

# An Elementary Calculation of the Combustion of Solid Propellants<sup>1</sup>

F. E. C. Culick

California Institute of Technology, Pasadena, California 91109

(Received 26 December 1967; in revised form 15 July 1968)

**Abstract**—An Elementary Calculation of the Combustion of Solid Propellants. The problem of the burning of a solid propellant is treated in an approximate manner by prescribing the spatial distribution of energy release in the gas phase. Adoption of this inverse approach converts the usual non-linear problem to a linear eigenvalue problem which is easily solvable. Results for concentrated combustion (a flame front) and special cases of distributed energy release are given. Qualitative aspects such as flame stand-off distance, flame thickness, and various components of heat transfer within the combustion region are clearly shown. Examination of the influence of energy loss by radiation from the solid-gas interface gives satisfactory agreement with previous computations based on the non-linear formulation. An application to the problem of unsteady burning, and the response to pressure fluctuations is discussed briefly. The ease with which useful results can be obtained seems to justify the imperfect nature of the analysis.

*Translated abstracts appear at the end of this article.*

## Nomenclature

$A$   $A = E_s/R_0(1 - T_0/T_s)$ ;  
 $C, C_p$  specific heats of solid and gas;  
 $E_s, E_f$  activation energies of surface and gas phase reactions;  
 $h$  total enthalpy;  
 $m$  mass flux ( $\text{g}/\text{cm}^2\text{-sec}$ );  
 $\dot{q}_C$  energy loss from interior of solid;  
 $\dot{q}_R$  energy loss by radiation from solid-gas interface;  
 $Q_s$  latent heat associated with surface reaction;  
 $Q_g$  heat release in gas phase ( $\text{cal}/\text{cm}$ );  
 $r$  linear burning rate ( $\text{cm}/\text{sec}$ );  
 $R_0$  universal gas constant;  
 $T_0$  temperature of cold propellant;  
 $T_1, T_2$  Eqs. (11) and (12);  
 $T_f$  flame temperature;  
 $T_{fa}$  adiabatic flame temperature;  
 $w$  gas phase reaction rate, Eq. (34);  
 $\alpha$  exponent in distribution of combustion, Eq. (40);  
 $\beta_1$  exponent in pyrolysis law, Eq. (21);  
 $\beta$  exponent in reaction rate, Eq. (34);  
 $\varepsilon$  exponent in thermal conductivity,  $\lambda_g \sim T_f^\varepsilon$ ;  
 $A^2$  eigenvalue, Eqs. (17) and (18);  
 $\rho_p$  density of solid;

$\dot{\omega}$  reaction rate ( $\text{g}/\text{cm}^3\text{-sec}$ ), Eq. (1);  
 $\tau$  normalized temperature, Eq. (10);  
 $\Omega$  Eq. (13);  
 $\bar{\Omega}$  Eq. (14);  
 $(\bar{\quad})$  mean value;  
 $(\delta)$  fluctuation;  
 $(\quad)_{0\pm}$  evaluated at mean position of solid-gas interface;  
 $(\quad)_{s\pm}$  evaluated at instantaneous position of solid-gas interface;  
 $(\quad)_f$  evaluated at flame;  
 $(\quad)^*$  reference values.

## Introduction

THERE exist several treatments of the combustion of a solid propellant, usually involving detailed calculations which are difficult to interpret until numerical results are obtained. The problem is obviously complicated because it not only encompasses chemical aspects which are poorly known, but also the fluid mechanics cannot be handled in a rigorous way. It is particularly true of composite propellants, which contain particles of oxidizer immersed in fuel, that analysis is at best a crude representation of reality.

For example, a laminar, one-dimensional flame is usually treated, with varying amounts of chemistry explicitly accounted for. The source of difficulty in even this simplified description is the non-linear dependence of reaction rates on temperature. Since

<sup>1</sup> Work performed under a personal services contract with Naval Weapons Center, China Lake, California.

the problem eventually comes down to solution of a differential equation for the temperature, further approximations are necessary. References [1-3] for example, treat essentially the same non-linear equation in different ways.

When properly handled, as in the references cited, the reaction rates, and hence the distribution of burning within the gas phase, must be treated as functions of the local temperature and composition; the distribution in space arises because those variables depend on position. However, it is conceptually appealing, and often very helpful, to think in terms of the spatial distribution directly. Thus, one frequently speaks of "flame stand-off distance" and "flame thickness" for example.

It is somewhat surprising, therefore, that analytical descriptions of a burning solid, based *ab initio* on the spatial distribution, have not, so far as the author is aware, been reported. Having adopted this approach, one immediately loses the opportunity for recovering some of the detailed information contained in a more careful treatment of the problem. However, in return, one gains a much more lucid representation and, it appears, some of the dominant features are readily accessible. This is the sole justification for the present work, which is bound to be less accurate than other available treatments.

Because the non-linear equation mentioned above is replaced by a linear, inhomogeneous equation, the calculations are straightforward, particularly for the two special cases treated here: a flame front, in which all combustion is concentrated in a plane parallel to the solid surface; and a flame of finite thickness in which the energy release is uniform or varies exponentially in space. An additional question examined is the effect of energy lost by radiation from the solid surface. This has been treated in [1] and [3]; the results found here agree fairly well with the more accurate computations of Johnson and Nachbar. Application of these steady-state results to the problem of the transient response of a burning is also discussed; owing to the necessary restriction to low frequencies, this may be of limited value.

### Formulation

The references given, and further works cited therein, provide adequate coverage of the background material. It is sufficient here to note that the usual set of conservation equations for the gas phase can be reduced to a single differential equation, taken in this work to be the energy equation written for the temperature. The most significant approximations are that pressure and viscous forces are ignored, and

that the mass diffusivity of any constituent is equal to the thermal diffusivity of the mixture (i.e. Lewis number is unity). It will also be assumed later, to simplify some calculations, that both the thermal conductivity and specific heat are constant; this is not essential to the argument. Thus, the equation to be solved is

$$mC_p \frac{dT}{dx} - \frac{d}{dx} \left( \lambda_g \frac{dT}{dx} \right) = Q_g \dot{\omega} \quad (1)$$

where  $Q_g$  is the total heat released in the gas phase, per unit mass, and  $\dot{\omega}$  is the reaction rate, mass per unit volume and time.

As defined here,  $Q_g$  depends on the composition of the propellant but not locally in the gas phase. The influence of composition appears wholly in  $\dot{\omega}$  (for example [1, 2] as a product of concentrations in a second order reaction involving only fuel and oxidizer). The dependence of  $\dot{\omega}$  on the local composition will not be shown explicitly since its spatial distribution will be specified.

