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A comprehensive fractal char combustion model[☆]Yuting Liu^{1,2,*}, Rong He¹¹ Department of Thermal Engineering, Tsinghua University, Beijing 100084, China² Institute of Materials, China Academy of Engineering Physics, Mianyang 621908, China

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ABSTRACT

The char combustion mechanisms were analyzed and a comprehensive fractal char combustion model was developed to give a better understanding and better predictions of the char combustion characteristics. Most of the complex factors affecting the char combustion were included, such as the coupling effects between the pore diffusion and the chemical reactions, the evolution of the char pore structures and the variation of the apparent reaction order during combustion, the CO/CO₂ ratio in the combustion products and the correction for oxy-char combustion. Eleven different chars were then combusted in two drop tube furnaces with the conversions of the partly burned char samples measured by thermogravimetric analysis. The combustion processes of these chars were simulated with the predicted char conversions matching very well with the measured data which shows that this char combustion model has good accuracy. The apparent reaction order of the char combustion decreases, stabilizes and then increases during the combustion process. The combustion rates in the oxy-mode are generally slower than in the air-mode and the effect of the char-CO₂ gasification reaction becomes obvious only when the temperature is relatively high and the O₂ concentration is relatively low. © 2016 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

The char particles are typical porous media with complex pore structures [1–3], so the combustion reactions can occur at both the external and the internal surfaces of the char particle. What's more, the pore structure in the char particles changes greatly during combustion [3]. Many factors affect char combustion including the gas diffusion in the char pores, catalysis or inhibition effects of the ash, graphitization of the char and so on, among which the pore diffusion is the most important [4]. The pore diffusion and the chemical reactions inside the pores are coupled with each other [5] which increases the complexities of the char combustion modeling. Since the char particle pore structure determines the pore diffusion resistance [2] and affects the collisions between the gas molecules and the pore surfaces, the pore structure significantly affects the char combustion kinetics [4,6].

However, the char pore structures are too complex to describe with the classical geometric method [7], so the fractal theory has been used instead [1,7–13]. The fractal dimension of the char pore structures, D_f , based on mercury intrusion measurements [7] is the most representative one:

$$D_f = -\frac{d \ln [dS_a(r_{\text{pore}})/dr_{\text{pore}}]}{d \ln (r_{\text{pore}})} \quad (1)$$

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* Corresponding author.

E-mail addresses: liuyuting10@mails.tsinghua.edu.cn (Y. Liu), rhe@mail.tsinghua.edu.cn (R. He).

where r_{pore} is the char pore radius (m) and $S_a(r_{\text{pore}})$ is the accumulated pore surface area (m²) corresponding to r_{pore} in the mercury intrusion measurements. D_f describes the complexity of the char pore structures with a larger D_f indicating a more complex structure and a higher pore diffusion resistance. The gas diffusion in a bulk space can be described by Fick's diffusion law. However, in small char pores with pore sizes close to the gas molecular mean free path, the gas molecular motion is restricted and the collision frequency between the gas molecules and the pore surface is much higher than the intermolecular collision frequency. In this situation, Fick's diffusion law is not suitable [14–16]. In either case, fractal theory can be used to describe the pore diffusion effects.

The pore diffusion effects have been extensively included in various char combustion models among which the traditional intrinsic model [6,17,18] is the most famous one. The tortuosity factor, τ , is used to describe the complexity of the pore structures in the intrinsic model. However, τ has no scientific definition and cannot be measured or calculated which makes the intrinsic model difficult to use. In the intrinsic model, the pore diffusion is described by the Fick's and Knudsen's diffusion law both of which cannot be conveniently used for the fractal char pores [14–16]. In addition, the intrinsic model does not include the evolution of the char pore structure during combustion.

In this article, a comprehensive fractal char combustion model was developed. The apparent reaction order, n , during combustion was allowed to vary. Four parameters (porosity, θ , specific surface area, S_g , fractal dimension D_f and particle diameter, d_p) were used to describe the char pore structures with these parameters also allowed to vary

during combustion. The model gives reasonable predictions of the CO/CO₂ ratio in the combustion products. A correction factor, α , was introduced to describe the effect of the high CO₂ concentration on the total char combustion rate to expand the scope of the char combustion model. Eleven different chars were combusted in two drop tube furnaces with the conversions of the partly burned char samples measured using thermogravimetric analysis. The combustion processes of these chars were then simulated by the model with the predicted char conversions compared with the measured data to determine the model parameters and verify the model. Finally, the model was used to study some phenomena in the char combustion.

2. Development of the Comprehensive Char Combustion Model

The comprehensive char particle combustion model in this article consists of five parts with the char combustion rate expression, the char particle pore structure evolution, the variation of the apparent reaction order, the CO/CO₂ ratio in the combustion products and the correction factor for oxy-char combustion. The first four parts have already been studied by our research group [3–5,19] and they are combined with the fifth part in this paper to form a complete model.

2.1. Char combustion rate expression

A char combustion rate expression was developed from a theoretical derivation in [4]. The coupling effects between the chemical reactions and the gas diffusion inside the char pores were considered. The final form of the char combustion rate expression is:

$$k_a = 3k_i \left(\coth Q / Q - Q^{-2} \right),$$

$$\text{where, } k_i = A_i \exp(-E_i/RT_p), Q = \frac{1}{2} \left[\frac{k_i}{\zeta \chi (T_p/0.032)^{1/2}} \right]^{1/2}, \quad (2)$$

$$\chi = \frac{2\theta^{5/3}}{S_g \rho_i^2 d_p^2 (1-\theta)^2} \exp(-D_f).$$

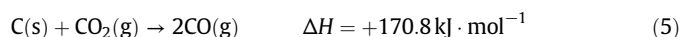
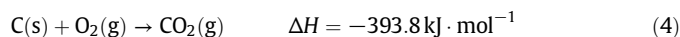
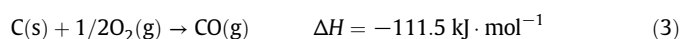
where k_a is the apparent reaction rate constant, k_i is the intrinsic reaction rate constant, Q is an intermediate variable, A_i is the pre-exponential factor, E_i is the intrinsic activation energy ($\text{J} \cdot \text{mol}^{-1}$), T_p is the particle temperature (K), R is the universal gas constant, ζ is a scale factor, θ is the porosity, S_g is the specific surface area ($\text{m}^2 \cdot \text{kg}^{-1}$), ρ_i is the char true density ($\text{kg} \cdot \text{m}^{-3}$), d_p is the particle diameter (m), D_f is the

fractal dimension defined in Eq. (1), χ is a dimensionless modulus which is a combination of pore structure parameters to indicate the pore diffusion resistance with a larger χ indicating a lower pore diffusion resistance [3–5]. In Eq. (2), A_i , E_i , and ζ are model parameters to be determined from experimental data.

2.2. Char particle pore structure evolution during combustion

Fractal pore models [20] generated by a random walk algorithm can be used to simulate real char particles. Fig. 1(a) shows a schematic diagram of a fractal pore model. The pore shapes in the model are irregular as in natural char particles (Fig. 1(b)) and the model also has good fractal properties. Thus, the fractal pore model is also called the numerical char particle model. The random walk process parameters can be adjusted to generate numerical char particle models with various porosities and fractal dimensions.

