Inline Measurement of the Residence Time Distribution in High-Pressure Extraction Columns

Axial backmixing lowers the efficiency of packed countercurrent high-pressure extraction columns. To quantify backmixing, a method of measuring the residence time distribution and calculating the axial dispersion coefficient in high-pressure extraction columns is introduced. Using a design of experiments, the effect of supercritical and liquid mass flow rates as well as the pressure at a constant temperature on the mean residence time and the axial dispersion coefficient are evaluated for the system water/supercritical CO₂. The experimental data is correlated to the Reynolds and Schmidt number.

Keywords: Axial dispersion, Countercurrent extraction, Design of experiments, Residence time distribution, Supercritical CO₂ extraction

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1 Introduction

Static or pulsed packed countercurrent liquid-liquid extraction columns are state-of-the-art for different separation processes. The advantages of packed columns are high flexibility and low investment costs [1]. High-pressure extraction columns are preferably operated in countercurrent mode and filled with static structured packings. Different applications were tested successfully [2]. For designing high-pressure extraction columns, the residence time distribution and the resulting axial dispersion coefficient of the continuous phase are important. By measuring the residence time distribution, the deviation from the ideal plug flow can be quantified. The non-ideal flow is caused by stagnant zones, backmixing, or channeling of fluid. The investigation of the backmixing is of importance, as it leads to reduced concentration gradients between the phases and therefore lowers the mass transfer rates significantly. All backmixing effects are summarized in the axial dispersion coefficient.

Especially for one-dimensional dynamic models describing a high-pressure extraction column, a value for the axial dispersion and its effect on the performance of the column is required. Low residence times and high axial dispersion coefficients negatively affect the mass transfer and therefore the performance of the whole column [3]. However, the most dynamic models neglect backmixing and the axial dispersion of the continuous phase. The first dynamic model of high-pressure extraction column for simulating the separation of methyl oleate and squalene with supercritical CO₂ was published by Ruivo et al. [4]. They considered both mass transfer and fluid dynamic aspects. Other model approaches were published by Fernandes et al. [5], Martin and Cocero [6], and Gañán et al. [7].

Different techniques for measuring the residence time distribution and calculating the axial dispersion can be found in literature. The residence time distribution is typically determined via a measured concentration profile. Therefore, either the substance used in production or dedicated tracer experiments can be used. A comprehensive overview of all methods for measuring and calculating the axial dispersion in packed extraction columns is given by Becker [1]. These methods are mainly applied in liquid-liquid extraction. For supercritical extraction processes, first correlations for the axial dispersion were developed using single-phase tracer experiments and fixed-bed extractors [8–10].

First axial dispersion measurements with supercritical CO₂ as continuous phase and a static packing were conducted by Heyrich [11] and Becker [1]. They employed o-xylene as tracer, which was detected by an UV-VIS measurement system. Here, the continuous phase was bypassed and the o-xylene concentration was determined in a high-pressure UV-VIS vial. They highlighted that a structured packing decreases the axial dispersion compared to a mesh wire packing. Moreover, the axial dispersion is independent from the liquid load and slightly decreases by increasing supercritical CO₂ load. The impact of different packing geometries on the axial dispersion coefficient was analyzed by Markmann [12].

The extraction from fermentation broth is described as a promising field in the literature. Different physical and reactive extraction processes were tested [13–15]. The aim of the
The present study is to measure the axial dispersion coefficient for the system supercritical CO\textsubscript{2}/water, which can be used as artificial system for describing fermentation broth. Therefore, a new inline measurement system for the rapid determination of the residence time distribution, the Péclet number, and the axial dispersion coefficient is presented. By applying this system, the influence of the operation pressure, supercritical and liquid mass flow rate was systematically varied according to a central composite design of experiments. Moreover, using the experimental data, a correlation for calculating the axial dispersion coefficient was derived. The correlation was validated using experimental results retrieved from literature and own experiments conducted at different operation settings.

