Pyrotechnic Modelling for the NSI Driven Pin Puller

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Review

Sources for guidance in model development:

- Pin-Puller tests: Bement, Schimmel, et al.
- Pyrotechnics chemistry: McLain, Conklin
- NSI ignition study: Varghese
- Multiphase combustion: Baer, Nunziato, Krier, Powers, etc.
- Automobile airbags: Butler
- Solid propellants: Williams, Kuo, Strehlow, etc.
- Solid state combustion synthesis: Varma
Engineering Problems

- Occurrence of operational failures.
- Qualification only after many tests.
- Difficult to predict behavior of new formulations.
- Difficult to quantify effects of modifications:
  - diffusive heat transfer,
  - molecular heat transfer,
  - pin puller geometry,
  - friction,
  - apparently random sample behavior.
Modeling Approaches

• Full Scale Models:
  
  – time-dependent,
  
  – three-dimensional spatial gradients,
  
  – multiple species, multiple reactions,
  
  – fully resolved chemical kinetics,
  
  – compressibility,
  
  – turbulence,
  
  – real gas effects,
  
  – boundary layers,
  
  – essentially no detailed kinetic data available,
  
  – more complex than justified by data.
Modeling Approaches, cont’d.

• Empirical Models:
  – experimentally-based correlations,
  – reliable in limited ranges,
  – somewhat inflexible.

• Simple Models - present approach:
  – analytically tractable,
  – judgement required,
  – simplicity at expense of loss of rigor,
  – introduction of ad hoc assumptions.

• Stochastic Models:
  – estimates for uncertainty required,
  – could be coupled with simple model.
Assumptions for the Preliminary Model

- Model total system as 3 subsystems:
  - solid pyrotechnic reactants \((s)\)
  - gas phase products \((g)\)
  - condensed phase products \((cp)\)

- Well stirred reactor:
  - spatial homogeneity
  - time-dependent variables
  - no mass, momentum, or energy diffusion
Assumptions cont’d.

Mass and Energy Exchange

- No mass exchange between total system and surroundings,
- Heat and work exchange between system and surroundings,
- Mass exchange from reactants to gas and condensed phase products,
- No work exchange between subsystems.
- Heat exchange between gas and condensed phase product subsystems.

Combustion Process

- Combustion products produced in ratios which minimize Gibbs free energy (CEC76 routine):
  - mass fractions frozen,
  - gas phase products described by single mixture specific heat and mixture gas constant,
  - condensed phase products characterized by a single mixture density,
- Global kinetic burn rate estimated from solid propellant data.
Assumptions cont’d.

Other assumptions

- Ideal gas with temperature dependent specific heat (CHEMKIN II data base and subroutines),
- Constant temperature vessel wall,
- No wall friction,
- Constant density solid pyrotechnic,
- Constant density condensed phase products,
- Kinetic energy of total system assumed negligible,
- Body forces assumed negligible.
Mass, Momentum, and Energy Principles

Mass Evolution Equations:

\[
\frac{d}{dt} [\rho_s V_s] = -\rho_s A_p r,
\]

\[
\frac{d}{dt} [\rho_{cp} V_{cp}] = \eta_{cp} \rho_s A_p r,
\]

\[
\frac{d}{dt} [\rho_g V_g] = [1 - \eta_{cp}] \rho_s A_p r.
\]

Energy Evolution Equations:

\[
\frac{d}{dt} [\rho_s V_s e_s] = -\rho_s A_p e_s r,
\]

\[
\frac{d}{dt} [\rho_{cp} V_{cp} e_{cp}] = \eta_{cp} \rho_s A_p e_s r - \dot{Q}_{cp,g},
\]

\[
\frac{d}{dt} [\rho_g V_g e_g] = [1 - \eta_{cp}] \rho_s A_p e_s r + \dot{Q}_{cp,g} + \dot{Q}_{in} - \dot{W}_{out}.
\]

Newton’s Second Law:

\[
m_p \frac{d^2 z_p}{dt^2} = F_p.
\]
Geometrical and Constitutive Relations

A. Geometry

*Total volume:*

\[ V = V_s + V_{cp} + V_g. \]

*Piston position:*

\[ z_p = \frac{V}{A_p}. \]
Geometrical and Constitutive Relations, cont’d.

