(article starts on next page)

16th International Conference on Fluidized Bed Combustion

May 13–16, 2001 • Reno, Nevada

Edited by Donald W. Geiling, P.E.

fbc

Copyright Information

Table of Contents

About FBC'01

About This CD

Towards a quantitative understanding of NO$_x$ and N$_2$O emission formation in full-scale circulating fluidised bed combustors

Kilpinen, P.*, Kallio, S., Konttinen, J., Mueller, C., Jungar, A., Hupa, M.
Åbo Akademi University - Process Chemistry Group
Lemminkäisenkatu 14-18 B, FIN-20520 TURKU, FINLAND

*) E-mail: pia.kilpinen@abo.fi

Åmand, L-E., Leckner, B.
Chalmers University of Technology
Department of Energy Conversion
S-412 96 GOTHENBURG, SWEDEN

ABSTRACT

A mathematical tool is being developed for studying the nitrogen oxide emission formation in circulating fluidised bed combustors. The model is based on detailed homogeneous and heterogeneous chemical kinetics and a simplified, reasonable description of CFB hydrodynamics with presumed temperature distribution *(Kilpinen et al, 1999a)*. With the model different fuels and fuel mixtures can be compared in regard to their nitrogen oxide emission formation tendency at typical CFBC conditions.

In this paper the structure of the CFBC model and its submodels are shortly described in present form. The CFBC model is tested for nitrogen oxide prediction at normal air staging conditions in a 12 MW CFB with bituminous coal and wood chips as the fuel, respectively. Comparisons of modelling results with detailed gas concentration profiles measured inside the furnace are made. The relative importance of homogeneous and heterogeneous reactions on NO and N$_2$O concentration profiles is illustrated based on a quantitative reaction rate analysis at different parts in the combustor. The importance of effects of radical removal on particle surfaces, and thus, a decreased CO burnout and, simultaneously, enhanced rates of catalytic bed/char reactions on nitrogen oxides' destruction are discussed.

1. INTRODUCTION

Circulating fluidised bed combustion technology (CFBC) has been established as reliable and flexible means of energy production. Fuels that can be utilised vary from different coals to various biomasses and wastes or waste-derived fuels such as refuse-derived fuels (RDF) or recycled fuels (REF). The properties of these fuels vary a lot, and thus, the combustion chamber conditions and the emission formation tendency may also vary within a wide range.

Ever tightening emission limits necessitate further development work for the reduction of the emissions from CFBC including components like NO$_x$, N$_2$O, SO$_2$, and CO. To render CFBC technology economically attractive, the emission reduction has to take place in the CFBC furnace itself. The challenge, however, is that the dependence on process operational parameters for the different emission components is different: reducing one emission component easily increases the formation of

others. In simple terms, the following conditions favour low levels of the different emission components at coal combustion (*Lyngfelt et al., 1995; Kilpinen et al, 1999a*):

-low N_2O: high temperature, air staging, high sorbent feeding rate.
-low NO_x: low temperature, air staging, low sorbent feeding rate.
-low SO_2: moderate temperature, no air staging, high sorbent feeding rate.
-low CO: high temperature, no air staging, high sorbent feed rate.

For fuel mixtures the large differences in the fuels' characteristics make it difficult to predict their combustion conditions in the furnace, and consequently, their effect on emission formation.

The purpose of the on-going development work presented in this paper is to create a general mathematical tool for studying emission formation in CFBC. Special interest with the model will be to rank different fuels and fuel mixtures according to their emission formation tendency for nitrogen oxides (Fig. 1).
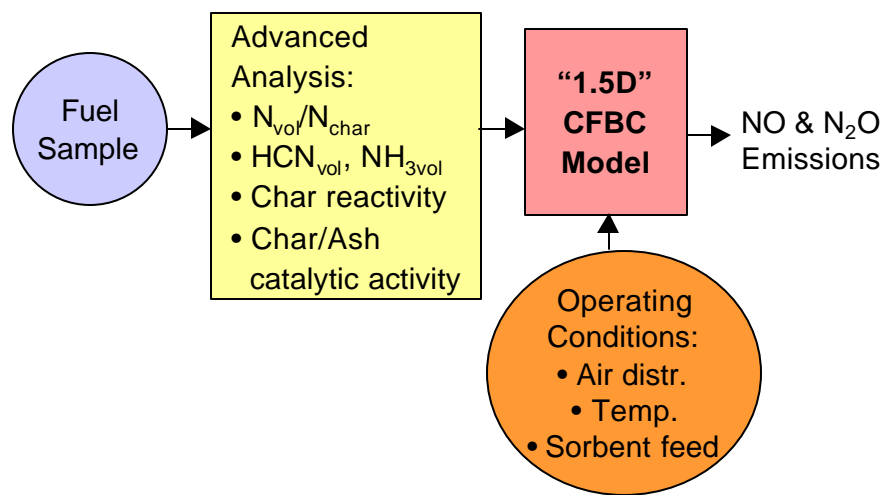

Fig.1. Principle of CFBC nitrogen oxide emission tendency prediction (modified from Hupa et al., *1999*).

Certain fuel-specific values are needed as input to the predictor in addition to the conventional ultimate and proximate analyses. Especially, information is needed on the behaviour of fuel-nitrogen including its split into volatiles (vol-N) and char (char-N), and the share of fixed-nitrogen components in the volatiles (NH_3, HCN, NO). Knowledge is also needed on the reactivity of char including char-carbon oxidation to CO and CO_2, and char-nitrogen oxidation to NO, N_2O, N_2, as well as the catalytic activities of char and ash in their reactions with nitrogen components (NO, N_2O, NH_3, HCN). These values can be experimentally determined at various laboratory reactors, and for many conventional fuels much of this information is already available. The data are then used in a comprehensive, one-and-a-half-dimensional CFBC chemistry model that calculates under given operating and boiler design conditions the NO and N_2O concentrations in the CFBC furnace and in the flue gases.

The CFBC model also allows for a detailed understanding for the chemical pathways of fuel-nitrogen conversion, and it may be used as a guiding tool for searching the optimum operating conditions for lowest emissions.

This paper is continuation to our earlier papers that deal with the development work of the CFBC model (*Kilpinen et al., 1999a; Kilpinen et al., 1999b; Kallio et al., 1999; Kallio et al., 2000; Kallio et al., 2001*). In this paper we will describe the model and its submodels in their present form.

We will show some simple tests with the chemistry submodels at idealised conditions in order to check their correct implementation, and to illustrate the importance of effects of radical removal and catalytic nitrogen reactions on the fate of nitrogen oxides. Further, we will test the CFBC model for nitrogen oxide prediction in a 12 MW CFB. The test cases deal with bituminous coal and wood chip combustion in normal air staging conditions without limestone addition. The modelling results are compared to detailed gas concentration profiles measured inside the furnace. The relative importance of homogeneous and heterogeneous reactions on NO and N_2O concentration profiles is illustrated based on a novel quantitative reaction rate analysis at different parts of the combustor as a function of combustor height.

Based on the results practical conclusions are drawn and future development needs and trends of the CFBC model are outlined.

2. DESCRIPTION OF THE MODEL AND TESTS WITH SUBMODELS

Modelling of nitrogen oxide emission from CFBC is complicated due to the complex nature of the two-phase hydrodynamics, heat transfer, and mixing processes involved. The description of fuel behaviour includes devolatilisation and particle fragmentation/attrition. The CFBC chemistry includes homogeneous, heterogeneous gas-solid, and heterogeneous catalytic reactions. The models for CFB combustion are usually based on a one or a 1.5-dimensional description of the hydrodynamics. For CFB combustion modelling the 1.5-dimensional models are preferred since internal solids recirculation, included in the 1.5D model but not in the 1D model, plays a crucial role in the hydrodynamics.

Also, 2- and 3-dimensional models for CFB combustion have been presented (e.g., *Werther and Knöbig, 1997; Knöbig et al., 1999*). With these models the mixing of gas and solids can be better described than in the 1.5D-models, especially in the regions where fuel and secondary air enter into the reactor, and in the region above the bottom bed where gas from bubbles and emulsion phase from the bottom bed are mixed. A challenge is, however, that the chemistry submodels that can be used in 2D and 3D models need to be largely simplified due to computational restrictions. For description of the fate of nitrogen components, whose oxidation kinetics is more complicated than that of the unburned components like the burn-out of carbon monoxide, no simplified expressions are available that would reliably describe, e.g., the gas-phase oxidation of NH_3/HCN to NO, N_2O, N_2 at FBC combustion conditions. For a proper description of nitrogen oxide formation from char, a treatment is also required that takes into account kinetics and transport phenomena both in the pore system of char.

