



Production of brown algae pyrolysis oils for liquid biofuels depending on the chemical pretreatment methods



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ABSTRACT

Based on observations of rapidly growing biochar in fluidization beds, kelp (*Saccharina japonica*), a species of brown algae, was pretreated for the efficient operation of pyrolysis processes to produce pyrolysis oils. The removal of catalytically active inorganic minerals and the softening of polymeric seaweed structures were performed by means of chemical treatments, including a CaCl_2 treatment to isolate valuable and sticky fucoidan and a sulfuric acid treatment to remove catalytically active minerals. The sulfuric acid pretreatment significantly reduced the inorganic elements but did not significantly affect the properties of the pyrolysis oil compared to the non-treated kelp pyrolysis oil. Whereas the non-treated kelp produced significantly large chunks of biochar, which hindered the continuous operation of pyrolysis, the kelp treated with sulfuric acid did not produce aggregated large particles of biochar, thereby offering a means of developing reliable continuous pyrolysis processes.

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1. Introduction

Macroalgae are promising biomass resources because of their rapid growth, less competition with foods, and cultivation in the sea. Brown algae, *Saccharina japonica* (*S. japonica*), used in this study is composed of alginate, laminarin, fucoidan, mannitol, and other inorganic elements [1]. Because other biomass sources, such as corn, sugarcane, wood, and grass, have been fermented into bioethanol and other bioalcohols, there have also been efforts to ferment macroalgae into bioalcohols [2,3]. Although bioalcohol production, one of the frequently used biofuel processes, can be selected for the macroalgae feedstocks, the smaller amount of fermentable sugars compared to cellulosic or carbohydrate types of biomass may hinder the use of macroalgae as a feedstock for bioalcohol production [1].

Under these circumstances, thermochemical conversions, including pyrolysis and hydrothermal liquefaction, have been sug-

gested to obtain hydrocarbon fuels from macroalgae [4], and thermochemical conversions of microalgae have been widely investigated in studies pertaining to microalgae-based biodiesel production [5–7]. As lignocellulosic biomass is processed [8], batch or fixed bed pyrolysis [9–12], continuous flow pyrolysis using a fluidized bed reactor or others [13–18], and batch hydrothermal liquefaction [19,20] have been assessed for the ability of these methods to produce bio-oils. The addition of a special treatment, such as a microwave treatment, was performed to valorize macroalgae-derived pyrolysis oils [4,12,21,22]. The kinetics of the combustion and pyrolysis of seaweeds was also studied in an effort to understand the thermal degradation characteristics [23–28].

In keeping with the research on producing pyrolysis oils using organic components in seaweeds, the production of the pyrolysis oils of *S. japonica* using a fluidized bed reactor was attempted, but rapidly growing biochar chunks were observed in the early stage of the process (see Fig. S1 in the supplementary information), which made it difficult to operate the process continuously. It was predicted that the robust char formed possibly because of the inorganic mineral-catalyzed gelation and then the carbonization of gel-like sticky organic polysaccharides, which was similar to observations of lignin pyrolysis [29]. To increase the pyrolysis oil

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yield, the removal of the major organic components of macroalgae, including alginate, laminarin, and mannitol was avoided. Two pretreatment methods were selected: a sulfuric acid and a CaCl_2 treatment. The sulfuric acid pretreatment of macroalgae was performed to remove a significant amount of the inorganic elements by exchanging metal cations with protons to convert the inorganic salts of alginates and fucoidan to acidic forms and thus to reduce the catalysis caused by these materials during the pyrolysis process. Because the inorganic elements do not contribute to the yields of macroalgae pyrolysis oils, the removal of these inorganic elements may improve the pyrolysis processability. A CaCl_2 treatment of macroalgae has been used to extract valuable fucoidan [30] and soften the networked structures of macroalgae [31]. The relatively small component (5–20 wt%) fucoidan was removed to suppress the gelation of organic components. In addition, because fucoidan is a valuable chemical that is extracted from seaweeds, this process can simulate the valorization of fucoidan-extracted seaweeds by pyrolysis. The removal of significant amounts of metal elements was also predicted because fucoidan exists as metal salts [1].

2. Experimental section

2.1. Materials

Kelp (*S. japonica*) was collected at Wando, Korea. Kelp was sieved to 600–1000 μm and dried at 60 °C for 24 h prior to use. Calcium chloride (CaCl_2 , anhydrous, 95.0%) was purchased from Wako (Osaka, Japan). Sulfuric acid (98.8%), D-mannitol, sodium alginate, laminarin (*Laminaria digitata*), fucoidan (*Fucus vesiculosus*), and tetrahydrofuran were purchased from Aldrich (Milwaukee, WI, USA). Deionized water (DI water, 18.2 M Ω cm) was prepared using an aquaMAX Ultra 370 water purification system (YL Instruments, Seoul, Korea).

2.2. Pretreatment of the kelp

Kelp was processed with (i) a CaCl_2 treatment (fucoidan removal) and (ii) a sulfuric acid pretreatment. (i) Fucoidan removal was performed by stirring the sieved kelp powder (420 g, 600–1000 μm) mixed with an aqueous calcium chloride solution (1 wt% CaCl_2 , 7 L) twice for 20 min each. The mixture was then filtered, washed with DI water, dried at 105 °C for 24 h, and stored in a desiccator (KelpF) [30]. (ii) The acid pretreatment was performed by stirring the sieved kelp powder (700 g, 600–1000 μm) mixed with an aqueous sulfuric acid (4 wt% H_2SO_4 , 7 L) solution for 30 min. This mixture was then filtered and washed with DI water to achieve a pH of 5.5. The washed product was further dried in air at 105 °C for 16 h and stored in a desiccator (KelpA).

