Combustion of Nitramine Propellants

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The composite solid propellant combustion model of Beckstead, Derr, and Price is modified to describe the combustion of nitramine propellants. Modifications are based upon experimental observations of the combustion characteristics of hydrocarbon binder propellants containing cyclotetramethylenetetranitramine (HMX).

Nomenclature[†]

a = exponent on inhibited surface diameter-dependence
K = coefficient of inhibited surface diameter-dependence
ℓ = exponent on diffusion pressure-dependence
N = surface structure penetration limit; number of diameters
s = exponent on diffusion diameter-dependence
T_m = particle melting point
κ = thermal diffusivity

Introduction

THE combustion process of nitramine propellants, and therefore the mechanism for observed shifts in the pressure-dependence of burning rate,[1,2] are not well understood. Nitramine propellants have not been researched as extensively as unfilled double-base propellants or hydrocarbon propellants containing ammonium perchlorate. Efforts directed toward combustion modeling or experiments that would uncover mechanisms for use in modeling have been very limited.[1-7]

A comprehensive model of ammonium perchlorate composite propellant combustion was developed by Beckstead, Derr, and Price.[8] The model has been able to predict particle size effects and limitations of particle size adjustment by direct computation.[8,9] Through parametric variation, it has also been possible to show the effect (and thereby the potential) of changing a given mechanism.[6,10] Therefore, this approach was selected as the starting point for the development of a nitramine propellant combustion model. The essential task is to model the role of nitramines as distinguished from ammonium perchlorate.

As part of this work, experiments have recently been completed which provide the basis for the model modifications. These have been reported elsewhere.[11]

Differences Between Nitramine and Ammonium Perchlorate Propellants

Fundamental differences between nitramine and ammonium perchlorate propellants as would bear upon the combustion modeling are summarized as follows:

1) Nitramines have much lower melting points than ammonium perchlorate.

2) Nitramines are nearly balanced stoichiometrically, ammonium perchlorate is oxidizer-rich.

3) The nitramine monopropellant flame is much more energetic, and nitramines burn faster as monopropellants than does ammonium perchlorate.

4) As a result of 1), nitramines can melt in bulk when the propellant burning rate is low such that a more planar surface structure results.[11]

5) As a result of 2), nitramine-hydrocarbon propellants are highly fuel-rich; thus the binder is exposed to an oxidative and thermal environment which is less severe.

6) As a result of 4) and 5), a thick binder melt layer can form which can interfere with the nitramine surface at low burning rates.[11]

7) Another result of 2) is that the diffusion process serves to inhibit the nitramine monopropellant flame, and any diffusion flame that might occur must be of lower rather than higher temperature.

8) It follows that the burning rate of the nitramine limits the burning rate of the propellant; the binder is inhibiting rather than augmenting combustion

9) It is found that, at some point, the combustion of the nitramine is able to propagate into the propellant to considerable depths and thereby alter the surface structure.[11] It is hypothesized that this is associated with cessation of bulk melting at a sufficiently high heating rate dependent upon particle size, and is accentuated by the extent of inter-crystal contact resulting from propellant manufacture. Such extreme penetration is not observed with ammonium perchlorate, perhaps because the binder pyrolysis rates never fall too far behind the crystal deflagration rates, which is consistent with the differences pointed out in 3) and 5).

Combustion Model Modifications

The following discussion makes liberal references to Ref. 8. Only the modifications are shown here. The nomenclature is the same except for the introduction of new parameters. Basically, burning rate is computed by iterative solution of a set of surface structure equations, flame structure equations, and equations representing the conservation of energy and the macroscopic continuity of the propellant.

Surface Structure Equations

The basic surface structure equation is Eq. (3) of Ref. 8. However, if the particle melts in bulk, a more proper representation of the surface structure is planar. Following Ref. 6

$$S_{ox}/S_o = \zeta \tag{1}$$

Additionally, if the binder melt can flow over the particle melt so as to inhibit a portion of the area, then Eq. (1) must incorporate some restriction. Although the experiments have revealed the existence of such restriction, it has not been possible to quantify it. Therefore, the restriction is assumed to

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[†] Also cf. Ref. (8).

be of the following form

$$S_{ox}/S_o = \zeta(K\,D_o{}^a) \tag{2}$$

where K and a are constants.

