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# A comparison study of extraction methods for bio-liquid via hydrothermal carbonization of food waste

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**Abstract** The hydrothermal carbonization method has received great attention because of the conversion process from biomass. The reaction produces various products in hydrochar, bio-liquid, and gas. Even though its yield cannot be ignored in amount, it is difficult to find research papers on bio-liquid generated from the hydrothermal carbonization reaction of biomass. In particular, the heterogeneity of feedstock composition may make the characterization of bio-liquid different and difficult. In this study, bio-liquid from the hydrothermal carbonization reaction of food wastes at 230 °C for 4 h was investigated. Among various products, fatty acid methyl esters were analyzed using two different extraction methods: liquid-liquid extraction and column chromatography. Different elutions with various solvents enabled us to categorize the various components. The eluents and fractions obtained from two different extraction methods were analyzed by gas chromatography with a mass spectrometer (GC/MS). The composition of the bio-liquid in each fraction was characterized, and seven fatty acid methyl esters were identified using the library installed in GC/MS device.

**Key words:** Bio-liquid, Food waste, GC/MS, Column chromatography, Liquid-liquid extraction, Fatty acid methyl ester

## 1. Introduction

The amount of food waste emission is recently increasing but treatment facilities and methods are decreasing in reverse proportion and legal limits on food emission are growing. In the result of a national survey, present status of the national waste generation and treatment, conducted by the Ministry of Environment in 2013, a proportion of food waste out of municipal waste was 33.1 % (311.3 g/day/person) and 16,224 ton a day was generated. In the result of ash measurement of food waste, moisture was 77.8 %, combustible was 17.7 % and ash was 4.45 %, and there was no big difference depending on the scale of a city or sources [1]. Food waste treatment methods have limitations and are not diverse. Food waste which is not properly treated may cause secondary pollution and therefore studies on how to treat food waste are required to sustain the environment.

Among various methods to treat food waste, hydrothermal carbonization (HTC) was performed [2]. HTC carbonizes wet biomass containing a large

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amount of moisture at relatively low temperature (200 °C ~ 250 °C) under the oxygen-limited condition [3-4]. Hydrochar, bio-liquids, and bio-gases are generated from these reactions and to date, many studies on hydrochar generated as a solid component have been conducted. Bio-gases generally include methane and ammonia, and studies on fuel production using catalysts or other methods are being performed. On the contrary, bio-liquids have a lot of moisture and low heat and therefore several studies on the improvement in bio-liquids, such as hydro-treating, hydro-cracking, solvent addition/esterification and emulsification, are being conducted to convert bio-liquids to fuels [5]. While most of bio-liquid analyses are based on pyrolysis (high-temperature carbonization), bio-liquid analyses by HTC reaction have not been intensively studied [6-8]. The components of bio-liquids generated through HTC reaction containing much moisture would be different from that of pyrolysis [9].

In general, the bio-liquid analysis is performed using liquid-liquid extraction (LLE) or column chromatography (CC) methods. LLE method is based on a difference in the solubility of various analytes, using solvents with different polarity and CC method uses analyte segregation analysis by interaction with the stationary phase and mobile phase. Based on references, each method has two different treatments and therefore there are four methods including LLE 1, LLE 2, CC 1, and CC 2 for the HTC bio-liquid analysis [10-13]. In this study, both LLE and CC methods were used for the bio-liquid analysis. Especially, we analyzed fatty acid methyl esters (FAMEs) which can be used as a biodiesel fuel and have been spotlighted as an alternative energy, out of bio-liquids generated by HTC reaction. Bio-liquid from food waste via HTC reaction was analyzed by Gas Chromatography/Mass spectrometer (GC/MS) after 4 extraction methods were conducted. Qualitative and quantitative information was compared to suggest the suitable extraction method for FAME detection.

## 2. Experimental

Bio-liquid from food waste used in the study were obtained by using its own reactor at 230 °C for 4 hr. Food waste was collected from the local restaurants located in Nowon-gu, Seoul, Korea and its composition was as follows (weight %): grain 41.5 %, vegetables 18.5 %, meat 4.5 %, fruits 27.8 %, and other mixture (paper, bark, etc.) 10.7 %. The sample was kept in a freezer to maintain homogeneous food waste and then thawed in a refrigerator just before the use.

