Plateau Region of Composite Propellants

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I. Introduction

A MAJOR concern with the development of some present and next-generation solid-propellant rocket motors is stability during operation. Considering the characteristic times of the instability modes in some motors and the characteristic time associated with composite solid-propellant burning rates, it is possible to speculate that solid propellants that exhibit plateau burning-rate regimes may be less prone to destructive instabilities. Although there have been various attempts to determine the reasons for plateau conditions, the phenomenon still remains an enigma to solid-propellant scientists. This Note offers a new qualitative analysis and concept, peculiar to composite propellants, that could provide further understanding as to why plateau conditions could occur and how they could be used beneficially.

II. Approach

The qualitative evidence has been that plateau burning-rate effects are most frequently found for polyvinyl chloride (PVC) plastisol propellants and particularly those with low concentrations of ammonium perchlorate (AP). Interestingly, propellants containing potassium perchlorate (KP) as an oxidizer have not appeared to exhibit a plateau burning region. A possible explanation of these trends based on kinetic and thermochemical analyses has been formulated and is offered in the following paragraphs.

A burning-rate mechanism for composite solid propellants based on a granular-diffusion-flame model was offered by Summerfield et al.[1] and led to the following burning rate expression:

$$1/\dot{r} = (a/P_c) + (b/P_c^{1/3})$$

where $\dot{r}$ is the linear burning rate, P_c is the chamber pressure, a is a parameter related to the gas-phase reaction kinetics of the propellants, and b is a parameter related to the diffusive character of oxidizer gas pockets in a gaseous fuel vapor. Although this characterization of the composite-propellant burning rate does not explicitly correlate with experimental results for all propellants, it does appear to correctly characterize the trend that at lower chamber pressures gas phase chemical kinetics play the dominant role in determining the burning rate and at higher pressures diffusion effects control.[1] With this general consideration, it is possible to offer a reasonable analysis as to why plateaus occur in $\ell n\, \dot{r}$ vs $\ell n\, P_c$ curves.

Burning composite propellants containing low concentrations of AP are considered to exhibit two compensating effects as the pressure is raised. Although the combustion (flame) temperature increases with pressure at low concentrations of AP, the actual temperature is relatively low for propellant systems. Thus, important kinetic effects can come into play, particularly for PVC plastisol propellants. The reason for these effects, particularly with PVC, appears to be due to the presence of the chlorine atom in the binder. Thus, PVC augments the chlorine atom concentration in perchlorate propellants.

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The chemical reaction rates that sustain the combustion process in propellant deflagrations are not that different from any hydrocarbon–oxygen flame process; i.e., the overall rate of the reactions is controlled by the extent of radical chain branching, which is dominated by the simple step[2]:

$$H + O_2 \rightarrow OH + O \tag{1}$$

As in the explanation of simple H_2–O_2 explosion limits, as the pressure is increased, the following effective three-body chain-terminating step begins to slow the reaction process:

$$H + O_2 + M \rightarrow HO_2 + M \tag{2}$$

where M is any third body removing the energy of association.[2] The general importance of the high-pressure competition between these two reactions, even at higher temperatures, has been shown recently.[3] At the higher pressures of composite propellant combustion the increase of temperature with pressure is mild, so that the more temperature-sensitive reaction 1 is overtaken by the more pressure-sensitive reaction 2 (Ref. 3). This aspect has been verified experimentally in premixed laminar flames,[4] as shown in Fig. 1, in which, at the stoichiometric equivalence ratio, it was found that the laminar flame speed of methane in air dropped by 44% in a change of pressure from 0.5 to 2 atm. The numerical calculation of the flame speed based on the chemical reaction of methane included the kinetic rates of both reactions 1 and 2.