Equation (2) has been incorporated into the model as the expression for the surface structure under the condition that the nitramine has melted in bulk. If the nitramine has not melted in bulk, then the original equation applies.

When the nitramine is not melted, there are two expressions for h/D_o to be used depending upon whether the particle protrudes or penetrates. If it protrudes, the positive form of Eq. (4) of Ref. 8 is still valid. If it penetrates, the negative form must be modified to allow the observed deep penetrations. The referenced Eq. (4) contains an inherent restriction that prevents the surface from becoming excessively unbalanced; this needs to be relaxed. The depth is now arrived at by comparing the particle size to the distance burned by the binder in the time it takes to consume that particle

$$(h/D_o)_N = D_o/\left[r_f\left(t_{\text{ign}} + \frac{D_o}{r_{ox}}\right)\right] \tag{3}$$

This expression would allow the penetration to become unbounded. A new restriction is imposed according to an assumed depth of particles in contact in an average particle cluster. This is denominated the "manufacturing parameter," N. Thus, for example, if $N=2$ as an input parameter, the penetration depth could not exceed two diameters. These surface structures are depicted in Fig. 1.

The melt/no-melt criterion is obtained by solution of the unsteady heat transfer equation representing the passage of the thermal wave across a particle. These results

$$r_m = \left[\left(\frac{T_s - T_o}{T_m - T_o} - 1\right)\frac{12\kappa_f\kappa_o}{D_o{}^2}\;\frac{\lambda_f}{\lambda_o}\right]^{1/2} \tag{4}$$

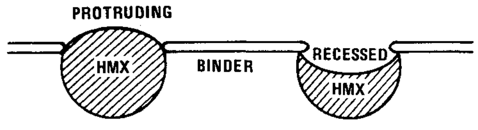
So if $r \geq r_m$, the iterations proceed along the no-melt path; if $r < r_m$, the iterations proceed along the melt path. Note that the critical burning rate, r_m, is inversely proportional to particle size.

Diffusion Equations

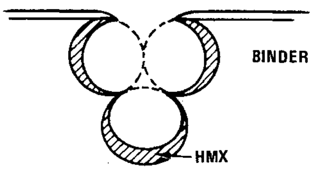
In an ammonium perchlorate propellant, a high-temperature diffusion flame is situated above the propellant surface in accordance with computed diffusional mixing and reaction kinetic distances.[6,8] The mixing length is taken to be a function of particle size only, and the diffusion flame can release its heat wherever it occurs—even at a distance much closer than the location of the oxidizer monopropellant flame. Such a model might be deemed unrealistic for nitramine propellants. Because there are no excess oxidizing species, it can be argued that there cannot be a flame in the literal sense that would be situated considerably closer to the surface than the monopropellant flame. Rather, the significance of diffusion in nitramine propellants is to produce a zone of dilution and cooling. To the extent that the diffusion distance is shorter than the monopropellant reaction distance, a portion of the monopropellant flame feeding heat back to the surface is cooled; in the extreme, it is all cooled to the temperature of the mixture. If the monopropellant reaction distance is shorter than the diffusion distance, there is no cooling at that point; the more distant eventual cooling is of no consequence to the heat feedback.

Beckstead et al, on the other hand, did conceive of the possibility of a diffusion flame occuring in nitramine composite propellants.[6] They referred to this process as "active cooling," in contrast to the "passive cooling," that would characterize the argument of the previous paragraph. In a situation where the nitramine reaction distance is larger than the diffusion distance, it is possible that the hydrocarbon species evolved from the binder could "rob" the oxidizing species initially evolved from the nitramine to produce a "less efficient" reaction than the monopropellant flame.

a) SURFACE STRUCTURE FOR BULK MELTING; $h/D_0=0$



b) SURFACE STRUCTURE FOR FROZEN PARTICLES (ANALOGOUS TO THE AMMONIUM PERCHLORATE MODEL); $|h/D_0| < 1$



c) SURFACE STRUCTURE FOR DEEP PENETRATION WITH N = 2; $-2 < h/D_0 < -1$

Fig. 1 Representations of nitramine propellant surface structure.

