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Identification of Dihydroxy Aromatic Compounds in a Low-Temperature Pyrolysis Coal Tar by Gas Chromatography–Mass Spectrometry (GC–MS) and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS)

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Dihydroxy aromatics in coal tar undergo rapid coupling reactions with each other and with some coal-derived species during coal pyrolysis and liquefaction. However, only limited information on the structure of dihydroxy aromatics is known. In this study, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and gas chromatography–mass spectrometry (GC–MS) were used to characterize the dihydroxy aromatics in a low-temperature pyrolyzed coal tar and its distillate and residue fractions. Negative-ion electrospray ionization (ESI) FT-ICR MS spectra of coal-tar-derived samples had low molecular masses and narrow mass ranges. Negative-ion ESI is extremely selective for the dihydroxy aromatics present in coal tar. The O₂ class species had the highest ion intensity among the species in the negative-ion FT-ICR mass spectrum for each sample. Dihydroxy compounds with an aromatic core structure of benzene, indan, biphenyl (and/or acenaphthene), and naphthalene were identified in the distillate fractions. Dihydroxy compounds in the residue fraction were dihydroxy fluorenes and phenanthrenes (and/or anthracenes). The O₂ class species with relatively high molecular masses were likely dihydroxy acenaphthylenes and/or hydroxy dibenzofurans but could not be distinguished from each other because these compounds have the same molecular mass.

1. Introduction

The physical properties and reactivity of coal are key parameters for developments in coal use in liquefaction, gasification, and pyrolysis. These parameters are affected by the oxygenated compounds, which are the key species found in coal.^{1,2} Many analytical techniques have been used to characterize the molecular structure and mass distribution of coal and coal-derived liquids. The most commonly used technique is mass spectrometry (MS)^{3,4} in combination with

techniques such as gas chromatography (GC),^{5–8} liquid chromatography (LC),^{9–12} and injection probe.¹³ Various ionization techniques have also been used, including chemical ionization (CI),^{3,14} field ionization (FI),^{9–11,3,15} field desorption (FD),^{3,15,16} fast atom bombardment (FAB),^{3,17} laser

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desorption (LD),^{18,19} matrix-assisted laser desorption ionization (MALDI),^{20,21} and electrospray ionization (ESI).^{4,22–24}

Phenolics are the major oxygen-containing compounds in coal tar⁸ and brown-coal-derived liquids.²⁵ Of those, the alkyl phenols are dominant.^{26,27} Other oxygen-containing compounds that have been found include tetralinol, indanol, hexahydrofluorene, fluorene, hydroxybiphenyl, and dihydroxybenzene.^{7,8,25,28} The high viscosity of coal-derived asphaltenes is likely due to intermolecular aggregation from hydrogen bonding of phenolic compounds. Therefore, when the phenol content in the asphaltenes fraction is decreased, the viscosity of coal-derived liquids will also be reduced.²⁹

Polyhydroxybenzenes are the basic units of lignin structure and are dominant in low-rank coal.² A large amount of dihydroxybenzenes³⁰ is produced under low-severity pyrolysis of low-rank coals, which minimizes secondary cracking reactions to produce volatiles. Catechol (1,2-dihydroxybenzene) and other dihydroxy benzenes have been identified in some coal liquids.^{31,32} Catechol undergoes self-coupling reactions at

a lower rate than resorcinol.² In the presence of donor solvents, 1,4-dihydroxynaphthalene undergoes dehydroxylation reactions at a reaction rate fast enough to prevent self-coupling reactions of dihydroxy aromatics.² Hybrid experiments with sub-bituminous coal and dihydroxyl aromatics showed that the coupling reaction rate of derived species with dihydroxyl aromatics is faster than the self-coupling reactions rate of dihydroxy aromatics.² Although phenols have been extensively analyzed by gas chromatography–mass spectrometry (GC–MS),^{6,26,27,33} only a few studies have been devoted to correlating the detailed composition of dihydroxy aromatics in coals and coal-derived liquids.^{7,8,25} The characterization of phenolic compounds requires prior fractionation to isolate them from a complex hydrocarbon matrix. This is a time-consuming and tedious separation procedure. GC–MS lacks the chromatographic and/or mass resolution to distinguish and identify the individual compounds of heavy fractions. Furthermore, dihydroxy aromatics have high boiling temperatures, and most of these compounds cannot be volatilized.

