**Highlights:**

Direct coal liquefaction residue was firstly extracted at 25 ℃by liquefied DME;

It achieved a higher yield than those by Soxhlet method using acetone or hexane;

The extract had a high content of C and low contents of S, O, and ash (< 0.1%);

Abundant polycyclic aromatic hydrocarbons in the extract were determined;

DME extraction is as good as acetone Soxhlet extraction on molecular compositions.

# Room-Temperature Extraction of Direct Coal Liquefaction Residue by Liquefied Dimethyl Ether

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## Abstract

Direct coal liquefaction residue (DCLR) is the main byproduct during the direct coal liquefaction process. The efficient recovery of organic components from DCLR at low temperatures is beneficial for improving the economy and reducing energy consumption and environmental pollution. Here, DCLR was extracted using liquefied dimethyl ether (DME), acetone, and hexane as the solvents. Compared with the other two solvent Soxhlet extraction, the DME extraction process was performed at room temperature with the shortest extraction time, the lowest energy consumption, and the highest extraction yield (16.2%). Owing to the high carbon contents, low sulfur and oxygen contents, and low ash contents (< 0.1%), the extracts obtained using liquefied DME and acetone naturally became the feedstock of carbon materials. Based on the results of the gas chromatography-mass spectrometry analysis, the extracts obtained using the three different solvents had similar compositions in light compounds and were abundant in polycyclic aromatic hydrocarbons with two-, three-, four-, five-, and six-membered benzene rings, indicating that all three DCLR extracts are potential raw materials for preparing high value-added carbon materials. Furthermore, the molecular composition analysis revealed that the room-temperature extraction using liquefied DME was as good as high-temperature Soxhlet extraction using acetone, considering the similarity of their compositions in high molecular weight species and the considerably higher efficiency than that of high-temperature Soxhlet extraction using hexane. Due to the low energy consumption, short extraction time, high extraction yield, and high performance of the extract, liquefied DME is an efficient and economic solvent for extracting DCLR.

**Keywords**: Direct coal liquefaction residue; extraction; room temperature; liquefied dimethyl ether; polycyclic aromatic hydrocarbons; molecular composition.

## 1. Introduction

The processes of direct coal liquefaction (DCL) and indirect coal liquefaction (ICL) are the two most important technologies used to convert coal into liquid fuels and chemicals [1]. In the DCL process, vast quantities (~0.5 million t/a) of an undesirable byproduct commonly called the DCL residue (Hereafter, referred to as DCLR), accounts for 20-30 wt% of the raw coal consumed in the DCL process and has emerged as a serious problem for industrial application [2, 3]. DCLR contains high-boiling-point liquefied oils, asphaltenes, unreacted coal, mineral matter, and liquefaction catalysts [4]. In light of the economic and environmental considerations, DCLR must be effectively utilized.

DCLR was primarily used as a feedstock for combustion, gasification, pyrolysis, and carbonization to produce heat, fuel gas, tar, and coke, respectively [5-8], which have low market values and may cause additional environmental problems. The organic components in DCLR, such as liquefied oil and asphaltenes, are valuable products. In particular, because of the abundance of polycyclic aromatic structures (PASs) [9], DCLR is considered an excellent precursor for preparing various high-grade carbon materials, such as carbon micro/nanofibers [10, 11] and porous carbons [12, 13].

The solvents, which have been used for extracting DCLR, can be classified into three groups: traditional organic solvents, water, and ionic liquids. Up to now, DCLR has been extracted by using various traditional organic solvents, such as acetone [2], methanol [14], ethanol [14], isopropanol [2, 14], dipropylamine [9, 15], toluene [16], and benzene [2, 16, 17]; the energy cost is moderate, but most of the solvents used are toxic. Subcritical water extraction, using hot water (100-374 °C) as the only solvent, is a green and efficient method to extract organic components from DCLR [18]; however, the high energy consumption due to high extraction temperature and requirements of apparatus resistant to high temperature and pressure may greatly limit its industrial application. By comparison, ionic liquids are more suitable for extracting DCLR, because the extraction is conducted at room temperature and most ionic liquids are green solvents [3, 19-24]. However, ionic liquids are much more expensive than other organic solvents, and the process of separating the extract from the solvent is highly complex [18].

**Table 1** The ultimate and proximate analyses of DCLR sample, and extracts and residues after extraction processes.

| Sample name | Ultimate analysis [wt%, daf] [a] | | | | | Atomic ratio [-] | | Proximate analysis [wt%, db] [b] | | | Moisture [wt%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | H | N | S | O (diff.) | H/C | O/C | FC | VM | Ash | |
| DCLR | 77.1 | 3.9 | 1.0 | 1.9 | 16.1 | 0.60 | 0.16 | 42.4 | 42.6 | 15.0 | 0.64 |
| DME-R | 75.6 | 3.8 | 0.9 | 2.1 | 17.6 | 0.59 | 0.17 | 47.4 | 36.9 | 15.7 | -- |
| DME-E | 88.9 | 6.8 | 1.2 | 0.3 | 2.8 | 0.92 | 0.02 | 7.8 | 92.1 | 0.1 | -- |
| Acetone-R | 75.3 | 3.7 | 0.9 | 2.0 | 18.1 | 0.59 | 0.18 | 49.9 | 34.4 | 15.7 | -- |
| Acetone-E | 88.9 | 6.4 | 1.3 | 0.2 | 3.2 | 0.86 | 0.03 | 5.2 | 94.7 | 0.1 | -- |
| Hexane-R | 77.0 | 3.9 | 1.0 | 1.9 | 16.2 | 0.60 | 0.16 | 46.7 | 38.8 | 14.5 | -- |
| Hexane-E | 82.6 | 6.7 | 0.6 | 0.1 | 10.0 | 0.97 | 0.09 | 2.5 | 96.0 | 1.5 | -- |

[a] daf means dry ash-free basis; [b] db means dry basis.

Therefore, a non-toxic, economical, and effective solvent is particularly desired for extracting organic components from DCLR.

Dimethyl ether (DME, $CH_3OCH_3$), which is the simplest ether, is a colorless gas with a slight ether-like fragrance at ambient temperature and pressure. The boiling point, critical temperature, and critical pressure of DME are -24.2 ℃, 128 ℃, and 5.4 MPa, respectively. At normal ambient temperature, DME is easily compressed, and liquefied DME dissolves 7-8% by the weight of water [25]. DME is non-reactive, non-toxic, non-carcinogenic, and does not induce pH change in aqueous solution [26]. Furthermore, it has a competitively low price and is a safe solvent for use in the field of food processing [27]. Thus, it can be adequately safe and economic to adapt DME in an extraction process.

Compared to other techniques, extraction using liquefied DME has the advantages of non-toxicity, low operating temperature (room temperature), short extraction time, simple operational process, and environmental compatibility. Liquefied DME can extract water, lipids, or functional ingredients from various feedstocks [28]. All the DME extraction processes are performed at low temperatures (including room temperature) in the range from 20 to 60 ℃ and under pressures ranging from 0.5 to 1.4 MPa. Herein, ‘room temperature’ is defined by the Japanese Pharmacopeia as 1-30 ℃ [29]. Furthermore, due to the low boiling point, liquefied DME can evaporate at room temperature after the extraction process without heating, which is beneficial for reducing energy consumption and improving the economy of the

