MEASUREMENT OF AXIAL DISPERSION IN PACKED BEDS AT LOW REYNOLDS NUMBERS BY IMPERFECT PULSE CHROMATOGRAPHY

A. J. KEHINDE, R. R. HUDGINS AND P. L. SILVESTON

Department of Chemical Engineering, University of Waterloo, Ontario, Canada

Studies were made of axial dispersion in packed beds at low Reynolds numbers (0.01 to 1) using imperfect pulse chromatography. Three types of experiments were used to measure dispersion. One set was done with non-porous particles, another with non-porous particles coated with a thin liquid film to which mass transfer occurred, and a third set was done with porous particles in which there was internal diffusion.

Measurements confirmed the presence of a maximum Peclet number in the low Reynolds number region, as was previously identified by other workers. At the lowest Reynolds number used, the Peclet number approaches a limit imposed by molecular diffusion.

Different values of the axial dispersion coefficient were obtained in the presence of mass transport and internal diffusion. This disturbing result calls into question the validity of the commonly accepted dispersion-fluid particle transport model of packed beds in the region of low Reynolds numbers.

Introduction

Axial spreading is common to many industrial operations; because of this, it has received considerable study since the early explorations in the 1950's. The literature on the subject is vast. It has been examined recently by Gangwal *et al.*⁽⁶⁾ At low flow rates, axial spreading is believed to be a function of the diffusion coefficient of the tracer material modified by a factor which accounts for tortuosity created by the packing. As the flow velocity increases, spreading becomes less dependent on the physical properties of the tracer and becomes a function of the hydrodynamics in the specific packing.

Despite the vast literature, little has been reported for the combination of fine particles and low flow rates ($N_{Re} < 1$). Since this combination is characteristic of pulse chromatography, these new data should be useful.

Experimental Procedure

Gangwal *et al.*⁽⁷⁾ pointed out that the dispersion model used in the treatment of chromatographic data does not correspond to the condition at the entrance to the column where the packing sees an abrupt jump in tracer concentration when impulses are used. Despite the simplification accruing with an impulse, this difficulty led Wakao *et al.*⁽²⁶⁾ to use an imperfect pulse technique in which the impulse is smoothed in a dispersive bed ahead of the test section. A third bed

following the test section allows infinite-bed boundary conditions to be used and reduces flow discontinuity at the outlet of the test section.

The essential features of the measurement system devised by Wakao *et al.*⁽²⁷⁻²⁹⁾ are shown in Fig. 1. Details of the packed bed chromatographic column are shown in Fig. 2. The packed column, made of 2-cm i.d. stainless steel tubes, consisted of three sections with thermal conductivity detectors between sections 1 and 2 and sections 2 and 3. Section 1 functioned as a disperser bed and was packed with non-porous glass beads. The length of section 1 could be varied from 2 to 10 cm. Dispersion measurements were made across section 2, which contained packing consisting of porous or non-porous liquid-coated spheres (balloons). Three particle sizes were used: 0.7, 3 and 4 mm. Packing depth could be varied between 5 cm and 10 cm. Section 3 was packed with non-porous glass beads; its purpose was to satisfy the outlet boundary conditions for the test bed as mentioned above. The packed bed was kept in a constant-temperature oven to insure isothermal conditions. Temperature variation was less than 0.5°C. Beds were oriented horizontally. Wakao⁽²⁵⁾ found that orientation did not affect the measurements. Average bed porosity was determined indirectly from the known volume of the column and the weight and density of the packing material.

Tracer concentration was detected by thermal conductivity using a matched quad of tungsten filaments, Gow Mac Model 13-002WX, housed in short connectors, 5 mm in length, between the sections (Fig. 2). The reference side of the thermal conductivity

Received October 2, 1982. Correspondence concerning this article should be addressed to P. L. Silveston. A. J. Kehinde is now at Dept. of Chem. Eng., Univ. of Lagos, Lagos, Nigeria.

