



Catalytic Pyrolysis of Oil Fractions Separated from Food Waste Leachate Over Nanoporous Acid Catalysts

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Oil fractions, separated from food waste leachate, can be used as an energy source. Especially, high quality oil can be obtained by catalytic cracking. In this study, nanoporous catalysts such as Al-MCM-41 and mesoporous MFI type zeolite were applied to the catalytic cracking of oil fractions using the pyrolysis gas chromatography/mass spectrometry. Mesoporous MFI type zeolite showed better textural porosity than Al-MCM-41. In addition, mesoporous MFI type zeolite had strong Brønsted acidity while Al-MCM-41 had weak acidity. Significant amount of acid components in the food waste oil fractions were converted to mainly oxygenates and aromatics. As a result of its well-defined nanopores and strong acidity, the use of a mesoporous MFI type zeolite produced large amounts of gaseous and aromatic compounds. High yields of hydrocarbons within the gasoline range were also obtained in the case of mesoporous MFI type zeolite, whereas the use of Al-MCM-41, which exhibits relatively weak acidity, resulted in high yields of oxygenates and diesel range hydrocarbons.

Keywords: Food Waste Oil Fractions, Catalytic Pyrolysis, Nanoporous Catalysts.

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. Measures for the appropriate treatment of organic waste are being considered in South Korea to limit the ocean disposal of organic waste.¹ In December 2008, the rate of food waste generation in South Korea was 13,000 ton/day, resulting in an annual economic loss of about \$15 billion.²

Food waste can be treated using various processes, including composting, feedstuff production, and 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 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. Usually, one liter of leachate contains 5 g of oil fractions, and is mainly composed of animal and vegetable oils.^{1,2} Therefore, the oil fractions are separated from the leachate can be used as an energy source.

Animal and vegetable oils can generally be converted to biodiesel via transesterification, and can also be converted to bio-oils via pyrolysis. In particular, the pyrolysis of biomass, such as wood, agricultural by-products and herbaceous plants, has been widely investigated. Bio-oils produced via biomass pyrolysis can be used as heating fuel, but the fuel quality is low.¹⁻⁶ Therefore, efforts have been made to produce reformed oils via the catalytic reactions of low-quality bio-oils, to give a product with improved quality.⁷⁻⁹ Recent investigations have been

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conducted to produce bio-fuels from vegetable oils via catalytic pyrolysis.^{10,11} To the best of our knowledge, Al-MCM-41 and mesoporous MFI type zeolite (meso-MFI) are utilized for the first time to produce bio-oils through reforming of food waste oil. The objective of this study was to investigate the performance of nanoporous catalysts for the catalytic cracking of oil fractions separated from food waste leachate. To test the catalytic activities of nanoporous catalysts, the pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) experiment was carried out because it allowed direct analysis of catalytic products.

2. EXPERIMENTAL DETAILS

2.1. Oil Fractions Separated from Food Waste Leachate

Oil fractions separated from food waste leachate was obtained from Korea Institute of Energy Research. More detailed procedure for the normal hexane extractive chemical test was reported in literature.²

2.2. Preparation of Catalyst

2.2.1. Preparation of Al-MCM-41

The MCM-41 samples were synthesized as described below.¹² Cetyltrimethylammonium bromide (CTAB) (24.3 g) was completely dissolved in 280 g of distilled water in a drying oven (100 °C). Then, 100 g of sodium silicate solution (SiO₂ 20 wt% in H₂O) was added dropwise at room temperature. After stirring for 1 h, to form a gel, the mixture was aged for 24 h at 100 °C. Acetic acid (50 wt%) was added until the pH of the mixture reached 10. The mixture was then aged further for 24 h at 100 °C. The pH was readjusted to 10 using the above-mentioned method. The final solid product was separated by filtration, then washed several times with distilled water and the solid product calcined for 4 h at 550 °C. The molar ratio of SiO₂:CTAB:H₂O was 0.5:0.1:30. Aluminum incorporation into MCM-41 was performed using the post-synthetic grafting method.¹³ Before baking, the prepared nanoporous material was introduced into a solution prepared by dissolving AlCl₃ in 100 mL of ethanol, according to the desired Si/Al ratio, and then stirred for 24 h, washed with ethanol, filtered, dried for 24 h, and calcined for 4 h at 550 °C.