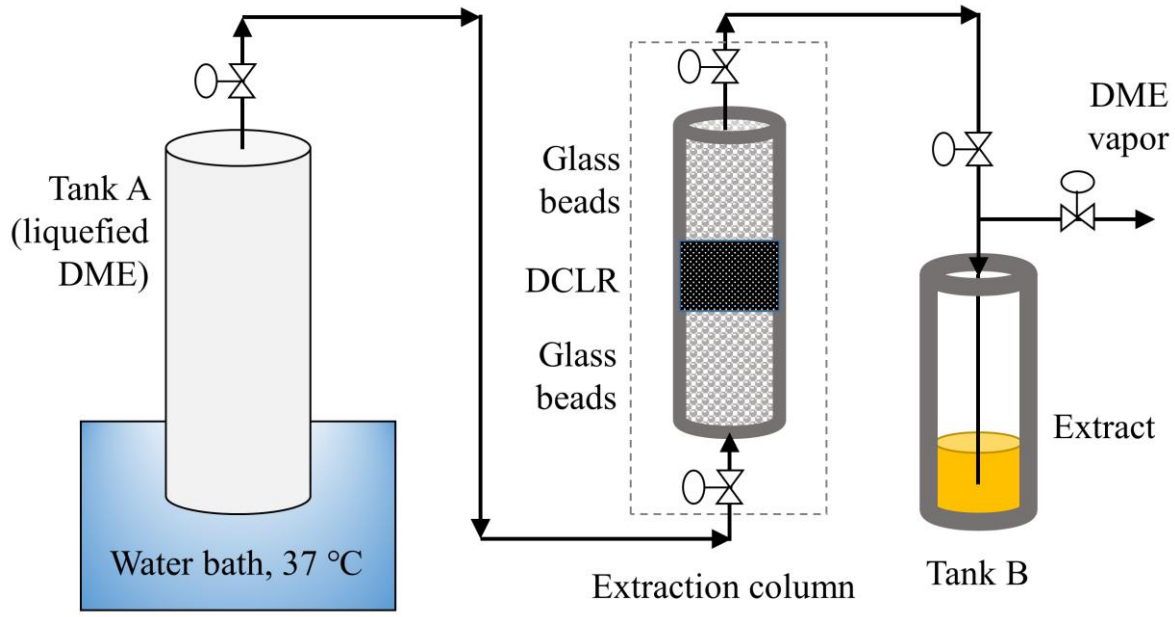


**Figure 1** Schematic diagram of the DME extraction apparatus.

DCL process.

Here, we conducted the room-temperature extraction of DCLR using liquefied DME as the solvent, compared it with those by the traditional Soxhlet method using acetone and *n*-hexane as the solvents, and studied the yield, elemental composition, compound composition, and molecular composition of the extracts in detail.

## 2. Material and Methods

### 2.1. Materials and solvents

The raw DCLR sample was obtained from Shenhua direct coal liquefaction plant in China. **Table 1** shows the ultimate and proximate analysis results of the DCLR sample. The DCLR sample has a low moisture content of 0.64 wt%, a high ash content of 15.0 wt%, and 77.1 wt% of C and 3.9 wt% of H (H/C = 0.60). The contents of volatile matter (VM) and fixed carbon (FC) are close, at 42.4% and 42.6%, respectively. Before the extraction process, the DCLR sample was grounded and sieved by a 250 μm sieve.

The solvents for extraction included acetone (for high performance liquid chromatography (HPLC); FUJIFILM Wako Pure Chemical Corp., Osaka, Japan), *n*-hexane (for HPLC; FUJIFILM Wako Pure Chemical Corp., Osaka, Japan), and liquefied DME (Spray-work aircan 420D; Tamiya Inc., Shizuoka, Japan).

**2.2. DME extraction process**

**Figure 1** schematically shows the laboratory-scale DME extraction apparatus. A tank containing liquefied DME (tank A; volume: 1000 $cm^3$; Taiatsu Techno Corp., Saitama, Japan), an extraction column (diameter: 11.6 mm, length: 190 mm; HPG-10-5; Taiatsu Techno Corp., Saitama, Japan), and a collection tank (tank B; HPG-96-3; Taiatsu Techno Corp., Saitama, Japan) were connected in series. In a typical experiment, 3 g of DCLR sample was used as the raw material. After the DCLR sample was loaded into the extraction column, glass beads (diameter between 1.5 and 2.5 mm; BZ-2, AS ONE Corp., Osaka, Japan) were loaded at the top and bottom ends of the column. The liquefied DME in tank A was maintained at 37 ± 1 ℃ in a water bath, and its saturated vapor pressure was 0.82 ± 0.02 MPa. The liquefied DME was supplied from tank A and flowed to the extraction column owing to the pressure difference between tank A and the extraction column. The DME flow rate was maintained at ~8 mL/min by controlling a valve at the outlet of the extraction column. Through a long tube between tank A and the extraction column, DME was cooled down, and the extraction was performed at 25 ℃ in the extraction column. After the liquefied DME passed through the extraction column at different time intervals, DME was evaporated by opening the pressure-reducing valve of tank B. The total extraction time was less than 60 min. After the extraction, the residue and extract (referred to as ‘DME-R’ and ‘DME-E’, respectively) were collected from the extraction column and tank B, respectively, and weighed. The consumption of DME during the extraction process was calculated by the mass difference of liquefied DME in tank A.

**2.3. Soxhlet extraction process**

DCLR was extracted by acetone and hexane (*n*-hexane), respectively, using a Soxhlet apparatus (Vidrolabor®). In each experiment, 3 g of DCLR sample and 200 mL of solvent were used for the extraction. The refluxing started at temperatures above the boiling points of the solvents, which are 56.5 ℃ and 69 ℃ for acetone and hexane, respectively. After the extraction proceeded for 6 h, the solvent was separated from the extract at 60 ℃ under reduced pressure using a rotary evaporator. The residues and extracts were dried, collected, kept in sealed glass vessels, and stored in a refrigerator until further analysis. They are referred to as 'Acetone-R', 'Hexane-R', 'Acetone-E', and 'Hexane-E', in which 'R' and 'E' refer to the residue and extract, respectively.

**2.4. Characterization**

The elemental composition of the solid product was determined using a CHNS analyzer (2400 CHNS/O Series II System; PerkinElmer Inc., MA, USA). The moisture content was tested by using a halogen moisture meter (65g0001g; AS ONE Corp., Osaka, Japan). The VM, FC, and ash contents were measured using a thermogravimetric analyzer (TG 8120; Rigaku Corp., Osaka, Japan). According to the National Institute of Standard and Technology (NIST) mass spectral database, light compounds in the extracts were identified by gas chromatography-mass spectrometry (GC-MS) (7890A GC system and 5975C inert XL MSD with a triple-axis detector; Agilent Technologies, Inc., CA, USA) using a diphenyl-dimethylpolysiloxan column (DB-5; 30 m × 0.25 mm ×0.25 μm; Agilent Technology Tokyo Ltd, Japan) and tetrahydrofuran (THF; stabilizer free for HPLC; ≥ 99.8%; Wako Pure Chemical Industries, Ltd., Osaka, Japan) as the solvent. The chromatograph was temperature-programmed from 40 to 300 °C at a rate of 5 °C/min. The injection volume of the sample was 1 μL and He was used as the carrier gas with a flow rate of 24 mL/min.

The extraction yield was defined as the percentage of the mass of extract against the total mass of the raw DCLR sample excluding moisture and ash. The calculation equation (Eq. 1) is shown as follows.

$$Extraction\ yield\ = \frac{Mass\ of\ extract\ (g)}{Mass\ of\ raw\ DCLR\ (g)} \times 100\% \quad (1)$$

## 2.5. Mass and Kendrick mass defect analyses

All the chemicals for mass analyses were purchased from Wako Pure Chemicals (Osaka, Japan) unless otherwise mentioned. The laser desorption ionization high-resolution mass spectra (LDI-HRMS) were recorded using a JMS-S3000 spiralTOF$^{TM}$ instrument (JEOL, Tokyo, Japan) operated in positive ion mode. First, 0.5 µL of the extracts solubilized in THF at 1 mg/mL was deposited on a disposable target plate (Hudson Surface Technology, NJ, USA) to form a thin layer. This was repeated three times for confirming repeatability of the LDI-HRMS fingerprint and three times for internal calibration using the sodium adducts of sodium trifluoroacetate (NaTFA) and [3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile for the low mass range of <300 Da and 600 g/mol poly(methylmethacrylate) for the high mass range up to 700 Da. The voltages, delay time, and laser fluence were adjusted once to record a satisfactory signal just above the desorption threshold with resolving at ~45000 along the entire mass range and further kept identical for all the extracts for the sake of comparison. Instrument control, data acquisition, and preliminary processing of all the experiments were achieved using MSTornado provided by JEOL.

