



Petrology and structural studies in liquefaction reactions of Late Permian coals from Southern China

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HIGHLIGHTS

- ▶ The liquefaction behavior of the samples having high hydrogen was studied.
- ▶ Some of the inertinites underwent liquefaction reaction for DHB.
- ▶ Barkinite reacted in liquefaction.
- ▶ The chemical structural change during liquefaction was studied by FTIR, Py-GC/MS.
- ▶ C₂-naphthalene and C₃-naphthalene become the main constitutions in the residues.

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ABSTRACT

Three coals from South China, having high contents of vitrinite, liptinite, hydrogen, volatile matter, and high H/C atomic ratios, were subjected to liquefaction in tubing-bomb microreactors at 430 °C for 1 h with tetralin, hydrogen, and iron sulfate catalyst. The optical characteristics of the liquefaction residues were studied by white-light and fluorescence microscopy. A comparative study on the chemical structural features of the raw coals and their respective liquefaction residues was conducted by Fourier transform infrared spectroscopy (FTIR) and flash pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). The liquefaction conversions were in the range of 79.0–87.1% (daf basis) under the conditions used. The optical examination of the liquefaction residues indicated that all of the liptinite and most of the vitrinite have reacted. For Dahebian coal, the observed liquefaction conversion was greater than the total vitrinite and liptinite content, indicating that some of the inertinite macerals must have participated in the reaction. Anisotropic semicoke was observed in the residue. Both FTIR and Py-GC/MS techniques showed that aliphatic groups, oxygen-containing functional groups, alkylbenzenes, and alkylphenol have reacted in liquefaction. C₂-naphthalene and C₃-naphthalene are main constitutions in residues.

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1. Introduction

In general, it is believed that coal liquefaction involves a two-step process. The first step is a breakdown of the coal macromolecular structure to release trapped molecules and break weak bonds to generate new species. The second step is to reduce these molecules in size and remove heteroatoms. So, coal liquefaction is a chemical process, which means that coal chemical structure will be changed during liquefaction. Various techniques, flash pyrolysis gas chromatography/mass spectrometry (Py-GC/MS), solid state cross-polarization magic angle spinning carbon-13 nuclear mag-

netic resonance (CPMAS ¹³C NMR), and Fourier transform infrared spectroscopy (FTIR), etc., have been widely used for studying the chemical structural change of coal during liquefaction at selected liquefaction conditions [1–7] and describing the characterization of coal liquefaction residue, even products of liquefaction and liquefaction residue [8–11]. It was shown that some functional groups (aliphatic C–H, carbonyl, carboxyl, etc.) reacted in liquefaction. However, the chemical structural changes obtained by these techniques in the liquefaction of coals, especially those with high hydrogen and volatile matter, from Southern China, has not been discussed.

Transformations of macerals during coal liquefaction at different conditions have been widely observed. Davis et al. [12] studied the insoluble residue from batch hydrogenation for two coals from 316 °C to 427 °C. Shibaoka [13] described in detail the formation and development of vitroplast in the hydrogenation and pointed

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out that the change of vitroplast is related to the experimental conditions. Shibaoka [14] also examined the changes of vitrinite macerals at various temperatures during treatment with tetralin. Mitchell [15,16] provided detailed information on the optical characteristics of hydrogenation residues (benzene-insoluble) of some specific coal macerals in both batch and continuous-flow processes over a range of temperature. Also, a classification of solid residues was proposed on the basis of morphology, size, relative reflectance, and anisotropy, as determined by examination of polished surfaces in reflected white light. Parkash et al. [17] made a petrographic analysis of residues from the liquefaction of the three subbituminous coals. Hower et al. [18] studied the petrographic analysis of liquefaction residue of coals from inertinite-rich Peach Orchard lithotype. Mitchell [19] summarized the maceral transitions and contributions during liquefaction.

The Late Permian coals (rich in barkinite), from the Leping coal basin in Jiangxi province, have relatively high values of hydrogen and volatile matter in comparison with other humic coals of similar rank [20–22]. Although barkinite, classified as a liptinite maceral in Chinese nomenclature, has been widely studied over the past 80 years, it has not yet been recognized as a maceral by organizations such as the International Committee for Coal and Organic Petrology (ICCP) or The Society for Organic Petrology (TSOP). Hower et al. [23] also pointed out that it was more appropriate to use the term “component” instead of “maceral” for barkinite. Regardless, coals rich in barkinite undergo intense thermal decomposition and abnormal thermoplastic behavior [24]. But, the liquefaction behavior of these coals, especially the change of optical characteristics during liquefaction, has not been reported. Furthermore, barkinite, classified as a liptinite maceral in Chinese nomenclature, should be a reactive maceral in liquefaction. Therefore, it is worthy to discuss the role of barkinite in liquefaction.

