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Oscillatory Combustion of Fine-AP/HTPB Propellants: Disproportionate Pyrolysis Response

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The combustion of hydroxyl-terminated polybutadiene (HTPB) propellants containing fine ammonium perchlorate (AP) was investigated using laser-excited, combustion recoil at 1–5 atm. At 1 atm, binder-rich (70–75% AP), monomodal fine-AP (2–50 θ m) propellants exhibit a prominent non-quasi-steady gas and surface reaction zone, homogeneous propellant, one-dimensional flame response peak at 100–300 Hz, with frequency varying inversely with AP size. Adding coarse AP (resulting in a wide, bimodal AP distribution) causes this response to disappear at 1 atm. Raising the pressure to 2 atm causes the response to reappear and increase in frequency to 600–800 Hz (2-θ m AP). This oscillatory combustion behavior is attributed to time-varying selective or disproportionate pyrolysis of AP and HTPB (unsteady accumulation and depletion of AP at the propellant surface) and the associated compositional (stoichiometric) fluctuations that occur in the fuel-rich, premixed gas-phase reaction zone adjacent to the fine-AP/HTPB solid region. A low Peclet number appears to be a requirement of achieving this condition. Combustion recoil and thermocouple measurements at 1 atm without laser excitation exhibited spontaneous oscillations in the monomodal fine-AP propellants and corroborate the disproportionate pyrolysis interpretation of the laser-excited resonant response. This finding of a strong disproportionation response in composite propellants with fine AP or binder-rich, fine-AP matrix regions has important implications for pressure-coupled response and solid rocket motor stability in that the same response mechanism could operate under oscillatory pressure conditions and at elevated pressures.

Nomenclature

c_p = specific heat
D = mass diffusivity
d = average diameter of ammonium perchlorate particles
E = activation energy
F = force per unit area
f = frequency, Hz
G_{xx} = one-sided autospectral density function (power of signal per Hertz)
$H(f)$ = thrust response function, units of force per unit area per heat flux, N/W
k = thermal conductivity
M = molecular weight
m = mass flux
Pe = Peclet number, ratio of bulk convective mass transport rate (streamwise direction only) to diffusive transport rate (streamwise and lateral), $u_g d/D$
p = pressure
R = universal gas constant
r_b = burning rate, cm/s
T = temperature
u_g = velocity of gases leaving propellant surface
α = thermal diffusivity
ρ = density
Ω = nondimensional frequency, $2\pi f_{\exp}\alpha_c/\bar{r}_b^2$

Subscripts or Superscripts

c = condensed phase
exp = experimental
g = gas phase
s = surface
$'$ = oscillatory or instantaneous quantity
$-$ = mean or time average quantity

Introduction

EVEN though ammonium perchlorate (AP) with nonenergetic polymer binder is a common propellant system, its combustion behavior is still not fully understood and certainly is not predictable. Important observations that have not been fully explained are intermediate pressure extinction and plateau/mesa burning-rate behavior in wide size distribution AP/hydroxyl-terminated polybutadiene (HTPB) propellants. The distinguishing feature of these systems is that they contain a fuel-rich pocket or matrix propellant region consisting of binder and fine-AP particles.[1–5] Conventional multiple-flame models that can be made to correlate steady burning-rate data for more typical AP–composite propellants reasonably well do not adequately simulate the behavior of such wide-distribution propellants, indicating a possible lack of some important basic physics or chemistry in these models.

This paper is concerned with combustion of HTPB composite propellants containing fine-AP. This includes both binder-rich, matrix propellants containing only monomodal fine-AP and bimodal (wide-distribution), nearly stoichiometric propellants. The binder-rich, monomodal fine-AP propellants are designed to be models of the pocket or matrix propellant that occupies the region between coarse AP in bimodal propellants. Earlier work[1] with binder-rich (70–75% AP) propellants containing monomodal fine AP indicated a prominent oscillatory response peak in the laser-excited combustion recoil response at 1 atm. This response was in addition to the classical thermal relaxation, or quasi-steady gas and surface reaction zone, homogeneous propellant, one-dimensional flame (QSHOD) response peak found with most homogeneous or quasi-homogeneous propellants. In the present work the oscillatory combustion of both monomodal and wide-distribution bimodal propellants was further investigated experimentally in an effort to better understand the governing fundamental combustion processes in AP/HTPB propellants. The results shed further light on the secondary or non-QSHOD combustion response peak that occurs in propellants containing fine AP, a phenomenon that is postulated to be associated with selective or disproportionate pyrolysis of AP and binder.

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Table 1 Propellant formulations

Propellant	Formulation
APF series	74% (5, 11, 23, 50, 100, 200, 400 μm) AP, 25% HTPB [isophorone diisocyanate (IPDI) with dioctyl adipate (DOA)] binder, 1% carbon black
JF1	74.0% (5 μm) AP, 25% HTPB (IPDI) binder, 1% carbon black
JF3	74% (11 μm) AP, 25% HTPB (IPDI) binder, 1% carbon black
M4	86% (200:2 μm) AP, 12% HTPB binder [dimeryl diisocyanate (DDI) with DOA], 2% transition metal oxide (TMO)
M6	70% (2 μm) AP, 26% HTPB binder (DDI with DOA), 4% TMO
FDT, FIT	70% (2 μm) AP, 26% HTPB binder (IPDI or DDI with DOA), 4% TMO

