Transport of Gases in Charring Solids

Howard R. Baum
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899

Arvind Atreya
Department of Mechanical Engineering
University of Michigan
Ann Arbor, MI 48109

1   Introduction

The analysis of thermal degradation of charring solids is complicated by the fact that the charring process results in the release of gaseous combustible materials at the char-virgin material interface. Initially, the interface is at or near the surfaces of the material being heated. Under these circumstances, it is often assumed that the gases are instantly expelled from the solid material into the adjacent oxidizing atmosphere, permitting combustion to take place in the gas phase. However, if the process goes on long enough, the interface will no longer be adjacent to the heated surfaces. The purpose of this document is to outline the development of a mathematical model of the transport of gases through the char. In the next section the basic equations and boundary conditions controlling the gas transport are derived. Following this, the model is used to study the time-dependent thermal degradation of a semi-infinite charring material heated above the charring temperature. This one-dimensional transient analysis is the simplest possible configuration for charring studies. A one-dimensional transient model is also the local approximation currently used in multi-dimensional studies of flame spread over complex surfaces. Then, the opposed flow flame spread over a plane surface treated by Atreya and Baum [1] is revisited. This permits the gas transport to be studied in a configuration for which the temperature distribution is already known. It also removes an assumption about the surface distribution of the gaseous fuel that was needed due to the absence of a physics based model of the transport process.

2   Gas Transport Model

The starting point for the analysis is the choice of dependent variables. Let ρ_v denote the density of the virgin material, and let ρ_c be the density of the char, where $\rho_c < \rho_v$. The lower char density is assumed to be caused by the creation of small void spaces through which the evolved gases pass. The void fraction ϵ is then given by the expression

$$\epsilon = (\rho_v - \rho_c)/\rho_v \tag{1}$$

The void fraction is an essential concept in what follows. In order to characterize the thermodynamic state of the gas in terms of the usual density, temperature, and pressure, we need to have ρ denote the gas density per unit volume of space *occupied by the gas*. On the other hand, the velocity $\vec{u}$ must be defined such that $\vec{m} = \rho \vec{u}$ is the local mass flux of gas through a macroscopic surface element in the char. The notion of a macroscopic surface element arises because the char will be treated as a continuum, with gas and solid matter coexisting in the volume occupied by the char. Adopting this approach means that the equation expressing conservation of mass for the evolved gas takes the form:

$$\frac{\partial (\rho \, \epsilon)}{\partial t} + \nabla \cdot (\rho \, \vec{u}) = 0 \tag{2}$$

The next step is to find a relationship between the local mass flux and the gaseous pressure gradient in the char. This is Darcy's Law, whose form can be justified by considering the relationship between mass flux and pressure drop in Poiseuille flow. The discussion by Batchelor [2] gives a useful insight into the fluid mechanical basis for this relationship in studying the percolation of water through ground soil. The argument needs to be modified for a gas percolating through the char [3]. A modified version of Landau's approach will be followed here. Consider the mass flux through a pipe of elliptical cross-section with semi-axes a and b. Using the fact that the cross-sectional area A of the pipe is given by the expression $A = \pi ab$, the relation between the mass flux and pressure gradient takes the form:

$$\vec{m} = -\frac{(ab) \, A}{4\pi \, (a^2 + b^2)} \left(\frac{p \, \nabla p}{\mu(T) \, \mathcal{R}T} \right) \tag{3}$$

Equation (3) shows that the local mass flux is composed of two parts; a shape dependent factor proportional to the cross-sectional area of the pipe, multiplied by a term which is proportional to the gradient of the pressure *squared*, and which depends

only on the properties of the gas. The shape factor will have to be replaced by an empirical factor, since there is no way of knowing the actual shape of the passages created by the gasification processes. Moreover, the shapes would be so complex that it would be impractical to use the information even if it were available. The gas properties, however, can all be readily measured if samples of the evolved gas can be obtained.

