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Development of reduced mechanisms applicable to CFD modeling of NO$_x$ emissions from biomass combustion

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Preface

The report deals with development of reduced kinetic mechanisms for ammonia oxidation that can be used for CFD modeling of NO_x formation in biomass combustors.

A computer code CARM was tested for generation of the reduced mechanisms. The code was obtained from Prof. Jyh-Yuan Chen at the Combustion Modeling Laboratory, Department of Mechanical Engineering, University of California, Berkeley. We want to thank him for supplying us with the code, as well as helping us to get started.

The report firstly describes shortly the general method for developing of the reduced mechanisms. Secondly, the development of the $CO/H_2/NH_3/O_2$ mechanism is described, and its performance is evaluated by comparing its predictions to full chemistry results and to results by alternative reduced mechanisms. Finally, the applicability of the mechanism is discussed in CFD calculations.

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Abstract

An 8-species 4-step reduced mechanism and a 9-species 5-step reduced mechanism have been developed. The mechanisms describe the oxidation of CO and H_2, and ammonia to NO and to N_2. The non-steady state nitrogen species are NH_3 and NO. The reduced mechanisms were developed using the computer code CARM from Berkeley. The mechanisms have been evaluated using PSR conditions. The temperature range covered was 600 K to 1600 K. The NH_3 mole fractions at the inlet ranged from 0 ppm to 1000 ppm and NO mole fractions at the inlet ranged from 0 ppm to 500 ppm. The investigated residence times were chosen as to correspond to those typically encountered in the Eddy Dissipation Concept developed by Magnussen for modeling of turbulent combustion, i.e., 0.1 – 10 ms. It was found that the 9-species reduced mechanism is more accurate, especially at longer residence times. However, it is likely that the 8-species mechanism too is accurate enough to be used in the modeling of turbulent flows, since other approximations are then probably more severe.

1. Introduction

Combustion of biomass is one way to reduce the growth of CO_2 in the atmosphere. A problem with biomass combustion is concerned with logistics [1]. Large areas need to be harvested in order to secure the supply of fuel for any larger installations. One option is to use smaller plants. However, for economical reasons these are often moving-grate combustors [1]. Such combustors are robust, but difficult to control. If the fuel quality is fluctuating, e.g. with regard to moisture content, such installation can have severe emissions of unburned components [1]. Another problem is concerned with NO_x emissions. Although in biomass combustion thermal-NO_x formation is of minor concern, the NO_x emissions can be high due to the high fuel-N content. Typically biomass may contain $0.1 - 1.0$ wt.-% nitrogen. Because of the limited economical possibilities to actively control combustion in smaller units, it is of great importance that they are designed properly. Here, it is interesting to use CFD as a tool in the design.

In Finland, e.g., the forest industry is a large producer of energy, although much of it is used for own use. In the pulping industry, the recovery process of the pulping chemicals involves combustion. Simultaneously, as the pulping chemicals are recovered, the part of the wood that does not consist of cellulose is combusted. The recovery boilers are usually large units so it is possible to apply more sophisticated technology to control emissions. Here too, the NO_x emissions stem from the nitrogen content of the fuel. For recovery boilers the emission levels are not particularly high, however, because of the large size of the units, there is an interest in reducing them to a minimum. In conjunction with the pulping process, there are often other possibilities to use biomass for energy conversion. For example, the bark is removed prior to the cooking. Often the bark is combusted in a fluidized bed. In the mechanical forest industry, sawdust is a by-product. This too can be combusted in fluidized beds. These latter processes, because of their size are usually built in such a way that there are possibilities to control the emissions actively. Nevertheless, for an optimal design, it is necessary to understand the emission formation in detail, as well as to be able to use this knowledge at the design stage.

The interest in reducing mechanisms has been driven by the fact that in the numerical simulation of even simple two-dimensional flames or three-dimensional flames, the use of full detailed mechanisms is prohibited. There are basically two advantages that can be obtained with the use of a reduced description: the fastest time scales are removed which makes the system less stiff and secondly, the number of species that has to be considered is reduced.

Reduced mechanism for simple fuels can be found in a number of textbooks, e.g. in [2,3]. Peters [2] describes in detail the development of a reduced mechanism for methane. In Rogg *et al.* reduced mechanisms for a number of fuels can be found [3]. These mechanisms are well established, and there is not much need for detailed descriptions. Later reduced mechanisms for hydrocarbons have been developed for special conditions, e.g. to describe oscillatory behavior, ignition, high pressure, and lean conditions [4,5,6].

Less reduced mechanisms are available in which nitrogen chemistry is included. Many include formation of thermal-NO [6,7], but this is not a complete enough description of the nitrogen chemistry to be applied in the modeling of biomass combustion where the main source of NO_x is fuel bound nitrogen. A mechanism that also includes prompt-NO formation has been presented by Røkke *et al.* [8] although their mechanism is not a pure reduced mechanism.

A few reduced mechanisms have been published which also include fuel-N chemistry. Glarborg *et al.* [9] has put forth a mechanism that describes the $CH_4/O_2/HCN/NO$ system. Although the $CO/H_2/O_2$-chemistry which is a subset of this mechanism, it is not well suited for use of biomass combustion modeling. It is usually assumed that in the devolatilization products of biomass fuels, the fuel-bound nitrogen is mainly existing as NH_3, whereas HCN is of major importance in coal combustion. Wendt [10] has been published a mechanism for nitrogen chemistry including NH_3. This mechanism is of the same type as that of Røkke *et al.* [8]. Although it included NH_3 it is only valid for fuel rich conditions since there is no reaction for oxidation of NH_3 to NO. Pedersen [11] has developed a reduced mechanism for description of volatile nitrogen conversion in pulverized

coal combustion. In the mechanism higher volatiles have been discarded. The mechanism describes the system $CO/H_2/O_2/HCN/NH_3/NO$ and could hence also work for biomass combustion conditions. Unfortunately, the temperature range of the mechanism was limited to 1200-2200K and the volatile nitrogen conversion was investigated at 1800 K, which is substantially higher than typical temperatures in biomass combustion. Consequently, the reactions between NH_2 and NO could successfully be described with a single reaction. This results in that the reduced mechanism cannot model reduction of NO by NH_3, a reaction that is of importance in biomass combustion. Marro et al. [12] has developed a reduced mechanism for nitric oxide in methane-air flames. In their mechanism NH_3, HNCO, HCNO, HCN, and NO were the non-steady state species. However, their model is intended for use with a laminar flamelet model and relies on that the C/H/O system is known. Lindstedt and Selim [13] have developed a number of reduced mechanisms for ammonia oxidation. None of these are applicable to the system of interest here, since in these mechanisms there is no C-chemistry.

The purpose of this work was to develop a reduced mechanism for the $CO/H_2/NH_3/NO/O_2$-system. The mechanism is developed for use in the modeling of biomass combustion where the NO_x emissions mainly stem from oxidation of NH_3. The mechanism has been developed using the CARM-code developed at Berkeley following the method outline by Chen [5]. This is the first project where this code has been utilized at Åbo Akademi University. At the same time as a new mechanism is reported this report also tries to discuss the use of such a tool for automatic construction of reduced mechanisms. A future goal is to use the reduced mechanism in CFD modeling. Therefore, computational efficiency is of uttermost importance. When modeling turbulent combustion with CFD, severe approximations have to be made to the description of the chemistry. As a consequence, the proposed mechanism does not include any radicals.

2. Techniques for developing reduced mechanisms

2.1 General procedure

The development of a reduced mechanism has been a tedious task that has required mathematical skills and a good knowledge of chemistry. First a skeletal mechanism has been established. This is a subset of the full mechanism that has been found to accurately describe the chemistry in the range of conditions the reduced mechanism will be used at. Secondly, quasi-steady state species are identified. Using the quasi-steady state assumptions an algebraic system will be obtained from which the concentrations of the quasi-steady state assumptions can be obtained. The algebraic system will be non-linear and may prove difficult to solve. To simplify the non-linear algebraic system a process termed truncation can be used. Truncation can be the use of partial-equilibrium assumptions or even the complete elimination of certain reactions in the quasi-steady state species equations.

The step in constructing a reduced mechanism for H_2 can be demonstrated following Peters [2] taking into account the following reactions:

1. $H+O2<=>O+OH$
2. $O+H2<=>OH+H$
3. $H2+OH<=>H2O+H$
4. $OH+OH<=>H2O+O$
5. $H+O2+M=>HO2+M$
6. $H+HO2=>OH+OH$
7. $H+HO2=>H2+O2$
8. $OH+HO2=>H2O+O2$

The mechanism is constructed assuming that OH, O, and HO_2 are steady state species. First balance equations are written for all species. Peters uses the notation $L(C_i)$ as a general linear differential operator for the concentration of species C_i that may not only contain the time derivatives. Using this operator the balance equations are

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$$L(C_H) = -\omega_1 + \omega_2 + \omega_3 - \omega_5 - \omega_6 - \omega_7$$
$$0 = L(C_{OH}) = \omega_1 + \omega_2 - \omega_3 - 2\omega_4 + 2\omega_6 - \omega_8$$
$$0 = L(C_O) = \omega_1 - \omega_2 + \omega_4$$
$$L(C_{H2}) = -\omega_2 - \omega_3 + \omega_7$$
$$L(C_{O2}) = -\omega_1 - \omega_5 + \omega_7 + \omega_8$$
$$L(C_{H2O}) = \omega_3 + \omega_4 + \omega_8$$
$$0 = L(C_{HO2}) = \omega_5 - \omega_6 - \omega_7 - \omega_8$$

Steady state assumption for a species leads to an algebraic relation between the rates. Using these relations it is possible to eliminate reactions from the balance equations of the non-steady state species. The justification for this operation is that the net reaction rates of the steady-state species are zero. Consequently these can be added to the balance equations of the non-steady state species without changing the reaction rates of the non-steady state species. As a rule the fastest consumption reactions for each species should be eliminated. If reaction 3 is eliminated for OH, reaction 2 for O, and reaction 7 for HO_2 the following linear combination results in balance equations for the non-steady state where the reactions 2, 3, and 7 have been eliminated. Note that simultaneously also other reactions are eliminated.

