Pyrolysis Temperature Effect on Compositions of Neutral Nitrogen and Acidic Species in Shale Oil Using Negative-Ion ESI FT-ICR MS

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1. INTRODUCTION

Oil shale is a fine-grained sedimentary rock rich in organic matter and has a schistose structure with the oil content between 3.5 and 30%. After burning, the ash content is generally higher than 40%, and the calorific value is generally higher than 4.19 kJ/kg. The organic matter of oil shale is present as an organic polymer. The total content of organic matter in oil shale is usually less than 35% of the total mass. It is filled in the framework of inorganic minerals and mainly consists of kerogen and bitumen. Furthermore, shale oil is the most important pyrolysis product of oil shale. The special composition and structure of oil shale determine that it has broad potential applications in energy, mineral, chemical, and architectural fields. The greatest utilization potential of oil shale is to produce shale oil by pyrolysis. Shale oil is a brown and sticky liquid fuel with a special irritating odor, very similar to crude oil. It can be used not only for refining gasoline and diesel oil for ships and airplanes but also for processing rubber softeners, asphalt additives, and other additional products. Furthermore, both shale oil and crude oil contain a large amount of heteroatom compounds, as well as crude oil asphaltene and interfacial material. This will decrease the catalyst activity and selectivity, corrode the metal equipment, and decrease oil stability during shale oil refining and processing. Moreover, the combustion of heteroatom compounds releases a large amount of nitrogen- and sulfur-containing oxides, polluting the environment. Therefore, it is of great scientific importance to analyze the distribution and characterization of heteroatom species and the effect of different pyrolysis conditions on their distribution characteristics.

The molecular composition of shale oil and other fuel oils is very complex and difficult to characterize in detail. Conventional analytical instruments such as gas chromatography–mass spectrometry (GC–MS), nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy, GC–nitrogen chemiluminescence detection, and GC–sulfur chemiluminescence detection were used for the molecular characterization of shale oil. However, the GC method cannot analyze the entire fraction of shale oil because of the limitation of the column temperature and peak capacity. NMR and FT-IR spectroscopy were used to analyze the distribution of H, C, and some functional groups. Therefore, these conventional analytical instruments have certain limitations in the molecular characterization of liquid fuel oils. Recently, FT-ICR MS has been successfully used for

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studying heteroatom compounds in crude oil,\textsuperscript{27−30} coal tar,\textsuperscript{31−34} shale oil,\textsuperscript{35,36} and other liquid fuel oils\textsuperscript{37,38} and in developed "petroleomics."\textsuperscript{39,40} Its high resolution makes it possible to identify thousands of components in complex samples without chromatographic separation and is often used to analyze the petroleum components with the relative molecular mass ranging from 200 to 1000 Da. FT-ICR MS combined with ESI can be directly used for the analysis of the liquid fuel oil without sample pretreatment. ESI FT-ICR MS has a high selectivity for polar components and can obtain the number of double-bond equivalence (DBE) and carbon number of compounds in the sample. In addition, acidic compounds and neutral nitrogen species can be detected under the negative-ion ESI mode.\textsuperscript{41}

In this study, negative-ion ESI FT-ICR MS was used to compare the compositions of acidic and neutral nitrogen species in Huadian shale oil produced at different temperatures. To more accurately analyze the effect of pyrolysis temperature on acidic and neutral nitrogen species, shale oils produced during the heat-up stage were abandoned. Instead, only shale oils produced by pyrolysis at the preset constant temperature in a complete pyrolysis process were collected as samples in this study. This is very different from other studies.\textsuperscript{42−44} The shale oil samples produced at different temperatures in most other studies were produced from room temperature to the preset temperature. However, shale oils produced at constant temperatures are more representative and can better represent the thermal evolution characteristics compared with the shale oils produced at different final pyrolysis temperatures. Hence, the experimental results obtained in this study are found to be more innovative and provide basic data for the oil shale pyrolysis mechanism and molecular simulations.