Low pressure burning rate data for Nitramine composite propellants lend support to the active cooling concept. For both RDX and HMX, it is found that low pressure burning rate increases with decreasing particle size and that pressure exponents are in the neighborhood of 0.6. A passive cooling concept would cause burning rates to decrease with decreasing particle size as the diffusion cooling becomes more efficient. Moreover, a passive cooling concept would produce pressure exponents of approximately 1 since the only point of heat feedback would be fixed at the monopropellant flame position (which follows second-order kinetics). Thus the low pressure burning rate data suggest a diffusion model similar to that of ammonium perchlorate propellants, differing quantitatively rather than conceptually.

Beckstead et al. discussed the subject of diffusion as would be applied to various composite propellant types.[6] Basically, the characteristic mixing length may be described in the following form

$$x_D^* \sim D_o{}^s/P^\ell \tag{5}$$

The exponent on particle size varies from 1.0-2.0 depending upon whether the flame structure may be characterized as short or tall. Beckstead found that a value of 1.0 best characterized ammonium perchlorate propellants. This value has been adopted here, except that it must be changed to the value of "a" to be consistent with the surface structure represented by Eq. (2) for the molten surface. The exponent on pressure varies from 0-1.0 depending upon whether the mixing is laminar or turbulent. Beckstead found that a laminar flame best described ammonium perchlorate propellants having a relatively smooth surface structure, but that a turbulent flame best described potassium perchlorate propellants having a comparatively rough surface structure. They were unable to come to a conclusion for HMX propellant because its modeling was rudimentary and not in adequate agreement with data at that time; suffice it to say for present purposes that the assumption of turbulent diffusion produced too high a pressure exponent at low pressure. Therefore, the value of ℓ was left to parametric study. The constant of proportionality is related to Eq. (13) of Ref. 8.

The remaining portions of the diffusion flame analysis remain the same as described in Ref. 8. The diffusion flame height is the sum of mixing and reaction lengths, the reaction length following second-order kinetics. The monopropellant flame is assumed to be premixed, and its postion is governed by second-order kinetics. Thus Eqs. (8), (9), (13), (14), (17), and (18) of Ref. 8 remains intact. With the addition of Eqs. (1, 2, 5, and 19) of Ref. 8, also unchanged, the problem is reduced to solving for the surface temperature.

Energy Equations

The energy equations for surface temperature, Eqs. (7, 20, and 22) of Ref. 8, remain unchanged except that there is no "final flame" and that the particle latent heat term (Q_L) must include a heat of fusion ($Q_L + Q_{LM}$) when there is bulk melting.

The original authors have received several inquiries regarding the operation of the β_F parameter appearing in the energy equation, so this is perhaps a good place for clarification. The value of β_F is determined from the intersection of the parabaloid representing the diffusion flame boundary and the plane representing the monopropellant flame. This is illustrated in Fig. 2. If the parabaloid peaks below the plane, all of the energy being projected onto the surface of the Nitramine comes from the diffusion flame and $\beta_F = 1$. In other words, the diffusion flame is situated closer to the surface than the monopropellant flame. If the parabaloid peaks above the plane, then the intersection represents that fraction of the Nitramine surface exposed to the monopropellant flame and the remainder is exposed to the diffusion flame, $\beta_F < 1$. As the plane becomes relatively close to the surface, $\beta_F \rightarrow 0$ and the Nitramine surface is fully exposed to the monopropellant flame. This geometry is solved as

$$\beta_F = (x^*_{ox} - x^*_{PF}/x^*_D) \tag{6}$$

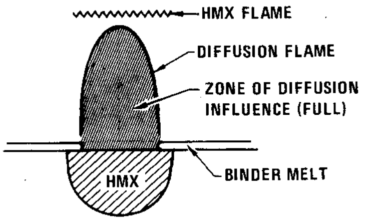
The authors referred to this process as "competing flames."

