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Catalytic pyrolysis of mandarin residue from the mandarin juice processing industry

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HIGHLIGHTS

- Catalytic pyrolysis of mandarin residue was performed using zeolites.
- HZSM-5 produced more aromatics from mandarin residue than from woody biomass.
- Ga/HZSM-5 increased further the production of valuable aromatics.

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ABSTRACT

In this study, the catalytic pyrolysis of mandarin residue from the mandarin juice processing industry was carried out using pyrolysis gas chromatography/mass spectroscopy and employing microporous zeolite catalysts, HZSM-5 (SiO_2/Al_2O_3 = 23 and 80) and HBeta (SiO_2/Al_2O_3 = 25). The effect of acidity of the catalyst was investigated by comparing the activity of two HZSM-5 catalysts with different SiO_2/Al_2O_3 ratios. The effect of catalyst structure was explored by comparing the results obtained using HZSM-5 (23) and HBeta. Most oxygenates produced from non-catalytic pyrolysis were removed by catalytic upgrading, whereas the yields of mono-aromatics, which are important feedstock materials for the chemical industry, increased considerably, improving the quality of the bio-oil produced. HZSM-5 (23), having the highest acidity among the catalysts used in this study, showed superior catalytic activity to those of HZSM-5 (80) and HBeta. Pt/HZSM-5 (23) and Ga/HZSM-5 (23) resulted in an even higher yield of aromatics.

1. Introduction

With the growing demand for alternative energy sources that can replace fossil fuels, biomass, including organic wastes, is gaining considerable attention as a sustainable energy source (Subramanian, 2009). Biomass is inherently carbon–neutral: its net greenhouse gas emission is zero.

Rapid growth of the world population and industrial development are causing an increase in the production of various organic wastes. Secondary air pollution problems, such as emissions of odorous substances and methane, can arise when organic wastes are landfilled without appropriate pretreatment. Recovering energy from these organic wastes not only produces energy but also reduces waste disposal.

Depending on the composition of the waste, biochemical and thermochemical processes are usually used to recover energy from organic waste. The biochemical processes include anaerobic digestion and ethanol fermentation of sugar-based biomass, whereas thermochemical processes include pyrolysis, gasification, and combustion (McKendry, 2002). Each process has advantages and disadvantages. Combustion is a simple and easy process to operate but it requires facilities to remove the various air pollutants emitted, such as SO_x, NO_x, and dioxins. High operational costs to maintain the high combustion temperatures are another drawback of combustion. Gasification can be operated at a lower temperature and emits less air pollutants, but large amounts of tar produced during the gasification reaction cause difficulties in the operation, calling

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for an additional tar removal process. Pyrolysis, the aim of which is to produce bio-oil, can also be operated at a lower temperature than combustion. The high moisture content, high viscosity, and acidity of the product bio-oil, however, impede its direct application as a fuel. Additional catalytic upgrading is usually employed to improve the quality of the bio-oil produced from pyrolysis processes (Park et al., 2011, 2012b; Bu et al., 2012; Ko et al., 2012).

In South Korea, an average of 650,000 tons of mandarins are produced annually, 120,000 tons of which are processed to produce mandarin juice. About half of the processed mandarins (60,000 tons) are left as waste residue. Conversion of this waste residue into biofuel would reduce the waste disposal costs as well as generate renewable energy. Pyrolysis of waste residue from grape, tomato, and orange juice production processes has been employed for the production of bio-oil (Aguiar et al., 2008; Encinar et al., 2008; Miranda et al., 2009; Xu et al., 2009; Demiral and Ayan, 2011). Pyrolysis of mandarin waste and mandarin peel was studied previously by the present authors (Kim et al., 2011a,b). Catalytic upgrading of the bio-oil produced from mandarin residue using microporous zeolites, however, has not previously been reported.

In this study, the catalytic pyrolysis of mandarin residue was carried out, for the first time, employing microporous zeolite catalysts. Fast pyrolysis experiments were performed using pyrolysis gas chromatography/mass spectroscopy (Py-GC/MS) for rapid analysis of the composition of the bio-oil produced. The effects of various characteristics of the catalyst on the composition of the bio-oil were investigated.

2. Experimental

2.1. Mandarin residue

To determine the contents of C, H, N and S in the waste mandarin, ultimate analysis was performed using an elemental analyzer (TruSpec, LECO Co., USA) and a sulfur analyzer (SC-432DR, LECO Co., USA). Proximate analysis was performed using a thermo-gravimetric analyzer (pyris1 TGA, Perkin Elmer). The ASTM D2016-74, ASTM E897-82, and ASTM D1102-84 standards were used to determine the moisture, volatile matter, and ash contents. First, 4–8 mg of the waste mandarin sample were heated in the TGA from room temperature to 110 °C under an N_2 atmosphere and then this temperature was maintained for 1 h to determine the moisture content. The volatile matter content was determined by raising the temperature to 900 °C. After changing to an oxygen atmosphere, the temperature was maintained at 800 °C until the sample mass reached an asymptotic value. The total mass change observed at this point was regarded as the fixed carbon content, whereas the remainder was regarded as the ash content.

