

DIFFUSION RATE INCREASE DURING EXTRACTION OF POROUS PRODUCTS : THE KRISCHER APPROACH FOR SUPERCRITICAL APPLICATIONS

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1. INTRODUCTION AND STATE OF THE ART

Various models have been applied to describe the batch extraction of natural products with supercritical fluids. As reference, one may use models which have been deduced from the simple single particle (SSP) approach, the shrinking core approach, and models which take into account dispersion as well as adsorption/desorption phenomena. One important branch is the reflection on crunched particles with easy accessible solute and bounded solute in the intact cell walls.

By means of the different modelling tools, one may adapt the diffusion coefficient, which depends strongly on the process parameters pressure and temperature, but also the pore geometry.

Especially in the SSP approach, it has been shown in the past that even the experimental time has an effect to the calculated diffusion coefficient, which is therefore often called “effective Diffusion coefficient”. This value differs strongly from the binary diffusion coefficient, which is a constant by definition.

Figure 1 shows the evolution of the effective diffusion coefficient for the extraction of soy bean, the increase depends strongly on the fluid velocity. Effective diffusion coefficient has been calculated by adapting the SSP approach to experimental values

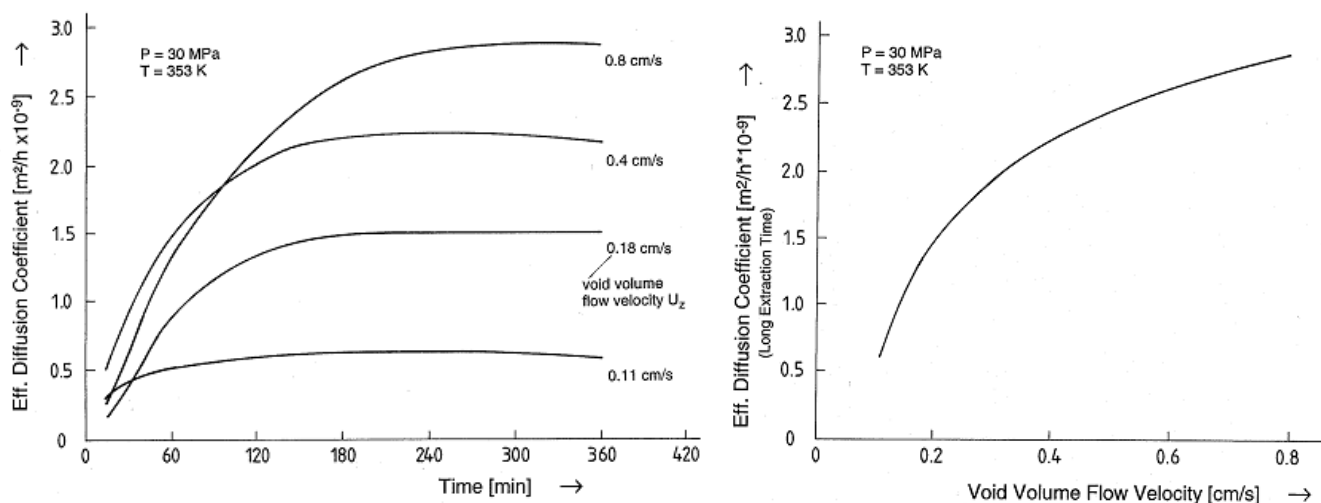


Figure 1 : Influence of fluid velocity on the effective diffusion coefficient [1]

Although the SSP approach may be criticized for the large number of neglects of physical side effects, the information implies clearly an increase of the effective diffusion during the initial part of the extraction. From some point of view this observation can be defined as contradictive to physicochemical definitions : a diffusion coefficient should be independent of time and velocity. In the following, a theoretical description from drying technologies is used for describing the increasing mass transfer.

