Unsteady Effects on Low-Pressure Extinction Limit of Solid Propellants

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Unsteady effects are introduced into the heat loss theory of low-pressure extinction of solid propellants to improve the prediction by the steady-state analysis. These effects include dynamic extinctions induced by the natural flame oscillation and by the forced flame vibration in response to external pressure disturbances. The analysis shows that a part of the steady-state solution at low pressure is linearly unstable and so it cannot be physically observed. In the linear stable region, flames that are close to the neutral stable point can still be quenched easily by a finite amplitude external pressure disturbance. The critical magnitude of this disturbance is computed in an approximate way. Both effects broaden the nonflammable range of the propellants.

Nomenclature

A = nondimensional parameter [see Eq. (9)]
B_s = linear pryolysis rate law coefficient, cm-sec^{-1}K$_I^{-\beta}$
C_s = solid-phase specific heat, cal/g K
C_p = mean isobaric specific heat of the gas-phase, cal/g K
E_s = activation energy for pryolysis rate law, kcal/mole
E_f = activation energy for gas-phase chemical reaction, kcal/mole
K = mean coefficient of thermal conductivity of the gas-phase, cal/cm-sec-K
L = heat of vaporization, cal/g
m_w = mass flux relative to burning surface, g/cm^2-sec
n = order of chemical reaction
P = pressure, atm
ΔP = critical amplitude of pressure oscillation for flame quenching
P_{SL} = low-pressure limit from steady-state theory
P_{DYL} = low-pressure limit from dynamic stability theory
Q_r = heat of combustion per unit mass of reference species consumed, cal/g
q_{RS} = rate of radiant energy loss from the propellant burning surface, cal/cm^2-sec
r = linear burning rate, cm/sec
R = ideal gas constant, 1.9867 cal/mole-K
t = time, sec
T = temperature, K
T_i = initial temperature, K
T_f = flame temperature, K
x = distance from propellant surface, cm
Z = nondimensional parameter [see Eq. (11)]
α = nondimensional parameter [see Eq. (10)]
β_I = temperature dependence of pre-exponential factor in linear pryolysis law
ϵ = nondimensional parameter [see Eq. (8)]
ϵ_s = total hemispherical emissivity of solid-phase burning surface
ω = frequency nondimensionalized by $\bar{m}_W^2 C_s/\rho_s\lambda$
η = amplification coefficient
ρ = mean density of gas phase, g/cm^3
ρ_s = density of solid phase
λ = coefficient of thermal conductivity of the solid-phase, cal/cm-sec-K
ξ = nondimensional parameter [see Eq. (12)]
γ = nondimensional parameter [see Eq. (13)]

Superscripts

$'$ = complex amplitude of perturbation quantity
$\hat{}$ = perturbation quantity
$\bar{}$ = mean or steady-state component

I. Introduction

AN analysis has been performed to study the mechanisms of inflammability of solid propellants at low pressure. Previous investigations on the subject have followed either the stability consideration[1] or the mechanism of heat losses.[2,3] The stability analysis which employs an adiabatic flame model has not been successful in producing a low-pressure flammability limit. On the other hand, the steady-state heat loss theory has given the correct qualitative trends consistent with the experimental results. Unfortunately, quantitative comparison with experiments has not been very successful; the theory always predicts a wider flammable range than is experimentally observed. The present study tries to improve this discrepancy by a combined consideration of nonsteady effects and heat loss mechanisms.

The unsteady effects include dynamic extinctions induced both by natural flame oscillation and by forced flame vibration in response to external pressure disturbances. The present analysis shows that part of the steady-state solution at low pressure is linearly unstable, so it cannot be physically observed. The existence of this branch of unstable solution is the consequence of heat loss from the flame. The heat loss also provides a mechanism to interpret the final outcome of the growing oscillatory unstable flame, i.e., dynamic extinction. Flame extinguishment due to pressure-forced oscillation is also studied. This phenomenon is observed in solid rockets with L-star instability. In general, the sensitivity of the low-pressure extinction limit to disturbances was known to many experimenters and it was specially stressed in Ref. 4.

II. Analysis

In the analysis of the propellant combustion, the principal assumptions include one-dimensional flame, single-step

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chemical reaction, homogeneous propellant, no reaction in the solid-phase, vaporization of the solid according to Arrhenius law, Lewis number equal to unity. Radiative heat loss from the hot propellant surface is the only heat loss mechanism considered in this analysis. Therefore, the steady-state model is the same as that given by Johnson and Nachbar.[2] In the unsteady part, the disturbances are assumed to have relatively low frequencies, so that the quasi-steady-gas phase, unsteady-solid-phase type analysis is made. The method of solution is similar to the one used by Denison and Baum,[6] except that we are treating a nonadiabatic model, which does make the important difference in the behaviors of propellant flame at low pressure. Only the essential steps will be presented here, more details can be found in Ref. 5.