The complete char combustion processes were simulated [3] with this numerical char particle model with four chemical reactions:

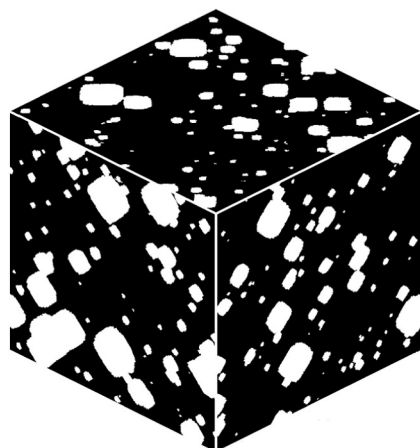


They were described by simple collision theory [21] with reaction rates expressed as:

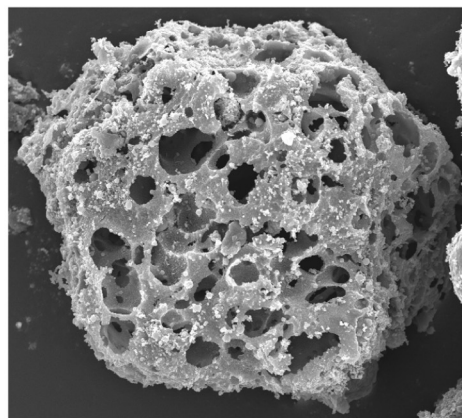
$$\text{Reaction rate} = (\text{Collision frequency}) \times (\text{Fraction of collisions with at least the threshold energy}) \quad (7)$$

Since the Fick's and Knudsen's diffusion law cannot be conveniently used for the fractal char pores [14–16], the diffusion law [22] based on the kinetic theory of gases [23] was used.

21 different numerical char particle models were used in the char combustion simulations with 756 cases in total for various operating conditions [3] to calculate the variations of the pore structure parameters (θ , S_g , D_f and d_p) with the char conversion, X , during combustion. Commonly used empirical expressions with some modifications were then used to associate these pore structure parameters with X . Then,



(a)



(b)

Fig. 1. Schematic diagram of the fractal pore model (a) and SEM photo of a bituminous char particle (b).

all the coefficients in each expression were related to the operating conditions and the initial pore structure parameters. Finally, the variations of the pore structure parameters during combustion were expressed as:

$$\theta = (1-a_1) - (1-a_1-\theta_0)(1-X)^{a_2} \quad (8)$$

$$a_1 = (1.0372 - 2687.8\chi_0)(1-\theta_0)ash_0 \quad (9)$$

$$a_2 = \exp[-1.4071 \times 10^{-5}T_0/(P_{O_2,0}\chi_0/101325)^{0.35}] \quad (10)$$

$$S_g = (S_{g0}-b_1)(1-X)[1-b_2 \ln(1-X)]^{b_3} + b_1 \quad (11)$$

$$b_1 = (0.8265 + 3142.1\chi_0)S_{g0}ash_0 \quad (12)$$

$$b_2 = 1.8042 \times 10^5 (P_{O_2,0}/101325)^{0.3} \chi_0^{0.2}/T_0 \quad (13)$$

$$b_3 = 2 \exp(-0.07283/\chi_0^{0.25}) \quad (14)$$

$$D_f = (D_{f0}-c_1) \exp(-c_2X) + c_1 \quad (15)$$

$$c_1 = 0.2879D_{f0}ash_0/\chi_0^{0.1} \quad (16)$$

$$c_2 = 3.1256 \times 10^5 (P_{O_2,0}/101325)^{0.3} \chi_0^{0.4}/T_0 \quad (17)$$

$$d_p = (d_{p0}-d_1)(1-X)^{d_2} + d_1 \quad (18)$$

$$d_1 = (0.9017 + 1435.9\chi_0)d_{p0}ash_0^{0.34} \quad (19)$$

$$d_2 = 0.3354(1-a_2) \quad (20)$$

$$\chi_0 = \frac{2\theta_0^{5/3}}{S_{g0}^2\rho_f^2d_{p0}^2(1-\theta_0)^2} \exp(-D_{f0}) \quad (21)$$

where T is the temperature (K), P_{O_2} is the O_2 partial pressure at the particle external surface (Pa), ash is the ash content, X is the char conversion, a_1 , a_2 , b_1 , b_2 , b_3 , c_1 , c_2 , d_1 and d_2 are constants for a given combustion process and the subscript 0 represents the initial value.

2.3. Variation of the apparent reaction order during combustion

The char combustion apparent reaction order, n , has been extensively studied in experiments, but only the values of n for specific chars for specific reaction conditions have been given and no clear universal relationships has been proposed [5,24]. This may be the reason why the assumption $n = 1$ is still commonly used in many simulations.

Recently, an expression for n was developed for different chars and different reaction conditions from the numerical simulations with the expression validated by experimental data [5]. The simulations used the numerical char particle model in Fig. 1(a) and the chemical reactions and pore diffusion model described in Section 2.2.

10 different numerical char particle models were used in the char combustion simulations with 600 cases in total for various operating conditions [5]. The values of n in each case were obtained. First, the relationships between n and the operating conditions were analyzed for each numerical char particle model to form 10 preliminary expressions. Then, the coefficients in the 10 expressions were correlated by introducing the effect of the particle category. Finally, the expression for n was written as:

$$n = \left\{ 1 + 1.0832(-73907.0\chi + 9.7345) \times \exp\left[-\left(6.5549 \times 10^6\chi + 2231.2\right)/T_p/(P_{O_2}/101325)^{0.3}\right] \right\}^{-1} \quad (22)$$

where T_p is the char particle temperature (K), P_{O_2} is the O_2 partial pressure at the particle external surface (Pa) and χ is the modulus which is the same as in Eq. (2).

2.4. Apparent CO/CO₂ ratio in the combustion products

The apparent CO/CO₂ ratio in the combustion products is an important factor affecting the char combustion [19]. Since the heat released when CO₂ is the combustion product is 3.5 times that when CO is the combustion product, a small difference in the apparent CO/CO₂ ratio will lead to differences of hundreds of degrees in the combustion temperature [25]. Usually, the apparent CO/CO₂ ratio is thought to be a function of the char particle temperature, T_p , and the O_2 partial pressure at the particle external surface, P_{O_2} , based on experimental studies [26].

The simulations in Section 2.3 also gave the values of the apparent CO/CO₂ ratio by counting the numbers of CO and CO₂ molecules diffusing out of the numerical char particle [5]. A correlation of the apparent CO/CO₂ ratio calculated in the simulations gave:

$$\text{Apparent CO/CO}_2 \text{ ratio} = 47.7645(P_{O_2}/101325)^{-0.2221} \exp(-3063.13/T_p) \quad (23)$$

which is very close to the experimental results in [25].

2.5. Correction factor for oxy-char combustion

In oxy-char combustion, CO₂ is used as the background gas instead of N₂. Since the physical properties of CO₂ and N₂ are very different and CO₂ is not an inert gas like N₂, the char combustion characteristics in oxy-mode will be a little different. The existing studies [27,28] of oxy-char combustion focused on the effects of the high-concentration CO₂ in an external environment on the combustion temperature, the flame stability and so on, but the effects of the high-concentration CO₂ inside the char pores were usually ignored. In the complex char pores, the four chemical reactions in Eqs. (3)–(6) are coupled with each other. If the CO₂ concentration in the pores is excessive, the original balance will be broken.

Since the char combustion model in this paper included all the reactions within the char particle pores, a correction factor, α , was defined as:

$$\alpha = R_{\text{oxy}}/R_{\text{air}} \quad (24)$$

where R_{oxy} is the char combustion rate (mol·s⁻¹) for the CO₂ background gas and R_{air} is the char combustion rate (mol·s⁻¹) for the N₂ background gas. Other operating conditions like the temperature, the O_2 concentration, and the char particle model were the same when R_{oxy} and R_{air} were solved. In this way, the effect of using CO₂ instead of N₂ is reflected in α .

