Oil Shale, Vol. 12, No. 1 pp. 15-30

https://doi.org/10.3176/oil.1995.1.02

STUDY ON REACTION KINETICS OF OIL SHALE AND SOURCE ROCK

LI SHUYUAN WANG JIANQIU WU ZHAOLIANG QIAN JIALIN

School of Chemical Engineering University of Petroleum Beijing, China

> This paper describes major results in the field of reaction kinetics of oil shale and source rock processing. These reactions include drying, pyrolysis, and combustion of oil shale and shale char. The resultant data are applied in retorting practice. The kinetic data of source rock kerogen thermodegradation are used to calculate the quantity of hydrocarbons formed in basins.

Preface

At the beginning of the nineteen-fifties, a study on pyrolysis of oil shale and coal was carried out in the fossil fuel laboratory of the Beijing Petroleum Institute [1]. At the beginning of the nineteen-sixties, due to the discovery and exploitation of Daqing Oil Field, much attention was paid to petroleum processing, thus suspending the research work on the pyrolysis of solid fossil fuel. In the nineteen-seventies, the world "oil crisis" occurred, so many countries resumed their research work on synfuels [2].

The International Conference of Oil Shale Experts sponsored by the United Nations took place in 1981 [3]. Research work on oil shale, mainly in the field of fundamentals, including oil shale composition, structure, and reaction kinetics was restored in the East China Petroleum Institute (the predecessor to the Petroleum University, China).

In this paper, achievements in oil shale reaction kinetics investigation are presented. These include pulverized, particulate and lump oil shale drying, pyrolysis and combustion reactions [4-6]. From the beginning of the nineteen-eighties, the authors of this paper conducted research work on source rock pyrolysis and hydrocarbon formation kinetics. This effort utilized prior results from oil shale pyrolysis research, thus enriching the current work. Not only fundamental research on oil shale and source rock reaction kinetics was carried out, but much attention was also paid to the practical problems, too. The theoretical results were applied in oil shale processing and provided explanations of hydrocarbon formation in basins.

1. Intrinsic Kinetics of Pulverized Oil Shale Pyrolysis and Hydrocarbon Evolution

Oil shale consists of organic - mainly kerogen - and mineral matter, commonly the latter being the chief constituent. Kerogen is a high-molecular compound with a complex spatial structure not yet totally defined. However, some simplified structural models were developed. Oil shale is retorted to produce shale oil, which is further processed for manufacturing liquid fuels and organic chemicals. Oil shale is also used for producing steam and electricity.

A thermogravimetric analyzer, thermodifferential apparatus, source rock evaluation apparatus (Rock Eval), and specially designed reactors were used for systematic detailed research on oil shale reaction kinetics. The use of pulverized oil shale (< 0.075 mm), eliminated heat transfer effects on the kinetic experiments. Hence, the tests could be considered as having been run purely in the kinetic range. As a rule, the experiments were carried out with a constant rate of heating, sometimes at a constant reaction temperature. Eight models of pyrolysis kinetics, along with their calculation codes, were used for processing and modelling experimental data. As for the samples, not only Chinese Fushun, Maoming, Huang County, and Haidian oil shales were used, but also foreign ones, such as Green River (Colorado, USA), Baltic (of Estonia), and Lajjun (of Jordan).

Overall First-Order Reaction

Assuming that the structure of oil-shale kerogen is uniform, like that of a simple compound (such as Type I kerogen), the reaction may be considered to fit the Arrhenius equation during the entire pyrolysis run, thus:

$$\frac{dx}{dt} = k(1-x)^n = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-x)^n$$

where, x - fraction of kerogen undergoing conversion;

t - time, s;

- k reaction rate constant, s^{-1} ;
- n reaction order;
- A apparent frequency, s^{-1} ;
- E apparent activation energy, J/mol;
- R gas constant, 8.314 J/mol·K;
- T absolute temperature, K.

When n=1,

$$\frac{dx}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-x)$$

at a constant rate of heating, m=dT/dt, thus:

$$\frac{dx}{dT} = \frac{A}{m} \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1-x)$$

(2)

(3)

(1)

Equation (3) may be solved by the differential method, or by the integration method.

$$\ln\left(\frac{dx/dT}{1-x}\right) = \ln\left(\frac{A}{m}\right) - \frac{E}{R} \cdot \frac{1}{T}$$
(4)

Using the differential method:

Taking the *T*-*x* curve obtained from experimental data, a series of *x*, *T*, dx/dT values can be obtained. Then a plot of $\ln(dx/(dT \cdot (1-x)))$ versus 1/T may be made. Using a least squares regression, *E* and *A* can be obtained. For example, the experimental data of the pyrolysis of Fushun and Maoming oil shales, carried out with a constant heating rate (5 K/min) in the Rock Eval apparatus, fits Equation (4) very well. The correlation coefficient, *r*, is greater than 0.988. Therefore, the pyrolysis of both Fushun and Maoming oil shales may be considered to fit the overall first order reaction model [7].

