Analysis of Kinetic Characteristics of Merey Crude oil Pyrolysis by Isoconversion Method

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Abstract. As an important chemical reaction during in-situ combustion, pyrolysis reaction is related to the whole combustion process. To understand the kinetic characteristics of the pyrolysis reaction more clearly, three models, FWO, Friedman and KAS, were used to fit and calculate the thermogravimetric data of Merey crude oil by three linear heating rates under air atmosphere and analyze the kinetic parameters of crude oil at different conversions. The results show that KAS model provides the fitting result similar to the FWO model, but Friedman model provides smaller result, and the FWO model provides the highest linear correlation and the most accurate calculation results among the three models; the gasification stage has the lowest activation energy, followed by low temperature oxidation stage, the pyrolysis stage has the highest activation energy and the highest energy consumption and is the core reaction in the whole process, and the high temperature oxidation stage has a bit lower activation energy than the pyrolysis stage among the four stages of thermal reaction of Merey crude oil.

1. Introduction

As a thermal recovery technology suitable for complicated formation conditions, the in-situ combustion technology has received increasing attention. Thermal recovery is a complicated chemical process in which the heat energy from combustion of crude oil and oxygen in the reservoir is used with other driving forces to thermally recover crude oil[1-2]. The in-situ combustion process includes low temperature oxidation, pyrolysis and high temperature oxidation of crude oil[3-5]. The pyrolysis reaction is the key reaction during in-situ combustion. The pyrolysis kinetics is helpful to understand the mechanism and characteristics of the reaction. However, the crude oil pyrolysis process is too complicated to accurately establish a reaction mechanism model. Thus, the non-model fitting method is used to study the pyrolysis reaction kinetics. As a typical non-model fitting method, isoconversion method has been widely used. Zhao R.B.[6] experimentally oxidized the heavy oil from Fengcheng in Xinjiang, divided the combustion stages and determined the activation energy by Friedman method. Tang J.S. et al. [7] used thermogravimetry for experimental oxidation of heavy oil in 2013 and found from calculation of Kinetic parameters by three different kinetic models that the single scan method provided inaccurate calculation results, but the isoconversion method provided more accurate calculation results. Tang X.D. [8] summarized the progress in research of crude oil oxidation during air injection and calculation of kinetic parameters both at home and abroad, and believed that the isoconversion method had a great development potential in the research of crude oil oxidation kinetics.
In this paper, three isoconversion models, Friedman model, Flynn-Wall-Ozawa (FWO) model and Kissinger-Akahira-Sunose (KAS) model, were used to process the thermogravimetric data of Merey crude oil heated linearly at different heating rates under air atmosphere in order to analyze the kinetic characteristics of Merey crude oil pyrolysis and provide a theoretical support for application of in-situ combustion technology at the oil fields.

2. Experiment

2.1. Equipment
WCT-2D thermogravimetric-differential thermal analyzer, made by Beijing Optical Instrument Factory; Air (99.99%), made by Qingdao Tianyuan Gas Manufacturing Co., Ltd.; Merey Crude Oil, provided by PetroChina.

2.2. Experimental Procedure
Merey crude oil was heated till 600 °C at a linear heating rate of 5, 10, and 15 mL/min in air with the flow rate of 50 mL/min in a thermogravimetric-differential thermal analyzer. According to the weight loss curve of the sample, the conversion, α, during thermal reaction of Merey crude oil was calculated.

2.3. Data Processing
The thermogravimetric data are calculated by the isoconversion model in order to obtain the activation energy and pre-exponential factor. After linear regression of thermogravimetric data, the slope of the fitting line is the activation energy at the corresponding conversion. The pre-exponential factor is calculated by taking the activation energy to the general formula. The reaction mechanism cannot be determined by the isoconversion method. Assuming that the crude oil pyrolysis process is an isothermal homogeneous reaction, the reaction mechanism is expressed as $f(\alpha) = (1 - \alpha)^n$. The three dynamic models used in this paper are listed as follows [9]:

(1) FWO Model
The general formula of FWO model is

$$\ln \beta = \ln \left( \frac{AE}{Rg(\alpha)} \right) - 5.331 - 1.052 \frac{E}{RT}$$ (1)

(2) Friedman Model
The general formula of Friedman model is

$$\ln \left( \frac{\beta d\alpha}{dT} \right) = \ln \left( Af(\alpha) \right) - \frac{E}{RT}$$ (2)

(3) KAS Model
The general formula of KAS model is

$$\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AR}{Eg(\alpha)} \right) - \frac{E}{RT}$$ (3)

3. Result and Discussion

3.1. Calculation of Activation Energy by Isoconversion
Fig. 1 shows the activation energies at different conversions obtained by using the above three models for fitting at the conversion, α, of 0.1-0.9. Zhang Q.X. et al. [3] believed that the Merey crude oil pyrolysis under linear heating conditions was divided into four stages: light component gasification, low temperature oxidation, pyrolysis and high temperature oxidation. Thus, the whole reaction process shows the four stages at the conversion, α, of 0.1-0.9. Assuming that the thermal reaction of crude oil is the first order reaction, the pre-exponential factor is calculated.
According to Fig. 1, the activation energies and pre-exponential factors calculated from the three models are summarized in Table 1.

### Table 1. Activation energies \((E)\) and pre-exponential factors \((A)\) at different conversions for Merey oil obtained by FWO, Friedman and KAS models.

| Model | \(\alpha\) | \(E\) (kJ·mol\(^{-1}\)) | \(A\) (s\(^{-1}\)) | \(R^2\) | \(E\) (kJ·mol\(^{-1}\)) | \(A\) (s\(^{-1}\)) | \(R^2\) | \(E\) (kJ·mol\(^{-1}\)) | \(A\) (s\(^{-1}\)) | \(R^2\) |
|-------|--------|-----------------|-----------------|------|-----------------|-----------------|------|-----------------|-----------------|------|
| FWO   | 0.1    | 11.61644        | 4.877×10\(^7\) | 0.98369 | 12.84344        | 7.81×10\(^6\) | 0.95973 | 9.253326        | 0.016           | 0.97392 |
|       | 0.2    | 22.19231        | 2.33×10\(^7\)  | 0.97125 | 22.13909        | 1.84×10\(^6\) | 0.93792 | 19.45981        | 1.74            | 0.95991 |
|       | 0.3    | 27.24398        | 3.84×10\(^7\)  | 0.91928 | 29.40504        | 7.60×10\(^6\) | 0.85327 | 23.99075        | 3.01            | 0.88784 |
|       | 0.4    | 44.46047        | 4.68×10\(^9\)  | 0.89336 | 50.0931         | 3.15×10\(^8\) | 0.91836 | 41.33872        | 7.63×10\(^6\)  | 0.86595 |
|       | 0.5    | 57.12037        | 4.79×10\(^9\)  | 0.8487  | 52.34662        | 7.88×10\(^7\) | 0.91132 | 53.92513        | 1.02×10\(^7\)  | 0.81577 |
|       | 0.6    | 130.4947        | 8.87×10\(^12\) | 0.89086 | 97.95689        | 6.94×10\(^11\) | 0.92263 | 130.2536        | 8.0×10\(^12\)  | 0.87958 |
|       | 0.7    | 104.7443        | 7.97×10\(^14\) | 0.9594  | 99.08092        | 2.46×10\(^13\) | 0.92539 | 102.6542        | 3.95×10\(^10\) | 0.95351 |
|       | 0.8    | 75.97555        | 7.74×10\(^10\) | 0.99969 | 24.54294        | 3.64×10\(^9\) | 0.73251 | 71.6569         | 1.61×10\(^7\)  | 0.99956 |
|       | 0.9    | 54.90912        | 3.52×10\(^8\)  | 0.98503 | 53.04203        | 7.39×10\(^8\) | 0.93461 | 49.07247        | 32.82           | 0.97997 |
| average |      | 58.7508         |                 |          |                  |                 |      | 0.939029        | 49.05001        | 0.899527 |
| Friedman |      |                 |                 |          |                  |                 |      | 55.73388        |         | 0.924001 |