2. THEORETICAL APPROACH:

Fixed beds are macroporous systems. In this case the diffusion takes place on the “macro”-particle surface as well as inside the particles. In both regions (macro- and micropores), different resistances for mass transfer exist and they can be summarized to a total one. The resistance is finally responsible for the mass flow of solvent and solute. The solvent will take the way of the minimal resistance, which is a sum of partial parallel and serial contributions. In common, the diffusional flow is considerably higher in the macropores which are filled with the fluid. For mass transfer, one can expect consequently the pathway with the lowest fraction of solids. This is in contrast to the pathway of heat transfer. The reason is based in the different behaviour of the thermal conductivity.

Krischer et al. [2] have defined the influence of macro-porosity on the diffusion with the resistance factor μ

$$\mu = \frac{\delta_{gas}}{\delta_{solid}} = \frac{1/\delta_{solid}}{1/\delta_{gas}} \quad (1)$$

Data bases exist for numerous applications (civil engineering, colorants, nutrition, drying). Values are greater than one (wood, concrete), and may reach dimensions in the range of 10^6 . A more precise approach takes into account the recent loading of the pores. At the beginning of the process, it is assumed that the pores are completely filled with the substrate, leading to a diffusion coefficient which is close to the wet pore one. During the extraction and the leaching of the substrate, the system can then be considered as a network of parallel and serial diffusional resistances, referring from the gaseous phase and the wet phase [3].

$$\Psi_l = \varepsilon \cdot \frac{C}{C_0} \quad (2)$$

$$\delta = 1 / \left(\frac{1-\alpha}{\delta_l} + \frac{\alpha}{\delta_{II}} \right) \quad (3)$$

$$\delta_l = \Psi_l \cdot \delta_{wet} + (\varepsilon - \Psi_l) \cdot \delta_{gas} \quad (4a)$$

$$\delta_{II} = \left[\frac{\Psi_l}{\delta_{liq}} + \frac{(\varepsilon - \Psi_{liq})}{\delta_{gas}} \right]^{-1} \quad (4b)$$

with

α : fraction of serial Resistances in the system
 ε : Porosity
 Ψ_l : fraction of the liquid phase saturation in the Pores

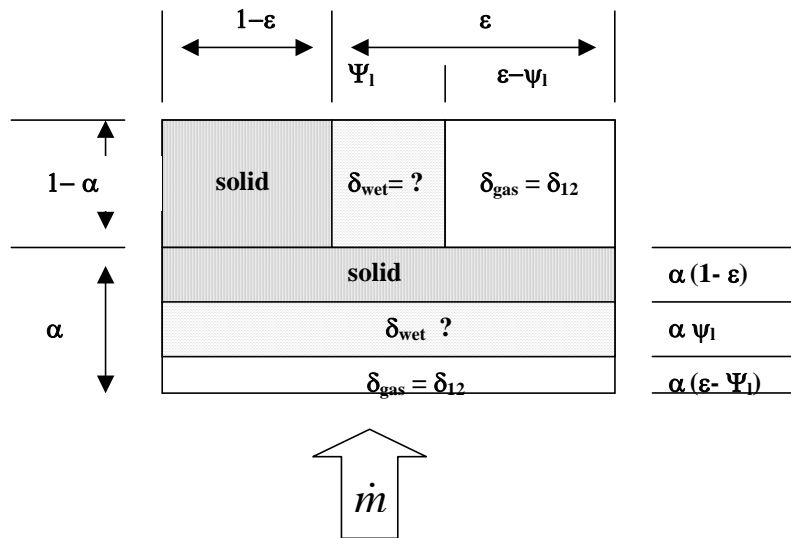


Figure 2: Network of parallel and serial mass transfer resistances for describing the macropore diffusion .

The development of the diffusion coefficient from equation 3 is visualised in figure 4. It shows the influence of pore saturation on the effective diffusion coefficient. At the beginning the coefficient is close to the (estimated) wet pore one, and it reaches the values of the gaseous one only at the very end of the process.

