

HYDROTHERMAL PROCESS FOR CELLULOSIC WASTE DEGRADATION INTO VALUABLE CHEMICALS

R. Sarwono

Pusat Penelitian Kimia-Lembaga Ilmu Pengetahuan Indonesia
Komp. PUSPIPTK, Serpong, Tangerang Selatan (15314)
Email: rach014@lipi.go.id

ABSTRAK

Pada tulisan ini dibahas tentang sifat-sifat air pada kondisi sub dan super kritis dalam kemampuannya untuk menguraikan biomasa selulosa. Air dalam kondisi super kritis mempunyai sifat oksidator yang kuat, yang mampu menguraikan biomasa selulosa menjadi molekul yang lebih kecil seperti dalam bentuk gas CO₂, H₂ dan air. Air pada kondisi sub kritis mempunyai sifat oksidator yang lebih rendah yang mampu menguraikan biomasa selulosa menjadi molekul yang agak besar seperti glukosa, asam-asam organik dan *biofuel*. Penguraian biomasa selulosa dengan proses *hydrothermal* biasanya menghasilkan gas, cairan dan padatan tar. Dengan mengubah-ubah kondisi operasi (temperatur dan tekanan), jenis katalis, dan waktu reaksi, dan juga komposisi dari biomasa selulosa maka produk yang akan dihasilkan bisa diperkirakan. *Hydrothermal upgrading* dan *liquefaction* menggunakan media air pada kondisi subkritis untuk menguraikan biomasa selulosa menjadi produk bentuk cair yang bisa dipakai sebagai bahan bakar.

Kata kunci: selulosa, hydrothermal, kondisi operasi, gas, bahan bakar

ABSTRACT

In this review paper discussed the properties of sub- and supercritical water in the ability to decompose of cellulosic materials. Supercritical water has strong oxidation power that decomposed cellulosic biomass into gases such as CO₂, H₂ and water. Subcritical water has lower oxidation power that decomposed cellulosic biomass into bigger molecules such as glucose, organic acids and biocrude or biofuel. Decomposition of cellulosic biomass in hydrothermal processing normally produced gas, liquid and tars. By manipulation of operating conditions (temperature and pressure), catalyst, residence time, and materials composition, the major product with certain range of molecule size can be predicted. Hydrothermal upgrading and liquefaction processes used a subcritical water conditions to convert cellulosic biomass into liquid range that can be used as a fuel.

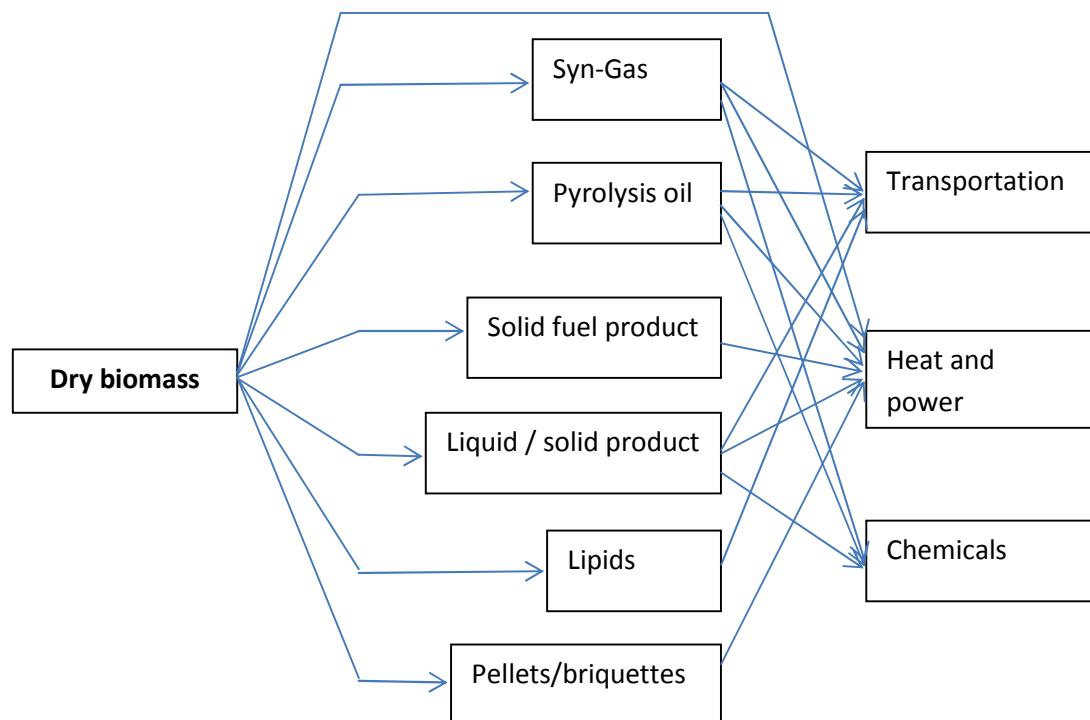
Key words: cellulosic, hydrothermal, operating conditions, gas, biofuel

INTRODUCTION

In recent years, the global issue in the energy field is that with the combination of increasing energy consumption and steady depletion of fossil fuel resources. This, together with the global environment issues of the appropriate treatment of increasing municipal solid waste (MSW) has prompted a global research to develop alternative energy resources as well as to reduce CO₂ emissions by using renewable energy from biomass and waste ^(1,2).

