SINGLE PARTICLE MODEL FOR CHAR CARBON AND CHAR NITROGEN OXIDATION

PARAMETRIC STUDIES AND COMPARISONS WITH EXPERIMENTAL RESULTS

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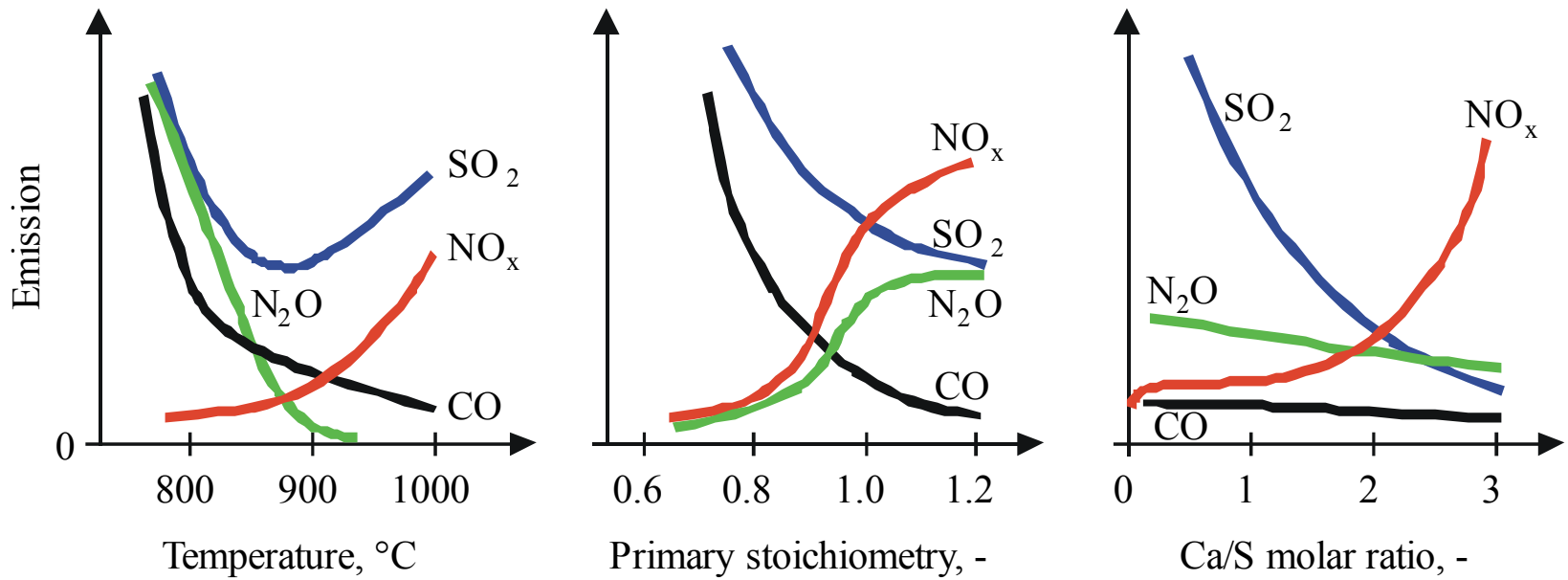
NO and N_2O Emission Tendency Predictor for Fluidized Bed Combustion of Solid Fossil Fuels

- CFBC technology has been established as reliable, environmentally friendly and flexible means of energy production

- the objectives of the project have been:
  - to create a general mathematical tool for studying the emission formation in a CFBC
  - to rank the different fuels and fuel mixtures according to their emission formation tendency for nitrogen oxides

- The project has been part of the CODE Technology programme of Finland. The CODE programme is coordinated by TEKES. The project was also a part of an ECSC project funded by the European community

Simplified overview of gaseous emissions' dependence on various process parameters in CFBC