The Kendrick mass defect (KMD) analyses and assignments of the ion series were done from the peak lists generated with mMass 5.5.0 (no deisotoping, threshold at 1% for a rapid comparison of the composition with simple KMD plots) using "Kendo" [30], which is a homemade Excel spreadsheet available upon request with Visual Basic for Application coding (VBA) [31]. The resolution-enhanced KMD plots displaying the mass defects (i.e., the fractional part of the accurate mass of an ion with regard to a chosen reference mass) as a function of the mass-to-charge ratio of the detected ions (noted *m/z*) were computed using a mathematical base unit, $CH_2/X$, with the $CH_2$ methylene chemical moiety at 14.01565 Da and X as the natural divisor. The separating power of the resolution-enhanced KMD plot was modified from its regular counterpart and computed with $CH_2$ only [32] depending on X. The values of X were set at 13 (actual base unit: $CH_2/13=1.07813$), 20 (actual base unit: $CH_2/13=0.70078$), and 21 (actual base unit: $CH_2/13=0.66741$) in the KMD plots reported below to separate the carbonaceous ion

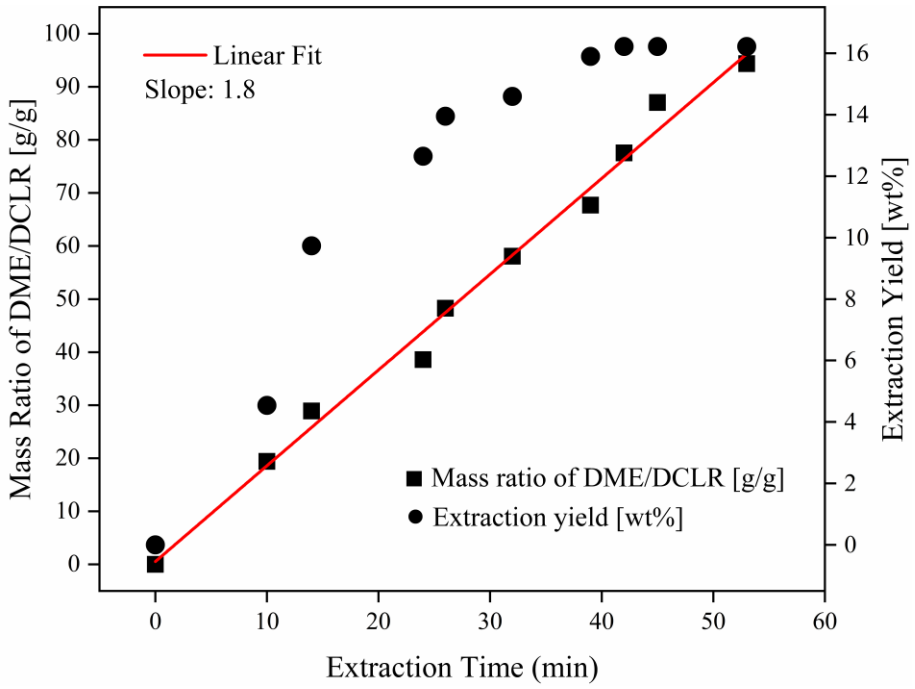


**Figure 2** The relationship among extraction time, DME consumption, and extraction yield. ■ Mass ratio of DME/DCLR; ● Extraction yield.

series by their contents of H, O, and N atoms and $^{13}C$ isotopes in visual graphs with unambiguous assignments.

## 3. Results and Discussion

### 3.1. Extraction of DCLR by liquefied DME

**Figure 2** shows the relationship between extraction time, DME consumption, and extraction yield. DME consumption exhibits a linear relationship with extraction time with a slope of 5.4 g/min and is displayed by black solid cubes and read line (linear fit) in **Figure 2**. The difference between the theoretical and actual values of the DME consumption can be attributed to the errors caused by the interval procedure. As shown by black solid circles in **Figure 2**, the extraction yield increases with the liquefied DME flow during the first 10 min. For an extraction time of 10 to 24 min, the mass ratio of DME/DCLR changed from 20 to 39, and the growth rate of the extraction yield reached a maximum. Subsequently, the extraction yield increased slowly and remained unchanged at 16.2%, indicating that the extraction was

**Table 2** Performance comparison of the extraction methods using liquefied DME and subcritical water as solvents.

| Solvents | Temperature [℃] | Pressure [MPa] | Time [min] | Mass ratio of Solvent/DCLR [g/g] | Yield 1 [wt%] [a] | Yield 2 [wt%] [b] | Yield 3 [wt%] [c] |
|---|---|---|---|---|---|---|---|
| DME | 25 | 0.6~0.8 | 40 | 70 | -- | 13.8 | 16.2 |
| Water [18] | 250 | 5.2 | 120 | 15 | 6 | 3.6 | -- |
| | 320 | 11.7 | 120 | 10 | ~6 | ~3.6 | -- |
| | 300 | 8.9 | 60~180 | 15 | 12~14 | 7.2~8.4 | -- |
| | 300 | 8.9~11.6 | 120 | 15 | ~14 | 8.4 | -- |
| | 320 | 11.7 | 120 | 15 | 24 | 14.4 | -- |
| | 320 | 11.7 | 120 | 30 | ~30 | ~18.0 | -- |
| | 320 | 11.7 | 120 | 90 | ~51 | ~30.7 | -- |

[a]: Yield reported [18] on the dry basis of THF-extractable fraction in the DCLR sample via Soxhlet extraction.

[b]: Yield recalculated on the dry basis of the DCLR sample.

[C]: Extraction yield defined in this paper, on the dry ash-free basis of the DCLR sample.

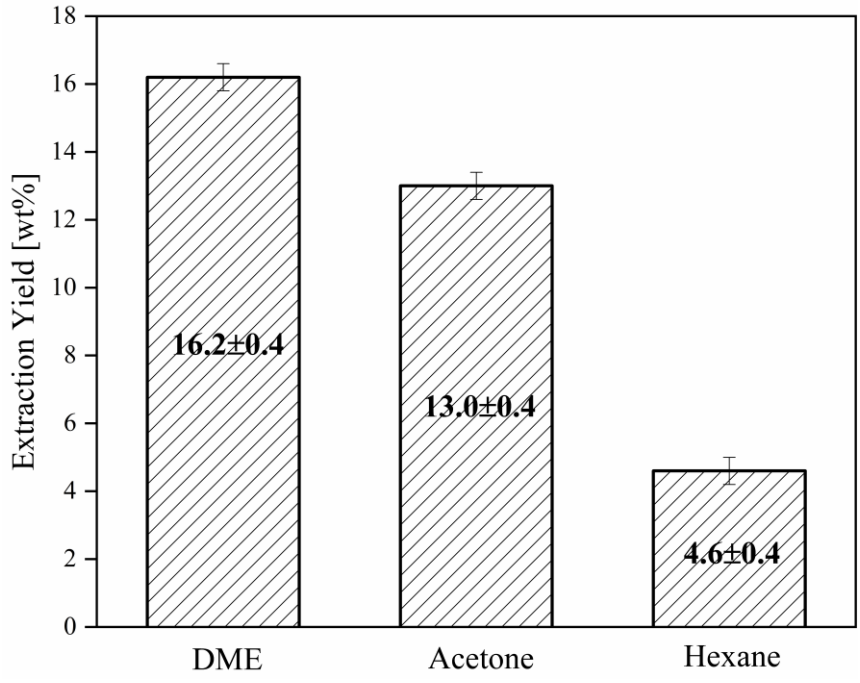


**Figure 3** Extraction yields for DCLR using liquefied DME, acetone, and hexane as the solvents.

almost complete; at this point, the mass ratio of DME/DCLR was approximately 70 and the extraction time was 40 min. Thus, approximately 40 min were required for complete extraction of 3g of DCLR at room temperature using 210 mL of liquefied DME as the solvent.

For an economical process, DME gas used for extraction must be recovered and recycled during the practical application. Based on our previous studies [33], except for the DME dissolved in water, most of the DME could be recovered. For example, when the feeding material was the coal with a moisture content of up to 66.7 wt%, the recovery rate of DME was 95% [33]. Considering the moisture content of the DCLR sample, which was quite low in this study, the recovery rate of DME could be ~100%.

