3.2 Combustion and Energetic Materials

Group Leaders: M. Quinn Brewster and John Buckmaster

Faculty: Quinn Brewster, John Buckmaster, David Ceperley, Eliot Fried, Herman Krier, Richard Martin, Todd Martinez, Mark Short, and D. Scott Stewart

Research Scientists and Programmers: Thomas Jackson, Kung-Chyun Tang, Xiaojian Wang, and Xu Zhou

Postdoctoral Associate: Luca Massa

Graduate Research Assistants: Matthew Culley, Mark Esler, Russell Fitzgerald, Pascal Genevieve, Thomas Hafenrichter, Sergei Kochevets, Igor Kuznetsov, Yanning Liu, William Mattson, Jason Quenneville, and Mark Ulrich, Jason Weber, Lanying Zeng

Consultant: Mitchell Smooke (Yale University)

Overview

Combustion of solid propellant composed of energetic materials is the driving thermomechanical force in the operation of a solid rocket motor. Accurate modeling and simulation of the combustion and resulting regression of solid propellants entails research activities in several areas, including the description and propagation of the propellant combustion interface, modeling of solid propellant flames, combustion instability analysis, and constitutive modeling of energetic materials.

Propellant Combustion

Two-dimensional Laminate Propellant Simulation and Validation (Brewster, Fitzgerald, Genevieve, and Tang)

The two-dimensional laminate propellant configuration is being used to develop and validate simplified kinetics models for AP/hydrocarbon composite solid propellant combustion. During the past year significant improvements were made in the AP combustion model to correct previous deficiencies. A multi-path condensed-phase decomposition model was implemented. This improved burning rate predictions near the low-pressure deflagration limit and resulted in significantly more accurate representation of AP burning surface profiles. Figure 3.2.1 shows a simulation (left) of steady burning at 15 atm with a 150-µm pure-binder fuel layer in the center and AP on the outside in comparison with an experimental image (right). The protrusion of the AP is simulated with much better accuracy than in our previous model and is satisfactory considering the differences in the outer boundary conditions. Figure 3.2.2 shows a simulation of steady burning at 5 atm with a 630 µm oxygenated-binder fuel layer in the center. The burning surface is flat due to the premixed flame created by incorporating fine AP into the binder. The inner burning surface (away from the outer boundaries) and flame structure are simulated well for this case also.

A shortcoming of the current model is the inability to correctly predict protrusion of fuel for oxygenated binders with wide fuel thickness and/or high pressure. This deficiency has its origins in thermochemical assumptions used in the simplified kinetics. This treatment, which has been adequate for the pure binder case, is apparently inadequate for treating oxygenated binders.
at high pressures. Future efforts will be directed at correcting this deficiency. Time dependence and ignition capability (radian and convective) will also be added to the model. As in the past the model will be validated by comparison with experimental laminate propellant observations.

Solid Propellant Ignition Theory and Validation (Brewster, Tang, and Weber)

Simulation of radiant ignition of a homogeneous energetic material, HMX, has been accomplished using a modified Zeldovich-Novozhilov (ZN) theoretical approach that is compatible with the nonlinear dynamic burning module (Rocburn) already implemented in the integrated code. A significant result of this effort was successful elimination of the need to assume a surface temperature ignition criterion. (Use of a surface temperature ignition criterion is almost universal among solid propellant ignition models and is almost universally recognized as an undesirable ad hoc feature.) By assuming a chemistry “activation” temperature (a concept analogous to the “cold-boundary” temperature of laminar flame theory) below 500 K, burning rate becomes invariant with the choice and no surface ignition temperature is required. That is, kinetics alone determine ignition. With this model we were able to successfully reproduce the experimentally observed domain of self-sustained ignition (e.g., the classical “go/no-go” ignition map), as shown in Figure 3.2.3. Validation was accomplished by comparison with experimental results. Simulation results showed that ignition behavior is strongly dependent on the condensed phase thermal relaxation process (e.g., in-depth heat storage). The effects of radiant heat flux level and propellant optical properties on the ignition corridor were also examined.