B. Combustion Model

Reaction occurs in a single step:

\[
\sum_{i=1}^{N_s} \nu_{s_i} X_{s_i} \rightarrow \sum_{i=1}^{N_{cp}} \nu_{cp_i} X_{cp_i} + \sum_{i=1}^{N_g} \nu_{g_i} X_{g_i},
\]

- \(X_{s_i}, X_{cp_i}, X_{g_i}\): chemical species,
- \(\nu_{s_i}, \nu_{cp_i}, \nu_{g_i}\): stoichiometric coefficients,
- \(\nu_{s_i}, X_{s_i}\): specified as inputs to the CEC76 code,
- \(Y’s, \eta_{cp}\) can be determined from knowledge of \(\nu’s\).

Linear pyrotechnic burn rate:

\[
r = r(P_g, T_g) = a(T_g) + b(T_g)P_g^n,
\]

- \(a(T_g), b(T_g), n\): empirically determined.
Geometrical and Constitutive Relations, cont’d.

C. Thermal Equation of State

\[ P_g = \rho_g R T_g, \]

where

\[ R = \mathbb{R} \sum_{i=1}^{N_g} \frac{Y_{g_i}}{M_{g_i}}, \quad Y_{g_i} = \frac{\nu_{g_i} M_{g_i}}{\sum_{j=1}^{N_g} \nu_{g_j} M_{g_j}}. \]

D. Caloric Equations of State

\[ e_s(T_s) = \sum_{i=1}^{N_s} Y_{s_i} e_{s_i}(T_s), \]
\[ e_{cp}(T_{cp}) = \sum_{i=1}^{N_{cp}} Y_{cp_i} e_{cp_i}(T_{cp}), \]
\[ e_g(T_g) = \sum_{i=1}^{N_g} Y_{g_i} e_{g_i}(T_g). \]

• Calculated using CHEMKIN II subroutines and data base.
Geometrical and Constitutive Relations, cont’d.

D. Model for $\dot{Q}_{in}$:

$$\dot{Q}_{in} = h A_w [T_w - T_g] + \sigma A_w [\alpha T_w^4 - \epsilon T_g^4],$$

- Parameters:
  - $h$, convective heat transfer coefficient,
  - $\epsilon$, emissivity of the gas,
  - $\alpha$, absorptivity of the vessel’s walls,
  - $T_w$, temperature of the vessel’s walls,
  - $\sigma$, Stefan-Boltzmann constant.

E. Model for $\dot{W}_{out}$:

$$\dot{W}_{out} = P_g \frac{dV}{dt}.$$

- Only allow for pressure volume work.

F. Model for $F_p$:

$$F_p = \begin{cases} 0 & \text{if } P_g A_p < F_{crit} \\ P_g A_p & \text{if } P_g A_p \geq F_{crit} \end{cases},$$

- $F_{crit}$, constant critical force necessary for shear pin failure.
Geometrical and Contitutive Relations, cont’d.

G. Model for $\dot{Q}_{cp,g}$:

$$\dot{Q}_{cp,g} = h_{cp,g} [T_{cp} - T_g].$$

- $h_{cp,g}$, heat transfer parameter.
Mathematical Reductions

Goal:

- To perform intermediate operations leading to a refined final model:
  - six O.D.E.’s for $V$, $V_s$, $V_{cp}$, $T_{cp}$, $T_g$, and $\dot{V}$
  - all other variables expressed as a function of these six variables.

- Final model suitable for numerical integration.

Step I. Determination of $\rho_g$.

- Add together *mass evolution equations*:

$$\frac{d}{dt} \left[ \rho_s V_s + \rho_{cp} V_{cp} + \rho_g V_g \right] = 0.$$ 

- Integrate, apply initial conditions, and solve for $\rho_g$:

$$\rho_g(V, V_s, V_{cp}) = \frac{\rho_s V_{so} + \rho_{cp} V_{cpo} + \rho_g V_{go} - \rho_s V_s - \rho_{cp} V_{cp}}{V - V_s - V_{cp}}.$$
Mathematical Reductions, cont’d.

Step II. Expression for mixture energy evolution.

- Add together energy evolution equations:

$$\frac{d}{dt} \left[ \rho_s V_s e_s + \rho_{cp} V_{cp} e_{cp} + \rho_g V_g e_g \right] = \dot{Q}_{in} - \dot{W}_{out}.$$  

- Note: this expression is not explicitly used in the analysis.

