CHROMATOGRAPHIC EFFECTS OF VARYING PARTICLE SIZE AND SIZE DISTRIBUTIONS OF SUPERFICIALLY POROUS PARTICLES

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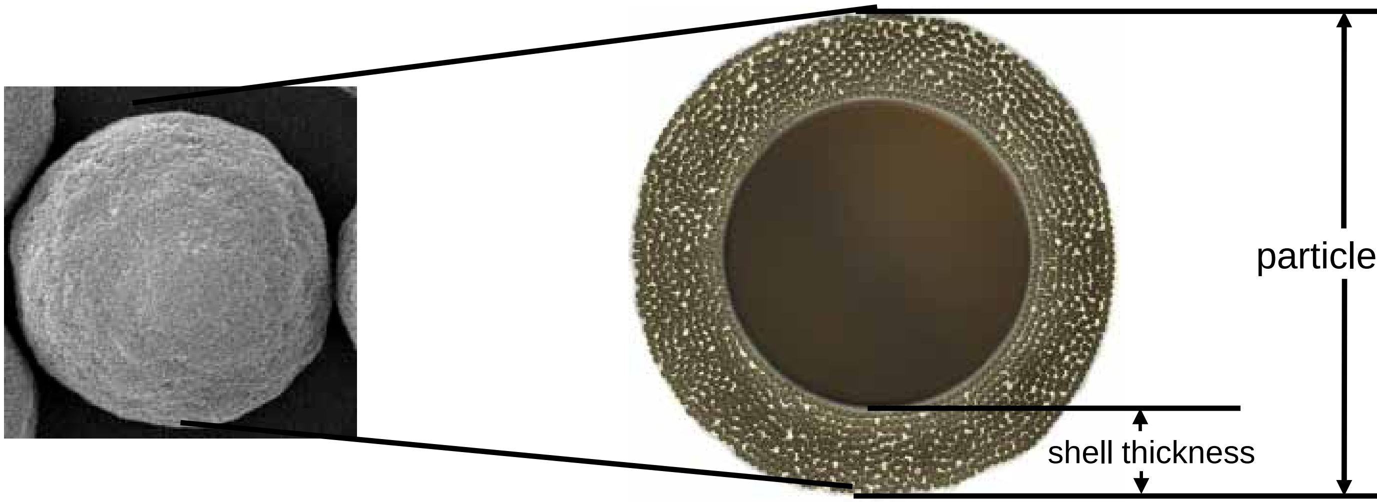
ABSTRACT

Sub-3-micron fused-core® (superficially porous, core-shell or porous shell) particles have been shown to have distinct performance advantages over comparable totally porous particles for separating small molecules. Columns of 2.7 µm fused-core particles show higher efficiency than totally porous particles of similar size, likely because of superior eddy diffusion properties (smaller van Deemter A term) resulting from exceptionally narrow particle size distributions, higher density and the ability to form homogeneous packed beds. The efficiency for columns of 2.7 µm fused-core particles actually rivals that for sub-2 µm totally porous particles with only about one-half the back pressure. Fused-core particles with a wide range of uniform particle sizes were synthesized to allow the preparation of stable, efficient packed columns for this study. These columns were used to measure the effects of particle size and size distributions (varied by mixing particles of different sizes in the 2 – 5 µm range) on chromatographic performance. This report describes the effect of these particle characteristics on several factors of separation importance, including reduced plate height and pressure. The performance of the larger fused-core particles (4.6 µm) exceeded expectations, likely because larger particles are easier to pack into more homogeneous packed beds than smaller particles.

HALO® Fused-Core Particles



SEM of HALO Fused-core

Graphical representation of HALO Fused-core

CHARACTERISTICS OF PARTICLES USED IN THIS STUDY

Total Particle Size	Shell Thickness	Core Diameter	Surface Area
2.0 microns	0.5 micron	1.0 micron	100 m^2/g
2.7 microns	0.5 micron	1.7 microns	125 m^2/g
4.1 microns	0.55 micron	3.0 microns	105 m^2/g
4.6 microns	0.6 micron	3.4 microns	95 m^2/g

