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Preparation of Mesophase Pitch through Supercritical Fluid Extraction of Coal Tar Pitch

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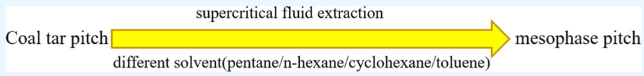
ABSTRACT: This paper explores the preparation of mesophase pitch by employing supercritical fluid extraction on coal tar pitch sourced from a coal chemical company. The raw material undergoes pretreatment using various extraction solvents, and the resulting refined components are thermally polycondensed in a laboratory microreactor to create mesophase pitch. Qualitative and quantitative analyses of the mesophase pitch's structure are conducted through polarized light microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and other analytical methods to identify an optimal supercritical fluid extraction pretreatment solvent for coal tar pitch. The results reveal that using *n*-hexane solvent in the supercritical fluid extraction process yields a mesophase pitch with a remarkable mesophase content of 90.07%, displaying excellent optical texture distribution, superior directional arrangement and order, the closest lamellar accumulation, and the highest degree of anisotropy and graphitization.



1. INTRODUCTION

China offers the highest coal reserves among its three major fossil resources.[1−3] Coal tar pitch, constituting approximately 50−60% of the total coal tar after the removal of liquid fractions, is a complex mixture of organic compounds.[4] Unfortunately, much of the coal tar pitch is currently limited to basic building materials and low-value-added applications like heavy fuel oil,[5−7] resulting in a significant waste of resources. This underutilization is problematic, considering that coal tar pitch has abundant resources, affordability, rich carbon content, low ash content, stable performance, excellent adhesion, high coking residual carbon value, and a propensity for easy graphitization. These characteristics make it a prime raw material for producing a wide range of carbon materials.[8,9] Consequently, it is imperative to address the challenge of efficiently utilizing and enhancing the value of the coal tar pitch.

Carbonaceous mesophase,[10,11] a nematic liquid crystal material with disk-like or rod-like molecular structures (average relative molecular mass of around 2500), is produced through the thermal polycondensation of polycyclic aromatic hydrocarbons. It was first identified by Brooks and Taylor.[12,13] Mesophase pitch offers outstanding properties, including easy graphitization and a high carbon residue rate, making it a crucial resource in various sectors, including national defense and everyday life. Thanks to its affordability and abundant sources, mesophase pitch is widely used in producing a variety of vital advanced carbon materials.[14,15] As a significant precursor for high-quality carbon materials, the properties of mesophase pitch significantly influence the properties of carbon materials, underscoring the importance of studying mesophase pitch.[16−18]

The composition of raw materials has a profound impact on the structure of the mesophase pitch. It is generally recommended that raw materials contain 30−50% aromatic content, possess 2−4 aromatic rings,[19−21] and exhibit minimal side chains,[22,23] particularly a linear arrangement of tricyclic and tetracyclic short side-chain aromatics. The greater their content, the better the outcome.[24,25] Therefore, raw material pretreatment is the primary process in mesophase pitch preparation. Zhongming et al.[26] achieved asphalt with a suitable softening point and molecular weight distribution through the flash evaporation−thermal polycondensation combination method, which has been industrialized. However, the control conditions are relatively stringent, limiting the prolonged production. Wu et al.[27] employed a solvent method to obtain refined asphalt with uniform molecular weight distribution and suitable aromaticity, making it a suitable raw material for high-quality needle coke production. Nevertheless, this method has high production costs, low processing capacity, and a complex operation process. Guo et al.[28] found that the solvent-hydrogenation method offers the advantages of low hydrogen consumption and high-quality refined raw materials, enabling the production of premium needle coke, although this method remains in the laboratory research phase. In comparison to the above references, it is evident that traditional raw material pretreatment methods have certain shortcomings. Consequently, it remains crucial to

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explore a rational and stable approach to raw material pretreatment.

In this article, coal tar pitch from a coal chemical company was utilized as the raw material. The raw material was subjected to supercritical fluid extraction[29−31] with various extraction solvents for pretreatment. The raw material and refined components were then subjected to thermal polycondensation in a laboratory microreactor to produce mesophase pitch. A comprehensive structural analysis of the mesophase pitch was conducted using a polarizing microscope, X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and other analytical methods to identify an optimal supercritical fluid extraction pretreatment solvent for coal tar pitch.

