Analysis of Distribution and Structures of Heteroatom Compounds in Asphaltene of Medium/Low Temperature Coal Tar by Negative Anion Mode ESI FT-ICR MS

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Abstract: The existence of heteroatomic compounds with complex structure and different polarity in the asphaltene of medium and low temperature coal tar (M/LTCT) limits its processing and utilization. Combined with negative ion electrospray ionization source (ESI), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was used to characterize the molecular composition of O, N, and S heteroatom compounds in M/LTCT asphaltenes. Acidic oxygen-containing compounds (OCCs) and non-basic nitrogen-containing compounds (NCCs) in asphaltenes were identified, except for sulfur-containing compounds (SCCs). The mass spectra showed that the heteroatom compounds in asphaltene mainly existed as \( X_1 O_X \), \( N_1 O_X \), \( S_1 O_X \), \( N_2 O_X \), \( N_3 O_X \), \( N_4 O_X \), \( N_5 O_X \), \( N_6 O_X \), and \( O_X \) class species (where \( x = 1–6 \)). The M/LTCT asphaltenes were enriched with \( O_X \), \( N_4 \), and \( N_1 O_1 \) class species. The core structure of \( O_X \) class species were likely to be composed of 1–7 aromatic rings with 4 phenolic hydroxyl groups, the core structure of \( N_4 \) class species were likely to be comprised of 4–7 aromatic rings with a piperazine ring and a pyrazole ring, and the core structure of \( N_1 O_1 \) was mainly 3–6 aromatic rings with a phenolic hydroxyl group and a pyrrole ring. These results suggest that more condensed NCCs and OCCs with short, substituted alky side chains are presented, which are more easily to undergo condensation to generate fused molecules, making it too difficult to be removed by hydrogenation. Through the analysis of the molecular structures of OCCs and non-basic NCCs in M/LTCT asphaltenes, important information about the molecular composition can be obtained, which can provide basic data for the hydrogenation of deasphaltene.

Keywords: M/LTCT asphaltenes; heteroatom compounds; negative ESI FT-ICR MS; core structure

1. Introduction

Medium and low temperature coal tar (M/LTCT) is a liquid by-product obtained from coal gasification, low-cohesive coal (lignite, bituminous coal, long flame coal, etc.) and dry distillation at a temperature below 600 °C. The daily output of M/LTCT has reached thousands of tons. As a suitable raw material for producing traditional liquid fuels (such as gasoline and diesel) with ultra-low heteroatom content through M/LTCT hydrogenation, it has received extensive attention in China [1]. Currently, two main types of M/LTCT HDT processing methods, i.e., the whole fraction and distillate fraction (<360 °C) fixed bed HDT processes, are used to produce gasoline and diesel. The world’s first whole fraction M/LTCT hydrogenation technology to produce clean fuel oil has been successfully applied in Shennu Fuyou Co., Ltd. in Yulin, China [2], which means that a large amount of asphaltenes have no choice but to enter the reactor to be processed.

As we all know, asphaltenes refer to carbonaceous resources that are insoluble in normal alkanes, but soluble in aromatics [3–5]. Asphaltenes are the most complex and
refractory components in M/LTCT, which account for 15–30 wt% [6]. The structure of M/LTCT asphaltenes is believed to be some fused aromatic ring, with several naphthenic and alkyl side chains, and it also contains amounts of sulfur, nitrogen, oxygen, and various metal heteroatom compounds [7]. The heteroatom compounds in asphaltenes are closely related to the operational problems in upstream and downstream M/LTCT processing. For instance, heteroatom compounds are relatively enriched in asphaltene. Aggregation are likely driven by polar heteroatom interactions, resulting in the instability of the M/LTCT processing system. Moreover, these heteroatom compounds will cause serious deactivation of the catalyst during the hydrogenation, and the remaining trace heteroatom compounds will reduce the stability of the products [8,9]. Therefore, the problem caused by asphaltenes in the hydrogenation of M/LTCT has attracted the attention of many researchers, who hope to reveal the structure and properties of asphaltenes through various characterization methods.

The characterization of asphaltenes is necessary for the formation of M/LTCT processing strategies. Recently, various analytical methods, such as nuclear magnetic resonance (NMR) [10], Fourier transform infrared (FTIR) spectroscopy [11,12], and X-ray photoelectron spectroscopy (XPS) [13], have been applied to successfully identify the heteroatom compounds from a macroscopic perspective. Compared with petroleum asphaltenes, M/LTCT asphaltenes were found to have the following characteristics: (1) A smaller relative molecular mass and higher aromaticity. (2) The chemical structure is mainly composed of fused ring aromatic hydrocarbons with a shorter alkyl side chain and rich in heteroatom functional groups. (3) The heteroatoms are mainly oxygen atoms, with fewer nitrogen and sulfur atoms. The oxygen-containing functional groups are mainly phenolic hydroxyl groups and ether oxygen bonds groups, the nitrogen-containing functional groups are mainly pyridine, pyrrole, and amines, and the sulfur-containing functional groups are mainly thiophene and sulfoxide. Recently, researchers also have been attempting to correlate chemical properties and behavior to the molecular composition of asphaltenes. Combined with various ionization techniques, such as electrospray ionization (ESI) [14], field desorption/ionization (FD/FI) [15,16], electron ionization (EI) [17], and atmospheric pressure photoionization (APPI) [18], Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been proven to efficiently reveal the composition of heteroatom-containing compounds in petroleum at the molecular level [19,20]. Among these ionization sources, electrospray ionization (ESI) is more convenient in use, and can highly selectively ionize N, S, and O heteroatom compounds with polarity [21]. Simultaneously, negative-electron ESI coupled with FT-ICR MS can also precisely determine the detailed molecular composition and distribution of acidic OCCs [22,23] and non-basic NCCs [24–26] in crude oils and sand oils asphaltenes.

The acidic OCCs in asphaltenes can not only cause corrosion [27] but also lead to fuel instability and reduction of the combustion performance [2]. Wang et al. [21] indicated that the acidic OCCs, such as O_2, O_2S, O_2S_2, O_3, and O_4, show high relative abundance (RA) in the asphaltenes of Venezuelan crude oil, of which the most abundant O_2 class species are mainly naphthenic acid compounds by negative-electron FT-ICR MS analysis. Zhang et al. [10] characterized the C_5 asphaltene of LTCT in Yulin, Shaanxi, by negative-electron FT-ICR MS and revealed that the predominant species was the O_2 class species, which mainly distributed the DBE (double bond equivalents) of 7–26 and carbon numbers of 14–36. The core structure of the O_2 class species was mainly dihydric phenolic OCCs with 2–8 aromatic rings. It showed that, in negative ion mode, the type and distribution of acidic OCCs in different asphaltenes are various.