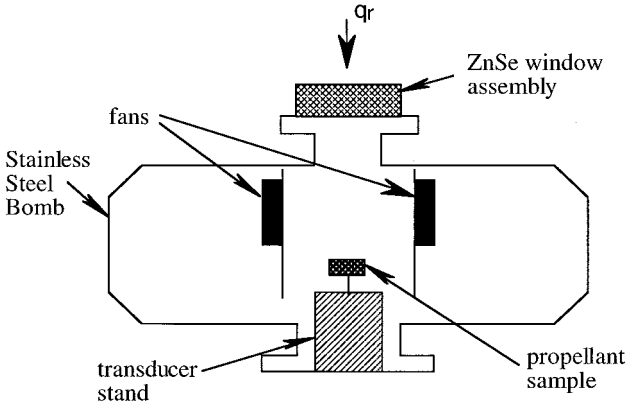

Fig. 1 Schematic diagram of pressurized chamber for laser-recoil response measurements.

Experimental Method

Measurement of laser-excited combustion recoil was conducted under both nonpressurized (1 atm) and pressurized (>1 atm) conditions. Open, nonpressurized measurements were made in a manner similar to those described previously.[1,2,6] Pressurized measurements were made possible by construction of a 4-ft^3, stainless steel chamber fitted with optical windows for laser access[7] as shown in Fig. 1. The chamber also included internal fans for removing the combustion product plume from the laser line of sight and a vented piezoelectric force transducer to minimize transducer sensitivity to pressure fluctuations. Because of a high-frequency (>3 kHz) mechanical response of the transducer loaded with propellant, there is a maximum measurable combustion response frequency on the order of kilohertz. In this study, identical 1000-Hz, low-pass filters were used on each channel to prevent aliasing, and the sampling rate was kept above the Nyquist frequency for the system. The sampling frequencies used in this set of experiments ranged from 2500 Hz per channel to 10,000 Hz per channel depending on the frequency range of interest. The sampling rate for each test was chosen to obtain a minimum of eight points per period at the highest frequency of interest. A CO_2 laser was used with the laser power modulated in a sine sweep. Typical mean laser flux values were 45–100 W/cm^2. Other details of the laser-recoil technique are the same as described previously and may be found in Refs. 6 and 7. Reference 6 also contains a description of the microthermocouple (platinum/platinum rhodium, 5-μm bead) method used. The propellant formulations are given in Table 1 (particle size distribution data for the APF, JF1, JF3, FDT, and FIT may be found in Ref. 7).

The primary measured quantity is the linear combustion recoil or thrust response function $H(f)$, defined as

$$H(f) = F'/q' \tag{1}$$

where F is the thrust force per unit area and q is the heat flux. The thrust response $H(f)$ is a measure of the oscillatory thrust response generated by the burning propellant (output signal) to the oscillatory heat flux (input signal). It is a complex quantity with the magnitude representing the ratio of the amplitude of the oscillatory thrust to the amplitude of the oscillatory laser flux and the phase representing the phase lead (>0) or lag (<0) of the output (thrust) relative to the input (laser flux). The magnitude of H is given in units of force per unit area per heat flux or newton per watt. Measured response data were found to be reproducible as long as the response was kept in the linear regime, that is, heat flux magnitudes small enough that the response of the propellant is linear. This was checked experimentally for every propellant.

The significance of the thrust response is twofold. First, it represents a detailed fingerprint or signature of the propellant combustion behavior, which is difficult to match with a physically erroneous combustion model. (In contrast, steady-state burning-rate data are relatively speaking easier to match.) Thus, it is a very useful diagnostic for developing mechanistic understanding and mathematical models, checking assumptions, and evaluating parameter values. Second, the thrust response is strongly related to the mass flux response, which is of importance in determining motor stability. Where there is a thrust response peak, it is likely that there is also mass flux response peak. Likewise, where there is a pressure-sensitive mass response peak, there is increased potential for combustor instability. Although theoretical obstacles still remain for reliable quantitative conversion of thrust response to mass response, the correspondence between the two is still strong enough that thrust response is a useful predictive diagnostic tool for mass response and instability potential. The thrust response phase is also useful for identifying mass response peaks because the phase usually crosses zero whenever there is a peak or valley of sufficient magnitude in the response, and the zero crossings should be nearly the same between thrust and mass response. In a laser-excited experiment, the phase is inconsequential in terms of affecting the growth or decay of oscillations as the heat flux is not affected by the changes in mass loss; however, in a pressure-excited mode (e.g., a rocket motor), the phase is of utmost importance because the amplitude of pressure oscillations is directly governed by the phase of the mass addition.

