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Combustion of Energetic Materials

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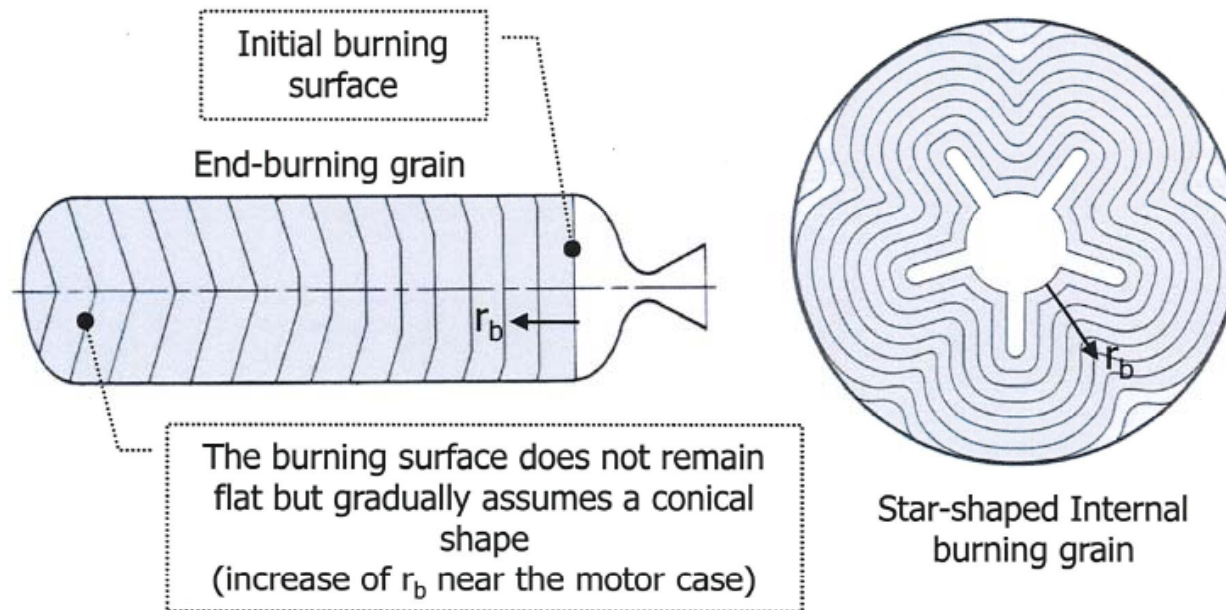
Burning Rate Experimental Techniques

Burning Rate of Solid Propellants

$$r_b = aP^n$$

Burning rate [mm/s] \rightarrow r_b \leftarrow Burning rate exponent
Burning rate coefficient [mm/s] \rightarrow a \leftarrow Pressure [bar]
 $\sim 0.3 - 0.7$ for rocket motors

- This equation is valid only when the gas cross-flow velocity over the propellant surface is low enough so convection effects on the burning rate can be neglected.
- In the case of high-velocity flow of combustion gases over the burning propellant surface a different equation must be used (erosive burning)



Figures adapted from
Beckstead, 2000

Temperature Sensitivity of Burning Rate

- The burning rate of a solid propellant is dependent on pressure ($r_b = aP^n$)
- However, it is also dependent on the initial temperature of the propellant T_i even when the pressure is kept constant
- The parameter “ a ” is not a true constant since it can be expressed as a function of initial temperature T_i and temperature sensitivity σ_p

$$a = a_{ref} e^{\sigma_p (T_i - T_{i,ref})} \quad (33)$$

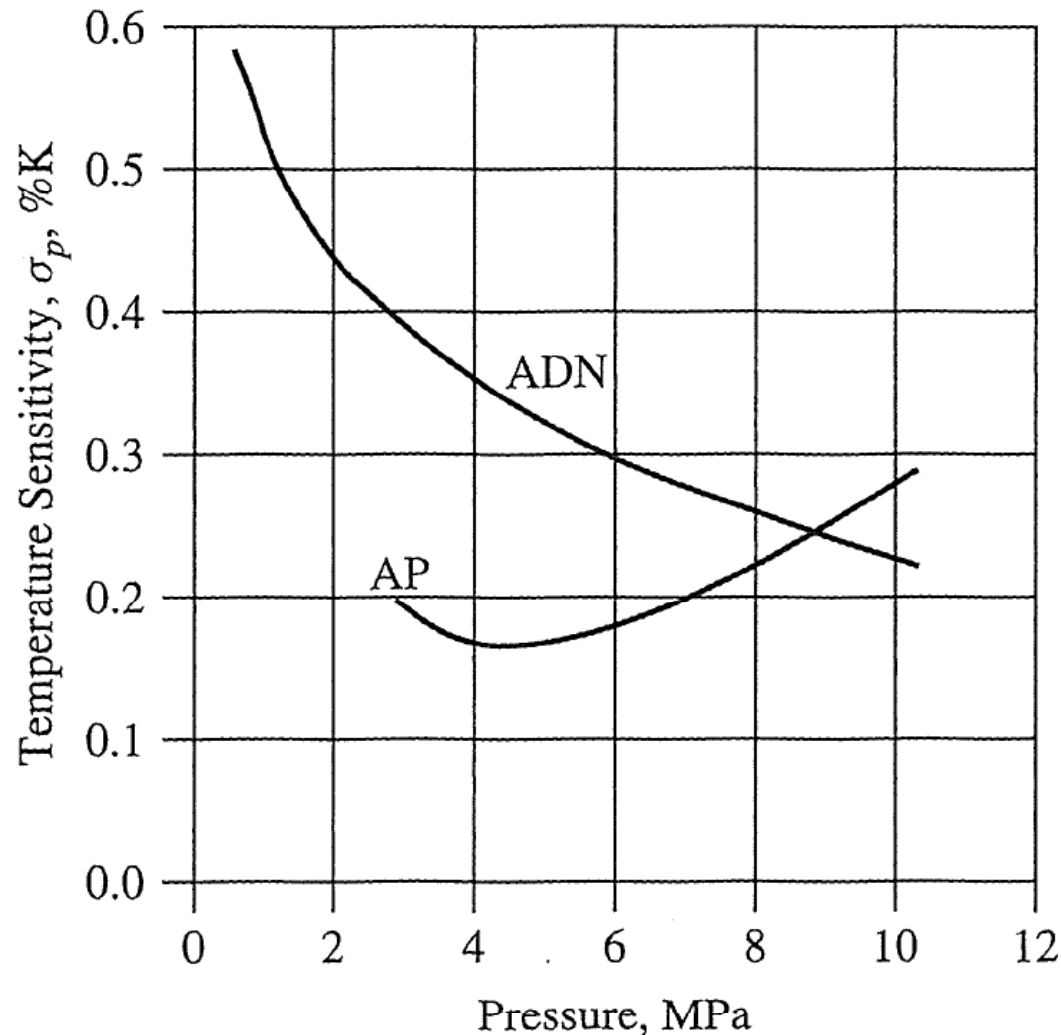
- The temperature sensitivity σ_p is defined as:

$$\sigma_p \equiv \frac{1}{r_b} \left[\frac{\partial r_b}{\partial T_i} \right]_P = \left. \frac{\partial \ln r_b}{\partial T_i} \right|_P \quad (34)$$

- Using equations (33) and (34), the burning rate can be expressed as:

$$r_b = \left[a_{ref} e^{\sigma_p (T_i - T_{i,ref})} \right] P^n \quad (35)$$

Dependency of σ_p on Pressure



- The temperature sensitivity σ_p of the propellant burning rate is a function of the propellant chemical composition, and usually depends on pressure
- As the pressure is increased, σ_p generally decreases. This is most apparent in the nitramines (HMX, RDX, CL-20)
- AP has shown an exception to the trend as σ_p first decreases and then increases with p
- In general, propellant ingredients with low σ_p are favored because they have more consistent performance under different operating conditions

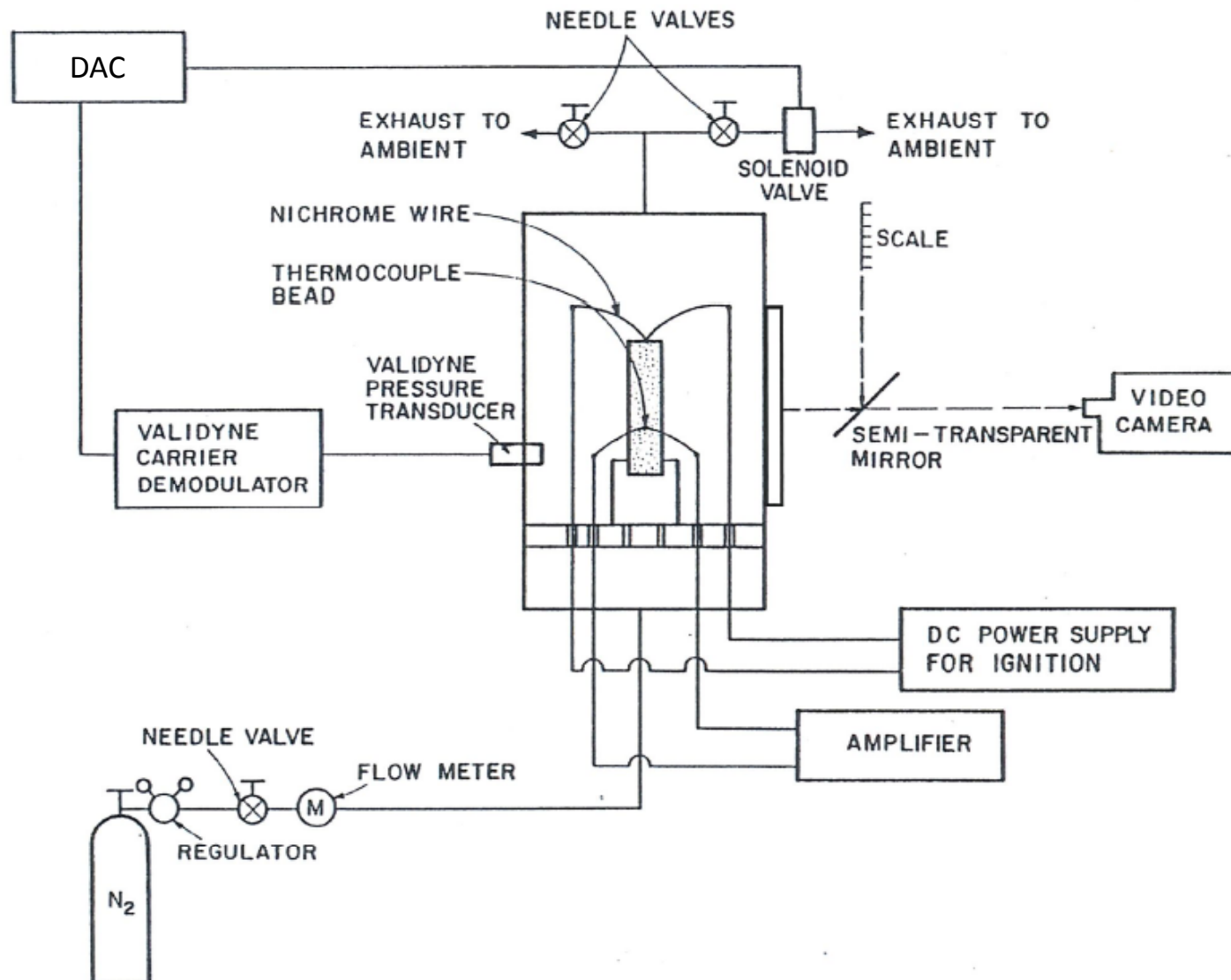
Burning rate measurement techniques

- Probe (break wires, Crawford bomb)
- Optical (windowed bomb necessary)
 - Direct (burning rate determined from high speed camera, simultaneously observe uniform planar burning, flame spread, melt, residue, ejection of particles, etc.)
 - Laser servo (feed-back system to maintain surface position)
- Pressure (closed bomb; measure pressure variation as a function of total burn time; based on equilibrium thermochemistry, burning rate calculated from correlation that requires knowledge of specific heat and heat of combustion; oil and water bath sometimes used)

