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Synthesis of biodiesel from an oil fraction separated from food waste leachate

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Abstract−Biodiesel was produced from an oil fraction separated from food waste leachate, using a batch reactor system, to evaluate its potential as a renewable energy source for the first time. In order to reduce the free fatty acid content of the leachate oil fraction, three different acid catalysts, H_2SO_4, zeolite and Amberlyst-15, were used in the pretreatment process. The residual oil fraction after pretreatment was further treated over KOH as a base catalyst to produce a fatty acid methyl ester (FAME). The FAME content in the product was analyzed using GC/MS. A large number of different FAMEs were detected, which is characteristic of the food-waste-derived raw material used in this study. The FAME content of the product was highest when pretreated over Amberlyst-15, followed by trans-esterification. Additional refining and process optimization would be expected to further increase the FAME content. Therefore, it was concluded that the production of biodiesel from the oil fraction separated from food waste leachate is promising.

Key words: Oil Fraction Separated from Food Waste Leachate, Biodiesel, Acid Catalyst, Base Catalyst

INTRODUCTION

While industrialization and economic growth have led to a richer life, they also have adverse side-effects, including increased municipal waste generation. In particular, the food waste, among other municipal wastes, has steadily increased in Korea, amounting to about 20,000 ton per day, most of which are organic wastes. Since the direct landfilling of food wastes was banned in 2005, to prevent soil and ground water pollution, these food wastes have been recycled for composting, animal feed production, and energy generation via pulverization and anaerobic digestion. While the processes of food waste recycling differ depending on the purpose, they all share a common step: pretreatment, including foreign material removal and dehydration [1].

During the dehydration step, liquid leachate and solid dewatered cake are separated. The dewatered cake is usually used as compost after drying, whereas the leachate is a sludge-like mixture of water and oil, and contains a considerable amount of solid particulate matter. The solid particulates in leachate, which generally account for about 20% [1], are separated from the liquid using a centrifugal separator, such as a decanter. The separated solid is transported to a drier, together with the dewatered cake, whereas the remaining liquid stays at a reservoir for any residual particles to be precipitated. The liquid with the particulates removed is then transferred to a pH adjustment tank. The pH-adjusted leachate contains various oil components, accounting for 5 g/L, which is mostly composed of vegetable/animal fats and oils [1]. If the oil fractions of food waste leachate can be upgraded into high-quality fuel oil, such as biodiesel, this would be desirable not only in terms of the creation of added-value but also of waste recycling.

Until now, there have been many reports about biodiesel synthesis [2-9]. Biodiesel is mostly produced from vegetable oils which could otherwise be used as food. This fact has raised the criticism that the production of biodiesel is causing food shortages and increased food prices [10]. Therefore, the application of non-food crops, marine biomass, or butchery animal fat by-products for the production of biodiesel is of great interest [11].

Non-food and/or waste fats and oils contain large amounts of free fatty acids (FFAs). It has been reported that trans-esterification, using an alkali catalyst, cannot be applied to fats and oils containing FFAs exceeding 3% [12]. Therefore, it is essential to remove these FFAs in advance for the production of biodiesel from waste fats and oils with high FFA content using acid catalyst. Sulfuric acid as a liquid catalyst has been used widely for the production of biodiesel. However, one drawback of sulfuric acid is that it may be contained in the biodiesel and glycerin after the reaction and require a further refining process. Erosion of the reactor is another potential risk of using liquid acid catalysts. Therefore, much attention has recently focused on solid acid catalysts [11-17]. The ion-exchange resin might have a greater potential for the synthesis of biodiesel. Amberlyst-15 is known as a catalyst with good properties in terms of its esterification efficiency [18]. Also, Pappu et al. investigated a kinetic model of Amberlyst-15 catalyzed transesterification of methyl stearate with n-butanol [19]. In addition, there are several reports about the use of zeolite catalysts to produce biodiesel. Carma et al. [20]

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studied the Al-MCM-41 mesoporous molecular sieves with Si/Al ratio of 8 for esterification of palmitic acid with methanol, ethanol and isopropanol. Zeolite beta modified with La (La/zeolite beta) had been tested as a solid acid catalyst for methanolysis of soybean oil [21].

