Forward sensitivity analysis of a supercritical extraction process

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Introduction

In the supercritical extraction process, a solvent in supercritical conditions is used to separate a solute from solid particles. A distributed-parameter model with three partial differential equations can be used to describe the fluid-solid extraction process. We study the effect of the parameters on the model solution using a forward sensitivity analysis method.

Process model

We consider a fluid-solid extraction process model which extends a reference model commonly used in the literature [1].

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

$$\frac{\partial c_s(t,z)}{\partial t} = \underbrace{r_e(t,z)}_{\text{Kinetic term}} \tag{1b}$$

$$\frac{\partial T(t,z)}{\partial t} = \underbrace{-\frac{F(t)C_p^f(T(t,z),P(t))}{A\left[(1-\varepsilon)\rho_f\left[T(t,z),P(t)\right]C_p^f\left[T(t,z),P(t)\right]+\varepsilon\rho_s C_p^s\right]}\frac{\partial T(t,z)}{\partial z}}_{\text{Convective term}} + \underbrace{D_e^T\left[T(t,z),P(t)\right]\frac{\partial^2 T(t,z)}{\partial z^2}}_{\text{Diffusive term}} \tag{1c}$$

- $c_f(t,z)$ - Concentration of the solute in the solvent $[kg\ m^{-3}]$
- $c_s(t,z)$ - Concentration of the solute in the solid phase $[kg\ m^{-3}]$
- $T(t,z)$ - Temperature of the pseudo-homogeneous phase $[^\circ C]$
- $F(t)$ - Flow rate of the solvent $[kg\ s^{-1}]$
- $P(t)$ - Pressure $[bar]$
- A - Cross-section of the extractor $[m^2]$
- ϵ - Void fraction $[-]$
- ρ_s - Density of the solid particles $[kg\ m^{-3}]$
- $\rho_f\left[T(t,z),P(t)\right]$ - Density of the solvent $[kg\ m^{-3}]$
- $D_e^M\left[T(t,z),P(t),F(t)\right]$ - Axial mass diffusion coefficient of the solute in the solvent $[m^2\ s^{-1}]$
- $C_p^f\left[T(t,z),P(t)\right]$ - Specific heat of the solvent $[J\ mol^{-1}\ K^{-1}]$
- $D_e^T\left[T(t,z),P(t)\right]$ - Axial heat diffusion coefficient of the pseudo-homogenous phase $[m^2\ s^{-1}]$
- C_p^s - Specific heat of the solid phase $[J\ mol^{-1}\ K^{-1}]$

Model assumptions and description

- One-dimensional model
- No radial profiles
- Plug flow
- No pressure drop
- Uniform particle size distribution
- Constant particle-size and void fraction
- Single component solute
- The amount of solute in the solvent is considered negligible
- Two-film theory
- Pseudo-homogeneous thermal properties

The solvent flows through a fixed bed of solid particles and dissolves the soluble substances. We consider the axial dispersion of the solute in the solvent and assume that radial dispersion is negligible. The mass balance for the fluid phase (Eq. 1a) consist of convection, diffusion, and kinetic terms.

The solid phase is fixed, which indicates lack of a convective movement of the solid particles. We assume that the diffusion of the solute between solid particles is negligible. The mass balance for the solid phase (Eq. 1b) consist of the kinetic term only.

- The mass transfer kinetic (Eq. 2) describe 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.

$$r_e(t,z) = -\frac{D_i(T(t,z))}{\mu l^2}\left(c_s(t,z) - \frac{\rho_s}{k_m\left[T(t,z)\right]\rho_f\left[T(t,z),P(t)\right]}c_f(t,z)\right) \tag{2}$$

- $D_i(T(t,z))$ - Overall diffusion coefficient $[m^2\ s^{-1}]$
- μ - Shape coefficient $[-]$
- l - Characteristic dimension of particles $[m]$
- $k_m(T(t,z))$ - Mass partition factor $[-]$

