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The Impact of Aqueous Medium on Gas Yields and Kinetic Behaviors of Hydrogen Isotope Fractionation during Organic Matter Thermal Degradation

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In order to recognize the impact of aqueous medium on gas yields and the kinetic behaviors of hydrogen isotope fractionation during organic matter thermal degradation, and to establish and calibrate the chemical kinetics models for quantitative description of the gas generation process and hydrogen isotope fractionation process, so that to reveal in depth the information like natural gas genesis, maturity evolution, aqueous medium environment and reservoir forming implied in the hydrogen isotope composition of natural gas, the gold tube apparatus was employed to conduct thermal simulation experiment by mixing the nC₁₈ with the water of different properties and proportions. By combining with GC and isotope analysis, the generation rate of natural gas components and the relation among hydrogen isotope composition of each component, experimental temperature and heating rates have been obtained. On such basis, the chemical kinetics models of methane generation and hydrogen isotope fractionation have been established and calibrated.

The results indicate that under the higher temperature conditions, hydrous experiment has obvious impact on the gas yields, such as the more the added water, the higher yields of hydrocarbon gas and H₂, and the existence of water obviously prolong the temperature interval with heavy hydrocarbon gas existence. It also shows that the hydrogen isotope of C₁, C₂ and C₃ hydrocarbon gas generated by hydrous experiment is obviously lighter than that generated by anhydrous experiment, and with the increasing amount of added water, the δD value of hydrocarbon gas gradually decreases (Fig. 1). Compared with gas yields, the variation of δD value is more sensitive to aqueous medium in the thermal simulation experiment. However, compared with the amount of the added water, the aqueous medium property has smaller impact on the gas yields, which still shows the inherit effect on hydrogen isotope composition of aqueous medium. Through the simulation and the isotope fractionation behavior analysis, it is validated that the hydrogen isotope fractionation process can be well described by the chemical kinetic model. The difference of reaction fraction of normal methane and D-containing methane is large, corresponding to the same activation energy. The reaction fraction of normal methane is obviously higher in the lower part of activation energy distribution, while that of D-containing

methane is higher in the higher part of activation energy distribution (Fig. 2). Therefore, it will result in larger hydrogen isotope fractionation, and the δD values will be more sensitive to the variation of maturity. Meanwhile, the average activation energies of methane generation from nC-18 in the hydrous experiments are higher than that in the anhydrous experiment, and the more amount of the added water, the larger the average activation energy of methane generation reaction (Table 1). This has laid foundation for its exploratory application in the study of gas reservoir forming history and the gas-source correlation, which indicates the research and application prospects in this orientation.

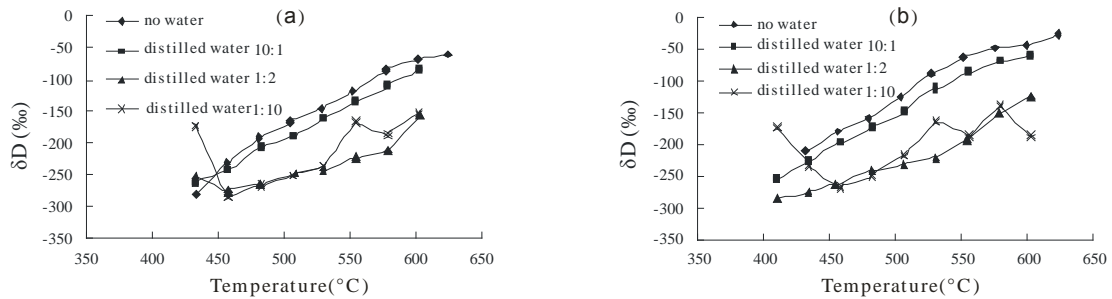


Fig. 1 - Evolution of δD_1 value with temperature in the experiment with different added water (a: heating rate $20\text{ }^{\circ}\text{C}/\text{h}$; b: heating rate $2\text{ }^{\circ}\text{C}/\text{h}$)

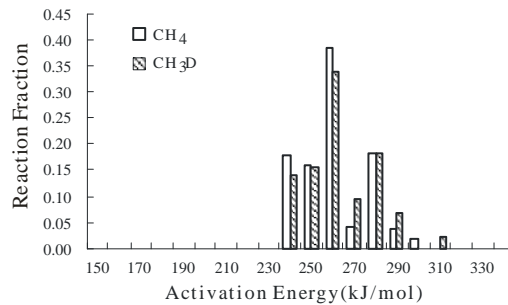


Fig. 2 - Distribution of activation energy in reaction of normal methane and Deuterium-containing methane generated from Octadecane cracking under anhydrous experiment

Table 1 - Difference of Kinetic Parameters of Normal Methane and D-containing Methane in Each Experiment

Experiment	E_{i_H} (kJ/mol)	E_D (kJ/mol)	A_D / A_{i_H}	$E_D - E_{i_H}$ (kJ/mol)
Octadecane	259.87	263.04	1.00	3.17
Octadecane added with distilled water (10:1)	260.73	263.40	1.00	2.67
Octadecane added with distilled water (1:2)	262.07	266.03	1.00	3.96
Octadecane added with water of Daqing Oilfield (1:2)	263.85	268.59	1.02	4.74
Octadecane added with water of Tarim Oilfield (1:2)	262.63	267.08	1.02	4.45
Octadecane added with distilled water (1:10)	267.56	274.12	1.10	6.57

Note: E_{i_H}, E_D - average activation energy