A COMPARATIVE STUDY ON THE CARBON PRODUCTS FROM HYDROTHERMAL CARBONIZATION AND TORREFACTION PROCESS USING WOOD FIBER WASTE

by

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Thesis submitted in fulfillment of the requirements

for the degree of Chemical Engineering

FEBRUARY 2013

SUPERVISOR DECLARATION

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

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STUDENT DECLARATION

I declare that this thesis entitled “A comparative study on the carbon products from hydrothermal carbonization and torrefaction process using wood fiber waste” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature	
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Special Dedication of This Grateful Feeling to My Beloved father and mother;

Mr. ABU BAKAR B. CHAR** and **Mrs. HAMISAH BT. MAT

Also loving siblings

This is for all of you…

ACKNOWLEDGEMENT

Praise is to God for His help and guidance that I finally able to complete this Undergraduate Research Project.

Firstly, I would like to show my greatest appreciation to my supervisor, Dr. Saidatul Shima for her guidance, constant attention. I can’t say thank you enough for her tremendous support and help. Without her encouragement and guidance this research would not have materialized. I believe that all of her advices and comment are for the benefit of producing the best research project.

Special thanks to all assistant vocational training officers (JP) of laboratory for Chemical and Natural Resources Engineering Laboratory for their permission and helping throughout this project in term of borrowing equipment and others. I would also extend my sincere appreciation to my partner, Norfatin Sahira Binti Saidi for always be there for me through my thick and thin to complete the experiment.

Special appreciation goes to my loving parents who always giving me support to complete my thesis.

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ABSTRAK

Sisa serat kayu adalah salah satu sumber tenaga biojisim penting untuk ditukarkan kepada produk nilai tambah iaitu zarah karbon. Karbonisasi hidroterma (HTC) adalah kaedah yang berkesan untuk menukar biojisim ini ke dalam zarah karbon. Ciri-ciri yang tidak diperlukan oleh biojisim seperti kandungan lembapan yang tinggi dan sifat heterogen memberi halangan dalam daya saing pasaran penjanaan tenaga. Satu pilihan yang terbaik untuk mengatasi isu-isu yang dihadapi oleh biojisim adalah untuk menjalankan satu proses prarawatan yang dipanggil torrefaction. Ciri-ciri fizikal zarah karbon telah ditentukan dengan menggunakan FTIR, BET dan FESEM. Objektif utama kajian ini adalah untuk menghasilkan zarah karbon dari karbonisasi hidroterma dan proses Torrefaction menggunakan sisa serat kayu dan untuk mengenal pasti ciri-ciri fizikal zarah karbon daripada kedua-dua proses. Analisis proksimat telah dilakukan untuk mengenal pasti perubahan komposisi kimia dalam produk.Berdasarkan analisis, produk dengan kepadatan tenaga yang lebih tinggi, kandungan lembapan yang rendah telah dihasilkan daripada proses Torrefaction. Torrefaction proses menghasilkan produk dengan kandungan lembapan terendah iaitu kira-kira 3.99% kepada 4.47%. Kandungan abu juga menunjukkan bahawa proses torrefaction menghasilkan produk dengan peratusan terendah kandungan abu berbanding HTC dan mentah sisa serat kayu. Bahan meruap yang terkeluar adalah dari 53% kepada 91% bagi semua sampel. Torrefaction juga menghasilkan nilai tertinggi kalori (24.894MJ/kg). Analisis FTIR menunjukkan hidroksil, karbonil, alifatik, eter, alkohol, kumpulan fenol dan karboksilik hadir pada permukaan sampel. Akhirnya, kesimpulan yang boleh dibuat bahawa kedua-dua proses adalah kaedah yang praktikal untuk menukar biojisim kepada produk tambah nilai.

ABSTRACT

Wood fiber waste is the one important biomass energy source to convert to value added product which is carbon particles. Hydrothermal carbonization (HTC) is the effective method to convert this biomass into carbon particles. The undesirable properties of biomass such as high moisture content and its heterogeneous nature pose a barrier to its competitiveness in the energy generation market. A best option to overcome the issues face with biomass is to carry out a pretreatment process called torrefaction. The physical characteristic of the carbon particles was determined by using FTIR, BET and FESEM. The main objectives of this study are to prepare carbon particles from hydrothermal carbonization and Torrefaction process using wood fiber waste and to identify physical characterization of carbon particle from the both processes. Proximate analysis has been done to identify the changes in chemical composition of the product. Based on the analysed, the product with higher energy density, low moisture content was produced from Torrefaction process. Torrefaction process produced lowest moisture content product which is about 3.99% to 4.47%. Ash content also shows that torrefaction process produced product with lowest percentage ash content compared to HTC and raw of wood fiber waste. The volatile matter left is from 53% to 91% for all the samples. Torrefaction also produce highest calorific value (24.894MJ/kg). FTIR analysis showed the hydroxyl, carbonyl, aliphatic, ethers, alcohol, phenol and carboxylic groups are present on the surface of the sample. Finally, it can be concluded that both processes is practicable method to convert biomass into value added product.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Biomass is a renewable, potentially sustainable and environmentally benign source of energy. According to Tye et al., (2011), Biomass contribute about 12% of today's world primary energy supply, while in many developing countrys, its contribution range from 40% to 50%. World production of biomass is estimated at 146 billion metric tons a year (Balat and Ayar, 2005). Some farm crops and trees can produce up to 20 metric tons per acre of biomass a year. Biomass in definition is any organic matter such as wood, crops, seaweed, animal wastes that can be used as an energy source. Traditionally biomass has been utilized through direct combustion.

There are abundant volumes of wood fiber waste production which normally being dumped to the landfill. The total land area in Malaysia is 32.98 million hectar (ha). According to the Malaysian Timber Council (MTC) in 2009, the total production of logs based on the total land area is 18.27 million cm^3 has produced 438,340 m^3 of logs, 270,891 m^3 of sawn timber and 683,498,732 m^3 of plywood in 2009. Wood, agricultural fiber residues also known as agrifibers, and other woody plants are composite materials whose main components are polysaccharides (cellulose and hemicelluloses) and lignin. Wood fiber waste also known as biomass which is a qualified carbon raw material for synthesis of valuable carbonaceous materials because it is available in high quality and huge amount.

There are several methods to convert this biomass waste product into value added product. Hydrothermal carbonisation (HTC) is the best method because their process is benign environment, versatile chemistry, enhanced reaction rate and economics cost. HTC can generate both solid carbonaceous material and water soluble organic liquid. The solid carbonaceous material are sometimes called biochar which is defined as fine grained charcoal, high in organic carbon and largely resistance to decomposition. HTC process can release one third of the combustion energy throughout dehydration (Funke and Ziegler, 2010). Its carbon efficiency is close to 1 after an adequate reaction time under proper condition. The conversion of biomass into carbon particle is promising potential applications in many fields such as water purification, carbon fixation, energy storage, fuel cell catalysis, carbon dioxide sequestration, bioimaging, drug delivery, and gas sensors (Hu et al., 2010). For the HTC process, the initial structure and composition of the biomass material can influence the size, shape, and surface structure of the final biochar.

Acccording to the Chew and Doshi (2011), biomass and its utilization have been intimately associated to renewable energy in the recent years. However, the undesirable properties of biomass such as high moisture content and its heterogeneous nature pose a barrier to its competitiveness in the energy generation market. A viable option to overcome the issues associated with biomass feedstock is to carry out a pretreatment process called torrefaction. Biomass torrefaction is gaining attention as an important preprocessing step to improve the quality of biomass in terms of physical properties and chemical composition. A recent study (Tumuluru et al., 2011) mentioned that torrefaction is the slow heating of biomass in an inert or reduced environment to a maximum temperature of approximately 300°C. Torrefaction can also be defined as a group of products resulting from the partially controlled and isothermal pyrolysis of biomass occurring in a temperature range of 200–280ºC. The process can be called a mild pyrolysis as it occurs at the lower temperature range of the pyrolysis process. Torrefaction proses can produce a solid uniform product with lower moisture content and higher energy content than raw biomass (Tumuluru et al., 2011). Most of the smoke-producing compounds and other volatiles are removed during torrefaction, which produces a final product that has a lower mass but a higher heating value.

1.2 Problem Statement

Biomass mainly in the form of wood is the oldest source of energy used by humans. Traditionally, biomass has been utilized through direct combustion. Burning biomass produces some pollutants, including dust and the acid rain gases sulphur dioxide (SO_2) and nitrogen oxides (NO_x). Burning wood produces 90% less sulphur than coal. These can all be reduced before releasing the fuel gases into the atmosphere. The demand for energy is increasing at an exponential rate due to the exponential growth of world population. This combined with the widespread depletion of fossil fuel and gradually emerging consciousness about environmental degradation. Biomass is carbon dioxide neutral. Substitution of fossil fuels for energy for energy production with biomass will result in a net reduction in greenhouse gas emissions and the replacement of a non-renewable energy source.

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. Due to environmental concerns because of abundant wood fiber waste from day to day, it is an attractive option to create new technologies to convert biomass waste especially wood fiber waste into value added product. The need for efficient biomass conversion technologies and high cost of conventional nanoparticle synthesis production such as arc discharge and steam explosion, hydrothermal carbonisation method represents one of the promising chemical routes to treat this biomass because of the intrinsic advantages such as benign environment, versatile chemistry, enhanced reaction rate and economic cost.

Biomass like any other energy source has its advantages and disadvantages. One of the most obvious drawbacks is the heterogeneous nature of biomass. Biomass feedstock can differ considerably in term of physical, chemical and morphological characteristics. Biomass has relatively low energy density and high moisture content in its untreated form compared to fossil fuel. Due to this issue faced with biomass, torrefaction is the pretreatment biomass that can be used to overcome this problem.

1.3 Research Objectives

This study outlines the following objectives:

1.3.1 To prepare carbon particles from hydrothermal carbonisation process using wood fiber waste.

1.3.2 To prepare torrefied biomass from wood fiber waste by torrefaction process

1.3.3 To identify physical characterization of carbon particle from hydrothermal carbonisation and torrefaction process using wood fiber waste.

1.4 Significance of Proposed Study

This research is about the development of advanced materials focusing on production of carbon particle from hydrothermal carbonisation process and production of torrefied biomass using wood fiber waste. In addition, analysis on the physical characterization of carbon particle from torrefaction and hydrothermal carbonisation process using wood fiber waste were also carried out. This proposed study will help to produce carbon particle using wood fiber waste from hydrothermal carbonisation which are facile, low cost, environmental friendly and non-toxic routes. The carbon particle also can be commercialized because of wide variety potential application either in environment, catalysis, energy, sensor, and biology application. Besides that, this proposed study also can reduce the amount of abundant wood fiber waste from the industries by adding the value of the solid material and avoid pollution to the environment.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass Uncover the Opportunities behind the Mess

2.1.1 Introduction to Biomass

Biomass, also known as biorenewable resources, which is defined as all materials of biological origin, excluded materials that have been imbedded in geological formations and have become fossilized such as oil and coal. Brown (2003), pointed out that biomass by definition is sustainable resources or resources that are renewed at such rate that they will be available for future generations. Biomass is any organic matter such as wood, crops, seaweed, animal wastes that can be used as an energy source. All organic matter contains stored energy from the sun.

During a process called photosynthesis, sunlight gives plants to the energy they need by converting water and carbon dioxide into oxygen and sugars. Biomass is a renewable energy source because its supplies are not limited.

$$\underset{\text{Carbon dioxide}}{6CO_2} + \underset{\text{Water}}{12H_2O} \xrightarrow[\text{Green plant}]{\text{Light}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Oxygen}}{6O_2} + \underset{\text{Water}}{6H_2O}$$

Biomass has been used as a substitute for fossil fuels in recent years. The energy in biomass is known as biomass energy or bio-energy. Bioenergy is defined as the conversion of biomass into heat or electric power. The growing interest in bio-energy will contribute to the reduction of poverty in developing countries, increase the sustainable energy supply and reduce the emission of CO_2.

2.1.2 Biomass resources

Biomass can be classified into biowaste and dedicated energy crops. A biowaste is a material that has been traditionally discarded because it has no apparent value or represents a nuisance or even a pollutant to the local environment. This was seen in the recent study (Brown, 2003) that biowastes include agricultural residues, yard waste, municipal solid waste, waste from food processing industry, sewage and manure. Dedicated energy crops are plants grown specifically for production of biobased products that is, for purposes other than food or feed. They are planted and harvested periodically. This does not include cutting down an old-growth forest for firewood. Dedicated energy crops can either be herbaceous energy crops or short-rotation energy crops (Brown, 2003), Brown (2003) pointed out that herbaceous energy crops are plants with no or little woody tissue. They can be thick stemmed grasses such as sugarcane, energy cane and corn, or thin-stemmed grasses such as reed canary grass and switch grass. Short-rotation energy crops are fast growing woody biomass, including hardwoods and softwoods. Softwoods are pine, spruce and cedar. Brown (2003) also highlighted that these species have considerable value as construction lumber or pulpwood, and are therefore mostly only available as logging and manufacturing residues. Examples on hardwood species for energy production are poplar, willows (*Salix spp*.) and eucalyptus.

Biomass energy resources come from wood and wood wastes, agricultural crops and their waste byproducts, municipal waste (MSW), animal waste and food waste. Presently, the available biomass resources could provide as much as 6.33–10.55 $\times10^{15}$ kJ of feedstock energy as mention in the literature (Demirbas and Ozturk, 2006). The average majority of biomass energy is produced from wood and wood wastes (64%), followed by MSW (24%), agricultural waste (5%), and landfill gases (5%) (Demirbas, 2001 ; Deshmukh et al, 2008 ; Demirbas, 2006 ; Demirbas, 2008).

Table 2.1 Biomass production in Malaysia (BioGen Resource Assessment 2004)

Type of industry	Production (Thousand tonne)	Residue	Residue product ratio (%)	Residue generated (Thousand Tonne)	Potential Energy PJ
Oil palm	59,800	EFB	21.14	12,642	59
		Fiber	12.72	7,607	113
		Shell	5.67	3,391	57
	Total			23,640	229
	Others (POME)			41,860	24
Paddy	2,141	Rice husk	22	471	7.6
		Paddy straw	40	856	8.8
Sugar	1,111	Bagasse	32	356	356
Wood	2,937,697 m^3	Sawn Timber	0.5-0.6	1,692,718 m^3	5.2
	523,336	Plywood and veneer	0.18-0.65	121,000 m^3	0.374
	147,813	Molding	0.2-1.0	75,600 m^3	0.232
MSW (Incenaration technology)	11,940 tonnes/day	MSW	-	-	-

Table 2.1 shows the biomass production in Malaysia. Oil palm industry produce 59,800 thousand tonne per year, and the residue generated is 23,640 thousand tonne which about 229 of potential energy. Production of sawn timber (2,937,697m^3), plywood & veneer (523,336 m^3) and molding (147,813m^3) from wood industry can generate potential energy of 5.2PJ for sawn timber, 0.374PJ of plywood and veneer and 0.232PJ of molding residue. Agricultural residues are basically biomass materials that are byproducts of agriculture. This includes cotton stalks, wheat and rice straw, coconut shells, maize and jowar cobs, jute sticks, rice husks, and etc, this was seen in the recent study (Demirbas, 2006). The most common agricultural residue is the rice husk, which makes up 25% of rice by mass as mentioned in the literature (Demirbas et al, 2006). Many developing countries

have a wide variety of agricultural residues in ample quantities. Demirbas, (2001) highlighted that large quantities of agricultural plant residues are produced annually worldwide and are vastly underutilized.

Municipal solid waste (MSW), also called urban solid waste, is a waste type that includes predominantly household waste (domestic waste) with sometimes the addition of commercial wastes collected by a municipality within a given area. They are in either solid or semisolid form and generally exclude industrial hazardous wastes. The term residual waste relates to waste left from household sources containing materials that have not been separated out or sent for reprocessing.

2.1.2.1 Wood fiber waste as a valuable biomass

Abundant of wood fiber waste derived from agricultural residue and forest byproduct has drawn little attention as a raw material to convert into more value added product since only simple combustion has been used to elevate the value of waste biomass. Wood waste is mostly found in logging activities. The total land area in Malaysia is 32.98 million ha. According to the Malaysian Timber Council (MTC) in 2009, the total production of logs based on the total land area is 18.27 million cm^3 has produced 438,340 m^3 of logs, 270,891 m^3 of sawn timber and 683,498,732 m^3 of plywood in 2009. In addition to profits, these industries generate a huge amount of abundant wood waste, which can potentially give rise to environmentally sensitive disposal issues. In order to fully utilize the waste, it can be converted into value added product.