Burning rate measurement techniques

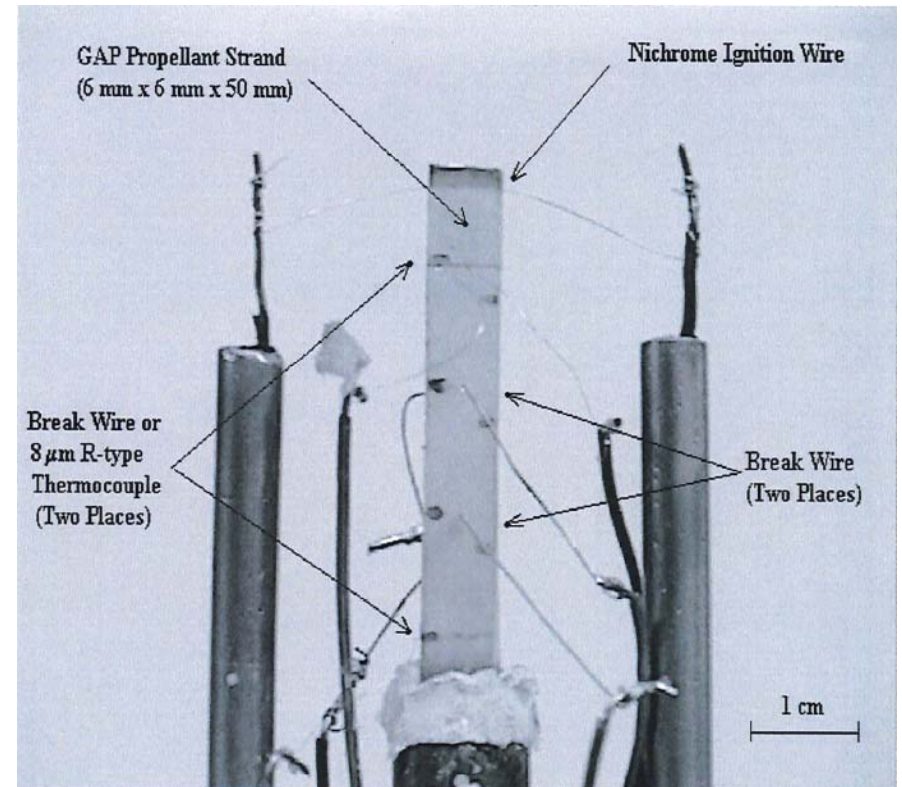
- Weight loss/thrust (applicable to transient burning also; microforce transducer used)
- Microwave Reflection Interferometry (propellant bonded in waveguide, microwaves reflected from surface by ions in reaction and phase shift recorded; applicable to transient burning; can be used with aluminized propellants)
- Ultrasonic (propellant attached to a coupling material with transducer; mechanical wave travels through sample and is reflected at the burning surface back to the transducer, applicable to transient burning; most often used in motors)
- X-ray (applicable to transient burning; most often used in motors)

Schematic Diagram of a Windowed Strand Burner

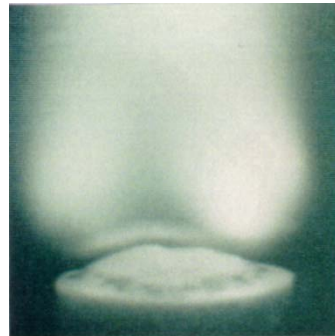


Measurement of Propellant Burning Rate by using Strand Burner

- Small propellant strands (~50 mm long, 6 mm diameter) are designed to burn as end-burning specimen for determining their rates under well-controlled P and T_i conditions
- All lateral surfaces are covered with inhibitor materials leaving only the top surface exposed
- The burning rate is deduced by measuring the time needed to burn a fixed length of the propellant (which is the distance between two consecutive break wires inserted in the strand), and/or by visual measurements through a windowed burner
- An inert gas such as nitrogen is used to pressurize the chamber, and is allowed to flow continuously as purged gas during the test
- The temperature of the purge gas can be controlled to desirable levels for preconditioning the initial temperature of the strand
- A fine wire thermocouple can be inserted in the specimen for determination of the thermal wave profile in the condensed phase



Solid Propellant Strand Burner



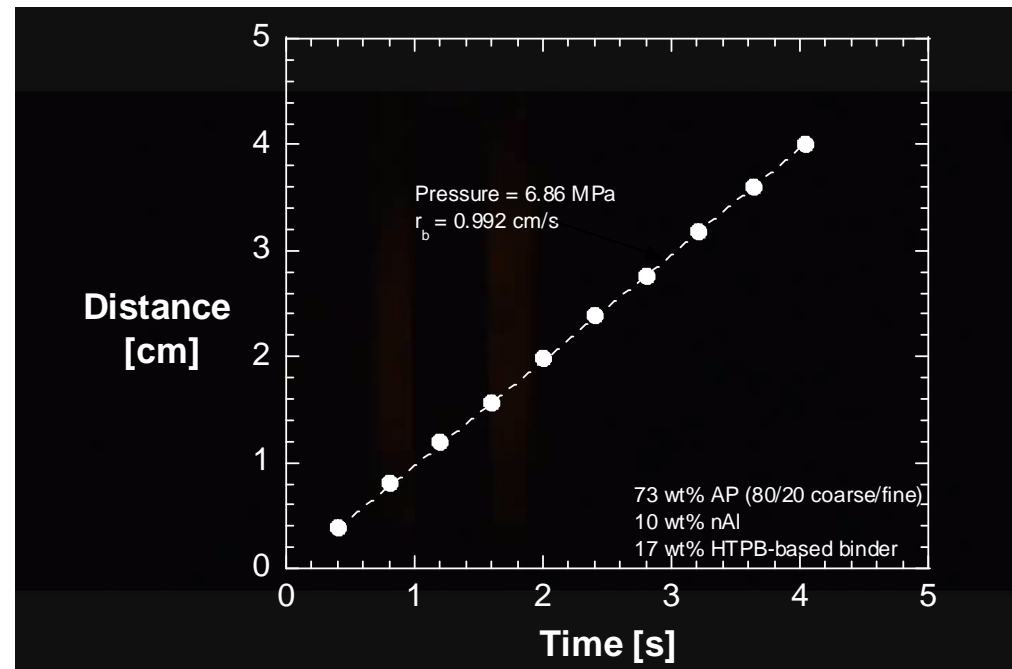
RDX Propellant



JA-2 Propellant

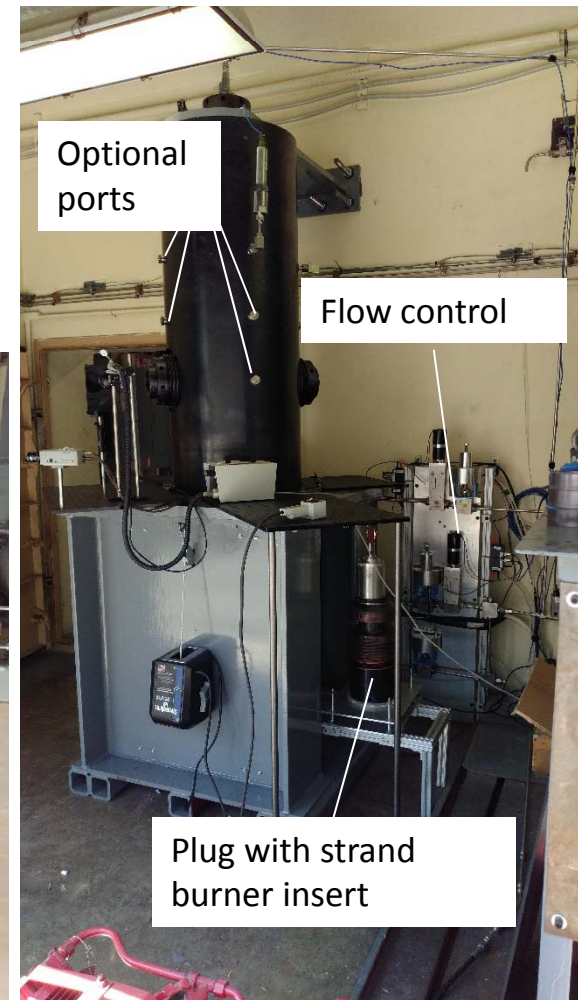
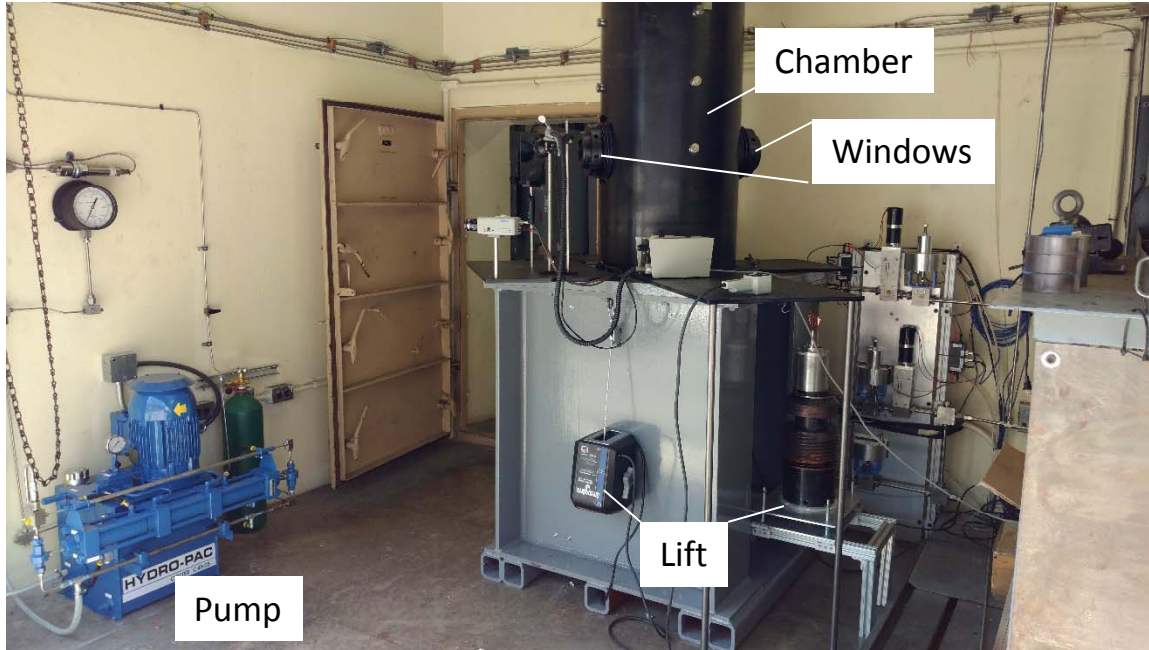


