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CHEMISTRY RESOLVED KINETIC FLOW MODELING OF TATB BASED EXPLOSIVES

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Abstract. Detonation waves in insensitive, TATB based explosives are believed to have multi-time scale regimes. The initial burn rate of such explosives has a sub-microsecond time scale. However, significant late-time slow release in energy is believed to occur due to diffusion limited growth of carbon. In the intermediate time scale concentrations of product species likely change from being in equilibrium to being kinetic rate controlled. We use the thermo-chemical code CHEETAH linked to an ALE hydrodynamics code to model detonations. We term our model chemistry resolved kinetic flow as CHEETAH tracks the time dependent concentrations of individual species in the detonation wave and calculates EOS values based on the concentrations. A HE-validation suite of model simulations compared to experiments at ambient, hot, and cold temperatures has been developed. We present here a new rate model and comparison with experimental data.

INTRO

While detailed chemical kinetics of detonations in homogeneous gases and liquids has been extensively studied, processes governing condensed solid insensitive energetic materials are much less understood. This is due to the higher densities, shorter reactive lengths and time scales, and more energetic nature of condensed detonations. For non-ideal explosives, such as those based on TATB, chemical reaction time scales can be comparable to the characteristic flow time scales leading to non-linear coupling between hydrodynamics and chemistry. Additionally, multi-phase products form for oxygen-deficient explosives composed primarily of C, H, N, and O (TATB has the chemical formula $C_6H_6N_6O_6$), where carbon has the possibility of forming stable solid phase detonation products.

Reactive flow modeling of a non-ideal insensitive explosive such as those based on TATB should consider multiple time scale rates. The initial burn rate of has a sub-microsecond time scale ($<\mu s$) with the gaseous product species nearly in chemical equilibrium with each other. At intermediate time scales ($\sim\mu s$) after the onset of detonation, concentrations of gaseous product species change from being in equilibrium to being approximately frozen in value. Additionally, significant late-time slow release in energy is believed to occur due to diffusion limited growth of carbon nano-clusters ($>10\mu s$) [1]

To self-consistently model the chemical kinetics of energetic material detonations the CHEETAH [2] thermochemical code has been coupled to a multi-dimensional Arbitrary Lagrangian Eulerian (ALE) hydrodynamic code. CHEETAH is used to determine the chemical properties of the reacting energetic material and to solve the chemical kinetic rate equations. CHEETAH uses a high-pressure fluid equation of state to determine the chemical composition of the reacting high explosive gases. We term our model chemistry resolved kinetic flow as CHEETAH tracks the time dependent concentrations of

individual species in the detonation wave and calculate EOS values based on their concentrations.

We model the transformation of the high explosives into a reacting fluid of small product molecules based on a simplified chemical kinetic rate scheme, whose coefficients were determined from fitting model results to measured detonation data. Non-rate controlled product species were assumed to be in thermodynamic equilibrium or frozen depending upon local conditions.

In this paper we expand upon our previous CHEETAH reactive flow modeling which used pressure power-law and Arrhenius kinetic rate laws [3-4]. Here we present a new CHEETAH reactive flow model for TATB based explosives that has been calibrated for hot, ambient, and cold PBX9502. Excellent agreement with experimental data is achieved.

REACTIVE FLOW RATES

A wide range of behavior is observed in non-ideal explosives experiments dealing with differing size, geometries, initial densities and initial temperatures. These experiments sample different regions of the phase space in the detonation wave. A good predictive detonation model should be able to reproduce the many observed phenomena including variations in the detonation velocity with the radial diameter of rate-sticks and wall velocity vs. time for confined cylinder experiments.

With the goal of creating a single initial temperature and initial density dependent physically motivated model treatment for TATB based explosive we have incorporated new rate forms into our CHEETAH reactive flow model. The model uses terms for Arrhenius ignition, pressure-dependent growth, Arrhenius bulk burn with an effective activation volume, pressure-dependent completion, and Arrhenius carbon kinetics. All rates except for the carbon kinetic term are used to treat the fast and slow chemistry of burning the initial explosive to product species. Carbon species are simplified to representative nano-carbon (C_s) and bulk detonation soot (C_b) species. Both are similar to graphite, but with higher energies. The carbon reaction is $C_s \rightarrow C_b$. C_s has higher energy than C_b due to surface bonding effects.

