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# Experimental Study on the Volatilization Dynamic of Long Flame Coal Pyrolysis

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**Abstract**: Long flame coal from the Shenfu-Dongsheng coal field in the Ordos Basin is pyrolyzed for volatilization dynamic experiments using HYLZ-2 cryogenic dry distillation furnace. The pyrolysis procedure is designed to contain the dry dewatering phase (20 to 245 ℃), the transition phase of slight pyrolysis (245 to 460 ℃ or other 485 ℃, and 510 ℃) both at 5 ℃/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 =214 KJ/mol, and the pre-exponential factor lnA=28.832. For the constant heating rate pyrolysis, the activation energy E =26.26 KJ/mol, and the pre-exponential factor lnA=2.714.

**Keywords**: temperature time sampling roadmap; constant heating rate pyrolysis; isothermal pyrolysis; volatilization dynamics.

## I. INTRODUCTION

Low-rank coal cryogenic dry distillation is a quality-raising pyrolysis process that overcomes the shortcomings of high moisture, high volatile fractions, and low thermal value, and low processing suitability [1, 2]. The cryogenic dry distillation is also considered to be the first step that must be followed in for advanced conversion process of low-rank coal, such as gasification, liquefaction, coking, and combustion. So, it is important to study the pyrolysis dynamics of low-rank coal in depth. The science studying how the properties of a particular characteristic of a reactant changing over time and temperature is chemical dynamics, which is a good example of a mass change curve over time or/and temperature obtained by thermal gravity analysis techniques [3-8]. As the temperature rises, the low-rank coal thermal dissociation, weight loss is caused by sulfur, water, and volatiles, which enter the gaseous product from the solid-state reactant according to their respective laws [9, 10]. The evaluation of coal quality, the determination of the degree of volatilization and the classification of coalification are closely related. The volatile matter contained in cryogenic dry distillation solid products is also very important for the applicability of processing [11, 12]. For example, the higher the volatile matter content in solid residues, the more flammable, they are more likely to catch fire. Therefore, volatile matter content and their release behavior during the pyrolysis has an important impact. To ensure the needs of the downstream process, it is necessary to control volatile matter content for metallurgical coke [13], gasification coke, and civil combustion of clean coal with half coke [14-16]. So far, there have been studies on the dynamics of heat solution weight loss and the phenomenon of thermal desulfurization, etc., but the experimental study on low-rank coal low-temperature dry distillation volatilization dynamics is rarely involved. To this end, this paper will prepare a series of different degrees of pyrolysis samples, and to study volatile dynamics.

## II. EXPERIMENTAL DETAIL AND VOLATILE MATTER CONTENT 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℃ to 245℃ at 5℃ /minute heat rate.

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

The strong pyrolysis phase to the end point employed of isothermal pyrolysis at 460℃ or designed temperature of 485℃ or 510℃. 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. Volatile matter content 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℃ 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℃ to 245℃ at 5℃ /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℃. The 2 before a dash is marked as the sample isothermal pyrolysis at 485℃. The 3 before a dash is marked as the sample isothermal pyrolysis at 510℃.

## III. DYNAMIC CALCULATIONS [17-20]

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:

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

A. Weight loss rate and conversion rate

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

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \qquad (2)$$

$W_0$: Sample original volatile amount, 17.17 grams

W: Residual volatile amount in standard stainless-steel retort for a pyrolysis experiment.

$W_f$: Final residual volatile amount in standard stainless-steel retort for the maximum pyrolysis experiment, which is 7.373 grams with a maximum temperature of 510℃ and a maximum temperature of 320 minutes.

B. Isothermal pyrolysis

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

$$-ln(1-\alpha) = kt + C \qquad (3)$$

According to equation (3), under isothermal pyrolysis condition, the -ln(1-a) 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:

$$lnk_i = lnA - \frac{E}{RT_i} \qquad (4)$$

According to equation (4), 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.:

$$\beta = \frac{dT}{dt} \qquad (5)$$

When E being treated as a constant, Equation (1), (4), and (5) can be treated as:

$$\frac{d\alpha}{dT} = \frac{A(1-\alpha)^n}{\beta} \exp\left(-\frac{E}{RT}\right) \qquad (6)$$

Set the initial conditions of a=0 when T=$T_{0,}$ and get:

$$\int_0^\alpha (1-\alpha)^{-n} d\alpha = \frac{A}{\beta}\int_{T_0}^{T} exp\left(-\frac{E}{RT}\right) dT \qquad (7)$$

According to Doyle approximate integrals and at n-1,

$$\ln[-\ln(1-\alpha)] = \ln\left(\frac{AE}{\beta R}\right) - 5.33 - \frac{E}{RT} \qquad (8)$$

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 °C, and time t=0 minute), and let a=0.999 at the final sampling point (temperature T=510 °C, and time t=320 minute).

D. Isothermal pyrolysis results

Table 1 listed 18 isothermal pyrolysis volatile loss (VL) data and their conversion rate and calculations.

