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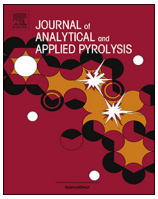

Effect of thermal pretreatment on the extraction of potassium salt from alga *Saccharina japonica*

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ABSTRACT

Interests in conversion of macroalgae to bioenergy via thermal treatment, namely pyrolysis or combustion has increased due to their distinctive composition and high photosynthetic rates. The resulting char byproducts could serve as a trove of precious mineral resources. Thermal pretreatment was compared with direct extraction of potassium salts from alga *Saccharina japonica* using deionized water for use as food additive, agricultural or pharmaceutical applications. Biomass was pyrolysed with fixed bed reactor or combusted with muffle furnace at 300, 450, 600 °C, and extracted using deionized water in shaker at 150 rpm and 30 °C for 2 h. Overall potassium salts recovery efficiency from raw biomass (52.55 ± 2.79%) was relatively lower than from 450 °C chars from pyrolysis (75.30 ± 0.81%) and combustion (62.07 ± 0.56%). Extracts from pyrolysed char at 600 °C had highest purity of KCl which is most abundant mineral in all products. SEM-EDX and ICP-OES elemental analysis confirmed absence of heavy metals such as As, Cu, Cd and Pb in extracts. Ratios of organic to inorganic fractions in extracts from thermally pretreated samples were much lower (~0.1) than that of raw biomass (8.42).

1. Introduction

Macroalgae are very rich source of minerals [1]. The content of such minerals in seaweeds could be as high as 40% [2], and usually more than from terrestrial biomass. This is due to the fact that seaweeds tend to accumulate metal ions from sea water and concentrate those substances in their fronds [3–5]. Particularly, a study on the effect of fir wood and kelp seaweed biochars on the field cultivation of corn showed that the biochar from kelp seaweed source contained more than 100 times potassium minerals than from fir wood [6]. During thermal treatment of biomass, there is generally a phase-mineral transformation that may result in the formation of several compounds such as silicates, hydroxides, phosphates, sulfates, carbonates, chlorides and nitrates which are salts of the various minerals present [7]. Thus, mineral extracts of macroalgae has been identified as a precious trove of biologically active compounds which have important benefits for humans, animals as well as plant growth.

Bioproducts from natural sources with functional properties with concentrates of compounds with desired properties, generally categorized "bio" or "organic", rather than being a product of synthesis from other non-organic sources are increasingly required by many consumers [8]. Organic source of potassium salts such as KCl has important health benefits and several other applications. Nowadays, a health conscious world is moving towards sodium replacement (low sodium diets or sodium-free substitutes) and source of potassium in diet [9]. The deficiency of K^+ has been implicated in many diseases such as cardiovascular disease and osteoporosis among others [10]. Furthermore, the world fertilizer trends and outlook report revealed that the capacity of

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Abbreviations: RKB, raw kelp biomass; RKR, residue after extraction from RKB; RKE, extract from RKB; PKC-300, PKC-450 and PKC-600 char from pyrolysis at 300,450 and 600 °C respectively; PKR-300, PKR-450 and PKR-600 residues after extraction from PKC-300 PKC-450 and PKC-600 respectively; PKE-300, PKE-450 and PKE-600 extracts from PKC-300 PKC-450 and PKC-600 respectively; CKC-300, CKC-450 and CKC-600 char from combustion at 300,450 and 600 °C respectively; CKR-300, CKR-450 and CKR-600 residues after extraction from CKC-300 CKC-450 and CKC-600 respectively; CKE-300, CKE-450 and CKE-600 extracts from CKC-300 CKC-450 and CKC-600 respectively; $Y_{C/B}$, yield of char per initial dry weight of biomass during pyrolysis or combustion; $Y_{E/C}$, yield of water extractable minerals based on mass of dry extract to initial dry mass of char; $Y_{E/B}$, yield of water extractable minerals based on mass of dry extract to initial dry mass of RKB; DW_E, dry weight of extract after extraction; DW_C, dry weight of char; NI_{KCL}, normalized intensities of KCl; I_{KCl}, intensities of only KCl species; $I_{S,total}$, intensities of all species including KCl; I-RKE, I-300, I-450 and I-600 normalized intensities denoted respectively for extracts obtained from RKB and both pyrolysis and combustion extracts at 300 450 and 600 °C respectively; E_K, total potassium minerals recovery efficiency; M_{KE}, amount of potassium in extract; M_{KF}, amount of potassium in dry RKB; A_{fs}, initial fraction of ash in feedstock; A_{extr}, ash fraction in extract; $f_{inorg,E}$, inorganics fraction in extract; $f_{org,E}$, organic fraction in extract; $f_{inorg,R}$, remaining inorganic fraction in char residues after extraction; $f_{org,R}$, remaining organic fraction in residues after extraction; $f_{inorg,S}$, total fraction of inorganics in sample; $f_{org,S}$, total fraction of organics in sample; r_f, ratio of amount of water extractable organics to inorganics in extract; $A_{C,est}$, estimated amount of ash in char; A_{RB}, ash amount in RKB

