PROPELLANT FORMULATION DEVELOPMENT FOR FUTURE ARMY WEAPONS SYSTEMS BY MEANS OF ADVANCED MODELING AND FLAME KINETICS RESEARCH

R. Sausa*, M. Grams[a], C. Conner[a], and W. Anderson
US Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ABSTRACT

We apply our experimental and modeling results of a number of burner-stabilized flames relevant to the combustion of solid propellants to calculate the burning rates of tri-amino-guanidinium-azotetrazolate (TAGzT) with and without a nitrate ester-based propellant using our CYCLOPS combustion model that we developed at US Army Research Laboratory. The model employs a detailed, chemical reaction mechanism containing 59 species and 368 reactions. Our calculations show that TAGzT enhances the burning rate of the base propellant over a range of pressures used for rockets and guns; a factor of three at 10 MPa.

1. INTRODUCTION

Predictive modeling of a solid propellant's burn rate is essential to guiding and developing novel propellant formulations for Future Combat Systems and for providing a fundamental screening tool that can result in substantial cost savings compared to experimental formulation and missile and gun firings. As a result, much recent research centers on computer models with detailed chemical mechanisms to predict the burning rate of materials (Miller and Anderson, 2004, and references therein; Miller, 2005). Essential to these models is an accurate knowledge of the gas-phase processes and reaction kinetics. Burner-stabilized flames provide a convenient method to test these mechanisms for accuracy of their reaction's rate constants over a wide temperature range (Grams and Sausa, 2008, and reference therein). In this paper, we report our experimental and modeling results of various burner-stabilized flames, NH_3, H_2, HN_3/O_2, N_2O, NO_2, and apply these results to predict the burning rate of TAGzT and TAGzT with nitrocellulose (NC), nitrate ester (NE), and nitroglycerine (NG) with our two-phase, combustion model CYCLOPS. TAGzT is a very promising, new high-nitrogen compound whose combustion products are environmentally-safe and also help decrease gun barrel and rocket nozzle erosion, thus increasing the life-time of those components (Leveritt et al., 2006).

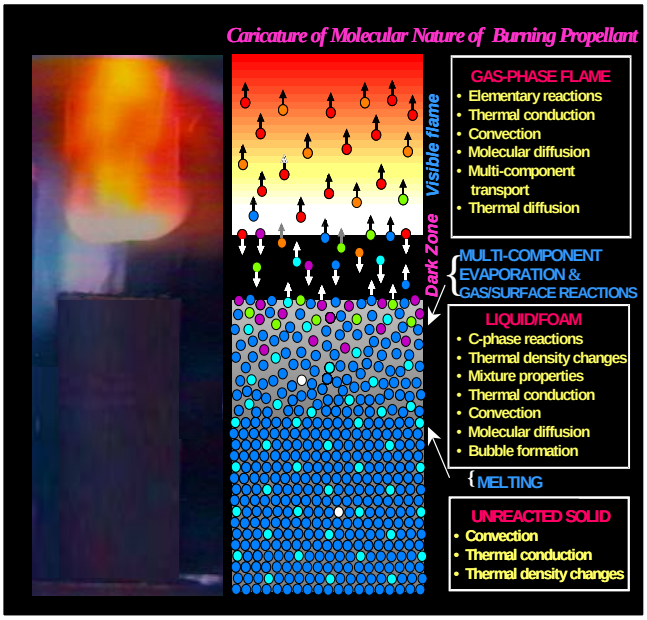

Fig. 1. Burning solid propellant (left) and associated molecular processes (right).

2. EXPERIMENT AND MODEL

We describe the details of our experimental apparatus elsewhere (Grams and Sausa, 2008; Venizelos and Sausa, 2000s; Miller and Anderson, 2004). Figure 1 shows a photograph of burning propellant strand and a drawing depicting the complex molecular processes associated with the event. Briefly, we calculate the burning rates of TAGzT and 20% TAGzT with an 80% nitrate ester-based propellant (NC:NE:NG::60:25:15) over a broad pressure range using Cyclops, a burn-rate predictor developed at the US Army Research Laboratory. The CYCLOPS predictor employs a detailed chemical mechanism containing over 350 elementary chemical reactions involving about sixty species. We derive this mechanism from a critical

[a] ***ARL Postdoctoral Research Associate***

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literature review, and test its H-N-O component with our unique, burner flame apparatus that is equipped with advanced laser spectroscopic and molecular beam, mass-spectrometric diagnostics. We measure the temperature of a number of NH_3, H_2, HN_3/ O_2, N_2O, NO_2 flames by thin-wire thermometry, and the stable and radical species concentrations by molecular beam-mass spectrometry, laser induced fluorescence, or both, as function of height above burner surface. We then compare the experimental species profiles to those we calculate with the Sandia PREMIX flame code containing the propellant's detailed chemical mechanism (Kee et al, 1991, 1994). Rate and sensitivity analyses reveal new chemical information relevant to H-O-N chemistry, which is unique to advanced, high-nitrogen, energetic ingredients such as TAGzT.