Non-basic NCCs are more difficult to remove than basic NCCs. In the process of hydrodenitrogenation, non-basic NCCs are first converted to basic NCCs and then can be removed [28]. In addition, NCCs can promote the formation of deposits in fuel oil and increase its instability during storage [29,30]. Xu et al. [31] found that the relative abundance of the non-basic N_1 class species was relatively high, which may have been carbazole compounds, mainly distributed with the DBE of 14–24 and the carbon numbers
of 21–49 in Sudan vacuum residue C7 asphaltenes by negative ESI FT-ICR MS mode. Shi et al. [32] showed that non-basic NCCs in asphaltenes of crude oil were mainly present as N1, N1O1, and N1O2 class species, and among them, the most abundant N1 class species were mainly distributed at the DBE values of 9–23 and carbon numbers of 15–50. The core structure was mainly pyrrole derivatives with 2–8 aromatic rings. Wang et al. [33] believed that the non-basic NCCs in Canadian oil sands asphaltenes mainly existed as N1 species, and these compounds were mainly distributed with DBE of 10–19 and carbon numbers of 16–50, and the core structure was mainly pyrrole compounds with low condensation. It shows that, in the negative ion mode, the non-basic nitrogen class species in petroleum and oil sand asphaltenes mainly existed as an N1 class species, and these compounds are considered to be pyrrole and carbazole species.

As mentioned above [28–30], the acidic OCCs and non-basic NCCs in M/LTCT asphaltenes will cause a large number of operation and transportation problems, which are also detrimental to the quality of the products. Recently, the characterization of petroleum asphaltenes from different regions shows that the OCCs, NCCs, and SCCs are also quite different. In addition, previous studies have shown that M/LTCT has relatively higher aromaticity and content of polar heteroatom compounds, which is conductive to condensation. Recently, the research on the molecular composition and distribution of OCCs, NCCs, and SCCs in M/LTCT asphaltenes has not been received as much attention, which will hinder the further understanding of the inherent characteristics for M/LTCT asphaltenes.

In this work, negative ion ESI FT-ICR MS was used to explore the occurrence and molecular composition of OCCs, NCCs, and SCCs in M/LTCT asphaltenes, including the RA distribution of heteroatom, DBE, and carbon number distributions. This work will be helpful and necessary for further research on the conversion mechanisms of S, N, and O heteroatom compounds in the process of M/LTCT hydrogenation.

2. Experimental Section

2.1. Precipitation of Asphaltenes

The raw material (whole fraction M/LTCT), provided by a coking enterprise in northern Shaanxi, was produced by pyrolysis of low-rank coal in an internal heating vertical furnace (the dry distillation temperature 400~600 °C). The specific steps for the precipitation of asphaltenes are as follows [8]: A certain amount of M/LTCT and n-heptane (50 mL per gram of coal tar sample) were mixed in a flat-bottomed flask, heated to reflux for 0.5 h, kept standing for 1 h in the dark, and then filtered with a filter paper to obtain the insoluble materials, which remained in the filtrate for about 1 h, until the reflux turned colorless, and then dissolved with toluene in an Erlenmeyer flask. At last, the asphaltenes were obtained after the solvents were driven out with rotary evaporator and vacuum oven (temperature 110 °C, vacuum degree 93 KPa, 1 h) and cooled to ambient temperature. The toluene and n-heptane used were analytical reagent grade solvents. Table 1 lists the properties of M/LTCT and precipitated asphaltenes. The data shows that the contents of N, S, and O in M/LTCT asphaltenes was significantly higher than that of M/LTCT, illustrating that heteroatom-containing compounds tended to be enriched in precipitated asphaltenes.

| Properties | M/LTCT | M/LTCT Asphaltenes |
|------------|--------|-------------------|
| Element analysis/% |
| C         | 81.46  | 81.72             |
| H         | 8.61   | 5.68              |
| N         | 1.26   | 2.33              |
| S         | 0.34   | 1.86              |
| O         | 8.03   | 8.92              |
| H/C atomic ratio | 1.268 | 0.818             |
| Density (20 °C)/g·cm⁻³ | 1.041 | -                 |
| M_w       | 420    | 663               |
2.2. Analytical Methods
2.2.1. Elemental Analysis

The contents of C, H, S, and N in asphaltene samples was analyzed by using a Vario MicroCube elemental analyzer from Elementar, Germany, and the content of O was calculated by differential subtraction. The combustion tube temperature was 1150 °C, and complete decomposition by high temperature combustion was used with a deviation of less than 0.1% and a repeat measurement error of less than 1%.

2.2.2. Relative Molecular Mass Analysis

The average relative molecular mass of the actual asphaltenes was determined using a high temperature gel permeation chromatograph (PL-GPC 220) from Agilent, Santa Clara, CA, USA. Tetrahydrofuran (THF) was used as the solvent, with a flow rate of 0.6 mL/min, an injection volume of 10 µL, and a column temperature of 40 °C.

2.2.3. ESI FT-ICR MS

The ESI source worked in negative ion mode. A certain amount of M/LTCT asphaltene samples were dissolved with toluene into a 10 mg/mL solution, then diluted to 0.2 mg/mL with toluene/methanol (1:3) mixture, and 15 µL of NH₄OH (20~30%) was added to promote the deprotonation of the compound. Finally, the prepared solution was injected into the ESI source at a rate of 150 µL/h by using a syringe pump. The asphaltenes were analyzed using Apex-ultra mass spectrometer FT-ICR MS (Bruker Company, Billerica, MA, USA), which was equipped with a 9.4T superconducting magnet (operating at 9.0 T) [32]. The operating procedure for negative-ion ESI FT-ICRMS has been described elsewhere [21,32,34]. The methods of FT-ICR MS quality calibration and data processing procedure have been described elsewhere [35,36].

2.3. Data Analysis Procedure

Since the information obtained by FT ICR MS was quite abundant, it was necessary to properly process and classify the data. In order to identify the homologous series (compounds with the same heteroatom composition and the same number of rings and double bonds, but a different number of CH₂ groups) in the sample, the measured mass was converted from International Union of Pure and Applied Chemistry (IUPAC) mass to Kendrick mass (KM), thereby the Kendrick mass differences (KMDs) were derived from the following formulas [37,38].

\[ KM = M \times \left(14.0000/14.0156\right) \quad (1) \]

\[ KMD = \left(INT(KM) - KM\right) \times 1000 \quad (2) \]

M represents IUPAC mass, INT(KM) is the integer closest to KM.

