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Research Article

EXPERIMENTAL COMPARISON OF THE VOLATILE MATTER LOSS DYNAMIC DURING PYROLYSIS BETWEEN LONG FLAME COAL AND OIL RICH COAL

[1]YalingWei, [2,*]Dong Li, [2]Xuemei Zhang, [2]Qinghua Ma, [3]Yang Wang and [4]Jingyuan Hao

[1]Ningxia Sanfang Coal Quality Testing Technology Co., Ltd., Yinchuan, Ningxia, China
[2]Energy and Chemical Industry Big Data Application Teaching and Research Center, Xi'an Siyuan University, Xi'an, Shaanxi, China
[3]Beijing Deqin Technology Development Co., Ltd., Beijing, China
[4]School of Chemical Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, China

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Abstract

For the isothermal pyrolysis of oil rich coal, the activation energy E =182.39 KJ/mol, and the pre-exponential factor lnA=24.12. The activation energy of oil rich coal under isothermal pyrolysis condition is smaller than that of long flame coal, E =239.73 KJ/mol, which means that the conversion rate of long flame coal is smaller than that of the oil rich coal. For the constant heating rate pyrolysis of oil rich coal, the activation energy E =37.338 KJ/mol, and the pre-exponential factor lnA=4.405. The activation energy of oil rich coal under constant heating rate pyrolysis condition is larger than that of long flame coal, E =26.255 KJ/mol, which means that, under constant heating rate pyrolysis phases, when the temperature from T_1 increased to T_2, the conversion rate change of oil rich coal is larger than that of the long flame coal.

Keywords: Oil rich coal, Long flame coal, Isothermal pyrolysis, Constant heating rate pyrolysis, Activation energy.

INTRODUCTION

According to the industrial manual of national mineral resources (2014 Revision) of China, the coal can yield 7%~12%tar, using Gray-King low temperature carbonization experiment, is called oil-rich coal. Therefore, oil-rich coal does not belong to the category of special coal resources, but coal-based oil and gas resources with oil and gas resource attributes. China's oil-rich coal resources are abundant, about 500billion tons, widely distributed in Shaanxi, Inner Mongolia, Xinjiang, Ningxia, Qinghai and other places (Xu Ting *et al.,* 2022). The oil-rich coal can be used to produce high-quality fuel products such as gasoline and diesel through lightweight treatment such as hydrogenation reaction and catalytic cracking (Yang Fu *et al.;* Shi Qingmin *et al.*). Therefore, the oil-rich coal has a huge resource potential advantage in increasing domestic oil and gas supply channels and ensuring the security of national oil and gas strategies. From the perspective of the degree of coalification, long-flame coal and gas coal can produce higher coal tar than lignite, high volatile content and high tar yield do not have a monotonic correspondence. Within the same coal level, the differences in sedimentary environment, material composition and other conditions also cause oil-rich coal to have obvious non-uniform distribution characteristics in the seam domain and region (MA Li *et al.,* 2022). Taking the Jurassic coal seam in Shaanxi province as an example, although oil-rich coal is widely distributed, the tar yield is distributed in the 3%~16% (SHI Qingmin *et al.,* 2021). There are oil-rich coal and oil-bearing coal being coexisted in different or same mining areas and coal seams. Low-rank coal, including oil rich coal and long flame coal has high moisture, high volatile fraction, and low thermal value, those characteristics are affecting its direct applications.

Corresponding Author:** ***Dong Li,
Energy and Chemical Industry Big Data Application Teaching and Research Center, Xi'an Siyuan University, Xi'an, Shaanxi, China.

Thus, the pyrolysis is used to improve their applicability (Qinghua Ma *et al.,* 2022). Until now, a same industrial pyrolysis procedure is used for the tar yield between 3%~16% low rank coal, not matter the raw material is oil rich coal or long flame coal, because no one discuss whether there was the pyrolysis dynamic difference between long flame coal and oil rich coal. This paper is designed to conduct an experimental comparison of the volatilization dynamic during pyrolysis between long flame coal and oil rich coal.

