Appendix A. Modeling of NO Reduction during Simultaneous Char Combustion in the Char-sand Bed

In the present paper, two models, named slow char-N to NO model and rapid char-N to NO model respectively, were applied to interpret the experimental results. The two models represent two extreme possibilities of char-NO reaction in the experiment. The net NO conversion ratio is calculated by Equation 3 and 4 in the paper. In the appendix A, calculations leading to Equation 3 and 4 are shown.

1. Basic assumptions of the simultaneous char combustion experiments

The following assumptions are considered in both of the models:

- The gas is plug flow in the char-sand bed.
- NO formation and reduction are independent of each other.
- The char-N is liberated from each particle as either NO or N_2 with a fixed ratio.
- NO could be reduced to N_2 by char while gas flowed through the char-sand bed.
- The char particle temperature is equal to gas temperature during char combustion.

When the gas flows through the char-sand bed, char-N was oxidized to NO and then partial NO was reduced by the downstream char. Schematic representation of NO formation and reduction during simultaneous combustion is shown in Fig. 1. The subscript ´t´ in this appendix denotes the time when gas reached the inlet of the char-sand bed, and the subscript ´τ´ denotes the residence time of the gas in the char-sand bed, e.g., $[NO]_{t,\tau}$ means NO concentration of the gas which reaches the inlet of char-sand bed at t and has flowed a period of τ in the bed.

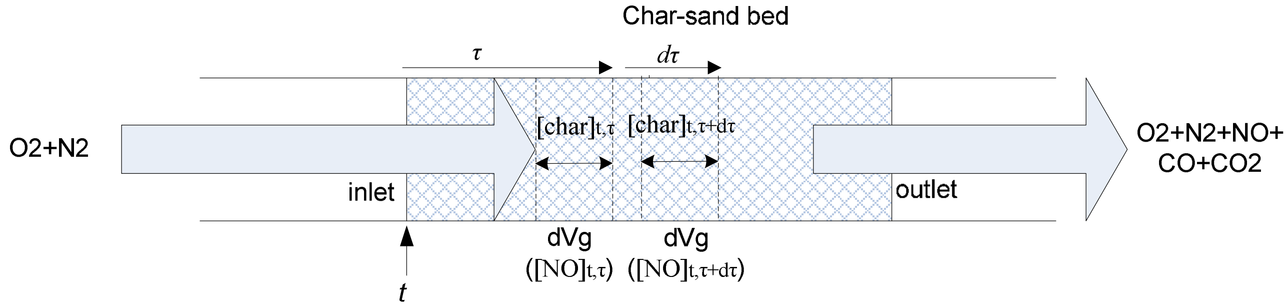

Figure a 1 Schematic representation of NO formation and reduction during simultaneous combustion

Considering the fate of the NO in a small volume gas ($d(V_g)$) with a small residence time ($d\tau$) in the reactor, Equation a1 is given:

$$\frac{d[NO]_{t,\tau}}{d\tau} = -k_{NO} \times ([char]_{t,\tau})^{\alpha} \times ([NO]_{t,\tau})^{\beta} + (NO - produced - in - d\tau) \quad \text{(a1)}$$

Here $[NO]_{t,\tau}$ is NO concentration of the gas, k_{NO} is the NO reduction rate constant, $[char]_{t,\tau}$ is char concentration, and NO-produced-in- $d\tau$ is the produced NO from char-N oxidation within $d\tau$. The three terms of Equation a1 from left to right denote variation of NO concentration, decrease of NO concentration due to NO reduction over char (NO-char reaction), as well as increase of NO concentration from char-N oxidation (char-N to NO reaction) respectively.

The NO reduction over char is assumed as first order with respect to both of NO concentration and char concentration, then the Equation a1 is described as Equation a2:

$$\frac{d[NO]_{t,\tau}}{d\tau} = -k_{NO} \times ([char]_{t,\tau}) \times ([NO]_{t,\tau}) + (NO - produced - in - d\tau) \quad \text{(a2)}$$

In the present experiments, the burnout times of char sample in 10% O_2 are 4-8 s according to CO and CO_2 gas profile as shown in Fig. a2, while the total residence time, simplified in Equation a3, is only 0.012 s at 850 ^{o}C. Thus, the variations of $[char]_{t,\tau}$ at 0-τ_0 with the certain t are neglect. So the Equation a2 is simplified as Equation a4:

$$\tau_0 = \frac{V_{fb}}{V_g} \quad \text{(a3)}$$

Here τ_0 is the total residence time of gas in the char-sand bed (in s), V_{fb} is volume of char-sand bed (in m^3), V_g is the volumetric gas flow rate (in m^3/s).

