

**EXPERIMENTAL STUDY ON THE COALIFICATION DYNAMIC OF LONG FLAME COAL PYROLYSIS****¹Yaling Wei, ^{2,*}Dong Li, ²Xuemei Zhang, ²Qinghua Ma, ³Xiaodong Zhao and ⁴Jingyuan Hao**¹Ningxia Sanfang Coal Quality Testing Technology Co., Ltd., Yinchuan, Ningxia, China²Energy and Chemical Industry Big Data Application Teaching and Research Center, Xi'an Siyuan University, Xi'an, Shaanxi, China³Beijing Deqin Technology Development Co., Ltd., Beijing, China⁴School of Chemical Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, China

Received 11th September 2022; Accepted 18th October 2022; Published online 23rd November 2022**Abstract**

Long flame coal from the Shenfu-Dongsheng coal field in the Ordos Basin is pyrolyzed for coalification dynamic experiments using HYLZ-2 cryogenic dry distillation furnace. The pyrolysis procedure is designed to contain three sequence phases: starting with the dry dewatering phase (20 to 245°C), following through the transition phase of slight pyrolysis (245 to 460°C or to 485°C, and to 510°C) both at 5°C/min constant heating rate, and ending by the strong isothermal pyrolysis phase at those three temperatures for certain time. For the isothermal pyrolysis, the activation energy of coalification $E = 168.77 \text{ KJ/mol}$, and the pre-exponential factor $\ln A = 22.316$. For the constant heating rate pyrolysis, the activation energy of coalification $E = 28.1 \text{ KJ/mol}$, and the pre-exponential factor $\ln A = 2.985$.

Keywords: Vitrinite reflectance, Constant heating rate pyrolysis, Isothermal pyrolysis, Coalification dynamics.

INTRODUCTION

From plant death, accumulation, transformation, coalification through rock formation and metamorphic two stages. In the early rock formation stage (peat), microorganisms participate in decomposition, compound and coalescence into peat and is called "biochemical coalification". Under temperature, pressure, and time, from tens of millions of years to hundreds of millions of years, nature metamorphism is a chemical reaction transition process, sequentially from peat, lignite, bituminous coal to anthracite [1-3]. Based on the general principle of thermal and chemical dynamics, Wu Chonglong and others introduced the concept of "coal metamorphic thermal dynamics" and took the coal grade of deep and superimposed Fujian and Guangdong overlapping basin as an example [4, 5], to discuss the theory and method of thermal dynamics analysis of ancient geothermal field and coal metamorphic action in the basin. The thermal dynamics of coal metamorphism has the following three points:

According to the curve [6] of Bostick et al, the mean reflectivity cross-coupling diagram of the ancient Geo temperature-rock layer was indicated, and the medium and newborn boundary measured data in Songliao, Ordos and Erlian basins with a single thermal history in China, and double regression was used to establish the T-t-Ro empirical formula:

$$\ln(T - 273) = \frac{646.32}{\ln t + 111.85} - \frac{0.492t^{0.093}}{R_0} \quad (1)$$

Equation (1) is not only a simplification of the Bostick curve diagram, but also a statistical expression of the Arrhenius equation in nature metamorphism.

A detailed division of thermodynamic evolution models of thermal transfer in the basin, such as segmentation, emergent rupture, and magmatic mass thermal evolution. In the case, the obtained results are replaced into the T-t-Ro empirical formula, and the total process is simulated with superimposed metamorphism. It is proposed that the paleo ground temperature calculation and analytical value of the mutual verification equation (1) under the average reflectivity of the known mirror mass group and the effective thermal time; again, the calculation and measured values of the Ro equation (1) of the known mild and effective thermal time.

In order to understand the mechanism of natural metamorphic coalification and the influence of hydrocarbon gas content, the artificial coal improvement process from lignite, bituminous coal to anthracite is simulated in the laboratory by artificial temperature and pressure in a short period of time, for example, artificial coal refined Shandong lignite and Yunnan lignite samples [7], lignite [8] in Hailar Basin, Inner Mongolia, with earlier carrion and algal coal, and peat to sub-bituminous. Although these coalification experiments are conducted, the thermal dynamics cannot be designed according to the data processing requirements of chemical dynamics. Therefore, the above problem will solve with the whole process from experimental design to data processing.