The boundary conditions which should be satisfied by the temperature profile are: at the downstream side of the flame

$$T = T_f \quad (x \rightarrow \infty) \quad (2a)$$

$$\frac{dT}{dx} \rightarrow 0 \quad (2b)$$

where  $T_f$  is the flame temperature, and at the surface

$$T = T_2 \quad (3a)$$

$$\begin{aligned} \left( \lambda_g \frac{dT}{dx} \right)_{0+} &= \left( \lambda_p \frac{dT}{dx} \right)_{0-} + m(h_{0+} - h_{0-}) \\ &= \left( \lambda_p \frac{dT}{dx} \right)_{0-} - mQ_s \end{aligned} \quad (3b)$$

Equation (3b) follows from the energy balance for the surface as shown in Fig. 1;  $(\lambda_p dT/dx)_{0-}$  is the heat passing from the interface to heat the solid material and  $Q_s$  is the heat released in the phase change at the surface ( $Q_s > 0$  for an exothermic reaction).

Following the notation of [3],  $\dot{q}_R$  represents heat lost (per unit area and time) by radiation from the interface itself, and  $\dot{q}_C$  represents a loss (undefined) from the interior of the solid. Both  $\dot{q}_R$  and  $\dot{q}_C$  are supposed completely lost in the sense that neither is absorbed by the gases in the region of interest. It follows from conservation of energy applied to the solid phase that

$$\left( \lambda_p \frac{dT}{dx} \right)_{0-} = mC(T_s - T_0) + \dot{q}_C \quad (4)$$

and the energy balance for the complete transformation, cold solid to hot gas, gives

$$T_f = \frac{C}{C_p} T_0 + \left(1 - \frac{C}{C_p}\right) T_s + \frac{Q_s + Q_g}{C_p} - \frac{\dot{q}_C + \dot{q}_R}{mC_p} \quad (5)$$

The boundary condition (2b) is superfluous, and automatically met if  $T$  remains finite to satisfy (2a). Moreover, with  $T_f$  set according to the global energy balance, rewritten as (5), then (2a) and (2b) will be simultaneously met. Hence, there really are only two boundary conditions for the second order equation (1). It happens, however, that even these cannot be satisfied for arbitrary values of the mass flux  $m$ , and one has an eigenvalue problem, as previous works have emphasized.

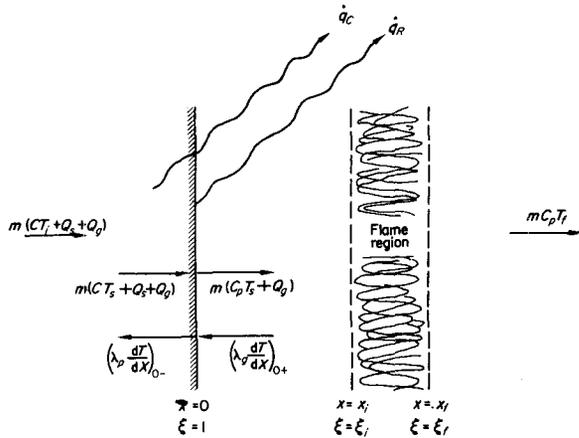


FIG. 1. Sketch of the model, showing contributions to the transfer of energy.

Intimately connected with the fact that this is an eigenvalue problem is a restriction on  $\dot{\omega}$ . First, the energy balance for the gas phase alone is

$$\left(\lambda_g \frac{dT}{dx}\right)_{0+} = m(h_f - h_{0+}) = m[C_p(T_f - T_s) - Q_g] \quad (6)$$

for which  $\dot{q}_R$  has been associated with the solid. Now integrate Eq. (1) from  $x = 0$  to  $x \rightarrow \infty$ :

$$m[C_p(T_f - T_s)] = -\left(\lambda_g \frac{dT}{dx}\right)_{0+} + Q_g \int_0^{\infty} \dot{\omega} dx. \quad (7)$$

Comparison of Eqs. (6) and (7) shows that  $\dot{\omega}$  must be normalized to satisfy

$$\int_0^{\infty} \dot{\omega} dx = m. \quad (8)$$

It will be a simple matter in the examples treated later to verify that this is in fact a formula for the eigenvalue of the differential equation (1) with the

boundary conditions (3a) and (3b). Equation (8) is therefore redundant, but it is a useful check.

It is considerably more convenient to carry out the analysis in dimensionless variables, and in particular those introduced by Rosen are especially nice. Let  $x \rightarrow \xi$ , defined as

$$\xi = \exp\left(\int_0^x \frac{mC_p}{\lambda_g} dx\right) \quad (9a)$$

or

$$\frac{d\xi}{dx} = \left(\frac{mC_p}{\lambda_g}\right) \xi. \quad (9b)$$

Also let

$$\tau = \frac{T - T_1}{T_2} \quad (10)$$

with

$$T_1 = \frac{C}{C_p} T_0 + \left(1 - \frac{C}{C_p}\right) T_s + \frac{Q_s}{C_p} - \frac{\dot{q}_C + \dot{q}_R}{mC_p} \quad (11)$$

$$T_2 = Q_g/C_p \quad (12)$$

and assume that  $\dot{\omega}$  has the form

$$\dot{\omega} = p^n \Omega \quad (13)$$

where  $\Omega$  can presumably depend on temperature ( $\tau$ ) and composition but here will be treated as a function of position  $x$  (or  $\xi$ ). The purpose of (13) is really to display the pressure dependence explicitly. Finally, set

$$\bar{\Omega} = \int_{\tau_s}^{\tau_f} \Omega d\tau \quad (14)$$

and

$$\phi = \Omega/\bar{\Omega} \quad (15)$$

so that

$$\int_{\tau_s}^{\tau_f} \phi d\tau = 1, \quad (16)$$

which is a condition on  $\phi$  arising from the definitions, and is not connected with (8).

With the preceding preliminaries, one can verify easily that Eq. (1) becomes

$$\xi^2 \frac{d^2\tau}{d\xi^2} = -A^2 \phi \quad (17)$$

where

$$A^2 = \frac{\lambda_g p^n \bar{\Omega}}{m^2 C_p} \quad (18)$$

and the boundary conditions (3a) and (3b) transform to

$$\tau = \tau_s \quad (\zeta = 1) \quad (19a)$$

$$\frac{d\tau}{d\zeta} = \tau_s \quad (19b)$$

By comparison of (11), (12) and (5), one finds

$$\tau_f = 1 \quad (20)$$

always, whether or not the losses  $\dot{q}_C + \dot{q}_R$  are included. In the real problem, the losses obviously reduce the flame temperature, as shown by (5), but in the transformed problem, their influence is thrown into the surface condition ( $\tau_s$ ).

