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Effective conversion of the carbohydrate-rich macroalgae (*Saccharina japonica*) into bio-oil using low-temperature supercritical methanol

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ABSTRACT

The use of supercritical methanol (scMeOH) for the liquefaction of the carbohydrate-rich macroalgae *Saccharina japonica* was investigated at low temperature (250–300 °C). At 300 °C, almost complete conversion (98.1 wt%) and a high bio-oil yield (66.0 wt%) were achieved. These values are higher than those achieved with supercritical ethanol (scEtOH, 87.8 wt% conversion, 60.5 wt% bio-oil yield) and subcritical water (subH_2O, 91.9 wt% conversion, 40.3 wt% bio-oil yield) under identical reaction conditions. The superior liquefaction in scMeOH is attributed to the beneficial physical properties of scMeOH, including its higher polarity, superior reactivity, and higher acidity. The superior reactivity of scMeOH was evident from the larger amount of esters (54.6 area%) produced in scMeOH as compared to that in scEtOH (47.2 area%), and the larger amount of methyl/methoxy-containing compounds (78.6 area%) produced in scMeOH than that of ethyl/ethoxy-containing compounds (58.2 area%) produced in scEtOH. The higher bio-oil yield combined with its higher calorific value (29.2 MJ kg^{-1}) resulted in a higher energy recovery of 135% for scMeOH as compared to those of scEtOH (118%) and subH_2O (96%). When considering the amount of alcohol consumed during the liquefactions and the production of light bio-oil fractions that evaporate during bio-oil recovery, the higher methanol consumption (5.3 wt%) than that of ethanol (2.3 wt%) leads to similar bio-oil yields (~51 wt%).

1. Introduction

Aquatic algae biomass is considered to be one of the most promising feedstocks for the production of biofuels and biochemicals, which is an increasingly important strategy for addressing current energy and environmental issues [1,2]. The use of algal biomass is extremely attractive owing to its natural abundance, global distribution, and the rapid CO_2 consumption that it exhibits during its growth, which is 10–20 times higher than that of terrestrial biomass [3,4]. Specifically, the use of multicellular macroalgae has enormous potential for integration with waste water treatment because multicellular macroalgae has the ability to grow in harsh conditions [5,6] and has a higher life-cycle yield compared to that of unicellular microalgae [7].

The thermochemical conversion of macroalgae into fuels and chemicals has received considerable attention recently owing to its shorter residence times and smaller space requirements than those of biochemical conversion, which is slow, requires large spaces for operation, and relies on the use of expensive enzymes. Furthermore, unlike biochemical approaches, a variety of biomass components can be treated simultaneously by thermochemical conversion [6]. On the other hand, as compared to biochemical conversion, the thermochemical conversion requires high-temperature reactor system and unspecific thermochemical reactions result in product mixtures comprised of many different types of chemicals.

Although fast pyrolysis is typically used for the thermochemical conversion of “dry” biomass into liquid fuels [8–10], hydrothermal liquefaction, which utilizes high-temperature water as a solvent, is considered to be a more appropriate choice for treating algal biomass because of its inherently high moisture content [11–16]. Indeed, there has recently been some progress in the large-scale production of bio-oil from algae using hydrothermal liquefaction [17]. Nonetheless, a significant problem with hydrothermal liquefaction is the inefficient separation of the liquid products after the liquefaction process. Liquid-liquid extraction using a non-polar or slightly polar solvent such as dichloromethane (DCM) [18], or ethyl acetate [19] is typically employed to recover the bio-oil product from the aqueous phase. However, many bio-oil components having medium-to-high polarities are not effectively extracted into the organic phase and remain in the aqueous phase [18–20]. This partitioning of products into the organic and aqueous phases during recovery not only lowers bio-oil yield, it also

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complicates the study of liquefaction behavior. Furthermore, distillation, the technique most typically used to separate water from water-soluble oil fractions, is highly energy intensive and thus difficult to implement on a practical scale. Therefore, to improve hydrothermal liquefaction, effective ways to utilize the aqueous phase, which is rich both in organic compounds and inorganic ash, are required.

Organic solvents such as alcohols, acetone, 1,4-dioxane, and tetralin, especially in their supercritical states, have been employed in biomass liquefaction as alternatives to water [19,21–26]. The advantages of employing organic solvents such as alcohols like methanol, ethanol, and propanol instead of water include higher bio-oil yields, the higher calorific values of the bio-oils produced, and the production of homogeneous liquid products that do not require liquid-liquid extraction.

A variety of organic solvents have been assessed for the liquefaction of different algal biomass species. For example, Yuan et al. liquefied the microalgae *Spirulina* in methanol, ethanol, and 1,4-dioxane, and reported that of the three solvents, methanol provided the highest conversions at all the temperatures tested (300–380 °C) and a maximum conversion of 82% at 380 °C [22]. They also reported that the bio-oil yield was higher using ethanol at 340 °C (55.6 wt%) as compared to that using methanol, but the yield using methanol exceeded than that using ethanol when the temperature was raised to 380 °C (ethanol yield: 60.6 wt%, methanol yield: 62.9 wt%). Furthermore, Duan et al. assessed ten different organic solvents (i.e., ethylene glycol, methanol, ethanol, n-propanol, isopropanol, acetone, ethyl acetate, 1,4-dioxane, tetralin, and benzene) and water in the liquefaction of the microalgae *Chlorella pyrenoidosa* at 350 °C and a solvent-to-biomass ratio of 4:2.5 for 60 min [23]. They reported that ethanol was the most effective liquefaction solvent, and that the highest bio-oil yield was 64.6 wt% and the lowest solid residue yield was 11.9 wt% using an ethanol-to-biomass ratio of 12:2.5 at 350 °C for 60 min. Similarly, in a study on the liquefaction of the macroalgae *Enteromorpha prolifera* performed by Zhou et al., methanol afforded a maximum bio-oil yield of 44 wt% at 280 °C and ethanol afforded a maximum bio-oil yield of 50 wt% at 300 °C. Further increase in temperature in each case decreased the bio-oil yield [27].