Although it is a common source of energy (especially in developing countries), biomass as such is not an ideal fuel due to its fibrous nature, low density and low heating value. Therefore biomass is treated in various processes to create products which can be efficiently and economically utilized in modern equipment. Lignocellulose such as agricultural and forestry waste (wood, bark, etc) should be used for energy purposes as these are not in direct competition with biomass for food and feed. Lignocellulose material mainly consists of cellulose, hemicellulose and lignin. Cellulose is a linear homopolymer of glucose units, while hemicellulose is a co-polymer of pentoses and hexoses, and lignin consists of aromatic units linked together in large structure.

Conversion processes are available or under development for both wet and dry feedstock. Examples of wet biomass are sewage sludge, sugar solutions, algae suspensions, waste streams from biomass processing, or from biorefineries. Dry biomass commonly has low moisture content. Examples of dry biomass are wood, straw, or other sun dried waste. Propose route processing is shown in Figure 1.



a)

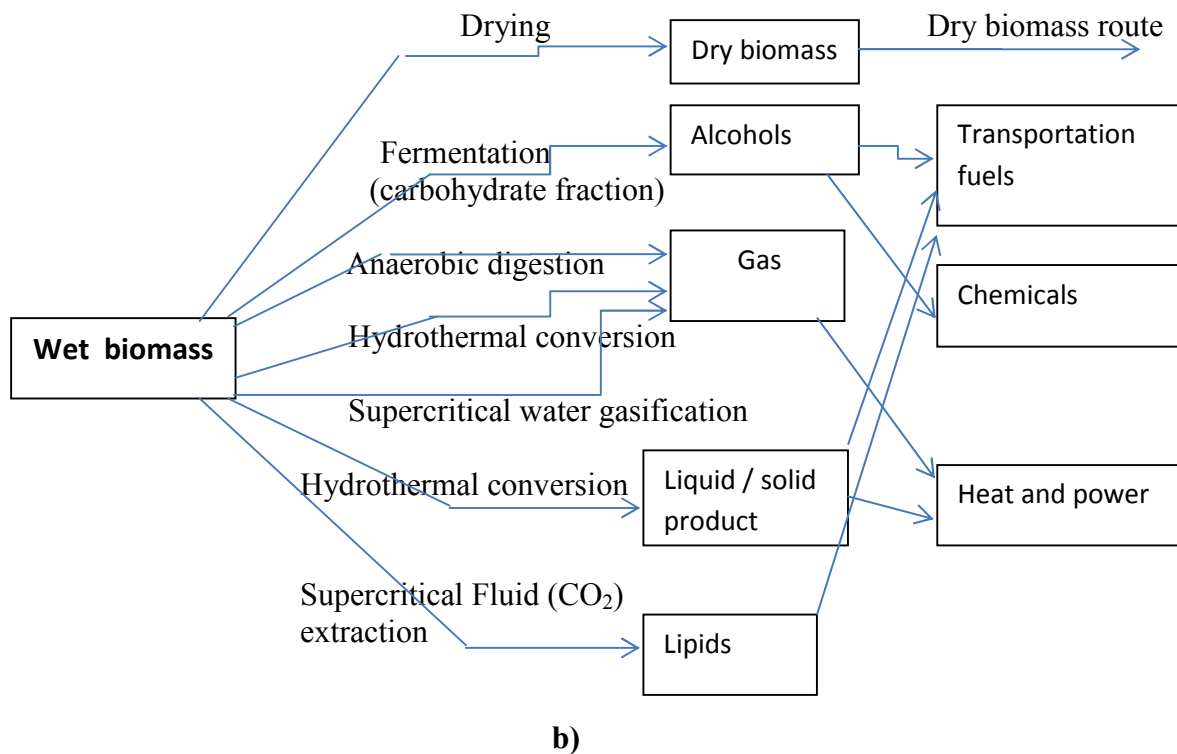


Figure 1. Conversion route and utilization options for a) dry and b) wet biomass ⁽³⁾.

For wet biomass conversion, processes which do not require water evaporation are desired. Biological conversion and also in hot compressed water, both sub- and supercritical, is possible aimed at the production of hydrophobic liquids, solids and gasses. By combining dry and wet conversion routes, a wide spectrum of interconnected thermo-chemical biomass conversion route towards final products are possible.

