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Research on the structural characteristics of vitrinite in different coal ranks

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HIGHLIGHTS

- ▶ Samples are high-purity vitrinite separated by isodensity separation technology.
- ▶ Analyses of organic geochemical characteristics.
- ▶ Functional groups of vitrinite were characterized by FT-IR.
- ▶ Structural parameters of the macromolecular structure of vitrinite is proposed.

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ABSTRACT

Based on the separation of vitrinite in Shanxi coal samples, high purity vitrinite was obtained. Kerogen type was determined for vitrinite obtained from each sample, along with the types of organic matter present and the hydrocarbon generation potential. The structural characteristics of vitrinite in different ranks of coal were studied using Fourier transform infrared spectroscopy (FT-IR) experiments in combination with the peak separation method. Our research shows that vitrinite structure is characterized by the presence of short aliphatic chains and that its high stability is due to a greater aromatic content in comparison to the aliphatic hydrocarbon component. Vitrinite also has a larger aliphatic hydrocarbon proportion than raw coal, which makes vitrinite a major hydrocarbon-generating maceral. The higher carboxyl content and H-bonding were an essential contributor to the stability of the macromolecular structure of vitrinite; oxygen-containing functional groups and alkyl side chains of vitrinite are lost at different rates with an increase in coal rank. The extent of aromatization increased with the coal rank. Combined with the results of elemental and industrial analysis, the content of each functional group in the FT-IR spectra was systematically analyzed. The related structural parameters of vitrinite were calculated, and the structural features are discussed. Finally, the pattern of functional group changes in the macromolecular structure in vitrinite with respect to coal rank was obtained. The structural parameters of vitrinite were calculated, and the structural features are discussed. Finally, the pattern of functional group changes in the macromolecular structure in vitrinite was obtained. The research results presented in this paper provide important new information that extends macromolecular structure in vitrinite. Structure of vitrinite in different coal ranks are substantially modified during the subsequent evolution process of the coals.

1. Introduction

Vitrinite is a large polymer and a hydrocarbon-generating maceral, and it is the main maceral in coal source rocks. With the progress of coalification in the natural evolution of coal ranks, the vitrinite macromolecule is fragmented into hydrocarbons as aromatization, aromatic ring polymerization, and aromatic layer superposition occurs [1–3]. In previous works, vitrinite was separated using different methods and a summary of the present situation and the existing problems encountered in maceral separation were presented. Separation and enrichment, according to the floating and sinking test and centrifugal separation, are mainly based on a difference in density for specific macerals [4–6]. Heavy-liquid separation remains the most widely used separation process. Based on vitrinite separation experiments, researchers have studied the hydrocarbon generation and coal structure of high-purity single macerals [7–9].

Previously, advanced technology was used to characterize and analyze the complex organic matter composition of macerals in

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coal and the structure of pyrolysis products. This work launched the beginning of simulation and modeling studies. However, these earlier studies lacked a systematic characterization model and comparisons between coal ranks in various hydrocarbon evolution stages. Fourier transform infrared spectroscopy is a useful technique for studying the chemical structure of coal and has precedence for use coal structure research [10–23].

FT-IR has been used mainly to study three aspects of coal structure: (a) The presence of functional groups, including hydroxyl, other oxygen-containing functional groups, and aliphatic and aromatic hydrocarbons, in different coal ranks. (b) Semi-quantitative and quantitative analyses of the amount of functional groups in different types of coal samples from different geographic areas using peak height or area. The reduction of carboxyls lasted past the fat coal stage, which mainly occurred before RVmax = 0.50%. The amount of aliphatic groups was found to decrease during the bituminization stage. The structural parameters of coal can be calculated by the content of the absorption peak. (c) There are only a few reports of quantitative studies on the structure of vitrinite in coal samples by physical chemistry treatments. Previous studies were on commonly used hydrocarbon source rocks, which were composed of mixtures of various components. The evolution of molecular structure of macerals with different components had a significant difference with respect to hydrocarbon generation. Nevertheless, the evolution of macromolecular structure and reaction kinetics are internal factors that lead to the diversity of hydrocarbon generation.

Coal is taken as the research object in previous researches. But coal consists of different macerals. Little research work has been done to the structure of vitrinite, the main hydrocarbon generating maceral. We took high purity vitrinite through the separation experiment. The systematic study of the structural evolution of vitrinite and secondary hydrocarbon generation has important implications for both theory and applications. This paper has elucidated the structure of vitrinite in different ranks of coal and analyzed the differences between structures in different coal ranks to reveal a structure evolution mechanism for vitrinite hydrocarbon generation.