Waste wood from the forest products industry such as bark, sawdust, board ends and others are widely used for energy production. Wood industry, in many cases, is now a net exporter of electricity generated by the combustion of wastes. Combustion also may lead to the air pollution and increasing carbon dioxide concentration in atmosphere. The comprehensive study (Schmidt and Daunenhauer 2007; Tilman, Hill & Lehman 2006) highlighted that carbon materials fabricated from waste biomass have shown promising applications as sorption materials, hydrogen storage, biochemicals and others.

Biomass is a qualified carbon raw material for the synthesis of valueable carbon materials because it is available in high quality, huge amount and environmental friendly renewable resource. The hard plant tissue, with structural, crystalline cellulose scaffolds, shows a different structural disintegration pathway. The melting point of crystalline cellulose is well above its decomposition temperature, which to a large extent can result in a preserved macro- and microstructure in the final carbonaceous material. The lignin fraction of biomass essentially goes unchanged through the hydrothermal carbonisation process (HTC). By cycloaddition, it can be cross linked to coal, but the essential lignin structure remains stable in the rather mild conditions of HTC as mentioned in the literature (Antonietti, 2007). Thus, for the hydrothermal carbonization of biomass, materials with low lignin contents and high cellulosic contents are preferred.

2.1.3 Biomass potential

The total contribution of biomass to the primary energy supply of Malaysia has been estimated to be at least 90 PJ. At present, the main contribution to biomass is from palm-oil waste, which is about 80% of the total utilized biomass. Poh and Kong, (2002) highlighted that the total technical potential of biomass in Malaysia is around 130 PJ, which is about 5% of the national energy requirement. For instance, Malaysian industries, such as sugar, palm oil, rice and wood, have been utilizing their biomass as fuel to cover some or all of their energy requirements as mentioned in the literature (Sumathi, Chai & Mohamed, 2008). In Malaysia, it is estimated that potentially 1340 MW of energy can be generated from biomass by 2030 (Tye et al., 2011). Biomass is considered to be one of the main renewable energy resources of the future due to its large potential for economic viability and various social and environmental benefits. Many different types of biomass can be grown for the express purpose of energy production.

2.2 Hydrothermal carbonisation (HTC)

2.2.1 History of HTC

Titirici, Thomas and Antonietti (2007) pointed out that hydrothermal carbonisation in material synthesis is a 100-year-old technique, with increasing interest originating from the charcoal formation. Bergius first described the hydrothermal transformation of cellulose into coal-like materials in 1913, this was seen in the recent study (Hu et al., 2010). As mentioned in the literature, detailed investigations were focused on the biomass source, the formation process, and the identification of the final coal composition. Since the discovery of carbon nanotubes in 1991 as mentioned in the literature (Hu et al., 2010) the high-temperature HTC process has been developed quickly. The comprehensive study (Wang et al., 2001; Sun and Li, 2004) highlighted that at the beginning of the new century, a renaissance in the low-temperature HTC process appeared with the reports on the synthesis of uniform carbonaceous particles from sugar or glucose. In the past few years, lots of functional carbonaceous materials from biomass have been produced via the HTC process and these materials have shown great potential in many fields, this was seen in the recent study (Hu et al. 2010). Nowadays, with the gradual acknowledgement of hydrothermal process and carbonization mechanism, the HTC has been widely used to smartly design novel carbon and carbonaceous materials from biomass with important applications (Titirici, Thomas & Antonietti, 2007 ; Hu et al. 2010).

2.2.2 The HTC process

Carbohydrate is important constituents of both plants and animals. Compounds classified as carbohydrates range from those consisting of a few carbon atoms to gigantic polymeric molecules. Carbohydrates that cannot be broken down into simpler units by hydrolysis reactions are known as monosaccharides. Examples of monosaccharides are glucose and fructose (both $C_6H_{12}O_6$) as mentioned in the literature (Lilliestråle, 2007). Carbohydrates in a slightly acidic, aqueous solution are mildly heated (180-205°C) in closed recipients, forming condensed, coal-like structures (Lilliestråle, 2007). Depending on the extent of the reaction, four to five water units per carbohydrate molecule are eliminated in the final product (Antonietti, 2006).

$$[C_6H_{12}O_6]_n \rightarrow n[C_6H_4O_2 + 4H_2O]$$

The elimination of water in the presence of water seems counterintuitive, but the reaction is both exothermic in character as well as strongly supported by entropy. This is due to the increment of the number of mole and the degree of freedom (Antonietti, 2006). For complex biomass, the chemical decomposition cascade of HTC is more complex than for pure glucose. Model examinations with glucose and GC-MS examinations of the intermediary states of biomass indicate that the main reaction channel of HTC is a very quick partial dehydration of the carbohydrate to hydroxymethylfurfural (chemical composition). The hydroxymethylfurfural subsequently undergoes cycloaddition and polymerization reactions, essentially resulting in structures rich in carbonyl, aliphatic and aromatic hydroxy groups. As mentioned above, four to five water units per saccharide unit are eliminated in the process, depending on the extent of the reaction (Lilliestråle, 2007). Author pointed out that due to the fact that the HTC process progresses through liquid intermediates, which later cyclize or polymerize to the final coal like material, the final product consists of nanometer scaled, globular carbon spheres. the spheres have highly hydrophilic surfaces, with a distribution of hydroxyl (OH) and carbonyl (C=O) groups that are formed from non- or just partially dehydrated carbohydrates (Lilliestråle, 2007). In a typical reaction with glucose as starting material, elemental analysis shows that 70 - 92 wt% of the product can be attributed to carbon. The remaining mass is made up of oxygen and hydrogen atoms in the hydrophilic shells and this was seen in the recent study (Lilliestråle, 2007).

Hydrothermal carbonization is a thermochemical conversion process which combined dehydration and decarboxylation of a fuel to raise its carbon content with the aim of achieving a higher calorific value of coallike product. It is realized by applying elevated temperatures (180–220°C) to biomass in a suspension with water under saturated pressure for several hours. Hydrothermal carbonisation is an exothermal process that lowers both the oxygen and hydrogen content of the feed by mainly dehydration and decarboxylation. With this conversion process, it’s easy to handle fuel with well-defined properties can be created from biomass residues, even with high moisture content.

Thus it may contribute to a wider application of biomass for energetic purposes. It has been used for almost a century in different sciences, mainly to simulate natural coalification in the laboratory. Nowadays, the hydrothermal process has become an important technique for the synthesis of various kinds of inorganic materials, such as functional oxide, and non-oxide nanomaterials with specific shapes and sizes, as well as for the synthesis of new solid (Hu et al., 2010). In principle, any kind of biomass can be carbonized hydrothermally. Namely model substances, such as cellulose and lignin, as well as wood, plant tissue, resin and peat have been successfully treated.

2.2.3 Classification of HTC

Hydrothermal carbonisation can be divided into two main parts by applied temperature. The high-temperature HTC process proceeds between 300 and 800 °C and is therefore clearly beyond the stability of standard organic compounds. Hydrothermal carbonization at high temperatures gave various carbon materials, multi-walled carbon nanotubes, fullerenes, and carbon spheres with different nanotextures. The low-temperature HTC process performs below 300 °C, and functional carbonaceous materials can be produced according to dehydration and polymerization schemes known from ordinary organic chemistry. A recent study (Titirici, Thomas and Antonietti, 2007) highlighted that for the coalification of biomass, the low-temperature HTC process is presumably close to natural coalification but, of course, at highly accelerated speed, decreasing the reaction time from some hundred million years to the time-scale of hours. In addition, it is a spontaneous, exothermic process, with the vast majority of the carbon of the starting products also found in the final product. In the hydrothermal carbonization at a low temperature, the pressure is usually built up by water vapor, and so depends on the volume of the autoclave and also on the amount of water. Therefore, the higher temperature causes the higher pressure, and consequently the pressure is not presented in most literatures. Hydrothermal carbonization at low temperatures was applied on various sugars, where carbon spheres were obtained as main products.

2.2.4 Process condition of HTC

There is no common definition of hydrothermal carbonization. A recent study (Funke and Ziegler, 2010) highlighted some conditions for hydrothermal carbonization process. The operation should be limited to subcritical conditions of water, due to physical and chemical reasons. Author also pointed out that the temperature must be above 100°C so at this range first reactions have been observed. Substantial hydrolysis starts at a temperature of about 180°C. There needs to be a liquid water phase or at least saturated pressure is necessary. The feed needs to be submerged during the whole process as mentioned in the literature (Funke and Ziegler, 2010). Besides that, author also has listed other condition which is the pH-value should be below 7 because alkaline conditions lead to a substantially different product. Due to byproducts, the pH value drops automatically during hydrothermal carbonization.

A recent study (Funke and Ziegler, 2010) highlighted that the residence time cannot be limited to a meaningful range because reaction rates are largely unknown. Typical published experimental times varied between 1 and 72 h. The term hydrothermal carbonization is refers to the formation of a solid residue under the above mentioned conditions. Despite these parameters, which are based on physical and chemical considerations, it appears unlikely that practical implementations of hydrothermal carbonization operate outside a temperature range of 180–250°C. Many researchers use the term ‘reaction severity’, which also proved useful for this survey. A higher reaction severity refers to both increasing temperature and/or longer residence time of the feed. With increasing reaction severity, a product with higher carbon content is produced at a lower theoretically possible yield.

2.2.5 Advantages with HTC

The HTC process is the best method for carbon conversion. It requires only heating process of a biomass dispersion under weakly acidic conditions in a closed reaction vessel for 4–24 h to temperatures of around 200 °C. This is indeed an extremely simple, cheap and easily scalable process. HTC inherently requires wet starting products or biomass, as effective dehydration only occurs in the presence of water, plus the final carbon can be easily filtered from the reaction solution. This way, complicated drying schemes and costly isolation procedures can be conceptually avoided. In addition, under acidic conditions and below 200 °C, most of the original carbon stays bound to the final structure. Carbon structures produced by this route either for deposit or materials use are therefore the most CO_2-efficient. Furthermore, the HTC process is a spontaneous, exothermic process.

Due to the high thermodynamic stability of water, it liberates about a third of the combustion energy stored in the carbohydrate. The carbon efficiency (CE) of HTC is close to 100% for dehydration. HTC can be seen as much more than just a technique for making carbon-rich substances. The comprehensive study (Lilliestråle, 2007) highlighted that for this value temperatures below 200 °C and a pH value between 5 and 7 are mandatory. The CEs of fermentation and anaerobic digestion are 66% and 50%, respectively (Lilliestråle, 2007). A schematic comparison of HTC with fermentation and anaerobic digestion from the literature (Lilliestråle, 2007) is shown below in the figure. This is proved that HTC produced high carbonaceous materials.

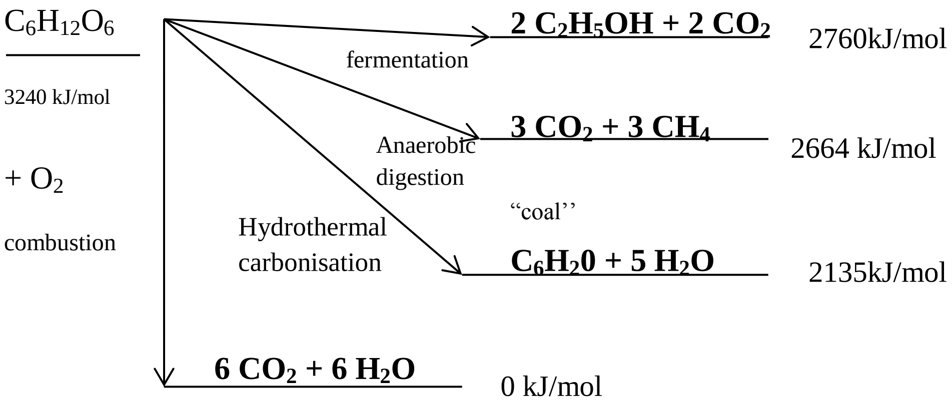


Figure 2.0 Energy distributions from conversion of biomass by different methods.

2.2.6 Potential applications of HTC

The HTC process could be used to sequester carbon from biomass for either material or energy use. Since all carbon in the starting product ideally stays bound to the final structure, large scale HTC of biomass can also be seen as an efficient carbon sink. A recent study (Lilliestråle, 2007), listed out one application is the technical synthesis of carbon nanostructures. Recently, it has been shown that the presence of metal ions effectively accelerates the HTC of starch and directs the synthesis towards various metal/carbon nanoarchitectures such as carbon nanocables, nanofibers and spheres as mentioned in the literature (Lilliestråle, 2007). Furthermore, the carbonaceous materials can be used as a raw material in the chemical industry, as isolation material in buildings, as sorption coal for drinking water purification as improvement of concrete materials (Lilliestråle, 2007).

Products from HTC could be used for energy production. HTC can convert biomass into energy, such as ethanol, biodiesel and biogas production. Other processes, such as the Fischer-Tropsch process, can covert coal into transportation fuels (Lilliestråle, 2007). Besides that, HTC can be used to degrade biowaste from agriculture, for example left-overs from sugarbead and rapeseed production. Orange peels contain flavones and limonenes; substances that will hinder microbial degradation of the biomass. HTC has proved to work well for orange peels and results in a product that is suitable as fertilizer as mentioned in the literature (Lilliestråle, 2007). The carbonaceous end-products could be used as a fertilizer to improve soil quality.

Furthermore, the HTC process can be used for carbon sequestration. More than 80% of the global terrestrial carbon stocks are found in soils, this was seen in the recent study (Lilliestråle, 2007). Stable humus produced with HTC will draw carbon dioxide from the atmosphere and keep it in the soil for hundreds to thousands of year (Lilliestråle, 2007). The growing concerns for global warming caused by increasing anthropogenic emissions of GHGs, mainly from the combustion of fossil fuels and deforestation, it would indeed be desirable to capture atmospheric carbon dioxide and store it as a stable carbon material.

2.3 Reaction mechanisms

There are various chemical reactions that can be used in hydrothermal carbonisation such as, hydrolysis, dehydration, decarboxylation, polymerization, aromatization and other mechanisms. Funke and Ziegler, (2010) highlighted that biomass components are being hydrolyzed to a vast amount of oligomers and monomers. Extractables are being eluted simultaneously and most of them exhibit very good water solubility (Funke and Ziegler, 2010). These solved fragments and extractables are subject to subsequent degradation mechanisms, such as dehydration and decarboxylation, while condensation reactions take place.

2.3.1 Hydrolysis

Hydrolytic reactions lead to the cleavage of mainly ester and ether bonds of the bio macromolecules by addition of 1 mole of water. The wide range of products includes (oligo-) saccharides of cellulose and phenolic fragments of lignin. Funke and Ziegler, (2010) pointed out that an impression of the complexity of the resulting reaction network is given by the hydrolysis of D-fructose, which is a specified substance in contrast to biomass. Other degradation mechanisms mentioned below, the resulting fragments are being further hydrolyzed for example 5-(hydroxymethyl) furfural (HMF) to yield levulinic and formic acid as mentioned in the literature Funke and Ziegler, (2010). Cellulose is being hydrolyzed tremendously under hydrothermal conditions above approximately 200°C (Peterson et al. 2008). Hemicellulose readily hydrolyzes at around 180°C, but detailed reaction pathways are less well understood. Alkaline conditions give the highest reaction rates compared to acidic and conditions, whereas further degradation reactions of glucose are highly enhanced by acidic conditions. Funke and Ziegler, (2010) highlighted that in a pH range from 3 to 7, the rate of reaction is largely independent of $H+$ and $OH-$ concentration, probably because the hydrogen bond between cellobiose and H_2O is stronger at high temperatures than the influence of pH in this region.

Funke and Ziegler, (2010) pointed out that hydrothermal degradation of lignin is most likely realizable at around 200°C due to its high amount of ether bonds. Highly reactive products with a low molecular weight are being formed by nucleophilic reactions. One of them with potential interest is acetic acid, which is most likely formed by hydrolysis of side chains as mentioned in the literature Funke and Ziegler, (2010). They highlighted that the amount of different fragments being formed is very high, even by hydrolysis of selected components. Many of these fragments are highly reactive and quickly form precipitates by condensation reactions. Interactions between the different biomass components and its fragments cannot be avoided. The effect of such interactions on hydrolysis is largely unknown. It has been supposed that hemicellulose fragments interact with lignin and thus enhance the solubility of its aromatic structures (Funke and Ziegler, 2010). It can be concluded that the rate of hydrolysis of biomass is primarily determined by diffusion and thus limited by transport phenomena within the matrix of biomass. This may lead to condensation of fragments within the matrix of the biomass at high temperatures as mentioned in the literature (Funke and Ziegler, 2010).