- For special case $\dot{Q}_{in} = \dot{W}_{out} = 0$, can integrate:

$$\rho_s V_s e_s + \rho_{cp} V_{cp} e_{cp} + \rho_g V_g e_g = \rho_s V_{so} e_{so} + \rho_{cp} V_{cpo} e_{cpo} + \rho_g V_{go} e_{go}.$$  

- Can use algebraic relation to evaluate code performance.

Step III. Determination of $P_g$.

- Use $\rho_g$ from Step I and thermal equation of state to obtain:

$$P_g(V, V_s, V_{cp}, T_g) = \rho_g(V, V_s, V_{cp})RT_g.$$
Mathematical Reductions, cont’d.

Step IV. Determination of $r$ and $F_p$.

- Using $P_g$ from Step III, can obtain:

$$ r = r(V, V_s, V_{cp}, T_g) = a(T_g) + b(T_g)P^n_g(V, V_s, V_{cp}, T_g), $$

$$ F_p = F_p(V, V_s, V_{cp}, T_g). $$

Step V. Simplify remaining differential mass equations.

- Since $\rho_s$ and $\rho_{cp}$ are constants:

$$ \frac{dV_s}{dt} = -A_p r(V, V_s, V_{cp}, T_g), \quad (1) $$

$$ \frac{dV_{cp}}{dt} = \eta_{cp} \left[ \frac{\rho_s}{\rho_{cp}} \right] A_p r(V, V_s, V_{cp}, T_g). \quad (2) $$
Mathematical Reduction, cont’d.

Step VI. Simplification of energy equations.

• Consider energy evolution equation for solid pyrotechnic:

\[
\frac{d}{dt} [\rho_s V_s e_s] = -\rho_s A_p e_s r,
\]

– subtract the following from this equation:

\[
\left[ \frac{d}{dt} [\rho_s V_s] = -\rho_s A_p r \right] e_s,
\]

– obtain:

\[
\frac{de_s}{dt} = 0, \quad \implies e_s = e_{so}.
\]

• Consider energy evolution equation for condensed phase products:

\[
\frac{d}{dt} [\rho_{cp} V_{cp} e_{cp}] = \eta_{cp} \rho_s A_p e_s r - \dot{Q}_{cp,g},
\]

– subtract the following:

\[
\left[ \frac{d}{dt} [\rho_{cp} V_{cp}] = \eta_{cp} \rho_s A_p r \right] e_{cp},
\]

– obtain:

\[
\rho_{cp} V_{cp} \frac{de_{cp}}{dt} = \eta_{cp} \rho_s A_p r (V, V_s, V_{cp}, T_g) [e_{so} - e_{cp}(T_{cp})] - \dot{Q}_{cp,g}(T_{cp}, T_g),
\]
Mathematical Reductions, cont’d.

– using caloric equation of state $e_{cp}(T_{cp})$:

\[
\frac{dT_{cp}}{dt} = \frac{\eta_{cp}\rho_s A_p r(V, V_s, V_{cp}, T_g)[e_{so} - e_{cp}] - \dot{Q}_{cp,g}(T_{cp}, T_g)}{\rho_{cp} c_{cp}(T_{cp})V_{cp}}. \tag{3}
\]

• Consider energy evolution equation for gas phase products:

\[
\frac{d}{dt} [\rho_g V_g e_g] = [1 - \eta_{cp}]\rho_s A_p e_s r + \dot{Q}_{cp,g} + \dot{Q}_{in} - \dot{W}_{out},
\]

– subtract the following:

\[
\left[ \frac{d}{dt} [\rho_g V_g] = [1 - \eta_{cp}]\rho_s A_p e_s r \right] e_g,
\]

– obtain:

\[
\rho_g V_g \frac{d e_g}{dt} = [1 - \eta_{cp}]\rho_s A_p r[e_{so} - e_g] + \dot{Q}_{in} - \dot{W}_{out},
\]

– using caloric equation of state $e_g(T_g)$:

\[
\frac{dT_g}{dt} = \frac{[1 - \eta_{cp}]\rho_s A_p r(V, V_s, V_{cp}, T_g)[e_{so} - e_g(T_g)] + \dot{Q}_{cp,g}(T_{cp}, T_g)}{\rho_g(V, V_s, V_{cp})c_{vg}(T_g)[V - V_s - V_{cp}]} + \frac{\dot{Q}_{in}(T_g) - P_g(V, V_s, V_{cp}, T_g)\dot{V}}{\rho_g(V, V_s, V_{cp})c_{vg}(T_g)[V - V_s - V_{cp}]}, \tag{4}
\]
Mathematical Reductions, cont’d.