Since the gas phase is quasi-steady, von Karman's integral is used

$$m_w \epsilon_{rw} = C \cdot P^{n/2} T_f^{(n/2+1)} \exp(-E_f/2RT_f) \tag{1}$$

Control volume analysis gives the temperature gradient on the gas side

$$K\left(\frac{\partial T}{\partial x}\right)_{x=0+} = -m_w C_p \left(T_f - T_w - \frac{Q_r}{C_p}\epsilon_{rw}\right) \tag{2}$$

Surface pyrolysis is given by

$$m_w = \rho_s B_s T_w^{\beta_1} \exp(-E_s/RT_w) \tag{3}$$

Surface energy balance is given by

$$\lambda\left(\frac{\partial T}{\partial x}\right)_{x=0-} = K\left(\frac{\partial T}{\partial x}\right)_{x=0+} + m_w(C_s T_w - C_p T_w - L) - q_{RS} \tag{4}$$

Where q_{RS} is the radiative heat loss from the propellant surface given by

$$q_{RS} = 1.36\,\epsilon_s (T_w/1000)^4 \text{cal/cm}^2\text{-sec} \tag{5}$$

Solid heat conduction equation is

$$\rho_s C_s (\partial T/\partial t) = -m_w C_s (\partial T/\partial x) + \lambda(\partial^2 T/\partial x^2) \tag{6}$$

The previous equations are solved, first, for the steady state, and then perturbed for small oscillations to obtain a set of linearized unsteady equations. For natural oscillations, the pressure is kept constant and exponential oscillatory solutions of the other perturbed quantities are sought. For example, $m'_W = m'_W \exp[\eta + i\omega)t]$. For a given propellant and pressure, the linearized equations can be solved for η and ω. When $\eta > 0$, the flame is linearly unstable, when $\eta < 0$, it is linearly stable. Setting $\eta = 0$, we can use the propellant parameters to obtain the neutral stability boundary. The corresponding ω is the natural frequency of the flame. It can be shown easily that the equation for the neutral stable boundary is

$$b - 1 - A + A\alpha - Z + [(b-1)/i\omega]A = 0 \tag{7}$$

where

$$\epsilon = (n+2)/2 + E_f/2R\bar{T}_f \tag{8}$$

$$A = [\beta_1 + (E_s/R\bar{T}_w)][1 - (T_i/\bar{T}_w)] \tag{9}$$

$$\alpha = C_p \bar{T}_f / C_s (\bar{T}_w - T_i)\epsilon \tag{10}$$

$$Z = (\bar{q}_{RS}/\bar{m}_w C_s \bar{T}_w)[(\beta_1 + E_s/R\bar{T}_w) - 4] \tag{11}$$

$$\xi = 1 + A - A\alpha + Z \tag{12}$$

$$\gamma = (n/2)(C_p/C_s)(1/\epsilon)(\bar{T}_f/\bar{T}_w) \tag{13}$$

The significance of Eq. (17) will be presented in Sec. III.

For forced oscillation in the linearly stable domain, the pressure is treated as the forcing function. Solutions are sought of the type $\hat{P}' = P' \exp(i\omega t)$, $\hat{m}'_w = m'_w \exp(i\omega t)$, etc. The burning rate response of the flame is found to be

$$\frac{(r'/\bar{r})}{(P'/\bar{P})} = \frac{A\alpha n/2}{[b - 1 - A + A\alpha - Z + [(b-1)/a]A]} \tag{14}$$

In Eq. (14), $a = i\omega$.

III. Results and Discussion

Figure 1 gives the steady-state burning rate curves for several values of the activation energy of the gas-phase reaction. All three curves have the same reference point, i.e., $\bar{m}_w = 1.603$ g/cm^2-sec at $\bar{P} = 6.8$ atm (the frequency factor of the chemical reaction is determined by this condition). The low-pressure limits predicted by the steady-state equation are given by P_{SL}. The lower branch of each surve has been shown by Spalding[7] to be statically unstable. The stability of the upper branch of the burning rate curve is investigated in this paper. The neutral stability boundary given by Eq. (7) is plotted in Fig. 2. The locus of one propellant ($E_f = 30$ kcal/mole) at different pressure levels is shown in this map. It can be seen that, at low pressure, the locus crosses the stability boundary into the unstable domain before it reaches P_{SL} (P_{SL} corresponds to the condition, $A\alpha - Z = 0$). The point of crossing P_{DYL} is a neutral stable point. From Fig. 1, it can be seen that there exists a pressure range ($P_{SL} < P < P_{DYL}$) in which the steady solution is dynamically unstable. In this region, the flame will oscillate spontaneously with increasing amplitude, although the pressure is kept constant. Unless some nonlinear mechanisms come in to limit the amplitude growth, the instantaneous burning rate will eventually drop below the value of the lower branch burning rate (at constant pressure), and dynamic extinction will occur, as suggested in Ref. 8 and 9. In such a case, P_{DYL} is the physical low-pressure extinction limit in the absence of finite amplitude disturbances.

