

# Separation and Analysis of Oxygen-Containing Compounds in a Shaanxi Middle/Low-Temperature Coal Tar

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**ABSTRACT:** A middle/low-temperature coal tar (M/LTCT) was obtained from a low-temperature carbonization plant in Shaanxi, China. The M/LTCT was separated into light components and coal tar pitch through extraction. A series of alkanes, aromatic hydrocarbons, oxygen-containing arenes (OCAs), and nitrogen-containing arenes were fractionated from light components by medium-pressure preparative chromatography with gradient elution using petroleum ether and ethyl acetate. They were analyzed using a gas chromatography–mass spectrometer (GC–MS) and a Fourier transform infrared spectrometer. The OCAs were analyzed by a Fourier transform Orbitrap MS (quadrupole exactive Orbitrap mass spectrometer), and the molecular distribution of the  $O_1$ – $O_6$  species was studied. OCAs are mainly oxygen-containing aromatic compounds, including aromatic phenols, furans, alkoxy aromatic hydrocarbons, aromatic ethers, aromatic aldehydes, aromatic ketones, and aromatic acids. The position of the oxygen atom on the aromatic ring and the condensation form of the aromatic ring are studied.

## 1. INTRODUCTION

Coal tar is one of the most important heavy carbon resources, and it contains complex chemicals that are otherwise difficult to acquire from other fossil fuels such as gas and oil.<sup>1</sup> The middle/low-temperature coal tar (M/LTCT) is a byproduct of coal carbonization and gasification.<sup>2</sup> This low-rank coal in China has reserves of nearly 500 billion tons, accounting for approximately 42% of the documented coal reserves.<sup>3–5</sup> With the large-scale exploitation and utilization of low-rank coal, the M/LTCT as an alternative fuel has great prospects in the future.<sup>6</sup> The M/LTCT is mainly composed of alkanes, aromatic hydrocarbons (AHCs), oxygen-containing arenes (OCAs), nitrogen-containing arenes (NCAs), and coal tar pitch.<sup>7–9</sup> Since 2015, the annual total production capacity of the M/LTCT in China has reached 4 Mt,<sup>10</sup> and most have been burned directly, causing serious environmental pollution and waste of resources.<sup>11</sup>

Most of the pure products separated from the M/LTCT are important fine chemicals. For example, AHCs, OCAs, and NCAs are important ingredients in the synthesis of

pharmaceuticals, dyes, resins, disinfectants, and pesticides.<sup>12</sup> The AHCs are completely hydrogenated as saturated hydrocarbons, and the resulting mixtures can be used as high-quality liquid fuels after fractionation.<sup>10</sup> However, the properties and composition of the M/LTCT are complex. Phenols are usually hydrogenated with water, which easily causes catalyst deactivation, and many nitrogen-containing organic compounds can cause catalyst poisoning.<sup>13</sup> Therefore, it is very important to explore an effective way to separate each component from the M/LTCT with low energy consumption and material consumption.

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**Table 1.** Some Properties and Ultimate Analysis of the M/LTCT<sup>a,b,c</sup>

some properties of M/LTCT					ultimate analysis (%)				
D	V	M	A	T	C	H	N	S	O <sub>diff</sub>
0.96	11.10	1.21	0.17	0.40	80.92	7.90	0.93	0.39	9.86

<sup>a</sup>D: density (20 °C/g·mL<sup>-1</sup>); V: viscosity (80 °C/mPa·s). <sup>b</sup>M: moisture (%); A: ash (%); T: toluene insoluble (%). <sup>c</sup>The M/LTCTNSP sample was collected from Shanbei (Northern Shaanxi Province) semicoke plant (Shuangyi Co., Ltd.).

Coal tar separation technology has been developed for a long time, and it mainly includes distillation,<sup>2</sup> acid and alkali treatments,<sup>14</sup> organic solvent extraction,<sup>15–20</sup> and column chromatography.<sup>21</sup> Distillation cannot effectively separate the hydrocarbons and phenolic compounds in the M/LTCT due to their similarity in boiling points. Extensive use of column chromatography faces difficult problems, and it is time-consuming. Solvent extraction has achieved good results in model compounds instead of the actual treatment of the M/LTCT samples. The trend of M/LTCT separation technology is to separate components of different groups under mild conditions. Liquid chromatography is an important technique for separating soluble organic matter from complex compositions,<sup>22–25</sup> and medium-pressure preparative chromatography (MPPC) is one of the most commonly used methods in liquid chromatography separations.

