

Parameter estimation

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ABSTRACT

Given a system of partial differential equations, $F(t, x, \dot{x}, p, u) = 0$, where x represents state variables, p are the parameters, and u are control variables, we describe the supercritical extraction process. The process model describes a partially filled extractor with a fixed bed, which work under constant operating conditions. We assume that the flow is uniform across any cross-section, although the area available for the fluid phase is a function of distance. We apply the concept of quasi-one-dimensional flow to mimic the modelling of a two-dimensional case. The collected dataset, obtained from the extraction of caraway seeds at different operating conditions, is used to estimate unknown parameters. The model-based parameter estimation applies the maximum likelihood method to estimate values of the extraction kinetic parameters such as mass partition factor, internal diffusion coefficient and radial diffusion.

1. Introduction

2. Materials and methods

2.1. Supercritical fluids

The properties of a fluid can be divided into two kinds, equilibrium properties and transport properties. The equation of state can be used accurately to predict the equilibrium properties, such as density, enthalpy, vapor pressure, fugacity and fugacity coefficient, vapor liquid equilibrium, and all kinds of excess properties.

Carbon dioxide above its critical point attains a supercritical state and exhibits certain peculiar properties such as higher density as a liquid but with a lower viscosity comparable to a gas. The supercritical carbon dioxide (S-CO₂) has a range of engineering applications.

The thermodynamic properties of S-CO₂ such as density, local speed of sound and specific heat capacity vary significantly for slight change in temperature and pressure due to real gas effects. Equation of state (EOS) which account these real gas effects is used to calculate the thermodynamic properties. In order to predict this real gas effects, the Peng-Robinson equation of state (P-R EOS) is used to compute properties of CO₂. The P-R EOS belongs to the specific class of thermodynamic models for modelling the pressure of a gas as a function of temperature and density and can be written as a cubic function of the molar volume (of the density). The P-R EOS is presented by equation 1

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2} \quad (1)$$

where a , b , α are parameters defined as presented in the appendix.

The properties of the CO₂ presented as a function of operating conditions (temperature and pressure) are presented on fig. 1

At standard atmospheric pressure and temperature, the CO₂ behaves as an ideal gas, and its compressibility factor

equals to unity. However, at high temperature and pressure, the compressibility factor varies from unity, due to real gas effects. As it is presented on Figure 1a, the compressibility factor obtained from the Peng-Robinson equation of state varies strongly depending on the operating conditions. The compressibility factor can be obtained by given temperature and pressure by solving the polynomial form of the P-R EOS given by equation 2.

$$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \quad (2)$$

where A and B are parameters as defined in the appendix. The roots of the polynomial can be found iteratively or by Cardano formula. Depends on the operating conditions, one or two roots can be found. In one-phase region the fluid can be describe as gas, liquid or super-critical. In the two-phase region the gas-liquid mixture is present. The biggest root is assigned to the gas phase and smallest root corresponds to the liquid phase.

The real gas effects are also visible on the density plot presented on the Figure 1b. The density can change significantly depends on the operating conditions. By analysing the compressibility and density plots more it can be noticed that very near to the critical point, the fluid can neither be called a liquid nor a gas and has a unique combination of gas-like and liquid-like properties.

The Figure 1c show behaviour of the heat capacity of a supercritical fluid at constant pressure (C_p). The details of the calculations can be found in the appendix. In contrary to the density which varies monotonically, the specific heat shows very high levels in a narrow region. In the sub-critical region, the phase transition is associated with an effective spike in the heat capacity (i.e., the latent heat). Approaching the critical point, the latent heat falls to zero but this is accompanied by a gradual rise in heat capacity in the pure phases near phase transition. At the critical point, the latent heat is zero but the heat capacity shows a diverging singularity. Beyond the critical point, there is no divergence, but rather a smooth peak in the heat capacity; the highest point of this peak identifies the Widom line. (ref: 10.1038/nphys1683, 10.3311/PPch.12871)