Then, the char combustion simulations were conducted to calculate α for the different operating conditions. 10 different numerical char particle models (as shown in Fig. 1(a)) were used with the particle diameters and the pore structure parameters listed in Table 1. The chemical reactions and the pore diffusion were described in the same way as in Section 2.2. The simulation conditions are summarized in Table 2. The combustion simulations were conducted for each char particle model for each temperature and each atmosphere listed. Thus, there were 600 cases in total, with one half in air-mode (in an O_2/N_2 atmosphere) and the other half in oxy-mode (in an O_2/CO_2 atmosphere). The total pressure for all cases was 101.325 kPa. The simulations gave the total char combustion rate including the effects of the chemical kinetics and the pore diffusion for the corresponding operating conditions. Then, 300 values of α were calculated using Eq. (24).

The C + CO₂ reaction rate is generally much lower than the C + O₂ reaction rate with the measurements giving a C + O₂ reaction rate that was 5 orders of magnitude higher than for the C + CO₂ reaction at

Table 1
Particle diameters and pore structure parameters of the numerical char particle models

Char particle model	Particle diameter/ μm	Porosity/%	Specific surface area/ $\text{m}^2 \cdot \text{g}^{-1}$	Fractal dimension
M01	100	40.09	0.727	2.153
M02	50	40.09	1.455	2.153
M03	100	60.28	1.129	1.146
M04	50	60.28	2.259	1.146
M05	100	31.41	0.513	1.991
M06	50	31.41	1.027	1.991
M07	100	51.10	0.924	1.419
M08	50	51.10	1.847	1.419
M09	100	69.84	1.620	1.104
M10	50	69.84	3.240	1.104

Table 2
Simulation conditions for char combustion in air-mode and oxy-mode

Char particle model	Temperature/K	Atmosphere (mole fraction)
M01, M02, M03, M04, M05, M06, M07, M08, M09, M10.	800, 1000, 1200, 1400, 1600, 1800.	2%O ₂ /98%N ₂ , 2%O ₂ /98%CO ₂ , 10%O ₂ /90%N ₂ , 10%O ₂ /90%CO ₂ , 21%O ₂ /79%N ₂ , 21%O ₂ /79%CO ₂ , 30%O ₂ /70%N ₂ , 30%O ₂ /70%CO ₂ , 40%O ₂ /60%N ₂ , 40%O ₂ /60%CO ₂ .

1073 K and 10 kPa pressure [29]. At higher temperatures, the difference was not so extreme, but the C + CO₂ reaction rate was still much lower than the C + O₂ reaction rate as long as comparable O₂ concentrations were present. So, the α obtained in the simulations were very close to 1.

At lower temperatures, $\alpha < 1$, while at higher temperatures, $\alpha > 1$. Also, the demarcation temperatures are different for different char particles. With lower O₂ partial pressures and higher CO₂ partial pressures, α differed more from 1. Thus, α was correlated as:

$$\alpha = 1 + m_1 \frac{P_{\text{CO}_2}}{P_{\text{O}_2}} \ln(T_p/m_2) \quad (25)$$

where P_{O_2} and P_{CO_2} are the partial pressures of O₂ and CO₂ at the char particle external surface (Pa), T_p is the particle temperature (K), and m_1 and m_2 are constants for a given char particle. The α calculated in the simulations were used correlated to obtain the m_1 and m_2 listed in Table 3.

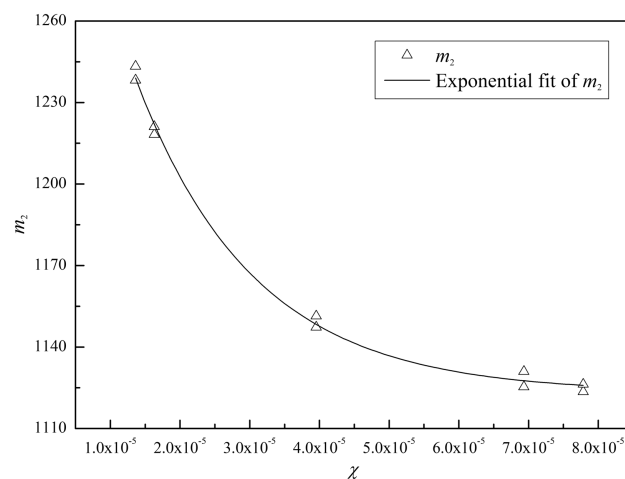
All the correlation coefficients in Table 3 are higher than 0.98, which shows the validity of Eq. (25). The values of m_1 for all the chars are in the range of $(6.02 \pm 0.017) \times 10^{-4}$ with small standard deviations, so m_1 is set to 6.02×10^{-4} for all the chars. m_1 seems to be a scale factor. However, m_2 changes greatly for the different char particles, so it cannot be taken as a constant. The major difference among the char particles is the pore structure which affects the diffusion and reactions in the

Table 3
 m_1 and m_2 for each numerical char particle model

Char particle model	$m_1 \times 10^4$	Standard error of $m_1 \times 10^4$	m_2	Standard error of m_2	Correlation coefficient
M01	6.0280	0.0137	1243.31	0.78	0.9954
M02	6.0116	0.0256	1238.22	1.46	0.9894
M03	6.0218	0.0228	1125.32	1.26	0.9905
M04	6.0281	0.0129	1130.99	0.71	0.9948
M05	6.0271	0.0162	1218.21	0.91	0.9925
M06	6.0283	0.0038	1221.12	0.22	0.9970
M07	6.0283	0.0049	1151.37	0.27	0.9972
M08	6.0331	0.0177	1147.27	0.98	0.9948
M09	6.0149	0.0260	1123.54	1.44	0.9898
M10	6.0368	0.0036	1126.28	0.20	0.9976

pores. The modulus χ defined in Eq. (2) is a combination of the pore structure parameters and m_2 correlates well with the modulus χ with Fig. 2 showing the relationship between m_2 and χ which is correlated as:

$$m_2 = 258.45 \exp(-59051.09\chi) + 1123.3 \quad (26)$$

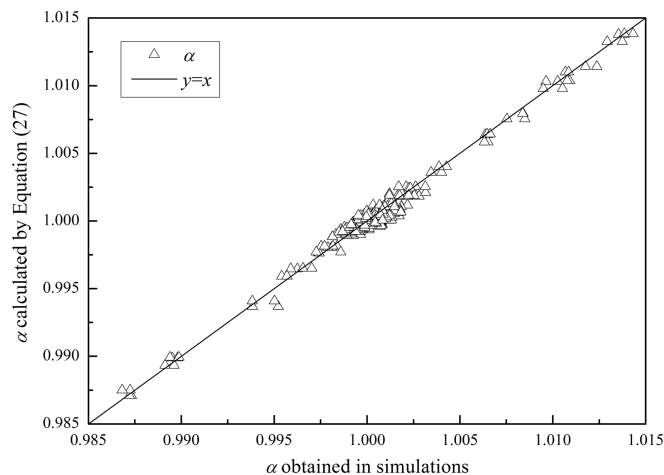
**Fig. 2.** Exponential relationship between m_2 and χ .

Thus, the correction factor, α , has the following form:

$$\alpha = 1 + 6.02 \times 10^{-4} \frac{P_{\text{CO}_2}}{P_{\text{O}_2}} \ln \left(\frac{T_p}{258.45 \exp(-59051.09\chi) + 1123.3} \right) \quad (27)$$

The α calculated by Eq. (27) are compared with those obtained in the simulations in Fig. 3. All the points are distributed along the diagonal which shows that the data correlation works well.