2. RESULTS AND DISCUSSION

2.1. Total Number of Neutral Nitrogen and Acidic Species. Acidic and neutral nitrogen species identified in this study mainly include carboxylic acid, phenolic, and pyrrole series compounds. Figure 1 shows the negative-ion ESI FT-ICR MS spectra of Huadian shale oils produced at five different temperatures. The spectra in Figure 1 are very similar, and the molecular weight ranges from 200 to 350 Da. This shows that there is little difference in the number and types of nitrogen and acidic species in shale oils produced at different pyrolysis temperatures. After data analysis, the acidic and neutral nitrogen species mainly include \( \text{N}_1, \text{N}_2, \text{N}_3, \text{N}_4, \text{N}_5, \text{N}_6, \text{N}_7, \text{N}_8, \text{N}_9, \text{O}_1, \text{O}_2, \text{O}_3, \text{O}_4, \text{O}_5, \text{O}_6, \text{O}_7, \text{O}_8, \text{O}_9, \text{O}_{10}, \text{O}_{11}, \) and \( \text{O}_{12} \) species. Among them, \( \text{O}_2 \) species were dominant. All the high peaks in Figure 1 were identified as \( \text{O}_2 \) species. Figure 2 shows the partial enlarged spectra at 250 and 354 \( m/z \). Moreover, the mass spectrum peak identifications of Figure 2 are listed in Table 1. The mass errors of qualitative compounds were less than 0.5 ppm, as shown in Table 1. Table 2 shows the total number of acidic and neutral nitrogen compounds in Huadian shale oils produced at 400, 430, 460, 490, and 520 °C. A total of 2123–2363 heteroatom compounds were identified, not significantly different with the increase of temperature. The number of heteroatom compounds has no obvious change rules with the pyrolysis temperature. However, this is significantly lower than the total number of heteroatom compounds detected by positive-ion ESI FT-ICR MS.\textsuperscript{45}

2.2. Characterization of Neutral Nitrogen Species. Neutral nitrogen species in Huadian shale oils included \( \text{N}_1, \) \( \text{N}_2, \) \( \text{N}_3, \) \( \text{N}_4, \) \( \text{N}_5, \) \( \text{N}_6, \) \( \text{N}_7, \) \( \text{N}_8, \) \( \text{N}_9, \) \( \text{O}_1, \) \( \text{O}_2, \) \( \text{O}_3, \) \( \text{O}_4, \) \( \text{O}_5, \) \( \text{O}_6, \) \( \text{O}_7, \) \( \text{O}_8, \) \( \text{O}_9, \) \( \text{O}_{10}, \) \( \text{O}_{11}, \) and \( \text{O}_{12} \) classes. Figure 3 shows the relative abundance of nitrogen-containing species of shale oils produced at five different pyrolysis temperatures. Furthermore, \( \text{N}_1 \) species were dominant, followed by \( \text{N}_2 \) and \( \text{N}_3 \) species. DBE was used to characterize the degree of unsaturation of polyheteroatom compounds. Figures 4–6 show the isoabundance plots of DBE versus carbon number for \( \text{N}_3, \text{N}_4, \text{N}_5, \text{N}_6, \text{N}_7, \text{N}_8, \text{N}_9, \text{O}_1, \) and \( \text{O}_2 \) classes in shale oils produced at different temperatures. In addition, the relative abundances of \( \text{N}_1, \text{N}_2, \text{N}_3, \text{N}_4, \text{N}_5, \text{N}_6, \text{N}_7, \text{N}_8, \text{N}_9, \text{O}_1, \) and \( \text{O}_2 \) classes were lower than 1%. Figures S1–S4 show the isoabundance plots of DBE versus carbon number for \( \text{N}_1, \text{N}_2, \text{N}_3, \text{N}_4, \text{N}_5, \text{N}_6, \text{N}_7, \text{N}_8, \text{N}_9, \text{O}_1, \) and \( \text{O}_2 \) class species in Huadian shale oils. For \( \text{N}_1 \) species, the nitrogen atom was determined to be a pyrrole in the negative-ion mode.\textsuperscript{35} As shown in Figure 4, the \( \text{N}_1 \) class species in Huadian shale oils were with DBE values of 3–21 and carbon numbers of 9–33. The content of \( \text{N}_1 \) species with DBE values of 9, 12, and 15 was higher, which were more likely carbazole, benzocarbazole, and dibenzocarbazole series of compounds.\textsuperscript{37,46−49} respectively. The \( \text{N}_1 \) class compounds with a DBE value of 12 and carbon numbers of 17, 18, and 19 were dominant, which were \( \text{C}_1 \)-benzocarbazoles, \( \text{C}_2 \)-benzocarbazoles, and \( \text{C}_3 \)-benzocarbazoles, respectively.