$$\frac{d[NO]_{t,\tau}}{d\tau} = -k_{NO} \times \frac{m_{char,0}(1-X_c)}{V_{fb}} \times ([NO]_{t,\tau}) + (NO - produced - in - d\tau) \quad \text{(a4)}$$

Here k_{NO} is the NO reduction rate constant (in m^3/kg/s), $m_{char,0}$ is initial char mass (kg carbon), X_c is carbon conversion ratio.

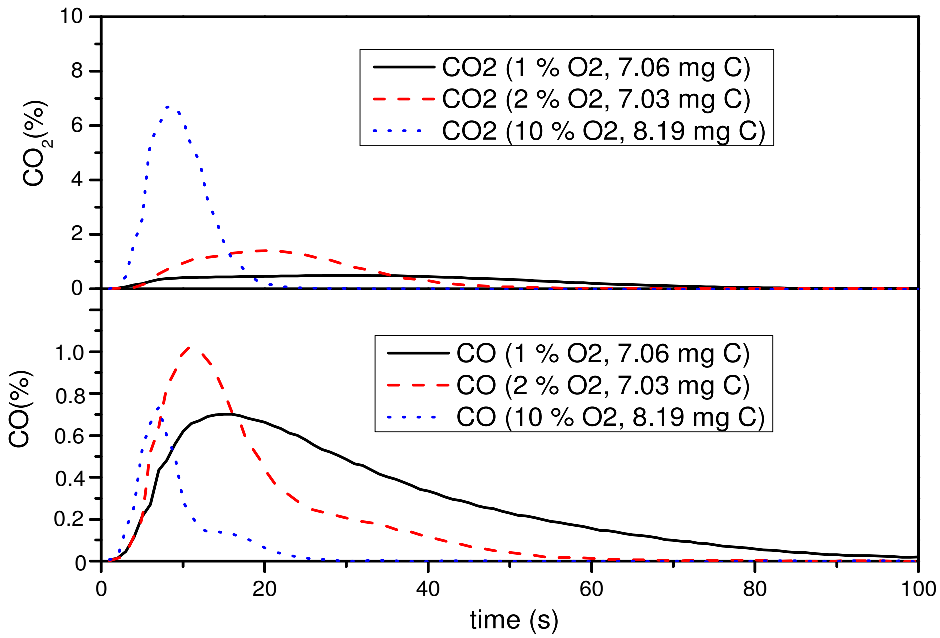

Figure a 2 Effect of O_2 concentration on CO and CO_2 concentration (combustion temperatures: 850 ^oC; gas flow: 1.5 NL/min; fuel: bituminous coal char) (Fig. 7 in paper)

2. Char-N to NO assumptions of the simultaneous char combustion experiments

2.1. Rapid char-N to NO model

Rapid char-N to NO model assumes that the char-N to NO reaction happened in the front of the char-sand bed, allowing the maximum possible extent of the char-NO reaction. The illustration of NO profile is shown in Fig. a3. In this case, the NO is only produced in the front of the bed and then the (NO-produced-in- dτ) is 0. Therefore, the Equation a4 is simplified as Equation a5:

$$\frac{d\left[NO\right]_{t,\tau}}{d\tau} = -k_{NO} \times \frac{m_{char,0}(1-X_c)}{V_{fb}} \times \left[NO\right]_{t,\tau} \qquad \text{(a5)}$$