Further, and of importance for propellant considerations, is that the presence of chlorine serves as a homogeneous catalyst for the recombination of H atoms, further reducing the reaction rate, according to the simple reaction sequence[2]:

$$H + Cl_2 \rightarrow HCl + Cl \tag{3}$$

$$H + HCl \rightarrow H_2 + Cl \tag{4}$$

$$Cl + Cl + M \rightarrow Cl_2 + M \tag{5}$$

$$\text{overall} \quad H + H \rightarrow H_2 \tag{6}$$

Note again that there is another pressure-sensitive three-body recombination reaction. The more chlorine present, the slower the reaction rate. This chlorine effect also has been verified in simple laminar flame speed studies.[5]

Thus, as the pressure is increased for a composite AP propellant, the burning rate will rise until a given pressure level is reached, then the reaction 2–5 sequence becomes chain terminating and slows the reaction. Thus, although the temperature will rise with an increase in pressure, due to the now slower reacting system, the propellant flame front moves further from the propellant surface. These two opposing effects compensate and no increase of burning rate with pressure should be observed; a plateau exists over a given range of pressures. Indeed, due to the character of the binder and the overall chlorine content there is no reason to preclude a mesa condition; i.e., a drop in burning rate with pressure, as observed in the drop in flame speed of halogenated hydrocarbons in air.[5] These halogenated hydrocarbon data are shown in Fig. 2 in which a 50–50% mixture of methane and chloromethane shows a drop in flame speed of about 50% over pure methane.

The plateau region is essentially limited since at still higher pressures the granular diffusion mechanism begins to dominate and diffusion effects become controlling.[1] In this high-pressure diffusion-controlled regime the combustion temperature continues to increase somewhat with pressure, the overall heat flux to the propellant surface increases due to this higher temperature, and an increase in the mass ($D\rho$ and/or thermal $\alpha\rho$) diffusivity term. D is the mass diffusivity, α the thermal diffusivity, and ρ is the gaseous density. $D\rho$ and $\alpha\rho$ are insensitive to pressure, but increase with temperature since D varies ap-

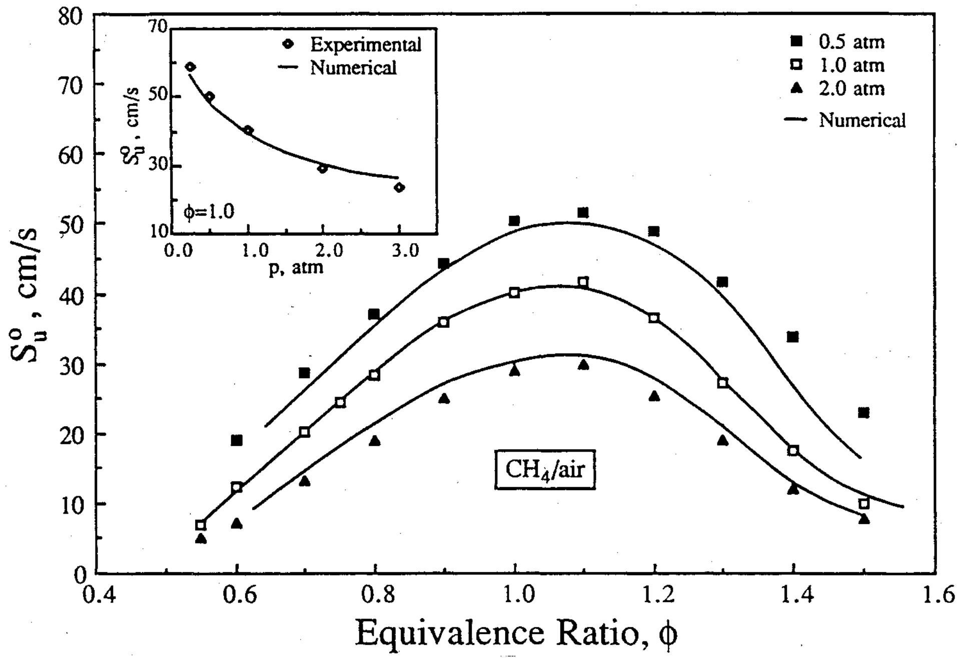

Fig. 1 Experimentally and numerically determined laminar flame speed S_u^o for methane/air as a function of equivalence ratio ϕ and pressure (Ref. 4).