Using the integration method, Equation (3) becomes

$$\int_{0}^{x} \frac{dx}{1-x} = \int_{T_0}^{T} \frac{A}{m} \cdot \exp\left(-\frac{E}{RT}\right) dT$$
(5)

when $T >> T_0$. Equation (5) is approximately integrated to the following:

$$-\ln(1-x) = \frac{ART^{2}}{mE} \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right)$$
$$\ln\left[\left(-\frac{\ln(1-x)}{T^{2}}\right) / \left(1 - \frac{2RT}{E}\right)\right] = \ln\frac{AR}{mE} - \frac{E}{R} \cdot \frac{1}{T}$$
(6)

For a series of experimental data x-T, Equation (6) may be solved by using the least squares method, thus obtaining E and A. It was shown that the experimental data obtained for Chinese (Fushun and Maoming), Australian (Queensland) and Moroccan (Timhadi) oil shales, using a thermogravimetric analyzer with a constant heating rate of 1 and 2 K/min, can be handled well with Equation (6) to get satisfactory results [8].

Overall nth-Order Reaction

Equation (1) is the model of overall *n*th order kinetics. When the experimental data of Fushun oil shale were analyzed using Equation (1), it was shown that n=0.9-1.2, i.e. $n\approx 1$ [9].

Different Stages of First-Order Reaction

When the overall first-order or *n*th order models do not fit the experimental data, kinetic curves may be divided into the beginning, major and end stages, and each of them treated as a first-order model, by using Equation (4) or Equation (6), with different values of E and A, but the overall x is equal to 1 [10-13].

Pyrolysis at Maximum Reaction Rate

At a constant rate of heating, and maximum rate of pyrolysis,

$$\frac{d^2x}{dT^2} = 0 \tag{7}$$

Differentiating Equation (3), and using Equation (7), with n=1, yields

$$\ln \frac{m}{T_m^2} = \ln \frac{AR}{E} - \frac{E}{RT_m}$$
(8)

where, T_m is the temperature at the maximum rate of pyrolysis, K.

Using the same sample, different values of T_m can be obtained at different pyrolysis curves for different rates of heating. A plot of $\ln(m/T_m^2)$ versus $1/T_m$ can be regressed in order to obtain *E* and *A* at the maximum reaction rate for this sample [14].

Parallel First-Order Reaction

Assuming that the pyrolysis of oil shale consists of a number of parallel reactions (No) with different *E* and *A* values, the model may be described as follows:

$$\frac{dx_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right) \cdot (X_{i0} - X_i)$$
⁽⁹⁾

where subscript *i* denotes the *i*th reaction, i_0 is the final state of *i*th reaction. Thus

$$\sum_{i=1}^{N_0} X_i = x, \qquad \sum_{i=1}^{N_0} X_{i0} = 1$$

Using the Monte Carlo method and the Simpson integration method, the values for E_i , A_i and X_{i0} , as well as x at t can be obtained [15]. It was found that $\ln A_i$ for parallel reactions is a linear function of E_i [16].

Parallel and Consecutive Reactions

Assuming that at pyrolysis of oil shale bitumen and small quantities of oil and gas are formed simultaneously followed by the formation of oil, gas and retorted shale from the pyrolysis of bitumen, as follows:

Kerogen
$$\begin{array}{c|cccc} X_1 & k_{11} & & k_{21} & & \\ X_1 & \stackrel{}{\longrightarrow} & \text{bitumen } (Y_1) & \stackrel{}{\longrightarrow} & \text{shale oil } (u_1) + \text{retorted shale} \\ & & & \\ & & & \\ & & & \\ X_{22} & & & \\ & & & \\ & & & \\ X_2 & \stackrel{}{\longrightarrow} & \text{shale oil } (Y_2) \\ & & & \\ & & & \\ & & & \\ X_3 & \stackrel{}{\longrightarrow} & \text{gas } (Y_3) \end{array}$$

where X_1, X_2, X_3 - the weight fractions of kerogen converted to bitumen, shale oil, and gas, respectively;

- Y_1, Y_2, Y_3 the weight fractions of bitumen, shale oil, and gas
 - formed, respectively (on a kerogen basis);
- u_1, u_2 the weight fractions of oil and gas formed, on a kerogen basis, respectively;
- k_{11}, k_{12}, k_{13} the reaction rate constants for pyrolysis of X_1, X_2, X_3 , with units of reciprocal seconds, s⁻¹;
 - k_{21} , k_{22} -reaction rate constants for formation of oil and gas from bitumen, respectively, with units of reciprocal seconds, s⁻¹.