As shown in Figure 5, the \( \text{N}_2 \) class species in the shale oil were spread over a wide range of DBE values (4–19) and carbon numbers (9–30). Moreover, for \( \text{N}_3 \) class species, the changes in the DBE value and carbon number with the
increase of pyrolysis temperature were not obvious. The N1O1 species can be divided into three series: DBE of 7 and 10; DBE of 8, 11, 14, and 17; and DBE of 9 and 12. The increment of the three DBE values is characteristic of a condensed aromatic ring. The N1O1 class compounds with a DBE value of 7 were likely a phenol fused with a pyridine core. Furthermore, as shown in Figures 4 and 5, two DBE increments were observed from the N1 species with DBE values of 9, 12, and 15 to the N1O1 species with DBE values of 11, 14, and 17. The DBE value of 2 is exactly the increment of furan core condensation. Therefore, these oxygen atoms were more likely furan cores. The N1O2 species with a DBE value of 8 was likely an indole fused with a furan core. Moreover, the N1O1 class compounds with a DBE value of 9 was likely the cores of species with a DBE value of 8 joined with a bridge bond or a phenol fused with an indole core. The N1O2 species with DBE values of 9 and 12 were dominant as shown in Figures S1, which were two DBE increments than the N1O1 species with DBE values of 7 and 10. The N1O2 species with a DBE value of 9 were likely two phenol cores fused with a pyrrole core or a phenol core fused with a furan core and a pyridine core.

Table 1. Identification of Singly Charged Ions at m/z Values of 250 and 354

| peak no. | formula [M − H]− | observed mass (Da) | theoretical mass (Da) | error (mDa) | error (ppm) |
|---------|------------------|--------------------|-----------------------|-------------|-------------|
| 1       | C15H9N2O2        | 250.07041          | 250.07045             | 0.04        | 0.2         |
| 2       | C16H12N1O2       | 250.08741          | 250.08735             | −0.06       | −0.2        |
| 3       | C17H13O2         | 250.09551          | 250.09548             | −0.03       | −0.1        |
| 4       | C18H14N1O1       | 250.12378          | 250.12374             | −0.04       | −0.2        |
| 5       | C19H15O2         | 250.13189          | 250.13187             | −0.02       | −0.1        |
| 6       | C19H19N1         | 250.16017          | 250.16012             | −0.05       | −0.2        |
| 7       | C20H20N1O1       | 250.18946          | 250.18941             | −0.05       | −0.2        |
| 8       | C21H20O2         | 354.12900          | 354.12883             | −0.17       | −0.5        |
| 9       | C22H20N1O2       | 354.15012          | 354.14995             | −0.17       | −0.5        |
| 10      | C22H20N2O1       | 354.15839          | 354.15851             | 0.12        | 0.3         |
| 11      | C23H21O2         | 354.16848          | 354.16834             | −0.14       | −0.4        |
| 12      | C23H21N1         | 354.22289          | 354.22273             | −0.16       | −0.5        |
| 13      | C24H22N1O1       | 354.28039          | 354.28024             | −0.15       | −0.4        |
| 14      | C25H23O2         | 354.28837          | 354.28839             | 0.02        | 0.1         |
| 15      | C25H23N1         | 354.31677          | 354.31662             | −0.15       | −0.4        |
| 16      | C26H25O2         | 354.34602          | 354.34592             | −0.10       | −0.3        |

Note: the numbers of * symbols indicate the number of isotopic peaks.

