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Determination of effective diffusivities and transport parameters of porous solids in the Single-Pellet-String-Column

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Abstract

The chromatographic technique which employs SPSC and takes into account the extra-column effects of the measuring system can provide consistent transport characteristics of porous solids. These characteristics are independent of the kind of gases which are transported through pores, as well of temperature and pressure. Dispersion of the tracer band in the interparticle spaces of the SPSC increases at higher carrier gas velocities when the non-porous column packing is replaced by a porous one. This points to some additional mechanism of band spreading caused by the presence of interface gas-porous solid.

Keywords: Effectice diffusivity; Porous solid; Single-pellet-string column (SPSC); Chromatography

1. Introduction

The chromatographic method for obtaining effective diffusivities in porous materials (catalysts, adsorbents, etc.) is well established [1,2]. Effective diffusivities are evaluated from response (chromatographic) curves of columns packed with particles of the tested porous material. The carrier-gas (C) flows at constant rate and a pulse of another gas (tracer – T) is injected into the carrier stream. Tracer concentration is monitored at the column outlet by a suitable detector (thermal conductivity, flame ionisation, etc.) and the recorded outlet response peak is then analysed. Several processes occur during the passage of the tracer band through the column: besides convection and axial dispersion, transport of tracer through the laminar film around the packing particles takes place followed by diffusion in the pore structure. Tracer (in case of adsorbable gas) is, then, adsorbed on the internal surface of the porous packing.

Porous particles can be packed in the column in two ways: Either a wide bed packed with particles is formed – to guarantee the axially dispersed plug flow hydrodynamics it is necessary to have the column diameter to particle diameter ratio larger than about 20. Or, particles are packed one by one into a column with a diameter exceeding that of the particles by only 10–20%. This arrangement, known as Single-Pellet-String-Column (SPSC) [3], is used usually for spherical or cylindrical porous particles. In SPSC high linear carrier-gas velocities – which suppress the tracer peak broadening due to axial dispersion – are easily attained. This is even more significant, when inert (non-adsorbable) gases are used as tracers which move through the column with the carrier-gas velo-

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city. The use of inert tracers prevents their adsorption and the possible surface diffusion which obscures the effective diffusion coefficients [4].

The analysis of outlet peaks is based on the model of processes in the column. Today the Kubín–Kučera model [5,6] which accounts for all the above mentioned processes, as long as they can be described by linear (differential) equations, is used nearly exclusively. Several possibilities exist for obtaining rate parameters of intracolumn processes (axial dispersion coefficient, external mass transfer coefficient, effective diffusion coefficient, adsorption/desorption rate constants, adsorption equilibrium constant) from the column response peaks. The moment approach in which the moments of the outlet peaks are matched to theoretical expressions developed from the system of model (partial) differential equations is widespread as a consequence of its simplicity [7]. Because of the availability of computers matching of whole column response peaks with model equations starts to be the predominant analysis method. Such matching can be performed in the Laplace- [8] or Fourier-domain [9], or, preferably in the time-domain [10,11].

The Kubín–Kučera model [5,6] describes correctly the intracolumn processes but neglects the effects of processes upstream and downstream of the column (extra column effects – ECE). Recently it was suggested [12] that these processes can be included in the time-domain matching through the application of the convolution theorem. This requires, besides the knowledge of the experimental system response, also the knowledge of the ECE response, i.e., the response of the system from which the SPSC is removed. It was shown that such an approach works satisfactorily for SPSC packed with non-porous particles – in this case only axial dispersion in the interparticle space is responsible for tracer band broadening. It is the aim of this work to verify the applicability of the time-domain matching combined with the convolution of ECE responses for the case of porous pellets packed in the SPSC. In addition to axial dispersion in the interparticle spaces also intraparticle diffusion in the pores of the SPSC packing is responsible for broadening of the tracer band. The responses of a SPSC packed with cylindrical particles of an industrial porous catalyst were obtained for a series of tracer and carrier gases in the same SPSC for which ECE responses and responses for non-porous packing of the same size were available [12]. It was believed that Peclet numbers (which characterise the interparticle mixing) determined for SPSC with non-porous packing could be used in matching the responses of porous packing. This would decrease the number of fitted parameters for SPSC with porous pellets and, thus, remove part of the undesirable parameter correlation. In an attempt to verify the width of the applicability field of the convolution approach also some adsorbable tracers were used.

