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Optimization of Molecular Composition Distribution of Slurry Oil by Supercritical Fluid Extraction to Improve the Structure and Performance of Mesophase Pitch

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Abstract: The composition distribution of slurry oil has a significant impact on the structure and performance of the mesophase. In this study, supercritical fluid extraction oil (SFEO) and extraction components were extracted from two slurry oils (SLOs) using the supercritical fluid extraction (SFE) technique. The fundamental properties and composition distribution of two SLOs and associated SFEOs were thoroughly investigated. Electron microscopy and spectroscopic techniques were employed to study the morphology and structures of mesophase pitch produced by carbonizing SLOs and their extraction components under the same conditions. The findings revealed that, compared to SLO-LH, SLO-SH has a higher proportion of 4–5 aromatic rings and a narrower hydrocarbon distribution range. In SLO-LH, O1, N1, and N1O1 molecules with long side chains and poor flatness make up the majority of the heterocyclic aromatic hydrocarbons. The distribution of CH compounds can be narrowed by using supercritical fluid extraction to efficiently separate various heteroatom-containing compounds with a higher condensation degree. After supercritical extraction, the mesophase content, texture distribution, and graphitization degree of the mesophase were improved. Polycyclic aromatic hydrocarbons with high planarity help polymer macromolecules stick together and build up in an orderly way. Heterocyclic aromatic hydrocarbons with high condensation and low planarity, on the other hand, play an important role in the formation of mosaic structures.

Keywords: slurry oil; supercritical fluid extraction; mesophase pitch



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1. Introduction

Fluid catalytic cracking (FCC), which generates a massive quantity of slurry oil (SLO), is a crucial procedure for heavy oil treatment to manufacture cracked gas, gasoline, and diesel. SLO, with a high concentration of aromatic compounds, can be utilized as a raw material in the manufacture of high-value-added carbon materials [1]. Nevertheless, the compositional distribution of SLO is not homogeneous, and substantial contaminants are hard to remove, which enhances the instability of the polymerization reaction and makes it challenging to maximize the SLO value [2,3]. In industrial production, needle coke is generally manufactured by delayed coking and can be applied as a filler for manufactured graphite electrodes [4]. The feedstock viscosity and mesophase development during the reaction determine the structure of the coke throughout the succeeding coking process, which affects the degree of graphitization, reactivity, and coefficient of thermal expansion (CTE) of the needle coke product [3,5,6]. CTE is an important performance parameter for measuring temperature-related expansion. Samples with lower CTE values exhibit less excessive expansion and contraction, and their structures are more stable. The type of the precursor's composition governs the development of the mesophase [7–9]. Heteroatoms such as S, N, and O not only make the feedstock more reactive during the reaction, but they are also more likely to form a mosaic structure in high-viscosity environments, which leads to a low yield of large, higher-order needle coke [10].

The thermochemical reaction activity and reaction rate of carbon precursors with various composition distributions were investigated at the same soaking temperature [8,11,12]. The anisotropic content and optical texture structure of mesophase pitch will differ based on the quantities of quinoline insoluble (QI) and asphaltene in the raw materials [13–20]. Supercritical fluid (SF) is highly compressible and solvable, and minor variations in pressure and temperature can cause significant changes in its properties. It can change the operating pressure and temperature to adjust the density of SF and its solubility in heavy oil, thereby increasing the extraction efficiency. SFE may eliminate contaminants from precursors and provide a higher quality fraction based on the solubility difference [21]. The performance of SFE technology for eliminating contaminants and heteroatom compounds was thoroughly investigated [22–25]. Zhang et al. employed the SFE technique to separate FCC SLO and coal tar to obtain aromatic-rich fractions, which greatly increased the yield of manufactured mesocarbon microspheres [26,27]. SFE is expected to have a strong potential for producing a high-quality mesophase pitch.

In the research on the preparation of carbonaceous mesophase based on slurry oil, there is no report on the research from the perspective of the difference in component distribution of different raw materials. To deepen the understanding of the influence of raw material composition, it is necessary to analyze the distribution of the overall composition. In this work, two types of SLO were extracted utilizing SFE technology, and carbonization experiments were performed on the corresponding fractions. The quality and performance of mesophase pitch obtained after carbonization were investigated as well as the optimization effect of SFE technology on the mesophase pitch. The distribution of SFEO and SLO compositions was investigated, and the effects of hydrocarbon composition and heterocyclic compound distribution on the structure and performance of mesophase pitch were correlated.

2. Materials and Methods

2.1. Raw Material

For simplicity, FCC slurry oil (SLO) from Lianhua (LH) refineries and Shihua (SH) refineries in China are labeled as SLO–LH and SLO–SH. Furthermore, the slurry oil has a low metal concentration and no toluene insoluble or QI component. This study's chemicals are all analytical reagents (AR).

2.2. Supercritical Fluid Extraction (SFE)

The two slurry oils (SLO–LH and SLO–SH) were treated with SFE using isobutane as a solvent. In Figure 1, the flow chart is displayed [27]. SFELO (extracted light oil), SFEO (extracted oil), and SFER (extracted residue) were obtained, with the designations SFEO–LH, SFEO–SH, SFER–LH, and SFER–SH, respectively. The extraction conditions were determined as a solvent-to-oil ratio of 4, an extraction temperature between 80 and 165 °C, a pressure of 5 Mpa. The slurry flow was 600 g/h. The extraction lasted 60 min in total.

2.3. Mesophase Pitch Preparation

Figure 2 depicts a thermal polymerization microreactor device made up of a tin bath heating furnace, nitrogen, a heating system controlled by an intelligent program, a back pressure valve, and a reaction system. Using the polycondensation process, with slurry and its extraction components as raw materials, MP was created. The 50 mL reactor was filled with 10 g of raw material, then it was locked. N₂ was purged for three minutes, and then the air was expelled. After that, N₂ was used to elevate the system pressure to a fixed value of 0.7 MPa, the heating rate to 3 °C/min, and the temperature to a constant temperature of 430 °C. The reactor was removed from the tin bath after the reaction had been running for 8 h, and the solid residue, known as mesophase pitch, was removed after naturally cooling in the air (MP–LH, MP–SH, MP–LHSFEO, MP–SHSFEO, MP–LHSFER, and MP–

SHSFER). Three repeated trials were carried out under identical conditions to guarantee the experiment's correctness. The measured yield and quantitative values are average.

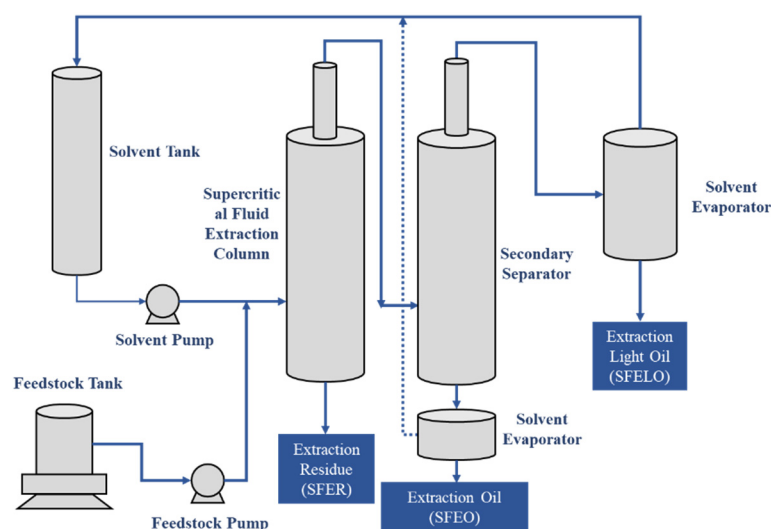


Figure 1. Flow chart of supercritical fluid extraction separation process.

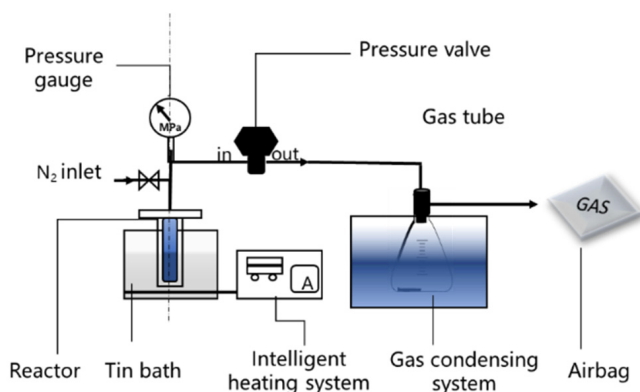


Figure 2. The thermal polymerization microreactor device.

