Hydrothermal Processing Converted Of Biomass with High Moisture Content into Energy Dence Materials

Rakhman Sarwono¹

¹Research Centre for chemistry – National Research and Innovation Agency, Serpong, Tang-sel, Banten (15314), Indonesia.

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I. INTRODUCTION

Biomass was estimated produce naturally above one trillion tons annually, is the most abundant biobased polymer on earth. Biomass produces 5×10 kJ of energy/year, this value is predicted to reach 150×10 kJ by 2050.¹It's found mainly in plants biomass. Biomass naturally consists of cellulose, hemi-cellulose, lignin, inorganic and metals trace, but the content is varies, as shown in Table 1. High moisture content biomass has a much lower net energy density by mass, as shown in Table 2.

Type of biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Other
Softwood	41	24	28	(70)
Hardwood	39	35	20	7
Wheat straw	40	28	17	15
Rice straw	30	25	12	33
Bagasse	38	39	20	3
Oak wood	34.5	18.6	28	-
Pine wood	42.1	17.7	25	-
Birch wood	35.7	25.1	19.3	-
Spruce wood	41.1	20.9	28	-
Sunflower seed hull	26.7	18.4	27	-
Coconut shell	24.2	24.7	34.9	-
Almond shell	24.7	27	27.2	-
Poultry litter	27	17.8	11.3	20
Deciduous plant	42	25	21.5	11.5
Coniferous plant	42	26	30	2
Willow plant	50	19	25	6
Larch plant	26	27	35	12

Tabel 1. Some biomass have difference content of cellulose, hemi-cellulose and lignin.²

Cellulose biomass can be used in a wide range of applications, from paper to transparent films, and from textile fibres to absorbing materials. Currently, cellulose is investigated as a renewable, non-food raw material for producing various glucose-derived chemicals, such asethanol³levulinic acid.⁴

Structurally, it is linear polymer with long chains of repeating anhydro-glucose units. Cellulose is also a polysaccharide made of glucose, the glucose units connected via b-1-4 glycosidic linkages. The difference in connectivity results in a profound difference in properties of the polysaccharides. Cellulose shows various



unique characteristics such as resistance to chemical or including water, and structural rigidity. It was found that crystalline cellulose underwent transformation to an amorphous state in hot and compressed water, which was followed by complete dissolution.⁵

Biomass can be converted into smaller molecules in the grade of fuels using thermo-chemical processes. Cellulose molecules are bound to each other by inter- and intra-molecular hydrogen linkages through their hydroxyl groups, and crystalline cellulose is difficult to decompose. Direct liquefaction of biomass in suband super-critical solvents water has proven to be an effective approach to convert lignocelluloses materials into low weight chemicals (Wang, 2009).⁶

The basic reaction mechanisms of biomass liquefaction can be described: (i) The first step is to dissolved the α -cellulose crystalline into liquid phase. (ii) depolimerization of the α -cellulose (iii) decomposition of the biomass monomers by cleavage, dehydration, decarboxylation and deamination; (iv) recombination of the reactive fragments through condensation, cyclization, and polymerization to form new compounds (Huang, 2011).⁷ In the first step cellulose is converted into glucose, hemi-cellulose into xylose, and lignin into polyols. The first step is very important step that influents to the whole reaction. Reaction between α -cellulose crystalline can be derived as a fluid-solid reaction.

Cellulose is one of the main components in lignocellulosis materials. It can be chemically converted into fermentables saccharides. This is usually hindered by but its great resistance to hydrolysis.³ Cellulose is a linear crystalline homopolymer consisting of β -1,4-linked d-glucopyranose units. In nature, cellulose has high degree of polymerization, in a range of about 6000-15000 glucopyranose units, which makes itshighly crystalline and not easy to be separated or dissolved in almost solvents.⁸ Thus, numerous biological, chemical, and physical treatments such as enzymatic sacharification, acid/alkali treatments, steam explosion, supercritical and subcritical treatments have been applied and developed foe cellulose hydrolysis.^{9,10}

