Lecture 17-18: Solid Propellants: Other Topics

Combustion of Solid Propellants

For a general discussion, read Sutton, Chapter 13. A detailed model of combustion of composite propellants is presented next.

Combustion of Composite Propellant
(Ref: Guy Lengellé, Jean-Robert Duterque, Jean-Claude Godon, Jean-Francois Trubert, ONERA, "Solid Propellant Steady Combustion – Physical Aspects". In AGARD-LS-180-Combustion of Solid Proplellants,1991 (TL507.N867, no. 180))

Composite propellants are heterogenous mixtures of oxidizer grains and powdered aluminum fuel, both embedded in a rubber-like binder, which is also a fuel. The most common oxidizer by far is Ammonium Perchlorate (AP), ($C\ell O_4 NH_4$), a crystalline substance with ρ = 1.95 g/cm^3, c_p = 0.31 $cal/g/K$, thermal diffusivity = $d_p = 2.5 \times 10^{-3} - 4.55 \times 10^{-6} T\left({}^0 C\right) cm^2/sec$, and an estimated m.p of 835K. AP is ground to sizes from a few to around $100\,\mu m$. The finer grades are dangerous, so grinding is done just prior to fabrication. AP has M = 116.5 $g/mole$ and 55% by mass is oxygen.

The aluminum is also ground to similar sizes at the last minute. Al is a very exothermic fuel, producing $A\ell_2 O_3$ which is liquid at the flame temperature ($\approx 3500K$), and condenses later to a solid.

The binder is often polybutadiene (synthetic rubber), either Carboxyl Terminated (CTPB) or Hydroxyl Terminated (HTPB). The composition of CTPB is $C_7 H_{11.24} O_{0.2}$, with thermal conductivity $\lambda_p = 3.6 \times 10^{-4} \dfrac{cal/sec}{(cm)(K)}$, $\rho_p = 0.97\, g/cm^3$, $c_p = 0.39\, cal/g/K$

Best performance is obtained with very high percentage of AP, although mechanical properties require a minimum of binder, and AP concentration ranges from $\approx$ 70% by mass when there is $A\ell$ ($\approx 16\%$), the balance being binder (14%), to about 80%-85%, with no $A\ell$ (as in "smoke-less" compositions), the balance then being all binder.

Overview of Combustion Mechanism – The burning of AP-binder propellants (no $A\ell$) is a complex series of phenomena, and the detailed geometry of the grains does matter (size, particularly). At $P \geq 20$ atm, AP itself can deflagrate exothermically, and it decomposes partly in a thin liquid layer on the surface of a grain, partly in an "AP flame" a few μm above it. The heat of decomposition raises T to $\approx 1205K$ by itself; heat from the outer flame (more below) can raise the AP flame temperature well above this, however.

Around the AP grains, the heat from the main flame decomposes the binder, which generates a mixture of short-chain hydrocarbons, while absorbing about 360 cal/g, plus the energy to heat it to the surface temperature $T_s \cong 1000K$-$1100K$.

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The O$_2$-rich gas generated in the AP flame co-flows outwards with the binder decomposition products, with interdiffusion along the way. This is a "diffusion flame", and the final combustion takes place in it, raising T to about 3540K.
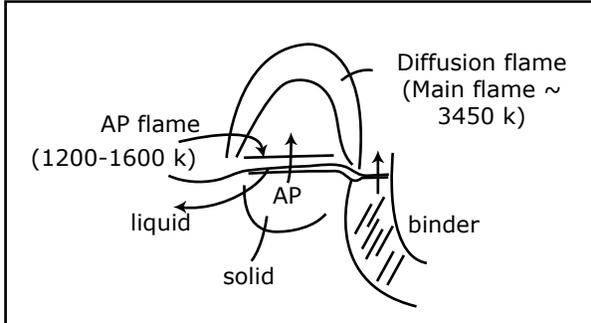
When there is Aluminum, the *Al* Particles are ejected when the binder holding them recedes; they then burn at several hundred μm from it; during this burning they agglomerate to several tens of μm (they are liquid, m.p=930K, but remain "encased" in Al_2O_3 until this shell breaks at 2300K, then the *Al* spews $\approx$ 1 μm microparticles which burn quickly)