2.4. Analytical Method

At 20 °C, the density was determined using specific gravity bottles according to GB/T 2540-81. The residual carbon value is based on the SH/T 0170-92 electric furnace process, at a temperature of 520 °C. The carbon and hydrogen contents were evaluated using a Flash EA 1112 organic trace element analyzer, while the sulfur and nitrogen contents were determined using an ANTEK7000NS sulfur and nitrogen analyzer. The molecular weight was determined utilizing gel permeation chromatography (GPC) with the Waters GPC515-2410 equipment. The SARA analytical technique was performed in consultation with SH/T0509-92, using neutral-Al₂O₃ with 1% water as the adsorbent. The Analytical and Testing Center of Tsinghua University carried out the analysis using the JOEL JNM-ECA 600 as the testing machine for ¹H-NMR. The hydrocarbon composition was analyzed by GC-MS following ASTM D2786 and ASTM D3239 standards. A Bruker Apex-Ultra FT-ICR MS equipped with a 9.4 T actively shielded superconducting magnet was used for the molecular characterization. It is equipped with electrospray ionization sources (ESI and APPI). Methodologies for FT-ICR MS mass calibration, data acquisition, and processing have been described elsewhere [28]. A final concentration of 0.2 g/L of a solvent mixture of toluene and methanol (1:1, v/v) was used to dissolve the oil samples. For each measurement, the conditions of the HR MS operating in positive-ion mode included a 3600 V positive ion spray voltage, 5 Arb sheath gas, and 2 Arb aux gas; a total of 20 scans

were averaged. The ion transfer tube temperature and the evaporation temperature were 300 and 20 °C. The mass resolution was 500,000 at m/z 200, and the mass range was 150–1200 Da.

Before observation, the mesophase pitch sample was hardened using epoxy resin following the prior procedure, and the section was polished [26]. A Leica DM 2700 P polarizing microscope was utilized. For the quantification of optical texture, “scan at a fixed distance between steps, obtain at least 50 images for each sample section to ensure full coverage” is added in line 124. Image feature analysis technology was used to classify and count a sequence of pictures collected using a polarizing microscope [29]. Eser and Mochida proposed categorization and calculation techniques appropriate for needle coke [30–32]. We enhanced the categorization of anisotropic texture as given in Table 1 to more clearly display the order of anisotropic texture. The anisotropic texture of mesophase pitch and its relative distribution were analyzed. The mesophase content is the percentage of the area of anisotropic texture statistically identified on the cut plane. The degree of order of anisotropic texture is evaluated according to the statistical relative distribution of texture classifications in Table 1. X-ray diffraction data were obtained by Bruker D8 Advance with a scanning angle of 10°–90°. Raman spectroscopy was performed on a Renishaw Raman 2000 System Spectrometer with a wavelength of 532 nm and a scan range of t . The scanning electron microscope (SEM) was performed on the Hitachi SU8010, and the optical texture analysis of the product was performed on the Leica DM 2700 P. The resistivity tester employed is an XH1000S-A102-FM powder resistivity tester, and the test method is GB/T 24521-2018.

Table 1. Nomenclature of microstructure types of optical texture.

Anisotropic Texture	Abbreviation	Size (μm)
Fine Mosaic	FM	<5
Coarse Mosaic	CM	Between 5 and 20
Flow	F	Between 20 and 60
Flow Domain (short)	FD(s)	Between 60 and 300
Flow Domain (long)	FD(l)	≥ 300

3. Results

3.1. Properties of SLO and SFEO

With isobutane as the solvent, two types of SLO were extracted to produce extracted light oil (SFEL), extracted oil (SFEO), and extracted residual (SFER). Table 2 shows the yield of the extractive fraction. Under the same working circumstances, the yield of SFEO–LH is higher than that of SFEO–SH, while the yield of SFER–LH is lower than that of SFER–SH, which may be due to differences in the composition selectivity of isobutane to slurry oil.

Table 2. Operating parameters of SFE and yield of extraction components.

Sample	Pressure (Mpa)	Solvent/Oil Ratio	SFEL (wt %)	SFEO (wt %)	SFER (wt %)
SLO-LH	5	4	5.14	87.91	7.01
SLO-SH	5	4	8.22	62.55	29.23

Table 3 displays the fundamental property information for the two types of SLO and SFEO. As can be observed, when compared to the two types of SLO, SFEO has lower density and viscosity, lower O and S contents, lower residual carbon contents, and zero ash content, all of which indicate that the solid impurities have been fully eliminated. Additionally, SLO–LH had a larger molecular mass but a lower density and viscosity when compared to SLO–SH. Table 2 shows that SFE extracts SLO–LH to separate SFEL fractions, and the low molecular weight fraction contributes more to the number average molecular

weight (Mn), causing Mn to rise after extraction. With a narrowed composition distribution, SFE technology separates more big molecular weight compounds from SLO-SH, leading to a drop in Mn. After SFE treatment, the number-average molecular mass and H/C of SFEO-SH both increased.

Table 3. Basic properties data of two kinds of SLO and SFEO.

Property	RC * wt %	Ash μg/g	Viscosity mPa·s	Density g/cm ³	Mn	Elemental Content wt %					H/C
						C	H	S	N	O	
SLO-LH	8.16	0.16	34.66	0.9909	486	88.16	10.93	0.37	0.3	<0.3	1.48
SFEO-LH	6.69	0	31.46	0.9694	475	88.1	11.15	0.35	0.32	<0.1	1.51
SLO-SH	16.08	0.32	42.06	1.0941	341	90.4	7.98	0.51	0.5	<0.3	1.05
SFEO-SH	7.97	0	14	1.0098	360	89.39	9.29	0.42	0.42	<0.1	1.24

* RC: Residual carbon.

3.2. Structural Differences between SLO and SFEO

The distribution of components having boiling points of less than 540 °C can be obtained with GC-MS. Figure 3 displays information on the hydrocarbon composition of SLO and SFEO. After SFE treatment, the relative content of chain alkanes and 1–3 rings cycloalkanes increased in SLO-SH, although the concentration of heavier components decreased. The total aromatic content of SLO-SH and SFEO-SH was greater than that of SLO-LH and SFEO-LH, respectively. Aromatics with 4–5 rings and unidentified aromatics had a greater relative content. Furthermore, the content of aromatic compounds in SFEO-SH rose more than that in SFEO-LH following SFE treatment, although the relative distribution of various aromatic compounds did not change considerably. Unidentified aromatic hydrocarbons accounted for 8–10% of them, which is greater than pentacyclic aromatic hydrocarbons and cannot be ignored.

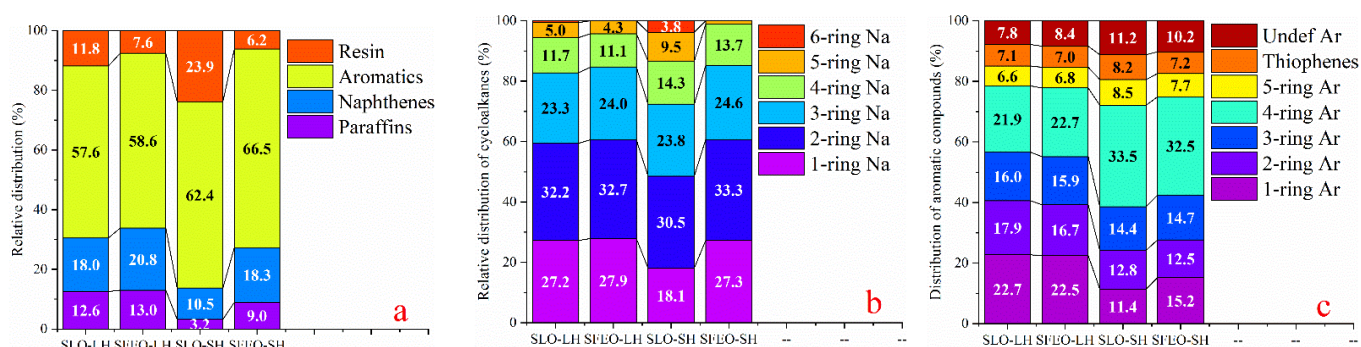


Figure 3. Hydrocarbon composition of SLO and SFEO by GC-MS. (a) Hydrocarbon composition (b) naphthenic hydrocarbon and (c) aromatic hydrocarbon.

High-temperature simulation distillation analysis was used to determine the boiling point distribution with a boiling point less than 750 °C, and the whole distillation range was divided into 10 fractions. The following temperature ranges are given: (1) <300 °C; (2) 300–350 °C; (3) 350–400 °C; (4) 400–450 °C; (5) 450–500 °C; (6) 500–550 °C; (7) 550–600 °C; (8) 600–650 °C; (9) 650–700 °C; (10) >700 °C. Figure 4 depicts the distribution of the two types of slurries' boiling points and the extraction oil's boiling points. Following SFE extraction, the components of 350–600 °C are found to be more narrowly focused: SFEO-SH (93.75%) > SLO-SH (90%) > SFEO-LH (70%) > SLO-LH. It is found that the boiling points of the slurry and the extracted oil are largely concentrated in the range of 350–600 °C (67.2%). After

supercritical extraction, the number of components with boiling points higher than 600 °C went down.

