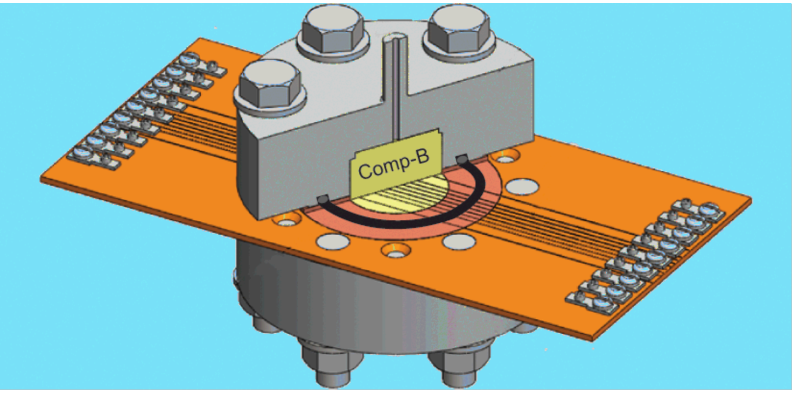
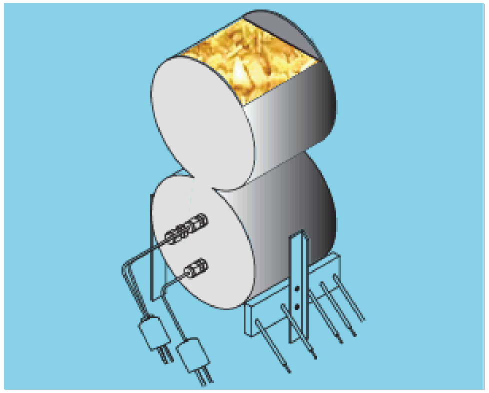
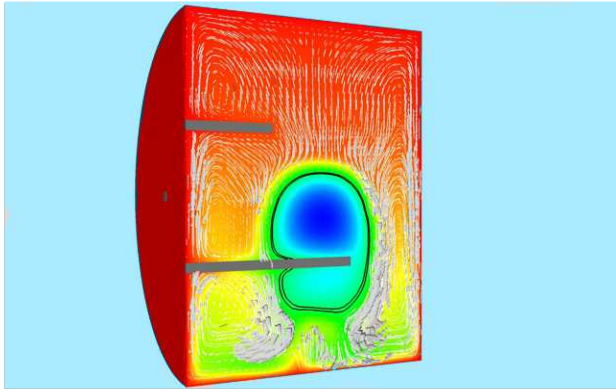
Exceptional service in the national interest

SAND2013-0079C

Sandia National Laboratories







Energetic Material and Foam Decomposition Modeling in Sierra

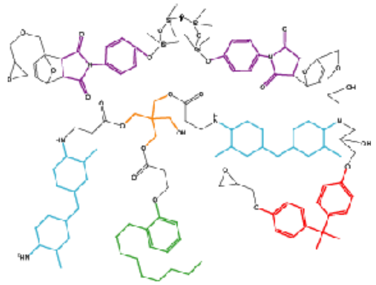
Michael L. Hobbs

1516, Nanoscale & Reactive Processes

Some materials of interest

Polymers

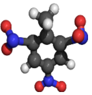
- Polyurethane foams, e.g. toluene diisocyanide (TDI) and methylene diphenyl diisocyanate (MDI)
- Epoxy foams, e.g. removable epoxy foam (REF)
- Syntactic foam, e.g. removable syntactic foam (RSF)
- Phenolic resins with chopped fiberglass, e.g. MXB-71
- Silicon encapsulant, e.g. Sylgard



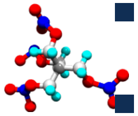
"vitrified"

Starting sample | 325˚C cure for 30 min | 525˚C cure for 30 min | 725˚C cure for 30 min | 925˚C cure for 30 min

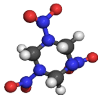
Explosives



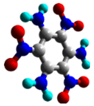
- TNT based (Comp-B, Octol, Pentolite, etc.)



- PETN based (xtx8003, LX2, LX8, LX16, Semtex, etc.)
- HMX based (LX4, LX7, LX9, LX10, LX11, LX14, PBX9402, PBX9501, etc.)



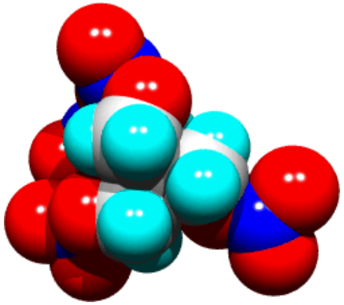
- RDX based (C4, PBX9205, PBX9407, etc.)



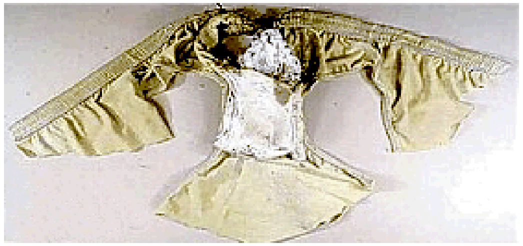
- TATB based (LX17, PBX9503, etc.)

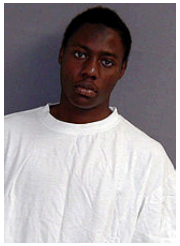
PETN detonator failure model

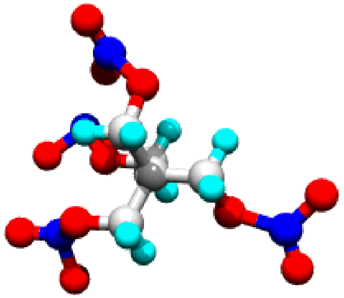
- 50 g PETN gained notoriety for shoe bomber Richard Reed (2002).



- 80 g PETN gained notoriety for the underwear bomber Umar Abdulmutallab (2009).



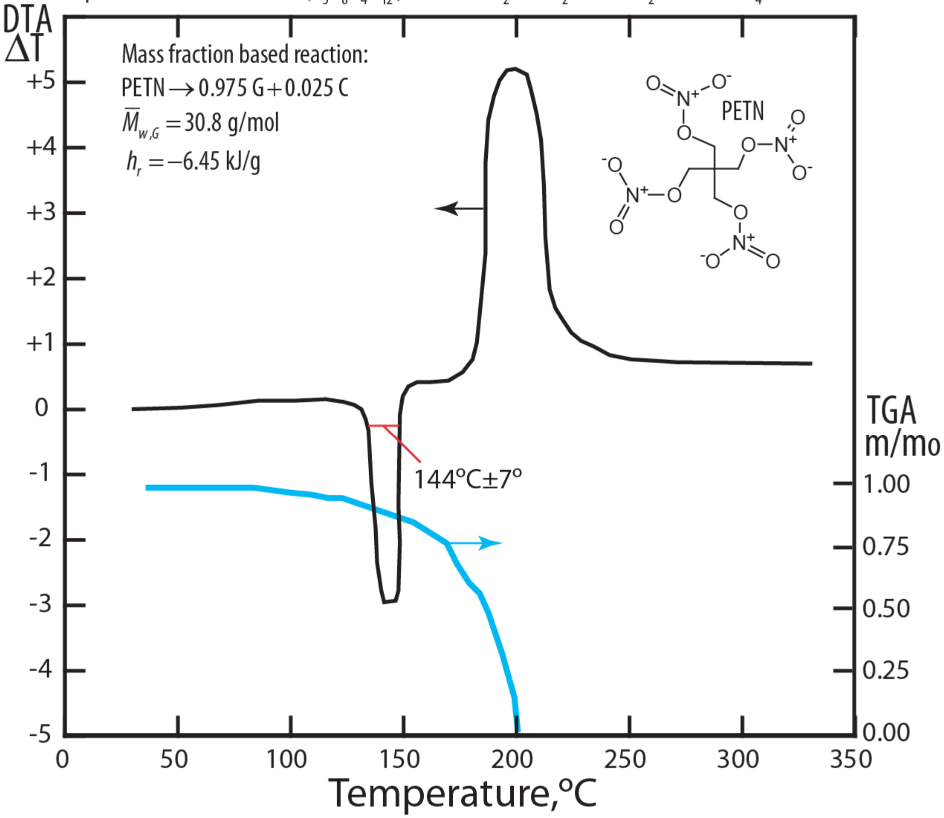




- YouTube video of 20 g of PETN cutting down Tree

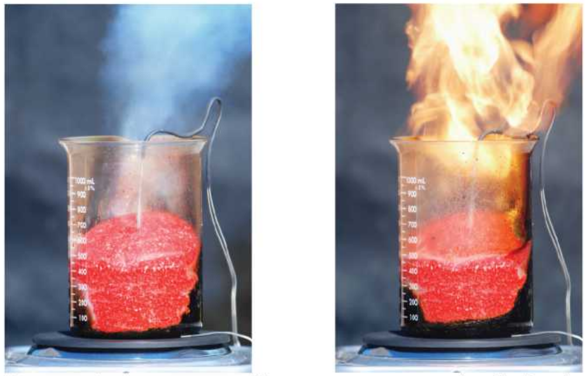
PETN detonator failure model

Equilibrium reaction: PETN ($C_5H_8N_4O_{12}$) $\rightarrow$ 4.17 CO_2 + 2 N_2 + 3.66 H_2O + 0.17 CH_4 + 0.66 C*



*G, C, $M_{w,G}$, and h_r represent gaseous reaction products, condensed carbon, average gas product molecular weight, and reaction enthalpy, respectively.

