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Effect of Multidimensional Flamelets in Composite Propellant Combustion

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This article reviews the results of a series of studies involving two-dimensional models of combustion of solid propellants. The results presented are selected to illustrate the role of the kinetically limited leading-edge portion of the oxidizer/fuel "diffusion" flamelets in controlling burning rate and aluminum agglomeration. Included are results from "sandwich burning," gas burner, numerical modeling of the two-dimensional flame, and tests on propellants to validate the applicability to propellants.

Introduction

THE mechanistic features of combustion of composite solid propellants differ conspicuously according to the kind of ingredients, scale of heterogeneity, and pressure. All propellants burn by decomposition, combustion, heat release, and heat return to the burning solid to sustain decomposition. Most analytical models are based on this "one-dimensional" view of burning. In this view of burning, the progress of chemical reactions is distributed in one dimension. It is recognized that heat release may occur at several locations, e.g., condensed-phase, surface, and gas-phase reactions. Problems arise in analytical modeling when the scale of heterogeneity of the propellant (e.g., particle size of oxidizer) is large enough for significant lateral temperature gradients in the microstructure, and for long enough mixing times of decomposition products (in surface liquid layers and gas phase) to limit reaction rates. The modeling problems are greatly aggravated when the melting and decomposition temperatures of the ingredients are markedly different. This is clarified by examples in Table 1. Another factor important to this article is the exothermicity of the oxidizer/fuel (O/F) flame (comparisons in Table 1). This article is concerned with propellant systems in which the oxidizer and binder decompose at comparable temperatures and in which the gas phase oxidizer/binder flame is strongly exothermic. These features are typical of combustion of most ammonium perchlorate/hydrocarbon (AP/HC) binder propellants. For such propellants a major part of the heat release can occur in an array of hot microflamelets standing in the mixing O/F flows ("mixing fans") formed above the oxidizer/binder contact lines on the burning surface. This is illustrated in idealized form in Fig. 1, using a two-dimensional microstructure for simplicity.

Modeling of AP/HC binder propellants[1,2] has sought to accommodate the deviations from one dimensionality in a variety of approximations involving the determination of some kind of average heat release and standoff distance of the AP flame and parts of the O/F flame. The averaging process is necessitated by the presence of a range of particle sizes, but usually ends up with some form of one dimensionalization that decouples the individual flamelets from the surface sites that feed the flamelet reactions. Considering the complexity of a rigorous model for a chaotic propellant structure, it is easy to understand why such approximations are used in models, and why the combustion details are often studied in simpler two-dimensional experiments as pictured in Fig. 1. The goal of this article is to look at the local details and nature of the O/F flamelets and see how they couple to the burning surface. The discussion will rely extensively on the experiments and analyses of two-dimensional models of propellants.

Before embarking on a discussion of O/F flamelets, it is appropriate for the sake of perspective to consider further the conditions under which such flamelets are present and are important. Under some conditions, such as those for which diffusion rates are high compared to O/F reaction rates, the O/F flame is premixed and approximately one dimensional (e.g., very fine AP or low pressure, or both). At very low pressure (i.e., low for rocket motor applications), all gas-phase reactions become so slow that little if any heat is returned to the burning surface and burning may be sustained by reactions in the condensed phase that are usually relatively unimportant at motor pressures (1000 psi). In heterogeneous propellants such low-pressure (subatmospheric) burning ordinarily occurs only if fine AP and/or catalysts are used in the propellant to enhance O/F reactions. The following observations are for typical AP/HC binder propellants in the pressure range 100–2000 psi:

1) The O/F reaction occurs in three-dimensional flamelets anchored in the mixing "fans" of oxidizer and fuel vapors that are in turn anchored at the contact lines of oxidizer and fuel on the surface.[3]

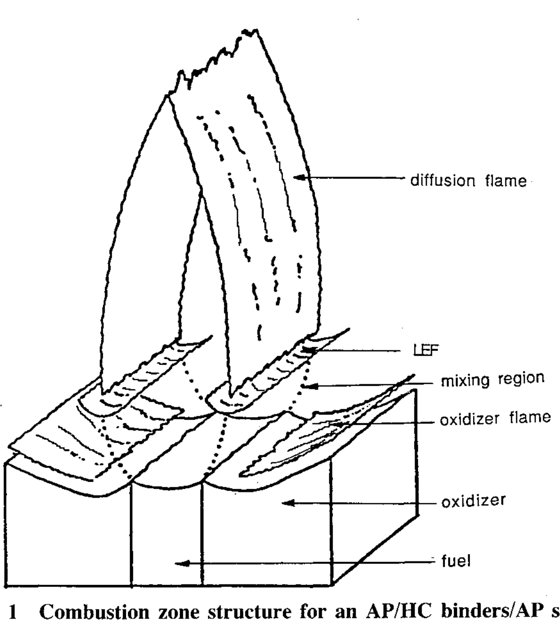

Fig. 1 Combustion zone structure for an AP/HC binders/AP sandwich.

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Table 1 Approximate comparison of ingredient thermal response and energetics of oxidizer/fuel flames

Ingredient	Melting temperature, °C	Vaporization (decomposition) temperature, °C	Energetics of decomposition	Energetics of O/F flame
PBAN binder	480	500	Endothermic	——
HTPB binder (DDI-cured)	260	500	Endothermic	——
NMMO binder	85	200	Mildly endothermic	——
AP oxidizer	~580[a]	Rapidly above 400	Exothermic	——
AN oxidizer	145	245	Endothermic	——
KP oxidizer	——	400	Endothermic	——
HMX oxidizer	255	290	Exothermic	——
ADN oxidizer	90	165	Exothermic	——
CL-20 oxidizer	——	270	Exothermic	——
Aluminum	673	2493	Very endothermic	——
AP/PBAN	——	——	——	Very exothermic
AN/PBAN	——	——	——	Exothermic
HMX/PBAN	——	——	——	Nearly neutral
ADN/PBAN	——	——	——	Very exothermic

[a] Decomposes before melting except at heating rates $>10^5$°C/s.

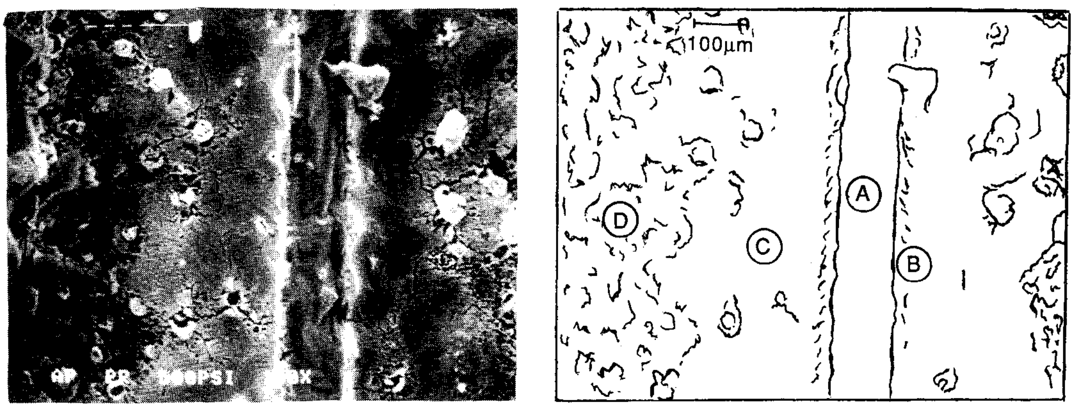

Fig 2 Details of an AP/PBAN/AP sandwich quenched by rapid depressurization from 500 psi (3.46 MPa): Ⓐ surface of the binder lamina, Ⓑ AP protruding along the laminas contact plane, Ⓒ location in a band of smooth surface (AP), concave upward. The leading edge of the burning front is located here, and Ⓓ frothy inclined surface typical of AP self-deflagration.

2) These flamelets are the principal site of heat release, coupled locally to the surface structure via the mixing fans.[3]

3) The part of each flamelet that is closest to the surface is most favorably located for returning heat to the surface, and is particularly intense because it consumes the accumulation of mixed O/F vapors prepared upstream of the "ignition point."

4) While the overall nature of the flamelet array is controlled by the rate of diffusion in the mixing fans, the location of the critical leading edge of each flamelet is also dependent on chemical kinetic rates in the mixing fans.