M43 Propellant



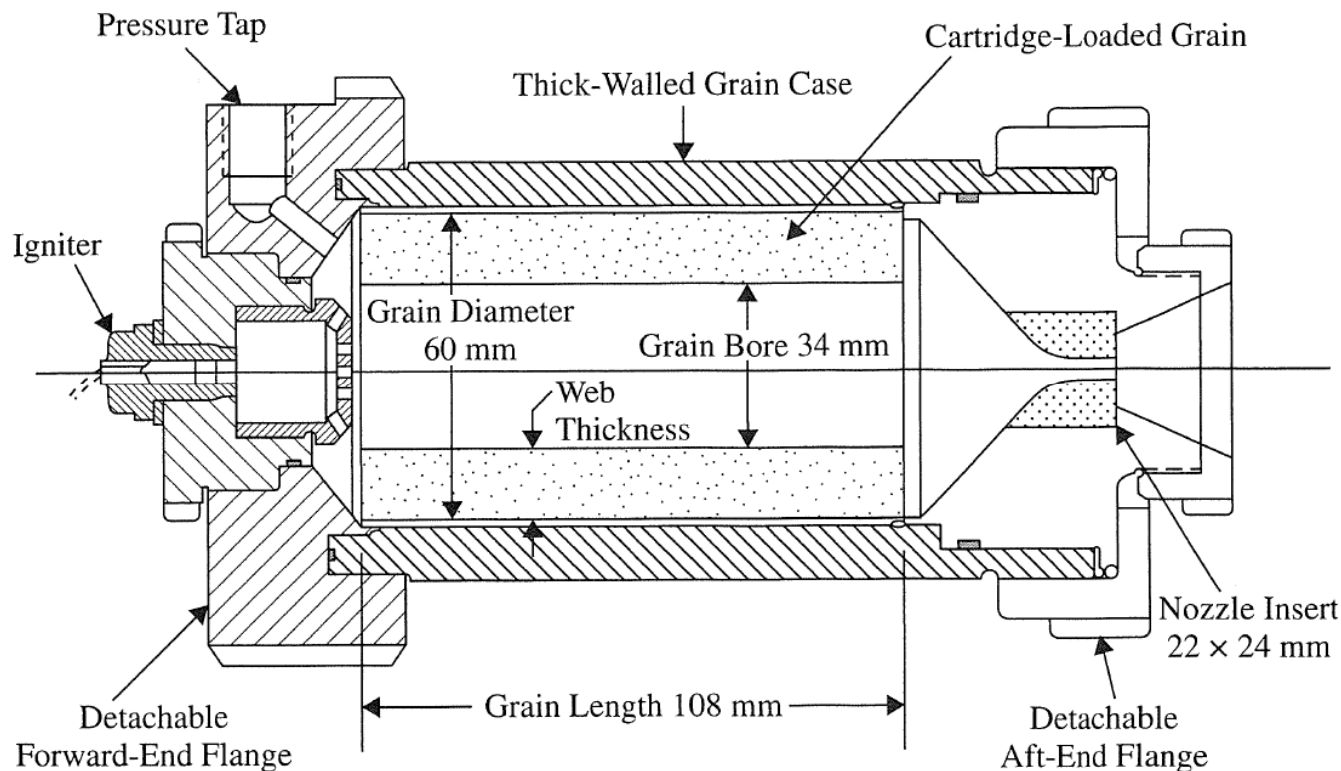
High Pressure Optical Combustion Chamber

- operational pressure from 0.03 to 300 MPa
- working volume of 0.012 m³ (12 liters) allowing for a variety of experiments



Measurement of Propellant Burning Rate by Sub-Scale Test Motor

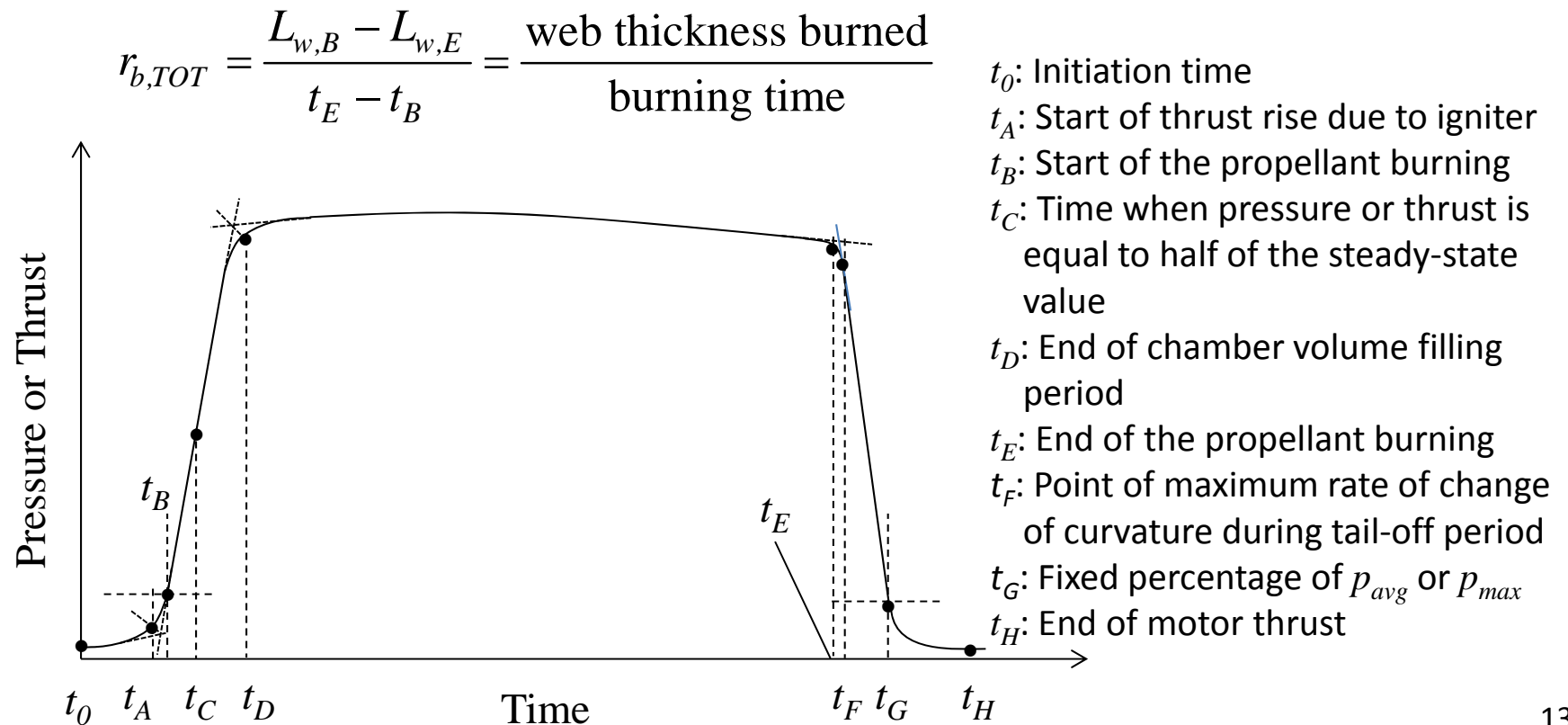
- Small-scale rocket motors used for propellant screening, development, performance verification, and production control
- Nozzle allows assessment of burning rate at a specific operational pressure and over a range of pressures
- Generic, heavy duty, small scale motor with flanges for easy cleaning and reuse, which enables testing propellants with various grain designs



From Kuo and Acharya, 2012

Burning Rate by Thickness/Time (TOT) Method

- Web thickness, L_w , is defined as the minimum thickness of the grain from the initial burning surface to the insulated case wall of the motor or to the intersection of another burning surface; examples are end burning grains and center perforated grains.
- Conventional method, based on propellant thickness and the burning time



Mass Balance Burning Rate Method

$$r_{b,MB} = \underbrace{\frac{L_{w,A} - L_{w,G}}{t_E - t_B} \frac{\int_{t_A}^{t_E} p dt}{\int_{t_B}^{t_G} p dt}}_{\text{first equality}} = \underbrace{\frac{\text{web thickness}}{\text{burning time}}}_{\text{second equality}} \times \alpha_m$$

- α_m is the correction factor
- More complicated than TOT method, but usually results in less data scatter than TOT method due to non-instantaneous burnout correction
- Methods require web thickness measurement
 - Obtained from design dimensions with shrinkage/deformation correction or a measured average
 - Mandrel imperfections can result in $\sim 10\%$ error causing burning rate inaccuracies $\sim 3\%$
- Burning times determined from pressure or thrust traces
- Difficult due to “real world” effects of non-uniform burning and non-instantaneous burn-out

Correlation to Full-Scale Motors

- In general, full-scale motors, small-scale motors, and propellant strands do not have the same burning rate at the same pressure and a correlation or scale factor is used to relate them
- Various parameters influence differences in burning rate:
 - Intrinsic parameters
 - Pressure
 - Temperature
 - Mechanical Properties
 - Global parameters
 - Principal (internal motor flowfield, real grain geometry (grain deformation effects), erosive burning, rheology of grain manufacture
 - Other (combustion stability, radiation, propellant composition at liner interface, thermoelastic coupling, nozzle design, acceleration)
- Lab scale strand burner experiments best for assessing statistically significant effects of formulation changes and validation of modeling and simulation efforts

Experimental Considerations

- Inhibitor

- 1-D burning is required
- Side burning is prohibited by covering the sides with an inhibitor
- Any inhibitor may be used as long as it does not react or dissolve the propellant or interfere with propellant burning (clear nail polish)

- Temperature Dependence

- Burning rates generally increase with propellant temperature
- The sensitivity of burning rate to propellant temperature must be quantified as well as the effect of temperature on pressure sensitivity
 - Temperature sensitivity appears to be highest at lower pressures so the pressure effect can be important
 - Measure r_b at a number of pressures, e.g., from 100 to 1500 psi, at three different temperatures or measure r_b at two or three pressures at a number of different temperatures
- Temperature sensitivity is different than the effect of thermal damage, burning rate will change based on thermal degradation of the propellant

Experimental Considerations cont'd

- Pressure Dependence

- $r_b \sim p$ to a power generally less than 1 (0.2 to 0.7)
- Propellants and solid rocket motors (SRMs) operate at pressures from 700-1500 psi (interest in higher pressures exist)
- Experimental measurements at such conditions are difficult
 - Premixed flame zone is drawn closer to propellant surface and final diffusion flame moves farther from surface
 - Gas properties not well defined or understood
 - Optical diagnostics complicated by sharp density gradients in the flow, spectroscopic line broadening, requirements for thick windows, etc.

