Study on the Pretreatment Process and Removal Rules of Sulfur-Containing Compounds for Medium- and Low-Temperature Coal Tar

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ABSTRACT: The heteroatoms (sulfur and nitrogen) and metals (ferrum and calcium) in coal tar can easily cause the corrosion of hydrogenation equipment, catalyst poisoning, and environmental pollution. These should be removed before coal tar is hydrogenated. In this study, with the acid refining method, the effects of three polyether demulsifiers (i.e., PD1, PD2, and PD3), polypamine carboxylate demetalizers (i.e., PCD1, PCD2, and PCD3), and separation temperature on the removal of ferrum, calcium, sulfur, and nitrogen in medium- and low-temperature coal tar were determined. PD2 was selected, and the added amount was 200 μg·g⁻¹. When the PD2 demulsifier was added alone or PD2 demulsifier with various demetalization agents was added, heteroatoms in coal tar could be effectively removed. For the experiments and analysis, the pretreatment conditions of coal tar were as follows: the addition amount of the PD2 demulsifier was 200 μg·g⁻¹, the addition amount of the PCD3-type demetalization agent was 400 μg·g⁻¹, and the stirring temperature was 80 °C. Before and after pretreatment, the methods of inductively coupled plasma−atomic emission spectrometer, gas chromatography−mass spectrometry (MS), and Fourier transform-ion cyclotron resonance MS were used in the present study to explore and analyze the distribution, occurrence form, and removal law of sulfur in coal tar. As revealed from the results, sulfur compounds in coal tar <360 °C fraction (light coal tar fraction, LF) before being pretreated had a lower content, which existed as benzothiophene and dibenzothiophene largely. Sulfur compounds S1 and S2 achieved the maximum relative abundance in >360 °C fraction (heavy coal tar fraction, HF). After the compounds were pretreated, the sulfur removal rate reached 40.0% in LF, and the sulfur compounds were primarily removed. For HF, the sulfur removal rate reached 20.1%. In addition, S1 compounds within the dibenzothiophene derivatives exhibiting more side chains and a larger condensation degree were basically removed. S2 compounds, mainly linked to several quinolines or more aromatic rings and thioether-aliphatic amine sulfur compounds exhibiting small molecular weight and simple structures, were relatively easy to remove. The SO class (e.g., the sulfones and thiophene-ketone group) was more difficult to remove.

1. INTRODUCTION

Over the past few years, as processable crude oil has been increasingly exhausted, people place stress on employing technologies (e.g., oil shale, hydrogen energy, and coal-derived oil) to process clean fuels.¹² By 2020, China’s external dependence on crude oil has become 70%. Such imbalance between supply and demand will severely impact China’s economic development and energy arrangements. As suggested by the BP World Energy Statistics Yearbook released in 2020, the world’s coal consumption was downregulated by 0.6%, taking up 27.0% of the energy mix, whereas for emerging economies (e.g., China), coal consumption continued to rise, and coal production increased the most. In China, coal remains the major energy source, with over 10 million tons of coal tar synthesized from coal pyrolysis each year.³⁴ Coal tar is optimally used by being converted into clean fuel (e.g., gasoline, diesel, and kerosene) or through catalytic hydrogenation to synthesize aromatic hydrocarbons and senior naphthenic base oils.³⁴ Three existing types of medium- and low-temperature coal tar (MLCT) processing methods are primarily adopted, that is, fine chemical engineering route, delayed coking route, and hydrogenation route. To be specific, hydrogenation acts as the primary means to treat coal tar.⁷−¹⁰ However, impurities (e.g., water, ferrum, calcium, and heteroatom compounds) in different forms can in coal tar significantly jeopardize hydrogenation units, hydrogenation catalysts, and the quality of products. Its main performance
refers to the corrosion of equipment, the aging and deactivation of catalysts, and the poor oil stability and inoxidizability of products. At the same time, they will also have a serious effect on the deep hydrogenation processing technology, product quality, and environmental protection. Heteroatoms in coal tar decrease the degree of coal tar deep processing and exploitation. The research on coal tar pretreatment technology turns out to be a research hotspot, arousing growing attention, which facilitates coal tar to be comprehensively exploited. On the one hand, gaining insights into the composition of coal tar and the occurrence and distribution of heteroatoms can theoretically underpin the removal of heteroatoms and subsequent hydrotreating of coal tar. On the other hand, the research of pretreatment technology helps clarify the relationship between the key equipment of coal tar pretreatment and is of reference significance in the design and industrialization of the whole coal tar pretreatment.