The formulation is completed with a statement of the way in which the solid is transformed to gaseous products. As usual, it will be assumed that this is governed mainly by a surface activation energy and the surface vaporizes at a rate

$$m = aT_s^{\beta_1} e^{-E_s/R_0T_s} \quad (21)$$

#### Flame Front Model

The simplest model of a burning solid is based on the supposition that the reaction rates are rapid compared with the transport of energy by heat conduction and convection. Then the combustion is completed within a region thin compared with its distance from the surface. In Fig. 1,  $x_1 = x_f$  for this case; the temperature profile is sketched in Fig. 2a.

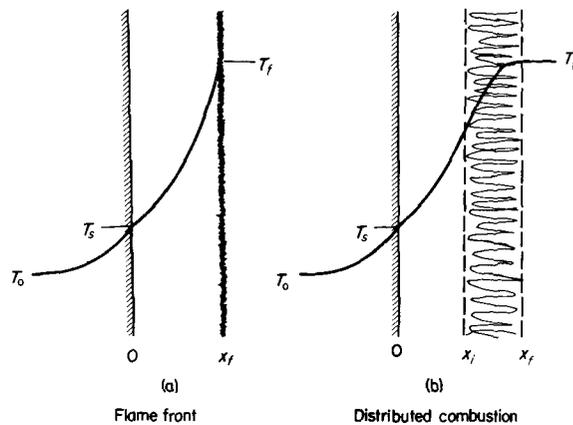


FIG. 2. Sketch of the temperature profiles.

The combustion distribution for a flame front is represented by a delta function at  $x_f$ , or  $\zeta_f$ :

$$\Omega = w\delta(\zeta - \zeta_f) \quad (22)$$

and the right-hand side of Eq. (17) is zero except at  $\zeta = \zeta_f$ . Hence, one has only to solve  $d^2\tau/d\zeta^2 = 0$  on

both sides of the front. The boundary conditions (19) and (20) are satisfied by

$$\tau = \begin{cases} \tau_s \zeta & 1 \leq \zeta < \zeta_f \\ 1 & \zeta_f < \zeta \end{cases} \quad (23)$$

and continuity of temperature requires

$$\zeta_f = \tau_f/\tau_s = 1/\tau_s \quad (24)$$

Thus, assuming  $\lambda_g$ ,  $C_p$  constant, the flame stand-off distance is

$$x_f = \frac{\lambda_g}{mC_p} \ln\left(\frac{1}{\tau_s}\right) = \frac{\lambda_g/\rho_p C_p}{r} \ln\left(\frac{1}{\tau_s}\right) \approx \frac{600}{r} \ln\left(\frac{1}{\tau_s}\right) \mu \quad (25)$$

for typical values of the properties and  $r$  in cm/sec.

It is instructive at this point to unravel some of the dimensionless quantities and find the meaning of  $\tau_s$ . From the boundary condition (19b) and the definitions of  $\xi$  [Eq. (9)] and  $\tau$  [Eq. (10)], one finds

$$\tau_s = \left(\frac{d\tau}{d\zeta}\right)_{\zeta=1} = \left(\frac{dx}{d\zeta}\right)_{\zeta=1} \frac{1}{T_2} \left(\frac{dT}{dx}\right)_{0+} = \frac{1}{mQ_g} \left(\lambda_g \frac{dT}{dx}\right)_{0+}$$

so that  $\tau_s$  is the fraction of heat released, in the gas flame, which is returned to the solid by heat conduction. By use of the energy balance for the gas phase alone, [Eq. (6)], it follows that  $\tau_s$  can be computed from the formula

$$\tau_s = \frac{1}{mQ_g} \left(\lambda_g \frac{dT}{dx}\right)_{0+} = 1 - \frac{C_p}{Q_g} (T_f - T_s) \quad (26)$$

Let  $T_{fa} = (CT_0 + Q_s + Q_g)/C_p$  be the flame temperature in the absence of heat losses, so that according to Eq. (5)

$$T_f = T_{fa} - \frac{\dot{q}_C + \dot{q}_R}{mC_p} \quad (27)$$

Hence,  $\tau_s$  becomes

$$\tau_s = 1 - \frac{C_p}{Q_g} (T_{fa} - T_s) + \frac{\dot{q}_C + \dot{q}_R}{mQ_g} \quad (28)$$

It will be assumed, for comparison with [3], that  $\dot{q}_C$  is a constant and that  $\dot{q}_R$  is purely black body radiation,

$$\dot{q}_R = 1.36 (T_s/1000)^4 \quad (29)$$

Consequently, for a given propellant,  $\tau_s$  is a function of surface temperature ( $T_s$ ), or burning rate through Eq. (21), only. Equation (25) will give the dependence of stand-off distance on burning rate.

In order to obtain the eigenvalue  $\Lambda^2$ , it is simplest

to multiply Eq. (2) by  $d\tau$  and integrate from the surface through the flame front. Since  $(d\tau/d\xi)(d^2\tau/d\xi^2) = (1/2)d/d\xi(d\tau/d\xi)^2$ .

$$\frac{1}{2} \int_{\tau_s}^{\tau_f} \xi^2 \frac{d}{d\xi} \left( \frac{d\tau}{d\xi} \right)^2 d\xi = -A^2 \int_{\tau_s}^{\tau_f} \phi d\tau = -A^2 \quad (30)$$

because  $\phi$  is normalized according to Eq. (16). Now at  $\xi = \xi_f$ ,  $d\tau/d\xi$  is discontinuous, being equal to  $\tau_s$  for  $\xi < \xi_f$  and zero for  $\xi > \xi_f$  [see Eq. (23)]. Thus, the integral on the left-hand side is non-zero only because of the singularity of the integrand at  $\xi = \xi_f$

$$\begin{aligned} \int_{\tau_s}^{\tau_f} \xi^2 \frac{d}{d\xi} \left( \frac{d\tau}{d\xi} \right)^2 d\xi &= \int_{\tau_s}^{\tau_f} \xi^2 d \left( \frac{d\tau}{d\xi} \right)^2 \\ &= \xi_f^2 \left[ \left( \frac{d\tau}{d\xi} \right)^2 \right]_{\xi_f^-}^{\xi_f^+} = -\xi_f^2 \tau_s^2. \end{aligned}$$

