

Technical University of Denmark



## Simplified Model for Reburning Chemistry

**Glarborg, Peter; Hansen, Stine Broholm**

*Published in:*  
Energy & Fuels

*Link to article, DOI:*  
[10.1021/ef100469h](https://doi.org/10.1021/ef100469h)

*Publication date:*  
2010

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Glarborg, P., & Hansen, S. (2010). Simplified Model for Reburning Chemistry. *Energy & Fuels*, 24(8), 4185-4192. DOI: 10.1021/ef100469h

## DTU Library

Technical Information Center of Denmark

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

## Simplified Model for Reburning Chemistry

Stine Hansen and Peter Glarborg\*

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

Received April 14, 2010. Revised Manuscript Received July 6, 2010

In solid fuel flames, reburn-type reactions are often important for the concentrations of  $\text{NO}_x$  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 ( $\text{NO}_x$ ), 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,<sup>1,2</sup> 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<sup>3–6</sup> and analytically reduced schemes.<sup>7,8</sup> 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,<sup>9</sup> sets based on partial equilibrium approaches,<sup>10–13</sup> and analytically reduced schemes.<sup>7,14–16</sup>

Two different simplified schemes for NO reduction by reburning reactions are employed in the commercial CFD code Fluent.<sup>17</sup> Both schemes, termed the instantaneous approach and the partial equilibrium approach, respectively, describe the reduction of NO by the reaction with the  $\text{C}_1$  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  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$ ; their concentrations are drawn from calculations with a detailed combustion mechanism. The partial equilibrium approach is based on the work by Dimitriou et al.<sup>11</sup> Here, the principal pathways of NO reduction are assumed to involve the reaction with the radicals  $\text{CH}_2$ ,  $\text{CH}$ , and  $\text{C}$ . The concentration of these radicals are found by assuming the following reactions to be in partial equilibrium:  $\text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2$ ,  $\text{CH}_3 + \text{OH} \rightleftharpoons$

\*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.

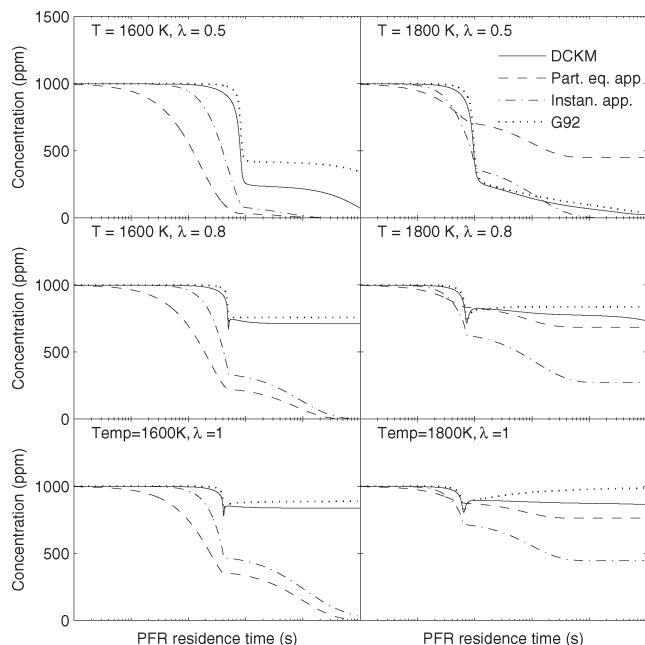
(13) Su, S.; Xiang, J.; Sun, L.; Zhang, Z.; Sun, X.; Zheng, C. *Proc. Combust. Inst.* **2007**, *31*, 2795–2803.

(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<sub>4</sub> in the N<sub>2</sub>/O<sub>2</sub> mixture with 1 vol % O<sub>2</sub> under isothermal plug-flow reactor conditions.

CH<sub>2</sub> + H<sub>2</sub>O, CH<sub>2</sub> + H ⇌ CH + H<sub>2</sub>, and CH + H ⇌ C + H<sub>2</sub>. The omission of reactions between CH<sub>3</sub> 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.<sup>18–20</sup> It is also noteworthy that neither of the Fluent schemes involves the HCCO radical, which even for combustion of CH<sub>4</sub> is predicted to be important for NO removal.<sup>18–20</sup>

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.<sup>7</sup> (denoted G92), and the recent detailed chemical kinetic model by Mendiara and Glarborg<sup>20,23</sup> (denoted DCKM). These calculations, as well as those shown below, were conducted using Chemkin<sup>21,22</sup> 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<sub>2</sub>/O<sub>2</sub> mixture with 1 vol % O<sub>2</sub> at selected excess air ratios ( $\lambda$ ) and temperatures. To exclude differences in the selected mechanisms caused by anything other than the nitrogen chemistry descriptions, other species concentrations (O<sub>2</sub>, H<sub>2</sub>, radicals, etc.) are drawn from the detailed mechanism.