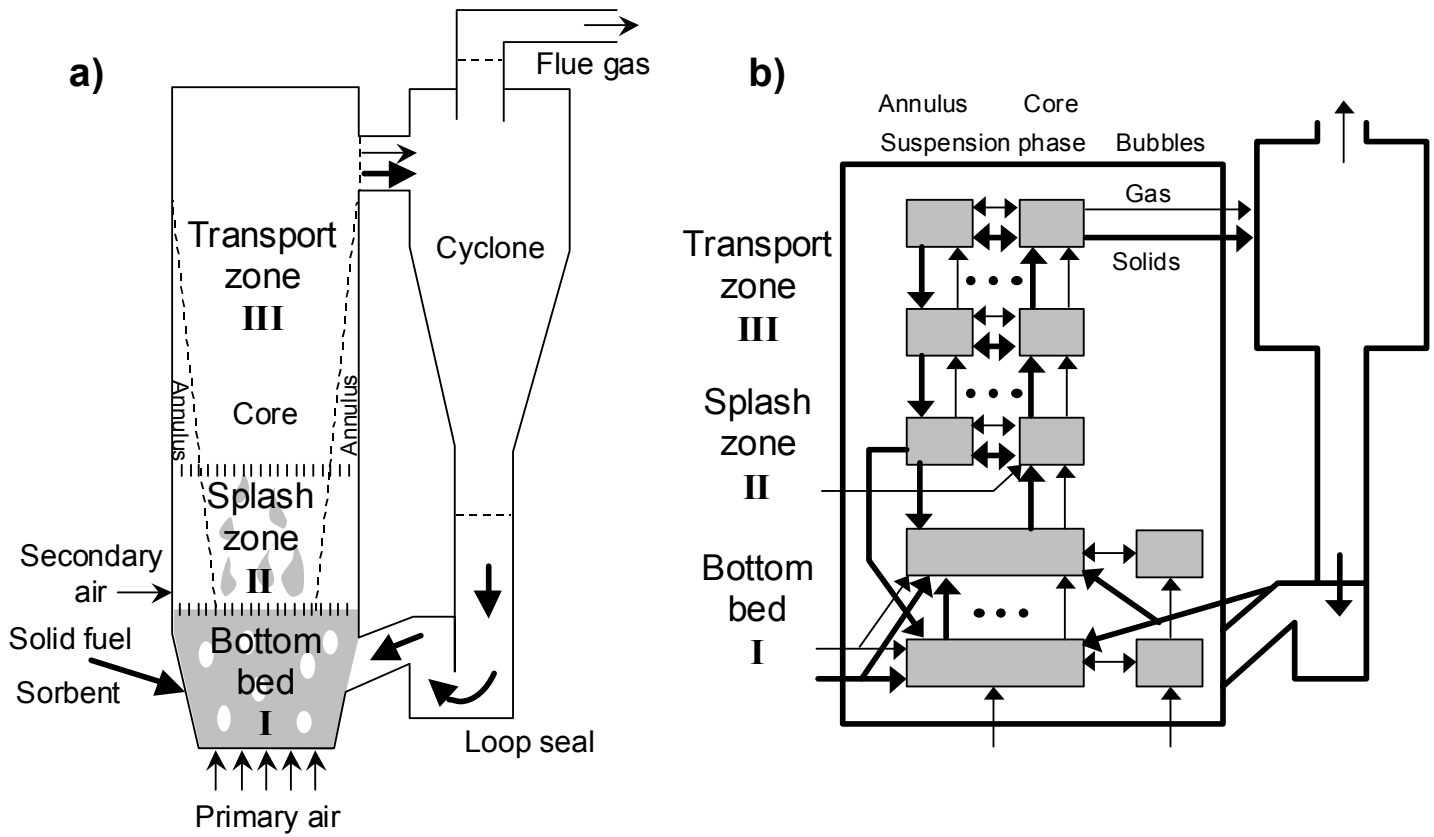


The CFBC model

- The model is based on a 1.5-dimensional description of CFBC hydrodynamics. It compasses the entire circulation loop.

- The model uses detailed homogeneous and heterogeneous chemical kinetics for main combustion and nitrogen reactions:
  - About 300 elementary gas-phase reactions
  - **An oxidation model for single char particles**

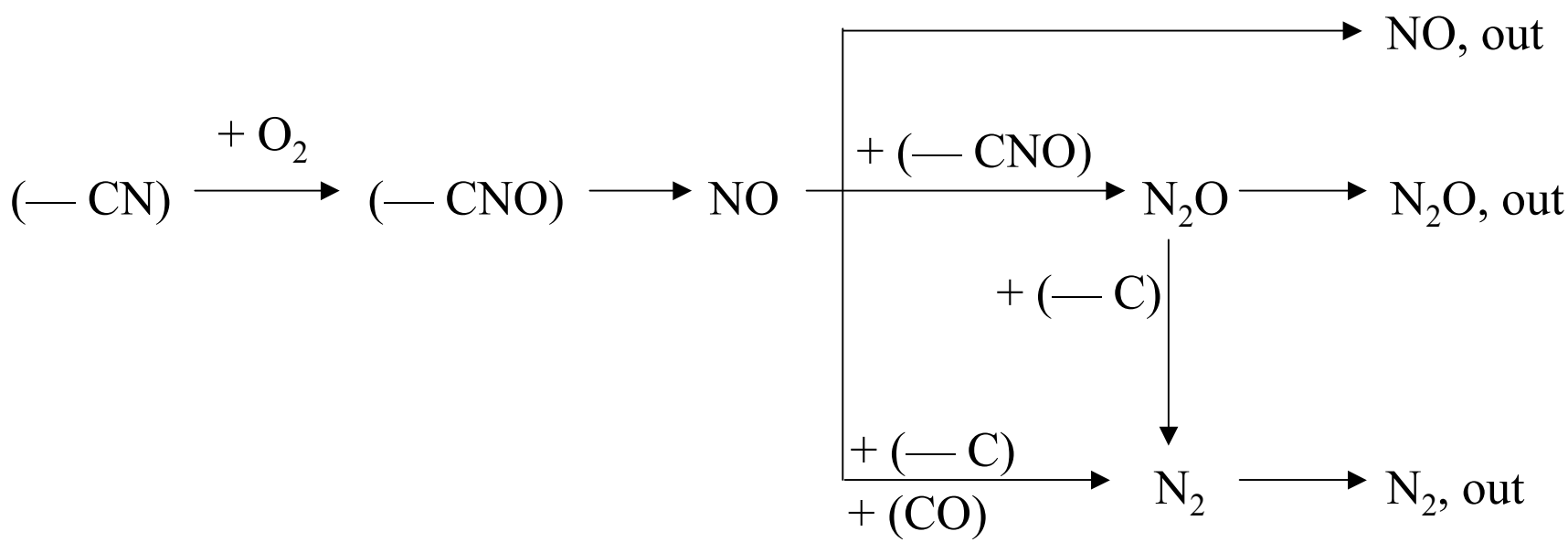
Schematic of detailed CFBC emission model at Åbo Akademi University



