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Thermal decomposition mechanisms of coal and coal chars under CO_2 atmosphere using a distributed activation energy model

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ABSTRACT

The thermal decomposition characteristics of Sanxing (SX) coal and coal chars (C500 and C850, produced at 500 and 850 °C, respectively) were tested by nonisothermal thermogravimetric analysis and a distributed activation energy model used to determine the kinetic parameters. The effects of char-making temperature were investigated. A sharp peak was seen in the relationship between X and activation energy (E) of the SX and C500 samples; no evident peak, but a ladder-shaped decline, was shown by C850. The temperatures at which E was maximized were relatively close for SX coal and C500, while the minimum value of activation energy was almost the same for the three samples. This showed the char-making process had less influence on the gasification reaction under high-temperature conditions. The results of the kinetic compensation effect between E and the pre-exponential factor (k_0) showed that different kinetic compensation mechanisms occurred for the pyrolysis- and gasification-dominated stages.

1. Introduction

Coal is widely available at relatively stable cost so many countries use it for power generation; however, its utilization creates many environmental problems [1,2], including the generation of NO_x and SO_x. The development of clean coal technologies is essential to minimize its future environmental impact. Gasification is a clean technology that can offer an attractive route for converting carbonaceous fuels cleanly and with high efficiency into synthesis gas and other valuable energy products [3].

In general, the gasification process is very complex and includes water evaporation, pyrolysis of volatiles, combustion, volatiles gasification, and char gasification. Pyrolysis is the first step in the thermochemical conversion of coal. This can be described as the thermal degradation of the organic matrix in an inert environment to obtain an array of solid, liquid, and gaseous products [4]. Pyrolysis influences char reactivity in terms of particle porosity and surface morphology, and carbon burnout in terms of amount of char remaining [5]. Char gasification is the rate-controlling step in a coal gasifier due to its low gasification rate [6]. In addition, the CO_2 gasification rate of chars is much slower than their steam and oxygen gasification rates, so the char CO_2 gasification rate is considered as the rate-determining step in practical gasification processes. Knowledge of char CO_2 gasification kinetics is required for reactor design and optimization of process operation.

Thermogravimetric analysis (TGA) is one of the most widely used techniques to study pyrolysis and gasification characteristics and is an important tool in determining reaction kinetics. Theoretically, kinetic parameters should comprise independent variables; in fact, the pre-exponential factor (k_0) is highly correlated with the activation energy (E), which is known as the kinetic compensation effect [7–9]. Specifically, $\ln(k_0)$ shows a linear relationship with E as follows:

$$\ln(k_0) = aE + b \quad (1)$$

where a and b are constants that depend on the reaction system.

Few references can be found on the compensation effect of coal and coal chars under nonisothermal CO_2 atmosphere. By applying the first-order Volume Reaction Model, Skodras et al. [8] analyzed the kinetic parameters and studied the compensation effect in isothermal coal CO_2 gasification; however, there was a large difference when compared with actual coal gasification under a nonisothermal environment. Few references could be found for the design of an industrial reactor under these conditions, so more work is still needed.

The method for studying pyrolysis kinetics can be divided into isothermal [10] and non-isothermal method [11–13]. Compared with the isothermal method, the non-isothermal method is simple and easy because of avoiding the change of chemical and physical properties of the tested sample, and providing useful information via fewer experiments [14]. Using TGA data, researchers have developed different mathematical models for establishing the kinetic mechanism of

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pyrolysis processes, including the homogeneous [15], random pore [16,17], shrinking-core [18], and distributed activation energy (DAEM) models [19,20]. Of these, the DAEM is proposed to describe the variation of activation energy during pyrolysis of coal and biomass, and has been widely used [21–23] The model assumes that many irreversible first-order parallel reactions that have different rate parameters occur simultaneously [24]. Miura and Maki [25] simplified the model to estimate the activation energy and corresponding pre-exponential factor from at least three TGA curves obtained at different heating rates. This simplified DAEM has been widely used to describe the kinetics of pyrolysis under inert atmosphere for different types of materials, such as biomass, coal, sewage sludge, oil shale, polymers, and medical waste [7,24,26–29]. Liu et al. [28] studied the kinetic behavior of both pyrolysis and gasification of coal samples under air atmosphere using the DAEM. There are few research reports concerning use of the simplified DAEM in the study of thermal decomposition processes of coal or char under a CO_2 atmosphere, which involve both coal/char pyrolysis and gasification of the newly generated char.

The kinetics characteristics of thermal decomposition of coal and chars originating from the Sanxing deposit under CO_2 atmosphere were investigated. The DAEM was selected to analyze the experimental TGA data. The three kinetic parameters were calculated and kinetic compensation parameters discussed.

