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# Hydrothermal Liquefaction Of Fresh Kale Stalk Of Water Spinach Into Bio-Crude In Sub- And Super-Critical Water Media

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**ABSTRAK**
Hydrothermal Liquefaction (HTL) proceeded fresh kale stalk of water spinach into bio-crude was attempted. Process parameters were attempted such as temperature (350, 375 and 400 $^{o}$C). Increase the temperature reaction increased the degradation rate, liquid and gaseous products. Residual solid decreased from 16% to 4%, liquid product was increased from 45.7 to 51.7%, and gaseous product was increased from 38.3 to 44.2%. Dry basis substrate kale stalk of water spinach load of (0.3, 0.6 and 0.9 gr), increase the substrate load decreased the degradation rate. Residual solid increased from 4% to 24.7%, liquid products were decreased from 51.7 % to 48.1%, and gaseous product was decreased from 44.2 to 27.2%. Reaction time of 1,2, 3 and 4 hrs. Increase the reaction time commontly increased the degradation rate, increased the liquid and the gaseous product. Residual solid were decreased from 21.4 to 2%, liquid products increased from 44.2 to 49.6%, and gaseous products increased from 34.2 to 48.4%. The optimum procees parameters were laid on substrate of kale stalk of water spinach load of 0.3 gr, reaction time of 2 hours, and temperature of 400 $^{o}$C, the residual solid was 4%, liquid product was 51.7%, and gaseous product was 44.2%.
**Key words:** kale stalk, HTL, bio-crude, conversion

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## I. INTRODUCTION

Exploration alternative energy to substitute fossil energy was very attractive, because of the rapid shortage of fossil energy. People has a big worry by the supply of energy in the future. 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.[1]

Fruits and vegetable wastes are a biodegradable material 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.[2] 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.[3] 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.[4]

Commontly, fruits and vegetable wastes treated by composting.[5] Other ways fruits and vegetables waste were proceeded become juice, and than juice was fermented by *Saccharomyces Cerevisiae* into ethanol.[3,6,7] Fruits and vegetable wastes can be converted into bio-oil by pyrolysis process, the wastes must be dried in appropriate moisture content to feed the reactor.[8] Brunerova[9] used fruit waste biomass for production of bio-briquetts fuel. More recently, Fruits and vegetable wastes were produced bioelectricity.[10,11]

The water spinach or kakung (Ipomoea reptans Poir) is popular vegetable in Asian region. Water spinach was cultivated along the districk in each province. In Indonesia the production of water spinach around 295.556 ton in 2019,[12] but the demand is more than the number. The water spinach harvesting mode was shown in Figure 1.

**Figure 1.** Harvesting mode of water spinach[13]

After harvesting water spinach was packed in consump's pack, as shown in figure 2.

Before being cooked, the water spinach was cut into two part, the first part is part of leaf that will be consumped, and the second part is kale stalk, is deposes as waste, as shown in figure 3. The waste approximately is a haft of weight of the amound of harvest of water spinach. For example the amount of water spinach harvested in the year 2019 was about 295.556 ton, the kale stalk was about 147.778 ton. The kale stalk of water spinach is usually use as compost material, because of high moisture content.[5]

Kale stalks of water spinach is biomass waste that can be converted into bio-crude as a fuel raw material. Hydrothermal liquefaction (HTL) process can proceed a material even has high moisture content like kale stalk of water spinach.

Hydrothermal liquefaction (HTL) process is used hot compressed water as the reaction medium, and HTL technology is totally environmentally friendly. HTL can proceed any biomass with high water content directly, without drying and extraction process. Not just extracted lipid, all content of tale stalk such protein, lipid and carbohydrate will distructed in the HTL process into bio-crude. The HTL process used pressures mainly up to 250 bars and temperature up to 350 $^{o}$C.[14,15]

The main objectives of this paper is to study the effect of various operation parameters affected to the converting of the tale stalk of water spinach into bio-crude, solid residue, liquid and gaseous products.

