Comprehensive View of the Combustion Models of Composite Solid Propellants

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Introduction

COMPOSITE solid propellants contain an inorganic oxidizer (generally ammonium perchlorate, AP) and a fuel binder (organic polymers) as the major ingredients. In order to understand the combustion phenomena of the propellant in its totality, it is worthwhile to examine the combustion of the ingredients, i.e., AP and the polymer, as a prelude to the propellant combustion. Some attempts have been made in the past to understand the combustion of AP, which also happens to be a monopropellant, and some similarities have been shown to exist between the combustion of AP and the combustion of the propellant. The binder combustion, from the viewpoint of propellant combustion, has not received adequate attention, which may perhaps be due to the belief that the binder occupies a smaller proportion in the propellant. However, combustion and physicochemical characteristics of a propellant do depend on the nature of the binder. Thus, there is a need to understand the combustion of AP and the polymer separately. Since the information available in the literature on the various aspects of combustion of the binder, AP, and the propellants is fragmentary, it is the purpose of the present review to bring together the information and examine it critically.

Combustion of AP

One of the most interesting aspects of AP deflagration which has not been explained adequately is the existence of nondeflagration pressure ranges (particularly low-pressure limit, LPL). At ambient temperature, the average of various reported values comes out to be 20 atm and the burning rate ($\dot{r}$) under these conditions is around 2 to 3 mm s^{-1} for both single crystals or high-density pellets. LPL strongly depends upon the initial temperature of the grain and the presence of additives. By using a scanning electron microscope, the presence of a melt layer on the surface has been shown by Hightower and co-workers.[1-3] They conclude that the thickness of the melt layer decreases as the pressure is increased, and that the melt layer plays a significant role in AP deflagration by providing an opportunity both for gas-phase and condensed-phase reactions. Similarly, Guirao and

Williams[4] believe that the thickness of the melt layer decreases as the pressure is decreased and approaches zero as the pressure goes to inifinity. None of the theories postulated so far satisfactorily explain the (1) cause of LPL, (2) effect of particle size, and (3) mechanism of catalyst action. The essential features of both the gas-phase and condensed-phase theories are discussed as follows.

A) Gas-Phase Theories

Johnson and Nachbar[5] proposed an elaborate model for steady-state deflagration by considering a one-dimensional adiabatic laminar flame model. This model could not predict LPL, so they added an arbitrary heat loss term from the solid phase. When this term was given a very large value, which is impossible from the known physical grounds, self-quenching could be predicted. They also concluded that the radiant heat losses from the gas phase, as calculated by Olfe and Penner,[6] and from the burning surface were too small to account for the observed LPL.

Sohn[7] proposed an adiabatic model based on the information of surface heterogenity by Boggs.[8] He considered the condensed-phase reactions to be negligible. He theoretically predicted that self-quenching occurs because of two- or three-dimensional heat losses. His theory could explain many characteristics, including the dependence of LPL on the initial temperature of the solid.

B) Condensed-Phase Theories

No elaborate mathametical theory based on a physical model (except that of Guirao and Williams,[4] which will be discussed at a later stage) is available which could satisfactorily explain and consider the importance of condensed-phase reactions. In the model developed by Beckstead et al.[9] it has been shown from calculations that there is a considerable heat release at the surface of the condensed phase. Evidence has also been given by various workers which demonstrates the importance of such condensed-phase reactions.

Beckstead and Hightower[3] have shown that during the combustion of AP the phase transition between orthorhombic

to cubic takes place into the solid phase. From cinephotomicrography they[10] further observed that the surface gets wet during the combustion of AP. Waesche and Wenograd,[11] from the results of differential scanning calorimetry (DSC), suggested that combustion of AP involves the participation of condensed-phase reactions. They further observed that thermal decomposition of AP is exothermic at atmospheric as well as higher pressures. Wenograd and Shinner[12] pointed out some interesting features which contradict the general concept of the gas-phase model. They are as follows: 1) with the deflagration flame temperature of 1000°C, the heat transfer to the surface should be conductive in nature rather radiative as assumed by gas-phase theory. For burning rate ($\dot{r}$) of 1 cm/s the calculated value of heat flux comes to 1300 cal cm^{-2} s^{-1}, which shows that it is conductive. 2) Friedman and Levy,[13] supporting the gas-phase model, calculated the flame zone thickness to be of the order of 0.2 to 1.0 μ. It has been observed by many investigators that 0.5% copper chromite doubles the $\dot{r}$. At 0.5% concentration, the distance between the catalyst particles should be 50 μ. To account for the catalyst action by a gas-phase model, the flame zone thickness should be far more than the observed value. Thus, the combustion appears to be much more complex than that proposed by the gas-phase mechanism. In order to account for the observed effects, the heat of evaporation has to be considered to be very small, or heat generated during the decomposition at the surface or below it should be taken into account. Such condensed-phase reactions can very well explain the observed catalytic effect of copper chromite.

Wise et al.[14] examined the contribution of reactions in the solid phase to both ignition and deflagration of AP. $\dot{r}$ measurements were made on AP and copper chromite systems. The experimental determinations of the condensed-phase temperature profile in a burning propellant indicated the existence of a heat release region close to the burning surface. Some of the strands quenched during deflagration revealed the existance of a subsurface layer, which is located in a zone at which the temperature has reached the level of the phase transition (240°C) of AP. The experimental results obtained and their correlation with the theoretical analysis emphasize the contribution of exothermic condensed phase reactions during steady-state burning. However, such condensed-phase reactions do not completely ignore the importance of the gas-phase reactions. They believe that propellants with higher $\dot{r}$ will have a diminished contribution from the condensed-phase reactions, since the enhanced rate of the propellant surface regression reduces the time available for exothermic heat release in the solid.