TEST CHROMATOGRAM

Test Conditions:
Columns: 3.0 x 50 mm
Mobile Phase: 60/40 ACN/H_2O
Flow Rate: varied
Temperature: ambient (ca. 22 ^oC)
Detector: semi-micro UV @ 254nm
Peak Identities:
1. **Uracil (t_0 marker)**
2. **Phenol**
3. **4-Cl-1-nitrobenzene**
4. **Naphthalene (k values 3.3 to 3.8)**

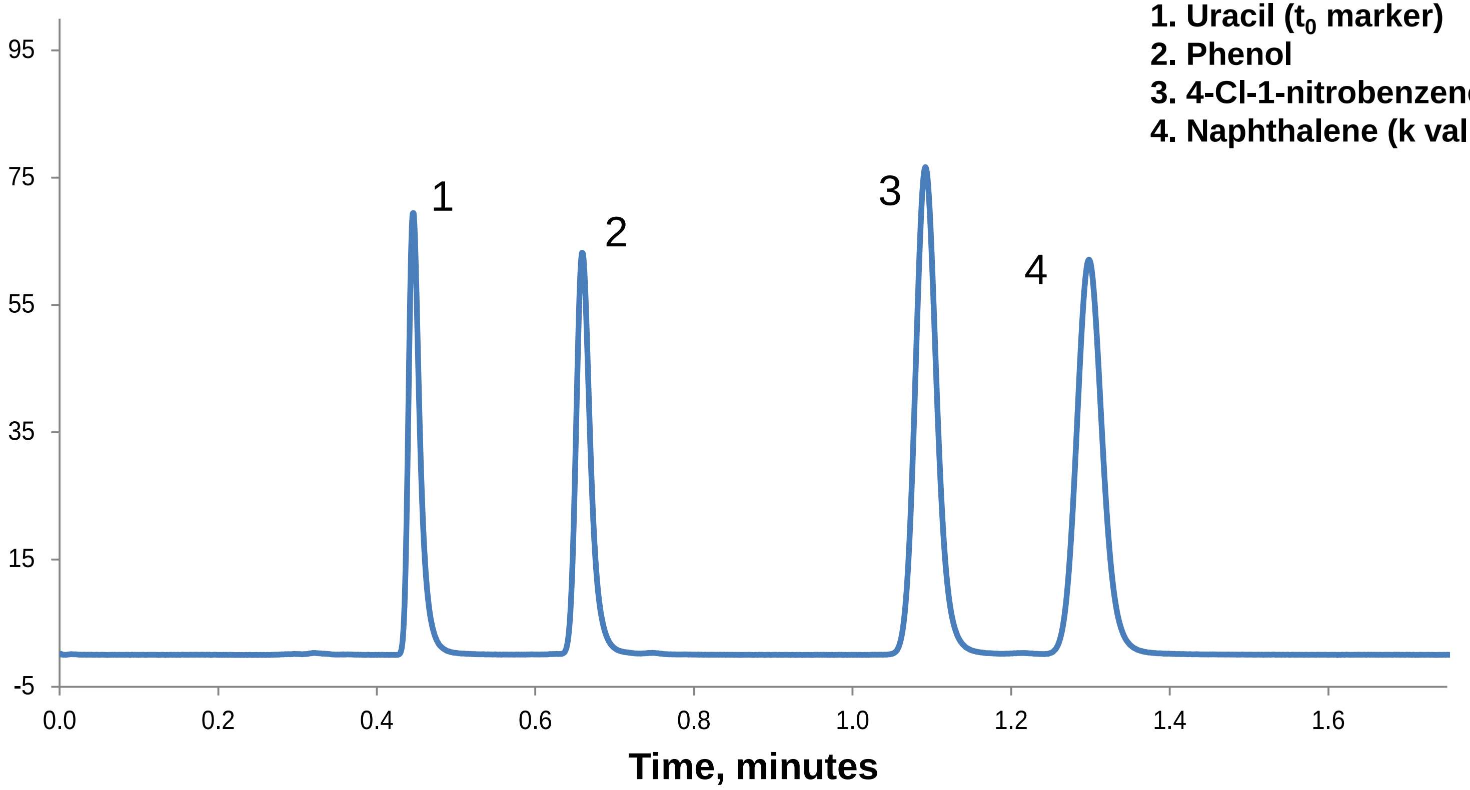
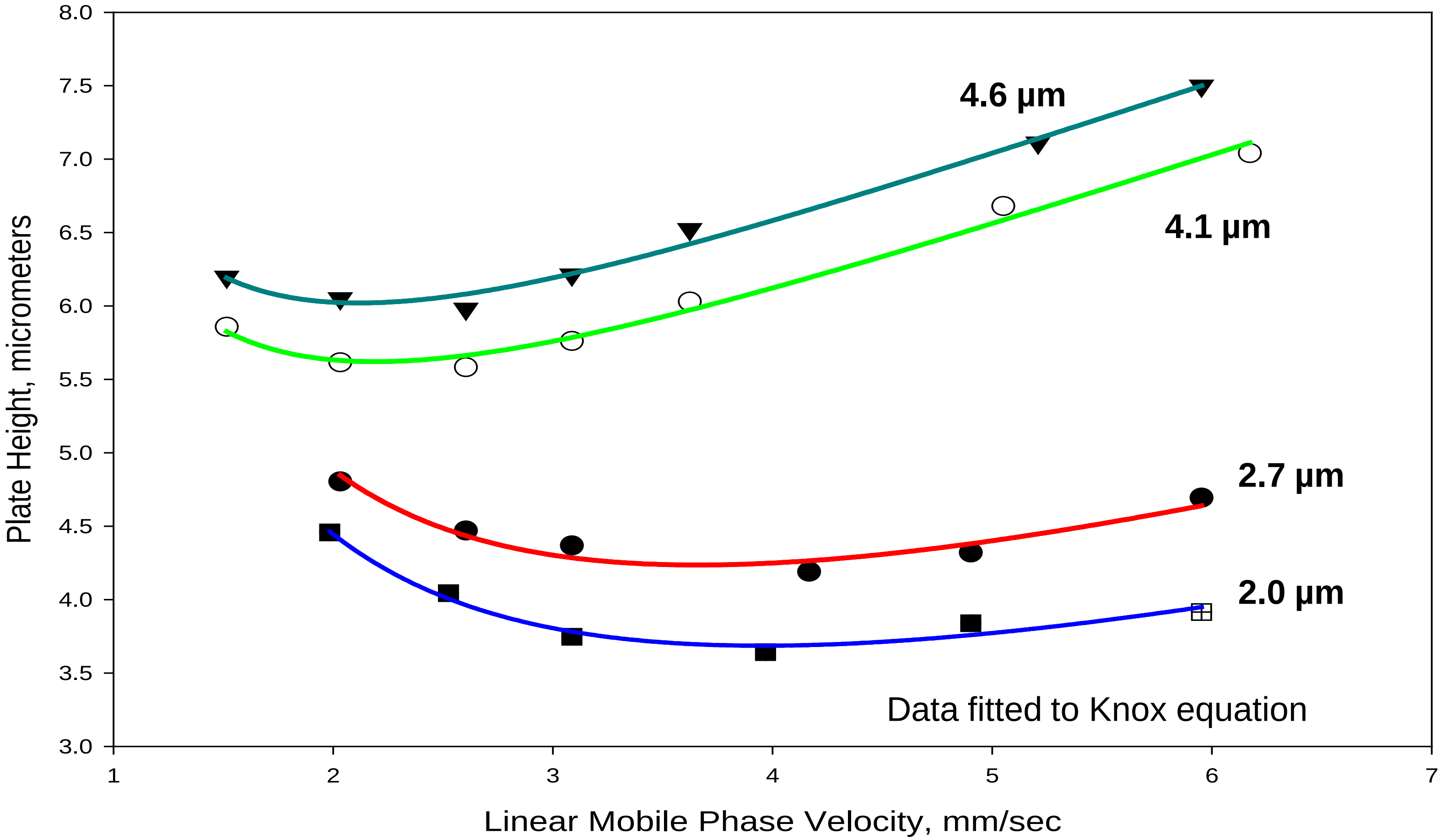
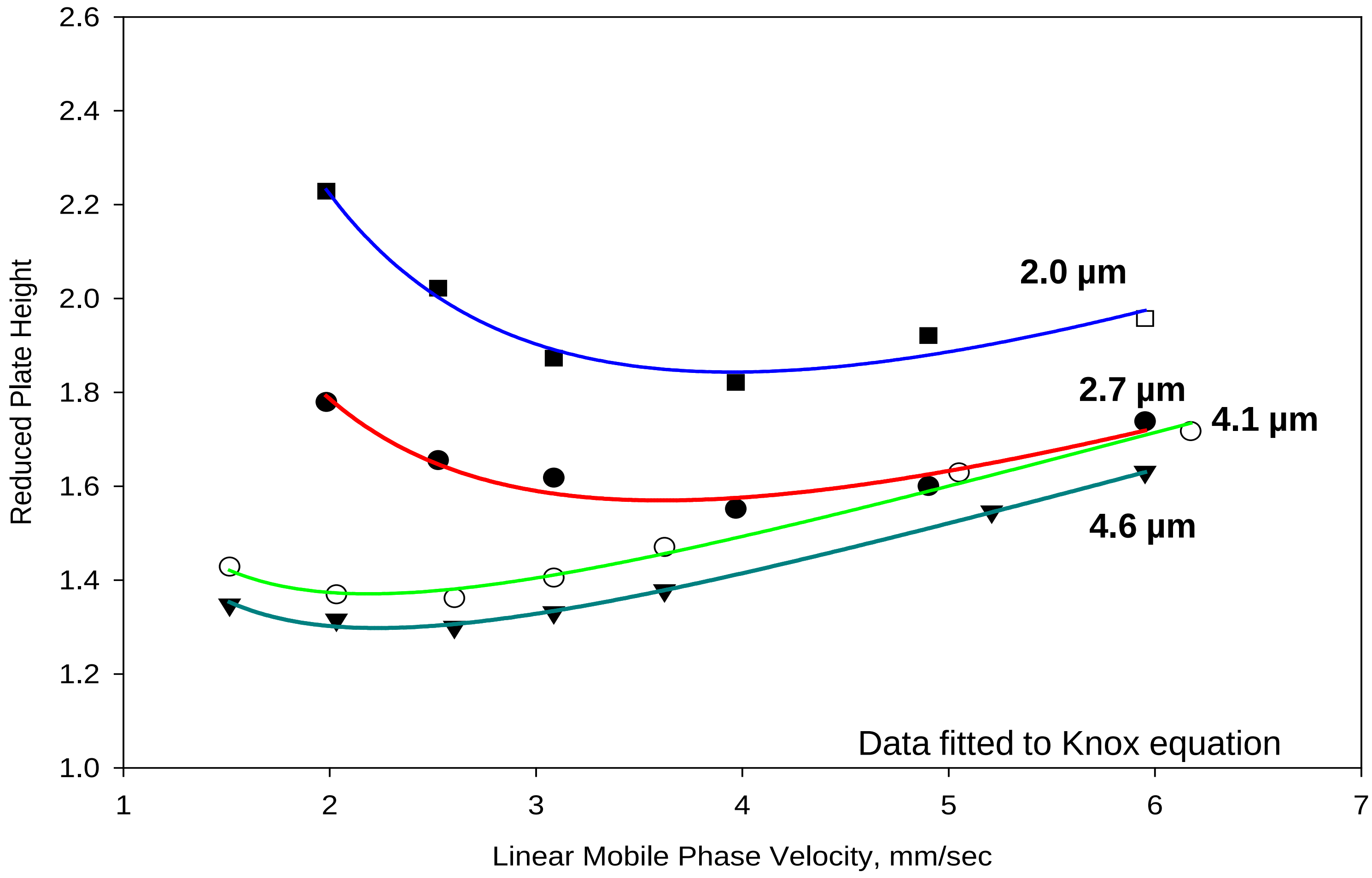