2. EXPERIMENTAL SECTION

2.1. Pretreatment of Coal Tar Pitch by Supercritical Fluid Extraction. Figure 1 presents the flowchart of the continuous supercritical fluid extraction pilot experimental device, with a processing capacity of 30 kg/h for raw materials. The device comprises a solvent and residue preheating and metering system, extractor, heavy deoiling sedimentation tower, and solvent recovery system. In the experiment, the hot solvent from the solvent heating furnace and the heated raw material from the raw material tank were mixed in a predetermined ratio and introduced into a section of the extractor. The deoiled asphalt settled and was separated from the deasphalted oil, which was then discharged from the bottom of the extractor. The deasphalted oil ascended to the preset temperature in the second-stage heating furnace, and it subsequently entered the second-stage separator. The heavy components in the deasphalted oil further precipitated from the solvent phase, entered the buffer tank as heavy deoiling, and the solvent in this process was recovered. The light deoiling, coming from the top of the separation tower, entered the solvent separator through depressurization, and the solvent was heated, evaporated, and cooled back to the solvent tank. The light deoiling was obtained at the bottom of the separator. The raw material refining components used in the preparation of mesophase pitch consist of heavy deoiling and light deoiling mixed oils.

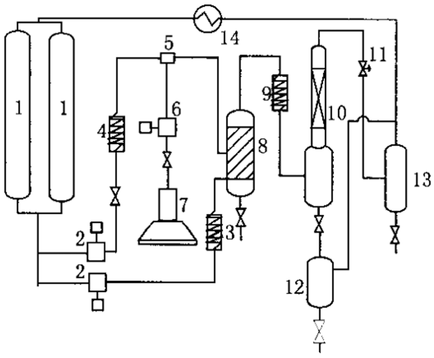

Figure 1. Schematic flow diagram of the pilot supercritical fluid extraction experimental device. Note: 1—Solvent tank, 2—Solvent pump, 3—Secondary solvent heating furnace, 4—Main solvent heating furnace, 5—Mixer, 6—Raw material pump, 7—Electronics, 8—Primary extractor, 9—Secondary heating furnace, 10—Secondary separator, 11—Pressure regulator, 12—Heavy deoiling solvent separator, 13—Light deoiling solvent separator, 14—Cooler.

In this experiment, coal tar pitch from a coal chemical company served as the raw material, and *n*-hexane, pentane, cyclohexane, and toluene were used as extraction solvents, respectively. The raw material underwent a supercritical fluid extraction pretreatment. The performance indicators of the raw material and refined components after extraction are displayed in Table 1, group composition analysis is presented in Table 2, and elemental analysis is shown in Table 3.

2.2. Preparation of Mesophase Pitch. The mesophase pitch was prepared using the thermal polycondensation method in a laboratory microreactor, as illustrated in Figure 2. Approximately 8 g of the raw material or refined components was weighed and placed into a high-temperature and high-pressure reactor. The temperature was raised to 350 °C with a heating rate of 5 °C/min and then increased to 490 °C at a rate of 2 °C/min. The temperature was maintained at a constant 30 h under a 0.7 MPa nitrogen atmosphere. After the reaction, the reaction kettle was removed and allowed to cool to room temperature naturally, and the product was retrieved for analysis and characterization.

2.3. Product Characterization Methods.

(1) Polarizing microscope (PM) analysis: Leica DM 2700P polarizing microscope with 200× magnification was used for qualitative and quantitative analysis of mesophase pitch. The product was cured with epoxy resin before observation, and the section was polished. Quantitative analysis employed the evaluation criteria and classification system proposed by Eser[33] and Li.[34] This paper also introduced a new evaluation criterion for mesophase microstructure, as detailed in Table 4. The calculation formula of the optical structure index optical texture index (OTI) is as follows:

$$\mathrm{OTI} = \sum f_i \times (\mathrm{OTI})i$$

where f_i is the proportion of each type of optical structure and $(\mathrm{OTI})_i$ is the optical structure index assigned to each texture type.

(2) Scanning electron microscope (SEM) analysis:[32,35] a Hitachi SU 8010 scanning electron microscope with a 5 kV acceleration voltage and magnification range of 3−10 k was used.