The general procedure for the production of biodiesel consists of two steps. At first, acid catalyst is used in the pretreatment process. Then the residual oil fraction after pretreatment is further treated over a base catalyst to produce a fatty acid methyl ester (FAME) [11]. The esterification reaction with alcohol over an acid catalyst converts the FFAs into fatty acid esters and water. The water can then be removed using a reduced pressure evaporation method.

In this study, the synthesis of the fatty acid methyl ester (FAME) from the oil fractions derived from food waste leachate was investigated using both acid and base catalysts to evaluate the potential of food waste leachate as a feedstock for the production of biodiesel for the first time. Sulfuric acid, Amberlyst-15 and HZSM-5 were used as acid catalysts and KOH was used as a base catalyst.

EXPERIMENTAL

1. Materials and Instruments

The oil fraction was provided by the Korea Institute of Energy Research, and prepared by extraction with normal hexane from a raw food waste leachate sample, with the evaporation of the normal hexane [1].

Methanol (Duksan, 99.8%) was used as the alcohol agent, while H_2SO_4 (SAMCHUN, 95%) was used as the acid catalyst for the pretreatment. To evaluate the potential of using a solid acid catalyst, Amberlyst-15 (SIGMA ALDRICH, dry) and HZSM-5 zeolite (Si/Al=15) were also tested. KOH (KANTO, 86%) was used as the base catalyst for trans-esterification reaction.

A batch reactor was used for the experiments under atmospheric pressure. The reaction temperature was controlled by circulating water through a 4-neck jacketed reactor, with a capacity of 1,000 ml, using a water bath circulator. A reflux condenser was installed to prevent evaporation of the methanol. The reactor was stirred using a stirrer with a Teflon impeller.

2. Reaction Method

The oil fraction and methanol were placed into the jacketed reactor, with a mixing ratio of 50 g : 100 ml. Although the stoichiometric molar ratios for esterification and trans-esterification reactions are 1 : 1 and 1 : 3, respectively, an excess of methanol is generally used in practical applications because it is difficult to maintain constant molar concentrations of the FFA and oil components in the leachate. Therefore, the experiments conducted in this study were aimed at confirming the production of FAME by the reaction with overdosed methanol. The reaction temperature was controlled at 60 °C, via the method described in section 2.1. It is important to maintain the reaction temperature below the boiling point of methanol to prevent the excessive loss of methanol. When the temperature of methanol and the oil fraction reached the designated temperature, the catalyst was introduced into the reactor, then stirred at 400 rpm, which was regarded as the beginning of reaction. On completion of the reaction, the product clearly separated into two phases. The upper phase solution was sampled and washed with distilled water to extract water-soluble species. After further water washing, the upper phase solution was sampled and analyzed.

3. Analysis Method

The FFA content is generally expressed by the acid value, which is the amount of KOH (mg) required to neutralize the fatty acid, and was measured using a method of KSHISO 660. Meanwhile, it should be understood that the acid values of the leachate oil fraction varied from sample to sample. Because the characteristic of food waste leachate was very inhomogeneous due to various sources of food waste and irregular supply, it was very difficult to perform a reaction with leachate oil fraction having constant acid values.

