

Development of an Improved NO_x Reaction Mechanism for Low Temperature Diesel Combustion Modeling

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ABSTRACT

The development of a new Nitric Oxide (NO_x) reaction mechanism has been conducted by adding species, including hydrogen cyanide (HCN) and the CH radical to a reduced chemistry diesel combustion model. The additional chemical reactions were added to the ERC's reduced 12-step NO_x mechanism, which consists of N, NO, N₂O, and NO₂. The new NO_x mechanism was implemented into the KIVA/ERC-CHEMKIN code and was found to be able to predict the experimentally observed trend that the amount of engine-out NO_x decreases as engine load is increased, which is not reproduced by the current reduced NO_x mechanism. HCN and CH were found to be species that bridge C_xH_y products and N radicals via the reaction $\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$ under high equivalence ratio conditions, and Zeldovich NO formation is suppressed by the formation of HCN, a species in the Fenimore NO formation pathway. The additional species and reactions were also found to influence the prediction of engine-out soot emissions. Predictions with the new NO_x mechanism and the ERC 2-step soot model showed a reduced amount of soot compared to the standard 12-step NO_x and 2-step soot models. Acetylene (C₂H₂), which is considered to be a precursor of soot in the 2-step soot model, serves as a CH radical precursor as well, and soot and CH radicals compete with C₂H₂ in fuel rich regions. It is concluded that the new NO_x reaction mechanism is able to predict NO_x emissions more accurately for fuel-rich, high-load diesel engine operating conditions.

INTRODUCTION

The development of NO_x and soot prediction models for multi-dimensional computations is important in order to analyze combustion processes and to realize the reduction of emissions efficiently. To meet mandated emissions regulations, several new concepts of diesel combustion, such as Low Temperature Combustion (LTC), are being developed and examined in the engine community, and the requirement of reaction chemistry models which can predict engine-out NO_x emissions for a wide range of engine operation is of increased importance.

Currently, the formation of NO emissions in engine applications is often modeled using the Zeldovich (thermal) NO mechanism [1], and less attention is paid to other pathways, such as the Fenimore (prompt) NO [2] formation mechanism. However, in contrast to thermal NO, prompt NO is produced at relatively low temperatures (i.e., ~1000 K). One of the important reactions, $\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$, in which HCN can react further to produce NO [3], has lower activation energy than the formation steps of the thermal NO reactions. Therefore, even though LTC engines have relatively low reaction temperatures, and consequently produce smaller amounts of NO_x, accounting for the formation of prompt NO might be necessary for more accurate NO_x prediction under LTC engine operating conditions.

Additionally, the conversion of NO into HCN and ammonia (NH₃) under fuel-rich conditions has been reported in studies of fuel-NO conversion [4]. With direct fuel injection, the conditions of the air-fuel mixture within the engine combustion chamber vary from fuel-rich to fuel-lean dynamically during the cycle. Thus, if the mixture is not perfectly homogeneous, the conversion of NO to HCN and NH₃ via fuel-rich pathways can influence the predicted NO_x emissions. This possibility occurs especially under high-load engine operating conditions where locally rich mixtures are likely to be more prevalent.

Furthermore, studies of the interaction between NO and soot formation have reported that there exists a coupling between NO and soot that is caused not only by radiation-induced thermal effects [5], but also by the reaction-induced chemical effects [6]. The chemical effect is brought about by the competition for C₂H₂ between CH and soot, where CH is one of the species that appears in the pathways for the formation of prompt NO, as indicated previously.

In the present study, a previous 12-step NO_x mechanism developed at the Engine Research Center of the University of Wisconsin-Madison (ERC) [7] was expanded by adding new species and reactions that describe prompt NO formation. The new species and reactions are abstracted from the GRI-Mech mechanism developed by Gas Research Institute (GRI) [8]. The new

mechanism, denoted hereafter as the “improved reduced NO_x mechanism” was studied and validated under several diesel engine operating conditions.