As basis for our nitrogen oxide emission tendency predictor we have chosen a comprehensive description of homogeneous and heterogeneous chemical kinetics and a sound representation of hydrodynamics. The main assumptions in the different submodels are shortly described below.

Hydrodynamics and mixing

The model illustrated in Fig. 2, encompasses the entire circulation loop. In the riser, the flow domain is vertically divided into three regions: a dense bubbling bed at the bottom, a vigorously mixed splash zone, and a transport zone. The two upper zones are horizontally split into a core region and an annular region.
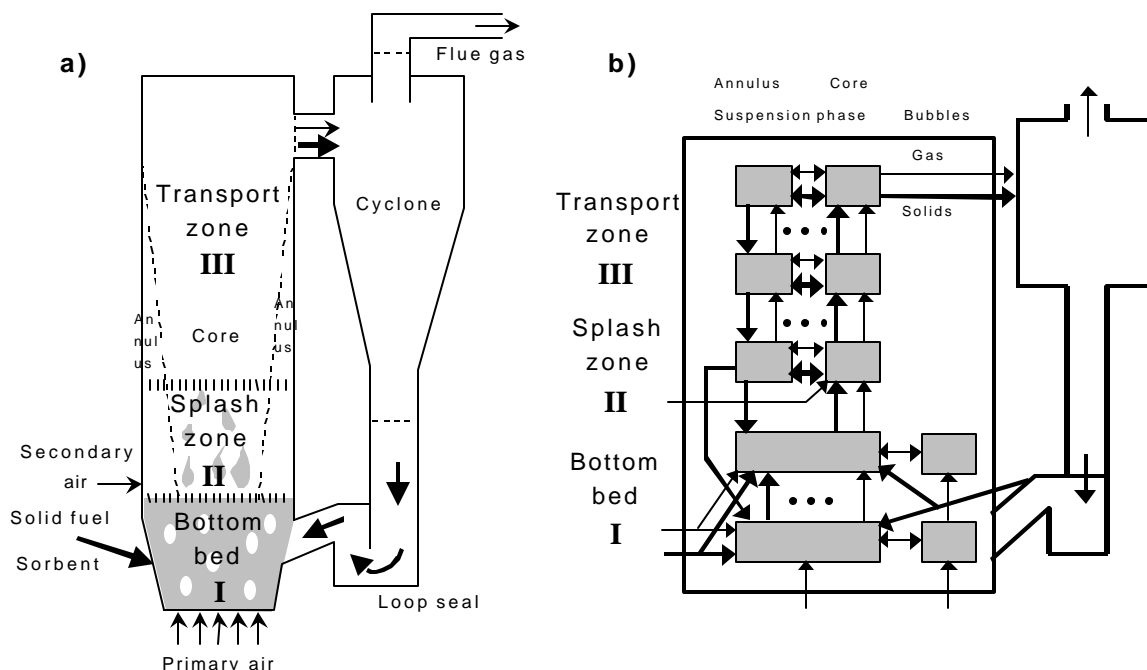

Fig. 2. Schematic of CFBC nitrogen oxide tendency predictor a) general model structure and b) calculation cells and flows. (*Kilpinen et al., 1999a*).

In the vertical direction, the three regions are further divided into cells for which balance equations for mass and chemical components are solved. When gas from level k-1 enters level k, it first undergoes diffusion between the different phases (gas, emulsion phase) followed by chemical reactions in a plug flow: heterogeneous reactions inside the char particle, homogeneous gas-phase reactions, and heterogeneous catalytic reactions on solid particle surfaces.

In the core both the gas and the solids are assumed to move upwards, whereas in the wall region (annulus) gas is assumed to move upwards and solids fall down. At the riser exit, a part of the up-flowing solids in the core is separated to the annulus, where it flows down, while the remaining solids are recycled through the cyclone back to the bottom bed. The exit separation efficiency is given in terms of an empirical parameter. The dense bed region is treated with a model for bubbling beds: the emulsion phase is assumed to be in the state of minimum fluidisation. In the axial direction, mass is transported by convection, whereas in the horizontal direction the

mass transfer is described by diffusion and dispersion parameters. The voidage in the bottom bed is constant.

Above the bottom bed in the splash and transport zones, the solids concentration is calculated from an exponential decay function. The overall hydrodynamics is assumed to be unaffected by the combustion process. The fuel is divided into four size classes. No particle fragmentation or attrition model is included at this moment.

A more detailed description of the hydrodynamic and mixing submodels is given in Kallio et al. (*2000,2001*) where also a comprehensive sensitivity test is shown on the effects of hydrodynamic parameters on the predictions. The study showed main physical factors and phenomena affecting nitrogen oxide emissions are particle size distribution, segregation, char loading, and mixing of bed gases (emulsion gas, bubbles) above the bottom bed.

Chemistry

A detailed reaction scheme consisting of about 300 elementary steps between around 50 chemical components describes the homogeneous chemistry. The mechanism includes the oxidation reactions of methane and ethane, HCN, and NH_3, as well as the interactions between hydrocarbon species (CH_i, HCCO) and nitrogen components (NO, NH_i, N_2), and N_2 fixation. The mechanism is called KILPINEN97, and is available from the net or from the authors. The mechanism is also completely listed in the recent reference by *Coda Zabetta et al. (2000)*. The mechanism is based on schemes developed by Glarborg, Miller, and co-workers. The mechanism has been shown to describe nitrogen reactions well at a number of combustion conditions in the FBC temperature range of 700-100 °C (*Kilpinen et al., 1999a*).

The presence of particles in CFBC can strongly influence the gas-phase chemistry by removal of the radicals. Our CFBC model allows for inclusion of radical quenching/recombination on particles. The removal has been assumed to be limited by mass transfer that is described by Sherwood number (Sh):

$$-d[i]/dt = SC \cdot (D_i \cdot Sh)/(2R) \cdot (A/V) \cdot [i] \qquad (1)$$

and where symbol *i* stands for radical species, *D* is diffusion coefficient (m^2/s), *R* is radius of particle (m), *A* is total surface area of solids (m^2), *V* is total volume of solids (m^3), and [ ] means molar concentration (mol/m^3). SC means so called sticking coefficient that tells what is the probability that the collision leads to removal of the radical. For example, sticking coefficient equal to 0.2 means that only every fifth of the collisions of the radical to the surface leads to removal of the radical.

Heterogeneous char oxidation to CO and CO_2, and char-nitrogen conversion to NO, N_2O, and N_2 are described by a single particle model that includes 15 reaction steps given in the form of 7 net reaction paths (*Goel et al., 1994*). The "shrinking particle model" yields the reaction rates inside the char particle as a function of particle radius. It assumes that mass transfer and chemical reactions inside the particle are always locally in balance. Mass transfer inside the particle – internal diffusion- is described by an effective diffusion coefficient. External mass transfer due to forced convection is calculated from Sherwood's number. In the present version of the model, particle

temperature is estimated and given as an input to the single particle model. In the future, an energy balance will be added to calculate the particle temperature.
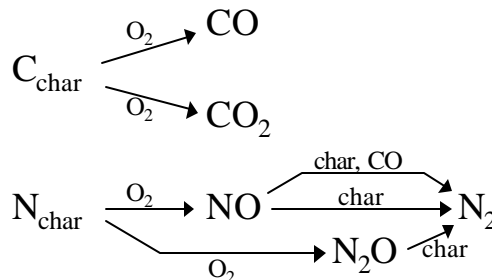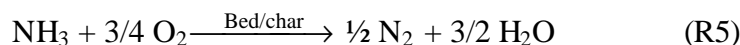
$$C_{char} \xrightarrow{O_2} CO$$
$$C_{char} \xrightarrow{O_2} CO_2$$

$$N_{char} \xrightarrow{O_2} NO \xrightarrow[char]{char, CO} N_2$$
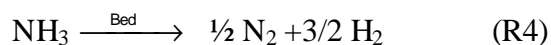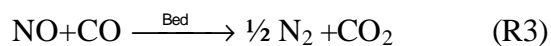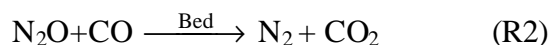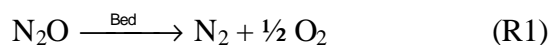$$N_{char} \xrightarrow{O_2} N_2O \xleftarrow{char} N_2$$
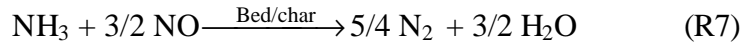
Fig. 3. The submodel of heterogeneous char oxidation.