Hydrothermal treatment in hot-compressed water (HCW) has been proposed as a promising method to hydrolyze cellulose mostly due to its non-toxic, non-catalytic and environmentally benign properties. ^{11,12} Over conventional method, it has advantages such as limited corrosion problem, no sludge generation, low capital and operational cost, no significant degradation of cellulose at normal operation conditions. Hot compressed water is highly pressurized, high-temperature liquid water at subcritical condition, below the critical point of water at 374 °C and 22.1 MPa.¹³ Temperature and pressure chart was drown to show the border area of each hydrothermal process.¹⁴

It is characterized by a higher ionic product and thus higher concentration of H^+ and OH^- ions compared to ambient water. Hydrothermal treatment allows water to access the inner structures of cellulosic biomass. Essentially, an arrangement of molecules of cellulose develops its structure into crystalline and amorphous domains. The amorphous fraction in cellulose is more reactive than the crystalline fraction.¹² Crystalline-to-amorphous transformation of cellulose takes place when water penetrates the inner structure.⁵



Figure 1. Temperature and pressure chart of water in hydrothermal process.¹⁴

In fact cellulose crystalline swells only in supercritical water. The crystalline of the unreacted cellulose was almost unchanged by the extent of conversion.^{15,16}Until now, different kinetic models have been presented for the HTC of cellulose.Cellulose reactions at hydrothermal conditions can proceed via the homogeneous route involving dissolution and hydrolysis or the path of surface hydrolysis.

Type of Biomass	Moisture (%) (wet basis)		
Water hyacinth	95.3		
Dairy cattle manure	88.0		
Rice straw	50 - 80		
Food waste	70		
Corn stalks	40-60		
Willow	60		
Wood bark	30 - 60		
Bagasse	45 - 50		
Poplar	45		
Saw dust	25 - 55		
Wheat straw	8 - 20		
Switchgrass	13 - 15		
RDF pellets	25 - 35		
Rice husk	7 - 10		
Miscanthus	11.5		
Danish pine	8		
Fir	65		

Cellulose biomass can be used in a wide range of applications, from paper to transparent films, and from textile fibres to absorbing materials. Currently, cellulose is investigated as a renewable, non-food raw material for producing various glucose-derived chemicals, such as ethanol,³levulinic acid.⁴Structurally, it is linear polymer with long chains of repeating anhydro-glucose units. Cellulose is also a polysaccharide made of glucose, the glucose units connected via b-1-4 glycosidic linkages. The difference in connectivity results in a profound difference in properties of the polysaccharides. Cellulose shows various unique characteristics such as resistance to chemical or including water, and structural rigidity. It was found that crystalline cellulose underwent transformation to an amorphous state in hot and compressed water, which was followed by complete dissolution.⁵

Tabel 2. The moisture content of some biomass.²

II. THERMOCHEMICAL PROCESS

II.1 Hydrothermal Carbonization (HTC)

Hydrothermal conversion is a thermo-chemical conversion technique which uses liquid sub- critical water as a reaction medium for conversion of wet biomass and waste stream. For wet biomass conversion, processes which do not require water evaporation are desired. Hydrothermal carbonization (HTC) is a thermo-chemical pretreatment process is treated under hot compressed water to produce hydrochar. Hydrochar is a stable, hydrophobic, friable solid product.¹⁷ The complex reaction chemistry of HTC offers a huge potential for producing a variety of products, from fuel to super-capacitors, from carbon nano-sphere to low cost adsorbents, from fertilizers to soil amenders.

Hydrothermal carbonization (HTC) is a promising technique among all conversion technologies. Hydrothermal carbonization is a thermochemical process for the pretreatment of high moisture content biomass under hot compressed water, making it applicable for diversified purposes. It is performed in a closed reactor at a temperature range of 180 - 280 °C under pressure of 2-6 MPa for 5 to 240 mins. ¹⁸ The primary product of hydrothermal carbonization is a coal-like product called hydrochar and also produces aqueous, and gas phases.¹⁹ The mechanism for this process mainly entails decarboxylation, dehydration and polymerization.²⁰ The water content in the wet biomass is an excellent solvent and reaction medium. Water can act as a base as well as an acid at temperature between 200°C and 280 °C because its ionic product is maximized. At this temperatures the dielectric constant of water is reduced so it acts more like a nonpolar solvent.²¹

Compared to biological treatment (anaerobic digestion or alcoholic fermentation), carbonization of biomass has various advantages. The reaction only takes hours compared to days or months needed for biological processes. The advantage of hydrothermal carbonization is that, without an energy-intensive drying method, the biomass can be transformed to carbonaceous solids. During the HTC phase, toxic organic molecules and residual micro-pollutants are also degraded.²² Reaction temperature, pressure, and time are the important factors that influences the process of hydrothermal carbonization, whereas the type of biomass used affects the products of HTC.

