Journal of Engineering Mathematics 23: 253–260, 1989

An entry-flow problem for a non-isothermal catalytic-wall reactor

S.A. THORNHAM[(1)] and J.A. KING-HELE*

*Mathematics Department, University of Manchester, Manchester M13 9PL, England (*author for correspondence); [(1)]present address: Wolfson Image Analysis Unit, Department of Medical Biophysics, University of Manchester, Manchester M13 9PL, England*

Received 1 October 1988; accepted in revised form 6 March 1989

Abstract. A reacting gas flows into a metal, thin-walled, tube which has a catalytic coating on its inner surface. A strong, temperature-dependent, exothermic reaction occurs giving a local hot spot. It is assumed that the surface temperature is controlled by heat conduction through the metal wall, heat transfer into the gas being negligible. A standard approximate technique is used to derive an integral equation which relates the mass transfer at the wall in the Blasius boundary layer to the wall temperature. A second integral equation is derived from the heat-conduction problem for the metal wall, and the coupled equations are solved numerically. The maximum temperature rise at the wall is found to be significantly higher than that obtained when a fully developed flow passes over a catalytic coating.

1. Introduction

Catalytic-wall reactors are often used when the desired gas-phase reaction is highly exothermic, for example, in the oxidation of naphtalene. In such a reactor a thin layer of catalyst is coated on the inner surface of a metal tube and hence the heat is produced at the wall where it can be efficiently removed. In the conventional fixed-bed catalytic reactor it is sometimes difficult to remove heat from the interior of the bed and so, to retain temperature control, the inlet concentration of the reacting gas has to be reduced. A summary of the advantages of catalytic-wall reactors over fixed-bed reactors has been given in review articles by Smith et al. [1] and Carberry [2]. These advantages include greater efficiency of catalytic use. The interior of the catalytic-wall reactor may be empty, as in the monolith converter used in car exhausts, or filled with inert beads to increase mixing. In this latter case, however, there may be an unacceptable pressure drop (Boersma et al. [3]). We shall consider the case where the tube is empty, at least in the inlet region.

In an ideal situation the operation is isothermal, so that the catalytic surface is used uniformly, but this is not always possible since 'hot spots' may occur on the metal wall where the unreacted gas first comes into contact with the catalyst. Such hot spots are undesirable since they lead to local degradation of the catalyst and may also trigger off some unwanted reaction. It is therefore important to know the temperature rise in such a hot spot and its spatial extent. These quantities will be determined by two main factors, (1) the rate of production of heat at the wall and (2) the efficiency with which heat can be removed through the metal wall. The key factor in (1) is the mass transfer to the wall which is influenced by the local gas-velocity field. In a previous paper [4], we found the wall-temperature distribution when a fully developed Poiseuille flow passed over a catalytic coating. In this paper we use a very similar method to determine the wall-temperature profile in an inlet region where the flow is of Blasius type. In this latter case the mass transfer to the wall is more efficient and consequently a greater temperature rise occurs. For our parameters the temperature rise for the developing flow is about two and a half times the temperature rise for the fully developed case. In the special case of an infinite reaction rate the wall-temperature profile has a universal form and an explicit formula for the temperature rise is derived.

The inlet hot-spot temperature profile is important because in practice the whole of the inner surface of the tube wall will be coated. Moreover if the coating was absent in the entry-length region, approximately 30 cms in our case, this length of reactor would essentially be wasted.

The efficiency with which heat can be removed depends on the thickness of the metal wall and the efficiency of the heat-transfer mechanism on the outer surface of the reactor. We shall assume here that the outer surface has a constant temperature which corresponds to the most efficient heat-transfer mechanism.

The study was motivated by experimental investigations carried out at Imperial Chemical Industries, Runcorn, U.K.