Gas chromatography–mass spectrometry (GC–MS) and Fourier transform infrared (FTIR) spectrometry are widely applied to realize the compositions of SPs. However, unknown structural details of complex heteroatom-containing species mixtures cannot be revealed by these analytical methods. In high-resolution mass spectrometry, an FT Orbitrap MS (quadrupole exactive orbitrap mass spectrometer) with an electron spray ionization source (ESI/FT Orbitrap MS) is more affordable compared with a Fourier transform ion cyclotron resonance MS, and it is of a higher resolving power (140,000) than time-of-flight MS.<sup>26–30</sup> Therefore, combining GC–MS with ESI/FT Orbitrap MS makes good sense of fully realizing the compositions of SPs in coal tar.

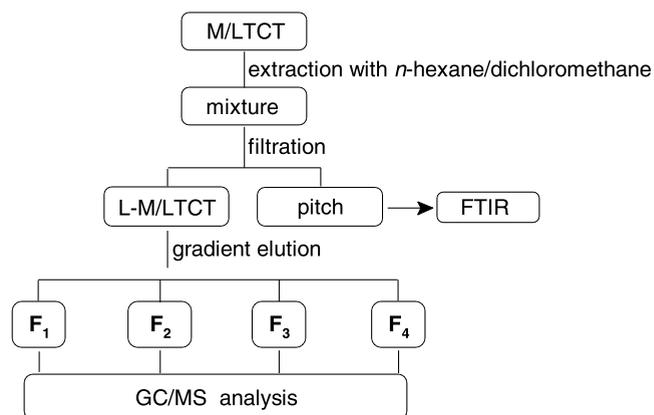
In this work, a new separation method of the M/LTCT by MPPC was designed and developed. The M/LTCT was separated into five parts: alkanes, AHCs, OCAs, NCAs, and coal tar pitch. The OCAs were analyzed by the ESI/FT Orbitrap MS in negative ion mode, and the distributions of the O<sub>1</sub>–O<sub>6</sub> species were studied.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** The M/LTCT sample was obtained from a semicoke plant. The M/LTCT sample was subjected to extraction separation producing coal tar pitch and light-M/LTCT(L-M/LTCT), which was approximately 83% of the M/LTCT material. The elemental compositions of the sample and some properties of the L-M/LTCT were analyzed according to the Chinese national standards and are included in Table 1.

**2.2. Chemicals and Materials.** Silica gel Si60 (SG, 60–100 mesh, Qindao Tenghai Fine Sine Silica Gel Chemical Co, Ltd), methanol, ethyl acetate, n-butanol, and petroleum (products of Fu Chen Chemical Company, Tianjin, China) were used in this study. The chemicals were all AR grade.

**2.3. Extraction and Fractionation.** Figure 1 shows the experimental process. Approximately 100 g of M/LTCT was extracted in a conical flask with an isometric *n*-hexane/dichloromethane mixed solvent for 2 h. The extract was filtered through a polytetrafluoroethylene membrane filter with a pore size of 0.5 μm. The extraction residue was deposited on the

**Figure 1.** Scheme of M/LTCT extraction and separation.

filter, and the filtrates were collected and concentrated to 50 mL with a Büchi R-134 rotary evaporator.

**2.4. Sample Preparation and Experimental Process.** The directional separation of the L-M/LTCT was accomplished by MPPC. One hundred grams of silica for gel chromatography (SG, 60–100 mesh) was weighed and vacuum dried at 110 °C for 2 h. A sample of L-M/LTCT (3 g) and *n*-hexane (10 mL) was prepared by sonication for 15 min. The slurry was mixed with 10 g of silica gel and sonicated for 20 min. The slurry was placed in a 50 °C rotary evaporator until the sample was dried into granules. The L-M/LTCT fractions were subjected to normal phase MPPC. The preparation for separation was performed on a Sepacore R Easy Extract purification system consisting of two C-605 pump modules, a C-615 control unit, and a C-640 UV detector (Puri Flash 450, Interchim Labortechnik, France). The initial separation was performed on a 70 × 460 mm plastic glass column (Interchim, France) loaded with silica gel Si60 (50–60 μm, Interchim). The ultraviolet wavelength of the UV detector was set at 212 and 254 nm. When an elution component entered the detector, the absorption peak curve begins to rise until the elution was complete, the absorption peak curve decreased when it reached a stable level, and the elution component was collected. The L-M/LTCT was divided into four components. The operation principles of the instrument are shown in Figures 2 and 3 and list the process of screening the eluting solvents by MPPC.

