Exceptional service in the national interest

SAND2016-3411PE

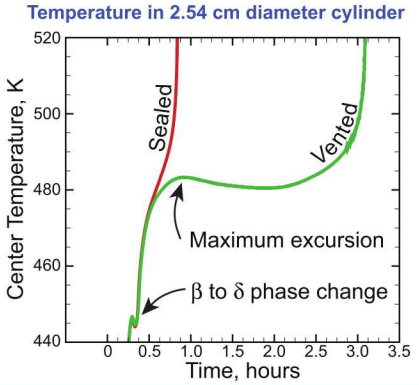
Sandia National Laboratories

NO_x signature

Damage and conductive burn

Cracking and spalling

Effect of nitro-plasticizer

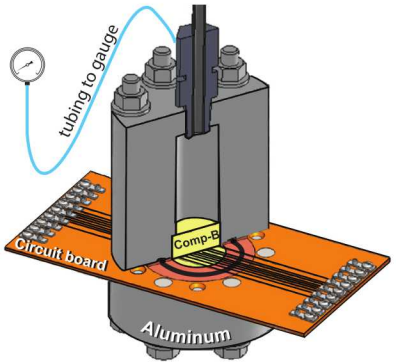


The Role of Pressure during Cookoff of Explosives

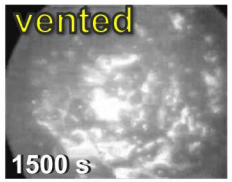
Adsorbent mixed with Nitrate Salts
- Clogged filter leading to heating
- Unclogged filter leading to cooling
- Yellow residue is a sign of NO_x products

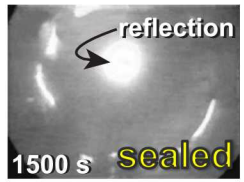
Plastic Bonded Explosive (PBX 9501, PBX 9502)
- Exotherm caused by limiting reactant
- Temperature excursions related to damage

Melt-castable Explosives (Comp-B)
- Pressure affects flow characteristics



Michael L. Hobbs
Michael J. Kaneshige





U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2013-5306C

Why model cookoff?

Sandia National Laboratories

- Need to know behavior in **accidental fires** to assess safety.
- Need to know the **time-to-ignition** for safety timing studies.
- Need to know the **amount of gas produced** to determine if confinement will rupture before ignition.
- Need to know how the damaged state of the material affects the subsequent **burn behavior**.
- Need to avoid **accidents** such as the breach of drum 68660 at WIPP. Initial upper bound cost estimate to restore WIPP to operation-- $550M.

Carrier	Deaths	Injured	Cost
Oriskany, 1966	44	156	$63.6M
Forestal, 1967	134	162	$758M
Enterprise, 1969	28	343	$554M
Nimitz, 1981	14	48	$150M
	220	**709**	**$1525M**

Atwood et al, "Experimental Support of a Slow Cookoff Model Validation effort," 2004 Insensitive Munitions & Energetic materials Technology Symposium (2004).

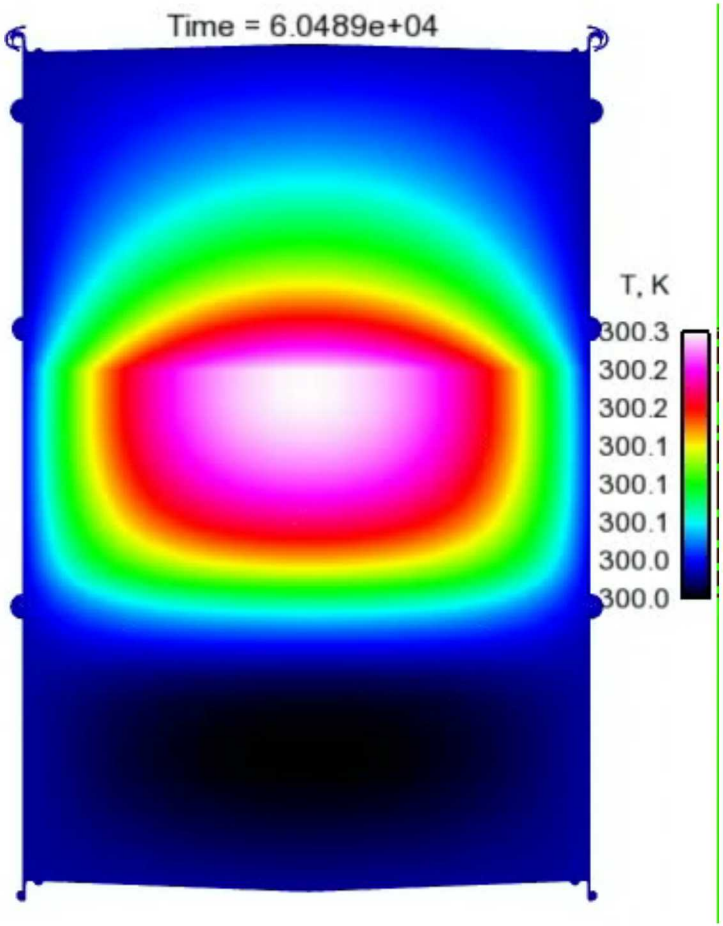
Tremendous cost considering none were under attack!

Organic adsorbent with nitrate salts

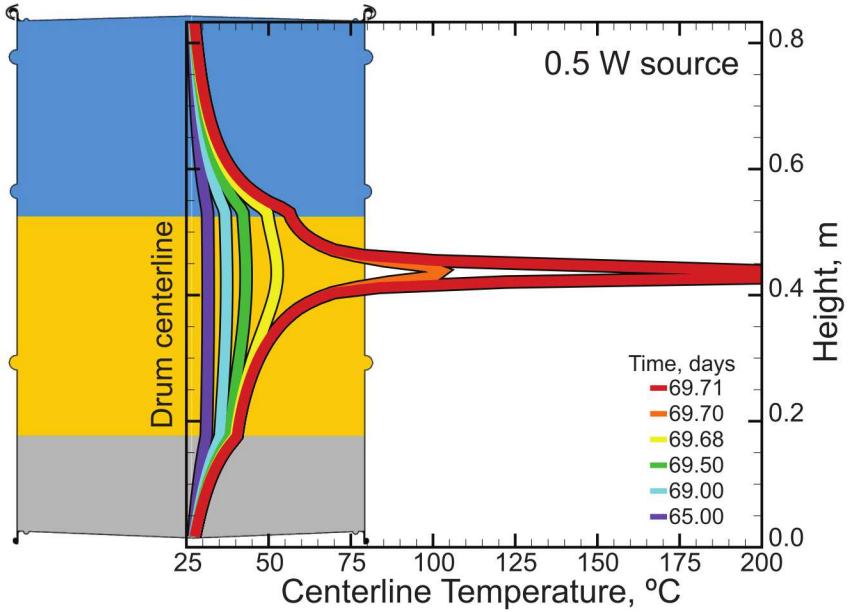
Sandia National Laboratories

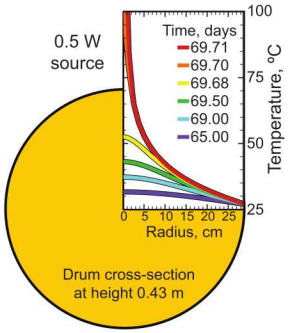
Model of drum 68660

(arrows represent heat generation)



Temperature after 70 days



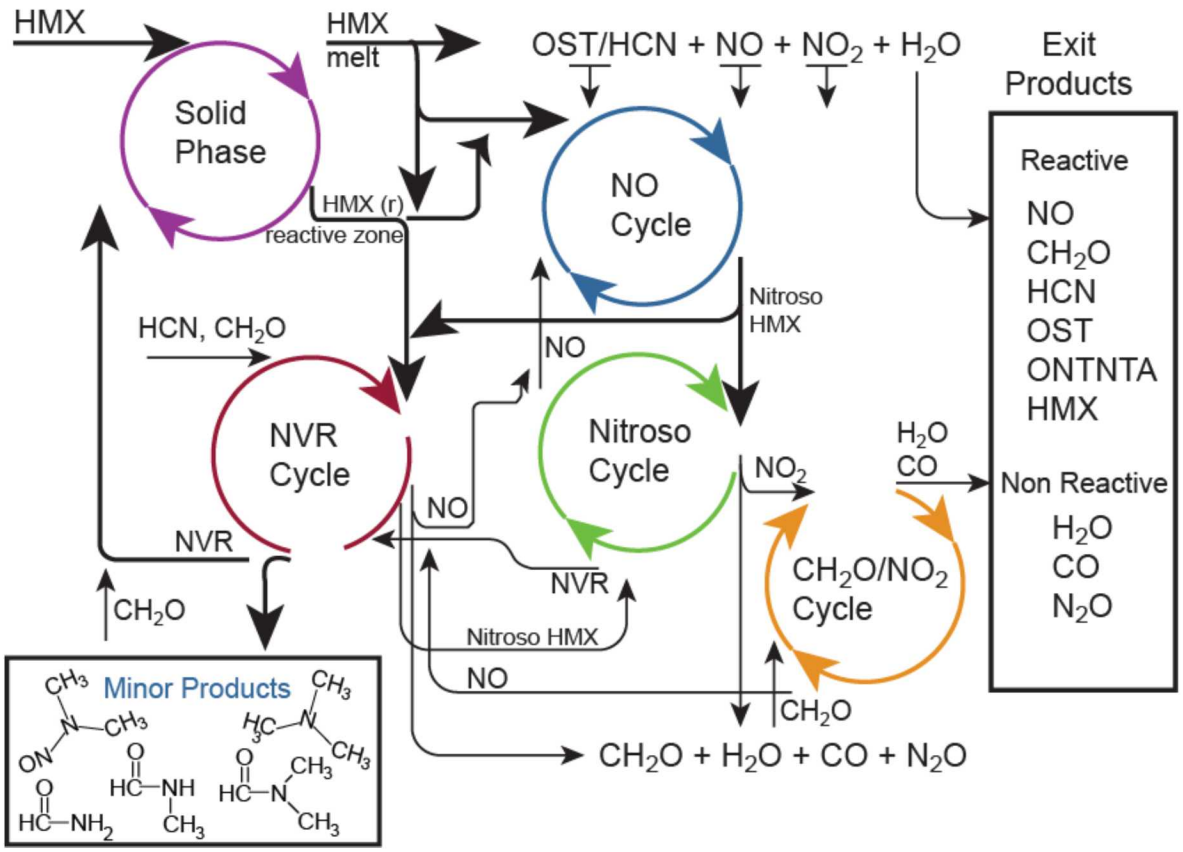


Yellow residue is a key sign of NO_x

Fuming nitric acid contaminated with yellow NO_2

Behrens also measured NO and NO_2 in STMBMS

Complex decomposition mechanism



Behrens R., "Thermal Decomposition of HMX: Morphological and Chemical Changes Induced at Slow Decomposition Rates, *Proceedings of the 38th JANNAF Combustion Subcommittee Mtg.*, 2002, CPIA Pub. 712, Vol. I: p. 397-408.