2. The mathematical model

We consider the steady flow of a single reacting gas with concentration C_0 and temperature T_0 into a tube of internal radius a. The metal wall of the tube is of thickness l. We shall assume that $l \ll a$ so that we can use local plane geometry. The coordinate x is measured along the pipe and entry-flow region starts at $x = 0$. The coordinate y is measured from the gas/metal interface. We assume that the gas velocity is u_0 at $x = 0$, where u_0 is a constant. The outer surface of the tube is maintained at a constant temperature T_0 as is the 'leading edge' surface $x = 0$.

We scale the x-coordinate with respect to l, the y-coordinate with respect to $l\,\mathrm{Re}^{-1/2}$ (where $\mathrm{Re} = lu_0/\nu$ is a Reynolds number for the flow and ν is the viscosity) and the x-component of velocity with respect to u_0. Then the boundary-layer equations governing the gas flow in the entry region may be written in the standard dimensionless form

$$u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = \frac{\partial^2 u}{\partial y^2}\,, \tag{1}$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0\,, \tag{2}$$

where $u = 1$ at $x = 0$, $y > 0$; $u \to 1$ as $y \to \infty$, $x > 0$ and $u = v = 0$ on $y = 0$, $x > 0$. The solution of these equations gives the Blasius profile [5], for which the stream function is

$$\psi(x, y) = x^{1/2}F(y/x^{1/2})\,. \tag{3}$$

The corresponding velocity components in the x- and y-directions are given by

$$u = \frac{\partial\psi}{\partial y}\,, \qquad v = -\frac{\partial\psi}{\partial x}\,. \tag{4}$$

The function $F(y/x^{1/2})$ is tabulated in Schlichting [5] and in particular, near $y = 0$, $u(x, y)$ and $\psi(x, y)$ may be written in the approximate form

$$u(x, y) = \gamma y / x^{1/2}, \qquad \psi(x, y) = \gamma y^2 / 2x^{1/2}, \tag{5}$$

where $\gamma = 0.33$. This approximate result will be used later, when we use the Lighthill method [6] to estimate the mass transfer at the wall.

The equation governing the gas concentration in the concentration boundary layer on $y = 0$ can be written in the dimensionless form

$$u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = \frac{1}{\mathrm{Sc}} \frac{\partial^2 c}{\partial y^2}, \tag{6}$$

where $\mathrm{Sc} = \nu / D$ is the Schmidt number. Here D is the diffusion coefficient and c is the gas concentration scaled on C_0. The boundary conditions to be satisfied by $c(x, y)$ are

$$\begin{aligned} &c = 1, \quad x = 0, \quad y > 0, \\ &c \to 1, \quad y \to \infty, \quad x > 0, \\ &\frac{\partial c}{\partial y} = \mathrm{Re}^{-1/2} \Lambda(T_w) c \quad \text{on} \quad y = 0, \quad x \geqslant 0, \end{aligned} \tag{7}$$

where $T_w(x)$ is the unknown wall temperature. The third equation in (7) expresses the condition that the mass flux of gas at the wall equals the rate of reaction at the wall. We have assumed a first-order reaction. The temperature dependence of the rate of reaction is determined by an Arrhenius factor so that

$$\Lambda(T) = \lambda_0 \exp\left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right], \tag{8}$$

where E is the activation energy, R is the gas constant and $\Lambda = \lambda_0$ when $T = T_0$. Here T_0 is the absolute temperature of the outer surface of the metal tube. Note that if r_0 is the true dimensional reaction rate at temperature T_0, with dimension LT^{-1}, then $\lambda_0 = l r_0 / D$. In practice r_0 is given, so this equation determines λ_0.

It is convenient to introduce a dimensionless temperature θ defined by

$$\theta = \frac{E}{R T_0^2} (T - T_0), \tag{9}$$

so that $\Lambda(T_w)$ in (7) is replaced by

$$\lambda(\theta_w) = \lambda_0 \exp\left[\frac{\theta_w}{1 + \varepsilon \theta_w} \right], \tag{10}$$

where $\varepsilon = R T_0 / E$ and $\theta_w(x)$ is the dimensionless temperature at the gas/metal interface $y = 0$.