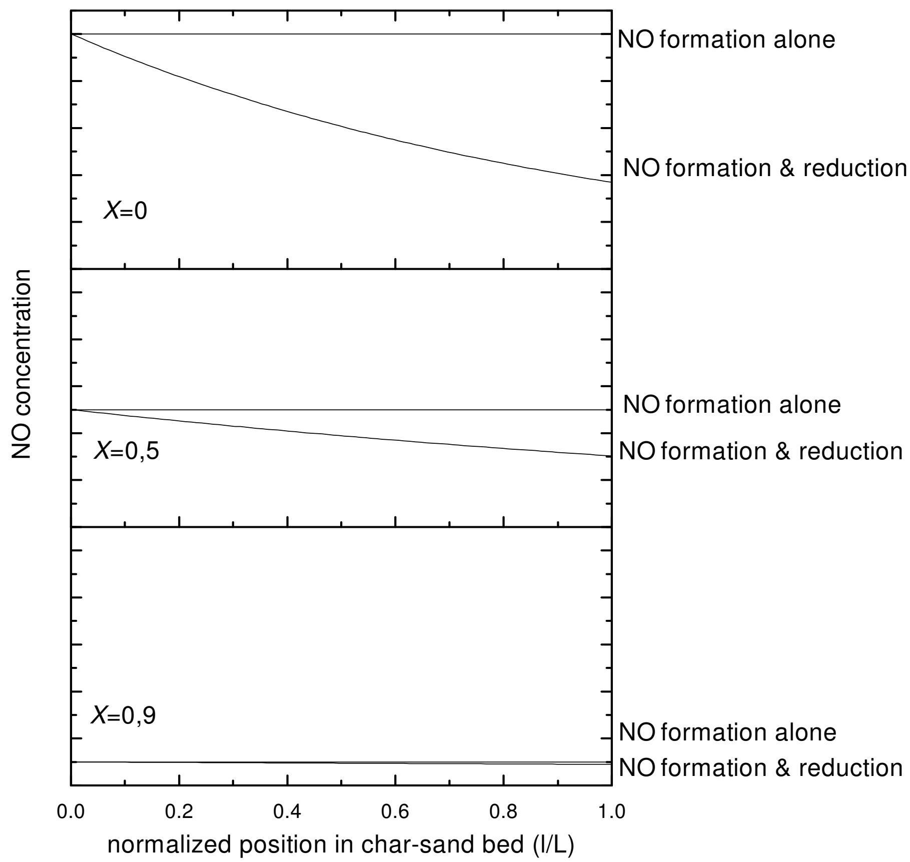

Figure a 3 Illustration of NO profile of the small volume gas (d(Vg)) within the char-sand bed with the rapid char-N to NO model

Equation a6 is achieved by integrating the Equation a5 throughout the residence time of gas in the char-sand bed (from $\tau=0$ to $\tau=\tau_0$)

$$\int_0^{\tau_0} \frac{d[NO]_{t,\tau}}{d\tau} d\tau = -\int_0^{\tau_0} k_{NO} \times \frac{m_{char,0}(1-X_c)}{V_{fb}} \times [NO]_{t,\tau}\, d\tau \tag{a6}$$

The τ_0 is defined by Equation a3 and then the following equation could be obtained:

$$\frac{[NO]_{t,\tau_0}}{[NO]_{t,0}} = \exp\left(-k_{NO} \times \frac{m_{char,0}(1-X_c)}{V_g}\right) \tag{a7}$$

Here $[NO]_{t,0}$ is the NO concentration in the inlet of char-sand bed, $[NO]_{t,\tau 0}$ is the NO concentration in the outlet of char-sand bed.

Integrating the Equation a7 throughout the char combustion period (from t=0 to t=t_0) could lead to the Equation a8 (Equation 4 in paper):

$$\overline{\eta_{NO}} = \eta_0 \times \frac{1-\exp(-k_{NO} \times m_{char,0} / V_g)}{k_{NO} \times m_{char,0} / V_g} \tag{a8}$$

Here $\overline{\eta_{NO}}$ is the net NO conversion ratio from char-N to NO, η_0 is the net conversion ratio from char-N to NO at single-particle condition, k_{NO} is the NO reduction rate constant (in m^3/kg/s), $m_{char,0}$ is the initial char mass (in kg carbon), V_g is the volumetric gas flow rate (in m^3/s).

2.2. Slow char-N to NO model

The slow char-N to NO model assumes that the char-N to NO reaction took place evenly throughout the char-sand bed, allowing the minimum possible extent of the char-NO reaction. The illustration of NO profiles with slow char-N to NO model is shown in Fig. a4. Thus, the Equation a4 could be described as Equation a9:

$$\frac{d[NO]_{t,\tau}}{d\tau} = -k_{NO} \times \frac{m_{char,0}(1-X_c)}{V_f} \times [NO]_{t,\tau} + \frac{d[m_{char,o} \times (1-X_c)]}{dt} \times \frac{N_{char} \times \eta_0}{M_N \times V_{fb}} \tag{a9}$$

Here N_{char} is nitrogen content in char, M_N is atomic weight of nitrogen.

