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Technical Comments

Comment on "Intrinsic Combustion Instability of Solid Energetic Materials"

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Nomenclature

A = $(T_s - T_0)(\partial\ \ell n\ r_b/\partial T_s)_{p,q}(=k/r)$
A_c = pre-exponential factor
B = $1/[(T_s - T_0)(\partial\ \ell n\ r_b/\partial T_0)_{p,q}](=1/k)$
C = specific heat of condensed phase
E_c = effective activation energy of condensed-phase decomposition
E_s = $E_c/2$
f = frequency, Hz
f_r = fraction of q absorbed below surface reaction zone
J = dimensionless mean radiant heat flux, $q/[mC(T_s - T_0)]$
K_a = absorption coefficient of condensed phase
k = $(T_s - T_0)(\partial\ \ell n\ r_b/\partial T_0)_{p,q}$
m, m' = mass burning rate, $\rho_c r_b$, $\Delta m e^{i(2\pi f t + \phi)}$
n = $(\partial\ \ell n\ r_b/\partial\ \ell n\ p)_{T_0,q}$ (same as ν)
n_q = $(\partial\ \ell n\ r_b/\partial\ \ell n\ q)_{T_s,p}$ $(=\delta_q/r)$
n_s = $(\partial\ \ell n\ r_b/\partial\ \ell n\ p)_{T_s,q}$ $(=\delta/r)$
p, p' = pressure, $\Delta p e^{i2\pi f t}$
Q_c = condensed-phase heat release (positive exothermic)
$\tilde{Q}_c$ = $Q_c/[C(T_s - T_0)]$
$\tilde{Q}_r$ = $f_r J$
q, q' = absorbed radiant heat flux in condensed phase, $\Delta q e^{i2\pi f t}$
R = universal gas constant
R_p = pressure-driven frequency response function, $(m'/\bar{m})/(p'/\bar{p})$ at constant q
R_q = radiation-driven frequency response function, $(m'/\bar{m})/(q'/\bar{q})$ at constant p
r = $(\partial T_s/\partial T_0)_{p,q}$
r_b = burning rate
T_0, T_s = initial temperature, surface temperature
α_c = condensed phase thermal diffusivity
β = optical thickness (absorption only) of conduction zone $(K_a\alpha_c/r_b)$
Δ = amplitude of fluctuating quantity
δ, δ_q = Jacobian parameters, $\nu r - \mu k$, $\nu_q r - \mu_q k$
λ = $\frac{1}{2} + (\frac{1}{2})(1 + 4i\Omega)^{1/2}$
μ = $[1/(T_s - T_0)](\partial T_s/\partial\ \ell n\ p)_{T_0,q}$
μ_q = $[1/(T_s - T_0)](\partial T_s/\partial\ \ell n\ q)_{T_0,p}$
ν = $(\partial\ \ell n\ r_b/\partial\ \ell n\ p)_{T_0,q}$ (same as n)
ν_q = $(\partial\ \ell n\ r_b/\partial\ \ell n\ q)_{T_0,p}$
ρ_c = condensed-phase density
ϕ = phase angle of R_p or R_q
Ω = dimensionless frequency, $2\pi f\alpha_c/r_b^2$

A RECENT paper by De Luca et al.[1] presents a review of the classical problem of intrinsic stability and linear frequency response of both pressure- and radiation-driven burning of solid propellants within the Zeldovich–Novozhilov (ZN) or QSHOD framework [quasisteady gas phase and condensed phase (surface) reaction; homogeneous propellant; one-dimensional heat feedback]. The purpose of this paper is to clarify some important unstated limitations of the results reported in Ref. 1, to note a few subtle errors, and to cite references where less restrictive results have previously been given.

First, the ZN radiation–Jacobian parameter relationship appearing in Eq. (46) of Ref. 1, $n_s = \delta_q/r$, is incorrect; it should read $n_q = \delta_q/r$. This error appears to be more than just typographical since n_q is used as a synonym for ν_q in the same Eq. (46), $n_q = \nu_q$. This usage reflects confusion about the basic definitions of the ZN Jacobian parameters, n_s and n_q. The n_s and n_q parameters can be given general partial derivative definitions, in a similar manner as the other ZN parameters[2–4]:

$$n_s \equiv \left(\frac{\partial\ \ell n\ r_b}{\partial\ \ell n\ p}\right)_{T_s,q} = \frac{\delta}{r}, \qquad n_q \equiv \left(\frac{\partial\ \ell n\ r_b}{\partial\ \ell n\ q}\right)_{T_s,p} = \frac{\delta_q}{r} \tag{1}$$