a) General model structure

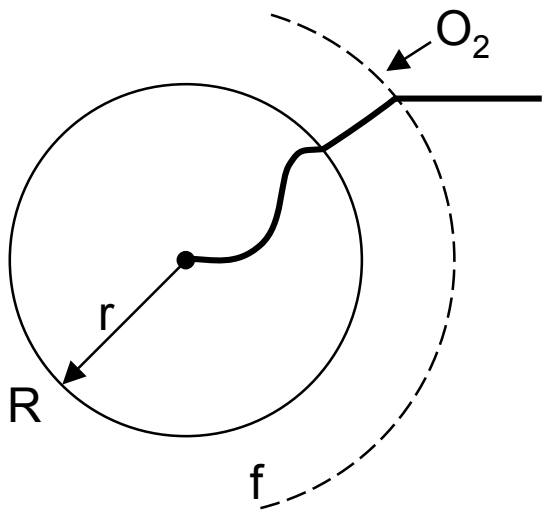
b) Calculation cells and flows

Heterogeneous nitrogen chemistry inside a burning char particle



Simplified mechanism according to Goel (1996) and de Soete (1999)

Single Particle Char Oxidation Model



$$k_g = \frac{D_f Sh}{2R}$$

$$Sh = 2.0 + 0.68 \cdot Re^{\frac{1}{2}} \cdot Sc^{\frac{1}{3}}$$

$$Sc = \frac{\mu_f}{\rho_f D_f}$$

$$Re = \frac{\mu_{slip} \cdot \rho_f \cdot 2R}{\mu_f}$$

- solves diffusive mass transport and chemical kinetics in a shrinking char sphere:

$$D_{p,i} \cdot \left(\frac{\partial^2 [i]}{\partial r^2} + \frac{2}{r} \frac{\partial [i]}{\partial r} \right) + R_i = 0$$

$$\begin{cases} r = 0 & \left. \frac{\partial [i]}{\partial r} \right|_{center} = 0 \\ r = R & D_{p,i} \cdot \left. \frac{\partial [i]}{\partial r} \right|_{surface} = k_g \cdot \left([i]_\infty - [i]_s \right) \end{cases}$$

The reaction rate expressions of the char particle model

$$R_{O_2}: \quad -\frac{1}{2}k_{O_2}[O_2]-\frac{1}{2}k_{CO}[CO][O_2]^{\frac{1}{2}}$$

$$R_{CO}: \quad k_{O_2}[O_2]-k_{CO}[CO][O_2]^{\frac{1}{2}}$$

$$R_{CO_2}: \quad k_{CO}[CO][O_2]^{\frac{1}{2}}$$

$$R_{NO}: \quad \frac{N}{C}k_{O_2}[O_2]\left(\frac{k_1}{k_1+k_2[NO]}\right)-k_{NO}[NO]-k_{NO-CO}[NO][CO]$$

$$-\frac{N}{C}k_{O_2}[O_2]\left(\frac{k_2[NO]}{k_1+k_2[NO]}\right)$$

$$R_{N_2O}: \quad \frac{N}{C}k_{O_2}[O_2]\left(\frac{k_2[NO]}{k_1+k_2[NO]}\right)-k_{N_2O}[N_2O]$$

Parameter determination for the single particle model

- Goel (1996) determined the 2*6 kinetic parameters and D_e for bituminous Newlands coal under a limited set of experimental conditions (1023 K, 1073 K and 1123 K, 4 vol % and 8 vol % O_2)

- model predictions with the original parameters do not fit well enough the experimental results of Tullin (1995) at different temperatures
  - also, the high NO reduction rates in a large-scale CFBC are not well predicted

- A better set of kinetic parameters (KKK_1) have been determined by:
  - using the small-scale fluidized bed combustion experimental data of Tullin (1995)