***Corresponding Author: Dong Li,**

Energy and Chemical Industry Big Data Application Teaching and Research Center, Xi'an Siyuan University, Xi'an, Shaanxi, China

However, because Chinese coal metamorphism has the characteristics of multi-stage evolution and multi-heat sources, the successful application of T-t-Ro thermal dynamics formula depends on the large accumulation of different earth crust thermal structure data, and reasonable analysis of coal metamorphism, initial state, progressive deterioration, deposition environment, sediment burial velocity, and ground temperature gradient. Similarly, the successful application of T-t-Ro thermal dynamics of improved coalification depends on the mutual reference and verification of metamorphic and improved coalification.

II. Experimental detail and coalification data

A. Laboratory instruments

HYLZ-2 cryogenic dry distillation furnace is selected as equipment with a standard stainless-steel retort.

B. Solid sampling

This experiment is designed to implement a temperature time sampling roadmap for 20 solid samples. The low ash, low sulfur, high volatile long flame coal from the Ordos Basin has been chosen as the coal sample. Two kinds of pyrolysis methods, constant heating rate pyrolysis and isothermal pyrolysis, have been used in the experimental operation. The temperature time sampling roadmap is consisted with three in turn phases and corresponding pyrolysis method:

The dry dewatering phase employed of constant heating rate pyrolysis from 20°C to 245°C at 5°C /minute heat rate.

The transition phase of slight pyrolysis employed of constant heating rate pyrolysis from 245°C to 460°C, or designed temperature of 485°C or 510°C, at 5°C /minute heat rate.

The strong pyrolysis phase to the end point employed of isothermal pyrolysis at 460°C or designed temperature of 485°C or 510°C. During this phase, total 6 samples are collected at each isothermal temperature. They are collected at 6 different times, 0, 20, 60, 120, 200, and 320 minutes.

C. Coalification data

The 3 kg of long flame coal produced in the Ordos Basin Shenfu-Dongsheng coal field is broken into a 1 mm sieve in a shredder, then baked in a 60°C oven for two hours, cooled in the air, put into a plastic bag, then placed in a drying dish. At the beginning of each new experiment, 70.0 grams has been weighted and sealed into the standard stainless-steel retort as the starting sample, marked as #0. The 70.0 g starting sample is heated from 20°C to 245°C at 5°C/minute heat rate as a dry dehydration phase sample, marked as #00. The 70.0 g starting sample is subjected to a dry dehydration phase, then continue heating to the designed isothermal pyrolysis temperature as a slight pyrolysis phase sample. The 1 before a dash is marked as the sample isothermal pyrolysis at 460°C. The 2 before a dash is marked as the sample isothermal pyrolysis at 485°C. The 3 before a dash is marked as the sample isothermal pyrolysis at 510°C.

III. Dynamic calculations [11-15]

The reactions of gas-solid multi-phase chemical reactions are complex and are commonly used to represent the relationship between reaction rate and conversion rate:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2)$$

A. Coalification rate and conversion rate

Since the conversion rate is represented by the vitrinite reflectance rate data [9, 10], there is

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \quad (3)$$

W_0 : Sample original vitrinite reflectance, 0.576%.

W : Residual vitrinite reflectance in standard stainless-steel retort for a pyrolysis experiment.

W_f : Final residual vitrinite reflectance in standard stainless-steel retort for the maximum pyrolysis experiment, which is 1.838% with a maximum temperature of 485°C and 320- minutes isothermal pyrolysis.

B. Isothermal pyrolysis

When n is 1, the conversion rate is only related to the isothermal pyrolysis time as:

$$-\ln(1 - \alpha) = kt + C \quad (4)$$

According to equation (3), under isothermal pyrolysis condition, the $-\ln(1-\alpha)$ is in a straight line with time t . The slope of the line is the velocity constant of isothermal pyrolysis k and the intercept is the integral constant C .

