CHEMICAL CHARACTERISTICS OF CARBON NANOPARTICLE CONVERTS FROM WOOD FIBER WASTE VIA SUBCRITICAL LIQUID AND PYROLYSIS CONDITIONS.

by

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A thesis submitted to the Faculty of Chemical and Natural Resources Engineering in partial fulfillment of the requirement for the Degree of Bachelor of Engineering in Chemical Engineering.

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FEBRUARY 2013

ABSTRACT

Hydrothermal carbonization and pyrolysis are the process transforms into a useful material in the life and environmental practice. In contrast, both of the process are different in term of reaction. Hydrothermal carbonization process is to remove water contain and pyrolysis to remove volatile content in product. The problem of abundant volume of wood fibre waste production which normally being dumped to the landfill. Thus wood manufacturing should control the output product to avoid natural pollution from illegal activities. The objective of this research is to determine the amount of carbon particle in each process This process not only forms carbon element but other chemical compound such as hydrogen, nitrogen and sulphur in small ratio. This research is also proposed to avoid environmental pollution from give harm to human and economic aspect. Hydrothermal carbonization is conducted by supercritical unit and pyrolysis conducted by furbnace with temperature, volume and time control. The required temperature for this research is 200 °C and proportional with time in 4 hours. Each experiment needs to change the volume of material to 150g ang 175g. After completing experiment, the product analyses using elemental analysis and TGA will be carry out to determine the chemical composition and the carbon present in product. Hydrothermal carbonization and pyrolysis are synthesis technique to convert waste material into a variety of application. Likewise, recycle a wood fibre waste to generate new application that gives a big impact to the economy and environment. The management of waste can be improved by the friendly technology that applies to avoid environmental problem.

ABSTRAK

Pengkarbonan hidroterma dan pirolisis ialah proses berubah menjadi satu bahan yang berguna dalam hidup dan alam sekitar. Sebaliknya, kedua-dua proses jadi berbeza di istilah tindak balas. Proses pengkarbonan hidroterma ialah untuk membuang air mengandungi dan pirolisis membuang kandungan turun naik dalam produk. Masalah jumlah amat banyak pengeluaran sia-sia serat kayu yang biasanya dibuang ke bahan buangan. Oleh itu, pembuatan kayu patut mengawal keluaran output mengelak pencemaran semulajadi dari kegiatan haram. Objektif penyelidikanini ialah untuk menentukan zarah banyaknya karbon dalam setiap proses. Ini bukan sahaja membentuk unsur karbon tetapi sebatian kimia lain seperti hidrogen, nitrogen dan sulfur dalam nisbah kecil. Penyelidikan ini juga dicadangkan untuk mengelak pencemaran alam sekitar dari memberi kerosakan oleh manusia dan segi ekonomik. Pengkarbonan hidroterma dijalankan oleh unit genting dan pirolisis dikendalikan oleh relau dengan suhu, jumlah dan kawalan masa. Suhu diperlukan untuk penyelidikan ini ialah 200 °C dan berkadar dengan masa dalam 4 jam. Setiap eksperimen perlu mengubah jumlah bahan kepada 150g dan 175g. Selepas menamatkan eksperimen,analisis produk menggunakan analisis unsur dan TGA akan melaksanakan untuk menentukan komposisi kimia dan karbon hadir dalam produk. Pengkarbonan hidroterma dan pirolisis ialah teknik menukar bahan buangan ke dalam pelbagai jenis keperluan. Begitu juga, kitar semula satu serat kayu membazirkan untuk menjana permohonan baru yang memberi satu impak besar bagi ekonomi dan persekitaran. Pengurusan sisa boleh diperbaiki dengan teknologi mesra alam yang digunakan untuk mengelak masalah persekitaran

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURE

LIST OF ABBREVIATION

g	-	Gram
TGA	-	Thermogravimetry
MDF	-	Medium density fiberboard
GCV	-	Gross calorific value
HHV	-	Higher heating valu
NCV	-	Nett calorific value
LHV	-	Lower heating value
CO_2	-	Carbon dioxide
H_3O	-	Hydromium
OH^-	-	Hydroxide
C	-	Carbon
N	-	Nitrogen
H	-	Hydrogen
S	-	Sulfur
O	-	Oxygen
Na	-	Natrium
K	-	Potassium
Mg	-	Magnesium
P	-	Phosphorus
Ca	-	Calcium
Ag	-	Silver
MJ/kg	-	mega Joule per kilogram
MJ/nm^{-3}	-	mega Joule per newton
kJ/mol	-	kilo Joule per mol
cm	-	centimeter