If we regard $\theta_w(x)$ as given, then (6), (7) can be solved to determine $c(x, y)$ and the mass flux at the wall. A good approximation to the mass flux at the wall may be obtained by using the Lighthill method [6]. In this method, first developed for the analogous heat-transfer problem, the near-wall velocity field is used in (6) rather than the complete Blasius profile. The error in this method is less than three percent if $\mathrm{Sc} \geqslant 0.7$. If we use x and ψ as independent variables, then equation (6) can be written in the Von Mises form

$$\frac{\partial c}{\partial x} = \frac{1}{\mathrm{Sc}} \frac{\partial}{\partial \psi}\left(u \frac{\partial c}{\partial \psi}\right). \tag{11}$$

Using the forms for u and ψ close to the wall given in (5), equation (11) becomes

$$\frac{\partial c}{\partial x} = \frac{1}{\mathrm{Sc}}\left(\frac{2\gamma}{\sqrt{x}}\right)^{1/2} \frac{\partial}{\partial \psi}\left(\psi^{1/2} \frac{\partial c}{\partial \psi}\right). \tag{12}$$

If we introduce the new variables $\xi = \sqrt{2\gamma}\, x^{3/4}/3\,\mathrm{Sc}$, $\eta = \psi^{1/2}$, equation (12) takes the simple form

$$\eta \frac{\partial c}{\partial \xi} = \frac{\partial^2 c}{\partial \eta^2}. \tag{13}$$

The boundary conditions (7) become

$$\begin{aligned} &c = 1, \quad \xi = 0, \quad \eta > 0, \\ &c \to 1, \quad \eta \to \infty, \quad \xi \geqslant 0, \\ &\frac{\partial c}{\partial \eta} = \left(\frac{6\xi\,\mathrm{Sc}}{\gamma^2}\right)^{1/3} \mathrm{Re}^{-1/2} \lambda(\theta_w(\xi))c, \quad \eta = 0. \end{aligned} \tag{14}$$

The boundary-value problem can now be formally solved in terms of an integral equation. If we introduce the Laplace transform

$$\bar{c}(p,\eta) = \int_0^\infty c(\xi,\eta)\,\mathrm{e}^{-p\xi}\,\mathrm{d}\xi, \tag{15}$$

then (13) becomes

$$\frac{\mathrm{d}^2\bar{c}}{\mathrm{d}\eta^2} = \eta(p\bar{c} - 1).$$

The solution which satisfies the first two boundary conditions in (14) may be written in the form

$$\bar{c}(p,\eta) = \frac{1}{p} + \frac{1}{p^{1/3}} \frac{\mathrm{d}\bar{c}}{\mathrm{d}\eta}(p,0) \frac{\mathrm{Ai}(\xi p^{1/3})}{\mathrm{Ai}'(0)}, \tag{16}$$

where Ai is the Airy function and Ai′ is its derivative. We now apply this result on $\eta = 0$ and, using the convolution theorem, obtain

$$c(\xi,0) = 1 - \frac{1}{\Gamma(\frac{1}{3})3^{1/3}} \int_0^\xi (\xi' - \xi)^{-2/3} \frac{\partial c}{\partial \eta}(\xi,0)\,\mathrm{d}\xi'. \tag{17}$$

Returning to the original dimensionless x, y variables, and using (7) to eliminate $c(x,0)$ in favour of $\partial c/\partial y$ on $y = 0$, we obtain

$$\frac{f(x)\,\mathrm{Re}^{1/2}}{\lambda(\theta_w(x))} = 1 - \frac{1}{\Gamma(\frac{2}{3})}\left(\frac{3}{16\gamma\,\mathrm{Sc}}\right)^{1/3} \int_0^x f(s)(x^{3/4} - s^{3/4})^{-2/3}\,\mathrm{d}s, \tag{18}$$

where $f(x) = (\partial c/\partial y)_{y=0}$ is the dimensionless diffusive mass flux at the wall. Equation (18) is a weakly-singular Volterra integral equation of the second kind for the function $f(x)$ given $\theta_w(x)$.