Highlights

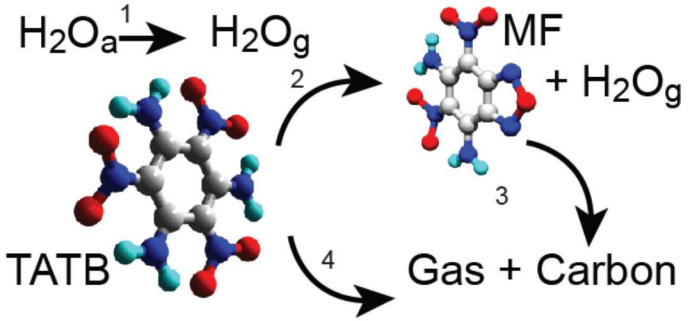
- Reactions occur in gas, solid, and molten phases and depend on physical and morphological changes in the HMX.
- β to δ phase transition creates grain structure and promotes cracking and nucleation sites.
- Nucleation sites fill with decomposition gases and NVR.
- Controlling mechanisms include unimolecular decomposition and gas phase reactions occurring within a closed pore network.

This is for HMX, PBX 9502 also contains 2.5% Estane and 2.5% BDNPA/F

Simplified Decomposition Mechanism

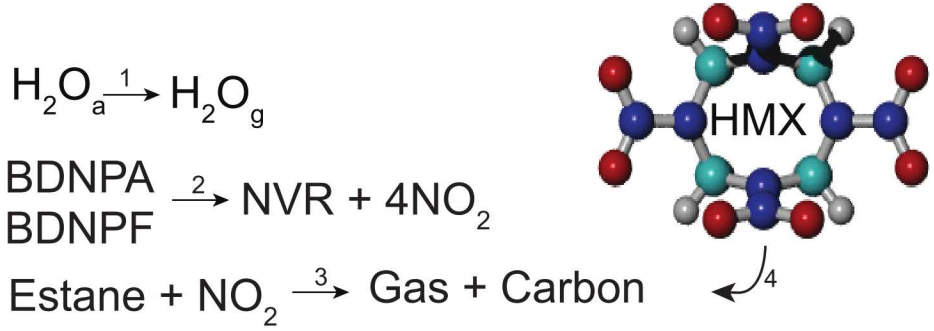
Sandia National Laboratories

PBX 9502 (95% TATB 5% Kel-F)



Hobbs ML and Kaneshige MJ, *J. Chem. Phy.* **140**, 124204 (2014).

PBX 9501 (95% HMX 2.5% Estane 2.5% BDNPAF)



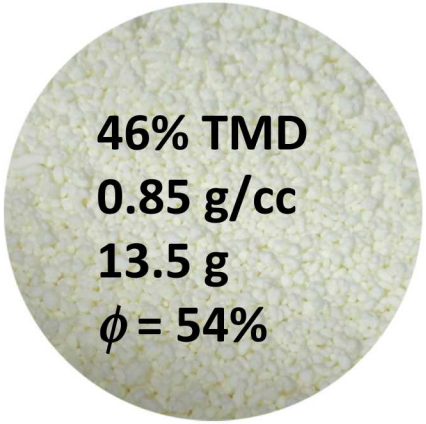
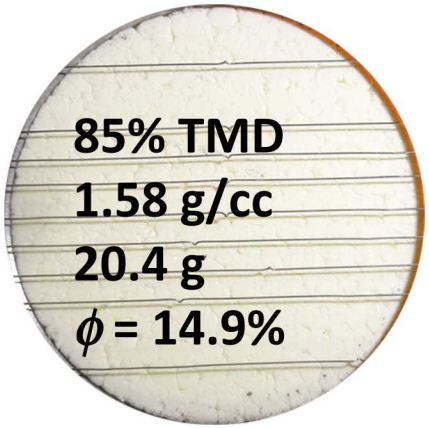
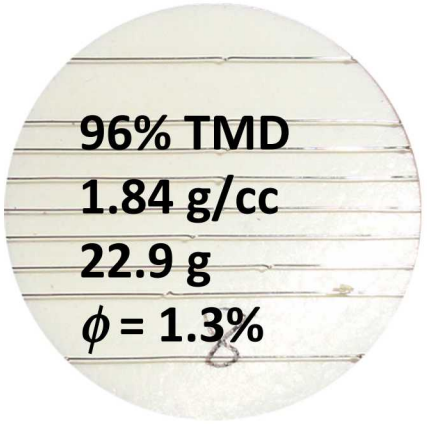
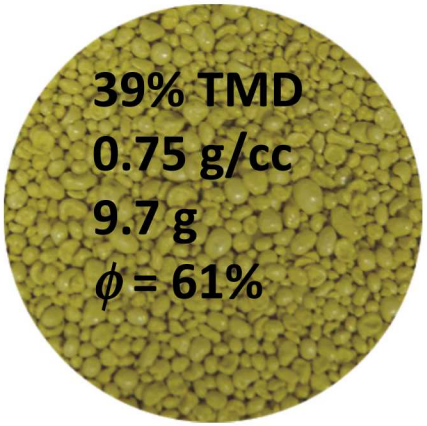
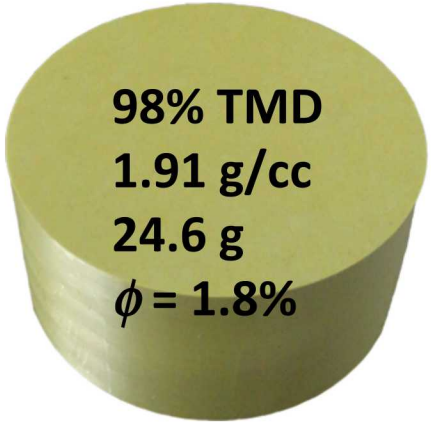
Highlights

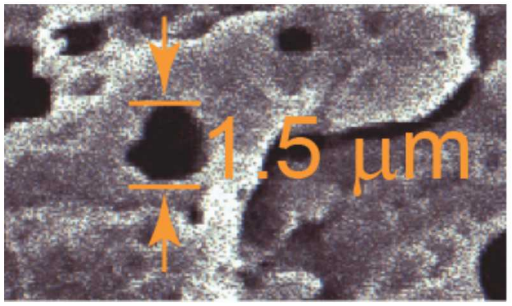
- Reactions occur in gas, solid, and molten phases and depend on physical and morphological changes in the PBX.
- Phase transitions create grain structure and promote cracking and nucleation sites.
- Nucleation sites fill with decomposition gases and NVR.
- Controlling mechanisms include unimolecular decomposition and gas phase reactions occurring within a closed pore network.

Binder: 9502 (Kel-F is assumed inert) 9501 (BDNPAF is a major reactant)

What do plastic-bonded explosives look like?

Sandia National Laboratories

	Prills	Pressed	Pressed
PBX 9501	 46% TMD 0.85 g/cc 13.5 g ϕ = 54%	 85% TMD 1.58 g/cc 20.4 g ϕ = 14.9%	 96% TMD 1.84 g/cc 22.9 g ϕ = 1.3%
PBX 9502	 39% TMD 0.75 g/cc 9.7 g ϕ = 61%	 98% TMD 1.91 g/cc 24.6 g ϕ = 1.8%	



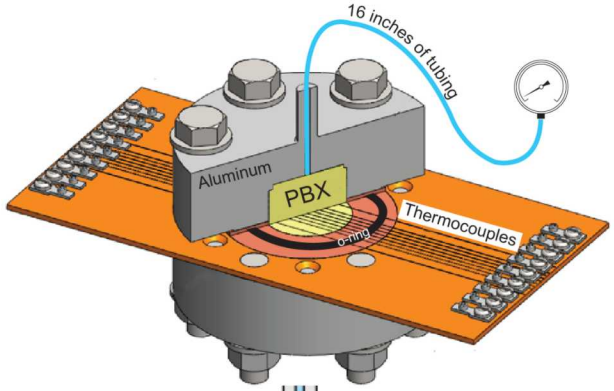
SEM of thermally degraded HMX grain

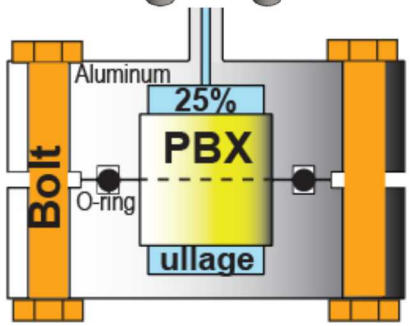
Behrens R. et al (1998)

If porosity is less than about 5%, the pores may not be connected and decomposition occurs in a closed pore network.

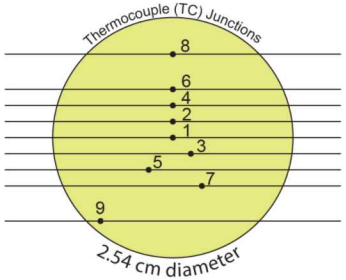
Sandia's Instrumented Thermal Ignition (SITI)

Sandia National Laboratories

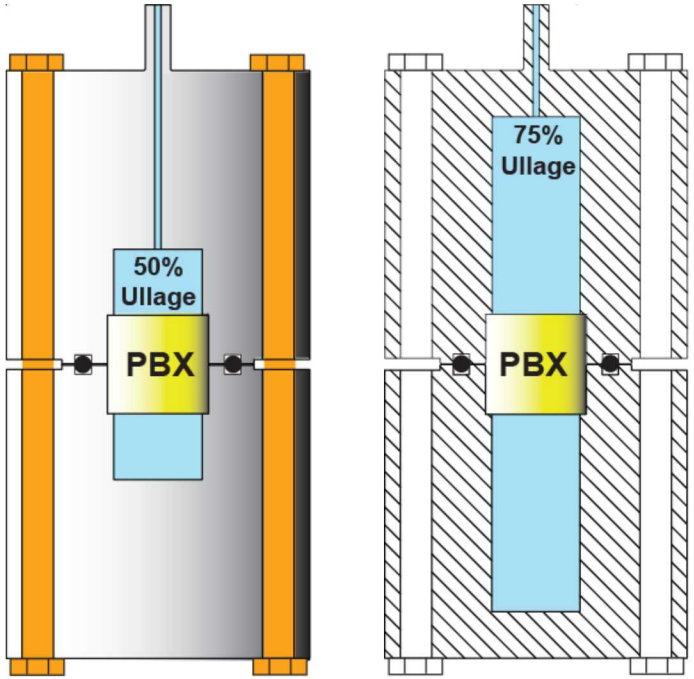




two 2.54 cm diameter by 1.27 cm tall pellets



Large ullage SITI



SITI:

$0.69 \le r \le 1.92$ g/cc

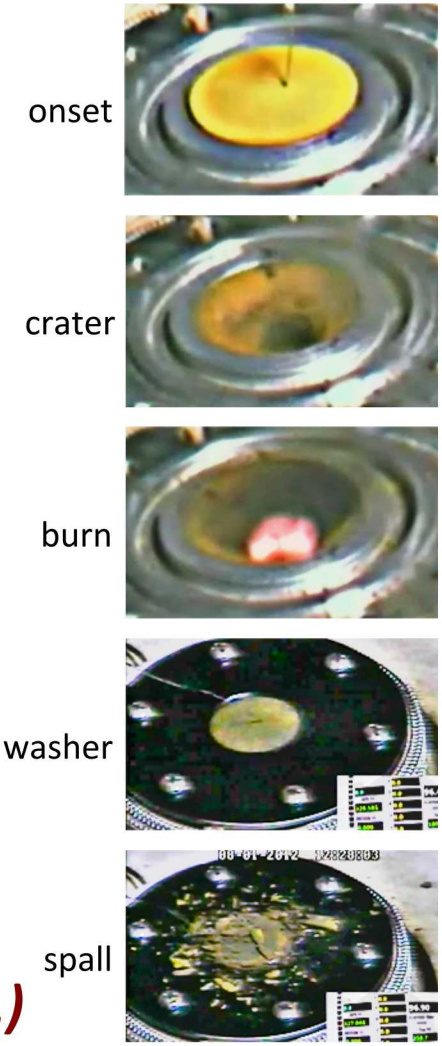
$533\ \text{K} \le T_{sp} \le 574\ \text{K}$

sealed & vented

20-75% ullage (excess gas volume)

Measures: Ignition time, temperature, pressure

Open half shell

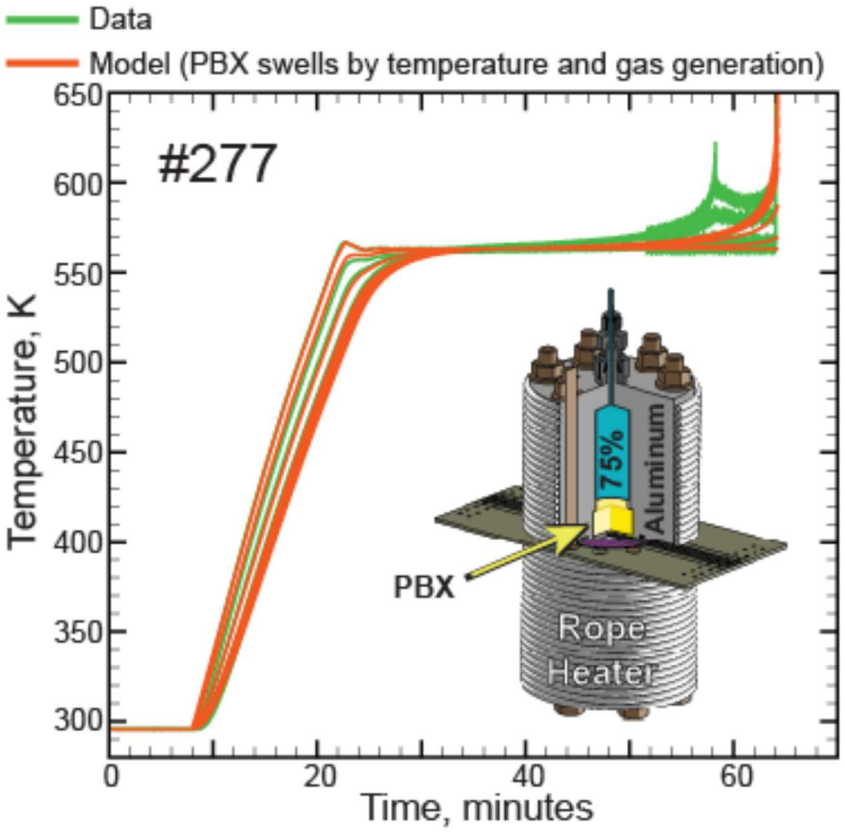


Incremental bursts heard as audible noises (pop, thud, etc.)

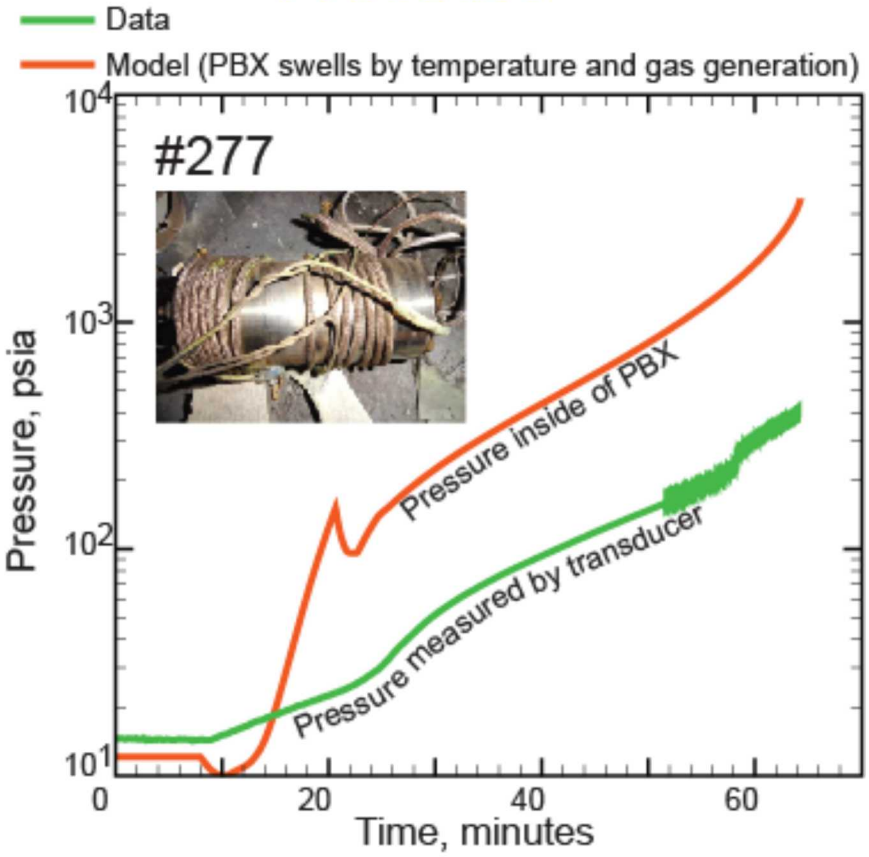
My Favorite PBX 9502 Experiment

Sandia National Laboratories

Temperature



Pressure

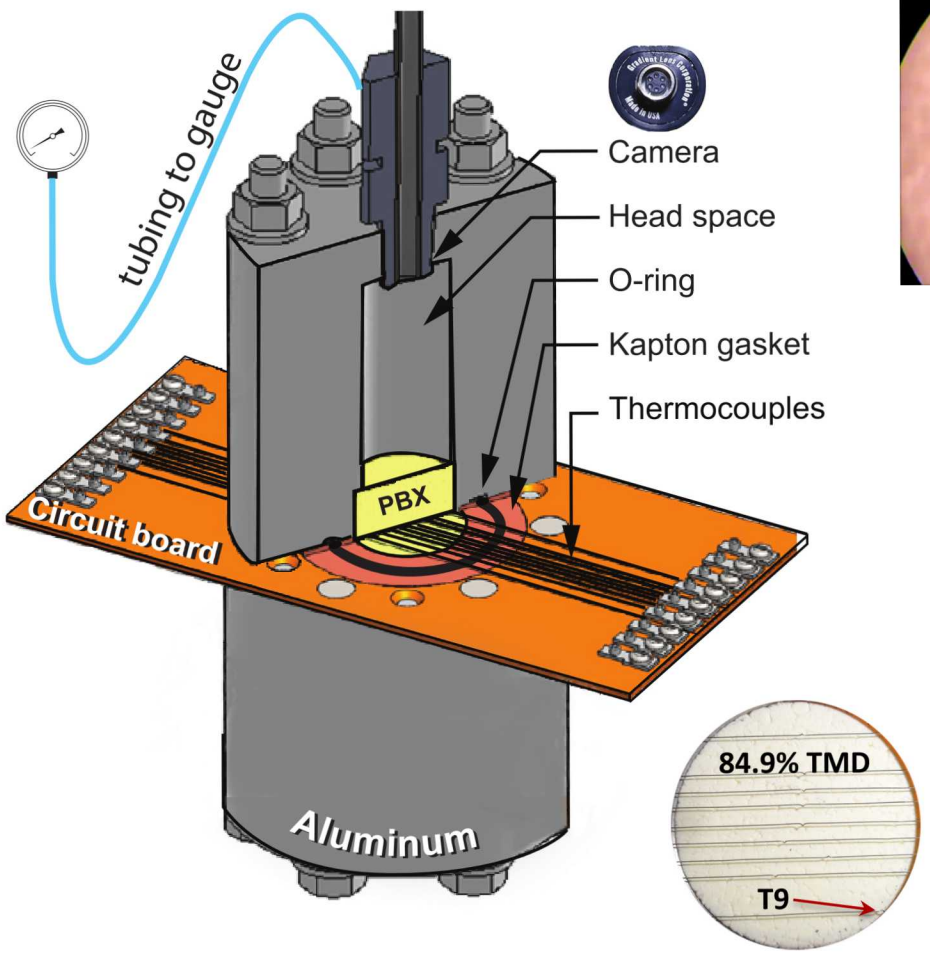


Hobbs ML and Kaneshige MJ, "Ignition experiments and models of a plastic bonded explosive (PBX 9502)," *J. Chem. Phys.*, **140**, 124203 (2014).

Anomalies may not be anomalies.