GC/MS was used to quantitatively analyze the FAMEs contained in the biodiesel produced as the area%. The final FAME yields were calculated by the following equation:

$$\text{Final yield } (\%) = \frac{(\mathrm{BD}_1 \times \mathrm{ME}_A + \mathrm{BD}_2 \times \mathrm{ME}_B)}{\text{Oil fraction (g)}} \times 100$$

Table 1. Effect of reaction temperature on acid value

Temperature (°C)	Acid value*		
	0 min	60 min	120 min
40	22.33	2.00	1.75
50	19.92	1.05	0.73
60	36.15	1.04	0.70

*Unit: mg KOH/g

H_2SO_4/Oil=3/100 (w/w), Oil to methanol ratio 50 g : 100 ml

Table 2. Effects of solid acid catalysts on acid value

Catalyst	Acid value*							
	0 min	30 min	60 min	90 min	120 min	150 min	180 min	210 min
H_2SO_4[a]	36.15	-	1.04	-	0.70	-	0.52	-
HZSM-5[b]	34.23	18.15	19.12	19.12	18.88	18.88	-	-
Amberlyst-15[c]	24.01	13.64	11.60	12.38	13.12	12.62	-	-
Amberlyst-15[d]	33.21	9.10	6.17	3.78	2.20	1.65	0.83	0.63

*Unit: mg KOH/g

[a] H_2SO_4/Oil=3/100 (w/w)

[b] HZSM-5/Oil=10/100 (w/w)

[c] Amberlysit-15/Oil=3/100 (w/w)

[d] Amberlysit-15/Oil=10/100 (w/w)

Oil to methanol ratio 50 g : 100 ml, 60 °C where BD_1 and ME_A are the mass of biodiesel (g) and the FAME content, respectively, obtained over the acid catalyst, and BD_2 and ME_B are the mass of biodiesel and the FAME content, respectively, obtained over the base catalyst.

RESULTS AND DISCUSSION

1. Esterification over Acid Catalyst

As the HHV of the oil was about 40 MJ/kg, the oil can be classified as a promising fuel [1]. However, the oil cannot be applied directly in industry due to its high viscosity and high fatty acid content; therefore, an additional process, such as esterification, will be required for its conversion into a valuable fuel.

The oil fraction separated from food waste leachate was shown to have high acid values, ranging from 20 to 36 mg KOH/g. The removal of FFAs using an acid catalyst is essential for the production of biodiesel from fats and oils with high FFA content [11,13]. The most widely used acid catalyst for the production of biodiesel

Table 3. Product distribution after Amberlyst-15 treatment

Compound		Contents (%)
Caprylic acid methyl ester	C8 : 0	0.083
Capric acid methyl ester	C10 : 0	0.069
Lauric acid methyl ester	C12 : 0	0.365
Myristic acid methyl ester	C14 : 0	0.887
Palmitic acid methyl ester	C16 : 0	22.656
Oleic acid methyl ester	C18 : 1	62.828
Eicosatetraenoic acid methyl ester	C20 : 4	4.535
Docosahexaenoic acid methyl ester	C22 : 6	2.465
Methyl-10-hydroxy octadecanoate	C18 : 0	2.176
Total		96.064

Amberlyst-15/Oil=10/100 (w/w), Oil to methanol ratio 50 g : 100 ml, 210 min, 60 °C

Table 4. Product distribution after H_2SO_4 treatment

Compound		Contents (%)
Caprylic acid methyl ester	C8 : 0	0.178
Capric acid methyl ester	C10 : 0	0.212
Lauric acid methyl ester	C12 : 0	0.678
Myristic acid methyl ester	C14 : 0	1.847
Palmitic acid methyl ester	C16 : 0	23.19
Oleic acid methyl ester	C18 : 1	42.145
Linoleic acid methyl ester	C18 : 2	2.069
Linolenic acid methyl ester	C18 : 3	4.054
Eicosenoic acid methyl ester	C20 : 1	2.184
Eicosupentaenoic acid methyl ester	C20 : 4	4.133
docosahexaenoic acid methyl ester	C22 : 6	2.954
Total		83.644