Table 1. Performance Index of the Raw Material and Refined Components

sample name	viscosity (mPa·s) 50 °C	viscosity (mPa·s) 100 °C	density (g/cm^3) (20 °C)	carbon residue (wt %)	ash (wt %)	molecular weight M_n
coal tar pitch	183,400	373.60	1.3544	41.58	0.0239	388
refined component of pentane extraction	148.50	10.51	1.1886	14.13	0	240
refined component of *n*-hexane extraction	323.40	14.15	1.1923	19.54	0	278
refined component of cyclohexane extraction	249.60	23.62	1.1516	24.96	0	317
refined component of toluene extraction	7568	114.60	1.2342	33.12	0	385

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Table 2. Analysis of Group Composition of the Raw Material and Refined Components

sample name	saturate (wt %)	aromatic (wt %)	colloid (wt %)	asphaltene (wt %)	TI (wt %)	QI (wt %)
coal tar pitch	0.08	33.49	13.98	37.93	14.52	0.02
refined component of pentane extraction	0.05	70.44	18.50	7.98	3.03	0
refined component of *n*-hexane extraction	0.05	60.94	23.55	11.28	4.18	0
refined component of cyclohexane extraction	1.29	47.30	13.55	29.00	8.86	0
refined component of toluene extraction	1.50	39.22	18.81	35.85	4.62	0

Table 3. Element Analysis of the Raw Material and Refined Components

sample name	C (wt %)	H (wt %)	O (wt %)	N (wt %)	S (wt %)	H/C
coal tar pitch	92.91	4.87	0.90	0.80	0.52	0.63
refined component of pentane extraction	92.55	5.27	0.88	0.80	0.50	0.68
refined component of *n*-hexane extraction	92.60	5.31	0.90	0.80	0.39	0.68
refined component of cyclohexane extraction	92.04	5.74	0.94	0.85	0.43	0.74
refined component of toluene extraction	92.42	5.40	0.98	0.80	0.40	0.70

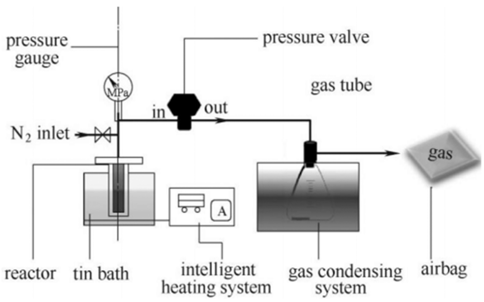

Figure 2. Sketch of miniature reactor.[32]

Table 4. Evaluation Criteria of Mesophase Microstructure

optical texture type	size (μm)	OTI value
fine mosaic	<5	1
coarse mosaic	5−20	10
flow	20−60	50
flow domain (short)	60−300	100
flow domain (long)	>300	200

(3) X-ray diffraction (XRD) analysis:[36,37] a Bruker D8 Advance X-ray diffractometer with a scanning angle of 5−90°, Cu target, 0.5°/min step frequency, and a 0.15406 nm X-ray wavelength was employed. The calculation method of microcrystalline degree I_g is as follows:

$$I_g = \frac{I_{26}}{I_{26} + I_{22}} \times 100\%$$

where I_{26} is the peak area of carbon crystallites with regular arrangement and I_{22} is the peak area of amorphous carbon.

(4) Raman spectrum analysis:[38−40] a Raman spectrometer of the Via Reflex type by Renishaw in the United Kingdom, with a 532 nm wavelength and scanning range of 500−2500 cm^{-1} was used.

3. RESULTS AND DISCUSSION

3.1. Product Yield and Mesophase Content. Figures 3 and 4 illustrate the yield and mesophase content of the mesophase pitch obtained through the thermal polycondensation of raw material and refined components.

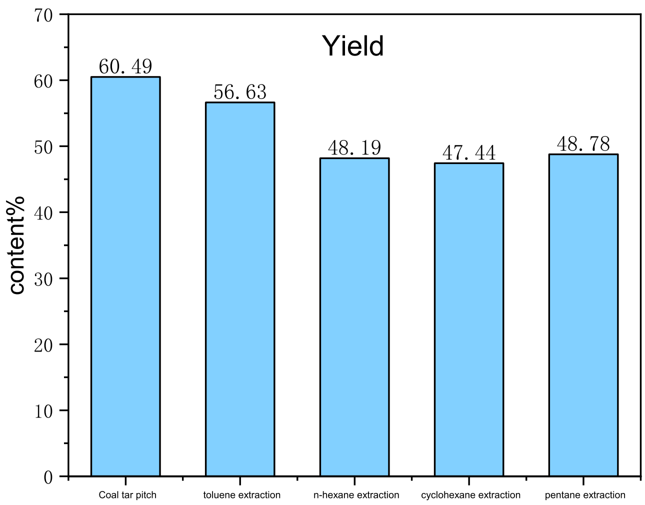

Figure 3. Solid yield of mesophase pitch obtained by the raw material and refined components.