- Erosive Burning

- Modification of burning rate by flow of product gases across the surface
- The cross velocity modifies the energy transport mechanisms to the propellant surface
- Erosive burning results in a dramatic increase in burning rate once a critical Reynolds number is reached
- Erosive burning effects do not scale well, and are generally less severe with increasing motor size

Experimental Considerations cont'd

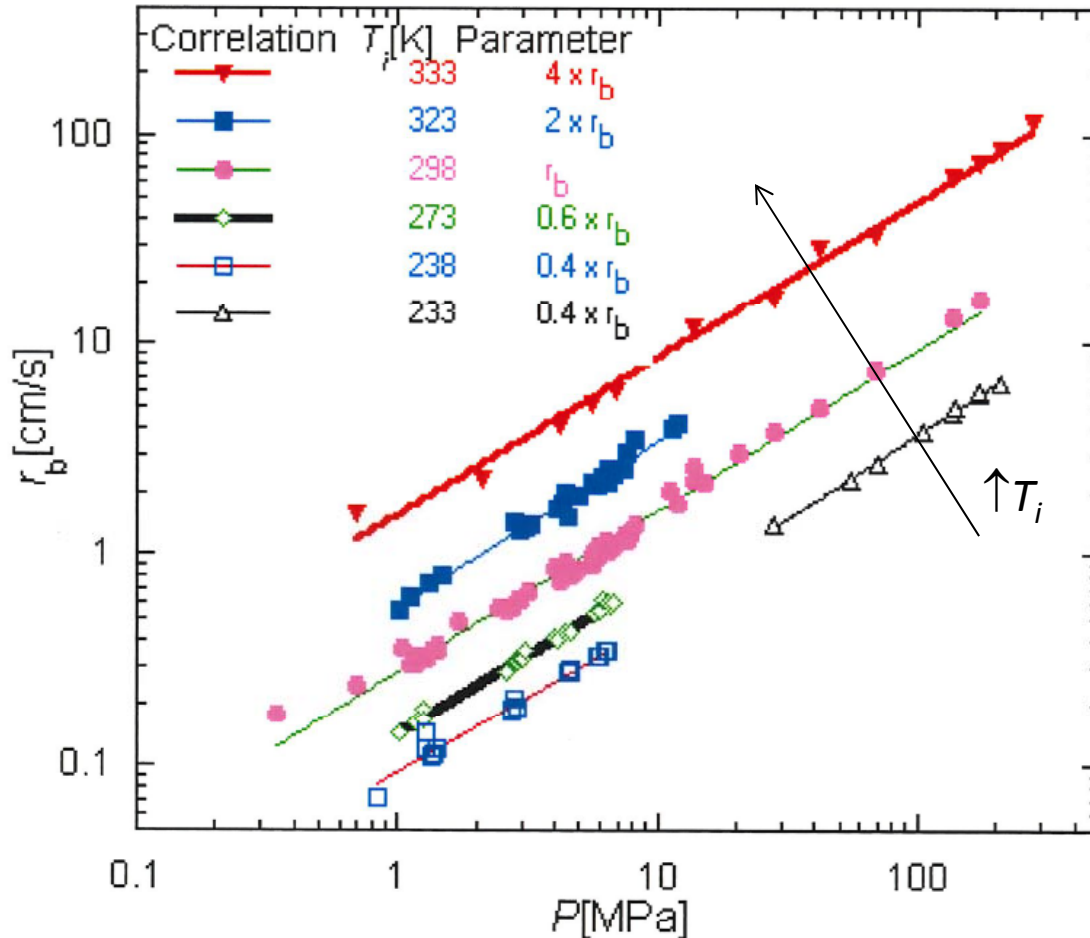
- Strain Augmented Burning

- Solid composite propellant strands subjected to tensile strain have shown burning rate augmentation once critical strain values are surpassed, due to dewetting of particle/binder forming voids and the ability of flame to penetrate the grain
- Also when propellant undergoes rapid strain, e.g., ignition, heat is generated in the propellant which modifies local burning rate
- Propellant stress-strain response can contribute to variations in motor burning rate

- Quasi-Steady vs. Transient Measurements

- Quasi-steady burning ; $r_b = f(p, T_i)$, p and T_i constants
- Transient burning ; what happens to r_b when pressure changes rapidly?
- Propellant reaction rates vary strongly with both pressure and temperature and local processes in the gas and condensed phases produce a dynamic response that exhibits significant frequency dependence
 - Some of the energy released in chemical reactions is transformed to mechanical energy of motions in the combustion products causing combustion instability

Comparison of Correlated Burning Rate Expression of JA2 Propellant with the Measured Burning Rate Data



$$r_b = a_{ref} P^n \exp \left[\sigma_p (T_i - T_{i,ref}) \right]$$

$$\sigma_p = \sigma_{p,c} + \frac{b}{c_1 + c_2 P}$$

The parameter values obtained from the burning rate curve fitting procedure are:

$$a_{ref} = 0.2478 \text{ (cm/s) (MPa)}^{-n}$$

$$n = 0.8222$$

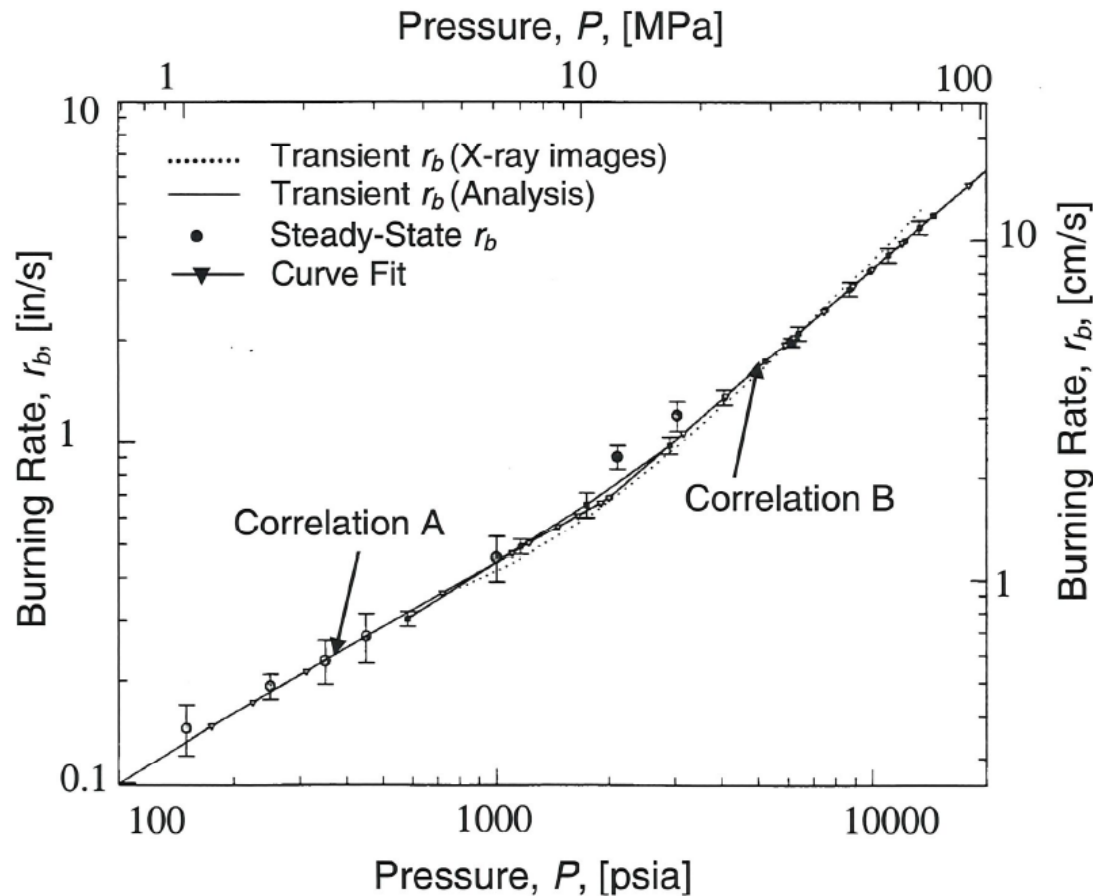
$$\sigma_{p,c} = 0.00240 \text{ K}^{-1}$$

$$b = 0.537 \text{ K}^{-1}$$

$$c_1 = 17.0425$$

$$c_2 = 2.2108 \text{ MPa}^{-1}$$

Comparison of Burning Rates of JA2 Propellant at Various Pressure Levels



For $0.7 < p < 13.8$ MPa, r_b at $T = T_{amb}$ can be represented by

Correlation A:

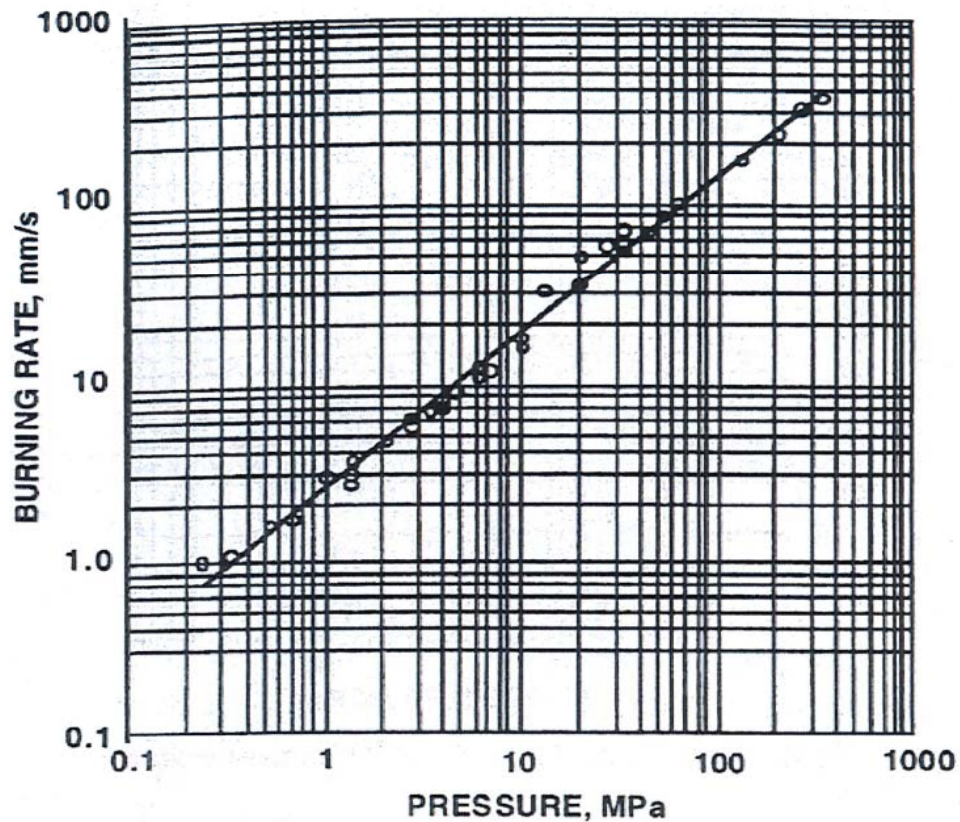
$$r_b(\text{cm/s}) = 1.127[p(\text{MPa})/6.894]^{0.63}$$