ESI is an effective approach to ionize polar compounds for MS analysis. Since it was introduced for heteroatom analysis in fossil fuels in 2000,³⁴ ESI coupled with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been widely used in petroleum analysis. Wu et al.²² applied negative-ion ESI FT-ICR MS, resolving 10 000 compositionally distinct components in polar coal extracts, and provided detailed molecular composition for acidic species in various coal extract fractions and liquefied coal products. However, ESI cannot ionize large molecules in coal-derived asphaltenes.³⁵ Herod et al.⁴ investigated the mass distribution of a low-temperature pyrolyzed coal tar and coal-derived liquids using positive-ion ESI. The results showed that, while the use of ESI provided information on only the small molecules, such as azarenes, it did not provide information on the high-molecular-weight compounds in coal-derived liquids. The results revealed that the mass range of ESI was slightly larger than that of GC–MS.

The composition of low-temperature coal tar is known to be different from those of high-temperature coal tar and other coal-derived liquids.¹⁹ In this study, negative-ion ESI FT-ICR MS and GC–MS were used to characterize the oxygen-containing compounds in a low-temperature pyrolyzed coal tar. The focus of this study was on the O₂ class species with dihydroxy groups.

2. Experimental Section

2.1. Material. A low-temperature coal tar sample was obtained from pyrolyzed Shenmu (Shanxi province, China) coal at 600 °C. The elemental composition of the coal tar sample was 82 wt % carbon, 9.42 wt % hydrogen, 1.37 wt % nitrogen, 6.89 wt % oxygen, and 0.27 wt % sulfur. The coal tar sample was atmospheric-distilled. The 200–350 °C distillate and residue was collected and characterized. The yields of 200–350 °C distillate and residue were 36.5 and 58.0 wt %, respectively.

2.2. GC–MS Analysis. A Thermo-Finnigan Trace DSQ GC–MS was used to analyze the composition of the coal tar

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sample and its distillate and residue fractions before and after derivatized with bis(trimethylsilyl)trifluoroacetamide (BSTFA). The mass spectrometer was operated with an electron impact (EI) source at 70 eV ionization energy and scanned from 35 to 500 Da/s interval. GC–MS was equipped with a HP-5MS (60 m × 0.25 mm × 0.25 μm) fused silica capillary column. The oven temperature was held at 50 °C for 1 min, increased to 300 °C at 4 °C/min, and then held constant at 300 °C for 30 min. The injector was maintained at 300 °C in split-less mode. The sample injected was 1 μL at 8 mg/mL concentration. Helium was used as a carrier gas at a flowing rate of 1 mL/min. Catechol, purchased from Beijing Chemical Reagent Company, was used as the model compound to validated the presence of this species in the distilled coal tar fraction.

2.3. FT-ICR MS Analysis. The coal tar sample and its fractions to be analyzed by ESI FT-ICR MS were dissolved with a solvent mixture of toluene and dichloromethane (3:1) to 10 mg/mL. A total of 20 mL of the sample solution was further diluted with 1 mL of toluene/methanol (1:1) solution. The resulting sample solutions were subjected to ESI FT-ICR MS analysis without spiking with a base or further treatment. All solvents used were analytical-grade reagents, which were distilled twice and stored in a glass bottle. Glassware was used for solvent handling and transfer, except for the steel pistons of 10 μL Hamilton syringes.

The MS analysis was performed using Bruker Apex ultra FT-ICR MS equipped with a 9.4 T superconducting magnet. Sample solution was injected into the electrospray source at 180 μL/h using a syringe pump. The typical conditions for negative-ion formation were 4.0 kV emitter voltage, 4.5 kV capillary column introduced voltage, and −320 V capillary column end voltage. Ionized samples were stored in an argon-filled collision cell for 0.1 s and transferred to the ICR cell with a 1.2 ms time-of-flight window. A sidekick voltage of 6 V was used to initially trap the ions. A total of 256 scans were accumulated and averaged to improve the signal-to-noise ratio of the resulting spectra. The mass range was set at m/z 100–800. The size of the data set was set to 2 M words.

