



中国石油大学
CHINA UNIVERSITY OF PETROLEUM

Study of oil shale pyrolysis in the presence of water

Yue Ma, Shuyuan Li, Guili Ma

China University of Petroleum, Beijing

厚积薄发 开物成务

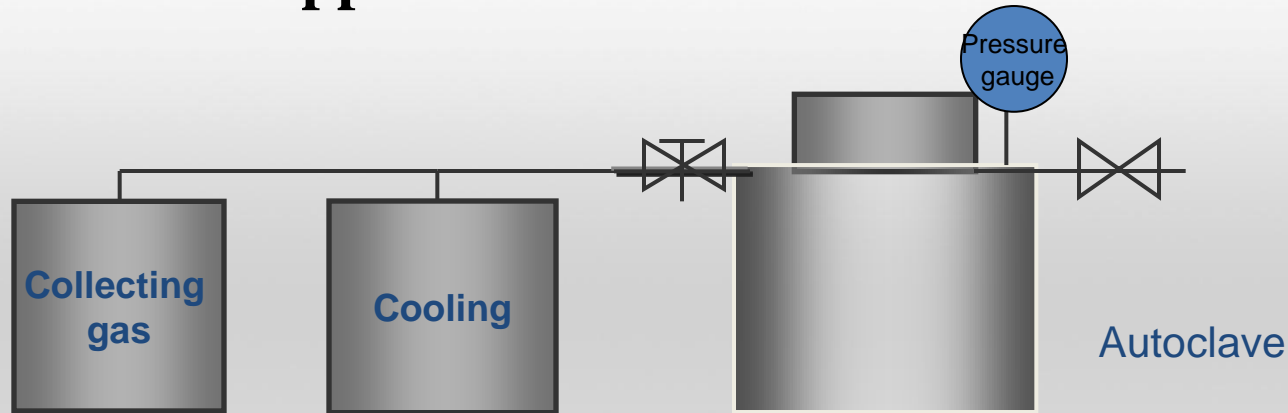
Background

- Oil shale pyrolysis technology is divided into two types: surface pyrolysis reactors and in-situ conversion processing.
- In recent years, more attention is being paid to the in-situ conversion processing technology by many researchers.
- To date, the commercial-scale application of in-situ conversion processing has not been demonstrated, but laboratory and pilot plant tests have been conducted.

Background

- The influential factors in in-situ conversion processing can be roughly determined using simple laboratory equipment.
- In general, the following factors were considered to be major concerns: hydrostatic pressure, effective pressure, maximum temperature, heating rate, heating time and the oil shale composition.
- It is very important to investigate oil shale pyrolysis in the presence of water.

● Experimental apparatus

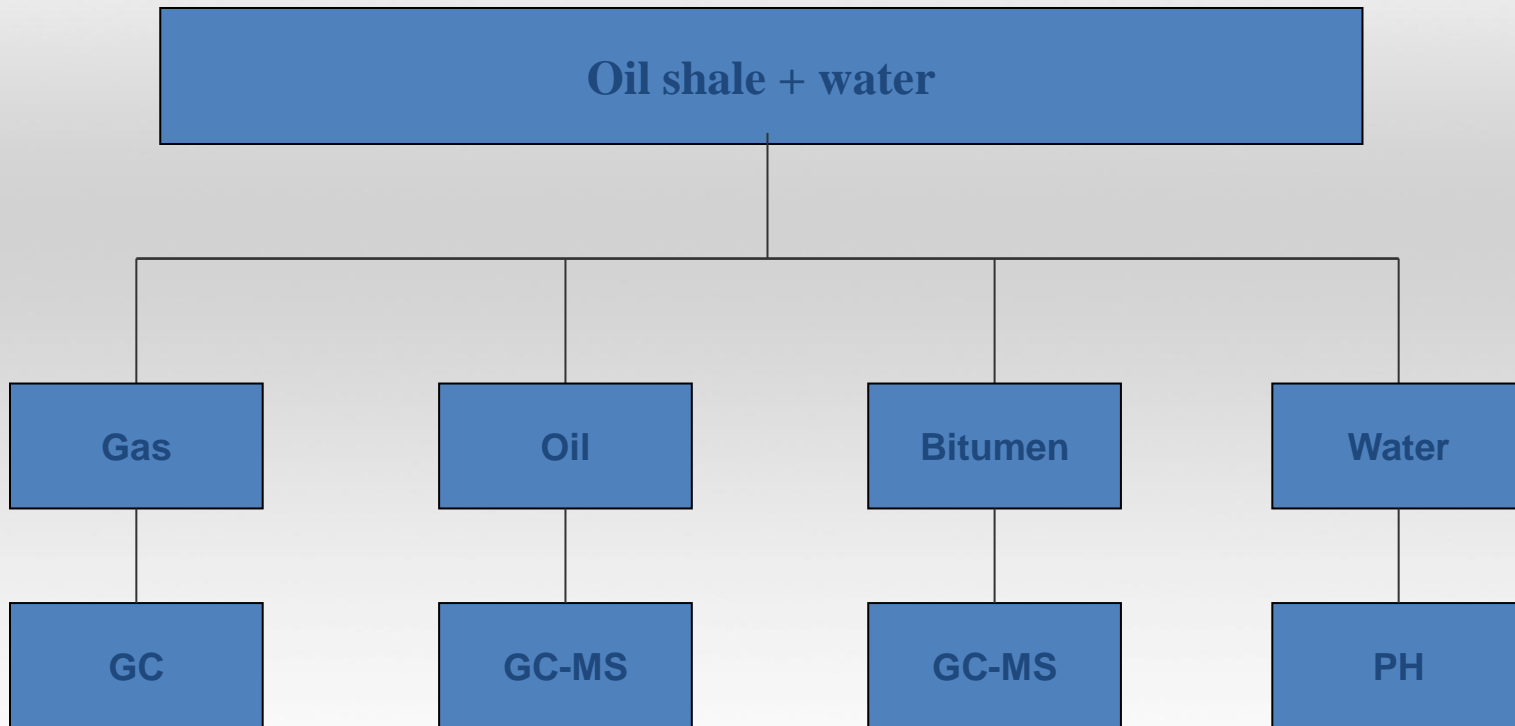


- 30 g oil shale was used in each experiment.
- To simulate water saturated in-situ conditions, 50 g of deionized water was added to the autoclave.
- To simulate unsaturated conditions, only 7.6 g of deionized water was added to the autoclave.

Experiment

- The oil shale and water were placed in a quartz beaker in the autoclave. The samples were heated to 200°C in 300 min, and then heated to different final temperatures at a heating rate of 2.5°C/h. The pyrolysates were cooled through a refrigerator and then collected when the temperature decreased to 300°C.

