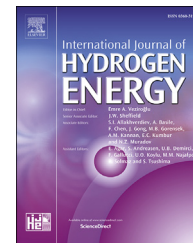


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Catalytic co-pyrolysis of polypropylene and *Laminaria japonica* over zeolitic materials

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ABSTRACT

Catalytic co-pyrolysis of polypropylene and *Laminaria japonica* was carried out using Py-GC/MS and a fixed-bed reactor over different catalysts: HZSM-5, mesoporous MFI, Pt/mesoporous MFI, and mesoporous Al-SBA-16. The contents of oxygenates, acids, and wax species were reduced substantially by catalytic upgrading, whereas the contents of aromatics and light hydrocarbons in the gasoline and diesel range were significantly increased, enhancing the economic value of the bio-oil. Among the catalysts used in this study, Pt/mesoporous MFI showed the highest catalytic upgrading capability, which was attributed to large pore size, strong Brønsted acid sites, and the catalytic effect of added Pt.

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Introduction

Nowadays, climate change and energy have been regarded as the most important issues to be studied [1,2]. In this regard, a number of different biomass materials have been attracting significant attention as an alternative energy, chemical and material resource replacing fossil fuels [3–6]. Various biofuels such as bioethanol [7], bio jet fuel [8], bio-oil [9,10], biogas [11–13], biochar [14–16] and biochemicals can be produced

from biomass. These biofuels can be produced using various methods, such as fermentation, transesterification, pyrolysis, and gasification. Among them, fast pyrolysis is a method which maximizes the yield of liquid bio-oil [17–19]. Bio-oil has a higher energy density and is easier to be transported than the feedstock biomass. A number of different biomass materials can be used for pyrolysis: lignocellulose (wood, grass, etc.), agricultural residue, waste sludge, microalgae, macroalgae, and waste wood material (construction waste, waste furniture, etc.). Nevertheless, biomass is inferior to

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petroleum-derived liquid fuels in terms of the fuel quality. For example, bio-oil has relatively large oxygen content ranging 30–40%, and its pH is very low (~2), making it very corrosive [17–19]. In addition, bio-oil has a lower heating value (about 19 MJ/kg) and a higher viscosity, limiting its fluidity, than those of petroleum-derived fuels [17–19]. Various techniques have been suggested to enhance the fuel quality of bio-oil, one of which is catalytic pyrolysis [20–22]. During the catalytic pyrolysis of biomass, deoxygenation reactions take place resulting in a lower oxygen content of bio-oil and acids are removed leading to a higher pH. The heating value of bio-oil is also increased by catalysis. One important drawback of catalytic pyrolysis is that dehydration, one of the deoxygenation reactions, leads to an increase in the water content in bio-oil. In addition, the oxygen content is still much higher (about 10–20%) than that of petroleum-derived fuels.

Another promising method to enhance the fuel quality of bio-oil is to pyrolyze biomass together with an organic material containing lots of carbon and hydrogen. Plastics consist mostly of carbon and hydrogen. Pyrolysis oil obtained from plastics is known to have similar properties with petroleum-derived fuels depending on the catalyst used: gasoline-range fuel (e.g., HZSM-5 and mesoporous MFI) and diesel-range fuel (e.g., mesoporous Al-SBA-16). Therefore, co-pyrolysis of biomass and a plastic material can significantly increase the carbon and hydrogen contents in bio-oil, resulting in improved fuel quality of bio-oil [23–26]. Miskolczi et al. [23] found that the yields of undesired oxygen containing pyrolysis products were decreased by the co-pyrolysis of poly-lactic-acid biopolymer and organic waste with HDPE. Brebu et al. [25] reported the thermal decomposition properties and product yields of grape seeds and PE by feeding their mixture and discussed their interaction during the pyrolysis. Synergetic formation of aromatic hydrocarbons was the main target of the catalytic co-pyrolysis of plastics and biomass over microporous catalysts such as HZSM-5 [25].