The final form of equation (3) comes from noting that the mass flux averaged over an area that is large compared with any individual pore passage must account for the fact that only a fraction of the area of order $\epsilon^{(2/3)}$ contains voids, if the char density is related to that of the virgin material through equation (1). Thus, the form of Darcy's law that will actually be used is:

$$\rho\,\vec{u} = -\epsilon^{(2/3)}K\,\left(\frac{p\,\nabla p}{\mu(T)\,\mathcal{R}T}\right) \tag{4}$$

The permeability K has the dimensions of an area. It is clearly an empirical parameter that characterizes the char as a porous medium. Hopefully, a given virgin material will have a unique value of K. The mass conservation equation, which controls the transport of gases through the char then takes the final form:

$$\frac{\partial}{\partial t}\left(\frac{p}{\mathcal{R}\,T}\epsilon\right) = \nabla\cdot\left(\frac{\epsilon^{(2/3)}K\,p}{\mu(T)\,\mathcal{R}T}\,\nabla p\right) \tag{5}$$

Note that equation (5) is a parabolic equation, in contrast to the elliptic equation that results from using this kind of model to represent liquid percolation phenomena. Moreover, the domain through which the evolved gases can percolate is not known in advance, but must be determined as part of the solution for the associated problem for the evolution of the temperature field.

The boundary condition at the interface between the char and the virgin material can be stated as follows: Let $\vec{V}$ be the local velocity of the interface and $\vec{n}$ be the unit normal to the surface defined with positive $\vec{n}$ pointing *into* the virgin material. Then:

$$\epsilon^{(2/3)}K\,\left(\frac{p\,\nabla p\cdot\vec{n}}{\mu(T)\,\mathcal{R}T}\right) = (\rho_v - \rho_c)\,\vec{V}\cdot\vec{n} \tag{6}$$

Physically, equation (6) states that the rate at which evolved gases are created is equal to the product of the velocity of the char front normal to itself multiplied by the density difference between the char and virgin material. Thus, all the mass lost to the solid phase is taken up by the gas, with the pressure adjusting accordingly. Finally, at an impermeable boundary between the char and an inert solid material, the gas cannot penetrate into the inert solid. Thus, if $\vec{\nu}$ denotes a unit normal to the impermeable boundary:

$$\nabla p\cdot\vec{\nu} = 0 \tag{7}$$

3 Initial Transient

Consider an idealized scenario in which the temperature at the surface of a semi-infinite solid is instantaneously raised from an initial ambient temperature T_∞ to a surface temperature $T_s > T_p$. Since the pressure field is determined by the temperature distribution in the char and the virgin material, we consider this first. The analysis is very similar to that outlined in Ref. [1]. Let $T_v(x\,t)$ be the temperature, λ_v be the thermal conductivity, and C_{pv} be the heat capacity of the virgin material, with an analogous notation in the char. Then:

$$\rho_c C_{pc}\frac{\partial T_c}{\partial t} = \lambda_c\frac{\partial^2 T_c}{\partial x^2}\,, \quad 0\leqslant x\leqslant X(t) \qquad \rho_v C_{pv}\frac{\partial T_v}{\partial t} = \lambda_v\frac{\partial^2 T_v}{\partial x^2}\,, \quad X(t)\leqslant x\leqslant\infty \tag{8}$$

Here, $x = X(t)$ is the position of the interface between materials, with x measured from the heated surface. The boundary conditions can be stated as follows: At the surface $x = 0, T_c = T_s$. Far from the surface, the virgin material is at the ambient temperature. Thus; $T_v = T_\infty$ as $x\to\infty$. Finally, at the interface $x = X(t)$, three conditions must be satisfied.

$$T_v = T_c = T_p \qquad \lambda_v\frac{\partial T_v}{\partial x} = \lambda_c\frac{\partial T_c}{\partial x} + \rho_v X'(t)Q \tag{9}$$

The first two conditions require that the temperature at the interface is continuous and equal to the char formation temperature. The final condition states that the heat flux transmitted from the char must supply an energy Q per unit mass of virgin material to liberate the gas at the char front, with the excess conducted into the interior of the solid. Solutions satisfying the temperature boundary conditions at the surface, interface, and in the interior can be obtained by noting that the absence of any independent length or time scale implies that all physical quantities depend only on a similarity variable η, defined as:

$$\eta = x/\sqrt{\alpha_v\,t} \qquad \alpha_v = \lambda_v/(\rho_v C_{pv}) \tag{10}$$

This implies that the interface position corresponds to a constant value of η. Denoting this value as $\eta = C$, the interface position can be expressed as:

$$X(t) = C\sqrt{\alpha_v\,t} \tag{11}$$

The solutions satisfying the first two of equations (9) can be written in the form:

$$T_v = T_p\,F(\eta) \qquad F(\eta) = \frac{T_\infty}{T_p} + \left(1 - \frac{T_\infty}{T_p}\right)\frac{\text{erfc}\,(\eta/2)}{\text{erfc}\,(C/2)} \tag{12}$$

$$T_c = T_p\,G(\eta) \qquad G(\eta) = \frac{T_s}{T_p} - \left(\frac{T_s}{T_p} - 1\right)\frac{\text{erf}\,(\eta^*/2)}{\text{erf}\,(C^*/2)} \tag{13}$$

$$C^* = \sqrt{(\alpha_v/\alpha_c)}\,C \qquad \eta^* = \sqrt{(\alpha_v/\alpha_c)}\,\eta \tag{14}$$

