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Bio-Crude Upgrading Into Fuel Grade From Hydrothermal Liquefaction Of Biomass In Sub- And Super-Critical Water Media

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ABSTRAK
Hydrothermal Liquefaction (HTL) proceeded of biomass into bio-crude have been studied. Bio-oil products were not ready to use as a fuel, because bio-oil content of high moisture content, high density, low heating value and inorganic elements. The bio-oil needs upgrading to improve the characteristic to fuel grade. Upgrade bio-oil included process of hydrotreatment, esterification and cracking, denitrogenation, deoxygenation, and demineralization. The high oxygen content in the bio-crude created undesirable properties in the oil such as low energy density, instability that leads to polymerization, high viscosity, and corrosion on contact surfaces during storage and transportation. The bio-oil treated to fuel grade properties lead on the high carbon content and high heating value, low impurities content, such as lower N,O,S and mineral contents. The resulted upgrade bio-oil should be mathed to the criteria of the fuel to be used.

Key words: HTL, biomass, convert, bio-oil, upgrading, fuel

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I. INTRODUCTION

Biomass as renewable resource, fixes carbon dioxide in the atmosphere through photosynthesis during growth, and is regarded as an alternative feedstock for fuel. Biomass resources include terrestrial and aquatic plants, food materials, biowastes, algae and bacteria. They are photosynthetic efficiency, high biomass production, rapid growth rate, low environmental impact and low competition for food.[1]

Biomass is one of the most abundant natural resources, which supplies around 10% of annual primary energy consumption.[2] It is generally agreed that the chemicals and fuel with low carbon footprint can be synthesized by the conversion of biomass using various catalytic strategies, which contribute to the reduction of CO_2 emission.[3] Exploration energy from biomass as alternative to supply the fossil energy becomes interesting works. There are three generations of biofuels, The first generation was converted edible feedstocks, for example soya beans, wheat corn, rape seed, sugarcane, molasses and carbohydrate into ethanol. Because those materials compete with human needs, the raw material supply will unsafe. The second generation was used lignocellulosic waste to convert into ethanol, but the cost was significantly increase. The third generation was used algae to convert into fuels.[4]

Fruits and vegetable wastes are biodegradable material that is generated in large quantities. Vegetable wastes occurs throughout the supply chain and very widely depending on its processing. Globally more than 30% waste occurs at the retail and consumer levels.[5] The generated wastes pose an environmental treat. Production of biofuel from fruits and vegetable has been carrieds out with singular aim that converting the waste to useful material.[6] Reducing food waste is one of the strategies which the food and Agricultural Organization is implementing to achieve its specific target in the sustainable development goals, designed to guarantee food security for the rapidly growing global population.[7] Mixed disposal is called municipal solid waste (MSW). Waste management meets two benefits, firstly, manage the environment properly will get the environment better souraounding life, and secondly, get usefull materials to increase the economic value. MSW included fruits and vegetable waste have a high moisture and low energy content. This material can be proceeded using HTL process into useful material, solid residue with high carbon content and soluble liquid can be upgraded into liquid fuels.

Hydrothermal liquefaction (HTL) process is an interesting technology that to produce a liquid bio-oil from wet biomass. In a HTL, wet biomass and a supplementary amount of water are heated 300 – 400 °C, under pressure comprised between 10 to 25 MPa, in several hours, that the solid degraded simultaneously into soluble liquid and gaseous.[8] Cassava pulp converted into bio-oil via hydrothermal liquefaction, bio-oil products is not more than 15%.[9] The HTL process can able to proceed biomass into three products, such as bio-oil, residual solid that rich of carbon, and gaseous.