In the present work, the objectives were to study the liquefaction behavior of the coal samples at selected liquefaction conditions and to determine the changes of optical characteristics and chemical structure during liquefaction with microscopy and FTIR and Py-GC/MS, respectively.

2. Samples and experimental

2.1. Samples selected and coal characteristics analysis

Three channel coal samples were collected from the Mingshan coal mine (LP) in Jiangxi province, the Changguang coal mine (CG) in Zhejiang province, and the Dahebian coal mine (DHB) in Guizhou province in the south of China. A Zeiss Universal reflected-light microscope fitted with a 40X-oil-immersion objective and 10X ocular lenses was used for determining maceral compositions following ASTM International D2779-11 test method [25]. The maceral analysis was conducted on polished pellets and their relative percentages were determined by the point-count method. A total of 1000 points was counted using an interpoint and interline distance of 0.5 mm. Reflectance reported was the mean value of 100 measurements. Proximate analysis and ultimate analysis were carried out following methods GB/T 212-2008 [26], GB/T 476-2008 [27], GB/T 214-2007 [28], and GB/T 215-2003 [29].

2.2. Coal liquefaction

Liquefaction experiments were carried out using a stainless steel tubing-bomb microreactor loaded with coal (–100 mesh) and solvent (tetralin) in the ratio of 1:3 and desired amount of catalyst (iron sulfide, FeS₂) under 6.90 MPa (1000 psig) cold hydrogen. Liquefaction temperature was chosen at 430 °C. The raw samples were ground to –100 mesh and dried in an oven at 100 °C for

60 min before reaction. The reactor was flushed with nitrogen and three times with hydrogen before final pressurization with hydrogen at room temperature. The reactor was agitated vertically during the experiment. After the reaction, the solid–liquid products were sequentially extracted by Soxhlet extraction with hexane and tetrahydrofuran (THF). Here, water yield was included in oil and gas yield. More details about the liquefaction procedures maybe found elsewhere [30].

2.3. Fourier transform infrared spectroscopy (FTIR)

Quantitative FTIR transmission spectra of coals were obtained using finely ground samples pressed in KBr pellets using a Nicolet model 6700 Fourier Transform infrared spectrometer. The mixture of coal and KBr (in the ratio of 1:300) were ground for 120 s and pressed into a pellet, then dried in a vacuum oven for 48 h. Spectra were recorded by co-adding 300 scans at a resolution of 2 cm^{–1}. Others details of the FTIR measurements have been published elsewhere [31].

2.4. Pyrolysis gas chromatography and mass spectroscopy (Py-GC/MS)

Pyrolysis gas chromatography and mass spectroscopy (Py-GC/MS) was performed using a Hewlett Packard 5890 Series II gas chromatograph and Hewlett Packard 5971 mass spectrometer equipped with a Pyroprobe 1000. The procedure and conditions of experiment used in this study as follows: Py-GC/MS analyses were carried out on whole channel samples. About 0.5–1.0 mg of sample was flash pyrolyzed (with a nominal heating rate of 5000 °C/s) by using a pyrolysis temperature of 610 °C for 10 s, during which time the pyrolyzates (pyrolysis products) were retained in the close-to-inlet section of the capillary column by cooling with liquid nitrogen. The sample was loaded into a thin quartz tube, which was then inserted into the horizontal filament coil in the pyroprobe. The pyrolysis unit was attached to a HP Hewlett Packard 5890 Series II gas chromatograph and the pyrolysis products were transferred directly to a capillary column (RXItm-5 ms Restek 30 m, 0.25-mm i.d.; 0.25-mm film thickness). The temperature of the interface was 270 °C. Helium was used as a carrier gas. The GC oven was cryogenically cooled to 40 °C with liquid nitrogen. This temperature was held for 1 min, then increased at a rate of 4 °C per min to 300 °C and held for 10 min. The HP 5890 GC was interfaced to a HP 5971 mass spectrometer. The mass spectrometer was operated in the electron-impact mode at 70 eV. The data were processed using Chemstation C1701BA software.

3. Results and discussion

3.1. Main characteristics of the selected samples

The general information on coal samples used is shown in Table 1. The elemental compositions of the samples were 6.00–6.34% hydrogen, 9.31–11.65% oxygen, and 1.05–4.68% organic sulfur, on a dry ash-free basis (daf), with 0.88–0.97 H/C atomic ratios. The samples have relatively high values of volatile matter, from 40.48% to 56.03% (daf). As can be seen in the maceral analysis data (Table 1), vitrinite and liptinite are the main maceral components of the samples. The samples have high barkinite content, especially LP and CG, ranging from 19.2 to 53.5 (vol.%). It can also be seen from Table 1 that the values of mean maximum reflectance of the samples range from 0.68% to 0.78%, indicative of the high volatile bituminous rank level, according to the ASTM correlation (D388).

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