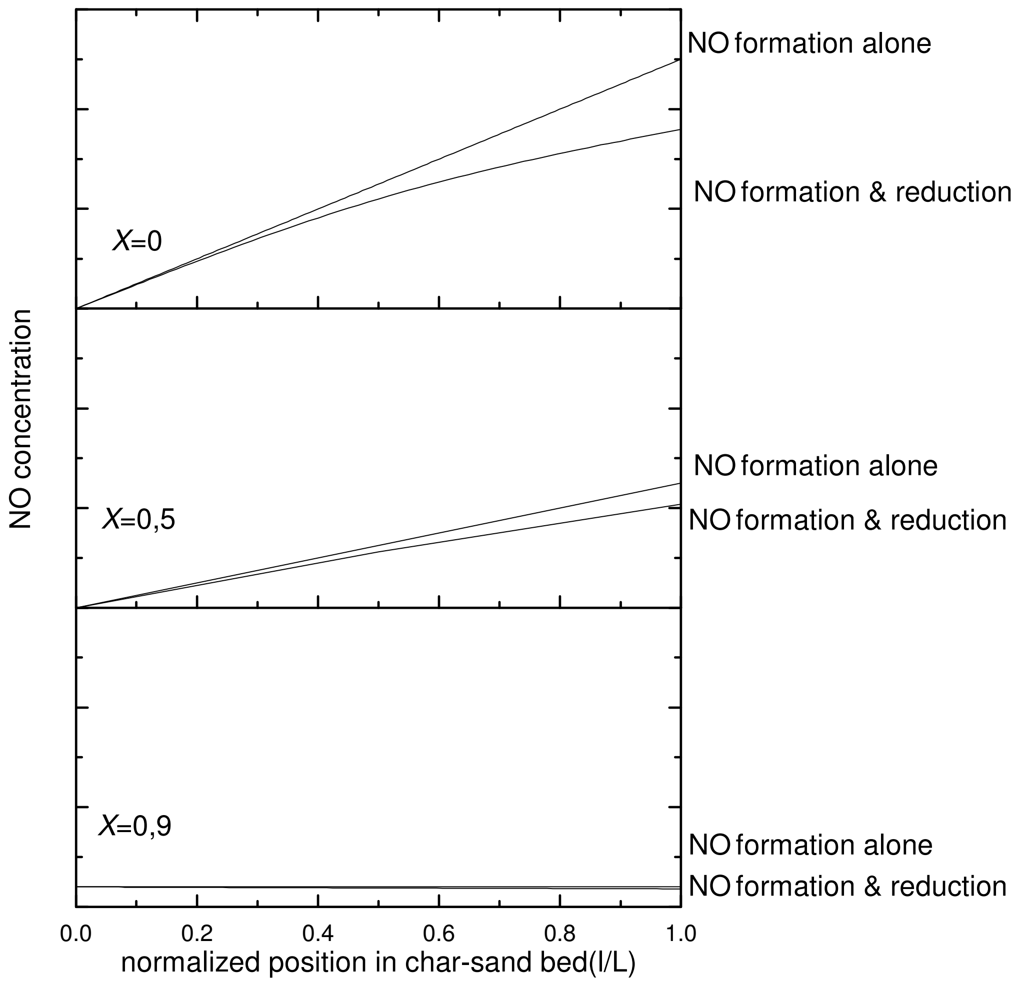

Figure a 4 Illustration of NO profile of the small volume gas (d(Vg)) within the char-sand bed with the slow char-N to NO model

The three terms of Equation a10 are integrated throughout the residence time (from τ=0 to $\tau=\tau_0$) and the char combustion period (from t=0 to $t = t_0$). The calculations of integration are shown in Equation a10-a12.

$$\int_0^{t_0}\left(\int_0^{\tau_0}\frac{d\left[NO\right]_{t,\tau}}{d\tau}d\tau\right)dt=\int_0^{t_0}\left(\left[NO\right]_{t,\tau_0}-\left[NO\right]_{t,0}\right)dt=\int_0^{t_0}\left(\left[NO\right]_{t,\tau_0}\right)dt \tag{a10}$$