For $13.8 < p < 96.5$ MPa, r_b at $T = T_{amb}$ can be represented by

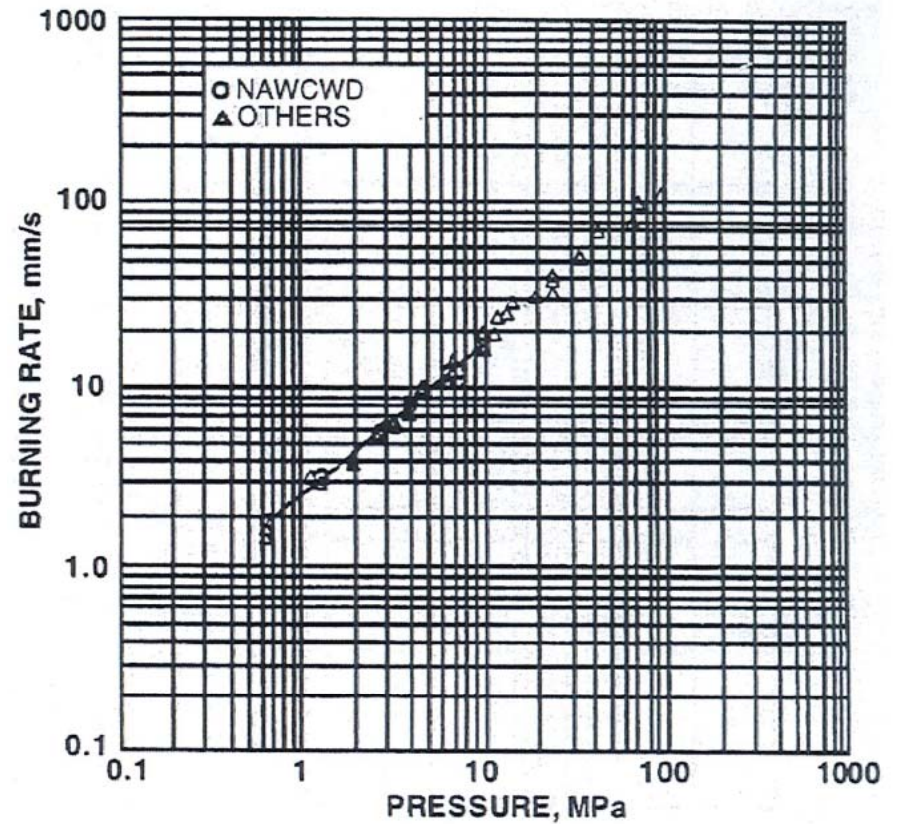
Correlation B:

$$r_b(\text{cm/s}) = 5.822[p(\text{MPa})/48.26]^{0.97}$$

Burning Rate of Pressed Nitramine Ingredients at $T = T_{\text{amb}}$

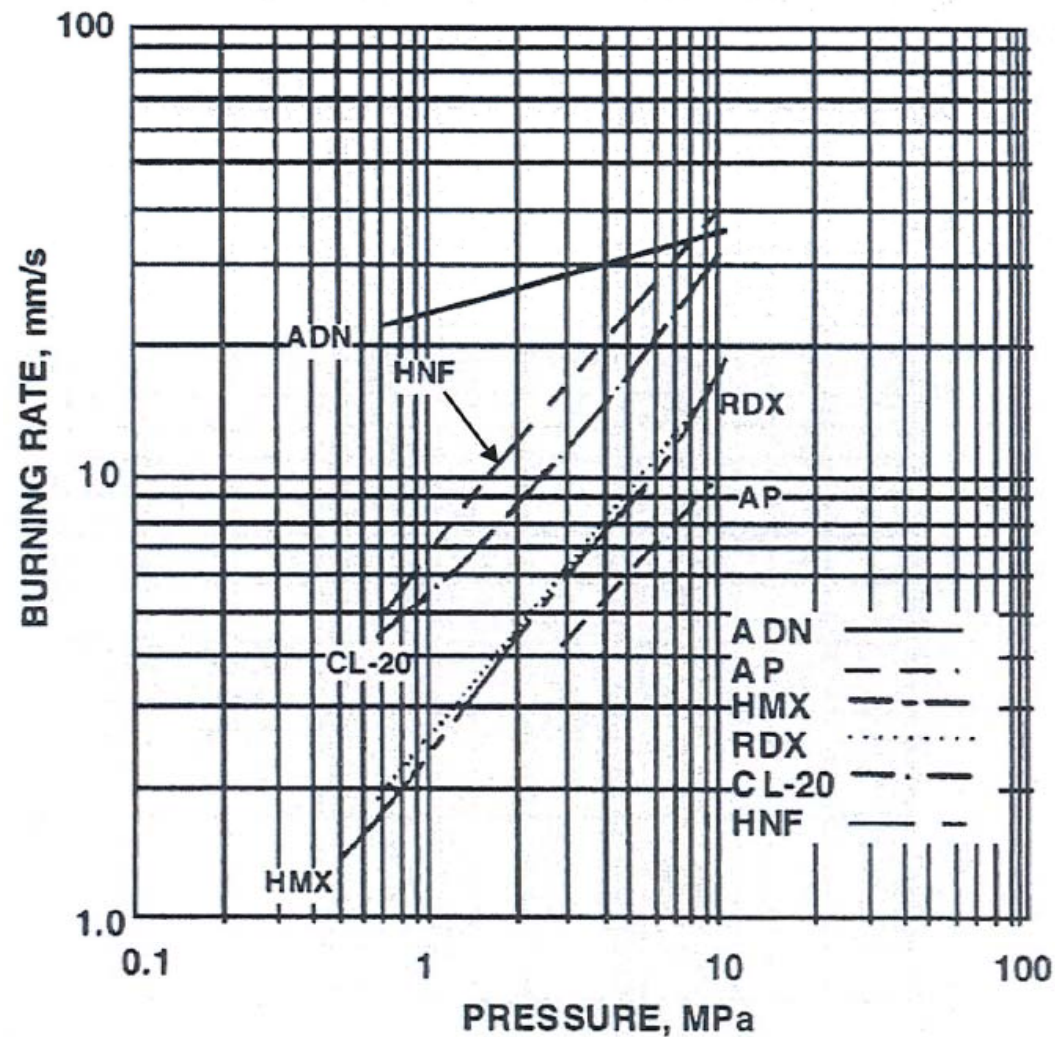


Burning rate data of HMX



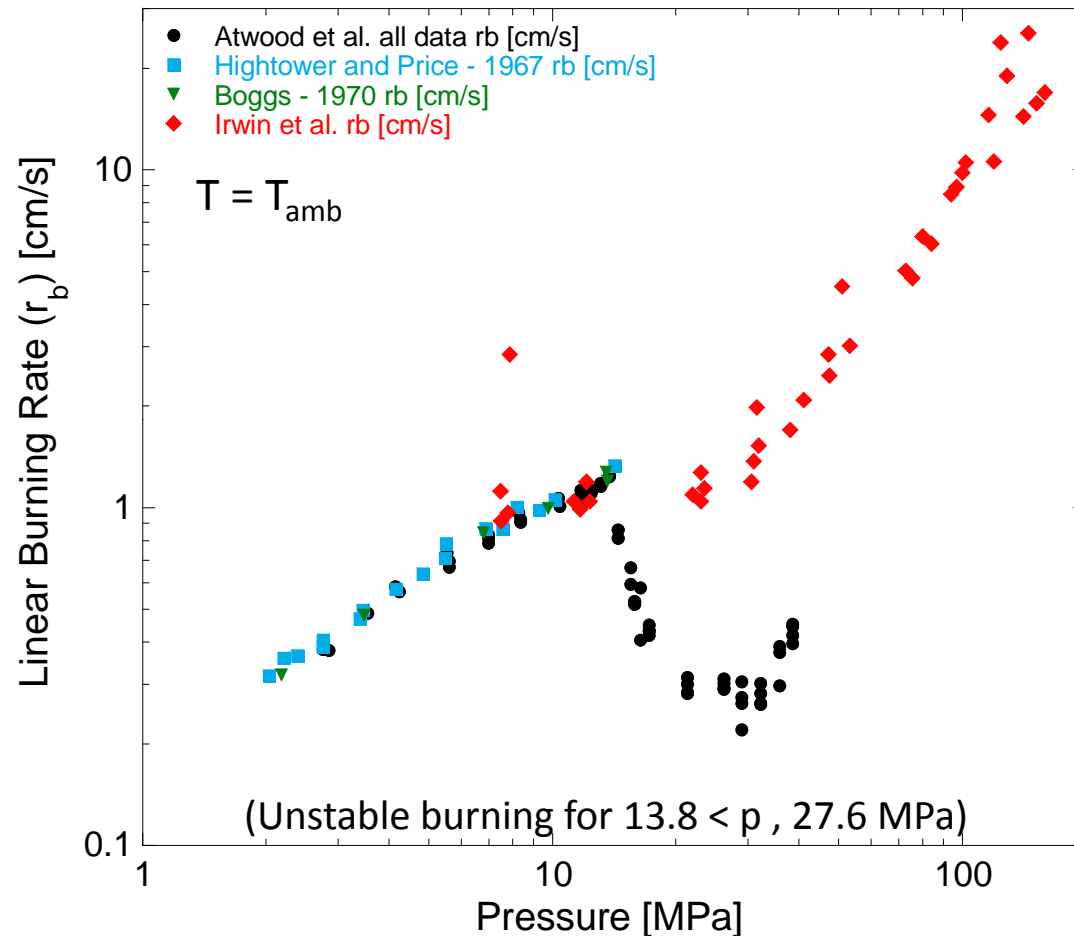
Burning rate data of RDX

Self-deflagration Rates of Six Monopropellants at $T = T_{\text{amb}}$



After Atwood et al., Journal of Propulsion and Power, 1999

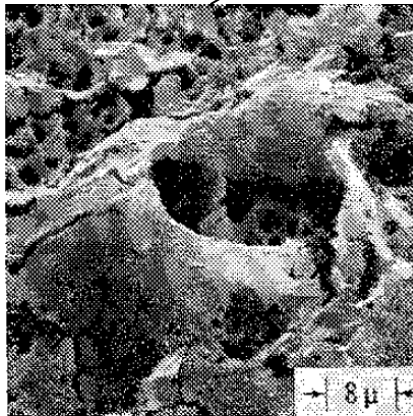
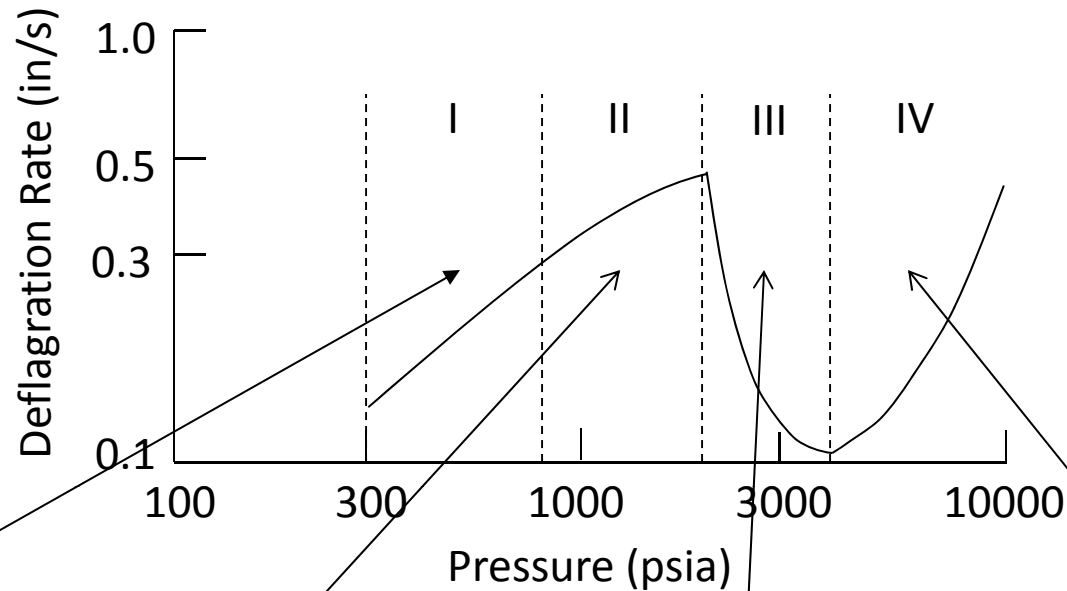
Phenomenological explanations of the AP burning rate as a function of pressure exist; however, can they be predicted?



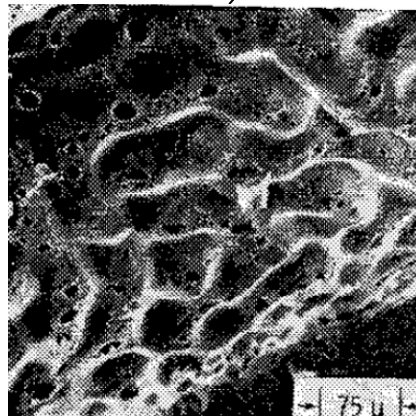
Atwood, A., Boggs, T. L., Curran, P. O., Parr, T. P., Hanson-Parr, D. M., Price, C. F., and J. Wiknich, *Journal of Propulsion and Power* 15 (1999) 740-747. References for the Hightower and Price, Boggs, and Irwin et al. data may be attained from Atwood et al.

Boggs, T.L., in *Fundamentals of Solid-Propellant Combustion*, K. K. Kuo, and M. Summerfield, Eds., New York, 1984, Vol. 90, p. 121.

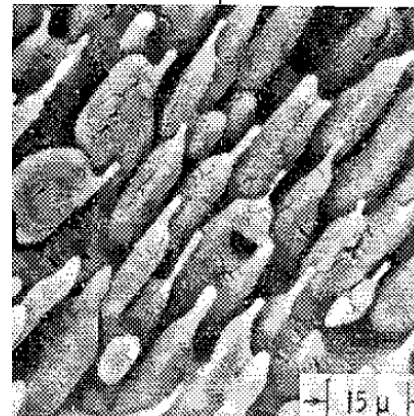
Surface Conditions of Deflagrating AP in N₂



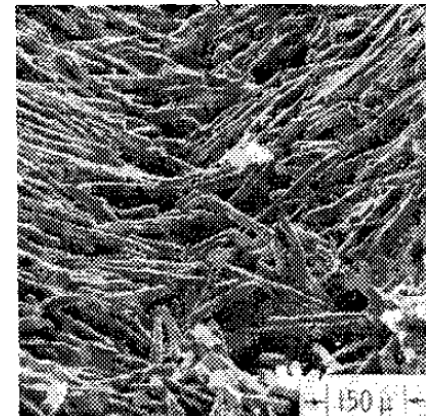
Steady planar
flame
Gas entrapped in
liquid resulting in
froth



Steady planar
Ridges and valleys
with activity sites
in valleys

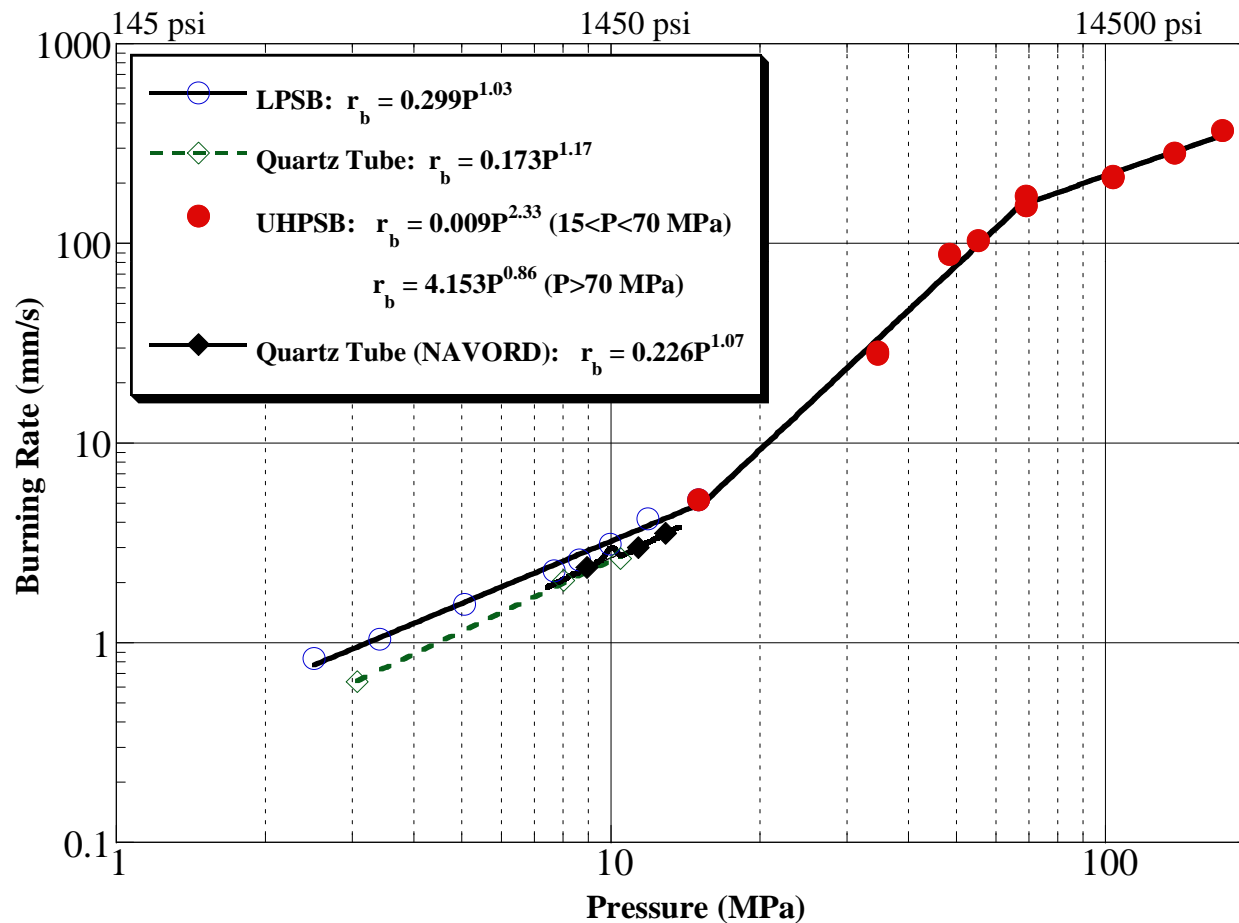


Intermittent, non-
planar
Needles in regions
of max. regression



Steady planar
Entirely covered
with needles

Current models predict the low pressure burning rates of liquid nitromethane (CH_3NO_2); can they predict it for $P > 10$ MPa



Condensed phase decomposition likely not important over the P range shown

High Pressure Burning Rate of Liquids

Deflagration speed (from Mallard and Le Chatelier)

$$S_L = \left[\alpha_u \frac{\dot{w}}{\rho} \left(\frac{T_f - T_i}{T_i - T_u} \right) \right]^{1/2}$$

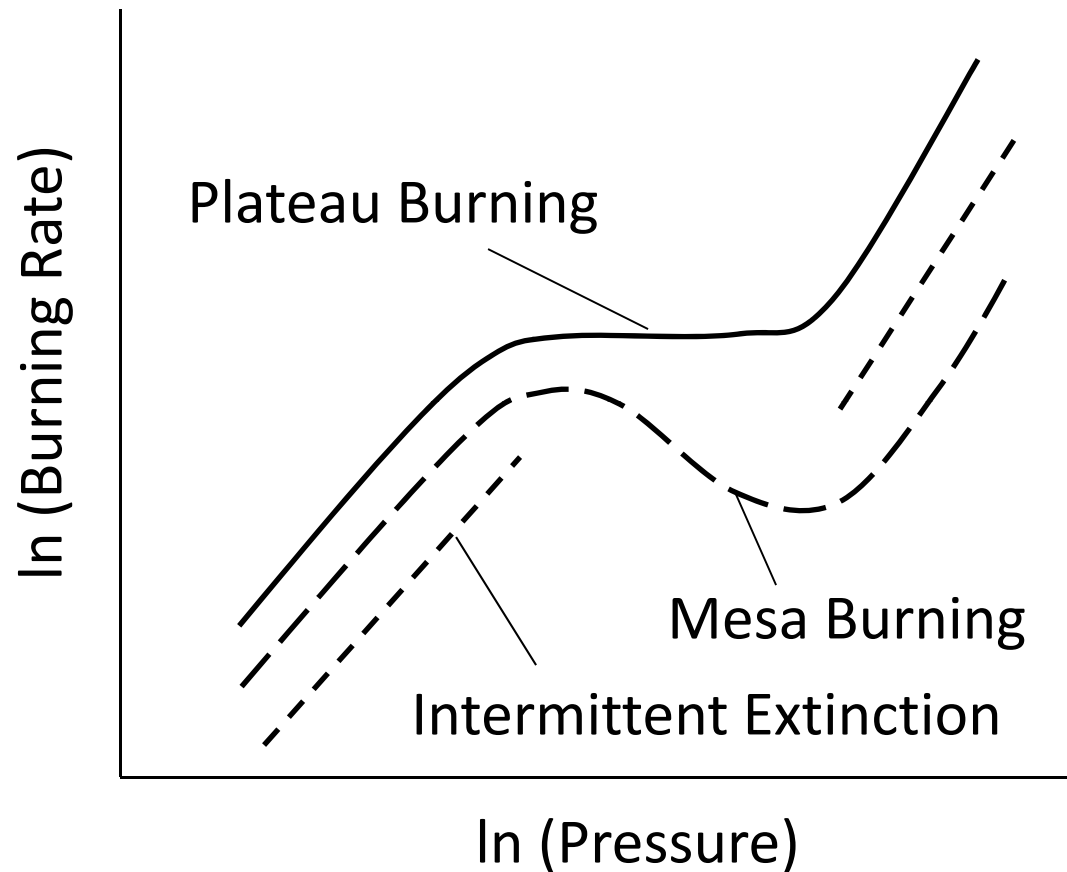
Propellant speed (from Kubota)

$$r_b = \left[\frac{k_g Q_g \dot{w}}{\rho_p^2 C_{pg} [C_c (T_S - T_u) - Q_s]} \right]^{1/2}$$