Plate Height Vs Velocity Plots



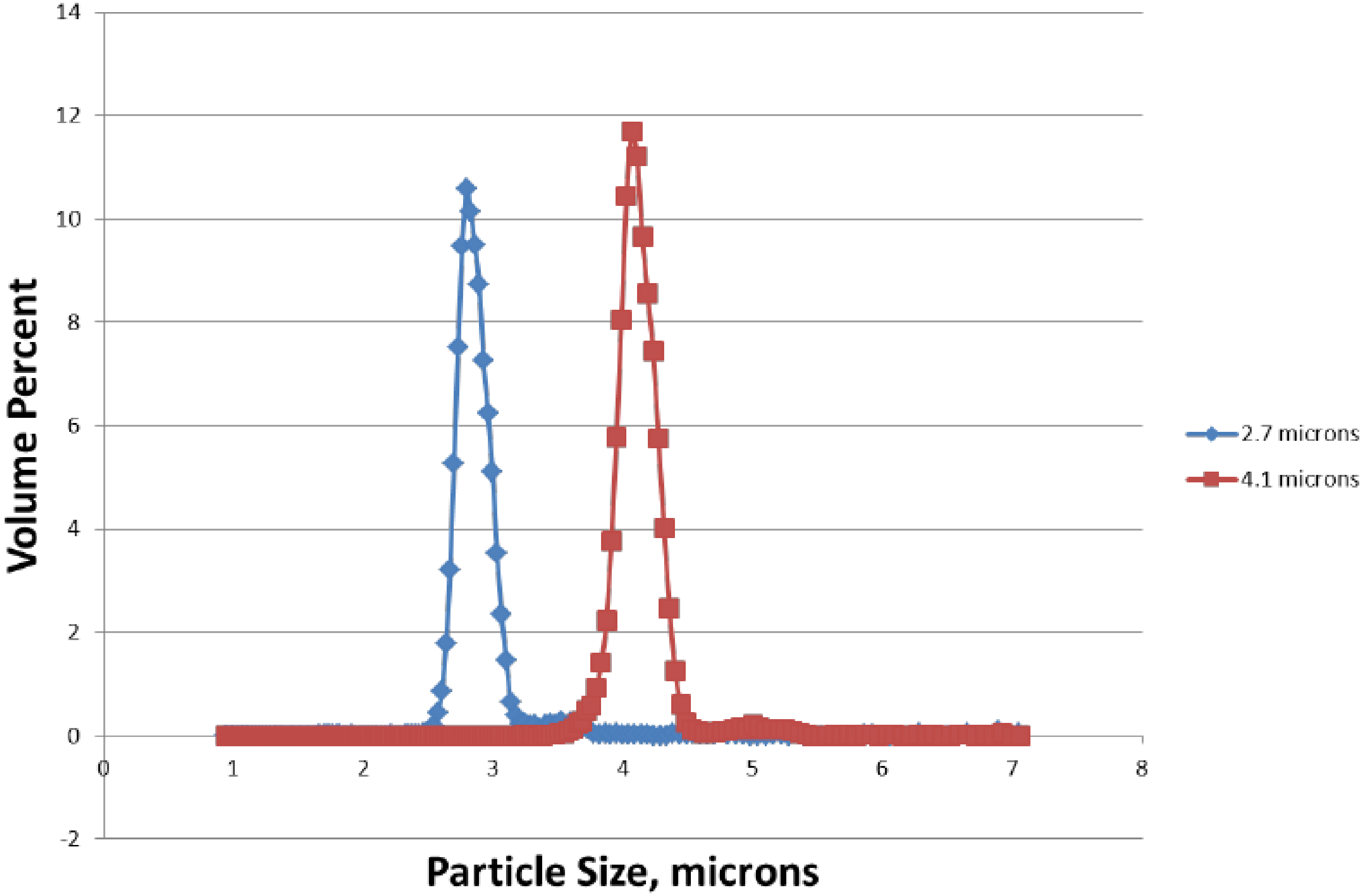
The Plate Heights of columns packed with particles of different sizes, as expected, get smaller as the particle size gets smaller.

