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Description	



Properties of bio-oil generated by a pyrolysis of forest cedar residuals with the movable Auger-type reactor

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Abstract. Our research project has developed the new movable reactor for bio-oil production in 2013 on the basis of Auger-type system. This package would be a great impact due to the concept of local production for local consumption in the hilly and mountainous area in not only Japan but also in the world. Herein, we would like to report the properties of the bio-oil generated by the developing Auger-type movable reactor. The synthesized bio-oil possessed C: 46.2 wt%, H: 6.5 wt%, N: 0.5 wt%, S: <0.1 wt%, O: 46.8 wt% and H₂O: 18.4 wt%, and served a good calorific value of 18.1 MJ/kg. The spectroscopic and mass analyses such as FT-IR, GC-MS, ¹³C-NMR and FT-ICR MS supported that the bio-oil was composed by the fine mixtures of methoxy phenols and variety of alcohol or carboxylic acid functional groups. Thus, it is suggested that the bio-oil generated by the new movable Auger-type reactor has a significant potential as well as the existing bio-oil reported previously.

Keywords. Auger-type movable reactor, cedar pyrolysis, bio-oil, FT-ICR MS.

INTRODUCTION

Fast pyrolysis of biomass resources towards liquid (called as pyrolysis oil or bio-oil) has much attraction as an effective tool for productions of liquid fuels and derived feedstocks for chemical materials. Since the product bio-oil was yielded up to 80 wt% on dry feed via a fast pyrolysis, this liquefaction approach is highly anticipated by many researchers. They have been developing the numerous system for fast pyrolysis affording to the bio-oil to meet the variety of biomass resources such as straw, olive pits, nus shells, miscanthus, sorghum and so on, nearly 100 types of biomass have been tested [1-4]. Predominantly, most technologies for the pyrolysis of wood have been studied on a static plant with a large scale in order to treat a large amount of biomass resources in a day, however, the plants cannot be moved out from the factory. The development of movable pyrolysis reactor was rarely reported in the world.

In our research project, we focused on the development of a compact/movable reactor package for bio-oil production. Especially, in the hilly and mountainous area in Japan, the unutilized resources of forest scraps and wood waste were kept intact a lot in the area, because no human power or high costs (low benefits) was ensured to collect such worthless resources into the business place. If the movable pyrolysis reactor could be transported into and operated in such field, *ex.* the timber basin area close to the mountain, the unutilized resources would be upgraded towards the bio-oil, useful energy and chemical resources, with more effective manner. This futural approach will

serve not only for encouragements in the utilization of unharnessed biomass resources but also for generation of new life-style and energy cycles in accordance with the bio-refinery.

In a recent few years, our research project has been developing the movable Auger-type reactor for bio-oil production in the mountain area. Herein, we would like to report and discuss the properties of the bio-oil generated by the new movable Auger-type reactor.

EXPERIMENTAL

Production of the bio-oil by movable Auger-type reactor

The Japanese cedar chips excluding bark (2-3 mm, 8.21% H₂O) was fed into with 45 kg/h rate and pyrolyzed at 450-500 °C in the Auger-type reactor with iron shots (SINTOKOGIO Ltd.; SB-20, $\phi = 1.4-1.7$ mm). The produced bio-oil was collected by the condenser composed with a scrubber and mist collector attached with the reactor (**Figure 1**) [5-6].