A) Semtex 1A (87% PETN with dye, antioxidant, plasticizer, and binder)



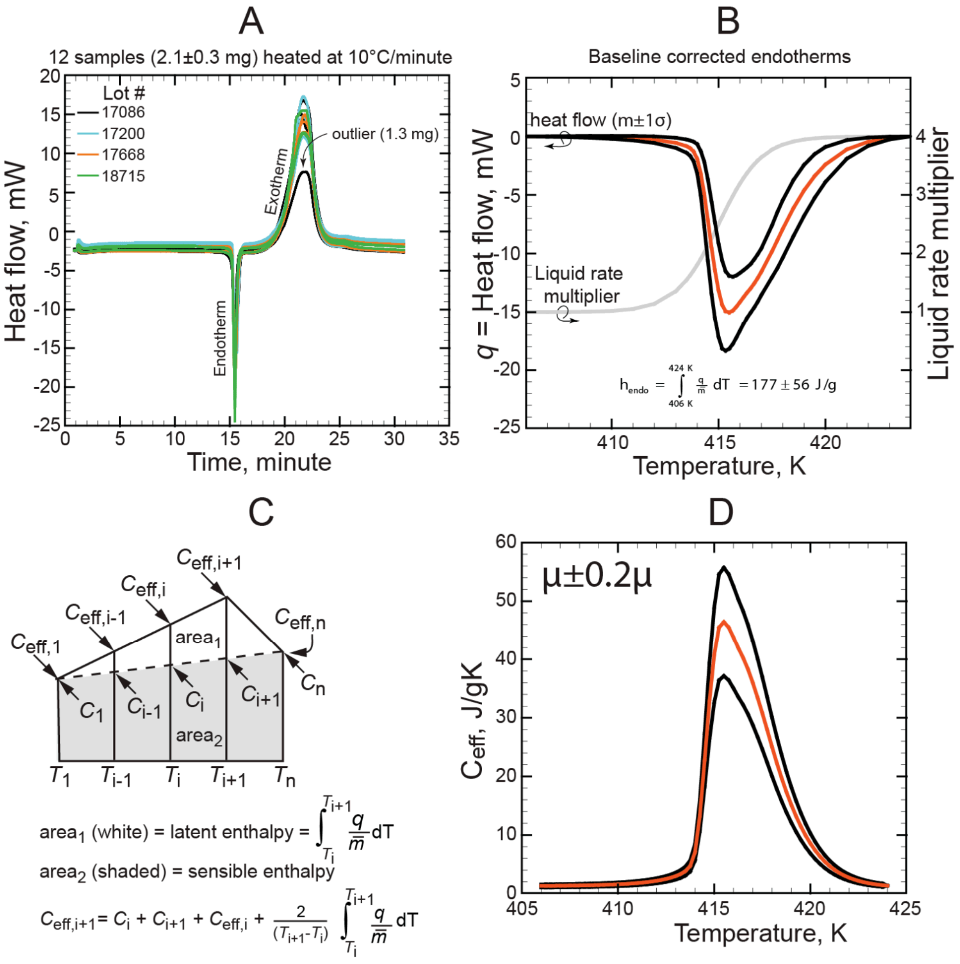
Does not slump as melting occurs, gases ignite in air.

B) Semtex 10 (82% PETN with dye, antioxidant, plasticizer, and binder)

Decomposes and ignites before melting completes.

Failure is based on two predictable events: 1) exceeding an activation temperature and 2) the extent of decomposition

PETN decomposition model



$h_{endo} = \int_{406\ K}^{424\ K} \frac{q}{m} dT = 177 \pm 56$ J/g

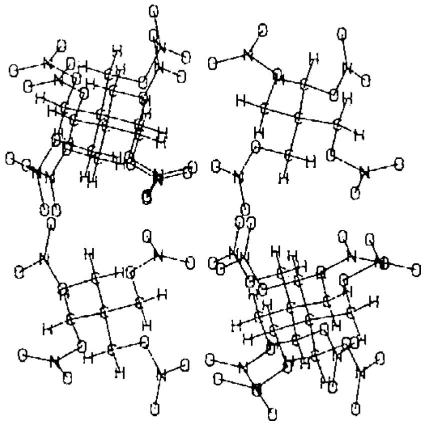
$area_1$ (white) = latent enthalpy = $\int_{T_i}^{T_{i+1}} \frac{q}{\bar{m}} dT$

$area_2$ (shaded) = sensible enthalpy

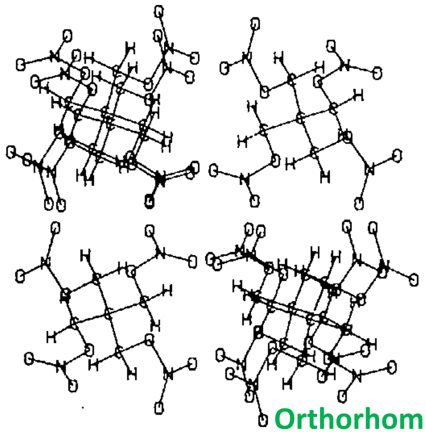
$$C_{eff,i+1} = C_i + C_{i+1} + C_{eff,i} + \frac{2}{(T_{i+1} - T_i)} \int_{T_i}^{T_{i+1}} \frac{q}{\bar{m}} dT$$

†Hobbs ML, Wente WB, Kaneshige MJ, *J. Phys. Chem. A (114), 5306 (2010)*

2 polymorphs



Tetragonal (1.778 g/cc)



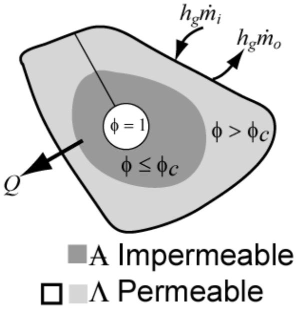
Orthorhombic (1.716 g/cc)

*Cady, HH; Larson, AC, *Acta Crystallographica B(31), 1864 (1975)*

Endotherms based on data

PETN decomposition model

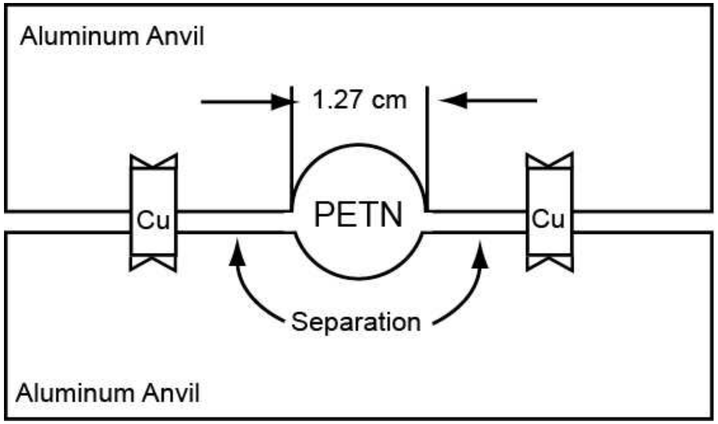
Gas continuity (integral)	$\frac{dM_g}{dt} = \int_\Lambda r\,dm_c^o + \dot{m}_i - \dot{m}_o$	(1)
Gas momentum (low Mach)	$P(x,y,z,t) = P(t) = M_g \Big/ \int_\Lambda \frac{M_{wg}}{RT}\,d\Lambda$	(2)
Energy (integral: bulk elements)	$\frac{dV_b \rho_g C_g T_b}{dt} = -\int_S h\left(T_b - T\right)dS + \dot{m}_i h_i - \dot{m}_o h_o$	(3)
Energy (field: material blocks)	$\rho_b C_b \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + qr$	(4)

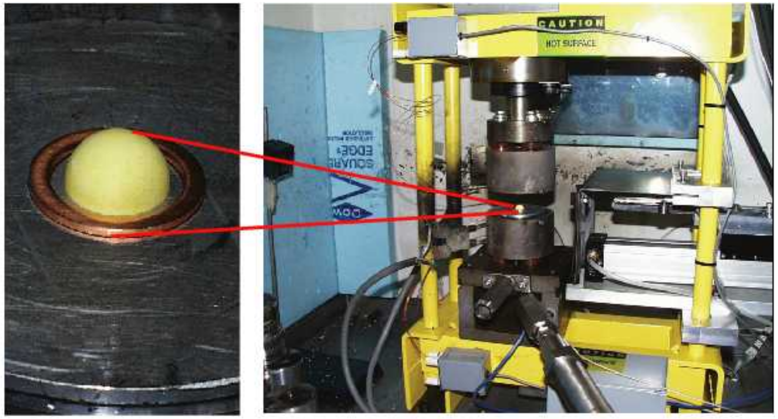


Mechanism	mole basis:	$C_5H_8N_4O_{12} \rightarrow 4.17\ CO_2 + 2\ N_2 + 3.66\ H_2O + 0.17\ CH_4 + 0.66\ C$ or	
	mass basis:	$petn \rightarrow 0.975\ gas + 0.025\ carbon$	(1)
Reaction Rate		$r = \frac{d}{dt}(petn) = \xi A \exp\left[-\left(E + z\sigma_E\right)/RT\right] petn$, where $petn_o = 1$	(2)
Distribution parameter		$1 - petn = \int_{-\infty}^{z} \frac{1}{\sqrt{2\pi}} \exp\left(\frac{-z^2}{2}\right) dz$ or $z = \mathbf{norminv}(1 - petn)$	(3)
Gas volume fraction		$\phi = 1 - \left[S_f \left(1 - \phi^o\right) \rho_c^o / \rho_c\right]$ where $S_f = petn + carbon$	(4)
Bulk density		$\rho_b = \phi\rho_g + (1-\phi)\rho_c$	(5)
Thermal conductivity		$k = \phi k_g + \frac{2}{3}(1-\phi)k_c + \frac{16\sigma T^3}{3\left[\phi\alpha_g + (1-\phi)\alpha_c\right]}$	(6)

