Parameter estimation

Oliwer Sliczniuk*^{a,*}, Pekka Oinas^a and Francesco Corona^a

^{a}*Aalto University, School of Chemical Engineering, Espoo, 02150, Finland*

ARTICLE INFO

ABSTRACT

Given a system of partial differential equations, $F(t, x, \dot{x}, p, u) = 0$, where x represents state variables, p are the parameters, and u are control variables, the process model is simultaneously solved for both x_i and a set of sensitivity functions, dx_i/dp_j, overall times t. These sensitivity functions measure the influence of the parameter change on the model's output. As an example, the supercritical extraction process is presented. The impact of mass flow rate, pressure, and inlet temperature on the model's output is discussed. The sensitivity analysis results prove that the considered variables can affect the extraction's yield and be used as control variables in optimization problems. Moreover, the local sensitivity analysis results are analyzed from a phenomenological point of view to enhance understanding of the process model.

1. Introduction

2. Materials and methods

2.1. Extraction model

~~The main components of the model are three one-dimensional differential equations related to mass balances (solid and fluid phase) and heat balance. As in all batch processes, our system has only one steady state. The steady-state occurs only if the solute is entirely taken out of the biomass. The extraction from a fixed bed is an unsteady process, implying that the solute concentrations in the solid and solvent phases vary over time and space. The convection and the diffusion of the mass and the heat are considered only in the axial direction. The radial distribution of such properties like a velocity is assumed to be flat in that direction. The assumption of the flat velocity profile allows considering a lack of back mixing. The pressure drop in the bed is assumed to be assumed to negligible. Under such conditions, the fluid flow can be considered a plug flow. Since the solute is assumed to be a single pseudo-component, there is only one mass balance equation for each phase (Eq. s 2 and 3). On the other hand, there is only one heat balance (Eq. 8) because the presence of a single pseudo-phase is assumed. Moreover, the process model does not consider the change of particle size or the void fraction during the process. The particles are assumed to be uniformly distributed along the bed and to have the same size.~~

A distributed-parameter model, based on Reverchon [1], is used to describe the solid-fluid extraction process. The process model consists of three partial differential equations: two mass balance equations relative to the concentration of solute in the fixed solid phase and the mobile fluid phase, and the heat balance equation relative to the temperature of the fluid phase. The amount of solute in the solvent is considered negligible. Therefore, the fluid phase can be described as pseudo-homogenous, and its properties are assumed to be the same as the solvent.

The movement of the mobile pseudo-homogeneous phase (Eq. 2) is considered only in the axial direction. The properties of the system in the radial direction is assumed to be uniform. In addition, it is considered that the boundary layer adjacent to the inner wall of the extractor does not exist. Therefore, the velocity profile is constant across any cross-section of the extractor perpendicular to the axial direction. As a result, the plug flow model can be introduced. The particle size distribution and the void fraction of the solid phase are assumed to be uniform in space and remain constant in time. Moreover, the pressure is considered to be constant along the fixed bed. The mass balance for the fluid phase consists of convection, diffusion, and kinetic terms.

Considering the solid phase to be fixed, the convection and diffusion terms in the corresponding mass balance are both assumed to be negligible or absent. Therefore, the mass balance for the solid phase (Eq. 3) consists of the kinetic term only.

As for the mass transfer from the solid to the fluid phase, a kinetic term based on two-film theory for the solute is considered. The mass transfer kinetic (Eq. 4) consists of the overall diffusion coefficient and the concentration gradient, which acts as a driving force for the process. A single pseudo-component is used to represent the extract collectively.

The heat balance (Eq. 8) consists of the convective and diffusive terms. It follows the assumption of a pseudo-homogeneous phase, which properties are the mean between fluid and solid phases. We consider no heat loss through the wall, and there is no heat generation in the system. Therefore, the temperature of the extractor can be changed only by manipulating the temperature of the inlet stream $T_{In}(t)$.

We assume that at a given section, where the cross-sectional area is A, the flow properties are uniform across that section. Hence, although the are of an extractor changes as a function of a distance along an extractor (e.g. if a fixed fill an extractor partially), z, and therefore in reality the

*Corresponding author

✉ oliwer.sliczniuk@aalto.fi (O. Sliczniuk*)

ORCID(s): 0000-0003-2593-5956 (O. Sliczniuk*); 0000-0002-0183-5558 (P. Oinas); 0000-0002-3615-1359 (F. Corona)

flow field is two-dimensional (the flow varies in the two-dimensional space), we make the assumption that the flow properties vary only with z; this is tantamount to assuming uniform properties across any given cross section. Such flow is defined as quasi-one-dimensional flow.

For the sake of clarity of the process model, different colors have been used in the equations to indicate: control variables, state variables, variables and parameters.

2.1.1. Continuity equation

The continuity equation for the fluid phase is given by Eq. 1. The details of derivation can be found in the appendix A.1.1

$$\frac{\partial \left(\rho_f \varepsilon(z) \right)}{\partial t} + \frac{\partial \left(\rho_f u \right)}{\partial z} = 0 \tag{1}$$

where u is the superficial velocity, ε is the bed porosity and ρ_f is the fluid density.