Compared with DME extraction, Soxhlet methods were conducted at higher temperatures for a longer extraction time of 6 h. The extraction yields using acetone and hexane as the solvents were 13.0% and 4.6%, respectively, which were lower than that using liquefied DME at 16.2% (**Figure 3)**. **Table 2** shows the performance of two extraction methods using liquefied DME and subcritical water as solvents. The extraction yield using subcritical water as the solvent was defined on the dry basis of THF-extractable fraction in the DCLR sample via Soxhlet extraction [18], which was different from that in this study which defined the extraction yield on the dry ash-free basis of the DCLR sample. For convenience and accuracy, the original extraction yields with different solvents were recalculated on the dry basis of the DCLR sample and are listed in the column labeled 'Yield 2' in **Table 2**. Despite the errors caused by the differences in used DCLR samples, the extraction yield (Yield 2) using liquefied DME is 13.8 wt%, which is similar to the yield (Yield 2) obtained via subcritical water extraction at 320 ℃ and 11.7 MPa for 2 h with a low mass ratio of solvent/DCLR (14.4 wt%). Therefore, it can be presumed that liquefied DME extraction method can be as effective as the subcritical water extraction after optimization of factors such as extraction temperature, pressure, time, mass ratio of solvent/DCLR, and the amount of water addition. This extraction method can be foreseen to have a stronger market competitiveness owing to a shorter extraction time, lower energy consumption, and more convenient separation of DME gas from the extract compared to conventional methods. Furthermore, the efficient extraction of dry DCLR sample extends the application range of liquefied DME extraction technology, as the previous studies regarding liquefied DME extraction mainly focused on wet feedstocks, such as

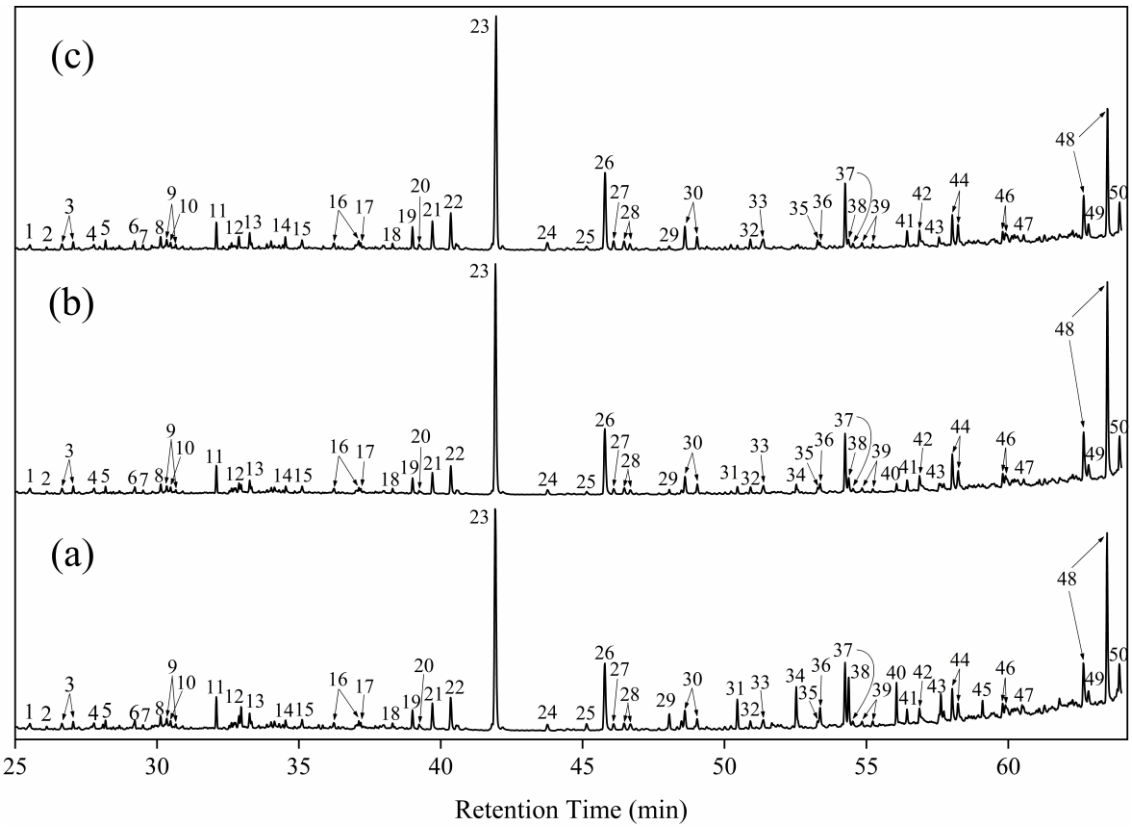


**Figure 4** GC-MS chromatogram of (a) DME-E, (b) Acetone-E, and (c) Hexane-E.

low-rank coal with high moisture contents, wet microalgae, and sludge.

### 3.2. Elemental composition of the extracts

**Table 1** shows the elemental compositions of the residues and extracts obtained using different solvents. Each residue contains a slightly lower carbon content and a higher oxygen content relative to the feedstock. However, hydrogen, nitrogen, and sulfur contents remain almost the same at 4%, 1%, and 2%, respectively, which can account for the similar ratios of H/C and O/C in the feedstock and residues. The elemental compositions of the extracts differ from the feedstock and residues, which include the highest carbon and hydrogen contents of > 80% and 6%, respectively, highest ratio of H/C of 1.0, lowest ratio of O/C of <0.1, and lowest content of sulfur of < 0.3%. These results are consistent with previous reports [2, 9]. Each extract had a VM content of > 90%, which was much higher than the feedstock (43%),

**Table 3** Light compounds determined using GC-MS in the extracts obtained from DCLR. [a]

| No | Compound name | No | Compound name |
|---|---|---|---|
| 1 | 2,3,4,4a,9,9a-hexahydro-1H-fluorene | 26 | 1-methylpyrene |
| 2 | 6-propyl-1,2,3,4-tetrahydronaphthalene | 27 | 5,6-dihydro-4*H*-benzo[*de*]anthracene |
| 3 | tetradecahydroanthracene | 28 | 4-methylpyrene |
| 4 | pentadecane | 29 | tricosane |
| 5 | 2-methyl-1,2-dihydronaphthalene | 30 | 1,3-dimethylpyrene |
| 6 | 6-butyl-1,2,3,4-tetrahydronaphthalene | 31 | Tetracosane |
| 7 | 1-ethoxynaphthalene | 32 | chrysen-6-ol |
| 8 | 1-(prop-1-en-2-yl)naphthalene | 33 | 2-methyl-7,12-dihydrotetraphene |
| 9 | 3-(*tert*-butyl)-1,2-dihydronaphthalene | 34 | pentacosane |
| 10 | hexadecane | 35 | 5-methoxybenzo[*c*]phenanthrene |
| 11 | hexadecahydropyrene | 36 | isooctyl phthalate |
| 12 | 2,2'-dimethyl-1,1'-biphenyl | 37 | 8,9-dihydro-7*H*-cyclopenta[*a*]pyrene |
| 13 | 1,2,3,4,5,6,7,8-octahydroanthracene | 38 | hexacosane |
| 14 | phenanthrene | 39 | 1,12-dimethyltetraphene |
| 15 | octadecane | 40 | heptacosane |
| 16 | 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene | 41 | 7,12-dimethyltetraphene |
| 17 | nonadecane | 42 | benzo[*e*]acephenanthrylene |
| 18 | 4,5,9,10-tetrahydropyrene | 43 | octacosane |
| 19 | 1,2,3,3a,4,5-hexahydropyrene | 44 | benzo[*a*]pyrene |
| 20 | icosane | 45 | nonacosane |
| 21 | 1,2,3,6,7,8-hexahydropyrene | 46 | 10-methylbenzo[*a*]pyrene |
| 22 | 4,5-dihydropyrene | 47 | triacontane |
| 23 | pyrene | 48 | 1,12-benzoperylene |
| 24 | 2,3-Dihydro-1H-cyclopenta[l]phenanthrene | 49 | 1-phenylpyrene |
| 25 | docosane | 50 | anthanthrene |

[a]: Serial numbers corresponds to the numbers included in Figure 4.

accompanied with low contents of FC and ash. Overall, the elemental compositions of the residues or extracts obtained using different solvents were similar to each other. However, there was a subtle difference between extraction methods using hexane and the other two solvents. The nitrogen content in the feedstock was 1.0%, which was lower than those in DME-E and Acetone-E but higher than that in Hexane-E. Furthermore, the ash contents of DME-E and Acetone-E were as low as < 0.1%, whereas that of Hexane-E was 1.5%. Owing to high carbon contents, low sulfur and oxygen contents, and low ash contents of < 0.1%, DME-E and Acetone-E were determined to be naturally good feedstocks for high-grade carbon materials.

