

# Effect of Confinement during Cookoff of TATB

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**Abstract.** In practical scenarios, cookoff of explosives is a three-dimensional transient phenomenon where the rate limiting reactions may occur either in the condensed or gas phase. The effects of confinement are more dramatic when the rate-limiting reactions occur in the gas phase. Explosives can be self-confined, where the decomposing gases are contained within non-permeable regions of the explosive, or confined by a metal or composite container. In triaminotrinitrobenzene (TATB) based explosives, self-confinement is prevalent in plastic bonded explosives at full density. The time-to-ignition can be delayed by orders of magnitude if the reactive gases leave the confining apparatus. Delays in ignition can also occur when the confining apparatus has excess gas volume or ullage. Understanding the effects of confinement is required to accurately model cookoff at various scales ranging from small laboratory experiments to large real systems that contain explosives.

## 1. Introduction

Predicting the response of energetic material during an accident, such as a fire, is important for high consequence safety analysis, even for insensitive high explosives (IHE). The ignition time, the amount of decomposed gas, the thermo-mechanical sensitization of the degraded energetic material (EM) at ignition, burning of the degraded EM, the possible run-up to detonation and subsequent violence is needed for safety assessments. Even if the EM does not thermally ignite, degraded HE at elevated temperatures are more sensitive to shock initiation than pristine HE. For example, the shock sensitivity of the IHE triaminotrinitrobenzene (TATB) was shown to be similar to conventional explosives such as 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) at elevated temperature [1].

Predictive models must be able to resolve phenomena across ten orders of magnitude in time from hours to sub-microseconds and six orders of magnitude in space from microns to meters. These models should include robust computational tools with solvers for numerically stiff sets of differential equations using adaptive gridding on massively parallel computers. Constitutive models for the EM should consider coupled thermal, mechanical, and chemical phenomena. Constitutive models for confining materials are also needed at elevated temperatures.

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<sup>1</sup> Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. SAND NO. 2013-5318C.

In the early stages of a cookoff event, the mechanical response and decomposition gas velocities are slower than acoustic wave speeds and can be determined in a quasistatic manner. During this time, heat transfer, decomposition, and gas generation are coupled. Reaction rates are dependent on temperature and, in some cases, pressure. Disparity in thermal expansion between the confinement and the EM can change heat transfer paths as well as available gas volume. The pressurization rate and the degree of confinement influence the probability of deflagration-to-detonation transition (DDT) in the EM.

Decomposition mechanisms are complex and may change with temperature and pressure. The dominant reaction pathways may be different prior to ignition than after ignition. Thermal decomposition of energetic materials produces an excess of heat which is subsequently dissipated by conduction, convection, and/or radiation. If internally generated heat is not dissipated fast enough, the energetic material self-heats catastrophically, and the EM ignites. At ignition, the temperature increases rapidly and a front starts to burn into the damaged EM. Initially, the burn is conductive, but may develop into a convective burn, form a high density plug, and transition into a detonation. Decomposition, ignition, and burning are material specific and can directly influence the outcome of a cookoff event, be it a detonation, thermal explosion, deflagration, or quench.

The focus of the current paper is on the effects of confinement on preignition chemistry. Cookoff of the IHE, triaminotrinitrobenzene (TATB) with a chlorotrifluoroethylene/vinylidene fluoride (Kel-F) binder, will be used as an example. In previous work [2], this plastic bonded explosive (PBX) was shown to be pressure dependent. Ignition times depend on the degree of confinement, the initial density of the PBX, and the amount of space in the confining apparatus not occupied by the PBX. These observations support the hypothesis that TATB decomposition is pressure dependent.

## **2. Pristine vs thermally damaged PBX**

Figure 1 shows the difference between pristine and thermally damaged IHE. A molding powder that is 29% of the theoretical maximum density (TMD) or  $0.79 \text{ g/cm}^3$  is shown in Figure 1.a; a fully pressed PBX that is 98%TMD, or  $1.9 \text{ g/cm}^3$ , is shown in Figure 1.b; and a thermally damaged PBX that was originally at 98% TMD is shown with some evidence of swelling in Figure 1.c. About 61% of the molding powder volume is gas and about 2% of the volume of the pressed PBX is gas. Decomposition gases can migrate through the molding powder and end up in the ullage volume. In contrast, decomposition gases formed in the pressed pellet cannot migrate out of the pellet until the pressure is high enough to damage the pellet. Figure 1.c shows a damaged pellet with several spall caps.