Modern combustion models for AP/HC binder propellants all incorporate these features (except the latter part of item 2) in one form or another.[4,5] The purpose of this article is to present and discuss studies aimed at determining the nature and role of the O/F flamelets more fully. These studies include edge burning of oxidizer-binder sandwiches, a gas burner study aimed at clarifying the nature of the leading-edge portion of the O/F flame, a numerical simulation of this leading-edge flame (LEF), and investigations aimed at determining the role of LEFs in ignition of aluminum. These studies used two-dimensional simulation of propellants to facilitate the observation, modeling, and interpretation of results. In this regard it should be understood that the critical features of the combustion zone occur on a dimensional scale of less than 100 μm (at motor pressures), below the spatial resolution of direct real-time experimental measurement. As a result, conclusions concerning experimental results are based on a variety of experimental data such as burning rate vs pressure and lamina thickness, observations of surfaces of quenched samples, and dependence of surface profiles on test variables. The gas burner studies were conducted at atmospheric pressure to facilitate detailed measurements.

Results from Combustion of AP/HC Binder Sandwiches

Studies of edge burning of laminates made up of alternate layers of oxidizer and fuel have been conducted by several investigators over the last 30 years; most of these studies are described in Ref. 5. For those studies that simulate propellant combustion, the features of the combustion zone are similar to those in the sketch in Fig. 1. The AP laminas are thick enough so that most of the edge surface of each self-deflagrates independently of the O/F flame, with an inclination that is determined by the relative burning rate of the sandwich and the AP (Fig. 1). The sketch shows the AP self-deflagration flame [which probably includes exothermic reactions in a surface froth (Fig. 2)]. The curvature of the AP surface profile closer to the lamina contact plane is an indication of heat flux from the O/F flame, with the point of maximum regression being the site of maximum net heat flux, and the rate-determining point (maximum heat in, minus heat loss by lateral heat flow). There is usually a region immediately adjacent to the binder lamina where the AP regression is retarded due to lateral heat loss to the (endothermic) binder lamina.[3] As can be seen in Fig. 2, the surface quality of the AP is different in the region that is heated by the O/F flame.

On theoretical grounds, one can argue that the stoichiometric surface in the mixing fan above each contact plane extends out over the AP surface because the oxidizer is relatively dilute compared to the binder. It can also be argued that the LEF will be centered on the stoichiometric surface, while the curvature of the AP surface profiles indicate that the LEF is close to the surface (e.g., 50 μm or so). As shown in Fig. 1, there is one LEF for each contact plane. Because the overall stoichiometry of the sandwiches discussed here are usually oxidizer-rich (i.e., thin binder laminae), the trailing diffusion flamelets "close" over the binder as in the sketch (Fig. 1). However, under propellant-like conditions, the sandwich binder lamina is usually very thin, the sandwich LEFs are close together, and the diffusion flame "tent" is very short. The LEFs are so close together that they may be coupled, consuming most of the fuel, leaving little for the diffusion limited parts of the flame tent (Fig. 3). The effect of this trend is evident in the dependence of sandwich burning rate on thickness of the binder lamina (Fig. 4). For binder thicknesses greater than 125 μm, the rate is relatively independent of thickness, indicating that burning is proceeding as two uncoupled burning fronts (with protruding binder in-between). A maximum burning rate occurs for thickness in the 50–75-μm range, a result that is explained[3] as optimum for LEF sharing of the fuel supply while minimizing heat "loss" through lateral heat flow to excess fuel that flows out between the LEFs without local exothermic reaction. For thinner fuel laminas the burning rate is lower because of insufficient fuel for the LEFs, so that the burning rate tends towards the AP self-deflagration rate as the thickness of the binder lamina approaches zero. These observations, described in more detail in Ref. 3, give an idea of the role of LEFs in sandwich burning, of the relevant dimensional scales, and of how they depend on pressure and lamina thickness. The relation to burning of a fuel-rich system with propellant-like microstructure is not too difficult to visualize (Fig. 5), except for the details of particle burnout, etc. The results are consistent with modern computational models in which it is found that LEFs are the primary source of heat to drive the combustion wave at intermediate pressures, with AP self-deflagration becoming more important above 1000 psi. There is direct evidence that condensed-phase or surface O/F interactions are not important in the >300-psi range in burning of AP/HC binder/AP sandwiches.[3]

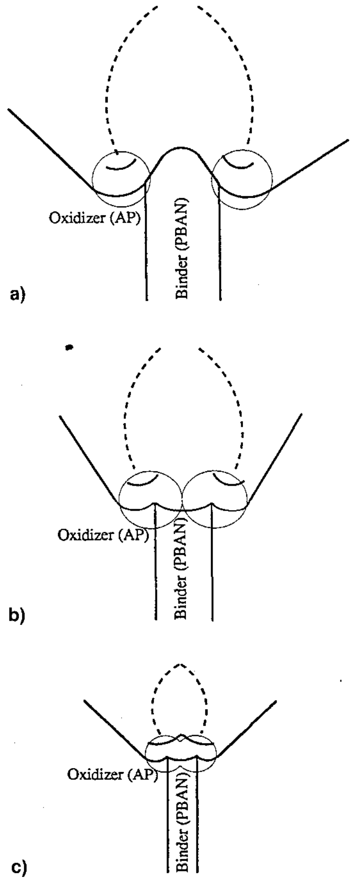

Fig. 3 Dependence of flame complex on thickness of binder lamina. Circles around LEFs indicate their domain of influence: a) thick binder lamina, b) 70–100 μm, and c) $\sim$50 μm.

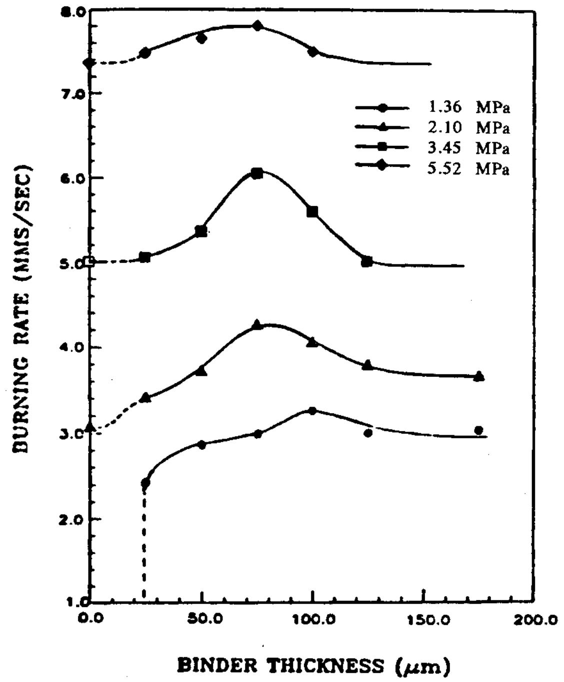

Fig. 4 Dependence of sandwich burning rate on thickness of the binder lamina.

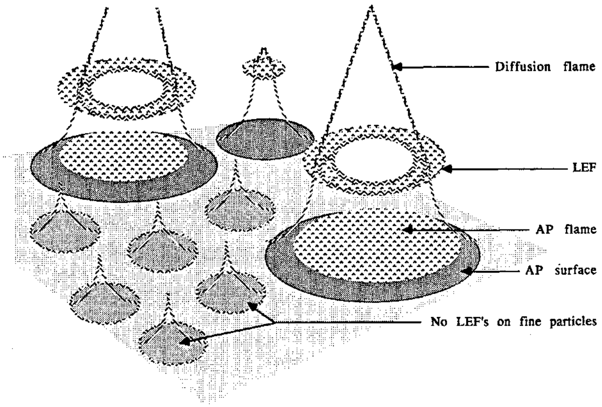

Fig. 5 Sketch of flame complex for a propellant with particulate AP.

As noted in Ref. 5, the results of sandwich burning studies by different investigators do not all agree. The disagreement appears to be due to the differences in binder and the failure to examine the effect of thickness of binder laminas (and widespread use of large thicknesses).

