8
Analysis of an Endothermic Reaction in a Packed Column

8.1 Introduction
In 1977 the British Steel Corporation presented a problem to the European Study Groups for Industry, concerning the analysis of a gas-solid reaction in a column packed with solid catalyst pellets. This is an industrial problem of common concern, arising in various kinds of reactor such as a blast furnace. BSC were coy about the details of the reaction involved, but were happy to provide details of relevant physical parameters, essential for any analysis, and this allowed for a fairly thorough study of the problem.

Much of the applied mathematical interest in this type of problem has been motivated by the occurrence of exothermic reactions, i.e. those which release heat, as multiple steady states may exist for such reactions, and the associated phenomenon of thermal runaway can occur. However, the BSC problem concerned an endothermic reaction, one which absorbed heat, and our challenge thus lay in seeking some analytical understanding of the dynamics of the reaction.

The specific problem as summarised by BSC was as follows:
The problem is to solve two simultaneous partial differential equations. Although a method has been found using finite differences, the method is very slow in convergence and the boundary conditions have to be solved by an indirect manner. This is because the boundary conditions are dependent on an external radiative heat transfer problem. It would be very useful if an alternative approach to the problem was available in which the external heat transfer problem and the partial differential equations were formulated as a single problem.

Then, as now, the industry really wanted an efficient numerical code; and then, as now, our approach was directed towards analytical understanding. For a problem as simple as that stated below, it is in fact feasible to provide a good description of the solution analytically; furthermore, a numerical solution requires a certain amount of analytical pre-treatment, to know what time and space steps should be used. In a sense, the challenge that this problem avoids raising, but which is also a suitable case for treatment, is the industrially relevant situation where ten, twenty, or a hundred reactions are going on. If we judge the state of the art by the extant literature (which is very substantial), then we find that much of the modelling and analysis that has been done is limited to the consideration of single-pellet dynamics, and also simple first- or second-order reaction kinetics (for examples of the gas-solid reaction literature, see [1], [3]–[6], [9]–[16], [18]–[22], [24], and [25]). It is thus perhaps a message yet to be realised, that applied analytic techniques can not only facilitate the solution of relatively simple problems such as that here, but are also capable of dealing with more realistic problems of practical concern.

8.2 The Problem and the Model
A cylindrical tube, of typical radius 10 cm and height 8 m, is packed with solid catalyst pellets, which react with a gas stream flowing through the tube. The situation is shown in figure 8.1.

Fig. 8.1. A schematic illustration of the reactor geometry
A first-order reaction occurs between the gas and the solid, and the reaction is endothermic. If the solid pellets are sufficiently small, then the solid pellet temperature \( s \) may be taken to be locally uniform (within each pellet). It is always the case that the pellets are much smaller than the reactor radius, and it is commonly also the case that the pellets are in thermal equilibrium, and at relatively uniform temperature. In the present instance, this is confirmed post hoc by the fact that the macroscopic heat conduction parameter \( \Gamma \) is \( O(1) \).

The gas (at mean temperature \( g \)) supplies heat to the solid through a viscous boundary layer (in the gas, next to the solid surface). For a typical gas velocity of 100 cm s\(^{-1}\), pellet radius 1 cm, and gas viscosity 1 cm\(^2\) s\(^{-1}\) (at reactor temperatures), the particle Reynolds number is 100, so that the flow would be laminar, although the irregular pore space is likely to make it highly unsteady. The Prandtl number of air at elevated temperatures is approximately one, so that the Peclet number is \( \sim 10^2 \), and a thermal boundary layer (slightly thicker than the viscous one) will exist next to the solid surface. It is not in fact essential that these boundary layers exist, since the model below will apply in any case, even if the particle Peclet number is small.

A steady-state model to describe this situation is

\[
\rho_g c_p u \frac{\partial g}{\partial x} - h_v(s - g) = k_g \nabla^2 g,
\]

\[
h_v(s - g) + \mathcal{R} \Delta H = k_s \nabla^2 s,
\]

\[
\frac{\partial c}{\partial x} = -\mathcal{R},
\]

\[
\mathcal{R} = K c e^{-\lambda/s},
\]

wherein \( u \) is the gas flux, \( \rho_g \) the gas density, and \( c_p \) the gas specific heat; \( h_v \) is a heat transfer coefficient (whose size will depend on the particle Reynolds and Peclet numbers), \( k_g \) and \( k_s \) are the effective thermal conductivities of gas and solid, and \( \mathcal{R} \) is the reaction rate, given by (8.1)\({\alpha}\) for a first-order reaction; \( c \) is the gas reactant concentration, and \( \Delta H \) is the heat of reaction absorbed per mole of reactant.