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the world potash which is one of the major components of crop fertilizers, was projected at 49,700,000 t as K_2O in 2013. It is estimated that by 2018, the total capacity is likely to be 60,700,000 t. From the total increment in this period, 49% would be in North America, 39% in East Europe and Central Asia and about 13% in East Asia [11]. Thus, the recovery of appreciable amount of potassium salts from seaweeds in regions like East Asia where there are abundant growth of many varieties of seaweeds, could address the imbalance between the supply and demand of domestic potash to promote agricultural and economic development.

Some studies have been reported on the extraction of organic and inorganic matter from biomass and biomass ash. A study on the alkali metal emission during pyrolysis of biomass showed that the major release takes place in the high-temperature region above 500 °C [12]. Also, there is significant release of alkali metals and other ash-forming elements during the thermal conversion of biomass [13]. The release behavior of the ash-forming elements during extraction is highly dependent on its mode or state of occurrence in the biomass structure [14,15]. Some studies have considered the extraction of potassium salts and focused on terrestrial biomass as feedstock sources [16,17]. For instance, Liaw and Wu [18] studied the difference between batch and semi-continuous operations on the leaching characteristics of organic and inorganic matter from mallee leaf and wood and found that the leaching of water-soluble monovalent species of Na and K were faster than those of divalent species of Ca and Mg. Wang et al. [19] found a total elemental potassium content of 43.1% from the product of repeated extraction and quantification of various potassium salts from straw ash. However, based on the issues of sustainability or availability of biomass source for extraction of such important mineral salts, seaweeds have more considerable advantages over terrestrial biomass sources. In addition to their relatively higher content of potassium and other minerals, seaweeds have a superior photosynthetic abilities of 6–8% higher as compared to terrestrial biomass of 1.8–2.2% [20]. Also, the mass cultivation of seaweeds from sea-farming scale could be much higher than terrestrial biomass [21], thus there can be a constant availability and supply of feedstock for extraction from seaweeds than from terrestrial biomass sources. Moreover, the harvesting of seaweeds from surface waters and their use as feedstock for mineral extraction would help reduce the load of biogenic compounds and clean the coast of unwanted biomass [22]. Due to their distinctive properties such as composition of some specific carbohydrates [21] among other advantages over terrestrial biomass, interests in pyrolysis of macroalgae [23–26] for the production of bioenergy is increasing. The byproducts (biochar) from pyrolysis of macroalgae have high ash contents, usually ranging from 3.5% to 46% [5,27,28] and thus, can serve as a useful resource for K extraction which could be used for fertilizer or other applications.

Previous few works have suggested leaching and extraction methods and focused on the effects mostly on terrestrial biomass. However, no thermal treatment effect of feedstock on potassium salt extract from seaweeds are reported. In this study, direct leaching from raw biomass was compared to the effect of thermal pretreatment, namely, pyrolysis and combustion at various temperatures to assess the extent of recovery and purity of potassium salt from macroalgal *Saccharina japonica*. The content and form of potassium salts in extracts were determined using X-ray powder diffraction (XRD) analysis, Inductively coupled-optical emission spectroscopy (ICP-OES), Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), Ultimate analysis (CHONS) and Proximate analysis.

