Process simulation of formation and emission of NO and N$_2$O during coal decoupling combustion in a circulating fluidized bed combustor using Aspen Plus

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**A R T I C L E I N F O**

Article history:
Received 30 April 2011
Received in revised form 17 October 2011
Accepted 21 October 2011
Available online 28 October 2011

Keywords:
Mathematical modeling
Systems engineering
Simulation
Combustion
NO and N$_2$O emission
Aspen Plus

**A B S T R A C T**

A process simulation model of coal decoupling combustion in a 30 kW circulating fluidized bed (CFB) combustor has been developed for predicting NO and N$_2$O emissions based on the built-in modules/blocks provided by Aspen Plus software as well as the external subroutines from FORTRAN compiler. The gas–solid hydrodynamics in the decoupling CFB combustor and macro-chemical reaction kinetics of coal combustion have been included in the process simulation model of CFB coal decoupling combustion. The profiles of average bed temperature and concentrations of gas components along the CFB riser height can be successfully predicted by the developed process simulation model. The effects of excess air percentage, first stage stoichiometry, and the introduction position of secondary air on concentrations of the emitted gaseous components, especially concentrations of NO and N$_2$O can be simulated by the developed process simulation model. The contribution ratios of all relevant combustion reactions to emissions of NO and N$_2$O can be quantitatively predicted. A good agreement between the simulated and measured results can be obtained during CFB coal decoupling combustion process under a large variation range of the CFB operation conditions.

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1. Introduction

The circulating fluidized bed (CFB) combustion technology has been rapidly developed and widely applied since the 1980s because of its high combustion efficiency and low pollution emission. The main advantages of CFB combustion technology from industrial application can be summarized as easy operation, low operation temperature, large adaptability of fuels, wide load adjustment range from 30% to 100%, and discharged high activity solid ash as raw material of high quality cements (Basu, 1999; de Diego et al., 1996; Muzio and Quartucy, 1997). However, high concentration of NO$_x$, especially N$_2$O, emitted from CFB coal combustion boilers is a conspicuous problem although it emits lower NO concentration than that of other coal combustion technologies.

In order to solve the problem that depleting N$_2$O emission and controlling NO emission during coal combustion in a CFB combustor, some new technologies have been developed and adapted in recent years beside traditional de-NO$_x$ technologies (Lyngfelt et al., 1996, 1998; Zhang et al., 2006b). As a new clean coal combustion technology, the CFB coal decoupling combustion process has been developed at the Institute of Process Engineering, Chinese Academy of Sciences (IPE, CAS) for decreasing NO$_x$ emission, especially depleting N$_2$O emission (Zhang et al., 2006b). Compared to the traditional CFB coal combustion technology, the CFB coal decoupling combustion process can be divided into three sub-steps: (1) coal particles are pyrolyzed in the CFB downer column/reactor; (2) the pyrolysis products are burned out in the CFB riser column/reactor; and (3) the gas and solid particles is separated in a CFB cyclone installed at the top of the CFB downer column/reactor. The emission behavior of NO and N$_2$O in the newly developed CFB coal decoupling combustion technology have been investigated in a 30 kW CFB combustor. The operation parameters include the excess air percentage, first stage stoichiometry, introduction position of secondary air, inletting position of coal, and coal types, which can effectively affect on NO$_x$ emission during CFB coal decoupling combustion process reported elsewhere (Xie et al., 2007, 2006; Zhang et al., 2006a).

A lot of researchers had put their attentions on developing the mathematical models for describing coal combustion performance in a fluidized bed combustor. Rajan and Wen had developed...
a unique coal combustion model in a fluidized bed combustor, which considered the related reactions in freeboard (Rajan and Wen, 1980). A three-phase model of coal combustion in a fluidized bed had been developed by Sriaram and et al. to embody the effects of gas mixing and solids circulation (Sriramulu et al., 1996). A mathematical modeling study of gaseous pollutants formation and destruction during the incineration of municipal solid wastes (MSW) in a CFB combustor had been conducted by Desroches-Ducarne et al. (1998). Meanwhile, Basu had summarized the progresses of combustion process (Basu, 1999). Kilpinen et al. had carried out a study of a single particle modeling for char-nitrogen (char-N) oxidation in a fluidized bed combustor (Kilpinen et al., 2002). Therefore, it is available to investigate the process simulation of NO and N2O emissions during CFB coal decoupling combustion process. The process simulation model considering the gas–solid hydrodynamics and combustion reaction kinetics can simulate and predict the emission schemes of NO and N2O during CFB coal decoupling combustion process with cost-saving and energy-saving benefits, because the experiments of CFB coal decoupling combustion are very difficult to obtain the related information.

Aspen Plus, as the sophisticated process simulation software, can realize the process optimization, technology reliability, economic benefit, and environmental assessment. It has been proved by many performances that Aspen Plus can be successfully applied to simulate the steady state process containing solids, electrolytes, coal, and biomass based on sequential modular method as well as equation oriented method for sensitivity analysis, design optimization, and case study (Cimini et al., 2005; Doherty et al., 2009; More et al., 2010; Nikoo and Mahinpey, 2008; Sahu et al., 2010). Sotudeh-Gharebaagh et al. (1998) have wonderfully simulated the emissions of gaseous components have been simulated and compared with the measured ones (Xie et al., 2007, 2006; Zhang et al., 2006a,b). Furthermore, the contribution ratios of the related reaction kinetics and gas–solid hydrodynamics and chemical reaction kinetics is very important and necessary to simulate the behavior of gaseous component emission during CFB coal decoupling combustion process in this study.

A process simulation model of coal decoupling combustion in a 30 kW CFB combustor for three coals has been developed in Aspen Plus environment considering gas–solid hydrodynamics (Löfler et al., 2003), and coal combustion kinetics (Desroches-Ducarne et al., 1998; Rajan and Wen, 1980) including macro-kinetics of char-N transformation to NO or N2O (Kilpinen et al., 2002). The effects of operation parameters for the CFB combustor, such as, excess air, first stage stoichiometry, position of secondary air, on the emissions of gaseous components have been simulated and compared with the measured ones (Xie et al., 2007, 2006; Zhang et al., 2006a,b). Furthermore, the contribution ratios of the related reactions in the CFB riser column on the formation and destruction of NOx, along the CFB riser height have been determined and discussed. The ultimate goal of this study is to optimize the operation conditions of the CFB coal decoupling combustor to control the emissions of NO and N2O, and find the emission mechanism and control measures of NOx during CFB coal decoupling combustion process.

2. Mathematical modeling

The most important reaction zone in the CFB coal decoupling combustion configuration is the CFB riser column, where combustion rate of fuel particles is affected by the gas–solid hydrodynamics and multiphase macro-kinetics. The gas–solid hydrodynamics affects the distribution of solid particles along the CFB riser height, and furthermore influences the contact area between solid particles and gas phase. The multiphase macro-kinetics in the CFB riser column contains the intrinsic kinetics of the related reactions combined with heat and mass transfer between solid particles and gas phase. Hence, the multiphase macro-kinetics will affect the consumption rates of fuel particles as well as formation rates of pollutants. Therefore, it is of great importance to accurately describe the gas–solid hydrodynamics and multiphase macro-kinetics in the CFB riser column for exactly simulating CFB coal decoupling combustion process.