Boroscope in SITI with PBX 9501

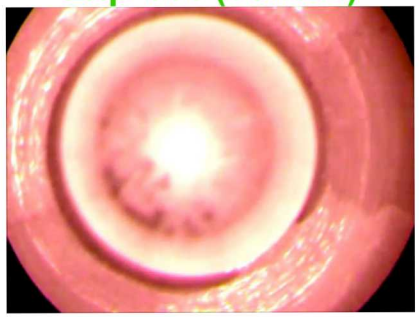
Sandia National Laboratories



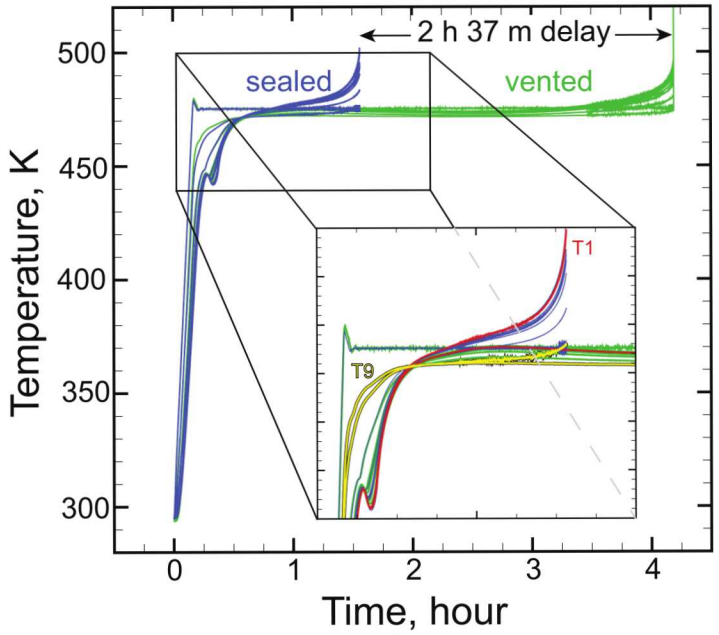
Exp 445 (sealed)

Minimal binder flow

Exp 444 (vented)

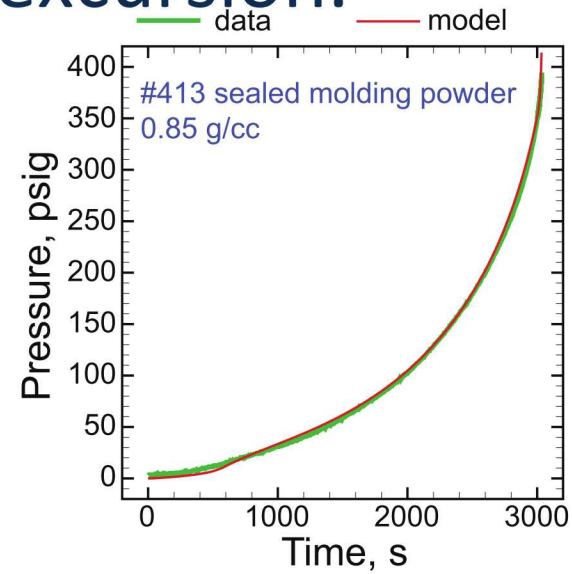


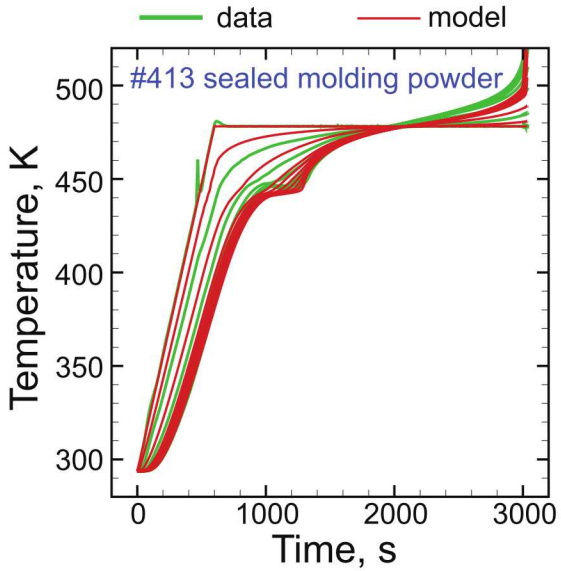
Binder flows to edges

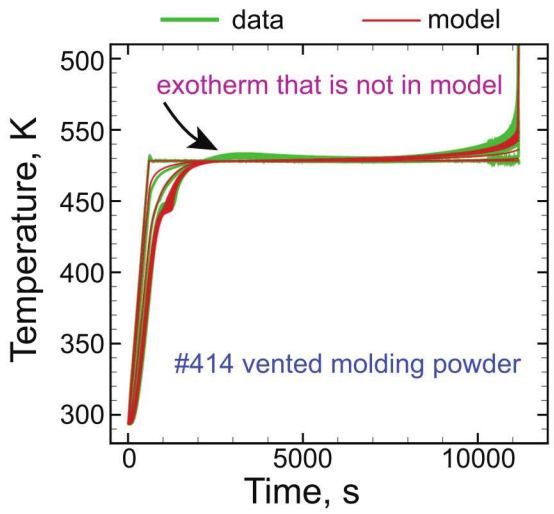


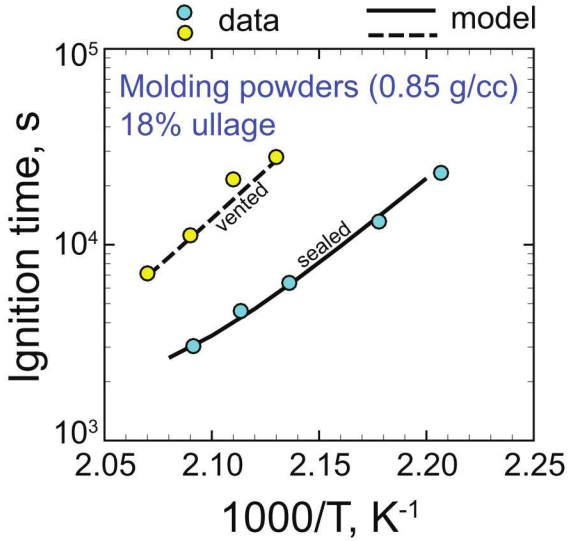
For unconfined decomposition, binder migrates to the edge. A wetted surface provides better heat transfer for the vented case.

Mechanism from 15th Det. Symp does not match excursion.









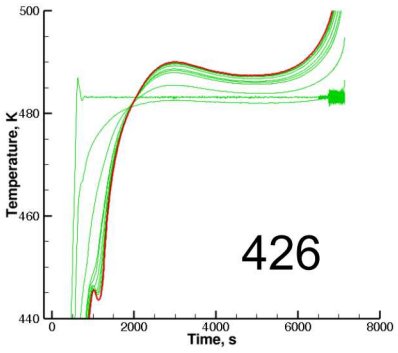
Observations

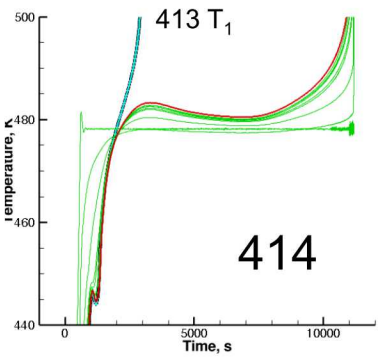
- Distributed activation energy model can be used to match curvature in pressure.
- Steric factor can be used to match slope of ignition curve.
- Poor agreement with T9 for sealed SITI may be due to contact resistance.
- Better agreement with T9 for vented SITI may be related to binder extruding preferentially along Al/EM interface causing better contact at this surface.
- Temperature excursion may be caused by a limiting reactant such as the binder.

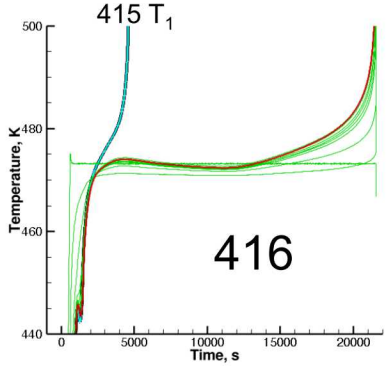
PBX 9501 molding powder (46% TMD)

