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High-yield bio-oil production from macroalgae (*Saccharina japonica*) in supercritical ethanol and its combustion behavior

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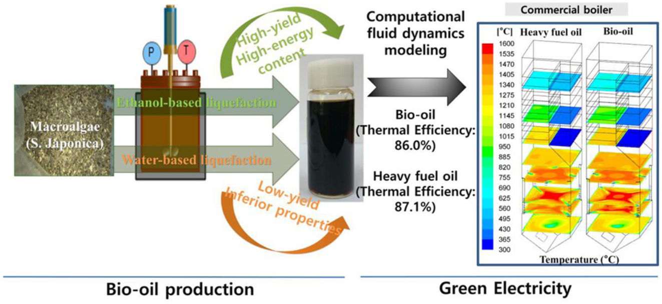
HIGHLIGHTS

- Almost complete conversion of macroalgae in supercritical ethanol (scEtOH).
- High-yield (88 wt%) and high-energy-content (35 MJ kg^{-1}) bio-oil produced in scEtOH.
- ScEtOH produced higher-yield and better-quality bio-oil than water-based reaction.
- Bio-oil can be used as a combustion fuel for green electricity generation.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of reaction parameters (temperature, time and biomass-to-solvent (BS) ratio) on properties (higher heating value (HHV) and O/C and H/C ratios) and yields of bio-oil produced from macroalgae (*Saccharina japonica*) liquefaction using supercritical ethanol (scEtOH) as a solvent was investigated. At 400 °C using a BS ratio of 1/10 and reaction time of 45 min, a high yield of bio-oil (88 wt%) with a HHV of 35.0 MJ kg^{-1}, O/C ratio of 0.14, and H/C ratio of 1.62 was obtained. Compared with water-based liquefaction, (subcritical water at 300 °C, bio-oil yield of 43 wt%, HHV of 20.7 MJ kg^{-1}, O/C ratio of 0.48, and H/C ratio of 2.01; supercritical water at 400 °C, bio-oil yield of 37 wt%, HHV of 29.0 MJ kg^{-1}, O/C ratio of 0.18, and H/C ratio of 1.76), the yield and energy content of the bio-oil produced using scEtOH were significantly higher. This enhancement was attributed to the reactivity of scEtOH with the intermediates generated from macroalgae. The utility of the generated bio-oil was demonstrated by application in a commercial 100 MW$_e$ generation plant. The thermal efficiency of the bio-oil (86.0%) was quite similar to that of heavy fuel oil (HFO) (87.1%), suggesting that the HFO could be fully replaced by the bio-oil.

1. Introduction

The finite oil reserves and greenhouse gas emissions have fueled immense interest in the development of renewable alternatives to fossil fuels. Production of biofuels from first-generation biomass such as corn and sugarcane and second-generation biomass such as lignocellulose faces severe socio-economic and environmental pressure because of the direct competition for food resources, arable land, and fresh water [1]. Algal biomass can offer certain advantages as third-generation biomass because of the high production rate (which enables high-rate carbon fixation due to the high photosynthetic efficiency) and the adaptability of algae to grow in both fresh and saline/wastewater (which can

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reduce its dependence on arable land) [2]. Microalgae have drawn considerable attention as a feedstock for biofuel mainly because of its relatively high lipid content. Recently, it was observed that the yield of bio-oil produced from microalgae liquefaction was higher than the lipid content in microalgae [3], suggesting other organic components of algal species (such as protein and carbohydrates) also contribute to the bio-oil yield. This opened up a gateway for utilizing low-lipid-content algal biomass, i.e. macroalgae, as a promising feedstock for the production of biofuel. There are obvious advantages in using macroalgae as a biomass feedstock; macroalgae has high biomass productivity and can grow in harsh environments by consuming nutrients from wastewater, which can offer a new opportunity for combining wastewater treatment, carbon capture, and biofuel production in one facility [2,4].

Currently, thermochemical conversion of solid biomass into liquid fuel is either performed in the presence or absence of a solvent (liquefaction versus pyrolysis). The primary function of the solvent in liquefaction is to solubilize the solid biomass to facilitate the subsequent decomposition reaction. Thus, the use of a solvent enables biomass conversion at lower temperatures (250–400 °C) as compared to pyrolysis (>500 °C), but requires elevated pressures (5–40 MPa) [5,6]. Pyrolysis of biomass requires severe operating conditions and often results in liquid fuel with inferior properties, such as a high oxygen content (O/C ratio of ~0.2), lower caloric value (higher heating values (HHVs) of ~20 MJ kg^{-1}), and high corrosiveness because of the low-carbon-number carboxylic acids [7–9]. Therefore, pyrolysis bio-oil is not suitable for direct use as a co-combustion or transportation fuel. On the other hand, thermochemical liquefaction (TCL) using water as the solvent can produce bio-oils with lower O/C ratios and higher HHVs when compared to those produced using pyrolysis, but the potential corrosiveness associated with sub- (subH$_2$O) and super-critical water (scH$_2$O), the complex product-separation procedures, and low energy recovery due to the low bio-oil yield (in the range of 19–35 wt%) are major drawbacks of hydrothermal liquefaction [2,10–12].

