Study on gas yields and generation kinetics of a type I kerogen sample by open and confined pyrolysis

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Abstract. A shale sample collected from the Neoproterozoic Xiamaling Formation in Xiahuayuan region, North China, was studied by a newly developed apparatus, Multiple-Gas Container Open Pyrolysis Device, and data were compared with those from confined gold tube pyrolysis. This device is mainly composed by a pyrolysis heater and 15 gas containers, a whole heating process was divided into 15 time/temperature segments, gases generated in different temperature segments with carrier gas were temporarily conserved in their gas container correspondingly. When pyrolysis completed, gases in each container were introduced to a gas chromatography for analysis. Sample was heated from room temperature to 650 ℃. Because oil generated from sample was removed by carrier gas immediately from heating area, oil cracking did not play an important role in gas generation. Maximum yield of methane is only 28.4% of that from confined gold tube pyrolysis. Trend of methane yield from open method is similar to that from confined method in EASY%Ro range from 0.58% to 1.80%, indicating that oil cracking in this maturity range is minor, but at higher temperature, gas yields produced in confined pyrolysis increased rapidly, much higher than those from closed method. Activation energies of methane generation from open method ranges from 53 to 72 kcal/mol, central value of C1,C2,C3 decline with their carbon number, showing a clear generating order that the gas with larger carbon number will be generated earlier. δ13C of methane from open method is similar to that from confined method in EASY%Ro range from 0.58% to 2.2%; But in later pyrolysis stage, it is much heavier than that from confined method. δ13C deviation of methane between open and confined methods provides a possible way to calculate proportion of the gas from oil cracking. This open pyrolysis device offers a convenient and efficient way to simulate gas generation potential and acquire kinetics parameters, especially for the source rock from open or semi open gas producing strata.

1. Introduction

Thermal simulation and kinetics research are common ways in hydrocarbon potential evaluation bitumen [1–3]. Generally speaking, there are 3 devices in this area [4-9]. The first is Rock-Eval [10-11], a very popular device. Rock or kerogen sample is heated at setting heating rates, the oil/gas generate is carried by carrier gas flow to a flame ionized detector (FID) to determine oil/gas yield. To derive kinetics parameters, 2-3 heating rates of pyrolysis are necessary. With its efficiency and convenience, this method has been widely used to obtain kinetics parameters. Though the equipment has been used long time, it can only provide bulk kinetics of whole oil/gas, rather than that of individual composition. In most cases, especially in natural gas researches, characteristics of
individual composition, such as kinetics of methane, C₂, C₃, is much important than buck parameter. Such a disadvantage limits application of Rock-Eval data in oil/gas research and exploration.

Another common method is closed pyrolysis in gold tubes [5,6,7,12]. Sample is sealed in series of gold tubes, and those tubes with sample are pressurized by water pump in autoclaves and heated in heating oven at setting heating rates. After pyrolysis, heated gold tubes are pierced in a vacuum glass tube to release gases for GC analysis. Based on gas yields and related temperature and heating time, kinetics of individual gas compound can be derived. In recent years, this closed pyrolysis method has been popularly used in gas/oil potential evaluation for source rocks [5-8,12-14]. In this method, since all products, oil and gas, whenever generated early or late, are sealed in a limited space; oil will crack in high temperature generating gases, which will mix with those gases generated directly from kerogen. The data from closed pyrolysis is suitable for the well-sealed gas bearing strata. But in some geological cases, strata of source rock were not fully sealed in all oil generation period, early generated oil might expel and would not participant in oil cracking. In such cases, total gas amounts in those open or semi-open strata are much fewer than experiment results by closed gold tube pyrolysis. This difference between natural gas reserve and experimental data may result in misunderstanding to gas generating potential of source rock.