The parallel pyrolysis kinetics model may be described as follows:

$$\frac{dx_j}{dt} = -k_{1j}X_j, \qquad j = 1, 2, 3 \tag{10}$$

$$\frac{dY_1}{dt} = k_{11}X_1 - k_2Y_1, \tag{11}$$

$$\frac{dY_j}{dt} = k_{ij}[Y_{j0} - Y_j], \qquad j = 2, 3$$
(12)

$$\frac{du_i}{dt} = k_{2i}Y_1, \qquad i = 1, 2$$
 (13)

Using the Monte Carlo method and the Simpson integration method, kinetic parameters can be obtained, and thus X_i , Y_i , and u_i can be calculated for different values of t [15, 16]. For clarification, the oil shale pyrolysis kinetics model, with bitumen as an intermediate product, was elaborated by Li et al. [17].

Infinite Number of Parallel First-Order Reactions

Assuming that the pyrolysis of kerogen includes an infinite number of reactions with a single value of A_i and infinite different values of E_i , then the reaction of maximum hydrocarbon evolution X_{i0} (of each reaction) *i* varies with E_i according to the Gaussian distribution function:

$$X_{i0} = \frac{1}{\sigma\sqrt{2\pi}} \exp[-(E - E_0)^2 / 2\sigma^2]$$
(14)

By deduction, the reaction kinetics at constant heating rate may be given by the following:

$$x = 1 - \frac{1}{\sigma\sqrt{2\pi}} \int_{E_0^{-2\sigma}}^{E_0^{+2\sigma}} \exp\left[-\frac{A}{m} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT - \frac{(E - E_0)^2}{2\sigma^2}\right] dE$$
(15)

where E_0 - mean apparent activation energy;

 δ - standard deviation for the Gaussian distribution function.

Using the Taylor method for obtaining linear functions, followed by the least square regression method, the values for A, E_0 , and δ can be calculated. This is based on the experimental data for pyrolysis carried out at a constant heating rate. This yields values of X for different values of t [8, 18].

Consecutive First-Order Reactions

or model with varying activation energy versus pyrolysis conversion fraction. This model is also called the Friedman Model. Kerogen is assumed to be a complex molecule with multi-functional groups and different chemical bonds. As the pyrolysis reaction proceeds, characteristics of the reactant change. Different kinds of chemical bonds break, and apparent activation energy and frequency factor change (the reaction order is assumed to be 1).

In this case, Equation (3) can be used. For different heating rates m_i ,

$$\ln\frac{dx}{dT} = \ln\left|\frac{A}{m_i}(1-x)\right| - \frac{E}{R} \cdot \frac{1}{T}$$
(16)

As an example, taking $m_i=1, 2, 5, 10, 15$ K/min in experiments, the pyrolysis curves, *X*-*T*, are obtained for different heating rates.

For each X-T curve, taking the same x_i value (e.g., $x_i=0.05, 0.10, 0.15 \dots 0.85, 0.90, 0.95$), the slope of the curve $(dx/dT)_i$ can be obtained. From the plot of $\ln(dx/dT)_i$ versus $(1/T)_i$, one can calculate values for A_i and E_i at different x_i [14].

Kinetic Parameters Calculated According to Different Models

For Fushun and Maoming oil shale samples, pyrolysis experiments at constant heating rate were carried out using a thermogravimetric apparatus. Figures 1 and 2 show X-T, and dx/dt-T curves obtained from experimental data. Using some of the different models which were described above, the calculated results are given in Tables 1-3 [14].

Sample	Overall first order		Maximum reaction rate	
	E, kJ/mol	A, s^{-1}	E, kJ/mol	A, s^{-1}
Fushun	169.1	4.07.109	230.6	2.36.1014
Maoming	161.1	1.46.109	219.2	3.25.1013

 Table 1. Results Calculated Using the Overall First-Order

 and Maximum Reaction Rate Model







Sample	Fushun		Maoming		
E _i , kJ/mol	x _{i0}	A_{i}, s^{-1}	X _{i0}	A_i , s ⁻¹	
80	0.0398	8.573·10 ³	0.0382	5.406·10 ³	
120	0.1208	2.751.106	0.1234	1.277.107	
160	0.3142	3.476.109	0.3146	3.923.109	
200	0.3313	1.025.1012	0.3506	2.944·10 ¹²	
240	0.1185	1.336.1016	0.0949	5.206.1015	
280	0.0713	1.425.1019	0.0781	1.672.1019	

Table 2. Results Calculated Using the Parallel Reaction Model

Table 3. Results Calculated Using the Model with Varying Activation Energy versus Conversion Fraction

