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The role of water during gas generation

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Abstract. Resources of coal-derived gas in the deep strata are found abundant in China. Recent advances in petroleum geochemistry suggest water may contribute hydrogen and oxygen to the formation of hydrocarbons and oxygenated alteration production. However, the role of water during gas generation has been in debate due to conflicting research results. In this study, a Jurassic coal sample from the Kuqa depression, Tarim Basin, China was artificially matured by nonhydrous pyrolysis and hydrous pyrolysis at isothermal (330 °C, 350 °C, 370 °C for 72h) and non-isothermal (440 °C, 470 °C and 500 °C at heating rate of 2 °C/h) temperatures. Both isothermal and non-isothermal experiments generated more methane but less C₃₋₅ hydrocarbon gases and CO₂ non-hydrocarbon gas in the nonhydrous system relative to hydrous conditions. In the isothermal experiment, the nonhydrous pyrolysis generated at most 24% more methane relative to the hydrous pyrolysis, but the hydrous pyrolysis generated 5%~87% more C₃₋₅ hydrocarbon gas and at most 28% more CO₂ relative to the nonhydrous pyrolysis. In the non-isothermal experiment, the nonhydrous pyrolysis generated 25%~94% more methane relative to the hydrous pyrolysis, but the hydrous pyrolysis generated at most 2.56 times more C₃₋₅ hydrocarbon gas and 1.04 times more CO₂ relative to the nonhydrous pyrolysis. In general, the compositional variation trend of hydrocarbon and non-hydrocarbon gases is similar between the isothermal and non-isothermal experiments. This indicates that contribution from the supercritical water in the non-isothermal pyrolysis is not essential. With the presence of water, the secondary cracking of C₃₋₅ alkanes in the hydrous experiments was significantly suppressed, as shown by the relatively higher yield of C₃₋₅ alkanes in the hydrous systems. The availability of exogenous hydrogen from water in the hydrous pyrolysis inhibits the carbon-carbon bond cross linking, thus the reaction pathway of hydrocarbon generation is dominated by the thermal cracking of carbon-carbon bonds. The significant increase in CO₂ in the hydrous pyrolysis indicates water is not only the source for exogenous hydrogen but also the source for the excess oxygen accounted for the formation of CO₂. The overall geochemical implication of these experimental results is that it is important to consider the role of water in the hydrocarbon generation, especially in the deep strata where both geological and geochemical conditions are complex.

1. Introduction

China's natural gas industry has made brilliant achievements after a long and arduous exploration. After 70 years' exploration and development, China's proven reserves and production of natural gas has changed from insignificant to the world's top, which makes China from a gas-poor country jump to the world's sixth largest gas production country. Among them, coal-derived gas made the most important contribution. By the end of 2018, the cumulative proven reserves of coal-derived gas accounted for 60.1% of the total and the gas production of giant coal-derived gas fields accounted for 50.9% of the total



national gas production [1-2]. A number of studies have demonstrated that resources of coal-derived gas in the deep strata are abundant in China [3-5].

Recently, the role of water and inorganic minerals during the gas generation in deep strata gets more and more attraction. It is proposed that water maybe facilitate reaction mechanism not available in dry environments and contribute hydrogen and oxygen for the formation of hydrocarbons, which may result in the significant increase of the amount of natural gas in the deep basin environment where mature kerogen is low in hydrogen [6]. Both pyrolytic experiments and field data proposed the exogenous source of hydrogen during the hydrocarbon generation, especially at high thermal mature stage [7-10]. Laboratory experiment even found extensive and reversible incorporation of water-derived hydrogen into C₂–C₅ n-alkanes on timescales of months under hydrothermal conditions [11]. However, pyrolytic experiments on lignite proposed that closed nonhydrous pyrolysis generates on the average 15% more gas than hydrous pyrolysis [12]. Therefore, understanding of the role of water during gas generation is still poor, especially in the deep basin environment. In order to further investigate the role of water during gas generation, in this study, two sets of pyrolytic experiments on a coal sample were carried out.