Experimental detail and volatile matter loss data

A pyrolysis under 300°C -600°C is defined as low temperature pyrolysis. The objective of this paper is to conduct an experimental comparison of the weight loss dynamic during pyrolysis between long flame coal (volatile matter content 29.95%) and oil rich coal(volatile matter content 37.65%). The HYLZ-2 cryogenic dry distillation furnace is selected as pyrolysis equipment with a standard stainless-steel retort too. The experiment is designed to implement a temperature time sampling roadmap for 20 solid samples. Constant heating rate pyrolysis and isothermal pyrolysis are two kinds of pyrolysis methods used in the experimental operation. The 3 kg of oil rich 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 have been weighted and sealed into the standard stainless-steel retort as the starting sample, marked as #0. The temperature time sampling roadmap is consisted with three in turn phases and corresponding pyrolysis method:

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

B. 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 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.
C. 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. The 1- is marked as the sample isothermal pyrolysis at 460°C. The 2- marked as the sample isothermal pyrolysis at 485°C. The 3- is marked as the sample isothermal pyrolysis at 510°C.

Volatile loss rate and conversion rate

Since the conversion rate is represented by the volatile loss rate data, there is

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \tag{1}$$

W_0: Starting volatile matter amount, 24.102 grams; the volatile matter amount for long flame coal is 19.16 grams.
W: Residual weight in standard stainless-steel retort for a pyrolysis experiment.
W_f: Final residual volatile matter in standard stainless-steel retort for the maximum pyrolysis experiment, which is 6.041 grams with a maximum temperature of 510°C and a maximum temperature of 320 minutes. The maximum volatile loss amount in 70 grams starting sample is 18.061 grams for oil rich coal. The maximum volatile loss amount in 70 grams starting sample is 11.787 grams for long flame coal.

Dynamic calculations (Liu Penghua *et al.*, 2019; Zhai Zhenyong *et al.*, 2019; Liang Dingcheng *et al.*, 2016; ZHANG Xue-mei *et al.*, 2021)

There are only constant heating rate pyrolysis and isothermal pyrolysis. These are two kinds of pyrolysis methods used in the oil rich coal pyrolysis experimental operation.

A. Isothermal pyrolysis

Under isothermal condition, when reaction order n is 1, the conversion rate is only related to the isothermal pyrolysis time as:

$$-ln(1-\alpha) = kt + C \tag{2}$$

According to equation (2), the -ln(1-a)is in a straight line with time t. The slope of the line is the velocity constant of isothermal pyrolysisk and the intercept is the integral constant C.

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

$$lnk_i = lnA - \frac{E}{RT_i} \tag{3}$$

According to equation (3), under isothermal pyrolysis condition, the velocity constant of isothermal pyrolysis is in a straight line with reciprocal of the temperature. With at least two isothermal temperatures, the slope of the line can be used to solve the activation energy E and the intercept is the pre-exponential factor A. Table 1 listed 18 isothermal pyrolysis volatile matter loss (VL) data and their conversion rate and calculations.

Table 1. 18 isothermal pyrolysis wl, conversion rate, and calculations

Item	VL/g	a	1-a	ln(1-a)
0#	0.001	0.0001	0.9999	-0.0001
00#	1.770	0.0980	0.9020	-0.1032
1-1	10.169	0.5630	0.4370	-0.8279
1-2	14.049	0.7779	0.2221	-1.5045
1-3	14.186	0.7854	0.2146	-1.5392
1-4	14.829	0.8210	0.1790	-1.7205
1-5	15.894	0.8800	0.1200	-2.1206
1-6	16.131	0.8931	0.1069	-2.2363
2-1	9.235	0.5113	0.4887	-0.7160
2-2	12.043	0.6668	0.3332	-1.0990
2-3	15.263	0.8451	0.1549	-1.8647
2-4	16.161	0.8948	0.1052	-2.2518
2-5	16.228	0.8985	0.1015	-2.2880
2-6	17.141	0.9491	0.0509	-2.9773
3-1	11.394	0.6308	0.3692	-0.9965
3-2	15.109	0.8366	0.1634	-1.8114
3-3	16.396	0.9078	0.0922	-2.3842
3-4	17.180	0.9512	0.0488	-3.0206
3-5	17.472	0.9674	0.0326	-3.4230
3-6	18.060	0.9999	0.0001	-9.8015

Based on Equation (3), the relationship between ln(1-a) and isothermal pyrolysis time t at three different temperatures are plotted in Figure 1.