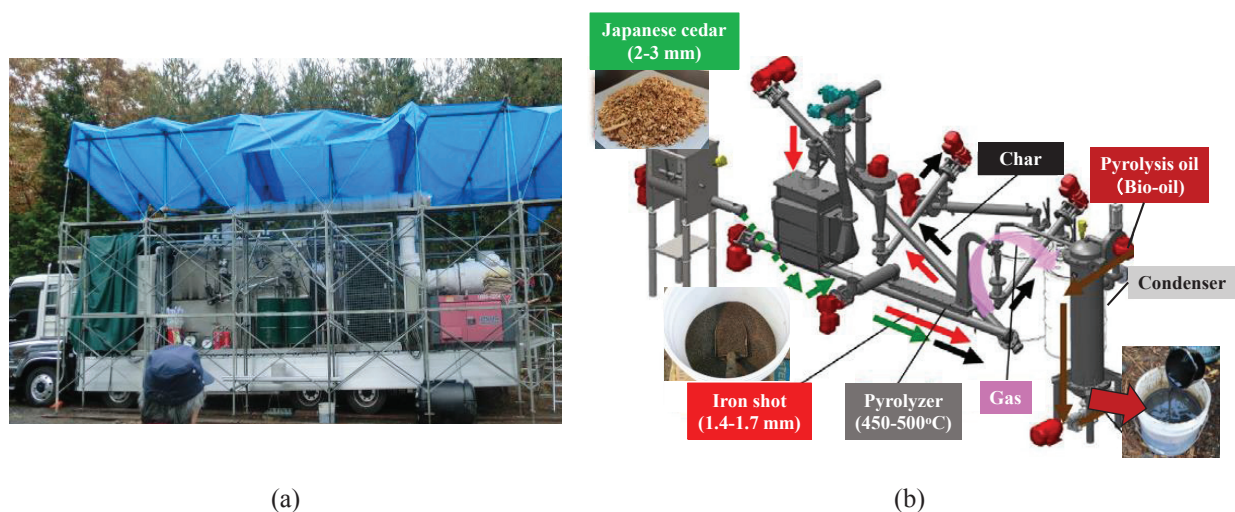


FIGURE 1. The developing movable Auger-type reactor; (a) overview on a truck bed and (b) schematic flow in the reactor.

Physical properties analysis

Elemental analysis for C, H, N and S was performed by the Vario EL3 elemental analyzer (Elementar). The reduction tube, CO₂ column, SO₂ column, and H₂O column was elevated to 850 °C, 100 °C, 210 °C and 150 °C, respectively. 5 mg of bio-oil was sealed within the Tin capsule (0.05 mL vol.), and introduced into the furnace at 1150 °C. Sulfanilic acid (Merck Millipore) was used as the standard for C: 41.61wt%, H: 4.07wt%, N: 8.09wt%, and S: 18.50 wt%.

Water content was determined by the Karl Fischer (KF) moisture titration with a volumetric titration mode (MKA-610, Kyoto Electronics Manufacturing Co., LTD.). HYDRANAL-KetoSolver (Fluka) and HYDRANAL-Composite 5K (Fluka) was used as solvent and titrant, respectively. 2.0 g of bio-oil was applied at a time for KF analysis.

NaOH titration was attempted to use for acidity test. 1.0 g of bio-oil was dispersed into 50 ml of pure water in a conical beaker, and then neutralized by a 0.500 N of NaOH aqueous solution till the pH approaching to the range of 8.30-8.50.

Higher heating value (HMV) of the bio-oil was assigned by a calorific meter (IKA C200). 0.4 g of bio-oil was sealed in 0.118 g of gelatin capsule (18759 J/g) with the firework fuel of 0.0318 g of paraffin films (46619 J/g), and then the ignition was occurred under the pressurized O₂ gas (30 bar). For standard correction, 1.0 g of benzoic acid tablet (26460 J/g) was also measured.

A cone-plate type viscometer (TOKI SANGYO TVE-35H) attached with a 0.8°×R24 cone and a D-52 pH meter (HORIBA) was used for the measurement of viscosity and pH value, respectively.

Spectroscopic and MS analysis

FT-IR (ATR) was obtained by a spectrum 100 meter (ParkinElmer) attached with the ATR accessory of a ZnSe crystal plate. The 123 scans of IR spectra were performed in the range of 4000-400 cm^{-1} with 4 cm^{-1} resolution. The characteristic peaks were identified by following literatures [7-8].