The heterogeneous char oxidation model is evaluated in comprehensive parametric studies (*Kilpinen et al., 1999a*; *Konttinen et al., 2001a*). The results show that the 15-step mechanism is somewhat too simple for an accurate description of formation and destruction of nitrogen oxides for the great variety conditions that exist in CFB furnace. For example, the model underestimates NO reduction in presence of CO. We have also shown that the data used by Goel et al. (*1994*) for kinetic parameter fitting (rate constants for the seven net paths) were too limited, and the original parameters proposed do not predict correctly the effect of temperature on the reactivity of char.

Konttinen et al. (*2001a*) have re-estimated the parameters based on a larger amount of available data while keeping the mechanism unchanged. Recently, however, we have also made additional, new experiments burning single bituminous char particles in a laboratory flow reactor under many different conditions. These data, together with available data from literature, will be used for further parameter estimation including some changes in the mechanism as well (*Konttinen et al., 2001b*). The aim is to include - in a simplified way - the following missing pathways at least: HCN formation during char oxidation and N_2O reduction by CO (*Winter 1999; Ashman et al., 2000; Aihara et al., 2000*).

Catalytic reactions play also an important role in the conversion of fuel-nitrogen to nitrogen oxides, and the kinetics of many catalytic reactions have also been measured (*Johnsson, 1994; Leckner, 1998; Kilpinen et al,1999a*). A first version of submodel for catalytic nitrogen reactions to our CFBC model was compiled during this work. The reactions included at the moment are the following. The rate constants were taken from the works by Johnsson et al. (*1990, 1991, 1995, 1999*).

$$N_2O \xrightarrow{Bed} N_2 + \tfrac{1}{2} O_2 \qquad \qquad (R1)$$

$$N_2O + CO \xrightarrow{Bed} N_2 + CO_2 \qquad \qquad (R2)$$

$$NO + CO \xrightarrow{Bed} \tfrac{1}{2} N_2 + CO_2 \qquad \qquad (R3)$$

$$NH_3 \xrightarrow{Bed} \tfrac{1}{2} N_2 + 3/2\ H_2 \qquad \qquad (R4)$$

$$NH_3 + 3/4\ O_2 \xrightarrow{Bed/char} \tfrac{1}{2} N_2 + 3/2\ H_2O \qquad \qquad (R5)$$

$$NH_3 + 5/4\ O_2 \xrightarrow{Bed/char} NO + 3/2\ H_2O \qquad \qquad (R6)$$

$$NH_3 + 3/2\ NO \xrightarrow{\text{Bed/char}} 5/4\ N_2 + 3/2\ H_2O \qquad (R7)$$
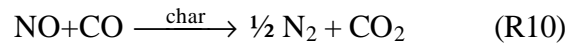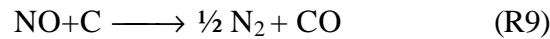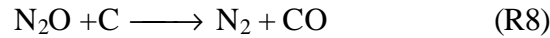
To test the implementation and to illustrate the effect of catalytic reactions on NO/N_2O destruction and reduction some simplified plug flow calculations were carried out at a constant solids concentration equal to 10 kg/m^3 that can be assumed to be a typical value in the upper parts of the riser (Fig. 4). A typical flue gas from coal combustion was assumed in the beginning of the calculations with the following composition: 200 ppm NO, 100 ppm N_2O, 1% CO, 6% H_2O, 13 % CO_2, 4 % O_2, rest N_2. Four principally different types of calculations were performed:

a) pure gas-phase kinetics without radical removal,
b) gas-phase kinetics with radical removal. The radicals H, O, OH, and HO_2 were considered and sticking coefficients equal to 0.2 for each radical.
c) gas-phase kinetics without or with radical removal (SC=0 or 0.2) and heterogeneous kinetics with sand bed conditions (char 2%, ash 10%, sand 88%),
d) gas-phase kinetics without or with radical removal and lime bed conditions (char 2%, ash 10%, CaO 44%, $CaSO_4$ 44%).

In calculations for the cases c and d, the following reactions were also included in addition to the reactions (R1)-(R7):

$$N_2O + C \longrightarrow N_2 + CO \qquad (R8)$$

$$NO + C \longrightarrow \tfrac{1}{2}\ N_2 + CO \qquad (R9)$$

$$NO + CO \xrightarrow{\text{char}} \tfrac{1}{2}\ N_2 + CO_2 \qquad (R10)$$

The rate constants in the simplified plug flow calculations were taken from Johnsson&Jensen (*1999*) for the reactions R8 and R9, and for the reaction R10 from Johnsson&Dam-Johansen (*1991*). In the CFBC simulations, however, all these three reactions are taken into account with the single particle model and using different reaction rate expressions. Further, it should be noted that no char oxidation reactions (heterogeneous generation of NO, N_2O, CO) were included in the simplified plug flow calculations whereas they are a part of the single particle model, and play typically a significant role in a CFBC riser.

From Fig. 4 we can see that when radical removal and sand or lime bed conditions are considered a strong NO reduction occurs at the conditions studied. This is due to less CO burn-out and enhanced NO reduction by reaction (R10), especially. Above 850°C no NO remains after 1s residence times under these conditions when we assume that no new NO is formed from char. For N_2O emission the radical removal will decrease the N_2O reduction efficiency at short times due to the otherwise very rapid N_2O destruction that would occur by radicals and especially by H radical. However, at residence times longer than 0.5s the decreased CO burn-out due to radical removal and the consequent enhanced rate of reaction (R2) takes over, and results in lower N_2O emission for lime and sand bed than without radical removal