Figures 1.d and 1.e show a closer view of thermally and chemically damaged TATB. Figure 1.d shows a  $50\times$  magnification of thermally damaged TATB that was confined, heated 5 K/minute to 523 K, and held at 523 K for one hour before the confinement burst at 100 bars with an estimated mass loss of about 5%. Figure 1.e shows a  $1000\times$  image with holes created by heating a TATB crystal to 573 K. The macro-pores are more than 2000 times larger than the micro-pores. Gases formed in a solid crystal stress and damage the crystals and create macro-pores. The macro-pores can maintain lower pressures associated with the larger volumes but they too eventually fail. Determination of the effect of thermally-damaged materials, including stress-strain laws for degraded materials, remains a major unsolved problem.

## **3. Sandia's Instrumented Thermal Ignition Experiments (SITI)**

The SITI experiments [2] have been modified to study the effects of ullage and confinement as shown schematically in Figure 2. Figure 2.a shows the TATB sample as two 2.54 cm diameter by 1.27 cm tall pressed pellets with 25% of the confined volume being ullage. The location of the internal thermocouples are shown in Figure 2.b. The type K 76  $\mu\text{m}$  thermocouples are held in place using a Kapton gasket that is not shown in Figure 2. Figure 2.c and 2.d show the SITI apparatus with 50% and 75% ullage. The ullage includes the expansion gap as well as the gas volume in the tubing above the expansion gap. The ullage volume is approximately 25%, 50%, and 75% of the overall internal volume.

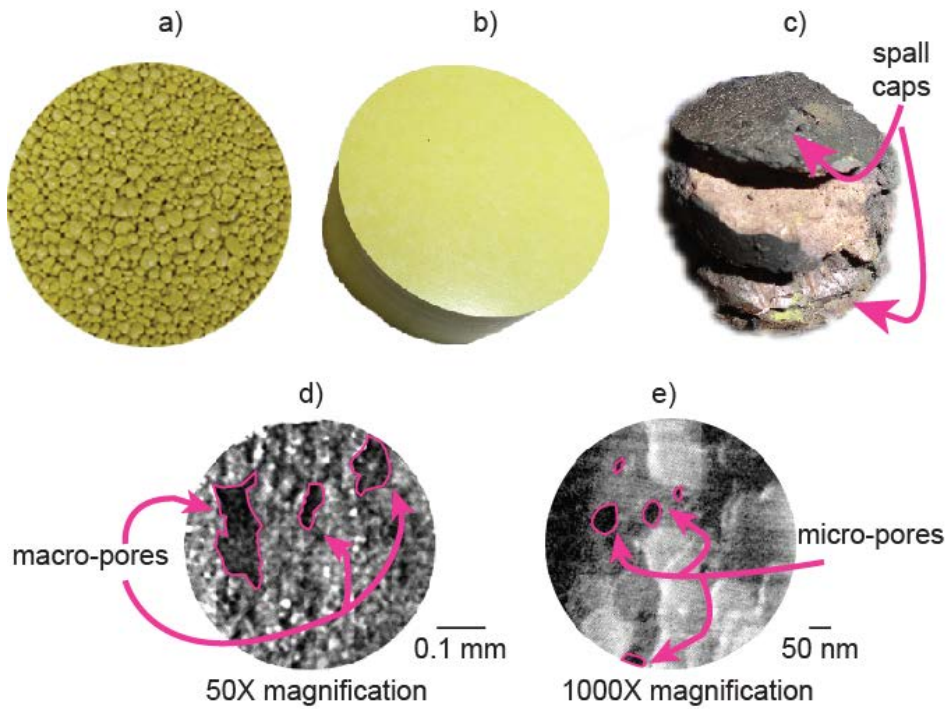


Figure 1. a) Pristine molding powder (39% TMD, 0.75 g/cm<sup>3</sup>, 61% gas volume), b) pressed PBX (98% TMD, 1.9 g/cm<sup>3</sup>, 1.8% gas volume), c) 50× magnification of thermally damaged TATB showing macro-pores, and d) 1000× magnification showing micro-pores.