**2.5. Analytical Methods.** The components were analyzed by the GC–MS (model 7890/5975, Agilent Technologies) with an HP-5MS (cross-link 5% PHME siloxane, 60 m length, 0.25 mm inner diameter, and 0.25 μm film thickness) and a quadrupole analyzer with an *m/z* range from 33 to 500 in the electron ionization (EI, 70 eV) mode. The FTIR spectrum of the samples was recorded from 4000 to 400 cm<sup>-1</sup> with a Nicolet Magna IR560 FTIR spectrometer. Each sample was mixed with KBr, and they were pressed into a pellet for FTIR analysis. OCAs were analyzed through an Orbitrap MS, which was equipped with an ESI in negative ion mode (model Q

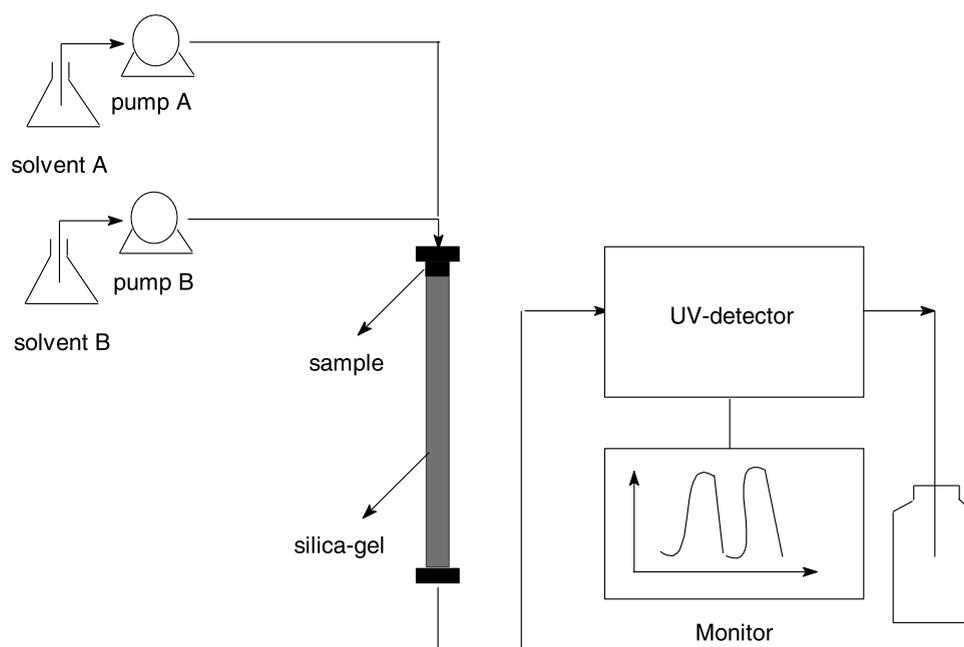


Figure 2. Schematic diagram of preparative liquid chromatography.

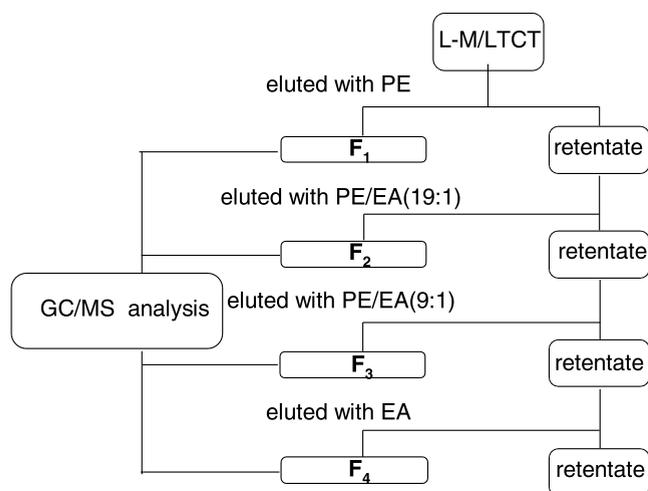


Figure 3. Process of screening the eluting solvents by MPPC.

Exactive, Thermo Scientific). The scanning mass range was 100–1000 Da, and the spectrum was scanned for 2 min. Thermo Xcalibur Quan Browser software was used for qualitative analysis.

### 3. RESULTS AND DISCUSSION

**3.1. Yield of Fractionations.** Figure 4 shows the yield of the group fraction collected by MPPC. The first eluted component ( $F_1$ ) was alkane, and the second eluted component ( $F_2$ ) was AHC. The third eluted component ( $F_3$ ) was OCA, and the final eluted component ( $F_4$ ) was NCA. The total yield of the four components was 89.5 wt %, reflecting the loss of low mass volatiles during the solvent removal and some retention of the heavy molecules in the silica gel. The separation experiment was repeated three times with an error of less than 0.5%.

