# Effect of Radiant Energy on the Burning Rate of a Composite Solid Propellant

M. D. Horton\* and L. Z. Youngberg†
Brigham Young University, Provo, Utah

This paper describes the measured effect of radiant energy flux on the atmospheric pressure burning rate of a solid propellant. It was concluded that the effect is negligible except when the propellant burning rate is very low as, for example, during the quench of a controllable motor. Also, from the experimental data, it was calculated that the PBAN-AP propellant had an apparent surface temperature of 560°C and an apparent exothermic solid decomposition that liberated 130 cal/g.

# Nomenclature $A_s/A_w={ m ratio}$ of burning propellant surface area to flux-chamber

 $\begin{array}{ll} C_p & = \text{ heat capacity of solid propellant} \\ C_{pf} & = \text{ heat capacity of propellant flame gases} \\ \mathfrak{T} & = \text{ gray body form factor for radiation from burning propellant surface to flux chamber wall} \\ F & = \text{ black body form factor} \\ k & = \text{ thermal conductivity of propellant flame gas} \\ q_s & = \rho_s r_0 [C_p (T_s - T_c) + \lambda] \\ q_f & = k/\delta_0 (T_f - T_s) \end{array}$ 

 $q_r$  = net rate of radiative energy flux to combusting propellant surface

wall area

r = burning rate of solid propellant  $r_0$  = burning rate of solid propellant when  $q_r$  is zero

 $T_c$  = conditioning temperature of solid propellant  $T_f$  = flame temperature for propellant combustion gases

 $f_{f0}$  = flame temperature for propellant combustion gases when  $q_r$  is zero

 $T_s$  = surface temperature of combusting solid propellant

 $T_w$  = wall temperature of flux chamber

δ = hypothetical flame thickness as defined by Eq. 4

 $\delta_0$  = hypothetical flame thickness as defined by Eq. 4 when  $q_r$  is zero

 $\epsilon_s$  = emissivity of combusting propellant surface

 $\epsilon_w$  = emissivity of flux chamber wall

λ = heat of decomposition of solid propellant

 $\rho_s$  = density of solid propellant  $\sigma$  = Stefan-Boltzmann constant

#### Introduction

It has long been known that an incident flux of radiant energy will cause an increase in the burning rate of a solid propellant. For example, Refs. 1-4 discuss the phenomenon. The effect is of practical interest in that during the course of a firing, the inert parts of a rocket become heated and radiate a significant amount of energy to the propellant. This radiation can alter the combustion of the propellant and affect the behavior of the motor. Also, the phenomenon is of theoretical interest in that the combustion of a solid propellant cannot be well understood until this phenomenon is quantitatively explained.

Accordingly, this research has undertaken to obtain quantitative data relating the burning rate of a solid propellant to the incident radiative flux. Also, the experimental data were to be interpreted and their theoretical significance explained.

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\* Associate Professor of Chemical Engineering.

† Masters Candidate.

# Analysis

In order to theoretically relate burning rate to radiation, one must select a combustion model. It is well to remember that any subsequent examination of experimental data will yield results dependent on the model chosen. Thus, different models may well lead to different interpretations. Be that as it may, the very simple model depicted in Fig. 1 is chosen and will be examined analytically. Note that the model represents a propellant that is passively heated to a characteristic temperature where it decomposes then subsequently reacts in the gas phase.

The general approach used is to first assume that at a given pressure the burning rate is a function of flame temperature and incident radiation. Then upon making appropriate heat balances and mathematical operations, a relation between radiant flux and burning rate is derived. In general

$$r = f(q_r, T_f) \tag{1}$$

so

$$dr = (\partial r/\partial q_r)dq_r + (\partial r/\partial T_f)dT_f \tag{2}$$

and

$$dr/dq_r = (\partial r/\partial q_r) + (\partial r/\partial T_f)dT_f/dq_r \tag{3}$$

The first partial derivative  $\partial r/\partial q_r$  is evaluated by making a heat balance at the interface which shows that at a given pressure

$$r\rho_s[C_p(T_s - T_c) + \lambda] = (k/\delta)(T_f - T_s) + q_r \qquad (4)$$

Now r,  $\delta$ , and  $T_f$  are all dependent on  $q_r$ . The unknown, inconvenient variable  $\delta$  can be eliminated by first defining a reference condition at a given pressure where the net radiative flux is zero. Hence

$$r_0 \rho_s [C_p (T_s - T_c) + \lambda] = (k/\delta_0) (T_{f0} - T_s)$$
 (5)

and then the assumption is made that

$$\delta = \delta_0(r/r_0) \tag{6}$$

This roughly corresponds to assuming that the time for the gaseous products to react is the sum of a diffusion and a chemical reaction time. This assumption has been used to derive a reasonable steady-state burning rate law<sup>5</sup> and hence should also give reasonable results here. Equations (4-6) are now combined then solved for r to yield

$$r = \frac{q_r \pm \{q_r^2 + 4\rho_s k r_0 \delta_0^{-1} (T_f - T_s) [C_p (T_s - T_c) + \lambda]\}^{1/2}}{2\rho_s [C_p (T_s - T_c) + \lambda]}$$