But since  $\xi_f = 1/\tau_s$ , Eq. (24), the eigenvalue is simply

$$A^2 = \frac{1}{2}. \quad (31)$$

With  $\Omega$  given by (22),  $\bar{\Omega}$  is

$$\bar{\Omega} = w \int_{\tau_s}^{\tau_f} \delta(\xi - \xi_f) d\tau = w \int_{\tau_s}^{\tau_f} \delta(\xi - \xi_f) \left( \frac{d\tau}{d\xi} \right) d\xi.$$

Again owing to the discontinuity in  $d\tau/d\xi$ , the delta function picks up the average value at  $\xi = \xi_f$  and

$$\bar{\Omega} = \frac{1}{2} w \tau_s. \quad (32)$$

It is easy to verify that the restriction (8) on  $\dot{\omega}$  leads to the same result (25). Substitute (22) and (13) into (8) and use (9b):

$$m = \int_0^{\infty} \dot{\omega} dx = p^n w \int_1^{\infty} \delta(\xi - \xi_f) \left( \frac{dx}{d\xi} \right) d\xi = \frac{p^n w \lambda_g}{m C_p \xi_f},$$

which, after use of (32) for  $w$ , can be rearranged to give

$$\frac{\lambda_g p^n \bar{\Omega}}{m^2 C_p} = \frac{1}{2} (\xi_f \tau_s) = \frac{1}{2},$$

and this is exactly the formula (31).<sup>1</sup>

From (31) and (32), the burning rate is found to be

$$m = p^{n/2} (w \tau_s)^{\frac{1}{2}} (\lambda_g / C_p)^{\frac{1}{2}}, \quad (33)$$

and if one assumes that the gas phase reaction rate follows an Arrhenius law,

$$w = k T_f^{\beta} e^{-E_f/R_0 T_f} \quad (34)$$

with  $k$  a constant,

<sup>1</sup> The result can also be obtained from Rosen's variational principle [2] and from formulas used by Johnson and Nachbar [3].

$$m = p^{n/2} T_f^{\beta/2} (\tau_s)^{\frac{1}{2}} \left( \frac{k \lambda_g}{C_p} \right)^{\frac{1}{2}} e^{-E_f/2R_0 T_f}. \quad (35)$$

As one might have anticipated, this is almost identical with results obtained by von Kármán [4] and Boys and Corner [5] for a thin propagating laminar flame. The presence of the solid surface (which reduces the flame speed) appears wholly in  $\tau_s < 1$ .

However, the limit representing a flame propagating in a premixed gas cannot be obtained directly from Eq. (35) because this result involves explicitly the value  $\xi_s = 1$  at the interface of the solid, according to the boundary condition (23). The preceding calculations can easily be carried through without specifying the value of  $\xi_s$ , and instead of (35) one finds

$$m = p^{n/2} T_f^{\beta/2} \left( \frac{k \lambda_g}{C_p} \right)^{\frac{1}{2}} \left[ \frac{1 - \xi_s/\xi_f}{\xi_f(1 - \tau_s)} \right]^{\frac{1}{2}} e^{-E_f/2R_0 T_f} \quad (35a)$$

Now let the interface recede to  $x \rightarrow -\infty$ , so  $\xi_s \rightarrow 0$ , and let  $\tau_s = \tau$ , the normalized temperature of the gas mixture. This gives exactly the formula one finds if the same analysis is applied *ab initio* to the problem of a laminar flame, in which case  $C = C_p$  and  $Q_s = 0$ , of course.

The use of a delta function evidently implies an "infinitely fast" reaction rate in order to achieve an infinitesimally thin reaction zone. Thus the appearance of an Arrhenius factor, in Eq. (34), which is associated with a finite reaction rate, seems a contradiction. This reflects the imperfect nature of the simple model. Strictly, the reaction zone must be spread out if the reaction rate is finite. Representation by a delta function is an approximation, good if the thickness  $\delta$  of the reaction zone is small compared to the other characteristic length in the problem, namely the scale of the temperature profile,  $l = \lambda_g/mC_p$ . Thus, the criterion for use of this model is  $\delta/l \ll 1$ . A measure of the reaction time is  $\tau = \rho_g/\dot{\omega}$  and the thickness is roughly  $\delta = u\tau = m/\dot{\omega}$ , which also follows from the normalization (8). Hence the inequality to be met is

$$\left( \frac{m}{\dot{\omega}} \right) \left( \frac{m C_p}{\lambda_g} \right) \ll 1$$

which is satisfied under some circumstances. However, the value of the analysis presented here is not intended to be accurately quantitative, and therefore does not rest critically on satisfaction of the inequality.

### The Influence of Radiative Loss

To check Eq. (35), comparison has been made with the results of [3], for the combustion of pure ammonium perchlorate. The multiplying factor in (35) is set

so as to obtain agreement with the data at one point,  $p = 100$  atm,  $r = 1$  cm/sec. It is also assumed that  $\lambda_g \sim T_f^e$  so that (35) leads to

$$\left(\frac{p}{100}\right)^{n/2} = r \left(\frac{\tau_s^*}{\tau_s}\right)^{\frac{1}{2}} \left(\frac{T_f^*}{T_f}\right)^{\frac{\varepsilon + \beta}{2}} \exp\left\{\frac{E_f}{2R_0} \left(\frac{1}{T_f} - \frac{1}{T_f^*}\right)\right\}, \quad (36)$$

where starred quantities are values for  $p = 100$  atm. Figure 3 shows calculations for which all remaining

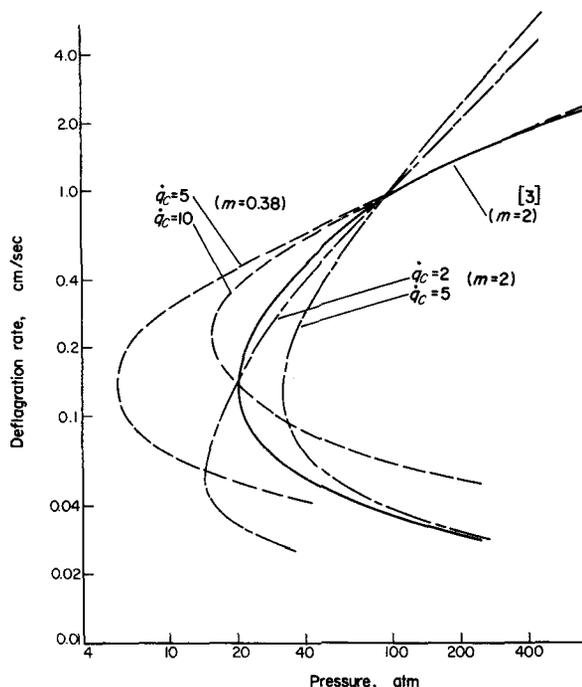


FIG. 3. Numerical results showing the effect of energy loss by radiation.

constants are assigned the values (in particular,  $n = 2$ ) associated with curve 1 of Fig. 4, Ref. [3]; experimental data [6] lie along the upper branch of that curve. The agreement of Eq. (35) is not satisfactory, especially as regards the slope in the pressure range  $p > 50$  atm. However, since the flame temperature doesn't change much along the upper branch (see remarks below),  $r \sim p^{n/2}$  and the slope is sensitive to the value of  $n$  used here. Calculations for  $n = 0.38$  are shown, for two values of  $\dot{q}_C$ , and the agreement is then quite good, although the remainder of the curve does not match that found in [3].