2.3.2 Dehydration

In this study, dehydration is used as main chemical reaction in hydrothermal carbonisation. This is because to the final product with high carbon content. Dehydration during hydrothermal carbonization can cover both chemical reactions and physical processes, which remove water from the biomass matrix without changing its chemical constitution. Chemical dehydration significantly carbonizes biomass by lowering the H/C and O/C ratios.

Early experiments with oil discovered that cellulose starts decomposing by pure dehydration according to

$$4(C_6H_{10}O_5)_n \quad \longleftrightarrow \quad 2(C_{12}H_{10}O5)_n + 10H_2O$$

Significant decarboxylation only appears after that specific amount of water is formed as mentioned in the literature (Funke and Ziegler, 2010). It is largely unknown to which extent biomass can be carbonized without major decarboxylation. During common hydrothermal carbonization, the rate of dehydration appears to be much higher than decarboxylation. Dehydration is generally explained by elimination of hydroxyl groups (Funke and Ziegler, 2010). For the case of lignin, the dehydroxilation of catechol is mentioned as well as the possible formation of water during the cleavage of phenolic and alcohol groups above 150°C and 200°C, respectively.

Another source of water during hydrothermal carbonization may be due to the condensation of fragments, which is discussed below. When hydrothermal conditions are applied to biomass, the physical dewatering is linked closely to the above mentioned chemical changes. These effects have been utilized for the drying of lignite (‘hydrothermal dewatering’) and peat (‘wet carbonization’) (Funke and Ziegler, 2010). Due to a lower viscosity of water, destruction of colloidal structures, less hydrophilic functional groups, and gas formation, physical dewatering is enhanced significantly under hydrothermal conditions.

2.3.3 Decarboxylation

Hydrothermal treatment causes a partial elimination of carboxyl groups. Carboxyl and carbonyl groups rapidly degrade above 150°C, yielding CO_2 and CO, respectively as mentioned in the literature (Funke and Ziegler, 2010). Author highlighted that more CO_2 is being formed than can be explained by elimination of carboxyl groups. Therefore, other mechanisms must be involved. One likely source for CO_2 is formic acid, which is formed in significant amounts during the degradation of cellulose and decomposes under hydrothermal conditions to yield primarily CO_2 and H_2O. Other possible sources may be the formation of CO_2 during condensation reactions as well as the cleavage of intramolecular bonds (Funke and Ziegler, 2010). Another assumption is that H_2O acts as an oxidizing agent at elevated temperatures (above 300°C) and that additional CO_2 is formed by the thermal destruction of such oxidized units (Funke and Ziegler, 2010).

2.3.4 Polymerization

Unsaturated compounds which polymerize easily are being created by the elimination of carboxyl and hydroxyl groups (Funke and Ziegler, 2010). The author also explained that condensation reactions are often accounted for some of the formation of CO_2. The rate of carbonization is increasingly determined by steric influences with a higher condensation degree of aromatics. It thus may be concluded that the formation of HTC-coal during hydrothermal carbonization is mainly characterized by condensation polymerization, specifically aldol condensation as mentioned in the literature (Funke and Ziegler, 2010). Condensation most likely proceeds mainly with the formation of H_2O. Condensation reactions of monosaccharides are even slower, especially as cross-linked polymerization competes with recondensation to oligosaccharides (Funke and Ziegler, 2010). Polymerization, which forms a solid precipitation, is widely regarded as an unwanted side reaction and therefore is minimized to a great extent in other hydrothermal processes.

2.3.5 Aromatization

Even though cellulose/hemicellulose consists of carbohydrates, it is able to form aromatic structures in both non-hydrous and hydrothermal conditions (Funke and Ziegler, 2010). Author also pointed out that alkaline conditions appear to enhance the formation of aromatic structures. Aromatic structures exhibit a high stability under hydrothermal conditions and therefore may be considered as a basic building block of the resulting HTC-coal. Cross-linking condensation of aromatic rings also makes up for major constituents of natural coal which might explain the good agreement between natural coalification and hydrothermal carbonization (Funke and Ziegler, 2010). On the basis of these considerations it becomes evident that the effect of hydrothermal treatment on the carbon content decreases with a rising number of aromatic bonds.

2.3.6 Other mechanism

Thermal pyrolysis is process in absence of oxygen. It is known to be efficient for large scale production of carbon nano particles at low operating cost (Funke and Ziegler, 2010). Pyrolytic reaction also competing reaction under hydrothermal conditions as mentioned in the literature (Funke and Ziegler, 2010). In general they might become significant above 200°C though typical products from pyrolysis such as CO and tars have not been reported to be formed in significant amounts during hydrothermal carbonization. A recent study (Hashaikeh et al, 2007; Shoji et al. 2005) highlighted that carbonization of biomacromolecules, which do not have contact to H_2O because they have been blocked by precipitation of condensing fragments, has also been explained by pyrolytic reactions.

Hydrolytic reactions lead to the cleavage of mainly ester and ether bonds of the biomacromolecules by addition of 1 mole of water. The wide range of products includes (oligo-) saccharides of cellulose and phenolic fragments of lignin. A recent study (Funke and Ziegler, 2010) highlighted that an impression of the complexity of the resulting reaction network is given by the hydrolysis of D-fructose, which is a specified substance in contrast to biomass.

2.4 Application of HTC carbon particles

Hydrothermal carbonization (HTC) process of biomass is a promising candidate for the synthesis of novel carbon-based materials with a wide variety of potential applications such as carbon fixation, water purification, fuel cell catalysis, energy storage, CO_2 sequestration, bioimaging, drug delivery, and gas sensors.

2.4.1. Environment Applications

As HTC operates with biomass, all chemistry and technology on the base of HTC products are essentially sustainable, close to ‘‘CO2-neutral’’ operations. It is known any open biomass is rapidly degraded by microbe or fungi, for example, and turned into CO_2 again. Biomass represents the biggest carbon converter with the highest efficiency to collect and bind CO_2 away from the atmosphere and any type of carbonization can transfer this biomass into less degradable coal compounds. Thus, using the HTC process to convert biomass into coal rapidly could represent a most efficient tool for CO_2 sequestration this was seen in the recent study (Titirici, Thomas & Antonietti 2007). The desirable acceleration of the coalification of biomass by a factor of 10^6–10^9 makes it a technically attractive and realistic ‘‘artificial’’ instrument for fixing the carbon of biomass on large scales. In addition, it is the most efficient strategy for carbon fixation, with carbon efficiency close to 1.

Water pollution now becomes a worldwide problem that threatens human health. Therein, heavy metal ions, pesticides, and drug residues are most hazardous. Recently, scientists began to test carbonaceous materials derived from biomass via HTC process as specific sorbents for those purposes, for their surfaces contain many functional groups to act as potential sorption sites. During the hydrothermal process, the glucose decomposes into HMF, and then undergoes cycloaddition with acrylic acid and polycondenses into derivatized CSPs. Compared with the product from pure glucose, the surface of the resulting product surface here has much more carboxylate groups that can bind to metal ions easily.

2.4.2 Generation of metal oxide nanostructures

The chemical and physical properties of nanomaterials are tightly related to their morphologies. Recently, porous hollow spheres draw an increasing attention for their low density, high surface area, and good permeability, which make these hollow materials good candidates for catalysis, sensing or other applications. The comprehensive study by (Hu et al., 2010) highlighted that the general synthesis method mainly includes the adsorption of metal ions from solution to the surface layer of carbonaceous spheres and subsequent removal of the carbonaceous cores via calcinations. Based on this method, some hollow spheres were successfully synthesized such as Ga_2O_3 (Hu et al., 2010).

It is worth mentioning that the sizes and structures of different metal oxide hollow spheres are predominantly determined by the templates. These as-synthesized hollow spheres showed high potential applications in the area of gas sensitivity or catalysis. Other kinds of templates have also been used for the synthesis of metal oxide hollow spheres via sacrificial-core techniques, such as colloidal nanoparticles for example Au, Ag, or CdS and sub-micrometer polystyrene spheres, but these templates are confined to the synthesis of a few particular compositions such as SiO_2, TiO_2, SnO_2, ZrO_2, and Fe_3O_4 and cannot be applied as widely as the HTC carbon templates.

(Hu et al., 2010).pointed out that carbonaceous nanofibre also has been used as template for the synthesis of hollow metal oxide fibres. This method can even be extending to the synthesis of uniform ternary oxide nanotubes such as $BaTiO_3$ (Hu et al., 2010). Compared to carbon nanotubes, the carbonaceous fibers by the HTC process have higher surface reactivity, making them more suitable for templating production of a variety of metal oxide nanotubes this was seen in the recent study (Hu et al., 2010). The HTC-generated carbonaceous materials can also sacrifice themselves to template some special core shell-like structures.

The carbon spheres produced during the HTC process can be profitably used as sacrificial templates for the production of new materials. After the hydrothermal treatment of mixtures of carbohydrates with different metal salts in water inside sealed steel autoclaves at 180 °C, carbon spheres with the metal oxide precursors tightly embedded in the microspheres were obtained. The removal of carbon directly resulted in hollow spheres of the corresponding metal oxide that were composed of nanoparticles with high surface areas.

Production of TiO2 hollow spheres was reported by (Hu et al., 2010). The hollow sphere was prepared hydrothermal carbon spheres using the hydrothermal carbonization of glucose. The authors afterwards took advantage of the oxygenated functional groups on the surface of the carbon spheres and dispersed the carbon spheres in a toluene solution of titanium tetraisopropoxide. Hydrolysis of the orthoesters by –OH on the surface layer generated a condensed glassy layer of amorphous TiO2. After thermal treatment under vacuum at 450 °C for 2 h, TiO2 of this composite crystallized, and the TiO2/C-v sample showed well-discerned characteristic peaks of anatase.

Mesoporous SnO2 microspheres were also prepared by hydrothermal treatment by using the salt addition/inclusion-scheme, of pre-formed 3–7 nm sized SnO2 nanoparticles in the presence of glucose this was seen in the recent study (Hu et al., 2010). Throughout the formation of carbon spheres, the nanoparticles are homogeneously incorporated into the carbon matrix and after the removal of the carbon matrix through calcination, these nanoparticles assemble together into mesoporous SnO2 microspheres, where the porosity and high surface area are brought about by the interstitial porosity between the agglomerated nanoparticles.

Porous hollow inorganic metal oxide can be used as gas sensors using the HTC process resulting carbon spheres as template. A recent study (Hu et al., 2010) highlighted that when the ionic oxygen species fixed on the surface of metal oxide react with the reducing gas molecules, the trapped electrons release back to the crystal grains, the potential barriers at the grain boundary decrease, and the resistance is dramatically reduced. For the porous hollow structures, the ionic oxygen can absorb onto both inner and outer surfaces and the detected gas molecules can penetrate through and react with them freely, thus increasing the sensitivity. Author also highlighted that a WO_3 hollow-sphere structure that showed certain selective response to the organic gas. Using glucose-derived carbon spheres as template synthesized porous In_2O_3 hollow nanospheres that had a satisfactory response for ethanol, methanol, and other organic gases even at a very low concentration. Besides, the sensors have good recovery ability.

2.4.3 Catalysis

It is known that the performance of heterogeneous catalysts is highly affected by their supporting materials. It was a straightforward trial to explore biomass-derived HTC-carbon materials and colloids as supports for metal particles for different catalytic applications because of their high surface area and functionality. The carbon spheres are obtained by a gentle HTC process and subsequent calcination at 600 °C. From the cyclic voltammogams, the as-prepared Pt@CMS and Pd@CMS show higher catalytic activity for methanol oxidation at alkaline media than commercial Pt (Pd)/carbon black. The comprehensive study (Sevilla, Lota, & Fuertes 2007; Kim et al., 2006; Yang et al., 2005; Yuan et al., 2007; Tan et al., 2008) highlighted that other carbon materials from HTC loaded with Pt nanoparticles show better performance for methanol oxidation.

The product generated from the HTC process shows excellent stability and high catalytic activity for methanol-tolerant oxygen electroreduction. The high stability is speculatively caused by a thin mesoporous carbon film on the Pt nanoparticles that enables the oxygen to touch the activity sites and keeps the methanol away. A recent study (Hu et al., 2010) highlighted that synthesized structures, constituted of uniform carbonaceous nanofibers embedded with noble-metal nanoparticles by using the HTC process. The catalytic activity depends sensitively on the type of metal loading, among which the Pt system has the most efficiency.

2.4.4 Electric and energy storage

Hydrocarbon materials promising application in the field of electric and energy storage. Reliable and affordable energy storage is a crucial for using renewable energy in remote locations, integration into the energy grid and the development of a future decentralized energy supply system. Mobile electric energy storage is also the most promising technology currently available to reduce fuel consumption in the transport sector. Hydrocarbon materials have been used and structurally improved as electrodes in Li ion batteries as mentioned in the literature (Hu et al., 2010). The author also highlighted the use of carbon colloids, prepared by the HTC process, as a fuel in order to increase the efficiency of the indirect carbon fuel cell.

2.4.4.1 Li ion batteries

Lithium ion batteries are widely used in laptops, cameras, cell phones and other electronic portables device due to the relative high energy density. However, for advanced applications such rechargeable batteries with higher power density, improved rate capability and longer cycle life are eagerly demanded. For high energy density, the electrode materials in the lithium-ion batteries must possess high specific storage capacity and coulombic efficiency. Hu et al., (2010), pointed out that graphite and $LiCoO_2$ are normally used as anode and cathode, respectively, and have high coulombic efficiencies (typically >90%) but rather low capacities (372 and 145 mAh g^{-1}, respectively). To solve these problems, scientists have developed some strategies, which, interestingly, are quite similar to each other. A first approach is to apply hollow or mesoporous nanostructures as an electrode, for the empty space serves as a good cushion for the volume change. A second approach is to coat a flexible carbon layer onto the particle surface to both increase the conductivity and absorb stress by volume change. The third approach is usually complemented or even substituted by a sealing layer of a stable but deformable solid–electrolyte interface (SEI) on the carbon particle composite to resist the harsh deformation.

The HTC process is a much more facile and green method. In addition, it is liquid-based and therefore cheap and scalable. A recent study (Hu et al., 2010) reported that by using the hydrothermal treatment from hydrothermal carbonization of glucose in the presence of pre-formed SnO_2 nanoparticles followed by subsequent removal of the carbon. Thus, mesoporous SnO_2 micrometer-sized spheres composed of small SnO_2-aggregated nanoparticles were produced and tested as anode materials in lithium ion batteries, showing high specific capacities (~960mA h g^{-1}) and good cycling performances. The micrometersized spheres enable easy handling in terms of separation or film formation in comparison with their nanometer-sized constituents.

2.4.4.2 Carbon fuel cells

Carbon fuel cells are conceptually the most effective way of converting the chemical energy of carbon into electrical energy, especially compared to classical combustion processes. As the global reserves of coal exceed by far those of other fossil fuels, there have been numerous attempts in the past decades to develop and generally improve applicable carbon fuel cells (Hu et al., 2010). promising higher efficiency compared to conventional coal combustion. Besides optimizing the fuel cell device, the efficiency of carbon fuel cells can also be optimized using carbon colloids as a fuel, as electrochemical oxidation of a solid certainly depends on the absolute surface area and its surface structure. Carbon colloids derived from hydrothermally treated biomass can indeed act as a potential fuel for decentralised energy generation with an overall zero-emission balance of CO_2.

2.4.5 Water purification

The system using the principle of adding water soluble organic monomers such as acrylic acid to the HTC process, carbon materials with a high loading of carboxylic groups on the surface could be produced. Besides conferring a high degree of functional groups, the organic monomer has also an important influence on the final morphology of the materials. A recent study (Hu et al., 2010) highlighted that these functional with high surface area materials were tested as adsorbents for the removal of heavy metal ions from water. Ion binding capability goes highly non-linear with the content of acrylic acid. Pure hydrocarbons as well as the samples with only 1 wt% acrylic acid have, expectedly, the lowest binding capacity for both cadmium and lead. The capacity increases slightly for the 2 wt% sample (11.00 $Cd_{(II)}$ mg/g, 77.7 $Pb_{(II)}$ mg/g), while a dramatic increase in adsorption capacity is observed upon further increasing the amount of acrylic acid in the samples. This is to be related to the development of a pore system and accessibility of binding sites. The 10 wt% acrylic acid containing carbon has the highest metal uptake capacity. The capacity of the 10AcA-C for lead ion is 351.4 mg/g (1.7 mmol/g) and for cadmium is 88.8 mg/g (0.79 mmol/g). Pb^{2+} ions are retained more strongly and in larger quantities than Cd^{2+} ions on all our carbon functional materials as mentioned in the literature (Hu et al., 2010).