● Experimental process



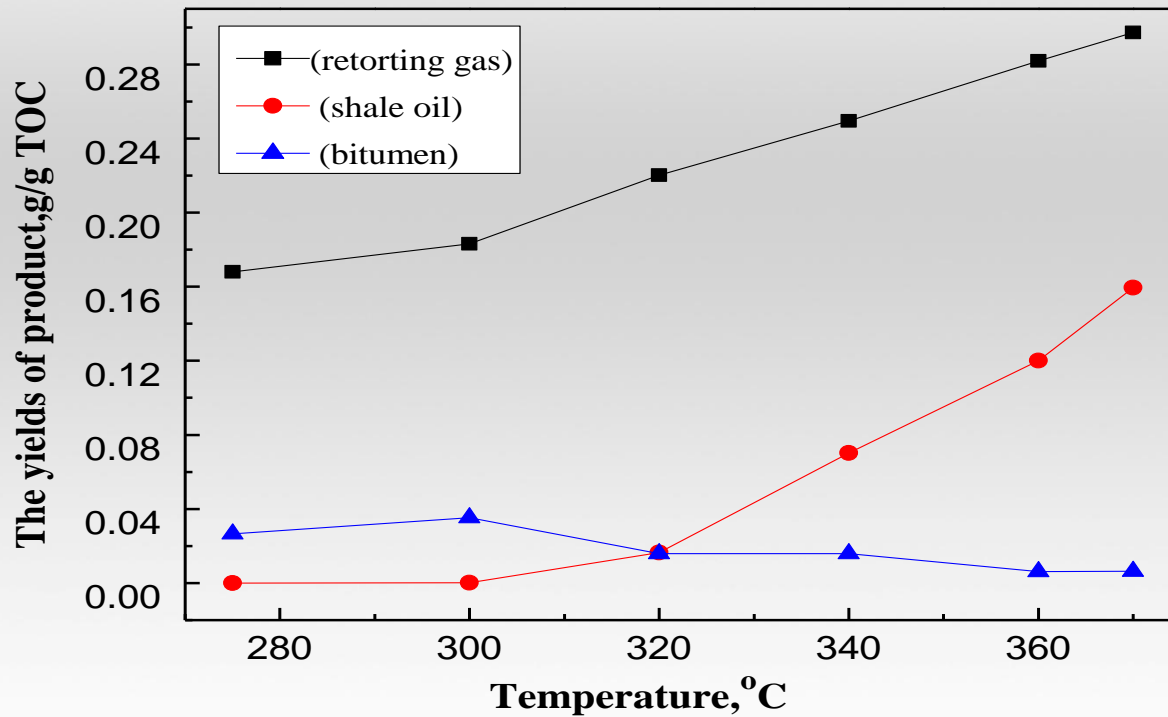
● Samples

The oil shale used in this study was taken from Liushuhe Basin in NE China. The oil shale sample was crushed and screened. The size range for samples used in these experiments was between 6 and 13 mm.

● The results of Fischer Assay and TOC

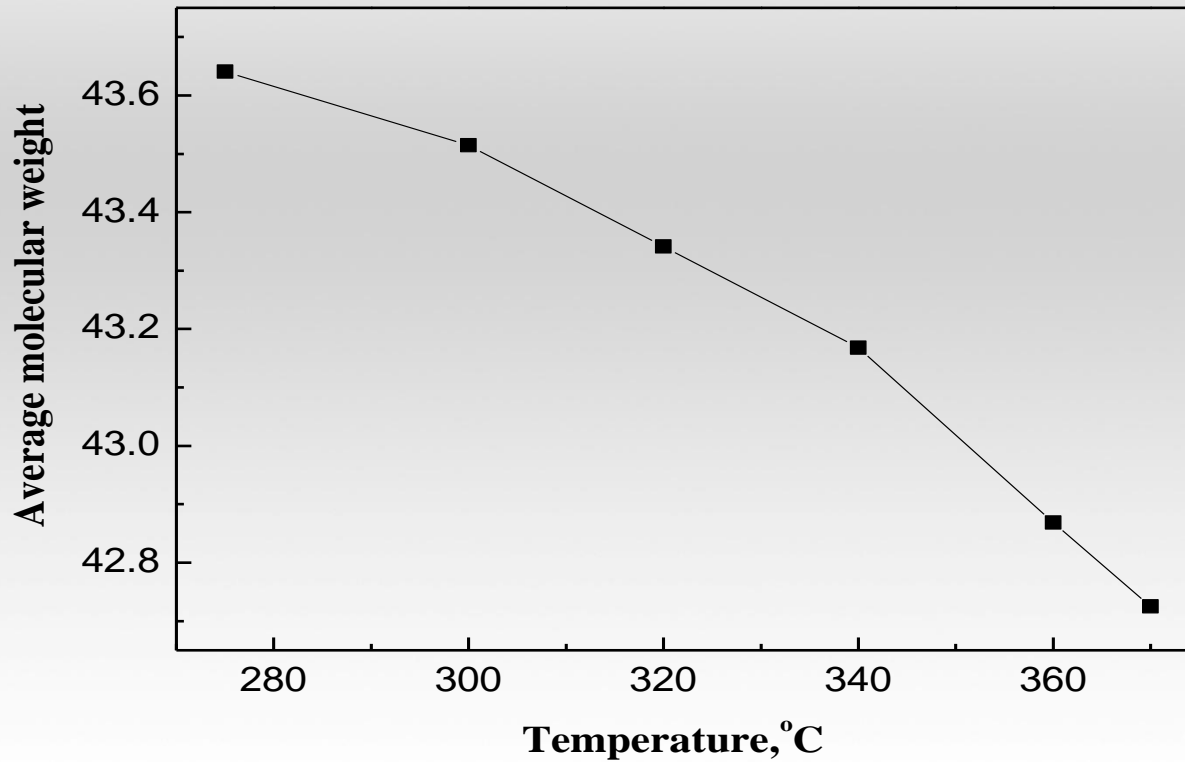
Oil Content %	Semi-coke %	Water %	Retorting Gas %	TOC %
11.63	64.88	8.75	14.73	49.54