Results

Externally Excited, Laser-Recoil Response

Figure 2 shows the laser-recoil thrust response for binder-rich, monomodal AP/HTPB propellants containing relatively coarse AP ($\geq$100 μm) at 1 atm. The main feature of these results is the low-frequency (<30 Hz) peak in the thrust response magnitude. This peak is thought to be the classical solid-phase thermal relaxation or unsteady heat conduction response. QSHOD theory indicates that the frequency of the solid thermal response peak should scale approximately with mean burning rate squared over solid thermal diffusivity, $\bar{r}_b^2/\alpha_c$ (see definition of Ω in the Nomenclature). To the degree that the nondimensional frequency Ω of the response peak is constant, the dimensional frequency of the response peak should vary as $\bar{r}_b^2/\alpha_c$. This behavior is generally observed to hold in low-frequency peaks in laser-recoil response measurements at 1 atm and is used to help identify solid-phase thermal relaxation peaks in the present data. At 1 atm, laser-recoil response measurements have shown no evidence of any secondary (higher frequency) response

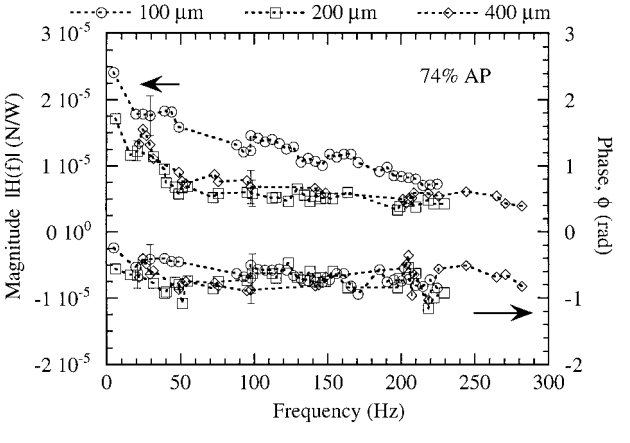

Fig. 2 Laser-recoil response function for monomodal coarse AP/HTPB fuel-rich propellants APF100, APF200, and APF400 at 1 atm.

Table 2 Propellant mean burning rates and response peak frequencies

Propellant	$\bar{p}$, atm	$\bar{q}$, W/cm^2	$\bar{r}_b$, cm/s	First peak frequency		Second peak frequency	
				f_{exp}, Hz	Ω^a	f_{exp}, Hz	Ω^a
APF5	1	0	0.117	<30	<10	——	——
	1	45	0.177	<30	<5	180	26
APF11	1	0	0.117	<30	<10	——	——
	1	45	0.176	<30	<5	180	26
APF23	1	45	0.137	<30	<8	105	25
APF50	1	45	0.146	<30	<7	110	23
APF100	1	45	0.126	<30	<9	——	——
APF200	1	45	0.113	<30	<11	——	——
APF400	1	45	0.099	<30	<14	——	——
FDT	1	60	0.137	<30	<8	365	87
FIT	1	60	0.171	<30	<5	360	55
JF1	1	45	0.158	<30	<6	190	34
	1.5	45	0.181	——	——	230	32
JF3	1	45	0.151	<30	<6	150	30
M6	1	0	0.115	——	——	260	88
	1	45	0.135	<30	<8	310	76
	2	45	0.139	50	12	650	150
	5	80	0.274	390	23	(>1000)	(>60)
M4	1	0	0.121	——	——	——	——
	1	45	0.131	<30	<8	400	94
	2	45	0.188	75	8.3	800	91
	5	80	0.304	——	——	(>1000)	(>44)

[a]For monomodal propellants (i.e., APF5–M6), α_c was assumed to be 7.2×10^{-4} cm^2/s and for M4, 6.4×10^{-4} cm^2/s.

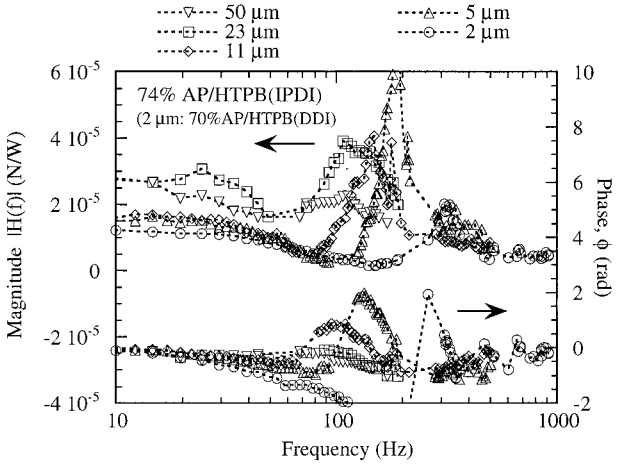

Fig. 3 Laser-recoil response function for monomodal fine AP/HTPB fuel-rich propellants M6, JF1, JF3, APF23, and APF50 at 1 atm.

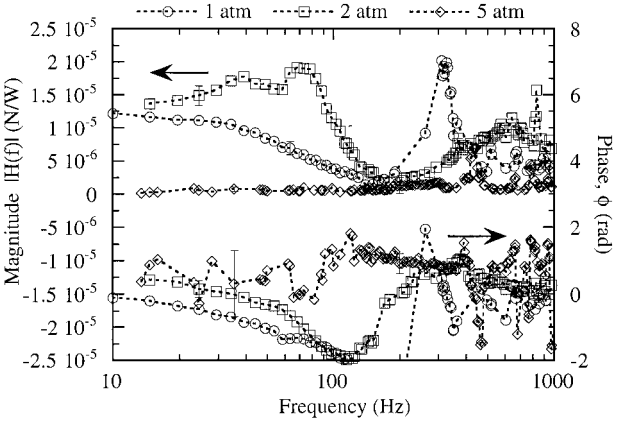

Fig. 4 Thrust response of binder-rich, monomodal fine-AP propellant M6; effect of pressure.

peaks above the solid thermal relaxation response up to 1000 Hz for coarse-AP monomodal propellants.