2.2.2. Preparation of Meso MFI

A meso-MFI with a Si/Al molar ratio of 20 was synthesized using a procedure described elsewhere.^{8,9} An amphiphilic organosilane, [(3-trimethoxysilyl)propyl] hexadecyldimethylammonium chloride (TPHAC), was used as a nanopore-directing agent. The catalyst thus obtained was

calcined, ion-exchanged with a 1.0 M ammonium nitrate solution at 80 °C repeatedly (4 times) to convert it into the NH₄⁺ form, and finally calcined again at 550 °C to convert it into the H⁺ form.

2.3. Catalyst Characterization

The powder X-ray diffraction (XRD) patterns were determined by X-ray diffractometer (Rigaku D/MAX-III) using Cu-K α radiation. The BET surface area of the catalyst was measured using an ASAP 2010 apparatus (Micromeritics). 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 an adsorption gas at the temperature of liquid nitrogen. The nitrogen adsorption-desorption isotherms and BET surface area were then obtained. The surface acidity of the catalysts was measured using temperature programmed desorption of ammonia (NH₃-TPD) employing a BEL-CAT TPD analyzer with a TCD detector.

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 μ l) and catalyst (1 mg) were placed in a sample cup and then 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-5MS/HT; 5% diphenyl and 95% dimethylpolysiloxane, length 30 m, i.d. 0.25 mm, film thickness 0.5 μ m, Frontier Laboratories Ltd. Japan). To prevent condensation of products, the interface and inlet temperatures were both maintained at 300 °C. The column temperature was programmed to change 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 a.m.u. at a rate of 2 scans/sec. The identification of peaks was performed using the NISTMS library, with the area percents calibrated to compare the catalytic performance for the formation of valuable aromatic compounds.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

The low angle of XRD pattern of Al-MCM-41 exhibits typical peaks of Al-MCM-41 (Fig. 1). Also, the high angle of XRD pattern of meso-MFI is in accordance with the conventional MFI zeolite. Figure 2(a) shows the N₂ adsorption-desorption isotherms of the prepared catalysts. All samples satisfied the type IV hysteresis loop

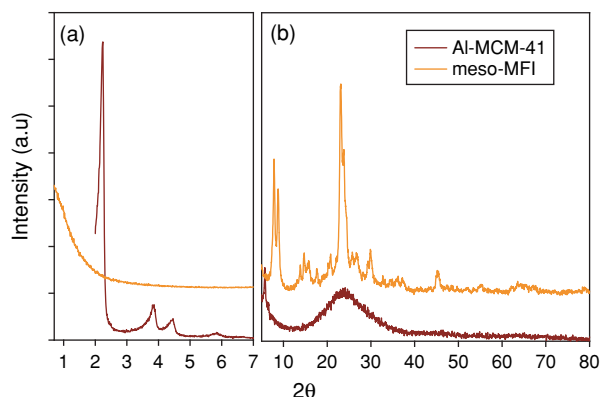


Fig. 1. X-ray diffraction patterns in the region of low (a) and high (b) angle.

in accordance with the IUPAC classification, and all catalysts showed type IV isotherms. Al-MCM-41 exhibited an isotherm analogous to that of a typical nanoporous material; whereas, the meso-MFI zeolite showed a slightly different isotherm from that of the hexagonal material, with increased adsorption in the range of $P/P_0 = 0.8 \sim 1.0$. This was attributed to capillary condensation in the open mesopores, as described previously,⁹ suggesting that the meso-MFI zeolite had a greater textural porosity than Al-MCM-41. The pore size distribution curves were obtained from isotherm curves using the BJH method (Fig. 2(b)). Table I shows the physical properties of the nanoporous catalysts. The BET surface areas and pore sizes of Al-MCM-41 and meso-MFI were 1054 and 471 m^2/g , and 2.6 and 4.1 nm, respectively. Also, pore volumes of Al-MCM-41 and meso-MFI were 0.93 and 0.51 cm^3/g , respectively. The Si/Al ratio of the catalysts was 20. NH_3 -TPD was obtained in order to characterize the amount and strength of acid sites, which are useful for the interpretation of the catalytic activity over those of solid acid catalysts (Fig. 3). The peaks at approximately 220 and 400 $^\circ\text{C}$ were attributed to NH_3 desorption from the weak acid and strong Brönsted acid sites, respectively.⁹ Al-MCM-41 was weakly acidic, while meso-MFI showed strong Brönsted