## 2 Materials and Methods

### 2.1 Experimental Setup

The experiments are carried out in a pilot plant equipped with a 4 m active height extraction column (B3) (Fig. 1). The column is filled with a Sulzer CY packing and has an inner diameter of 38 mm. The maximum operation pressure is 550 bar and the maximum operation temperature is 100°C. Liquid CO\textsubscript{2} is pumped pulse-free from the CO\textsubscript{2} tank K1 into the high-pressure extraction column by pump P1 (Lewa LDE 1). The mass flow rate and the density of the fluid are measured with a Coriolis flowmeter (Siemens SITRANS CT030). The high-pressure extraction column is equipped with a level detector (Aquasant SEK 35/20 SB R GH P) at the bottom of the column. The operation pressure within the extraction column is automatically controlled by a backpressure regulator valve and expands the supercritical CO\textsubscript{2} into the separator B2. The gaseous CO\textsubscript{2} flows via heat exchanger W3 back into the tank K1. The liquid aqueous phase is pumped via pump P2 (Lewa LDB 1) into the extraction column at the top and leaves it through a level controlled pneumatic valve at the bottom of the column.

In order to measure the residence time distribution, the tracer component \textit{o}-xylene is pumped via an HPLC pump (Knauer P4.15), a time-controlled valve (Rheodyne MX Series II), and a high-pressure check valve (Sitec-Sieber Engineering) into the bottom of the high-pressure extraction column. \textit{o}-Xylene is pumped with a volumetric flow rate of 10 mL min\textsuperscript{–1} into the extraction column. This setup allows to reproducibly pump 0.13 g s\textsuperscript{–1} ± 0.003 g s\textsuperscript{–1} tracer substance. For one tracer impulse, the valve is open for 1 s. Becker [1], Heydrich [11], and Brockkött and Jupke [16] already stated that \textit{o}-xylene is a suitable tracer substance for supercritical CO\textsubscript{2}. At the top of the extraction column two optical fibers are installed at the heated sapphire glasses. The individual heating of the sapphire glasses of +5 K above operation temperature is necessary to prevent condensation at the glasses. The optical fibers are connected to a SAM Collimator measuring continuously at 255–265 nm. Transmittance and absorbance are measured with the multispectrometer (tec5). The measured absorbance is directly correlated to the concentration due to the Beer-Lambert law.

![Experimental setup consisting of a 4 m (active height) countercurrent extraction column](image)
No calibration is conducted. The settings of the UV-VIS-NIR spectrophotometer are stated elsewhere [16].

After each tracer experiment, the supercritical CO\textsubscript{2} is pumped under operation conditions into the fixed-bed extractor (B1) filled with an adsorber (Blücher Saratech). Here, the tracer substance is adsorbed completely. This can be stated by reaching always the same baseline signal at the beginning of each tracer experiment. All chemicals used for these experiments are listed in Tab. 1. Each tracer experiment is conducted three times.

### 2.2 Residence Time Distribution and Axial Dispersion Coefficient

In countercurrent extraction columns the desired flow pattern is the plug flow, resulting in the highest mass transfer rates and therefore in the highest separation performance. The deviation from the ideal plug flow is experimentally obtained using tracer experiments. Therefore, tracer impulse experiments were conducted to measure the residence time distribution.

The residence time distribution can be quantitatively described by the time that the individual fluid elements spend in the high-pressure extraction column. \(E(\theta)\) defines the probability that a fluid element spends a total time \(t\) in the column. Its density function is defined by Eq. (1):

\[
E(t) = \frac{c(t)}{\int_0^\infty c(t) dt}
\]

In Eq. (1), its density function is defined. Here, \(c(t)\) is the effluent concentration-time curve. The mean residence time \(t_m\) represents the mean time the tracer substance spends in the high-pressure extraction column.

\[
t_m = \int_0^\infty tE(t) dt
\]