^{13}C -NMR spectrum was examined by an Avance III 400 spectrometer (400 MHz, Bruker BopSin Inc.) at room temperature. Methanol- d_4 (99.8 atm% D, Acros Organics) was used as solvent. The 5,000 numbers of scan were operated to brush up the S/N ratio.

For GC-MS analysis (Shimadzu QP-5000), the produced bio-oil was resolved in methanol to *ca.* 50 $\mu\text{l}/\text{ml}$, and a 0.1 μl of the sample was analyzed using a commercial NEUTRA ND-5 capillary column (GL Science, 0.25 mm ID \times 30 m) under He gas flow (99.9999% purity, 20 ml/min). The injection temperature was 250 $^{\circ}\text{C}$. The temperature of GC column oven was conducted to the program: an initial 50 $^{\circ}\text{C}$ for 5 min, a ramp to 250 $^{\circ}\text{C}$ at a rate of 5.0 $^{\circ}\text{C}/\text{min}$, and a constant 250 $^{\circ}\text{C}$ for 15 min. Ionization of the sample was treated by the electron ionization (EI) method. A full MS spectrometry scan was acquired in the range of $m/z = 35-700$ at a rate of 0.5 s per scan. The GC chromatographic peaks were characterized by the CLASS-5000 library (Shimadzu ver. 2.22).

FT-ICR MS (Bruker Daltonics Inc., Solarix) was obtained by using a 9.4 T superconducting magnet. The diluted samples were prepared by mixing the bio-oil samples and methanol (1 $\mu\text{l}/\text{ml}$). Oleic acid ($\text{C}_{18}\text{H}_{33}\text{O}_2$; 281.24860 Da (Monoisotopic)) was used as an internal standard for adjustment of the m/z axis in MS spectrum. The electrospray ionization (ESI) method at 4.5 kV was applied for negatively-ionization of the sample. A 2 Mega-byte data set (3.84 M points) was acquired in the range of $m/z = 100-1200$. A number of 5 scans of FT-ICR data sets were added to enhance the S/N ratio. From the obtained negative-ion FT-ICR MS spectrum, the estimated composition formulas determined by the actual m/z value below ± 1.0 ppm error were listed up as the expected compounds ($\text{C}_\alpha\text{H}_\beta\text{O}_\chi\text{N}_\delta$) in the sample.

RESULTS AND DISCUSSIONS

Physical properties

The physical properties of the produced bio-oil are listed in **Table 1**. The elemental analysis indicated that as-produced bio-oil contained C: 46.2 wt%, H: 6.5 wt%, N: 0.5 wt%, S: <0.1 wt% (below limit), and O: 46.8 wt%. The pH value was 2.60. The NaOH titration led to the acidity of 4.66 (NaOH g/ 100 g oil) corresponding to the 7.0 wt% of acetic acid (if these were derived from acetic acid all). As is usual in bio-oil properties, high oxygen content, no sulfur production, and acidic pH were also detected in our product.

TABLE 1. Physical properties of the as-prepared bio-oil.

Indexes	Values	Note
C	46.2 wt%	Limit value: 0.1 wt%
H	6.5 wt%	Limit value: 0.1 wt%
N	0.5 wt%	Limit value: 0.1 wt%
S	<0.1 wt%	Limit value: 0.1 wt%
O	46.8 wt%	Difference of CHNS values
pH	2.60	
H ₂ O	18.4 wt%	
Acidity (NaOH g/ 100 g oil)	4.66	
Viscosity	0.467 Pa•s (at 25 $^{\circ}\text{C}$) 0.019 Pa•s (at 50 $^{\circ}\text{C}$)	Limit value: 3.33 mPa•s
Kinetic viscosity	17 cSt (at 50 $^{\circ}\text{C}$)	
Calorific value	18.1 MJ/kg (Higher) 16.8 MJ/kg (Lower)	

The viscosity was 0.467 Pa·s measured at 25 °C and 0.019 Pa·s at 50 °C. When the specific gravity of the bio-oil was set as 1.1 g/cm³ tentatively, the kinetic viscosity was estimated to 17 cSt at 50 °C. This value was superior than that of the heavy fuel oil A grade based on the Japan standard (JIS K 2205-1991) (< 20 cSt). The high calorific value was 18.1 MJ/kg which was approximately half value of the conventional fuel oils such as gasoline, light diesel oil and heavy fuel oil (42-45 MJ/kg). Since the latent heat of the contained/produced water produced *ca.* 1.33 kJ/g heat, the lower calorific value was calculated to be 16.8 MJ/kg.