2.4.6 Bioapplications

Application in biological from HTC carbon materials such as bioimaging and drug delivery. By changing the concentration or the molar ratio of the starting materials, different architectures with tunable size can be obtained, such as monocore shell, multicore shell, and eccentric core shell. These nanospheres give strong green emission under excitation at 340 nm. The fluorescent imaging showed that the particles could be internalized into living human lung-cancer cells and exhibited almost no cytotoxic effects on the cells. Modification of the surface of the polymer shell may allow for core shell spheres that are more specifically targeted to cells or deliver drugs or genes in a tissue of specific fashion. Fluorescent surface functional CSPs derived from the hydrothermal treatment of glucose can deliver a membrane impermeable molecule into the mammalian cell nuclei and further modulate gene expression in vivo (Hu et al., 2010). The fluorescent images and Ramman spectrum also showed that the CSPs could cross the blood–brain barrier and penetrate into the brain. Thus, the CSPs are potential carriers to deliver drugs against brain tumors.

2.5 Torrefaction

2.5.1 History of torrefaction

Research focused on torrefaction has been started in France in the 1930s, but publications about this research are limited. According to the Van der Stelt et al., (2011) Pentananunt studied the combustion characteristics of (torrefied) wood in a bench scale torrefaction unit. It was shown that torrefied wood has a significantly higher combustion rate and produces less smoke than wood. Also it was found that torrefied briquettes were practically water resistant and torrefaction appeared a good technique for upgrading briquettes. The comprehensive study (Van der Stelt et al., 2011) highlighted that the structure of the torrefied biomass is changed in comparison to the raw biomass which makes it brittle and hydrophobic. Ferro et al., (2004), studied the effect of the raw material, temperature, residence time and nitrogen flow on the properties of the torrefied products. The Energy research Centre Netherlands (ECN) has been working on the principle of torrefaction since 2002 and published various reports (Bergman et al., 2005; Bergman et al., 2004; Bergman, 2005; Pels, 2006). In particular the influence of feed, particle size, torrefaction temperature and reaction time on torrefaction characteristics such as mass and energy yield and product properties has been investigated.

As torrefaction is not available commercially at the moment, much of the generated knowledge is used to develop this technology. On the basis of the principles of torrefaction it is strongly believed that it is has high potential to become a leading biomass pretreatment technology as mentioned in the literature (Weststeyn, 2004). Prins et al., (2006) performed thermodynamic analysis of coupled biomass gasification and torrefaction. The research was focused on weight loss kinetics of wood torrefaction (Prins, Ptasinski & Janssen, 2006), analysis of products from wood torrefaction (Prins, Ptasinski & Janssen, 2006), and more efficient biomass gasification via torrefaction (Prins, Ptasinski & Janssen, 2006). It was shown that weight loss kinetics for torrefaction of willow can be accurately described by a two-step reaction in series model and moreover deciduous wood types, such as beech and willow torrefaction (Prins, Ptasinski & Janssen, 2006), were found to be more reactive than coniferous wood. Prins concluded that the overall mass and energy balances for torrefaction at 250 and 300 °C showed that the process of torrefaction is mildly endothermic. The general conclusion was that the concept of wood torrefaction, followed by high temperature entrained flow gasification of the torrefied wood, is very promising (Prins, 2005).

2.5.2 Biomass conversion from torrefaction

Biomass and its utilization have been intimately associated to renewable energy in the recent years. However, the undesirable properties of biomass such as high moisture content and its heterogeneous nature pose a barrier to its competitiveness in the energy generation market. A viable option to overcome the issues associated with biomass feedstock is to carry out a pretreatment process called torrefaction. Torrefaction is a thermolysis process that subjects the feedstock to thermal treatment at relatively low temperatures of 200–300 ◦C in the absence of oxygen.

Definition for torrefaction is commonly associated with roasting, mild pyrolysis, slow pyrolysis, and thermal pretreatment, according to its utilization. The process is characterized by relatively long reactor residence times, with the final product being a solid uniform product called tor-coal, which can be transformed into tor-briquettes or tor-pellets.Once torrified, the material will have a higher energy density in order of 22.000 kJ/ KG (or 9.600 BTU/lb). Overall the mass of the feedstock will reduce with 25% and it will retain 90% of the original biomass feed energy content. Feedstock for torrefaction is not limited to wood and lumber waste, but includes also forrest debris, agriculture-and-industry waste, animal-and-biohousehold waste, seaweed, algea, peat, energy grasses (elephant grass, miscanthus) among many others.

The comprehensive study (Prins, Ptasinski & Janssen ,2006; Pimchuai, Dutta & Basu ,2010 ; Bridgeman et al, 2010) highlighted that during the process of torrefaction, the changes have been accounted to the release of carbon dioxide as well as water, favorable for gasification and combustion. The decomposition mechanism of torrefaction involves significant dehydration as the changes in the H:C and O:C atomic ratios of biomass follows the dehydration pathway. The higher loss in oxygen and hydrogen compared to carbon is highly related to the increase in energy value of the biomass as mentioned in the literature (Bergman et. al, 2005 ; Couhert, Salvador & Commandré , 2009). One of the main disadvantages of biomass has been related to the presence of moisture which penalizes its performance especially in thermochemical processes. Felfli et al., (2005), Pimchuai, Dutta & Basu, (2010) highlighted that moisture absorption of thermal treated sample is comparatively lower than untreated biomass using immersion test. The effect of torrefaction on equilibrium moisture content was examined across relative humidity range of 11.3–97.0% (Acharjee et al., 2009)

2.5.3 Reaction mechanism of torrefaction

In the torrefaction temperature regime, water is one of the main products release along with volatiles. Physical drying of biomass is first initiated at approximately 100 ◦C whereby the free water in biomass feedstock is liberated. Light organic volatiles are evolved in the post drying steps as the organic molecules dehydrate. From the literature (Chew and Doshi, 2011) has pointed out that as the temperature gradually increases to the excess of 200 °C, bound water in biomass is released. Depolymerization of long polysaccharide chains shortens the polymeric structure of biomass, mainly from the hemicelluloses fractions (Chew and Doshi, 2011). This is coupled with limited devolatization and carbonization of the lignin and cellulose. During torrefaction, the breakage of the hydroxyl group on the cellulose microfibrils monomers introduces hydrophobic properties to torrefied biomass as mention in the literature (Chew and Doshi, 2011). This non-reversible reaction preserves the quality of the product as the torrefied biomass molecules are non-polar and prolongs the storage duration (Chew and Doshi, 2011). Combustion behavior of torrefied biomass becomes more exothermic and ignition time is shorter compared to untreated biomass (Chew and Doshi, 2011). The aforementioned improved properties of torrefied biomass are favorable for transportation, utilization and storage of biomass because of its increased stability and durability.

2.5.4 Torrefied biomass applications

Wood pellets have some limitations in terms of energy content and moisture uptake during storage and transportation. Besides that, pulverized fuel combustion in coal-fired power stations and entrained flow gasification are particularly interesting product outlets for biomass. In both applications, biomass has to be fed to the reactor as a powder, which is difficult, costly, and achievable only at very low capacity in classical coal-mills. Due to this limitation, wood pellets are currently the state-of-the-art for co-firing, as they consist of sufficiently small particles. Torrefied biomass being energy dense and hydrophobic in nature can be a good replacement for wood pellets in cofiring and gasification plants. The high fuel quality of torrefied biomass makes it very attractive for combustion and gasification applications. Due to high CVs, the thermal energies of the combustion and gasification system can be improved significantly (Tumuluru et al., 2011). Other applications include high-quality smokeless solid fuels for industrial, commercial, and domestic applications solid fuel for cofiring directly with pulverized coal at electric power plants an upgraded feedstock for fuel pellets, briquettes, and other densified biomass fuels and high quality biomass solid fuel for advanced bioenergy application (Tumuluru et al., 2011).

2.6 Physical characterization

Fourier-transform infrared (FTIR) also use to identify its physical characterization. The FTIR has been widely used to characterize the surface groups of different oxides and also applied to various types of carbon and carbonaceous materials like coals, carbon blacks, chars and activated carbon structures. Since IR transmission spectra had peaked shapes where the specific chemical bonds existed, it was possible to know which functionalities were created on the surface of activated carbon by comparing locations and depths of the peak. FTIR was mainly used as a qualitative technique for the evaluation of the chemical structure of carbon materials.

CHAPTER 3

METHODOLOGY

3.1 Research Design

This study is about preparing carbon particles from hydrothermal carbonization and torrefaction process using wood fiber waste. This research intends to achieve three main goals. Firstly, how to prepare carbon particle from hydrothermal carbonisation using wood fiber waste. Secondly, how to produce torrefied biomass from torrefaction process and lastly to identify physical characterisation of product from both process.

3.2 Production of carbon particles

3.2.1 HTC Process

3.2.1.1 Material and Equipment

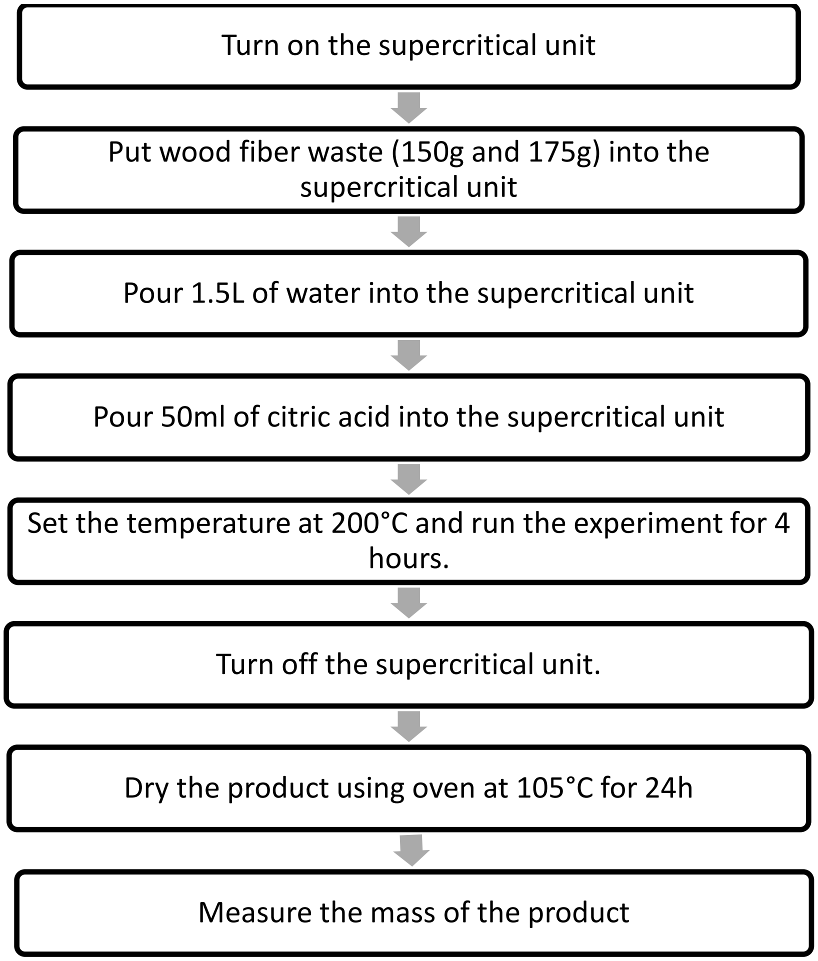
1. Supercritical Unit (2L Pressure Vessel)

2. Wood Fiber waste

3. Citric acid

4. Water

3.2.1.2 Procedure for HTC Process



Turn on the supercritical unit

Put wood fiber waste (150g and 175g) into the supercritical unit

Pour 1.5L of water into the supercritical unit

Pour 50ml of citric acid into the supercritical unit

Set the temperature at 200°C and run the experiment for 4 hours.

Turn off the supercritical unit.

Dry the product using oven at 105°C for 24h

Measure the mass of the product

Figure 3.1 Supercritical unit Buchiglauster model

The hydrothermal carbonization of wood fiber waste was carry out according to the following procedure by using the supercritical unit Buchiglauster model shown in Figure 3.1. The unit and the monitor were switched on. The reactor was lift down so that the sample can be put in the reactor. 175g of wood fiber waste was put into the supercritical unit. The wood fiber waste was dispersed in 50 ml citric acid and 1.5L of water and stirred it. After the mixture was mixed well, the reactor was lifted up and was tied with twelve screws to avoid any pressure release. As the reactor was tied up, the temperature was set at 200^{o}C and the stirrer was on at 50 rpm. The over limit 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. The sample was then dried in the oven at 105°C for 24hours. The cleaning process was done to continue with the next experiment (150g of WFW).

Table 3.1: Operating Conditions

Items	Value
Water (L)	1.5
Temperature (°C)	200
Time (h)	4
Citric acid (ml)	50

3.2.2 Torrefaction process

3.2.2.1 Material and equipment

1. Wood Fiber Waste (WFW)
2. Glass Furnace
3. Clay bowl
4. Aluminium foil

3.2.2.2 Procedure for Torrefaction

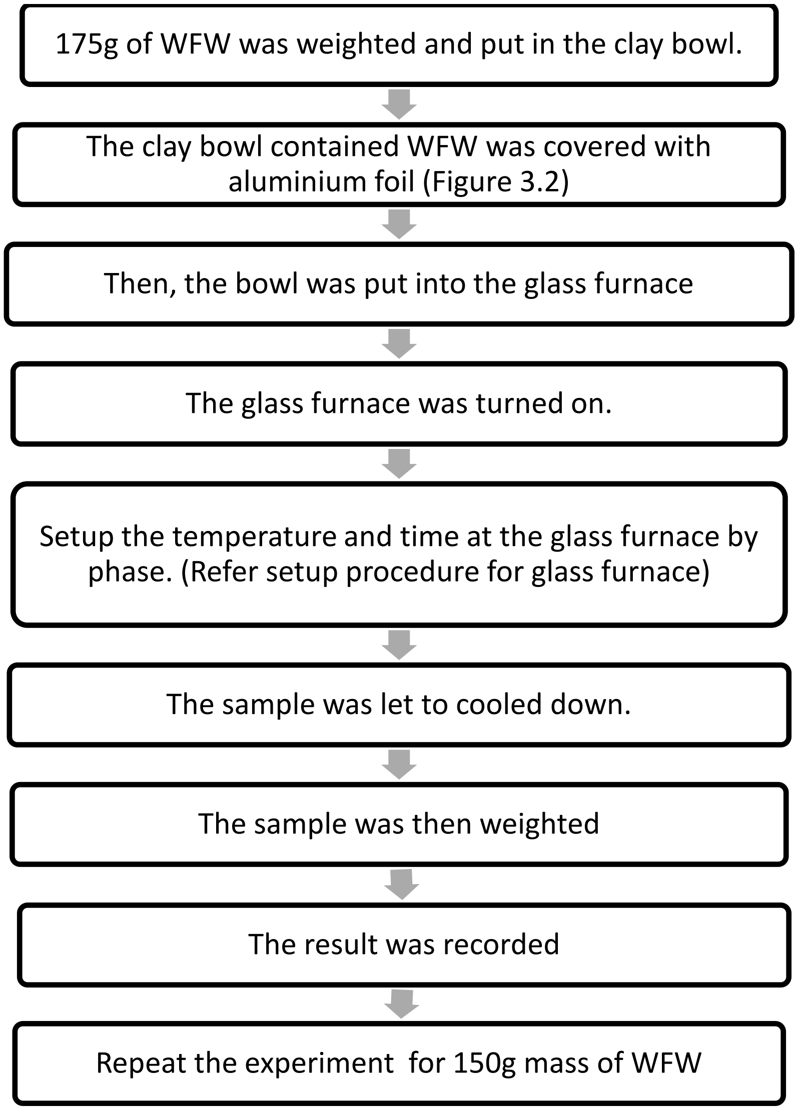


Figure 3.2 Clay bowl filled with WFW covered with aluminium foil

3.2.2.3 Setup procedure for Glass furnace

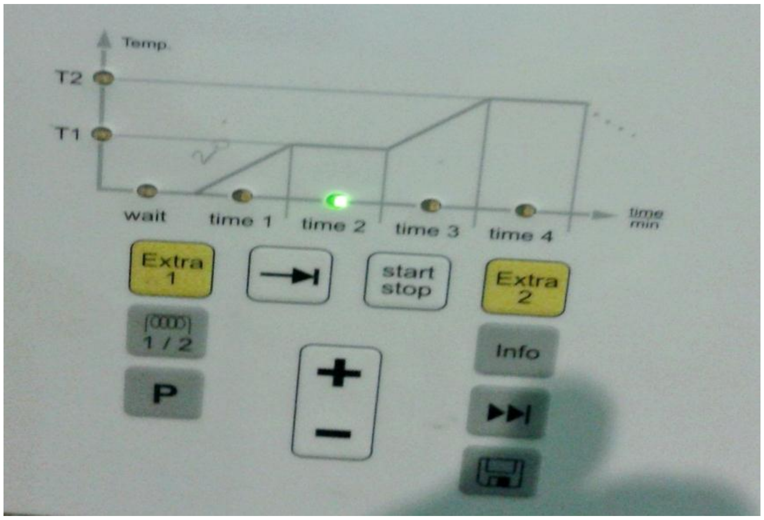


Figure 3.3 Ramp setup button at glass furnace

1. The switch was turned on.
2. The ramp of the glass furnace was setup by phase (see Figure 3.3)
3. 5min was set at phase ‘wait’, the enter button was pressed.
4. 10min was set at phase ‘time 1’, then the enter button was pressed.
5. The temperature at T1 was set 100°C, then the enter button was pressed.
6. The ‘time 2’ was set at 5min. then the enter button was pressed.
7. Next, ‘time 1’ was set 10min, then the enter button was pressed.
8. T2 was set at 200°C and enter button was pressed.
9. Time 4 was set at 4 hours, and then press enter button. Start button was pressed.