2. Experimental

Porous catalyst: The industrial unreduced low temperature water-gas conversion and methanol synthesis catalyst ICI 52-1 (Imperial Chemical Industries, UK; composition: 45% ZnO, 20% CuO, Al_2O_3) in the form of cylindrical pellets (5.5×3.8 mm=height×diameter; diameter of (equivalent) sphere with the same volume to geometric surface ratio, d_p=0.465 cm) were used for packing of SPSC. The pellet porosity, β=0.623, was determined by the combination of mercury and helium pycnometry and the column void fraction, α=0.459, was calculated from the SPSC volume and the weight of packed pellets.

Non-porous pellets: Brass pellets 5.7×3.8 mm (height×diameter) with d_p=0.47. The column void fraction, α=0.491.

Gases: Hydrogen, helium, nitrogen and argon were used as carrier-gases (C). Hydrogen, helium, nitrogen, argon, methane, ethane and propane were used as tracer-gases (T).

SPSC column: stainless steel tube (i.d. 6.8 mm, length 48.6 cm).

Chromatographic system consisted of calibrated mass flow-meter/controllers for carrier and tracer gases, a six-way sampling valve for tracer with sampling loop 0.273 cm^3, SPSC and thermal conductivity detector (Micro-TDC 10-955, Gow-Mac Industries, Gillingham, UK; cell volume 20 μl). Metal capillaries (i.d. 1 mm) with minimised length were employed for connecting the system components.

Column and ECE responses: All measurements were made at laboratory temperature and pressure. Signal from the TCD was recorded in a digital data logger (1000 data points). After zero-line correction (less than 0.1% of the maximum response height) about 80 uniformly distributed points, normalised to the maximum tracer concentration, were retained for further processing. Because the system responses were quite rapid the positions of maxims of replicated peaks differed slightly (0.1–0.2 s). Therefore, the mean maximum position was determined and replicated peaks were shifted to this maximum. The final response peak was, then, obtained by averaging the individual responses. Three responses were obtained for every pair of gases. The ECE responses were acquired with removed column. Injection of tracer T into carrier C is denoted in the following as T→C.

3. Results and discussion

3.1. *Extra-column-effects*

Fig. 1 compares the SPSC and ECE responses for one carrier and four tracer gases at the same carrier flow-rate. As can be seen ECE peaks have nearly the same shape for all tracers (N_2, Ar, methane and ethane). The effect of the carrier flow-rate on the shape of ECE and SPSC responses is illustrated in Fig. 2 for the $N_2 \rightarrow H_2$ pair. The carrier-gas flow-rate has a marked effect on the ECE peaks. The peaks start at nearly the same time but their width decreases with the increase of the carrier flow-rate. Tailing of the ECE responses is also more marked for lower carrier flow-rates. The same is true also for other T→C systems (not shown). Evidently, the ECE responses differ from the expected signal that should start immediately after the tracer injection and have the form of a square wave. Thus, there is not only a tracer time delay in the system parts outside the SPSC but also some signal spreading mechanisms operate. We have tried to model the ECE peaks as: (i) a response of an ideal mixer with a time delay section and (ii) as an ideal mixer with time delay and dead volume. The matching parameters (two in case (i) and three in case (ii)) were, however, not constant. They changed with carrier gas flow-rate and with the kind of tracer and carrier. Hence, such modelling of ECE response does not reveal the true nature of processes that cause the response delay and spreading in the extra column spaces and could be used merely for data interpolation. This is, in fact, the reason for using the convolution theorem with experimentally determined ECE responses in the process of time-domain matching of the SPSC signals.