The results of Figure 1 show that the schemes employed by Fluent<sup>17</sup> 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.<sup>15,16</sup> 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<sup>24</sup> or the four-step mechanism by Jones and Lindstedt,<sup>25</sup> offer estimates of the fuel oxidation rate and concentrations of intermediates, such as CO,<sup>26</sup> but they are unable to predict radical levels.

Recently,<sup>27</sup> we developed a simple approach for estimating O/H radical concentrations and combined it with the analytically reduced N scheme by Pedersen et al.<sup>8</sup> 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,<sup>28,29</sup> 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.<sup>27</sup> Scheme II combines an analytically reduced scheme for C<sub>1</sub> radicals<sup>7</sup> with semi-empirical correlations for C<sub>2</sub> radicals (present work). Finally, the NO<sub>x</sub> model (scheme III) is a combined scheme describing volatile N oxidation with HCN and NH<sub>3</sub> 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.<sup>8</sup> and Glarborg et al.<sup>7</sup> 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<sup>27</sup>**

fuel number <sup>b</sup>	composition (vol %) <sup>a</sup>			
	1	2	3	4
H <sub>2</sub> O	16.5	12.5	5.0	1.7
CO	12.3	8.5	6.9	38.2
CO <sub>2</sub>	5.0	3.2	1.2	9.1
H <sub>2</sub>	46.7	39.1	37.5	41.4
CH <sub>4</sub>	3.4	4.6	6.9	9.6
C <sub>2</sub> H <sub>4</sub>	1.1	1.6	2.9	
soot <sup>c</sup>	14.9	30.5	39.7	0

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

recent work<sup>27</sup> to provide a good description of the oxidation chemistry of HCN and NH<sub>3</sub>, but it does not involve hydrocarbon/nitrogen interactions. The scheme of Glarborg et al. provides a satisfactory description of C<sub>1</sub>/NO interactions (Figure 1) but excludes reactions of NH<sub>3</sub>.

Similar to the work by Han et al.,<sup>15</sup> 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.<sup>27</sup> 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.<sup>20,23</sup> Subsets of the full mechanism have been evaluated against a range of experimental data for oxidation of HCN<sup>34</sup> and NH<sub>3</sub><sup>19,23,35</sup> and for reduction of NO.<sup>20</sup> 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.<sup>7</sup> The C<sub>1</sub> radicals needed in the reburning model are those belonging to the sequence CH<sub>3</sub> → CH<sub>2</sub>(s) → CH<sub>2</sub> → CH → 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.<sup>7</sup> The methyl radical, CH<sub>3</sub>, is involved in reactions R5–R16 in Table 2. However, because the influence of reactions R11, R12, and R14 on CH<sub>3</sub> is minor, these steps are omitted from the steady-state approximation describing CH<sub>3</sub>. Furthermore, the reverse of reaction R17 is neglected (Table 3). The set of equations to determine CH<sub>3</sub> then becomes (eq 1)

$$\begin{aligned}
 D_{\text{CH}_3} &= k_{\text{r},\text{R5}}[\text{H}_2] + k_{\text{r},\text{R7}}[\text{H}_2\text{O}] + (k_{\text{f},\text{R8}} + k_{\text{f},\text{R9}})[\text{O}_2] \\
 &+ k_{\text{f},\text{R10}}[\text{H}] + k_{\text{f},\text{R13}}[\text{O}] + (k_{\text{f},\text{R15}} + k_{\text{f},\text{R16}})[\text{OH}] \\
 [\text{CH}_3] &= \frac{[\text{CH}_4](k_{\text{f},\text{R5}}[\text{H}] + k_{\text{f},\text{R6}}[\text{O}] + k_{\text{f},\text{R7}}[\text{OH}])}{D_{\text{CH}_3}}
 \end{aligned} \quad (1)$$