The parameter C that determines the location of the interface is found by requiring that the last of equations (9) be satisfied. The result is identical with that obtained for the interface condition in the flame spread problem considered in [1]. In slightly different notation it can be expressed as follows:

$$\frac{Q}{C_{pv}\,(T_p - T_\infty)} = \frac{\lambda_c}{\lambda_v}\left(\frac{T_s - T_p}{T_p - T_\infty}\right)f_1\,(C^*) - f_1\,(C) \tag{15}$$

$$f_1\,(C^*) = \frac{2}{\sqrt{\pi}\,C^*}\frac{\exp\left(-(C^*)^2/4\right)}{\text{erf}\,(C^*/2)} \tag{16}$$

We now turn to the calculation of the mass transport through the char. In what follows, it will be assumed that the interface is endothermic. The mass transport and hence the pressure distribution is confined to a domain bounded by the interface $x = X(t) = C^*\sqrt{\alpha_c\,t}$ and the char surface $x = 0$. The coefficients in equation (5) depend only on the variable η^*, while the char interface and surface correspond to the fixed values $\eta^* = C^*$ and $\eta^* = 0$ respectively. Thus, it makes sense to assume that the pressure is a function of η^* only. Denoting the pressure at the char surface by p_s, the pressure in the evolved gas is written in the form:

$$p(x,\,t) = p_s P\,(\eta^*) \tag{17}$$

Moreover, since the evolved gas viscosity is a function of temperature only, a reasonable assumption is that $\mu/\mu_p = (T/T_p)^n$. Using the solution for the temperature field obtained above, equation (5) takes the form:

$$\beta\frac{\eta^*}{2}\frac{d}{d\eta^*}\left(P\,(\eta^*)/G\,(\eta^*)\right) + \frac{d}{d\eta^*}\left(P\,(\eta^*)/[G\,(\eta^*)]^{n+1}\frac{dP}{d\eta^*}\right) = 0 \tag{18}$$

$$\beta = (\epsilon)^{1/3}\,\alpha_c\,\mu_p/\,(p_s\,K) \tag{19}$$

The boundary conditions at the interface and the char surface respectively take the form:

$$P\frac{dP}{d\eta^*}\,(\eta^* = C^*) = \frac{C^*}{2}\beta\,(\rho_v T_p)\,/\,(\rho_s T_s) \equiv M \qquad P(0) = 1 \tag{20}$$

Equations (18) - (20) reveal some important physics, even before any solutions are obtained. Clearly, the parameter β plays a major role in the mass transport. Small values of β correspond to nearly instantaneous transport of the evolved gases from the interface to the surface, with little accumulation in the interior of the char. Thus, models that postulate instant surface emission of gases assume (whether consciously or not) that the material in question has small values of β. This includes virtually all charring models developed to date. A natural starting point for the analysis of equations (18) - (20) is the observation that when $\beta = 0$, an analytical solution can be found for any value of M. Denoting the resulting pressure distribution by $P = P^{(0)}$, the solution takes the form:

$$P^{(0)}\,(\eta^*) = \left(1 + 2M\int_0^{\eta^*}[G(x)]^{(1+n)}\,dx\right)^{1/2} \tag{21}$$