Figure 3 indicates that the raw material yields the highest mesophase pitch, at 60.49%, followed by the mesophase pitch obtained from toluene extraction refining components, at 56.63%. The yield of mesophase pitch from cyclohexane extraction refining components, *n*-hexane extraction refining components, and pentane extraction refining components is

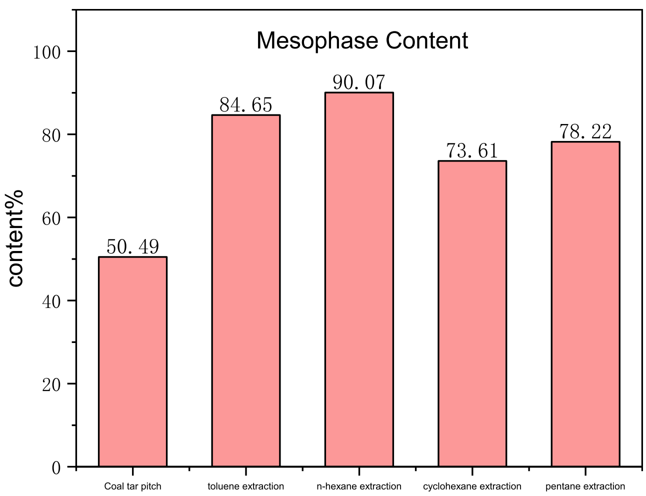

Figure 4. Mesophase content of the mesophase pitch obtained by the raw material and refined components.

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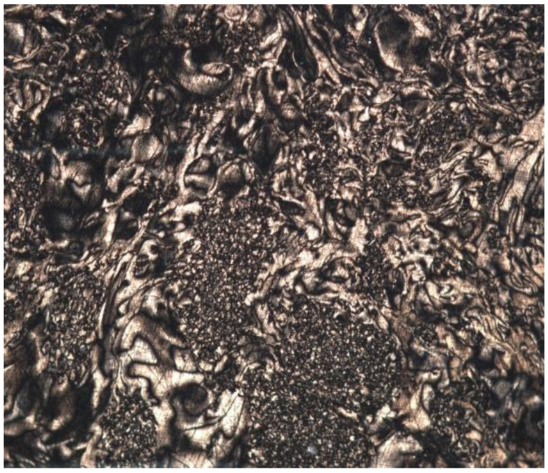
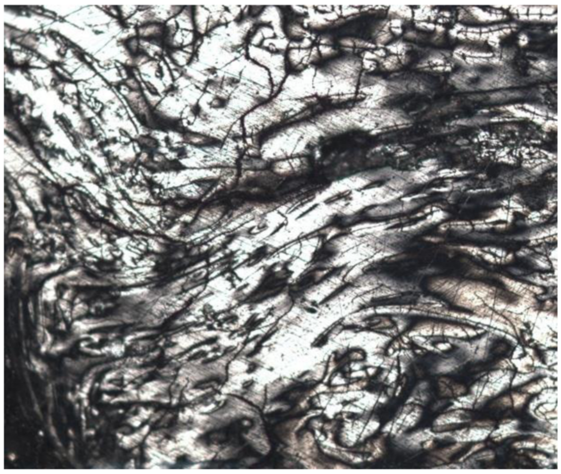


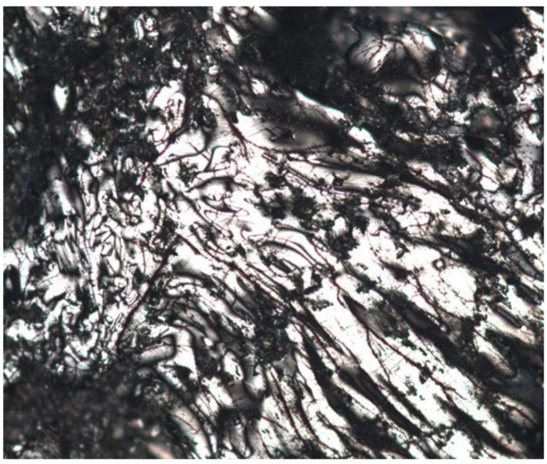
(a) Coal tar pitch

(b) Refined component of toluene extraction

(c) Refined component of n-hexane extraction



(d) Refined component of cyclohexane extraction



(e) Refined component of pentane extraction

Figure 5. Polarizing micrographs of mesophase pitch obtained by the raw material and refined components.

quite similar, fluctuating around 48%. This demonstrates that supercritical fluid extraction pretreatment of the raw material effectively removes impurities and heavy components such as QI,[41−44] significantly increasing the presence of light components in the refined components. During thermal polycondensation, a substantial number of light components are released as gas from the system, resulting in lower yields of mesophase pitch from the refined components compared with those obtained from the raw material.

