A Theoretical Study on the Advantage of Core-shell Particles with Radially-oriented Mesopores

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Abstract

We report on a first-principles numerical study explaining the potential advantage of core-shell particles with strictly radially-oriented mesopores. Comparing the efficiency of these particles with fully porous and core-shell particles with a conventional (i.e., randomly oriented) mesopore network, the present numerical study shows a similar strong reduction in minimal reduced plate height (h_{min}) as was very recently observed in an experimental study by Wei et al (resp. a h_{min}-reduction on the order of about 1 and 0.5 reduced plate height-units). As such, the present work provides a theoretical basis to understand and confirm their experimental findings and quantifies the general advantage of "radial-diffusion-only" particles. Determining the effective longitudinal diffusion (B-term contribution) in a series of dedicated, independent simulations, it was found that this contribution can be described by a very simple, yet fully exact mathematical expression for the case of "radial- diffusion-only" particles. Using this expression, the significant increase in efficiency of these particles can be fully attributed to their much smaller B-term band broadening, while their C-term band broadening (representing the mass transfer resistance) remains unaffected.

1. Introduction

In the past 10 years, core-shell (CS) particles have revolutionized the speed and efficiency of chromatographic separations [1-7]. The introduction of these CS particles can be considered as a rejuvenation of the pellicular particle concept proposed by Horvath and Lipsky back in the 1960's [8]. These particles owe their advantage for a small part to the shorter internal diffusion distances, but especially to their significantly lower B-term band broadening [9-10], their lower internal volume (leading to a lower zone retention factor for a given phase retention factor [11]) and to their apparent lower eddy-dispersion [10]. Although the latter is still under debate, it could be related to the fact that core-shell particles can typically be produced with a much narrower particle size distribution than fully-porous particles [12-13], except for some notable exceptions [14-15]. Because of the aforementioned advantages, core-shell particles rather have a reduced minimal plate height of around $h_{min}=1.5$, compared to $h_{min}=2$ for fully-porous particles. In addition, the lower internal volume also leads to a lower t_0-time-based flow resistance, adding further to the kinetic advantage of this particle type [16].

In a very recent publication, Wei et al. [17] have proposed a new type of core-shell particle that has the potential to make another leap in efficiency and speed. This material is of the core-shell type but, being based on pseudomorphic transformation (PMT) micelle templating, has all its mesopores oriented purely radially. Because of this orientation (and the presence of the core), it can be expected that the longitudinal diffusion (B-term contribution) will be strongly suppressed, while the C-term mass transfer processes can still go on nearly undisturbed. With

this material they could demonstrate unprecedented reduced minimal plate heights of $h_{min}=1.0$, thus reaching a new "magical" boundary.

To support these findings from a theoretical point of view and delimit the potential efficiency and kinetic performance limits of core-shell particles with radially-oriented mesopores (CS-ROM), we report here on a series of computational fluid dynamics simulations to accurately simulate the band broadening in simplified, perfectly ordered CS-ROM particle beds. The obtained reduced plate height curves are compared with data sets previously obtained for fully porous and core-shell particles with conventional isotropic internal diffusion. To allow for a fair comparison, the different particle types are compared for the same particle arrangement, the same values for the mobile zone and porous zone diffusion coefficients, as well as the same zone retention factor k" (defined via the relation $u_R=u_i/(1+k")$, wherein u_R is the effective band migration speed and u_i is the interstitial velocity).

The results are analyzed using the general plate height model of packed bed chromatography [18-23], according to which the dimensionless plate height can be written as the sum of 4 different contributions:

$$h=h_{inhom}+h_B+h_{Cm}+h_{Cs} \qquad (1)$$

wherein h_B represents the effective longitudinal diffusion (which is the only remaining source of band broadening when the flow is arrested), wherein h_{Cm} and h_{Cs} arise from the finite time needed for the mass transfer between the interstitial space and the particles, and wherein h_{inhom} groups all band broadening contributions arising from the heterogeneities of the velocity field of the bed. According to the general plate height model, the way in which h varies with the reduced interstitial velocity ν_i is, apart from the bed geometry, fully determined by the value of the zone retention factor k" defined above and the ratio between the porous zone and the mobile diffusion coefficient (D_{pz}/D_{mol}) [20,24]. In the present study, we have considered two widely differing values for this ratio, one corresponding to a value that, at least for the case of small molecular weight compounds in reversed phase LC, can be considered as very large ($D_{pz}/D_{mol}=0.5$) and one very small ($D_{pz}/D_{mol}=0.1$).