2.1. Modeling of gas–solid hydrodynamics in CFB riser

To simplify the description of gas–solid hydrodynamics model in a CFB riser column, some assumptions should be applied and can be summarized as follows: (1) CFB coal decoupling combustion is considered as a steady state process; (2) fuel particles are burned turbulently, and have a very good internal back-mixing at each location in a CFB riser column (Sotudeh-Gharebaagh et al., 1998); (3) the unburned fuel particles separated from the exhaust flue gas by a cyclone are mixed with the newly added coal particles and returned to the bottom of CFB riser column for further combustion, thus all solid particles can be well circulated and mixed by an ideal external recirculation (Sotudeh-Gharebaagh et al., 1998); and (4) the size variation of solid particles by friction is neglected.

As a key reactor of a CFB combustor, the CFB riser column can be divided into several reaction sub-units along the CFB riser height according to the characteristics of gas–solid hydrodynamics. These sequentially divided sub-units along the CFB riser height are closely dependent on each other through the exchanges of materials and heat streams. The relationship between the voidage $e_i$ and CFB riser height $z$ in the five divided sub-units along the CFB riser height during CFB coal combustion process in a 30 kW CFB combustor is presented in Fig. 1. The difference of gas superficial velocity $U_g$ caused by introducing the secondary air can divide the CFB riser column into two regions as the dense phase region and dilute phase region. In order to describe the voidage distribution along the CFB riser height, the dense phase region can be further divided into two reaction regions as turbulent region 1 and turbulent region 2. The solid particles in the dense phase region are only fluidized by the sum of primary air and relaxation air from a U-type valve installed at the bottom of the CFB downer column. Therefore, gas phases and solid particles are turbulent and both of them are mixed perfectly in the dense phase region because $U_g$ is usually higher than the critical velocity $U_c$ (Sotudeh-Gharebaagh et al., 1998). Therefore, the average voidage at a constant is assumed in the dense phase region as

$$\bar{e}_1 \approx \bar{e}_2 = \bar{e}_i(z_2)$$

The solid particles are fluidized in the dilute phase region by the sum of primary air, relaxation air and secondary air, can be divided into three reaction regions as lower acceleration region 3, upper acceleration region 4 and completely fluidized region 5. The distribution of solid particles in the above-mentioned three sub-regions of the dilute phase region has an exponential decay relationship with the CFB riser heights $z$ as (Sotudeh-Gharebaagh et al., 1998)

$$\frac{e^i - \bar{e}(z)}{e^i - \bar{e}_\infty} = e^{-dz}$$

Therefore, the average voidage in the lower acceleration region 3, upper acceleration region 4 and completely fluidized region 5 in the upper dilute phase region can be also calculated as
follows:

\[ \xi_i = \int_{Z_{i-1}}^{Z_i} \varepsilon(z)dz = \frac{1}{g_i} \int_{Z_{i-1}}^{Z_i} \left( e^a - (e^a - e^{-a \nu_i})e^{-a \nu_i} \right) dz \]

\[ = e^a - \frac{1}{g_i} \left( e^{-a \nu_i} - e^a \right)(e^{-a \nu_i} - e^{-a \nu_{i-1}}), \quad i = 3, 4, \text{and } 5 \] (3)

The relationship among the decay index \( a \), average particle diameters \( d_i \), and gas superficial velocity \( U_g \) based on Kunii and Levenspiel (Kunii and Levenspiel, 1991; Sotudeh-Gharebaagh et al., 1998). The average solid particle size \( d_s \) in this study is larger than 80 \( \mu \)m. The calculated \( U_g \) is in a range of 4–7 m s\(^{-1} \). The constant \( C \) is taken as 4.0–5.0. The symbol \( \varepsilon^* \) represents the voidage at the top of CFB riser column in the dilute phase under the saturated condition, and can be calculated by (Sotudeh-Gharebaagh et al., 1998)

\[ \varepsilon^* = \frac{1}{1 + ((C/P_{C})/(U_g/\nu_g))]} \] (4)

where the crushing index \( \Phi \) is related with Froud number \( Fr \) as (Kunii and Levenspiel, 1991; Patience and Chaouki, 1993)

\[ \Phi = 1 + \frac{5.6}{Fr} + 0.47 Fr^{0.41}, \quad Fr = \frac{U_{mf}}{g d} \]

\[ U_{mf} = \frac{d_s^2 (\rho_g - \rho_s)g}{1650 \mu} \]

(5)

2.2. Modeling of equivalent pyrolysis process

It is recommended by Aspen Plus that coal can be treated as a mixture composed of series of stable elementary substances, such as, carbon, hydrogen, oxygen, nitrogen, sulfur, and ash-forming elements because no molecular formula can be applied to describe the coal chemical composition due to its structural complexity and composition diversity (Aspen Technology, 2002). The chemical compositions and particle size distributions of three coals are listed in Table 1. Therefore, the proximate and ultimate analyses of three coals have been applied to describe the coal pyrolysis process using the equivalent pyrolysis model. During the equivalent pyrolysis modeling, the rapid pyrolysis process of three coals in the CFB downer column can be treated as two cascade steps in this study: the first step is the equivalent DECOMPOSITION of coal to above-mentioned stable elementary substances; the second step is the SYNTHESIS of coal pyrolysis products from the above-mentioned stable elementary substances according to the principle of material balance.

It is well-known that the gaseous volatile matters and char are two main pyrolysis products of coal. The main components of gaseous volatile matters are \( CH_4, H_2, CO_2, CO, H_2O, \) and tar. The yield of gaseous volatile matter for three coals can be calculated from the correlation developed from the experimental data of Loison and Chauvin (Rajan and Wen, 1980) as

\[ V_{yield} = VM - \alpha - \beta \] (6)

\[ \alpha = \exp(26.41 - 3.961 \ln T + 1.15 VM) \] (7a)

\[ \beta = 0.2(VM - 10.9) \] (7b)

The mass fraction \( w_i \) of each component in volatile matters from coal rapid pyrolysis can be calculated by

\[ w_{CH_4} = 0.201 - 0.469(VM/100) + 0.241(VM/100)^2 \] (8a)

\[ w_{H_2} = 0.157 - 0.868(VM/100) + 1.388(VM/100)^2 \] (8b)

\[ w_{CO_2} = 0.135 - 0.900(VM/100) + 1.906(VM/100)^2 \] (8c)

\[ w_{CO} = 0.428 - 2.653(VM/100) + 4.845(VM/100)^2 \] (8d)

Table 1

<table>
<thead>
<tr>
<th>Coal type</th>
<th>Proximate analysis (mass%)</th>
<th>Ultimate analysis (mass%)</th>
<th>Particle size distribution (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatile matter</td>
<td>Ash</td>
<td>Fixed carbon</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal A</td>
<td>36.2</td>
<td>5.5</td>
<td>58.3</td>
</tr>
<tr>
<td>Coal B</td>
<td>30.7</td>
<td>18.4</td>
<td>50.9</td>
</tr>
<tr>
<td>Coal C</td>
<td>26.4</td>
<td>13.1</td>
<td>60.5</td>
</tr>
</tbody>
</table>

* Based on dry basis.