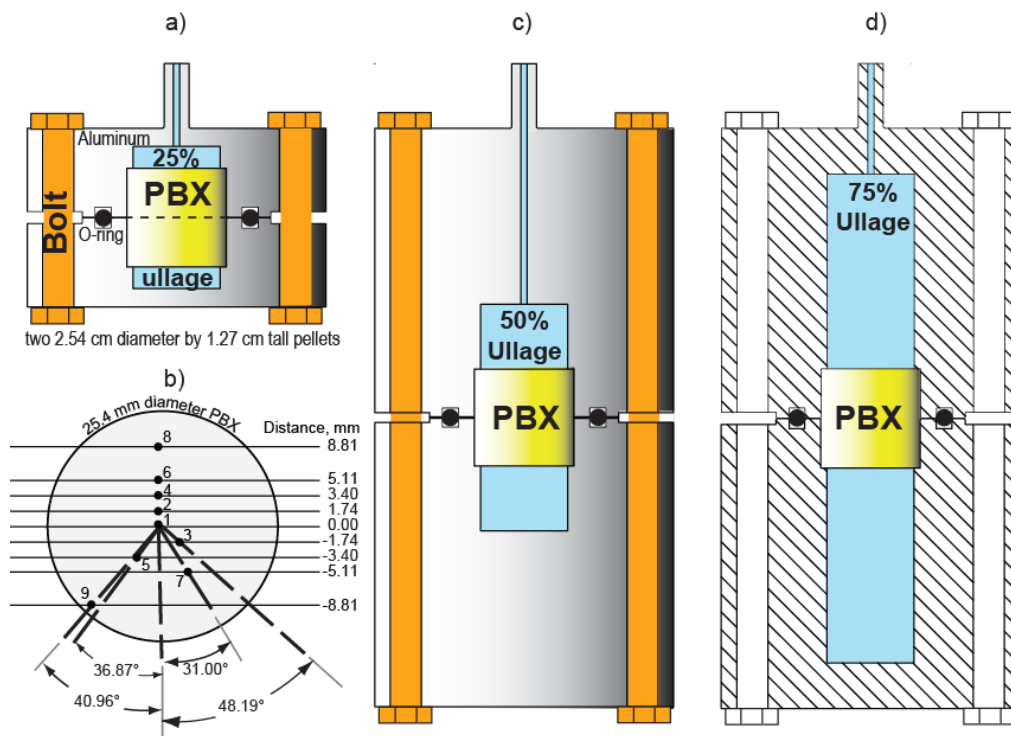


Figure 2. a) SITI schematic with 25% ullage, b) thermocouple locations, and SITI schematic with c) 50% and d) 75% ullage.

The outside temperature of the confining aluminum cylinders was maintained at a controlled set point using a coil heater. Typically, the outside temperature of the aluminum confinement was ramped from room temperature until the set point temperature was reached. The ramp rate was controlled so that the set point temperature was reached in 10 minutes. Pressure was monitored with a transducer connected to the top of the apparatus through various lengths of tubing. More information regarding this modified SITI experiment can be found in reference [2].

Figure 3 shows an example of the measured temperature and pressure profiles for a low density and high density SITI experiment. The low density experiments, #225 and #223, contained molding powder similar to that shown in Figure 1.b with a density of 0.75 and 0.74 g/cm<sup>3</sup>, respectively. For these experiments, the ullage was 19% of the overall internal volume. The boundary temperatures for both of these experiments were controlled so that the outside temperature reached 573.5 K in 10 minutes. For experiment #225, the experiment was sealed and the ignition occurred at 50.6 minutes. For experiment #223, the gases were vented from the tube and the ignition occurred after 125.1 minutes from the start of the ramp. Clearly, confinement affects the time to ignition.