The results presented here are for polybutadiene acrylonitrile acrylic acid (PBAN) binder laminas of low thickness compared to most other sandwich-burning studies (for relevance to propellants). Tests with other binders showed some differences (example in Fig. 6) that appear to be related to tendency of some binders to form a melt layer that flows onto the AP surface. This is uneven and nonsteady along the edge of the laminas, causing a loss of two dimensionality of the combustion, including sometimes faster burning down one

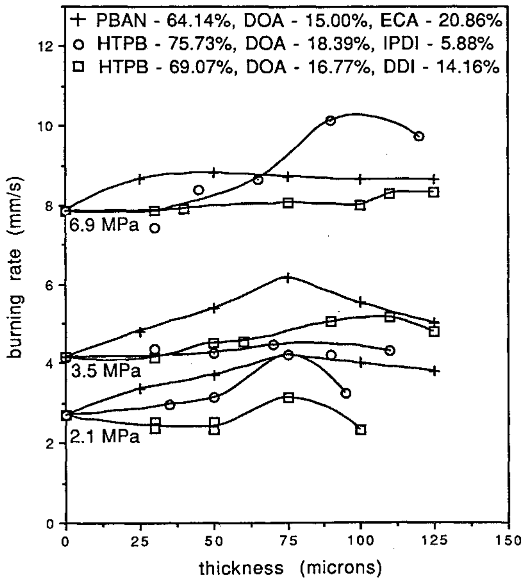

Fig. 6 Comparison of sandwich burning rates for different binders: burning rate vs binder lamina thickness.

interface than the other. The test results are simpler and easier to interpret when melt flow effects are minimized as with PBAN binder, but more attention to melt flow effects is needed because widely used binders such as dimeryl diisocyanate (DDI)-cured hydroxyl-terminated polybutadiene (HTPB) are prone to melt effects, evident even in sandwich burning rates (Fig. 6). It is not yet clear what O/F flamelet arrays result when binder melts encroach on the oxidizer surface, and it seems unlikely that all past sandwich burning studies (or propellant burning studies) can be reconciled without learning more about how the melt flow proceeds, and about the corresponding effects on surface pyrolysis and flamelet arrays. Melt flow is minimal with the PBAN binder used in most of the studies reported here.

Effect of Burning Rate Catalysts in AP/HC Binder/AP Sandwiches

A number of investigators have added catalysts to the AP laminas, binder lamina, or contact planes, with various proposed catalytic mechanisms.[5] In the present studies, catalysts were added to the binder lamina, in order to simulate propellants.[6,7] An example of test results is shown in Fig. 7. In interpreting the results the following was noted:

1) There is only limited exposure of the catalyst to the AP decomposition region or to the AP-binder interface (because the catalyst particles are in the binder), suggesting that rate enhancement involves the binder decomposition or the LEF, or both.[7]

2) Simple catalysis of decomposition of the binder would not in itself affect burning rate much because the effect would primarily be to cause the binder surface to be recessed a little more.[8]

3) The presence of particulate catalyst in the mixing fan and LEFs would not have much catalytic effect because of limited collision rate with catalyst.

4) The effective catalysts were observed to concentrate on the binder surface, where preliminary binder-decomposition fragments have high collision probabilities in passing through the "catalyst bed"; even the Catocene catalyst produced iron oxide concentration on the binder surface.

5) The catalysts are known to be effective in "cracking" heavy hydrocarbons.

6) Flames with heavy hydrocarbons are known to form only where the hydrocarbons have pyrolyzed to more reactive light species.

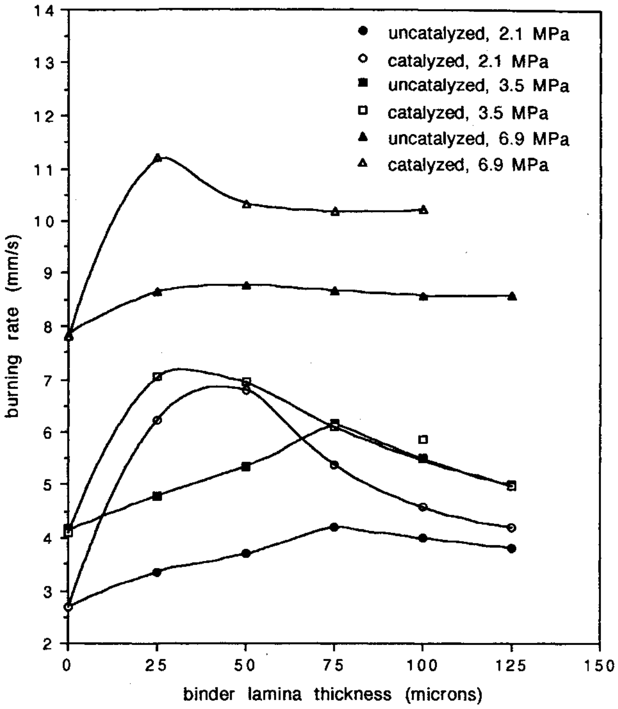

Fig. 7 Effect of Fe_2O_3 catalyst (10%, 2 μm, in the binder lamina) on the burning rate of AP/PBAN/AP sandwiches (from Ref. 6).

From these observations it was concluded[6,7] that in these tests the catalyst acted by supplying more reactive fuel fragments to the LEFs, allowing the LEFs to locate closer to the surface with correspondingly higher heat flux to the surface. This interpretation is supported by the fact that the burning rate and surface profiles showed dependence on thickness of the binder lamina and on pressure similar to that observed with uncatalyzed sandwiches. Thus, the catalysts effectively catalyze the LEF, but actually act at the binder surface by decomposing the heavy binder-vapor fragments. In this regard, it is emphasized that the response of the LEF is responsible for the burning rate increase. It will be seen in a later section that the catalyst may act in a different way when higher contact area of AP, binder, and catalyst exists.

Conditions for Presence of LEFs, and LEF Coupling

An investigation was made[9–12] of the burning of sandwiches in which the "binder" lamina was a matrix of PBAN binder and fine AP (10 or 33.5 μm) with AP contents of 50 and 70%. With such fine AP particles, the AP and fuel vapors can diffuse together before appreciable O/F reaction, giving a premixed flame if the mixture (e.g., 70% AP) is not too fuel rich to burn. At high pressure with 33.5-μm particles, there was evidence in quenched samples that LEFs and AP self-deflagration occurred on individual particles, (no such evidence for 10-μm particles, or for 33.5-μm particles at 300 psi). For 50/50 matrices this was evident only adjoining the lamina contact planes, indicating coupled behavior between lamina LEFs (LLEFs) and particle LEFs (PLEFs). The burning rates of the sandwiches with AP-filled binder laminae are shown in Fig. 8 (PBAN binder).

In interpreting the results in Fig. 8, it should be noted that the matrix mixtures are fuel-rich, even at a 70/30 ratio. The 50/50 mixture would not burn on its own, and quenched sandwiches showed matrix surfaces that were dominated by solidified binder melt (except as noted above). If one looks at the matrix as a "diluted fuel lamina" and repeats the argument about location of the interlamina mixing fan, stoichiometric surface and LLEF, one would expect them to be shifted closer to the "extended" plane of the lamina contact surface (Fig. 9), reflecting the effect of a less concentrated fuel. One effect

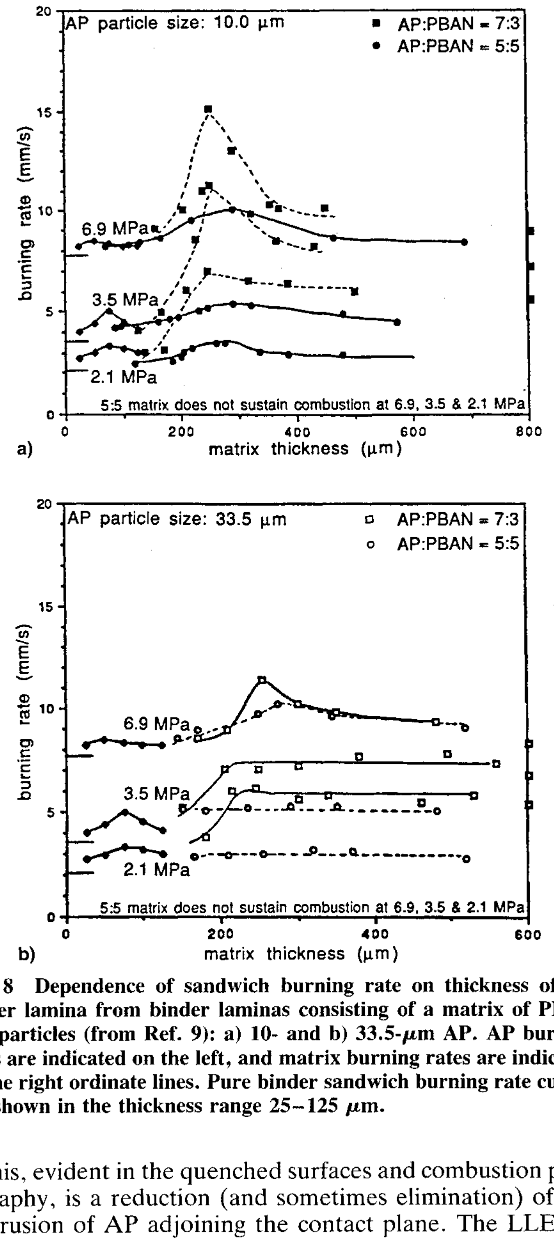

Fig. 8 Dependence of sandwich burning rate on thickness of the binder lamina from binder laminas consisting of a matrix of PBAN and particles (from Ref. 9): a) 10- and b) 33.5-µm AP. AP burning rates are indicated on the left, and matrix burning rates are indicated on the right ordinate lines. Pure binder sandwich burning rate curves are shown in the thickness range 25–125 µm.

of this, evident in the quenched surfaces and combustion photography, is a reduction (and sometimes elimination) of the protrusion of AP adjoining the contact plane. The LLEF is located more favorably to heat this region than in the pure binder case, and also more favorably to reduce lateral heat loss to the fuel lamina by supplying more LEF heat directly to the fuel lamina.

