AAPG HEDBERG CONFERENCE
"NATURAL GAS GEOCHEMISTRY: RECENT DEVELOPMENTS, APPLICATIONS, AND TECHNOLOGIES"
MAY 9-12, 2011 – BEIJING, CHINA

Bulk Pyrolysis Characteristics of Coal under High-over Mature Stages

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Bulk pyrolysis characteristics of coal sample have been reported in many references (Liu et al. 2009; Erdmann and Horsfield, 2006; Dieckmann, et al., 2006; Mahlstedt, 2008), and the difference of chemical kinetic parameters obtained from different thermal apparatus (Rock-Eval-II and gold tube) also have been investigated (Wang and Lu, 2011). However, the recent research demonstrate that the gas generation potential of coal have not been exhausted at the termination temperature (600℃) for Rock-Eval-II pyrolysis equipment (with the heating rate of 10℃/min), and the same is true for gold tube pyrolysis equipment (with the heating rate of 2℃/min and termination temperature of 650℃). To investigate the terminal temperature of gas generation from coal under open and closed pyrolysis apparatus, the TG-MS combination equipment was employed. And the objective of this research is to compare the bulk pyrolysis characteristics of coal under TG-MS and gold tube apparatus, and then throw lights on the thermal experiment.

1. Sample and experiment

1.1 Sample

Coal was selected from Yingcheng coal mine in Southern of Songliao Basin, which was belong to the Shahezi Group Formation, the TOC content is 73.39%, nitrogen content is 0.51%, carbon content is 69.95%, hydrogen content is 5.24%, oxygen content is 12.46%. Sample of organic matter is belonged to type III and geochemical parameters are given in Table 1.

Table 1 Fundamental geologic and geochemical information of coal sample

Area	Yingcheng coal mine in Songliao Basin Southern Area
Lithology	Coal
Layer	Shahezi Group
TOC (%)	73.39
Tmax (°C)	427
IH (mg/gTOC)	217
IO (mg/gTOC)	3
Ro (%)	0.5

1.2 Experiments

This research designed two kinds of experiments. Open system experiment was carried out with TG-MS combined analysis equipment, and closed system experiment was carried out with gold tube experimental device.

1.2.1 TG-MS experiment

Samples were covered by inert gas (Argon, flows 45ml/min), with the heating rate of 10℃/min The sample is milled by hand and heated from 30℃ to 1000℃with the weight of 11mg. TGA apparatus was produced by the French SETARAM company. The yield information was detected by OmniStar^{TM}200 small online mass spectrometer (four mass filter mass spectrometer QMS422). MS specific parameters are as the following: detection charge-mass ratio range is from 1~300amu, and the scan rate is 0.2s/aum~60s/aum, in order to assure detection accuracy, the sample should be constant temperature for two hours before the heating experiment, and two hours purge process simultaneously, starting the pyrolysis with the pre-selected heating rate when all of the analysis production baseline smoothly.

1.2.2 Gold tube experiment

The gold tube experiment can utilize the good plasticity of the gold tube, and then it can setup and control experimental pressure flexibility, and the experiment pressure is the pressure of the fluid required. The experimental apparatus composition of gold tube experiment can be seen in reference (Lu Shuangfang et al., 2007).

Injection sample weight range of 10 ~ 60mg, under the pressure of 60 MPa, with the heating rate of 20°C/h and 2°C/h respectively, samples were heated from 200°C to 620°C or so. At a temperature point target closed the valve which connected to the autoclave, removed the autoclave from the incubator, and took out the gold tube after cooling. The gold tube placed in a special gas collection, quantitative system for accurate measurement, and used HP6890 gas chromatograph for GC analysis. After the gold tubes frozen by liquid nitrogen, cut it and put it into the solvent quickly, ultrasonic vibration for 5 minutes, and no loss of light hydrocarbons. To draw each gas production of every experimental sample point, per unit sample weight by hydrocarbon gas volume and the amount. The ratio of the gas production rate and the limit gas production rate of the experimental points is the gas conversion rate of each point. Based upon this we can get the gas conversion rate vs. heating temperature curve for the calibration of chemical kinetic model.

2. The comparison of pyrolysis yields

The temperature range of methane occurrence is 200-850℃from the pyrolysis result with TG-MS experiment (Fig.1). Combined with the extended Easy Ro% model (Everlien, 1996), the flowing relations can be obtained. For examples, when the methane transformation ratio (TR) is 10% (or 0.1), the corresponding Ro value is 0.7%; when the methane TR is 50%, Ro value is 1.3%; and when the methane TR is 90%, Ro is 3.2%. For gold tube experiment, the quantities of gas generation are almost equal under the two heating rates condition with the Ro value 3.2% (Fig.2), which are approximately 110ml/g sample. It demonstrates that the same amount of hydrocarbons generated from the coal under the same thermal effect. In Gold tube experiment, because of gas generation potential has not been terminated at the termination temperature, so we can not obtain the ultimate production rate and can not also get the TR correspond to Ro value of 3.2%. However, if taking the termination temperature production rate (160ml/g sample) as the maximum yields, the TR would be 68.75%, while the actual TR rate should be smaller than this value.

