

The GRI-Mech™ Model for Natural Gas Combustion and NO Formation and Removal Chemistry

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ABSTRACT

The Gas Research Institute has sponsored an ongoing 4-institution project to develop for the natural gas combustion community a detailed, comprehensively optimized and validated chemical model that describes the combustion of natural gas and pollutant formation under the wide range of conditions encountered in industrial practice and in laboratory experiments. In this presentation, new applications of the GRI-Mech optimization method to extend the GRI-Mech chemistry describing NO_x formation and removal, toxic emissions, and presence of higher hydrocarbons will be described. Comparisons will be made to data from a number of recently reported studies of natural gas combustion.

Key Words: combustion, chemical kinetics, flames, ignition, pollutant formation and removal

INTRODUCTION

Concern for combustion-generated pollution of the environment has led to intense research on the subject. Some of it has already spawned significant technical innovations, particularly in the industrial sector. Still more stringent control of pollutant emissions is being demanded by the public, however, and for this reason continued fundamental research on pollution control aspects of the combustion process is being supported in the industrial countries.

One of the least understood aspects of combustion is the underlying chemical reaction itself, even for relatively simple fuels like natural gas. In part this is due to the restrictions on experimental methods imposed by the harsh conditions under which combustion proceeds, and in part it is caused by the inherent chemical complexity of combustion. In addition to these obstacles, the fragmented history of combustion chemistry research has generated a bewildering variety of incomplete information about the elementary chemical reactions responsible both for the main chemistry converting fuel to water and carbon oxides and for the side reactions that lead to undesirable pollutants such as oxides of nitrogen and sulfur. To overcome this historical problem, the Gas Research Institute has supported a 4-institution collaboration of chemical kinetics researchers to develop methodology for a unification of the knowledge that has been gained about the detailed chemistry of natural gas combustion and pollutant formation. This effort led to release in 1995 of the first version of the GRI-Mech™ model for methane combustion, which was followed in 1997 by its extension to describe the chemistry underlying formation and reduction of oxides of nitrogen. (Frenklach et al. 1995; Bowman et al. 1997) This research has continued, with focal points on improving the chemical description of nitrogen oxides and air toxics formation, the influences of higher hydrocarbons on natural gas combustion chemistry, and including in the parameter optimization process additional data obtained by the collaborators and others.

THE GRI-MECH OPTIMIZATION PROCESS

Full details of the optimization procedures developed for this project have been reported elsewhere. (Frenklach et al. 1995; Bowman et al. 1997) In brief, starting sets of elementary reactions are assembled from the archival literature and earlier reaction mechanisms; thermodynamic data for all chemical species are reviewed; each rate coefficient expression is critically examined against the data used to derive it and against gas phase rate coefficient theory; the trial collection of elementary reactions is used to survey a wide selection of candidate optimization targets—that is, laboratory combustion data—to select appropriate ranges of reaction conditions and to determine the sensitivities of the candidate data points to rate and thermochemical parameters; a starting set of parameters and targets is chosen and optimization undertaken by a “solution mapping” procedure, wherein polynomial representations of numerical solutions to the initial value problems simulating each optimization target are adopted to serve in lieu of the solutions themselves in a factorial design optimization of the initial parameter set against the initial target set. The results of the initial round of optimization are then

values. Optimizations are repeated until eventually a globally—in the sense of best representing all of the data that appears to be internally consistent—optimum model emerges. Finally, the model is compared in validation tests to all relevant data.

RESULTS

The trial model used for the current GRI-Mech optimization differed from the 1.2 and 2.11 models in a number of items of detail that reflect recent experimental results from the authors' laboratories and elsewhere. Some of these, for example the reaction channels of vinyl radical C₂H₃ with O₂ and the rate coefficient for the water-catalyzed formation of HO₂ from H+O₂, were confirmed to have major chemical implications under conditions typical of natural gas combustion. New optimization targets were also added.

