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

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

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
F – Mass flow rate
Σ – Covariance matrix
Θ – Vector of parameters

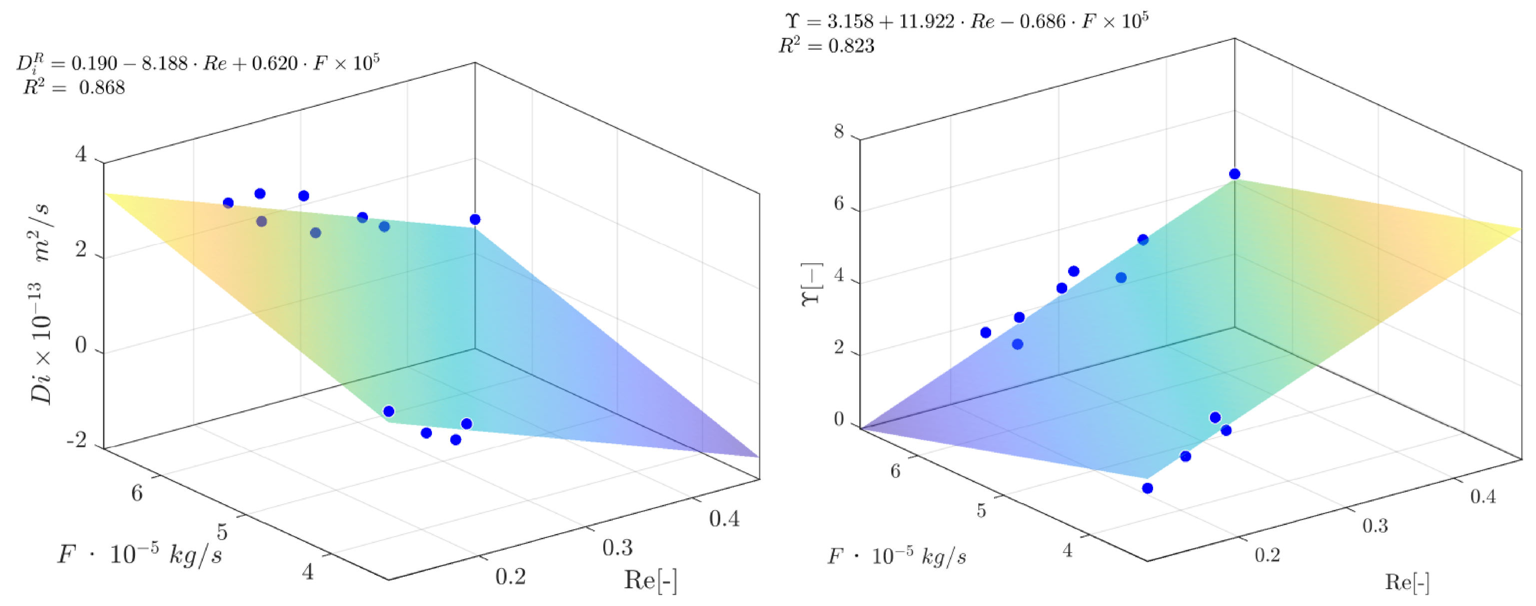

Figure 1: Empirical correlations

Model-based optimal design of experiment

Fisher information $\mathcal{F}$ (Hessian of the likelihood function) measurs the amount of information observable random variables carry about a parameters of a distribution that models these variables[3]:

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

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.

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

This work aims to improve the precision of the correlation for D_i^R by designing an experiment with dynamically changing operating conditions (F and T^{in}).

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.

Results

The system operates for 300 minutes, with a sampling interval of 10 minutes and decision variables adjusted every 15 minutes. Each of the five analysed cases assumes a constant pressure, set at 100, 125, 150, 175, and 200 bar. To identify the global solution, the optimization problem is solved multiple times, each starting from a random initial solution sampled from a uniform distribution.

