Strand Size and Low-Pressure Deflagration Limit in a Composite Propellant

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The low-pressure deflagration limit, LPDL, has been determined for a composite ammonium perchlorate propellant over a range of pressures from 35 to 235 torr. The independent variable was strand cross section area. A linear relation was found between the LPDL and the inverse of the "hydraulic radius" of the strand. It was thus possible to extrapolate and determine the low-pressure limit for a strand of infinite extent. It can be argued that such an infinite strand is adiabatic. A possible mechanism to explain a finite extinguishing pressure for an adiabatic strand is the lack of sufficient oxidant in the gas phase due to differences in the rate of change of fuel and oxidizer gasification rates with decreasing pressure.

I. Introduction

SOME time ago we attempted to examine the structure of the combustion zone above a strand of composite solid propellant by means of interferometry. In order to increase spatial resolution we expanded the zone by burning propellant strands at subatmospheric pressure in a chamber which could be continuously pumped and which was provided with windows for observation. For reasons that we probably should have anticipated we fell somewhat short of our primary objective. In the course of our experiments, however, we did obtain some data on the low-pressure deflagration limit, LPDL, for two composite propellant compositions. In particular, we determined the dependence of LPDL on strand size. It seems in order to record these results because they may provide some grist for the theorist's mills and shed some light on the nature of the combustion process mechanics.

The realization that LPDL depends on strand size is not new. Sutherland noticed when he ignited wedge-shaped strands of a composite propellant from the thick end that the point at which they extinguished depended on the ambient pressure.[1] That is, the higher the pressure the thinner could be the web of the wedge at which combustion could be sustained. He did not present any quantitative details. More recently, Steinz and Summerfield[2] report that the LPDL for one of their propellants was decreased by a factor of two when the strand size was increased in cross section from 0.25 to 0.6 in.[2] In common with Sutherland these investigators explained this trend in terms of relative heat loss by convection and conduction to the ambient atmosphere. On the other hand, in their studies of the deflagration of pure ammonium perchlorate strands Levy and Friedman indicate that the LPDL was independent of sample size.[3] Consequently, Johnson and Nachbar ascribed the important heat loss to radiation from the burning surface in their attempt at an exact treatment of the LPDL of ammonium perchlorate.[4] Most theoretical treatments of solid-propellant combustion attribute the existence of an LPDL to the nonadiabaticity of real experimental systems.[4,5] However, Barrère and Williams do suggest that mechanisms other than heat loss might be responsible.[6] Our results hint that alternatives to the heat loss explanation might well be contemplated. We emphasize the point that all of our considerations relate to "ordinary" deflagration and not to the kind of flameless combustion which was observed by Wenograd et al.[7]

II. Experimental Apparatus and Procedures

The main features of the apparatus are shown schematically in Fig. 1. The low-pressure chamber comprised a standard 6-in. Pyrex pipe cross (Corning). The open ends of the cross were closed by covers made of aluminum plate with O-ring seals between the plate and grooves ground into the Pyrex. Various leads for electrical, mechanical, and gas connections were introduced through the cover, which also were provided with plane windows for viewing and photography. Many features of the apparatus relate primarily to interferometry problems and will not be discussed here. The chamber was continuously exhausted by a mechanical rotary vane pump, which had sufficient capacity to maintain the chamber pressure at any desired value from 40 to 200 torr with propellant strands up to 1 in.[2] in cross section. Control of the pressure was by means of a globe valve in the exhaust line between the pump and the chamber. It is noteworthy that at subatmospheric pressures the burning rate for most propellants is directly proportional to the first power of the pressure. Thus, the volume flow of combustion gases is almost independent of pressure. Because the volumetric efficiency of the pump increases slightly with pressure there is an inherent stability in the pressure control loop. This is fortunate from the safety standpoint as well as for experimental convenience. We noted that with the large strands the increased heat release could lead to "uncomfortably" high temperatures in the chamber. In one case some soldered joints in the top cover actually were melted. Dousing with water was required to avoid failure. We strongly advise provision of effective cooling in future experiments of this sort, not only to preserve the integrity of the equipment but to prevent the increase in volume flow rate that would accompany high temperatures.

