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Research article

A modified Arrhenius equation to predict the reaction rate constant of Anyuan pulverized-coal pyrolysis at different heating rates

Rui-Ling Du *, Keng Wu, Da-An Xu, Chang-Yao Chao, Li Zhang, Xiao-Dong Du

State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China
School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

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ABSTRACT

The pyrolysis performance of pulverized-coal varies with different heating conditions. Therefore, the influence of heating rates on the pyrolysis kinetic of pulverized-coal is studied in this paper. Based on previous researches and large amounts of experimental data, the kinetic compensation effect for different heating rates is expressed as $\ln A_i = aE_{ai} + b$, and the influence of heating rate β on activation energy E_{ai} is described as $E_{ai} = \Delta E_a \ln\beta_i + E_{a0}$. Then, a modified Arrhenius equation ($\ln k_i = -E_{a0}/RT + \Delta E_a(a - 1/RT)\ln\beta_i + \ln A_0$) is proposed to describe the influence of heating rate on the rate constant k_i of pulverized-coal pyrolysis. The parameters of a, E_{a0}, and ΔE_a could be obtained from at least three sets of experimental data under different heating rates. Finally, the extrapolation reliability of the modified Arrhenius equation is validated by the experimental data at other different heating rates. The results show that the modified Arrhenius equation not only provides an expedient way to depict the pyrolysis kinetics at different heating rates, but also presents extrapolation reliability over a broad range.

1. Introduction

The pyrolysis of coal is the first step in most coal conversion processes, which is crucial to subsequent steps, such as carbonization, gasification and combustion [1]. The pyrolysis performance differs greatly under different heating conditions [2,3]. While the relevant reports in quantitative analysis are rare, Guo's investigation showed that the heating rate had a big influence on both initial and final temperatures for thermal chemical reaction as well as the activation energy of coal pyrolysis [4]. Nevertheless, in Guo's work, the relationship between heating rates and rate constant was not quantitatively obtained. Yu found that with increasing heating rate, the rate constant increases as well [5]. Furthermore, Yu proposed a method for predicting the rate constants at fast heating rates presented by correlating with coal rank and rate constants at low heating rates. The relation between the pyrolysis rate constant k and the heating rate m was expressed as $k_1/k_2 = (m_1/m_2)^n$. The exponent n denotes the degree of influence of heating rate on the kinetic rate. However, the formula merely provided a simple method to calculate the mean value of k. The effect of temperature on the rate constant was ignored, which could not reflect the essence of the pulverized-coal pyrolysis. Moreover, the function of the rate constant with the heating rate and temperature was not presented. Thus, the influence of heating rate on pyrolysis kinetics of pulverized-coal was focused on this thesis.

Under the isothermal condition, the Arrhenius equation was used to describe the relationship between the rate constant and temperature. With the development of thermal analysis kinetics, the Arrhenius equation is applied to the non-isothermal system. However, no matter how thermal analysis methods (such as: model fitting method [6], model-free method [7], distributed activation energy model (DAEM) method [8,9]) are adopted, the activation energy and rate constant are changed with heating rates at same temperature. Therefore, the heating rate was introduced into the modified Arrhenius equation to describe the influence of heating rate on the rate constant in non-isothermal dynamics. The modified law aims to predict pyrolysis rates without assuming pyrolysis product distribution. Finally, the extrapolation reliability of function was validated using experimental data at different heating rates.

2. Materials and methods

Anyuan coal mine is located in Jiangxi Province, China. There are a lot of advantages of Anyuan coal: low ash, low sulfur impurities, and high calorific value. It is widely used in different industries (e.g. thermal power industry, steel industry). The fuel properties of Anyuan coal samples used in this study are shown in Table 1.

A Netzsch No. STA 449 F3 analyzer was used for the measurements of pyrolysis kinetics. The schematic of the apparatus is shown in Fig. 1. The sample was heated automatically according to the setting program and the experimental data was collected automatically by the computer.

* Corresponding author at: School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China.
E-mail address: durling_ustb@163.com (R.-L. Du).

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Table 1
Proximate and ultimate analyses (wt.%) of Anyuan coal.

Proximate analysis (air-dried basis)				Ultimate analysis (dry basis)				
Fixed carbon	Ash	Moisture	Volatiles	C	H	N	O	S
49.6	2.6	40.0	7.8	69.07	4.44	1.20	12.17	1.07

Anyuan coal with the average particle sizes 112.5 μm (75–150 μm; 100–200 mesh) was used in this study. The mass of sample was 10 ± 1 mg in each experiment. During the entire experimental process, the gas flow 2.5 mL·s^{-1} of argon was adopted to protect the sample from oxidation. The sample was placed inside the analyzer at room temperature for 40 min to remove the air, heated to 105 °C at the rate of 10 °C·min^{-1}, held for 10 min to remove the adsorbed water, and heated to 900 °C at different heating rates (15, 30, 45, and 60 °C·min^{-1}). To ensure consistency among the experimental results, every set of experiments was conducted at least three times.

