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Chemical kinetics study of hydrocarbon regeneration from organic matter in carbonate source rocks and its significance

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In the comparison research of hydrocarbon regeneration, a low maturity carbonate source rock is heated to different temperatures in a gold tube to obtain a series of samples with different maturities. Then, the heated samples, before and after extraction, are subjected to Rock-Eval pyrolysis through a thermal simulation of hydrocarbon regeneration in order to inspect pyrolysis characteristics and probe into the characteristics of the chemical kinetics of each sample. The results indicate that, whether hydrocarbon regeneration peak is delayed or advanced, the potential of hydrocarbon regeneration is closely related to the expulsion amount and breakdown maturity of primary hydrocarbon generation. After extraction, the average activation energy of artificially maturated samples increases with the increasing maturity, but the chemical kinetic properties of un-extracted samples decrease. The calibrated chemical kinetic models that describe extracted and un-extracted samples are applied to the Bohai Bay and the Songliao Basin, and the results indicate that the combination of the two models can explain some contradictory conclusions previously reported. These results also facilitate the quantitative evaluation of the amount of hydrocarbon regeneration by the chemical kinetic method.

carbonate, hydrocarbon regeneration, chemical kinetics, thermal simulation, quantitative evaluation of hydrocarbon regeneration

Many hydrocarbon-bearing basins, especially in carbonate rocks basins, are multistage basins in China. These kinds of basins usually undergo complicated and multistage tectonic movements, so the hydrocarbon regeneration of organic matter is a common issue in superimposed basins. It is also one of the scientific "hard nuts to be cracked" in hydrocarbon source rock evaluation and petroleum exploration. As a result, the knowledge and research on this issue are very significant to superimposed basin evaluation, especially to the carbonate rock related to the petroleum exploration prospect and the exploration direction. Because of this issue, in recent years a number of scholars [1−15] have been conducting massive discussions about this matter in terms of simulation experiments and geological analysis in China. Currently, no reports from abroad about using the laboratory thermal simulation method to study the functional mechanism of hydrocarbon regeneration are available.

It is generally agreed that the prerequisite of organic matter existing in the source rock undergoing hydrocarbon regeneration is that the reheated temperature should reach the termination point of primary hydrocarbon generation. Because the compensation relationship between time and temperature in the course of hydrocarbon generation is complicated, the relationship between re-startup critical point of hydrocarbon regeneration and hydrocarbon generation efficiency is highly uncertain.

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As a result, there is a strong disputation[2−12] about the hydrocarbon regeneration onset of source rock, its potential, and the appraisal method.

One viewpoint is that the hydrocarbon regeneration function does not follow the track of primary hydrocarbon generation but it bears an obvious hysteresis, the extent of which is related to the initial maturity of the source rock during (upon the occurrence of) hydrocarbon regeneration. The results of adding the quantity of primary hydrocarbon to that of hydrocarbon regeneration are not equal to the results of successive hydrocarbon generation[2−5]. Another viewpoint is that the hydrocarbon regeneration is closely followed by primary hydrocarbon generation, and the hydrocarbon regeneration peak has no obvious "hysteresis" or "advancement". The hydrocarbon regeneration function does not affect the results of hydrocarbon generation[6,7]. But Zou Yanrong[11] deems that the delay or advancement of the hydrocarbon regeneration peak temperature correlates to the maturity after primary hydrocarbon generation.

There are several factors leading to the above contradictory conclusions. First, samples with a narrow scope of maturity used in the thermal simulation cannot make up a natural section of evolution; therefore, it is difficult to reveal the function mechanism of hydrocarbon regeneration through the experimental results. The explanation of experimental results is, to some extent, unilateral. Second, the experimental methods employed are entirely different (e.g. high-pressure experiment, normal-pressure experiment, closed-system experiment, and open-system experiment). The experimental results obtained from hydrous experiments in the autoclave closed system and the prevailing gold tube experiments are regarded as the best results indicative of geological fact. The closed system experimental method cannot accurately measure light hydrocarbon (C_6—C_{14}) components, which are generated in large quantities in these experiments. The advantages of open system experimentation are that all experimental results can be measured accurately online. Third, the hydrocarbon retention quantity in samples is different. Because these samples, which possess the same quality and maturity, come from different geological sections and have different hydrocarbon retention quantities in closed and open system simulation experiment, there will be vast differences in the hydrocarbon generation appearance point, peak, yield, and curved shape in subsequent experiments.