Ignition presented something of a problem because it was desirable to provide combustion initiation that was uniform across the strand surface. The most satisfactory method of the several tried was to lower onto the surface a section of nichrome strip wider than the propellant strand. Passing an electric current through the strip raised the temperature and resulted in fairly uniform ignition. In most cases the burning surface tended to level out during burning even though

Presented as Paper 69-144 at the AIAA 7th Aerospace Sciences Meeting, New York, January 20–22, 1969; submitted May 1, 1969; revision received November 7, 1969. This work was supported by the Office of Naval Research through Project SQUID, Contract No. 1858 (25) NR-098-038.

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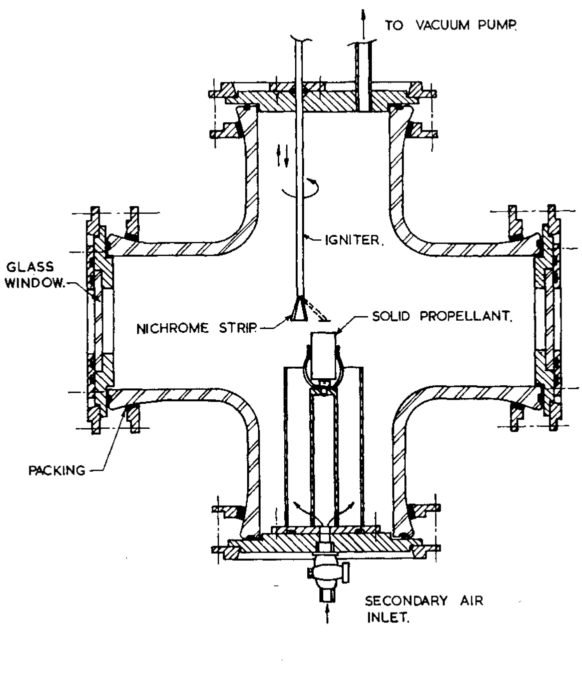
initiation was not uniform. In order to obtain the minimum burning pressure each sample was ignited at a pressure above the minimum value and the pressure was gradually decreased by opening the control valve until the strand ceased to burn. The process was repeated at least once for each strand size. It was found that the pressure had to be reduced fairly slowly in order to obtain reproducibility. Rapid reduction in pressure resulted in large variations in apparent extinguishing pressure. With care, reproducibility was within a few per-cent.

The propellant composition was essentially the same as that used by Silla in his measurements of burning velocity at low pressure.[8] The fuel binder was P13 polyester resin. The oxidizer was ammonium perchlorate in one of two particle grinds: 25 μ or less and 80 μ or less. Measurements were made with compositions having either 78 or 80% by weight of oxidizer. No inhibitor was used. The strands were rectangular in cross section. The long dimension was always 1 in. The short dimension ranged from $\frac{1}{16}$ to 1 in.

III. Results and Discussion

The raw experimental data are summarized in Fig. 2, which shows a plot of extinction pressure vs strand thickness. There is a clear functional dependence of LPDL on strand size. The hotter propellant (80% oxidizer) burns to a lower pressure than the cooler one for a given strand size. The two points for the finer grind 78% oxidizer composition indicate little dependence on particle size in this range. There are too few data to draw firm conclusions on this point. The form of the curves indicates two asymptotes. In one limit there appears to be a minimum strand size below which combustion cannot obtain no matter what the pressure. This apparent limit probably is neither meaningful nor realistic because we know that the character of the combustion changes from a premixed to a diffusion flame mode as the pressure increases. Consequently, any conclusions drawn from extrapolation would have to be treated with great caution.

The other and more interesting asymptotic limit relates to the apparent possibility that there is a pressure below which steady-state combustion will not occur no matter what the size of the strand. As we already have indicated, such a low-pressure limit has been predicted by theoretical treatments for the case in which the system is not completely adiabatic, i.e., there is heat loss to the surroundings.[4,5] Such heat losses in the case of one-dimensional strand models generally can be attributed to conductive and convective loss to the ambient gas and to radiant loss from the surface as well as from the burned gases. It is to be expected that the relative heat losses due to convection and conduction and to radiation from the burned gas would depend upon the surface to volume ratio of the hot gas column rising from the burning surface. It is instructive, therefore, to recast the data in terms which will reflect this surface to volume ratio.



