Research Article

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Kinetic analysis of CO₂ gasification of biochar and anthracite based on integral isoconversional nonlinear method

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Abstract: The nonisothermal thermogravimetric analysis was implemented for gasification of sawdust char (SD-char), wheat straw char (WS-char), rice husk char (RH-char), bamboo char (BB-char) and anthracite coal (AC) in the presence of CO₂. The dependence of activation energy upon conversion for different biochars and AC was obtained by the integral isoconversional nonlinear (NL-INT) method which is a model-free method. Based on the activation energy values from the NL-INT method, a model-fitting method called random pore model (RPM) was used to estimate the kinetic parameters including the preexponential factor and pore structure parameter from the experimental data. The results are shown that the gasification reactivity of different samples from high to low can be sorted as that of WS-char, SD-char, BB-char, RH-char and AC. In the early stage of gasification, the activation energy values of biochars increase generally with an increase in the

conversion degree, whereas the value of AC decreases. Thereafter, the activation energy values remain almost unchanged when the conversion is up to some extent. When the conversion degree varies between about 0.3 and 0.9, these carbon materials can be sorted in the order of average activation energy from low to high as WS-char, SD-char, AC, RH-char and BB-char, respectively, 134.3, 143.8, 168.5, 184.8 and 193.0 kJ/mol. It is shown that a complex multistep mechanism occurs in the initial stage of gasification, while a single-step gasification mechanism exists in the rest of the gasification process. The RPM is suitable for describing the gasification of biomass chars and AC except the initial gasification. Additionally, it is found that the kinetic compensation effect (KCE) still exists in the gasification reactions of biochars and AC. However, the AC deviates markedly from the KCE curve. This may be caused by the similarity of carbonaceous structure of biochars and the difference in reactivity between biochars and AC.

Keywords: biochar, gasification, integral isoconversional nonlinear method, random pore model, kinetic compensation effect

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1 Introduction

Biomass energy, as an important renewable and clean energy and the only renewable carbon source, is characterized by wide distribution, rich reserves, renewability, carbon neutrality, fungibility and low pollution. It occupies the fourth place of the total world energy consumption after coal, oil and natural gas [1]. Currently, biomass conversion and utilization technologies can be divided into physical, chemical and biological transformations. The thermal chemical transformation methods, mainly including direct combustion, pyrolysis, gasification and liquefaction technologies, are widely used in the industries of biomass power generation, gas and liquid fuels [2]. Gasification is usually referred to thermal chemical conversion of biomass to gas by using a gasification medium, e.g., air, oxygen, nitrogen,

steam, carbon dioxide or a combination of them [3]. Moreover, in the steel industry, renewable biomass-based fuels are considered as a promising opportunity to decrease fossil-based energy consumption and CO₂ emissions. Especially, in the processes of iron making such as blast furnace (BF) iron making and direct-reduction iron making (DRI), biomass-derived reducing agents have gained more and more attention [4–6]. Generally, the auxiliary reducing agents are injected into the BF from the tuyeres located in the lower part of the BF via injection lances with oxygen-enriched hot blast. The biochars experience rapid heating, devolatilization, gas-phase combustion, char combustion and gasification. In fact, once all the oxygen are consumed at the border of the raceway, the main char consuming reaction is char gasification with CO₂ [7]. In addition, for reducing carbon composite agglomerates (CCAs) in DRI process, the carbon gasification reaction with CO₂ is an important step that induces the fast self-reduction process of CCAs [8]. It is noteworthy that high gasification reactivity of chars with CO₂ is beneficial to decrease the amount of unreacted char, which either blocks the stock column in the lower region of a BF and inhibits the flow of reducing gas or decreases the reduction efficiency of CCAs.