Several important features still need to be developed in the next phase of this effort. One is to extend the radiative properties, radiative transfer and combustion model descriptions from
homogeneous materials to composite propellants. Another is to include convective heating of the propellant.

**Nonlinear Dynamic Burning Rate Simulation (Brewster and Tang)**

The phenomenological Zeldovich-Novozhilov nonlinear dynamic combustion model (*Rocburn ZN*) has been successfully implemented in the new integrated simulation codes (GEN2.5). A newly developed *Rocburn_2D* interface (to communicate with *Rocman*) allows different combustion models to be integrated into the *Rocburn_2D* module without changing interface code significantly. In addition, the implementation of individual combustion models is now totally independent from model to model. Additional validation of *Rocburn_ZN* has been extended to the combustion of a relatively new oxidizer Hydrazinium Nitroformate. Results show good agreement compared with experimental observations including steady regression rate (pressure, initial temperature, and radiant flux sensitivities), surface temperature, condensed phase temperature profile, and linear frequency response to radiation. As for nonlinear dynamic result, the calculated pressure-time history for the ignition event in an end burner is shown in Figure 3.2.4 with Schoyer’s experimental result shown in the inset. The prediction of a strong initial pressurization spike in a low-$L^*$ (high $dP/dt$) end-burning (no crossflow) motor with HNF propellant confirms our recent hypothesis that initial pressurization spikes may be due to nonlinear dynamic combustion in addition to (or instead of) erosive burning.

Model development and validation will continue with emphasis on extending the nonlinear dynamic burning theory to include ignition. Ignition of AP-composite propellant will be considered including integration with the system codes. The effects of radiant flux level, spectral energy distribution, and propellant optical properties on ignition delay will be investigated.

**Modeling Heterogeneous Propellant Combustion (Buckmaster, Jackson, Massa, and Wang)**

*Rocfire* is a tool currently being built to analyze the burning characteristics of heterogeneous solid propellants. The ultimate goal is an unsteady three-dimensional simulation of heterogeneous propellant burning that can be used to generate a subgrid combustion model for the CSAR system integrated code.

One accomplishment this past year was the development of a homogenization tool. Industrial propellant packs contain a large volume of fine AP, particles too small to be numerically
resolved, and they are accounted for by homogenizing them into the binder. When this is done, it is necessary to know the properties of the blend in terms of the properties of the individual (AP, binder) components. The two properties of concern are the effective heat conduction coefficient of the blend, and the effective pyrolysis law for the surface. Formulas are derived, and verified by numerical simulations. For validation, burning rate simulations were carried out for Miller packs SD-III-17 and SD-III-21. The volume fraction of homogenized binder blend that is AP is 0.323 for SD-III-17 and 0.425 for SD-III-21. The propellant morphology for each pack was computed using Rocpack, an in-house particle packing code. Figure 3.2.5 shows the pack SD-III-17, while Figure 3.2.6 are level surfaces of the total heat output in the gas phase. Figure 3.2.7 depicts the experimental burning rates Miller observed, as well as the simulated results from Rocfire using the homogenization tool described above. Each data point derives from a computer run on ASCI Blue Pacific using 25 processors and took about four wall clock hours. Note the good agreement between the simulations and the experimental data for Miller SD-III-17, but discrepancies exist for Miller SD-III-21, especially at the higher pressures. The most likely candidate for this discrepancy is the use of over simplified gas phase kinetics. Future work will focus on generating reduced kinetic mechanisms appropriate for heterogeneous propellants. Future work will also focus on further development and validation of Rocfire, relevant modeling and physics issues, and the development of an efficient algorithm for the implementation of a subgrid model into the CSAR system framework.

In the course of validating the homogenization strategy, periodic sandwich configurations, alternating slices of AP and binder, were burned numerically where a blend of binder and AP of a specified volume fraction replaced the pure binder. The use of a blend rather than pure binder generates a richer variety of solution responses. One unexpected response was the generating of intrinsic instabilities at low pressure when the sandwich is very fuel rich (equivalence
ratios below 0.15). It is suggested that experiments could be performed to confirm these instabilities.