In addition, recent simulation experiment researchers concentrate on revealing the mechanism and process of hydrocarbon regeneration from coal samples, especially focusing on secondary gas generation from coal samples[7,9−14]. The involved studies of the hydrocarbon regeneration from organic matter in carbonate rocks are not systematic or revealing. In view of the common high maturity of carbonate source rock in China, it is difficult to obtain samples with maturity ranging from low-maturity to over-maturity. Systematic analysis of the issue of hydrocarbon regeneration in terms of experiment and chemical kinetics is not available, which obviously affects the evaluation of hydrocarbon regeneration results and resource potential.

Based on this background information, this study employs limestone with high organic matter and low maturity, which comes from the Permian carbonate in the Santanghu Basin of Xinjiang, China. The gold tube experiment is employed because it is considered to be contiguous with the development of geology. First, samples are heated in gold tubes to different temperatures (primary hydrocarbon generation). Next, a series of samples from low-maturity to over-maturity are obtained through the thermal simulation experiment using different temperatures of the closed gold-tube system under high pressure. Then, the heated samples are divided into two groups: one is treated by extracting and the other is not. They are both put into Rock-Eval for the thermal simulation experiment of hydrocarbon "regeneration". While examining the relationships between the product productivity of pyrolysis and the initial maturity, the heated temperature, and the heating rate, this experiment also probes into the characteristics and the significance of diverse chemical kinetics.

1 Samples and experiments

The surveyed limestone sample comes from the Permian limestone (Carbonate extent: 73.75%. See Table 1 for essential geochemical characteristics) in the Santanghu Basin of Xinjiang, China. The low maturity (R_o=0.59%) and high organic matter of the sample are its most valuable features. It is one of China's only carbonate samples with such a low maturity level; therefore, it is the most suitable carbonate sample for the simulation experiment of the hydrocarbon generation mechanism.

1.1 Simulation experiment of primary hydrocarbon generation

The experimental procedure begins by selecting geo-

Table 1 Essential geochemical characteristics of original and artificially matured samples

Samples		TOC (%)	T_{max} (℃)	S_1 (mg/gC)	S_2 (mg/gC)	S_1+S_2 (mg/gC)	HC(mg/gC)	HI (mg/gC)
R_o (%)	Processing method							
0.59	Un-extracted	3.882	443	0.07	10.95	11.02	1.8	282.07
0.82		3.829	443	0.23	11.19	11.42	6.01	292.24
0.95		3.239	445	4.41	16.24	20.65	136.15	501.39
1.45		2.734	436	9.01	3.2	12.21	329.55	117.04
1.96		2.355	557	1.42	0.49	1.91	60.3	20.81
2.41		2.538	590	0.78	0.16	0.94	30.73	6.3
2.56		1.807	600	0.05	0.06	0.11	2.77	3.32
0.82	Extracted	3.542	447	0.05	20.73	20.78	1.41	585.26
0.95		2.593	447	0.05	4.89	4.94	1.93	188.58
1.45		2.434	462	0.05	0.57	0.62	2.05	23.42
1.96		2.187	569	0.07	0.3	0.37	3.2	13.72
2.41		1.916	594	0.05	0.1	0.15	2.61	5.22

logically sectioned samples with different maturities as samples for experimental simulation. In China's stratified rock basins, it is almost impossible to obtain a perfect series of low- to over-mature carbonate samples for this experiment[16,17]. Therefore, using the artificial maturation method to obtain different samples in maturity is the only feasible strategy. Using the "gold-tube" method (an accurate imitation of genuine geological evolution)[18], limestone samples (Santanghu Basin, Xinjiang, China) with low maturity and an abundance of highly organic matter are artificially heated (viz. primary hydrocarbon generation) to different temperatures under a closed system and high pressure (50 MPa) for 48 hours (namely: 300℃, 330℃, 360℃, 400℃, 450℃, and 500 ℃), resulting in 6 carbonate samples with different maturities. Then the heated samples are divided into two groups. In order to compare the difference between the two groups, one group is treated by extraction and the other is not. This method avoids the difficulty in explaining and comparing experiment results. The difficulty is usually caused by the hydrocarbon retention quantity in samples after the primary hydrocarbon generation.

