Extending Semi-parallel Reaction Model of Pulverized Coal Particle to Various Coal Types

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A new concept for modeling the overlap between devolatilization and char oxidation was extended to various coal types. Quasi-steady mass transfer analysis around a single coal particle with devolatilization was performed, and the overlap between devolatilization and char oxidation was modeled with a semi-parallel reaction model. The semi-parallel reaction model can capture the differences in the char oxidation rates of each coal by a single fitting parameter called the inhibition factor. The combustion simulation of the single coal particle indicated the superiority of the semi-parallel reaction model over the previously reported modeling concepts because the semi-parallel reaction model could describe the decrease in char oxidation rate during devolatilization, which is not represented by other reaction models. Although the inhibition factor is not correlated with the proximate analysis of the volatile matter, it is correlated with the temperature at which the rate-controlling step of char oxidation shifts. This is because the proximate analysis does not include information on char reactivity. Therefore, it is suggested that the inhibition effect of devolatilization on char oxidation strongly correlates with the parameter that describes the sensitivity of char oxidation to the mass transfer processes of the oxidant.

Key Words
Coal reaction model, Mass transfer analysis, Devolatilization, Char oxidation

1. Introduction

Pulverized coal combustion is one of the most important techniques for generating electricity, and oxyfuel combustion and gasification techniques have been developing as new coal utilization technologies. Pulverized coal combustion includes many kinds of factors, such as fluid flow, chemical reactions and radiation in not only a gas phase but also solid phase and gas-solid interactions. Numerical investigations of pulverized coal combustion have provided reasonable insights, which cannot be obtained from experiments. Particularly, the reaction model of the solid phase plays important roles in CFD (Computational Fluid Dynamics) in accurately predicting the phenomena in industrial coal combustors. The pulverized coal combustion process involves the following two processes: devolatilization and heterogeneous reactions of char. These two processes
are considered as separate processes in CFD through completely independent reaction models. For devolatilization, the mass-based reaction model has often been employed in CFD [13-16], and FLASHCHAIN [18] and CPD [18-19] have been proposed to determine the appropriate reaction parameters. For char reactions, the surface reaction model by Field [18], the random pore model by Bhatia [20], and the Langmuir-Hinshelwood-type equations [20-23] are famous and used in numerical simulations.

Devolatilization occurs because of the heating of particles, whereas char oxidation occurs if oxidants are present around the char particles. In other words, the time when each process occurs can partially overlap. Since devolatilization is not a steady-state phenomenon, its reaction rate becomes smaller after the peak. At close to the end of devolatilization, char oxidation can occur although the overlap duration may be short. Char oxidation includes the mass transfer of oxidant to the particle surface as well as chemical reactions on the char particles [23-26]. Thus, the devolatilization process, which leads to convective flow around the coal particles, significantly affects the char oxidation rate. This phenomenon has been discussed in previous studies [26-28]. Howard and Essenhigh reported that devolatilization and char oxidation occur simultaneously when the convective flow induced by devolatilization is weak [24]. Saastamoinen et al. investigated the dependency of char oxidation on the convective flow by experiments and analytical calculations [25]. They concluded that devolatilization and char oxidation would progress sequentially as both the particle size and gas temperature increase. Gurgel et al. focused on the effect of devolatilization on the burnout time of char. From the analytical investigation, they suggested that the time in which devolatilization and char oxidation overlap extends as the particle diameter decreases [26].

The order of devolatilization and char oxidation is an important issue in the modeling of char reaction in CFD because researchers have to determine whether the reaction processes are sequential or parallel prior to simulation. When the two processes are considered sequential processes, char oxidation does not occur during devolatilization. This assumption is implemented into ANSYS Fluent as the default method for the modeling of devolatilization and char oxidation [20]. Asotani et al. carried out the simulation of a coal boiler to predict the ignition position [20]. In the simulations, although devolatilization and char oxidation occurred simultaneously, they were completely independent processes. However, only a few articles describe the details of the modeling for devolatilization and char oxidation because the appropriate modeling concept has not yet been established.