Current work is also being carried out using level-set technology to remove the restriction of the representation of the surface by a mapping function. This would allow the surface to develop complex shapes, as would be expected when, say, aluminum particles are present or when the pack is fuel rich. Preliminary results show good agreement between the current solver Rocfire and the present method; see Figure 3.2.8. Future work will concentrate on validation and parallelization before aluminum particles are added.

**Thermomechanical Structure Modeling of Solid Propellant Flames (Stewart and Kuznetsov)**

This work has focused on two effects that are clearly important and yet have not been accounted for in the past: thermal expansion in the narrow layer close to the surface of the propellant, and the effects that are introduced by curvature of the burning solid surface. The theoretical effort is aimed at a rigorous derivation of a class of surface evolution equation that relates the regression rate with surface curvature and thermal expansion parameters, similar to that carried out for pure gas-phase flames.

Last year we derived a nonlinear heat equation valid only in the solid that looked at the effects of thermal expansion on heat transfer. This year we have added additional effects of variable material properties coupled with the full structure of the gaseous part of the propellant flame to study and identified the influence of temperature dependent material properties on the propellant regression rate, surface temperature and burnt gas temperature. Explicit formulas were derived (using asymptotic methods) for the regression rate of the propellant surface as a function of surface temperature, with corrections due to the expansion. Figure 3.2.9 shows that a comparison of the burning rate we derived compared against experimental data for the explosive HMX, with fair success.

Other analytical work undertaken was towards the rigorous derivation of surface evolution equation for the combustion surface that relates the surface regression rate

Fig. 3.2.8: Good agreement shown between Rocfire and present method.

Fig. 3.2.9: Burning rate of HMX as function of pressure, for high ($E = 40,000$) and low ($E = 10$) activation energy, including effects of thermal expansion Experimental data by Boggs and comparison with classical Merzanov formula.
with curvature and thermal expansion parameters. This work assumes that the curvature is asymptotically small and seeks to generalize results in classical flame theory to solid monopropellants. Part of this work is in collaboration with Prof. M. Matalon at Northwestern University.

Work also started on the development of a computational simulation tool that has a representation of both the solid and the gas phase regions of the solid propellant flame. In the gas region we solve the viscous reactive flow equations in the combustion approximation for a gas with a one step exothermic reaction. The region in the solid is modeled by a heat equation that may allow for thermal expansion heat flux effects. The combustion interface is allowed to move according to the solution of the moving boundary problem that couples both sides. This work is ongoing and is part of what we plan to do next year. A 2-D combustion code, PLAYMA, was developed as part of an advanced course on theory and simulation of combustion and it serves as the basis of our initial developments. Figure 3.2.10 shows examples of diffusion flames computed with PLAYMA.

This work will continue with development of a numerical model that will simulate combustion of an arbitrarily shaped solid propellant surface. Tracking of the surface position will be performed by a fast-tube level-set method. In the solid phase, we will solve the 2-D version of the nonlinear heat equation with the thermal expansion term. For the gas phase, we are going to use the low mach number solver PLAMYA. Figure 3.2.11 shows a schematic diagram of the regions of the solver.

The first revision of the code, PLAMYA2 is currently under development and will be an optimized version of its predecessor. PLAYMA2 will be able to solve propellant flames with complex non-rectangular geometries such as regressing two dimensional combustion interfaces (solid propellant fin regions inner walls, cracks in energetic materials, etc.) At the time of this writing, the 1-D time dependent version of PLAMYA2 is being tested against exact solutions of steadily propagating flames found by solving the appropriate ODEs, in order to test the surface propagation algorithm. Once appropriate propagation al-

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**Fig. 3.2.10:** Reaction rate distribution (top) and fuel distribution (bottom) for 2-D diffusion flame computed with PLAYMA.