(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<sup>a</sup>**

number	reaction	A (cm, mol, s)	b	E (cal/mol)
R1	C <sub>2</sub> H <sub>2</sub> + O → CH <sub>2</sub> + CO	1.4 × 10 <sup>7</sup>	2.00	1900
R2	C <sub>2</sub> H <sub>2</sub> + O → HCCO + H	6.1 × 10 <sup>6</sup>	2.00	1900
R3	HCCO + H → CH <sub>2</sub> (s) + CO	1.5 × 10 <sup>14</sup>	0.00	0
R4	HCCO + O <sub>2</sub> → CO <sub>2</sub> + CO + H	4.9 × 10 <sup>12</sup>	−0.142	1150
R5	CH <sub>4</sub> + H ⇌ CH <sub>3</sub> + H <sub>2</sub>	4.1 × 10 <sup>3</sup>	3.156	8755
R6	CH <sub>4</sub> + O → CH <sub>3</sub> + OH	4.4 × 10 <sup>5</sup>	2.50	6577
R7	CH <sub>4</sub> + OH ⇌ CH <sub>3</sub> + H <sub>2</sub> O	1.0 × 10 <sup>6</sup>	2.182	2506
R8	CH <sub>3</sub> + O <sub>2</sub> → CH <sub>3</sub> O + O	7.5 × 10 <sup>12</sup>	0.00	28297
R9	CH <sub>3</sub> + O <sub>2</sub> → CH <sub>2</sub> O + OH	1.9 × 10 <sup>11</sup>	0.00	9842
R10	CH <sub>3</sub> + H → CH <sub>4</sub>	2.6 × 10 <sup>28</sup>	−5.10	−2630
R11	CH <sub>3</sub> + H ⇌ CH <sub>2</sub> + H <sub>2</sub>	9.0 × 10 <sup>13</sup>	0.00	15100
R12	CH <sub>3</sub> + H ⇌ CH <sub>2</sub> (s) + H <sub>2</sub>	1.2 × 10 <sup>17</sup>	−0.80	16483
R13	CH <sub>3</sub> + O → CH <sub>2</sub> O + H	6.9 × 10 <sup>13</sup>	0.00	0
R14	CH <sub>3</sub> + OH ⇌ CH <sub>2</sub> + H <sub>2</sub> O	1.1 × 10 <sup>3</sup>	3.00	2780
R15	CH <sub>3</sub> + OH ⇌ CH <sub>2</sub> (s) + H <sub>2</sub> O	6.9 × 10 <sup>14</sup>	−0.4884	0
R16	CH <sub>3</sub> + OHC ⇌ H <sub>2</sub> OH + H	5.4 × 10 <sup>10</sup>	1.00	3554
R17	CH <sub>2</sub> + H → CH <sub>3</sub>	5.3 × 10 <sup>24</sup>	−3.90	829
R18	CH <sub>2</sub> + H ⇌ CH + H <sub>2</sub>	1.2 × 10 <sup>14</sup>	0.00	0
R19	CH <sub>2</sub> + O → CO + H + H	1.2 × 10 <sup>14</sup>	0.00	536
R20	CH <sub>2</sub> + O → CO + H <sub>2</sub>	8.0 × 10 <sup>13</sup>	0.00	536
R21	CH <sub>2</sub> + OH → CH <sub>2</sub> O + H	2.8 × 10 <sup>13</sup>	0.1228	−161
R22	CH <sub>2</sub> + OH ⇌ CH + H <sub>2</sub> O	8.6 × 10 <sup>5</sup>	2.019	6776
R23	CH <sub>2</sub> + O <sub>2</sub> → CH <sub>2</sub> O + O	2.9 × 10 <sup>11</sup>	0.00	0
R24	CH <sub>2</sub> + O <sub>2</sub> → CO <sub>2</sub> + H <sub>2</sub>	1.5 × 10 <sup>12</sup>	0.00	0
R25	CH <sub>2</sub> + CO <sub>2</sub> → CO + CH <sub>2</sub> O	1.0 × 10 <sup>11</sup>	0.00	1000
R26	CH <sub>2</sub> (s) + M ⇌ CH <sub>2</sub> + M	1.0 × 10 <sup>13</sup>	0.00	0
third body enhancements: H <sub>2</sub> = 20, O <sub>2</sub> = 3.1, and H <sub>2</sub> O = 3				
R27	CH <sub>2</sub> (s) + N <sub>2</sub> ⇌ CH <sub>2</sub> + N <sub>2</sub>	1.3 × 10 <sup>13</sup>	0.00	430
R28	CH <sub>2</sub> (s) + O <sub>2</sub> → CO + OH + H	3.1 × 10 <sup>13</sup>	0.00	0
R29	CH <sub>2</sub> (s) + CO <sub>2</sub> → CH <sub>2</sub> O + CO	1.1 × 10 <sup>13</sup>	0.00	0
R30	CH + H ⇌ C + H <sub>2</sub>	1.5 × 10 <sup>14</sup>	0.00	0
R31	CH + O → CO + H	5.7 × 10 <sup>13</sup>	0.00	0
R32	CH + OH → HCO + H	3.0 × 10 <sup>13</sup>	0.00	0
R33	CH + OH ⇌ C + H <sub>2</sub> O	4.0 × 10 <sup>7</sup>	2.00	3000
R34	CH + O <sub>2</sub> → HCO + O	3.3 × 10 <sup>13</sup>	0.00	0
R35	CH + H <sub>2</sub> O → CH <sub>2</sub> O + H	5.7 × 10 <sup>12</sup>	0.00	−755
R36	CH + CO <sub>2</sub> → HCO + CO	8.8 × 10 <sup>6</sup>	1.75	−1040
R37	C + OH → CO + H	5.0 × 10 <sup>13</sup>	0.00	0
R38	C + O <sub>2</sub> → CO + O	2.0 × 10 <sup>13</sup>	0.00	0

