



Application and thermal properties of hydrogen-rich bark coal



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ABSTRACT

The thermal properties of hydrogen-rich bark coal were investigated by thermogravimetric analysis, Gieseler fluidity analysis, and polarized light microscopy with a heated stage. The liquefaction behavior was studied separately using an autoclave and a stainless-steel microautoclave reactor. The results showed that the thermal behaviors of hydrogen-rich bark coal are anomalous compared to humic coals, with high fluidities (>180,000 ddpm) and intense thermal reaction (the highest mass loss rate is 1.11%/°C). The most interesting temperature range for heating bark coal is 410–450 °C: the temperatures of maximum volatile loss of the samples used are in this range, the temperatures of maximum fluidity are about 440 °C, and the particle size was drastically reduced on heating to 430 °C or above. But in this temperature range, liquefaction conversion values were almost the same, even though oil plus gas yield, and preasphaltenes and asphaltene yield were clearly influenced by temperature. Considering the thermal behavior and properties of bark coal, some effective utilization ways are suggested, including low-temperature carbonization, co-coking, direct liquefaction, co-processing, and hydrogen production.

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1. Introduction

The thermal properties of coal are critical in understanding certain reactivity properties of coal, and provide guidance for reasonable utilization of coal in some processes, such as liquefaction, coke-making, and carbonization. Various aspects of the thermal properties of coal have been widely studied and numerous useful reviews are available [1–4]. The products and behavior of coal pyrolysis depend on many factors, including rank, maceral composition, temperature, heating rate, particle size, and mineral content. Certain bituminous coals (usually high volatile A bituminous (hvAb), medium volatile bituminous (mvb), and low volatile bituminous (lvb)) on heating can pass through a transient plastic state in which they successively soften, swell, and resolidify into a cellular coke [5–10]. The onset of plasticity is related to decomposition temperature, and the plastic range is entirely contained in the temperature range in which by active decomposition occurs. Some factors controlling the thermoplastic behavior of coal are rank, petrographic composition, heating rate, and the degree of oxidation of the coal [11]. The production of liquid fuels from coal has also been widely studied. Four schemes have been introduced to convert solid coal to liquids: solvent extraction, direct catalytic

hydrogenation, indirect liquefaction (Fischer–Tropsch), and pyrolysis. The results of coal liquefaction are also related to coal characteristics (such as rank, macerals, and mineral composition) and to the processes conditions (temperature, pressure, catalyst, and solvent) [12–17]. The mechanism of the thermoplastic behavior of coal is similar to that of liquefaction [18].

Hydrogen-rich bark coal is widely distributed in the Late Permian Longtan Formation in South China. Some well-known examples are the Leping coal basin in Jiangxi province and the Changguang coal basin in Zhejiang province. Bark coal is named because of its high content of barkinite, although barkinite has not yet been accepted as a maceral classification by the International Committee for Coal and Organic Petrology and The Society for Organic Petrology. In the past 80 years, general information on bark coal has been discussed, including the chemical composition, petrology, and chemical structure [19–27]. Recently, the processing of bark coal and/or barkinite was reviewed by Tang et al. [28] and Sun [29], and chemical compositional and structural characteristics were discussed by Wang et al. [30]. The thermal behavior of bark coal has also been studied [24,27,31]. The thermal decomposition of coals with different barkinite contents at different heating rates has been discussed [31], and the evolution of gaseous compounds (i.e. H₂, H₂O, CO, CO₂, and CH₄) from coal during pyrolysis was investigated by Wang et al. [24]. The thermoplastic properties at heating rates of 3 °C min⁻¹ were also studied [31].

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However, the systemic information on thermal behavior of hydrogen-rich bark coal is not so extensive, especially direct observation on the coal particle changes under microscopy when heated.

Hydrogen-rich bark coal is a special coal type, and has potential commercial applications in several technologies due to its high hydrogen content and high volatile matter yield [25,30]. However, bark coal is nowadays mainly used as source for combustion, which not only causes energy waste, and but also leads to pollution in the environment. Meanwhile, a regulation in China was issued, pointing out that special coal types should be protected and be reasonably and responsively used. The feasible availability of hydrogen-rich bark coal must be considered in future for keeping long-term production projections. Therefore, a discussion on the effective utilization of hydrogen-rich bark coal is necessary.

In this work, the objectives were (1) to systemically analyze the thermal properties of hydrogen-rich bark coal and (2) to discuss the effective utilization ways of bark coal.

2. Samples and experimental

2.1. Samples selected and coal characteristics analysis

The samples were selected from the Mingshan mine (LP, LP-4, MS-6) and Changuang mine (CG, CG-3) in the south of China. Barkinite was separated from Mingshan mine by combining hand picking and the density gradient centrifugation (DGC) method. The detailed procedure for maceral separation was described in the work of Guo et al. [32]. The general characteristics of the samples used are shown in Table 1. The hydrogen content ranges from 5.33% to 6.91%. The values of volatile matter are >40.00%, the highest is up to 62.16%. The content of barkinite of these samples (LP, LP-4, MS-6, CG, and CG-3) varies from 45.6% to 80.6%. The purity of barkinite is over 96.0%.