LIST OF SYMBOL

°C	-	degrees Celcius
%	-	percent

CHAPTER 1

INTRODUCTION

1.1 Background

Wood fibre, classified as organic material can be extracted from tree, bamboo, corn, soy and other plant-based material. The physical properties of wood fiber are thermal expansion, high density, good moisture content and electrical resistance. These elements are the main factor to choose the best quality of wood in manufacturing. Thermal expansion is a percentage of length change affected by the temperature change between -51.1°C to 54.4°C. Moisture content can be defined as water content in wood. Wood has the ability to absorb water or moisture and it depend on the temperature and humidity from the surrounding. Hence, wood will lose or gain the water moisture in certain condition that called equilibrium moisture content. Conductivity refers to the electric flow within electric power supply. While, dielectric constant is the quantity of the electric in the material when it supplied to the electric power and dielectric power factor is the requirement to generate heat from the quantity of the electric supply (Jerrold 1994). Furthermore, it also has chemical compositions in wood such as carbon, hydrogen, oxygen, nitrogen and sulphur.

Table 1.1 Percentage of chemical composition in wood fibre (Jerrold, 1994).

Chemical composition	% of dry matter weight
Carbon	45-50
Hydrogen	6.0-6.5
Oxygen	38-42
Nitrogen	0.1-0.5
Sulphur	max 0.05

The quality of wood fiber is depend on the condition and properties of the wood. Because of this, wood has a high demand to produce furniture, construction material, particle board, pallet and others. According to this, the waste of wood fiber is not dispelled in proper way to avoid environmental problem. The waste management face a problem to solve this situation due to give a sensitive disposal issues. The management should reduce the problem by a new technology and research. For example, in bioprocess or chemical that offer the latest improvement in order to achieve a good sustainable life.

Mohan and his friends explored that pyrolysis process have been improved and widely used in charcoal production and convert to liquids fuels (Mohan et al., 2006). Pyrolysis convert biomass by heating in absence of air to produce carbon solid, char and volatiles product (Brownsort,2009). In pyrolysis reaction, wood fiber waste produce a large number of chemical substance which is can be used as additional for conventional fuels In high temperature, the component in biomass present a sufficient energy since it highly influenced of inorganic materials and different heat treatments condition (Mohan et al, 2006)..

For recent decade, hydrothermal carbonization is introduced that can be approach to increase the technology in waste material. Various type of lignocellulosic material had been use in hydrothermal treatment to reduce a natural pollution and reuse a waste material due to save an energy usage. Hydrothermal carbonization is a friendly environmental process that applies energy to form a new item for more application. It releases a small amount of energy input into a heat. The current hydrothermal applications are water purification, reducing CO_2 and energy storage (Hu et al., 2010). The main reactions occur in hydrothermal are hydrolysis dehydration. These two reaction encourage in hydrothermal process with temperature condition. In generally, the effective dehydration occurs only in water presence which is the wood fiber waste must in wet condition. Hydrothemal carbonization process convert the biomass directed to complex structural under a control of surface polarity of the biomass (Titirici et al., 2007).

1.2 Problem statement

Disposal method of wood fibre is a main problem in manufacturing industry. Nowadays, hydrothermal is a technique to reduce environment pollution in an authority of engineering field (Lykidis et al., 2008). In hydrothermal process, wood fibre is a suitable raw material due to the character and capability to use in a process. This material did not require high energy and complicated process to produce a new product. Pyrolysis is a another process that applicable to convert the wood waste to valuable composition (Bridewater et al., 1999). Another problem is high cost of conventional nanoparticle synthesis production to treat a waste into a useful material. Nanoparticle synthesis needs a variety of medium and specific character to complete the reaction according to the material (Kim et al., 2009). Thermochemical process is pyrolysis which is protion of the lignocellulose is integrated with the production of valuable chemicals. This process occur when absence of oxygen and produce char, liquid and gas where liquid and gas are volatile component.

1.3 Research objective

The objectives of this study are

i. To analyze the carbon nanoparticles produced from hydrothermal carbonization and pyrolysis process.

ii. To investigate the chemical characterization of the waste material.

iii. To determine the ash, volatile , moisture content in hydrothermal and pyrolysis product.

