Supercritical Extraction

A process model and a sensitivity analysis

Oliwer Sliczniuk

15.05.2021

Aalto University

Table of contents

Supercritical extraction - process description

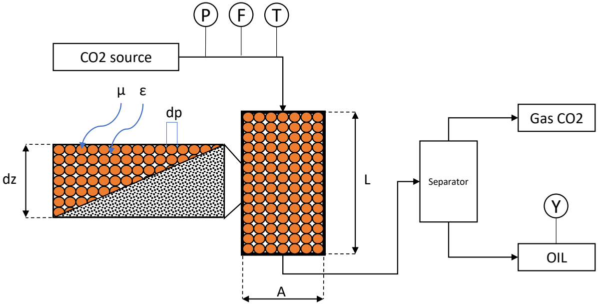


Figure 1: Schematic representation of SFE process

Model description

Model of the extractor

control variables, state variables, variables and parameters

(1) Fluid phase mass balance

$$\frac{\partial c(t,z)}{\partial t} = -\frac{1}{\epsilon A}\frac{F(t)}{\rho(T(t,z)P(t))}\frac{\partial c(t,z)}{\partial z} + D_e^M(T(t,z)P(t))\frac{\partial^2 c(t,z)}{\partial z^2} + \frac{1-\epsilon}{\epsilon} r_e(t,z)$$

(2) Solid phase mass balance

$$\frac{\partial q(t,z)}{\partial t} = r_e(t,z)$$

(3) Heat balance

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

Extraction kinetic

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

Output function

$$y(t) = g(x(t)) = \frac{\sum_{i=1}^{N_z}\left(\frac{1}{N_z}(m_0 - m_i(t,z))\right)}{m_0} = \frac{\sum_{i=1}^{N_z}\left(\frac{V}{N_z}(q_0 - q_i(t,z))\right)}{q_0 V}$$

SFE - assumptions

- One-dimensional model
- Plug flow
- No pressure drop
- Negligible external diffusion
- Single component
- Pseudo-homogeneous thermal properties
- Uniformly distribution of the particles

Model dependencies

(1) Density - Peng-Robinson

$$P(t) = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

(2) Solid phase mass balance

$$C_p(T(t,z)P(t)) = Cp_{Ideal} + Cv_{corr} + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P - R$$

(3) Axial diffusion of the mass

$$D_e^M(T(t,z)P(t)) = \frac{u(T(t,z)P(t))d_p}{\epsilon P_e}$$

(4) Axial diffusion of the heat

$$D_e^T \left[\frac{m^2}{s}\right](T(t,z)P(t)) = \frac{k^T(T(t,z)P(t))}{\rho(T(t,z)P(t))C_p(T(t,z)P(t))}$$

(5) Internal diffusion

$$D_i(T(t,z))\left[\frac{m^2}{s}\right] = D_{i_0} \exp\left(\frac{-EA_{D_i}}{RT(t,z)}\right)$$

(6) Partition coefficient

$$k_m(T(t,z))\,[-] = k_{m_0} \exp\left(\frac{-EA_{k_m}}{RT(t,z)}\right)$$

SFE - state-space model

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

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

SFE - discretization

$$
\frac{dx(t)}{dt} = \begin{bmatrix} \frac{dc_1(t)}{dt} \\ \vdots \\ \frac{dc_{N_z}(t)}{dt} \\ \frac{dq_1(t)}{dt} \\ \vdots \\ \frac{dq_{N_z}(t)}{dt} \\ \frac{dT_1(t)}{dt} \\ \vdots \\ \frac{dT_{N_z}(t)}{dt} \end{bmatrix} = \begin{bmatrix} F_1\left(c(t), q(t), T(t); p\right) \\ \vdots \\ F_{N_z}\left(c(t), q(t), T(t); p\right) \\ F_{N_z+1}\left(c(t), q(t), T(t); p\right) \\ \vdots \\ F_{2N_z}\left(c(t), q(t), T(t); p\right) \\ F_{2N_z+1}\left(c(t), q(t), T(t); p\right) \\ \vdots \\ F_{3N_z}\left(c(t), q(t), T(t); p\right) \end{bmatrix} = F\left(t; p\right)
$$

where $x \in \mathbb{R}^{N_x = 3N_z}$ and $p \in \mathbb{R}^{N_p = N_\theta + N_u}$

Sensitivity Analysis

Sensitivity Analysis

Local derivative-based methods involve taking the partial derivative of the output with respect to an input parameter. In sensitivity analysis the original system of equations is solved simultaneously with $\frac{\partial F(x(t);p)}{\partial p}$, where p is a vector of all the parameters and the control variables.

