

Title: Development of Comprehensive Detailed and Reduced Reaction Mechanisms for Syngas and Hydrogen Combustion

PI: Chih-Jen Sung
Case Western Reserve University
Department of Mechanical and Aerospace Engineering
Cleveland, OH 44106
Tel: (216) 368-2942
Fax: (216) 368-6445
E-mail: cjs15@case.edu

Subcontractor: Hai Wang, University of Southern California
Angela Violi, University of Michigan

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ABSTRACT

Objective

This project aims to develop tools necessary for the design of future coal derived syngas and hydrogen (SGH) fueled combustion turbines. A set of benchmark experiments and computations will be carried out to map laminar flame speeds, autoignition delays, and extinction limits of SGH/oxidizer mixtures over a wide range of mixture compositions, inlet temperatures, and pressures. These fundamental combustion properties will in turn be used to develop comprehensive detailed and reduced kinetic models for H₂/CO/H₂O/O₂/N₂ chemistry. Additionally, the resulting experimental database will be of practical use in determining the desired syngas compositions for optimal IGCC operation, as well as improving the design and operation of advanced combustors fueled by SGH.

Accomplishments to Date

Using the counterflow burner apparatus, laminar flame speed measurements were conducted for a CO-rich fuel gas mixture, H₂/CO mole ratios of 5/95, at a preheat temperature of 323 K. Effects of water addition on flame propagation over a wide range (0 to 35% of the fuel mixture) were studied for equivalence ratios of 0.6–0.9. The molar percentage water addition is defined as $[(X_{H_2O})/(X_{H_2}+X_{CO}+X_{H_2O})] \times 100\%$. It was found that with water addition the laminar flame speed responded non-monotonically for the CO-rich fuel mixture. The flame speed increased with water addition from 0 to 15% and then decreased from 15 to 35%. Detailed integrated flux flow analysis was also carried out using a recently developed chemical kinetic mechanism to understand the controlling chemistry responsible for such non-monotonic behavior.

To further examine the effect of water addition for various H₂/CO ratios, laminar flame speeds for fuel gas mixtures with H₂/CO ratios of 5/95, 10/90, 15/85 and 20/80, were determined at equivalence ratio of 0.6 and water addition of 0–35%. It was found that the non-monotonic behavior was most pronounced for H₂/CO=5/95. The extent of non-monotonicity decreases with increasing H₂/CO ratio. It was also noted that the peak of laminar flame speed occurred at a lower value of water addition when the H₂/CO ratio was increased. For H₂/CO ratio of 20/80, the laminar flame speed response with water addition was strictly monotonically decreasing. The results indicate that for H₂/CO ratio less than 15/85, laminar flame speed varies non-monotonically with addition of water. However, beyond this value of H₂/CO ratio of 15/85, water addition decreases the laminar flame speed.

Furthermore, ab initio quantum chemical calculations, master equation modeling, and detailed kinetic modeling were used to resolve the remaining kinetic issues in syngas combustion. The reaction CO + HO₂ → CO₂ + OH was examined using the single-reference CCSD(T) method with Dunning's cc-pVTZ and cc-pVQZ basis sets and multireference CASPT2 methods. It was found that the classical energy barriers are about 18 and 19 kcal/mol for CO + HO₂ addition following the trans and cis paths. The HOOCO adduct has a well-defined local energy minimum in the trans configuration, but the cis conformer is either a very shallow minimum or an inflection point on the potential energy surface. This observation led us to treat the cis pathway with conventional transition state theory and the trans pathway with a master equation analysis. The computation showed that the overall rate is independent of pressure up to 500 atm. Upon a careful treatment of the hindered internal rotations in the HOOCO

adduct and relevant transition states, a rate coefficient expression k_1 ($\text{cm}^3/\text{mol}\cdot\text{s}$) = $1.57 \times 10^5 T^{2.18} e^{-9030/T}$ for $300 \leq T \leq 2500$ K was obtained. This rate expression is within 10% of that obtained on the basis of an analysis of rapid compression machine (RCM) experiments of H_2/CO oxidation in the temperature range of 950-1100 K. Considering the underlying uncertainties in the theoretical energy barriers, we carried out a parameter sensitivity analysis for k_1 and estimated the uncertainty factor for the theoretical expression to be 8, 2, and 1.7 at temperatures of 300, 1000, and 2000 K, respectively. These error bars reject almost all of the rate values reported in earlier studies, with the exception of the RCM experiments reported by Mittal and Sung (2006).

