Study on the Influence of the Activation Energy on the Simulation of Char Combustion

Yuan Fang *, Lei Qiao, Cheng Wang, Xiaoyu Luo, Teng Xiong, Rongli Tian, Zhengming Tang, Haijun Sun
Wuhan Second Ship Design and Research Institute, Wuhan, China.

*Corresponding author e-mail: 786523702@qq.com

Abstract. The numerical simulation of coal char combustion process can quickly obtain the combustion characteristics of char. It has guiding significance for the design and operation industrial boilers. But during the numerical simulation, how to choose the appropriate kinetic parameters is a difficult problem. The values of combustion activation energy in previous literatures were different. This paper focused on the influence of activation energy on the simulation results of char combustion. The activation energies of 20 Chinese typical coals were measured by a two-step in-situ reaction analyzer. CBK (Carbon burnout kinetics) model was used to simulate char combustion process. Results showed that when activation energy varied greatly, the the predicted combustion rate and particle temperature were very different, especially in the later stage of char combustion.

1. Introduction
With the rapid development of computer technology, numerical simulation has received more and more attention. Through numerical simulation of combustion process, the design and operation of boiler can be optimized to improve the coal combustion efficiency and reduce the pollutant emissions. Compared with cumbersome experiments, numerical simulation is not only fast, but also able to predict the combustion characteristics in commercial boilers.

At present, the commonly used commercial computational fluid dynamics software Fluent include the diffusion/kinetics reaction control model of Baum and Street [1] and the intrinsic reaction model of Smith et al [2]. The diffusion/kinetics reaction control model could predict char reaction rate based on the external surface area. However, the model didn't take the complexity and variation of pore structure into consideration. The influence of internal pore diffusion on the chemical reaction, the change of external surface area of the particles during combustion process were both neglected. Thus, although the diffusion/kinetics reaction control was relatively simple, it was necessary to determine the apparent kinetic parameters of coal under specific conditions in actual application. In addition, changing the coal type or combustion condition also had great influence on the simulation calculation results of diffusion/kinetics reaction model. Smith's intrinsic reaction model established the relationship between pore structure and pore diffusion by effectiveness coefficient η. The extent of oxygen diffusion in the inner pore of coal char was related to char structures and temperatures. Then the combustion rate of coal char under different combustion conditions was calculated based on the intrinsic kinetic parameters, which increased the applicability and generality of intrinsic reaction model. However, the relationship
between the intrinsic reactivity and char structures was not clear. The intrinsic reactivity of different types of chars varies greatly.

Based on the intrinsic reaction model, Hurt et al. [3, 4] further considered the effects of char deactivation at high temperature, inhibition of oxygen transfer due to vitrified ash layer on reaction rate. The proposed model (CBK) summarized the initial reactivity data of various coals and established the relationship between the initial reactivity and carbon content. The value of intrinsic activation energy $E$ in CBK was 146 kJ/mol. In the intrinsic reaction model of Smith, $E$ was 180 kJ/mol. The average activation energy of various coals measured by Russell et al. [5] was 130 kJ/mol. The values of various coals measured by Hargerve et al. [6] were 155-167 kJ/mol. In the model of Solomon et al. [7], the preset value was 125 kJ/mol. It could be found that the intrinsic kinetic parameters of coke measured or used in different literatures varied greatly. Further research was needed about the influence of the activation energy of the kinetic parameters on the simulation results of char combustion.

Based on the CBK model, this paper studied the influence of activation energy $E$ on the CBK model simulation results. The values of in-situ char combustion measured in this paper and those reported in previous literatures were used to predict the char conversion rate. The influence of the value of activation energy $E$ on the simulation results of CBK model was investigated.

2. Experiment and Simulation

2.1. Experimental methods

20 types of Chinese typical coals were selected and grounded within 74-100 μm. Compared with previous experiments, this paper used a two-step in-situ reaction analyzer to measure the intrinsic activation energy of in-situ char combustion. The influence of the cooling process on char structure was avoided during the whole test process, and the combustion reaction kinetics of the in-situ char coke was realized [8]. The specific combustion test procedure has been introduced in the previous literature [9].

2.2. Kinetic analysis

In this paper, the isothermal method was used to obtain the kinetic parameters of coal char. The detailed analytical calculations had been introduced in the previous literature [8]. The main formula was as follows.

$$\ln k = \ln A - \frac{E}{RT} \quad (1)$$

With ln$k$ as the ordinate and $1/T$ as the abscissa, a line was fitted. $-E/R$ and ln$A$ were the slope and intercept, respectively. Then, the activation energy $E$ and the pre-exponential factor $A$ were obtained.

