

DEVELOPMENT AND IMPLEMENTATION OF REDUCED CHEMISTRY FOR COMPUTATIONAL FLUID DYNAMICS MODELING OF SELECTIVE NON-CATALYTIC REDUCTION

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The development of reduced chemistry for implementation in a turbulent reacting computational fluid dynamics (CFD) code for simulations of selective noncatalytic reduction (SNCR) performance in boilers and furnaces is discussed in this paper. To obtain realistic estimates of SNCR performance in large boilers and furnaces, it is important to couple together the important physical processes, heat transfer, reagent mixing, and finite rate chemistry in one simulation. Decoupling the mixing from the chemistry or oversimplification of the finite rate chemistry can lead to erroneous predictions of performance. Using an automated strategy, based on conventional reduced mechanism techniques, a 10-species reduced mechanism was developed based on conditions suitable for the application of lean SNCR with NH_3 or urea reagents. Comparisons between the detailed, reduced, and previously used global mechanisms demonstrated excellent agreement between the new 10-species reduced mechanism and the detailed chemistry on which it was based over a range of conditions appropriate for SNCR. The results also showed significant improvement over the previously used global mechanism. The 10-species reduced mechanism also was incorporated into a three-dimensional, turbulent reacting CFD code for simulation of industrial-scale SNCR systems. Comparisons with detailed chemistry in a simple plug flow geometry showed excellent agreement in predictions of NO reduction, NH_3 slip, as well as N_2O and H₂CO emissions. Comparisons between model predictions and data obtained in a pilot-scale furnace also showed good qualitative and quantitative agreement.

Introduction

Conditions for the selective noncatalytic reduction (SNCR) of NO to N_2 by ammonia in the presence of excess oxygen were first identified by Lyon nearly 25 years ago [1]. Since that time researchers have investigated the effectiveness of other reagents, such as urea [2] and cyanuric acid [3] and effects of process parameters such as temperature, residence time, normalized stoichiometric ratio (i.e., chemical N/ NO_x molar ratio, NSR), equivalence ratio, initial NO_x level, and various additives [4]. There has been significant industrial interest in SNCR as a low-cost, effective, and retrofittable NO_x control strategy. SNCR has demonstrated NO_x reduction capabilities from 25% to 75% over a range of industrial applications including (1) utility boilers, (2) refinery process units and industrial boilers, (3) municipal waste combustors, (4) wood-fired/co-gen plants, and (5) the chemical industry [5]. The variation in observed NO_x reduction capability depends on site-specific considerations and the amount of unreacted ammonia (ammonia slip) that is considered tolerable.

Although simple in concept, the design of actual SNCR installations can become quite complicated. Non-uniformities in velocity and temperature at the reagent injection location can pose operational difficulties because of the inherent sensitivity of the process to these parameters. The physical location of the optimal temperature window depends on operating factors such as unit load, fuel type, burner firing strategy, among others. Generally, these factors require the utilization of multiple injection elevations in full-scale systems, especially for those boilers or furnaces operated with a cycling load profile. There are also other balance-of-plant issues including (1) ammonia contamination of fly ash in coal-fired boilers, (2) air heater pluggage in regions of high ammonia slip, (3) formation of ammonium chloride plumes, and (4) the emission or production of undesirable byproducts, such as NH_3 or N_2O [6,7]. These are concerns that must be considered in the design and operation of an SNCR system.

In practical combustion systems, NO_x reduction efficiencies are primarily dependent on three factors: (1) mixing, (2) temperature, and (3) residence

time. Efficiencies increase when all three act in concert so that the reagent is fully mixed with the flue gas at optimum temperatures over a sufficient residence time. In practical combustion systems, severe design constraints are placed on the reagent injection system that must disperse the reagent throughout the entire combustion product stream while the gases are within the appropriate temperature window. Thus, the design of an SNCR injection system requires an analysis capability that takes into account the nonlinear coupling between these processes. Accurate representation of mixing, temperature, and residence time requires coupling between turbulent fluid mechanics, radiative and convective heat transfer, spray droplet dynamics, and gas-phase chemistry.