Table 2. Total Number of Heteroatom Compounds of Shale Oils Produced at Different Temperatures

| temperature (°C) | N1 | N1O1 | N1O2 | N1O3 | N2 | N2O1 | N2O2 | N3 | N3O1 | O1 | O2 | O3 | O4 | O4S1 | N1S1 | total |
|------------------|----|------|------|------|----|------|------|----|------|----|----|----|----|------|------|-------|
| 400              | 263| 257  | 178  | 99   | 224| 143  | 78   | 76 | 45   | 255| 298| 191| 95 | 108  | 53   | 2363  |
| 430              | 219| 235  | 163  | 88   | 210| 130  | 71   | 71 | 50   | 222| 259| 177| 82 | 86   | 69   | 2132  |
| 460              | 235| 241  | 160  | 100  | 209| 139  | 88   | 74 | 39   | 228| 269| 161| 87 | 91   | 75   | 2196  |
| 490              | 213| 237  | 154  | 96   | 211| 133  | 77   | 73 | 29   | 229| 256| 176| 84 | 96   | 59   | 2123  |
| 520              | 227| 246  | 175  | 110  | 222| 151  | 90   | 92 | 38   | 244| 273| 182| 76 | 101  | 69   | 2296  |
15 is really high. The three DBE increments were for the additional aromatic ring. The \( \text{N}_2 \) species must have at least a pyrrole core. Therefore, the \( \text{N}_2 \) species with a DBE value of 6 were likely a pyrrole core fused with a pyridine core. The relative abundance of \( \text{N}_2 \) class species with a DBE value of 6 decreased with the increase of pyrolysis temperature. Furthermore, the \( \text{N}_2 \) species with a DBE value of 12 were likely two indoles joined by a bridge bond. According to Figure 6, the \( \text{N}_2 \) classes with a DBE value of 12 in all samples were abundant, and the relative abundance advantage was more obvious with the increase of pyrolysis temperature. It can be concluded that under the negative-ion ESI mode, the pyrolysis temperature has an effect on the DBE distribution of \( \text{N}_2 \) class species. Therefore, the DBE distribution of the \( \text{N}_2 \) class species in Huadian oil shale produced at 520 °C was mainly concentrated at 9 and 12. Moreover, a large number of \( \text{N}_2 \) species with DBE values of 7 and 10 were identified. The \( \text{N}_2 \) species with a DBE value of 7 were likely a pyrrole core and a pyridine core joined by a bridge bond. In addition, the relative abundance of \( \text{N}_2 \) species with DBE values of 8, 11, and 14 series was relatively low, especially in Huadian shale oil produced at high temperatures, which were likely an indole and a pyrrole fused with 0–2 aromatic rings.

In the negative-ion ESI mode, many nitrogen-containing species can be ionized; it is difficult to determine their detailed structures directly, especially for \( \text{N}_3 \) and \( \text{N}_3\text{O}_1 \) species. Their structures must have at least one carboxylic acid, phenol, or pyrrole core.