| t = 0 | t = 2x10^{-4}s | t = 4x10^{-4}s | t = 6x10^{-4}s | t = 8x10^{-4}s | 10^{-3}sec |
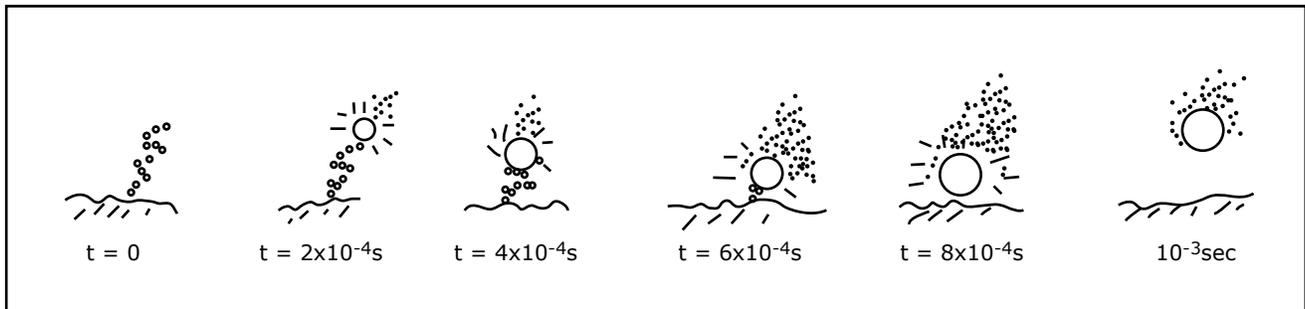
From the surface regression point of view, *Al* "burns" instantly, as its particles are ejected.

Overall Burn Rate from Burn Rates of Constituents

Let υ_p be the mean surface regression speed (cm/sec), and υ_{AP}, υ_b the corresponding rates for the AP and the binder individually and in isolation. Although the geometry is more complex, we can idealize the propellant as a layered medium, with alternative thicknesses δ_{AP}, δ_b. The time to burn through both δ_{AP} and δ_b is

$$t = \frac{\delta_{AP} + \delta_b}{\upsilon_p} = t_{AP} + t_b = \frac{\delta_{AP}}{\upsilon_{AP}} + \frac{\delta_b}{\upsilon_b}$$

Calling $\xi_{AP} = \dfrac{\delta_{AP}}{\delta_{AP} + \delta_b}$, $\xi_b = 1 - \xi_{AP} = \dfrac{\delta_b}{\delta_{AP} + \delta_b}$ the <u>volume fractions</u> of the constituents

$$\frac{1}{\upsilon_p} = \frac{\xi_{AP}}{\upsilon_{AP}} + \frac{\xi_b}{\upsilon_b} \tag{1}$$

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The mass flux (g/cm²/sec) burnt is

$$\dot{m}_p = \rho_p \, \upsilon_p \tag{2}$$

where ρ_p is the mean density

$$\rho_p = \frac{m_{AP} + m_b}{\dfrac{m_{AP}}{\rho_{AP}} + \dfrac{m_b}{\rho_b}} \qquad\qquad \frac{1}{\rho_p} = \frac{\alpha_{AP}}{\rho_{AP}} + \frac{\alpha_b}{\rho_b} \tag{3}$$

where α_{AP} is the <u>mass fraction</u> of AP, and $\alpha_b = 1 - \alpha_{AP}$ is that of the binder.

<u>Note</u>: ρ_{AP} = 1.95 g/cm^3, ρ_b = 0.91 g/cm^2

The mass fluxes of the individual constituents are, similarly,

$$\dot{m}_{AP} = \rho_{AP} \, \upsilon_{AP} \qquad ; \qquad \dot{m}_b = \rho_b \, \upsilon_b \tag{4}$$

From (1) and (2),

$$\frac{1}{\rho_p \upsilon_p} = \frac{1}{\dot{m}_p} = \frac{\xi_{AP} \dfrac{\rho_{AP}}{\rho_p}}{\rho_{AP} \, \upsilon_{AP}} + \frac{\xi_b \dfrac{\rho_b}{\rho_p}}{\rho_b \, \upsilon_b}$$

and since $\xi_i \dfrac{\rho_i}{\rho_p} = \left(\dfrac{V_i}{V}\right)\left(\dfrac{M_i}{V_i}\right) \Big/ \dfrac{M}{V} = \dfrac{M_i}{M} = \alpha_i$

$$\frac{1}{\dot{m}_p} = \frac{\alpha_{AP}}{\dot{m}_{AP}} + \frac{\alpha_b}{\dot{m}_b} \tag{5}$$
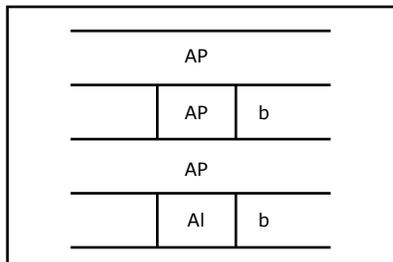
For aluminum loaded propellants, we noted that the *Al* particles are ejected when the binder holding them burns through. Looking at the simplified geometry below, it can be seen that the mean burning speed υ_p would be the same if the binder were really "filling in" for the *Al*.