The gasification characteristics of different chars can be evaluated using thermogravimetric methods [9–13]. As a result, the kinetic parameters of gasification can provide a fundamental understanding of the gasification process. At present, the methods of thermogravimetric dynamic analysis mainly include model-fitting method and model-free method (isoconversional method) [14]. In the model-fitting method, the models including volume reaction model (VM) [15,16], unreacted core model (URCM) [17] and random pore model (RPM) [11,12,18,19] are usually used to estimate the kinetic parameters. For a type of carbon material, the activation energy value obtained from the model-fitting methods is constant throughout the gasification process. Whereas the isoconversional method can be used to evaluate the activation energy values without assuming or identifying any particular form of the reaction model [20–22]. The activation energy value obtained by the model-free method is not a constant but a function of conversion during the gasification process. Generally, for a multistep kinetic process, it is difficult to find a suitable mechanism function for the model-fitting method. However, the isoconversional (model-free) method is suitable for obtaining reliable kinetic information from at least three sets of experimental data obtained at different heating rates, by which the activation energy obtained varies significantly with the conversion degree. Moreover, the activation energy obtained by the model-free method can be used to verify that gained by the model-fitting method.

In this work, the gasification reactivity and kinetic process of different chars such as sawdust char (SD-char), wheat straw char (WS-char), rice husk char (RH-char), bamboo char (BB-char) and anthracite coal (AC) were studied using the nonisothermal thermogravimetric analysis (TGA). Based on four sets of thermogravimetric (TG) curves under different heating rates, the apparent activation energy values at different conversion degrees were solved by the integral isoconversional nonlinear (NL-INT) method [22]. On the basis of the activation energy values calculated by the NL-INT method, the kinetic parameters of gasification of different carbon materials with CO₂ were estimated using the RPM [18,19]. It is expected that this research will be helpful for understanding the mechanism of gasification reaction and improving the co-gasification of biochar and coal in the gasifier.

2 Materials and methods

2.1 Raw materials

The biomass feedstock sawdust (SD), wheat straw (WS), rice husk (RH) and bamboo (BB) were used for producing biochars by slow pyrolysis. Before carbonization, the biomass raw materials were rinsed, dried and smashed to the size of 0.25–5 mm. These pretreated samples were pyrolyzed in a controlled temperature tube-type resistance furnace with a flowing nitrogen atmosphere at a temperature of 973 K for 120 min. The biochars derived from pyrolysis were then grinded and screened for characterization analysis and gasification experiment. The AC raw material was taken from Yangquan city, Shanxi Province in China. The proximate and ultimate analyses of biomass and coal raw materials and biochars were conducted using the Chinese standard GB/T 212-2001 and GB/T 476-2001, respectively (Table 1). As shown in Table 1, after pyrolysis, the volatile matter content of the biochars is lower than that of AC, and the main contents are fixed carbon and ash. The ash content of WS-char and RH-char is as high as 32.52% and 42.44%, respectively.

The SEM images of biochars and anthracite are shown in Figure 1. The alveolate structure and rough surface of the biochars can be clearly seen from Figure 1a–d. At the same magnification, the pore sizes of different biochars vary significantly. The pore diameter of WS-char is large and the pore wall is thin, whereas the pore size of RH-char is small. Some biochar particles maintain a larger particle size, while others are crushed. The regular pore structure of large char

Table 1: Proximate and ultimate analyses of carbonaceous materials (wt%)

Sample	Proximate analysis				Ultimate analysis				
	H ₂ O	FC _d	A _d	V _d	C _d	H _d	O _d	N _d	S _d
SD	8.67	16.83	2.45	80.72	48.89	6.75	41.39	0.44	0.08
SD-char		90.54	3.89	5.57	92.24	1.23	1.63	0.95	0.06
WS	6.95	18.41	7.28	74.31	41.51	4.02	46.54	0.43	0.22
WS-char		62.16	32.52	5.32	63.73	0.91	1.41	0.92	0.51
RH	7.02	15.13	17.66	67.21	42.23	4.41	35.22	0.41	0.07
RH-char		52.85	42.44	4.71	54.59	0.83	1.09	0.84	0.21
BB	9.01	13.81	3.33	82.86	45.04	5.37	45.54	0.65	0.07
BB-char		79.77	16.21	4.02	79.52	1.01	2.37	0.78	0.11
AC	7.50	75.76	11.25	12.99	78.25	3.53	5.19	1.05	0.73

Note: FC_d, A_d and V_d are fixed carbon, ash and volatile matter with regard to dry basis, respectively; d, dry basis.

particles is clearly visible, while that of the small particles is not easily observed. When the large char particle is crushed, the pore walls are broken and the small particles are mostly flaky and rough with cracks. By contrast, as shown in Figure 1e, the surface of AC granule is smooth with dense structure. According to the research [23], the porosity of biochars is about 3 times more than that of coal and the specific surface of biochars is high compared to coke and coal.

