Prediction of Axial Concentration Profiles in Catalytic Fluidized Reactors

D. R. van der Vaart
Virginia Polytechnic Institute and State University, Pennwood Laboratory, Charlottesville, VA 22902

A previous study by Fryer and Potter (1976) of the catalytic decomposition of ozone in a bubbling fluidized-bed reactor is considered in the light of a recently developed reactor model. It is shown that since in-bed sampling leads to an averaged concentration that is biased toward the emulsion-phase gas composition, an increase in the ozone concentration in the sampled gas is predicted as the probe is raised above the bubbling bed. The analysis, which does not have to assume gas backmixing, shows that the minima in the ozone concentration profiles associated with this transition occurs between H_{mf} and H, the expanded bed height, and may even occur at lower points in the bed at higher excess fluidizing velocities. The model also correctly predicts the overall conversion of ozone as a function of the reaction rate constant and gas velocity without resorting to the fitting of any parameters.

Introduction

Several different physical descriptions of the catalytic conversion of gaseous reactants in a bubbling gas-fluidized bed were proposed which have led to many mathematical models (Yates, 1983; van Swaaij, 1985). Since the immediate goal of any model is the prediction of the overall performance of the reactor, most experimental studies have focused only on the effluent gas composition. It can be argued, however, that the measurement of the in-bed concentration profile could lead to a greater understanding of the reactor dynamics of the fluidized bed. Nevertheless, few investigators have studied axial profiles. One exception is the extensive study reported by Fryer and Potter (1976) (referred to as F & P here), in which ozone decomposition was used as a test reaction. In that study, ozone kinetics were carefully measured under controlled conditions (that is, in a fixed bed) and used in conjunction with the countercurrent backmixing model proposed by Latham et al. (1968) to correlate experimental concentration profiles. The authors concluded that the results supported the existence of backmixing, citing as evidence the minimum in the ozone concentration measured near the surface of the bubbling bed.

More direct proof of gas backmixing using nonadsorbing tracer gases has been reported by, for example, Latham and Potter (1970) and Li and Weinstein (1989), although the link between these studies and the chemical reaction studies is less clear. This article presents another explanation of the shape of the axial concentration profiles measured by F & P which rests on: a) the effect that sampling from within the bed has on the probe composition; b) a reactor model recently developed by van der Vaart (1992).

Theory

If a gas-sampling probe immersed in a bubbling fluidized bed is assumed to draw gas at a constant flow rate regardless of what phase it samples from, the composition of the gas drawn by the probe, C_p, would depend on the length of time the probe spends in each phase. In addition, if the time period of sampling is long enough to ensure a smooth average of all phases and the two-phase theory of fluidization is assumed, it can be shown that:

$$C_p = \delta C_b + \left(\frac{1}{\psi} - 1\right)\delta C_{cld} + \left(1 - \frac{\delta}{\psi}\right)C_e \qquad (1)$$

where δ is the volumetric fraction of bed occupied by bubbles given by Davidson and Harrison (1963):

$$\delta = \frac{U - U_{mf}}{U_{abs}} \qquad (2)$$

The nomenclature used here is the same as that of van der Vaart (1992). In fact, this temporal average was given first by Fryer and Potter (1972) for a three-phase system (assuming that the wake and cloud phases are equivalent).

In the freeboard, however, the gases from the individual phases have mixed according to the two-phase theory so that a sample probe placed there would draw a gas with a composition given by a volumetric average due to Chavarie and Grace (1975),

$$C_p = \frac{U-U_{mf}}{U} C_b + \frac{U-U_{mf}}{U}\left(\frac{1}{\psi}-1\right)\epsilon_{mf}C_{cld} + \left[1-\frac{U-U_{mf}}{U}\left(1-\epsilon_{mf}+\frac{\epsilon_{mf}}{\psi}\right)\right]C_e \quad (3)$$

Note that Eqs. 1 and 3 are identical when $U_{br}=U_{mf}$ and $\epsilon_{mf}\rightarrow 1$. For smaller particle systems, however, $U_{br}>U_{mf}$, and the temporal average, Eq. 1, predicts that the probe concentration will be biased toward the emulsion phase relative to the volumetric average represented by Eq. 3. Now, if a probe is used to sample gas from different points along the axial coordinate of the reactor, this theory would indicate that the gas is averaged (by the probe) according to Eq. 1 when the probe is immersed in the bubbling bed. In the freeboard, the gases have mixed according to Eq. 3 and, as such, that average describes the gas sampled by the probe there. The transition, occurring somewhere near the bed surface from a sample biased toward the emulsion phase to the one that is not, would lead to a minimum in the concentration profile, since for practically any chemical reaction occurring in a fluidized reactor, the conversion will be higher in the emulsion phase than in the bubbles. This is due to both the generally greater residence time of the gas in the emulsion phase and, for heterogeneous reactions, the much greater gas-solid contact there. The only possible exception is an extremely exothermic homogeneous reaction such as gas combustion (see van der Vaart, 1992).