Reduced Plate Height Vs Velocity Plots



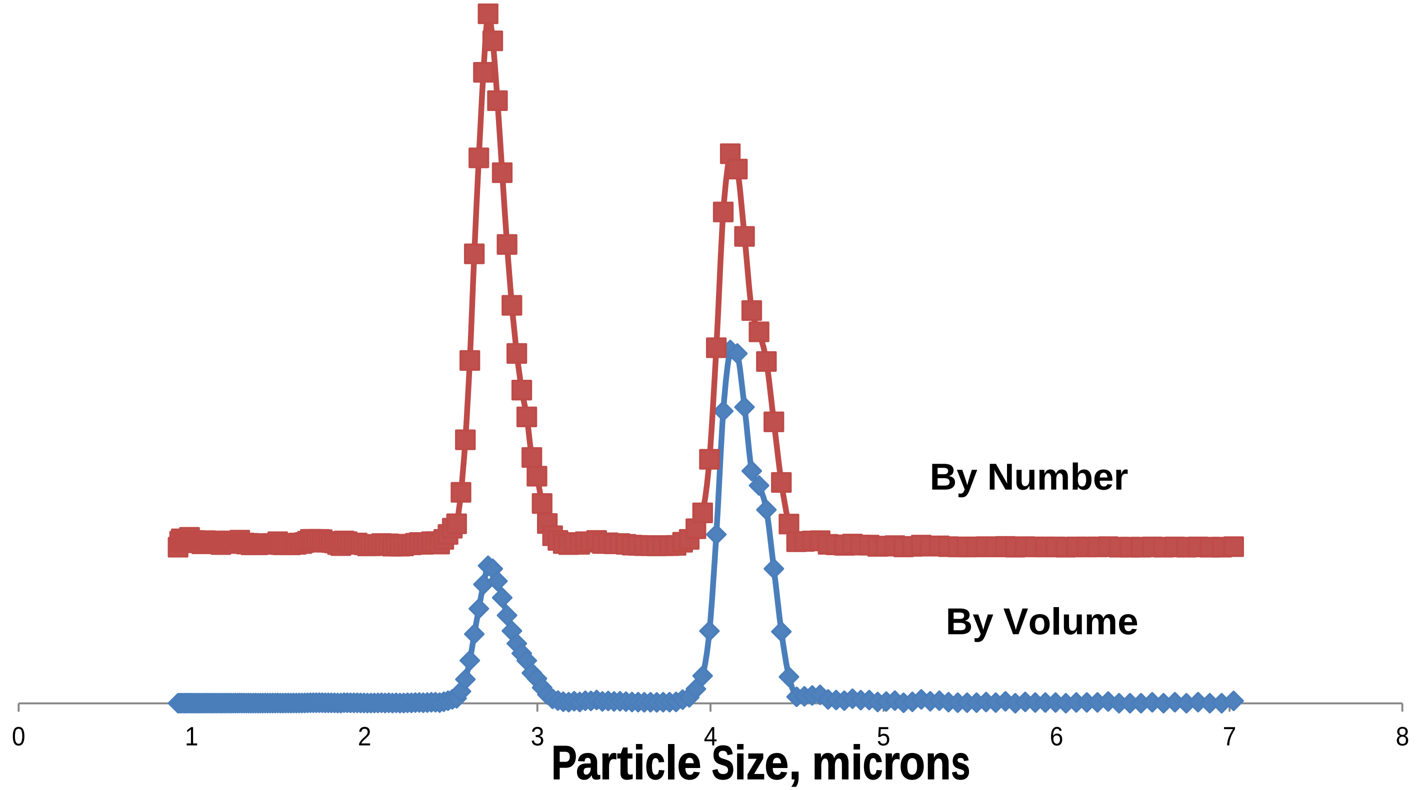
Reduced Plate Heights ($h = H/d_p$) get smaller as the particle size is increased, indicating more homogeneity in packed beds for the larger particles.

Overlay of Size Distributions of Individual Batches of 2.7 µm and 4.1 µm Fused-core Particles