Single particle model performance with the new kinetic parameters

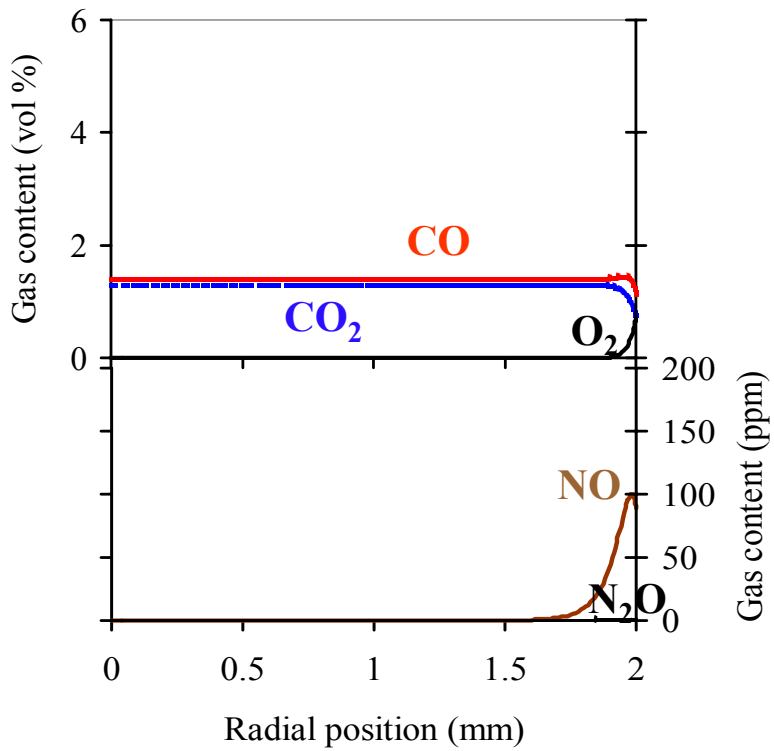
- the char carbon combustion rates at different temperatures of Tullin (1995) are well predicted ***)**

- the trends of char-nitrogen conversion to NO and N_2O at different temperatures (Tullin, 1995) are correctly predicted ***)**

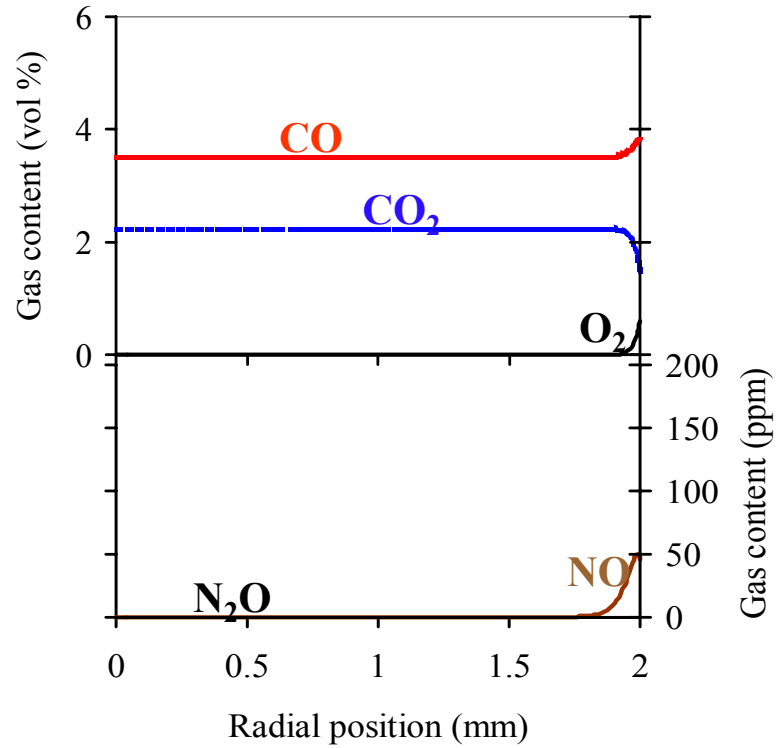
  ***)** these results are presented in the proceedings of the 40th IEA-FBC meeting in Turku, Finland, May 24-25, 2000

- the recent literature indicates that the reaction mechanism consisting of 15 steps (7 net reactions) is too simple and should be improved for better predictions