Conversion x	Fushun oil shale		Maoming oil shale	
di un presidente chromatoeran	E, kJ/mol	A, s^{-1}	E, kJ/mol	A, s ⁻¹
0.05	167.7	3.304.109	173.3	1.605.1010
0.10	194.0	3.000.1011	195.9	7.170.1011
0.20	212.3	6.400·10 ¹²	216.1	1.945.1013
0.30	218.7	1.800.1013	219.1	2.770·10 ¹³
0.40	221.1	2.520.1013	220.5	3.100.1013
0.50	232.4	1.470.1014	221.2	3.187.1013
0:60	239.8	3.870.1014	227.0	7.742.1013
0.70	242.2	3.950.1014	249.1	2.500.1015
0.80	242.8	3.070.1014	264.0	1.600.1016
0.90	249.6	5.520.1014	282.2	7.000.1016
0.95	288.6	1.478.1017	286.8	4.600.1016

For Type I or II kerogens (such as Fushun and Maoming oil shales) the overall firstorder reaction model, or the model with varying E with x (Friedman Model) can be used for calculations in the main range of pyrolysis temperatures.

Time Required for Pyrolysis of Pulverized Oil Shale at Constant Temperature

Using Equation (2) for the overall pyrolysis reaction rate with constant reaction temperature,

$$t = -\frac{1}{A} \cdot \ln(1-x) \cdot \exp\left(-\frac{E}{RT}\right)$$
(17)

Using *E* and A, which are calculated from the experimental data obtained at constant heating rate, and assuming x=0.95, the time, *t*, required for keeping the reaction temperature constant was calculated from Equation (17) (Table 4) [14].

Table	4. Time	Required	for (Constant	Pyrolysis	Temperature
with	Pulverize	ed Fushun	and	Maomin	g Oil Sha	le

Şample Temp., °C	Fushun Oil S	hale	Maoming Oil Shale	
	475	500	475	500
Time, min	7.83	3.26	6.04	2.62

It is shown that for pulverized oil shales, the pyrolysis reaction proceeds quickly - at pyrolysis temperatures of 475-500 °C only a few minutes are required.

Kinetics of Product Evolution

Kerogen, which was obtained from oil shale by treating it with HCl and HF, was pyrolyzed by rapid heating (500 °C/min). This was followed by thermal treating at constant temperature. Products were analyzed by using gas chromatography, and the overall first-order pyrolysis kinetic model was used for calculation of the evolution of different products, such as $<C_7$, C_7 , C_{11} , C_{13} , C_{16} , C_{18} , C_{20} , C_{22} , etc. It was shown that the values of *E* and *A*, for the formation of light hydrocarbons smaller than C_7 , are higher than for the evolution of toluene [19].

Kinetics of Pyrolysis of Oil Shale under Pressure

Using an high-pressure thermodifferential apparatus, pyrolysis experiments of Fushun, Maoming and Colorado oil shales at constant heating rate (10 °C/min), and under pressure ($0.1\cdot10^6$ - $6.0\cdot10^6$ Pa) were carried out. The data were analyzed using an overall first-order reaction rate model, and kinetic parameters were obtained. It was shown that pressure has a hindering effect on pyrolysis. Therefore, a pressure factor, *f*, was proposed and introduced into the kinetic model of pyrolysis under pressure [20].

$$\frac{dx}{dT} = \frac{A}{mf} \cdot (1-x) \cdot \exp\left(-\frac{E}{RT}\right)$$
(18)

$$f = A_1 + A_2 p + A_3 p^2 + A_4 p^3$$
(19)

where

f - pressure factor;

 A_1, A_2, A_3, A_4 - coefficients varying with oil shale;

p - pressure.

2. Kinetics of Particulate Oil Shale Pyrolysis

Cylindrical samples of Fushun and Maoming oil shales, with equal height and diameter (3, 4, 7, 9, 10 mm), were used for pyrolysis studies in a modified thermogravimetric apparatus with constant heating rate (5 °C/min). The weight loss curve was obtained, as well as temperature data for both the interior and the surface of the oil shale. It was shown that for particles smaller than 10 mm, the pyrolysis data may be processed by the overall first-order reaction model. This occurred when the interior and surficial temperature difference did not exceed 4 °C. It was also found that *E* and *A* are different for different sample sizes of the same oil shale. Finally, the time required for pyrolysis at constant temperature of Maoming oil shale is proportional to the diameter, when the particles have a diameter of 2-10 mm. This is due to the strongly laminated structure of the oil shale. During heating and pyrolysis, Maoming oil shale easily breaks into thin pieces. For Fushun oil shale, the time required for pyrolysis at constant temperature is proportional to the square of its diameter [21].