### 2.1. LLE 1 method

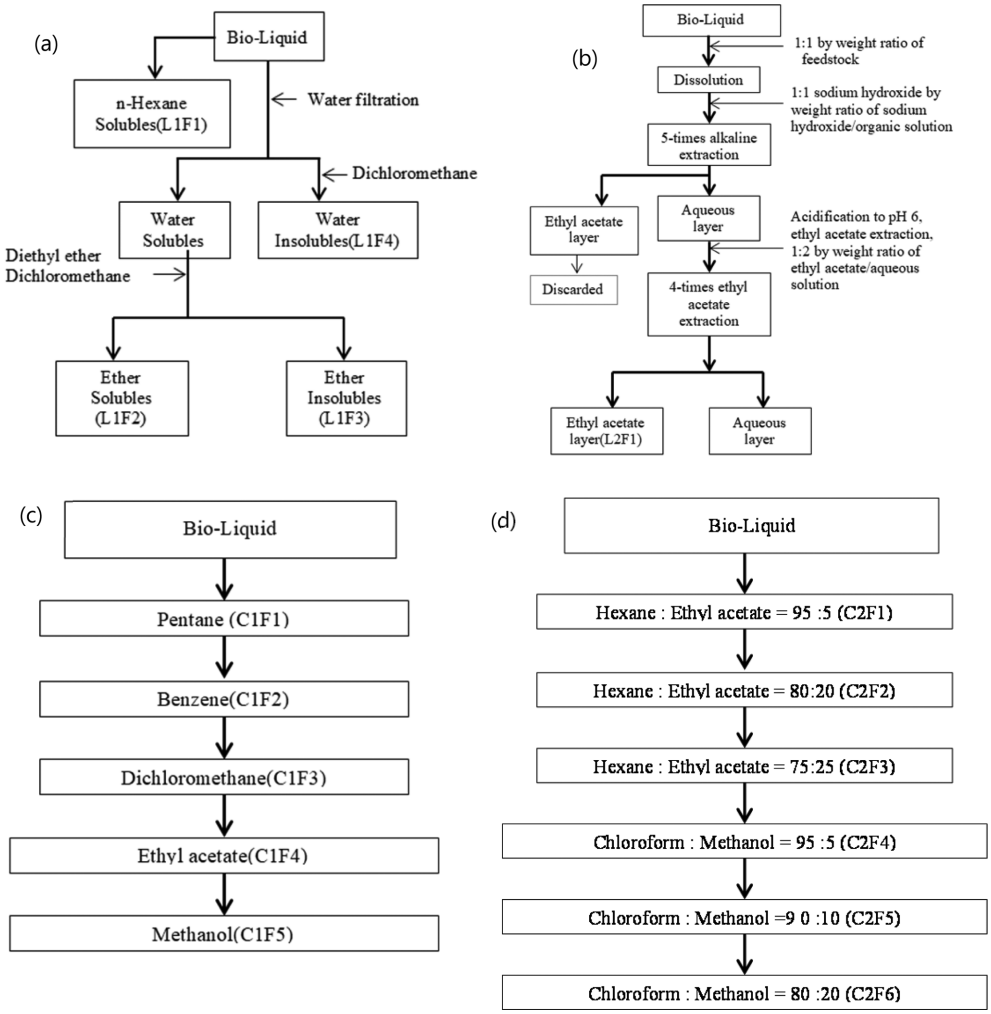
In the LLE 1 method, food waste was classified by fraction according to the method suggested by Oasmaa *et al.* (2003) and then analyzed [10] as shown in *Scheme* 1(a). All the tests were conducted in duplicate.

n-Hexane soluble fraction (L1F1): The 10 mL of bio-liquid and 10 mL of n-hexane were mixed in the ratio of 1:1(v/v). After layer separation, n-hexane supernatant was taken and evaporated at 50 °C. The residue was dissolved in 2 mL n-hexane and then filtered through a 0.45 μm syringe filter to obtain the n-hexane soluble fraction.

Ether soluble fraction (L1F2): The 10 mL of bio-liquid and 30 mL of water were mixed for 30 min. After rotary evaporation, the solution was divided into the water soluble fraction and water insoluble fraction using a membrane filter. The residue remaining on the filter was dried in the oven for water insoluble fraction. Then, the 30 mL of mixture of dichloromethane and diethyl ether (1:1, v/v) and 30 mL of water soluble fraction were transferred into a separatory funnel for extraction. The ether soluble and ether insoluble fractions were divided. The ether soluble fraction was evaporated at 40 °C and then was dissolved in 2 mL of diethyl ether for syringe filtration. Finally, the ether soluble fraction was obtained.

Ether insoluble fraction (L1F3): The ether insoluble fraction separated during ether soluble fraction extraction underwent rotary evaporation at least at 80 °C and then was dissolved in 3 mL of dichloromethane for syringe filtration.

Water insoluble fraction (L1F4): The residue on the filter dried during ether soluble fractionation (LIF2) was put into a bottle and 5 mL of dichloromethane was added. Then, it was sonicated approximately for 30 min.




*Scheme* 1. Procedure of 4 extraction methods used in this study. (a) liquid-liquid extraction 1 method, (b) liquid-liquid extraction 2 method, (c) column chromatography 1 method, and (d) column chromatography 2 method.

