with preparation for acquisition. This step is to ensure the desired sample temperature can be set at the command line. After that the sample was inserting into the NMR tube. The tube must be held in a plastic spinner. After insert the sample the next step is locking. Lock signal can be seen in the lock display window. The appropriate solvent was selected at this step and “lock finished” message was appear at the bottom of the topspin. The next step of NMR procedure is tuning and matching the probe. The resonance frequency of the coils will vary depending on the content of the sample. Thus, it is necessary tune the coil to the correct value to yield the correct resonant frequency for the magnetic field strength that was using. The last step is shimming which the process in which minor adjustment re is made to the magnetic field until uniform magnetic field is achieved around the sample.

Figure 3.6 Image of NMR used for characterization.

3.6 Proximate Analysis

3.6.1 Moisture Content

Moisture content was determined in order to know the percentage of the water content in the sample after drying process. Firstly empty crucible without lid was weighted. About 1g of sample was put in the crucible. Then, the crucible with the sample was weighted again. After that the crucible and the contents was placed in an oven for about one hour under temperature 105°C. After one hour the crucible was cooling down by using desiccators and reweight. Lastly the amount of moisture content in the sample was calculated by using the following equation:

$$\% \text{ moisture} = \frac{mass\ of\ water\ removed\ (g)}{mass\ of\ original\ sample\ (g)}$$

3.6.2 Ash Content

Firstly the empty clay crucible was weighted. Then about 1g of sample was put in the crucible. After that the crucible and the content was reweighted. The crucible and the content then were placed in the furnace at temperature 750°C for about one hour. The crucible was placed in the desiccators for cooling process. Lastly the crucible and the remain content was weighted and the calculation of the ash content was done by using the following equation:

$$\% \text{ ash} = \frac{mass\ of\ residue\ after\ combustion\ (g)}{mass\ of\ original\ sample\ (g)}$$

3.6.3 Volatiles Content

Firstly empty crucible clay with lid was measured. Then 1g of sample was put in the crucible and the new weight of the crucible clay with lid and contents was measured. The crucible with lid was placed in the furnace at temperature 925°C for only 7 minutes. After that the crucible was removed and was placed in the desiccators for cooling process. The new weight of crucible and content was measured the value of volatile content was calculated by using following equation:

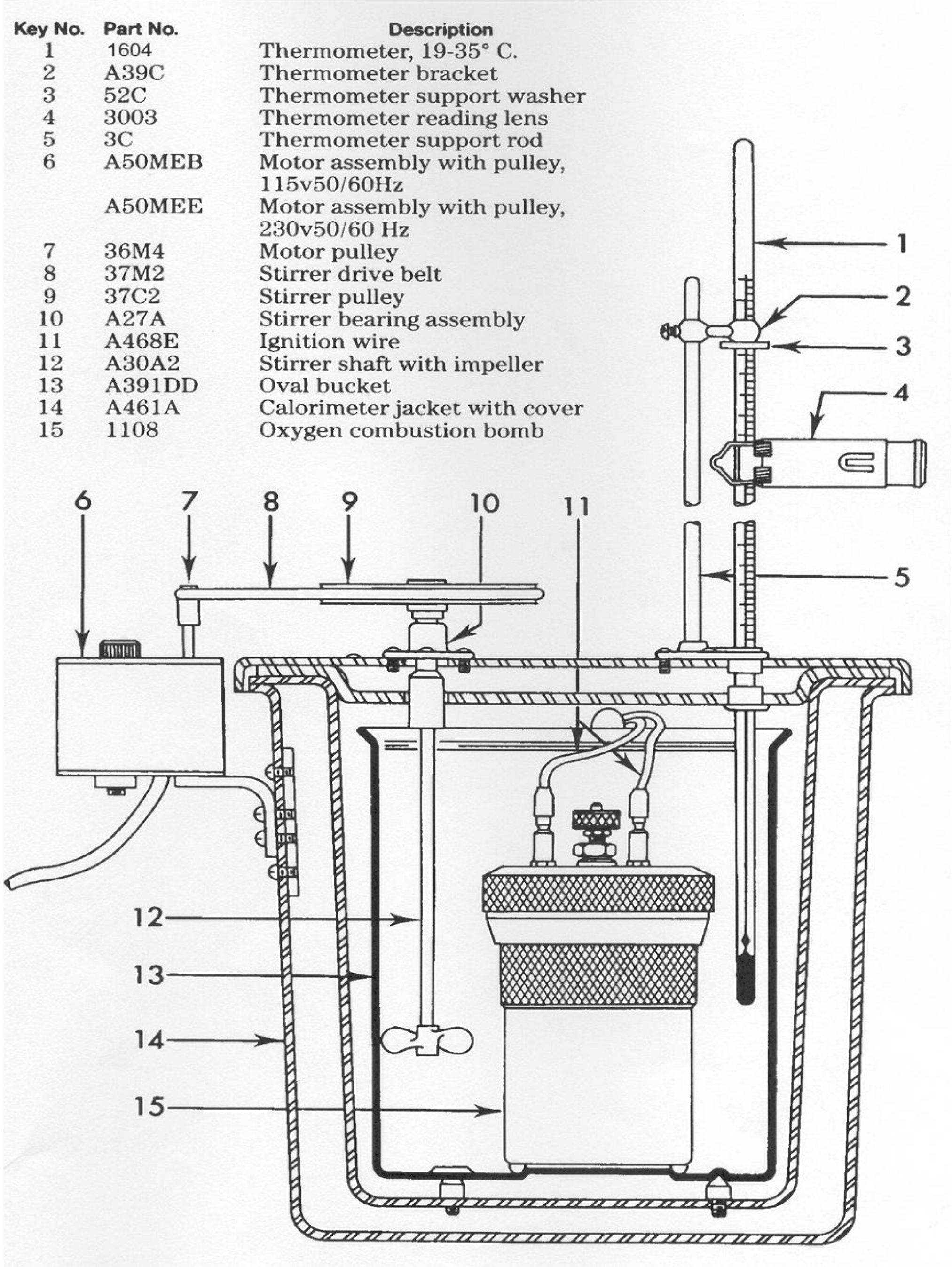
$$\% \text{ volatile} = [\ \frac{mass\ loss\ of\ sample\ after\ heating\ (g)}{mass\ of\ original\ sample\ (g)}\ x\ 100\ ] - \text{moisture}\%$$

3.6.4 Calorific Value

A combustion capsule was cleaned and dried and 0.5g of sample was weighted accurately using analytical balance. The sample was filled inside the combustion capsule and it was weighted to get the mass of samples in gram. The combustion capsules were fix on bomb head. Then about 10 cm of fuse wire was cute. The fuse wire was attached on bomb head by raise the cap, the wire was inserted through the eyelet; a ‘U’ shape was made and the cap was pulled downward. The fuse wire must immersed or touch the sample but should not touch the combustion capsule to prevent short circuit. Then, carefully the bomb head was attached with combustion bomb until it is tight. The bomb was filled with oxygen gas. The oval bucket was filled with accurately 2 L of distilled water. The lifting handle was attached to the two holes in the side of the screw cap and the combustion bomb was lower into the water. The combustion bomb was handled carefully so the sample will not be disturbed. Make sure that there’s no bubbles (leaking) going out from combustion bomb.

The handle was removed and any drops of water were shaking back into the bucket. The ignition lead wire was pushed into the terminal sockets on the bomb. The cover was put vertically on the jacket with the thermometer facing toward the front. After that the stirrer was turned on by hand to be sure that it runs freely. The drive belt was slip onto the pulleys and the motor was started. As the stirrer was run the temperatures was read and recorded at one minute intervals. After 1 minute, the bomb was fire by pressing the ignition button and holding it down until the indicator light goes out. The temperature was read and recorded at one minute interval until the temperature being constant (minimum 3 same temperature reading). After the last temperature reading, the motor was stopped, then the belt was removed and the cover was lift from the calorimeter vertically. The cover was put on the support stand and the ignition leads wires were removed. The bomb was lifted out of the bucket. Then the bomb was wipe with a clean towel. The knurled knob on the bomb head was slowly opened to release the gas pressure. After all pressure has been released, the cap was unscrewed, the head was lifted out of the cylinder and it was placed on the support stand. All unburn pieces of fuse wire was removed from the bomb electrodes, made them straight and their combined length was measured in centimeter. The same procedure was repeated for others sample.

