The effect of process water recycle on hydrothermal treatment of yard long bean (Vigna unguiculata ssp. sesquipedalis) and water spinach (Ipomoea reptans) seeds

D Kurniasari¹, A T Yuliansyah² and C W Purnomo*²

¹ Magister of System Engineering, Faculty of Engineering, Gadjah Mada University
² Department of Chemical Engineering, Engineering Faculty, Gadjah Mada University

* Email: chandra.purnomo@ugm.ac.id

Abstract. Hydrothermal treatment is one of thermal biomass conversion method that the solid product can be used as fuel. The main problem of hydrothermal system is the liquid product that usually become waste. The water requirements of hydrothermal treatment need to be assessed to determine commercial feasibility. This research aims to study the influence of reusing liquid product to become process waster in hydrothermal treatment of yard long bean and water spinach seed with temperature variation of 180, 200 and 220 °C, biomass and water ratio of 1:5, and residence time of 40 minutes. Solid product was characterized in terms of mass yield and heating value (HHV). It is found that the solid yield value increased 8% from the first to the sixth process using recycle water. The biggest HHV of solid product was the hydrothermal process with temperature of 220°C using the 5th recycle liquid at 5499 cal/g for water spinach seed and 5466 cal/g for long bean seed.

Keyword: biomass seeds, water recycle, hydrothermal treatment.

1. Introduction:
Biomass is an abundant renewable energy source in nature and it is considered one of the most promising alternatives to fossil fuels for the production of bio-fuels. One of the large available biomass in Indonesia has been not widely studied is vegetable seeds such as yard long bean (Vigna unguiculata ssp. sesquipedalis) and water spinach (Ipomoea reptans) seeds. The statistical data of Indonesian Agriculture show that the amount of yard long bean production was 313 tons, and 3980 ton for water spinach seed in 2017 [1]. The seed industry will sell the seeds that pass the selection section. In the selection process, at about 10% seed will not pass the quality control and become solid waste. Since seed is hard and have strong mechanical integrity it is difficult to be decomposed and recycle. By hydrothermal carbonization (HTC), biomass could be converted into a solid fuel, liquid and condensat [2].

Usually, hydrothermal treatment processing uses temperature from 180 to 320°C in suspension with pressurized water for a period time [3]. The aqueous products contain various sugars, organic acids, and furfurals and can be potential feed for valuable chemical recovery. Another studies report that process water from hydrothermal treatment biomass contained fenol, oligomer glucose, alcohol and organic acid [4]. The process water of hydrothermal treatment is an essential, a large demand for process water can be minimized by recycle. Recycling process water can reduce wastewater treatment costs, since it has to be treated before discharges into the environment [5]. Previous reports were studied the effect of
recycle process water of hydrothermal of poplar wood [6], municipal green waste (MGW), and orange pomace [7]. However, these studies still use common solid waste and did not consider the effect of recycling water to the alteration of solid product properties such as heating values.

In this study, the effect of process water recycle from hydrothermal treatment was studied using water spinach seed and ipomoea sp seed with temperature variation of 180, 200, 220ºC with biomass and water ratio of 1:5, residence time of 40 minutes and procedure was repeated ten times at 180ºC, 200ºC and nine times at 220ºC. The hydrochar was analyzed in terms of mass yield and heating value (HHV).

2. Material and methods

2.1 Material

The long bean (Vigna unguiculata ssp. sesquipedalis) and water spinach (Ipomoea reptans) seeds were collected from a seed industry (East West Seed Indonesia) in Purwakarta, West Java, Indonesia. The seed were collected from off spec. portion (rejected seed) and characterized for lignocellulosic content and shown in Table 1.

| Seed variety      | Cellulose, %wt. | Hemicellulose, %wt. | Lignin, %wt. |
|-------------------|-----------------|---------------------|--------------|
| Yard long bean (RKP) | 18.1            | 35.1                | 7.4          |
| Water spinach (RBK)  | 29.5            | 30.5                | 10.2         |

2.2 Experimental procedure

Hydrothermal treatment process were conducted in 2L batch type autoclave reactor with a shaking system, temperature controller and pressure control. For each of the intial runs, a mixture of seed and demineralized water was loaded into the glass liner with a mass ratio of 1:5 of biomass:water (100 gr biomass : 500 mL water) and maximum temperature was set on 180, 200 or 220ºC. The residence time during processing time was forty minutes and then reactor was naturally cooled and after that the solid product was collected by filtration. The hydrothermal reactor scheme is provided in Figure 1.