2. Materials and methods

2.1. Materials

Raw kelp seaweed (*Saccharina japonica*) used in this study was purchased from a local market in Daejeon, Korea. The as-received raw kelp was further dried for 12 h at 105 °C in an oven. This dried raw kelp biomass as well as various chars from pyrolysis and combustion used for extraction were crushed and ground to a size range of −710 μm to +75 μm. The feedstocks were kept in glass containers which were tightly sealed, and placed in a desiccator until use. The following designations are used for samples: raw kelp biomass (RKB), chars obtained from pyrolysis at 300, 450 and 600 °C (PKC-300, PKC-450 and PKC-600 respectively) and that from combustion at 300, 450 and 600 °C (CKC-300, CKC-450 and CKC-600 respectively).

2.2. Pyrolysis and combustion of biomass

A fixed bed pyrolysis reactor system was used to carry out pyrolysis of *S. japonica*. The dimensions of the reactor system are as follows: cylindrical heater with 200 mm height × 170 mm outer diameter and a hollow inner (152 mm height × 70 mm diameter) with a 30 mm width lagged area in which is a cylindrical quartz reactor (260 mm height × 60 mm diameter). Nitrogen gas flow of 200 mL/min was ensured to maintain anaerobic conditions of the reactor. Pyrolysis was achieved from room temperature to different set temperatures (300, 450, and 600 °C) at a heating rate of 10 °C/min. The holding time at each final temperature was 60 min. A K-type thermocouple was positioned in the middle to measure the internal reactor temperature during pyrolysis. The cylindrical quartz reactor was charged with 20 g of the biochar precursor prior to pyrolysis. Products of pyrolysis reactions were separated into three phases namely biochar, bio-oil and bio-gas. The vapor products released were separated into condensable liquid (bio-oil) or non-condensable gas (bio-gas) after passing through the condenser connected to a water thermostat circulator at about −4 °C. The yield of recovered biochar and bio-oil were determined gravimetrically by weighing, after reaching room temperature whiles the bio-gas yield was calculated by mass balance in the system. The biochars were preserved in an air tight 70 mL borosilicate glass vials and used for extraction experiments.

An electrical programmable controller muffle furnace, NOVA Series SP570 designed by Samheung Energy (Model SH-MF2C, Sejong, South Korea) was used for the combustion of *S. japonica*. The volume of the furnace was 4200 cm^3. During combustion, 20 g of dried biomass in 450 cm^3 porcelain crucible was burned at the center of the furnace with the furnace door opened. Combustion was achieved from room temperature to different set temperatures (300, 450, and 600 °C) at a heating rate of 10 °C/min with a 60 min holding time at each final temperature. The yield of remaining char in crucible was computed after cooling in a desiccator to room temperature and samples preserved as in the case of pyrolysis for extraction experiment.

Thermogravimetric analysis was carried out using 10.0 ± 0.5 mg of dried raw kelp seaweed to understand the thermal decomposition and the weight percent of each resulting mass change as a function of temperature. Each experiment was carried out from 30 °C to the set temperature at a constant rate of 10 °C/min using a TG analyzer (Model TGA/SDTA 851e, Mettler Toledo, USA). An inert atmosphere of pure nitrogen at a flow rate of 100 mL/min was used.

2.3. Minerals extraction

The experimental scheme including crushing, thermal pretreatment, leaching, filtration, concentration, crystallization and drying among other operations are shown in Fig. 1. A 10 g sample of raw dried biomass, pyrolysed and combusted chars were weighed into separate 200 mL vials containing 100 mL of deionized water. Using a shaking incubator (Model VS-8480SF, Vision Scientific, Korea) at 150 rpm and 30 °C for 2 h, maceration was done. Supernatant solutions and solid residues were separated by vacuum filtration with an electric aspirator (Model VE-11, Lab Companion, Korea) and a filtration apparatus (Nalgene®, Waltham, USA) through 0.3 μm Whatman filter paper. The filtrate was heated in silicone oil bath at 135 °C to facilitate rapid

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