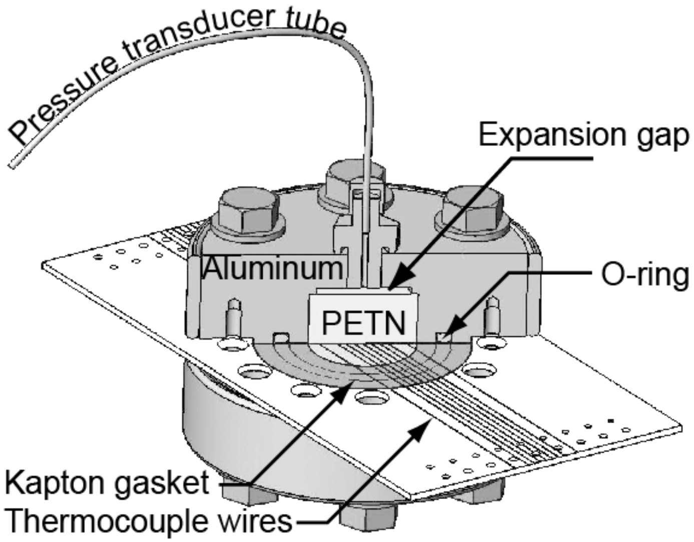
PETN validation experiments

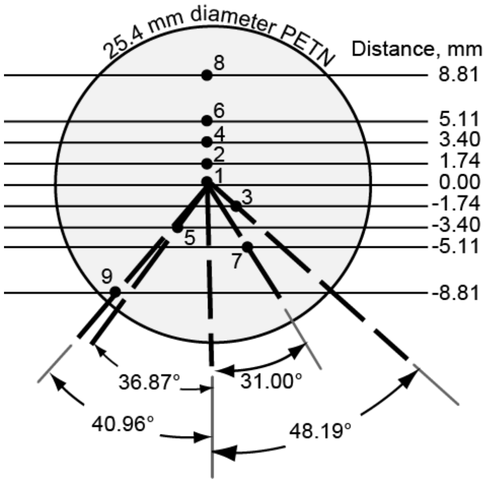
ODTX

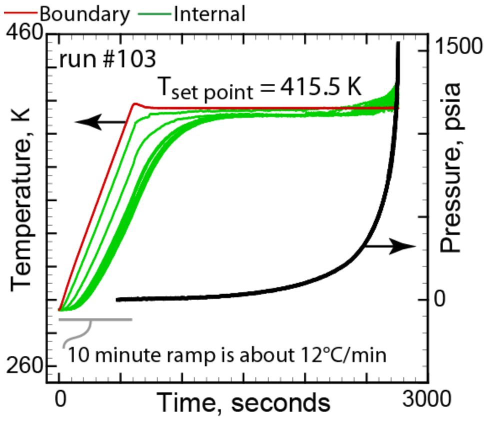




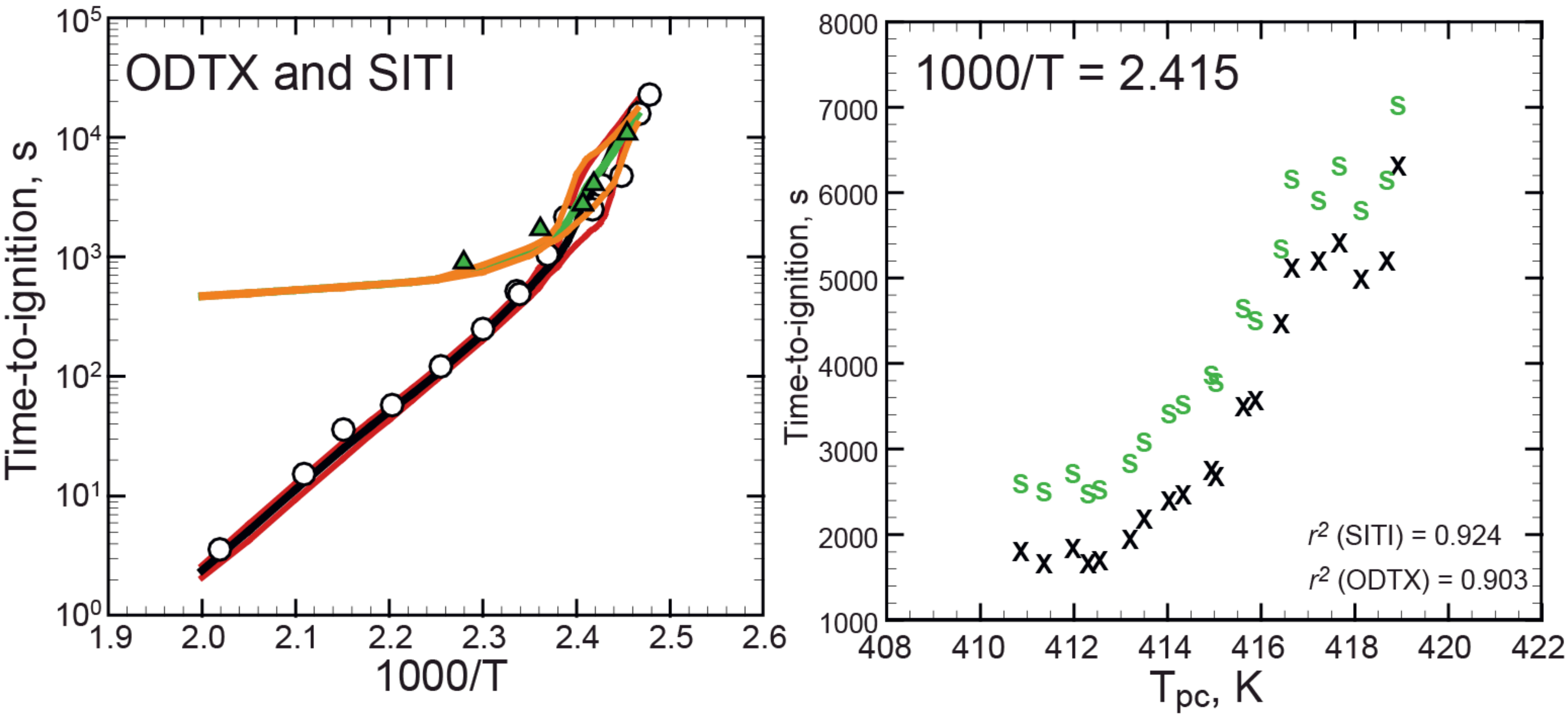
SITI







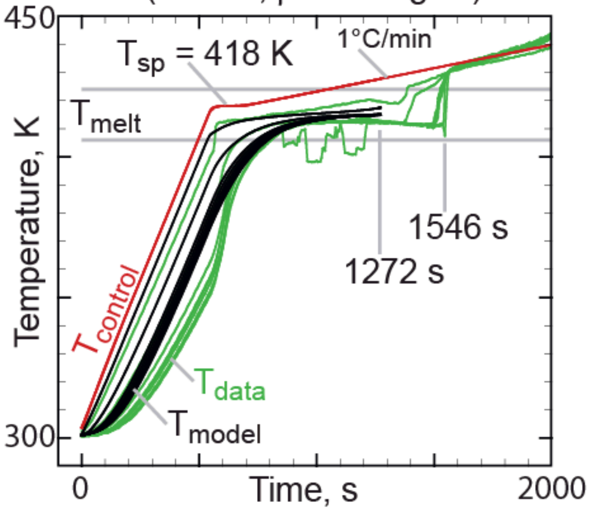
PETN model predicts ignition time



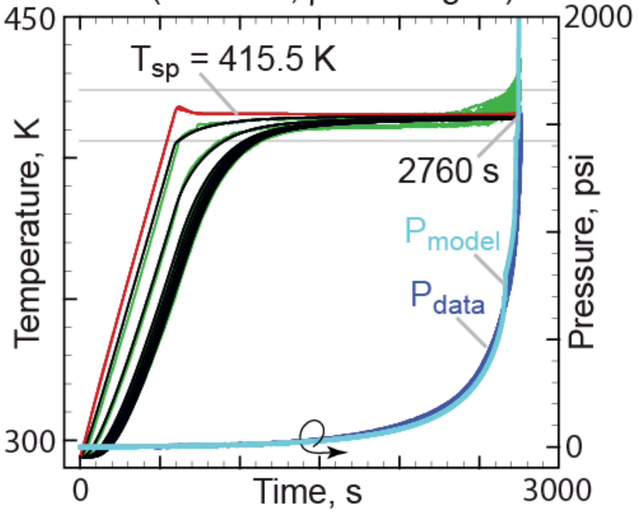
Uncertainty calculated with 20 LHS samples

Model predicts temperatures/pressures

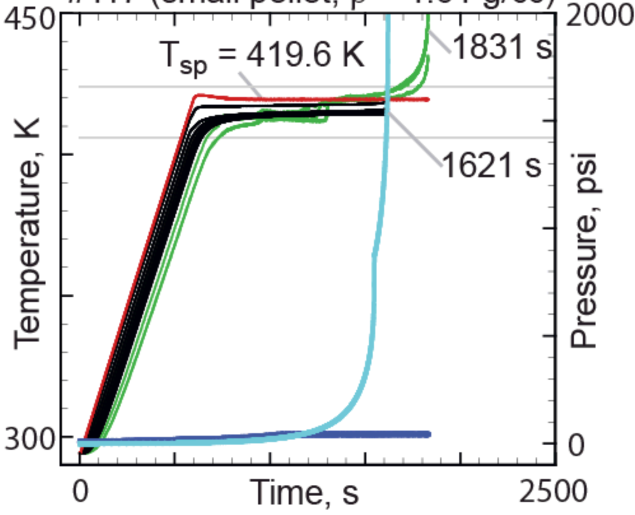
#102 (vented, ρ = 1.10 g/cc)

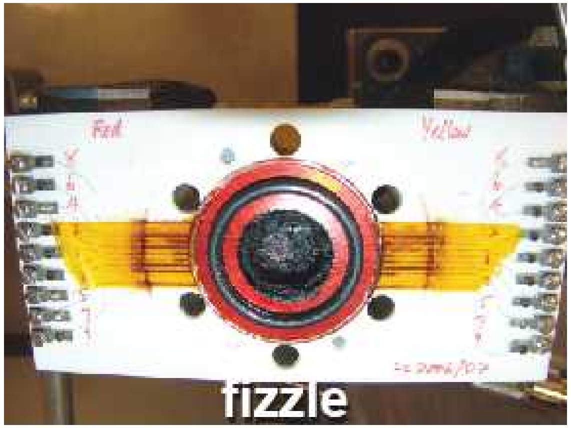


#103 (confined, ρ = 1.69 g/cc)



#117 (small pellet, ρ = 1.61 g/cc)

