

Title: Chemical Kinetics in Support of Syngas Turbine Combustion

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ABSTRACT

Objective

The objective of this project is to further investigate fundamental chemical kinetic modeling issues for CO/hydrogen/oxygen systems at pressures, temperatures, and diluent concentrations of CO₂ and H₂O typical of those expected in gas turbine syngas combustion, with particular emphasis on the effects of third body collision partners and NO_x chemistry. Computational design tools will utilize such a model either directly or as a skeletal model from which lower dimensional representations more suitable for computations can be derived. This project aims to further extend our own prior work in developing and validating kinetic models for the CO/hydrogen/oxygen system by providing additional experimental data using a Variable Pressure Flow Reactor (VPFR), carefully analyzing the individual and interactive behavior of specific elementary and subsets of elementary reactions at the conditions of interest, and by using comparisons of both data obtained in this program and those appearing in the literature to further test and refine the model presently in hand. Additionally, it is clear that other species such as small hydrocarbons (e.g., methane) and other combustion gas components (e.g. NO_x) can be present in gas turbine combustion systems, particularly in mixing regions of entering fuel and air. These contaminants can have significant influence on some of the kinetic behavior. These interactions are also a relevant aspect of the present work.

Accomplishments to Date

As a result of further analyses under syngas gas turbine combustion conditions and using a C₁ reaction mechanism that we have been developing, the reactions $H + O_2 + M = HO_2 + M$ (R1), $H + O_2 = OH + O$ (R2), $H + OH + M = H_2O + M$ (R3), $CO + OH = CO_2 + H$, (R4), $HCO + M = H + CO + M$ (R5), $HCO + O_2 = HO_2 + CO$ (R6), $HO_2 + OH = H_2O + O_2$ (R7), $HO_2 + H = OH + OH$ (R8), $HO_2 + H = H_2 + O_2$ (R9), $HO_2 + H_2 = H_2O_2 + H$ (R10), $CO + O + M = CO_2 + M$ (R11), and $CO + HO_2 = CO_2 + OH$ (R12) affect various facets of the carbon-monoxide-hydrogen-oxygen kinetic reaction system behavior at high pressures. The reactions $CO + O + M = CO_2 + M$ (R11) and $CO + HO_2 = CO_2 + OH$ (R12) primarily affect chemical induction time in *pure* carbon-monoxide-hydrogen-oxygen mixtures diluted by nitrogen, water, and/or carbon dioxide. Post induction destruction of the

reactants and energy release are not affected by these reactions. CSP-based analyses show that under different high pressure conditions (represented here by rapid compression machine and very high-pressure shock tube experiments), important reactions participating in the induction period vary. As pressure is increased, the change in overall reaction rate before and after crossing the explosion limit of importance decreases, while the overall activation energy of the average rate of reaction is essentially the same at all pressures from 0.5 to 40 atm. The CSP analyses (which include consideration of thermochemical contributions) are also confirmed by sensitivity analyses that consider separately the pre and post induction chemical processes.

The presence of small amounts of NO_x has the potential to essentially remove the importance of the above $\text{HO}_2\text{-H}_2\text{O}_2$ reactions altogether. A simple example of autoignition under adiabatic compression shows that varying the small amounts of NO present as residual gas from exhaust gas recirculation in reciprocating engines, leads to changes in autoignition timing. Similar effects are likely in continuous flow systems with back-mixing of reaction products.

We have also shown that the interactions of third bodies of very different collisional efficiencies (such as water and nitrogen) are sufficiently small such that linear combinations of pressure fall-off descriptions are accurate for predictions of syngas combustion involving water and carbon dioxide as diluents. Further measurements of the third body efficiency uncertainty issues for water and carbon dioxide at high dilutions will be the principal issue in future work under this effort.

Future Work

We are investigating experimentally the collisional efficiency of carbon dioxide in the reaction $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ (R1) using the Variable Pressure Flow Reactor and hydrogen-oxygen-nitrogen-carbon dioxide mixtures seeded with NO and quantities of carbon dioxide diluent. Experiments are at temperatures between 800 and 900 K and at pressures between 10 and 14 atm.

Publications/Presentations

J. Li, Z. Zhao, A. Kazakov, F. L. Dryer, and J. Scire, "A Comprehensive Kinetic Mechanism for CO, CH_2O , CH_3OH Combustion", *Int. J. Chem. Kin.* (submitted).

F.L. Dryer, "Fundamental Issues: Hydrogen/Syngas Energy Technologies", Hydrogen Combustion Workshop, National Science Foundation, Arlington VA, March 9-10, 2006.

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