The existence of unstable solution at low pressure is a consequence of heat loss from the flame. This can be seen from Fig. 2; the dotted line which corresponds to an adiabatic

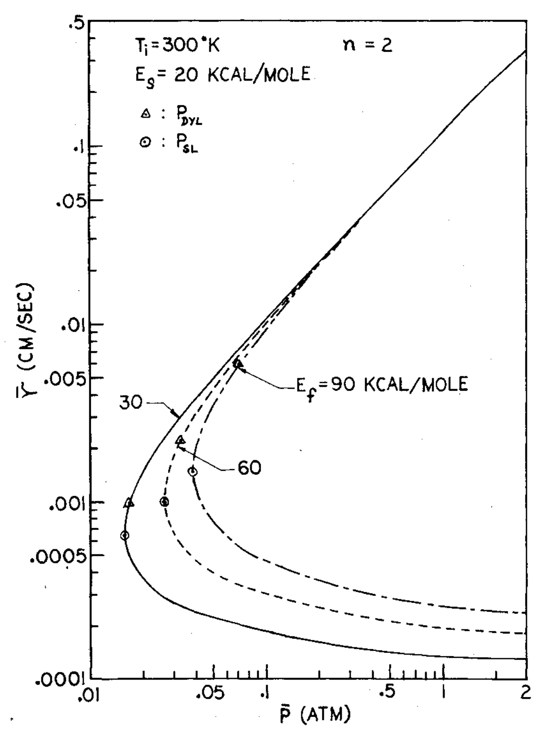

Fig. 1 Steady-state burning rate vs pressure according to heat loss theory. P_{SL} is low pressure extinction limit from steady theory, P_{DYL} is limit from linear stability theory.

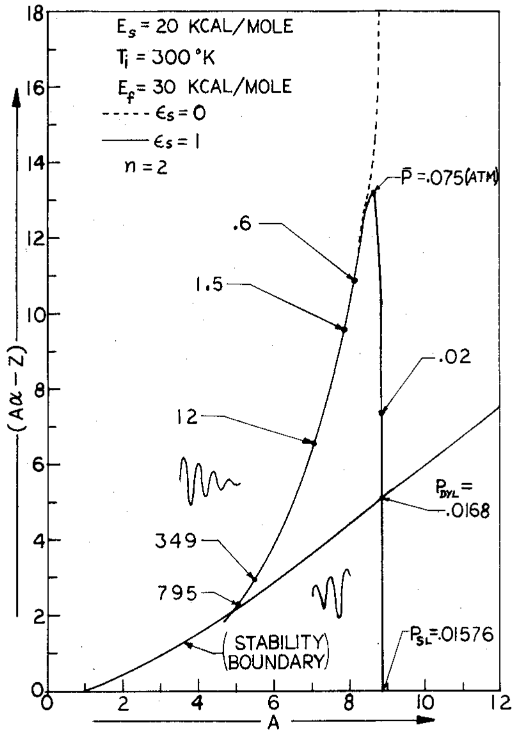

Fig. 2 Locus of one propellant at different pressures in the stability map.

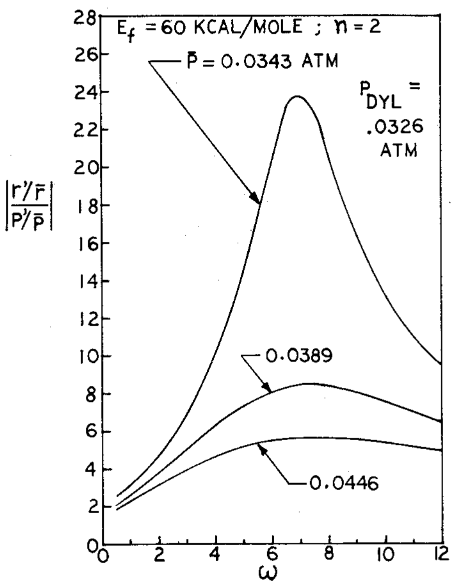

Fig. 3 Absolute magnitude of burning rate response vs nondimensional frequency for near-limit flames.

flame never crosses the stability boundary at low pressure. This result checks with the conclusion of Strahle.[1]