3. Pyrolysis of Lump Oil Shale

A pyrolysis apparatus was specially designed for treating one lump of oil shale sample. Fushun and Maoming lump oil shales (20-60 mm) were pyrolyzed in this apparatus, each at three different heating rates (1, 2 and 5 °C/min). The following data were obtained at various temperatures: the temperature difference between the surface and the center of the oil shale, the weight loss, and the shale oil and pyrolysis gas yields. A pyrolysis kinetics model, including heat transfer effects, was developed. Apparent activation energies for weight loss, shale oil evolution and gas formation were calculated. These were 105-120, 125-165 and 100-200 kJ/mol, respectively. It was shown that the heat transfer inside the shale lump is the controlling step for pyrolysis. It was calculated that the time required for pyrolysis at constant temperature is proportional to the square of the lump diameter [22-24].

4. Kinetics of Oil Shale Drying

When Maoming oil shale is processed in an industrial retort, it breaks into pieces during the drying stage. This effect was studied in the laboratory. A thermogravimetric apparatus and specially designed drying oven were used to obtain drying kinetics data for particulate and lump Maoming oil shale. The apparent activation energy was about 16-20 kJ/mol, indicating that the drying stage is a physical process. It was also shown that when the temperature reaches 180-200 °C, drying and evaporation proceed rigorously, thus breaking the oil shale into pieces. Based on the drying mechanism and experimental data, a three-stage drying kinetics model was proposed [25, 26].

5. Kinetics of Combustion of Oil Shale and Shale Char

Pulverized Oil Shale

Using a thermodifferential analyzing apparatus, Fushun, Maoming, Huang County, Colorado, and Yugoslavian pulverized oil shale samples (<0.074 mm) were used for combustion studies. These were run under atmospheric air pressure and at a constant heating rate (10 °C/min). It was shown that the combustion process may be treated as a two-stage, first-order reaction model, *E* and *A* were calculated. Among the samples studied, combustion of Colorado oil shale takes place the most quickly, while that of Fushun oil shale occurs the most slowly [27, 28].

Combustion of Pulverized Oil Shale under Pressure

Using an high-pressure thermodifferential analyzer, Fushun, Maoming, and Estonian pulverized oil shales were used for combustion studies with air at 0.1, 0.7, 1.3, 1.9 MPa and at a constant heating rate (10 K/min). Two exothermic peaks appeared during the combustion: the first one due to the volatile matter and the second one from the fixed carbon. The data were processed by using a first order reaction model, and a pressure factor was introduced. It was shown that the pressure favours the combustion reaction [29, 30].

Particulate Oil Shale

Using a thermogravimetric apparatus, Fushun, Maoming and Jordanian particulate oil shales (2.5-7.5 mm) were first quickly heated up, and then burned at constant temperature. The fluidized-bed combustion boiler was used for modelling the reaction. It was shown that the high-rate heating stage can be modeled with an overall first-order reaction model. While the combustion period at constant temperature can be simulated by a shrinking core reaction model [31]. For Fushun oil shale, more than 90 % of the combustible material was already burned during the high-rate heating step (1.5-2.5 min, 200-350 °C/min). For Maoming oil shale, the high-rate heating step (1.4-2.3 min, 300-400 °C/min), burned about 70-86 % [32].

A combustion efficiency model was developed based on the feed size distribution and a representative residence time for a Maoming fluidized-bed combustion furnace (35 t/h). The calculated combustion efficiency was about 95.1 %, which is close to the real value [33].

Pulverized and Particulate Shale Char

Using a thermodifferential analyzer, Maoming and Colorado pulverized shale char were used for combustion studies. The experimental data were well matched using an overall first-order reaction model [28].

Using a thermogravimetric analyzer, particulate Fushun and Maoming shale char (5, 8, 11 and 14 mm diameter) were used for combustion studies at constant temperatures (600-950 °C). A combustion kinetic model, involving gas film diffusion, chemical combustion kinetics, and ash layer diffusion, was developed. Related parameters and the time required for combustion were obtained [34-36].

6. Kinetics of Source Rock Pyrolysis and Hydrocarbon Evolution

Just like oil shale, source rock is also composed of organic (mainly kerogen) and mineral matter but its organic content is much lower. Thermogravimetric apparatus, Rock-Eval apparatus, etc., can also be used for study of source rock pyrolysis and hydrocarbon evolution. The different kinetic models used for oil shale study can also be used for source rock [37-41], i.e. for modelling the *in situ* thermal degradation of source rock, for estimating its maturity, and for calculation of the hydrocarbon evolution. Due to the large content of minerals in source rock, Rock-Eval apparatus is normally used for modelling of its pyrolysis [42-43].