However, unlike the standard ZN sensitivity parameters (ν, ν_q, k, μ, μ_q, and r) that involve derivatives of the natural dependent variables (r_b and T_s) with respect to the natural independent variables (T_0, p, and q), n_s and n_q are mixed in the sense that T_s is treated like an independent variable in being held constant in the derivative. Often, the literature (usually Western) that prefers the use of n_s over δ does not clearly identify this more fundamental definition or recognize the relation of n_s to the standard ZN parameters (almost no references to n_q exist). To avoid such confusion as appears in Ref. 1, we recommend that the formal definitions [Eq. (1)] be adopted and that n_q not be used as a synonym for ν_q.

Second, the radiation-driven frequency response function, Eq. (42) of Ref. 1, is not general in the same sense that the companion pressure response expression Eq. (32) of Ref. 1 is, i.e., for nonzero Jacobian parameter. Rather, Eq. (42) is limited to the case of zero Jacobian parameter ($\delta_q = 0$). A more general (nonzero Jacobian) response function expression within the QSHOD framework has been reported previously[2,5]:

$$R_q = \frac{\nu_q + \delta_q(\lambda - 1) - \dfrac{k\tilde{Q}_r(\lambda - 1)}{\beta + \lambda - 1}}{\lambda r + \dfrac{k}{\lambda} - (r + k) + 1 - \dfrac{k\tilde{Q}_r(\lambda - 1)}{\lambda(\beta + \lambda - 1)}}$$

$$= \frac{\nu_q AB + n_q(\lambda - 1) - \dfrac{A\tilde{Q}_r(\lambda - 1)}{\beta + \lambda - 1}}{\lambda + \dfrac{A}{\lambda} - (1 + A) + AB - \dfrac{A\tilde{Q}_r(\lambda - 1)}{\lambda(\beta + \lambda - 1)}} \tag{2}$$

The term involving δ_q (or n_q) in Eq. (2) is missing in Eq. (42)

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of Ref. 1. [The validity of Eq. (2) has been verified by numerical solution of the unsteady differential equations for species and energy for the case of single-step, zero-order, condensed-phase controlled burning.[3,6]]

Third, the condensed-phase pyrolysis relations assumed [Eqs. (6) and (7) of Ref. 1], need commenting on. Equation (6) of Ref. 1 is unnecessarily and perhaps inappropriately restrictive, as well as of questionable validity, for real materials under unsteady combustion, whereas Eq. (7) of Ref. 1 is not compatible with Eq. (32) of Ref. 1 for R_p or Eq. (42) of Ref. 1 for R_q.

Equation (6) of Ref. 1

$$r_b = A_s p^{n_s} \exp(-E_s/RT_s) \tag{3}$$

can be represented functionally as

$$r_b = r_b(T_s, p) \tag{4}$$

where neither q nor T_0 appear explicitly. Clearly, the radiation–Jacobian parameters δ_q and n_q are zero for this particular case and presumably this led to the zero-Jacobian condition in the expression for R_q found in Ref. 1. However, for a general pyrolysis condition, q or T_0 can appear explicitly in the pyrolysis relation in addition to T_s and p. That is,

$$r_b = r_b(T_s, p, q) \tag{5}$$

$$r_b = r_b(T_s, p, T_0) \tag{6}$$

or both q and T_0 can appear explicitly in place of p

$$r_b = r_b(T_s, q, T_0) \tag{7}$$

Transformation among these various forms [Eqs. (5–7)] is easily accomplished by use of the steady burning rate law

$$r_b = r_b(p, T_0, q) \tag{8}$$

and eliminating either p, T_0, or q. For these more general pyrolysis expressions [Eqs. (5–7)], the radiation–Jacobian parameters δ_q and n_q will not necessarily be zero. {It should be noted that even with pyrolysis relations [such as Eq. (9), zero-order decomposition[2,7]] where q appears explicitly, it is possible to have $\delta_q = 0$. This is true, for example, when there is an equivalent effect on burning rate and surface temperature by radiant flux and initial temperature. Conditions for the applicability of this case are discussed in Refs. 2, 4, and 7.} These relations also show that it is an error to think that T_0 is not a parameter in the problem just because it doesn't appear explicitly in a pyrolysis relation [e.g., Eq. (3)], or because it is set to some value and not varied; it is a parameter in that if its value is changed r_b and T_s change just as surely as if the values of p or q are changed.