After 1 minute, fire the bomb by pressing the ignition button and holding it down until the indicator light goes out. Read and record the temperature at one minute interval until the temperature being constant (minimum 3 same temperature reading). After the last temperature reading, stop the motor, remove the belt and lift the cover from the calorimeter vertically. Put the cover on the support stand. Remove the ignition leads wires and lift the bomb out of the bucket. Wipe the bomb with a clean towel. Open the knurled knob on the bomb head slowly to release the gas pressure. After all pressure has been released (no sound), unscrew the cap, lift the head out of the cylinder and place it on the support stand. Remove all unburn pieces of fuse wire from the bomb electrodes, straighten them and measure their combined length in centimeter. Repeat the same procedure for Sample 2 & Sample 3. Wash and clean up the combustion capsules, combustion bomb and oval bucket.



Key No.	Part No.	Description
1	1604	Thermometer, 19-35° C.
2	A39C	Thermometer bracket
3	52C	Thermometer support washer
4	3003	Thermometer reading lens
5	3C	Thermometer support rod
6	A50MEB	Motor assembly with pulley, 115v50/60Hz
	A50MEE	Motor assembly with pulley, 230v50/60 Hz
7	36M4	Motor pulley
8	37M2	Stirrer drive belt
9	37C2	Stirrer pulley
10	A27A	Stirrer bearing assembly
11	A468E	Ignition wire
12	A30A2	Stirrer shaft with impeller
13	A391DD	Oval bucket
14	A461A	Calorimeter jacket with cover
15	1108	Oxygen combustion bomb

Figure 3.7 Bomb Calorimeter

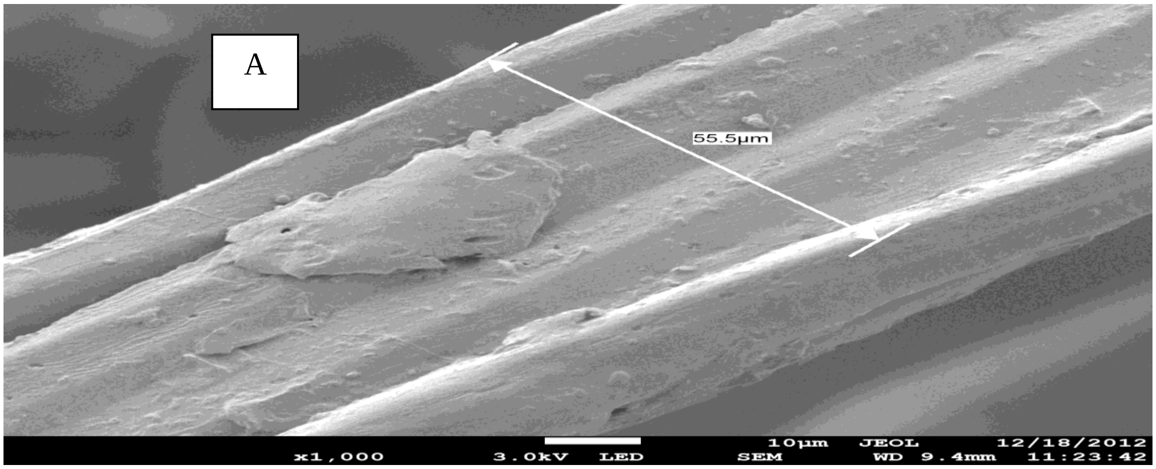
CHAPTER 4

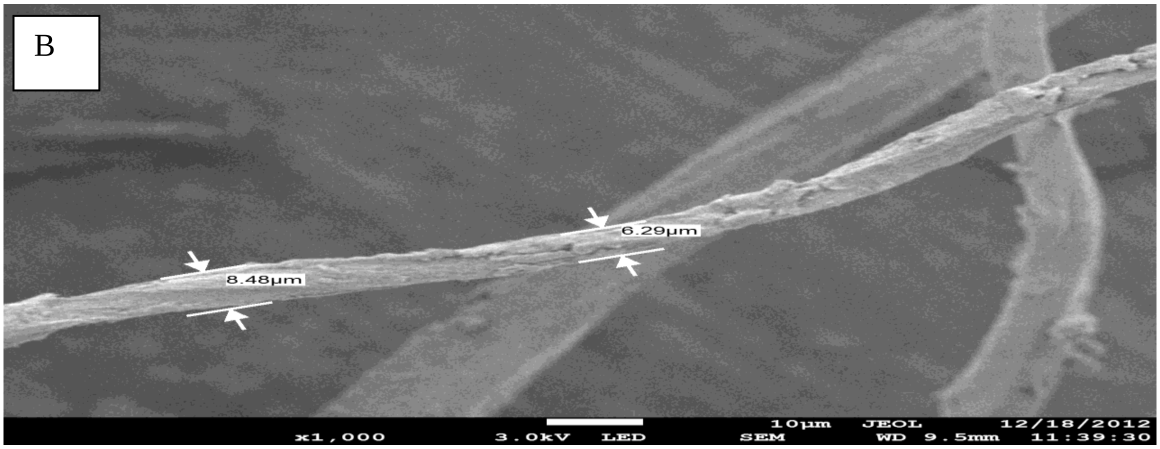
RESULT AND DISCUSSION

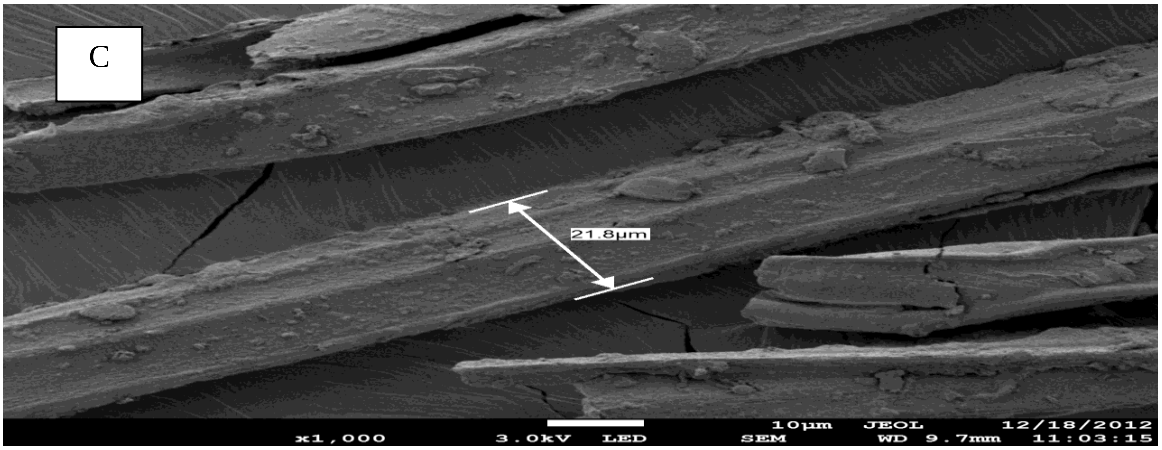
4.1 Field Emission Scanning Electron Microscopy (FESEM)

4.1.1 Fiber Size

Field emission scanning electron microscopy was used to characterize the diameter of the sample produces and the morphology structure from the hydrothermal carbonization process and pyrolysis processes. The diameter of the raw wood fiber waste before undergo the process was measured too in order to determine the effect of the process towards the diameter of the sample. Firstly, the comparison between the sample from HTC using 150g of wood fiber waste and from pyrolysis sample using 150g of wood fiber waste was done. The comparison was done in order to determine the effect of the different process towards the morphology characteristic. The results obtain from the FESEM characterization was shown in figure below:


A
55.5µm
10µm JEOL 12/18/2012
x1,000 3.0kV LED SEM WD 9.4mm 11:23:42


B
6.29µm
8.48µm
10µm JEOL 12/18/2012
x1,000 3.0kV LED SEM WD 9.5mm 11:39:30


C
21.8µm
10µm JEOL 12/18/2012
x1,000 3.0kV LED SEM WD 9.7mm 11:03:15

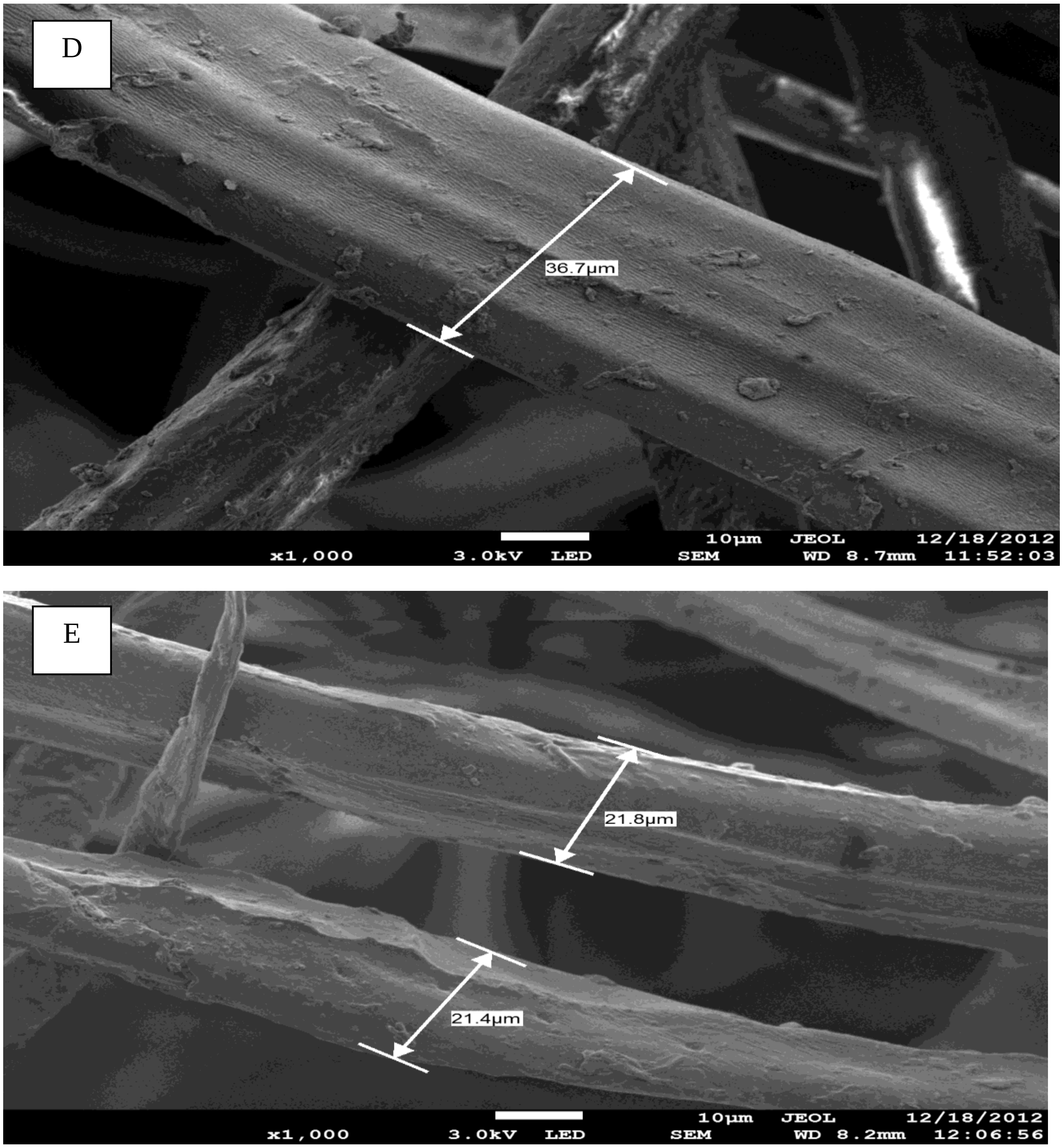


Figure 4.1 Diameter of the sample from HTC and pyrolysis process. (A= WFW, B=HTC, 150g wood fiber, C=HTC, 175g wood fiber, D=Pyrolysis, 150g wood fiber, E=Pyrolysis, 175g wood fiber)

Based on the figure 4.1 above, the comparison can be made between the picture A and C. Picture A is the diameter of the sample from HTC process while picture C is from pyrolysis process. Both process used 150g of wood fiber waste as the initial weight of raw material. From the picture it shows that diameter from sample A is smaller than diameter in picture C. This is due to the reaction during the HTC process where, the surface contact of water and the outer surface of the wood fiber waste is high. As the surface contact is high the damage at the outer layer of the wood fiber is become large. Since the pyrolysis is not including water during the process, there is no surface contact with water and the rupture is less. The processes occur during the pyrolysis is only heating and the water content inside the wood fiber molecule will be evaporate. Same theory was apply for the comparison of picture B and D.

The comparison between the different weights of wood fiber waste use also needs to consider. The parameter that needs to study is the weight of raw material used. From figure 4.1, the picture A and B shows the diameter of the sample that using the same process and condition during process but different in amount of wood fiber waste use initially. From the picture it shows that the diameter in picture A is smaller than the diameter in picture B. With same amount of water used during the reaction, the sample from picture B will be more concentrated as the amount of wood fiber waste use as raw is larger than 150g. The amount of wood fiber waste as raw material is really effect the physical characteristic of carbon produce. As the mixture become more concentrated, the surface contact between the outer layer of wood fiber waste and water is less and contributing to the diameter size of the particles after reaction.

For pyrolysis process in pictures C and D, the differences of the diameter is not too much as the process of pyrolysis is only the pre treatment of the wood fiber waste. There is no surface contact with water and the rupture at the surface also less since water is not including during the reaction. The major differences between both sample C and D is only the color of the product obtain which is for sample from picture C which using 150g of wood fiber waste is more brown compare to the sample from picture D. It proves that as the amount of the wood fiber waste used is large, with same operation condition the rate of heating will be slower. The comparison between the initial raw wood fiber waste used and the carbon particles produces after the process was done. From four samples that was done sample form picture A shows the higher differences in diameter with the initial of wood fiber waste. Picture A is the sample from HTC process using 150g of wood fiber waste shows the diameter at average of 7.3µm and the initial diameter of wood fiber waste used is about 55.5µm.

4.1.2 Morphology

The effect toward the diameter of the sample produce is directly contributed to the change in morphology of the sample which is the rupture effect at the surface area. The same theory was applied toward the morphology effect. The rupture effect at the surface area of the sample was effect by the surface contact with the water if the HTC process is considered. For the pyrolysis process the rupture is caused by the heating rate at the surface area which are as the amount of the wood fiber waste used the heating rate at the surface is less and less rupture occur. The morphology effect after the process was shown in figure 4.2

