DTU Library

Simplified Model for Reburning Chemistry

Glarborg, Peter; Hansen, Stine

Link back to DTU Orbit

energy&fuels
article

Simplified Model for Reburning Chemistry

Stine Hansen and Peter Glarborg*

*Department of Chemical Engineering, Technical University of Denmark,
2800 Lyngby, Denmark*

In solid fuel flames, reburn-type reactions are often important for the concentrations of NO_x in the near-burner region. To be able to model the nitrogen chemistry in these flames, it is necessary to have an adequate model for volatile/NO interactions. Simple models consisting of global steps or based on partial-equilibrium assumptions have limited predictive capabilities. Reburning models based on systematic reduction of a detailed chemical kinetic model offer a high accuracy but rely on input estimates of combustion intermediates, including free radicals. In the present work, an analytically reduced nitrogen scheme is combined with simplified correlations for estimation of O/H and hydrocarbon radicals. Correlations are derived for volatile compositions representative of solid fuels ranging from bituminous coal to biomass, for temperatures of $1200-2000$ K and excess air ratios in the range of $0.6 \leq \lambda \leq 2.0$. The combined model is tested against reference calculations with a comprehensive mechanism. The results indicate that the approximations in the simplified hydrocarbon radical scheme are satisfactory. However, when this scheme is combined with the semi-empirical correlations for the O/H radicals, the modeling predictions for the radicals become less accurate. Despite these deviations, the combined model provides a satisfactory prediction of NO under reburning conditions over the range of fuels, temperatures, and stoichiometries tested.

1. Introduction

Computational fluid dynamic (CFD) models are often used to predict pollutant formation, in particular, nitrogen oxides (NO_x), in combustion systems. Although significant efforts have been aimed at modeling and understanding NO formation and destruction, it remains a challenge to quantitatively predict NO emissions from practical systems. Because of the complexity of turbulent combustion, simplified schemes are often required to describe the chemistry,[1,2] to reduce the computational load. Several simplified approaches for modeling nitrogen chemistry in combustion have been reported. Typically, they involve either an empirical fitting of a set of global reaction parameters to experimental data or an analytical reduction of comprehensive models through sensitivity analysis and/or equilibrium considerations.

Simplified schemes developed to predict volatile N oxidation in combustion include both global models[3-6] and analytically reduced schemes.[7,8] Under reducing conditions, reburn-type reactions recycling NO to cyanide species may become important. Here, the nitrogen chemistry is closely coupled to details of the fuel oxidation chemistry, i.e., the formation and destruction of hydrocarbon radicals, and the prediction of NO constitutes a demanding test of simplified mechanism concepts. Published schemes for reburning include global mechanisms,[9] sets based on partial equilibrium approaches,[10-13] and analytically reduced schemes.[7,14-16]

Two different simplified schemes for NO reduction by reburning reactions are employed in the commercial CFD code Fluent.[17] Both schemes, termed the instantaneous approach and the partial equilibrium approach, respectively, describe the reduction of NO by the reaction with the C_1 radical pool to form HCN (or CN). The difference between the schemes concerns the choice of radicals and the way their concentration is estimated. The instantaneous approach involves the hydrocarbon radicals CH_3, CH_2, and CH; their concentrations are drawn from calculations with a detailed combustion mechanism. The partial equilibrium approach is based on the work by Dimitriou et al.[11] Here, the principal pathways of NO reduction are assumed to involve the reaction with the radicals CH_2, CH, and C. The concentration of these radicals are found by assuming the following reactions to be in partial equilibrium: $CH_4 + H \rightleftharpoons CH_3 + H_2$, $CH_3 + OH \rightleftharpoons$

*To whom correspondence should be addressed. Fax: +45-45882258. E-mail: pgl@kt.dtu.dk.

(1) Andersen, J.; Jensen, P. A.; Meyer, K. E.; Hvid, S. L.; Glarborg, P. *Energy Fuels* **2009**, *23*, 5773–5782.
(2) Andersen, J.; Jensen, P. A.; Hvid, S. L.; Glarborg, P. *Energy Fuels* **2009**, *23*, 5783–5791.
(3) De Soete, G. G. *Proc. Combust. Inst.* **1975**, *15*, 1093–1102.
(4) Mitchell, J. W.; Tarbell, J. M. *AIChE J.* **1982**, *28*, 302–311.
(5) Chen, W.; Smoot, L. D.; Fletcher, T. H.; Boardman, R. D. *Energy Fuels* **1996**, *10*, 1036–1045.
(6) Brink, A.; Kilpinen, P.; Hupa, M. *Energy Fuels* **2001**, *15*, 1094–1099.
(7) Glarborg, P.; Lilleheie, N.; Byggstøyl, S.; Magnussen, B.; Kilpinen, P.; Hupa, M. *Proc. Combust. Inst.* **1992**, *24*, 889–898.
(8) Pedersen, L. S.; Glarborg, P.; Dam-Johansen, K. *Combust. Sci. Technol.* **1998**, *131*, 193–223.

(9) Chen, W.; Smoot, L. D.; Hill, S. C.; Fletcher, T. H. *Energy Fuels* **1996**, *10*, 1046–1052.
(10) Mereb, B. J.; Wendt, J. O. L. *Proc. Combust. Inst.* **1990**, *23*, 1273–1279.
(11) Dimitriou, D. J.; Kandamby, N.; Lockwood, F. C. *Fuel* **2003**, *82*, 2107–2114.
(12) Su, S.; Xiang, J.; Sun, X.; Zhang, Z.; Zheng, C.; Xu, M. *Energy Fuels* **2006**, *20*, 1434–1443.
(13) Su, S.; Xiang, J.; Sun, L.; Zhang, Z.; Sun, X.; Zheng, C. *Proc. Combust. Inst.* **2007**, *31*, 2795–2803.
(14) Giral, I.; Alzueta, M. U. *Fuel* **2002**, *81*, 2263–2275.
(15) Han, X.; Rückert, F.; Schnell, U.; Hein, K. R. G.; Koger, S.; Bockhorn, H. *Combust. Sci. Technol.* **2003**, *175*, 523–544.
(16) Lv, Y.; Wang, Z.; Zhou, J.; Cen, K. *Energy Fuels* **2009**, *23*, 5920–5928.
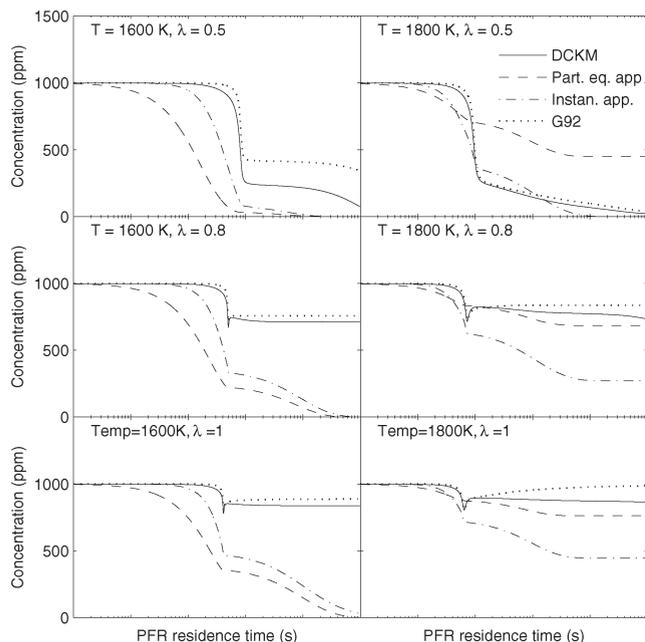(17) *Fluent 6.3 Users Guide*; Fluent, Inc.: Lebanon, NH, 2005.

Figure 1. Predictions of NO reburning during combustion of the CH_4 in the N_2/O_2 mixture with 1 vol % O_2 under isothermal plug-flow reactor conditions.