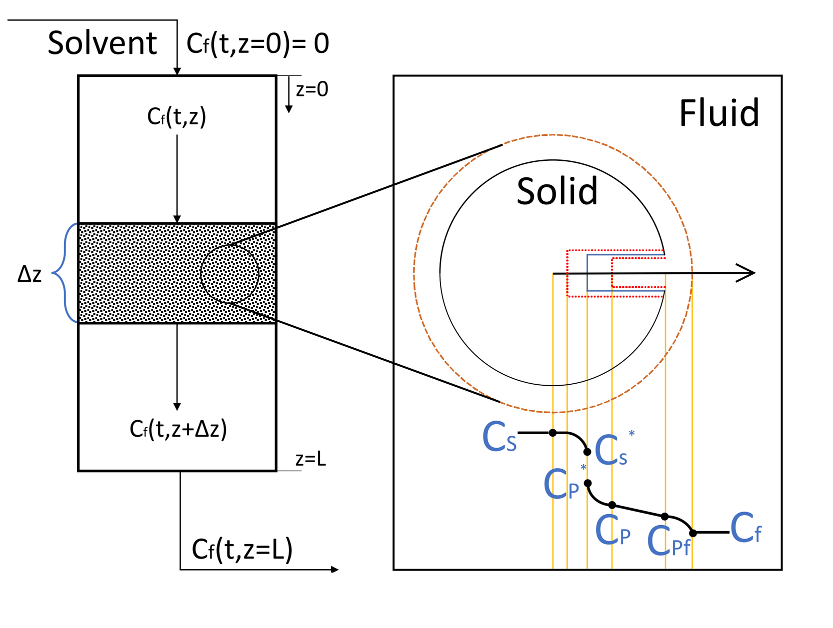

Figure 1: Schematic representation of the extracting bed

- L - Length of the fixed bed
- z - Axial coordinate of the fixed bed
- Δz - Length interval
- c_s - Concentration of the solute in the core of the particle
- c_s^* - Equilibrium concentrations of the solute in the solid phase at the solid-fluid interface
- c_P^* - Equilibrium concentrations of the solute in the fluid phase at the solid-fluid interface
- c_P - Concentration of the solute in the fluid phase in the centre of the pore
- c_{Pf} - Concentration of the solute in the fluid phase at the end of the pore
- c_f - Concentration of the solute in the solvent

The heat balance (Eq. 1c) 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 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 manipulating the temperature of the inlet stream $T_{Inlet}(t)$.

Observations:
The efficiency of the process (the yield) is calculated according to Eq. 3, and is based on the change of solutes concentration in the solid phase. It is defined as ratio the ratio between the difference of its initial value c_s^0 and the actual value $c_s(t,z)$, compared to the initial one.

$$y(t) = \frac{\left(c_s^0 - c_s(t,z)\right)}{c_s^0}100\% \tag{3}$$

Numerics:
The method of lines is used to transform the process model equations into a set of ODEs denoted as $G(x(t);\theta)$, where $x(t)$ is the discretized state and the θ represents the collection of model parameters and the control variables (assuming they are constant).
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 derivatives, while the central difference scheme is used to approximate second-order derivatives.
The length of the fixed bed is divided into N_z equally distributed points in the z-direction.

Sensitivity analysis

The sensitivity analysis aims to measure the effect of the parameters on process model solution. The sensitivity analysis equations ($\dot{Z}$) are obtained by taking the total derivative of the discretized system $G(x(t);\theta)$ with respect to θ, as presented in [2]. In this work, the direct method is considered and restricted to the analysis of linear sensitivity coefficients.

$$Z(x(t);\theta) = \frac{\partial x(t)}{\partial \theta} \tag{4}$$

As the process model depends on parameters θ and initial conditions, each parameter's sensitivity depends on time t. Therefore, the new system of equations can be obtained by taking derivatives with respect to time t and applying the chain rule.