II. UPGRADING

Bio-oil upgraded with combination of hydrotreatment, esterification, and cracking under supercritical conditions**.** Bio-oil upgrading in supercritical fluids used catalytic and non-catalytic. Metal catalysts Pd, Ru and Pt on various supports are chosen for catalytic bio-oil upgrading. This is reportedly due to their favourable catalytic activity during the process including hydrotreating, hydrocracking and esterifation, which leads to improvements in liquid yield, heating value, and pH of the upgraded bio-oil.[10]

Process variable of hydrothermal processing affected to the bio-oil quality and yield.[11] The maximum bio-oil yield 38.35 wt% was obtained at 359 °C for 10 min. Catalytic hydrothermal liquefaction by CuO-CeO_2 and Ni-Co improve bio-oil . 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%, and the S content is reduced by 83.3%.[12]

Catalytic hydrothermal upgrading, supercritical ethanol under hydrogen at mosphere by using Pd/SO_4^{2-} / ZrO_2 / SBA-15 catalyst.[13] Catalytic upgrading of crude oilover platinum on gamma alumina (Pt/Υ-Al_2O_3) in supercritical (SCW) at 400 °C for 1 hour.[14] Catalytic hydrotreatment of crude bio-oil over palladium on carbon (5% Pd/C), in supercritical water (SCW) at 400 °C and 3.4 MPa high-pressure H_2, time 1 to 8 hours.[15]

The fuel grade could be summerised that the colorific value has high, its can be reached by the content of oxygen, nitrogen, and sulfur are lower, as shown in Fig.1, the elements content of bio-oil produces by several methods. Bio-oil upgrade using HZSM-5 at 500 °C resulted olefins $C_2 – C_4$.[16] Catalytic transformation of crude bio-oil in a two-step process produce olefins $C_2 – C_4$.[17]

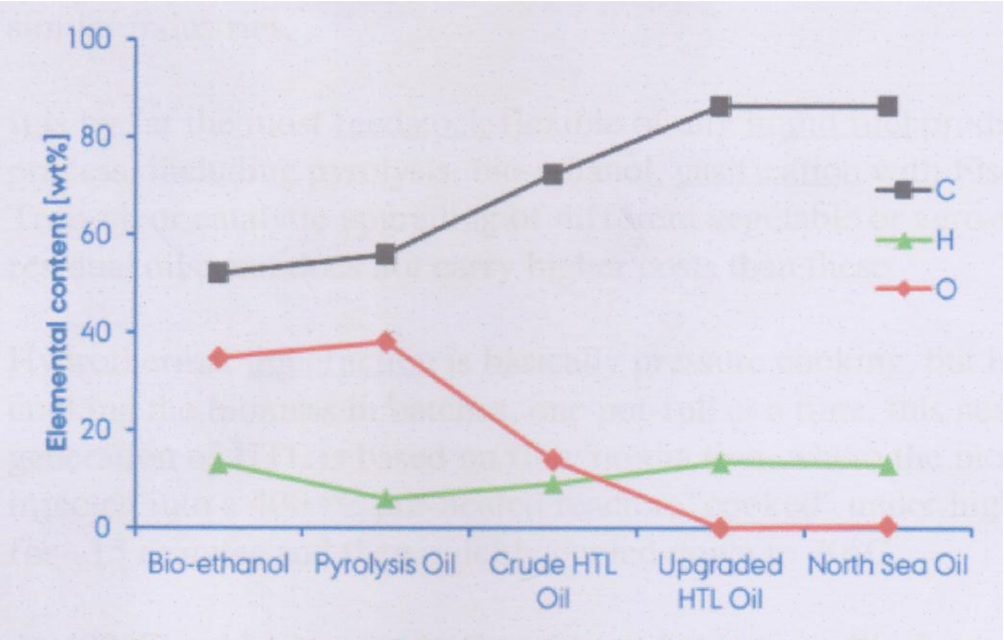

Figure 1. Elemental content of HTL oil compared to other fuel types.[18]