2. Material and method

A Jurassic coal sample from the Kuqa River section in the Kuqa depression, Tarim Basin, China was collected and used for the pyrolytic experiments. Jurassic coal measures are widely distributed in the Kuqa depression and are the main source rocks of coal-derived gas in the deep strata. For the coal sample, the vitrinite reflectance Ro% value is 0.7%, total organic carbon (TOC) is 81.0%, S₁ and S₂ are 6.7 mg/g and 114.8 mg/g, respectively, T_{max} is 436.0 °C, and HI is 141.7 mg/g.TOC (Table 1). Elemental composition of the coal sample was also analyzed. The coal sample was composed of 1.52% of nitrogen, 76.88% of carbon, 5.21% of hydrogen, and 9.47% of oxygen (Table 1). The H/C ratio is 0.81 and O/C ratio is 0.09. Water used in the hydrous experiments was sea water and bought from the Chinese Academy of Geological Sciences. It is a standard material with hydrogen isotope of −4.8‰ (GBW (E) 070016).

Table 1. Rock-Eval pyrolysis and elemental composition of the Jurassic coal sample

TOC %	T _{max} °C	S ₁ mg/g	S ₂ mg/g	HI mg/g.TOC	Ro %	N %	C %	H %	O %	H/C	O/C
81.0	436.0	6.7	114.8	141.7	0.7	1.52	76.88	5.21	9.47	0.81	0.09

The coal sample was crushed and sieved with a size less than 0.125 mm. The crushed sample was placed in an oven at a temperature of 100 °C for two hours to get rid of the free water inside the sample. During the whole loading process, the sample was placed in a jar with desiccants.

Considering the potential effects from supercritical water, the experiments were divided into two sets. Both sets of experiments were conducted under hydrous and nonhydrous closed system under pressure of 40 MPa. Here the word “nonhydrous” is referred to the experiment with no added water, and the word “hydrous” is referred to the experiment with added water. It is reported that pyrolytic experiments on lignite either with added water or with no added water generated 14.6~15.2 wt.% water [12]. So this study prefers to adopt nonhydrous rather than anhydrous for the experiment with no added water. The first set is isothermal pyrolytic experiments for 72 hours. The temperatures are 330 °C, 350 °C, 370 °C, corresponding to the final Easy Ro% value of 1.34%, 1.64% and 1.99%, respectively [13]. In this set, the temperature is not more than 370 °C, which is below the critical temperature of pure water (374 °C), so water is normal liquid water. The second set is non-isothermal pyrolytic experiments. In this set of experiment, temperature increased to 300 °C in two hours from room temperature, hold for half an hour, then increased to 440 °C, 470 °C and 500 °C at heating rate of 2 °C/h, which corresponds to a final Easy Ro% value of 1.82%, 2.35% and 2.92%, respectively [13]. In this set, due to the high temperature water is supercritical water. The pyrolytic experiments were conducted in a gold tube system in the PetroChina Research Institute of Petroleum Exploration and Development, China (RIPEd). The pyrolytic products of hydrocarbon and non-hydrocarbon gases are determined using a two-channel Wasson-Agilent 7890

Series gas chromatograph (GC), which was calibrated by an external standard. Certified gas standards were prepared at a precision of better than ± 1 mol% for each component made by BAPB Inc.

3. Results

3.1. Gas product of the isothermal experiments

In the isothermal experiment, the methane yield is 42.08, 47.23 and 62.86 ml/g for the nonhydrous experiment at thermal maturity of 1.34%, 1.64% and 1.99%, respectively, and it is 33.84, 38.25 and 58.36 ml/g for the hydrous experiment at thermal maturity of 1.34%, 1.64% and 1.99%, respectively. The methane yield clearly increases with increasing thermal maturity in both nonhydrous and hydrous experiments, however, the yield of methane in nonhydrous experiment is higher than that in the hydrous experiment. The difference of methane yield between nonhydrous and hydrous experiments decreases with increasing thermal maturity, i.e., 24% at Ro% of 1.34%, 23% at Ro% of 1.64% and 8% at Ro% of 1.99%. The yield of C₃₋₅ alkanes is 0.77, 0.71 and 0.26 ml/g for the nonhydrous experiment at thermal maturity of 1.34%, 1.64% and 1.99%, respectively, and it is 0.84, 0.75 and 0.49 ml/g for the hydrous experiment at thermal maturity of 1.34%, 1.64% and 1.99%, respectively. In contrast to methane, with increasing thermal maturity, the yield of C₃₋₅ alkanes decreases both in nonhydrous and hydrous experiments. Moreover, the yield of C₃₋₅ alkanes in hydrous experiment is higher than that in the nonhydrous experiment. The hydrous pyrolysis generated about 9%, 5% and 87% more C₃₋₅ hydrocarbon gases at thermal maturity of 1.34%, 1.64% and 1.99%, respectively relative to the nonhydrous pyrolysis (Figure 1).