$CH_2 + H_2O$, $CH_2 + H \rightleftharpoons CH + H_2$, and $CH + H \rightleftharpoons C + H_2$. The omission of reactions between CH_3 and NO in the partial equilibrium approach would be expected to limit the accuracy, at least at temperatures below 1500 K, where methyl has been shown to be active in reducing NO.[18−20] It is also noteworthy that neither of the Fluent schemes involves the HCCO radical, which even for combustion of CH_4 is predicted to be important for NO removal.[18−20]

Figure 1 compares modeling predictions of NO reburning with the simplified schemes employed in Fluent (instantaneous and partial equilibrium approaches), the analytically reduced scheme by Glarborg et al.[7] (denoted G92), and the recent detailed chemical kinetic model by Mendiara and Glarborg[20,23] (denoted DCKM). These calculations, as well as those shown below, were conducted using Chemkin[21,22] and Matlab, respectively, assuming conditions of an isothermal plug-flow reactor. The calculations show the NO reduction during combustion under isothermal conditions of methane in the N_2/O_2 mixture with 1 vol % O_2 at selected excess air ratios (λ) and temperatures. To exclude differences in the selected mechanisms caused by anything other than the nitrogen chemistry descriptions, other species concentrations (O_2, H_2, radicals, etc.) are drawn from the detailed mechanism.

The results of Figure 1 show that the schemes employed by Fluent[17] have considerable shortcomings. The instantaneous

approach also predicts a large reduction of NO at all of the conditions examined, partly because it does not account for recycling of the cyanides to NO. The partial equilibrium approach provides a reasonable description of the NO emission level at the high temperature and $\lambda \geq 0.8$. At more reducing conditions or lower temperatures, the predictions are less accurate. The discrepancies may be attributed partly to the selection of reactions between hydrocarbons and NO and partly to the prediction of hydrocarbon radical concentrations.

Contrary to the Fluent schemes, the reduced mechanism by Glarborg et al. provides a good description of NO reburning at all of the examined conditions, except at very reducing conditions and lower temperatures. A similar level of accuracy would be expected from the more recent analytically reduced reburn schemes.[15,16] Even though these schemes are superior to the global models in terms of accuracy, their use has thus far been limited because they are computationally more demanding and rely on input estimates of combustion intermediates. In particular, these schemes require estimates of free-radical concentrations, values which in the past have been available only from modeling with either comprehensive mechanisms or analytically reduced fuel oxidation schemes. Global schemes, such as the two-step hydrocarbon oxidation mechanism by Westbrook and Dryer[24] or the four-step mechanism by Jones and Lindstedt,[25] offer estimates of the fuel oxidation rate and concentrations of intermediates, such as CO,[26] but they are unable to predict radical levels.

Recently,[27] we developed a simple approach for estimating O/H radical concentrations and combined it with the analytically reduced N scheme by Pedersen et al.[8] to yield a modeling tool for volatile N oxidation. In the present work, we extend this approach to involve also hydrocarbon radicals, to develop a simplified modeling tool for reburning-type chemistry. Simplified relations are derived for volatile compositions representative of solid fuels ranging from coal to biomass. The combined model, which describes the important gas-phase formation and consumption mechanisms for NO,[28,29] is tested against reference calculations with a comprehensive mechanism.

2. Numerical Procedure

The model developed in the present work consists of three parts: a simple approach for estimating O/H radical concentrations (scheme I), a scheme for prediction of hydrocarbon radical concentrations (scheme II), and an analytically reduced mechanism to describe the nitrogen chemistry (scheme III). Scheme I, consisting of semi-empirical correlations for H, O, and OH, is adopted from previous work.[27] Scheme II combines an analytically reduced scheme for C_1 radicals[7] with semi-empirical correlations for C_2 radicals (present work). Finally, the NO_x model (scheme III) is a combined scheme describing volatile N oxidation with HCN and NH_3 as intermediates, as well as a reduction of NO by reburning. It is set up initially by combining the reduced mechanisms of Pedersen et al.[8] and Glarborg et al.[7] but modified in the present work. The Pedersen scheme was shown in our

(18) Glarborg, P.; Alzueta, M. U.; Dam-Johansen, K.; Miller, J. A. *Combust. Flame* **1998**, *115*, 1–27.

(19) Skreiberg, Ø.; Kilpinen, P.; Glarborg, P. *Combust. Flame* **2004**, *136*, 501–518.

(20) Mendiara, T.; Glarborg, P. *Energy Fuels* **2009**, *23*, 3565–3572.

(21) Kee, R. J.; Rupley, F. M.; Miller, J. A. Chemkin II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics. *Sandia Report SAND89-8009B · UC-706*; Sandia National Laboratories: Livermore, CA, 1989.

(22) Lutz, A. E.; Kee, R. J.; Miller, J. A. Senkin: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics With Sensitivity Analysis. *Sandia Report SAND87-8248 · UC-401*; Sandia National Laboratories: Livermore, CA, 1990.

(23) Mendiara, T.; Glarborg, P. *Combust. Flame* **2009**, *156*, 1937–1949.

(24) Westbrook, C. K.; Dryer, F. L. *Combust. Sci. Technol.* **1981**, *27*, 31–44.

(25) Jones, W. P.; Lindstedt, R. P. *Combust. Flame* **1988**, *73*, 233–249.

(26) Andersen, J.; Rasmussen, C. L.; Giselsson, T.; Glarborg, P. *Energy Fuels* **2009**, *23*, 1379–1389.

(27) Hansen, S.; Glarborg, P. *Energy Fuels* **2010**, *24*, 2883–2890.

(28) Glarborg, P.; Jensen, A. D.; Johnsson, J. E. *Prog. Energy Combust. Sci.* **2003**, *29*, 89–113.

(29) Miller, J. A.; Bowman, C. T. *Prog. Energy Combust. Sci.* **1989**, *15*, 287–338.

Table 1. Estimated Volatile Compositions of the Selected Fuels[27]

	composition (vol %)[a]			
fuel number[b]	1	2	3	4
H_2O	16.5	12.5	5.0	1.7
CO	12.3	8.5	6.9	38.2
CO_2	5.0	3.2	1.2	9.1
H_2	46.7	39.1	37.5	41.4
CH_4	3.4	4.6	6.9	9.6
C_2H_4	1.1	1.6	2.9	
soot[c]	14.9	30.5	39.7	0

[a] When the volatile composition is entered into the simulations, the remaining components are normalized to yield 100%. [b] Fuel types: (1) Montana lignite,[30] (2) Dietz sub-bituminous coal,[31] (3) Pittsburgh number 8 bituminous coal,[32] and (4) biomass (poplar wood).[33] [c] Not included in the modeling.

recent work[27] to provide a good description of the oxidation chemistry of HCN and NH_3, but it does not involve hydrocarbon/ nitrogen interactions. The scheme of Glarborg et al. provides a satisfactory description of C_1/NO interactions (Figure 1) but excludes reactions of NH_3.

Similar to the work by Han et al.,[15] the model is developed for use in solid fuel combustion. The radical schemes are applicable to fuels belonging to four different ranks, ranging from bituminous coal to biomass. The assumed volatile compositions of these fuels are listed in Table 1. For each of the fuels, a set of semi-empirical equations describing the formation and consumption of the O/H radical pool has been developed in previous work.[27] On the basis of reference calculations with a full reaction mechanism (see below), equations are derived in the present work to describe also the formation and consumption of relevant hydrocarbon radicals.

The combined model, i.e., the schemes for the O/H and hydrocarbon radical pools and the reduced scheme for nitrogen chemistry, is tested by a comparison to reference calculations with a full mechanism, adopted from the work by Mendiara and Glarborg.[20,23] Subsets of the full mechanism have been evaluated against a range of experimental data for oxidation of HCN[34] and NH_3[19,23,35] and for reduction of NO.[20] As documented in these references, the detailed mechanism provides a good description of volatile N oxidation and reburn-type chemistry over a wide range of conditions. For this reason, we find it appropriate to use modeling predictions with the detailed mechanism as reference calculations for the simplified schemes.

