Experimental evidence for formation water promoting crude oil cracking to gas

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Crude oil cracking to gas is the key to determining the exploration potential and strategy for deep hydrocarbon resources. Identifying the factors that affect the threshold and potential of crude oil cracking to gas as well as other possible influencing factors will provide the scientific basis for deep hydrocarbon exploration. A comparison of pyrolysis simulation experiments of crude oil, hydrous crude oil, and various water media under a constant temperature (350°C) and pressure (50 MPa) shows that water plays a large role in crude oil cracking to gas. (1) When water is added, the gas yields increase significantly, including those of alkane gases and non-hydrocarbon gases: the yield of alkane gases increases 1.8–3 times; the yields of H₂ and CO₂ also increase significantly. This means that water takes part in the process of crude oil cracking to gas, and supplies hydrogen. Therefore, the presence of water will dramatically enhance the potential of crude oil cracking to gas. (2) Mg²⁺ ions in the formation water promote the crude oil + water reaction to some extent and increase the total yield of alkane gases and the yields of both H₂ and CO₂; more interestingly, the *i*-C₄/*n*-C₄ and *i*-C₅/*n*-C₅ ratios increase significantly. This indicates that Mg²⁺ ions in formation water act as a catalyst, and a disproportionation reaction is involved in the crude oil + water reaction. This study helps us to understand the factors influencing crude oil cracked gas and to evaluate the hydrocarbon resources in deep sedimentary basins.

H₂, natural gas, formation water, pyrolysis simulation experiment, crude oil

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As worldwide hydrocarbon exploration gradually deepens, deep layers will become a future target and part of the sustainable development of hydrocarbon exploration in mature basins. There are currently diverse opinions regarding deep exploration potential. Some believe that it is almost impossible to find oil and natural gas in places where the temperature is higher than 120°C. For example, in 2007, scientists from Statoil and the Faculty of Science and Technology, University of Stavanger, Norway, suggested the theory of “golden zones for oil and natural gas development” (90% of oil and natural gas in the world are reserved in places where the temperature is in the range 60–120°C). However, a relatively optimistic viewpoint is becoming popular in the pe-

troleum industry: “The natural gas and oil reserves would be as deep as the basin”.

With global exploration and further studies, some viewpoints have gradually changed with regard to our knowledge of crude oil cracking to gas. In the 1970s and 1980s, geochemists believed that liquid hydrocarbons would be completely cracked into gas when the temperature reached 149°C [1,2]; however, later researchers insisted that crude oil was stable and would not be cracked and transformed into natural gas except under high-temperature conditions (160–200°C) [3–6]; furthermore, Price [7] concluded that C₁₅₊ hydrocarbons were still stable even when *R*_o (Vitrinite reflectance) is significantly higher than 1.35%, and could still exist in the *R*_o range 7.0%–8.0%.

A number of simulation experiments were therefore

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conducted to study the possible factors influencing crude oil cracking to gas, such as mineral (element) catalysis, TSR (Thermal sulfate reduction), pressure, and geological background (heating history) [8]. Although mineral catalysis in the reservoir has attracted most attention [9–13], it is undeniable that the mineral catalysis effect on crude oil cracking under real reservoir conditions has not been apparent since only slight differences have been found. Mango [14] strongly advocated the influence of transition metals on crude oil cracking to gas as a result of thermo-catalysis. However, the geochemical characteristics of simulated experimental gaseous products are obviously different from those of natural gas in nature in many respects [15–17]. The TSR effect can promote rapid cracking of crude oil into gas at low temperatures [18,19], simultaneously producing a lot of H_2S [18,20–26]. The available data show that TSR primarily takes place in carbonate reservoirs containing gypsum, and the TSR effect is mainly restricted to these areas.

In fact, geological conditions are extremely complicated, and many of the factors influencing crude oil cracking to gas are as yet unknown. In this paper, we present the results of some recent simulation experiments and try to illustrate that the media-formation water existing widely under geological conditions could also promote the process of crude oil cracking to gas. The influence of formation water on crude oil cracking has never received sufficient attention because it is commonly believed that water would suppress the cracking of crude oil and the generation of gaseous products [27,28]. Early simulation experiments were mostly conducted in incompressible pyrolysis reactors, such as autoclaves or quartz tubes, in which water was involved in vapor form; an overpressure would be created in the incom-

pressible environment. Generally, crude oil cracking is a reaction which is characterized by a relative increase in volume. Simulation experiments in such pyrolysis systems would therefore certainly suppress crude oil cracking. A gold tube experimental simulation system could avoid such shortcomings. Because of the ductility of gold, the water vapor pressurization can be compensated for by a volumetric change in the gold tube [29], thus minimizing the artificial impact caused by the experimental system. Simulation experimental results in a gold-confined reaction system are presented in this paper and the effects of formation water and ions on crude oil cracking to gas are discussed.