3. RESULTS AND DISCUSSION

Overall, our PREMIX flame calculations predict very well the stable species H_2, HN_3, N_2O, NH_3, NO_2, N_2, NO, O_2, and radical species OH and NH for a number of flames. We present representative data in figure 2. Figure 2a (top) shows both the NH LIF and modeled profiles of an $H_2/O_2/HN_3$ flame. The experimental profile is normalized to the modeled profiles near 6 mm for comparison purposes. Figure 2a reveals that the NH concentration decreases rapidly from the burner surface and is zero above 10 mm. The modeled profiles agree very well with the experimental profile at burner distances greater than 4 mm, but not as well near the burner surface. Sensitivity analysis reveals that the reactions $HN_3+OH=N_3+H_2O$ (R1) and $HN_3+NH=N_3+NH_2$ (R2) are important in determining the NH, HN_3, and NO concentrations throughout the flame, particularly near the burner surface, and that their rate constants are much higher than those reported in the literature (LeBras and Combourieu, 1973; Li et al., 2006). Our model does a better job predicting our experimental NH data near the burner surface when we decrease the rate expression of reactions R1 and R2 by a factor of four and three, respectively (see figure 2a, model-modified).

The slopes of the NH profiles near the burner surface, 2 to 4 mm, are about two orders of magnitude more than the slope from 4 to 9 mm. This dramatic change in slope suggests that there are two or more reactions that are responsible for NH production and consumption, and that their interplay determines the observed shape of the NH profile. A plot of the calculated NH rate as a function of burner distance, presented in figure 2b (bottom), shows that NH is produced by the reaction $N_3+H=NH+N_2$ and consumed by the reactions $HN_3+NH=NH_2+N_3$, $NH+NH=N_2+H+H$, and $NH+OH=H+HNO$ near the burner surface, less than 2 mm. The reaction $NH_2+H=NH+H_2$ plays an important role in forming NH from 2 to 8 mm. The NH peak at 5 mm corresponds to the shoulder in the experimental NH profile near 5mm.

