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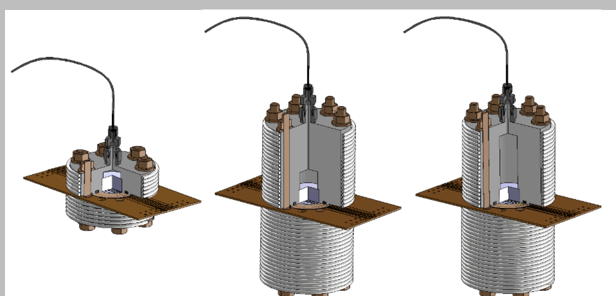

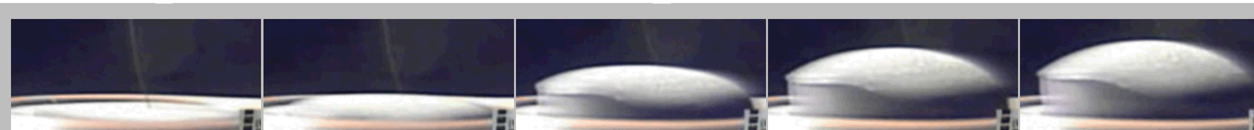

JANNAF 46th CS, 34th APS, 34th EPSS and 28th PSHS Joint Subcommittee Meeting, Albuquerque NM, Dec. 8-11, 2014

Pressure and Free Volume Dependence in the Cook-off of AP Composite Propellants

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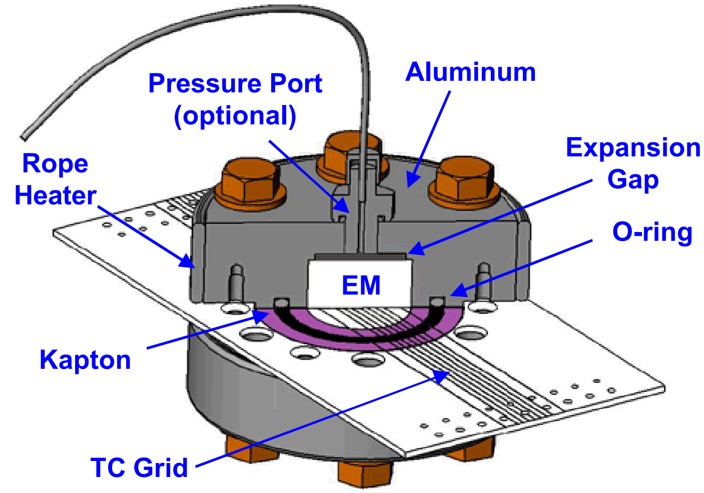
Outline

- Introduction
- SITI Devices
- Propellant
- Experiments
- Analysis
- Modeling
- Summary and Conclusions

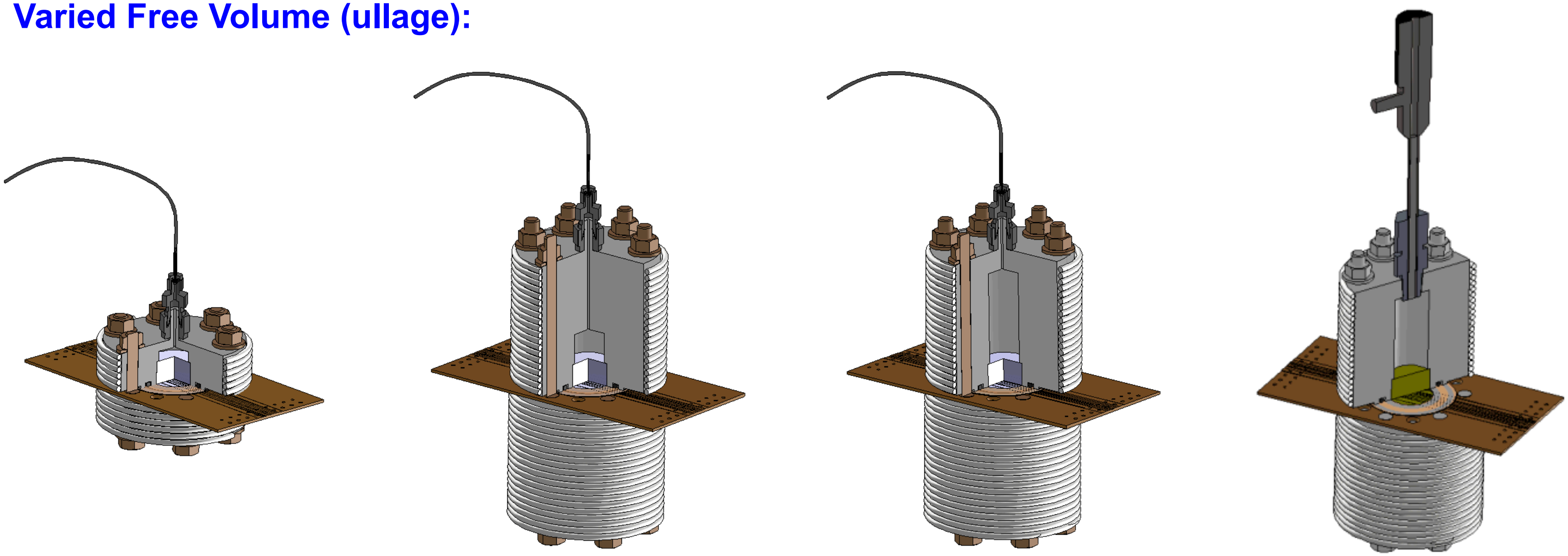
Sandia Instrumented Thermal Ignition (SITI) Devices

Baseline SITI (figure at right):

- Two 1” diameter, ½” thick samples of EM
- samples confined within aluminum (near isothermal boundary condition)
- expansion gap at end of sample
- optional pressure transducer port or vent
- 9 TCs along midplane of EM allow measurement of internal temperatures
- heated via rope heater around perimeter to follow a designated temperature history
- symmetric about axis



Varied Free Volume (ullage):



25% free volume (33.3% of EM volume)

50% free volume (100% of EM volume)

75% free volume (300% of EM volume)

75% free volume with borescope

SITI data on AP/HTPB/AL Propellant

"Propellant A"

- Class 1.3, AP/Al/HTPB-IPDI

Samples:

- Original: 1" diam. 0.5" high
- Shredded: turned on lathe to form ribbons

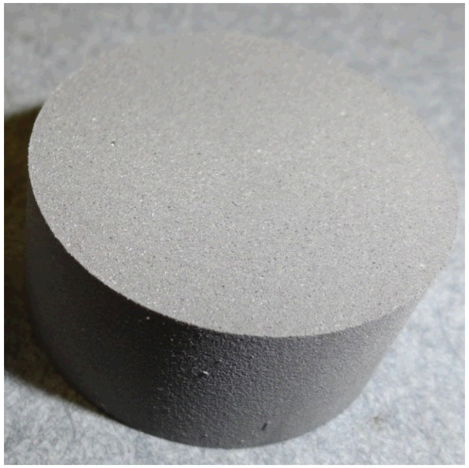
Tests:

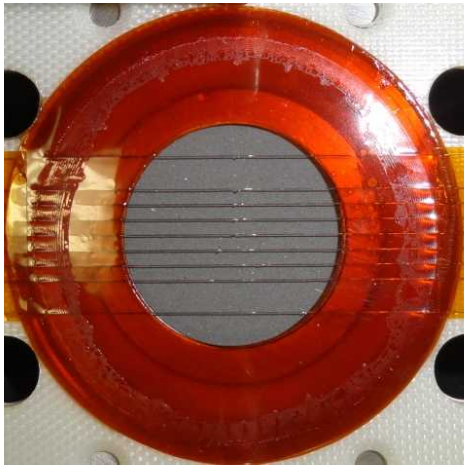
- Temperature Profiles:
  (Constant Ramp or Ramp & Hold)
- Confinement
  (Unvented or Vented)
- Free Volume
  (8.7%, 18.7%, 25%, 50%, 75%)

Diagnostics:

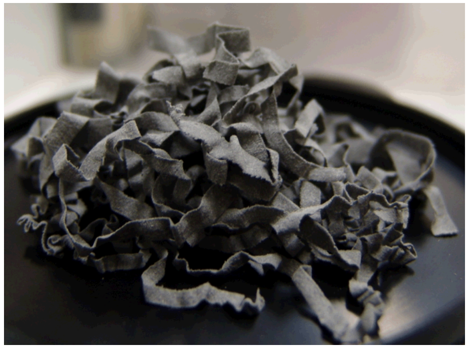
- Temperature (internal & external)
- Pressure (some unvented tests)
- Heater power
- Borescope (selected tests)

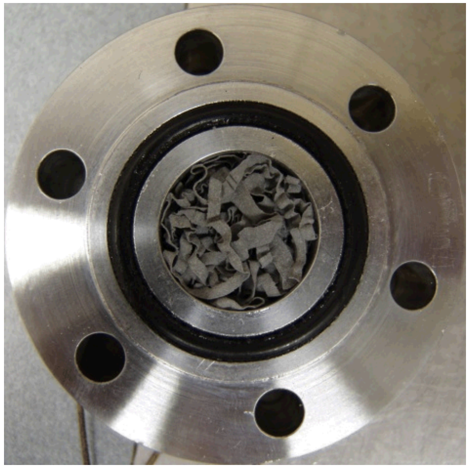
AP / HTPB / AL Propellant Sample in SITI





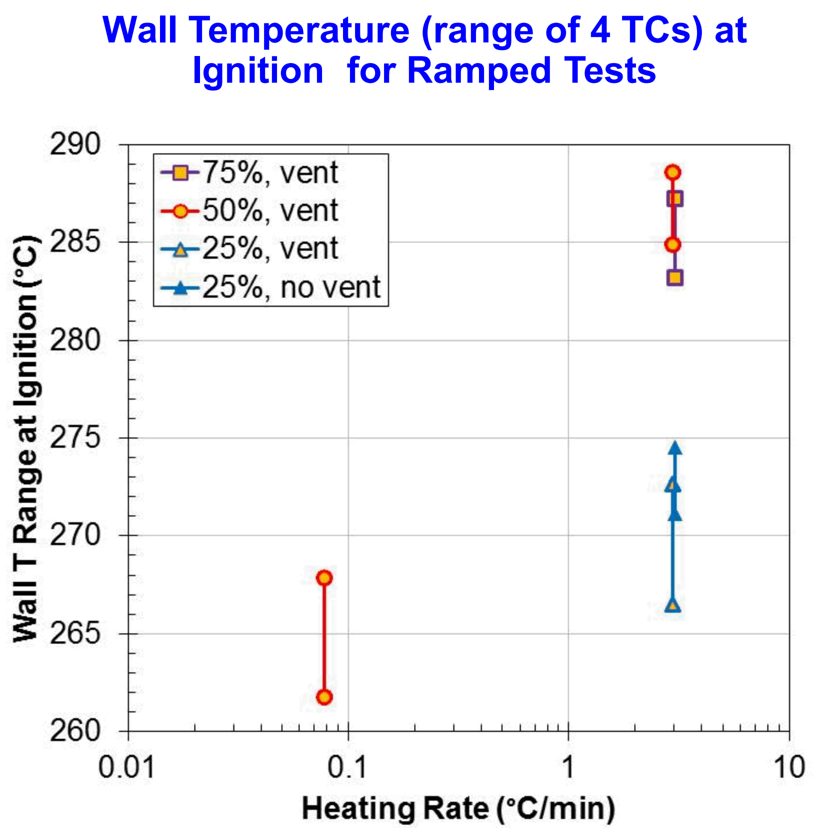
Shredded Propellant Samples





Ramped Test Data

- Only a few tests were done in temperature-ramped configuration (main purpose was for determining thermal diffusivity/conductivity)*
- Tests at 3 ºC/min or 0.7 ºC/min
- Effect of heating rate is significant (as expected)
- No appreciable difference between 50% and 75% free volume (vented)
- Similar results between vented & unvented at 25% free volume
- Significant difference between 25% and 50 & 75% free volume.

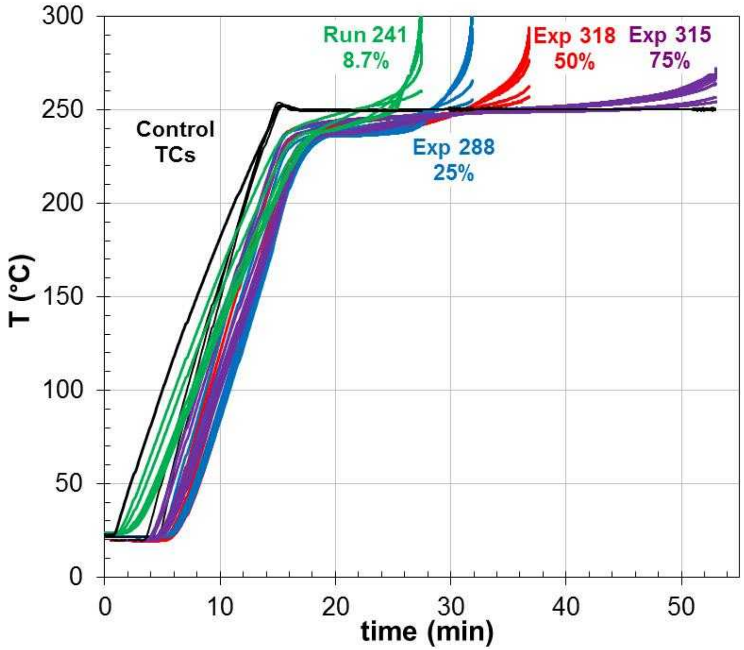


* W.W. Erikson, M.A. Cooper, M. L. Hobbs, M. J. Kaneshige, M.S. Oliver, and S. Snedigar, "Determination of Thermal Diffusivity, Conductivity, and Energy Release from the Internal Temperature Profiles of Energetic Materials," *International Journal of Heat and Mass Transfer*, Vol. 79, pp. 676-688, 2014.