Considering the great difference in the structure and the composition of different kinds of kerogen occurring in source rock, its pyrolysis characteristics also vary. It was shown that different pyrolysis kinetics models are suitable for various kinds of kerogen. The overall first-order reaction kinetics model is most suitable for Type I kerogen, but neither for Type II nor for Type III. The maximum reaction rate model may be used for indicating the pyrolysis characteristics at the point of maximum pyrolysis rate. The model with varying activation energy versus conversion fraction, i.e. the Friedman Model, is suitable for all Types of kerogen [44].

Equation (2) is used for the calculation of the fractions of hydrocarbon evolution from source rock at different burial depths. This is based on experimental kinetic data of source rock pyrolysis. It also uses the model with varying activation energy versus conversion fraction, in addition to geologic parameters, such as sedimentation rate, ancient geothermal gradients, etc. The quantity of hydrocarbon evolved in a given basin can then be calculated by the following equation:

$$\frac{dQ}{dt} = SprVcx$$

where Q - quantity of hydrocarbon evolved;

S - evolution area of the source rock within the basin;

- λ density of source rock;
- *r* volumetric fraction of source rock within the basin;
- V sedimentation rate of the evolution layer;
- c potential hydrocarbon evolution of source rock;
- x hydrocarbon evolution fraction.

Erosion and compression of the layer may also be considered in the calculation. In recent years, we successfully made the hydrocarbon evolution calculation for Dongpu, Linqing, Liao Dong, Gin Hu, and Hui Min Basins [40, 41, 45]. This method can not

(20)

only be used for calculation of the hydrocarbon evolution quantity, but also for its evolution distribution in the basin. Therefore, this method is very useful for oil and gas exploration and exploitation.

REFERENCES

- 1. Cao C. Y., Wang J. Q., Zhu Y. J. Study on fluidized retorting of pulverized coal // Journal of Beijing Petroleum Institute. 1959. V. 1, No. 1. P. 1-7 (in Chinese).
- Qian J. L., Wang J. Q. The development of world's oil shale processing and research // Journal of Fuel Chemistry and Technology. 1982. No. 3. P. 266-278 (in Chinese, with English Abstract).
- 3. Decora A., Freitas I., Qian J. L., et al. Final Report of the Technical Panel on oil shale and tar sands // United Nations General Assembly, A/Conf. 100/PC/26, 1981.
- 4. Zhu Y. J. Collected Papers on Oil Shale Research. East China Petroleum Institute Press, Dong Ying, China, 1984 (in Chinese, with English Abstract).
- 5. Hou S. L. Shale Oil Industry in China. Petroleum Industry Press, Beijing, 1984.
- 6. Zhu Y. J. Proceedings of International Conference on Oil Shale and Shale Oil.- Beijing, Chemical Industry Press, 1988.
- Wang J. Q., Qian J. L., Wu L. Y. Kinetic Study on Hydrocarbon Forming Pyrolysis of Fushun and Maoming Oil Shales: Preprints. // Symposium on Characteristization and Chemistry of Oil Shales. Div. of Fuel Chemistry and Petroleum Chemistry, American Chemical Society. St. Louis Meeting, April, 1984, P. 143-147.
- Nuttall H. E., Guo T. M. Pyrolysis Kinetics of Several World Key Oil Shales // ACS Symposium Series. 1983. 230. P. 269-300.
- Wang T. F., Lu S. S. Study on Fushun Oil Shale Pyrolysis Kinetics Equation // Journal of East China Petroleum Institute. 1981.No. 3. P. 1-8 (in Chinese, with English Abstract).
- Yang J. T., Chen T. R. Nonisothermal Pyrolysis Kinetics Study of Maoming Oil Shale // Petroleum Refining. 1983. No. 12. P. 41-47 (in Chinese).
- 11. Yang J. T., Chen T. R. Thermogravimetric Study on the Pyrolysis of Fushun Oil Shale // Acta Petrolei Sinica. 1984. V. 5, No. 2. P. 107-117 (in Chinese, with English Abstract).
- Yang J. T., Chen T. R., Qin K. Z. A Study on the Pyrolysis of the Organic Matters and Mineral Matters Separated from Maoming Oil Shale In: Zhu Y. J. ed. Collected Papers on Oil Shale Research. East China Petroleum Institute Press, Dong Ying, 1984. P. 111-119 (in Chinese, with English Abstract).
- Yang J. T. Investigation on Pyrolysis of Huangxian Oil Shale between 550-750 °C. In: Zhu Y. J. ed. Proceedings of International Conference on Oil Shale and Shale Oil. Beijing, Chemical Industry Press, 1988. P. 263-270.
- Li S. Y., Qian J. L., Qin K. Z., Zhu Y. J. Study on Intrinsic Kinetics of Oil Shale Pyrolysis.
 Kinetic Parameters Determined by Different Models // Acta Petrolei Sinica (Petroleum Processing Section). 1986. V. 2, No. 3. P. 1-10 (in Chinese, with English Abstract).
- Wang D. Y., Wang D. J., Qian J. L. Study on Parallel and Consecutive Pyrolysis Models on Oil Shale and Source Rock // Journal of East China Petroleum Institute. 1985. No. 3. P. 1-8 (in Chinese, with English Abstract).
- Li S. Y., Qian J. L., Qin K. Z., Zhu Y. J. Study on Intrinsic Kinetics of Oil Shale Pyrolysis.
 Activation Energy Distribution and its Correlation with Frequency Factor in Parallel Model // Acta Petrolei Sinica (Petroleum Processing Section). 1986. V, 3, No. 2. P. 1-12 (in Chinese, with English Abstract).

