Catalytic conversion of *Laminaria japonica* over microporous zeolites

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ABSTRACT

The catalytic pyrolysis of *Laminaria japonica* was carried out over four different microporous zeolite catalysts, HZSM-5 (SiO_2/Al_2O_3 = 23, 80), HBETA (SiO_2/Al_2O_3 = 25) and HY (SiO_2/Al_2O_3 = 30). The effects of the catalysts on the properties of the resulting pyrolysis products were examined. Py-GC/MS (pyrolysis gas chromatography/mass spectrometry) was used to compare the composition of the bio-oils obtained from the non-catalytic and catalytic pyrolysis. Catalytic upgrading decreased the oil yield but increased the gas yield. The composition of bio-oil was changed to a large extent by catalytic upgrading. Among the oxygenate species contained in the bio-oil, the contents of 1,5-anhydro-d-mannitol and 1,4-anhydro-d-galacitol were reduced considerably by catalytic upgrading, whereas the proportions of furans and cyclopentanones were increased. The formation of high value-added aromatics was enhanced considerably by catalytic upgrading, which was attributed to the acid characteristics of the zeolite catalysts. HZSM-5 (SiO_2/Al_2O_3 = 23), which had the strongest acid sites, showed the highest selectivity for aromatics production.

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1. Introduction

The world is facing an energy crisis caused by the increasing demand for fossil fuels and corresponding price rises, requiring the development of new and sustainable energy resources. Biomass is the most widely exploited renewable energy resource [1–9]. Biomass refers to organic matter that originates from photosynthesis, and includes animals, plants and microorganisms on land and in water. The pyrolysis of various types of biomass to energy products has been studied widely [1–15].

Algae are photosynthetic plants that can be divided into microalgae and macroalgae according to their ecological characteristics. Macroalgae show much higher growth rates than other plants, and can be harvested 4–6 times each year in subtropical regions. Another advantage of macroalgae is that they can be cultivated in the sea, resulting in much higher productivity per unit area (565 ton/ha) than that of land plants (9 ton/ha). In addition, macroalgae require less expensive resources, such as fresh water, land and fertilizer. Furthermore, the level of CO_2 absorption by macroalgae is 36.7 ton/ha/year, which is 5–7 times higher than that of lignocellulosic biomass.

Laminaria japonica is a brown algal species. Approximately 30–67% of the dry mass of brown algae is carbohydrates, composed mainly of alginate, laminaran, mannitol and fucoidan, whose fractions vary depending on the harvest time and species. *L. japonica* absorbs more than twice the amount of CO_2 than tropical rainforest and has the highest primary productivity among all photosynthetic plants on Earth [16–18]. Therefore, application of *L. japonica* to the production of bio-fuel is important for the development of new renewable energy sources.

Pyrolysis refers to the process, in which biomass polymer is decomposed to low-molecular-mass species by heat under an oxygen-free atmosphere. The liquid product obtained from the pyrolysis of biomass is called bio-oil, whose yield is generally 50–65 wt% depending on the type of biomass pyrolyzed. Compared to conventional liquid fuels, however, bio-oil has several shortcomings including low heating value, high oxygen content, high acidity (pH <2.3) and large viscosity, all which deteriorate the fuel quality.

Catalytic upgrading is the most common method to upgrade bio-oil and can be operated under atmospheric pressure leading to a low operation cost. Recently, a range of zeolite catalysts, such as HZSM-5, HY and HBETA, have been applied to the catalytic pyrolysis of biomass to examine their effects on the product selectivity and energy efficiency [19–21]. On the other hand, the catalytic pyrolysis of macroalgae has rarely been reported despite their large potential as a bio-fuel. Therefore, the catalytic pyrolysis of macroalgae for the production of upgraded bio-oil is worthy of investigation.

In this study, four different microporous zeolite catalysts, HZSM-5 (SiO_2/Al_2O_3 = 23, 80), HBETA (SiO_2/Al_2O_3 = 25) and HY (SiO_2/Al_2O_3 = 30), were used for the catalytic pyrolysis of *L. japonica* to determine the effect of catalytic upgrading on the bio-oil quality.

2. Experimental

2.1. L. japonica

The ultimate and proximate analyses of *L. japonica* are reported elsewhere [17]. The sample was pulverized and sieved with standard mesh to a mean particle size of 0.6–1.0 mm. To minimize the moisture condensed onto the pyrolysis product, the sample particles were dried in an oven at 80 °C for more than 48 h before the pyrolysis experiments. A 5.0 g sample was used for each experiment.

2.2. Catalysts

The zeolite catalysts, HZSM-5 (SiO_2/Al_2O_3 = 23, 80), HBETA (SiO_2/Al_2O_3 = 25) and HY (SiO_2/Al_2O_3 = 30), were purchased from Zeolyst International. The specific surface areas and SiO_2/Al_2O_3 ratios of these catalysts were provided by the company. NH_3-TPD (NH_3-Temperature programmed desorption) experiments were performed to compare the acid characteristics of the catalysts. Prior to each measurement, samples were treated in a He stream at 450 °C. After cooling to 100 °C, NH_3 adsorption was performed. After purging samples in the He stream for 1 h to completely remove the physically adsorbed NH_3, the catalysts were heated from 100 °C to 700 °C at a rate of 10 °C/min. The desorbed NH_3 was detected using a TCD (thermal conductivity detector).