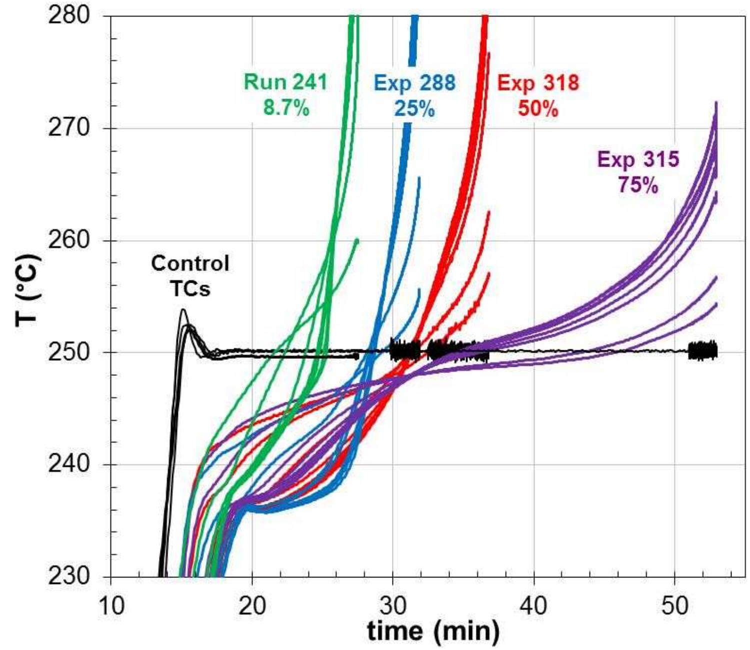
Ramp and Hold Test Data (Original Propellant)

Unvented Tests at 4 levels of Free Volume at 250ºC Hold Temperature

Overall Temperatures



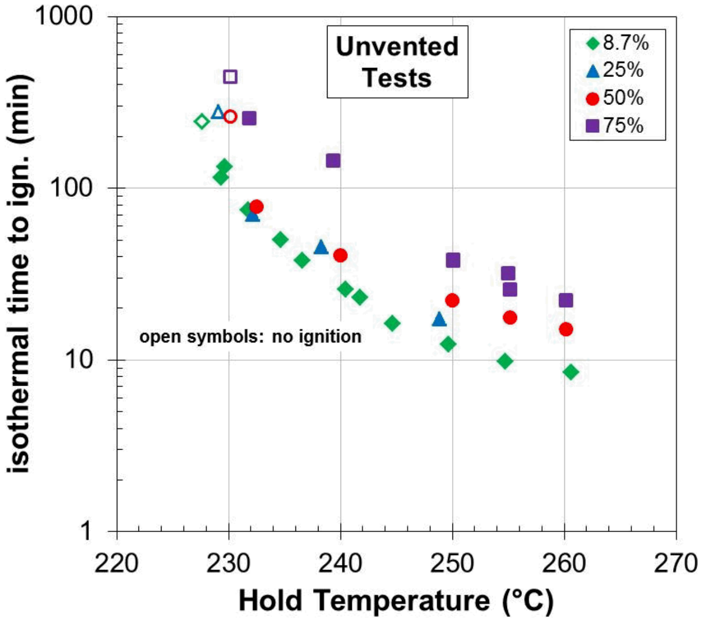
Detail of Runaway

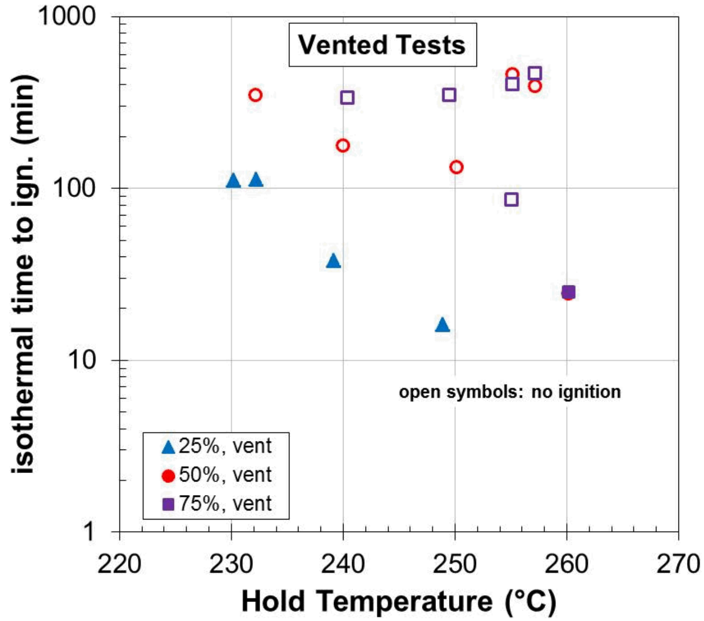


- Free volume has a noticeable effect on ignition time
- AP crystal Phase change at 240ºC is apparent; reactions likely have begun prior to that being reached (note shape of Run 241).

Ramp-and-Hold Test Data (Original Propellant)

Time to Ignition as a Function of Hold Temperature and Free Volume (open symbols = no ignition, symbol is time that test was ended)

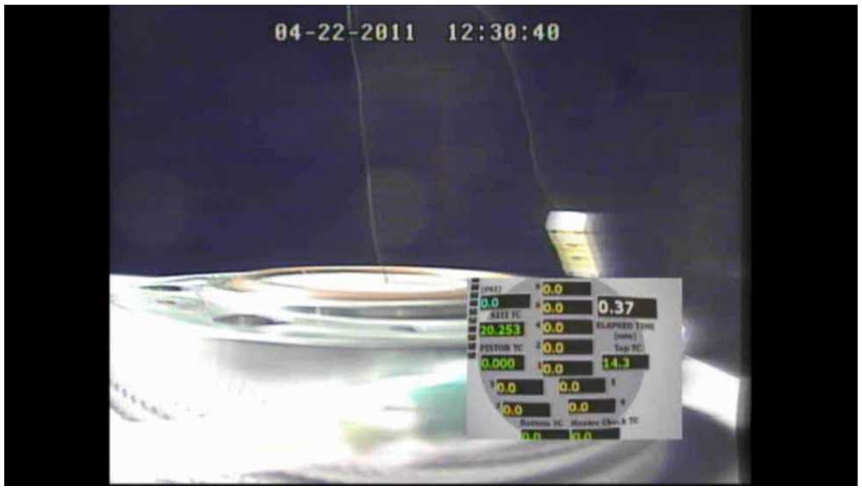




- Significant effect of free volume in unvented tests (more volume → longer ignition time)
- Significant effect of venting; ignition failed (open symbols on graphs) for hold T <260 ºC at 50 & 75% free volume
- Little or no effect of venting at 25% free volume, ignition down to 230 ºC

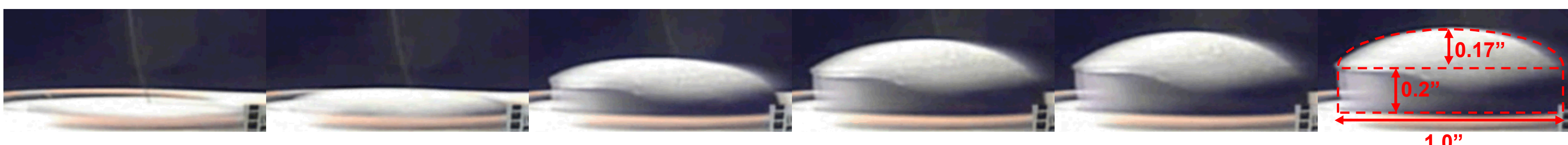
AP / HTPB Propellant Swelling/Expansion in SITI Experiments