Gas concentration profiles inside a burning char particle



4 vol % O2 at 800°C
De = 1e-5, u_sl = 0.5



2 vol % O2, 4 vol % CO at 800°C
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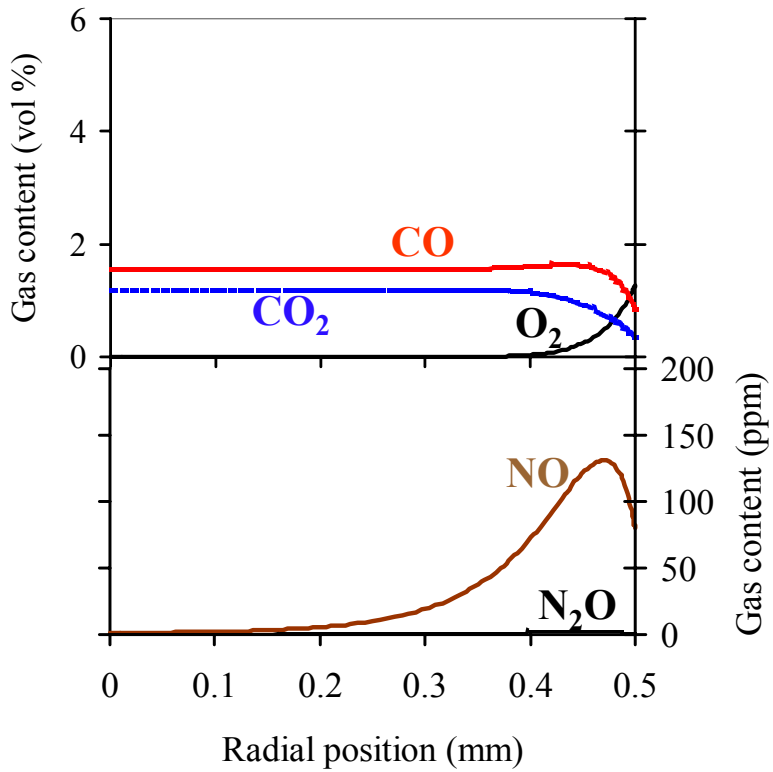

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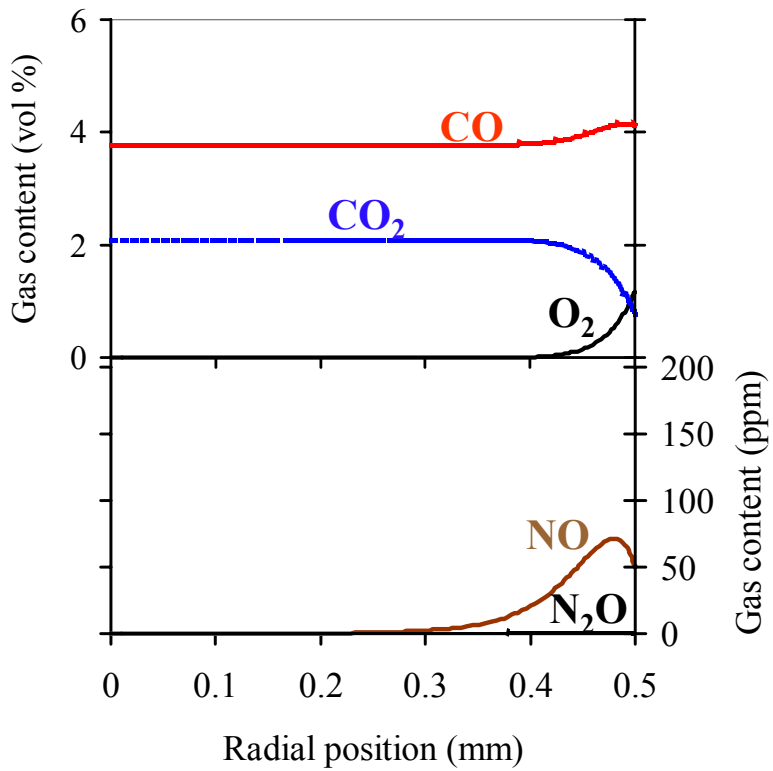

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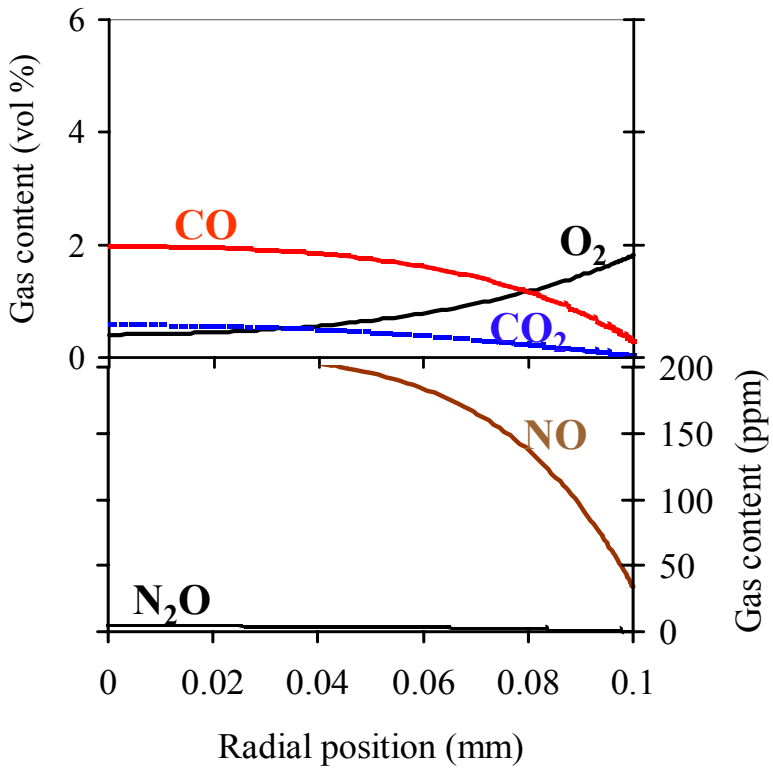