Although the coal tar pretreatment technology has been extensively explored, such as static separation, centrifugal separation technique, electrolytic salt technology, extraction technology, hydrogenation technology, and so on, most of the relevant studies stayed at the stage of pretreatment condition and the occurrence form. Moreover, the removal rule of heteroatoms in coal tar before and after pretreatment has been rarely studied in depth. The heteroatoms (sulfur and nitrogen) and metals (ferrum and calcium) in coal tar have higher content and are harmful to further processing.

In the present study, on the basis of the research group’s previous exploration, the pretreatment process of acid refining method at MLCT was systematically studied. By comparing the water content in coal tar and the removal effect of ferrum, calcium, sulfur, and nitrogen, the types of auxiliaries and better technological parameters were screened out. Gas chromatography–mass spectrometry (GC–MS), inductively coupled plasma–atomic emission spectrometry (ICP–AES), and Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) were used for characterization analysis, the content and distribution of sulfur heteroatoms in coal tar before and after pretreatment were investigated, and the removal rule of sulfur compounds in coal tar was found. It can provide a reference for the development of coal tar pretreatment technology and the analysis of sulfur compounds in heavy oil.

2. EXPERIMENTAL SECTION

2.1. Experimental Material. The raw material of the experiment here comes from the full fraction MLCT produced in a coking plant in the north of Shaanxi Province. The basic physical and chemical properties are shown in Table 1.

| Table 1. Properties of Full-Range MLCT |
|----------------------------------------|
| property                  | value     |
| density at 293 K (g·mL⁻¹)        | 1.0351    |
| viscosity/mm²·s              | 35.82     |
| saturates/wt %               | 20.01     |
| aromatics/wt %               | 32.32     |
| resins/wt %                  | 32.74     |
| asphaltenes/wt %             | 14.93     |
| Elemental Analysis           |           |
| C                          | 84.40     |
| H                          | 8.26      |
| N                          | 0.82      |
| S                          | 0.37      |
| O                          | 6.15      |
| Distillation Range (°C)      |           |
| IBP                       | 145       |
| 30%                        | 285       |
| 50%                        | 341       |
| 70%                        | 372       |
| EBP                       | 512       |

Considering the considerable alkaline substances, which are harmful, and the polyamine carboxylic acid salt demetalization agent is acidic, the removal effect is significant. Hence, this study preliminarily selected three commercially available polyether demulsifiers (i.e., PD1, PD2, and PD3) and three polyamine carboxylate demetalization agents (i.e., PCD1, PCD2, and PCD3). During the experiment, coal tar and additives (acid extract preparation, demulsifier, and demetalization agent) were synthesized with the self-assembled pretreatment device, and the fully mixed reaction was performed at a constant temperature. After the samples stood for a certain time, stratified, and reached equilibrium, the oil phase and water phase were separated, and the oil phase (coal tar) was taken for detection.

2.3. Measuring Techniques. The contents of S and N in coal tar were detected with a sulfur–nitrogen meter (Jiangsu Jiang Electricity Analysis Instrument Co. Ltd.), a type of TSN-2000v. The detection conditions comprised the temperature at 1030 °C, the oxygen and argon inlet pressure under 0.25 MPa, the ozone flow rate at 80 mL·min⁻¹, the split oxygen flow reaching 350 mL·min⁻¹, the imported oxygen flow reaching 90 mL·min⁻¹, and the inlet oxygen flow of 130 mL·min⁻¹. By using ICP–AES (OPTIMA8000DV, PerkinElmer, USA), the contents of ferrum and calcium in coal tar were detected. To detect coal tar samples <360 °C, this study employed OP2010 Plus meteorological chromatography–MS combined with electron ionization (EI) source detection (GC–MS) produced in Tsujima, Japan. The detection conditions included the shunt ratio at 100:1, the carrier gas as high-purity helium, the flow rate at 1.5 mL·min⁻¹, the inlet temperature at 300 °C, the EI ion source temperature at 230 °C, and the column as RXI-5ms capillary column (30 m × 0.25 mm × 0.25 μm). Given the NIST08S map data, the structure information of the components was determined in accordance with the confidence or similarity. To detect >360 °C coal tar sample, the present study adopted FT-ICR MS combined with atmospheric pressure photoionization ionization source detection. The detection conditions and methods consisted of magnetic field intensity of 7.0 T, ion APCI ionization mode, a sampling frequency of 1 S; toluene dissolved the >360 °C coal tar sample into a 10 mg·mL⁻¹ solution, and then the mixture was diluted with toluene/methanol to 0.2 mg·mL⁻¹.
The prepared solution was injected into the APCI ion flow for detection with the injection pump.