Fig. 1. Schematic flow diagram.

CRR chromatographic reactor, reference; CRS chromatographic reactor, sample; D dryer; GC gas cylinder, carrier/reference; GS gas cylinder, sample; ID input detector; IO isothermal oven; MFC Moore flow controller; OD output detector; RC rotameter carrier gas; RR rotameter reference gas; SMB soap bubble meter; SV sample valve.

Fig. 2. Reactor bed system for imperfect pulse chromatography.

DH detector housing; DSP detector-seal plate; GR guard ring (to support WG, WM); LW lead wire; OR O-ring; PT pressure tap; TCF thermal conductivity detector filament; WG wire gauze; WM wire mesh.

detection system was identical to the sample side. The detectors, however, were mounted in an empty column which was kept inside the constant-temperature oven. This arrangement minimized drift of the detection system. Current to the filaments was supplied by a constant-voltage DC-power supply. A two-channel recorder provided strip-chart recording of the response signals. The signals were simultaneously fed to the low-level side of analog-to-digital converter of a Hewlett-Packard 21 MX computer. The bridge circuits were similar to those employed in gas chromatographs. Details of the circuitry and of the instruments employed are given elsewhere.¹²⁾ The linearity of the recorders was checked and was found to be adequate. Recorded voltages were used for data re-

duction without conversion to concentrations.

After the columns were assembled and leak-tested, they were pretreated in helium at a temperature of about 125° for about 24 hours. Before a set of experimental runs was made, the equipment was allowed a stabilization time of about 8 hours and the computer was pre-programmed to sample the bridge voltages at a specified rate. In each measurement, the recorder and computer were started when the tracer was injected upstream of the first bed. A run was completed after the output peak had eluted completely. During a measurement series, a stabilization time for the system of about 10 minutes was allowed between changes in the flow rates of the carrier and reference gases. Further details of the experimental technique, including computerized data acquisition, are available.¹²⁾

Data smoothing was not employed, but corrections for baseline drift were made assuming that it was linear with time. The tail region of the response curves was extended as suggested by Edwards^{4,5)} and Sater and Levenspiel.²⁰⁾ Figure 3 shows the data processing employed. The moment method, shown on the left, was used to obtain starting values for fitting in the Fourier domain. In addition to the two methods shown, fitting in the time and imaginary domains was also employed. No significant differences were found for the dispersion measurement. Details are discussed by Kehinde.¹²⁾

The chromatographic technique requires a model to relate the pulse dispersion to the various processes occurring in the column. Of the models described in the literature, only the Kubin-Kucera model¹⁴⁻¹⁶⁾ was used.

For the dispersion measurements with non-porous glass beads, the model employed was

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x} \quad (1)$$

with boundary/initial conditions:

$$C(x, 0) = 0 \quad (2a)$$

$$\left. \frac{\partial C(t)}{\partial x} \right|_{x=L^-} = 0 \quad (2b)$$

$$C(-\infty, t) = \frac{D_L}{U} \left. \frac{\partial C(t)}{\partial x} \right|_{x=0^+} + C_{x=0^+}(t) \quad (2c)$$

Boundary conditions [(2b), (2c)] have occasioned controversy in past years. A recent study by Ioannidis¹¹⁾ has confirmed that the choice in this development is adequate. Laplace and Fourier transforms of the model and the first absolute moment and variance are given by Gangwal *et al.*⁶⁾ and Wen and Fan.³⁰⁾

Model parameters were obtained by fitting the above model to the experimental response in the

Fig. 3. Flow chart of data processing.

Fourier or imaginary domain. This procedure was chosen because it required appreciably less time than fitting in the time domain even when a fast Fourier transform was used to evaluate the convolution integral. Application of the procedure generated parameters virtually identical to those obtained by fitting in the time domain even for porous particles. Indeed, when dispersion alone occurs in the test section, evaluation of the transfer function as described by Hopkins *et al.*¹⁰⁾ and even the moment method give an adequate value of D_L .