Homologous series have the same KMD and same core structural, but have different CH₂ numbers, or rather to say, the same type of compounds with different substituents have the same KMD value. According to the value of KMD, the types of compounds can be quickly and accurately distinguished, which was conducive to programmatic processing of data [39].

DBE was the number of double bonds in each molecular structure plus the number of rings, indicating the degree of condensation of the molecule. The DBE value can be directly derived from the general formula \( C_c H_h N_n O_o S_s \), \( DBE = c - h/2 + n/2 + 1 \), where \( c, h, \) and \( n \) were the number of carbon, hydrogen, and nitrogen atoms [40–42]. Carbon number\( (c) \) played a role in the characterization of degree of alkyl substitution.

3. Results and Discussions
3.1. Negative Ion ESI FT-ICR Mass Spectra

The mass spectrum of FT-ICR MS contains abundant molecular composition information. In the negative-ion ESI mode, the broadband mass spectrum of M/LTCT asphaltene
is shown in Figure 1. The value of m/z on the abscissa can directly reflect the relative molecular mass of asphaltenes, and the intensity value on the ordinate represents the relative mass fraction. In Figure 1, it appears that the molecular weight distribution of M/LTCT asphaltenes was relatively wide, mainly concentrated between 200 and 750 Da. After the partial enlargement, it can be seen that there were multiple mass spectrum peaks at m/z = 332 Da. The identified compounds with relatively high mass spectrometry peaks of mass spectra at m/z = 332 are listed in Table 2.

### Figure 1. Mass spectra of the M/LTCT asphaltenes. The narrow segment of mass spectra at 332 Da.

| NO   | Formula [M + H]⁻ | Theoretical Mass (Da) | Measured Mass (Da) | Error (m/z) | Resolving Power |
|------|------------------|-----------------------|--------------------|-------------|-----------------|
| N₁O₁ | C₂₂H₃₆N₁O₁      | 332.1465              | 332.1363           | 0.0102      | 132,193         |
| O₁   | C₂₁H₂₃O₄        | 332.3495              | 332.2229           | 0.1266      | 126,027         |
| N₂O₂ | C₂₀H₃₂N₂O₂      | 332.4932              | 332.4841           | 0.0091      | 121,912         |
| N₁O₂ | C₂₁H₃₂N₁O₂      | 332.6737              | 332.6715           | 0.0022      | 134,457         |

#### 3.2. Heteroatom-Containing Compounds Distribution

In order to describe the distinct in molecular composition, all identified mass spectrum peaks were classified according to the heteroatom type, and the relative abundance (RA) of each class was defined as the magnitude of each peak divided by the sum of the magnitudes of all identified peaks (excluding the isotopic peaks) in the mass spectrum. In the negative ESI mode, the RA map of various acidic and non-basic species in the M/LTCT asphaltenes identified were shown in Figure 2. It can be seen that the heteroatom compounds in asphaltenes mainly existed as Oₓ, Nₓ, N₁Oₓ, N₂Oₓ, N₃Oₓ, N₄Oₓ, N₅Oₓ, and N₆Oₓ class species (x = 1–6).

Figure 2 shows that Oₓ class species were the predominant species, due to the high oxygen content of M/LTCT, which was consistent with the results found in other studies [8,38]. In addition, the Nₓ class species have lower ionization efficiency, due to their weak acidity [43]. The Oₓ compounds existed mainly in the O₂, O₃, and O₄ class species. Of these, the O₄ class species accounted for 11.19%, which seems much higher than that of any other acidic and non-basic class species, indicating that they have the strongest response to ion sources. Nₓ compounds in asphaltenes mainly existed in the form of N₁, N₂, N₃, and N₄ class species. Relative to the O₄ class species, the RA of N₄ class species was much lower, but it was still the most abundant of all non-basic nitrogen species. Of these multi-heteroatom (N₁Oₓ, N₂Oₓ, N₃Oₓ, N₄Oₓ, N₅Oₓ, and N₆Oₓ), N₁O₁ was the predominant class species, followed by N₂O₁, N₃O₂, and N₄O₃, which have an extremely lower RA, accounting for about 2.20%, 2.06%, 1.85%, and 1.49%, respectively. The RA of the N₁O₁ species was approximately equal to that of the N₁ species.
Compared to the dominant O\textsubscript{2} and N\textsubscript{1} class species in oil sand asphaltenes [31], O\textsubscript{4} and N\textsubscript{4} species are the most abundant species in M/LTCT asphaltenes. No sulfur-containing heteroatom species, (such as the N\textsubscript{1}S\textsubscript{1}, N\textsubscript{1}O\textsubscript{1}S\textsubscript{1}, O\textsubscript{2}S\textsubscript{1}, and O\textsubscript{2}S\textsubscript{2} class species) were identified in the M/LTCT asphaltenes. There are supposed to be two reasons. For one, the concentration of sulfur compounds in M/LTCT asphaltenes is much lower than that of oil sand. For another reason, the negative ion ESI cannot directly ionize the sulfur-containing functional groups, and the non-basic nitrogen or acidic oxygen-containing compounds that can be ionized in the asphaltenes do not contain sulfur heteroatom. This conclusion is similar to the results reported in the literature [31].

3.3. The Molecular Structure of Heteroatom-Containing Compounds

Although the accurate molecular mass value allows for unique elemental formulas to be assigned to each peak in the mass spectrum, it does not provide the molecular structures of each species. Combined with the molecular element composition determined by FT ICR MS, the iso-abundance point coding map was constructed, and the DBE and carbon number distribution of various species in asphaltenes were investigated. Based on the DBE value and carbon number, the molecular structure of the compounds can be inferred.

3.3.1. O\textsubscript{x}(x = 2–4) Class Species in M/LTCT Asphaltenes

Previous studies [44–46] believed that the oxygen atoms in the M/LTCT asphaltenes mainly existed in the form of single-bonded oxygen (such as C-OH, Ar-OH, and C-O-C) and double-bonded (ketones and carboxylic acid) oxygen by XPS and FT-IR analysis. Of these, acidic OCCs are phenols and carboxylic compounds. Therefore, in the negative ion mode, the identified OCCs should be phenol hydroxyl and carboxylic acid compounds.