Sensitivity Analysis

$$Z = \frac{\partial x(t, p)}{\partial p}$$

$$\dot{Z} = \frac{\partial Z(t, p)}{\partial t} = \frac{\partial}{\partial t}\left(\frac{\partial x(t, p)}{\partial p}\right) = \frac{\partial}{\partial p}\left(\frac{\partial x(t, p)}{\partial t}\right) = \frac{\partial F(x(t); p)}{\partial p}$$

$$\begin{aligned} \frac{dF(x(t); p)}{dp} &= \frac{\partial F(x(t); p)}{\partial x(t)} \frac{\partial x(t)}{\partial p} + \frac{\partial F(x(t); p)}{\partial p} \\ &= J_x(x(t); p) S(x(t); p) + J_p(x(t); p) \end{aligned}$$

$$\underset{(N_x \times N_p)}{\boxed{\frac{\mathbf{dF(x(t);\, p)}}{\mathbf{dp}}}} = \underset{(N_x \times N_x)}{\boxed{\mathbf{J}_x}} \; \underset{(N_x \times N_p)}{\boxed{\mathbf{S}}} + \underset{(N_x \times N_p)}{\boxed{\mathbf{J}_p}}$$

Sensitivity Analysis

$$\frac{dF(x(t);p)}{dp} = \begin{pmatrix} \frac{\partial F_1(x(t);p)}{\partial x_1(t)} & \frac{\partial F_1(x(t);p)}{\partial x_2(t)} & \cdots & \frac{\partial F_1(x(t);p)}{\partial x_{N_x}(t)} \\ \frac{\partial F_2(x(t);p)}{\partial x_1(t)} & \frac{\partial F_2(x(t);p)}{\partial x_2(t)} & \cdots & \frac{\partial F_2(x(t);p)}{\partial x_{N_x}(t)} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial F_{N_x}(x(t);p)}{\partial x_1(t)} & \frac{\partial F_{N_x}(x(t);p)}{\partial x_2(t)} & \cdots & \frac{\partial F_{N_x}(x(t);p)}{\partial x_{N_x}(t)} \end{pmatrix} \begin{pmatrix} \frac{dx_1(t)}{dp_1} & \frac{dx_1(t)}{dp_2} & \cdots & \frac{dx_1(t)}{dp_{N_p}} \\ \frac{dx_2(t)}{dp_1} & \frac{dx_2(t)}{dp_2} & \cdots & \frac{dx_2(t)}{dp_{N_p}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{dx_{N_x}(t)}{dp_1} & \frac{dx_{N_x}(t)}{dp_2} & \cdots & \frac{dx_{N_x}(t)}{dp_{N_p}} \end{pmatrix} +$$

$$+ \begin{pmatrix} \frac{\partial F_1(x(t);p)}{\partial p_1} & \frac{\partial F_1(x(t);p)}{\partial p_2} & \cdots & \frac{\partial F_1(x(t);p)}{\partial p_{N_p}} \\ \frac{\partial F_2(x(t);p)}{\partial p_1} & \frac{\partial F_2(x(t);p)}{\partial p_2} & \cdots & \frac{\partial F_2(x(t);p)}{\partial p_{N_p}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial F_{N_x}(x(t);p)}{\partial p_1} & \frac{\partial F_{N_x}(x(t);p)}{\partial p_2} & \cdots & \frac{\partial F_{N_x}(x(t);p)}{\partial p_{N_p}} \end{pmatrix}$$

Sensitivity Analysis

The$F(x(t);p)$ is augmented with sensitivity equations and denoted as $\mathbf{F}(x(t);p)$. The size of $\mathbf{F}(x(t);p)$ is equal to $N_s = N_x(N_p+1)$.

$$\mathbf{F}\left(x(t);p\right) = \begin{bmatrix} F(x(t);p) \\ J_x(x(t);p)S(x(t);p) + J_p(x(t);p) \end{bmatrix}$$

The initial conditions are described as

$$\mathbf{F}\left(x(t_0);p\right) = \begin{bmatrix} x(t_0), & \frac{\mathrm{d}x(t_0)}{dp_1}, & \cdots, & \frac{dx(t_0)}{dp_{N_p}} \end{bmatrix}^T$$