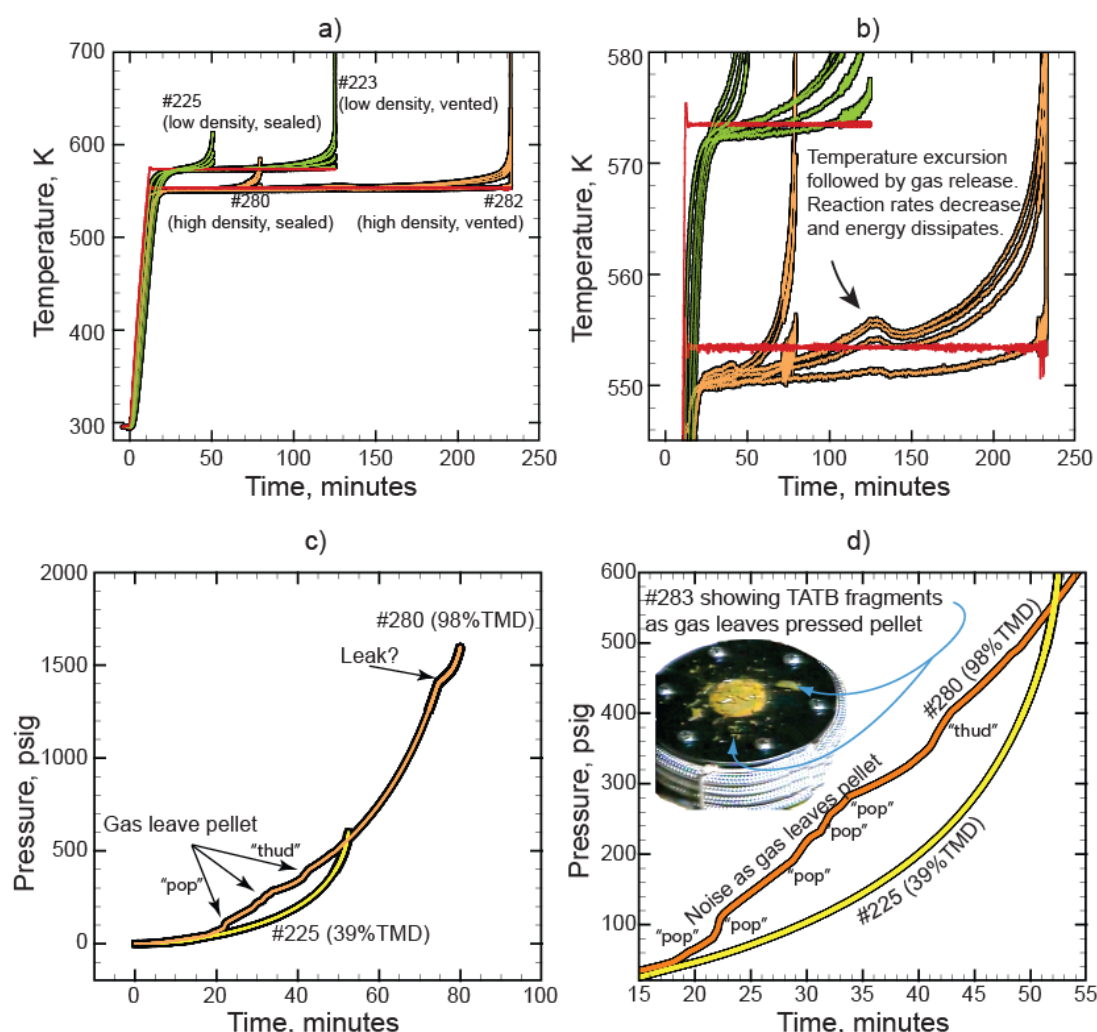


Figure 3. Measured temperature (a,b) and pressure (c,d) for two low density and two high density experiments. The gases are either vented or sealed for both experiments. Both low density experiments have the same set point temperature shown in red. Both high density experiments also have the same set point temperature.

Figure 3 also shows the measured temperature and pressure for the high density experiments #280 (sealed) and #282 (vented), which contained pellets pressed to 1.90 and 1.87 g/cm<sup>3</sup>, respectively. The boundary temperature for both of these experiments was ramped from room temperature to 554.4 K in 10 minutes. The ullage in experiments #280 and #282 were 25.1 and 25.7% of the overall internal volume, respectively. The ignition time for the sealed experiment #280 was 79.4 minutes; and, the ignition time for the vented experiment #282 was 232.1 minutes. Again, venting increases the ignition time significantly.