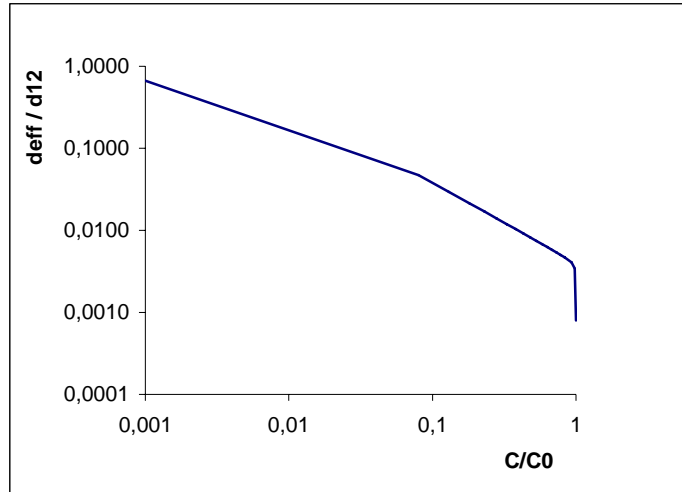


Figure 4 :Influence of Pore Saturation on the diffusion coefficient , here : Pore wetting C/C_0 from $1 \rightarrow 0$, $\delta_{wet} = 1/10000 * \delta_{12}$, $\alpha = 0,5$, $\epsilon = 0,5$

3. IMPLICATION OF THE NETWORK TO THE EXTRACTION MODEL

The Simple Single Plate Model is the most attractive approach for the fast evaluation of the extraction yield curve. The fixed bed may be considered as a homogeneous continuum (e.g. a simple plate, sphere or cylinder) with an equilibrated concentration profile inside the particle.

This model allows a reduction of number of unknown parameters to one, as the mass balance reduces to

$$\frac{Y(t)}{Y_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2} \exp\left[-\frac{\delta_{eff} (2n+1)^2 \cdot \pi^2 \cdot t}{(2 \cdot L_{part})}\right] \quad (5)$$

which is a direct functional solution when dispersion may be neglected. The experimental curve allows consequently to calculate the *effective diffusion coefficient* δ_{eff} , which may differ strongly from the binary one δ_{12} . The reason of this is the fact that all mass transfer resistances (inner phase of the solid, micropores, and fluid phase pores) are implied to the particle phase. The equation above leads to a change in the effective diffusion coefficient with time, when adapting δ_{eff} to different flow rates and experimental run times (Figure 1).

III.1 Modified Simple Single Plate Model during the constant extraction rate

The use of the operational solubility may allow a fast simulation of the total extraction yield : it is valid for the condition that the natural matrix delivers constantly the same substrate flow, which is dissolved and transported from the fluid phase (constant mass transfer rate. Consequently the concentration of the fluid at the extractor output is constant, the upper limit is defined by the thermodynamic solubility.

Simplified mass balance ($D_{ax} = 0$, substrate flow = constant) gives:

$$\frac{\bar{C}_{solt,solid} - C_{solt,out}}{C_{solt,solid} - C_{ein}} = \exp\left(-\frac{\kappa \cdot A}{\dot{V}}\right) \quad \text{with } \kappa = \frac{\delta}{s} \quad (6)$$

Output concentration is measured as the experimental value. Surface concentration is considered as saturation concentration of the fluid. Mass transfer is consequently infinite when the output concentration has the same value as the surface concentration.

The length s is referring to the pathway of diffusion. In spherical particles, s defines the radius.

The term $\frac{\kappa \cdot A}{\dot{V}} = a \cdot H_{autocl} \cdot \frac{Sh}{Pe} = \text{NTU}$ is defined as number of transfer units , it describes the ratio between residence time and the necessary relaxation time of the fluid flow.

Considering a spherical shape particle with $s = R(\text{radius})$, the minimum Sherwood number of a single particle in an immobile fluid environment is $Sh=2$.