The data in Table 1 also give the geochemical characteristics of the primary artificially matured samples after extraction. The data also show that the six different artificially matured samples contain maturities of 0.59%, 0.82%, 0.95%, 1.45%, 1.96%, 2.41% and 2.56%, respectively. These samples represent all maturity stages from low to high, indicating that they can accurately represent all the possible initial maturities of hydrocarbon regeneration found in the stratified rock basin.

1.2 Simulation experiment of hydrocarbon regeneration

After artificially maturated samples are divided into extracted and un-extracted parts, they are put in the OGE-II workstation. This workstation is an improvement on the French Rock-Eval-III by the Research Institute of Petroleum Exploration and Development of China National Petroleum Corporation. Samples are heated from 250℃ to 600℃ at the heating rates of 5℃, 15℃, 30℃, and 50℃ per minute to stabilize hydrocarbon regeneration in order to accurately maintain correlation between the productivity of hydrocarbon generation and temperature (Figure 1). Precision enhances the study and comparison of the relationship among the threshold maturities of hydrocarbon regeneration, heating rates, and heating temperatures. At the same time the experimental data aids in calibrating the chemical kinetic models.

2 Results and discussions

2.1 Hydrocarbon conversion characteristics of hydrocarbon regeneration

Due to the limited space, Figure 1(a), (b) shows the relationship between hydrocarbon "regeneration" productivity and temperature through heating extracted and un-extracted samples with different maturities in Rock-Eval pyrolysis. (Because of the same relationship among different heating rates, only 5℃ per minute heating rate is given). In Figure 1(a), (b), the hydrocarbon conversions of different samples are normalized in relation to the original samples. After primary hydrocarbon generation, the hydrocarbon regeneration starting temperatures of extracted samples become higher with the increasing maturities of samples (hysteresis). This phenomenon, perhaps, has something to do with the lower activation energy of components first consumed in the process of primary hydrocarbon generation. The hysteresis is also in agreement with the gradually

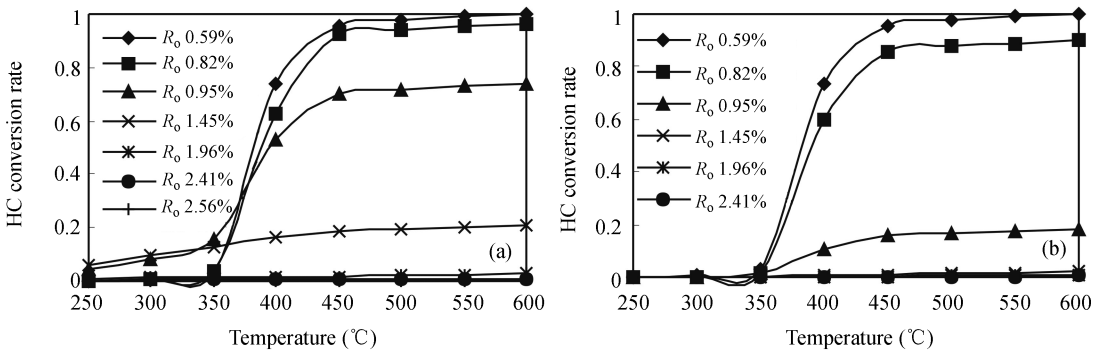

Figure 1 Relationships between temperatures and HC conversion rates of artificially matured (heating rate: 5℃/min). (a) Un-extracted samples; (b) extracted samples.

increasing activation energy calibrated from chemical kinetic models of the samples. During hysteresis, the produced hydrocarbon amounts decrease. The samples heated at temperatures higher than 360℃ (the corresponding R_o is higher than 1.41%) have limited hydrocarbon regeneration potential. However, the un-extracted samples are quite different from the extracted ones in hydrocarbon regeneration characteristics. For the samples heated at 330℃ and 360℃, the corresponding R_o are 0.95%, 1.45%, respectively. Because preponderant hydrocarbons produced from primary hydrocarbon generation still exist in samples, starting temperatures are obviously lower in the process of "hydrocarbon regeneration". Because the sample under the temperature of 300℃ has low hydrocarbon amounts, and because hydrocarbon-generating potential of samples over 400℃ has been mostly consumed and even the primary products have been expulsed under the high experiment temperature, there is little difference between the extracted and un-extracted samples. Regardless of the fact that the total hydrocarbon amounts are less than those from the primary samples, there is still a substantial hydrocarbon increase in relation to the extracted samples.