By using Eq. (2), the mean velocity within the packing geometry of the supercritical CO\textsubscript{2} can be calculated:

\[
u_m = \frac{L_M}{t_m}
\]

Here, \(L_M\) is the distance between the tracer injection and the SAM collimators at the top of the high-pressure extraction column. In this study, \(L_M\) is equal to 4.19 m. In order to compare the residence time distribution at different process parameters, the use of dimensionless magnitudes is common. The dimensionless time is defined as:

\[
\theta = \frac{t}{t_m}
\]

Table 1. Chemicals used in this study to measure the residence time distribution

| Component | CAS reg. no. | Source                 | Initial purity \([\text{mol mol}^{-1}]\) | Purification method          | Final purity |
|-----------|-------------|------------------------|------------------------------------------|-----------------------------|--------------|
| CO\textsubscript{2} | 124-38-9    | Westphalen Gas         | 99.995 %                                  | None                         | –            |
| Water     | 7732-18-5   | In-house               | –                                        | Deionization, distillation   | <0.7 \(\mu\)S cm\textsuperscript{-1} |
| o-Xylene  | 95-47-6     | Merck KGaA             | 98.0 %                                    | None                         | –            |

and the density function as function of the dimensionless time is expressed as:

\[
E(\theta) = \frac{c(\theta)}{\int_0^\infty c(\theta) d\theta}
\]

For the analysis of the dimensionless residence time distribution function, different methods for an impulse tracer injection and a single measurement point are available in the literature. In this study, the maximum method suggested by Vergnes [17] is applied. The method only requires the maximum coordinate of the dimensionless residence time distribution and is used for calculating the axial dispersion coefficient from a single point. Due to constructive constraints, no axial dispersion coefficient based on two measuring points was calculated.

Based on the reduced equation for the density function proposed by Levenspiel and Smith [18], the following relationship can be derived from the extreme value condition \(\frac{dE}{d\theta} = 0\) for the respective maximum of the measured tracer concentration curve [17]:

\[
4\pi(E_{\text{max}} \theta_{\text{max}})^2 = Pe - 1.5 + \frac{1.125}{Pe}
\]

Here, \(Pe\) is the dimensionless Pécelt number, which is defined by:

\[
Pe = \frac{\mu_{\text{channel}} L_M}{D_{\text{ax}}}
\]

The Pécelt number describes the ratio of convective and diffusive mass transfer. A Pécelt number \(Pe \rightarrow \infty\) corresponds to a plug-flow regime. The Pécelt number depends on both the flow behavior within the column and on the column geometry. For Pécelt numbers \(Pe > 10\), the last term on the right-hand side of Eq. (6) can be neglected. In this study, the Pécelt numbers resulting from the experiments are higher than 25. Therefore, Eq. (6) can be rearranged to:

\[
Pe = 4\pi(E_{\text{max}} \theta_{\text{max}})^2 + 1.5
\]

### 2.3 Model Geometries of Static Packing

Structured packing geometries are characterized by the volume-specific surface area \(a_S\) and the void fraction of the packing \(\varepsilon\).

\[
a_S = \frac{A_P}{V_K}
\]
\[ e = \frac{V_K - V_P}{V_K} \]  

(10)

In these equations, \( A_P \) denotes the surface of the packing, \( V_P \) is the volume of the packing geometry, and \( V_K \) is the volume of the extraction column. The equivalent spherical particle diameter \( d_p \) is chosen in this paper for selecting a suitable length scale. This scale is used to define dimensionless numbers for the flow patterns within the packing geometry. According to Stockfleth [19], the particle model represents best the fluid dynamics in a packed extraction column. The spherical particle diameter is calculated by:

\[ d_p = \frac{6(1 - e)}{a_S} \]  

(11)

Detailed information and data about the characteristics of the packing Sulzer CY can be found elsewhere [16].

