# Optimal design of experiment:
*supercritical fluid extraction case*

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## Introduction

This study investigates the extraction of valuable components from biomass using supercritical carbon dioxide as a solvent. The interest is in essential oils extracted from chamomile flowers in cylindrical extractors operated in a semi-batch mode. The process is described by a distributed-parameter model, and set of empirical correlations. This work aims to validate empirical correlations by designing a new experiment with dynamically changing operating conditions.

## Process Model

- 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
$\rho_f$ – Density of fluid
$A_f$ – Cross-section of the bed
$u$ – Darcy velocity
$\phi$ – Void fraction
$D_i^R$ – Internal mass diffusivity
$D_e^M$ – Axial mass diffusivity
$\mu$ – Particle shape coefficient
$l$ – Particle length
$\Upsilon$ – Decaying factor
$\rho_s$ – Bulk density of solid bed
$k_m$ – Partition factor
$P$ – Pressure
$T$ – Temperature
$F$ – Mass flow rate

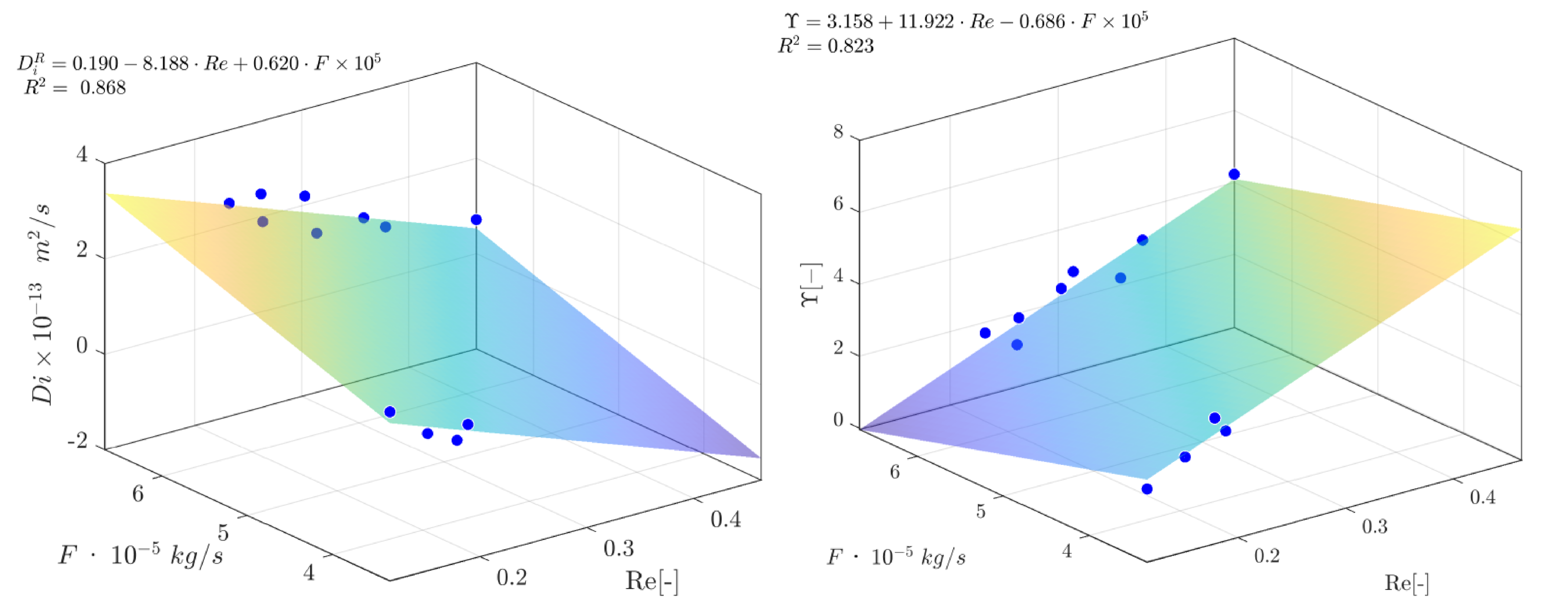


**Figure 1:** Empirical correlations

## Model-based optimal design of experiment

Fisher information $\mathcal{F}$ measures the amount of information that an observable random variable carries about an unknown parameter of a distribution that models the random variable. $\mathcal{F}$ is defined as Hessian of the likelihood function with respect to parameters $\Theta$, given the covariance matrix $\Sigma$.

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

The optimal design of experiments is a concept that refers to planning an experiment, which allow parameters to be estimated without bias and with minimum variance. The D-optimality criterion is selected as the objective function, which leads to the minimisation of the volume of the ellipsoidal confidence region of parameter estimates given the experimental condition $\Xi$.