Figure 4 reveals that the mesophase content in the mesophase pitch prepared from refined components is higher than that from the raw material, with a noticeable difference. In descending

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order of mesophase content: *n*-hexane extraction refining component, toluene extraction refining component, pentane extraction refining component, cyclohexane extraction refining component, and the raw material. Remarkably, the mesophase content in the mesophase pitch from the *n*-hexane extraction refining component reaches an impressive 90.07, 39.58% higher than the 50.49% mesophase content in the mesophase pitch obtained from the raw material. This underscores the significant optimization effect of supercritical fluid extraction pretreatment on the raw material, particularly when *n*-hexane is used as the extraction solvent.

Qualitative and quantitative characterization analysis of the microstructure of the mesophase pitch, obtained from both the raw material and refined components, was conducted using various analytical methods. The results are as follows.

3.2. Polarization Microscope Analysis. Figure 5 displays polarized microscopic images of mesophase pitch obtained through the thermal polycondensation of the raw material and refined components. Notably, the optical structure of the mesophase pitch derived from the four refined components is significantly superior to that of the mesophase pitch from the raw material. The short-watershed and long-watershed structures in the mesophase pitch obtained from each refined component are notably increased, indicating a tendency toward regular alignment and a fibrous structure.

With the assistance of ImageJ software, the mesophase pitch was subjected to quantitative analysis using the new evaluation standard for the mesophase microstructure proposed in this paper. The results are presented in Figures 6 and 7.

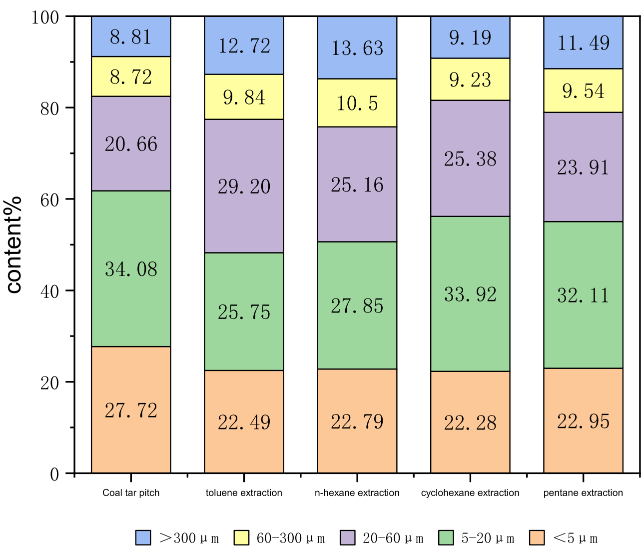

Figure 6. Optical texture distribution of mesophase pitch obtained by the raw material and refined components.

Figure 6 illustrates the optical texture distribution of the mesophase pitch obtained through the thermal polycondensation of the raw material and refined components. It is apparent from Figure 6 that the mosaic structure in the mesophase pitch obtained from the four refined components is significantly reduced compared with that in the mesophase pitch obtained from the raw material. The fine mosaic structure hovers around 22%, and structures exceeding 20 μm, such as streamlined and basin-type structures, have increased significantly. Among them, the mesophase pitch obtained through *n*-hexane extraction refining has the most excellent optical texture distribution, with long-watershed and short-watershed structures reaching 13.63 and 10.5%, respectively.

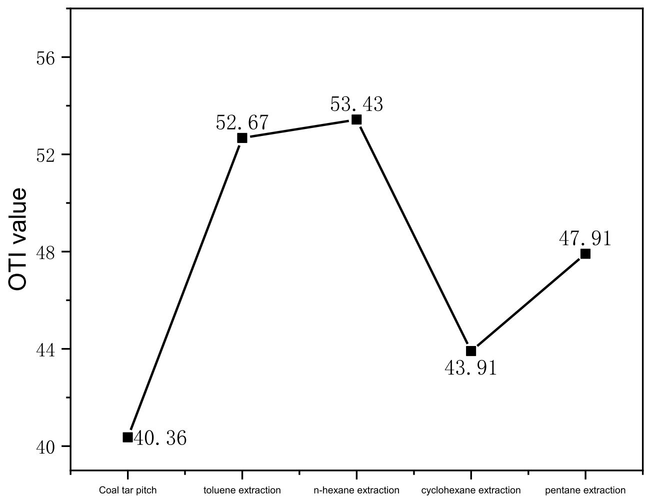

Figure 7. OTI value of the mesophase pitch obtained by the raw material and refined components.