1 Experiments

A gold tube in a closed system was used in the simulation experiments. The crude oil samples were collected from Well LN58 in the Tarim Basin (4335.5–4337.5 m, specific gravity 0.7565, and sulfur content undetermined). Crude oil (8 mg) was placed in each gold tube, and then a corresponding amount of water (120 μL) or mineral water solution (120 μL) was added. The molar concentrations of water and mineral water solutions were 1 mol/L for all tubes (Table 1).

All the gold tubes loaded with samples were solder-sealed under argon. The gold tubes were then placed inside interconnected autoclaves. The autoclave pressures were held at 50 MPa using an external fluid pressure method. The autoclaves were placed outside a furnace chamber. The furnace chamber was heated to the preset temperature of 350°C, and when the temperature became constant, the

Table 1 Conditions for simulation experiments on crude oil cracking and compositions of produced natural gases at 350°C and 50 MPa

Type	Time (h)	Natural gas compositions (mL/g)											$\delta^{13}C_1$ (‰)
		C_1	C_2	C_2H_4	C_3	C_3H_6	<i>i</i> - C_4	<i>n</i> - C_4	<i>i</i> - C_5	<i>n</i> - C_5	H_2	CO_2	
Oil	48	3.01	1.75		1.98	0.02	0.48	1.09	0.52	0.65	0.37	2.26	−43.14
	96	5.32	3.41	0.01	4.12	0.03	1.10	2.55	1.30	1.56	0.46	2.12	−53.60
	192	11	6.98	0	8.94	0.05	2.56	5.89	3.37	4.25	0.33	2.23	−55.17
Oil+ H_2O	48												
	96	14.77	9.55	0.13	10.06	0.59	2.44	5.61	2.62	3.43	13.00	2.46	−53.54
	192	23.71	14.76	0.10	14.31	0.39	4.69	10.96	4.62	6.33	21.04	3.28	−54.97
Oil + $MgCl_2$ solution	48	11.57	5.26	0.18	4.59	0.59	1.90	2.06	1.33	0.92	35.70	11.89	−53.84
	192	23.75	14.85	0.09	16.99	0.39	9.99	9.23	8.86	5.12	19.83	7.07	−54.04
Oil + $CaCl_2$ solution	48	9.55	4.00	0.07	2.99	0.22	0.74	1.25	0.73	0.69	13.56	2.79	−53.08
	96	16.61	10.84	0.08	12.25	0.36	4.05	6.95	4.63	3.86	13.42	4.09	−53.82
	192	26.82	16.21	0.06	17.53	0.26	5.76	9.31	6.26	4.91	13.66	5.16	−54.74
Oil+ Na_2SO_4 solution	48	9.95	4.83	0.09	3.86	0.31	0.74	1.64	0.61	0.78	12.51	5.64	−60.43
	96	19.45	12.00	0.09	12.49	0.41	3.04	6.80	3.07	3.81	1.64	6.21	
	192	21.19	15.03	0.05	18.35	0.27	5.21	12.43	6.14	7.93	8.26	2.91	−56.89
Oil+ K_2SO_4 solution	48	10.87	4.55	0.09	3.12	0.27	0.57	1.25	0.54	0.75	14.68	4.29	−55.95
	192	24.23	16.41	0.07	17.83	0.30	4.77	11.02	5.45	7.21	10.98	5.29	−56.85

autoclaves were placed in the furnace chamber one by one, and then kept at 350°C for 48, 96, and 192 h. After the specified time, the autoclaves were removed and quenched in cool water. The fluctuation error in the furnace temperature was kept to within 0.5°C, and the pressure error was kept within 1 MPa. To reduce errors caused by the experiments themselves, the pyrolysis simulations all needed to be performed at one time using the same furnace; because of the restricted number of autoclaves, the pyrolysis simulations for some time points were reduced selectively. However, as the experimental analysis is correlative, the overall trends and correlation results were not affected by the partial lack of experimental points.

Once pyrolysis was complete, the gaseous product compositions were quantitatively analyzed by an external standard method using an Agilent 6890N gas chromatograph (GC). A Poraplot Model Q chromatographic column (30 m $\times$ 0.25 mm $\times$ 0.25 μ m) was used with helium as the carrier gas. The initial temperature of the GC oven was set at 50°C for 2 min, and then the oven was heated to 180°C for 15 min at a rate of 4°C/min. The quantitative analytical error was within 1%. Stable carbon isotope analysis of the gaseous products was conducted using an Isochrom Model II GC-IR-MS isotope mass spectrometer and a Poraplot Model Q chromatographic column with helium as the carrier gas. The GC oven temperature was initially set at 50°C for 3 min, and then the oven was heated to 150°C at a rate of 15°C/min, and kept at a constant temperature for 8 min. The analytical error of three runs for isotope analysis was within 0.3‰.