Besides those two methods, Tang developed a device to obtain kinetics of oil generation by open method [15,16]. Like Rock-Eval, the device has a similar heater with RE, but it is equipped with 10 cold traps to collect oil, whole heating time is cut into 10 time fragments, oil generated from each fragment is sent and collected into a cold trap. When pyrolysis completed, oil in cold traps will be heated and blew into GC for qualitative and quantitative analysis. This device is suitable to gain oil generation kinetics, but is not available in gas generation research, because their cold traps are not so effective catch methane.

As we discussed above, it is a challenge to collect methane by cold trap. To solve this problem, we developed a new device, like Tang’s device except that our device installed 15 gas containers to substitute for cold traps.

2. Equipment and experimental

2.1. Pyrolysis equipment

Diagram of the apparatus is shown in figure 1. 5 to 10 mg kerogen sample was filled in a quartz tube, a few quartz wools was packed in both ends of sample column to prevent sample powder from being blew out of the heating area. A thermal couple was inserted into center of sample column to detect accurate temperature for pyrolysis control. 15 gas containers were connected to sample heater chamber through close/open valves. There is an oil trap between sample heater and gas containers to remove oil from carrier gas flow.

![Figure 1. Schematic diagram of pyrolysis apparatus.](image-url)
In our experiment, whole pyrolysis process, from 250 °C to 630 °C, was divided into 15 temperature/time segments, gas from each segment was led to its related gas container to be preserved temporarily, so each container will keep the gas generated from one time segment for further analysis. At any moment of gas collection or GC sampling, only one gas container opened to receive or output gas. Before experiment, all gas containers were evacuated by vacuum pump. During pyrolysis, carrier gas flow was controlled just not to over fill gas container in the time segment. When pyrolysis is completed, gas samples in each gas container will be led to GC for quantitative and qualitative analysis. Finally, kinetics of individual composition of gases will be derived though a software KINETIS based on gas yields with related temperature/time endured. Oil generated during pyrolysis was trapped before gas container, and will not be discussed in this paper.

2.2. Sample and pyrolysis experiments
The shale sample was collected from an outcrop of Neoproterozoic Xiamaling Formation in Xiahuayuan region, Hebei Province, North China. Because the shale is one of important source rock in many gas producing strata in China, it has been frequently applied in thermal simulate experiments. This strata usually has very high maturity in gas producing positions because it is buried deep, but samples from the outcrop in basin margin is premature and suitable for oil/gas potential simulation (table 1). The rock sample was crashed, kerogen was isolated from rock powder.5 to 10 mg kerogen sample was used in 1 heating rate run, pyrolysis of 2 heating rates, 20 °C/h and 4 °C/h was performed in our experiments.

| S1 (mg/g) | S2 (mg/g) | S3 (mg/g) | Tmax (°C) | TOC (%) |
|-----------|-----------|-----------|-----------|---------|
| 14.00     | 292.35    | 7.36      | 431       | 84.28   |

3. Results and discussion
For one heating rate, pyrolysis was repeated 2 times, data of the 2 runs at the same heating rate behave excellent reproducibility (Figure 2). There is only 1 set of data for each heating rate was listed in table 2.

| Gas container number | Temperature (°C) | Heating rate (°C/min) | C1 (mL/g) | C2 (mL/g) | C3 (mL/g) | C4+/C5 (mL/g) |
|----------------------|------------------|-----------------------|-----------|-----------|-----------|---------------|
| 1                    | 349              | 20                    | 0.127     | 0.107     | 0.091     | 0.068         |
| 2                    | 369              | 20                    | 0.363     | 0.297     | 0.255     | 0.161         |
| 3                    | 389              | 20                    | 0.801     | 0.643     | 0.563     | 0.365         |
| 4                    | 409              | 20                    | 1.593     | 1.283     | 1.113     | 0.719         |
| 5                    | 429              | 20                    | 3.068     | 2.463     | 2.099     | 1.281         |
| 6                    | 449              | 20                    | 5.726     | 4.668     | 3.647     | 2.125         |
| 7                    | 469              | 20                    | 9.829     | 7.711     | 5.807     | 3.231         |
| 8                    | 489              | 20                    | 15.612    | 11.429    | 8.190     | 4.363         |
| 9                    | 509              | 20                    | 22.782    | 14.952    | 10.096    | 5.124         |
| 10                   | 529              | 20                    | 30.480    | 17.542    | 11.484    | 5.717         |
| 11                   | 549              | 20                    | 38.470    | 18.935    | 12.118    | 5.881         |
| 12                   | 569              | 20                    | 44.469    | 19.706    | 12.273    | 5.881         |
| 13                   | 589              | 20                    | 49.055    | 20.093    | 12.273    | 5.881         |
3.1. Comparison of gas yields from open method with confined methods

