Contact Time Distributions in a Large Fluidized Bed

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Fluidized-bed chemical reactors have found many applications in the chemical and petroleum industries, perhaps the most important being catalytic cracking. Such reaction systems have been the focus of considerable research, and numerous mathematical models have been proposed to describe reactor performance and fluidized-bed behavior. Beginning with the pioneering work of Gilliland and Mason (1952), residence time measurements using inert (nonadsorbed) tracers have been used to analyze the general flow patterns in fluidized beds. It soon became apparent, however, that inert tracer experiments have little bearing on the yield of a heterogeneous reaction catalyzed by fluidized particles. Orcutt et al. (1962) introduced the concept of contact time as a measure of the time reactant molecules spent on the catalyst surface in an adsorbed state. Nauman and Collinge (1968a,b) refined the concept of contact time distribution and showed it to be the exact heterogeneous analogue of the residence time distribution. They also developed a method of measuring the contact time distribution using adsorbable tracers. These researchers and, later, Doheim and Collinge (1980) used this technique to measure contact time distributions in a 0.14-m-diameter fluidized bed. Orth and Schlugerl (1972) also used adsorbable tracers as an aid to understanding the yield of a heterogeneous reaction but analyzed their data using a specific mixing model, axial dispersion. Adsorbable tracer experiments were carried out on a large, 0.6-m-diameter fluidized bed by Krambeck et al. (1987). They also analyzed their data in terms of the axial dispersion model. This work analyzes the same data using the methodology of Nauman and Collinge (1968a,b). In this way, a model-free estimate of the contact time distribution is obtained.

Mobil Research & Development Corp. built a 0.6-m-diameter fluidized bed as a full-scale, cold-flow model for a nominal 100-bbl/d (16-kL/d), methanol-to-gasoline, demonstration plant. The cold-flow model was subjected to a variety of tracer experiments using sulfur hexafluoride as an adsorbable tracer. The extent of adsorption was adjusted by varying the moisture content of the catalyst. The cold-flow reactor and the tracer experiments were discussed in detail by Krambeck et al. (1987).

Theory and Data Analysis

In this section, the theory of Nauman and Collinge (1968) is summarized briefly, as well as a more recent account by Nauman and Buffham (1983).

The contact time distribution is the heterogeneous analogue of the residence time distribution. It can be used to estimate yields for isothermal, heterogeneous reactions in the same way that the residence time distribution can be used to estimate yields for isothermal, homogeneous reactions. For a first-order reaction, a unique prediction of the yield is obtained. For other reaction orders, fairly close bounds on the yield can be obtained using the concepts of complete segregation and maximum mixedness. For the first-order case, the fraction unreacted is given by:

$$\frac{C_{\text{out}}}{C_{\text{in}}} = \int_0^\infty e^{(-kt_c)} f_c(t_c)\,dt_c \qquad (1)$$

where f_c is the differential distribution of contact times and k is a pseudo-homogeneous rate constant. In principle, k can be determined from laboratory-scale experiments done say in a spinning basket reactor or in a small bed operated at incipient fluidization.

In what follows we prefer to use the contact time washout function $W_c(t_c)$, rather than the differential distribution function. The washout function $W_c(t_c)$ is defined as the fraction of entering reactant molecules that experience a contact time greater than t_c. It can be determined using a pair of washout experiments made at identical operating conditions, but different extents of adsorption. Suppose a washout experiment has been made using an adsorbable tracer. Then, the integral under the washout curve can be used to define a dimensionless constant N_1:

$$\int_0^\infty W_1(t_1)\,dt_1 = N_1\bar{t} = N_1 V/Q \qquad (2)$$

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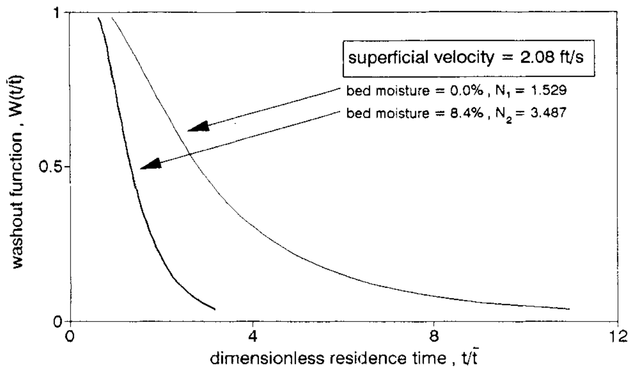