The obvious conclusion from this simplified study is that the radical removal effects play an important role in determining the final nitrogen oxide emission amounts. The removal of radicals greatly affects the CO oxidation rate, and thus, the CO concentration in the furnace, and the rates for nitrogen oxides' reduction. If no radical
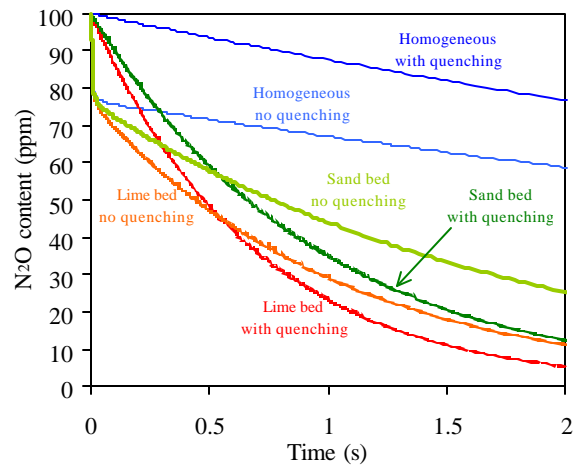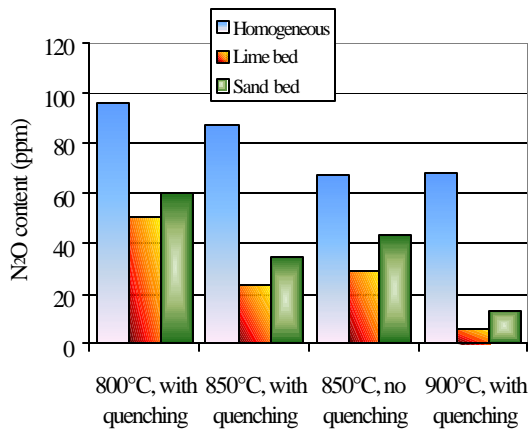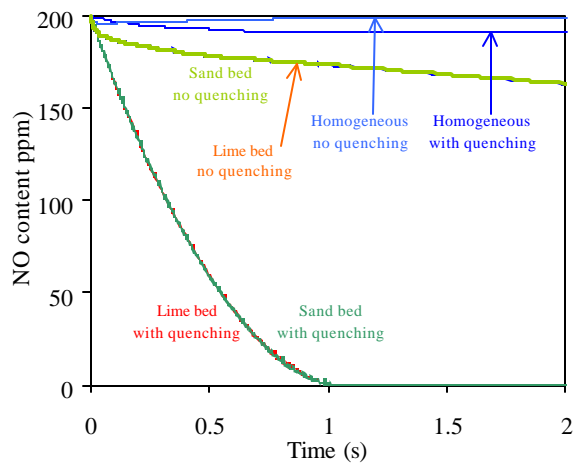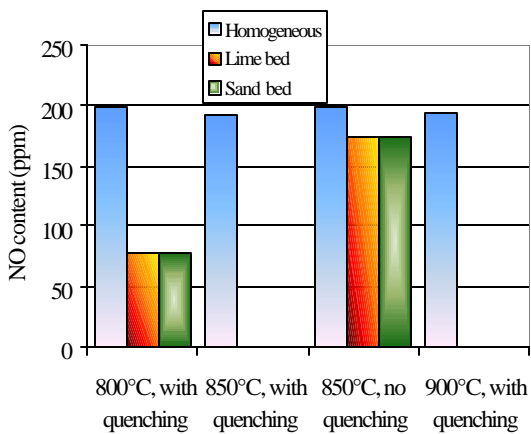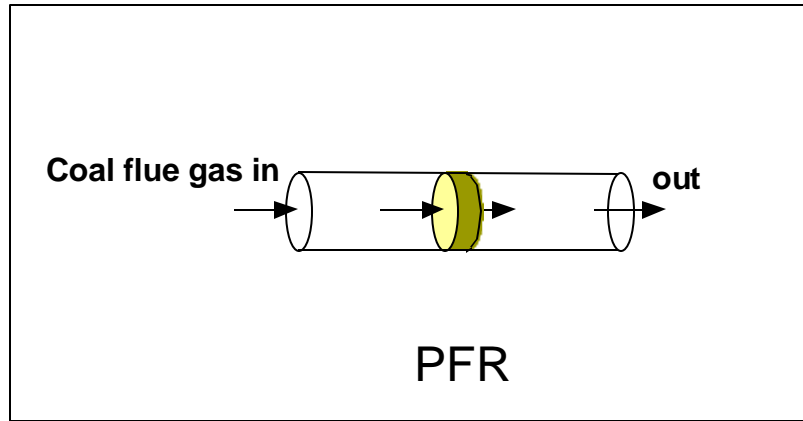
Fig. 4. a) The calculated effect of radical removal on nitrogen oxides' destruction in a plug flow reactor after 1s residence time at a temperature of 800, 850, or 900°C. b) The effect of radical removal on nitrogen oxides' destruction as a function of time in a plug flow reactor at 850°C. Inlet gas: 200 ppm NO, 100 ppm N_2O, 1% CO, 6% H_2O, 13 % CO_2, 4 % O_2, rest N_2. In the calculations the NO formation from char was excluded.

removal is assumed no CO will be left at the exit of the furnace, and too high nitrogen oxide emission values were predicted (Tallsten, 2000). For realistic prediction of nitrogen oxides from CFBC the effect of radical removal needs to be considered.

The simplified calculations shown above were carried out only as a test of the compilation of the submodel for catalytic nitrogen reactions. The implementation of the submodel to the CFBC model is in progress. In the present version, the bed (either sand or lime) was treated as a single component but the future plan is to complement the submodel to include a option where the effects of bed components could be taken into account separately (ash, sand, CaO, CaS, $CaSO_4$). This gives better possibilities to model the effects of operating conditions on the reactions. It is well known that for both NO and N_2O reduction CaS is a very important material at reducing conditions because of the reductive decomposition of sulphated limestone. However, modelling the effects of rapid local changes between oxidising and reducing conditions in a CFBC on nitrogen chemistry still remains a challenge as also discussed by Johnsson&Jensen (1999).

Recently, it has also been shown that for oxidation of, e.g., ammonia on calcined limestone (CaO) the presence of flue gas components, especially of water vapour (H_2O), can significantly reduce the catalytic acitivity due to blocking of active sites (Zijlma et al., 2000). Since the kinetic investigations for catalytic reactions have so far been made without the presence of flue gas components, there is a need of re-checking the kinetic constants in the presence of flue gas components as well.

3. SIMULATION RESULTS AND DISCUSSION

To test the performance of the CFBC model two simulations were made corresponding to cases that have been measured in a 12 MW CFBC at Chalmers University. A comparison of model predictions to nitrogen oxides' profiles inside the combustor measured during coal and wood chips combustion is illustrated in Fig. 5. The most important reactor, operational, material, and other input data for the simulations are given in Tables 1-3.

The coal simulation in Fig. 5 is further illustrated for two different sets of char particle oxidation parameters: the blue curve refers to the original parameters determined by Goel et al. (1994) and the green one to a set of new parameters fitted to laboratory FBC data and data from pilot CFBC conditions, as described by Konttinen et al. (2001a). In the latter simulation case as well as in the wood chip simulation effects of radical removal were included. No catalytic nitrogen reactions were yet taken into account, however.

Coal was assumed to release its volatiles evenly to the emulsion phase in the bottom bed whereas volatiles from wood chips were also released in the volume above the bottom bed up to 2m furnace height. The volatile components were taken in the simulations as CH_4, CO, H_2, H_2O, HCN, NH_3, N_2. The same C/N ratio as in fuel was assumed to remain in char. The split of volatile-nitrogen to HCN/NH_3/N_2 was assumed equal to 35/35/30 for coal, and 0/70/30 for wood chips, respectively. The volatiles composition for coal and wood chips are specified in Table 4.

Table 1. Reactor parameters for the conditions of Fig. 5.

Riser height / m	13.5
Cross-section up to 2.2m / m^2	2.07
Cross-section above 2.2m / m^2	2.37
Riser exit location / m	10
Exit separation efficiency / %	25
Secondary air inlet location / m	2.1
Temperature in core,annulus,bottom bed/^oC	850

Table 2. Operational parameters for the conditions of Fig. 5.

	Coal	Wood chips
-Primary gas feed / (kg/s)	2.94	2.45
-Secondary gas feed / (kg/s)	1.25	1.33
-air via the particle seal at 0.99m	0.25	0.10
-air via the bed material classifier at 1.29m	0.15	0.20
-Fuel feed / (kg/h)	1430	3340
-Fuel density / (kg/m^3)	1400	60
-Bed material density / (kg/m^3)	2600	2600
-Diameter of bed material / (μm)	320	320

Table 3. Material properties for the fuels of Fig. 5.

	Coal	Wood chips
Proximate analysis (wt-%, raw)		
-moisture	14.8	44.1
-ash	6.6	0.6
-combustibles	78.6	55.3
Ultimate analysis (wt-%, daf)		
C	79.8	50.5
N	1.56	0.22
S	0.72	0.03
H	5.3	6.0
O	12.6	43.3
Volatiles (wt-%, daf)	40	80

Table 4. Composition used for the volatiles in simulations of Fig. 5. One kg of combustibles yielded volatiles as follows (kmol/kg comb.):

	Coal	Wood chips
CO	0.00788	0.0269
CH_4	0.0104	0
NH_3	1.071e-4	7.5e-5
HCN	1.071e-4	0
N_2	4.59e-5	1.5e-5
H_2	0.00523	0.0292
H_2O	0	2.22e-4

One can see from the Figure 5 that the NO emissions for both fuels are about the same despite the much higher fuel-nitrogen content in coal than in wood. This is in agreement with other additional measurements carried out in a laboratory and a pilot-scale CFBC (*Åmand et al., 2001*). The N_2O emission, on the other hand, is much higher for coal than for wood chips. According to the measurements coal results to a much higher NO concentrations at the lower part of the boiler than wood chips, and the measured NO profile is clearly decreasing for coal as a function of boiler height.