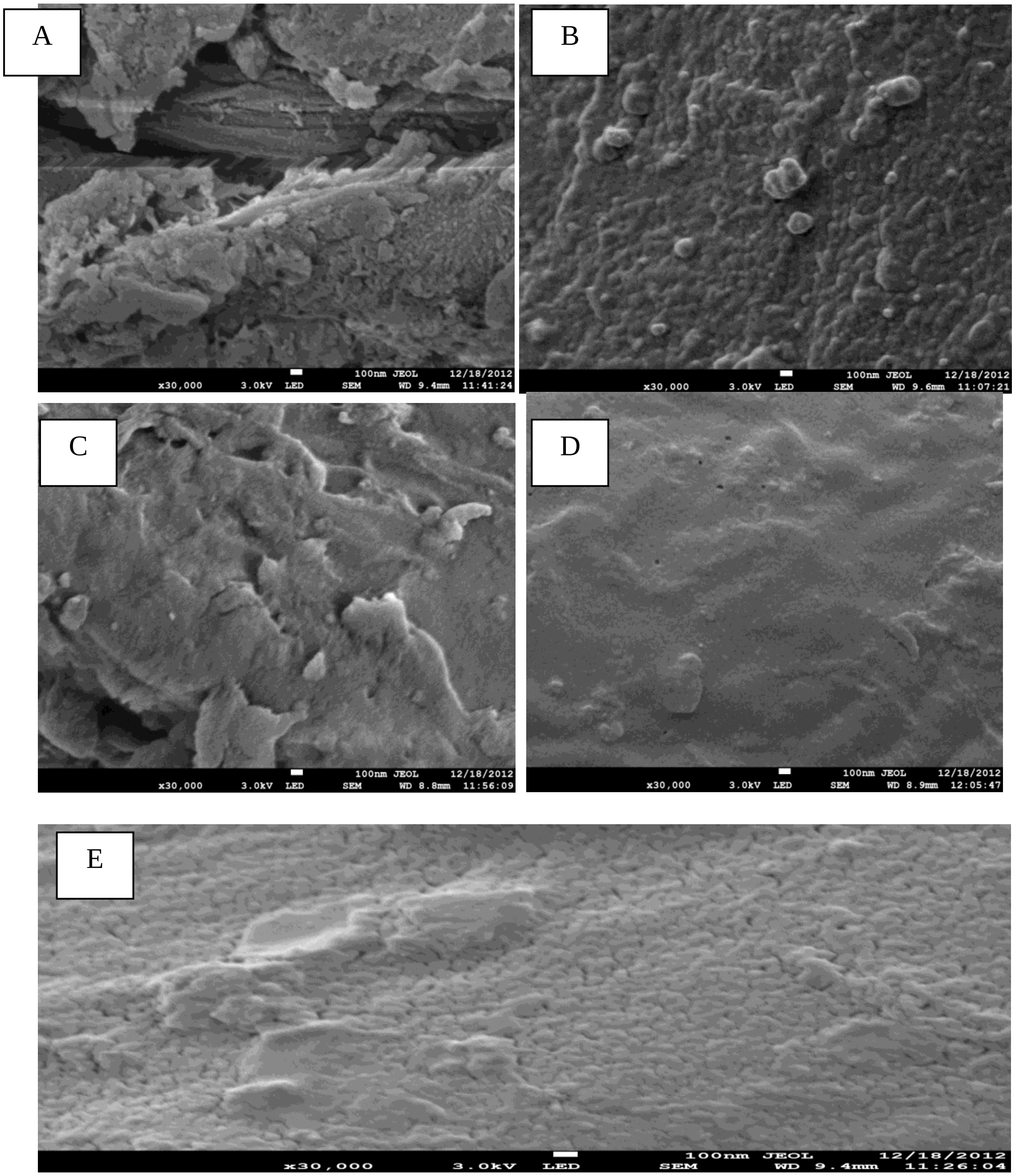


Figure 4.2 Morphology effect (A=HTC,150g wood fiber , B=HTC,175g wood fiber , C=pyrolysis,150g wood fiber,D=Pyrolysis,175g wood fiber , E=Raw material wood fiber waste)