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

**Table 3. Reverse Reaction Rates for Reversible Reactions<sup>a</sup>**

number	reaction	A (cm, mol, s)	b	E (cal/mol)
R5	CH <sub>4</sub> + H ⇌ CH <sub>3</sub> + H <sub>2</sub>	1.30 × 10 <sup>−1</sup>	4	5540
R7	CH <sub>4</sub> + OH ⇌ CH <sub>3</sub> + H <sub>2</sub> O	1.63 × 10 <sup>5</sup>	2.18	16429
R11	CH <sub>3</sub> + H ⇌ CH <sub>2</sub> + H <sub>2</sub>	3.90 × 10 <sup>9</sup>	1	6930
R12	CH <sub>3</sub> + H ⇌ CH <sub>2</sub> (s) + H <sub>2</sub>	7.20 × 10 <sup>13</sup>	0	0
R14	CH <sub>3</sub> + OH ⇌ CH <sub>2</sub> + H <sub>2</sub> O	3.18 × 10 <sup>1</sup>	3.4	11018
R15	CH <sub>3</sub> + OH ⇌ CH <sub>2</sub> (s) + H <sub>2</sub> O	2.42 × 10 <sup>13</sup>	0	−951
R16	CH <sub>3</sub> + OH ⇌ CH <sub>2</sub> OH + H	1.80 × 10 <sup>14</sup>	0.16	111
R18	CH <sub>2</sub> + H ⇌ CH + H <sub>2</sub>	8.42 × 10 <sup>13</sup>	0	2950
R22	CH <sub>2</sub> + OHCH + H <sub>2</sub> O	5.58 × 10 <sup>13</sup>	0	30420
R26	CH <sub>2</sub> (s) + M ⇌ CH <sub>2</sub> + M	3.99 × 10 <sup>12</sup>	0	8919
third body enhancements: H <sub>2</sub> = 20, O <sub>2</sub> = 3.1, and H <sub>2</sub> O = 3				
R27	CH <sub>2</sub> (s) + N <sub>2</sub> ⇌ CH <sub>2</sub> + N <sub>2</sub>	4.90 × 10 <sup>12</sup>	0	9369
R30	CH + H ⇌ C + H <sub>2</sub>	5.55 × 10 <sup>14</sup>	0	24065
R33	CH + OH ⇌ C + H <sub>2</sub> O	6.62 × 10 <sup>8</sup>	2	41667

<sup>a</sup>Numbering is the same as in Table 2.

Here,  $k_{\text{f}}$  and  $k_{\text{r}}$  denote forward and reverse rate constants, respectively. The steady-state approximations for CH<sub>2</sub> and CH<sub>2</sub>(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<sub>2</sub>; the contribution from CH by the reverse reactions is expected to be small. The equations for CH<sub>2</sub>

are as follows:

$$\begin{aligned}
 D_{\text{CH}_2} &= k_{f, R11}[\text{H}_2] + k_{f, R14}[\text{H}_2\text{O}] + (k_{f, R17} + k_{f, R18})[\text{H}] \\
 &\quad + (k_{f, R19} + k_{f, R20})[\text{O}] + (k_{f, R21} + k_{f, R22})[\text{OH}] \\
 &\quad + (k_{f, R23} + k_{f, R24})[\text{O}_2] + k_{f, R25}[\text{CO}_2] + k_{f, R26}[\text{M}] + k_{f, R27}[\text{N}_2] \\
 N_{1, \text{CH}_2} &= \frac{k_{f, R1}[\text{C}_2\text{H}_2][\text{O}] + (k_{f, R11}[\text{H}] + k_{f, R14}[\text{OH}])(\text{CH}_3)}{D_{\text{CH}_2}} \\
 N_{2, \text{CH}_2} &= \frac{k_{f, R26}[\text{M}] + k_{f, R27}[\text{N}_2]}{D_{\text{CH}_2}} \\
 [\text{CH}_2] &= N_{1, \text{CH}_2} + N_{2, \text{CH}_2}[\text{CH}_2(\text{s})]
 \end{aligned} \quad (2)$$

The equations for  $\text{CH}_2(\text{s})$  are as follows:

$$\begin{aligned}
 D_{\text{CH}_2(\text{s})} &= k_{f, R12}[\text{H}_2] + k_{f, R15}[\text{H}_2\text{O}] + k_{f, R26}[\text{M}] + k_{f, R27}[\text{N}_2] \\
 &\quad + k_{f, R28}[\text{O}_2] + k_{f, R29}[\text{CO}_2] \\
 N_{1, \text{CH}_2(\text{s})} &= \frac{k_{f, R3}[\text{HCCO}][\text{H}] + (k_{f, R12}[\text{H}] + k_{f, R15}[\text{OH}])(\text{CH}_3)}{D_{\text{CH}_2(\text{s})}} \\
 N_{2, \text{CH}_2(\text{s})} &= \frac{k_{f, R26}[\text{M}] + k_{f, R27}[\text{N}_2]}{D_{\text{CH}_2(\text{s})}} \\
 [\text{CH}_2(\text{s})] &= N_{1, \text{CH}_2(\text{s})} + N_{2, \text{CH}_2(\text{s})}[\text{CH}_2]
 \end{aligned} \quad (3)$$

The concentration of  $\text{CH}_2$  can, by simultaneously solving eqs 2 and 3, be calculated by eq 4.

$$[\text{CH}_2] = \frac{N_{1, \text{CH}_2} + N_{2, \text{CH}_2} N_{1, \text{CH}_2(\text{s})}}{1 - N_{2, \text{CH}_2} N_{2, \text{CH}_2(\text{s})}} \quad (4)$$