3. RESULTS AND DISCUSSION

3.1. Optimization of Demulsifier Type and Additive Amount. To explore the performance of three kinds of demulsifiers, we took an appropriate amount of coal tar; the emulsification and stirring processes were conducted at an oil−water ratio of 1:1 and the mixing temperature was 80 °C. 5 wt % H₂SO₄ and 200 μg·g⁻¹ PD1, PD2, and PD3 were added to record the water dewatering at different times. The experimental results are shown in Figure 1. The water content in coal tar was almost unchanged. Therefore, the optimal amount of demulsifier was selected as 200 μg·g⁻¹, ensuring the dehydration effect and keeping it economical. In brief, among the three types of demulsifiers, PD2 was selected, and the added amount was 200 μg·g⁻¹.

3.2. Optimization of Demetalizing Agent Type and Additive Amount. According to the physicochemical properties of coal tar, and the content of heteroatomic ferrum, calcium, sulfur, and nitrogen are taken as indicators to screen out the demetalizing agents with better effects in our experiment. Using the same conditions as above, the removal ability of different heteroatoms in coal tar were explored by PCD1, PCD2, and PCD3 under 200 μg·g⁻¹ PD2 demulsifier and 400 μg·g⁻¹ demetalized additives. The results are shown in Figure 3.

Figure 1. Water content of coal tar under different demulsifiers.

![Figure 1](image1.png)

Figure 2. Effect of demulsifier (PD2) addition on water content in coal tar.

![Figure 2](image2.png)

Figure 3. Effects of different types of demetallicants on the content of heteroatoms in coal tar.

![Figure 3](image3.png)
acid, and then neutralize and sulfonate with sulfur and nitrogen heteroatoms, so the heteroatoms enter the water phase and are removed. For the heteroatom compounds in polymer complexes, such as metalloporphyrins and petroleum acids, the effect is not obvious. Since the demineralizer is acidic, the addition of demineralizer produces H⁺ for the system, and the demetallization agent molecules can be used in cooperation with metal ions to form chelates exhibiting high stability of five-membered rings or above. Thus, the impurities of the polymer complex can be removed. In addition, there are −COOH and −OH functional groups in the demetallization agent, capable of being complexed with nitrogen atoms and converted into water-soluble complexes, which can be removed together.

Accordingly, with the addition of the demetallizing agent, the removal effect of heteroatoms in coal tar was significantly improved by strengthening the strong acid action and enhancing the chelating and complexing synergy. The overall removal effect of the three groups is presented as PD2 + PCD3 > PD2 + PCD2 > PD2 + PCD1. In this study, PCD3 was taken as the optimal demetallization agent.

To explore the influence of the additive amount, 100, 200, 300, 400, and 500 μg·g⁻¹ PCD3 additions were selected under the same experimental conditions as above. As shown in Figure 4, with the increase of PCD3 addition, the heteroatom content in coal tar decreased first and then leveled off. When the amount of PCD3 was increased to 400 μg·g⁻¹, the heteroatom removal effect was not obvious. The analysis shows that the heteroatom content decreases first because with the increase of the addition amount the demetallizer provides more H⁺ and −COOH functional groups for the system, which makes the degree of acidification, complexation, and chelation between the demetallizer and heteroatom increase. Thus, metal porphyrin and oil acid compounds, as well as most of the alkali nitrides and part of the alkali nitrides, could be more effectively removed. When the amount of the demetallization agent is increased, the removal effect of heteroatoms is almost unchanged, indicating that the remaining heteroatoms in coal tar are difficult to remove with this method, and such heteroatom compounds may exist in coal tar asphalts and other recombination components. From the above experimental results, it is found that the amount of 400 μg·g⁻¹ added demetallization agent is a more appropriate amount for the pretreatment process of MLCT. PCD3 demetallization with the additive amount of 400 μg·g⁻¹ has the best performance.