Figure 7 shows the optical texture index (OTI) of the mesophase pitch obtained through the thermal polycondensation of the raw material and refined components. The OTI value is used to characterize the degree of anisotropy in mesophase pitch, where higher values indicate greater anisotropy and better performance. The OTI values for mesophase pitch obtained from the four refined components are higher than the OTI value for mesophase pitch obtained from the raw material, with *n*-hexane extraction refining reaching an impressive 53.43. This underscores the excellent optimization effect of supercritical fluid extraction pretreatment on the raw material. The anisotropy of the mesophase pitch obtained from pretreated refined components has increased, enhancing performance. The refined component obtained using *n*-hexane as the extraction solvent exhibits the highest degree of anisotropy and the best performance after thermal polycondensation.

3.3. Scanning Electron Microscope Analysis (SEM). Figure 8 presents SEM images of the mesophase pitch obtained through the thermal polycondensation of the raw material and refined components, magnified by 5000 times. Notably, the fiber lamellar structure in the mesophase pitch from the four refined components is denser than that in the mesophase pitch from the raw material. Large granular material is significantly reduced, the layered stacking structure is more regular and orderly, and the height gap between the layers is more uniform. Upon comparison, it is evident that the microstructure of the mesophase pitch obtained from the refined component of *n*-hexane extraction is the most excellent. The surface is smooth and flat with almost no large granular material. The lamellar accumulation is dense and uniform, aligning with the conclusions drawn from polarizing microscope analysis.

3.4. X-ray Diffraction Analysis (XRD). Figure 9 presents the XRD spectrum of the mesophase pitch obtained through thermal polycondensation of the raw material and refined components. Notably, both the raw material and refined components' mesophase pitch exhibit a 002 crystal plane characteristic peak at approximately 26°, with the peak intensity ranking from highest to lowest as *n*-hexane extraction refining component, toluene extraction refining component, pentane extraction refining component, cyclohexane extraction refining

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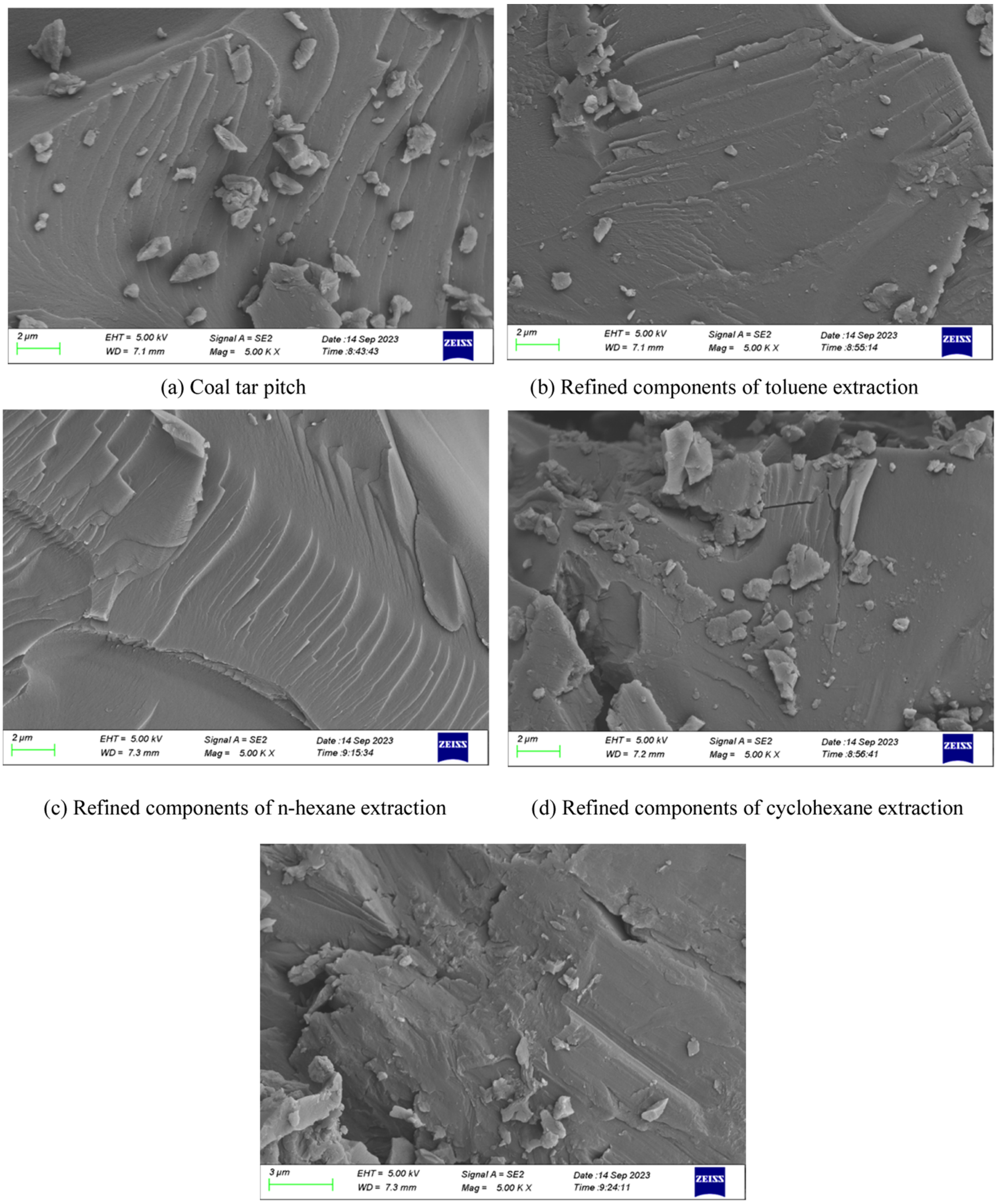