* H_2SO_4/Oil=3/100 (w/w), Oil to methanol ratio 50 g : 100 ml, 120 min, 60 °C

Table 5. Product distribution after Amberlyst-15 and KOH treatment

Compound		Contents (%)
Octanoic acid methyl ester	C8 : 0	0.02
Decanoic acid methyl ester	C10 : 0	0.34
Dodecanoic acid methyl ester	C12 : 0	1.54
12-Methyl-tridecanoic acid methyl ester	C14 : 0	5.06
4,8,12-Trimethyl-tridecanoic acid methyl ester	C14 : 3	0.09
Pentadecanoic acid methyl ester	C15 : 0	0.97
Hexadecanoic acid methyl ester	C16 : 0	17.66
7-Hexadecenoic acid methyl ester,(Z)-	C16 : 1	9.52
Heptadecanoic acid methyl ester	C17 : 0	0.83
11-Octadecenoic acid methyl ester	C18 : 1	45.22
9,12-Octadecadienoic acid methyl ester, (E,E)-	C18 : 2	1.11
9,12,15-Octadecatrienoic acid methyl ester, (Z,Z,Z)-	C18 : 3	1.12
Nonadecanoic acid methyl ester	C19 : 0	0.21
10-Nonadecenoic acid methyl ester	C19 : 1	0.56
Eicosanoic acid methyl ester	C20 : 0	1.17
11-Eicosenoic acid methyl ester	C20 : 1	3.87
5,8,11,14-Eicosatetraenoic acid methyl ester, (all-Z)-	C20 : 4	1.04
5,8,11,14,17-Eicosapentaenoic acid methyl ester, (all-Z)-	C20 : 5	1.51
Docosanoic acid methyl ester	C22 : 0	0.27
13-Docosenoic acid methyl ester, (Z)-	C22 : 1	1.46
4,7,10,13,16,19-Docosahexaenoic acid methyl ester, (all-Z)-	C22 : 6	2.13
15-Tetracosenoic acid, methyl ester, (Z)-	C24 : 1	0.12
Total		95.82

* KOH/Oil=1/100 (w/w), Oil to methanol ratio 50 g : 100 ml, 30 min, 60 °C

is sulfuric acid. Besides sulfuric acid, two representative solid acid catalysts, i.e., the ion exchange resin, Amberlyst-15, and the zeolite catalyst, HZSM-5, were evaluated in this study.

First, the performance of sulfuric acid for reduction of the acid value was investigated at three different temperatures: 40, 50 and 60 °C. The mass ratio of sulfuric acid/the oil fraction was 3/100. The reaction time was 120 min. As shown in Table 1, the acid value was observed to decrease with increasing reaction temperature. The esterification reaction of the food-waste-derived oil fraction should be continued for 120 min at a temperature of 50 °C or higher to achieve an acid value lower than 1.

Table 2 shows that the effect of solid acid catalysts on acid values. These reactions were conducted at 60 °C for 210 min, with sampling performed every 30 min. After removing the solid catalysts by filtration, the acid value was measured. The catalytic activity of HZSM-5 for the lowering the acid value was observed to be low. The low catalytic activity of HZSM-5 may be due to diffusion limitation of bulky reactants (FFAs) into the microporous structure of HZSM-5 [1]. Also, it may be difficult for bulky products to diffuse out the micropore of HZSM-5. Furthermore, it was difficult to separate the HZSM-5 catalyst from the samples by filtration due to the high viscosity of the oil fraction. Also, the activity of lowering acid value with Amberlyst-15 (mass ratio of Amberlyst-15/oil=3/100) was not sufficiently high. When large amount of Amberlyst-15 (mass ratio of Amberlyst-15/oil=10/100) was used in the experiment, however, the acid value, 0.63, was obtained by continuing the reaction for 210 min, which was lower than that achieved by the reaction with sulfuric acid for 120 min. Therefore, it would be expected that