Arrhenius equation is an empirical relationship between the velocity constant of isothermal pyrolysis and temperatures as:

$$\ln k_i = \ln A - \frac{E}{RT_i} \quad (5)$$

According to equation (5), under isothermal pyrolysis condition, the velocity constant of isothermal pyrolysis is in a straight line with reciprocal of the temperature. The slope of the line can be used to solve the activation energy E and the intercept is the pre-exponential factor A.

C. Constant heating rate pyrolysis

Constant heating rate means that both temperature and time are variables, but temperature is rising at a constant rate, i.e.:

$$\beta = \frac{dT}{dt} \quad (6)$$

When E being treated as a constant, Equation (2), (5), and (6) can be treated as:

$$\frac{d\alpha}{dT} = \frac{A(1-\alpha)^n}{\beta} \exp\left(-\frac{E}{RT}\right) \quad (7)$$

Set the initial conditions of $\alpha=0$ when $T=T_0$, and get:

$$\int_0^\alpha (1-\alpha)^{-n} d\alpha = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (8)$$

According to Doyle approximate integrals and at $n-1$,

$$\ln[-\ln(1-\alpha)] = \ln\left(\frac{AE}{\beta R}\right) - 5.33 - \frac{E}{RT} \quad (9)$$

According to Equation 8, the $\ln[-\ln(1-a)]$ vs the reciprocal of the temperature is a straight line. The slope and intercept of the line can be used to solve the activation energy E and the intercept is the pre-exponential factor A. To avoid the mathematic difficulty, let $a=0.001$ at the starting point (temperature $T=20^\circ\text{C}$, and time $t=0$ minute), and let $a=0.999$ at the final sampling point (temperature $T=485^\circ\text{C}$, and time $t=320$ minute).

D. Isothermal pyrolysis results

Table 1 listed 17 isothermal pyrolysis vitrinite reflectance (VR) data and their conversion rate and calculations.

Based on Equation (4), the relationship between $\ln(1-a)$ and isothermal pyrolysis time t at three different temperatures are plotted in Figure 1.

Table 1. 18 isothermal pyrolysis Vitrinite Reflectance (VR) conversion rate, and calculations

Item	VR/%	a	1-a	$\ln(1-a)$
0#	0.001	0.0008	0.9992	-0.0008
00#	0.057	0.0452	0.9548	-0.0462
1-1	0.895	0.7092	0.2908	-1.2351
1-2	0.861	0.6823	0.3177	-1.1465
1-3	0.938	0.7433	0.2567	-1.3597
1-4	1.087	0.8613	0.1387	-1.9757
1-5	1.093	0.8661	0.1339	-2.0106
1-6	1.154	0.9144	0.0856	-2.4583
2-1	0.476	0.3772	0.6228	-0.4735
2-2	0.963	0.7631	0.2369	-1.4400
2-3	1.025	0.8122	0.1878	-1.6724
2-4	1.024	0.8114	0.1886	-1.6682
2-5	1.06	0.8399	0.1601	-1.8322
2-6	1.261	0.9992	0.0008	-7.1405
3-1	0.893	0.7076	0.2924	-1.2297
3-2	0.969	0.7678	0.2322	-1.4603
3-3	1.152	0.9128	0.0872	-2.4400