**Fig. 3.2.11:** Schematic of combined PLAYMA2 that solves SP-front motion.
algorithm is finalized, the 2-D implementation will use the Narrow Band Level Set recently proposed.

Combustion in Cracks of Homogeneous and Inhomogeneous Propellants (Short and Liu)

This work continues the study on dynamics of combustion in thin propellant cracks, with widths on the order of 5-100 microns. In particular, we have extended our study on homogeneous materials to inhomogeneous systems, applicable, say to AP/binder propellants. Specifically, fracture of such materials may lead to cracking at the interface between AP and binder. To address this problem, we have examined the dynamics of diffusion flames between two opposed injection surfaces, one fuel and one oxidizer. A typical burning reaction rate structure for a model rectangular crack is shown in Figure 3.2.12; the top injection surface is fuel, the bottom oxidizer. These problems are examined in the context of a variable density Navier-Stokes model.

Currently we are examining the problem of flame spread and ignition of propellant cracks. Here the dynamics of solid propellant regression and behavior is being included. We also plan to continue collaborating with Geubelle in examining combustion driven crack propagation.

Computational Study of Ammonium Perchlorate Diffusion Flames (Smooke)

Most composite propellants based on AP contain bimodal or trimodal particle size distributions of AP. A typical formulation would contain 85% solids (AP) with 15% binder (e.g., HTPB). The AP would consist of a mixture of coarse and fine AP particles (e.g., 62% 200 μm and 38% 25 μm). In prior counterflow studies with AP (at Yale University), methane and ethylene were used as representatives of the HTPB decomposition gases that would burn with the fine AP. In the present work, the fuel is a mixture of H₂ and CO in the ratio of 52 to 48 mole percent, respectively. This simulates the chemistry of the combustion products from the binder (HTPB) and fine AP fraction of a composite propellant, which go on to react in a diffusion flame with the large diameter AP fraction. Similar concepts have been investigated in which the combustion of a fuel-rich AP/binder blend, contiguous with large AP particles, has been studied in a multidimensional computational model. In addition to contributing to our basic understanding of the fundamental kinetics in AP/hydrocarbon binder propellants, the present work, when combined with previous results on AP/CH₄ and AP/C₄H₄ flames, provides insight into how the flame chemistry will vary with AP crystal particle size. (The final report for this subcontracted work with Yale University appears as an Appendix to this section.)

Energetic Materials

Meta-Stable Forms of Nitrogen at High Temperatures and Pressures (Martin and Mattson)
We have simulated the meta-stability of various forms of nitrogen under high pressure. When nitrogen is compressed at low temperature to pressures in excess of 190 GPa it forms a non-molecular solid that has a path dependent range of meta-stability. The experimental evidence indicates that the solid may be an amorphous network, with ~2.6 nearest neighbors per atom. We performed ab initio molecular dynamics simulations of both the most energetically favorable crystal structure, cubic gauche, with three nearest neighbors, and several amorphous structures from previous work, with ~2.4 nearest neighbors. The cubic gauche structure showed a range of meta-stability greater than experiment. The amorphous structure’s range was consistent with the meta-stability experiments with higher temperature paths. Examination of the reaction processes revealed that atoms in the amorphous structure with less than three nearest neighbors were reaction centers. An amorphous structure, with hydrogen atoms inserted to fully passivate it, has an intermediate range of meta-stability. This indicates that meta-stability is a function of the number of nearest neighbors.

We intend to complete our work on the meta-stability of the high-pressure phases of nitrogen with simulations to higher temperatures. In addition we have constructed a Hugoniostat routine for SIESTA the ab initio molecular dynamics code we use. With this modification we will be able to refine our previous work on the shock Hugoniot of nitrogen, using significantly less computation for each point on the Hugoniot. Experiment shows a very unusual double shock induced cooling, which is not supported in current theoretical calculations. This will hopefully result in a more complete principal shock Hugoniot and secondary Hugoniots from points of interest on the principal Hugoniot.
Path Integral Monte Carlo Simulations of Hot, Dense Hydrogen (Ceperley and Esler)

We have further developed, tested and applied to dense hydrogen, better methods for Quantum Monte Carlo. We have demonstrated that the newly devised “Coupled Electronic-Ionic Monte Carlo” method is efficient for calculations of warm dense matter such as occurs in combustion. We have developed novel forms for the wavefunction of hot dense hydrogen, allowing much more accurate calculations, particularly at lower temperatures. In particular we performed simulations of molecular and metallic hydrogen in the temperature range of 300-1000K without assuming an intermolecular potential or a density functional for the electrons. We have developed a new method to eliminate core electrons and are in the progress of testing these pseudopotentials on heavier elements.