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We then get the approximate expression

$$\frac{1}{\upsilon_p} = \frac{\xi_{AP}}{\upsilon_{AP}} + \frac{\xi_b + \xi_{A\ell}}{\upsilon_b} \; ,$$

identical to the Eq. (1), even with $A\ell$ particles. Eq. (5) also follows, with $1 - \alpha_{AP}$ in place of α_b. The only difference is that the mean density ρ_p in $\dot{m}_p = \rho_p \upsilon_p$ is modified by the $A\ell$

$$\left(\frac{1}{\rho_p} = \frac{\alpha_{AP}}{\rho_{AP}} + \frac{\alpha_b}{\rho_b} + \frac{\alpha_{A\ell}}{\rho_{AI}} \right)$$

Separate Burning of AP

Heat penetrates into the receding AP particle to a small depth only. This can be seen from the heat balance written <u>in the receding frame</u>:
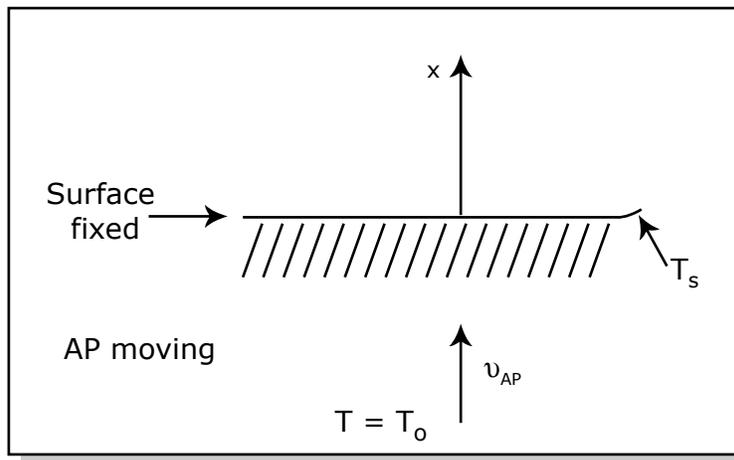
$$\rho_{AP} \, \upsilon_{AP} \, c_{AP} \frac{dT}{dx} - \frac{d}{dx} \left(\lambda_{AP} \frac{dT}{dx} \right) = 0 \qquad\qquad \text{Define } d = \frac{\lambda}{\rho c} \text{ (heat diff., cm}^2\text{/sec)}$$

$$\upsilon_{AP} T - d_{AP} \frac{dT}{dx} = \upsilon_{AP} T_0 \; ; \; d_{AP} \frac{d(T - T_0)}{dx} = \upsilon_{AP}(T - T_0)$$

$$T - T_0 = c \, e^{\frac{\upsilon_{AP}}{d_{AP}} x} \rightarrow \frac{T - T_0}{T_s - T_0} = e^{x / \left(\frac{d_{AP}}{\upsilon_{AP}} \right)}$$

Note: $d_p \cong 1.2 \times 10^{-3} \, cm^2 / s$, $c \cong 0.31 \, cal / g / K$.

This shows an exponential temperature decay into the solid, with a characteristic thermal thickness $x^* = \left(\dfrac{d}{\upsilon}\right)_{AP}$. Assuming $\upsilon = 1\,cm/s$, $d_{AP} \cong 1.2 \times 10^{-3}\,cm^2/sec$, this gives $x^* = 1.2 \times 10^{-3}\,cm = 12\,\mu m$.

The top few microns of the AP are molten when its temperature exceeds $T_{AP} \cong 835\,K$ (which may not happen if the pressure is so low, under $\approx 20\,atm$, that the flame-surface distance is too large to provide sufficient heating to it. Note this rate is

$$q_s = -\lambda_{AP}\left(\frac{dT}{dx}\right)_o = -\left(\lambda_{AP}/x^*\right)\left(T_s - T_0\right) = -\rho_{AP}\,\upsilon_{AP}\,c_{AP}\left(T_s - T_0\right),\ \text{so}$$

$|q_s|_{MIN} = \left(\rho\upsilon c\right)_{AP}\left(835 - 298\right)$ typically.

In this molten layer, about 70% of the AP undergoes complete decomposition to final (onydizing) gaseous products, according to

$$NH_4ClO_4 \rightarrow 0.285N_2 + 0.12N_2O + 0.23NO + 1.62H_2O + 0.76HCl + 0.12Cl_2 + 1.015O_2$$
$$(7)$$
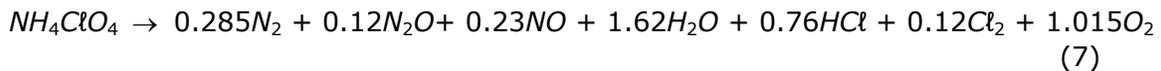
whereas the remaining 30% sublimates as a mixture of ammonia, NH_3, and perchloric acid, $HClO_4$; this mixture then completes the decomposition to the final products of (7) in a premixed (AP) flame about $1\mu m$ from the surface.