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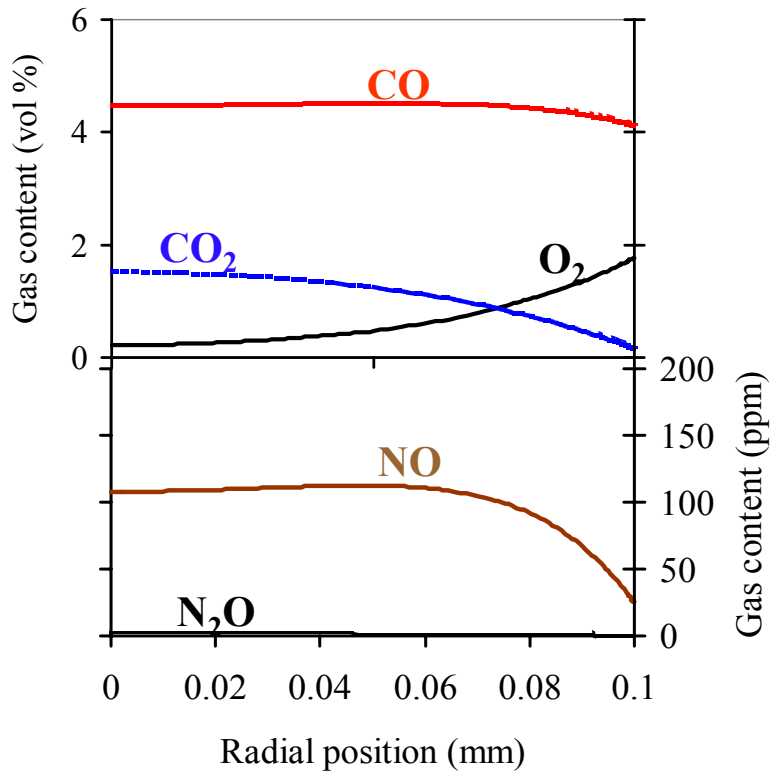

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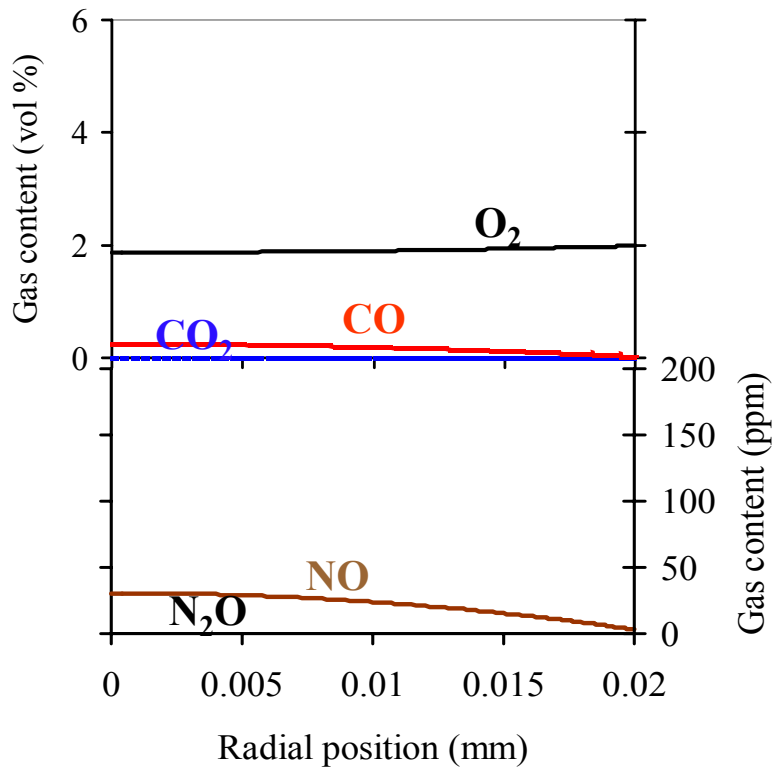