2.2 Experimental procedure

The CO₂ gasification experiments of biochars and anthracite were conducted by means of thermal gravimetric analyzer (TGA, METTLER TOLEDO STARE 9.20). Each sample weighing about 25 ± 2 mg was put into a crucible, which was moved to the hot zone of the reaction furnace. For the biochars, each experiment was conducted under nonisothermal condition from room temperature to the final temperature of 1,473 K at different heating rates of 5, 10, 15 and 20 K/min; whereas for the anthracite, the final temperature is 1,553 K. The flow rate of the gasifying agent (CO₂, with purity of 99.9%) for the reaction zone is 50 mL/min. The experimental data were continuously recorded in real time by a computer.

2.3 Characteristic parameters of gasification

2.3.1 Gasification conversion

The gasification conversion degree (α) can be calculated by the following equation:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty} \quad (1)$$

where W_0 , W_t and W_∞ (mg) are the initial sample weight, sample weight at the time of t and final sample weight during the gasification process, respectively. In this study, the temperature of 600 K is regarded as the starting temperature at which the sample mass is the initial one. In this way, the effect of nonreactive weightlessness on the extent of conversion can be avoided by eliminating the volatilization of moisture.

2.3.2 Conversion rate

The conversion rate γ (1/min) can be described by the following equation based on the first derivative of α :

$$\gamma = \frac{d\alpha}{dt} \quad (2)$$

where t (min) is the reaction time during the gasification process.

2.4 Kinetic equation

Generally, the rate of solid-state reactions can be given by the equation:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

For the nonisothermal process, when the temperature rises at a constant rate ($\beta = dT/dt$), Equation (3) can be written as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (4)$$

Figure 1: SEM images of samples: (a) SD-char; (b) WS-char; (c) RH-char; (d) BB-char and (e) AC.

where A and E are the kinetic parameters, the preexponential factor (1/min) and the activation energy (kJ/mol), respectively, and R is the universal gas

constant (8.314 J/mol K), T is the thermodynamic temperature (K) and β is the heating rate (K/min), $\beta = dT/dt$.

2.5 The NL-INT method

The NL-INT method was proposed by Vyazovkin [20–22], and it can be used to calculate the credible activation energy without choosing the model functions by means of multistrip curves from different heating rates.

The integral formula of the abovementioned non-isothermal dynamic equation (Equation (4)) can be presented as follows:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (5)$$

$$\approx \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{A}{\beta} I(E, T)$$

where $f(\alpha)$ and $G(\alpha)$ are, respectively, the differential and integral forms of kinetic model functions and T_0 is the initial reaction temperature (K).

Therefore, for a given conversion degree α and a series of experiments performed at different heating rates β_i ($i = 1, \dots, n$), it follows from Equation (6) that:

$$\frac{A}{\beta_1} I(E_\alpha, T_{\alpha,1}) = \frac{A}{\beta_2} I(E_\alpha, T_{\alpha,2}) = \dots = \frac{A}{\beta_n} I(E_\alpha, T_{\alpha,n}) \quad (6)$$

Thereby, the E_α values can be determined by the minimizing evaluation function [20] as follows:

$$\Phi(E_\alpha) = \min \left| \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} - n(n-1) \right| \quad (7)$$

where the temperature integral

$$I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} \exp\left(-\frac{E_\alpha}{RT}\right) dT \quad (8)$$

is solved numerically by the fourth-order Senum–Yang approximation equation:

$$I_{SY-4}(E, T) = \left[T \exp(-u) \cdot \left(\frac{u^3 + 18u^2 + 86u + 96}{u^4 + 20u^3 + 120u^2 + 240u + 120} \right) \right] \quad (9)$$

where $u = E/RT$. The experimental data β_i and $T_{\alpha,i}$ ($i = 1, 2, 3, \dots, n$), based on the same conversion from a series of nonisothermal TG curves at different heating rates, can be substituted into Equation (7) to obtain the E_α values. The golden section method which is one-dimensional search optimization algorithm was employed for the solution of Equation (7). For the NL-INT method, since at least three curves are needed from three

different heating rates, the E_α values are determined from four different heating rates for each type of the material in this study.