Sensitivity Analysis

$$y(t) = g(x(t)) = \frac{\sum_{i=1}^{N_z} \left(\frac{1}{N_z} (m_0 - m_i(t,z)) \right)}{m_0} = \frac{\sum_{i=1}^{N_z} \left(\frac{V}{N_z} (q_0 - q_i(t,z)) \right)}{q_0 V}$$

By taking a total derivative of $y(t)$ with respect to p, the new sensitivity equation can found.

$$\frac{dy(t)}{dp} = \frac{dg(x(t))}{dp} = \frac{\partial g(x(t))}{\partial x(t)} \frac{\partial x(t)}{\partial p} + \frac{\partial g(x(t))}{\partial p}$$

$$\frac{\partial g(x(t))}{\partial p} = \frac{\partial g(x(t))}{\partial x(t)} \frac{\partial x(t)}{\partial p} + 0 = \frac{\partial g(x(t))}{\partial x(t)} S(x(t);p) =$$

$$\begin{pmatrix} \frac{\partial g_1(x(t))}{\partial x_1} & \frac{\partial g_1(x(t))}{\partial x_2} & \cdots & \frac{\partial g_1(x(t))}{\partial x_{N_x}} \\ \frac{\partial g_2(x(t))}{\partial x_1} & \frac{\partial g_2(x(t))}{\partial x_2} & \cdots & \frac{\partial g_2(x(t))}{\partial x_{N_x}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial g_{N_g}(x(t))}{\partial x_1} & \frac{\partial g_{N_g}(x(t))}{\partial x_2} & \cdots & \frac{\partial g_{N_g}(x(t))}{\partial x_{N_x}} \end{pmatrix} \begin{pmatrix} s_{(1,1)} & s_{(1,2)} & \cdots & s_{(1,N_p)} \\ s_{(2,1)} & s_{(2,2)} & \cdots & s_{(2,N_p)} \\ \vdots & \vdots & \ddots & \vdots \\ s_{(N_x,1)} & s_{(N_x,2)} & \cdots & s_{(N_x,N_p)} \end{pmatrix}$$

Sensitivity Analysis

Because the output function returns only one value, the equation becomes

$$
\left(\frac{\partial y(x(t))}{\partial p_1}, \frac{\partial y(x(t))}{\partial p_2}, \dots, \frac{\partial y(x(t))}{\partial p_{N_p}} \right) =
$$

$$
= \left(\frac{\partial g(x(t))}{\partial x_1}, \frac{\partial g(x(t))}{\partial x_2}, \dots, \frac{\partial g(x(t))}{\partial x_{N_x}} \right)
\begin{pmatrix}
s_{(1,1)} & s_{(1,2)} & \cdots & s_{(1,N_p)} \\
s_{(2,1)} & s_{(2,2)} & \cdots & s_{(2,N_p)} \\
\vdots & \vdots & \ddots & \vdots \\
s_{(N_x,1)} & s_{(N_x,2)} & \cdots & s_{(N_x,N_p)}
\end{pmatrix}
$$

$$
\underbrace{\boxed{\frac{\mathbf{dg(x(t))}}{\mathbf{dp}}}}_{(1 \times N_p)} = \underbrace{\boxed{\frac{\mathbf{dg(x(t))}}{\mathbf{dx(t)}}}}_{(1 \times N_x)} \underbrace{\boxed{\mathbf{S}}}_{(N_x \times N_p)}
$$

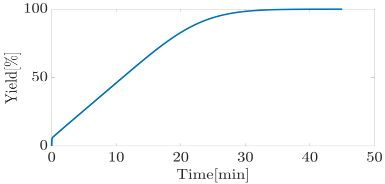
Results

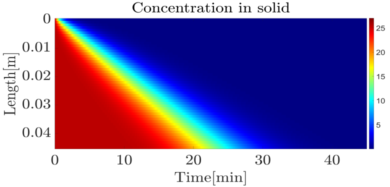
Results of the simulation

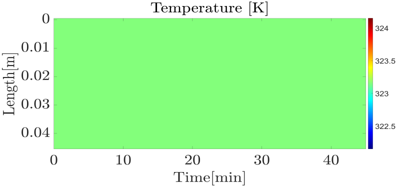
Product: CARQUEJA essential oil

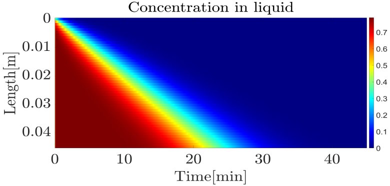
Ref	$F[kg/hr]$	$T_{Inlet}[C]$	$T_{extractor}[C]$	$P[bar]$	$c[kg/m^3]$	$q[kg/m^3]$
Vargas	0.035	50	50	90	0	27