The extracted solution was taken for rotary evaporation at 40 °C and dissolved in 2 mL of dichloromethane for syringe filtration. Finally, the water insoluble fraction was prepared.

### 2.2. LLE 2 method

The LLE 2 method was based on the method suggested by Amen-Chen *et al.* (1997) [11] and proceeded step by step in order to obtain one ethyl acetate fraction (*Scheme* 1(b)).

Ethyl acetate fraction (L2F1): The 4 g of bio-liquid and 4 g of ethyl acetate (1:1, w/w) were mixed thoroughly and transferred into a separatory funnel. Then, various concentrations of NaOH solution including 0.05 M, 0.3 M, and 2.0 M was added (1:1, w/w), respectively. When the layer was divided after shaking the separatory funnel, the NaOH fraction, the lower part, was separated for next step. After discarding ethyl acetate layer, NaOH solution at various concentrations were mixed to the NaOH fraction in the ratio of 1:1(w/w) and then the same extraction process was repeated 5 times. After the final extraction, the NaOH layer, an aqueous layer, was mixed with 50 % $H_2SO_4$ to adjust pH to 6.

Then, the mixture of ethyl acetate and the NaOH solution (1:2, w/w) was added to the aqueous layer to remove NaOH layer and to separate the ethyl acetate layer 4 times. Then, syringe filtration was performed prior to further use.

### 2.3. CC 1 method

The CC 1 method was based on the method suggested by Ba (2004) [12] and proceeded as shown in *Scheme* 1(c).

A glass column (I.D. 16 mm × 450 mm) was filled with 10 g silica gel (70-230 mesh) and then with 5 g of bio-liquid. In order of a polarity increase, each 100 mL of pentane (C1F1), benzene (C1F2), dichloromethane (C1F3), ethyl acetate (C1F4), and methanol (C1F5) were added for elution to obtain total 5 fractions. After rotary evaporation to remove the solvent from the eluent, the 1 mL of same solvent as each fraction (3 mL for pentane) was added for syringe filtration.

### 2.4. CC 2 method

The CC 2 method was based on the method suggested by Das *et al.* (2004) [13] as shown in *Scheme* 1(d). A glass column (I.D. 25 mm × 450 mm) was filled with 20 g of silica gel (70-230 mesh) and then with 10 g of bio-liquid. In order of a polarity increase, solvents were added to obtain each fraction. The 100 mL of mixture of hexane and ethyl acetate in the ratio of 95:5 (v:v) (C2F1) was added to the same column and then a vial was filled with the fraction. Next, the 100 mL of mixtures of hexane and ethyl acetate (80:20, v:v) (C2F2), hexane and ethyl acetate (75:25, v:v) (C2F3), chloroform and methanol (95:5, v:v) (C2F4), chloroform and methanol (90:10, v:v) (C2F5), and chloroform and methanol (80:20, v:v) (C2F6), respectively, were eluted to the same column and then a vial was filled with each fraction. Moisture was removed from the solvents of each fraction using $MgSO_4$. After rotary evaporation, each fraction was reconstituted with same solvent but different volumes: 1 mL for C2F1, C2F2, C2F3, C2F4, and 6 mL for C2F5, C2F6. Prior to GC injection, syringe filtration was applied.

### 2.5. GC/MS analysis

Bio-liquid extracted by total 4 extraction methods were prepared and qualitative and quantitative analyses were determined by GC/MS. GC system (Agilent 7820) was equipped with MSD 5977E quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Separation was performed using a capillary column HP5-MS fused-silica capillary column (30 m × 0.25 mm × 0.25 μm) with helium (99.999 %) carrier gas at a flow rate of 1 mL/min. The injection was performed in splitless mode and the injector temperature was set at 290 °C. The oven temperature program was varied according to the extraction methods. For LLE1 method, the temperature was started at 30 °C held for 2 min increased by 10 °C/min to 300 °C held for 5 min. For LLE2 method, it was started at 50 °C held for 2 min increased by 10 °C/min to 200 °C, and continued to increase to 270 °C by rate of 30 °C/min held for 15 min. For CC1 method, it was started from 50 °C held for 2 min and increased by 5 °C/min to 290 °C. For CC2 method, 40 °C held for 2 min and increased by 5 °C/min to 270 °C (He flow rate: 0.7 mL/min). The MS transfer line was maintained at 280 °C. Electron ionization was performed at 70 eV with the source temperature at 230 °C and quadrupole at 150 °C. Full scan MS acquisition was done, m/z range of 35 Da–500 Da, for selecting the most appropriate m/z for the detection of each analyte in selected ion monitoring (SIM) mode.

