Experimental study on the desulfurization dynamic of long flame coal pyrolysis

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

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

Abstract: Long flame coal from the Shenfu-Dongsheng coal field in the Ordos Basin is pyrolyzed for desulfurization dynamic experiments using HYLZ-2 cryogenic dry distillation furnace. The pyrolysis procedure is designed to contain three sequence phases: 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 of desulfurization E =201 KJ/mol, and the pre-exponential factor lnA=26.508. For the constant heating rate pyrolysis, the activation energy of desulfurization E =34.29 KJ/mol, and the pre-exponential factor lnA=5.267.

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

I.   INTRODUCTION

Long flame coal cryogenic dry distillation is one of the quality-raising pyrolysis used in China to improve the suitability of coal quality by reducing high moisture, high volatile fractions, and increasing thermal value [1, 2]. In the process of coal utilization, sulfur not only pollutes the environment but also affects the quality of coal chemical and downstream steel products. Scholars from all over the world have carried out a lot of desulfurization research projects involving before, during, or after pyrolysis process. Among which, the desulfurization during the pyrolysis has been paid much attention due to a high desulfurization efficiency. Sulfur in coal is mainly organic sulfur and inorganic yellow iron ore sulfur. There are a lot of researches involved the coal desulfurization, such as the study of the law of desulfurization in the coal combustion process [3, 4], the study of the sulfur migration during various types of coal pyrolysis [5-8], the study of the law of organic sulfur migration for high sulfur coal and biomass co-pyrolysis together [9-11], the study of hydrogen-rich atmosphere coal pyrolysis [12-16], and the study of additive desulfurization reagents [17-19]. These studies pay attention to the specific forms of sulfur thermal migration law in coal so that all kinds of thermal desulfurization methods have sufficient basic theoretical research support. But for the long flame coal cryogenic dry distillation is rarely involved, the most basic reason is that the Shenfu long flame coal is low sulfur content and low ash coal. Therefore, the desulfurization dynamic of has not been mentioned on the agenda. According to the process of semi-coke production plant in northern Shaanxi Province of China and the way of constant heating rate pyrolysis and isothermal pyrolysis used, some experiments of the desulfurization dynamic of long flame coal pyrolysis have been conducted to calculate desulfurization rate constant, active energy, and pre- exponential factor.

II. EXPERIMENTAL DETAIL AND DESULFURIZATION 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. Desulfurization 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 [20-25]

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. Desulfurization rate and conversion rate

Since the conversion rate is represented by the desulfurization rate data, there is

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

W_0: Sample original sulfur amount, 105.64 milligrams

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

W_f: Final residual sulfur amount in standard stainless-steel retort for the maximum pyrolysis experiment, which is 66.02 milligrams with a maximum temperature of 510°C 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:

$$ln k_i = ln A - \frac{E}{RT_i} \qquad (4)$$

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 desulfurization (DS) data and their conversion rate and calculations. Based on Equation (3), 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 DS, CONVERSION RATE, AND CALCULATIONS

Item	DS/g	a	1-a	ln(1-a)
0#	0.01	0.0003	0.9997	-0.0003
00#	16.45	0.4151	0.5849	-0.5363
1-1	30.98	0.7817	0.2183	-1.5220
1-2	32.2	0.8125	0.1875	-1.6741
1-3	34.62	0.8736	0.1264	-2.0682
1-4	35.42	0.8938	0.1062	-2.2421
1-5	35.58	0.8978	0.1022	-2.2809
1-6	36.25	0.9147	0.0853	-2.4617
2-1	28.02	0.7070	0.2930	-1.2277
2-2	35.29	0.8905	0.1095	-2.2117
2-3	35.68	0.9003	0.0997	-2.3059
2-4	36.5	0.9210	0.0790	-2.5386
2-5	35.46	0.8948	0.1052	-2.2517
2-6	35.5	0.8958	0.1042	-2.2613
3-1	33.57	0.8471	0.1529	-1.8779
3-2	34.89	0.8804	0.1196	-2.1235
3-3	37.01	0.9339	0.0661	-2.7164
3-4	38.34	0.9674	0.0326	-3.4249
3-5	39.04	0.9851	0.0149	-4.2072
3-6	39.62	0.9997	0.0003	-8.2848

In the figure:
$$y = -0.0027x - 1.7178$$
$$y = -0.0017x - 1.9303$$
$$y = -0.0187x - 1.5259$$

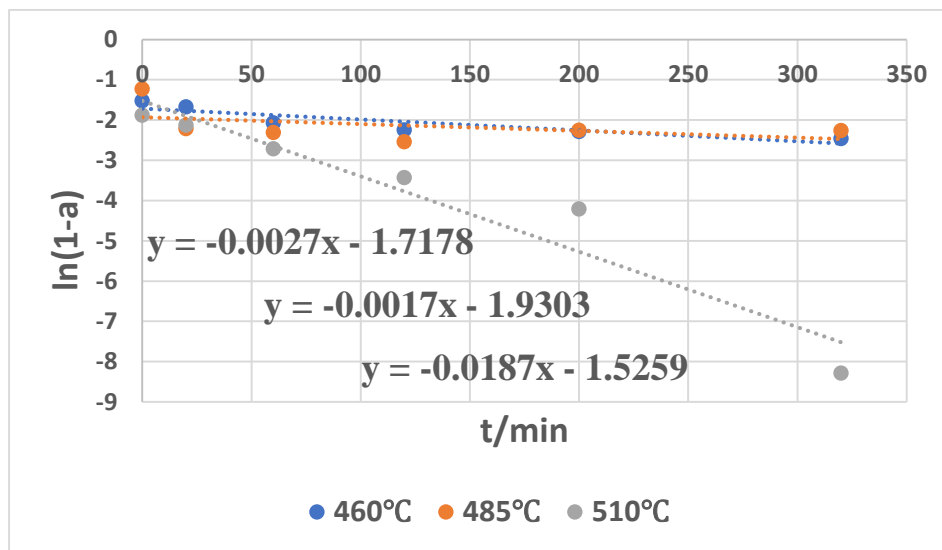Axis labels: ln(1-a) (vertical), t/min (horizontal)