Combustion Model Results

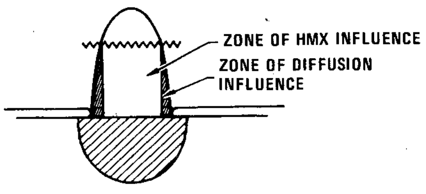
Input Parameters

Values of the input parameters are changed from those listed in Ref. 8 in accordance with the obvious propellant differences. Thus, constants for HMX as reported in Ref. 6 replace ammonium perchlorate constants. Constants for the binder have since been measured,[10] and these are now adopted. Diffusion flame constants are arbitrarily assumed to be the same, except for the diffusion coefficient adjustment necessary to compensate optimized values for a (0.25), K ($1.3\mu^{-0.25}$), and ℓ(0.6). The value of Q_{LM} was optimized as 132 cal/gm. The melting point of the nitramine, and the required thermal and thermochemical properties, are known. The penetration limit N was taken to be 3 for particle sizes of the order of 100μ, 2 for sizes of the order 10μ, and 1 for sizes of the order 1μ.[11]

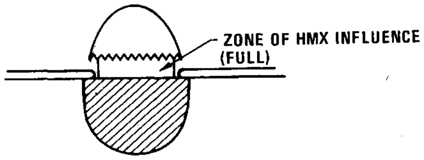
Any time a sophisticated model attempts to address a complex process, there is bound to be a number of unknown input quantities. This leads to the criticism of fudging. However, once optimized quantities are established for a standard propellant, they are fixed and must then accommodate a broad range of propellant variables in terms of correctly showing changes in burning rate characteristics over a wide pressure range. If the model correctly reproduces the trends, then it has value in the overall combustion tailoring scheme.



a) $\beta_F = 1$ (LOW PRESSURE)



b) 0 $\beta_F < 1$ (INTERMEDIATE PRESSURE)



c) $\beta_F \rightarrow 0$ (HIGH PRESSURE)

Fig. 2 Representations of diffusion flame structure.

Results for LPC Propellants

The model was first applied to the two propellants which were processed in the course of this work for experimental study.[11] These are hydroxyl-terminated polybutadiene (HTPB) propellants containing 75 wt% HMX. One contains a mean particle size of 195μ, the other contains a mean particle size of 5μ. Results are comapared with the experimental burning rates in Fig. 3. It is observed that the following trends are correctly predicted. 1) The coarse HMX propellant has lower burning rate at low pressure, higher burning rate at high pressure. 2) The pressure exponent shift is much more abrupt for the coarse propellant, in fact appearing as a discontinuity in the model, and occurs at lower pressure. 3) The pressuure exponents at low pressure are approximately equal and of a value about 0.5; the pressure exponents at high pressure are approximately equal and of a value about 1.0. 4) The high pressure burn rate of the coarse HMX propellant approaches the extrapolated burn rate of HMX itself; the high pressure burn rate of the fine HMX propellant does not.

The exponent shift for the coarse HMX propellant results from the change in surface structure accompanying cessation of bulk melting. At the same time, the controlling process shifts from the diffusion flame to the HMX flame in order to drive that surface structure in the iterative solution of the equations. The deep penetrations result in relatively high surface area exposed to HMX flame control. Thus the burning rate jumps to the burning rate of HMX as though no binder were present. This appears as a discontinuity because of the idealization of a single particle size. The second exponent shift is merely the proceeding along the path of HMX flame control. Thus the very high slope is but a transition between two mechanisms: diffusion flame control over a planear melt surface at low pressure, HMX flame control over a pitted surface at high pressure.

The exponent shift for the fine HMX propellant does not result from a change in the surface structure. The fine HMX is always melted over the pressure range, so that the surface remains planar. Here, what is happening is only that the flame structure is shifting from diffusion control to HMX flame control. This is precisely the mechanism for the same kind of exponent shift in ammonium perchlorate propellants. Because the surface remains planar, and does not open up to the high areas of the penetrations, the burning rate cannot jump to the HMX rate. There is simply a transition to the high exponent associated with HMX flame control, but not to the HMX rate itself. The propellant rate is limited by the relatively low surface area of the HMX associated with the planar surface.

It is therefore concluded that there are two types of exponent shifts in intramine composite propellants: 1)That caused by cessation of bulk melting, resulting in a marked

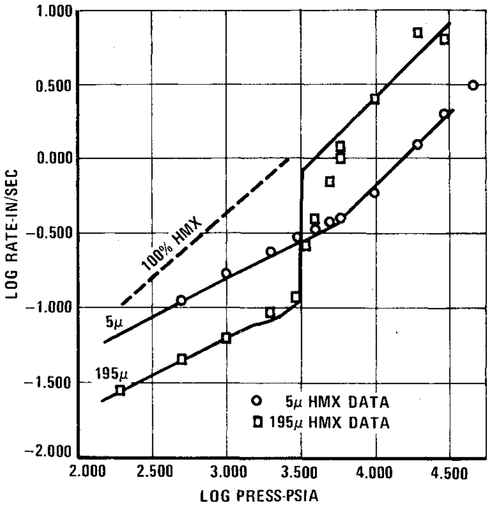


Fig. 3 Effect of HMX particle size in HTPB propellant; 75% HMX.

