

CHARACTERIZATIONS OF THERMAL BITUMEN AS A PYROLYTIC INTERMEDIATE FROM FUSHUN OIL SHALE

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ABSTRACT

To obtain a deep understanding of the pyrolysis mechanism of oil shale kerogen, critical organic intermediate—thermal bitumen was firstly prepared by heating Fushun oil shale up to the critical temperature point (450 °C), and then extracted by IL(BmimCl) which was mixed with NMP. Scanning electron microscope, X-ray diffraction, Fourier transform infrared spectrophotometry and flash pyrolysis-gas chromatography-mass spectrometry were employed to investigate the physical and chemical transformation in oil shale pyrolysis and extraction processes. Results showed that thermal bitumen was mainly composed of aliphatic structures. In the thermolysis and extraction courses, aliphatic structures have poor stability by comparison of peak intensities. Thermal bitumen mainly comprised short and middle-chain alkanes/alkenes in the range from C4 to C26 .

Keywords: oil shale, Ionic liquid, thermal bitumen, structure

1. INTRODUCTION

Complex macromolecular organic compounds in oil shale are collectively referred to as kerogen. The pyrolysis of kerogen in oil shale covers a series of complex chemical reactions. The pyrolysis products are shale oil and gas. The properties of shale oil are similar to those of crude oil.

The macromolecular organic matters in kerogen split into soluble extracts, including the critical organic intermediates—thermal bitumen and gas products. With the temperature increasing, thermal bitumen disintegrates into shale oil, gas, and semi-coke[1].

It is very significant to study the formation and pyrolysis of thermal bitumen. However, few experimental and theoretical analyses have been conducted to explain what happens from kerogen to thermal bitumen.

A promising new treatment method for lignocellulosic materials and coal is the use of ionic liquids (ILs). ILs are non-volatile solvents that exhibit unique extracting properties. ILs are a class of organic salts, comprised entirely of cations (usually organic) and anions (usually inorganic). Unlike molten salts which is liquid at high temperatures, room temperature ionic liquids exist as liquid at relatively low temperatures. A large number of works show that ILs have excellent ability to dissolve cellulose and lignite at considerably mild conditions with close to 100% recovery.[2]

In this review, the dissolution of semi-coke in ionic liquid(BmimCl) was mixed with NMP which was a dispersant. Few experimental and theoretical analyses about ionic liquids have been applied to oil shale.

2. EXPERIMENTAL SECTION

2.1 Materials

Oil shale samples used in this work were obtained from Fushun city in China. The samples were crushed and sieved to small particles (less than 0.1 mm in size), dried at 40 °C to a constant weight, and then stored for use in a desiccator. Oil shale was heated to 450 °C to obtain the semi-coke. Thermal bitumen in semi-coke was extracted for 48h by an ultrasonic extractor. The elemental analyses of 4 samples are illustrated in Table 1.

Table 1. Elemental Analyses of Samples

	C	H	O	N	S
Oil shale	11.879	2.118	8.617	0.761	0.400
Semi-coke	7.978	1.304	5.013	0.699	0.290
Residue	6.884	1.235	4.336	0.719	0.200
Bitumen	43.126	4.685	50.730	2.029	0.890

2.2 Samples Preparation

Through a large amount of retorting experiments of the studied oil shale, it was observed that the critical temperature was close to 450 °C [3-4]. To obtain the thermal bitumen, the oil shale was heated to 450 °C in the retorting reactor. The reactor was slowly heated from room temperature to the pyrolysis temperature at a heating rate of 2 °C/min, and then kept the pyrolysis temperature for 0.5h to guarantee the whole sample was evenly heated.

Then, When the sample was cooled to room temperature, the semi-coke in the reactor were taken out and stored in a desiccator. Thermal bitumen was then extracted from semi-coke by an ultrasonic extractor with 1-butyl-3-methylimidazolium chlorid (BmimCl)/NMP as the solvent at 75 °C for 48 h. The solution was separated from residues with a filter, and then deionized water was injected into the solution for reverse extracting the organic matter. The bitumen precipitate was finally separated with a filter and evaporated in a vacuum drying oven.

2.3 Characterization

SEM images of samples were carried out on JEOL JSM-6510LV SEM instruments.

The XRD patterns of the kerogen sample were recorded on a Bruker D8 Venture XRD analyzer equipped with a Co tube operating at 36 kV and 20 mA. The samples were scanned in the range from 10 to 80° (interval: 0.01°; measurement speed: 0.3 s-step-1)

FTIR spectra were obtained with a Nicolet-6700 spectrometer. The samples were prepared by grinding 1 mg of thermal bitumen with 100 mg of ground KBr. The FTIR spectrum of the bitumen sample was collected at a resolution of 2 cm⁻¹ and in the wavelength range of 4000–400 cm⁻¹.