The first two equations represent heat transfer in the gas and solid phases. The terms in the gas temperature equation describe heat advection, interfacial heat transfer, and heat conduction respectively. In the second equation, the heat advection term is neglected on the basis that the solid velocity is negligible, so that heat conduction is balanced by the interfacial heat transfer and also the endothermic heat of reaction \( \mathcal{R} \Delta H \). This term affects the solid temperature because the reaction occurs at the gas–solid interface. Depending on the nature of the pellet, this is either the pellet surface or, if the pellets are porous, the internal surface area. In either event, the heat of reaction is removed from the solid.

The third equation represents the depletion of reactant in the gas stream. The rate of reaction \( \mathcal{R} \) acts as a volume sink for the reactant, while the effect of diffusion can be ignored, being small. The final equation is the Arrhenius term for the rate of a first-order reaction, dependent on the solid (surface) temperature.

A good deal of physics is present in these equations, and we shall have some comments to make concerning the validity of the model in the discussion. For now we focus our attention on the model (8.1), supplemented by boundary conditions as indicated below. The inlet and outlet conditions are controlled by the fast gas flow through the tube. In general, continuity of heat flux across a boundary has two components, due to advective flux and conductive heat transfer. When the advective term is large (as we suppose here), this essentially means that the temperature will be continuous. At the inlet, the gas flow carries in its external temperature, which we therefore consider prescribed, thus

\[
g = s = g_0, \quad c = c_0 \quad \text{on} \quad x = 0,
\]

where in addition we prescribe the entry reactant concentration of the gas stream. At the outlet, the same principle applies, except that the gas carries its temperature out of the tube. In the absence of any external control at the outlet, it is natural to suppose that there is no thermal boundary layer at the outlet, and a mathematically consistent way of ensuring this is to prescribe

\[
\frac{\partial s}{\partial x} = \frac{\partial g}{\partial x} = 0 \quad \text{on} \quad x = L,
\]

although further consideration of the validity of this might be necessary in differing circumstances. In the present case, the outlet conditions will not actually affect the discussion.

Finally, on the wall,

\[
k_g \frac{\partial g}{\partial r} = h_0(T - g),
\]

\[
k_s \frac{\partial s}{\partial r} = \varepsilon_G \sigma (T^4 - s^4).
\]

These Neumann boundary conditions differ in form because it is assumed that heat transfer to the gas from the wall at temperature \( T \) is by thermal conduction, whereas transfer to the solid pellets occurs through radiation; \( \sigma \) is the Stefan–Boltzmann constant and \( \varepsilon_G \) is the emissivity.
We nondimensionalise these equations by writing
\[ g = g_0 + (T - g_0)g^*, \quad s = g_0 + (T - g_0)s^*, \]
\[ x = r_0x^*, \quad r = r_0^*, \quad c = c_0e^*, \]
so that when the exponent is expanded to two terms of its Taylor series, we obtain
\[ e^{-\lambda / s} \approx e^{-\lambda / g_0} e^{\lambda x^*} \]
where
\[ \lambda = \frac{\lambda(T - g_0)}{g_0^2} \]
(Apparently the assumption (8.6) is not supported by the values \( T = 1300 \) K and \( g_0 = 700 \) K, but in fact we later find that \( s^* \approx 1/\Lambda \), so that (8.6) is equivalent to \( g_0 \ll \lambda \), which is valid. The model (8.1) can then be written in the dimensionless form, dropping the asterisks,
\[ \frac{\partial g}{\partial x} - (s - g) = \mu \nabla^2 g, \]
\[ h(s - g) + ce^{\lambda x^*} = \Gamma \nabla^2 s, \]
and the boundary conditions are
\[ c = 1, \quad g = s = 0 \text{ on } x = 0; \]
\[ \frac{\partial g}{\partial x} = \frac{\partial s}{\partial x} = 0 \text{ on } x = 1/\delta; \]
The presence of several small parameters suggests a variety of possible asymptotic limits, but before we proceed to their consideration, we append some comments on the model as supplied by the company.