Solubility test

To select the solvent having nice affinity for bio-oil, several solvents (4 ml) were mixed with the bio-oil (1 ml), and the solubility was tested. The **Figure 2** shows the photograph for the mixed solvent after shaking. The water made clouded brownish yellow suspension with non-soluble bio-oil precipitation (ii) whereas the hexane (iv) and petroleum ester (viii) were hardly mixed with the bio-oil at all. From the observation in the case of benzene (vii), the bio-oil supposedly included two phase of soluble (light brownish yellow color) and insoluble (dark brown) in benzene. The cases of AN (v) and THF (vi) were visualized that almost all bio-oil was miscible, however a few precipitants and/or extractions were observed at the bottom of the glass tube. The MeOH was only the solvent nicely mixable with bio-oil, homogeneously (iii).

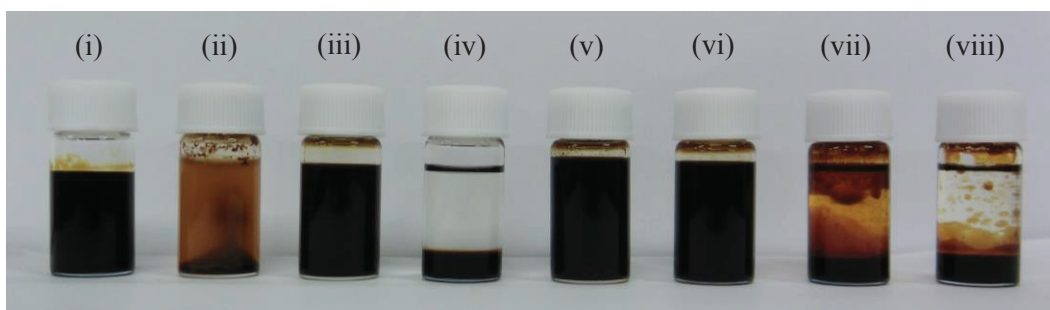


FIGURE 2. Solubility tests of the bio-oil in (i) None (itself), (ii) Water, (iii) Methanol, (iv) Hexane, (v) Acetonitrile, (vi) Tetrahydrofuran, (vii) Benzene, and (viii) Petroleum ester.

FT-IR spectroscopy

Figure 3 shows the FT-IR spectrum of the bio-oil. There is a large/broad peak around at 3000-3800 cm⁻¹ which attributed to the O-H stretching vibration in alcohol, phenol or water. Because the large quantity of water was detected in the bio-oil (18.4 wt%), it will be mainly originated from co-existence water molecule. The peak at 1713 cm⁻¹ was assigned to the stretching vibration of carboxylic acid (COOH) or ketone (C=O). The C-H bending vibration in alkane and O-H bending/C-O stretching vibrations in alcohols or phenol were detected at 1363-1452 cm⁻¹. The latter would be also assigned at 1033-1073 cm⁻¹. The peaks appeared at 1270-1235 cm⁻¹ would be derived from ester in arylalkyl group (aryl-O-C). The multiple connected C-C stretching mode in aromatic compounds and C-H bending vibration in substituted benzenes were at around 1600-1650 cm⁻¹ and 860 cm⁻¹, respectively. Though it is a large quantity at 1514 cm⁻¹, it seems to be difficult to estimate its derivations: *i.e.* a lot of candidates were proposed. Possibility of surfer compounds such as sulfuric acid (R-SO₃H at 1210-1150 cm⁻¹, 1060-1030 cm⁻¹ and 650 cm⁻¹) and sulfoxide (R-SO-R at 1070-1030 cm⁻¹) were negligible, because of the result in elemental analysis (*vide supra*). The nitro compounds such as amide and imide are not listed up too in the sentences because of low contents (N: 0.5 wt%).