2.2 Chemical kinetic model of hydrocarbon generation and calibration

The parallel first-order reaction model with a wide applicability and the Variable-yardstick principle of optimality and algorithm[19−21] aid in the calibration and discussion of the chemical kinetic model used to describe the hydrocarbon regeneration of different maturity samples. The calibration program employed is the software developed by author in the early 1990s and perfected over the decade (contact the author for more information). Figure 2 shows the activation energy distribution of extracted and un-extracted samples. Figure 3 shows the relationships between the weighted average activation energy and its maturity of extracted and un-extracted samples. These figures show that the average activation energy of artificially maturated samples increases with the increasing maturity after extraction (viz. all of the hydrocarbon from primary generation is expulsed), especially at 400℃ (R_o = 1.96%) and above. This occurrence is clearly related to the preferential consumption of components with low activation energies. It is also in accordance with the initial temperature when the extracted samples generate hydrocarbon (Figure 1). But the chemical kinetic characteristics of un-extracted samples (corresponding to some, or even most of, the hydrocarbon from the primary generation retained in the source rock) are opposite. Also, the average activation energy of most samples is lower than that of original samples (unheated). An inevitable conclusion is that the hydrocarbon generation rate of un-extracted samples reaches a high value (Figure 2). With the increasing maturity, the average activation energy noticeably decreases until the highest point of oil generation (R_o) reaches about 0.95%, and then it has a tendency to increase. Low activation energy indicates a more easily generated hydrocarbon; therefore, hydrocarbon regeneration in artificial samples is easier than that of original samples. In fact, the first hydrocarbon regeneration is the product of primary generation in the Rock-Eval experiments rather than the real regeneration. The residual pyrolysis products gradually release from samples during the course of heating, then outflow by the carrier gas in the experiment.

2.3 Initial application of chemical kinetic model

Figure 4 shows the relationships between the hydrocarbon generation conversion and the depth of all extracted and un-extracted samples. The hydrocarbon gen-