In fact, in the 1980-90s, the combustion mechanism of a pulverized coal particle received much attention, and many researchers performed experiments and simulations on the combustion of single coal particle [29-33]. Timothy et al. measured the burning history of a single coal particle with a two-color optical pyrometer and compared the obtained data with model predictions [29]. In the model calculation, the energy transfer from the flame to the particle was considered, and the transient phases (i.e., heat-up, devolatilization, and char oxidation phases) were described. Choi and Kruger developed a radiative transfer model during devolatilization and performed the heat transfer calculation around a single coal particle [30]. In their calculations, the radiative heat transfer in the volatile cloud was described, and they discussed the effect of soot generated by volatile matter, VM combustion on the energy balance between the particle and surrounding gas. Mussara et al. investigated the heat and mass transfer around a single coal particle during overall reaction process by using two-dimensional simulations [31]. They considered not only heterogeneous reaction of char but also homogeneous reactions of volatile matter and CO and showed the invalidity of flame sheet assumption for homogeneous reactions. The most interesting point is that the oxygen mass fraction was not zero even though during devolatilization. This result suggested that the char oxidation can occur during devolatilization. Chun Wai and Niksa also modeled the initial stage of pulverized coal combustion for various coal types [33]. They evaluated the amount of feedback heat generated by volatile combustion to a particle and revealed that the ratio to the particle in overall heat did not depend on coal rank. In addition, the dependence of the maximum flame temperature and flame lift-off on coal rank was discussed. Although the coal combustion mechanism has already been discussed well, it is difficult to implement the acknowledge obtained from the above studies into CFD. This is because the handling method of gas phase in the vicinity of a coal particle is not consistent between the mass transfer analysis and Lagrangian framework in CFD. For examples, the chemical reactions in the vicinity of the particle cannot be considered in CFD, whereas the above studies considered them. Thus, the reaction model which can represent the mass and/or heat transfer around a single coal particle in CFD is desired while the consistency of handling method of the gas phase is ensured.

Recently, we successfully modeled the overlap between devolatilization and char oxidation of Newlands coal and developed a semi-parallel reaction model that considers the overlap of devolatilization and char oxidation [30].
Applying the semi-parallel reaction model to CFD, we are able to perform numerical simulation without any arbitrary assumptions on the reaction order of devolatilization and char oxidation. If the applicability of the semi-parallel reaction model to another coal types can be confirmed, this model would be a de facto standard model for pulverized coal particles. The objective of this work is the extension of the semi-parallel reaction model to various coal types. One-dimensional mass transfer analysis around a single coal particle was performed with various coal types. Thereafter, we confirmed the applicability of the semi-parallel reaction model to various coal types and the differences in the relationship between devolatilization and char oxidation.

2. Numerical methods for quasi-steady mass transfer analysis around a single coal particle

2.1 Computational domain and numerical conditions

Fig. 1 shows the schematic of the computational domain using a spherical coal particle as the target. To describe the gas phase around the coal particle, a one-dimensional spherical coordinate system was used. The computational domain extended 50 \(d_p\) to the bulk side of the computational region from the particle center, with \(d_p\) being the particle diameter. Then, the domain was divided into several control volumes having a width of 1 \(\mu\)m. The independence of the computational region and grid density of the numerical results was examined. The temperatures of the particle and gas phase were constant over time and space. As for the assumptions of spatially uniform temperature in the gas phase, the motivations were described in the previous article 34). In the mass transfer analysis, the chemical species were transported by convective and diffusive flows, and the steady-state profiles were obtained. The release rate of volatile matter, VM was then fixed at an initial release rate. The accumulation effect is known to be significant to capture the transient phenomena around a droplet and coal particles 38, 39). However, since gas phase reactions, which enhance the accumulation effect, were not considered to minimize the difference of handling method of gas phase between mass transfer analysis and CFD 34, the fuel vapor accumulation effect was also ignored in the present study. It is noted that the relative velocity of the coal particle to the gas phase is also not considered. In fact, the relative velocity of the particle to gas flow is not zero in realistic combustors. However, the effect of relative velocity on coal reactions is not considered in all of reaction models which are often used in CFD of the pulverized coal combustor because the phenomena around the coal particle become at least two-dimensional and its modeling is difficult. Despite this simplification of the previous reaction models, the CFD predicts temperature and species distributions with relatively high accuracy. Thus, our proposed model would perform well in CFD of realistic facilities. The numerical conditions are summarized in Table 1. The target ranges of particle diameter and temperature were 10-150 \(\mu\)m and 1000-2500 K, respectively. Table 2 presents the proximate and ultimate analyses of the coals. In this study, five kinds of coals were employed to investigate the applicability of the semi-parallel reaction model to coal samples. The details of the method and the assumptions have been described in our previous work 34).