However, the point is that the qualitative aspects, especially the reversal of the  $r - p$  curve, are reproduced. Also, owing to the simplicity of the results, one can easily determine what physical aspects are reflected in the calculations.

The main purpose of [3] was to relate the lower deflagration limit,  $p_{DL}$  (here identified as the minimum value of pressure on the  $r - p$  curve), to radiation losses. A lower limit does arise for non-zero values of  $\dot{Q}_L = (\dot{q}_C + \dot{q}_R)/mC_pT_2$ ; the shape of the  $r - p$  curve is almost entirely a result of a lower flame temperature due to the loss ( $\dot{Q}_L > 0$ ), which in turn changes the reaction rate. On most of the upper branch away from  $p_{DL}$ ,  $\dot{Q}_L$  is negligible; on the lower branch  $\dot{q}_C$  is 6–10 times as large as  $\dot{q}_R$ . As Johnson and Nachbar have noted, it is not possible to obtain a lower deflagration limit, in the sense suggested here, unless  $\dot{q}_C$  is rather large. No interpretation of  $\dot{q}_C$  has been given, but it is hard to understand how, in the present model, it can be anything but radiation, coming from the colder solid. If so, it may be doubted that  $\dot{q}_C$  can be so large. The experiments reported in [7] showed also that the burning rate was negligibly affected by externally applied incident radiation until the intensity reached about 8 cal/cm<sup>2</sup>-sec. This may be compared with black body radiation losses from the surface equal to approximately 0.5–2.6 cal/cm<sup>2</sup>-sec. The higher value occurs in the range of pressure where the radiative loss has negligible effect on the burning rate, according to the calculations. Consequently, this proposed explanation of the lower deflagration limit is open to question, as in fact statements in [3] suggest.

For the calculations shown, the stand-off distance increases from the high pressure end of the upper branch and continues increasing along the lower branch. For example, with  $\dot{q}_C = 5$  cal/cm<sup>2</sup>-sec, at  $p = 100$  atm, Eq. (25) gives  $x_f \cong 50$  microns for  $r = 1$  cm/sec (upper branch),  $x_f \cong 1500 \mu$  for  $r = 0.038$  cm/sec (lower branch), and  $x_f \cong 800 \mu$  at  $p_{DL} \cong 20$  atm. Calculated estimates of a few microns and less which have been reported [7] have been based incorrectly on a linear temperature profile from the surface to the flame. The correct exponential variation used here forces a "thicker" flame. The values computed here are in the range of the experimental observations of Bobolev, *et al.* [8]. The values of  $\tau_s$  are 0.93, 0.90, and 0.83, respectively, so that, since  $\tau_s = q_{0+}/mC_pQ_g$ , the fractional amount of heat released and returned to the surface tends to a minimum in the vicinity<sup>1</sup> of  $p_{DL}$ . As the burning rate decreases on the upper branch,  $\tau_s$  also decreases because the surface temperature is lower [see Eq. (28)]. But on the lower branch,  $\tau_s$  increases as the surface temperature is lowered further because the

<sup>1</sup> Contrary to what one might guess,  $\tau_s$  is not a minimum exactly at  $p_{DL}$ , but nearly so. There seems to be no simple interpretation of this fact, nor of the precise condition prevailing at  $p_{DL}$ .

relative effect of the radiative loss increases and dominates. It should be noted that the heat transfer to the surface ( $q_{0+}$  itself) decreases continuously along the curve, reaching its lowest values at the high pressure end of the lower branch.

It has been speculated [3], following [1] that the lower branch represents unstable states; this can be supported, although not strictly proved, by the following argument. At the flame front there is no heat transfer downstream, but there is a loss upstream, given as

$$q_{f-} = \left( \lambda_g \frac{dT}{dx} \right)_{f-} = \lambda_g T_2 \left( \frac{d\xi}{dx} \frac{d\tau}{d\xi} \right)_{f-} = m Q_g \xi_f \tau_s = m Q_g$$

The heat loss from the gas phase to the solid is  $q_{0+} = m C_p Q_g \tau_s$ , Eq. (26), so that the net heat transferred to the region between the solid surface and the flame is

$$q_{f-} - q_{0+} = m C_p Q_g (1 - \tau_s), \quad (37)$$

which, in view of the behavior of  $\tau_s$ , passes through a maximum in the vicinity of  $p_{DL}$ . On the upper branch,  $q_{f-} - q_{0+}$  therefore increases as the burning rate goes down, and on the lower branch  $q_{f-} - q_{0+}$  decreases as the burning rate decreases. Now suppose that the burning is taking place at some condition ( $p_0, r_0$ ) on the lower branch and that a pressure disturbance is introduced, say  $\delta p < 0$ . Because the chemical reactions respond more rapidly than the processes of thermal conduction, one may suppose that the flame assumes in the first instance a new condition characterized by higher values of the burning rate, surface temperature, and flame temperature, while the net heat lost from the flame,  $q_{f-} - q_{0+}$ , maintains sensibly the initial value. But according to the above observations, the initial value is less than the value required for steady state burning at the new pressure  $p_0 + \delta p < p_0$ . There is therefore a tendency for the flame temperature to rise further, enforcing the original perturbation. In this way, one can show that operating points are unstable on the lower branch and stable on the upper branch.

This is not intended to be a rigorous proof that the lower branch must be experimentally unattainable, and the argument is less satisfactory near  $p_{DL}$ . But the explanation seems to be qualitatively appealing otherwise.

### Distributed Combustion

No further numerical calculations will be given here, but it is instructive to examine the more realistic problem of a flame with energy release distributed in space. Only the simplest case will be discussed, namely  $\Omega$  proportional to a power of  $\xi$  and hence exponential in  $x$ . Actually, three cases must be treated—uniform energy release,  $\Omega$  linear in  $\xi$ , and  $\Omega$  varying as  $\xi^\alpha$  with  $\alpha \neq 1$ :

$$\Omega_1 = w_1, \text{ (here, } \bar{\Omega} = \int \Omega d\tau) \quad (38)$$

$$\Omega_2 = w_2(\xi - \xi_i), \quad (39)$$

$$\Omega_3 = w_3(\xi^\alpha - \xi_i^\alpha). \quad (40)$$

Since the calculations are similar in the three cases and involve nothing novel, they will only be described and certain results quoted as appropriate.

