

Prediction of NO_x Emissions in Recovery Boilers

— An Introduction to NO_x Module

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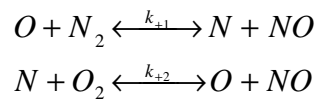
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1. Introduction

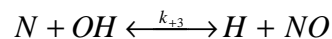
In laminar flames, and at the molecular level within turbulent flames, the formation of NO_x can be attributed to three distinct chemical kinetic processes. The NO_x formed by these three processes is described as thermal NO_x, prompt NO_x, and fuel NO_x. Thermal NO_x is formed by the oxidation of atmospheric nitrogen present in the combustion air. Prompt NO_x is produced by high-speed reactions at the flame front, and fuel NO_x is produced by oxidation of nitrogen contained in the fuel.

Thermal NO_x

The formation of thermal NO_x is determined by a set of highly temperature-dependent chemical reactions known as the extended Zeldovich mechanism. The principal reactions governing the formation of thermal NO_x from molecular nitrogen are as follows:



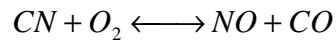
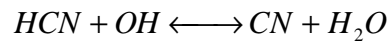
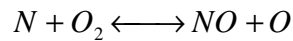
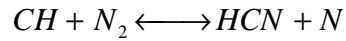
A third reaction has been shown to contribute, particularly at near-stoichiometric conditions and in fuel-rich mixtures:



The rate of formation of thermal NO_x is significant only at high temperatures (greater than 1800 K) because fixation of nitrogen requires the breaking of the strong N₂ triple bond.

Prompt NO_x

Prompt NO_x is most prevalent in rich flames. The actual formation involved a complex series of reactions and many possible intermediate species. The route now accepted is as follows:



Many investigations have shown that the prompt NO_x contribution to total NO_x from stationary combustors is small.

Fuel NO_x

It is well known that nitrogen-containing organic compounds present in liquid or solid fuel can contribute to the total NO_x formed during the combustion process. The extent of conversion of fuel nitrogen to NO_x is dependent on the local combustion characteristics and the initial concentration of nitrogen-bound compounds. Fuel-bound nitrogen-containing compounds are released into the gas phase when the fuel droplets or particles are heated during the devolatilization stage. From the thermal decomposition of these compounds, in the reaction zone, radicals such as HCN, N, CN, and NH can be formed and converted to NO_x.

2. NO_x Formation and Destruction in Recovery Boilers

As mentioned above, thermal NO_x is significant only at the temperature higher than 1800 K. Normally in recovery boilers, fuelled by black liquor, bark, or hogfuels, the maximum gas temperature is lower than 1800 K. Prompt NO_x also contributes less to the total NO_x emission from recovery boilers because the flame is less rich comparing with the normal gas flames. Therefore, both thermal NO_x and prompt NO_x can be neglected in the NO_x emission prediction at present. However, the NO_x emission from recovery boilers is in a lower level comparing with utility boilers fuelled by fossil fuels. The relative importance of thermal NO_x and prompt NO_x may increase. Tao *et al.* [1]

predicted the NO_x emission from a Kraft recovery boiler, and found that 19 ppm is from thermal-NO_x among the total NO_x emission of about 48 ppm. For further study, both thermal NO_x and prompt NO_x should be included in the NO_x prediction.

Fuel NO_x makes the greatest contribution to the total NO_x emission from recovery boilers, especially when the nitrogen content in the fuel is high. The nitrogen-containing compounds in the fuel may release into gas phase at both devolatilization stage and char burning stage. We name the nitrogen-containing compounds released during the devolatilization stage as volatile-N, while those released during the char burning stage as char-N. The distribution of fuel nitrogen in volatile-N and char-N depends on the fuel properties, and may vary from fuel to fuel. As a normal treatment, it is acceptable to assume that the mass fractions of volatile-N and char-N are proportional to the mass fractions of volatile and fixed carbon respectively if no related experimental data are available.

The volatile-N may appear as different forms of chemical species, such as HCN, NH₃, CN and so on, when it is released into the gas phase. According to the investigation by Forssen *et al.* [2] and Iisa *et al.* [3], the volatile-N mainly releases into gas phase in the form of NH₃ in the case of black liquor combustion in the recovery boiler. In this model, therefore, we assume the form of volatile-N to be NH₃ only. It is also assumed that the volatile-N evolution has the same rate as the devolatilization. In the gas phase, NH₃ will be oxidized by O₂ into NO, or reduced by NO into N₂.