### 2.4 Design of Experiments

For the experimental analysis and optimization of supercritical extraction processes from solid matter, a design of experiments (DoE) is a standard tool [20]. Different approaches are available in literature with the aim of gaining as much information as possible and simultaneously saving time and resources. The DoE methods can be subdivided into screening and optimizing design of experiments.

Temperature, pressure, and supercritical \( \text{CO}_2 \) mass flow are often chosen as independent variables for analyzing and optimizing the extraction from solid matter. Likewise, this has been done in this study for analyzing the axial dispersion coefficient. The response surface method (RSM) is chosen, as it embodies linear and quadratic interactions between inputs. In contrast to the extraction from solid matter, the aqueous mass flow rate might have an impact on the axial dispersion coefficient in packed countercurrent high-pressure extraction columns. As most of the extraction processes from aqueous phase are conducted at an operation temperature of \( T = 313.15 \text{K} \), the temperature is set constant. In most cases, a higher temperature would negatively affect the partition coefficient. This was demonstrated for the extraction of alcoholic components [21, 22], as well as the reactive extraction of carboxylic acids [15].

Therefore, the three variables pressure, supercritical and liquid mass flow are examined using a central composite design (CCD). A central composite circumscribed (CCC) method is applied. The CCC is characterized by star points located outside the cubic design of the DoE. In Tab. 2, the experiments related to the star points are denoted with a \(-2 \) and \( 2 \), whereas experiments related to the cubic points are denoted with \(-1 \) and \( 1 \), and the central point with \( 0 \). Compared to other CCD, the CCC explores the largest process space.

### 3 Results

The reproducibility and the reliability of the data were checked at first conducting single and multiphase experiments at an operation pressure of \( P = 100 \text{bar} \) and an operation temperature of \( T = 313.15 \text{K} \). Afterwards, the multiphase experiments of the DoE were conducted. Fig. 2 states that the experimental setup allows to conduct reproducible tracer experiments. Here, an operation pressure of 110 bar, an operation temperature of 313 K, a supercritical \( \text{CO}_2 \) mass flow rate of 9 kg h\(^{-1}\), and a liquid mass flow rate of 1.5 kg h\(^{-1}\) were used. In this figure, three multiphase experiments were conducted and plotted as dimensionless concentration as a function of the dimensionless time. Despite the reproducibility of the tracer experiments, each experiment of the DoE is conducted three times. The arithmetic mean of these experiments is used in the following diagrams.

#### 3.1 Mean Residence Time and Average Channel Velocity

The mean residence time is a first simple indicator for bypassing or channeling and is defined by Eq. (2). According to the DoE, the impact of supercritical mass flow rate and operation pressure on the mean residence time and the channel velocity is evaluated. The resulting response surface is plotted in Fig. 3. On the left, the mean residence time and on the right the Reynolds number of the supercritical phase in the packing are plotted as a function of the pressure and the supercritical mass flow rate. The liquid mass flow rate is held constant at 1 kg h\(^{-1}\).
On the left-hand side of Fig. 3 it can be seen that the residence time of the supercritical CO\textsubscript{2} can be adjusted by the operation pressure, which has a direct effect on the solvent’s density and viscosity. Especially the solvent’s density is directly linked to its ascend velocity. By increasing the pressure, both density and viscosity increase. For instance, raising the pressure from 90 to 110 bar, the density rises from 485.5 to 683.52 kg m\textsuperscript{-3} whereas the viscosity increases from 34.806 to 54.123 m\textsuperscript{2}\textper\textsecond. The higher the density of the solvent, the higher the mean residence time.