The premixed AP vapors in the "diluted" matrix outflow are, of course, more than a diluent. On the fuel-rich side of the LLEF they are a combustible mixture, that extends the fuel rich side of the LLEF out over the matrix. This increases the total heat release in the LLEF, enabling the flame to stand closer to the surface and give a higher burning rate than resulted with pure binder laminas (Fig. 3), and higher than the matrix burning alone (indicated at the right in Fig. 8). The thickness of matrix lamina for maximum burning rate is around 250 µm, as compared with 50–75 µm for pure binder lamina. This is consistent with the interpretation described for pure binder laminas if one allows for 1) the greater extent of the fuel-rich side of the LEFs that leads to attainment of LLEF coupling at greater thickness of the matrix laminas and 2) the fuel supply becomes deficient with decreasing lamina thickness at greater matrix thickness because the fuel is dilute.

The nature of the O/F flame complex for matrix sandwiches is sketched in Fig. 10, based on theoretical reasoning and experimental results. For a 70/30 mixture with 10-µm AP, the LLEFs act as flameholders for a premixed "canopy" flame over the matrix lamina (Figs. 10b and 10d). For a 50/50 matrix the canopy is open (thick laminas) because the matrix does not support a flame alone (Figs. 10a and 10c). However, the fuel-rich side of the LLEF extends further than with pure binder, as noted earlier, because a flammable mixture is present. The burning rate of the samples with 70/30 matrices is higher than with 50/50 matrices at all matrix thicknesses except the lowest, suggesting that the size and location of the LLEFs (Fig. 10) are 1) closer to the surface and 2) more favorably

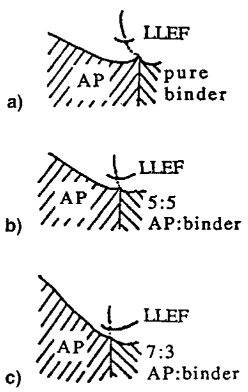

Fig. 9 Shift in LLEFs when the binder is "diluted" with AP a) narrow LLEF, over AP lamina. Heat flow from AP lamina to binder lamina, AP regression retarded at laminas contact plane; b) wider LLEF, stoichiometric point closer to surface and shifted toward laminas contact plane. Less lateral heat flow in solid, less retardation of AP at contact plane. More conservative LLEF, closer to surface, correspondingly higher rate; and c) wider LLEF, stoichiometric point over outer edge of AP lamina. LLEF extends well over matrix lamina, probably minimal lateral heat flow in solid.

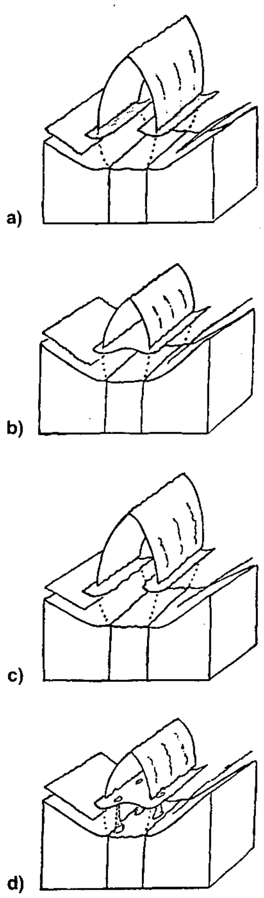

Fig. 10 Flame complex for sandwiches with AP-filled binder laminae (300-µm matrix lamina, 500 psi, 3.45 MPa): a) 50/50 AP/PBAN matrix, 10-µm AP; b) 70/30 AP/PBAN matrix, 10-µm AP; c) 50/50 AP/PBAN matrix, 33.5-µm AP; and d) 70/30 AP/PBAN matrix, 33.5-µm AP. Refer to Fig. 1 for an explanation of general features.

located laterally to heat the matrix surface and minimize lateral heat loss in the condensed phase into the matrix lamina. The quenched samples indicate that the sandwich burning rate is determined by LLEF-assisted regression of the AP lamina, as noted earlier for pure binder laminae.

The effect of particle size of the AP in the matrix gives important clues to the details of the O/F flamelets, as follows:

1) Effect of particle size (i.e., 10 and 33.5 μm) is small for 50/50 matrix ratio, and for 70/30 ratio at 300 psi. This suggests that under these conditions the matrix outflow is essentially premixed at the LLEF standoff height and premixed canopy flames (Figs. 10a and 10c) result.

2) Burning rates are higher with 10-μm AP than with 33.5-μm AP in the 70/30 matrix at 500 and 1000 psi, suggesting that mixing is not complete for the 33.5-μm AP (thereby limiting the contribution of the fuel-rich side of the LLEF to the rate).

3) A relatively strong maximum occurs in the rate vs lamina thickness curves (70/30 matrix at 500 and 1000 psi), especially for 10-μm AP. This indicates that the matrix flame does not