2. Materials and methods

2.1. Vitrinite separation

For this experiment, vitrinite was separated from bituminous coal. The working procedure for separating vitrinite from coal, which was performed strictly according to the standard (MT/T807-1999), was to manually crush the coal to 200 mesh, float it in zinc chloride solution, and separate the components using an isodensity gradient supercentrifuge with a rotation speed of 6000 r/min. The separation density of different ranks of vitrinite was obtained by condition experiments. The results show that the jet coal density liquid used in sample M1 had a high density of 1.35 g/cm^3 and a low density of 1.28 g/cm^3, the density liquid used in sample M2 had a high-density of 1.31 g/cm^3 and a low density of 1.26 g/cm^3, the density liquid used in samples M3 and M4 had a high density of 1.36 g/cm^3 and a low density of 1.30 g/cm^3, and the density liquid used in sample M5 had a high density of 1.38 g/cm^3 and a low density of 1.32 g/cm^3. Separated vitrinite was cleaned in a bath until the pH was 7.0 and then heated at 45 °C in a thermostatic drying chamber and stored in glass bottle for latter experiments.

The degree of enrichment of vitrinite is high. The purity of vitrinite samples was greater than 80% except for jet coal. When the purity was more than 90%, the vitrinite separation experiment from coking coal and lean coal using zinc chloride solution was feasible. The vitrinite separating effect for jet coal is 76% because of containing some inertinite macerals.

2.2. FT-IR analysis

Five vitrinite samples were studied using FT-IR (model VERTEX-70, made by Bruker in Germany). The experimental procedure for the FT-IR analysis involved placing 80 mg of KBr into an agate mortar, adding 0.9 mg of a coal sample, grinding the KBr and coal sample into a fine powder with a pestle, and then pressing this powder into a transparent sheet for 10 min using a tablet machine.

2.3. Main characteristics of the separation samples

Five vitrinite samples were selected from the Lower Permian shanxi Formation in North China and characterized by proximate analyses, ultimate analyses, and rock–eval (Table 1). Sample M1 was taken in Sela mine located at Dongsheng city Inner Mongolia Autonomous Region. Sample M2 was taken in Linnancang mine located at Tangshan city Hebei province. Sample M3 was taken in Fangezhuang mine located at Tangshan city Hebei province. Sample M4 was taken in Lujiatuo mine located at Tangshan city Hebei province. Sample M5 was taken in Xiandewang mine located at Xingtai city Hebei province. RVmax and purity of samples were determined according to the standard (GB6948-86) and (GB/T 1558-2001).

3. Results and discussion

3.1. Organic geochemical characteristics

The kerogen types, organic matter types and the hydrocarbon generation capacity of samples can be observed in Table 1. S1, S2, and S1 + S2 first increased and then decreased with increasing coal rank and change as parabola. Pyrolyzed hydrocarbons (S2) and CO_2 mg/g (S3) of coking coal was greater than in jet coal and lean coal. According to the linear relationship between T_{max} and reflectance, we obtained a fitted formula, $y = 48.035x + 396.24$, with a linear step relationship. The organic matter type present in jet coal (M1) and gas coal (M2) is type III2, while the organic matter in coking coal (M3, M4) and lean coal (M5) is type III1 (Fig. 1a). According

Table 1
Results of rock–eval, proximate, and ultimate analyses of samples.

Coal sample	RVmax (%)	Results of rock–eval							Proximate analysis (wt%)						Ultimate analysis (wt%)			
		S1 (mg/g)	S2 (mg/g)	S1 + S2 (mg/g)	TOC (%)	T_{max} (°C)	PI (S1/S1 + S2)	S3 (mg/g)	HI	OI	Mad	Ad	Vdaf	Q (MJ/kg)	C	H	O	N
M1	0.58	0.17	33.53	33.7	72.92	428	0.01	11.68	46	16	10.88	3.82	32.55	21.91	78.21	4.15	16.69	0.77
M2	0.80	0.57	83.41	83.98	56.17	426	0.01	0.62	148	1	2.26	49.58	48.58	15.86	69.19	6.37	22.57	1.25
M3	1.59	2.09	87.36	89.45	38.15	470	0.02	3.10	229	8	0.83	10.35	23.99	25.00	87.73	5.02	4.96	1.71
M4	1.61	1.00	102.14	103.14	40.28	468	0.01	2.26	254	6	0.66	18.37	27.35	25.30	87.24	5.29	5.17	1.63
M5	2.46	0.18	29.71	29.89	28.78	519	0.01	3.38	103	12	1.34	4.80	13.80	28.38	90.28	4.26	3.45	1.61