Peclet number defines the ratio of fluid velocity to mass transfer. Consequently, mass transport coefficient is defined via particle shape and fluid velocity:

$$Sh = \frac{\kappa \cdot L_{particle}}{\delta_{eff}} \quad Pe = \frac{u_o \cdot L_{particle}}{\delta_{eff}} \quad (7)$$

Provided that either Sherwood number or the effective diffusion coefficient is known, the system is consequently completely defined. The recent equations for the description of $Sh = f(u_{fluid})$ are based on the same structure, and can be found elsewhere [4]:

$$\frac{Sh}{\sqrt[3]{Sc}} = A Re^n \quad (8)$$

It may be concluded that the wet pore diffusion coefficient has an important influence on the precise modelling of the system, respectively the effective diffusion coefficient. As the

saturation of the pores varies during the process depending on time and position, this approach would require a local re-calculation at each position of the extractor.

Axial dispersion and bypass effects includes additionally important influences (“apparent Sherwood Number”) on the internal concentration profile, in contrast to the homogeneous approach of the global SSP model.

III.2 Application

Flow rate is the changing parameter in the following discussion, whereas the other model parameters and modeling routines have been constant. The procedure for discussing the influence of mass flow on the local, concentration dependent parallel/serial mass transfer is noted in the following.

From the modified SSP model, it is possible to calculate the liquid pore diffusion coefficient for the constant extraction rate section. The *liquid* pore diffusion itself is considered as constant, i.e. independent from external parameters like mass flow and pore shape. Gas phase (binary) diffusion coefficient is considered as constant too, and estimated in the range of 10^{-9} m²/s [4]. Considering one reference extraction, the experimental shape is a given input information, and Krischer modelling approach gave a solid phase diffusion coefficient $\delta_{liq} = 7,69 \cdot 10^{-13}$ m²/s, = $\delta_{es}(t=0)$, based on a serial/ parallel fraction of $\Psi = 0,5$. It is proposed that, due to surface tension effects, the serial/parallel fraction reduces to low values at high flow rates.

Based on the results from the SSP approach, it is consequently possible to develop the total extraction yield curve according the shrinking core (SC) [5] or the diffusion/desorption/dispersion algorithm (DDD) [1].

For the reference experiment, the linear Desorption coefficient is $K_{DDD} = 0,75$

The shrinking core approach uses on the one hand the estimated diffusion coefficient for the solid phase, on the other hand the Biot number, as the linking factor with the external mass transfer. External mass transfer coefficient is considered as constant. Consequently, with changing internal concentrations, the Biot number will also be a function of the local concentration, this means Biot itself will change during the extraction run. Fluid phase mass transfer coefficient was constant at $\kappa_{fluid} = 2,82 \cdot 10^{-7}$ m/s.

In the following figure 5, the network approach was applied strictly at each time step and each position in function of the local substrate concentrations, for three flow rate scenarios.

The applicant of Batch SFE may expect an increased mass transfer at higher flow rates, whereas the convective influence is the most important parameter. However, doubling the flow rate will not lead to a proportional result in process efficiency, only the fluid phase mass transfer coefficient increases in the same way.

One may conclude that the intraparticle diffusion coefficient is the process determining parameter, this reduces the increase of the overall mass transfer coefficient, and finally induces only a light increase of the process Sherwood number,