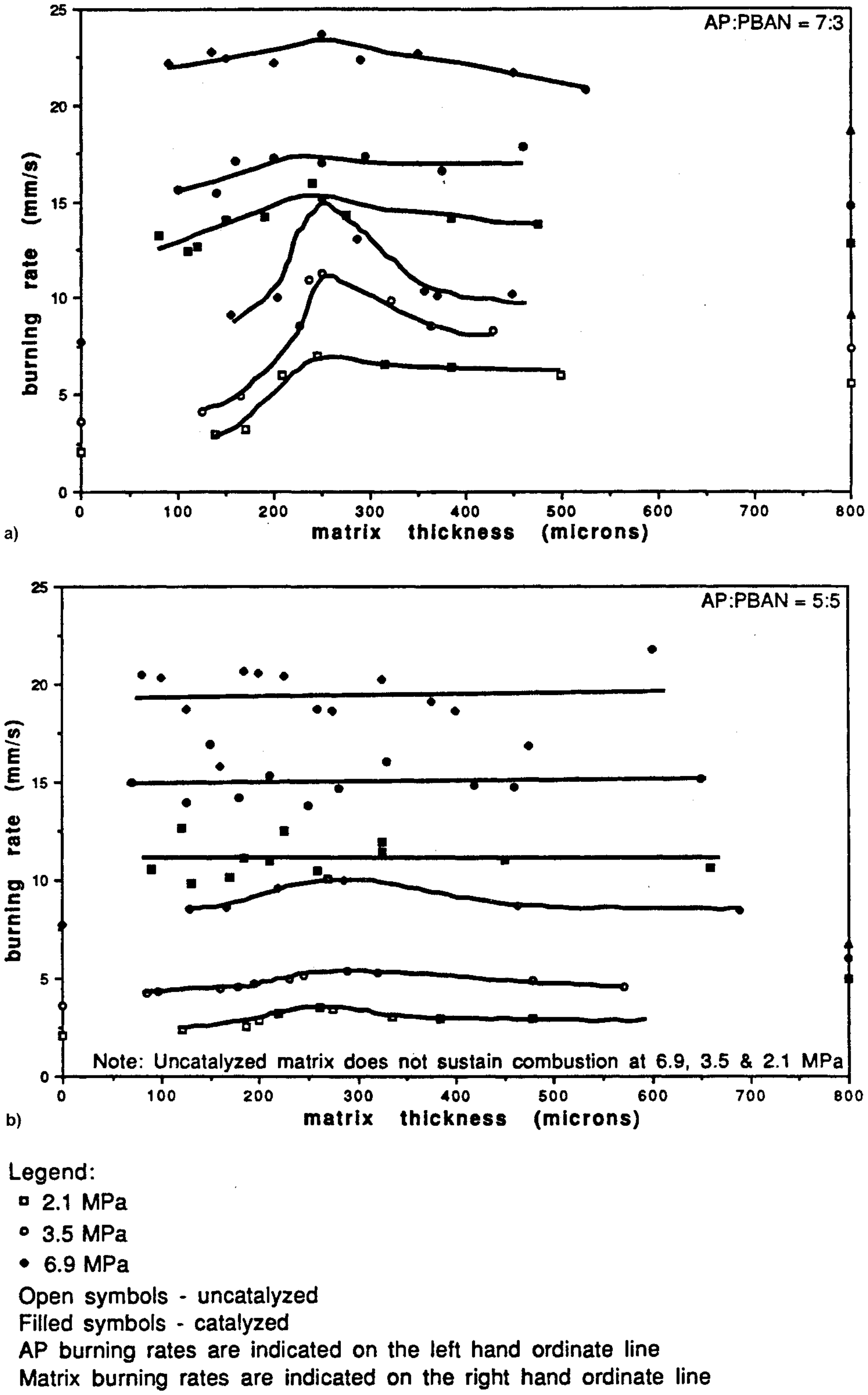

Fig. 11 Dependence of sandwich burning rate on thickness of the binder lamina for binder laminas consisting of a matrix of PBAN binder, fine AP (10 μm and 1% "Pyrocat" Fe_2O_3 catalyst: AP:PBAN = a) 7:3 and b) 5:5 (from Ref. 13).

control the rate, but rather enhances it via augmentation of the LLEFs. Extra matrix (i.e., thick lamina) apparently acts to drain heat (and possibly oxidizer species) from the rate controlling region of the sandwich.

4) The weaker maximum of the rate curves in 3 with 33.5-μm AP presumably reflects the weaker contribution of the fuel-rich side of the LLEFs due to incomplete mixing of the matrix outflow.

5) The quenched 70/30 samples that were burned at 500 and 1000 psi showed evidence that the 33.5-μm particles adjoining the AP laminae were burning individually (i.e., with PLEFs and AP self-deflagration). This may have been a factor in the burning rate, but it is notable that the same behavior was not evident with 10-μm AP, which gave higher burning rate.

Taken collectively, the results indicate that, for the conditions tested, the LLEFs dominate the burning rate, and that AP in the binder lamina enhances the LLEF effect by shifting the LEFF position and extending the fuel-rich side (and, hence, increasing LLEF heat release). Fine AP is more effective because more complete mixing has occurred at the LLEF height. The optimum lamina thickness for rate enhancement is around 250 μm for the conditions tested. Under the conditions tested the individual particles of AP either did not establish their own flamelets, or when they did (33.5 μm, 70/30, 500, and 1000 psi) no major effect on burning rate was evident. This suggests that in a typical bimodal propellant, the fine AP/binder matrix does not control the burning rate directly, but rather enhances the burning rate of the coarse AP particles. As the fine particle size and pressure increase, the fine particles burn more independently and enhance the coarse particle burning less (transition somewhere in the 500–1000-psi range for 33.5-μm AP in a 70/30 matrix, above 1000 psi in a 50/50 matrix).

Combination of Fine AP and Fine Fe_2O_3 in the Binder Lamina

An extension of the "filled" binder lamina studies was initiated by adding Fe_2O_3 to the matrix. Initially 10% of the 2-μm Fe_2O_3 used in the catalyzed binder lamina studies (described above and in Refs. 7 and 8) was attempted, using 10-μm AP and PBAN binder. Samples with 70/30 AP/PBAN ratio could not be processed, and samples with 50/50 ratio gave very erratic burning rates. A change was made to 1% of "Pyrocat" Fe_2O_3 (described by the manufacturer as 0.003-μm particles). Satisfactory results were obtained (Fig. 11, Ref. 13) with a major increase in the burning rate over similar samples without catalyst (Fig. 8). Addition of the catalyst increased the burning rate of the 70/30 matrix by about 100% at all three pressures, and caused the burning of the 50/50 matrix to be self-sustaining (matrix rates shown at the right in Fig. 11). The burning rates of the sandwiches with 50/50 matrix were about double the rate of the matrix alone and insensitive to lamina thickness. The rates of the sandwiches with 70/30 matrix were somewhat higher than the corresponding matrix, only mildly dependent on lamina thickness. The features of quenched samples are not yet completely available, but limited results show only a narrow portion of the AP laminas with the smooth surface quality, a narrow ledge that is no longer clearly "horizontal" (i.e., compared to the vertical laminas contact plane). As a preliminary conclusion, it appears that the LLEF plays a less important role in the burning rate in the catalyzed matrix sandwiches (some role is indicated by the fact that the sandwiches burn faster than the matrix alone). Many authors have argued that Fe_2O_3 acts by catalysis of reactions at the oxidizer/binder contact surfaces, an argument that is supported most strongly by burning tests of propellants at pressures near 1 atm. The evidence described in a preceding section for catalyzed binder laminas supported a contrary argument, but the situation is very different in the AP-filled binder laminas, because the amount of AP-binder contact area is enormously increased, and the very fine Fe_2O_3 has far greater surface area, more uniformly available in the solid. Thus, it seems plausible to assume that catalyzed contact-surface reactions contribute significantly or predominantly to the heat flow that determines burning rate in the catalyzed matrix sandwiches (the reactions may involve gas phase in microscopic interface crevises at contact surfaces). If LLEF heating were the primary factor in rate, one would expect a greater dependence of rate on lamina thickness than is evident in Fig. 11. It is possible that catalytic cracking of binder vapors also contributes to burning rate enhancement by bringing the LLEFs and the premixed matrix flame closer to the matrix surface in the manner argued earlier for the LLEFs in the case of sandwiches with catalyzed binder. Further study is needed.

Role of LLEFs in Behavior of Aluminum in the Combustion Zone

When powdered aluminum is used in AP propellants, the aluminum is observed to concentrate on the burning surface and depart as large agglomerates, a condition that can pose problems with combustion efficiency, slag formation, and prediction of combustor stability. A critical factor in agglomerate formation is the inflammation of the accumulating aluminum, which leads abruptly to the formation of a burning droplet that is too hot to remain on the burning surface. Several studies[14,15] suggested that inflammation of accumulating aluminum did not occur until exposed to the high temperatures of the O/F flamelets. This issue was examined by the introduction of aluminum powder in the binder laminae of AP/PBAN/AP sandwiches (binder laminae around 70 μm thick, pressure 500–1000 psi). Combustion photography and quenched samples showed sintered accumulations of aluminum, with inflammation always starting at locations nearest to the contact planes. Aluminum leaving the surface near the center of the binder lamina did not ignite near the surface (no oxidizer vapors). Sandwiches were then tested in which the aluminum was mixed with the AP before dry pressing (i.e., the AP laminae contained the aluminum). During burning, the AP surface became covered with a layer of sintered aluminum. This accumulation ignited only at the edge adjoining the contact plane where LLEF heating was present. Once ignited locally, the inflammation spread rapidly along the contact plane, and more slowly outward over the covered AP surface, forming one or more large burning agglomerates. Tests were

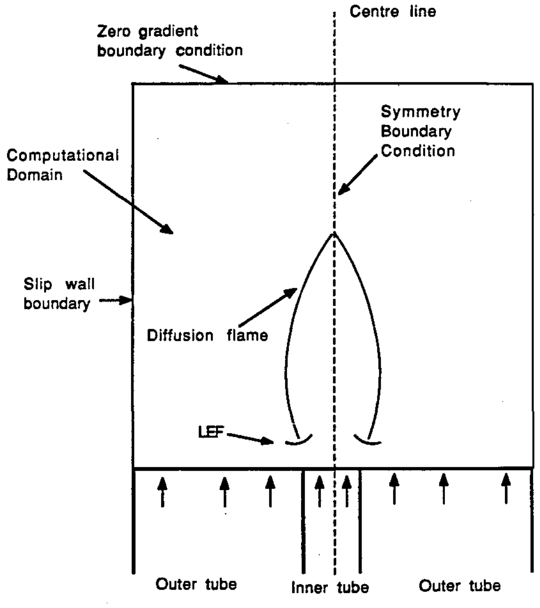

Fig. 12 Arrangement for a two-dimensional gas diffusion flame burner (numerical model and experiment).

also run on aluminized AP laminae alone (no binder lamina). The aluminum was observed to concentrate on the burning surface and leave the surface as large sintered accumulations with ignition and agglomeration being only occasional and apparently starting at sites where the sintered accumulations experienced break up. These results showed the critical role of the O/F flame in igniting surface aluminum accumulations, thereby limiting agglomerate size.