Inami et al.[15] studied the heat release rate of AP-fuel and AP-catalyst mixtures as a function of temperature. Studies on AP-fuel mixture show that measurable heat release occurs at temperatures below the phase transition of AP and that the rate of heat generation per mass of material is greater than that of pure AP. The rate of exothermic decomposition of AP is unaffected by an increase of pressure. This observation suggests that the heat release is controlled by homogeneous and heterogeneous reactions in the condensed phase.

Guirao and Williams[4] developed a comprehensive theory for the deflagration of AP which assumes that most of the heterogenous condensed-phase reactions occur in liquid melt, which covers the surface completely. They emphasized the occurence of condensed-phase surface and subsurface reactions and incorporated them into the theory. This model assumes that endothermic vaporization occurs at the liquid-gas interface. They assumed the rate controlling step in the condensed phase to be the breakage of the Cl-O bond.

The effect of ionic impurities like SO_4^{-2} and Ca^{+2} on thermal decomposition of AP has been studied by Maycock and Pai Verneker.[16] They have observed that a reversal in the thermal decomposition characteristics takes place at a particular concentration of the impurities, viz., SO_4^{-2} doping
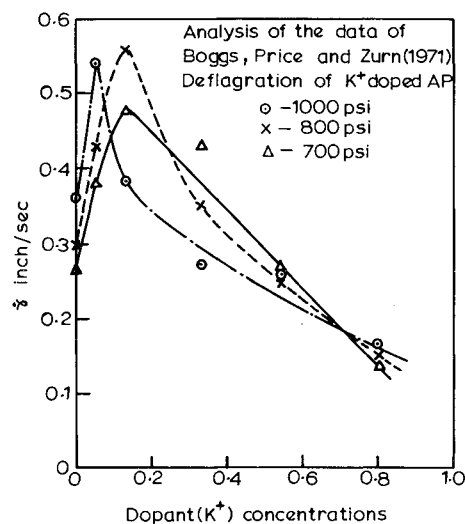

Fig. 1 Effect of dopant concentration on the deflagration rate of AP.

showed a sensitization initially at lower concentrations but then it showed a desensitizing effect at higher concentrations. An exactly reverse trend was observed for Ca^{+2} doping, i.e., it showed a desensitization and then a sensitization. Generally, such behavior is observed when a crystal is doped with impurities, and it is believed that a crystal can take only a limited amount of impurity. Boggs et al.[17] have studied the effect of K^+ dopant on the $\dot{r}$ of AP. In the analysis of their data (Fig. 1) it was found that at a particular pressure, $\dot{r}$ shows a sensitization and then a desensitization as the dopant concentration is increased. This behavior is similar to that observed for dopant effects on thermal decomposition. This then shows that thermal decomposition and, therefore, condensed-phase reactions play a significant role during the combustion.

Combustion of Binders

Polymer combustion[18] is characterized either by a smoldering or vigorous and flaming degradation of organic material. In polymer combustion the rate is more dependent on nonchemical factors: gas turbulence; diffusion; conductive, convective, and radiative heat flows; and polymer volatility, melting, and dripping enormously influence ignition and burning rates. In a typical burning of polymer, the material is first heated from an external source, and, depending upon the flammability, it ignites at some point. It sustains steady-state combustion depending upon the environmental conditions and the heat feedback to the material. In a candle-like burning, most of the heat feedback will be via conduction, although there may be some radiative heating. Igniting and quenching are non-steady-state flame processes because the parameters of these phenomena change rapidly with time.

The lean premixed methane-oxygen flame can be considered as a model for the more complex polymer flames. Hydrocarbon diffusion flames of methane, propane, paraffin, linear and branched polyethylene (PE), and polypropylene have all have been probed for simple products, and the reported results are remarkably consistent. Other polymers have been probed for reaction products including polymethylmethacrylate, polyoxymethylene, and polytetrafluoroethylene (PETF). The first two polymers give results similar to PE except that large amounts of monomer were found early in the flame. This observation seems to be reasonable since both materials are known to degrade almost exclusively via depolymerization reactions. PETF also unzips during burning to give large amounts of monomer along with other products.

Flame temperature measurements have also been carried out in polymer flames using small thermocouples. Valans[18]

reported that PE candle gives a surface temperature of 230-540°C and a flame temperature of 490-740°C in air. PE burning in air exhibited surface and flame temperatures as 400°C and 700°C, respectively. Stnetz[18] recorded PE flame temperatures higher than 1000°C. Finnimore[18] observed that PE burning in O_2(22%)-Ar gives flame temperatures over 1500°C.

Overall combustion of a polymer is quite complex and involves different classes of reactions like 1) gas phase, 2) surface, and 3) subsurface condensed phase. These are discussed below.

A) Gas-Phase Reactions

The chemistry of gas-phase reactions[19] in polymer combustion is similar to that of diffusion flames of hydrocarbons and substituted hydrocarbons. Polymer combustion can be viewed as a solid surface reaction forming a hydrocarbon flame. The process becomes more complicated by unsaturation, aromatization, and by the presence of various substitutient groups. Hydrocarbon flames are limited by a rate controlling step, $H + O_2 \rightarrow OH + O$, which is associated with activation energy (E) of 16 Kcal mole^{-1} and represents the attack of oxygen and the main radical branching step. This step is rapid only at high temperature (~ 1000 K) which agrees with the fact that the lowest final temperature in these flame systems is of the order of 1000 K.