3 Results and discussion

3.1 Gasification characteristics of biochars and AC

To quantitatively describe the gasification characteristics of different samples, the parameters including the initial gasification temperature (T_i), the peak conversion temperature corresponding to the maximum conversion rate (T_p) and the final gasification temperature (T_f) were defined according to the previous research [24]. As shown in Figure 2, the initial gasification temperature (T_i), the peak conversion temperature (T_p) and the final gasification temperature (T_f) from the conversion curves and conversion rate curves were defined and evaluated using the graphic method as described in the literature [25]. First, through the conversion rate peak point A, a vertical line is made upward to intersect the conversion curve at point B, which corresponds to the peak conversion temperature (T_p). Second, a tangential line to conversion curve is made at point B, which meets the extended final-level line of conversion curve at point C and meets the initial-level line at point D. Third, another vertical line is made downward through point C, which corresponds to the final gasification temperature (T_f). The corresponding temperature of point D is defined as the initial gasification temperature (T_i).

Figure 2: Initial gasification temperature (T_i), the peak conversion temperature (T_p) and the final gasification temperature (T_f).

Figure 3: Gasification curves of different carbonaceous materials with CO₂: (a) SD-char; (b) WS-char; (c) RH-char; (d) BB-char and (e) AC.

Conversion degree and reaction rate curves of gasification of different biochars and anthracite at different heating rates are shown in Figure 3. It can be seen that with an

increase in heating rate from 5 to 20 K/min, the curves of conversion ratio and reaction rate move toward the high temperature. By increasing the heating rate, the temperature

corresponding to the same conversion ratio increases, whereas the conversion ratio corresponding to the same temperature decreases. The main reason is that the residence time in each temperature is shortened and the heat transfer hysteresis is strengthened with an increase in the heating rate. It can also be seen that the peak of the reaction rate curve increases by increasing the heating rate. The reason is that the total reaction time shortens when the heating rate increases.

Overall, for different samples (biochars and AC), the shape of these reaction curves is similar except the differences in the initial gasification temperature, final gasification temperature, peak conversion temperature and conversion rate during the gasification process. As can be seen in Figure 3, the gasification process of the different carbonaceous materials can be divided into three stages, using the conversion and reaction rate curves as shown in examples in Figure 3a, at the heating rate of 5 K/min. For the first stage, below the temperature of T_i , the conversion degree changes slowly and the conversion rate is low. The removal of volatiles is dominant and it almost ends at this stage. In the second stage, carbon gasification mainly occurs with CO₂ and weight loss occurs rapidly, and a peak can be observed in the reaction rate curve. For the third stage, above the temperature of T_f , the carbon gasification is almost over and the mass of residue tends to be constant. Gasification and weight loss mainly occur in the second stage. The gasification characteristic parameters of the different carbonaceous materials are shown in Table 2. It can be seen that the order of T_i and T_p for the samples is, from high to low, AC, BB-char, RH-char, SD-char and WS-char. Whereas T_f of the samples has a different order which is AC, RH-char, BB-char, WS-char and SD-char. At the same time, the order of maximum reaction rate for these samples is, from high to low, WS-char, SD-char, BB-char, RH-char and AC. Therefore, the gasification reactivity cannot be described only by means of T_i and T_f . In order to describe the gasification reactivity of the different carbonaceous materials, the comprehensive gasification characteristic index S is used for this work. The equation of index S can be written as follows [11,26,27]:

$$S = \frac{(\mathrm{d}\alpha/\mathrm{d}t)_{\max} \cdot (\mathrm{d}\alpha/\mathrm{d}t)_{\text{mean}}}{T_i^2 \cdot T_f} \quad (10)$$

where $(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$ and $(\mathrm{d}\alpha/\mathrm{d}t)_{\text{mean}}$ are the maximum and average gasification reaction rates, respectively. As shown in Table 2, the index S of different samples from high to low can be sorted as that of WS-char, SD-char, BB-char, RH-char and AC. Thus, from high to low, the gasification reactivity of five samples can be ranked as that of WS-char, SD-char, BB-char, RH-char and AC. Meanwhile, the maximum and average reaction rates of five carbon samples have almost the same

sequence. Therefore, the index S is mainly determined by the reaction rate. According to the literature [11], the carbon crystalline structure of carbonaceous materials plays an important role in carbon gasification reactivity. The carbon structure of biochars is mostly amorphous carbon structure and the structure of anthracite is graphitic carbon. The gasification reactivity of carbonaceous materials decreases with an increase in the graphitization degree of its carbon structure.