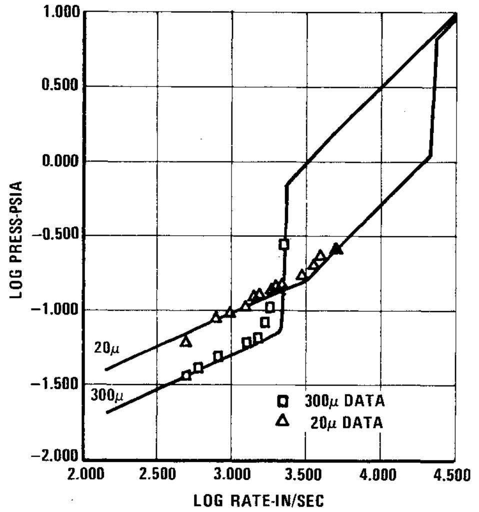


Fig. 4 Effect of RDX particle sixe in polyurethane propellant; 71% RDX.

change in surface structure, necessarily accompanied by a change in flame structure, and which will produce a zigzag in the burning rate curve to approach the nitramine rate itself; and 2) that caused by the natural change in flame structure with pressure, which also occurs in ammonium perchlorate propellants, and does not require marked changes in surface structure to bring it about.

Results for Other Propellants

The model was also applied to the RDX (cyclotrimethylenetrinitramine) propellants studied by Zimmer-Galler.[2] Input parameters were appropriately changed in accordance with the 71% concentration, the polyurethane binder, and the particle sizes of 20μ and 300μ. The RDX parameters were changed where known to be different from HMX, otherwise they were assumed the same. Unknown constants optimized for HMX were left unchanged. The results are compared with data in Fig. 4. It is observed that the trends are correctly predicted and that the burning rate magnitudes are predicted very well. The absence of high pressure data precludes a complete assessment, however.

The model was next applied to a 75 wt% HMX/polyurethane propellant tested at the U.S. Naval Weapons Center.[12] This propellant contained 2μ HMX. Results are shown in Fig. 5. The burning rate magnitude is predicted quite well, but the pressure at which the flame structure shift occurs is somewhat overpredicted. Comparing either Figs. 3 and 5 or Figs. 4 and 5 shows a combined effect of diffusion flame structure and temperature. Flame temperature increases when HTPB is replaced by polyurethane, or when Nitramine concentration is increased. Diffusion distances become shorter when particle size decreases or when concentration increases. Thus the burning rate in Fig. 5 is higher than that of either the 5μ propellant of Fig. 3 or the 20μ propellant of Fig. 4. Also, the flame structure and pressure exponent shift at higher pressure. Note well, however, that these trends can be superseded and appear to become unsystematic if the surface structure is able to shift through cessation of bulk melting. This point of parametric confusion can be magnified in real propellants whose finite particle size bandwidths preclude jump discontinuities in burning rates, so the mechanistic distinctions are not so evident.

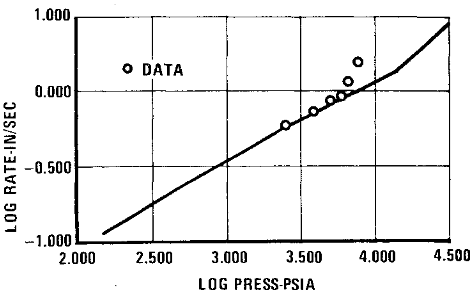


Fig. 5 75% HMX in polyurethane propellant; 2μ HMX.

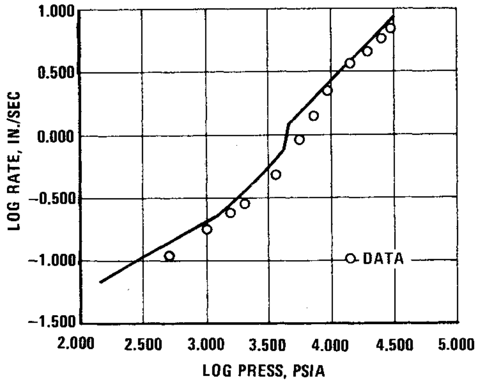


Fig. 6 85% HMX in CTPB propellant; 100μ HMX.