The response surface was calculated by allowing a linear and quadratic interaction of the variables and minimizing the quadratic error of the resulting function. The resulting function has a coefficient of determination of 0.95 and is stated in Eq. (12):

\[
\frac{t_m}{s} = -97.45 \frac{m_{sc}}{kg\ h^{-1}} + 21.66 \frac{P}{bar} + 58.19
\]

(12)

On the right-hand side of Fig. 3, the impact of the operation pressure and the supercritical CO\textsubscript{2} mass flow rate on the Reynolds number within the packing channels is shown. The Reynolds number is calculated by:

\[
Re_{sc} = \frac{u_{superficial}}{\eta_{sc}}
\]

(13)

In this equation, \(\rho_{sc}\) denotes the density of the supercritical CO\textsubscript{2} and \(\eta_{sc}\) its viscosity. The Reynolds number within the packing is calculated using the particle model introduced in Sect. 2.3.

Like the mean residence time, the Reynolds number can be varied by changing the operation pressure and mass flow rate. The Reynolds number of the supercritical CO\textsubscript{2} in the packing geometry just above the critical point can be adjusted easily which is also a relevant factor for enhancing the mass transfer, as the interaction time of disperse and continuous phase can be simply increased. The resulting function for the response surface of the Reynolds number has a coefficient of determination of 0.94 and is stated in Eq. (14):

\[
Re_{sc} = 5.204 \frac{m_{sc}}{kg\ h^{-1}} + 10.7 \left(\frac{P}{bar}\right)^2 + 610.6
\]

(14)

In order to evaluate the interaction of the supercritical phase and the packing geometry, the measured velocities and the calculated channel velocities are compared in Fig. 4. The channel velocity is defined as:

\[
u_{Channel} = \frac{u_{superficial}}{(1 - \delta)\epsilon}
\]

(15)

In this equation, \(u_{superficial}\) defines the velocity of the supercritical CO\textsubscript{2} without any interaction with the packing; \(\delta\) is defined as the holdup of the high-pressure extraction column. The holdup is calculated by using the correlation suggested by Brockkötter and Jupke [16]. The equation indicates that the supercritical fluid will be faster than the superficial velocity due to the tapered free volume in the extraction column. In Fig. 4, the relationship between the measured velocity \(u_{c}\) from the tracer experiments and the calculated channel velocity \(u_{Channel}\) is plotted.

Fig. 4 indicates that Eq. (15) systematically overestimates the measured velocity of the supercritical phase. This phenomenon is well known in the literature for extraction columns in pilot scale and describes the bypass flow between the packing and the column wall. In the specific case, the Sulzer CY has a diameter of 28 mm, whereas the column diameter is 38 mm. Therefore, 45.7% of the column diameter is not covered with a packing and can therefore be bypassed.
Beside that, the impact of the liquid phase on the measured channel velocity is neglectable. Therefore, Eqs. (12) and (14) can be used to calculate the mean residence time \( t_m \) and the \( \text{Re}_{sc} \) in the packing geometry.

### 3.2 Impact of the Liquid Mass Flow Rate on the Axial Dispersion

In Fig. 5, the axial dispersion coefficient is plotted over the supercritical mass flow rate at an operation pressure of \( P = 100 \) bar and an operation temperature of \( T = 313 \) K. The liquid mass flow rate in all countercurrent experiments was \( 1 \) kg h\(^{-1}\).

With increasing supercritical \( \text{CO}_2 \) mass flow rate, backmixing inside the packing channels increases which results in a higher axial dispersion coefficient. The axial dispersion coefficient is slightly lowered by the liquid mass flow rate, having a maximum deviation of 7.5\% compared to the single-phase experiments. The small deviation is caused by the small holdup of less than 5\%. This phenomenon was also observed for packed liquid-liquid extraction columns [23–25] and for packed high-pressure extraction columns [12].