Legend: 460°C, 485°C, 510°C

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 INTERGRAL CONSTANT C AT THREE ISOTHERMAL TEMPRATURES

T/°C	k/min^{-1}	C
460	0.0027	-1.7178
485	0.0017	-1.9303
510	0.0187	-1.5259

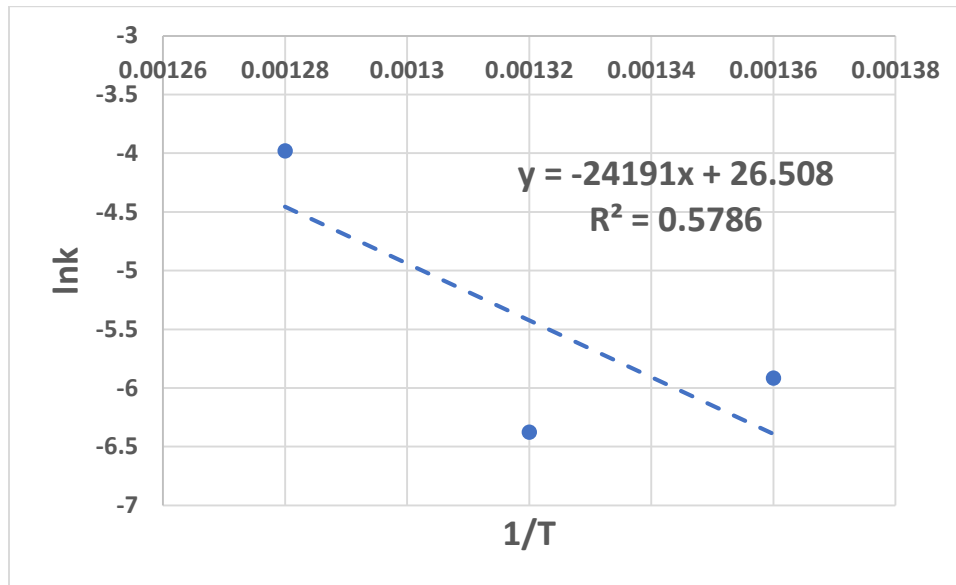Figure 2 is the plotted of the relationship between lnk and 1/T of the isothermal pyrolysis.

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 =201 KJ/mol, and the pre-exponential factor lnA=26.508.

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

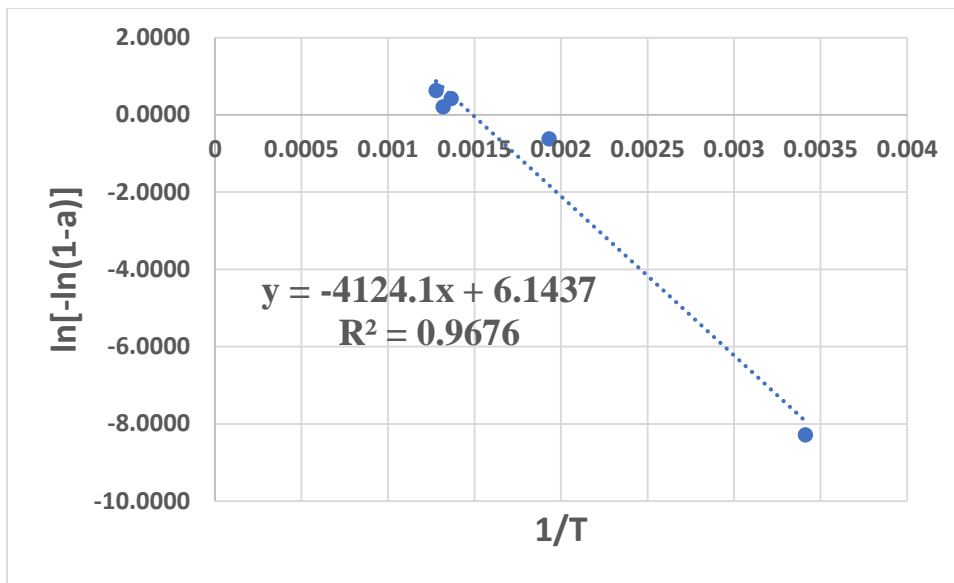*Fig. 3: The relationship between ln(-ln(1-a)) and 1/T of the constant heating rate pyrolysis*

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

$$-\frac{E}{R} = -4124 \qquad (9)$$

Therefore, E =34.29 KJ/mol for constant heating rate pyrolysis.

The intercept can be presented as:

$$ln\left(\frac{AE}{\beta R}\right) - 5.33 = 6.1437 \qquad (10)$$

Put every constant into Equation (10), the pre-exponential factor lnA=5.267.

IV.   CONCLUSIONS

Long flame coal from the Shenfu-Dongsheng coal field in the Ordos Basin is pyrolyzed for desulfurization 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 =201 KJ/mol, and the pre-exponential factor lnA=26.508. For the constant heating rate pyrolysis, the activation energy E =34.29 KJ/mol, and the pre-exponential factor lnA=5.267.

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

V. REFERENCES

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Xuemei Zhang (1987 -), female, master, associate professor, majored in chemical engineering, mainly engaged in research on reclaimed water reuse, published more than 20 academic papers, undertaken and participated in 3 projects of Shaanxi Provincial Department of education and water resources department.