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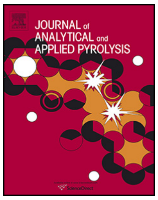

Feasibility of *Laminaria japonica* as a feedstock for fast pyrolysis in a bubbling fluidized-bed reactor

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ABSTRACT

Laminaria japonica, brown algae, was used as a feedstock for fast pyrolysis in a bubbling fluidized-bed (BFB) reactor by manipulating the pyrolysis temperature, feeding rate, and ratio of the fluidizing velocity to the minimum fluidizing velocity (U/U_{mf}), which exhibited optimum operating conditions of a feeding rate of 600 g/h, a U/U_{mf} of 18.3 and a pyrolysis temperature of 425 °C. The maximum yield of *L. japonica*-derived bio-oil (approximately 35 wt%) was lower than that of lignocellulose. When fractionated, the *L. japonica*-derived bio-oil was found to be composed of several major compounds, including cyclic aliphatic compounds, which were very different from aromatic molecules, the major compounds of lignocellulose-derived bio-oil.

1. Introduction

The depleting levels of fossil fuels and global climate change have initiated the development of sustainable sources of biofuels and biochemicals. Among biomass resources, including plants and crops, lignocellulose has been studied to produce valuable platform chemicals [1–4]. Due to several issues related to biomass resources obtained from the land, including the use of vast amounts of land and the irrigation required for cultivation [5–7], marine macroalgae, particularly brown algae, have been suggested as a potential resource, especially considering that the use of marine macroalgae avoids the issues associated with land biomass [8]. The possible mass production of brown algae also supports their industrial use: for example, the annual production capacity of *Laminaria japonica* (LJ), a typical brown alga, in Republic of Korea was roughly estimated to be 285 kt in 2008 [9]. Macroalgae grow rapidly in nature, absorbing phosphorous and nitrogen compounds [10,11], which facilitates the minimization of the energy input and the cost of the nutrient supply. Depending on the species, brown algae contain a high carbohydrate fraction composed of alginic acid, laminarin, mannitol and fucoidan, of which the proportions are 10–40 wt%, 2–34 wt%, 5–25 wt% and 5–20 wt%, respectively [11–14].

Recently, there have been a number of studies on the pyrolytic conversion of brown algae [12,15,16], where the performance of the pyrolysis process of brown algae was assessed using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and thermogravimetry (TG), by which the identification of reaction products and the kinetics study were accomplished. Four major carbohydrates exhibited different thermal degradation behaviors, producing furfural from alginate, 5-methyl-2-furancarboxyaldehyde from fucoidan, 1-(2-furanyl) ethanone from mannitol, and 1,2-cyclopentanedione and 2-hydroxy-3-methyl-2-cyclopenten-1-one from laminarin [12]. In addition, a packed tube reactor was used to produce a 37.5–47.4 wt% bio-oil yield at 300–600 °C [17]. However, the fast pyrolysis of brown algae in a fluidized-bed reactor, which may be useful for industrial applications, has not much been investigated.

In this study, we performed the fast pyrolysis of brown algae, *Laminaria japonica* (*L. japonica* or LJ) using a bubbling fluidized-bed (BFB) reactor. Three operating parameters, the feeding rate, gas velocity, and reaction temperature, were optimized and the effects of these parameters on the fast pyrolysis performance were investigated. The thermal decomposition of *L. japonica* was studied using a thermogravimetry (TG). The bio-oil produced using the BFB reactor

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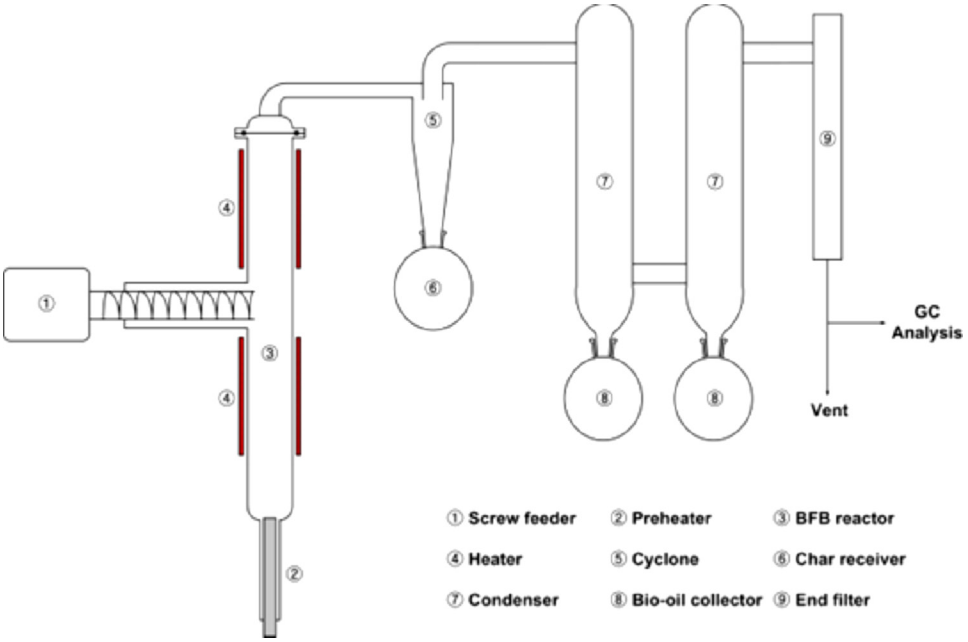