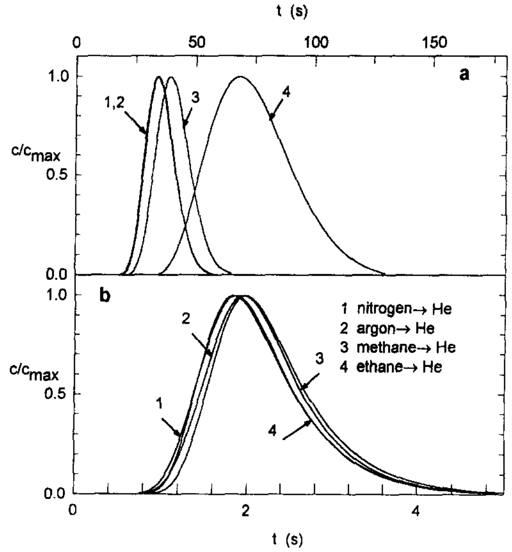

Fig. 1. Comparison of SPSC (a) and ECE responses (b) for different T→C systems. He flow-rate: 10 cm^3/min.

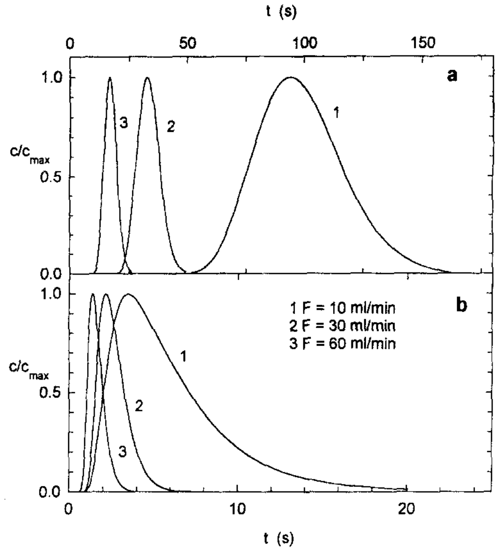

Fig. 2. Comparison of SPSC (a) and ECE responses (b) for $N_2 \rightarrow H_2$ and different hydrogen flow-rates.

3.2. Response matching

for a T→C system the impulse response (i.e., response to a tracer Dirac pulse) of a column packed with porous spherical particles of radius, R, in which tracer equilibrium adsorption in the Henry region of the adsorption isotherm (characterised by the adsorption equilibrium constant, K_T) and intraparticle diffusion characterised by an effective diffusion coefficient D_{TC} takes place is given by [14]

$$h(t) = Q \int_0^\infty \exp\left(\frac{\mathrm{Pe}}{2} - f_1\right) \cos\left(\frac{2\gamma\lambda^2 t}{\delta_0 t_{\mathrm{dif}}} - f_2\right) \lambda \, \mathrm{d}\lambda, \tag{1}$$

where

$$\begin{aligned} f_{1,2} &= \sqrt{\frac{\sqrt{A^2+B^2} \pm A}{2}}, \\ A &= \mathrm{Pe}\left(\frac{\mathrm{Pe}}{4} + \frac{3\gamma H_1 t_c}{t_{\mathrm{dif}}}\right), \\ B &= \mathrm{Pe}\frac{t_c}{t_{\mathrm{dif}}}\left(\frac{2\gamma\lambda^2}{\delta_0} + 3\gamma H_2\right), \\ H_1 &= \lambda\frac{\sinh(2\lambda) + \sin(2\lambda)}{\cosh(2\lambda) - \cos(2\gamma)} - 1, \\ H_2 &= \lambda\frac{\sinh(2\lambda) - \sin(2\lambda)}{\cosh(2\lambda) - \cos(2\gamma)} \end{aligned} \tag{2}$$

and t_c is the tracer mean residence time in the column of length L ($t_c = L/v$) with carrier gas linear velocity, v. Pe is the Peclet number ($\mathrm{Pe} = vL/E$ and E is the axial dispersion coefficient), t_{dif} denotes the diffusion time of the tracer in the pore structure of a pellet, $t_{\mathrm{dif}} = (d_p/2)^2\beta/D_{TC}$, δ_0 is the tracer adsorption parameter $\delta_0 = \gamma(1 + K_T)$, and $\gamma = \beta(1+)/\alpha$. β is the pellet porosity and α is the column void fraction (interstitial void volume/column volume). Thus, γ, is the pore volume per unit interstitial volume. For an inert tracer $K_T = 0$ and $\delta_0 = \gamma$. Q is a normalisation constant defined so that at the calculated SPSC response maximum the tracer concentration equals unity, $c(t_{\max}) = 1$. Eq. (1) assumes no resistance between the bulk stream and the external surface of porous pellets.