Let us look at the energetics of these effects:

(a) Enthalpy per gram to bring AP to its surface (molten) temperature (including some intermediate phase transitions):

$$\Delta h_{H,AP} = 266 + 0.328\left(T_{s,AP} - 835\right)\quad\text{(cal/g)}\qquad\qquad(8)$$

(b) Heat of the sublimation into $NH_3 + HClO_4$

$$\Delta h_{s,AP} = 476\ \text{to}\ 510\ \text{cal/(g/sublimed)}\qquad\text{(493 average)}\qquad(9)$$

(c) Heat of "combustion" of NH_3 with $HClO_4$

$$\Delta h_{C,AP} = -850\ \text{to}\ -885\ \text{cal/(g.reacted)}\qquad\text{(heat \underline{released})}\qquad(10)$$

(d) Heat released per gram of AP directly degraded in the liquid phase:

$$\Delta h_{D,AP} = -375\,cal/g\qquad\qquad(11)$$

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Note: We must have $\Delta h_s + \Delta h_c = \Delta h_D$)

We can combine these values to obtain the Adiabatic Flame Temperature $T_{f,AP}^{ad}$ of the "AP flame":

$$\Delta h_{H,AP} + 0.7\Delta h_{D,AP} + 0.3\left(\overbrace{\Delta h_{s,AP} + \Delta h_{C,AP}}^{\Delta h_{D,AP}}\right) + c_g\left(T_{f,AP}^{ad}T_{s,AP}\right) = 0 \qquad (12)$$

which, using for the gas a specific heat

$$c_g = 0.3 cal/g/K$$

gives $\underline{T_{f,AP}^{ad} = 1205 K}$ \qquad (13)

Rates and AP flame structure. The rate of pyrolization is found experimentally to depend on the surface temperature according to an Arrhenius-type expression

$$\dot{m}_{AP} = A_{S,AP}\, e^{-E_{s,AP}/RT_s} \qquad (14)$$

with $E_{S,AP}$ = 20 $Kcal/mol$ \qquad $A_{S,AP}$ = 96000 $g/cm^2/sec$

The reaction rate for the premixed AP flame obeys a similar law, except that, being primarily a bimolecular reaction, its rate is proportional to p^2:

$$\dot{\omega} = p^2 A_{g,AP}\, e^{-E_{g,AP}/RT_{f,AP}} \qquad (15)$$

with p in atm, $\dot{\omega}$ in $g/cm^3/sec$, and with

$$E_{g,AP} = 15 Kcal/mol; \; A_{g,AP} = 650 g/cm^3/sec/atm^2$$

If the velocity υ_g of the gas normal to the surface were known, Eq. (15) would allow calculation of the flame standoff distance, $x_{f,AP}$. The time to "burn" the gas is $\tau_{ch} = \rho_g/\dot{\omega}$, and then

$$x_{f,AP} = \upsilon_g \tau_{ch} = \upsilon_g \rho_g / \dot{\omega} = \frac{\upsilon_g \rho_g}{p^2 A_{g,AP}} e^{+\frac{E_{g,AP}}{RT_g}} \qquad (16)$$

(and notice $\rho_g \upsilon_g = \dot{m}_{AP}$)

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A separate expression for x_f can be obtained from the fact that the AP flame has to supply to the vaporizing surface the required heat of reaction, so if the flame moves too far, the reaction is too slow, and vice versa. The net (convection + conduction) heat flux in the gas between surface and flame is constant (no heat evolves there)

$$\dot{m}_{AP} \, c_g \frac{dT}{dx} - \frac{d}{dx}\left(\lambda_g \frac{dt}{dx} \right) = 0 \quad (c_g \cong 0.3 cal \, / \, g \, / \, K, \; \lambda_g = 1.9 \times 10^{-4} cal \, / \, sec \, / \, cm \, / \, K \;) \quad (17)$$

with the boundary conditions T=T$_{S,AP}$ at x=0 and

$$\left(\lambda_g \frac{dT}{dx} \right)_{x=0} = \dot{m}_{AP} \, Q_c = \dot{m}_{AP} \left(\Delta h_{H, AP} + Q_S \right) \quad (18)$$

Here Q$_s$ is the net heat required to take the AP from liquid at T$_s$ to gaseous products (before the AP "flame")

$$Q_s = 0.3 \times 493 + 0.7(-375) = -115 \; cal/g \quad (19)$$

Integrating (17) with (18),

$$\dot{m}_{AP} \, c_g T - \lambda_g \frac{dT}{dx} = \dot{m}_{AP} \, c_g T_{S,AP} - \dot{m}_{AP} \, Q_c$$

$$\frac{dT}{dx} - \frac{\dot{m}_{AP}}{\lambda_g} \left(T - T_{S, AP} \right) = \frac{\dot{m}_{AP}}{\lambda_g} Q_c$$

and imposing $T = T_{S, AP}$ at x = 0 again, $c = \dfrac{Q_c}{c_g}$, so

$$T \text{ -} T_{S, AP} = \frac{Q_c}{c_g}\left[e^{\frac{\dot{m}_{AP} \, c_g}{\lambda_g}x} - 1 \right] \quad (20)$$

The "AP flame" is at x = x $_{f, AP}$, where T reaches T$_{fAP}$ (adiabatic T$_f$ for AP alone, but maybe higher if there is heat supply from the main flame). Solving for x$_{f,AP}$ then,

$$x_{f, AP} = \frac{\lambda_g}{\dot{m}_{AP} \, c_g} \, \ell n \left[1 + \frac{c_g \left(T_{f, AP} - T_{s, AP} \right)}{Q_c} \right] \quad (21)$$