2. Geometries and numerical methods

2.1 Geometries and flow, retention and diffusion parameters
Fig. 1 shows an axial cut of the simulation geometries used in the present study for each of the three different particle types: fully porous (Fig. 1a), CS particles with conventional (i.e., isotropic) diffusion (Fig. 1b) and CS-ROM particles (Fig. 1c). The default domain length was 153 µm but was extended to 307 µm for those cases (typically at high reduced velocity) where the standard length was too short to reach the long-time limit plate height value (see Section 2.3). The color pattern in overlay represents the species distribution recorded at a given moment in time.

The flow domain was composed of a 2D ordered arrangement of disks (representing the cross-section of cylindrical pillars with an infinite height) with an outer diameter d_o=2μm. Their centers were arranged on the vertices of a tile pattern made up of equilateral triangles. The flow direction was perpendicular to one of the sides of these triangles. During the calculation of the velocity and the species distribution fields, the sidewalls were put at symmetry, to mimic an infinitely wide domain. To account for the presence of an impermeable core, the core-shell disks contained a smaller concentric disk (radius r_i=1.26, relative radius=0.63) that was made impermeable to the species.

2.2 Simulation Methods

All simulations were performed with Ansys® Workbench version 16.2 from Ansys, Inc., purchased from Ansys Benelux, Wavre, Belgium. Within this software platform all flow domains were drawn with Ansys® Design Modeler and meshed with Ansys® Meshing. All simulations were performed with Ansys® Fluent.

Mesh

The shortest flow domains (153 μm) were divided in 5.10^5 mesh cells, the longer domains (307 μm) contained twice as many cells. Mainly quadrilateral cells were used, with a small fraction (less than 0.2%) of triangular cells. Mesh inflation layers were imposed on the disk walls on both sides (in the mobile zone as well as in the stationary zone) to capture the steepest velocity- and concentration gradients. Fifteen layers with a thickness growth rate of 1.1, resulting in a cumulative thickness of 0.17 μm were used. To check mesh independency, a mesh containing cells half the original size, resulting in a quadruple cell count, was used. At $\nu_{l=}16$, the difference in plate height recorded with this finer mesh was only 0.15% smaller than in the original mesh. Therefore it was concluded the original mesh yields sufficient accuracy.

Solver

First, the velocity fields were computed solving the Navier-Stokes equations using the segregated pressure-based steady-state solver. For spatial discretization, the least squares cell based method was used to calculate gradients, the SIMPLE scheme for pressure-velocity coupling, the second order interpolation scheme for pressure and second order upwind scheme for momentum. Boundary conditions were set to symmetry (for the side walls) and the in- and outlet planes were put at a fixed pressure, respectively at 112487.39 Pa and 101325.00 Pa. The outer walls of the disks were set to the no-slip condition. Material properties in the mobile zone were these of water.

Subsequently, the outer wall of the disks was set to interior, to allow diffusion of the species from the mobile zone to the stationary zone and vice versa. The transient solver, with second order implicit temporal discretization and second order upwind scheme for spatial discretization was then used to solve the convection diffusion equation yielding the transient

concentration field of tracer band migrating through the flow domain. A fixed time stepping method with 500 to 3000 steps of size $5.10-5$ s was used. The tracer was assigned the same properties as the water it was dissolved in.

Diffusion in the mobile zone was always isotropic and was characterized by the diffusion coefficient D_{mol}. Its value was tuned to produce different values of ν_i. The diffusion in the stationary zone was either put at $D_{pz}/D_{mol}=0.5$ or at $D_{pz}/D_{mol}=0.1$. To mimic the special case of the radial-only diffusion in the CS-ROM particles, the diffusion in the disks was made anisotropic, using user defined functions to assign each disk its proper anisotropic diffusion tensor (Cartesian coordinates), resulting in diffusion only in the radial direction of the respective disk.