Theoretical-Numerical Analysis of Leading-Edge Flames

Because of the emergence of LEFs as a critical factor in edge-burning of AP sandwiches and propellants, it was decided to attack the problem of rigorous modeling of two-dimensional diffusion flames.[12,16,17] This effort was started because of the absence of direct observations of LEFs in propellant-sandwich combustion studies (because of inability to make such observations on microflamelets). In the modeling work the gases were assumed to emerge at the upstream boundary (Fig. 12) at specified velocity, density, and temperature (simulating a Wolfhard-type gas burner), and pressures near atmospheric were assumed (simulating a companion experimental study). Nonsteady laminar Navier–Stokes flow was assumed. Inlet gases were assumed to be $CH_4 + N_2$ in the center flow, and $O_2 + N_2$ in the outer flow. The chemistry was represented by a set of 48 elementary reactions involving 18 species. Temperature-dependent transport properties were used for each chemical specie. Details and computational methods are described in Ref. 16. Some notable results about LEFs are discussed here.

Figure 13 shows plots of distribution of species concentration, heat release rate (per unit volume), pressure, and flow direction (streamlines). Figure 13a shows the concentration of CHO, which is a short-lived intermediate product present only in the flame. There are locally high concentrations at the LEF sites. Figure 13b shows very high heat release rates at the same sites (high rates compared to the diffusion limited part of the flame further downstream), indicative of abrupt

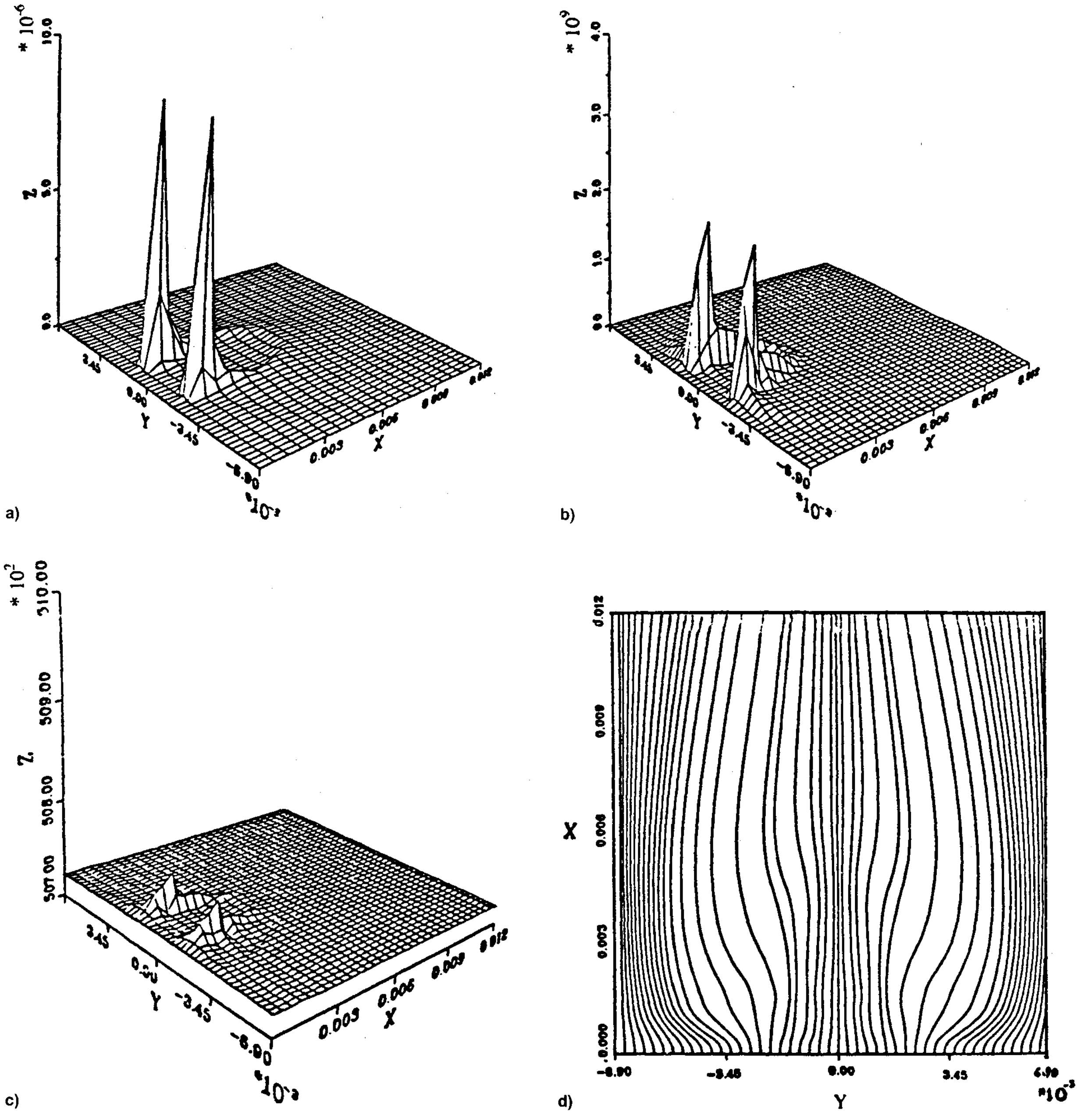

Fig. 13 Computed features of two-dimensional methane-air diffusion flame (N_2 diluted), burner configuration as in Fig. 12; *X* and *Y* dimensions are in meters; flow enters at lower left: a), b) and c), and at the bottom in d): a) CHO concentration (mass fraction); b) volumetric heat release rate (J/m^3 s); c) pressure [N/m^2]; and d) streamlines (Ref. 16).

consumption of the reactants that have mixed upstream of this site. Figure 13c shows that this concentrated reaction and the associated volume increase produce local pressure increases at the LEF sites, and Fig. 13d shows that this produces a divergence of the approach flow, as a result of which the vertical component of the velocity of the approach flow to the LEFs is reduced (i.e., does not increase as much as in a one-dimensional flame). These results support the idea of an intense leading-edge flame, an extended, less intense diffusion limited "tent" flame (Fig. 1). These computed LEFs show little lateral extent, contrary to those suggested in earlier sketches and discussion here. This "narrowness" is a feature of LEFs produced by combinations of pure fuel and oxidizer flows (i.e., diluted only by relatively inert gas). In a following section on LEFs in gas burner flames, crescent LEFs resulted when some fuel was included in the oxidizer inflow and some oxidizer in the fuel inflow. In the sandwich burning tests, the products of AP pyrolysis are a mixture of fuel and oxidizer species (e.g., NH_3 and $HClO_4$); and most of the binders, and especially the AP/binder matrix laminae, have oxidizer species in the laminae outflow. Thus, the propellant LEFs probably have appreciable lateral extent as suggested earlier in the discussion of the effect of addition of AP to the binder lamina.

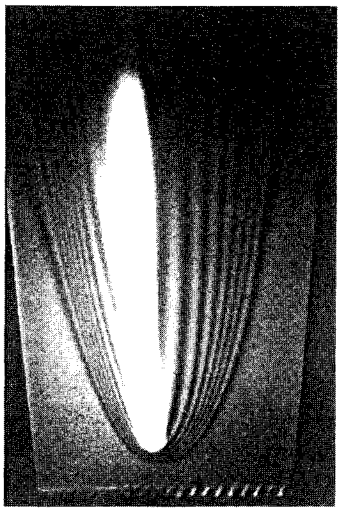

Fig. 14 Double exposure images of one of the two diffusion flames in the gas burner, viewed edge-on. The bright central plume is the flame viewed by self-luminosity. The surrounding lines correspond to isotherms, produced by monochromatic light interference fringes (M-Z interferometry) (Ref. 18).