The physical properties of CO₂ are very different from those of N₂. For example, the molar specific heat of CO₂ is significantly higher than that of N₂ and the O₂ diffusion coefficient in CO₂ is much lower than that in N₂. Both factors restrict the char combustion in an O₂/CO₂ atmosphere [27,28]. Thus, the char combustion rate in oxy-mode is usually lower than that in air-mode. However, CO₂ is not inert, especially at high temperatures. As the temperature increases, the C + CO₂ reaction

**Fig. 3.** Data correlation results for α .

rate increases, so the char combustion rate in oxy-mode may exceed that in air-mode.

The transition process can be quantitatively described by defining a critical temperature based on Eq. (27) as $T_{\text{critical}} = m_2 = 258.45 \exp(-59,051.09\chi) + 1123.3$. When $T_p > T_{\text{critical}}$, the char combustion in oxy-mode is enhanced ($\alpha > 1$). When $T_p < T_{\text{critical}}$, the char combustion in oxy-mode is reduced ($\alpha < 1$). T_{critical} is a characteristic of the char particle which only depends on the particle structure. When χ increases, T_{critical} will decrease which indicates that the decreasing pore diffusion resistance tends to compensate for the slower oxy-char combustion caused by the lower O_2 diffusion coefficient in CO_2 . However, T_{critical} has a limit of 1123.3 K. Thus, if the particle temperature is below 1123.3 K, the char combustion rate in oxy-mode will be always lower than that in air-mode.

These conclusions are only for the combustion process inside the char particle, without considering the effect of the bulk diffusion and the reactions in the bulk space. At the same time, only a very short combustion time was simulated since only the char combustion rate for the given operating conditions was needed. Thus, the environmental conditions did not change much in such a short time. As a result, the results do not show the effect of the lower combustion temperature caused by the higher CO_2 molar specific heat in oxy-mode. However, these factors will not affect the use of Eq. (27) in oxy-char combustion simulations as α only depends on the current conditions and α can be used in conjunction with some process simulation programs. α makes the char combustion rates in oxy-mode more accurate and makes the reaction process closer to the real situation.

2.6. Model summary

Sections 2.1–2.5 introduced the five parts of the char particle combustion model. Thus, the combustion rate ($\text{mol} \cdot \text{s}^{-1}$) of a char particle, R_s , can be expressed as:

$$R_s = \alpha k_a m S_g (1 - \text{ash}) C_s^n \quad (28)$$

where α is the correction factor for the oxy-char combustion given by Eq. (27), k_a is the apparent reaction rate constant described by Eq. (2), m is the char particle mass (kg), S_g is the specific surface area ($\text{m}^2 \cdot \text{kg}^{-1}$), ash is the ash content in the char particle, C_s is the O_2 concentration at the particle external surface ($\text{mol} \cdot \text{m}^{-3}$) and n is the apparent reaction order of the char combustion given by Eq. (22). The variations of all the pore structure parameters in Eqs. (2), (22), (27) and (28) during combustion are described by Eqs. (8)–(21). The apparent CO/CO_2 ratio in the combustion products is given by Eq. (23). All these model equations together can give a better description of the complex pore diffusion effects on the char combustion.

Table 4
Proximate and ultimate analyses of the parent coals

Samples	Heating values/ $\text{kJ} \cdot \text{g}^{-1}$	Proximate analysis (dry air basis)				Ultimate analysis (dry basis)				
		Inherent moisture/%	ash/%	Volatile matter/%	Fixed carbon/%	C/%	H/%	N/%	O/%	S/%
No. 1	27.85	0.8	12.0	33.2	54.0	71.39	4.78	1.56	9.81	0.46
No. 2	25.56	5.4	11.2	44.8	38.6	67.75	5.99	0.91	13.94	0.21
No. 3	17.22	9.1	8.8	44.7	37.4	59.7	5.11	0.27	25.73	0.39
No. 4	28.63	1.65	18.4	8.8	71.2	74.7	2.9	0.8	2.8	0.4
No. 5	29.22	1.4	16.8	14.2	67.6	74.7	3.7	1.3	3.2	0.3
No. 6	28.74	3.3	15.9	26.3	57.8	70.7	4.2	1.3	7.6	0.3
No. 7	28.84	1.7	16.2	11.5	70.6	75.1	3.5	1.3	3.5	0.4
No. 8	24.91	14.2	1.0	43.8	41.0	72.3	5.4	0.8	20.4	0.1
No. 9	29.22	1.72	14.3	13.0	71.0	77.1	3.8	1.2	3.2	0.4
No. 10	27.84	7.0	9.7	28.1	55.2	72.3	4.7	0.9	11.6	0.8
No. 11	29.38	2.7	14.5	10.2	72.6	77.9	3.6	0.8	2.8	0.4

3. Drop Tube Furnace Experiments

Experiments were conducted [4] to determine the unknown model parameters (A_i , E_i and ζ) and to verify the model.

11 different chars were combusted in two drop tube furnaces (DTFs) with the proximate and ultimate analyses of the 11 parent coals listed in Table 4. These chars were divided into two groups with Nos. 1–3 in Group 1 tested in furnace 1 and Nos. 4–11 in Group 2 tested in furnace 2. The two furnaces were similar with the same schematic diagram shown as in Fig. 4. Both furnaces had 50 mm inner diameters. The length of furnace 1 was 750 mm and the length of furnace 2 was 1000 mm. In furnace 1, the char particle injector was 310 mm from the inlet and the sampling points were distributed along the furnace tube to obtain char samples with different conversions. In furnace 2, the char particle injector was 200 mm from the inlet and the chars were only sampled at the furnace tube outlet.

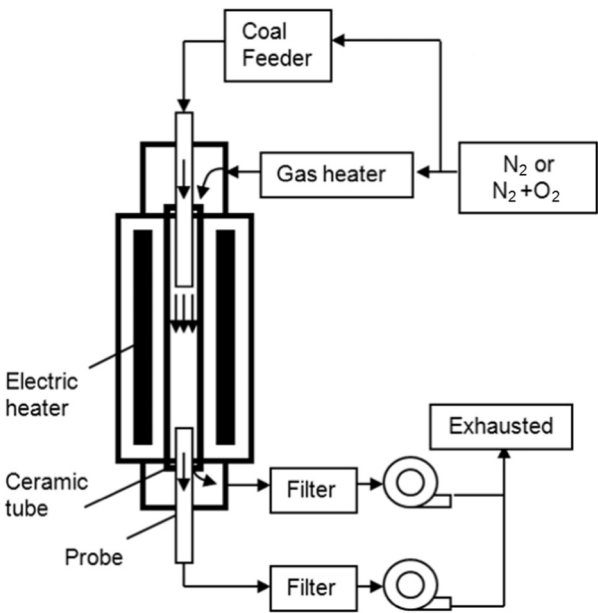


Fig. 4. Schematic diagram of the drop tube furnace.

The chars were produced by pyrolysis of the parent coals in a N_2 atmosphere at around 1473 K in the drop tube furnaces. The experimental conditions for the char combustion are listed in Table 5. The conversions of the char samples, X , were calculated as:

$$X = \frac{1 - \text{ash}_0 / \text{ash}}{1 - \text{ash}_0} \quad (29)$$

Table 5
Drop tube furnace experimental conditions

	Group 1	Group 2
Char	Nos. 1–3	Nos. 4–11
Wall temperature	1473.15 K, 1673.15 K, 1873.15 K	1273.15 K
Gas	Air	Air
DTF inner diameter	50 mm	50 mm
Gas flow rate	120 L·min ⁻¹ (293.15 K, 0.1 MPa)	0.5 Nm ³ ·h ⁻¹
Gas velocity	5.12 m·s ⁻¹	0.33 m·s ⁻¹
Feed rate	0.35 g·min ⁻¹	1 g·h ⁻¹
Residence time	0.086 s	1.67 s
Evaluation point	Local	End

where ash_0 is the initial ash content of the char and ash is the ash content of the partly burned char sample both of which were measured by a Q500 thermogravimetric analyzer produced by TA Instruments, US. The measurement error of this analyzer was only $\pm 0.1\%$ of the full scale.