To further increase the liquefaction yield and to improve the quality of bio-oil, organic solvents have been tested as TCL media [12–14]. Organic solvents can solubilize decomposed intermediates and products, can stabilize reaction intermediates to retard tar/char formation, and can remove oxygen from the organic species to some degree, thereby improving the energy content of bio-oil. For example, supercritical alcohols meet the aforementioned criteria owing to their high solubilizing power for bio-oil and their ability to donate hydrogen, which not only retards recombination of the reaction intermediates to increase the bio-oil yield, but also removes oxygen via hydrodeoxygenation [10,12,15,16]. The beneficial properties of supercritical alcohols have been exploited in the TCL of various types of biomass, including wood [10,17,18], rice husk [19], lignin [20–22], manure [23], lipid-rich microalgae [24], cornstalk [25], sewage sludge [26], and upgrading of fast pyrolysis bio-oil [27]. However, according to our knowledge, only few studies have investigated TCL of macroalgae in supercritical alcoholic media. Summary of previous macroalgae and microalgae liquefaction in supercritical fluids is listed in Table S1. When *Enteromorpha prolifera* was liquefied in supercritical ethanol (scEtOH) at 300 °C for 15 min using a biomass-to-solvent (BS) ratio of 1/10, a bio-oil yield (on dry ash-free basis) of 50.5 wt% with an O/C ratio of 0.24, and a HHV of 30.68 MJ kg^{-1} were obtained, whereas the use of scMeOH at 280 °C for 15 min with a BS ratio of 1/10 produced a bio-oil yield of 44.5 wt%, O/C ratio of 0.34, and HHV of 26.04 MJ kg^{-1} [15]. Whereas Singh et al. liquified *Ulva fasciate* in scEtOH as well as in scMeOH and concluded that scMeOH produced higher yield of bio-oil (75.1 wt%) as compared to scEtOH (68.3 wt%) [28]. Among the two solvents employed previously for macroalgae liquefaction, ethanol was preferred to be the solvent in this work because of environmental concerns about the use of methanol for biomass liquefaction, as methanol is toxic and is mainly derived from petroleum sources [29,30].

In this study, efforts are directed towards determining the optimum parameters for achieving high-yield and high-energy-content bio-oil from *Saccharina japonica* using scEtOH. At 400 °C using a reaction time of 45 min, a high yield of bio-oil (88 wt%) with a high HHV of (35.0 MJ kg^{-1}) could be achieved. This is the highest reported yield of bio-oil obtained using algal biomass as a feedstock (Table S1). The scEtOH-based liquefaction process is compared with subcritical water (subH$_2$O) and supercritical water (scH$_2$O) based liquefaction to gain insight into the liquefaction mechanisms. Lastly, the feasibility of replacement of heavy fuel oil (HFO) produced from petroleum resources by macroalgae-based bio-oil for electricity generation in a commercial-scale boiler with 100 MWe-capacity is examined using computational fluid dynamics (CFD).

2. Experimental

2.1. Materials

The raw macroalgae, *Saccharina japonica*, was purchased from a local market in Suwon, South Korea. The macroalgae was dried and ground to particle sizes of 600–1000 μm using an IKA A11 basic analytical mill. Considering the seasonal variation in the chemical composition of the macroalgae, one batch of the feedstock was used for the entire study. Table 1 lists the results of proximate analysis, ultimate analysis, and the chemical composition of the inorganic species in the raw macroalgae. The moisture content was measured by drying the raw macroalgae at 105 °C until a constant weight was obtained. The protein content was calculated by multiplying the organic nitrogen content by a factor of 6.25 (Kjeldahl method) [31]. The total lipid content was measured by separating the lipids from the raw feedstock using a mixture of dichloromethane and methanol (2:1 v/v) [32]. To improve the phase separation, NaCl (5 wt%) was added to the aqueous phase. The lignin content was measured using the Klason method [33,34]. The carbohydrate content was calculated by difference after determination of the ash content using thermogravimetric analysis (TGA, see Fig. S1) in air environment. Ethanol (HPLC grade, used as a liquefaction solvent), methanol (HPLC grade, used for lipid content measurement), toluene (HPLC grade, for Klason method), and acetone (HPLC grade, used as a washing solvent after the reaction) were obtained from Sigma-Aldrich Company (USA). Reagent grade ethyl acetate (EA, 99.0% pure), sulfuric acid (72% pure), and dichloromethane (99.0% pure) were obtained from Daejung Metal & Chemical (South Korea). Distilled and deionized (DDI) water was prepared using an AQUAMaxTM-Basic 360 water purification system equipped with a 0.22 μm filter (Young Lin Instrument Co., Ltd., South Korea). High-purity nitrogen (99.99%), helium (99.99%), hydrogen (99.99%), and air (99.99%) for purging the reactor and for use in gas chromatography were obtained from JC Gas Company (South Korea).

2.2. Liquefaction procedure

Prior to the liquefaction experiment, the macroalgae was dried overnight in a vacuum oven at 70 °C. The details of the reactor setup and experimental protocol are described elsewhere [35]. Briefly, the batch reactor with an inner volume of 140 mL was equipped with a magnetically driven stirrer and two heating sources (heat furnace and cartridge heaters). After charging with the pre-determined amount of raw macroalgae and the solvent, the reactor was sealed, purged with N$_2$ three times using a purge