Retention

In all considered cases, the zone retention factor of the analytes was put at $k''=8$, which, assuming a typical values for the intra-particle porosity $\varepsilon_{pz}=0.35$, corresponds to a phase retention factor of $k'=4.9$ for the fully-porous particles and to a phase retention factor of $k'=5.8$ for both core-shell types. Both can be considered as very typical for an LC separation.

Hardware

All simulations were performed on Dell Power Edge R210 Rack Servers each equipped with an Intel Xeon x3460 processor (clock speed 2,8 GHz, 4 cores) and 16 Gb, 1333 MHz ram memory, running on Windows server edition 2008 R2 (64-bit). Simulations of the steady-state velocity field in the aforementioned geometries took about 1 hour, while the transient species concentration field simulations took about 24 hours.

2.3 Determination of plate heights

Plate heights were determined by following the variance of a tracer band migrating through the flow domain. The initial species concentration of this band was defined by implementing a Gaussian distribution curve ($\sigma_x=1$ µm) near the inlet of the domain. Depending on the reduced velocity, the position of this band was adapted to be far enough downstream to avoid any tracer leaking from the inlet (going from 7 µm from the inlet at high ν_i to 50 µm at low ν_i).

At the end of each time step the 0th, 1st and 2nd order non-central moments (μ_0, μ_1 and μ_2) of the tracer concentration as function of the x-coordinate (flow direction) were reported. These were used to calculate the band's variance σ_x^2 [25-26]. After each time step, a local plate height was calculated by dividing the difference with the variance at the preceding time by the elapsed distance during this time step.

The resulting local plate height is then followed as a function of the band's position. After a sufficient distance this curve reaches an asymptotic value, which is then reported as the plate height representative for the studied condition.

2.4 Determination the effective diffusion coefficient (B-term constant)

The diffusion-only component of the band broadening was also computed independently. This was done by carrying out the same type of diffusion-only simulations as already described in [27]. In brief, this method consists of assigning fixed, but different values for the tracer concentration at the inlet and outlet of a flow domain containing only one representative unit cell. Subsequently, the steady-state concentration field is calculated in the absence of any fluid motion by solving the diffusion equation. Reporting the value of the species flux at either the inlet or outlet plane then allows to directly calculate the effective diffusion coefficient.

3. Results

3.1 Plate height data and analysis

Fig. 1 shows images of the species distribution at the moment when the band has moved to some intermediate position in the bed for the case of a reduced interstitial velocity of 16 (ν_i=16). As can be seen from the axial width of the color distribution, as well as from the C_{max}-values in the caption to Fig. 1, the amount of band broadening decreases significantly going from the fully porous (Fig. 1a), to the CS (Fig. 1b) and finally to the CS-ROM particles (Fig. 1c).

Fig. 2 summarizes and quantifies the results from all conducted band broadening simulations. Confirming the images in Fig. 1, the three considered particle types lead to important differences in reduced plate height. According to the general plate height model, the differences between the different particle types observed in Fig. 2 should be exclusively due to the differences in the intra-particle geometry, because all simulations have been carried out for the same particle arrangement, as well as the same zone retention factor k" and the same values for the diffusion coefficients D_{pz} and D_{mol}. Considering the strong emphasis this field has always been putting on packing uniformity and external mass transfer when discussing column efficiency, much more than on the intra-particle properties, the observed differences are impressively large.

Whereas the conventional CS particles already have a h_{min}-value that is, depending on the D_{pz}/D_{mol}-ratio, between 0.28 and 0.41 h-units smaller than the fully porous particles, the CS-ROM particles display h_{min}-values that are yet significantly smaller than the conventional CS-particles, between 0.48 and 0.22 h-units (again depending on the D_{pz}/D_{mol}-ratio). Interesting to note is the fact that the CS-ROM particles have clearly lower h-values in the B-term dominated region than conventional CS particles and at the same time this is not penalized by a steeper C-term, as the CS-ROM curve always remains below the conventional CS curve, even up till the highest ν_i (in practice columns are not operated much higher than ν_i=15 to 20).