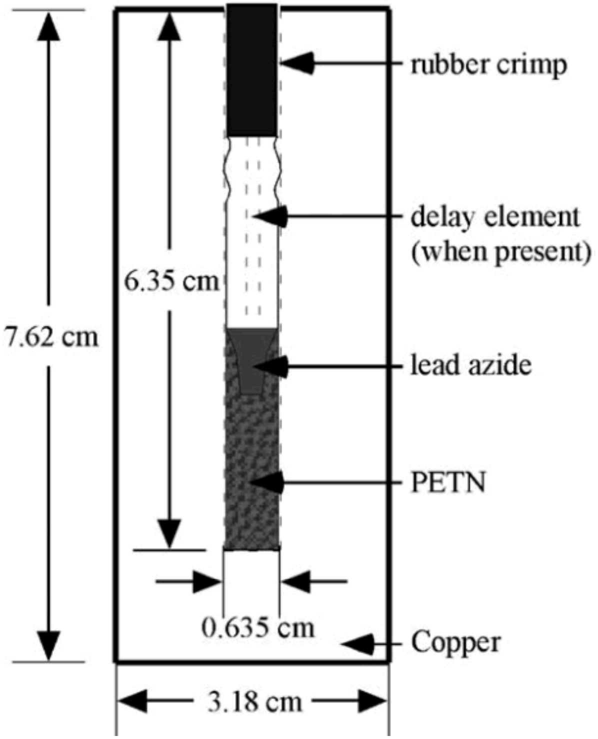




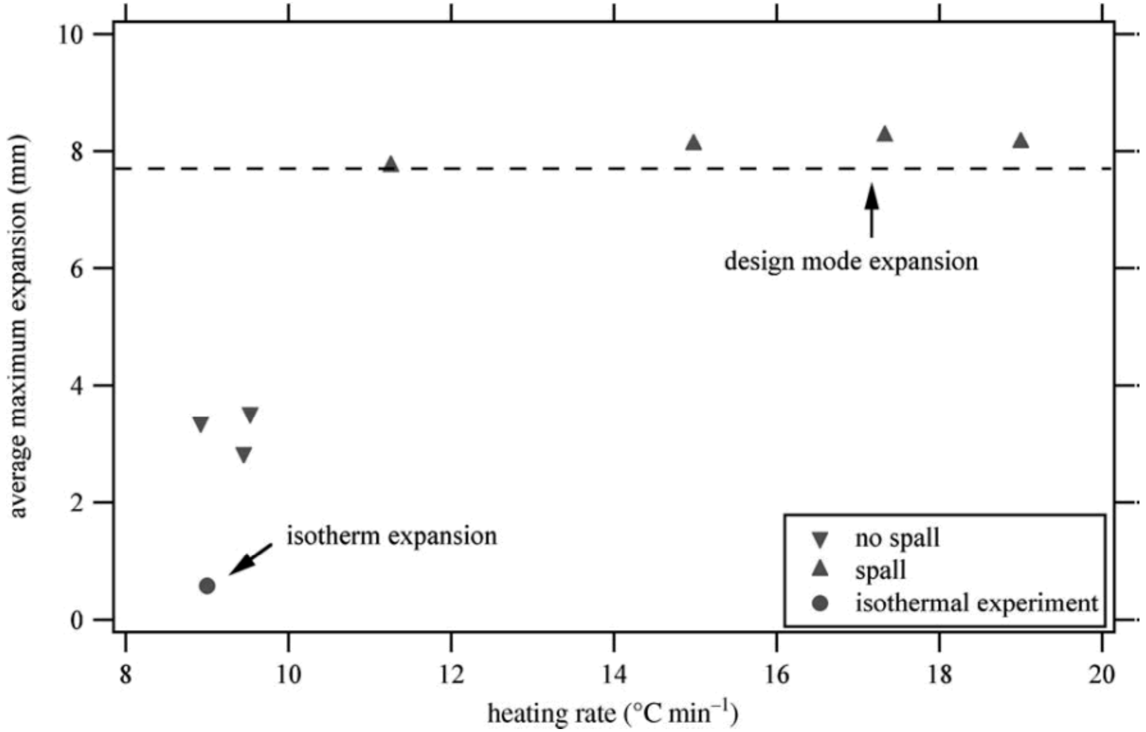
Model does not calculate violence

Does ignition guarantee failure?

NONEL Detonator in copper



Expansion of copper

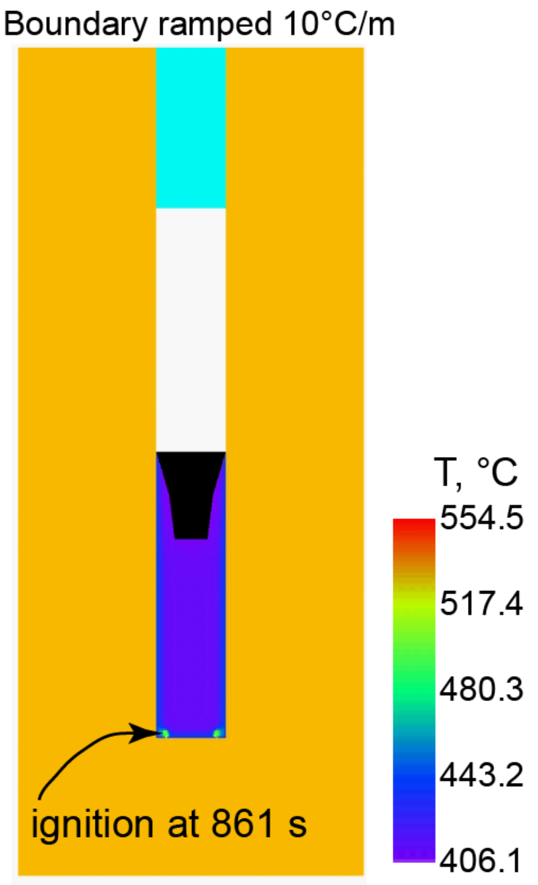


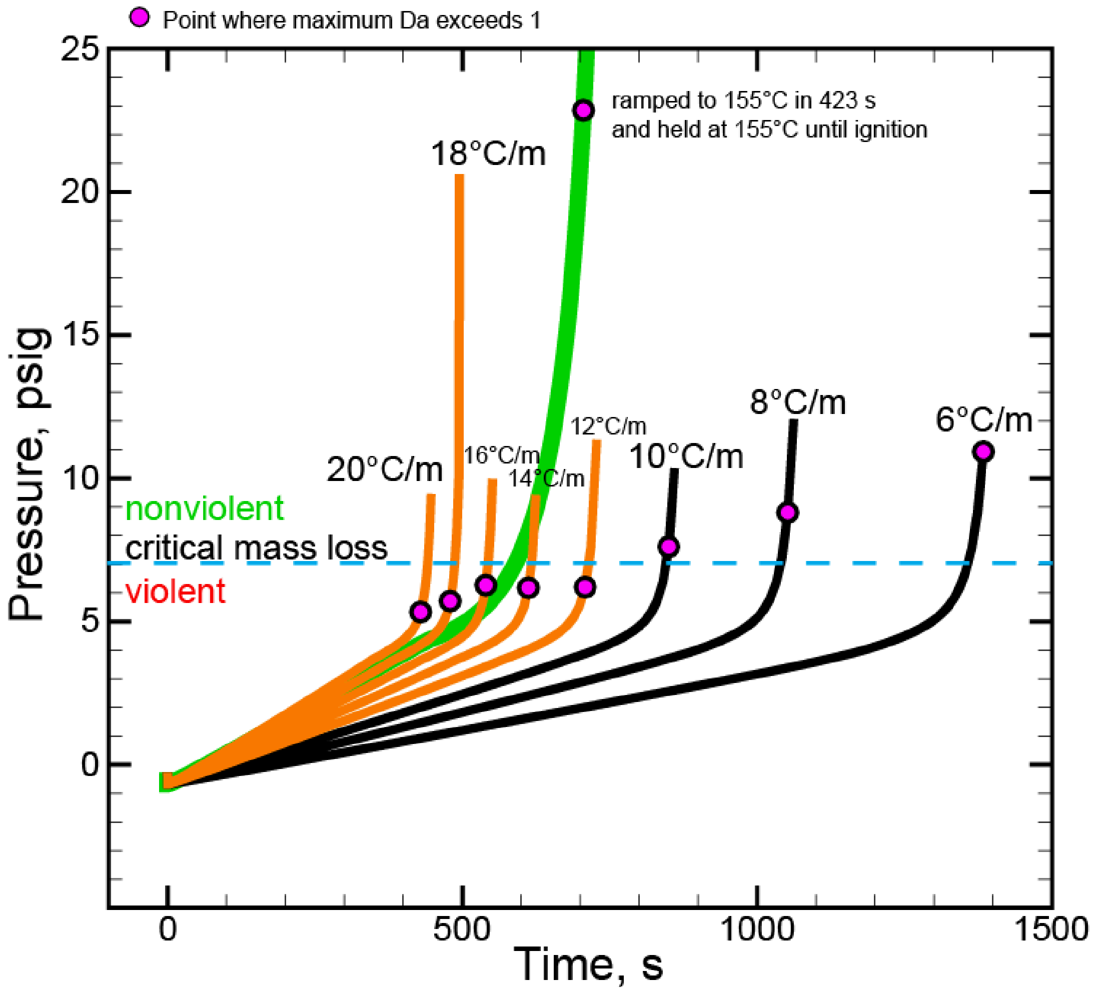
*J.M. Zucker, P. Dickson, V.E. Sanders, *Propellants Explos. Pyrotech.*, **34**, 142 (2009).

Correlate reaction extent with Damköhler number by relating chemical reaction timescales to conduction timescales.

$$Da = \frac{\sum q_i r_i}{c_p \, {}^{dT}\!/_{dt}}$$

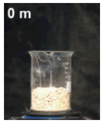
Sierra simulation of NONEL detonator





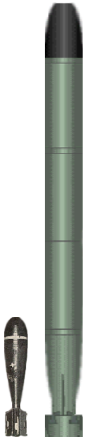
Failure assumed when Damköhler # exceeds 1 before critical mass loss is achieved.

What about flow? Comp-B example



- Composition B (Comp-B) explosives consist of mixtures of RDX and TNT, and a desensitizing wax. In the current work, Comp-B is assumed to be composed of 60/40 RDX/TNT by weight.

- Developed prior to WWI and used in mortar shells, torpedoes, demolition charges, warheads, shaped charges, and bombs.



- Prepared by melting TNT in a steam-jacketed kettle, adding wet RDX slowly, heating and stirring until the water is evaporated. Comp-B is cast into desired shape and cooled.

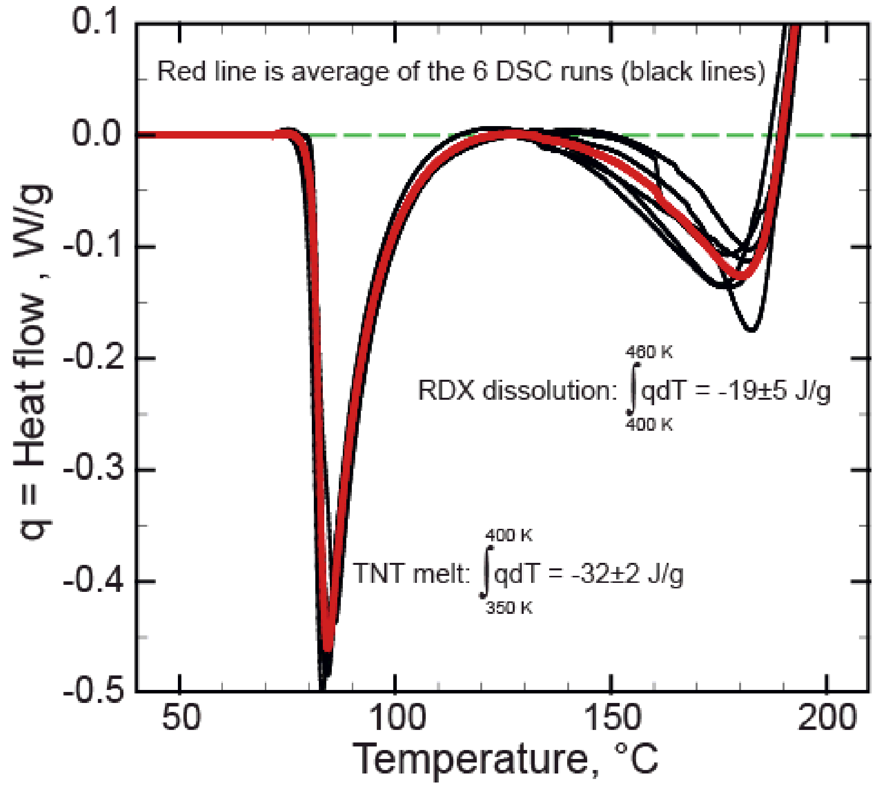
- Comp-B is easy to process, has a high detonation pressure, but fails many insensitive munitions (IM) requirements.