Figure 3.b shows a close-up view of the temperatures in Figure 3.a. An arrow highlights a temperature excursion occurring at 130 minutes for the high density, vented experiment #282. Accumulating gases within the high density PBX may have caused high pressures and increased reaction rates within the PBX causing the temperature to rise. High pressure gases may have caused the PBX to spall or crack, similar to the degraded pressed explosive shown in Figure 1.c. The temperature decreased as the internal pressure was relieved.

Figure 3.c shows the pressure for the low density experiment #225 as being smooth. The pressure for the high density experiment #280 was not smooth. Small increases in pressure between 20 and 50 minutes were also associated with a loud “pop” or a “thud.” Similar audible noises have been observed during the vented high density experiments. As the pellet is damaged by cracking or spalling, these gases are released into the ullage space for the sealed experiments where the pressure is measured. The inset picture in Figure 3.d is a frame of a video of an open test that shows spalling. The drop in temperature could be due to expansion cooling, reduced reaction rates, and energy dissipation.

#### 4. Model

Details of the model have been given by Hobbs and Kaneshige [2] and are only briefly discussed in this section. Thermal ignition is determined by solving the conductive energy equation using a volumetric source for the chemical reactions. The pressure dependent decomposition is accounted for by using a nonstandard Arrhenius reaction model using distributed activation energies. The pressure model is based on a low Mach flow assumption, where the gas velocity is much less than sound speeds and the pressure within the system is only a function of time, that is  $P(x,y,z,t) = P(t)$ . Pressure changes temporally because of increasing temperature and reaction. Condensed and gas-phase temperatures are assumed to be equal, that is,  $T_c = T_g = T(x,y,z,t)$ . The engineering model does not 1) track gas flow, 2) calculate separate gas and condensed temperatures, and 3) determine permeability due to reactions or strain.

Figure 4 presents the four-step pressure dependent reaction mechanism used by Hobbs and Kaneshige [2]. The first step represents drying of the adsorbed water following the work of Glascoe et al. [3]. The amount of adsorbed water is assumed to be 0.15% by weight for all of the simulations. The water desorption enthalpy is the enthalpy of vaporization of water. Desorption of water from TATB was first order in the amount of adsorbed water. The desorption reaction was distributed with respect to the extent of reaction and was not pressure dependent.

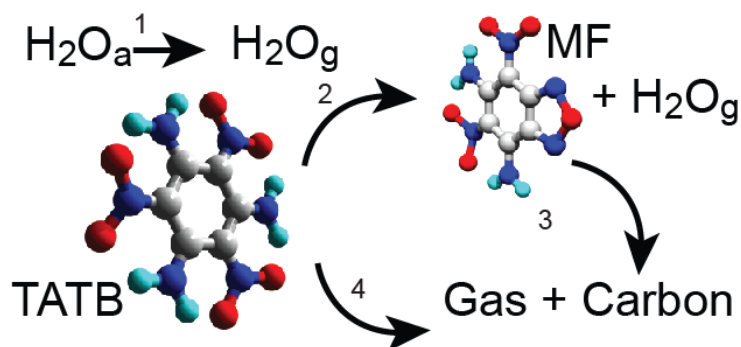


Figure 4. Simple TATB decomposition mechanism.

Mono-, di-, and tri-furazan compounds were observed during decomposition of TATB by Land et al [4], with mono-furazan being the most prevalent furazan. Following the observations of Land, we have taken the second reaction step to be the formation of mono-furazan (MF) with the loss of a single molecule of water from the TATB molecule. The reaction enthalpy for the second reaction is assumed to be thermally neutral. Using this assumption with Hess's law, the heat of formation of MF is +87.6 kJ/mol. The heat formation of the MF is needed to determine the enthalpy change associated with the decomposition of MF to form equilibrium products, which is the third reaction step.

The third and fourth reaction steps represent the decomposition of MF and TATB into the final equilibrium products. The product hierarchy was determined using equilibrium calculations over a broad temperature and pressure space. The products composition did not change appreciably over this range. The reaction enthalpy for the 3<sup>rd</sup> reaction was determined using Hess's law with the heat of formation of MF determined from the neutral 2<sup>nd</sup> reaction. The final reaction is the decomposition of TATB directly into equilibrium products.