The thermal bitumen sample (5 mg, < 0.2 mm) was placed in a multi-shot pyrolyzer (Frontier Laboratories EGA/PY-3030D) using a double-shot sampler, and then the pyrolysis products were directly used for GC–MS analysis (Perkin Elmer SQ8 GC–MS) coupled with the pyrolyzer using He as the carrier gas. Pyrolysis

condition: Pyrolysis time = 10 s; pyrolyzer furnace temperature = 600 °C. GC–MS acquisition parameters: Oven initial temperature 50 °C for 5 min; ramp rate 10 °C/min to 280 °C; hold = 20 min; injection port temperature = 250 °C; transfer temperature = 250 °C; source temperature = 250 °C; scan range = 50 to 450 Da; and column = 30.0 m × 250 μm [6].

3. RESULTS

3.1 SEM analysis

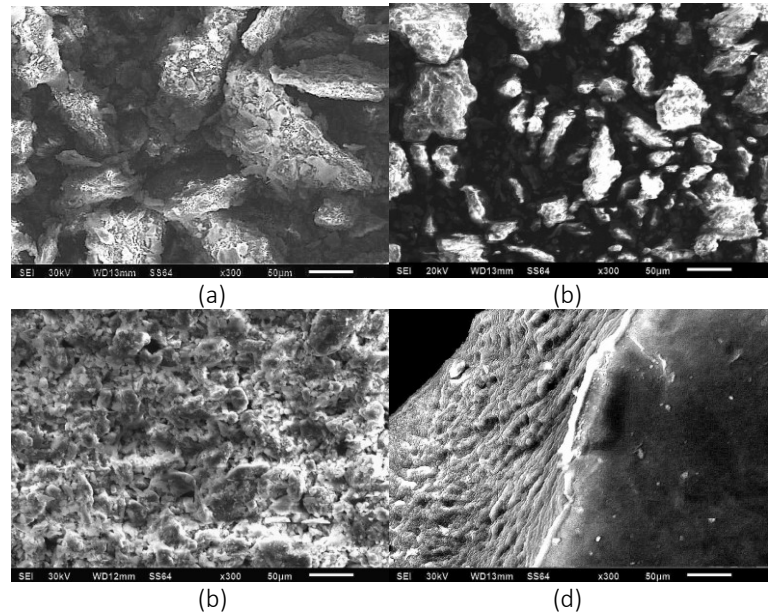


Figure.1 The SEM images of Fushun oil shale, semi-coke, residue and thermal bitumen.

Fig.1 shows the SEM images of oil shale, semi-coke, residue and bitumen. The sizes of the particles and pores in oil shale and semicoke decrease due to the volatilization of internal water and the decomposition of organic matter. It reflects that pyrolysis impacts thermal damage effect upon oil shale. In the extraction process, parts of the organic matter are dissolved in the solvent so that the particle sizes of the samples decrease. Residue particles adhere to each other, and the surface presents a dense gully shape. Thermal bitumen emerges the lamellar structure with smooth surface.

3.2 XRD analysis

Fig.2 shows the XRD spectra of oil shale, semicoke and residue. There are five groups of minerals: kaolinite, illite, calcite, quartz and pyrite. The comparison of the X-ray diffraction intensities reflects the Quartz and calcite are the primary minerals determined from the oil shale. The pyrolysis process of

450°C from oil shale to semicoke did not affect the mineral composition. In the extraction process from semi-coke to residual, mineral composition had a little change.

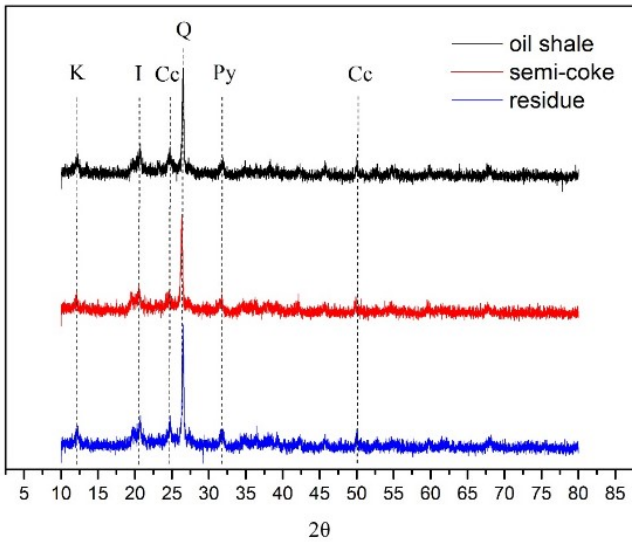


Figure.2 XRD spectra of oil shale,semi-coke and residue.