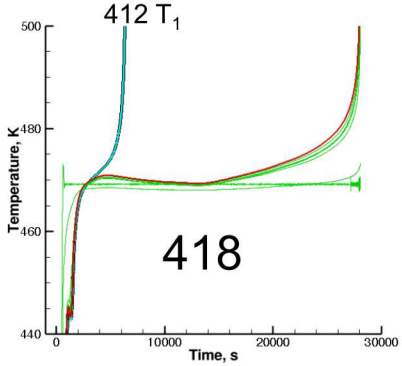
Sandia National Laboratories

Vented

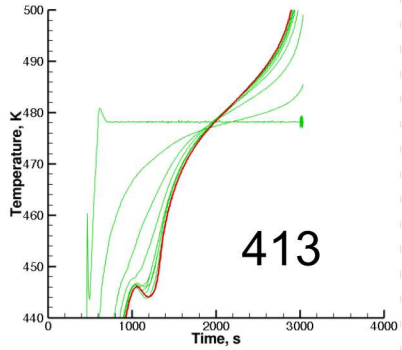


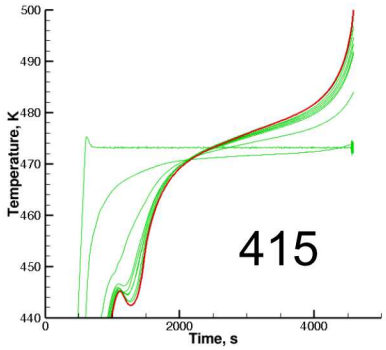


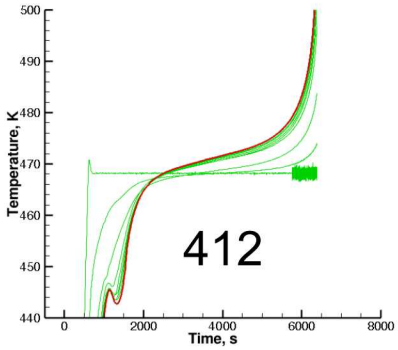


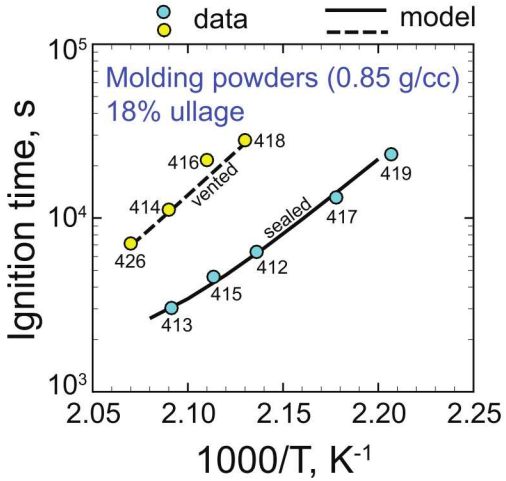


Sealed





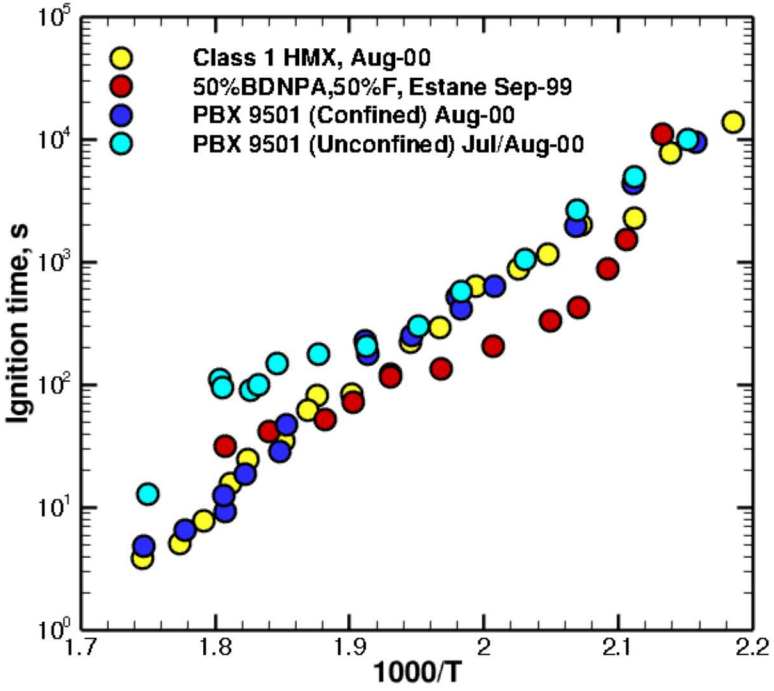




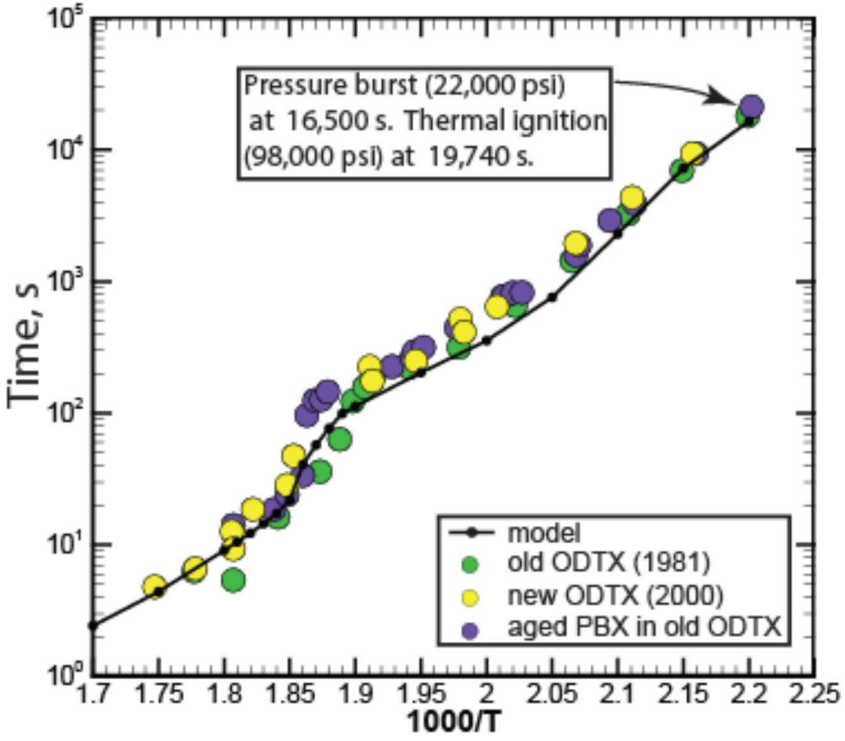
Similar trend shown with 85% TMD SITI experiments.

Could the binder be a major player in cookoff of PBX 9501?

ODTX data shows reactive binder



Tarver CM and Tran TD, *Combustion and Flame* **137**, 50 (2004)

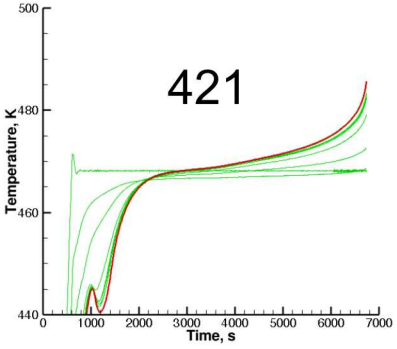


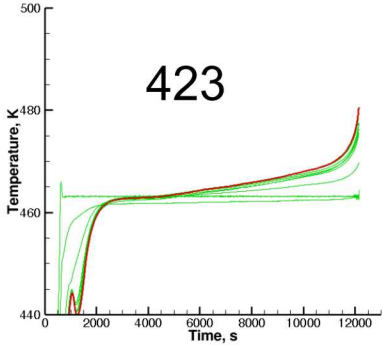
ODTX data does not show a strong effect of venting possible due to gases remaining in PBX. ODTX densities are 95-97%TMD.

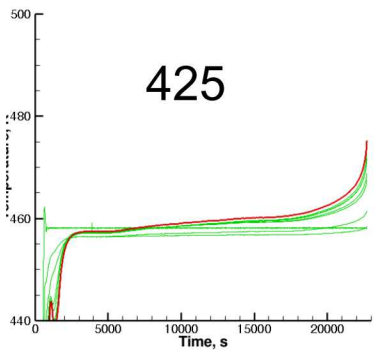
PBX 9501 pressed pellets (95% TMD)

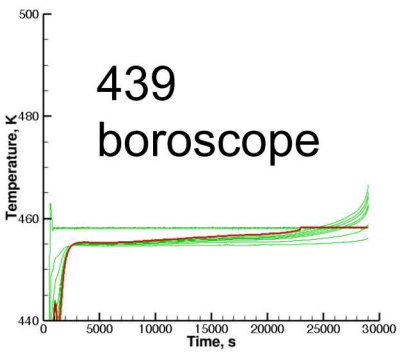
Sandia National Laboratories

Vented

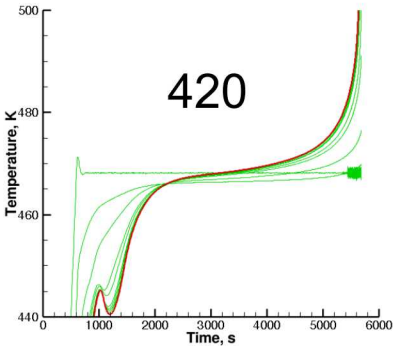


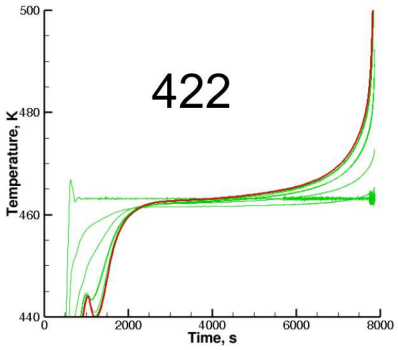


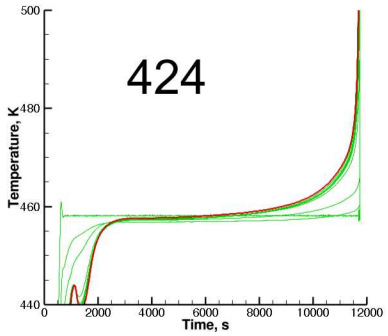


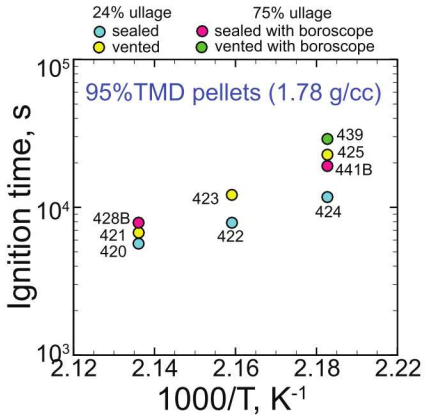


Sealed









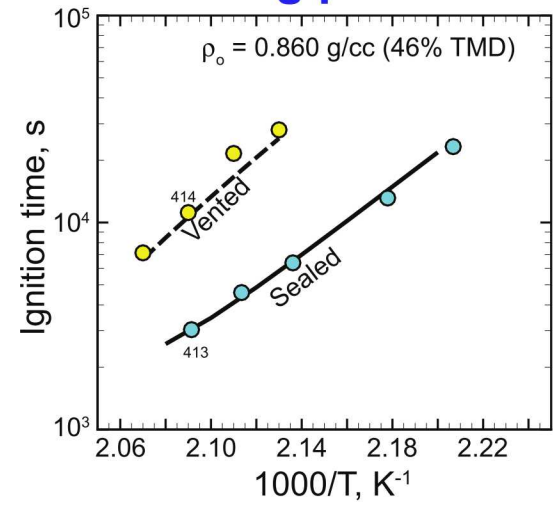
Is this evidence of closed pore decomposition?