Expansion in Open Air SITI Test (Exp 208)
Played at 240 x real time (1 sec = 4 min)



Expansion in 75% Ullage SITI Test (Exp 362) w/Borescope
Played at 240 x real time (1 sec = 4 min)

Images taken 2 min apart

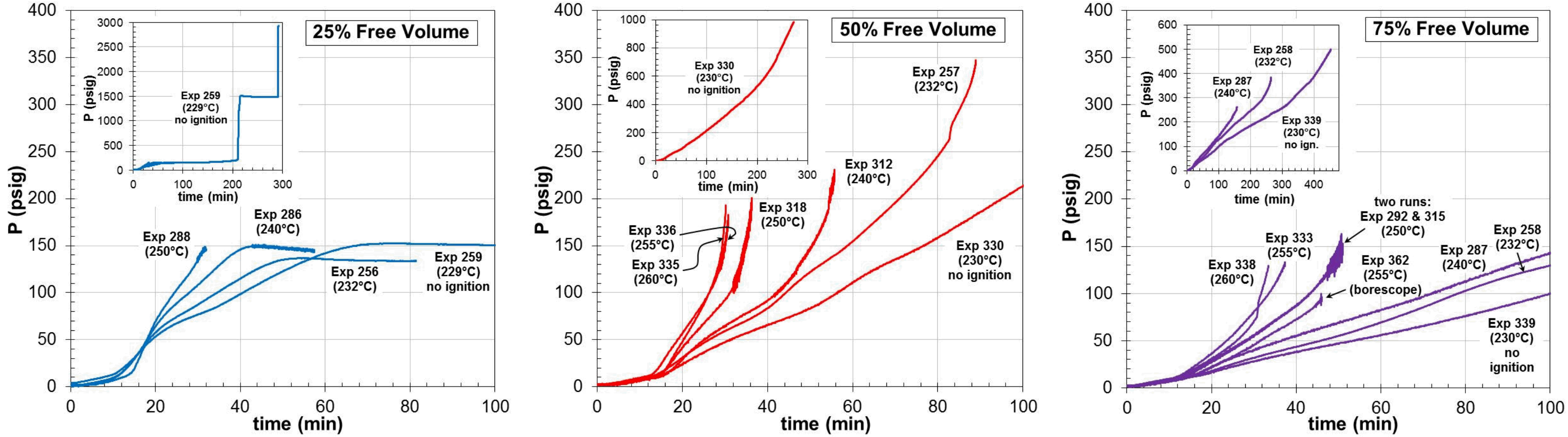


- Estimate of expansion by assuming half ellipsoid on top of cylinder, results in ~63% vol. expansion.
- The crystal phase change should result in ~10% volume increase.
- Thermal expansion should be ~7% (assume α ~ 1 x 10^{-4}/°C, and ∆T = 220°C).

- Are evolved internal gases are causing it to swell (“bread loafing”) beyond amount expected from thermal expansion/phase change? Or is something nonlinear happening with the polymer binder?

SITI data on AP/HTPB/AL Propellant

Pressure Histories for SITI tests at various levels of Free Volume (Ullage)

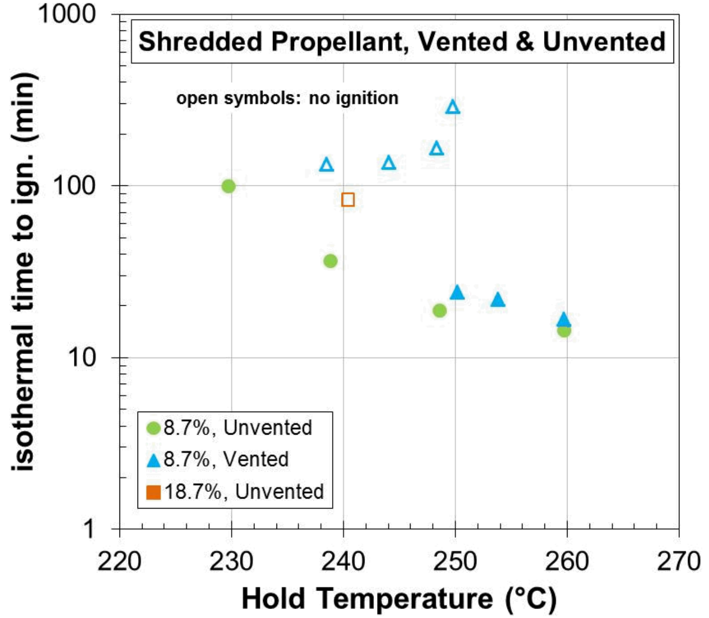


- At 25% ullage, pressure seems to always plateau at about 150 psi.
- In contrast, 50% or 75% ullage, pressure always grows (concave up)
- We believe that the material in the 25% ullage cases had all expanded to completely fill the available free volume and reached the pressure transducer tube, leading to plugging.
- Interesting behavior in Exp 259 (25% ullage with a 230C hold temperature, see inset graph) (Plateau at ~150 psi, sudden jump to ~1500 psi where it remains steady, another sudden jump to ~3000 psi)
- Implies that there are high pressure gases within the propellant itself which is suddenly released as a flow path opens up

Ramp-and-Hold Test Data (Shredded Propellant)

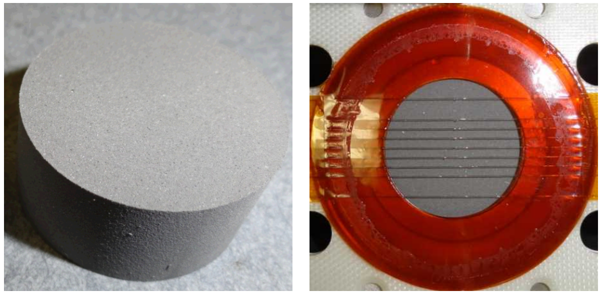
- Venting affects the temperature threshold for ignition
- But above threshold temperature, the effect on ignition time is minimal

Time to Ignition as a Function of Hold Temperature and Free Volume (open symbols = no ignition)