O\textsubscript{2} Class Species

As described in Figure 3b, O\textsubscript{2} species in asphaltenes have a relatively narrow distribution range centered at DBE values of 6–14 and carbon numbers of 17–25. The O\textsubscript{2} species with a DBE value of 8 might be a naphthalene combined with a naphthenic ring, two phenolic hydroxyl groups or acenaphthene with two phenolic hydroxyl groups, or one naphthalene with a carboxyl group. The species with a DBE value of 12 were suspected of pyrene with two phenolic hydroxyl groups, fluoranthene with two phenolic hydroxyl groups, or benzofluorene with two phenolic hydroxyl groups were also suspected of phenanthrene plus a naphthenic ring with a carboxyl group or anthracene plus a naphthenic ring with a carboxyl group. Therefore, the O\textsubscript{2} species might be highly condensed aromatic acids phenols. The possible core structure of the acidic O\textsubscript{2} species are 0–6 aromatic rings with a carboxylic group or 0–6 aromatic rings with two phenolic hydroxyl groups.
As described in Figure 3a, O4 species in asphaltenes have the highest RA, mainly centered at DBE values of 6–14 and carbon numbers of 17–25. The O2 species were concentrated at DBE of 7–27 and carbon numbers of 14–27. Among them, species with DBE of 10 have the highest relative abundance (as shown in Figure 3a), which have a formula of C16H13O3, were suspected of a core structure of phenanthrene with three carboxyl groups or anthracene with three carboxyl groups. The O3 species with a DBE value of 13 were likely to be a pyrene plus a naphthenic ring with three phenolic hydroxyl groups. The O3 species with a DBE value of 15 were likely to be benzopyrene with three phenolic hydroxyl groups or triphenylene plus a naphthenic ring with a carboxyl group and a phenolic hydroxyl group. The DBE value of the O3 species was higher than the O2 species, thus most additional oxygen atoms should have an aromatic ring with a carboxylic group and a phenolic hydroxyl. The O3 species with a DBE value of 14 were suspected to be a pyrene plus two naphthenic rings with three phenolic hydroxyl groups. The O3 species with a DBE value of 15 were likely to be benzopyrene triphenols compounds. Therefore, the core structure of the O3 class species was higher RA in O2, O3, and O4 class species.

According to Figure 3b, the O3 species were concentrated at DBE of 7–27 and carbon numbers of 14–27. Among them, species with DBE of 10 have the highest relative abundance (as shown in Figure 3a), which have a formula of C16H13O3, were suspected of a core structure of phenanthrene with three carboxyl groups or anthracene with three carboxyl groups. The O3 species with a DBE value of 13 were likely to be a pyrene plus a naphthenic ring with three phenolic hydroxyl groups or a fluoranthene plus a naphthenic ring with three phenolic hydroxyl groups. The O3 species with a DBE value of 15 were likely to be a pyrene with a phenolic hydroxyl group and a carboxyl group or a fluoranthene with a phenolic hydroxyl group and a carboxyl group. The O3 species with a DBE value of 16, 17, and O4 class species...
14 were suspected to be a pyrene plus two naphthenic rings with three phenolic hydroxyl groups, a fluoranthene plus two naphthenic ring with three phenolic hydroxyl groups, or chrysene plus one naphthenic ring with three phenolic hydroxyl groups were also likely to be a pyrene plus a naphthenic ring with a phenolic hydroxyl group and a carboxylic acid group, a fluoranthene plus a naphthenic ring with a carboxylic acid group and a phenolic hydroxyl group, or chrysene with a carboxylic acid group and a phenolic hydroxyl group. The O3 species with a DBE value of 15 were suspected of a core structure of benzopyrene with three phenolic hydroxyl groups or triphenylene plus a naphthenic ring with a carboxyl group and a phenolic hydroxyl group. The DBE value of the O3 species was higher than the O2 species, thus most additional oxygen atoms should have an aromatic group. Therefore, the possible core structure of the acidic O3 species were mainly composed of 2–6 aromatic rings with three phenolic hydroxyl groups or 2–6 aromatic rings with a carboxylic group and a phenolic hydroxyl.

O4 Class Species

As described in Figure 3c, O4 species in asphaltenes have the highest RA, mainly centered at a DBE of 4–15 and carbon numbers of 12–27. Previous studies [22] have shown that O2 class monomers will form O4 molecular aggregates with double DBE values and carbon number when the oil sample concentration is too high. However, the carbon number distribution range shows that O4 species were monomers. There are few O4 species with a DBE value of 0, indicating that there were only a small amount of tetrahydric alcohol compounds. The O4 species with a DBE value of 8 were likely to be acenaphthylene tetraphenols compounds. The O4 species with a DBE value of 12 were likely to be pyrene tetraphenols or fluoranthene tetraphenols. The O4 species with a DBE value of 15 were likely to be benzopyrene tetr phenols compounds. Therefore, the core structure of the acidic O4 species were suspected of 0–6 aromatic rings with four phenolic hydroxyl groups.

Different from that of the oxygen-containing species in other asphaltenes (as shown in Table 3), the O4 species dominated in the M/LTCT asphaltenes, and they were likely quaternary phenolic OCCs with a relatively higher DBE values and smaller carbon numbers, while the O2 naphthenic acids species dominated in sand oil asphaltenes with a lower DBE value. Obviously, the O4 phenolic OCCs have a high condensed structure with either additional short or multi-substituted alkyl side chains, which were difficult to remove by hydrogenation, in comparison to the O2 naphthenic acid compounds. In addition, the presence of a large amount of phenolic compounds adversely affected high-quality diesel products through M/LTCT hydrogenation [47].

Table 3. Main oxygen-containing heteroatom species in asphaltenes of different raw material.

| Feed                  | Most Abundant Oxygen Species | DBE Center | Carbon Numbers Center | Possible Core Structure               |
|-----------------------|-----------------------------|------------|-----------------------|--------------------------------------|
| The present work      | M/LTCT asphaltenes          | O4         | 4–15                  | Quaternary phenolic hydroxyl          |
| Wang et al. [33]      | Oil sands bitumen asphaltenes | O2         | 3–5                   | Naphthenic acid                       |
| Xu et al. [31]        | Sudan sand oil asphaltenes  | O2         | 0–8                   | Naphthenic acid                       |
| Shi et al. [32]       | Crude Oil asphaltenes       | O1         | 4–6                   | Phenolic hydroxyl                     |

3.3.2. Distribution of N_X Class Species

N1 class species. Among all non-basic N1 species, pyrrole and its derivatives are typical NCCs that can be effectively ionized in negative ion mode, which has been confirmed in other reports [32,43,48]. In addition, the GC-MS results also showed that indole and carbazole are the main components of non-basic NCCs in coal tar [3,8]. As described in Figure 4b, the N1 species are concentrated at DBE of 15–21 and carbon numbers of 27–37. Among them, the compounds of C_{36}H_{39}N_{1} with a DBE value of 18 have the highest RA.
(as shown in Figure 4a). The compounds were suspected of a benzopyrene combined with two naphthenic rings and a pyrrole ring or benzonaphthocarbazoles. The N1 species with a DBE value of 19 were likely to be dibenzopyrene with a pyrrole ring. The N1 species with the DBE values of 20 might have been a dibenzopyrene plus a naphthenic ring and a pyrrole ring. Therefore, the core structure of the N1 species in M/LTCT asphaltenes was suspected of a pyrrole ring with higher degree of condensation. However, the N1 species were also the most abundant in crude oil asphaltenes, with the core structure of carbazoles with 2–7 aromatic rings [25,32,49].