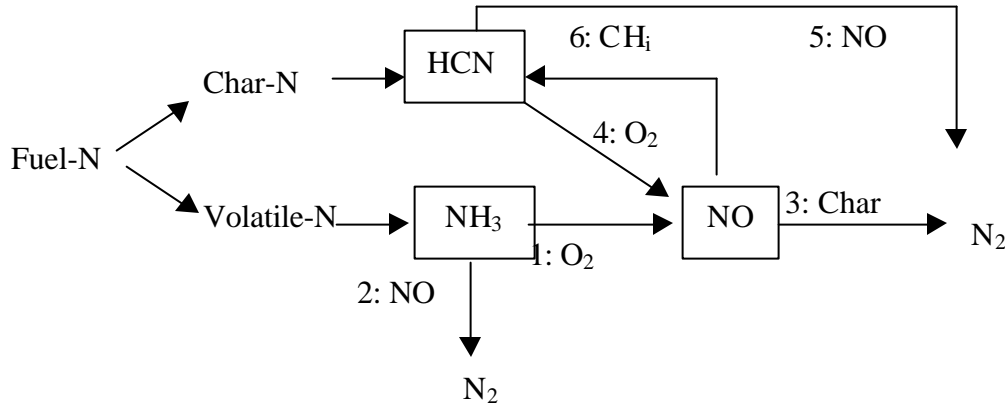
The char-N may be oxidized into NO if oxygen can reach the surface of the char particle. It may also release into gas phase in the form of N₂ if oxygen cannot reach the surface of the char particle [2, 3]. It is possible to simulate this process, but it needs to make improvements on the existing black liquor combustion program. As an alternative way, it is assumed in this model that the char-N releases out during the char burning stage in the form of HCN. In the gas phase, HCN will be oxidized by O₂ into NO, or reduced by NO into N₂. The release rate of char-N is assumed as the same as char burning rate.

The heterogeneous reaction of NO reduction on the char particle surface has been found in our experiment [4], and also by Iisa *et al.* [3]. The reduction rate determined by Iisa *et*

al. has been adopted in this model.

If the fuel staging technique is adopted in the recovery boiler, the NO reduction by reburning mechanism will be significant. When the secondary fuel is injected into the furnace to form a fuel rich zone, named reburning zone, the hydrocarbon radicals CH_i will react with the formed NO from the main combustion zone to produce HCN. Under the reducing atmosphere, HCN is mainly reduced by NO into N₂. Many investigations have proved that the NO reduction rate can be as high as 60 % by using reburning technique. In this model, the global reaction rate between CH_i and NO derived by Chen [5] is adopted.

The NO_x formation and reduction in recovery boilers, as discussed above, can be summarized by the reaction pathway as follows:



The reaction rates of above six reactions are as follows:

$$R_1 = A_1 x_{NH_3} x_{O_2}^a \exp(-E_1 / RT)$$

$$R_2 = A_2 x_{NH_3} x_{NO} \exp(-E_2 / RT)$$

$$R_3 = [A_{31} \exp(-E_{31} / \overline{RT}) + A_{32} x_{CO} \exp(-E_{32} / \overline{RT})] x_{NO}$$

$$R_4 = A_4 x_{HCN} x_{O_2}^a \exp(-E_4 / RT)$$

$$R_5 = A_5 x_{HCN} x_{NO} \exp(-E_5 / RT)$$

$$R_6 = A_6 x_{HC} x_{NO} \exp(-E_6 / RT)$$

where R_1, R_2 = conversion rate of NH₃ (1/s)

R_3 = NO reduction rate by char particle (m³/s/m_{BET}²)

R_4, R_5 = conversion rates of HCN (1/s)

R_6 = NO reduction rate by reburning (1/s)

T = instantaneous temperature (K)

\bar{T} = mean temperature (K)

x = mole fractions

A_1 = 4.0×10^6 1/s

E_1 = 32,000 cal/mol

A_2 = 1.8×10^8 1/s

E_2 = 27,000 cal/mol

A_{31} = $0.204 \text{ m}^3/\text{m}_{\text{BET}}^2/\text{s}$ (if $T \leq 923$ K)
= $1.26 \times 10^9 \text{ m}^3/\text{m}_{\text{BET}}^2/\text{s}$ (if $T > 923$ K)