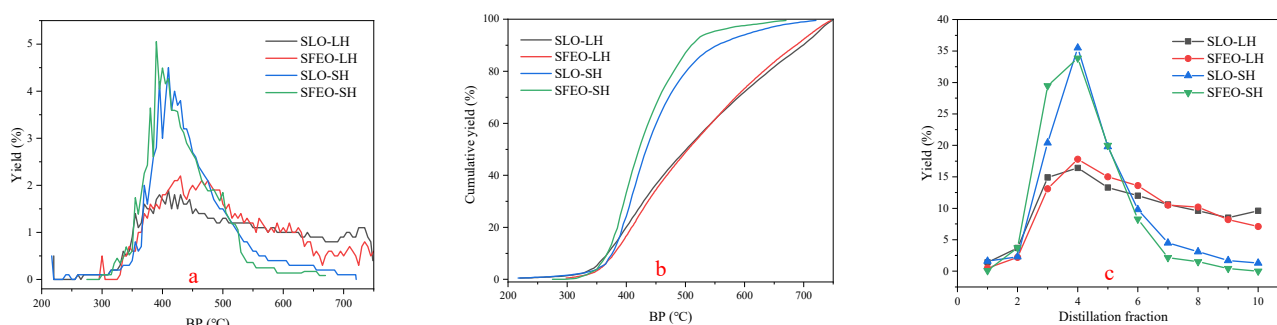


Figure 4. The boiling point distribution of SLO and SFEO ((a): yield; (b): cumulative yield; (c): the yield of distillation fraction).

According to the ^1H NMR spectra, the average molecular structure parameters of SLOs and SFEOs were calculated by the improved B-L method as shown in Table 4 [33]. When compared to SLO-SH, SLO-LH exhibits a larger alkyl carbon rate f_P , lower aromaticity f_A , and cycloalkyl carbon rate f_N , as well as a higher condensation degree, indicating that SLO-LH contains heavier components. This is consistent with the boiling point distribution analysis shown above. SFEO-SH has greater aromaticity f_A , aromatic ring R_A , and naphthenic-ring number R_N than SFEO-LH, although the alkyl carbon number is much lower. Furthermore, the condensation degree parameter of SFEO-SH is lower, indicating that the condensation degree in the component's average molecular structure is bigger.

Table 4. Average molecular structure parameters of SLO and SFEO obtained by H^1 -NMR.

Structural Parameter	SLO-LH	SFEO-LH	SLO-SH	SFEO-SH
f_A	0.33	0.33	0.63	0.50
f_P	0.45	0.49	0.14	0.25
f_N	0.22	0.18	0.23	0.26
H_{AU}/C_A	0.72	0.79	0.75	0.72
R_A	2.47	2.33	3.57	2.83
R_N	1.93	1.57	1.47	1.71
R_T	4.39	3.91	5.04	4.54
C_A	11.86	11.33	16.26	13.33
C_N	7.71	6.29	5.90	6.83
C_P	16.10	17.22	3.51	6.64

SFE with isobutane can remove components with large molecular mass, reducing the carbon number C_T in the average molecular structure and increasing the total ring number R_T and aromatic ring number R_A . The naphthenic carbon parameter is larger in SFEO-SH than in SFEO-LH, which may lower the SFEO condensation activity at the start of the process. SLO-SH contains more aromatic structures than SLO-LH. However, the aromatic compounds in SFEO-SH were reduced following extraction. It can be seen that isobutane has a certain separation impact on high aromatic compounds, which is consistent with the previous findings of Zhang that the aromaticity of SFEO is reduced [27].

Using an FT-ICR MS with an APPI ionization source, the molecular composition of the two types of slurry oil and their extraction oil was analyzed. The mass spectra of SLO and SFEO are shown in Figure 5. The molecular mass distribution of SLO-SH is more concentrated than that of SLO-LH. As shown, the number of heavier molecules decreases after SFE extracts SLO-LH and SLO-SH, but the center of distribution for SFEO-LH stays the same, with two centers at 240 and 400.

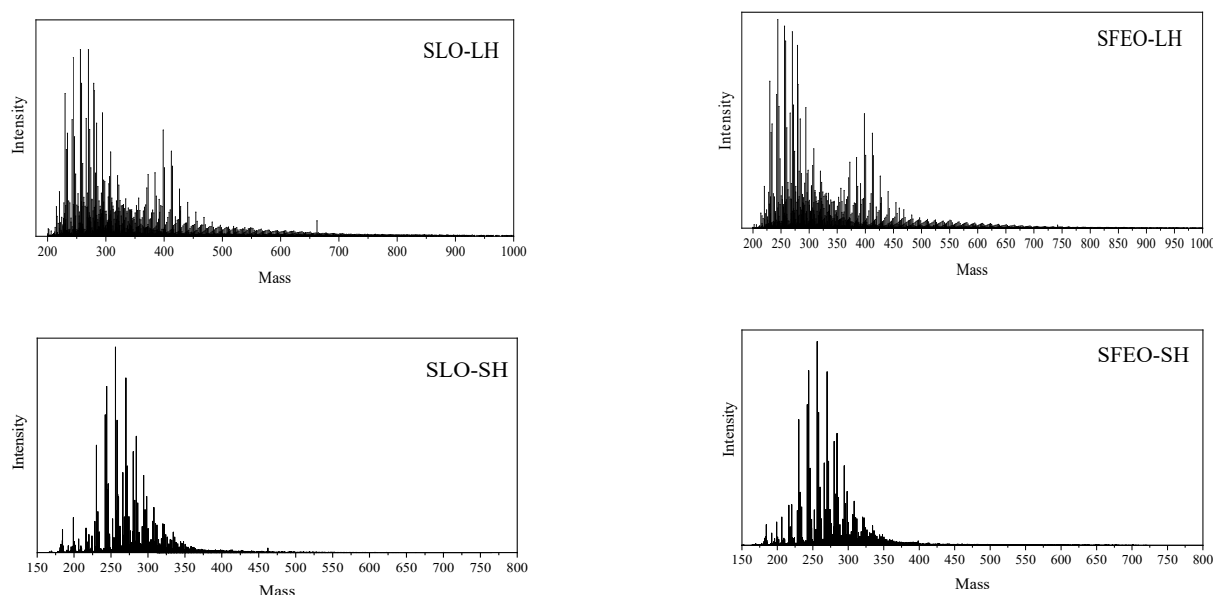


Figure 5. Mass spectra of SLO and SFEO were obtained by FT-ICR MS (APPI).

Figure 6 displays the distribution outcomes of CH compounds with various double bond equivalents (DBE) as well as the relative abundances of various compounds identified by APPI. It can be seen from Figure 6a,b that the contaminant compounds were partly eliminated, the proportion of CH compounds increased, and the proportion of higher condensation CH compounds declined in the two types of slurry oil after SLO-LH and SLO-SH were extracted by SFE. While the hydrocarbon compounds in SFEO-LH have two distribution centers, mostly at DBE = 5 and DBE = 12, those in SFEO-SH have a higher percentage and a narrower distribution, with the distribution center being about DBE = 3. The distribution of CH compounds was more narrowly focused, even though SFE did not alter the CH compound's distribution center. Supercritical isobutane has a greater separation efficiency for CH compounds with a DBE > 12 in SLO-SH compared to SLO-LH.

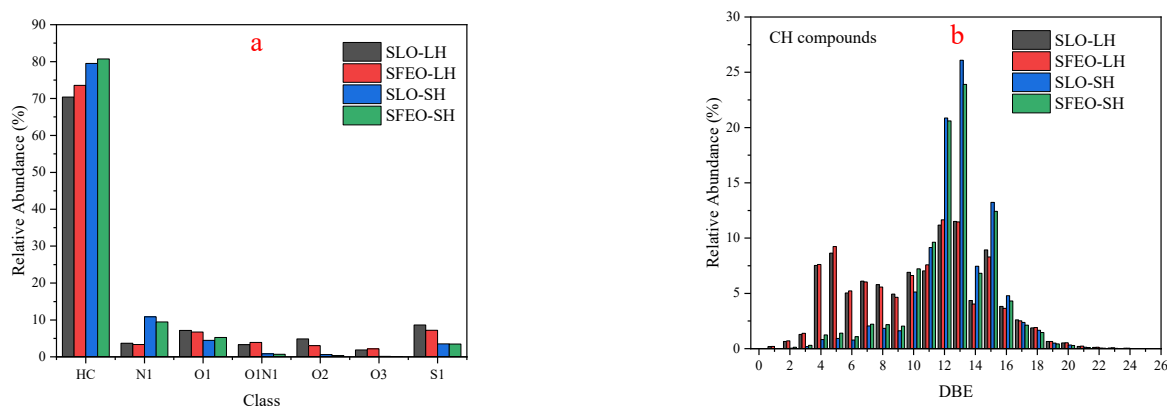


Figure 6. Relative abundance of various class compounds, (a,b) relative distribution of CH compounds with different condensation degrees in SLO-LH and SFEO (APPI).