**3.2. Analysis of the Fractionations with GC–MS.** Figure 5 shows the GC–MS total ion chromatograms of  $F_1$ ,  $F_2$ ,  $F_3$ , and  $F_4$ , which are alkanes, AHCs, OCAs, and NCAs. In the

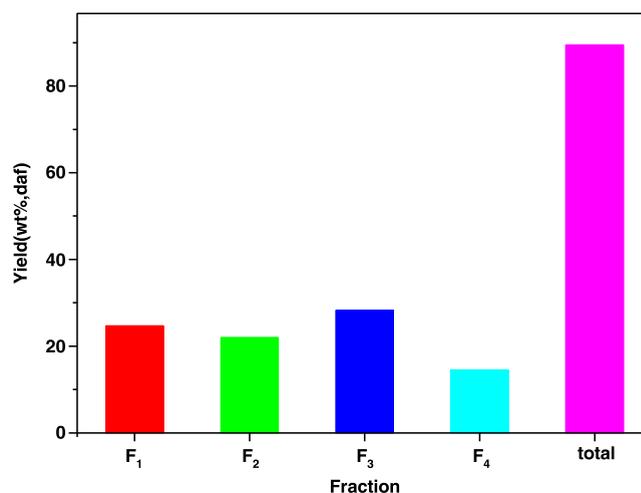


Figure 4. Yield of each fraction.

elution process, the alkanes were eluted first. However, the eluent of the  $F_1$  component became a white crystal at room temperature below 10 °C after purification by rotary evaporation. Because the structure of the alkanes is relatively simple and the adsorption of the alkanes on the silica gel is minimal, the alkanes are eluted first. The linear alkanes are mainly  $C_{10}$ – $C_{30}$ . The relatively pure fraction of alkanes can be further cut and separated by distillation to obtain light oil products, such as diesel oil.  $F_2$  are mainly aromatic hydrocarbons with different number of aromatic rings, including alkyl benzene, alkyl naphthalene, alkyl hydrazine, and alkyl phenanthrene. Interestingly, abundant alkyl-substituted benzene rings and naphthalene rings were detected by GC–MS, and the substituents were mainly methyl and ethyl.  $F_3$  are OCAs, which are mainly phenols containing  $O_1$  and minor amounts of  $O_2$ ,  $O_3$ , and  $O_4$  compounds. The types of alkyl phenols are numerous, and most of the alkyl phenols have methyl and/or ethyl substituents, such as methyl phenol, ethyl phenol, and methyl ethyl phenol. NCAs are predominant in  $F_4$ .