CFD-Based SNCR Model

Overview

In the Twenty-Sixth Symposium, Brouwer et al. [8] outlined the development and incorporation of a seven-step global mechanism for SNCR chemistry into a steady-state, three-dimensional, turbulent reacting, computational fluid dynamics (CFD) code (GLACIER) [9]. GLACIER fully couples reacting gases, solids, and liquids with turbulent mixing and radiative heat transfer. Coupling turbulence and heat transfer with finite-rate reaction chemistry requires the number of chemical kinetic steps to be relatively small. GLACIER uses a set of reduced kinetic steps for slow reactions and minimizes Gibbs free energy for all other species. Mean species concentrations, density, and temperature are calculated using an assumed probability density function (PDF) approach. One important difference between this model and other CFD-based SNCR models is that the SNCR chemistry is incorporated into and coupled with the CFD calculation.

Brouwer et al. used the seven-step global chemistry within GLACIER and compared predictions with new pilot-scale data. Effects of reagent composition, injection temperature, thermal quench rate, mixing rates, and CO concentration were examined, and the comparisons showed overall good agreement with measured data.

Application of SNCR Model to Large-Scale Systems

Following the incorporation of the seven-step global chemistry into GLACIER, a number of investigations of SNCR performance in coal-fired utility boilers have been conducted using GLACIER. These investigations have been used to assess expected performance of SNCR in particular boiler geometries and to aid in the design of actual SNCR

injection systems. Many boiler types and sizes have been investigated, including tangentially fired, wall-fired, cyclone-fired, and turbo-fired boilers ranging in size from 150 to 600 MW. In several of the studies, CFD simulations were combined with in-boiler measurements of temperature, CO, O₂ and NO_x, as well as cold flow measurements in subscale models to quantify effects of injection location on reagent mixing [10–12].

The overall results of these investigations indicated that NO_x reductions from 20% to 45% with less than an average of 5 ppm ammonia slip were possible. Conditions that limited the effectiveness of SNCR in these boilers included the following:

1. Existence of convective surfaces that limited reagent mixing
2. Large cross-sectional areas over which reagent needed to be mixed
3. Infeasibility of injector placement in “optimal” locations due to existing hardware
4. High furnace exit gas temperatures followed by fast temperature quench in the convective section

The advantage of the use of GLACIER over other commonly used models [13] for prediction of SNCR performance is the level of coupling that exists within the model. In particular, mechanisms controlling reagent mixing (i.e., turbulence, droplet dynamics) are coupled with the finite rate calculations of SNCR chemistry. The importance of coupling the calculations of reagent mixing with the finite rate chemistry has been observed, and it has been shown that poor mixing can result in lower NO reduction compared with ideal mixing [14].

The importance of this degree of coupling can be seen in Fig. 1, which shows calculations of NO_x reduction versus normalized stoichiometric ratio (NSR) for a 600 MW tangentially fired coal utility boiler [11]. The GLACIER results (with the incorporated seven-step global SNCR chemistry) show the range of predicted overall NO_x reductions in this boiler. These predictions are compared with corresponding CHEMKIN [15] calculations along computed streamlines originating in locations of urea release predicted in the GLACIER calculations. The time/temperature history along these representative streamlines was used within CHEMKIN calculations, assuming a specified initial NSR for urea. Both the seven-step global SNCR chemistry and the detailed chemistry on which it was based were used in these streamline calculations. Fig. 1 shows that for all of the streamlines chosen in the region of the urea release, the predicted NO_x reduction along the streamline was higher than that predicted in the GLACIER simulations at the same NSR. This difference highlights the role of mixing limitations on SNCR performance and the necessity of utilizing an analysis tool that couples mixing with chemistry.