Figure 4. (a) The RA of N1, N2, and N4 class species as a function of DBE. (b–d) The plots of DBE versus carbon number for N1, N2, and N4 class species. (e) The suggested core structures of N1, N2, and N4 class species.
N₂ class species. The N₂ species contains double nitrogen atoms. As shown in Figure 4c, the N₂ species in the M/LTCT asphaltenes were concentrated at the DBE of 17–25 and the carbon numbers of 26–35. Compared with the N₁ species, N₂ species have higher DBE values and lower carbon numbers, indicating that molecules of N₂ species have a high degree of condensation. Of them, the compounds of C₃₄H₃₀N₂ with DBE of 21 have the highest RA (as shown in Figure 4a). The compounds were suspected of a benzopyrene plus two naphthenic rings and a pyrazole ring or a dibenzopyrene plus a naphthenic ring and an imidazole ring. The N₂ species with DBE of 20 might be a benzopyrene plus a naphthenic ring and a pyrazole ring and were also likely a dibenzopyrene with an imidazole ring. The N₂ species of 22 DBE were likely a benzopyrene combined with three naphthenic rings and a pyrazole ring and were also likely a dibenzopyrene combined with two naphthenic rings and an imidazole ring. Therefore, the core structure of N₂ species were suspected of 4–7 aromatic rings with a pyrazole ring.

N₄ class species. As described in Figure 4d, the N₄ species in the asphaltenes have the highest RA, mainly centered at the DBE of 16–24 and carbon numbers of 12–23. Of these, the compounds of C₂₆H₁₆N₄ with a DBE value of 22 have the highest RA (as shown in Figure 4a). The compounds were suspected to be a naphthopyrene plus a naphthenic ring with a piperazine ring and a pyrazole ring. The N₄ species with DBE of 22 might be a naphthopyrene plus two naphthenic rings with a piperazine ring and pyrazole ring and also might be a naphthopyrene plus three naphthenic rings with a piperazine ring and an imidazole ring. The N₄ species with a DBE value of 23 might be a naphthopyrene plus three naphthenic rings with a piperazine ring and a pyrazole ring and might be a benzonaphthopyrene plus a naphthenic ring with a piperazine ring and an imidazole ring. Therefore, the core structure of the N₄ species were suspected of 4–7 aromatic rings with a pyrazole ring.

In short, the N₄ species dominated in the Nₓ species, which have a higher degree of condensation with short and multi-substituted alkyl side chains, and the core structure was likely a pyrazole ring or piperazine ring with an imidazole ring. Compared with the research results of other asphaltenes (as shown in Table 4), the RA of N₁ species were most abundant in crude asphaltenes, which have the core structure of pyrrole rings or carbazole rings. The DBE values for N₁ species in M/LTCT asphaltenes were distributed in a wide range, indicating that the species have higher aromaticity than that of the crude oil asphaltenes. Thus, not only the N₁ species but also the N₄ species in M/LTCT asphaltenes are more difficult to remove by hydrogenation.

### Table 4. Main nitrogen-containing heteroatom species in asphaltenes of different raw material.

| Feed                          | Most Abundant Nitrogen Species | DBE Center | C Center | Possible Core Structure                      |
|-------------------------------|--------------------------------|------------|----------|---------------------------------------------|
| The present work M/LTCT asphaltenes | N₄                             | 16–25      | 12–23    | A piperazine ring with a pyrazole ring       |
| Wang et al. [33] Oil sands bitumen asphaltenes | N₁                             | 14–24      | 22–37    | Pyrrole                                     |
| Xu et al. [31] Sudan asphaltenes     | N₁                             | 10–16      | 22–35    | Carbazole ring                              |
| Shi et al. [32] Crude Oil asphaltenes  | N₁                             | 9–19       | 21–37    | Carbazole ring                              |
| Wang et al. [21] Petroleum asphaltenes | N₁                             | 9–20       | 20–46    | Carbazole ring                              |

3.3.3. Distribution of Muti-Heteroatom Class Species

N₁O₁ class species. The N₁O₁ species contains two heteroatoms of nitrogen and oxygen and have the most abundant contents in multi-heteroatom containing species. As shown in Figure 5b, the N₁O₁ species were concentrated at DBE of 12–18 and the carbon numbers of 19–28. Of these, the compounds of C₂₁H₁₉N₁O₁ with 13 DBE have the highest RA. The compounds might be naphthopyrene plus two naphthenic rings with a phenolic hydroxyl and a pyrazole ring. The N₁O₁ species of 15 DBE might be a pyrene plus a
naphthenic ring with a phenolic hydroxyl and a pyrazole ring. The N$_1$O$_1$ species of 16 DBE might be a pyrene plus two naphthenic rings with a phenolic hydroxyl and a pyrazole ring. The N$_1$O$_1$ species of 17 DBE might be benzopyrene plus naphthenic rings with a phenolic hydroxyl and a pyrazole ring.

Figure 5. (a) The RA of N$_1$O$_1$, N$_1$O$_2$, and N$_2$O$_1$ class species as a function of DBE. (a–d) show the plots of DBE versus carbon number of N$_1$O$_1$, N$_1$O$_2$, and N$_2$O$_1$ class species. (e) The suggested core structures of N$_1$O$_1$, N$_1$O$_2$, and N$_2$O$_1$ class species.

N$_1$O$_2$ class species. As described in Figure 5c, the N$_1$O$_2$ species in the asphaltenes were concentrated at DBE of 17–22 and carbon numbers of 29–36. Of these, the compounds of C$_{30}$H$_{27}$N$_1$O$_2$ with a DBE value of 18 have the highest RA (as shown in Figure 5a). The compounds were suspected of a benzopyrene with two naphthenic rings, two phenolic
hydroxyl, and a pyrazole ring were also likely to be the combination of a pyrene with a naphthenic ring, a carboxyl, and a pyrazole ring. The \( N_2O_1 \) species with a DBE value of 19 were likely to be the combination of a dibenzopyrene with two phenolic hydroxyl and a pyrazole ring and were also likely to be the combination of benzopyrene with naphthenic rings, a carboxyl, and a pyrazole ring. The \( N_2O_1 \) species of 20 DBE might be dibenzopyrene with naphthenic ring, two phenolic hydroxyl, and a pyrazole ring and were also likely to be dibenzopyrene with a carboxyl and a pyrazole ring. The \( N_1O_2 \) species with a DBE value of 21 were likely to be the combination of benzopyrene with two naphthenic rings, two phenolic hydroxyl, and a pyrazole ring and were also likely to be the combination of a benzopyrene with a naphthenic ring, a carboxyl ring, and a carboxyl.