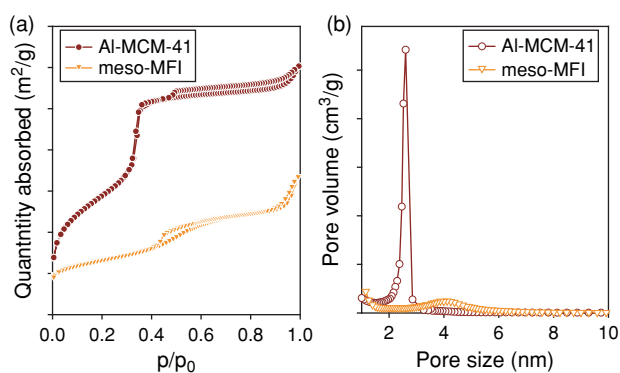


Fig. 2. Nitrogen sorption isotherms (a) and pore size distributions (b) of nanoporous catalysts.

Table I. Physical properties of nanoporous catalysts.

Catalyst	Surface area (m^2/g) ^a	V_p (cm^3/g) ^b	D_p (nm) ^c	Si/Al ^d
Al-MCM-41	1054	0.93	2.6	20
Meso-MFI	471	0.51	4.1	20

^aCalculated in the range of relative pressure (P/P_0) = 0.05 – 0.20. ^bMeasured at $P/P_0 = 0.99$. ^cMesopore diameter calculated by the BJH method. ^dMeasured by ICP-AES.

acidity. In addition, the number of acid sites in Al-MCM-41 was much lower than that of the meso-MFI, particularly strong acid sites.

3.2. Catalytic Activity

Table II shows the main products obtained from the non-catalytic pyrolysis of the oil fractions separated from the food waste leachate. The product of pyrolysis is usually a mixture of a number of different species. In this study, for convenience, the product species were divided into several groups: gases, oxygenates, acids, hydrocarbons, aromatics and PAHs. The removal of the acid components contained within bio-oils is very important because they cause erosion. With the noncatalytic cracking, the yield of acids, especially oleic acid (32.35%), was very high.

Figure 4 shows the product distributions obtained from the pyrolysis of the food waste oil fractions. When the nanoporous catalysts were used; Al-MCM-41 and meso-MFI, most of the acidic components were converted to other species. This can be attributed to the large nano-sized pores of Al-MCM-41 and meso-MFI, which are beneficial for the decomposition of large molecules, such as oleic acid. Therefore, it is believed the use of Al-MCM-41 and meso-MFI catalysts to pyrolyze acid components of food waste oil fractions would be desirable.

When Al-MCM-41 was used, oxygenates were most dominant product, followed by hydrocarbons and aromatics. The oxygenates obtained by using Al-MCM-41, as

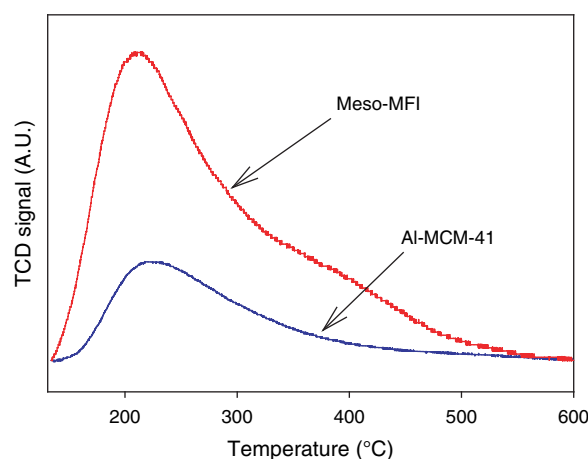


Fig. 3. NH_3 TPD of nanoporous catalysts.