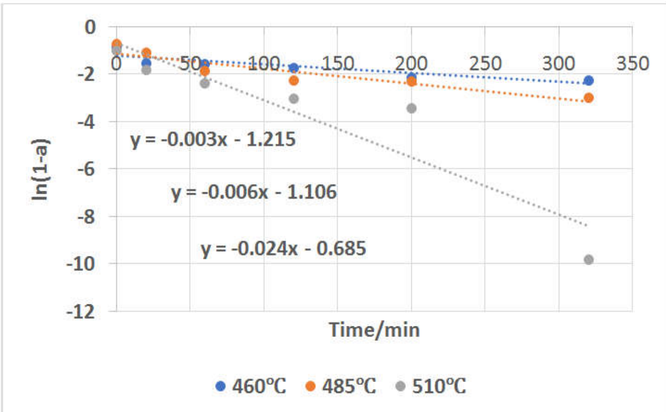

Figure 1. The relationship between ln(1-a) and isothermal pyrolysis time t at three different temperatures

The Table 2 lists the velocity constants k and integral constants C are obtained for three isothermal temperatures.

Table 2. The velocity constants k and intergral constants c at three isothermal temperatures

T/°C	k/min^{-1}	C
460	0.0037	-1.215
485	0.0063	-1.1068
510	0.0214	-0.6852

Figure 2 is the plotted of the relationship between lnk and 1/T of the isothermal pyrolysis for oil rich coal as one set of data. The relationship between lnk and 1/T of the isothermal pyrolysis for long flame coal as another set of data.

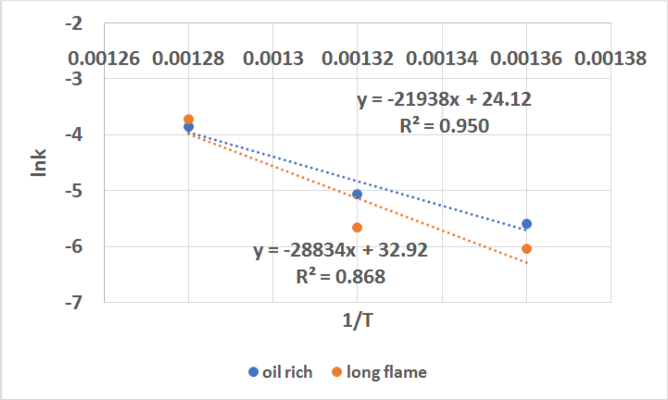

Figure 2. The relationship between lnk and 1/T of the isothermal pyrolysis for oil rich coal and long flame coal

According to equation 3, the slope of the line can be used to solve the activation energy E and the intercept is related to pre-exponential factor lnA.

Table 3 listed the activation energy and pre-exponential factor of both oil rich coal and long flame coal under isothermal pyrolysis condition.

Table 3. The activation energy and pre-exponential factor under isothermal pyrolysis condition

	Long flame	Oil rich
E/KJ/mol	239.73	182.39
lnA	32.924	24.12

From the Table 3, both activation energy and pre-exponential factor of oil rich coal are smaller than that of long flame coal. Activation energy is a chemical term, also known as threshold energy. The term was introduced by Arenas in 1889 to define the energy barriers that need to be overcome to occur in the event of a chemical reaction. Activation energy can be used to represent the minimum energy required for a chemical reaction to occur, so the higher the activation energy, the more difficult the reaction is. The chemical reaction rate is closely related to the size of its activation energy, the lower the activation energy, the faster the reaction rate. Under isothermal pyrolysis phase, the conversion rate of oil rich coal is larger than that of the long flame coal.