Krawietz et al., Eglin AFB

- Comp-B does not pass slow and fast cookoff IM tests. Consequently, the response of Comp-B during an accident, such as a fire, is important for safety analysis.

Comp-B experiments: melt & dissolution

Baseline corrected DSC

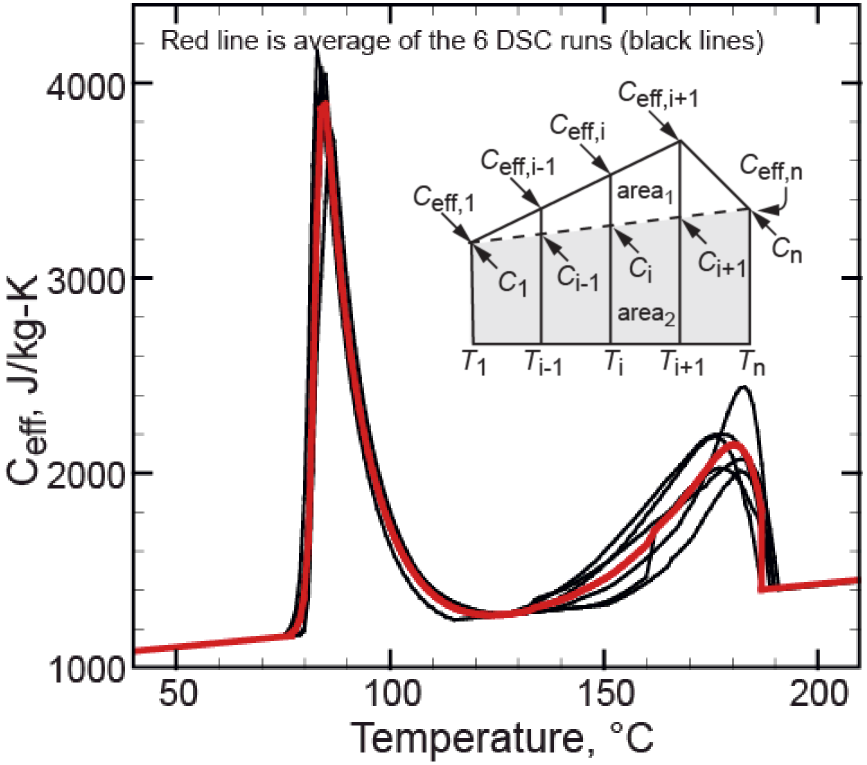


Red line is average of the 6 DSC runs (black lines)

RDX dissolution: $\int_{400\,K}^{460\,K} q\,dT = -19 \pm 5$ J/g

TNT melt: $\int_{350\,K}^{400\,K} q\,dT = -32 \pm 2$ J/g

Effective capacitance model

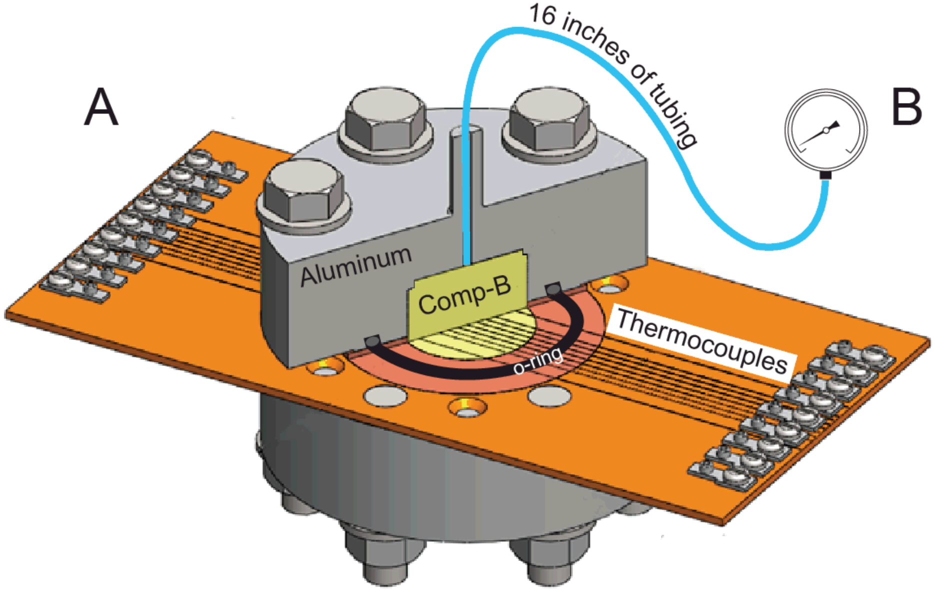


Red line is average of the 6 DSC runs (black lines)

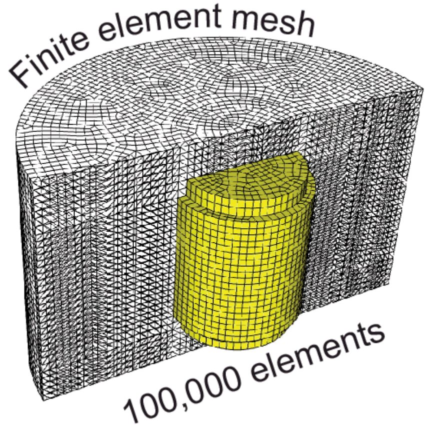
Latent enthalpy taken directly from DSC data. TNT latent enthalpy matches literature. Energy of RDX dissolution is less than RDX melt.

Sandia's Instrumented Thermal Ignition (SITI)

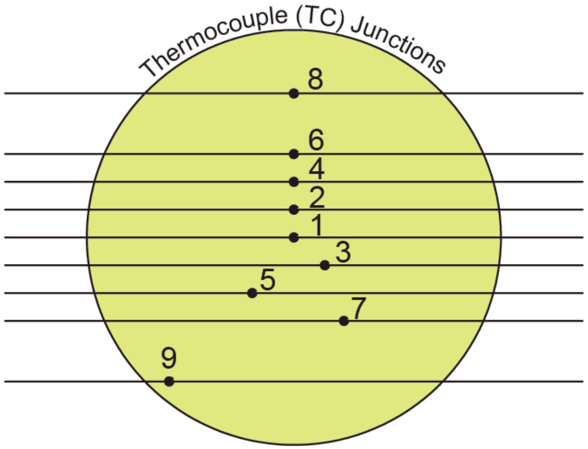
A



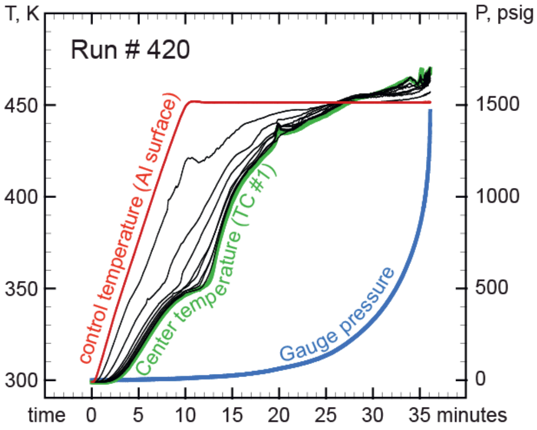
B



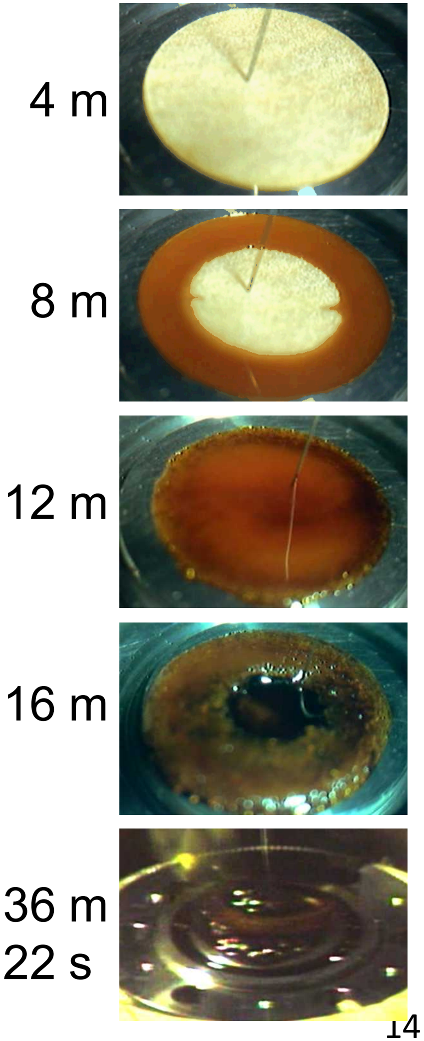
C



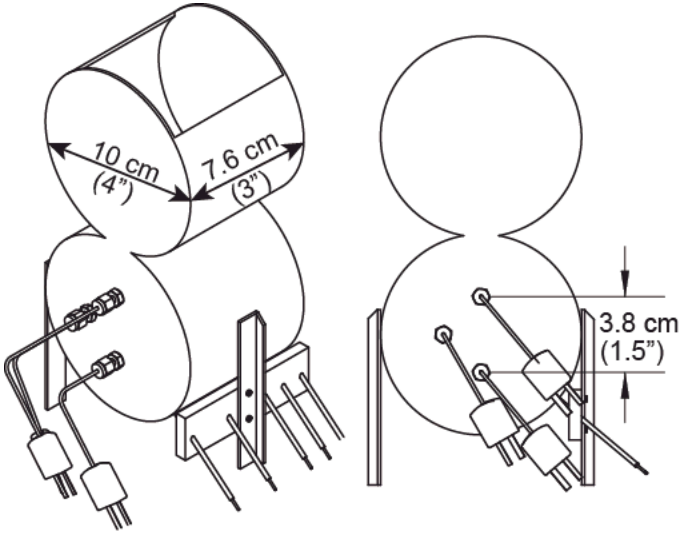
D



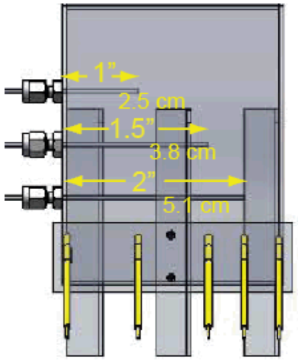
Open half shell



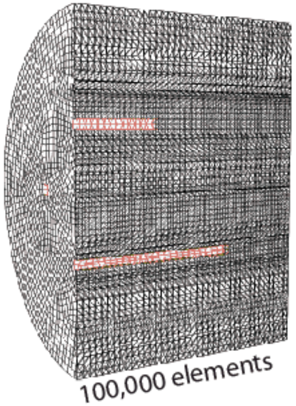
Comp-B Oven Test

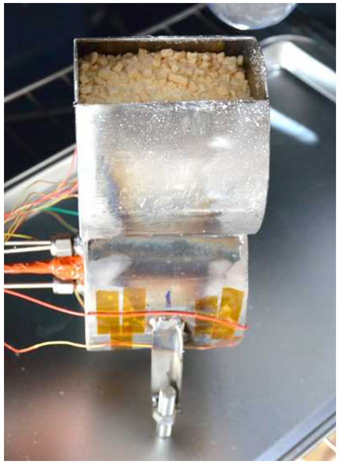


Lower cylinder fills with liquid



Mesh





45 minutes

135 minutes

270 minutes

Post test oven

Comp-B Model Features

- One-step, first-order mechanism, products from equilibrium

$$\text{Comp-B}(C_{4.58}H_{5.61}N_{4.82}O_6) \rightarrow 2.24H_2O + 2.41N_2 + 1.88CO_2 + 0.064H_2 + 2.54C + 5.82\times 10^6\,\frac{J}{kg}$$