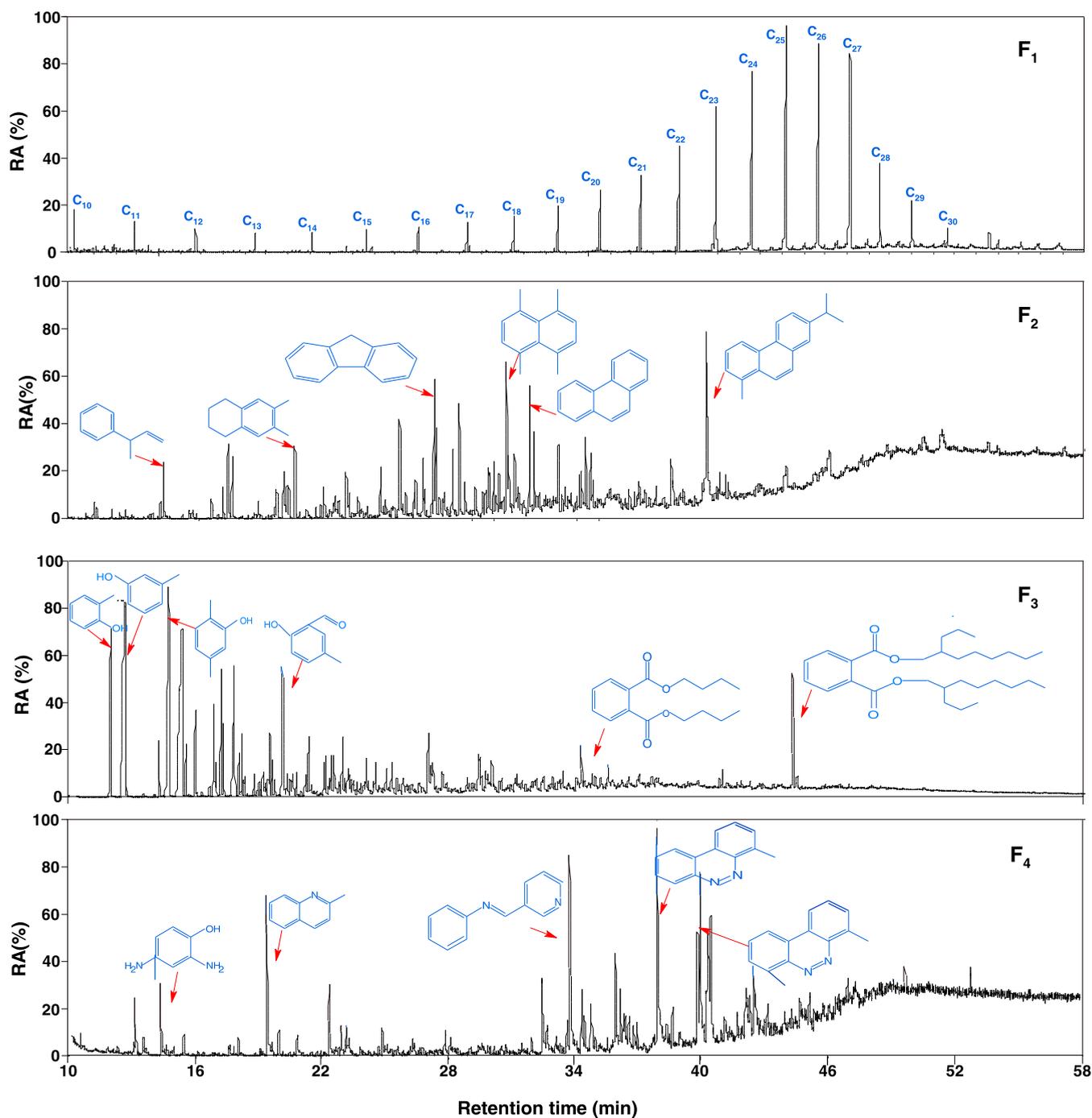


Figure 5. Total ion chromatograms of F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, and F<sub>4</sub>.

Different types of alkyl quinolones are abundant, including methyl and ethyl quinolones.

**3.3. FTIR Analysis of Coal Tar Pitch.** FTIR spectroscopy is one of the most common analysis techniques used to determine the functional groups of compounds. In Figure 6, the absorbances around 803 and 741  $\text{cm}^{-1}$  are ascribed to the flexural vibration of the C–H plane of a condensed aromatic hydrocarbon, while the absorbances around 1580 and 1460  $\text{cm}^{-1}$  are assigned to an aromatic skeleton vibration, and the absorbance around 2920  $\text{cm}^{-1}$  results from the alkanes. In addition, the absorbance around 3050  $\text{cm}^{-1}$  is ascribed to a C–H stretching vibration in an aromatic hydrocarbon, and the absorbance around 3440  $\text{cm}^{-1}$  results from a heteroatom X–H.

**3.4. FT Orbitrap MS Analysis of Organic Compounds (OCAs).** As shown in Figure 7, the range of their molecular masses is from 100 to 1000  $u$ , and most of them range from 150 to 350  $u$ . For the ions near 229  $u$ , 4 distinct compounds identified were assigned to the O<sub>1</sub>–O<sub>4</sub> species. The relative contents of O<sub>1</sub>–O<sub>6</sub> species with an FT Orbitrap MS analysis were 29.23, 35.28, 17.14, 13.1, 4.23, and 1.01%, respectively (Figure 8). Double-bond equivalence (DBE) is an important structural parameter used in an FT Orbitrap MS analysis for OCAs. As exhibited in Figure 9, the DBE values and carbon numbers (CNs) for the O<sub>1</sub>–O<sub>6</sub> species vary from 0 to 25.

Referring to the analytical method of petroleum omics,<sup>26,27</sup> the compounds detected by the FT Orbitrap MS can be

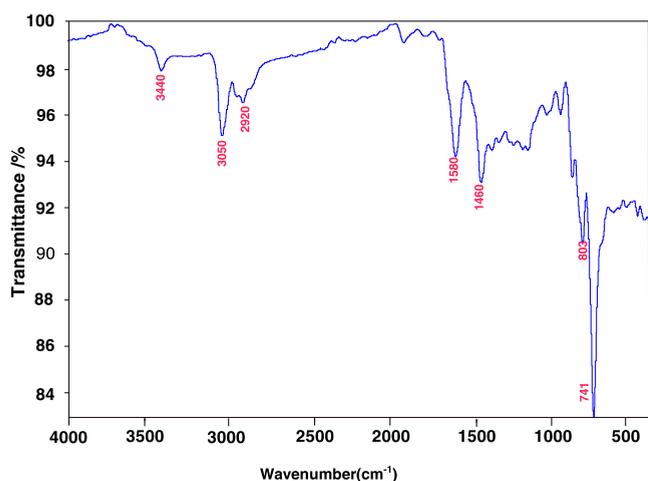


Figure 6. FTIR spectrum of coal tar pitch from the M/LTCT.

classified by “class” and “type” according to the number of heteroatoms and the number of equivalent double bonds (DBE, the number of rings plus double bonds). The value of DBE can be calculated by the general formula  $C_cH_hO_oN_nS_s$ , and DBE is equal to  $c - h/2 + n/2 + 1$ . DBE is an important structural parameter for organic compounds. For each double bond or lipid ring added, the DBE value increases by 1. In general, the condensation degree of the aromatic ring increases by 1, and the DBE value of the compound increases by 3; hence, different aromatic ring structures are speculated. As shown in Figure 10, according to the different positions of the oxygen atom on the aromatic ring, the possible compounds were deduced.

