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Catalytic upgrading of oil fractions separated from food waste leachate

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In this work, catalytic cracking of biomass waste oil fractions separated from food waste leachate was performed using microporous catalysts, such as HY, HZSM-5 and mesoporous Al-MCM-48. The experiments were carried out using pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) to allow the direct analysis of the pyrolytic products. Most acidic components, especially oleic acid, contained in the food waste oil fractions were converted to valuable products, such as oxygenates, hydrocarbons and aromatics. High yields of hydrocarbons within the gasoline-range were obtained when microporous catalysts were used; whereas, the use of Al-MCM-48, which exhibits relatively weak acidity, resulted in high yields of oxygenated and diesel-range hydrocarbons. The HZSM-5 catalyst produced a higher amount of valuable mono aromatics due to its strong acidity and shape selectivity. Especially, the addition of gallium (Ga) to HZSM-5 significantly increased the aromatics content.

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1. Introduction

The generation of organic waste continues to increase. The abandoning, landfilling and ocean disposal of organic waste, such as food waste, livestock excretion, wastewater sludge and butchery waste, has caused severe environmental pollution. Thus, the direct landfilling of organic waste has been banned in a number of countries. Methods for the appropriate treatment of organic waste are being considered in South Korea to limit the ocean disposal of organic waste. In 2006, 13,300 ton/day of food waste was generated in South Korea, resulting in an annual economic loss of about $15 billion (Lee et al., 2009).

Food waste can be treated using various processes, including composting, feedstock production, anaerobic digestion for energy production and pulverization for the production of fuel. While the detailed procedures of these processes vary depending on the purpose of the treatment, dehydration, usually by press rolling, and the removal of impurities are common pre-treatment steps. Water and particulate matter are separated as leachate during the press rolling dehydration stage, with the dehydrated cake sent to a dryer. The leachate is a sludge that contains water, solid particulate matter and oil fractions. Existing food waste leachate treatment processes, without oil separation, result in blocking of the gate screens within water treatment plants with clotted oil. Moreover, there is a build-up of oil layers on the water surface of the aeration tank, hindering the air supply for microorganism breeding. The danger of fire has been a serious problem in the drying process of the sludge separated from food waste leachate due to the oil layer accumulating on the wall of the discharge duct. Therefore, a process to separate oil from food waste leachate has been developed (Kim, 2010). Usually, one liter of leachate contains 5 g of oil fractions, which are mainly composed of animal and vegetable derived oils (Kim, 2010). The oil fractions separated from the leachate can be used as an energy source. At the same time, the oil fractions can be converted to a more useful product, biofuel, which is also an alternative energy source.

Animal and vegetable oils can generally be converted to biodiesel via transesterification, and can also be converted to bio-oils via pyrolysis. The bio-oils produced via biomass pyrolysis can be used as heating fuel, but the fuel quality is low (Park et al., 2010a). Therefore, numerous efforts have been made to produce reformed oils with improved quality, via catalytic reactions of the low-quality bio-oils (Lee et al., 2008; Park et al., 2010b,c). Investigations...
have recently been conducted to produce bio-fuels from vegetable oils via catalytic pyrolysis (Ngo et al., 2010; Ong and Bhatia, 2010; Prado and Filho, 2009). To the best of our knowledge, catalytic pyrolysis has never been applied to the production of valuable oils via the reforming of food waste oil. Also, Al-MCM-48, a mesoporous material with cubic symmetry, has not been applied to the catalytic pyrolysis of biomass, despite its higher catalytic ability than Al-MCM-41 (Park et al., 2008). One objective of this study was to investigate the performance of microporous and mesoporous catalysts, such as HY, HZSM-5 and Al-MCM-48, for the catalytic cracking of oil fractions separated from food waste leachate. Another objective was to increase the fractions of valuable aromatic compounds in bio-oil using HZSM-5 with the addition of Ga.

The experiments were carried out using the Py-GC/MS instrument to allow the direct analysis of the pyrolytic products. Several Py-GC/MS studies have been carried out before using different catalysts (Adam et al., 2005; Lu et al., 2009, 2010; Pattiya et al., 2008). The product distribution after the catalytic reaction was compared to reveal the catalytic effects of different catalysts.