Table II. Main Products of noncatalytic conversion of oil fractions separated from food waste leachate.

Compounds	Area %	Compounds	Area %
Carbon dioxide	2.48	2-Tetradecene, (E)-	1.03
1,3-Butadiene	1.62	1-Pentadecene	0.5
2-Propenal	3.45	Pentadecane	1.66
1,3-Pentadiene	0.18	Cyclododecene	1.77
1-Buten-3-yne, 2-methyl-	0.36	1-Hexadecene	0.79
Cyclopentene	0.32	8-Heptadecene	2.47
2-Propen-1-ol	0.45	Heptadecane	0.65
1-Hexene	1.01	1,13-Tetradecadiene	0.36
Hexane	1.46	1-Octadecene	0.35
Benzene	0.44	Ethyl 9-hexadecenoate	0.67
1-Heptene	1.26	Hexadecanoic acid, ethyl ester	2.26
Heptane	0.59	Nonadecane, 2-methyl-	2.94
1-Octene	0.77	Z,E-3,13-Octadecadien-1-ol	0.66
Octane	0.46	Linoleic acid ethyl ester	3.89
1-Nonene	0.46	Octadecanoic acid, ethyl ester	3.99
Cyclooctene	0.35	cis-9-Hexadecenal	0.43
1-Decene	0.53	9-Nonadecene	6.41
5-Undecene	1.72	Oleic acid	32.35
Cyclooctene	0.65	9-Octadecenal, (Z)-	8.92
1-Dodecene	0.51	E-2-Octadecadecen-1-ol	2.86
Cycloheptene	0.58	Tetracosanoic acid	1.23
1-Tridecene	0.54	Cholesta-3,5-diene	3.18
Tridecane	0.45		

Table III. Main oxygenate compounds obtained by using Al-MCM-41.

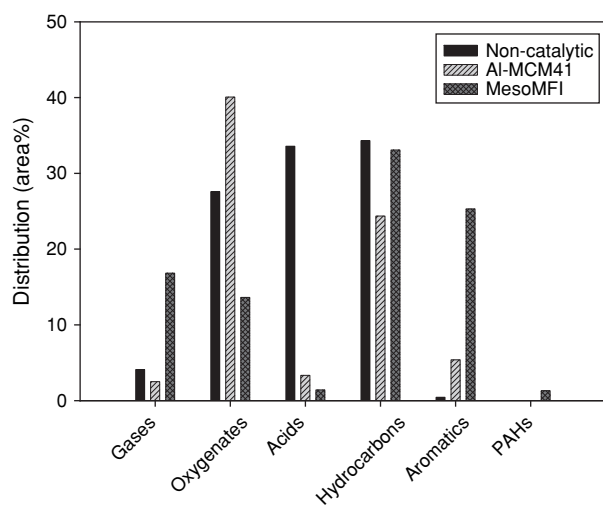
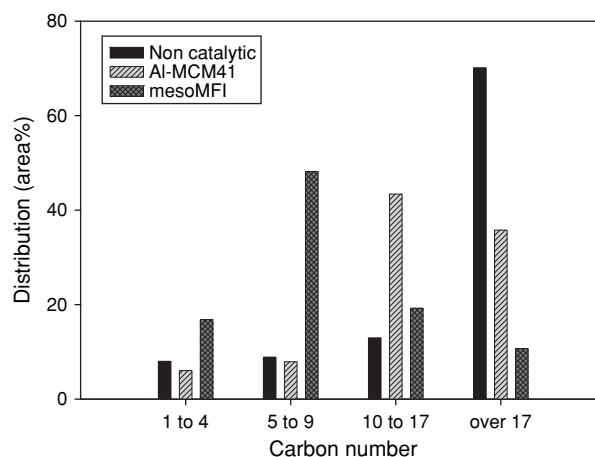
Compounds	Area %
2-Propenal	3.52
Cyclohexanone	0.57
Tetradecanal	1.72
2-Heptadecanone	1.50
2-Cyclopenten-1-one, 2-pentyl-	1.00
[1,1'-Bicyclopentyl]-2-one	4.19
9-Tetradecenal, (Z)-	4.26
2-n-Heptylcyclopentanone	4.25
2-Cyclopenten-1-one, 2-pentyl-	9.58
9,17-Octadecadienal, (Z)-	2.64
Hexadecanoic acid, ethyl ester	3.42
Linoleic acid ethyl ester	3.42

