



Impacts on Bitumite's Structure and Properties During Low-Temperature Oxidation†

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Published online: 10 March 2014;

AJC-14877

Low temperature oxidation could change the structure and properties of bitumite. Experimental results showed that the calorific value of coal decreased and the structure changed after low-temperature oxidation. Vitrinite and inertinite have almost the same radical groups. Radical groups' content in vitrinite was significantly higher than that in inertinite. Hydrogen peroxide oxidation altered less the thermodynamic property of the bituminite. Thermogravimetric graph slightly moved to low temperature zone after hydrogen peroxide oxidation and thermal enthalpy decreased.

Keywords: Low temperature oxidation, Bituminite, FTIR, Attenuated total reflectance micro-Fourier transform infrared.

INTRODUCTION

Low-temperature oxidation of coal is an important research subject in coal chemistry field. Research theory of low-temperature oxidation in coal mainly covers three aspects: firstly, research of coal molecular structure and oxidation relationship; secondly, research of coal spontaneous combustion theory based on activation energy indicators; thirdly, research of chemical kinetics and mechanism of coal oxidation¹. Many authors studied coals' molecular structure and oxidation relationship by means of infrared spectroscopy, X-ray diffraction and nuclear magnetic resonance (¹³C NMR) after the coal was oxidized through different temperature rises, oxygen supply, oxidation with oxidant, *etc.*²⁻⁵.

Directly detect the FTIR of vitrinite and inertinite with attenuated total reflectance micro-Fourier transform infrared (ATR-FTIR) spectroscopy is more convenient than the traditional method which firstly separates vitrinite and inertinite from coal and then detects their FTIR. The method was used in this research.

In coal inspection agencies, there are many reference samples which was placed in containers for several months. During that time, those properties and structure will change. Investigate and confirm this problem in this case is a matter of interest for many people.

EXPERIMENTAL

The coal sample was taken from the Aiweiergou Mine of Chinese Xinjiang Coking Coal (Group) Duty Limited Company and was prepared and divided for properties analysis.

Oxidized the coal sample at low temperature by two means: place them in bottle at room temperature for different time or moisten them with hydrogen peroxide, keep them in dark for 24 h and dry it in an oven at (105-110) °C for 2 h. The calorimeter was used to determine the samples' calorific value prior to and after oxidation. Divide the sample for maceral and reflectance determination into two parts, oxidize one with hydrogen peroxide. Make briquettes out of the two parts based on the standard and then determine the infrared spectra of vitrinite and inertinite in the two briquettes with ATR-FTIR. Use simultaneous thermal analyzer to estimate the thermodynamic properties of the original sample and the one oxidized by hydrogen peroxide.

RESULTS AND DISCUSSION

Properties of coal sample: The proximate analysis and ultimate analysis was following: M_{ad} 1.53 %, A_{ad} 24.67 %, V_{ad} 27.98 %; C_d 60.34 %, H_d 3.69 %, O_d 7.67 %, N_d 1.08 %, S_d 2.67 %. The content of vitrinite, inertinite, exinite and mineral content are 55.3, 23.1, 5.7 and 15.9 %, respectively, mean vitrinite

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

reflectance is 0.82. The coal ash chemical composition was: SiO_2 39.73 %, Al_2O_3 39.43 %, Fe_2O_3 3.42 %, CaO 6.80 %, MgO 0.39 %, SO_3 0.33 %, TiO_2 1.18 %, K_2O 0.37 %, Na_2O 0.08 %, P_2O_5 0.17 %.

Impact on calorific value during low-temperature oxidation: Calorific value of the samples which were placed for different periods (15d, 30d, 45d and 60d) and oxidized by hydrogen peroxide, compared to the original samples, decreased by 0.16, 0.27, 0.40, 0.52 and 0.91 MJ/kg, respectively, the reduction rate were 0.64, 1.09, 1.61, 2.09 and 3.66 %, respectively.

Impact on structures of vitrinite and inertinite in bitumite: The study explored the structure changes of vitrinite and inertinite with ATR-FTIR. As shown in Fig. 1, infrared spectra of vitrinite in original and oxidized coal samples were detected. As shown in Fig. 2, infrared spectra of inertinite in original and oxidized coal samples were detected. Main groups in inertinite and vitrinite of the original sample were identical, which indicated that compound types in the both do not differ significantly. However, the content of hydroxyl, methylene, carbonyl, benzene ring and C-O-C in the vitrinite were significantly higher than those in the inertinite, still the inertinite contained more carboxyl than the vitrinite. After being oxidized by hydrogen peroxide, reduction of hydroxyl, methylene, carbonyl, benzene ring and C-O-C content in vitrinite was higher than that in inertinite, which indicated that the hydrogen peroxide mainly reacted with the vitrinite in coal, while impacted the inertinite to a lower extent.