The gas pressure was calculated using the BKWS [5] equation of state (EOS) in conjunction with conservation of gas volume. The thermal expansion of the TATB was determined using the temperature dependent volumetric expansion coefficient from Maienschein and Garcia [6], until reactions became significant. Material strain caused by gas generation was determined by using an empirical swelling model.

Hobbs and Kaneshige list four typical model scenarios encountered when using a decomposition model for safety analysis: 1) sealed high density,  $\rho \geq 95\%$  TMD; 2) sealed low density,  $\rho < 95\%$ ; 3) vented high density, and 4) vented low density. Each of these scenarios is based upon the permeability of the PBX. The interested reader can find details regarding these model scenarios, the model equations, and the model parameters in reference [2].

## 5. Model comparisons to data

Figure 5.a and 5.b shows a comparison of the measured and predicted temperature and pressure for experiment #225, respectively. The inset pictures show the finite element mesh and a color contour plot of the temperature at the onset of ignition. Ignition times for experiment #225 and other SITI experiments run with 18.6-25.7% ullage is shown in Figure 5.c and 5.d.

Figure 5.c shows the effect of density and venting. Ignition time increases with venting and decreases with higher density. The simulations of the high density PBX were done by assuming the gases remain in the pellet and cannot diffuse into the ullage space. This type of decomposition is referred to as closed pore decomposition. Open pore decomposition is assumed when the gases can access all of the internal gas volume as well as the ullage volume. A simulation done assuming both open and closed pore decomposition is shown in Figure 5.d. The simulations with the closed pore assumption match the data better, except for experiment #172. The temperatures and pressures predicted for experiment #172 are shown in Figure 6 with the data. The data shows the gas release from the pellet with an accompanying increase in measured pressure, a leak with a decrease in the measured pressure, a clog causing the measured pressure to increase, and gas release. The leak likely caused the rates to drop and the ignition time to increase.

Figure 7 shows a simulation of experiment #277. In this high density sealed experiment, a large temperature excursion is seen prior to ignition. The measured pressure is labeled external pressure in Figure 7.b since the pressure is measured with a transducer outside of the pellet. The pressure predicted in the model is the pressure within the PBX. The internal pressure drop is caused by thermal expansion and swelling of the PBX. The internal pressure starts to increase as decomposition gases are produced. Eventually, thermal runaway is predicted at the first temperature excursion. The data indicates that the gases broke through the pellet at the first thermal excursion and the reaction rates decreased. Eventually the pressure and reaction rates were high enough to ignite the PBX.