For pressure higher than P_{DYL}, the flame is in the linearly stable region where small disturbances will die down. However, a finite amplitude perturbation can still quench the flame. In Refs. 8 and 9, a dynamic extinction criterion was suggested based on the magnitude of the departure of the instantaneous burning rate (or the instantaneous flame temperature) from its steady-state value. Since most disturbances are in the form of pressure and velocity fluctuations, a calculation of the burning rate response of the flame to these fluctuations is needed to apply the extinction criterion. Only the pressure disturbance is considered in this analysis because of the limitation of the one-dimensional assumption in the combustion model. Furthermore, the disturbance will be

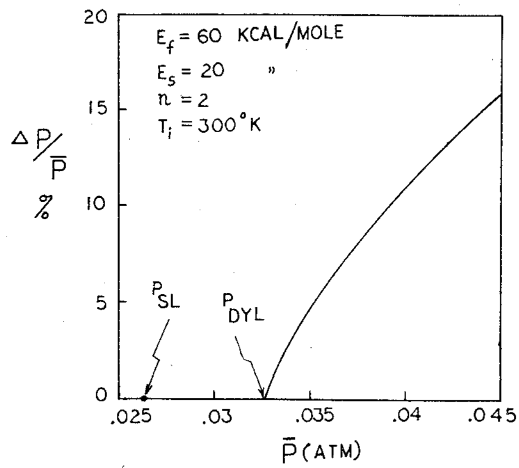

Fig. 4 Critical amplitudes of pressure oscillation for flame quenching in near-limit region (oscillation frequency is close to natural frequency of the flame).

assumed sinusoidal. The response of the flame to the pressure forced oscillation is given by Eq. (14) and it is plotted in Fig. 3 for one propellant ($E_f = 60$ kcal/mole) at several different pressures. For pressure closer to P_{DYL}, larger resonance peak of the response function is observed. This is a direct consequence of the fact that P_{DYL} is a neutral stable point. The larger excursion of the burning rate from its steady-state value in the presence of a relatively small pressure disturbance makes the dynamic extinction of the flame highly likely. In the following a method will be presented to calculate the critical (minimum) magnitude of the pressure disturbance above which the flame will be quenched. The method is approximate in nature, and its validity will be discussed later.

For a given steady-state pressure level, the magnitude of the burning rate excursion Δr that is needed for dynamic extinction can be found from Fig. 1. It is simply equal to the difference of the burning rates between the upper and lower branch curves at the given steady-state pressure.[9] To relate the burning rate deviation to the pressure disturbance, we calculate the response function $(r'/\bar{r})/(P'/\bar{P})$ according to Eq. (14) and substitute the amplitude of r' by Δr. We can then compute the amplitude of $P'/\bar{P}$ and it is denoted by $\Delta P/\bar{P}$. ΔP is the critical magnitude of the pressure disturbance that is necessary to quench a flame dynamically. It is a function of the frequency of the oscillation. Its minimum value occurs near the peaking frequency (natural frequency of the flame) as shown in Fig. 3. In Fig. 4, $\Delta P/\bar{P}$ is calculated using the peaking frequency for one propellant ($E_f = 60$ kcal/mole) in the pressure range close to P_{DYL}. It can be seen that, for pressure very close to P_{DYL}, a very small pressure disturbance can quench the flame, but the critical magnitude increases rapdily as we go away from P_{DYL}. It should also be noted that ΔP has been found (at least for the case in Fig. 4) to be smaller than $(\bar{P} - P_{DYL})$, the extinction process we referred to should not be confused with the static ones.

The above procedure of calculating $\Delta P/\bar{P}$ deserves some discussion. The dynamic extinction criterion suggested in Refs. 8 and 9 is derived from stability considerations. Stability analysis requires that the boundary conditions of the problem remain unperturbed with time, i.e., no external forcing. In the situation we considered here, this was not true. Since the pressure across the flame is assumed to be uniform, the oscillation is externally forced. Dynamic extinction in such a situation has not been rigorously analyzed. The application of the above procedure to calculate the critical pressure disturbance $\Delta P/\bar{P}$ is based on the premise that near P_{DYL}, $\Delta P/\bar{P}$ is much smaller than unity. And for a small pressure deviation, the extinction criterion remains close to what it is when the pressure is held constant.

This study indicates that both the natural flame oscillation and the forced flame vibration widen the nonflammable range of the solid propellants at low pressure. However, the extent of the influence of the pressure-forced vibration on extinction is narrower than we first expected, i.e., $\Delta P/\bar{P}$ increases very fast as the pressure goes away from P_{DYL}. Influence of the velocity disturbance may have a much larger effect on the flammability limits, but two or three dimensional analyses are required to analyze this.

This analysis cannot be applied directly to solid-propellant strand burning in air[10] because most solid propellants are fuel rich and a diffusion flame surrounding the normal flame zone will modify the rate of heat loss. The model is, however, expected to be valid for propellant burning in inert gases and in rocket combustors.

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