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

This work aims to design a dynamic experiment to improve precision of correlation for $D_i^R$. The system is assumed to run for 300 min, with sampling time of 10 min. The set of decision variables consists of $T^{in}$ and $F$, and each of them is manipulated every 15 min. Each of five analysed cases assumes that P is kept constant at 100, 125, 150, 175 and 200 bar, respectively.

## Results

To identify the global solution, the optimization problem is solved multiple times, each starting from a random initial solution. Figure 2 compares the initial and final values of the cost function across multiple optimization runs for different cases of pressure value.

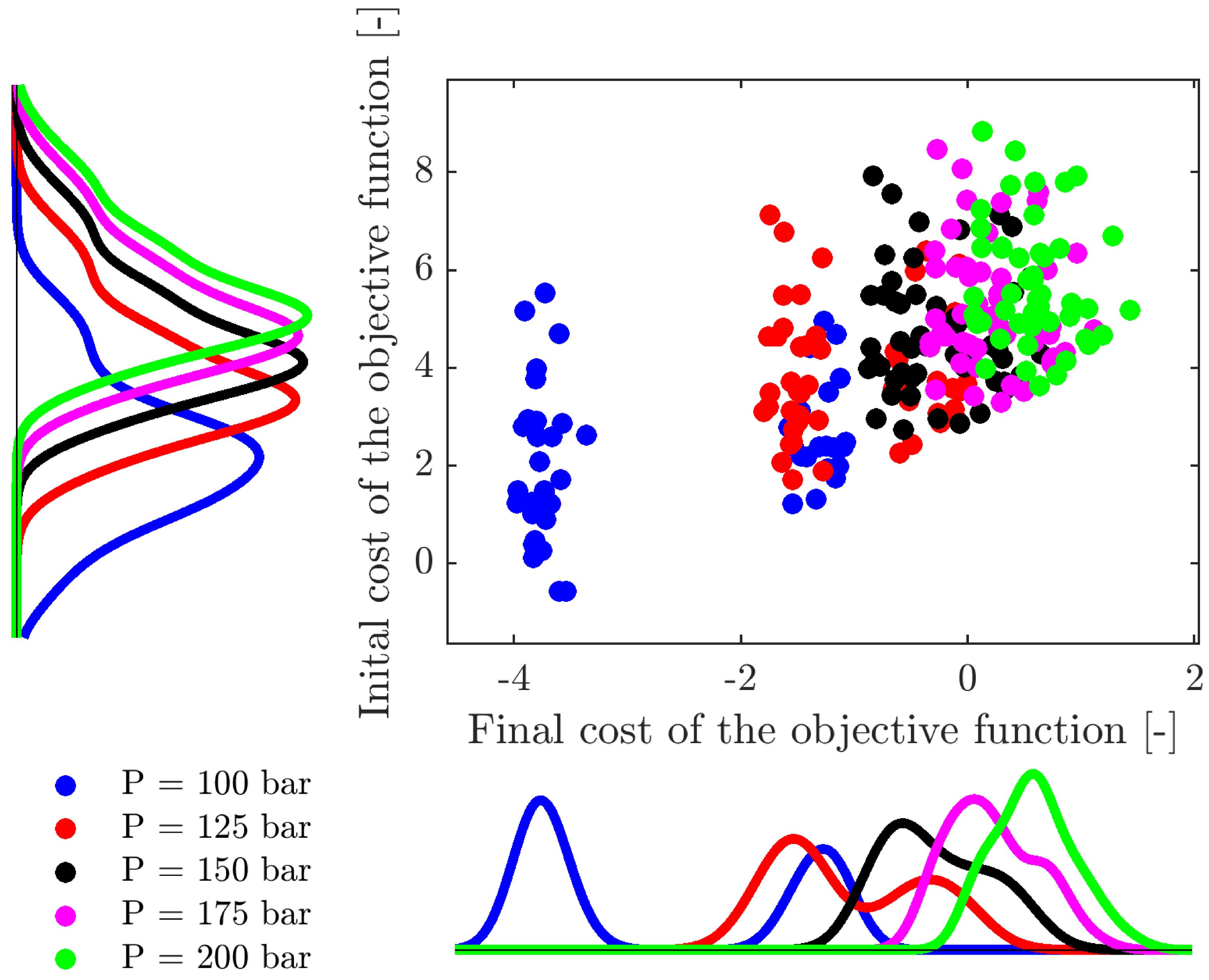


**Figure 2:** Values of the objective function

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