4.2 Nuclear Magnetic Resonance

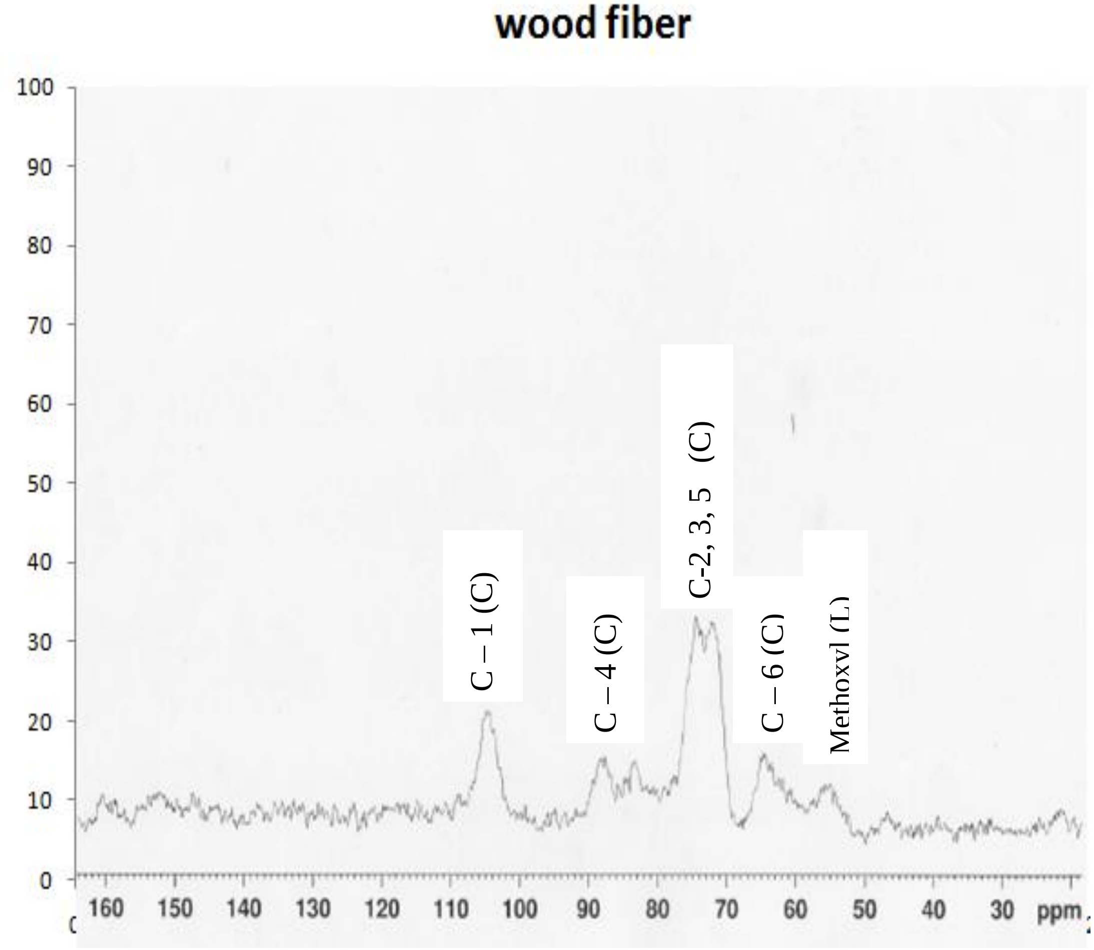


Figure 4.3 NMR result for wood fiber waste

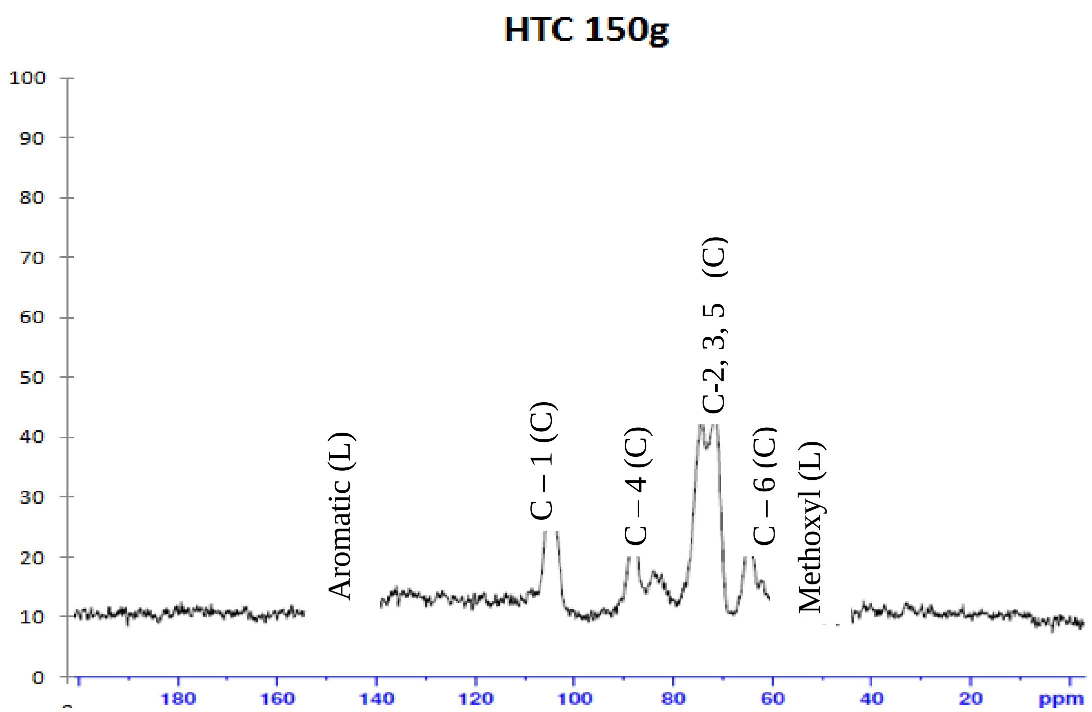


Figure 4.4 NMR result sample from HTC 150g

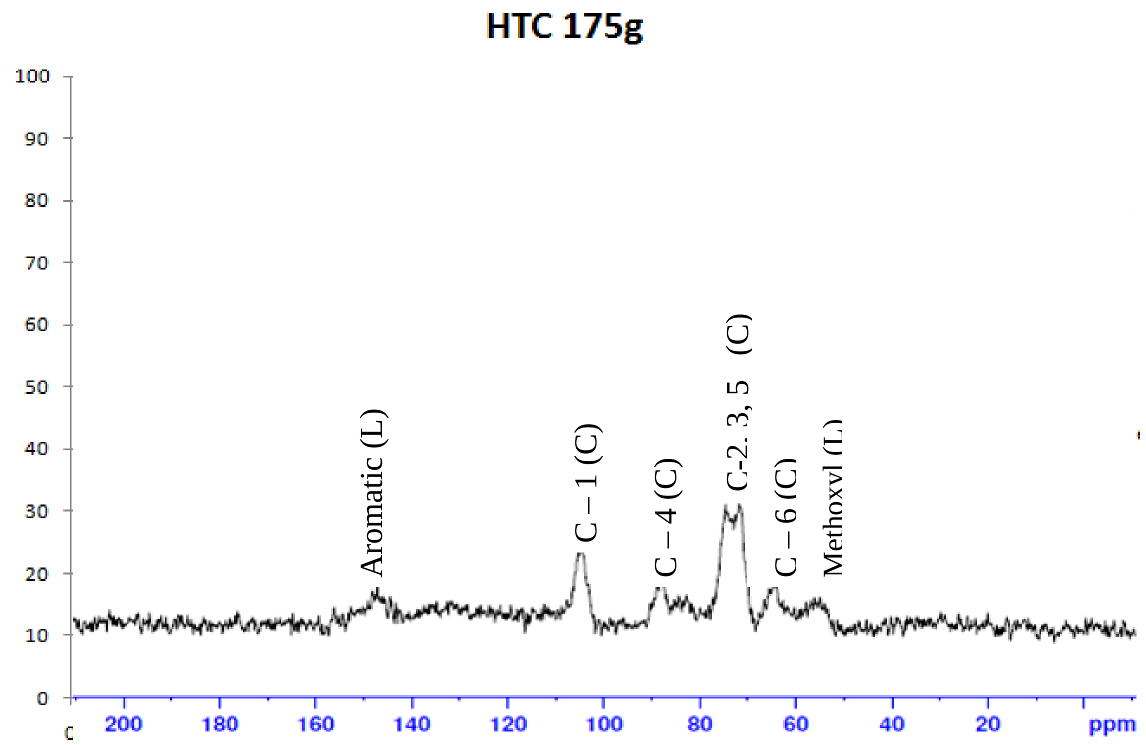


Figure 4.5: NMR result for sample from HTC 175g

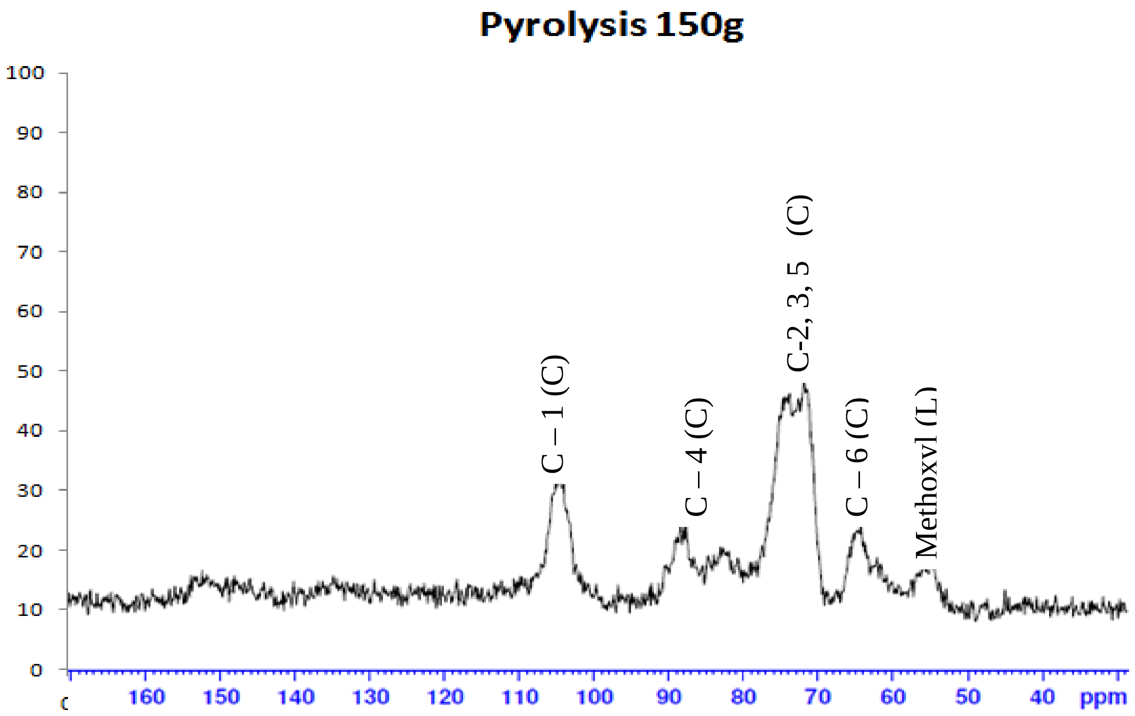


Figure 4.6 NMR result for sample from pyrolysis 150g

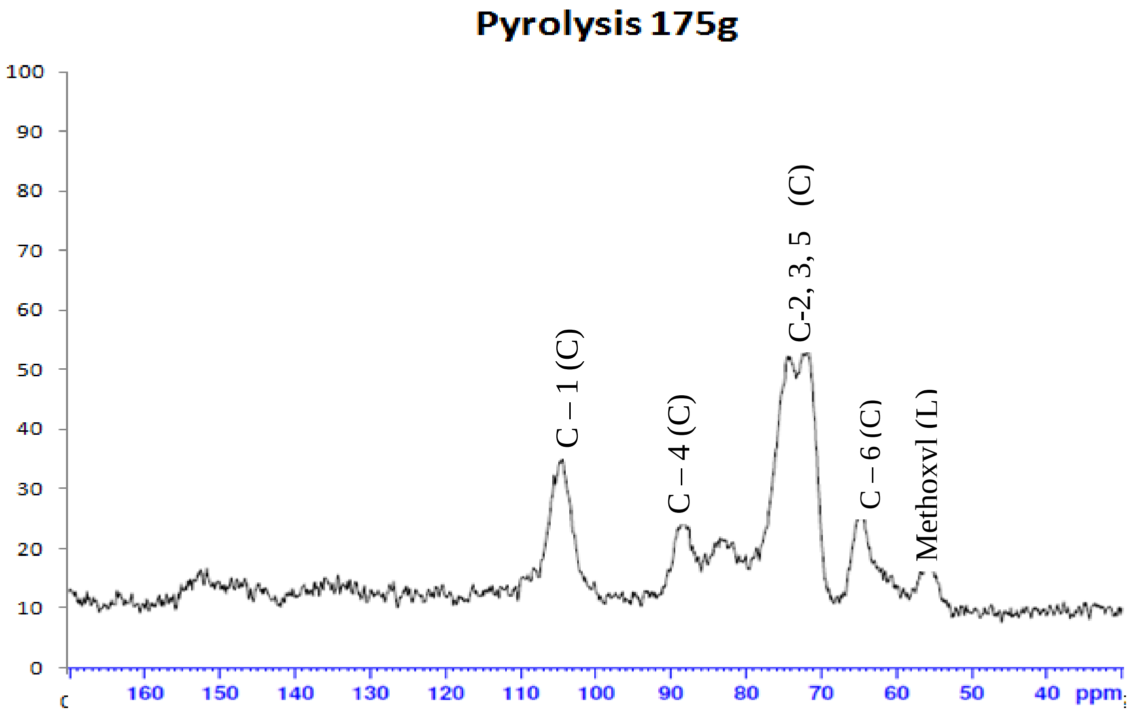


Figure 4.7 NMR result for sample from pyrolysis 175g

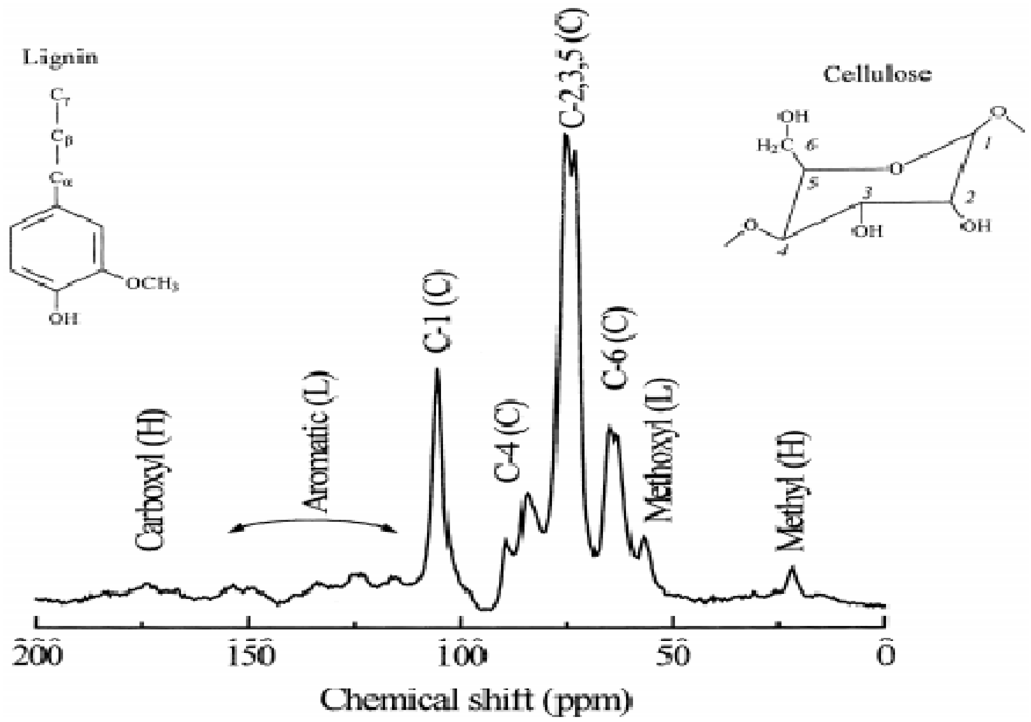


Figure 4.8 ^{13}C NMR Spectrum (Jair *et al*, 2000)