- Li S. Y., Qian J. L., Qin K. Z., Zhu Y. J. Study on the Kinetics of Oil Shale Pyrolysis with Bitumen as an Intermediate Product // Journal of Fuel Chemistry and Technology. 1987. V. 15, No. 2. P. 118-123 (in Chinese, with English Abstract).
- Nuttall H. E., Guo T. M., Schader S., Thakur D. S. The Pyrolysis Kinetics of Several Key World Oil Shale. In: Collected Papers on Oil Shale Research, Zhu Y. J. ed. Dong Ying, East China Petroleum Institute Press, 1984. P. 128-148 (in Chinese, with English Abstract).
- Lu Q. H., Qin K. Z., Wang T. F., Zhu Y. J. Isothermal Pyrolysis Gas Chromatography for Study of Hydrocarbon Formation Kinetics for Kerogen. In: Proceedings of International Conference on Oil Shale and Shale Oil, Zhu Y. J. ed. Beijing, Chemical Industry Press, 1988. P. 287-294.
- Ding F. C., Wang J. Q., Qian J. L. Kinetic Study on Oil Shale Pyrolysis under Pressure // Acta Petrolei Sinica (Petroleum Processing Section). V. 7, No. 4. P. 20-27 (in Chinese, with English Abstract).
- 21. *Wang J. Q., Li S. Y., Yang K. Y.* Study on Pyrolysis of Particulate Oil Shale with an Improved Thermogravimetric Apparatus. In: Proceedings of International Conference on Oil Shale and Shale Oil, Zhu Y. J. ed. Beijing, Chemical Industry Press, 1988. P. 271-278.
- Li S. Y., Qian J. L, Wang J. Q., Zhu Y. J. Study on the Pyrolysis of Single Oil Shale Lump.
 Pyrolysis Kinetics Parameters // Acta Petrolei Sinica (Petroleum Processing Section).
 1990. V. 6, No. 4. P. 86-93 (in Chinese, with English Abstract).
- Li S. Y., Qian J. L., Wang J. Q., Zhu Y. J. Study on the Pyrolysis of Single Oil Shale Lump.
 Intra-Lump Heat Transfer // Acta Petrolei Sinica (Petroleum Processing Section). 1991.
 V. 7, No. 1 (in Chinese, with English Abstract).
- Li S. Y., Qian J. L. Study of the Pyrolysis of Maoming Oil Shale Lumps // Fuel. 1991.V. 70, No. 12. P. 1371-1375.
- Wang J. Q., Di F. C., Li S. Y., Qian J. L. Drying Mechanism and Kinetics Model of Lump-Size Maoming Oil Shale with High Moisture Content. In: Zhu Y. J., ed. Proceedings of International Conference on Oil Shale and Shale Oil. Beijing, Chemical Industry Press, 1988, P. 225-232.
- Wang J. Q., Li S. Y., Wang X. Q., Qian J. L., Zhu Y. J. Drying and Disintegration of Particulate Maoming Oil Shale // Journal of Fuel Chemistry and Technology. 1987. V. 5, No. 4. P. 369-372 (in Chinese, with English Abstract).
- 27. Wang T. F. Investigation of Combustion Properties of Oil Shale by DTA Method // Journal of East China Petroleum Institute. 1983. No. 1. P. 97-107 (in Chinese, with English Abstract).
- Wang T. F. Differential Thermal Analysis of the Reaction Properties of Raw and Retorted Oil Shale with Air // ACS Symposium : Preprints. Div. of Petrochemistry. St. Louis Meeting, April 1984. P. 239-245.
- Wang J. Q., Zhang Q., Qian J. L. Pressurized Combustion Behavior of Oil Shale and Coal and its Kinetics. In: Xu X. C., ed. Proceedings of the 2nd International Sumposium on Coal Combustion. Beijing, China, Machine Press, 1991. P. 137-143.
- 30. Wang J. Q., Zhang Q. Comparison of Combustion Behavior between Oil Shale and Coal under Atmospheric and Elevated Pressure // Oil Shale. 1991. V. 8, No. 3. P. 210-219.
- Zhang Q. X., Wang X. Q., Qian J. L., Zhu Y. I. Study on the Combustion Kinetics Model of Oil Shale Particle // Acta Petrolei Sinica (Petroleum Processing Section). 1992. V. 8, No.2. P. 85-93 (in Chinese, with English Abstract).
- Wang X. Q., Zhang Q. X., Qian J. L., Zhu Y. J. A Study on Combustion and Sulfur Transition of Oil Shale Particle // Journal of Fuel Chemistry and Technology. 1992. V. 20, No. 2. P. 160-167 (in Chinese, with English Abstract).