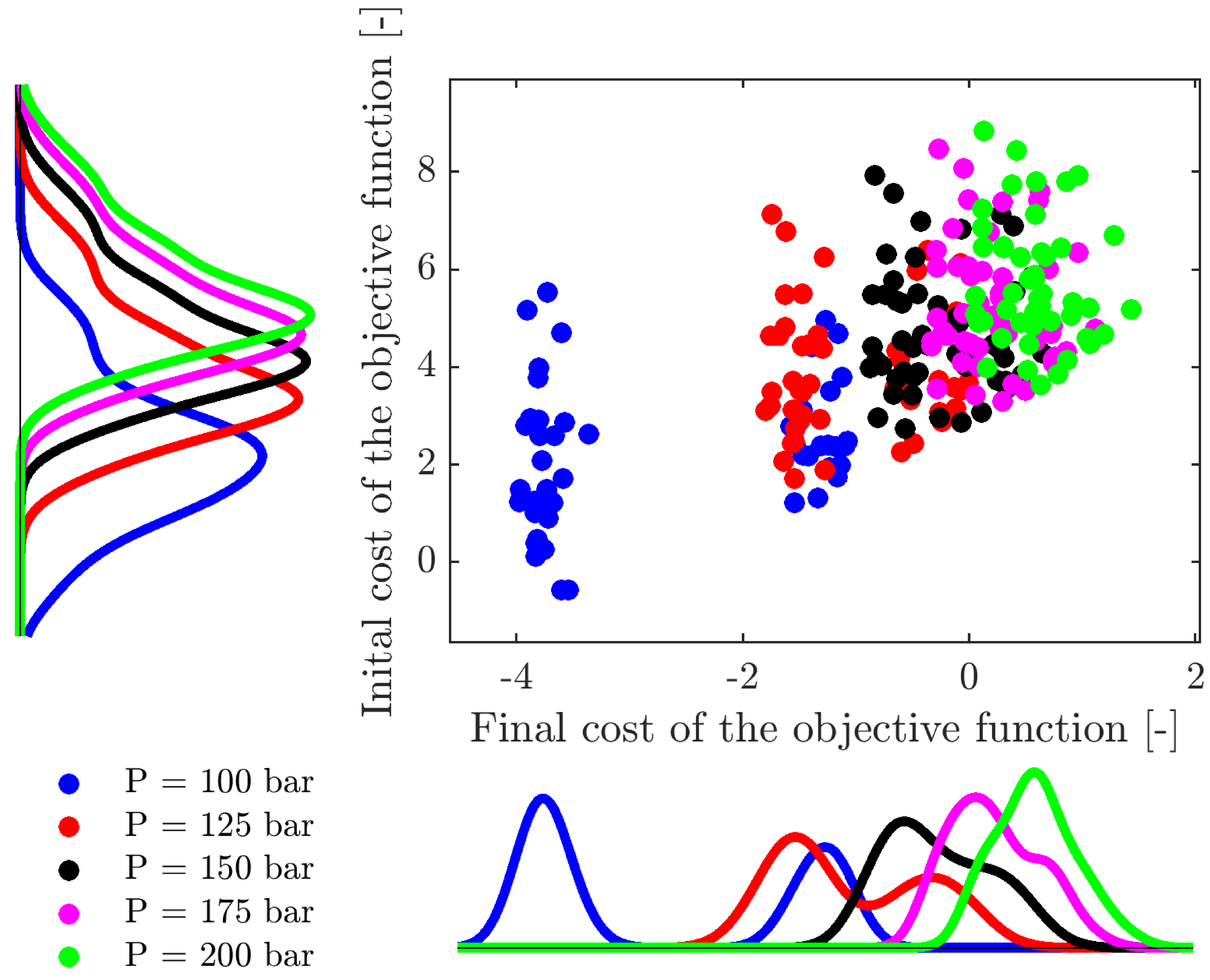

Figure 2: Values of the objective function

The optimal profiles of the inlet temperature and flow rates for each case are showed in Figure 3