\( N_2O_1 \) class species. As presented in Figure 5d, the \( N_2O_1 \) species in the asphaltenes were concentrated at the DBE values of 15–20 and carbon numbers of 30–40. Of these, the compound of \( C_{36}H_{40}N_2O_1 \) with a DBE value of 18 had the highest RA (as shown in Figure 5a). The compounds were most likely to be the combination of benzopyrene with two naphthenic rings, a phenolic hydroxyl, and a pyrazole ring and were also likely to be the combination of benzopyrene with two naphthenic rings, a phenolic hydroxyl, and an imidazole ring. \( N_2O_1 \) species with a DBE value of 17 were likely to be a benzopyrene with a naphthenic ring, a phenolic hydroxyl, and a pyrazole ring. The \( N_2O_1 \) species of 19DBE were likely to be the combination of benzopyrene with three naphthenic rings, a pyrazole ring, and a phenolic hydroxyl.

Compared with the \( N_1O_1 \) species, the more abundant \( N_1O_1 \) species have higher DBE values and lower carbon numbers, suggesting that they contained more condensed molecular structures. The nitrogen and oxygen atoms existed in the form of pyrrole rings and phenolic hydroxyl, respectively. The oxygen atoms in \( N_1O_1 \) species were considered to be phenolic hydroxyls, rather than furans. There are two reasons for it. Hydroxy compounds are more polar than furan compounds. Highly polar hydroxyl compounds were more likely to exist in the asphaltenes during the separation process. In addition, based on the knowledge of the phenolic compounds that is abundant in coal tar [50], there were a large number of pyrrole compounds containing phenolic hydroxyl groups in M/LTCT. Thus, unlike \( N_1O_1 \) species of hydroxyl-containing carbazole compounds in petroleum asphaltenes, the core structure of \( N_1O_1 \) compounds in M/LTCT asphaltenes may be hydroxyl-containing pyrrole compounds. In addition, the distributions of \( N_1O_1 \) compounds were dispersed in a relatively wide range. Moreover, the nitrogen-containing heteroatom compounds with additional oxygen are easier to remove than pure nitrogen-containing heteroatom compounds through hydrogenation [51].

4. Conclusions

A variety of acidic OCCs and non-basic NCCs, except for SCCs, were identified in M/LTCT asphaltenes by negative ESI FT-ICR MS. The distributions of relative molecular weight were mainly concentrated between 200 Da and 750 Da. The acid OCCs identified in M/LTCT asphaltenes include the \( O_x(x=1–6) \) class species, which were comprised of a significant proportion of all species. Different from petroleum asphaltenes, the \( O_4 \) species were predominant in the M/LTCT asphaltenes. The non-basic NCCs were identified, including \( N_X, N_1O_X, N_2O_X, N_3O_X, N_4O_X, N_5O_X, \) and \( N_6O_X(x = 1–6) \), in which the \( N_4 \) species were the most abundant species.

The distributions of DBE values and carbon numbers indicated that the core structure of the \( O_4 \) species was suspected to be 0–6 aromatic rings with four phenolic hydroxyl groups and \( N_4 \) species, probably consisting of a core structure of 4–7 aromatic rings with a piperazine ring and a pyrazole ring. The multi-heteroatom compounds mainly existed as the \( N_1O_1 \) species, which may have a core structure of 3–6 aromatic rings with a pyrrole ring and phenolic hydroxyl group.

Furthermore, compared to the molecular composition of petroleum asphaltenes, the most abundant \( O_4 \) and \( N_4 \) species contained in M/LTCT asphaltenes have higher DBE values centered at 4–15 and 16–24 and lower carbon numbers centered at 12–27 and 12–23,
indicating that more condensed nitrogen-containing and oxygen-containing heteroatom compounds with short substituted alky side chains existed, which more easily undergo condensation to generate more refractory molecules, making it too difficult to remove by hydrogenation. The detailed description of these compounds can provide guidance for revealing the properties of asphaltenes and the basic data for the hydrogenation of deasphaltene.

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**References**

1. Li, D.; Li, Z.; Li, W.; Liu, Q.; Feng, Z.; Fan, Z. Hydrotreating of low temperature coal tar to produce clean liquid fuels. *J. Anal. Appl. Pyrolysis* 2013, 100, 245–252. [CrossRef]
2. Zhu, Y.; Zhang, Y.; Dan, Y.; Yuan, Y.; Zhang, L.; Li, W.; Li, D. Optimization of reaction variables and macrokinetics for the hydrodeoxygenation of full range low temperature coal tar. *React. Kinet. Mech. Catal.* 2015, 116, 433–450. [CrossRef]
3. Tian, Y.; Zhang, B.; Chen, J.; Zhan, Z.; Yang, C.; Zou, Y.; Peng, P. Characterisation by ESI FT-ICR MS of heteroatomic compounds in catalytic hydropyrolysates released from marine crude oil asphaltenes. *Org. Geochem.* 2021, 167, 104391. [CrossRef]
4. Merdrignac, I.; Quoineaud, A.A.; Gauthier, T. Evolution of Asphaltene Structure during Hydroconversion Conditions. *Energy Fuels* 2006, 20, 2028–2036. [CrossRef]
5. Ancheya, J.; Centeno, G.; Trejo, F.; Marroquin, G. Changes in asphaltene properties during hydrotreating of heavy crudes. *Energy Fuels* 2003, 17, 1233–1238. [CrossRef]
6. Yuan, Y.; Li, D.; Zhang, L.N.; Zhu, Y.H.; Wang, L.; Li, W.H. Development, Status, and Prospects of Coal Tar Hydrogenation Technology. *Energy Technol.* 2016, 4, 1338–1348. [CrossRef]
7. Sun, Z.H.; Li, D.; Ma, H.; Tian, P.; Li, X.; Li, W.; Zhu, Y. Characterization of asphaltene isolated from low-temperature coal tar. *Fuel Process. Technol.* 2015, 138, 413–418. [CrossRef]
8. Ruiz-Morales, Y.; Miranda-Olvera, A.D.; Portales-Martínez, B.; Domínguez, J.M. Experimental and Theoretical Approach To Determine the Average Asphaltene Structure of a Crude Oil from the Golden Lane (Faja de Oro) of Mexico. *Energy Fuels* 2020, 34, 7985–8006. [CrossRef]
9. Cai, X.; Shi, R.; Wang, W.; Hou, H.; Peng, D.; Wang, N.; Deng, Z.; Liu, Z.; Zhang, Q. Molecular Structures of Refractory Sulfur Compounds in Heavy Oil Hydrodesulfurization Characterized by Collision-Induced Dissociation Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* 2022, 36, 1326–1337. [CrossRef]
10. Zhang, Q.; Xu, Z.; Zhao, S. Separation and characterization of C5-asphaltenes from low temperature coal tar. *J. Fuel Chem. Technol.* 2016, 44, 1318–1325.
11. Ahmed, A.; Sriram, R.; Nagu, D. Review of Asphaltenes Deposition Modeling in Oil and Gas Production. *Energy Fuels* 2021, 35, 965–986.
12. Zeinab, T.; AmirHossein, S.; Shahab, A. A New Insight to the Assessment of Asphaltene Characterization by Using Fortier Transformed Infrared Spectroscopy. *J. Pet. Sci. Eng.* 2021, 205, 108824.
13. Deng, W.; Wu, L.; Wang, X.; Lu, J.; Li, C. Characteristics of surface functional groups from coal tar asphaltene and its influence on the selection of assistants in slurry-bed hydrocracking. *Acta Pet.* *Sin.* *Pet. Process. Sect.* 2015, 31, 1262–1268.
14. Noah, M.; Forsythe, J.; di Primio, R.; Mehay, S.; Mullins, O.C.; Mahlstedt, N.; Horsfield, B. Heavy End Evaluation in Oils and Associated Asphaltenes Deposits from Two Adjacent Reservoirs by High-Resolution Mass Spectrometry. *Energy Fuels* 2022, 36, 8866–8878. [CrossRef]
Sustainability 2022, 14, 15497

