

Effect of Temperature on the Burning Rate of Solid Propellants: A Review

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Abstract

THE initial temperature of a solid propellant influences the burning rate and affects the performance of a rocket motor. A review of the literature reveals that a very thin zone beneath the burning surface is conceived to be effectively heated and important. However, this is not fully recognized in the quantitative prediction of the effect of temperature on the burning rate. Therefore, studies emphasizing the role of condensed and gas phase processes in different solid propellants are presented in this review so that there is some basis for unifying theories for predicting the effect of temperature on burning rate and other related properties like extinction, radiation effect, and deflagration pressure limit.

Contents

Generally, burning rate (\dot{r}) will increase with initial temperature (T_0) and this variation of \dot{r} with T_0 at constant pressure (P) is defined as the temperature sensitivity (σ_P) of \dot{r} and display $\sigma_P = 1/\dot{r}(\partial\dot{r}/\partial T_0)_P = (\partial \ln \dot{r}/\partial T_0)_P$. The influence of T_0 on a very thin zone beneath the burning surface² and the physico-chemical processes must have measurable effect on \dot{r} and other related properties in homogeneous solid propellants, ammonium perchlorate (AP) monopropellant, and composite solid propellants.

Homogeneous Solid Propellant

The work of Zenin and Nefedova,³ over a wide temperature interval, supports the fact that increase in σ_P ($\sigma_P = 22.4 \times 10^{-10} \times T_0^{2.6}$) is determined by the heat liberated in the condensed phase (CP) in which the residence time of the intermediate products of gasification is also important. Suggestive reasons for the nonuniform combustion at $T_0 < 50^\circ\text{C}$ and $P = 1$ atm include processes like the detachment of yellow nitrocellulose fibers from the surface which forms the char. Considering the mutual interplay of the regimes of CP and gas phase (GP), Miller⁴ has attempted to elucidate the relation between the fundamental chemical and physical properties with σ_P , P , and T_0 . In the work of Suh et al.,⁵ it is quite implicit that by varying T_0 and P , i.e., by disrupting the rate of thermal energy required for the steady state burning and the rate of heat transfer, the effects of reactions responsible for the flatness of the temperature distribution in CP, self extinction, and steady burning could be explored.

Externally imposed radiation, which is equivalent to increasing the T_0 , accelerates CP reactions in a thin layer and increases the \dot{r} . Reflectivity considerations of the carbonaceous material on the burning surface and sufficient opacification by particulate additives account for lower \dot{r} values. If higher radiative heat fluxes induced extensive surface reactions,

assumptions that σ_P is constant break down due to changes in the values of σ_P and the theory fails.⁶ The photochemical processes responsible for the enhanced surface heat release have to be considered and re-examined. The "equivalence principle" (equivalence between heat absorbed and increase in T_0), which has been established⁷ to explain why the \dot{r} in motors exceeds strand burning rates, provides sufficient information to determine the surface heat release, and supports the fact that radiant influences are thermal. However, precise conditions under which equivalence exists have not been reported.

Ammonium Perchlorate Monopropellant

One of the interesting aspects of AP is the existence of a low-pressure deflagration limit (P_L), which decreases with increase in T_0 . Most of the studies reported earlier were directed towards explaining the existence of P_L and its interrelationship with T_0 . Watt and Petersen⁸ ascribe the existence of P_L to the molten zone and not to any interparticle processes. It is felt that the influence of melt and its enhancement on deflagration may be so profound that by altering the temperature of the reaction layer in the CP, (i.e., T_0), one could possibly observe the conditions for the existence of P_L . Although Guirao and Williams⁹ have considered exothermic CP reactions in a liquid layer at the burning surface, the effect of T_0 has not been predicted. However, the Naval Weapon Centre (NWC) model¹⁰ appears to predict the σ_P and considers the CP as an important energy source for self-deflagration. Based on the criterion of mass burning rate at P_L , general agreement that \dot{r} increases with T_0 and decreases with P_L is found from the equation $K = P_L^{0.5} \exp \sigma_P (T_0 - T_0^*)$ where K is a constant and T_0^* is the reference temperature. However, the basis for incorporating a value of 0.5 for the pressure exponent is not indicated.¹¹ A plausible explanation for the variation of σ_P with P has been provided by Boggs et al.¹² and the differences between the authors on this aspect is clarified as due to the potassium impurity present to different levels in the sample used. Another explanation by Strunin and Manelis¹³ is based on a simple expression $\sigma_P = E/2L (1/T_{m'} - T_s) + 1/T_s - T_0$ where L is a parameter representing saturated vapor pressure and $T_{m'}$ is the maximum temperature of decomposition. At low pressure, the decrease in σ_P is found to depend on T_0 and slightly on the decomposition and vaporization activation energies, while at higher pressures, increase in σ_P is determined by the decomposition and vaporization activation energies only. Therefore, it seems that a concerted and more definite explanation for the variation of σ_P as a function of P is necessary.