B) Condensed-Phase Reactions

The condensed-phase reactions[16] include surface and subsurface reactions. The subsurface reactions are the solid-phase degradation reactions which occur due to degradation before vaporization. If the polymers contain no dissolved free radicals or oxidizing species, pure thermal initiation requires rupture of C-C or C-X bonds with E 50-100 Kcal mole^{-1}. The subsequent depropagation results in either gaseous products or crosslinking with char formation. uv sources can also initiate chain breaking and radical production which lowers the initiation threshold of polymers.

For surface reactions two cases can be distinquished: liquid surface and solid char surface. A melt at the surface of polymer may be several millimeters thick. A char at the surface of a polymer has a large surface area due to its porous structure. The chemistry of the interfacial region differs from the regions of pyrolysis in the polymer bulk. Some studies of polymer combustion have provided an indication of oxygen penetration into the solid, but the question is still being debated and such reactions may well depend on the polymer substrate and geometry.

Cohen et al.[20] have carried out surface pyrolysis studies on propellant binders like CTPB, HTPB, PBAN, polyurethane, polysulphide, etc. It was found that they exhibit a molten boiling surface together with the formation of char over a wide range of heating rates and pressures. Addition of AP or Cl_2 atmosphere increases the char formation. However, kinetics were found to be independent of pressure, AP, and the presence of catalysts, but they were affected by an oxidizing gas atmosphere. The proposed combustion model predicts that major alterations in pyrolysis kinetics will affect binder surface temperature significantly, but propellant $\dot{r}$ will not be changed greatly. Major changes in the heat of decomposition of polymer was also found to have a smaller effect.

The contribution of the condensed-phase reactions in the polymer combustion is not precisely known. However, the following specific examples demonstrate the importance of condensed-phase reactions.

Fennimore and Martin[18] studied the effect of Cl_2 and HCl on combustion of PE and other plastics. They inferred, on the basis of oxygen index measurements, that Cl_2 when chemically bound to the polymer retarded the combustion much more effectively than when Cl_2 was added to the atmosphere around the burning polymer.

Fennimore and Jones[21] studied the polymer flammability in the different oxidizing atmosphere ($N_2O + N_2$) and ($O_2 + N_2$) and found that the nature of the combustion behavior of the polymer containing $Al_2O_3 \cdot 3H_2O$ filler was the same in both cases, showing thereby that the effect of filler is in the condensed phase. Fennimore and Jones[21] also studied the combustion of the two polymers having similar Cl_2 contents, PVC and poly 3,3, bis (chloromethyl) oxetane, and found that the oxygen index of the two was vastly different, showing that polymer combustion strongly depends upon polymer structure.

Martin and Rice[22] studied the effect of $Al_2O_3 \cdot 3H_2O$ and Al_2O_3 on the combustion of epoxy resins. $Al_2O_3 \cdot 3H_2O$ was found to increase the oxygen index tremendously after 40% loading. Anhydrous Al_2O_3 acted only as an inert filler. These results supported the occurrence of condensed-phase reactions in polymer combustion. The authors also have shown that various phosphorous additives in epoxy resins retard the flame in the condensed phase, since it is known that various phosphorous and boron compounds significantly increase the char formation in the condensed phase.

According to Boilet et al.,[23] the combustion of polyurethane foam is controlled by a combination of vapor and solid-phase mechanisms. Phosphates modify the solid-phase mechanism while nonreactive PO_4 and phosphine oxides are active in the vapor phase.

According to Yoshinga et al.,[24] inorganic additives in PVC increase its ignitiion temperature by either an inhibiting effect in the vapor phase by thermal decomposition or in the solid phase by a shielding effect. H_3PO_4 which is converted into $(H_3PO_4)_4$ showed a large condensed-phase effect on flammability.

Kwan-Nangeh et al.[25] determined the effectiveness of H_3PO_4, $(NH_4)_2HPO_4$, and tetrakis-(hydroxymethyl) phosphonium hydroxide as a fire retardant on cotton from rate of heat release data. These retardants acted in the solid phase by reducing the amount of fuel evolution into the gaseous phase.

Combustion of Composite Solid Propellants

Research has provided a qualitative and to some extent quantitative understanding of the propellant combustion which occurs in varying degrees in the gas phase, on the burning surface, and in the condensed phase. In practical situations the importance of these steps in the combustion zone is not known. There are two schools of thought concerning the importance of the condensed-phase reactions in combustion. There are those who consider it negligible; on the other hand, the condensed-phase reactions have been suspected to play an important role.

The gas-phase models are generally based on the solution to the energy and mass balance equations. The conservation equations for the solid and the combusting gas are first laminarized and then solved under an appropriate set of boundary conditions.[5,26-28] It is also assumed that the surface regression rate is described by an Arrhenius-type pyrolysis law. This approach is more comprehensive because it includes a method for determining the appropriate value of surface temperature in terms of dynamic processes occuring in the gas phase and in the condensed phase.