The simulations for coal also show a very high NO peak at the bottom bed part of the boiler, but above the bed a very high NO reduction is predicted, and the NO concentration at about 1m height is much lower than what is measured. When secondary air streams are added the NO concentrations predicted start to increase, and continue to increase along the whole riser height for the original char oxidation parameters (blue) whereas the new parameters (green) lead to no net formation of NO after the final secondary air addition. This difference is mainly due to the enhanced NO reduction by CO catalysed by char at these conditions. The radical removal that was applied in the latter simulation leads to higher CO concentration profile in the riser which together with the higher rate constant for the reaction between NO and CO on char enhance the NO reduction.
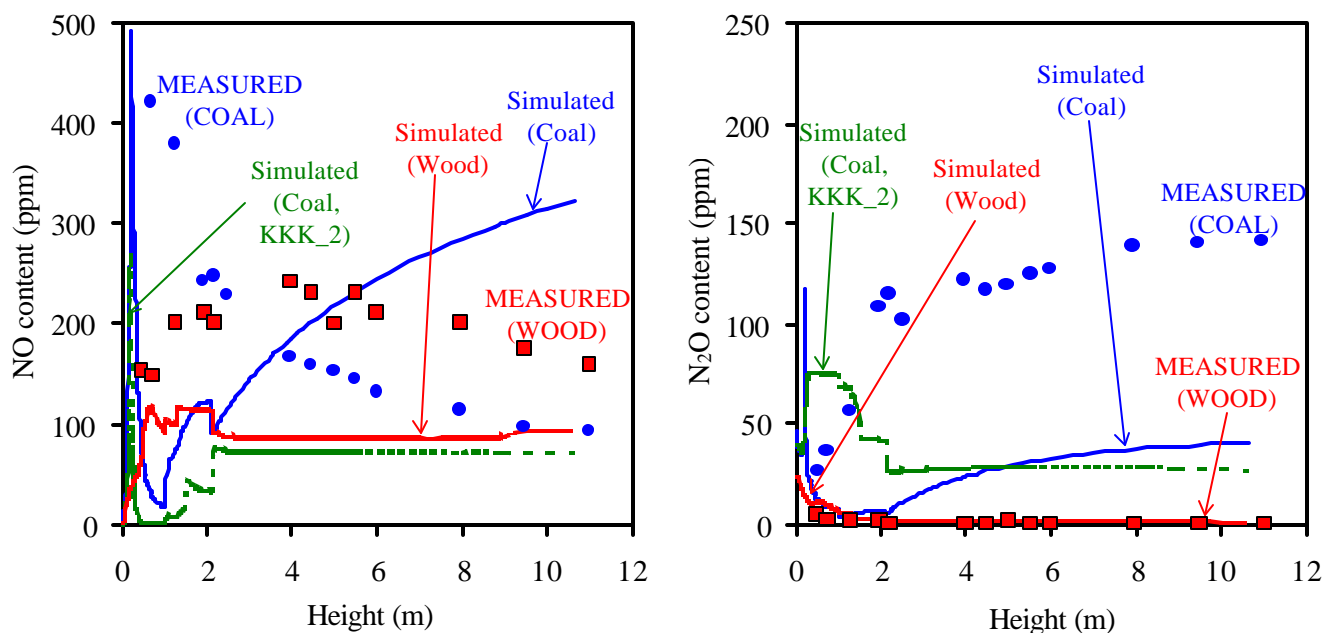

Fig. 5. Comparison of model predictions to measurements from a 12 MW CFBC. Homogeneous and heterogeneous chemistry included in all simulations. For simulation of wood chip combustion and coal combustion with KKK_2 parameters (green) also radical removal was taken into account. No catalytic reactions were though included.

However, also the latter simulation (green) fails to predict the decreasing NO trend which is likely an indication that important additional catalytic reactions for NO reduction must be missing from the calculations. For example, important catalytic reactions that can easily lead to enhanced NO reduction could be NO reduction by CO on ash components that contain iron or iron oxides, e.g. (*Hayhurst and Lawrence, 1997*):

$$3CO + Fe_2O_3 = 3CO_2 + 2Fe$$
$$2Fe + 3NO = 3/2 N_2 + Fe_2O_3$$
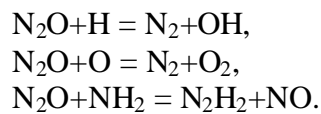
net: $NO + CO = \frac{1}{2} N_2 + CO_2$.
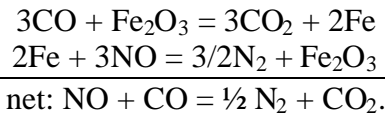
The discrepancies in measured and predicted concentration profiles may also be due to many other reasons like the uncertainties in determination of values for the process input data that was used in the simulations. In addition, it should be remembered that the measured profile applied for centerline concentrations only, and considerable radial concentration gradients can exist especially in the lower parts but also in the upper parts of the combustor in practise. The strong drop in NO concentration that was predicted at 1m height could also be controlled by slowing down the mixing of the bed gases above the bottom bed (*Kallio et al, 2001*).

In summary, with the new parameters for char oxidation (green) the model ranks the two tested fuels in the correct order with respect to the final NO and N_2O emission tendency. The final concentrations are in the correct order of magnitude.
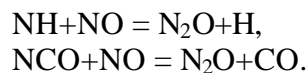
Contribution analysis

To investigate the relative importances of various reactions a postprocessing routine was created for a quantitative analysis of contribution of different homogeneous or heterogenous reactions for formation/destruction of chemical components at different heights in the combustor. Figure 6 shows examples of the results with the contribution analysis for the conditions shown in Fig. 5 and with the original *Goel et al. (1994)* parameters for the heterogeneous char oxidation.
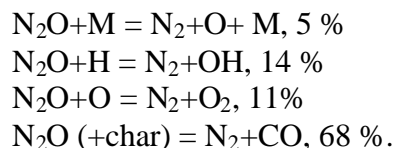
In Figs. 6a-d the formation and destruction of NO/N_2O are given in ppm/s units in the bubbles. The curves in the figures are plotted in cumulative way which means that the area between the curves stands for the contribution of the indicated reaction. For example, we can see that for N_2O destruction the important reactions are in the bubbles:
$$N_2O+H = N_2+OH,$$
$$N_2O+O = N_2+O_2,$$
$$N_2O+NH_2 = N_2H_2+NO.$$
Formation of N_2O occurs via:
$$NH+NO = N_2O+H,$$
$$NCO+NO = N_2O+CO.$$
In Figs. 6e-h the formation and destruction of NO/N_2O are given in moles/s in the whole bed (emulsion phase and bubbles together). The Figures show that both NO and N_2O formation and destruction are mainly dominated by heterogeneous char reactions at these conditions. The same conclusion applied for the freeboard region. For example, one could calculate by integration of the curves the following relative importances for N_2O destruction in the freeboard:

$$N_2O+M = N_2+O+ M,\ 5\ \%$$
$$N_2O+H = N_2+OH,\ 14\ \%$$
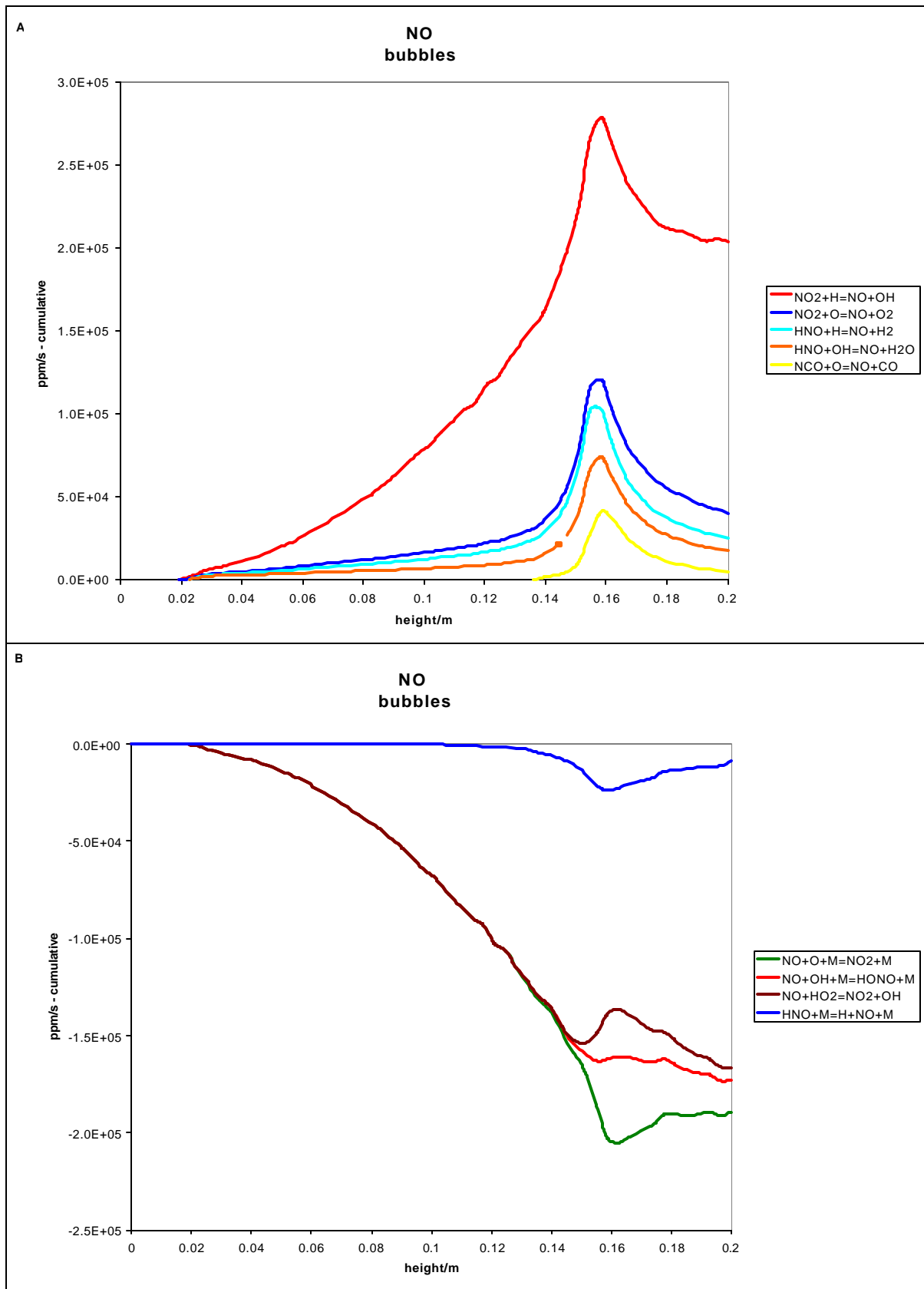$$N_2O+O = N_2+O_2,\ 11\%$$
$$N_2O\ (+char) = N_2+CO,\ 68\ \%.$$

Fig. 6a-b. Formation and destruction of NO in the bubbles. Rates are calculated for each computational cell and plotted in a cumulative way. Conditions apply for coal combustion in Fig. 5.

Fig. 6c-d. Formation and destruction of N_2O in the bubbles. Rates are calculated for each computational cell and plotted in a cumulative way. Conditions apply for coal combustion in Fig. 5.
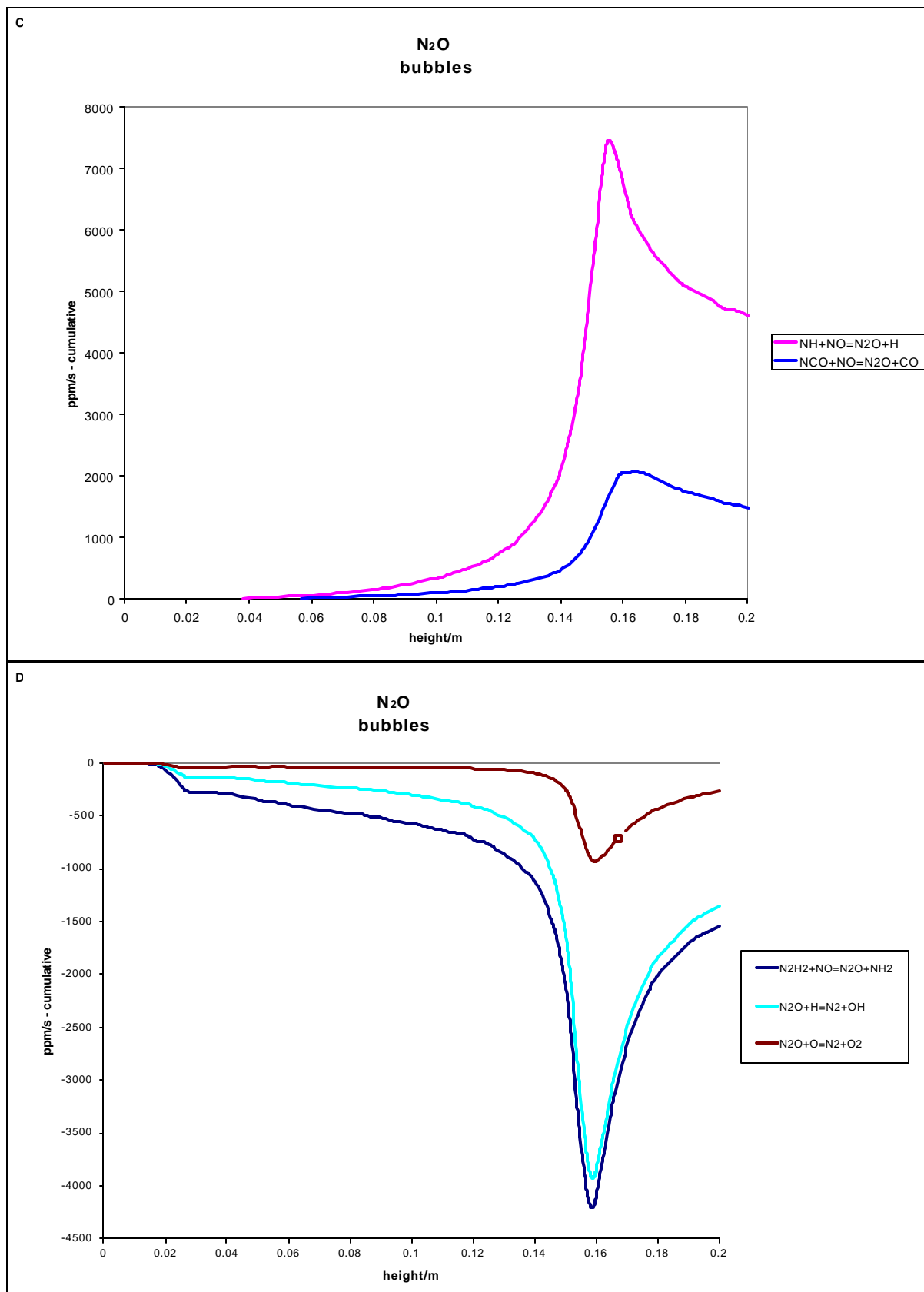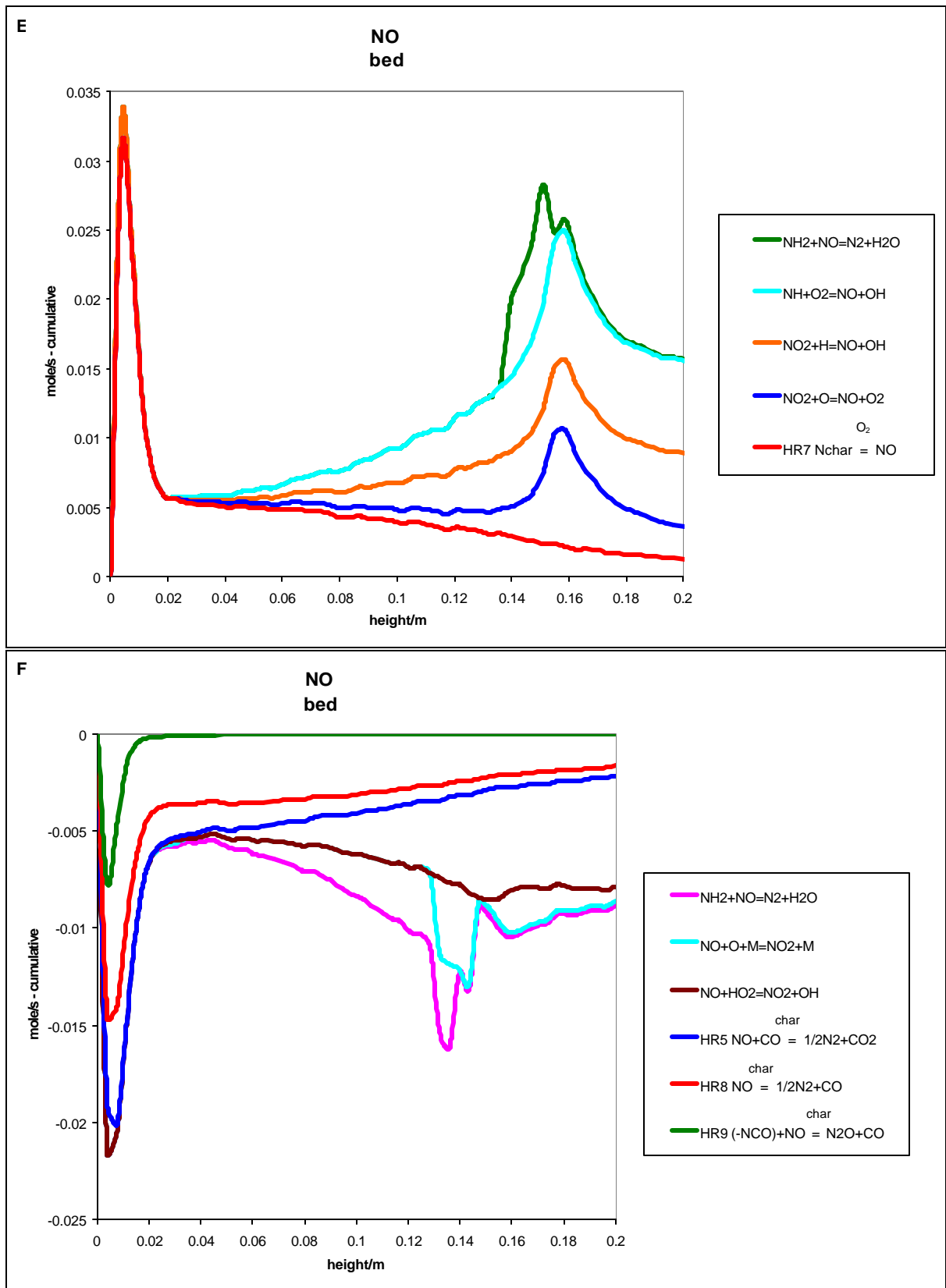
Fig. 6e-f. Formation and destruction of NO in the bottom bed. Rates are calculated for each computational cell and plotted in a cumulative way. Conditions apply for coal combustion in Fig. 5.