* By difference.
2.3. Modeling of macro-combustion reaction kinetics

To simplify the macro-combustion kinetics model of pyrolysis products in a CFB riser column, the basic assumptions proposed in this study are summarized as follows: (1) the surface temperature of char particles $T_p$ is higher than gas temperature $T_g$ and $T_r$ can be calculated by $T_p = T_g + 6.6 \times 10^4 C_{O_2}$ (Hu, 2007); (2) the combustion of char particles in the CFB cyclone as well as in the CFB downdown column is negligible because the residence time of char particles and silica sands as heat carrier in the CFB cyclone is very short, and oxygen concentration in the CFB downdown column is very low (Sotudeh-Gharebaagh et al., 1998); (3) the reduction of char particle diameter during combustion process is also omitted; and (4) the primary crack of coal particles and the secondary crack of char particles are also neglected (Sotudeh-Gharebaagh et al., 1998).

The chemical reaction equations, expressions of chemical reaction rates, and corresponding reaction rate constants for describing the combustion of pyrolysis products in the CFB riser column are summarized in Table 3 (Liu et al., 2011). The number of char particles in the ith sub-unit $N_{char, i}$ defined as the ratio of char particles volume $V_{char, i}$ to the average volume of single char particle $V_{char}$ can be calculated by

$$N_{char, i} = \frac{V_{char, i}}{V_{char}} = \frac{V_i(1-T_r)\eta_i}{(1/6)\pi d_e^3 \eta_{char}}$$  \hspace{1cm} (9a)

The volume fraction of char particles in the ith sub-unit $\eta_i$ can be calculated by

$$\eta_i = \frac{q_{char, i}/V_{char}}{q_{char} + q_{SiO_2}} \frac{V_{char}}{V_e} \eta_{char}$$  \hspace{1cm} (9b)

The Sherwood number $Sh_p$ of R(1) in Table 3 for describing $k_{l,d}$ can be calculated as follows (Basu, 1985):

$$Sh_p = 2e + 0.69 \frac{Re_p \sqrt{Sc}}{e}$$  \hspace{1cm} (10a)

where the Reynolds number $Re_p$ and Schmidt number $Sc$ can be defined as follows:

$$Re_p = \frac{Ar \varepsilon^{0.75}}{18 + 0.61 \sqrt{Ar \varepsilon^{0.75}}} , \quad Sc = \frac{\mu_g}{\rho_g D_g}$$  \hspace{1cm} (10b)

The Archimedes number $Ar$ and diffusivity coefficient of $O_2$ in nitrogen $D_g$ (Hu, 2007) in Eq. (10b) can be calculated by

$$Ar = \frac{g_d \rho_g (\rho_d - \rho_g)}{D_g}, \quad D_g = 3.13 \times 10^{-4} \left( \frac{T}{1500} \right)^{1.73}$$  \hspace{1cm} (10c)

The mechanism factor $\phi$ for describing char combustion in the definition of $k_{l,d}$ in R(1) in Table 3 can be calculated by (Rajan and Wen, 1980)

$$\phi = \frac{1}{1 + \left( \frac{2c + 2 - \frac{d_{char} - 0.05}{d_{char} + 2}}{0.05 \leq d_{char} \leq 1.0 \text{ mm}} \right)}$$  \hspace{1cm} (11)

where $z$ is the concentration ratio of $CO$ to $CO_2$ generated during char combustion, and can be calculated by (Rajan and Wen, 1980)

$$z = 2500 \exp(-51,900/R_d T_p)$$  \hspace{1cm} (12)

Therefore, the above-mentioned kinetics model of macro-combustion reactions for pyrolysis products can be developed by combining Eqs. (9)–(12) with all macro-reaction rates listed in Table 3 to simulate the coal decoupling combustion in the 30 kW CFB combustor.

2.4. Construction of process simulation model based on Aspen Plus

2.4.1. Description of CFB coal decoupling combustion process

According to the above-mentioned principle of the coal decoupling combustion technology, a CFB coal decoupling combustion reactor has been modified from a 30 kW traditional CFB combustor reported elsewhere (Xie et al., 2007, 2006), as shown in Fig. 2. The coal particles were charged from a port at the lower zone of the solid–solid mixer below the particle storage hopper in the CFB downdown column using nitrogen as carrying gas. The char and pyrolysis gases generated in the CFB downdown column via a U-type valve at the bottom of the CFB downdown column and further combusted with the primary air and the secondary air along the CFB riser height. The unburned char, gases and silica sands were separated in a cyclone at the top of the CFB downdown column, and the separated gas was emitted as flue gas to a vent. Meanwhile, the separated solid particles containing the unburned char particles and silica sands were stored in a particles storage chamber. The secondary air with ambient temperature was tangentially introduced to the CFB riser column through a gas distributor chamber. The secondary air and the char combustion process must be described by the built-in modules/blocks of Aspen Plus. Six kinds of built-in modules/blocks of Aspen Plus have been applied in this study.
as shown in Fig. 3. The characteristics and purposes of the applied six kinds of modules have been reported elsewhere (Aspen Technology, 2001; Liu et al., 2011). It can be seen from Fig. 3 that the fully steady state of CFB coal decoupling combustion process can be represented by six kinds of modules as follows: (1) The pyrolysis process of the charged coal particles in the CFB downer column is represented by the built-in modules of yield reactor (Ryield) with the chemical composition and particle size distribution, and stoichiometry reactor (RStoic) with the specified reaction extents or conversion ratios based on Aspen Plus. (2) The mixing process between silica sands and pyrolysis products is represented by a module of a hopper-type mixer (Hopper). (3) The heat exchange among the existing silica sands, unburned char particles, and pyrolysis products in the CFB downer column is represented by a module of a heater (Heater 2). (4) The ash discharging operation from the U-type valve at the bottom of the CFB downer column is represented by a module of a separation (Sep1). (5) The combustion process of pyrolysis products along