2. Experimental

2.1. Oil fractions separated from food waste leachate

The oil fractions separated from food waste leachate were obtained from the KIER using the normal hexane extractive chemical test. For more details on the procedure for the normal hexane extractive chemical test, one can refer to the literature (Kim, 2010). Pyrolysis tests were performed using a TGA analyzer (PerkinElmer, Pyris 1 TGA). A typical sample mass of 20 mg was heated at 10 K/min, with nitrogen purging, to a final temperature of 873 K.

2.2. Preparation of catalyst

Microporous catalysts, such as HY (Si/Al = 2.6) and HZSM-5 (Si/Al = 15, 40), were purchased from Zeolyst. 1 wt.% Ga was impregnated into HZSM-5 using Ga(NO₃)₃ by incipient wetness method. The impregnated Ga/HZSM-5 catalyst was dried overnight at 110 °C and calcined in air at 550 °C for 4 h, and finally calcined in air at 550 °C for 5 h. The MCM-48 was prepared using the following procedure. First, to prepare pure MCM-48, 10.0 g of CTABr, 1.5 g of Brij-30 and 190.5 g of distilled water were mixed. When the mixture became transparent, 46.13 g of sodium silicate solution (Na/Si = 0.5) was slowly added, drop wise, with stirring. The prepared solution was placed in an oven at 100 °C for 48 h for the reaction to take place. After 48 h, the solution was cooled and its pH adjusted to 10 using 50 wt.% acetic acid. The solution was then placed in the oven at 100 °C for the reaction to take place for a further 48 h. The pH adjusting process was repeated three times. The solution was then washed with distilled water, filtered and dried in the oven for 24 h, which was followed by another washing with ethanol, filtering, drying for 24 h and baking at 550 °C for 4 h. Aluminum incorporation into MCM-48 was performed using the post-synthetic grafting method (Park et al., 2008). Before baking, the prepared mesoporous material was introduced into a solution prepared by dissolving AlCl₃ in 100 mL of ethanol, according to the desired Si/Al ratio. The solution was stirred for 24 h, washed with ethanol, filtered, dried for 24 h and calcined for 4 h at 550 °C.

2.3. Catalyst characterization

The BET surface area of the catalyst was measured using an ASAP 2010 apparatus (Micrometrics). The catalyst sample was dried, with 0.3 g of the dried sample taken, and outgassing under vacuum for 5 h at 250 °C, using nitrogen as the adsorption gas at the temperature of liquid nitrogen. The nitrogen adsorption-desorption isotherms and BET surface area were then obtained. The surface acidities of the catalysts were measured using temperature programmed desorption of ammonia (NH₃-TPD), employing a BEL-CAT TPD analyzer with a TCD detector (Park et al., 2010d).

2.4. Py-GC/MS analyses

A double-shot pyrolyzer (Frontier-Lab Co., Py-2020ID), coupled directly to GC/MS, was used for identification of the catalytic cracking products. For the sample preparation, the food waste oil fraction (1 μl) and catalyst (1 mg) were placed in a sample cup, which was then placed into a 500 °C furnace under a He atmosphere. The gaseous species generated during the catalytic cracking were directly introduced into a GC inlet port (split ratio of 1/100) and onto a metal capillary column (Ultra ALLOY-5MSHT: 5% diphenyl and 95% dimethylpolysiloxane, length 30 m, i.d. 0.25 mm, film thickness 0.5 μm; Frontier Laboratories Ltd., Japan). To prevent condensation of the products, the interface and inlet temperatures were both maintained at 300 °C. The column temperature was programmed to ramp from 40 (5 min) to 320 °C (10 min), at a heating rate of 5 °C/min. The temperature of the GC/MS interface was 280 °C, with the MS operated in the EI mode at 70 eV. The program was run in the scanning range from 29 to 400 amu, at a rate of 2 scans/s. The identification of peaks was performed using the NISTMS library.

The experiments were conducted at least three times for each catalyst to confirm the reproducibility of the reported procedures. The average values of the peak area and peak area% as received were calculated for each identified product.

3. Results and discussion

3.1. Characteristics of oil derived from food waste leachate

The elemental composition of the oil derived from food waste leachate was C 75.45 wt.%, H 13.85 wt.%, N 0.53 wt.%, S 0.01 wt.% and O 10.16 wt.% (by difference). The HHV was calculated following the formula suggested in the literature (Demibras, 1997). As the HHV of the oil (39.52 MJ/kg) was slightly lower than that of soybean oil (40.09 MJ/kg) (Ngo et al., 2010), the oil can be classified as a promising fuel. However, the oil cannot be applied directly to industry due to its high viscosity and high fatty acid content; therefore, an additional process, such as catalytic pyrolysis, will be required for its conversion into a valuable fuel.