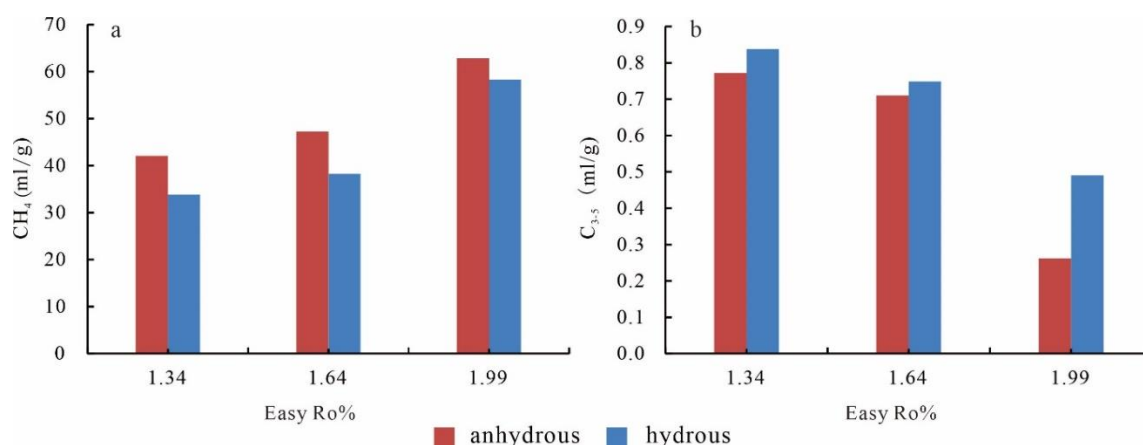


Figure 1. The yields of CH₄ and C₃₋₅ alkanes under anhydrous and hydrous conditions in the isothermal experiment

3.2. Gas product of the non-isothermal experiments

In the non-isothermal experiment, either hydrous or nonhydrous, methane yield increase with increasing thermal maturity, while the yield of C₃ to C₅ alkanes decrease with increasing temperature. For example, the yields of methane are 44.35, 55.91 and 68.62 ml/g for the nonhydrous experiment and 22.91, 44.71 and 54.87 ml/g for the hydrous experiment, at thermal maturity of 1.82%, 2.35% and 2.92%, respectively. While the yields of C₃₋₅ alkanes are 0.56, 0.15, 0.12 ml/g for the nonhydrous experiment and 0.69, 0.53, 0.13 for the hydrous experiment, at thermal maturity of 1.82%, 2.35% and 2.92%, respectively. In general, the methane yield in nonhydrous experiment is much higher than that in the hydrous experiment, especially at thermal maturity of 1.82%, the methane yield in nonhydrous experiment is around 94% higher than that in the hydrous experiment. With increasing thermal maturity, the differences of methane yield between nonhydrous and hydrous experiments decrease to 25% at Ro% of 2.35% and 2.92%. In contrast to the methane, the yield of C₃₋₅ hydrocarbon gases decreases with increasing thermal maturity. The yield of C₃₋₅ hydrocarbon gases in hydrous experiment is higher than that in the nonhydrous

experiment. The hydrous pyrolysis generated about 23%, 256%, 7% more C_{3-5} hydrocarbon gases at thermal maturity of 1.82%, 2.35% and 2.92%, respectively relative to the hydrous pyrolysis (Figure 2).