Figure 3 shows the laser-recoil thrust response for binder-rich, monomodal AP/HTPB propellants containing relatively fine (<100 μm) AP at 1 atm. In addition to the low-frequency solid thermal relaxation peak, AP sizes below 50 μm exhibited a prominent secondary response peak. The frequency of this secondary response increased with decreasing AP size even down to the smallest AP size tested, 2 μm. As will be discussed later, the frequency of this second peak scales with $\bar{r}_b/d$ at 1 atm. Table 2 gives a summary of the frequencies of the response peaks, both primary and secondary, where they are identifiable. The mechanism responsible for the secondary response observed in the binder-rich fine-AP propellants of Fig. 3 is a question of primary interest in this paper. As discussed hereafter, we conclude that the secondary peak is due to selective or disproportionate pyrolysis of the AP and HTPB ingredients (and associated gas-phase compositional fluctuations), and that name (selective or disproportionate pyrolysis) will be used here to designate the second response peak. The following results focus on formulations that contain monomodal, fine AP and exhibit a noticeable disproportionate pyrolysis response.

Figure 4 shows the thrust response of binder-rich, monomodal, 2-μm AP/HTPB (DDI) propellant (M6) as a function of pressure (1, 2, and 5 atm). The 1-atm curve is the same as in Fig. 3, with a solid-phase thermal relaxation response peak somewhere below 30 Hz and a disproportionate pyrolysis response peak at 310 Hz. At 2 atm, the solid thermal relaxation peak, nominally at 50 Hz, actually consists of two separate minor peaks near 40 and 70 Hz, and has shifted upward in frequency from its location at 1 atm. The upward shift in frequency is consistent with the slight increase in $\bar{r}_b$ (see Table 2) through the $\bar{r}_b^2$ scaling of QSHOD theory noted earlier. The splitting into two separate peaks is not in accordance with QSHOD theory, however, and is evidence of non-QSHOD effects. The selective pyrolysis response peak has also shifted up in frequency from 310 to 650 Hz. Table 2 gives an estimate of the nondimensional frequency values associated with each identifiable response peak. At 5 atm the thrust response magnitude of M6 seen in Fig. 4 has decreased significantly compared with 2 atm. This decrease is a general feature observed in thrust response measurements with composite propellants and is elaborated in the following paragraph.

Generally a decrease in response magnitude with increasing pressure is expected for propellants with steady-state burning-rate pressure exponent less than one-half, $n < 0.5$, based on one-dimensional momentum considerations. As pressure increases, gas density increases (as p^1) and, for a nearly constant mass flux ($\rho_g u_g$), mean gas velocity would therefore decrease. Because recoil force varies as momentum flux, $\rho_g u_g^2$ or m^2/ρ_g, the variation of recoil force

with pressure depends on how strongly m varies with pressure, where $m \sim p^n$. For $n < 0.5$ (which applies to all propellants at all pressures considered here) the time-averaged or steady momentum flux and recoil force decrease with increasing pressure by one-dimensional theory. This trend, which is based on assuming steady conditions, generally carries over into the unsteady response, although exceptions occur where response peaks at a higher pressure coincide in frequency with response valleys at a lower pressure. Thus, over most of the measured frequency range, Fig. 4 shows a lower response magnitude for propellant M6 at 5 atm in comparison with that at 2 atm. A noticeable response peak does appear near 390 Hz at 5 atm that is thought to be associated with the solid thermal relaxation mechanism. As at 2 atm, this response seems to be split into a weaker response (below 390 Hz) and a stronger response (above 390 Hz). The selective pyrolysis response peak at 5 atm is presumably beyond the frequency limit of the measurement, 1000 Hz, assuming it still exists.

The results of Figs. 3 and 4 show that the effect of fine-AP size on second-peak frequency (increasing frequency with decreasing AP size) persists down to 2-μm AP (see also Table 2) and that with increasing pressure the selective pyrolysis response frequency increases.

Figure 5 shows the thrust response of a nearly stoichiometric (overall), bimodal 200:2 μm AP/HTPB (DDI) propellant (M4). At 1 atm, a broad, solid thermal relaxation peak is clearly evident at low frequencies. At 400 Hz, there is a weak signal indicating a possible weak disproportionate pyrolysis response but it is not as strong as that seen for M6 at 1 atm in Fig. 4. At 2 atm, however, M4 exhibits a relatively strong disproportionate pyrolysis peak at 600–800 Hz, which is the same frequency range as the disproportionation response of M6 (650 Hz). That the composition of M6 and the matrix (fine AP and binder) of M4 are so similar and that the secondary response peak occurs at nearly the same frequency suggest that the same mechanism (disproportionate pyrolysis) is responsible. The increasing prominence of the disproportionation response peak in the bimodal propellant (M4) with increasing pressure may be related to a change in flame structure. The flame zone may be closer to being premixed (compositionally more uniform across coarse AP and matrix) at 1 atm and less so (compositionally less uniform across coarse AP and matrix) at 2 atm. At 5 atm, the thermal relaxation peak in M4 seems to have broadened and bifurcated into two peaks above and below 130 Hz. This split in M4 is probably associated with the large-scale heterogeneity between coarse AP and matrix. Perhaps the idea of separate QSHOD response peaks being manifested for coarse AP and matrix has some applicability here. However, simple extrapolation of QSHOD ideas to individual components (AP vs binder or coarse AP vs matrix) in a composite propellant is probably too simplistic. For example, QSHOD theory applied to individual components does not appear to be adequate to describe the broad, two-peaked thermal relaxation response observed for propellant M4 at 5 atm in Fig. 5. As for the disproportionation response in M4 at 5 atm, this peak, if it still exists, might have been out of the measurement range (being above 1000 Hz).