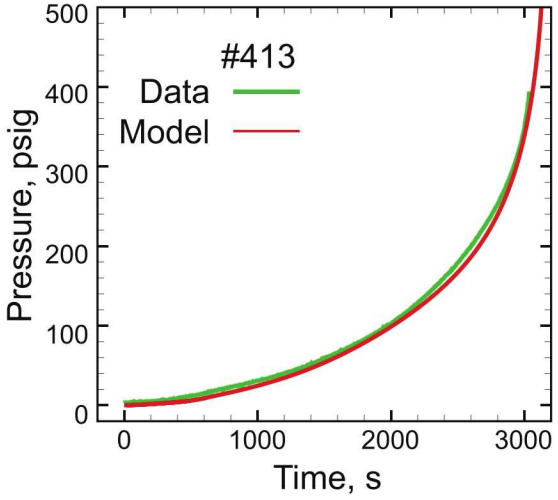
SITI Predicted vs. Measured Ignition Times

(Symbols are data and lines are model)

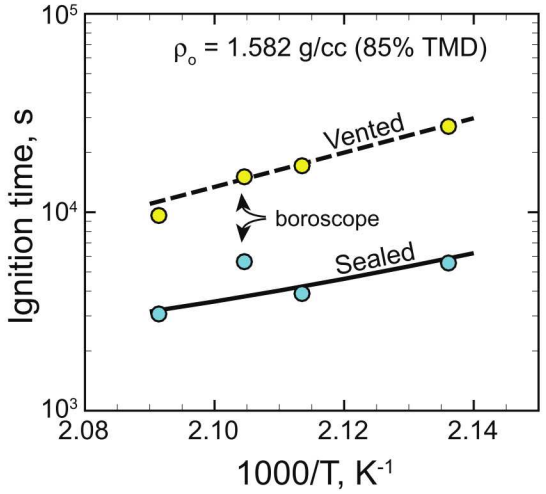
Sandia National Laboratories

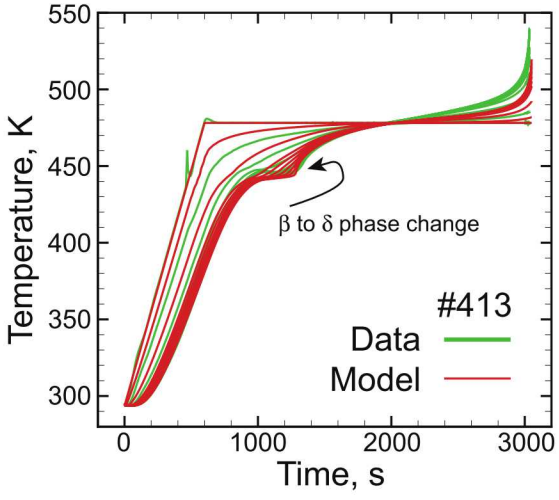
Molding powders



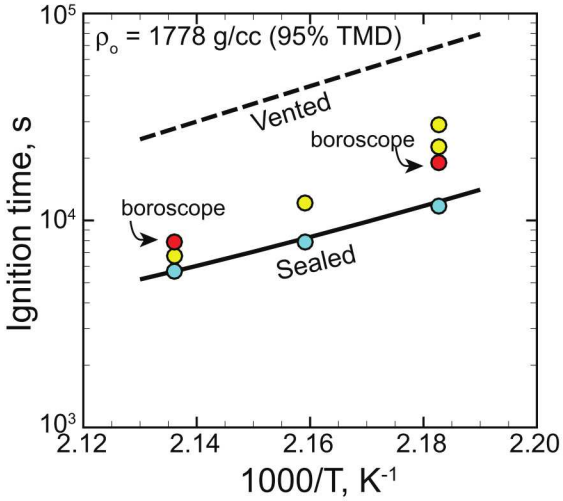


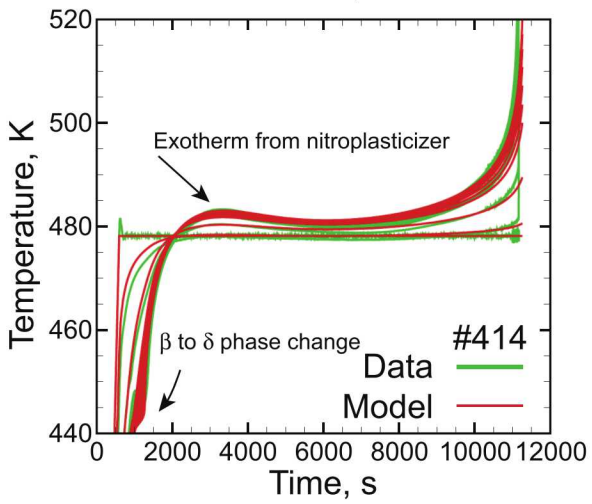
Lightly pressed





Fully pressed



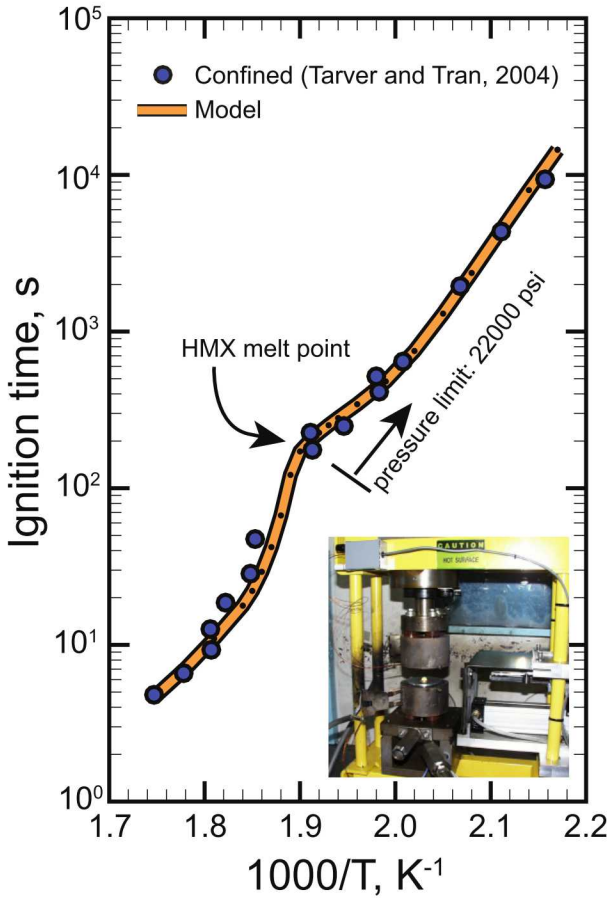


Nitroplasticizer migrates to explosive exterior for high density PBX

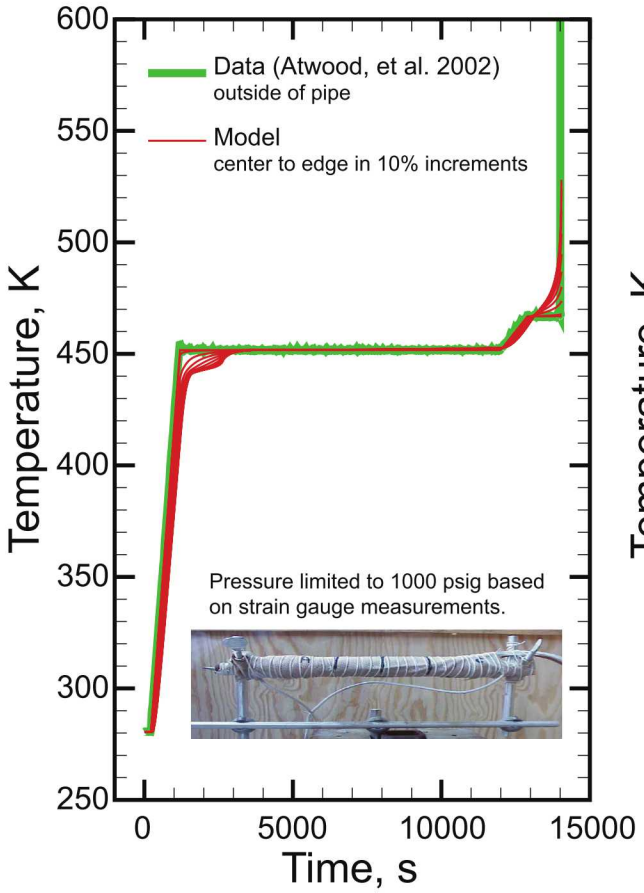
Validation with experiments from other labs

Sandia National Laboratories

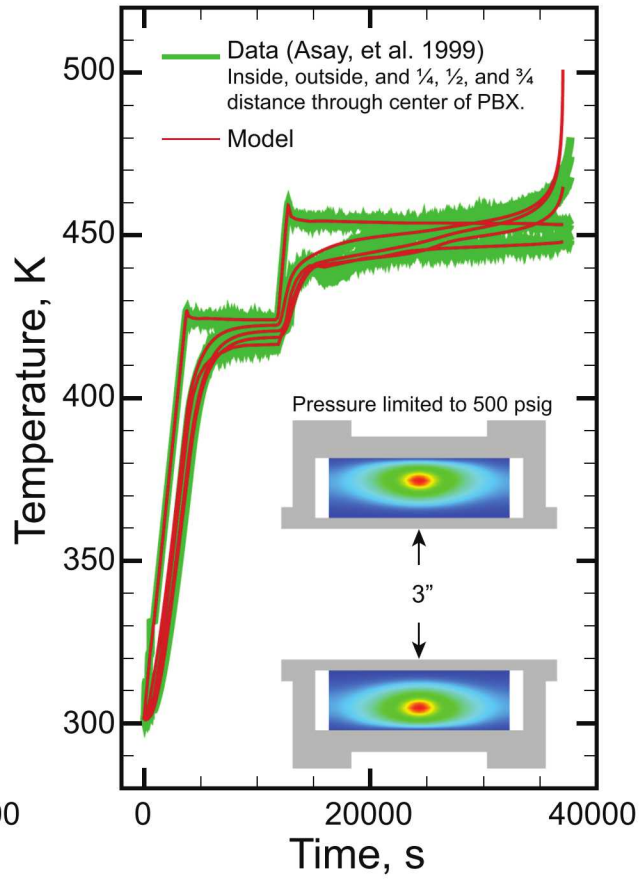
LLNL ODTX



NAWC pipe



LANL LASC



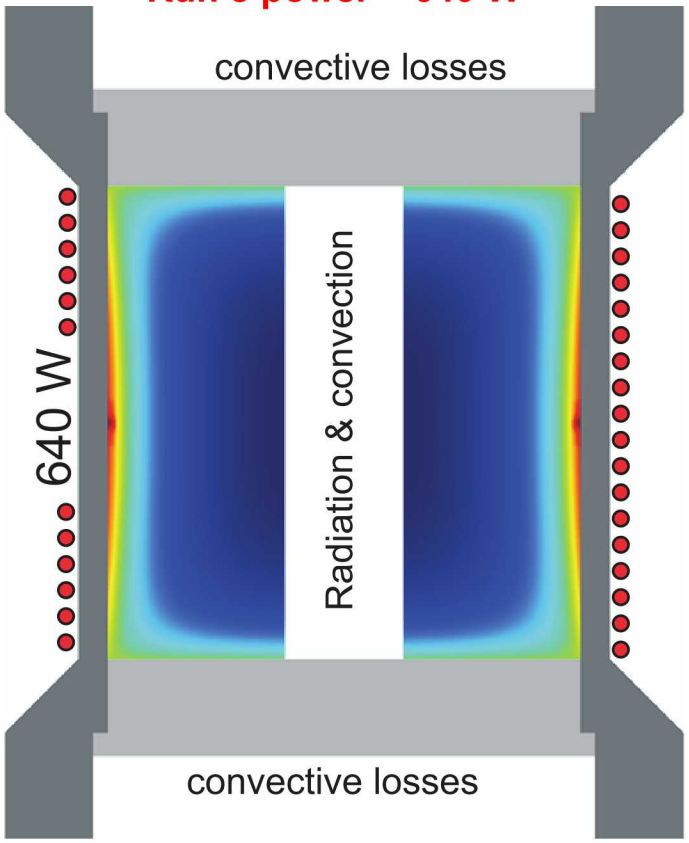
Model predicts scales from 2 g → 36 g → 2540 g. However, we need to know volumes and working pressures accurately!

