

SOLID-STATE THERMOCHEMISTRY OF FLAMING COMBUSTION

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Introduction

A large amount of research has been conducted on the gas phase thermochemistry of flaming combustion [1], undoubtedly due to the commercial importance of this process in heating and internal combustion engines. In contrast, the solid-state processes of flaming combustion are poorly understood—probably because this knowledge is relevant mainly to the problems of fire and incineration, neither of which have a large enough economic impact to justify significant research activity. To date, only the thermochemical processes that occur in burning wood have been studied systematically [2]. At the Federal Aviation Administration we are attempting to develop a fireproof aircraft cabin [3, 4]. Since commercial aircraft cabins are comprised primarily of synthetic organic polymers and polymer composites, we require a fundamental understanding of the solid-state processes of flaming combustion and the relationship of these processes to polymer chemical structure in order to achieve this goal. Therefore, the present work attempts to extend the existing research on the solid-state thermochemistry of burning wood to include polymers.

Fire Behavior of Combustible Solids

Once sustainable ignition has occurred, steady, one-dimensional burning of the thermally thick polymer is assumed [5]. Steady burning at a constant net surface heat flux \dot{q}_{net} is treated as a stationary state by choosing a coordinate system that is fixed to the surface and receding at velocity v as the polymer gasifies (see Figure 1).

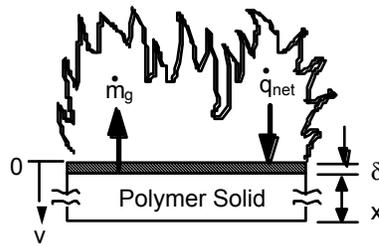


Figure 1. Geometry of burning process.

If there is no internal heat generation or absorption and pyrolysis is restricted to a thin surface layer of depth δ the steady-state, one-dimensional heat conduction equation for a constant recession velocity is

$$\frac{d^2T}{dx^2} + \frac{v}{\alpha} \frac{dT}{dx} = 0 \quad (1)$$

where T is the temperature at location x in the solid polymer of constant thermal diffusivity α . Solution of Equation 1 for the appropriate boundary conditions gives the steady recession velocity of the surface $x = 0$ at surface temperature $T(x = 0) = T_s$

$$v = \frac{1}{\rho} \frac{\dot{q}_{\text{net}}}{\left(c(T_s - T_o) + \Delta h_v \right)} = \frac{1}{\rho} \frac{\dot{q}_{\text{net}}}{h_g} \quad (2)$$

where ρ and c are the density and heat capacity of the polymer, respectively, Δh_v is the heat of vaporization of the volatile thermal degradation products, and $h_g = c(T_p - T_o) + \Delta h_v$ is the total heat of gasification per unit original mass of polymer. The steady-state temperature distribution in the burning solid polymer of thermal conductivity κ is

$$T(x) - T_o = (T_s - T_o) \exp\left(-\frac{c \dot{q}_{\text{net}}}{\kappa h_g} x \right) \quad (3)$$

from which the surface heating rate is

$$\beta = \left. \frac{dT}{dt} \right|_{x=0} = v \left. \frac{dT}{dx} \right|_{x=0} \approx \frac{\dot{q}_{\text{net}}^2}{\kappa \rho h_g} \quad (4)$$

Conservation of mass in the pyrolysis layer where virgin polymer of density ρ pyrolyzes to an inert or char fraction $\mu = \text{mass of char/original mass}$, gives

$$\rho v = \frac{\dot{m}_g}{1 - \mu} \quad (5)$$

where \dot{m}_g is the mass loss rate of pyrolysis gases per unit surface area. Defining a heat of gasification per unit mass of volatiles

$$L_g = \frac{h_g}{1 - \mu} \quad (6)$$

and combining Equations 5 and 6

$$\dot{m}_g = \frac{\dot{q}_{\text{net}}}{h_g / (1 - \mu)} = \frac{\dot{q}_{\text{net}}}{L_g} \quad (7)$$

Multiplying Equation 7 by the heat of complete combustion of the fuel gases h_c^0 and the gas phase combustion efficiency, χ gives the steady-state energy balance for the heat release rate in flaming combustion

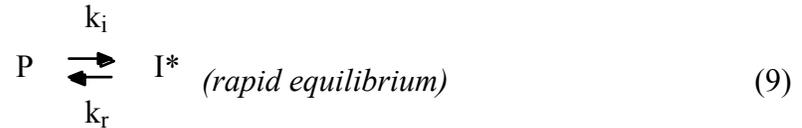
$$\dot{q}_c = \chi h_c^o \dot{m}_g = \chi(1-\mu) \frac{h_c^o}{h_g} \dot{q}_{\text{net}} = \chi \frac{h_c^o}{L_g} \dot{q}_{\text{net}} \quad (8)$$

Fuel Generation Kinetics

A simple solid-state fuel generation model has been proposed [6] based on the following assumptions about the process of polymer thermal degradation as it occurs in fires:

1. A reactive intermediate I^* is generated in the polymer dissociation (initiation) step which is in rapid dynamic equilibrium with the parent polymer (P) but is consumed in the process of gas (G) and char (C) formation such that its concentration never becomes appreciable. This is the stationary-state hypothesis.
2. Char and gas formation is a single step process.
3. The thermal degradation environment in the pyrolysis zone of a burning solid polymer is non-oxidizing or anaerobic.