The effect of binder curative (IPDI vs DDI) on the laser-recoil response for fuel-rich, monomodal, fine-AP propellants FDT and FIT at 1 atm is shown in Fig. 6. IPDI curing gives a noticeably stronger disproportionation response than DDI. Curative type has previously been observed to affect steady-state burning rate, with IPDI-cured propellants generally burning faster than DDI-cured propellants.[4] Here a similar effect is observed in the unsteady response.

Spontaneous Oscillating Combustion

Combustion recoil measurements without laser irradiation were performed at 1 atm on propellants M6 and M4 to check for spontaneous oscillatory behavior. Propellants were ignited using an integrated CO_2 laser to ensure uniform ignition. After ignition, the laser was turned off. The results are shown in Fig. 7 in terms of the autospectral density function of the recoil force. All data points are included without distinction being made for noise. Peaks between 100 and 200 Hz occurred in all of the tests. These peaks were caused by systematic noise sources such as gas flow or electrical noise. (In laser-excited tests, this noise can be distinguished from the driven response signal and eliminated by use of the coherence function, which is a measure of the output signal caused by the input signal.) Figure 7 shows a strong spontaneous recoil oscillation at 250 Hz in binder-rich, monomodal M6 that is absent in bimodal M4. This peak is thought to be mechanistically the same as the secondary peak found in the laser-excited response of M6 (310 Hz). The slight difference in frequency (250 vs 310 Hz) is probably due to the slightly higher mean burning rate with laser augmentation. Bimodal M4, however, shows only a weak spontaneous oscillatory component of thrust at 250 Hz, just as the excited laser-recoil measurement showed little response in that same frequency range at 1 atm (Fig. 5).

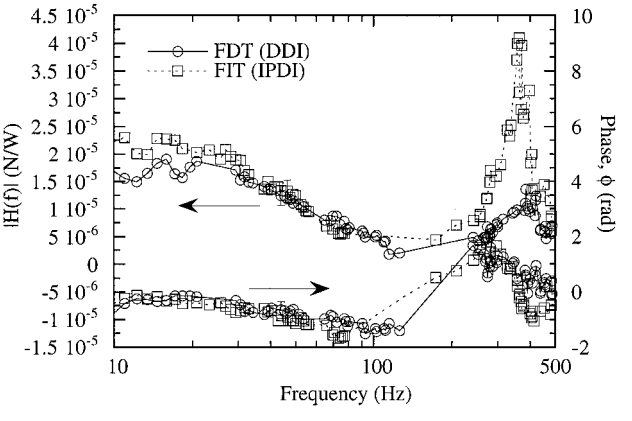

Fig. 6 Effect of binder curative on thrust response of binder-rich, monomodal fine-AP propellants FDT (DDI) and FIT (IPDI) at 1 atm.

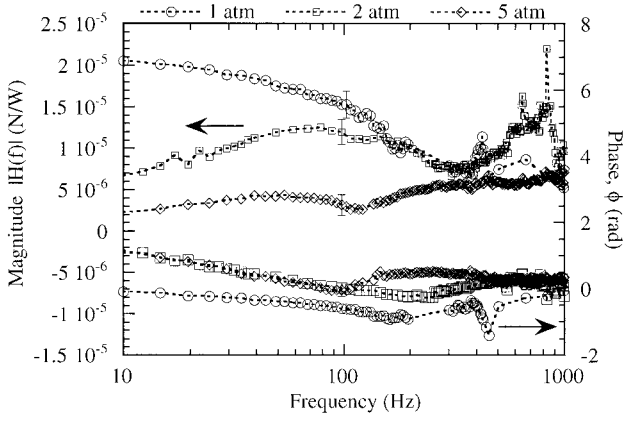

Fig. 5 Thrust response of bimodal AP propellant M4; effect of pressure.

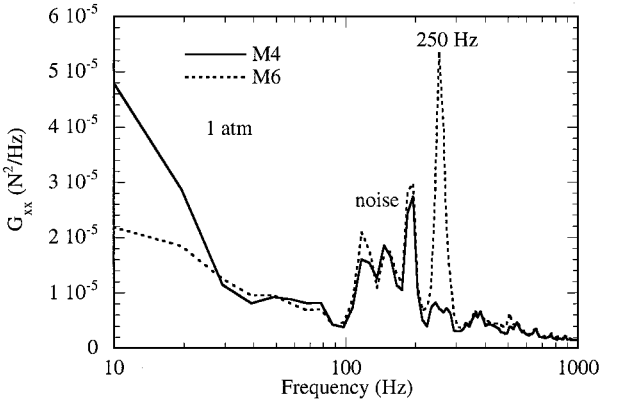

Fig. 7 Thrust response of M4 and M6 propellants without laser augmentation, 1 atm.