2.4. Data Analysis. FT-ICR mass spectra were internally calibrated with sodium formate aqueous solution. The m/z values between 100 and 500 Da with relative abundance greater than 6 times the standard deviation of the baseline noise were exported to a spreadsheet. Data analysis was performed by custom software.^{36,37}

3. Results and Discussion

3.1. Heteroatoms Identified by Negative-Ion ESI FT-ICR MS. Figure 1 shows the negative-ion ESI FT-ICR MS mass spectra of the coal tar sample and its distillate and residue fractions. Although the physical appearance of coal tar is similar to that of petroleum asphaltenes, the spectra of the coal-tar-derived sample had lower m/z values and narrower mass ranges. Peaks with a relative abundance of more than 1% were at a m/z range of 100–300. These were mainly the species with mass series of m/z 109 + 14*n* and 183 + 14*n*. The mass values of spectral peaks of the coal tar distillate fraction were less than 250. The m/z 183 + 14*n* mass peaks were the most abundant in the spectra of coal tar and its residue but

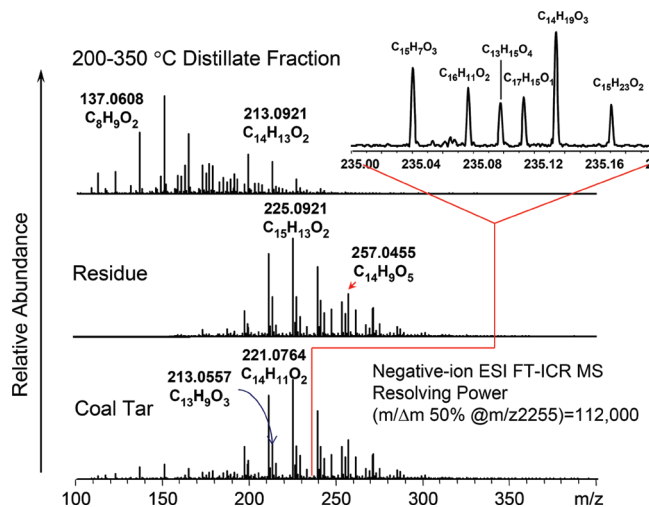


Figure 1. Negative-ion ESI FT-ICR MS mass spectrum of the coal tar and its distillate and residue fractions.

not the distillate. This suggests that these low-molecular-weight compounds have low volatility. The ESI FT-ICR MS spectra for the low-temperature coal tar in this work were different from the negative-ion ESI MS spectra reported by Wu et al.^{22–24} for coal extracts and coal liquefaction products, which contained 3000–10 000 peaks over the m/z range of 300–700. The FT-ICR MS spectra were simple, and almost no abundant masses (peak heights were 6 times the standard deviation of the noise level for each spectrum) were observed at the m/z range above 300 (Figure 1).

The precise mass measurement and high-resolution power of FT-ICR MS allows for the unambiguous assignment of molecular formulas for ions up to 400 Da³⁸ and distinct separation of low mass peaks. The inset in Figure 1 shows the close-up view of the expanded mass spectrum obtained under the resolving power of 120 000 ($m/\Delta m$ 50% at m/z 235). Heteroatoms were distinctly identified in the spectra. These consisted of N₁, N₂, N₁O₁, N₁O₂, O₁, O₂, O₃, O₄, and O₅ class species. However, in this study, the discussion is focused on the predominant O₂ class species.