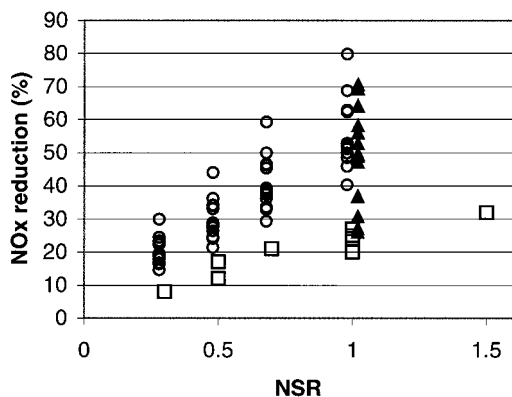


FIG. 1. Comparison of NO_x predictions using GLACIER (\square), seven-step global chemistry along streamlines (\circ), and detailed NO_x chemistry along streamlines (\blacktriangle) as a function of normalized stoichiometric ratio (NSR). Initial properties for the streamline calculations were based on the local conditions computed by the CFD model. The global and detailed calculations at $\text{NSR} = 1$ are offset only to distinguish the data.

An additional observation that can be made from Fig. 1 is the difference in predictions of NO_x reduction along the streamlines due to the chemical kinetics. Streamline calculations were performed using both detailed and global chemistry at $\text{NSR} = 1$. In the figure, the data are offset slightly along the abscissa from $\text{NSR} = 1$ to distinguish the symbols even though the calculations were indeed for $\text{NSR} = 1$. The difference in these results is a direct indication of inadequacies in the global chemistry in its representation of the detailed chemistry over the non-isothermal history of the streamlines.

Figure 1 motivates the remaining discussions in this paper that describe the method used to improve the reduced SNCR chemistry as well as the actual implementation procedure and results obtained with the new reduced chemistry.

Development of a Reduced Mechanism for SNCR

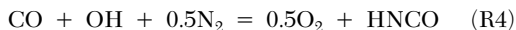
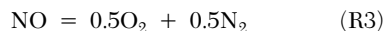
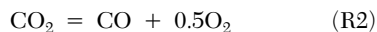
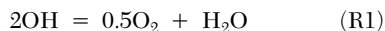
The detailed NO_x mechanism that we have been using to evaluate the kinetics governing reactions between ammonia or urea and coal flue gases containing NO_x is the mechanism of Miller and Bowman [16] with literature modification [17]. This detailed mechanism contains over 60 chemical species and 250 reversible elementary reactions [18]. Incorporation of this chemical mechanism into a CFD code, which would require the solution of transport equations for the same number of species that exist in the mechanism, is prohibitive from the standpoint of both CPU time and memory. Thus, a reduced description of the detailed chemistry is necessary.

The approach that we have taken is based on the assumption that certain species contained within the detailed mechanism are in steady state (i.e., rate of production equals rate of destruction) [19,20]. This is a more rigorous and universal approach than curve-fitting approaches that are often used to generate simple global mechanisms. Historically, reduced mechanism methods have been difficult to generate due to the amount of human time necessary in deriving them. To overcome this difficulty, we have been using an approach that automates the reduction process. The computer-assisted reduction method (CARM) [21,22] automates this process and produces FORTRAN source code for the calculation of the chemical source terms defined by the reduced mechanism. The inputs for the subroutine are pressure, temperature, and the mass fractions of the major species. The output is the instantaneous reaction rate for the major species.