$$\begin{aligned}&\int_0^{t_0}\left(\int_0^{\tau_0}k_{NO}\times\frac{m_{char,0}(1-X_c)}{V_{fb}}\times\left[NO\right]_{t,\tau}d\tau\right)dt\\&=\left(k_{NO}\times\frac{m_{char,0}}{V_{fb}}\right)\times\int_0^{t_0}\left((1-X_c)\left(\int_0^{\tau_0}\left[NO\right]_{t,\tau}d\tau\right)\right)dt\\&\approx\left(k_{NO}\times\frac{m_{char,0}}{V_{fb}}\right)\times\int_0^{t_0}\left((1-X_c)(\left[NO\right]_{t,\tau_0}\times\frac{V_{fb}}{2V_g})\right)dt\\&=\left(k_{NO}\times\frac{m_{char,0}}{2V_g}\right)\times\int_0^{t_0}\left((1-X_c)\times\left[NO\right]_{t,\tau_0}\right)dt\end{aligned} \tag{a11}$$

$$\int_0^{t_0}\left[\int_0^{\tau_0}\frac{d(m_{char,o}(1-X_c))}{dt\times V_{fb}}\times\frac{N_{char}\times\eta_0}{M_N}\times d\tau\right]dt=\frac{m_{char,0}\times N_{char}\times\eta_0}{M_N\times V_g} \tag{a12}$$

Thus, the Equation a13 is achieved from Equation a9-12.

$$\int_0^{t_0}\left(\left[NO\right]_{t,\tau_0}\right)dt=-\left(k_{NO}\times\frac{m_{char,0}}{2V_g}\right)\times\int_0^{t_0}\left((1-X_c)\times\left[NO\right]_{t,\tau_0}\right)dt+\frac{m_{char,0}\times N_{char}\times\eta_0}{M_N\times V_g} \tag{a13}$$

In the Equation a13, the three terms from left to right denote the net produced NO, the reduced NO by char and the intrinsic released NO from char-N. The net NO conversion ratio could also be calculated by its definition directly and shown following.

$$\begin{aligned}\overline{\eta_{NO}}&=\frac{net-produced-NO}{(net-produced-NO)+(reduced-NO-by-char)}\\&=\frac{\int_0^{t_0}\left(\left[NO\right]_{t,\tau_0}\right)dt}{\int_0^{t_0}\left(\left[NO\right]_{t,\tau_0}\right)dt+\left(k_{NO}\times\frac{m_{char,0}}{2V_g}\right)\times\int_0^{t_0}\left((1-X_c)\times\left[NO\right]_{t,\tau_0}\right)dt}\end{aligned} \tag{a14}$$

Here $\overline{\eta_{NO}}$ is the net NO conversion ratio from char-N to NO, k_{NO} is the NO reduction rate constant (in $m^3/kg/s$), $m_{char,0}$ is the initial char mass (in kg carbon), V_g is the volumetric gas flow rate (in m^3/s),

$[NO]_{t,\tau 0}$ is the NO concentration in the outlet of char-sand bed (in mol/m^3), X_c is carbon conversion ratio.

Appendix B. Modeling of External NO Reduction in the Char Combustion Experiment

In the appendix B, how to model the external NO reduction in the char combustion experiment (modeling data in Fig. 9) are shown.

1. Rapid char-N to NO model

In this model, the modeling data of NO concentration at the outlet of char-sand bed is calculated by Equation a15 (from Equation a7).

$$\frac{[NO]'_{t,\tau_0}}{[NO]_{t,0}} = \exp\left(-k_{NO} \times \frac{m_{char,0}(1-X_c)}{V_g}\right) \tag{a15}$$

Here $[NO]'_{t,\tau0}$ is the modeling data of NO concentration at the outlet of char-sand bed (in mol/m^3), $[NO]_{t,0}$ is the NO concentration at the inlet including the external NO and produced NO from char (in mol/m^3), k_{NO} is the NO reduction rate constant (in m^3/kg/s) from rapid char-N to NO model achieved from simultaneous combustion experiments in this paper.

The modeling data of the net conversion ratio could be described by Equation a16.

$$\overline{\eta_{NO}} = \frac{\int_0^{t_0} ([NO]'_{t,\tau_0} - [NO]_{inlet-gas})dt \times V_g \times M_N}{m_{char,0} \times N_{char} \times \eta_0} \tag{a16}$$

Here $[NO]_{inlet\text{-}gas}$ is the NO concentration at the inlet gas (in mol/m^3).