The molecular compositions of the O₂ class species in the coal-tar-derived samples were determined using the isoabundance plot of double bond equivalent (DBE) as a function of the carbon number. Figure 2 shows the isoabundance plots of the O₂ class species in the coal tar sample and its derived fractions. In the distillate fraction, the O₂ class species had DBE values of 4–9 and carbon numbers of 8–16. The species with a DBE value of 4 were the most abundant. The O₂ class species with a DBE value of 9 were predominant in the coal tar and its residue fraction. This shows that the core structure of the O₂ class species in the coal tar distillate is different from that in the coal tar and its residue fraction. Each of the abundant species had a narrow carbon number distribution, indicating the presence of short side chains on the core of the molecule. The O₂ class species are usually identified as carboxylic acids in petroleum and coal liquefaction products.^{22–24} However, carboxylic compounds decompose at elevated temperatures. Therefore, it is not likely that there will be abundant carboxylic acids in the pyrolyzed coal tar. To perform a more in-depth characterization of the O₂ class species, which were low-molecular-weight

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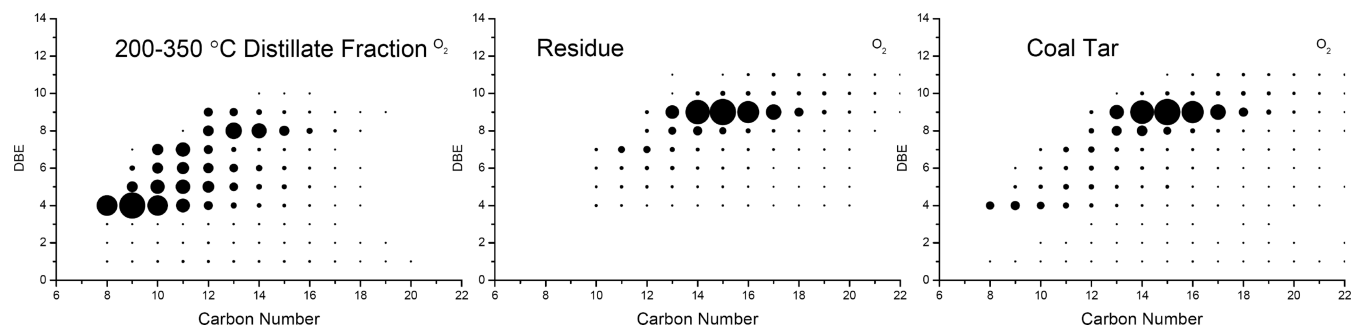


Figure 2. Iso-abundance plots of DBE versus the carbon number of O_2 class species in the coal tar and its distillate and residue fraction. The area of each dot is directly proportional to the peak relative abundance. The maximum dot size was normalized for each plot.

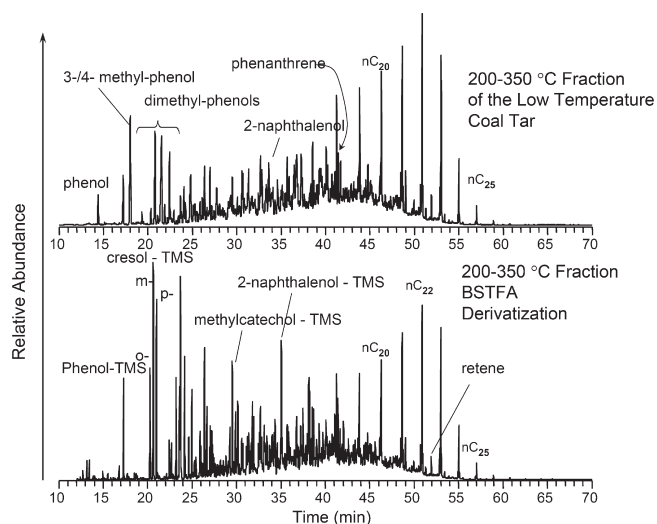


Figure 3. TICs of coal tar 200–350 °C distillate fraction before and after derivatization with BSTFA. “TMS” denotes the trimethylsilyl group.

compounds, the coal-tar-derived samples were subjected to GC–MS analysis.

3.2. Identification of Dihydroxybenzenes by GC–MS. The coal tar samples before and after derivatization reactions with BSTFA were analyzed by GC–MS. Figure 3 shows the total ion chromatograms (TICs) of the 200–350 °C distillate fraction before and after derivatization, indicating that alkyl phenols were abundant in the coal-tar-derived samples. Figure 4–7 show segments of the TICs and mass chromatograms of the dihydroxy compounds. On the basis of the results of GC–MS analysis, dihydroxy compounds with an aromatic core structure, such as benzene, biphenyl, indan, acenaphthene, and naphthalene, were identified in the distillate fraction. These dihydroxy aromatic compounds were not carboxylic acids or non-dihydroxy aromatic compounds with two oxygens.