Recently, the pyrolysis of seaweed was intensively investigated by many researchers because its growth rate is faster than those of other land plants [17,19]. Lorenzetti et al. [26] reported that large amounts of aromatic hydrocarbons can be obtained from the catalytic pyrolysis of seaweed over HZSM-5 with high denitrogenation effect for nitriles, amines and amides. However, a large amount of coke was indicated as the problem. Lee et al. [27] achieved an increased yield of aromatic hydrocarbons via the catalytic co-pyrolysis of seaweed and PP over mesoporous Al-SBA-15 and they pointed out that the pore size of the catalyst is an important factor for enough reaction in the catalyst pores. Another candidate catalyst for the catalytic co-pyrolysis of seaweed and plastics is mesoporous MFI because it has larger pore size than HZSM-5 and its acidity is also relatively high [28]. However, its use for the catalytic co-pyrolysis of seaweed and plastics has not been reported yet. Therefore, its catalytic performance for the production of value added fuels via catalytic co-pyrolysis needs to be investigated.

In this study, thermal and catalytic co-pyrolysis of polypropylene (PP) and *Laminaria japonica* over four different catalysts, microporous HZSM-5, mesoporous Al-SBA-16 and MFI, and Pt/mesoporous MFI, was carried out using various kinds of analytical systems. Thermogravimetric (TG) analysis was

applied to examine the thermal behaviors observed from the non-isothermal pyrolysis of PP, *L. japonica*, and their mixture. The yields of gas, oil, and char and their detailed chemical compositions were obtained from isothermal fast pyrolysis reactions using a fixed-bed reactor and pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS), respectively. Results obtained from this study will be used as valuable information to produce hydrocarbons, one of important hydrogen carriers, via the pyrolysis, one of the thermal conversion technologies.

Experimental

Feedstock for pyrolysis

According to the proximate analysis of *L. japonica* sample, the contents of moisture, volatile matter, fixed carbon, and ash were 7.65 wt%, 53.10 wt%, 10.97 wt%, and 28.28 wt%, respectively. Volatiles comprised the majority of PP sample (99.8 wt %) and the remainder (0.2 wt%) was ash. Elemental analysis showed that *L. japonica* consisted of 30.60 wt% C, 4.89 wt% H, 62.44 wt% O, 1.51 wt% N, and 0.54 wt% S, whereas PP consisted of only 85.4 wt% C and 14.6 wt% H.

Catalysts

Microporous HZSM-5 was purchased from Zeolyst International. Mesoporous MFI and Al-SBA-16 were synthesized and 0.5 wt% Pt-impregnated mesoporous MFI (0.5 wt% Pt/mesoporous MFI) were prepared according to the procedures reported in previous studies [29,30]. To examine the properties of the catalysts, temperature-programmed desorption of NH₃ (NH₃-TPD) and N₂ adsorption–desorption were measured according to the procedures reported in a previous study [29]. Detailed experimental procedures for the preparation and characterization of the catalysts are shown in Supplementary Information.

Pyrolysis experiments using TGA

To investigate the non-isothermal decomposition behaviors of feedstocks over catalysts, TG analysis was performed using a TG analyzer (Perkin Elmer Pyris 1, USA). For this, 10 mg of PP, *L. japonica* and their mixture (1:1) were heated from ambient temperature to 600 °C at a heating rate of 10 °C/min under a 30 mL/min of nitrogen gas.

Pyrolysis experiments using a fixed-bed reactor

Isothermal pyrolysis experiments of feedstocks were performed using a U-type quartz fixed-bed reactor, which is the same instrument used in a previous study [31], under oxygen-free conditions. The reactor was purged for 30 min using N₂ gas (50 mL/min) prior to each experiment. A constant temperature 500 °C and a uniform N₂ flow of 50 mL/min were maintained during each experiment that lasted 1 h. For each experiment, 5 g of feedstock sample was used: either 5 g of *L. japonica* or a mixture of 2.5 g of PP and 2.5 g of *L. japonica*. For catalytic pyrolysis, the catalyst/sample ratio of 1/10 was used.

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