This must be the same as (16). Equating them,

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$$\frac{\dot{m}_{AP}}{p^2 A_{g,AP}} e^{\frac{E_{g,AP}}{RT_{f,AP}}} = \frac{\lambda_g}{\dot{m}_{AP} c_g} \ell n [\cdots]$$

or $\qquad \dot{m}_{AP} = p \sqrt{\dfrac{\lambda_g A_{g,AP}}{c_g} e^{-\frac{E_{g,AP}}{RT_{f,AD}}} \ell n \left[1 + \dfrac{c_g \left(T_{f,AP} - T_{s,AP} \right)}{Q_c} \right]}$ (22)

So, for AP <u>alone</u>, where $T_{f,AP} \cong 1205\,K$ is known, and $T_{s,AP}$ can be estimated (not too much higher than 835 K), the regression rate is <u>proportional to pressure</u> ($n_{AP} \cong 1$).

<u>Pyrolysis of Inert Binder</u>. A similar formulation can be used for the calculation of the heating rate due to the <u>main flame,</u> which serves to pyrolyze the surface of the binder (and also to elevate the temperature of the AP flame).
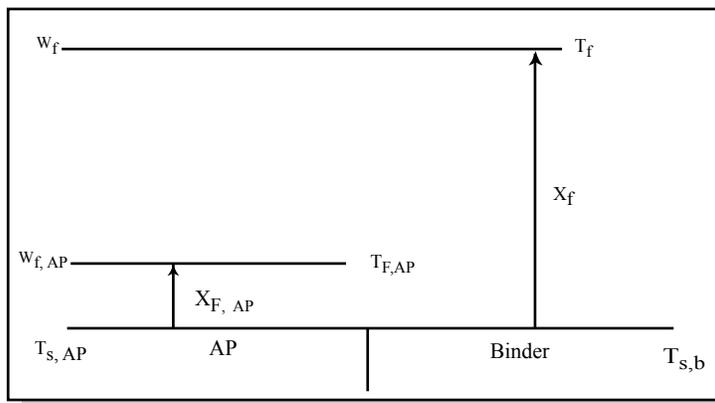
The paper by Lengellè et al. Simplifies the model by treating for this purpose the flow of gas as 1-D (even though it really is 2-D or 3-D due to the heterogeneity of the surface. It also assigns a uniform mass flux m_p above both, AP and binder. This is questionable, but we'll press on.

Similar to Eq. (17), we have now

$$\dot{m}_p c_g \frac{dT}{dx} - \frac{d}{dx} \left(\lambda_g \frac{dT}{dx} \right) = 0$$

and, defining $q = \lambda_g \dfrac{dT}{dx}$ the magnitude of the (surface-directed) conduction heat flux,

$$\frac{dq}{dx} - \frac{\dot{m}_p c_g}{\lambda_g} q = 0 \tag{23}$$

We integrate the condition $\dot{m}_p Q_f = q(x_f)$ (24)

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where x_f is the location of the main flame, at which the energy of combustion $Q_f \cong 700 \, cal/g$ is released (q=0 <u>above</u> it, $q = \dot{m}_p Q_f$ below it):

$$q = \dot{m}_p Q_f \, e^{-\frac{\dot{m}_p c_g (x_f - x)}{\lambda_g}} \tag{25}$$

At x=0, on the binder surface, the heat flux q(0) is used to pyrolyze the binder at the rate $\dot{m}_b$ (p.u. area), and if $Q_{c,b}$ is the required heat (cal/g), we obtain $q(0) = \dot{m}_b Q_{c,b}$, or

$$\dot{m}_b = \dot{m}_p \frac{Q_f}{Q_{c,b}} e^{-\frac{\dot{m}_p c_g x_f}{\lambda_g}} \tag{26}$$

The pyrolisation heat $Q_{c,b}$ is composed of that required to heat the binder form T_0 to $T_{s,b}$, plus the heat of decomposition Q_s=360 cal/g:

$$Q_{c,b} = c_b \left(T_{s,b} - T_0 \right) + 360 \qquad (c_b \cong 0.39 \, cal/g/k) \tag{27}$$

For $T_{s,b}$=1100K, $Q_{c,b}$=675 cal/g.

Eq. (25) is also useful to estimate the rate of arrival of heat from the main flame at the location of the AP flame ($x=x_{f,AP}$):

$$q_{f,AP} = \dot{m}_p Q_f e^{-\frac{\dot{m}_p c_g \left(x_f - x_{f,AP} \right)}{\lambda_g}} \tag{28}$$

and, from this, the AP flame temperature, using a modification of Eq. (12):

$$\dot{m}_{AP} \left[\Delta h_{H,AP} + \Delta h_{D,AP} + c_g \left(T_{f,AP} - T_{s,AP} \right) \right] = q_{f,AP} \tag{29}$$

or

$$\dot{m}_{AP} \, c_g \left(T_{f,AP} - T_{f,AP}^{ad} \right) = q_{f,AP} \tag{29b}$$

where $T_{f,AP}^{ad}$ is the value of $T_{f,AP}$ with no $q_{f,AP}$ present ($T_{f,AP}^{ad} \cong 1205K$, as we found).