3.3 FTIR analysis

Fig.3 shows that most of the peak positions of oil shale, semi-coke and residue change insignificantly. However, the samples have markedly different peak intensities. These distinct peaks can be assigned to six regions: 3621 cm^{-1} , 3699 cm^{-1} (O-H), 2854 cm^{-1} , 2925 cm^{-1} (aliphatic C-H), 1628 cm^{-1} (C=C), 1433 cm^{-1} (aliphatic C-H), 700-900 cm^{-1} (aromatic C-H) and 480-1200 cm^{-1} (minerals) [5]. In the thermolysis and extraction courses, aliphatic structures have poor stability by comparison of peak intensities. Residue has less C-H (2854 cm^{-1} , 2925 cm^{-1}) and C=C (1628 cm^{-1}) than those in oil shale and semi-coke. The pyrolysis and extraction processes mainly make a big difference for aliphatic C-H. The absorption bands between 1060-1170 cm^{-1} due to Si-O in the mineral. The absorption zones overlap by quartz, clay minerals, kaolinite, illite and montmorillonite. FTIR data consistent with the results of XRD.

Two peaks around 2923 and 2850 cm^{-1} in Fig.4 arising from the asymmetrical and symmetrical alkyl CH₂ stretching vibrations have the strongest signal in spectra, showing that CH₂ has an absolute advantage in quantity. The sharp peak appearing at about 796 cm^{-1} and 748 cm^{-1} proves the presence of the skeletal vibration of straight chains with more than four CH₂ groups. The weak absorption peak at about 1700 cm^{-1} indicates the presence of a carbonyl group, although

with less content. C=C stretching contributes to the relatively broader peak at 1606 cm^{-1} and shows that thermal bitumen contains a certain amount of olefins and aromatic rings. The weak peaks between 1454 and 1374 cm^{-1} are due to the symmetric bending vibration of CH₃. The peak at 1288 cm^{-1} proves the presence of ethers and alcohols, and the signal around 3423 cm^{-1} is mainly attributed to OH stretching of phenols.

3.4 Py-GC-MS analysis

Table.2 summarizes the corresponding pyrolysis products. The relative content of the products was calculated by the integration of the peak area. The pyrolysis products are straight carbon chains mainly ranging from C₄ to C₂₆, and the other components include alcohols, esters and ethers, etc. n-Alkanes and the corresponding alkenes with an equal number of carbon atoms are the predominant products from pyrolysis. Thus, 46 representative chromatographic peaks are identified from the TIC.

n-Alkanes/alkenes and iso-alkanes/alkenes exhibit absolute dominance, which account for 74.64% of the

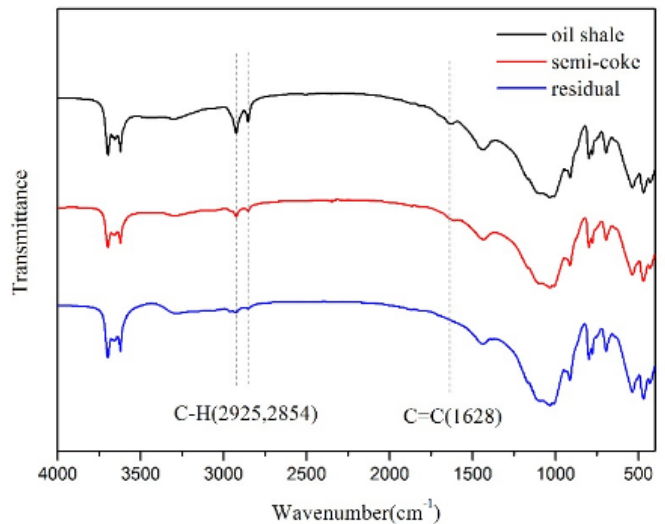


Figure.3 FTIR spectrum of oil shale,semi-coke and residue.

