



Full Length Article

The evolution of chemical groups and isotopic fractionation at different maturation stages during lignite pyrolysis



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ABSTRACT

In this study, the evolution of different chemical groups and isotopic fractionation at different maturation stages of coals were investigated by gold-tube pyrolysis, detailed geochemical analysis and theoretical calculations based on Density Function Theory (DFT). The results from non-isothermal pyrolysis of lignite revealed that the conversion and hydrocarbon generation of lignite can be divided into four maturation stages in the range of R_o from 0.35 to 4.66%. Fourier-transform infrared spectra (FTIR) results of residual coals showed that the evolution of different functional groups dominates the generation of oil and gas products at different maturation stages. Correspondingly, the activation energy for methane generation was fitted into four Gaussian distributions, which elucidated different formation mechanisms or precursors of methane. Theoretical calculations indicated that the difference of isotopic fractionation kinetics for the cleavage of different chemical groups dominates carbon and hydrogen isotopic compositions of methane during lignite pyrolysis. By calculation of the isotopic fractionation factor ($\alpha = k^*/k$) for the cleavage of ethyl and methyl radical, a simplified model was established to predict the carbon isotopic ratios of ethane ($\delta^{13}C_2$) with and without cracking. Moreover, thermodynamic calculations confirmed that the occurrence of recombination between ethane and polycyclic aromatics is available at temperatures between 25 and 650 °C. It is also demonstrated that the isotopic exchange between ethane and methyl aromatics can occur and will result in the depletion of D for residual coals and ^{13}C for ethane during this process. Hence, the recombination reactions should be responsible for the rollover of $\delta^{13}C_2$ at extremely high maturity both in experimental and geological conditions.

1. Introduction

Generally, humic coals have been recognized as important sources for the accumulation of hydrocarbon gases in sedimentary basins [1]. Till now, numerous researches have been carried out to ascertain the geochemical features of coal-derived gas and the maturation of coals [2–9]. Previous works established several empirical relationships and criterion based on field data to identify the origin of coal-derived gas in particular reservoirs [2–5]. Meanwhile, the evolution of chemical groups of bulk coals and their macerals with increasing maturity were well observed by elemental analysis and in-situ spectroscopy, including Raman spectroscopy, Fourier Transform infra-red spectroscopy (FTIR) and ^{13}C NMR spectroscopy [10–16]. In addition, pyrolysis experiments were applied to address the potential, kinetics and isotopic fractionation for gas generation from type-III kerogen and humic coals [17–23]. These studies significantly enhance our understanding of the process for the generation and accumulation of coal-derived gas in the subsurface.

The upper thermal maturity limit for gas generation from coal was

an important parameter for the gas resource prediction in deep formation and has been re-studied recently [15,24,25]. Early works based on geological observations suggested vitrinite reflectance (R_o) of 2.0% or 3.0% as the upper thermal maturity limit of gas generation from coals [1,26,27]. However, the most recent discovery of deep coal-derived gas reservoirs [8,28,29] and experimental results from coal pyrolysis [15,25,30], indicated that considerable amounts of methane can be generated at higher maturity or temperature. Recent pyrolysis experiments and NMR analysis in our group demonstrated that the upper limit of gas generation from coal should be of R_o at 5.0% [15,24]. The decreasing of H/C ratios of coals with increasing R_o can be divided into several different stages [15]. FTIR detections on natural coals with various ranks also implied that the evolution of different functional groups during coalification can be discriminated into different stages [12]. Hydrocarbon generation from organic matter is a process of side chain cleavage and polymerization of aromatic rings accompanied by carbon-enrichment and dehydrogenation [1,15,26]. Although the relationship between the evolution of coal chemical structures with

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maturity was well observed [10–13], the kinetics for the cleavage of different chemical groups and the isotopic fractionation in different maturation stages for coals are still uncertain [6]. Moreover, recombination reactions are suggested to generate neofomed organic matters and to affect the hydrocarbon generation and isotopic compositions at high maturity or temperature [9,21,30]. However, limited work has focused on the thermodynamic effects of isotopic fractionation during this process.

In this study, a series of non-isothermal gold-tube pyrolysis of lignite were firstly conducted to simulate the maturation of coals. Combined with detailed analysis of the products and residual coals including chemical and isotopic compositions and FTIR detections, the maturation stages during coal pyrolysis were identified. Moreover, theoretical calculations based on DFT were carried out to address the kinetics of the isotopic fractionation for the cleavage of different chemical groups and the effects of recombination reactions on the isotopic fractionation at extremely high maturity.

2. Material and methods

2.1. Sample

The lignite was collected from Late Tertiary Formation in the Chuxiong Basin, located in Yunnan Province (Southwest China). The sample contains 51.0 wt% TOC, H/C of 1.01 and O/C of 0.43. In addition, the value of vitrinite reflectance (R_o) is 0.35%. The geochemical characteristics of this sample, including Rock-Eval data, elemental and isotopic compositions, are shown in Table 1. Prior to pyrolysis, the sample was crushed into powder (~100 mesh).