2.1.2. Mass balance for the fluid phase

The fluid phase is a mobile phase, which means that the fluids mass balance (Eq. 2) is made of convection, diffusion, and mass transfer kinetic terms.

$$\frac{\partial c_f(t,z)}{\partial t} = \underbrace{- \frac{1}{\varepsilon A} \frac{F(t)}{\rho_f \left[T(t,z), P(t) \right]} \frac{\partial c_f(t,z)}{\partial z}}_{\text{Convective term}}$$

$$+ \underbrace{D_e^M \left[T(t,z), P(t), F(t) \right] \frac{\partial^2 c_f(t,z)}{\partial z^2}}_{\text{Diffusive term}} + \underbrace{\frac{1-\varepsilon}{\varepsilon} r_e(t,z)}_{\text{Kinetic term}} \tag{2}$$

where $c_f(t,z), c_s(t,z), T(t,z)$ correspond to concentration of solute in the fluid phase, concentration of solute in the solid phase and the temperature, respectively. $r_e(t,z)$ is a mass transfer kinetic term. $F(t)$ is the mass flow rate, $P(t)$ is the pressure, ϵ is the void fraction of the bed, A is the extractor's cross section, $\rho(T(t,z), P(t))$ is the fluid's density, ρ_s is the solids density, $D_e^M(T(t,z), P(t), F(t))$ is the axial mass diffusion coefficient.

2.1.3. Mass balance for the solid phase

The solid phase is a stationary phase, which indicates a lack of convection and diffusion terms in the mass balance (Eq. 3). Therefore, the only term present in this equation is the kinetic term (defined as presented in equation 4), which links solid and fluid phases.

$$\frac{\partial c_s(t,z)}{\partial t} = \underbrace{r_e(t,z)}_{\text{Kinetics}} \tag{3}$$

2.1.4. Kinetic term

As the solvent flows through the bed, ~~it forms a film around the porous solid particle and occupies its pores.~~ the CO_2 molecules diffuse into the pores and adsorb on the particle surface to for an external fluid film around the solid particles through the solvent–solid matrix interactions. Assuming that the mean free path of the molecule is much smaller than the pore diameter, the effect of Knudsen diffusion is small and can be neglected. In this work, the molecular diffusion is assumed.. The dissolved solute diffuses from

the particle's core through the solid-fluid interface, the pore, and the film into the bulk. The graphical representation of the mass transfer mechanism is shown in Figure 1. The mean solute concentration in the solid phase is denoted as c_s. At the solid-fluid interface, the equilibrium concentrations are given as c_s^* and c_P^*, respectively for solid and fluid phases. The concentration of the solutes in the fluid phase in the centre of the pore is denoted as c_P. As the solute diffuses through the pore, its concentration changes and reaches c_{Pf} at ~~the end~~ the opening of the pore. The solute diffuses through the film around the particle and reaches a concentration in the bulk c_f. It can be assumed that the two-film theory describes the solid-fluid interface inside the pore. The overall mass transfer coefficient can be introduced if the relation between the solute concentration in one phase and its equilibrium concentration is known.
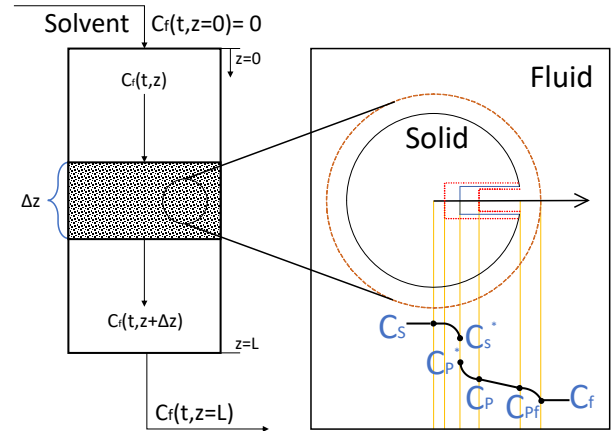

Figure 1: The extraction mechanism

Bulley et al. [2] suggest a process where the driving force for extraction is given by the difference between concentration of the solute in the bulk, c_f, and in the centre of the pore, c_P^*. The concentration c_P^* is in equilibrium with c_s according to an equilibrium relationship. The rate of extraction is thus $r_e \left(c_f - c_P^*(c_s) \right)$.

On the other hand, Reverchon [1] proposes a driving force given by the difference between c_s and c_P^*. c_P^* is determined by an equilibrium relationship with c_f and the extraction rate is $r_e \left(c_s - c_P^*(c_f) \right)$.