Parameters obtained through fitting in the Fourier domain were always checked by comparing predicted response to experimental response in the time domain. This was accomplished by evaluating the convolution integral using the procedure developed by Wakao and co-workers.^{28,29)}

Measurements with Non-Adsorbing, Non-Porous Particles

Test bed lengths of 5.0 and 10.0 cm were used in dispersion experiments with tracer pulses of nitrogen, ethylene and benzene vapour in a helium carrier. Two different temperatures, 30 and 60°C, were employed.

A typical pair of Gaussian-like input-output curves

is shown in Fig. 4. Time zero is chosen as the time when a tiny switching disturbance pulse appears; zero point for the response is the voltage where the tracer pulse begins to form. The mean residence time in the test bed is taken as the time difference between the maxima of the input and output curves.

Axial dispersion measurements, expressed as Peclet number, are plotted against the particle Reynolds number for the three particle sizes used in Fig. 5. Points for two separate sets of measurements made with the 0.7-mm particles under identical conditions are shown. The agreement demonstrates the high level of reproducibility attained in this study.

Results for the 3- and 4-mm particles fall together and become asymptotic to the dashed line representing molecular diffusion in the bed at Reynolds numbers below 0.1. This behaviour is expected and, as Fig. 6 shows, it is widely observed.

The D_L data for the 0.7-mm particles fall below the line for molecular diffusion. They do not agree with the data of Gunn and Pryce,⁹⁾ which are also shown in Fig. 5. These data were obtained for 0.37- and 0.7-mm particles using an Ar-air system. Deviations from the molecular diffusivity limit indicate hydrodynamic mixing or short-circuiting resulting in increased axial

Fig. 4. Typical input-output curves in pure dispersion studies.

Fig. 5. Effect of particle size ($L = 10.0$ cm, $d_t = 1.905$ cm, N_2 (Tracer)/He, $T = 25.6^\circ\text{C}$).

dispersion.

Figure 5 shows an unexpected difference between the fine and coarse particles. The maximum in the Peclet number (N_{Pe}) has been observed before^{5,9}; what is surprising is the order of magnitude difference in N_{Pe} at the same Reynolds number using identical equipment and operating conditions (except for velocity).

One possible explanation, the influence of the tube diameter, was considered. With a tube diameter of 2 cm, the tube-to-particle diameter ratio ranged from 4.8 to 26.5 for the measurements. At lower ratios, the velocity profile in the column is no longer flat. According to Fig. 5, this seems to cause less mixing at lower N_{Re} than the situation where flow is essentially uniform except at the walls. To prevent velocity profile effects in packed beds, most investigators have used high values of the d_t/d_p ratio, generally larger than 10. Denbigh³ claims that when $d_t/d_p > 30$ the

Fig. 6. Summary of dispersion data.

To the original graph by Urban & Gomezplata²⁴ have been added data from Lee¹⁷ and from this study.

deviation from the flat velocity profile assumed in plug flow is not more than 20%. Stahel and Geankoplis,²³ however, suggest that if $d_t/d_p > 15$, the velocity profile is essentially flat or can be assumed so.

Carberry¹ allows for the tube diameter effect by defining an equivalent diameter, d_e , as

$$d_e = \frac{\varepsilon d_t}{\frac{3}{2} \frac{d_t}{d_p} (1 - \varepsilon) + 1} \quad (3)$$

where ε is the void fraction of the column. Employing this diameter, we may compare measurements with the 3- and 4-mm particles with those reported in the literature. Figure 6 is adapted from Scott, Lee and Papa²¹ and plots a Peclet number based on a velocity parameter, $u d_e$, introduced by Urban and Gomezplata.²⁴ Our data for the 3- and 4-mm particles agree well with the literature. This agreement confirms the usefulness of Carberry's proposal for particles greater than 3 mm.