2.3. Pyrolysis

Pyrolysis of the kelp was performed using batch and continuous reactors (Fig. 1). When the fixed-bed-type batch reactor (quartz, ID = 2.4 cm) was used (Fig. 1(a)), each run processed 40 g of kelp powder pre-dried in air at 105 °C. The reaction was processed under an N_2 flow (0.5 L/min) at 470 °C for 10 min. The pyrolysis oil was collected at the first (25 °C) and second condensers (0 °C). The continuous flow pyrolysis reaction was performed using a fluidized bed reactor (Fig. 1(b)). Pre-sieved kelp powder (600–1000 μm) was dried in air at 105 °C and conveyed using a screw-type solid feeder at a rate of 150 g/h to a reactor filled with alumina particles (260 μm). The N_2 carrier gas flow rate was fixed at 45.37 L/min (at 470 °C). The residence time of the kelp particles in the reactor was held to 2 s or shorter. The formed char particles

were collected at the cyclone, and the volatile products were collected using two chilled condensers (first condenser at 22 °C; second condenser at –10 °C).

2.4. Characterization of kelp powders and pyrolysis oils

For all the GC/MS analyses, the concentrations of the identified materials were determined using the relative peak areas [28,32]. The prepared kelp powder was observed by means of Py-GC/MS, which was performed using an Agilent 6890 GC equipped with a CDS pyroprobe 5000 and a 5973 mass selective detector. The pyroprobe was operated at a ramping rate of 450 °C/s to reach a temperature of 450 °C and hold it there for 20 s; it was thermally protected by the surrounding air at 270 °C. GC/MS was performed using a DB-1701 capillary column (60 m \times 0.25 mm \times 0.25 μm) [33]. The pyrolysis oil was observed using a GC/MS (the Agilent Technologies 7890A GC system with a HP-5MS column, 60 m \times 0.25 mm \times 0.25 μm). Prior to the GC/MS analysis, the pyrolysis oil was mixed with tetrahydrofuran to form a 50% w/w mixture, after which a biphasic mixture composed of a transparent bottom and dark top layer formed, whose GC/MS results were separately obtained. The amount of volatile compounds in the kelp powder was measured by means of a proximate analysis under an air flow using a TGA SDT Q600 instrument (TA Instruments). The kelp powder (~15 mg) was heated to 120 °C at a ramping rate of 10 °C/min and kept at 120 °C for 30 min, heated to 575 °C at 10 °C/min and kept at 575 °C for 30 min, and then heated to 800 °C at 10 °C/min and kept at 800 °C for 30 min. The weight losses up to 120 and 575 °C were attributed to water and volatile compounds, respectively. The remaining weight was assigned as ash. Thermogravimetry of the kelp powders, oils, and other compounds was performed under an N_2 flow using a TGA SDT Q600 instrument (TA Instruments). The compositions of C, H, N, and S in the kelp powders and oils were measured using a Flash 2000 series CHNSO analyzer (Thermo Scientific, USA). The oxygen content was measured using a Fisons-EA-1108 (Thermo Scientific, USA). The inorganic compositions of the kelp powders and oils were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Polyscan-61E, Thermo Electron Corp., Winsford, Cheshire, UK). To measure the solid contents in the pyrolysis oils, the oil (5 g) was dissolved in a mixture of dichloromethane and methanol (50% w/w, 50 g), which was stirred for 30 min. The resulting mixture was filtered using a paper filter (0.45 μm) and dried in air at 60 °C for 24 h prior to the measurement of the remaining weight. The total acid number (TAN) of the oil was measured by stirring the oil (0.05 g) dissolved in acetone (20 mL) for 10 min. Three drops of phenolphthalein (0.1 g) dissolved in methanol (20 mL) were added to the oil/acetone solution, which was titrated with 0.1 M KOH, and the TAN was determined as $\text{TAN (mmol KOH/g)} = (\text{KOH volume, mL}) \times (0.1 \text{ mmol/mL KOH}) / (\text{weight of oil, g})$. The thermogravimetry results for the kelp and pyrolysis oil were obtained using the TGA SDT Q600 instrument; this process was performed in an N_2 flow by heating ~15 mg of the sample to 1000 °C at a ramping rate of 20 °C/min. FT-IR was performed on the kelp powder using a Nicolet iS10 FT-IR system. The Karl Fischer titration method was used to measure the water content of the pyrolysis oil (3 mg) using a Karl Fischer Moisture Titrator MKC-520 with the addition of HYDRANAL-Coulomat AG-H. For the bi- or multi-phasic oil mixture, each phase was separately observed. The viscosity of the pyrolysis oil was measured at 25 °C using an AR2000 (TA Instruments, New Castle, DE, USA) cone and plate stress control type rotational rheometer. The shear rate was 0.1–1000 s^{-1} . The density of the pyrolysis oil, prepared by stirring for 30 min, was measured using a pycnometer (Lenz Laborglas, Wertheim, Germany). The heating values of the pyrolysis oils were determined using the Dulong equation [34]: $\text{HHV (higher heating value, MJ/kg)} = 33.742 \times [\text{C}] + 143.905 \times ([\text{H}] - [\text{O}]/8) + 9.396 \times [\text{S}]$, where [C], [H], [O], and [S]

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