E_{31} = 16,000 cal/mol (if $T \leq 923$ K)
= 57,300 cal/mol (if $T > 923$ K)

A_{32} = $37.8 \text{ m}^3/\text{m}_{\text{BET}}^2/\text{s}$ (if $T \leq 923$ K)
= $7.12 \times 10^{10} \text{ m}^3/\text{m}_{\text{BET}}^2/\text{s}$ (if $T > 923$ K)

E_{32} = 18,160 cal/mol (if $T \leq 923$ K)
= 57,300 cal/mol (if $T > 923$ K)

A_4 = 3.5×10^{10} 1/s

E_4 = 67,000 cal/mol

A_5 = 3.0×10^{12} 1/s

E_5 = 60,000 cal/mol

A_6 = 2.72×10^6 1/s

$$E_6 = 18,800 \text{ cal/mol}$$

$$R = \text{universal gas constant equal to } 1.986 \text{ cal/(mol}\cdot\text{K)}$$

The oxygen reaction order a is calculated from the following equation:

$$a = \begin{cases} 1.0, x_{O_2} \leq 4.1 \times 10^{-3} \\ -3.95 - 0.9 \ln x_{O_2}, 4.1 \times 10^{-3} < x_{O_2} \leq 1.11 \times 10^{-2} \\ -0.35 - 0.1 \ln x_{O_2}, 1.11 \times 10^{-2} < x_{O_2} < 0.03 \\ 0, x_{O_2} \geq 0.03 \end{cases}$$

3. Turbulence-Chemistry Interaction Model

The flow in recovery boiler is fully three-dimensional and turbulent. There are interactions between turbulence and chemistry. Additional effort is necessary in order to calculate the mean reaction rate correctly. The influence of turbulence on the reaction is taken into account by employing combined Arrhenius and eddy breakup model. In the eddy breakup model, the rate of reaction $R_{i,k}$ (kg/m³/s) is given by the smallest of the two expressions below:

$$R_{i,k} = \nu'_{i,k} M_i A \rho \frac{\varepsilon}{k \nu'_{R,k} M_R}$$

$$R_{i,k} = \nu'_{i,k} M_i A B \rho \frac{\varepsilon}{k \sum_P \nu'_{P,k} M_P}$$

where $\nu'_{i,k}$ = molar stoichiometric coefficient for species i in reaction k

M_i = molecular weight of species i (kg/kmol)

ε = dissipation rate of turbulent kinetic energy (m²/s³)

k = turbulent kinetic energy (m²/s²)

m_R = the mass fraction of a particular reactant, R, giving the smallest value of $R_{i,k}$

m_P = the mass fraction of any product species, P

A = an empirical constant equal to 4.0

B = an empirical constant equal to 0.5

In the combined Arrhenius and eddy breakup model, the reaction rates are calculated from the Arrhenius expression (the chemical reaction rate shown above) and the eddy breakup model. The limiting (slowest) rate is used as the reaction rate, and the contribution to the source terms in the species conservation equations are calculated from this reaction rate.

According to the above models, the source terms of species NH₃, HCN and NO conservation equations can be arranged as follows.

Source terms for NH₃ (kg/s/m³)

$$S_{NH_3-V} = S_V M_{NV} M_{NH_3} / M_N / V$$

$$S_{NH_3-1} = -\min\left\{ R_1 \frac{M_{NH_3} P}{RT}, M_{NH_3} x_{NH_3} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{NH_3} \frac{M_{NO}}{M_{NO} + M_{H_2O}} x_{NO} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

$$S_{NH_3-2} = -\min\left\{ R_2 \frac{M_{NH_3} P}{RT}, M_{NH_3} x_{NH_3} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{NH_3} \frac{M_{N_2}}{M_{N_2} + M_{H_2O}} x_{N_2} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

Source terms for HCN (kg/s/m³)

$$S_{HCN-C} = S_C M_{NC} M_{HCN} / M_N / V$$

$$S_{HCN-1} = -\min\left\{ R_4 \frac{M_{HCN} P}{RT}, M_{HCN} x_{HCN} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{HCN} \frac{M_{NO}}{M_{NO} + M_{HCO}} x_{NO} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

$$S_{HCN-2} = -\min\left\{ R_5 \frac{M_{HCN} P}{RT}, M_{HCN} x_{HCN} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{HCN} \frac{M_{N_2}}{M_{N_2} + M_{HCO}} x_{N_2} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

$$S_{HCN-3} = \min\left\{ R_6 \frac{M_{HCN} P}{RT}, M_{HCN} x_{NO} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{HCN} \frac{M_{HCN}}{M_{HCN} + M_{H_2O}} x_{HCN} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