Measurements with 0.7-mm particles fall on an extension of the data cluster of previous work and at low values of $u d_e$ approach a line representing the binary diffusivity for the gas mixture N_2 -He. The modified Peclet numbers are, however, an order of magnitude lower. The decrease in the Peclet numbers as velocity increases has been observed for both larger and smaller particles. Gunn⁸ suggests that the greater dispersion and the velocity effect arise from regions of anomalous packing in the bed which lead to channeling of the flow (and short-circuiting) or to local

fluidization. Moulijn and Van Swaaij¹⁹⁾ also suggest channeling as the source of the observation and identify it particularly as a problem with fine particles.

Two additional tracers (ethylene and benzene) were used with the 0.7-mm glass beads at 30 and 60°C. The Peclet numbers measured are compared with the N₂ tracer results at 25.6° in Fig. 7, with correction for different molecular diffusivities by plotting the ratio of the Peclet and Schmidt numbers vs. the Reynolds number. Below a N_{Re} of 0.02, the curves for all tracers and temperatures converge; some divergence of the ethylene tracer data, however, are evident above this Reynolds number. Results with these other tracers confirm the N₂-He data and indicate that the high levels of axial dispersion must arise from the bed and not from the signal detection or data reduction procedures.

Measurements with Absorbing, Non-Porous Particles

Dispersion measurements were repeated using glass beads coated with a methyl silicone liquid phase, OV-101, supplied by Chromatographic Specialities Ltd. This treatment introduced mass transfer into the system and required a different model. Only 0.7-mm glass beads were used. The test section length for these measurements was 5 cm. Details of the measurements and the model used are discussed elsewhere.¹³⁾

In the measurement series, loading of the liquid substrate, temperature, tracer and carrier gas were varied. Figure 8 shows that liquid loading, the thickness of the film coating the particle, does not affect axial dispersion. The scatter is experimental uncertainty. Measurements at temperatures of 30, 45 and 60°C with a constant liquid loading also showed scatter, but no temperature trend. Similarly, a change of tracer affected only the Peclet number at the lowest N_{Re} to the extent predicted by the change in the Schmidt number.

Figure 9 compares measurement of axial dispersion with and without the presence of mass transfer from the fluid to the particle surface. At the lowest Reynolds number used, where we have previously shown that mixing is due to molecular diffusion, the two curves coincide as would be expected. The interpretation of the shape of the Peclet number curves is that hydrodynamic or Taylor dispersion becomes unimportant when $N_{Re} < 0.02$ for this particle size. Consequently, the difference in the Peclet numbers for measurements on absorbing and non-absorbing particles arises in the region where Taylor diffusion must be considered. Significantly, the curve for measurements made in the presence of mass transfer lies above the measurements for pure dispersion. This suggests that less Taylor dispersion occurs with mass transfer, or rather, with coated particles. Three explanations seem possible. The silicone coating may form bridges

Fig. 7. Effect of tracer.

$L = 10.0$ cm, $d_p = 0.7$ mm, $t = 30^\circ\text{C}$; helium carrier with various tracers.

Fig. 8. Effect of liquid film thickness ($L = 5.0$ cm, $d_p = 0.7$ mm; benzene tracer in He carrier; 45°C).

Fig. 9. Comparison of dispersion (as Peclet number).

Measured in pure dispersion experiments and in presence of mass transfer ($d_p = 0.7$ mm, benzene tracer in He carrier).

between 0.7-mm particles, thereby altering the channel structure of the bed to promote more uniform flow. We implicate bed packing heterogeneity or

channeling to explain low values of N_{Pe} for the 0.7-mm particles. Bridging would close off the finer channels, but since the liquid coating is very thin, it will have little effect on the larger channels. Consequently, the distribution of velocities at points in the cross-section of the bed may be smaller and reduce mixing by Taylor dispersion.

A second explanation is that bridging may lead to aggregates in the bed, thereby raising the effective diameter which appears in the numerator of both the Peclet number and the Reynolds number. The results would be almost exactly described if bridging doubles the effective size of particles, since the curves would be shifted upwards along a 45° line in Fig. 9.