Obviously, the relative position of the curves in Figs. 2a-b depends on the relative magnitude of the intra-particle diffusion coefficient. When D_{pz}/D_{mol} is large (cf. Fig. 2a), the difference between the curves for the conventional CS and the CS-ROM particles is larger than the

difference between the fully porous and the conventional CS particles. When D_{pz}/D_{mol} is small (cf. Fig. 2b), the strongest difference in plate height curve is observed when going from the fully porous particles to the conventional CS particles, whereas the difference between the conventional CS and the CS-ROM particles is smaller here. This is further analyzed and explained in below sections.

3.2 B-term contribution and modelling

As is evident from Fig. 2, the h,ν_i-curves of the different particle types most strongly differ in their B-term dominated part (i.e., to the left of the optimum). In this velocity range, the band broadening is essentially dominated by the effective longitudinal diffusion coefficient D_{eff}. In this nomenclature, the word "effective" relates to the fact that D_{eff} is to be considered as the weighted contribution of two diffusion paths, one through the interstitial (=mobile) zone and the other through the porous particle zone (see Fig. 4 further on). The required weighing factor is not a straightforward value, but can be calculated to a very high degree of accuracy be calculated using the effective medium theory [28]. This has been introduced in the area of chromatography in [29-30].

The separate numerical diffusion experiments that were conducted in the present study (see Sections 2.3 and 2.4) provided independent values for D_{eff}. Given the speed with which this type of calculations can be run, a broad range of different zone retention factors was considered. In addition, we also considered one extra value for the relative porous zone diffusion coefficient ($D_{pz}/D_{mol}=0.3$). The results are plotted in Fig. 3a in a dimensionless format, i.e., as $\gamma_{eff}=D_{eff}/D_{mol}$.

Considering first the series for the fully-porous and the conventional CS particles, the perfect coincidence between the data points and the dashed model curves readily shows that these particles produce D_{eff}-values that can be perfectly fitted by the effective medium expressions established in ref. [29]. This agreement reflects the high accuracy of the model as well as of our computations. The effect of the relative porous zone diffusion coefficient (D_{pz}/D_{mol}) on the D_{eff}-curves for the fully-porous and the conventional CS-particles is also quite straightforward, as the curves are arranged following the order of the D_{pz}/D_{mol}-value (higher means higher effective diffusion). The difference between the fully-porous and the conventional CS-particles for the same D_{pz}/D_{mol}-value reflects the obstructive effect of the core on the effective diffusion [9,29,30].

Turning now to the CS-ROM particles, it is first of all striking to observe that, unlike for the two other materials, the data points for the different D_{pz}/D_{mol}-value all fall on the same curve. This curve also decreases in a much steeper way with the zone retention factor k" than the curves for the two other particles, where the porous zone diffusion is isotropic. "

It is a well-established fact from the theory of chromatography that the B-term band broadening part of the reduced plate height h is given by [29,31]:

$$h_B = B/\nu_i, \text{ with } B = 2 \cdot \gamma_{eff} \cdot (1+k'') \tag{2}$$

Using Eq. (2), the γ_{eff}-values shown in Fig. 3a transform into the B-values shown in Fig. 3b. This figure readily reveals an important property of the CS-ROM particles: i.e., their B-term band broadening is fully independent of the retention factor, and remains at its minimal level, i.e., the one obtained at zero retention. This is in contrast with the two other particle types, where B quite strongly increases with k'', reflecting the fact that, although γ_{eff} drops with increasing k'' (cf. Fig. 3a), this drop is not sufficiently strong to outweigh the multiplication with (1+k'') in the expression for h_B. According to Eq. (2), the constant B-value observed for the CS-ROM particles automatically implies that γ_{eff} should vary inversely proportional with (1+k''). Since the observed γ_{eff} should equal that of a packed bed of fully solid particles at zero zone retention (i.e., when the particles are fully solid and impermeable and k''=0), we can readily express that the effective diffusion in a bed of CS-ROM particles can be exactly described by the following simple law:

$$\gamma_{eff, \text{CS-ROM}} = \gamma_{eff,\text{fully solid}} / (1+k'') \tag{3}$$

As can be witnessed from the good agreement between the computed data points and the solid line curve added to Figs. 3a-b, this expression indeed perfectly describes the observed effective diffusion in CS-ROM particles.