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In order to calculate thermodynamic properties from a real gas, the departure function for that property with respect to the chosen equation of state has to be evaluated. The departure function for any thermodynamic property of a real gas is defined as the difference in the value of that property determined from the chosen real gas equation of state and the value of the same property for an ideal gas under the same conditions of temperature and pressure. (0.1007/s10494-017-9872-4)

On the other hand, transport properties (viscosity and conductivity) are also important quantities required in engineering design for production, fluid transportation, and processing. According to (10.1007/BF00500714), there is no satisfactory theory of transport properties of real dense gases and liquids. The main difficulties in the study of transport properties are twofold: one is the inherent difficulties involved in accurate measurements, and the other is the complexity involved in theoretical treatments. Therefore, the generally used correlations of transport coefficient are either empirical or based on some theoretical foundation. Enskog (REF) developed a popular theory for the transport properties of dense gas based on the distribution function. However, the Enskog theory was proposed for rigid spherical molecules. For real gases, some modification is needed. Following the Enskog theory, many correlations have been proposed in the form of the reduced density and reduced temperature. The correlations of (10.1063/1.556013) and (10.1063/1.4977429) implemented and compared as presented on Figure 2. Eventually the NIST correlation was selected to be used. The viscosity formulation proposed by NIST consists of four contributions: (i) for the limit of zero density, (ii) for the initial density dependence, (iii) for the residual viscosity, and (iv) for the singularity of the viscosity at the critical point. The NIST correlation covers temperatures from 100 to 2000 K for gaseous CO_2 and from 220 to 700 K with pressures along the melting line up to 8000 MPa for compressed and supercritical liquid states.

Similarly, several correlations for thermal conductivity of CO_2 were compared on Figure 3. The presented figures are focused around critical point, where the singularity is present. Similarities between specific heat and the thermal conductivity can be observed. Eventually, the NIST correlation were selected. The correlations are applicable for the temperature range from the triple point to 1100 K and pressures up to 200 MPa.

2.2. Governing equations

The detail derivation of the governing equation can be found in the appendix (??). Let's assume that any properties of the flow are uniform across any given cross-section of an channel (or any device like an extractor). Such a flow is called quasi-one-dimensional. The variation of the cross-section might be an result of its irregular shape (or partial filling of an extractor).

The quasi-one-dimensional compressible Navier-Stokes equations in Cartesian coordinates is given by equations 2.2

$$\frac{\partial(\rho_f A_f)}{\partial t} + \frac{\partial(\rho_f A_f v)}{\partial z} = 0 \quad (3)$$

$$\frac{\partial(\rho_f v A_f)}{\partial t} + \frac{\partial(\rho_f A_f v^2)}{\partial z} = -A_f \frac{\partial P}{\partial z} \quad (4)$$

$$\frac{\partial(\rho_f e A_f)}{\partial t} + \frac{\partial(\rho_f A_f v e)}{\partial z} = -P \frac{\partial(A_f v)}{\partial z} + \frac{\partial}{\partial z} \left(\frac{\partial T}{\partial z} \right) \quad (5)$$

where ρ_f is the density of the fluid, A_f is the function which describe change of the cross-section, v is the velocity, P is the total pressure, e is the internal energy of the fluid, t is time and z is the spacial direction.

2.3. Low Mach number expansion

As discussed by Lions [1], the low Mach number equations are a subset of the fully compressible equations of motion (continuity, momentum and energy). Such a set of equations allow for large variations in gas density but it is consider to be acoustically incompressible. The low Mach number equations are preferred over the full compressible equations for low speed flow problems ($M_a = \frac{|V|}{\sqrt{\partial P / \partial \rho}} \ll 1$) to avoids the need to resolve fast-moving acoustic signals. The equations are derived from the compressible equations based on the perturbation theory. The perturbation theory develops an expression for the desired solution in terms of a formal power series known as a perturbation series in some "small" parameter ζ , that quantifies the deviation from the exactly solvable problem. The leading term in this power series is the solution of the exactly solvable problem, while further terms describe the deviation in the solution, due to the deviation from the initial problem.