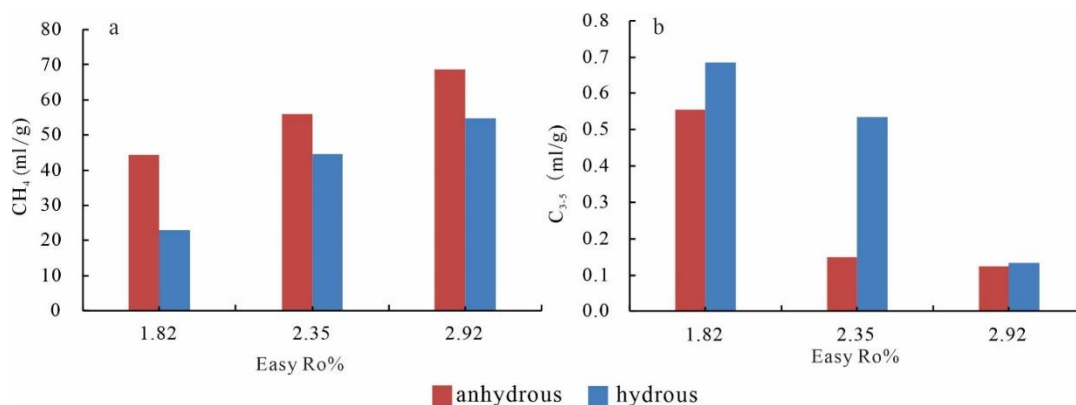


Figure 2. The yields of CH_4 and C_{3-5} alkanes under anhydrous and hydrous conditions in the non-isothermal experiment

4. Discussion

Previous studies reported on average 15 wt.% more methane in the closed nonhydrous pyrolysis than that in the hydrous pyrolysis for the lignite sample [12], however, this difference increases to 52-76% for nonhydrous pyrolysis relative to hydrous pyrolysis of source rocks with Type-II kerogen [10]. These experiments are all conducted at isothermal temperatures not more than 370 °C for different duration, which is similar to the isothermal experiment that used in this study. In these experiments, supercritical water is avoided. This is because supercritical water with temperature above 374°C (i.e., critical temperature for pure water) has very different properties than the liquid water. For example, supercritical water has high reactivity, thus very high solubility, where water molecules are not held by hydrogen bond and they can float around as free radicals. However, compared to the non-isothermal experiments which was conducted with supercritical water, the compositional variation trend of the hydrocarbon gas and non-hydrocarbon gas (CO_2) between hydrous and nonhydrous conditions is very similar (Figure 3). This indicates that contribution from supercritical water on gas yields is not essential.

In both sets of experiments (isothermal and non-isothermal), the yield of methane in nonhydrous experiment is always higher than that in the hydrous experiment, however, such differences decrease with increasing thermal maturity (Figure 3). In contrast to methane, the yield of C_{3-5} alkanes in nonhydrous experiment is always lower than that in the hydrous experiment. While the ethane yield in nonhydrous experiment is higher than that in the hydrous experiment at low maturity, but with increasing thermal maturity, the ethane yield in nonhydrous experiment gets lower than that in the hydrous experiment. In sum, the nonhydrous pyrolysis generated 18%~84% more hydrocarbon gas relative to hydrous pyrolysis in the non-isothermal system, while the nonhydrous pyrolysis generated 5%~22% more hydrocarbon gases relative to hydrous pyrolysis in the isothermal system. The significant bigger increase amplitude in the non-isothermal system is likely due to the higher thermal maturity in the non-isothermal system.

With the presence of liquid water, the reaction pathway of hydrocarbon generation is dominated by thermal cracking of carbon-carbon bonds, while in the absence of liquid water, the dominant reaction pathway is carbon-carbon bond cross linking, therefore, under the hydrous experiment, the availability of exogenous source of hydrogen will reduce the rate of thermal decomposition, promote thermal cracking, and inhibit carbon-carbon bond cross linking [10]. A possible delay of secondary cracking reactions in hydrous conditions compared to anhydrous conditions was proposed in the isothermal experiments [10, 12]. Experimental results also demonstrated that the destruction of crude oil to gas was significantly inhibited by the presence of water [14]. This explains why the methane yield in the nonhydrous system is higher relative to the hydrous condition. The conflicting results between Gao et al. [15] and this study