These results indicated that the bio-oil was composed by various aromatic alcohols and variety of alcohol or carboxylic acid functional groups.

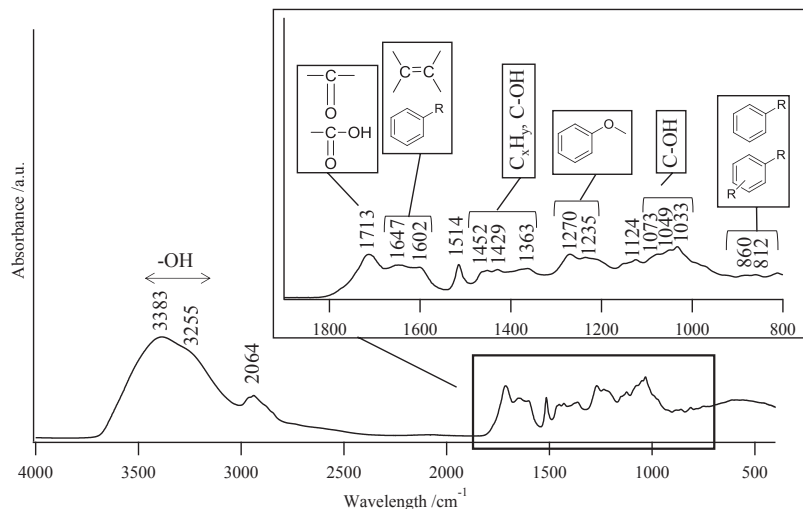


FIGURE 3. FT-IR(ATR) spectrum of the bio-oil with indexes of the estimated functional structure.

¹³C-NMR spectrum

The ¹³C-NMR spectrum of bio-oil is shown in **Figure 4**. The *x*-axis (chemical shift) was adjusted by the solvent (MeOH-d₄; 49.00 ppm) [9]. The indexes in the spectrum were assisted by the previous report for bio-oil analysis [10]. The values were calculated with an integration of the area in the range of 215-163 ppm (carbonyl, C: 15.94%), 163-110 ppm (aromatic, C: 34.36%), 110-84 ppm (carbohydrate, C: 12.65%), 84-53 ppm (methoxy/hydroxyl, C: 19.47%) and 42-0 ppm (alkyl carbons, C: 17.58%) except for solvent in 53-42 ppm (MeOH). It is clearly suggested that the aromatic carbon was the major component (C: 34.36%). According to the another paper [11], aromatic C-O, aromatic C-C, and aromatic C-H would afford signals at 166.5-142.0 ppm, 142.0-125.0 ppm, and 125.0-95.8 ppm, respectively. Therefore, aromatic C-O and aromatic C-H accounted a large quantity among aromatic compounds in the bio-oil. The methoxy/hydroxy O-C-H group, carbonyl group and alkyl carbons were detected as the similar content value of C value (15-20%).