Table 1 shows that the fitting curves of three isoconversion models have good linear fitness \((R^2)\); FWO has the highest fitness and higher accuracy in the three models; the activation energy \((58.75\text{ kJ} \cdot \text{mol}^{-1})\) calculated from FWO model is closer to the activation energy \((55.73\text{ kJ} \cdot \text{mol}^{-1})\) calculated by KAS model, but the activation energy \((49.05\text{ kJ} \cdot \text{mol}^{-1})\) calculated by Friedman model is lower mainly because (1) both FWO and KAS models use the integral method, in which the change of activation energy with conversion is averaged, and therefore provide calculation errors; and (2) Friedman model uses the differential method and makes no assumption and approximation, and therefore provides more accurate results, but this model is sensitive to experimental noise.

### 3.2. Characteristics of Different Reaction Stages

The four reaction stages during thermal reaction of crude oil at the heating rate of 5℃/min correspond to the activation energies at different conversions. The results are shown in Table 2.

### Table 2. The relation of activation energy and four intervals of the thermal reaction.

| Reaction | \(E\) (kJ·mol\(^{-1}\)) | \(\alpha\) |
|----------|-----------------|--------|
| Gasification | 11.62-37.57 | 0.1-0.36 |
| LTO | 37.57-93.81 | 0.36-0.55 |
| Pyrolysis | 93.81-93.24 | 0.55-0.74 |
| HTO | 93.24-54.91 | 0.74-0.9 |

Table 2 shows that the activation energy of Merey crude oil increases first and then decreases in the four stages during thermal reaction; the highest activation energy occurs at the pyrolysis stage, which is...
related to the composition of crude oil and its reaction type. The gasification stage has the lowest activation energy because the gasification of light components is a physical process; the low-temperature oxidation stage has lower activation energy because of incomplete oxidation of some organic substances; as the key stage during thermal reaction, the pyrolysis stage has the highest activation energy because of its high energy consumption.

According to the weight loss percentage at varying temperature, the relationship between the conversion, $\alpha$, and temperature, $T$, during thermal reaction of Merey crude oil in air at different heating rates is shown in Fig. 2.

![Figure 2. $\alpha$-T curves of Merey crude oil mass loss at different heating rates under air.](image)

Fig. 2 shows the linear relationship between conversion and temperature during thermal reaction of crude oil at different heating rates, i.e. the relationship between conversion and temperature is very linear below 400°C, and fluctuates slightly between 400°C and 550°C, maybe because with the increase of temperature, the reaction becomes more complicated, the mechanism functions change more diversely, resulting in the errors of Kinetic data processing.

3.3. Comparison of Experimental Data and Fitting Results

It is concluded from Table 1 that the FWO model has the best linear correlation and the highest accuracy. Therefore, the curve of conversion vs. temperature obtained by this method is compared with that obtained by experimental data, as shown in Fig. 3.

![Figure 3. Comparison of experimental data and simulated data with FWO model for Merey crude oil.](image)
Fig. 3 shows that the fitting curve obtained by FWO model coincides almost completely with the curve obtained by experimental data, i.e. the two curves have good correlation. Thus, FWO model is the most suitable for calculation of the related kinetic parameters of Merey crude oil, and provides the most accurate calculation results in three models.

4. Conclusion
(1) FWO, Friedman and KAS models were used to process the thermogravimetric data of Merey crude oil at three different heating rates to obtain the kinetic parameters at the conversion from 0.1 to 0.9. The FWO model has the highest linear correlation and provides more accurate calculation results. The KAS model provides similar results to the FWO model, but the Friedman model provides smaller results.

(2) Among the four stages during thermal reaction of Merey crude oil, the gasification stage has the lowest activation energy, followed by low temperature oxidation stage; the pyrolysis stage has the highest activation energy and the highest energy consumption, which is the core stage in the whole reaction process.

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