1.4 Scope of study

Wood fibre waste is a main element to describe the chemical composition and carbon compound. The process will analyze the carbon conversion using chemical characteristic. Citric acid is used as a catalyst to increase a process rate without change the reaction. The duration time to conduct the experiment is 4 hours at 200 °C

1.5 Expected outcomes

Hydrothermal carbonizationand and pyrolysis are synthesis techniques which carried out waste material into a variety of application. For example, recycle a wood fibre waste to generate new application that gives a big impact to the economy and environment. The management of waste will be improving by the friendly technology applies to avoid environmental problem. Wood fibre wastes contain higher carbon than hydrogen, nitrogen and sulphur. Thus, wood fibre waste can be used as a fuel to save the fuel sources in earth.

1.6 Conclusions

In this chapter, conversion process waste material to valuable material is discussed. Hydrothermal carbonization is a process to reduce CO_2 in product which is to control global warming. Meanwhile, pyrolysis is a combustion process that react wihout oxygen and no oxidation take place in this process. Wood fibre is one of the waste materials that easy to process to produce a reuse material for future application.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass

Biomass is the material that can be derived directly or indirectly from plant which is consumed as energy or materials in a significant amount of existing via animal farming and food industry. The term of biomass is called a "phytomass" and translated bioresource or bio-derived-resource (UN Energy, 2007). Meanwhile, McKendry stated that the carbohydrates formation by plant derivation by the reaction between CO_2 in the air, water and sunlight through photosynthesis process (McKendry, 2001). The basis resource contains hundreds of thousands of plant species, terrestrial and aquatic, several agricultural, forestry and industrial residues and process waste, sewage and animal wastes. Definitely, biomass means wood, rape seed, water hyacinth, sawdust, wood chip, rice husk, rice straw, pulp sludge, kitchen garbage and animal dung. The types of plantation in biomass are eucalyptus, hybrid poplar, oil palm, sugar cane and switch grass (UN Energy, 2007).

In 1934, biomass term appeared first in the literature of Oxford English Dictionary. Russian scientist, Bogorov used biomass as nomenclature. He analyse the periodic growth change of plankton by measured the weight after drying process. He named dried plankton as biomass (Bogorov, 1934). Biomass is renewable resource and renewable energy conversion from biomass to energy. But, in Japan, biomass is designated a new energy and it authorized term to this country. The concerning law of the use of new energy was obligated in April 1997. However, biomass not approved as a new energies and officially accepted in January 2002 when the law was revised (H.Sano, 2002). The power generation by photovoltaic, wind energy, fuel cell and biomass by means of thermal use of waste selected as a new energy. The law provide a permitting new energy that what have to be the invention, generation and utilization of petroleum possibilities, what is inefficiently infiltrated by the economic control and what the recommended in order to support the use of new energy by the government regulation (Yokoyama, 2008).

The derivation energy of biomass will increase the overall energy supply as the price of fossil fuels increase over the next decades. The energy source from biomass is very attractive, and then it can be a zero CO_2 of energy source. Hence, greenhouse gas emission will decrease. The emission of CO_2 is caused by combustion of biomass, though the consumption of fossil fuels occurs when the carbon converts to CO_2. The zero of CO_2 achieving by the new trees or other plants replanted to the range that the CO_2 released can be reduced during the consumption of biomass energy. The appropriate management in energy plantations, it not concern in developing countries where the forest used for biomass energy not being replanted (Yokoyama,2008).

The availability of land is significant of widespread expansion of biomass energy otherwise used for food production or other commercial such as timber production (Yokoyama, 2008).The estimation of future biomass energy potential is ranging from 42 EJ to 350 EJ that closes to the total energy production by year 2100. Therefore, biomass energy should be wisely utilized in accordance with the food or valuable material production as well as environmental protection (H. Sano, 2002).

Biomass involves various and different in chemical property, physical property, moisture content, mechanical strength in biomass and transformation of technology to material and energy to materials and energy also diversified. Developing of effective cost and environmentally friendly to conversion technologies have been complete to reduce the dependency of fossil to restrain CO_2 emission and active the rural economics (H. Sano, 2002).

Plant and natural resource is the living thing that can be used in biomass. Biomass contain of carbon, hydrogen, oxygen, nitrogen. Apart from that, it also contains small quantities of alkali, alkali earth and heavy metals. The chemical and physical properties of biomass enable to produce coal and petroleum by transformation of fossil by geological processes. The carbon contain in fossil was removed and released from the atmosphere under different environmental conditions in. Therefore, utilization of biomass creates a closed loop carbon cycle in short of time. The higher energy density can be found in fossil fuel due to the oxidation of the carbon to carbon dioxide and hydrogen to water.