In open method, methane generated from 300°C to 600°C; while C2 and C3 exhausted at temperature points of 560°C and 520°C (Figure 2), suggesting that those gas compositions with more carbon number will be generated earlier.

\[
\begin{array}{cccccc}
14 & 609 & 20 & 51.766 & 20.262 & 12.273 & 5.881 \\
15 & 629 & 20 & 53.183 & 20.262 & 12.273 & 5.881 \\
1 & 330 & 4 & 0.252 & 0.226 & 0.207 & 0.141 \\
2 & 350 & 4 & 0.652 & 0.608 & 0.559 & 0.353 \\
3 & 370 & 4 & 1.362 & 1.304 & 1.207 & 0.727 \\
4 & 390 & 4 & 2.493 & 2.380 & 2.162 & 1.243 \\
5 & 410 & 4 & 4.281 & 3.995 & 3.494 & 1.965 \\
6 & 430 & 4 & 7.268 & 6.428 & 5.289 & 2.904 \\
7 & 450 & 4 & 11.951 & 9.784 & 7.491 & 4.005 \\
8 & 470 & 4 & 18.432 & 13.544 & 9.845 & 5.025 \\
9 & 490 & 4 & 26.073 & 16.714 & 11.467 & 5.605 \\
10 & 510 & 4 & 33.895 & 18.560 & 12.036 & 5.802 \\
11 & 530 & 4 & 41.182 & 19.625 & 12.219 & 5.862 \\
12 & 550 & 4 & 47.064 & 20.180 & 12.275 & 5.882 \\
13 & 570 & 4 & 50.153 & 20.266 & 12.293 & 5.882 \\
14 & 590 & 4 & 51.977 & 20.308 & 12.293 & 5.882 \\
15 & 610 & 4 & 53.169 & 20.333 & 12.293 & 5.882 \\
\end{array}
\]

\[\text{Figure 2. Gas yields from open pyrolysis at 2 heating rates.}\]
Maximum methane yield from open method is much lower than that from confined methods. When EASY%Ro ≤ 1.80%, methane yields curves of both open and confined methods are very close each other, implying that major sources of methane in this range is kerogen itself rather than oil cracking. When EASY%Ro > 1.80%, gas increasing speed was dominated by oil cracking. Yield of C_2-C_5 from open and confined method increased almost synchronously in EASY%Ro ranging from 0.5% to 1.2%, reached its peak at EASY%Ro point 1.80%. When EASY%Ro > 1.80%, cumulative C_2-C_5 from confined method began to decrease due to gas cracking, however, such oil cracking did not happen at open method (figure 3).

In many gas producing strata, source rock may intermittently open by uplift or formation of faults, causing oil expelled and moved to the adjacent area with lower temperature. In this situation, effect of oil cracking to provide gases is minor or negligible, just like pyrolysis by our open pyrolysis device. So, for those open and semi-open geological conditions, open pyrolysis method is a more suit means than confined method to evaluate gas generation potentials. In figure 3, for both open and confined methods, gas yields related to EASY%Ro from different heating rates located at a common curve, indicating that EASY%Ro is a reliable common scale to gas generation content for both open and confined experiment.