Figure 1. show the contents of oxygen, hydrogen and carbon in HTL-oil before and after upgrading, compared to other fuel types. Bio-oil with high carbon content increased in the high heating value (HHV), bio-oil with high moisture, nitrogen, oxygen and sulfur content will decreased in the HHV value. Total value of sulphur and acidity obtained the gross calorific value or final GCV of coal decreased.[19] Elemental content of fulewood species influenced to the colorific value.[20] Combination of hydrothermal pretreatment and pyrolysis of sewage sludge resulted of bio-oil with low oxygen and nitrogen contents.[21]

A new generation of the HTL process can convert all kinds of biomasses to crude bio-oil, which is sufficiently similar to fossil crude oil that a simple thermal upgrade and existing refinery technology can be employed to subsequently obtain all the liquid fuels we know today. What is more, the HTL process only consumes approximately 10-15 percent of the energy in the feedstock biomass, yielding an energy efficiency of 85-90 percent. To emphasize, the HTL process accepts all biomasses from modern society – sewage sludge, manure, wood, compost and plant material along with waste from households, meat factories, dairy production and similar industries.[18]

II.1. Hydrodeoygenation

Hydrodeoxygenation (HDO) is one of the hydrotreatment approaches, HDO is highly effective in removing oxygen form bio-crude through water formation. The yield and properties of upgraded bio-crude obtanined from HDO are dependent on the temperature, residence time, pressure, solvent, catalyst type, and reactor configuration.[22] HDO is an upgrading process applied to produce a high-quality oil with higher carbon content. The process involves removing oxygen from a hydrocarbon by applying different catalytic reactions at pressure up to 200 bars and temperature up to 400 ^oC.[23] HDO process occurs through different reactions, including the hydrogenation of C- O, C=O, and C=C bonds, the dehydration of the C-OH groups, condensation and the decarbonylation of the C – C bonds and hydrogenolysis of C – O – C bonds,[24] which breaks down the C-O bonds and liberates the oxygen in the form of water.

HDO reaction is to reduce the bio-crude oxygen content commontly used catalysts of Ni_2Fe_3, this catalyst is showed good activity in improving the bio-crude quality by increasing the heating value.[25] Several NiMo catalysts were also used for upgrading of fast pyrolysis bio-oil into products.[26] Zeolite cracking is an alternative catalysts, where HZSM-5 are used as catalysts for the deoxygenation.[27]

The high oxygen content in the bio-crude created undesirable properties in the oil such as low energy density, instability that leads to polymerization, high viscosity, and corrosion on contact surfaces during storage and transportation. Therefore, various upgrading techniques have been developed for bio-oil upgraded.[22] It was found that temperature up to 350 ^oC, the degree of deoxygenation is mainly driven by temperature, whereas the degree of denitrogenation also relies on initial H_2 pressure and temperature-pressure interaction.[28] Catalysts CoMo and NiMo used for hydrotreating of biocrude reduced the oxygen content by 3.8 to 2.4 wt% in increasing temperature of 320 to 370 ^oC.[29] Catalysts CuO-ZnO used for hydrodeoxygenation resulted increase in C and H content accompanied by a reduction in oxygen content with a degree of deoxygenation reaching 72.9%, and an increase in higher heating value (HHV).[30]

II. 2 Deoxygenation

Deoxygenation is also process to reduce oxygen content, its used CaO as adsorber.[31] Bio-oil was reacted with H_2 gas to reduce oxygen into water.[32] Catalytic pyrolysis is able to produce bio-oil with a low O and N content and high levels of aliphatics and H from spent grains by using activated serpentine and olivine at 430–460 °C. Using absorbers at the same temperature, there are any different of oxygenation power from activated olivine > activated turpentine > alumina.[33]

Biomass fast pyrolysis yields oxygen rich hydrocarbons that are of inferior quality for transportation fuel. They contain upwards of 40 dry-weight % oxygen, whereas petroleum-based fuels contains around 1%, so these bio-oils must be upgraded to be rightfully considered an equivalent replacement.