The average char particle diameters were measured by a Mastersizer 2000 Laser Particle Size Analyzer. This analyzer could measure particle sizes from 0.02 to 2000 μm and the measurement errors were less than 1%. Repeated measurements show differences of less than 0.5%. The char particle pore structure parameters (θ , S_g and D_f) were measured by an Autoscan 33 mercury porosimeter with an operating pressure range of 0–232 MPa. The smallest pore which this mercury porosimeter could measure was a diameter of 3.23 nm and the nonlinearity was $\pm 0.05\%$ of the full scale. The measured average particle diameters and the pore structure parameters of the 11 chars listed in Table 6 were used in the following simulations. The measured pore structure parameters were only for the large pores, while the small pores which nearly had no effect on the char combustion were excluded [1,7].

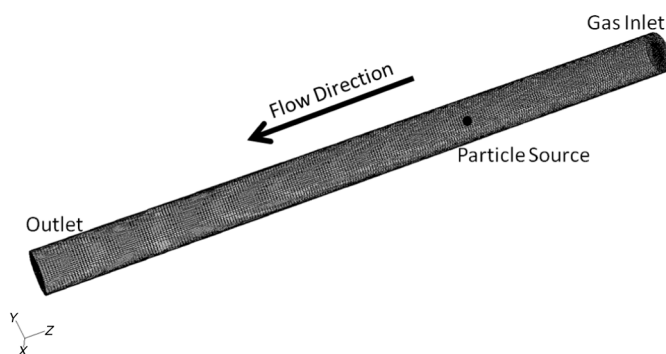
Table 6
Measured average particle diameters and pore structure parameters of the 11 chars

Char	Average particle diameter/ μm	Porosity/%	Specific surface area/ $\text{m}^2\cdot\text{g}^{-1}$	Fractal dimension
No. 1	49.4	42.66	1.69	1.31 ± 0.004
No. 2	48.3	47.96	1.99	1.32 ± 0.002
No. 3	40.6	57.19	2.21	1.42 ± 0.004
No. 4	69.4	35.48	1.47	1.38 ± 0.003
No. 5	119.0	47.27	2.16	1.03 ± 0.001
No. 6	28.2	31.5	1.24	1.26 ± 0.003
No. 7	101.0	41.69	1.86	1.12 ± 0.001
No. 8	82.6	50.6	1.68	1.46 ± 0.003
No. 9	64.2	45.4	2.46	0.99 ± 0.002
No. 10	40.0	36.6	1.05	1.04 ± 0.001
No. 11	124.8	34.5	0.98	0.95 ± 0.004

4. Model Validation

Since the flow in the drop tube furnace was a typical gas–solid two-phase flow, the Euler–Lagrange approach was used to simulate the drop tube furnace experiments. The air was treated as a continuum described by the Navier–Stokes equations, while the char particles were tracked through the calculated flow field. The char particles exchange mass, momentum and energy with the air in the simulations. Since both the average particle diameters in Table 6 and the feed rates in Table 5 are very small, the interactions among particles and the effects of the particles on the flow field were assumed to be negligible. The detailed equations were given in [4].

A three-dimensional grid was generated for the cylindrical furnace tube with a total of 222,400 nodes as shown in Fig. 5. The air entered the furnace at the gas inlet. The particle injector was inserted into the

**Fig. 5.** Grid for the drop tube furnace.

furnace in the experiments but its influence on the flow field was neglected. Thus, the particles were assumed to be injected from a particle source location in the furnace.

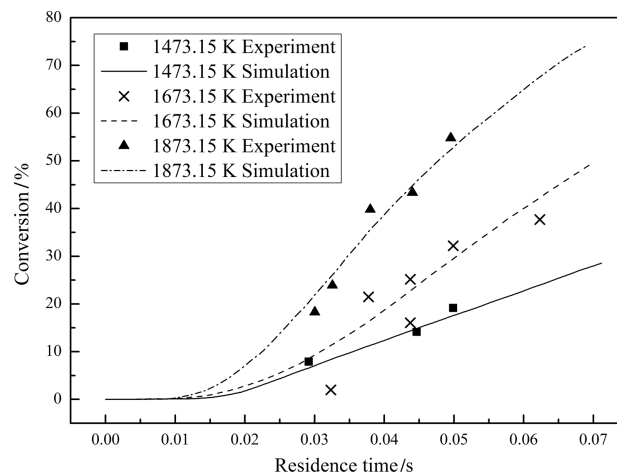
The combustion rates of each char particle were described by the model introduced in Section 2. The model parameters (A_i , E_i and ζ) given in [4] were initially used as the initial values. The predicted char conversions were then compared with the measured values (only used the experimental results of chars Nos. 1–3) with the model parameters (A_i , E_i and ζ) adjusted by trial and error to minimize the differences. The final model parameters for all the chars were determined to be:

$$A_i = 45.8415, E_i = 54000 \text{ J} \cdot \text{mol}^{-1}, \zeta = 2.4872 \quad (30)$$

which completes the char particle combustion model. The value of E_i is the same with that in [4,5], which reconfirms its physical meaning as the intrinsic activation energy.

Figs. 6–8 compare the predicted char conversions with the experimental values for chars Nos. 1–3 at all temperatures. The dots represent the measured char conversions and the lines represent the predicted char conversions. The good agreement shows that the comprehensive char particle combustion model is very accurate. Table 7 lists the root mean square errors of the predictions from the experimental results for both the present model and the model of He *et al.* [4] which shows that the present model gives a much better representation of the data.

Only the final conversions were measured for chars Nos. 4–11 in the experiments since furnace 2 only had one sampling point at the furnace tube outlet. The measured final conversions are listed in Table 8 together with the ash contents of the char samples. Then, the

**Fig. 6.** Measured and predicted conversions for char No. 1.

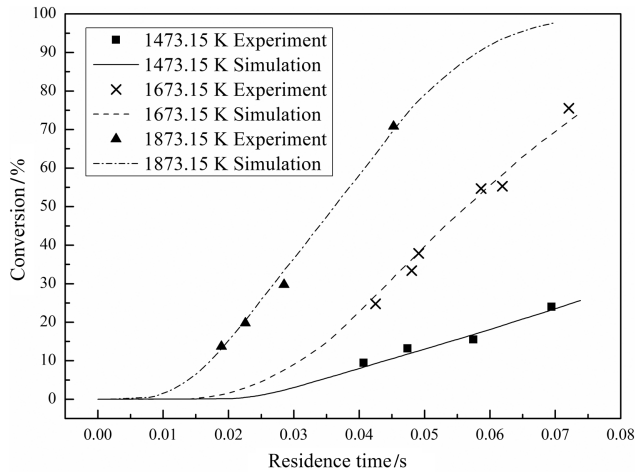


Fig. 7. Measured and predicted conversions for char No. 2.