2 Results

The results for natural gases generated are listed in detail in Table 1. The experimental preset temperature (350°C) did not exceed the maximum critical temperature of water (373°C), in order to determine the roles of water and salt solutions during the crude oil cracking process. As a result,

the crude oil transformation ratio was relatively low within the experimental control range. The maximum transformation ratio was about 30%, which basically corresponds to the early stage of crude oil cracking. The overall consistency of the experimental results is obvious, despite the low transformation ratio. These points will be discussed one by one below.

2.1 Gas yields

As shown by the experimental results (Table 1 and Figure 1), for both C_1 and C_{1-5} , the yields for the water-involved experimental groups are significantly higher than the quantity produced from cracking of pure crude oil. The gas yields of the water-involved experimental groups are 1.8–3 times that of gas cracked from pure crude oil. As the pyrolysis time increases, the differences are significantly enhanced. Compared to the effect in the pure water + crude oil experimental groups, the impact of water solutions of mineral salts ($Na^+/Ca^{2+}/K^+$, Cl^-) on the yield of crude oil cracked gas is insignificant (Figure 1); however, for those groups with Mg^{2+} ions, the yield of C_{1-5} increased a little, which is mainly a result of the significant increase in the C_{3+} content of the wet gas components, especially the increased yields of *i*- C_4 and *i*- C_5 isoalkane gases. This means that water is the major factor accelerating crude oil cracking to gas; the metal ion which had the most significant effect was Mg^{2+} .

2.2 Hydrocarbon gas compositions

There is a very good linear relationship between the yields of methane and wet gas components in crude oil cracked gas, and both increased with pyrolysis time; the relative contents of methane in water-involved and various water-solution experimental groups are higher than that in pure crude oil cracked gas; the effect of various metal ions on the yields of alkane gases is insignificant. Such a variation is also clearly seen from the relationship between the drying coefficient and the alkane yield. The drying coefficient of

Figure 1 Comparison of yields of crude oil cracked gases in different solutions. (a) C_1 yields; (b) C_{1-5} yields.

natural gas from the cracking of pure crude oil is significantly lower than those of the water-involved experimental groups. Moreover, the transformation degree of crude oil cracked gas is fairly low, and the content of wet gas components is significantly higher than the yield of methane, so the drying coefficient of the produced hydrocarbon gases is generally low, basically in the range 30%–40%; as the pyrolysis time increases, almost all the drying coefficients decrease, indicating that crude oil cracking is dominated by cracking of long chains, and the yield of wet gas components is fairly high during the initial stage of crude oil cracking to gas. In general, the role of water is dominant, and the effects of various common ions in water on the hydrocarbon components in crude oil cracked gas are insignificant (Figure 2).

As shown in Figure 3, the ratios of isoalkanes to the corresponding normal alkanes in natural gases obtained from water-involved pyrolysis simulations are similar to that in pure crude oil cracked gas; the $i\text{-C}_4/n\text{-C}_4$ ratios remain consistently within the range 0.4–0.5 and the $i\text{-C}_5/n\text{-C}_5$ ratios are in the range 0.75–0.85. Solutions containing Na^+ and K^+ exhibit the same ratios, indicating that they have no effect on the ratios of normal alkanes to isoalkanes in the generated gaseous hydrocarbons; moreover, none of these ratios is affected by pyrolysis time, indicating that the ratio is not controlled by the transformation degree during the early stage of crude oil cracking.

However, for those pyrolysis experimental groups containing Mg^{2+} and Ca^{2+} ions, the proportion of isoalkanes increases significantly. It should also be noted that the ratio increases significantly as the pyrolysis time increases. This is especially true for Mg^{2+} -containing solutions, whose $i\text{-C}_4/n\text{-C}_4$ and $i\text{-C}_5/n\text{-C}_5$ ratios at 192 h reached 1.08 and 1.73, respectively. This indicated that alkaline-earth metal ions such as Ca^{2+} and Mg^{2+} do have a catalytic role in crude oil cracking to gas.

2.3 Non-hydrocarbon gas compositions

H_2 and CO_2 are the major non-hydrocarbon gases in crude oil cracked gas. During the pure crude oil cracking process,

only a trace amount of H_2 is produced; in the experimental groups involving water, however, the H_2 yields increase significantly (Figure 4(a)); the highest H_2 yields occurred in the Mg^{2+} -containing experimental groups. The $\text{H}_2/(\text{H}_2 + \text{C}_{1-5})$ ratios show similar results: the lowest ratio occurred in pure crude oil cracked gas.