Aside from the formulational issues discussed earlier and the question of zero vs nonzero Jacobian, the larger question with Eq. (6) of Ref. 1 is, how well does it represent real materials, even with $n_s \neq 0$ or $n_q \neq 0$ (assuming a q^{n_q} term was added in the same ad hoc manner that the p^{n_s} term appears)? That question can only be answered by comparison with observations. We have previously examined a rigorously derived pyrolysis relation based on high activation energy, single-step, zero-order decomposition[6]

$$r_b^2 = \frac{A_c \alpha_c \exp[(-E_c)/RT_s]}{(E_c/RT_s)[1 - (T_0/T_s)][1 - (\tilde{Q}_c/2) - \tilde{Q}_r]} \tag{9}$$

[which corresponds functionally with Eq. (7)], and found that it matches both steady-state burn rate data and unsteady response function data for homogeneous materials (when quasisteady conditions are satisfied) using realistic parameters, whereas the ad hoc relation (3) does not.[2,4,6] The failure of Eq. (3) can be seen in part by comparing the sensitivity parameter relation for Eq. (9) (see Ref. 2)

$$n_s = \frac{-\nu}{k(2 - \tilde{Q}_c - \tilde{Q}_r) - 1} \tag{10}$$

with that for Eq. (3):

$$n_s = \nu - \mu[1 - (T_0/T_s)](E_s/RT_s) \tag{11}$$

[The term $\ell n\, p(\partial n_s/\partial\, \ell n\, p)_{T_0,q}$ has been dropped from Eq. (11) for the n_s in Eq. (6) of Ref. 1 to be compatible with that appearing in Eq. (10), i.e., the ZN definition (see the Nomenclature and Ref. 2). Whether this term is indeed negligible has not been demonstrated.] Equation (10) indicates that n_s and ν should have opposite signs (the denominator is positive for realistic conditions). The behavior of Eq. (11) appears to be quite different: when ν is negative, n_s must also be negative (μ is presumably positive), and when n_s is positive, ν must also be positive. This alone shows that the two pyrolysis relations have very different behaviors at the sensitivity parameter level. Experimental response function data (laser-recoil and T-burner) obtained for AP and double-base propellant have shown favorable comparison with sensitivity parameters derived from Eq. (9),[8] but not from Eq. (3). Quasisteady, oscillatory response comparison is an important exercise because it magnifies error in the steady-state burning rate laws. This is because the quasisteady, linear response function is based on the steady-state sensitivity parameters that are the derivatives of the steady-state functions. Since derivatives amplify error in the original function, unsteady response is a sensitive discriminator with respect to determining the accuracy of a steady-state burning model. We think the evidence so far suggests that the formally derived zero-order decomposition relation is significantly more accurate at the sensitivity parameter level than the ad hoc surface pyrolysis relation, Eq. (6) of Ref. 1, even with $n_s \neq 0$ or $n_q \neq 0$ (assuming a q^{n_q} term was added).

The other pyrolysis relation quoted [Eq. (7) of Ref. 1], also needs commenting (although it apparently was not used extensively). Equation (7) of Ref. 1 (referred to as Eq. (12) here)

$$r_b = B_s p^{n_s}(T_s - T_0)^{w_s} \tag{12}$$

can be expressed functionally by Eq. (6). The important point is that T_0 appears explicitly. By using the steady burning rate law [Eq. (8)] to eliminate T_0, this relation can be written as Eq. (5), from which it is evident that neither the pressure nor radiation–Jacobian parameters will be zero (see the definitions of n_s and n_q). Therefore, Eq. (7) of Ref. 1 is not compatible with Eq. (42) of Ref. 1, because, in general, $n_q \neq 0$, whereas Eq. (42) of Ref. 1 assumes $n_q = 0$. Another problem that arises because of the explicit appearance of initial temperature in Eq. (12) is that the n_s parameter appearing in Eq. (12) is not the same as that appearing in Eq. (32) of Ref. 1. The n_s parameter appearing in Eq. (32) of Ref. 1 is the ZN parameter, which is defined by a partial derivative holding constant T_s and q, not T_0. Therefore, Eq. (7) of Ref. 1 is also not compatible with Eq. (32) of Ref. 1, unless it is recognized that the two n_s parameters appearing there are not in general the same.