<table>
<thead>
<tr>
<th>Reaction no.</th>
<th>Chemical reaction equation</th>
<th>Reaction rate</th>
<th>Constant of reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(1)</td>
<td>$C + \frac{1}{\varphi} O_2 \rightarrow (2 - \frac{2}{\varphi}) CO + (\frac{2}{\varphi} - 1) CO_2$</td>
<td>$-\frac{dn_C}{dt} = N_{char} \pi d^2 \varphi k_{10} C_{02}$</td>
<td>$k_1 = \frac{(R_T/M_C)}{(1/k_{10}) + (1/k_{11})}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$k_{10} = 8710 \exp(-1.4947 \times 10^3)$</td>
</tr>
<tr>
<td>R(2)</td>
<td>$CO + \frac{1}{2} O_2 \rightarrow CO_2$</td>
<td>$-\frac{dC_{CO}}{dt} = k_2 \varphi C_{CO}^2 \varphi O_2$</td>
<td>$k_2 = 1.9 \times 10^6 \exp(-8956)$</td>
</tr>
<tr>
<td>R(3)</td>
<td>$C + CO_2 \rightarrow 2CO$</td>
<td>$-\frac{dn_{CO}}{dt} = N_{char} \pi d^2 \varphi k_{3} C_{CO_2}$</td>
<td>$k_3 = 4.1 \times 10^6 \exp(-29.787)$</td>
</tr>
<tr>
<td>R(4)</td>
<td>$CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2H_2O$</td>
<td>$-\frac{dCH_4}{dt} = k_{4} C_{CH_4}^0.8$</td>
<td>$k_4 = 1.585 \times 10^{10} \exp(-24.157)$</td>
</tr>
<tr>
<td>R(5)</td>
<td>$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$</td>
<td>$-\frac{dH_2}{dt} = k_{5} C_{H_2} C_{0.5}$</td>
<td>$k_5 = 1.63 \times 10^{7} \exp(-3240)$</td>
</tr>
<tr>
<td>R(6)</td>
<td>$NH_3 + \frac{5}{4} O_2 \rightarrow NO + \frac{3}{2} H_2O$</td>
<td>$-\frac{dNH_3}{dt} = k_{6} C_{NH_3} C_{O_2}$</td>
<td>$k_6 = 3.38 \times 10^7 \exp(-10,000)$, $k_6 = 0.054$</td>
</tr>
<tr>
<td>R(7)</td>
<td>$NH_3 + \frac{3}{4} O_2 \rightarrow 2H_2 + \frac{3}{2} N_2 + \frac{3}{2} H_2O$</td>
<td>$-\frac{dNH_3}{dt} = k_{7} C_{NH_3} C_{O_2}$</td>
<td>$k_7 = 3.38 \times 10^7 \exp(-10,000)$, $k_7 = 0.054$</td>
</tr>
<tr>
<td>R(8)</td>
<td>$HCN + \frac{3}{4} O_2 \rightarrow 2H_2 + CO + \frac{1}{2} N_2 + \frac{1}{2} N_2O$</td>
<td>$-\frac{dHCN}{dt} = k_{8} C_{HCN} C_{O_2}$</td>
<td>$k_8 = 2.14 \times 10^{9} \exp(-10,000)$</td>
</tr>
<tr>
<td>R(9)</td>
<td>$[N]_{char} + \frac{1}{2} O_2 \rightarrow NO$</td>
<td>$-\frac{dn_{NO}}{dt} = \frac{N_{char} \pi d^2 \varphi}{N_{char} \varphi} \left( \frac{dn_C}{dt} \right) \frac{1}{1 - k_{9} C_{NO}}$</td>
<td>$k_9 = 900 \exp(-3551)$</td>
</tr>
<tr>
<td>R(10)</td>
<td>$\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightarrow NO_{thermal}$</td>
<td>$-\frac{dn_{NO_{thermal}}}{dt} = k_{10} C_{N_2} C_{O_2}$</td>
<td>$k_{10} = 3 \times 10^{14} \exp(-65,300)$</td>
</tr>
<tr>
<td>R(11)</td>
<td>$[N]_{char} + \frac{1}{4} O_2 \rightarrow \frac{1}{2} N_2O$</td>
<td>$-\frac{dn_{N_2O}}{dt} = \frac{N_{char} \pi d^2 \varphi}{N_{char} \varphi} \left( \frac{dn_C}{dt} \right) \frac{k_{11} C_{NO}}{1 + k_{11} C_{NO}}$</td>
<td>$k_{11} = 900 \exp(-3551)$, $k_{11} = 3$</td>
</tr>
<tr>
<td>R(12)</td>
<td>$NO + C \rightarrow CO + \frac{1}{2} N_2$</td>
<td>$-\frac{dn_{NO}}{dt} = N_{char} \pi d^2 \varphi k_{12} C_{NO}$</td>
<td>$k_{12} = 5.85 \times 10^7 \exp(-12,000)$</td>
</tr>
<tr>
<td>R(13)</td>
<td>$NO + CO \rightarrow CO_2 + \frac{1}{2} N_2$</td>
<td>$-\frac{dn_{NO}}{dt} = f(C_{NO}, C_{CO})$</td>
<td>$f(C_{NO}, C_{CO}) = k_{13} C_{NO} (k_{11} C_{CO} + k_{14}) / (k_{11} C_{SO} + k_{14} C_{CO} + k_{15})$</td>
</tr>
<tr>
<td>R(14)</td>
<td>$N_2O + C \rightarrow CO + N_2$</td>
<td>$-\frac{dn_{N_2O}}{dt} = N_{char} \pi d^2 \varphi k_{14} C_{N_2O}$</td>
<td>$k_{14} = 2.9 \times 10^6 \exp(-16,983)$</td>
</tr>
<tr>
<td>R(15)</td>
<td>$N_2O + CO \rightarrow CO_2 + N_2$</td>
<td>$-\frac{dn_{C_2O}}{dt} = k_{15} C_{NO} C_{CO}$</td>
<td>$k_{15} = 5.01 \times 10^3 \exp(-5292)$</td>
</tr>
<tr>
<td>R(16)</td>
<td>$N_2 + \frac{1}{2} O_2 \rightarrow N_2 + O_2$</td>
<td>$-\frac{dn_{N_2}}{dt} = f_{char} \pi d^2 \varphi k_{16} C_{N_2}$</td>
<td>$k_{16} = 43.5 \exp(-10,000)$</td>
</tr>
</tbody>
</table>
the CFB riser height is represented by five modules of the continuous stirred tank reactor RCSTR with \( i = 1, 2, 3, 4, \) and 5, respectively. (6) The cyclone separation of the unburned char particles and silica sands from flue gas is represented by a module of a separator (Sep2). (7) The heating process of primary air is represented by a module of a heater (Heater1). The mixing of the heated primary air with solid substances from the CFB downer column is represented by a mixer module (Mixer1). (8) The mixing of secondary air at ambient temperature and substances from RCSTR2 is represented by a mixer module (Mixer2).

2.4.3. Function of calculator modules

To describe the influence of gas superficial velocity \( U_g \) on the voidage profile \( \varepsilon(z) \) along the CFB riser height using Aspen Plus, the gas superficial velocity \( U_g \) must be recalculated at each iteration to get a new value as initial value of \( U_g \) at the next iteration. The calculator module labeled as EPSS was developed to implement this function. The information streams illustrated in Fig. 3 show that the calculated \( U_g \) at one iteration for describing \( \varepsilon(z) \) in five modules of RCSTR with \( i = 1, 2, 3, 4, \) and 5 are the initial value of \( U_g \) at the next iteration for the purpose of decreasing the number of iterations in this study.
The calculator module assigned as NDC was developed to calculate the mole ratio of char-N to carbon in char particles, i.e., \( n_{\text{char-N}} / n_{\text{char-C}} \). The calculated \( n_{\text{char-N}} / n_{\text{char-C}} \) in five cascade modules of RCSTR(i) with \( i = 1, 2, 3, 4, \) and 5 is applied to simulate the gas–solid heterogeneous reaction rate of char-N in each module of RCSTR \( i \) with \( i = 1, 2, 3, 4, \) and 5.

The calculator module labeled as COALN was established to calculate the mole ratio of unburned char-N to total char-N in char particles in a module of RCSTR5 based on the mole ratio from N to C in coal particles from chemical composition of the investigated coals. The other function of calculator module COALN was used to make N from the introduced air into the flue gas in module Sep2, and let the unburned char-N in coal particles into the module Hopper, which was used to describe the gas–solid separation by a cyclone at the top of the CFB downer column.