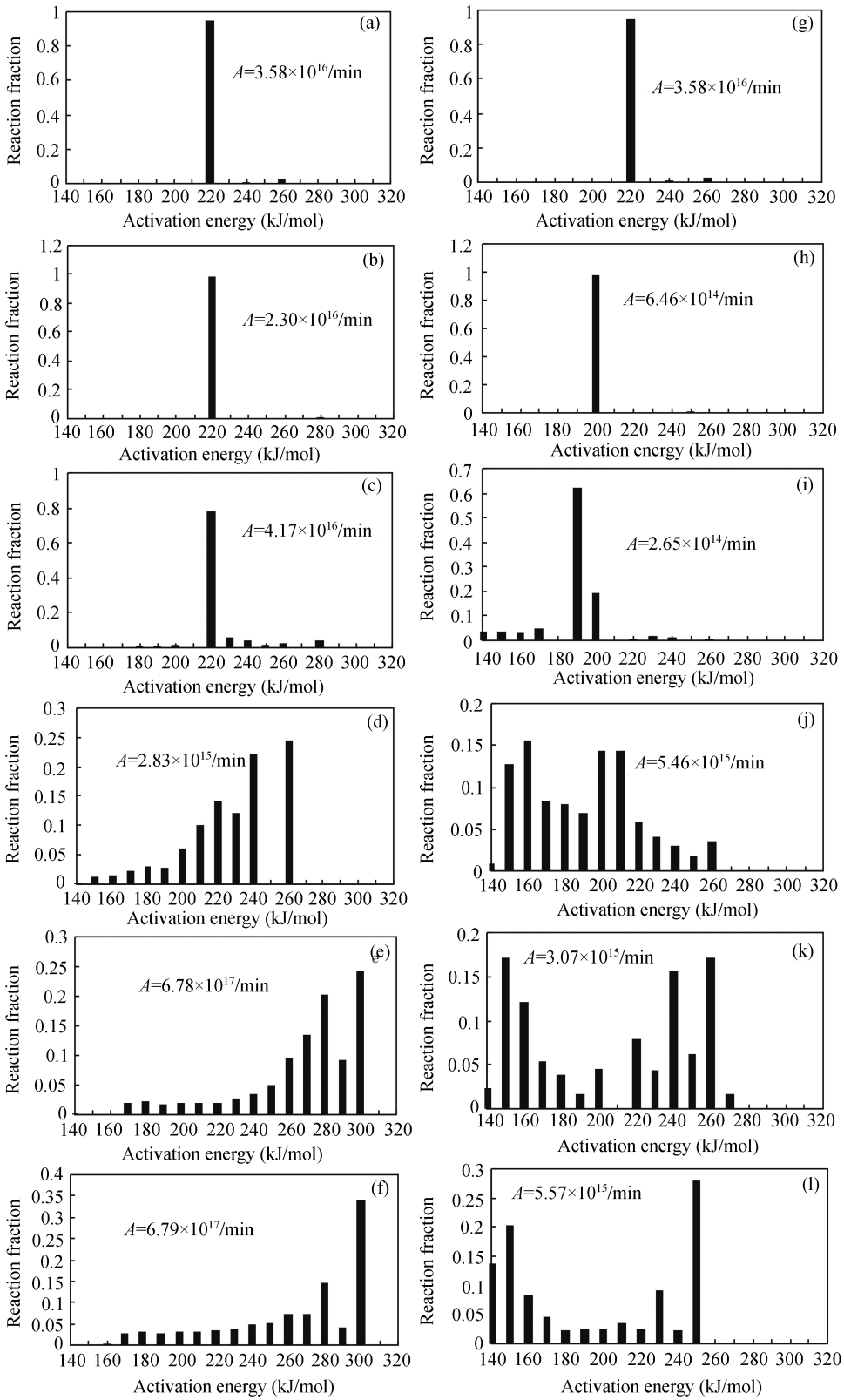

Figure 2 Hydrocarbon regeneration activation energy distributions of samples with different initial maturities ((a)—(f): extracted, (g)—(l): un-extracted). (a), (g) R_o 0.59%; (b), (h) R_o 0.82% ; (c), (i) R_o 0.95%; (d), (j) R_o 1.45% ; (e), (k) R_o 1.96%; (f), (l), R_o 2.41%.

eration conversions are obtained by combining the calibrated chemical kinetic parameters and the geothermal history of the Bohai Bay basin. The hydrocarbon generation process of an artificially matured extracted sample is a little more delayed than that of an original sample because of the hydrocarbon's retention quantity (Figure 4(a)). For this reason, previous researchers came to the conclusion that activation temperatures of hydrocarbon regeneration are lower than breakdown temperatures of primary hydrocarbon generation.

Whether the sample is extracted or not, the hydrocarbon regeneration potential of over-matured samples is very low when the temperature is higher than 400℃ (R_o = 1.96%). Figures 5 and 6 illustrate hydrocarbon generation history of carbonate rock in the Jiyang Depression (O) and the Songliao Basin (C-P) calculated by the chemical kinetic model. Different from Figure 4, the kinetic process of gas cracked from oil[22,23] has been taken into consideration. The oil directly generated from kerogen accounts for 70%, and the gas directly generated from kerogen 30%. The primary hydrocarbon generation of the Ordovician depression in Jiyang mainly occurred in the early Jurassic period, and only a little hydrocarbon regeneration occurred after the deposit of the Guantao Formation. However, a certain amount of hydrocarbon regeneration occurred in source rocks of the Songliao Basin (C-P) during the period of the Denglouku Formation deposit (about 150 Ma). Therefore, it is convenient to quantitatively evaluate the amount of hydrocarbon regeneration by combining the chemical kinetic method and geothermal history.

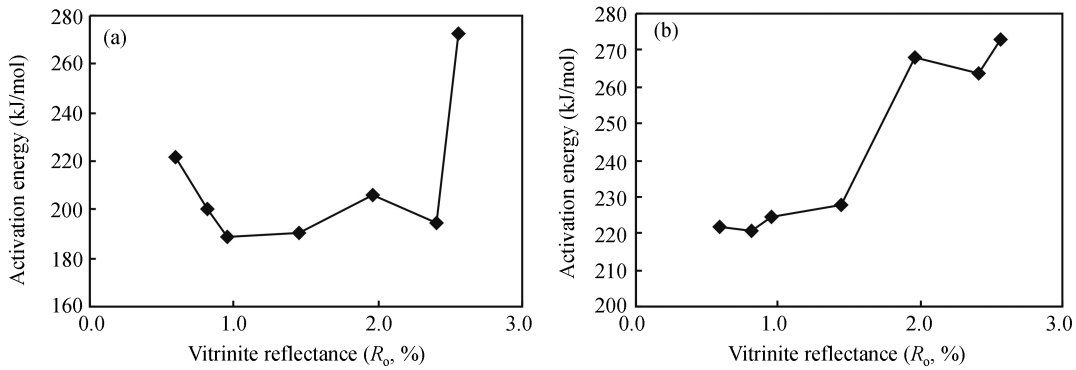

Figure 3 Relationship between average activation energy of artificially matured samples and R_o. (a) Un-extracted; (b) extracted.