To determine a second relationship between $\theta_w(x)$ and $f(x)$ we need to examine the temperature field in the metal produced by the heating at the gas/metal interface $y = 0$. The exact condition which holds at this interface is that the jump in heat flux there equals the rate of production of heat due to the chemical reaction. However, the conductivity of the metal K exceeds the conductivity of the gas k by a factor of order 400 and consequently we expect that most of the heat generated will flow into the metal. This approximation can be checked afterwards.

The temperature in the metal wall satisfies the equation

$$\frac{\partial^2\theta}{\partial X^2} + \frac{\partial^2\theta}{\partial Y^2} = 0\,, \tag{19}$$

where $X = x$ and $Y = y\,\mathrm{Re}^{1/2}$. Note that Y is found by scaling the real physical coordinate perpendicular to the wall with respect to l.

If the heat transfer into the gas is neglected compared with that into the wall then the flux of heat into the metal equals q times the mass flux at the wall, where q is the heat of reaction. Then the boundary conditions on $\theta(X, Y)$ are

$$\begin{aligned}
&\frac{\partial\theta}{\partial Y} = Q\,\mathrm{Re}^{1/2} f(x)\,, && Y = 0\,, && X > 0\,, \\
&\theta = 0\,, && Y = -1\,, && X > 0\,, \\
&\theta \to 0\,, && X \to \infty\,, && -1 \leq Y \leq 0\,, \\
&\theta = 0\,, && X = 0\,, && -1 \leq Y \leq 0\,,
\end{aligned} \tag{20}$$

where $Q = qDC_0E/KRT_0^2$, and q is the heat of reaction. The parameter Q is therefore a measure of the strength of the heating effect of the chemical reaction. The last boundary condition in (20) assumes that the 'leading edge' of the tube is maintained at a temperature T_0.

The solution for $\theta(X, Y)$ is

$$\theta(X, Y) = \frac{Q\,\mathrm{Re}^{1/2}}{2\pi}\int_0^\infty f(X')\{G(X' - X, Y) - G(X' + X, Y)\}\,\mathrm{d}X'\,, \tag{21}$$

where

$$G(X, Y) = \mathrm{Real}\left\{\ln\coth^2\left(\frac{\pi}{4}\,(X + \mathrm{i}Y)\right)\right\}. \tag{22}$$

Thus, in particular on $Y = 0$,

$$\theta_w(X) = \frac{Q\,\mathrm{Re}^{1/2}}{2\pi}\int_0^\infty f(X')\ln\left\{\frac{\coth^2\frac{\pi}{4}\,(X' - X)}{\coth^2\frac{\pi}{4}\,(X' + X)}\right\}\mathrm{d}X'\,. \tag{23}$$

This is an equation for $\theta_w(X)$ given $f(X)$.