The carbon number (NC)-DBE distribution of CH, O1, and S1 compounds in SLO-LH and SFEO-LH is shown in Figure 7. As can be shown, the distribution of carbon numbers in CH compounds ranges from 16 to 34, whereas DBE is 4 to 18, with the majority of them being hydrocarbons having 3–5 rings and alkyl side chains. After SFE extraction, the relative abundance of CH compounds with longer side chains was reduced, and the distribution of DBE was mainly between 4 and 20, while the range of NC in O1 compounds changed from 15–29 to 15–26. In SLO-LH, SFE eliminated oxygenated aromatic compounds with rings 5

and 6. In S1 compounds, the distribution of NC ranged from 15 to 24, whereas that of DBE ranged from 9 to 16. After SFE extraction, the distribution range of S1 compounds remained constant, although the relative abundance of naphthalene benzo-thiophene compounds with short side chains (DBE = 12) increased in SFEO-LH.

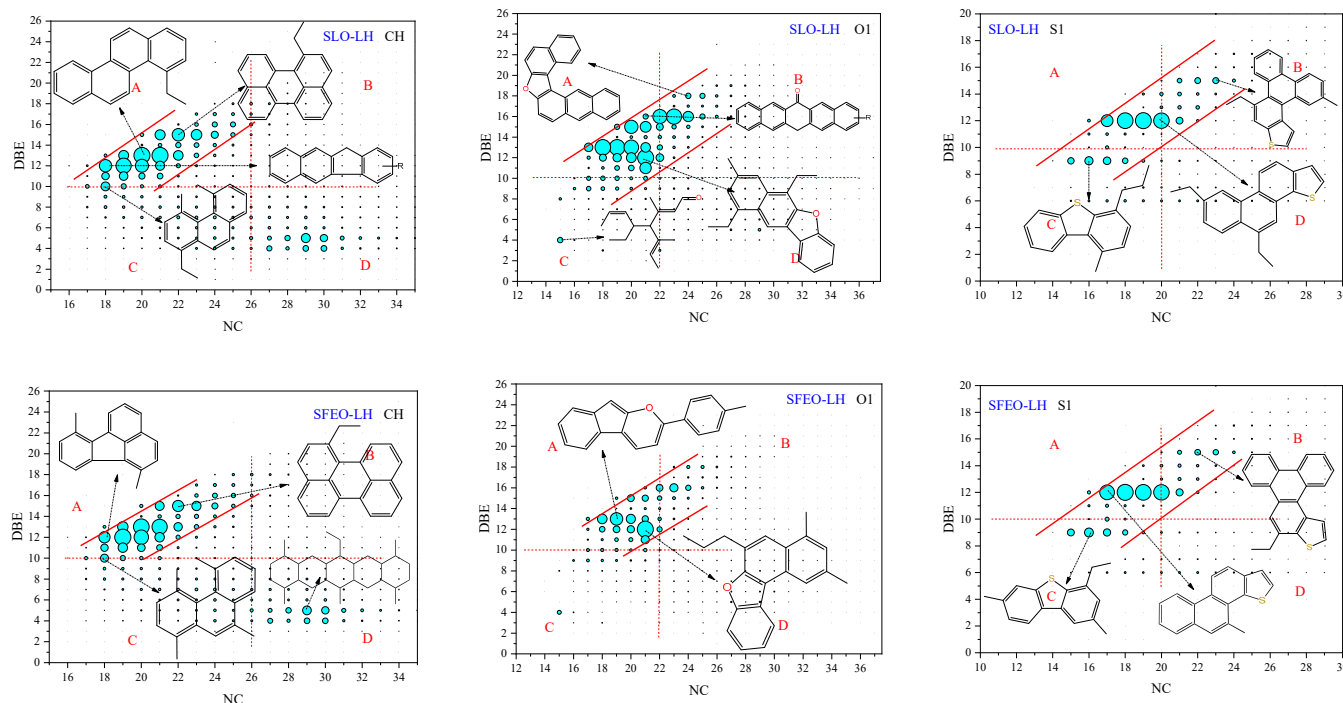


Figure 7. NC-DBE distribution of compounds in SLO-LH and SFEO-LH (APPI). (NC, number of carbon; DBE, double bond equivalents, The NC regions of CH, O1 and S1 compounds are demarcated at 26, 22, and 20, respectively. The DBE regions of CH, O1, and S1 compounds are demarcated at 10. For example, CH compounds in the A region (NC < 26 and DBE > 10)).

The NC-DBE distribution of CH, O1, and S1 molecules in SLO-SH and SFEO-SH is shown in Figure 8. The CH compounds are dominated by 3–5 rings of aromatic hydrocarbons with alkyl side chains. The NC distribution spans 18 to 24, while the DBE distribution spans 11 to 15, primarily in the A region. After SFE extraction, the relative abundance of highly condensed CH, S1, and O1 compounds dropped. The distribution of DBE is 12–16 and that of NC is 18–25 in O1 compounds. The distribution of DBE was 9–16 and that of NC was 16–24 in S1 compounds. After extraction, the relative abundance of compounds with a higher degree of condensation was determined. In summary, SFE may effectively separate O1 and S1 compounds with high condensation degrees from the two types of slurries, increasing the concentration of CH compounds while scarcely modifying their dispersion state.

High-resolution mass spectrometry in association with a +ESI ionization source was used to investigate the structures of SLO and SFEO to fully understand the separation effect of supercritical extraction on various polar heteroatomic compounds in slurry oil. In Figure 9, the mass spectrum is displayed. The compounds with high molecular mass and small molecular mass in SLOs have been reduced by SFE, making the molecular composition distribution in SFEOs narrower. It is found that the NC distribution of polar heterocyclic compounds in SLO-LH is wider than that in SLO-SH. The supercritical extraction efficiency of the two types of oil differed. With isobutane as the solvent, more components with molecular weights larger than 600 were extracted from SLO-SH than from SLO-LH.

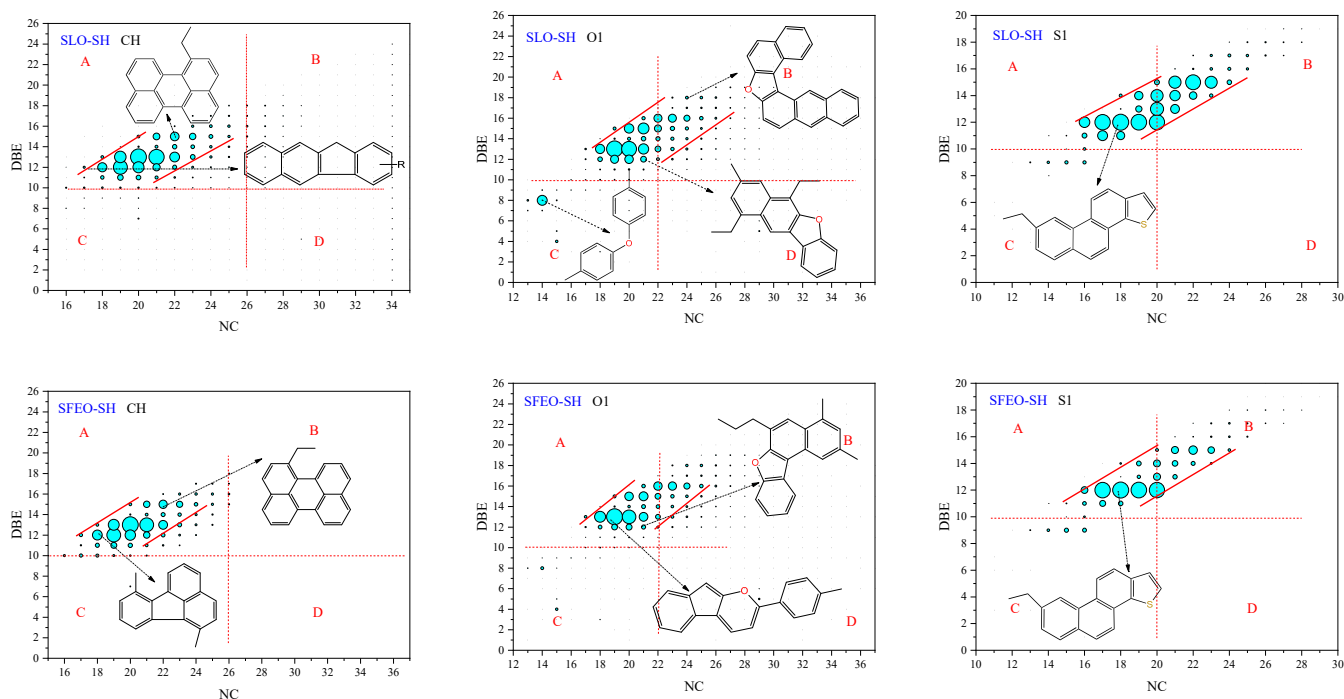


Figure 8. NC-DBE distribution of compounds in SLO-SH and SFEO-SH(APPI). (NC, number of carbon; DBE, double bond equivalents, The NC and DBE regions of CH, O1 and S1 compounds are demarcated at 26, 22, and 20, respectively. The DBE regions of CH, O1, and S1 compounds are demarcated at 10. For example, CH compounds in the A region ($NC < 26$ and $DBE > 10$)).