Physically, the form of Eq. (3) can be understood as follows. According to the general effective medium theory, D_{eff} is a mix of series and parallel connection effects of the diffusion paths through the mobile zone and the stationary zone [29]. In Fig. 4, these are represented respectively by arrows (1) and (2). Since the longitudinal contribution of the diffusion path through the particles (path 2) is completely blocked in the CS-ROM particles, this only leaves path (1) as the only remaining diffusion route (cf. Fig. 4b). This route is the same as the one that would be followed when the particles would be fully solid (in which case $\gamma_{eff}=\gamma_{eff,\text{fully solid}}$). However, since the CS-ROM particles can effectively take up species, and since these species have a zero contribution to the longitudinal diffusion when residing in that state, the net effective diffusion should be weighed by a factor 1/(1+k'') to express that the species are only effectively diffusing along path (1) during a fraction 1/(1+k'') of the time they spend in the column. During the remainder of the time (fraction k''/(1+k'')), they have a zero net diffusion in the longitudinal direction.

Returning now to Fig. 3, and considering the conditions used to obtain the reduced plate height data shown in Fig. 2, it can readily be verified that, for the $D_{pz}/D_{mol}=0.5$-case, the CS-ROM particles produce a B-term contribution that is 7.05 times lower than that of the fully

porous and 5.89 times lower than the conventional core-shell particles. For the D_{pz}/D_{mol}=0.1-case, the values are respectively 2.78 and 2.32 times smaller.

3.3 Detailed analysis of the relative magnitude of the different plate height contributions

To understand the impact of the differences in B-term band broadening observed in the previous Section, Fig. 5 revisits the data of Fig. 2, but now after subtracting the h_B-contribution.

As can be noted, the conventional CS and the CS-ROM curves now produce nearly perfectly coinciding curves. This clearly demonstrates that the extra gain in efficiency one can expect by going from a CS particle with isotropic diffusion to one with radial-only diffusion can be fully attributed to the (large) difference in B-term band broadening (all other parameters are the same). There is however still a significant difference between (h-h_B)-curve for the fully-porous and the CS particles, reflecting that the difference in band broadening between a CS and a fully-porous particle is not only due to the difference in B-term band broadening.

Obviously, the explanation for this remaining difference is to be found in the difference in mass transfer resistance inside the particles (cf. the h_{Cs}-term). As was shown in [32], this contribution can, for the considered case of 2-D cylindrical particles, be written as:

$$h_{C_s} = \frac{k''}{\left(1+k''\right)^2} \cdot \frac{v_i}{2\,Sh_{pz}\dfrac{D_{pz}}{D_{mol}}} \tag{4}$$

$$\text{with} \quad Sh_{pz} = \frac{1-\rho^2}{\dfrac{1}{8} - \dfrac{1}{2}\rho^2 + \dfrac{3}{8}\rho^4 - \dfrac{\rho^4}{2}\ln\rho} \tag{5}$$

wherein ρ is the ratio of the solid core to the total cylinder radius. For the fully porous case, ρ=0 and hence Sh_{pz}=8. For the presently considered CS-geometry, ρ=0.63, and Eq. (5) returns a value of Sh_{pz}=27.35. This implies the CS-particles can be expected to approximately have a 3.4 times smaller h_{Cs}-term than the fully porous. Since the theory [32-34] underlying the above expressions does not distinguish between isotropic and radial diffusion, this 3.4-fold lower h_{Cs}-contribution applies to both the conventional CS as well as to the CS-ROM particles, at least according to the theory underlying the general plate height model (see end of Section for some moderating comments).

To account for the difference in h_{Cs}-contribution between the fully porous and the CS particles, Fig. 6 shows the plate height values remaining after subtracting the h_{Cs}-contribution from the (h-h_B)-curves shown in Figs. 5a-b. As can be noted, all particle types now produce nearly perfectly coinciding (h-h_B-h_{Cs})-curves. This confirms that the only important remaining

difference between the fully-porous and the CS-particles in Fig. 5 is indeed due to the difference in h_{Cs}-term.

Since we consider a perfectly ordered system, without heterogeneities at the multi-particle level, the h_{Cs}-contribution is the only remaining contribution in Fig. 5 that depends on the D_{pz}/D_{mol}-ratio according to the general plate height model. This, together with the identical packing structure for the three different particle types, explains the (near-perfect) agreement between the h-h_B-h_{Cs}-curves for both D_{pz}/D_{mol}-ratio's. This also explains why we opted to represent the two data sets in Fig. 6 in the same graph.

