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The Effect of Biomass-Water Ratio on Bio-crude Oil Production from *Botryococcus braunii* using Hydrothermal Liquefaction Process

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ABSTRACT

The increasing demand of energy in Indonesia has led to the urgency to conduct research and development in renewable energy. Biomass is one of the largest renewable energy sources in Indonesia. For biomass to energy conversion, hydrothermal liquefaction (HTL) has been considered as one of the potential methods where biomass is processed using subcritical water to produce bio-oil, aqueous phase, gas, and solid product. In this research, the effect of biomass-water ratio on hydrothermal liquefaction (HTL) process of microalgae Botryococcus braunii has been investigated. The HTL was conducted using biomass/water ratio 1:10, 1:20 and 1:30 with various holding time for each ratio. The product was bio-crude oil with similar characteristics to crude oil. Experimental results showed that biomass-water ratio affected the distribution of bio-crude oil yields. For biomass-water ratio of 1:10 and 1:20, it was found that bio-crude oil yields reached a maximum at 20 minutes, while the highest bio-crude oil yield of 4% was obtained at biomass-water ratio of 1:10. On the other hand, with biomass-water ratio of 1:30, bio-crude oil yield was continuously increasing with holding time until it reached the maximum yield of 4% at 40 minutes of holding time. The aforementioned results indicated that the highest bio-crude oil yield was obtained using biomass-water ratio 1:10 and 20 minutes of HTL processing time.

Keywords: bio-crude oil; biomass-water ratio; Botryococcus braunii; hydrothermal liquefaction; microalgae

ABSTRAK

Peningkatan permintaan energi telah mendorong kesadaran pengembangan energi terbarukan di Indonesia. Biomassa adalah salah satu sumber bahan baku energi terbarukan yang melimpah di Indonesia. Proses konversi biomassa menjadi energi dapat dilakukan dengan proses Hydrothermal Liquefaction (HTL). *Metode ini telah dianggap sebagai salah satu metode yang menjanjikan dalam mengolah biomassa. Dalam proses ini, biomassa diproses menggunakan air subkritis untuk menghasilkan bio-oil, fase larut air, gas, dan produk padat. Dalam penelitian ini, dipelajari pengaruh rasio biomassa-air pada proses HTL terhadap mikroalga* Botryococcus braunii. *Pengaruh rasio biomassa / air dipelajari dengan variasi 1:10, 1:20 dan 1:30 pada berbagai waktu pemrosesan* (holding time) *untuk masing-masing rasio. Produk yang dihasilkan adalah minyak* bio-crude oil *yang memiliki kemiripan sifat dengan minyak mentah. Hasil eksperimen menunjukkan bahwa rasio biomassa-air memiliki pengaruh pada distribusi hasil* bio-crude oil. *Untuk rasio biomassa-air 1:10 dan 1:20, hasil percobaan menunjukkan bahwa puncak* yield *dari* bio-crude oil *nilai maksimum diperoleh pada waktu pemrosesan 20 menit dengan nilai* yield *dari* bio-crude oil *maksimum 4% pada rasio biomassa-air 1:10. Di lain pihak, hasil percobaan dengan rasio biomassa-air 1:30 menunjukkan tren* yield *yang meningkat terus-menerus dan mencapai nilai* yield *tertinggi sebesar 4% dengan waktu pemrosesan 40 menit. Hasil*

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percobaan ini menunjukkan bahwa yield *dari* bio-crude oil *tertinggi dengan proses HTL diperoleh pada rasio biomassa-air 1:10 dengan waktu pemrosesan selama 20 menit.*

Kata kunci: bio-crude oil; Botryococcus braunii; hydrothermal liquefaction; *jumlah air; mikroalga*

1. Introduction

Due to rapid population growth, Indonesia has to face imminent threat on national energy security. Recent data shows that population in Indonesia is expected to grow up to 305.62 million in 2035 (BPS, 2013). Increasing population will certainly affect energy demand in the future. In 2019, it is predicted that final energy demand in Indonesia is around 1,019 million BOE and will keep rising up to 4,569 million BOE in 2050 (BPPT, 2018). On the other hand, Indonesia's fossil fuel reserves are depleting in a considerable rate (BP, 2018). By using business-as-usual assumption, it is predicted that oil and coal reserve in Indonesia will be depleted in 10 and 60 years, respectively (BP, 2017). Therefore, it is mandatory for Indonesia to utilize other resources as renewable resources for energy. The situation is actually in-line with government's decree which plans to increase renewable energy proportion in national energy mix (Mujiyanto and Ties, 2013).