also supports that a delay of secondary cracking reactions exist in hydrous experiments. Previous study by Gao et al. [15] found that hydrous pyrolysis generated more hydrocarbon gases relative to the nonhydrous pyrolysis, where the pyrolysis was conducted at constant temperatures of 400 °C, 430 °C, 450 °C, 500 °C, 550 °C for 72 hours. Considering the temperatures are above 374 °C (critical temperature of pure water), the non-isothermal pyrolysis in this study has temperatures of 440 °C, 470 °C, and 500 °C, which is above the critical temperature of water as well. The temperatures were raised from 300 °C to the designed temperate at a heating rate of 2 °C/h. The heating duration was 70 hours from 300 °C to 440 °C, 85 hours from 300 °C to 470 °C and 100 hours from 300 °C to 500 °C. Though the heating duration of the non-isothermal experiment in this study is similar or even longer than 72 hours, the duration staying at high temperature is short, which results in the delay of the secondary cracking reactions in the hydrous experiment. In addition, according to the lower concentration of C₃₋₅ heavy hydrocarbon gases in the nonhydrous pyrolysis, it is concluded that the presence of water may suppress the cracking of C₃₋₅ heavy hydrocarbon gases, resulting the higher yield of C₃₋₅ heavy hydrocarbon gases in the hydrous pyrolysis. Pyrolytic experiments showed that open nonhydrous pyrolysis of coal generated hydrocarbon gases extremely enriched in C₂₊ hydrocarbons relative to closed nonhydrous pyrolysis [16]. This indicates, cracking of heavy hydrocarbons occurred in the closed nonhydrous pyrolysis. With the presence of water, the secondary cracking of C₃₋₅ alkanes in the hydrous experiments was significantly suppressed, as shown by the relatively higher yield of C₃₋₅ alkanes in the hydrous systems (Figure 3).

The maximum increase in CO₂ in hydrous condition can be up to 104% in the non-isothermal system and 28% in the isothermal system. The significant increase in CO₂ in hydrous system relative to nonhydrous conditions in both isothermal and non-isothermal experiments also supported the generation of exogenous hydrogen in hydrous system. Isothermal pyrolysis on lignite also demonstrated a 37% increase of CO₂ in the hydrous system relative to the nonhydrous condition [12]. Water is not only the source of hydrogen, but also the source of excess oxygen needed to account for the CO₂ generated under hydrous conditions [10]. Considering the low temperature (not more than 370 °C in isothermal experiment) and low content of CO, reactions such as steam-methane reaction or water-gas shift reaction are unlikely to be responsible for the formation of CO₂ in the hydrous experiment. One possible explanation includes the reaction that water may oxidize the existing carbonyl groups and thus form hydrogen and carboxyl groups, and the carboxyl groups will form CO₂ by decarboxylation with increasing thermal maturity [10]. Such interaction between water and carbonyl groups has been reported to happen at temperature as low as 150 °C [17] or even 350 °C [18].

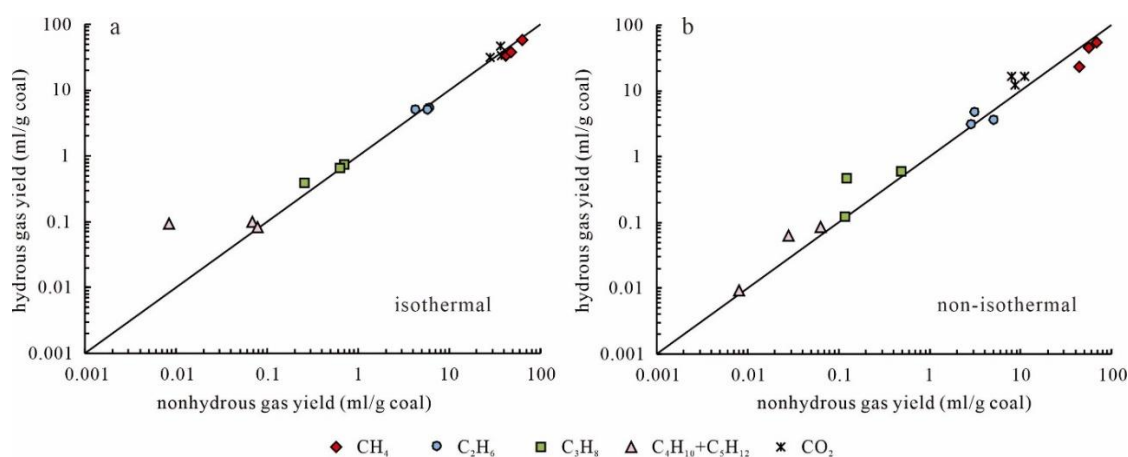


Figure 3. Plot of gas yields generated by nonhydrous pyrolysis against those by hydrous pyrolysis at isothermal (a) and non-isothermal (b) temperatures

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