(7)

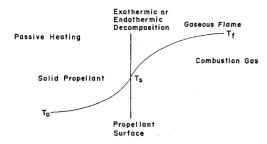


Fig. 1 Model of propellant combustion zone.

where only the positive root has physical significance. Defining  $\rho_s r_0[C_p(T_s - T_c) + \lambda]$  as  $q_s$  and  $(k/\delta_0)(T_f - T_s)$  as  $q_f$ , then taking the derivative

$$\partial r/\partial q_r = (r_0/2q_s)[1 + q_r/(q_r^2 + 4q_sq_f)^{1/2}]$$
 (8)

Also from Eq. (7)

$$\partial r/\partial T_f = kr_0/\delta_0 (q_r^2 + 4q_s q_f)^{-1/2}$$
 (9)

The other unknown derivative  $dT_f/dq_r$  can be evaluated by noting from a heat balance that

$$r\rho_s C_{pf}(T_f - T_{f0}) = q_r \tag{10}$$

and hence

$$\frac{dT_f}{dq_r} = \frac{1 - \rho_s C_{pf} (T_f - T_{f0}) \ dr/dq_r}{r \rho_s C_{pf}}$$
 (11)

Upon combination of Eqs. (3, 8, 9, and 11) the desired equation is found to be

$$\frac{dr}{dq_r} = \left\{ \frac{r_0}{2q_s} \left[ 1 + q_r (q_r^2 + 4q_s q_f)^{-1/2} \right] + \frac{kr_0}{r\rho_s C_{pf} \delta_0} \left( q_r^2 + 4q_s q_f \right)^{-1/2} \right\} \times \left[ 1 + \frac{kr_0 (T_f - T_{f0}) (q_r^2 + 4q_s q_f)^{-1/2}}{r\delta_0} \right]^{-1} \tag{12}$$

This expression may be simplified when, as in the present study, the radiative fluxes are a small (less than 10%) part of the total heat flux to the propellant. When this is so,  $r_0 \simeq r$ ,  $q_r^2 \ll 4q_sq_f$ ,  $(T_f - T_{f0})/(T_f - T_s) \ll 1$ , and  $q_s \approx q_f$ . These approximations can be used to simplify Eq. (12) and obtain

$$dr/dq_r = \{1 + [C_p(T_s - T_c) + \lambda][C_{pf}(T_{f0} - T_s)]^{-1}\} + \{2\rho_s[C_p(T_s - T_c) + \lambda]\}^{-1}$$
(13)

which is the desired equation relating the burning rate of the propellant to the incident radiative flux. Equation (13) predicts a straight line relationship between r and  $q_r$  which conclusion can be examined experimentally.

Table 1 Propellant burning rates, in./sec

Strands $\frac{1}{2} \times \frac{1}{2} \times 1^{\frac{1}{2}}$ in. long		Hollow cylinders 0.25-in i.d. $\times$ 0.80-in. o.d. $\times$ 1.25-in. long	
4.9 psia	$12.6 \mathrm{\ psia}$	4.9 psia	12.6 psia
0.0192	0.0385	0.0224	0.0408
0.0192	0.0382	0.0222	0.0386
0.0193		0.0219	0.0380
0.0193		0.0206	0.0436
		0.0243	0.0394
		0.0191	0.0422
		0.0188	0.0394
		0.0207	

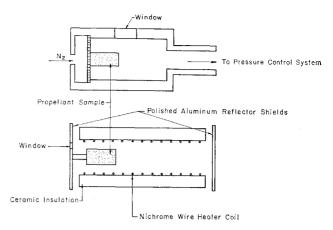


Fig. 2 Burning rate apparatus.

## Experiment

The object of the experimental program, which is described in detail in Ref. 6, was to determine the burning rate of the propellant as a function of radiative flux. The propellant selected for study was composed of 24% PBAN and 76% eighty-micron ammonium perchlorate. This propellant was furnished by the Naval Weapons Center and was the propellant used for Round Robin testing by the committee concerned with T-burner standardization.

The burning rate of the propellant was measured at room temperature (75°F) in the two types of apparatus illustrated in Fig. 2. The upper combustion chamber was a standard strand-burner and was used to determine propellant burning rates at atmospheric and at one subatmospheric pressure. The bottom chamber was a furnace used to determine the burning rate as a function of the radiant flux to the burning propellant surface at atmospheric pressure.