**Industrial Specification**

The model as presented by BSC was not quite in the above form. The sign of the \( h_v \) term in (8.1) was positive, the mass flow was given as \( M = \rho_x u \), and the reaction equation for \( c \) was absent, with the heat absorption \( R \Delta H \) being given as \( Q = \Lambda e^{-\lambda t/\Lambda} \). Presumably (it was over twenty years ago) the reaction equation for \( c \) was added during the study group, and a relevant value for \( \Delta H \) was then applied. Presumably the gas is air and the gaseous reactant is oxygen (21% by volume). At 400°C, the density of air is about \( 0.5 \times 10^{-3} \) gm cm\(^{-3} \), and with its molecular weight being about 30 (gm mole\(^{-1} \)), this is a molar density of about \( 1.65 \times 10^{-5} \) mole cm\(^{-3} \), and 0.21 of this is \( 0.35 \times 10^{-5} \) mole cm\(^{-3} \), consistent with the supplied value. On the other hand, \( M = \rho_x u \) must be the mass flow rate of air, so that the molar density \( \rho_x \) is about 5c0. If we use the supplied value of \( c_0 \), then we derive \( u \approx 100 \text{ cm s}^{-1} \). In fact, in the original report, a value of \( u \approx 450 \text{ cm s}^{-1} \) was used, which reduces the value of \( \kappa \) by a factor 4.5. Presumably this oversight was due to neglect of what the gaseous reactant actually was.

Another comment worth making is that the heat transfer coefficient \( h_v \) and thermal conductivity \( k_v \) and \( k_g \) should be phase-averaged in some way (the superficial velocity \( u \) (i.e. the volume flux per unit area) is already effectively phase-averaged); no information is available as to whether this was in fact done, although it would only make cosmetic differences to the results.

The other parameters were supplied by BSC, though with some inaccuracies: \( r \) given as \( 1.38 \times 10^{-2} \), mass flow \( M \) as mole cm\(^{-2} \).

### 8.3 Analysis

The original presentation of this problem was concerned, as is often the case, with the numerical solution of the model. The company had not nondimensionalised the model, and one can infer that the nature of their concern was such that the accurate solution of this particular model was perhaps less relevant than a qualitative understanding of how the model ought to be solved. In particular, the choice of a first-order reaction is presumably a gross simplification of the realistic chemistry. In this context, it ought to be pointed out that the inclusion of detailed chemistry is likely to lead to other, faster, reactions with associated short relaxation distances, and this will also cause difficulties in straightforward numerical schemes.

We now proceed to an analysis of the model. The parameter \( \Lambda \) is relatively large, particularly as it is present in an exponent. If we suppose that \( s \) is negative (and \( O(1) \)), then the heat absorption term is exponentially small and negligible. However, there is then no mechanism which can reduce \( s \) to such low values, and this assumption seems unwarranted. In a similar vein, if \( s \) is positive and \( O(1) \), then the exponential term is dominant, suggesting to leading order either that \( c \approx 0 \) (which cannot be valid near the inlet), or that \( s \) is small and negative. And if this is the case, it seems likely that \( g \) also will be small and negative. This provides the motivation to rescale the temperatures to satisfy

\[
  g \sim s \sim \frac{1}{\Lambda},
\]

so that the corresponding dimensional temperature scales are \( \frac{g_0^2}{\lambda} \). Of course we might have scaled this way initially, but it is more illuminating of the solution process to indicate the rescalings as they are discovered.

Adopting (8.15), the (rescaled) model is

\[
  \alpha g_x - (s - g) = \mu \nabla^2 g,
\]

\[
  H(s - g) + \frac{c}{\varepsilon} e^s = \nabla^2 s,
\]

\[
  c_s = -\kappa c e^s,
\]

where

\[
  H = h/\Gamma \sim 2.2, \quad \varepsilon = \Gamma/\Lambda \sim 0.06,
\]

with the side wall conditions being

\[
  \frac{\nu}{\Lambda} \frac{\partial g}{\partial r} = 1 - \frac{g}{\Lambda},
\]

\[
  \frac{\beta}{\Lambda} \frac{\partial s}{\partial r} = 1 - \left( \frac{\beta_1 + \beta_2 x}{\Lambda} \right)^4 \quad \text{on} \quad r = 1,
\]

the other conditions being unaltered.