It is supposed that  $\Omega$  is non-zero only in the region  $\xi_i \leq \xi \leq \xi_f$ . Hence, in the space between the surface and  $\xi_i$ , the dimensionless temperature profile satisfying conditions (19a) and (19b) is

$$\tau = \tau_s \xi \quad (1 \leq \xi \leq \xi_i). \quad (41)$$

As noted already,  $\tau = 1$  for  $\xi \geq \xi_f$ . Integration of (17) with any one of (38)–(40) is trivial and the results are summarized in Table 1; the integration constants  $C_1$  and  $C_2$  are, of course, different in the three cases.

Now there are five quantities required to complete the solution of the problem:  $C_1, C_2, \xi_i, \xi_f$  and the eigenvalue  $\Lambda^2$ . The inner boundary of the flame ( $\xi_i$ ) may be specified by an ignition temperature  $T_i$ , and  $\xi_i$  is found from (41),

$$\xi_i = \tau_i / \tau_s. \quad (42)$$

Table 1. Temperature Profile and First Derivative for a Flame Having Distributed Combustion

	Temp. ( $\tau$ )	Heat transfer ( $d\tau/d\xi$ )
$\alpha = 0$	$\tau = \Lambda^2 \ln \xi + C_1 \xi + C_2$	$\frac{d\tau}{d\xi} = \frac{\Lambda^2}{\xi} + C_1$
$\alpha = 1$	$\tau = \Lambda^2 [\xi - (\xi + \xi_i) \ln \xi] + C_1 \xi + C_2$	$\frac{d\tau}{d\xi} = -\Lambda^2 \left[ \ln \xi + \frac{\xi_i}{\xi} \right] + C_1$
$\alpha \neq 1$	$\tau = -\Lambda^2 \left[ \frac{\xi^\alpha}{\alpha(\alpha-1)} + \xi_i^\alpha \ln \xi \right] + C_1 \xi + C_2$	$\frac{d\tau}{d\xi} = -\Lambda^2 \left[ \frac{\xi^{\alpha-1}}{\alpha-1} + \frac{\xi_i^{\alpha-1}}{\xi} \right] + C_1$

The remaining four quantities are set by the conditions that the temperature and heat transfer (hence  $\tau$  and  $d\tau/d\xi$ ) must be continuous at the edges  $\xi = \xi_i$  and  $\xi = \xi_f$  of the flame.

For each case, the two continuity conditions give separate formulas for  $A^2$ , and equating these gives a transcendental equation for the ratio  $\xi_f/\xi_i$ . The normalization of  $\hat{\omega}$ , Eq. (8), also gives a formula for  $A^2$  which can easily be shown equivalent to the other two. The final results are summarized in Table 2, showing the three separate formulas obtained in this way for each case.<sup>1</sup> Equating any two for a fixed value of  $\alpha$  gives an equation for  $\xi_f/\xi_i$ .

Consequently, if one specifies the state and composition of the cold propellant (and therefore  $T_f$ ), the pyrolysis law, kinetic properties ( $w$ ,  $Q_g$ , etc.) for the gas phase, the ignition temperature, and the distribution of combustion, the problem can be solved. No additional assumptions are required to find the position and boundaries ( $\xi_f$ ,  $\xi_i$ ) of the flame.

Combinations of the three cases can of course be used to approximate other combustion profiles if desired. Although one can obviously obtain more detailed information from the treatment of a flame with distributed combustion, it is likely that no new qualitative features will be discovered. For example, the effect of radiative losses is in any case quite like that for the flame front; the numerical results will differ only in relatively minor respects.

#### Application to Unsteady Combustion

In connection with the problem of unstable pressure oscillations in solid propellant rockets, it is necessary to know the response of a burning solid to pressure disturbances. The response is defined as the ratio of the mass or velocity fluctuation to the impressed pressure fluctuation, evaluated at the downstream edge of the flame. Almost all calculations presently available make use of the fact that the processes in the gas phase respond much more rapidly than those in the solid phase [9]; the gas phase is assumed to behave "quasi-statically." This means that at any time, the temperature profile can be computed from the steady state solution, but using the instantaneous values of the boundary conditions. The temperatures at the boundaries of course vary in time, and generally are not in phase with one another or with the pressure disturbance. Thus, results such as those found already in this work may be used directly.

Let primed quantities denote deviations from the steady state so that  $p = \bar{p} + p'$ ,  $m = \bar{m} + m'$ , etc. The

problem then is to compute  $m'_f/p'$  or a normalized multiple of it. Within the quasi-static approximation,  $m'_f = m'_s$ , the value of  $m'$  at the surface. Perhaps the simplest way to find this quantity is to use the perturbed energy balance at the solid-gas interface, deduced from Eq. (3b), but with radiation ignored for simplicity

$$\left(\lambda_p \frac{dT}{dx}\right)'_{s+} = \left(\lambda_p \frac{dT}{dx}\right)'_{s-} + (C_p - C) \bar{m} T'_s - Q_s m'_s \quad (43)$$

Subscript ( )<sub>s</sub> refers to the instantaneous position of the solid-gas interface which fluctuates about the mean position denoted by ( )<sub>0</sub>. The solution for the temperature in the solid phase, in the presence of harmonic oscillations of pressure, gives [9] and many earlier works)

$$\left(\lambda_p \frac{\partial T}{\partial x}\right)'_{s-} = \bar{m} C \left(\lambda + \frac{A}{\lambda}\right) T'_s \quad (44)$$

where  $A = E_s/R_0 \bar{T}_s (1 - T_0/\bar{T}_s)$  and  $\lambda$  is a complex function of frequency. From the pyrolysis law (21),  $m'_s$  is related to the fluctuation of surface temperature according to

$$\frac{m'_s}{\bar{m}} = \left(\beta_1 + \frac{E_s}{R_0 \bar{T}_s}\right) \frac{T'_s}{\bar{T}_s} \quad (45)$$

Since also  $(\partial T/\partial x)'_{s+} \cong (\partial T/\partial x)'_{0+}$  for quasi-static behavior, then the left hand side of (43) is  $q'_{0+}$  in the notation used here. Equations (43)–(45) combine to relate the fluctuations of surface temperature and heat transfer from the gas to the solid phase

$$q'_{0+} = \bar{m} C \left\{ \left(\lambda + \frac{A}{\lambda}\right) + \left(\frac{C_p}{C} - 1\right) \left(1 + \beta_1 + \frac{E_s}{R_0 \bar{T}_s}\right) + \frac{Q_s}{C \bar{T}_s} \left(\beta_1 + \frac{E_s}{R_0 \bar{T}_s}\right) \right\} T'_s \quad (46)$$

The right-hand side of this equation is the expression for the fluctuation of heat transfer, from the gas to the solid, required to satisfy the conduction of heat in the solid, energy balance at the surface and the pyrolysis law.