To investigate the pyrolytic behavior of food waste leachate, TGA and DTG analyses were carried out (data not shown). When 20 mg of leachate was analyzed using TGA, DTG peaks were observed at 110, 280 and 430 °C, which appeared to be the results of reductions of water, low-molecular-weight hydrocarbons and high-molecular-weight acids, respectively, in the leachate due to pyrolysis. Also, a considerable mass reduction was achieved below 500 °C. Based on this result, the catalytic pyrolysis reactions in this study were conducted at 500 °C.

3.2. Characterization of catalysts

Table 1 shows the physical properties of the catalysts used in this study. HZSM-5 had the smallest surface area, while the surface area of Al-MCM-48 was largest. Zeolite catalysts were shown to have sub-nanometer pores (0.7 nm for HY and 0.5 nm for HZSM-5); whereas, Al-MCM-48 had nano pores (2.97 nm). Fig. 1 shows the TPD results. The number of acid sites on the Al-MCM-48 catalyst was smaller than those of the other catalysts, and Al-MCM-48...
Table 1
Physical properties of catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
<th>Average pore diameter (nm)</th>
<th>Si/Al ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>HY</td>
<td>730</td>
<td>0.74 × 0.74 [1 1 1]</td>
<td>2.6</td>
</tr>
<tr>
<td>HZSM-5 (15)</td>
<td>400</td>
<td>0.51 × 0.55 [1 0 0]</td>
<td>15</td>
</tr>
<tr>
<td>HZSM-5 (40)</td>
<td>425</td>
<td>0.51 × 0.55 [1 0 0]</td>
<td>40</td>
</tr>
<tr>
<td>Al-MCM-48</td>
<td>1380</td>
<td>2.97</td>
<td>20</td>
</tr>
</tbody>
</table>

* Channel diameter viewed along [111] direction.

had weak acid sites that exhibited a maximum peak at about 250 °C. Conversely, the HY catalyst had the largest number of acid sites: weak acid sites with a peak at about 220 °C and medium acid sites with a shoulder peak at about 330 °C. HZSM-5 had weak acid sites and strong Brønsted acid sites, with peaks at about 220 and 400 °C, respectively. The order of the numbers of acid sites was HY > HZSM-5 (15) > Al-MCM-48; whereas, the order of the strengths of acid sites was HZSM-5 > HY > Al-MCM-48. When the Si/Al ratio of HZSM-5 was increased from 15 to 40, the number of acid sites decreased. The addition of Ga to HZSM-5 decreased the number of acid sites of HZSM-5.

### 3.3. Noncatalytic pyrolysis

The oil fraction of the food waste leachate was pyrolyzed using Py-GC/MS. One of the drawbacks of Py-GC/MS is that it does not allow product collection, thus, the exact bio-oil yield cannot be determined. Moreover, the GC/MS technique cannot provide quantitative analyses of the volatile products. However, the chromatographic peak area of a compound was considered to be linear with respect to its quantity, and the peak area% with its content. Therefore, the corresponding chromatographic peak area% can be compared to show the change in the relative content of the pyrolysis vapors (Adam et al., 2005; Lu et al., 2010; Heo et al., 2010a,b; Pattiya et al., 2008; Wang et al., 2010).

Supplementary data. Table S1 shows the results of the decomposition of the food waste leachate oil fraction at different temperatures between 400 and 700 °C. The product species accounting for the largest area% at every temperature tested was oleic acid, the main component of olive oil. Fatty acid esters, such as octadecanoic acid ethyl ester, hexadecanoic acid ethyl ester and linoleic acid ethyl ester, were also contained in the products. These species stem from the animal and vegetable oils that comprise the food waste leachate. As the pyrolysis products were a mixture of a number of species, these species were roughly grouped into five categories: gases (CO, CO₂, and hydrocarbons up to C₄), oxygenates, acids, hydrocarbons (aliphatic alkanes and alkenes) and aromatics. Fig. 2 shows that with increasing temperature, the fatty acids were decomposed into low-molecular-weight hydrocarbons, aromatics and gases. In particular, the amount of oleic acid, which accounted for the largest amount of the product, was shown to decrease dramatically with increasing pyrolysis temperature (Table S1). Fig. 3 illustrates the results of the product grouping based on the number of carbon atoms in the molecules. With increasing pyrolysis temperature, the fractions of low-molecular-weight species increased; C₇–C₁₀ species accounted for the largest fraction at 700 °C. This result suggests that the food waste oil fraction can be converted to high-quality fuels by pyrolysis at high temperature. However, a high-temperature decomposition reaction requires a lot of energy. Therefore, it would be better to make the same reaction take place at a lower temperature using catalysts.

