Influence of Buoyancy Forces on the Flow of Gases through Packed Beds at Elevated Pressures

A. H. Benneker, A. E. Kronberg, and K. R. Westerterp
Chemical Reaction Engineering Laboratories, Dept. of Chemical Engineering, Twente University of Technology, 7500 AE Enschede, The Netherlands

The flow of gases through packed-bed columns at elevated pressures was investigated by displacement experiments with a stepwise change in the tracer concentration. The experiments with different tracers, flow rates, pressures, particle sizes, tube diameters, and flow directions were used to illustrate the effect of buoyancy forces on the apparent fluid mixing in packed beds. The experimental results exhibit a strong influence of the density differences between the tracer and carrier gas on the flow behavior at higher pressures. Axial dispersion significantly increases due to hydrodynamical instabilities when the density increases with the height, and is reduced in the presence of stable density gradients. The effect of density differences on the fluid flow becomes more pronounced with increasing tube diameters. It can be argued that in pressure equipment the usual correlations for mass and heat transfer may not be valid any more and that plug flow in such equipment is hardly possible to achieve.

Introduction

When designing and modeling packed-bed reactors, it is a common practice to uncouple the momentum transfer equations from the energy and mass balances. Inherent to this uncoupling, the effect of changes of fluid density and viscosity is assumed to be unimportant and free convection phenomena are neglected. However, in chemical reactors, variations in the composition of the fluid and heat effects due to chemical reaction create density and viscosity differences within the fluid and may induce free convection. In the case of an exothermic reaction in a downflow packed-bed reactor, the fluid density decreases in the direction of gravity, giving rise to an increase in buoyancy forces compared with the viscous and inertial forces. Consequently, the flow can become unstable—slow- and fast-flow regions are formed—resulting in hot and cold spots. The complex interaction between free convection and reaction is believed to be a major factor in many of the instabilities observed in reacting flows (see Nguyen and Balakotaiah, 1995).

So the flow behavior in the reactor can be completely distinctive from that in the experimental apparatus, in which the model parameters are measured. These parameters are usually determined by experiments on a laboratory scale and under idealized conditions, that is, at ambient pressure and—in the case of mass dispersion experiments—with a "perfect" tracer not affecting the hydrodynamics. It is disputable whether the transport parameters experimentally obtained at conditions definitely different to those in industrial equipment are reliable for the description of the flow behavior in real chemical apparatus.

The effect of density and viscosity differences can be quantified by the measurement of the fluid–solid mass and heat transfer as well as the hydrodynamical dispersion of mass and heat in the axial and radial directions. In this article we focus on the influence of the effects of density and viscosity on the axial dispersion in gases flowing through packed beds. The investigation of axial dispersion demonstrates the region where free convection affects the fluid flow. Moreover, the magnitude of axial dispersion under those conditions is itself interesting.

While considerable advances have been made in understanding the axial dispersion in fluids with constant density and viscosity flowing through packed beds, less attention has been paid to the dependence of the fluid flow on density and viscosity variations. It is recognized that density differences in liquids flowing through porous media give rise to significant changes in the nature of the dispersion, even for liquids

Correspondence concerning this article should be addressed to K. R. Westerterp.

with very small variations in the density (see Nunge and Gill, 1969). Lindfors (1979) performed displacement experiments with aqueous solutions of KCl in a packed, vertical column, and he showed that density differences as small as 0.02% resulted in differences in the axial dispersion coefficient of a factor of 2.

The major part of experimental research on effects of density and viscosity differences has focused on liquid systems. Some data are available for supercritical fluids. Interfacial mass transfer in packed beds with flowthrough of supercritical fluids was strongly affected by free convection caused by density differences, as was pointed out theoretically and proven experimentally by Debenedetti and Reid (1986). The significant influence of free convection on the interfacial mass transfer in supercritical fluid extraction was confirmed experimentally by Lim et al. (1994), Lee and Holder (1995), and Stüber et al. (1996). In the latter article, particle-to-fluid mass-transfer coefficients of 1,2,-dichlorobenzene and toluene in supercritical carbon dioxide were measured. At conditions near the critical point, the extraction time for 50% recovery of solute with upflow of carbon dioxide was almost triple the time for the same recovery with downflow of the fluid.

The importance of differences in the fluid properties on the hydrodynamics of gases through packed beds has never been quantified, although Mikuš et al. (1980) have observed nonsymmetrical temperature profiles in a catalytic bed for upflow and downflow during the oxidation of carbon monoxide, indicating that free convection phenomena are significant in packed-bed reactors with gas throughflow. In addition, Westerterp et al. (1996) recently found that the RTD of gases flowing through a packed bed was significantly different at higher pressures. They investigated axial dispersion in an upward gas flow by pulse experiments in a packed column at pressures up to 2.0 MPa. The results were attributed to free convection phenomena due to the density differences between the tracer and carrier gas (see Benneker et al., 1996). In the latter article, displacement experiments were carried out with a stepwise change in tracer concentration. Differences in Bodenstein numbers (Bo) of a factor of 10 were found for step changes from nitrogen to a helium/nitrogen mixture and vice versa in upward gas flow. These were attributed to gravitation-driven instabilities due to vertical density gradients in the case of a heavy gas displaced by a light gas. Density gradients in the reverse experiments evidently inhibited axial dispersion.