Hydrothermal carbonization is understood to be coalification of organic material in aqueous phase under applied high temperature and pressure. Hydrothermal carbonization is based on a single chemical process, namely the splitting of water from carbohydrate (dehydration).

$C_{6}H_{12}O_{6}$	C_6H_2O	+	5 H ₂ O	+ -950 kj/mol
Carbohydrate	HTC-Biochar		water	Heat

A simple energy balance of the process already indicates that it is exothermic, during the reaction, energy is released. ²³ A further advantage of HTC is that the liquid phase can be separated considerably more efficiently from HTC-biochar than from original biomass. HTC is a mimicry of the natural coal formation. ²⁴ HTC products depend on the type of biomass, temperature, pressure, catalysts used, residents time of reaction and biomass water ratio. The size and the size distribution of colloidal carbon spheres prepared by HTC were influenced by processing temperature, ²⁵ reaction time, and concentration of starting material. ²⁶

Energy production will play a key role in this process and several routes will be needed. Biomass is one of the options for renewable and sustainable energy. Hydrothermal conversion of biomass (HTC). In this process, hot compressed water (subcritical water) is used as the reaction medium. Therefore this technique is suitable for conversion of wet biomass/ waste streams. The evaporation of water and its high energy consumption can be avoided in this process by operating at high pressures. Biomass is not ready for ideal fuel due to its fibrous nature, low density and heating value.²⁷Hydrothermal carbonization (HTC) is a thermochemical process that coverts biomass into coal-like material called HTC-coal by applying high temperature to biomass in a suspension with water under saturated pressure for several hours.²⁸

Residual algal biomass proceeded by HTC resulted carbon materials about 67.3%.²⁹Hydrothermally of wastewater sludge and sugarcane bagasse at 210 °C resulted highest bio-coal of 23.36%, and the highest calorific value of 20.21 MJ/kg.³⁰ Sewage sludge was hydrothermally under optimum conditions of 150 °C, 30 min residence time and 30% solid loading, 80.56% of hydro-char was recovered, and a high heating value of 18.49 MJ/kg.³¹ Algae of *Eucommiaulmoides* was hydrothermally resulted the char yield of 66.5% at temperature of 220 °C.³² Grape marc was hydrothermally resulted bio-char with HHV in the range 19.8 – 24.1 MJ/kg (Basso.³³Hydrothermal carbonization process of peat conversion into bio-coal in the temperature of 230 °C resulted hydro-char with carbon content of 52.09% from initial peat carbon of 68.17%, oxygen content decreases from 33.1% -initial peat to 19.4%.³⁴Hydrothermally wheat straw at temperature 230 °C resulted bio-char with HHV 21 MJ/kg.³⁵

II.2 Hydrothermal liquefaction (HTL)

HTL is promising technology for converting high-moisture waste biomass into energy dense "biocrude" oil. Biomass can be converted into solid, liquid and gaseous biofuels for generating bioenergy, as well as into some chemicals. HTL has been applied to a wide-range of wastewater feed-stocks, including swine and cattle manure, microalgae, macroalgae and sludge.³⁶ The advantage with employing HTL process is that water can serve as a solvent, a reactant, and even a catalyst in the reaction medium.³⁷

Hydrothermal liquefaction (HTL) occurs at high pressure (10–25 MPa) and high temperatures ($280^{\circ}C$ – $370^{\circ}C$). The bio-oil is produced as the chief product when wet biomass reacts and produces co-products of solid, liquid, and gas phases. The use of biofuels offers advantages over existing fuels because they come from renew sources, they are biodegradable, their storage and transport are safer, and their emissions into atmosphere are lower.³⁸

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recombination of the reactive fragments through condensation, cyclization, and polymerization to form new compounds.⁷ In the first step cellulose is converted into glucose, hemi-cellulose into xylose, and lignin into polyols. The first step is very important step that influents to the whole reaction. Reaction between α -cellulose crystalline can be derived as a fluid-solid reaction.