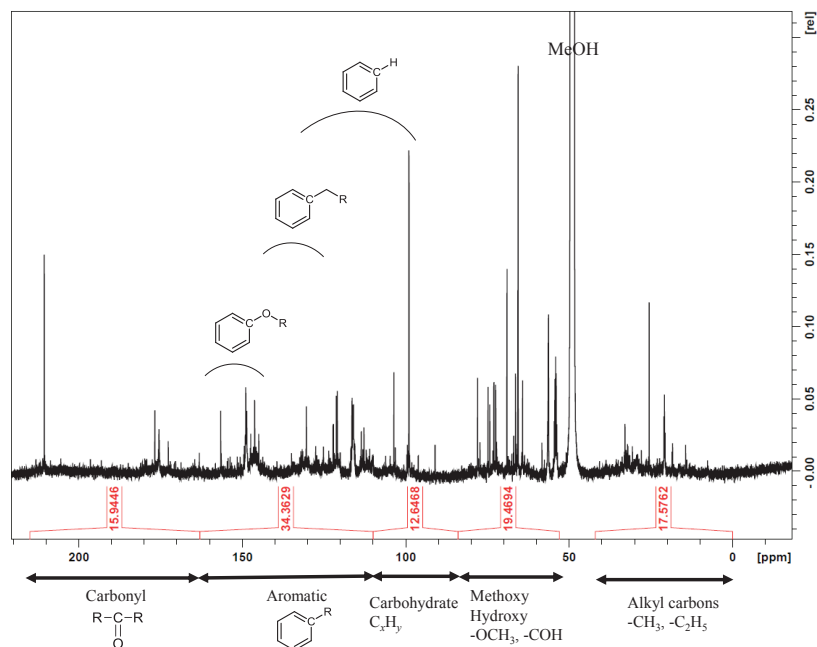


FIGURE 4. ¹³C-NMR spectrum of the bio-oil produced by Auger-reactor with the expected structure.

GC-MS analysis

To further examine the structure of the compounds in bio-oil, GC-MS was measured. **Figure 5** shows GC chart of the bio-oil. The expected structure by MS analysis in the top ten peaks from the largest area were also described in the **Figure 5**. As shown with the orange dialogs, phenol, catechol, and methoxy phenols were the main compounds in the bio-oil. Some furan derivatives, ketone and aldehyde were also detected in top 10 materials (blue dialogs). The large architectonics of $C_{20}H_{30}O$ (black dialog) was detected at 46.43 min. The wood generally consists of cellulose (40-50%), hemicellulose (20-40%), lignin (18-35%) and others (1-4%) [12]. Therefore, cellulose and hemicellulose, comparative easily-decomposable sources under pyrolysis, will convert into gases or furans and aliphatic aldehydes/carboxylic acids detected in bio-oil, whereas the tough lignin was partially decomposed and a lot of methoxy phenols were remained in bio-oil. These observations agreed well with the previous reports for bio-oil analyses [13-14].

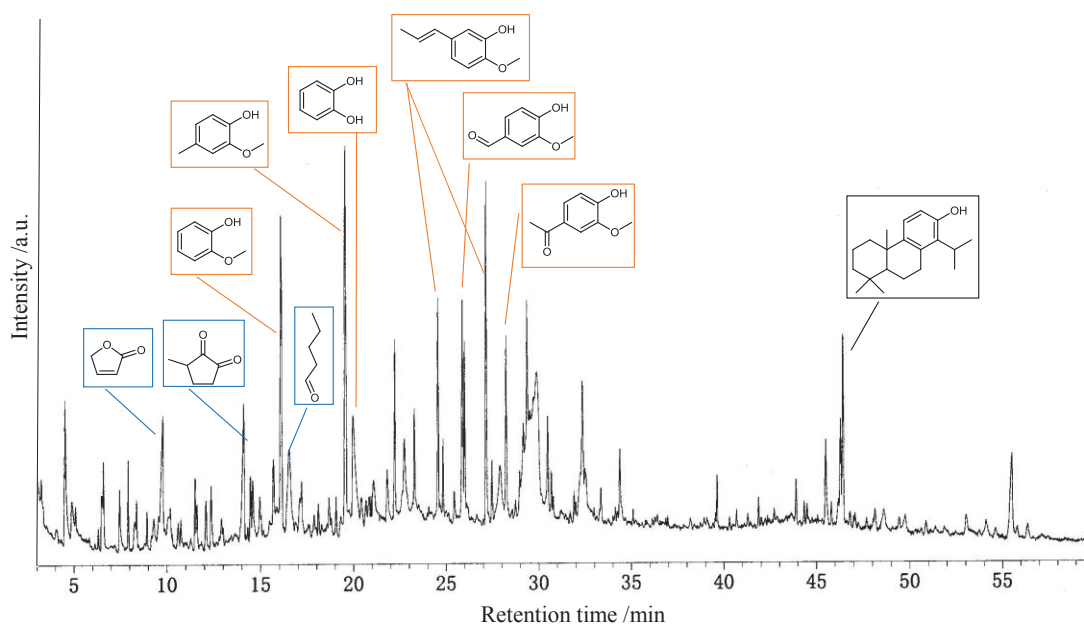


FIGURE 5. GC chart of the bio-oil produced by Auger-reactor with the top 10 expected structure by MS spectrum.