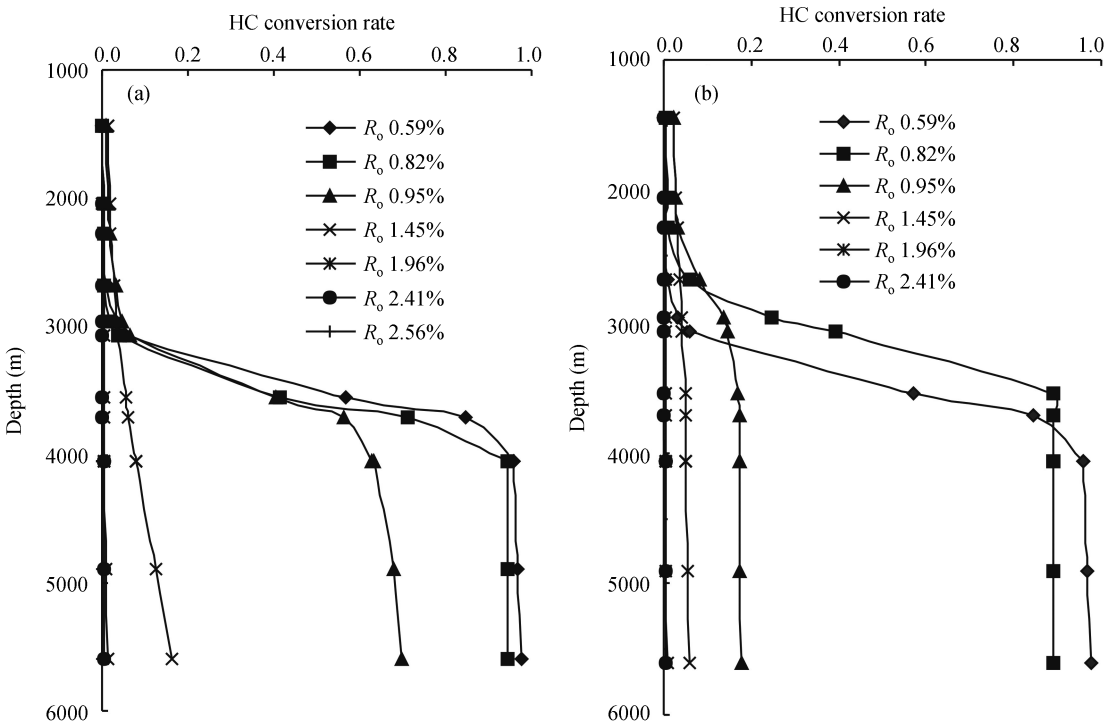

Figure 4 Relationships between HC conversion rate and depth calculated by the chemical kinetic model. (a) Extracted samples; (b) un-extracted samples.

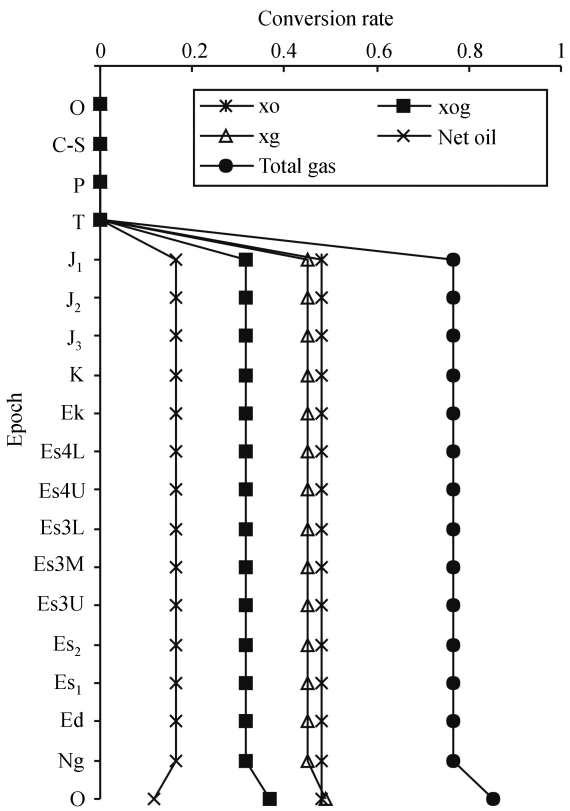

Figure 5 Hydrocarbon generation history of the Ordovician source rock in the Jiyang Depression calculated by the chemical kinetic model (hydrocarbon regeneration).