### 2.4.4. Function of external FORTRAN subroutine

To accurately describe the combustion process of pyrolysis products along the CFB riser height based on Aspen Plus, it is necessary to input or provide the related data of reaction rates for all indispensable reactions in the divided five sub-units represented by five cascade modules of RCSTR with \( i = 1, 2, 3, 4, \) and 5. The applied expressions of reaction rates for all indispensable reactions in five cascade modules of RCSTR \( i \) with \( i = 1, 2, 3, 4, \) and 5 are summarized in Table 3. However, it is difficult to directly apply the standard interface of data in Aspen Plus to calculate the reaction rates for all indispensable reactions in five cascade modules of RCSTR \( i \) with \( i = 1, 2, 3, 4, \) and 5 listed in Table 3, or to directly use the gas–solid hydrodynamics model described in detail in Section 2 as the complexity. An external FORTRAN subroutine code must be developed to link the applied five cascade modules of RCSTR with \( i = 1, 2, 3, 4, \) and 5 in Aspen Plus for simulating the CFB coal decoupling combustion process, respectively. This means five external FORTRAN subroutine codes have to be developed for above-mentioned five cascade modules of RCSTR \( i \) with \( i = 1, 2, 3, 4, \) and 5 to exchange data information with the main simulation program of Aspen Plus, as shown in Fig. 3.

The external FORTRAN subroutine code contains the macro-combustion reaction kinetics, as listed in Table 3, which is invoked when the module of RCSTR \( i \) with \( i = 1, 2, 3, 4, \) and 5 is executed, respectively. Therefore, the external FORTRAN subroutine code needs the input stream information with 51 variables, such as, temperature, pressure, component concentration, flow-rate of reactants, etc. Calculating the reaction rates of chemical reactions listed in Table 3 is the main task of the developed external FORTRAN subroutine code. The programming method has been reported in the Aspen Plus guide of user (Aspen Technology, 2001). The calculated results from the external FORTRAN subroutine code are written as the output stream of modules of RCSTR \( i \) with \( i = 1, 2, 3, 4, \) and 5.

### 2.4.5. Physical properties of related substances and initialization in process simulation model

The physical properties of the related gaseous components in 15 built-in blocks are calculated by the built-in IDEAL method in Aspen Plus at high temperature and atmospheric pressure (Aspen Technology, 2002). The related solid components of those are determined by a built-in method in Aspen Plus for conventional substances at high temperature. Thus, the decided physical properties of gas and solid substances can be applied to calculate the parameters of combustion reactions, such as, enthalpies and densities, by Aspen Plus. The major initial conditions of six kinds of applied modules in this study are summarized in Table 4.

<table>
<thead>
<tr>
<th>Sub-process</th>
<th>Applied module</th>
<th>Input variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition</td>
<td>Ryield</td>
<td>(1) Temperature ( T = 298.15 \text{K} ) &lt;br&gt;(2) Pressure ( p = 101,325 \text{kPa} ) &lt;br&gt;(3) Component yield (see coal ultimate analysis in Table 1) &lt;br&gt;(4) Chemical composition of ash</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>Rstoic</td>
<td>(1) Temperature ( T = 298.15 \text{K} ) &lt;br&gt;(2) Pressure ( p = 101,325 \text{kPa} ) &lt;br&gt;(3) Chemical stoichiometry (see Table 2) &lt;br&gt;(4) Conversion ratio of key component (see Table 2)</td>
</tr>
<tr>
<td>Combustion</td>
<td>RCSTR</td>
<td>(1) Heat duty ( Q = 0 \text{J} ) &lt;br&gt;(2) Pressure ( p = 101,325 \text{kPa} ) &lt;br&gt;(3) Available chemical reactions in CSTR with ( i = 1,2,3,4, ) and 5 &lt;br&gt;(4) The volume of CSTR ( (i=1,2,3,4,5) )</td>
</tr>
<tr>
<td>Heat exchange</td>
<td>Heater</td>
<td>(1) Temperature ( T_{\text{heater}} = 473 \text{K} ), ( T_{\text{heater}} = 1023 \text{K} ) &lt;br&gt;(2) Pressure ( p = 101,325 \text{kPa} )</td>
</tr>
<tr>
<td>Mixing</td>
<td>Mixer</td>
<td>(1) Temperature ( T = 298.15 \text{K} ) &lt;br&gt;(2) Pressure ( p = 101,325 \text{kPa} )</td>
</tr>
<tr>
<td>Separation</td>
<td>Sep</td>
<td>Split fraction of all components in one outlet</td>
</tr>
</tbody>
</table>

### 3. Simulation results and discussion

The process simulation model of CFB coal decoupling combustion in a 30 kW CFB combustor based on Aspen Plus including the gas–solid hydrodynamics model and the macro-combustion reaction kinetics model can be developed according to above-mentioned steps. To compare the simulated results of gas concentrations with those in other references and literatures, all gas concentrations listed in tables or illustrated in figures have been converted to those of flue gases containing 6 vol% of \( \text{O}_2 \) on dry basis by

\[
y_{li,6\%} = \frac{y_{li,\text{out}} \cdot \lambda_{\text{O}_2,\text{out}}}{1.4}, \quad \lambda_{\text{O}_2,\text{out}} = \frac{21}{2T_{\text{out}} - y_{\text{O}_2,\text{out}}} \tag{13}
\]

where \( y_{li,6\%} \) is the converted concentration of component \( i (\times 10^{-2} \) or \( \times 10^{-6}) \), \( y_{li,\text{out}} \) is the measured concentration of component \( i (\times 10^{-2} \) or \( \times 10^{-6}) \), \( \lambda_{\text{O}_2,\text{out}} \) is the excess air percentage number based on the measured \( \text{O}_2 \) concentration (dimensionless), 1.4 is the excess air percentage number based on the measured concentration of \( \text{O}_2 \) as 6 vol% (dimensionless), \( y_{\text{O}_2,\text{out}} \) is the measured \( \text{O}_2 \) concentration (\( \times 10^{-2} \)).

#### 3.1. Simulation of temperature profile along CFB riser height

The simulated and measured temperature profiles along the CFB riser height during CFB coal decoupling combustion in a 30 kW CFB combustor for three coals are shown in Fig. 4, respectively. The operation parameters of the 30 kW CFB combustor are listed in Table 5 for three coals. It can be observed from Fig. 4 that the temperature increases sharply with an increase of the CFB riser height in the dense phase region; while, a smooth increase of temperature can be observed in the dilute phase region of the CFB riser column. The temperature increasing along the CFB riser height can be explained as follows: (1) the released heat from combustion of both char particles and pyrolysis gases with the primary air can contribute on temperature sharp
improvement in the dense phase region of the CFB riser column; the released heat from char combustion with the secondary air can lead to the further improvement of temperature in the dilute phase region; (2) the heat accumulation effect is another factor to improve the temperature along the CFB riser height because five modules of RCSTRI with \( i = 1, 2, 3, 4, \) and 5 as five adiabatic reactors have been applied to describe the combustion reactions in the CFB riser column; and (3) a small jump of the simulated temperature can be observed at the position of inletting the secondary air for Coal B and Coal C except Coal A, because no secondary air at ambient temperature is introduced for Coal A.