As a side note, it should be remarked that the reason why the h_{Cs}-term appears more dominant in our simulations than in real world experiments on real columns (see for example the strong difference in h-curves between the D_{pz}/D_{mol}=0.5- and 0.1-cases in Figs. 2 and 5) is that the simulations relate to a perfectly ordered system. In real packed beds, the contribution of the eddy dispersion is so large that it makes the h_{Cs}-contribution much less important.

The fact that the (h-h_B-h_{Cs})-curves in Fig. 6 still display some small subtle differences (which are largest in the D_{pz}/D_{mol}=0.5-case) is not due to any simulation inaccuracies. This was checked by going to extreme high computational cell densities and low time steps and finding that this did not affect the position of the curves. The differences are anyhow relatively small, on the order of some h=0.05-reduced plate height units, and are hence not really relevant for real packed bed columns where they are overshadowed by the other contributions. The observed differences can be attributed to the fact that the mass transfer phenomena inside and outside the particles are not completely independent of each other in a packed bed medium, such that the pure additivity of the different band broadening sources in the general plate height model (as expressed in Eq. 1) is not 100% accurate (as was already demonstrated in [35]). The strict independence and additivity in fact only holds in coated capillary systems, where the mobile and the stationary zone remain uniform in thickness all along the x-coordinate. As a consequence of the mutual influence the different mass transfer processes have on each other, the D_{pz}/D_{mol}-ratio and the presence or absence of the core have a small effect on how the mass transfer inside the particles (h_{Cs}-contribution) interacts with the mass transfer outside the particles (h_{Cm}-contribution). As a result, the different cases in Fig. 6 do not yield perfectly coinciding h-h_B-h_{Cs}-curves, despite they all relate to the same bed geometry, velocity field and zone retention factor.

3.4 Extrapolations of the results to the performance of real packed beds and practical considerations

Whereas the degree of simplification of the bed geometry is very high, the insights from the present study are sufficiently general to conclude that any bed of CS-ROM particles (be it 2D or 3D, and be it ordered or disordered) will always have the advantage to produce a very low

B-term band broadening (remaining at the minimal value of $h_B=2.\gamma_{eff,fully\ solid}$, independently of the retention factor), without affecting the speed of the C-term mass transfer.

Given the above, the magnitude of the corresponding drop in h_{min} observed in the present study is certainly also indicative for the potential gain in real packed beds, provided this drop is considered in absolute terms (drop of 0.22 to 0.48 in reduced plate height units compared to the regular core-shell particles), rather than in relative terms. Because in real packed beds, the total reduced plate height values are higher due to the significant eddy-dispersion. It could be that the latter will be somewhat larger for CS-ROM particles, because of their lower permeability and the correspondingly smaller multi-particle radial velocity equilibration. Nevertheless, the presently observed gains in h_{min} are very similar in absolute values compared to that in the Wei et al. study [17].

Another important remark is that, whereas the comparison in the graphs shown in Fig. 2 assumes the three particle types have the same D_{pz}/D_{mol}-value, it can be inferred that the straight running mesopores of the CS-ROM particles will lead to higher D_{pz}-values than can ever be expected in the random pore networks of conventional particles. This might lead to a further reduction of the h_{Cs}-contribution. Maybe this could also counter the above mentioned possibility of a slightly higher eddy-dispersion.

The fact that the B-term contribution of CS-ROM particles remains at the minimal value of $h_B=2.\gamma_{eff,fully\ solid}$ for any value of k", while B and hence also h_B rather strongly increase with the retention factor for particles with an isotropic internal diffusion (cf. Fig. 3b) also allows to conclude that the advantage of CS-ROM particles will be largest for components eluting with high retention factors (which is unfortunately the region where the h_{Cs}-contribution becomes ever and ever smaller such that the above mentioned advantage of higher D_{pz}-values of CS-ROM particles would vanish likewise)

The fact that the lower h_{min} of the CS-ROM particles is obtained via a lower B-term also implies the optimal velocity shifts to lower velocities. This is also observed in the Wei et al. study [17]. This obviously has a consequence on the achievable maximal speed, although the kinetic advantage is clear over the entire range of velocities (see the kinetic plot in Fig. 14 of ref. [17]).