### 4 Development of a Correlation for the Axial Dispersion Coefficient

The DoE was conducted to gain a correlation with a high range of validity. Based on the response surface method, a correlation having a standard deviation of 0.6 is developed. Therefore, a more accurate, empirical correlation is elaborated, considering every relevant relationship between different physical quantities. According to Delgado [26], axial dispersion is a function of the velocity \( u_i \), density \( \rho_i \), viscosity \( \eta_i \), and diffusion coefficient \( D_m \) of the phases and the particle diameter \( d_p \).

\[
D_{ax} = f(u_i, \rho_i, \eta_i, D_m, d_p)
\]  
(16)

According to the Buckingham \( \pi \) theorem, Eq. (16) can be rearranged to:

\[
D_{ax} = F \left( \frac{d_p u_i \rho_{sc}}{\eta_{sc}}, \frac{d_{ml} u_i \rho_{li}}{\eta_{li}}, \frac{\eta_{sc}}{\rho_{sc} D_m} \right)
\]  
(17)

The first argument of \( F \) in Eq. (17) is the Reynolds number of the supercritical phase within the packing geometry. The second term is the Reynolds number of the liquid phase. Due to the fact that the liquid holdup is too low, the impact of liquid phase on the axial dispersion coefficient is negligible.

The last argument of Eq. (17) is the Schmidt number of the supercritical phase describing the ratio of viscous diffusion and molecular diffusion. According to Levenspiel [3], the molecular diffusion has an impact on the dispersion coefficient in a laminar flow regime. As the tracer experiments state that a laminar flow regime in the packing is present, the Schmidt number is considered for the correlation (see Fig. 3).

The diffusion coefficient is calculated by a rearranged Wilke and Chang [27] equation, valid for supercritical fluids [28].

\[
D_m = 8.6 \times 10^{-15} \left( \frac{T \sqrt{M_{\text{CO}_2}}}{n_{sc} (V_{BP, \text{CO}_2})^{0.6}} \right)
\]  
(18)

The diffusion coefficient \( D_m \) is a function of the temperature \( T \), the molecular mass of \( \text{CO}_2 M_{\text{CO}_2} \), its viscosity \( \eta_{sc} \) and its molecular volume at the normal boiling point \( V_{BP, \text{CO}_2} \). The diffusion coefficient is on the order of \( 1 \times 10^{-8} \) m s\(^{-1}\) as stated by Zehnder [29].

The following expression for Eq. (17) is used for fitting the data:

\[
D_{ax} = \alpha \left( \text{Re}_{sc} \text{Sc}_{sc}^{0.6} \right)
\]  
(19)
In this equation, $\alpha$, $\beta$, and $\gamma$ are empirical fitting parameters. The parameters are fitted to all experiments from the DoE resulting in:

$$D_{kk} = 0.119 \, \text{cm}^2 \text{s}^{-1} \left( \frac{R_e}{S_c} \right)^{0.845} \left( \frac{S_c}{S_e} \right)^{0.496}$$

(20)

The correlation is valid for Reynolds numbers from 30 to 170 and Schmidt numbers from 0.6 to 1.8. In this case, the Schmidt numbers are in the range of gases due to the gas-like viscosity and a diffusion coefficient between gases and liquids. The correlation has a coefficient of determination of 0.803. The results are plotted in Fig. 6.

![Figure 6. Parity plot of the experimental and calculated axial dispersion coefficient.](image)

This correlation was validated by measuring the single-phase axial dispersion coefficient at 100 bar and 333.15 K resulting in lower Schmidt numbers but higher Reynolds numbers. Moreover, results from Markmann [12] for the Sulzer Mellapak 500 were taken to validate the empirical correlation of this study. In comparison to the Sulzer CY packing geometry, the Sulzer Mellapak has a lower volume-specific surface area of $a_s = 500 \, \text{m}^2 \text{m}^{-3}$ but a higher void fraction of $\varepsilon = 0.96$. Markmann conducted his single-phase experiments at an operation pressure of $P = 300$ bar and a temperature of $T = 333.15 \, \text{K}$ resulting in a maximum Schmidt number of 2.4 and a maximum Reynolds number of 68.