~~The kinetic term, denoted as equation 4, corresponds to a solute transfer rate between both phases. This term is made of the overall diffusion coefficient and the concentration gradient (between one phase and its equilibrium concentration), which acts as a driving force for the process.~~ The mass transfer kinetic (Eq. 4) describes a diffusion rate of the solute from solid particles to the solvent. The kinetic term consists of the overall diffusion coefficient and the concentration gradient, which acts as a driving force for the process. Based on the work of Bulley et al. [2], Reverchon [1] proposed to define the kinetic terms as

$$r_e(t,z) = \frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - q^*(t,z)\right) \tag{4}$$

where $D_i(T(t,z))$ corresponds to the overall diffusion coefficient and $q^*(t,z)$ is a concentration at the solid-fluid interface (which according to the internal resistance model is supposed to be at equilibrium with the fluid phase). $q^*(t,z)$ can be calculated based on the equilibrium relationship (Eq. 5).

~~The kinetic term of the model takes into account the properties of the biomass like a sphericity (through the shape coefficient μ equal to 1/3 for slabs and 3/5 for spheres), a characteristic dimension of particles (through the parameter $l = r/3$ where r is the mean particle radius), and the solid density ρ_s. The fixed bed is characterized by a void fraction ϵ.~~

The kinetic term of the model takes into account properties of the solid particles like a sphericity (through the shape coefficient μ), a characteristic dimension of particles (through the parameter $l = r/3$ where r is the mean particle radius), and the bulk density ρ_s. The fixed bed is characterized by a void fraction ϵ.

According to Bulley et al. [2], a linear equilibrium relationship (Eq. 5) can be used to find an equilibrium concentration of the solute in the fluid phase $c_f^*(t,z)$ is based on concentration of the solute in the solid phase $c_s(t,z)$

$$c(t,z) = k_p(T(t,z),P(t))q^*(t,z) \tag{5}$$

The volumetric partition coefficient $k_p(T(t,z),P(t))$ behaves as an equilibrium constant between the solute concentration in one phase and the corresponding equilibrium concentration at the solid-fluid interphase. ~~The $k_p(T(t,z),P(t))$ can be expressed as mass partition factor $k_m(T(t,z))$ according to~~ Spiro and Kandiah [3]. According to Spiro and Kandiah [3], the term $k_p(T(t,z),P(t))$ can be expressed as the function of mass partition factor $k_m(T(t,z))$

$$k_m(T(t,z)) = \frac{k_p(T(t,z),P(t))\rho_s}{\rho(T(t,z),P(t))} \tag{6}$$

Equation 7 is the full representation of the kinetic term.

$$r_e(t,z) = -\frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - \frac{\rho_s}{k_m(T(t,z))\rho(T(t,z),P(t))}c(t,z)\right) \tag{7}$$

2.1.5. Heat balance

~~The heat balance equation (Eq. 8) was developed, assuming the existence of a pseudo-homogeneous phase, which properties are the mean between fluid and solid phases (the amount of solute is considered small enough not to affect the overall heat balance). Equation 8 contains the convection and the diffusion terms. It is considered that there is no heat loss through the wall, and there is no heat generation in the system. The temperature of the extractor can be changed only by increasing the temperature of the inlet stream. The pseudo-homogenous phase is assumed to flow only in the axial direction. The numerator of the factor in front of the convection term of the heat equation contains only the specific heat of the fluid $C_p(T(t,z),P(t))$ because~~ the solid phase is stationary. Therefore, this factor can be understood as the fraction of the fluid's total heat through convection. On the other hand, the axial heat diffusion is calculated based on the definition of thermal diffusivity for the fluid, as explained in the appendix.

The heat balance (Eq. 8), is based on Srinivasan and Depcik [4], and consists of convective and diffusive terms. It follows the assumption of a pseudo-homogeneous phase, which properties are the mean between fluid and solid phases. It is considered that there is no heat loss through the walls, and there is no heat generation in the system. The temperature of the extractor can be changed only by manipulating the temperature of the inlet stream $T_{Inlet}(t)$.

$$\frac{\partial T(t,z)}{\partial t} = -\underbrace{\frac{F(t)C_p(T(t,z),P(t))}{A[(1-\epsilon)\rho(T(t,z),P(t))C_p(T(t,z),P(t)) + \epsilon\rho_s C_{ps}]}\frac{\partial T(t,z)}{\partial z}}_{\text{Convection}} +$$
$$+ \underbrace{D_e^T(T(t,z),P(t))\frac{\partial^2 T(t,z)}{\partial z^2}}_{\text{Diffusion}} \tag{8}$$

where $D_e^M(T(t,z),P(t),F(t))$ is the axial mass diffusion coefficient, $C_p(T(t,z),P(t))$ is the fluid's specific heat, C_{ps} is the specific heat of the solid phase, $D_e^T(T(t,z),P(t),F(t))$ is the axial heat diffusion coefficient.