Source terms for NO (kg/s/m³)

$$S_{NO-1} = \min\left\{ R_1 \frac{M_{NO} P}{RT}, M_{NO} x_{NH_3} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{NO} \frac{M_{NO}}{M_{NO} + M_{H_2O}} x_{NO} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

$$S_{NO-2} = -\min\left\{ R_2 \frac{M_{NO}P}{RT}, M_{NO}x_{NH_3} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{NO} \frac{M_{N_2}}{M_{N_2} + M_{H_2O}} x_{N_2} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

$$S_{NO-3} = -A_{BET} c_s R_3 \frac{M_{NO}P}{RT}$$

$$S_{NO-4} = \min\left\{ R_4 \frac{M_{NO}P}{RT}, M_{NO}x_{HCN} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{NO} \frac{M_{NO}}{M_{NO} + M_{HCO}} x_{NO} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

$$S_{NO-5} = -\min\left\{ R_5 \frac{M_{NO}P}{RT}, M_{NO}x_{HCN} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{NO} \frac{M_{N_2}}{M_{N_2} + M_{HCO}} x_{N_2} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

$$S_{NO-6} = -\min\left\{ R_6 \frac{M_{NO}P}{RT}, M_{NO}x_{NO} A \frac{\varepsilon}{k} \frac{P}{RT}, M_{NO} \frac{M_{HCN}}{M_{HCN} + M_{H_2O}} x_{HCN} AB \frac{\varepsilon}{k} \frac{P}{RT} \right\}$$

where S_{NH_3-V} = source of NH_3 from volatiles ($kg/s/m^3$)

S_{HCN-C} = source of HCN from char ($kg/s/m^3$)

S_V = source of volatiles originating from fuel droplets into the gas phase (kg/s)

M_{NV} = mass fraction of nitrogen in the volatiles

S_C = char burnout rate (kg/s)

M_{NC} = mass fraction of nitrogen in char

V = cell volume (m^3)

P = the pressure of combustion system (atm)

R = universal gas constant equal to $8.206 \times 10^{-2} m^3 \cdot atm / (kmol \cdot K)$

A_{BET} = BET surface area of char particle (m^2/kg)

c_s = concentration of particles (kg/m^3)

4. NOx Module

NOx concentrations generated in the combustion process in recovery boilers are generally low. As a result, NOx chemistry has negligible influence on the predicted flow field, temperature, and major combustion product concentrations. It follows that the

most efficient way to use the NOx module is as a postprocessor to the main combustion calculation.

In the NOx module, the species conservation equations of NH₃, HCN and NO will be solved in iteration. The procedure to calculate these three equations will be the same as to other scalar equations except the diffusion coefficient and the source terms as discussed above. The calculated data from the main combustion simulation will be used in the module, such as velocities, temperature, density, turbulent kinetics, and so on. Also the calculated values of fuel droplet combustion process, such as volatile releasing rate, char burnout rate, and particle concentration, are very important for the NOx simulation.

4.1 Input Data

The necessary input data for NOx module are listed as follows:

f_{N_2} – mass fraction of nitrogen in fuel

f_{VM} – mass fraction of volatile in fuel

f_{FC} – mass fraction of fixed carbon in fuel

S_V – mass rate of volatile released into gas phase at each cell (kg/s), calculated from droplet combustion program

S_C – consumption rate of fixed carbon at each cell (kg/s), calculated from droplet combustion program

c_s – concentration of particles at each cell (kg/m³), calculated from droplet combustion program

A_{BET} – BET surface area of char particle (m²/kg). According to the measurement by Iisa *et al.* [3], the BET area has a value of 14,000 m²/kg at the temperature of 1023 K, and 1,000 m²/kg at the temperature of 1173 K.