2.2 Chemical reactions

For VM, we considered CO, CO\(_2\), H\(_2\)O, HCN, N\(_2\), CH\(_4\), C\(_2\)H\(_2\), and tar. To calculate the devolatilization rate of each chemical species, the first-order reaction rate equation 36 was used for each chemical species. Pyrolysis simulations with commercial software, PC Coal Lab\(^{15}\), provided the pre-exponential factor, activation energy, and the molecular weight of tar. The tar species were modeled based on the molecular weight obtained from the pyrolysis simulation. Then, the transport properties of polycyclic aromatic hydrocarbons were given to the tar according to the molecular weight. Thereafter, the heating rate of coal particle was set as 10\(^5\) K/s, based on the numerical results of the previous work 37). Since the target system in this study is a rapid heating system, which the ambient temperature in the furnace reached at 1600 K, the main

| Table 1 Numerical conditions |
|-----------------------------|
| Particle diameter (\(\mu\)m) | Particle density (\(kg/m^3\)) | Reaction temperature (K) | Mole fraction of N\(_2\) | Mole fraction of O\(_2\) | Gas pressure (Pa) |
|-----------------------------|
| 10-150                      | 800                         | 1000-2500                  | 0.8                       | 0.2                       | 10325             |
products by char oxidation would be CO according to the previous studies \(^{38} - 41\). Thus, only the partial oxidation reaction (R1) was employed for char oxidation.

\[
C + 0.5 \text{O}_2 \rightarrow \text{CO} \quad (\text{R1})
\]

The chemical reaction rate was expressed in the surface reaction model or volume reaction model as follows:

\[
r = k P_{\text{O}_2} S_p
\]

\[
r = k' P_{\text{O}_2} m_p
\]

Here, \(k\) and \(k'\) are the rate constants represented by the Arrhenius form per surface area or volume of coals, and \(P_{\text{O}_2}\), \(S_p\), and \(m_p\) denote the partial pressure of the oxidant and the external surface area and mass of the coal chars, respectively. The reaction rate parameters of each coal are summarized in Table 3. It is noted that the chemical reactions in the gas phase are not considered with the perspective of simplification and implementation in CFD. The reason for this has been discussed in detail in our previous work \(^{34}\).

2.3 Governing equations

To describe the mass transfer on the one-dimensional spherical coordinate system, the continuity equation, conservation equations for the chemical species, and the ideal gas law were solved as follows.

\[
\frac{1}{x^2} \frac{\partial}{\partial x} (x^2 \rho u) = S_p
\]

\[
S_p \ AV = \left\{ \sum_{i} \nu_i r_{\text{a},i} + \sum_{i} \nu_i r_{\text{dev},i} \right\}_p, \quad \text{at particle surface}
\]

(4)

\[
\frac{1}{x^2} \frac{\partial}{\partial x} \left( x^2 \rho v \right) = \frac{1}{x^2} \frac{\partial}{\partial x} \left( x^2 \rho D \frac{\partial f_m}{\partial x} \right) + S_p
\]

(5)

\[
S_p \ AV = \left\{ \sum_{i} \nu_i r_{\text{a},i} + \sum_{i} \nu_i r_{\text{dev},i} \right\}_p, \quad \text{at particle surface}
\]

(6)

\[
\rho = \frac{PM}{RT}
\]

(7)

Here, \(\rho\), \(u\), \(AV\), \(v_i\), \(f_m\), and \(D\) are the gas density, gas velocity, volume of control volumes, stoichiometric coefficients of char oxidation, mass fraction, and diffusion coefficient of chemical species, respectively. Employing a finite volume method, the above governing equations were discretized on staggered grids. The convection and diffusion terms in the conservation equations for the chemical species were discretized with the power-law scheme. The system of equations was solved based on the tri-diagonal matrix algorithm. The validity of our calculation method has already been confirmed in our previous work \(^ {34}\).