15. Shi, Q.; Zhang, Y.; Chung, K.; Zhao, S.; Xu, C. Molecular Characterization of Fossil and Alternative Fuels Using Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: Recent Advances and Perspectives. Energy Fuels 2021, 35, 18019–18055. [CrossRef]

16. Schaub, T.M.; Hendrickson, C.L.; Quinn, J.P.; Rodgers, R.P.; Marshall, A.G. Instrumentation and Method for Ultrahigh Resolution Field Desorption Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry of Nonpolar Species. Anal. Chem. 2005, 77, 1317–1324. [CrossRef]

17. Fu, J.; Kim, S.; Rodgers, R.P.; Hendrickson, C.L.; Marshall, A.G.; Qian, K. Nonpolar Compositional Analysis of Vacuum Gas Oil Distillation Fractions by Electron Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Energy Fuels 2006, 20, 661–667. [CrossRef]

18. Park, J.W.; Cho, Y.; Son, S.; Kim, S.; Lee, K.B. Characterization and Structural Classification of Heteroatom Components of Vacuum-Residue-Derived Asphaltenes Using APPI (+) FT-ICR Mass Spectrometry. Energy Fuels 2021, 35, 13756–13765. [CrossRef]

19. Klein, G.C.; Rodgers, R.P.; Marshall, A.G. Identification of hydrotreatment-resistant heteroatomic species in a crude oil distillation cut by electrospray ionization FT-ICR mass spectrometry. Fuel 2006, 85, 2071–2080. [CrossRef]

20. McKenna, A.M.; Purell, J.M.; Rodgers, R.P.; Marshall, A.G. Identification of Vanadyl Porphyrins, in a Heavy Crude Oil and Raw Asphaltene by Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometry. Energy Fuels 2009, 23, 2122–2128. [CrossRef]

21. Wang, S.S.; Yang, C.; Xu, C.M.; Zhao, S.Q.; Shi, Q. Separation and characterization of petroleum asphaltene fractions by ESI FT-ICR MS and UV-vis spectrometer. Sci. China Chem. 2013, 56, 856–862. [CrossRef]

22. Wang, L.T.; He, C.; Zhang, Y.H.; Zhao, S.Q.; Chung, K.H.; Xu, C.M.; Hsu, C.S.; Shi, Q. Characterization of Acidic Compounds in Heavy Petroleum Residue by Fractionation and Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Analysis. Energy Fuels 2013, 27, 4555–4563. [CrossRef]

23. Headley, J.V.; Kumar, P.; Dalai, A.; Peru, K.M.; Bailey, J.; McMartin, D.W.; Rowland, S.M.; Rodgers, R.P.; Marshall, A.G. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Characterization of Treated Athabasca Oil Sands Processed Waters. Energy Fuels 2015, 29, 2768–2773. [CrossRef]

24. Zhu, X.; Shi, Q.; Zhang, Y.; Pan, N.; Xu, C.; Chung, K.; Zhao, S. Characterization of Nitrogen Compounds in Coker Heavy Gas Oil and Its Subfractions by Liquid Chromatographic Separation Followed by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Energy Fuels 2010, 24, 281–287. [CrossRef]

25. Liao, Y.; Shi, Q.; Hsu, C.S.; Pan, Y.; Zhang, Y. Distribution of acids and nitrogen-containing compounds in biodegraded oils of the Liaohe Basin by negative ion ESI FT-ICR MS. Org. Geochem. 2012, 47, 51–65. [CrossRef]

26. Gaspar, A.; Zellermann, E.; Lababidi, S.; Reece, J.; Schrader, W. Characterization of Saturates, Aromatics, Resins, and Asphaltenes Heavy Crude Oil Fractions by Atmospheric Pressure Laser Ionization Fourier Transform Cyclotron Resonance Mass Spectrometry. Energy Fuels 2012, 26, 3481–3487. [CrossRef]

27. Merino-Garcia, D.; Andersen, S.I. Application of Isothermal Titration Calorimetry in the Investigation of Asphaltene Association. In Asphaltenes, Heavy Oils, and Petroleumics; Springer: New York, NY, USA, 2007; pp. 329–352.

28. Bej, S.K.; Dalai, A.K.; Adjaye, J. Comparison of hydrodenitrogenation of basic and nonbasic nitrogen compounds present in oil sands derived heavy gas oil. Energy Fuels 2001, 15, 377–383. [CrossRef]

29. Sharma, Y.K. The Instability of Storage of Middle Distillate Fuels: A Review. Liq. Fuels Technol. 2012, 30, 1839–1850. [CrossRef]

30. Mushrush, G.W.; Speight, J.G. Petroleum Products: Instability and Incompatibility; Taylor & Francis: Abingdon, UK, 1995.

31. Xu, C.M.; Liu, Y.; Zhao, S.; Shi, Q. Compositional analysis of petroleum asphaltenes by negative ion electrospray high resolution FT-ICR mass spectrometry. J. China Univ. Pet. 2013, 37, 190–195.