Most of the proposed models are gas-phase models and treat the burning surface as being planar, dry, and homogenous, whereas in practice it has been found to contain a molten layer and also to be rough. The gas-phase models can predict the trend of the dependence of $\dot{r}$. The phenomenon of "flameless combustion,"[29,30] where the combustion wave propagates through the propellant after the extinguishment of the gas-phase flame by lowering the pressure, cannot be explained by the gas-phase model. The $\dot{r}$ in the flameless combustion is dependent on pressure and particle size where no gas-phase flame is present. The gas-phase model predicts the disappearance of the particle size effect at sufficiently low
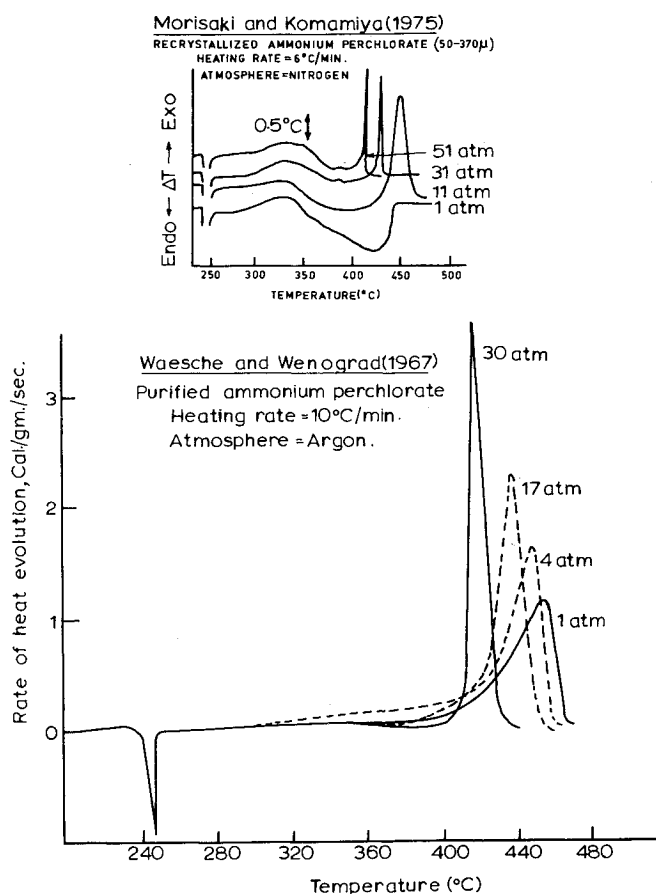
Morisaki and Komamiya (1975)

RECRYSTALLIZED AMMONIUM PERCHLORATE (50-370μ)
HEATING RATE = 6°C/MIN.
ATMOSPHERE = NITROGEN

Waesche and Wenograd (1967)

Purified ammonium perchlorate
Heating rate = 10°C/min.
Atmosphere = Argon.

Fig. 2 DTA and DSC thermograms of ammonium perchlorate at higher pressures.

Schmidt (1969)
Trimodal blend ammonium perchlorate
Heating rate = 20°C.min^{-1}

1. 15 psi
2. 100 psi
3. 250 psi
4. 500 psi
5. 750 psi
6. 1000 psi
7. 2000 psi

Fig. 3 DTA of AP at high pressures.

Fig. 4 Dependence of burning rate on decomposition characteristics of ammonium perchlorate at elevated pressures.

Table 1 Calculated data of various authors on the decomposition and $\dot{r}$ of AP at higher pressures

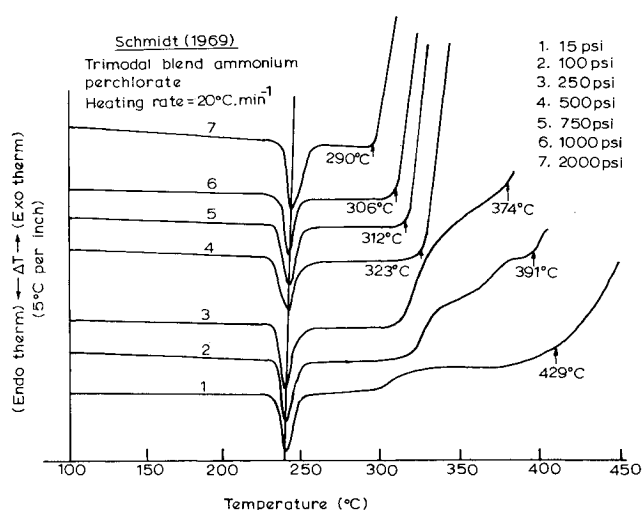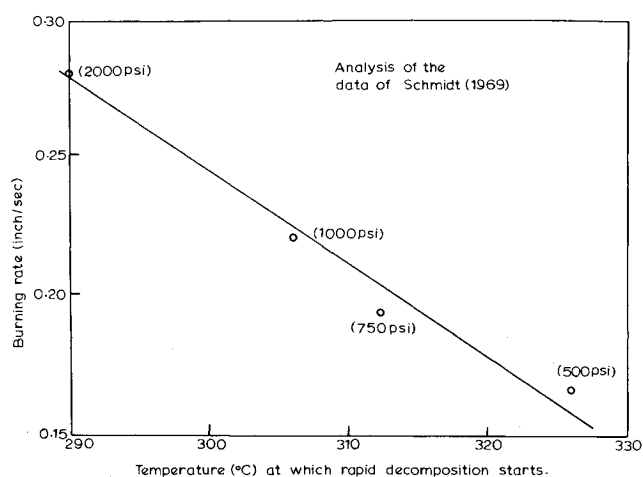| Pressure atm	Decomposition temp, °C	Remarks	$\dot{r}$ cm/s	Reference
1	...	End temperature (DTA)	...	33
11	445		...	
31	432		...	
51	515		...	
1	458	Peak temperature in (DSC)	...	11
4	451		...	
17	440		...	
30	425		...	
1	429	Temperature at which rapid decomposition starts (DSC)	...	34
6.8	391		...	
17.0	374		...	
34.0	327		0.166	
51.0	317		0.194	
68.0	313		0.220	
136.1	294		0.280	

pressures, although in actual practice the effect persists at the lowest pressure at which the propellant burns. The gas-phase model does not explain the effect of particle size distribution and cannot predict 1) the effect of changing binder on $\dot{r}$, 2) variation of pressure index n with pressure (ambient to 4000 psi), 3) prediction of surface temperature, 4) effect of many catalysts, 5) condensed-phase heat release, and 6) temperature sensitivity of $\dot{r}$.