2.1. Prediction of Hydrocarbon Radicals. The elementary reactions taken into consideration for estimating concentrations of hydrocarbon radicals are listed in Table 2. It is mostly drawn from the skeletal mechanism of Glarborg et al.[7] The C_1 radicals needed in the reburning model are those belonging to the sequence $CH_3 \rightarrow CH_2(s) \rightarrow CH_2 \rightarrow CH \rightarrow C$. These radicals can all be assumed to be in steady state. The equations describing the steady-state approximations are mostly drawn from Glarborg et al.[7] The methyl radical, CH_3, is involved in reactions R5−R16 in Table 2. However, because the influence of reactions R11, R12, and R14 on CH_3 is minor, these steps are omitted from the steady-state approximation describing CH_3. Furthermore, the reverse of reaction R17 is neglected (Table 3). The set of equations to determine CH_3 then becomes (eq 1)

$$D_{CH_3} = k_{r,R5}[H_2] + k_{r,R7}[H_2O] + (k_{f,R8} + k_{f,R9})[O_2]$$
$$+ k_{f,R10}[H] + k_{f,R13}[O] + (k_{f,R15} + k_{f,R16})[OH] \quad (1)$$

$$[CH_3] = \frac{[CH_4](k_{f,R5}[H] + k_{f,R6}[O] + k_{f,R7}[OH])}{D_{CH_3}}$$

(30) Suuberg, E. M.; Peters, W. A.; Howard, J. B. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 37–46.
(31) Niksa, S.; Cho, S. *Energy Fuels* **1996**, *10*, 463–473.
(32) Neoh, K. G.; Gannon, R. E. *Fuel* **1984**, *63*, 1347–1352.

Table 2. Reactions Considered for Estimating Hydrocarbon Radical Concentrations[a]

number	reaction	A (cm, mol, s)	b	E (cal/mol)
R1	$C_2H_2 + O \rightarrow CH_2 + CO$	1.4×10^7	2.00	1900
R2	$C_2H_2 + O \rightarrow HCCO + H$	6.1×10^6	2.00	1900
R3	$HCCO + H \rightarrow CH_2(s) + CO$	1.5×10^{14}	0.00	0
R4	$HCCO + O_2 \rightarrow CO_2 + CO + H$	4.9×10^{12}	−0.142	1150
R5	$CH_4 + H \rightleftharpoons CH_3 + H_2$	4.1×10^3	3.156	8755
R6	$CH_4 + O \rightarrow CH_3 + OH$	4.4×10^5	2.50	6577
R7	$CH_4 + OH \rightleftharpoons CH_3 + H_2O$	1.0×10^6	2.182	2506
R8	$CH_3 + O_2 \rightarrow CH_3O + O$	7.5×10^{12}	0.00	28297
R9	$CH_3 + O_2 \rightarrow CH_2O + OH$	1.9×10^{11}	0.00	9842
R10	$CH_3 + H \rightarrow CH_4$	2.6×10^{28}	−5.10	−2630
R11	$CH_3 + H \rightleftharpoons CH_2 + H_2$	9.0×10^{13}	0.00	15100
R12	$CH_3 + H \rightleftharpoons CH_2(s) + H_2$	1.2×10^{17}	−0.80	16483
R13	$CH_3 + O \rightarrow CH_2O + H$	6.9×10^{13}	0.00	0
R14	$CH_3 + OH \rightleftharpoons CH_2 + H_2O$	1.1×10^3	3.00	2780
R15	$CH_3 + OH \rightleftharpoons CH_2(s) + H_2O$	6.9×10^{14}	−0.4884	0
R16	$CH_3 + OH \rightleftharpoons CH_2OH + H$	5.4×10^{10}	1.00	3554
R17	$CH_2 + H \rightarrow CH_3$	5.3×10^{24}	−3.90	829
R18	$CH_2 + H \rightleftharpoons CH + H_2$	1.2×10^{14}	0.00	0
R19	$CH_2 + O \rightarrow CO + H + H$	1.2×10^{14}	0.00	536
R20	$CH_2 + O \rightarrow CO + H_2$	8.0×10^{13}	0.00	536
R21	$CH_2 + OH \rightarrow CH_2O + H$	2.8×10^{13}	0.1228	−161
R22	$CH_2 + OH \rightleftharpoons CH + H_2O$	8.6×10^5	2.019	6776
R23	$CH_2 + O_2 \rightarrow CH_2O + O$	2.9×10^{11}	0.00	0
R24	$CH_2 + O_2 \rightarrow CO_2 + H_2$	1.5×10^{12}	0.00	0
R25	$CH_2 + CO_2 \rightarrow CO + CH_2O$	1.0×10^{11}	0.00	1000
R26	$CH_2(s) + M \rightleftharpoons CH_2 + M$	1.0×10^{13}	0.00	0
	third body enhancements: H_2 = 20, O_2 = 3.1, and H_2O = 3			
R27	$CH_2(s) + N_2 \rightleftharpoons CH_2 + N_2$	1.3×10^{13}	0.00	430
R28	$CH_2(s) + O_2 \rightarrow CO + OH + H$	3.1×10^{13}	0.00	0
R29	$CH_2(s) + CO_2 \rightarrow CH_2O + CO$	1.1×10^{13}	0.00	0
R30	$CH + H \rightleftharpoons C + H_2$	1.5×10^{14}	0.00	0
R31	$CH + O \rightarrow CO + H$	5.7×10^{13}	0.00	0
R32	$CH + OH \rightarrow HCO + H$	3.0×10^{13}	0.00	0
R33	$CH + OH \rightleftharpoons C + H_2O$	4.0×10^7	2.00	3000
R34	$CH + O_2 \rightarrow HCO + O$	3.3×10^{13}	0.00	0
R35	$CH + H_2O \rightarrow CH_2O + H$	5.7×10^{12}	0.00	−755
R36	$CH + CO_2 \rightarrow HCO + CO$	8.8×10^6	1.75	−1040
R37	$C + OH \rightarrow CO + H$	5.0×10^{13}	0.00	0
R38	$C + O_2 \rightarrow CO + O$	2.0×10^{13}	0.00	0

[a] Rate constant expressed as $k = AT^b \exp(-E/(RT))$.

Table 3. Reverse Reaction Rates for Reversible Reactions[a]

number	reaction	A (cm, mol, s)	b	E (cal/mol)
R5	$CH_4 + H \rightleftharpoons CH_3 + H_2$	1.30×10^{-1}	4	5540
R7	$CH_4 + OH \rightleftharpoons CH_3 + H_2O$	1.63×10^5	2.18	16429
R11	$CH_3 + H \rightleftharpoons CH_2 + H_2$	3.90×10^9	1	6930
R12	$CH_3 + H \rightleftharpoons CH_2(s) + H_2$	7.20×10^{13}	0	0
R14	$CH_3 + OH \rightleftharpoons CH_2 + H_2O$	3.18×10^1	3.4	11018
R15	$CH_3 + OH \rightleftharpoons CH_2(s) + H_2O$	2.42×10^{13}	0	−951
R16	$CH_3 + OH \rightleftharpoons CH_2OH + H$	1.80×10^{14}	0.16	111
R18	$CH_2 + H \rightleftharpoons CH + H_2$	8.42×10^{13}	0	2950
R22	$CH_2 + OH \rightleftharpoons CH + H_2O$	5.58×10^{13}	0	30420
R26	$CH_2(s) + M \rightleftharpoons CH_2 + M$	3.99×10^{12}	0	8919
	third body enhancements: H_2 = 20, O_2 = 3.1, and H_2O = 3			
R27	$CH_2(s) + N_2 \rightleftharpoons CH_2 + N_2$	4.90×10^{12}	0	9369
R30	$CH + H \rightleftharpoons C + H_2$	5.55×10^{14}	0	24065
R33	$CH + OH \rightleftharpoons C + H_2O$	6.62×10^8	2	41667

[a] Numbering is the same as in Table 2.