$$L(C_H) + L(C_{OH}) + 2\,L(C_O) - L(C_{HO2}) = 2\omega_1 - 2\omega_5 + 2\omega_6$$
$$L(C_{H2}) - L(C_{OH}) - 2\,L(C_O) + L(C_{HO2}) = -3\omega_1 + \omega_5 - 3\omega_6$$
$$L(C_{O2}) + L(C_{HO2}) = -\omega_1 - \omega_6$$
$$L(C_{H2O}) + L(C_{OH}) + L(C_O) = 2\omega_1 + 2\omega_6$$

In the balance equations the L-operator of the steady state species should be neglected. Next step is to arrange the reaction rate in such a way that those rates with equal stoichiometric coefficients are added. Now the balance equations for the non-steady state species become

$$L(C_H) = 2(\omega_1 + \omega_6) - 2\omega_5$$
$$L(C_{H2}) = -3(\omega_1 + \omega_6) + \omega_5$$
$$L(C_{O2}) = -(\omega_1 + \omega_6)$$
$$L(C_{H2O}) = 2(\omega_1 + \omega_6)$$

The stoichiometry of these corresponds to the following global mechanism

(I)   3H2+O2 = 2H + 2H2O
(II)   2H = H2

with the rates

$$\omega_I = \omega_1 + \omega_6$$
$$\omega_{II} = \omega_5.$$
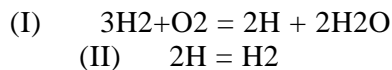
Peters choose to write the second global equation

$$\text{(II)} \quad 2H + M = H2 + M$$
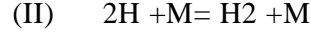
to remind that ω_5 is a third body reaction.

Since the construction of the reduced mechanism mainly involves algebraic operations, the problem is well suited to be formulated using matrix notation. First the rates of all species are put into a matrix $\mathbf{W}$.

$$\mathbf{W} = \begin{bmatrix} \mathbf{w}_H \\ \mathbf{w}_{OH} \\ \mathbf{w}_O \\ \mathbf{w}_{H_2} \\ \mathbf{w}_{O_2} \\ \mathbf{w}_{H_2O} \\ \mathbf{w}_{HO_2} \end{bmatrix}$$

where $\mathbf{w}_i$ is the product of stoichiometric vector describing the reactions of species i multiplied by the rate of the reactions i is involved in.

Using this matrix two matrices are constructed using only the columns corresponding to the reaction rates, i, j, and, k, that are chosen to be eliminated; one for the non-steady state species and one for the steady state species.

$$\mathbf{W}_{ns,e} = \begin{bmatrix} \mathbf{w}_{H,i} & \mathbf{w}_{H,j} & \mathbf{w}_{H,k} \\ \mathbf{w}_{H_2,i} & \mathbf{w}_{H_2,j} & \mathbf{w}_{H_2,k} \\ \mathbf{w}_{O_2,i} & \mathbf{w}_{O_2,j} & \mathbf{w}_{O_2,k} \\ \mathbf{w}_{H_2O,i} & \mathbf{w}_{H_2O,j} & \mathbf{w}_{H_2O,k} \end{bmatrix}$$

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$$\mathbf{W}_{ss,e} = \begin{bmatrix} \mathbf{w}_{OH,i} & \mathbf{w}_{OH,j} & \mathbf{w}_{OH,k} \\ \mathbf{w}_{O,i} & \mathbf{w}_{O,j} & \mathbf{w}_{O,k} \\ \mathbf{w}_{HO_2,i} & \mathbf{w}_{HO_2,j} & \mathbf{w}_{HO_2,k} \end{bmatrix}$$

Next a matrix $\mathbf{X}$ is determined that eliminates the rates of reactions i, j, and k, i.e.,

$$\mathbf{W}_{ns,e} + \mathbf{X}\mathbf{W}_{ss,e} = \mathbf{0}$$

The matrix $\mathbf{X}$ contains information how the balance equations of the steady state species should be added in order to eliminate the chosen reaction rates. The reaction rates of the non-steady state species with the reactions i, j, and k are now given by.

$$\mathbf{W}_{ns} + \mathbf{X}\mathbf{W}_{ss} = \begin{bmatrix} \mathbf{w}_H \\ \mathbf{w}_{H_2} \\ \mathbf{w}_{O_2} \\ \mathbf{w}_{H_2O} \end{bmatrix} + \mathbf{X} \begin{bmatrix} \mathbf{w}_{OH} \\ \mathbf{w}_O \\ \mathbf{w}_{HO_2} \end{bmatrix}$$

Next the reaction rates has to be arranged in such a way that rates with equal stoichiometric coefficients are added, which then helps to find the balance equations of the global mechanism as well as the global rates. This can be done by determining which columns in the resulting matrix are linearly dependent.

The rule of eliminating the fastest consumption rate can be an arbitrary choice since which reaction is the fastest depends upon the conditions. For the present example OH was consumed by reactions 3 and 8, O by reactions 2 and 4 and HO_2 by reactions 6,7, and 8. The reactions that are eliminated has to be chosen such that the rank of the matrix $\mathbf{W}_{ss,e}$ is full. This means that reaction 8 cannot be chosen both for OH and HO_2. Still, there are ten different possible combinations giving rise to three different global mechanisms. The global mechanisms are listed below.

$$3H_2 + O_2 = 2H + 2H_2O$$
$$2H = H_2$$

$$3H_2 + O_2 = 2H + 2H_2O$$
$$2H_2 + O_2 = 2H_2O$$

$$H_2 + 1/3\ O_2 = 2/3\ H + 2/3\ H_2O$$
$$1\ 1/3\ H + 1/3\ O_2 = 2/3\ H_2O$$
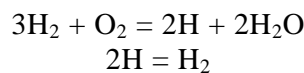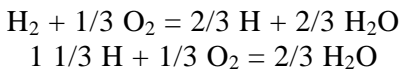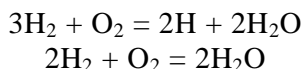
Although these global reactions differ, their rates of the global reactions differ in such a way that by using the steady state relations they can be transferred into each other. Eliminating in all possible ways, the 8-step mechanism can be used to formulate a 2-step reduced mechanism in 54 ways, which results in all together 11 different versions of the global reactions. Since it is unlikely that the steady state assumptions are strictly valid for all conditions a reduced mechanism will be applied to, they will all result in different predictions.

2.2 CARM

Today, a number of automatic methods exist for the construction of reduced mechanisms. Some of this are closely related to the traditional way of making reduced mechanisms, they consist mainly of a mathematical way of identifying quasi-steady state species or reaction groups as well as sometimes the skeletal mechanism. Chen [5,14] has put one such method forth. This is an automatic algorithm that starts by establishing a skeletal mechanism. The skeletal mechanism is developed by identifying and eliminating reaction steps in the detailed mechanism that are not of importance at the conditions being investigated. The algorithm uses the normalized sensitivity coefficients obtained using the PSR code [15] from the CHEMKIN-package [16] to identify the most important reactions. Here a cut-off level has to be specified. Reactions having a higher sensitivity than the specified cut-off level are added to a preliminary set of reactions that will form the skeletal mechanism. Then the normalized rate-of-production and normalized rate-of-destruction of the species in the preliminary set of reactions are examined for those reactions that are not included. Then reactions that have a large enough rate-of-production or rate-of-destruction are added to the preliminary set. Finally, it is checked that no new species are included in the set of reactions. If new species are added the steps including the

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check of the rate-of-production and rate-of-reaction and the check for new species are repeated until no new species are being added.

Next the algorithm identifies quasi-steady state species. A species is approaching quasi-steady state if the net rate compared to the net production rate or destruction rate is small enough, i.e.,

$$\frac{\left|\dot{\omega}_k^p - \dot{\omega}_k^c\right|}{\max\left(\left|\dot{\omega}_k^p\right|, \left|\dot{\omega}_k^c\right|\right)} << \delta$$

where δ is a cut-off level, $\dot{\omega}_k^p$ the rate of production of species k and $\dot{\omega}_k^c$ its rate of consumption. A modified criterion can also be utilized in which also the concentration level is taken into account,

$$X_k \frac{\left|\dot{\omega}_k^p - \dot{\omega}_k^c\right|}{\max\left(\left|\dot{\omega}_k^p\right|, \left|\dot{\omega}_k^c\right|\right)} << \delta$$

Finally the algebraic set of equation obtained applying quasi-steady state assumptions. In the algorithm put forth by Chen [5,14] the reaction associated with the smallest sensitivity coefficients are eliminated. Care is being taken that reactions are being eliminated that are independent of those eliminated earlier.

2.3 KINALC

Another method has been put forth by Tomlin *et al.* [4]. They use an index

$$B_i = \sum_{n=1}^{N} \left(\frac{\partial \ln f_n}{\partial \ln C_i}\right)^2$$

to identify redundant species that may be excluded from the model. This step requires that a threshold must be defined. Tomlin *et al.* [4] state that the threshold will be different for each model studied, but that in most cases there will exist a

gap between the values of the B_i index for those species that should be kept in the model and those that can be eliminated. Principally this examination has to be carried out for every condition the reduced mechanism is going to be applicable to. However, the method depends on that important species first are specified, e.g. major reactants or products. The next step of their algorithm consists of the identification of redundant reactions. Here they use principal component analysis of the rate sensitivity matrix $\widetilde{\mathbf{F}}$, where

$$\widetilde{F}_{ij} = \frac{\partial \ln f_i}{\partial \ln k_j} = \frac{\nu_{ij} R_j}{f_i}$$

The principal component analysis is based on an eigenvalue-eigenvector decomposition of the matrix $\widetilde{\mathbf{F}}^T \widetilde{\mathbf{F}}$. The eigenvectors represents sets of coupled reactions and the eigenvalues measures the relative contribution of each set. By disregarding eigenvectors associated with small enough eigenvectors, but also by disregarding small enough eigenvector-elements redundant reactions will be automatically eliminated. The method of Tomlin *et al.* [4] also includes treatment of non-isothermal systems. In their paper they conclude that it is crucial first to identify redundant species before identifying the redundant reactions. So far, the method has only provided a skeletal mechanism or a minimal mechanism. To obtain a reduced mechanism steady state assumptions has to be applied. Tomlin *et al.* [4] suggest a method how to select the quasi-steady species. The method consists of a combination of analysis of the species lifetime obtained from analyzing the Jacobian and the use of a concentration sensitivity analysis. Tomlin *et al.* [4] conclude that their method give some indication as to why H is not a successful quasi-steady state species, which indicates that the reduced mechanism still has to be extensively evaluated before it finally can be applied. A CHEMKIN-based package for executing, e.g., principal component analysis of the rate sensitivity matrix $\widetilde{\mathbf{F}}$, KINALC, can be found at http://chem.leeds.ac.uk/Combustion/Combustion.html.