3. Results and discussion

3.1. The influence of heating rates on pulverized-coal pyrolysis

Coal is a kind of heterogeneous polymer compound. The main decomposed products of coal are combustible gas, tar, and coke [10]. In Fig. 2, thermal gravity (TG) curves and differential thermal gravity (DTG) curves show a thermal hysteresis phenomenon with increasing heating rate. In the research performed by Guo and Zhang, the pyrolysis temperature range of Shenhua, Datong, and Xinglongzhuang coals was divided into various stages according to the weight loss rate and released gas species [4,11]. However, the effects of heating rates were not considered. In this paper, because the changes of the kinetic mechanism are often accompanied with the radical changes of mass loss rate, the temperature range of Anyuan coal is divided into three parts at the temperatures where the variation of mass loss rate reaches the maximum [12]. As listed in Table 2, the divided temperature ranges vary at different heating rates due to the effects of heating rates in the pyrolysis process. The sectioning temperature point T_i (for $i = 1, 2$) increases with the heating rates.

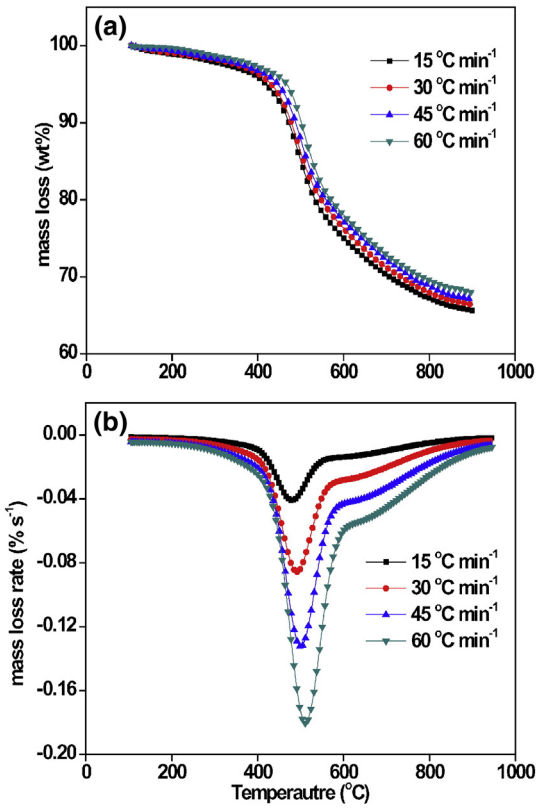

Fig. 2. Mass loss and mass loss rate of pyrolysis process at different heating rates (standard deviation δ = 0.002).

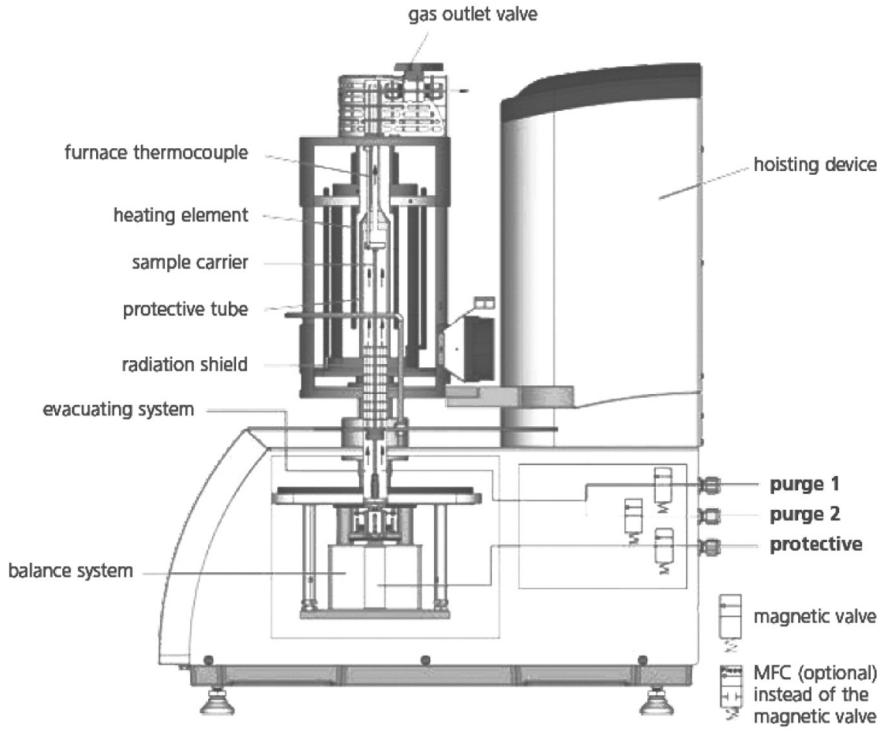

Fig. 1. Schematic diagram of Netzsch STA 449 F3 analyzer.