LOW PRESSURE TEST VESSEL.

Fig. 1 Low-pressure combustion chamber.

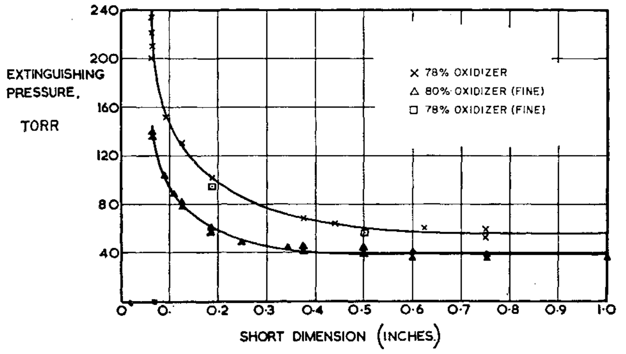


Fig. 2 Dependence of extinguishing pressure on strand size. Variation of minimum composite propellant strand dimension with extinguishing pressure.

Figure 3 shows a plot of the LPDL vs the ratio of strand perimeter to cross section area. This ratio is, of course, simply the inverse of the "hydraulic radius" which has been very useful as a measure of wall effects in flow through conduits of various shapes. The data for each composition appear to fall on a straight line that is extrapolated readily. The abscissa intercept would seem to correspond to the LPDL for a strand of infinite cross section. In such a case the main heat loss should be by radiation from the surface. It is just this kind of heat loss that the theoretical treatments have contemplated. Unfortunately, it is not easy to relate the exact theories to our experimental situation. Our composite propellant is much more complex than the theoretical models and we cannot assign appropriate values to the important parameters. Moreover, it is not entirely clear to us that extrapolation to infinite cross section does not also eliminate loss due to radiation from the surface. In a real limit of infinite cross section the surface would effect a net loss of heat by radiation only if it could "see" cool surroundings through an infinite depth of hot gas that is not entirely transparent. In fact, therefore, it would not see the surroundings. Thus, from the perspective of the surface the system might be adiabatic. If this is the case and if our extrapolation limit really corresponds to a burning surface of infinite area, we would have to seek an explanation for the LPDL of an infinite strand in some mechanism other than simple heat loss.

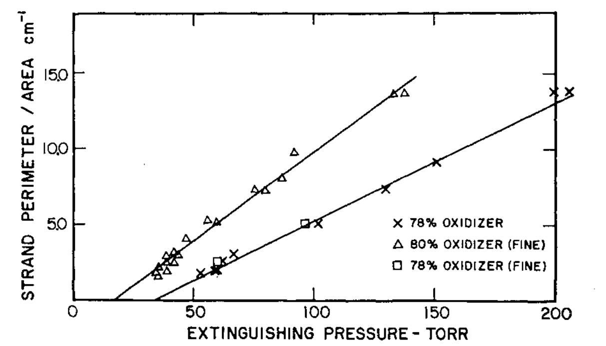


Fig. 3 Dependence of extinguishing pressure on inverse hydraulic radius.

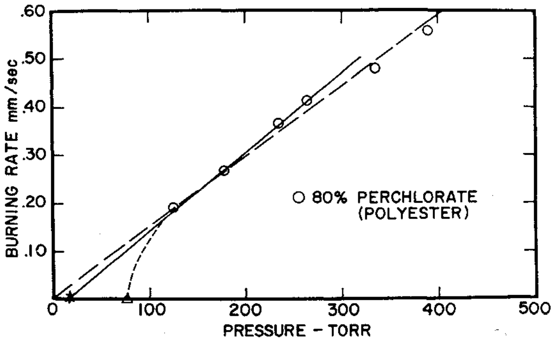


Fig. 4 Silla's data on pressure dependence of burning rate.