When the oxygen atom is located outside the aromatic ring, it is mainly aromatic phenolic compounds. According to the change of DBE, its aromatic rings are mainly benzene ring, indane ring, indene ring, fluorene ring, acenaphthene ring, naphthalene ring, anthracene ring, phenanthrene ring, pyrene

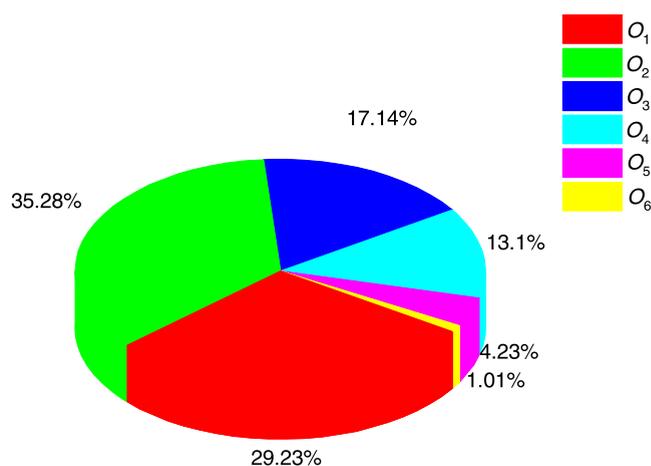


Figure 8. Relative contents of  $O_1$  to  $O_6$  species from the M/LTCT by the ESI/FT Orbitrap MS in negative ion mode.

ring, etc. When the DBE is the same and the CNs are different, this is mainly a series of aromatic phenols with the same aromatic ring and different side-chain substituents. Generally, the larger the CNs, the longer the side-chain substituents. When  $DBE < 13.5$ , the aromatic ring of aromatic phenol is mainly condensed at the metaposition; when  $DBE > 13$ , the aromatic rings in aromatic phenols are mainly condensed in the peri-position.

When the oxygen atom is located on the aromatic ring, it is mainly aromatic ketone compounds. There are mainly indanone, tetralone, anthranone, pyrene, and so on. The aromatic rings of aromatic ketones were partially saturated, and their aromaticity decreased. Decalin in coal tar as a hydrogen-donating solvent can promote the hydrogenation of aromatic phenolic compounds to generate aromatic ketones. In aromatic ketones, when  $DBE < 10$ , the aromatic ring is metacondensed. While  $DBE > 10$ , the aromatic ring is peri-condensed.