3.3. Separation Temperature Optimization. In order to explore the separation of oil–water at different temperatures, as well as the removal effect of impurity atoms in coal tar mixed material, we designed an experiment to optimize the separation temperature. The conditions of the experiment were as follows: Suitable amount of coal tar in the oil–water ratio of 1:0.2, acid extract preparation of 5 wt %—H₂SO₄, PD2 demulsifier of 200 μg·g⁻¹, and PCD3 demetallization agent of 400 μg·g⁻¹, stirring at 80 °C, the mixing time was 0.5 h, the flow rate of the feed pump was controlled, and the separation time was ensured as 120 min. Figures 5 and 6 illustrate the water content and removal effect of heteroatoms in coal tar after pretreatment at different separation temperatures.

![Figure 4. Effect of the amount of demetallizer (PCD3) added on the content of heteroatoms in coal tar.](image)

![Figure 5. Water content in coal tar at different separation temperatures.](image)

![Figure 6. Heteroatom content in coal tar at different separation temperatures.](image)
decreased, thereby reducing the resistance of oil and water molecules and accelerating the oil and water coalescence. On the other hand, as the separation temperature rose, the internal energy of oil and water molecules increased, significantly enhancing the thermal movement of molecules and upregulating the probability of collision and fusion between water molecules. In the meantime, the density difference between oil and water phases increased, facilitating the separation of oil and water phases. However, since the increase in density between oil and water phases is limited, when the temperature reached 80 °C, with its increase, the water content in coal tar did not decrease significantly and tended to be stable.

As indicated in Figure 6, with the extension of the separation temperature, ferrum, calcium, sulfur, and nitrogen contents in coal tar first decreased and then turned stable, basically complying with Figure 6. Thus, the present study tested different separation temperatures after pretreatment. With the effect of water content and impurity atom content in coal tar, the optimal separation temperature was 80 °C, the coal tar moisture content was 0.9%, heteroatom ferrum, calcium, sulfur, and nitrogen removal rates were 78.2, 90.5, 25.1, and 74.6%, respectively, and the pretreatment of coal tar could satisfy the requirement of subsequent processing.

Combined with the above experiments and analysis, the pretreatment conditions of coal tar were as follows: the addition amount of the PD2 demulsifier was 200 μg g⁻¹, the addition amount of the PCD3-type demetalization agent was 400 μg g⁻¹, and the stirring temperature was 80 °C.

3.4. Analysis of Sulfur in Coal Tar Components before and after Pretreatment. 3.4.1. Analysis of Sulfur in Coal Tar Components before and after Pretreatment. According to the previous distillation range detection, it was found that the LF accounted for 50% of the total fraction. Therefore, coal tar samples were cut into LF and HF by vacuum distillation apparatus before and after pretreatment in the experiment. The distribution of yield and sulfur content is shown in Table 2.

| Table 2. Sulfur Content in Coal Tar and Distillates<sup>a</sup> |
|---------------------|---------------------|---------------------|
|                     | <360 °C distillates | >360 °C distillates |
| before              | fraction distribution/% | 58.8                | 41.2                |
| pretreatment        | S content/μg g⁻¹      | 2351.5              | 5463.9              |
|                     | S distribution/wt %  | 35.9                | 64.1                |
| after               | fraction distribution/% | 56.3                | 43.7                |
| pretreatment        | S content/μg g⁻¹      | 1350.2              | 4374.2              |
|                     | S distribution/wt %  | 27.5                | 72.4                |
|                     | removal rate/%       | 40.0                | 20.1                |

<sup>a</sup> The total sulfur content of coal tar before pretreatment is 3684.3 μg g⁻¹, and the total sulfur content after pretreatment is 2759.5 μg g⁻¹. The total sulfur removal rate is 25.1%.