Although Waesche and Wenograd[30] have attempted to calcuate r from the condensed-phase concept, this approach, in general, cannot predict the pressure dependence of $\dot{r}$. This approach has potentialities to predict 1) condensed-phase heat release, 2) temperature sensitivity of $\dot{r}$, and 3) explanation of

catalyst action. According to this concept, thermal decomposition of the propellant should have a correlation with the $\dot{r}$. In the past few years our laboratory has shown[31,32] that propellant $\dot{r}$ is altered when decomposition characteristics of the propellant are changed. However, such dependence has been shown only under ambient conditions. There is a need to demonstrate that at higher pressures, where $\dot{r}$ is increased with pressure, the decomposition characteristics should also be altered in similar directions. Although no direct evidence of this is available, an attempt has been made to analyze the existing data in the literature.

Waesche and Wenograd[11] have investigated the decomposition of AP by employing the DSC technique. They have examined the effect of pressure on thermal decomposition (TD) of AP (Fig. 2). They observed that when the pressure is increased, the high-temperature peak becomes sharper and it occurs at lower temperatures, but the phase transition temperature remains unaltered. Thus, the thermal decomposition of AP is sensitized as the pressure is increased. Morisaki and Kamamiya[33] have obtained DTA of AP in N_2 and O_2 at various pressures (Fig. 2). Their results show that 1) phase transition remains unaltered, 2) low-temperature exotherm does not show any appreciable change, 3) high-temperature exotherm gets affected appreciably—the peak becomes sharper as the pressure is increased and also the temperature
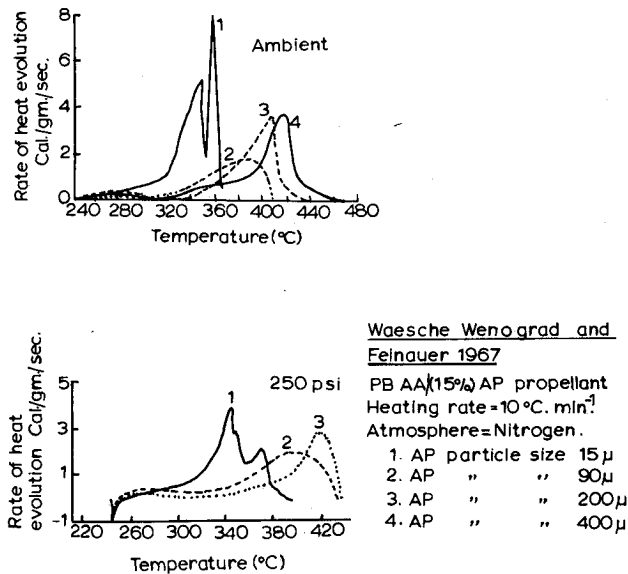
Fig. 5 DSC thermograms of PB AA/AP propellant at ambient and 250-psi pressure.

at which the decomposition is complete is lowered. Their results also show that the decomposition of AP is sensitized as the pressure is increased. Schmidt[34] has also studied the thermal decomposition of AP at higher pressures using DSC technique. He has not reported the complete thermograms; however, it is possible to note the temperature at which the onset of fast decomposition in the high-temperature region occurs (Fig. 3). This point perhaps represents the starting point of the high-temperature exotherm. The $\dot{r}$ values obtained by them were taken from their $\dot{r}$ vs pressure plot and the above decomposition temperatures at different pressures were obtained from the DSC thermograms. The derived high-pressure AP deflagration and decomposition data from various authors are summarized in Table 1. A plot of $\dot{r}$ vs decomposition temperature (Fig. 4) was obtained from the data of Schmidt, which clearly indicate the dependency of $\dot{r}$ on the thermal decomposition of AP at higher pressures. Although the actual data of Bouck[35] are not available to the author, it is believed he also found that the temperature for the onset of runaway exothermic reaction of solid propellant is a function of pressure and heating rate. Waesche et al.[36] have studied the thermal decomposition and burning rate of polybutadiene-acrylic acid (PBAN) based propellants. The studies were carried out at ambient pressure and 250 psi to
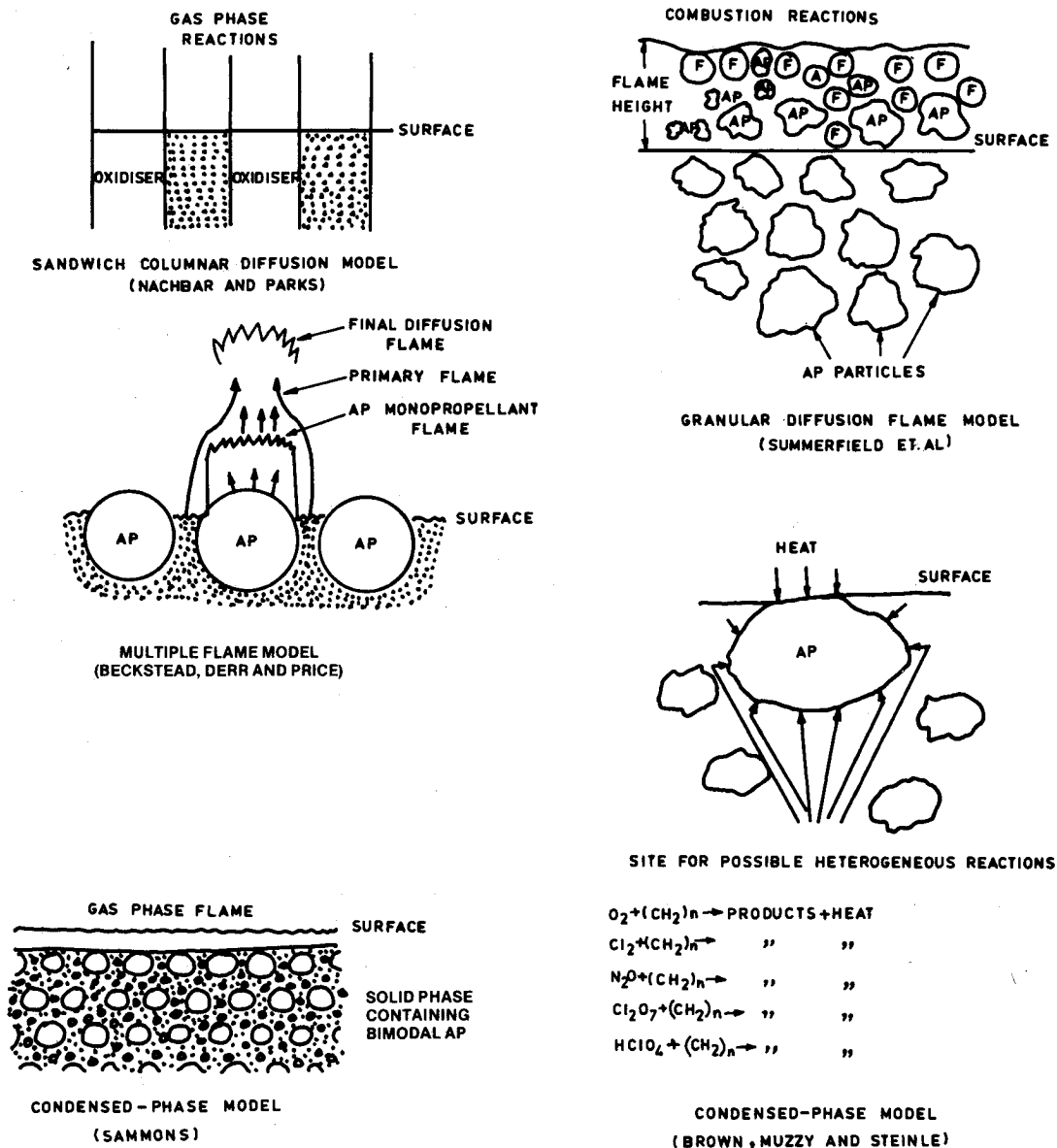