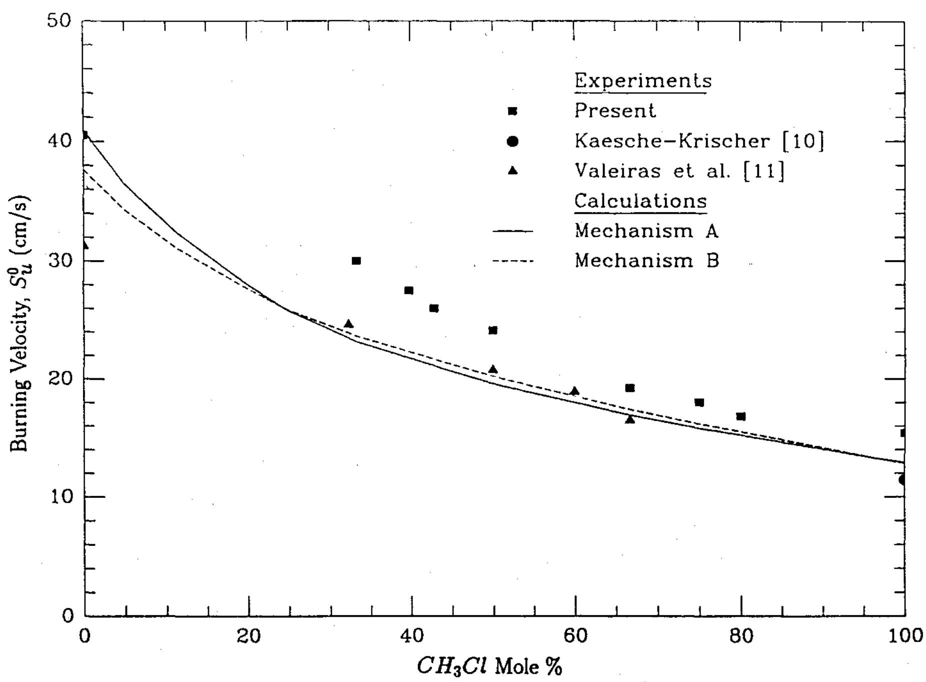

Fig. 2 Variation of stoichiometric values of the burning velocity S_u^o of chloromethane, methane, and air as a function of chloromethane mole % in the fuel (Ref. 5).

proximately as T to about the 1.76 power and ρ as T to the inverse first power. The mass diffusion effect means the gaseous oxidizer pockets[1] are consumed faster and the flame moves closer to the surface. The thermal effect $\alpha\rho$, as well, increases the rate of heat transfer.

The situation is quite different for KP propellants because thermodynamics reveal that KCl is the preferred product to HCl. Thus, the likelihood of chlorine being an inhibitor to the radical pool decreases substantially. This effect, and the fact that KP propellants produce higher temperatures than AP propellants, are the most probable reasons no plateau is observed with KP propellants. These factors could explain, as well, the higher pressure coefficients found with KP propellants.

It is important to note that because of the higher temperatures reached with highly loaded AP and aluminized propellants, pressure plateaus should be mostly nonexistent in these systems. Nevertheless, a concept has been proposed that suggests it may be possible by the control of kinetic rates to create plateau-like conditions for particular composite propellant formulations existing today and to be developed in the future. Such propellants may be less prone to combustion instabilities.

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Magnetic Flow Meter Measurement of Solid Propellant Pressure-Coupled Responses Using an Acoustic Analysis

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Introduction

THE traditional methods for measuring solid propellant pressure-coupled responses such as the T-burner and modulated exhaust burner[1] are based on deducing the response by matching measured pressure oscillations, both amplitude and phase, with an acoustic analysis of the flow inside the test apparatus. The pressure-coupled response in the acoustic analysis is varied until the predicted pressure oscillations match the measured ones. These methods are indirect and are only as accurate as the acoustic analyses themselves.