NUMERICAL MODELS

SOOT MODEL

In this study soot emissions were predicted using a phenomenological 2-step soot model [9] which employs acetylene (C₂H₂) as the inception precursor species for the calculation of the soot formation rate. The rate of change of soot mass M_s in a computational cell is computed as a competing balance between the rate of soot formation, M_{sf}, and the rate of oxidation, M_{so}. The soot formation rate is specified to be of Arrhenius form, based on the Hiroyasu and Nishida model [10]. The soot oxidation rate is determined by the Nagle-Strickland-Constable (NSC) model in which surface chemistry with two reaction pathways are taken into account [11], and

$$\frac{dM_s}{dt} = \frac{dM_{sf}}{dt} - \frac{dM_{so}}{dt}$$

$$\frac{dM_{sf}}{dt} = A_{sf} M_{C_2H_2} P^{0.5} \exp\left(-\frac{E_{sf}}{RT}\right)$$

$$\frac{dM_{so}}{dt} = \frac{6MW_c}{\rho_s D_s} M_s R_{Total}$$

where the soot particle diameter, D_s=25 nm, the activation energy, E_{sf}=12.5 kcal/mol, and the soot density, ρ_s=1.8 g/cm³. M_{C₂H₂}, P, and MW_c are the mass of C₂H₂, pressure, and carbon molecular weight, respectively. R_{Total} is the net reaction rate [12]. The pre-exponential factor A_{sf} was changed according to the engine operating cases in the validation. This model was incorporated into the KIVA/ERC-CHEMKIN code and in the reaction mechanism file for SENKIN [13] calculations.

IMPROVED REDUCED NO_x MODEL

A reduced NO_x chemistry mechanism based on the GRI-Mech 2.11 mechanism was previously developed by Sun [7]. This NO_x mechanism has 4 species and 12 reactions, respectively, and it was validated by combining it with the ERC n-heptane mechanism [7,14,15]. This NO_x reaction mechanism only deals with thermal NO, and it gave satisfactory NO_x trend predictions while saving computer time compared to use of the full-size GRI-Mech mechanism, which needs an additional 29 species and 198 reactions. However, the reduced 12-step NO_x mechanism does not consider prompt NO_x or the conversion of N-atom containing species into NH₃ and HCN [4], which may be important in fuel-rich conditions, such as at high load. Lack of consideration of these mechanisms in the NO_x model may be responsible for the observed discrepancies between measured and model predicted NO_x at fuel-rich conditions. Thus, the present improved reduced NO_x

reaction mechanism was developed to account for the behavior of N radicals in fuel-rich conditions. The development was based on GRI-Mech 3.0 [8] (the current ERC 12-step reduced NO_x mechanism was developed based on GRI-Mech 2.11) because GRI-Mech 3.0 was optimized for a more extensive range of combustion conditions than GRI-Mech 2.11. Since the combination of the ERC n-heptane chemistry and the 12-step NO_x mechanism based on the GRI-Mech 2.11 mechanism has provided reasonable predictions of thermal NO (even though the GRI-Mech mechanism was originally optimized for methane and natural gas as the fuel), it was felt that the GRI-Mech 3.0 mechanism would contain additional benefits for new NO_x mechanism development.

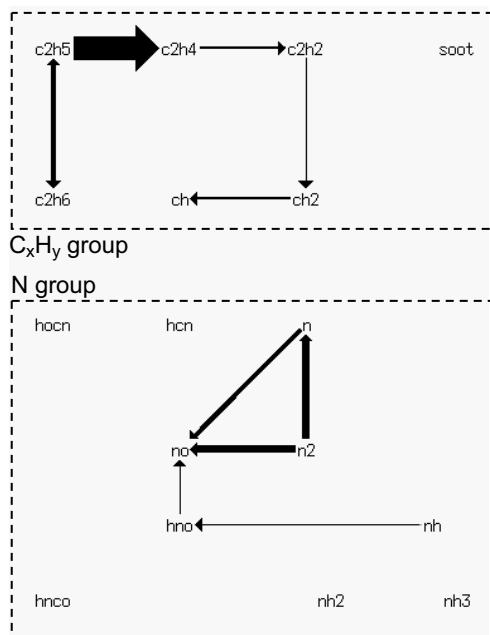
The steps in the present development of the improved reduced NO_x mechanism were:

1. Observe and identify the important species of the GRI-Mech 3.0 mechanism, especially under fuel-rich conditions, and then add the species and reactions to the ERC 12-step NO_x model using GRI-Mech 3.0 reaction coefficients to obtain the base mechanism.
2. Eliminate omissible species and reactions from the mechanism produced by step 1, and then assimilate two or more reactions into a single reaction to downsize the base mechanism. Add new species and reactions if additional paths are needed.

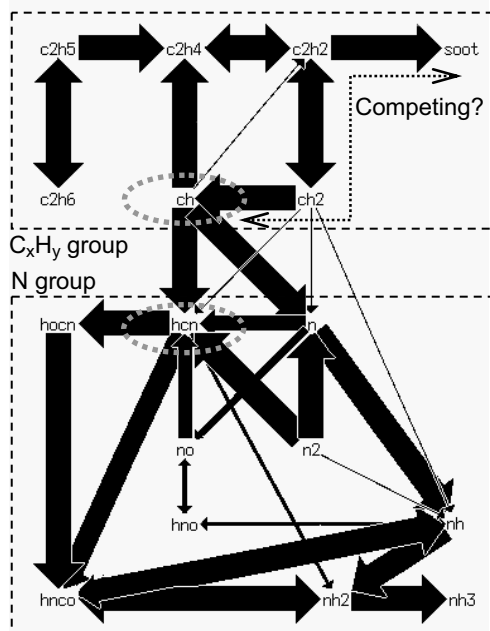
Step 1: Formulate base NO_x mechanism

SENKIN and XSENKPLOT [17] were used to observe the behavior of the GRI-Mech 3.0 mechanism when combined with the ERC n-heptane mechanism. Figure 1 shows the reaction pathways of representative species for two different equivalence ratios (1.0 and 3.0) as obtained using XSENKPLOT. The calculation was conducted at constant volume, with initial pressure, P_{ini}=40 bar, initial temperature, T_{ini}=769 K, and computational time, T_{end}=100 ms using SENKIN. The arrows in the figure denote the direction of the reaction, and the width of the arrows represents the net absolute reaction fluxes normalized to that of NO. It is seen that the radicals CH and HCN bridge the hydrocarbon group species and the nitrogen group under the high equivalence ratio condition, while these groups are not linked significantly under stoichiometric and low equivalence ratio conditions.

Additionally it is seen that the radical CH plays a role in connecting the C_xH_y group to the N group and also leads to C₂H₂ and soot. This suggests that taking account of the prompt formation pathway of the N group will influence the formation of soot emissions under fuel-rich conditions. It is seen that the most important additional species are the radicals CH and HCN, and these two species and their related reactions were thus added to the 12-step NO_x mechanism.

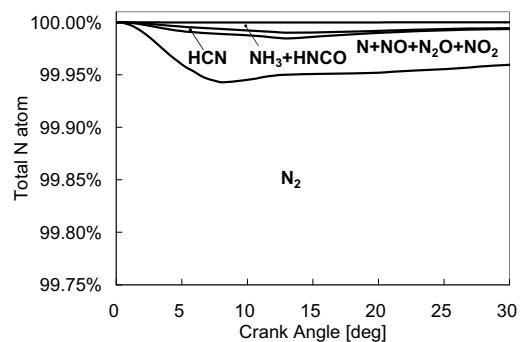


(a) Equivalence ratio=1.0.