There are many kinds of MSW treatments such as mechanical biological treatment, mechanical treatment, and biological treatment. However, mechanical and biological treatment stage have common problems requiring long treatment time, it more than 1 week to 1 month, with unpleasant smells ^(4,5). The hydrothermal treatment is one of the thermo-chemical processes, treating waste in high temperature and high-pressure water media to upgrade the material in a short time ^(6,7). That is one of progressive technologies for converting MSW and biomass into useful energy resources because it can improve the dehydration and drying performance of high moisture content of biomass as well as upgrade the property of the fuel produced from MSW.

Hydrothermal treatment has been applied in various field, such as synthesis and decompositions of organic materials ⁽⁸⁾. Recently, application field of hydrothermal treatment expanding to biomass gasification and biomass liquefaction. Nowadays hydrothermal treatment was applied in the field of biomass saccharification as one of the efficient techniques. By applying a hydrothermal treatment on ligno-cellulose biomass, cellulose and hemi-cellulose components is decomposed to the oligosaccharide or mono-saccharide, such as glucose, xylose and sugar. Therefore, research works on a hydrothermal pre-treatment process for bio-ethanol production are actively implemented. Sakaki⁽⁹⁾,

Ando⁽¹⁰⁾ and Minowa et al.⁽¹¹⁾ conducted hydrothermal treatment on cellulose materials in batch reactor. After these research works, many researchers involved in biomass hydrothermal treatment as a pre-treatment technique of enzyme saccharification. Funke and Ziegler⁽¹²⁾ discussed of chemical decomposition and hydrolysis mechanism of biomass during a hydrothermal reaction and optimum hydrothermal conditions in various biomass species with batch type reactors.

With expanding hydrothermal applications on biomass saccharification, new application units and systems are introduced in order to increase an efficiency and productivity of saccharine from ligno-cellulose. There are three categories as the system, which are batch, semi-batch and continuous reactor. In batch reactor, water and reactant is sealed in a same reactor. Reactor is heated up from the outside or inside with microwave. Since hydrothermal operation could be conducted easily by this reactor, many hydrothermal reaction results and data has been accumulated in various operation conditions. However the productivity can not satisfy commercial demands. In semi-batch reactor, reactant is filled in a reactor and hot compressed water is introduced to the reactant. Temperature and flow rate control is simple and product can be obtained continuously, but reactants have to be refilled in the reactor for continuous production. Sakaki⁽⁹⁾ developed semi-batch system, but the productivity of the semi-batch was still very low. In continuous system, there are two methods; one is separate type and the other is slurry type. Operation in separation process has difficulties on the solid-liquid feeding. Because solid feed stock to be fed into a high pressure into the reactor. On the other hand, continuous feeding of slurry is able to demonstrate easy with a commercial high pressure slurry pump, productivity can be increased significantly.

HYDROTHERMAL PROCESSES

Supercritical water oxydation (SCWO) is based on the unique properties of water at conditions near and beyond its thermodynamic critical point of 374 °C and 22.1 MPa, as shown in figure 2. In that conditions water has a diference properties as usual. Hydrogen bonding is almost entirely disrupted, so that the water molecules lose the ordering responsible for many of liquid water's characteristic properties. In particular, solubility behavior is closer to that of high-pressure steam than to liquid water. The loss of bulk polarity by the water phase has striking effects on normally water-soluble salts. No longer readily solvated by water molecules, they frequently precipitate out as solids.

Small polar and nonpolar organic compounds, with relatively high volatility, will exist as vapors at typical SCWO conditions, and hence will be completely miscible with supercritical water. Larger organic compounds and polymers will hydrolyze to smaller molecules, thus resulting in solubilization via chemical reaction.

The earliest tests on gasification in supercritical water were carried out by Modell and coworkers at the Massachusetts Institute of Technology (MIT) in the late of 1970's⁽¹³⁾. An advantage of the supercritical water gasification (SCWG) process, is expected to extend to

the SCWO process. It is known that the formation of high molecular weight hydrocarbon (tar and char) is a function of feed heat-up time, with longer heat-up times yielding higher amounts of these products.

SCWO involves carrying out oxidative reactions in the supercritical water (SCW) environment in the presence of sub-stoichiometric quantities of oxidant, typically pure oxygen or air, and as such is related to the technology of SCWO. Application of SCWO technology have thus far been primarily targeted at waste destruction applications, where the high destruction efficiencies attainable in compact equipment are very desirable.

The molecular dispersion of the organic and oxidant reactants within a single phase, in conjunction with the high diffusivity, low viscosity, and relative dense SCW reaction medium, is conducive to rapid oxidation reactions. Furthermore, the temperature is sufficiently high that reaction completion is usually attained within seconds to tens of seconds. Rapid reaction rates have been demonstrated for virtually all types of organic materials, including solids.

SCWO has proven to be a robust method for the complete oxidation and mineralization of a wide spectrum of materials. It is particularly suited to feedstocks with a high water content, such as biomass-derived materials, as well as dirty fuels such as high-sulfur coal. It is a natural complement to the process of supercritical water gasification (SCWG), with the matched pressure of the processes facilitating heat interchange.