The final explanation for the difference is that at extremely low Reynolds numbers the dispersion-mass transfer model becomes unsatisfactory. After all, the model implies that mass transfer occurs to isolated particles in the fluid stream, whereas in the real bed we are dealing with particles which are members of clusters or aggregates.

Measurements with Porous Particles

A further set of experiments was performed with porous alumina particles whose mean diameter was approximately 0.7 mm. Internal diffusion as well as mass transfer is introduced in this way. Again, a different model must be used to reduce the data.¹³⁾ The length of the test column for these experiments was 10 cm. The measurements were carried out using nitrogen as the tracer gas.

No variation of axial dispersion was found over a temperature range of 45 to 119°C. This may be seen in Fig. 10. The figure compares data taken with three types of systems. It is evident that in the region of low Reynolds numbers, the data converge to the molecular diffusion limit. In the region where Taylor dispersion becomes important, Peclet numbers are substantially different even though they show the same trend with Reynolds number. Measurements made with porous particles indicate less axial mixing than would be observed if the particles had no porosity. It is difficult to find an explanation because the measured bed porosities are identical for both porous and non-porous particles. Perhaps particle shape is a factor because this did differ, or homogeneity of the packing is affected. The dependence of the pressure drop in packed beds on particle shape is well established at Reynolds numbers higher than those used in this study.

Perhaps these results signal a failure of the model at the low Reynolds numbers studied. It is interesting that in the data-fitting exercise, mass transfer from the fluid to the porous particle contributes a resistance which makes a negligible contribution to spreading. Thus, we cannot use the argument of aggregation

Fig. 10. Comparison among dispersion (as Peclet number) measured in pure dispersion experiments and in the presence of mass transfer and internal diffusion ($L=10$ cm; $d_p=0.7$ mm, $\varepsilon_p=0.564$ benzene tracer in He carrier).

invoked in the previous section.

Measurements for the silicone particles were made with benzene and ethylene tracers. Dividing by the diffusivity or the Schmidt number brings the data points at $N_{Re} \sim 0.02$ together but it fails to desegregate the data at higher Reynolds numbers. Indeed, it causes Peclet numbers measured with porous particles to show the largest departure from the Peclet numbers representing pure dispersion.

Measurements with the porous particles were also made using ethylene as a tracer. Ethylene chemisorbs on alumina at the temperatures used. Although Peclet numbers measured in the presence of adsorption showed considerable scatter, they were in general agreement with the data shown in Fig. 10.

Conclusion

Our purpose in this paper has been to supplement the scanty data on axial dispersion in packed beds of particles at Reynolds numbers less than one. Our measurements found in the low Reynolds number region a maximum Peclet number seen previously by Edwards and Richardson,⁵⁾ and by Urban and Gomezplata.²⁴⁾ It seems likely that this phenomenon arises from non-homogeneous regions in the packing.

Perhaps the most significant finding is that even with a parameter such as axial dispersion, one of the easiest parameters to measure experimentally, the values obtained seem to reflect the local environment in the bed. We have demonstrated that different val-

ues of axial dispersion are obtained when other processes such as mass transport and internal diffusion are present. Wakao²⁶⁾ made a similar claim but presented no experimental verification. This disturbing result can only call into question, at Reynolds numbers less than one, the validity of the conventional dispersion-fluid particle transport model used to describe packed beds.

Acknowledgments

Grateful acknowledgment is made of financial support from the Natural Sciences and Engineering Research Council, Ottawa, as well as fellowship support (for A.J.K.) from the Government of Nigeria and the University of Lagos. Helpful advice and computer programs were provided by Professor N. Wakao, Yokohama National University, Japan, and Mr. T. Funazukuri, formerly of Yokohama National University and currently of our own laboratory.