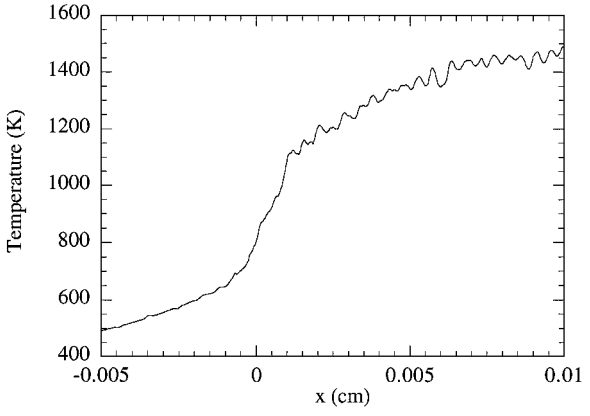

Fig. 8 Temperature profile for M6 propellant (without laser), 1 atm.

Thermocouple Measurements

Thermocouples (5-μm bead, platinum/platinum–rhodium) were used to measure the temperature through the combustion zone for propellant M6 at 1 atm, which has a theoretical equilibrium adiabatic flame temperature of 1460 K and an estimated surface temperature of 800 K, as shown in Fig. 8. The temperature in the gas phase oscillates at 250 Hz, corresponding to the 250-Hz peak in its spontaneous combustion recoil oscillation (Fig. 7) and the 310-Hz peak in its laser-driven thrust response (Fig. 4). [A similar correspondence can be seen at 180 Hz for similar propellant with slightly larger, 5–11 μm, fine-AP and IPDI curing (APF5 and APF11) in Ref. 6; spectral analysis is given in Ref. 7.] Corroborating evidence of this phenomenon was also reported in Ref. 8, where high-speed emission imaging of the burning surface of M6 at 1 atm showed incandescent material (presumably carbon residue from the binder and transition metal oxide) accumulating on and departing from the burning surface at 250 Hz.

Discussion

The experimental observations just presented provide useful information that can possibly help unravel the complicated combustion mechanisms of propellants containing fine AP. In particular, oscillatory combustion behavior that appears under certain conditions with fine AP is an opportunity to gain insight. This behavior has been observed in two ways: as a pronounced secondary response function peak for laser-augmented combustion and as spontaneous oscillating combustion recoil and gas-phase temperature without laser augmentation. The primary condition that appears to be necessary for a pronounced secondary response peak is a binder-rich mixture with fine AP.

The cause of the secondary response peak is postulated to be disproportionate ingredient (AP and binder) pyrolysis. Significant differences in thermophysical and/or chemical kinetic decomposition properties, particularly activation energy, between different ingredients in a composite propellant (or even in a supposedly homogeneous propellant, e.g., NC/NG) can cause selective or disproportionate pyrolysis of these ingredients. This means instantaneous pyrolysis rates or mass fluxes that are out of proportion with the relative mass fractions of the ingredients in the propellant. HTPB cured with IPDI has been reported to have a decomposition activation energy of 11 kcal/mol (Refs. 9 and 10, Chen and Brill[10] reported 12.5 kcal/mol for DDI-cured HTPB), whereas near 1 atm AP decomposes (mostly via dissociative sublimation) with an activation energy of 29 kcal/mol (Ref. 11). There is also a minor difference in thermal diffusivities. This primary difference in activation energies means AP's decomposition rate is more temperature sensitive than that of the binder. Therefore, in the presence of an oscillatory flame with its associated oscillatory conductive heat feedback, AP has a greater propensity to decompose in an oscillatory manner compared to HTPB. This raises the question of what conditions might cause an oscillatory flame. One possible cause is the process of disproportionate decomposition itself. When AP and binder disproportionately decompose, the gas composition feeding the gas flame also experiences disproportionation.[12–15] That is, the gas flame experiences compositional fluctuations that change its fuel/oxidizer ratio. If the gas flame is premixed and fuel rich (both of which appear to be necessary conditions for a prominent secondary response peak) the gas-flame volumetric heat release and temperature would experience significant fluctuations, resulting in a significant oscillatory component of conductive heat feedback to the solid ingredients (as evidenced in Fig. 8). Thus, a feedback loop is established and conditions are favorable for either a strong systemwide resonant response when the entire propellant is excited by a correlating external stimulus (e.g., laser radiation or pressure) at the appropriate frequency or self-sustained local oscillatory combustion in the absence of a correlating external influence.

The idea of disproportionation (a term coined by Price et al.[13]) has previously been cited as a factor that theoretically might influence the pressure-coupled combustion response.[12–16] Price[16] predicted in 1969 that kinetic differences among propellant ingredients could produce mixture oscillations in the gas phase and produce oscillatory burning that could either amplify or attenuate a perturbing environmental oscillation, depending on the phase of the mixture fraction oscillations relative to the perturbation, for example, pressure. Indeed the present observations seem to support Price's early hypothesis. Other references to possible effects of disproportionate pyrolysis on unsteady combustion have also appeared. King[12] considered the effect of disproportionation in the context of the primary (QSHOD) response; however, no secondary response was mentioned. Cohen and Strand[14] calculated separate (i.e., primary and secondary) response peaks due to the thermal relaxation (QSHOD) mechanism and gas-phase compositional fluctuations, but predicted that the selective pyrolysis-gas compositional fluctuation peak would occur at a lower frequency than the QSHOD response, which is opposite the present laser-recoil observations. The later report[15] of Cohen's work recognizes or emphasizes more than the earlier paper[14] does the potential importance of gas-phase temperature fluctuations (via composition) in influencing the acoustic admittance function.