2.3. Simulation approach

The CBK model was used to simulate the combustion process. The single char particle combustion rate was described as follows.

$$R = \eta A_0 S e^{-E/RT} P_s^n m_p \quad (2)$$

$R$—combustion rate, g/s

$A_0$—Pre-exponential factor under unit external surface area and oxygen partial pressure, g•s$^{-1}$•cm$^{-2}$•atm$^{-1}$

$S$—total surface area, cm$^2$/g

$P_s$—oxygen partial pressure of the particle surface, atm

$n$—Apparent reaction order

$m_p$—the carbon mass in the particle, g

$\eta$—the dimensionless effectiveness coefficient

$T_p$—the surface temperature of the carbon particle outer surface, K

The dimensionless validity factor $\eta$ was calculated by the following equation.
According to the heat balance equation, the surface temperature of single-particle coke was as follows.

\[
m_p C_p \frac{dT_p}{dt} = R(\Delta H_{rec}) / MW_c - hS(T_p - T_b) - \varepsilon \sigma S(T_p^4 - T_b^4) \eta = \frac{1}{\phi} \left[ \coth(3\phi) - \frac{1}{3\phi} \right]
\]

The first item on the right represented the heat release during char combustion. The middle term represented convective heat transfer between particles and gas. The last term represented radiation heat transfer.

3. Results and discussion

3.1. Experimental results

In-situ char combustion activation energies \( E \) of 20 typical Chinese coal species were measured by a two-step in-situ reaction analyzer. The result of fitting the reaction rate \( \ln k \) to \( 1/T \) was shown in Figure 1. The average value of the combustion activation energy \( E \) of these 20 in-situ chars was 132 kJ/mol. In Hurt's CBK model, the measured coal char combustion averages \( E = 146 \) kJ/mol. The average value measured by Smith is 180 kJ/mol. This is related to the different materials selected by authors. Most of the coals selected in this paper were sub-bituminous coal and bituminous coal. In Hurt's experiment, bituminous coal was the main material and in Smith's experiment, different types of carbon were chosen. Therefore, the average value of \( E \) in this paper was lower.

![Figure 1. The reaction rate \( \ln k \) versus \( 1/T \).](image)

3.2. Simulation results

According to the above test results, combined with the previous literature reports, the effects of the values of the combustion three activation energy \( E \) (132 kJ/mol, 146 kJ/mol, 180 kJ/mol) on the simulation results of the CBK model were compared.

3.2.1. The effects of \( E \) on the carbon conversion rate. Figures 2(a) and Figures 2(b) gave the effects of different activation energies on the carbon conversion rate of char at the temperature of 1673 K and 1273 K, respectively. In Figure 2(a), it could be found that the two burnout curves calculated by 146
kJ/mol and 132 kJ/mol were very close. When the combustion temperature was 1673 K, the combustion was in the pore diffusion zone. When the value of E decreased by 14 kJ/mol, the burn-out time of the CBK simulation was similar. When E increased from 146 kJ/mol to 180 kJ/mol, the char combustion process was very different. When E was 146 kJ/mol, the burnout time was less than 0.25 s. But when E was 180 kJ/mol, the carbon conversion rate was only 0.7 at the same time, and then the burning rate became slower and slower. When the combustion temperature was 1273 K in Fig2 (b), the chemical reaction rate of the char decreased and the influence of E on char combustion process increased.

When the value of E is reduced by 14 kJ/mol at 1273K, the two burnout curves were still close, but compared with Figure Fig2(a), the influence of E on the combustion process increased, and when the value of E increased by 34 kJ/mol, the simulation results of CBK model showed that char burnout time was significantly increased. This result indicated that when E varied within a small range (±15 kJ/mol), the calculated results in the pulverized coal furnace of CBK model were relatively close. However, when the value of E varies greatly (±30 kJ/mol), the simulation results of CBK model also varied greatly.

**Figure 2.** The effect of activation energy E on the carbon conversion rate X. (a) T=1673K, (b) T=1273K

3.2.2. The effects of E on the char combustion rate. Figures 3(a) and Figures 3(b) showed the char combustion rate versus carbon conversion rate X at the temperature of 1673 K and 1273 K, respectively. Results showed that the decrease of E from 146 kJ/mol to 132 kJ/mol had little effect on the simulated combustion rate. However, when the reaction temperature decreased (T = 1273 K), the difference between the two curves increased. This was because the effect of the chemical reaction rate on combustion rate increased. When the combustion temperature decreased.

