

Hydrothermal Liquefaction Of Coconut Dregs Into Bio-Crude In Super-Critical Water Media

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ABSTRACT

Hydrothermal Liquefaction (HTL) proceeded of coconut dregs into bio-crude was attempted. Process parameters were attempted such as reaction time (2,3,4,5,6 hours), and substrate load of 0.3 – 2.5 grams. Increased in reaction time was increased degradation rates. There was decreased of the residual solid. The liquid and gaseous products were increased by increasing the reaction time. Increased the substrate load reduced the degradation rate and gaseous products, and liquid products were increased slightly, it's indicated that the residual solid was increased. In lowest substrate load of 0.3 gram there was higher degradation rate, it's mostly 50% of substrate was degraded into liquid and gaseous. Increase the substrate load the degradation rate was stagnant in about 70%, and liquid product was increased slightly, gaseous product was decreased slightly.

Keywords: coconut dregs, HTL, bio-crude, conversion

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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 CO₂ 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 carried 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 surrounding life, and secondly, get usefull materials to increase the economic value.

Commonly, fruits and vegetable wastes were treated by composting [8]. Traditional composting takes along time, but using EM4 inoculum reduced the incubation time to 20 days [9]. The powerfull ways is that they used waste to feed the black soldier fly larvae (BSFL). BSFL are highly effective in their consumption of waste, and the biological transformation of this into higher value organic oils with a variety of chemical applications [10]. BSFL was dried to supply the animal proteins. Fruits and vegetables waste were extracted into sugar juice, and than sugar juice was fermented by *Saccharomyces Cerevisiae* into ethanol [6,11-13]. The ethanol producton was less then 1 mg/ml,[6] Khandaker [12] conducted a production of bioethanol resulted less then 6%. Promon [13] conducted bioethanol production from vegetable peels and effective *cellulolytic* bacterial resulted 14.17 % ethanol. Fruits and vegetable wastes can be converted into bio-oil by pyrolysis process, the wastes must be dried in appropriate moisture content to feed to the reactor.¹⁴ Pyrolysis process needs high

temperature compared to HTL process [15]. Fruit and vegetables waste biomass converted for production of bio-briquettes fuel [16]. Fruit and vegetables waste also used as biofuel precursors [17]. More recently, Fruits and vegetable wastes were produced into bioelectricity [18,19]. Coconut dregs is one of the fruit and vegetable waste come from the coconut milk industries. Coconut dregs still contain of 12.2 – 15.9% oil [20]. Coconut dregs was fermentation to extract the oil, than the oil in-situ directly transesterification using catalysts to produce bio-diesel [21-23]. Coconut dregs can be used for several purposes, for animal feed,²⁴ to substitute of flour [25].

Coconut is widely cultivated in Asia, Oceania, Latin America and Africa was predicted a total of 55 million ton production in the year 2013. According to the study of Ng [26] coconut pulp residues contains 72.6% cellulose. Total sugars as carbohydrates were determined to have 84.5% [27]. The coconut pulp residue converted into biofuel in three steps, firstly, coconut residue pulps were alkaline delignification and enzymatic hydrolysis resulted reducing and total sugars, and then reducing sugars were fermented into ethanol or bio-fuel [28].

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 [29]. Cassava pulp converted into bio-oil via hydrothermal liquefaction, bio-oil products is not more than 15% [30]. The HTL process can able to proceed the coconut dregs into three products, such as biocrude, residual solid that rich of carbon, and gaseous.

II. EXPERIMENTAL

Materials and chemicals

Coconut pressed cake come from coconut milk industries was used as raw materials. The materials were sieved into several fraction of sizes. After that the biomass was contained into the reactor in certain weight. The moisture content of coconut pressed cake is about 80%. All solvents are analytical reagent grade provided by Merck.

Experimental procedures

Liquefaction experiments were carried out in a reactor volume of 60 ml stainless steel cylindrical, and 0.3 – 2.5 gram of dry basis of coconut dregs was contained into the reactor, water was added until the reactor is full and then the reactor was sealed properly and make sure that there is no leakage. The reactor was mounted into the furnace that the temperature can be set in certain point as the reacting temperature of 400°C. The reactor leave for several hours as the reacting time (2, 3, 4, 5 and 6 hrs). After reacting time was reached the reactor was pull out from the furnace and poured with tap water to chill and stop the reaction until at ambient temperature, and then the reactor valve was open to leave the gas out, and then the reactor was opened properly to pull out the reaction products. The solid and liquid products are separated by filtering. The solid was rinsed with same solvent and dried at 105 °C until the weight remained unchanged as residual solid product. The liquid was dried in vacuum dryer at temperature 50 °C, until weight remained unchanged as liquid products.

$$\text{Yield of bio-oil} = \text{Mass of bio-oil} / \text{mass of coconut drega} \times 100\% \quad (1)$$

$$\text{Yield of solid residue} = \text{Mass of carbon} / \text{mass of coconut dregs} \times 100\% \quad (2)$$

$$\text{Conversion rate} = 100 \text{ wt\%} - \text{yield of solid residue} \quad (3)$$

$$\text{Gaseous product} = 100\% - \text{residual solid} - \text{liquid product} \quad (4)$$

III. RESULTS AND DISCUSSION

The experimental results were shown in figures 1 and 2. The effect of substrate load and reaction time were examined in water media at 400 °C. HTL process resulted into three products such as residual solid, liquid water soluble and gaseous. Increased the reaction time increase the degradation of coconut dregs, it's showed that the residual solid was decreased slightly. The liquid and gaseous products increase slightly (Fig.1).