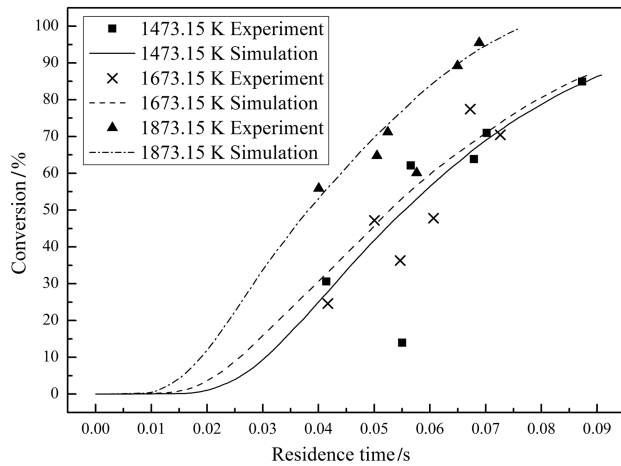


Fig. 8. Measured and predicted conversions for char No. 3.

final char conversions were predicted by both the intrinsic model [6,17, 18] and the present model with the results also listed in Table 8. All the predicted final conversions are plotted in Fig. 9 versus the measured final conversions to show that the present model is more accurate than the intrinsic model.

5. Discussion

The combustion of a single char particle in a bulk space was simulated with the present model to get more details about the char

Table 7

Root mean square errors for the model of He *et al.* [4] and the present model relative to the experimental data

Char	Temperature /K	Error for the model of He <i>et al.</i> [4] /%	Error for the present model/%
No. 1	1473.15	1.99	1.26
	1673.15	5.84	5.68
	1873.15	5.04	2.94
No. 2	1473.15	1.42	1.19
	1673.15	4.64	2.39
	1873.15	4.81	1.94
No. 3	1473.15	16.72	15.21
	1673.15	12.62	10.06
	1873.15	9.88	8.89

Table 8

Comparisons of the predicted final conversions with the measured data for chars in Group 2

Samples	Experimental results			Predicted conversions/%	
	ash ₀ /%	ash/%	Conversion/%	Intrinsic model	Present model
No. 4	22.5	25.5	15.2	30.35	14.52
No. 5	25.2	71.5	86.6	23.5	77.91
No. 6	31.0	35.7	19.1	16.74	21.63
No. 7	25.7	37.2	41.6	30.7	39.16
No. 8	11.3	22.4	55.9	58.9	53.06
No. 9	20.2	53.2	77.7	46.3	65.9
No. 10	18.3	35.8	59.8	61.5	63.28
No. 11	16.1	18.9	17.7	8.3	14.17

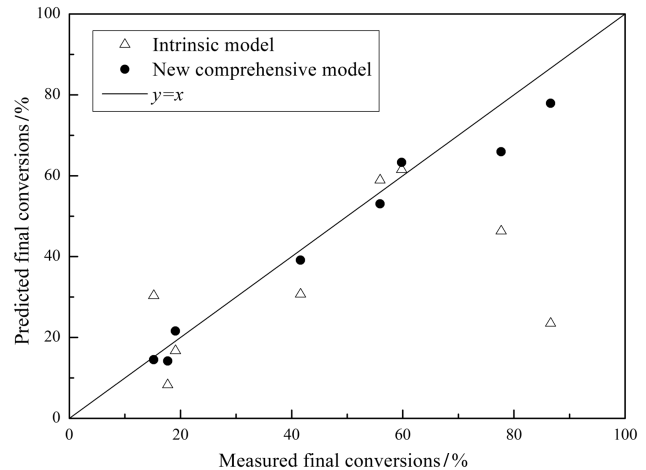


Fig. 9. Comparison of the present model with the traditional intrinsic model.

combustion process. The char particle was assumed to be spherical and isothermal. The equations describing the char particle were the same with those in the drop tube furnace experiment simulations [4]. The one-dimensional conservation equations for multicomponent reacting systems in spherical coordinates [30] were used to describe the heat and mass transfer processes and the chemical reactions in the flow field around the char particle. The effects of the char particle combustion on the flow field were used as the boundary conditions. The No. 2 char in Tables 4 and 6 was used with the detailed simulation conditions listed in Table 9. In all the cases, the total pressure is 101.325 kPa and the initial char particle temperature is 300 K.

Figs. 10–15 show the simulation results in which “Air” means that the case used the air-mode (in an O₂/N₂ atmosphere) and “Oxy” means the case used the oxy-mode (in an O₂/CO₂ atmosphere). The results in Figs. 10–14 were obtained with an initial O₂ mole fraction at the char particle external surface of 21% while the results in Fig. 15 were obtained with an initial temperature of 1200 K. The other simulation conditions are indicated in the figures.

Table 9

Simulation conditions for a single char particle combustion

Temperature/K	Atmosphere (mole fraction)
1200	5%O ₂ /95%N ₂ , 5%O ₂ /95%CO ₂
1200	21%O ₂ /79%N ₂ , 21%O ₂ /79%CO ₂
1200	35%O ₂ /65%N ₂ , 35%O ₂ /65%CO ₂
1200	50%O ₂ /50%N ₂ , 50%O ₂ /50%CO ₂
900	21%O ₂ /79%N ₂ , 21%O ₂ /79%CO ₂
1500	21%O ₂ /79%N ₂ , 21%O ₂ /79%CO ₂
1800	21%O ₂ /79%N ₂ , 21%O ₂ /79%CO ₂

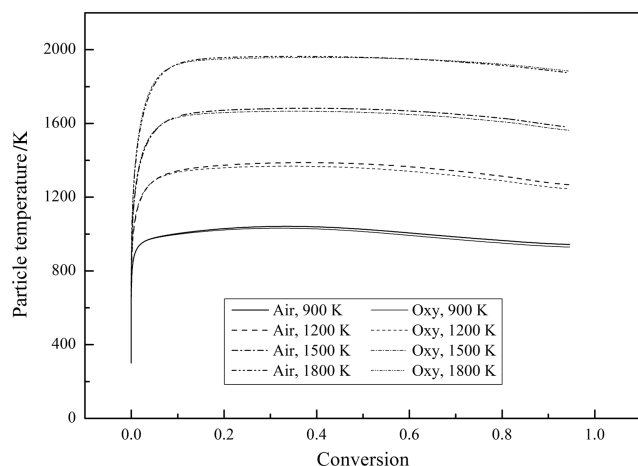


Fig. 10. Variations of the char particle temperature during combustion (21%O₂).

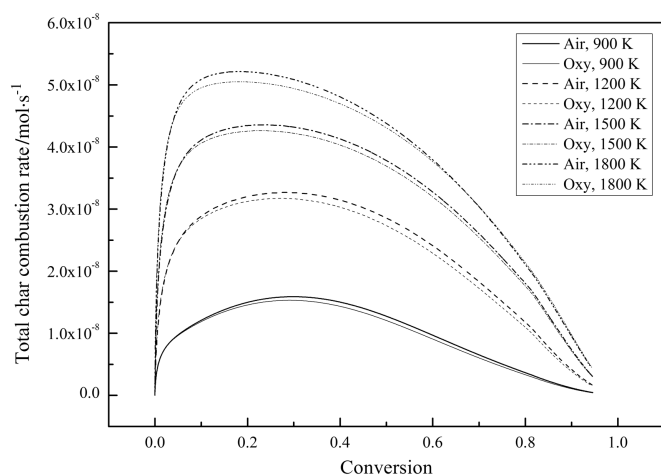


Fig. 11. Variations of the total char combustion rate for different temperatures during combustion (21%O₂).