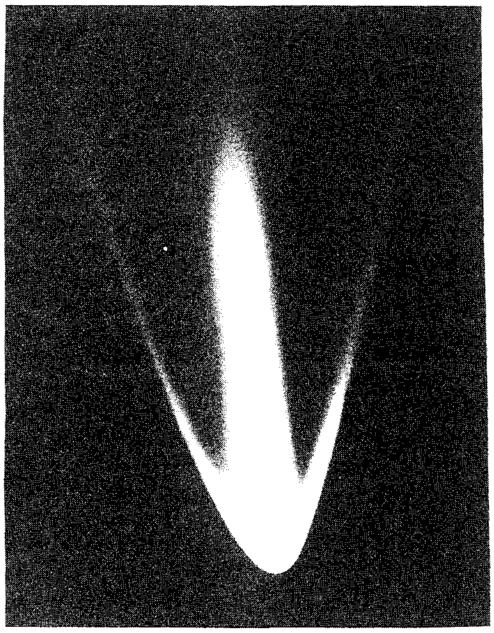

Fig. 15 Leading-edge flame in the gas burner when O and F inflows were enriched with F and O (mixtures well below flammability limits: methane-air with N_2 and CO_2 dilution, atmospheric pressure).

LEFs in Gas Burner Flames

To further verify the presence and nature of LEFs, a gas burner study was made[12,18] using a rectangular atmospheric pressure burner with a fuel flow in the middle and oxidizer flows on the outside (analogous to sandwiches and to the numerical study). A methane-air combination was used, with N_2 and CO_2 used as diluents. Outflow velocities were matched, but varied together from 15–50 cm/s. The flames were viewed edge-on photographically, including viewing with a Mach–Zehnder interferometer that permitted determination of the temperature field (example in Fig. 14). Temperatures were also measured with a traversing thermocouple. In addition, the flames were viewed side-on for intensity of CH radiation, a good indicator of heat release rate. The results of this study are detailed in Ref. 18. Some highlights are summarized here.

1) An intense leading-edge region of the flame was indicated in the CH intensity and temperature measurements, and the flame standoff distance from the burner surface was measured from photographs.

2) These LEFs were of limited lateral extent, consistent with results of the computational studies.

3) When fuel was added to the oxidizer flow and oxidizer added to the fuel flow, a crescent LEF resulted (Fig. 15).

4) The approach flow was deemed to be laminar, because turbulence would smear out interference fringes, an effect that was not observed (Fig. 14).

5) The "effective flame speed" of the LEF was taken to be the flow velocity from the burner, and was compared with the flame speed of one-dimensional premixed methane-air flames of the same temperature (Fig. 16). This effective flame speed was as much as 2.5 times the premixed flame speed.

In general, the experimental results were consistent with the numerical modeling results, indicating an intense, local LEF in the mixing fan, followed by a trailing diffusion limited flame with much lower heat release rate. The high effective

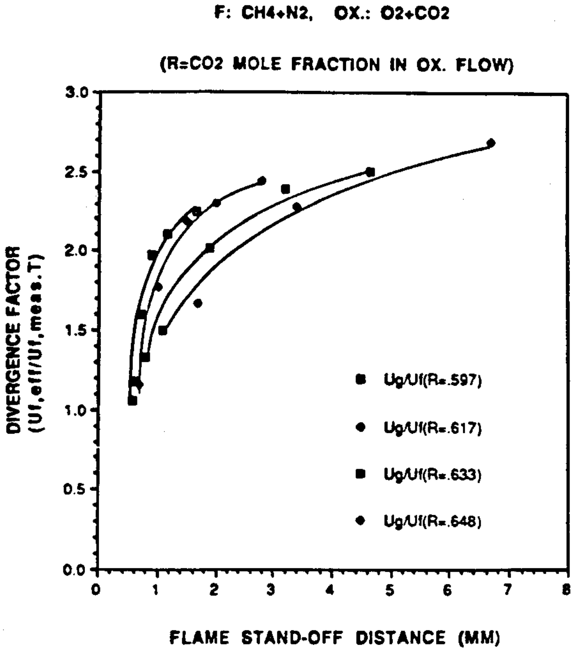

Fig. 16 Ratio of LEF speed to speed of methane-air flames of the same flame temperature (measured temperatures) (Ref. 18).

flame speed is presumably due to divergence and retardation of the approach flow to the LEF due to the pressure "island" (Fig. 13c) at the site of the LEF. The crescent flame (Fig. 15) supports the interpretation of sandwich burning tests in which the fuel flow was enriched by inclusion of oxidizer in the binder lamina. Similar LEF behavior (crescent LEF and high flame speed) has been reported[19,20] in stratified fuel-air mixtures in horizontal ducts. It may be worth re-emphasizing that this high effective flame speed is due to the high local heat release rate in the LEF, the resulting local pressure rise, and the resulting multidimensional convective flow in the neighborhood of the LEF. Not only is the upstream heat flow to the surface localized by the local nature of the heat source, but the location of the heat source is dependent on multidimensional aspects of both heat flow and gas flow.

Results with Propellants

The understanding of combustion of AP/HC binder sandwiches was applied in the present program to the granular AP propellant situation by two studies by Sambamurthi[21,22] and Beiter.[23,24] These investigations are summarized briefly here to demonstrate the role of the leading-edge flame in propellant burning.

In view of the critical role of the LEF in precipitating the ignition and agglomeration of aluminum accumulations on the burning surface, it was proposed[21,22] that this mechanism could be demonstrated by making and testing an aluminized propellant with bimodal oxidizer-particle-size distribution. In such propellants the burning surface consists of irregular arrays of coarse AP particles (400-μm mass mean diameter was used), with intervening areas consisting of a fuel-rich mixture of binder, fine AP, and aluminum. At low pressures the fine AP particles will decompose without "attached" LEFs (analogous to the results of Lee noted earlier), and the accumulating aluminum on the surface will be ignited by the PLEFs on the coarse particles. The whole area of accumulation between coarse particles will then coalesce, to give large agglomerates. If test pressure is increased, a threshold will be reached where PLEFs will occur in the O/F mixing fans of the fine AP particles. This in turn will provide a large increase in number and proximity of sites for ignition of the accumulating aluminum, with a corresponding decrease in agglomerate size. This postulate was tested by Sambamurthi, who prepared bimodal propellants with four different fine AP particle sizes. According to the mechanistic argument, the threshold pressure for onset of PLEFs on the "fine" AP particles would be lower for fine particles of larger size, so the corresponding threshold for decreases in agglomerate size would be at lower pressures. Sambamurthi used combustion photography and agglomerate quench tests[22] to determine agglomerate size. Figure 17 shows the trend of agglomerate size (mass average mean diameter) with pressure for the four sizes of fine AP used (17.5, 49, 82.5, and 196 μm). The results show an abrupt decrease in agglomerate size at a threshold pressure, as predicted in the foregoing scenario. The threshold pressure decreases with increases in AP particle size, as predicted. Keeping in mind that this rather singular trend in agglomerate size was forecast in advance on the basis of sandwich burning-based results and mechanistic arguments about leading-edge flames and aluminum ignition, the results are a good validation of the mechanistic argument. The results provide a mechanistic basis for the empirical "pocket" model of agglomeration proposed originally by Crump[25] and Price et al.,[26] and provide a more complete basis for the heuristic bimodal pocket model proposed by Cohen.[27]

The propellant study by Beiter has to do with the dynamic response of the combustion zone to pressure oscillations. In particular, the study considered the possibility that a large part of the dynamic response might result from the LEF behavior when the conditions are close to the threshold noted in the last paragraph. When the small particle LEFs are on the brink of detachment, their stability is marginal, and they may oscillate between an attached PLEF condition and a more remote premixed canopy flame configuration. It was proposed that, if a bimodal propellant with very narrow size distribution of the fine AP were tested for pressure-coupled response function, a large portion of the fine AP particles would reach PLEF threshold conditions at the same pressure. Above that pressure, dynamic response would be typical of burning with the PLEF flame complex, and below it the response would be typical of coarse AP PLEFS with premixed canopy flames over the areas of fine AP-Al-binder matrix. In-between those two domains it seemed likely that a greatly increased response might occur due to the marginal stability of the fine particle LEFs. This postulate was tested by running a series of T-burner tests over the relevant pressure range.[23,24] Figure 18 shows the response function vs pressure for tests at 500 Hz with a propellant with 17.5-μm fine AP. While the data scatter in this type of test is rather appreciable, it seems clear that a peak in the response function curve occurred at 275 psi (1.91 MPa). Tests with the other sizes of fine AP were less decisive,

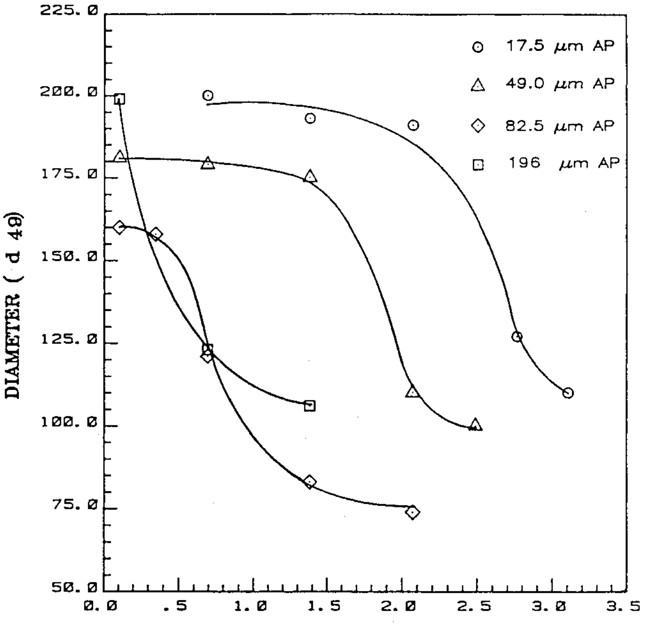

Fig. 17 Effect of pressure on mass average aluminum agglomerate size for propellants with coarse/fine AP in the ratio 8:2 (Ref. 22).