- 33. *Li S. Y., Qian J. L.* A Mathematical Model for Evaluating Fluidized Bed Combustion Efficiency of Oil Shale // Oil Shale. 1992. V. 9, No. 2. P. 97-102.
- Wang X. Q., Wang J. Q., Qian J. L., Zhu Y. J. The Reaction Model and Diffusional Effects in the Ash Layer of the Oil Shale Char Combustion. In: Gary J. H., ed. 20th Oil Shale Symposium Proceedings. Colorado School of Mines Press, Golden, 1987. P. 206-216.
- Wang X. Q., Lin M., Qian J. L., Zhu Y. J. A Study on the Combustion Kinetics of Fushun and Maoming Shale Char Particles. In: Zhu Y. J., ed. Proceedings of International Conference on Oil Shale and Shale Oil. Chemical Industry Press, Beijing, 1988. P. 495-505.
- Lin M., Wang X. Q., Qian J. L., Zhu Y. J. A Study on Effectiveness Factor for Combustion Process of Oil Shale Char Particles // Acta Petrolei Sinica (Petroleum Processing Section). 1990. V. 6, No. 1. P. 45-52 (in Chinese, with English Abstract).
- Wang J. Q., Wu L. Y., Qian J. L. Kinetic Study of Hydrocarbon Forming Pyrolysis of Source Rock by using Rock Evaluation Apparatus // East China Petroleum Institute. 1984. No. 1. P. 55-63 (in Chinese, with English Abstract).
- Jin Q., Qian J. L., Huang X. H. Study on Thermal Degradation Kinetics of Source Rock Kerogen and Quantitative Estimation of Hydrocarbon Transformation // Acta Petrolei Sinica. 1986. V. 7, No. 3. P. 11-19 (in Chinese, with English Abstract).
- 39. Wu Z. L., Wang J. Q., Huang X. H. Pyrodynamics of Source Rocks in Dong Pu Depression // Oil and Gas Geology. 1986. V. 7, No. 4. P. 428-432 (in Chinese, with English Abstract).
- Wu Z. L., Wang J. Q., Qian J. L. Application of Maximum Reaction Rate Method for the Calculation of the Quantity of Hydrocarbon Evolution in the Source Rock // Acta Petrolei Sinica. 1990. V. 11, No. 1. P. 32-39 (in Chinese, with English Abstract).
- Qian J. L., Wu Z. L., Wang J. Q. A Study of Different Mathematic Models for Evaluation of Hydrocarbon Generation from Source Rock Kerogen Thermal Degradation // Journal of Southeast Asian Earth Science. 1991. V. 5, No. 1-4. P. 63-66.
- 42. Wang J. Q., Turner T. F., Miknis F. P., Chong S. L. A New Method for Identifying Kerogen Types Based on Pyrolysis Characteristics. 1992. V. 16, No. 1. P. 108-114 (in Chinese, with English Abstract).
- Yang G. H., Wu Z. L., Liu Q. H. Study on Kinetics of Hydrocarbon Generating Pyrolysis of Different Kinds of Kerogen. 1 // Journal of the University of Petroleum. 1990. V. 14, No. 1. P. 72-80 (in Chinese, with English Abstract).
- Yang G. H., Wu Z. L., Shi W. M., Qian J. L. Study on Kinetics of Hydrocarbon Generating Pyrolysis of Different Kinds of Kerogen. 1 // Journal of the University of Petroleum. 1990. V. 14, No. 2. P. 74-84 (in Chinese, with English Abstract).
- 45. *Wu Z. L., Wang S. H.* The Calculation Method of Quantity of Hydrocarbon Evolution with the Model of Hydrocarbon Kinetics // Journal of East China Petroleum Institute. 1986. V. 10, No. 3. P. 1-9 (in Chinese, with English Abstract).

Received January 12, 1994