The corresponding reactions are:



Equations 9-11 reduce thermal degradation of polymer P to a single step involving parallel reactions of an active intermediate I^* to form to gas G and char C, where k_i is the rate constant for initiation, and k_r , k_g , and k_c are the rate constants for termination by recombination, hydrogen transfer to gaseous species, and char, respectively.

For the usual case where the global activation energy for pyrolysis E_a is much greater than RT_p with $T_p = T_s$ the thermal decomposition temperature, Equations 9-11 can be solved for the maximum fractional mass loss rate during a constant heating rate (e.g., thermogravimetric analysis) experiment

$$\frac{\dot{M}_{\text{max}}}{M_0} = \left. \frac{-1}{M_0} \frac{dM}{dt} \right|_{\text{max}} \approx (1-\mu) \frac{\beta E_a}{eRT_p^2} \quad (12)$$

where β is the heating rate, T_p is the temperature at peak fractional mass loss rate, M and M_0 are the instantaneous and initial mass of the sample, e is the natural number, and R is the gas

constant. Multiplying Equation 12 by the heat of complete combustion of the pyrolysis gases gives the specific heat release rate

$$\dot{Q}_c^{\max} \text{ (W/kg)} = -h_c^o \frac{\dot{M}_{\max}}{M_o} \approx h_c^o \frac{\beta(1-\mu) E_a}{eRT_p^2} \quad (13)$$

Dividing Equation 13 by the heating rate β (K/s) gives a material flammability property with the units (J/kg-K) and significance of a heat release capacity.

$$\eta_c \equiv \frac{\dot{Q}_c}{\beta} = \frac{h_c^o (1-\mu) E_a}{eRT_p^2} \quad (14)$$

The heat release capacity is measurable by different techniques [7, 8] and is calculable from molar group contributions [9], suggesting that it is a true material property. If the global mass loss rate kinetic constant at depth x is a function only of the temperature $T(x)$ then $k(x) = A \exp[-E_a/RT(x)]$, and with $T(x)$ as per Equation 3, the steady flaming heat release rate is related to the heat release capacity [5, 10] as

$$\dot{q}_c = \chi h_c^o \dot{m}_g = \chi h_c^o \left\{ \rho \int_0^\infty k(x) dx \right\} = \chi \rho \delta \dot{Q}_c^{\max} = \chi \rho \delta \beta \eta_c \quad (15)$$

For an external heat flux of 50 kW/m² the net heat flux is approximately $\dot{q}_{net} = 40$ kW/m² at a typical surface burning (reradiation) temperature of 750K. Under these conditions the pyrolysis zone thickness δ for steady burning is [5, 10]

$$\delta = \frac{\kappa}{q_{net}} \frac{eRT_p^2}{E_a} \approx 0.4 \text{ mm} \quad (16)$$

Equation 4 gives an effective surface heating rate $\beta = \dot{q}_{net}^2 / \kappa \rho h_g = (40 \text{ kW/m}^2)^2 / [(0.2 \text{ W/m-K})(1100 \text{ kg/m}^3)(3 \text{ MJ/kg})] = 2.4 \text{ K/s}$, so for an external heat flux of 50 kW/m² the steady flaming heat release rate should be proportional to the heat release capacity with (typical) slope $\chi \rho \delta \beta = (0.9)(1100 \text{ kg/m}^3)(4 \times 10^{-4} \text{ m})(2.4 \text{ K/s}) = 1 \text{ kg-K-m}^2\text{-s}^{-1}$. Figure 2 is a plot of steady (average) heat release rate in flaming combustion for several pure polymers tested at an external heat flux of 50 kW/m² *versus* their measured heat release capacity. Approximate proportionality and slope predicted by Equation 15 are observed. Substituting Equations 4, 13, and 16 into Equation 15 recovers the energy balance for flaming combustion (Equation 8) showing that the solid state thermochemistry is self-consistent.

Conclusions

The heat release rate in steady, flaming combustion is derived from nonisothermal pyrolysis kinetics by assuming that the rates of solid state (pyrolysis) and gas phase (combustion) reactions

are rapid in comparison to the rate of heat transfer. Detailed thermal degradation chemistry is foregone in favor of a transient mass balance on the polymer, fuel gases, and solid char in a thin anaerobic pyrolysis layer at the surface.

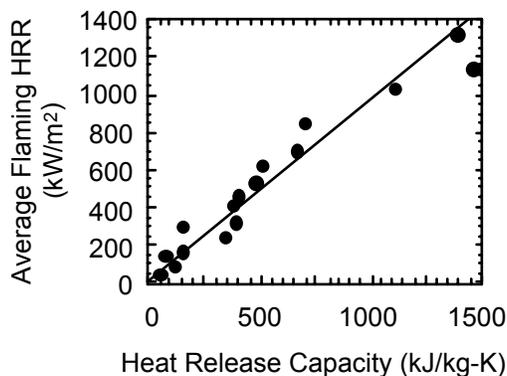


Figure 2. Average Flaming Heat Release Rate *versus* Heat Release Capacity for Some Commercial Polymers.

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