As indicated from Table 2, the LF before and after pretreatment were both greater than 50% and similar in value, indicating that this kind of coal tar has many light components and is suitable for hydrogenation of raw materials to produce light oil products. At the same time, pretreatment had little influence on the composition of coal tar fraction and did not change its internal structure. Sulfur is mainly concentrated in HF. Although the sulfur distribution of the LF decreased after pretreatment and the sulfur distribution of the HF increased after pretreatment, the sulfur content decreased after pretreatment in both cases, demonstrating that pretreatment could remove the thioheteroatomic compounds in both fractions. According to the calculation, the removal rate of sulfur was 40.0 and 20.1%, respectively, after pretreatment under the two conditions of LF and HF. This is primarily explained as HF being mainly asphaltic with large molecular weight and complex sulfur type, and the pickling pretreatment has certain limitations, so the removal rate is relatively low.

3.4.2. Analysis of Sulfur in <360 °C Coal Tar before and after Pretreatment. As the LF is relatively light, GC–MS was used to analyze its sulfur compounds, as shown in Table 3. According to Table 3, a total of eight types of sulfur compounds were detected, sulfur heterocompounds account for less in LF, including thionaphthene, dibenzothiophene, 1-methylbenzothiophene, 3-methylbenzothiophene, benzonaphthothiophene, benzothiazole, and mainly benzothiophene and dibenzothiophene. No sulfur-containing heteroatomic compounds were detected after pretreatment, which indicates that sulfur compounds in LF have been largely removed after pretreatment.

3.4.3. Analysis of Sulfur in >360 °C Coal Tar before and after Pretreatment. Since HF is heavy, its molecular weight is relatively large and its boiling point exceeds the temperature range of GC–MS gasification chamber, GC–MS is no longer applicable to the detection of this fraction. Based on the weak polarity of sulfur heteroatomic compounds in coal tar, APCI soft ionization source combined with FT-ICR MS was used to directly conduct molecular level analysis of >360 °C distillate oil before and after pretreatment. To visually describe the composition differences of various sulfur-containing heteroatoms before and after pretreatment, all identified mass spectrum peaks were classified by complying with the type of heteroatoms, and the distribution of various sulfur-containing compounds is presented in Figure 7.

The sulfur compounds identified included five types, that is, S1, S2, S3, S4, and S5 (Sx type denotes the compound containing x sulfur atoms in the molecule). Before pretreatment, the relative abundance of the respective type of sulfur-containing compound in HF ranged from S1 > S2 > S3 > S5 > S4, and the relative abundance of S1 and S2 was significantly higher than that of other types. As revealed from the results, the sulfur heteroatomic compounds in HF largely existed in S1 and S2. The distribution pattern of the relative abundance of each type of thioheteroatomic compounds in HF after pretreatment complied with that of HF before pretreatment, whereas the relative abundance of the various compounds changed significantly, in which S1 and S5 compounds’ relative abundance values that were 45.5 and 9.5%, respectively, before pretreatment reduced to 34.0 and 8.4% and those for S2, S3, and S4 compounds, respectively, that were 25.3, 11.2, and 8.5% before pretreatment rose to 28.6, 16.6, and 12.4%, which explains that the pretreatment process had a certain removal effect on some sulfur atoms, and in S1 heteroatomic, easier sulfur removal. Given the complexity and polydispersity of sulfur heteroatomic compounds in coal tar, this study correlated the carbon number, double-bond equivalences (DBE) value, and relative abundance of S1, S2, S3, S4, and S5 compounds in HF before and after pretreatment to generate a DBE distribution diagram of various sulfur heteroatomic compounds.
DBE represent the number of rings plus the number of double bonds in a given molecular formula. DBE values can be calculated by the following equation: \[ \text{DBE} = c - h/2 + n/2 + 1 \]
where \( c \) denotes the number of carbon atoms in the compound, \( h \) expresses the number of hydrogen atoms, and \( n \) is the number of nitrogen atoms. Figure 8 presents DBE and carbon number distribution diagrams of S1 compounds in HF before and after pretreatment. As indicated in it, there are more S1 compounds in HF before and after pretreatment, and their distribution areas are also relatively wide. Before pretreatment, the C-number distribution range of S1 compounds was 5−55, and the DBE distribution range fell to 0−54 in HF. Therefore, S1 compounds exhibit a complex structure, and there are considerable sulfur heteroatomic compounds with different condensation degrees. DBE ranged from 0 to 15, and carbon numbers ranged from 5 to 30. If the entire distribution interval falls into four intervals according to DBE value, DBE = 0−2, DBE = 3−5, DBE = 6−9, and DBE above 9, due to the high oxygen content in tar and the easy decomposition of thioether compounds, the corresponding structure in the first interval may be that the parent nucleus is sulfoxide or mercaptan derivatives, but through chemical formula analysis, it is found that S1OyNz is the main type, so the main structure in this interval is sulfoxide derivatives; the corresponding structure of the second interval may be explained as the parent nucleus is a thiophene derivative linked to the alkyl side chain or naphthenic ring, and the relative abundance of such compounds is larger than that of the first interval; since benzo thiophene DBE = 6 and compounds are primarily of SxOyNz type, the third interval compound is speculated to be the parent nucleus of dibenzo thiophene linked to N and O heteroatoms alkyl side chains or naphthenic ring derivatives, and the relative abundance of such compounds is also relatively large; the corresponding structure of the fourth interval may be that the parent nucleus is dibenzoxy thiophene, which is widely distributed with the maximum DBE up to 54, indicating the existence of dibenzo thiophene derivatives with higher condensation degree.