$$\dot{Z}(x(t);\theta) = \frac{dZ(x(t);\theta)}{dt} = \frac{\partial}{\partial t}\left(\frac{\partial x(t)}{\partial \theta}\right) = \frac{\partial}{\partial \theta}\left(\frac{\partial x(t)}{\partial t}\right) = \frac{dG(x(t);\theta)}{d\theta} \tag{5}$$

By applying the definition of the total derivative to the Eq. 5, the sensitivity equation can be obtained.

$$\frac{dG(x(t);\theta)}{d\theta} = \underbrace{\frac{\partial G(x(t);\theta)}{\partial x(t)}}_{J_x(x(t);\theta)}\underbrace{\frac{\partial x(t)}{\partial \theta}}_{S(x(t);\theta)} + \underbrace{\frac{\partial G(x(t);\theta)}{\partial \theta}}_{J_p(x(t);\theta)} \tag{6}$$

This equation consists of three terms: Jacobian $J_x(x(t);\theta)$, sensitivity matrix $S(x(t);\theta)$ and Jacobian $J_p(x(t);\theta)$. The Jacobians are obtained by automatic differentiation. The sensitivity equations are coupled with the process model and solved simultaneously. As the result, the gradients of the solution with respect to each parameter along the time series are obtained.

Results

The model parameters and the operating conditions come from Vargas et al. [3], who conducted the supercritical extraction to obtain essential oil, known as 'carqueja', from 'Baccharis Trimera' leaves. The experiments were performed in a temperature range from 313.15 [K] to 343.15 [K] at 90 [bar]. The inital conditions and the operating conditions are presented in the table 1.

$c_f^0(t,z)\ [kg\ m^{-3}]$	$c_s^0(t,z)\ [kg\ m^{-3}]$	$T^0(t,z)\ [^\circ C]$	$T_{Inlet}(t)\ [^\circ C]$	$F(t)\ [kg\ hr^{-1}]$	$P(t)\ [bar]$
0	27	50	50	0.035	90

Table 1: Initial conditions and operating conditions

The solution of the process model is presented in figure 2

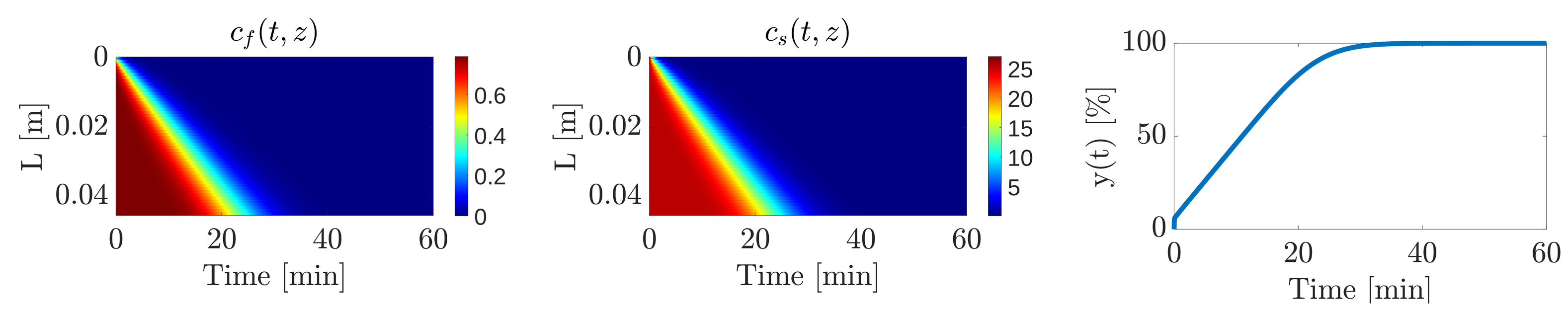

Figure 2: Solution of the process model

We examine the effect of the operating conditions: $F(t)$, $P(t)$, $T_{Inlet}(t)$ on the state variables: $c_f(t,z)$, $c_s(t,z)$ and on the observation function $y(t)$. The obtained results of the sensitivity analysis are presented in figure 3