● Pyrolysates



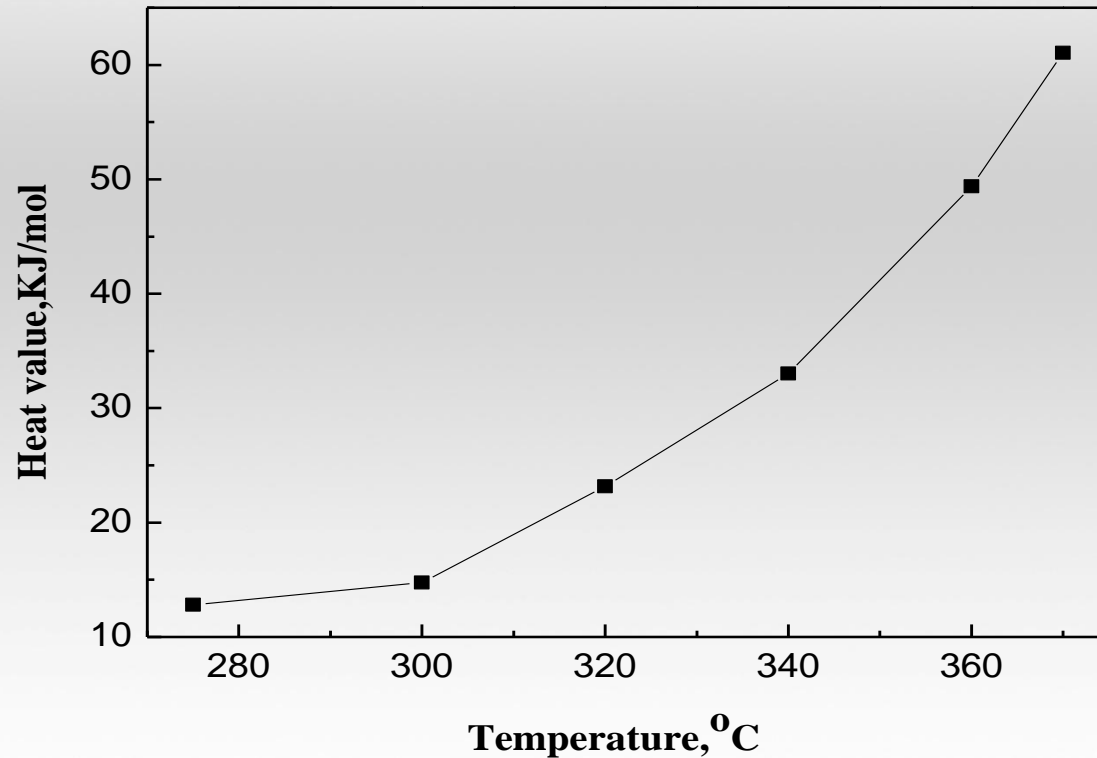
The retorting gas and shale oil yields increased with temperature.
The bitumen content increases initially and then decreases slightly.

● Retorting gas



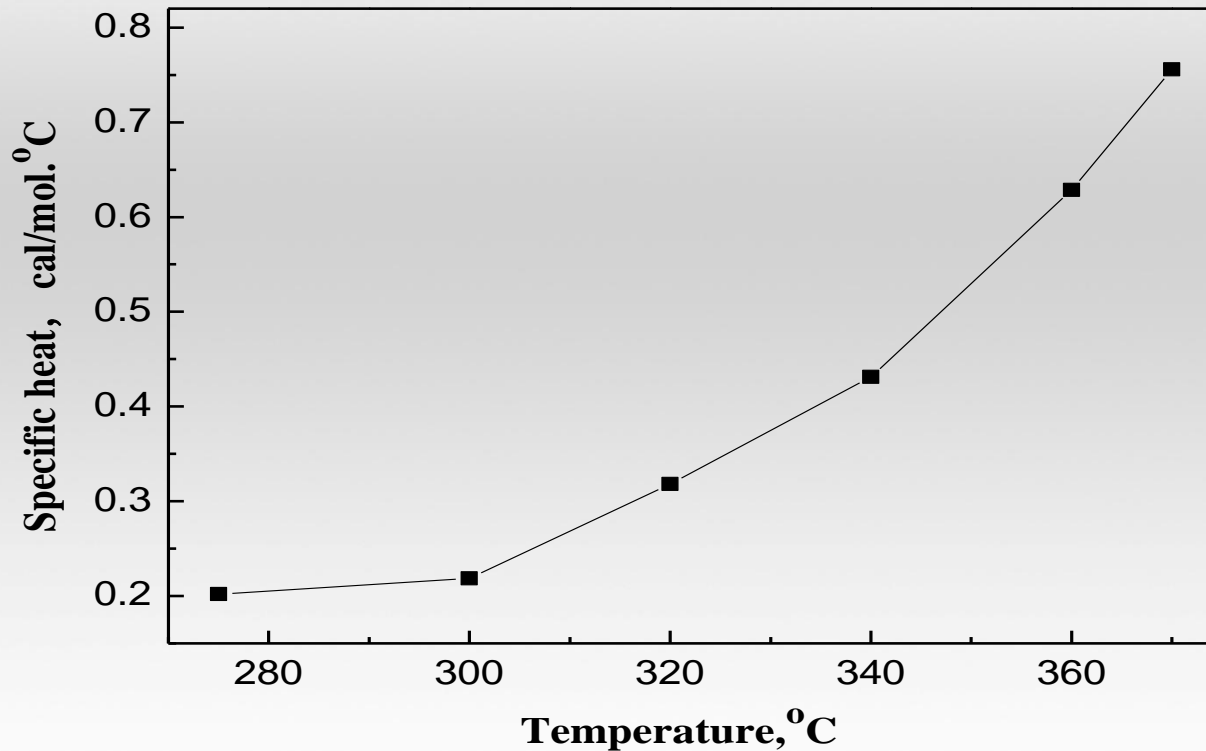
→ The average molecular weight decreases gradually with an increasing temperature.