### 3.2. Simulation of concentration profiles for gaseous pollutants along CFB riser height

The simulated concentration profiles of \( O_2, CO_2, N_2O, NO, \) and \( CO \) along the CFB riser height during CFB coal decoupling combustion in the 30 kW CFB combustor for three coals are illustrated in Fig. 5, respectively. The operation parameters of the 30 kW CFB combustor are the same as that listed in Table 5 for three coals. The measured concentrations of \( O_2, CO_2, N_2O, NO, \) and \( CO \) in flue gas for three coals are also given in Fig. 5 for comparison. Certainly, the operation parameters of 30 kW CFB combustor for three coals are also shown in Fig. 6 for comparison.

It can be observed from Fig. 6(a) that increasing the excess air percentage can lead to an improvement of NO emission. This result can be explained as follows: (1) A larger excess air percentage implies a higher \( O_2 \) concentration in the CFB combustor. Thus, a larger reaction probability of char-N with \( O_2 \) can make more NO formed, i.e., the reaction R(9) listed in Table 3 will be enhanced. (2) The oxidation of \( NH_3 \) by \( O_2 \) can be intensified to form more NO with a larger excess air percentage. Therefore, the reaction R(6) listed in Table 3 will be promoted. (3) A higher excess air percentage corresponds to a less number of char particles and a smaller CO concentration in the dilute phase region at the upper CFB riser column. Therefore, the reactions R(12) and R(13) listed in Table 3 will be weakened. Hence, more NO can be generated with a larger excess air percentage during CFB coal decoupling combustion process.

The simulated results in Fig. 6(b) show that increasing excess air percentage can result in obvious improvement of \( N_2O \) emission for three coals as reported elsewhere \( (de\ Diego\ et\ al.,\ 1996;\ Zhang\ et\ al.,\ 2006a;\ Zhao\ et\ al.,\ 1994) \). However, a relative complex effect of the excess air percentage on \( N_2O \) emission has been measured for three coals as that increasing the excess air percentage can lightly improve \( N_2O \) emission for Coals A and B, and slightly decrease \( N_2O \) emission for Coal C. The result that increasing the excess air percentage can lead to an improvement of \( N_2O \) emission for Coal A and Coal B is similar as that reported elsewhere \( (de\ Diego\ et\ al.,\ 1996;\ Zhang\ et\ al.,\ 2006a) \), but the obtained results show that the excess air percentage corresponding to a less number of char particles and a smaller \( CO \) concentration in the dilute phase region at the upper CFB riser column. Therefore, the reactions R(12) and R(13) listed in Table 3 will be weakened. Hence, more NO can be generated with a larger excess air percentage during CFB coal decoupling combustion process.
applied Coal A and Coal B has higher volatile matters as 36.2 mass% and 30.7 mass%, respectively. Therefore, N₂O emission from Coals A and B is mainly decided by the homogenous oxidation reaction R(8) in Table 3. A greater excess air percentage can result in a greater N₂O emission for Coals A and B. The result that a lower volatile matter as 26.4 mass% and a higher fixed

applied Coal A and Coal B has higher volatile matters as 36.2 mass% and 30.7 mass%, respectively. Therefore, N₂O emission from Coals A and B is mainly decided by the homogenous oxidation reaction R(8) in Table 3. A greater excess air percentage can result in a greater N₂O emission for Coals A and B. The result that a lower volatile matter as 26.4 mass% and a higher fixed
carbon as 60.5 mass% in Coal C can make the reverse reactions of reduction NO on surface of char particles play an important role in N₂O emission, i.e., a greater excess air percentage can lead to a lower or stable N₂O emission for Coal C.

The same treatment method has been applied for three coals in the developed process simulation model based on Aspen Plus. The variation of coal ranks of three coals has not considered in the developed process simulation model. This maybe is the main reason for not accurately simulating the relationship between the excess air percentage and N₂O emission for Coal C. Therefore, accurately describing coal composition based on Aspen Plus is a challenging task to be solved in further study.

### 3.4. Simulation and prediction of first stage stoichiometry on NO and N₂O emissions

The comparison of the simulated and measured emissions of NO and N₂O during CFB coal decoupling combustion process in a 30 kW CFB combustor with changing the first stage stoichiometry from 0.69 to 1.21 under the condition of keeping the excess air percentage as 30% for three coals is illustrated in Fig. 7. The operation parameters of the CFB are listed in Table 7 for three coals.

It can be observed from Fig. 7(a) that decreasing the first stage stoichiometry can effectively result in a decrease of NO emission.
for three coals. Decreasing the first stage stoichiometry can largely increase the O$_2$-lean region in the dense phase region of the CFB riser column, furthermore, deplete the reaction rate of forming NO by reaction R(9) in Table 3. A higher mass ratio of the charged char particles and a greater amount of reducing components, such as CO in the dense phase region of the CFB riser column, can promote the reduction reactions of the formed NO into N$_2$ by reactions R(12) and R(13) in Table 3.

However, the complex relationships between the first stage stoichiometry and N$_2$O emission can be observed for three coals from the simulated and measured results illustrated in Fig. 7(b). The simulated relationship between the first stage stoichiometry and N$_2$O emission for three coals is basically consistency with that of the measured one for Coals A and B. This implies that decreasing the first stage stoichiometry can lead to a limited decrease of N$_2$O emission for Coals A and B. The reasons of these results can be summarized as follows: (1) The O$_2$-lean region in the dense phase region at the lower CFB riser column as deceasing the first stage stoichiometry is benefit to promote the decomposition reactions of forming N$_2$O by homogenous reaction R(8) and heterogeneous reaction R(11) in Table 3 (Zhang et al., 2006a, b). (2) More amounts of precursors of N$_2$O, such as HCN and NH$_3$, especially HCN, can be generated in the dense phase region of the CFB riser column with an increase of the first stage stoichiometry. Hence, the generated HCN will increase N$_2$O formation. The comprehensive or interaction effects of promotion or depletion of N$_2$O emission can weaken the effect of decreasing the first stage stoichiometry on N$_2$O emission. Therefore, no obvious or slight decrease of N$_2$O emission can be found from Fig. 7(b) for Coals A and B by decreasing the first stage stoichiometry.

The inconsistent result between the simulated and measured emission N$_2$O for Coal C shown in Fig. 7(b) can be explained with the same reasons as described in Section 3.3, i.e., a lower volatile matters and a higher fixed carbon in Coal C compared with Coals A and B can make a higher N$_2$O emission under the condition of the smaller first stage stoichiometry because N$_2$O formation is controlled by the heterogeneous reaction R(11) in Table 3 (Zhang et al., 2006a), but not by the homogenous reaction R(8) in Table 3 (Zhang et al., 2006a,b). Therefore, the characteristics of coal composition considering the coal rank differences by Aspen Plus should be given more attentions in the developed process simulation model.