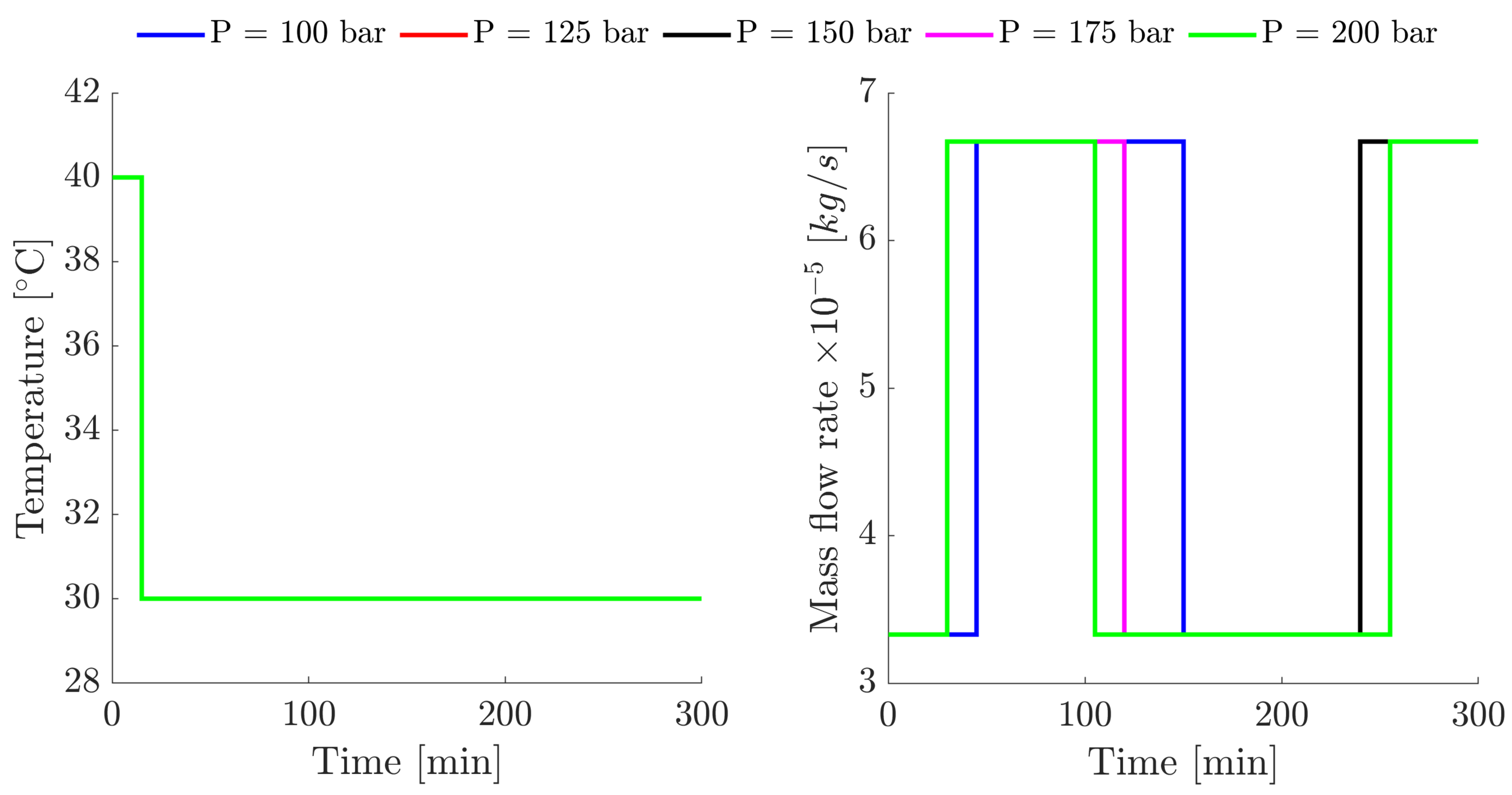


**Figure 3:** Optimal profiles

## Conclusions

- The optimal profiles of controls are similar for all the cases
- Low values of the objective are obtained at pressures close to supercritical point, where the variation in the inlet temperature cause large deviation in the physical properties of $CO_2$ and Reynolds number
- The mass flow rate is used as main control variable, which suggest that the system is more sensitive to the mass flow rate than the inlet temperature

## Forthcoming Research

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## References

[1] A. B. Jones and J. M. Smith. Article Title. *Journal title*, 13(52):123–456, March 2013.

[2] J. M. Smith and A. B. Jones. *Book Title*. Publisher, 7th edition, 2012.

## Acknowledgements

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