Figure 4 shows the mass chromatograms of alkyl dihydroxy benzene (benzenediol). The inset in Figure 4 shows a close-up view of the mass chromatograms of three dihydroxy benzene isomers in the coal tar distillate fraction before and after derivatization. EI mass spectra were characteristics of these isomers. Furthermore, the use of pure catechol as the model compound validated the presence of this species in the distilled coal tar fraction. Before derivatization, the dihydroxy benzenes were masked by co-eluted compounds, such as dimethyl phenols and naphthalenes. The only distinct peak on the mass chromatogram was from catechol. However, Figure 3 shows that the silylated dihydroxy benzenes

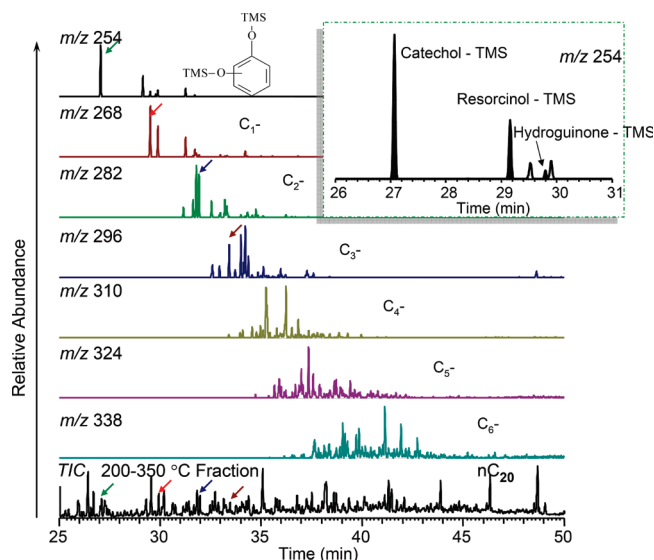


Figure 4. Mass chromatograms of silylized dihydroxy benzenes of coal tar distillate fraction after derivatization with BSTFA. “TMS” denotes the trimethylsilyl group, and “ C_n ” denotes the carbon number of substitute alkyl(s). Colored arrow pairs indicate identified peaks in the mass chromatograms and TIC.

had three symmetrical sharp peaks in the chromatogram of the derivitized sample. The relative abundance of these compounds is greater than that in the spectrum of the underivatized sample. Dihydroxy benzenes had substitute side chains containing 0–10 carbon atoms, in which C_0 – C_3 alkyl homologues were the most abundant.

Three other mass series were identified as dihydroxy aromatics in the mass chromatograms of distillate fraction derivatives in addition to the dihydroxy benzenes. The base values of the mass series were 330, 294, and 304, corresponding to dihydroxy compounds with a core structure of biphenyl (or acenaphthene), indan, and naphthalene, respectively. The mass chromatograms of these compounds are shown in Figures 5–7. The identification and assignment of these compounds was based on the following: (1) the mass spectra appeared in the derivitized analyte were not in the underivatized sample; (2) the mass spectra of these compounds had the correct molecular masses and characteristic mass fragments of trimethoxysilane (m/z 73); (3) these compounds had

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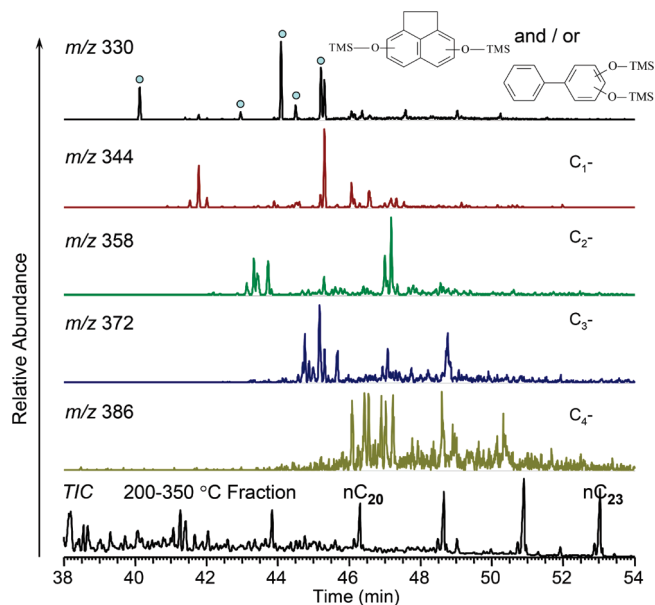