3.2 Kinetic analysis

According to a series of conversion curves at the heating rates of 5, 10, 15 and 20 K/min, the E_α values corresponding to each conversion degree of gasification for different carbonaceous materials were obtained by means of the NL-INT method. By plotting the numerical E_α values against the corresponding conversion degree, α , a dependence of activation energy upon conversion has been manifested in Figure 4. It can be seen that the E_α values of biochars increase generally with an increase in the conversion degree, whereas the value of AC decreases from 314 to 180 kJ/mol in the early stage of gasification. Except for AC, the activation energy sequence of the four biochars is basically unchanged and the order from low to high is WS-char, SD-char, RH-char and BB-char. However, as the conversion degree increases to more than 0.3, the activation energy value of AC becomes lower than that of RH-char and BB-char. It can be explained that the pyrolysis of volatiles in AC induces the significant increase in the specific surface area and active points at the early stages of gasification. By contrast, due to the pre-pyrolysis, the volatile matter content of the biochars is lower than that of AC, and the pore structure of the biochars has been well developed. The volatile matter content should not be the main factor affecting the gasification of biochars. On the other hand, when the conversion degree is lower than 0.3, the gasification reaction of carbon with CO₂ does not take place appreciably and the residual volatile matter in the chars is pyrolyzed slowly. Structural ordering, carbonization, existing pore collapse and micropore coalescence led to a decrease in the surface area and thermal deactivation of the chars [28]. When the conversion degree is up to some extent, the removal of volatile matter comes to an end and carbon gasification develops, resulting in the immutability of E_α value for different materials. For AC, RH-char and BB-char, the values of E_α remain nearly unchanged when the conversion degree is in the range of 0.25–0.95. While for SD-char and WS-char, the corresponding range of conversion is $0.30 < \alpha < 0.90$. Therefore, at a certain range of

Table 2: Gasification characteristic parameters of different samples

Samples	Heating rate (K/min)	T_i (K)	T_p (K)	T_f (K)	$(d\alpha/dt)_{max}$ (1/min)	$(d\alpha/dt)_{mean}$ (1/min)	$S \times 10^{12}$
SD-char	5	1043.8	1140.8	1159.1	0.07378	0.00872	0.52
	10	1103.9	1194.4	1222.8	0.11953	0.01589	1.30
	15	1123.4	1221.9	1247.9	0.17200	0.02297	2.56
	20	1135.4	1244.6	1284.2	0.17501	0.02901	3.16
WS-char	5	1008.0	1089.8	1182.3	0.09207	0.00845	0.70
	10	1086.4	1136.3	1232.6	0.17500	0.01570	2.05
	15	1105.6	1161.2	1289.4	0.21871	0.02164	3.33
	20	1117.2	1176.9	1297.3	0.24864	0.02858	4.84
RH-char	5	1122.8	1212.3	1257.2	0.03985	0.00756	0.20
	10	1164.8	1266.5	1313.8	0.07160	0.01393	0.58
	15	1180.0	1280.2	1332.2	0.10622	0.02038	1.21
	20	1200.4	1319.1	1377.9	0.12201	0.02560	1.64
BB-char	5	1135.0	1223.8	1239.8	0.07390	0.00781	0.37
	10	1173.5	1271.1	1292.2	0.11600	0.01445	0.96
	15	1193.1	1289.1	1316.2	0.15760	0.02091	1.80
	20	1218.9	1340.5	1373.8	0.15134	0.02573	1.96
AC	5	1215.9	1313.8	1384.8	0.03151	0.00611	0.10
	10	1260.0	1378.2	1444.9	0.05794	0.01121	0.30
	15	1280.2	1410.3	1465.7	0.07687	0.01551	0.52
	20	1296.1	1423.5	1492.4	0.09889	0.02047	0.85

Figure 4: Relation between activation energy and conversion for different biochars and anthracite.

conversion degree, the activation energy is nearly independent of the conversion degree, and a single reaction mechanism function can be used for describing the gasification of each biochar or AC. It can also be obtained that, at the range of $0.30 < \alpha < 0.90$, the mean values of E_α from low to high can be sorted as that of WS-char, SD-char, AC, RH-char and BB-char, respectively, 134.3, 143.8, 168.5, 184.8 and 193.0 kJ/mol.

