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Steam co-gasification of brown seaweed and land-based biomass

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ABSTRACT

Alkali and alkaline earth species in biomass have self-catalytic activity on the steam gasification to produce hydrogen-rich gas. In this study, three types of biomass, i.e., brown seaweed, Japanese cedar, apple branch containing different concentrations of alkali and alkaline earth species, and the mix of both of them were gasified with steam in a fixed-bed reactor under atmospheric pressure. The effects of reaction temperature, steam amount and mixing ratio in co-gasification on gas production yields were investigated. The results showed that higher gas production yields (especially for H_2 and CO_2) were obtained when the brown seaweed was used than the other two types of biomass since the ash content in brown seaweed was much higher than in land-based biomass and contained a large amount of alkali and alkaline earth species. The yield of hydrogen increased with an increase in the amount of steam, but excessive steam use reduced the hydrogen production yield. From the co-gasification experiments, the gas production yields (especially for H_2 and CO_2) from the land-based biomass increased with the increase in brown seaweed ratio, suggesting that the alkali and alkaline earth species in brown seaweed acted as the catalysts to enhance the gasification of land-based biomass in co-gasification process.

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1. Introduction

With the depletion of fossil fuel sources as well as the global warming issues, much attention has been paid to those renewable energy sources such as biomass which can be converted to clean fuels via thermo-chemical and biochemical routes [1,2]. Among all biomass thermochemical conversion processes, gasification is considered one of the promising ways carried out at high temperatures to convert the energy content of biomass into a more practical and clean fuel, which can be used for synthesis of methanol and other liquid fuels by Fischer-Tropsch synthesis, chemical production, and electricity generation (turbine, gas engine or fuel cell) [3-5]. However, in biomass gasification, significant amounts of tar generally generated together with syngas should be removed out from the gas lines. In fact, tar can condense into more complex structures and can be difficult to remove [6–8]. To date, it is found that steam gasification of biomass can produce a gaseous fuel with a relatively higher H₂ content having relatively low tar content [9]. A large number of papers have been published dealing with the gasification of various land-based biomass, including sawdust [10], cedar wood [11], camphor wood [12], pine wood [13], rice straw [14], white oak [15], and so on. Besides land-based biomass, seaweeds (macroalgae) are gaining increasing interest as a feedstock for sustainable fuel production. Some seaweeds really have numerous advantages over other land-based biomass for the following reasons: high growth rate, high mass productivity per area, no need for internal transport of nutrients or water and no competition with food production [16]. Many researches in energy and fuels relating to algae have been devoted towards methane production and biodiesel production from microalgae, and very few studies have investigated the conversion of macroalgae to syngas by gasification which can be used directly for energy production [17,18]. Seaweeds can be subdivided into three broad groups, namely, red algae, brown algae and green algae, based on their pigmentation [19]. Among different types of seaweeds, brown seaweed has relatively low protein content but is very rich in carbohydrate content. This feature of brown seaweeds may be useful in carbonization process [20]. In addition, seaweed has high ash content which contains larger amount of alkali and alkaline earth species than land-based biomass [21,22]. It is well known that the gasification activity of carbon in carbonaceous materials can be greatly enhanced by various alkali and alkaline earth metal compounds [23–28]. Several studies also indicated that alkali and alkaline earth species such as K and Ca play a key role in the formation of active sites for the surface

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carbon gasification reaction. It can reduce tar production by means of either stopping tar formation initially or catalyzing tar decomposition and decreasing the formation of char [27].

Recently, co-gasification of coal and biomass has been widely studied. Brown et al. [29] investigated the catalytic activity of alkalirich biomass on co-gasification of coal and switchgrass and found that switchgrass, especially switchgrass ash, which contains large quantities of potassium, displayed excellent catalytic activity in coal gasification. Howaniec et al. [30] investigated the synergy effect of steam cogasification of coal and biomass and found that the observed synergy effect was mainly attributed to the catalytic effect of K₂O present in the ash blend. However, few studies are related to the co-gasification of land-based biomass and seaweeds. Particularly, the effect of alkali and alkaline earth species in seaweed ash on the gasification of landbased biomass has not been explored. Large quantities of alkali and alkaline earth species contained in the brown seaweed may provide a potential source of inexpensive catalysts in the co-processing of landbased biomass and brown seaweed. In the present study, the steam gasification of brown seaweed (Sargassum horneri), land-based biomass (Japanese cedar and apple branch) and mixed biomass between brown seaweed and Japanese cedar was carried out, and the effects of varying the gasification operating parameters on gas production yields were investigated and discussed. The objective was to clarify the promoting effects of seaweeds on the gasification of land-based biomass.

2. Experimental

2.1. Materials

Brown seaweed (*S. horneri* (Turner) C.Agardh), apple branch and Japanese cedar obtained from Aomori Prefecture, Japan were used as biomass samples. Brown seaweed was first washed in fresh water to remove the impurity adhered on the surface and dried in an oven at 105 °C before storage and further use; apple branch and Japanese cedar were also dried at the same conditions. Proximate analyses were performed according to ASTM D7582 standards, while ultimate analyses were conducted using Vario EL cube elemental analyzer. The compositions of biomass ash after calcination at 800 °C for 3 h in air

were analyzed by XRF analysis (Energy Dispersive X-Ray Spectrometer, EDX-800HS, Shimadzu).

2.2. Steam gasification of biomass

Steam gasification of biomass was carried out by using a fixed-bed reactor with an internal diameter and a length of 18 and 350 mm, respectively. A schematic diagram of the experimental setup is shown in Fig. 1. For each run, 0.6 g of oven-dried biomass was loaded into the vertical fixed-bed reactor. The reactor was placed inside an electrical furnace, which provided the heat for reactions. The heater was started at room temperature with a heating rate of 20 °C/min and held at the desired temperature. The reactions were performed at atmospheric pressure with a temperature in the range of 650-750 °C. Water was introduced by peristaltic pump into a vaporization furnace (250 °C) and then was carried to the reactor by argon (carrier gas) with flow rate of 50 cm³/min. In our previous study [31], it is found that the gas yield after 2 h reaction was very low. Therefore, in this study, the reaction time was fixed at 2 h for each test. The gases produced were passed through a cold trap and collected in a gas bag. The gas compositions were analyzed using a gas chromatograph (Agilent 7890A GC system), in which one TCD with 3 packed columns (1 molecular sieve $5A \operatorname{column} + 1 \operatorname{HayeSep} O \operatorname{column} + 1 \operatorname{molecular sieve} 5A \operatorname{column}$ was for the separation of CO, CH₄ and CO₂ using He as carrier gas while the other TCD with a molecular sieve 5A for H₂ measurement using Ar as the carrier gas. The carbon content in the remained char was estimated by using the elemental analyzer.

For the cogasification process, gas production yield was compared with the predicted yield of gas production (Y_{pred}), which was the total yield when the two kinds of biomass were separately gasified. Predicted production yield was calculated as follow:

$$Y_{\text{pred}} = X_{\text{bio1}} \times Y_{\text{bio1}} + (1 - X_{\text{bio1}}) \times Y_{\text{bio2}} \tag{1}$$

where X_{bio1} is the mass fraction of biomass 1 in the mix sample while Y_{bio1} and Y_{bio2} are gas or char production yields from biomass 1 and biomass 2 when they were separately gasified, respectively.



Fig. 1. Schematic diagram of a fixed bed steam gasification system.

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