The integral in equation (21) represents the effect of the temperature dependence of the viscosity of the evolved gases. If it is further assumed that $\mu \sim T$ so that $n = 1$, the integral can be evaluated explicitly. Figure 1 shows how the pressure distribution of the evolved gases in the char changes as the mass flux parameter increases, assuming that the transport parameter $\beta = 0$.
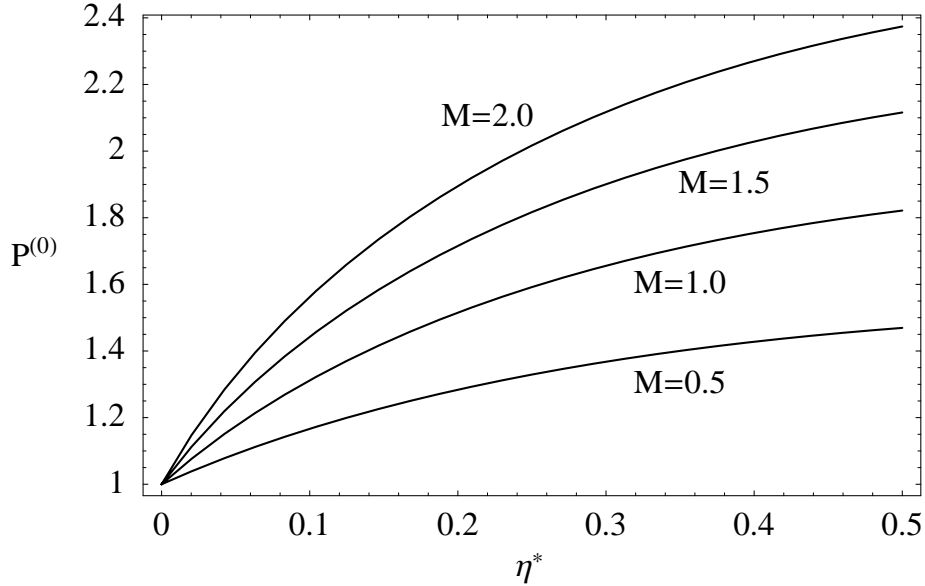
Figure 1: Evolved gas pressure distribution $p/p_s = P^{(0)}(\eta^*)$ in char for different values of mass flux parameter M. The solutions are valid for values of the transport parameter $\beta = 0$. The remaining parameters are $T_s/T_p = 2$, and $C^* = 0.5$.

Note that since $P^{(0)}$ represents a pressure normalized with respect to the ambient pressure at the char surface, the pressure rise is quite significant. Thus, a linearized treatment of this equation would be very inaccurate.

The above solution, although derived for $\beta = 0$ and M fixed, has a much wider range of validity. Indeed, if we write $M = \beta\tilde{M}$ and treat $\tilde{M}$ as a large parameter with β fixed, then it is easy to see that the same solution holds with an error $O\left(1/\sqrt{\tilde{M}}\right)$. The accuracy of the analytical solution has been confirmed by testing it against numerical results computed for $\beta = 1$, $M = 10, 100$, and 1000. The errors are actually much smaller for the cases investigated than the error estimate. This is in fact the most realistic case for this particular problem, since $\tilde{M}$ takes the form:

$$\tilde{M} = \frac{C^*}{2}\left(\rho_v T_p\right)/\left(\rho_s T_s\right) \tag{22}$$

In general, C^* is a number of order one, as is the temperature ratio T_p/T_s. However, the density ratio of the virgin wood to the gas at the char surface will almost always be large. Finally, as will become evident in the next Section, the solution is also valid for the pressure distribution in the opposed flow flame spread problem studied in [1].

4 Opposed Flow Flame Spread

The steady progression of a laminar flame over the surface of a combustible material into a stream containing the oxidizer is one of the oldest and most well studied problems in combustion science. Any analysis of this problem requires the solution of a coupled problem involving both the gas and condensed phases. Most of the research on this problem has focused on the description of the combustion phenomena in the gas phase. The thermal degradation of the condensed phase material is typically treated using a surface pyrolysis model coupled to a simple heat conduction analysis in the interior of the solid. There has been almost no work on charring materials like wood, where the gaseous "fuel" is liberated at an interior surface whose location must be found as part of the solution.