Using a similar method, we examined the controversy reaction $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$. Measurements made by the Karlsruhe group suggested that the rate coefficient has an anomalous drop at a temperature around 1000 K and rises again towards high temperature. Yet the recent experiments at the Argonne National Laboratory suggested that the anomaly is probably caused by experimental artifacts. Our previous modeling studies on high-pressure shock tube experiments on syngas-like mixtures shows that this anomalous temperature dependency impacts the prediction. For this reason, we used the single-reference CCSD(T) method with Dunning's cc-pVDZ basis sets to examine the potential energy of the reaction. Combined with a consideration of the reaction rate theory, we found that the anomaly, if it exists, cannot be explained by the ab initio potential energy of interactions. Taken the theoretical results on the two reactions together, we are now in the position to finalize the H_2/CO reaction model.

Future Work

Conduct further laminar flame speed measurements, with varying H_2/CO ratio and water addition. The measurements will be carried out at a higher value of H_2/CO ratio for a range of equivalence ratios and water addition. Flame studies will be extended to obtain the extinction limits of various syngas flames, using the counterflow burner configuration. Autoignition delay studies for moist syngas mixtures using the rapid compression machine are in progress. In addition, future work will focus on completing the master equation analysis for the rate constant of $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$, and finalize the reaction model of H_2/CO combustion.

List of Publications/Presentations

1. G. Mittal, C.J. Sung, M. Fairweather, A.S. Tomlin, J.F. Griffiths, and K.J. Hughes, "Significance of the HO_2+CO reaction during the combustion of $\text{CO}+\text{H}_2$ mixtures at high pressures," *Proceedings of the Combustion Institute* 31, 419-427 (2007).
2. R. Sivaramakrishnan, A. Comandini, R.S. Tranter, K. Brezinsky, S.G. Davis, and H. Wang, "Combustion of CO/H_2 mixture at elevated pressures," *Proceedings of the Combustion Institute* 31, 429-437 (2007).
3. X. You, E. Goos, C.J. Sung, and H. Wang, "Reaction kinetics of $\text{CO}+\text{HO}_2 \rightarrow \text{CO}_2+\text{OH}$ ab initio study and master equation modeling," work-in-progress poster, 31st International Symposium on Combustion, Heidelberg, Germany, August 2006.
4. G. Mittal and C.J. Sung "Ignition of moist syngas in a rapid compression machine", 5th US Combustion Meeting, San Diego, CA, March 2007.
5. X. You, H. Wang, E. Goos, C.J. Sung, and S. J. Klippenstein "Reaction kinetics of $\text{CO}+\text{HO}_2 \rightarrow$ products: ab initio study and master equation modeling," 5th US Combustion Meeting, San Diego, CA, March 2007.
6. You, X., Wang, H., Goos, E., Sung, C. J., Klippenstein, S. J. "Reaction kinetics of $\text{CO}+\text{HO}_2 \rightarrow$ products: ab initio transition state theory study with master equation modeling," *Journal of Physical Chemistry A* 111, 4031-4042 (2007).
7. C.J. Sung and C.K. Law "Fundamental combustion properties of H_2/CO mixtures: ignition and flame propagation at elevated pressures," *Combustion Science and Technology*, in press.
8. A.K. Das, K. Kumar, and C.J. Sung "Laminar flame speeds of moist H_2/CO mixtures," Spring Technical Meeting of the Central States Section of the Combustion Institute, Tuscaloosa, AL, April 2008.

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1. Apurba K. Das, graduate student in the Department of Mechanical and Aerospace Engineering, Case Western Reserve University.
2. Xiaoqing You, graduate student in the Department of Aerospace and Mechanical Engineering, University of Southern California.