Results

To illustrate this effect, the reactor model developed by van der Vaart (1992) was applied to the system of F & P. Briefly, this model includes three phases: bubble, cloud, and emulsion. Gas in all three phases are assumed to flow as a plug. The reaction rate expression given by F & P was used (converted to a catalyst-volume basis), and reaction was assumed to occur in all three phases. The conversion in the bubble phase with its small volumetric concentration of solids is, of course, much lower than the other two phases. Bubble (and cloud) growth is taken into account and described by the correlation due to Darton et al. (1977),

$$D_b = \frac{0.54(U-U_{mf})^{0.4}(x+4\sqrt{A_o})^{0.8}}{g^{0.2}} \quad (4)$$

To investigate the generality of the reactor model rather than that of Eq. 4, A_o, a parameter which is given by Darton et al. (1977) to be dependent on the distributor, was used to fit the bubble growth data given by F & P (for the lowest value of U). Equation 4, with $A_o = 1.6\times10^{-3}$ m^2, is compared with the data in Figure 1 showing fair agreement for comparatively shallow beds. F & P noted that slugging began at those bed conditions that led to bubble diameters greater than 0.1 m which may explain in part the poorer fit at higher gas velocities and bed heights.

Comparison of the model with the data of F & P for ozone conversion as sampled from the freeboard as a function of superficial fluidizing velocity is shown in Figures 2a and 2b. Note that the ozone concentration was calculated for these figures using the volumetric average (Eq. 3). The dependence

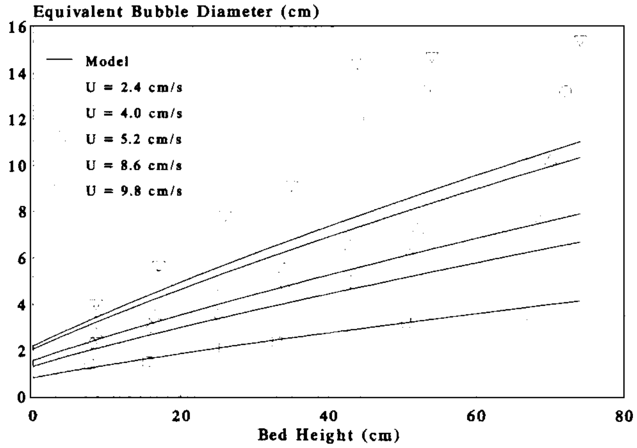

Figure 1. Variation of bubble size with bed height.

Data from Fryer and Potter (1976).

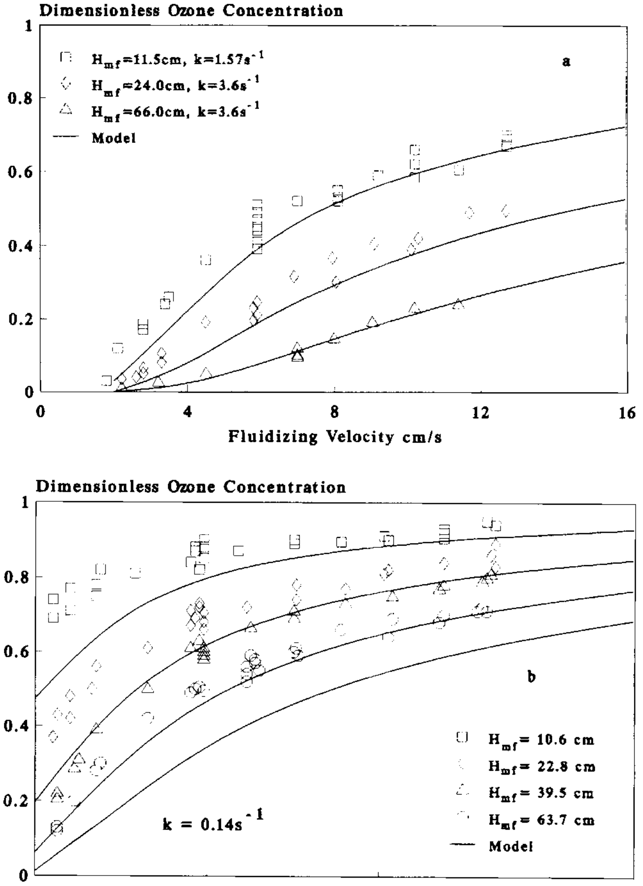

Figure 2. Conversion data as a function of *U* compared with predictions of model.