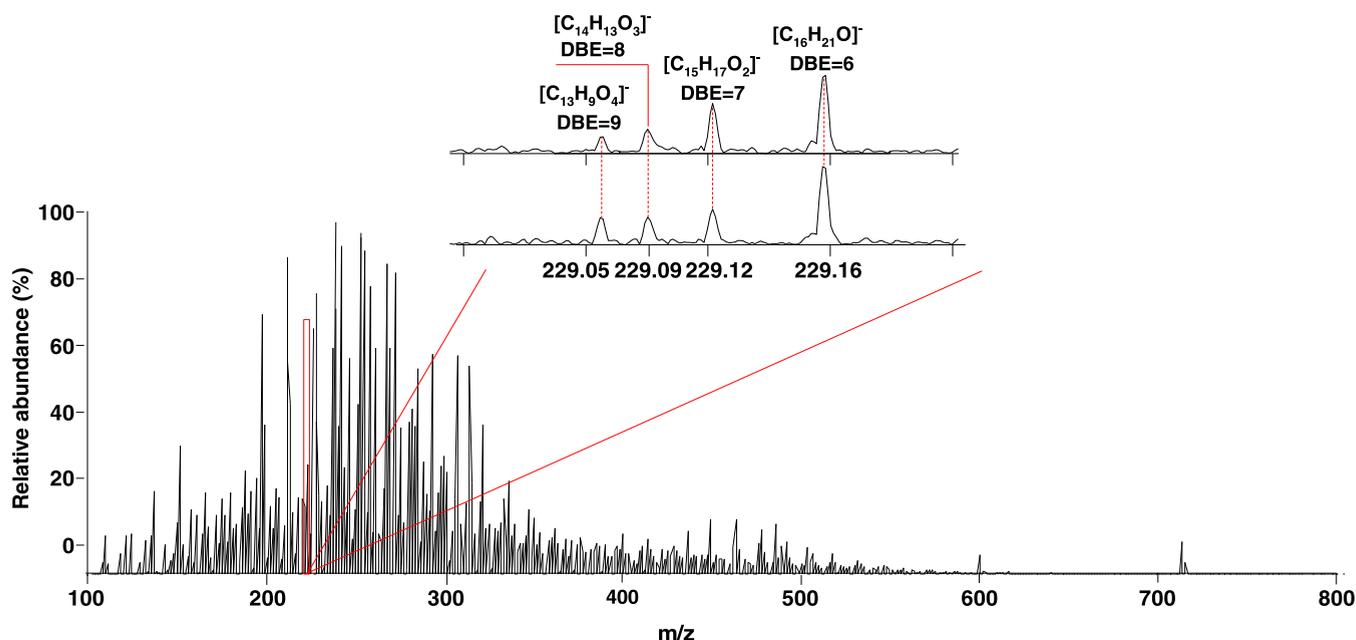
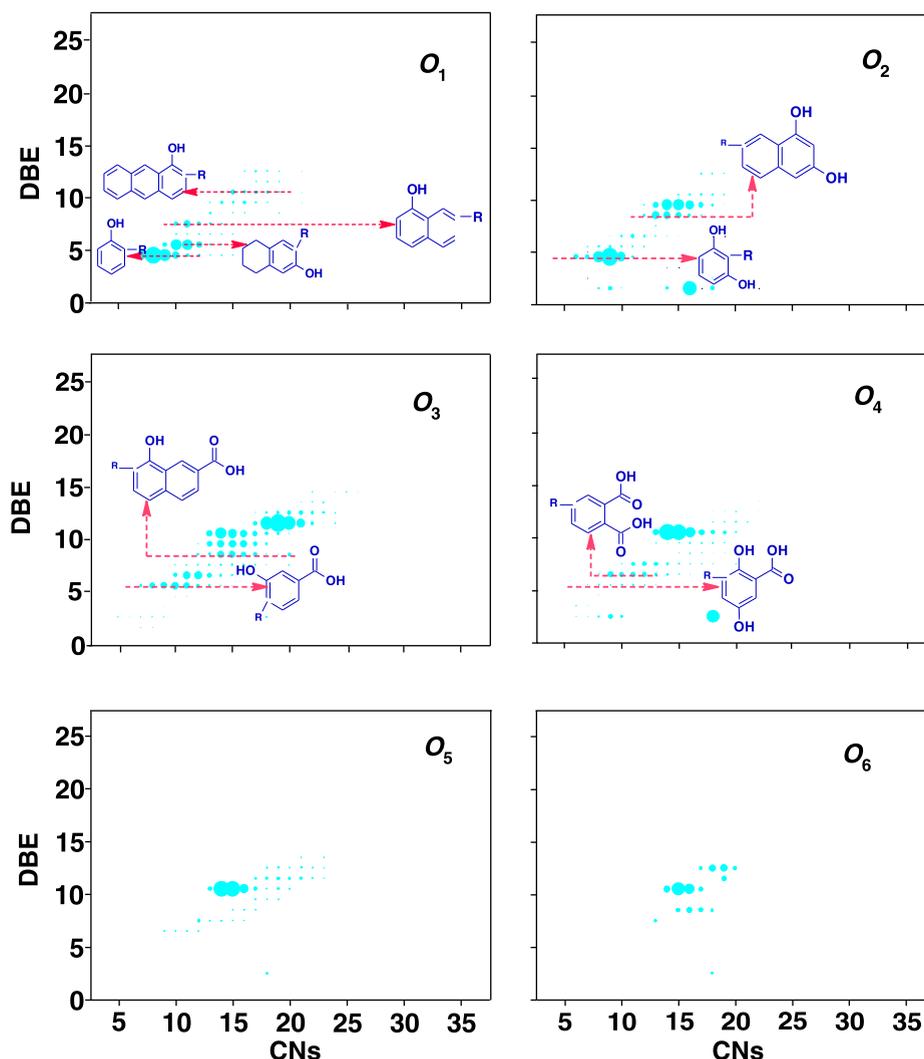


Figure 7. Broadband mass spectra of oxygenated compounds by the ESI/FT Orbitrap MS in negative ion mode and mass scale-expanded segments (inserted figure) at 229u.



**Figure 9.** Iso-abundance plots of DBE versus CNs for the  $O_1$ – $O_6$  species in OCs identified by the ESI/FT Orbitrap MS in negative ion mode.

When the position of the oxygen atom is in the aromatic ring, the main furan compounds are mainly benzofuran, naphthofuran, benzonaphthofuran, and other compounds. The DBE value increases with the increase of aromatic ring condensation degree.

The  $O_2$  compounds are mainly alkanoids, arenediols, and aromatic acids. The  $O_2$  compounds with the DBE of 4, 7, and 10 are most likely alkyl benzenediols, alkyl naphthalenediols, and alkyl anthracenediols, respectively. The higher levels of  $O_2$  compounds are bisphenols (DBE = 4) and benzofurans (DBE = 9). Most of the  $O_2$ – $O_6$  compounds are not easily detected by GC–MS due to their high polarities and boiling points.