Other simulations

Fast

CSAFE (1.42 kg PBX)

Run 8 power = 640 W

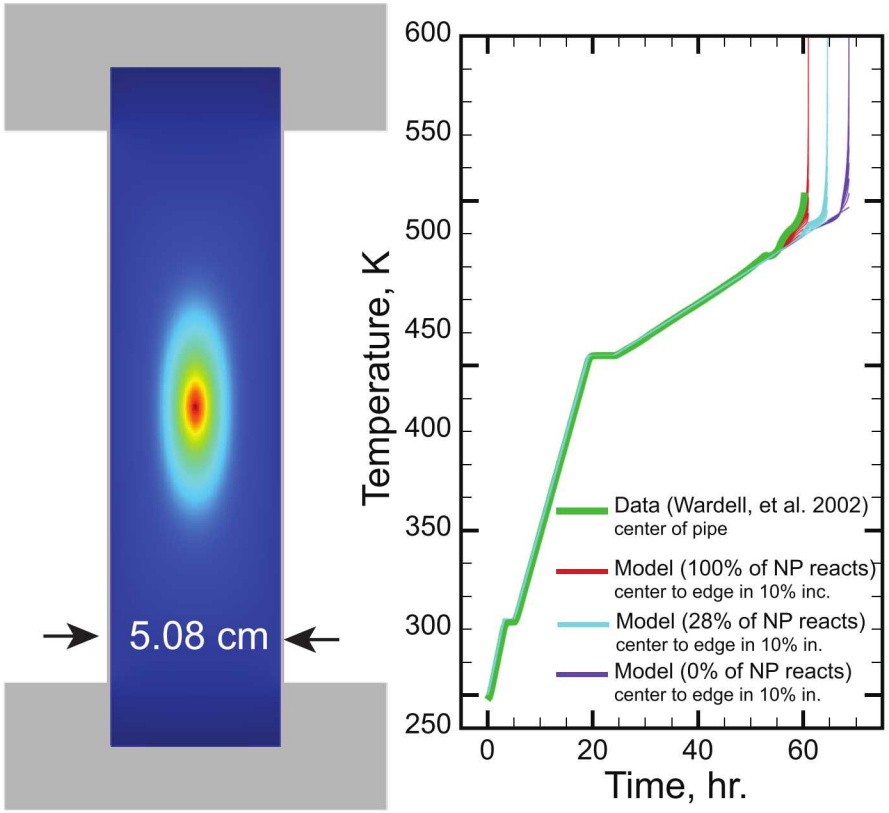


Ignition in 1545 s (model predicts 1500 s)

Slow

STEX (705 g PBX)

Run 27 with thin walls

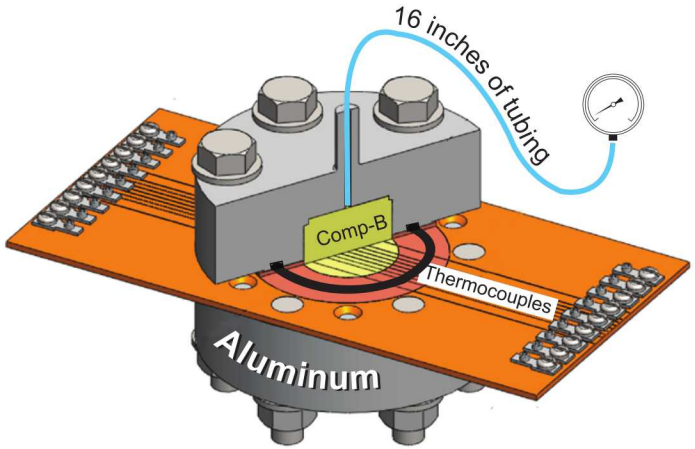


Need accurate boundary conditions, ullage, vessel working pressure.