Carbon materials produced through the hydrothermal carbonization process and pyrolysis process of wood fiber waste were investigated by using ^{13}C high resolution solid state Nuclear Magnetic Resonance (NMR). The result obtained for every sample was shown in figure 4.4 until 4.7 and it was compared by the ^{13}C NMR Spectrum shown in figure 4.8 in order to identify what types of carbon content in every sample. Based on the figures above, all the samples shows the same behavior of NMR trend which means that all the sample have the same of carbon content. The differences between all these sample data are the percent of carbon type content in sample. Besides that, the details revealed by the high-field NMR spectra provide important information about chemical changes in the initial raw of wood fiber.

Since all the sample data shown the same pattern, it can be assume that all the samples contained same type of carbon. Based on the figures it shown that, at chemical shift (ppm) in range of 100 -110 ppm the sample contained of C-1 (C) type carbon. At chemical shift range 80 – 90 ppm sample was assumed to have C-4 (C) carbon type, while at range 70 – 80 ppm it was founded C-2,3,5 (C) carbon type. At range 60 – 70 ppm sample was contained C-6 (C) carbon type and in range 50 – 60 ppm methoxyl (L) was founded. Based on Jair *et al* (2000), peak labels refer to the typical building units associated with cellulose (C) and Lignin (L) as shown in the Figure 4.8.

The difference between HTC samples and pyrolysis samples is the HTC sample contained aromatic compound (L) while pyrolysis does not contain it. From the figures, it showed the changes of wood fiber occur before and after undergo the HTC and pyrolysis process. The changes were in terms of composition of carbon in the sample. Initially the raw wood fiber waste was founded to contain about 20% of C-1 (C), 14% of C-4 (C), 32% of C-2,3,5 (C), % C-6 (C), and % methoxyl. After undergo the HTC process, the changes was occurred in which the carbon content was increased. For HTC using 150g WF, the sample was founded to contain about 16% of aromatic lignin, 30% of C-1 cellulose, 21% C-4 cellulose, 45% of C-2, 3, 5 celluloses, 22% C-6 cellulose and 15% of methoxyl lignin. While for HTC 175g shows about 18g of aromatic lignin, 21% of C-1 cellulose, 16% of C-4 cellulose, 30% pf C-2,3,5 cellulose, 15% of C-6 cellulose and only 13% of methoxyl lignin. Same goes for pyrolysis process in which the content is increase. The data for all the sample was illustrated in the table below:

Table 4.1 NMR Results

	WFW	HTC 150g	HTC 175g	Pyrolysis 150g	Pyrolysis 175g
Aromatic (L)	-	16	18	-	-
C-1 (C)	20	30	21	30	35
C-4 (C)	14	21	16	22	23
C-2,3,5 (C)	32	45	30	48	50
C-6 (C)	18	22	15	22	25
Methoxyl (L)	11	15	13	18	15

4.3 Proximate Analysis

4.3.1 Moisture Content

Table 4.2 Mass of sample before drying

Sample	Run 1	Run 2	Run 3	Average
Pyrolysis 175g	1.0043	1.000	1.0053	1.0031
Pyrolysis 150g	1.0039	1.0037	1.0061	1.0046
HTC 175g	1.0057	1.0187	1.0149	1.0131
HTC 150g T	1.0007	1.0091	1.0091	1.0063
WF	1.0015	1.0048	1.0039	1.0034

Table 4.3 Mass of sample after 1hr drying

Sample B	Run 1	Run 2	Run 3	Average
Pyrolysis 175g	0.9791	0.9571	0.9523	0.9628
Pyrolysis 150g	0.9879	0.9489	0.9424	0.9597
HTC 175g	0.6434	0.6664	0.6405	0.6501
HTC 150g	0.8999	0.8957	0.9004	0.8987
WF	0.9244	0.9180	0.9172	0.9199

By using the moisture content formula the percentage of moisture for every sample was determined by using the following equation:

$$\% \text{ moisture} = \frac{mass\ of\ water\ removed\ (g)}{mass\ of\ original\ sample\ (g)}$$

Table 4.4 Moisture content for every sample

Sample	% moisture
Pyrolysis 175g	4.00
Pyrolysis 150g	4.50
HTC 175g	35.8
HTC 150g	10.70
WF	8.30

Table above shows the percentage of moisture for all samples and the raw of wood fiber waste. From the value above it shows that the higher moisture content is the sample from the process of hydrothermal carbonization (HTC) process using 175g of wood fiber waste. This is due the using of water during the process and since the process is closed system the water content inside the reactor cannot vaporize to the atmosphere. As the cooling process occurs the water that vaporizes in the reactor will be condensed to be water again. Besides that the reason for the moisture content of that sample is high is the sample is not drying with excess heat during the drying process. Without proper drying the sample will become wet and the particle to become swallow increase the moisture content inside the particles. Same goes for the sample from HTC using 150g wood fiber waste. The using of water during the reaction and improper drying process will affect the moisture content inside the particles of sample.

Both pyrolysis samples show the less moisture content than the raw of wood fiber waste. The reason is during the pyrolysis process, the heating of the sample in the absence of oxygen will absorb the water molecule inside the particles. That is why the sample will become drier than the raw wood fiber.

4.3.2 Ash Content

Table 4.5 Mass of sample before drying

Sample	Run 1	Run 2	Average
Pyrolysis 175g	1.0092	1.0092	1.0092
Pyrolysis 150g	1.0017	1.0028	1.0022
HTC 175g	1.0041	1.0039	1.0040
HTC 150g	1.0088	1.0075	1.0082
WF	1.0063	1.0023	1.0043

Table 4.6 Mass of sample after drying

Sample	Run 1	Run 2	Average
Pyrolysis 175g	0.0307	0.0193	0.0250
Pyrolysis 150g	0.0188	0.0622	0.0405
HTC 175g	0.1160	0.0501	0.0831
HTC 150g	0.1129	0.1910	0.1519
WF	0.1205	0.0785	0.0995

By using the ash content formula the percentage of ash for every sample was determined and it was illustrated in table below:

Table 4.7 Ash content for every sample

Sample	% ash
Pyrolysis 175g	2.48
Pyrolysis 150g	4.04
HTC 175g	8.28
HTC 150g	15.07
WF	9.90

Ash content is defined as a measure of the total amount of minerals or inorganic present in the carbon particles. Based on the result shown in the table, the sample from HTC process using 150g of wood fiber waste shows the highest ash content with 15.07% follows by raw wood fiber gave the value of ash content with 9.9%. This is because the original wood fiber still contains a lot of mineral and inorganic materials in molecules. After undergo the HTC process and the pyrolysis process, the mineral and inorganic contain inside the molecule will decrease based on the condition of the process.

HTC using 150g of wood fiber wastes give the high of ash content since the process including the excess water. Excess water but non excess drying will cause the sample to become wet and the moisture content inside the sample is high. Water is inorganic compound and as the sample is wet, the inorganic content inside the sample is high which is contributing to the high ash content. HTC process using 175g of wood fiber wastes shows the ash value lesser than the HTC using 150g. This is caused by the both process used the same amount of water during the process. HTC using 175g of wood fiber waste and 1L of water is more concentrated compare to the HTC process using 150g of wood fiber waste with same amount of water. Besides that, the sample from HTC using 175g of wood fiber was assumed to undergo the excess drying process and the sample obtained was assumed hundred percent dry which contributing towards the less ash content.

Pyrolysis process using 150g and 175g of wood fiber waste show the less of ash content with 4.04% and 2.48% respectively. The both sample shows the less ash content than the others sample since the pyrolysis process not including water during process. Pyrolysis process was considered as the pre treatment of wood fiber waste into the value added product. The process is about heating the samples with absence of oxygen. The heating process during the pyrolysis itself was contributed in evaporation of water molecule inside the sample. Since the water is inorganic compound, the ash content for the pyrolysis sample was less than the other sample.