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:

$$\begin{aligned}
 D_{\text{CH}} &= k_{f, R18}[\text{H}_2] + k_{f, R22}[\text{H}_2\text{O}] + k_{f, R30}[\text{H}] + k_{f, R31}[\text{O}] \\
 &\quad + (k_{f, R32} + k_{f, R33})[\text{OH}] + k_{f, R34}[\text{O}_2] \\
 &\quad + k_{f, R35}[\text{H}_2\text{O}] + k_{f, R36}[\text{CO}_2] \\
 N_{1, \text{CH}} &= \frac{[\text{CH}_2](k_{f, R18}[\text{H}] + k_{f, R22}[\text{OH}])}{D_{\text{CH}}} \\
 N_{2, \text{CH}} &= \frac{k_{f, R30}[\text{H}_2] + k_{f, R33}[\text{H}_2\text{O}]}{D_{\text{CH}}} \\
 [\text{CH}] &= N_{1, \text{CH}} + N_{2, \text{CH}}[\text{C}]
 \end{aligned} \quad (5)$$

The C radical concentration is calculated by eq 6.

$$\begin{aligned}
 D_{\text{C}} &= k_{f, R30}[\text{H}_2] + k_{f, R33}[\text{H}_2\text{O}] + k_{f, R37}[\text{OH}] + k_{f, R38}[\text{O}_2] \\
 N_{\text{C}} &= \frac{k_{f, R30}[\text{H}] + k_{f, R33}[\text{OH}]}{D_{\text{C}}} \\
 [\text{C}] &= N_{\text{C}}[\text{CH}]
 \end{aligned} \quad (6)$$

(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	$\varepsilon = A_\varepsilon T + B_\varepsilon$		
	$A_\varepsilon$	$B_\varepsilon$	
1	$4.43 \times 10^{-4}$	$-4.71 \times 10^{-1}$	
2	$4.78 \times 10^{-4}$	$-4.74 \times 10^{-1}$	
3	$5.25 \times 10^{-4}$	$-4.44 \times 10^{-1}$	
4	$6.49 \times 10^{-5}$	$-7.09 \times 10^{-2}$	
fuel number	$\kappa = A_\kappa T^2 + B_\kappa T + C_\kappa$		
	$A_\kappa$	$B_\kappa$	$C_\kappa$
1	$-4.38 \times 10^{-7}$	$1.77 \times 10^{-3}$	$-1.96$
2	$-4.40 \times 10^{-7}$	$1.79 \times 10^{-3}$	$-1.20$
3	$-4.40 \times 10^{-7}$	$1.80 \times 10^{-3}$	$-2.01$
4	$-3.93 \times 10^{-7}$	$1.71 \times 10^{-3}$	$-1.95$

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

$$[\text{CH}] = \frac{N_{1, \text{CH}}}{1 - N_{2, \text{CH}} N_{\text{C}}} \quad (7)$$

The  $\text{C}_2$  chemistry added in the present work to the scheme of Glarborg et al.<sup>7</sup> aims at estimating the concentration of HCCO, which is formed from  $\text{C}_2\text{H}_2$ . Inclusion of an analytically reduced submodel for the  $\text{C}_2$  chemistry would complicate the model significantly. Instead, semi-empirical correlations, similar to those reported for the O/H radical pool,<sup>27</sup> 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  $\text{C}_2\text{H}_2$  during combustion show similarities to the profile predicted for  $\text{CH}_3$ . Accordingly,  $\text{C}_2\text{H}_2$  may be described by eq 8.

$$[\text{C}_2\text{H}_2] = Q_3[\text{CH}_3] \quad (8)$$

Values of  $Q_3$  were then determined from the peak concentrations of  $\text{C}_2\text{H}_2$  and  $\text{CH}_3$  predicted by the detailed mechanism for temperatures in the range of 1200–2000 K, inlet oxygen concentrations of 1–21 vol %, and values of  $\lambda$  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:

$$Q_3 = \frac{1}{\sqrt{\lambda}} \varepsilon(T) [\text{O}_2]_{\text{in}}^{\kappa(T)} \quad (9)$$

For biomass, where the volatiles were not assumed to contain  $\text{C}_2\text{H}_4$  (Table 1),  $\text{C}_2$  hydrocarbons are formed only through recombination of  $\text{C}_1$  compounds. Here, the correlation is

$$Q_3 = \frac{1}{\lambda^2} \varepsilon(T) [\text{O}_2]_{\text{in}}^{\kappa(T)} \quad (10)$$

The constants,  $\varepsilon$  and  $\kappa$ , 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.

$$[\text{HCCO}] = \frac{k_{f, 2}[\text{O}][\text{C}_2\text{H}_2]}{k_{f, 3}[\text{H}] + k_{f, 4}[\text{O}_2]} \quad (11)$$

**2.2. N Chemistry Scheme.** The scheme developed in this work describes reburn-type chemistry along with oxidation of  $\text{NH}_3$  and HCN. The basis of the model is the scheme of Pedersen et al.,<sup>8</sup> which describes well the HCN and  $\text{NH}_3$  oxidation chemistry.<sup>27</sup> 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<sup>a</sup>**

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

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

NO reduction reactions from the mechanism of Glarborg et al.<sup>7</sup> (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.<sup>20,23</sup> For several of these steps, more accurate kinetic parameters have become available since the publication of the reduced mechanism of Glarborg et al.,<sup>7</sup> 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<sub>2</sub> 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

**Table 6. Equilibrium Constants for Reversible Reactions<sup>a</sup>**

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

<sup>a</sup> Numbering is the same as in Table 5.

steps from Table 5.