2.3. Characterization of Oxygen- and Sulfur-Containing Compounds. Oxygen- and sulfur-containing species in
Huadian shale oils contain O$_1$, O$_2$, O$_3$, O$_4$, O$_{1S}$, and N$_{1S}$ species. Figure 7 shows the relative abundance of O$_1$, O$_2$, O$_3$, O$_4$, O$_{1S}$, and N$_{1S}$ species of shale oils produced at five different pyrolysis temperatures using negative-ion ESI FT-ICR MS. Figures 8-12 show the isoabundance plots of DBE versus carbon number for O$_1$, O$_2$, O$_3$, O$_4$, O$_{1S}$, and N$_{1S}$ species in Huadian shale oils produced at different temperatures. The oxygen-containing species in this study were mainly O$_1$ and O$_2$ species: phenols and carboxylic acids. Figure 13 shows the DBE distributions of oxygen- and sulfur-containing species identified in Huadian shale oils produced at different temperatures. For O$_2$ species, no compound with a DBE value <4 was found, indicating the absence of alcohols in the samples. However, the relative abundance of O$_1$ species with DBE values of 4, 7, and 10 was relatively high: phenols, naphthols, and anthracenols (phenanthrenols). Furthermore, the O$_1$ species with DBE values of 9 and 12 were likely unsaturated isoprenoid higher phenols. Under the negative-ion ESI mode, O$_2$ species were dominant with the relative abundance ranging from 26.68 to 37.07% in Huadian shale oils produced at five different temperatures, as shown in Figure 7. Furthermore, most of them were carboxylic acids with a DBE value of 1. The relative abundance of carboxylic acids with carbon numbers of 16 and 18 was higher: palmitic acid and stearic acid, respectively. Moreover, the O$_2$ class compounds with carbon numbers of 16 and 18 were also dominant in isoprenoids (DBE = 2): palmitoleic acid and oleic acid, respectively. The C=C bond of palmitoleic acid and oleic acid was between the ninth and tenth carbons (starting with the carboxyl carbon atom). In addition, palmitic acid, stearic acid, palmitoleic acid, and oleic acid are biological markers. Nevertheless, the relative abundance of O$_2$ species with DBE = 6, 9, and 12 was also higher. The O$_2$ species with a DBE of 6 were likely a phenol core fused with a furan core. Furthermore, Orrego-Ruiz and Rojas-Ruiz$^{50}$ concluded that the O$_2$ compounds found in the acidic fraction are confined to DBE <10, while the nonacids to DBE >10. The relative abundance of O$_3$ class compounds with DBE values of 2, 9, 11, and 14 was higher than that of compounds with adjacent DBE values, as shown in Figure 13. The O$_3$ classes with a DBE value of 2 were also likely naphthenic and isoprenoid acids. Nevertheless, the O$_3$ classes with DBE values of 9 and 11 were a furan core fused with two phenol cores and a phenol core fused with two furan cores, respectively. For O$_4$ species in Huadian shale oils produced at different temperatures, the relative abundances were all less than 1%. According to Figure S5, the abundant O$_4$ species in Huadian shale oils have DBE values of 2–16 and carbon numbers of 10–26. It was confirmed that the O$_4$ species with a DBE of 2 were dicarboxylic acids.$^{12}$ Because both phenol and carboxylic acid can be identified, it is difficult to determine the structure of O$_4$ species with higher DBE values. In addition, the selective ionization of ESI may cause errors in the qualitative analysis of polyheteroatom compounds.$^{51,52}$

The relative abundances of O$_{1S}$ and N$_{1S}$ species were very low, less than 1% as shown in Figure 13. For O$_{1S}$ species, the molecular structure has a phenol core. The O$_{1S}$ species with a DBE of 6 were likely a phenol core fused with a thiophene

Figure 6. Isoabundance plots of DBE vs carbon number for N$_{2}$ species.

Figure 7. Relative abundance of oxygen- and sulfur-containing species of shale oils.