Figure 1. Washout functions for adsorbed tracers for unbaffled bed.

where $\bar{t} = V/Q$ is a mean residence time in the gas phase. $N_1 = 1$ for a nonadsorbed tracer, while $N_1 > 1$ for an adsorbed species that spends time on the catalyst surface as well as in the gas phase. A second washout experiment is performed at a different extent of adsorption:

$$\int_{\infty}^{0} W_2(t_2)dt_2 = N_2\bar{t} = N_2 V/Q \tag{3}$$

The two washout functions are equated,

$$W_1(t_1) = W_2(t_2) \tag{4}$$

to define corresponding values of the total (gas phase + surface) residence times, t_1 and t_2, for the two experiments. The contact time is then calculated from:

$$t_c = \frac{t_2 - t_1}{N_2 - N_1} \tag{5}$$

These calculated results for t_c correspond to the same values of the washout function as used to determine t_1 and t_2. Specifically,

$$W_c(t_c) = W_1(t_1) = W_2(t_2) \tag{6}$$

This methodology produces a model-free estimate of $W_c(t_c)$ that can be used in Eq. 2 to estimate conversion. The validity of the estimate of $W_c(t_c)$ depends on the assumptions of contact time theory as developed by Nauman and Collinge (1968a). One necessary assumption is that the contact time be a monotonic function of the gas-phase residence time. Flow paths with longer residence times must have longer contact times, although direct proportionality is not required. A second assumption is that motion of the solids phase does not significantly affect gas-phase residence times, even for adsorbable molecules. These assumptions were addressed by Nauman and Collinge (1968a,b), and the possible effects of solids motion have been discussed by them and by Shinnar and Rumschitzki (1989). As stated by Nauman and Collinge (1968a), the experimental data suggest that the assumptions are satisfied for small fluidized beds. The internal consistency of the present data suggests that they are also satisfied for industrial-scale fluidized beds.

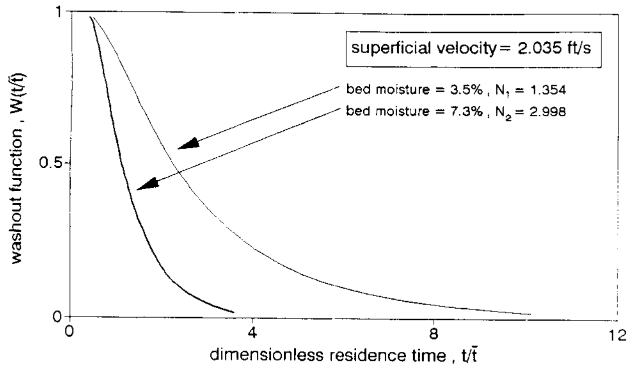

Figure 2. Washout functions for adsorbed tracers for vertically baffled bed.

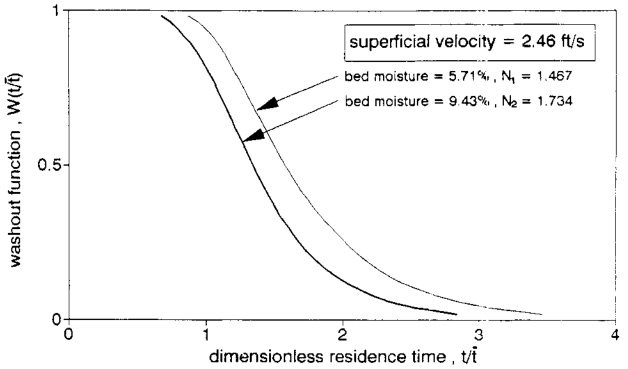

Figure 3. Washout functions for adsorbed tracers for horizontally baffled bed.