FT-ICR MS analysis

Recently, it has been reported that the FT-ICR MS technique well serves the detailed information to characterize extremely complex mixtures such as heavy oil and bio-oil [15-16]. Thus, we attempted to use the FT-ICR MS for the bio-oil generated by the new Auger-type reactor. **Figure 6** shows the negatively-ion FT-ICR MS broadband spectrum of the bio-oil. On this time, two projecting peaks were observed at $m/z = 129.01925$ and 143.0349 . For instance, these were assigned to the composition formula of $C_5H_5O_4$ and $C_6H_7O_4$, respectively, by the accurate mass. In total, the 720 expected compounds with $C_\alpha H_\beta O_\gamma N_\delta$ formula (± 1.0 ppm error) were assigned in the sample. The carbon number and oxygen number counted up based on each given compound ($C_\alpha H_\beta O_\gamma N_\delta$ formula) were described as 2D and 3D polts in **Figure 7**. The cohesive distributions exhibited the average around at $C = 14-15$ and $O = 8-9$. The 3D polts indicated that the main component in the bio-oil had a linearity between carbon and oxygen: *i.e.* the $C_\alpha H_\beta O_\gamma N_\delta$ with a larger carbon number also possessed a larger oxygen number. Therefore, it is suggested that the Auger-type reactor served a comparatively fine bio-oil in quality.

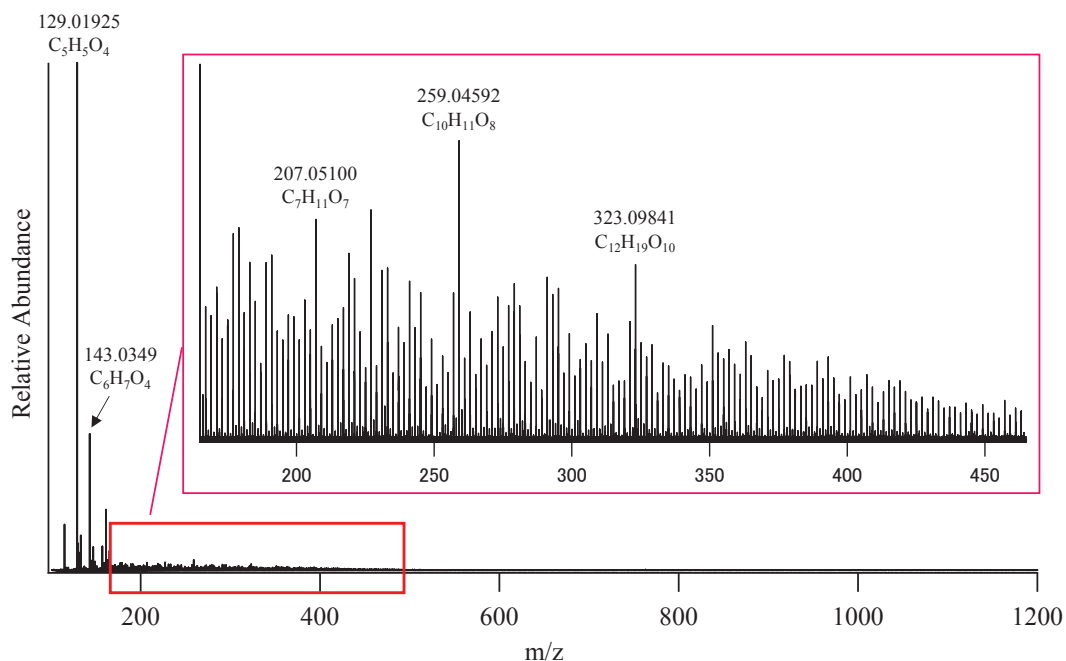


FIGURE 6. Negative-ion FT-ICR MS broadband spectrum of the bio-oil with examples for the estimated composition formula.