### 3.3 Determination of light compounds

**Figure 4** displays the GC-MS chromatograms of DME-E, Acetone-E, and Hexane-E, and **Table 3**

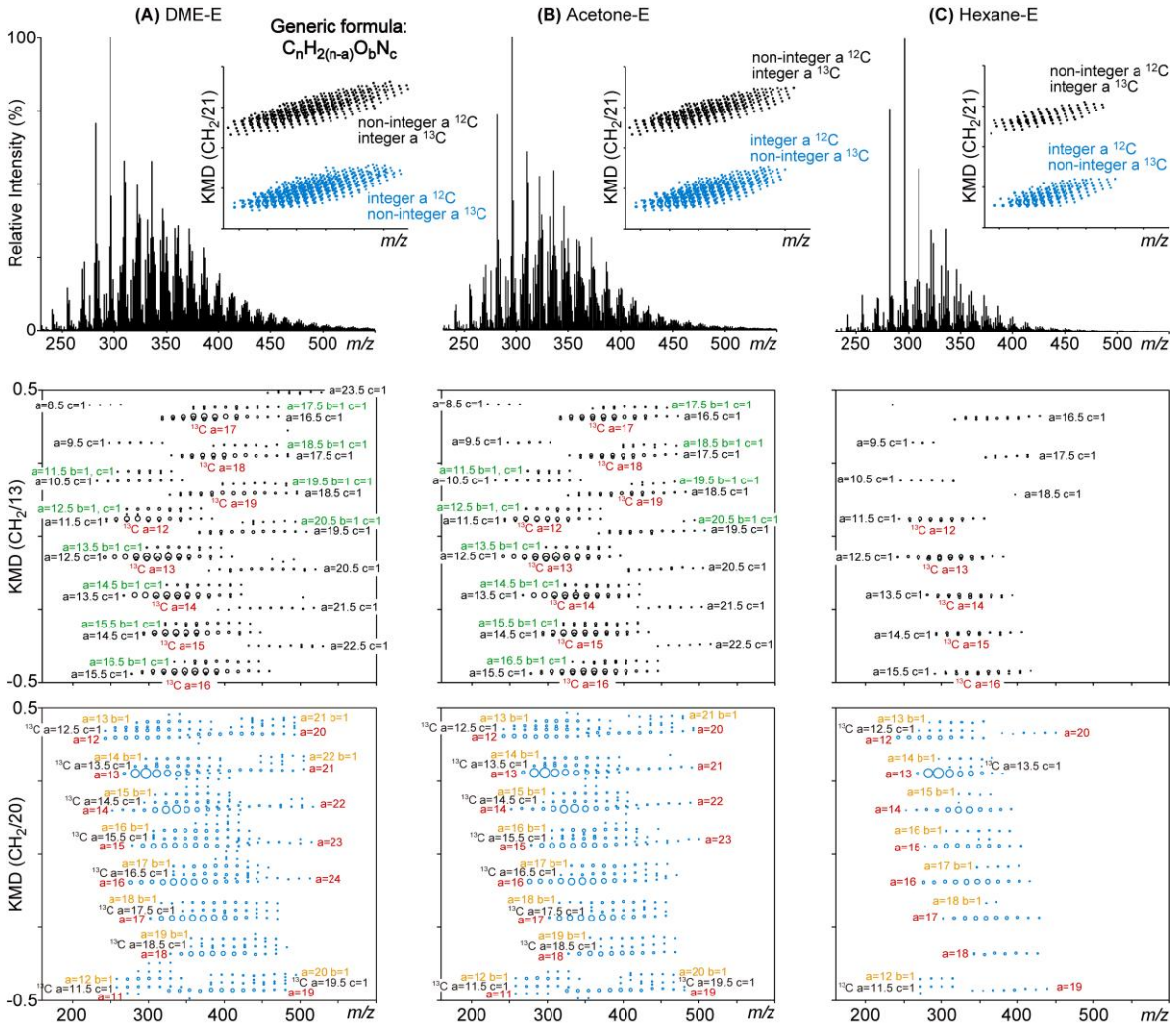


**Figure 5** Mass and KMD analysis of (A) DME-E, (B) Acetone-E, and (C) Hexane-E. From top to bottom: LDI-HRMS spectrum and resolution-enhanced KMD plot (base unit: $CH_2$/21, threshold 1%); Filtered resolution-enhanced KMD plot from the monoisotopic $C_nH_{2(n-a)}O_bN_c$ with non-integer a and $^{13}C$ isotopes of $C_nH_{2(n-a)}O_bN_c$ with integer a (black points, base unit: $CH_2$/13); Filtered resolution-enhanced KMD plot from the monoisotopic $C_nH_{2(n-a)}O_bN_c$ with integer a and $^{13}C$ isotopes of $C_nH_{2(n-a)}O_bN_c$ with non-integer a (blue points, base unit: $CH_2$/20).

includes a list of light compounds identified by GC-MS. The compositions of the determined compounds in all three extracts are similar, including alkanes ($C_{14}H_{24}$~$C_{30}H_{62}$), cycloalkanes (such as

tetradecahydroanthracene and hexadecahydropyrene), and various monocyclic and polycyclic aromatic compounds. The abundance of polycyclic aromatic hydrocarbons (PAHs) with two-, three-, four-, five-, and six-membered benzene rings, which are represented by phenanthrene, pyrene, tetraphene, benzo[*a*]pyrene, benzoperylene, anthanthrene, or their derivatives, supports that all the DCLR extracts are potential materials that could be used to prepare high value-added carbon materials [15]. The elemental composition of all the detected species can be conveniently denoted as $C_nH_{2(n-a)}O_b$ with parameter *n* (C content) ranging from 11 to 30, parameter *a* (inverse of H content ~ degree of unsaturation, a=(2C-H)/2) ranging from -1 for alkanes to 16 for highly unsaturated PAHs, and parameter *b* (oxygen content) ranging from 0 to 4 in the fifty low molecular weight species detected by GC-MS (**Figure 4)**. This generic notation will be used in the next section for description of the carbonaceous series with an identical unsaturation number and identical O content but a varying number of methylene $CH_2$ moieties.

Compared to DME-E and Acetone-E, Hexane-E lacks some peaks of alkanes including tetracosane ($C_{24}H_{50}$, No 31 in **Table 3**), pentacosane ($C_{25}H_{52}$, No 34 in **Table 3**), and heptacosane ($C_{27}H_{56}$, No 40 in **Table 3**). However, the difference is small, and it can be concluded that liquefied DME, acetone, and hexane can extract similar light compounds. To reveal the reason for a big difference in the extraction yields of the three solvents, an additional characterization technique that allowed the detection of higher molecular weight compounds was employed.

### 3.4. Molecular composition

In our previous studies, a simple LDI-HRMS mass analysis method combined with an appropriate Kendrick mass defect analysis has been confirmed to be effective in characterizing the molecular composition of coal or biomass extracts [32, 34]. The two LDI mass spectra recorded for DME-E and Acetone-E are similar (**Figure 5** A-B, top) while the third spectrum from Hexane-E appears different at first sight (**Figure 5** C, top). In the three spectra, the major ion series was assigned as $C_nH_{2(n-a)}$ with a=13 thanks to an accurate internal calibration (errors at ~1 ppm over the entire mass range). Nevertheless, a

thorough comparison of the chemical compositions requires the tedious assignment of the peaks one by one in time-consuming processing.