zeolites have been shown to have high hydrogenation and deoxygenation capabilities. Zeolites were catalytic performance in the HDO process of bio-oil. Its resulted that the higher heating value (HHV) of bio-oil increased from 12 to 18 MJ/kg, the viscosity value doubled, the degree of deoxygenation increased to 77%, and the water content reduced dramatically to about one-third of that of raw bio-oil.[34]

II.3. Denitrogenation

Microalgae has high nitrogen content, commonly 20 – 40% of the N in the raw biomass. Nitrogen content would distribute into bio-oil during HTL process.[35] biocrude is related to the algal type. Liquefaction with water generates nitrogen in the form of ammonia transferred to the aqueous phase.[36] Small molecule aliphatic nitrogen compounds can be dissolved in water, while the macromolecules remain in the biocrude, such as palmitamide, hexadecanenitrile and stearonitrile, hydrodenitragenation (HDN) is converting them into hydrocarbons.[37]

Increaesed the concentration of nitrogen elements in the bio-oil used of activated carbon to treat to reduce nitrogen contents.[38] Catalytic upgrading of biocrude that had been produced via the HTL was conducted by Duan.[39] The maximum upgraded yield of 83% at 400 ^oC for 240 minutes with a 20% Pt/C catalyst. This upgraded biocrude still contained a high nitrogen content of 3.68%. The nitrogen content decreased as the amount of catalyst increased. Another trial that upgrade biocrude with lowest nitrogen content of 1.5% was conducted at 530 °C for 360 min with a 10% Pt/C catalyst.[40] Using two-stage hydrotreated upgrading, resulted N contents of 1.95% and oxygen content of 0.72%.[41]

II.4. Desulfurization

Nitrogen (N) and sulphur (S) play an important role in algae cultivation as they are important nutrients for growth. They also affect the conversion route, the product distribution, elemental and chemical composition of the end products. Bio-crude from HTL of algae produces of high N (5-8 wt%) and S (0.5-1.5 wt%) content generating lower quality biofuel and requiring upgrading.[42] There is no limitation on N content. N problematic due to possible gum or sediment formation and low thermal and storage stability of the fuel.[43]

The present of N and S in biofuel has very different roles in combustion and subsequent emissions. N in biofuel will disassociate under combustion and undergo chemical transformation to form either N_2 of NO and NOx. N_2 and NOx were highly variable and depends signifantly on engine operation conditions.[44] In contrast to N, S in the biofuel will always produce emissions that are considered to be harmful. The major S emission product is SO_2 and SO_3. S compounds have a strong tendency either in the form particles or attack to existing particles.[45] In general, at least 20 wt% of S will be present in the exhaust emissions in aerosol form.[46] Upgrading of biocrude was conducted in hydrothermal liquefaction at 450 °C and 20 min with added H_2 and catalyzed Ni-Ru/CeO_2 + H_2, the catalysts had good catalytic desulfurization effect.[47]

Hydrotreating includes hydrodemetallization for metal removal, hydrodesulfurization for S removal, hydrodenitrogenation for N removal, and hydrodeoxygenation for oxygen removal. Hydrotreating processes usually occur in the presence of catalyst, and the most traditional catalysts used for hydrotreatment are NiMo, NiW and CoMo.[48]

II.5. **Mineralization**

Lignocellulosic biomass contains inorganic element (ash) resulted in a decrease of the desired liquid product. Removal of inorganic elements from agricultural residues was investigated. Reducing the elements used by washing with water or solution of nitric or acetic acid are usually used. Washing with water was effective for removal of up to 42% of the inorganics in the biomass, whereas washing with acidic solution achieved inorganic removal higher than 90%.[49] Rice husk as the raw material was treated by washing water and acid solution.[50] Raw materials such as palm oil empty fruit bunch (EFB) have high alkali and alkaline earth metals (AAEMs) content. This problem leads to the low bio-oil yield with high char formation.[51]

III. Standard quality of fuel

Certain fuels have a certain properties for their usefulness, such as density, specific gravity, viscosity, flash point, pour point, specific heat and calorific value.