It is well-known that combustion and gasification of char involve a gas–solid reaction. In general, the kinetic

models include the VM, URCM and RPM, which are used to describe the gas–solid reaction [12,29]. The governing equations of RPM have been developed for the first-order reaction by Bhatia and Perlmutter [18,19]. In the RPM model, the pore size distribution and the pore structure and its evolution were taken into account during the reaction process. It was confirmed that the RPM is suitable for describing the gasification of biochars. In this work, based on the activation energy values from the NL-INT method, the RPM was used to evaluate the kinetic parameters of gasification. The mechanism functions of the RPM can be written as follows:

$$f(\alpha) = (1 - \alpha) \sqrt{1 - \psi \ln(1 - \alpha)} \quad (11)$$

where ψ is the pore structure parameter. Thus, the differential and integral expressions of nonisothermal kinetic equations can be given as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (12)$$

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (13)$$

With regard to Equation (13), the integral on the right-hand side of the equation is an unconventional integral which was written as an approximate expression by Coats and Redfern [30] and Marini *et al.* [31] as follows:

Table 3: Kinetic parameters fitted to Equation (15) for the gasification reaction of different samples

Sample	β (K/min)	E (kJ/mol)	RPM			
			A (1/min)	ψ	R^2	$\ln A$
SD-char	5	143.8	3.6705×10^5	0.9605	0.9892	12.8133
	10		2.3519×10^5	4.6281	0.9967	12.3681
	15		2.6708×10^5	4.1016	0.9964	12.4953
	20		3.2428×10^5	1.8320	0.9962	12.6894
WS-char	5	134.3	2.3803×10^5	0.4157	0.9768	12.3802
	10		6.2551×10^4	39.5279	0.9964	11.0437
	15		8.4914×10^4	21.9138	0.9962	11.3494
	20		9.7843×10^4	20.3093	0.9960	11.4911
RH-char	5	184.8	1.0778×10^7	0.3013	0.9938	16.1930
	10		9.6694×10^6	0.2339	0.9939	16.0845
	15		1.1121×10^7	0.3999	0.9942	16.2243
	20		9.1348×10^6	0.2137	0.9955	16.0276
BB-char	5	193.0	1.9663×10^7	1.3952	0.9950	16.7942
	10		1.9145×10^7	1.1209	0.9949	16.7676
	15		1.9810×10^7	1.4022	0.9950	16.8017
	20		1.7234×10^7	0.2306	0.9914	16.6624
AC	5	168.5	2.9166×10^5	0.8198	0.9947	12.5833
	10		3.0077×10^5	0.5514	0.9907	12.6141
	15		3.3362×10^5	0.1963	0.9870	12.7178
	20		3.6102×10^5	0.2172	0.9842	12.7967

$$\frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AR}{\beta E} \left[T^2 \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) - T_0^2 \left(1 - \frac{2RT_0}{E}\right) \exp\left(-\frac{E}{RT_0}\right) \right] \quad (14)$$

where T_0 is the starting temperature of reaction, K . Combining Equations (11)–(14) followed by integrating, the dependence of conversion α on temperature T can be given as Equation (15):

$$\alpha = 1 - \exp\left\{ \frac{1 - \left[1 + \frac{\psi A_{\text{RPM}} R}{2\beta E} \left(T^2 \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) - T_0^2 \left(1 - \frac{2RT_0}{E}\right) \exp\left(-\frac{E}{RT_0}\right) \right) \right]^2}{\psi} \right\} \quad (15)$$

where A_{RPM} denotes the preexponential factor (1/min) in kinetic equation of RPM.

