The Rock-Eval Pyrolysis and Hydrocarbon Generation Kinetic of Four Coal Samples from Different Areas, China

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Abstract. Rock-Eval pyrolysis and hydrocarbon generation kinetic are effective and extensive methods to evaluate source rock. In this study, we chose four coal samples from different areas in China including Fuxing, Guangyuan, Fushun and Taiyuanzu. The results show that Fushun has the highest hydrocarbon generation capacity (399-427mg/g), the lowest dominant activation energy (47Kcal/mol) and frequency factor (1.32*10^{12}/s), which has the highest transformation ratio at different heating rates. It is easy to evaluate the hydrocarbon potential of Fushun. But Fuxing, Guangyuan and Taiyuanzu have different frequency factors and activation energies. In the multiple frequency factors (MFF) model, it is difficult to evaluate hydrocarbon potential by activation energies when frequency factors are different. This study evaluates hydrocarbon potential by comparing transformation ratio at universal and geological heating rate. This is because transformation ratio is a comprehensive result of frequency factor and activation energy. In addition, different heating rates affect the hydrocarbon generation rate of coal samples, the hydrocarbon generation rate is positive with heating rates. For example, the hydrocarbon generation rate of Fushun at 5, 25℃/min are 0.0013 and 0.0051 mg/g.s^{-1}. And the temperature difference (ΔT) of main hydrocarbon generation period heated at 3℃/my and 5,15,25℃/min are different, which are 21-52 and 53-99℃.

1. Introduction
Coal is significant source rock, and has good potential of hydrocarbon generation. Rock-eval pyrolysis and hydrocarbon generation kinetic are prevailing methods to evaluate the resource potential of source rock. Rock-eval pyrolysis results can determine the hydrocarbon capacity and kerogen type of coal samples[1, 2]. Kinetic can describe the process of hydrocarbon generation with a mathematical mode[3-5]. Kinetic parameters come from rock-eval pyrolysis experiment in open system, which can be extrapolated to geological condition[6]. In this study, we compare the hydrocarbon generation characteristics of four coal samples in the laboratorial and geological condition. The results will provide data for the exploration in Fuxing, Guangyuan, Fushun and Taiyuanzu areas.

2. Sample information
As shown in table 1, the HI range of M-FS, M-TYZ, M-FX and M-GY samples are 399-427, 197-205, 113-130 and 107-112 mg/g, respectively. The Tmax range of four samples are 425-446℃. Figure 1 shows that Kerogen type of M-FS(II1), M-TYZ(II2), M-FX and M-GY(III). M-FS sample has the...
highest capacity of hydrocarbon generation, which is almost four times than M-FX and M-GY samples.

Table 1. The Rock-eval data of four samples.

| Sample ID | S1(mg/g) | S2(mg/g) | S3(mg/g) | Tmax(℃) | TOC(%) | HI(mg/g) | OI(mg/g) |
|-----------|----------|----------|----------|---------|--------|----------|----------|
| M-GY-1    | 1.01     | 76.89    | 7.1      | 446     | 71.92  | 107      | 9.87     |
| M-GY-2    | 1.01     | 77.37    | 7.7      | 439     | 70.75  | 109      | 10.88    |
| M-GY-3    | 1.09     | 80.3     | 7.08     | 442     | 71.97  | 112      | 9.84     |
| M-FX-1    | 0.71     | 73.04    | 5.71     | 433     | 56.08  | 130      | 10.18    |
| M-FX-2    | 0.5      | 64.92    | 8.49     | 426     | 56.13  | 116      | 15.13    |
| M-FX-3    | 0.65     | 69.58    | 5.68     | 433     | 61.35  | 113      | 9.26     |
| M-FS-1    | 6.05     | 286.01   | 7.68     | 428     | 66.99  | 427      | 11.46    |
| M-FS-2    | 4.4      | 253.11   | 5.28     | 429     | 63.39  | 399      | 8.33     |
| M-FS-3    | 4.95     | 278.27   | 7.2      | 427     | 66.32  | 420      | 10.86    |
| M-TYZ-1   | 3.28     | 141.63   | 4.0      | 427     | 71.91  | 197      | 5.56     |
| M-TYZ-2   | 3.9      | 139.95   | 4.12     | 425     | 68.27  | 205      | 6.03     |
| M-TYZ-3   | 3.34     | 129.12   | 4.6      | 430     | 64.32  | 201      | 7.15     |

Figure 1. The kerogen type of four samples in HI-Tmax diagram.