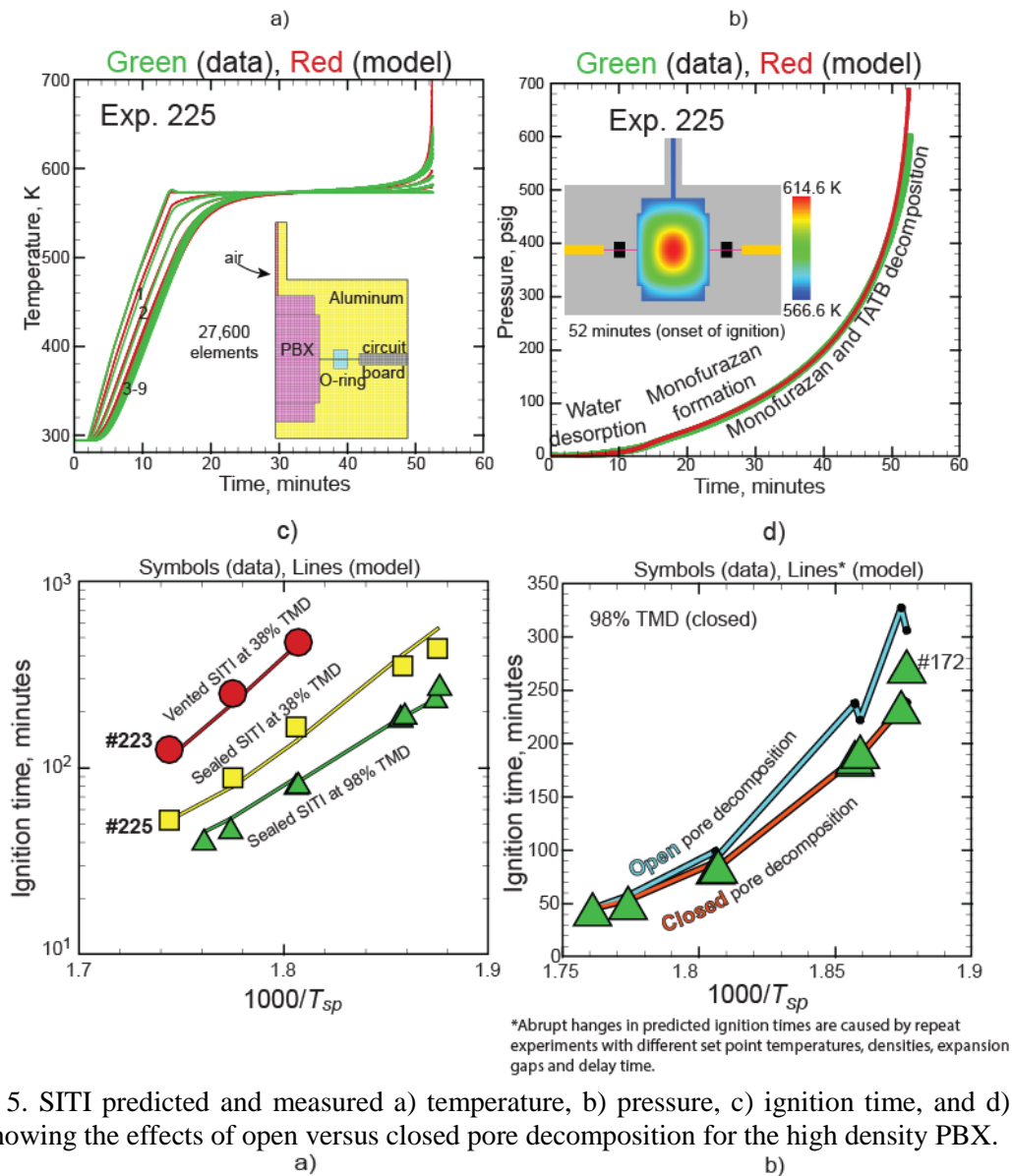


Figure 5. SITI predicted and measured a) temperature, b) pressure, c) ignition time, and d) ignition time showing the effects of open versus closed pore decomposition for the high density PBX.

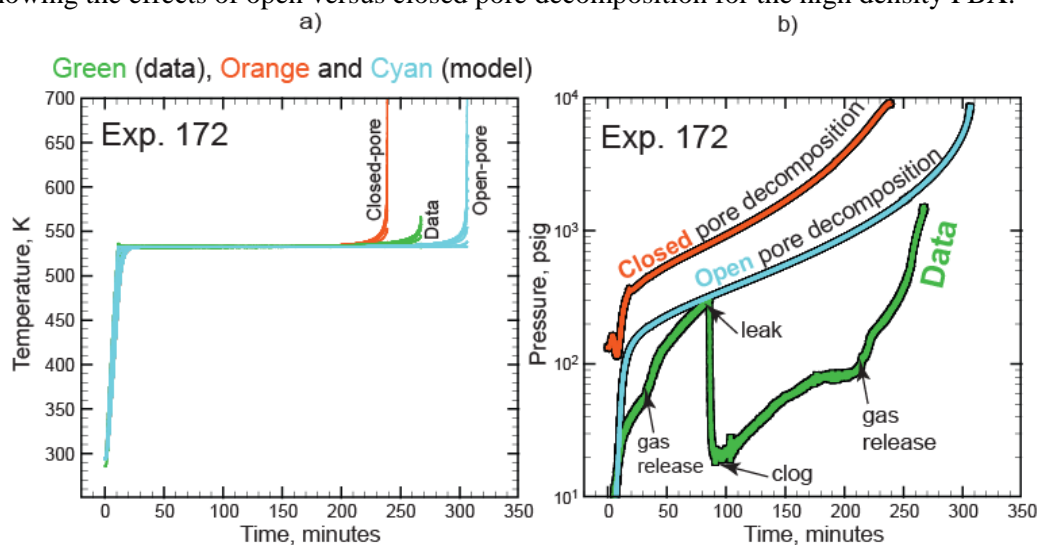


Figure 6. Measured and predicted a) temperature and b) pressure for experiment #172.