In the work of Benneker et al. (1996) the obtained *Bo's* reflect a significant influence of buoyancy forces on the flow of gases through packed beds at elevated pressures. But, based on the performed experiments, the physical mechanism responsible for the differences in Bo at different pressures and the role of other parameters were not fully elucidated. The role of the physical properties of the tracer gas and the influence of particle size, tube diameter, and flow direction had not been studied.

To clarify the physical mechanism responsible for the differences in Bo at different pressures, the influence of other parameters has been investigated. In the current article, the experimental results are presented and an analysis of the data is given. Displacement experiments have been done with different tracers, with up- and downflow of the gas, and the influence of particle size and tube diameter has been studied. By changing the flow direction of the gas with otherwise constant conditions, the previous results of Benneker et al. (1996) have been confirmed: the differences in the Bo are caused by the effect of buoyancy forces due to density differences. In principle, hydrodynamic instabilities caused by a density increase with height can have a twofold effect on the axial mixing: they increase the flow irregularities, resulting in greater axial dispersion, and also enlarge the transverse mixing, resulting in smaller axial dispersion. The experimental results demonstrate the first effect to be greater: the magnitude of axial dispersion is increased in the case of unstable density gradients, where the density increases with height. In the opposite case, where the density decreases with height, the magnitude of the axial dispersion is decreased by buoyancy effects. Differences in the viscosity have no noticeable influence on the hydrodynamical behavior in the investigated system. Experiments with different tracers have shown the role of the physical properties of the gases on the stability of the gas flow. In the case of unstable density gradients, the gas mixing due to molecular diffusion decreases the density gradients and stabilizes the flow. The effect of buoyancy becomes more pronounced at elevated pressures since the stability condition for fluids initially at rest, characterized by the Grashof · Schmidt numbers ($GrSc$), and the ratio of the buoyancy to the inertial forces, Gr/Re^2, are proportional to the pressure squared at fixed Reynolds numbers (Re). An increase in the tube diameter with otherwise constant conditions causes the buoyancy forces to have a greater effect, indicating that flow irregularities are determined by the tube diameter. For a fixed Re, an increase in the particle size obviously destabilizes the gas flow in the experiments where the density increased with height. Experiments with ethylene as tracer and nitrogen as carrier—where these two components have the same molar mass—confirm that density differences are responsible for the increased magnitude of axial dispersion. For this case, the Bo is not measurably influenced by the pressure and by the direction of a step change in the tracer concentration.

The obtained information on the flow of gases through packed beds can be very important for the description and design of packed-bed reactors. Since many processes operate at elevated pressures of up to 30 MPa and, in the case of adiabatic reactors, large tube diameters are used, we can expect that the effect of the buoyancy forces on the flow behavior can be large, especially in high-pressure equipment.

Experimental Setup and Procedure

The flow of gases through packed beds has been investigated by measuring an apparent axial dispersion coefficient using experimental techniques described in more detail in Benneker et al. (1996). Displacement experiments with constant volumetric flow rates were carried out in two vertical columns with 25 and 50 mm internal diameters packed with glass spheres of 2.2, 3.9 or 6.8 mm. The responses to the introduced step changes were measured at two locations in the bed—at 0.7 m and 3.7 m, respectively, beyond the tracer injection plane—at pressures between 0.13 and 1.5 MPa and for Re between 5 and 300.

In the experimental program, the flow rate, the particle diameter, the tracer concentration, and the pressure were

Table 1. Physical Properties of the Gases Used in the Experimental Study*

	Carbon Dioxide	Ethylene	Helium	Nitrogen
Molec. wt.	44.00	28.03	4.00	28.02
Density,** kg/m^3	1.9768	1.2644	0.1769	1.2507
Vis.,† 10^{-5} Pa·s	1.463	1.010	1.946	1.766
Diff. coeff. in nitrogen,† 10^{-5} m^2/s	1.63	1.63 (298 K)	7.05	—

*Under the experimental conditions the density can be considered as proportional to the pressure, the viscosity as pressure-independent, and the diffusion coefficient as inverse proportional to the pressure.
**at Standard Conditions (273 K, 0.1 MPa)
†at 293 K and 0.1 MPa, unless otherwise indicated.

varied. Helium, carbon dioxide, and ethylene were used as tracers, and nitrogen was used as the carrier gas. The physical properties of the gases are shown in Table 1. The column was operated with both upflow and downflow of the gas. The mole fractions of helium and carbon dioxide were measured with thermal conductivity detection cells (see Westerterp et al., 1996; Benneker et al., 1996). Ethylene was analyzed by means of a flame ionization detector (FID). To this end, a gas chromatograph HP3300 with an internal FID was installed and connected to the two sample points by 1-mm-ID sample tubes. The sample flows were regulated by means of two mass-flow controllers at a rate of 25 NmL/min. To reduce the response time of the sample system, these mass-flow controllers, which also operated as pressure relievers, were placed near the sample point: the pressure decrease enhanced the volumetric flow rate through the sample tubes. The two sample streams were brought together in the FID and the mV-signal was sent to the data-acquisition and control unit. The extent of axial dispersion, represented by the *Bo*, and the average residence time were determined by curve fitting in the time domain (see Benneker et al., 1996). The physical properties of pure nitrogen were used to calculate the *Re*'s.