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

$$r_{\text{NH}_3} = -w_{21} - w_{22} - w_{23} \tag{13}$$

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

$$r_{\text{N}_2} = w_{16} + w_{26} + w_{33} + w_{36} - w_{37} - w_{38} \tag{15}$$

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  $i$ th 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

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

$$[\text{CN}] = (k_{f,N1}/K_{N1}[\text{HCN}][\text{H}] + k_{f,N4}/K_{N4}[\text{HCN}][\text{OH}] + k_{f,N38}[\text{C}][\text{N}_2] + k_{f,N42}[\text{C}][\text{NO}]) / (k_{f,N1}[\text{H}_2] + k_{f,N4}[\text{H}_2\text{O}] + k_{f,N9}[\text{OH}] + k_{f,N10}[\text{O}_2]) \tag{18}$$

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

$$D_{\text{NCO}} = k_{f,N11}/K_{N11}[\text{H}_2\text{O}] + k_{f,N12}[\text{H}_2] + k_{f,N13}[\text{M}] + k_{f,N14}[\text{H}] + k_{f,N15}[\text{O}] + k_{f,N16}[\text{NO}]$$

$$N_{1,\text{NCO}} = ([\text{HOCN}](k_{f,N7}[\text{O}] + k_{f,N8}[\text{OH}]) + [\text{CN}](k_{f,N9}[\text{OH}] + k_{f,N10}[\text{O}_2]) + k_{f,N2}[\text{HCN}][\text{O}] + k_{f,N39}[\text{CH}_2][\text{NO}]) / D_{\text{NCO}}$$

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

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

The steady-state concentration of HNCO is

$$D_{\text{HNCO}} = k_{f, N11}[\text{OH}] + k_{f, N12}/K_{N12}[\text{H}] + k_{f, N17}[\text{M}] + k_{f, N18}[\text{O}_2] + k_{f, N19}[\text{H}] + k_{f, N20}[\text{O}]$$

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

$$N_{2, \text{HNCO}} = (k_{f, N11}/K_{N11}[\text{H}_2\text{O}] + k_{f, N12}[\text{H}_2])/D_{\text{HNCO}}$$

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

By solving eqs 19 and 20 simultaneously

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

The steady-state concentration of HCNO is found from

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

The equations for the species  $\text{NH}_2$ ,  $\text{NH}$ , and  $\text{N}$  are also solved simultaneously. The steady-state concentration for  $\text{NH}_2$  is

$$D_{\text{NH}_2} = k_{f, N21}/K_{N21}[\text{H}] + k_{f, N22}/K_{N22}[\text{H}_2\text{O}] + k_{f, N23}/K_{N23}[\text{H}_2] + k_{f, N24}[\text{H}] + k_{f, N25}[\text{OH}] + k_{f, N26}[\text{NO}]$$

$$N_{1, \text{NH}_2} = (k_{f, N19}[\text{HNCO}][\text{H}] + [\text{NH}_3](k_{f, N21}[\text{M}] + k_{f, N22}[\text{OH}] + k_{f, N23}[\text{H}]))/D_{\text{NH}_2}$$

$$N_{2, \text{NH}_2} = (k_{f, N24}/K_{N24}[\text{H}_2] + k_{f, N25}/K_{N25}[\text{H}_2\text{O}])/D_{\text{NH}_2}$$

$$[\text{NH}_2] = N_{1, \text{NH}_2} + N_{2, \text{NH}_2}[\text{NH}] \quad (23)$$

The steady-state concentration for  $\text{NH}$  is

$$D_{\text{NH}} = k_{f, N24}/K_{N24}[\text{H}_2] + k_{f, N25}/K_{N25}[\text{H}_2\text{O}] + (k_{f, N27} + k_{f, N28})[\text{O}_2] + k_{f, N29}[\text{H}] + k_{f, N30}[\text{O}] + (k_{f, N31} + k_{f, N32})[\text{OH}] + k_{f, N33}[\text{NO}]$$

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

$$N_{2, \text{NH}} = (k_{f, N29}/K_{N29}[\text{H}_2] + k_{f, N32}/K_{N32}[\text{H}_2\text{O}])/D_{\text{NH}}$$

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

$$[\text{NH}] = N_{1, \text{NH}} + N_{2, \text{NH}}[\text{N}] + N_{3, \text{NH}}[\text{NH}_2]$$