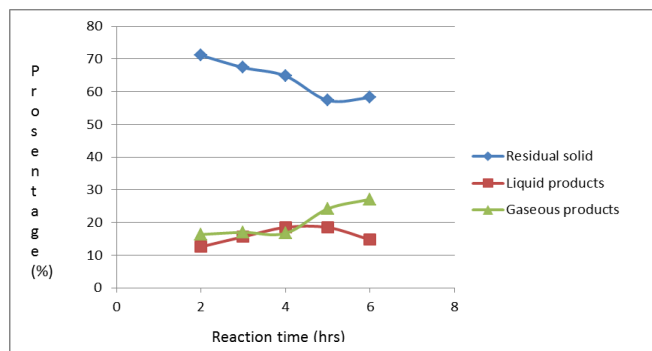


Fig.1 Solid residue, liquid and gaseous products for coconut dregs of 1.53 gram at T=400 °C For increasing reaction time (hours).

Increased the reaction time more liquid was converted into gaseous. It's meant that increase the reaction time the gasification rate more higher then the liquefaction rate. After 4 hours reaction time gaseous products were increased and liquid products were decreased.

Loading rate at 0.3 gram there was a high degradation rate, almost 50% solid degraded into liquid and gaseous. Increase of substrate load more then 0.3 gram there was stagnant of degradation rate of solid, it's around in 70%. Increase the loading rate the liquid products increased slightly, and gaseous products decreased slightly. After loading rate of 2 gram liquefaction rate was increase slightly, and gasification rate was decrease slightly. It's meant that in higher loading liquefaction rate is increased.

The bio-crude resulted from HTL process is not ready to use as fuel, because the bio-crude still have high moisture content, high density, low heating value. Bio-crude needs upgrading process that to improve it's properties. Biocrude mainly contents of organic acid, ketones and alkakes [31]. Biocrude has high content of oxygen, nitrogen and sulfur resulted harmful emission after combustion. Improving quality of biocrude needs upgrading proses that to reduce heteroatoms content.

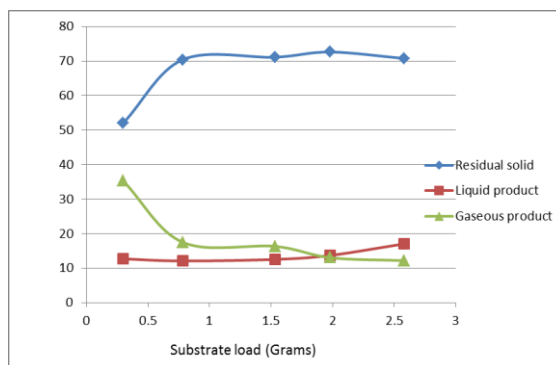


Fig. 2 Solid residue, liquid and gaseous products in reaction time of 2 hours, and temperature of 400 °C for increasing substrate load.

Hydrodeoxygenation

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 obtained from HDO are dependent on the temperature, residence time, pressure, solvent, catalyst type, and reactor configuration [32]. 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 °C [33]. 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,[34] 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 commonly used catalysts of Ni₂Fe₃, this catalyst is showed good activity in improving the bio-crude quality by increasing the heating value [35]. Several NiMo catalysts were also used for upgrading of fast pyrolysis bio-oil into products [36]. Zeolite cracking is an alternative catalysts, where HZSM-5 are used as catalysts for the deoxygenation [37]. 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 [32]. It was found that temperature up to 350 °C, the degree of deoxygenation is mainly driven by temperature, whereas the degree of denitrogenation also relies on initial H₂ pressure and temperature-pressure interaction [38]. 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 °C [39].

Denitrogenation

Nitrogen content of biocrude is related to the algal type. Liquefaction with water generates nitrogen in the form of ammonia transferred to the aqueous phase [40]. Small molecule aliphatic nitrogen compounds can be dissolved in water, while the macromolecules remain in the biocrude, such as palmitamide, hexadecanenitrile and stearonitrile, hydrodenitrogenation (HDN) is converting them into hydrocarbons [41].

Duan [42] conducted catalytic upgrading of biocrude that had been produced via the HTL. The maximum upgraded yield of 83% at 400 °C 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 [43]. Using two-stage hydrotreated upgrading, resulted N contents of 1.95% and oxygen content of 0.72% [44].

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 [45]. 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 [46].

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 N₂ or NO and NO_x. N₂ and NO_x were highly variable and depends significantly on engine operation conditions [47]. In contrast to N, S in the biofuel will always produce emissions that are considered to be harmful. The major S emission product is SO₂ and SO₃. S compounds have a strong tendency either in the form particles or attack to existing particles [48]. In general, at least 20 wt% of S will be present in the exhaust emissions in aerosol form [49]. Upgrading of biocrude was conducted in hydrothermal liquefaction at 450 °C and 20 min with added H₂ and catalyzed Ni-Ru/CeO₂ + H₂, the catalysts had good catalytic desulfurization effect [50].

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 [51].

IV. CONCLUSION

HTL process was successfully to degrade the coconut dregs resulted three phases, residual solid that was not degraded in the process, insoluble liquid that can be upgraded into biofuel, gaseous products. Increased the reaction time increase the degradation of coconut dregs, it's showed that the residual solid was decreased slightly and the liquid and gaseous products increase slightly. Loading rate at 0.3 gram there was a high degradation rate, almost 50% solid degraded into liquid and gaseous. Increase of substrate load more than 0.3 gram there was stagnant of degradation rate of solid, it's around in 70%. Increase the loading rate the liquid products increased slightly, and gaseous products decreased slightly. After loading rate of 2 gram liquefaction rate was increase slightly, and gasification rate was decrease slightly. Biocrude resulted from HTL process needs more treatment to improve the quality of biocrude. Treatment needs to reduce the heteroatoms of the biocrude into standart fuel.

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