**Figure 2.** Water spinach a consump's packs size


**Figure 3.** Part of leaf and kale stalk waste of water spinach

## II. EXPERIMENTAL

### 2.1. Materials and chemicals

Fresh kale stalk of water spinach were cut about a haft cm (Fig. 5). After that the biomass was contained into the reactor in certain weight. The moisture content of kale stalk is about 95%. All solvents are analytical reagent grade provided by Merck.

### 2.2 Experimental procedures

Liquefaction experiments were carried out in a reactor volume of 60 ml stainless steel cylindrical. 0.3, 0.6, and 0.9 dry basis of kale stalk was contained into the reactor, water was added until 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 ( 350, 375 and 400$^{o}$C) . The reactor leave for several hours as the reacting time

(1, 2,3 and 4 hrs). After reacting time was reached the reactor was pull out 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 $^{o}$C until the weight remained unchanged as residual solid product. The liquid was dried in vacuum dryer at temperature 50 $^{o}$C, until weight remained unchanged as liquid products.

Yield of bio-oil = Mass of bio-oil / mass of bryophyte x 100% (1)

Yield of solid residue = Mass of carbon / mass of bryophyte x 100% (2)

Conversion rate = 100 wt% - yield of solid residue (3)

Gaseous product= 100% - residual solid - liquid product (4)

**2.3 Products analysis**

The gas produced was leave out not to be analyzed. The soluble liquid products were analyzed using GC-MS, Agilent technologies 7890B, with DB5 Column (30 m x 0.32 mm x 0.25 µm, detector MSD 5977A, Helium (He) was used for mobile phase or carrier gas with flow rate 1 ml/min. Injector temperature was 250 $^{o}$C. The temperature of ion source and MS Quadruple were 230 $^{o}$C and 150 $^{o}$C, respectively. Extracted bio-oil from solvent of water was diluted with acetone until the end of volume 4 ml aliquot.

## III. RESULTS AND DISCUSSION

In hydrothermal liquefaction (HTL) biomass such as kale stalk of water spinach surface has been exposing to the chemical reactions, such as hydrolysis to single molecule, those molecule was separated from the solid material and dissolved to the media. By the time exposing, the solid material was degraded into soluble and gas. Resulted the residual solid has high carbon content.

Coal is formed by the decomposition of organic plant matter. In nature in this gradual transformation takes place in the course of millions years. In this process, hydrogen and oxygen contents of the material decrease while $H_2O$ and $CO_2$ are released from the molecule structure.[16] This lead to an increase the carbon content of the materials. The higher degree of the transformation is the higher of carbon content, that resulted material rich carbon (Fig.5)

**Figure 4.** Fresh kale stalk of water spinach as feed

3.1. The results of the experiment were shown in Figures 6 - 8. The effects of temperatures, substrate load and reaction times were examined in water media. HTL process with kale stalk as a raw materials have produced of liquid, gas and residual solid.

**Figure 5.** Kale stalk after process as a material rich carbon

Increase the reaction time (1, 2, 3, and 4 hrs) commontly, increased conversion of solid that indicated by reducing residual solid. The liquid products decreased slightly and gaseous products increased. The residual solid was decreased from 21.4% to 2%, it’s almost completed degradation. The liquid products were increased slightly from 44.2% to 49.6%, gaseous products were increased from 34.2% to 48.4% (Fig.6). It’s meant that increase the reaction time more liquid were converted into gaseous products. Other words gasification rate increase by increasing reaction time. Increase the reaction time, the degradation of solid also increased, it can be seen that the residual solid was decreased.

Temperature is important parameter that has high influent to the reaction rate. Degradation of biomass increases with increasing temperature, indicated that the solid residues were decreased.

Increase the temperature (350, 375 and 400 $^{o}$C) might cause increase the conversion rate, the gaseous products and also liquid products increased slightly (Fig.7). By increasing temperature 350 to 400 $^{o}$C, residual solid decreased from 21.4% to 2%, liquid products were increased from 44.2% to 49.6%, gaseous products were increased from 34.2% to 48.4%.