## 3. Results and Discussion

### 3.1. Qualitative analysis

#### 3.1.1. LLE 1 method

The result of GC/MS with analysis using LLE 1 is summarized by each fraction as shown in *Table* 1 and *Fig.* 1(a). In the chromatogram, FAMEs were detected or its peak area had high fractions. The n-hexane soluble fraction (L1F1) was transparent because it was not well mixed with a bio-liquid and hydrocarbon and amines were mainly detected in this fraction. Hydrocarbons are generated by decarboxylation reaction in which CO or $CO_2$ is lost during HTC reaction [14]. Amines with a heavy molecular weight

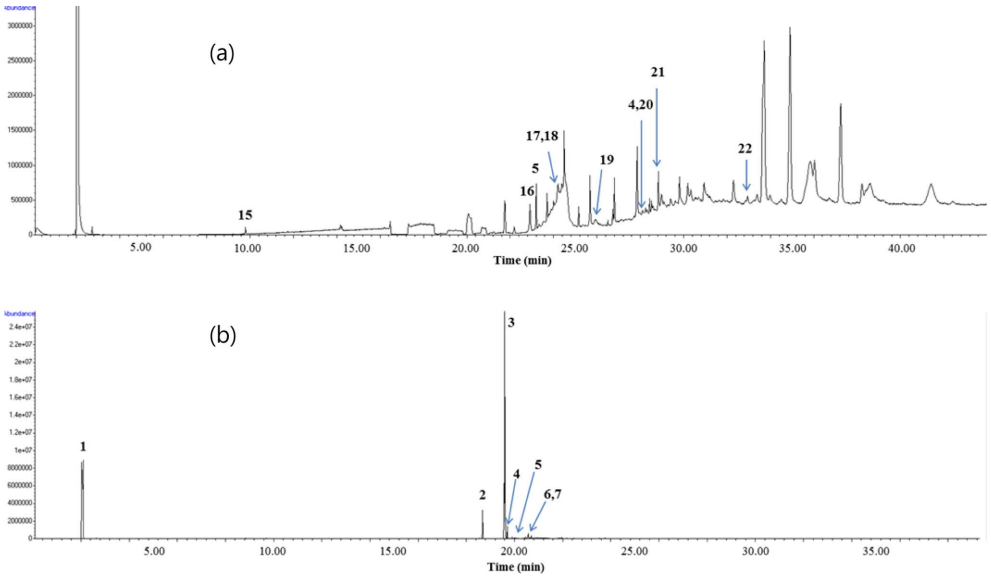



*Fig.* 1. Chromatograms of liquid-liquid extraction methods. (a) water insoluble fraction (L1F4) using liquid-liquid extraction 1 method and (b) 2 M NaOH extraction (L2F1) using liquid-liquid extraction 2 method. Peak numbers of *Fig.* 1(a) and *Fig.* 1(b) are same as in *Tables* 1 and 2, respectively.

*Table* 1. Normalization method for bio-liquid analysis extracted by LLE1 method and identified by GC/MS

| Peak No. | Compound | Normalized peak area % | | |
|---|---|---|---|---|
| | | Fraction* | | |
| | | L1F1 | L1F3 | L1F4 |
| 1 | 1,3-bis(4-methoxyphenyl)-5-phenyl-1,3,5-triazinane-2-thione | 0.93 | | |
| 2 | eicosane | 1.74 | | |
| 3 | tris(2-methyl-3-indolizinyl)methane | 50.36 | | |
| 4 | octadecane | 19.28 | | 2.97 |
| 5 | N,N-diethyl-N',N'-diphenyl-6-(1H-pyrrol-1-yl)-1,3,5-triazine-2,4-diamine | 27.69 | | 14.87 |
| 6 | 4-oxopentanoic acid | | 3.61 | |
| 7 | 2-pyrrolidinone | | 10.29 | |
| 8 | 4(1H)-pyridone | | 21.95 | |
| 9 | 3-methyl-2(1H)-pyridinone | | 2.66 | |
| 10 | 6-methyl-3-pyridinol | | 31.08 | |
| 11 | 2,6-dimethyl-3-pyridinol | | 4.02 | |
| 12 | 5-hydroxymethyldihydrofuran-2-one | | 13.63 | |
| 13 | hexahydro-pyrrolo[1,2-a]pyrazine-1,4-dione | | 5.25 | |
| 14 | 3,9-diazatricyclo[7.3.0.0(3,7)]dodecan-2,8-dione | | 7.50 | |
| 15 | 1-methyl-4-(1-methylethenyl)-cyclohexene | | | 1.82 |
| 16 | 8-octadecenoic acid, methyl ester | | | 19.01 |
| 17 | 1-chloroeicosane | | | 8.93 |
| 18 | propanoic acid,3,3'-thiobis-, 1,1'-didodecyl ester | | | 21.49 |
| 19 | dotriacontane | | | 2.97 |
| 20 | nonadecane | | | 4.62 |
| 21 | 2-methyl-eicosane | | | 17.03 |
| 22 | 1-iodo-octadecane | | | 6.29 |