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Estimating the Main Flame Distance. Let D_{ox} be the diameter of the oxidizer particle. The surface of the particle evolves oxidizing gas (after AP flame), while the binder around it generates fuel gas.
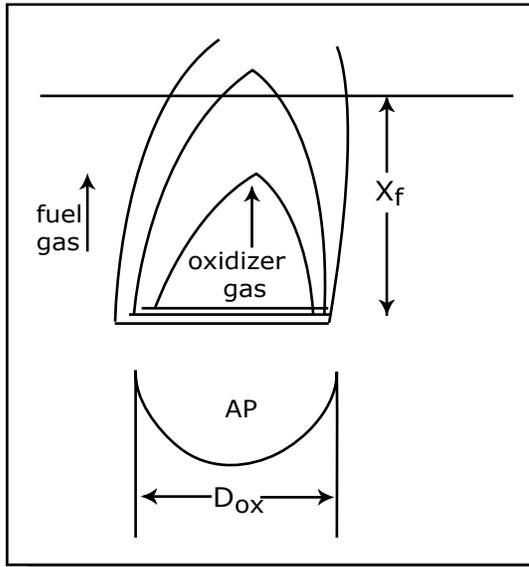
These inter-diffuse to form a diffusion-flame, similar to that from a Bunsen burner (but inside-out). The radial distance covered by a substance diffusing with a diffusivity D, in a time t, is of the order of $\sqrt{2Dt}$. We say the flame's end is at the point when this equals $D_{ox}/2$ (times some factor of order 1, to account for real geometry):

$$\frac{D_{ox}}{2} \cong A_d^{1/2} \sqrt{2Dt} \; (A_d \approx 1)$$

Equating the time t to $x_f / \upsilon_g = x_f \dfrac{\rho_g}{\dot{m}_p}$ (notice we again use the overall mass flux $\dot{m}_p$ here),

$$\frac{D_{ox}}{2} \cong A_d^{1/2} \sqrt{2D\rho_g x_f / \dot{m}_p}$$

or

$$x_f = \frac{\dot{m}_p D_{OX}^2}{8 A_d \left(\rho_g D \right)} \tag{31}$$

The diffusivity D is inversely proportional to the gas density, so that $\rho_g D$ is independent of P at a given T (and weakly dependent on T). Thus, (31) gives a main flame distance which is independent of pressure, and scales with the square of AP particle diameter.

To a good approximation, the mass diffusivity D is equal to the heat diffusivity:

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$$D \cong d_g = \frac{\lambda_g}{\rho_g c_g} \Rightarrow \rho_g D \cong \frac{\lambda_g}{c_g} \tag{32}$$

which can be substituted into (31):

$$x_f \cong \frac{\dot{m}_p \, c_g}{8 A_d \lambda_g} D_{ox}^2 \tag{32}$$

The final gas temperature (after the main flame) can be estimated now from

$$\alpha_{AP} T_{f,AP} + \alpha_b T_{s,b} + \frac{Q_f}{c_g} = T_f \tag{34}$$

Using $\alpha_{AP} = 0.8$, $\alpha_b = 0.2$, $T_{f,AP}^{ad} = 1205\ K$, $T_{s,b} = 1100\ K$, $c_g = 0.3\,cal/g/K$, $Q_f = 700\ cal/g$. We calculate $T_f = 3250\ K$.

Actually, Eq.(33) is appropriate only when the diffusion time (distance) is much more than the reaction time (distance), as at high P (short reaction times), and/or large AP particle diameters (long diffusion times). In the opposite limit, x_f is really dictated by the chemical reaction time (distance); similar to Eq. (16), this distance can be written as

$$x_{f,r} = \frac{\dot{m}_p}{p^2 A_{g,f}} e^{+\frac{E_{g,f}}{RT_f}} \tag{35}$$

The values of $A_{g,f}$ and $E_{g,f}$ are not given by Langellé et al. This is especially regrettable for $E_{g,f}$ which is very sensitive. We here take tentatively $A_{g,f} = 650\,g/cm^3/sec/atm^2$, as for AP, and determining $E_{g,f}$ by matching approximately one of the small-diameter data points quoted in the paper. This leads to

$$E_{g,f} \cong 29.4 Kcal\ /\ mol \tag{36}$$

For the general case, then, we take x_f to be the sum of the reaction and diffusion distances:

$$x_f = \dot{m}_p \left[\frac{c_g}{8 A_d \lambda_g} D_{ox}^2 + \frac{1}{p^2 A_{g,f}} e^{+\frac{E_{g,f}}{RT_f}} \right] \tag{37}$$