2.2. Thermogravimetric analysis of samples

Temperature-programmed pyrolysis tests were performed in a Perkin Elmer TG47 thermogravimetric analyzer (TGA). Three samples (LP, CG, and LP-4) were tested at a heating rate of 10 °C min⁻¹. The detailed procedure can be found elsewhere [31]. To assess the effect of heating rate on pyrolysis behavior, the barkinite sample was chosen, and pyrolysis tests were carried out with a TGA/DSC 1/1600HT thermogravimetric analyzer (TGA). The conditions were as follows: heating rates, 10, 20, and 40 °C min⁻¹; temperature, ambient to 900 °C; nitrogen atmosphere with a flow rate of 50 mL min⁻¹; and about 8 mg sample weight.

Table 1
General information on coal samples used.

	Barkinite	LP-4	MS-6	LP	CG	CG-3
<i>Proximate analysis (wt.%)</i>						
Ash, dry basis	0.97	14.16	19.29	17.99	16.52	14.54
Volatile matter, dry ash free basis	62.16	57.51	41.44	56.03	49.75	44.80
<i>Ultimate analysis (wt.%, daf)</i>						
Carbon	81.59	78.87	80.00	76.21	81.12	83.34
Hydrogen	6.91	6.36	5.33	6.13	6.34	6.23
H/C atomic ratio	1.01	0.97	0.80	0.97	0.94	0.90
<i>Maceral composition (Vol.%)</i>						
Vitrinite	<3.0	15.0	39.2	34.2	34.0	20.0
Barkinite	>96	80.6	45.6	52.9	53.5	68.6
Other liptinite + inertinite	0.0	4.4	15.2	12.9	12.5	11.4
Ro (%)	–	0.67	0.65	0.69	0.73	0.71

Ro, mean maximum vitrinite reflectance; daf, dry-ash-free. "–": no value.

2.3. Thermoplasticity measurement

The fluid properties of each coal were determined using a constant-torque Gieseler plastometer following the ASTM D2639-04 standard procedure. Four samples (LP, LP-4, CG, and CG-3) were selected. Detailed experimental procedures have been described elsewhere [31]. LP-4 and CG-3 were sent to Pearson Coal Petrography, Inc., to measure the fluid properties independently of our laboratory. In Pearson Coal Petrography, Inc., the experiment was carried out using the Model 4000 Plastometer following the ASTM standard. The samples was heated from 320 °C to 550 °C at the standard 3 °C min⁻¹. The machine automatically picks the softening, solidification, and maximum fluidity temperatures. The machine used has a fluidity limit of 180,000 ddpm (dial divisions per minute). The data were collected by the touch screen computer controller.

2.4. Liquefaction experiment

Two liquefaction conditions were used. For LP and CG samples, liquefaction experiments were carried out using a stainless-steel tubing-bomb microautoclave reactor. More details about the liquefaction procedures maybe found elsewhere [33]. To study the effect of temperature on liquefaction behavior of the MS-6 sample, a series of experiments were conducted in a 500-mL autoclave with shaken frequency of 67-times per minute. Approximately 10 g of coal sample was charged with 15.0 g of de-crystallized anthracene oil as a solvent and 0.3 g of catalyst (Fe₂O₃: sulfur:1:0.4) into the autoclave. After displacing the air in the autoclave with hydrogen, the hydrogen pressure was increased to 8 MPa. The autoclave was heated at a rate of 5 °C/min up to a selected reaction temperature from 410 °C to 450 °C and held at this temperature for 60 min. In both kinds of liquefaction experiments, the solid and liquid products were sequentially separated by Soxhlet extraction with hexane and tetrahydrofuran (THF). The products were classified as oils (hexane-soluble), preasphaltenes and asphaltenes (THF-soluble and hexane-insoluble), and residue (THF-insoluble).

2.5. Polarized light microscopy with heated stage

To investigate the change in morphology of coal particles when heated, the experiment was carried out by programmed polarized light microscopy with a heated stage (DMLP, Leica Company) and with a high-definition camera (MC-D900U(C)). The LP sample was ground to –80 mesh. The sample was placed between two glass sheets (ordinary glass microscope slides) and this assembly was put into the sample cell together, and finally fixed in place by a top cap. Heating procedures were as follows: from room temperature to 200 °C at the heating rate of 10 °C/min, and from 200 to 500 °C at 5 °C/min. The temperature range from room temperature to 500 °C was used due to the temperature limitations of the instrument. Nitrogen was used for preventing samples from being oxidized. The figures were analyzed by Phmias 2008 Cs version 3.0 software.

3. Results and discussion

3.1. Thermal behavior during pyrolysis

Figs. 1 and 2 show the curves of mass loss (TGA) and their derivatives (DTG) for all coals used, respectively, at a 10 °C/min heating rate. Some significant parameters obtained are listed in Table 2. As described in Section 2.2, the pyrolysis procedures for these samples were different. Regardless, the shapes of DTG curves

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