The  $O_3$  species has a DBE value in the range of 1.5–14.5 and a carbon number in the range of 5–26. The three oxygen atoms contained are in the form of hydroxyl groups, carboxyl groups, carbonyl groups, and/or methoxy groups. When the DBE is less than 4, they are hydroxy-substituted alkanoids (DBE = 1) and carbonyl-substituted alkanoids (DBE = 2). When the DBE is 8 and 11, the corresponding species may be alkyl hydroxyl naphthoic acids and alkyl hydroxyl anthracene-carboxylic acids, respectively.

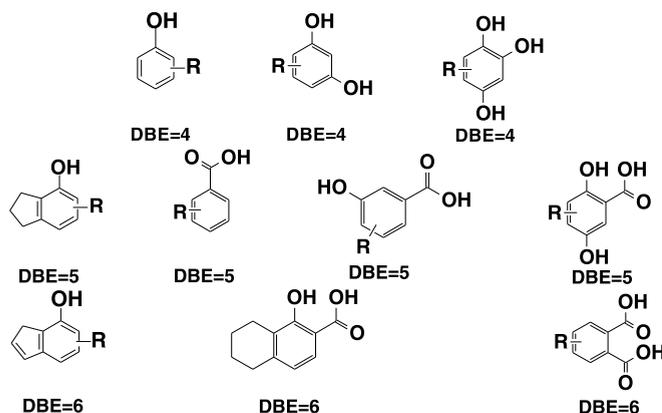
In  $O_4$  class, the DBE values of 5, 8, and 11 may be alkyl dihydroxyarene dicarboxylic acids with aromatic rings from 1 to 4, while the DBE values are 6 and 9, the compounds could be alkyl arenedicarboxylic acids with 1–2 aromatic rings.

Since the combination of oxygen in  $O_5$ – $O_6$  species may be varied, determining the precise molecular structure of these species is quite difficult. Compounds in the  $O_5$  class may be alkanedioic acids with 2 hydroxyl groups or alkyl hydroxyphthalic acid and alkyl hydroxy naphthalene dicarboxylic acid. The  $O_6$  species may be alkyl tricarboxylic acid.

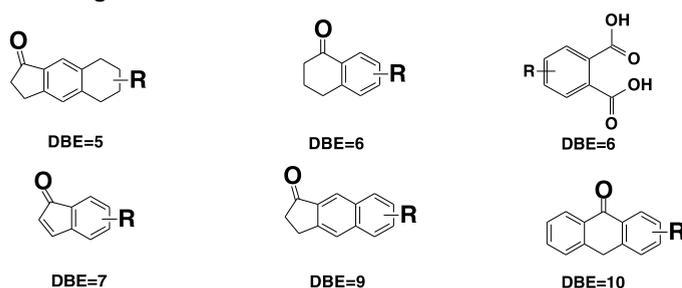
#### 4. CONCLUSIONS

MPPC is used to separate components of different groups from an M/LTCT under mild conditions. The results of GC–MS and FT Orbitrap MS analyses demonstrate that MPPC with solvent elution and gradient elution is a scientific and efficient method for the separation of group components from the M/LTCT. Based on the polarity and the elution order of the component groups, the MPPC instrumentation can separate alkanes, aromatic hydrocarbons, OCAs, and NCAs from the M/LTCT. The molecular masses of OCAs range from 150 to 350 *u* by an FT Orbitrap MS. They are mainly condensed aromatic compounds containing oxygen. The composite

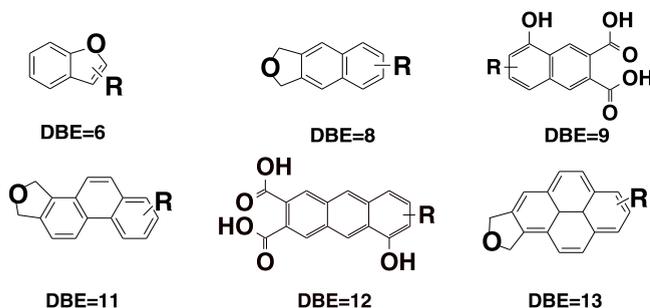
## Over the aromatic ring



## On the aromatic ring



## In the aromatic ring



**Figure 10.** Possible structures of the  $O_N$  base on CNs and DBE.

number of aromatic rings, the position and existing form of oxygen atoms on the aromatic ring, and the types of substituents on the aromatic ring of these compounds are studied.

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## Notes

The authors declare no competing financial interest.

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## NOMENCLATURE

AHCs, aromatic hydrocarbons

DBE, double-bond equivalence

FTIR, Fourier transform infrared

FT Orbitrap MS, Fourier transform Orbitrap mass spectrometer

GC–MS, gas chromatography–mass spectrometer

L-M/LTCT, light-middle/low-temperature coal tar

M/LTCT, middle/low-temperature coal tar

MPPC, medium-pressure preparative chromatography

NCAs, nitrogen-containing compounds

OCA, oxygen-containing arenes

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