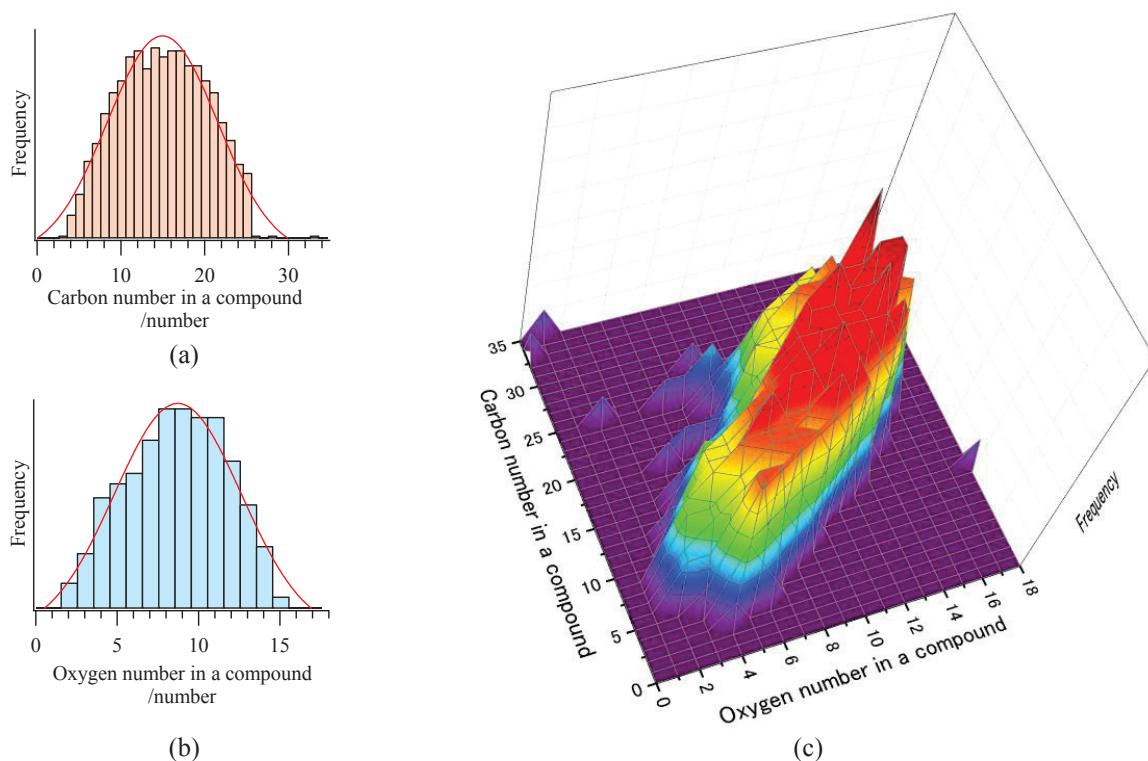


FIGURE 7. Result of FT-ICR MS analysis; (a) oxygen, (b) carbon, and (c) oxygen-carbon number contributions in the estimated compounds in the bio-oil.

SUMMARY

We have been developing the new movable Auger-type reactor for bio-oil production. The produced bio-oil possessed good calorific value (18.1 MJ/kg) and flow property (17 cSt at 50 °C). Physical, spectroscopic and mass analyses indicated that the bio-oil was clean, no sulfur and low nitrogen contents, and mainly composed by methoxy phenols and variety of alcohol or carboxylic acid with fine mixture. The developing movable Auger-type reactor for bio-oil production would be a strong candidate for bio-refinery technology.

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