After the pretreatment, the composition and relative content of the compounds with sulfur heteroatoms varied significantly, and most of the sulfur compounds in the C-number >30 distribution interval were removed; this kind of compound mainly exists in the SxNz class or SxOyNz class, mainly dibenzo thiophene derivatives with more side chains and larger condensation degree, and a small amount of thiophene and benzothiophene derivatives with lower condensation degree but more side chains; the content of sulfur-containing compounds in the distribution interval of C-number <30 also decreased, whereas it was not easy to remove because it mainly existed in the SxOy class.

Figure 9 presents DBE and C-number distribution diagrams of S2 compounds in HF before and after pretreatment. As shown in Figure 9, before pretreatment, S2 compounds were also widely distributed in >360 °C distillate of coal tar, with C-
number distribution ranging from 6 to 55 and DBE distribution ranging from 0 to 10, and C-number distribution ranging from 5 to 25 being concentrated. The mentioned compounds are mainly SNO and SN compounds, and the former is in the majority. Since coal tar is measured under the condition of positive ions, there are fewer acidic sulfides, indicating that the oxygen atoms of these compounds mainly exist in the form of −OH functional groups or ketones. To be specific, compounds with DBE = 0 may be sulfone-aliphatic amine, compounds with DBE = 3 may be sulfone-thioether-piperidine, compounds with DBE = 5 may be thioephene-thioether-tetrahydrofuran or thiouindene, and those with DBE = 9 may be thiophene-pyrrrole or benzothiazole-piperidine. Specific to DBE >10, the compounds have relatively complex compositions, which may be benzothiophene linked to multiple quinolines (DBE = 17) or sulfone linked to multiple aromatic rings and aliphatic amines (DBE = 25).

After pretreatment, the relative abundance of compounds with C-number >30 and higher DBE value in S2 compound and compounds with C-number <10 significantly decreased, as revealed from the results; the sulfides with multiple quinolines or aromatic rings and piperidines and the simple thioether-aliphatic amines with small molecular weight were easy to remove. However, the abundance of sulfur compounds with lower C-number and DBE decreased less, demonstrating that sulfones, thiophene-ketone groups, and other SO groups are more difficult to remove. Nevertheless, the sulfur compounds with lower C-number and DBE had less decrease in abundance, indicating that sulfone, thiophene-ketone group, and other SO groups are difficult to remove.

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Figure 10 illustrates DBE and C-number distribution diagrams of S3 compounds in HF before and after pretreatment.

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As indicated in this figure, the relative abundance of S3 compounds in HF before pretreatment was significantly lower than that of S1 and S2, its distribution range was relatively wide and uniform, C-number was distributed between 7 and 55, DBE was distributed between 0 and 49, and no C-number and DBE centralized distribution interval was identified, mainly SNO compounds. Structurally, only one more sulfur atom exists in S3 than S2, so S3 may have one more thioether ring or sulfone structure than S2. Furthermore, compounds with DBE = 0 may be sulfone-aliphatic amines-sulfones; compounds with DBE = 4 may be sulfone-sulfide ring-pyrrole class; those with DBE = 9 may be sulfone-sulfide ring-pyrrole class; those with DBE = 10 may be sulfone-thiophene-pyrazines; and those exhibiting DBE higher than 15 may be benzoethiophenes linked to multiple indoles or quinolines, with the main compounds of long chains.