Figure 2 (taken from [1]) shows the overall geometry of the flame spread problem in a coordinate system moving with the flame. While this paper will be concerned only with the condensed phase model, it is important to explain certain features of the overall problem, in order to understand the sense in which the condensed phase analysis presented below represents a solution. To begin with, it is assumed that the whole problem can be regarded as a steady state phenomenon in a frame of reference moving with the flame speed V. The objective of the analysis is to determine V as a function of the material properties of the solid fuel, the gaseous oxidizer, and the ambient speed U_∞ of the opposed flow.
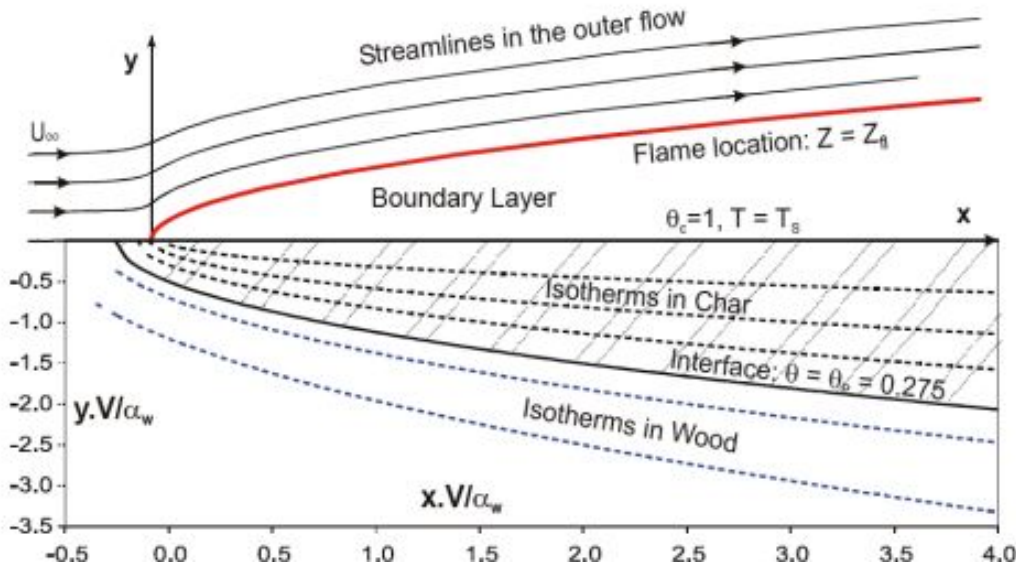
Figure 2: **Schematic showing combined gas phase and condensed phase analysis for charring material. The char region is shaded. Note that both the char and virgin material are heated upstream of the flame front.**

Two simplifications are introduced that permit the gas phase and condensed phase analyses to be considered separately, with the results of each analysis combined at the end to produce the desired results. First, it is assumed that there is no heat or mass transfer between the gas and condensed phase upstream of the flame front. Note that this does *not* mean that there is no pre-heating of the gas or solid. In fact, Figure 2 clearly shows that upstream conduction of heat plays a significant role in the heat transfer process. Moreover, while the gas phase dynamics is not of interest here, it should be noted that both the flow and temperature distributions depart from their ambient values ahead of the flame. The second assumption is that the surface temperature of the char is uniform downstream of the flame front. This assumption yields an internally consistent coupled solution to the heat transfer problem in both phases, provided that the first simplification is accepted. Specification of a value for this temperature, together with all the material properties and upstream flow conditions, then uniquely determines the flame speed.

Up to this point, all assumptions and simplifications are contained in the solutions described in [1]. However, that analysis required a third major assumption, that relates the spatial distribution of the mass flux of gas liberated at the char-virgin material interface to that at the surface. The analysis presented below removes that assumption, and replaces it with a physics based model for the evolved gas transport. It will be demonstrated that the results obtained using this model are entirely consistent with the earlier analysis, and thus complete the solution for the opposed flow flame spread over charring materials.

The starting point for the analysis is the representation of the steady state version of equation (5) in the coordinate system shown in Figure 2.

$$V \frac{\partial}{\partial x}\left(\frac{p}{\mathcal{R}T}\epsilon\right) = \frac{\partial}{\partial x}\left(\frac{\epsilon^{2/3}Kp}{\mu(T)\mathcal{R}T}\frac{\partial p}{\partial x}\right) + \frac{\partial}{\partial y}\left(\frac{\epsilon^{2/3}Kp}{\mu(T)\mathcal{R}T}\frac{\partial p}{\partial y}\right) \tag{23}$$

Equation (23) must be solved subject to the following boundary conditions at the gas-solid interface $y = 0$.

$$p(x, 0) = p_s \qquad x \geqslant 0 \qquad\qquad \frac{\partial p}{\partial y}(x, 0) = 0 \qquad x < 0 \tag{24}$$

The boundary condition at the char-virgin material interface will be derived below. The first of equations (24) states that at the surface of the solid, downstream of the flame front, the pressure must be the surface pressure (essentially ambient pressure when the flow Mach number is small, as is the case here). This generates the flow of gasified fuel that supports the flame. The second of these equations states that there is no mass flux of gasified fuel through the surface upstream of the flame front. If this were not true, the flame would begin upstream of the origin, violating the geometry on which the analysis is based.