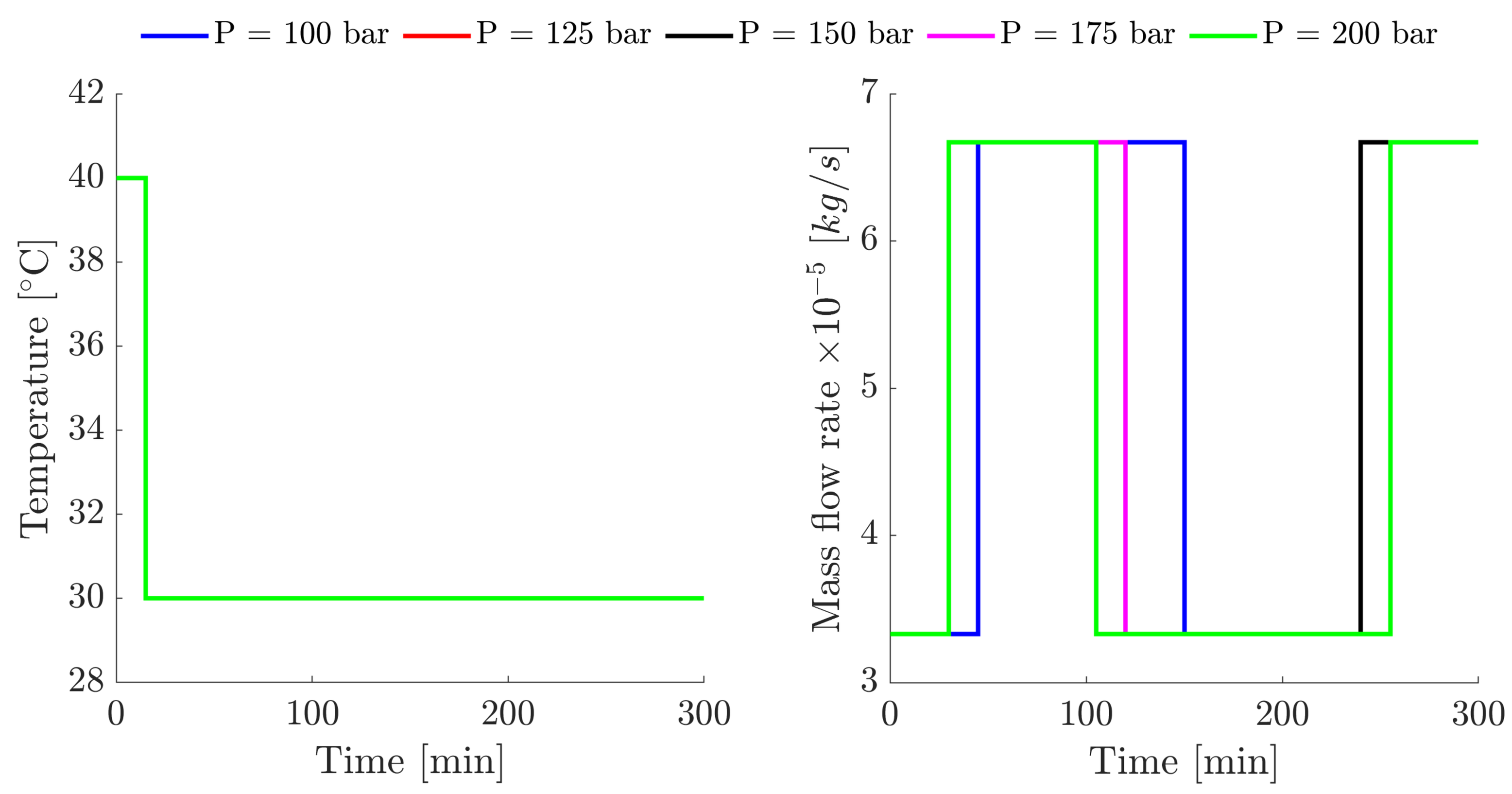

Figure 3: Optimal profiles

Conclusions

- The optimal control profiles are similar across all cases.
- Low objective values are achieved at pressures near the supercritical point, where variations in the inlet temperature cause significant deviations in the physical properties of CO_2 and consequently in the Reynolds number
- 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.

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.

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