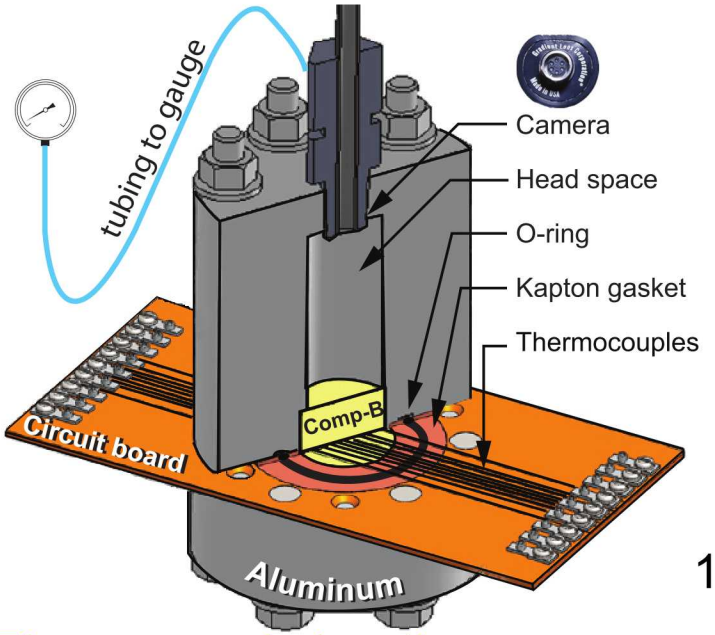
Comp-B experiments

Sandia National Laboratories

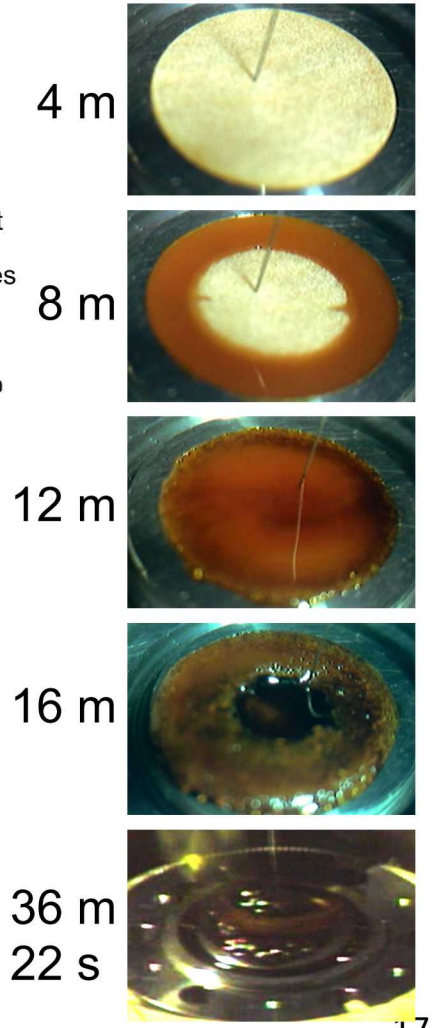
Limited head space



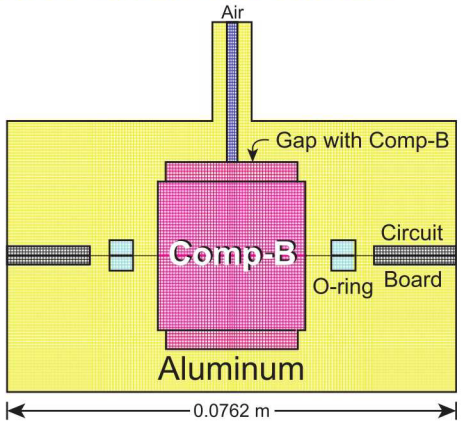
Ample head space



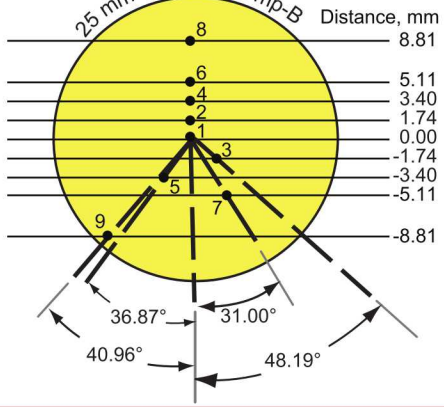
Open half shell



Finite element mesh



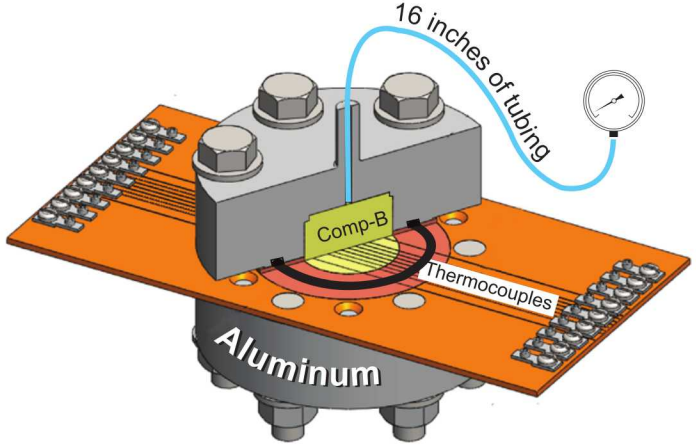
Thermocouple locations



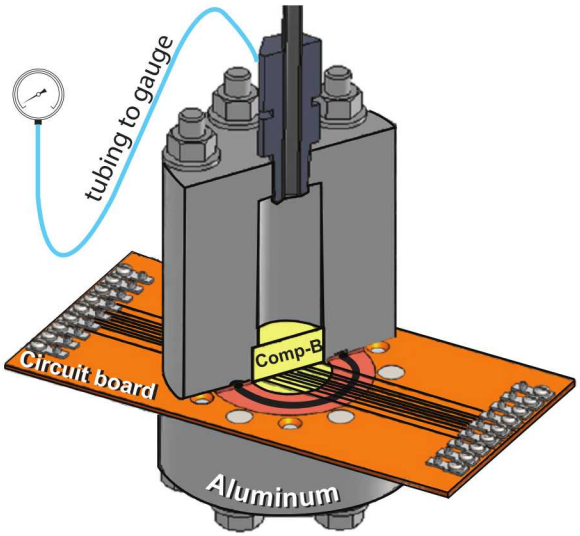
Pressure affects mixing/heat transfer

Sandia National Laboratories

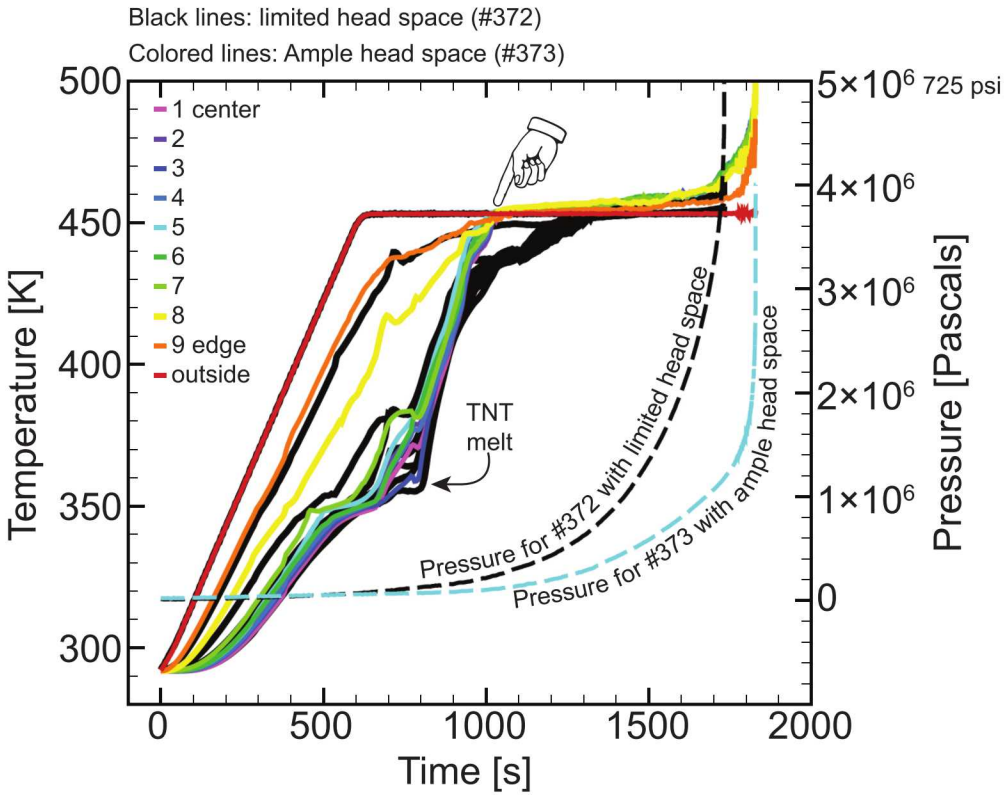
Limited head space, #372



Ample head space, #373



Large head space (colored) shows increased heat transfer

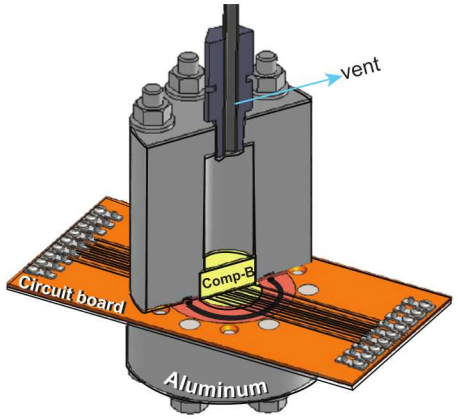


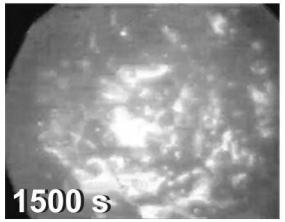
Pressure affects heat transfer more than chemistry since ignition times are similar.

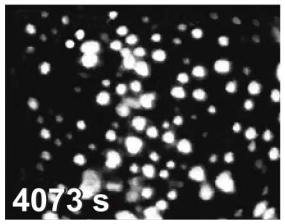
Venting has a *significant* effect

Sandia National Laboratories

Vented, #370

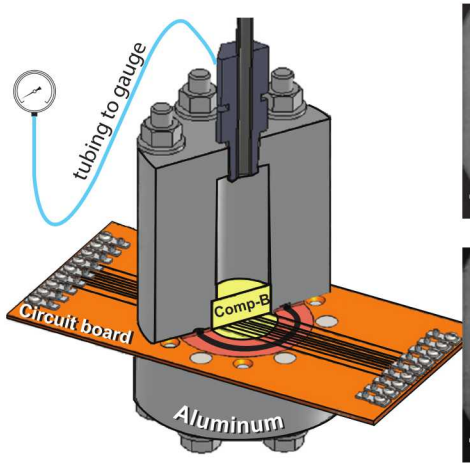


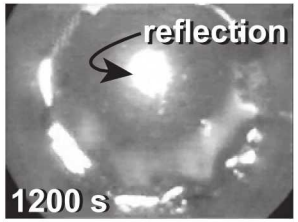


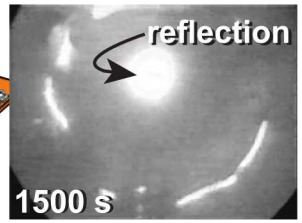


vigorous motion

Sealed, #373

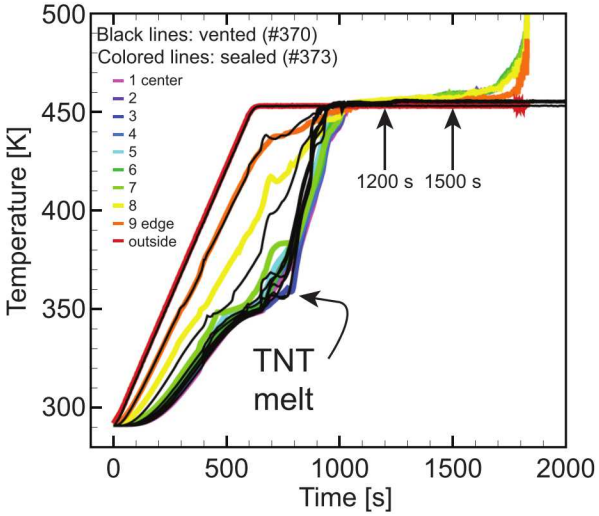


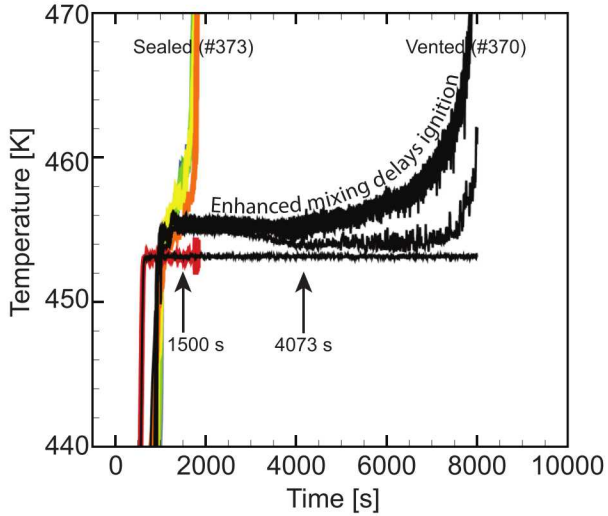




quiescent motion

Temperatures





Observations

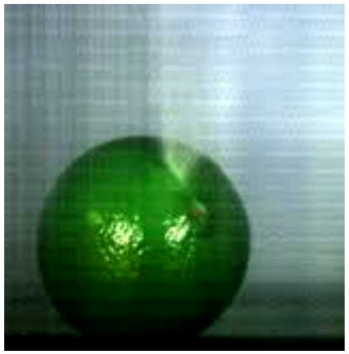
- Bubbly two-phase flow increases heat transfer and delays ignition.
- Higher pressure causes large bubbles to escape along the edge of the Comp-B.

Summary and Conclusions

Sandia National Laboratories

- Pressure effects are different in PBX's vs melt-castables explosives
- Pressure effects chemistry in PBX's
- Pressure effects flow in melt-castable
- Ignition time depends on the degree of confinement of the PBX 9501, which is similar to PBX 9502. Phase change may release trapped gases and open up the structure.
- A temperature excursion during unconfined decomposition of PBX 9501 may be associated with an limiting reactant such as the reactive binder. Perhaps NO_x reacts with the organic fuel, which is pressure dependent.

Internal gas generation in closed pore system leads to failure.

Mechanism Details

Sandia National Laboratories

PBX 9502 (95% TATB 5% Kel-F)

DAE
1) **Drying** (h_{r1} = 2.26×10^6 J/kg, endothermic)
2) **Mono-Furazan formation** (h_{r2} = 0 J/kg, neutral)
TATB → MF + H_2O (h_{r2} = 0 J/kg, neutral)
3) **MF decomposition into equilibrium products** (h_{r3} = -4.82×10^6 J/kg, exothermic)
MF → 3 N_2 + 1.66 H_2O + 1.67 CO_2 + 0.15 CH_4 + 0.04 H_2 + 4.18 C
MF → 6.52 Gas_m + 4.18 C_m

DAE, f(P)
4) **TATB decomposition into equilibrium products** (h_{r4} = -4.48×10^6 J/kg, exothermic)
TATB → 3 N_2 + 2.4 H_2O + 1.8 CO_2 + 0.3 CH_4 + 3.9 C
TATB → 7.5 Gas_t + 3.9 C_t

PBX 9501 (95% HMX 2.5% Estane 2.5% BDNPAF)

DAE
1) **Drying** (h_{r1} = 2.26×10^6 J/kg, endothermic)

DAE
2) **NO_2 evolution** (h_{r2} = -2.01×10^6 J/kg, exothermic)
BDNPAF ($C_{7.5}H_{13}N_4O_{10}$)→ NVR ($C_{7.5}H_{13}O_3$) + 4 NO_2

DAE, f(P)
3) **Oxidation of Estane** (h_{r3} = -3.32×10^6 J/kg, exothermic)
Estane ($C_{10}H_{14.6}N_{0.4}O_{3.5}$) + NO_2 → 0.7 N_2 + 4.5 H_2O + 0.5 CO_2 + 1.4 CH_4 + 0.04 H_2 + 8.1 C
Estane + NO_2 → 7.1 Gas_E + 8.1 C_E

DAE, f(P)
4) **HMX decomposition into equilibrium products** (h_{r4} = -6.2×10^6 J/kg, exothermic)
HMX → 4 N_2 + 3.6 H_2O + 2.2 CO_2 + 0.2 CH_4 + 1.6 C
HMX→ 10 Gas_X + 1.6 C_X

Equations solved in finite element code with conductive energy equation.
Rates are pressure dependent using distributed activation energy models.