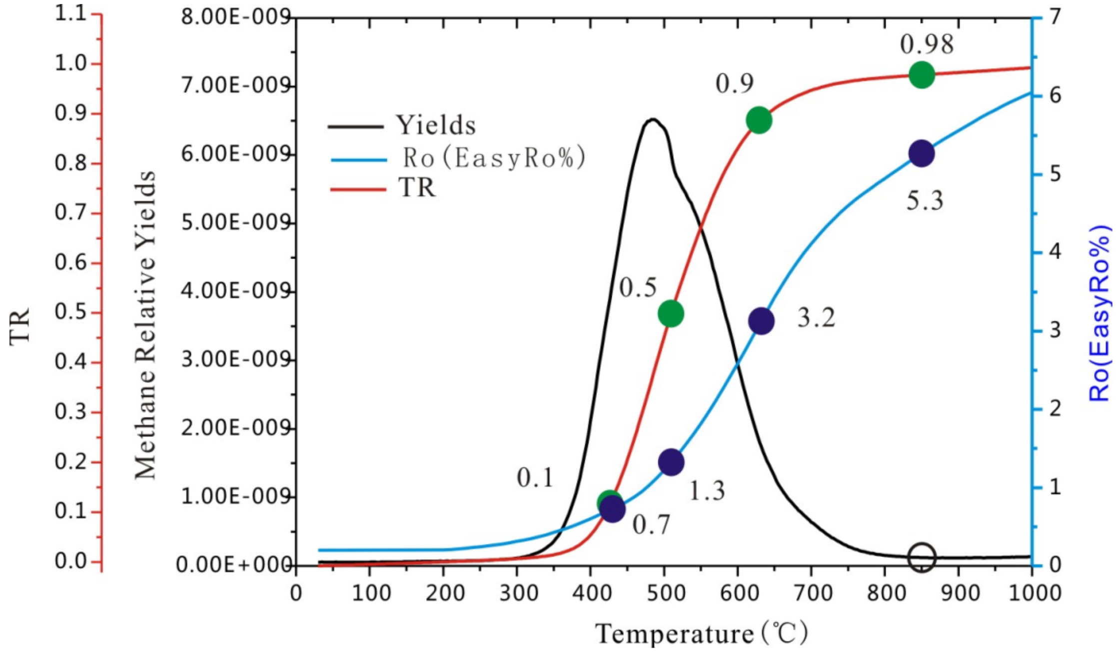

Fig. 1 Relation between CH_4 yields of coal sample from TG-MS experiment and Ro (open system, temperature range is from 30 to 1000℃, heating rate is 10℃/min)

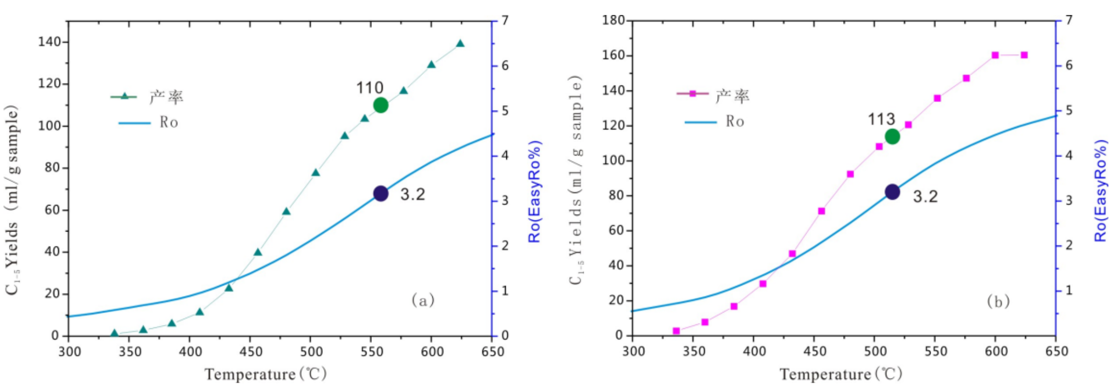

Fig. 2 Relation between CH_4 yields of coal sample from gold tube experiment and Ro (closed system, temperature range is from 300 to 650℃; a: 20°C/hour; b: 2°C/hour)

Judging from the results of gold tube experiments (Fig.2), coal still own higher gas generation ability when Ro value reach to 4.5% or above. While under the open system (TG-MS), methane TR reaches to 90% when Ro value is 3.2%. The termination temperature of methane generation from coal sample under TG-MS experiment is about 850℃ (with 10℃/min heating rate), and the corresponding Ro is about 5.3% calculated by extended EasyRo% model. However, the C_{1-5} mass yields increase all the while even at the end experiment temperature under the closed system experiment (the corresponding Ro is about 4.9% and with 2℃/hour heating rate), which indicates coal sample has gas potential at higher maturity stage. It may be caused by the recombined reaction of C_{6+} liquid hydrocarbons with kerogen or bitumen under closed environment, which will be formed new products with high thermal stability and the new formed products will generate methane at higher maturity stage. For open system, such as TG-MS experiment and Rock-Eval experiment, this recombined reaction cannot take place because the C_{6+} liquids are swept off by the carried gas. As gas generation capacity of coal did not depleted under the gold tube experiment, the gas limited threshold can not be known, so if replace the limited threshold by the maximum value, the relative gas TR is higher than the real one. It is also seen from the reference (Shuai et al., 2006), who heated coal rocks in a closed system with the heating rate of 1°C/h, termination temperature 600°C, the methane generation curve showed a growing trend all the detected points. Under the closed system, the limited value of gas generated from coal and the difference of gas generation limited values to the kinetic model parameters will be reported by other paper.

3. Kinetic characteristics in different experimental systems

Calibration the activation energy of gas generated from coal by using chemical kinetics. The activation energy of methane of gold tube experiments (average activation energy: 243.47kJ/mol, exponential factor: $7.67\times10^{13}min^{-1}$) is obviously higher than that of TG-MS (open system) experimental (average activation energy: 220.12kJ/mol, exponential factor: $1.11\times10^{14}min^{-1}$). The sources of methane under gold tube experiment are organic matter and liquid hydrocarbons (from the initial organic matter cracking), however, the sources of methane under TG-MS (open system) experiment is only the direct cracking of organic matter. Therefore, the activation energy of methane in gold tube experiment is higher than that in the TG-MS experiment.

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