O$_{1S}$ and N$_{1S}$ species of shale oils produced at five different pyrolysis temperatures using negative-ion ESI FT-ICR MS. Figures 8-12 show the isoabundance plots of DBE versus carbon number for O$_1$, O$_2$, O$_3$, O$_4$, O$_{1S}$, and N$_{1S}$ species in Huadian shale oils produced at different temperatures. The oxygen-containing species in this study were mainly O$_1$ and O$_2$ species: phenols and carboxylic acids. Figure 13 shows the DBE distributions of oxygen- and sulfur-containing species identified in Huadian shale oil produced at five different temperatures. For O$_2$ species, no compound with a DBE value <4 was found, indicating the absence of alcohols in the samples. However, the relative abundance of O$_1$ species with DBE values of 4, 7, and 10 was relatively high: phenols, naphthols, and anthracenols (phenanthrenols). Furthermore, the O$_1$ species with DBE values of 9 and 12 were likely unsaturated isoprenoid higher phenols. Under the negative-ion ESI mode, O$_2$ species were dominant with the relative abundance ranging from 26.68 to 37.07% in Huadian shale oils produced at five different temperatures, as shown in Figure 7. Furthermore, most of them were carboxylic acids with a DBE value of 1. The relative abundance of carboxylic acids with carbon numbers of 16 and 18 was higher: palmitic acid and stearic acid, respectively. Moreover, the O$_2$ class compounds with carbon numbers of 16 and 18 were also dominant in isoprenoids (DBE = 2): palmitoleic acid and oleic acid, respectively. The C=C bond of palmitoleic acid and oleic acid was between the ninth and tenth carbons (starting with the carboxyl carbon atom). In addition, palmitic acid, stearic acid, palmitoleic acid, and oleic acid are biological markers. Nevertheless, the relative abundance of O$_2$ species with DBE = 6, 9, and 12 was also higher. The O$_2$ species with a DBE of 6 were likely a phenol core fused with a furan core. Furthermore, Orrego-Ruiz and Rojas-Ruiz$^{50}$ concluded that the O$_2$ compounds found in the acidic fraction are confined to DBE <10, while the nonacids to DBE >10. The relative abundance of O$_3$ class compounds with DBE values of 2, 9, 11, and 14 was higher than that of compounds with adjacent DBE values, as shown in Figure 13. The O$_3$ classes with a DBE value of 2 were also likely naphthenic and isoprenoid acids. Nevertheless, the O$_3$ classes with DBE values of 9 and 11 were a furan core fused with two phenol cores and a phenol core fused with two furan cores, respectively. For O$_4$ species in Huadian shale oils produced at different temperatures, the relative abundances were all less than 1%. According to Figure S5, the abundant O$_4$ species in Huadian shale oil have DBE values of 2–16 and carbon numbers of 10–26. It was confirmed that the O$_4$ species with a DBE of 2 were dicarboxylic acids.$^{12}$ Because both phenol and carboxylic acid can be identified, it is difficult to determine the structure of O$_4$ species with higher DBE values. In addition, the selective ionization of ESI may cause errors in the qualitative analysis of polyheteroatom compounds.$^{51,52}$

The relative abundances of O$_{1S}$ and N$_{1S}$ species were very low, less than 1% as shown in Figure 13. For O$_{1S}$ species, the molecular structure has a phenol core. The O$_{1S}$ species with a DBE of 6 were likely a phenol core fused with a thiophene
core. In addition, the O1S1 species with a DBE of 9 were dominant in sulfur-containing species, likely a naphthol core fused with a thiophene core. For N1S1 species, a pyrrole core must be present in the molecular structure. Two DBE increments were observed from the N1 species with DBE values of 9 and 12 to N1S1 species with DBE values of 11 and 14. Hence, the sulfur atoms in N1S1 are mainly present in thiophene cores.