After pretreatment, the C-number >30 and exhibiting a higher DBE value of the S3 compounds decreased significantly, indicating that sulfoxide-thiophene-containing compounds with high C-number and linked to the azogen structure are easy to remove, consistent with the rule of S2 compound removal. However, the C-number ranged from 15 to 25, DBE varied from 0 to 10, and considerable thiophene-pyrazole compounds were generated. As suggested from the results, some indole-derived compounds exhibiting higher molecular weight can be converted to pyrazole as impacted by sulfuric acid. Accordingly, the mentioned compounds are more difficult to remove.

Figure 11 illustrates DBE and C-number distribution diagrams of S4 compounds in HF before and after pretreatment. As indicated in this figure, the relative abundance of S4 compounds in HF before pretreatment was also low, its
distribution range was relatively wide and uniform, and the distribution characteristics of C-number and DBE were not obvious, mainly SNO compounds. Because the combination of sulfur and sulfur atoms in S4 compounds varies a lot, it is difficult to determine exactly the molecular structure of this type of compound. It can also indicate that the structure of sulfur heteroatomic compounds in coal tar is complex, compounds with a DBE of 0 may be sulfone-aliphatic amines or sulfoxone-alcohols, and compounds with DBE = 9 may be benzothiazole-sulfonic acids or thiophene-sulfonamides.

After treatment, a large number of S4 compounds were removed, and a few thiazole-nitrogen heterocycle (DBE = 0) and thiazole-thioketone (DBE = 5) S4 compounds with low condensation degree appeared. These results indicate that there is a conversion between compounds in the pretreatment process of impurity removal, and the appearance of the compounds may be the product of the reaction of S4 macromolecules with other compounds.

Figure 12 illustrates DBE and C-number distribution diagrams of S5 compounds in HF before and after pretreatment. As indicated in this figure, the characteristics of the distribution of S5 compounds in HF before pretreatment were similar to those of S3 and S4, that is no C-number and DBE centralized distribution characteristics, C-number was distributed between 20 and 55, and DBE was distributed between 0 and 47. Through the analysis of distribution, it can be concluded that S5 is a class of compounds with higher molecular weight, and this type of compound consists mainly of five sulfur atoms combined with different nitrogen and oxygen atoms. Hence, it is difficult to determine the structure of this type of compound from the only characterization available.

After pretreatment, the relative abundance of S5 compounds in HF decreased significantly; most of the materials had been removed and transformed, leaving only a small amount of materials with higher original content. It also showed that the acid refining pretreatment had a good effect on the removal of complex thioheteroatomic compounds.

4. CONCLUSIONS

In the present study, full fraction MLCT acted as the raw material. In addition, the removal of three polyether demulsifiers (i.e., PD1, PD2, and PD3) and polyamine carboxylate demetalizing agents (i.e., PCD1, PCD2, and PCD3) on ferrum, calcium, sulfur, and nitrogen in coal tar was investigated, respectively. Given the experiment, the optimal pretreatment conditions for coal tar were obtained (e.g., the addition amount of PD2 demulsifier as 200 μg·g⁻¹, the addition amount of PCD3 type demetalization agent as 400 μg·g⁻¹, and the stirring temperature at 80 °C). Moreover, ICP–AES, GC–MS, and FT-ICR MS were adopted to analyze the distribution, occurrence form, and removal rule of sulfur in coal tar before and after pretreatment. As revealed from the results, before pretreatment, sulfur compounds in LF had a lower content, mainly existing as benzothiophene and dibenzothiophene, and the relative abundance of S1- and S2-containing sulfur compounds was the maximum in HF. After pretreatment, the sulfur removal rate reached 40.0% in LF, and the sulfur heteroatomic compounds were largely removed; the sulfur removal rate was 20.1% in HF; class S1 was basically
removed for dibenzothiophene derivatives with more side chains and larger condensation degree, as well as a small amount of thiophene and benzothiophene derivatives exhibiting lower condensation degrees but more side chains; S2 compounds were mainly sulfides linked to multiple quinolines or multiple aromatic rings and piperidines and simple thioether-aliphatic amines exhibiting small molecular weight and were easy to remove, while sulfones, thiophene-ketones, and other SO compounds were more difficult to remove.

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Notes

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