The comprehensive effects of both the excess air percentage and the first stage stoichiometry on the simulated NO and N$_2$O emissions during CFB coal decoupling combustion in a 30kW CFB combustor for three coals are illustrated in Fig. 8, respectively. The optimal parameters of the excess air percentage and first stage stoichiometry can be obtained from Fig. 8 for three coals.

3.5. Predicted effect of introduction position of secondary air on gaseous pollutant emission

3.5.1. Predicted effect of introduction position of secondary air on concentration profiles of gas components along the CFB riser height

The reasonable introduction position of secondary air is an important CFB operation parameter for optimizing the effect of the first stage stoichiometry on NO and N$_2$O emissions during CFB coal decoupling combustion. Artificially changing the introduction position of secondary air in a CFB combustor with the fixed CFB configuration is very limited. The process simulation can be considered as a cost-low method to determine the optimal introduction position of secondary air. The simulated concentration profiles of O$_2$, CO$_2$, N$_2$O, NO, and CO along the CFB riser height with introducing the secondary air at 1.66 m, 2.80 m, and 4.00 m during CFB coal decoupling combustion in a 30kW CFB combustor for Coal C are illustrated in Fig. 9. The operation parameters are the same as that for Coal C in Table 5.

It can be seen from Fig. 9(a) and (b) that improving the introduction position of secondary air from 1.66 m to 4.00 m through 2.80 m above the gas distributor for Coal C can make an obvious variation of the concentration profiles of O$_2$ and CO$_2$ along the CFB riser height, but no obvious change at the outlet of flue gas or in flue gas. This means that changing the introduction position of secondary air cannot negatively affect on the coal combustion efficiency. The simulated results show that improving the secondary air position from 1.66 m to 4.00 m via 2.80 m can make the flow rate of O$_2$ at outlet of module RCSTR2 decrease from 2.20 × 10$^{-5}$kmol s$^{-1}$ to 1.29 × 10$^{-5}$kmol s$^{-1}$ via 1.66 × 10$^{-5}$kmol s$^{-1}$; meanwhile, the flow rate of CO$_2$ at outlet of module of RCSTR2 increases from 1.88 × 10$^{-5}$kmol s$^{-1}$ to 2.80 × 10$^{-5}$kmol s$^{-1}$ via 2.42 × 10$^{-5}$kmol s$^{-1}$ in the dense phase region of the CFB riser column.

It can be also observed from Fig. 9(c) that improving the introduction position of secondary air from 1.66 m to 4.00 m can result in a decrease of formation and emissions of NO and N$_2$O along the CFB riser height. The reasons of decreasing NO profile from improving the introduction position of secondary air can be explained as follows: (1) Improving the introduction position of secondary air can expand the O$_2$-lean zone; meanwhile, gas and solid particles will have a longer residence time in the dense phase region of the CFB riser column, where a stronger reducing atmosphere can be formed to benefit NO decomposition via reactions R(12) and R(13) in Table 3. (2) The formed NO in the expanded O$_2$-lean zone in the dense phase region of the CFB riser column can be reduced by the accumulated char particles to form N$_2$O.

Although the inconsistency results of changing the introduction position of secondary air on N$_2$O emission haven been reported from different researchers (Zhao et al., 1994), such as improving or depleting, or no influence on N$_2$O emission. Not only expanding the O$_2$-lean zone, but also the circulating characteristics of solid particles, residence time and temperature profile (Zhao et al., 1994) can be changed by improving the introduction position of secondary air. The simulated results from Fig. 9(d) show that improving the introduction position of secondary air can lead to a decrease of N$_2$O emission. This result is similar to that reported by Zhao et al. (1994). The lower temperature profile is maybe the major reason to the decrease of N$_2$O emission (Zhao et al., 1994) by improving the introduction position of secondary air for Coal C. Therefore, changing the introduction position of secondary air is a valid method to decrease emissions of NO and N$_2$O without influence on combustion efficiency during CFB coal decoupling combustion process.

Improving the introduction position of secondary air has also an effect on decreasing CO emission for Coal C as shown in Fig. 9(e). The simulated residence time of O$_2$ in the dense phase region of the CFB riser column increases from 0.40 s to 0.71 s and then to 1.03 s with improving the introduction position of secondary air from 1.66 m to 4.00 m via 2.80 m above the gas distributor. Therefore, the char particles can not be sufficiently burned in the dense phase region of the CFB riser column with improving the introduction position of the secondary air as the shorter resident time of O$_2$. Meanwhile, the simulated flow rate of CO at outlet of module RCSTR2 decreases from 3.28 × 10$^{-7}$kmol s$^{-1}$ to 1.60 × 10$^{-7}$kmol s$^{-1}$ via 2.16 × 10$^{-7}$kmol s$^{-1}$. The simulated results show that the flow rate of CO at outlet of module RCSTR5 decreases from 9.35 × 10$^{-8}$kmol s$^{-1}$ to 8.05 × 10$^{-8}$kmol s$^{-1}$ via 8.44 × 10$^{-8}$kmol s$^{-1}$ with improving the introduction position of secondary air. However, the total residence time of O$_2$ in
modules RCSTR3, RCSTR4, and RCSTR5 is 1.08 s, 0.83 s, and 0.58 s at above-mentioned three introduction position of secondary air as 1.66 m, 2.80 m, and 4.00 m, respectively. Therefore, it can be concluded that increasing O₂ concentration by introducing the secondary air is the main reason of complete CO combustion in the dilute phase region, but not the longer residence time of O₂.

3.5.2. Comprehensive effect of both secondary air introduction position and excess air percentage on NO and N₂O emissions

The effect of excess air percentage on NO and N₂O emissions during CFB coal decoupling combustion process in a 30 kW CFB combustor with three above-mentioned introduction positions of secondary air at a feeding rate of 2.83 kg h⁻¹ for Coal C is illustrated in Fig. 10. The operation parameters of the CFB
It can be obviously shown from Fig. 10 that improving the introduction position of secondary air from 1.66 m to 2.80 m above a gas distributor can lead to a slight increase of NO emission; however, further improving the introduction position of secondary air from 2.80 m to 4.00 m has an obvious active effect on depleting NO emission although increasing the air excess percentage from 5% to 35% shows a clearly tendency to promote NO emission during CFB coal decoupling combustion process.

Fig. 9. Predicted concentration profiles of O$_2$, CO$_2$, NO, N$_2$O, and CO along CFB riser height under the condition of charging secondary air at 1.66, 2.80, and 4.00 m during CFB coal decoupling combustion process in a 30 kW CFB combustor for Coal C, respectively.

Fig. 10. Comparison between simulated and measured concentrations of NO and N$_2$O in flue gas under the condition of various excess air percentages with charging secondary air at 1.66, 2.80, and 4.00 m along CFB riser height during CFB coal decoupling combustion process in a 30 kW CFB combustor for Coal C, respectively.
1.66 m | 2.80 m | 4.00 m
Position of secondary air

Table 8

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Flow rate of air at 298.15 K (m³ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test no.</td>
<td>Excess air</td>
</tr>
<tr>
<td>1</td>
<td>17.952</td>
</tr>
<tr>
<td>2</td>
<td>19.074</td>
</tr>
<tr>
<td>3</td>
<td>20.196</td>
</tr>
<tr>
<td>4</td>
<td>21.318</td>
</tr>
<tr>
<td>5</td>
<td>22.440</td>
</tr>
<tr>
<td>6</td>
<td>23.562</td>
</tr>
<tr>
<td>7</td>
<td>24.684</td>
</tr>
</tbody>
</table>

Fig. 11. Comparison between simulated and measured concentrations of NO and N₂O in flue gas under the condition of various values of first stage stoichiometry with charging secondary air at 1.66, 2.80, and 4.00 m along CFB riser height during CFB coal decoupling combustion process in a 30 kW CFB combustor for Coal C, respectively.
by O2 accounts for at least 44.11% on N2O decomposition in the upper dilute phase region of the CFB riser column.