TABLE I: 18 ISOTHERMAL PYROLYSIS VL, CONVERSION RATE

AND CALCULATION

| Item | VL/g | a | 1-a | ln(1-a) |
|---|---|---|---|---|
| 0# | 0.01 | 0.000848 | 0.999152 | -0.00085 |
| 00# | 0.19 | 0.016106 | 0.983894 | -0.01624 |
| 1-1 | 7.043 | 0.597016 | 0.402984 | -0.90886 |
| 1-2 | 7.422 | 0.629143 | 0.370857 | -0.99194 |
| 1-3 | 8.818 | 0.747478 | 0.252522 | -1.37626 |
| 1-4 | 8.629 | 0.731457 | 0.268543 | -1.31474 |
| 1-5 | 9.413 | 0.797915 | 0.202085 | -1.59907 |
| 1-6 | 9.627 | 0.816055 | 0.183945 | -1.69312 |
| 2-1 | 3.402 | 0.288378 | 0.711622 | -0.34021 |
| 2-2 | 6.799 | 0.576333 | 0.423667 | -0.85881 |
| 2-3 | 8.094 | 0.686107 | 0.313893 | -1.1587 |
| 2-4 | 8.927 | 0.756718 | 0.243282 | -1.41353 |
| 2-5 | 8.758 | 0.742392 | 0.257608 | -1.35632 |
| 2-6 | 9.744 | 0.825973 | 0.174027 | -1.74854 |

| | | | | |
|---|---|---|---|---|
| 3-1 | 5.792 | 0.490972 | 0.509028 | -0.67525 |
| 3-2 | 7.982 | 0.676613 | 0.323387 | -1.1289 |
| 3-3 | 9.325 | 0.790455 | 0.209545 | -1.56282 |
| 3-4 | 10.141 | 0.859625 | 0.140375 | -1.96344 |
| 3-5 | 11.441 | 0.969823 | 0.030177 | -3.50067 |
| 3-6 | 11.787 | 0.999152 | 0.000848 | -7.07302 |

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

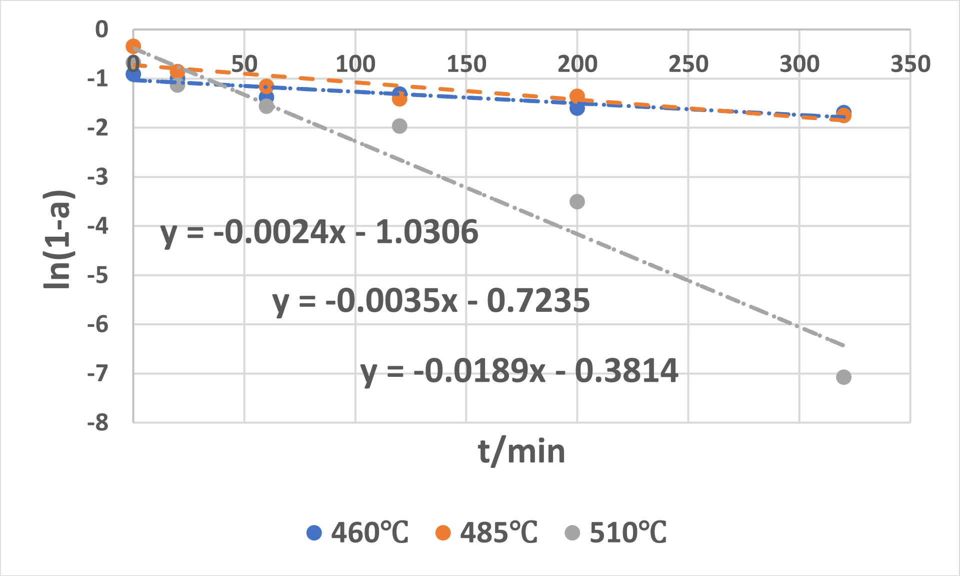

Fig. 1: The relationship between ln(1-a) and isothermal pyrolysis time t

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 II: THE VELOCITY CONSTANTS k AND INTEGRAL CONSTANTS C

AT THREE ISOTHERMAL TEMPERATURES

| T/°C | k/$\text{min}^{-1}$ | C |
|---|---|---|
| 460 | 0.0024 | -1.0306 |
| 485 | 0.0035 | -0.7235 |
| 510 | 0.0189 | -0.3814 |