Data from Fryer and Potter (1976).

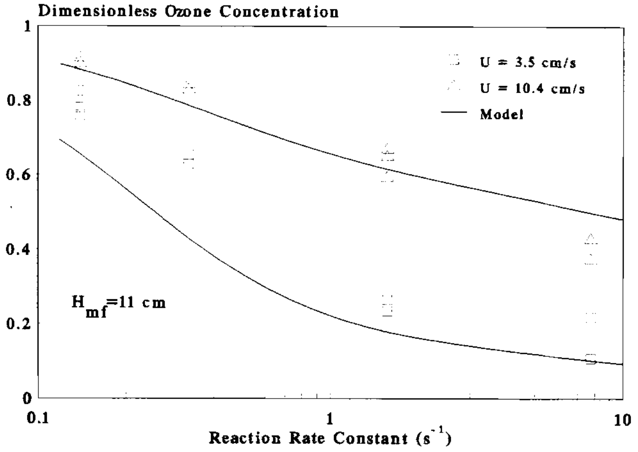

Figure 3. Comparison of model predictions with experimental data for conversion as a function of *k*.

Data from Fryer and Potter (1976).

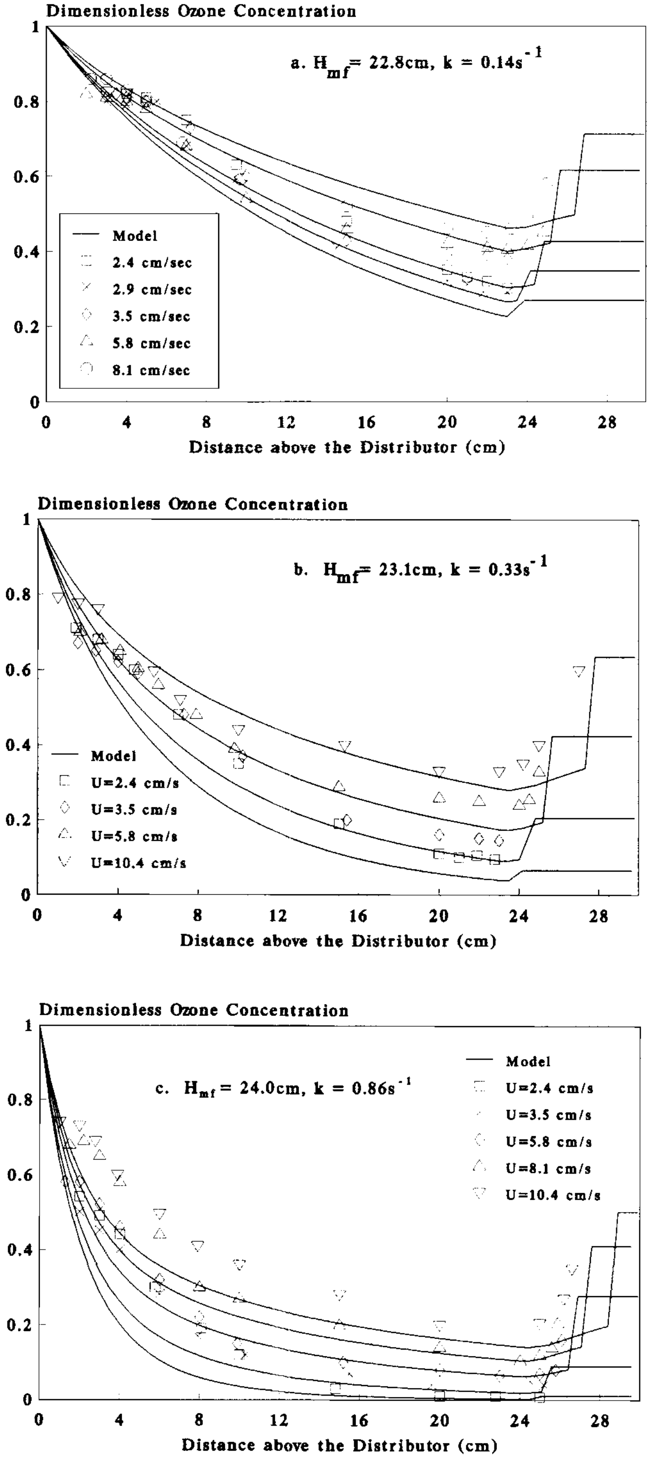

Figure 4. Predicted and experimental concentration profiles.