3. Experiment method

3.1. pyrolysis
Rock-eval 6 is widely used to gain pyrolysis data including total organic content(TOC), thermo-vaporized free hydrocarbon(S1), pyrolysis hydrocarbon from cracking of organic matter(S2), carbon dioxide organic source(S3) and temperature of peak S2 maximum(Tmax)[1]. The kinetic results of single heating rate pyrolysis experiments are inconsistent with results from multiple-heating rate experiments[7]. In this study, each sample was divided into three parallel groups and performed pyrolysis experiment at 5, 15, 25℃/min, respectively. Thus, accidental errors brought by single heating rate experiment can be avoided.

3.2. kinetic model
The laboratory artificially maturate organic matter in source rock samples and this process can be described by kinetic model based on a series of independent first-order reactions[8]. The kinetic can be approximately described by the Arrhenius equation[6, 9]. In the equation 1, t is time, T is temperature, xi is the residual potential of oil and gas formation associated to reaction i, R is the molar gas constant and A is the frequency factor while Ei is the assumed activation energies[3, 6].

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dx_i/dt = -A_i \exp(-E_i/RT), \quad i=1\ldots N \quad \text{(Equation 1)}
\]
Kinetics parameters from the laboratory can be extrapolated to the geological condition[6]. Kinetic can be used to compute hydrocarbon yield, generation rates and the transformation ratio in the petroleum system[7].

![Figure 2. Hydrocarbon generation rate and transformation ratio of four samples at 5, 15, 25°C/min.](image)

| Sample ID | Heating rate(°C/min) | T_{start} (°C) | T_{end} (°C) | ΔT (°C) |
|-----------|----------------------|----------------|--------------|---------|
| M-FS      | 5                    | 406            | 459          | 53      |
|           | 15                   | 428            | 482          | 54      |
|           | 25                   | 438            | 494          | 56      |
| M-GY      | 5                    | 432            | 522          | 90      |
|           | 15                   | 449            | 544          | 95      |
|           | 25                   | 458            | 554          | 96      |
| M-FX      | 5                    | 420            | 513          | 93      |
|           | 15                   | 440            | 536          | 96      |
|           | 25                   | 450            | 549          | 99      |
| M-TYZ     | 5                    | 409            | 481          | 72      |
|           | 15                   | 428            | 504          | 76      |
|           | 25                   | 438            | 514          | 76      |

4. Results and discussion

4.1 Hydrocarbon generation characteristics
As shown in the figure 2, M-FS has the highest hydrocarbon (HC) generation rate at 5, 15 and 25°C/min heating rates, which is 0.0013, 0.0032 and 0.0051 mg/g.s⁻¹, respectively. The rate at 25 °C/min is near five times to the rate at 5°C/min. Therefore, HC generation rates are positive with heating rates. M-FX and M-GY always have similar HC generation rates, which are the lowest rate among four samples. The transformation ratio of four samples have same characteristic at different heating rates. TR from high to low are M-FS, M-TYZ, M-FX and M-GY samples before reaction ending.

In this study, we divided transformation ratio between 20% and 80% as main hydrocarbon generation period (MHGP). For each sample, the starting and ending temperature of MHGP at 5°C/min is smaller than 15 and 25°C/min. And the temperature difference(ΔT) between starting and ending temperature is near constant at three heating rates (Table 2). This is because the temperature and reaction time complement each other. The smaller heating rate means more heating time, which is consistent with equation 1 that the increase of time(t) leads the decrease of temperature(T) while other parameters are constant, such as xi, A, E and R. And the MHGP means Δxi is constant for 60%, which means ΔT is also constant. Hence, different heating rates would not change ΔT.