Step VII. Newton’s second law governing piston motion.

- Split 2\textsuperscript{nd} order O.D.E. into two 1\textsuperscript{st} order O.D.E.’s:

\[
\frac{dV}{dt} = \dot{V}, \tag{5}
\]

\[
\frac{d\dot{V}}{dt} = \frac{F_p(V, V_s, V_{cp}, T_g) A_p}{m_p}. \tag{6}
\]
Final Form of Preliminary Model

Governing O.D.E.’s:

\[
\frac{dV}{dt} = \dot{V},
\]

\[
\frac{dV_s}{dt} = -A_p r(V, V_s, V_{cp}, T_g),
\]

\[
\frac{dV_{cp}}{dt} = \eta_{cp} \left( \frac{\rho_s}{\rho_{cp}} \right) A_p r(V, V_s, V_{cp}, T_g),
\]

\[
\frac{dT_{cp}}{dt} = \frac{\eta_{cp} \rho_s A_p r(V, V_s, V_{cp}, T_g) [e_{so} - e_{cp}] - \dot{Q}_{cp,g}(T_{cp}, T_g)}{\rho_{cp} c_{cp}(T_{cp}) V_{cp}},
\]

\[
\frac{dT_g}{dt} = \frac{[1 - \eta_{cp}] \rho_s A_p r(V, V_s, V_{cp}, T_g) [e_{so} - e_g(T_g)] + \dot{Q}_{cp,g}(T_{cp}, T_g)}{\rho_g(V, V_s, V_{cp}) c_{vg}(T_g)[V - V_s - V_{cp}]}
+ \frac{\dot{Q}_{in}(T_g) - P_g(V, V_s, V_{cp}, T_g) \dot{V}}{\rho_g(V, V_s, V_{cp}) c_{vg}(T_g)[V - V_s - V_{cp}]},
\]

\[
\frac{d\dot{V}}{dt} = \frac{F_p(V, V_s, V_{cp}, T_g) A_p}{m_p},
\]

Initial Conditions:

\[
V(t = 0) = V_o, \quad V_s(t = 0) = V_{so}, \quad V_{cp}(t = 0) = V_{cpo},
\]

\[
T_{cp}(t = 0) = T_{cpo}, \quad T_g(t = 0) = T_{go}, \quad \dot{V}(t = 0) = 0.
\]
Initial Results

The following results are presented:

- pressure-time predictions for a 10 cm$^3$ closed bomb combustion of 114 mg of Zr/KClO$_4$,
- pressure-time predictions and piston energy calculations for typical operation of NSI driven pin puller.

**Balanced Stoichiometric Equation:**

\[
3.6162\text{Zr}(s) + 2.6849\text{KClO}_4(s) \rightarrow 3.2354\text{Zr}(l) + 1.9712\text{O}(g) \\
+1.6988\text{KCl}(g) + 0.9766\text{Cl}(g) \\
+0.9041\text{K}(g) + 0.7454\text{O}_2(g) \\
+0.3407\text{ZrO}_2(g) + 0.0790\text{KO}(g) \\
+0.0401\text{ZrO}(g) + 0.0065\text{ClO}(g) \\
+0.0009\text{K}_2\text{ClO}_2(g) + 0.0006\text{Cl}_2(g) \\
+0.0006\text{K}_2(g).
\]

**NSI Pyrotechnic Composition:**

- 114 mg of a Zr/KClO$_4$ mixture:
  - 53.6 mg of Zr(s),
  - 60.4 mg of KClO$_4$. 
Closed Bomb Combustion (10 cm³)

- NASA specifications: firing an NSI containing 114 mg of Zr/KClO₄ mixture into a 10 cm³ volume shall produce a peak pressure of 650±125 psi within 5 ms.