2. Slow char-N to NO model

In this case, integrating the three terms of Equation a9 throughout the char-sand bed (from τ=0 to τ=τ_0) and the char combustion period (from t=0 to $t = t_0$) could achieve the Equation a17-a19.

$$\int_0^{t_0}\left(\int_0^{\tau_0}\frac{d\left[NO\right]'_{t,\tau}}{d\tau}d\tau\right)dt=\int_0^{t_0}\left(\left[NO\right]'_{t,\tau_0}-\left[NO\right]_{t,0}\right)dt$$
$$=\int_0^{t_0}\left(\left[NO\right]'_{t,\tau_0}-\left[NO\right]_{t,inlet-gas}\right)dt \tag{a17}$$
$$=\overline{\eta_{NO}}\times\frac{m_{char,0}\times N_{char}\times\eta_0}{V_g\times M_N}$$

$$\int_0^{t_0}\left(\int_0^{\tau_0}k_{NO}\times\frac{m_{char,0}(1-X_c)}{V_{fb}}\times\left[NO\right]_{t,\tau}d\tau\right)dt$$
$$=\left(k_{NO}\times\frac{m_{char,0}}{V_{fb}}\right)\times\int_0^{t_0}\left((1-X_c)\left(\int_0^{\tau_0}\left[NO\right]_{t,\tau}d\tau\right)\right)dt$$
$$\approx\left(k_{NO}\times\frac{m_{char,0}}{V_{fb}}\right)\times\int_0^{t_0}\left((1-X_c)(\frac{\left[NO\right]_{t,\tau_0}+\left[NO\right]_{inlet-gas}}{2}\times\frac{V_{fb}}{2V_g})\right)dt \tag{a18}$$
$$=\left(k_{NO}\times\frac{m_{char,0}}{2V_g}\right)\times\int_0^{t_0}\left((1-X_c)\times\frac{\left[NO\right]_{t,\tau_0}+\left[NO\right]_{inlet-gas}}{2}\right)dt$$

$$\int_0^{t_0}\left[\int_0^{\tau_0}\frac{d(m_{char,o}(1-X_c))}{dt\times V_{fb}}\times\frac{N_{char}\times\eta_0}{M_N}\times d\tau\right]dt=\frac{m_{char,0}\times N_{char}\times\eta_0}{M_N\times V_g} \tag{a19}$$

Thus, the modeling data of the net conversion ratio are shown as following:

$$\overline{\eta_{NO}}=1-\frac{k_{NO}\times M_N}{2\times N_{char}\times\eta_0}\times\int_0^{t_0}\left((1-X_c)\times\frac{\left[NO\right]_{t,\tau_0}+\left[NO\right]_{inlet-gas}}{2}\right)dt \tag{a20}$$

Here $[NO]_{t,\tau0}$ is the NO concentration in the outlet of char-sand bed (in mol/m^3), $[NO]_{inlet\text{-}gas}$ is the NO concentration at the inlet gas (in mol/m^3), k_{NO} is the NO reduction rate constant from slow char-N to NO model achieved from simultaneous combustion experiments in this paper (in m^3/kg/s) .

Notation of Appendix

η_0	net conversion ratio from char-N to NO at single-particle condition
$\overline{\eta_{NO}}$	net NO conversion ratio from char-N to NO
τ	the residence time of gas in char-sand bed
τ_0	the total residence time of gas in char-sand bed
$d\tau$	a small residence time of the $d(V_g)$
$[char]_{t,\tau}$	char concentration, kg/m^3
k_{NO}	the NO reduction rate constant, $m^3/kg/s$
$m_{char,0}$	the initial char mass and calculated by CO and CO_2 gas profiles, kg
M_N	atomic weight of nitrogen, kg/mol
N_{char}	nitrogen content in char and achieved from Table 2 in paper
$[NO]_{t,\tau}$	NO concentration, mol/m^3
$[NO]_{t,0}$	NO concentration in inlet of char-sand bed, mol/m^3
$[NO]_{t,\tau 0}$	NO concentration in the outlet of the char-sand bed and measured by gas analyzer, shown as C_{NO} in paper, mol/m^3
$[NO]'_{t,\tau 0}$	modeling data of NO concentration at the outlet of char-sand bed, mol/m^3
$[NO]_{inlet\text{-}gas}$	NO concentration at the inlet gas, mol/m^3
t	the time of gas reaching the inlet of char-sand bed, s
t_0	burn out time of char sample, s
V_{fb}	volume of char-sand bed, m^3
V_g	the volumetric gas flow rate, m^3/s
$d(V_g)$	a small volume gas
X_c	carbon conversion ratio, calculated by CO and CO_2 gas profiles and $m_{char,0}$