2.4 Computational Singular Perturbation

Another possibility to reduce the chemistry is to use the Computational Singular Perturbation (CSP) technique [17]. In short this technique is based on the fact that the reaction rate for each species can be expressed using another representation than that given by the stoichiometric matrix and the reaction rate matrix. With the CSP technique a set of basis vectors that are found which describes the fastest reaction groups. It is then possible to discard those that do not contribute significantly. In this way only a certain number of reactions and species needs to be taken into account and the concentration of the other can be calculated from algebraic relations in the usual way. The CSP technique provides a local minimal set of species that needs to be treated exactly in the equations describing the system. Consequently, both the individual reactions and the number of reactions in the reduced mechanism will be a function of the local conditions.

2.5 S-STEP

Massias *et al.* [18] has put forth an algorithm, which is based on CSP data, for constructing reduced mechanisms that do not vary with the local conditions. First, the number of steady state species or number of steps in the reduced mechanism has to be selected. No recommendations are given for this step, but the problem is common to the methods described above. One option is to try different numbers and see which species are identified as quasi-steady state species. This is the approach used by Massias *et al.* [18] in the construction of a reduced mechanism for methane. They use as many step as necessary in order to get H as a non-steady state species with the motivation that in the literature it has been reported that H should be a major species. In order to check whether the species that are considered as major species by the investigator is included in the set of non-steady state species the following steps has to be performed. First, the number of steady state species is guessed. Then the basis vectors as calculated by the CSP technique with the specified number of steady state species are analyzed at each condition that is to be taken into consideration. In this way the CSP technique will provide a "pointer" which points to the species that are in steady state. By integrating a criterion which takes into account the CSP-pointer, the concentration, and that the rate is significant over the whole domain, an index is

obtained which shows which species are most non-steady state species. Unfortunately, a species which is a non-steady state species when the reduced mechanism will be of a certain size, may not necessary be included in a reduced mechanism containing more non-steady state species. Once the steady state species have been selected the reactions that are to be eliminated are determined. This is done by calculating the mean rate of destruction of the species in steady state starting from that "most" in steady state according to index used to determined which ones are in steady state. The reaction that is fastest on an average is eliminated. This is repeated for each species in turn for all steady state species. Here too, care has to be taken that the reactions that are eliminated form a set of independent reactions. S-STEP, a FORTRAN program for automatically producing global reduced chemical kinetic mechanisms of prescribed size can be found at http://euklides.iceht.forth.gr:8000/SD/.

2.6 Intrinsic Low-Dimensional Manifold

Another method for constructing a reduced representation of the chemistry is the Intrinsic Low-Dimensional Manifold (ILDM) method [19,20]. This method is related to the CSP method in that it is a function of the compositions. In contrast to the CSP method the size of the reduced chemistry is constant. First the number of "steps" in the reduced chemistry has to be specified although no formal reactions are introduced. Instead the number of "step" are associated with the number of control variables needed to describe the system. In common with the CSP method the ILDM method do not use steady state of individual species but for reaction groups. The reaction groups are calculated from an eigenvector analysis of the Jacobian matrix of the source term. In contrast tot the CSP method the number of steady state assumptions do not vary with composition. Nevertheless, in contrast to the traditional steady state assumption the steady state assumptions themselves vary with composition. Usually, the reaction rates are pre-calculated and stored in a table. It is interesting to note that Eggels *et al.* [21] who compared the conventional steady state based technique to the ILDM method found that the conventional method provided superior results. The reason for this surprising founding was that the time scale of the reaction groups in steady state and those not, i.e., those describing the manifold was small. In their investigation

they studied a CO/H2-air flame. Since the ILDM method requires tabulation the method has mainly been applied to chemically simple systems. However, it would be a trivial task to decompose the Jacobian matrix of the source term for any system and based on this judge the potentials of the ILDM method for that particular system.

2.7 Repro-modeling

As an alternative to the approaches outlined above Turánayi [22] has suggested that repro-modeling can be an alternative. Repro-modeling is a technique where the input-output relation is approximated by explicit empirical equations. Turánayi has successfully tested this approach on a wet CO combustion. In order to obtain coefficients for the polynomials a large simulation matrix is required, but once the coefficients are established the technique provides a fast way of calculating reaction rates. Turánayi [22] suggests two ways of use of the repro-modeling technique. In the first the polynomials provides reaction rates, in the second it provides change of composition in a small time interval. In the latter case a considerable speed-up is achieved since the solution of stiff kinetic equations is replaced by the evaluation of polynomials.

3. Mechanism development

The computer code CARM based on the algorithm put forth by Chen [5,14] was used as a tool for developing the reduced mechanism. CARM requires as input results from a PSR simulation with the PSR-code [15] from the CHEMKIN-package [16]. Bases on the results the code establishes a skeletal mechanism, identifies quasi-steady state species, formulates the algebraic equations, and finally writes a PSR-code compatible FORTRAN routine for calculation of reaction rates. The full mechanism can be found in Appendix 1. The mechanism has been compiled by Kilpinen *et al*. [23] using the mechanism of Miller and Glarborg [24] as a starting point. Two conditions, as described in the input file to the PSR-code are shown in Table 1, were used as input to the CARM code. The first condition corresponds to a fuel rich mixture of air and pyrolysis gas, whereas

the second condition corresponds to flue gas conditions. The NH_3 and NO level could probably have been chosen a bit higher.

Table 1. Keywords in the input files to the PSR-code that specify the conditions the calculations the reduced mechanisms are based on.

	Base case I	Base case II
TEMP	1300.00	1500.00
PRES	1.0	1.0
TAU	0.010	0.001
REAC CO2	0.000000	0.110000
REAC CO	0.114286	0.005000
REAC O2	0.090000	0.020000
REAC H2O	0.000000	0.140000
REAC H2	0.142857	0.005000
REAC NH3	0.000100	0.000005
REAC NO	0.000000	0.000020
REAC N2	0.652757	0.719975

Four different mechanisms were developed. First a 9-species reduced mechanism was developed using the full mechanism. The sorting of the species according to how well they fulfill the quasi-steady state requirements were not used in choosing the non-steady state species found in the set of formal reactions. The main reason for discarding the recommendations was that because of the low input levels of NH_3 and NO, these species were found by the code to be unimportant compared to many radicals known to be of little importance. As a consequence, the 9 species where chosen to correspond to the species transport equations will be solved for in CFD-modeling. The only possible exception here is the H-radical that was retained because of its reported importance in literature. The reduced mechanism established using the full reaction mechanism and having all species but CO_2, CO, O_2, H_2O, H_2, H, NH_3, NO, and N_2 in quasi-steady state is:

$$NH_3 + NO = H + H_2O + N_2$$
$$NH_3 + NO + H = H_2 + H_2O + N_2$$
$$5\ H_2O + 4\ N_2 = 3\ NH_3 + 5\ NO + H$$
$$1/2\ O_2 + 3\ H_2O + 3\ N_2 = 2\ NH_3 + 4\ NO$$
$$3\ H_2O + CO + 2\ N_2 = 2\ NH_3 + 2\ NO + CO_2$$
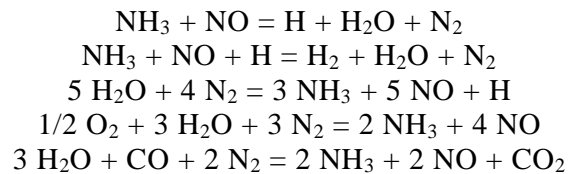
When solving the analytic set of algebraic equations, those reactions suggested as candidates by the CARM-code were eliminated. A separate listing of all reduced reaction mechanisms can be found in Appendix 2.

Then a skeletal mechanism was developed using the recommended cut-off level for redundant reaction steps. Of the original 137 reactions and 26 species, 86 reactions were retained. Only one species, NO_3, was discarded compared to the full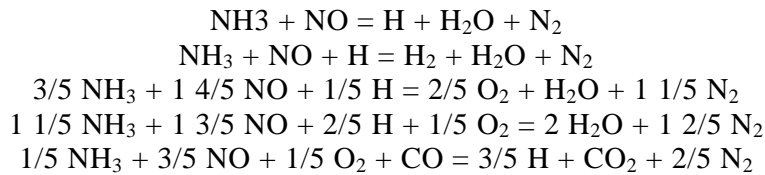 mechanism. In this mechanism the same non-steady state species were used as in the development of the reduced mechanism based on the full mechanism. The formal reactions of this mechanism are

$$NH_3 + O_2 = NO + H + H_2O$$
$$NH_3 + H + O_2 = NO + H_2 + H_2O$$
$$NH_3 + 1\ 1/4\ O_2 = NO + 1\ 2/4\ H_2O$$
$$2\ NO = O_2 + N_2$$
$$1/2\ O_2 + CO = CO_2$$
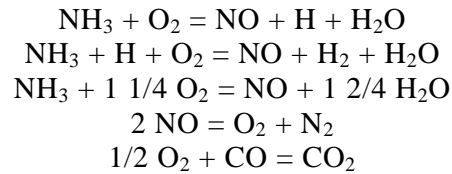
Another reduced mechanism including the same non-steady state reactions were also developed using a higher value for the cut-off for non-significant reactions in the step where the skeletal mechanism was developed. Here a value 0.1 was used, whereas the recommended value is 0.05. In this case the skeletal mechanism consisted of 65 reactions between 22 species. Compared to the skeletal mechanism obtained with the cut-off value 0.05 also N_2H_2, N_2H_3, and N_2H_4 were eliminated. Here, the following formal reactions were obtained

$$NH3 + NO = H + H_2O + N_2$$
$$NH_3 + NO + H = H_2 + H_2O + N_2$$
$$3/5\ NH_3 + 1\ 4/5\ NO + 1/5\ H = 2/5\ O_2 + H_2O + 1\ 1/5\ N_2$$
$$1\ 1/5\ NH_3 + 1\ 3/5\ NO + 2/5\ H + 1/5\ O_2 = 2\ H_2O + 1\ 2/5\ N_2$$
$$1/5\ NH_3 + 3/5\ NO + 1/5\ O_2 + CO = 3/5\ H + CO_2 + 2/5\ N_2$$