The yields and ratios in the other experimental groups show similar variations; they decrease as the pyrolysis temperature and gaseous hydrocarbon yields increase. During the initial stage of pyrolysis, the H_2 content reaches 30%–60% (Figure 4(b)). The H_2 yields relative to the C_{1-5} gaseous hydrocarbons decrease sharply (Figure 4(b)). Apparently, as a transitional unstable product, H_2 is continuously consumed by unsaturated hydrocarbons, resulting in generally low yields of olefins in the product (Table 1).

No apparent trends are seen in the CO_2 yields (Figure 5(a)), but, generally, the CO_2 yields are higher in the water-involved experimental groups; this is consistent with previous studies [7,30,31] (Figure 5(a)). The low yields of CO_2 generated from pure crude oil cracking remain consistent. For the water-involved + crude oil experimental groups, however, the CO_2 yields increase slightly with increasing pyrolysis time; the CO_2 yields in solutions containing saline minerals are slightly higher than those in the pure water + crude oil experimental groups; the $\text{CO}_2/(\text{CO}_2 + \text{C}_{1-5})$ ratio decrease gradually as the yield of crude oil cracked gas increases.

2.4 Stable carbon isotopes of methane

The stable carbon isotope ratios of methane obtained from the experiments remained low, and mainly occurred in the range -55‰ to -53‰ (PDB) (Figure 6). These values were similar to those in the early stages of high-temperature pyrolysis simulation experiments [32]. Compared to the large amount of published stable isotope data for pyrolysis simulation experiments, the stable carbon isotope ratios of methane in this study are much lighter, mainly because of the relatively low transformation degree of the crude oil. In terms of the methane yield, the transformation ratio of crude

Figure 2 Compositional characteristics of gaseous hydrocarbons in the simulation experiments. (a) C_1 vs. C_{2-5} ; (b) drying coefficient ($\text{C}_1/\text{C}_{1-5}$) vs. C_{1-5} yield.

Figure 3 Relationships between ratios of isoalkanes and normal alkanes in crude oil cracked gas.

oil cracked gas is only 5%, which agrees quite well with such extremely light stable carbon isotope compositions of methane.

3 Discussion

The experimental results indicate that water promotes the

process of crude oil cracking to gas, leading to a significant increase in alkane gas yields; the high H_2 and CO_2 yields in water-involved systems further prove that water takes part in crude oil cracking to gas and provides H and O (Figure 7) [30]. This is consistent with the experimental results regarding the effect of water on source-rock oil-generation reported in the literature [33]. When water is involved, the amounts of liquid hydrocarbons in the crude oil increase by 29%, with the amount of C_{15+} hydrocarbons increasing by 33% [33].

It is generally believed that water basically does not play a part in the generation of hydrocarbons, because the H derived from water is believed to be able to suppress free-radical reactions [33]. In fact, free-radical reactions are secondary in such conditions. Carbocation reactions induced by disproportionation occurring between water and organic molecules are important, which accelerate the crude oil cracking gas generation process [33]:

The experimental results also indicate that Mg^{2+} ions play a significant role in promoting the disproportionation reaction between crude oil and water. On the one hand, the quantities of H_2 and CO_2 are far higher than those in the

Figure 4 H_2 yields in crude oil cracked gas. (a) H_2 and C_{1-5} yields; (b) $H_2/(H_2 + C_{1-5})$ and C_{1-5} .

Figure 5 CO_2 yields in crude oil cracked gas. (a) CO_2 and C_{1-5} yields; (b) $CO_2/(CO_2 + C_{1-5})$ and C_{1-5} .

Figure 6 Relationship between methane yield and stable carbon isotopes in crude oil cracked gas under different solution conditions.

Figure 7 Relationship between H_2 and CO_2 yields.

other experimental groups (Figure 7); on the other hand, the proportion of isoalkanes increases greatly. It is generally believed that during the maturing of organic matter, straight-chain normal alkanes are formed mainly through free-radical fragmentation reactions, whereas isoalkanes with branched chains are formed mainly through carbocation reactions [21,34]. The higher proportion of isoalkanes indirectly indicates that Mg^{2+} ions accelerate carbocation reactions as well as the disproportionation reactions between crude oil and water [24].

4 Conclusions

Formation water plays a role in promoting crude oil cracking. The yields of alkane gases in water-involved experimental groups are 1.8–3 times those in pure crude oil experimental groups. The H_2 and CO_2 yields increase significantly. This means that water provides hydrogen and oxygen for crude oil cracking to gas, thereby significantly enhancing the gas-generation potential. This is of great significance for re-evaluating the potential of hydrocarbon resources in deep sedimentary basins.

Mg^{2+} ions in water play a significant role in catalyzing and promoting the disproportionation reaction between crude oil and water, leading to significant increases in the proportion of isoalkanes, and H_2 and CO_2 yields.

However, more elaborate experimental studies are needed to understand how water takes part in the cracking of crude oil, the reaction path and mode during pyrolysis, and the extent to which these reactions help to promote the crude oil cracked gas potential.

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