**Figure 3.** The char combustion rate versus carbon conversion rate X. (a) T=1673K, (b) T=1273K
3.2.3. The effect of $E$ on the effectiveness coefficient. Figures 4(a) and Figures 4(b) showed the effectiveness factor $\eta$ versus carbon conversion rate $X$ at the temperature of 1673 K and 1273 K, respectively. The effectiveness factor $\eta$ was the ratio of the combustion rate of char in the case of pore diffusion to the burning rate in the absence of pore diffusion. $\eta$ could represent the extent of oxygen diffusion in the inner pore during char combustion. For $\eta=1$, oxygen could be completely in contact with the carbon surface and reaction was in the kinetic control zone. For $\eta=0$, the reaction occurs on the outer surface of the carbon, and the reaction is controlled by the external diffusion. The results in Figure 4 showed that with the combustion proceeding, the intrinsic reactivity of the heat-treated char is lowered, and the influence of the chemical reaction rate was increased. Thus $\eta$ increased during the combustion process. In addition, when the temperature decreased, the char chemical reaction rate decreased, and $\eta$ increased. Therefore, the simulation result of CBK model was more sensitive to the value of $E$ when the temperature is lowered.

Figure 4. The effectiveness factor $\eta$ versus carbon conversion rate $X$. (a) $T=1673K$, (b) $T=1273K$

3.2.4. The effect of $E$ on the particle temperature. Figures 5(a) and Figures 5(b) showed the particle temperature $T_p$ versus carbon conversion rate $X$ at the temperature of 1673 K and 1273 K, respectively. Figures showed that when $E$ increased, the carbon consumption rate decreases, and heat release of combustion reaction decreases. Thus the particle temperature $T_p$ calculated by CBK model decreased.

Figure 5. The particle temperature $T_p$ versus carbon conversion rate $X$. (a) $T=1673K$, (b) $T=1273K$
4. Conclusion

The influence of the activation energy $E$ on the simulation results of CBK model was investigated in this paper. When $E$ varied within a small range ($\pm 15$ kJ/mol), the calculated results of CBK model were relatively close. When $E$ varies greatly ($\pm 30$ kJ/mol), the simulation results of CBK model also varied greatly. The predicted burnout time, combustion rate and particle temperature were very different. Moreover, in the later stage of combustion, the chemical reaction rate played a leading role in the combustion rate. This was because the influence of the chemical reaction rate on char combustion rate increased in the later stage.

References

[1] M.M. Baum, P.J. Street, Predicting the Combustion Behaviour of Coal Particles, Combustion Science and Technology. 1971 3 (5) 231-243.

[2] I.W. Smith, The combustion rates of coal chars: a review, Proceedings of the Combustion Institute. 1982 19 (1) 1045-1065.

[3] R.H. Hurt, J. Sun, M. Lund, A kinetic model of carbon burnout in pulverized coal combustion, Combustion and flame. 1998 113 (1) 181-197.

[4] J. Sun, R.H. Hurt, Mechanisms of extinction and near-extinction in pulverized solid fuel combustion, Proceedings of the Combustion Institute. 2000 28 (2) 2205-221304.

[5] N.V. Russell, T.J. Beeley, C. Man, J.R. Gibbins, J. Williamson, Development of TG measurements of intrinsic char combustion reactivity for industrial and research purposes, Fuel Processing Technology. 1998 57 (2) 113-130.

[6] G. Hargrave, M. Pourkashanian, A. Williams, The combustion and gasification of coke and coal chars, Proceedings of the Combustion Institute. 1988 21 (21) 221-230.

[7] P.R. Solomon, D.G. Hamblen, M.A. Serio, S. Charpenay, A characterization method and model for predicting coal conversion behaviour, Fuel. 1993 72 (4) 469-488.

[8] Y. Fang, R.H. Zou, G.Q. Luo, J. Chen, Z.H. Li, Z.J. Mao, X.Q. Zhu, F.L. Peng, S.Q. Guo, H. Yao, Kinetic study on coal char combustion in a microfluidized bed, Energy and Fuels. 2017 31 (3) 3243-3252.

[9] Y. Fang, G.Q. Luo, J. Li, K.D. Li, C. Chen, H. Zhao, R. Duan, H. Yao, Kinetic study on in-situ and cooling char combustion in a two-step reaction analyzer, Proceedings of the Combustion Institute. 2017 36 (2) 2147-2154.