Finally, the steady-state concentration of  $\text{N}$  is

$$D_{\text{N}} = k_{f, N29}/K_{N29}[\text{H}_2] + k_{f, N32}/K_{N32}[\text{H}_2\text{O}] + k_{f, N34}[\text{OH}] + k_{f, N35}[\text{O}_2] + k_{f, N36}[\text{NO}] + k_{f, N44}[\text{CH}_3]$$

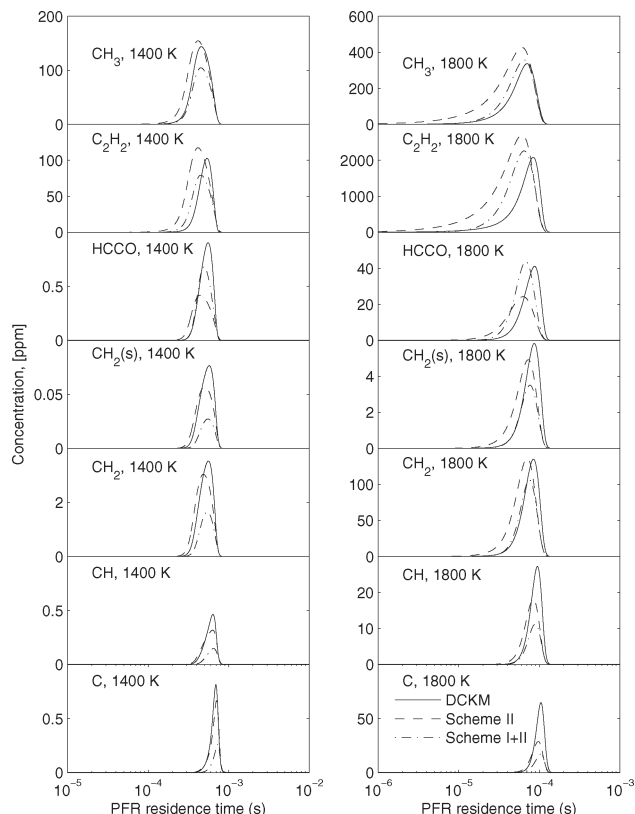
$$N_{1, \text{N}} = (k_{f, N13}[\text{NCO}][\text{M}] + [\text{NO}](k_{f, N34}/K_{N34}[\text{H}] + k_{f, N35}/K_{N35}[\text{O}]) + k_{f, N36}/K_{N36}[\text{N}_2][\text{O}] + k_{f, N37}[\text{CH}][\text{N}_2] + k_{f, N38}[\text{C}][\text{N}_2] + k_{f, N43}[\text{C}][\text{NO}])/D_{\text{N}}$$

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

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

Equations 23–25 are solved simultaneously.

$$[\text{NH}] = \frac{N_{1, \text{NH}} + N_{2, \text{NH}}N_{1, \text{N}} + N_{3, \text{NH}}N_{1, \text{NH}_2}}{1 - N_{2, \text{NH}}N_{2, \text{N}} - N_{3, \text{NH}}N_{2, \text{NH}_2}} \quad (26)$$



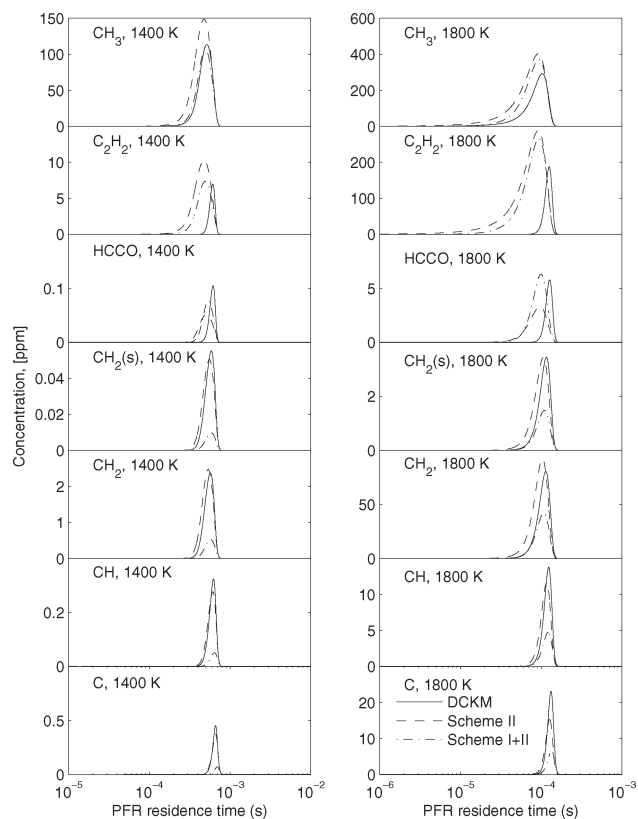
**Figure 2.** Radical concentrations during combustion of bituminous coal at two temperatures and reburning conditions.  $\lambda = 0.8$ , and  $\text{O}_2$  inlet concentration = 1 vol %.