Here, k_f and k_r denote forward and reverse rate constants, respectively. The steady-state approximations for CH_2 and $CH_2(s)$ are solved simultaneously, because these radicals are linked through reactions R26 and R27. For simplification, reactions R18 and R22 are assumed to be irreversible in the determination of CH_2; the contribution from CH by the reverse reactions is expected to be small. The equations for CH_2

are as follows:

$$D_{CH_2} = k_{r,R11}[H_2] + k_{r,R14}[H_2O] + (k_{f,R17} + k_{f,R18})[H]$$
$$+ (k_{f,R19} + k_{f,R20})[O] + (k_{f,R21} + k_{f,R22})[OH]$$
$$+ (k_{f,R23} + k_{f,R24})[O_2] + k_{f,R25}[CO_2] + k_{r,R26}[M] + k_{r,R27}[N_2]$$

$$N_{1,CH_2} = \frac{k_{f,R1}[C_2H_2][O] + (k_{f,R11}[H] + k_{f,R14}[OH])[CH_3]}{D_{CH_2}}$$

$$N_{2,CH_2} = \frac{k_{f,R26}[M] + k_{f,R27}[N_2]}{D_{CH_2}}$$

$$[CH_2] = N_{1,CH_2} + N_{2,CH_2}[CH_2(s)]$$

$$(2)$$

The equations for $CH_2(s)$ are as follows:

$$D_{CH_2(s)} = k_{r,R12}[H_2] + k_{r,R15}[H_2O] + k_{f,R26}[M] + k_{f,R27}[N_2]$$
$$+ k_{f,R28}[O_2] + k_{f,R29}[CO_2]$$

$$N_{1,CH_2(s)} = \frac{k_{f,R3}[HCCO][H] + (k_{f,R12}[H] + k_{f,R15}[OH])[CH_3]}{D_{CH_2(s)}}$$

$$N_{2,CH_2(s)} = \frac{k_{r,R26}[M] + k_{r,R27}[N_2]}{D_{CH_2(s)}}$$

$$[CH_2(s)] = N_{1,CH_2(s)} + N_{2,CH_2(s)}[CH_2]$$

$$(3)$$

The concentration of CH_2 can, by simultaneously solving eqs 2 and 3, be calculated by eq 4.

$$[CH_2] = \frac{N_{1,CH_2} + N_{2,CH_2}N_{1,CH_2(s)}}{1 - N_{2,CH_2}N_{2,CH_2(s)}}$$

$$(4)$$

The concentrations of the radicals CH and C are also solved simultaneously because they are linked through reactions R30 and R33. The equation for determining the CH radical concentration is as follows:

$$D_{CH} = k_{r,R18}[H_2] + k_{r,R22}[H_2O] + k_{f,R30}[H] + k_{f,R31}[O]$$
$$+ (k_{f,R32} + k_{f,R33})[OH] + k_{f,R34}[O_2]$$
$$+ k_{f,R35}[H_2O] + k_{f,R36}[CO_2]$$

$$N_{1,CH} = \frac{[CH_2](k_{f,R18}[H] + k_{f,R22}[OH])}{D_{CH}}$$

$$(5)$$

$$N_{2,CH} = \frac{k_{r,R30}[H_2] + k_{r,R33}[H_2O]}{D_{CH}}$$

$$[CH] = N_{1,CH} + N_{2,CH}[C]$$

The C radical concentration is calculated by eq 6.

$$D_C = k_{r,R30}[H_2] + k_{r,R33}[H_2O] + k_{f,R37}[OH] + k_{f,R38}[O_2]$$

$$N_C = \frac{k_{f,R30}[H] + k_{f,R33}[OH]}{D_C}$$

$$[C] = N_C[CH]$$

$$(6)$$

(33) Vilas, E.; Skifter, U.; Jensen, A. D.; López, C.; Maier, J.; Glarborg, P. *Energy Fuels* **2004**, *18*, 1442–1450.

(34) Dagaut, P.; Glarborg, P.; Alzueta, M. U. *Prog. Energy Combust. Sci.* **2008**, *34*, 1–46.

(35) Tian, Z.; Li, Y.; Zhang, L.; Glarborg, P.; Qi, F. *Combust. Flame* **2009**, *156*, 1413–1426.

Table 4. Values for the Calculation of Q_3

fuel number	$\varepsilon = A_\varepsilon T + B_\varepsilon$	
	A_ε	B_ε
1	4.43×10^{-4}	-4.71×10^{-1}
2	4.78×10^{-4}	-4.74×10^{-1}
3	5.25×10^{-4}	-4.44×10^{-1}
4	6.49×10^{-5}	-7.09×10^{-2}

fuel number	$\kappa = A_\kappa T^2 + B_\kappa T + C_\kappa$		
	A_κ	B_κ	C_κ
1	-4.38×10^{-7}	1.77×10^{-3}	-1.96
2	-4.40×10^{-7}	1.79×10^{-3}	-1.20
3	-4.40×10^{-7}	1.80×10^{-3}	-2.01
4	-3.93×10^{-7}	1.71×10^{-3}	-1.95

When eqs 5 and 6 are solved simultaneously, the CH concentration can be determined by eq 7.

$$[CH] = \frac{N_{1,CH}}{1 - N_{2,CH}N_C}$$

$$(7)$$

The C_2 chemistry added in the present work to the scheme of Glarborg et al.[7] aims at estimating the concentration of HCCO, which is formed from C_2H_2. Inclusion of an analytically reduced submodel for the C_2 chemistry would complicate the model significantly. Instead, semi-empirical correlations, similar to those reported for the O/H radical pool,[27] were developed. These were based on reference calculations with the full mechanism, assuming isothermal plug-flow conditions and representing the fuel by the different volatile compositions given in Table 1. It was found that the formation and consumption of C_2H_2 during combustion show similarities to the profile predicted for CH_3. Accordingly, C_2H_2 may be described by eq 8.

$$[C_2H_2] = Q_3[CH_3]$$

$$(8)$$

Values of Q_3 were then determined from the peak concentrations of C_2H_2 and CH_3 predicted by the detailed mechanism for temperatures in the range of 1200–2000 K, inlet oxygen concentrations of 1–21 vol %, and values of λ in the range of 0.6–2.0. Various functional forms describing Q_3 as a function of combustion conditions were tested. The following simple correlation was found to be satisfactory for the three coals:

$$Q_3 = \frac{1}{\sqrt{\lambda}} \varepsilon(T)[O_2]_{in}^{\kappa(T)}$$

$$(9)$$

For biomass, where the volatiles were not assumed to contain C_2H_4 (Table 1), C_2 hydrocarbons are formed only through recombination of C_1 compounds. Here, the correlation is

$$Q_3 = \frac{1}{\lambda^2} \varepsilon(T)[O_2]_{in}^{\kappa(T)}$$

$$(10)$$

The constants, ε and κ, are functions of the temperature and, furthermore, dependent upon the coal type. These can be calculated according to the correlations in Table 4.