To explore the conditions where free convection effects become large and to clarify the physical mechanism, we studied the influence of several variables on those effects. Displacement experiments were used to illustrate the effect of free convection on the flow behavior of gases flowing through a packed bed. To find the role of gravity, the direction of the flow was changed. The information obtained with the up- and downflow experiments can help us to discriminate between the role of density and viscosity differences between tracer and carrier gas. To investigate the effect of the physical properties, different tracers were used. Experiments using a tracer and a carrier with equal densities were performed to rule out any buoyancy effects. Further, both the particle size as well as the tube diameter were varied. Moreover, the strong influence of the pressure on the *Bo* found by Benneker et al. (1996) was investigated further.

Results

Effect of the direction of flow

Step changes have been executed from pure nitrogen to a mixture of helium and nitrogen with up- and downflow and with otherwise constant conditions. Differences in the experimental results are therefore caused by gravity effects. At pressures (P) close to 0.1 MPa the *Bo* found for the up- and downflow experiments are almost equal. When the pressure increases, the *Bo* for the upflow experiments are substantially lower than for the downflow at the same column pressure. The *Bo* for the upflow mode decreases considerably and for downflow increases slightly with higher pressure. Typical results are shown in Figure 1a, where ▲ and ■ represent the up- and downflow experiments, respectively. The influence of the buoyancy forces on the flow behavior at elevated pressures can be seen: in the case of upward flow, gravitation-driven instabilities due to unstable density gradients —the density increases with height—increase the axial dispersion coefficient; in downward flow experiments, where the density decreases with height, the axial dispersion is inhibited by buoyancy forces. When a reverse step change is performed from mixture to pure nitrogen in the downflow mode—an unstable density gradient—the *Bo-P* dependency coincides with that of the unstable displacement in the upflow experiments (see Figure 1a). The experimental results as shown in Figure 1a indicate that under those experimental conditions the differences in the *Bo*'s can be attributed solely to the influence of buoyancy forces on the fluid flow. Since no considerable differences are measured for the two unstable flow

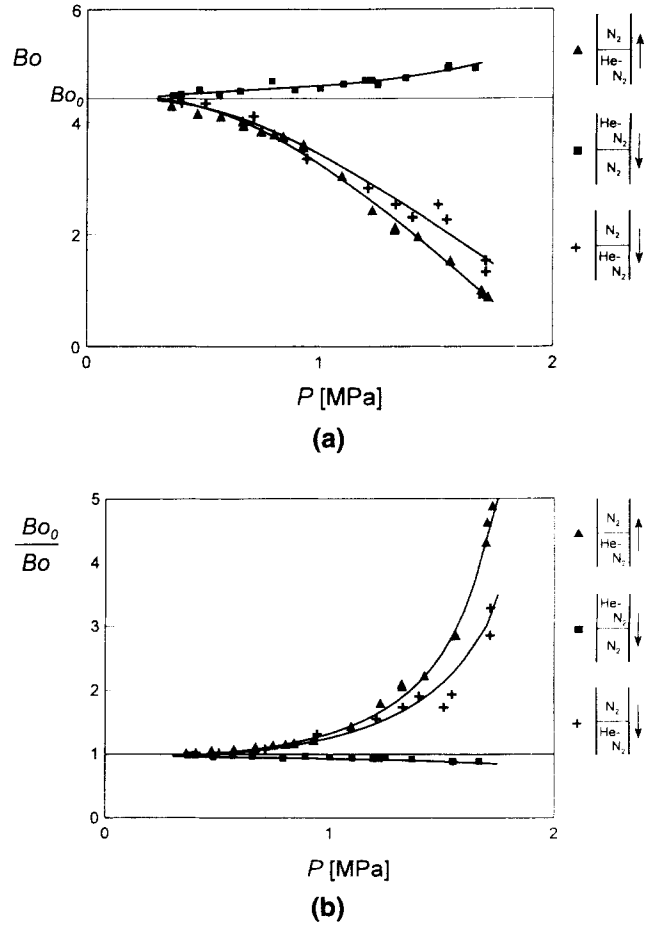

Figure 1. Axial dispersion at constant *Re* as a function of the flow direction and of the pressure. (a) *Bo*; (b) enhancement factor.

Conditions: $Re = 35$; $\Delta\rho^* = 0.17$; $d_p = 3.9$ mm; $d_t = 25$ mm; $L = 3.0$ m.

experiments, viscosity differences evidently have no remarkable influence.

Bo_0, given in Figure 1a, is the Bodenstein number measured at low pressures and at the same *Re* and *Sc*; it represents the magnitude of axial dispersion due to the combined action of molecular diffusion and forced convection. It is possible to define an enhancement factor for axial dispersion due to buoyancy forces as Bo_0/Bo; this factor is plotted vs. the pressure in Figure 1b. The factor Bo_0/Bo represents the ratio of the measured axial dispersion coefficient $1/Bo$ over the dispersion coefficient $1/Bo_0$ that would be measured when buoyancy effects are negligible.