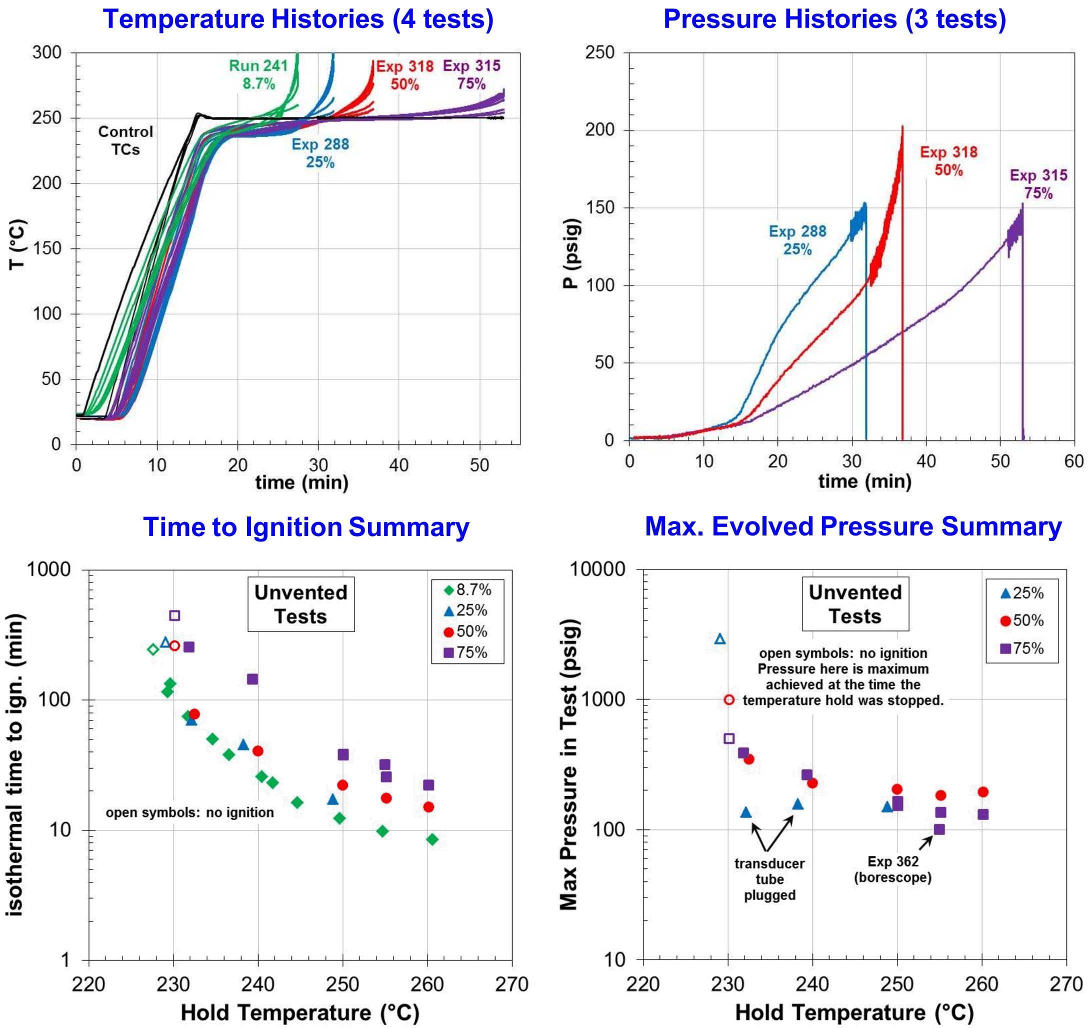
SITI data on AP/HTPB/AL Propellant

AP / HTPB / AL Propellant Sample in SITI



- Effect of free volume seems to be significant.
- Why?
  - Pressure-dependent chemistry?
  - Enthalpy loss?
  - Migration of reactive intermediate species?
- How to model this?
  - Assume all volume is accessible?
  - Porous flow?
  - More complicated, coupled mechanics, etc.?

Effect of amount of Free Volume on Ignition



Model 1: AP/HTPB Propellant Thermal Decomposition (based on Behrens & Minier, 1996*)

Three-step Chemical Reaction Mechanism:

(1) Dissociative sublimation of AP:

$NH_4ClO_4(s) \leftrightarrow NH_3(g) + HClO_4(g)$

(2) Hydrogen extraction from HTPB (represented as $[-C_4H_6-]_n$):

$[-C_4H_6-]_n(s) + \frac{1}{2}\,HClO_4(g) \rightarrow [-C_4H_6-]_{n-1}(s) + [-C_4H_2-](s) + \frac{1}{2}\,HCl(g) + 2\,H_2O(g)$

(3) Reaction of carbonaceous residue with perchloric acid:

$[-C_4H_2-]_n(s) + 2\,HClO_4(g) \rightarrow [-C_4H_2-]_{n-1}(s) + 2\,HCl(g) + H_2O(g) + CO + 3\,CO_2$

Notes:

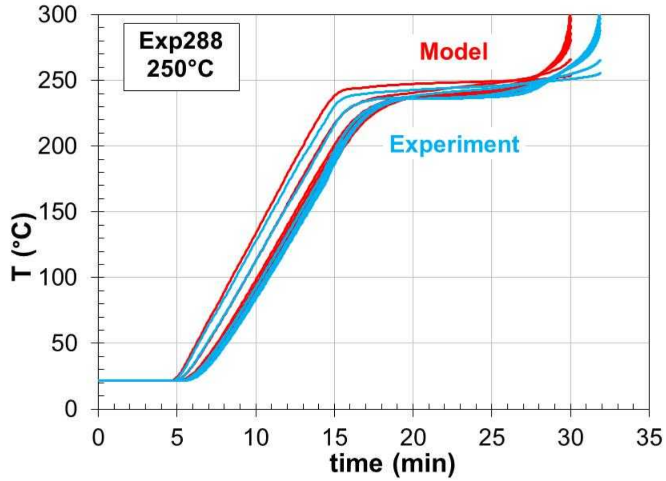
- **Reaction 1 is endothermic: (+247.3 kJ per mole of AP reacted)**
- **Sum of Reactions 2 & 3 is exothermic: (-2252 kJ per mole of HTPB reacted to final products)**
- **Net 9.5 moles of gas formed per mole of C_4H_6 reacted**
- **Hydrogen extraction from HTPB, results in a residue which can undergo cross-linking, resulting in a hardening/embrittlement of binder**

*R. Behrens and L. Minier, "The Thermal Decomposition of Ammonium Perchlorate and of an Ammonium-Perchlorate-Based Composite Propellant," 33rd JANNAF Combustion Subcommittee Meeting, Monterey, CA, Nov. 1996.

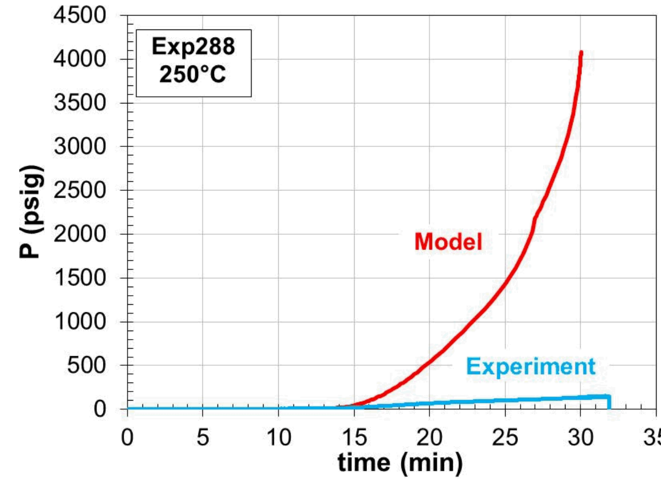
Model 1 Applied to SITI

- **Kinetic constants:**
  - $\ln A_1 = 17.0$, $Ea_1 = 28$ kcal/mol
  - $\ln A_2 = 26.8$, $Ea_2 = 40.8$ kcal/mol
  - $\ln A_3 = 26.8$, $Ea_3 = 40.8$ kcal/mol
- **Model appears to get time-to-ignition about right**
- **Model over-predicts the gas generation and pressure**
- **Unclear where model needs adjustment (AP decomposition? AP + HTPB?)**
- **Is gas evolved but trapped within propellant?**