4.2 Hydrocarbon generation kinetic
The kinetic models with a discrete distribution of activation energies have two kinds: single frequency factor (SFF) model and multiple frequency factors (MFF) model[10]. SFF model has a universal frequency factor, and allow scholars to easily compare the kinetic difference of all samples. MFF model has different frequency factors, which is difficult to compare the difference. This is the reason many scholars take SFF model to evaluate source rock. But the SFF model underestimates the hydrocarbon generation potentials of some organic matter with lower and higher activation energies[10, 11]. MFF model can avoid that situation[10]. Hence, this study used MFF model. As shown in the figure 3, the frequency factor of M-FS, M-TYZ, M-GY and M-FX samples are 1.32*10^{12}/s, 1.41*10^{13}/s, 6.94*10^{14}/s, 4.96*10^{12}/s, respectively. And the activation energy range is 40-63, 42-65, 49-73 and 41-65Kcal/mol, respectively. The activation energy distribution of M-FS is very concentrated, and has only one dominant activation energy (47kcal/mol). In contrast, the activation energy distribution of M-GY and M-FX are very dispersed, and both have three dominant activation energy (56, 58, 60Kcal/mol and 48, 49, 50Kcal/mol). The dominant activation energy of M-GY is higher than M-FX, and the frequency factor of M-GY (6.94*10^{14}/s) is bigger than M-FX (4.96*10^{12}/s). Transformation ratio as a comprehensive result of frequency factor and energy, can reflect the difference of kinetic parameters in MFF model. As shown in the figure 2, the transformation ratio of M-GY is always lower than M-FX at different heating rates. M-FS has the highest transformation ratio.

4.3 Application to geological condition

The laboratory kinetic parameters can be extrapolated to geological heating rate[6]. We chose 3°C/ky (million years) as a universal and geological rate. After temperature reaches 250°C, four samples gradually reach ultimate yield. Although M-GY has highest frequency factor (6.94*10^{14}/s), the transformation ratio of M-GY is lowest (94.64%) while other samples have almost same transformation ratio (98.71-99.94%) at 250°C. The dominant activation energy of M-GY is highest (56, 58, 60Kcal/mol), and activation energy may have bigger influence to transformation ratio than frequency factor. The starting and ending temperature of main hydrocarbon generation period of M-FS, M-TYZ, M-FX and M-GY, are 112-133, 125-162, 123-174 and 152-204°C, respectively (Table 3). Table2 and Table 3 show that the temperature difference (ΔT) of main hydrocarbon generation period heated at 3°C/ky and 5,15,25°C/min are different, which are 21-52 and 53-99°C.

| Sample ID | Heating rate(°C/ky) | T_{start} (°C) | T_{end} (°C) | ΔT (°C) |
|-----------|---------------------|----------------|--------------|---------|
| M-FS      | 3                   | 112            | 133          | 21      |
| M-GY      | 3                   | 151            | 203          | 52      |
| M-FX      | 3                   | 123            | 174          | 51      |
| M-TYZ     | 3                   | 123            | 162          | 39      |

5. Conclusions

In this study, we compared the hydrocarbon generation characteristics of four coal samples from Fuxing, Guangyuan, Fushun and Taiyuanzu. Four samples have different frequency factors and
activation energies. It is difficult to compare the hydrocarbon potential by activation energies when frequency factors are different. Especially, samples only have high frequency factor or low dominant activation energy. The transformation ratio is a comprehensive result of frequency factor and activation energy, which can reflect the hydrocarbon potential of different samples at universal heating rate. Fushun sample has the lowest dominate activation energy (47 kcal/mol) and lowest frequency factor ($1.32 \times 10^{12}$/s), which has the highest transformation ratio at different heating rates. In contrast, Guangyuan sample has the highest frequency factor ($6.94 \times 10^{14}$/s) and the highest domain activation energy (56, 58, 60Kcal/mol), which has the lowest transformation ratio at different heating rates. In the geological condition, Fushun has highest transformation ratio. Although Taiyuanzu and Fuxing have different frequency factors and activation energies, the transformation ratio of Taiyuanzu and Fuxing are near. Therefore, comparing transformation ratio at geological temperature can evaluate the hydrocarbon potential of samples in the multiple frequency factors (MFF) model.

In addition, different heating rates will affect the hydrocarbon generation rate of coal samples, the hydrocarbon generation rate is positive with heating rates. The temperature difference ($\Delta T$) of main hydrocarbon generation period heated at 3°C/my is smaller than that heated at 5,15,25 °C/min.

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