● Retorting gas



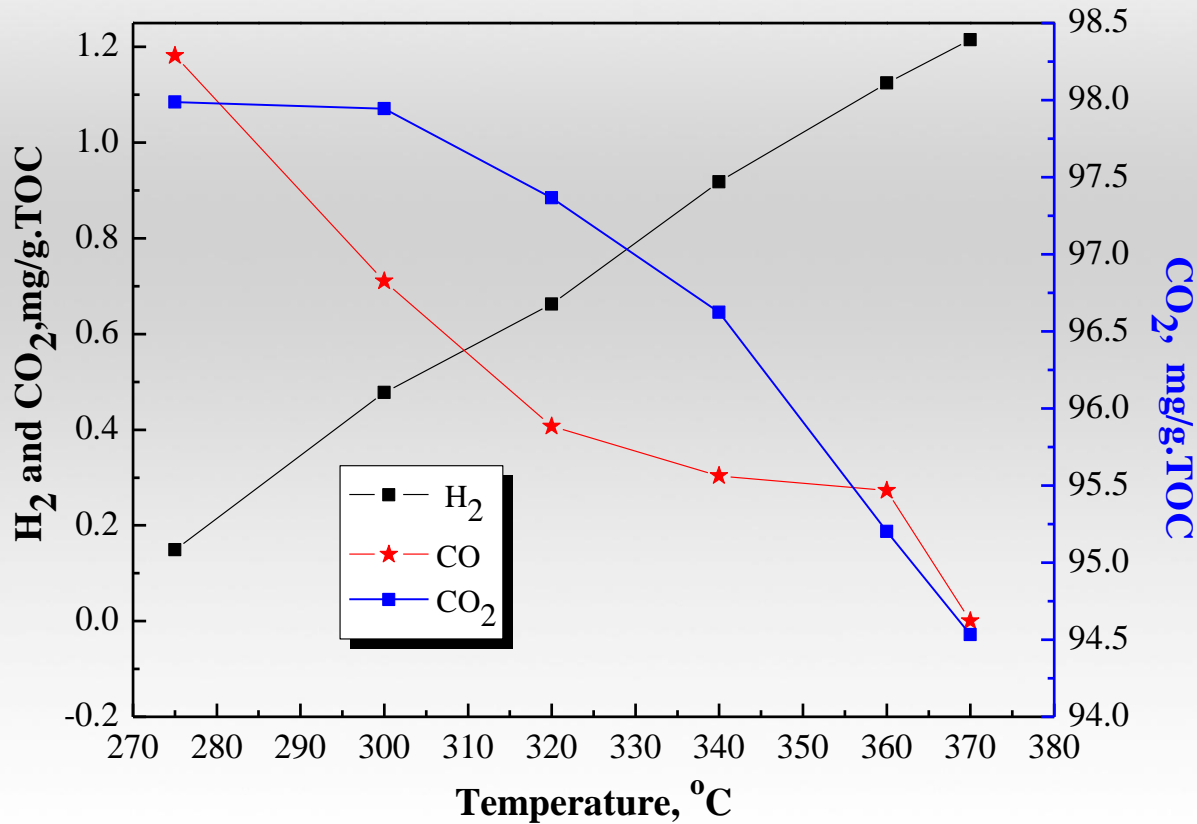
→ The heat value increases gradually with an increasing temperature.

● Retorting gas



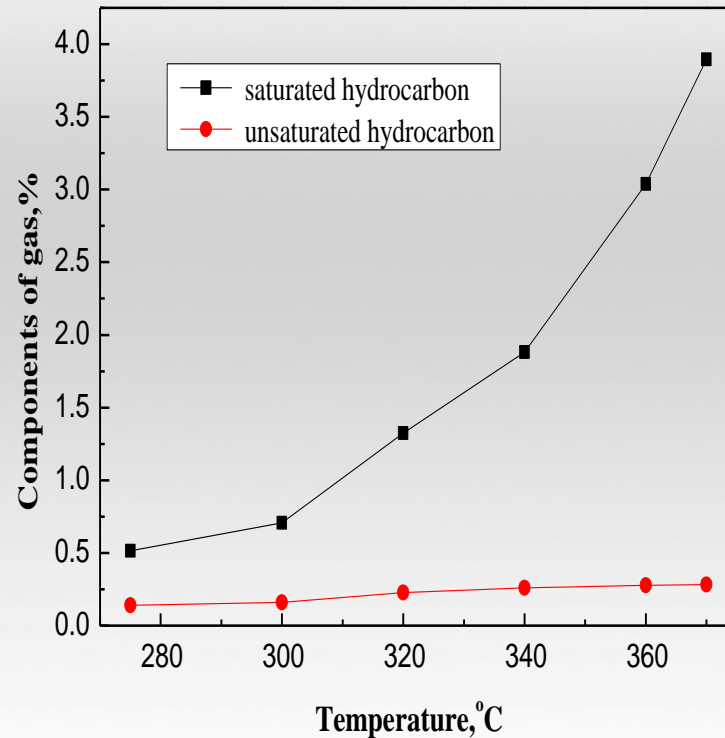
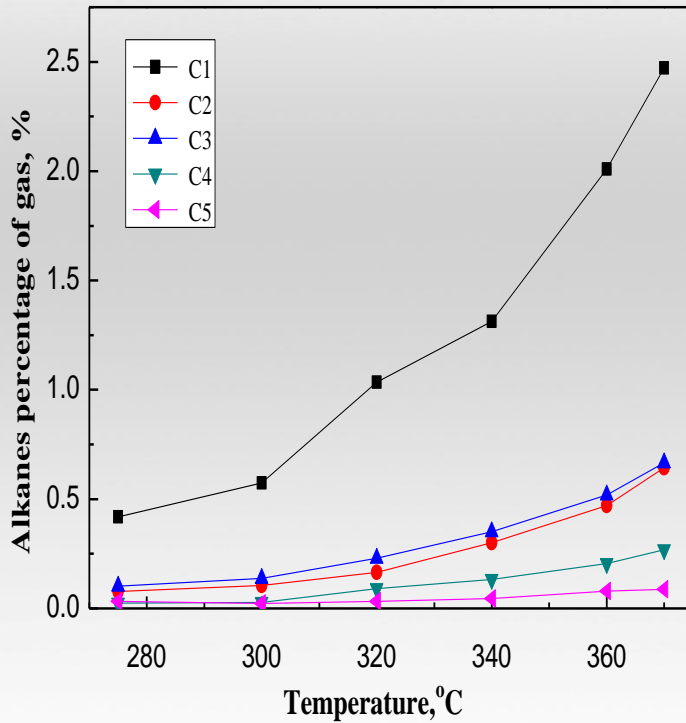
→ As temperature increases, the specific heat increases gradually .

● Non-hydrocarbon gas



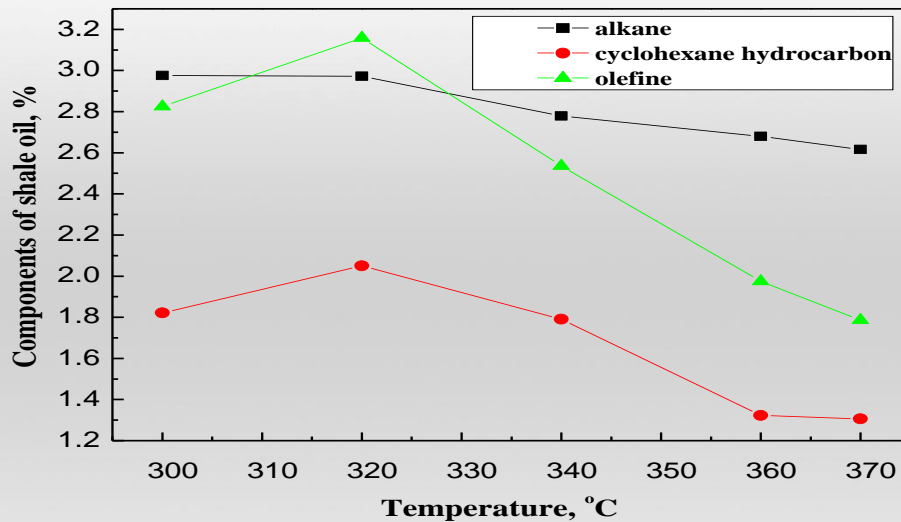
As the temperature increases, the amount of CO and CO₂ decreased and the H₂ increases.