4. Conclusions

A process simulation model of CFB coal decoupling combustion in a 30 kW CFB combustor has been developed based on Aspen Plus. The process simulation model has been constructed by 18 built-in modules in Aspen Plus including the gas–solid hydrodynamics via in–line calculator modules and macro-combustion reaction kinetics via the external FORTRAN subroutine codes comprehensively. The developed process simulation model has been verified by comparing the measured results. The main summary remarks can be obtained as follows:

(1) Not only the concentrations of gaseous components in flue gas but also the concentration profiles of gaseous components along the CFB riser height during coal decoupling combustion process in a 30 kW CFB combustor can be successfully predicted by the developed process simulation model based on Aspen Plus.

(2) Increasing the excess air percentage and first stage stoichiometry can lead to an increase of the simulated NO and N2O concentration in flue gas during coal decoupling combustion process. Not considering the coal rank properties or differences is the main reason for not accurately simulating the effect of excess air percentage or first stage stoichiometry on NO and N2O emission for coal with low volatile matters and high fixed carbon, such as, Coal C in this study.

(3) A reasonable improving the introduction position of secondary air can lead to an decrease of NO and N2O emissions during coal decoupling combustion process for coal with low volatile matter and high fixed carbon, such as, Coal C in this study.

(4) The optimal introduction position of secondary air can be obtained from the simulated results of NO and N2O emissions during coal decoupling combustion process only from the viewpoint of decreasing NO and N2O emissions.

(5) The contribution ratios of the related chemical reactions in the CFB riser column on formation and decomposition of NO and N2O along CFB riser height can be quantitatively determined from the developed process simulation model. The
simulated results show that the NO formation is absolutely controlled by fuel-N combustion; N2O formation is mainly controlled by HCN from coal pyrolysis gas in the dense phase region, while, oxidation of fuel-N will make a dominative role on N2O formation in the dilute phase region. The NO decomposition is dominated by char particles reduction; while, N2O decomposition in flue gas is comprehensively controlled by char particles, CO and O2 species, the contribution ratio of char particles, CO and O2 species accounts for 44.57%, 9.57% and 45.86% to N2O decomposition in flue gas during CFB coal decoupling combustion process in a 30kW CFB combustor with the fixed CFB configuration and operation parameters, respectively.

Conflict of interest

None.

Nomenclature

- $a$: decay index of cluster in free board, m$^{-1}$
- $Ar$: Archimedes number, dimensionless
- $C$: constant, 4–5
- $C_i$: concentration of component $i$ in gas, mol m$^{-3}$
- $C_{O_2}$: volume molar concentration of O$_2$ on surface of char particles, kmol m$^{-3}$
- $d_{e, char}$: equivalent or average diameter of char particles, m
- $D_g$: diffusivity coefficient of oxygen in nitrogen, m$^2$ s$^{-1}$
- $F_i$: relevant physical quantity
- $Fr$: Froude number, dimensionless
- $g$: gravitational acceleration, m s$^{-2}$
- $h_i$: height of the $i$th reaction sub-unit in riser column m
- $N_{char, i}$: number of char particles in the $i$th reaction sub-unit in riser column, dimensionless
- $M_r$: relative atom weight of carbon element, dimensionless
- $q_{m, SiO_2}$: mass flow of silica sands to reaction sub-units in riser column, kg s$^{-1}$
- $q_{m, SiO_2}$: mass flow of silica sands to reaction sub-units in riser column, kg s$^{-1}$
- $Q$: heat duty, J
- $R_u$: universal gas constant, 8.314 J mol$^{-1}$ K$^{-1}$
- $Re_p$: Reynolds number of particles, dimensionless
- $Sc$: Schmidt number, dimensionless
- $Sh_p$: Sherwood number of particles, dimensionless
- $t$: time, s
- $T$: absolute temperature, K
- $T_p$: absolute temperature of particles, K
- $T_g$: absolute temperature of gas, K
- $U_g$: gas superficial velocity, m s$^{-1}$
- $U_{ref}$: critical fluidization velocity, m s$^{-1}$
- $V_i$: volume of $i$th reaction sub-unit in riser column, m$^3$
- $V_{char, i}$: volume of char particles in $i$th sub-unit in riser column, m$^3$
- $V_{e, char}$: equivalent volume of single char particles in riser column, m$^3$
- $V_{yield}$: yield of volatile matter during pyrolysis, kg (100 kg coal)$^{-1}$
- $V_{e, SiO_2}$: average volume of single silica particle, m$^3$
- $VM$: content of volatile matters in coal, kg (100 kg coal)$^{-1}$
- $W_i$: mass fraction of component $i$ in pyrolysis gas, dimensionless
- $X_i$: weight fraction of particles at $d_i$ interval, dimensionless
- $y_i$: volume fraction of component $i$ in gas, $\times 10^{-2}$ or $\times 10^{-6}$
- $z$: height of the CFB riser column, m

Greek letters

- $\alpha$: coefficient for describing yield of volatile matters, kg (100 kg coal)$^{-1}$
- $\beta$: coefficient for describing yield of volatile matters, kg (100 kg coal)$^{-1}$
- $\epsilon$: voidage, dimensionless
- $\epsilon(z)$: voidage at height of $z$ in the CFB riser column, dimensionless
- $\epsilon^*$: voidage under saturated conditions, dimensionless
- $\epsilon_{\infty}$: voidage equivalent to the value at the height as $\infty$ in the CFB riser column, dimensionless
- $\tau_i$: average voidage in $i$th reaction sub-unit, dimensionless
- $\eta_i$: volume fraction of char particles in $i$th reaction sub-unit, dimensionless
- $\lambda$: excess air number, dimensionless
- $\mu_g$: viscosity of gas, Pas
- $\xi$: ratio of CO concentration to CO$_2$ concentration formed during char combustion, dimensionless
- $\rho_p$: density of solid particles, kg m$^{-3}$
- $\rho_{char, i}$: density of char particles in the $i$th reaction sub-unit, kg m$^{-3}$
- $\rho_{SiO_2}$: density of silica sands in reaction sub-units, kg m$^{-3}$
- $\rho_g$: density of gas, kg m$^{-3}$
- $\varphi$: mechanism factor of char combustion, dimensionless
- $\phi$: crushing index, dimensionless

Subscript

- $i$: $i$th reaction sub-unit or component $i$, dimensionless

Acknowledgment

The finical support of this work by the Natural Sciences Foundation of China (Project no. 50576101) is gratefully appreciated.

Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ces.2011.10.050.

References