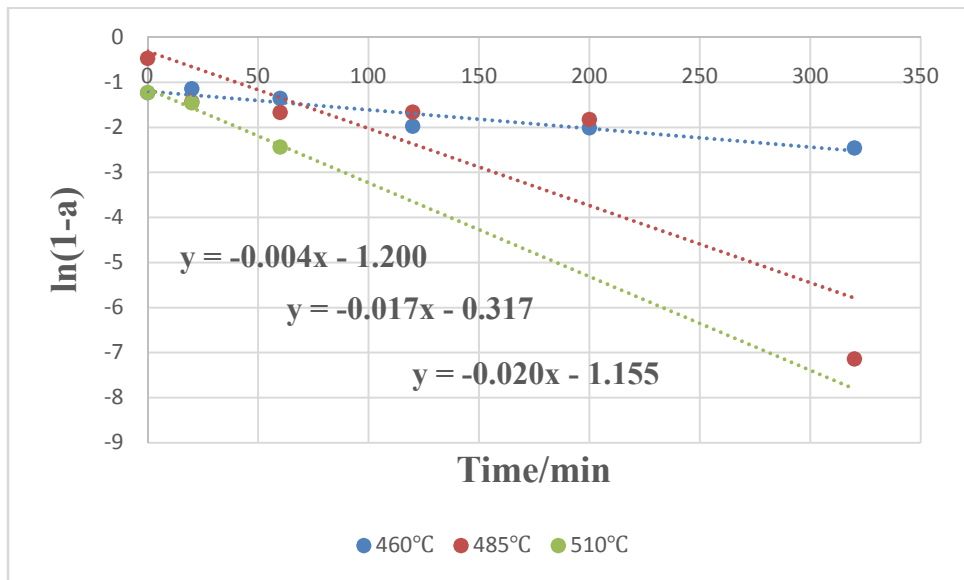


Fig. 1. The relationship between ln(1-a) and isothermal pyrolysis time t at three different temperatures

Thus, the velocity constants k and integral constants C are obtained for three isothermal temperature and listed in Table 2.

Table 2. The velocity constant k and integral constant c at three isothermal temperatures

T/°C	k/min ⁻¹	C
460	0.0041	-1.2008
485	0.0017	-0.3171
510	0.0208	-1.1556

Figure 2 is the plotted of the relationship between lnk and 1/T of the isothermal pyrolysis.

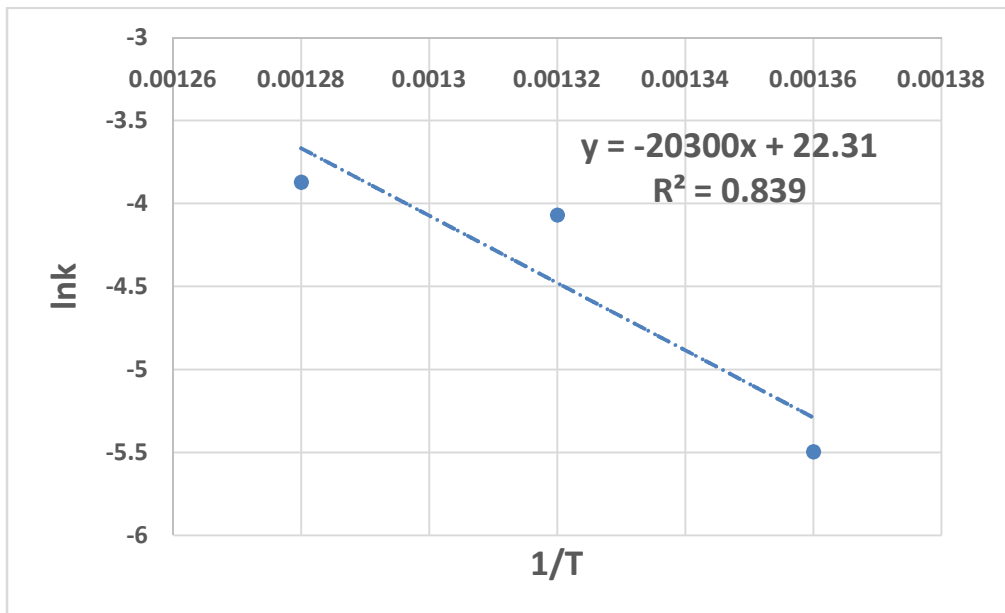


Fig. 2. The relationship between lnk and 1/T of the isothermal pyrolysis

The slope of the line can be used to solve the activation energy E =168.77 KJ/mol, and the pre-exponential factor lnA=22.316.