**Outer Solution**

The parameters \( \alpha, \mu, \) and \( \varepsilon \) are all small, and so we can neglect the corresponding terms in (8.16), an approximation that should be valid away from the boundaries:

\[
  s \approx g \approx \ln \varepsilon + S.
\]
where \( S \) satisfies
\[
\nabla^2 S = ce^S, \tag{8.20}
\]
with boundary conditions to be determined below. The reactant concentration satisfies
\[
c_0 = -\varepsilon \ln e^{-c} = c e^S, \tag{8.21}
\]
and suggests that the relevant length scale for the reaction is \( x \sim 1/\varepsilon \kappa \).

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Suppose, for simplicity, that in fact \( c \approx c(x) \). Then
\[
S \approx \frac{8}{c} - 2 \ln(1 - r^2). \tag{8.29}
\]
Thus, in the variables scaled by \( \beta_0^2/\lambda \approx 70 \text{ K} \), the centre line (minimum) temperature is
\[
s \approx \ln \left[ 8 \varepsilon / c \right]. \tag{8.30}
\]
while the solid temperature at the wall is
\[
s_0 \approx \ln \left[ \frac{\varepsilon \Lambda^2 (1 - \beta_1^2)^2}{2c \beta^2} \right]. \tag{8.31}
\]

Gas Temperature Boundary Layer

Evidently, the assumption \( \varepsilon \ll 1 \) is hardly relevant to the above solution, since \( S \) can be found \((c = c(x))\) explicitly. For the gas thermal boundary layer we put
\[
r = 1 - \sqrt[4]{\mu} \eta, \tag{8.32}
\]
and if \( \sqrt[4]{\mu} \ll \sqrt[4]{\varepsilon} \), then \( s \approx s_0 \) and to satisfy the approximate condition
\[
- \frac{\gamma}{\Lambda \sqrt[4]{\mu}} s_0 \approx 1, \tag{8.33}
\]
we have
\[
g \approx s_0 + \frac{\Lambda \sqrt[4]{\mu}}{\gamma} e^{-\eta}, \tag{8.34}
\]
while the gas temperature at the wall is
\[
g_0 \approx s_0 + \frac{\Lambda \sqrt[4]{\mu}}{\gamma}. \tag{8.35}
\]

Inlet Boundary Layers

We omit details. There will be an adjustment layer for \( s \) of thickness \( O(\sqrt[4]{\varepsilon}) \) and a thinner layer for \( g \) of thickness \( \sqrt[4]{\mu} \) (since \( \sqrt[4]{\mu} \gg \alpha \)). In addition, (8.29) becomes valid (if \( c = c(x) \)) for distances \( x \gg 1 \), i.e. beyond the inlet region.
Temperature and Reactant Profiles

From (8.27) and (8.28), we can write a uniform approximation to the particle temperature as

\[ s \approx \ln \frac{8\varepsilon}{c} - 2 \ln \left[ 1 - r^2 + \frac{2\varepsilon}{\nu} \right]. \tag{8.36} \]

and the reactant concentration then satisfies (8.21), with \( s \) given as above. From this we have

\[ c \approx 1 - \frac{8\varepsilon\kappa x}{(1 - r^2 + \frac{2\varepsilon}{\nu})^2}. \tag{8.37} \]

and the reaction zone boundary (where \( c = 0 \)) is given by

\[ x \approx \frac{\left(1 - r^2 + \frac{2\varepsilon}{\nu}\right)^2}{8\varepsilon\kappa}. \tag{8.38} \]

and is shown in figure 8.2. The maximum extent of the reaction zone at the centre line is

\[ x_m \approx \frac{\left(1 + \frac{2\varepsilon}{\nu}\right)^2}{8\varepsilon\kappa}. \tag{8.39} \]

Similarly, a uniform expansion for the dimensionless gas temperature is

\[ g \approx s + \frac{\Lambda \sqrt{\mu}}{\gamma} \exp \left[ -\frac{(1 - r)}{\sqrt{\mu}} \right]. \tag{8.40} \]

Figure 8.3 shows the cross-sectional profiles of the solid temperature given by (8.36) and (8.37) at various values of \( x \). The core temperature varies slowly with \( x \), while the solid warms up at the wall as the reaction proceeds. After the reaction front leaves the wall at \( x \approx 1.4 \), the core temperature begins to increase as the reactive core shrinks towards the centre. Figure 8.4 compares gas and solid temperatures given by (8.36), (8.37) and (8.40) at \( x = 0.2 \) near the tube inlet. The temperatures are the same in the core, but the gas has a hot boundary layer at the tube wall due to its relatively low thermal conductivity (as indicated by the low value of \( \mu \)).