Biomass can replace a minor problem of the fuel and energy via combustion and fermentation of carbohydrates to ethanol fuel, enlargement of oil seed and invention of biogas through anaerobic digestion (Powlson et al., 2005). Gustavsson and his friend analyzed the energy efficiencies, costs and and biological impact on biomass energy in 1995. In Brazil, oil car fuel had been replace with sugarcane which is it converted into ethanol but the process growth highly inefficient. Nevertheless, production of biological fuel simply increases in CO_2 emission and fossil resources cannot compensate for past and currently emitted CO_2 (McKendry, 2002).

Biomass material can be categories into four:

i. Wood and wood waste
ii. Energy crops
iii. Agricultural residues
iv. Food waste

Wood and wood waste consist of bark and sawdust which is no chemical treatments but the physical and chemical properties influenced it sources. This type of wood is suitable used in energy applications. At a variety of scales, it can burn for heat and power for new developing technologies of produce a liquid and gaseous in biofuels (Koopmans, 1997). Meanwhile, it can distribute in energy crops which is have a high demand in fuel and output of potential performed. Therefore, it should be maximize the output of crops to energy supply and gives a big impact on crop management practice (Bain et al., 2002). The characteristic of energy crop are high

production, low energy input and cost, minimum in contamination of composition and required a low nutrient. These characteristics influenced on local climate change and soil conditions (McKendry, 2002).

Natural resources play an important role in conversion energy of biomass. The development of bioenergy industry, agricultural residues implied in renewable energy resources (Blasi et al., 1997). In general, residues presently related to the growing and selecting of product that consuming nutritional value or processing in industrially (Unal et al., 2010). Food waste embraces the highest potential of economic utilization due to high amount of carbon and effectively exchanges into biogas and organic fertilizer (Zafar, 2012).

2.1.1 Properties of Biomass

The characteristics of the biomass are important to determine the optimal of conversion process. Similarly, the selection of biomass is influenced by the process in which the energy is needed. These two features are interactive to be introduced in energy source of biomass. The specific material properties become important in processing that depending on the energy transformation processes. have classified the main material properties in subsequent process of biomass: (McKendry 2002)

i. Moisture content
ii. Calorific value
iii. Proportions of fixed carbon and volatiles
iv. Alkali metal content
v. Ash content
vi. Lignocellulosic ratio

2.1.1.1 Moisture Content

Two type of moisture content are importance in biomass which is intrinsic and extrinsic moisture. The intrinsic moisture means that the moisture contains in biomass without the influenced of weather effect, however extrinsic moisture contains influence of normal weather condition in harvesting (Khan et al., 2009). The moisture content in biomass is determined by the weather conditions during harvesting. In thermal conversion, woody and low moisture content herbaceous plant species are the most efficient biomass sources to liquid fuels, methanol. In high

moisture of herbaceous plant species, sugarcane is suitable for produce ethanol by biochemical (fermentation) conversion (McKendry, 2002).

2.1.1.2 Calorific Value

In biomass, calorific value is express as energy content or heat value when burnt in air. the calorific value can be measure in solid, liquid and gas phase. In solid phase, the measurement of calorific value in term of the energy content per unit mass or volume, MJ/kg, MJ/l for liquid and MJ/Nm^3 for gas. For fuel ,calorific value can be expressed in two forms such asthe gross calorific value (GCV) or higher heating value (HHV) and the nett calorific value (NCV) or lower heating value (LHV) (Khan et., 2009). The higher heating value present the total energy content released when the fuel burn in air. It also include the latent heat that contained in water vapour , so it describe recoverable the maximum amount of energy potential in biomass. In technology, the actual amount of energy had been described as the combustible gas, oil and steam. The lower heating value is applicable use for incompatible latent heat contained in water vapor (McKendry, 2001).

2.1.2.3 Propotions of Fixed Carbon and Volatile Matter

Solid fuel has been developed as coal which consists of chemical energy stored in fixed carbon and volatiles. The fixed carbon content refer to the mass remaining after releases of volatile, eliminating the ash and moisture contents. Meanwhile, the volatile content in solid is portion convert as gas by heating process. The fuel analysis used to determined volatile content, ash and moisture continued