One must obtain, from the solution to the problem in the gas phase, a similar formula expressing the fluctuation of heat transfer which the gas phase will provide. So far as this computation is concerned, there are two unknown quantities,  $q'_{0+}$  and the fluctuation of the flame temperature (just downstream of the combustion region). The two available relations are the overall energy balance [6] for the gas phase,

<sup>1</sup> Note that  $\bar{Q}$  has been replaced by  $w$  in  $A^2$  in Table 2.

Table 2. Formulas for the Eigenvalue  $\lambda^2 = \lambda_g p^0 w / m^2 C_p$

	Normalization of $\phi$ (Eq. 8)	Continuity of heat transfer	Continuity of temp.
$\alpha = 0$	$\frac{1}{\ln(\xi_f/\xi_i)}$	$\frac{\tau_i}{1 - \xi_i/\xi_f}$	$\frac{1 - \tau_i}{\ln \frac{\xi_f}{\xi_i} - \left(1 - \frac{\xi_i}{\xi_f}\right)}$
$\alpha = 1$	$\frac{1 - \xi_i}{\left(\frac{\xi_f}{\xi_i} - 1\right) - \ln \left(\frac{\xi_f}{\xi_i}\right)}$	$\frac{\tau_i/\xi_i}{\ln \left(\frac{\xi_f}{\xi_i}\right) - \left(1 - \frac{\xi_i}{\xi_f}\right)}$	$\frac{(1 - \tau_i)/\xi_i}{2 \ln \frac{\xi_f}{\xi_i} - \frac{\xi_f}{\xi_i} \left(1 - \frac{\xi_i^2}{\xi_f^2}\right)}$
$\alpha \neq 1$	$\frac{\alpha/\xi_i^{\alpha}}{\left[\left(\frac{\xi_f}{\xi_i}\right)^{\alpha} - 1\right] - \alpha \ln \left(\frac{\xi_f}{\xi_i}\right)}$	$\frac{1}{\alpha - 1} \left[ \left(\frac{\xi_f}{\xi_i}\right)^{\alpha-1} - 1 \right] - \frac{\tau_i/\xi_i}{\xi_i}$	$\frac{(1 - \tau_i)/\xi_f^{\alpha}}{\left(1 - \frac{\xi_f}{\xi_i}\right) \left[ \frac{1}{\alpha - 1} + \left(\frac{\xi_i}{\xi_f}\right)^{\alpha} \right] - \frac{1}{\alpha(\alpha - 1)} \left[ 1 - \left(\frac{\xi_i}{\xi_f}\right)^{\alpha} \right] - \ln \xi_f + \left(\frac{\xi_f}{\xi_i}\right)^{\alpha} \ln \xi_i}$

and the eigenvalue itself,  $\Lambda^2$ , which essentially contains all the information extracted from the solution to the gas phase. Thus, linearization of (6) gives

$$g'_{0+} = -mC_p T'_f + \bar{m}C_p \left\{ 1 - \left( \frac{\bar{T}_f}{\bar{T}_s} - 1 - \frac{Q_g}{C_p \bar{T}_s} \right) \times \left( \beta_1 + \frac{E_s}{R_0 \bar{T}_s} \right) \right\} T'_s \quad (47)$$

and linearization of, for example, the eigenvalue for a flame front [i.e. Eq. (35) or (36)] leads to

$$\frac{m'_s}{\bar{m}} = \frac{n p'}{2 \bar{p}} + \left( \frac{\varepsilon + \beta}{2} + \frac{E_f}{2R_0 \bar{T}_f} \right) \frac{T'_f}{\bar{T}_f} + \frac{1}{2} (g'_{0+} / \bar{g}_{0+}) \quad (48)$$

where  $g_{0+}$  correctly appears.

Substitution of (47) and (48) in (46) then gives the ratio  $T'_s/p'$  and the completion of the calculation to give  $m'/p'$  follows easily. The final result is very similar to that found by Denison and Baum [10], but two points should be noted. First, since they used Kármán's result for a pre-mixed laminar flame, the dependence of the burning rate, in the gas phase, on the surface temperature (through  $\tau_s$ ) does not appear; and second, it is not necessary to force the fluctuations of flame temperature to be isentropic, although this restriction can incorrectly be imposed.

Both points have been discussed by Krier *et al.* [11], who present a calculation of the response function based on the assumption of uniform combustion between the solid surface and the position  $\xi_f$ .<sup>1</sup> However, since they did not carry out a complete calculation of the steady state problem, they did not determine either the eigenvalue  $\Lambda^2$  or the flame thickness  $\xi_f$ ; alternative estimates and assumptions were required. In contrast, the calculations covered here will yield complete results once the distribution of combustion has been chosen. Thus, with  $\xi_i = 1$ ,  $\tau_i = \tau_s$  for the flame region extending to the solid surface, one finds from Table 2 a relation between  $\xi_f$  and  $\tau_s = (d\tau/d\xi)_{0+}$ :

$$\xi_f = 1 + (d\tau/d\xi)_{0+} \xi_f \ln \xi_f. \quad (49)$$

If  $w$  is given by (34), and  $\lambda_g \sim T_f^z$  as before, the eigenvalue gives

$$m = p^{n/2} \left( \frac{T_f}{T_f^*} \right)^{\frac{\varepsilon + \beta}{2}} \left( \frac{k\lambda_g^*}{C_p} \right)^{\frac{1}{2}} \left( \frac{(d\tau/d\xi)_{0+}}{\ln \xi_f} \right)^{\frac{1}{2}} \times e^{-E_f/2R_0 T_f}. \quad (50)$$

<sup>1</sup> This may be regarded as a rough approximation to the sort of flame associated with combustion of a composite propellant.

The linearized form of (49) relates fluctuations of the flame thickness to fluctuations of heat transfer and mass flux.