It is apparent that the solution for \( s \) becomes invalid if \( c \to 0 \) at the wall, since \( s \) must be bounded (by \( \Lambda \)) there, in contrast to (8.31), which indicates \( s_0 \to \infty \) as \( c \to 0 \). At the wall, (8.37) implies that \( c = c_0 \) satisfies

\[ c_0 \approx 1 - 2\nu^2\kappa x. \tag{8.41} \]

with a termination front at \( x_0 = 1/2\nu^2x \). Beyond the reaction front, we can expect a dead zone where \( c = 0 \), and in fact we see that the approximation for \( s \) is invalid for \( x \gg 1 \), both because (8.37) implies \( c \) depends on \( r \), and also because of the dead zone. Despite this, we might expect the general characteristics of the reaction zone to be similar to that described here; that is to say, a central reactive core of inverted paraboloidal shape (as in figure 8.2) in which the gas and solid temperatures are depressed.

Reaction Front

The preceding analysis with \( c = c(x) \) is inaccurate at large \( x \) but suggestive of the existence of a well-defined front at \( r = r_f(x) \), say. If we now suppose...
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c = c(x, r), then the problem we have to solve in r < r_f for s and c is

\[
\frac{c}{\varepsilon} \frac{d^2 c}{dr^2} = \frac{1}{r} s_r + \frac{1}{r} s_x + s_{xx},
\]

\[c_x = -\kappa c e^\xi,\]  
(8.42)

with \(c = 1\) on \(x = 0\), and

\[\frac{\partial s}{\partial r} \approx \frac{\nu}{\sqrt{\varepsilon}} \text{ on } r = 1.
\]
(8.43)

The solution with \(c = c(x)\) is in fact valid so long as \(\varepsilon k x \ll 1\), and in particular while \(c_0\) (on the wall, see (8.41)) is greater than zero, i.e. \(x < x_0 = 1/2\nu^2k\). For \(x > x_0\), we suppose that \(c = 0\) in \(r > r_f\), so that

\[s = s_0 + \frac{\nu}{\sqrt{\varepsilon}} \ln r, \quad r > r_f,
\]
(8.44)

and the problem to determine \(r_f\) and \(s_0\) is found from the solution for \(S\)

\[c e^\xi = S_r + \frac{1}{r} S_x,
\]

\[c_x = -\varepsilon k c e^\xi,
\]
(8.45)

with

\[c = 1 \text{ on } x = 0, \quad c = 0 \text{ and } S_x = \frac{\nu}{\sqrt{\varepsilon} r_f} \text{ on } r = r_f.
\]
(8.46)

It is straightforward to solve this problem numerically. Although \(\nu/\sqrt{\varepsilon} \approx 3\)
is hardly large, it is useful to take the limit \(\sqrt{\varepsilon} \ll 1\) seriously. In this case, a genuine reaction front exists. We revert to the variable \(s\), and put

\[r = r_f - \sqrt{\varepsilon} R
\]
(8.47)

(cf. (8.23)), so that, to leading order,

\[s_{RR} \approx c e^\xi,
\]

\[\rho c R \approx c e^\xi,
\]
(8.48)

where we define

\[r_f' \approx -\kappa \sqrt{\varepsilon} \rho \ll 1.
\]
(8.49)
Thus the reaction zone will be of length \( O(1/\kappa \sqrt{\varepsilon}) \) in this case, and we can take \( c \approx 1 \) in \( r < r_f \), so that suitable boundary conditions for matching purposes are

\[
s \sim s^* - \frac{v}{r_f} \quad c \to 0 \quad \text{as} \quad R \to -\infty;
\]

\[
s_R \to 0, \quad c \to 1 \quad \text{as} \quad R \to +\infty;
\]

(8.50)

here (cf. (8.44))

\[
s^* = s_0 + \frac{v}{\sqrt{\varepsilon}} \ln r_f.
\]

(8.51)

It follows that \( \rho = v/r_f \), and thus from (8.49),

\[
r_f^2 = 1 - 2\kappa \sqrt{\varepsilon} \ln(x - x_0),
\]

(8.52)

where \( x_0 \) is given by \( x_0 = 1/2v^2\kappa \) (see (8.41)), and also

\[
c = 1 + \frac{s_R}{\rho}.
\]

(8.53)

Thus \( s \) satisfies

\[
s_{RR} \approx \left(1 + \frac{s_R}{\rho}\right) e^s,
\]