Figure 3 depicts the three propellant geometries used in the study; a simple strand, an externally burning cylinder and an internally burning cylinder. With each of these geometries the sample was machined to the desired dimensions then the surface to be ignited was coated with a pyrotechnic igniter and later ignited by the use of a hot wire. During each test, the output of a Raytheon EM 1502 optical sensor which "saw" the propellant flame was recorded on a Visicorder. Subsequently, the burning rate was calculated from the duration on the flame radiation and the known thickness of the propellant.

Use of this optical technique demands that the ignition transient be negligible compared to the total burn time. Theoretically, for the times and dimensions involved, the transient was small and the experimental evidence also indicated the transient was small. Thus it is felt that the aforementioned technique did yield valid burning rate data. This conclusion is supported by the fact that at room temperature

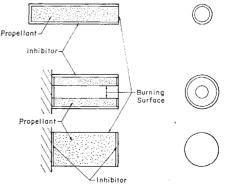


Fig. 3 Propellant geometries.

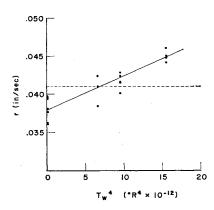


Fig. 4 Burning rate of externally burning cylindrical propellant grains as a function of chamber wall temperature. The dashed line is the burning rate for internally burning cylinders.

the same burning rate was determined from the strands as for externally burning cylinders.

The flame front seemed to uniformly reach the outer surface of the internal-burning cylinder and hence erosive burning did not appear to be important.

Table 1 is a list of the data obtained from the burning of strands and internally-burning cylinders in the strand burner. Table 2 contains the burning rate data obtained from the flux chamber whose operation is described as follows.

Reflective aluminum plates were placed at the ends of the chamber, power was applied to the heating coil and then sufficient time allowed so that steady state was reached. One end plate was removed and the temperature read with an InfRed Pyrometer Model BF-713. Then the propellant sample was inserted, quickly ignited (within 2 sec), and the burn time recorded.

### **Calculations**

By comparing the burning rate obtained at atmospheric pressure in the strand burner with that from the flux chamber,

Table 2 Burning rate data of externally burning cylinders 0.8-in. o.d.  $\times$  0.8-in. long

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Chamber wall	Calculated flux	<b>7</b> 5
temperature,	to surface, a	Burning rate
$^{\circ}R$	Btu/in.² sec	in./sec
535	-0.015	0.0381
535	-0.015	0.0397
535	-0.015	0.0395
535	-0.015	0.0381
535	-0.015	0.0362
535	-0.015	0.0360
535	-0.015	0.0395
535	-0.015	0.0393
535	-0.015	0.0376
1600	+0.0036	0.0423
1600	+0.0036	0.0384
1600	+0.0036	0.0410
1760	0.013	0.0424
1760	0.013	0.0428
1760	0.013	0.0401
1760	0.013	0.0416
1760	0.013	0.0415
1760	0.013	0.0415
1985	0.030	0.0448
1985	0.030	0.0448
1985	0.030	0.0460
1985	0.030	0.0450
1985	0.030	0.0448
1985	0.030	0.0441

<sup>&</sup>lt;sup>a</sup> For a propellant emissivity of 0.9 and a surface temperature of 1500°R.

Table 3 Propellant heat of decomposition

$\epsilon_8$	$rac{dr/dq_{r},}{ ext{in.}^{3}/ ext{Btu}}$	λ, Btu/lb
0.9	0.15	-250
0.8	0.14	-240
0.7	0.12	-230

it is possible to calculate the surface temperature of the burning propellant. This is done by assuming that the gas is transparent and noting that because the hole in the internal-burning cylinder was long and small, radiation losses from the burning surface were negligible. Thus the net radiative flux was zero because any portion of the propellant surface was only interchanging radiant energy with other propellant surface at the same temperature.

An equivalent situation must also have existed when the externally-burning cylindrical propellant grains were burned in the flux chamber. That is, at some chamber-wall temperature the net radiant flux to the propellant surface would be zero. Obviously, when this condition existed, the burning rate would be the same for the internally-burning cylinder and for the externally-burning cylinder. This is because the pressures are the same and both combustion processes are adiabatic.

The wall temperature which caused equal burning rates was found by plotting as in Fig. 4 the burning rate as a function of  $T_w^4$ . Then, the data were fit by a least-mean-squares technique and it was found that a chamber wall temperature of 1500°R (560°C) caused the burning rate to be the same as in the internally burning cylinder, 0.040 in./sec. Because the net radiative flux is zero only when the temperatures are equal, the surface temperature of the propellant was also  $560^{\circ}$ C.