(a) Coal tar pitch

(b) Refined components of toluene extraction

(c) Refined components of n-hexane extraction

(d) Refined components of cyclohexane extraction

(e) Refined components of pentane extraction

Figure 8. Scanning electron micrograph of mesophase pitch obtained by the raw material and refined components.

component, and raw material. Upon comparison, the intensity of the characteristic peak of the 002 crystal plane in the mesophase pitch obtained from the refined component of *n*-hexane extraction is the highest, signifying a dense and uniform carbonaceous microcrystalline layered stacking structure.

The characteristic parameters of XRD were obtained through peak fitting calculations of the XRD spectra, as displayed in Table 5. A comparison of Table 5 reveals that the microcrystalline layer spacing d_{002} in the mesophase pitch obtained from the four refined components is smaller than that in the mesophase pitch obtained from the raw material. The average height L_c, average size L_a, and regular carbon microcrystalline content I_g in the mesophase pitch obtained from the refined components are larger than those in the mesophase pitch obtained from the raw material. Upon analysis, it is evident that the microstructure ranking from excellent to poor among the products obtained through thermal polycondensation is as follows: *n*-hexane extraction refining component, toluene extraction refining component, pentane extraction refining component, cyclohexane extraction refining component, and raw material. Among these, the microstructure of the mesophase pitch obtained from the *n*-hexane extraction refining component is the most favorable. The minimum microcrystalline layer spacing d_{002} is 0.34, and the average microcrystalline height L_c, average microcrystalline size L_a, and regular carbon microcrystalline content I_g are 2.93, 3.61, and 84.27%, respectively. This aligns

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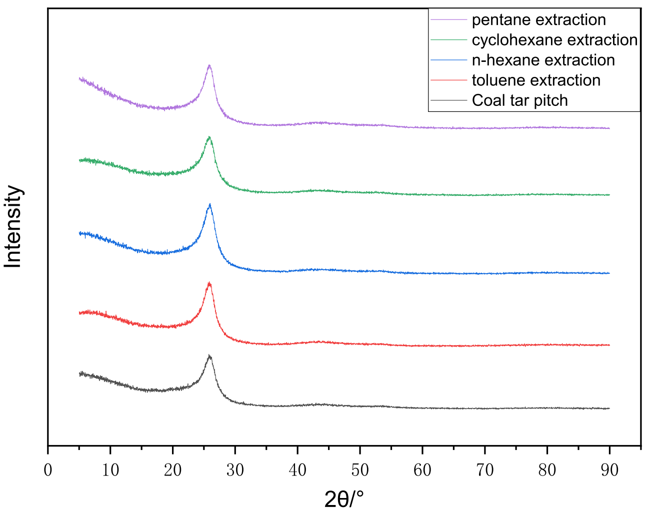

Figure 9. XRD spectra of mesophase pitch obtained by the raw material and refined components.