2.4. Effect of Pyrolysis Temperature on Molecular Composition. As shown in Figure 3, with the increase of the pyrolysis temperature, the content of N1 species increased first, then decreased, and reached the highest at 460 °C. However, the relative abundance of N1O1, N1O2, and N1O3 species first decreased and then increased with increasing pyrolysis temperature and reached the highest at 520 °C. Moreover, the content of N2, N3O2, N3O3, and N3 classes also reached their maximum at 520 °C, indicating that the increase in the pyrolysis temperature is beneficial to the formation of neutral nitrogen species with polyheteroatoms. Generally, the effect of pyrolysis temperature on the composition and structure of shale oil is mainly reflected in two aspects: (i) different pyrolysis temperatures lead to different molecular fragments cleaved from kerogen macromolecules and (ii) a higher pyrolysis temperature leads to the secondary reaction of pyrolysis products. Nevertheless, the secondary reaction during oil shale pyrolysis is complex where both cracking and polymerization reactions (aromatization reaction) occur simultaneously. For the pyrolysis of coal, Xu et al. and Shi et al. suggested that the cleavage of Cal−Cal, Cal−H, and Car−N bonds occurs at a pyrolysis temperature of 428 °C and
the cleavage of the Ca–O bond occurs at 350 °C. However, the cleavage of C_ar–Ca, C_ar–O, and C_ar–S occurs at a pyrolysis temperature of >500 °C. The ring-opening reaction of aromatic and heteroatomic aromatic rings (furan, pyridine, pyrrole, and thiophene rings) occurs at a higher temperature. Nevertheless, compared with the ring-opening reaction during pyrolysis, the polymerization reaction occurs more easily. For example, alkylbenzene reacts with acetylene to form naphthalene.56−58 Dong et al.59 studied the formation of polycyclic aromatic hydrocarbons (PAHs) during the coal pyrolysis at a pyrolysis temperature ranging from 400 to 1300 °C. With the increase in the pyrolysis temperature, the content of PAHs increased first and then decreased, reaching the maximum at 800 °C. Hou et al.60 reported that the content of thiophene-type sulfur and pyrrole-type nitrogen in coal semicoke increased with the increase in the pyrolysis temperature from 300 to 700 °C. However, the content of pyridine-type nitrogen decreased. The results indicate that the relative content of pyrolysis products with aromatic rings, thiophene, and pyrrole cores increases with the increase in the pyrolysis temperature in a certain temperature range. For the pyrolysis of Huadian oil shale in this study, because of the effect of polymerization reaction, the content of nitrogen-containing compounds with pyrrole cores increased with the increase in pyrolysis temperature. The relative abundance of N1O1, N1O2, N1O3, N2, N2O1, and O3 species was the highest in the Huadian shale oil produced at 520 °C. Similarly, the polymerization reaction also increased the content of thiophene compounds in pyrolysis products, resulting in the highest relative abundances of O1S1 and N1S1 classes in the oil sample obtained at 520 °C.
Moreover, the relative abundance of O1 species in shale oils produced at 490 and 520 °C was higher, as shown in Figure 7. The O1 species in shale oils were monophenolic compounds. However, with the increase of pyrolysis temperature, it is interesting that the relative abundance of O2 and O4 species decreased obviously. Furthermore, the decrease in the relative abundance of O2 species was mainly attributed to the decrease in carboxylic acid with a DBE of 1, as shown in Figure 13. Because of the cracking reaction, the cleavage of the Cα−O bond occurs at higher temperatures. However, the oxygen atoms in O2 classes with DBE values of 9 and 12 were mainly present in furan and phenol cores. Hence, because of the polymerization reaction, their relative abundances were higher at a pyrolysis temperature of 520 °C than those at other temperatures.

In addition, different boiling points of pyrolysis products can also affect the compound distribution. Under negative-ion ESI FT-ICR MS, considering the boiling points of pyrolysis products and the secondary reaction, the effect of pyrolysis temperature on the molecular composition of neutral nitrogen and acidic species is complex. Still, characteristic rules are followed.

3. CONCLUSIONS

The composition analysis of Huadian shale oil produced at five different temperatures by negative-ion ESI FT-ICR MS was conducted in this study. The results show valuable information about the molecular composition of heteroatom species in shale oil. The probable heteroatom core structures are suggested based on the DBE values. The effect of pyrolysis temperature on the distribution of acidic and neutral nitrogen
compounds in shale oil was analyzed. The conclusions are as follows:

(1) The content of N1 species first increased and then decreased with increasing pyrolysis temperature and reached the highest at 460 °C. The relative abundance of N1O2, N1O3, N2O, N2, N2O3, N2O4, and N3 species is the highest in shale oil produced at 520 °C, indicating that an increase in the pyrolysis temperature is beneficial for the formation of nitrogen-containing compounds with polyheteroatoms.