Classification the cases in which SCW is used to gasify different compounds was described by Youssef⁽¹⁴⁾ is below:

1. **Pyrolysis in SCW** which stands for the hydrolysis of the organic compounds at SCW conditions in the absence of both catalyst and oxidant.
2. **Total oxidation in SCW** which stands for gasifying the organic compounds in the absence of catalyst and the presence of excess oxidant at oxygen to carbon molar ratio (MR) of 1.0 or higher (the stoichiometric requirement i.e. $M.R \geq 1.0$)
3. **Gasification in SCW (SCWG)** which stands for gasifying the organic compounds in the absence of oxidant while using catalyst, which is also known as low temperature gasification.
4. **Partial oxidation in SCW (SCWPO)** which stands for oxidizing the organic compounds in the presence of oxidant at oxygen to carbon molar of lower 1.0 ($M.R. < 1.0$) and with an absence of catalyst.
5. **Sequential gasification partial oxidation** which stands for gasifying the organic compounds in the presence of active catalyst (heterogeneous or homogeneous) followed by further gasifying the organic compounds in the presence of oxidant at oxygen to carbon ratios below the theoretical requirements i.e. an approach using a combination of step 3 followed by step 4.

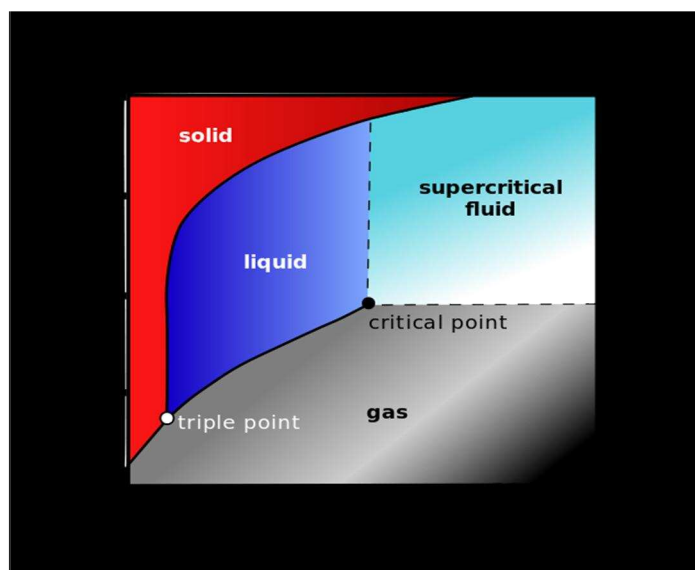


Figure 2. Water pressure and temperature diagram ⁽²⁾.

SCWO has several advantages over conventional processes and even some of the relatively modern processes such as wet-air oxidation and incineration. As a medium for chemical reactions, depending on its density, SCW has low dielectric constant promotes dissolution of non-polar organic compounds where as gas-like low viscosity promotes mass transfer and the solvation is enhanced by the liquid-like density.

DECOMPOSITION OF BIOMASS

The proton-catalyzed mechanism, direct nucleophilic attack mechanism, hydroxide ion catalyzed mechanism, and radical mechanism play important roles in the hydrolysis of biomass waste. The most likely source of hydroxide and hydroxide ions is the high temperature water itself because subcritical and supercritical water have a stronger tendency to ionize than ambient water, which makes water a Bronsted base acid and acts as an effective catalyst ⁽¹⁵⁾.

The decomposition of biomass waste under hydrothermal conditions including hydrolysis, dissolution, pyrolysis, and all of them favor decomposition and gassification. At the same time, the process under hydrothermal conditions shows similarities to other methods as well as significant differences due to the presence of water as the reactant, reaction medium, and catalyst ^(16,17). Usually, detailed chemical reaction pathways with well-defined single reaction steps cannot describe the degradation of biomass in supercritical and subcritical water. The reason is that biomass is a combination of cellulose, hemicellulose, and lignin. These components interact each other, leading to a very complex chemical mechanism. The chemical mechanisms including hydrogen formation from raw biomass and decomposition are very complex and cannot be easily summarized ^(11,19). It is possible to say that pyrolysis, hydrolysis, steam reforming, water gas shift, methanation, and other reactions play a role in the gasification chemistry. The heterogenous reaction cannot be directly compared to homogenous reactions of other organic compounds.

At low temperature regions, the oligomer is the main liquefaction product of biomass; it is the most part lower organic compound. At the same time, the conversion rate of oligomer is much faster than the hydrolysis rate of biomass waste. When the temperature is higher than 400 °C, the breakage of interior and intermolecular H-H bonds happen with easy and produce a large number of H₂, CO, CH₄, and tar^(19,20,21).

Cellulose hydrolysis produces oligomers and glucose. Glucose epimerizes to fructose and further transformation or decomposes to erythrose plus glycolaldehyde or glyceraldehydes plus dihydroxyacetone. Produced fructose also decomposes to erythrose plus glyceraldehydes or glyceraldehyde plus dihydroxyacetone. Glyceraldehyde converts to dihydroxyacetone and both glyceraldehyde and dihydroxyacetone dehydrated into pyruvaldehyde. Pyruvaldehyde, erythrose, and glycolaldehyde further decompose to smaller species, which are mainly acid, aldehydes, and alcohols of 1-3 carbons.