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

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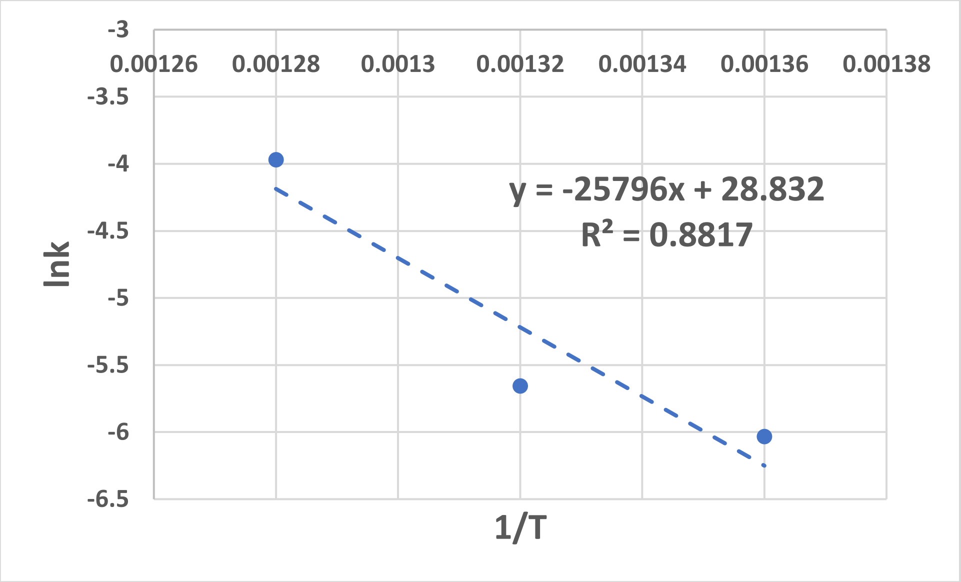

Fig. 2: The relationship between lnk and 1/T of the isothermal pyrolysis

The slope of the line can be used to solve the activation energy E =214 KJ/mol, and the pre-exponential factor lnA=28.832.

E. Constant heating rate pyrolysis results

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

TABLE III: THE RELEVANT DATA OF THOSE TWO CONSTNT

HEATING RATE PYROLYSIS

| Item | 1/T | ln(-ln(1-a)) |
|---|---|---|
| 0# | 0.003413 | -7.07259 |
| 00# | 0.001931 | -4.12046 |
| 1-1 | 0.001364 | -0.09556 |
| 2-1 | 0.001319 | -1.07819 |
| 3-1 | 0.001277 | -0.39266 |

Based on the Equation (8), the relationship between ln(-ln(1-a)) and 1/T of the constant heating rate pyrolysis is plotted in Figure 3.

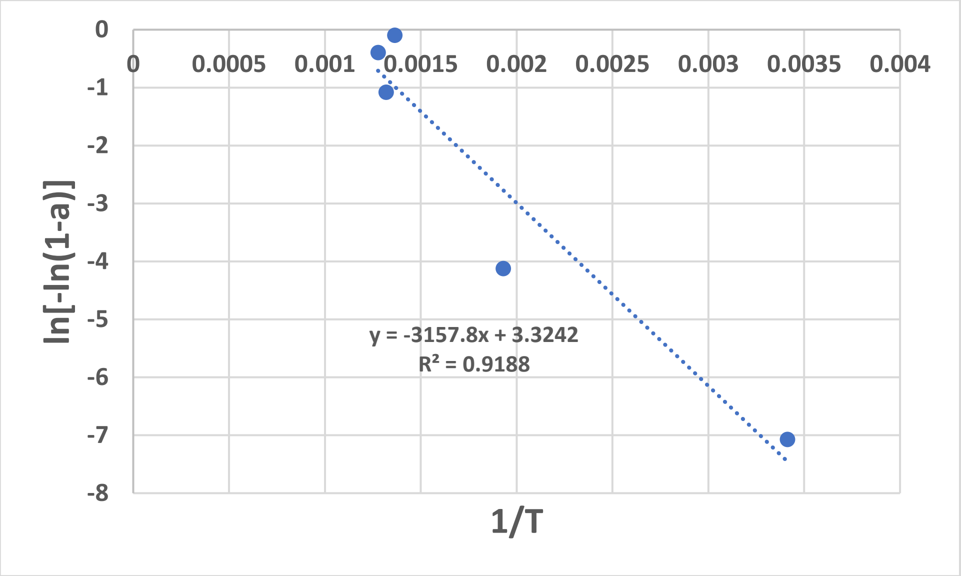

Fig. 3: The relationship between ln(-ln(1-a)) and 1/T of the constant heating rate pyrolysis

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

$$-\frac{E}{R} = -3158 \qquad (9)$$

Therefore, E =26.26 KJ/mol for constant heating rate pyrolysis.

The intercept can be presented as:

$$ln\left(\frac{AE}{\beta R}\right) - 5.33 = 3.3242 \qquad (10)$$

Put every constant into Equation (10), the pre-exponential factor lnA=2.714.

## IV. CONCLUSION

Long flame coal from the Shenfu-Dongsheng coal field in the Ordos Basin is pyrolyzed for volatile loss 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 ℃), the transition phase of slight pyrolysis (245 to 460 ℃ or other 485 ℃, and 510 ℃) both at 5 ℃/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 =214 KJ/mol, and the pre-exponential factor lnA=28.832. For the constant heating rate pyrolysis, the activation energy E =26.26 KJ/mol, and the pre-exponential factor lnA=2.714.

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

□: conversion rate

□: constant heating rate, K/min

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