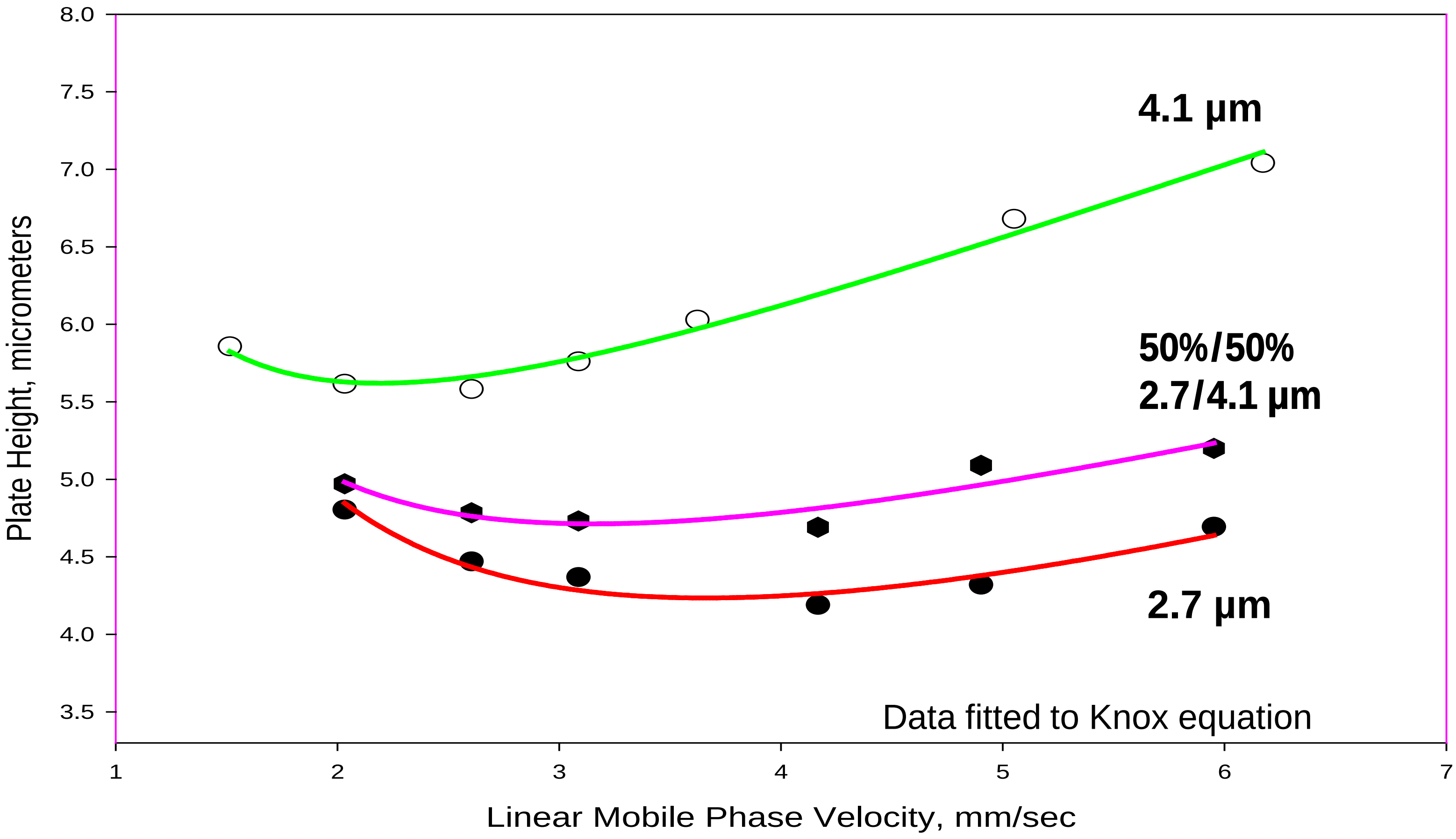
Individual batches of Fused-core particles exhibit very narrow particle size distributions.

Actual Size Distributions of a 50/50 Mixture of 2.7 and 4.1-Micron Particles



- Mixtures of different sized particles can be measured by Coulter Counter and give different values if assessed by number or volume.
- Measurement of particle size by volume is more representative of the contents of a column than is size by number.

Plate Height Vs Velocity Plots Including Mixed Particles



50/50 mix of 2.7 and 4.1 µm particles produces a column with plate heights intermediate to the components of the mixture.

Comparison of Single-Sized Particles and a Mixture

Packing Particles	d_p90[a]	d_p10[b]	d_p90/d_p10	Plate Number (N)*	Plate Height (H)*	Pressure (bar)*	Plates per bar
4.1 µm	4.30	3.89	1.11	8590	5.58	34	253
2.7 µm	3.02	2.69	1.12	11950	4.19	128	93
50/50 mix 4.1/2.7 µm	4.26	2.63	1.62	10650	4.69	94	113