To faithfully represent behavior in the furnace corresponding to fuel-rich or fuel-lean NH_3 (or urea) injection, the reduced mechanism must be robust enough to capture the kinetics of NO reduction/formation in both fuel-rich and fuel-lean regions with and without the presence of NH_3 . Using CARM, we have constructed and evaluated several reduced mechanisms over a wide range of conditions. CARM uses a set of input test problems (perfectly stirred reactor [PSR] solutions) to rank species by the errors, ε_i , introduced by assuming they are in steady state. This error is evaluated by the expression

$$\varepsilon_i = X_i \frac{|\omega_i^p - \omega_i^c|}{\max(|\omega_i^p|, |\omega_i^c|)} \quad (1)$$

where ω_i^p and ω_i^c are, respectively, the rates of production and consumption for species i , and X_i is the mole fraction. To create reduced mechanisms for modeling SNCR chemistry, fixed temperature PSR solutions covering the range of temperatures (1100–1700 K) and flue gas stoichiometric ratios (1–1.5, lean conditions) were obtained, where the stoichiometric ratio is defined as the inverse of the fuel equivalence ratio. A number of reduced mechanisms were developed and tested, utilizing an imposed error criterion of $\varepsilon_i = \times 10^{-7}$. Although the test problems utilized by CARM are based on PSR solutions, the resulting reduced mechanisms were tested under both PSR and plug flow reactor (PFR) conditions. A six-step reduced mechanism retaining 10 major species (48 species in steady state) was found to give excellent agreement with the detailed chemistry. The six steps of this reduced mechanism are



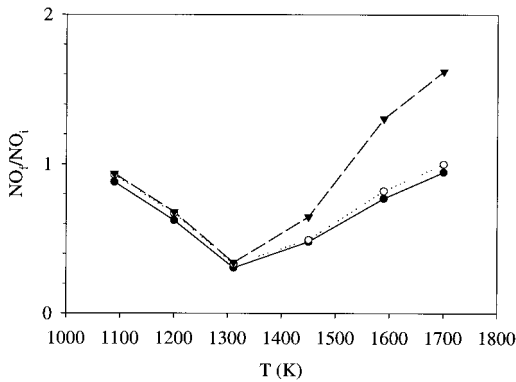


FIG. 2. Comparison of isothermal plug flow calculations in CHEMKIN using seven-step global (\blacktriangledown), 10-species reduced (\circ), and detailed (\bullet) chemistry versus gas temperature for a residence time of 0.1 s. The initial flue gas composition was that of equilibrated coal products with 3% O₂, 300 ppm NO, 150 ppm NH₃ and, 150 ppm HNCO.

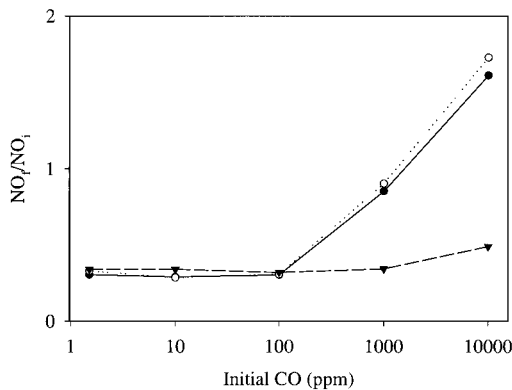
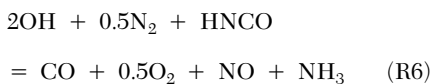
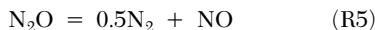


FIG. 3. Comparison of isothermal plug flow calculations in CHEMKIN using seven-step global (\blacktriangledown), 10-species reduced (\circ), and detailed (\bullet) chemistry versus initial CO concentration for a residence time of 0.1 s. Initial flue gas composition corresponded to that of equilibrated coal products with 3% O₂, but varying levels of CO from 2 to 10,000 ppm, 300 ppm NO, 150 ppm NH₃, and 150 ppm HNCO at $T = 1311$ K.



The steady-state species, although not shown in the six-step mechanism, play a direct role in the computation of the chemical reaction rates of the 10 major species, which are computed by CARM.