Dividing one by the other

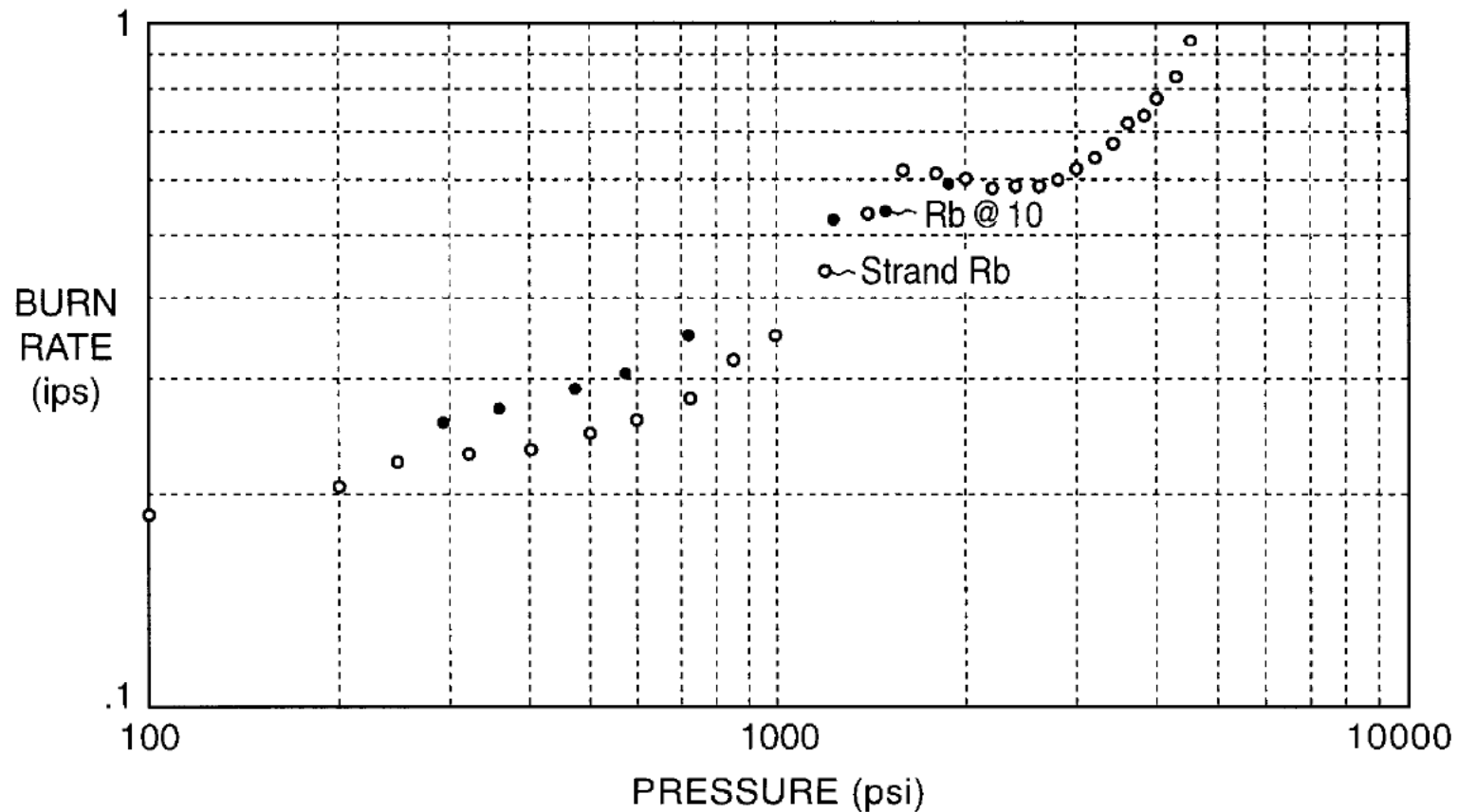
$$r_b = S_L \left[\frac{C_{pg}}{C_c} \left(\frac{\rho_g}{\rho_p} \right)^2 \left(\frac{1}{1 - \frac{Q_s}{C_c (T_S - T_u)}} \right) \left(\frac{T_i - T_u}{T_S - T_u} \right) \left(\frac{T_f - T_S}{T_f - T_i} \right) \right]^{1/2}$$

Three Types of Anomalous Burning



- In plateau burning, the burning rate levels off over a pressure range
- In mesa burning, the burning rate is inversely proportional to pressure over a specific range
- In intermittent extinction burning, the propellant is unable to sustain burning over a range of pressures

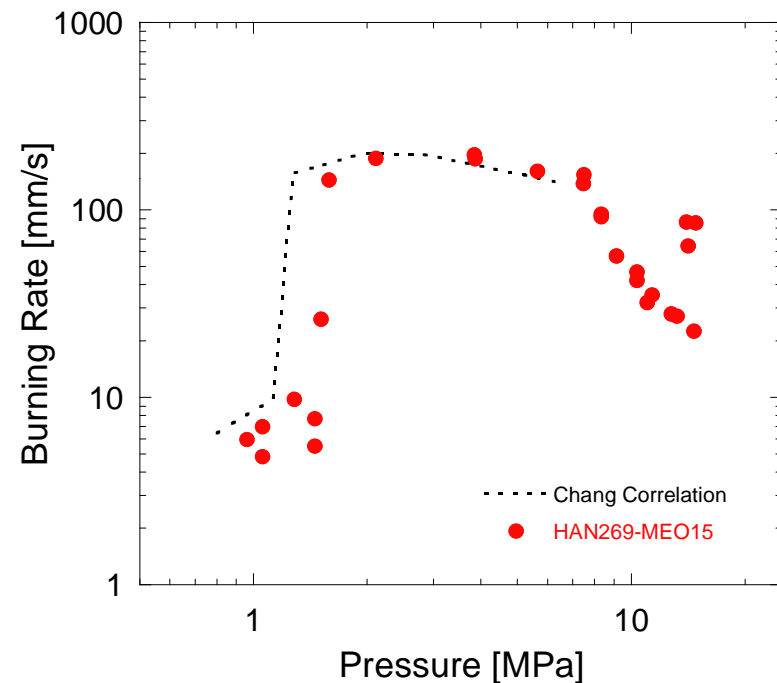
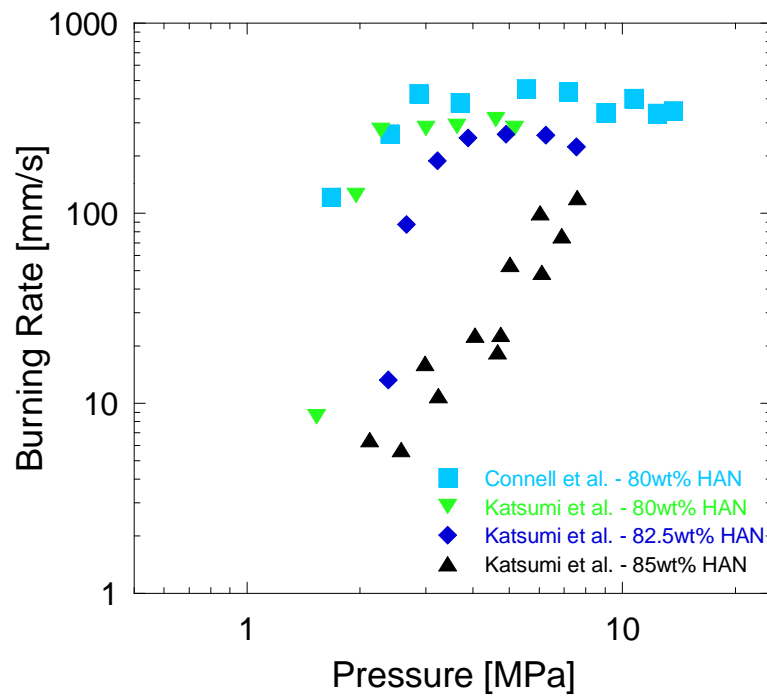
Aluminized AP-based Solid Composite Propellant



R.H Taylor and C.J. Hinshaw, US patent 5,771,679, June 30, 1998

Are HAN (NH_3OHNO_3) plateau burning behaviors controlled by the gas-phase, condensed phase, or the interface?