Fig. 6 Combustion models.

examine the effect of particle size and catalysts. A close look at their results (Fig. 5) shows that those formulations which increase $\dot{r}$ also sensitize the thermal decomposition both at ambient pressure as well as at 250 psi. The foregoing analysis, therefore, clearly demonstrates that condensed-phase reactions play a significant role even at higher pressures.

Most of the support for condensed-phase reactions has come from the thermal studies using DTA, DSC, and TG techniques which have also received criticism. Caveney and Pittman,[37] supporting the gas-phase model, believe that the time available for subsurface consensed-phase reactions to occur in practical propellants is less than 10^{-3}s, which is several orders of magnitude less than the heating rates used in DTA/DSC. They also believe that DTA/DSC measure large amounts of gas-phase heat release close to the surface in addition to the condensed-phase reactions. Northam et al.[38] studied the correlation between the low-temperature decomposition rate (TG at 158°C and 760 mm pressure) of CTPB propellants containing doped AP (0.16% PO_4^{-3} and 0.03 ClO_3^{-1}) and their respective $\dot{r}$. They found that $\dot{r}$ does not show any difference, whereas the TG measurements show a tenfold change in the decomposition rate.

Without taking recourse to thermal techniques, we have recently found, from the chemical analysis of the binder separated from decomposition and combustion residue, that common intermediates are formed during the decomposition and combustion of solid propellants.[39] These results very strongly support the occurence of condensed-phase reactions during combustion. The salient features of the gas-phase and condensed-phase approaches will be discussed now.

A) Gas-Phase Theories

Schultz and Dekker[40] developed the "two-temperature model," which states that the decomposition of the solid oxidizer and binder are essentially independent processes and assumes the regression rate of the fuel and binder to be governed by the Arrhenius equation according to which the solid-phase decomposition rate is expressed as a function of surface temperature. Satisfactory predictions for ammonium nitrate and to some extent AP propellants have been made using this theory. However, the model is not completely in accordance with the experimental findings.

Nachbar and Parks[41] proposed the "sandwich columnar diffusion flame model" (Fig. 6), which assumes that the propellant is made up of slabs of fuel and oxidizer of finite thickness. The solid-gas interface where the solid is converted into gas in assumed to be dry. The condensed-phase reactions are not taken into consideration. In spite of the elaborate mathematical treatment, this theory cannot predict the dependence of $\dot{r}$ on pressure.

Chaiken and Anderson[42] proposed the "thermal layer theory," which is based on the two-temperature postulate and is applicable to ammonium nitrate propellants. It assumes that the solid-phase decomposition is a result of the heat transfer from the flame zone or thermal layer surrounding the oxidizer particles and that this flame zone is a result of the gas-phase redox reactions between the oxidizer fuel pyrolysis products.

Rosen[26] developed a mathematical model based on premixed laminar flame which yields the following expression for the dependence of $\dot{r}$ on pressure (P): at low pressure $\dot{\gamma}/a$ $\propto P/b$, at high pressures $\dot{\gamma}/a \propto (P/b)^{1/3}$ where a and b are constants. It was found that the preceding relation does not hold good for every propellant, and it was not exact at low pressures.