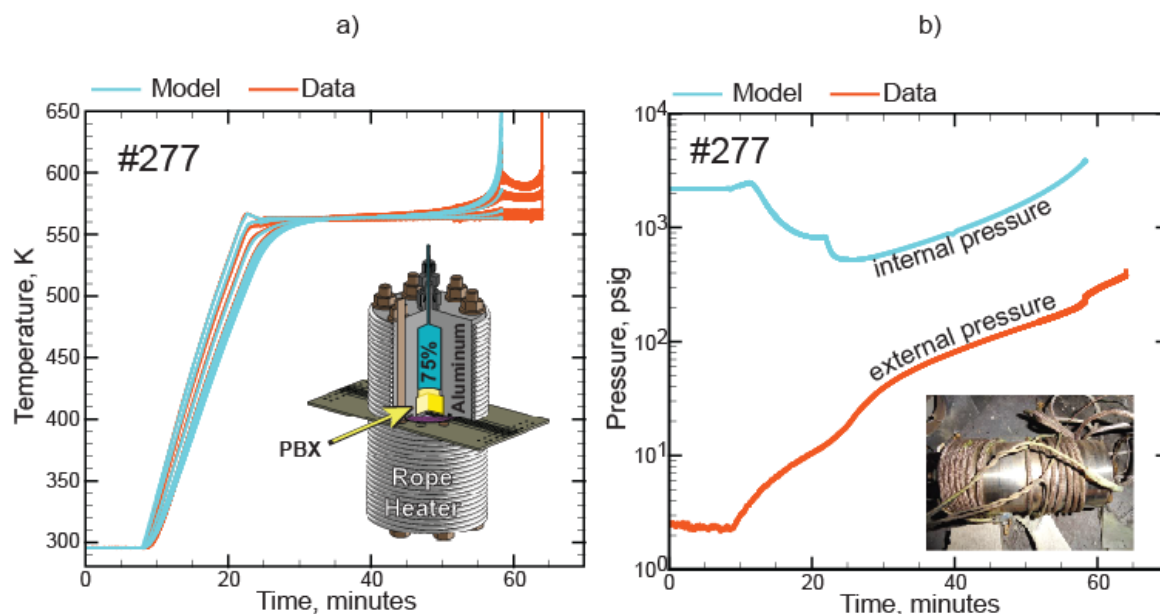


Figure 7. Measured and predicted a) temperature and b) pressure for experiment #277.

## 6. Summary and Conclusions

The effects of confinement on decomposition of a plastic bonded explosive containing TATB have been studied both with experiments and models. The decomposition is dependent on the density and the degree of confinement of the PBX. For low density PBX, the decomposition gases permeate through the explosive and mix with the ullage gases within the confining apparatus. For high density pressed PBX, the decomposition gases are retained within the explosive. Periodically the high pressure gases vent from the PBX by cracking, spalling or some other damage mechanism. The release of the trapped gases is associated with temperature excursions and acoustic noise. The release of trapped gases causes the decomposition rates to drop and the ignition to be delayed. Decomposition of TATB is highly dependent on pressure and confinement.

## Acknowledgments

I would like to thank Michael J. Kaneshige for allowing me to use his SITI data. Mike should have been a coauthor on this paper, but could not since APS does not allow multiple authors for invited papers. More details regarding our joint work can be found in [2]. I would also like to thank Shane Snedigar for running all of the SITI experiments, Bill Erikson for reducing the SITI data to determine thermal conductivity, Tolulope Okusanya for helping to implement the pressure dependent model, Eric Harstad for leading the energetics team and obtaining funding, and Marty Pilch, Leanna Minier for their constant interest and enthusiasm regarding our experimental and modeling activities.

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