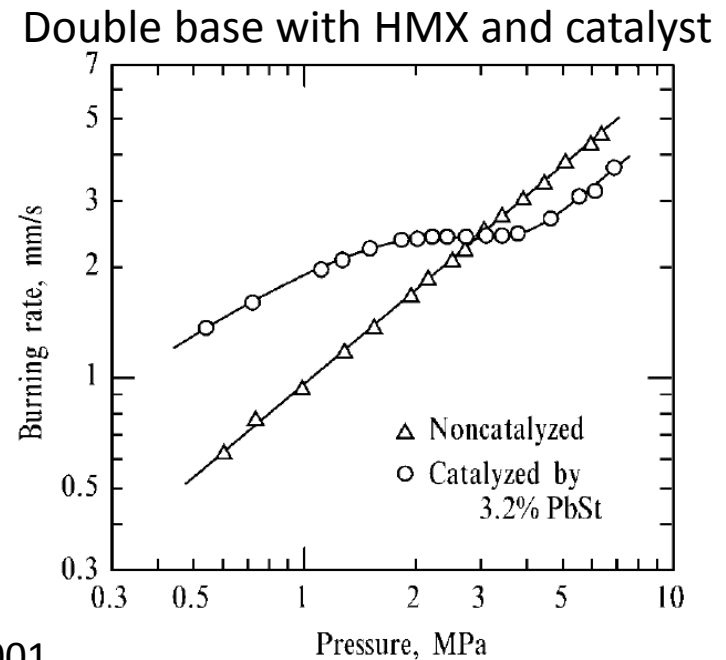
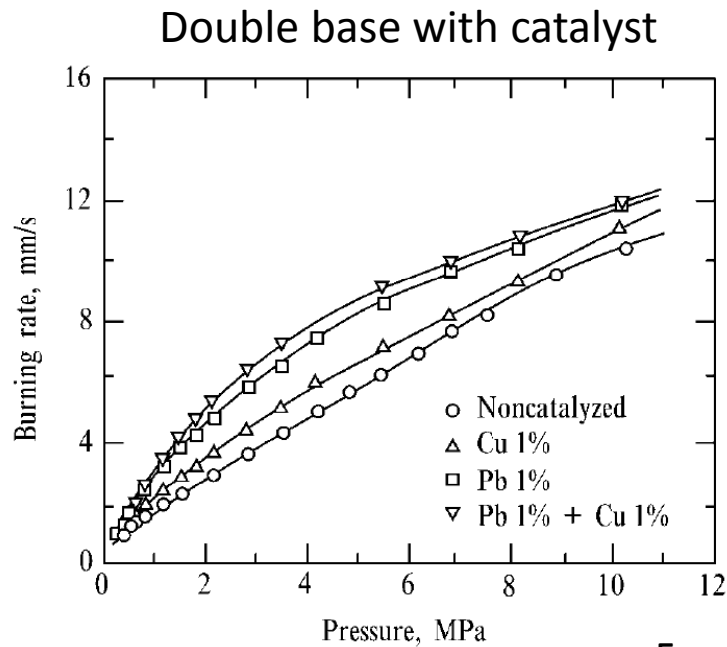
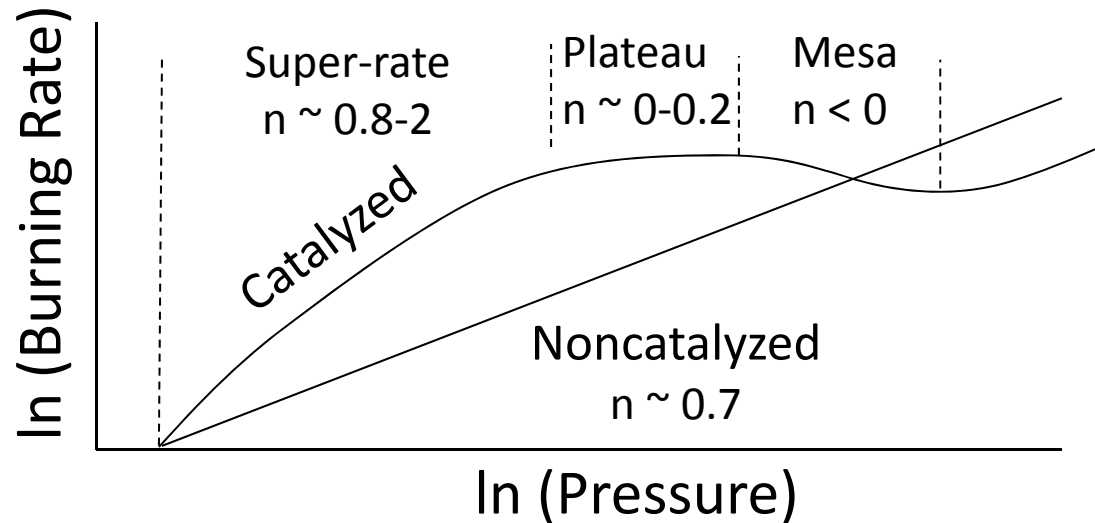
HAN/water burning rates at ambient temperature with various weight percentages of HAN (left); HAN/ $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ burning rate at ambient temperature (right)



Condensed phase decomposition known to occur over the P range shown

Katsumi, T., Hori, K., Matsuda, R., and Inoue, T., "Combustion Wave Structure of Hydroxylammonium Nitrate Aqueous Solutions," 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, AIAA Paper No. 2010-6900, Nashville, TN., 2010.
Chang, Y., "Combustion Behavior of HAN-Based Liquid Propellants," PhD. Dissertation, The Pennsylvania State University, 2002.

The effects of catalysts on burning rate



From Kubota, 2001

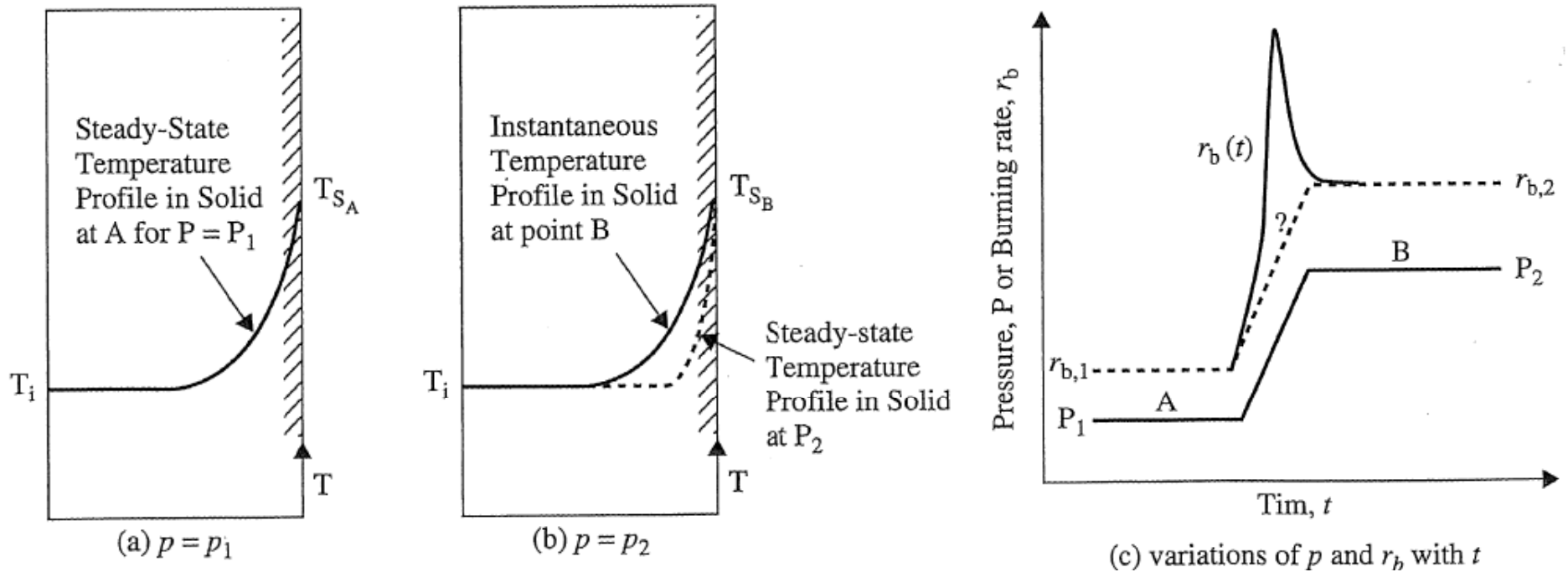
Transient Burning Characterization

- Ignition: involves transition from non-reactive to reactive state
- Flame spreading: deals with the rate of propagation of a flame front over solid propellant
- Transient (or dynamic) burning: addresses the problem that the instantaneous burning rate of solid propellant under rapid pressure change is different from those under corresponding steady state pressure
- Extinction: deals with extinction phenomena and establishes both static and dynamic extinction boundaries
- Combustion instability: deals with processes contributing to the stability of solid rocket motors in terms of gain or loss mechanisms associated with different modes of instability

What is dynamic burning?

- The dynamic (or transient) burning process often occurs under rapid pressure excursion
- It is caused by the finite relaxation times required for solid and/or gas phases to adjust their temperature profiles
- The instantaneous burning rate under transient conditions can differ significantly from the steady state burning rate corresponding to the instantaneous pressure
- The temperature profile (or thermal wave) thickness is a function of pressure
- The thermal wave thickness (and hence thermal energy content in the heated region of solid propellant) decreases when pressure is increased
- The main reason for dynamic burning is that during rapid p excursion the relatively thicker wave that existed at lower pressure does not have time to adjust to a thinner thermal wave at higher pressure
- Thus the propellant contains more thermal energy in the heated region than required for steady state burning at the new higher pressure
- The extra energy storage results in sudden increase in burning rate during the pressure ramp up period

Dynamic Burning



- The instantaneous burning rate cannot be determined by using the instantaneous pressure level in $r_b = ap^n$

Characteristic times associated with transient burning phenomenon

- τ_c : Characteristic time for nonreacting condensed phase with surface regression of r_b
- τ_s : Characteristic time for the surface reaction region
- τ_g : Characteristic time for the gaseous flame
- τ_p : Characteristic time for the pressure transient (related to the rate of pressurization or frequency of pressure oscillations)

$$\tau_c \equiv \frac{\alpha_c}{r_b^2}$$

$$\tau_s \equiv \left(\frac{R_u T_s}{E_{a,s}} \right) \tau_c = \varepsilon \tau_c$$

$$\tau_g \equiv \frac{\alpha_g}{U_g^2} = \left(\frac{k_g C_c \rho_g}{k_c C_g \rho_c} \right) \tau_c$$

$$\tau_p \equiv \frac{\Delta p}{dp/dt} \quad \text{or} \quad \tau_p \propto \frac{1}{f}$$

Steady-State Flame (Steady-state burning)	Quasi-steady Flame (Dynamic burning)	Unsteady flame (Dynamic burning)
$\tau_c \ll \tau_p$	$\tau_c \sim \tau_p$	$\tau_c \sim \tau_p$
$\tau_s \ll \tau_p$	$\tau_s < \tau_p$	$\tau_s \sim \tau_p$
$\tau_g \ll \tau_p$	$\tau_g \ll \tau_p$	$\tau_g \sim \tau_p$
Steady state in both gas and condensed phases	Quasi steady state in gas and transient in solid	Transient in both gas and solid phases

Pressure Deflagration Limit

- The low pressure deflagration limit (PDL) of a solid propellant is the limiting pressure below which the flame cannot sustain burning
- For AP crystals (and pressed AP pellets), this is near 20 bar
- For AP/HTPB composite propellants, many factors influence the limit, e.g., particle size, percent of binder, catalyst, void fraction, cross-sectional areas of samples, etc.
- Near the PDL, the flame can become unstable and oscillatory, produce local flame spots across the burning surface depending on the propellant type
- This unstable burning is different from the unstable burning for $n > 1$ for the rocket motor

Smoky, Reduced Smoke, and Minimum Smoke Propellants

- Smoky propellants produce particles during the combustion process, e.g., alumina from the addition of aluminum to the propellant
- Reduced smoke propellants produce particles during the expansion process, e.g., hydrochloric gas (HCl) and water condensation. Composite propellants without aluminum are referred to as reduced smoke propellants because there is no primary smoke in the exhausts, but secondary smoke formation is possible
- Minimum smoke propellants (or smokeless propellants) are generally CMDB because there are very few condensed phase species in the nozzle exhausts and no secondary condensation

Basic Scientific Issues (Things we would like to know more thoroughly)

1. Controlling factors that determine the value of the pressure exponent n , in $r_b = ap^n$
2. Reaction channels affected by catalysts
3. Reaction channels triggered by combustion instability
4. Contributing factors to plateau burning effects (often by ionic compounds)
5. Decomposition chemical kinetics in condensed phase
6. Surface phenomena of metallic additives and oxide growth and size distribution