3.3 Product preparation and characteristic analysis

3.3.1 Proximate analysis

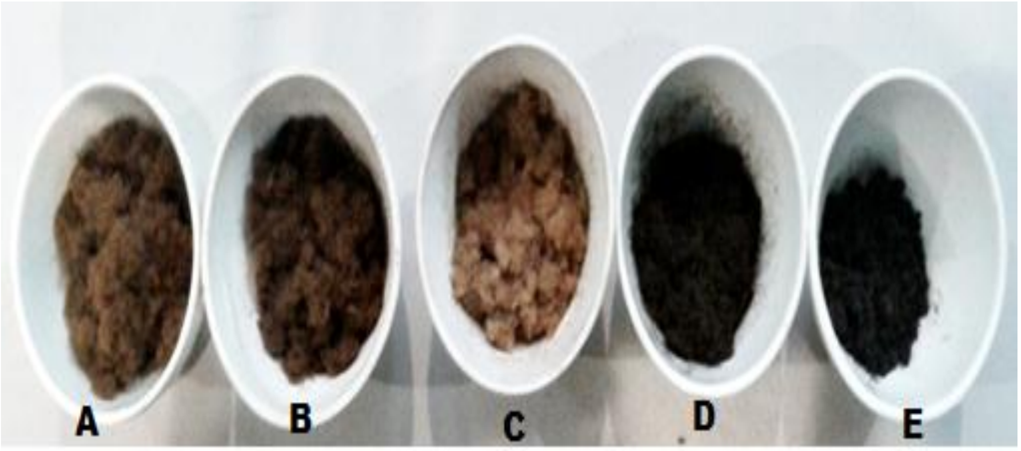


Figure 3.4 Sample of treated and untreated WFW, A: TF 175g, B: TF 150g, C: Raw of WFW, D: HTC 150g and E: HTC 175g

a) Moisture Content

The moisture content of the samples was determined by simple step of experiment. Firstly, empty crucible clay was weighted. Approximately 1 grams of each sample were placed in crucible clay and the initial weights of samples were measured. These samples were kept in an oven to maintain the temperature at 105 ± 5°C for 1 hour. After 1 hour, samples were removed from the oven and then cooled in a desiccator and the weights were measured. This process was repeated 3 times to get accurate result. The percentage of total moisture and dry content of each sample was the calculated by using equation below:

$$\%\ \text{Moisture} = \frac{Mass\ of\ water\ removed\ (g)}{Mass\ of\ original\ sample\ (g)} \times 100$$

b) Ash content

The different between moisture and ash experiment procedure was the operating conditions. Firstly, empty crucible clay was weighted. Approximately 1 grams of each sample were placed in crucible clay and the initial weights of samples were measured. The sample was placed in the furnace for one hour at a higher temperature (750°C). The crucible was then cooled at room temperature for approximately 1 minute and then put in the desiccator. Finally, the sample was reweighed and %Ash was determined using equation below;

$$\%\text{Ash} = \frac{Mass\ of\ residue\ after\ combustion\ (g)}{Mass\ of\ original\ sample\ (g)} \times 100$$

c) Volatiles content

The empty crucible was weighted and 1 ± 0.1 g of sample was added and the weight was recorded. This crucible was placed in a high temperature furnace (preheated to 925°C) for 7 minutes. After that, the crucible was removed from the furnace and cooled down at room temperature for 1 minute. The crucible was then transferred to the desiccator and cooled to room temperature before being reweighed. The amount of volatiles in the sample can be calculated using equation below:

$$\% \text{ Volatile} = \left(\frac{Mass\ loss\ of\ sample\ after\ heating\ (g)}{Mass\ of\ original\ sample\ (g)} \times 100 \right) - \%\ Moisture$$

d) Calorific Value

The combustion capsule was cleaned and dried and 0.3g of sample was weight accurately using analytical balance. The combustion capsule was fixed on bomb head. 10 cm of fuse wire was cut. The fuse wire was attached on bomb head by raised the cap, the wire was inserted through the eyelet, make a ‘U’ shape and pulled the cap downward. The fuse wire must immersed or touch the sample but should not touch the combustion capsule to prevent short circuit. The bomb head was carefully attached with combustion bomb until it is tight. Then, the bomb was filled with oxygen gas. The oval bucket was filled with accurately 2 L of distilled water. The lifting handles were attached to the two holes in the side of the screw cap and lower the combustion bomb 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. Removed the handle and shake any drops of water 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. The stirrer was turned by hand to be sure that it runs freely. The drive belt was slip onto the pulleys and starts the motor. Stirrer was on. The temperature was recorded at one minute intervals. The temperature was recorded at one minute interval until the temperature being constant. After the last temperature reading, stopped the motor, the belt is removed and lifted the cover from the calorimeter vertically. The cover was put on the support stand. The ignition leads wires were removed and lifted the bomb out of the bucket. The knurled knob was opened slowly on the bomb head to release the gas pressure. After all pressure has been released (no sound), the cap was unscrewed, lifted the head out of the cylinder and placed it on the support stand. All unburn pieces of fuse wire was removed from the bomb electrodes, the combined length was measured.

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

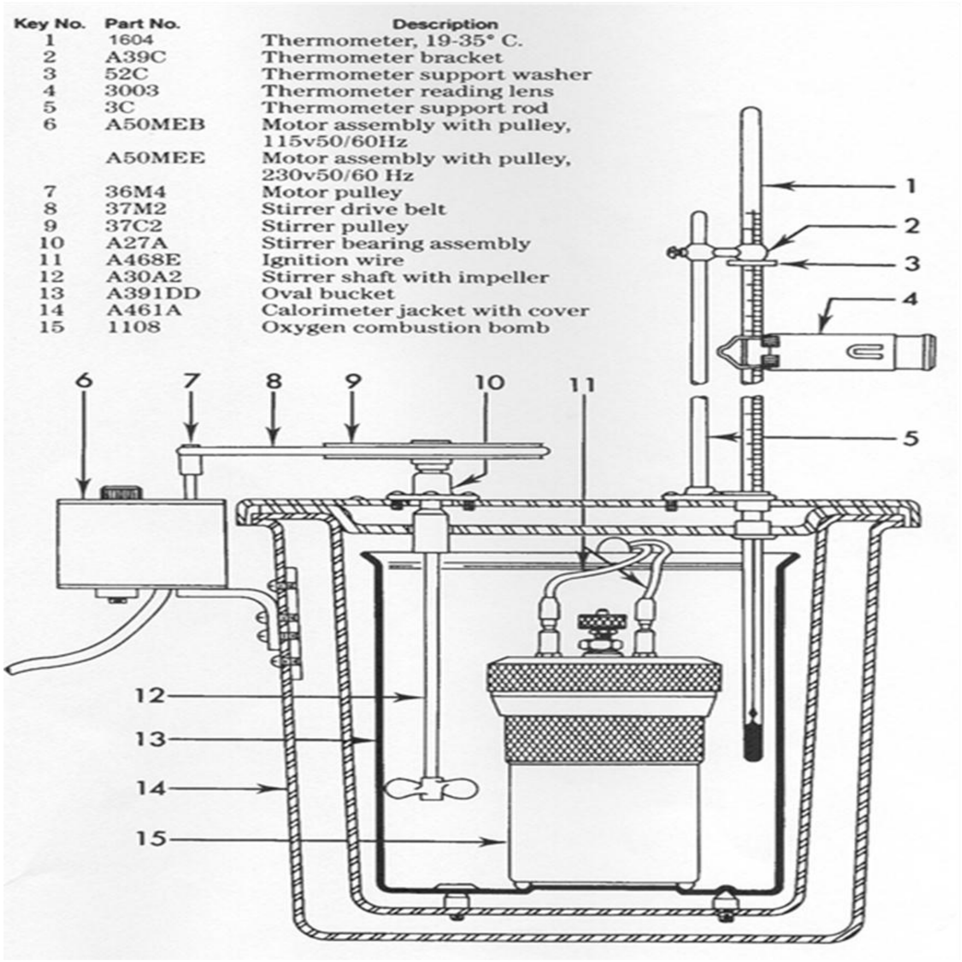
e_1 = correction in calories for heat of formation of nitric acid (HNO_3) (assumed =0)

e_2 = correction in calories for heat of formation of sulphuric acid (assumed=0)

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

= 2.3 x centimeters of fuse wire consumed in firing

m = mass



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 3.5 Bomb calorimeter

3.3.2 Characterization analysis

3.3.2.1 FTIR Analysis

Figure 3.6 FTIR for powder sample

1. The sample was grind by using grinder machine to produced fine powder sample. The sample was mixed with proper amount of KBr and pressed into a pellet.
2. Storage compartment on top of the Smart Diffuse Reflectance accessory was opened and the sample holder that has two sample cups was removed.

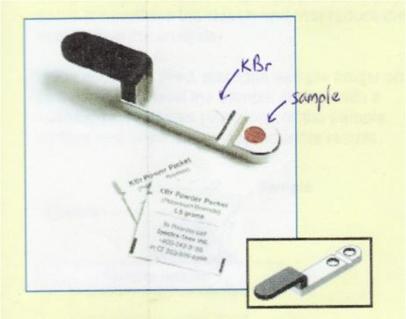


Figure 3.7 Sample holder with sample cups

3. Front cup was filled overflowing with the sample. When the cup was filled, sample holder was placed on a flat surface and the sample surface was leveled with a spatula.

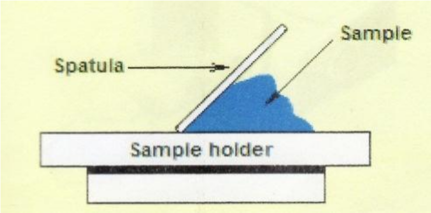


Figure 3.8 Sample leveled with spatula

4. Sample holder was inserted into the Smart Diffuse Reflectance accessory. To position the background material under the IR beam, the sample holder was pushed all the way in and then pulled it out slightly until felled the holder click into position.

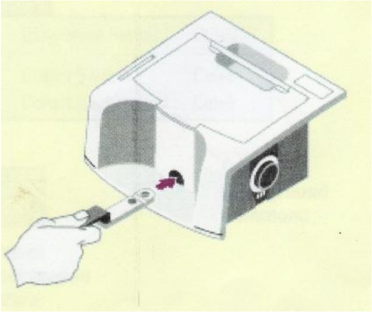


Figure 3.9 Sample holder inserted into the Smart Diffuse Reflectance accessory

5. The collect background command in the OMNIC collect menu was used or clicks the Collect Background button on the toolbar if it is displayed.

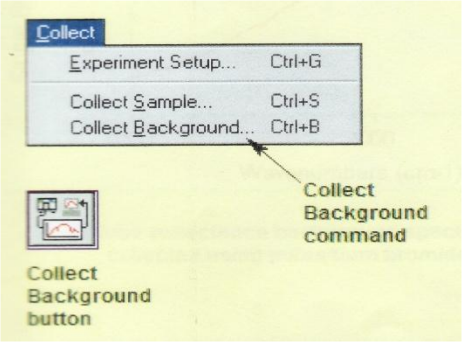


Figure 3.10 Command in the OMNIC collect menu

6. The sample holder was the slide out about 3cm (1inch) until felled it click into position.

7. The collect sample command in the OMNIC collect menu was used or clicks the Collect Sample button on the toolbar if it is displayed.

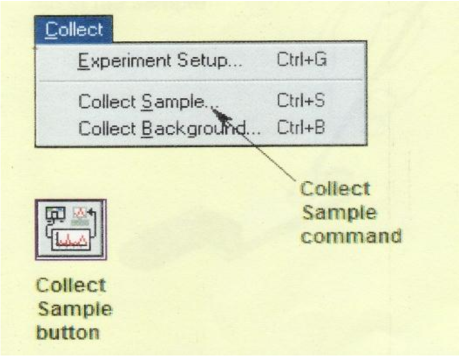


Figure 3.11 Collect sample command in the OMNIC collect menu

8. The data collection was then saved.
9. The sample holder was gently sliding removed it out of the sample port. the sample holder was cleaned by removed the sample.

10. The accessory was then pulled out to release it. The accessory was continued lifting straight up until it is completely free of the sample compartments.

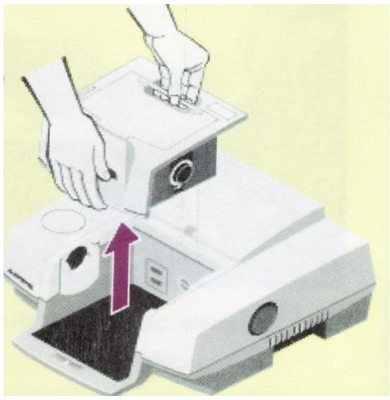


Figure 3.12 Pulled out the accessory

3.3.2.2 BET Analysis

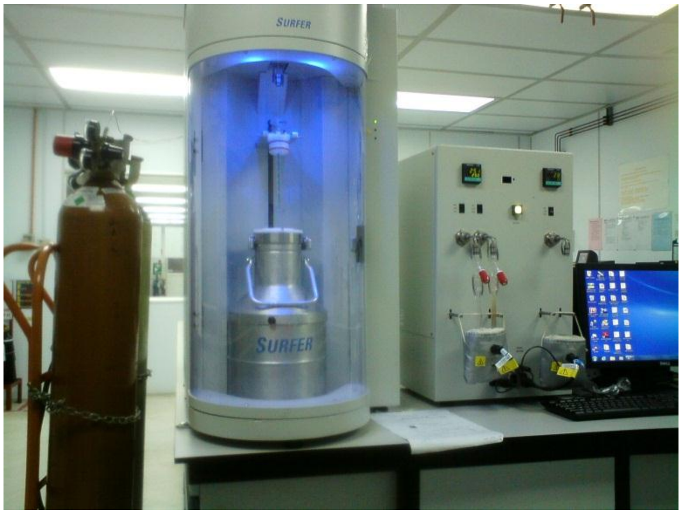


Figure 3.13 Brauneur Emmet Teller (BET) equipment.

The specific surface area of the samples was determined from a BET analysis of nitrogen absorption isotherms using a Thermo Scientific Surfer. The total pore volume is obtained as the volume of the adsorbed nitrogen at a relative pressure approximating unity. Ten minutes were allowed for each adsorption point. Sample of 0.3g were weighted, placed into sample tubes, and degassed under vacuum at 250°C for 6 hours. The surface area was calculated using BET equation from selected N_2 adsorption data within the range of relative pressure , p/p_0, from 0.1 to 0.3.

3.3.2.3 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 needs 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 3.14 FESEM used in Central Laboratory University Malaysia Pahang.

3.4 Conclusions

As a conclusion, this chapter had discussed the methodology for this research. The research questions are how to produce carbon particles from hydrothermal carbonization and Torrefaction process using wood fiber waste and what is the physical characterization of carbon particle from both processes using wood fiber waste. FTIR and BET is used to identify physical characteristic of carbon particle from hydrothermal carbonization using wood fiber waste. Field emission scanning electron microscopy (FESEM) was used to characterize the morphology structure from the hydrothermal carbonization process and pyrolysis process. The determination of the moisture content, ash content, volatiles content, calorific value was identified by simple experimental work. The results and discussion will be discussed in the next chapter which is chapter 4.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Proximate Analysis

4.1.1 Moisture Content

Table 4.1 Percent moisture content in the sample

%Moisture	Run 1	Run 2	Run 3	Average % moisture
Raw	8.96	8.64	8.64	8.75
HTC 175g	35.99	34.59	36.85	35.81
HTC 150g	9.37	11.17	10.77	10.44
Torrefaction 175g	2.51	4.29	5.18	3.99
Torrefaction 150g	1.59	5.46	6.35	4.47

From the Table 4.1 above, the result shown the percent moisture content is decrease after undergo Torrefaction process which are (3.99%: Torrefaction 175g, and 4.47%: Torrefaction 150g) compared to HTC process (35.81%: HTC 175g and 10.44%: HTC 150g). Torrefaction process also decreased about 3-4% moisture from the raw material. This is proved that Torrefaction is a pre-treatment process for the biomass in order to reduce the moisture in the biomass particle. Besides that, the results also shown that HTC process produce high moisture content compared to Torrefaction process and raw material. This is because, HTC required a lot amount of water in order to increase the efficiency of the dehydration process. The contact between water and polymeric structure at a certain temperature is able to influence the reaction process and speed up the physical and chemical interactions.