Instead, a sequential KMD analysis dramatically facilitates the comparison using visual graphs and speeds up the ability to make assignments via simulation of the theoretical KMDs (one KMD value per series instead of one *m/z* value per ion) [32]. A first resolution-enhanced KMD plot was computed from each of the full LDI mass spectra with $CH_2/21$ as the mathematical base unit (chemical moiety: $CH_2$ at 14.01565, divisor X=21). The plots instantly sorted the ~850-900 points that were generically labeled as $C_nH_{2(n-a)}O_bN_c$ in two clouds by varying their contents of H (parameter a being integer or non-integer) and $^{13}C$ isotopes (insets in **Figure 5** A-C, top). Each cloud that was composed of ~400-450 points was then isolated and independently re-processed using $CH_2/13$ (**Figure 5** A-C, middle) and $CH_2/20$ (**Figure 5** A-C, bottom) to further separate all the ion series depending on their O (parameter b), N (parameter c), and unsaturation (parameter a, inverse of H content) contents. The resulting KMD plots display clear horizontal alignments with one line per ions series with the elemental composition of the congeners within a given series varying by +/- n*$CH_2$ groups. There is no overlap because the resolution-enhanced methodology takes advantage of the full spectral width of the plots from -0.5 to 0.5, which is in contrast to the clustered KMD plots usually reported in the literature [35]. The Kendo spreadsheet now incorporates a simulator which computes the theoretical KMD and mass-to-charge ratios (*m/z*) for a set of parameters [36 13C, n] to instantly assign the ion series in the KMD plots. Several $C_nH_{2(n-a)}O_bN_c$ series are readily highlighted with a=8.5-23.5 (non-integer a, from lowest to highest degree of unsaturation) / a=12-24 (integer a), b=0-1, and c=0-1 with their combination of b=c=1 and $^{13}C$ isotopes in the two sets of plots for DME-E and Acetone-E (**Figure 5**, A-B, middle and bottom; red series: b=c=0, $^{12}C/^{13}C$ isotopes; orange series: b=1, c=0; black series: b=0, c=1, $^{12}C/^{13}C$ isotopes; green series: b=c=1). The high similarity of their fully resolved KMD plots graphically confirms the high similarity of the overall chemical composition of the two extracts in terms of high molecular weight species.

Considering its KMD plots, Hexane-E is also formed from similar classes of ion series that are generally labelled $C_nH_{2(n-a)}O_bN_c$; however, the ranges of a, b, and c clearly differ with a=9.5-18.5 (non-integer a) / a=12-20 (integer a), b=0-1, and c=0-1, while their combination is missing (**Figure 5**, C, middle and bottom). Indeed, no singly oxygenated / nitrogenated series denoted as $C_nH_{2(n-a)}O_1N_1$ and labeled in green in the previous KMD plots was detected for Hexane-E regardless of the mass range or the values of n or a. The higher molecular weight compounds observable by LDI were clearly depleted in Hexane-E in spite of being characterized under identical conditions of sample preparation and the parameters for mass analysis. The potential of this last DCLR extracted with hexane is questionable due to a lower amount and lower polycyclic character of the detected PAHs, as indicated by the narrower range for parameter a, which revealed an overall lower degree of unsaturation. Thus, the extraction performed with liquefied DME at room temperature, which was as good as the extraction with acetone at high temperature considering their similar high molecular weight species, is preferred over extraction with hexane at high temperature especially in terms of recovered PAHs.

## 4. Conclusions

The extraction of DCLR was performed at room temperature using liquefied DME. Approximately 40 min were required for the complete extraction of 3g of DCLR with 200-210 mL of liquefied DME. For comparison, DCLR was extracted by the Soxhlet method using acetone and hexane; the extraction temperature was above the boiling point of the solvent, and the extraction time was 6 h. Even so, the extraction yield with liquefied DME was 16.2%, which was higher than the yields obtained from the Soxhlet method with acetone and hexane, at 13.0% and 4.6%, respectively. Furthermore, the energy consumption during the DME extraction process was low because the extraction was performed at room temperature and DME gas separated from the extract without heating. DME-E and Acetone-E contain high carbon contents, low sulfur and oxygen contents, and low ash contents of < 0.1%; thus, they can be used as feedstocks of carbon materials. The GC-MS results showed that the extracts obtained using the three different solvents had similar light compound compositions and are abundant in PAHs with two-,

three-, four-, five-, and six-membered benzene rings, represented by phenanthrene, pyrene, tetraphene, benzo[*a*]pyrene, benzoperylene, anthanthrene, and their derivatives. The molecular compositions of the extracts were investigated by a simple LDI-HRMS mass analysis combined with an appropriate Kendrick mass defect analysis. It revealed that the extraction performed with liquefied DME at room temperature was equally effective as the extraction with acetone at high temperature considering their compositional similarity in high molecular weight species and should be preferred over extraction with hexane at high temperature, particularly consierting the recovered PAHs. All results above confirm that liquefied DME is an efficient and economic solvent for extracting DCLR.

## Abbreviations

DME dimethyl ether

DCL direct coal liquefaction

ICL indirect coal liquefaction

DCLR direct coal liquefaction residue

PASs polycyclic aromatic structures

PAHs polycyclic aromatic hydrocarbons

HPLC high-performance liquid chromatography

THF tetrahydrofuran

VM volatile matter

FC fixed carbon

GC/MS gas chromatograph/mass spectrometer

LDI-HRMS laser desorption ionization high-resolution mass spectra

NaTFA sodium trifluoroacetate

KMD Kendrick mass defect

VBA Visual Basic for application coding

## Acknowledgements

This work was supported by JSPS KAKENHI Grant Numbers JP23686117 (H. Kanda).

## Competing Interests

There are no competing interests.

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Figure 1

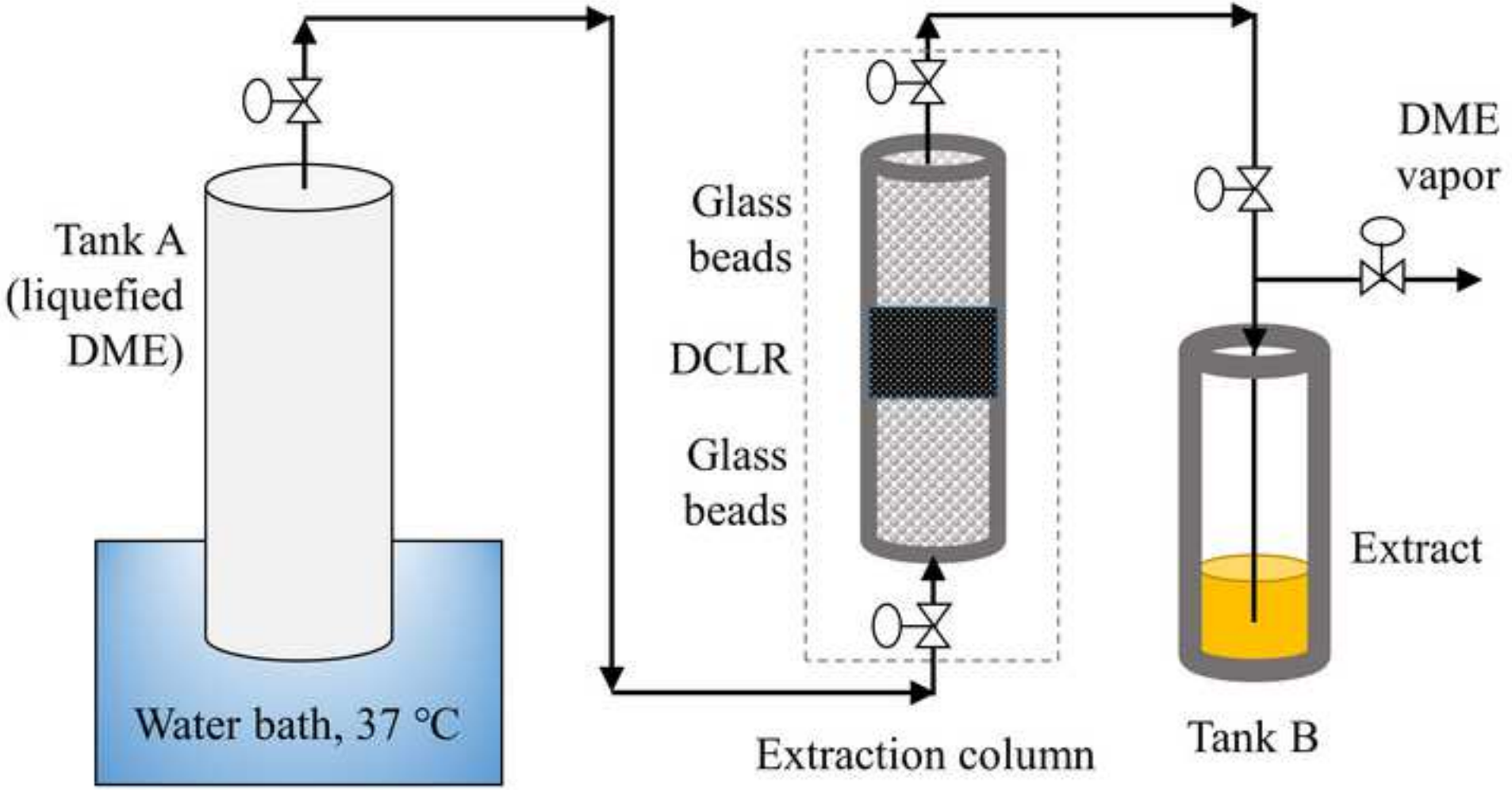

Tank A
(liquefied
DME)
Water bath, 37 °C
Glass
beads
DCLR
Glass
beads
Extraction column
DME
vapor
Extract
Tank B