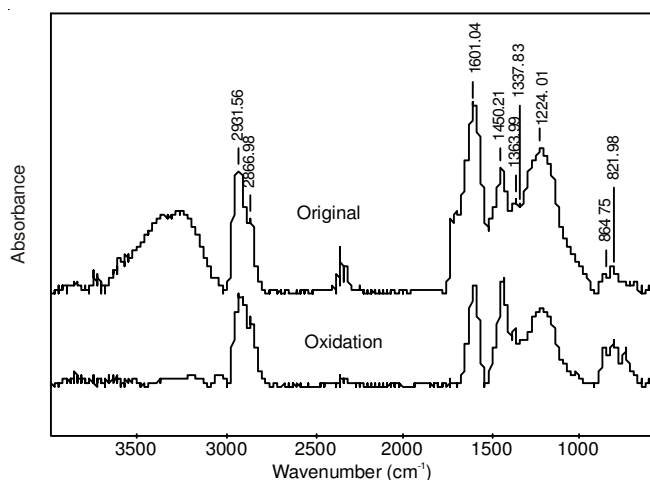


Fig. 1. Infrared spectra of vitrinite in original and oxidized coal samples

Impact on thermodynamic properties: As shown in Fig. 3, TG/DSC curve of original and oxidized coal samples was detected. TG/DSC curves of the original and oxidized samples were similar, which indicated that hydrogen peroxide oxidation had little impact on samples thermal properties. The greater the degree of coal samples metamorphism is experienced, the more compact the structure will be, the lower the amount of oxygen-bearing functional groups generated by hydrogen peroxide during oxidation, the smaller the impact on chemical reaction will be. The sample before oxidation experienced a slight weightlessness process at room temperature of 180 °C, which was mainly caused by the volatilization of a small amount of volatiles in the coal samples, such as moisture. As

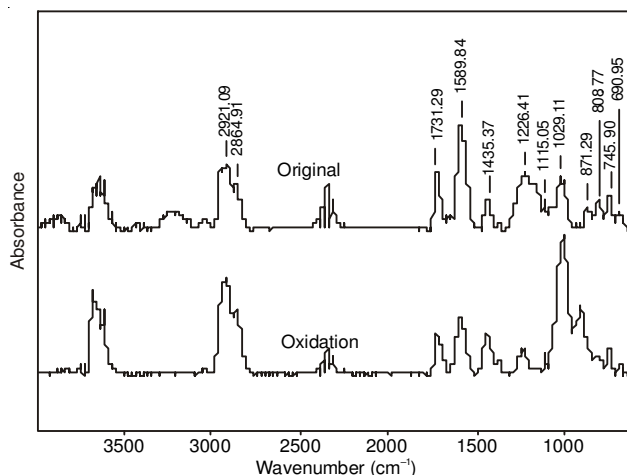


Fig. 2. Infrared spectra of inertinite in original and oxidized coal samples

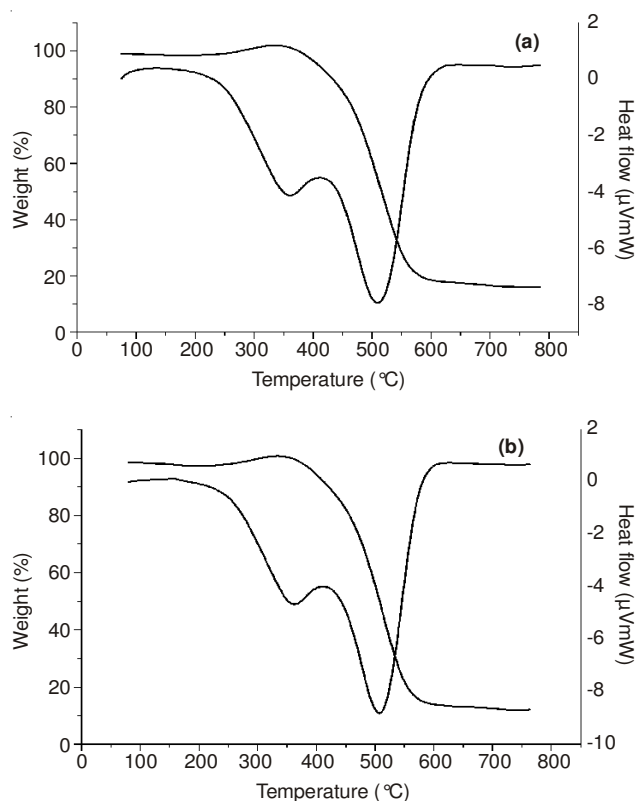


Fig. 3. TG/DSC curve of original (a) and oxidized (b) coal samples

the temperature further increased, the macromolecular chain ruptured, so chemisorption and chemical reaction were further enhanced. The original and oxidized coal samples experienced a weight gain process at 180-310 °C, which was due to a further enhancement of the macromolecular chain rupture and increase of the number of exposed active groups, oxygen uptake exceeded amount of the volatile gas and reactant gas, so coal samples showed a significant weight gain within this temperature range. At 310 °C, active groups and oxygen uptake of the nearby coal reached the maximum value. At this point, experimental temperature continued to rise, molecular chain split fully and generated a large amount of liquid volatiles, then the sample went through the major pyrolysis stage, experiencing a rapid combustion and eventually burning completely at 590 °C. Additionally, enthalpy of the oxidized sample was smaller than

the original one by comparing the DSC curve before and after oxidation.

Conclusion

The calorific value of the coal sample decreased after being oxidized. ATR-FTIR is convenient to detect the FTIR of maceral in coal and all the main groups in inertinite and vitrinite in the coal samples were identical. The structure changes a little during low temperature oxidation; hydrogen peroxide oxidation affected the thermodynamic properties of the bitumite to a lower extent, enthalpy of the oxidized samples decreased.

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