A drawback of the CS-ROM particle might be that they have yet a lower loadability than conventional CS particles, as they can maybe only be produced with a limited shell thickness. The nature of the pore network (parallel cylindrical versus randomly connected pores) furthermore also suggests a lower specific retention surface. Another potential issue could be their weaker mechanical strength, although no data are available to either support or contradict this.

4. Conclusions

Compared to conventional core-shell particles, core-shell particles with radially-oriented mesopores (CS-ROM particles) enable an additional strong reduction of the minimal plate height because their pore network produces the lowest possible B-term band broadening h_B, remaining at the minimal value of $h_B=2.\gamma_{eff,fully\ solid}$ instead of increasing with the retention factor as is the case for particles with isotropic internal diffusion. This advantage is realized without affecting the speed of the C-term mass transfer, such that the lower B-term band broadening is not penalized by an increase in C-term band broadening.

Comparing for the same zone retention factor (k"=8, corresponding to a phase retention factor of the order of 4.9 to 5.8), CS-ROM particles can be expected to produce a B-term which is between 2.32 (D_{pz}/D_{mol}=0.1) and 5.89 (D_{pz}/D_{mol}=0.5) times lower than that of a conventional core-shell particle with the same relative core, and between 2.78 (D_{pz}/D_{mol}=0.1) and 7.05 (D_{pz}/D_{mol}=0.5) times lower than for a fully porous particle.

In the perfectly ordered beds considered in the present simulation study, the CS-ROM particles displayed a h_{min}-value that was 0.76 and 0.48 h-units smaller than the ordinary fully porous and core-shell particles respectively for D_{pz}/D_{mol}=0.5 and 0.63 and 0.22 h-units smaller in case D_{pz}/D_{mol}=0.1. These values are of the same order as in the recent experimental study reported by Wei et al [17].

Observing such large differences under conditions of identical packing quality suggests that column efficiency is also strongly determined by the intra-particle properties (diffusion, geometry,..), whereas the field of LC has always been more pre-occupied with packing uniformity and external mass transfer.

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Figure captions

Figure 1. Bed geometries and computed species distribution for **(a)** fully porous particles, **(b)** core-shell particles with conventional (i.e., isotropic) diffusion and **(c)** CS-ROM particles. Conditions in all cases: k"=8, ν_i=16, D_{pz}/D_{mol}=0.5. The color scale varies in a linear way from the highest (red) to the lowest concentration (blue). Maximal concentration values respectively are: C_{max}=0.135 g/l (a), C_{max}=0.152 g/l (b), C_{max}=0.211 g/l (c).

Figure 2. Reduced plate height values h versus ν_i for the different particle types and the two considered D_{pz}/D_{mol}-values: **(a)** D_{pz}/D_{mol}=0.5 and **(b)** D_{pz}/D_{mol}=0.1.

Figure 3. Results of the numerical diffusion experiments, represented as **(a)** a plot of $\gamma_{eff}=D_{eff}/D_{mol}$ versus k" and **(b)** a plot of B versus k" for the 3 different particle types and the three considered D_{pz}/D_{mol}-values (squares D_{pz}/D_{mol}=0.5, circles 0.3 and triangles 0.1). Solid curve represents Eq. (3), modelling the CS-ROM stacking. Dashed and dash-dotted curves calculated using Eq. (31) of [29], modelling the fully porous and core-shell stacking respectively.

Figure 4. Schematic difference between the diffusion paths in a core-shell particle with **(a)** random diffusion and **(b)** one with radial-only diffusion. Arrows (1) and (2) are discussed in the text. The radial lines added to the shell in (b) schematically represent the blockage of the diffusion in the circumferential direction.

Figure 5. Plot of h-h_B versus ν_i using the h-values shown in Fig. 2 and the h_B-values shown in Fig. 3b. **(a)** D_{pz}/D_{mol}=0.5 and **(b)** D_{pz}/D_{mol}=0.1.

Figure 6. Plot of h-h_B-h_{Cs} versus ν_i using the h-values shown in Fig. 2 and the h_B-values shown in Fig. 3b. (squares D_{pz}/D_{mol}=0.5 and triangles 0.1)