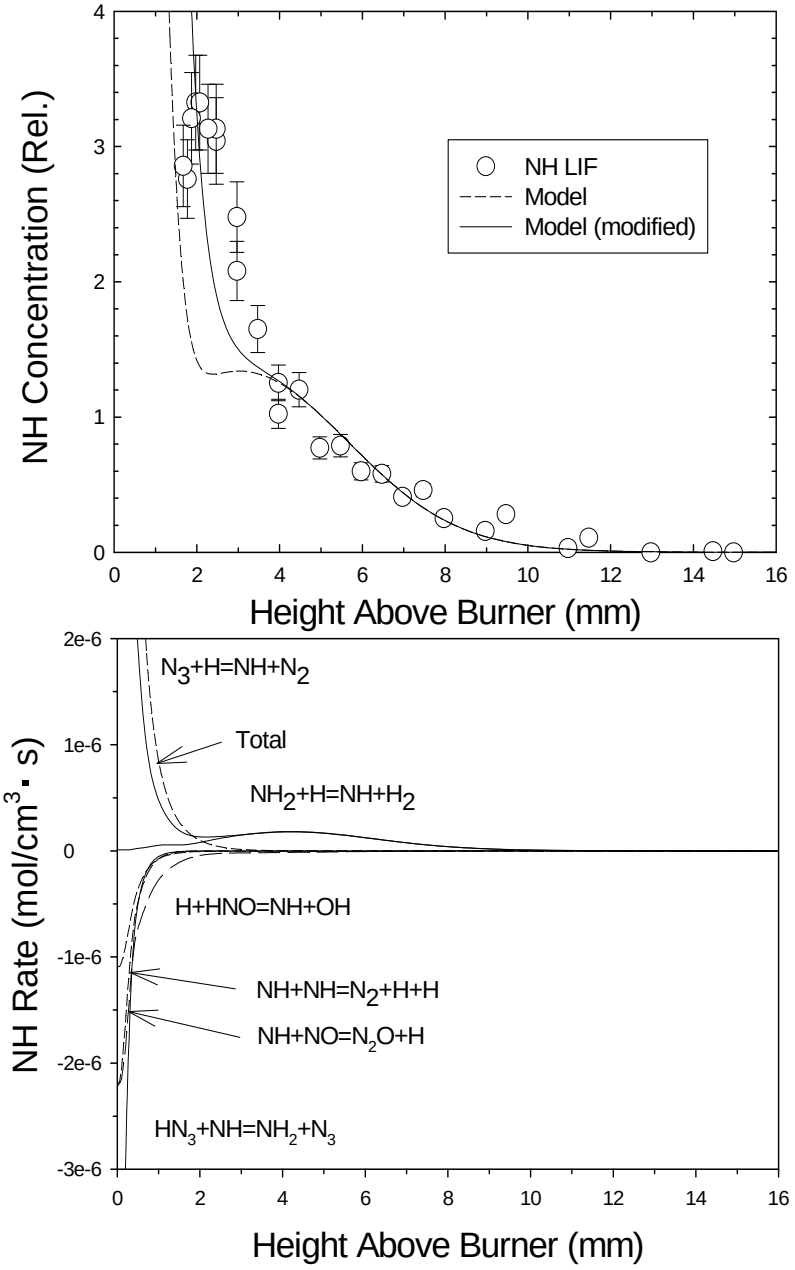

Fig. 2. NH LIF and flame model data (top) and modeled NH rates.

Figure 3 shows a chemical pathway diagram from our in-house, post processing program for the $H_2/O_2/HN_3$ flame. It reveals how HN_3, a four atom, high-nitrogen compound, decomposes to its intermediate and final products. HN_3 reacts predominantly with OH, H, and NH to form N_3, which mostly reacts with H and itself to form N_2. N_3 also reacts with H to form NH, which in turn forms additional N_2. The attack of H and NH on HN_3 to form NH_2 is another channel for HN_3 decomposition. The resulting NH_2 reacts mostly with OH to form NH_3. NO is formed mainly from the reactants HNO+H, NO_2+H, and NH+O, directly or by means of the N intermediate which reacts with OH. Some of the NO converts to N_2 directly, by reacting with N, NH, or N3, or indirectly, by reacting with NH and N_3 to form N_2O, which subsequently reacts with H. We observe the major and most of the minor species experimentally, and their profiles agree with those we calculate with Sandia PREMIX flame code (Grams and Sausa, 2008).

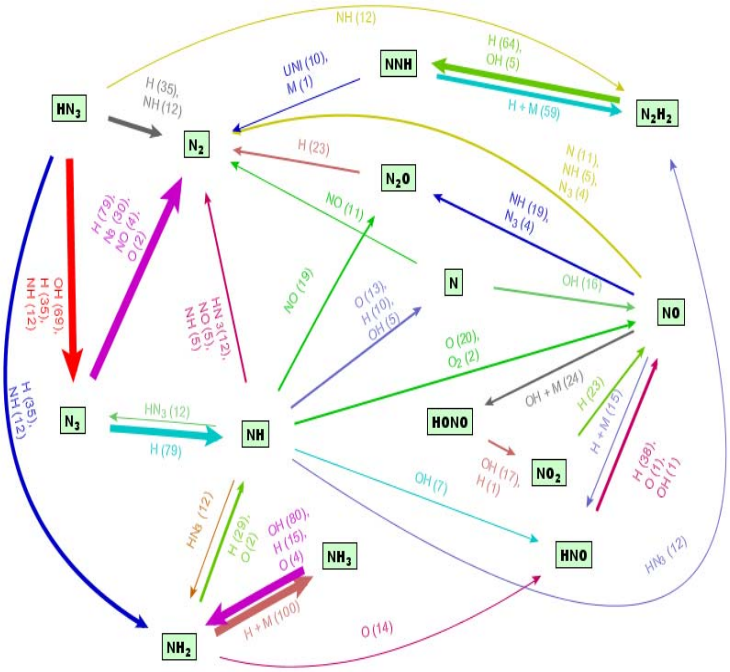

Fig. 3. Pathway diagram of an $H_2/O_2/HN_3$ flame

Figure 4 shows the experimental and predicted burning rates of neat TAGzT over the 0.1 to 200 MPa range. The model predicts the experimental data very well at pressures less than 10 MPa (Tappan et al., 2006; Korobeinichev et al., 2006). Above 10 MPa, the burning rate curve plateaus. Unfortunately, we are not aware of any corresponding experimental data for comparison purposes. A plausible explanation in the rate's leveling off is the decrease in heat feedback to the burner surface at the higher pressures. Our sensitivity analyses reveal that many temperature-sensitive reactions associated with the gas-phase chemistry are both operable at 0.1 MPa and 300 MPa. Table 1 lists the reactions for 0.1 MPa. Many

Table 1. Temperature sensitive reactions near the propellant surface showing endothermic or exothermic character at 0.1 MPa for pure TAGzT

$NH + NH = N_2 + H + H$	Endothermic
$2H + M = H_2 + M$	Exothermic
$N + H_2 = NH + M$	Exothermic
$HCN + H (+M) = H_2CN (+M)$	Exothermic
$2H + H_2 = 2H_2$	Exothermic
$H_2CN + N \Leftrightarrow N_2 + H (+M)$	Endothermic
$NH_3 (+M) = NH_2 + H (+M)$	Exothermic