Finally, an 8-species reduced mechanism was developed. Here the skeletal mechanism obtained with the recommended cut-off value for redundant reactions steps were used, but the H-radical was described as a quasi-steady state species. According to source is the literature, H should be treated as a non-steady state species, but in CFD modeling other simplifications in the description of turbulence-chemistry interactions are often severe enough that some discrepancy

between a reduced mechanism and the full chemistry can be tolerated. Assuming that H can be described with the quasi-steady state assumption, the following formal reactions were obtained:

$$NH_3 + 3/4\ O_2 = NO + H_2 + 2/4\ H_2O$$
$$NH_3 + 1\ 1/4\ O_2 = NO + 1\ 2/4\ H_2O$$
$$2\ NO = O_2 + N_2$$
$$1/2\ O_2 + CO = CO_2$$
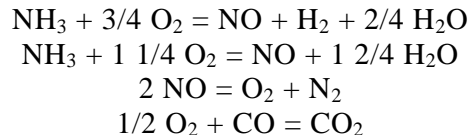
4. Evaluation of the mechanisms

The reduced mechanisms were evaluated at a broad range of conditions in a PSR. Basically two different compositions of the main components were investigated and four combinations of the NH_3-NO levels. In addition to the O_2 content, also the residence time of the PSR, and the temperature was changed in a broad range. Most of the simulations used for evaluation purpose were isothermal. Altogether 1344 different conditions were investigated for each of the reduced mechanisms. In addition, a few non-isothermal cases were also studied. The input to the PSR-code for the isothermal cases is shown in Table 2.

The reduced mechanism based on the full mechanism and the 9-species mechanism based on the skeletal mechanism where 0.1 was used as cut-off limit in the identification of redundant reactions caused numerical problems to the PSR-code. The reduced mechanism based on the full mechanism was almost impossible to converge. The 9-species mechanism converged, but the solutions were not sensible. Possible reasons for this behavior was investigated. It was found that the skeletal mechanism was valid, i.e., it was able to accurately reproduce the results obtained with the full mechanism. The species that were eliminated only were present at trace amount that indicated that the behavior could not directly be caused by their elimination. As a possible cause for the behavior could be the formal reactions. In the mechanism causing this kind of problem, the CO oxidation is coupled with the N-chemistry. Since the CO and CO_2 concentrations are several magnitude higher that the NH_3 and NO concentrations, a small error in the CO and CO_2 levels would be seen as a large error in the N-chemistry. However, no direct evidence for this could be given.
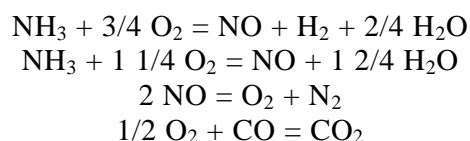
16

Nevertheless, there was some indications of that not all quasi-steady state assumptions were valid. There was a considerable difference between the reaction rates of the nitrogen containing species in the reduced mechanism compared to those based on the skeletal mechanism. When calculating the reaction rates with the skeletal mechanism, the rates were taken as the sum of production rates and destruction rates of the elementary reactions evaluated using quasi-steady state levels of the steady state species.

Table 2. Keywords in the input files used to specify the conditions used to evaluate the reduced mechanisms.

	"Pyrolysis gas"				"Post gas"			
TEMP	600, 900, 1100, 1300, 1500, 1700, 1900, 2100				600, 900, 1100, 1300, 1500, 1700, 1900, 2100			
PRES	1.0				1.0			
TAU	0.0001, 0.001, 0.01				0.0001, 0.001, 0.01			
REAC CO2	0.060000				0.110000			
REAC CO	0.040000				0.005000			
REAC O2	0.0001, 0.0004, 0.001, 0.0004, 0.01, 0.04, 0.1				0.0001, 0.0004, 0.001, 0.0004, 0.01, 0.04, 0.1			
REAC H2O	0.060000				0.140000			
REAC H2	0.040000				0.005000			
REAC NH3*	0	100 0	0	500	0	100 0	0	500
REAC NO*	0	0	500	500	0	0	500	500
REAC N2	rest				rest			

* The concentrations of NH_3 and NO are here given in ppm-vol. In the input-file they has to be given as mole fractions together with the REAC-keyword

All subsequent results from the calculations used in the evaluation procedure are presented for the reduced mechanisms obtained using the 0.05 cut-off limit in the establishing of the skeletal mechanism. From here on, the 8-species 4-step mechanism based on the skeletal mechanism containing 86 reactions between 25 species, i.e,

$$NH_3 + 3/4\ O_2 = NO + H_2 + 2/4\ H_2O$$
$$NH_3 + 1\ 1/4\ O_2 = NO + 1\ 2/4\ H_2O$$
$$2\ NO = O_2 + N_2$$
$$1/2\ O_2 + CO = CO_2$$

will be referred to as the 4-step mechanism and the 9-species 5-step based on the same skeletal mechanism, i.e.,

$$NH_3 + O_2 = NO + H + H_2O$$
$$NH_3 + H + O_2 = NO + H_2 + H_2O$$
$$NH_3 + 1.25\ O2 = NO + 1.5\ H_2O$$
$$2\ NO = O_2 + N_2$$
$$0.5\ O_2 + CO = CO_2$$
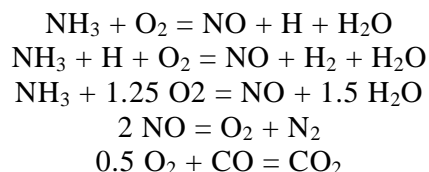
will be referred to as the 5-step mechanism. It can be noticed that a similar situation as compared to the CO oxidation coupling with the N-chemistry also exists for the H_2 oxidation. The global reaction $H_2 + 0.5\ O_2 = H_2O$ is obtained by subtracting the first reaction from the second reaction in the 4-step mechanism. In the 5-step mechanism case the coupling is even more complicated. Here the global reaction $H_2 + 0.5\ O_2 = H_2O$ is obtained by subtracting reaction 1 and 2 from twice reaction 3.

In the "pyrolysis gas" mixture the chemistry appeared frozen at 600 K. Here the full mechanism, the 4-step mechanism and the 5-step mechanism all produced similar results.

At 900 K the agreement between the full mechanism and the 5-step were good, although the $NH_i + NO = N_2 +...$ reaction was more important with the full mechanism. The 4-step mechanism was not fully able to describe the chemistry at 900 K. When equal amounts of NH_3 and NO was present the 4-step mechanism predicted a conversion of NO to NH_3, which is not in agreement with the results obtained with the full mechanism. Figure 1 shows the NH_3 and NO as a function of O_2-mole fraction for the three mechanisms.

Figure 1. NO mole fraction (dash-dotted line) and NH₃ mole fraction (full line) as a function of O₂ mole fraction at the inlet of an isothermal PSR. The temperature of the PSR was 900 K. At the inlet equal amounts of NO and NH₃ was present (500 ppm). The top row shows result obtained with the detailed mechanism, the middle row with the 5-step reduced mechanism and the bottom row with the 4-step reduce mechanism. The left, middle and right columns show results for τ=10 ms, τ=1 ms, and τ=0.1 ms, respectively. O₂ = 10⁻⁴ corresponds to λ=0.0025 and O₂ = 10⁻¹ corresponds λ=2.5. In these values, the effect on NH₃ on λ was not taken into account.

At 1100 K also the 4-step mechanism produces excellent results. At this temperature the reduction of NO by H was overestimated using the 5-step mechanism. Figure 2 shows the NH$_3$ and NO as a function of O$_2$-mole fraction for the three mechanisms.

Figure 2. NO mole fraction (dash-dotted line) and NH₃ mole fraction (full line) as a function of O₂ mole fraction at the inlet of an isothermal PSR. The temperature of the PSR was 1100 K and the residence time was 1 ms. For the different columns, different concentrations of NH₃ and NO have been present at the inlet. These are indicated in the top of the figure.

At temperatures higher than 1300 K, the agreement between the full mechanism and the 5-step mechanism is excellent. With the 4-step mechanism the chemistry is slightly slower at fuel rich conditions. This can be seen in Figure 3 that shows CO and H₂ profiles for the three mechanisms. Apart from some problems at fuel rich conditions, the 4-step mechanism is able to reproduce the N-chemistry, although the 5-step mechanism performs better than the 4-step mechanism. The difference between the full mechanism and the 4-step mechanism becomes more pronounced at longer residence times and at higher temperatures.