Fig. 10 shows the variations of the char particle temperature, T_p , during combustion. The differences in T_p between the air-mode and the oxy-mode are very small and T_p in air-mode is slightly higher than that in oxy-mode. Fig. 11 shows the variations of the total char combustion rate during combustion. The combustion rates in air-mode are higher than those in oxy-mode for all temperatures. These phenomena are mainly due to the higher molar specific heat of CO₂ and the lower O₂ diffusion coefficient in CO₂ which slow the char combustion in oxy-mode [27,28]. Even though the char can react with CO₂, the contribution is insignificant since the reaction rate of char with CO₂ is much lower than that of char with O₂ as long as comparable O₂ concentrations are present [29]. Since the complete char combustion processes were simulated with the bulk diffusion effects included, the reaction rate differences between the air-mode and the oxy-mode in Fig. 11 are higher than those in Fig. 3.

Fig. 12 shows the variations of the gas mole fractions at the char particle external surface during combustion. Since O₂ is a reactant in the combustion reactions, the O₂ mole fractions decrease as the combustion proceeds. During the final stage of the combustion, the combustion rates decrease significantly and the amount of O₂ diffusing from the ambient to the char particle surface is greater than the amount of O₂ consumed in the combustion reactions. Thus, the O₂ mole fractions gradually increase. At lower temperatures, the O₂ mole fractions decrease more in the air-mode than in the oxy-mode since the combustion

rates in the air-mode are faster. However, at higher temperatures, although the combustion rates in air-mode are still faster, the O₂ mole fractions decrease more in the oxy-mode. This is because more CO is generated in the oxy-mode at higher temperatures as can be seen in Fig. 12 and the combustion of CO will consume more O₂. The char-CO₂ gasification reaction rate is faster at higher temperatures, especially in oxy-mode with a large amount of CO₂ in the atmosphere. What's more, the apparent CO/CO₂ ratio is also higher at higher temperatures.

The variations of the CO mole fractions in Fig. 12 are the opposite of the O₂ mole fractions with the reasons being analogous to those for the variations of the O₂ mole fractions. In air-mode, there is no CO₂ in the atmosphere before combustion, so the CO₂ mole fractions first increase and then decrease during combustion, which is similar to the CO mole fractions. The CO mole fractions are higher than the CO₂ mole fractions especially at higher temperatures, which shows that CO is the main product of the char combustion. In oxy-mode, the CO₂ is used as the background gas with relatively high mole fractions before combustion, so the CO₂ mole fractions first decrease as the reactant. Then, the CO₂ mole fractions increase significantly and even exceed the original level, because CO₂ is also one of the combustion products.

Fig. 13 shows the variations of the char particle specific surface area, S_g , during combustion. Since the char particle pore structure evolution model in Section 2.2 has the same form for both the air-mode and the oxy-mode, only the relationships between S_g and the char conversion, X , in air-mode are shown. The results show that the temporal variations of S_g differ for the two modes. S_g first increases to a maximum and then decreases with increasing X which is the same as in some experiments [31–38]. The increase of S_g is caused by the pore growth and the opening of closed pores and the decrease of S_g is caused by the collapse of the pores and the coalescence of the pore walls [3]. The variations of S_g are similar to the variations of the total char combustion rates in Fig. 11. The porosity, θ , increases (not linearly) while the fractal dimension, D_f , and the particle diameter, d_p , decrease (not linearly) during combustion, which is the same as in [3]. The decrease of D_f means the char pore structures become less complex after combustion [3].

Fig. 14 shows the variations of the apparent reaction order, n , during combustion. During the initial stage of combustion, n decreases rapidly from 1. Then, n becomes stable. During the final stage of combustion, n increases gradually. As the O₂ concentration at the particle surface changes, the pore diffusion resistance and the time constant for the flow and diffusion into the pores postpone the variations of the O₂ concentration at the reactive surface inside the char pores and n is not always 1 [5]. In the simulations, the initial char particle temperature is very low (300 K) and the pore diffusion is not the key factor restricting the chemical reactions, so n is approximately equal to 1. As the char particle heats and burns, the particle temperature rises quickly and the effect of pore diffusion is significantly enhanced, so n decreases rapidly. As the combustion reaches steady state, n becomes stable. During the final stage of combustion, most of the carbon has been consumed and the pore structure becomes less complex [3] which means that the pore structure provides less pore diffusion resistance, so n gradually increases. Liu and He [5] also studied the variations of n during combustion and found that n decreased first and then became stable towards the end of the combustion process without increasing because the char pore structure evolution was not included in their simulations.

Fig. 15 shows the variations of the total char combustion rate for different O₂ concentrations at a higher temperature of 1200 K. Overall, the total char combustion rates in the air-mode are still higher than those in the oxy-mode and the differences become larger at higher O₂ concentrations. However, with an initial O₂ mole fraction of 5%, the total char combustion rates in the two modes are nearly the same. The total char combustion rates are actually a little higher in oxy-mode at this time but the difference cannot be seen in Fig. 15. This shows that the effect of the char-CO₂ gasification reaction is important only when

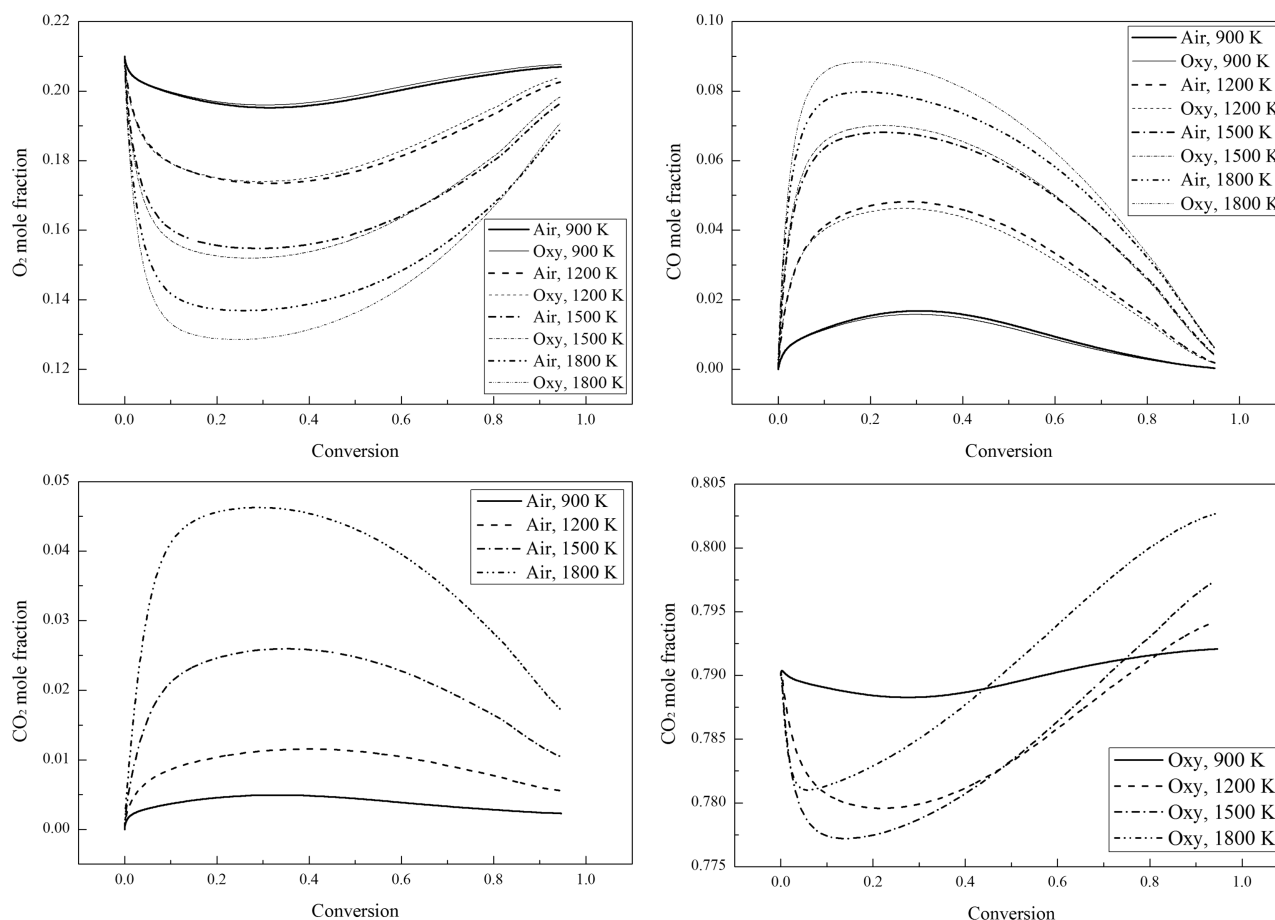


Fig. 12. Variations of the gas mole fractions at the char particle external surface during combustion (21%O₂).

the temperature is relatively high and the O₂ concentration is relatively low.