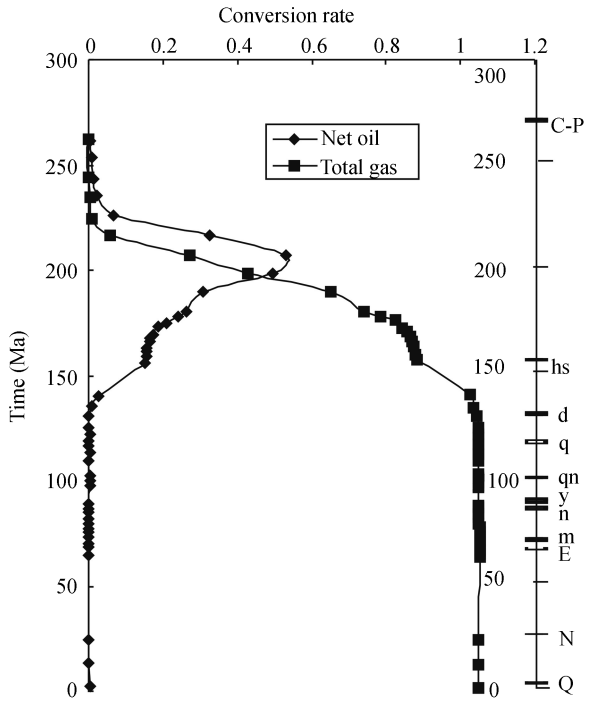

Figure 6 Hydrocarbon generation history of the source rock in the Songliao Basin (C-P) calculated by the chemical kinetic model (hydrocarbon regeneration).

3 Conclusions

The preliminary study shows that the difficulty in obtaining series carbonate source rocks with different maturities, which are used to probe into the hydrocarbon regenera- tion, can be solved by the artificial maturation method.

The potential of hydrocarbon regeneration and the delay or advancement of the hydrocarbon regeneration peak is related to the hydrocarbon expulsion amount and the breakdown maturity of the primary hydrocarbon generation. These phenomena are also associated with expulsion. Little or no expulsion in the amount of hydrocarbon will advance the maturity of hydrocarbon "regeneration" and will increase the potential of hydrocarbon generation. If the hydrocarbon generation and expulsion efficiency are high, the hydrocarbon "regeneration" will be delayed and the hydrocarbon generation potential will be low. Over-matured samples tend to have low hydrocarbon regeneration potential, e.g. when the artificial temperature is over 400℃, the corresponding R_o is 1.96%.

The chemical kinetic characteristics of samples after primary hydrocarbon generation are also associated with hydrocarbon generation and expulsion efficiency. In spite of the fact that the component with lower activation energy in organic matter is first consumed in the process of primary hydrocarbon generation. If most of the generated hydrocarbon is retained in source rock, the general apparent activation energy of hydrocarbon regeneration from organic matter will decrease, or the activation energy of hydrocarbon regeneration will increase with the process of primary hydrocarbon generation.

Clearly, in the hydrocarbon regeneration research, contradictory conceptions and conclusions will be derived if no consideration is taken into the source rock maturity, primary hydrocarbon generation, and expulsion efficiency.

The initial application demonstrates that it is convenient to achieve the quantitative evaluation of the amount of hydrocarbon regeneration by combining the chemical kinetic method and geothermal history.

