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Project Summary

Kinetic Modeling of NO_x Formation and Destruction and Combustibles Burnout

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A model of the gas-phase chemistry involved in the combustion of simple hydrocarbon fuels and the interconversion of fixed nitrogen species has been developed. One focus of the work was on modeling the chemistry involved in reburning and other advanced NO_x control strategies. A second focus was on the decay rate of various hydrocarbon species under high-temperature conditions. This provided an initial step towards the chemistry needed to model fuel burnout in small combustors, e.g., wood stoves.

The approach was to compare rates for elementary reactions as represented in the different compilations available in the literature. Where inconsistencies appeared, the original literature on the rates was consulted. The mechanism was tested against benchmark data so that the key reactions that controlled any inconsistencies could be identified. Adjustments to the rates were allowed if they fell within the error bounds of the original determination.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The control of nitrogen oxides (NO_x) from practical sources has become a relatively mature science. However, the basis for many of the technologies are understood only qualitatively. Thus, a major research thrust is to develop the quantitative understanding necessary to optimize NO_x control. Ultimately, this will aid in the design of scaled-up units.

A good example of such an NO_x control technology is reburning. Over the last several years, a diagram showing the key reactions that govern the reburning process would have changed only in its minor details. However, calculations of reburning would have changed considerably because the kinetic rates associated with many of the key reactions have evolved over this time frame.

This report describes the development of a chemical kinetic mechanism for NO_x formation and destruction, and fuel fragment burnout. The goal of this development is to provide a state-of-the-art tool for the analysis, optimization, and generalization of NO_x control technologies. In other words, the reported work is intended to help shift a qualitative understanding of these processes toward a quantitative understanding.

This program focused on the NO_x chemistry of the reburning process. Experimental studies of reburning have raised many questions. Fuel type, reburning temperature, and mixing

configuration all impact the final NO_x concentration. Also important are the primary and secondary (reburning) stoichiometries. Because of the many parametric studies of reburning and NO_x reduction, the overall understanding is fair. However, all of the key mechanisms are still not fully understood.

In order to better understand and ultimately predict this process, a homogeneous kinetic mechanism was assembled. Currently, the mechanism consists of the modified Arrhenius rate constants for 192 chemical reactions obtained from the open literature, plus two "phenomenological" reactions which were added to improve the model predictions. Forty chemical species are considered in the mechanism. It is solved with a model for one-dimensional (non-diffusional) chemical kinetics. The model contains options for temperature and pressure control, in addition to adiabatic operation. It also permits sidestream addition (fuel or air staging) and can simulate either well-stirred- or plug-flow-reactor chemistry.

The hydrocarbon combustion portion of the mechanism was first validated against shock-tube data. The nitrogen chemistry and modeling format was then tested against reliable bench-scale data on the reburning process.

Development of Kinetics

Rate Selection

A thorough search of the primary literature for kinetic rate data was beyond the scope of this program. Many highly regarded researchers are specialists in the evaluation of chemical kinetic data. Therefore, their work was used as references in order to assemble a specialized mechanism. Eight existing compilations and critical evaluations of kinetic rates were used as the principal sources for this study.

An important tool developed for the selection of rate constants was a collection of utility programs, written in-house, linked to a commercial graphics software package. This tool was used to produce Arrhenius plots of all of the rate data for each reaction.

For many reactions the differences between cited expressions were negligible and so the choice became immaterial. This prevailed in the H_2 - O_2 subset where rate data are relatively accurate for most reactions. A complete set of 254 Arrhenius plots is contained in the Appendix to the subject report.

Validation

Validation of a kinetic model involves a comparison of the model's predictions with reliable data. An important consideration here is whether the experimental conditions can be accurately represented. Heat losses, wall effects, mixing, and inhomogeneities all constitute modeling issues which go beyond chemical kinetics.

The present mechanism was compared with shock-tube data. The correlation parameter was a function containing CH_4 and O_2 concentrations (mole/cm^3) and an induction time defined as that time (seconds) required for 10% of the CH_4 to be destroyed. The model predictions fell well within the range of the data.

Reburning Modeling

Modeling the reburning process requires attention to the details of the physical, as well as chemical processes occurring in combustion systems. The model was applied against bench-scale data obtained in the EER Controlled Temperature Tower (CTT) in order to address some of these needs. Systematic variations of reburning parameters were applied to modeling the reburning process in order to improve the model predictions and to provide insight into the processes occurring during reburning in practical combustion systems. By examining the influence of physical parameters, such as temperature profile and staging rate, the chemistry of the reburning system was found to be very sensitive. However, the uncertainty in the physical situation was not sufficient to allow the model predictions to match the data. It was necessary to assume two phenomenological chemical reactions.