### 3. Results and Discussion

In the following, we define the schemes used in modeling as follows: DCKM, detailed chemical kinetics model;<sup>20,23</sup> 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  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , and  $\text{N}_2$ , from the detailed mechanism), and with schemes I, II, and DCKM ( $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , and  $\text{N}_2$  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  $\text{CH}_3$  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.



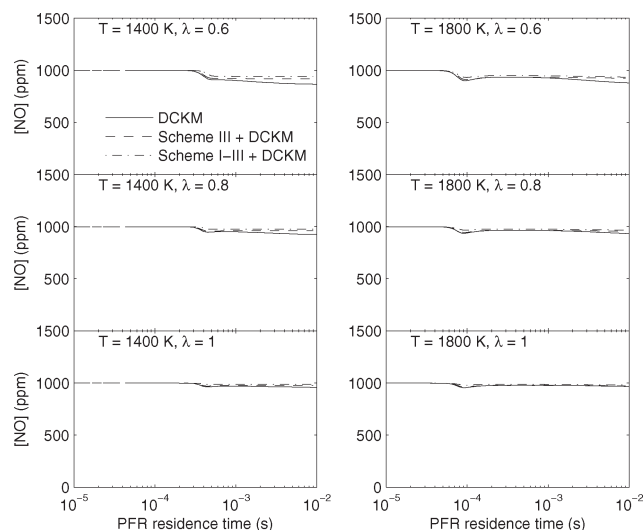
**Figure 3.** Radical concentrations during combustion of biomass at two temperatures and reburning conditions.  $\lambda = 0.8$ , and  $O_2$  inlet concentration = 1 vol %.

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).

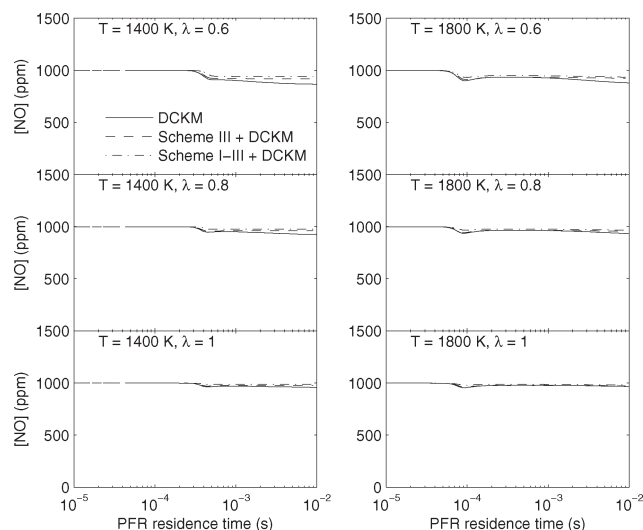
Figures 4 and 5 show results for reburning with volatiles from biomass and bituminous coal, respectively, as a function of stoichiometry ( $0.6 \leq \lambda \leq 1.0$ ) and temperature (1400–1800 K). Under the conditions investigated, the reduction in NO is modest. It increases as the stoichiometry becomes 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 simplified 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.



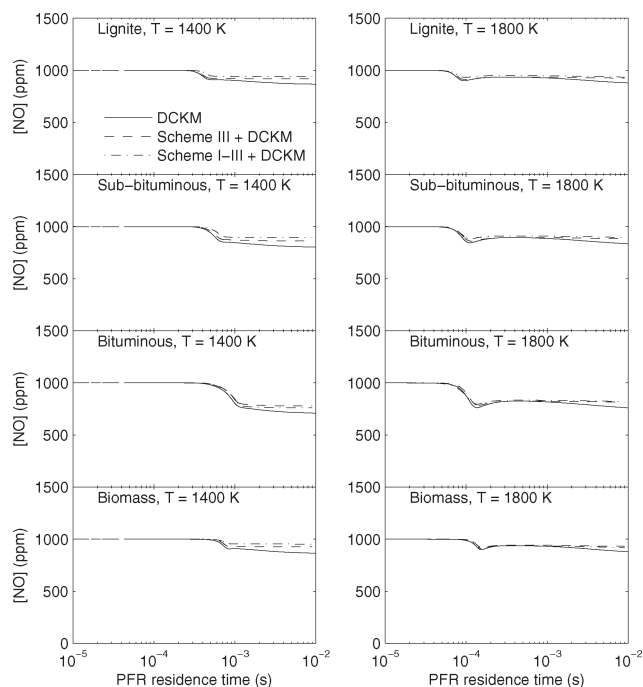
**Figure 5.** Predictions of NO reburning with bituminous coal volatiles in  $N_2/O_2$  mixtures with 1000 ppm NO and 1 vol %  $O_2$  in the inlet. The calculations are conducted under isothermal conditions. The figure compares modeling predictions from three levels of calculations: with DCKM, with scheme 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.<sup>2,27</sup> 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,<sup>36</sup> 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<sup>27</sup>), 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.<sup>27</sup> 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.<sup>27,37</sup> 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<sup>24,38,39</sup> 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<sup>25</sup> 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.

**Acknowledgment.** The work was funded by Vattenfall Research and Development AB and DONG Energy A/S.

**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.