In a previous study, we found that the use of supercritical ethanol (scEtOH) in the liquefaction of the carbohydrate-rich macroalgae *Saccharina japonica* at 350 °C and 29.8 MPa for 45 min resulted in high conversion (~90%) but only a moderate bio-oil yield (58.4 wt%) [28]. As the reaction temperature was increased to 400 °C, the conversion marginally increased (~94%), but the bio-oil yield increased to an exceptional 79.2 wt%. This indicated that the increase in bio-oil yield was not primarily due to the increase in biomass conversion, but because of the use of scEtOH as a reaction medium. The amount of ethanol consumed during the liquefaction at 400 °C was 18 wt%, much higher than that at 350 °C (6 wt%), indicating the more active participation of ethanol in the reaction at higher temperature. Considering the amount of ethanol consumed, the bio-oil yields were estimated to be 53.9 wt% at 400 °C and 40.0 wt% at 350 °C. Even though almost complete conversion of the carbohydrate-rich macroalgae was obtained in scEtOH at high temperature, the high consumption of ethanol, which is an expensive solvent, should be addressed carefully. In addition, because ethanol can be directly used as a transportation fuel, its high consumption during the macroalgae liquefaction makes the process less attractive in a practical-scale production of bio-oil as compared to those using water or other cheap organic solvents.

Herein, to address the problems outlined above, supercritical methanol (scMeOH) is employed as a reaction medium for the liquefaction of the macroalgae *Saccharina japonica*. We demonstrate that, at the low reaction temperature of 300 °C, almost complete conversion of the macroalgae and the high bio-oil yield of 66.0 wt% can be achieved in scMeOH. These values are much higher than those achieved with scEtOH at 300 °C (conversion: 88.0%, bio-oil yield: 60.5 wt%). In fact, the yields and conversion values obtained with scMeOH at 300 °C without the use of a catalyst are unprecedented for macroalgae liquefaction. In addition, the bio-oil produced in scMeOH exhibits a higher heating value (HHV) of 29.2 MJ kg^{-1}, which is higher than that of the bio-oil produced in scEtOH (27.8 MJ kg^{-1}). To gain insight into the liquefaction behavior of *Saccharina japonica* in scMeOH, gas chromatography coupled with time-of-flight mass spectrometry (GC-TOF/MS) was used to analyze the liquid product collected immediately after the reaction, and the analysis results are compared with those for the dried bio-oil collected after product separation. The results of scMeOH liquefaction are compared with those of scEtOH and subcritical water (subH_2O) liquefaction. The consumption of the alcohol solvents during the liquefactions and the energy recoveries are also discussed.

2. Experimental

2.1. Materials

The macroalgae *Saccharina japonica*, which is a type of kelp, was used in this study and was purchased from a local market in South Korea. The macroalgae was thoroughly washed to remove any salts present on its surface and then dried overnight in a drying oven at 105 °C. The dried macroalgae was crushed using a model IKA A11 basic analytical mill and sieved to 600–1000 μm. Because the chemical composition of the macroalgae is highly affected by seasonal variations, one batch of the feedstock was used for all the experiments in this study. Chemical composition, ultimate analysis, and inorganic content analysis results for the raw macroalgae are presented in Table 1. HPLC-grade methanol, ethanol, acetone, and DCM were purchased from Sigma-Aldrich Co. (USA). High-purity nitrogen (99.99%), helium (99.99%), hydrogen (99.99%), and air (99.99%), used for purging the reactor and in the gas chromatography experiments, were purchased from JC Gas Co. (South Korea).

2.2. Liquefaction procedure

A schematic diagram of the liquefaction and product separation protocol is shown in Fig. S2. The details of the liquefaction and product separation are described elsewhere [32]. Briefly, after adding the prerequisite amounts of macroalgae and solvent into a custom-built 140-mL SUS 316 reactor, the reactor was purged three times with nitrogen to remove the oxygen in the liquid and reactor head using a purge line dipped into the liquid. The reactor was then pressurized to 1 MPa with nitrogen. The amount of solvent (65 g) and macroalgae (6.5 g dry basis) were fixed for all the reactions. The reactor was heated to the target temperature at 15 °C min^{-1}. After the appropriate reaction time, the reactor was quenched to 100 °C in less than 5 min using cold water. After the reactor had cooled to room temperature, the gas produced during the liquefaction was passed through a wet gas meter (W-NK-2 type, Shinagawa Co., Japan) to measure its volume (the volume of 1 MPa of initially pressurized nitrogen was subtracted from the total volume), and then it was collected in a 0.5 L Tedlar® bag for compositional analysis (Step 1, Fig. S2). A small fraction of the liquid product in the reactor (~3 mL) was taken for Karl Fischer titration, chemical composition analysis via GC-TOF/MS, and for solvent quantification using GC coupled with flame ionization detection (FID) (Step 2). The solid and liquid products were poured into a beaker, weighed, and the amount of light fractions was calculated by mass balance (explained in detail in Section 3.4.3) (Step 3). The reactor was then further rinsed with acetone to collect the residual liquid and solid products. The residual solid products were separated from the liquid products using filtration (Step 4). The filter cake was dried in a drying oven at 80 °C for 24 h in order to estimate the amount of solid residue and calculate conversion (Step 5). The filtrate was evaporated using a rotary evaporator at 60 °C and 0.08 MPa for 30 min to estimate the bio-oil yield (Step 6). A control experiment was performed under identical separation conditions to ascertain that neither the liquefaction solvent