Modeling Parameters

Significant parameters which were investigated were:

Reburning fuel addition rate

Burnout air addition rate

Temperature change during reburning fuel addition

Temperature change during burnout air addition

The impacts of staging rate and heat release staging on model predictions of NO_x destruction during reburning were investigated. The heat of combustion of the remaining fuel was found to be important in determining reburning behavior during fuel addition, although less so during burnout (air staging). The rate at which mixing and reaction are assumed to occur during staging is important to the model predictions in both cases. This, of course, also implies that mixing is an important parameter in determining reburning effectiveness.

Phenomenological Modeling

Even accounting for the physical parameters, the model did not adequately predict the concentrations of the reduced nitrogen species NH_3 and HCN. In order to predict the observed HCN concentration, it was necessary to include a mechanism for fixation of N_2.

Two reactions which are proposed and their *a priori* rate expressions are:

$$C_2H_2 + NO = CHO + HCN$$
$$k = 8.133E5 * \exp(+14140/RT).$$

$$C_2H + N_2 = CN + HCN$$
$$k = 1.26E12 * \exp(-21000/RT).$$

These reactions were appended to the reaction mechanism and evaluated against the CTT reburning data. Their rate expressions were then adjusted parametrically to best fit the data over the range of SR2 = 1.0 to SR2 = 0.7. The resulting "best fit" rate expressions are:

$$C_2H_2 + NO = CHO + HCN$$
$$k = 2.2E5 * \exp(+14140/RT).$$

$$C_2H + N_2 = CN + HCN$$
$$k = 1.26E12 * \exp(-25000/RT).$$

HCN concentrations predicted with the two phenomenological reactions included in the reaction mechanism were very good over the range of SR_2 = 1.0 - 0.7. The trend of NH_3 concentration was quite good, although the predicted values were generally low. Predictions of NO concentrations were excellent, except at SR = 1.0.

Burnout NO_x Predictions

The chemistry occurring during burnout air addition is complicated. A large volume of air relative to the total system volume is needed to effect burnout. This results in a quench of the radical species concentrations followed by reignition and reaction at leaner stoichiometry. Initially the radical species reignite the reburning reaction responsible for NO_x reduction. However the excess oxygen and increasing radical levels soon begin to oxidize the remaining fixed nitrogen species.

The model predictions for NO concentration after burnout show the qualitative features of the data. However the predicted concentrations of NO_x v

SR_2 are too high. This indicates that the predicted oxidation of the remaining fixed nitrogen species is too efficient. An analysis of the reactions taking place indicates that about 80% of the HCN at the end of the reburning zone is oxidized to NO, using the current mechanisms.

Summary and Conclusions

The developed kinetic mechanism represents the current state of knowledge in homogeneous combustion modeling. The rate data are a compilation of the most reliable and up-to-date reviews available in the field of gas-phase chemical kinetics. By accounting for environmental factors and with the addition of two phenomenological reactions the present mechanism is able to adequately model NO_x destruction during the reburning process.

In summary, several things were required to develop the mechanism and carry out the modeling efforts described in the report:

- Reliable rate data and references.
- Reliable fundamental and bench-scale data against which to compare the model and mechanism.
- Computer programs to assist in the organization and selection of rate data.
- Understanding of the complexities involved in the reburning process.

Several points can be made based upon the experience gained during this program:

1. Real processes result from complex coupling of fundamental processes; i.e. mixing, heat transfer, diffusion, etc. These can be effectively modeled one dimensionally if certain key parameters can be correctly identified. The key parameters will vary between different experimental or full-scale configurations.
2. Physical processes (mixing, heat transfer, etc.) set the environment for the chemistry.
3. Chemistry is the means of NO_x removal, but chemistry can modify the physical environment; e.g., through heat release during combustion.
4. Development of the kinetic mechanism was only one step toward developing a valid model of the reburning process. Understanding the physical processes and accommodating them in the modeling format were equally important in not only modeling reburning, but also in deciding where changes could be made in the mechanism itself.

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The complete report, entitled "Kinetic Modeling of NO_x Formation and Destruction and Combustibles Burnout," (Order No. PB 89-124 358/AS; Cost: $42.95, subject to change) will be available only from:
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