Fourth and finally, it should be noted that in the response function expressions [Eqs. (32) and (42) of Ref. 1] there is no need to differentiate the B parameters as B_p and B_q. In the general ZN theory they are the same parameter, defined as a partial derivative, $1/k$ [Eq. (19) of Ref. 1]. The flame model expressions for B_p and B_q in Eqs. (34/44) and (37/45) of Ref. 1 are equivalent when it is observed that zero radiative flux has been assumed in the pressure-driven case, which is not necessarily a good assumption, particularly for rocket motor conditions.[4] A more general expression for R_p, including radiative heat feedback, is [see Eq. (20) in Ref. 5, Eq. (7) in Ref. 2, Eq. (37) in Ref. 6, or Eq. (31) in Ref. 4]

$$R_p = \frac{\nu + \delta(\lambda - 1)}{\lambda r + \dfrac{k}{\lambda} - (r + k) + 1 - \dfrac{k\tilde{Q}_r(\lambda - 1)}{\lambda(\beta + \lambda - 1)}} = \frac{nAB + n_s(\lambda - 1)}{\lambda + \dfrac{A}{\lambda} - (1 + A) + AB - \dfrac{A\tilde{Q}_r(\lambda - 1)}{\lambda(\beta + \lambda - 1)}} \qquad (13)$$

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Reply by the Author to M. Q. Brewster and S. F. Son

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THE paper under discussion[1] was devoted to the problem of intrinsic burning stability of solid energetic materials. The analysis was performed by 1) a general nonlinear approach for chemically inert condensed-phase and 2) a less general linear frequency response function to include condensed-phase reactions (for which the general approach could not be applied); both approaches were developed in the flame modeling framework. The results obtained by the authors of the Comment[2] in the Zeldovich–Novozhilov (ZN) framework were mentioned. However, the objective was understanding of intrinsic burning stability, not of frequency response function (although this can help as indeed shown in the paper). The Comment[2] only pays attention to details of the ZN linear frequency response function for chemically inert condensed phase.

Within this framework, the following is our Reply.

The general Arrhenius pyrolysis function was tacitly assumed of the form

$$r_{b,\mathrm{Arr}} = \tilde{A}_s p^{n_s} I_s^{n_{sq}} \exp[-(\tilde{E}_s/\mathcal{R}T_s)] \qquad (1)$$

with $n_{sq} = 0$ for lack of experimental data.

Equation (46) (Ref. 1) should read $n_{sq} = \delta_q/r$.

It is true that Eq. (42) (Ref. 1), although general, is limited to $n_{sq} = 0$.

Both Arrhenius and KTSS pyrolysis laws are fine if the proper compatibility relationships are used. For pressure-driven burning only, these compatibility relationships (related to the pyrolysis Jacobian) are discussed in detail for Arrhenius pyrolysis in Ref. 3 and for KTSS pyrolysis in Ref. 4. For pressure-driven burning with arbitrary initial temperature, the proper compatibility relationships are discussed in Ref. 5. A more general treatment allowing for radiation-driven burning is under preparation. Notice that in the paper under discussion, initial temperature is not a parameter (see line 3 subsection II.A on page 806, Ref. 1). In addition, please consider that any mathematically smooth and increasing (with temperature) pyrolysis laws are allowed for the general nonlinear approach developed to test intrinsic burning stability. The Arrhenius surface pyrolysis is a particular pyrolysis law used to compute linear frequency response functions only, whereas the KTSS surface pyrolysis was never implemented.

The overall problem of simultaneous pressure- and radiation-driven burning is fully analyzed under broad terms in of Ref. 1, Fig. 4 page 810; an even more general treatment, allowing for radiation penetration, is in Ref. 6. Whether to use B_p or B_q is irrelevant, as shown by Eqs. (53) and (54) on page 810 of Ref. 1, whereby several parameters used in the literature, including B_q or B_p, are simply particular expressions of the more general a and b formalism (see definitions on page 807 of Ref. 1). Perhaps the confusion is because of another minor, but important, misprint: Ref. 1, Eq. (54) should read

$$K = q_{\mathrm{DB}} = A_{\mathrm{KTSS}} = 1 + A - AB_q = b = 1 + k/r - 1/r \qquad (2)$$

(b disappeared in the final print).

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