Table 1: Initial conditions







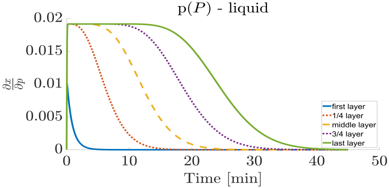


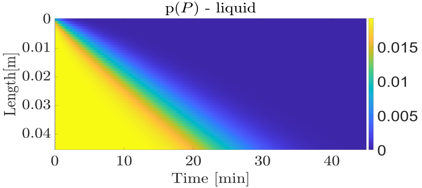
Sensitivity Analysis - Pressure

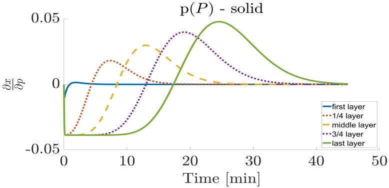
$$\frac{\partial c(t,z)}{\partial t} = -\frac{F(t)}{\epsilon A \rho(T(t,z)P(t))}\frac{\partial c(t,z)}{\partial z} + D_e^M(T(t,z)P(t))\frac{\partial^2 c(t,z)}{\partial z^2} + \frac{1-\epsilon}{\epsilon}\frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - \frac{c(t,z)\rho_s}{k_m(T(t,z))\rho(T(t,z)P(t))}\right)$$

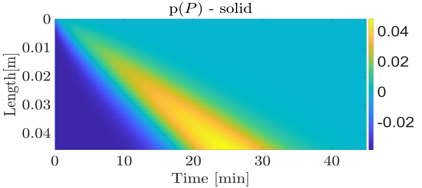
$$\frac{\partial q(t,z)}{\partial t} = -\frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - c(t,z)\frac{\rho_s}{k_m(T(t,z))\rho(T(t,z)P(t))}\right)$$

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







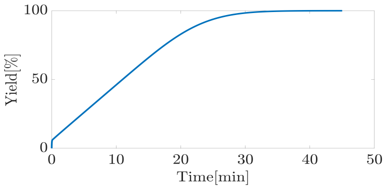


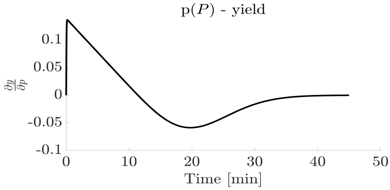
Sensitivity Analysis - Pressure

$$\frac{\partial c(t,z)}{\partial t} = -\frac{F(t)}{\epsilon A \rho(T(t,z)P(t))}\frac{\partial c(t,z)}{\partial z} + D_e^M(T(t,z)P(t))\frac{\partial^2 c(t,z)}{\partial z^2} + \frac{1-\epsilon}{\epsilon}\frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - \frac{c(t,z)\rho_s}{k_m(T(t,z))\rho(T(t,z)P(t))}\right)$$

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

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



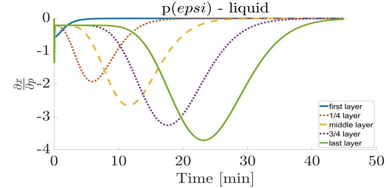


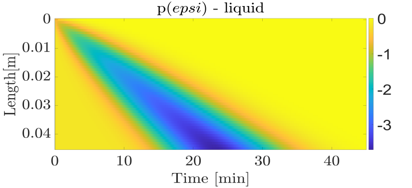
Sensitivity Analysis - Void Fraction

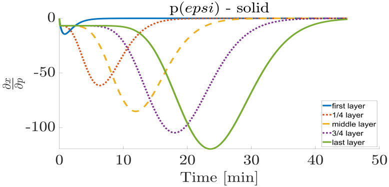
$$\frac{\partial c(t,z)}{\partial t} = -\frac{F(t)}{\epsilon A \rho(T(t,z)P(t))}\frac{\partial c(t,z)}{\partial z} + D_e^M(T(t,z)P(t))\frac{\partial^2 c(t,z)}{\partial z^2} + \frac{1-\epsilon}{\epsilon}\frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - \frac{c(t,z)\rho_s}{k_m(T(t,z))\rho(T(t,z)P(t))}\right)$$