To calculate the flux to the burning surface, it was assumed that not only was the flame transparent, but also that the radiative surfaces were "gray." Then,

$$q_r = \sigma \mathfrak{F}(T_w^4 - T_s^4) \tag{14}$$

with

$$1/\mathfrak{F} = F + (1/\epsilon_s - 1) + A_s/A_w(1/\epsilon_w - 1) \tag{15}$$

For the externally-burning cylinders in the flux chamber, F was calculated by the "crossed-strings" method of Hottel<sup>7</sup> to have an average value of 0.86. The chamber wall emissivity was measured as 0.80 so the radiative flux could be calculated if the emissivity of the burning propellant surface were known. Unfortunately, no reliable way of measuring this parameter is known and so several reasonable values were used in subsequent calculations. The slope  $dr/dq_r$  was then evaluated from the burning rate measurements and the flux calculations based on an assumed value for  $\epsilon_s$ .

As previously mentioned, the value for  $T_s$  was calculated to be 1500°R. Thermochemical calculations gave values for  $T_{f0}$  and  $C_{pf}$  to be 3910°R and 0.45 Btu/lb °R respectively. The specific heat and density of the solid propellant were measured experimentally and were 0.31 Btu/lb °R and 0.058 lbs/in³. With values known for the preceding parameters and also  $T_s$ , Eq. (13) could be used to calculate the heat of decomposition ( $\lambda$ ) of the solid propellant. Table 3 summarizes the results of the calculations and indicates a value of about -240 Btu/lb (-130 cal/g).

#### Discussion

It is interesting to note before proceeding that the relatively simple procedure described previously has made it possible to calculate both the surface temperature and the heat of decomposition of the solid propellant. Both of these parameters, in some form or another appear in all solid pro-

pellant combustion theories. Hence a method of determining their values is of considerable utility in evaluating theoretical models.

Because of the many assumptions used in the treatment and because of the fact that the answers are dependent on the combustion model chosen, the numerical values are best considered as qualitative. However, other investigators<sup>8,9,10</sup> have also performed measurements from which  $T_s$  was deduced or measured. Powling and Smith report values ranging from 500 to 550°C for an AP polyisobutylene propellant and Sabadell et al. report values of 510–660°C for several PBAA-AP propellants. Studies with pure AP crystals have indicated a  $T_s$  value of 525–600°C. Thus the present value of 560°C agrees very well with other work.

The heat of decomposition determined in this study compares very well with values of about -130 cal/g which are inferred from the temperature profile of the combustion zone. Such good agreement is not noted, however, when the comparison is made with values calculated from rapid depressurization tests. The rapid depressurization technique typically yields values of about 50 cal/g. When the present computational technique is applied to other radiation-burning rate studies,  $^{2,18}$  it is found that the heats of decomposition are calculated to be 35, -120, -175, and -50 cal/g for respectively pressed AP, pressed AP containing 0.5% copper chromite, pressed AP containing 0.5% copper chromite, propellant containing 0.5% copper chromite.

It can be seen from Table 3 that the value of  $\lambda$  is only weakly dependent on the assumed value for the emissivity. Larger uncertainty exists because of the scatter in the burning rate data. Use of the 70% confidence level for the burning rate data shows that the propellant surface temperature is between 1230 and 1700°R (422–672°C). Also, to the same confidence level the value of  $\lambda$  is between about -175 and -330 Btu/lb. This rather large difference is caused by the uncertainty in the value of the surface temperature and the uncertainty in the slope of the burning rate-heat flux curve.

The utility of the method presented in this paper can be seen when the results are applied also to transient combustion. Reference 12 utilizes the same simple combustion model to treat the process in which a rapid pressure decrease extinguishes a burning solid-propellant flame. When the  $T_s$  and  $\lambda$  values determined in this paper were used to generate theoretical extinction results for the same propellant, it was found that theory and experiment disagreed and hence the combustion model was oversimplified. Thus, the approach makes it possible to see if a combustion theory can consistently explain both steady-state and transient data. This is very important since further methods to evaluate transient combustion theories have been badly needed.

The results of this investigation are also of practical interest. First of all, as can be seen from Eq. (13) and Table 1, a given flux level causes a given change in burning rate. For most operational rocket motor geometries and inert part temperatures, radiation-induced changes in burning rate are

negligible. This can be seen by considering the aforementioned data which show that a wall temperature of 560°C increases the strand burning rate by 0.003 in./sec at both 4.9 and 12.6 psia. At a typical operating pressure of 500 psi, the burning rate would be increased from 0.336 to 0.339 in./sec which is a negligible 1% change. This effect does, however, become important when the burning rate is low. For example, when a propellant is extinguished by depressurization, the heat feedback from the hot nozzle to the nearly extinguished propellant would be expected to have a significant effect. All of the preceding discussion applies to propellants that produce relatively transparent flames. Heavily aluminized propellants produce gases that are so opaque that the combusting surface is effectively screened from the surroundings.

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