Figure 3, most of the acid sites of Al-MCM-41 were weak and, thus, the acidic components were converted to oxygenated hydrocarbons only, without further conversion to aromatics. On the contrary, the use of meso-MFI, having strong Brönsted acid sites, could lead to a significantly higher production of aromatics. The strength of the acid sites also affected the production of gaseous species.¹⁴⁻¹⁷ Stronger acid sites can crack food waste oil fractions with large molecules more easily, resulting in higher gas yields. Therefore, the use of meso-MFI, having a greater number of stronger acid sites, resulted in a significantly larger gas yield.

Figure 5 shows the carbon number distributions of the products obtained using the different pyrolysis methods. Again, catalytic pyrolysis has been shown to lead to a greater conversion of large molecular mass species into those with small molecular masses than noncatalytic pyrolysis. Diesel range compounds, i.e., those with carbon numbers between 10 and 17, dominated the product obtained when Al-MCM-41 was used, which has nano-sized pores. This result was ascribed to the large pore size of Al-MCM-41, which was advantageous to the production of species with large molecular masses. The weak

shown in Table III, contained appropriate amounts of oxygen atoms, resulting in a high octane number. Therefore, the use Al-MCM-41 is recommended to obtain a high oxygenate yield.

Conversely, when the meso-MFI catalyst was used, an even greater proportion of acid components were converted to other species compared to the use of Al-MCM-41. Furthermore, a considerable amount of aromatic components, especially PAHs, were produced when meso-MFI was used. Usually, strong Brönsted acid sites are required to produce aromatic species.^{9,14} As shown in

**Fig. 4.** Product distributions obtained from pyrolysis of food waste oil fractions.**Fig. 5.** Carbon number distributions of the products obtained from different pyrolysis methods.

acid sites of Al-MCM-41, which restrain the over-cracking of oils, were also thought to contribute to the production of species with large molecular masses. Meanwhile, when meso-MFI was used, gasoline range compounds, i.e., those with carbon numbers between 5 and 9, were mostly produced, which was attributed to its strong acidic sites, which facilitate these decomposition reactions. When the MFI catalyst such ZSM-5 was also used, which has a similar acid strength to that of meso-MFI, the production of aromatic compounds was significantly increased (data not shown).

In summary, the use of Al-MCM-41 is recommended to obtain greater proportions of oxygenates and diesel range compounds; whereas, the use of meso-MFI would be more desirable for the production of greater proportions of aromatic and gasoline range compounds.

4. CONCLUSIONS

Nanoporous catalysts, Al-MCM-41 and meso-MFI, were used for the catalytic pyrolysis of oil fractions separated from food waste leachate using Py-GC/MS. Meso-MFI zeolite with strong Brönsted acidity had a greater textural porosity than Al-MCM-41 with weak acidity. Oil fractions separated from food waste leachate contained significant amount of acid compounds and most of these compounds were converted to valuable products over nanoporous catalysts. In particular, meso-MFI produced high yields of gas and aromatics, with gasoline range hydrocarbons as the main products due to its strong acidic sites which facilitate decomposition reactions. On the other hand, the use of Al-MCM-41 resulted in higher yields of oxygenates and diesel range hydrocarbons because weak acid sites of Al-MCM-41 restrain the over-cracking of oils.

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Received: 8 July 2010. Accepted: 15 January 2011.