Density

This is defined as the ratio of the mass of the fuel to the volume of the fuel at a reference temperature of 15°C. Density is measured by an instrument called hydrometer. The knowledge of density is useful for quantity calculations and assessing ignition quality. The unit of density is kg/m^3.[52]

Specific gravity

This is defined as the ratio of the weight of a given volume of oil to the weight of the same volume of water at a given temperature. The density of fuel, relative to water, is called specific gravity. The specific gravity of water is defined as 1. Since specific gravity is a ratio, it has no units. The measurement of specific gravity is generally made by a hydrometer. Specific gravity is used in calculations involving weights and volumes.[54]

Viscosity

The viscosity of a fluid is a measure of its internal resistance toflow. Viscosity depends on temperature and decreases as thetemperature increases. Any numerical value for viscosity has nomeaning unless the temperature is also specified. Viscosity is measured in Stokes / Centistokes. Sometimes viscosity is also quoted in Engler, Saybolt or Redwood. Each type of oil has its own temperature - viscosity relationship. The measurement of viscosity is made with an instrument called Viscometer. Viscosity is the most important characteristic in the storage and use of fuel oil. It influences the degree of pre-heat required for handling, storage and satisfactory atomization. If the oil is too viscous, it may become difficult to pump, hard to light the burner, and tough to operate. Poor atomization may result in the formation of carbon deposits on the burner tips or on the walls.Therefore pre-heating is necessary for proper atomization. Vegetable-oil-based fuels have been attracting greater attention as a promising alternative to fossil diesel fuel in compression ignition (CI) engines.[54]

Flash Point

Flash point is the lowest temperature at which a liquid (usually a petroleum product) will form a vapor in the air near its surface that will flash.[55] The flash point of a fuel is the lowest temperature at which the fuel can be heated so that the vapour gives off flashes momentarily when an open flame is passed over it. Flash point for furnace oil is 66°C.

Pour Point

The pour point of a fuel is the lowest temperature at which it will pour or flow when cooled under prescribed conditions. It is a very rough indication of the lowest temperature at which fuel oil is readily pumpable.[56]

Specific Heat

Specific heat is the amount of kcals needed toraise the temperature of 1 kg of oil by 1°C. Theunit of specific heat is kcal/kg °C. It varies from 0.22 to 0.28 depending on the oil specific gravity. The specific heat determines how much steam or electrical energy it takes to heat oil to a desired temperature. Light oils have a low specific heat, whereas heavier oils have a higher specific heat.[57]

Calorific Value

Calorific value is amount of released energy when a known volume of gas is completely combusted.[58] The calorific value is the measurement of heat or energy produced, and is measured either as gross calorific value ornet calorific value. The difference being the latent heat of condensation of the water vapour produced during the combustion process. Gross calorific value (GCV) assumes allvapour produced during the combustion process is fully condensed. Net calorific value (NCV) assumes the water leaves with the combustion products without fully being condensed. Fuels should be compared based on the net calorific value. The calorific value of coal varies considerably depending on the ash, moisture content and the type of coal while calorific value of fuel oils are much more consistent.

IV. CONCLUSION

HTL process was successfully to degrade biomass resulted into three phases, residual solid, insulable liquid that its called bio-oil and can be upgraded into biofuel, and gaseous products. Residual solid have a high carbon content, it can be used as soil amendment, carbon sequestration, and another treatment resulted carbon fungsional, such adsorbent, capacitor, hydrogen storage. Bio-oil is containing in many type of hydrocarbon such as polimers, hydrocarbons, acids, amins and alcohols. Bio-crude produce from HTL process have undesirable properties in the oil such as low energy density, instability that leads to polymerization, high viscosity, and corrosion on contact surfaces during storage and transportation. The bio-oil is not ready to use as fuel, because of the properties is needed rightfully upgrading. Upgrading bio-oil to fuel grade is needed that increase the charge and replace the fossil oil.

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