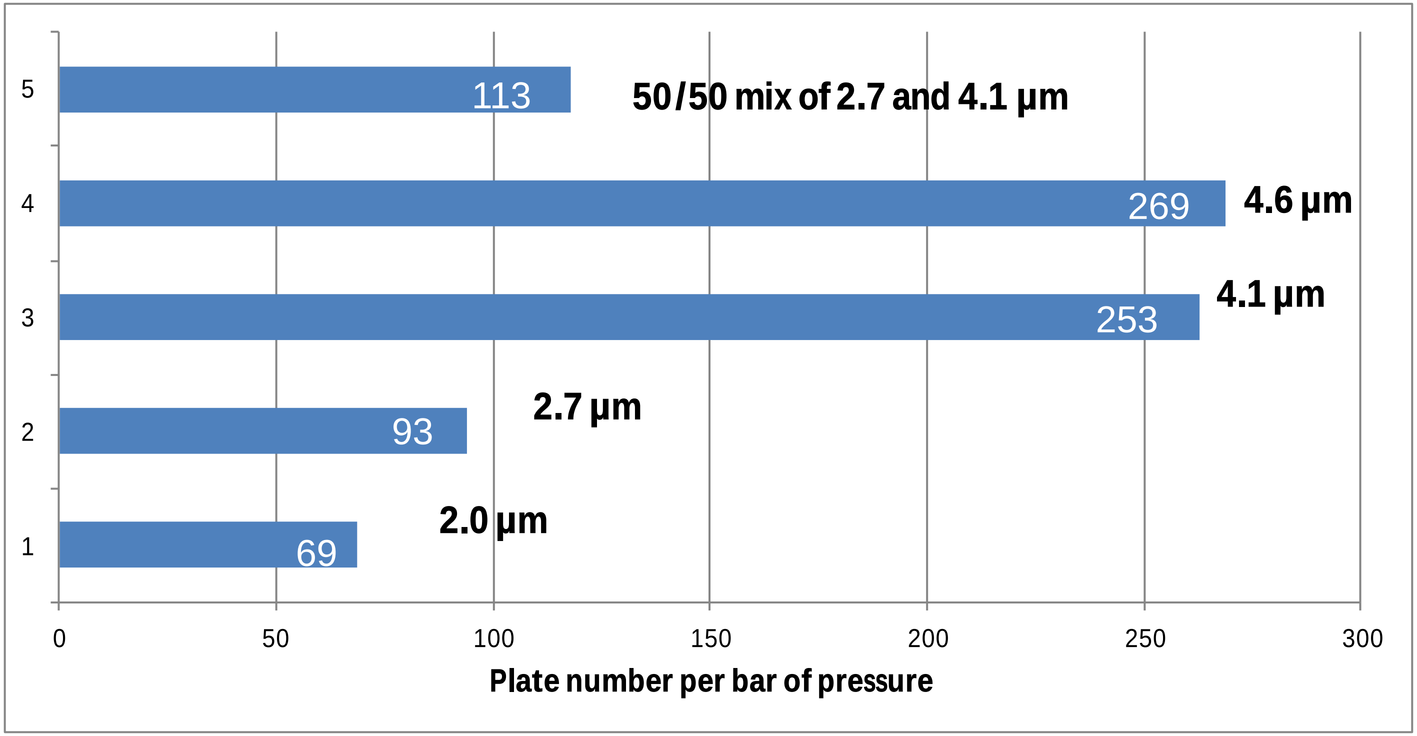
*** Values taken at optimum flow**

[a] d_p90 indicates that 90% of the particles are smaller than the given size
[b] d_p10 indicates that 10% of the particles are smaller than the given size

- High efficiency is still possible for a mixed bed of particles of different sizes, but the pressure increase is not favorable.

Plate Number Per Unit of Pressure

(Plate number and pressures taken at optimum flow for each particle size)



- **The plate number available per unit of pressure greatly increases as the particle size is increased.**
- **The column containing a mixture of large and small particles is not a good compromise of performance features because pressure changes faster than plate number with changes in average particle size.**

Conclusions

1. **Fused-core particles can be synthesized with different particle diameters to produce columns with high efficiencies.**
2. **Columns packed with Fused-core particles of different diameters show improvement in Plate Heights as the particle size is reduced.**
3. **Reduced Plate Heights (column efficiencies normalized for particle size) show the opposite effect – with columns of larger particles having smaller Reduced Plate Heights than smaller particles – indicating larger particles may be easier to pack into homogeneous beds.**
4. **Mixtures of larger and smaller particles can provide good column performance but the resulting pressure makes this a bad compromise.**
5. **Narrow particle size distributions for Fused-core packings may not be solely responsible for the exceptionally high performance of columns packed with superficially porous particles as predicted by recent computer modeling studies (e.g., J. Chrom. A , 1218 (2011) 6654–6662; High performance liquid chromatography column packings with deliberately broadened particle size distribution: Relation between column performance and packing structure; Anuschka Liekens, Jeroen Billen, Ron Sherant, Harald Ritchie, Joeri Denayer, Gert Desmet).**

Acknowledgements

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