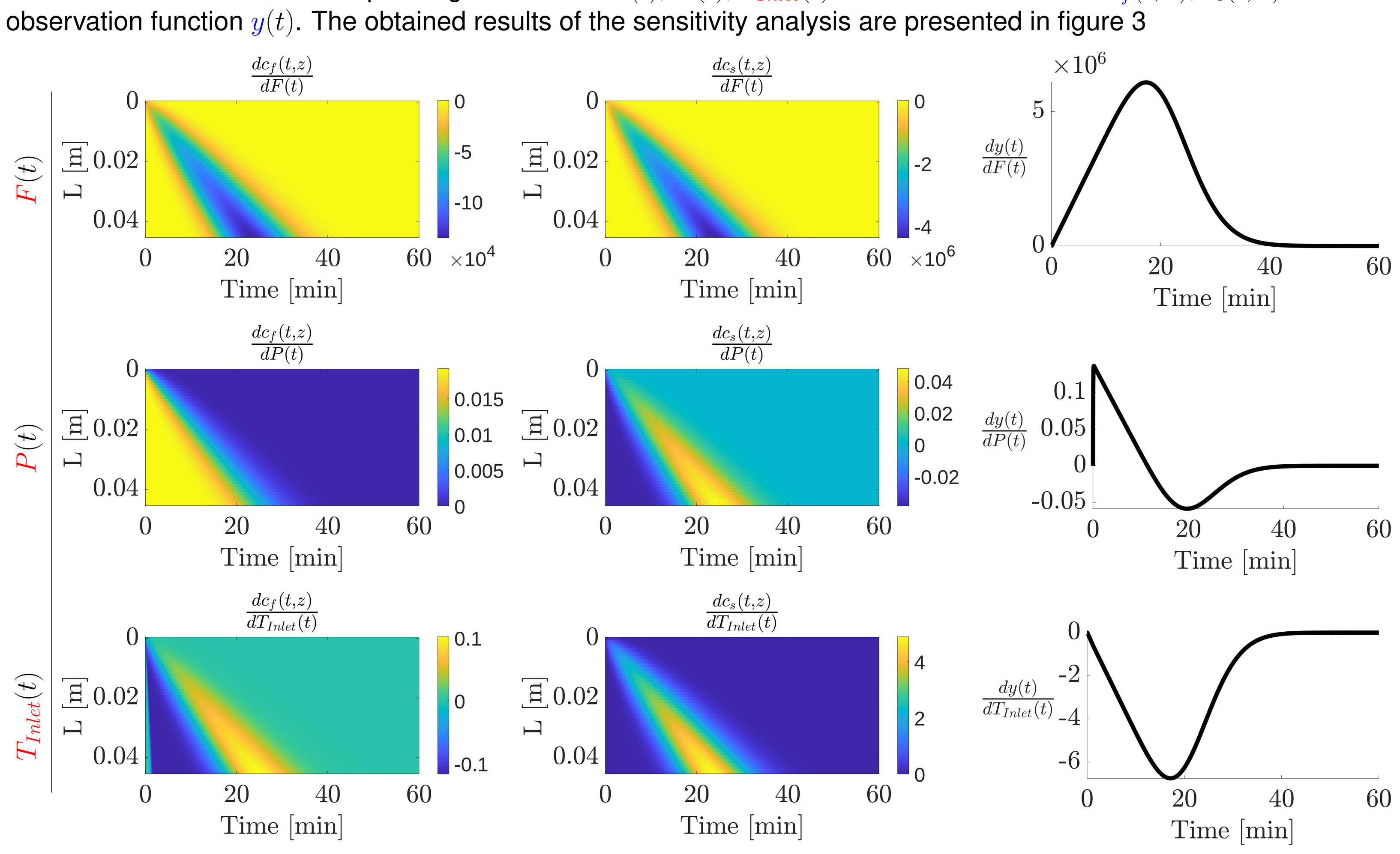

Figure 3: Results of the sensitivity analysis with respect to operating conditions