1 Xiong Y Q, Geng A S, Wang Y P, et al. Kinetic simulating experiment on the secondary hydrocarbon generation of kerogen, Sci China Ser D-Earth Sci, 2002, 45(1): 13－20
2 Guan D S, Wang Z Y, Qin Y, et al. Quantitative evaluation method of secondary hydrocarbon generation and its application in Bohai Bay basin. Acta Sedimentol Sin (in Chinese), 2003,21(3): 533－538
3 Zhang Y S, Qin Y, Liu H J, et al. Investigation on the hydrocarbon regeneration from sedimentary organic matters by pyrolytic simulation. Geochimica (in Chinese), 2002, 31(3): 273－282
4 Qin Y, Zhang Y S, Zhu Y M, et al. Lagging and reaction kinetic mechanism of hydrocarbon regeneration from organic matters in coals. Earth Sci-J Chin Univ Geosci (in Chinese), 2000, 25(3): 278－282
5 Zeng F G, Cheng K M. Research on secondary hydrocarbon generating mechanism of lower Palaeozoic marine carbonate rocks in North China. Geol-Geochem (in Chinese), 1998, 26(3): 40－46
6 Liu L F, Wang W H, Li S Y. Investigation on secondary generation of hydrocarbons by thermal modelling of Kerogen. Acta Sedimentol Sin (in Chinese), 1995, 13(s): 147－150
7 Zhang R H, Zhao Z J, He X S, et al. Simulation and potential evaluation of hydro-carbon regeneration of coal in the Shanxi Formation Huainan Coalmine. Petrol Explor Dev (in Chinese), 2004, 31(4): 25－28
8 Dong X F, Study on the oil-forming periods of Cambro-Ordoviclan source rocks in the Tarim basin and also on the secondary generation of oil in the late Himalayan epoch. Mar Geol Quat Geol (in Chinese), 1994, 14(3): 51－60
9 Zheng L Q, Li X Q, Zhong N N. Discussion on thermal evolution and secondary hydrocarbon generation of organic matter from Upper Paleozoic Coal Measures in Northern China. Coal Geol Chin (in Chinese), 2001, 13(4): 16－19
10 Zhong N N, Mu H Z. Hydrocarbon regeneration condition of Carboniferous-Permian coal in North China. Recent Progress Study of Natural Gas Geology (in Chinese). Beijing: Petroleum Industrial Press, 1997. 134－144
11 Zou Y R, Yang Q, Liu D M. Kinetic model of hydrocarbon re-generation from late Paleozoic coal, North China. Earth Sci-J Chin Univ Geosci (in Chinese), 1999, 24(2): 189－203
12 Ran Q G. Study on hydrocarbon generation and regeneration of later Paleozoic coal in North China. Petrol Explor Dev (in Chinese), 1995, 22 (Supp.): 6－9
13 Tang D Z, Wang J L, Lin S Y et al. An experimental study of program pyrolytic modeling on secondary hydrocarbon generation of coals. Exp Petrol Geol (in Chinese), 2000, 22(1): 9－15
14 Gong S, Li J, Zhang Y, et al. Discussion on the secondary hydrocarbon-generation mechanism of coal. Exp Petrol Geol (in Chinese), 2002, 24(6): 542－546
15 Rao D, Guo D X, Zhang X G, et al. Evaluation on efficient source rocks of Upper Paleozoic in North China. Fault Block Oil & Gas Field (in Chinese), 2004, 11(3): 10－14
16 Lewan M D, Williams T A. Evaluation of petroleum generation from Resinites by hydrous pyrolysis. AAPG Bulltin, 1987, 71(2): 207－214
17 Behar F, Kressmann S, Rudkiewicz J L, et al. Experimental simulation in a confined system and modeling of Kerogen and oil cracking. Org Geochem, 1991, 19: 173－189. [DOI]
18 Liu J Z, Tang Y C. Method to predict methane generation amount by using the hydrocarbon generating kinetics from Kerogen. Chin Sci Bull (in Chinese), 1998, 43(11): 1187－1191
19 Lu S F, Wang Z W, Huang D F, et al. Hydrocarbon generation kinetics of coal maceral. Sci China Ser B-Chem (in Chinese), 1995, 25(1): 101－107
20 Lu S F, Fu G, Wang P Y, et al. Quantitative Study of the Main Control Factors of Natural Gas (in Chinese). Beijing: Petroleum Industrial Press, 2002. 14－49
21 Zhai G M. Petroleum Geology of China (Vol. 6 Shengli Oilfield). Beijing: Petroleum Industrial Press, 1993. 96－195
22 Lu S F, Fu X T, Chen X, et al. Chemical kinetic models of generation of gas by various groups in crude oil and their calibration. Acta Geol Sin, 1997, 71(4): 365－373
23 Lu S F. Kinetics Theory of Hydrocarbon Generation From Organic Matter and Its Application (in Chinese). Beijing: Petroleum Industrial Press, 1996. 54－130