*L1F1: n-hexane solubles fraction
L1F2: ether solubles fraction
L1F3: ether insoluble fraction
L1F4: water insoluble fraction

might be present in the hexane fraction because of insolubility in water. In ether extraction, the ether soluble fraction (L1F2) was relatively transparent and the ether insoluble (L1F3) fraction was light brown. The analyte was not detected in the L1F2 fraction whereas acid, ketone, pyridinol, and pyridone were detected in the L1F3 fraction. The water insoluble fraction (L1F4) was slightly yellow and hydrocarbons were mostly observed, and ester and acid were also detected as a result of HTC reaction. By the LLE 1 method, one type of FAMEs, 8-octadecenoic acid methyl ester, was identified in L1F4 fraction.

#### 3.1.2. LLE 2 method

The result of LLE 2 method analyzed by GC/MS is shown in *Table* 2 and *Fig.* 1(b). In the result of GC/MS analysis, there was no trend that the amount of components increased or decreased depending on increased concentrations of NaOH solution added. The most components identified by this method were FAMEs. We propose that volatile or nonvolatile organic acids might be converted to ester by NaOH, a base catalyst (esterification: RCOOH + R'-OH → RCOOR' + $H_2O$). In addition, it was also assumed that they were converted to ester by solid acids [15]. Among FAMEs detected in this method, 10-octadecenoic acid methyl ester was largest based on the normalized peak area and they were detected at all the concentrations of NaOH solution added. Further studies on potential utilization of bio-liquids with esterification using a base catalyst would be meaningful according to the result of LLE2 method.

#### 3.1.3. CC 1 method

The analysis of bio-liquid using CC 1 followed by GC/MS is shown in *Table* 3 and *Fig.* 2(a). Paraffin solvents such as pentane were used for aliphatic compounds and benzene for aromatic compounds analyses. Methanol was used for other polar compounds [16]. Based on the solvent properties, extraction was performed using pentane, benzene, dichloromethane, ethyl acetate, and methanol in order of a polarity increases in the column. As the polarity increased, the color of the fraction was getting dark. The pentane and benzene fractions were almost transparent while the dichloromethane and ethyl acetate fractions were light yellow, and the methanol fraction was light brown. Various components were identified depending on different fractions. Most of hydrocarbons were rapidly separated from bio-liquid and extracted by non-polar solvents because bio-liquid has high polarity [7]. An aliphatic hydrocarbon compounds were mostly detected in the pentane fraction (C1F1). In the benzene fraction (C1F2), various types of hydrocarbons and FAMEs were detected. In the dichloromethane fraction (C1F3), esters and ketones were detected. FAMEs were also detected in the ethyl acetate fraction (C1F4) while phenol was detected. Phenol is generated by hydrothermal treatment of cellulose and first extracted from coal tar [17]. In the methanol fraction (C1F5), esters were mainly detected and acid and ketone were also identified. Overall, FAMEs were detected in all fractions except the pentane fraction.

*Table* 2. Normalization method for bio-liquid analysis extracted by LLE2 method and identified by GC/MS

| Peak No. | Compound | Normalized peak area % | | |
|---|---|---|---|---|
| | | NaOH concentration (M) | | |
| | | 0.05 | 0.3 | 2 |
| 1 | acetic acid, ethyl ester | 44.20 | 69.08 | 40.22 |
| 2 | hexadecanoic acid, methyl ester | 2.98 | 1.78 | 4.23 |
| 3 | 10-octadecenoic acid, methyl ester | 46.81 | 27.24 | 51.54 |
| 4 | octadecanoic acid, methyl ester | 1.50 | 1.01 | 1.91 |
| 5 | 9-octadecenoic acid(Z)-, ethyl ester | 3.20 | - | 0.38 |
| 6 | 13-eicosenoic acid(Z)-, methyl ester | 0.92 | 0.60 | 1.18 |
| 7 | eicosanoic acid, methyl ester | 0.40 | 0.28 | 0.54 |

*Table* 3. Normalization method for bio-liquid analysis extracted by CC1 method and identified by GC/MS