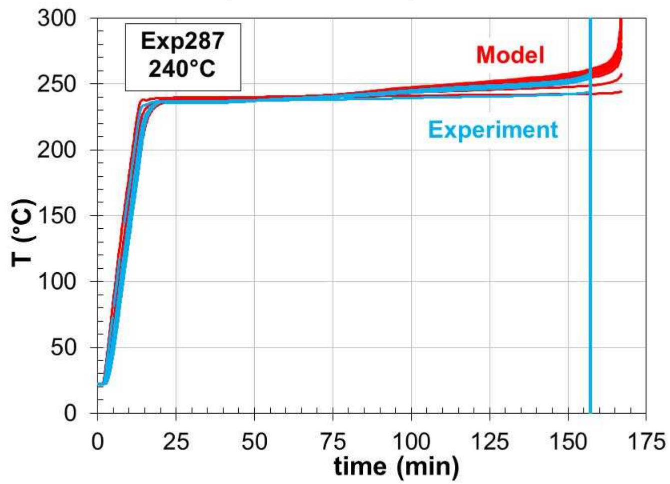
Exp288: Temperature



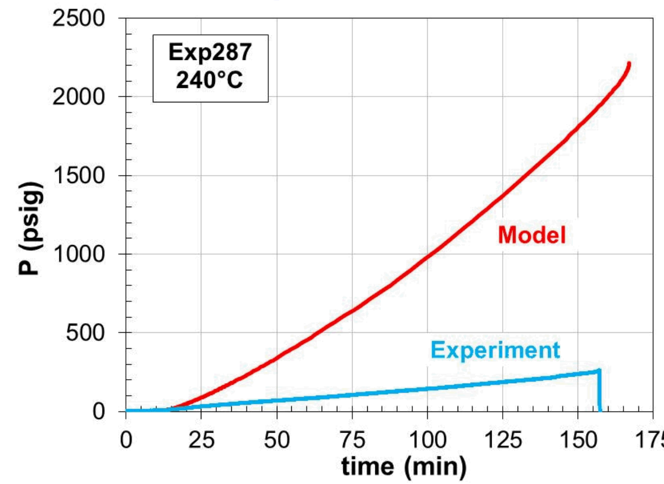
Exp288: Pressure



Exp287: Temperature



Exp287: Pressure



Model 2: Decomposition with Porous Flow

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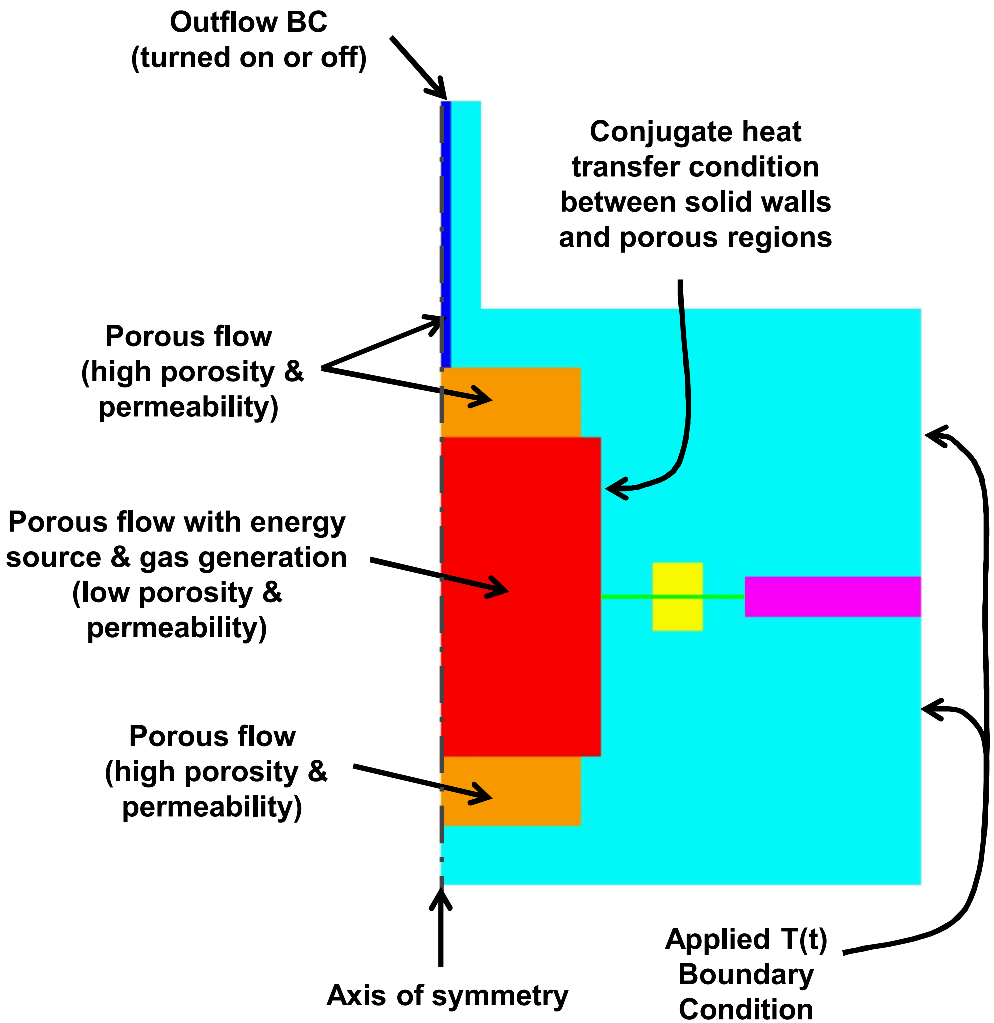


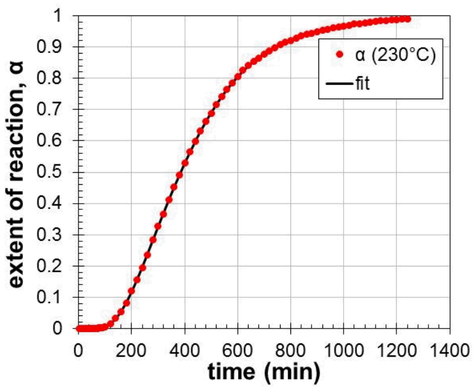
- Simple global chemistry model:
  - Propellant → x Gas + (1-x) Solid
    (x is a tunable constant)
  - Rate is function of extent of reaction and T:
    rate=f(α)*Aexp(-E/RT)
    f(α) based on literature for AP (next slide)
  - Could potentially use alternate chemistry form (pressure-dependent, etc.); have not done this yet.
- Porous flow model:
  - Darcy's law
  - Separate gas and condensed phase temperatures (heat transfer coefficient between them)
  - Enthalpy carried with gas—investigate whether enthalpy loss can effect ignition time

Model 2: Chemistry

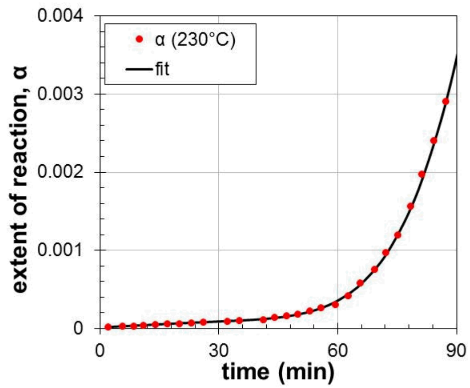
- **Assumption**: **AP decomposition is rate-limiting step** (e.g. data from Inami et al.* show AP propellant decomposition following same slope as AP decomposition but at a higher energy release).
- AP decomposition data from Jacobs & Ng† and Vyazovkin & Wight‡ processed to yield reaction model, f(α).