Solutions are obtained by recasting the problem in parabolic coordinates defined as follows (see Figure 2):

$$\tau^* + \imath\,\omega^* = \sqrt{\frac{\alpha_v}{\alpha_c}}\,(\tau + \imath\,\omega) = \sqrt{\frac{V}{\alpha_c}}\,(x + \imath\,y) \tag{25}$$

The isotherms shown in the figure are lines of constant ω^* (or constant ω). The transformation is defined so that the branch cut is taken to be the positive x axis. Thus, $\tau^* = 0$ on the negative x axis, and $\tau^* = -\sqrt{V x / \alpha_c}$ on the positive x axis in the char. The positive x axis corresponds to $\omega^* = 0$. Assuming all physical quantities to be functions of ω^* then ensures that the gradient of all physical quantities in the solid is parallel to the surface for $x < 0$. Moreover, since the temperature and pressure take on constant values for $x \geqslant 0$, assigning these values at $\omega^* = 0$ completes the enforcement of the boundary conditions at the gas-solid interface.

The next step is the transformation of the equations to parabolic coordinates, taking advantage of the fact that the pressure and temperature depend only on ω^*. Introducing the dimensionless variables $T = T_p G\left(\omega^*\right), \mu = \mu_p \left(T/T_p\right)^n$, and $p = p_s P\left(\omega^*\right)$, the conservation of mass for the evolved gases takes the form:

$$2\beta\,\omega^*\,\frac{d}{d\omega^*}\left(P/G\left(\omega^*\right)\right) + \frac{d}{d\omega^*}\left(P/\left[G\left(\omega^*\right)\right]^{n+1}\frac{dP}{d\omega^*}\right) = 0 \tag{26}$$

Here, $\beta = \epsilon^{1/3}\alpha_c\mu_p/\left(p_s K\right)$ is the accumulation parameter identified in the previous section in equation (19). A similar (but less complex) analysis yields the analogous equations for the char temperature function $G\left(\omega^*\right)$ and virgin material temperature $T_v = T_p F\left(\omega\right)$. It is clear from the discussion of the boundary conditions on the temperature that if the identification $\omega^* = \eta^*/2$ and $\omega = \eta/2$ is made, then the solutions for the temperature field given in equations (12) and (13) are also the solutions for the flame spread problem. Since we also require that $P(0) = 1$ to enforce the surface pressure boundary condition, if we can demonstrate that the interface condition for the flame spread problem is identical with that shown in equation (20), then the equivalence of the two problems is complete.

The mass flux $\dot{m}$ of evolved gas at the interface is given by the expression:

$$\dot{m} = -\left(\rho_v - \rho_c\right)V\vec{\imath}\cdot\vec{n} \;=\; \epsilon^{2/3}K\frac{p\nabla p \cdot \vec{n}}{\mu(T)\mathcal{R}T} \tag{27}$$

Here, $\vec{\imath}$ is a unit vector in the flow direction, while $\vec{n}$ is a unit normal to the interface pointing *into* the virgin material. Since the pressure and temperature are only functions of ω^*, the interface is a surface defined by $\omega^* = C^*$. Then, introducing the dimensionless pressure P and using the equation of state for the evolved gas in the form $p_s = \rho_s\mathcal{R}T_s$, the two expressions for $\dot{m}$ can be combined to yield the following condition at the interface:

$$P\frac{dP}{d\omega^*} = 2C^* \frac{\rho_v T_p}{\rho_s T_s}\,\beta \tag{28}$$

This result is identical with that obtained in equation (20) of the previous section if we again make the identification $\omega^* = \eta^*/2$ and note that the value of C^* obtained here must satisfy the same condition.

This completes the identification of the solution of the one-dimensional impulsively heated problem with the solution of the condensed phase portion of the opposed flow flame spread problem. The solution obtained in Ref. [1] assumed that the mass flux of gas emerging at the interface moved along a curve of constant τ^* without change until it reached the surface of the char layer where it is oxidized by the gas to produce the flame. That is equivalent to assuming that $\beta \ll 1$ in the present analysis. Thus, the analytical solution for P obtained in the previous section completes the solution obtained by Atreya and Baum, and provides a self-consistent physics based model of opposed flow flame spread over charring materials.

References

[1] Atreya, A. and Baum, H.R., "A Model of Opposed-Flow Flame Spread Over Charring Materials", *Proc. Combustion Institute*, Vol. 29, pp. 227-236, (2002).

[2] Batchelor, G.K., *An Introduction to Fluid Dynamics*, Cambridge Univ. Press, Cambridge, pp. 223-224, (1967).

[3] Landau, L.D. and Lifshitz, E.M., *Fluid Mechanics*, Addison-Wesley, Reading, pp. 57-59, (1959).