Plans for future work include initiating work to calculate electric and thermal conductivity of warm hydrogen; developing and applying a method for using pseudo-potentials in Quantum Monte Carlo to allow simulations of heavier elements such as energetic materials at high temperatures and pressures; and further development of the Coupled-Electronic Ionic Monte Carlo and application to hot dense hydrogen, calculating the melting curve and extending to heavier elements.

Quantum Dynamics Methods (Martinez and Quenenneville)

This work has been developing first-principles quantum dynamics methods (ab initio multiple spawning or AIMS) and extending these to large molecules and condensed phases. In previous years, they have shown the feasibility of this approach for gas phase reactions of energetic molecules and also demonstrated the accuracy of the methods by direct comparison of simulations with experimental results for short time dynamics as probed by femtosecond spectroscopy. This year, they have extended the method to larger hydrocarbons such as stilbene and investigated the possibility of using semiempirical techniques for treatment of electronic structure. They have also probed the role of electronic excited states in detonating materials, focusing on TATB. We were able to conclude that electronic excitation does not play an important role in detonation for this material.
Appendix: Subcontract Final Report
Computational Study of Ammonium Perchlorate Diffusion Flames

Mitchell D. Smooke
Yale University
Department of Mechanical Engineering
15 Prospect Street
New Haven, CT 06520-8284
Phone (203) 432-4344
Fax (203) 432-6775
mitchell.smooke@yale.edu

Overview

Many solid rocket propellants are based on a composite mixture of ammonium perchlorate (AP) oxidizer and polymeric binder fuels. In these propellants, complex three-dimensional diffusion flame structures between the AP and binder decomposition products, present on the length scales of the heterogeneous mixture, drive the combustion via heat feedback to the surface. Changing the AP crystal size modifies the burn rate of such propellants. Large AP crystals are governed by the cooler AP self deflagration flame and burn more slowly while small AP crystals are governed more by the hot partially premixed flames formed with the binder and burn faster. This allows control of composite propellant ballistic properties via particle size variation. Previous measurements on these diffusion flames in the planar two-dimensional (2-D) sandwich configuration [1,2] yielded insight into controlling flame structure, but there are several drawbacks that make comparison with modeling difficult. First, the flames are 2-D by definition and this makes modeling much more computationally complex than with one-dimensional problems, such as the prior work on RDX self- and laser-supported deflagration [3]. In addition, little is known about the nature, concentration, temperature, and evolution rate of species that come off the various binders as they decompose. This makes comparison with models quite difficult. Finally, the spatial resolution required for sandwich work is extreme: prior results show that the hot burning rate-controlling flame is only about 100 microns off the surface at the interface between AP and fuel even at one atm. The counterflow diffusion flame configuration studied here separates the fuel and oxidizer and it greatly extends this region spatially, allowing diagnostics to measure quantitative species and temperature profiles. The resolved profiles can then be used to validate kinetic modeling, which, in turn, can then be applied to 2-D composite propellant configurations. Counterflow diffusion flames of AP with CH₄ and separately AP with C₂H₄ have been studied previously, with excellent agreement between experimental results and modeling [4,5]. In a typical counterflow diffusion flame experiment two laminar plug flow jets, one of fuel and one of oxidizer, are directed at each other so they impinge in the middle of the domain. Properly designed, this configuration leads to one-dimensional (1-D) flames that can be modeled with the lower CPU demand of 1-D codes. In addition, the experimenter has complete control over many flame parameters including fuel chemistry, fuel thermal properties, flame strain rate, etc. In our case the oxidizer side is not a jet but a solid pellet of AP. AP does not normally self deflagrate at pressures below about 1.38-5.52 MPascal, but in the counterflow diffusion flame configuration, AP flames were observed to be self-sustained even at one atm, with nearly perfect planar multi-flame structures.
Research Program