Solution Procedure. Given $P, T_0, D_{ox}, \alpha_{AP}$, we want to calculate $\dot{m}_p$, as well as several of the intermediate variables. The equations are fairly complex, so some iteration must be devised. First, from the averaging law (Eq. (5)) with $\alpha_b = 1 - \alpha_{AP}$,

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$$\frac{\dot{m}_b}{\dot{m}_p} = \frac{1 - \alpha_{AP}}{1 - \alpha_{AP} \dfrac{\dot{m}_p}{\dot{m}_{AP}}} \tag{38}$$

But $\dfrac{\dot{m}_b}{\dot{m}_p}$ is also calculable from Eq. (26); this involves x_f, which is given by Eq. (37):

$$\frac{\dot{m}_b}{\dot{m}_p} = \frac{Q_f}{Q_{c,b}} e^{-\dfrac{\dot{m}_p c_g}{\lambda_g} \dot{m}_p \left[\dfrac{c_g}{8 A_g \lambda_g} D_{ox}^2 + \dfrac{\exp\left(+E_{g,f} / Q T_s\right)}{p^2 A_{g,f}} \right]} \tag{39}$$

Equate (38) and (39) and solve for $\dot{m}_p$:

$$\dot{m}_p = \sqrt{\frac{\lambda_g \ell n \left[\dfrac{Q_c}{Q_{c,b}} \dfrac{1 - \alpha_{AP} \dot{m}_p / \dot{m}_{AP}}{1 - \alpha_{AP}} \right]}{c_g \left[\dfrac{c_g}{8 A_d \lambda_g} D_{ox}^2 + \dfrac{\exp\left(-E_{g,f} / R T_f\right)}{p^2 A_{g,f}} \right]}} \tag{40}$$

This is similar to the expression Eq. (22) for $\dot{m}_{AP}$. In fact, the ratio of both equations provides a relationship between $\dfrac{\dot{m}_p}{\dot{m}_{AP}}$, and $T_{f,AP}$ with D_{ox} and p as parameters:

$$\frac{\dot{m}_p}{\dot{m}_{AP}} = \sqrt{\frac{e^{E_{g,AP} / R T_{f,AP}}}{A_{g,AP}} \frac{\ell n \left[\dfrac{Q_f}{Q_{c,b}} \dfrac{1 - \alpha_{AP} \dot{m}_p / \dot{m}_{AP}}{1 - \alpha_{AP}} \right]}{\ell n \left[1 + \dfrac{c_g \left(T_{f,AP} - T_{s,AP} \right)}{Q_c} \right]}} \cdot \frac{1}{\sqrt{\dfrac{c_g}{8 A_d \lambda_g} p^2 D_{ox}^2 + \dfrac{\exp\left(+E_{g,f} / R T_f\right)}{A_{g,f}}}} \tag{41}$$

The AP flame temperature $T_{f,AP}$ depends, in turn, on $\dfrac{\dot{m}_p}{\dot{m}_{AP}}$, as can be seen by combining Eqs. (28) and (29):

$$\dot{m}_{AP} \left[\Delta h_{H,AP} + \Delta h_{D,AP} + c_g \left(T_{f,AP} - T_{s,AP} \right) \right] = \dot{m}_p Q_f e^{-\dfrac{\dot{m}_p c_g \left(x_f - x_{f,AP} \right)}{\lambda_g}} \tag{42}$$

Here, we notice that the factor $e^{-\dfrac{\dot{m}_p c_g x_f}{\lambda_g}}$ is

$$e^{-\frac{\dot{m}_p\, c_g x_f}{\lambda_g}} = \frac{Q_{c,b}}{Q_f}\frac{\dot{m}_b}{\dot{m}_p} = \frac{Q_{c,b}}{Q_f}\frac{1-\alpha_{AP}}{1-\alpha_{AP}\dfrac{\dot{m}_p}{\dot{m}_{AP}}} \tag{43}$$

Also, the factor $e^{+\frac{\dot{m}_p\, c_g x_f ,AP}{\lambda_g}}$ can be expressed, using (21) as

$$e^{-\frac{\dot{m}_p}{\dot{m}_{AP}}\frac{\dot{m}_{AP}\, c_g x_{f,AP}}{\lambda_g}} = \left[1 + \frac{c_g\left(T_{f,AP}-T_{s,AP}\right)}{Q_c}\right]^{\dot{m}_p/\dot{m}_{AP}} \tag{44}$$

Combining (42), (43) and (44)

$$\Delta h_{H,AP} + \Delta h_{D,AP} + c_g\left(T_{f,AP}-T_{s,AP}\right) = Q_{c,b}\frac{1-\alpha_{AP}}{1-\alpha_{AP}\dfrac{\dot{m}_p}{\dot{m}_{AP}}}\left[1 + \frac{c_g\left(T_{f,AP}-T_{s,AP}\right)}{Q_c}\right]^{\frac{\dot{m}_p}{\dot{m}_{AP}}} \times \left(\frac{\dot{m}_p}{\dot{m}_{AP}}\right) \tag{45}$$

Here we recall that Q_c depends on $T_{s,AP}$ (Eqs. (18), (19) and (8))

$$Q_c \cong 266 + 0.328\left(T_{s,AP}-835\right) - 115 = 0.328 T_{s,AP} - 123\,(cal\,/\,g) \tag{46}$$

For the present purposes, it is sufficient to assume a value for $T_{s,AP}$ somewhat above 835K; this could be refined later by matching heat fluxes at the liquid surface. We adopt for most of the following $T_{s,AP}$=925K.