- Initial Conditions:

<table>
<thead>
<tr>
<th>initial condition</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₀</td>
<td>10.0 cm³</td>
</tr>
<tr>
<td>V₀₀</td>
<td>0.038 cm³</td>
</tr>
<tr>
<td>Vₙ₀</td>
<td>5.10×10⁻⁷ cm³</td>
</tr>
<tr>
<td>Tₙ₀</td>
<td>288.0 K</td>
</tr>
<tr>
<td>T₀₀</td>
<td>288.0 K</td>
</tr>
<tr>
<td>V</td>
<td>0.0 cm³/s</td>
</tr>
</tbody>
</table>

- Parameters:

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>burn area, A_p</td>
<td>2.0 cm²</td>
</tr>
<tr>
<td>pyrotechnic density, ρₚ</td>
<td>3.0 g/cm³</td>
</tr>
<tr>
<td>temperature of pyrotechnic, Tₚ</td>
<td>288.0 K</td>
</tr>
<tr>
<td>condensed phase density, ρₙ₀</td>
<td>1.51 gm/cm³</td>
</tr>
<tr>
<td>convective heat transfer coefficient, h</td>
<td>1.25×10⁵ g/sec³/K</td>
</tr>
<tr>
<td>emissivity of the gas, ε</td>
<td>0.80</td>
</tr>
<tr>
<td>absorptivity of the vessel’s walls, α</td>
<td>0.80</td>
</tr>
<tr>
<td>heat transfer parameter, hₙ₀ₐ</td>
<td>12.0×10⁹ gcm²/sec³/K</td>
</tr>
</tbody>
</table>

- Pyrotechnic Burn Rate:

\[ r = 0.004P_g^{0.69} \]
Closed Bomb Combustion, cont’d.
NSI Driven Pinpuller Results

• Initial Conditions:

<table>
<thead>
<tr>
<th>initial condition</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0$</td>
<td>0.824 cm$^3$</td>
</tr>
<tr>
<td>$V_{so}$</td>
<td>0.038 cm$^3$</td>
</tr>
<tr>
<td>$V_{cpo}$</td>
<td>$3.40 \times 10^{-6}$ cm$^3$</td>
</tr>
<tr>
<td>$T_{cpo}$</td>
<td>288.0 K</td>
</tr>
<tr>
<td>$T_{go}$</td>
<td>288.0 K</td>
</tr>
<tr>
<td>$V$</td>
<td>0.0 cm$^3$/s</td>
</tr>
</tbody>
</table>

• Parameters:

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>burn area, $A_p$</td>
<td>0.634 cm$^2$</td>
</tr>
<tr>
<td>pyrotechnic density, $\rho_s$</td>
<td>3.0 g/cm$^3$</td>
</tr>
<tr>
<td>pyrotechnic temperature, $T_s$</td>
<td>288.0 K</td>
</tr>
<tr>
<td>condensed phase density, $\rho_{cp}$</td>
<td>1.51 gm/cm$^3$</td>
</tr>
<tr>
<td>convective heat transfer coefficient, $h$</td>
<td>$1.25 \times 10^5$ g/sec$^3$/K</td>
</tr>
<tr>
<td>emissivity of the gas, $\epsilon$</td>
<td>0.60</td>
</tr>
<tr>
<td>absorptivity of the vessel’s walls, $\alpha$</td>
<td>0.60</td>
</tr>
<tr>
<td>heat transfer parameter, $h_{cp,g}$</td>
<td>$12.0 \times 10^9$ gm$^2$/sec$^3$/K</td>
</tr>
<tr>
<td>critical shearing force, $F_{crit}$</td>
<td>$3.56 \times 10^7$ dynes (80 lb)</td>
</tr>
</tbody>
</table>

• Pyrotechnic Burn Rate:

$$r = 0.004 P_g^{0.69}.$$
NSI Driven Pinpuller Results, cont’d.

- Pressure – time prediction:
Outline of Future Directions

• Study solution near equilibrium states,

• examine simplest possible case – constant volume, no heat transfer, constant specific heats,

• better justify heat transfer coefficients,

• study wall surface effects on heat transfer,

• continue search for accurate burn rate data,

• perform sensitivity analysis,

• include grain size effects,

• study spatially resolved field,

• include more detailed chemistry.