Biomass is undoubtedly one of the promising renewable energy resources for Indonesia. This is due to the fact that Indonesia has diverse biomass feedstock, including microalgae biomass (Phang et al., 2016). Microalgae has attracted a great deal of attention due to its vast advantages, including more efficient photosynthesis, less area consumption for cultivation, many important chemicals (carbohydrate, lipid, protein and antioxidant) content, and suitability for water treatment (for some species) (Valdez et al., 2014; Susilaningsih et al., 2014).

In order to harness microalgae potential to become renewable energy resources, hydrothermal liquefaction (HTL) is considered as one of the potential thermochemical processess to convert biomass into bio-crude oil (Huber et al., 2006). In HTL process, biomass will be contacted with subcritical water to produce bio-crude oil, aqueous phase, solid and gas (Valdez et al., 2014). Bio-crude oil is blackish compound that contains various hydrocarbon (Huber et al., 2006) and considered similar with petroleum oil in terms of straight-chain hydrocarbon content (Gai et al., 2012). Production of bio-crude oil using HTL offers several advantages to be compared to production via pyrolysis, including higher calorific value and removal of drying process (Gollakota et al., 2016). However, previous researches by Biswas et al. (2017) and Savage (2017) suggested that high-lipid content of biomass is more suitable for HTL.

Botryococcus braunii is one of the microalgae which contains relatively higher lipid content (Gollakota et al., 2016). Moreover, the potential use of *Botryococcus braunii* for HTL feedstock is still scarcely reported in the present literatures (Sari et al., 2013). Several factors were reported to affect HTL product yield, including feedstock composition (Vardon, et al., 2011), temperature (Valdez et al., 2014), temperature and water loading (Valdez et al., 2012). Many works regarding HTL reported the influence of temperature towards product yield (Caprariis et al., 2017; Gollakota et al., 2016; Dimitriadis and Bezergianni, 2017). However, water also has essential role to conduct the HTL process (Peterson et al., 2008). In previous researches, Gai et al. (2012) and Thiruvenkadam et al. (2015) found that reactions occurred during HTL process were started after carbohydrate, protein and lipid were hydrolized into its monomers. Different amount of water will likely affect hydrolysis reaction (Kang et al., 2018). From this standpoint, it is clear that the amount of water fed to the reactor, which can be represented as water-biomass ratio is necessary to be studied. Therefore, this current research aimed to study the effect of biomass-water ratio on product yield of HTL process.

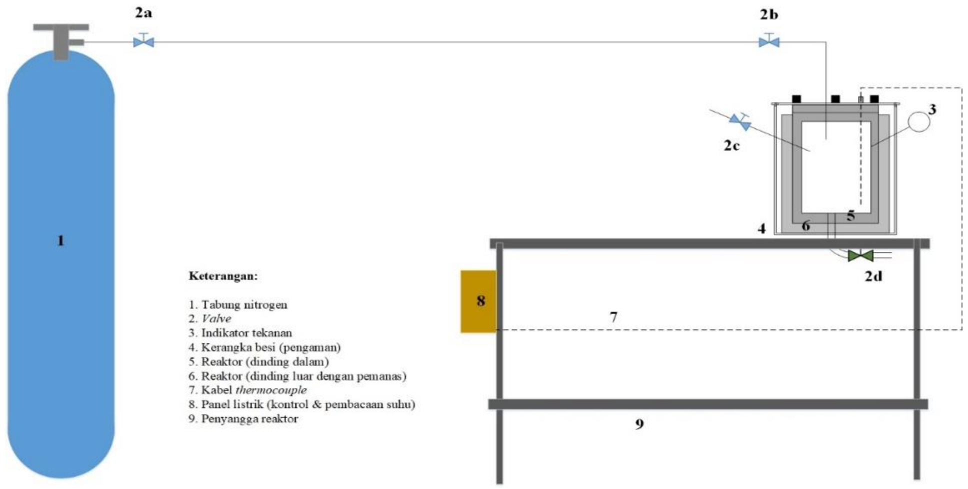

Figure 1. Apparatus of Hydrothermal Liquefaction Process

2. Research Methodology

2.1 Materials

The materials used in this research were *Botryococcus braunii* microalgae from Balai Budidaya Air Payau (BBAP) Situbondo East Java, nitrogen gas (technical grade) from PT Samator Gas, and n-hexane (technical grade) from Merck.