The model was finally applied to an 85 wt% HMX/CTPB propellant.[1] This propellant contained a mean particle size of 100μ. Results are shown in Fig. 6. The agreement with data is good except that the zigzag transition shown by the actual propellant is more gradual. The interpretation is that the propellant contained a broad-banded size distribution, typical of the as-received HMX used in practical developmental propellants, and skewed toward sizes finer than the mean. Note that the idealized discontinuity appears abated because the burning rate jump is shorter at this high concentration; the entire plot is approaching the 100% HMX rate line. Note also that the post-transition high pressure data in Figs. 6 and 3 (coarse) follow the same "zag" line. This is considered an important validation of the theory.

Conclusions

It is concluded that an analytical model of the combustion of nitramine composite propellants has been developed which explains observed burning rate characteristics, and the effects of particle size, concentration, and binder type, in an internally consistent manner. There are basically 2 mechanisms responsible for observed shifts in pressure exponent, one involving the surface structure and one involving the flame structure. The surface structure and the monopropellant flame control "high pressure" burning rate. The role of diffusion in nitramine propellants is more accurately described by a reactive process than a passive cooling of the monopropellant flame, and it controls "low pressure" burning rate. The interaction of the two mechanisms can produce what would appear to be unsystematic formulation effects on burning rate characteristics.

References

[1] Moy, B. K., "Nitramine Combustion Problems," AFATL-TR-72-190, Sept. 1972, Air Force Armament Lab., Eglin Air Force Base, Fla.

[2] Zimmer-Galler, R., "Correlations Between Deflagration Characteristics and Surface Properties of Nitramine-Based Propellants," *AIAA Journal*, Vol. 6, Nov. 1968, pp. 2107-2110.

[3] Gross, D. and Amster, A., "Thermal Explosions: Adiabatic Self-Heating of Explosives and Propellants," Eighth International Combustion Symposium, Williams and Wilkins, Baltimore, Md., 1962, pp. 728-734.

[4] Taylor, J. W., "A Melting Stage in the Burning of Solid Secondary Explosives," *Combustion and Flame*, June 1962, pp. 103-107.

[5] Taylor, J. W., "The Burning of Secondary Explosives by a Convective Mechanism," *Transactions of the Faraday Society*, Vol. 58, 1962, pp. 561-568.

[6] Beckstead, M. W., Derr, R. L., and Price, C. F., "The Combustion of Solid Monopropellants and Composite Propellants," Proceedings of the Thirteenth International Combustion Symposium, Combustion Institute, Pittsburgh, Pa., 1971, pp. 1047-1056.

[7] Kumar, R. N., and Strand, L. D., "Analytical Investigation of the Combustion Processes Occurring in Nitramine Propellants," Final Rept. MIPR FY7621-73-90062, 1974, Jet Propulsion Lab., Pasadena, Calif.

[8] Beckstead, M. W., Derr, R. L., and Price, C. F., "A Model of Composite Solid Propellant Combustion Based on Multiple Flames," *AIAA Journal*, Vol. 8, Dec. 1970, pp. 2200-2207.

[9] Cohen, N. S., Derr, R. L., and Price, C. F., "Extended Model of Solid Propellant Combustion Based on Multiple Flames," Proceedings of the 9th JANNAF Combustion Meeting, CPIA Publication 231, Vol. II, Dec. 1972, pp. 25-42.

[10] Cohen, N. S., Fleming, R. W., and Derr, R. L., "Role of Binder in Solid Propellant Combustion," *AIAA Journal*, Vol. 12, Feb. 1974, pp. 212-219.

[11] Cohen, N. S., "Combustion of Nitramine Propellants," *Proceedings of the 11th JANNAF Combustion Meeting* (CPIA Publication 261), Vol. I, 1974, pp. 267-283.

[12] Derr, R. L., et al., "The Combustion Characteristics of HMX," *Proceedings of the 11th JANNAF Combustion Meeting* (CPIA Publication 261), Vol. I, 1974, pp. 231-241.