The Mobil experimental plan used positive and negative step changes and impulse experiments. The present study reports selected runs of the impulse type. The runs were selected to have the same (or almost the same) operating conditions, but different moisture contents. An impulse response gives differential distribution functions when the experimental data are scaled to have unit integral:

$$f_1(t_1) = \frac{c_1(t_1)}{\int_0^{\infty} c_1(t_1)dt_1} \tag{7}$$

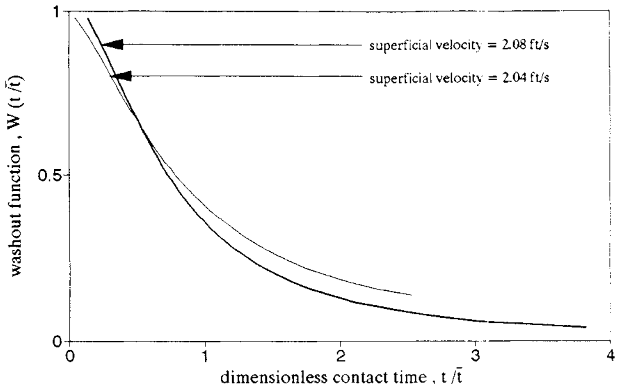

Figure 4. Contact time distributions for unbaffled bed.

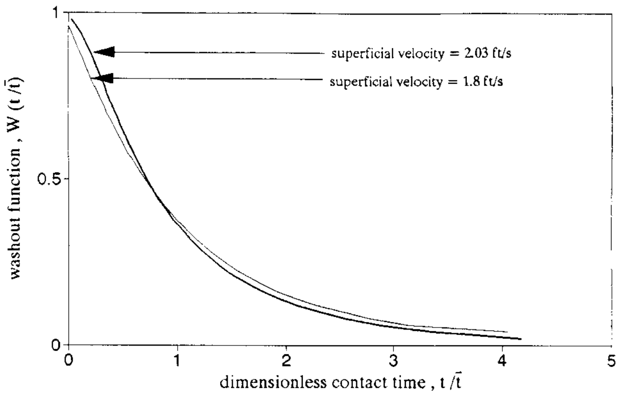

Figure 5. Contact time distributions for vertically baffled bed.

where c_1 is the measured concentration of the adsorbable tracer. The integral in Eq. 7 was evaluated using numerical integration over the finite data set and then by extrapolation of the tail using an exponential decay curve fit to the last few points. $f(t)$, thus obtained, was integrated to give the washout function:

$$W_1(t_1) = 1 - \int_{t_1}^{0} f_1(t)dt \qquad (8)$$

This, in turn, was integrated to find N_1 according to Eq. 2. Exponential extrapolation of the tail was used again.

The above procedure was repeated for a second run made with a different water concentration to obtain $W_2(t_2)$. Equations 5 and 6 were then applied to calculate $W_c(t_c)$. Had all calculations been precise, the integral under this washout function would have been equal to $\bar{t}$. In practice, integrals from $\bar{t}$ to about 1.1 $\bar{t}$ were observed. The results for $W_c(t_c)$ presented in the next section have been normalized to give unit integrals when the time axis is scaled by $\bar{t}$.

Results

Fourteen paired runs at seven operating conditions were analyzed using the above methodology. Three reactor configurations were evaluated: an open fluidized bed without baffles, the same bed with vertical baffles, and the same bed with horizontal baffles. Details of the bed and of the baffling arrangements were provided by Krambeck et al. (1987).

