LETTERS TO THE EDITOR

To the Editor:

With reference to the journal review "Coal Devolatilization and Hydrogasification" by D. B. Anthony and J. B. Howard [*AIChE J.*, 22, 625 (1976)], Table 6, reporting the composition of gas products has interchanged the percentage of CH_4 and H_2, as reported by Loison and Chauvin (1964). This error has been repeated for all three coals reported.

Consequently, the conclusion drawn in the third paragraph of page 637 based on Table 6, which says "Methane is a major constituent in all cases, while carbon oxides and hydrogen account for most of the rest" is erroneous. In fact, further experiments by other workers have never shown methane as a major product of devolatilization, for conditions similar to those reported in the paper.

N. S. Subramanian
Chemical Engineering Department
West Virginia University

Reply:

The H_2 and CH_4 data of Loison and Chauvin were unfortunately interchanged in our table. However, our discussion was based on the original data, and our conclusion stands correct as we stated it, namely, CH_4 is a major constituent of the pyrolysis gases in all cases presented in our Table 6.

This conclusion is not equivalent to the version implied by Subramanian, who apparently equates relative importance as a constituent of the gases with relative importance as a pyrolysis product. As can be seen from our Tables 5 and 6, methane can be as much as 50% by volume of the gases, and hence a major constituent of the gases, and at the same time be only a few percent by weight of the original coal.

Jack B. Howard
Department of Chemical Engineering
Massachusetts Institute of Technology

To the Editor:

Liaw et al. (*AIChE J.*, 25, 376, 1979) present an approximate result for the analytical solution obtained by Rosen (1952, 1954). Rosen's solution describes the kinetics of a fixed-bed adsorber in response to a step change in feed concentration for a linear equilibrium system having mass transfer resistance in both the mobile and stationary phases. It is in the form of a semi-infinite integral which converges rather slowly and his technique for obtaining numerical values is difficult to apply.

Stuart and Camp (1967) provide a method of numerically evaluating Rosen's integral solution for any desired parameter values to any accuracy chosen. The key to its efficiency is the manner of placing an upper bound on the truncation error. Rosen's entire table of 279 values was checked without excessive computer time. Given the decrease in the cost of computer calculations over the last decade, it seems unnecessary to substitute an approximate method which appears to involve a similar amount of computation.

Liaw et al. show increasing agreement with Rosen's results as the bed length parameter increases. They argue that the "shallow beds" for which their method shows appreciable deviations from the exact values "are not likely encountered in real adsorber operation and design." In my present affiliation with a supplier of adsorbent beads, I am sympathetic to the suggestion that "shallow" beds should not be encountered in industrial adsorbers. However, it must be conceded that at some point smaller beds with more frequent regeneration are more economical. Furthermore, it should be noted that the dimensionless bed length parameter involves an interplay between particle size, effective diffusivity, adsorption equilibrium constant, bed porosity, and fluid velocity as well as bed length. Therefore, a small dimensionless number does not necessarily correspond to a physically shallow bed.

Finally, it seems appropriate to note that solutions for fixed-bed adsorbers having mass transfer resistance in the fluid phase, diffusional resistance in the stationary phase and various non-linear equilibrium systems have been developed (Stuart 1967, Brecher 1967, Stuart and Camp 1973).

D. T. Camp
Dow Chemical Company
Midland, Michigan

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Reply:

Camp is right in pointing out that a small dimensionless number does not necessarily correspond to a physically shallow bed. As a result of the interplay between particle size, effective diffusivity, etc. a small bed length parameter may actually correspond to a realistic bed length.

It is interesting to observe in this connection the behavior of our solution at $\theta = 0$, corresponding to $Y/Z = 0$ in our figures. This is the time that the step input function would arrive at a fixed point in the bed, if there were no adsorption. The figures show that u moves higher up at smaller values of Z. The same observation can be made from our Eq. (33) upon setting $\Theta = 0$. Indeed then $u = e^{x}$. For a shallow bed of zero depth, $X \rightarrow 0$ and $u \rightarrow 1$, i.e. the stream exiting at the inlet concentration. For non-zero but small x there can be a finite stream concentration at $\theta = 0$. These characteristics of shallow beds are correctly reproduced in our solution.

R. A. GREENKORN and
K. C. CHAO
School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907

To the Editor:

Liaw, Wang, Greenkorn and Chao (*AIChE Jour.*, **25**, 376, 1979) are to be congratulated on reducing the complexity of Rosen's exact solution to the problem of fixed bed sorption in the presence of film and particle resistances. However, I am surprised the authors did not recognize that their Laplace transform result has an exact inversion which is tabulated in the literature (i.e. the Brinkley function, Perry (1963)).