The equations 2.2 describe the fully compressible equations of motion (respectively the transport of mass, momentum and energy) for quasi-one-dimensional case. We rescale the time variable, considering finally

$$\rho_\zeta = \rho(z, t/M_a), \quad V_\zeta = \frac{1}{\zeta} V(z, t/M_a), \quad T_\zeta = T(z, t/M_a), \quad k_\zeta = \zeta k(\rho_f, T)$$

The conservative non-dimensional equations of motion becomes

$$\begin{aligned} \frac{\partial(\rho_\zeta A_f)}{\partial t} + \frac{\partial(\rho_\zeta A_f V_\zeta)}{\partial z} &= 0 \\ \frac{\partial(\rho_\zeta A_f V_\zeta)}{\partial t} + \frac{\partial(\rho_\zeta V_\zeta A_f V_\zeta)}{\partial z} + \frac{A_f}{M_a^2} \frac{\partial P_\zeta}{\partial z} &= 0 \\ \frac{\partial(\rho_\zeta e_\zeta A_f)}{\partial t} + \frac{\partial(\rho_\zeta e_\zeta V_\zeta A_f)}{\partial z} - \frac{\partial}{\partial z} \left(k \frac{\partial T_\zeta}{\partial z} \right) + P_\zeta \frac{\partial A_f V_\zeta}{\partial z} &= 0 \end{aligned}$$

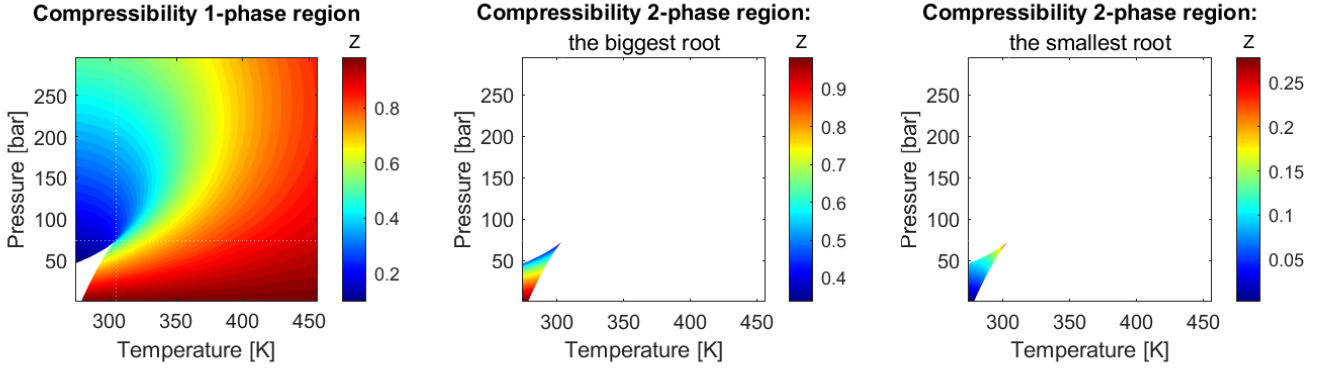
Let's define $\zeta = M_a^2$ and assume small Mach numbers, $M_a \ll 1$, then the kinetic energy, viscous work, and gravity work terms can be neglected in the energy equation since those terms are scaled by the square of the Mach number. The inverse of Mach number squared remains in the momentum equations, suggesting singular behaviour. In order to explore the singularity, the pressure, velocity and temperature are expanded as asymptotic series in terms of the parameter ζ