Researchers have tried to convert many kind of biomass and algae to produce bio-oil. Microalgae as a raw material for biofuels production due to high oil content.³⁹ There were 34 types of microalgae, including species of *Nitzschia, sp* and *Com* which had cell compositions in the form of cellulose, glucan and oil that have potential to be manufacture of renewable fuels.⁴⁰*Nannochloropsissp* was hydrothermally to biocrude, biocrude obtained contains of 84% carbon.⁴¹ Biomass as raw material to produce bio-oil in the hydrothermal liquefaction process. The operating conditions were temperature range of 250 - 374 °C and pressure of 4-25 MPa resulted three products such biochar, soluble liquid and gases. Hydrothermal of pine wood resulted the maximum bio-oil yield of 38.35 wt%, and HHV of obtained bio-oils varied in the range of 24 28 Mj/kg.⁴²

To increase the conversion catalyst Na_2CO_3 was used in the reaction. Hydrothermal liquefaction of *Entermorphaprolifera* into bio-oil in optimum conditions, such as temperature of 300 °C, 5% Na_2CO_3 catalyst, reaction time of 30 minutes, resulted the highest bio-oil yield of 23.0 wt%, and HHV were around 28- 30 MJ/kg.⁴³ Catalyst K_2CO_3 used for duckweed hydrothermal liquefaction resulted bio-oil with HHV 32 – 36 MJ/kg.⁴⁴ Metal catalysts also used in catalytic hydropyrolysis of microalgae. Catalysts Mo_2C was identified as the most suitable catalyst, Mo_2C promoted the in situ deoxygenation and desulfurization of the hydropyrolysis oil which has a HHVs varying between 35.3 – 39.3 MJ/kg.⁴⁵ Solvent ethanol-water used for hydrothermal liquefaction of *Chlorella pyrenoidosa* resulted highest bio-crude yield of 57.3 wt%.⁴⁶

The Results showed that the lowest production cost for bio-crude oil is achieved when HTL is performed at 340°C with Fe as catalyst (450 \notin /t or 13.6 \notin /GJ). At these conditions, the bio-crude oil produced has an oxygen content of 16.6wt% and a LHV of 33.1 MJ/kg.⁴⁷ In the case of hydrothermal conversion, additives to adjust the pH such as sodium hydroxide increase oil yields, lower its viscosity but do little to further improve the quality of the oils. For pyrolysis oils, increasing the severity does reduce acidity but at the expense of more unsaturations and a loss in yield.⁴⁸

II.3 Hydrothermal gasification (HTG)

Hydrothermal gasification processes are promising technologies for an efficient valorization of wet biomass feed-stocks or wastes. HTG process take placed in temperature up to critical temperature > 374 °C and pressure > 221 bars.⁴⁹The dominant result was synthetic natural gas.⁵⁰ Hydrothermal gasification of palm shell biomass resulted bio-syn gas of H₂ and CO with small amounts of carbon monoxide and methane.⁵¹Supercritical water gasification of organic feedstock resulted a mixture of H₂, CO₂, CO, CH₄. The composition and yield of the final gas mixture depends highly on reaction temperature, feed concentration and catalyst.⁵² Hydrothermal gasification of biomass resulted gases rich hydrogen and high heating value of 141.8 MJ/kg.^{53,54}

The different agricultural residues including almond shell, walnut shell, barley straw, canola stalk, rice straw and wheat straw have different gases production.⁵⁵Maximun hydrogen yield of 8.38 mmol/g was for barley straw, canola stalk has highest gas yield of 25.3 mmol/g.⁵⁶ The hydrogen production from hydrothermal gasification of forestry residue, sewage sludge, MSW have a high heating value approximately of 141.8 MJ/kg.⁵⁴Among the three model compounds, hydrogen yields increased in the order of lignin (0.73 mmol/g) < cellulose (1.95 mmol/g) < xylose (2.26 mmol/g). Lignocellulosic biomass (soybean straw and flax straw) were gasified under similar conditions as those of the model compounds in Phase two. Soybean straw exhibited superior H₂ yield (6.62 mmol/g) and total gas yield (14.91 mmol/g).⁵⁷