Our initiation rate (eq. 1) uses Arrhenius kinetics because hot spot chemistry is driven primarily by elevated local temperatures.

$$\frac{dF}{dt} = A(F_1 - F)(1 - F)e^{-T_O^*/T}$$
$$\frac{dF}{dt} = 0 \quad F \geq F_1 \tag{1}$$

We consider surface reactions as being responsible for run to detonation in shock initiation and completion and are represented by the rate form

$$\frac{dF}{dt} = A(F - F_1)^a (1 - F_2 - F)^b (P + Q)^c$$
$$\frac{dF}{dt} = 0 \quad F \leq F_1 \tag{2}$$
$$= 0 \quad F \geq 1 - F_2$$
$$= 0 \quad F < F_3 \ \& \ P + Q < P_0$$

The reaction mechanism changes for full detonation to a form that depends on temperature, T, local pressure, P, and shock pressure, P_S

$$\frac{dF}{dt} = A(F_1 - F)^a (1 - F)^b Z(P_s)e^{T^*(P)/T}$$
$$Z(P_S) = \tanh\left((P_S / P_A)^n\right)$$
$$T^*(P) = T_0\left(1 - \tanh\left((P / P_B)\right)^m\right) \tag{3}$$
$$\frac{dF}{dt} = 0 \quad F \geq F_1$$

The need to modify the rate from a simple power law form is supported by experiments (e.g. extrapolating the pop plot to detonation). The physical basis for form of Z(P) is the observation that very high pressure significantly reduces activation barriers. F is the HE burn mass fraction. In CHEETAH calculations, $1 - F$ is the mass fraction of the unburned explosive species concentration. Q is the artificial viscosity. $P + Q$ (rather than P) is used in the local pressure power

law terms to optimize model performance for coarse zoning. Arrhenius kinetics are used for carbon cluster growth

$$\frac{dC_b}{dt} = A\,C_s\,e^{-T_C^*/T} \qquad . \ (4)$$

Species concentrations that are not kinetic rate controlled are calculated as being in chemical equilibrium for pressures greater than a specified "freezing pressure" P_F, and are held approximately constant below this pressure.

Simplifying assumptions were made to treat initial temperature effects in our kinetics model. In this model, only the early (small F) reaction rates depend explicitly on initial temperature. The pre-factor of the reaction rate A is the only portion of the rate which depends explicitly on initial temperature. The late part the reaction rates (large F) and the carbon kinetics rate do not have explicit dependence on initial temperature. The same Cheetah EOS library is used for TATB based explosives at all temperatures. In some cases the EXP-6 gas interaction energy (ε) is scaled by a factor close to 1. This allows the apparent C-J detonation velocity to be brought into close agreement with experiment.

To test our CHEETAH reactive flow model we are developing a HE-validation suite. The validation suite allows for automated, systematic comparison of model simulations to historic and recent high fidelity metal push experiments at cold, ambient and hot temperatures. Current TATB based materials supported are LX-17, PBX9502, EDC-35, and Ultrafine. The current experiments considered include hot, ambient, cold rate sticks; ambient and cold Cu cylinder tests; ambient plate push; and ambient run to detonation. The total number of experiments in suite is about 50.

The HE-validation suite and the models account for the following physical properties of the explosive. The high explosive expands or contracts with changing temperature. Expansion or contraction changes part sizes, which may open gaps in some tests. The initial thermal energy of the explosive changes with temperature. Kinetic rates change with temperature. TATB-based explosives have a fast and slow component to their HE burn reaction rates. TATB-based explosives have late time graphite production.

RESULTS AND DISCUSSION

We considered here two rate model variants applied to PBX9502. The basic model uses 2 pressure power-law surface reaction rates (eq. 2) and a carbon Arrhenius rate. This model was calibrated using 80 zones/cm. The second rate model is our advanced model which has an Arrhenius ignition rate, 2 pressure power-law rates, a full detonation rate and a carbon Arrhenius rate. This rate was calibrated using 160 zones/cm.