### 3.4. Catalytic pyrolysis

Supplementary data. Table S2 shows the list of the products obtained from the decomposition of the food waste leachate oil fraction, with the aid of various catalysts, at 500 °C. It can be seen that...
the use of catalysts led to the decomposition of high-molecular-weight species into those with low-molecular-weights. In particular, most of the oleic acid was decomposed when catalysts were used. In order to illustrate the trend in the fractions of different species in the reaction products according to the catalysts used, as shown in Fig. 4, the product species were grouped into seven categories: gases, oxygenates, acids, hydrocarbons, aromatics (monocyclic aromatic hydrocarbons), polycyclic aromatic hydrocarbons (PAHs) and unknowns. A considerable amount of fatty acids produced under the non-catalytic conditions were decomposed further with the use of catalysts. The product distribution was, to a large extent, dependent on the catalyst used. When the Al-MCM-48 catalyst, with a large pore size, was used, the amounts of oxygenates, hydrocarbons and monomeric aromatics (benzene, toluene and alkylated derivatives) were higher than in the case of non-catalytic pyrolysis. When the HY zeolite catalyst was used, most oxygenates and fatty acids were converted into gases, hydrocarbons and monomeric aromatics. HZSM-5 showed a similar effect to that of HY zeolite: oxygenates and fatty acids were converted into gases, hydrocarbons and monomeric aromatics. In particular, when HZSM-5 was used, the amounts of monomeric aromatics and gases were very high compared to the cases where the other catalysts were used. It is well known that hydrocarbons and aromatics are regarded as valuable products due to their contribution to the calorific value of the bio-oil. However, HY and HZSM-5 also produced PAHs, which are well known to be toxic and mutagenic compounds.

Fatty acids are decomposed on the acid sites of the catalysts. Mesoporous catalysts, such as Al-MCM-48, are advantageous for the decomposition of high-molecular-weight species due to their large pore size. Nevertheless, the number and strength of their acid sites are lower than those of HY zeolite and HZSM-5 (Fig. 1), leading to a relatively lower decomposition efficiency. Therefore, when Al-MCM-48 was used, the fatty acids contained within the food waste leachate were mainly decomposed into oxygenates and hydrocarbons, with slight conversion to aromatic compounds. Lukyanov et al. (1994, 1995) reported that the presence of strong Brønsted acid sites in a catalyst, such as HZSM-5, enhanced the production of aromatics. HZSM-5 could accelerate the oligomerization of ethylene and propylene to form C4-C10 olefins, which then undergo dehydrogenation to form diolefins (or dienes). The subsequent cyclization and further dehydrogenation resulted in the formation of aromatic hydrocarbons. In this study, more aromatic compounds were generated when HY or HZSM-5, which have a greater number of Brønsted acid sites, was used compared to the case where a mesoporous catalyst with fewer Brønsted acid sites was used. In particular, with the use of HZSM-5, which has greater acid site strength than the HY catalyst, considerable amounts of hydrocarbons were converted into aromatics. It can be suggested that some higher-molecular-weight compounds in the oil separated from food waste would react on the surface of the HZSM-5 catalyst and generate many low-molecular-weight hydrocarbons, such as ethylene and propylene. These low-molecular-weight hydrocarbons then subsequently enter the three-dimensional pore system of the HZSM-5 catalyst and undergo further polymerization and aromatization to form aromatic hydrocarbons.

Fig. 4. Product distribution of catalytic pyrolysis of oil fractions separated from food waste leachate.