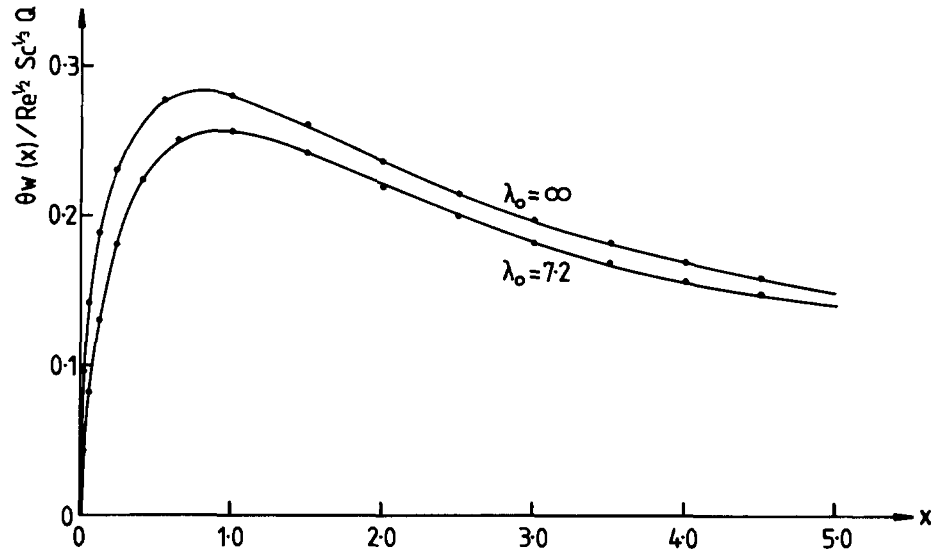

Fig. 1. The graph of $\theta_w(x)/\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/2}Q$ as a function of x for $\lambda_0 = 7.2$ ($\varepsilon = 0.15$, $Q = 0.37$, $\mathrm{Sc} = 0.75$), and $\lambda_0 = \infty$.

We have solved the coupled integral equations (18), (23) numerically, by an iterative technique very similar to that used in [4]. We initially took $\theta_w(x) = 0$, and solved (18) for $f(X)$ (see, for example, Baker [7]). We then formed a new approximation to $\theta_w(x)$ from (23) which was substituted back into (18). Convergence was obtained after about six iterations. The graph of $\theta_w(x)$ for the case $\varepsilon = 0.15$, $\lambda_0 = 7.2$, $Q = 0.37$, $\mathrm{Sc} = 0.75$ and $\mathrm{Re} = 120$ is shown in Fig. 1. These are the parameter values associated with the experiments which motivated this study. The scaling of $\theta_w(x)$ with respect to $Q\,\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3}$ was suggested by the infinite-reaction-rate case, $\lambda_0 \to \infty$, which we discuss next.

3. The solution for an infinite reaction rate

In the case $\lambda_0 \to \infty$ the concentration at the gas/metal interface is zero. The function $f(x)$ can then be determined from the limiting form of (18),

$$\int_0^x f(s)(x^{3/4} - s^{3/4})^{-2/3}\,\mathrm{d}s = \Gamma(\tfrac{1}{3})\left(\frac{16\gamma\,\mathrm{Sc}}{3}\right)^{1/3}, \tag{24}$$

which can be integrated to give

$$f(x) = \frac{\sqrt{3}\,\Gamma(\frac{2}{3})}{2\pi}\left(\frac{9\gamma\,\mathrm{Sc}}{4}\right)^{1/3} x^{-1/2}. \tag{25}$$

Thus the corresponding wall temperature $\theta_w^\infty(x)$ is given by

$$\theta_w^\infty(x) = \frac{\sqrt{3}\,\Gamma(\frac{2}{3})}{4\pi^2}\,Q\,\mathrm{Re}^{1/2}\left(\frac{9\gamma\,\mathrm{Sc}}{4}\right)^{1/3}\int_0^\infty \frac{1}{\sqrt{x'}}\ln\left\{\frac{\coth^2\left(\frac{\pi}{4}(X'-x)\right)}{\coth^2\left(\frac{\pi}{4}(X'+x)\right)}\right\}\mathrm{d}X' \tag{26}$$

This expression shows that for an infinite reaction rate the shape of the temperature profile has a universal character and the magnitude of the temperature rise depends only on the single parameter $Q\,\mathrm{Sc}^{1/3}\,\mathrm{Re}^{1/2}$. The graph of $\theta_w^\infty(x)$ is shown in Fig. 1, and shows that, for the numerical values chosen, the results for a finite reaction are very comparable with those for the infinite reaction rate. The numerical results also indicate, as expected, that the highest temperatures will be reached with an infinite reaction rate and the maximum temperature rise will be approximately $0.29Q\,\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3}$.