2.1.6. Extraction yield

~~The efficiency of the process (the yield) is calculated according to equation 9. The yield is defined as the ratio between a difference of initial solute's mass in the solid phase m_0, and an actual amount of solute in the same phase m, compared to the initial amount of the solute in the fixed bed m_0. The yield can also be calculated based on the change of solutes concentration in the solid phase if the volume of the extractor V is constant. An output function $y(t)$ returns a yield curve that represents the fraction of the solute's mass over time. The yield is obtained by function $g(q(t,z))$. Function $g(q(t,z))$ corresponds to a 'measurement device' that allows to calculate the yield based on the state variable $q(t,z)$.~~ The efficiency of the process (the yield) is calculated according to Eq. 9, and is based on the change of solute's mass in the solid phase. It is defined as ratio the ratio between the difference of its initial value m_0 and the actual value $m(t,z)$, compared to the initial one. The yield can also be calculated based on the change of solutes concentration in the solid phase if the volume of the extractor V is constant.

$$y(t) = g(q(t,z)) = \frac{(m_0 - m(q(t,z)))}{m_0} = \frac{V(q_0 - q(t,z))}{Vq_0} \tag{9}$$

where ~~$q(t,z)$ is concentration of solute in a solid phase and a temperature, respectively. m_0 is a initial mass of the solute in the solid phase, q_0 is a initial concentration of the solute in the solid phase, V is an extractor volume.~~

2.1.7. Dependencies

The Peng-Robinson equation of state is used to describe the thermodynamics of the fluid phase. The thermal

properties of the pseudo-homogeneous phase are assumed to vary along the extractor, though always remaining equal to the corresponding mean values between the fluid and solid phase.

In the process model, properties of the supercritical fluid such as the density $\rho(T(t,z), P(t))$, the specific heat $C_p(T(t,z), P(t))$, the thermal conductivity $k^T(T(t,z), P(t))$, or the viscosity $\eta(T(t,z), P(t))$ are calculated based on the local temperatures along the fixed bed and the pressure. The Peng-Robinson equation of state is used to find values of a $\rho(T(t,z), P(t))$ and $C_p(T(t,z), P(t))$.

The inter-particle diffusion coefficient $D_e^M(T(t,z), P(t), F(t))$ is calculated from the empirical correlation, as the function of the Reynolds number $R_e(T(t,z), P(t), F(t))$ and the Peclet's number $P_e(T(t,z), P(t), F(t))$. The values of the internal diffusion $D_i(T(t,z))$ and the partition coefficient $k_m(T(t,z))$ come from the laboratory experiments. The expressions and the detailed information of the parameter fitting can be found in the appendix.

2.1.8. State-space representation

It is assumed that the solvent is free of solute at the entrance of the extractor and that all the solid particles have the same initial solute content q_0. Moreover, it is considered that the initial temperature of the extractor in every place is equal to T_0. Therefore, the initial conditions employed in the simulation are:

$$c(t=0,z) = 0$$
$$q(t=0,z) = q_0$$
$$T(t=0,z) = T_0$$

The process model can be written in a general form:

$$\begin{bmatrix} \dfrac{\partial c(t,z)}{\partial t} \\ \dfrac{\partial q(t,z)}{\partial t} \\ \dfrac{\partial T(t,z)}{\partial t} \end{bmatrix} = \begin{bmatrix} \phi_1(c(t,z), q(t,z), T(t,z); \theta) \\ \phi_2(c(t,z), q(t,z), T(t,z); \theta) \\ \phi_3(c(t,z), q(t,z), T(t,z); \theta) \end{bmatrix} = \phi(t,z;\theta) = \dfrac{\partial \chi(t,z)}{\partial t}$$

(11)

where θ is a set of parameters present in the model, ϕ is a set of functions that correspond to state equations of the model, and χ is the state-space model.

The method of lines is used to transform the process model equations into a set of ODEs denoted as $G(x(t); p)$. The partial derivatives in z-direction are computed using a first-order and second-order finite difference approximation. The backward finite difference is used to approximate first-order derivative, while the central difference scheme is used to approximate second-order derivative. The length of the fixed bed is divided into N_z equally distributed points in z-direction. Each function ϕ_i is transformed to a corresponding set of N_z discretized equations denoted as $G_{i \times N_z + 1}$ to $G_{(i+1) \times N_z}$, where i corresponds to the process model equation. The state-space model $\chi(t,z)$ after the discretization is represented by $\dot{x}(t)$ (Eq. **??**).

$$\dot{x}(t) = \frac{dx(t)}{dt} = \begin{bmatrix} \dfrac{dc_{f,1}(t)}{dt} \\ \vdots \\ \dfrac{dc_{f,N_z}(t)}{dt} \\ \hline \dfrac{dc_{s,1}(t)}{dt} \\ \vdots \\ \dfrac{dc_{s,N_z}(t)}{dt} \\ \hline \dfrac{dT_1(t)}{dt} \\ \vdots \\ \dfrac{dT_{N_z}(t)}{dt} \end{bmatrix} = \underbrace{\begin{bmatrix} G_1(x(t), q(t), T(t); p) \\ \vdots \\ G_{N_z}(c(t), q(t), T(t); p) \\ \hline G_{N_z+1}(c(t), q(t), T(t); p) \\ \vdots \\ G_{2N_z}(c(t), q(t), T(t); p) \\ \hline G_{2N_z+1}(c(t), q(t), T(t); p) \\ \vdots \\ G_{3N_z}(c(t), q(t), T(t); p) \end{bmatrix}}_{G(x(t); p)}$$

where $x \in \mathbb{R}^{N_x = 3N_z}$ and $p \in \mathbb{R}^{N_p = N_\theta + N_u}$, N_θ is the number of model parameters, N_u is the number of control variables.