The mandarin residue used in this study contained 70.5 wt.% volatiles and 14.3 wt.% fixed carbon, which is similar to typical woody biomass. Also, the contents of moisture and ash were 1.2 and 14.0 wt.%, respectively. The contents of C, H, O and N were 36.54, 7.33, 41.64, and 0.49 wt.%, respectively. The nitrogen content was low and sulfur was not detected, indicating good potential to produce a low-emission fuel. The heating value of the mandarin residue was also relatively high (3284.5 kcal/kg).

2.2. Preparation and characterization of catalysts

Two microporous zeolite catalysts, HZSM-5 (SiO_2/Al_2O_3 = 23, 80) (CBV 2314, 8014) and HBeta (SiO_2/Al_2O_3 = 25) (CP814E*) were purchased from Zeolyst International. Hereafter the number in parentheses means the SiO_2/Al_2O_3 ratio. Using the incipient wetness method, HZSM-5 (23) was impregnated with 1 wt.% Ga and 0.5 wt.% Pt using gallium nitrate and $Pt(NH_3)_4(NO_3)_2$, respectively. After the impregnated catalysts were dried in an oven at 110 °C, the temperature was increased to 550 °C at a rate of 3 °C/min under oxygen-free conditions. Calcination was conducted for 4 h under an N_2 atmosphere (Araujo and Schmal, 2000).

The surface area was determined using the Brunauer–Emmett–Teller (BET) equation. The acidity was measured using a BEL-CAT TPD/TPR analyzer (BEL JAPAN INC.) based on the NH_3-temperature-programmed desorption (TPD) method. 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 30 min to completely remove the physically adsorbed NH_3, the catalysts were heated to 100–550 °C at a rate of 10 °C/min. The desorbed NH_3 was detected using a thermal conductivity detector.

2.3. Pyrolysis experiment

The vapor product produced from the catalytic pyrolysis process in a single-shot pyrolyzer (Frontier-Lab Co., Py-2020iD) was introduced into a GC/MS. The temperature of the pyrolyzer was set to 500 °C. After putting 1.5 mg of the mandarin residue onto the bottom of a sample cup and covering it with quartz wool, 1.5 mg of catalyst was laid over the quartz wool layer. In this system, the pyrolyzed vapor product is upgraded when it passes through the catalyst layer. The metal capillary column used for the analysis was an Ultra ALLOY-5 (MS/HT) (5% diphenyl and 95% dimethylpolysiloxane, length 30 m, i.d. 0.25 mm, film thickness 0.5 μm, Frontier Laboratories Ltd. Japan). The product composition was calculated as the peak area%. More detailed information on the experimental procedure can be found in the literature (Heo et al., 2011; Park et al., 2012b; Jeon et al., 2013). The detailed procedure for quantitative analysis of the yields of solid (char + coke), gas, and liquid can be seen in the literature (Ma et al., 2012). The yield of aromatics was quantified using the calibration curves of standards of known concentration.

3. Results and discussion

3.1. Characteristics of the catalysts

Table 1 shows the BET surface areas of the catalysts used in this study. The specific surface area of HZSM-5 was 382 m^2/g. The addition of Pt or Ga decreased the specific surface area of HZSM-5, which might be attributed to partial blockage of the pores of the catalyst. Of the two catalyst types used in this study, HBeta had a larger pore size and specific surface area.

The NH_3-TPD patterns of each catalyst are shown in Fig. 1 and Table 1 to compare the acid properties of the catalysts. The number of acid sites of HZSM-5 increased as the SiO_2/Al_2O_3 ratio decreased (1.47 mmol NH_3/g_{cat} for HZSM-5 (23) and 0.46 mmol NH_3/g_{cat} for HZSM-5 (80)). HZSM-5 showed strong Brønsted acid sites at approximately 410 °C. The number of acid sites of HBeta (1.03 mmol NH_3/g_{cat}) was smaller than that of HZSM-5 (23), but larger than that of HZSM-5 (80). Fig. 1 also shows that the acid strength of HBeta, with a peak at approximately 310 °C, was weaker than that of HZSM-5. Pt/HZSM-5 (23) (1.39 mmol NH_3/g_{cat}) and Ga/HZSM-5 (23) (1.11 mmol NH_3/g_{cat}) catalysts had fewer acid sites than HZSM-5 (23) because Pt and Ga replaced some of the acid sites (Park et al., 2010, 2012a).

3.2. Catalytic pyrolysis

3.2.1. Effect of the SiO_2/Al_2O_3 ratio on the product distribution

A detailed list of the pyrolysis products is provided in the Supporting material (Table S1). The products were divided into several categories (Fig. 2). The composition of the bio-oil is shown to