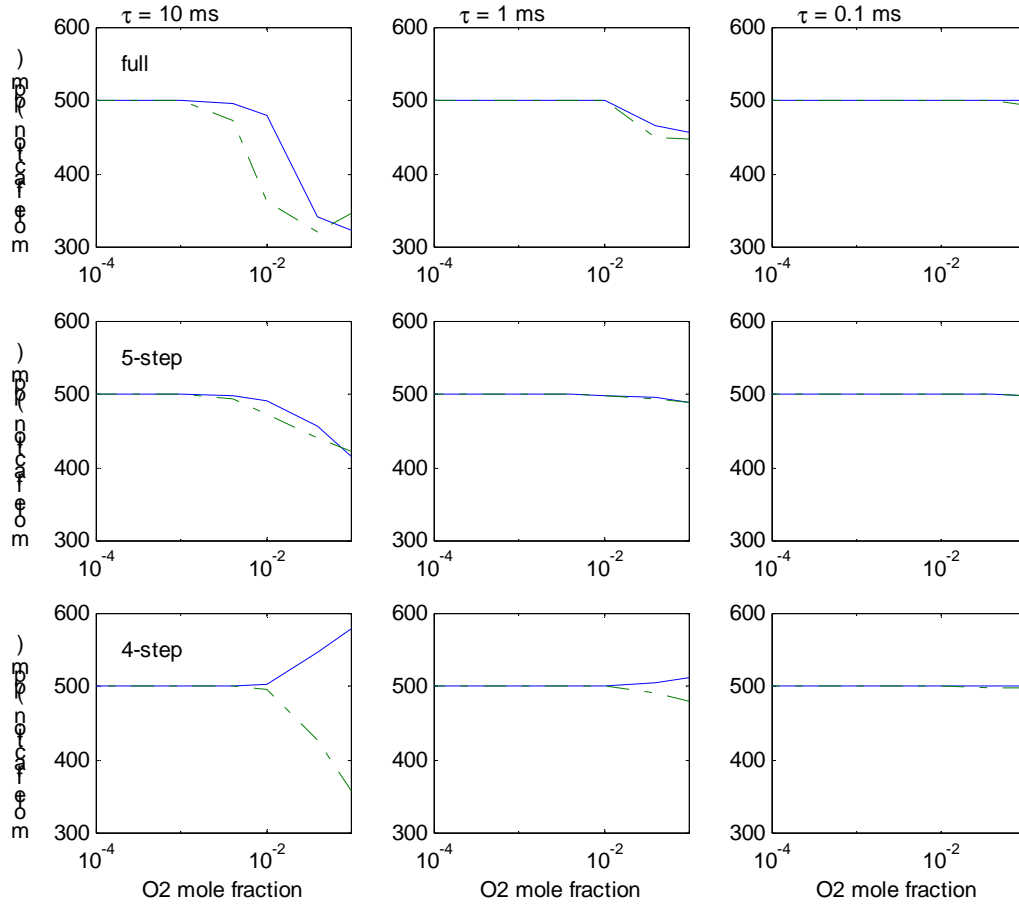*Figure 3. CO mole fraction (dash-dotted line) and H₂ mole fraction (full line) as a function of O₂ mole fraction at the inlet of an isothermal PSR. The temperature of the PSR was 1300 K. The left, middle and right columns show results for τ=10 ms, τ=1 ms, and τ=0.1 ms, respectively.*

The "pyrolysis gas" mixture was also investigated at adiabatic conditions. Here, two inlet temperatures were tested: 1100 K and 1300 K. Figure 4 shows NH_3 and NO profiles for the three mechanisms for the T_{in}=1100 K case. From the figure it can be seen that the trend is similar to that found in the isothermal case. It can be seen that the 4-step mechanism underestimates the NO reduction by H is as well as the reaction between NH_3 and NO. All in all though, the agreement is good. The agreement between the full mechanism and the 5-step mechanism is excellent here too.
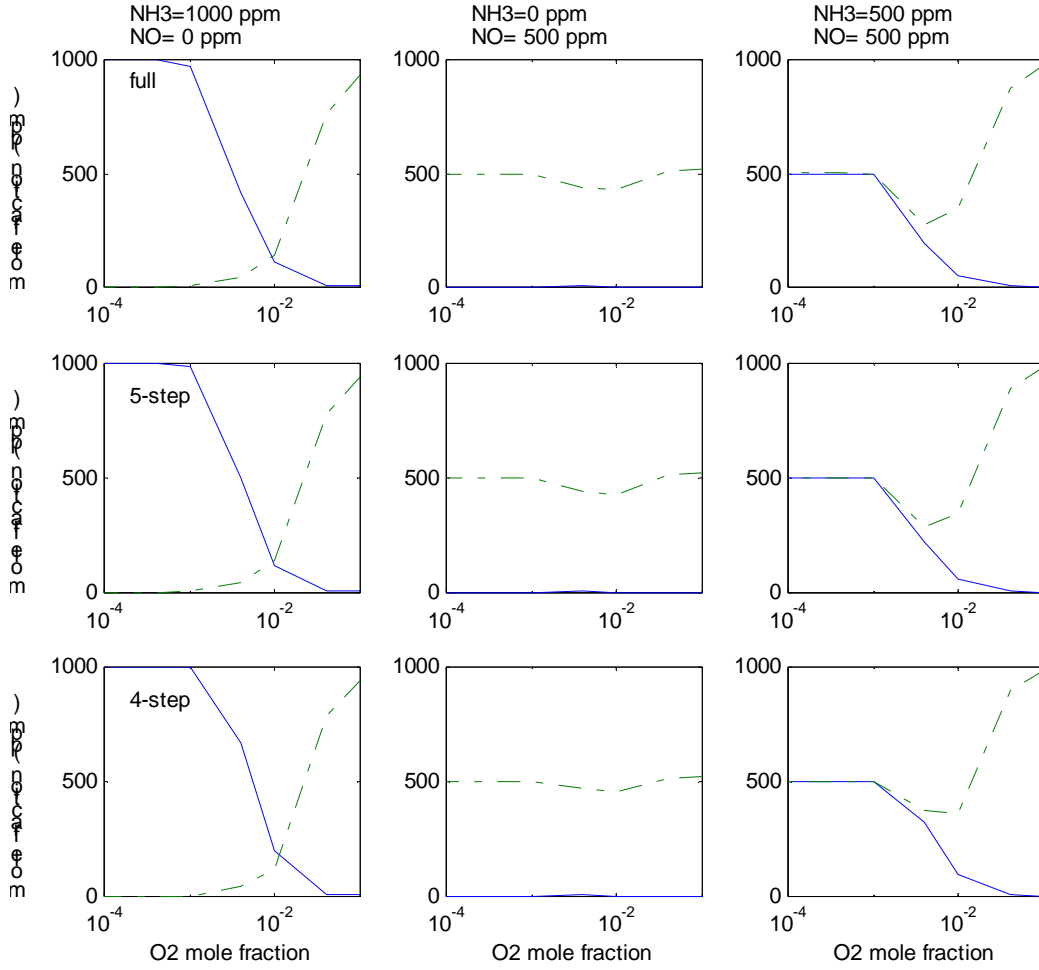
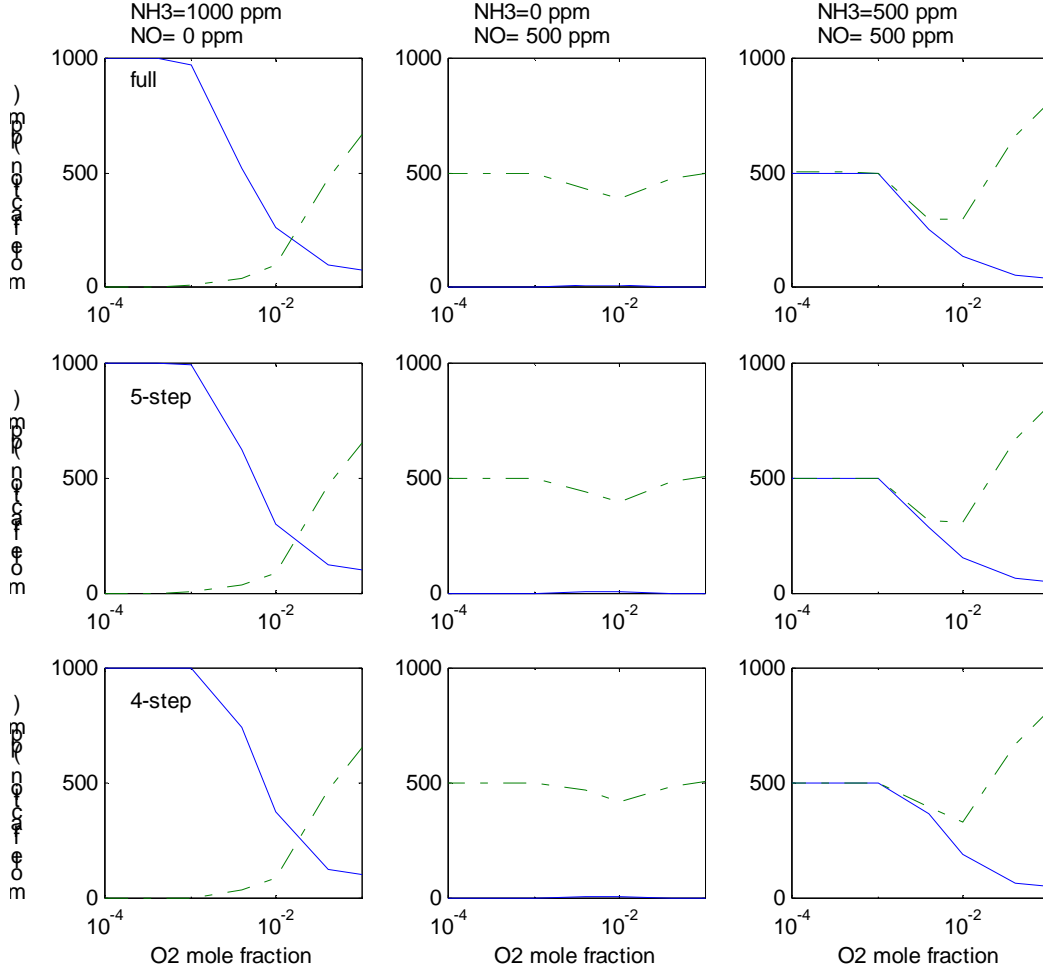*Figure 4. NO mole fraction (dash-dotted line) and NH₃ mole fraction (full line) as a function of O₂ mole fraction at the inlet of an adiabatic PSR with a 1 ms residence time. The temperature at the inlet of the PSR was 1100 K. The inlet concentrations of NO and NH₃ are indicated in the top of the figure. $O_2 = 10^{-4}$ corresponds to $\lambda=0.02$ and $O_2 = 10^{-1}$ corresponds $\lambda=20$.*