The prediction of HCCO is obtained by setting up a steady-state balance involving reactions R2–R4 in Table 2. The HCCO concentration is thus calculated by eq 11.

$$[HCCO] = \frac{k_{f,2}[O][C_2H_2]}{k_{f,3}[H] + k_{f,4}[O_2]}$$

$$(11)$$

2.2. N Chemistry Scheme. The scheme developed in this work describes reburn-type chemistry along with oxidation of NH_3 and HCN. The basis of the model is the scheme of Pedersen et al.,[8] which describes well the HCN and NH_3 oxidation chemistry.[27] The Pedersen scheme draws on reactions N1–N36 in Table 5. This scheme was then extended with eight

Table 5. Reactions Considered for Estimating the Nitrogen Chemistry[a]

number	reaction	A (cm, mol, s)	b	E (cal/mol)
N1	$CN + H_2 \rightleftharpoons HCN + H$	3.60×10^8	1.55	3000
N2	$HCN + O \rightarrow NCO + H$	1.40×10^4	2.64	4980
N3	$HCN + O \rightarrow NH + CO$	3.50×10^3	2.64	4980
N4	$CN + H_2O \rightleftharpoons HCN + OH$	8.00×10^{12}	0.00	7450
N5	$HCN + OH \rightleftharpoons HOCN + H$	5.90×10^4	2.40	12500
N6	$HOCN + H \rightarrow HNCO + H$	2.00×10^7	2.00	2000
N7	$HOCN + O \rightarrow NCO + OH$	1.50×10^4	2.64	4000
N8	$HOCN + OH \rightarrow NCO + H_2O$	6.40×10^5	2.00	2560
N9	$CN + OH \rightarrow NCO + H$	6.00×10^{13}	0.00	0
N10	$CN + O_2 \rightarrow NCO + O$	7.50×10^{12}	0.00	−389
N11	$HNCO + OH \rightleftharpoons NCO + H_2O$	6.40×10^5	2.00	2560
N12	$NCO + H_2 \rightleftharpoons HNCO + H$	7.60×10^2	3.00	4000
N13	$NCO + M \rightarrow N + CO + M$	3.10×10^{16}	−0.50	48000
	third body enhancement: $N_2 = 1.5$			
N14	$NCO + H \rightarrow CO + NH$	5.00×10^{13}	0.00	0
N15	$NCO + O \rightarrow NO + CO$	4.70×10^{13}	0.00	0
N16	$NCO + NO \rightarrow N_2 + CO_2$	1.40×10^{18}	−1.73	763
N17	$HNCO + M \rightarrow CO + NH$	1.10×10^{16}	0.00	86000
	third body enhancement: $N_2 = 1.5$			
N18	$HNCO + O_2 \rightarrow H + NO + CO_2$	1.00×10^{12}	0.00	35000
N19	$HNCO + H \rightarrow NH_2 + CO$	2.20×10^7	1.70	3800
N20	$HNCO + O \rightarrow NH + CO_2$	9.60×10^7	1.41	8520
N21	$NH_3 + M \rightleftharpoons NH_2 + H + M$	2.20×10^{16}	0.00	93470
N22	$NH_3 + OH \rightleftharpoons NH_2 + H_2O$	2.00×10^6	2.04	566
N23	$NH_3 + H \rightleftharpoons NH_2 + H_2$	6.40×10^5	2.39	10171
N24	$NH_2 + H \rightleftharpoons NH + H_2$	4.00×10^{13}	0.00	3650
N25	$NH_2 + OH \rightleftharpoons NH + H_2O$	4.00×10^6	2.00	1000
N26	$NH_2 + NO \rightarrow N_2 + H_2O$	1.30×10^{16}	−1.25	0
N27	$NH + O_2 \rightarrow H + NO + O$	4.60×10^5	2.00	6500
N28	$NH + O_2 \rightarrow NO + OH$	1.30×10^6	1.50	100
N29	$NH + H \rightarrow N + H_2$	3.00×10^{13}	0.00	0
N30	$NH + O \rightarrow NO + H$	9.20×10^{13}	0.00	0
N31	$NH + OH \rightarrow H + NO + H$	2.00×10^{13}	0.00	0
N32	$NH + OH \rightleftharpoons N + H_2O$	5.00×10^{11}	0.50	2000
N33	$NH + NO \rightarrow N_2 + O + H$	2.90×10^{14}	−0.40	0
N34	$N + OH \rightleftharpoons NO + H$	3.80×10^{13}	0.00	0
N35	$N + O_2 \rightleftharpoons NO + O$	6.40×10^9	1.00	6280
N36	$N + NO \rightleftharpoons N_2 + O$	3.30×10^{12}	0.30	0
N37	$CH + N_2 \rightarrow HCN + N$	3.70×10^7	1.42	20730
N38	$C + N_2 \rightarrow CN + N$	6.31×10^{13}	0.00	46000
N39	$CH_2 + NO \rightarrow NCO + H + H$	8.98×10^7	1.66	13910
N40	$CH_2(s) + NO \rightarrow HCN + OH$	2.00×10^{13}	0.00	0
N41	$CH + NO \rightarrow HCN + O$	7.90×10^{13}	0.00	0
N42	$C + NO \rightarrow CN + O$	2.00×10^{13}	0.00	0
N43	$C + NO \rightarrow N + CO$	2.80×10^{13}	0.00	0
N44	$N + CH_3 \rightarrow HCN + H + H$	2.40×10^8	1.50	−894
N45	$HCCO + NO \rightarrow HCNO + CO$	5.90×10^{12}	0.09	−457
N46	$HCNO \rightarrow HCN + O$	4.20×10^{31}	−6.12	61210
N47	$HCNO + H \rightarrow HCN + OH$	7.20×10^{10}	0.84	8612

[a] Rate constant expressed as $k = AT^b \exp(-E/(RT))$.

Table 6. Equilibrium Constants for Reversible Reactions[a]

number	reaction	A	b	$-E/R$
N1	$CN + H_2 \rightleftharpoons HCN + H$	1.2×10^{-4}	0.9545	10650
N4	$CN + H_2O \rightleftharpoons HCN + OH$	8.3×10^{-3}	0.6244	2599
N5	$HCN + OH \rightleftharpoons HOCN + H$	2.2×10^{-2}	0.1689	−3764
N11	$HNCO + OH \rightleftharpoons NCO + H_2O$	4.2×10^{-1}	-4.13×10^{-2}	3862
N12	$NCO + H_2 \rightleftharpoons HNCO + H$	3.4×10^{-2}	0.3713	4190
N21	$NH_3 + M \rightleftharpoons NH_2 + H + M$	1.6×10^6	0.2232	−55580
N22	$NH_3 + OH \rightleftharpoons NH_2 + H_2O$	9.6×10^1	−0.4878	4984
N23	$NH_3 + H \rightleftharpoons NH_2 + H_2$	6.8×10^3	−0.8179	−3068
N24	$NH_2 + H \rightleftharpoons NH + H_2$	3.4×10^1	−0.3772	5764
N25	$NH_2 + OH \rightleftharpoons NH + H_2O$	4.8×10^{-1}	-4.71×10^{-2}	13820
N29	$NH + H \rightleftharpoons N + H_2$	8.1×10^{-1}	−0.1602	12120
N32	$NH + OH \rightleftharpoons N + H_2O$	1.2×10^{-2}	0.1699	20170
N34	$N + OH \rightleftharpoons NO + H$	2.8×10^{-2}	0.3095	24580
N35	$N + O_2 \rightleftharpoons NO + O$	1.1×10^1	-9.64×10^{-2}	15930
N36	$N + NO \rightleftharpoons N_2 + O$	5.0×10^{-1}	-9.70×10^{-2}	37710

[a] Numbering is the same as in Table 5.

steps from Table 5.