Beginning with the authors' equation (27) and using their symbols:

$$U(s,x) = \frac{1}{s} \exp\left[- Kx \frac{s}{1 + \xi s} \right] \tag{1}$$

we rearrange this Laplace transform to read

$$U = \frac{1}{s} \exp\left[- \frac{\zeta s}{s + b} \right] \tag{2}$$

with $b = 1/\xi$ and $\zeta = Kx/\xi$.
We note that

$$\exp\left(- \frac{\zeta s}{s + b} \right) = 1 - \left(\frac{s}{s + b} \right) \int_0^{\zeta} \exp\left(- \frac{s}{s + b} \eta \right) d\eta \tag{3}$$

therefore (2) becomes

$$U = \frac{1}{s} \left[1 - \left(\frac{s}{s + b} \right) \int_0^{\zeta} \exp\left(- \frac{s}{s + b} \right) \eta \, d\eta \right] \tag{4}$$

This is nearly ready to invert in terms of tabulated functions if one notes that

$$\frac{s}{s + b} = 1 - \frac{b}{s + b} \tag{5}$$

and uses this in equation (4), to give:

$$U = \frac{1}{s} - \int_0^{\zeta} \exp(-\eta) \frac{\exp\left(\dfrac{b\eta}{s + b} \right)}{s + b} d\eta \tag{6}$$

This is a well-known result and can be inverted quite easily by noting that

$$L^{-1} \frac{1}{s} \exp(k/s) = I_0(\sqrt{4k\theta}) \tag{7}$$

and this along with the shifting theorem

$$L^{-1} f(s + b) = e^{-b\theta} f(\theta) \tag{8}$$

gives the final solution

$$u(\theta,\zeta) = 1 - \int_0^{\zeta} \exp(-\eta - b\theta) I_0(\sqrt{4b\eta\theta}) \, d\eta \tag{9}$$

This tabulated function can be expressed using the authors' symbols as:

$$u(\theta,x) = 1 - \int_0^{\frac{Kx}{\xi}} \exp(-\eta - \theta/\xi) I_0(\sqrt{4\eta \, \theta/\xi}) \, d\eta \tag{10}$$

This result, expressed as the J function, is presented graphically in Perry (1963) as

$$J(s,\tau) = 1 - \int_0^{s} e^{-\tau-\beta} I_o(\sqrt{4\tau\beta}) \, d\beta \tag{11}$$

for a wide range of independent variables; here we note the equivalence $s = Kx/\xi$ and $\tau = \theta/\xi$. This result is easily adapted to computer applications by using a simple integration routine along with a polynomial representation of the Bessel function. An approximation to the J function has been reported by Thomas (1948)

$$J(s,\tau) \approx \tfrac{1}{2}\left[1 - \operatorname{erf}(\sqrt{s} - \sqrt{\tau}) + \frac{\exp[- (\sqrt{s} - \sqrt{\tau})^2]}{\pi(\sqrt{\tau} - \sqrt[4]{s\tau})} \right] \tag{13}$$

The last term can be dropped when $\sqrt{s\tau} \geqslant 60$ which is the simple Klinkenberg approximation (1948).

We note in passing the above result was originally reported for the analogous heat transfer problem by Anzelius (1926) and is a well-known classical solution to the packed bed sorption problem when the only dissipative force is film resistance. It is demonstrated here that the classical result can be used to account for both film and intraparticle diffusive resistances by summing the two according to the formula of Liaw et al.

$$\xi = R\left(\frac{K}{3k} + \frac{R}{15D} \right) \tag{14}$$

This would seem to be a very practical and easily implemented result.

R. G. RICE
University of Queensland
Department of Chemical Engineering
St. Lucia, Queensland, Australia

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NOTATION

b = $1/\xi$
C_0 = inlet fluid concentration
D = effective particle diffusivity
k = mass transfer coefficient
K = linear adsorption equilibrium constant, q/C^*
R = particle radius
t = time
u = C/C_0, dimensionless fluid concentration
U = Laplace transform of u
v = interstitial velocity
x = $z/\eta v$
z = local bed length

Greek

ϵ = void fraction
ζ = Kx/ξ
η = $\epsilon/1 - \epsilon$, also used as dummy integration variable
θ = $t - z/v$, relative time
ξ = $R(K/3k + R/15D)$

Reply:

It is gratifying to see our results extended by Rice leading to a closed solution, and an approximate solution. These solutions are known to apply to systems of no mass transfer resistance in the solid, and are discussed in a number of books, for instance, by Aris and Amundson (1973), who also gave some other forms of solution. As pointed out by Rice, the combination of the film and intraparticle resistances suggested in our notes makes possible the extended use of the classical closed solutions.

We should, nevertheless, point out that Equation (33) of our notes remains the most efficient working formula for obtaining a numerical solution. It is implemented with a few FORTRAN statements and the convergence is established. In view of the above discussion it is indeed also the most efficient implementation of the classical solution to solids of no mass transfer resistance.

R. A. GREENKORN and
K. C. CHAO
School of Chemical Engineering
Purdue University
West Lafayette, IN 47907

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