To describe the SPSC response it is necessary to include the ECE effects into calculation. From the convolution theorem it follows that the column response $c(t)$ is given by the convolution theorem as

$$c(t) = \int_0^t g(t-u)h(u)\,\mathrm{d}u, \tag{3}$$

where $g(t)$ describes the shape of the signal entering the column instead of the Dirac pulse. In linear systems it is immaterial if the ECE are distributed in different places of the system or if they are concentrated in one place and in what order they are arranged. Therefore, it is possible to use the experimental ECE responses obtained in the system without the column, in place of $g(t)$. We have found that interpolation of experimental ECE response peaks with cubic splines [13] is quite satisfactory.

There are four unknown parameters in $c(t)$, viz., the pellet diffusion time, t_{dif} (which contains D_{TC}), the mean residence time of the carrier-gas in the interparticle space, t_c, Peclet number, Pe, and the adsorption parameter, δ_0. The parameter t_c can be obtained from the SPSC volume, V_c, bed porosity, α, and the carrier gas flow-rate, F, as $t_c = \alpha V_c/F$. Thus, only t_{dif}, Pe and δ_0 have to be obtained by matching. These parameters are not correlated and the matching is straightforward. From our experience the simplex algorithm [15] for minimisation of the sum of squared differences between the calculated and experimental SPSC responses proved to be sufficiently rapid and stable.

3.3. Axial dispersion

As stated above, it was at first supposed, that ECE peaks and responses of the SPSC packed with non-porous particles can be used for evaluation of Peclet numbers for the given carrier flow-rate and kind of carrier and tracer gases. This would decrease the number of matching parameter from three (t_{dif}, Pe, δ_0) to two (t_{dif}, δ_0). It appeared, however, that the Peclet numbers obtained by three parameters matching agreed with the Peclet numbers from matching of responses of SPSC packed with non-porous cylindrical pellets only at low carrier gas velocities. At higher carrier velocities the Peclet numbers in SPSC packed with porous pellets are higher than in SPRC packed

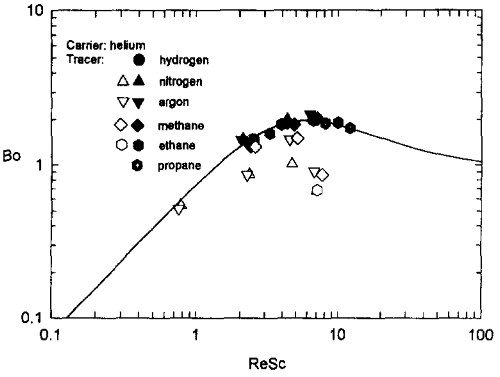

Fig. 3. Bo numbers for SPSC with porous and nonporous cylindrical pellets Points: experimental; empty symbols – porous packing, full symbols – nonporous packing. Line: calculated from $1/\mathrm{Bo} = (\gamma/\mathrm{ReSc}) + [\lambda \mathrm{ReSc}/(\beta + \mathrm{ReSc})]$ with $\gamma = 1.28$, $\lambda = 1.09$, $\beta = 16.4$.

with non-porous particles. This is demonstrated in Fig. 3 where the obtained optimum Peclet number (in the form of Bodenstein numbers, Bo: $\mathrm{Bo} = (d_p/L)\mathrm{Pe}$) are plotted versus the product of Reynolds and Schmidt numbers, ReSc. This suggests that in the interparticle space of SPSC packed with porous pellets operates some (unknown) additional dispersion mechanism. Therefore, it was necessary to use three-parameter matching for SPSC with porous packing.