4.1.2 Ash Content

Table 4.2 Summary of % Ash content

Sample	Run 1	Run 2	Average % Ash
Raw	11.97	7.83	9.90
HTC 150g	11.19	9.03	10.11
HTC 175g	11.55	4.99	8.27
TF 150g	1.88	6.20	4.04
TF 175g	3.04	1.91	2.48

Table 4.2 illustrated that HTC for 150g have highest percentage of ash content which is 10.11%. Then followed by raw for 9.90%. HTC for 175g have about 8.27% ash content. While, Torrefaction process has the lowest percentage ash content which are 4.04% for 150g and 2.48% for 175g. The purpose of measuring ash content was to determine the amount of incombustible solid after the combustion process. Ash content is expected to contain minerals and inorganic matter. In the HTC and Torrefaction process, the mineral and inorganic content within a material did not give any significant impact as the process occurs is dominated by dehydration rather than combustion. Clear viewed of percent ash content was showed in the Figure 4.1 below.

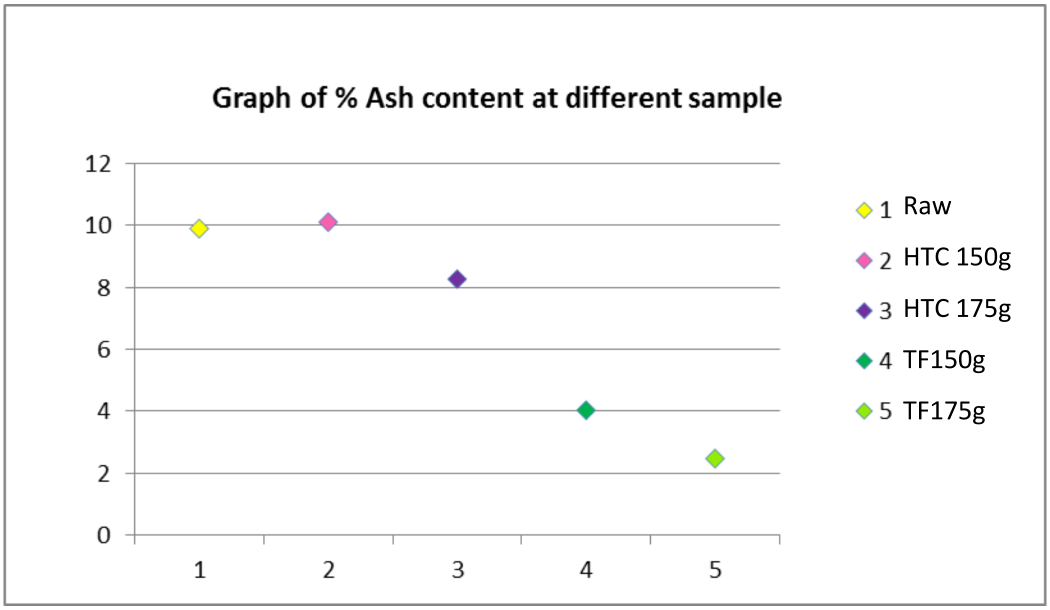


Figure 4.1 % ash content at different sample

4.1.3 Volatiles Content

Table 4.3 Summary of % Volatiles content

Sample	Run 1	Run 2	Average % volatile
Raw	80.95	81.66	81.31
HTC 150g	76.83	79.79	78.31
HTC 175g	53.48	53.46	53.47
TF 150g	90.32	88.22	89.27
TF 175g	90.33	93.47	91.90

Table 4.3 showed percentage volatiles content at different sample. Torrefaction process has the highest percentage volatiles which around 91-89% followed by raw of

WFW. The lowest percentage volatiles was HTC process which only 53-78% volatiles content. The volatile matters were fully converted into gaseous material and leave the solid. Torrefaction and HTC process increases the amount of atomic carbon while decreases the amount of atomic hydrogen and oxygen. A consequence of this change in the chemical composition was a decrease in O/C and H/C ratio of torrefied biomass in comparison to raw biomass. This is due to the release of volatiles rich in hydrogen and oxygen, such as water and carbon dioxide. This change in the chemical composition of biomass improves its quality as an energy source through an increase in energy density, since more oxygen than carbon is lost in the form of volatiles.

4.1.4 Calorific Value

Table 4.4 Calorific value at various samples

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
Torrefaction 175g	24.72	16.62	33.29	24.88
Torrefaction 150g	13.31	16.19	16.44	15.31

Table 4.3 illustrated calorific value produce from different sample. Torrefaction process of 175g produce highest calorific value (24.88MJ/kg) followed by Raw of WFW (21.39MJ/kg), HTC 150g (17.05MJ/kg), Torrefaction 150g (15.31MJ/kg). The lowest calorific value was HTC 175g, which about 13.54MJ/kg. Calorific value is the amount

of energy released during the combustion process. The efficiency of any future energy application process depends on the calorific value of the inlet, where high calorific value will increase the amount of energy released. The decomposition mechanism of torrefaction involves significant dehydration as the changes in the H:C and O:C atomic ratios of biomass follows the dehydration pathway. The higher loss in oxygen and hydrogen compared to carbon is highly related to the increase in energy value of the biomass. Compared to oxygen and hydrogen, the bond between carbon atoms is more stable. Therefore, more energy is required to break the bonds, which will reduce the ability of the combustion process. The table 4.5 below showed overall proximate analysis for raw, torrefaction and HTC process.

Table 4.5 Proximate analysis of treated and untreated WFW

Sample/ Process Proximate analysis	Raw	Torrefaction		Hydrothermal Carbonization (HTC)	
		150g	175g	150g	175g
Moisture (%)	8.75	4.47	3.99	10.44	35.81
Ash (%)	9.90	4.05	2.48	10.11	8.27
Volatiles (%)	81.31	89.27	91.90	78.31	53.47
Calorific Value (MJ/kg)	21.39	15.31	24.88	17.05	13.54
Mass Yield (%)	-	86.80	89.71	84.87	87.54

4.2 Characterization Analysis

4.2.1 Fourier Transform Infrared Spectrophotometer (FTIR)

FTIR was carried out to identify the component and chemical compositions which exist in the WFW after the HTC and Torrefaction process. FTIR analysis showed the hydroxyl, carbonyl, aliphatic, ethers, alcohol, phenol and carboxylic groups are present on the surfaces of the raw materials. Raw of wood fiber waste (WFW) consist of lignin, cellulose and hemicellulose. Determination of the main functional groups present were based on the comprehensive study by (Monthioux and Landais, 1988, Orem et al., 1996, Mursito et al., 2010). Table below show details on the spectra group detected using FTIR.

Table 4.6 Details on the spectra group detected using FTIR

Wavelenght (cm^{-1})	Functional Group	Description
3700-3000	O-H stretch	Detect the presence of water, alcohols from cellulose or phenols from lignin
3000-2800	C-H stretch	Small double peaks showing vibration of aliphatic C-H bond
1800-1650	C=O stretch	The vibration occur mainly from the esters, carboxylic acid or aldehydes from cellulose and lignin
1650-1500	C=C stretch	Vibration from the aromatic ring from lignin
1450-1200	C-H bend	Small peaks of absorption from CH bridge of aliphatic carbon, methylene, methyl

1200-950	C-O stretch	Vibration from esters, phenols, aliphatic alcohols
900-750	C-H bend	Deformation of CH bond in aromatic compounds

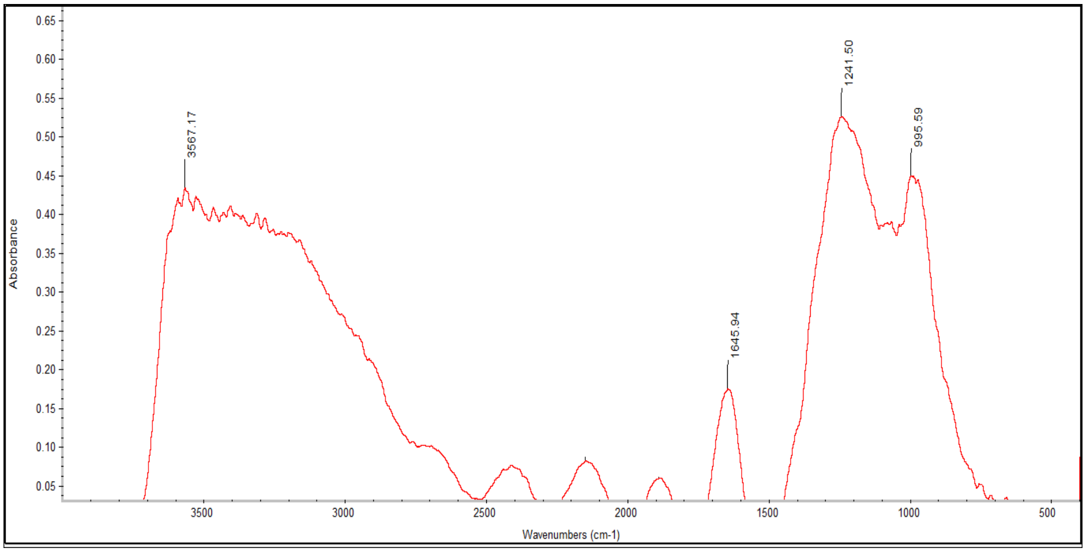


Figure 4.2 FTIR spectra for Raw material (WFW)

A peak appeared at 3567.17 cm^{-1} in the Figure 4.2, which corresponds to the stretching of O-H functional group and this is shows the presence of bonded hydroxide in the raw sample. There was another peak observed at 1645.94 cm^{-1} corresponding to the C=O stretching. A strong peak of C-H bend also observed around 1241.50 cm-1. This sample also shows another one peak at C-O stretching band at 995.59 cm^{-1} confirmed the formation of ester bonds. It can be suggested from the spectrum that the main oxygen groups present in the raw are carbonyl, ethers and alcohols group which are normally present in plant cellulose. Table 4.7 showed the summary of wave number present in the other samples.