It should be noted that the relative density difference in the experiments presented in Figure 1 is only 17%. In practice, in chemical reactors and contactors, the differences in the density can be much larger because of the additional variations in temperature and composition of the gas. Moreover, the maximum pressure in this study is only 1.7 MPa, while in many processes the pressure is higher.

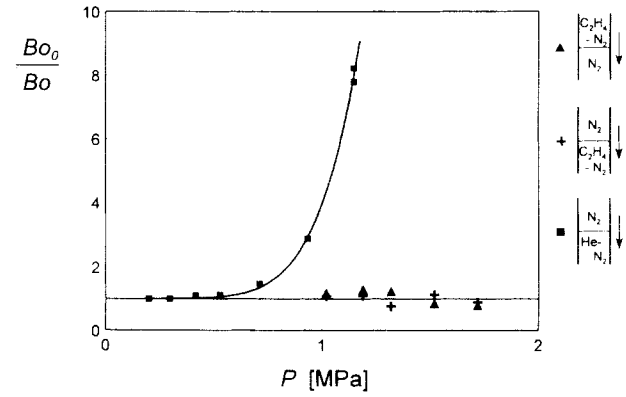

Figure 3. Enhancement factor of the axial dispersion due to buoyancy forces vs. the pressure for helium and ethylene as tracers in nitrogen.

Conditions: Downflow, $Re = 35$, 20 vol % He; 0.2 vol % ethylene; $d_p = 6.8$ mm; $d_t = 25$ mm; $L = 3.0$ m.

Influence of the tracer

The influence of the physical properties of the gas on the flow through a packed bed was investigated by changing the tracer gas and using nitrogen as the carrier gas. Experiments were performed with carbon dioxide, ethylene, and helium.

Both for carbon dioxide and helium as a tracer, the magnitude of the axial dispersion is larger for the negative density step changes where the heavier gas is displaced by the lighter one. *Bo*'s for upflow experiments with both helium and carbon dioxide as tracer at 1.0 MPa are presented in Figure 2 as a function of the *Re*. Although the relative density differences between the displacing and displaced fluids were equal for both tracers, the difference between the positive and negative step changes is considerably larger in the experiments with carbon dioxide. In the case of negative density step changes, the *Bo*'s were significantly lower for the experiments with carbon dioxide as compared to those for helium; in the reverse experiments, the *Bo*'s for carbon dioxide were obviously higher. These differences for the two tracers can be attributed to the difference in molecular diffusivity for the different gas pairs. During gravitation-unstable displacements, gas mixing due to molecular diffusion decreases concentration gradients and as a consequence stabilizes the flow. In this case, the molecular diffusion opposes the influence of buoyancy forces at lower *Re*'s. Since the molecular diffusion coefficient for the carbon dioxide/nitrogen mixture is approximately a factor of 4 smaller than for the helium/nitrogen mixture, the stabilizing effect in the case of carbon dioxide will be smaller, resulting in lower *Bo*'s. For gravitation-stable experiments the *Bo* curve will follow the molecular diffusion line at sufficiently low *Re*'s. The slope of the molecular diffusion line for the carbon dioxide/nitrogen mixture is four times the slope for helium/nitrogen, resulting in larger *Bo*'s for the experiments with carbon dioxide. The effect of molecular diffusion on the magnitude of the axial dispersion is therefore opposite for stable and unstable flows. At higher *Re*'s the influence of the molecular diffusion on the concentration field in the bed diminishes and no significant effect of the tracer type can be expected.

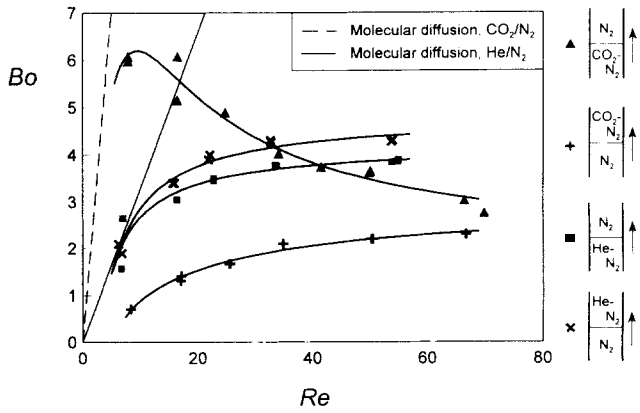

Figure 2. Bodenstein number as a function of the Reynolds number for different tracers.

Conditions: Upflow, $P = 1.0$ MPa; $\Delta\rho^* = 0.11$; $d_p = 3.9$ mm; $d_t = 25$ mm; $L = 3.0$ m.

To prove that density differences are responsible for the deviations in the magnitude of axial dispersion, displacement experiments with a tracer and a carrier of equal densities have been performed using ethylene and nitrogen. In this case, the direction of the step change or a change in the pressure should not have any influence on the *Bo*, because the molar masses of the tracer and the carrier are equal. This is confirmed by the results shown in Figure 3. The *Bo*'s now lie in between 1.5 and 2.0, which is considerably smaller than expected from previous experiments with helium and carbon dioxide. The *Bo*'s do not depend noticeably on the pressure and on the direction of the step change for the case of ethylene/nitrogen.