Summerfield et al[28] put forward an elaborate model known as the "granular diffusion flame model" (Fig. 6) according to which the heat reaching the burning surface comes from the main diffusion flamelets at the boundaries of the oxidizer and fuel vaporizer streams. The overall combustion speed is determined by both diffusional transport during mixing and by homogeneous gas-phase reactions. This theory illustrates

that the fuel pockets of variable dimensions burn in an atmosphere of oxidizing gaseous reaction products and some fuel vapor. In this unidimensional model the burning surface is assumed to be dry. The surface temperature has been assumed to be independent of pressure, particle size, and composition, but its dependence on catalysts has been suggested. The following $\dot{r}$ law has been derived from theory:

$$P/\dot{r} = a + bP^{2/3}$$

where empirically determined constants a and b are dependent on homogeneous gas-phase reaction rates and diffusion rates, respectively. It was found that theory could not explain the combustion of condensed mixtures. Validity of the theory was found to be generally true only below 100-atm pressure. Although the theory credibly makes use of the heat feedback concept coupled with diffusional transport, it suffers from too many assumptions which are open to question. For eample, the studies on surface topography have revealed that the surface is not dry, contrary to what is assumed in the theory.

Penner[43] proposed an alternative mathematical treatment to that of Summerfield.[28] According to him the following equation shows the pressure dependence of $\dot{r}$

$$\left(\frac{1}{\dot{r}}\right)^2 = \left(\frac{a}{p}\right)^2 + \left(\frac{b}{p^{1/3}}\right)^2$$

This equation becomes identical to that proposed by Summerfield et al.[28] when the a/b ratio is zero or infinity.

Barrer and Nadaud[44] developed a theory analogous to that of Summerfield,[28] but it does not include the concept of a granular diffusion flame.

According to Rice[45] and Von Elbe et al.,[46] fuel-oxidizer gases emerge from the regressing surface in columnar streams and this model gives the equation.

$$\frac{1}{\dot{r}} = \left[\frac{a}{p} + C\right]$$

where a and C are constants representing chemical reaction rate and diffusional mixing rate, respectively.

Beckstead, et al.[47] developed a "multiple flame model" which is based on the concept of multiple flames (Fig. 6) involving the following picture: 1) preheating of binder and oxidizer occurs via conduction, 2) binder and oxidizer decompose endothermically, 3) exothermic condensed-phase reactions occur between the products of decomposition, and 4) gaseous products escape and react in the gas phase. Three separate flames are considered at low pressures: a) primary flame between the decomposition products of binder and the oxidizer, b) a premixed oxidizer flame, and c) final diffusion flame between the products of the other two flames. This model describes various quantitative predictions such as dependence of $\dot{r}$ on oxidizer loading, dependence of $\dot{r}$ on initial grain temperature, prediction of mean surface temperature and flame standoff distance. The predicted effect of oxidizer particle size is somewhat greater than the observed value.

Hertzberg[48] proposed two theories, namely, "quasilaminar diffusion (QLD) theory" and "quasilaminar diffusion and monopropellant (QLDM) theory." QLD theory is applicable to propellant systems that contain pure fuel and pure oxidizer particles, neither of which can sustain combustion independently. QLDM theory is applicable to AP based propellants where the monopropellant combustion of AP is considered. QLD theory includes the diffusion process and is developed by comparing the spatially averaged thermal conductive heat feedback for an ideal interdiffusion flame

with a laminar premixed flame of identical overall stoichiometry. This theory satisfactorily predicts the limiting effects of the diffusion process. The difference between QLDM and QLD theory is that in the former the limiting effect of the diffusion process is not as severe as in the latter. This is because the AP monopropellant flame provides a heat flux to the surface that is present regardless of the structure of the diffusion flame.

B) Condensed-Phase Theories

Selzer[49] measured the temperature profile of a solid propellant by an optical method and showed that phase transition of AP occurs within 1 mm of the surface, which strongly suggests that the temperature in the solid phase is at least 240°C. According to Selzer there is a possibility of some heat source in the solid due to binder-oxidizer interactions.

Hermance[50] postulated one of the most elaborate mathematical treatments, which includes condensed-phase reactions. In contrast to some models, this model has no arbitrary or empirically derived constants, although some of the parameters are difficult to obtain. An $\dot{r}$ vs pressure curve was computed with no variables left to be determined from the data. The model incorporates heterogeneity of the surface and heat release at or below the surface. It assumes that the binder and the oxidizer decompose endothermically and exothermically, respectively, at or below the surface and also that exothermic reactions occur between the fuel binder and decomposed oxidizer particles. The model predicts 1) an $\dot{r}$ vs pressure relationship which agrees with the experimental findings, 2) a surface temperature which agrees with the experimental value, and 3) a reasonable value for the heat generation in the condensed phase.

Waesche et al.[36] studied the decomposition (by DSC technique) and combustion behavior of PBAA/AP propellants. The results show that those formulations that increase $\dot{r}$ also cause the major exotherms to occur at lower temperatures and with faster rates. Furthermore, they observed that heat release rate indicated that condensed phase reactions were rapid and intense enough to supply a significant portion of energy required to maintain the combustion wave at observed $\dot{r}$. Waesche and Wenograd[30] also tried to calculate $\dot{r}$ theoretically. They considered the "Zeldovich flameless combustion regime model," where there is no significant heat feedback from the flame to the surface. By adopting the surface temperature data of Inami et al.[51] and Powling et al.,[52] they calculated $\dot{r}$ for PBAA/AP (75%) propellants containing AP of different particle sizes. They found that most of the calculated $\dot{r}$ compared reasonably well with experimental values, but were consistently lower. This they attributed to the lack of additional gas-phase heat flux, which also contributes to the regression process.

Brown et al.[53] gave a physical model (Fig. 6) in which interfacial condensed-phase reactions are considered. The exothermic surface and subsurface interfacial reactions release sufficient heat to expel partially burned products into the flame zone. The incorporation of exothermic chemical processes on and within the solid phase represents an important addition to the analysis of the propellant transient combustion phenomenon. According to them, such reactions depend exponentially on the solid-phase temperature.