Among the principal modifications and expansions of the Versions 1.2 and 2.11 chemistry are the following. Detailed oxygenate chemistry was incorporated to better describe acetaldehyde and formaldehyde reactions, for the purpose of better representing air toxics chemistry. A limited set of propane species and reactions was added in order to represent the effects of higher hydrocarbons on the ignition of natural gas. Reactions of the NH₂ radical and other species important in nitrogen chemistry at lower temperatures were added to the model. On the target side, more reliable flame speed data were available for the current optimization, as were recent measurements of the kinetics of formaldehyde formation and oxidation and targets describing propane ignition.

In the following paragraphs a selection of the optimization and validation results is presented.

An optimization target of primary interest was the laminar flame speed for methane–air at ambient conditions, especially its dependence on equivalence ratio. The optimization result, as shown in Fig. 1, proved to be quite satisfactory. Similarly improved results were found for the dependence of laminar flame speeds on temperature and pressure. As in the earlier GRI-Mech optimizations, shock tube ignition experiments also provided a number of optimization targets. In most cases the current optimization led to matches that were as good or better than was found in earlier optimizations. An exception is shown in Fig. 2. Shock tube data were also used as optimization targets for extending the GRI-Mech chemistry to describe the effects of higher hydrocarbons on natural gas ignition. For this purpose, a skeleton 2-species propane mechanism was used. It proved to describe reasonably well not only the accelerating effect of propane on methane ignition, but also the ignition of propane-oxygen mixtures. This is illustrated in Fig. 3.

The aspects of natural gas combustion concerned with the production and control of air pollutants, in particular of nitrogen oxides, have been of concern to the natural gas industry for many years. These involve not only the high-temperature (over 2000 K) reactions that lead to thermal NO_x, but also the lower temperature reactions that in flame zones produce NO_x and in reburning environments can be used for NO_x control. Examples of the ability of the current GRI-Mech model to account for nitrogen chemistry under flame and reburning conditions are shown in Figs. 4 and 5.

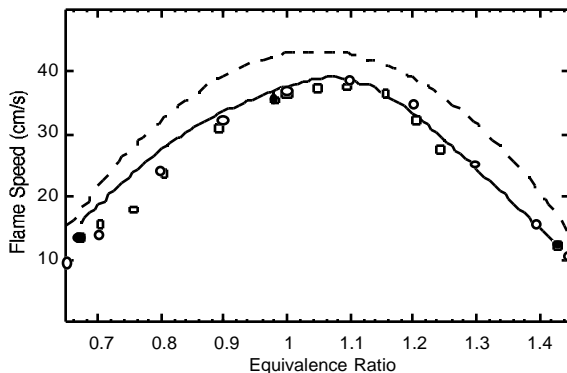


Fig. 1. Comparison of base (dashed line) and final (solid line) mechanisms for predicting 1 atm, 298 K laminar flame speeds in methane–oxygen mixtures. The squares are the data of Vagelopoulos et al. (1994, 1998), the open circles are the data of Van Maaren et al. (1994), and the solid circles are the flame speed values used as optimization targets.

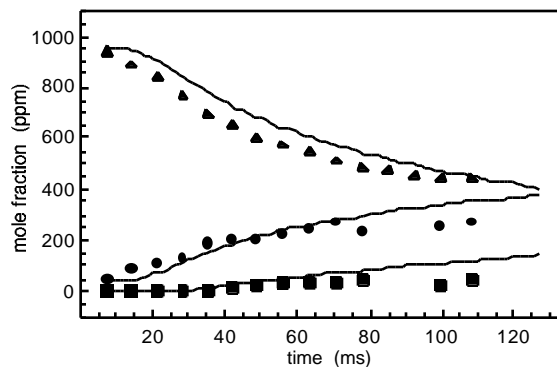


Fig. 4. Concentrations of NO (triangles), HCN (circles) and NH_3 (squares) in simulated flue gas containing 0.12% O_2 at 1573 K and 1 atm reported by Stapf (1994). The solid lines show calculation done with the current GRI-Mech model.