2.2 Research Procedure

The schematic diagram of HTL process is depicted in Figure 1. Microalgae and water was placed into the reactor, which was then operated at 250°C and 40 bar as initial pressure. Upon completing the reaction, several separation steps were performed to purify the bio-crude oil.

Bio-crude oil was extracted from the liquid mixture by using n-hexane as solvent. After solvent extraction process, there were two distinct phase, which were non-polar (n-hexane & bio-crude oil phase) and polar (aqueous phase). Separation of n-hexane/bio-crude oil phase from aqueous phase was done by decantation. Dissolved bio-crude oil was separated from the solvent via distillation. The distillation of bio-crude oil from n-hexane was conducted for 2 hours at 80°C. The elevated temperature, which was set to be much higher than n-hexane boiling point, and relatively long distillation time had ensured that remaining n-hexane in bio-crude oil was negligible. Aqueous phase was then filtered to obtained solid product. Prior to measuring the weight, solid product was then dried using oven. In this research, aqueous phase was measured by weighting solid that left after evaporating water from aqueous phase. In this step, temperature was set slightly above boiling point of water. This step led to good elimination of any trace of n-hexane which was carried from the decantation step.

After the dried-solid was weighted, it was burned in the furnace at 700°C to determine its ash content. Gas production (m_{gas}) was calculated by using Eq. (1), while microalgae production in term of $m_{microalgae\ (organic)}$ was obtained from Eq. 2. Gravimetric analysis was used in order to obtain the value of ash and moisture content of the *Botryococcus braunii*.

$$m_{gas} = m_{microalgae\ (organic)} - m_{bio-oil} - m_{AP} - m_{solid} \quad (1)$$

$$m_{microalgae\ (organic)} = m_{microalgae} - m_{ash} - m_{moisture} \quad (2)$$

2.3 Data Analysis

Yield for each product was calculated from weight data for all products. The calculation was based on Eq (3)-(6).

$$Y_{bio-crude\ oil} = \frac{m_{bio-crude\ oil}}{m_{microalgae\ (organic)}} x100\% \quad (3)$$

$$Y_{aqueous\ phase} = \frac{m_{aqueous\ phase}}{m_{microalgae\ (organic)}} x100\% \quad (4)$$

$$Y_{solid} = \frac{m_{solid}}{m_{microalgae\ (organic)}} x100\% \quad (5)$$

$$Y_{solid} = \frac{m_{gas}}{m_{organik\ alga}} x100\% \quad (6)$$

In Eq. (3)-(6) Y is product yield. Analysis was also performed to characterize *Botryoccus braunii* raw material in terms of carbohydrate, lipid, and protein. Gas Chromatography- Mass Spectrofotometer (GCMS) was used to identify product composition

3. Results and Discussion

The first part of the work focused on the influence of biomass-water ratio to the yields of various products as a function of processing time. Fig. 2 shows the effect of biomass-water ratio on bio-crude oil yield. According to Fig. 2, it was generally observed that bio-crude oil yield was increasing in the early holding time followed by the steady decrease with longer holding time. This phenomenon indicated the presence of other reaction which consumed produced bio-crude oil. During HTL process, various reactions, such as hydrolysis, decarboxylation, deamination, polymerization, Maillard reactions, etc. occurred to produce bio-crude oil, aqueous phase, solid and gas product (Gai et al., 2012; Thiruvenkadam et al., 2014). It was possible that each of those products were interconnected. Therefore, the decrease in bio-crude yield could be caused by further conversion into aqueous phase and gas. It was also found that biomass-water ratio 1:10 produced the highest bio-crude oil yield, which was around 4% at holding time of 20 min. The yield for biomass-water ratio of 1:20 was fluctuated between 1-2% for various holding time. On the contrary, the experiment with biomass-water ratio of 1:30 showed different trend with continuous increase of bio-crude oil yield with holding time reaching the peak at about 4% with 40 minutes of holding time.