$$r_{HCN} = w_1 - w_2 - w_3 + w_4 - w_5 + w_{37} + w_{40} + w_{41} + w_{44}$$
$$+ w_{46} + w_{47} \tag{12}$$

$$r_{NH_3} = -w_{21} - w_{22} - w_{23} \tag{13}$$

$$r_{NO} = w_{15} - w_{16} + w_{18} - w_{26} + w_{27} + w_{28} + w_{30} + w_{31} - w_{33}$$
$$+ w_{34} + w_{35} - w_{36} - w_{39} - w_{40} - w_{41} - w_{42} - w_{43} - w_{45} \tag{14}$$

$$r_{N_2} = w_{16} + w_{26} + w_{33} + w_{36} - w_{37} - w_{38} \tag{15}$$

The net rate of reaction, w_i, is for the reaction $A + B \rightleftharpoons C + D$ calculated as

$$w_i = k_i([A][B] - [C][D]/K_i) \tag{16}$$

Here, k_i and K_i are the forward rate constant and the equilibrium constant, respectively, for the ith reaction. The equilibrium constants are listed in Table 6. To solve the equations for the key nitrogen species, a number of steady-state equations must be solved for nitrogen radicals and intermediates. For HOCN and CN, we obtain

$$[HOCN] = \frac{k_{f,N5}[HCN][OH]}{k_{f,N5}/K_{N5}[H] + k_{f,N6}[H] + k_{f,N7}[O] + k_{f,N8}[OH]} \tag{17}$$

$$[CN] = (k_{f,N1}/K_{N1}[HCN][H] + k_{f,N4}/K_{N4}[HCN][OH]$$
$$+ k_{f,N38}[C][N_2] + k_{f,N42}[C][NO])/(k_{f,N1}[H_2] + k_{f,N4}[H_2O]$$
$$+ k_{f,N9}[OH] + k_{f,N10}[O_2]) \tag{18}$$

The equations for NCO and HNCO are solved simultaneously. The steady-state concentration for NCO is

$$D_{NCO} = k_{f,N11}/K_{N11}[H_2O] + k_{f,N12}[H_2] + k_{f,N13}[M] + k_{f,N14}[H]$$
$$+ k_{f,N15}[O] + k_{f,N16}[NO]$$

$$N_{1,NCO} = ([HOCN](k_{f,N7}[O] + k_{f,N8}[OH]) + [CN](k_{f,N9}[OH]$$
$$+ k_{f,N10}[O_2]) + k_{f,N2}[HCN][O] + k_{f,N39}[CH_2][NO])/D_{NCO}$$

$$N_{2,NCO} = (k_{f,N11}[OH] + k_{f,N12}/K_{N12}[H])/D_{NCO}$$

$$[NCO] = N_{1,NCO} + N_{2,NCO}[HNCO] \tag{19}$$

NO reduction reactions from the mechanism of Glarborg et al.[7] (reactions N37−N44 in Table 5).

For the reburn reactions (N37−N44), we have updated the rate constants according to the detailed mechanism by Mendiara and Glarborg.[20,23] For several of these steps, more accurate kinetic parameters have become available since the publication of the reduced mechanism of Glarborg et al.,[7] but the changes had only a small impact on modeling predictions.

In the present work, the three reactions N45−N47 were added to the mechanism. These steps describe the reduction of NO by the reaction with the HCCO radical and the subsequent conversion of the HCNO intermediate. Removal of NO by HCCO was found to be most important in combustion of coals, which release significant amounts of C_2 hydrocarbons with the volatiles.

The rates of production and consumption of the key nitrogen species are determined by the net rate of the reaction of selected

The steady-state concentration of HNCO is

$$D_{HNCO} = k_{f,N11}[OH] + k_{f,N12}/K_{N12}[H] + k_{f,N17}[M]$$
$$+ k_{f,N18}[O_2] + k_{f,N19}[H] + k_{f,N20}[O]$$

$$N_{1,HNCO} = k_{f,N6}[HOCN][H]/D_{HNCO} \qquad (20)$$

$$N_{2,HNCO} = (k_{f,N11}/K_{N11}[H_2O] + k_{f,N12}[H_2])/D_{HNCO}$$

$$[HNCO] = N_{1,HNCO} + N_{2,HNCO}[NCO]$$

By solving eqs 19 and 20 simultaneously

$$[NCO] = \frac{N_{1,NCO} + N_{2,NCO}N_{1,HNCO}}{1 - N_{2,NCO}N_{2,HNCO}} \qquad (21)$$

The steady-state concentration of HCNO is found from

$$[HCNO] = \frac{k_{f,N45}[HCCO][NO]}{k_{f,N46} + k_{f,N47}[H]} \qquad (22)$$

The equations for the species NH_2, NH, and N are also solved simultaneously. The steady-state concentration for NH_2 is

$$D_{NH_2} = k_{f,N21}/K_{N21}[H] + k_{f,N22}/K_{N22}[H_2O] + k_{f,N23}/K_{N23}[H_2]$$
$$+ k_{f,N24}[H] + k_{f,N25}[OH] + k_{f,N26}[NO]$$

$$N_{1,NH_2} = (k_{f,N19}[HNCO][H] + [NH_3](k_{f,N21}[M] + k_{f,N22}[OH]$$
$$+ k_{f,N23}[H])/D_{NH_2}$$

$$N_{2,NH_2} = (k_{f,N24}/K_{N24}[H_2] + k_{f,N25}/K_{N25}[H_2O])/D_{NH_2}$$

$$[NH_2] = N_{1,NH_2} + N_{2,NH_2}[NH] \qquad (23)$$

The steady-state concentration for NH is

$$D_{NH} = k_{f,N24}/K_{N24}[H_2] + k_{f,N25}/K_{N25}[H_2O]$$
$$+ (k_{f,N27} + k_{f,N28})[O_2] + k_{f,N29}[H] + k_{f,N30}[O]$$
$$+ (k_{f,N31} + k_{f,N32})[OH] + k_{f,N33}[NO]$$

$$N_{1,NH} = (k_{f,N3}[HCN][O] + k_{f,N14}[NCO][H]$$
$$+ [HNCO](k_{f,N17}[M] + k_{f,N20}[O])))/D_{NH} \qquad (24)$$

$$N_{2,NH} = (k_{f,N29}/K_{N29}[H_2] + k_{f,N32}/K_{N32}[H_2O])/D_{NH}$$

$$N_{3,NH} = (k_{f,N24}[H] + k_{f,N25}[OH])/D_{NH}$$

$$[NH] = N_{1,NH} + N_{2,NH}[N] + N_{3,NH}[NH_2]$$

Finally, the steady-state concentration of N is

$$D_N = k_{f,N29}/K_{N29}[H_2] + k_{f,N32}/K_{N32}[H_2O] + k_{f,N34}[OH]$$
$$+ k_{f,N35}[O_2] + k_{f,N36}[NO] + k_{f,N44}[CH_3]$$

$$N_{1,N} = (k_{f,N13}[NCO][M] + [NO](k_{f,N34}/K_{N34}[H]$$
$$+ k_{f,N35}/K_{N35}[O]) + k_{f,N36}/K_{N36}[N_2][O] + k_{f,N37}[CH][N_2]$$
$$+ k_{f,N38}[C][N_2] + k_{f,N43}[C][NO])/D_N$$

$$N_{2,N} = (k_{f,N29}[H] + k_{f,N32}[OH])/D_N$$

$$[N] = N_{1,N} + N_{2,N}[NH] \qquad (25)$$

Equations 23–25 are solved simultaneously.

$$[NH] = \frac{N_{1,NH} + N_{2,NH}N_{1,N} + N_{3,NH}N_{1,NH_2}}{1 - N_{2,NH}N_{2,N} - N_{3,NH}N_{2,NH_2}} \qquad (26)$$
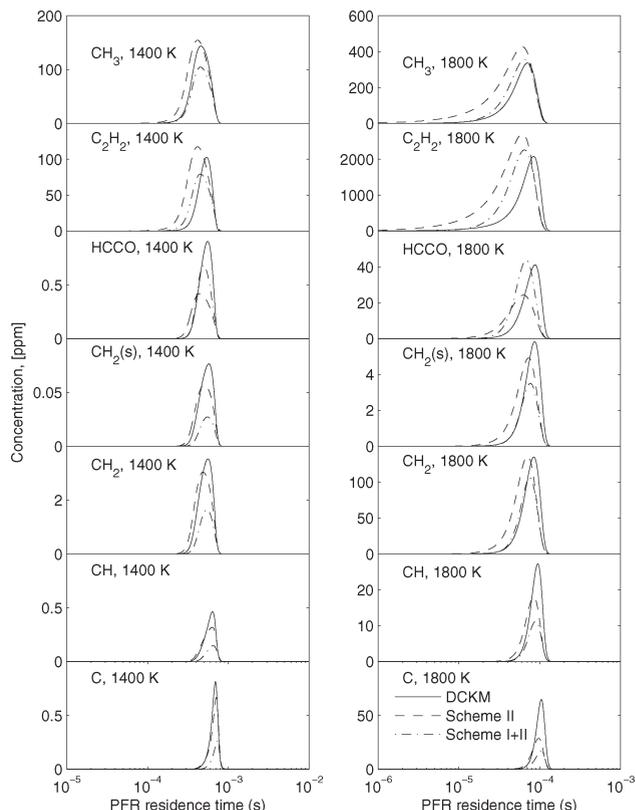

Figure 2. Radical concentrations during combustion of bituminous coal at two temperatures and reburning conditions. $\lambda = 0.8$, and O_2 inlet concentration = 1 vol %.