III. QUALITY OF HYDROTHERMAL PRODUCTS

The bio-oil quality its depended on the feedstock quality and operating conditions that used in the processes. Good quality of bio-oil lies on the content of oxygen in the fraction of bio-oil it self. The caloric results of the each process is difference, mainly in the chemical composition. Elemental content of oxygen, hydrogen and carbon in HTL oil before and after upgrading, compared to other fuel type.⁵⁸



Figure 2. Elemental content of HTL-oil compared to other fuel types.⁵⁸

Oils produced from the fast pyrolysis of four feed-stocks contained oxygen contents of 16, 21, 26 and 27 wt.%.⁵⁹ The pyrolysis of pine sawdust was carried out in a fixed bed reactor heated from 30 °C to a maximum of 700 °C in atmospheric nitrogen and pressurized hydrogen (5 MPa). The result shows that the oxygen content of the bio-oil (17.16%) obtained under the hydrogen atmosphere was lower while the heating value (31.40 MJ/kg) was higher than those of bio-oil produced under nitrogen atmosphere.⁶⁰ Catalytic fast pyrolysis (CFP) bio-oils with different organic oxygen contents (4–18 wt%) were prepared in a bench-scale dual fluidized bed reactor system by ex situ CFP of southern pine over HZSM-5, and the oils were subsequently hydro-treated over a sulfitedCoMo catalyst at 170 bar.⁶¹

Hydrothermal liquefaction processes (HTL) comprise complex chemical and physical transformations of biomass under the conditions of high temperature and pressure, commonly near- or supercritical water. The maximum bio-oil yield (38.35 wt.%) was obtained at 350 °C for 10 min. The HHV of the obtained resultant bio-oils varied in the range of 24-28 MJ/kg. Bio-oils from HTL of pine wood are complex mixtures of aromatic and cyclic compounds with numerous hydroxyl and carboxyl functional groups, the increase in the temperature results in a deeper decomposition of biomass manifested by the higher yield of bio-oil and its gradual de-oxygenation.⁴² Typical elemental content of bio-oil as shown in Figure 2.

III.1 Bio-oil upgrading

Bio-oil resulted from hydrothermal liquefaction or pyrolysis needs upgrading to improve the quality in fuel grade. Bio-oil upgrading using catalytic and non-catalytic supercritical fluid conditions are very common. The precious metal catalysts Pd, Ru, and Pt on various supports are chosen for catalytic bio-oil upgrading in supercritical fluid.⁶² Catalysts (Ni/C, ZSM-5, Ni/ZSM-5, Ru/C and Pt/C) at 300°C and 350°C. The upgraded bio-oil yields were higher at 300°C; however, higher quality upgraded bio-oils were obtained at 350°C. Ni/C gave the maximum upgraded bio-oil yield (61wt%) at 350°C. However, noble metal catalysts (Ru/C and Pt/C) gave the better upgraded bio-oils in terms of acidity, heating values, and nitrogen values.⁶³Biocrudes were catalytically hydrotreated with a commercial NiMo/Al₂O₃ catalyst at different temperatures and pressures.⁶⁴Commercial catalyst nickel-alumina-silica in a single-stage process. The 18% and 26% oxygen feed reduced to 52 and 61%, respectively.⁶⁵ Bio-oil obtained from pyrolysis of waste corn cobs was catalyse thermal cracking with zeolite as catalyst reduce high molecular weight oxygenated compounds.⁶⁶