(8.54)

with first integral

\[
s_R - \rho \ln \left(1 + \frac{s_R}{\rho}\right) = \frac{1}{\rho} e^s;
\]

(8.55)

the constant of integration has been chosen uniquely so that a monotone decreasing trajectory exists with \( s_R \to 0 \) as \( R \to +\infty \). The solution of (8.54) can be written parametrically as

\[
s = 2\ln \rho + \ln[\xi - 1 + e^{-\xi}],
\]

\[
R = \frac{1}{\rho} \int_{\xi}^{K} \frac{du}{u - 1 + e^{-u}},
\]

(8.56)

where \( \xi > 0 \), and the value of \( K \) simply fixes the origin. For example, if we choose \( c = \frac{1}{2} \) at \( R = 0 \), then \( K = \ln 2 \). The value of \( s_0 \) is then fixed via (8.50), together with the behaviour of (8.55) as \( R \to -\infty \) (\( \xi \to -\infty \)); we find

\[
s_0 = \frac{v}{\sqrt{\varepsilon}} \ln \frac{1}{r_f} + \ln K + 2 \ln \frac{v}{r_f} - \int_{-\infty}^{0} \frac{(1 - e^{-u})du}{u(u - 1 + e^{-u})},
\]

(8.57)

so the wall temperature increases as the reacting core shrinks.

8.4 Discussion

In \( r < r_f \), \( S = s - \ln \varepsilon \) then satisfies (with \( c \approx 1 \))

\[
S_{rr} + \frac{1}{r} S_r = e^S
\]

(8.58)

as before, with the matching condition obtained from (8.54),

\[
S \sim \ln 2 - 2 \ln(r_f - r) \quad \text{as} \quad r \to r_f.
\]

(8.59)

with solution

\[
S = \ln \left[ \frac{8r_f^2}{(r_f^2 - r^2)^2} \right].
\]

(8.60)

8.4 Discussion

This basically concludes the analysis. We now have a good idea of how the solution behaves. There is a detailed reactive core of dimensional length (from (8.51)) \( \approx (2\kappa \varepsilon \sqrt{\varepsilon})^{-1}c_0 \). Ignoring \( \beta_1 \ll 1 \), this is

\[
x_c \approx \frac{\beta c_0}{2\kappa \Gamma} = \frac{uc_0 c_0 \Delta H}{2\varepsilon G \sigma T^4}.
\]

(8.61)

There is a preceding attached reactive core of length \( x_a \approx (2v^2\kappa)^{-1}c_0 \); this is

\[
x_a \approx \frac{\beta^2 c_0}{2\kappa \Lambda \Gamma} = \frac{uc_0 c_0 \Delta H}{2\lambda c_0^2 \sigma T^4}.
\]

(8.62)

In the reactive core, the temperature is low, and if the radiative heat flux is high enough (\( v/\varepsilon > 1 \)), i.e. \( \Lambda > \beta \), i.e.

\[
\lambda c_0 \varepsilon G \sigma T^4 \left(\frac{\beta^2 c_0}{2\kappa \Lambda \Gamma} \right) \gg 1,
\]

(8.63)

then the reaction occurs in a thin front.

There are three concluding statements to make concerning the success of this case study. Firstly, it is a good illustration of the efficacy of applied mathematics. In a matter of days, an experienced researcher can essentially solve this problem far beyond the ability of a numerical solution. Numerical solution of this problem is best provided as an illustration and confirmation of the analytic results.

Secondly, did this study answer the question as posed in the introduction? The answer is yes, in passing. One only has to nondimensionalise the equations to realise that the existence of thermal boundary layers at the walls...
8.5 Further Modelling Considerations

The reaction between a gas stream and a solid catalyst pellet is a surface reaction; it may occur at the pellet surface, or within the pellet if it is permeable. The simplest case is the "shrinking unreacted core" model, where the pellet is impermeable, and the heat of reaction is absorbed at the surface; see [23] or [8] for a discussion of this. It is then appropriate to include the heat absorption in the \( s \) equation, as we have done here, together with the macroscopic heat conduction term, since we can assume (since \( \Gamma \sim 1 \)) that the pellets are in local thermal equilibrium.