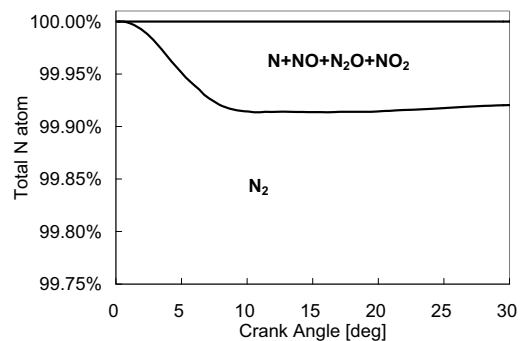


(b) Equivalence ratio=3.0.

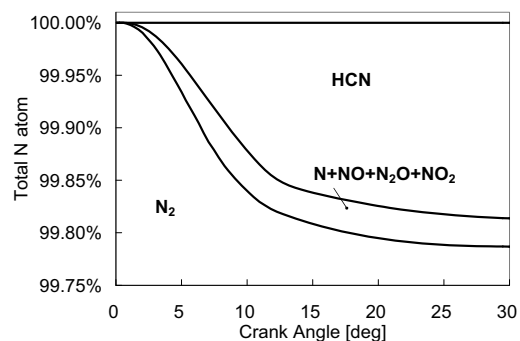
Figure 1: Representative reaction pathways using GRI-Mech 3.0 mechanism by SENKIN/XSENKPLOT.



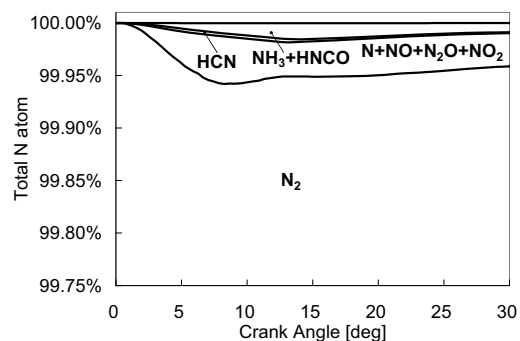
(a) GRI-Mech 3.0.



(b) ERC 12-step NO_x.



(c) ERC 12-step NO_x with CH and HCN.



(d) Base NO_x mechanism by step 1.

Figure 2: Concentration histories of N radicals for an arbitrary engine operation (overall equivalence ratio=approx. 0.77).

A NO_x mechanism that included CH and HCN was validated by comparing the results to those obtained with the GRI-Mech 3.0 mechanism under an arbitrary high-load diesel engine operating condition. In this case each NO_x mechanism was combined with the ERC n-heptane chemistry. Figure 2 (a), (b), and (c) show comparisons of the N atom history over the engine cycle for the GRI-Mech 3.0, 12-step NO_x, and 12-step NO_x with CH and HCN mechanisms, respectively. To clarify the influence of additional species, the four species already taken into account in the 12-step NO_x mechanism, N, NO, N₂O, and NO₂, are grouped in the figure, and the group is denoted as NO_x just in this section, although NO_x is generally considered as the sum of just NO and NO₂. It was found that the addition of only the two species, CH and HCN, led to excessive formation of HCN and consumption of N₂, even though the amount of NO_x was reduced compared to that predicted by the 12-step NO_x mechanism. This result indicates that the suppression of NO_x emissions is caused by the formation of HCN, and the reaction CH+N₂→HCN+N has a large impact on NO_x formation under fuel-rich conditions. It should be noted that it has been pointed out that the CH+N₂ reaction to form HCN and N in the ground electronic state is “spin-forbidden” (Sutton et al. [18]). Moskaleva and Lin [19] proposed instead the reaction CH+N₂→NCN+H which has spin-allowed products. However, they also point out that NCN can react to produce HCN. Thus, for the purpose of the present study, direct conversion to HCN is assumed.