Then by using that result in the linearized form of (50), one finds an equation corresponding to (48) for the flame front. An added chore is the determination of the average flame thickness from (49), which must be solved for each value of  $\tau_s$ . It appears that the burning rate—pressure curve one finds for this case is not very different from that associated with the flame front model. The assumption that  $\dot{\omega} \sim p^n$ , and also that fluctuations of  $\dot{\omega}$  can be computed directly from that relation, is similar to an approximation made in Ref. 11, and the final results will differ only in the definition of the parameter  $B$  below. It should be possible to improve upon this assumption, but it is not clear at the present time how this can best be done.

There is little need to complete the calculation of the response function here. The final result will necessarily [9] have the form common to calculations based on quasi-static behavior of the gas phase

$$\frac{1}{n} \frac{m'/\bar{m}}{p'/\bar{p}} = \frac{AB}{\lambda + A/\lambda - (1 + A) + AB}$$

where  $B$  is a constant independent of the frequency. The dependence of  $B$  on the remaining quantities in the problem ( $\bar{T}_f$ ,  $E_f$ , etc.) will be determined by the particular model of the gas phase one chooses. While  $A$  has values of 10–30, roughly,  $B$  generally lies in the range 0.7–1.2.

## References

1. SPALDING, D. B., Theory of burning of solid and liquid propellants, *Combustion and Flame* **4**, 59–76 (1960).
2. ROSEN, G., Burning rates of solid propellants, *J. chem. Phys.* **32**, 89–93 (1960).
3. JOHNSON, W. E. and NACHBAR, W., Deflagration limits of a monopropellant with application to ammonium perchlorate, *Eighth International Symposium on Combustion*, pp. 678–689. Williams & Wilkins, Baltimore (1962).
4. VON KÁRMÁN, TH., The present status of the theory of laminar flame propagation, *Sixth International Symposium on Combustion*, pp. 1–11. Reinhold, New York (1957).
5. BOYS, S. F. and CORNER, J., The structure of the reaction zone in a flame, *Proc. R. Soc.* **A197**, 90–106 (1949).
6. LEVY, J. B. and FRIEDMAN, R., Further studies of pure ammonium perchlorate deflagration, *Eighth International Symposium on Combustion*, pp. 663–672. Williams & Wilkins, Baltimore (1962).
7. FRIEDMAN, R., LEVY, J. B. and RUMBEL, K. E., The mechanism of deflagration, of pure ammonium perchlorate, Air Force Office of Scientific Research, AFOSR-TN-59-173, AD 211-313 (February, 1959).

8. BOBOLEV, J. K., GLASKOVA, A. P., ZENIN, A. A. and LEIPUNSKII, O. I., Temperature profiles upon burning ammonium perchlorate, *Dokl. Akad. Nauk U.S.S.R. Fis. Khim.* **151**, 604–607 (1963).
9. CULICK, F. E. C., A review of calculations of the admittance function for a burning surface, Appendix A in NOTS TP 4244, Naval Ordnance Test Station, China Lake, Calif. (Sept. 1967). (To be published in *AIAA JI*).
10. DENISON, M. R. and BAUM, E., A simplified model of unstable burning in solid propellants, *ARS JI* **31**, 1112–1122 (August, 1961).
11. KRIER, H., T'IEH, J. S., SIRIGNANO, W. A. and SUMMERFIELD, M., Non-steady burning phenomena of solid propellants: Theory and experiments, *AIAA JI* **6**, 278–285 (February, 1968).

F. E. C. Culick: *Associate Professor of Engineering, California Institute of Technology, Pasadena, California, 91109, U.S.A.*

**Résumé**—Un calcul élémentaire de la combustion des propulseurs solides. Le problème de la combustion d'un propulseur solide est traité d'une manière approximative en établissant la répartition spatiale du dégagement d'énergie au stade gazeux. L'adoption de cette méthode d'étude inverse transforme le problème non linéaire habituel en un problème linéaire à valeur eigen d'une solution facile. On donne des résultats pour la combustion concentrée (un front de flamme) et des cas spéciaux de dégagement d'énergie répartie. On montre clairement des aspects qualitatifs tels que distance d'éloignement de la flamme, épaisseur de la flamme, et différentes composantes du transfert de la chaleur dans la zone de combustion. L'examen de l'influence de la perte d'énergie par radiation de l'interface du solide et du gaz s'accorde de façon satisfaisante avec des calculs précédents basés sur les formules non linéaires établies. On discute brièvement d'une application du problème de combustion irrégulière, et de la réaction aux variations de pression. La facilité avec laquelle des résultats utiles peuvent être obtenus paraît justifier la nature imparfaite de l'analyse.

**Zusammenfassung**—Eine elementare Berechnung der Verbrennung fester Treibstoffe. Das Problem der Verbrennung eines festen Treibstoffes wird annäherungsweise durch Festlegung der Raumverteilung von Energie-Abgabe in der Gasphase behandelt. Die Einführung dieses umgekehrten Verfahrens verwandelt das übliche nichtlineare Problem in ein lineares Eigenwertproblem, das leicht lösbar ist. Die Ergebnisse für konzentrierte Verbrennung (eine Flammenfront) und Einzelfälle von verteilter Energieabgabe werden angeführt. Qualitative Aspekte wie Flammen-Abstand, Flammendicke und verschiedene Komponenten der Wärmeübertragung innerhalb der Verbrennungszone werden deutlich gezeigt. Die Prüfung des Einflusses von Energieverlust durch Strahlung aus der Festkörper-Gas-Grenzfläche ist in guter Übereinstimmung mit früheren, auf nichtlinearer Formulierung beruhenden Berechnungen. Eine Anwendung auf des Problem der unstenen Verbrennung und die Reaktion auf Druckschwankungen werden kurz besprochen. Die Leichtigkeit, mit der nützliche Ergebnisse erhalten werden können, scheint die unvollkommene Art der Analyse zu rechtfertigen.

**Резюме**—Элементарное Вычисление сгорания твёрдого топлива. Приближенно обсуждается проблема сгорания твёрдого топлива, предписывая пространственное распределение освобождения энергии в газовой фазе. Принятие этого обратного подхода преобразовывает обычную не-линейную проблему в линейную легко разрешимую проблему. Даны результаты для концентрированного сгорания (пламенный фронт) и специальные случаи распределения освобождения энергии. Ясно показаны качественные аспекты, такие, как расстояние расположения пламени, толщина пламени и различные компоненты передачи тепла в районе сгорания. Исследование влияния потери энергии радиацией с поверхности раздела газа и твердого топлива, даёт удовлетворительное согласование с предыдущими вычислениями, основанными на не-линейной формулировке. Кратко обсуждается применение к проблемы непостоянного горения и ответная реакция на флуктуацию (случайные изменения) давления. Лёгкость, с какой могут быть получены полезные результаты, видимо оправдывает несовершенную сущность анализа.