Optimal design of experiment:
supercritical fluid extraction case

Oliwer Sliczniuk, Pekka Oinas
School of Chemical Engineering, Aalto University, Finland
Aalto University

Introduction

This study investigates the extraction of essential oils from chamomile flowers using supercritical carbon dioxide as a solvent in a semi-batch mode. The process is described by a mathematical model incorporating empirical correlations. The goal of this work is to improve the precision of the model parameters by designing a new experiment and validating the model against it.

Process Model

The process is described by a first-principle distributed-parameter model [1,2] with a set of empirical correlations [2]. The model assumptions are

- One-dimensional
- Plug flow
- No pressure drop
- Uniform particle distribution
- Two-film theory for a single component
- Peng-Robinson equation of state
- Decaying extraction kinetic
- Empirical correlations

$$\dot{x} = \frac{dx}{dt} = \begin{bmatrix} \frac{\partial c_f}{\partial t} \\ \frac{\partial c_s}{\partial t} \\ \frac{\partial \left(\rho_f h A_f\right)}{\partial t} \\ \frac{dy}{dt} \end{bmatrix} = \underbrace{\begin{bmatrix} -\frac{1}{\phi}\frac{\partial (c_f u)}{\partial z} - \frac{1-\phi}{\phi}\frac{\partial c_s}{\partial t} + \frac{1}{\phi}\frac{\partial}{\partial z}\left(D_e^M \frac{\partial c_f}{\partial z}\right) \\ -\frac{D_i^R \exp\left(\Upsilon\left(1-\frac{c_s}{c_{s0}}\right)\right)}{\mu l^2}\left(c_s - \frac{\rho_s c_f}{k_m \rho_f}\right) \\ -\frac{\partial\left(\rho_f h A_f v\right)}{\partial z} + \frac{\partial\left(P A_f\right)}{\partial t} + \frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right) \\ \left.\frac{F}{\rho_f} c_f\right|_{z=L} \end{bmatrix}}_{G(x,t,\Theta;\Xi)}$$