Figure 2

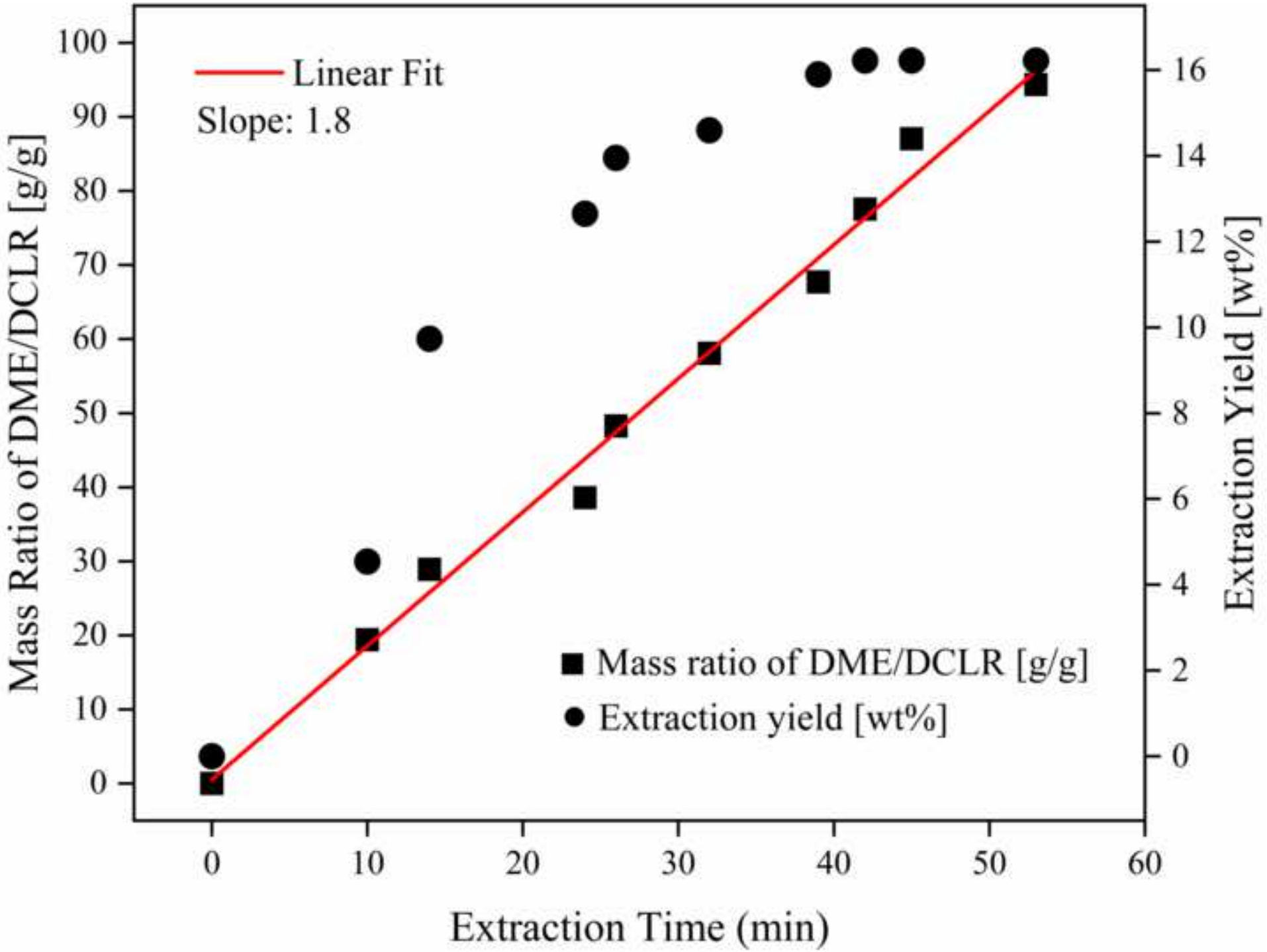

Linear Fit
Slope: 1.8
Mass ratio of DME/DCLR [g/g]
Extraction yield [wt%]
Mass Ratio of DME/DCLR [g/g]
Extraction Yield [wt%]
Extraction Time (min)
0
10
20
30
40
50
60
70
80
90
100
2
4
6
8
12
14
16

Figure 3

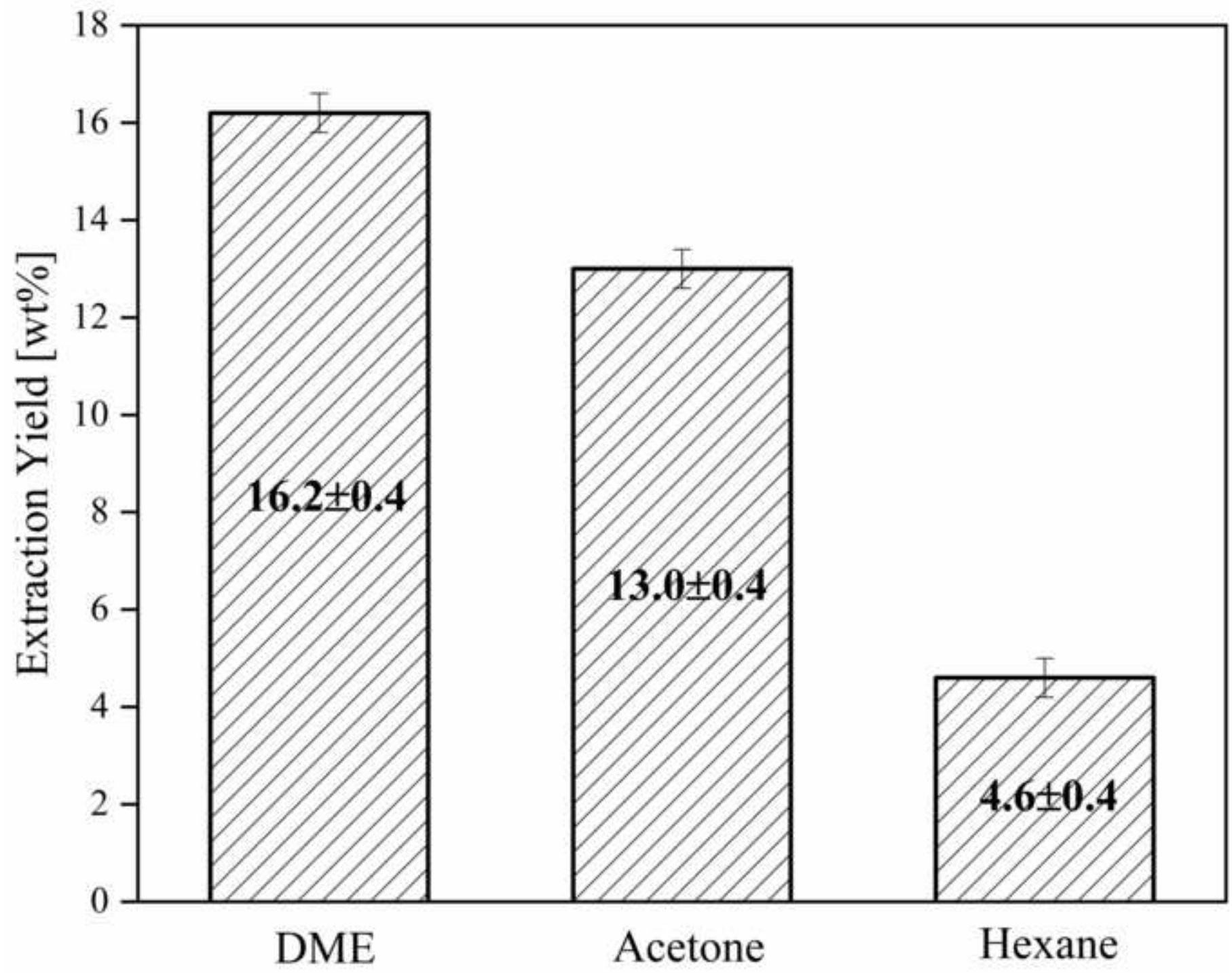

Extraction Yield [wt%]
18
16
14
12
10
8
6
4
2
0
16.2±0.4
13.0±0.4
4.6±0.4
DME
Acetone
Hexane