Nomenclature

C	= concentration in bulk gas	[mol/cm ³]
d_e	= equivalent diameter defined in Eq. (7)	[cm]
d_t	= column diameter	[cm]
d_p	= particle diameter	[cm]
D_L	= axial diffusivity	[cm ² /s]
L	= bed length	[cm]
$N_{Pe,p}$	= particle Peclet number	[—]
$N_{Re,p}$	= particle Reynolds number	[—]
N_{Sc}	= Schmidt number	[—]
t	= time	[s]
T	= half-time	[s]
U	= interstitial velocity	[cm/s]
x	= axial coordinate	[cm]
ε	= column void fraction	[—]

Literature Cited

- Carberry, J. J.: "Chemical and Catalytic Reaction Engineering," McGraw-Hill, New York (1976).
- Cerro, R. L. and J. M. Smith: *AIChE J.*, **16**, 1034 (1970).
- Denbigh, K.: "Chemical Reactor Theory," Cambridge University Press, Cambridge 1966.
- Edwards, M. F.: Ph. D. Dissertation, University of Wales (1966).
- Edwards, M. F. and J. F. Richardson: *Chem. Eng. Sci.*, **23**, 109 (1968).
- Gangwal, S. K., R. R. Hudgins and P. L. Silveston: *Can. J. Chem. Eng.*, **57**, 609 (1979).
- Gangwal, S. K., R. R. Hudgins and P. L. Silveston: *Can. J. Chem. Eng.*, **58**, 33 (1980).
- Gunn, D. J.: *Trans. Inst. Chem. Engrs.*, **49**, 109 (1971).
- Gunn, D. J. and C. Pryce: *Trans. Inst. Chem. Engrs.*, **47**, 341, 351 (1969).
- Hopkins, M. J., A. J. Sheppard and P. Eisenklam: *Chem. Eng. Sci.*, **24**, 1131 (1969).
- Ioannidis, G.: M. A. Sc. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1978.
- Kehinde, A. J.: Ph. D. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1980.
- Kehinde, A. J., R. R. Hudgins and P. L. Silveston: *J. Chem. Eng. Japan*, **16**, 483 (1983).
- Kubin, M.: *Collect. Czech. Chem. Commun.*, **30**, 1104 (1965).
- Kubin, M.: *Collect. Czech. Chem. Commun.*, **30**, 2900 (1965).
- Kucera, E.: *J. Chromatogr.*, **19**, 237 (1965).
- Lee, W.: Ph. D. Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1975.
- McHenry, Jr., K. W. and R. H. Wilhelm: *AIChE J.*, **3**, 83 (1957).
- Moulijn, J. A. and W. P. M. van Swaaij: *Chem. Eng. Sci.*, **31**, 845 (1976).
- Sater, V. E. and O. Levenspiel: *I/EC Fund.*, **5**, 86 (1966).
- Scott, D. S., W. Lee and J. Papa: *Chem. Eng. Sci.*, **29**, 2155 (1974).
- Sinclair, R. J. and O. E. Potter: *Trans. Inst. Chem. Engrs.*, **43**, T3 (1965).
- Stahel, E. P. and C. J. Geankoplis: *AIChE J.*, **10**, 174 (1964).
- Urban, J. C. and A. Gomezplata: *Can. J. Chem. Eng.*, **47**, 353 (1969).
- Wakao, N.: personal communication.
- Wakao, N.: *Chem. Eng. Sci.*, **31**, 1115 (1976).
- Wakao, N., Y. Iida and S. Tanisho: *J. Chem. Eng. Japan*, **7**, 438 (1974).
- Wakao, N., K. Tanaka and H. Nagai: *Chem. Eng. Sci.*, **31**, 1109 (1976).
- Wakao, N. and S. Tanisho: *Chem. Eng. Sci.*, **29**, 1991 (1974).
- Wen, C. Y. and L. T. Fan: "Models for Flow Systems and Chemical Reactors," Marcel Dekker, New York (1975).