In a state-space sense, the state variables of the system are the local concentrations of solute in the fluid and solid phases ($c(t,z)$ and $q(t,z)$, respectively), and the local temperature of the pseudo-homogeneous phase ($T(t,z)$). The controllable input variables are the mass flow-rate and temperature of the solvent in the feed ($F_{in}(t) = F(t)$ and $T_{in}(t) = T(t, z=0)$, respectively) and the pressure in the extractor ($P(t,z) = P(t)$). We also assume that extraction yield can be modelled as a function of a known initial mass of solute in the solid phase and it can be measured after the separator ($Y(t)$). The system is controllable by manipulating the flow-rate and temperature of CO2 in the feed, and the pressure in the extractor.

2.2. Parameter estimation

3. Results

4. Conclusions

References

[1] E. Reverchon. Mathematical modeling of supercritical extraction of sage oil. AIChE Journal, 42(6):1765–1771, jun 1996. doi: 10.1002/aic.690420627.

[2] N. R. Bulley, M. Fattori, A. Meisen, and L. Moyls. Supercritical fluid extraction of vegetable oil seeds. Journal of the American Oil Chemists' Society, 61(8):1362–1365, aug 1984. doi: 10.1007/bf02542243.

[3] M. Spiro and M. Kandiah. Extraction of ginger rhizome: partition constants and other equilibrium properties in organic solvents and in supercritical carbon dioxide. International Journal of Food Science & Technology, 25(5):566–575, jun 2007. doi: 10.1111/j.1365-2621.1990.tb01116.x.

[4] A. Srinivasan and C. Depcik. One-dimensional pseudo-homogeneous packed-bed reactor modeling: I. chemical species equation and effective diffusivity. Chemical Engineering & Technology, 36(1):22–32, dec 2012. doi: 10.1002/ceat.201200458.

A. Appendix

A.1. Governing equations

A.1.1. Mass continuity

Let's assume that any properties of the flow are uniform across any given cross-section of an extractor. The variation of the cross-section might be an result of partial filling of an extractor or its irregular shape. In reality, such a flow is two-dimensional, because with the area changing as a function of z, in actuality there will be flow-field variations in both directions. The assumption of quasi-one-dimensional flow dictates that the flow properties are function of z only. The equations described by quasi-one-dimensional assumption hold: (1) mass conservation, (2) Newton's second law, and (3) energy conservation. To ensure that these physical principles are satisfied the modified governing equation can be derived. Let's start with the integral form of the continuity equation:

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f}\rho_f d\mathcal{V}_f + \iint_S \rho_f \mathbf{V}\cdot\mathbf{dS} = 0 \tag{12}$$

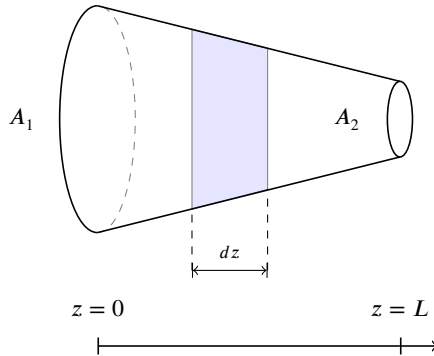We apply this equation to the shaded control volume shown in Fig. 2.

Figure 2: Control volume for deriving partial differential equation for unsteady, quasi-one-dimensional flow

This control volume is a slice of an extractor, where the infinitesimal thickens of the slice is dz. On the left side of the control volume, consistent with the quasi-one-dimensional assumptions, the density, velocity, pressure and internal energy denoted by ρ_f, V, P, and e, respectively, are uniform over the are A. Similarly, on the right side of the control volume, the density, velocity, pressure, and internal energy $\rho_f + d\rho_f$, $V + dV$, $P + dP$, and $e + de$, respectively, are uniform over the area available for fluid phase $A_f + dA_f$. Applied to the control volume in Fig. 2, the volume integral in Eq. 12 becomes, in the limit as dz becomes very small,

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f}\rho_f d\mathcal{V}_f = \frac{\partial}{\partial t}\left(\rho_f A_f dz\right) \tag{13}$$

where $A\,dz$ is the volume of the control volume in the limit of dz becoming vanishingly small. The surface integral in Eq. 12 becomes

$$\iint_S \rho_f \mathbf{V}\cdot\mathbf{dS} = -\rho_f V A_f + (\rho_f + d\rho_f)(V + dV)(A_f + dA_f) \tag{14}$$

where the minus sign on the leading term on the right-hand side is due to the vectors $\mathbf{V}$ and $\mathbf{dS}$ pointing in opposite directions over the left of the control volume, and hence the dot product is negative. Expending the triple product term

$$\iint_S \rho_f \mathbf{V}\cdot\mathbf{dS} = -\rho_f V A_f + \rho_f V A_f + \rho_f V dA_f + \rho_f A_f dV + \rho_f dV dA_f$$
$$+ V A_f d\rho_f + V d\rho_f dA + A_f d\rho_f dV + d\rho_f dV dA_f \tag{15}$$