The volcano shape plot of bio-crude oil production might be attributed to the presence of side reaction which consumed produced bio-crude oil, bio-crude oil decreased which was probably caused by further conversion into aqueous phase and gas product. However, based on Fig. 2, the trend is not always consistent as the highest biomass-water ratio gave continuous increase of yield with the increase of holding time. This inconsistency is often found when dealing with the processing of natural resources which has large variation. Previous studies regarding the effect of the biomass-water ratio gave relatively different results. In Valdez et al. (2012) for example, it was showed that the increase of biomass-water ratio gave higher bio-oil yield. On the other hand, Jena et al. (2011) and Xu and Savage (2017) reported that the variation of the ratio of biomass-water had no effect on bio-crude oil yield. According to Valdez et al. (2012) these different results were caused by the use of different microalgae, i.e. in Valdez et al. (2012) the experiments used *Nannochloropsis sp*. while Jena, et al. (2011) used *Spirulina platensis*.

However, unclear trend of water-biomass ratio variation was also investigated by Xu and Savage (2017). Researchers observed that varying water loading from 19.5% to 41.4% did not give consistent results. In this current study, unclear trend was caused by biomass-water 1:30 which produced rising yield trend after 30 minutes of reaction. This phenomenon might be caused by further cell disruption in 1:30 ratio. During HTL, microalgae cell was partially or fully destroyed due to process condition (Alba et al., 2012). It was possible that for biomass-water ratio of 1:30, microalgae cell was more hydrolyzed compare to other ratios of 1:10 and 1:20. This could lead the cell to be relatively weaker than the ratios of 1:10 and 1:20, which which made it ruptured and released more materials to produce bio-crude oil.

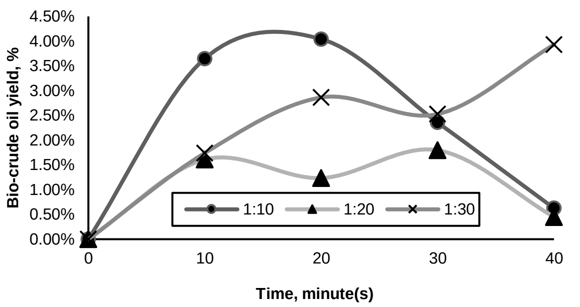

Figure 2. Correlation between biomass-water ratio and bio-crude oil yield

Fig. 3 shows the yield of aqueous phase as a function of holding time. It appears that the aqueous phase yield varies with biomass-water ratio and residence time. The aqueous phase yield for biomass-water ratio of 1:10 and 1:30 were similar, in the sense that there was an increase of yield in the first 10 minutes followed by steady decrease up to 40 minutes. The trend for biomass-water ratio 1:20 is somewhat different as it oscillates up to 40 minutes. This trend was also observed for bio-crude oil and solid, although in different magnitude. The patterns suggested that at 20 minutes, gas production was dominant. Gas was formed through several reactions including decarboxylation, deamination (Gai et al., 2012), and other reactions which produced short-chain hydrocarbons. It was possible that biomass-water ratio was the determining condition for gas formation reactions. As optimum condition had passed, rising trend for bio-crude oil and aqueous phase took place, which confirmed previous researches that showed gas formation from bio-crude oil and aqueous phase (Valdez et al., 2014; Vo et al., 2016). Correlation pathway between HTL products were previously explored by several researchers (Valdez et al., 2014; Vo et al., 2016). Those investigations validated that raw material was initially converted to bio-crude oil and aqueous phase, which later degraded to form gas products. In addition, conversion of bio-crude into aqueous phase and vice versapossibly happened in this current research.