Most composite propellants based on AP contain a bimodal or trimodal particle size distribution of AP. A typical formulation would contain 85% solids (AP) with 15% binder (e.g., HTPB). The AP would consist of a mixture of coarse and fine AP particles (e.g., 62% 200 μm and 38% 25 μm). In our prior counterflow studies with AP, we used methane and ethylene as representatives of the HTPB decomposition gases that would burn with the fine AP. In the present work, the fuel is a mixture of H₂ and CO in the ratio of 52 to 48 mole percent, respectively. This simulates the chemistry of the combustion products from the binder (HTPB) and fine AP fraction of a composite propellant, which go on to react in a diffusion flame with the large diameter AP fraction. Similar concepts have been investigated in [6] in which the combustion of a fuel-rich AP/binder blend contiguous with large AP particles has been studied in a multidimensional computational model. In addition to contributing to our basic understanding of the fundamental kinetics in AP/hydrocarbon binder propellants, the present work, when combined with our previous results on AP/CH₄ and AP/C₂H₄ flames, provides insight into how the flame chemistry will vary with AP crystal particle size.

Calculations were made to determine what fractions of H₂ and CO to use in the exit flow. Assuming the 85% solids loading example given above, with 62% coarse AP by weight to 38% fine AP, the actual products of the fine AP fraction with binder would be: 44% H₂ + 39% CO + 10% HCl + 5% N₂ + 0.7% C + 0.7% H₂O. In this study, we chose to ignore the HCl since it destroys flow meters and is present in the flame via diffusion from the AP side. Therefore, a 52/48 molar mixture of hydrogen and carbon monoxide was used as a surrogate mixture for the products of the fine AP binder flame.

The flame configuration used in both the modeling studies and the experimental measurements (carried out independently by Drs. T. P. Parr and D. M. Hanson-Parr at China Lake, CA) is illustrated in Figure 3.2A.1. The fuel exit diameter is 7.75 mm and the AP pellets 10.1 mm. Both the AP and fuel flows are surrounded by nitrogen shroud flows (26.8 mm diameter for the fuel and 22 mm for the AP). The shroud flows were set to match the fuel and AP decomposition gas flows. The fuel flow rate is controllable with a calibrated flow meter, but the AP decomposition gas flow rate is governed by the AP solid regression rate, over which we had no control. Hydrogen was included in the fuel-side nitrogen shroud flow to decrease the radial concentration gradient for hydrogen. With a fuel flow speed of 89.4 cm/s, the fuel exit temperature was measured with a 50 μm bead chromel-alumel (type K) thermocouple to be 540 ± 11 K, and the AP regression rate was 0.113 ± 0.024 mm/s, with an approximate gas flow speed at the AP surface of 48.4 cm/s. The AP used was Ultra High Purity (UHP) from Kerr McGee Corporation, pressed to 98.2% theoretical maximum density (TMD). UHP AP was used because the flame structure and even regression rate is sensitive to impurities in normal research grade AP [7].

Fig. 3.2A.1: Schematic of counterflow burner
The flame structure was imaged in separate experiments at 0.0932 MPascal (0.92 atm). Optical diagnostics applied to the flame included saturated planar laser-induced fluorescence (PLIF) imaging of OH and OH rotational temperature as well as PLIF imaging of CN, NH, and NO, ultraviolet-visible (UV-vis) absorption spectroscopy for NO, NO vibrational temperature, and OH, and spontaneous Raman spectroscopy for the major species, CO, H₂, N₂, O₂, HCl, CO₂, and H₂O. Temperature was also obtained via Stokes/Anti-Stokes spontaneous Raman scattering and Stokes sum density. A spring-loaded sample holder, with a tungsten-rhenium wire stretched taut across the sample, was used in the experiments. The AP surface location was held constant with this spring-loaded sample holder, thus offsetting the regression rate. The separation distance between the AP surface and the fuel jet exit, d, was maintained at 5 mm.