In the limit as dz becomes very small, the terms involving products of the differential in Eq. 15, sych as $\rho_f dV dA_f$, $d\rho_f dV dA_f$, go to zero much faster than those terms involving only one differential. Hence, all terms involving products of differentials can be dropped, yielding in the limit as dz becomes very small

$$\iint_S \rho_f \mathbf{V}\cdot\mathbf{dS} = \rho_f V dA_f + \rho_f A_f dV + V A_f d\rho_f \tag{16}$$

Substituting Eqs. 13 and 16 into 12, we have

$$\frac{\partial\left(\rho_f A_f\right)}{\partial t} + \frac{\partial\left(\rho_f A_f V\right)}{\partial z} = 0 \tag{17}$$

Above partial differential equation form of the continuity equation suitable for unsteady, quasi-one-dimensional flow. It ensures that mass is conserved for this mode of the flow. The $A_f(z)$ is an arbitrary function, which describe change of the cross-section of an extractor. The function $A_f(z)$ can be defined as $A_f(z) = \mathbf{A}\varepsilon(z)$, where ε is the bed porosity and $\mathbf{A}$ is the cross-section of an empty extractor.

$$\frac{\partial\left(\rho_f \mathbf{A}\varepsilon(z)\right)}{\partial t} + \frac{\partial\left(\rho_f \mathbf{A}\varepsilon(z)V\right)}{\partial z} = 0 \tag{18}$$

The equation can be simplified by cancel out a constant $\mathbf{A}$

$$\frac{\partial\left(\rho_f \varepsilon(z)\right)}{\partial t} + \frac{\partial\left(\rho_f \varepsilon(z)V\right)}{\partial z} = 0 \tag{19}$$

If so called superficial velocity is defined $u = \varepsilon V$, the mass continuity becomes

$$\frac{\partial\left(\rho_f \varepsilon(z)\right)}{\partial t} + \frac{\partial\left(\rho_f u\right)}{\partial z} = 0 \tag{20}$$

A.1.2. Transport of a species

The transport of a chemical species, in this case a solute, can be described by analogous equation to the Eq. 12 with additional terms on the right-hand side. The first term on the right-hand side describes that a substance goes from high density regions to low density regions and is based on the Fick's law $\left(J_{diff} = -D\dfrac{\partial C_f}{\partial z}\right)$. The other term correspond for the mass transfer between solid and fluid phases, which is treated as a source term.

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f} C_f d\mathcal{V}_f + \iint_S C_f \mathbf{V}\cdot\mathbf{dS} = \iint_S J_{diff}\cdot\mathbf{n}\,\mathbf{dS} + \frac{\partial}{\partial t}\iiint_{\mathcal{V}_s} C_s d\mathcal{V}_s \tag{21}$$

Similarly to the continuity equation, in the limit as dz becomes very small

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f} C_f d\mathcal{V}_f = \frac{\partial}{\partial t}\left(C_f A_f dz\right) \tag{22}$$

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_s} C_s d\mathcal{V}_s = \frac{\partial}{\partial t}\left(C_s A_s dz\right) \tag{23}$$

The surface integrals in the limit of dz becomes

$$\iint_S C_f \mathbf{V} \cdot \mathbf{dS} = C_f V dA_f + C_f A_f dV + V A_f dC_f \qquad (24)$$

From the Divergence theorem in multi-variable calculus, we have

$$\iint_S J_{diff} \cdot \mathbf{n}\, \mathbf{dS} = \iiint_{\mathcal{V}_f} \nabla J_{diff} dV_f = \nabla \iiint_{\mathcal{V}_f} J_{diff} dV_f = \nabla \left(J_{diff} A_f dz \right) \qquad (25)$$

By substituting the equations derived above into Eq. 21 we obtain

$$\frac{\partial (C_f A_f)}{\partial t} + \frac{\partial (C_f A_f V)}{\partial x} = \frac{\partial (C_s A_s)}{\partial t} + \frac{\partial (J_{diff} A_f)}{\partial z} \qquad (26)$$

By defining $A_f = A \cdot \varepsilon$, $A_s = A \cdot (1 - \varepsilon)$ and $u = V \cdot \varepsilon$, and assuming that A is constant, the above equation becomes

$$\frac{\partial (C_f \varepsilon)}{\partial t} + \frac{\partial (C_f u)}{\partial x} = \frac{\partial (C_s (1-\varepsilon))}{\partial t} + \frac{\partial (J_{diff} \varepsilon)}{\partial z} \qquad (27)$$