3.2. Gas generation kinetics from open and confined methods
Activation energy of methane generation from open method distributes between 52 and 72kcal/mol, its overall shape is near symmetrical, central value is 65kcal/mol (figure 4). This distribution shape accords with first order reaction, without oil cracking involved in. Compared with open method, activation energy of methane generation by confined method composed of two groups, group 1 is from 51 to 59 kcal/mol, mainly came from kerogen; group 2 is from 61 to 65 kcal/mol, this group represents gases from oil cracking. It is worth noting that the 2 groups could not be absolutely isolated, actually, gas generation and cracking co-existed at most range of pyrolysis, especially at EASY%Ro range from 1.5 to 2.5 (figure 3). In group 2, a portion of gases generated from kerogen; also in group 1, some of gases came from early oil cracking stage. Total percent of activation energies in group 2 is 52%
(figure 4); roughly referring the gases generated at middle and late oil cracking stages and the gas generated from kerogen in this temperature range. Activation energies of methane and C₂-C₅ from open experiment are bigger than those from confined method, suggesting that the gases need longer time and/or higher temperature to be generate in open or partially open basins than those in closed basins. Because of lack of the data from open method, yet it is not very clearly if the result from our experiment is common or only a special case. For data from our open device, it needs more evidences to check its feasibility to be extrapolated into geological conditions.

**Figure 4. Activation energy distribution of gas generation from open and confined pyrolysis.**

### 3.3. Gas Isotopes (δ¹³C) from open and closed methods

In early stage of pyrolysis (EASY%Ro=0.60-2.2%), δ¹³C of methane from open and closed method behaved similarly. In early pyrolysis stage, δ¹³C curves of methane went down ward, most light value is -45.12‰; Then two curves went up synchronously until reached the point at which EASY%Ro=2.2%. This range agree with the turning point of methane yield at figure 3 at which oil
cracking started to play more important role. In late part of pyrolysis, $\delta^{13}C$ of methane from open method became much heavier than those from confined method. At end of pyrolysis, deviation of $\delta^{13}C$ of the two curves was as much as -8.80‰. The light value of $\delta^{13}C$ was due to input of the gases from oil cracking. In figure 5, $\delta^{13}C$ data in initial and end of oil cracking are at 2 extreme conditions, between the 2 special points, difference between two curves is controlled by gas amount generated from oil cracking. On the other hand, at certain Ro, by $\delta^{13}C$ difference of methane in open and confined methods, cracked oil amount can be estimated. For open method, ethane generation finished at the point with EASY%Ro 3.0%, $\delta^{13}C$ in open and confined method is very similar.

![Figure 5](image.png)

**Figure 5.** $\delta^{13}C$ of methane and ethane in open and confined methods.

### 4. Conclusions

A newly developed apparatus was applied in pyrolysis on a type I kerogen sample. Gases generated from different temperature segments were collected and temporarily preserved in gas containers for further analysis. Gas yields, $\delta^{13}C$ of methane and C$_2$-C$_5$ were analyzed. Those data are compared with those from confined gold tube pyrolysis.

Maximum methane yield from open method is only 28.5% of that from confined method; this difference depends on cracked oil amount in confined method. Methane and ethane yields are similar compared with those from closed method at EASYRo% range of 0.65%~1.80%; all gases in this range are generated from kerogen. In further heating stage, the proportion of the gases from cracked oil increase. Activation energy from open method distributed from 53 to 72 kcal/mol, its overall shape is symmetric, showing a first order reaction of gas generation from kerogen. Activation energy distribution of methane from confined method can be divided into 2 groups, roughly representing gases generated from kerogen and oil cracking. Trend of $\delta^{13}C$ of methane from open method is similar with that from confined method at EASY%Ro range from 0.65% to 2.20%. When EASY%Ro >2.2%, $\delta^{13}C$ of methane from closed method is lighter than that from open method due to added gases from oil cracking. Cracked oil amounts can be calculated based on deviation value of the
2 curves. $\delta^{13}$C of ethane from open and confined method is similar in whole pyrolysis temperature range.

This open pyrolysis device provides an efficient way to acquire gas generation potential and kinetics parameters, especially suitable for the research on open and semi-open gas producing strata.

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