3. Results and Discussion

In the following, we define the schemes used in modeling as follows: DCKM, detailed chemical kinetics model;[20,23] I, prediction of H, O, and OH from the semi-empirical correlations of ref 27; II, prediction of hydrocarbon radicals from eqs 1–11; and III, prediction of the nitrogen chemistry from eqs 12–26.

Figures 2 and 3 show predictions of hydrocarbon radical concentrations during combustion of bituminous coal and biomass, respectively. The figures compare modeling predictions from three levels of calculations: with DCKM, with scheme II and DCKM (the O/H radical pool, as well as CH_4, O_2, CO_2, H_2O, H_2, and N_2, from the detailed mechanism), and with schemes I, II, and DCKM (CH_4, O_2, CO_2, H_2O, H_2, and N_2 from the detailed model). The results show that the peak hydrocarbon radical concentrations are mostly predicted within a factor of 2 compared to the reference calculations. In general, the accuracy is better at higher temperatures and not too fuel-rich conditions ($\lambda \geq 0.6$). Also, radicals, such as CH_3 and HCCO, formed directly from stable species are predicted more accurately than radicals, such as CH and C, estimated from a sequence of steady-state approximations. Bituminous coal and biomass represent extremes in terms of volatile composition and rank (Table 1). Still, the deviations from the reference calculations are similar for the two fuels.

The results indicate that the approximations in the simplified hydrocarbon radical scheme are satisfactory. However, when this scheme is combined with the semi-empirical correlations for the O/H radicals, the modeling predictions become less accurate.
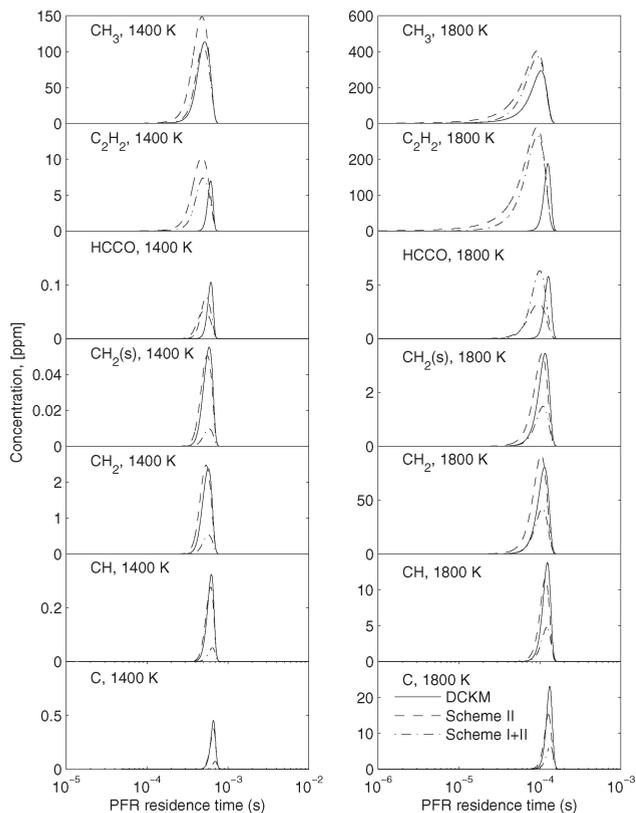
Figure 3. Radical concentrations during combustion of biomass at two temperatures and reburning conditions. $\lambda = 0.8$, and O_2 inlet concentration = 1 vol %.

The empirical equations developed to describe the formation and consumption of the hydrocarbon (scheme II) and O/H radical pool (scheme I) are combined with the reduced scheme for reactive nitrogen conversion established in this work (scheme III) to yield a model for volatile nitrogen reburning in solid fuel combustion. The following figures compare modeling predictions from three levels of calculations: with DCKM, with scheme III and DCKM (all radicals as well as CH_4, O_2, CO_2, H_2O, and H_2 from the detailed mechanism), and with schemes I−III and DCKM (CH_4, O_2, CO_2, H_2O, and H_2 from the detailed model).

Figures 4 and 5 show results for reburning with volatiles from biomass and bituminous coal, respectively, as a function of stoichiometry ($0.6 \leq \lambda \leq 1.0$) and temperature (1400−1800 K). Under the conditions investigated, the reduction in NO is modest. It increases as the stoichiometry becomes more fuel-rich, while the temperature has only a small impact. The combined simplified model (I + II + III) provides a satisfactory estimate of the NO concentration for both fuels.

Figure 6 compares predictions with the simplied model to reference calculations with the full mechanism for all four fuels at the two temperatures and $\lambda = 0.6$. Again, there is good agreement between the full mechanism and the simplified schemes. The calculations indicate that the major hydrocarbon radicals, CH_3 and HCCO, are responsible for most of the reduction in NO. For this reason, the shortcomings in predicting the concentrations of the smaller hydrocarbon radicals (Figures 2 and 3) do not significantly deteriorate modeling predictions.

3.1. Practical Application. It is most efficient in terms of computational efforts to conduct the calculations on the
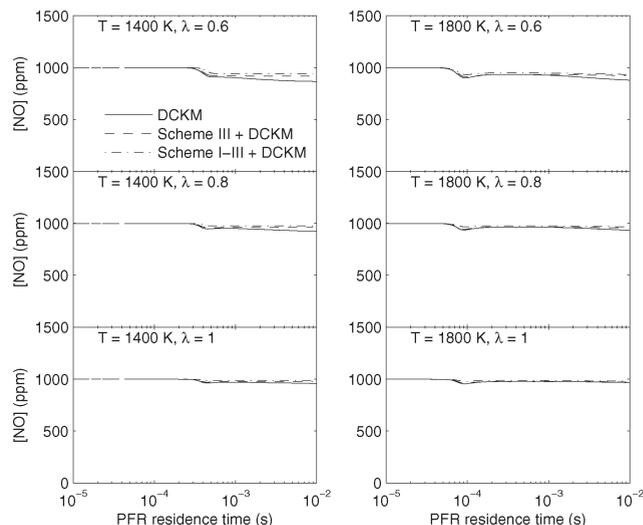