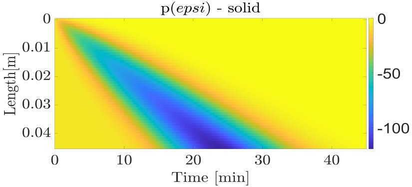
$$\frac{\partial q(t,z)}{\partial t} = -\frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - c(t,z)\frac{\rho_s}{k_m(T(t,z))\rho(T(t,z)P(t))}\right)$$

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







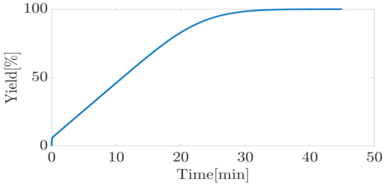


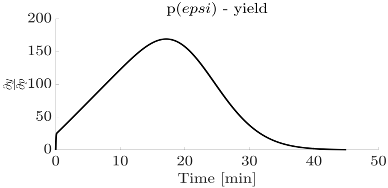
Sensitivity Analysis - Void Fraction

$$\frac{\partial c(t,z)}{\partial t} = -\frac{F(t)}{\epsilon A\rho(T(t,z)P(t))}\frac{\partial c(t,z)}{\partial z} + D_e^M(T(t,z)P(t))\frac{\partial^2 c(t,z)}{\partial z^2} + \frac{1-\epsilon}{\epsilon}\frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - \frac{c(t,z)\rho_s}{k_m(T(t,z))\rho(T(t,z)P(t))}\right)$$

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

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



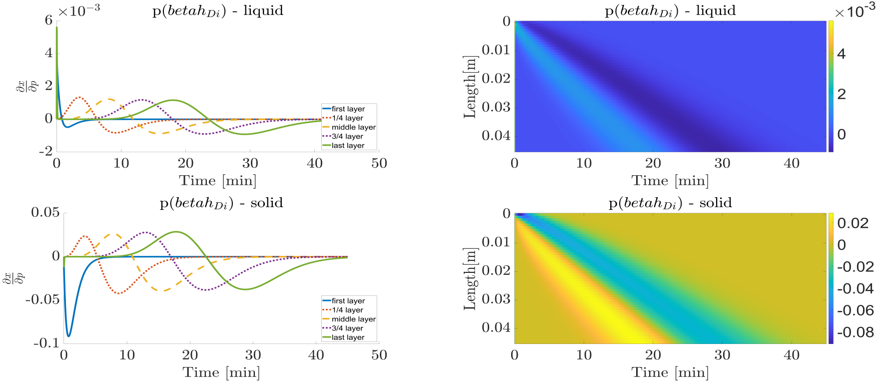


Sensitivity Analysis - Internal Diffusion

$$\frac{\partial c(t,z)}{\partial t} = -\frac{F(t)}{\epsilon A \rho(T(t,z)P(t))}\frac{\partial c(t,z)}{\partial z} + D_e^M(T(t,z)P(t))\frac{\partial^2 c(t,z)}{\partial z^2} + \frac{1-\epsilon}{\epsilon}\frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - \frac{c(t,z)\rho_s}{k_m(T(t,z))\rho(T(t,z)P(t))}\right)$$

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

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

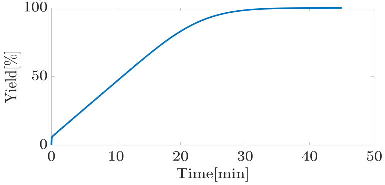


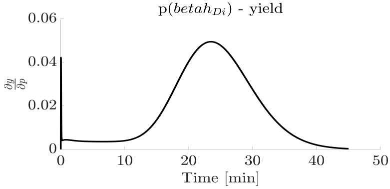
Sensitivity Analysis - Internal Diffusion

$$\frac{\partial c(t,z)}{\partial t} = -\frac{F(t)}{\epsilon A \rho(T(t,z)P(t))}\frac{\partial c(t,z)}{\partial z} + D_e^M(T(t,z)P(t))\frac{\partial^2 c(t,z)}{\partial z^2} + \frac{1-\epsilon}{\epsilon}\frac{D_i(T(t,z))}{\mu l^2}\left(q(t,z) - \frac{c(t,z)\rho_s}{k_m(T(t,z))\rho(T(t,z)P(t))}\right)$$

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

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





What's next?

- Paper related to the sensitivity analysis
- Control of the extraction process
- NovelBaltic
- Laboratory work