Particle size

Downflow displacements of a mixture of helium and nitrogen by pure nitrogen have been carried out with three particle diameters, 2.2, 3.9, and 6.8 mm, at a fixed *Re*. The ratio Bo_0/Bo for the different packings has been plotted as a function of the pressure in Figure 4. As shown, at a given pressure an increase of the particle diameter leads to an increase of the enhancement factor. Thus, in the case of unstable den-

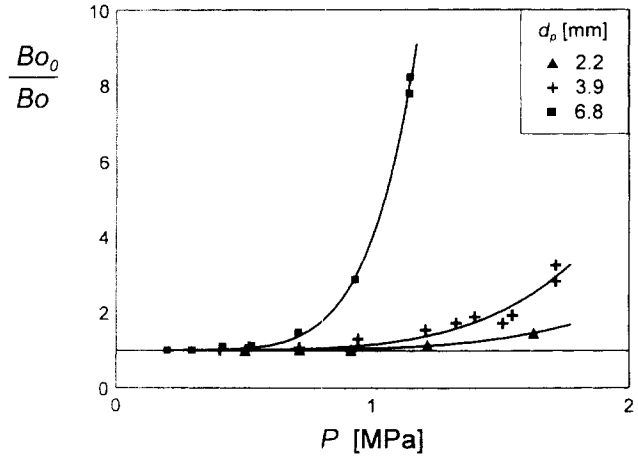

Figure 4. Influence of the particle diameter on the enhancement factor at different pressures.

Conditions: Downflow, displacement of helium/nitrogen mixture by pure nitrogen; $Re = 35$; $\Delta\rho^* = 0.17$; $d_t = 25$ mm; $L = 3.0$ m.

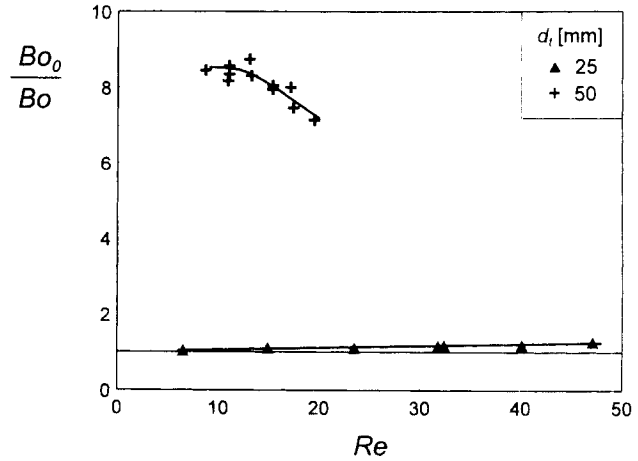

Figure 5. Influence of the tube diameter on the enhancement factor.

Conditions: Upflow, displacement of nitrogen by helium/nitrogen mixture; $P = 1.5$ MPa; $\Delta\rho^* = 0.14$; $d_p = 2.2$ mm; $L = 3.0$ m.

sity gradients, as for the experiments in Figure 4, the increase in the magnitude of axial dispersion with pressure is more pronounced for larger particle diameters. Evidently, when the resistance of the packing to the fluid flow is decreased by increasing particle size, secondary flows caused by density differences are more easily induced and have a larger effect on the flow pattern.

Tube diameter

Displacement experiments with upflowing gas and a stepwise change from nitrogen to a helium/nitrogen mixture have been performed in packed columns with different tube diameters. It has been found that, at a given pressure, the effect of buoyancy forces on the axial dispersion is more significant at larger tube diameters: the enhancement factor Bo_0/Bo is around eight in the 50-mm tube at 1.5 MPa, whereas in the 25-mm tube $Bo_0/Bo \approx 1$ (see Figure 5). Thus, the unstable density gradient in these displacement experiments influences the axial dispersion more significantly in larger tubes. This effect indicates that flow irregularities are present on the scale of the tube diameter.

To our knowledge, in the analyses of the hydrodynamical stability in porous media or packed beds with flowthrough, the influence of the tube wall on the stability has never been demonstrated. Only Wooding (1959) studied the effect of the tube diameter on the hydrodynamical stability of a viscous liquid at rest in a vertical tube containing porous material. According to his stability condition, an increase in the tube radius leads to an easier inducement of hydrodynamical instabilities.

Experiments at higher Reynolds numbers

The previously presented data were obtained at *Re*'s lower than 125. It is interesting to know what happens at higher *Re*'s. With increasing *Re*'s, the influence of buoyancy forces is expected to decrease, since the ratio of buoyancy to inertial forces—characterized by Gr_L/Re^2—decreases. In this case, the *Bo* must become independent of pressure and of the direction of flow and step change. As a consequence, the different curves measured at low *Re*'s must approach each other. At pressures around 0.5 MPa this was indeed the case: the difference in *Bo* disappeared around a *Re* of 60. However, at higher pressures the values for *Bo* did not converge when *Re* was increased, and strange results were obtained: the *Bo*'s for step changes from the helium/nitrogen mixture to pure nitrogen decreased significantly as a function of the *Re*, independently of the flow direction. Here, small values for *Bo* were measured at high *Re*'s. The *Bo*'s for the reverse step changes—from nitrogen to the helium/nitrogen mixture—were only slightly decreased with *Re*. Typical results are shown in Figure 6. Note that the density difference between the helium/nitrogen mixture and pure nitrogen is only 4%. These results, which cannot be explained with available hydrodynamical stability theories, may be of major interest for flow behavior through packed-bed reactors, since many reactors operate at even higher *Re*'s and higher pressures.