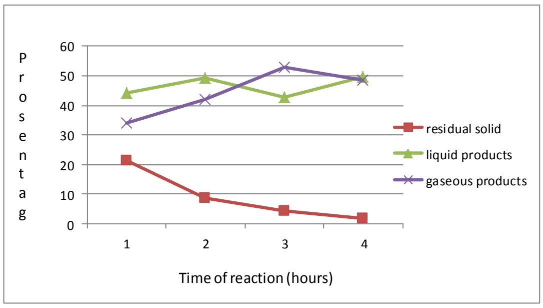


**Figure 6.** Solid residue, liquid and gaseous product, by influence of increasing reaction time.

By increase the substrate load of (0.3, 0.6 and 0.9 gr dry basis) decreased of the degradation rate, gaseous and the liquid product. The residual solid was increased from 4% to 24.7%. It's meant that degradation rate was reduced by increasing the load. liquid product was decreased slightly from 51.7% to 48.1%, and gaseous products were decreased 44.2% to 27.2% (Fig. 8). It's meant that gassification rate was reduced with increasing substrate load.

The basic reaction mechanisms of biomass liquefaction can be described: (i) depolimerization of the biomass; (ii) decomposition of the biomass monomers by cleavage, dehydration, decarboxylation and deamination; (iii) recombination of the reactive fragments through condensation, cyclization, and polymerization to form new compounds.[17] In the first step cellulose is converted into glucose, hemi-cellulose into xylose, and lignin into polyols.[18]

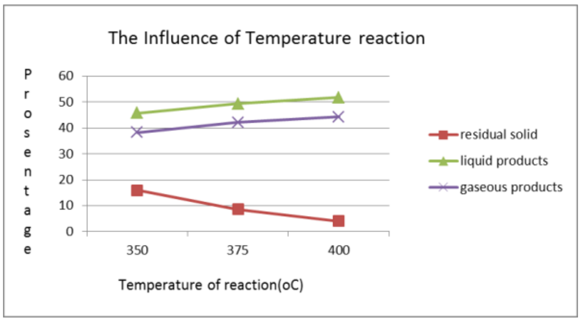


**Figure 7.** Solid residue, liquid and gaseous product, by influence of increasing temperature reaction.

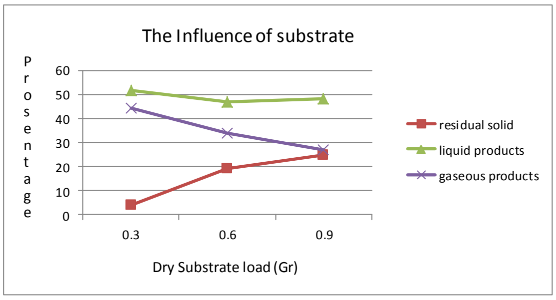


**Figure 8.** Solid residue, liquid and gaseous product, by influence of substrate load.

Before chemical reaction acts, the microcrystalline of cellulose reacts in sub- and supercritical solvents require an extra step and time to break down the cellulose crystallite. In subcritical water, the crystallite is hydrolyzed at the surface region without swelling or dissolving. Therefore, the overall conversion rate of microcrystalline cellulose is slow, and there is no cellulose crystal formed in the residue. In contrast, in near-critical and super-critical water, the crystallite can swell or dissolve around the surface region to form amorphous-like cellulose molecules. These molecules are inactive; therefore, they can be easily hydrolyzed to celluloses and cellooligosaccharides. Some of the hydrolysate can pass from the polymer phase to the water phase by cleavage of their hydrogen-bond networks.[19]

In the first step of reaction hydrolysis, dehydration and hydration were take places, celluose was converted into glucose and then into carboxylic acid in strong alkalines. In weak alkaline glucose converted into carboxylic acid and 5-hydroxymethyl furfurol (5-HMF). In medium alkaline both reaction pathways take places.[20] In acidic pathway 5-HMF further converted into formic acid and levulinic acid by hydration reaction, further dehydration reaction into 1,2,4 benzentriol.[21]

In the whole process, the substances of biomass are first hydrolyzed to small molecul compounds, then further reaction of repolimerization, decomposition and condensation of the intermediates from the different phase may be favored with the increment of reaction temperature and residence time.[22] Carbohydrate is hydrolyzed to produce reduced sugar and non-reduced sugar. Glucose itself reversibly isomerizes into fructose, this is an important reaction since a number studies have confirmed that fructose is more reactive than glucose.[22]

Pedersen[23] made overall reaction system for the formation of biocrude from lignocellulosic material macromolecules. Macromolecules were hydrolyzed into monomers. Further reaction involves reaction formation $C_{1-4}$ compounds through retro aldol reaction, and $C_{5-6}$ compounds formation through dehydration reaction. The reactive fragments still continoue reaction into bio-oil through condensation to form ketones and derivatives. Through reaction of dehydration to form oxygenated aromatic derivatives. The last reaction was gasification to form gaseous products.