3. Numerical methods for zero-dimensional combustion simulation of a single coal particle

Using the semi-parallel reaction model developed in the mass transfer analysis, zero-dimensional combustion simulations of the coal particle with 150-\(\mu\)m diameter were
performed. The temperatures of the gas phase and the wall were fixed at 1500 and 1200 K, respectively. The initial particle temperature was 300 K, and the mole fractions of O$_2$ and N$_2$ were set as 0.2 and 0.8, respectively. The governing equations are the mass and energy conservation equations as follows:

$$\frac{dm_r}{dt} = -r - r_{\text{oxid}}$$  \hspace{1cm} (8)

$$m_v C_{vp} \frac{dT_r}{dt} = Q_{\text{conv}} + Q_{\text{trad}} + Q_{\text{reac}}$$  \hspace{1cm} (9)

Here, $r$ is calculated using Eq. (1) or (2), $C_{vp}$ is the specific heat of coal particle, and $Q_{\text{conv}}, Q_{\text{trad}},$ and $Q_{\text{reac}}$ are the amounts of convective, radiative, and reaction heat transfers, respectively, and were calculated using the following equations.

$$Q_{\text{conv}} = h^* (T_g - T_r) S_r$$  \hspace{1cm} (10)

$$Q_{\text{trad}} = \varepsilon_r \sigma (T_r^4 - T_g^4) S_r$$  \hspace{1cm} (11)

$$Q_{\text{reac}} = \xi_r \Delta h + r_{\text{oxid}} \Delta h_{\text{oxid}}$$  \hspace{1cm} (12)

Here, $h^*, T_g, T_r, \sigma,$ and $\Delta h$ denotes corrected convective heat transfer coefficient, gas temperature, wall temperature, Stefan-Boltzmann constant, and reaction heat, respectively. The particle emissivity, $\varepsilon_r$, was set as 0.9. Following the previous works, the corrected convective heat transfer coefficient was estimated as follows.

$$h^* = \frac{\lambda N_u}{(\varepsilon - 1) d_p}$$  \hspace{1cm} (13)

$$z = \frac{(-dm_r/dt) \varepsilon_{\text{eff}}}{h S_p}$$  \hspace{1cm} (14)

$$h = \frac{\lambda N_u}{d_p}$$  \hspace{1cm} (15)

Here, $\varepsilon_{\text{eff}}, N_u, h^*, \lambda,$ denotes specific heat of ambient gas, Nusselt number, convective heat transfer coefficient and thermal conductivity of ambient gas, respectively. The relative velocity between the gas phase and coal particle was assumed to be zero, and the Nusselt number was set as 2.0. The contribution of reaction heat to the particle phase, $\xi$, was set to 1.0. The ordinary differential equations, Eq. (8) and (9), were solved with the second-order Runge-Kutta method.

To show the difference between the semi-parallel reaction model and the previous reaction model, the calculations were also performed with sequential and parallel reaction models. In the sequential reaction model, which is often employed in coal combustion simulations, char oxidation does not occur until devolatilization is complete, even if the particle temperature becomes high enough for the oxidation reaction. In the parallel reaction model, devolatilization and char oxidation occur simultaneously, and the effect of overlap between devolatilization and char oxidation is ignored because the two reaction processes are completely independent. The details of the algorithm of each reaction model are provided in our previous work.

4. Results and Discussion

4.1 Inhibition effect of convective flow induced by devolatilization on char oxidation rates

Fig. 2 shows the Arrhenius plots of the oxidation rates of Adaro coal char with 50-\(\mu\)m diameter. The oxidation rates of char increase exponentially with the elevation of particle temperature; however, the temperature dependence decrease above 2000 K. This implies that the rate-controlling step shifts from a chemical reaction to mass transfer of the oxidant. When devolatilization is considered, the oxidation rate of char, restrained, is lower than that without devolatilization, $r$, because the convective flow caused by devolatilization inhibits the mass transfer of the oxidant.