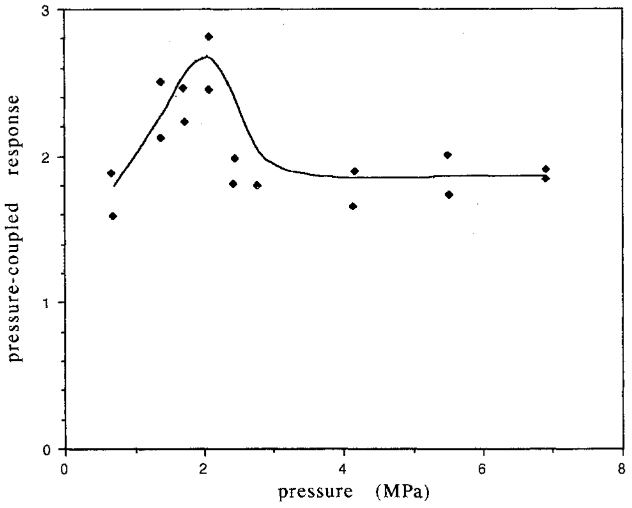

Fig. 18 Response function (vs pressure) for an AP/PBAN propellant with bimodal AP size distribution, obtained from pulsed T-burner tests at a frequency of 500 Hz (Ref. 24).

apparently due to scatter in T-burner data and difficulty in achieving uniform particle size of the fine AP. The design of the experiment requires that the fine AP particles all experience threshold conditions for PLEFs at the same pressure to produce a recognizable singularity in the collective dynamic response. In propellants with more conventional particle-size blends, the contribution of marginally stable LEFs is present to lesser degree over a wide pressure range, but is not distinguishable from other contributions to global dynamic response.

Summary

Studies of the edge-burning of laminates of oxidizer and binder layers ("sandwiches") have been conducted for some 30–35 years as a means to observe the combustion of heterogeneous solid propellants without the chaotic field of three-dimensional flamelets typical of AP propellants. The accumulating results of the sandwich burning tests led to increased attention to the leading-edge portion of the oxidizer/fuel diffusion flamelets. This portion of the flamelet (referred to variously as the "flame root," "phalanx flame," "primary flame," and "LEF") was not well-understood or modeled analytically, primarily because it is too small to observe experimentally, is not one dimensional, and cannot be modeled realistically without realistic description of species reaction and diffusion rates. However, it has been clear that this portion of the O/F flamelets is important to the propellant combustion because it is the part of the hot O/F diffusion flame that is closest to the propellant surface.

This article summarizes studies that clarify the nature of LEFs (gas burner and numerical modeling) and shows them to be local sites of high heat release rate, so high that they produce a local pressure peak and divergence in the approach flow, a result consistent with the interpretations of the sandwich-burning test results. This leads to close local coupling between the LEF and the surface regions close to the oxidizer contact lines (coupling via the O/F mixing fans). Tests on AP/PBAN/AP sandwiches with Fe_2O_3 burning rate catalyst in the binder lamina indicate that the catalyst acts by accelerating the breakdown of heavy binder product molecules to more reactive fragments, enabling the LEF to stand closer to the burning surface and thus increase burning rate.

Sandwich-burning tests on sandwich samples with AP-filled binder lamina matrix indicate that the AP in the matrix acted as a source of a reactive diluent in the fuel vapor, that caused a shift in position and size of the LLEF in a manner that enhanced burning rate. The results indicated that the sandwich burning rate was controlled by regression of the AP lamina under the influence of the LLEF. With the finer AP (10 μm), the mixing of the AP and binder vapors was apparently near complete before it reached the LLEF standoff distance (without appreciable exothermic reaction). With the coarser AP (33.5 μm), mixing was apparently less complete, resulting in less enhancement of the rate-controlling lamina LEF, and correspondingly less enhancement of burning rate. At higher pressure, PLEFs were apparently established on the individual particles (1000 psi, 70% 33.5-μm AP). However, the sandwich rate does not seem to have been enhanced by this condition, since the rate remained lower than for 10 μm AP, for which particle LEFs were not indicated. The collected results localize a boundary between two long recognized domains of burning of the matrix of fine oxidizer and binder. In one domain (fine AP, low AP content, low pressure) AP vapors mix and yield a premixed flame. In the other domain mixing is incomplete at lamina LEF height. At high enough pressure, PLEFs may be present in association with the larger exposed (fine) oxidizer particle surfaces. In all cases the sandwich burning rate is controlled by the lamina LEF-assisted regression of the AP laminas, indicating a complex coupling of the nature and pyrolysis of the matrix lamina with the lamina LEFs and the rate-controlling AP lamina regression.

Some preliminary results were presented of tests on sandwiches with both fine AP and fine Fe_2O_3 in the PBAN lamina. This combination resulted in very high burning rates. Details of the results indicate that the catalyst does more than break down heavy fuel molecules for easier reaction in the lamina LEF. There appears to be exothermic O/F reaction in the surface layer of the matrix. It seems likely that the high AP/binder surface contact area, in combination with very fine catalyst particle size, allows significant interfacial reactions at or very near the surface that are not manifested in results with simpler sandwiches.

Sandwich burning tests with aluminum powder in the PBAN lamina showed concentration of the aluminum on the binder surface, and showed that ignition-agglomeration of the aluminum initiated only in the region exposed to the hot LEF. Tests on single laminas of AP/aluminum mixture burned with aluminum concentration on the surface, but showed detachment from the surface with minimal ignition and agglomeration. These results indicate that LEFs provide the source of high temperature needed to break down the oxide coating on the sintered aluminum concentrations. In propellants this role of LEFs is the event that terminates accumulation and, hence, limits agglomerate size.

The tests on propellants were designed to test the importance of LEFs in two important aspects of propellant combustion: 1) aluminum agglomeration and 2) dynamic response to pressure oscillations. The propellants were designed to test the mechanistic arguments convincingly on the basis of qualitative trends in results, and results were consistent with the sandwich burning-derived mechanistic arguments.

At issue were possible effects of the transition (for propellants with bimodal AP) from a condition of attached PLEFs to a region where there are attached PLEFs on coarse particles only. The results indicated a strong transition in aluminum agglomerate size and a peak in response function associated with the flame transition. The 400/17.5-μm AP particle combination was used in both studies, with the indicated transition pressure being comparable (1.91 MPa for peak response function, 2.43 MPa for agglomerate size distribution). The moderate difference may be due to the large mass fraction of aluminum and to lower AP/binder ratio in the fine AP/binder matrix of the aluminized formulation.

It is important to note that the studies reported here were designed to study (and clarify) aspects of combustion that are not well-encompassed in current models of propellant combustion, aspects such as the following:

1) The nature and role of LEFs.

2) The localized coupling of each LEF with the specific site of the solid surface that is the source of the mixing O/F flow that feeds the LEF.

3) The nature of and conditions for interaction of adjoining LEFs, associated lateral heat flow (and species flow in the gas phase), and dependence of effect on LEF spacing (scale of heterogeneity).

4) The nature of the transition from LEF-controlled burning to premixed O/F flame-controlled burning.

5) The special contribution to pressure-coupled combustion response that is made by particle burning in the transition region noted in 4.

6) The critical role of PLEFs in limiting aluminum concentration (by initiating its burning) and the corresponding effect of AP particle size and pressure on agglomerate droplet size.

7) The consequences of combination of large and small particle sizes (AP laminas and matrix laminas), and the relation to difficulties in model correlation of burning rates of bimodal AP propellants with wide mode separation.

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