Gaseous hydrocarbon

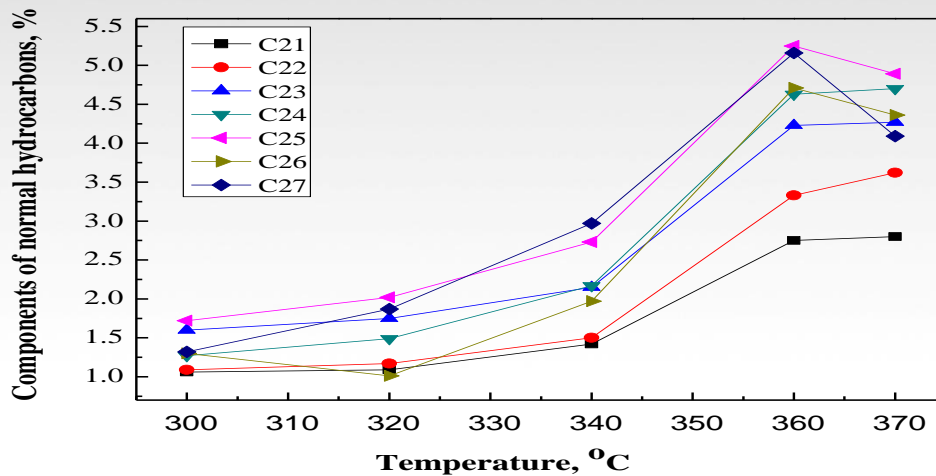


The gaseous hydrocarbon increases with temperature, and the contents of C_1 and saturated hydrocarbon increased significantly.

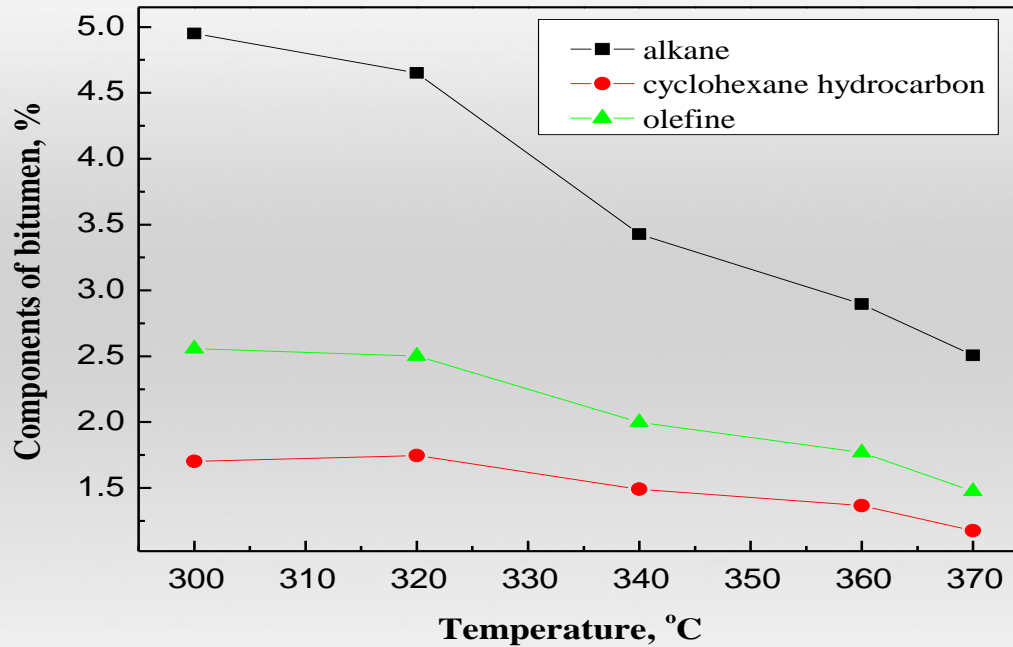
The analysis of shale oil



As the temperature was increased, some components initially increased, then decreased (e.g., cyclohexanes, olefins, and normal hydrocarbons between C_{21} and C_{27}).