Data from Fryer and Potter (1976).

of the effluent ozone concentration on the rate constant is shown in Figure 3. In each of these figures the agreement between the data and the model predictions is comparable to the backmixing model without resorting to the fitting of any parameters (such as the wake fraction). As was pointed out by F & P, the reactant gas actually entered the bed 1.3 cm above the distributor in their study, while the model assumed the gas to enter at $x=0$. Although the fit was improved in each case when this condition was included, the results are not given here so that a direct comparison with the backmixing model would be possible.

The model is compared with the axial concentration profiles reported by F & P in Figures 4a–4c. Here, the individual concentration profiles of the three phases predicted by the model were mixed according to Eq. 1 for $x<H$, the expanded bed height, and by Eq. 3 above H. As expected, the transition to the volumetric average above H results in a jump in the ozone concentration. Note, however, that the predicted profile actually shows a minimum between H_{mf} and H. This is because, in accordance with the study by Bakker and Heertjes (1960), van der Vaart (1992) assumed the volumetric fraction of solids $(1-\epsilon_i)$ decreases exponentially between H and H_{mf} for all three phases. Thus, due to the decreased particle concentration above H_{mf}, the interphase mass-transfer rate exceeds the reaction rate (with the reaction rate put on a catalyst-volume basis) before H. That is, the rate of ozone entering the emulsion and cloud phases from the bubble phase exceeds the rate of reaction in those two phases since the concentrations of catalyst there are dropping. The transition shown in these figures at $x=H$ is so abrupt because the model treats the freeboard $(x \geq H)$ as a single-plug-flow reactor with an initial ozone concentration given by Eq. 3. Note that Eq. 1 does equal Eq. 3 when $\epsilon_i \rightarrow 1$ (as is assumed in the model) *and* $U_{abs} \rightarrow U-U_{mf}$ (not assumed at present). A smoother transition would require describing the latter phenomenon in some way.

It should be noted that according to Bakker and Heertjes (1960), the volumetric fraction of solids actually begins to decrease at progressively lower values of $x<H_{mf}$ as the superficial fluidizing velocity is increased. This means that the concentration minimum could occur lower in the bed than is predicted here, as U is increased. Note also that for small values of U, $U_{br} \approx U_{mf}$, and the difference between the temporal and volumetric average is small. Consequently, the effect of the probe is less pronounced when U is only slightly greater than U_{mf} and therefore is perhaps more difficult to measure. This is in contrast to the result of the backmixing model which

predicts a critical excess fluidizing velocity that must be exceeded before a concentration minimum is predicted. Finally, it should be noted that concentration profiles obtained by Chavarie and Grace (1975) by sampling from the individual phases did not show any concentration minima. This would also indicate that in-bed sampling as practiced by F & P leads to biased sampling.

This analysis does not imply that backmixing does not occur at all. Studies by Latham and Potter (1970) and Li and Weinstein (1989), in which samples were drawn below the tracer-injection point within a fluidized bed, clearly show that backmixing does indeed occur. The theory given here simply means that when drawing gas samples from within a fluidized reactor, the biasing of the composition of the gas must be taken into account. It is likely that a more complete theory would include both mechanisms. In any event, more experimental studies such as the one by Fryer and Potter (1976) are needed to assess their relative importance.

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Notation

A_o = constant dependent on distributor plate, m^2
C_i = concentration in phase i, mol/m^3
C_p = concentration of gas drawn by chemical probe, mol/m^3
D_b = equivalent bubble diameter, m
g = gravitational acceleration, m/s^2
H = expanded bed height, m
k = reaction rate constant based on volume of dense phase, s^{-1}
U = superficial fluidizing velocity, m/s
U_{abs} = absolute bubble rise velocity, m/s
U_{br} = relative bubble rise velocity, m/s
U_{mf} = minimum fluidizing velocity, m/s
x = axial distance from distributor, m

Greek letters

δ = volumetric fraction of bubbles
ϵ_i = void fraction in phase i
ϵ_{mf} = void fraction at minimum fluidization
ψ = ratio of bubble volume to cloud and bubble volume

Subscripts

b = bubble phase
cld = cloud phase
e = emulsion phase
mf = evaluated at minimum fluidizing velocity

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