In the isothermal "post gas" evaluation set the chemistry was almost frozen below 1300 K. At 1100 K the detailed mechanism predicted some reaction between NH₃ and NO, which the reduced mechanism the reaction rate was almost negligible. At higher temperatures the agreement improves. Figure 5 shows results from the 1300 K calculations. The 5-step mechanism is in good agreement with the full mechanism at all conditions that were investigated. The trend that the 4-step mechanism performed less satisfactorily than the 5-step at low O₂ levels was also confirmed at the post gas conditions. Once again, largest discrepancy occurred at $\tau=10$ ms.
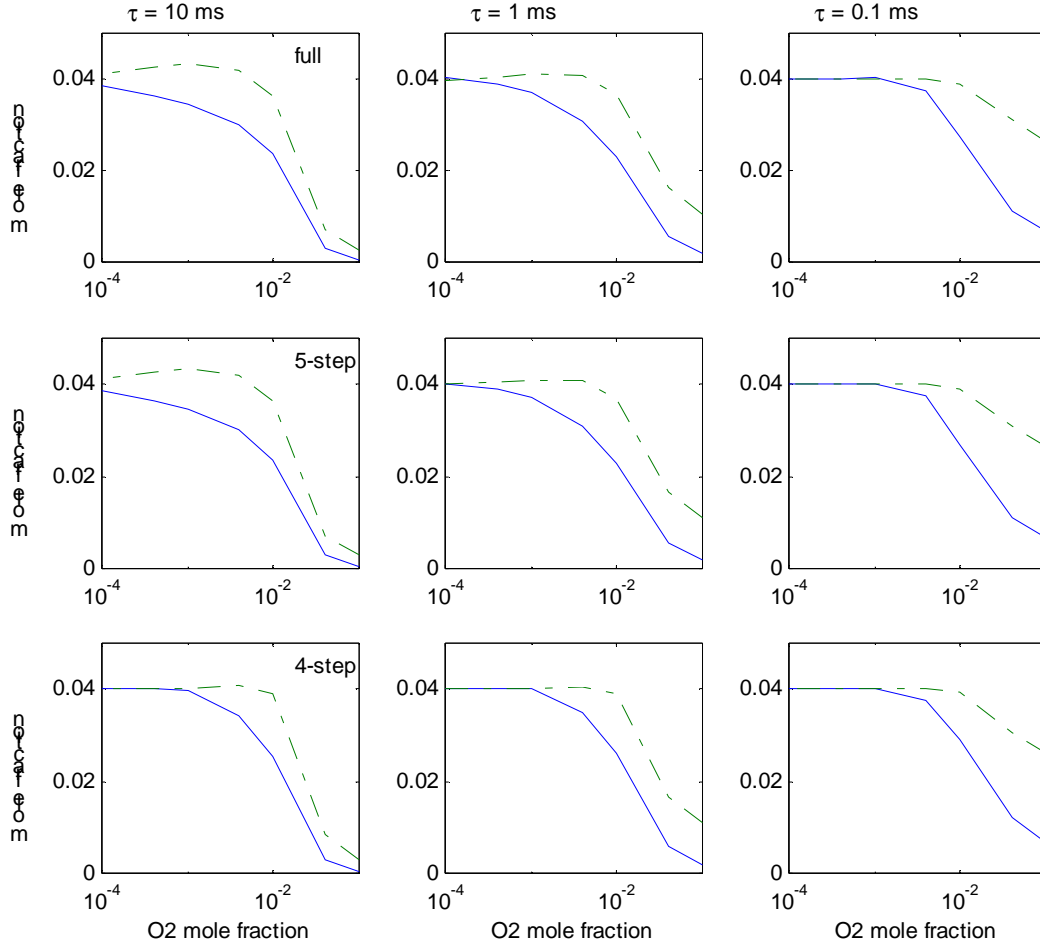
22
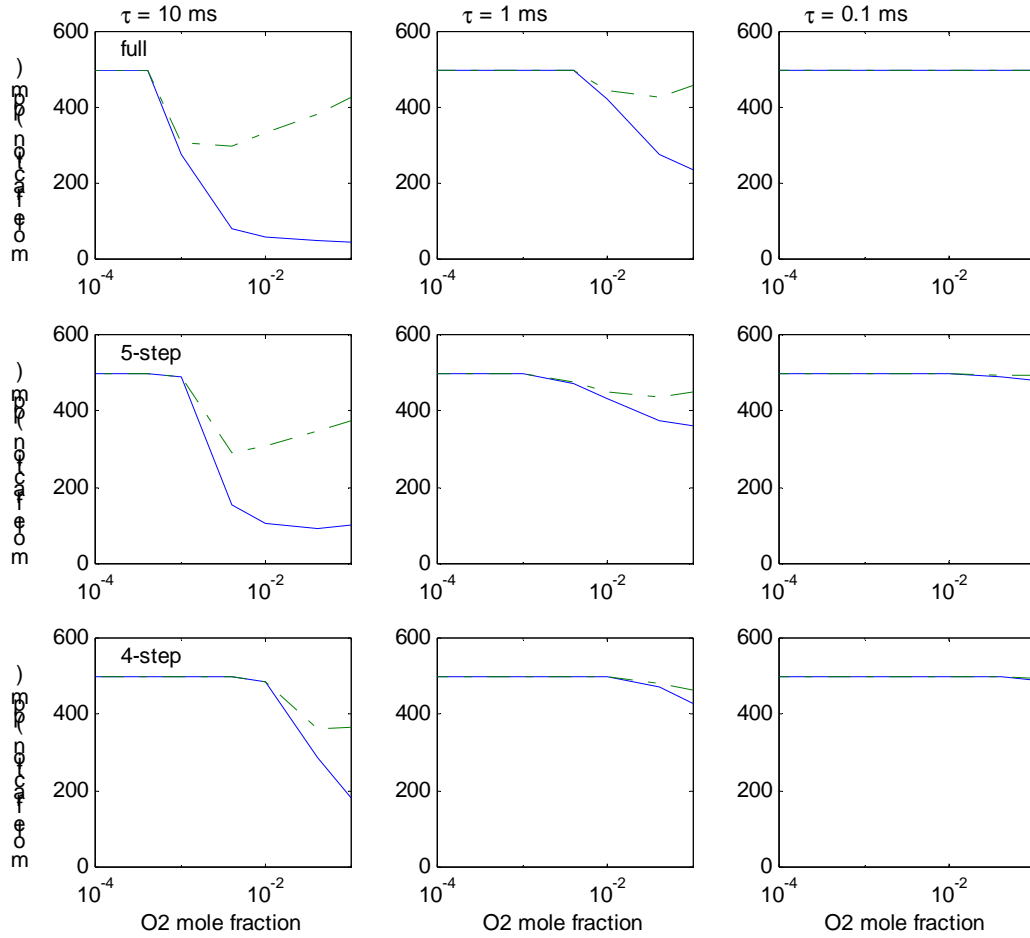
Figure 5. NO mole fraction (dash-dotted line) and NH₃ mole fraction (full line) as a function of O₂ mole fraction at the inlet of an isothermal PSR. The temperature of the PSR was 1300 K. The top column shows result obtained with a detailed mechanism, the middle column with a 5-step reduced mechanism and the bottom with a 4-step reduce mechanism. The left, middle and right row show results for τ=10 ms, τ=1 ms, and τ=0.1 ms, respectively. In all cases the inlet stream contained 500 ppm NO and 500 ppm NH₃.

5. Achieved speed-up of calculations

One reason for using reduced mechanisms is that a speed-up of the calculations is anticipated. To test the speed up, a single calculation with the PSR-code was performed. The CPU-need for the whole calculation was recorded. This included, e.g. the calculation of the initial guess, so this value should only be taken as an indication of the trend. However, the results were surprising in that the use of the 5-step mechanism only lead to a factor of 2 speed-up and the 4-step mechanism to a factor of 4 speed-up. This speed-up is in line with the linear speed up in term with the number of species in the reduced mechanism and the full mechanism as reported by Somers and de Goey [25] and Massias *et al.* [18]. Massias *et al.* [18] reported that for a laminar diffusion flame calculation approximately 90% of the CPU time per Newton iteration was taken by calculations of the steady state species.

Although the difference in the speed up between 4-step mechanism and the 5-step mechanism was not dramatic, it is likely that the 4-step mechanism will be the more adequate to use in CFD calculations of turbulent combustion devices. This, despite the superior description obtained with the 5-step mechanism. The reason for this is that an advanced enough turbulence-chemistry interaction model cannot probably be used for most technical applications, which is a prerequisite for a realistic description of highly reactive radicals such as the H-radical in the transport equations. As important as the speed-up is the reliability of the calculations. During the evaluation of the reduced mechanism it was found that the 4-step mechanism and the 5-step mechanism were numerically more stable than the detailed mechanism. Especially in the adiabatic PSR calculations the detailed mechanism caused numerical problems. Least numerical problems were encountered at with the 4-step mechanism.

6. CARM-code skeletal mechanism

The skeletal mechanism produced with the CARM code seems to include more reactions than necessary. For example, at the conditions used as the basis for the

development of the reduced mechanism, thermal-NO is of minor importance. Nevertheless, the reactions needed to describe thermal-NO formation are included in the reduced mechanism proposed by the CARM-code. To test possibilities to automatically produce reduced mechanisms the principal component analysis of the rate sensitivity matrix as proposed by Tomlin *et al*. [4] was tested. The calculations were performed using MATLAB®; i.e. the calculations are performed using the description of the method given by Tomlin *et al.* [4]. Modifications to the PSR-code where made such that the log-normalized rate sensitivity matrix where calculated in the CKWYP-routine. The skeletal mechanism was established for the conditions referred to as "base case II" in Table 1. First a skeletal mechanism was computed using the CARM-code. This consisted of 21 species taking part in 61 reactions. The following formal reactions were included in the reduced mechanism obtained using this skeletal mechanism