Similarly, we examine the effect of selected parameters: ϵ and l on state variables: $c_f(t,z)$, $c_s(t,z)$ and on the observation function $y(t)$. The obtained results of the sensitivity analysis are presented in figure 4

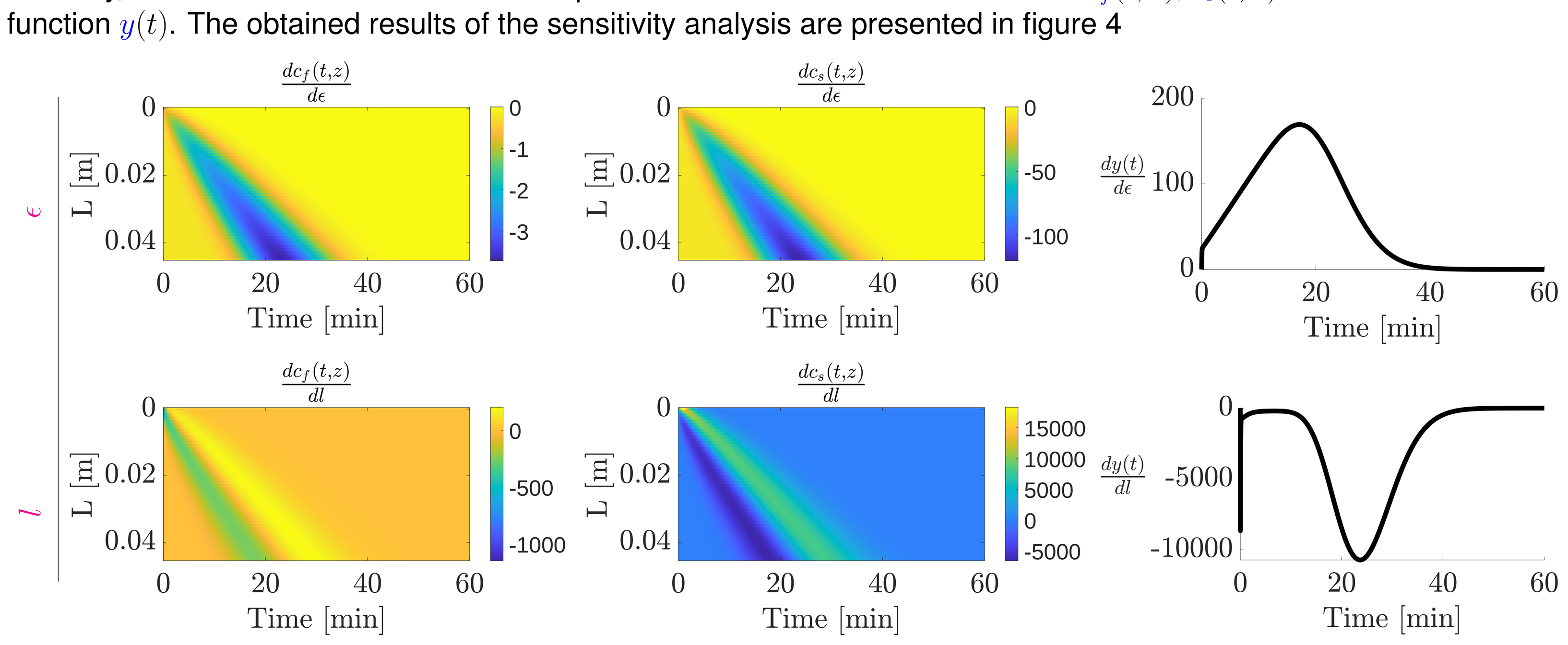

Figure 4: Results of the sensitivity analysis with respect to selected model parameters

References

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