Table 6. Product distribution after H_2SO_4 and KOH treatment

Compound		Contents (%)
Butanoic acid methyl ester	C4 : 0	0.02
Hexanoic acid methyl ester	C6 : 0	0.07
Octanoic acid methyl ester	C8 : 0	0.17
Decanoic acid methyl ester	C10 : 0	0.26
Undecanoic acid methyl ester	C11 : 0	0.01
Dodecanoic acid methyl ester	C12 : 0	1.11
Tridecanoic acid methyl ester	C13 : 0	0.03
4,8,12-Trimethyl-tridecanoic acid methyl ester	C13 : 3	0.06
Methyl tetradecanoate	C14 : 0	3.68
Methyl-Z-11-tetradecenoate	C14 : 1	0.34
Pentadecanoic acid methyl ester	C15 : 0	0.8
Hexadecanoic acid methyl ester	C16 : 0	20.30
7-Hexadecenoic acid methyl ester,(Z)-	C16 : 1	0.03
7-Methyl-6-hexadecenoic acid methyl ester, (Z)-	C16 : 1	0.16
9-Hexadecenoic acid methyl ester, (Z)-	C16 : 1	6.68
14-Methyl-hexadecanoic acid methyl ester	C16 : 1	0.17
Heptadecanoic acid methyl ester	C17 : 0	0.55
Octadecanoic acid methyl ester	C18 : 0	6.86
9-Octadecenoic acid methyl ester, (Z)-	C18 : 1	0.43
10,13-Octadecadienoic acid methyl ester	C18 : 2	40.83
9,12-Octadecadienoic acid methyl ester, (E,E)-	C18 : 2	0.43
9,12,15-Octadecatrienoic acid methyl ester, (Z,Z,Z)-	C18 : 3	0.74
Nonadecanoic acid methyl ester	C19 : 0	0.12
10-Nonadecenoic acid methyl ester	C19 : 1	0.17
Eicosanoic acid methyl ester	C20 : 0	0.87
11-Eicosenoic acid methyl ester	C20 : 1	2.22
7,10,13-Eicosatrienoic acid methyl ester	C20 : 3	0.15
5,8,11,14,17-Eicosapentaenoic acid methyl ester, (all-Z)-	C20 : 4	0.1
5,8,11,14,17-Eicosapentaenoic acid methyl ester, (all-Z)-	C20 : 5	1.85
Heneicosanoic acid methyl ester	C21 : 0	0.02
Docosanoic acid methyl ester	C22 : 0	0.1
13-Docosenoic acid methyl ester, (Z)-	C22 : 1	0.83
4,7,10,13,16,19-Docosahexaenoic acid methyl ester, (all-Z)-	C22 : 6	2.78
Tricosanoic acid methyl ester	C23 : 0	0.01
15-Tetracosenoic acid methyl ester	C24 : 1	0.14
Total		93.09

* KOH/Oil=1/100 (w/w), Oil to methanol ratio 50 g : 100 ml, 30 min, 60 °C

with a sufficient reaction time, Amberlyst-15 could be used for the lowering the acid value by removal of FFAs.

After the reaction and water washing steps, the FAMEs contained in the product were identified and quantified using GC/MS (Tables 3 and 4). Various FAMEs, ranging from C8 : 0 to C22 : 6, were found to exist in the product. Oleic acid methyl ester, palmitic acid methyl ester, and other methyl esters, in order of abundance, were shown to be the dominant FAME species contained in the product. The FAMEs content was larger with the use of Amberlyst-15 than with sulfuric acid. In particular, the total FAMEs content obtained with Amberlyst-15 was 96.1%, which was very close to the biodiesel quality standard of 96.5%, while that obtained with sulfuric acid was much lower (83.6%). Therefore, it was expected that the production of high quality biodiesel from oil fraction separated from food waste leachate would be possible if additional refining and process optimization were performed.