M_{NV} – mass fraction of nitrogen in volatile. According to the assumption in this model, it can be calculated as

$$M_{NV} = \frac{f_{N_2}}{f_{VM} + f_{FC}}$$

M_{NC} – mass fraction of nitrogen in char. It is the same as M_{NV} because of the assumption in this model.

$$M_{NC} = \frac{f_{N_2}}{f_{VM} + f_{FC}}$$

4.2 Linearization of Source Terms

To ensure the convergence of the iteration, the source terms of NH₃, HCN and NO should be linearized as

$$S = S_C + S_P \phi_P$$

Here, S_P can not be positive. The linearized source terms of NH₃, HCN and NO are as follows:

$$S_{C-NH_3} = S_{NH_3-V}$$

$$S_{P-NH_3} = (S_{NH_3-1} + S_{NH_3-2}) / x_{NH_3}$$

$$S_{C-HCN} = S_{HCN-C} + S_{HCN-3}$$

$$S_{P-HCN} = (S_{HCN-1} + S_{HCN-2}) / x_{HCN}$$

$$S_{C-NO} = S_{NO-1} + S_{NO-4}$$

$$S_{P-NO} = (S_{NO-2} + S_{NO-3} + S_{NO-5} + S_{NO-6}) / x_{NO}$$

Reference

- [1] L. Tao, W. Blasiak, and R. Fakhrai, Use of A Computer Model for Evaluation of Combustion and NOx Control Alternatives in A Kraft Recovery Boiler, Proceedings of 1998 International Chemical Recovery Conference, pp.299-312
- [2] M. Forssen, P. Kilpinen and M. Hupa, NOx Reduction in Black Liquor Combustion – Understanding Reaction Mechanisms Reveal Novel Operation Strategy Options,

Proceedings of 1998 International Chemical Recovery Conference, pp.747-762

- [3] K. Iisa, Q. Jing, J. Conn, N. Rompho, V. Tangpanyapinit, and R. Pianpucktr, Model for NO Formation in Recovery Boilers, Proceedings of 1998 International Chemical Recovery Conference, pp. 763-776
- [4] I. Naruse, H. Kim, G. Lu, J. Yuan, and K. Ohtake (now deceased), Study on Characteristics of Self-desulfurization and Self-denitrification in Biobriquette Combustion, Presented at the 27th Symposium (International) on Combustion, Colorado, Aug. 1998
- [5] W. Chen, A Global Reaction Rate for Nitric Oxide Reburning, PhD thesis of Brigham Young University, 1994
- [6] Fluent Inc., User's Guide Index, 1994

Appendix: Calculation of Thermal NO_x and Prompt NO_x

Thermal NO_x

The NO source term due to thermal NO_x mechanisms is

$$S_{thermal-NOx} = M_{NO} \frac{d[NO]}{dt}$$

Here $d[NO]/dt$ can be calculated as

$$\frac{d[NO]}{dt} = \frac{2[O](k_1 k_2 [O_2][N_2] - k_{-1} k_{-2} [NO]^2)}{k_2 [O_2] + k_{-1} [NO]}$$

Using partial equilibrium [O] approach, [O] is formulated as

$$[O] = 36.64T^{1/2} [O_2]^{1/2} \exp(-27123/T)$$

The rate coefficients in above formulates are as follows (in unit of $m^3 \text{ mol}^{-1} \text{ s}^{-1}$).

$$k_1 = 1.8 \times 10^8 \exp(-38370/T)$$

$$k_{-1} = 3.8 \times 10^7 \exp(-425/T)$$

$$k_2 = 1.8 \times 10^4 T \exp(-4680/T)$$

$$k_{-2} = 3.8 \times 10^3 T \exp(-20820/T)$$

All concentrations are in unit of mol m^{-3} .

Prompt NO_x

The NO source term due to prompt NO_x mechanisms is

$$S_{prompt-NOx} = M_{NO} \frac{d[NO]}{dt}$$

Here $d[NO]/dt$ can be calculated as

$$\frac{d[NO]}{dt} = k_{pr} [O_2]^a [N_2] [Fuel] \exp\left(-\frac{E_a}{RT}\right)$$

where

$$k_{pr} = 1.2 \times 10^7 (RT/P)^{a+1} \quad (m^3 \cdot \text{mol})^{a+1} \cdot s^{-1}$$

$$E_a = 60 \text{ kcal} \cdot \text{mol}^{-1}$$

$$R = 1.986 \times 10^{-3} \text{ kcal} \cdot \text{mol}^{-1} \cdot K^{-1} = 8.206 \times 10^{-5} m^3 \cdot \text{atm} \cdot \text{mol}^{-1} \cdot K^{-1}$$

P is pressure in unit of atm. If the main combustible species released from bark or wood chip is CH₄, [Fuel] in the above equation can be replaced by the concentration of CH₄.

Here all concentrations are also in unit of mol m⁻³.