Table 5. XRD Parameters of Mesophase Pitch of the Raw Material and Refined Components

sample name	d_{002} (nm)	L_c (nm)	L_a (nm)	I_g (%)
coal tar pitch	0.35	2.65	3.19	82.13
refined component of pentane extraction	0.34	2.89	3.42	83.47
refined component of *n*-hexane extraction	0.34	2.93	3.61	84.27
refined component of cyclohexane extraction	0.34	2.75	3.24	82.33
refined component of toluene extraction	0.34	2.76	3.33	82.50

with the findings of the polarizing microscope and XRD spectrum analysis.

3.5. Raman Spectroscopy. Figure 10 illustrates the Raman spectrum of the mesophase pitch obtained through the thermal polycondensation of the raw material and refined components. It is clearly visible in Figure 10 that both the mesophase pitches obtained from the raw material and refined components exhibit two typical graphite Raman peaks, D and G, located near 1360 and 1580 cm^{-1}, respectively. The peak near 1360 cm^{-1} is attributed to structural defects and a disordered state in carbon materials, while the peak near 1580 cm^{-1} arises from the vibration of the C−C bond on the graphite aromatic molecular layer plane, representing a graphite peak. The intensity ratio (I_D/I_G) of these two peaks indicates the relative content of disordered and graphite structures in carbon materials. A smaller ratio suggests a higher degree of graphitization. Figure 10 demonstrates that the I_D/I_G intensity ratio, from strong to weak, is as follows: *n*-hexane extraction refining component, toluene extraction refining component, pentane extraction refining component, cyclohexane extraction refining component, and raw material. This corresponds with the XRD pattern analysis. Notably, the I_D/I_G intensity ratio of the mesophase pitch obtained from the *n*-hexane extraction refining component is the smallest at 1.40, indicating the highest degree of graphitization. This conclusion aligns with the analysis of the XRD spectrum.

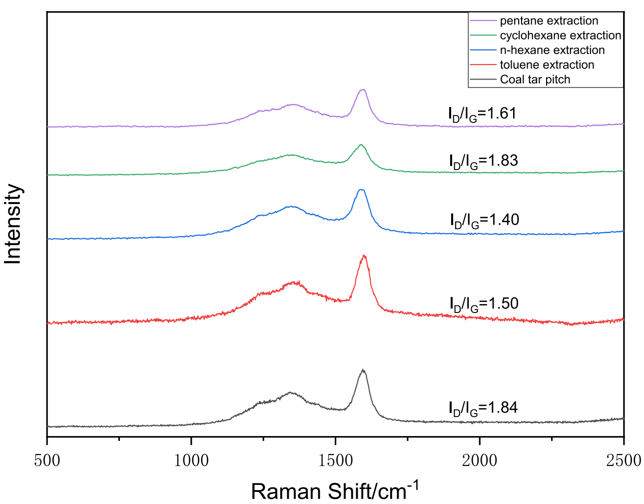

Figure 10. Raman spectra of the mesophase pitch obtained by the raw material and refined components.

4. CONCLUSIONS

(1) Supercritical fluid extraction pretreatment has an excellent optimizing effect on the raw material. The microstructure and properties of mesophase pitch obtained from refined components surpass those obtained from the raw material.

(2) Through the analysis and comparison of various analytical methods, it is evident that the optimization effect of supercritical fluid extraction pretreatment with four different solvents on the raw material and the microstructure and properties of mesophase pitch obtained from refined components are as follows, in descending order of excellence: refined component of *n*-hexane extraction, refined component of toluene extraction, refined component of pentane extraction, and refined component of cyclohexane extraction.

(3) Through comparison and analysis, it is clear that *n*-hexane is a superior solvent for supercritical fluid extraction pretreatment. The mesophase content of mesophase pitch prepared from the refined component is as high as 90.07% after pretreatment of the raw material with *n*-hexane solvent using supercritical fluid extraction. Additionally, the optical texture distribution is excellent, the directional arrangement and order are superior, the lamellar accumulation is compact, and the degree of anisotropy and graphitization are the highest.

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Notes

The authors declare no competing financial interest.

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