| Peak No. | Compound | Normalized peak area % | | | | |
|---|---|---|---|---|---|---|
| | | Fraction* | | | | |
| | | C1F1 | C1F2 | C1F3 | C1F4 | C1F5 |
| 1 | hexadecane | 3.66 | | 0.66 | | |
| 2 | pentadecane | 12.23 | | | | |
| 3 | tetradecane | 9.04 | | | | |
| 4 | octadecane | 4.87 | | 0.61 | | |
| 5 | heptacosane | 18.16 | | | | |
| 6 | methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate | 1.71 | | | | |
| 7 | heptadecane | 11.58 | | | | |
| 8 | hentriacontane | 4.82 | | | | |
| 9 | eicosane | 6.39 | | | | |
| 10 | 2,5-di-tert-butyl-1,4-benzoquinone | 3.15 | | | | |
| 11 | docosane | 9.13 | 0.20 | 0.58 | | |
| 12 | tricosane | 1.48 | | | | |
| 13 | tetratriacontane | 9.41 | | | | |
| 14 | pentacosane | 1.99 | | | | |
| 15 | octacosane | 2.36 | | | | |
| 16 | cyclohexane | | 0.45 | | | |
| 17 | cyclopentane | | 0.51 | | | |
| 18 | norbornane | | 0.53 | | | |
| 19 | toluene | | 1.20 | | | |
| 20 | hexadecanoic acid, methyl ester | | 9.60 | 10.66 | 6.34 | 4.54 |
| 21 | 9,12-octadecadienoic acid(Z,Z)-, methyl ester | | 14.17 | | 11.38 | 14.98 |
| 22 | 9-octadecenoic acid(Z)-, methyl ester | | 71.34 | | | 52.13 |
| 23 | (Z)-11-eicosenoic acid, methyl ester | | 1.22 | | | |
| 24 | nonadecanoic acid, methyl ester | | 0.78 | | | |
| 25 | 9,12-octadecadienoic acid(E,E)-, methyl ester | | | 10.67 | | |
| 26 | 9-octadecenoic acid(E)-, methyl ester | | | 61.34 | 48.18 | |
| 27 | octadecanoic acid, methyl ester | | | 2.31 | | |
| 28 | 1,2-benzenedicarboxylic acid, mono(2-ethyl hexyl)ester | | | 2.87 | | |
| 29 | 6,8-dibromo-2-(3-pyridyl)-4-phenyl-quinazoline | | | 10.30 | | |
| 30 | 3-pyridinol | | | | 5.39 | |
| 31 | 3-hydroxy-5-methyl pyridine | | | | 6.76 | |
| 32 | (+)-(s)-5-hydroxymethyloxolan-2-one | | | | 1.39 | |
| 33 | phenol, 4-amino | | | | 0.70 | |
| 34 | pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- | | | | 2.69 | |
| 35 | 13-octadecenoic acid(Z)-, methyl ester | | | | 1.65 | |
| 36 | 13-eicosenoic acid(Z)-, methyl ester | | | | 1.05 | |
| 37 | cyclo(-pro-phe) | | | | 1.35 | |
| 38 | 2(3H)-furanone, dihydro-5-methyl- | | | | 3.14 | |
| 39 | 3-pyridinol, 6-methyl- | | | | 0.86 | |
| 40 | 2,6-dimethyl-3-hydroxypyridine | | | | 2.13 | |
| 41 | dianhydromannitol | | | | 2.36 | |
| 42 | pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro- | | | | 4.64 | |
| 43 | 3,9-diazatricyclo[7.3.0.0(3,7)]dodecan-2,8-dione | | | | | 5.77 |
| 44 | di-n-octyl phthalate | | | | | 22.58 |

*C1F1: pentane fraction
C1F2: benzene fraction
C1F3: dichloromethane fraction
C1F4: ethyl acetate fraction
C1F5: methanol fraction

*Table* 4. Normalization method for bio-liquid analysis extracted by CC2 method and identified by GC/MS