$$D_i^R = 0.190 - 8.188 \cdot Re + 0.620 \cdot F \qquad R^2 = 0.868$$

$$\Upsilon = 3.158 + 11.922 \cdot Re - 0.686 \cdot F \qquad R^2 = 0.823$$

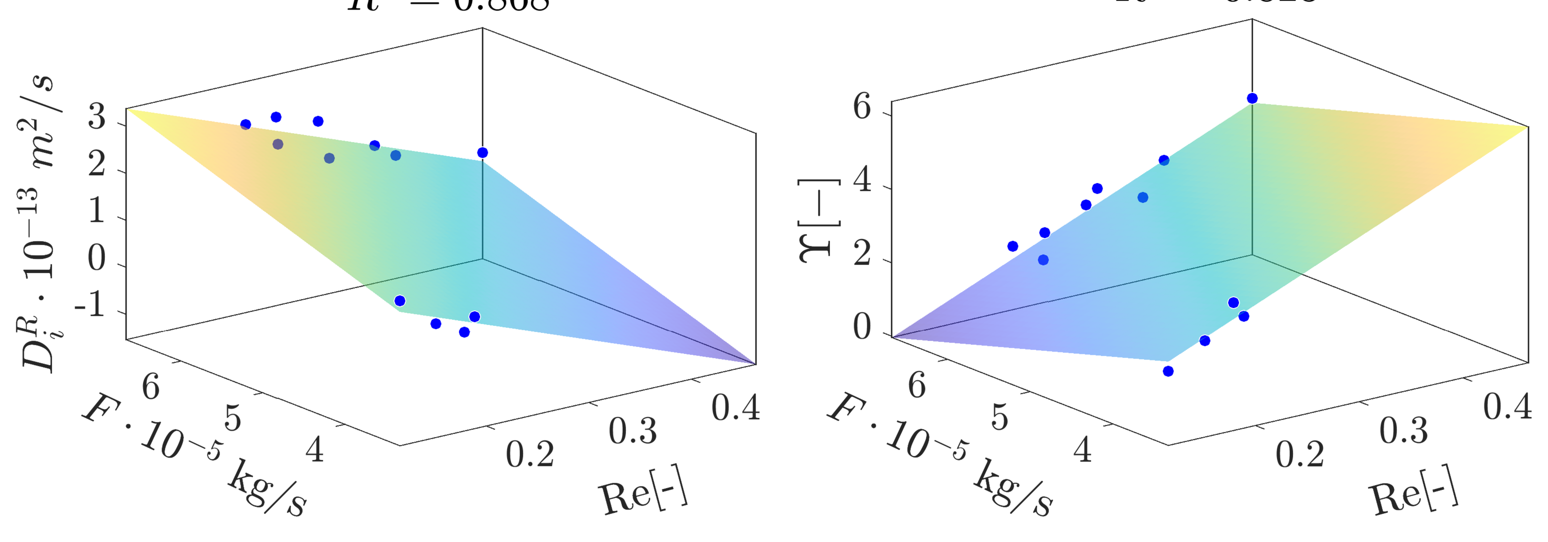

Figure 1: Empirical correlations

Model-based optimal design of experiment

$$\underbrace{\mathcal{F}(t,\Theta;\Xi)}_{\text{Fisher Information}} = \frac{\partial y(t,\Theta;\Xi)}{\partial \Theta}\Sigma\frac{\partial y(t,\Theta;\Xi)}{\partial \Theta^\top}$$

The D-optimality criterion is chosen as the objective function, aiming to minimize the volume of the ellipsoidal confidence region of parameter estimates under the experimental conditions Ξ [3].

$$\begin{aligned} \Xi^* &= \arg \min_{T^{in},\, F \in \Xi} \int_{t_0=0\text{min}}^{t_f=300\text{min}} -\ln\det \mathcal{F}(t,\Theta;\Xi)\, dt \\ \text{subject to} \quad \dot{x} &= G\ (x,t,\Theta;\Xi) \\ T^0 &= T^{in}(t=0) \\ 30°C \leq\ & T^{in}(t) \leq 40°C \\ 3.33 \cdot 10^{-5}\ \text{kg/s} \leq\ & F\ (t) \leq 6.67 \cdot 10^{-5}\ \text{kg/s} \\ 100\ \text{bar} \leq\ & P\ (t) \leq 200\ \text{bar} \end{aligned}$$

The aim is to improve the precision of the correlation for D_i^R by designing an experiment with dynamically changing operating conditions for five cases of constant pressure: 100, 125, 150, 175, and 200 bar. The yield is measured every 10 min and decision variables are adjusted every 15 min.

Numerics

The method of lines is employed to transform the process model equations into a set of ODEs. The first- and second-order derivatives are approximated using the backward and central difference schemes, respectively. The time integral and all time-dependent functions are discretized using the single-shooting approach with piecewise-constant controls to obtain a static non-linear program.

Legend

- c_f – Solutes concentration in the fluid phase
- c_s – Solutes concentration in the solid phase
- h – Enthalpy
- y – Extraction yield
- ρ_f – Density of fluid
- A_f – Cross-section of the bed
- u – Darcy velocity
- ϕ – Void fraction
- D_e^M – Axial mass diffusivity
- D_i^R – Internal mass diffusivity
- μ – Particle shape coefficient
- l – Particle length
- Υ – Decaying factor
- ρ_s – Bulk density of solid bed
- k_m – Partition factor
- P – Pressure
- T – Temperature
- T^{in} – Inlet temperature
- F – Mass flow rate
- Σ – Covariance matrix
- Θ – Vector of parameters

Results

To identify the global solution, the optimization problem is solved multiple times, each starting from a random initial solution sampled from a uniform distribution.