$$NH_3 + NO = H + H_2O + N_2$$
$$1\ 1/2\ NH_3 + 1\ 1/2\ NO + 1/2\ H + 1/2\ O_2 = 2\ 1/2\ H_2O + 1\ 1/2\ N_2$$
$$1/2\ H + 1\ 1/2\ H_2O + 1/2\ N_2 = 1/2\ NH_3 + 1/2\ NO + H_2 + 1/2\ O_2$$
$$O_2 + N_2 = 2\ NO$$
$$1/2\ H + 1/2\ O_2 + 1/2\ H_2O + CO + 1/2\ N_2 = 1/2\ NH_3 + 1/2\ NO + CO_2$$
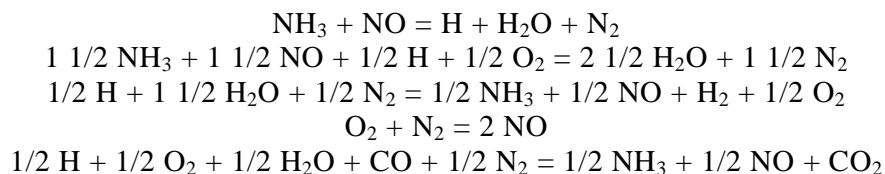
Then all reactions of the original mechanism where the 21 species identified by the CARM-code as necessary species are involved were used to form a new starting mechanism. Using this mechanism the method outlined by Tomlin *et al*. [4] was used to establish a skeletal mechanism. This resulted in a skeletal mechanism consisting of only 39 reactions. With the CARM code a reduce mechanism using this skeletal mechanism was established. The following formal reactions were obtained

$$NH_3 + H + O_2 = NO + H_2 + H_2O$$
$$2\ H = H_2$$
$$1\ 1/3\ H + 1/3\ O_2 = 2/3\ H_2O$$
$$1/3\ O_2 + 1/3\ H_2O + CO = 2/3\ H + CO_2$$
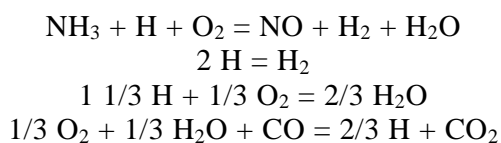
The mechanism was evaluated using the "pyrolysis gas" cases. It was found that the validity range of the reduced mechanism was very limited as compared to those obtained when the skeletal mechanism was produced with the CARM-code. For example, no thermal-NO path is included in the description of the chemistry.

However, the mechanism was computationally very stable and was able to well reproduce the results obtained with the skeletal mechanism it was based on. The results confirmed that the skeletal mechanism produced with the CARM-code is not a pure skeletal mechanism. On the other hand, as long as a stabile reduced mechanism is obtained, the "too" wide applicability range is only beneficial.

7. Conclusions

Reduced mechanisms able to describe the faith of ammonia at conditions typical of biomass combustion have been developed. The number of species in the reduced mechanisms was kept at a minimum since the result should be possible to use in CFD calculations. Based on the results obtained here, an 8-species 4-step reduced mechanism can be recommended since in this one no transport equations are needed for highly reactive radicals.

- The automatic construction of a reduced mechanism for biomass combustion systems can successfully be performed.
- Using the CARM-code the skeletal included more reactions than necessary. As long as the reaction mechanism is numerically stabile this only broadens its applicability range
- The reduced mechanisms where the CO oxidation was coupled with the nitrogen chemistry were computationally unstable. The reason for this could not be revealed.
- A 5-step mechanism performed well for all investigated conditions. The 4-step were not able to catch the chemistry in detail, but the result was satisfactorily, especially at residence time of 1 ms and below.
- The speed up of the calculations was only modest. A probable reason for this is that the calculations of the concentrations of the quasi-steady state species require a substantial computational effort.
- The proposed 4-step reduced mechanism and 5-step reduced mechanism was numerically more stabile than the full mechanism for PSR calculations.

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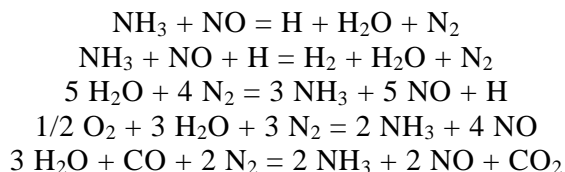
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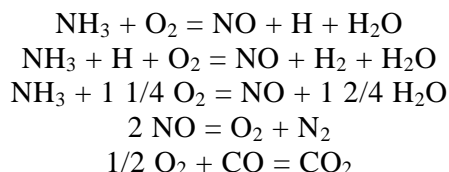
Appendix 1