2.2. Gold-tube pyrolysis

All pyrolysis experiments were conducted using a gold-tube pyrolysis system. The tubes used in our experiments were 50 mm in length with an inner diameter of 5.0 mm and a wall thickness of 0.50 mm. In a typical procedure, the samples (100 mg) were initially accurately weighted and loaded into a tube with one end sealed. The air in the tube was evacuated by flushing inert argon, and the other end of the tube was crimped and sealed using an argon arc welder with most of the sealed one emerged in liquid nitrogen. The detailed method for sample loading and tube sealing can be seen in He et al. [31]. Pyrolysis temperature was programmed as follows: the tube with sample loaded was firstly heated from room temperature to 300 °C in two hours, and then heated up again from 300 °C to desired temperature at 1 °C/h and 10 °C/h. A constant pressure of 50 MPa was applied in all the pyrolysis experiments. When the desired temperature was reached, the pressure was released, and the gold tubes were withdrawn. Before analysis, the tubes were weighed to ensure that there was no leakage during pyrolysis.

2.3. Gas determination and analysis

The collection of gas in each gold tube was performed by a custom-

made unit that was connected with a vacuum pump. The detailed method for volume and molar determination of gas products was conducted according to Zhang et al. [32].

Identification and quantification of the individual hydrocarbon and non-hydrocarbon gaseous components were conducted by a two-channel Agilent 7890 Series Gas Chromatograph (GC) integrated with an auxiliary oven, which was custom-configured by Wasson-ECE instrumentation (For Collins, CO.). The instrument was fitted with two capillary and six packed analytical columns, a flame ionization detector (FID) and two thermal conductivity detectors (TCD). The carrier gas for FID and fist TCD (for CO₂ determination) were high-pure He, and that for second TCD (for H₂ and H₂S determination) was high-pure N₂. The temperature program of the GC oven was: heating from initial 68 °C (held for 7 min) to 90 °C (held for 1.5 min) at 10 °C/min, then to 175 °C (held for 5 min) at 15 °C/min. The external standard method was employed for the chromatograph response calibration; the certified gas standards were prepared at a precision of less than ± 1 mol% for each component by BAPB Inc.

Stable carbon isotope analysis of gas products were performed using Thermo Delta V Advantage isotope ratio mass spectrometry (IRMS). All gas samples were firstly separated using a Thermo Trace GC Ultra gas chromatograph with a 60 m J & W fused silica DB-1MS capillary column (30 × 0.25 mm i.d.; 0.25 μm film thickness of 100% methylsilicone). The oven temperature program was initially from 33 °C to 80 °C at 8 °C/min, then to 250 °C at 5 °C/min, He was used as carrier gas at a constant flow of 1 ml/min, the injection port temperature was 300 °C. Stable hydrogen isotope ratios (δD) were measured by Thermo Mat253 mass spectrometers, which was composed of an Agilent 6890N GC and Mat253 IRMS. Carbon and hydrogen isotope values are referenced to the PDB and SMOW standards respectively. An external reference of pure methane with known isotope ratio was injected for calibration at five samples intervals to enhance precision and reliability. The precision in the measurements is ± 0.5‰ for δ¹³C and ± 5.0‰ for δD, respectively.

2.4. Oils and residual coals collection and determination

The oils generated during the pyrolysis were collected by solvent extraction of the solid residuals using dichloromethane (DCM). The total organic carbon (TOC) and Rock-Eval analysis of residual coals (solid residuals after DCM extraction) were conducted by a Rock-Eval II equipment (Vinci Technologies, France). The elemental compositions of lignite and residual coals were determined using a Vario Micro Cube element analyzer (Elementar, Germany) according to the national criterion of PR China (GB/T 19143–2011). The temperatures of the combustion and reducing tubes were set at 1140 ± 10 °C and 840 ± 10 °C, respectively. The test substance or external standard was acetanilide (Merck KGaA, Germany). The stable carbon and hydrogen isotopic ratios of the original lignite, oils and residual coals were determined with a Flash EA 1112Series stable isotope mass-spectrometry instrument. The Fourier-transform infrared spectra (FTIR) were collected from a Nicolet continuum Micro-IR spectrometer at a resolution of 2 cm⁻¹. Bulk samples for FTIR spectroscopy were prepared using the

Table 1
The essential geochemical characteristics of lignite.

TOC wt%	S content wt%	T _{max} °C	S ₁ wt.%	S ₂ wt.%	S ₃ wt.%	HI mg/g.C	OI mg/g.C	C wt.%	H wt.%	O wt.%	N wt.%	H/C	O/C	δ ¹³ C ‰	δD ‰
51.0	0.46	425	4.29	57.79	27.13	113	57	50.77	4.28	29.40	1.91	1.01	0.43	-26.6	-162.5

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