Given $T_{s,AP}$, we can see that Eq. (45) uniquely relates to $T_{f,AP}$ to $\dot{m}_p/\dot{m}_{AP}$. The following calculational procedure can than be followed:

(a) Take a value of $\dot{m}_p/\dot{m}_{AP}$ (typically in the range 0.2-0.6)
(b) Solve (45) for $T_{f,AP}$ (non-linear equation, requires some internal iteration)
(c) Solve (41) for the group

$$\psi \equiv \frac{c_g}{8A_d\lambda_g}\left(pD_{ox}\right)^2 + \frac{e^{+E_{g,f}\,/\,RT_f}}{A_{g,f}} \tag{47}$$

and, hence, for the product p_{Dox}. Given p_{Dox}, This gives p.

(d) Calculate $\dot{m}_{AP}$ from Eq. (22).

(e) $\dot{m}_p = \left(\dfrac{\dot{m}_p}{\dot{m}_{AP}}\right)\dot{m}_{AP}$

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This produces a curve of $\dot{m}_p$ vs. p, with $\dfrac{\dot{m}_p}{\dot{m}_{AP}}$ as the running parameter (for a fixed D_{ox}, particle diameter).

Notice how $T_{f,AP}$ and $\dot{m}_{AP}$ depend on the combination pD_{ox} rather than on the separate variables. However, since $\dot{m}_{AP}$ contains the factor p directly, the final burning rate of $\dot{m}_p$ is of the form

$$\dot{m}_p = p\ f(p\ D_{ox}) \tag{48}$$

where f is some complicated function. This is an important scaling law (not pointed out in Lengelle et al's paper). To verify it, we can use the data reported in Fig. 31 of the paper.

Fig.3   Pressure (atm)
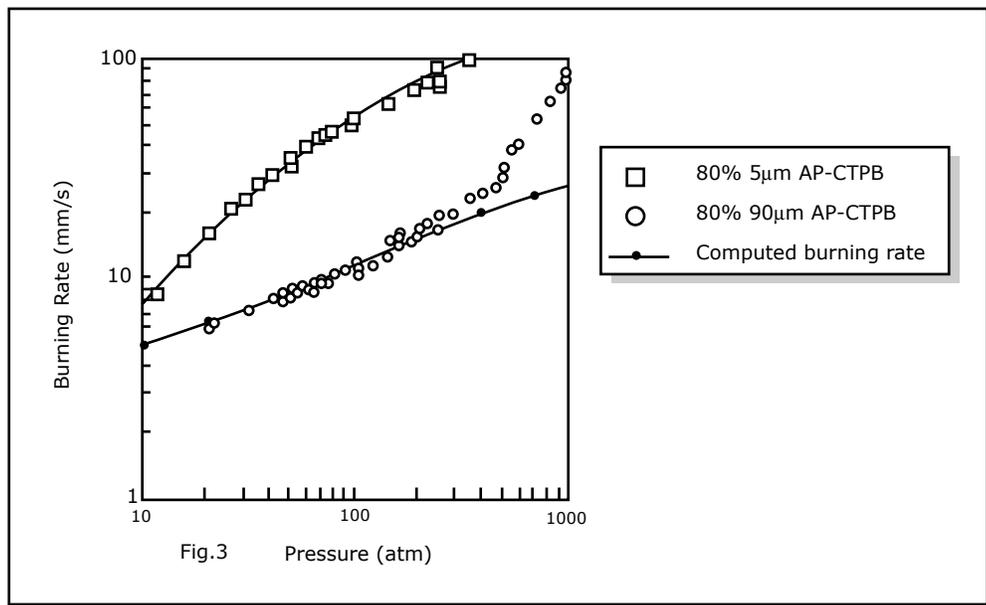
For Dox=5 μm , we have

P(cm)	10	30	100	300
υ_p (mm/sec)	7.8	21	61	92
PD$_{ox}$ (atm μm)	50	150	500	1500
$\upsilon_p / p\,(mm/\sec/atm)$	0.78	0.70	0.61	0.307

For Dox=90 μm ,

P(cm)	10	30	100	300
υ_p (mm/sec)	5	7.2	10.2	20.0
PD$_{ox}$ (atm μm)	900	2700	9000	27,000
$\upsilon_p / p\,(mm/\sec/atm)$	0.5	0.24	0.102	0.0667

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Plotting now both curves as (υ_p/p) vs. (pD$_{ox}$), <u>they do coincide</u>:

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