Increase the reaction time increased the degradation rate, liquid and gaseous products increased slightly. Increase the temperature increased the liquid products, and increased degradation rate of solid. It was similar to the HTL that microalgae as raw material.[24] Increased reaction time decreased residual solid, and liquid and gaseous products were increased slightly. Increase the substrate load decreased the degradation rate, liquid and gaseous products.

a. GCMS analysis

The GCMS results are (Fig.9 and Table 1), the compounds resulted from the degradation of kale stalk was dominated by n-Hexadecanoic acid

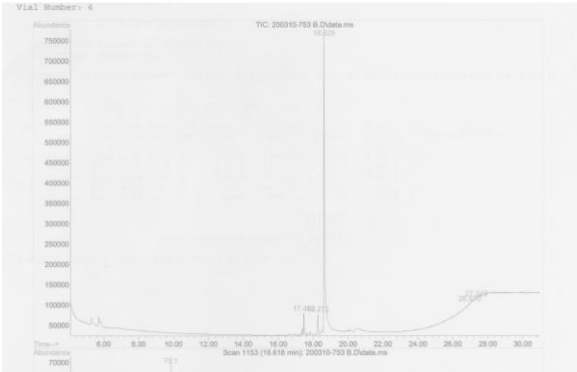

**Figure 9**. GCMS monograph of liquid products of kale stalk

**Table 1.** Typical composition of liquid products.

| Peak | R.T (min) | Area | Compounds | % of total |
|---|---|---|---|---|
| 1. | 17.469 | 1332905 | 2-Pentadecanone,6,10,14-trimethyl | 4.64 |
| 2. | 18.272 | 1386759 | Hexadecanoic acid, methyl ester | 4.83 |
| 3. | 18.631 | 25724552 | n-Hexadecanoic acid, methyl ester | 89.53 |
| 4. | 27.974 | 286461 | 1,1,1,3,5,5,5,-Heptamathyltrisiloxane | 1.0 |
| | | | Total | 100 |

We can trace the possibilities of the degradation reactions where n-Hexadecanoic acid come from. According to Pedersen,[23] firstly, cellulose is hydrolyzed become glucose, and then glucose was further reactions into reactive compound. Reactive compounds were further reaction into bigger molecule and repolymerization

Smaller molecules were further degradation become gaseous like $H_2$, $CO$,$CO_2$ and methan. Bigger molecule like acids, ketones polimers were doing continuous reaction along the prosess.

The reactive compound still take a chemical reaction, even the bio-crude have been separated in filtering the reaction still occurs, stable chemical reaction will take several minutes.

Stable biocrude consisted of a complex mixture of esters, aldehydes, ketones, alcohols, phenols, acids, cyclic compounds, acetates, ethers, and furans.[25]

## IV. CONCLUSION

Hydrothermal liquefaction process can convert the kale stalk to residual solid, liquid and gaseous products. Liquid product is called bio-crude or bio-oil as a fuel raw material. Increase the reaction time of (1, 2,3 and 4 hrs) commontly, conversion of solid and gaseous products were increased, but the liquid products were decreased slightly. Increase the substrate load of (0.3, 0.6 and 0.9 gr) decreased of the degradation rate and gaseous products, and the liquid product was inceeased. Increase the temperature (350, 375, and 400 $^oC$) might cause solid increase the conversion rate, the gaseous products and also liquid products increased slightly. The optimum operation parameter of hydrothermal liquefaction was come from substrate kale stalk of 0.2 gram, temperature of 400 $^oC$, and reaction time of 2 hours, resulted solid residue 8%, liquid product 49%, and gaseous product 43%.

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