An important consideration in the disproportionate response mechanism is the nature of the flame structure, premixed vs diffusion. The principal parameter characterizing the degree of reactant premixedness in a composite solid propellant is the mass Peclet number[17]:

$$Pe = u_g d/D = md/\rho_g D = c_p md/k_g, \qquad (Le \approx 1) \qquad (2)$$

The Peclet number is the ratio of mass or energy transport via axial convection to that via lateral or radial diffusion. A low Peclet number indicates rapid lateral diffusive mixing between binder and AP decomposition products and a premixed flame structure, whereas a large Peclet number indicates that a compositionally less sensitive, partially premixed leading edge and trailing diffusion flame structure is occurring near the AP and binder interface.[17,18] Figure 9 shows the estimated dependence of the Peclet number on AP particle size for 1-atm combustion of 75% monomodal AP/HTPB

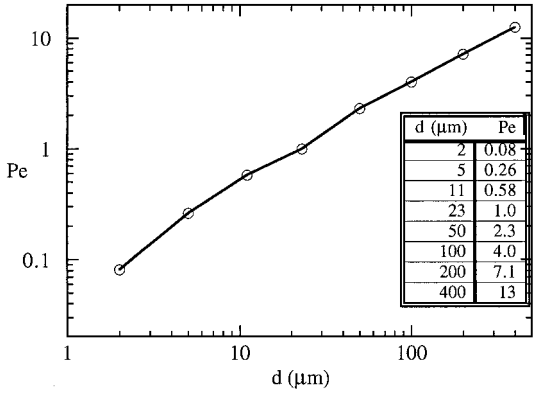

Fig. 9 Peclet number as a function of AP size [using Eq. (1), c_p = 0.45 cal/g-K, $m = \rho_c \bar{r}_b$, k_g = 0.217 mcal/cm-K-s].

propellant (transport and thermochemical properties for estimating Peclet number were obtained from the NASA thermochemical code). APF50 (50-μm AP), which has a Peclet number of 2.3, displayed a small-magnitude second peak (Fig. 1) and was the largest AP particle size to be used that produced a discernable second peak. A Peclet number of 1 corresponds to APF23 (23-μm AP), which showed a strong second peak. The experimental evidence for monomodal propellants at 1 atm suggests that a Peclet number of order 1 or less is needed for a sufficiently premixed flame structure and the occurrence of a disproportionate pyrolysis response peak. For $Pe \gg 1$ (AP size > 50 μm at 1 atm) diffusive transport is sufficiently slow relative to advection that significant compositional nonuniformity will exist in the gas region adjacent to the AP and binder. Therefore, a diffusion-flame structure with a partially premixed leading edge will be established near the AP-binder interface. Such a flame structure is less sensitive to compositional fluctuations, and the feedback loop necessary for the disproportionate pyrolysis response mechanism is broken. For 2-μm AP the Peclet number is 0.1 or less for pressures less than 5 atm, indicating that the flame structure governing the responses of Fig. 4 is definitely premixed. At 130 atm the Peclet number would still be of order one (assuming a burning rate of 3 cm/s), and the flame structure would still possibly be sufficiently premixed for a distinct disportionation response. Thus, 2-μm AP could be of particular concern for rocket motor stability at actual operating conditions.

Bimodal propellant with a wide AP size distribution, such as 200:2 μm, will have bimodal Peclet numbers, with $Pe \sim 10$ for the coarse AP relative to the surrounding matrix and $Pe \sim 0.1$ for the binder–fine-AP matrix at 1–5 atm. Figure 9 indicates $Pe = 7$ for the coarse AP at 1 atm, which is large enough that some nonpremixed flame structure between coarse AP and matrix may be expected. However, it is apparently small enough that sufficient oxidizer species from the coarse AP are diffusively transported into the matrix gas-phase region to mitigate the otherwise fuel-rich condition there and weaken the disproportionation effect. This could explain the absence of a strong disproportionate pyrolysis response at 1 atm in Fig. 5. At 2 atm, the disproportionate pyrolysis response appears prominently even in the bimodal propellant (Fig. 5). This could be partially due to the increase in Peclet number associated with an increase in mean burning rate. However, the increase in Peclet number would be rather modest for that pressure change. Other effects, such as a change in chemical kinetics (i.e., Damkohler number effect), should also be considered as contributing to the change in flame structure that causes the restoration of the disproportionate pyrolysis response at 2 atm in M4.

In the absence of a proven mathematical model that can describe the disproportionate pyrolysis-gas compositional fluctuation mechanism, a preliminary attempt at theoretical description was made by searching for correlation between the observed secondary response peak frequency and simple models that have been proposed. In Fig. 10, the experimentally observed secondary response frequency

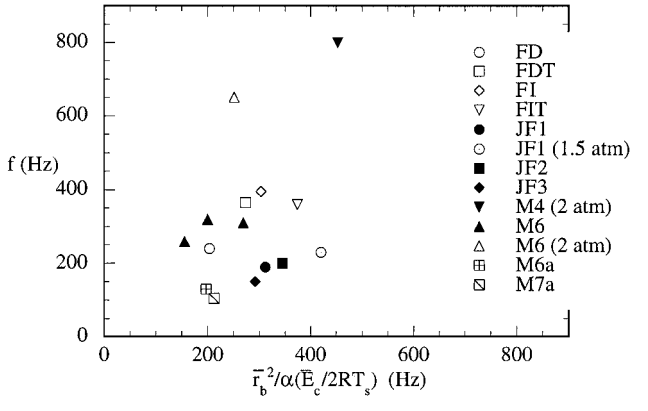

Fig. 10 Measured secondary response peak frequency for a variety of binder-rich, monomodal fine-AP propellants vs theoretical decomposition zone characteristic frequency.