Figure 4. Predictions of NO reburning with biomass volatiles in N_2/O_2 mixtures with 1000 ppm NO and 1 vol % O_2 in the inlet. The calculations are conducted under isothermal conditions. The figure compares modeling predictions from three levels of calculations: with DCKM, with scheme III and DCKM, and with schemes I−III and DCKM.
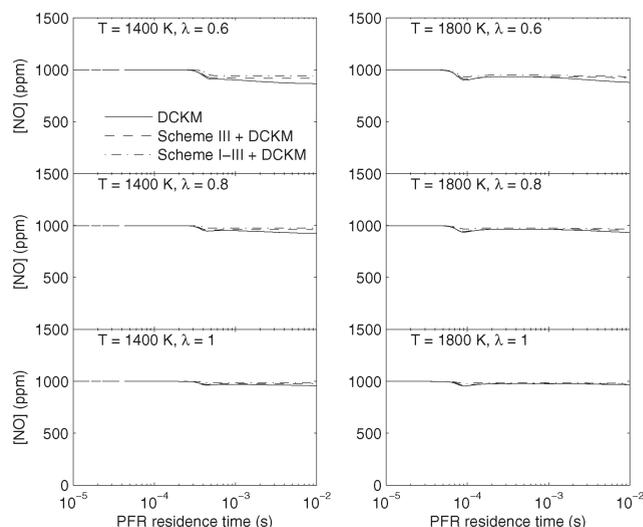

Figure 5. Predictions of NO reburning with bituminous coal volatiles in N_2/O_2 mixtures with 1000 ppm NO and 1 vol % O_2 in the inlet. The calculations are conducted under isothermal conditions. The figure compares modeling predictions from three levels of calculations: with DCKM, with scheme III and DCKM, and with schemes I−III and DCKM.

nitrogen chemistry as either post-processing or activated in a final iteration upon convergence of the main scalars.[2,27] These approaches imply that the nitrogen chemistry does not affect the overall flow pattern and temperature. Even though trace species including NO have been reported to affect emissions and combustion rates,[36] the assumption is justifiable because only a small fraction of the overall gas flow is involved in the active nitrogen chemistry.

To facilitate the practical implementation of the NO_x model, i.e., schemes I (the O/H radical model[27]), II (the hydrocarbon

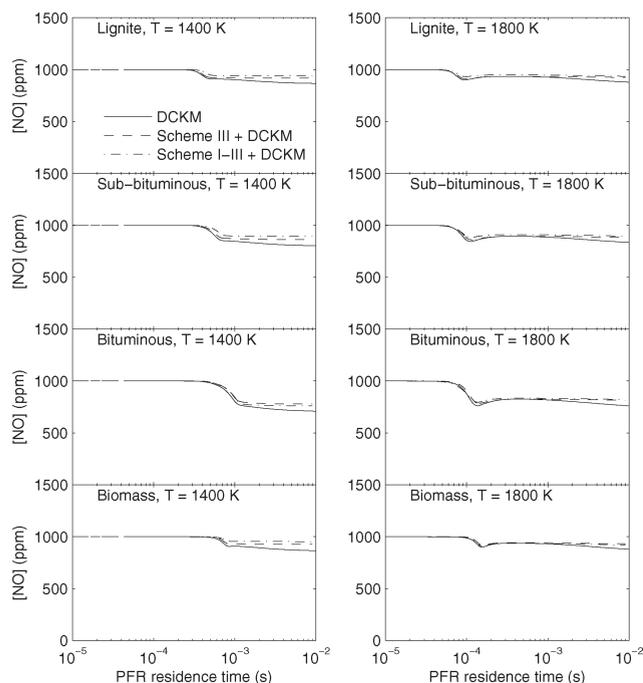(36) Glarborg, P. *Proc. Combust. Inst.* **2007**, *31*, 77–98.

Figure 6. Predictions of NO reburning in the N_2/O_2 mixture with 1000 ppm NO and 1 vol % O_2 in the inlet and $\lambda = 0.6$. The calculations are conducted under isothermal conditions. The figure compares modeling predictions from three levels of calculations: with DCKM, with scheme III and DCKM, and with schemes I−III and DCKM.

radical model), and III (the N scheme), we discuss below the implications for the main calculation and the post-processing. Matlab scripts for the NO_x model are included as Supporting Information.

3.1.1. Main Combustion Calculation. The main calculation establishes the flow field, the temperature field, and the major species concentrations. The main issue for the present purpose is the choice of models for pyrolysis and volatile oxidation. Dependent upon the complexity of the volatile oxidation model, the major species may comprise just a single volatile component, together with final products CO_2 and H_2O, or a more complete set of fuel components, intermediates, and products. The use of a simple one- or two-step volatile oxidation model is compatible with the NO_x model, as described below. However, while this approach will save computational resources, it could also be expected to yield less accurate modeling predictions compared to using a more advanced pyrolysis/volatile oxidation model. If a more complex model is chosen for pyrolysis and volatile oxidation, it is important that it is compatible with the NO_x model in terms of composition of the volatiles. This issue is discussed in detail below.

3.1.2. Nitrogen Chemistry Calculation. The calculations of the nitrogen chemistry can be conducted in a post-processing step. The main calculation provides information on flow field, temperature field, and major species concentrations. However, the time-dependent concentration profiles of O_2, H_2, and H_2O for each cell, required as input for schemes I−III, are not available from the main calculation. For this reason, the post-processing calculations must combine a volatile oxidation model with the radical schemes (I and II) and the N oxidation model (III).

The fitting parameters in the functional form chosen for the radical schemes are fuel-specific, in both I and II. The

volatile composition entering the post-processing calculation should be consistent with the data for one of the fuels listed in Table 1.[27] The data in the table are categorized according to fuel rank (bituminous coal, sub-bituminous coal, lignite, and biomass) and cover most solid fuels of importance. The correlations for the four fuels developed in this work may be applicable to other fuels within the same rank, because minor variations in volatile composition will only have a small impact on modeling predictions. If the pyrolysis model used in the main calculation provides only a simplified volatile composition, the split between the chosen fuel components (hydrocarbons, H_2, and CO) needed for the post-processing computations must be estimated algebraically.

The volatile model must describe the oxidation of the fuel elements, i.e., hydrocarbons, hydrogen, and carbon monoxide. The estimated concentrations of O_2, H_2, and H_2O for each time step are then used as input to schemes I−III. The choice of the volatile oxidation model will affect the computational effort as well as the expected accuracy.[27,37] The model could be a collection of global reactions, i.e., a single oxidation reaction for each fuel component in the volatiles. Rate constants for global oxidation steps are available for a range of fuel components[24,38,39] and may be readily available in the chosen CFD software. Even in a combination with a set of global reactions for volatile oxidation, the present model (schemes I−III) offers an improved prediction of the nitrogen chemistry compared to CFD standard models. For a more accurate prediction, the Jones and Lindstedt global four-step combustion mechanism[25] can be implemented. Four-step mechanisms are offered for several hydrocarbon fuels and also involve steps for oxidation of H_2 and CO.

4. Conclusion

In the present work, an analytically reduced nitrogen scheme was combined with simplified correlations for estimation of O/H and hydrocarbon radicals. This way, the predictive capability of the analytically reduced models is combined with the robustness and speed of more simplified schemes. Correlations were derived for volatile compositions representative of solid fuels ranging from bituminous coal to biomass, for temperatures of 1200−2000 K and excess air ratios in the range of $0.6 \leq \lambda \leq 2.0$. The combined model is tested against reference calculations with a comprehensive mechanism. The results indicate that the approximations in the simplified hydrocarbon radical scheme are satisfactory. However, when this scheme is combined with the semi-empirical correlations for the O/H radicals, the modeling predictions for the radicals become less accurate. Despite these deviations, the combined model provides a satisfactory prediction of NO under reburning conditions over the range of fuels, temperatures, and stoichiometries tested.

Supporting Information Available: Matlab scripts for the NO_x model. This material is available free of charge via the Internet at http://pubs.acs.org.

(37) Andersen, J.; Rasmussen, C. L.; Giselsson, T.; Glarborg, P. *Energy Fuels* **2009**, *23*, 1379–1389.
(38) Hautman, D. J.; Dryer, F. L.; Schug, K. P.; Glassman, I. *Combust. Sci. Technol.* **1981**, *25*, 219–235.
(39) Babushok, V. I.; Dakdancha, A. N. *Combust., Explos. Shock Waves* **1993**, *29*, 464–489.