4 vol % O2 at 800°C
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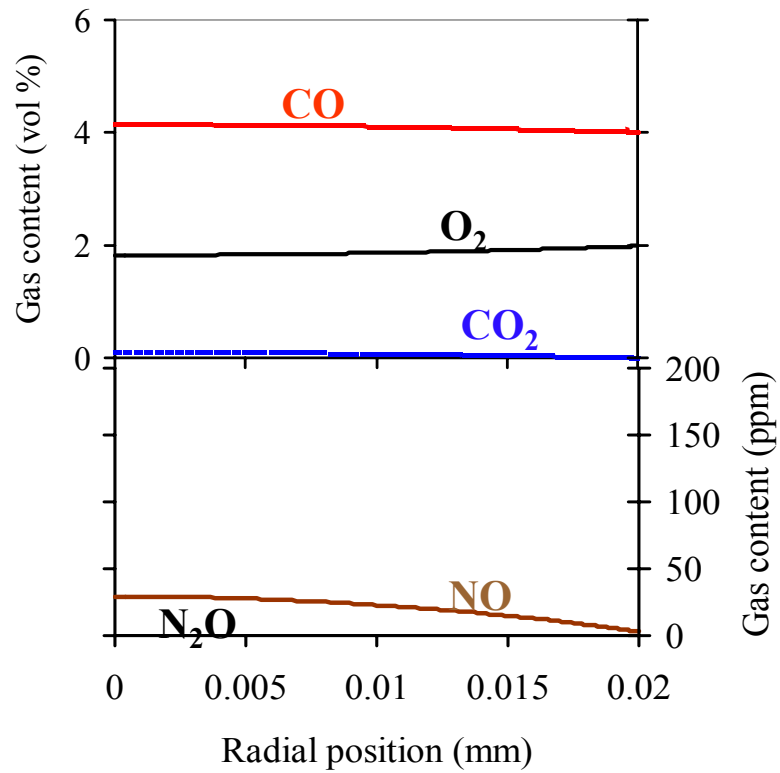
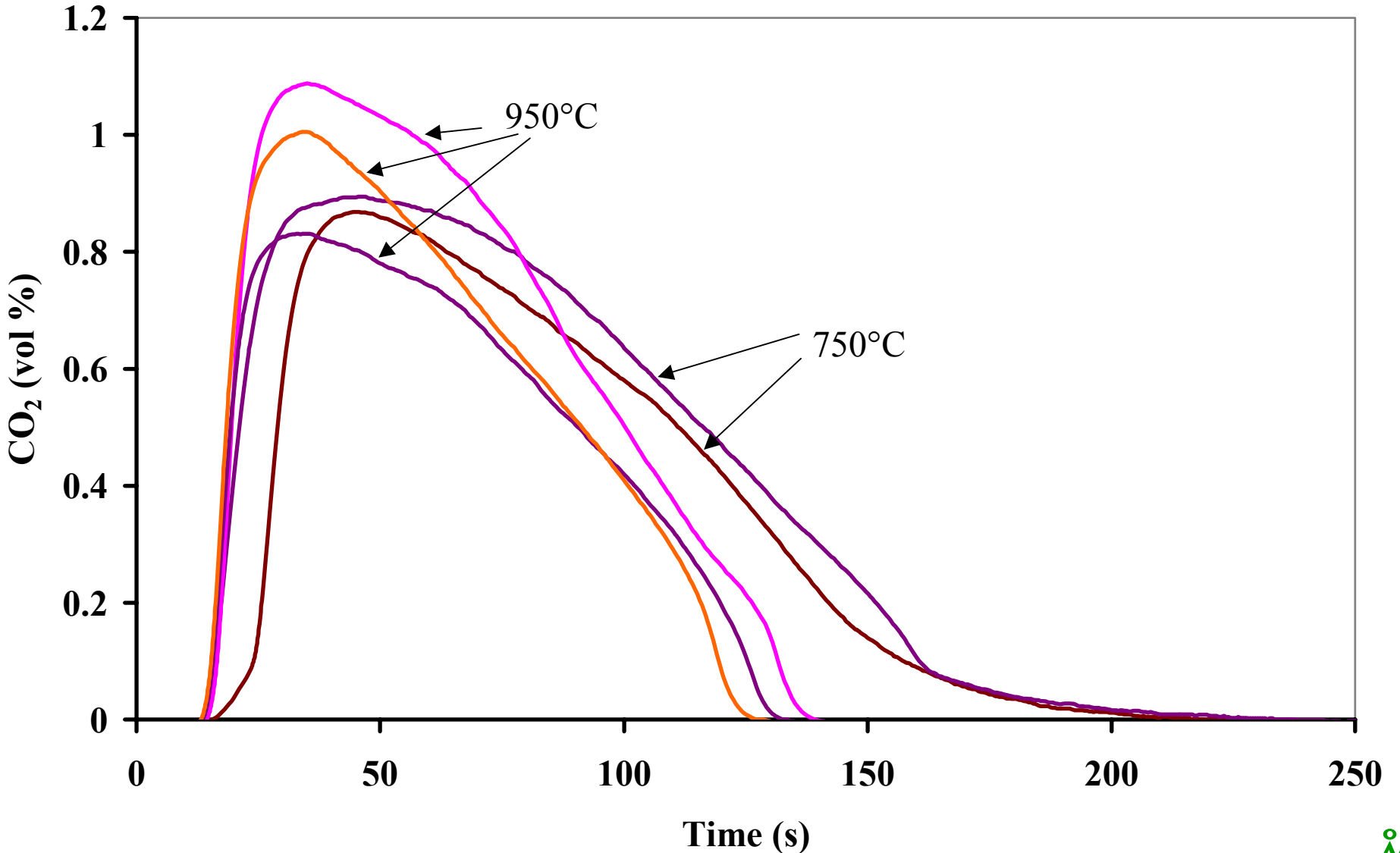
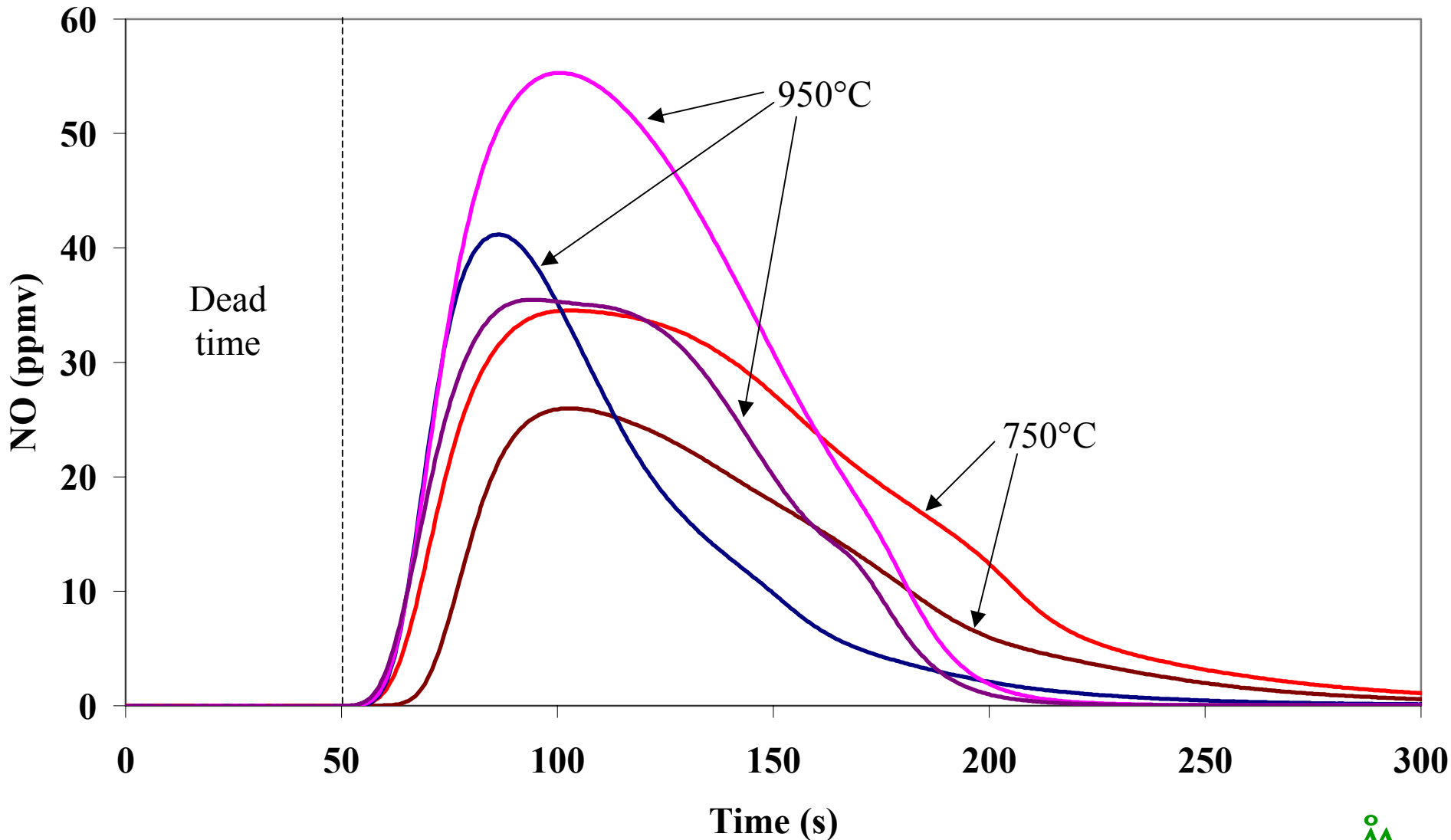