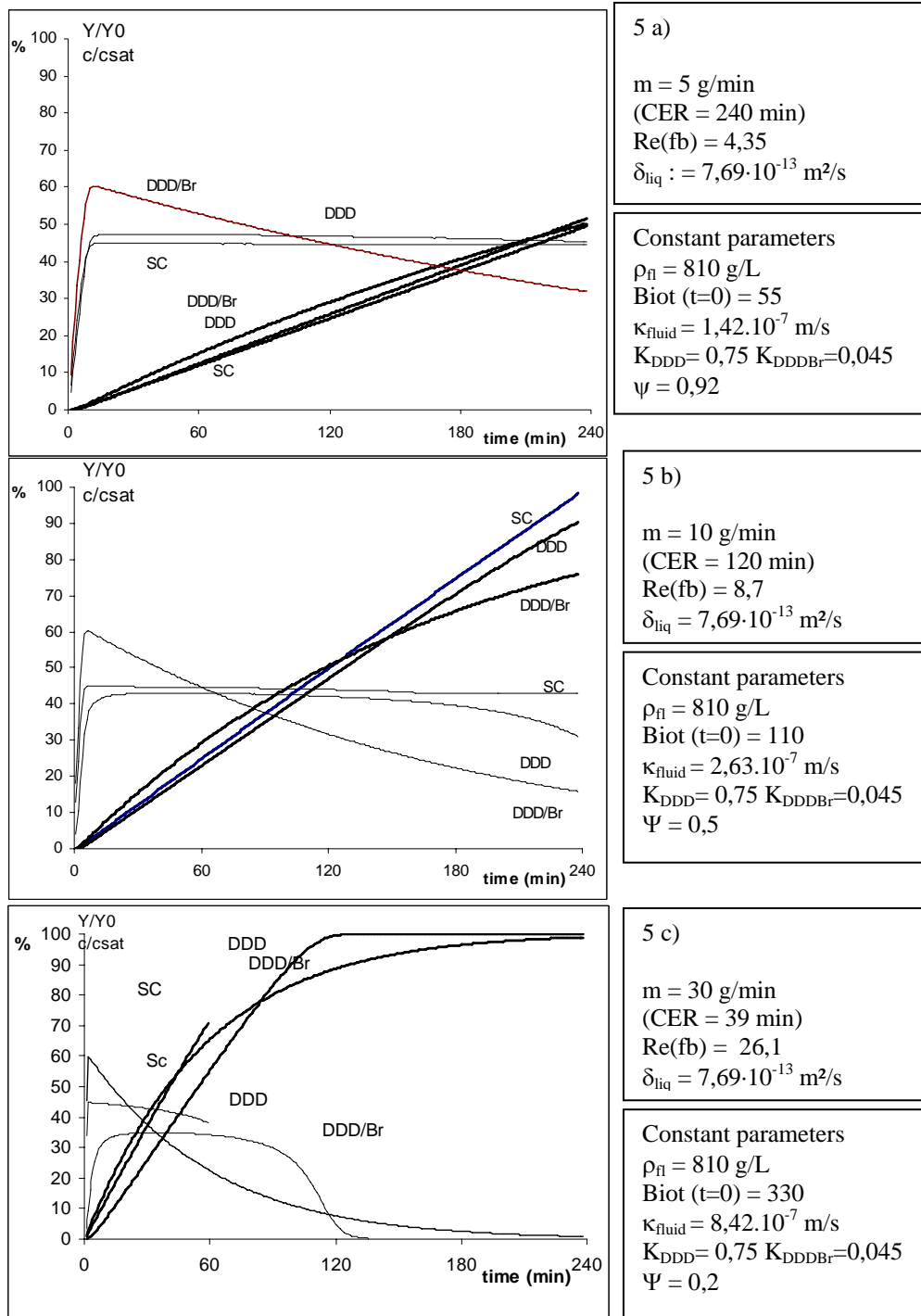


Figure 5 . Parameter Variation : influence of flow rate on total extraction yield

REFERENCES

- [1] BRUNNER (1994) : Gas Extraction, Chapter 7 , Springer
- [2] Krischer "Trocknungstechnik", 1956
- [3] Schlünder and Tsotsas (1988), "Wärmeübertragung in Festbetten,..", Thieme Verlag Stuttgart
- [4] Catchpole , King ,Ind. And Engineering Chem Res 33 (1994), 1828 –1837
- [5] GOTO, ROY, HIROSE ., J. Supercrit. Fluids, 9 (1996), 128.