In light of this possibility it is instructive to look at burning rates in the low pressure range. In particular the results of Silla are relevant because he used a propellant that was essentially identical with our 80–20 composition.[8] Figure 4 shows his results. The dashed line through the origin is equivalent to the line he drew through his points. The asterisk on the abscissa is the intercept value for the same propellant resulting from the extrapolation to infinite strand size in Fig. 3. It becomes inviting to draw the solid line shown in Fig. 4 as the extrapolation of burning rate data to the vanishing point. Clearly, the intercept is the same for both extrapolations. It is noteworthy that for the strand size used by Silla (0.25 × 0.25 in.) the pressures at which he made measurements are quite far to the right of the corresponding curve in Fig. 3. Thus, they may be considered free of heat-loss effects. This consideration is confirmed by the absence of any downward curvature in the solid line of Fig. 4.

Of course, strands of the size that Silla used will show a vanishing burning rate at pressures much higher than the "possibly adiabatic" limit shown by the asterisk on Fig. 4. We can estimate from Fig. 3 at what pressure this should occur for a 0.25 × 0.25 in. strand. The result is shown by the triangle on the abscissa of Fig. 4. The dotted curve represents a guess as to what the intermediate burning rate/pressure relation might be.

In sum, the extrapolation of Silla's burning rate data to zero velocity and the extrapolation of our LPDL data to infinite strand size both lead to the same finite positive value of pressure at which the burning rate vanishes, i.e., the flame is extinguished. Because it can be argued that both limits relate to adiabatic conditions, the possibility materializes that the existence of an LPDL may stem from a mechanism other than heat loss. We would be the first to insist that the arguments are by no means conclusive. However, we are able to suggest one possible alternative mechanism.

Measurements by several methods indicate that the activation energy for linear pyrolysis is larger for ammonium perchlorate than for many substances used as fuels. There are, of course, many questions raised about the meaning of linear pyrolysis measurements. Nevertheless, it seems quite certain at least that the vaporization rate for perchlorate decreases with decreasing surface temperature faster than the vaporization rate for fuel. As pressure is decreased without limit the surface temperature also will decrease. Consequently, at some value of the pressure the vaporization rate may become so much less for oxidizer than for fuel that the rich limit for combustion in the gas phase will be exceeded. This trend is illustrated in Fig. 5. On the ordinate is plotted the logarithm of the ratio of the linear pyrolysis rate for ammonium perchlorate to that for polymethyl-methacrylate. The abscissa is the inverse of the temperature in degrees Kelvin. We chose data from ONERA as reported by Barrère and Williams because both fuel and oxidizer rates were determined under the same conditions.[6] The break in the

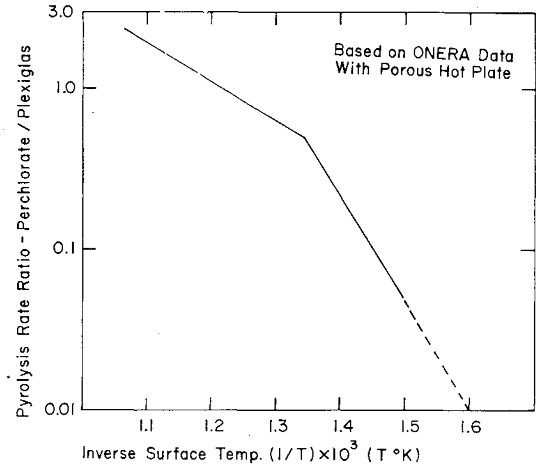


Fig. 5 Temperature dependence of relative pyrolysis rates for typical fuel and oxidizer.

curve corresponds to the change in slope in the pyrolysis curve for ammonium perchlorate that has been observed by several investigators. It is clear that, indeed, the gas phase will become fuel-rich as temperature decreases. To be sure, a propellant strand will try to compensate for the decrease in oxidizer vaporization rate by providing a larger surface area of perchlorate as the fuel recedes more rapidly. There must be a limit to this compensation because if the fuel surface goes too far "below" the oxidizer surface it will be shielded from the hot gas and will not receive enough heat to vaporize. Even before extinction occurs it might be expected that a fragile superstructure of oxidizer particles would develop that might periodically be swept away by the burning gas. Steinz and Summerfield have observed just this phenomenon in their studies of propellant burning at low pressure.[2] Our suggestion merely complements their proposal that extinction may occur because of oxidizer depletion.

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