Sewage sludge is first hydrothermally pre-treated (HTP) at 160 – 250 °C, and subsequently pyrolyzed at 550 °C to produce bio-oil. The characteristic of sewage sludge are improved during hydrothermal treatment, decreased N content and enhanced the aromaticity. The bio-oil contents of Oxygen and Nitrogen compounds are significantly decreased. The H/C ratio and higher heating value (HHV) of bio-oil in sample 190 – 550 °C increase 0.136 to 36.382 MJ/kg. The optimum HTP temperature is 190 °C for the HHV and energy recovery rate 44.23%.⁶⁷ Catalytically hydrothermal liquefaction of biomass resulted bio-oil with low oxygen content and high

heating value.⁶⁸ Catalytic hydrothermal liquefaction of CuO-CeO₂/Y-Al₂O3 was used as an in situ hydrogen donor and Ni-Co/SAPO-34 was synthesized for hydro-processing to improve bio-oil production process. When the two catalysts were mixed the yield of bio-oil increased from 51% to 64.51%, the carbon recovery rate raised from 69.53 to 88.18%, the energy recovery rate grew from 63.42 to 80.22%, and the S content is relatively reduced by 83.3%.⁶⁹ Hydrothermal liquefaction (HTL) of microalgae process over different metal supported of Co,Ni, and Fe on carbon nanotube CNT). Maximum bio-oil yield 43.6 wt% was found with Co/CNT catalyst 290 °C under ethanol solvent.⁷⁰Hydrothermal liquefaction of cassava pulp, KOH is suitable catalyst because it provides the highest Bio-crude oil.⁷¹

III.2 Carbon treatment

Materials carbon resulted from hydrothermal liquefaction needs another treatment before can be used in application. Functional carbonaceous materials can be produced via dehydration and polymerization reactions in the low-temperature HTC, below 300 °C. The carbon content is increased during the carbonization phase. HTC appears more appropriate to less-valuable organic residues. HTC with higher temperature and longer time, hydrochar tended to become darker in colour.⁷² The content of C element in hydrochar is usually greater than 60%, and the other elements contained in it are mainly H,O,N,S.⁷³ The hydro-char, rich in carbon, can be utilized as fuel, enrichment, or as an adsorbent or precursor for activated carbon.

Carbon materials have attracted interests as electrode materials for electrochemical capacitors, because their high surface area, electrical conductivity, chemical stability and low cost. Activated carbons produced by different activation processes from various precursors are the most widely used electrodes.⁷⁴The activity in materials science is the development of new materials for many purposes. This includes high-performance materials with specific characteristics, for example employed as electrode materials for lithium-ion batteries and super-capacitors, in fuel cells, and as host materials for hydrogen storage. Carbons have previously been utilized in various electrochemical energy storage system.⁷⁵

Materials carbon can be produced by pyrolysis or hydrothermal carbonization. For biomass with high moisture content hydrothermal carbonization is suitable to process this material to produce carbonbiochar.Biochar is suitable as a solid fuel energy regarding with carbon content itself. Agricultural waste was thermochemical decomposition, temperature was raised from 450 to 850 °C over 30 minutes. The resulted biochar have a net calorific value between 27 and 32 MJ/kg, which is comparable than good quality coal of 24-26 MJ/kg, its can be considered as a valuable source of energy (Kosakowski, 2020).⁷⁶ Increase temperature process of 250, 350 and 450 °C resulted biocharhas reduced the HHV of 24, 23.64 and 23.08 MJ/kg (Waqas, 2018).⁷⁷

IV. CONCLUSION

Hydrothermal process is suitable to process biomass with high moisture content. Biomass with high moisture content like algae, plants, forest wastes, and agricultural residue, biomass with high moisture content up 80%. Hydrothermal process is a thermochemical process that converts biomass into a coal-like material to biomass in a suspension with water under saturated pressure for several hours. Hydrothermal carbonization (HTC) was operated in temperature between 180 to 280 °C, and pressure of 2-6 MPa for 5 to 240 mins. Hydrothermal liquefaction (HTL) occurs at high pressure (10–25 MPa) and high temperatures (280°C–370°C). Hydrothermal gasification (HTG) occurs at super-critic temperature > 374 °C and pressure > 221 bar. The production of HTC mainly materials rich carbon that can be used as soil amendment for soil improvement. With another more treatments the material carbon can be used as carbon functional in many application such as adsorbent, capacitor, batteries, and energy storage. HTL mostly produced soluble liquid that based a liquid production. The catalytic upgrading of soluble liquid into liquid grade of fossil fuel replacement.

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