Figures 2 and 3 compare results in an isothermal PFR configuration representing urea injection into

a typical lean flue gas composition. Results using detailed, reduced, and seven-step global chemistry are compared. For these calculations, it was assumed that urea decomposes into equal parts NH₃ and HNCO. Fig. 2 shows that the 10-species reduced mechanism gives excellent agreement with the detailed chemistry over the SNCR temperature window, while the global model fails for temperatures above 1300 K. Fig. 3 makes a similar comparison between detailed, reduced, and global chemistry with variation in the initial CO concentration in the flue gas. Again, the global model works well over the narrow range of conditions for which it was developed, but it is unable to predict the increase in NO at higher CO concentrations that is accurately predicted by both the reduced and detailed mechanisms. Similar improvement over the global model was found when varying initial O₂ and NO concentrations, as well as the NSR. Other species of interest such as NH₃, HNCO, and N₂O (not shown) show similar agreement between the reduced and detailed chemistry and similar improvement over the global model. The reduced mechanism has also been found to yield excellent results under fuel-rich conditions.

Implementation in a CFD Model

The following four primary issues were addressed regarding implementation of the reduced mechanism:

1. Calculation of chemical reaction rates for major species
2. Accounting for turbulence/chemistry interaction in calculation of mean reaction rates
3. Solution of additional transport equations for the major species
4. Addressing numerical "stiffness" problems associated with solution of new transport equations

The CPU time required by the reduced mechanism can become expensive when it is integrated into a CFD code and used for predictions in a full-scale application. In a "postprocess" implementation, in which the temperature and velocity fields are assumed fixed, the calculation of the chemical reaction rates can take up to 80% of the total CPU time of the simulation. Of this time, about 90% is spent on converging the steady-state species concentrations, and about 10% is spent on calculating the elementary forward and backward reaction constants. The time needed to converge the steady-state species concentrations depends on the number of steady-state species, the initial guess, the convergence criteria, and the iteration method. The use of good initial guesses for the steady-state species concentrations, for example, can significantly reduce the overall CPU time required.

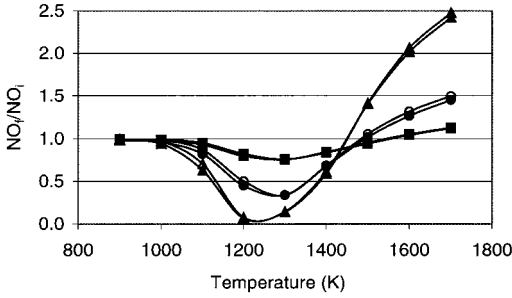


FIG. 4. Comparison of NO_x predictions for isothermal plug flow with initial coal flue gas composition CO_2 : 14.19%, H_2O : 12.43%, N_2 : 70.46%, O_2 : 2.89%, NO_i : 200 ppm, $\text{NH}_3/\text{NO}_i = 0.3, 1.0, \text{ or } 3.0$ at residence time 0.2 s (■ ~ detailed with NSR = 0.3, □ ~ reduced with NSR = 0.3, ● ~ detailed with NSR = 1.0, ○ ~ reduced with NSR = 1.0, ▲ ~ detailed with NSR = 3.0, △ ~ reduced with NSR = 3.0).

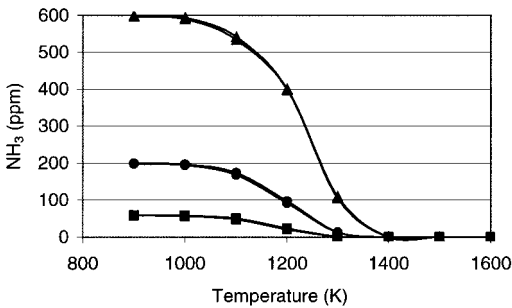


FIG. 5. Comparison of NH_3 slip predictions for the same conditions as in Fig. 4.