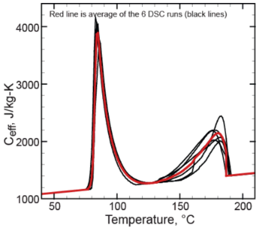
- Distributed Arrhenius rates modified by $(P/P^o)^n$

$$r = A\left(\tfrac{P}{P^o}\right)^n \lambda \exp\left[-\left(E+\xi\sigma_E\right)/RT\right][\text{compb}]$$

$$r_{compb} = \tfrac{d}{dt}[\text{compb}] + \vec{v}\cdot\nabla[\text{compb}] = -r$$

$$r_{carbon} = \tfrac{d}{dt}[\text{carbon}] + \vec{v}\cdot\nabla[\text{carbon}] = +2.450r$$

$$r_{gas} = \tfrac{d}{dt}[\text{gas}] + \vec{v}\cdot\nabla\left[\text{gas}\right] = +6.845r$$



- Liquefaction modeled thermodynamically
- Liquid rates are 15 times larger than solid rates,
- Thermal expansion, TNT phase change, RDX dissolution
- One energy equation, one momentum equation, three continuity equations (Comp-B, Gas, Carbon), various auxiliary equations for gas volume fraction, pressure, etc.

Model Features (continued)

- Single energy equation with convection and reaction source.

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \vec{v}\cdot\nabla T = \nabla\cdot(k\nabla T) + qr$$

- Single momentum equation with Boussinesq volume force.

$$\rho \frac{d\vec{v}}{dt} + \rho\vec{v}\cdot\nabla\vec{v} = -\nabla P + \mu\nabla^2\vec{v} + \left(\rho - \rho_o\right)gh$$

- All wetted surfaces assumed to have a no-slip boundary.

$$\vec{v}_{\text{wetted surfaces}} = 0$$

- Local gas/solid velocities/temperatures equal.

$$T_C = T_g = T(x,y,z,t) \;\text{ and }\; \vec{v}_C = \vec{v}_g = \vec{v}(x,y,z,t)$$

- Low Mach flow (velocities much less than sound speeds).

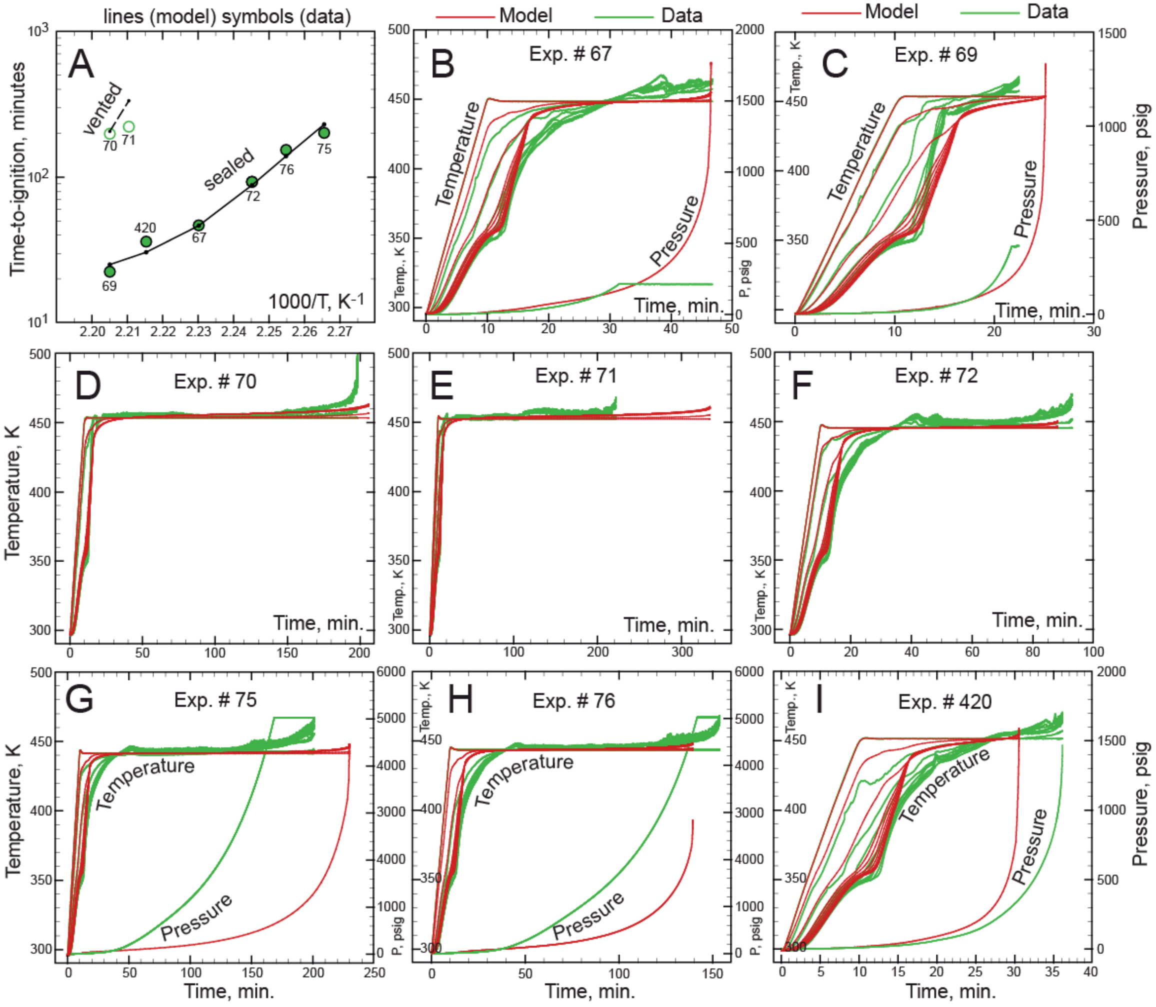
$$P(x,y,z,t) = P(t)$$

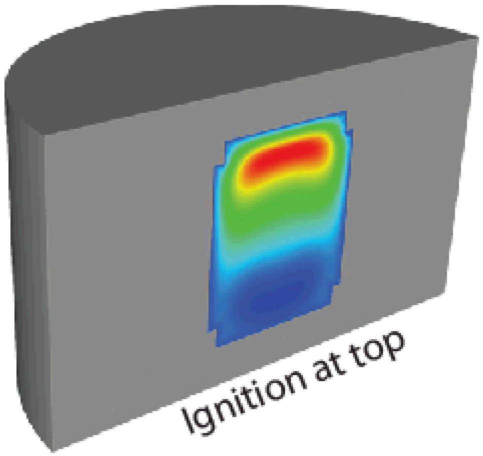
- BKWS-EOS used for pressure $P_g(x,y,z,t) = P_g(t) = \dfrac{\bar{z}nR\bar{T}}{V_g}$

$$\bar{z} = 1 + X\exp(0.298X)$$

$$X = \left(\frac{n}{V_g}\right)\left(\frac{0.0105\times Covol}{\sqrt{\bar{T} + 6620}}\right)$$