| Peak No. | Compound | Normalized peak area % | | | | | |
|---|---|---|---|---|---|---|---|
| | | Fraction* | | | | | |
| | | C2F1 | C2F2 | C2F3 | C2F4 | C2F5 | C2F6 |
| 1 | 7,9-dimethyl hexadecane | 0.06 | | | | | |
| 2 | pentadecane | 0.52 | 0.63 | 0.16 | 7.41 | | |
| 3 | hexatriacontane | 0.06 | | | | | |
| 4 | octadecane | 0.26 | 0.11 | 0.65 | 3.65 | 0.14 | |
| 5 | tetradecane | 0.24 | 0.08 | 0.10 | 0.21 | | |
| 6 | 1-dodecanol | 0.39 | | | | | |
| 7 | docosane | 1.07 | 0.32 | 0.71 | 5.26 | 0.25 | |
| 8 | nonanedioic acid, dimethyl ester | 0.13 | 0.04 | | | | |
| 9 | hexadecane | 0.52 | 0.04 | 0.29 | 2.91 | | |
| 10 | heneicosane | 1.30 | 0.59 | 0.64 | 0.66 | | |
| 11 | tetradecanoic acid, methyl ester | 0.19 | 0.20 | 0.23 | | | |
| 12 | hexadecanoic acid, methyl ester | 10.87 | 10.42 | 9.71 | 13.10 | 7.14 | 7.19 |
| 13 | 9,12-octadecadienoic acid(E,E)-, methyl ester | 10.19 | | | | 16.53 | 22.97 |
| 14 | 9,12-octadecadienoic acid(Z,Z)-, methyl ester | | | | 7.89 | | |
| 15 | 9-octadecenoic acid(Z)-, methyl ester | 62.46 | | | | 52.24 | 63.53 |
| 16 | 9-octadecenoic acid(E)-, methyl ester | | 20.05 | 74.69 | 40.17 | 3.06 | |
| 17 | 11-octadecenoic acid(Z)-, methyl ester | 3.98 | | | | | |
| 18 | octadecanoic acid, methyl ester | 4.15 | 4.92 | 3.13 | 2.46 | 2.63 | 2.94 |
| 19 | docosane | 0.80 | | | | | |
| 20 | 11-eicosenoic acid(Z)-, methyl ester | 1.78 | 3.48 | 2.02 | 1.54 | 1.43 | 1.79 |
| 21 | eicosanoic acid, methyl ester | 1.04 | 2.03 | 1.00 | | | 0.95 |
| 22 | 2,6,11-trimethyldodecane | | 0.11 | | | | |
| 23 | 9-oxo-nonanoic acid, methyl ester | | 0.08 | 0.10 | 0.36 | | |
| 24 | 2,6-di(tert-butyl)benzo-1,4-quinone | | 0.04 | | | | |
| 25 | 2-methyloxine | | 0.03 | | | | |
| 26 | 2-ethyl-2-methyl, tridecanol | | 0.04 | | | | |
| 27 | dodecanoic acid, methyl eater | | 0.04 | 0.07 | | | |
| 28 | heptadecane | | 0.20 | | | | |
| 29 | 9-hexadecenoic acid(Z)-, methyl ester | | 0.56 | 1.00 | | | |
| 30 | 13-octadecenoic acid(Z)-, methyl ester | | 53.76 | | | | |
| 31 | 9(Z),11(E)-octadecadienoic acid | | 0.77 | | | | |
| 32 | 13-docosenoic acid, methyl ester | | 0.41 | | | | |
| 33 | docosanoic acid, methyl ester | | 1.04 | 0.54 | | 0.44 | 0.63 |
| 34 | dodecane | | | 0.15 | 1.47 | | |
| 35 | 4-methylquinolin-8-ol | | | 0.12 | | | |
| 36 | hexadecanoic acid, ethyl ester | | | 0.33 | | | |
| 37 | eicosane | | | 0.58 | 4.31 | 0.16 | |
| 38 | 9,12-octadecadienoic acid(Z,Z)-, ethyl ester | | | 0.59 | | | |
| 39 | 9-octadecenoic acid(Z)-, ethyl ester | | | 2.44 | | | |
| 40 | 9-octadecenamide | | | 0.75 | 6.16 | 0.96 | |
| 41 | tetracosane | | | | | 1.88 | |
| 42 | tetradecanal | | | | 0.50 | | |
| 43 | cyclododecane | | | | 0.97 | | |
| 44 | cyclotetradecane | | | | 0.97 | | |
| 45 | 2-pyrrolidinone | | | | | 0.95 | |
| 46 | 3-pyridinol | | | | | 4.56 | |
| 47 | 6-methyl-3-pyridinol | | | | | 4.75 | |
| 48 | pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- | | | | | 0.61 | |
| 49 | 3,9-diazatricyclo[7.3.0.0(3,7)]dodecan-2,8-dione | | | | | 2.27 | |

*C2F1: hexane and ethyl acetate fraction (95:5, v/v)
C2F2: hexane and ethyl acetate fraction (80:20, v/v)
C2F3: hexane and ethyl acetate fraction (75:25, v/v)
C2F4: chloroform and methanol fraction (95:5, v/v)
C2F5: chloroform and methanol fraction (90:10, v/v)
C2F6: chloroform and methanol fraction (80:20, v/v)