Additional experiments were carried out to investigate the effect of the acidity of the catalysts. Fig. 4 also shows the results obtained by using different Si/Al ratios for the HZSM-5 catalyst. As shown in this figure, the HZSM-5 catalyst with a Si/Al ratio of 40 led to the production of more hydrocarbons and less aromatics than that with a Si/Al ratio of 15. This result indicated that a significant amount of hydrocarbons was converted into aromatics when the catalyst with a Si/Al ratio of 15 was used. The use of the catalyst with a Si/Al ratio of 15 also resulted in the production of higher amounts of gases. The results of these experiments indicated that the catalyst with a Si/Al ratio of 15, which has a greater number of Brønsted acid sites, effectively enhanced the catalytic cracking and aromatization, implying that Brønsted acid sites play an important role in the production of aromatics. The shape selectivity of HZSM-5 also affects the selectivity for aromatics production (Adjaye et al., 1996). The pores of HZSM-5, with intersecting channels, are ideal for producing aromatic compounds. The newly formed aromatic compounds can then either diffuse from the catalyst or remain inside the pores to form coke. Williams and Horne (1994) reported that the unique pore structure of HZSM-5 led to a high yield of aromatics in bio-oil. Pan et al. (2010) also reported the importance of the three-dimensional pore system of HZSM-5 catalyst in the production of aromatic hydrocarbons.

Fig. 5 shows the product distribution according to the number of carbon atoms in the molecules. The use of catalysts was shown to facilitate the conversion of high-molecular-weight species into...
those with low-molecular-weights. Mesoporous Al-MCM-48 led to the largest production of diesel-range compounds, with the number of carbon atoms ranging from 9 to 19. It is believed that the large pore size of Al-MCM-48 would be favorable for the production of high-molecular-weight species; whereas, its weak acidity would suppress excessive decomposition. When HY zeolite and HZSM-5 were used, the dominant products were gasoline-range compounds, with the number of carbon atoms ranging from 5 to 9, which can be attributed to their small pore sizes and strong Brønsted acid sites. In particular, when HZSM-5, which has the strongest Brønsted acidity, was used, the production of low-molecular-weight gases was the highest. The use of HY, which has a weaker acid strength and a larger pore size than HZSM-5, resulted in a higher proportion of C6-C17 compounds and PAHs, but a lower fraction of gases than HZSM-5.

In another set of experiments, Ga was added to HZSM-5. As shown in Table 2, the addition of Ga resulted in the decreased production of hydrocarbons, but increased aromatics. In particular, the fraction of monomeric aromatics, with high economic values, e.g., benzene, toluene and xylene, were significantly increased from 42.41% to 58.07%. The fraction of hydrocarbons decreased as much, while the other species were affected much less by the addition of Ga. The addition of Ga to HZSM-5 is known to result in an interaction between the Brønsted and Lewis acid sites, which promotes the conversion of hydrocarbons and bio-oil components into aromatics. Kwak and Sachlier (1994) reported that Brønsted acid sites catalyze oligomerization and ring closure, but Ga, with respect to protons, acts as a dehydrogenating site. Park et al. (2007, 2010d) also suggested that the incorporation of Ga cations into a MFI type zeolite increased the initial dehydrogenation rates of alkanes, as well as the subsequent dehydrogenation rates required to more rapidly transform alkenes to aromatics, leading to considerably larger aromatics production than obtained by the parent MFI type zeolite. It is believed that Ga played a similar role in this study: a considerable amount of hydrocarbons may have been converted into aromatics at the Ga and Brønsted acid sites. When Ga was added, the carbon number distribution of the product was similar to that obtained without the addition of Ga, but the production of gases was slightly decreased while the C5-C8 and C10-C17 hydrocarbon fractions were slightly increased (data not shown). This result was attributed to the loss of some strong acid sites from HZSM-5 due to the addition of Ga, resulting in partial suppression of the decomposition reactions (Park et al., 2007, 2010d).

4. Conclusions

The pyrolysis of the food waste leachate oil fraction was conducted using Py-GC/MS. The use of catalysts resulted in a significant improvement in the production of bio-oil, Al-MCM-48 suppressed excessive decomposition and converted the oil fraction mainly into diesel-range compounds. Conversely, HY and HZSM-5 showed high selectivity to gasoline-range compounds. In particular, HZSM-5 provided a high aromatics yield, which can be attributed to its strong Brønsted acid sites and shape selectivity. When Ga was added to HZSM-5, the interaction between the Ga and Brønsted acid sites led to a significantly enhanced production of aromatic compounds.

Appendix A. Supplementary data


References


Kim, S.G. System for separation of oil and sludge from food waste leachate. Korea Patent 2010-0053238.