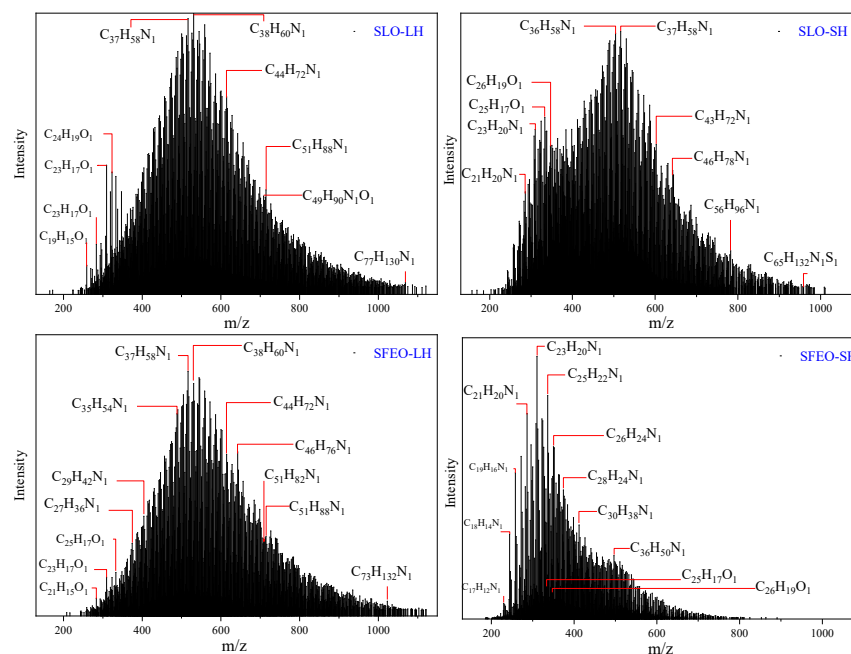


Figure 9. Mass spectra of SLO and SFEO were obtained by FT-ICR MS. (+ESI).

Figure 10 depicts a comparison of the types and relative abundances of various chemicals in the two types of slurry oil and its extraction oil. It can be noted that nine different kinds of heterocyclic compounds were found, including N1, O1, O1S1, N1O1, and N2 compounds, with the N1 compound having the largest relative abundance, followed by N1O1 and O1. Heteroatoms can enhance reaction activity and so generate a wide variety of intermolecular crosslinks, affecting mesophase development [34,35]. SLO-LH contains

more heteroatoms than SLO-SH. After SFE treatment, the relative amount of heteroatomic compounds, such as O1, N1O1, and O1S1, in SFEO went down.

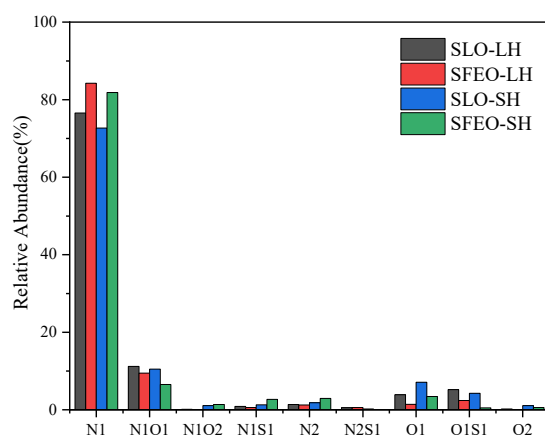


Figure 10. The relative abundance distribution of main heteroatomic compounds was detected characterized by FT-ICR MS(+ESI).

The DBE distributions of N1, O1, and N1O1 compounds are given in Figure 11 to clarify the variations in the distribution of heteroatomic compounds with varying DBE in SFEO following supercritical extraction of SLO. The relative abundance of N1, O1, and N1O1 compounds with DBE > 23 in SFEO-SH decreased, and the distribution centers of these compounds in SFEO shifted towards lower DBE. To clarify the molecular structure of N1, O1, and N1O1 compounds, the NC-DBE distribution of N1 compounds in two SLOs and their SFEOs is shown in Figures 12 and 13.

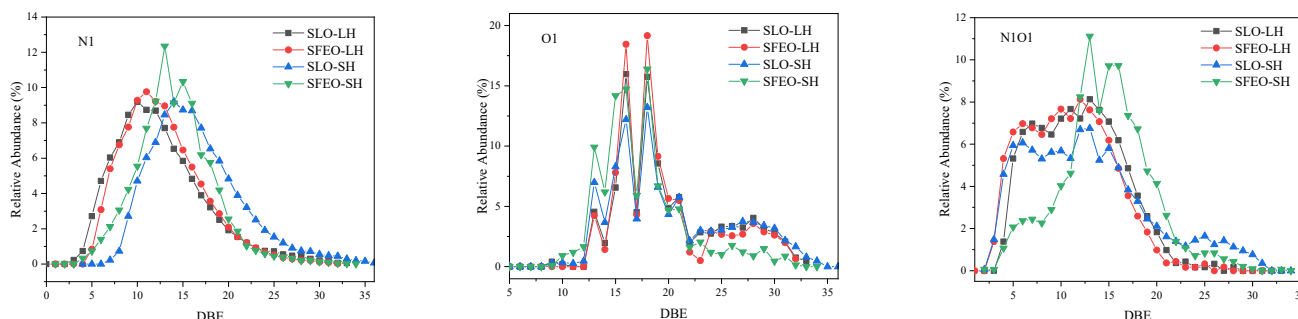


Figure 11. Relative abundance distribution of DBE for three species (N1, O1, N1O1) in SLO and SFEO (+ESI).

It can be observed that following SFE extraction, the NC range of N1 compounds remained constant at 20 to 80, while the DBE range changed from 4 to 30 (DBE = 4) to 4 to 32 (DBE = 10), with the highest concentrations being $C_{38}H_{59}N_1$ and $C_{36}H_{57}N_1$ (DBE = 10). It is speculated to be a long side-chain molecule with an aromatic ring serving as the core and pyridine as the center. Figure 14a depicts the three-dimensional molecular structure of the acridine compounds it represents. The abundance of the region (DBE > 20, NC45) in the N1 compound dropped after SFE treatment. The NC range of the O1 compound was changed from 19–47 to 19–45 after SFE extraction, while the DBE range was changed from 13–34 to 13–32. $C_{23}H_{16}O_1$ (DBE = 16) was speculated to be three-dimensional molecular structure diagrams of ketone compounds with polycyclic aromatic hydrocarbons as the core, as seen in Figure 14c. After SFE treatment, the relative abundance of O1 compounds (NC < 45, DBE > 20) in the D region dropped. The DBE range in N1O1 compounds changed from 3–31 to 3–27, and the NC range changed from 20–57 to 20–55. The proportion of $C_{38}H_{53}N_1O_1$ (DBE = 13) was rather high, and the three-dimensional molecular structure of ketone compounds with extended side chains centered on phenanthridine is presented

in Figure 14e. After SFE treatment, the higher degree of condensation of the N1 compound (DBE > 20) was lowered.

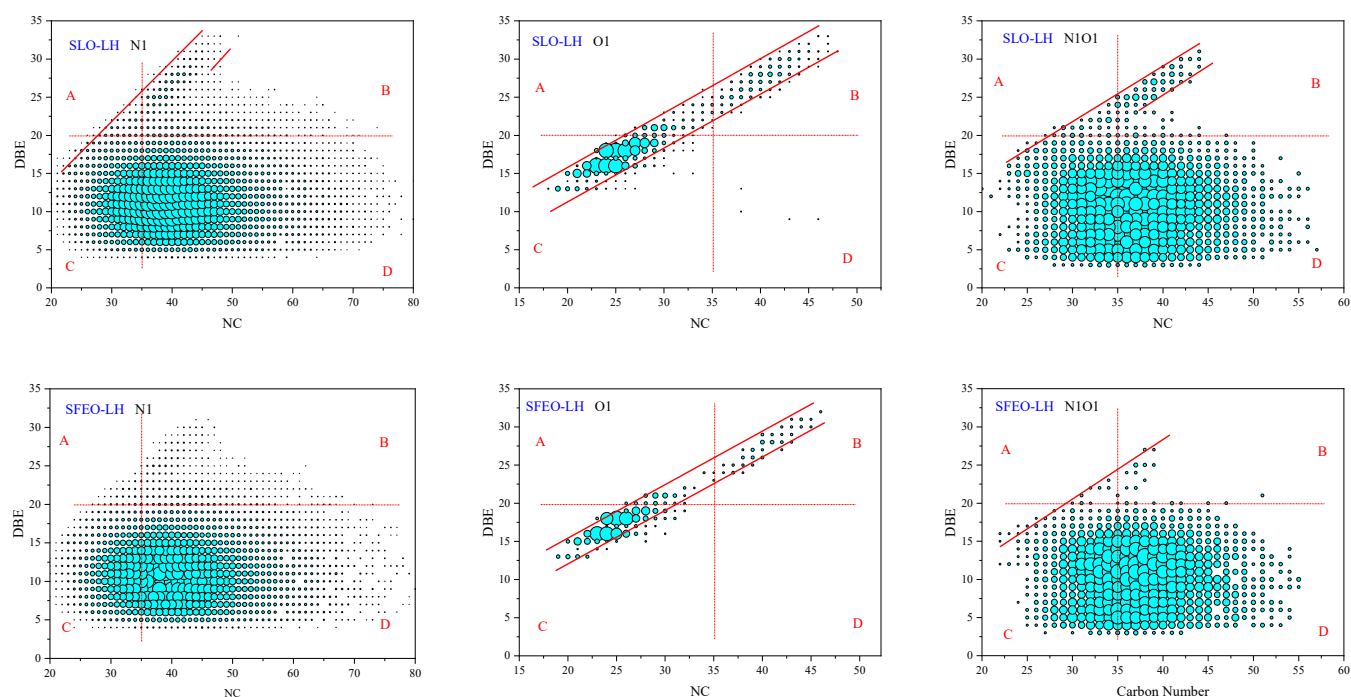


Figure 12. NC-DBE distribution of compounds in SLO-LH and SFEO-LH detected by FT-ICR MS (+ESI). (NC, number of carbon; DBE, double bond equivalents. The NC and DBE regions of N1, O1, and N1O1 compounds are demarcated at 35. The DBE regions of N1, O1, and N1O1 compounds are demarcated at 20. For example, N1 compounds in the A region (NC < 35 and DBE > 20)).