To model the AP/(H₂+CO) flame system, we consider a laminar reacting flow stabilized in the vicinity of the stagnation plane between two axisymmetric, counterflowing streams. One stream contains methane and the other the AP decomposition products as determined in [8]. The complete formulation of the mathematical model for solving the finite burner separation problem with plug flow boundary conditions [9,10] starts with the elliptic form, in cylindrical coordinates, of the two-dimensional equations describing the conservation of total mass, individual chemical species mass, momentum and energy for the reactive flow occurring between the fuel and the AP solid. To reduce the complexity of the problem, we seek a similarity solution [9] of the form \( v = v(z) \), \( u = rU(z) \), \( Y_k = Y_k(z) \), \( T = T(z) \), in which \( r \) and \( z \) are the independent radial and axial coordinates; \( u \) and \( v \) are the radial and axial components of the flow velocity; \( Y_k \) is the mass fraction of the \( k \)th chemical species; and \( T \) is the temperature. If the expressions for \( u \) and \( v \) are substituted into the continuity and momentum equations, one finds that the reduced radial pressure gradient must be a constant, i.e., \( (1/r)(\partial p/\partial r) = J = \text{constant} \) in which \( p \) is the pressure. This result, coupled with the similarity transformation, reduces the governing equations to a nonlinear, two-point boundary value problem in the axial direction along the stagnation point streamline. These equations are discretized with an adaptive finite difference algorithm and solved using Newton’s method. The system is closed with an equation of state (in this case, the ideal gas law) and appropriate boundary conditions at each end of the computational domain. The chemical production rates, binary diffusion coefficients, mixture viscosity and mixture thermal conductivity are evaluated using vectorized and highly optimized transport and chemistry libraries [11]. We utilize temperature, species [8] and regression rate (velocity) information from the experiments for both the AP and the (H₂+CO) fuel jet boundary conditions. The chemical kinetic mechanism is identical to our previous mechanism used to model AP/CH₄ flames [12] and consists of a total of 86 chemical species participating in 531 reversible reactions.

Results and Discussion

Species profiles of CO, H₂, HCl, H₂O, CO₂, N₂, and O₂, obtained from spontaneous Raman measurements, are shown in Figures 3.2.1.2 and 3.2.1.3. In all the plots, the measured scalars are compared with the model predictions. With the exception of NO on the fuel rich side, and the CO₂ profile, model predictions and experiment are generally in good agreement.

In Figure 3.2.1.4 we illustrate comparisons between the experimental and computational profiles of the temperature, NO, OH and NH mole fractions. The NO peaks close to the AP surface and decays throughout the rest of the flame. With CH₄ and C₃H₄ as the fuels, a peak NO concentration of 8.2% was seen compared with a current NO concentration of 5.7%. The NO
profile shapes for the methane case (and ethylene) are similar to the current results near the AP surface, as might be expected if the NO near the surface were controlled mostly by the AP decomposition and conversion of NO₂ to NO. The chemistry towards the AP surface is probably similar to the current results near the AP surface, as might be expected if the NO near the surface were controlled mostly by the AP decomposition and conversion of NO₂ to NO. The chemistry towards the AP surface is probably similarly independent of the fuel. In the current counterflow flame, the NO decreases more slowly towards the fuel exit than in the hydrocarbon fueled cases, implying a slower NO reduction rate. The NO disappeared well downstream of the fuel exit for the hydrocarbon flames, whereas just downstream of the exit in the present case the NO back diffuses all the way to the fuel exit plane to almost 1 mole percent.