Conversion of biomass into gas

Thermo-chemical gasification of biomass has been identified as a possible system to produce renewable hydrogen. SCWG which takes advantage of the characteristic of supercritical water, has high gasification efficiency and can deal directly with wet biomass without drying⁽²²⁾. The SCWG process generally takes at the temperature over 600 °C and a pressure higher than the critical point of water, with hydrogen as the target product.

Hydrothermal process for baby food treatment with conditions at 310 – 410 °C, 30 – 50 MPa, and 15 minutes resulted large amounts of CO₂⁽²³⁾. Water in supercritical conditions acts as strong oxidant, and oxygen in water can be transferred to the carbon atoms of the biomass. As a result of the high density, carbon is preferentially oxidized into CO₂ but also low concentrations of CO are formed⁽²⁴⁾.

In the real cases, all of the biomass do not react with supercritical water that every organic molecule is not transformed into hydrogen or carbon dioxide gases. As a result, tars and chars can be formed during the biomass gasification, especially for real biomass wastes⁽²⁵⁾. Because of sedimentation of these tars and chars usually plug reactors after several hours of running.

Considering the stability of carbon in supercritical water, especially when hydrogen gas is present, especially on the use of activated carbons as catalysts in supercritical water^(22,26). Their experiments showed that extraordinary yields of gas with high content of hydrogen (57 mol%). Watanabe et al.⁽²⁷⁾ studied of catalytic effects of NaOH and ZrO₂ for partial oxidative gasification of n-hexadecane and lignin in supercritical water (40 MPa and 400 °C) using of a batch type reactor. They show that the yield of H₂ from *n*-C₁₆ and lignin with zirconia was twice as same as that without catalyst at the same condition. The H₂ yield with NaOH was four times higher than that without catalyst. The catalytic effect of NaOH and ZrO₂ was found to be the enhancement of decomposition of intermediate into CO.

Conversion biomass into glucose

The production of glucose by hydrolysis is an important step of cellulose conversion, from which a wide range of chemical can be synthesized. From glucose, for example, one can form ethanol by fermentation or sorbitol and vitamin C from hydrogenation. By using sulfuric acid as catalyst, enhanced reaction rate and high glucose yield could be obtained. Generally, in the case of non-catalyzed hydrothermal degradation of cellulose (215 – 295 °C), the hydrolysis rate is much lower than that of acid-catalyzed hydrolysis and the glucose yield is lower⁽²⁸⁾. However, high yields of hydrolysis products were obtained by ⁽⁹⁾, in the non-catalytic hydrolysis of cellulose in sub- and supercritical water. At 400 °C the yield of hydrolysis products were as high as 65 – 77% at 0.01 – 0.05 s residence times. Although they got high yields of hydrolysis products in a very short residence time, the glucose yields showed relatively low values, comparing to those obtained by acid-catalyzed processes. The reactions in pure SCW, the conversions of cellobiose increase from 36.7 to 59.3% while the selectivities of glucose decrease from 19.9 to 12.8% by changing residence time between 0.05 and 0.15 s at 400 °C and 30 MPa. When extremely small amount of sulfuric acid (6.4×10^{-5} and 3.3×10^{-4} mol/l) was added to SCW, the conversions of cellobiose reached high values between 54.2 and 93.9% and the selectivity of glucose showed 35.4 – 73.5%.

Conversion biomass into organic acids

Hydrothermal oxidation is effective for treatment of organic waste, and the acetic acid is a stable intermediate product. As an important organic chemical, one important industrial use of acetic acid is to produce calcium magnesium acetate as a noncorrosive road deicer for cold area in winter. In order to convert organic wastes to useful materials, Jin et al.⁽²⁹⁾ proposed a method to produce an acetate deicer using various organic wastes, such as garbage, rice hulls, and straw. The result is that the direct oxidation of cellulose would produce formic acid but not acetic acid. In the interest of improvement of the conversion efficiency to acetic acid, a comprehensive research on wet air oxidation (WAO) mechanisms, properties of a solution at high temperatures and pressures were carried out. They showed that the production of acetic acid could be improved by a two-step hydrothermal process⁽¹⁵⁾. The two-step process consists of both a hydrothermal reaction process without a supply of oxygen (the first step reaction) and an oxidation reaction process (the second step reaction). From the studies on acetic acid production by WAO of ligno-cellulosic biomass and the mixture of cellulose and lignin, they found that lignin played an important role to increase the acetic acid⁽³⁰⁾.

Conversion of biomass into liquid fuel

Water in sub-critical conditions has less oxidation power. The biomass was degraded into bigger molecule than its degrade in the supercritical conditions. The process used the sub-critical condition is hydrothermal upgrading and hydrothermal liquefaction.