4.3.3 Volatile Content

Table 4.8 Mass of sample before heating

Sample	Run 1	Run 2	Average
Pyrolysis 175g	1.0041	1.0013	1.0027
Pyrolysis 150g	1.0022	1.0043	1.0033
HTC 175g	1.0031	1.0038	1.0035
HTC 150g	1.0031	1.0099	1.0069
WF	1.0057	1.0029	1.0043

Table 4.9 Mass of sample after heating

Sample	Run 1	Run 2	Average
Pyrolysis 175g	0.0570	0.0254	0.0412
Pyrolysis 150g	0.0522	0.0734	0.0628
HTC 175g	0.1075	0.1077	0.1076
HTC 150g	0.1277	0.0987	0.1132
WF	0.1039	0.0962	0.1001

Table 4.10 Mass loss of sample after heating

Sample	Run 1	Run 2	Average
Pyrolysis 175g T	0.9471	0.9759	0.9615
Pyrolysis 150g	0.9500	0.9309	0.9405
HTC 175g	0.8956	0.8961	0.8959
HTC 150g	0.8754	0.9112	0.8933
A WF	0.9018	0.9067	0.9043

Table 4.11 Volatile content for every sample

Sample	% volatile
Pyrolysis 175g	91.89
Pyrolysis 150g	89.24
HTC 175g	53.48
HTC 150g	78.03
WF	81.74

Volatile content expressed as percent weight of coating that is loss under specific conditions of temperature and time. Based on results showed in table 4.9, the highest value of volatile content is the sample from pyrolysis processes that using 175g of wood fiber with value 91.89%. This is because of the sample have the less of moisture content in the sample. As the moisture content is less, the volatile content is high which means that the sample is easy to burn and the weight loss during the heating process is high. The smallest value of volatile content is the sample from HTC process using 175g of wood fiber with the value 53.48%. The weight loss of that sample is small since it has the high moisture content. The high moisture content of that sample is because water was including during the process. Besides that the sample was assumed not undergo a complete drying process and the sample still wet and has some moisture content. Based on the result above, it was prove that as the moisture content is less, the volatile content was high due to the percent of weight loss under specific conditions of temperature and time.

4.3.3 Calorific Value

The heat of combustion is the energy released as heat when a compound undergoes complete combustion with oxygen. The chemical reaction is typically a hydrocarbon reacting with oxygen to form carbon dioxide, water and heat. It may be expressed with the quantities:

- energy/mole of fuel
- energy/mass of fuel
- energy/volume of fuel

The heat of combustion is traditionally measured with bomb calorimeter. It may also be calculated as the difference between the heat of formation of the products and reactants. The heat released in the combustion reaction is absorbed by the water and the other parts of the calorimeter, thereby causing the temperature of the calorimeter to rise. The calorimeter is adiabatic, that is, all of the heat librated by the reaction remains in the calorimeter. None is lost to the surrounding. The temperature rise of the calorimeter can be measured by a sensitive thermometer or other temperature measuring device. The reaction occurs under constant volume conditions, and hence the heat librated by the reaction is equal to the internal energy change:

$$q_{rxn} = \Delta U_{rxn}$$

The actual process occurring in the calorimeter involves the conversion of reactants at some initial temperature, T_1 to reactants at some final temperature, T_2. Since the calorimeter is adiabatic, no heat is transferred between the calorimeter and the surroundings, and the internal energy change for the calorimeter as a whole is zero, that is $\Delta U_{cal} = 0$. However, heat transfers occurs within the calorimeter. If the reaction is exothermic, heat is released by the reaction. Some of this heat raises the temperature of the products and the rest is transferred to the water bath and the other parts of the calorimeter

Thus, since U is a state function:

$$\Delta U_{CAL} = 0 = \Delta U_{RXN} + \Delta U_{HEATING}$$

$$\Delta U_{RXN} = \Delta U_{HEATING} - \int_{T_1}^{T_2} C dT = -C(T_2 - T_1)$$

By using calorimeter, the heat of combustion of a compound can be calculated using a formula:

$$H_g = \frac{tW - e_1 - e_2 - e_3}{m}$$

t = temperature rise/different

W = 2409.26 cal/^{o}C

e_1 = correction in calories for heat of formation of nitric acid (HNO_3)

e_2 = correction in calories for heat of formation of sulphuric acid

e_3 = correction in calories for heat of combustion of fuse wire

= 2.3 x centimeters of fuse wire consumed in firing

m = mass

Data Collection for Calorific value experiment

Table 4.12 HTC 175g

Run	Run 1	Run 2	Run 3
Mass of sample (gram)	0.3077	0.3054	0.3029
Unburn fuse wire (cm)	4.9	8.4	5.1
Time (minute)	Temperature Reading (°C)		
0	29.5	29.5	29.75
1	29.5	29.5	30.0
2	29.75	29.75	30.0
3	30.0	29.75	30.0
4	30.0	30.0	
5	30.0	30.0	
6		30.0	

Table 4.13 HTC 150g

Run	Run 1	Run 2	Run 3
Mass of sample (gram)	0.3014	0.3065	0.3046
Unburn fuse wire (cm)	3.5	1.7	1.7
Time (minute)	Temperature Reading (°C)		
0	29.0	29.0	29.25
1	29.0	29.5	29.5
2	29.5	29.5	29.75
3	29.5	29.5	29.80
4	29.5		29.80
5			29.80

Table 4.14 Pyrolysis 175g

Run	Run 1	Run 2	Run 3
Mass of sample (gram)	0.3048	0.3010	0.3028
Unburn fuse wire (cm)	2.7	3.8	1.9
Time (minute)	Temperature Reading (°C)		
0	30.0	30.0	29.0
1	30.5	30.25	29.5
2	30.5	30.50	29.5
3	30.75	30.50	29.75
4	30.75	30.50	29.80
5	30.75		30.0
6			30.0
7			30.0

Table 4.15 Pyrolysis 150g

Run	Run 1	Run 2	Run 3
Mass of sample (gram)	0.3013	0.3074	0.3056
Unburn fuse wire (cm)	2.3	6.5	1.8
Time (minute)	Temperature Reading (°C)		
0	28.2	29.0	29.25
1	28.4	29.0	29.5
2	28.5	29.25	29.60
3	28.6	29.5	29.75
4	28.6	29.5	29.75
5	28.6	29.5	29.75

Table 4.16 Raw of WFW

Run	Run 1	Run 2	Run 3
Mass of sample (gram)	0.3076	0.3050	0.3193
Unburn fuse wire (cm)	1.1	5.9	2.9
Time (minute)	Temperature Reading (°C)		
0	29.5	29.5	29.0
1	29.6	29.6	29.5
2	29.75	29.75	29.75
3	30.0	29.75	29.9
4	30.0	29.80	29.95
5	30.0	29.90	30.0
6		30.0	30.0
7		30.0	30.0
8		30.0	

Table 4.17: Calorific value for every sample in MJ/kg

Sample	Run 1 MJ/kg	Run 2 (MJ/kg)	Run 3 (MJ/kg)	Average MJ/kg
Raw of WFW	16.35	16.34	31.48	21.39
HTC 175g	16.23	16.24	8.16	13.54
HTC 150g	16.61	16.39	18.15	17.05
Pyrolysis 175g	24.72	16.62	33.29	24.88
Pyrolysis 150g	13.31	16.19	16.44	15.31

1 J/kg=0.000238846cal/g

Based on the values given in table 4.15, it shows that the highest value of calorific is from the sample Pyrolysis with 175g of wood fiber waste used with 24.88 MJ/kg. Pyrolysis is known as the pre treatment process in which the wood fiber waste is heat at certain range of temperature in absence of oxygen. As the calorific value of the pyrolysis sample is high than the raw of material, it proves that the pyrolysis process is the good of the pre treatment process. The calorific value for pyrolysis using 150g of wood fiber waste was smaller compared to the raw of wood fiber waste with 21.39 MJ/kg. Knowing that pyrolysis value should give more calorific value compared to the raw of wood fiber waste as they was undergo the pre treatment. In this cases, the pyrolysis process using 150g of wood fiber was assume incomplete and the process the sample was not covered completely with aluminum coil which contribute to the presence of oxygen during the process. Heating of the sample in the presence of oxygen was considered as the combustion and as the amount of oxygen presence during the process is high the calorific value will be small and the quality of pre treatment process is not good.