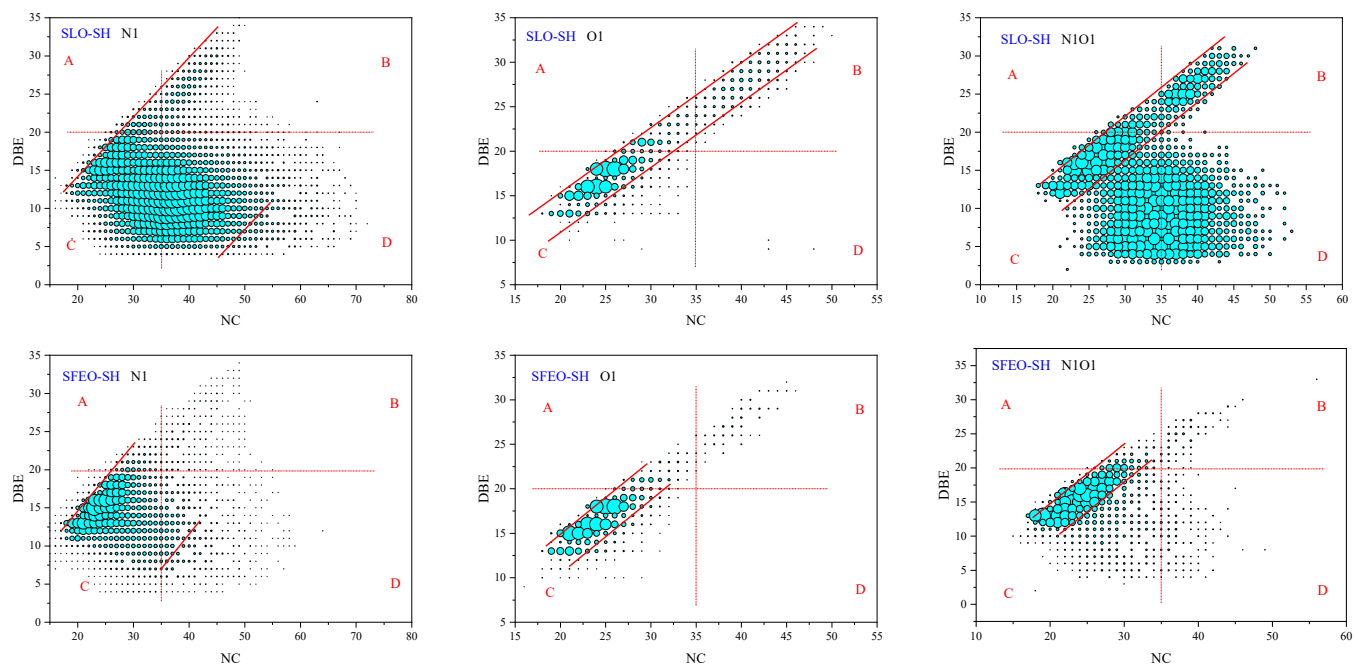


Figure 13. NC-DBE distribution of compounds in SLO-SH and SFEO-SH detected by FT-ICR MS(+ESI). (NC, number of carbon; DBE, double bond equivalents. The NC and DBE regions of N1, O1, and N1O1 compounds are demarcated at 35. The DBE regions of N1, O1, and N1O1 compounds are demarcated at 20. For example, N1 compounds in the A region (NC < 35 and DBE > 20)).

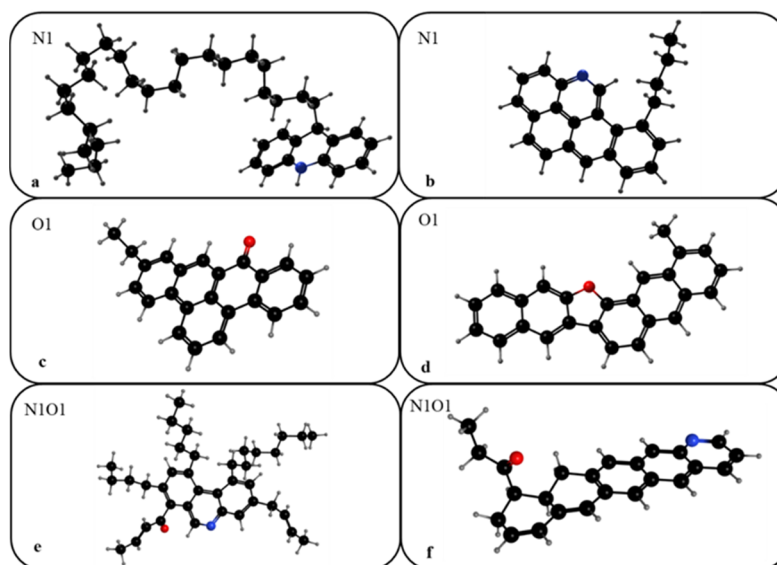


Figure 14. The 3D molecular structure of several representative heteroatom compounds. (SLO-LH and SFEO-LH: (a,c,e); SLO-SH and SFEO-SH: (b,d,f). The red balls represent oxygen atoms and the blue balls represent nitrogen atoms.).

According to the distribution of NC-DBE of various compounds in SLO-SH and SFEO-SH in Figure 13, the range of DBE of N1 compounds did not change from 5 to 34, while the range of NC changed from 17–70 to 17–59. $C_{23}H_{19}N_1$ (DBE = 15) possesses the highest content of SFEO-SH and is suggested to be a nitrogen-containing pentacyclic aromatic compound along with butyl. After SFE, highly condensed N1 compounds with DBE > 20 in SLO-SH were eliminated. The NC range of the O1 compound was changed from 19–48 to 18–45, while the DBE range was changed from 11–34 to 11–31. The most abundant compound was $C_{25}H_{16}O_1$ (DBE = 18), which was speculated to be a compound with a core of furan and polycyclic aromatic hydrocarbons. Figure 14d depicts a three-dimensional molecular structure diagram. O1 compounds with NC > 30 and DBE > 20 were separated after SLO-SH was treated with SFE. For N1O1 compounds, the DBE range changed from 3–32 to 4–30, and the NC ranged from 18–52 to 16–45. It was speculated that the $C_{24}H_{21}N_1O_1$ detected in SLO-SH (DBE = 15) was a ketone compound with the N-containing pentacene as its core. Figure 14f displays its molecular structure diagram in three dimensions. The N1O1 compounds in the lower DBE region (DBE < 20 and NC > 25) were separated after SFE treatment.

In the same DBE range of the two SLOs, the NC ranges of O1 compounds were much lower than those of N1 and N1O1 compounds, which is caused by the shorter side chains of O1 compounds. The high condensation degree O1 compounds in SLO-SH are extracted by SFE, and the separation efficiency is higher. The compounds with multi-directional stretching flatness changes affect the orientation of the polymerization and the ordered arrangement of the mesophase pitch, which will cause major variances in the mechanical, optical, and thermal characteristics. SLO-SH has more N1 and N1O1 compounds with short side chains and higher DBE than SLO-LH, and the molecular structure shows higher flatness. The separating effectiveness of SFE technology on compounds containing heteroatoms with higher condensation in SLO was consistent with the findings that the total number of rings in SFEO in ^1H -NMR dropped, as did the aromaticity and condensation degree. Therefore, the SFE separation efficiency of heterocyclic compounds was much higher than that of CH compounds. SFE reduces the content of heteroatom-containing compounds and narrows the distribution range of NC-DBE by eliminating heteroatom-containing compounds with higher condensation, resulting in a more concentrated distribution of CH compounds, but it cannot fundamentally change the dispersion status of CH compounds.