3.4. Tracer adsorption

The adsorption equilibrium constants, K_T determined from the matched parameter δ_0 are summarized in Table 1. It can be seen that tracer adsorption equilibrium constants, K_T, increase roughly with increasing tracer molecular weight except for helium which has the lowest K_T (helium<hydrogen<nitrogen≈argon<methane<ethane). At the same time adsorption equilibrium constants for the weakly-absorbable gases (H_2, He, N_2, Ar) are nearly independent of the kind of carrier gas. Adsorption equilibrium constants for methane and ethane show dependence on the carrier; in heavier carrier gases K_T decrease.

3.5. Pore diffusion

The effective diffusion coefficients, D_{TC}, obtained from the parameter t_{dif} include contributions from the Knudsen diffusion mechanism and molecular diffusion mechanism. The Bosanquet formula Eq. (4)

$$\frac{1}{D_{TC}} = \frac{1}{\langle r \rangle \psi \mathscr{K}_T} + \frac{1}{\psi \mathscr{D}_{TC}^m} \tag{4}$$

includes the molecular diffusion coefficient of the pair C-T, $\mathscr{D}_{TC}^m$, and the tracer Knudsen constant $\mathscr{K}_T = (2/3)\sqrt{(8R_g T/\pi M_T)}$ with the universal gas constant R_g, temperature, T, and tracer molecular weight M_T. ψ and $\langle r \rangle \psi$ are parameters characterising the porous medium and are independent of the kind of tracer and carrier gases as well as of temperature and pressure (material parameters of the porous solid [16]). $\langle r \rangle$ stands for the mean radius of pores through the majority of the mass transport takes place (transport pores) and ψ is the ratio of transport pore porosity and tortuosity. Eq. (4) can be rearranged into the form given in Eq. (5), which permits easy graphical data plotting

$$t_{dif} \mathscr{K}_T = \frac{(d_p/2)^2 \beta}{\langle r \rangle \psi} + \frac{(d_p/2)^2 \beta}{\psi} \frac{\mathscr{K}_T}{\mathscr{D}_{TC}^m}. \tag{5}$$

The diffusion times, t_{dif}, determined by three-parameter matching for sixteen T→C pairs and several

Table 1
Adsorption equilibrium constants, K_T, of tracers on ICI pellets

Carrier	Tracer					
	Helium	Hydrogen	Nitrogen	Argon	Methane	Ethane
Helium	—	—	0.37	0.34	0.75	3.32
Hydrogen	—	—	0.34	0.32	0.70	3.22
Nitrogen	0.11	0.17	—	0.34	0.61	2.65
Argon	0.16	0.24	0.38	—	0.74	2.67

carrier gas velocities are plotted in co-ordinates $t_{\mathrm{dif}}\mathscr{K}_{\mathrm{T}}$ versus $\mathscr{K}_{\mathrm{T}}/\mathscr{D}^{m}_{\mathrm{TC}}$ in Fig. 4. From the slope and intercept of the fitted straight line $\langle r\rangle\psi = 2.55$ nm and $\psi = 0.0249$. Hence, the mean radius of transport pores $\langle r\rangle = \langle r\rangle\psi/\psi = 102$ nm. The same transport parameters were obtained by non-linear least-squares fitting of experimental t_{dif}'s to calculations based on the Bosanquet formula Eq. (4). The 95% confidence region of transport parameters is depicted in Fig. 5. The obtained transport parameters are in good agreement with results obtained for the same catalyst by another method in which simultaneous permeation and diffusion of gases takes place [17].