SITI Test Results



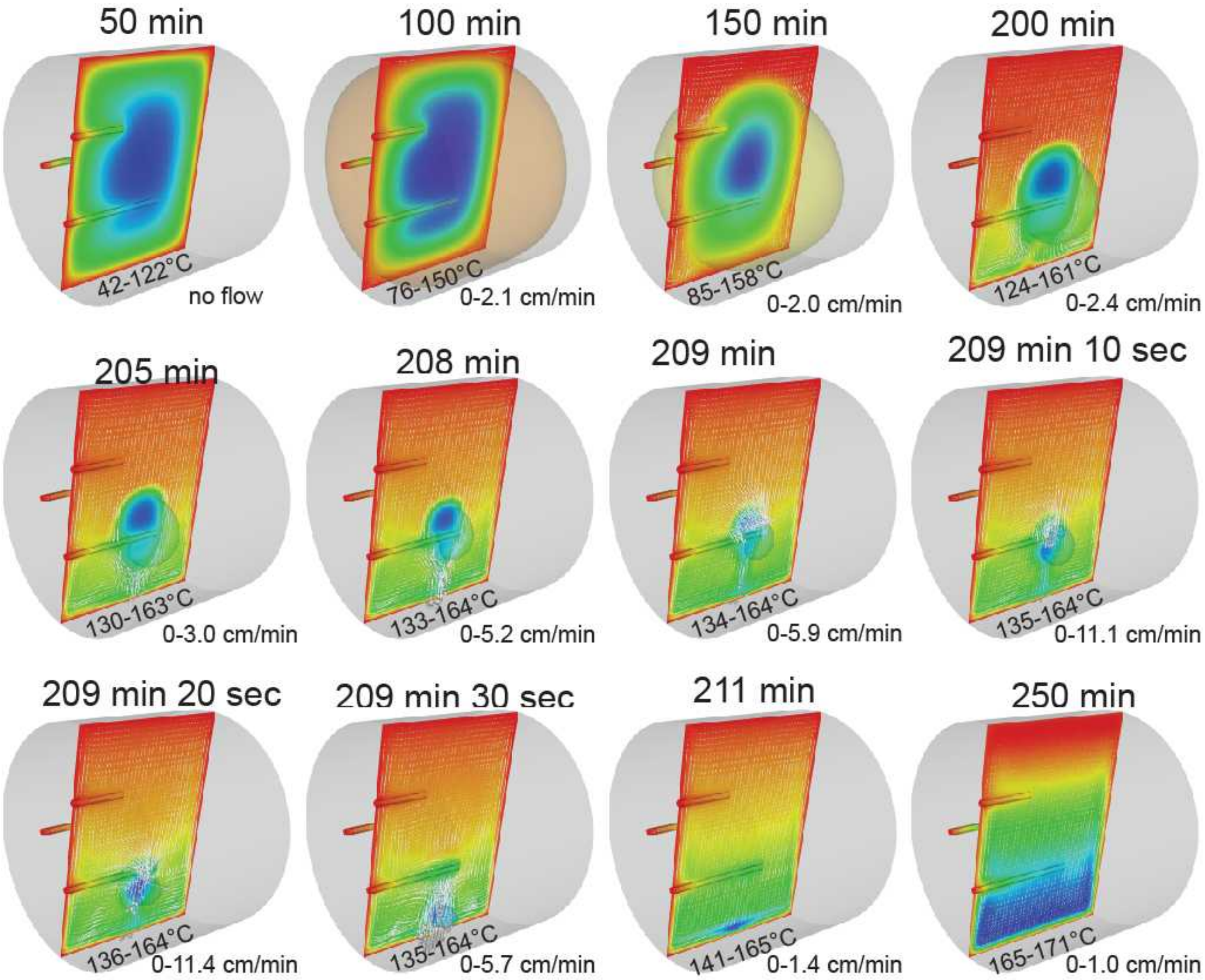


- #71 ignited faster than predicted. Possible plug?
- Good temperature match to 430 K, then model transition from solid to liquid is too fast.

$$T < 412.5K \qquad \mu = 0.25\times10^{6}\ \mathrm{Pa\cdot s}$$

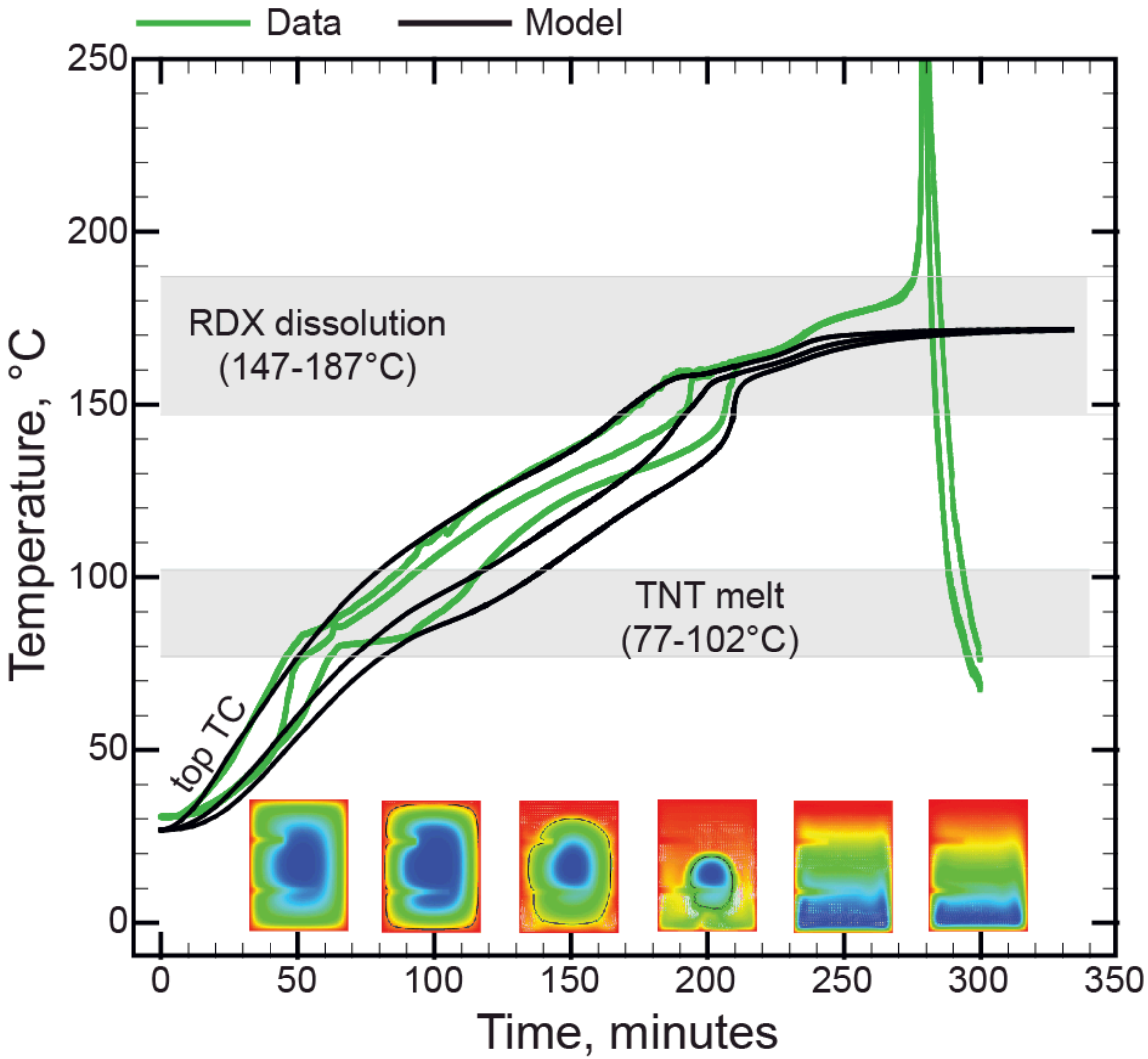
$$T > 413.5K \qquad \mu = 0.2\ \mathrm{Pa\cdot s}$$

Oven Test Results



- Melts from outside to the inside.
- Solid plug gets smaller and starts to fall toward the bottom of the can.
- Liquid heats up and eventually self-heats and ignites at the top of the can.

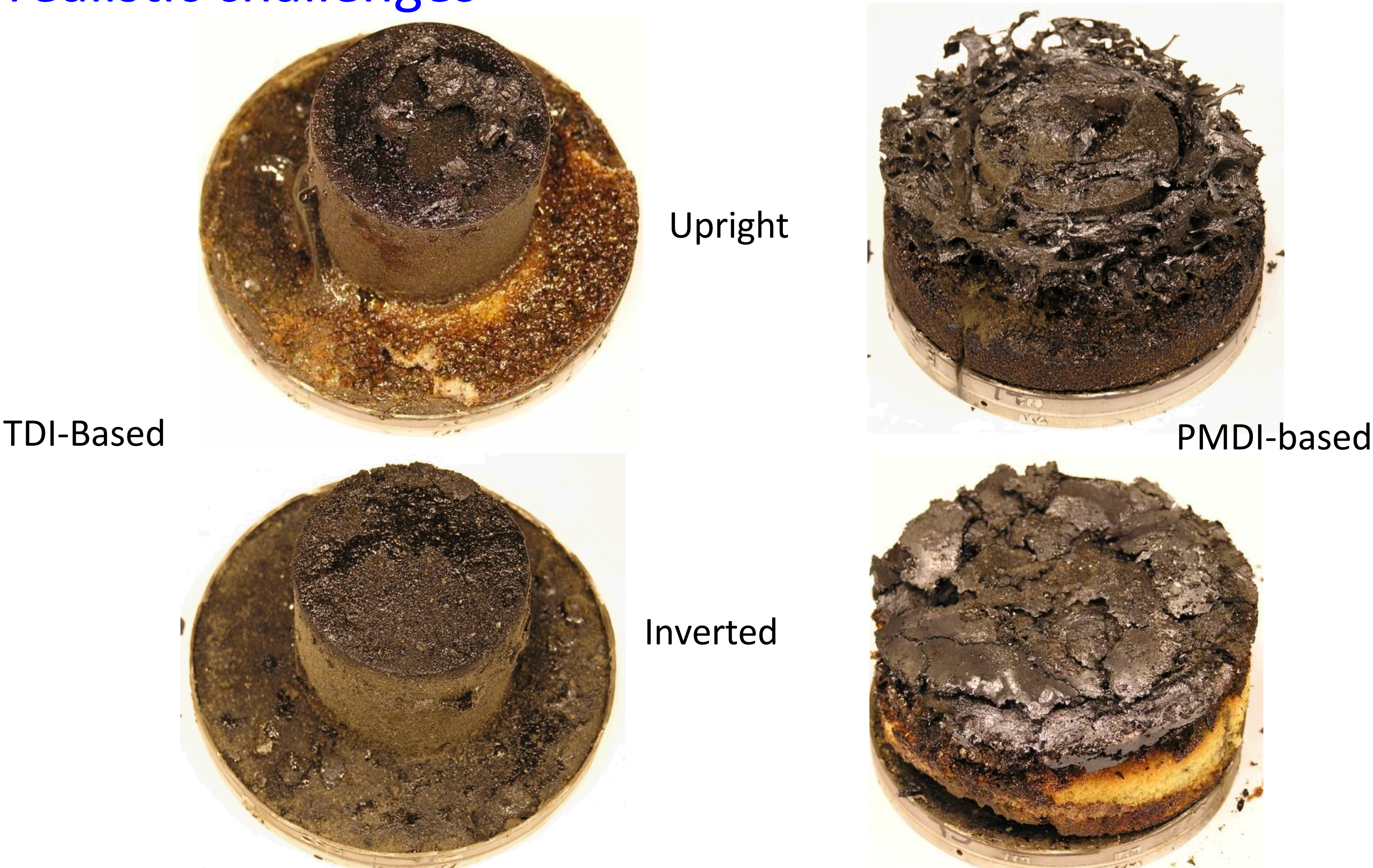
Oven Test Results



- Temperature pinch occurs in middle of RDX dissolution range.
- Model predicts longer ignition times.
- Discrepancy in ignition time could be related to the method of melting the Comp-B flakes.
- In the experiment, the flakes were melted in the combined system.