2 vol % O2, 4 vol % CO at 800°C
De = 1e-5, u_sl = 0.5

Char-carbon combustion in 21 vol % O_2



Char-nitrogen combustion in 21 vol % O_2



Conclusions

- Single particle model is used as an important submodel of the 1.5 dimensional CFBC model
  - the heterogeneous chemistry on the formation and reduction of NO_x and N_2O is described by the model
  - the internal and external mass transfer effects of particles of different size are described by the model

- The kinetic parameters of the model were refitted based on fluidized bed data on different scales.
  - the temperature trends of char carbon and char nitrogen oxidation are correctly predicted
  - significant differences in the model performance can be observed, when comparing the results with Goel (1994) parameters and KKK_1 parameters

Conclusions

- The recent literature indicates that the reaction mechanism consisting of 15 steps (7 net reactions) is too simple and should be improved for better predictions
- Under the simulated combustion conditions , film mass transfer has an effect to particles of larger than 0.1 mm in radius
- Chemical reaction controls the reaction rate with very small particles
  - with the most relevant particle sizes, both chemical reaction and mass transfer effects affect the reaction rate

Conclusions

- Some simulation results by the model indicate that the experimental conditions in the literature used in determination of the kinetic parameters for N_2O formation/destruction may have suffered from diffusional resistances.