(2) A higher pyrolysis temperature makes pyrolysis products more likely to polymerize into aromatic rings and N-, O-, and S-heteroatom aromatic molecules except pyridines. This varies the relative abundances of N1O1, N1O2, N1O3, N2, N2O1, O1, and O3 species in the Huadian shale oil produced at 490 and 520 °C. Similarly, the polymerization reaction also increased the content of thiophene compounds in pyrolysis products, resulting in the highest relative abundances of O3S3 and N3S3 of S-heteroatom compounds in shale oil obtained at 520 °C.

(3) Because of the cracking reaction, the cleavage of the C3O bond occurs at higher temperatures. The relative abundance of O2 and O4 species decreased with the increase of the pyrolysis temperature. This can be mainly attributed to the decrease in carboxylic acid with a DBE of 1. Because of the polymerization reaction, the content of O5 species with DBE values of 9 and 12 is higher at a pyrolysis temperature of 520 °C than that at other temperatures.

(4) The secondary reaction during oil shale pyrolysis is complex; both cracking and polymerization reactions occur simultaneously. Considering the boiling points of pyrolysis products and the secondary reaction, the effect of pyrolysis temperature on the molecular composition of acidic and neutral nitrogen species is complex. Still, characteristic rules are followed.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials and Pyrolysis Experiment

A crushed Huadian oil shale sample with <6 mm size was selected for the pyrolysis experiment. The oil shale pyrolysis experiment was carried out using a self-made vertical fixed-bed pyrolysis unit equipped with a temperature control device. Electric heating was the heating mode of the pyrolysis unit. Oil shale was heated at a rate of 10 °C/min from room temperature. When the temperature increased to 400 °C, it was maintained at this temperature for 20 min, and the liquid products produced by pyrolysis were collected by condensation of an ice–water mixture at the same time. The heating process was continued after 20 min. The liquid products produced by pyrolysis at different temperatures were collected using the same method when the temperatures reached 430, 460, 490, and 520 °C.

Then, the liquid products produced at different temperatures were centrifuged to reduce moisture. The shale oils were stored in a refrigerator at −4 °C for further analysis. Moreover, the ultimate analysis of shale oils by pyrolysis at different temperatures is shown in Table 3.

#### 4.2. Negative-Ion ESI FT-ICR MS Analysis

The instrument used in the experiment was an Apex-Ultra FT-ICR mass spectrometer of Bruker Daltonics, USA, equipped with an Agilent ESI source. The shale oils produced at different constant temperatures were dissolved in toluene to prepare 10 mg/mL sample solutions. Then, 20 μL of sample solution was diluted to 0.2 mg/mL concentration with methanol/toluene (3:1 v/v). Next, 15 ml of ammonia water was added to promote the production of [M − H]- ions, and the mixture was made homogeneous by gentle shaking. The inlet flow rate was 180 μL/h. The capillary voltages of the outlet and the inlet were set to 320 and 4000 V, respectively. Furthermore, the ion accumulation time in the collision cell was 0.5 s. Furthermore, the ion extraction time was 0.9 ms. The radio-frequency excitation was attenuated at 15 dB. In addition, the excited ions’ mass range is from 124 to 800 Da in this study.

#### 4.3. Data Analysis

Mass spectrum peaks with relative abundance of higher than 5 times the signal-to-noise ratio were exported. The data analysis work was performed using custom software. The species with the same class of heteroatom compounds and isotopes with different values obtained from the DBE value and carbon numbers were searched within ±0.0015 Kendrick mass defect tolerance.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03198.

Isoabundance plots of DBE versus carbon number for N1O2, N1O3, N2O, N2O3, N3O2, and O1 species (PDF)

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Notes
The authors declare no competing financial interest.

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