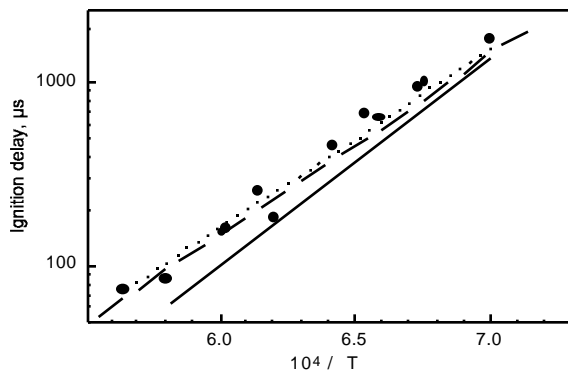


Fig. 2. Comparison of earlier GRI-Mech models (dotted and dashed lines) with current model (solid line) for ignition delays in a 9.1% CH_4 , 18% O_2 mixture in argon reduced to a constant post-shock density of 14.6 mol/m^3 . This shows one of the very few cases where the current optimization matches experiments less well than the earlier optimizations. The data are from Seery and Bowman (1971).

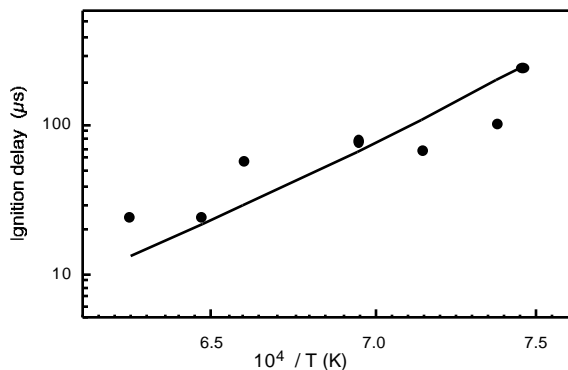


Fig. 3. Ignition delay times in 4% C_3H_8 , 20% O_2 in N_2 reported by Borisov et al. (1988). The post-shock pressures in these experiments ranged from 0.6 to 8 atm. In order to make a comparison between modeling and experiment, the $P^{-0.7}$ pressure dependence measured by these authors was used to reduce all of the data to a post-shock pressure of 4 atm.

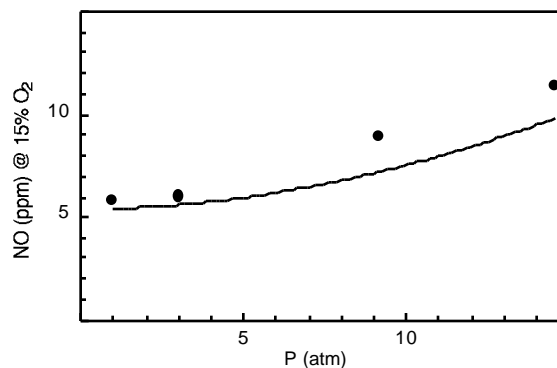


Fig. 5. Dependence of NO production on pressure. The data is from Klassen et al. (1995).

The optimization provided a more robust model and greater confidence in its ability to represent natural gas chemistry over wider ranges of combustion conditions. Still there are notable problems left to be addressed. These include especially the limited ability one has, caused by lack of experimental data, to describe natural gas combustion at very fuel-rich conditions, including the formation of polycyclic aromatic hydrocarbons and soot.

CONCLUSIONS

Continued development of the GRI-Mech detailed chemistry model for natural gas combustion and its associated formation and reduction of oxides of nitrogen has resulted in a more robust and more complete model. It is capable of representing laboratory data over wider ranges of combustion conditions and incorporates a number of important mechanistic discoveries made since the release of earlier versions. The mechanism development research uncovered further discrepancies in the literature of natural gas combustion and suggested a variety of experiments to clarify them.

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