Fig. 6e-f. Formation and destruction of N_2O in the bottom bed. Rates are calculated for each computational cell and plotted in a cumulative way. Conditions apply for coal combustion in Fig. 5.
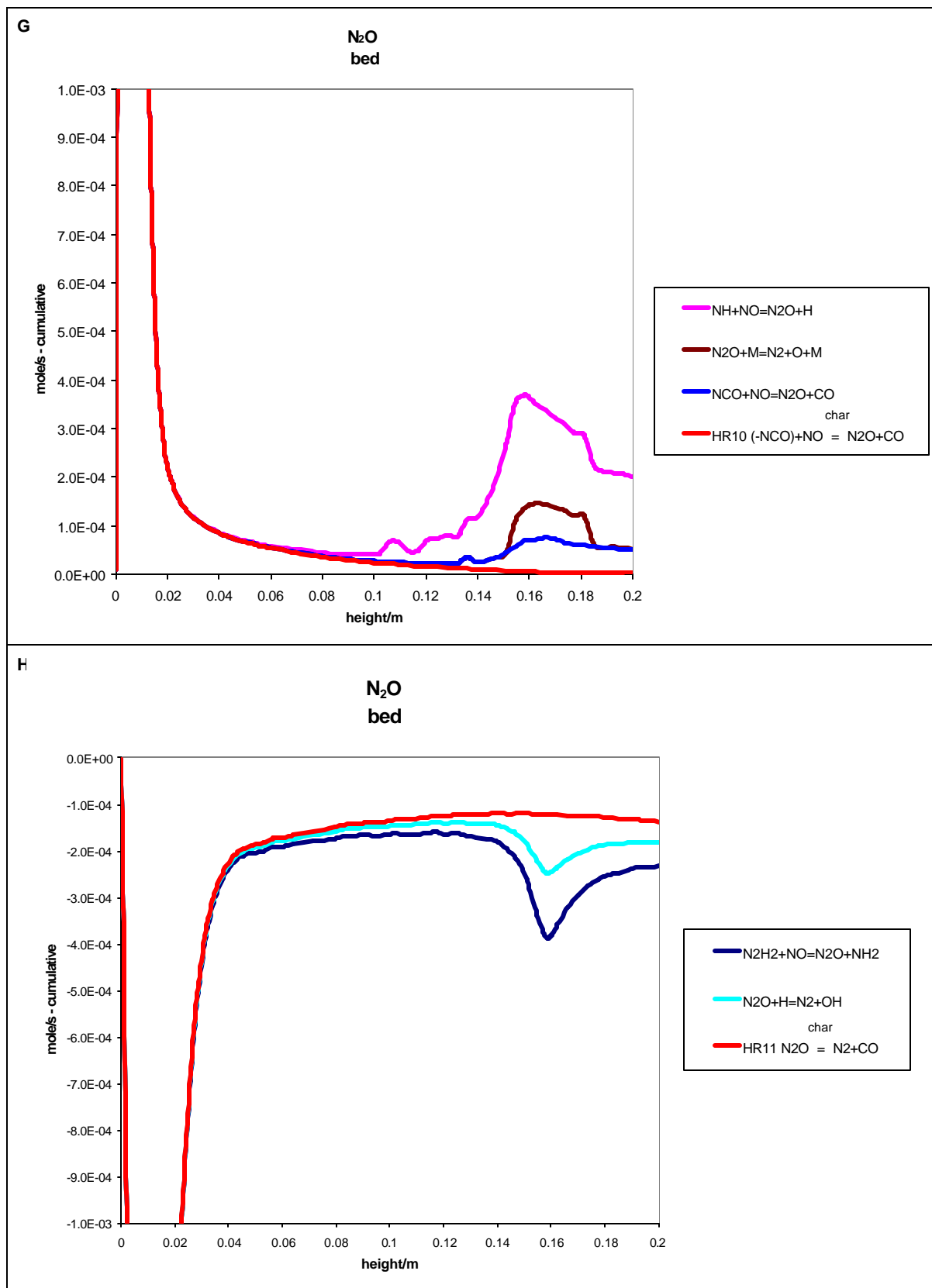
4. CONCLUDING REMARKS

The paper deals with work-in-progress aimed at developing a detailed emission model for circulating fluidised bed combustors. It is especially aimed that the model will perform as a predictor for nitrogen oxide emission tendency for various conventional fuels or fuel mixtures including fuels like renewable fuels and waste-derived fuels. The predictor will help the boiler manufacturers in estimating the warranties for nitrogen oxide emissions and in designing the combustor setup needed. The model is based on detailed homogeneous and heterogeneous chemical kinetics and a simplified, reasonable hydrodynamics with presumed temperature distribution. For particles a higher temperature than the gas temperature can be assumed.
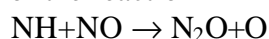
In this work the model was tested for nitrogen oxide prediction at coal and wood chip combustion in a 12 MW CFBC. A first version of the submodel for catalytic nitrogen reactions was also compiled but not yet implemented to the predictor. A postprocessing routine was also created for a quantitative analysis of the contribution of different homogeneous or heterogenous reactions for formation/destruction of chemical components at different heights in the combustor.

Based on the results the following conclusions can be drawn:

- The predictor ranked the two tested fuels (coal and wood chips) in the same order as in measurements with respect to the final NO and N_2O emission. The final concentrations were also in the correct order of magnitude. In concentration profiles, however, clear discrepancies could be seen between the predicted and measures ones.

- The knowledge of the homogeneous reactions and kinetics is good. The kinetics for many heterogeneous gas-solid and catalytic nitrogen reactions have also been measured. The knowledge of principal chemical pathways for NO/N_2O formation and destruction under practical FBC conditions is still not good, however. The quantitative reaction path analysis showed to be a powerful tool for obtaining a better understanding of the main routes for final nitrogen oxide emissions. Obviously, the radical removal effects play an important role for final nitrogen oxide emissions.