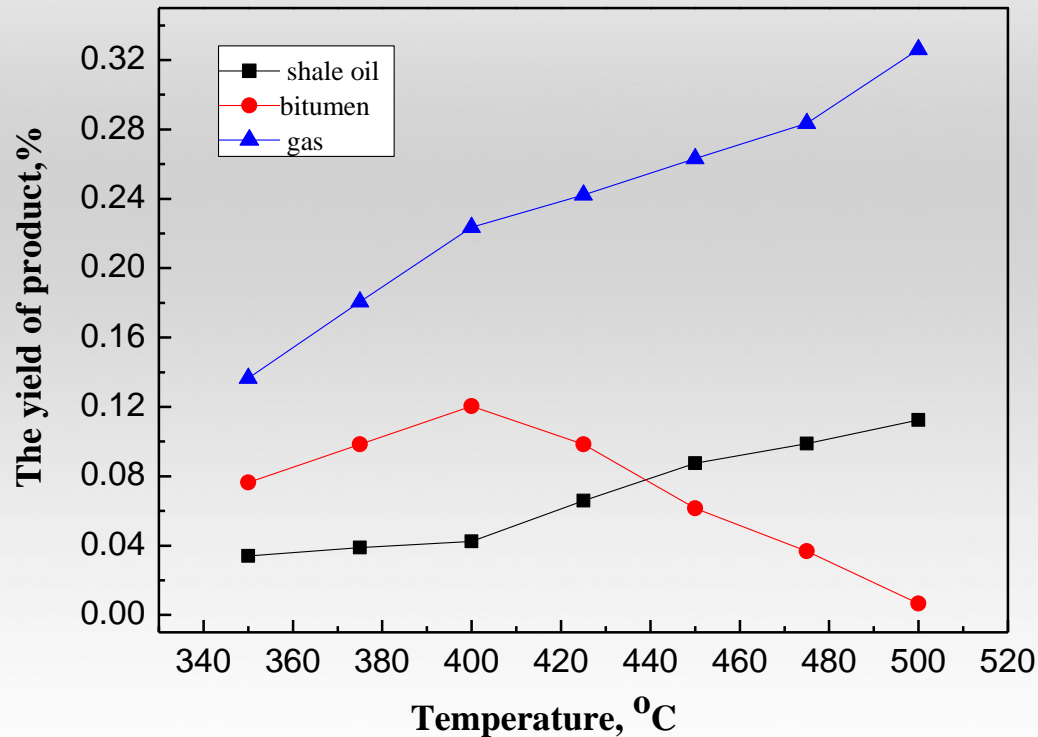
● The analysis of bitumen



● The analysis of pyrolysis water

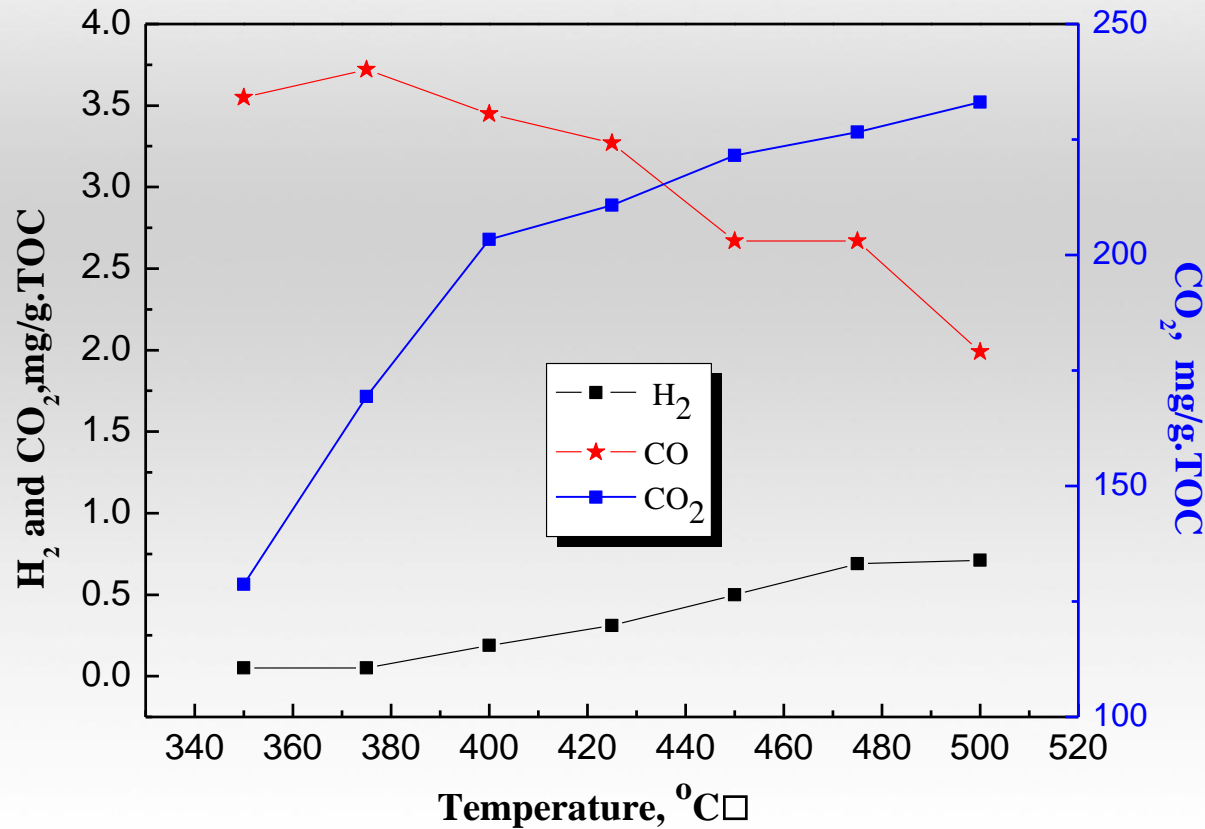
Temperature °C	300	320	340	350	360
pH	4.12	4.09	4.01	3.96	3.94

● Pyrolysis products



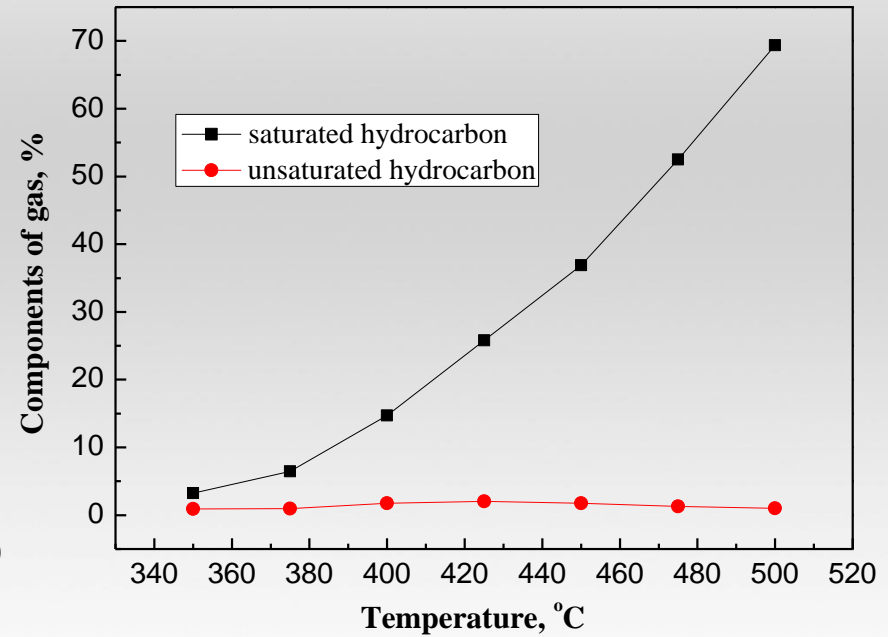
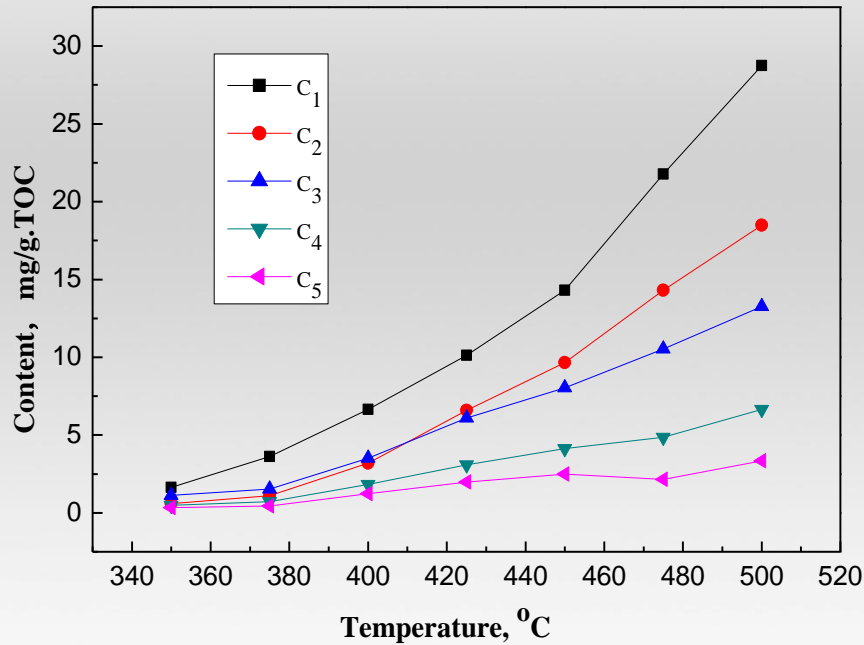
The changing trends are the same as the reaction under saturated water condition.