6. Conclusions

The char combustion mechanisms were analyzed in terms of (1) the pore diffusion effects on the char combustion, (2) the char particle pore structure evolution during combustion, (3) the variation of the apparent reaction order during combustion, (4) the apparent CO/CO₂ ratio in the combustion products, and (5) the effects of high CO₂ concentration on

the char combustion. A comprehensive char particle combustion model was then developed with all these mechanisms. Nearly all the complex factors affecting the char combustion are considered except for the catalysis of the trace elements in the ash and the graphitization of the chars which will be studied in a future work.

Eleven different chars were used in combustion experiments in two drop tube furnaces. The conversions of the partly burned char samples were measured using thermogravimetric analysis. The predicted char conversions matched very well with the measured values which showed the reliability of the present model. What's more, this model

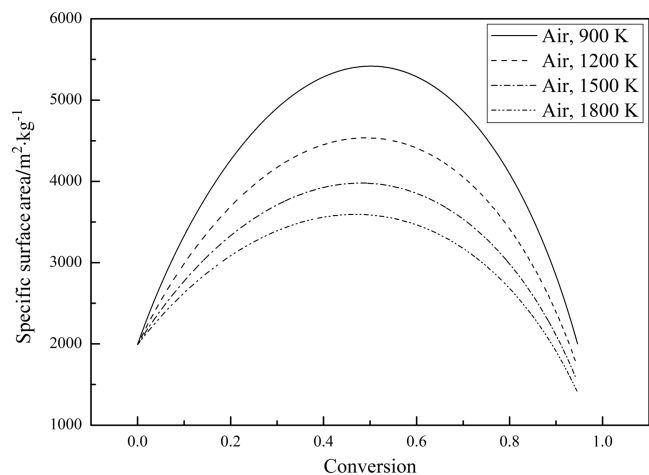


Fig. 13. Variations of the char particle specific surface area during combustion (21%O₂).

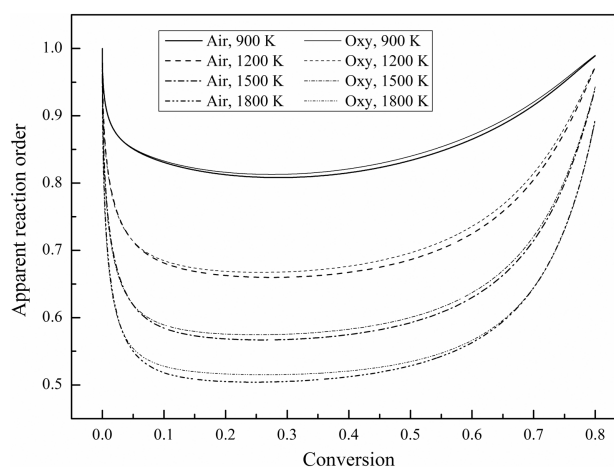


Fig. 14. Variations of the apparent reaction order during combustion (21%O₂).

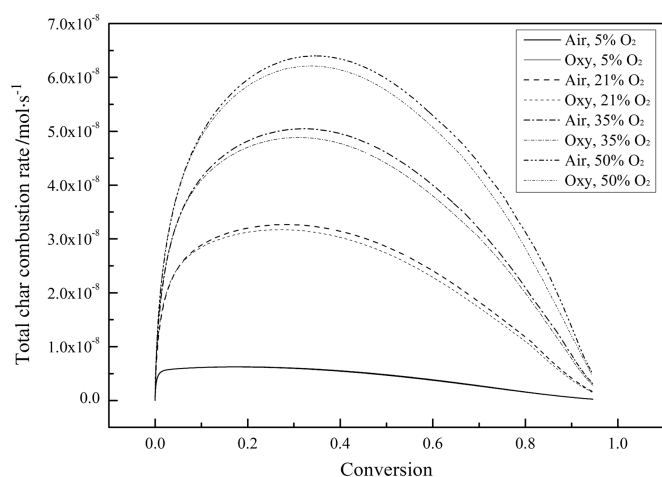


Fig. 15. Variations of the total char combustion rate for different O₂ concentrations during combustion ($T_0 = 1200$ K).

is significantly more accurate than the model of He *et al.* [4] and the traditional intrinsic model.

The apparent reaction order first decreases, then stabilizes and finally increases during the combustion process. The specific surface area of the char particle first increases and then decreases with a maximum during combustion. The combustion rates in oxy-mode are generally slower than those in air-mode due to the higher CO₂ molar specific heat and the lower O₂ diffusion coefficient in CO₂ which slow the char combustion in oxy-mode. The effect of the char-CO₂ gasification reaction becomes important only when the temperature is relatively high and the O₂ concentration is relatively low.

Nomenclature

A_i	pre-exponential factor
a_1, a_2	constants in Eq. (8)
ash	char particle ash content
b_1, b_2, b_3	constants in Eq. (11)
C_s	O ₂ molar concentration at the char particle external surface, mol·m ⁻³
c_1, c_2	constants in Eq. (15)
D_f	fractal dimension of the char pores
d_1, d_2	constants in Eq. (18)
d_p	char particle diameter, m
E_i	intrinsic activation energy, J·mol ⁻¹
k_a	apparent reaction rate constant
k_i	intrinsic reaction rate constant
m	char particle mass, kg
m_1, m_2	constants in Eq. (25)
n	apparent reaction order of char combustion
P_{CO_2}	CO ₂ partial pressure at the char particle external surface, Pa
P_{O_2}	O ₂ partial pressure at the char particle external surface, Pa
Q	intermediate variable
R	universal gas constant ($R = 8.314$ J·mol ⁻¹ ·K ⁻¹)
R_{air}	char particle combustion rate in the O ₂ /N ₂ atmosphere, mol·s ⁻¹
R_{oxy}	char particle combustion rate in the O ₂ /CO ₂ atmosphere, mol·s ⁻¹
R_s	char particle combustion rate, mol·s ⁻¹
r_{pore}	char pore radius, m
S_a	accumulated pore surface area in mercury intrusion measurements, m ²
S_g	specific surface area of the char particle, m ² ·kg ⁻¹
T	temperature, K
$T_{critical}$	critical temperature defined based on Eq. (27), K
T_p	char particle temperature, K
X	char conversion

α	correction factor for oxy-char combustion defined in Eq. (24)
ΔH	reaction heat, kJ·mol ⁻¹
ζ	scale factor
θ	char particle porosity
ρ_i	true density of the char particle, kg·m ⁻³
τ	tortuosity factor of the char pores
χ	dimensionless modulus defined in Eq. (2)

Subscript

0	initial value of the variable
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