2. Experimental

2.1. Preparation of samples

Sanxing (SX) coal, a bituminous coal from Inner Mongolia, China, was selected for the experiments. The coal chars were prepared in a fixed-bed reactor. A crucible containing 3 g of coal sample (< 125 μm) was placed in the cooled upper zone of the reactor prior to heating under a N_2 atmosphere (2 L/min) from ambient temperature to 500 °C or 850 °C. The crucible was then quickly pushed into the constant-temperature zone and held at the selected temperature for 30 min. The crucible was returned to the cooled zone for 20 min to obtain the char samples. The chars produced were labelled as C500 and C850, according to the final temperature applied in the pyrolysis stage. For TGA analysis, the char samples were ground and sieved again to ensure that their particle sizes were smaller than 125 μm.

2.2. Measurements of nonisothermal thermal decomposition reactivity under CO_2 atmosphere

TGA of coal and char thermal decomposition under a CO_2 atmosphere was carried out using the thermogravimetric–differential scanning calorimetry (TG–DSC) mode on an STA449C thermal analyzer (Netzsch-Gerätebau GmbH, Germany). In each nonisothermal gasification experiment, approximately 5 mg sample was loaded into an alumina crucible and heated under a CO_2 atmosphere (120 mL/min) up to 1200 °C at heating rates of 20, 30, and 40 °C/min. This range of heating rates (< 50 °C/min) [30–34] and the 3 TGA curves [35–39] are widely employed in the literatures which investigate thermal decomposition mechanisms. A separate blank run was conducted for each heating rate using an empty pan; this was used for baseline correction.

The carbon conversion (X) of samples in the nonisothermal thermal decomposition process was calculated by the following equation:

$$X = \frac{W_0 - W_t}{W_0 - W_{ash}}, \tag{2}$$

where W_0 is the sample mass at the start of the thermal decomposition; W_t is the sample mass at time t; and W_{ash} is the mass of ash remaining after complete decomposition.

3. Kinetic analysis

The DAEM assumes that a number of parallel, irreversible first-order reactions with different activation energies occur simultaneously. All activation energies have the same k_0 at the same conversion rate. The activation energies have a continuous distribution. Miura [40] conducted extensive research of DAEM based on coal pyrolysis, not only presenting a simple method to estimate the distribution curve of the activation energy ($f(E)$) and pre-exponential factor (k_0), but also proving that the method can be used to describe a single chemical reaction system. Miura's method was used to estimate E and k_0 for the thermal decomposition of SX coal and chars under CO_2 atmosphere. The model is expressed as:

$$1\text{-}X = \int_{\infty}^{0} \exp\left(-\frac{k_0}{\alpha}\int_{T}^{0} e^{-E/(RT)}dT\right)f(E)dE \tag{3}$$

where α is heating rate; R is the gas constant; T is temperature. The values of E and k_0 were obtained from three experiments using different heating profiles without assuming any functional forms for E and k_0. The calculation of Eq. (4) was then carried out:

$$\ln\left(\frac{\alpha}{T^2}\right) = \ln\left(\frac{k_0 R}{E}\right) + 0.6075\text{-}\frac{E}{RT}. \tag{4}$$

The procedure [25] used to estimate E and k_0 is summarized by the following steps: (i) X was measured as a function of T at three different heating rates; (ii) the values of $\ln(\alpha/T^2)$ and $-1/(RT)$ were calculated for the same X; (iii) $\ln(\alpha/T^2)$ was plotted against $-1/(RT)$ at selected X ratios; the activation energies E were calculated from the slopes and k_0 from the intercepts.

4. Results and discussion

4.1. Elemental characteristics of SX coal and chars

Table 1 presents the proximate and ultimate analyses of the SX coal and chars. The carbon content of the chars increased from 79.91% to 98.23% as the temperature increased from 500 °C to 850 °C. Concurrently, the hydrogen and oxygen contents decreased from 4.89% to 0.41% and from 13.89% to 0.15%, respectively. This is indicative of polycondensation and aromatization taking place [41]. Sample mass loss increased from 26.44% to 35.23% as the temperature increased from 500 °C to 850 °C, and the volatiles content reduced from 32.51% to 1.68%. These values indicated that the chars underwent differing degrees of pyrolysis.

4.2. Pore structures of Sanxing coal and chars

Images of the SX coal and chars obtained by scanning electron

Table 1
Proximate and ultimate analyses of Sanxing coal and chars.

		SX coal	C500	C850
Proximate Analysis	Ash (wt%, d)	10.41	11.74	13.43
	Volatiles (wt%, d)	32.51	12.04	1.68
	Fixed carbon (wt%, d)	57.08	76.22	84.89
	HHV, (kcal kg^{-1})	6614	7055	7165
Ultimate Analysis (wt%, daf)	C	79.91	90.29	98.23
	H	4.89	2.78	0.41
	N	0.92	0.76	0.54
	S	0.40	0.53	0.67
	O[a]	13.88	5.64	0.15
Weight loss[b] (wt%)		/	26.44	35.23

[a] Obtained by difference.
[b] As percentage resulting from pyrolysis (from room temperature to desired temperature).