● Nonhydrocarbon gas



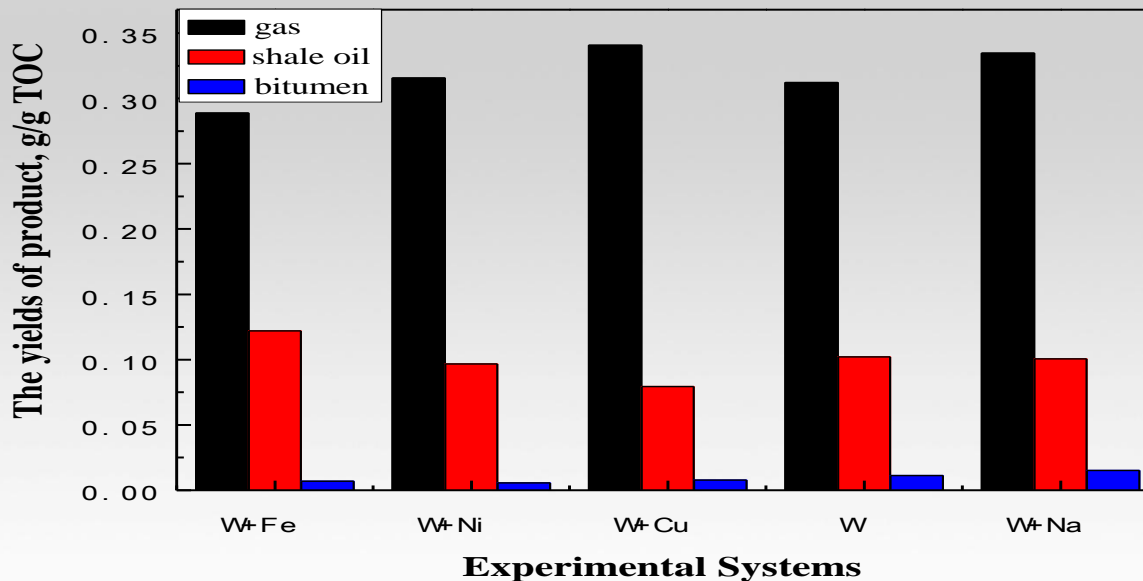
As the temperature increased, the amount of CO₂ generated increased. This is mainly because of the reaction of water gas.

Gaseous hydrocarbon



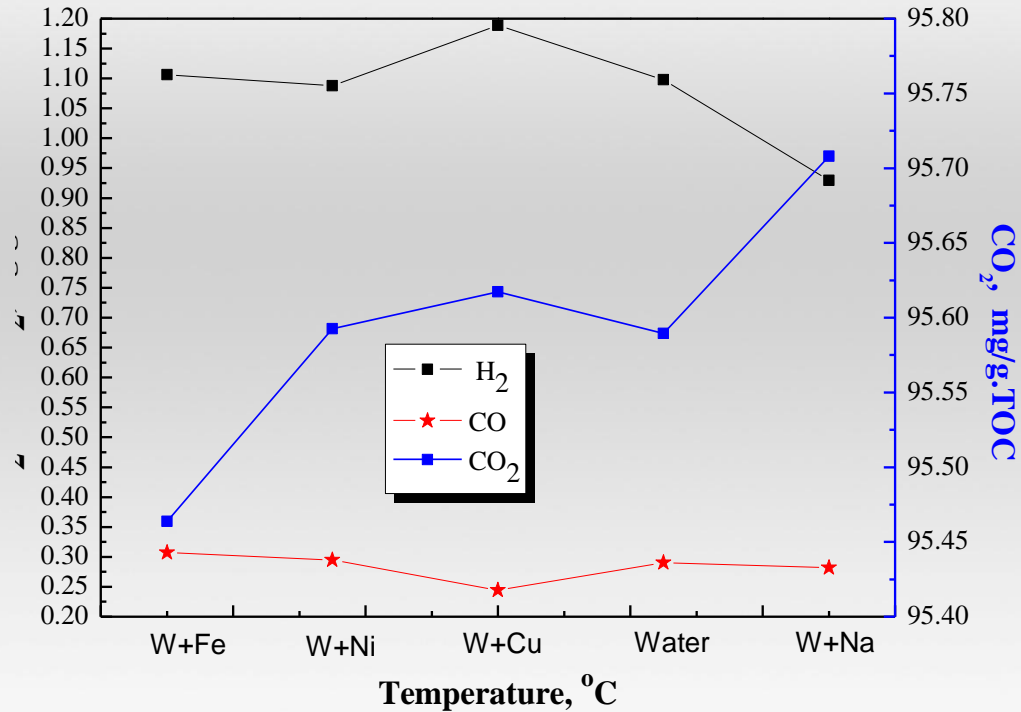
The changing trends of gaseous hydrocarbon are the same as the reaction under saturated water condition.

- According to the metal ion content in groundwater, four kinds of sulphate ions mixed with water, such as Cu^{+2} , Fe^{+3} , Ni^{+1} , Na^{+1} , were investigated, respectively.



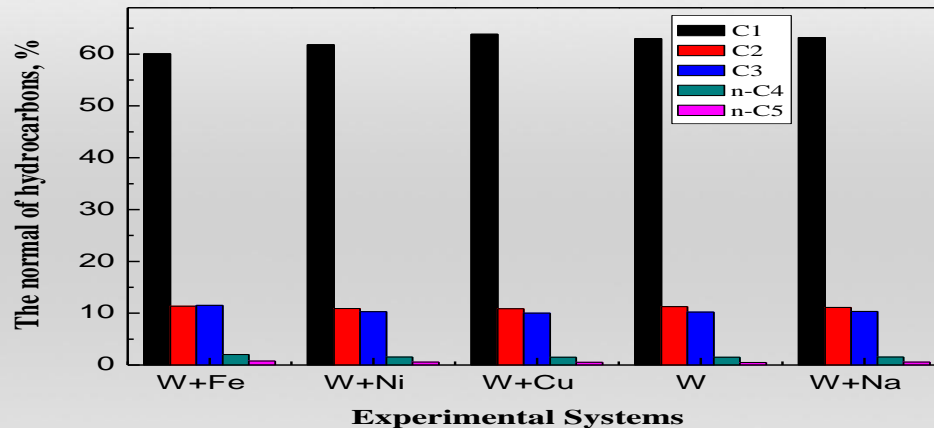
➔ The production of shale oil from bitumen was promoted in the presence of Fe^{+3} and Ni^{+1} .