In the previous studies, the parameters E_a and A were simultaneously obtained by using the model-fitting methods. However, in this study, based on the mean E_a values from the NL-INT method, Equation (15) is used to solve the kinetic parameters including A and ψ from

experimental data by means of nonlinear least squares fitting methods. Table 3 shows the mean E_a values calculated by using the NL-INT method and the fitted parameters (A and ψ) determined from the data obtained at different heating rates for each sample. Figure 5 shows a comparison of experimental and fitted conversion degree as a function of reaction temperature for (a) SD-char, (b) WS-char, (c) RH-char, (d) BB-char and (e) AC. Overall, the RPM fits the experimental data well for the different samples due to the high R^2 values. However, the RPM cannot describe very well the gasification of the samples in the initial stage ($\alpha < 0.3$). Especially for WS-char, the R^2 for the fitted and experimental conversion curves at heating rate of 5 K/min gets the minimum value of 0.9768. This is related to the variation in activation energy value in the initial stage of gasification. This indicates that a complex multistep mechanism occurs in the initial stage of gasification. On the contrary, thereafter, it seems to be true that there is a single-step gasification mechanism for the rest of the gasification process.

Comparing the mean activation energy with the reactivity of char gasification, it can be seen that the order is different. The main reason is that the gasification reaction rate is determined by both activation energy (E) and preexponential factor (A) as shown in Equation (3). Even so, it is quite clear that by increasing the

Figure 5: Experimental and fitted conversions for different biochars and anthracite during gasification with CO_2 : (a) SD-char; (b) WS-char; (c) RH-char; (d) BB-char and (e) AC.

preexponential factor and decreasing the activation energy, the gasification reaction rate increases. Thus, although the activation energy of AC decreases to be

lower than that of RH and BB, its lower preexponential factor leads to a lower reaction rate. Furthermore, the relation of the mean value of logarithmic preexponential

Figure 6: Relation between the values of apparent activation energy and preexponential factor for different biochars and AC.

factor and the activation energy value E_a for the gasification of different chars under different heating rates is shown in Figure 6. The clear linear relationship between $\ln A$ and E is the well-known kinetic compensation effect (KCE), which is caused by fitting a conversion curve at a single-heating rate by using single kinetic function model-fitting method based on the Arrhenius equation [32]. Thus, the expression of KCE in this study can be given as:

$$\ln A = 0.085E - 0.07054 \quad (16)$$

From Figure 6, it can also be observed that the biomass chars maintain strong correlation and the AC deviates from the KCE curve. This could be due to the similarity of carbonaceous structure of biochars and the difference in reactivity between biochars and AC. This also means that the KCE exists in the same or similar types of reactions under the same experimental conditions for the same type of materials, i.e., they have the same or similar reaction mechanisms.

4 Conclusions

In this work, the gasification behavior of different biomass chars and AC with CO₂ was investigated by nonisothermal TGA. The dependence of activation energy upon the conversion of gasification for different biochars and AC was achieved by using the NL-INT method which is a model-free method. Based on the activation energy values from the NL-INT method, the kinetic parameters of gasification of different chars with

CO₂ were obtained using the RPM. The results obtained can be summarized as follows:

- (1) The comprehensive gasification characteristic index S can well represent the gasification characteristics of different carbon materials. The CO₂ gasification reactivity of different biomass chars and anthracite from high to low can be sorted as that of WS-char, SD-char, BB-char, RH-char and AC. The gasification reactivity of biochars is stronger than that of anthracite.
- (2) In the initial stage of gasification, the activation energy values of biochars increase generally with increasing conversion degree, whereas the value of AC decreases. However, the values remain almost unchanged when the conversion degree is up to some extent. At the range of $0.30 < \alpha < 0.90$, the mean values of E_a from low to high can be sorted as that of WS-char, SD-char, AC, RH-char and BB-char, respectively, 134.3, 143.8, 168.5, 184.8 and 193.0 kJ/mol. It is shown that a complex multistep mechanism occurs in the initial stage of gasification, while a single-step gasification mechanism exists in the rest of the gasification process.
- (3) The RPM as a model-fitting method is suitable for describing the gasification of biomass chars and AC except the initial gasification. It is found that the KCE exists in the gasification reactions of biochars and AC. However, the AC deviates markedly from the KCE curve. This could be due to the similarity of carbonaceous structure of biochars and the difference in reactivity between biochars and AC.

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