Note:
1. Chasis
2. On or Off switch
3. Temperature controller
4. Heater Switch
5. Heater Indicator
6. Motor Indicator
7. Alarm
8. Power Indicator
9. Reactor
10. Reactor switch
11. Stirrer
12. Pressure gauge
13. Pressure valve
14. Motor shaker

Figure 1. Hydrothermal reactor scheme

The solid products was dried in oven with temperature of 180ºC for three hours. The hydrochar was analyzed to obtain heating value and the liquid products was measured for its pH using Hanna.
instrument. Some liquid by the volume of 250 mL was separated and mixed with deionized water to become 500 mL of liquid mixture and then used for the next hydrothermal batch. The solid yield can be calculated using the following equation

$$Y (%) = \frac{W_{db\ Product}}{W_{db\ feed}} \times 100\%$$ \hspace{1cm} (1)

where, Y is solid yield (%) and Wdb is mass of dried solid basis in grams.

For ease of identification the sample code for long bean is RKPx and for water spinach is RBKx with x is the recycle time of the process water, while for the first process using all fresh water is x=0. For example, the data of RKP3 means the hydrothermal process of yard long bean seed using the third recycle of process water.

3. Results and Discussion

Hydrothermal treatment is a process of thermal degradation of solid to form gases, liquids and solid products. In addition, the thermal degradation can decompose long chain molecules into simple structures with some of these molecules are dissolved into liquid and dispersed into gases and residues [8]. Commonly, the water demand for hydrothermal process is always use clean water in every batch. This can cause a huge quantity of wastewater since the water requirement in every batch is at about 5 times larger than the solid. In this study, hydrothermal process water is recycled at around 10 times.

The first batch of liquid product is collected and mixed with fresh water (1:1) and reused for the second batch and so on. In every batch the seed is always fresh only the water is half recycled. The solid yield of the seeds hydrothermally treated with water recycle is shown in Figure 1 and 2. In general, the yield of solid for RBK is higher than RKP this because the higher content of cellulose and lignin in water spinach seed that will contribute to the char production.

The solid products from long bean seeds increases from the first to the sixth recycle. Meanwhile for the other seed, the increase in solid products occured until the third recycle. After the increase, the solid yields are mostly decrease by the recycling progression. The yield of cowpea seeds with a temperature of 180°C increased from the first recycle process by 53.42% to 62.08% in the sixth recycle and then remain steady to the end of recycle. This increase of solid product is caused by compounds accumulation in the hydrothermal treatment process water from the previous processes. This results was confirmed by Uddin et al. [9] which shows that the optimization of the recycle of process water was very important because biomass pretreatment could be influenced by the presence of organic and inorganic materials remaining in the liquid product. An increase in the mass of solids could be generated from the deposition of compounds such as dissolved sugar from the decomposition of hemicellulose and cellulose that came out during the initial hydrothermal process.

After experiencing an increase, most of the solid yields are decrease in the later recycle. The hydrochar solids of water spinach with treatment temperature of 200°C has a peak at 61.56% in sixth recycle and then decrease to 55.46% in the last run. Meanwhile, the hydrochar yield of long bean in the same temperature has an optimum level in the third recycle at 55.48% and decrease to 47.76% in the last process. The decrease in solid yield could be due to the increase of pH in the hydrothermal solution by the progressing of the recycle sequence. The increase of pH will accelerate the solid decomposition and catalyze the compound cracking. Thus, somehow there is a kind of optimum recycling step for obtaining the solid yield.