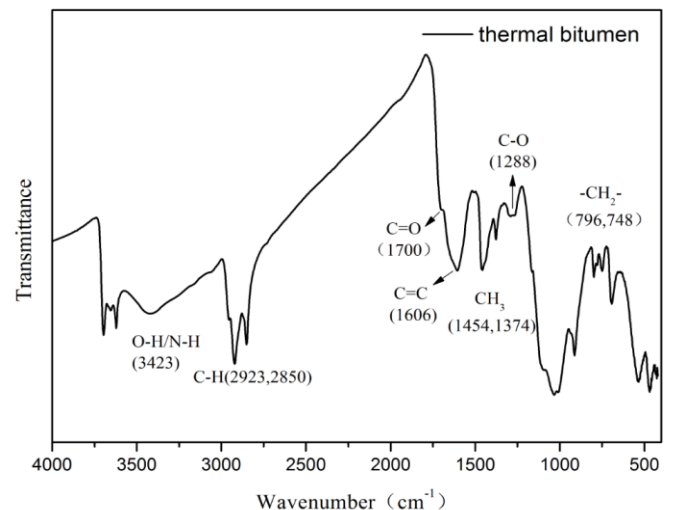


Figure.4 FTIR spectrum of thermal bitumen.

pyrolysis products. Aliphatic hydrocarbon products in high yield are mainly distributed in the range from C4 to C26, indicating that the thermal bitumen mainly comprises short and middle-chain alkanes/alkenes.

Table.2 Products obtained from the pyrolysis of Yaojie kerogen by Py–GC–MS.

No	Compounds (chemical formula)	Percent of peak area	No.	Compound s(chemical formula)	Percent of peak area
1	CO ₂	4.58%	24	C ₈ H ₄ O ₃	2.21%
2	C ₄ H ₈	6.34%	25	C ₁₁ H ₁₀	0.57%
3	C ₅ H ₁₀	2.33%	26	C ₁₄ H ₂₈	1.51%
4	C ₆ H ₁₂	2.22%	27	C ₁₄ H ₃₀	1.38%
5	C ₆ H ₆	1.59%	28	C ₉ H ₇ NO ₂	1.40%
6	C ₇ H ₁₄	1.24%	29	C ₁₅ H ₃₀	1.71%
7	C ₇ H ₁₆	0.87%	30	C ₁₅ H ₃₂	2.07%
8	C ₇ H ₈	1.63%	31	C ₁₄ H ₂₂ O	0.79%
9	C ₈ H ₁₆	6.41%	32	C ₁₆ H ₃₄ O	1.64%
10	C ₈ H ₁₈	2.59%	33	C ₁₆ H ₃₂	2.56%
11	C ₈ H ₁₀	0.64%	34	C ₁₆ H ₃₄	1.47%
12	C ₉ H ₁₈	1.22%	35	C ₁₇ H ₃₆	3.33%
13	C ₉ H ₂₀	1.62%	36	C ₁₅ H ₂₂ O ₂	2.59%
14	C ₁₀ H ₂₀	1.63%	37	C ₁₈ H ₃₆	1.80%
15	C ₁₀ H ₂₂	0.81%	38	C ₁₈ H ₃₈	3.77%
16	C ₈ H ₁₈ O	5.29%	39	C ₁₉ H ₃₈	1.83%
17	C ₁₁ H ₂₂	1.53%	40	C ₂₀ H ₄₀	4.93%
18	C ₁₁ H ₂₄	0.80%	41	C ₁₆ H ₃₂ O ₂	1.78%
19	C ₇ H ₆ O ₂	1.23%	42	C ₂₀ H ₄₂	1.42%
20	C ₁₂ H ₂₄	1.38%	43	C ₂₁ H ₄₄	4.89%
21	C ₁₂ H ₂₆	0.90%	44	C ₂₁ H ₄₄ O	1.21%
22	C ₁₁ H ₂₄ O	1.50%	45	C ₂₄ H ₅₀ O	1.13%
23	C ₁₃ H ₂₈	1.10%	46	C ₂₆ H ₅₄	4.56%

4. Conclusions

This study aimed to reveal evolution of organic structures in pyrolysates during the pyrolysis process. Therefore, we performed SEM, XRD, FTIR and Py-GC-MS to investigate the structural features of the thermal bitumen derived from Fushun oil shale.

SEM and XRD show the physical properties of samples and experiments. Pyrolysis and extraction processes have a significant impact upon the microstructure of samples. FTIR and Py–GC–MS analyses demonstrate that n-Alkanes/alkenes and iso-alkanes/alkenes exhibit absolute dominance in the thermal bitumen. The asymmetrical and symmetrical alkyl CH₂ stretching vibrations have the strongest signal in spectra, showing that CH₂ has an absolute advantage in quantity Aliphatic hydrocarbon products in high yield were mainly distributed in the range from C4 to C26.

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