Hydrothermal Upgrading procesess is the hydrothermal conversion of biomass into an organic crude oil (biocrude). During this process, the oxygen content of the organic material is claimed to be reduced from about 40% to between 10 and 15%, the removed oxygen ends

up mainly in CO₂ and water^(31,32). HTU was invented long time ago at least by the end of the 1970's to early 1980's, in HTU process, the reaction temperature range from 300 to 360 °C, and the pressure is 17 – 27 MPa and the residence time 5 – 20 mins. The HTU process has great opportunities for the production of fuel and chemicals. Its efficiency can be improved in many ways. One of the them is to exploit insights into the mechanism of the chemical reactions during the biomass decomposition.

In hydrothermal process, lignocellulose waste was converted to smaller molecule with the reaction mechanisms, such as hydrolysis, dehydration, dicarboxylation, aromatization, and condensation polymerization⁽¹²⁾. Lawn grass with higher water content resulted higher protein fraction⁽⁷⁾. High moisture content of 59% of Loy yang brown coal, increase the colorific value as of coal after processing⁽³⁴⁾. Municipal solid waste (MSW) of 10% moisture resulted similar quality to low-grade sub-bitumious coal⁽³³⁾.

Hydrothermal liquefaction (HTL) is also called hydrous pyrolysis, is a process for the reduction of complex organic materials such as bio-waste or biomass into crude oil or other chemicals. HTL converts feedstock into oil rather than gasses or alcohol. There are some unique feature of the HTL process and its product compared with other biological processes. First, the end product is crude oil which has a much higher energy content than syngas or alcohol. Secondly, if the feedstock contains a lot of water, HTL does not require drying as gasification or pyrolysis. The energy used to heat up the feed stock in the HTL process could be recovered effectively with the existing technology.

Zhou et al.⁽³⁴⁾ converted macroalgae into bio-oil. The bio-oil was a complex mixture of ketones, aldehydes, phenols, alkenes, fatty acids, ester, aromatics, and nitrogen containing heterocyclic compounds. The bio-oil obtained at moderate temperature 300 °C, 5% Na₂CO₃ catalyst, and retention time 30 min resulted 23% of bio-oil, and the heating value around 28 – 30 MJ/kg. The acetic acid was the main component of the water-soluble products. Using conditions temperature 300 °C, pressure of 10 - 12 Mpa, and 30 min residence time, spirulina algae waste converted into biocrude on hydrothermal processing resulted biocrude 9.4 – 32.6%, and heating value around 32.0-34.7 MJ/kg⁽³⁵⁾. Two-step process of hydrothermal liquefaction increase the efficiency of conversion.

Hydrothermal upgrading (HTu) is a promising liquefaction process, which can be used to convert a broad range of biomass feedstocks to liquid fuel is called “biocrude”⁽²⁴⁾. Treated in water in temperature range of 300 – 350 °C and a pressure range of 10 – 18 MPa, the biomass is depolymerized into biocrude with a heating value of 30 – 35 MJ/kg^(32,36). During this process, the oxygen content of the organic material is reduced from about 40% to between 10 and 15%, the removed oxygen ends up in CO₂, H₂O, H₂, methane and CO.

Many researchers investigated the conversion of lignocellulosic waste into biofuel on the HTL processes. Goudriaan et al.⁽³⁷⁾ applied the HTL process to artificial garbage prepared by mixing cabbage, boiled rice, boiled and dried sardines, butter, and the shell of short-necked clams. Three temperatures (250, 300 and 340 °C) and three retention times (0.1, 0.5, and 2 hours) were tested with out catalyst. The oil yield and its properties strongly

depended on the catalyst addition and reaction temperature, while retention time showed no significant effect⁽³⁷⁾. Higher oil yield of 27.6% is on an organic basis. The oil had a heating value of 36 MJ/kg. Minowa et al.⁽³⁸⁾ applied the HTL process for 18 kinds of agricultural and forest residues in Indonesia. The process conditions were set up such as temperature of 300 °C, pressure of 3 MPa, residence time 30 minutes, and 5 wt% Na₂CO₃ as the catalyst. The oil yields were the range of 21 – 36%, and the heating value were around 30 KJ/kg.

Suzuki et al.⁽³⁹⁾ investigated optimum starting materials and catalyst loading for conversion of sewage sludge to heavy oil. Various kinds of sewage sludge were liquified at 300 °C, 12 MPa, and a catalyst loading of 0 – 20 wt %. The average oil yield about 43%. Murakami et al.⁽⁴⁰⁾ converted activated sludge from a cornstarch processing plant into oil with the HTL process. The oil yield was 30% at 300 °C, 60 minutes retention time without catalyst. Oil yield was not significantly affected by catalyst loading. Properties of the oil product were not influenced to any great extent by temperatures between 225 – 300 °C. He et al.⁽⁴¹⁾ studied HTL process for swine manure. The process was evaluated by the oil production and waste reduction efficiency. The key factors of the HTL process were the operating temperature, the retention time, and the addition of a process gas. A process gas addition was necessary to achieve the oil product. Without the process gas addition, there is no oil products formed. The process gases addition include carbon monoxide, hydrogen, nitrogen, carbon dioxide and compresses air. Carbon monoxide was the most effective gas processes.