4.2 Quantification of the inhibition effect of convective flow induced by devolatilization on char oxidation rates

According to our previous work, the inhibition ratio, which represents the effect of devolatilization on the oxidation rate of char, was employed. The inhibition ratio was calculated based on the following equation:

$$I = 1 - \frac{r_{\text{oxid}}}{r_{\text{inhibited}}}$$  \hspace{1cm} (16)

where $r_{\text{oxid}}$ and $r$ denote the apparent reaction rates with and without devolatilization, respectively. As the value of $I$ approaches unity, the inhibition effect of devolatilization on the mass transfer of the oxidant becomes greater. Our previous work revealed that the inhibition ratio was well reproduced by the following curve:

$$I = 1 - (c - 0.75) \frac{r_{\text{oxid}}}{r_{\text{inhibited}}}$$  \hspace{1cm} (17)

![Fig. 2](image-url) Arrhenius plots of oxidation rates of Adaro coal char particles
where \( c \) is the single model fitting parameter, referred to as "inhibition factor" in the present study. \( r_M \) is mass transfer rate of oxidant to the particle surface. Thus, the same type of equations was used in this study.

Fig. 3 shows the relationship between the inhibition ratio and the ratio of devolatilization rates to mass transfer rates of the oxidant without devolatilization, \( r_{\text{dev}}/r_M \) (the plotted points show the numerical solutions and the solid line is the fitted curve). As can be seen in Fig. 3, the fitting curve is in agreement with the inhibition ratio regardless of the coal type. Table 4 shows the inhibition factor of each coal; the inhibition factors are slightly different for different coal types and are in the range of 0.85-0.95. This is because the chemical reactivities of char depend on coal types. Thus, if the intensities of convective flows induced by devolatilization are the same, the effects on the overall reaction rate of char would vary for different coal types. All the model equations of each coal were plotted in Fig. 4, which clearly demonstrate the difference in inhibition ratios. If the \( r_{\text{dev}}/r_M \) values are the same, the inhibition ratio would increase with a decrease in inhibition factor. Accordingly, it is suggested that the inhibition factor represents the sensitivity of char oxidation rate to the devolatilization rate.

### 4.3 Superiority of semi-parallel reaction model over previous reaction models by combustion simulation of a single coal particle

Fig. 5 shows the histories of the devolatilization rates and oxidation rates of the char using three reaction models. Since the histories of the devolatilization rates in the three reaction models are almost the same, only that of the sequential model is shown. In the present numerical conditions, the devolatilization process ended at 45 ms in the case of Adaro coal. In the sequential reaction model, the char oxidation rates rapidly increased at that time. This behavior is due to the assumption that the char oxidation reaction does not occur until the devolatilization processes end. Since the coal particle already attained a high temperature sufficient for the commencement of char oxidation at 45 ms, a sudden rise in char oxidation rate is observed. Thus, the semi-parallel or parallel reaction model is more appropriate for char oxidation modeling compared to the sequential reaction model. Although only the results of Adaro coal and Bituminous coal are shown in Fig 5, the same trends are observed for the other coals.

The histories of char oxidation rates in the semi-parallel and parallel reaction models seem to be the same.
This is because the devolatilization rate rapidly attained the maximum value before the particle temperature became high enough for the commencement of char oxidation in this numerical condition. Given that the previous numerical simulation using parallel reaction model captured the actual combustion behavior with a reasonable accuracy, the same trend of semi-parallel reaction model as parallel reaction model is acceptable. However, between 20 and 30 ms, the char oxidation rate predicted by the semi-parallel reaction model was slightly smaller than that predicted by the parallel reaction model. This decrease in char oxidation rate represents the effect of overlap between devolatilization and char oxidation. Although the difference between parallel and semi-parallel reaction models was small in this numerical condition, the effect is possible to become larger and more important for the prediction accuracy of important phenomena, such as igniting time. Given that the strong convective flow is caused by released volatile matter, mass transfer of oxidant would be hindered, and char oxidation rate would also decrease. While this effect is completely ignored in the parallel reaction model, the semi-parallel reaction model includes this important effect of devolatilization on char oxidation rate. Since arbitrary assumptions are not required for the semi-parallel reaction model, it is considered superior to the parallel reaction model.