Foam Decomposition:

realistic challenges*



*see Amanda Dodd, Org 8365, ajbarra@sandia.gov

Current foam model formulation

Energy Equation

Based on diffusive approximation for optically thick material

$$\rho c \frac{\partial T}{\partial t} = \nabla \bullet \left(k + k_e\right)\nabla T + \sum_i \rho r_i \left(-\Delta H_i\right)$$

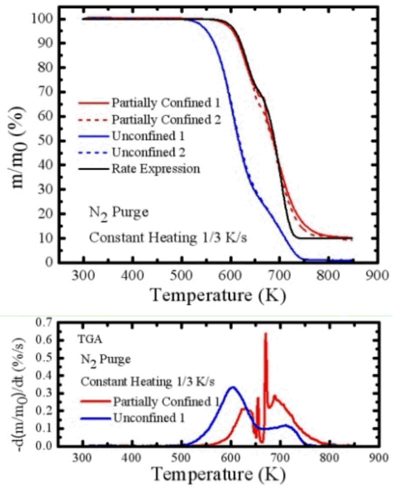
$$k_e = \frac{16\sigma}{3\left(a+\sigma_s\right)} T^3$$

Effective radiative conductivity k_e depends on absorption coeff. a and scattering coeff. σ_s[1]

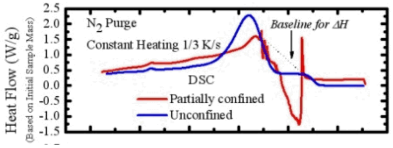
Note: Absorption coeff. a and scattering coeff. σ_s were calculated using an analytical two-flux model for radiative transfer and the measured values of reflectance R and transmittance T [2,3]

Decomposition Model

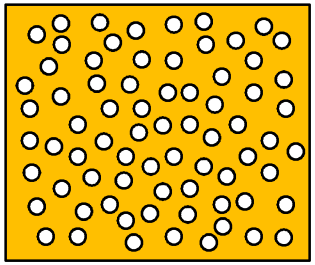
ThermoGravimetric Analysis (TGA)



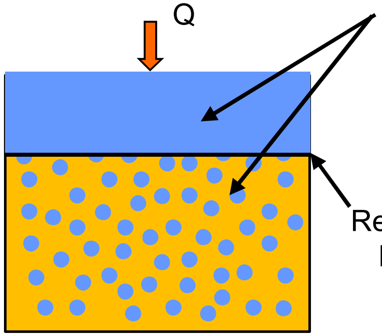
Differential Scanning Calorimetry (DSC)



Initial Foam



Partially Reacted



Gas/Vapors: CO_2, Cyclopentanone, Toluenediamine, Ethylacrolien, Other

Reaction Front

Pressure

Moles of gas

$$P = \frac{n_g R}{\int_{V_g} \frac{1}{T}\, dV_g} = \frac{n_g R}{\left(\underbrace{\int_{V_{fv}} \frac{1}{T}\, dV_{fv}}_{\text{Free volume/ temperature}} + \underbrace{\int_{V_B^0} \frac{\Phi}{T}\, dV_B^0}_{\text{Gas Volume: reacted area and pore space}} \right)}$$

n_g= gas moles, , $f(K_{Bij}, T)$

Φ=porosity, $f(\varphi_0, SF, f_p)$

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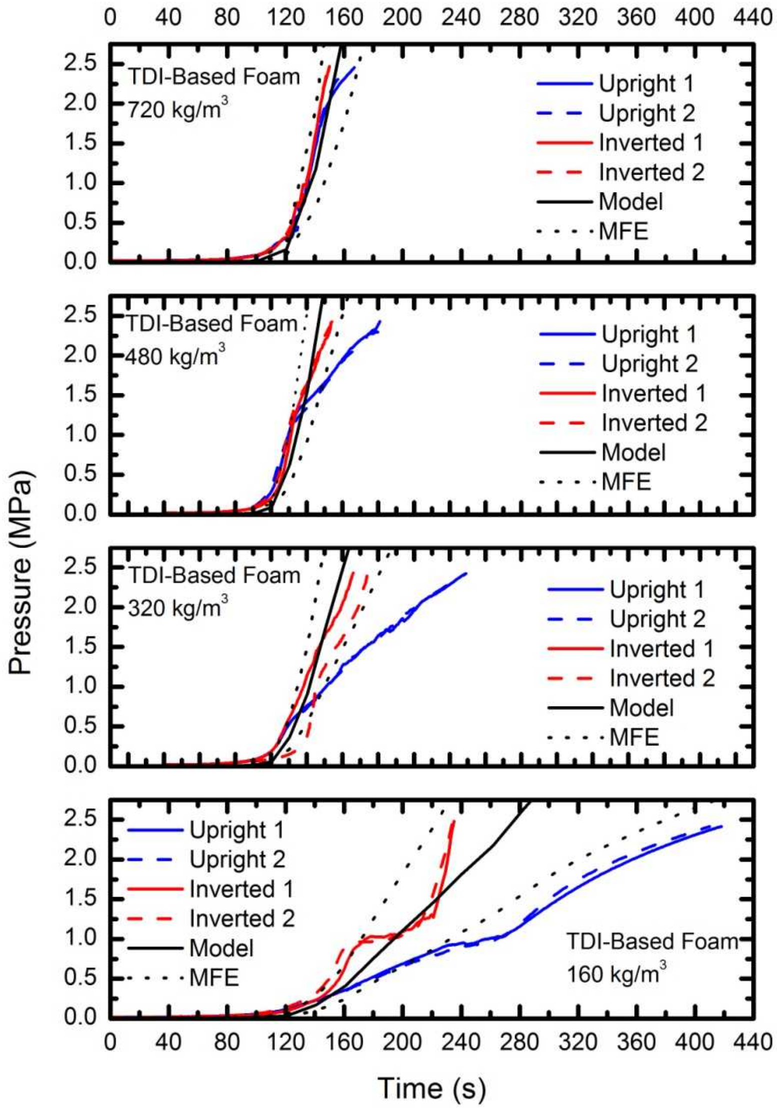
[1] Siegel, R. and Howell, J. R., Thermal Radiation Heat Transfer, 2nd ed., Hemisphere Publishing Corp., Cambridge, 1982, p497-p501.

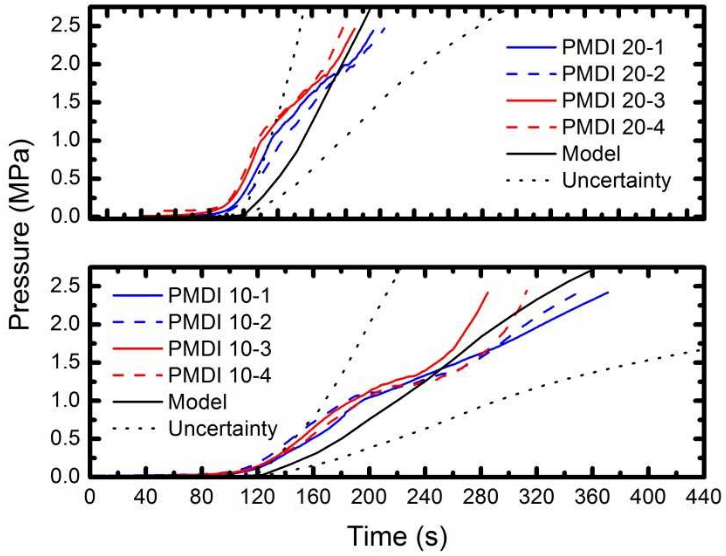
[2] Reichman, J., *Applied Optics*, 12 (8), August 1973, p1811-p1815.

[3] Erickson et al., BCC 2009.

Time to vent pressure (2.4 MPa) decreased as initial bulk density of foam increased

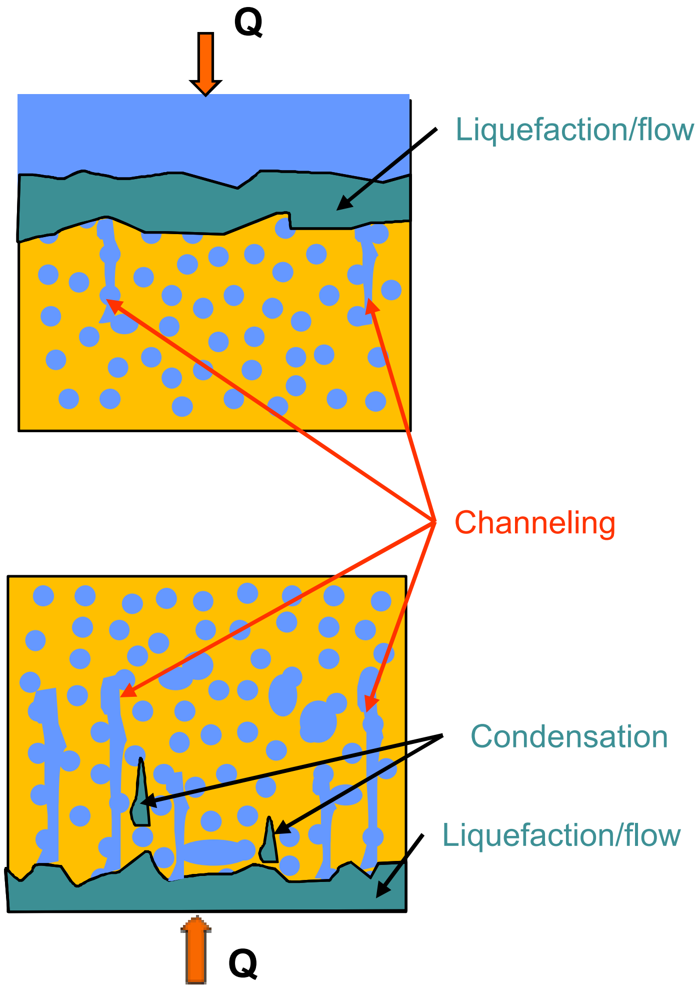


- Multiplier on pressure to incorporate model form error
  - Moles of gas
    - Distribution of decomposition products between gas and condensed phases (K_{Bij})
    - Temperature of condensed phase
  - Volume gas occupies
    - Erosive channeling (f_p)
  - Gas Temperature
- Multiplier does NOT capture convective heat transfer



Path Forward

- Estimating partial pressure of volatile organic decomposition products
- Liquefaction/flow of decomposition products
  - *Significantly impacts heat transfer to foam / rate of gas generation and container pressurization*
- Erosive channeling by hot gas-phase decomposition products



*see Amanda Dodd, Org 8365, ajbarra@sandia.gov

Summary and Conclusions

- Sierra tools used to simulate reactive materials.
- Models based on various experimental observations.
- Heat transfer, reactive chemistry, fluid flow were modeled with SIERRA-thermal.
- Three models discussed (PETN, Comp-B, and foam).
- PETN failure in abnormal thermal environment is based on predicted activation temperature and extent of reaction.
- Decomposition of Comp-B involves complex buoyancy driven flow.
- Foam decomposition is a difficult problem with complex physics. Affects such as liquefaction and flow, erosive channeling, and vapor-liquid equilibrium need to be considered. See Amanda Dodd for more information.