2. Trans-esterification over Base Catalyst

The residual oil fraction not converted into FAMEs by the acid-catalyzed pretreatment was used for trans-esterification experiments, where KOH was used as the catalyst (mass ratio of KOH/oil fraction=1/100). To investigate the effect of temperature on the FAME yield, the reaction experiments were carried out for 30 min at three different temperatures: 40, 50 and 60 °C. Of the reaction products, which separated into two phases, the upper phase solution was sampled and washed with distilled water to remove the methanol and catalyst. Based on the GC-MS analysis, the final yield was calculated. Tables 5 and 6 show the FAMEs identified and quantified by GC/MS. In both cases where Amberlyst-15 and sulfuric acid were used in the pre-treatment, oleic acid methyl ester (C18 : 1) was the most abundant component, followed by palmitic acid methyl ester (C16 : 0). The inclusion of methyl esters derived from saturated fatty acids, such as palmitic acid methyl ester, however, implied a poor low-temperature property of the product.

When vegetable oils are used for the production of biodiesel, the FAME products usually have even numbered carbon chains. In this study, where food-waste-derived oil fraction was used, however, FAMEs with odd numbered carbon atoms, e.g. C17 : 0 and C19 : 1, were also detected, because the food waste leachate oil fraction contained not only vegetable oils but also animal fats and oils. In this case, the conventional standard FAME analysis method (KS H ISO 5508), which analyzes samples using methyl heptadecanoate (C17 : 0) as the calibration standard, was not adequate due to the existence of methyl heptadecanoate in the samples. Another method recently suggested for the analysis of biodiesel from animal fats, prEN14103, uses nonadecanoic acid methyl ester (C19 : 0) as the calibration standard. This method, however, was also not acceptable for this study, because nonadecanoic acid methyl ester was also present in the samples. Therefore, the FAME content in this study was analyzed using GC/MS via the area%. The FAME content was higher when Amberlyst-15 was used for the pre-treatment (95.8%), which was slightly lower than the biodiesel quality regulation of 96.5%; therefore, an additional refining process would be required to meet the standard.

The final FAME yields are summarized in Table 7. The FAME yield was observed to increase with increasing temperature; in particular, the esterification reaction was not complete at 40 °C and caused the formation of a large amount of metal salt. When Amberlyst-15 was used, compared to sulfuric acid, the mass of biodiesel produced was smaller, although the FAME content was higher. Therefore, we concluded that sulfuric acid would be most effective in terms of FAME yield as the pre-treatment for the trans-esterification reaction.

Table 7. FAME yield from food waste oil using a two-step treatment

Two step treatment	Yield (%)
H_2SO_4 120 min+KOH 30 min (40 °C)	16.18
H_2SO_4 120 min+KOH 30 min (50 °C)	16.94
H_2SO_4 120 min+KOH 30 min (60 °C)	26.15
Amberlyst-15 210 min+KOH 30 min (60 °C)	18.65

H_2SO_4/Oil=3/100 (w/w)
KOH/Oil=1/100 (w/w)
Amberlysit-15/Oil=10/100 (w/w)

CONCLUSIONS

As a method of recycling a waste resource and contributing an energy supply, the synthesis of biodiesel using the oil fraction separated from food waste leachate as the raw material was investigated. The food waste leachate oil fraction exhibited a very high acid value, which necessitated a pretreatment over an acid catalyst. Sulfuric acid was shown to be the most effective acid catalyst, while Amberlyst-15 also seemed to be applicable if a sufficient reaction time was allowed.

The oil fraction not converted into FAMEs by the pretreatment was further treated via trans-esterification over KOH as a base catalyst. Large amounts of different FAMEs were produced from the food-waste-derived oil fraction, which was distinct from biodiesels produced from usual vegetable oils. Therefore, the physicochemical properties of these FAMEs need to be satisfactorily characterized in the future.

The FAME content obtained in this study was close to the biodiesel quality standard, without any post processing. Therefore, it would be expected that, with additional refining and process optimization, it will be possible to produce high-quality biodiesel from the food-waste-derived oil fraction.

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