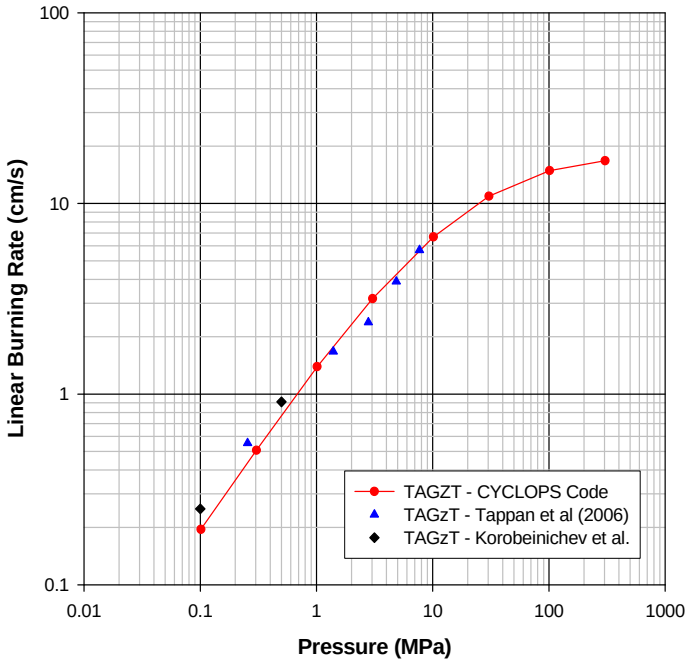

Fig. 4. Modeled and experimental rates of TAGzT

of these reactions are exothermic and provide heat feedback to the surface to gasify the surface products, which in general increase the propellant's burning rate. Near 300 MPa and above, many of these reactions become endothermic and thus provide less heat feedback to the surface compared to the 0.1 MPa reactions. As a result, the propellant's burning rate is less than the expected rate for that pressure and its burning curve deviates from linearity.

Figure 5 shows the experimental and predicted burning rates of TAGzT with and without the base propellant. The model predicts very well the base propellant's burning rates over the pressure regions of 0.3 to 10 MPa (Miller, M., private communication) and 14 to 500 MP (Juhasz et al., 1999). Figure 5 also shows that TAGzT increases the burning rate of the base propellant over the 0.1 to 1000-MPa pressure range. This enhancement is as much as a factor of six at lower pressures, but becomes less significant at 100 MPa and is negligible above 200 MPa.

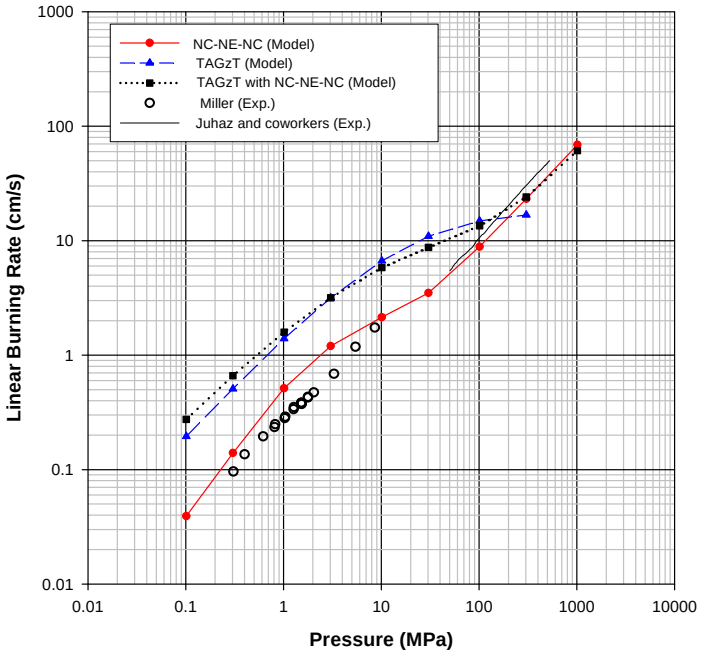

Fig. 5. Modeled and experimental rates of NC-NE-NG with and without TAGzT

CONCLUSION

Advanced flame diagnostics and modeling capabilities provide the necessary tools for characterizing new, propellant formulations for Future Force weapons systems. Our CYCLOPS model predicts very well the burning rates of TAGzT over a wide rage of pressure, and reveals that TAGzT enhances the burning-rate of the selected nitrate ester propellant. The agreement between experiment and model is a testament to the high quality of the extremely intricate chemical mechanisms that we have developed. Interaction between the flame kinetic studies and propellant models is synergistic in that the flame studies provide mechanistic testing and refinements, while the propellant models highlight features needing further study in the flame experiments

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