3.3. Effect of Supercritical Fluid Extraction on Mesophase Structure and Performance

Under the same conditions, thermal polycondensation processes were performed on the slurry and its extraction components to investigate the effect of supercritical fluid extraction on mesophase structure and performance. The carbonization-produced mesophase pitch is denoted as MP-LH, MP-SH, MP-LHSFEO, MP-SHSFEO, MP-LHSFER, and MP-SHSFER, respectively. The yield of mesophase pitch is represented by the yield of toluene insoluble (TI) after the carbonization reaction. Figure 15 depicts the results of TI yield and mesophase content obtained by the carbonization of slurry oil and its extraction components.

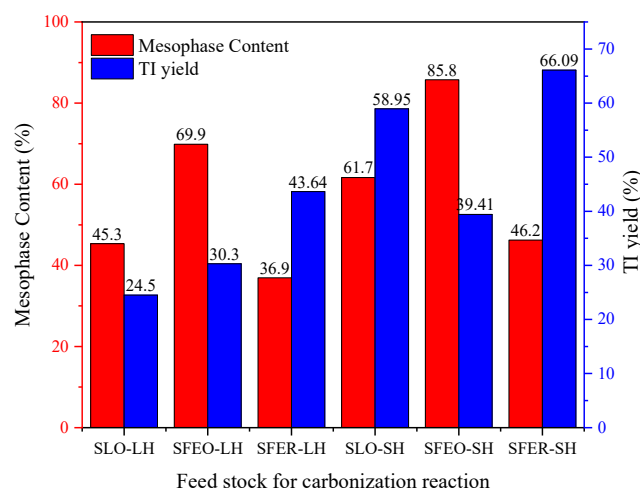


Figure 15. The diagram of TI yield and mesophase content.

Combined with the previous investigation, it was discovered that the molecular weight of SLO-LH with a scattered molecular composition distribution was larger than that of SLO-SH, while carbonization products with lower TI yield and lower mesophase content were formed. During the reaction, aromatic hydrocarbons with long side chains will be pyrolyzed. After carbonization, polycyclic aromatic hydrocarbons with short side chains in SLO-SH produce a mesophase pitch with a greater yield. Although the yield of the TI product of SFEO-SH was reduced, the mesophase content of the carbonation products obtained after SFE treatment was optimized. It is worth noting that SFE narrows the SFEO composition distribution by removing components with larger and smaller molecular masses, increasing the content of the mesophase. The TI yields of products produced by carbonizing SFER-LH and SFER-SH with heavy extractive components were greater than those of SLO-LH and SFEO-SH, but the mesophase content was low since SFER, which enriches more heteroatomic molecules with high DBE but poor flatness, cannot be stacked in an orderly manner to generate less anisotropic structures.

Figure 16 shows SEM images of the carbonized solid products of SLO, SFEO, and SFER, which reveal that the morphology of the solid products varies. MP-LH showed irregular blocky solids with a rough surface and an unobvious layered structure. MP-SH had more noticeable layered structures and less internal structural adhesion than MP-LH. Most of the layers in MP-LHSFEO are more visible and have better orientation, dense interlayer spacing, and smoother surfaces than in MP-LH. Small particles with no noticeable adherence on the surface were seen in MP-SHSFEO after SFE treatment, and the block's lamellar layer was more apparent with an orderly orientation.

A considerable number of unsmooth surfaces and unobvious layered structures were observed in the carbonized solid products MP-LHSFER and MP-SHSFER of supercritical extractives, along with apparent adhesion within the solid particles. Because of the presence of heteroatoms in SFER, chemical polarity becomes the dominant cohesive force, disturbing the parallel stacking process of polycyclic aromatic hydrocarbons, and a lower graphitization degree may correspond to a less lamellar stripe structure [36]. Detaching a

certain number of heteroatomic compounds helps mesophase spheres melt smoothly into the bulk mesophase with a smooth surface.

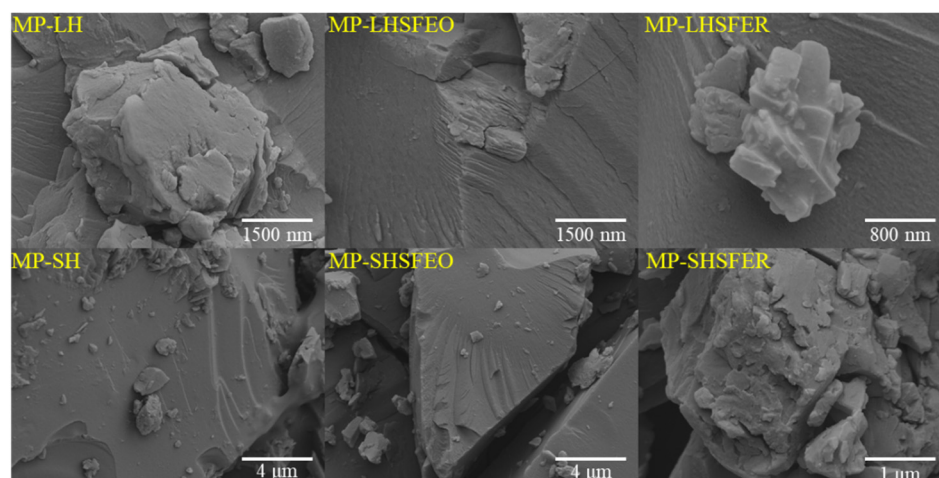


Figure 16. SEM images of SLO and SFE thermal conversion products.

Figure 17 depicts the polarization images of the mesophase of SLO and extracted fractions. MP-LH features more mosaic structures, whereas MP-SH has a large-area bulk mesophase. After SFE, the anisotropic structures in MP-LHSFEO and MP-SHSFEO were significantly superior to those in MP-LH and MP-SH. SLO-LH has a scattered hydrocarbon composition, with many more nitrogen and oxygen-containing heterocyclic aromatic hydrocarbons with long side chains, high molecular weight, high DBE, and poor flatness. SLO-LH included acridine chemicals, according to the aforesaid analysis. Mochida proposed that the presence of nitrogen-containing compounds, such as acridine compounds, would cause a large amount of naphthenic hydrogen in the raw material to be struggled with in the early carbonization process, making the π - π interaction of PHA become a strong polar dipole–dipole interaction, and the increase in the insolubility of the mesophase pitch was not favorable to planar stacking [37,38]. In polycyclic aromatic hydrocarbons with substantial steric hindrances, it is difficult to form a broad area of an ordered planar structure in the early stage of carbonization, and a mesophase pitch with poor orientation is formed in a high viscosity environment. Mesophase's optical structure will affect the electrothermal properties of carbon-based materials, such as carbon fiber and needle coke.

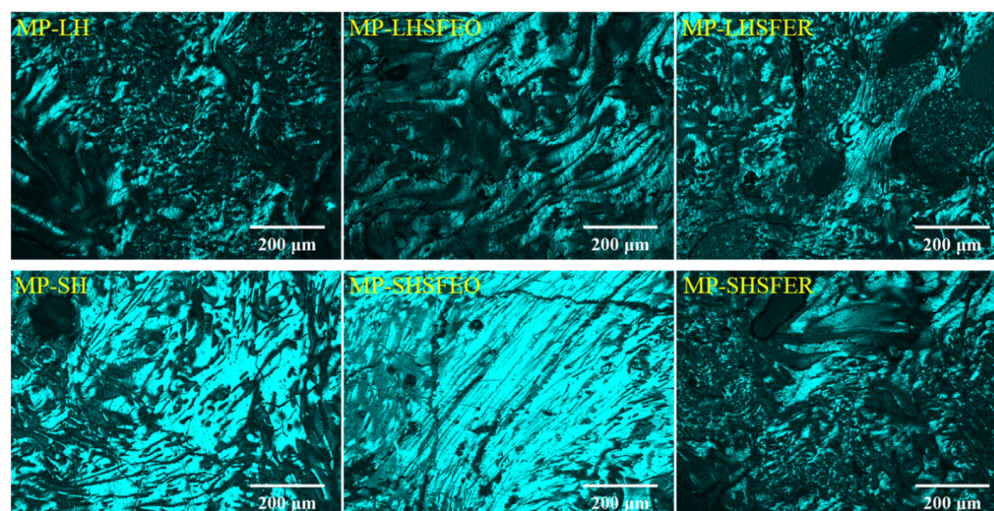


Figure 17. Polarized microscope images of several mesophase pitches.

Figure 18 depicts the anisotropic texture distribution of the two types of slurries and their extraction components in the mesophase. Compared to MP-LH and MP-SH, MP-LHSFEO and MP-SHSFEO have a less-pronounced mosaic texture, the relative abundance of FD (l) ($>300\ \mu\text{m}$) is higher, and the anisotropy of the bulk mesophase is stronger. The polarized images of MP-SHSFEO show larger bulk mesophase, better anisotropic orientation, and internal structural orderliness when compared to MP-LHSFEO. The mosaic structure is hardly noticeable in the texture of solid products, and the FD (l) type ($>300\ \mu\text{m}$) accounts for 97% of all textures, which is more consistent with the more apparent layered orientation of MP-SFEO showed in SEM. A better anisotropic texture in mesophase products often leads to lower coefficients of thermal expansion (CTE) values [39]. The two MP-SFERs showed a few FD (l), but the mosaic (less than $20\ \mu\text{m}$) and F-Type ($20\text{--}60\ \mu\text{m}$) structures presented more, which was consistent with the findings of the SEM pictures.