By expanding above equation, splitting variable and assuming that $\dfrac{\partial \varepsilon}{\partial t} = 0$ we get

$$\frac{\partial C_f}{\partial t} + \frac{u}{\varepsilon}\frac{\partial C_f}{\partial z} + \frac{C_f}{\varepsilon}\frac{\partial u}{\partial z} = \frac{1-\varepsilon}{\varepsilon}\frac{\partial C_s}{\partial t} - \frac{D}{\varepsilon}\frac{\partial C_f}{\partial z}\frac{\partial \varepsilon}{\partial z} - \frac{\partial}{\partial z}\left(D\frac{\partial C_f}{\partial z} \right) \qquad (28)$$

The equation can be further simplified if $\dfrac{\partial u}{\partial z} = \dfrac{\partial \varepsilon}{\partial z} = D = 0$, which corresponds to the assumptions of constant velocity along the bed(which might be a case of isothermal and low-mach number flow), constant porosity(which comes from the assumption of constant area for both solid and fluid phase) and no radial diffusion.

$$\frac{\partial C_f}{\partial t} + \frac{u}{\varepsilon}\frac{\partial C_f}{\partial z} = \frac{1-\varepsilon}{\varepsilon}\frac{\partial C_s}{\partial t} \qquad (29)$$

The Eq. 29 is equivalent to the equation presented by Reverchon [1].

A.1.3. Momentum conservation

Similarly to the mass conservation, the momentum conservation is derived for inviscid fluid with no body forces

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f} (\rho_f V_z)\, d\mathcal{V}_f + \iint_S (\rho_f V_z \mathbf{V})\, \mathbf{dS} = \iint_S (PdS)_z \qquad (30)$$

where V_z is the z component of the velocity.

We the momentum conservation to the shaded control volume in Fig. 2, the integrals on the left side are evaluated in the same manner as discussed above in the regard to the continuity equation. That is,

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f} (\rho_f V_z)\, dV_f = \frac{\partial}{\partial t}(\rho_f V A_f dz) \qquad (31)$$

equation
and

$$\iint_S (\rho_f V_z \mathbf{V})\, dS = -\rho_f V^2 + (\rho_f + d\rho_f)(V + dV)^2 (A + dA) \qquad (32)$$

The evaluation of the pressure force term on the right side of Eq. 30 can be understood based on the Fig. 3. Here, the z components of the vector PdS are shown on all four side of the control volume. Remember that $\mathbf{dS}$ is
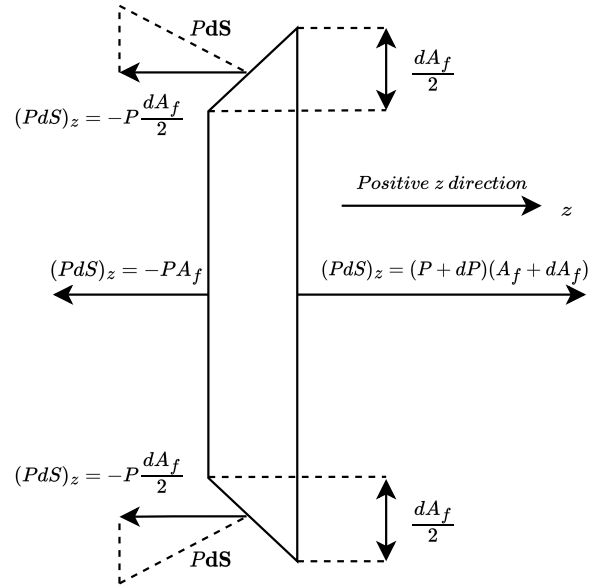

Figure 3: The forces in the z direction acting on the control volume

assumed to points away from the control volume; hence any z component $(PdS)_z$ that acts toward the left (in the negative z direction) is a negative quantity, and any z component that acts toward the right (in the positive z direction) is a positive quantity. Also note that the z component of PdS acting on the top and the bottom inclined faces of the control volume in Fig. 3 can be expressed as the pressure P acting on the component of the inclined are projected perpendicular to the z direction, $dA_f/2$; hence, the contribution of each inclined face (top or bottom) to the pressure integral in Eq. 30 is $-P(dA_f/2)$. All together, the right-hand side of Eq. 30 is expressed as follows:

$$\iint (PdS)_z = -PA_f + (P + dP)(A + dA_f) - 2P\frac{dA_f}{2} \qquad (33)$$

Substituting Eqs. 31 to 33 into Eq. 30, we have

$$\frac{\partial}{\partial t}(\rho_f V A_f dz) - \rho_f V^2 A_f + (\rho_f + d\rho_f)(V + dV)^2 (A_f + dA_f)$$
$$= PA_f - (P + dP)(A + dA_f) + PdA_f \qquad (34)$$

Cancelling like terms and ignoring products of differentials, equation above becomes in the limit dz becoming very small

$$\frac{\partial}{\partial t}(\rho_f V A_f dz) + d(\rho_f V^2 A_f) = -AdP \qquad (35)$$

Dividing above equation by dz and taking the limit as dz goes to zero, we obtain

$$\frac{\partial (\rho_f V A_f)}{\partial t} + \frac{\partial (\rho_f V^2 A_f)}{\partial z} = -A_f\frac{\partial P}{\partial z} \qquad (36)$$