According to Sammons,[54] in order for combustion to take place the solid has to gasify since the condensed-phase reactions are of importance since they lead to the generation of combustible gaseous species. Since the surface temperature in solid propellants is in the range of 725-1000 K there must be a thermal gradient in the subsurface region where the propellant will decompose in the solid phase. He proposed a model exhibiting condensed-phase reactions (Fig. 6). AP and binder both decompose in the solid phase and the products mix and interact in the interstices between AP particles. The fine AP particles are primarily responsible for the oxidizer gases or

liquids in the interstices because of the larger surface area. Oxidizer gases and liquids come only from the interfaces of the fuel and the larger AP, making the heat production in the interstices diffusion controlled. This reasoning quite satisfactorily explains the effect of fine AP on $\dot{r}$. The gas-phase model, on the other hand, can explain the pressure dependence of $\dot{r}$ on the propellant containing very large monomodal particles. But it cannot explain the temperature sensitivity of $\dot{r}$ and the effect of fine oxidizer particles on $\dot{r}$, which, however, can be adequately explained by considering the condensed-phase reactions. On the basis of the observations of Hightower and Price,[55] Sammons believes that with large particles of AP ($\sim 200\mu$) there are no interfacial AP/fuel reactions, and, due to the greater depth of the subsurface reactions, their contribution to condensed-phase reactions is small. At higher heating rates encountered during combustion, AP of 10μ or lower particle size can be assumed to be completely decomposed in the liquid binder layer, resulting in the generation of large exothermic condensed-phase reactions which consequently increase the $\dot{r}$. In a bimodal mixture, the $\dot{r}$ will be still higher because of the rapid decomposition of smaller particles, which also increases the number of subsurface reactions in the larger particles.

According to Kumar,[56,57] between the high-temperature gas-phase chemical reactions at high pressures and condensed-phase chemical reaction at low temperatures the overall rate determining step is more likely to be the latter. According to him, the pressure index in the power law is a composite quantity and incorporates the pressure dependent chemical reactions in the condensed phase. It is suggested that under certain circumstances surface reactions in a thin layer augment subsurface reactions. After the material travels from the deep solid region and reaches the surface, the binder and the oxidizer mix thoroughly.

Pantoflicek and Lebr[58] have proposed a theoretical model for the combustion of solid propellants at low pressures below 30-50 kg/cm². It has been assumed that the $\dot{r}$ is influenced only by reactions occurring during liquefaction and gasification of the propellants and that the amount of the heat transferred from the luminous zone is negligible. The theory developed explains the effect of small changes in the propellant compositions on the burning process in ignition energy. The calculated and measured $\dot{r}$ values are in good agreement.

Manelis and Strunin[59] have given a theoretical treatment of the combustion of AP and composite solid propellants. The results have been compared with experimental data and evidence supporting the contribution of condensed-phase reactions in combustion has been given.

Rastogi et al.[60] studied decomposition of PS/AP propellant along with its ingredients using DSC technique and found that the sum of the enthalpy change in the solid state for the ingredients was much less than the enthalpy change for the corresponding propellant decomposition, showing thereby that heterogeneous condensed-phase reactions occur in the propellant during thermal decomposition.

From mass-spectrometric analysis of the decomposition gases of PS/AP propellant, Kishore et al.[61] found that the mass spectra of the propellant were different from the sum of the mass spectra of ingredients PS and AP. This behavior was explained on the basis of the interaction of AP and PS decomposition products in the porous matrix of the propellant.

The results on the enthalpy measurements of PS/AP propellant from DSC data and calorimetric values showed that condensed-phase reactions contribute about one-third to the overall combustion process.[62] Recently, from $\dot{r}$ and thermal decomposition studies on a number of propellant systems, a correlation was found to exist between the thermal decomposition and $\dot{r}$. From the slope of the plot between TD number and $\dot{r}$ number, it was again found that condensed-phase reactions contribute one-third to the total combustion

process at ambient pressure.[32] Similar studies at higher pressures will reveal the contribution of condensed-phase reactions at higher pressures.

Kishore et al.[39] carried out a detailed analysis of the decomposition and combustion residue of PS/AP propellant using the TLC technique. It was observed that some peroxide intermediate is formed during decomposition, which was also present during combustion; thus, direct evidence of the existence of condensed-phase reactions was given. Further, they found that the introduction of peroxy intermediate enhanced the burning rate.

Conclusions

Although many of the experimental observations on AP combustion have been interpreted by various theories, no theory is perfect in itself. Phenomena like low-pressure quenching and catalyst action need special attention to be explained adequately by mathematical models.

Polymer combustion has been studied in the past in various geometries such as thin sheets, flat slab, centrally perforated cylinder, oxidizer-polymer sandwich, spherical particle, and a rod. Of special interest is the combustion in the form of a rod which would be similar to a propellant combustion. It is surprising that no appropriate theory is available which could describe the polymer combustion in the form of a rod. Therefore, there is need to develop a theoretical model for polymer combustion in rod form. To the best of our knowledge, high-pressure combustion studies of polymers are also not available, and there is a need to explore this aspect also. Such studies on polymer combustion may be quite useful in deriving useful predictions about propellant combustion.

Many theoretical models are available for propellant combustion which describe many of the observed experimental facts. However, some of the parameters, like quantitative predictions of $\dot{r}$, mechanism of catalyst action, and predictions of condensed-phase heat release, have yet to be incorporated to make a complete theory. Of these, the condensed-phase contribution, which has amply been demonstrated qualitatively by many workers, must be accounted for in developing a sound theory.

In summary the mathematical modeling of combustion in AP, polymers, and propellants is not perfect and needs a renewed look in the light of important experimental findings. Recent work of King[63] and Price et al.[64] is a welcome attempt in this direction.

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