SUMMARY

Water in sub- and supercritical conditions acts as oxidator to react with the surrounding, including biomass to degrade into smaller molecules. The degradation reaction included hydrolysis, decarboxylation, dehydration and aromatization. Near critical water acts not only as a solvent but also as a reactant. Vary in operation conditions such as temperature, pressure, catalysts and residence time produces wide range of products, such H₂, CO₂, glucose, organic acids and liquid fuels. Spesific operation condition will get narrow product fraction. The main goal is to remove oxygen and other heteroatoms (nitrogen, sulphur, phosphorous) from the biomass, leaving behind the initial carbon and hydrogen atoms in the form of low molecular weight compounds.

Hydrogen gas was produced in the conditions above supercritical water. This conditions water acts as strong oxidator, that oxidize the biomass into smaller molecule included gas CO₂ and hidrogen. While biocrude and other chemicals were produced in the sub-critical water and lower temperature and used a proper catalyst. The main route is liquefaction and then decompose of biomass into smaller molecules.

REFERENCES

1. Y. Kuzuhara, (2005). Biomass Nippon strategy-why “biomass Nippon” now?. *Biomass and Bioenergy*, vol.29, pp331-335.
2. P.E. Alexander, (2010). Technoeconomic aspects of alternative municipal solid wastes treatment methods. *Waste Management*, vol.30, pp 707-118.
3. D. Knezevic,(2009). *Hydrothermal conversion of Biomass*. PHd Thesis, The University of Twente. The Netherlands.
4. Y.S. Yun, J.I. Park and J.M. Park, (2005). High-rate slurry-phase decomposition of wood waste:indirect performance estimation from dissolved oxygen. *Process Biochemistry*, vol.40,pp. 1301-1306.
5. R. Barrena, G. Imporzano, S. Ponsa, T. Gea, A. Artola, F. Vazquez, A. Sanchez, and F.Adani, (2009). “In search of a reliable technique for the determination of the biological stability of the organic matter in the mechanical-biological treated waste”. *J.Hazardous Materials*, vol. 162, pp 1062-1072.
6. C. Serrano-Ruiz, D.J. Braden, R.M. West, and J.A. Dumesic, (2010). Conversion of cellulose to hydrocarbon fuel by progressive removal of oxygen. *Applied Catal. B: Environmental*,vol.100,pp 184-189
7. G. Luo, X. Cheng, W. Shi, P.J. Strong, H. Wang, and W. Ni, (2011). Response surface analysis of the water: feed ration influence of hydrothermal recovery from biomass. *Waste Management*, vol.31, pp 438-444.
8. G. Brunner,(2009). Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes. *The Journal of Supercritical Fluids*, 47, 373-381.
9. T. Sakaki, (1998). Mono and Oligo Saccharine of Cellulose in Hot-compressed Water (in Japanese), *Bio industry*, 15,28-36.
10. H. Ando, (1998). Components Separation of Ligno-cellulose with Hot-compressed Water Method. *Kagaku Kogaku*, 62, 700
11. T. Minowa, F. Zhen, and T. Ogi, (1999). Liquefaction of cellulose in hot-compressed water using sodium carbonate: production distribution at different reaction temperature. *J.Chem.Eng.Jpn.* 30:186-190.
12. A. Funke, and F. Ziegler, (2010). Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels, bioprod. And bioref.*,vol.4, pp 160-177.
13. M. Modell, R.C. Reid, and S.I. Amin, “Gasification Process”,U.S.Pat.4,113,446, 1978
14. E.A. Youssef, (2011). *Supercritical Water Gasification of Biomass & Biomass Model Compounds*. PHd Thesis, The University of Western Ontario. Ontario, Canada.