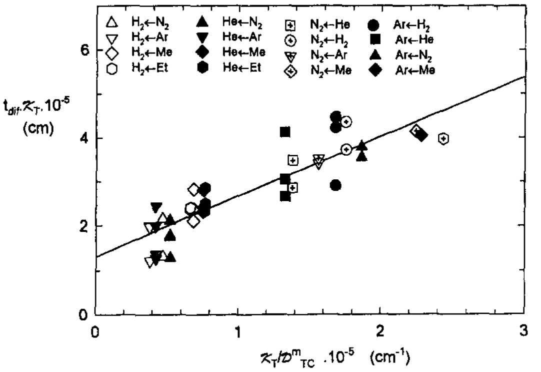

Fig. 4. Diffusion times from parameter matching in co-ordinates $t_{\mathrm{dif}}\mathscr{K}_{\mathrm{T}}$ versus $\mathscr{K}_{T}/\mathscr{D}^{m}_{TC}$.

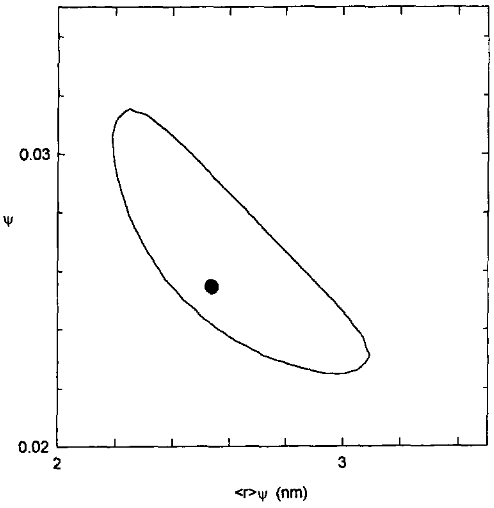

Fig. 5. 95% confidence region of transport parameters $\langle r\rangle\psi$ and ψ. The optimum parameter pair is shown as point.

4. Conclusion

It was verified that the chromatographic technique that employs SPSC and takes, via convolution, into account the extra-column effects of the measuring system can provide consistent transport characteristics of porous solids. These characteristics are material parameters of the porous solid and, hence, independent of the kind of gases that are transported through pores, as well of temperature and pressure.

The suggested method can detect even slight adsorption of the gases forming the T→C pairs. The usually assumed inertness of helium and hydrogen is not supported by the present results.

Dispersion of the tracer band in the interparticle spaces of the SPSC increases at higher carrier gas velocities when the non-porous column packing is replaced by a porous one. This points to some additional mechanism of band spreading caused by the presence of interface gas–porous solid.

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References

[1] H.W. Haynes, Jr. Catal. Rev.-Sci. Eng., 30 (1988) 563.
[2] M. Suzuki and J.M. Smith, Adv. Chromatogr., 13 (1975) 213.
[3] D.S. Scott, W. Lee and J. Papa, Chem. Eng. Sci., 29 (1974) 2155.
[4] P. Schneider and J.M. Smith, AICHE J., 14 (1968) 886.
[5] M. Kubín, Collect. Czech. Chem. Commun., 30 (1965) 1104.
[6] E. Kučera, J. Chromatogr., 19 (1965) 237.
[7] P. Schneider and J.M. Smith, AICHE J., 14 (1968) 237.
[8] K. Kamiyanagi and S. Furusaki, Internat. Chem. Eng., 25 (1985) 301.
[9] K. Zygourakis and K. Moudgalya, Chem. Eng. Commun., 61 (1987) 107.
[10] M.A. Fahim and N. Wakao, Chem. Eng. J., 25 (1982) 1.

[11] N. Wakao, S. Kaguei and J.M. Smith, J. Chem. Eng. Jpn., 12 (1979) 481.
[12] O. Šolcová and P. Schneider, Collect. Czech. Chem. Commun., 61 (1996) 844.
[13] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.A. Vetterling, Numerical Recipes, Wiley, New York, NY, 1986.
[14] P. Schneider, Chem. Eng. Sci., 39 (1984) 927.
[15] D.M. Himmelblau, K.B. Bischoff, Process Analysis and Simulation, Wiley, New York, NY, 1968.
[16] P. Fott and G. Petrini, Appl. Catal., 2 (1982) 367.
[17] P. Čapek, V. Hejtmánek, O. Šolcová, K. Klusáček and P. Schneider, Catal. Today, 38 (1997) 31–38.