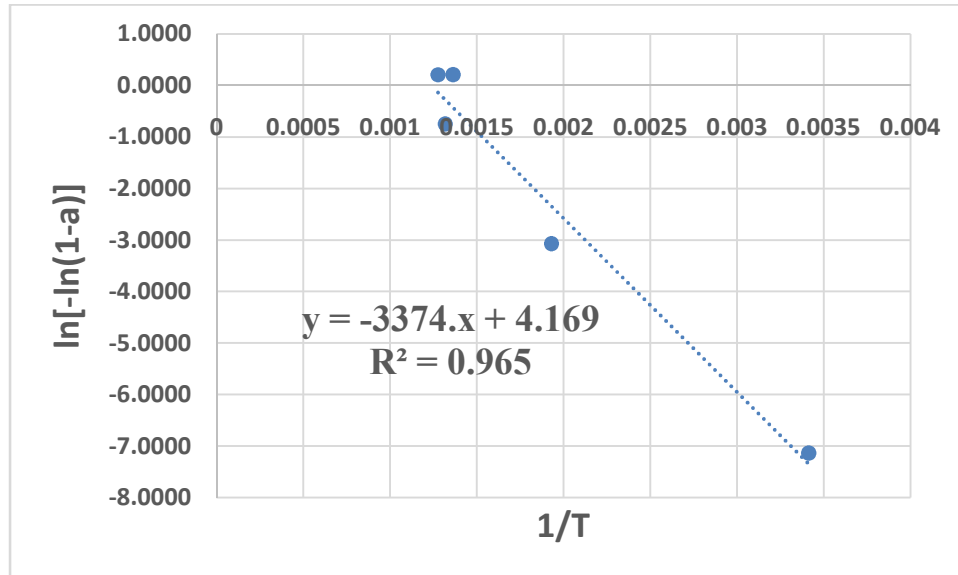
Constant heating rate pyrolysis results

The constant heating rate, 5°C/min), pyrolysisinvolved the dry dewatering phaseand the transition phase of slight pyrolysis. The relevant data of those two phases are listed in Table 3.

Table 3. The relevant data of those two constant heating rate pyrolysis

Item	1/T	ln(-ln(1-a))
0#	0.003413	-8.2846
00#	0.001931	-0.6231
1-1	0.001364	0.4200
2-1	0.001319	0.2052
3-1	0.001277	0.6301

Based on the Equation(9), the relationship between $\ln(-\ln(1-a))$ and $1/T$ of the constant heating rate pyrolysis is plotted in Figure 3.

**Fig. 3. The relationship between $\ln(-\ln(1-a))$ and $1/T$ of the constant heating rate pyrolysis**

The slope of the line can be used to solve the activation energy as:

$$-\frac{E}{R} = -3374.1 \quad (10)$$

Therefore, $E = 28.1$ KJ/mol for constant heating rate pyrolysis.

The intercept can be presented as:

$$\ln\left(\frac{AE}{\beta R}\right) - 5.33 = 4.1697 \quad (11)$$

Put every constant into Equation (11), the pre-exponential factor $\ln A = 2.985$.

Conclusion

The 17 improved coal samples were prepared in the low-temperature dry distillation furnace at constant temperature in the laboratory. All quality coal samples were analyzed by the vitrinite reflectance according to national standards. Defining improved transformation rates as characterized by vitrinite reflectance. The rate constants at three temperatures were calculated by the kinetic equation for the constant temperature lift, as well as the activation energy. The leading factor and activation energy of constant temperature acceleration are calculated by the kinetic equation for constant temperature acceleration. This proposes new analytical ideas and methods for solving the thermal dynamics relationship of T-t-Ro for coalification. The successful application of T-t-Ro thermal dynamics of quality coalification depends on the vitrinite reflectance and verification of metamorphic and quality coalification. For example, the calculation of the vitrinite reflectance characterization of the conversion rate and other considerations require relevant suggestions and verification by geologists and geochemists. Long flame coal from the Shenfu-Dongsheng coal field in the Ordos Basin is pyrolyzed for coalification experiments using HYLZ-2 cryogenic dry distillation furnace to collect the solid residual. The pyrolysis procedure is designed to contain the dry dewatering phase (20 to 245°C), the transition phase of slight pyrolysis (245 to 460°C or other 485°C and 510°C) both at 5°C /min constant heating rate, and the strong isothermal pyrolysis phase at those three temperatures to the end point. For the isothermal pyrolysis, the activation energy $E = 168.77$ KJ/mol, and the pre-exponential factor $\ln A = 22.316$. For the constant heating rate pyrolysis, the activation energy $E = 28.1$ KJ/mol, and the pre-exponential factor $\ln A = 2.985$.