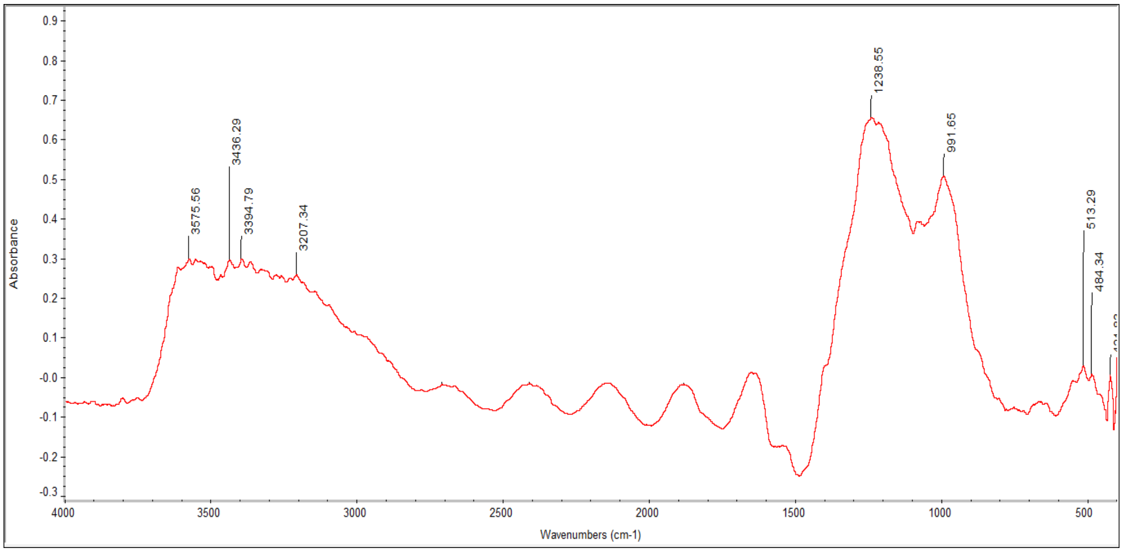


Figure 4.3 FTIR spectra for HTC 150g

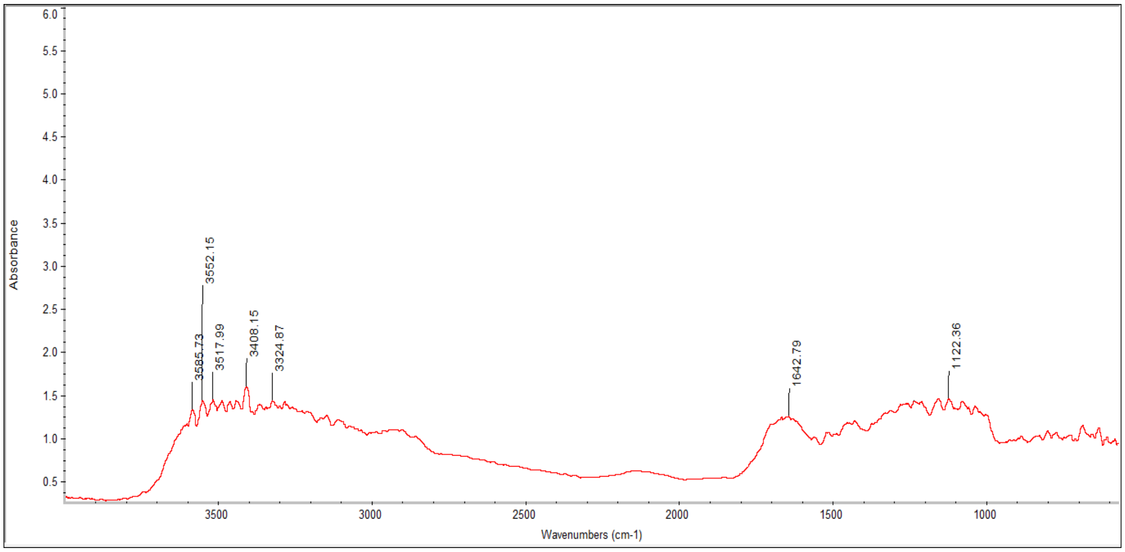


Figure 4.4 FTIR spectra for HTC 175g

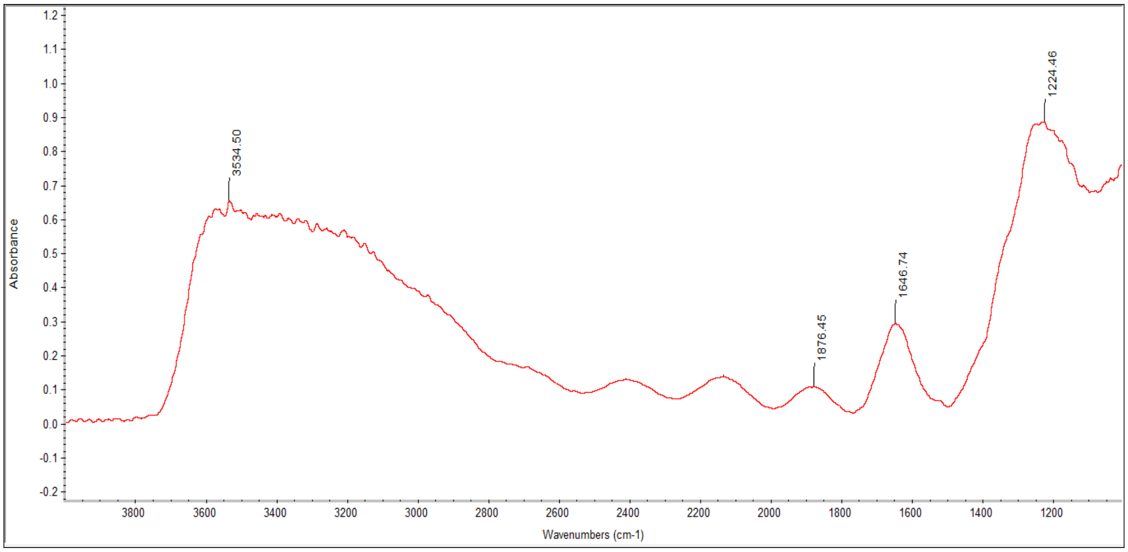


Figure 4.5 FTIR spectra for TF 150g

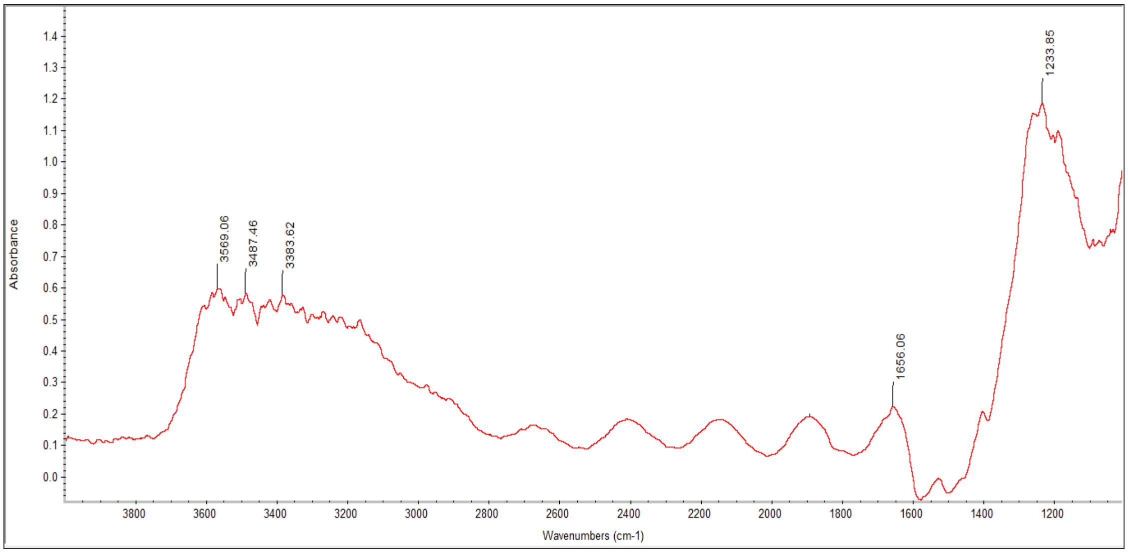


Figure 4.6 FTIR spectra for TF 175g

Table 4.7 Summary of wave number of some functional group present in the samples

Sample	Wave number (cm^{-1})	Functional Group
Raw WFW	3567.17	O-H stretch
	1645.94	C=O stretch
	1241.50	C-H bend
	995.59	C-O stretch
HTC 150g	3207.34 – 3575.56	O-H stretch
	1238.55	C-H bend
	991.65	C-O stretch
HTC 175g	3324.87 – 3585.73	O-H stretch
	1642.79	C=C stretch
	1122.36	C-O stretch
Torrefaction 150g	3534.50	O-H stretch
	1876.45	C=O stretch
	1646.74	C=C stretch
	1224.46	C-H bend
Torrefaction 175g	3383.62 – 3569.06	O-H stretch
	1656.06	C=O stretch
	1233.85	C-H bend

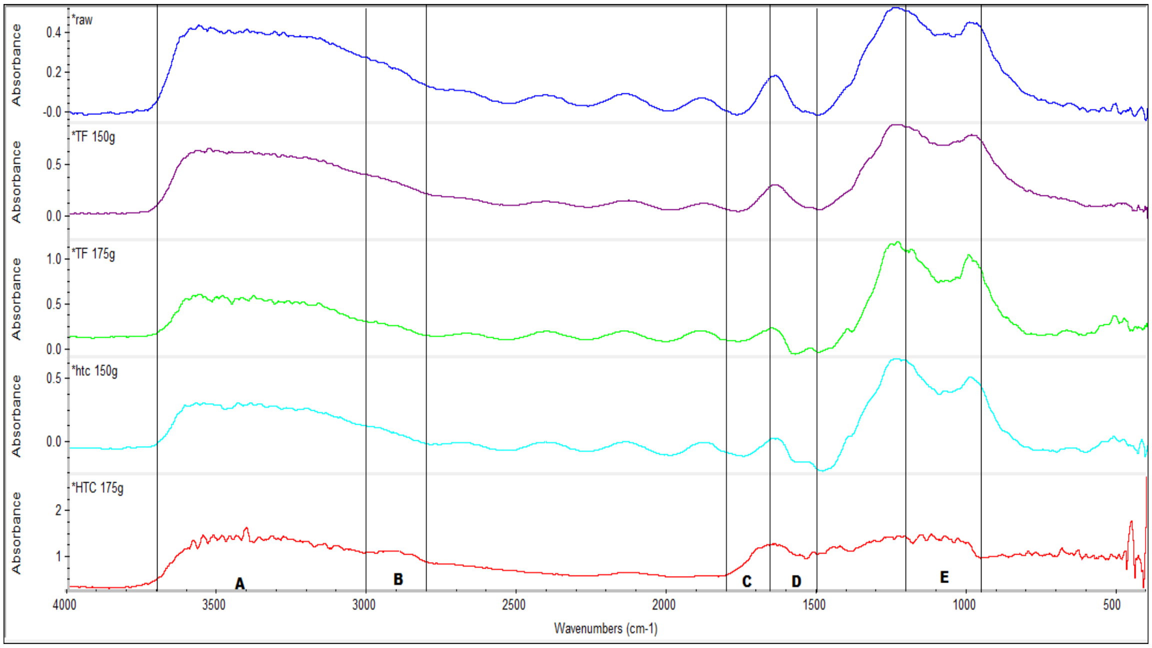


Figure 4.7 FTIR spectra of untreated and treated WFW at different process condition

Figure 4.7 shows the FTIR spectra of unmodified raw of wood fiber waste (WFW) and chemically modified at two different process conditions (HTC and TF). Clear differences can be detected in the infrared spectra, both in the different absorbance values and shapes of the bands and in their location. A decrease in the intensity of the O–H absorption band was observed in range A (data refer Table 4.7) indicating that the hydroxyl group contents in the product reduced after reaction. The spectrum peaks at range C, decrease compared to raw which is for C=O stretching. There are no significant differences between spectra for unmodified and chemically modified lignin samples. These are caused probably by the interactions between the functional groups. Generally, WFW contains hemicellulose and lignin. Therefore, stronger presence of single bonds components, such as O-H, C-H and C-O bonds, are expected in the surface of WFW. Small peaks of C=O and C=C bonds were also detected in these spectra proving the existence of hemicellulose and lignin on the raw materials surface structure.

4.2.2 Brauneur Emmet Teller (BET) analysis

BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m2/g yielding important information in studying the effects of surface porosity and particle size in many applications. Two sample was chose for BET analysis which were sample of HTC 150g and raw of WFW. Generally, the product has high surface area compared to raw as the purposed is to produce carbon particle. High surface area is the common characteristic of the carbon particle. From data shown in figure 4.8 below, both figure of a) and b) shows the negative isotherm linear plot. This might because of the sample preparation not followed correct procedure. Besides that, the sample is easier to degass only if the sample is dry. The sample is better in the form of powder, so the sample should grind first before run the BET analysis. Some problem might come from the equipment itself. It might be some leakage at the sample burette that can affect degassing process.

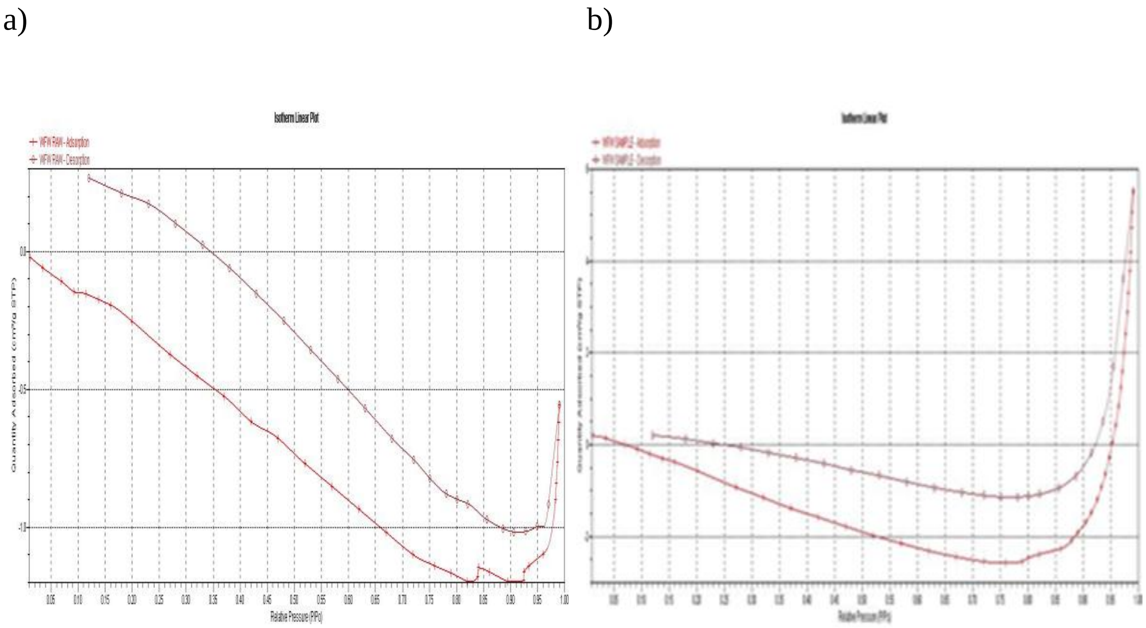
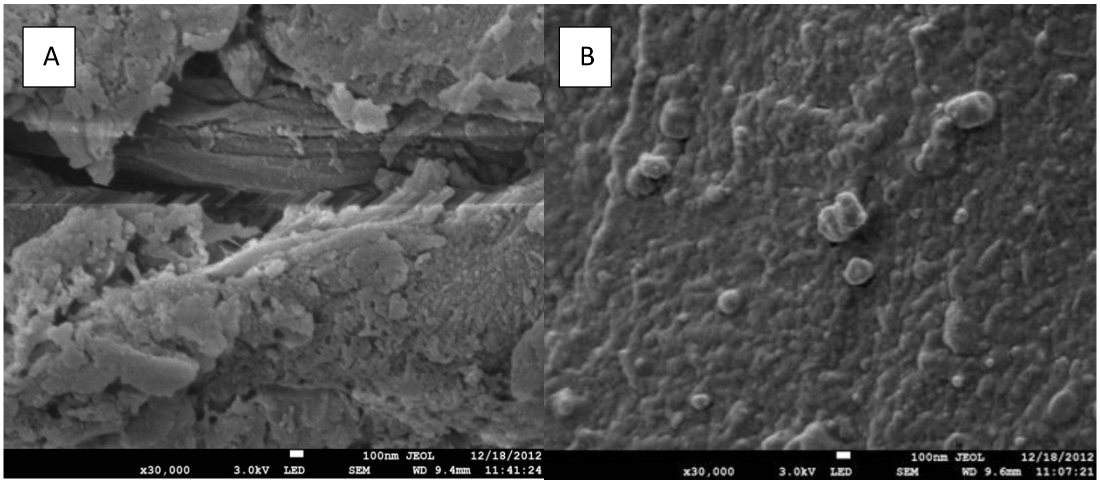


Figure 4.8 Isotherm linear plot at a) Raw of WFW, b) HTC 150g

4.2.3 Relationship of FESEM and FTIR Analysis

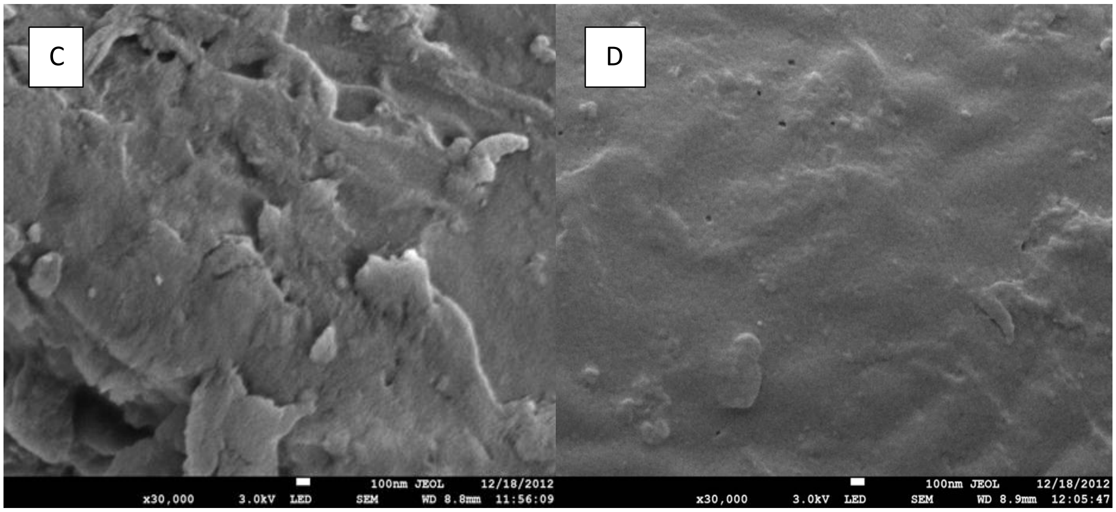
Field emission scanning electron microscopy (FESEM) was used to characterize the morphology structure from the hydrothermal carbonization process and pyrolysis process. In Figure 4.9, a comparison on the surface morphology and spectroscopy of HTC process at (A) HTC 150g (B) HTC 175g were illustrated.



Sample	Wave number (cm^{-1})	Functional Group	Sample	Wave number (cm^{-1})	Functional Group
HTC 150g	3207– 3575	O-H stretch	HTC 175g	3324 – 3585	O-H stretch
	1238.55	C-H bend		-	-
	-	-		1642.79	C=C stretch
	991.65	C-O stretch		1122.36	C-O stretch

Figure 4.9: Relationship of the surface morphology and spectroscopy of HTC process (A = HTC 150g, B = HTC 175g).

The morphology differences of the surface carbon particles can be seen, where the structure in Figure 4.9B show a significant difference with the HTC 150g (Figure 4.9A). In term of spectroscopy results, differences can be reported on HTC 150g which the peak are identified is C-H bend which do not exist in the data of Figure B as it's only shows a peak of C=C stretch . The peak of C-H bend in the Figure A explain the existence of small peaks of aliphatic carbon. Besides that, logically 150g of raw immersed in 1L of water during HTC process have higher surface contact with water, compared to 175g of raw with 1L of water. Highest rupture occurs 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.



Sample	Wave number (cm^{-1})	Functional Group	Sample	Wave number (cm^{-1})	Functional Group
Torrefaction 150g	3534.50	O-H stretch	Torrefaction 175g	3383.62 – 3569.06	O-H stretch
	1876.45	C=O stretch		1656.06	C=O stretch
	1646.74	C=C stretch		-	-
	1224.46	C-H bend		1233.85	C-H bend

Figure 4.10 Relationship of the surface morphology and spectroscopy of Torrefation process (C = TF 150g, D = TF 175g).

In Figure 4.10, a comparison on the surface morphology and spectroscopy of torrefaction process at (C) TF 150g (D) TF 175g were illustrated. The morphology differences of the surface carbon particles can be seen, where the structure in Figure 4.10D show a significant difference with the TF 150g (Figure 4.10C). In term of spectroscopy results, dissimilarities can be reported on the components as more peaks are identififed in Figure 4.10C, such as O-H stretch, C=O stretch, C=C stretch and C-H bend which C=C stretch lack in the data of Figure D. Torrefaction of 150g WFW proved the vibration of the aromatic ring from the lignin. This might due to the large surface area exposed to the heat during the process as only small amount of quantity WFW compared to 175g of WFW. So, fast reaction takes place in 150g of raw.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Through this study, the following summary and conclusions were obtained due to the several achievements from conversion of wood fiber waste (WFW) into carbon particle via hydrothermal carbonization and torrefaction process:

a) Both process increase the amount of carbon content in the final products, automatically improves its quality as an energy source.

b) The torrefaction process was able to improve the characteristic of the wood fiber waste in term of moisture content in the products. Lowest moisture content was obtained in the range of 3.99% - 4.47% moisture.

c) FTIR study revealed that from the spectrum shows the main oxygen groups present in the raw are carbonyl, ethers and alcohols group which are normally present in plant cellulose.

5.2 Recommendation

There are some recommendations were discussed for the improvement of the comparative study on the carbon products from the HTC and torrefaction process practice in future;

(i) The sample can be varies at other operating temperature and at different time taken for reaction to take place.

(ii) The pressure vessel for the supercritical unit must be firmly tightened to avoid any pressure release during the experiment.

(iii) The sample should be fully covered with the aluminium foil as torrefaction process occurs at the absent oxygen.