The Eq. 36 can be expanded further by assuming that $A_f = \mathbf{A}\varepsilon$

$$\frac{\partial (\rho_f V \mathbf{A}\varepsilon)}{\partial t} + \frac{\partial (\rho_f V^2 \mathbf{A}\varepsilon)}{\partial z} = -\mathbf{A}\varepsilon\frac{\partial P}{\partial t} \qquad (37)$$

The equation can be further simplified by assuming that the cross-section of an extractor $\mathbf{A}$ is constant and cancel out

$$\frac{\partial \left(\rho_f V \varepsilon\right)}{\partial t} + \frac{\partial \left(\rho_f V^2 \varepsilon\right)}{\partial z} = -\varepsilon \frac{\partial P}{\partial t} \tag{38}$$

If the superficial velocity $u = \varepsilon V$ is introduced, then the momentum conservation becomes

$$\frac{\partial \left(\rho_f u\right)}{\partial z} + \frac{\partial \left(\rho_f u^2/\varepsilon\right)}{\partial z} = -\varepsilon \frac{\partial P}{\partial z} \tag{39}$$

Eq. 36 represents the conservative form of the momentum equation for the quasi-one-dimensional flow. The equivalent non-conservative form can be obtained by multiplying the continuity equation by V and subtracting it from Eq. 36

$$\frac{\partial \left(\rho_f V A_f\right)}{\partial t} - V \frac{\partial \left(\rho_f A_f\right)}{\partial t} + \frac{\left(\rho_f V^2 A_f\right)}{\partial z} - V \frac{\left(\rho_f V A_f\right)}{\partial z} = -A_f \frac{\partial P}{\partial z} \tag{40}$$

Expanding the derivatives on the left-hand size of above equation and cancelling like terms, gives

$$\rho_f A_f \frac{\partial V}{\partial t} + \rho_f A_f V \frac{\partial V}{\partial z} = -A_f \frac{\partial P}{\partial z} \tag{41}$$

Dividing above equation by A_f the non-conservative form of the momentum can be obtained

$$\rho_f \frac{\partial V}{\partial t} + \rho_f V \frac{\partial V}{\partial z} = -\frac{\partial P}{\partial z} \tag{42}$$

The Eq. 42 is stylistically the same as the general momentum conservation for one-dimensional flow with no-body forces. The momentum equation can be expressed in terms of superficial velocity $u = V\varepsilon$. If $\dfrac{\partial \varepsilon}{\partial t} = 0$

$$\frac{\rho_f}{\varepsilon}\left(\frac{\partial u}{\partial t} + \frac{u}{\varepsilon}\frac{\partial u}{\partial z} + u^2 \frac{\partial \varepsilon^{-1}}{\partial z}\right) = -\frac{\partial P}{\partial z} \tag{43}$$

If the porosity is constant along an extractor, then the momentum conservation equation becomes

$$\frac{\rho_f}{\varepsilon}\left(\frac{\partial u}{\partial t} + \frac{u}{\varepsilon}\frac{\partial u}{\partial z}\right) = -\frac{\partial P}{\partial z} \tag{44}$$

Table 1
Notation

Symbol	Description	Unit
A	cross-section	m^2
c	concentration in fluid phase	$kg\ m^{-3}$
Cp	specific heat of the fluid	$J\ mol^{-1}\ K^{-1}$
Cp_s	specific heat of the solid	$J\ mol^{-1}\ K^{-1}$
D_e^M	axial mass diffusion coefficient	$m^2\ s^{-1}$
D_e^T	axial heat diffusion coefficient	$m^2\ s^{-1}$
Di	internal diffusion coefficient	$m^2\ s^{-1}$
dp	particle diameter	m
$F(t)$	mass flow-rate	$kg\ s^{-1}$
km	partition coefficient	$[-]$
k^T	thermal conductivity	$W\ m^{-1}\ K^{-1}$
l	characteristic dimension	m
L	total length of the bed	m
m	mass of the oil in solid phase	kg
m_0	initial mass of the oil in solid phase	kg
M_{CO_2}	molecular mass of CO2	$mol\ kg^{-1}$
Np	number of model parameters and control variables	$[-]$
N_θ	number of model parameters	$[-]$
Nu	number of control variables	$[-]$
Nz	number of grid points in z-direction	$[-]$
p	vector of model parameters and control variables	$[-]$
$P(t)$	pressure	bar
Pe	Peclet's number	$[-]$
q	concentration in solid phase	$kg\ m^{-3}$
R	gas constant	$J\ K^{-1}\ mol^{-1}$
Re	Reynolds number	$[-]$
t	time	s
T	temperature	K
T_0	initial temperature	K
V	volume of the extractor	m^3
y	yield	$[-]$
z	length	m
Z	compressibility factor	$[-]$
ϵ	void fraction	$[-]$
ρ	density of the fluid	$kg\ m^{-3}$
ρ_s	solid density	$kg\ m^{-3}$
μ	shape coefficient	$[-]$
θ	vector of model parameters	$[-]$
η	viscosity	cP
Subscript		
0	initial conditions	$[-]$
$*$	equilibrium conditions	$[-]$