The calorific values for the sample from HTC process using 150g and 175g of wood fiber shows the smaller value compared to the sample from pyrolysis and raw of wood fiber with 17.05 MJ/kg and 17.05 MJ/kg respectively. This is because of the HTC is not the pre treatment process and the process is about to convert the wood fiber waste into the value added product which is carbon particles. Water is the main solvent required during the HTC process. The results showed the calorific value of HTC using 150g owf wood fiber waste is higher compared to the HTC using 175g of woof fiber. As the same amount of water used during both process, the sample from HTC 150g of wood fiber was assumed to have high surface contact with water as the mixture during the process is less concentrated than HTC using 175g of wood fiber waste. As the surface contact between sample and water is high, the dehydration process during HTC was occurring in the high rate which means that lowering both oxygen and hydrogen content of the sample. The high oxygen and hydrogen removed from the sample, the high carbon content of the product which contributes to the high calorific value.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Hydrothermal carbonization and pyrolysis process are the main process consider in the research which the sample from both process was characterized in order to make a comparison between these processes. The first objective which is to develop and demonstrate the hydrothermal carbonization process to produce the carbon particle was already achieved as 2 samples from the process was already run. The second objective which is to make a comparison between these processes has been achieved. After analyzing the sample from both process through Field Emission Scanning Electron (FESEM) and Nuclear Magnetic Resonance (NMR) the comparison was made. Through the FESEM characterization, the diameter of the sample and the morphology effect was determined. The comparison was made and the best sample shown by the sample from HTC process using 150g of wood fiber waste. The diameter of the sample shown about 7.3µm and the highest rupture occur at the surface of the particles. This is due to the surface contact between the outer layer of the fiber and the water. As the excess water the rupture will be more and the diameter will become smaller. Results from NMR proves that the carbon content inside the sample was changes after undergo the HTC and pyrolysis process. The comparison was made and it shows that after undergo the HTC process the carbon content for cellulose and lignin was increased and HTC sample shows the content of aromatic lignin. Differ with pyrolysis process which does not contain aromatic lignin but for other content still increase after undergo the pyrolysis process. The proximate analysis also was done and it was found that HTC 175g WF gives the highest value of moisture content, HTC 150g WF gives the highest values of ash content with 15.07%. for volatile content the highest values was the sample from pyrolysis 175g WF with 91.89% and lastly for calorific value proves the pyrolysis with 175g of WF give the highest calorific value with 24.88 MJ/kg.

There is some recommendation that should be considering for the future work. Firstly by using various catalyst concentrations in order to find out how the concentration of catalyst will affect the sample in terms of morphology. Catalyst plays an important role in increasing the rate of reaction of the process. Second is by considering the various operation conditions in order to find the high conversion of the wood fiber waste. The example of operations conditions is time of reaction, the weight of wood fiber waste used as raw, amount of water used as solvent and others. All these parameters will affect the morphology of the sample. The best operation condition should be finding in other to produce the best carbon particles in terms of morphology and diameter of the carbon produced. Besides that the testing of the sample should be done in the other application in order to find out the ability of the product to perform in their application. For example by using it as additives for increasing the strength of the medium fiber (MDF) board. Testing result will help to find out which sample from the process used in the research is more able to perform in the application and the comparison between the samples can be done.

References

Aaron. E. (2012). The Carbon Cycle of Woody Biomass. Retrieved on 23th November 2012 from http://logging.about.com/od/Biomass-Fueling/tp/The-Carbon-Cycle-Of-Woody-Biomass.htm

Bo. H, Kan. W, Liheng . W, Shu. H. Y, Markus. A, Maria. M. T. (2010). Engineering Carbon Materialsfrom the Hydrothermal Carbonization Process of Biomass. Retrieved on 27th November 2012 from http://www.ebah.com.br/content/ABAAAAhN4AL/engineering-carbon-materials-from-the-hydrothermal-carbonization-process-of-biomass

Bridgwater. A.V. (2003). Renewable Fuels and Chemicals by Thermal Processimg of Biomass. Chemical Engineering Journal, Vol.91, pp.87-102, ISSN 1358-8947

Charalampos. L, Athanasios. G. (2007). Hydrothermal Recycling of Waste amd Performance of the Recycled Wooden Particleboards. Retrieved on 24th March 2012 from www.sciencedirect.com/science/article/pii/S0956053X06003497

De Anna. S. B. (2011). Woody Biomass Facts: A Look at the Myths Regarding a Sustainable Energy Source. Retrieved on 27th November 2012 from http://www.palletenterprise.com/articledatabase/view.asp?articleID=3433

Helmut. H, Detlef. S, Marc. B, Pierluigi. C, Yves. D, Mogens. H, Ole. H, Richard. K. J, Ulrike. K, Pierre. L, Eckart. L, Peter. N, Jouni. P, Anette. R, Sybille. V. D. H, Theo. V, Peter. W, Timothy. S. (2012). Correcting a Fundamental Error in Greenhouse Gas Accounting Related to Bioenergy. Retrieved on 24th November 2012 from http://www.cccep.ac.uk/Publications/research-articles/error-greenhouse-gas-accounting-bioenergy.pdf

International Carbon Black Association. (2006). What is Carbon Black?. Retrieved on 24th March 2012 from www.carbon-black-org/what_is.html

Jair. C. C. F, Tito. J. B, Francisco. G. E. (2000). Investigation of Biomass and Polymer Based Carbon Materials using ^{13}C High Resolution Solid State NMR. Retrieved on 10th January 2013 from http://144.206.159.178/FT/145/35034/599877.pdf

Jay. O. (2012). Biomass Economic 101: Opportunities and Challenges. Retrived on 26th November 2012 from http://www.palletenterprise.com/articledatabase/view.asp?articleID=3715

Kai. D. L. K. (2004). Nanocarbon: Properties and Applications. Retrieved on 24th March 2012 from www.authorstream.com/Presentation/Funschool-19102-Nanocarbon1-Nanocarbon-Properties-Applications-nano-Carbo-Bonding-Fullerence-Nanotube-Nanotubes-Cones-black-as-Entertainment-ppt-powerpoint/

Kim. K. (2001). Electrochemical Uses of Carbo. Retrieved on March 23th 2012 from http://electrochem.cwru.edu/encycl/art-c01-carbon.htm

Marcela. G, Claudia. M. B. F. M, Carlos. R. R, Dachamir. H. (2011). Synthesis of Carbon-Based Materials by Microwave Hydrothermal Processing. Retrieved on 24th March 2012 from www.cdn.intechopen.com/pdfs/17018/InTech-synthesis_or_carbon_based_materials_by_microwave_assisted_hydrothermal_process.pdf

Maria. M. T, Markus. A, Niki. B. (2008). Hydrothermal Carbon from Biomass: A comparison of the Local Structure from Poly-to Monosaccharides and Pentose/Hexoses. Retrieved on 23th March 2012 from http://pubs.rsc.org/en/Content/ArticleLanding/2008/GC/b807009a

Nicole. B, Kyoung. S. R, Jingdong. M, Joseph. R. V. F, Mark. A. C, Sunyoung. B. (2011). Hydrothermal Carbonization of Mucipal Waste Streams. Retrieved on 26th November 2012 from http://www.ars.usda.gov/SP2UserFiles/Place/66570000/Manuscripts/2011/Man864.pdf

Roger. S, Jennifer. O. (2010). A Synthesis of Research on Wood Products and Greenhouse Gas Impacts. 2nd Edition. Technical Report No. TR-19R. Retrieved on 25th November 2012 from http://www.forintek.ca/public/pdf/Public_Information/technical_rpt/TR19%20Complete%20Pub-web.pdf

Salman. Z. (2008). Biomass Pyrolysis. Retrieved on 23th November 2012 from http://www.altenergymag.com/emagazine.php?issue_number=09.02.01&article=pyrolysis

Sevilla. M. (2009). The Production of Carbon Materials by Hydrothermal Carbonization of Cellulose. Retrieved on 23th March 2012 from http://www.sciencedirect.com/science/article/pii/S0008622309002486

Titirici. M. M, Thomas. A, Yu. S. H, Muller. J, Antonietti. M. (2007). A Direct Synthesis of Meosporous Carbons with Bicontinuous Pore Morphology from Crude Plant Material by Hydrothermal Carbonization. Chemistry of Materials, Vol. 19, pp.4205-4212, ISSN 1520-5002

Yoshimura. M, Byparra. K. (2008). Hydrothermal Processing of Materials: Past, Present and Future. Journal of Materials Science, Vol. 48, pp.2085-2103, ISSN 0022-2461

University of Texas. (2010). Nanotube Thermocells Hold promise as Energy Source. Retrieved on 24th <arch 2012 from www.understandingnano.com/nanotube-thermocells.htm