AP isothermal decomposition data from Jacobs & Ng, fit with piecewise cubic splines (α=1 is 30% decomposed)

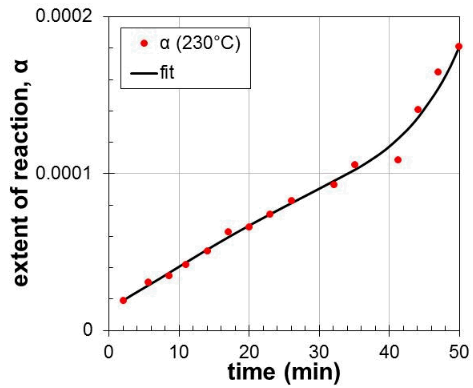
Overall Sigmoidal Shape



Early Time: Accelerating Growth

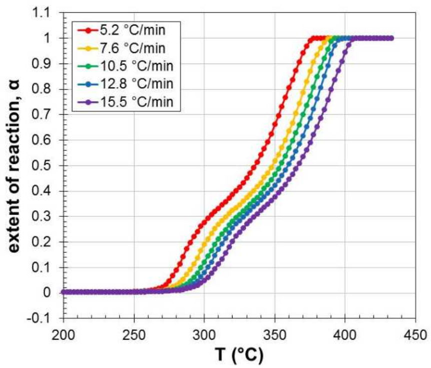


Very Early: Linear Induction

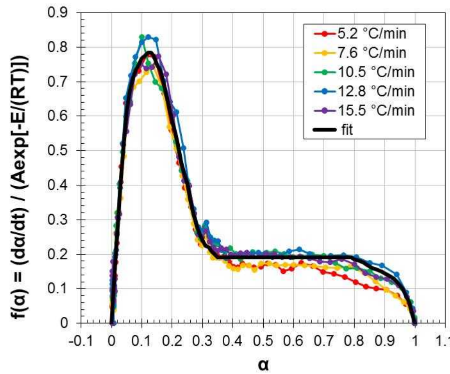


process data & scale to obtain f(α)

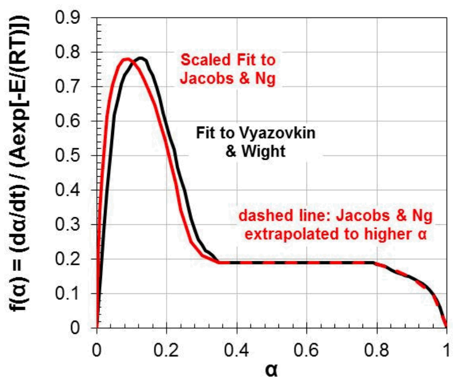
AP non-isothermal decomposition data from Vyazovkin & Wight



process data to obtain f(α)



Reaction Model, f(α)



*S. H. Inami, W. A. Rosser, and H. Wise, "Heat-Release Kinetics of Ammonium Perchlorate in the Presence of Catalysts and Fuel," *Combustion and Flame,* V. 12, pp. 41-44, 1968

† P. W. M. Jacobs and W. L. Ng, "A Study of the Thermal Decomposition of Ammonium Perchlorate Using Computer Modelling," *Reactivity of Solids*, Proceedings of 7th International Symposium on the Reactivity of Solids, Bristol, England, July 1972, J. S. Anderson, M. W. Roberts, and F. S. Stone, eds., pp. 398-410.

‡S. Vyazovkin and C. A. Wight, "Kinetics of Thermal Decomposition of Cubic Ammonium Perchlorate," *Chemistry of Materials*, Vol. 11, pp. 3386-3393,1999

Model 2: Test Case

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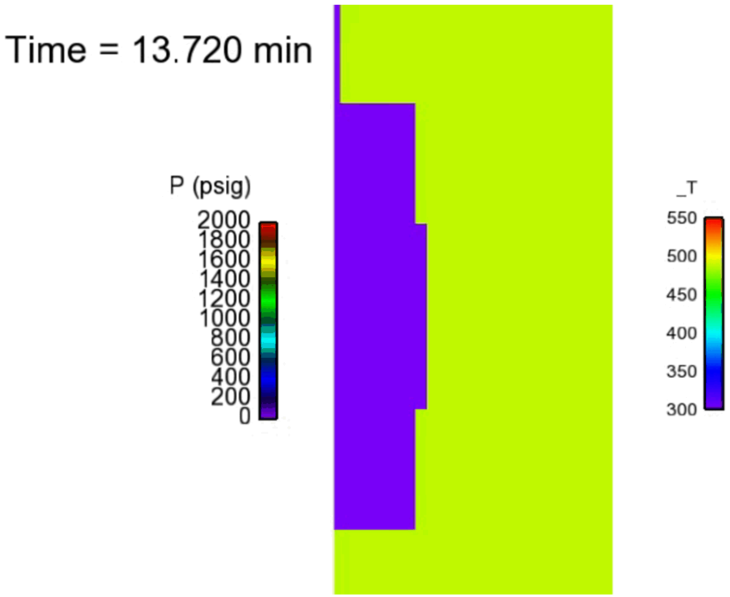
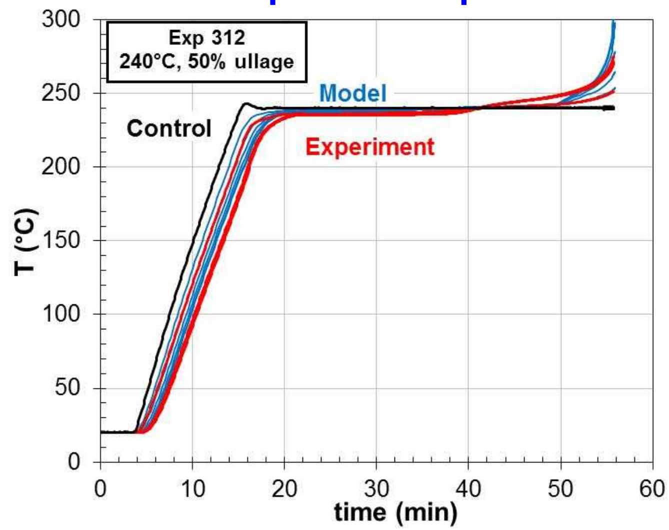
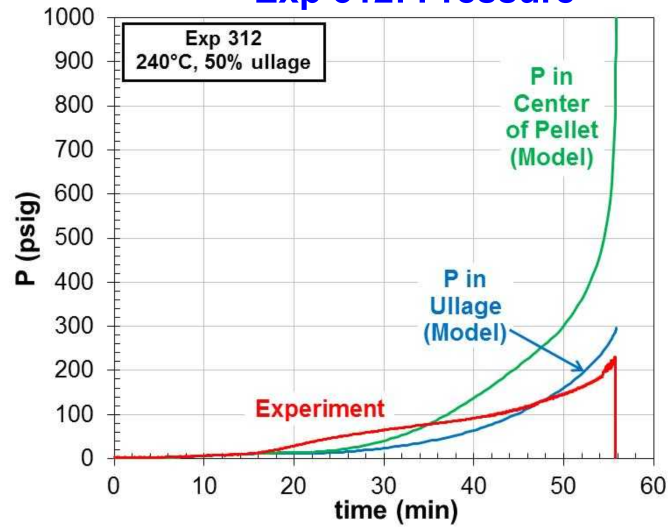
Simulation of Exp 312: Animation of Temperature, Internal Pressure, and Velocity Vectors