B. Constant heating rate pyrolysis results

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

$$\beta=\frac{dT}{dt} \tag{4}$$

The constant heating rate, 5°C /min, pyrolysis involved the dry dewatering phase and the transition phase of slight pyrolysis. According to Doyle approximate integrals and at n=1, the conversion rate under constant heating rate pyrolysis is expressed as:

$$\ln[-\ln(1-\alpha)] = \ln\left(\frac{AE}{\beta R}\right) - 5.33 - \frac{E}{RT} \tag{5}$$

According to Equation 5, 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.

The relevant data of those two phases of oil rich coal pyrolysis are listed in Table 4.

Table 4. The relevant data of those two phases, under constant heating rate, 5°C /min, pyrolysis condition

Item	1/T	ln(-ln(1-a))
0#	0.003413	-9.61027
00#	0.001931	-2.27139
1-1	0.001364	-0.18887
2-1	0.001319	-0.33404
3-1	0.001277	-0.00347

The relationship between ln(-ln(1-a)) and 1/T of the constant heating rate, 5°C /min, pyrolysis of both oil rich coal and long flame coal are plotted in Figure 3.

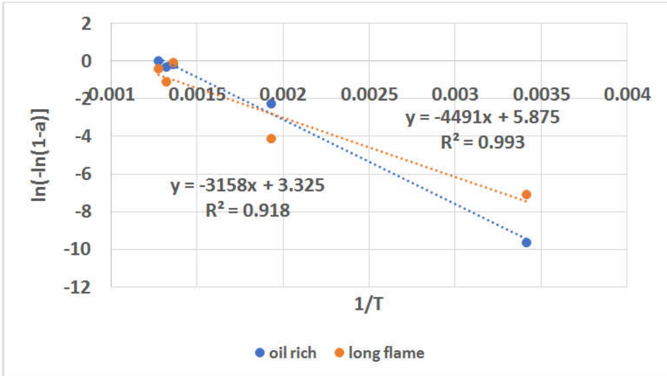

Figure 3. The relationship between ln(-ln(1-a)) and 1/T of oil rich coal and long flame coal under constant heating rate, 5°C/min, pyrolysis condition

Table 5. The activation energy and pre-exponential factor under constant heating rate, 5°C /min, pyrolysis condition

	Oil rich	Long flame
E/KJ/mol	37.338	26.255
lnA	4.405	2.207

From the Table 5, both activation energy and pre-exponential factor of oil rich coal are larger than that of long flame coal. We can draw a conclusion: generally, if the same temperature is raised, the reactor energy is large, and the rate constant is expanded by a large multiple. Under constant heating rate pyrolysis phases, when the temperature from T_1 increased to T_2, the conversion rate change of oil rich coal is larger than that of thelong flame coal.

Conclusion

For the isothermal pyrolysis of oil rich coal, the activation energy E =182.39 KJ/mol, and the pre-exponential factor lnA=24.12. The activation energy of oil rich coal under isothermal pyrolysis condition is smaller than that of long flame coal, E =239.73 KJ/mol. Based on the principle of lower activation energy, the conversion rate of long flame coal is smaller than that of the oil rich coal. For the constant heating rate pyrolysis of oil rich coal, the activation energy E =37.338 KJ/mol, and the pre-exponential factor lnA=4.405. The activation energy of oil rich coal under constant heating rate pyrolysis condition is larger than that of long flame coal, E =26.255 KJ/mol. Based on the principle of larger activation energy, under constant heating rate pyrolysis phases, when the temperature from T_1 increased to T_2, the conversion rate change of oil rich coal is larger than that of the long flame coal. Based on two facts of °C the Jurassic coal seam in Shaanxi province having the tar yield in the 3%~16% and °C a same industrial pyrolysis procedure is used for the tar yield between 3%~16% low rank coal, not matter the raw material is oil rich coal or long flame coal, the products contents of gas, tar, and blue carbon for pyrolysis should be always unpredictable and fluctuated.

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)
T: thermodynamic temperature, K
t: time, minute
α: conversion rate
β: constant heating rate, K/min

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