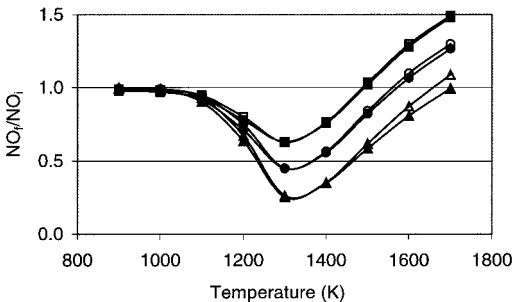


FIG. 6. Comparison of NO_x predictions for isothermal plug flow with initial composition CO_2 : 14.19%, H_2O : 12.43%, N_2 : 70.46%, O_2 : 2.89%, NO_i : 100ppm, 200ppm, or 500 ppm, urea/ NO_i :0.5 at residence time 0.2 s (■ ~ detailed with $\text{NO}_i = 100$ ppm, □ ~ reduced with $\text{NO}_i = 100$ ppm, ● ~ detailed with $\text{NO}_i = 200$ ppm, ○ ~ reduced with $\text{NO}_i = 200$ ppm, ▲ ~ detailed with $\text{NO}_i = 500$ ppm, △ ~ reduced with $\text{NO}_i = 500$ ppm).

Since the rates of reaction associated with the SNCR chemistry are the same order of magnitude as the rates of turbulent mixing, the effects of turbulence can have a significant effect on the mean rates of chemical reaction. Based on the approach developed by Smoot and Smith [23], GLACIER uses an assumed PDF approach to account for the effects of turbulence. The mean reaction rates ($\bar{\omega}_i$) for turbulent reacting gases are approximated by convoluting the instantaneous rates over the mixture fraction PDFs, as shown in equation 2:

$$\bar{\omega}_i = \bar{p} \int_f \int_{\eta} \frac{\omega_i(f, \eta, h)}{\rho(f, \eta, h)} \tilde{P}(f) \tilde{P}(\eta) d\eta df \quad (2)$$

where f and η represent two mixture fraction variables used within GLACIER and \sim denotes Favre averaging. This PDF approach is extremely CPU intensive and can require up to approximately a factor of 20 to 25 times increase in CPU time over the assumption of laminar chemistry (not accounting for turbulence effects on the mean reaction rates).

The addition of transport equations for the new species is a relatively straightforward procedure. However, the stiffness associated with the chemical reaction rates can cause some difficulty in converging the new transport equations. In the current approach, only six species transport equations (CO , OH , NO , N_2O , HNC O , and NH_3) are solved with chemical source terms, while the other four species in the reduced mechanism (CO_2 , O_2 , H_2O , and N_2) are calculated through the principle of conservation of atoms. The use of conservation of atoms reduces the number of transport equations that must be solved and improves the overall convergence of the remaining transport equations.

Application to Simple Plug Flow Geometry

To compare the reduced SNCR mechanism implemented in GLACIER with the detailed chemistry on which it was based, plug flow calculations over a range of conditions were performed. The detailed chemistry calculations were performed in CHEMKIN, while the GLACIER calculations were performed in a pipe flow geometry under the same conditions. Fig. 4 shows the comparisons over a range of temperatures and NSRs utilizing NH_3 as the SNCR reagent. Fig. 5 shows the corresponding calculations of NH_3 slip for the same conditions as in Fig. 4. The agreement between the GLACIER calculations and the detailed chemistry calculations is quite remarkable; note that in Fig. 5, the results are nearly indistinguishable. Fig. 6 shows a similar comparison using urea reagent for three different initial NO levels. Again, agreement is extremely good. Note that the effect of reduction in the initial NO , seen in Fig. 6, is to decrease the maximum NO removal and to reduce the optimal temperature where