We note, in conclusion, that this result is based upon the Lighthill approximation valid for $\mathrm{Sc} \geq 0.7$. The validity of this approximation can be tested in the case of infinite reaction rates since (6) has an exact similarity solution and the solution of the analogous heat-transfer problem has been widely studied (see Stewartson [8]). Using the results given in [8], with the Prandtl number replaced by the Schmidt number, we find that the ratio of the approximate dimensionless mass flux, given by (25), to the exact mass flux is $1.02/s\,\mathrm{Sc}^{1/3}$ where s, a function of Sc, is the Reynolds analogy factor. This ratio is a slowly varying function of Sc for $\mathrm{Sc} \geq 0.7$. It tends to unity as $\mathrm{Sc} \to \infty$ and is less than 1.04 when $\mathrm{Sc} = 0.6$.

4. Conclusions

We have assumed that the heat transfer into the gas stream is small compared with that into the metal. If δ is the thickness of the thermal boundary layer, this approximation is valid provided that

$$\frac{kl}{K\delta} \ll 1 . \tag{27}$$

where K and k are the metal and gas thermal conductivity, respectively, with $K = 400k$. The thickness of the thermal boundary layer on the gas/metal interface is of order $\delta = l\,\mathrm{Re}^{-1/2}\,\mathrm{Sc}^{1/3}$ if we take the thermal diffusivity α to equal D. For $\mathrm{Re} = 120$ and $\mathrm{Sc} = 0.75$ we deduce that $kl/K\delta = 0.03$, which clearly satisfies (27).

In our previous paper [4] we showed that the maximum temperature rise when a fully developed flow passes over a catalytic coating is, in dimensional terms,

$$(\Delta T)_{FD} = 0.55\,\frac{qDC_0}{K}\left(\frac{u_0 l^2}{aD}\right)^{1/3} . \tag{28}$$

In the case of developing flow, the corresponding result, from Fig. 1, is

$$(\Delta T)_D = 0.29\,\frac{qDC_0}{K}\left(\frac{lu_0}{\nu}\right)^{1/2}\left(\frac{\nu}{D}\right)^{1/3} . \tag{29}$$

The ratio of these temperatures rises is

$$\frac{(\Delta T)_D}{(\Delta T)_{FD}} = 0.53\left(\frac{u_0 a^2}{\nu l}\right)^{1/6} = 2.4 , \tag{30}$$

if, for example, $l = a/8$ and $lu_0/\nu = 120$. Since the reaction rate is often a sensitive function of the temperature this result shows that very fast reactions must be expected in the entry-flow region, with a hot spot of characteristic length l.

References

1. T.G. Smith and J.J. Carberry, Design and Optimization of a tube-wall reactor, *Chem. Eng. Sci.* 30(2) (1975) 221–227.
2. J.J. Carberry, Some aspects of catalytic reactor engineering. *Trans. Inst. Chem. Eng.* 59(2) (1981) 75–82.
3. M.A. Boersma, J.A. Spierts, W.J. van Lith and H.S. van Der Baan, The oxidation of ethane in an empty and packed reactor operating in the reaction and diffusion controlled regimes, *Chem. Eng. J.* (Lausanne) 20(3) (1980) 177–183.
4. J.A. King-Hele and S.A. Thornham, Non-isothermal catalytic wall reactions, *J. Eng. Math.* 17 (1983) 345–353.
5. H. Schlichting, *Boundary layer theory*, McGraw-Hill, New York (1979).
6. M.J. Lighthill, Contributions to the theory of heat transfer through a laminar boundary layer, *Proc. Roy. Soc.* A202 (1950) 359–377.
7. C.T.H. Baker, *The numerical treatment of integral equations*, Clarendon Press, Oxford (1977).
8. K. Stewartson, *The theory of laminar boundary layers in compressible flow*, Oxford Univ. Press (1964) p. 42.