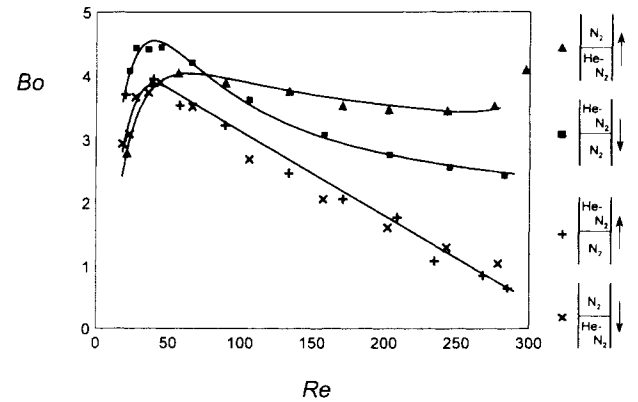

Figure 6. Bodenstein numbers for up- and downflow experiments at higher Reynolds numbers.

Conditions: $P = 1.5$ MPa; $\Delta\rho^* = 0.04$, $d_p = 3.9$ mm; $d_t = 25$ mm; $L = 3.0$ m.

Discussion

From the standard dimensional analysis, one would expect the axial mass dispersion in packed beds to be described by relationships of the form $Bo = f(Re, Sc)$ (see Hiby, 1962). As demonstrated in this article, this view is not adequate in the case of gas flow through packed beds at elevated pressures. Here buoyancy effects may have a large impact on the magnitude of axial dispersion and should be considered. Hydrodynamical instabilities, caused by buoyancy effects when the density increases with height, can significantly enhance the axial dispersion, as shown in Figure 1. In the opposite case, where densities decrease with height, axial dispersion may decrease due to buoyancy effects (see Benneker et al., 1996).

The obtained *Bo*'s elucidate the significance of the influence of free convection on flow behavior. It should be noted that the one-dimensional model with an apparent dispersion coefficient can hardly be a useful tool for accurately describing our experiments. To describe the experiments with a highly unstable flow, a more refined model is necessary. The *Bo*'s determined in this study were used solely to define the region where free convection effects were significant and to quantify roughly the impact of these effects. It was not our purpose to describe the complicated mixing phenomena in the presence of hydrodynamical instabilities with a simple, one-dimensional model.

Since the early experiments and analysis of Hill (1952), there has been a growth in the literature published on hydrodynamical instabilities due to density and viscosity variations in porous media (Homsy, 1987; Manickam and Homsy, 1995). These were thought to be important in enhanced oil recovery, groundwater flows, packed-bed regeneration, geothermal wells, and so forth. Because of the excessive complications, most theoretical analyses were restricted to the determination of the stability region. For example, Darcy's law was used to describe the resistance to the flow neglecting any inertial effects. A quantified description of the effect of differences in fluid density and viscosity on the solute transport in miscible fluid displacement in porous media was given by Welty and Gelhar (1991). Implicit in their analysis was the number of assumptions and approximations that was required to obtain analytical results. Because Welty and Gelhar (1991) were interested in the effect of variations in the density and viscosity in enhanced petroleum recovery operations and in environmental problems such as seawater intrusion and the sinking of contaminent plumes in aquifers caused by gravity, they did not consider the influence of the physical boundaries of the porous medium.

Available results of thorough investigations of unstable flows during miscible displacements in porous media (see Manickam and Homsy, 1995; Liu and Dane, 1996) cannot be used to describe our experiments. Since a detailed theoretical analysis of our complicated problem is impossible, we restrict ourselves to a dimensional analysis of the experimental data. Because our current data give evidence that viscosity variations are not important in our system, we focus on the influence of density differences on the stability of a fluid in a porous medium. The experimental data with an enhanced axial dispersion have been analyzed, since this enhancement is undesirable in chemical reactors and contactors.

Whereas in almost all investigations of the stability of fluids in vertical tubes filled with porous media, the physical boundaries were not taken into consideration, Wooding (1959) studied the effect of the tube wall on stability. He found that in a long vertical tube filled with porous material, a liquid is at rest for the case of the density increasing with height, provided that the density gradient $d\rho/dz$ does not exceed