Exp 312: Temperature



Exp 312: Pressure



- Gas fraction ('x') set to 20%
- Permeability set to 1e-18 m^2 (pristine HTPB propellant surrogate ~1e-21 m^2, but increases with temperature*).
- Time to ignition, temperature history fits pretty well
- Pressure in ullage is comparable to measurement; significant pressure gradient exists within propellant.
- Effect of swelling ignored … is it important?

*Celina, M. and Gillen, K. T., "Oxygen Permeability Measurements in Elastomers at Temperatures up to 225°C," *Macromolecules*, Vol. 38, pp. 2754-2763, 2005.

Next Steps for AP Propellant Model

- Improve performance in porous flow models—couple with true "fluid region"
- Do we need to include material expansion, coupled mechanics, etc.?
  - Including may help with being able to represent damage evolution and the associated increase in burning surface area (affects reaction violence, see next item)
- Anecdote on pipe bomb experiments with vent holes of various sizes.
  - If vent hole was just the right size (not too big, not too small) an extremely violent explosion resulted. With no vent, too large, or too small, the reaction violence was much less.
  - Process for the violent events:
    - A short time (a few seconds?) before final ignition, a "worm" of propellant was extruded/ejected from the vent hole (think Play Doh Fun Factory).
    - Presumably this resulted in the material shearing and creating a lot of surface area which, when ignited, burned very fast.
- How does the gas which evolves escape from the propellant matrix to reach the transducer?
  - Porous flow (Darcy's law)?
  - Micro fracture/cracking?
- Examine more closely "shredded propellant" results—since gases should be able to escape more easily we can perhaps use that information to explicitly examine pressure dependency.
- Adjust chemistry models as needed.

Summary and Conclusions

- Free volume and venting effects were systematically studied in cook-off experiments with an AP/HTPB/Al propellant.
- Significant effect of free volume and venting on the time to ignition.
- Swelling in heated propellant samples with expansion of > 60% has been observed, likely caused by gas accumulation within the material.
- The expansion and swelling of propellant in some SITI tests caused the pressure transducer tubes to be clogged.
- Two simple decomposition models were developed and attempts to compare with SITI data were partially successful.
  - Model 1 used chemistry to full reaction products.
  - Model 2 used global chemistry, a parameterized gas generation term and a porous flow representation.
  - Time-to-ignition for particular tests could be represented with either model
  - Gas generation way too high with Model 1, improved by Model 2
  - As yet have not shown the free volume or venting effects (work in progress).
- Identified areas for future work

Acknowledgements

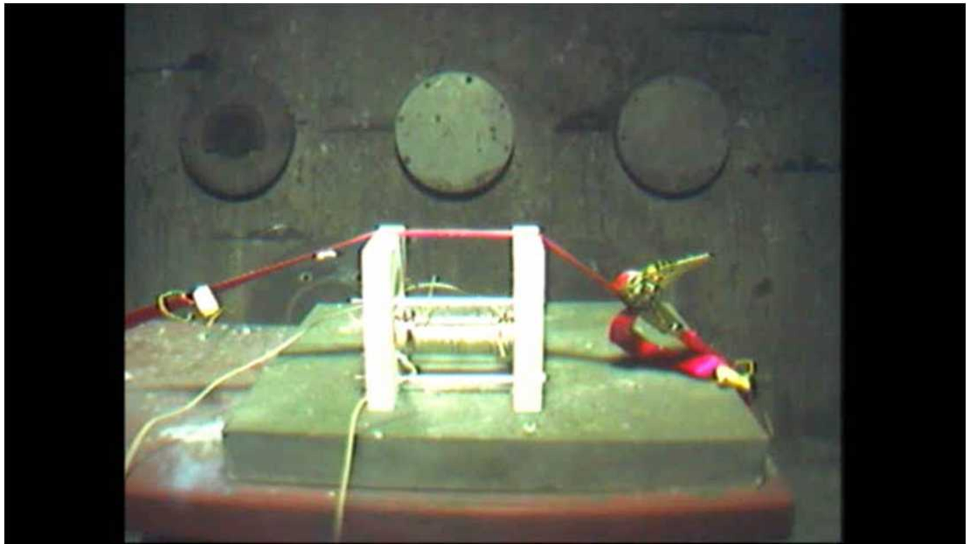
- Thanks to Shane Snedigar for his efforts in performing the experiments.
- Thanks to C. Yarrington and M. Cooper for manuscript review and helpful comments.
- Funding for this work was provided by DoD/DOE Joint Munitions Program under Technical Coordination Group – III

The End

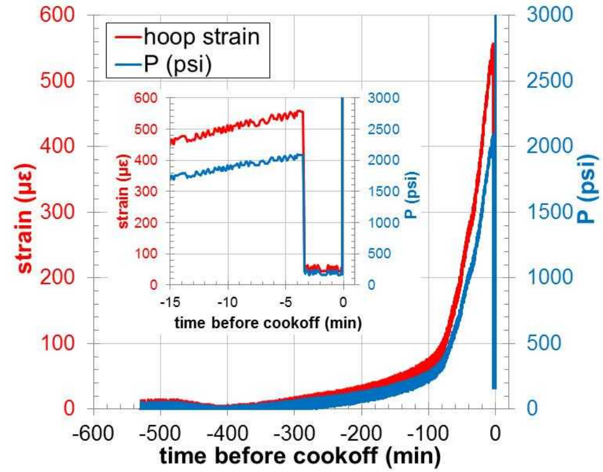
Back up Material

Vented Pipe Bomb with an AP/HTPB Propellant

Last ~34 min of Pipe Bomb Test with AP Propellant (60x; 1 sec = 1 min)



Pressure Calculated from Strain Gage in Pipe Bomb Test
(pressure drops when extrusion pops out)



- 0.2” diameter hole in end caps.
- Propellant extruded (one side) and popped out about 3.5 min before final ignition.
- Reaction was very violent compared with non-vented or larger vented tests (extrusion process generated internal surface area which burned very fast?)

Final Result
(extrusion pieces near top of photo)

detail showing propellant extrusion and pop-out