Figure 4

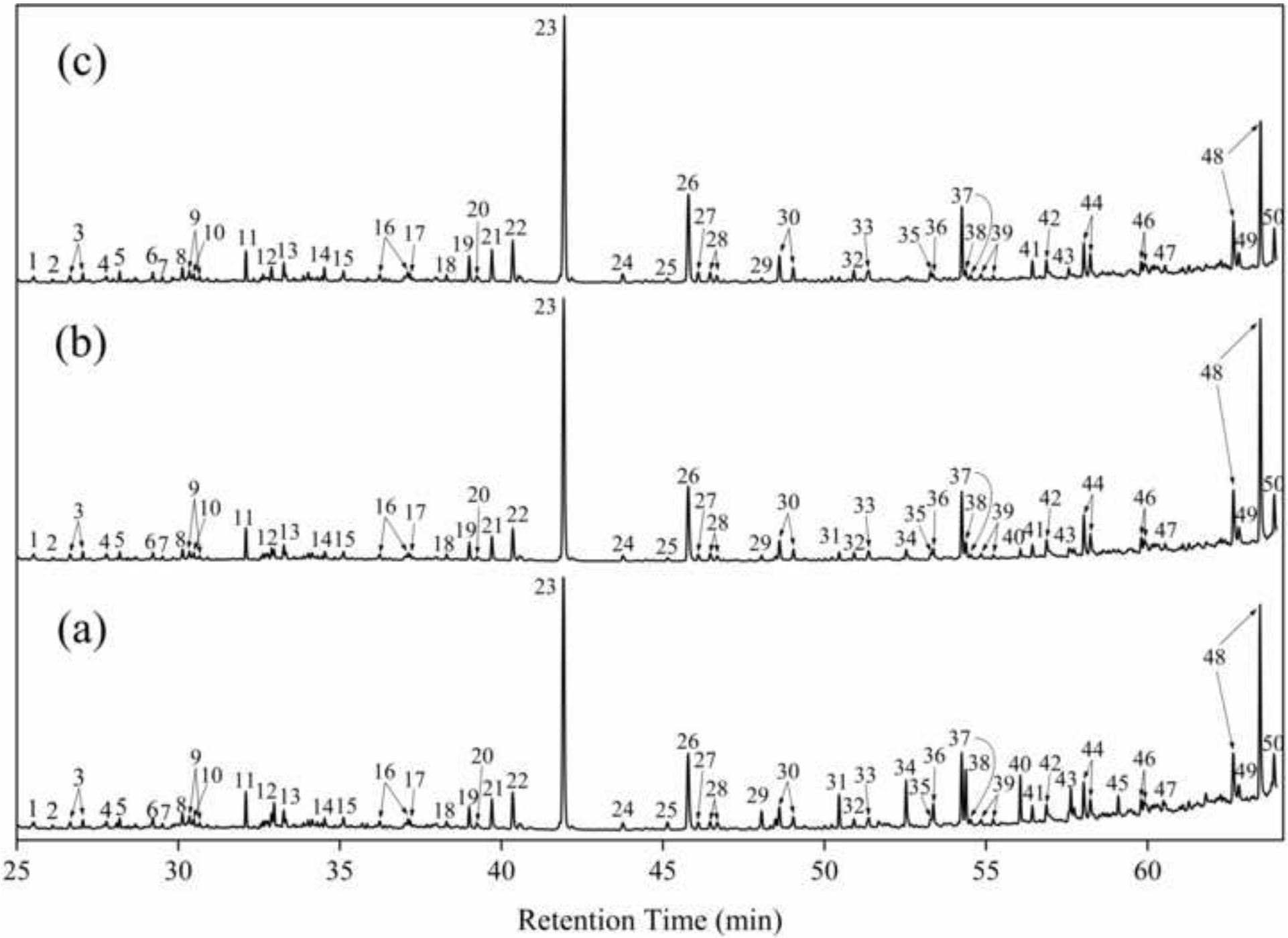
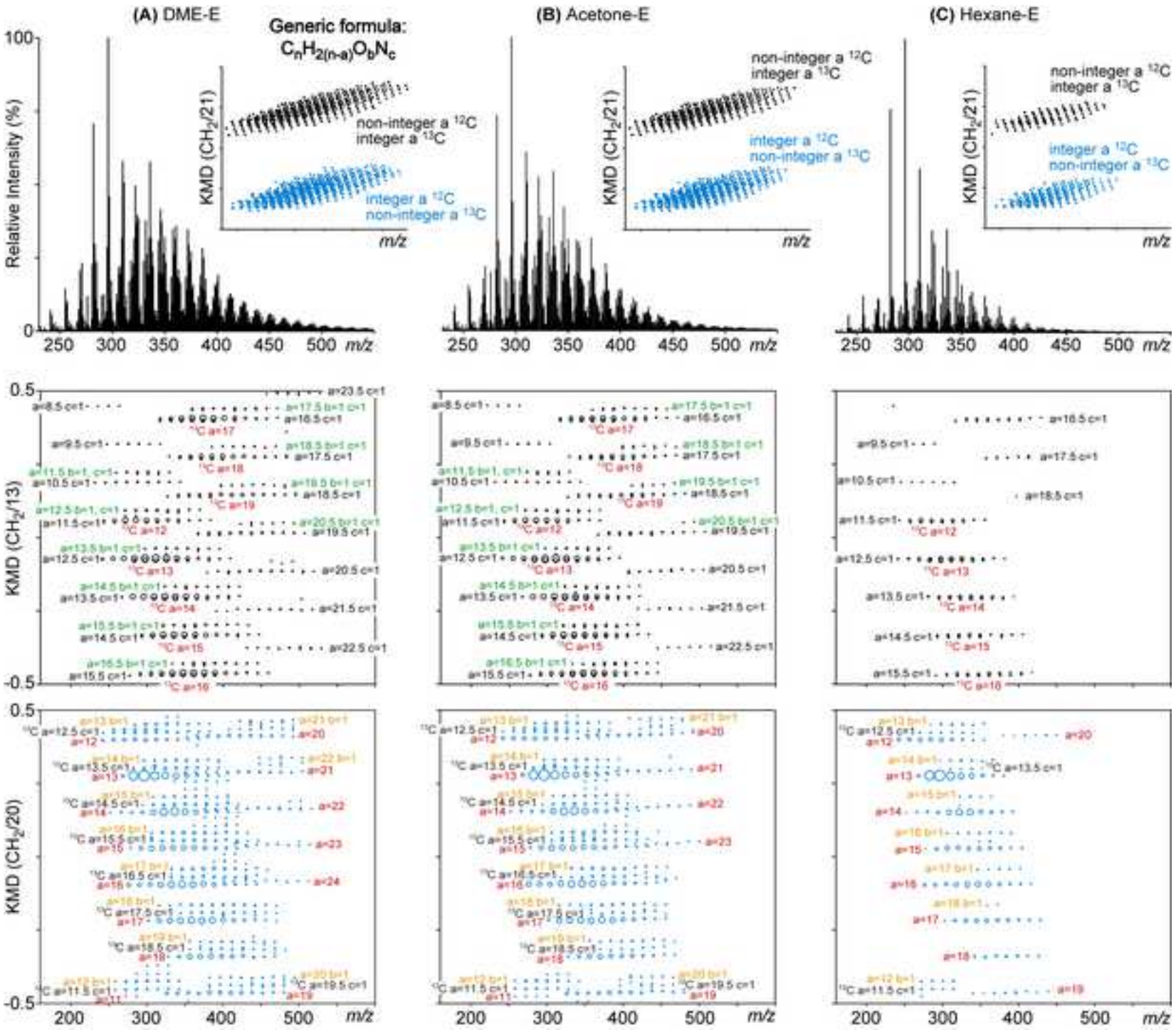


Figure 5


(A) DME-E
(B) Acetone-E
(C) Hexane-E
Generic formula:
$C_nH_{2(n-a)}O_bN_c$
Relative Intensity (%)
KMD (CH2/21)
non-integer a 12C
integer a 13C
integer a 12C
non-integer a 13C
m/z
KMD (CH2/13)
KMD (CH2/20)