$$\frac{d\rho}{dz} = \frac{3.390\eta\kappa}{gk_p b^2}.$$

where η is the viscosity; κ is the diffusivity through the medium of the solute producing the variation in ρ; g is the acceleration due to gravity; k_p is the permeability; and b is the radius of the tube filled with porous material. Thus, the stability condition requires that the Raleigh number, $Ra = d\rho/dz \cdot gk_p b^2/\eta\kappa = Gr \cdot Sc$, should not exceed 3.39, below which neutral stability is possible. Wooding (1959) did not consider the intensity of the hydrodynamical instabilities, but only the existence or absence of those instabilities. For fluids flowing through porous media theoretical results similar to those of Wooding taking into account the tube walls are unknown to us. In our analysis, we assume that the influence of the tube radius on the stability of slowly flowing fluids is the same as for fluids at rest. We further suppose that the Raleigh number is the governing parameter for the intensity of the instabilities in systems with low flow rates, say in the laminar region. In this region the tendency of a density gradient to produce a convective flow is opposed by mixing due to molecular diffusion. The effect of molecular diffusion becomes visible when the results for helium and carbon dioxide as the tracer are compared (see Figure 2). In the opposite case of higher flow rates, the influence of molecular diffusivity on the axial dispersion and on the stability of the flow diminishes, and the axial dispersion is mainly determined by convection only. It is well known that under these circumstances the relative importance of free compared to forced convection in determining flow patterns depends on Gr/Re^2, which is the ratio of buoyancy forces over inertial forces (see Bird et al., 1960). From dimensional analysis we can expect that the enhancement factor is determined by the same dimensionless groups as are present in the stability criteria. Hence, it has been assumed that for low Reynolds numbers the enhancement factor is determined by the product of the Grashof and Schmidt number, so $Bo_0/Bo = f(GrSc)$, and that for higher Reynolds numbers, $Bo_0/Bo = f(Gr/Re^2)$. A simple expression that satisfies the two limiting situations is $Gr/(k/Sc + Re^2)$. If $Re \to 0$, the ratio approaches $GrSc$, and if $Re \to \infty$ it approaches Gr/Re^2.

A difficulty in the analysis is the density gradient $d\rho/dz$, which in our experiments, depends on both time and the axial coordinate. During the displacement, the density gradient decreases along the reactor length and therefore the influence of free convection on the axial dispersion diminishes. We have measured the integral effect of free convection by comparing the concentration-time response curves at two positions in the bed. As a first estimate we have used $\Delta\rho/L$ to represent the density gradient in the Grashof number and $Gr_L = \Delta\rho/\rho_{N_2} \cdot gd_p^2 d_t^2/L\nu_{N_2}^2$.

In Figure 7, the enhancement of axial dispersion due to free convection is plotted as a function of $Gr_L/(k/Sc + Re^2)$.

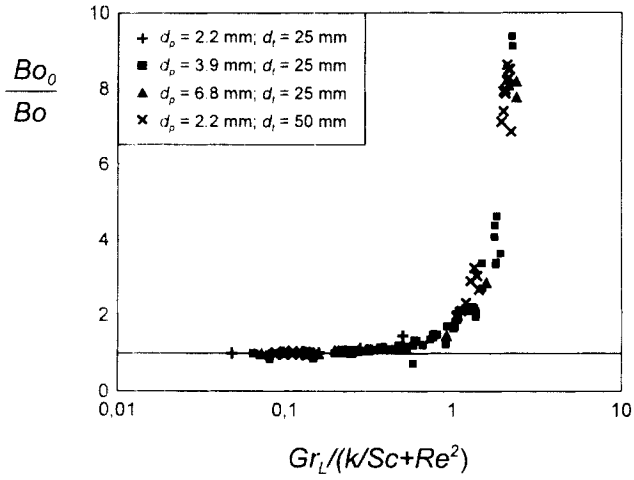

Figure 7. Enhancement of axial dispersion due to buoyancy forces as a function of the dimensionless group $Gr_L/(k/Sc + Re^2)$.

k = 600; for experimental conditions: see Table 2.

As can be seen, it is possible to adequately correlate our data obtained in the wide range of conditions given in Table 2. Of course, this simple correlation has not been proven to be universal, but it clearly reflects the effect of several parameters on the significance of the buoyancy forces on the mixing in the axial direction. The empirical constant k is 600 and determines the relative importance of the two mechanisms, which stabilize the flow: the stabilizing effects by gas mixing due to molecular diffusion and to forced convection are equal for $Re = \sqrt{(k/Sc)}$. Thus, when $Re < 50$ for helium and $Re < 25$ for carbon dioxide, molecular diffusion is the governing stabilizing mechanism. In the opposite case of larger Re's the forced convection is mainly responsible for the stabilization of the flow. Note that in the latter case of large Re's—where our expression, governing the enhancement of axial dispersion due to buoyancy, is reduced to $Gr_L/Re^2 = \Delta\rho/\rho \cdot d_t^2 g/L(u_0/\epsilon)^2$—the particle size does not play a role in the density effect.

From Figure 8 it follows that the dimensionless axial dispersion coefficient grows exponentially with Gr_L at fixed Re's and Sc's. Knowing Gr_L to be proportional to P^2, the significance of the effect of hydrodynamical instabilities on the axial dispersion at elevated pressures is evident.