Examination of the results obtained using GRI-Mech 3.0 showed that the eight species, N₂, N, NO, N₂O, NO₂, HCN, NH₃, and HNCO contain 99.99 % of the total N atoms in the cycle. However, the conversion of HCN to NH₃ takes place through the other species, NH and NH₂. In the pathway from HCN to HNCO, the intermediate species HOCN connects a higher flux pathway between HCN and HNCO than the direct pathway. However, HOCN was not added as a new species by combining the related reactions, HCN+OH⇌HOCN+H and HOCN+H⇌HNCO+H, into a direct pathway between HCN and HNCO: HCN+OH⇌HNCO+H. The resulting 10 species mechanism with N, N₂O, NO, NO₂, CH, HCN, NH, NH₂, NH₃, and HCNO is shown in Figure 2 (d). It is seen that the result obtained with the 10 species mechanism is very similar to the result obtained with the full GRI-Mech 3.0 mechanism. The final base mechanism thus consists of 10 species and 49 reactions.

Step 2: Downsizing the base NO_x mechanism

To make the base NO_x mechanism even more compact, a sensitivity analysis was conducted to further eliminate unimportant reactions over a wide range of conditions. SENKIN was used to conduct the study under constant temperature and pressure reactor combustion conditions. The conditions of the equivalence ratio were 0.2, 0.5, 1.0, 1.5, 2.0, and 3.0. The temperature conditions were 1200, 2000, and 2800 K. The reaction time was T_{end}=2 ms while the pressure was fixed constant at 60 bar. The first and second most important reactions for the species

formation and oxidation extracted by SENKIN were maintained, while the others were eliminated. Some reactions were assimilated, for example by combining HCN+OH⇌HNCO+H and HNCO+H⇌NH₂+CO into HCN+OH⇌NH₂+CO, for further elimination of species.

The base mechanism was found to lack a pathway from NH to prompt NO via HNO, which can be seen in Figure 1. Therefore, a new reaction NH₂+O⇌H₂+NO was added which allows NH₂ to be treated as a surrogate species of NH by combining the elementary steps NH₂+O⇌NH+OH, NH+OH⇌HNO+H, and HNO+H⇌NO+H₂. Additionally, NH₂ was treated as a surrogate species for NH₃ to further reduce the number of species and reactions. Then the rate coefficients of the reactions were modified so as to produce similar NO and NO₂ reaction curves to those of the GRI-Mech 3.0 mechanism. The final improved reduced NO_x mechanism consisted of 7 species, N, NO, N₂O, NO₂, CH, HCN, and NH₂, and 19 reactions, and the mechanism is presented in Appendix A.

Using a sensitivity analysis with GRI-Mech 3.0, it was found that the most C₂H₂ consuming reaction was C₂H₂+O⇌H+HCCO and the second most important one was C₂H₂+O⇌CH₂+CO. Thus, C₂H₂ that remains from the first reaction is consumed to form soot and CH₂. CH₂ reacts further to form CH, one of the C_xH_y-N radical bridging species. However, the magnitude of the reaction rate of the soot formation reaction is much lower than that of the other reactions. Thus, the influence of NO_x formation on soot formation could not be clarified by SENKIN analysis. Although the HCCO species is not included in the improved reduced mechanism, the reaction C₂H₂+O⇌CH₂+CO, became important when HCCO was not listed in the mechanism.

RESULTS AND DISCUSSION

CONVENTIONAL DIESEL COMBUSTION

The present improved reduced NO_x mechanism was combined with the ERC n-heptane reaction mechanism [14,15], and the mechanism was applied to engine cases and compared with experimental data [20]. The engine is a research single-cylinder direct-injection (DI) 4-cycle diesel, adapted from a Cummins N14-series engine. Three operating conditions, Modes 1, 2, and 3, were selected to test the model predictions. Hereafter, Modes 1, 2, and 3 would be denoted by their gross Indicated Mean Effective Pressures (glMEP), viz., 6.7, 9.2, and 10.8 bar, respectively. All conditions had the same engine speed, of 1800 rev/min, Start of Injection (SOI) timing of -2° Crank Angle After Top Dead Center (CA ATDC), and intake air conditions, but different loads. Further details of the engine specifications and operating conditions are given by Kweon and Foster [20]. For the model predictions, a 45 degree sector mesh with an average 5 mm grid size was used for all cases. The pressure and emissions curves for all cases are shown in Appendix B.



Documents

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