15. F. Jin, Z.Y. Zhou, T. Moriya, H. Higashijima, and H. Enomoto,H.(2005). Controlling hydrothermal reaction pathways to improve acetic acid production from carbohydrate biomass. *Environ.Sci.Technol.* 39:1893-1902.
16. K. Peter, (2004). Corrosion in high-temperature and supercritical water and aqueous solutions: A Review. *J.supercrit.Fluids.* 29:1-29
17. H. Oka, S. Yamago, J. Yoshida, (2002). Evidence for a hydroxide ion catalyzed pathway in ester hydrolysis in supercritical water. *Angew.Chem.Int.Ed.* 41:623-625.
18. T. Minowa, F. Zhen, and T. Ogi, (1998). Cellulose decomposition in hot-compressed water with alkali or nickel catalyst. *J.supercrit.Fluids.* 13:253-259
19. S. Mitsuru, F. Zhen, F. Yoshiko, (2000). Dissolution and hydrolysis of cellulose in sub-critical and supercritical water. *Ind.Eng.Chem.Res.* 39:2883-2890.
20. S. Mitsuru, A. Tadafumi, and A. Kunio, (2003). Fractionation of sugarcane bagasse by hydrothermal treatment. *bioresour. Technol.* 86:301-304.
21. I.C. Kim, S.D. Park, and S. Kim, (2004). Effects of sulfates on the decomposition of cellobiose in supercritical water. *Chem.Eng.Process.* 43:997-1005.
22. J.M. Antal, S. Allen, D. Schulman, X. Xu, and R.Divilio,(2000). Biomass gasification in supercritical water. *Ind Eng Chem Res*;39:40 -9.
23. A. Kruse, and A. Gawalik, (2003). Biomass conversion in water at 330-410 and 30-50 Mpa. Identification of key compounds for indicating different chemical reaction pathways. *Ind.Eng.Chem.Res.*;42:267-79
24. W. Feng, J. Hedzer, and J.S. Kooi, (2004). Phase equilibria for biomass conversion processes in subcritical and supercritical water. *Chem Eng J*; 98: 105-13.
25. J. Herguido, J. Corella, and S.J. Gonzales, (1992). Steam gasification of lignocellulosic residues in fluidized bed at small pilot scale. Effect of the type of feedstock. *Ind Eng Chem Res*;31:1274-82.
26. Y. Matsumura, X. Xu, and J.M. Antal,(1997). Gasification characteristics of an activated carbon in supercritical water. *Carbon*; 35:819-26.
27. M. Watanabe, H. Inomata, M. Osada, T. Sato, T. Adschiri, and K. Arai, (2003). Catalytic effects of NaOH and ZrO₂ for partial oxidative gasification of n-hexadecane and lignin in supercritical water. *Fuel*; 82: 545-52.
28. O. Bobleter, (1994). Hydrothermal degradation of polymers derived from plants. *Prog.Polym.Sci.*,vol.19,pp 797-841.
29. F. Jin, A. Kishita, T. Moriya, H. Enomoto, and N. Sato, (2002). A new process for producing Ca/Mg acetate deicer with Ca/Mg waste and acetic acid produced by wet oxidation of organic waste. *Chem Lett.*; 1:88 - 9.

30. F. Jin, Z. Zhou, A. Kishita, and H. Enomoto, (2006). Hydrothermal conversion of biomass into acetic acid. *J.Mater.Sci.*; 41:1495 - 501.
31. L. Petrus, and M.A. Noordermeer, M.A.; *Green Chem.*, 2006, 8, 861
32. F. Goudriaan, and D.G.R. Peferoen, (1990). Liquid fuels from biomass via a hydrothermal process; *Chem.Eng.Sci.*; 45 :2729.
33. P. Prawisudha, T. Namioka, and K. Yoshikawa, (2011). "Coal alternative fuel production from municipal solid waste employing hydrothermal treatment. *Applied Energy*. Vol.90, issue 1, february 2012, 298-304.
34. D. Zhou, L. Zhang, S. Zhang, H. Fu, and J. Chen, (2010). Hydrothermal Liquefaction of *Macroalgae Enteromorpha prolifera* to Bio-oil. *Energy Fuel*; 24: 4054 – 61.
35. D.R. Vardon, B.K. Sharma, J. Scott, G. Yu, Z. Wang, L. Schideman, Y. Zhang, and T.J. Strathmann, (2011). Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina*, swine manure, and digested anaerobic sludge. *Bioresour Technol*; Sep; 102(17): 8295-303.
36. T. Minowa, Y. Dote, S. Sawayama, S. Yokoyama, and S. Mukarami. (1995). Phase changing of garbage from solid to liquid slurry by thermal liquefaction. *J. Chem Eng Japan*, 28(6): 727-731.
37. F. Goudriaan, B. Van de Beld, F.R. Boerefijn, G.M. Bos, J.E. Naber, S. Van der Wal, J.A. Zeevalkink, (2001). Thermal efficiency of the HTU process for biomass liquefaction. Progress in thermochemical biomass conversion. Vol.2. Oxford: Balckwell Science; p. 1313.
38. T. Minowa, T. Kondo, and S. Sudirjo, (1998b). Thermochemical liquefaction of Indonesian biomass residues. *Biomass and bioenergy*; 14(5): 517-524.
39. A. Suzuki, T. Nakamura, S. Yokoyama, T. Ogi, and K. Koguchi, (1988). Conversion of sewage sludge to heavy oil by direct thermochemical liquefaction. *J. Chem Eng Japan*; 21(3): 288-293.
40. M. Murakami, S. Yokoyama, T. Ogi, and K. Koguchi, (1990). Direct liquefaction of activated sludge from aerobic treatment of effluents from the cornstarch industry. *Biomass*, 23: 215 – 228.
41. B. He, Y. Zhang, T. Funk, G. Riskowski, and Y. Yin, (2000). Thermochemical conversion of swine manure: An alternative process for waste treatment and renewable energy production. *Trans Amer Society Agri Eng*; 43(6): 1827 – 1833.