Figure 5. Mass chromatograms of silylanized dihydroxy biphenyls and/or acenaphthenes of coal tar distillate fraction after derivatization with BSTFA. “TMS” denotes the trimethylsilyl group, and “C_n” denotes the carbon number of substitute alkyl(s). Dotted peaks were but not always all of the dihydroxy biphenyl (and/or acenaphthene) isomers.

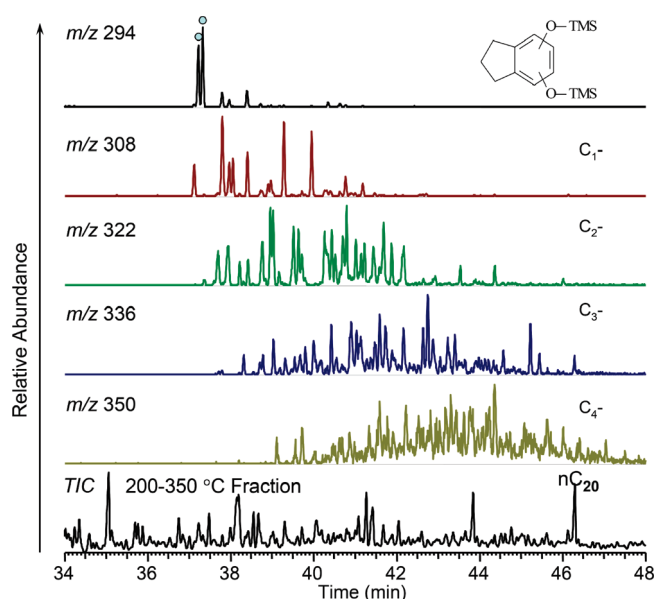


Figure 6. Mass chromatograms of silylanized dihydroxy indans of coal tar distillate fraction after derivatization with BSTFA. “TMS” denotes the trimethylsilyl group, and “C_n” denotes the carbon number of substitute alkyl(s). Dotted peaks were but not always all of the dihydroxy indan isomers.

the correct base mass values; (4) the number of isomers for the non-substituted and methyl-substituted compounds were consistent with theoretical values; and (5) retention behavior of these compounds was consistent with the published GC data.^{7,39}

The GC–MS analysis indicated that dihydroxy aromatics were the dominant O₂ class species in the coal tar distillate fraction. Although carboxylic acids are the abundant O₂ class species found in fossil fuels,²³ no mass spectra for these