Fig. 1. Schematic of the fast pyrolysis system.

was fractionated into three phases whose chemical compositions were identified using a gas chromatography/mass spectrometry (GC/MS). The properties of *L. japonica* and its pyrolyzed products were compared to those of lignocellulose, i.e., oak sawdust (OS) in this case. Based on these observations, we attempted to assess the feasibility of a fast pyrolysis process of brown algae.

2. Material and methods

2.1. Sample preparation

L. japonica (LJ), harvested from wild stock in June, was supplied from Wan-do located on the southern coast of the Republic of Korea. Raw LJ was crushed and sieved into a particle size range between 50 and 250 μm. Oak sawdust (OS) was purchased by SL Trading (Yesan-gun, Korea) and used as representative lignocellulosic material in fast pyrolysis. Raw OS was sieved and particles of size ranging between 250 and 710 μm were used. Prior to the fast pyrolysis experiments, biomass powders were dried in an oven at 105 °C overnight.

2.2. Sample characterization

A proximate analysis was conducted to determine the contents of water, volatile matters, fixed carbon and ash in the LJ. The compositions of C, H, N, O, and S in the sample were measured using an automatic elemental analyzer (Flash EA1112), subsequently followed by the calculation of the H/C and O/C ratios. Inorganic elements including alkali and alkaline earth metals were analyzed using an atomic absorption spectrophotometer (Thermo Electron Corp.) and an inductively coupled plasma spectrometer (ICP) with optical emission spectrometry (Thermo Electron Corp.). Higher heating values (HHV) were theoretically calculated using Dulong's equation based on the elemental analysis results [18]. In order to observe the major thermal decomposition of *L. japonica* and determine the operating temperature for the pyrolysis processes, thermal gravimetry results (TA instruments, TGA 2000) were obtained by heating the powder from room temperature to 900 °C at a ramping rate of 5–20 °C/min under a nitrogen flow (30 mL/min) using a sieved dry powder (20.0 ± 1.0 mg, <100 μm).

2.3. Fast pyrolysis in a bubbling fluidized bed reactor

The fast pyrolysis system used in this study consists of a screw feeder, two heaters, a bubbling fluidized bed (BFB) reactor, a cyclone, two condensers, and a filter (Fig. 1). The BFB reactor was made from SUS 306 stainless steel pipe with a height of 400 mm and an inner diameter of 50 mm. The dry LJ powder was continuously fed into the BFB reactor using a screw feeder with a maximum feed rate of 700 g/h. The reaction temperature of the BFB reactor was maintained by two heaters which were manipulated with a PID temperature controller. Nitrogen, as a fluidizing gas, was introduced into the reactor through a preheater to minimize the heat loss during the pyrolysis process. The fluidized bed was filled with sea sand (100 g, with a mean particle diameter of 180 μm, Kanto). The minimum fluidizing gas velocity (U_{mf}) was experimentally determined by measuring the pressure difference between the inlet of the fluidizing gas and the reactor exit. This was determined to be 0.028 m/s under ambient conditions in this study. The product stream from the top of the reactor was first passed through the cyclone to remove solid particles including char and ash. Two glass condensers were then connected in a series to cool the hot gas stream and collect pyrolysis vapors, where the temperature at the exit of the condensers was approximately 10 °C. Non-condensable aerosols were recovered using an end filter. The experiments were repeated at least twice at the same pyrolysis temperature, and the experimental error was less than 0.5%, which indicated the reproducibility of the data.

In order to optimize the operating parameters for fast pyrolysis in the BFB reactor, the pyrolysis temperature (400–500 °C), the ratio between the fluidizing gas velocity and the minimum fluidizing gas velocity ($U/U_{\mathrm{mf}} = 5–28$), and the feeding rate (400–700 g/h) were adjusted. Collected char and bio-oil were weighed for the calculation of the solid and liquid yields, while the gas yield was calculated from the overall material balance. It is important to note that all of the yields reported in this work are expressed on the basis of the weight of the LJ sample fed into the reactor. Non-condensable gas products, including H_2, CO, CO_2 and C_1–C_4 hydrocarbons, were also measured using a gas chromatography (Younglin, 600D).