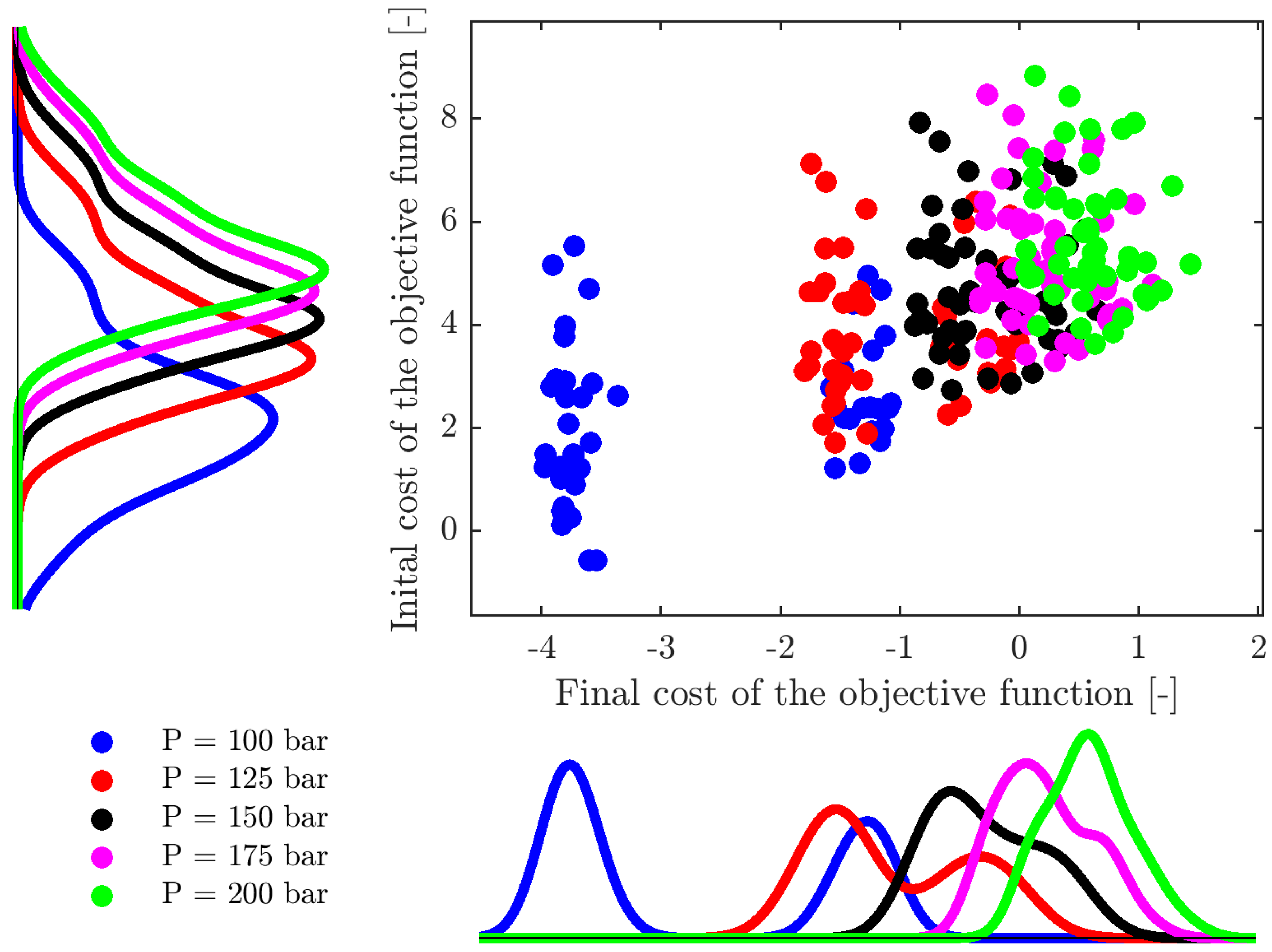

Figure 2: Values of the objective function

The optimal profiles of the controls and the yield curves are showed below

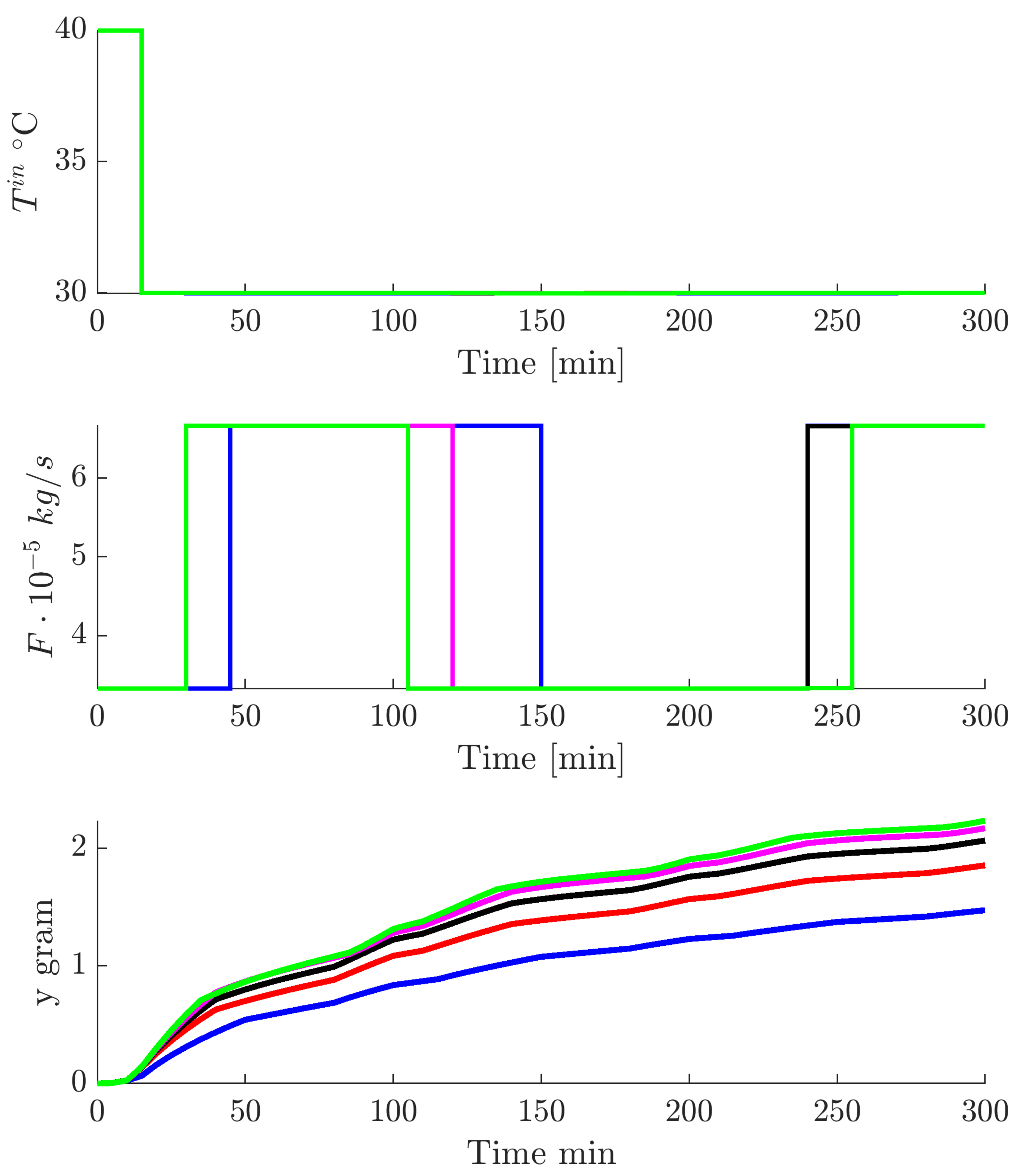

Figure 3: Optimal profiles

Conclusions

- The lowest values of the cost function are achieved near the supercritical point, where variations in the inlet temperature cause significant deviations in the physical properties of CO_2 and Re
- The optimal profiles of the controls are similar across all cases
- The mass flow rate is the primary control variable, indicating that the system is more sensitive to mass flow rate changes than to inlet temperature variations
- The optimal yield profiles are characterized by waving behaviour
- Experiments which result in the highest yields are not necessary the most informative

References

[1] E. Reverchon. Mathematical modeling of supercritical extraction of sage oil. AIChE Journal, 42(6):1765–1771, June 1996. ISSN 1547-5905. doi: 10.1002/aic.690420627.

[2] O. Sliczniuk and P. Oinas. Supercritical fluid extraction of essential oil from chamomile flowers: modelling and parameter estimation. CJCE Journal. June 2024. Under review.

[3] E. Walter and L. Pronzato. Identification of parametric models from experimental data. Communications and control engineering. Springer, London, 2010. ISBN 9781849969963