● Nonhydrocarbon gas

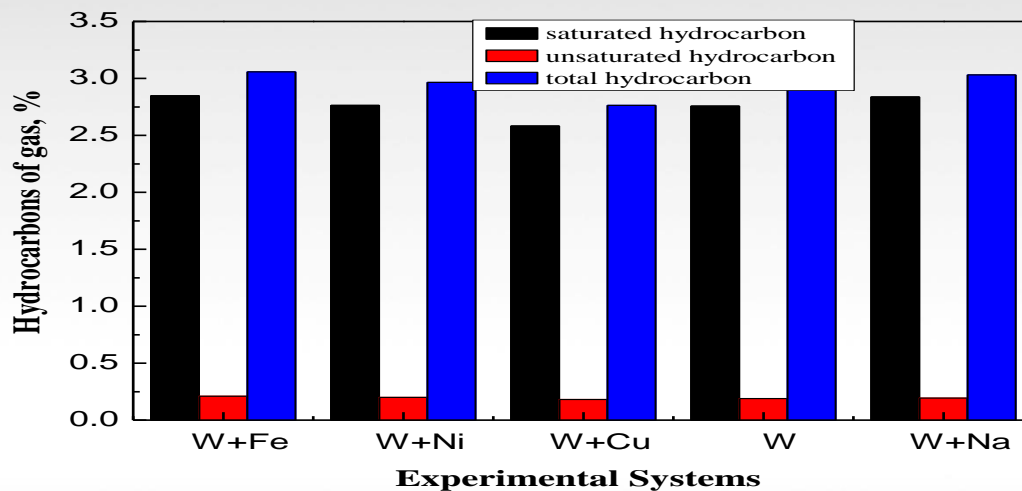


More H₂ was obtained when water was mixed with Cu ions.

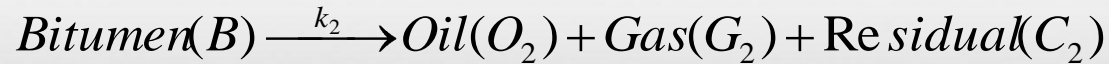
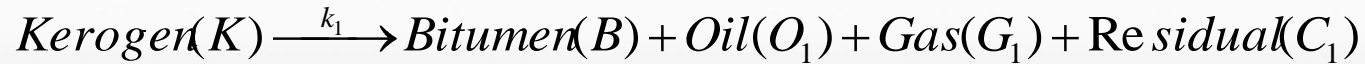
Hydrocarbon gas



More normal paraffins and other saturated hydrocarbons were found in the retorting gas when Fe was present in the system.



Kinetics of oil shale pyrolysis at presence of water



If two reactions in series are taken as first order, the kinetic equations can be shown as follows:

$$\frac{dK}{dt} = -k_1 \times K$$

$$\frac{dB}{dt} = f_1 \times k_1 \times K - k_2 B$$

$$\frac{dO}{dt} = f_3 \times k_1 \times K + f_2 \times k_2 \times B$$

- Using the Arrhenius formula, the following equations can be derived:

$$\frac{dy_1}{dT} = \frac{f_1 A_1}{\phi} \exp\left[-\frac{E_1}{RT} - \frac{A_1 R T^2}{\phi(E_1 + 2RT)} \exp\left(-\frac{E_1}{RT}\right)\right] - \frac{A_2}{\phi} y_1 \exp\left(-\frac{E_2}{RT}\right)$$

$$\frac{dy_2}{dT} = \frac{f_3 A_1}{\phi} \exp\left[-\frac{E_1}{RT} - \frac{A_1 R T^2}{\phi(E_1 + 2RT)} \exp\left(-\frac{E_1}{RT}\right)\right] + \frac{A_2}{\phi} f_2 y_1 \exp\left(-\frac{E_2}{RT}\right)$$

- The equations can be solved using the LongBei Coulthard and nonlinear damped least-square methods to determine the kinetic parameters according to the experimental data.

Kinetics of in-situ oil shale pyrolysis

● The pyrolysis kinetic parameters

Condition	f_1	f_2	f_3	A_1 s^{-1}	A_2 s^{-1}	E_1 kJ/mol	E_2 kJ/mol	F_1	F_2
Saturated	0.588	0.883	0.061	2.92×10^6	1.1×10^{11}	110.1	191.4	0.096	0.041
Unsaturated	0.798	0.785	0.077	2.12×10^6	1.0×10^{11}	134.2	190.5	0.069	0.121

- K: mass fraction of kerogen; B: mass fraction of bitumen; O: oil content; k_1 : rate constant of kerogen pyrolysis to bitumen; k_2 : rate constant of decomposition of the bitumen to oil and gas; f_1 : mass fraction of bitumen produced by kerogen pyrolysis; f_2 : mass fraction of oil produced by bitumen pyrolysis; f_3 : mass fraction of oil produced by kerogen pyrolysis; E_1 : activation energy of kerogen pyrolysis; E_2 : activation energy of bitumen pyrolysis; R: constant for gas ($8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); T: temperature of reaction (K); A_1 : frequency factor of kerogen pyrolysis; A_2 : frequency factor of bitumen pyrolysis

Kinetics of in-situ oil shale pyrolysis

- The magnitude of E_2 is larger than E_1 . The lower E_1 , under saturated condition, can be attributed to water due to the near critical state water decreasing the energy required to break chemical bonds by swelling under water saturated condition.
- The results of f_1 , f_2 , f_3 indicate that the pyrolysate of kerogen is mainly bitumen; only about 6% is converted to oil. Most of the residual kerogen was obtained in the first stage.

Kinetics of in-situ oil shale pyrolysis



- The consecutive first order reaction model involving bitumen as an intermediate product can be reasonably used to describe the oil shale pyrolysis at the presence of water.
- Actually, this process is the depolymerization of macromolecular polymer. The shale oil is mainly produced from bitumen cracking, little oil is generated from original kerogen.

Conclusion

- As temperature is increased, the yields of retorting gas, shale oil and saturated hydrocarbon increase. The amount of bitumen and CO increase initially and then decrease slightly in the presence of water. The CO₂ yield in the retorting gas is highest, CH₄ is the next most abundant component.
- Compared to anhydrous pyrolysis, the pyrolysis temperature under saturated water condition was about 100°C lower, and under unsaturated condition it was about 50°C lower.
- This indicates that water promotes shale oil production during pyrolysis.

Conclusion

- The presence of metal ions promoted the production of saturated hydrocarbons. The complex compounds were generated when Fe and Ni were present, leading to a reduction in activation energy of the reaction.
- The consecutive first order reaction model involving bitumen as an intermediate can be reasonably used to describe oil shale pyrolysis. The calculated results coincide with the experimental data. The activation energy of kerogen conversion to bitumen is less than that for the conversion of bitumen to shale oil.