- For homogeneous N_2O formation the main paths from volatile nitrogen are:
$$HCN \xrightarrow{\;+O\;} NCO \xrightarrow{\;+NO\;} N_2O.$$

$$NH_3 \xrightarrow{\;+OH\;} NH_2 \xrightarrow{\;+H\;} NH \xrightarrow{\;+NO\;} N_2O.$$
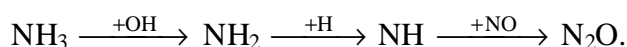
  New recommendations of kinetic and thermodynamic data *(Kilpinen et al., 1999c)* have increased the importance of the reaction
$$NH+NO \rightarrow N_2O+O$$
  as compared to the reaction
$$NCO+NO \rightarrow N_2O+CO.$$
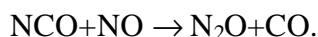
- The submodel for char-nitrogen oxidation to NO, N_2O, N_2 is based on a single particle model that includes 15 reaction steps in the form of 7 net reaction paths *(Goel et al., 1994)*. The "shrinking particle model" yields the reaction rates inside

the char particle as a function of particle radius. Mass transfer inside the particle is described by an effective diffusion coefficient. Our results have, however, suggested that the 15-step mechanism is too simple, and leads to underestimation of NO reduction in presence of CO. We have also shown that the data used for kinetic parameter fitting was too limited, and the parameters do not predict correctly the temperature effect on char reactivity (*Konttinen et al., 2001a*).

In summary, it may be concluded that a"first version" of predictor is finished and it gave promising results in the tests performed. Still, some fine-tuning will be needed in the future. This will include an implementation of a fragmentation model for the fuel particle, and a re-estimation of the single char particle oxidation mechanism based on experimental data at wider conditions and including the energy balance equation in the char combustion model. At high oxygen concentrations the particle may experience high temperature gradients that can significantly affect the reaction rates (*Konttinen et al., 2001b*). Work is also on-going on the extension of the fuel-specific nitrogen database for the predictor. Finally, some more validation simulations for real fuel mixtures are needed.

5. ACKNOWLEDGEMENT

6. REFERENCES

Aihara, T., Matsuoka, K., Kyotani, T., Tomita, A.: "Mechanism for N2 formation during char oxidation", paper presented at the 28th Symp. Int. on Comb., Edinburgh, August, 2000.

Ashman, P., Haynes, B., Nicholls, P., Nelson, P.: "Interactions of gaseous NO with char duringthe low temperature oxidation of coal chars", paper presented at the 28th Symp. Int. on Comb., Edinburgh, August, 2000.

Coda Zabetta, E.; Kilpinen, P.; Hupa, M.; Ståhl, K.; Leppälahti, J.; Cannon, M.; Nieminen, J., *Energy Fuels*, 14:4, 751-761, 2000.

Goel, S., Morihara, A., Tullin, C., Sarofim, A.: *25th Symp. Int. on Comb.*, The Combustion Institute, pp. 1051-1059 (1994).

Hayhurst, A.N. & Lawrence, A.D*.: Combustion and Flame*, 110:351-365 (1997).

Hupa, M., Kilpinen, P., Kallio, S., Konttinen, J., Skrifvars, B-J., Zevenhoven, M., Backman, R.: "Predicting performance of different fuels in fluidised bed *ITIT Symposium on Effective Utilisation of low grade fuels by fluuidised bed technology*, AIST-NIRE-NEDO, Tsukuba, Japan, December 1-2, 1999.

Leckner, B.: *Progress in Energy and Combustion Science*, Vol. 24, No. 1, 31-36, 1998.

Johnsson, J.E.: "Kinetics of heterogeneous NO reactions at FBC conditions", Technical University of Denmark, CHEC Report, No. 9003, March, 1990.

Johnsson, J.E. & Dam-Johansen, K.: "Formation and reduction of NO in a fluidised bed combustor", Fluid Bed Combustion – Clean Energy for the World, ASME, (ed. E.J. Anthony), pp. 1389-1396, 1991.

Johnsson, J-E.: *Fuel*, 73 (1994) pp. 1398-1415.

Johnsson, J.E. & Dam-Johansen, K.: "Reduction of N_2O over char and bed material from CFBC", 13th Int. Conf. on FBC, Vol 2, pp.859-869, 1995.

Johnsson, J.E. & Jensen, A.: "Investigation of N_2O reduction processes in circulating fluidised bed combustion chambers", Research Final Report, ECSC Coal RTD Programme, 1999.

Johnsson, J.E.&Jensen, A.: "Heterogeneous NO and N_2O chemistry in CFBC", IEA Workshop on NOx/N2O Formation and Destruction in Fluidised Bed Combustors, *38th IEA Fluidised Bed Conversion Meeting*, Savannah, May 16, 1999 (Eds. Winter, F.&Anthony, E.J.).

Kallio, S., Kilpinen, P., Hupa, M.: "Advanced modeling of nitrogen oxide emissions in circulating fluidized bed combustors: parametric study of hydrodynamics", *6th Int. Conference on Circulating Fluidized Beds*, Wurzburg, August 22-27, 1999.

Kallio, S., Kilpinen, P., Hupa, M.: "Study of effects of hydrodynamical modeling on the predicted nitrogen oxide emissions in CFB combustors", *3rd European conference on fluidization*, Toulouse, May 29-31, 2000.

Kallio, S., Kilpinen, P., Konttinen, J., Hupa, M.: "Numerical study of effects of gas mixing and solids segregation on nitrogen oxides formation in CFB combustors", *10th Int. Conference on Fluidisation*, Beijing, May, 2001, (to be published).

KILPINEN97, http://www.abo.fi/fak/ktf/cmc.

Kilpinen, P., Kallio, S., Hupa, M.:"Advanced modeling of nitrogen oxide emissions in circulating fluidized bed combustors: parametric study of coal combustion and nitrogen compounds chemistries", *Proc. 15th Int. FBC Conference*, CD-ROM, Paper No. FBC99-0155, Savannah, May 9-13, 1999a.

Kilpinen, P., Kallio, S., Hupa, M.. Leckner, B., Åmand, L-E., Johnsson, J-E., Jensen, A., Werther, J., Lucke, K., Sänger, M., Gulyurtly, I., Boavida, D.H., Abelha, P.: "Investigation of Processes in Circulating Fluidised Bed Combustion Chambers for N_2O Reduction*", Fifth International Conference on Technologies and Combustion for a Clean Environment*, Lisbon, July 12-15, 1999b.

Kilpinen, P., Norström, T., Mueller, C., Kallio, S., Hupa, M.: "Homogeneous NO and N_2O chemistry in FBC", IEA Workshop on NOx/N2O Formation and Destruction in Fluidised Bed Combustors, *38th IEA Fluidised Bed Conversion Meeting*, Savannah, May 16, 1999c (Eds. Winter, F.&Anthony, E.J.).

Knöbig, T., Lucke, K., Werther, J.: Chem. Eng. Science, 54, pp. 2151-2160 (1999).

Konttinen, J., Kilpinen, P., Kallio, S.: "Validation of a single particle model for char carbon and char nitrogen oxidation under fluidised bed combustion conditions", Char-nitrogen oxidation to NO and N_2O – a single particle modelling study", 16th Int. Conf. on Fluidised Bed Combustion, Reno, May 13-16, 2001a.

Konttinen, J, Kilpinen, P., Kallio, S., Forssen, M.: manuscript under preparation, 2001b.

Lyngfelt, A., Åmand, L-E., Leckner, B.: "Obtaining low N_2O, NO, and SO_2 emissions from circulating fluidised bed boilers by reversing the air staging conditions", *Energy and Fuels*, 9, pp. 386-387 (1995).

Tallsten, M.:"Test and validation of a detailed CFBC emission model for nitrogen oxides", M.Sc. Thesis, Åbo Akademi University, 2000.

Zijlma, G.J., Jensen, A., Johnsson, J.E., van den Bleek, C.M.: "The influence of H_2O and CO_2 on the reactivity of limestone for the oxidation of NH_3", *Fuel* 79 (2000) 1449-1454.

Winter, F.: "The concept of chemical similarity for optimisation and design of gas-solid processes", Habilitation, Vienna, September, 1999.

Werther, J., Knöbig, T.: Proc. Int. Symp. on Multiphase Flow (Eds. X. Chen and M. Ge), Beijing, International Academic Publishers, pp. 293-300 (1997).

Åmand, L-E., Miettinen-Westberg, H., Karlsson, M., Leckner, B., Lucke, K., Budinger, S., Hartge, E-U., Werther, J.: "Co-combustion of dried sewage sludge and coal/wood in CFB – a search for factors influencing emissions", 16th Int. Conf. on Fluidised Bed Combustion, Reno, May 13-16, 2001.