Symbol description

A: pre-exponential factor, min^{-1} .

C: integrated constant.

E: activation energy, KJ/mol.

n: reaction order.

R: gas constant, 8.314 J/(mol.K).

R₀: vitrinite reflectance, %.

T: thermodynamic temperature, K.

t: time, minute in artificial pyrolysis, Equation (2), Equation (4), and Equation (6),.

t: time, million years in nature metamorphism, Equation (1).

α : conversion rate

β : constant heating rate, K/min

REFERENCES

1. Yang Qi. A study on coal metamorphism in China. *Earth science*. vol. 14, iss.4, pp. 341-345, 1989.
2. Cao Daiyong, Li Xiaoming, Deng Juemei. Study on the Coupling Effects of Coalization and Tectonic-Thermal Events: A Geological Record of Basin Dynamic Processes. *Geological Frontiers*. vol. 16, issue 4, pp. 52-60, 2009.
3. Yang Qi. Superposition metamorphism of coal in China. *Geological Frontiers*. vol. 6, issue Z1, pp. 1-8, 1999.
4. Wu Chonglong, Yang Qi, Liu Gang, etc. Principles and methods of thermodynamic analysis of coal metamorphism. *Journal of Coal Society*. vol. 22, issue 3, pp. 225-229, 1997.
5. Yang Qi, Wu Chonglong. Coal metamorphism in China. *Earth Sciences: Journal of China University of Geosciences*. Vol. 21, issue 3, pp. 311-319, 1996.
6. Bostick N H, Cashman S M, McCulloh T H, et al. Gradients of vitrinite reflectance and present temperature in the Los Angeles and Ventura Basins, California. In: Oltz D F, ed. *Low temperature metamorphism of kerogen and clay minerals*. Los Angeles: Pacific Section, SEPM (Society for Sedimentary Geology). 1979, 65-96
7. Zhao Xigao, Liu Xiaoyan, Dang Changtao, etc. Characteristics of simulated experimental products of lignite coalification and their localization significance. *Journal of Daqing Petroleum Institute*. vol. 16, issue 3, pp. 1-5, 1992.
8. Huo Qiuli, Du Hongwen, Zhou Ping. Simulation experiment of lignite coalification. *Xinjiang Petroleum Geology*. vol. 19, issue 4, pp. 275-277, 1998.
9. Method of determining microscopically the reflectance of vitrinite in coal. GB/T 6948-2008
10. Classification of the degree of coalification of the reflectivity of the mirror body. Coal industry standard. MT/T 1158-2011
11. Li Ai-hsun, Wu Daohong, Wang Qicheng, etc. Non-isothermal re-analysis of the thermal process and dynamic characteristics of long flame coal. *Fuel and chemicals*. vol. 44, Issue6, pp. 7-11, 2013.
12. Li Wenjun, Chen Shanshan, Chen Yanpeng, etc. Experimental study of thermally heavy coal thermolytic reaction dynamics. *China Coal*, vol. 46, Issue3, pp. 84-89, 2020.
13. Zheng Mingdong, Bai Dayong. Dongsheng coal non-isothermal thermolytic properties and dynamic parameters are determined. *Coal Chemical*, vol. 34, Issue 2, pp. 13-16, 2006.
14. Zhou Zhijie, Fan Xiaolei, Zhang Wei, etc. Non-isothermal re-analysis to study coal coking aerodynamics. *Journal of Coal*, vol. 31, Issue 2, pp. 219-222, 2006.
15. Guo Yanhong, Cheng Fan. Adaptive analysis of hybrid coal thermolytic dynamics models. *Burning Science and Technology*, vol. 25, Issue6, pp. 509-518, 2019.