Wilson and Micci[2] have developed a technique based on magnetic velocimetry for directly measuring a solid-propellant pressure-coupled response by simultaneously measuring the pressure and velocity oscillations (both amplitude and phase) in the combustion product gas above the surface of the burning solid propellant. The nondimensionalized ratio of the velocity to the pressure oscillations gives the complex acoustic admittance of the burning propellant surface from which both the real and imaginary components of the pressure-coupled response can be calculated. The technique developed by Wilson and Micci used the measured pressure and velocity oscillations immediately above the burning propellant surface as the propellant surface regressed past the measuring station. The data that was used to obtain the acoustic admittance was taken during a very small fraction of the total propellant strand burn time and several tests at each frequency of interest were required to obtain statistical confidence in the results.

This study used an improved version of the magnetic flow meter burner developed at ONERA Palaiseau Center combined with an acoustic analysis of the standing wave above the surface of the burning propellant strand to use velocity and pressure oscillation data taken from the surface of the propellant to as far as 1.2 cm above it, increasing the statistical confidence in the calculated acoustic admittance. The analysis itself is not required to obtain the propellant pressure-coupled response, shown by Wilson and Micci,[2] unlike the case with the T-burner and the modulated exhaust burner. Its validity is also ensured because it is applied only over a short distance above the burning propellant surface, minimizing heat losses that are not modeled. This analysis also allowed the simultaneous derivation of the magnetic flow meter calibration coefficient, eliminating the need for separate calibration tests.

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Experiment

The magnetic flow meter burner measures the velocity of the combustion product gas by applying a strong magnetic field (1860 G in this experiment) and measuring the strength of the electric field generated by the ionized combustion product gas moving through the magnetic field.[2] The electric field is equal to the cross product of the gas velocity and the magnetic field:

$$\boldsymbol{E} = \boldsymbol{u} \times \boldsymbol{B} \tag{1}$$

The electric field is measured by placing two electrodes in the periphery of the flow at right angles to both the magnetic field and the flow direction. The voltage measured is given by

$$V = \alpha u B l \tag{2}$$

where α is a nondimensional coefficient between 0.0-1.0 and l is the distance between the electrodes. The coefficient α is a function of a phenomenon known as end-shorting caused by a nonspatially uniform magnetic field[3] and must be determined experimentally. The magnetic field was generated by a permanent magnet. Both mean and oscillatory pressures were measured with a piezoelectric transducer. The propellant strands were cylinders that end burned on the flat surface. A pressure oscillation at the frequency of interest was generated

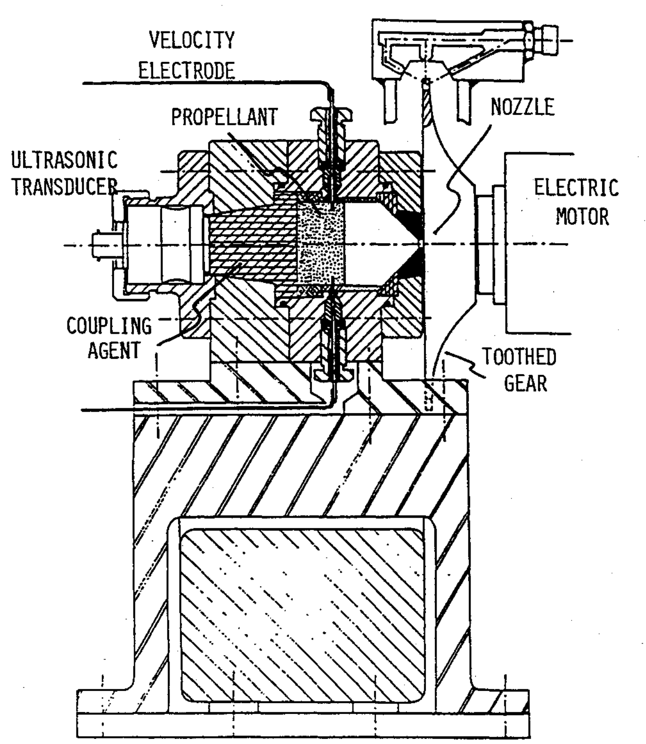

Fig. 1 Magnetic flow meter burner viewed perpendicular to the axis of the motor showing the installation of the velocity electrodes and the ultrasonic transducer.