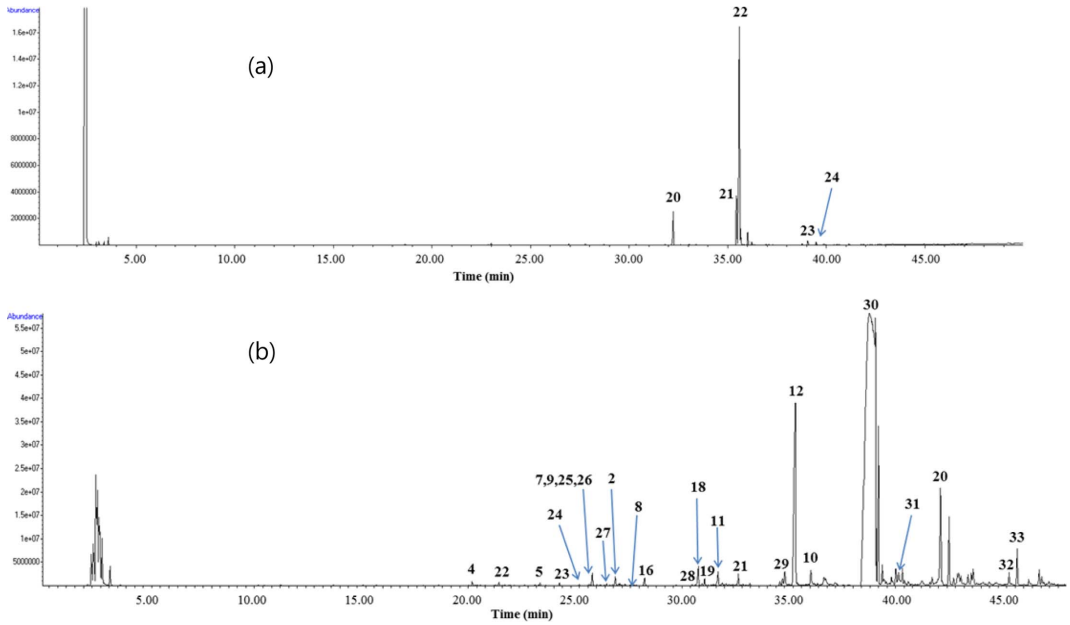



*Fig.* 2. Chromatograms of column chromatography methods. (a) benzene soluble fraction (C1F2) using column chromatography 1 method and (b) hexane: ethyl acetate = 80:20 soluble fraction (C2F2) using column chromato- graphy 2 method. Peak numbers of *Fig.* 2(a) and *Fig.* 2(b) are same as in *Tables* 3 and 4, respectively.

#### 3.1.4. CC 2 method

The results of GC/MS analysis of bio-liquid using CC 2 method is shown in *Table* 4 and *Fig.* 2(b). Similar to CC1 method, solvents with different polarity were used for extraction in the column. In the fraction using a mixed solvent with non-polar hexane and ethyl acetate, hydrocarbons were mostly detected and esters and acids were also observed. In this analysis, FAMEs were considerably detected like CC1 method as described in section 3.1.3. In the fraction of a solvent containing methanol, amount of hydrocarbons decreased while esters and ketones increased as methanol increased. In particular, esters were detected but hydrocarbons were not in the fraction containing 20 % methanol (C2F6).

### 3.2. FAMEs analysis depending on the extraction methods

In the results of HTC bio-liquid analysis using LLE 1, LLE 2, CC 1, and CC2 methods, various types of FAMEs with saturated or unsaturated hydrocarbons were identified and summarized in *Tables* 1 through 4. Especially, FAMEs with unsaturated hydrocarbons were more detected than that of saturated hydrocarbons resulting in thermal stability. FAMEs with long chains might play a role to increase viscosity.

By normalization of GC/MS areas of each FAME identified by different extraction methods, 7 FAMEs were selected for comparison including hexadecanoic acid methyl ester, octadecanoic acid methyl ester, 9-octadecenoic acid(E)-methyl ester, 9-octadecenoic acid(Z)-methyl ester, 9,12-octadecadienoic acid(E,E)-methyl ester, 9,12-octadecadienoic acid(Z,Z)-methyl ester, and 10-octadecenoic acid methyl ester. Out of 7 FAMEs, the normalized areas obtained by GC/MS analysis of hexadecanoic acid methyl ester, 9-octadecenoic acid(E)-methyl ester, and 9-octadecenoic acid(Z)-methyl ester were relatively large. In addition, relatively large amounts of 7 FAMEs were analyzed in the CC 2 method comparing to other extraction methods investigated in this study. Therefore, it was suggested that CC2 extraction method is the most appropriate method to analyze FAMEs among 4 extraction methods in the study.

## 4. Conclusion

Bio-liquids obtained from HTC reaction of real food waste were analyzed using LLE and CC methods. Each experiment was divided into 2 methods and therefore total 4 methods were investigated. In the result, various components of bio-liquid were detected in the analysis using CC and analytes were differently detected depending on solvent polarity. In particular, FAMEs being able to be used as a biodiesel fuel was diversely detected in CC. Different compounds generated through a decomposition reaction were generated from bio-liquid including alcohols, organic acids, ethers, esters, aldehydes, ketones, and phenol. It was confirmed that bio-liquid used in the study mostly consisted of esters and hydrocarbons. It shows that non-volatile compounds such as benzoic acid and benzene dicarboxylic acid known to be products of bio-liquid from pyrolysis were not detected. FAMEs and hydrocarbons being considered as tentative alternative energy obtained from bio-liquid of food waste via HTC reaction was effectively identified by CC extraction method. It is suggested to conduct further study on potential utilizations as alternative energy and other applications of bio-liquid based on the results of this study.

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