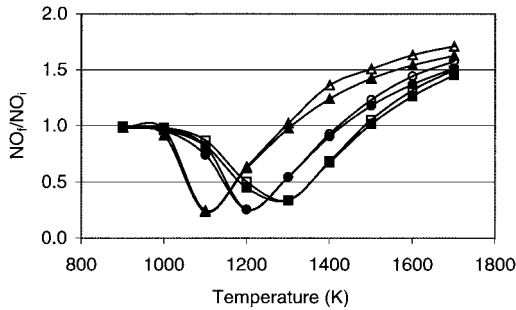


FIG. 7. Comparison of NO_x predictions for isothermal plug flow with initial composition CO₂: 14.19%, H₂O: 12.43%, N₂: 70.46%, O₂: 2.89%, NO: 200 ppm, NH₃/NO_i: 1.0, CO: 0 ppm, 100 ppm, 500 ppm at residence time 0.2 s (■ ~ detailed with CO = 0 ppm, □ ~ reduced with CO = 0 ppm, ● ~ detailed with CO = 100 ppm, ○ ~ reduced with CO = 100 ppm, ▲ ~ detailed with CO = 500 ppm, △ ~ reduced with CO = 500 ppm).

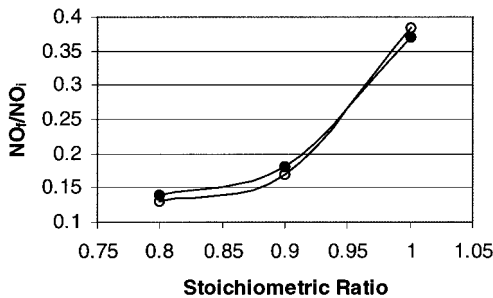


FIG. 8. Comparison of NO_x predictions for isothermal plug flow under fuel-rich (coal) conditions, $T = 1800$ K, with urea/NO_i: 1.0, NO_i = 600 ppm, at a residence time 0.5 s (● ~ detailed, ○ ~ reduced).

NO removal is a maximum, in agreement with reported data [24]. Fig. 7 shows similar comparisons over a range of CO levels. The reduced chemistry performs very well in capturing the effect of increased CO in both lowering and narrowing the SNCR temperature window. Comparisons with NH₃, HNCO, and N₂O concentrations show similar agreement. Comparisons also show excellent agreement under fuel-rich conditions as shown in Fig. 8.

Application to Pilot-Scale Test Facility

To compare predictions of the new model with measurements made under industrial conditions, small pilot-scale experiments were conducted in a 29 kW refractory lined furnace (16 cm in diameter, 7.3 m in length). Brouwer [8] and Heap [25] previously reported results of SNCR measurements in this facility.

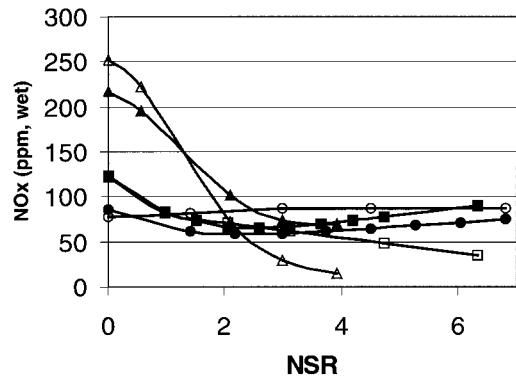


FIG. 9. Comparison of measured (solid symbols) and predicted (open symbols) furnace outlet NO_x concentrations with NH₃ injection in the fuel-rich region of the furnace upstream of the burnout of the burner addition. Comparisons are made for stoichiometric ratios of 0.90 (●), 0.95 (■), and 1.00 (▲) over a range of NSRs.

NH₃ was injected with N₂ carrier through a 1.25 cm water-cooled stainless steel injector located on the chamber axis. This stream was injected into the hot (1700 K), fuel-rich combustion products downstream of the natural gas burner, similar to the application described by Brogan [26]. The burner stoichiometric ratio was varied from 0.90 to 1.00, and burnout air was added approximately 2.2 meters downstream of the NH₃ injection to bring the combustion products to a stoichiometric ratio of 1.15 upstream of the furnace exit. Experiments were conducted over a range of NSRs based on the measured outlet NO in the absence of NH₃ injection for each burner stoichiometric ratio. The measured outlet NO, in the absence of NH₃ injection, varied from a minimum of 104 ppm to a maximum of 263 ppm for burner stoichiometries of 0.90 and 1.0, respectively.