Significance

To elucidate the practical significance of the results obtained, the value of the group $Gr_L/(k/Sc + Re^2)$ is estimated for typical industrial conditions. Consider an adiabatic, packed-bed reactor of 3-m diameter and 8-m height with a downward gas flow at 10 MPa. An exothermic reaction proceeds with dimensionless adiabatic temperature rise $\Delta T_{ad}/T_0 = 0.3$. Here T_0 denotes the inlet gas temperature in degrees Kelvin. The superficial gas velocity is 0.2 m/s and the bed porosity 0.4. The average molar weight of the gas mixture is assumed to be uniform over the reactor length; density variations due to differences in gas composition are therefore neglected. Since the density of the gas mixture in downflow decreases over the reactor length due to the temperature rise, the flow is potentially unstable. Now we assume our correlation in Figure 7 can be extrapolated. For a high flow rate of 0.2 m/s, the influence of molecular diffusion on the axial-dispersion is, of course, negligible. Therefore we can approximate our correlation by $Gr_L/Re^2 = \Delta\rho/\rho \cdot d_t^2 g/L(u_0/\epsilon)^2$. Because $\Delta T_{ad}/T_0 = 0.3$, the relative density difference $\Delta\rho/\rho$ is also approximately 0.3, and $Gr_L/Re^2 = 13$. On the basis of the correlated results in Figure 7, the flow in the reactor would be highly unstable. As a consequence, slow- and fast-flow regions may be formed, resulting in hot and cold spots. This phenomenon may promote the occurrence of undesirable side reactions due to temperature fluctuations and a wide range of residence times of the reactants. Moreover, hot spots may deactivate the catalyst, thus shortening the catalyst's life.

This simple estimation questions the hydrodynamical conditions in industrial reactors. Estimates of the group $Gr_L/(k/Sc + Re^2)$ in adiabatic-bed reactors—such as reactors for the synthesis of ammonia, ethylbenzene, and methanol—suggest that hydrodynamical instabilities may be expected. We realize that the extrapolation cannot be used with confidence. Knowledge of the phenomenon discussed is important, since the hydrodynamical instabilities may complicate the operation of packed-bed reactors. Therefore, much more research is desirable with larger vessel diameters and at higher pressures.

Table 2. Experimental Conditions of the Data Correlated in Figure 7

Pressure, MPa		0.2–1.7
Superficial velocity, m/s		0.002–0.10
Particle diameter, mm		2.2, 3.9, 6.8
Porosity		0.36–0.44
Tube diameter, mm		25, 50
Tracer (mole fraction)		Helium (5–20%)
		Carbon dioxide (20%)
Flow direction		Up, down
Grashof no., Gr_L		$(0.8–300)\times 10^3$
Reynolds no, Re		5–125
Schmidt no., Sc	He in N_2	0.23
	CO_2 in N_2	0.98

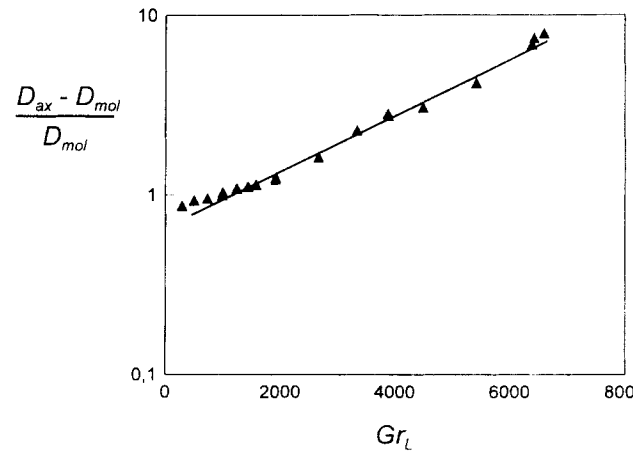

Figure 8. Dimensionless axial dispersion coefficient as a function of the Grashof number.

Conditions: Upflow, displacement of nitrogen by helium/nitrogen mixture; $Re = 35$; $\Delta\rho^* = 0.17$; $d_p = 3.9$ mm; $d_t = 25$ mm; $L = 3.0$ m.

Conclusions

The results obtained in the present study give evidence of free convection to affect significantly the gas flow through packed beds in situations of interest in practice, especially in packed beds under pressure. Axial dispersion significantly increases due to free convection in the case of unstable density variations, where the density increases with height. When the density decreases with height, axial dispersion is reduced. The density effects become more pronounced for gas flow through packed beds with larger tube diameters and at higher pressures.

The main implication of our results is that for packed beds at elevated pressures, density effects can be significant at even modest composition or temperature differences. The idealized conditions in laboratory experiments—isothermal, ambient pressure, and a perfect tracer not affecting the hydrodynamics—have masked density effects. However, since packed-bed reactors are ordinarily operated at extreme conditions, the phenomenon observed may be of major importance for the operation of those reactors and their design. It can be expected that free convection plays a considerable role in all mass- and heat-transfer processes in packed beds at elevated pressures. Therefore all available mass- and heat-transfer correlations, measured under different conditions than those in high-pressure packed-bed reactors and contactors, cannot be used with confidence.

The hydrodynamical instabilities observed disturb the plug-flow character in packed beds; they may eventually lead to hot spots and deactivated catalyst. Measures can be taken to prevent or reduce hydrodynamical instabilities in pressure equipment. Probably thinner and longer columns will reduce the effects. Much more research in these phenomena is desirable, above all in equipment of larger diameters and at high pressures.

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Notation

d_p = particle diameter
d_t = tube diameter
D = molecular diffusion coefficient
D_{ax} = axial dispersion coefficient
Gr_L = modified Grashof number, $\Delta\rho/\rho_{N_2} \cdot g d_p^2 d_t^2 / L \nu_{N_2}^2$
L = length of test section
u_0 = superficial velocity
Δ_ρ^* = dimensionless density difference $(= |\rho_{N_2} - \rho_{mixture}|/\rho_{N_2})$
ϵ = bed porosity
ν = kinematic viscosity
ρ = density

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