2.3. TGA (thermogravimetric analysis)

A thermogravimetric analyzer (TGA Pyris 1, Perkin Elmer) was used to determine the volatilization temperatures of the moisture and volatile fraction of *L. japonica* and examine the thermal decomposition characteristics. A ~6 mg sample was used for each analysis. N_2 gas with a flow rate of 40 mL/min was used as the purge gas, while N_2 gas at a flow rate of 20 mL/min was used as the sample gas. During the analysis, the temperature was increased to 700 °C at a heating rate of 20 °C/min.

2.4. Pyrolysis reactor and reaction conditions

The pyrolysis experiments were carried out using a batch-type fixed-bed reactor. The catalytic reactor was consecutively installed at the latter part of the main pyrolysis reactor. The main pyrolysis reactor was a quartz reactor into which the *L. japonica* (5.0 g) was charged. The fixed catalyst bed reactor was a tubular quartz type reactor which was filled with 0.5 g of catalyst. All the catalysts were pelletized, crushed and screened with standard sieves (1.7–2.4 mm) prior to their use in the experiments. For non-catalytic pyrolysis, the catalyst was replaced with quartz beads to maintain the same space velocity within the fixed catalyst bed. Prior to the experiments, all the experimental systems were purged with inert nitrogen, at a flow rate of 50 mL/min, for 1 h. Both reactors were indirectly heated electrically to the desired reaction temperature. Thereafter, the pyrolysis and upgrading reaction continued for 1 h. The carrier gas was N_2 and its flow rate was 50 mL/min. The temperatures of the experimental systems were adjusted using a PID (proportional-integral-derivative) temperature controller and monitored with two thermocouples (K type). The errors in the average reaction temperatures were within ±5 °C. Condensable bio-oil was collected in a glass condenser cooled to a temperature of −25 °C, using a circulator (RW-2025G, JEIO TECH), with ethyl alcohol as the cooling solvent. The non-condensable gases passing through the quenching system were sampled using Teflon gasbags, at 30 min intervals, with their compositions then analyzed. The experiments were conducted at least three times for each catalyst to confirm the reproducibility of the reported procedures. Mass balance for all experiments was calculated as follows: char (wt.%) + bio-oil (wt.%) + gas (wt.%) = 100. The reproducibility of the runs was above 97%.

2.5. Analysis of pyrolysis products

The gaseous products were analyzed by GC (gas chromatograph) (ACME 6000, Young Lin Instrument Co., Ltd) with a TCD and an FID (flame ionization detector). CO, CO_2, H_2 and CH_4 were analyzed using the TCD equipped with a Carboxen 1000 column (15 ft × 1/8 in), whereas the hydrocarbons were analyzed using the FID equipped with an HP-plot Al_2O_3/KCl column (50 m × 0.322 m × 8.00 μm). The moisture content of the bio-oil was quantified using a Karl Fischer titrator (Metrhom 870 KF Titrino) using the ASTM E203 method. HYDRANAL Composite 5 K (Riedel-de Haen) and methanol were used as the titrant and solvent, respectively.

2.6. Py-GC/MS (pyrolysis gas chromatography/mass spectrometry) analysis of bio-oil

The vapor-phase product upgraded indirectly by a single-shot pyrolyzer (Frontier-Lab Co., Py-2020iD) was introduced into a GC/MS apparatus for composition analysis. The temperature of the pyrolyzer was set at 500 °C. For the Py-GC/MS experiments, 2 mg of the *L. japonica* sample was placed at the bottom of the sample cup and covered with an intermediate quartz wool layer. 2 mg of the catalyst layer was laid over the quartz wool layer so that the vapor-phase pyrolysis product could be upgraded as it passed through the catalyst layer. Analysis was performed with a metal capillary column (Ultra ALLOY-5MS/HT; 5% diphenyl and 95% dimethylpolysiloxane; length: 30 m; i.d.: 0.25 mm; film thickness: 0.5 μm). Each experiment was repeated at least three times. The contents of the analyzed products were summarized as peak area %.

3. Results and discussion

3.1. Characteristics of the catalysts

Table 1 lists the physical characteristics of the catalysts. The specific surface areas of the HZSM-5 (SiO_2/Al_2O_3 = 23), HZSM-5 (SiO_2/Al_2O_3 = 80), HBETA, and HY catalysts were 425 m^2/g, 420 m^2/g, 680 m^2/g and 780 m^2/g, respectively. The order of the pore size was HY (0.74 nm) > HBETA (ca. 0.66 nm) > HZSM-5 (ca. 0.55 nm). NH_3-TPD analyses were performed to examine the acid characteristics of the catalysts, whose results are shown in Fig. 1. All 4 catalysts have weak acid sites represented by peaks appearing at approximately 225 °C. The peaks appearing at approximately 350 °C indicate that HY and HBETA have medium-strength acid sites. HZSM-5 has strong Brönsted acid sites [22], which are represented by the peak appearing at approximately 400–450 °C. Fig. 1