Figure 9 shows a comparison between the predicted outlet NO values and those measured in the furnace. The overall agreement is quite good, with the model predictions showing the same behavior of NO versus NSR as was measured. In addition to the measured difference in initial NO as a function of burner stoichiometric ratio, the average gas temperature was measured to be 50 K higher in the NH₃ injection region under stoichiometric conditions than existed at 0.9. As a result, the model results showed significantly higher NO reduction under stoichiometric conditions than under the two fuel-rich conditions, in agreement with the measurements. Although this trend is opposite to that observed in Fig. 8, the reduced temperature and reduced initial NO both would favor decreased NO reduction. Nevertheless, the model results compare very well with the measured data under these conditions.

Conclusions

Practical constraints such as imperfect reagent dispersion, non-uniform and non-isothermal temperature profiles, and local flue gas composition can have a significant effect on SNCR performance in industrial furnaces and boilers. The heat transfer, extent of mixing, and finite rate chemistry control the effectiveness of SNCR. Since these controlling mechanisms are tightly coupled, it is important that predictions of SNCR performance take it into account. Decoupling the mixing from the chemistry can significantly impact the predictions. However, oversimplification of the finite rate chemistry also can lead to erroneous predictions.

To develop an improved description of reduced SNCR chemistry, an automated strategy that utilizes conventional reduced mechanism techniques to reduce detailed chemical mechanisms (CARM) was utilized in this study. Using CARM, a 10-species reduced mechanism describing SNCR chemistry within both the fuel-rich and fuel-lean regions of a furnace was developed and implemented into a CFD-based turbulent reacting flow code (GLACIER). Comparisons with detailed chemistry calculations showed that the reduced mechanism is able to represent the detailed chemistry over a much wider range of conditions than was previously obtained with a seven-step global mechanism. Effects of gas temperature, CO concentration, initial NO concentration, and local stoichiometry on NO and NH₃ concentrations were represented very well in a simple plug flow geometry. CFD model predictions using the reduced mechanism also compared very well with measured pilot-scale data under fuel-rich conditions.

Acknowledgments

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COMMENTS

Hakan Serhad Soyhan, Lund University, Sweden.

1. What kind of output do you get from the PIR calculations to reduce the mechanism?
2. How do you reduce your detailed mechanism?

Author's Reply. The PSR test problems are defined by the user and represent the range of conditions over which the reduced mechanism is intended for use. CARM uses these test problems to rank species by the error that is introduced by assuming they are in steady state. So, the desired outputs of the PSR calculations are the solutions themselves. Based on the error analysis (equation 1), the user chooses which species to retain in the reduced mechanism. All other species are assumed to be in steady state. This assumption is used, within CARM, to generate a set of nonlinear algebraic equations for the steady-state species concentrations, in terms of the non-steady-state species. The rate equations for the non-steady-state species, as given by the detailed mechanism, along with the steady state species concentrations, are used to solve for the reaction rates for the non-steady-state species. This approach is described in more detail (Ref. [22] in paper).

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William Gardiner, University of Texas at Austin, USA.

How does the stiffness of the ODE system depend on the number of species left at the end of the reduction procedure you used?

Author's Reply. You might expect that as more species are assumed to be in steady state, the stiffness of the ODE system would decrease. This assumes that the timescales associated with the steady state species are the shortest while the timescales associated with the non-steady-state species that are retained in the mechanism are the slowest. This is the basis of the intrinsic low dimensional manifold method [1], in which increasing manifold dimensionality relates directly to shorter chemical timescales. However, with the reduced mechanisms that we have developed with CARM, we have not always seen this relationship between the number of species retained in the reduced mechanism and numerical stiffness of the ODE system.

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