In Heidari et al. [10] study, by recycling hydrothermal process water it had a positive effect on hydrochar yield value, the yield increased after the first recycle was 10.26%, while, the second recycle the increase in yield value was only 1.65% from the first recycle. On the other hand, Tercero et al. [11] stated that the amount of recycled water process carried out has not significantly affected the increase in hydrochar yield, but the yield of hydrochar value was significantly affected by temperature. Other
reported that the decrease in hydrochar was caused by the competition reaction of decomposition and depolymerisation of cellulose and hemicellulose content [12]. In addition, hemicellulose compounds were almost completely hydrolyzed at a temperature of 180ºC while lignin was hydrolyzed at 200ºC and cellulose was not hydrolyzed at temperatures below 220ºC. Lignin is a lignocellulose compound which is very difficult to be degraded since it has a stable phenolic structure that allows it to resist decomposition into liquids and gas fractions [13].

According to Kumar [14] hydrolysis occurred because of the formation of hydronium acid ions (H₃O⁺) and alkaline hydroxide ions (OH⁻) derived from ionization of water as reactants. The higher the reaction temperature used, the higher the ion dissolved in the water.

![Figure 2. Yield of hydrochar products from water spinach seeds](image1)

![Figure 3. Yield of hydrochar products from yard long bean seeds](image2)

In this study, HHV was analyzed for char at early, middle and end of recycle sequence as shown in Figure 4 and 5. In general, the solid product of water spinach seed has a higher heating value by the increase of temperature, with the highest value of 5499.0 cal/g at the 5th recycle, but slightly reduced at the last recycle. Whereas the heating value at 200ºC increased from 4807.7 cal/g on the first recycle to 5284.7 cal/g fifth recycle and slightly increasing at the end step. The similar trend also happened to the HHV of long bean chars with the highest HHV is for HTC 220 at 5465.6 cal/g.
The increasing of HHV at the middle of recycle number has a similar correlation with the solid yield. Thus, it can be said that the optimum solid product as a solid fuel with high yield and calorific value can be reached by the fifth recycle of process water.

**Figure 4.** Higher heating value of hydrochar from water spinach seeds

**Figure 5.** Higher heating value of hydrochar from yard long bean seeds

The energy content of hydrochar was influenced by water, ash, volatile and fixed carbon content. Thermal decomposition process or devolatization which was influenced by increase of the HTC temperature will remove the volatile content and leave the ash and carbon causing creating solid with high calorific value [15].

Uddin et al. [9] stated that the recycled water gives an influence on increasing the heating value of about 4% increased from the initial process which could be due to the content of organic acids such as acetic acid produced from previous decomposition. More acidic solution will fasten the decomposition process and removal of volatile content thus increase the heating value. The liquid products pH for selected sample is provided in Table 2.

**Table 2.** pH of some liquid product with number of recycle process at 220°C

| Seeds | Liquid pH of number of recycle |
|-------|-------------------------------|
|       | 1    | 5    | 7    | 9    |
| RBK   | 4.2  | 4.1  | 4.0  | 4.2  |
| RKP   | 4.6  | 4.2  | 4.3  | 4.5  |
Heidari et al. [10] stated that the amount of acid components formed in process water was due to decomposition and depolymerization reactions of biomass when the temperature rises. The solid mass increased when pH was low, based on the results obtained the highest acidity level occurred in bio-oil from both seeds. Reza et al. [16] stated that liquid will increase the acidity with the same time as the sugar content also increases in liquid products. Sugar contents can increase the solid yield through condensation and carbonization [17]. The progression of water recycle lead to the saturation with the balance of acid compounds, as demonstrated by Biller et al. [18] where the pH had increased from 7.6 in the initial recycle of process water to pH 10 at the final recycle.

4. Conclusion

Process water recycles of hydrothermal treatment could give effect to increasing solid mass yield as well as heating value of the solid product. This effect is mainly due to the content inside the recycled liquid by the combination of acidic and sugar compounds. The optimum recycle has to be determined for each waste in order to get the highest solid yield and calorific value of the solid product.

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