(iv) Personal protective equipment (PPE) is needed while handling proximate analysis which at high temperature.

(v) Further study on the surface area of the product need to be carried out by using Brauneur Emmet Teller (BET) analysis.

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APPENDIX A

A.1 Calculation for dilution of citric acid

SG= 1.665

Molecular weight = 192.13g/mol

SG_{water}= 1

Assume M_2= 0.5

V_2 required = 50ml

$$SG = \frac{\rho_{Subs}}{\rho_{Water}}$$

$$1.665 = \frac{\rho_{Subs}}{1000}$$

$$\rho_{Subs} = 1665g/L$$

$$\begin{array}{l|l} 1665g & mol \\ \hline L & 192.13g \end{array} \quad M1=$$

= 8.66601mol/L

$M_1V_1=M_2V_2$

8.66601mol/L × V1 = 0.5mol/L × 0.05L

V1= 0.002885

Mass =0.002885 L × 1665 g/L

Mass of citric acid = 4.8g

A.2 Result and calculation from excel

A.2.1 Data Collection for Mass Yield (%)

Table A.1 Mass yield conversion

Sample	Initial Weight (g)	Final Weight (g)	Mass Yield (%)
HTC 175g	175	153.2	87.54
HTC 150g	150	127.3	84.87
TF 175g	175	157.0	89.71
TF 150g	150	130.2	86.80

A.2.2 Data Collection for Moisture content experiment

Table A.2 Initial mass of sample (moisture content)

Mass of sample (g)	Run 1	Run 2	Run 3
Torrefaction 175g	1.0043	1.000	1.0053
Torrefaction 150g	1.0039	1.0037	1.0063
HTC 175g	1.0051	1.0187	1.0149
HTC 150g	1.0007	1.0091	1.0091
Raw	1.0154	1.0048	1.0039

(A)

Table A.3 Mass of sample and clay

Mass sample after 1h drying process + clay (g)	Run 1	Run 2	Run 3
Torrefaction 175g	41.5672	41.5452	41.5413
Torrefaction 150g	32.9556	32.9166	32.9101
HTC 175g	24.2090	24.2320	24.2065
HTC 150g	24.8992	24.8887	24.8927
Raw	32.8921	41.5061	24.4828

(B)

Table A.4 Mass of clay

Sample	Mass of clay (g)		
HTC 175g	23.5656		
HTC 150g	23.9923		
Torrefaction 175g	40.5881		
Torrefaction 150g	31.9677		
Raw	Run 1= 31.9677	Run 2= 40.5881	Run 3= 23.5656

(C)

Table A.5 Mass of sample after drying

Mass of sample after drying 1h (g)	Run 1	Run 2	Run 3
Torrefaction 175g	0.9791	0.9571	0.9532
Torrefaction 150g	0.9879	0.9489	0.9424
HTC 175g	0.6434	0.6664	0.6409
HTC 150g	0.9069	0.8964	0.9004
Raw	0.9244	0.918	0.9172

(D= B-C)

Table A.6 Mass of water removed

Mass of water removed (g)	Run 1	Run 2	Run 3
Torrefaction 175g	0.0252	0.0429	0.0521
Torrefaction 150g	0.016	0.0548	0.0639
HTC 175g	0.3617	0.3523	0.374
HTC 150g	0.0938	0.1127	0.1087
Raw	0.091	0.0868	0.0867

(E=A-D)

Table A.7 Percentage moisture content

%Moisture	**Run 1**	**Run 2**	**Run 3**	**Average % moisture**
Torrefaction 175g	2.509210395	4.29	5.182532577	3.993914324
Torrefaction 150g	1.593784241	5.459798745	6.349995031	4.467859339
HTC 175g	35.98646901	34.58329243	36.85092127	35.80689424
HTC 150g	9.373438593	11.16836785	10.77197503	10.43792716
Raw	8.961985424	8.638535032	8.636318358	8.745612938

(F= (E/A)×100)

A.2.3 Data Collection for Ash content experiment

Table A.8 Calculation of percentage ash content

Sample		A	B	C	D = C-B	E = A-D	F = (E/A × 100)
		Weight of sample (g)	Weight of empty crucible (g)	Weight of crucible + sample after heating (g)	Mass final sample after heating (g)	Mass of residue after combustion (g)	% Ash
RUN 1	Raw	1.0063	36.5295	36.65	0.1205	0.8858	88.02543973
	HTC 150g	1.0088	34.3571	34.47	0.1129	0.8959	88.80848533
	HTC 175g	1.0041	39.154	39.27	0.116	0.8881	88.4473658
	TF 150g	1.0017	31.8512	31.87	0.0188	0.9829	98.12319058
	TF 175g	1.0092	33.8193	33.85	0.0307	0.9785	96.95798652
RUN 2	Raw	1.0023	32.3415	32.42	0.0785	0.9238	92.16801357
	HTC 150g	1.0075	40.569	40.76	0.191	0.8165	81.04218362
	HTC 175g	1.0039	34.9599	35.01	0.0501	0.9538	95.00946309
	TF 150g	1.0028	36.9578	37.02	0.0622	0.9406	93.79736737
	TF 175g	1.0092	31.8107	31.83	0.0193	0.9899	98.08759413

Table A.9 Average percentage ash content

Sample	RUN 1	RUN 2	Average % Ash
Raw	88.02543973	92.16801357	90.10
HTC 150g	88.80848533	81.04218362	84.93
HTC 175g	88.4473658	95.00946309	91.73
TF 150g	98.12319058	93.79736737	95.96
TF 175g	96.95798652	98.08759413	97.53

A.2.4 Data Collection for volatile content experiment

Table A.10 Calculation of percentage volatile content

Sample		A	B	C	D = C-B	E = A-D	F = (E/A × 100) - % Moisture
		Weight of sample (g)	**Weight of empty crucible (g)**	**Weight of crucible + sample after heating (g)**	**Mass final sample after heating (g)**	**Mass loss of sample after heating (g)**	**% Volatile**
RUN 1	Raw	1.0057	40.5683	40.6719	0.1036	0.9021	80.95
	HTC 150g	1.0031	33.8134	33.9411	0.1277	0.8754	76.83
	HTC 175g	1.0031	34.3246	34.4321	0.1075	0.8956	53.48
	TF 150g	1.0022	31.998	32.0502	0.0522	0.95	90.32
	TF 175g	1.0041	39.322	39.379	0.057	0.9471	90.33
RUN 2	Raw	1.0029	32.3338	32.43	0.0962	0.9067	81.66
	HTC 150g	1.0099	34.9264	35.0251	0.0987	0.9112	79.79
	HTC 175g	1.0038	37.0322	37.1399	0.1077	0.8961	53.46
	TF 150g	1.0043	31.8587	31.9321	0.0734	0.9309	88.22
	TF 175g	1.0013	36.529	36.5544	0.0254	0.9759	93.47

Table A.11 Average of percentage volatiles content

Sample	RUN 1	RUN 2	Average % volatile
Raw	80.95	81.66	81.31
HTC 150g	76.83	79.79	78.31
HTC 175g	53.48	53.46	53.47
TF 150g	90.32	88.22	89.27
TF 175g	90.33	93.47	91.90

A.2.5 Data Collection for Calorific value experiment

Table A.12 Data collection for 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 A.13 Data collection for 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
6			

Table A.14 Data collection for torrefaction 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 A.15 Data collection for torrefaction 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 A.16 Data collection for 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 A.17 Calorific value in MJ/kg

Sample	Run 1	Run 2	Run 3	Average (cal/g)	MJ/kg
HTC 175g	3878.323	3881.172233	1949.769	3236.421392	13.55025
HTC 150g	3970.073	3917.520392	4337.436	4075.009789	17.06125
Torrefaction 175g	5907.923	3973.056478	7956.605	5945.861576	24.89413
Torrefaction 150g	3180.929	3870.13663	3928.305	3659.790303	15.32281
Raw of WFW	3907.997	3905.114754	7524.554	5112.555288	21.40525

1 J/kg=0.000238846cal/g

A.3 Report for BET analysis

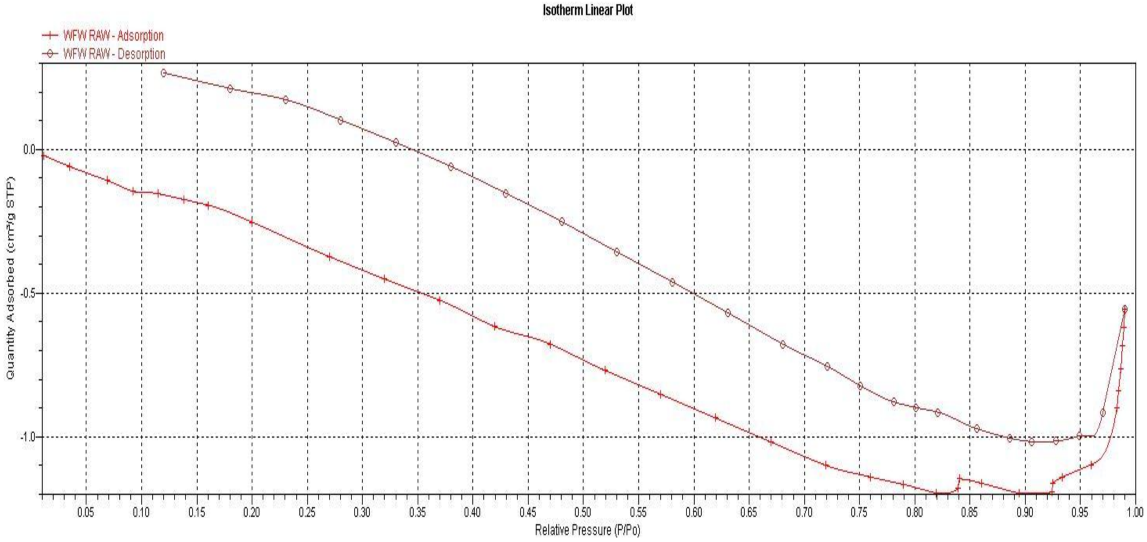


Figure A.1 Isotherm linear plot for raw

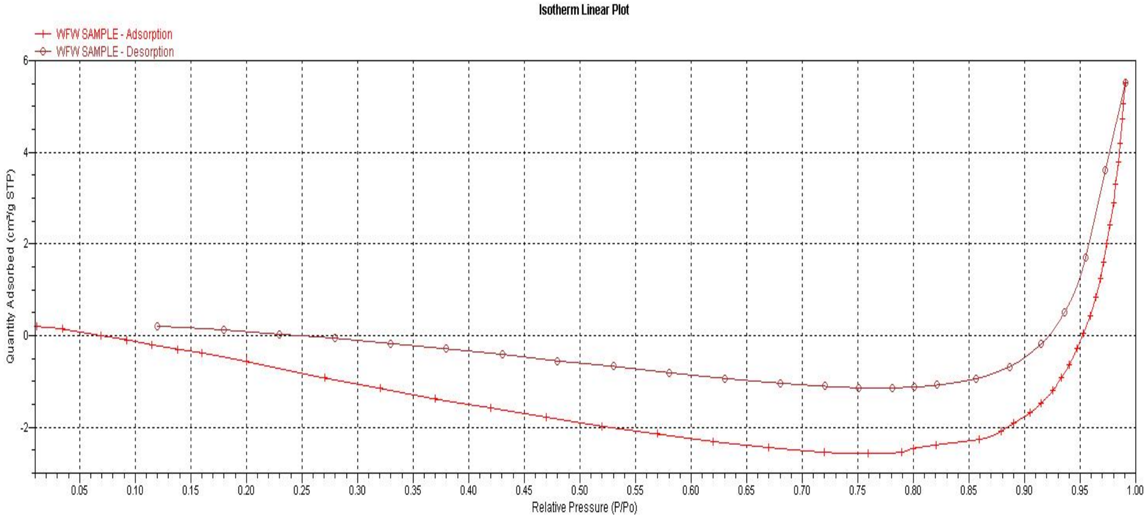
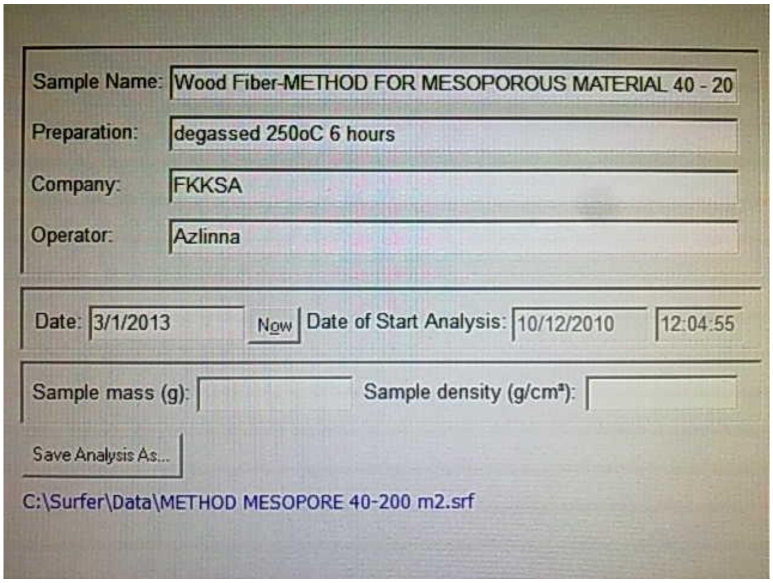


Figure A.2 Isotherm linear plot for sample (HTC 150g)



Sample Name: Wood Fiber-METHOD FOR MESOPOROUS MATERIAL 40 - 20

Preparation: degassed 250oC 6 hours

Company: FKKSA

Operator: Azlinna

Date: 3/1/2013

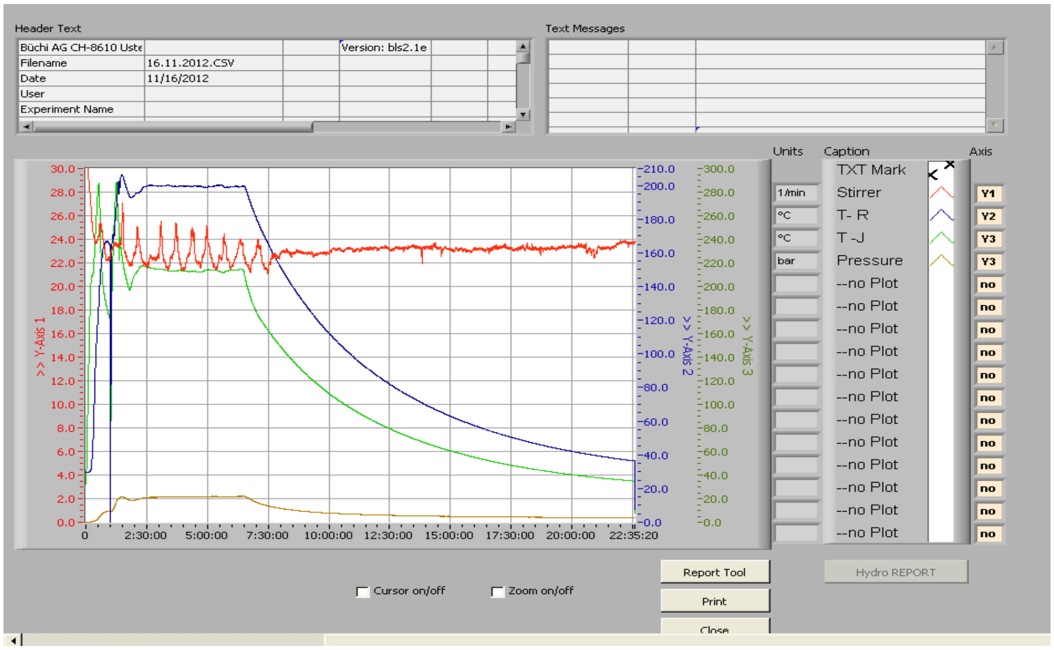
Date of Start Analysis: 10/12/2010 12:04:55

Sample mass (g):

Sample density (g/cm³):

C:\Surfer\Data\METHOD MESOPORE 40-200 m2.srf

Figure A.3 Software of Surfer



Header Text

Büchi AG CH-8610 Uste			Version: bls2.1e		
Filename	16.11.2012.CSV				
Date	11/16/2012				
User					
Experiment Name					

Text Messages

Units	Caption	Axis
	TXT Mark	
1/min	Stirrer	Y1
°C	T- R	Y2
°C	T -J	Y3
bar	Pressure	Y3
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	--no Plot	no
	--no Plot	no
	--no Plot	no
	--no Plot	no
	--no Plot	no
	--no Plot	no
	--no Plot	no
	--no Plot	no
	--no Plot	no
	--no Plot	no

Figure A.4 Analyze data plot of Supercritical unit