Solvent Extraction and Continuous Hydrothermal Liquefaction of Native Microalgae for Biofuel Production

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Abstract

Earthquake (March 2011) followed by a tsunami caused severe damage to the coastal areas in the Tohoku region, Northeast Japan, and consequently, many non-arable emerges. In this study, native microalgae cultivated in open raceway ponds at Minamisoma, Fukushima prefecture, Japan were assessed for crude oil production by direct organic solvent extraction and continuous hydrothermal liquefaction (HTL). These native microalgae had shown high biomass productivity (>29 $g/m^2/day$) even in cold temperate zone of Japan (Demura et al., 2018).

This thesis includes five chapters. Chapter 1 includes the general introduction of thesis contents and purpose of the study. Biofuel production from biomass grown on arable lands not only have raised the food prices but also competed for land with the agricultural resources. Microalgae have been recognized as a promising solution to this increasing global food-fuel due to several significant advantages provided by them. The advantages include smaller cultivation area, 10-100 times higher oil productivity and short growth cycle compared to terrestrial oil-crops (L. Zhu et al., 2015).

The native microalgae culture offers several additional advantages over monocultures regarding biomass productivity, nutrient utilization, and biomass stability (Demura et al., 2018; Hamilton et al., 2014; Stockenreiter et al., 2016). The operation and maintenance of these types of culture are comparatively more straightforward (Chen et al., 2015). However, previous studies mainly focused on biofuel production employing monocultures. Biofuel production potential of native microalgae is not well established. Therefore, the purpose of the thesis was to compare yield and quality of crude oil produced by direct solvent extraction and continuous HTL of native microalgae.

In chapter 2, effect of solvent extraction and thermogravimetric analysis on crude oil production from native microalgae was studied. Crude oil yields obtained from native microagae exhibited a good, positive relationship with the Hildebrand solubility parameter, which explained the observed differences in extraction yield obtained using different organic solvents. Crude oil

extracted with hexane indicated the presence of only neutral lipids and showed an excellent weight loss of 37% at temperatures from 250 to 350 °C, but its low crude oil yield of 1.5% limited its usage. In contrast, crude oil extraction with methanol not only exhibited the highest yield but also resulted in better thermogravimetric properties than all other solvents examined, making it an ideal solvent for crude oil production from native microalgae. Native microalgae not only exhibited a reasonable crude oil yield in the range of 1.5 to 11.4% depending on the solvent type but also shown good thermogravimetric properties.

In chapter 3, continuous HTL of a wet native microalgal feedstock was performed in a bench-scale tubular reactor system, using a microalgal slurry (19.4 wt%) at 350 °C and 19.5 MPa. The HTL process successfully converted this feedstock into biocrude. Additionally, a stoichiometric equation summarizing the HTL reaction was derived based on the elemental concentrations in the dry algae and biocrude, considering CO_2, NH_3 and H_2O as by-products of the reaction. According to this equation, the biocrude yield (60.7 wt%), carbon balance (72%) and nitrogen balance (44.9%) obtained in this study were each 80% of their respective maximum attainable values. The crude oil yield from the biocrude was significantly increased (by factors of 1.47 and 1.7 on a daf basis) compared with the crude oil directly extracted from dry algae with chloroform:methanol (2:1 v/v) and hexane, respectively. The crude oil products were characterized based on their thermogravimetric properties and were found to primarily fall in the distillation range of light and heavy oils (250–500 °C). Crude oil obtained from the biocrude showed a significant increase in light oils and a reduction in heavy oil components. These results suggest that the continuous HTL of native microalgae produces a superior biocrude with more light oil components, which is beneficial for biodiesel production.

In chapter 4, native microalgae were converted to biocrude by continuous HTL process as described in chapter 3 and effects of biomass concentration and HTL reaction temperature on biofuel production and crude oil extraction were evaluated. The increment in biomass concentration and reaction temperature positively influenced the biocrude as well as crude oil yield. The performance of native microalgae was comparative to that of monocultures used in previous studies on continuous HTL in terms of biomass composition and biocrude production.

Chapter 5 includes the summary and conclusion of the thesis. Represented results revealed that solvent extraction and HTL are the two efficient ways for biofuel production from native microalgae. Organic solvents are highly efficient in penetrate the algae cell wall and attaining high crude oil yield. Crude oil yield comparable to high temperature could be attained by direct solvent extraction at ambient temperature for 24 h. However, solvent extraction requires an additional step of feed drying which is energy consuming and overall process cost increases. On the other hand, organic matters of native microalgae could be successfully converted to biocrude by continuous HTL. However, biomass concentration and HTL reaction temperature greatly influences the biocrude and crude oil yield. Continuous HTL is more effective compared to direct solvent extraction since it could result higher crude oil yield probably due to conversion of carbohydrates and proteins into lipids. HTL of microalgae provide additional advantage of directly converting wet algal biomasses into liquid biocrude, thus eliminating the need to expend energy to dry the feedstock. Also, continuous HTL could offer a superior quality crude oil product compared to direct solvent extraction i.e. reach in light oil components desired for biofuel production.

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