Composite Solid Propellant

Attempts to explain satisfactorily the temperature dependence of \dot{r} have been renewed and devoted to model studies. The existing analysis based on GP and CP consideration is fragmentary. According to Glick,¹⁴ the rate controlling process is believed to occur in the GP in which the reaction zone acts to reduce the temperature-induced \dot{r} changes. AP flame temperature, explained as being more sensitive to T_0 than the primary flame,¹⁵ is questionable from the considera-

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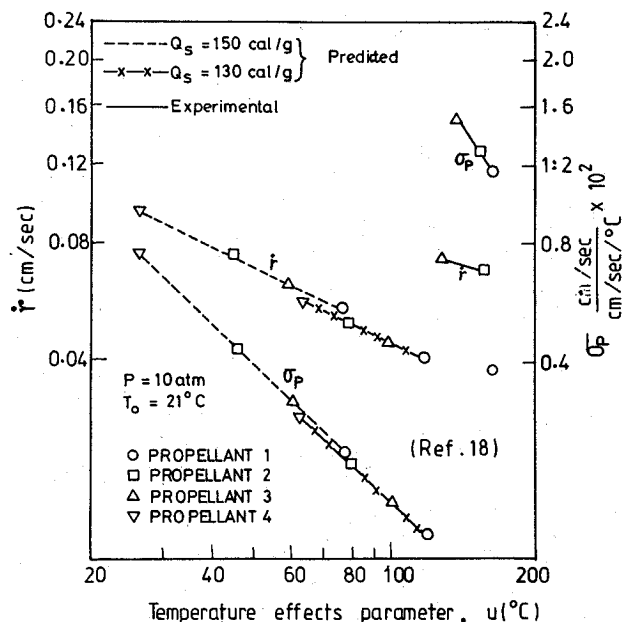


Fig. 1 Effect of activation energy and surface heat release on \bar{r} , u , and σ_P .

independent of T_0 . From a study of the relative effects of T_0 on the reaction time and diffusion time parameters, Blair¹⁶ has found that certain models neither represent the data nor predict the extinction phenomenon. If the pressure deflagration limit in composite solid propellants is to be explained, modification of theories, like that of Ref. 11, where the pressure exponent is not a function of T_0 , is required.

From CP considerations, the most significant parameter is probably the value of heat released (Q_s) at the burning surface.¹⁷ The parametric study of Ewing and Osborn¹⁸ shown in Fig. 1 indicates that some propellants follow the predicted trend while others do not. The intermittent burning, explained as due to the molten fluid nature of the binder covering the oxidizer at the surface, casts some difficulty in explaining the behavior of the polybutadiene acrylic acid based propellant as the binder does not melt in a certain pressure range. The pressure at which it occurs is also not predicted. It is believed¹⁹ that the presence of cracked carbonaceous layer covering the oxidizer perturbs the oxidizer-fuel ratio causing local self-extinction. Catalyzed studies have indicated that the increase in \bar{r} or reduction in σ_P is not produced solely by changes in T_s and surface heat release but by decrease in the diffusion time parameter than the reaction time parameter.

Prospective

1) There is a need to develop a suitable model for predicting the temperature dependence of \bar{r} ; 2) attention must be given to the use of the thermocouple and other exploring techniques for extracting information from the temperature profile over a wider range of T_0 ; 3) more efforts are needed to understand the dependence of P_L on T_0 ; 4) precise explanation for the variation of σ_P with P is needed; 5) a contour diagram between

\bar{r} , P , and T_0 might be helpful to get a real picture of \bar{r} dependence on P and T_0 ; 6) since catalysts alter reactions at the surface, supplementary studies of the effect of T_0 need to be applied to unravel the processes responsible for intermittent burning, propellant extinction, and mesa effects.

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