The choice of the reaction rate \( R \) in (8.1) also omits any consideration of the surface nature of the reaction. In fact the conservation of gas reactant in (8.1) would prescribe the supply from the gas stream to the particles, thus

\[
\frac{\partial c}{\partial x} = -h_c(c - c_s),
\]

where \( h_c \) is a mass transfer coefficient, and \( c_s \) the pellet surface gas concentration. A first-order reaction would then prescribe the reaction rate as

\[
R = K c_s e^{-\lambda/\mu},
\]

and it remains to determine \( c_s \). (More generally \( c_s \) would be replaced by the fraction of adsorbed sites at the surface, but at low values of \( c_s \), this is proportional to \( c_s \), at least for the Langmuir isotherm.)

Finally, the rate of supply must equal the rate of reaction, so that

\[
c_s = \frac{c}{1 + (K/h_c)e^{-\lambda/\mu}}.
\]

In particular, we regain (8.1) if \( h_c \) is large enough; otherwise, the Arrhenius factor is modified.

Further understanding of how the surface reaction term is included requires a discussion of the detailed pellet dynamics. This is discussed in [23], and is lucidly reviewed in [17] and [7]. For the simplest model, the nonporous pellet alluded to above, the reaction causes the pellets to shrink. For complete gasification, or if any resulting ash is removed by spalling, the pellet size is given by the dimensionless radius \( \xi \) (\( = 1 \) initially), and this varies as the reaction proceeds. The volumetric rate of reaction then depends on \( \xi \) (see [8], pp. 195 ff.), and in a steady-state model the time evolution of \( \xi \) is described by an advective evolution equation which incorporates the solids' settling velocity.

The other type of pellet model describes porous pellets. When the pellet is formed from compacted grains, this is also referred to as a grain model. Following [8], the dimensionless temperature and concentration fields in a porous (compacted grain) pellet can be written in the form

\[
\theta_t = \nabla^2 \theta - \beta r,
\]

\[
c_t = \frac{1}{Le} \nabla^2 c - \mu r,
\]

where the length scale is the pellet radius. If we realistically assume \( \mu \ll 1 \), then the pellet temperature \( \theta \) is quasi-steady; and if also \( \beta \ll 1 \), then the pellets are isothermal. In this case, the evolution of the reaction in the pellet can be described through the reactant equations

\[
\frac{\partial c}{\partial \tau} = \frac{1}{\phi^2} \nabla^2 c - c \xi \tau^{-1} H(\xi),
\]

\[
\frac{\partial \xi}{\partial \tau} = -c H(\xi)
\]

for a first-order reaction. The pellet temperature is normalised to zero here. In these equations, \( \xi \) is the (dimensionless) grain (not pellet) radius, \( H(\xi) \) is the Heaviside step function, \( \delta = c_s/\rho_s \) is the ratio of gas molar concentration to solid molar concentration, \( \tau = \delta \mu t \), and \( \phi = (\mu Le)^{1/2} \) is the Thiele modulus.
The exponent $F_g$ represents grain shape, being equal to 1, 2, or 3 for plates, cylinders, or spheres respectively.

Realistically, $\delta \ll 1$, and the time derivative of $c$ can be ignored (the quasi-static assumption). In general, solutions must be numerical, but analytic results are possible for large or small Thiele modulus. If $\phi \ll 1$ (chemical control), the reactant concentration is uniform in the pellet, and reaction proceeds uniformly throughout. More interesting mathematically is the diffusion-controlled limit $\phi \gg 1$, when a reaction front moves into the pellet (see below).

Many other aspects of the modelling may be considered as exercises. For example:

- Why does the fact that $\Gamma \sim 1$ imply that we can assume that pellets are in thermal quasi-equilibrium?
- Follow the discussion in [8] to modify the model (8.1) to allow for shrinking nonporous pellets, and examine the effect of this modification on the analysis presented here.
- Use the discussion in [8] (pp. 190 ff.) and [23] (pp. 133 ff.) to derive (8.68). For the quasi-static chemically controlled pellet, derive the appropriate form of the heat sink term in (8.1).
- Show that for the quasi-static diffusionally controlled pellet with spherical grains ($F_g = 3$), a reaction front at $r = r_f$, which separates a reacted fringe ($\xi = 0$) from an unreacted core ($c \approx 0$, $\xi \approx 1$), moves into the pellet at a rate

$$\dot{r}_f \approx -\frac{3}{\phi^2 r_f (1 - r_f)}.$$

Deduce the corresponding form of the heat sink term in (8.1).

References


Analysis of an Endothermic Reaction in a Packed Column


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