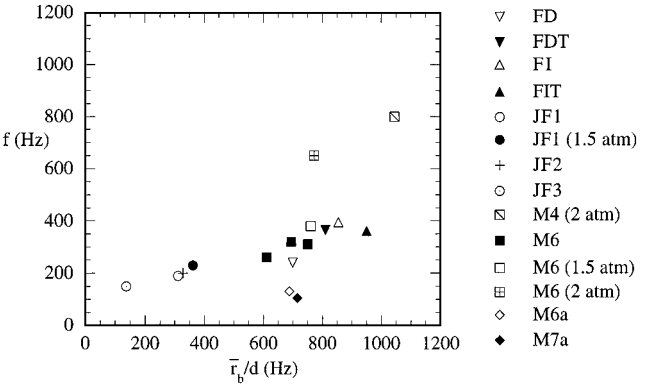

Fig. 11 Measured secondary response peak frequency for a variety of binder-rich, monomodal fine-AP propellants vs theoretical AP particle packing frequency.

for a variety of propellants and conditions is plotted vs the theoretical homogeneous condensed-phase decomposition zone characteristic frequency,[19] $\bar{r}_b^2/\alpha_c(E_c/R\bar{T}_s)$. Properties of AP (being the more plentiful ingredient) were used. The correlation with $\bar{r}_b^2/\alpha_c(E_c/R\bar{T}_s)$ in Fig. 10 is poor. A better correlation is observed in Fig. 11 with the AP particle packing frequency, or so-called layer or preferred frequency,[20,21] $\bar{r}_b/d$. However, the expected slope of close to one ($f \sim \bar{r}_b/d$) is not observed, at least for 1-atm data. (A slope of one follows if it is assumed that the disproportionate pyrolysis peak is due to a periodic accumulation and depletion of AP near the surface, in a manner similar to that proposed by Gany and Caveny[22] for aluminum accumulation on the surface in aluminized propellant. AP would differ from aluminum in that AP would be continuously decomposing although at a slower rate during the accumulation phase whereas the aluminum in Gany and Caveny's model was assumed not to decompose at the surface.) Evidently, there is more complex behavior occurring to produce the secondary response peak than just burning through alternate layers of relatively more or less binder-rich material.

As noted, an important implication of the disproportionate pyrolysis response is that it may be expected to appear in the pressure-coupled response also. Pressure-coupled response data for propellant M4 at 20 atm have been reported that indicate the possibility of a strong secondary (disproportionate pyrolysis) response.[23] This has important implications for solid rocket motors with wide-distribution AP/HTPB propellants because coupling between motor acoustic modes and the disproportionation response could lead to combustion instability.

Finally, note that the response features discussed here are for the recoil force or thrust response, not mass flux response. In past applications of recoil force measurements to homogeneous materials,[11] a simple one-dimensional momentum balance

$$F' = 2\bar{m}m'(R\bar{T}_f/PM) + \bar{m}^2(RT_f'/PM) \tag{3}$$

has been used to relate the mass flux response to the recoil response with the flame temperature fluctuation term neglected. Indeed for pure, single-component materials like HMX (or even two-component materials like NC/NG whose decomposition kinetics are not as disparate as those of AP/HTPB), neglecting flame temperature fluctuations seems justified. However, in AP/HTPB, particularly binder-rich mixtures where the flame temperature is quite sensitive to gas composition, this assumption may not hold. Preliminary estimates[7] indicate that the temperature fluctuation term could contribute as much to the measured recoil response as the burning-rate fluctuation. Independent measurements of burning-rate response and acoustic admittance, as previously suggested by Cohen,[15] as well as measurements of fluctuating gas temperature and recoil response, would be useful in quantifying the relation between gas velocity, density, mass flux, and temperature, and for verifying modeling assumptions.

Conclusions

The combustion of HTPB propellants containing fine AP exhibits both spontaneous and externally excitable, resonant oscillatory behavior. At 1 atm, binder-rich (70–75% AP), monomodal, 2-μm AP propellants exhibit spontaneous oscillation at 250 Hz and a prominent secondary (non-QSHOD) laser-excited response peak at 310 Hz that increases to 650 Hz at 2 atm. This behavior is attributed to selective or disproportionate ingredient (AP and HTPB) pyrolysis and the resulting compositional fluctuations that occur in the premixed (low Peclet number) gas flame. Bimodal (nearly stoichiometric) propellants comprising fine-AP/HTPB matrix and coarse (200-μm) AP exhibit no prominent selective pyrolysis response at 1 atm but do at 2 atm. The absence of a strong disproportionate pyrolysis response from the fine-AP/HTPB matrix region in the bimodal propellant at 1 atm is attributed to diffusive mixing of gaseous decomposition species between the coarse AP and matrix regions, which mitigates the fuel richness of the gas-phase composition issuing from the matrix region. Raising the pressure to as little as 2 atm, however, restores the necessary fuel richness and the disproportionation response reappears. The implication of these results is that a strong secondary (non-QSHOD) response peak related to selective or disproportionate ingredient pyrolysis could be expected to occur in wide-distribution AP–composite propellants even for pressure-coupled response.

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