4.4 Discussion on the correlation of inhibition factor

Correlation with coal properties is often used to predict the thermal swelling behavior of coal. In previous works, the swelling ratio, which represents the degree of swelling of coal during coal pyrolysis, was found to correlate well with coal properties and some experimental conditions. Since the target phenomenon, that is, the decrease in char oxidation rate by convective flow induced by devolatilization, is also related to coal pyrolysis, we investigated the relationship between inhibition factor and coal properties.

Fig. 6 (a) shows the correlation of inhibition factor with...
proximate analysis of VM. The inhibition factors become larger with an increase in the proximate analysis of VM below 30 % d.b., but a decrease in the range of 30-50 % d.b. The correlation with the proximate analysis of VM was not observed because the proximate analysis of VM does not include the effect of char reactivity. Unlike thermal swelling of coal, the target phenomenon is related to the char reaction process as well as the devolatization process. Thus, the parameter for rearrangement of inhibition factor must include information on char reactivity.

As described in section 4.1, the contribution of mass transfer of the oxidant affects the degree of inhibition by devolatilization. Since the rate-controlling step of char oxidation changes with temperature, the important factor for the target phenomenon would be temperature. Thus, the temperature at which the rate-controlling step of char oxidation shifts from a chemical reaction to mass transfer of the oxidant, Tshift was employed as the candidates of correlation parameter with inhibition factors. In this study, we defined Tshift as the temperature at which the chemical reaction rate of char becomes higher than the mass transfer rate of oxidant to the particle surface. At relative low temperature, the chemical reaction rate of char is lower than the mass transfer rate of oxidant. However, when the temperature increases, the difference between two reaction rates becomes smaller because the chemical reaction rate increases exponentially to temperature, whereas the diffusion coefficient of oxidant increases linearly to temperature to the power of 1.75. The schematic of Tshift is shown in Fig. 7. The chemical reaction rates were represented with Eqs. (1) and (2), and the mass transfer rate of oxidant was estimated by the reaction rate equation by Mulcahy and Smith [46].

![Fig. 7 Schematic of the temperature at which the rate-controlling step of char oxidation shifts from a chemical reaction to mass transfer of the oxidant, Tshift (Adaro coal, d_p = 50 μm)](image)

Fig. 6 (b) shows the correlation of inhibition factor with Tshift. As an example, Tshift is estimated with a particle diameter of 50 μm. As can be seen, almost all the inhibition factors increase with Tshift, demonstrating a good correlation. Although Tshift slightly changes with particle diameter, we confirmed that this correlation is valid for other particle diameters. This result suggests that Tshift could predict the inhibition effect of devolatilization on char oxidation before mass transfer analysis.

5. Conclusion

The semi-parallel reaction model was extended to various coal types. Although the model equation is the same for all the examined coal types, the semi-parallel reaction model could describe the difference in the inhibition ratios. Since the inhibition factor represents the difference in the effect of devolatilization on char oxidation, their values changed with coal types. Combustion simulation of a single coal particle suggested that the sequential reaction model does not capture the actual reaction behavior of coal because the char oxidation rate unrealistically increases. The char oxidation rate predicted by the semi-parallel model showed almost the same behavior as that predicted by the parallel reaction model; however, a decrease in reaction rate was observed during the last half of the devolatilization process. The decrease in reaction rates is attributed to the inhibition effect of devolatilization on char oxidation. The semi-parallel reaction model, which can be used without any arbitrary assumption about the commencement of char oxidation, will be appropriate for practical char combustion modeling. Although the inhibition factor does not correlate with the proximate analysis of VM, it correlates with the temperature at which the rate-controlling step of char oxidation shifts from a chemical reaction to mass transfer of the oxidant. This is because the proximate analysis does not include information on char reactivity. Therefore, it is suggested that the inhibition effect of devolatilization on char oxidation strongly correlates with the parameter that describes the sensitivity of char oxidation to the mass transfer process of the oxidant.

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