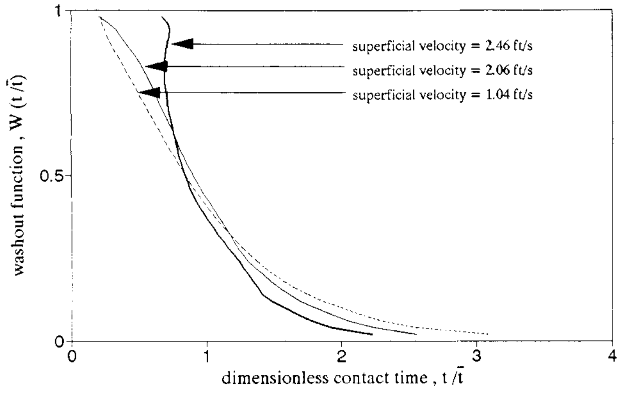

Figure 6. Contact time distributions for horizontally baffled bed.

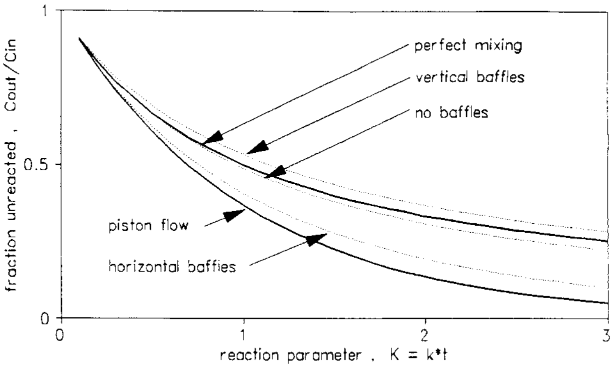

Figure 7. Predicted conversions for all reactor configurations.

Figures 1–3 show the washout curves for a representative pair of runs for each of the reactor configurations. The contact time is proportional to the horizontal distance between the paired washout functions. It is perhaps apparent from these curves that the results with no baffles and with vertical baffles are similar and that the results with horizontal baffles are qualitatively different. The results are quantified in Figures 4–6, which show the contact time washout functions for each of the reactor configurations.

The washout functions in Figures 4 (no baffles) and 5 (vertical baffles) closely correspond to the exponential distribution of a single stirred tank. No bypassing is exhibited, but bypassing is not expected in the high-velocity fluidization regime used industrially. The vertical baffles have no discernable advantage from a reaction engineering viewpoint. The results in Figure 6 do indicate an advantage with horizontal baffles. Horizontal baffles appear to stage the bed and thus provide a more uniform reaction environment. The reaction can be modeled as stirred tanks in series or as a piston flow reactor in series with a single stirred tank. There appears to be a trend with respect to superficial velocity, with high velocities giving a more uniform reaction environment. This trend is qualitatively reasonable for a fluidized bed.

Figure 7 shows predicted conversions for a solid catalyzed reaction that is first order with respect to the gas-phase concentration. Equation 1 was evaluated as a function of dimensionless rate constant, $K = k\bar{t}$, for each of the reactor configurations. In this figure, the lines showing predicted conversion represent averages of the contact time distributions for the various configurations. Specifically, the two washout functions in Figure 4 for the unbaffled case were averaged, and then Eq. 1 was evaluated using the averages $F_c(t_c)$. The data in Figures 5 and 6 were treated similarly. The results in Figure 7 confirm the large advantage of the horizontal baffles.

Acknowledgment

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Notation

c = measured concentration of the adsorbable tracer
C_{out} = outlet concentration of reactant
C_{in} = inlet concentration of reactant
f = differential distribution of residence times
f_c = differential distribution of contact times
k = pseudo-homogeneous rate constant
N = dimensionless holdup for an adsorbed tracer
Q = volumetric flow rate
t = residence time
t_c = contact time
$\bar{t}$ = mean residence time
V = volume of gas phase
W = washout function of residence times
W_c = washout function of contact times

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