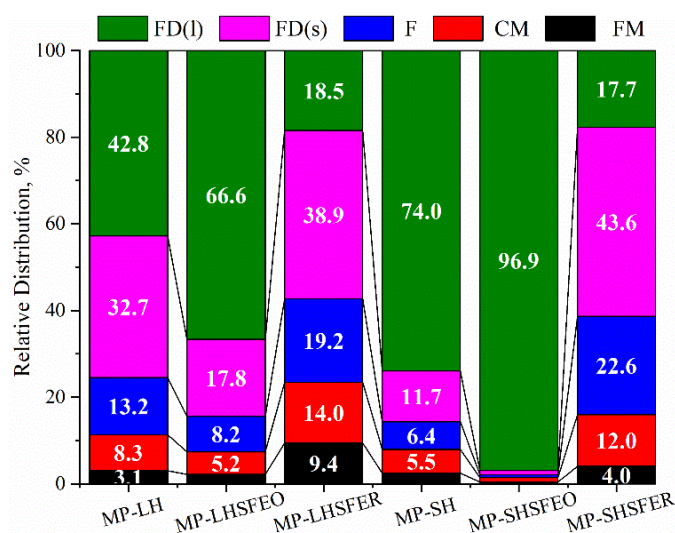


Figure 18. Anisotropic texture distribution of several mesophase pitches.

The carbonaceous mesophase's structure is similar to that of a crystal. The microstructure of several mesophase pitches was analyzed using XRD and Raman, as shown in Figure 19a,b and Table 5. The interlayer spacing of the (002) peak of MP-SFEO is smaller than that of the two MP-SLOs. The interlayer spacing of MP-SHSFEO is about $0.344\ \text{nm}$, while that of MP-LHSFEO is about $0.347\ \text{nm}$.

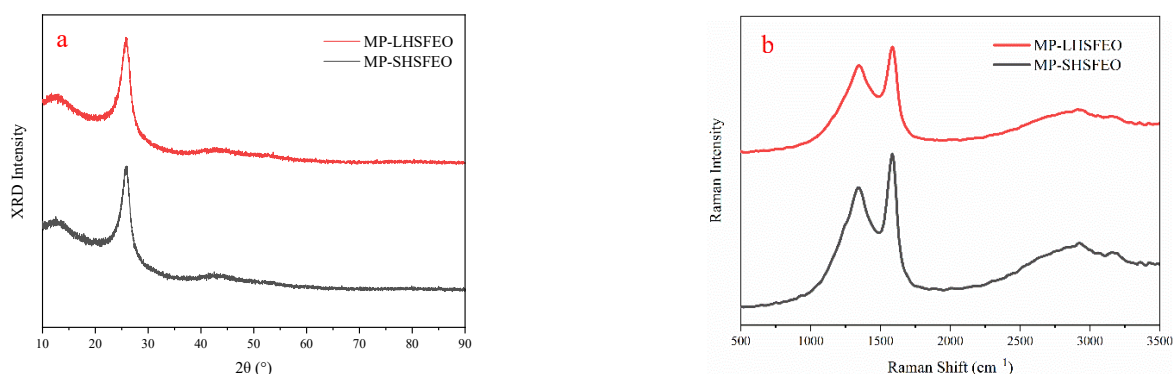


Figure 19. XRD (a) and Raman (b) spectra of MP-SFEO.

Raman spectra typically contain G peaks ($1580\ \text{cm}^{-1}$) indicating perfect graphite and D peaks ($1360\ \text{cm}^{-1}$) representing disordered carbon. Previous studies have shown an inverse relationship between the degree of graphitization of the material and the strength ratio of the D peak to the G peak. As the I_D/I_G value decreases, so does the disordered

structure [40,41]. MP-LHSFER has the greatest I_D/I_G ratio at 2.07, indicating a low degree of graphitization. MP-SHSFEO has the lowest I_D/I_G ratio at 1.35. Several mesophase pitch products were evaluated for resistivity. The resistivity of the two types of SFEO carbonization products was lowered when compared to MP-SLO. MP-SHSFEO has the lowest resistivity of 10.135 m Ω ·m and MP-SLHSFEOR has the maximum resistivity of 1340.9 m Ω ·m. This is consistent with the polarization and SEM results, which demonstrate that supercritical isobutane extraction may enhance the structure and performance of the mesophase pitch by optimizing the composition distribution in SLO.

Table 5. Structural performance parameters of several mesophase pitch.

Sample	L_C /nm	L_a /nm	d_{002} /nm	Resistivity/m Ω ·m	I_D/I_G
MP-LH	2.9612	1.7498	0.3474	19.959	1.82
MP-LHSFEO	2.9484	1.2546	0.3470	16.805	1.48
MP-LHSFER	2.6938	1.4335	0.3475	1340.910	2.07
MP-SH	3.0452	1.3407	0.3469	13.121	1.64
MP-SHSFEO	2.9700	2.2157	0.3444	10.135	1.35
MP-SHSFER	2.8214	1.2974	0.3470	1131.1	1.67

4. Discussion

Raw materials having a high ash content and heteroatom content are thought to provide lower-quality products. However, studies have revealed that SLO-LH has fewer ash heteroatoms, resulting in inferior product quality, whereas SLO-SH has more molecular planarity, resulting in a better structure of the mesophase product. The higher molecular planarity of the compounds in SLO-SH results in a better structure of the mesophase product. Due to the difficulty of parallel accumulation of three-dimensional structural macromolecules insoluble in the matrix, which results in the obstruction and dislocation of grain boundaries, heterocyclic aromatic hydrocarbons with high molecular mass and high DBE have high reactivity and seem to be difficult to form the FD (I) texture. When the two SLOs were compared, it was discovered that the overall composition of the feedstock and the planarity of various compounds contributed more to the structure of the mesophase. SLO-LH had lower viscosity than SLO-SH at 50 and 100 °C (before the reaction), but MP-LH had more mosaic structures, indicating that the viscosity throughout the reaction process had a greater influence than the beginning viscosity. To guarantee appropriate flowability and allow for ordered stacking of the carbonaceous molecules, the carbonation speed must be moderate enough. The balance between mild growth and fusion, which is governed by the viscosity of the carbonized matrix before hardening, determines the size and form of anisotropic units [42]. SLO-SH includes more polycyclic cycloalkanes, and the hydrogen donating of cycloalkanes during the reaction may lower viscosity, allowing for the creation of ordered textures. More saturated hydrogen is detected on the long side chains of SLO-LH and SFEO-LH, which are commonly broken during the early carbonization level to create a gas escape system, making it challenging to provide transferrable hydrogen and unable to reduce high reactivity. The early formation of highly condensed macromolecules renders them intractable in the carbonized matrix, boosting viscosity throughout the process. However, the mesophase's performance cannot be predicted only by the source material's molecular mass or viscosity. The distribution of molecular composition and the impact of viscosity during the reaction must be thoughtfully taken into account, yet it is challenging to keep track of the viscosity as the reaction progresses. Additional crosslinking increases the hardness of the interface between mesophase spheres, which hinders rearrangement and tends to form isotropic structures, and more microstructures with larger interlayer spacing and disorder are formed. This happens when many heteroatoms substitute the carbon atoms of aromatic molecules [43]. To handle the orderly development of the mesophase at a high solubility, the heteroatom-containing compounds in the composition slurry are separated utilizing SFE technology. This makes the precursor less likely to react at the beginning of the carbonization process. After the SFER

and SFEO are removed by the SFE technology, the composition distribution of SFEOs is more narrowed and hetero compounds are fewer. The interlayer spacing of MP-SFEO is reduced, the disordered structure is reduced, and the degree of graphitization is higher. The distribution is more concentrated, the compound distribution is more layered, the orientation is better, the interlayer spacing is dense, and the surface is smoother.

5. Conclusions

Two types of SLO were extracted by supercritical fluid extraction using isobutane as the solvent, and the ash in SFEO was eliminated. SFE successfully separated N1, O1, and N1O1 polycyclic aromatic hydrocarbons with higher condensation degrees, increasing the hydrocarbon concentration and narrowing the composition distribution. SFE technology was used to produce two types of SFEO, and the anisotropic texture of the mesophase pitch was optimized. The fraction of FD (I) structure increases, and the microstructure becomes more ordered. The performance test findings showed that MP-SHSFEO and MP-LHSFEO had better graphitization degrees and lower resistivity. The correlation between feedstock composition and carbonation products indicated that SLO-SH contained heterocyclic aromatic compounds with high DBE and flatness, showing strong synchronism in the thermal polycondensation reaction system and generating more orderly flow type structures. Many heterocyclic aromatic molecules with long side chains, such as acridine compounds, were easily condensed into macromolecules that are difficult to stack in parallel, affecting the flatness of the entire system to cause mosaic and inhibiting the development of mesophase pitch.

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