Own validation experiments are in a good agreement with the empirical correlation resulting in a maximum error of 14.8%. By using Markmann’s experimental results, the correlation constantly overestimates the axial dispersion coefficient. This is due to the fact that his experimental results exceed the validity range. Therefore, it can be concluded that the correlation has a limited extrapolability but can be employed to get a first valid impression on the axial dispersion coefficient. It can be stated that the use of the developed empirical correlation using the Reynolds and Schmidt number in the channels of the packing geometry is suitable for describing axial backmixing and axial dispersion for a wide range of operation parameters in high-pressure extraction columns.

### 5 Conclusion

The residence time distribution for supercritical CO$_2$ in a high-pressure extraction column equipped with a static structured packing was measured using o-xylene as tracer substance. The tracer absorbance was measured at the top of the high-pressure extraction column with two SAM collimators coupled to a UV-VIS NIR spectrometer. A central composite design of experiments was conducted to evaluate the impact of the supercritical and liquid mass flow rates as well as the operation pressure on the axial dispersion coefficient. The operation pressure was chosen at $P = 100$ bar ± 20 bar, which are typical values for the physical and reactive extraction from aqueous solutions. Moreover, applying this design of experiments, a broad range of resulting Reynolds and Schmidt numbers can be analyzed and characterized.

The liquid mass flow rate had a negligible impact on the mean residence time and on the axial dispersion coefficient due to the low holdup of less than 5%. As the diffusive flow influences the axial dispersion at a laminar flow regime, the axial dispersion is correlated to the Reynolds and Schmidt number. To validate the correlation, single-phase experiments under different operation conditions were used, having a maximum percentage error of 14.5%. Moreover, experiments from Markmann at an operation pressure of $P = 300$ bar and an operation temperature of 333.15 K conducted in a Sulzer Mellapak were compared resulting in a maximum percentage error of 37.5%. It was concluded that the developed correlation is valid for different structured packings and operation conditions of Reynolds numbers smaller than 170 and Schmidt numbers less than 1.8.

The range of determined axial dispersion coefficients means that axial backmixing in structured packings operating under supercritical conditions cannot be neglected. This is mainly due to the low viscosity of the supercritical fluid. The developed correlation can be applied in dynamic models in order to simulate the separation performance in a high-pressure extraction column more precisely.

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The authors have declared no conflict of interest.

### Symbols used

- $A$ [m$^2$] surface
- $a_s$ [m$^2$ m$^{-3}$] volume-specific surface
- $c$ [kg m$^{-3}$] concentration
- $d$ [m] diameter
\(d_{s2}\) [mm] Sauter diameter
\(D_{ax}\) [cm\(^2\)s\(^{-1}\)] axial dispersion coefficient
\(D_m\) [m\(^2\)s\(^{-1}\)] diffusion coefficient
\(E\) [s\(^{-1}\)] portion of the flow of tracer per second
\(L\) [m] length
\(\dot{m}\) [kg h\(^{-1}\)] mass flow rate
\(P\) [bar] pressure
\(P_e\) [-] Péclet number
\(Re\) [-] Reynolds number
\(Sc\) [-] Schmidt number
\(t\) [s] time
\(u\) [m s\(^{-1}\)] velocity

Greek letters
\(\theta\) [-] dimensionless time
\(\varepsilon\) [-] void fraction of the packing

Sub- and superscripts
i component \(i\)
K column
l liquid
m mean
max maximum
P packing
rs relative velocity
sc supercritical CO\(_2\)

Abbreviations
CCC central composite circumscribed
CCD central composite design
DoE design of experiments
RSM response surface methodology

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Research Article: To quantify axial backmixing in a high-pressure extraction column, an innovative method of measuring the residence time distribution is introduced. Using a design of experiments, the impact of supercritical and liquid mass flow rates as well as the pressure at a constant temperature on the mean residence time and the axial dispersion coefficient are evaluated for the system water/supercritical CO₂.

Inline Measurement of the Residence Time Distribution in High-Pressure Extraction Columns

J. Brockkötter, A. Welkner-Hoffmann, A. Jupke*  

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