PBX9502 modeling is complicated by there being two variants: recycled, which uses reground HE parts and virgin, which does not. We present results here for only recycled PBX9502. Calibrations with slight variations in parameters agree equally well with virgin results. Figure 1 shows the agreement between the calibrated basic model and size effect data for base rate sticks. The knee in the CHEETAH results is achieved by switching from a fast to a slow surface reaction rate as the burn fraction increases. The basic model does not show failure for small rate sticks.
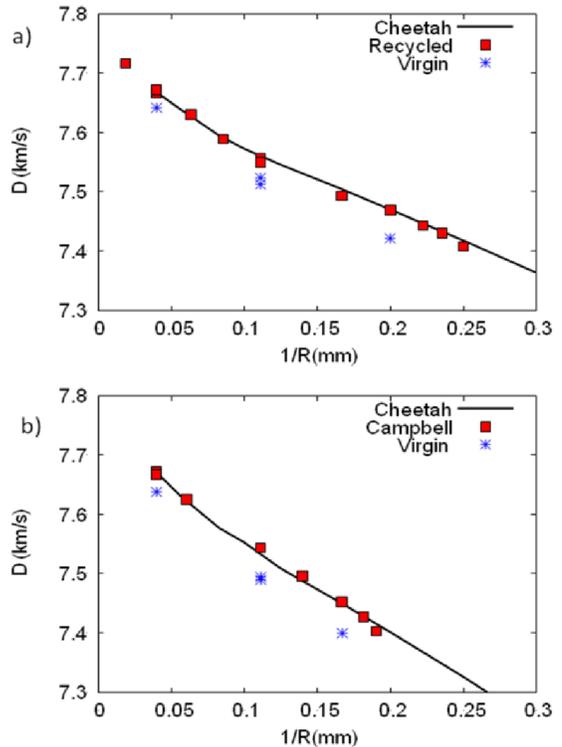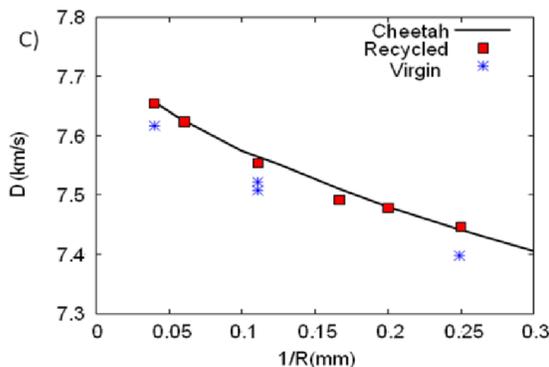
Figure 1. PBX9502 size effect detonation velocity for (a) ambient 25C, (b) cold -55C, and (c) hot 75C. The basic CHEETAH rate model used has been calibrated to the recycled data.

Our advanced rate model is able to treat detonation a broader range of behavior than the basic model. Shown in Figure 2 is the ambient recycled PBX9502 size effect curve for this model, which correctly fails below 4mm radii. The advanced model also gives good agreement with run to detonation experimental data (see Figure 3).
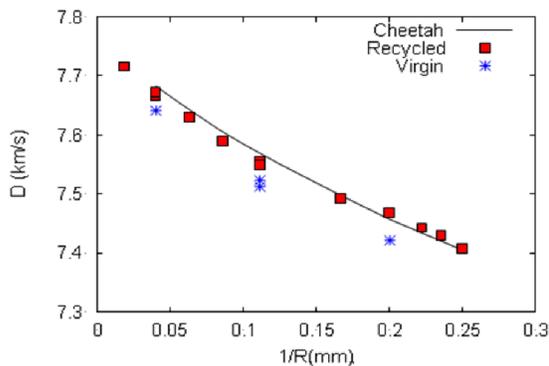

Figure 2. Size effect detonation velocity for ambient PBX9502. The CHEETAH rate model used was our advanced model calibrated to recycled data.

CONCLUSIONS

Our Chemically resolved kinetic flow model has proven successful in modeling TATB based explosives at different temperatures. We have shown here that we can correctly treat many aspects of HE behavior, including run to detonation and failure. Further calibration work needs to be done to fit all experiment types. Mesh resolved calibration also needs to be done. The CHEETAH EOS treatment for TATB explosives continues to be improved and we will be making use of new carbon and partial ionization EOS and rate models in the future.
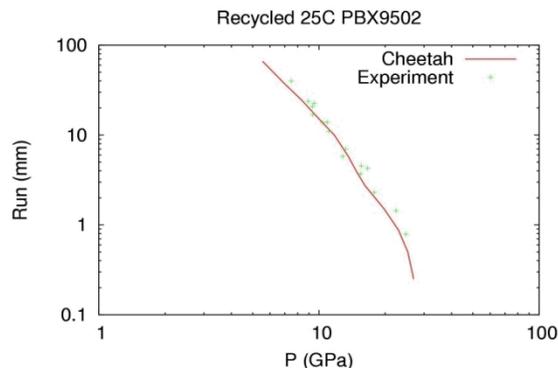

Figure 3. Run to detonation for ambient PBX9502. The CHEETAH model gives very good agreement for all initial pressure values.

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