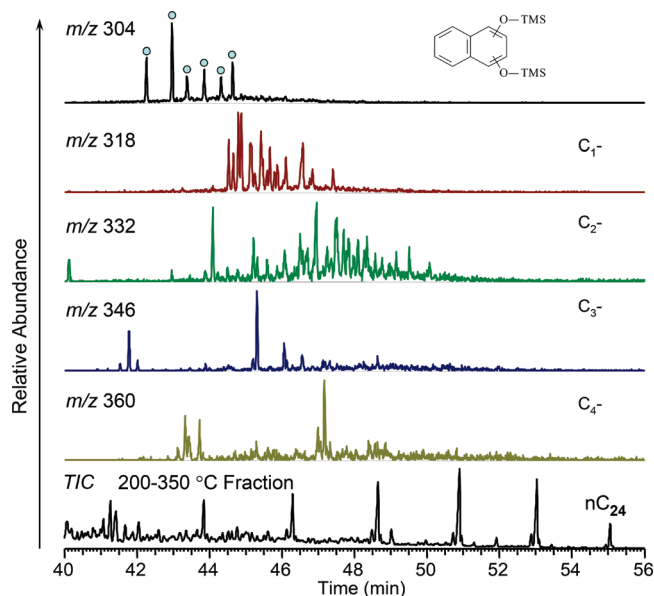


Figure 7. Mass chromatograms of silylanized dihydroxy naphthalenes of coal tar distillate fraction after derivatization with BSTFA. “TMS” denotes the trimethylsilyl group, and “C_n” denotes the carbon number of substitute alkyl(s). Dotted peaks were but not always all of the dihydroxy naphthalene isomers.

compounds were found in the samples before and after derivatization reactions. However, this does not confirm that carboxylic acids are not present in the coal tar samples, because the separation efficiency of the chromatograph may not be adequate to cause a clean separation among the compounds. The co-eluted compounds could mask the carboxylic acids if they are present in trace amounts.

The coal tar residue fraction and its silylanization derivative were also subjected to GC–MS analysis. A portion of dihydroxy aromatics identified in the coal tar distillate fraction were also observed in the residue fraction. In addition, the mass series of $342 + 14n$ and $354 + 14n$ were observed in the silylanization-derivatized analyte. These compounds were likely dihydroxy fluorenes and dihydroxy phenanthrenes (and/or anthracenes). Dihydroxy compounds with more aromatic ring core structures were identified by their molecular masses from FT-ICR MS spectra, but there was insufficient GC–MS information to confirm that these compounds are present in the samples.

3.3. Structure of Dihydroxy Aromatics. According to the GC–MS analysis, the most abundant peaks present in the FT-ICR MS spectra in the coal tar distillate fraction was dihydroxy benzenes. Although alkyl phenols are the most common and abundant oxygen compounds found in coal tar and can be ionized by ESI, their abundance was low in the FT-ICR mass spectra. This suggests that the ionization efficiency of dihydroxy aromatics is higher than that of phenols. Hence, negative-ion ESI is an appropriate technique for analyzing dihydroxy aromatics in complex mixtures, such as fossil fuels.

As shown in Figure 1, the FT-ICR mass spectrum peaks with the greatest ion intensity for the coal-tar-derived samples are the m/z $183 + 14n$ mass series, with a normal distribution centered at m/z 225. Accurate molecular mass indicates these compounds are O₂ class species with a DBE value of 9 (Figure 2). The DBE and carbon number distribution were coincident with those for dihydroxy acenaphthylene. However, the presence of dihydroxy acenaphthylenes was

not supported by the GC–MS analysis. Because dihydroxy acenaphthylenes are high boiling point compounds, if they are present in coal tar, they will likely not volatilize and pass through the GC column. Structural deduction based on the molecular weight and DBE value also suggests that this compound could be another type of O₂ class species, namely, hydroxy dibenzofuran. This is because the hydroxy groups can be ionized in ESI and GC–MS analysis shows dizenofuranes are abundant in the distillate fraction. However, the presence of dihydroxy acenaphthylenes and/or hydroxy dibenzofurans in the high-boiling fraction of coal tar samples could not be distinguished.

4. Conclusions

FT-ICR MS and GC–MS were used to investigate dihydroxy aromatics in a low-temperature pyrolyzed coal tar and

its distillate and residue fractions. Negative-ion ESI FT-ICR MS spectra of coal-tar-derived samples had low m/z values and narrow mass ranges. FT-ICR MS was extremely selective for the dihydroxy aromatics present in coal tar. The O₂ class species had the highest ion intensity among the species in the negative-ion FT-ICR mass spectrum of each sample. Dihydroxy compounds with an aromatic core structure of benzene, indan, biphenyl (and/or acenaphthene), and naphthalene were identified in the distillate fractions. Dihydroxy compounds in the residue fraction were dihydroxy fluorenes and dihydroxy phenanthrenes (and/or anthracenes). The O₂ class species with relative high molecular masses were likely dihydroxy acenaphthylenes and/or hydroxy dibenzofurans but could not be distinguished because these compounds have the same molecular mass.

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