32. Shi, Q.; Hou, D.; Chung, K.H.; Xu, C.; Zhao, S.; Zhang, Y. Characterization of Heteroatomic Compounds in a Crude Oil and Its Saturates, Aromatics, Resins, and Asphaltenes (SARA) and Non-basic Nitrogen Fractions Analyzed by Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Energy Fuels 2010, 24, 2545–2553.

33. Wang, L.; He, C.; Liu, Y.; Zhao, S.; Zhang, Y.; Xu, C.; Chung, K.; Shi, Q. Effects of experimental conditions on the molecular composition of maltenes and asphaltenes derived from oil sands bitumen: Characterized by negative-ion ESI FT-ICR MS. Sci. China Chem. 2013, 56, 863–873. [CrossRef]

34. Suleiman, S.; Wang, C.; Zhang, M.; Gao, H.; Han, Z.; Shi, L.; Su, F.; Xu, G. A Review on the Reaction Mechanism of Hydrodesulfurization and Hydrodenitrogenation in Heavy Oil Upgrading. Energy Fuels 2021, 35, 10998–11016.

35. Hua, R.; Li, Y.; Liu, W.; Zheng, J.; Wei, H.; Wang, J.; Lu, X.; Kong, H.; Xu, G. Determination of sulfur-containing compounds in diesel oils by comprehensive two-dimensional gas chromatography with a sulfur chemiluminescence detector. J. Chromatogr. A 2003, 1019, 101–109. [CrossRef] [PubMed]

36. Shi, Q.; Xu, C.; Zhao, S.; Chung, K.; Zhang, Y.; Gao, W. Characterization of Basic Nitrogen Species in Coker Gas Oils by Positive-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Energy Fuels 2009, 24, 563–569. [CrossRef]

37. Chen, X.; Shen, B.; Sun, J.; Wang, C.; Shan, H.; Yang, C.; Li, C. Characterization and Comparison of Nitrogen Compounds in Hydrotreated and Untreated Shale Oil by Electrospray Ionization (ESI) Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). Energy Fuels 2012, 26, 1707–1714. [CrossRef]

38. Zheng, J.; Li, D.; Fan, X.; Huang, Y.; Gao, F.; Shao, R.; Li, W.; Dan, Y. Characterization of heteroatom class species in asphaltenes from medium/low temperature coal tar. Energy Sources Part A 2020, 1–15. [CrossRef]
39. Shi, Q.; Pan, N.; Long, H.; Cui, D.; Guo, X.; Long, Y.; Chung, K.; Zhao, S.; Xu, C.; Hsu, C. Characterization of Middle-Temperature Gasification Coal Tar. Part 3: Molecular Composition of Acidic Compounds. *Energy Fuels* **2013**, *27*, 108–117. [CrossRef]
40. Zhang, N.; Zhao, S.; Shi, Q.; Xu, Z.; Sun, X.; Xu, C.M. Heteroatomic compositional analysis of venezuela orinoco AR and thevis breaking product by negative ion ESI-FT-ICR MS. *J. Fuel Chem. Technol.* **2011**, *39*, 37–41.
41. Mapolelo, M.; Rodgers, R.; Blakney, G.; Yen, A.; Asomaning, S.; Marshall, A. Characterization of naphthenic acids in crude oils and naphthenates by electrospray ionization FT-ICR mass spectrometry. *Int. J. Mass Spectrom.* **2011**, *300*, 149–157. [CrossRef]
42. Pereira, T.M.C.; Vanini, G.; Tose, L.V.; Cardoso, F.M.R.; Fleming, F.P.; Rosa, P.T.V.; Thompson, C.J.; Castro, E.V.R.; Vaz, B.G.; Romão, W. FT-ICR MS analysis of asphaltenes: Asphaltenes go in, fullerenes come out. *Fuel* **2014**, *131*, 49–58. [CrossRef]
43. Hughey, C.A.; Rodgers, R.P.; Marshall, A.G.; Qian, K.; Robbins, W.K. Identification of acidic NSO compounds in crude oils of different geochemical origins by negative ion electrospray Fourier transform ion cyclotron resonance mass spectrometry. *Org. Geochem.* **2002**, *33*, 743–759. [CrossRef]
44. Zhu, Y.; Huang, J.; Dan, Y.; Wang, L.; Li, W.; Li, D. Analysis and Characterization of Medium/Low Temperature Coal Tar Asphaltene. *Acta Pet. Sin. Pet. Process. Sect.* **2016**, *32*, 334–342.
45. Pei, L.; Li, D.; Yuan, Y.; Xue, F.; Li, W. Composition and structural changes of low temperature coal tar asphaltene precipitated in different n-alkane solvents. *Chem. Ind. Eng. Prog.* **2017**, *36*, 2101–2108.
46. Shao, R.; Li, D.; Pei, L.; Yuan, Y.; Liu, X.; Li, W. Effect of Deasphalting solvent on structure of coal tar asphaltene. *Acta Pet. Sin. Pet. Process. Sect.* **2017**, *33*, 1209–1217.
47. Xie, Z.; Zhang, M.; Wang, X.; Guo, L.; Du, Z.; Li, W. Mechanism of dibenzofuran hydrodeoxygenation on the Ni (1 1 1) surface. *Chin. J. Chem. Eng.* **2021**, *35*, 204–210. [CrossRef]
48. Shi, Q.; Zhao, S.; Xu, Z.; Chung, K.; Zhang, Y.; Xu, C. Distribution of Acids and Neutral Nitrogen Compounds in a Chinese Crude Oil and Its Fractions: Characterized by Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2010**, *24*, 4005–4011. [CrossRef]
49. Pan, Y.; Liao, Y.; Shi, Q.; Hsu, C. Acidic and neutral polar NSO compounds in heavily biodegraded oils characterized by negative-ion ESI FT-ICR MS. *Energy Fuels* **2013**, *27*, 2960–2973. [CrossRef]
50. Yang, Z.; Ma, Z.; Lu, C.; Zhu, Y.; Li, D. Analysis on the occurrence forms and removal rules of nitrogen in heavy fraction of medium and low temperature coal tar. *Energy Chem. Ind. 2020*, *41*, 1–8.
51. Fu, J.; Klein, G.C.; Smith, D.F.; Kim, S.; Rodgers, R.P.; Hendrickson, C.L.; Marshall, A.G. Comprehensive Compositional Analysis of Hydrotreated and Untreated Nitrogen-Concentrated Fractions from Syncrude Oil by Electron Ionization, Field Desorption Ionization, and Electrospray Ionization Ultrahigh-Resolution FT-ICR Mass Spectrometry. *Energy Fuels* **2006**, *20*, 1235–1241. [CrossRef]