Reaction flux analysis indicates that the major steps consuming NO are the recombination of H atoms with NO, H+NO+M=HNO+M, the reaction of N+NO=N₂+O, and the reaction NH+NO=N₂O+H. Of lesser importance is the formation of NOCl by recombination of NO with Cl. The HNO, produced in the first of these reactions, reacts further with H atoms and OH radicals reforming much of the NO. However, the net process is still responsible for the majority of the NO consumption with HNO being destroyed in several other channels. Variations in the rate constants of these reactions improve the agreement between model and experiment, but to identify the particular reaction or reactions responsible for the discrepancy, further research is needed on the individual HNO, NH, and NOCl reactions. The NO consumption rate of the AP/(CO+H₂) flame is approximately half that found in the

![Fig. 3.2A.2: Comparison of computational and experimental Raman profiles.](image)

![Fig. 3.2A.3: Comparison of computational and experimental Raman profiles.](image)
AP/CH\textsubscript{4} flame (2.5 mm from the fuel jet). In the AP/CH\textsubscript{4} flame, CH\textsubscript{3}, CH\textsubscript{2}, and HCCO reactions are responsible for the increased consumption of NO. These reactions are the expected reburn reactions observed in fuel rich mixtures of hydrocarbons and NO\textsubscript{x}, for which their kinetics have recently received a considerable amount of attention.

The CN concentration was below our detection limit: the upper bound on the measured CN concentration was about 23 ppb (parts per billion), based on comparison with CN signal from HMX (210 ppm). This is in stark contrast to the prior AP methane counterflow flame where large concentrations of CN were seen. No carbon species with a CH or CC bond is in the current system. In addition, this flame does not seem to reduce NO as well as the hydrocarbon case. The maximum NH in the flame was about 0.7 - 0.8 ppm. No off-resonance signal could be subtracted from the NH because there was some other species present in the flame, possibly S\textsubscript{2} impurity from the H\textsubscript{2} that produced LIF at the wavelength off-resonant for NH. The signal obtained off-resonance to NH appeared to be similar in shape (but more intense) to some of the signal obtained when the laser was tuned on-resonance for NH. A background subtraction was attempted by comparing the on-resonance signal to a scaled off-resonance signal and then the signals were subtracted. A broad peak (shown) appeared in the flame region, and at about the same distance from the fuel exit as for the AP/CH\textsubscript{4} case and another peak near the surface also appeared. The peak near the surface is approximately equal to the same mole fraction as the maximum in the flame. Modeling results for the AP/CH\textsubscript{4} counterflow flame [5] showed an NH mole fraction near the surface of about 1.5 ppm, similar to that for AP/(H\textsubscript{2}+CO). However, the prior work on AP methane and AP ethylene counterflow flames showed much higher NH concentrations in the central diffusion flame than are seen in the present AP/(H\textsubscript{2} + CO) flame.

The incorporation of condensed phase chemistry into the counterflow model required the coupling of a solid monopropellant model (no liquid layer) to the counterflow flame. In the AP layer near the solid/gas interface, temperatures are high enough for AP decomposition reactions to take place. In the condensed phase, the radial velocity and species diffusion velocities are all set to zero. Unlike the previous system in which gas phase boundary conditions are applied at the AP side of the domain, boundary conditions are specified directly for the AP pellet.

Several condensed phase reaction mechanisms were investigated. Results are illustrated in Figure 3.2A.5 for the burning rate as a function of the strain rate for the semi-empirical model of Beckstead et al. [13]. Regression rates are predicted quite well over the entire strain rate variation.

**Publications and Presentations**
Archival Publications


Presentations

• Eastern States Section of the Combustion Institute, Hilton Head, South Carolina, December 2001.
• 9th International Conference on Computational Combustion, Sorrento, Italy, April 2002.
• 29th International Combustion Symposium, Sapporo, Japan, July 2002.

Staff Supported

Graduate Student

Mikhail Noskov; Thesis Title: High-Order Computational Methods for Energetic Materials

Research Assistant

Brian Dobbins

Summer Student

Jesse Celeste

References


Fig. 3.2A.5: Comparison of computational and experimental burn rate versus strain rate.