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ELEMENTS
O H C N
END
SPECIES
  NH3  N2O  NO2  NO
  H  O  OH  H2  O2  HO2  H2O  H2O2
  CO CO2
  N NH NH2 NNH N2H2 N2H3 N2H4
  HNO HONO NO3 H2NO N2
END
!**********************************************************
!*            The NH3/NO/O2 System                       *
!*            a: IJCK paper (1994)                        *
!*            b: IJCK paper (1995)                        *
!*            c: Bodenstein (1995)                        *
!**********************************************************
REACTIONS
! *** NH3 Reactions ***
NH3+M = NH2+H+M            2.2E16   0    93470 ! a
NH3+H = NH2+H2            6.4E05  2.39  10171 ! a
NH3+O = NH2+OH            9.4E06  1.94   6460 ! a
NH3+OH = NH2+H2O         2.0E06  2.04    566 ! a
NH3+HO2 = NH2+H2O2       3.0E11   0    22000 ! a
! *** NH2 Reactions ***
NH2+H = NH+H2            4.0E13   0     3650 ! a
NH2+O = HNO+H            6.6E14 -0.5      0 ! a
NH2+O = NH+OH            6.8E12   0        0 ! a
NH2+OH = NH+H2O         4.0E06  2.0   1000 ! a
NH2+HO2 = H2NO+OH       5.0E13   0        0 ! a
NH2+HO2 = NH3+O2        1.0E13   0        0 ! a
H2NO+O = NH2+O2         2.0E14   0        0 ! c
NH2+NH2= N2H2+H2        8.5E11   0        0 ! a
NH2+NH2= NH3+NH         5.0E13   0    10000 ! a
NH2+NH2(+M)=N2H4(+M)    1.5E13   0        0 ! a
   LOW/1.0E18 0 0/
   N2/2.5/  H2O/5/  NH3/10/
NH2+NH = N2H2+H         5.0E13   0        0 ! a
NH2+N  = N2+2H          7.0E13   0        0 ! a
NH2+NO = NNH+OH        8.9E12 -0.35      0 ! c
NH2+NO = N2+H2O        1.3E16 -1.25      0 ! a
DUP
NH2+NO = N2+H2O       -8.9E12 -0.35      0 ! c
DUP
NH2+NO2 = N2O+H2O      3.2E18 -2.2       0 ! a
NH2+NO2 = H2NO+NO      3.5E12   0        0 ! b
! *** NH and N Reactions ***
NH+H = N+H2            3.0E13   0        0 ! a
NH+O = NO+H            9.2E13   0        0 ! a
NH+OH = HNO+H          2.0E13   0        0 ! a
NH+OH = N+H2O          5.0E11  0.5    2000 ! a
NH+O2 = HNO+O          4.6E05  2.0    6500 ! a
NH+O2 = NO+OH          1.3E06  1.5     100 ! a
NH+N = N2+H            3.0E13   0        0 ! a
NH+NH = N2+2H          2.5E13   0        0 ! a
NH+NO = N2O+H          2.9E14 -0.4       0 ! a
DUP
NH+NO = N2O+H         -2.2E13 -0.23      0 !
DUP
NH+NO = N2+OH          2.2E13 -0.23      0 ! a
NH+NO2 = N2O+OH        1.0E13   0        0 ! a
N+OH = NO+H            3.8E13   0        0 ! a
N+O2 = NO+O            6.4E09  1.0    6280 ! a
N+NO = N2+O            3.3E12  0.3       0 ! a
! *** NO Reactions ***
NO+O+M = NO2+M         7.5E19 -1.41      0 ! b
   N2/1.7/  O2/1.5/  H2O/10/
NO+OH+M = HONO+M       5.0E23 -2.51   -68  ! b
   N2/1.0/  H2O/5.0/
NO+HO2 = NO2+OH        2.1E12   0     -480 ! a
! *** Consumption of NO2 ***
NO2+H = NO+OH          8.4E13   0        0 ! b
NO2+O = NO+O2          3.9E12   0     -238 ! b
NO2+O(+M) = NO3(+M)    1.3E13  0.00      0 ! b
   LOW/1.0E28 -4.08 2470/
   N2/1.5/ O2/1.5/ H2O/18.6/
NO2+NO2 = NO+NO+O2     1.6E12   0    26123 ! b
NO2+NO2 = NO3+NO       9.6E09  0.73 20900 ! b
! *** Reactions of HNO, HONO, H2NO, NO3 ***
HNO+M = H+NO+M         1.5E16   0    48680 ! a
   H2O/10/ O2/2/ N2/2/ H2/2/
HNO+H = NO+H2          4.4E11  0.72   650 ! a
HNO+O = NO+OH          1.0E13   0        0 ! a
HNO+OH = NO+H2O        3.6E13   0        0 ! a
HNO+O2 = NO+HO2        1.0E13   0    25000 ! a
HNO+NH2= NO+NH3        2.0E13   0     1000 ! a
HNO+NO = N2O+OH        2.0E12   0    26000 ! a
HNO+NO2 = HONO+NO      6.0E11  0.00  2000 ! b
HNO+HNO = N2O+H2O      4.0E12   0     5000 ! a
HONO+H = NO2+H2        1.2E13  0.0   7350 ! b
HONO+O = NO2+OH        1.2E13  0.0   6000 ! b
HONO+OH = NO2+H2O      4.0E12   0        0 ! b
HONO+NH = NH2+NO2      1.0E13   0        0 ! b
HONO+NH2 = NH3+NO2     5.0E12   0        0 ! b
HONO+HONO=NO+NO2+H2O   2.3E12   0     8400 ! b
H2NO+M = HNO+H+M       2.5E16   0    50000 ! c
H2NO+H = HNO+H2        3.0E07  2.0   2000 ! a
H2NO+H = NH2+OH        5.0E13   0        0 ! a
H2NO+O = HNO+OH        3.0E07  2.0   2000 ! a
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H2NO+OH = HNO+H2O         2.0E07  2.0   1000 ! a
H2NO+NO = HNO+HNO         2.0E07  2.0  13000 ! a
H2NO+NH2 = HNO+NH3        3.0E12   0    1000 ! a
H2NO+NO2 = HONO+HNO       6.0E11  0.00  2000 ! b
NO3+H = NO2+OH            6.0E13  0.0      0 ! b
NO3+O = NO2+O2            1.0E13  0.0      0 ! b
NO3+OH = NO2+HO2          1.4E13  0.0      0 ! b
NO3+HO2 = NO2+O2+OH       1.5E12  0.0      0 ! b
NO3+NO2 = NO+NO2+O2       5.0E10  0.00  2940 ! b
! *** N2-amine Subset ***
N2H4+H = N2H3+H2          1.3E13   0    2500 ! a
N2H4+O = N2H2+H2O         8.5E13   0    1200 ! a
N2H4+OH = N2H3+H2O        4.0E13   0       0 ! b
N2H4+NH2 = N2H3+NH3       3.9E12   0    1500 ! a
N2H3+M = N2H2+H+M         3.5E16   0   46000 ! a
N2H3+H = NH2+NH2          1.6E12   0       0 ! a
N2H3+O = N2H2+OH          5.0E12   0    5000 ! a
N2H3+O = NH2+HNO          1.0E13   0       0 ! a
N2H3+OH = N2H2+H2O        1.0E13   0    1000 ! a
N2H3+OH = NH3+HNO         1.0E12   0   15000 ! a
N2H3+NH = N2H2+NH2        2.0E13   0       0 ! a
N2H2+M = NNH+H+M          5.0E16   0   50000 ! a
   H2O/15.0/  H2/2.0/  N2/2.0/  O2/2.0/
N2H2+H = NNH+H2           5.0E13   0    1000 ! a
N2H2+O = NH2+NO           1.0E13   0    1000 ! a
N2H2+O = NNH+OH           2.0E13   0    1000 ! a
N2H2+OH = NNH+H2O         1.0E13   0    1000 ! a
N2H2+NH = NNH+NH2         1.0E13   0    1000 ! a
N2H2+NH2 = NNH+NH3        1.0E13   0    1000 ! a
N2H2+NO = N2O+NH2         3.0E12   0       0 ! a
NNH = N2+H                1.0E07   0       0 ! c
NNH+H = N2+H2             1.0E14   0       0 ! a
NNH+O = N2O+H             1.0E14   0       0 ! a
NNH+O = NH+NO             5.0E13   0       0 ! b
NNH+OH = N2+H2O           5.0E13   0       0 ! a
NNH+O2 = N2+HO2           2.0E14   0       0 ! c
NNH+O2 = N2+H+O2          5.0E13   0       0 ! c
NNH+NH = N2+NH2           5.0E13   0       0 ! a
NNH+NH2 = N2+NH3          5.0E13   0       0 ! a
NNH+NO = N2+HNO           5.0E13   0       0 ! a
! *** N2O Subset ***
N2O+M = N2+O+M            4.0E14   0   56100 ! a
   N2/1.7/ O2/1.4/ CO2/3.0/ H2O/12/  !
N2O+H = N2+OH             3.3E10   0    4729 ! b
DUP
N2O+H = N2+OH             4.4E14   0   19254 !
DUP
N2O+O = NO+NO             2.9E13   0   23150 ! a
N2O+O = N2+O2             1.4E12   0   10800 ! a
N2O+OH = N2+HO2           2.0E12   0   40000 ! b
! *** H2/O2 Subset ***
O+OH = H+O2               2.0E14 -0.40     0 ! a
O+H2 = OH+H               5.1E04  2.67  6290 ! a
OH+H2 = H2O+H             2.1E08  1.52  3450 ! a
OH+OH = H2O+O             4.3E03  2.70 -2486 ! a
H+OH+M = H2O+M            8.4E21 -2.00     0 ! a
   N2/2.6/ H2O/16.5/
O+O+M = O2+M              1.9E13   0   -1788 ! a
   N2/1.5/
H+H+M = H2+M              1.0E18 -1.0      0 ! a
   H2/0.0/ H2O/0/
H+H+H2 = H2+H2            9.2E16 -0.6      0 ! a
H+H+H2O = H2+H2O          6.0E19 -1.25     0 ! a
H+O+M = OH+M              6.2E16 -0.6      0 ! a
   N2/1.5/
H+O2+M = HO2+M            2.1E18 -1.0      0 ! a
   N2/0/ O2/1.5/ H2O/10.0/
H+O2+N2 = HO2+N2          6.7E19 -1.42     0 ! a
HO2+H = H2+O2             4.3E13   0    1411 ! a
HO2+H = OH+OH             1.7E14   0     875 ! a
HO2+H = O+H2O             3.0E13   0    1721 ! a
HO2+O = OH+O2             3.3E13   0       0 ! a
HO2+OH = H2O+O2           2.9E13   0    -497 ! a
HO2+HO2 = H2O2+O2         1.3E11   0   -1630 ! a
  DUP
HO2+HO2 = H2O2+O2         4.2E14   0   11980 ! a
  DUP
H2O2+M = OH+OH+M          1.3E17   0   45500 ! a
   N2/1.5/ O2/1.5/ H2O/10/
H2O2+H = H2O+OH           1.0E13   0    3576 ! a
H2O2+H = HO2+H2           1.7E12   0    3755 ! a
H2O2+O = HO2+OH           6.6E11   0    3974 ! a
H2O2+OH = H2O+HO2         7.8E12   0    1330 ! a
  DUP
H2O2+OH = H2O+HO2         5.8E14   0    9560 ! a
  DUP
! *** CO Subset ***
CO+O+M = CO2+M            6.2E14   0    3000
   N2/1.5/ O2/1.5/ H2O/16/
CO+OH = CO2+H            1.4E05  1.95  -1347
CO+HO2 = CO2+OH         6.0E13   0   22950
CO+O2 = CO2+O            2.5E12   0   47700
END
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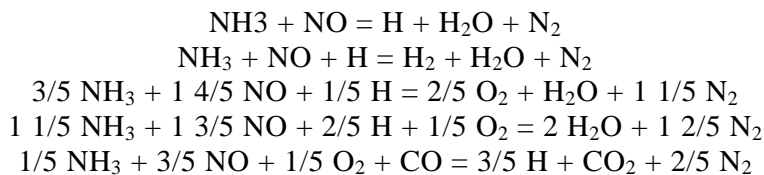
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Appendix 2

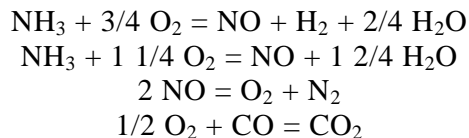**9-species, 5-reactions, (full mechanisms, δ=0.05):**

$$NH_3 + NO = H + H_2O + N_2$$
$$NH_3 + NO + H = H_2 + H_2O + N_2$$
$$5\ H_2O + 4\ N_2 = 3\ NH_3 + 5\ NO + H$$
$$1/2\ O_2 + 3\ H_2O + 3\ N_2 = 2\ NH_3 + 4\ NO$$
$$3\ H_2O + CO + 2\ N_2 = 2\ NH_3 + 2\ NO + CO_2$$

9-species, 5-reactions, (86-reaction and 25-species skeletal, δ=0.05):

$$NH_3 + O_2 = NO + H + H_2O$$
$$NH_3 + H + O_2 = NO + H_2 + H_2O$$
$$NH_3 + 1\ 1/4\ O_2 = NO + 1\ 2/4\ H_2O$$
$$2\ NO = O_2 + N_2$$
$$1/2\ O_2 + CO = CO_2$$

9-species, 5-reactions, (65-reaction and 22-species skeletal, δ=0.1):

$$NH3 + NO = H + H_2O + N_2$$
$$NH_3 + NO + H = H_2 + H_2O + N_2$$
$$3/5\ NH_3 + 1\ 4/5\ NO + 1/5\ H = 2/5\ O_2 + H_2O + 1\ 1/5\ N_2$$
$$1\ 1/5\ NH_3 + 1\ 3/5\ NO + 2/5\ H + 1/5\ O_2 = 2\ H_2O + 1\ 2/5\ N_2$$
$$1/5\ NH_3 + 3/5\ NO + 1/5\ O_2 + CO = 3/5\ H + CO_2 + 2/5\ N_2$$

8-species, 4-reactions, (86-reaction and 25-species skeletal, δ=0.05):

$$NH_3 + 3/4\ O_2 = NO + H_2 + 2/4\ H_2O$$
$$NH_3 + 1\ 1/4\ O_2 = NO + 1\ 2/4\ H_2O$$
$$2\ NO = O_2 + N_2$$
$$1/2\ O_2 + CO = CO_2$$

9-species, 4-reactions, (61-reaction and 21-species skeletal, δ=0.1):

$$NH_3 + NO = H + H_2O + N_2$$
$$1\ 1/2\ NH_3 + 1\ 1/2\ NO + 1/2\ H + 1/2\ O_2 = 2\ 1/2\ H_2O + 1\ 1/2\ N_2$$
$$1/2\ H + 1\ 1/2\ H_2O + 1/2\ N_2 = 1/2\ NH_3 + 1/2\ NO + H_2 + 1/2\ O_2$$
$$O_2 + N_2 = 2\ NO$$
$$1/2\ H + 1/2\ O_2 + 1/2\ H_2O + CO + 1/2\ N_2 = 1/2\ NH_3 + 1/2\ NO + CO_2$$
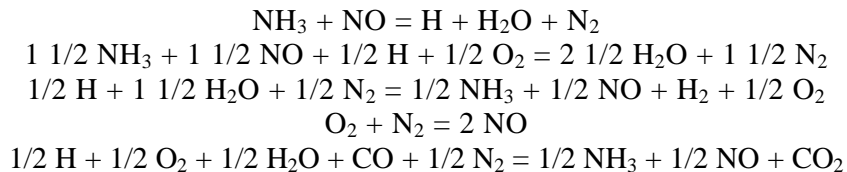
9-species, 4-reactions, (39-reaction and 21-species skeletal, PCA):

$$NH_3 + H + O_2 = NO + H_2 + H_2O$$
$$2\ H = H_2$$
$$1\ 1/3\ H + 1/3\ O_2 = 2/3\ H_2O$$
$$1/3\ O_2 + 1/3\ H_2O + CO = 2/3\ H + CO_2$$