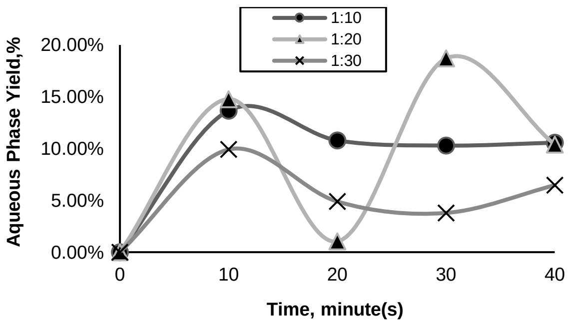

Figure 3. Correlation between biomass-water ratio and aqueous phase yield

Figs. 4 and 5 described solid and gas yield as function of biomass-water ratio. From Fig. 4, it was known that biomass:water ratio of 1:30 gives the lowest solid yield that indicates more solid is hydrolysed or converted into other products. In addition, the ratio of 1:30 has the highest gas yield and the lowest bio-oil and aqueous phase yield. It was due to the conversion of bio-oil and aqueous phase into gas which increased with higher amount of water. Unique tendency of solid yield increase were pictured after 20 minutes residence time. This indicated the presence of other reaction pathway that converted some products into long-chain hydrocarbons which later were also collected as solid product. Thiruvenkadam et al. (2015) explained that solid product of HTL was possibly produced via polymerization of furfural derivatives and melanoidin by Maillard reaction. Furfural derivatives were the product of carbohydrate decomposition, while Maillard reaction took place due to the presence of glucose and amino acid from hydrolysis of raw material (Thiruvenkadam et al., 2015).

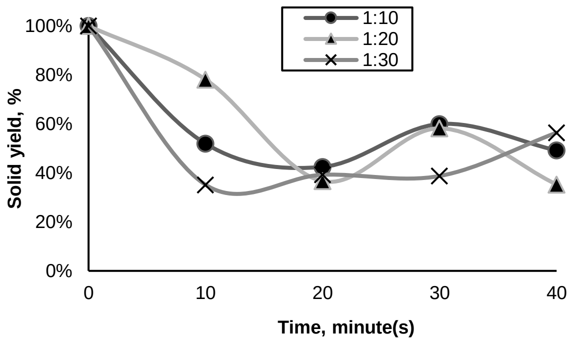

Figure 4. Correlation between biomass-water ratio and solid yield

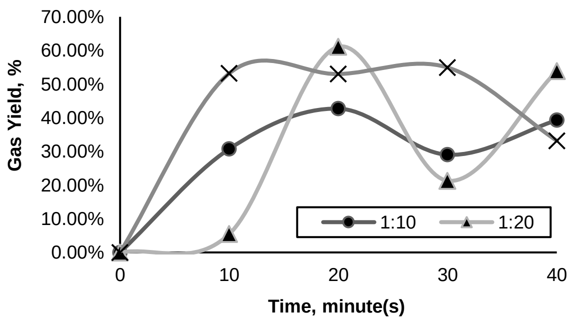

Figure 5. Correlation between biomass-water ratio and gas yield

Fig. 5 showed a consistent trend to those mentioned in Fig. 2 and 3. In Fig. 2 and 3, it was suspected that bio-crude oil and aqueous phase decreased to form other products, which more likely to be identified as gas product. In Fig. 5, it was seen that gas yield increased and became relatively steady as the holding time proceeded. It implied that gas was constantly produced from other products and was not further converted into other product. Distinct spiking trend observed in minute 20 corresponds to optimum condition for gas producing reaction as suspected to happen in oscillating trend of 1:20 ratio in Fig. 2-4.

By comparing product yields as presented in Figs. 2-5, it was revealed that bio-crude oil yield was the lowest among all product yields of *Botryococcus braunii* extraction. This was probably caused by *Botryococcus braunii* natural composition. Analysis of carbohydrate, lipid, and protein revealed that lipid content in the biomass was very small (Table 1). On the other hand, it was mentioned also that lipid is the main precursor of bio-crude oil in HTL process (Gai et al., 2012).

Table 1. Composition of *Botryococcus braunii*

Parameter	Weight fraction, %
Carbohydrate	56,81
Lipid	1,16
Protein	42,04

4. Conclusions

Experimental evidence presented in the current study indicates that biomass-water ratio affects the yields of HTL process. The biomass-water ratio variable affected the bio-oil yield, aqueous phase yield, and solid yield as well. However, the trends related to yields and ratios were not consistent. The highest bio-crude oil yield (4,04%) was acquired in biomass:water ratio 1:10 and 20 minutes. Compared to other product yield, bio-crude oil yield was the lowest due to the lack of lipid content in *Botryococcus braunii*. There was also indication that the reduction of bio-crude oil yield after a certain duration of residence time was due to further conversion on bio-crude oil into other products.

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