$$P_\zeta = P_0 + P_1 \zeta + P_2 \zeta^2 + \mathcal{O}(\zeta^3)$$

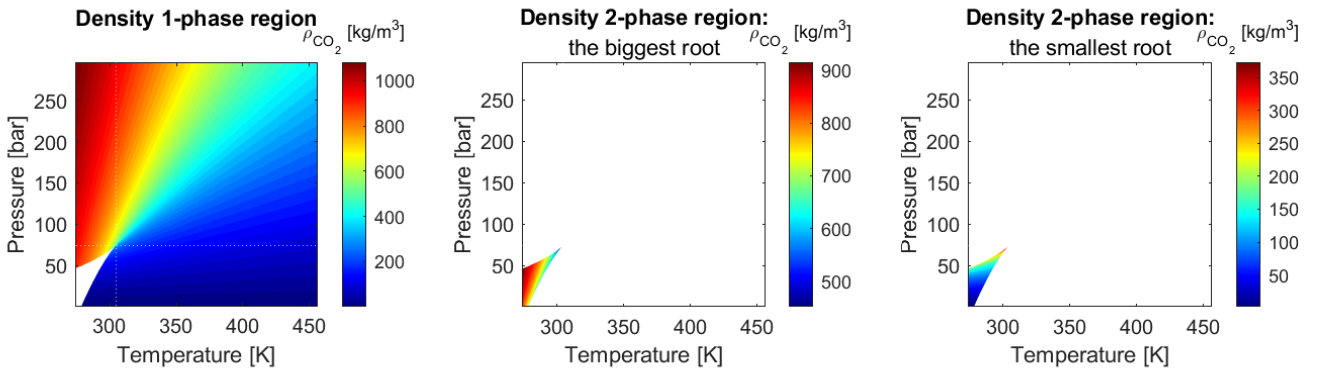
$$\rho_\zeta = \rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2)$$

$$V_\zeta = V_0 + V_1 \zeta + \mathcal{O}(\zeta^2)$$

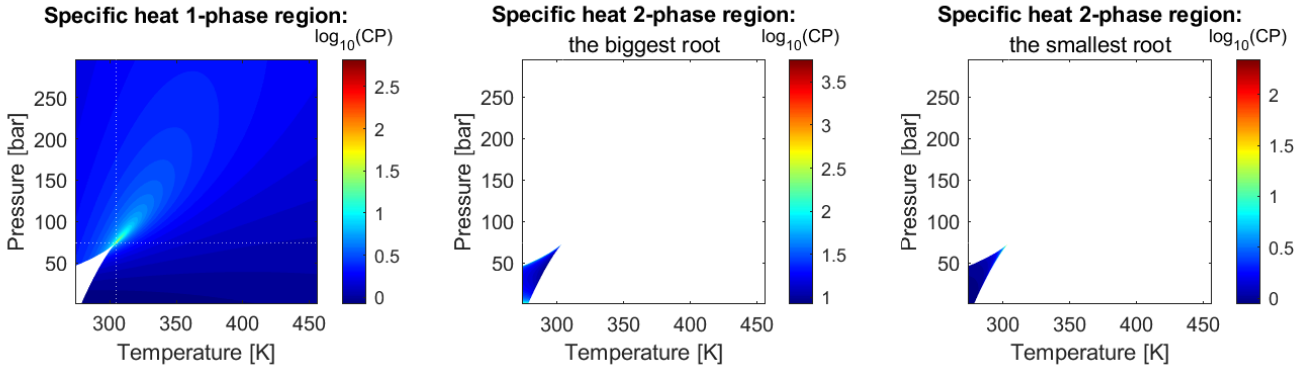
Parameter estimation



(a) The compressibility factor based on the Peng-Robinson equation of state



(b) The fluid density based on the Peng-Robinson equation of state



(c) The specific heat of the CO_2 based on the Peng-Robinson equation of state

Figure 1: Properties of CO_2 based on the equation of state

$$T_\zeta = T_0 + T_1 \zeta + \mathcal{O}(\zeta^2)$$

$$e_\zeta = e_0 + e_1 \zeta + \mathcal{O}(\zeta^2)$$

By expanding performing power expansion on the continuity equation and taking the limit of ζ from the positive side we get

$$\lim_{\zeta \rightarrow 0^+} \frac{\partial ((\rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2)) A_f)}{\partial t} + \frac{\partial ((\rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2)) A_f (V_0 + V_1 \zeta + \mathcal{O}(\zeta^2)))}{\partial z} = 0$$

The continuity equation become

$$\frac{\partial (\rho_0 A_f)}{\partial t} + \frac{\partial (\rho_0 A_f V_0)}{\partial z} = 0 \quad (6)$$

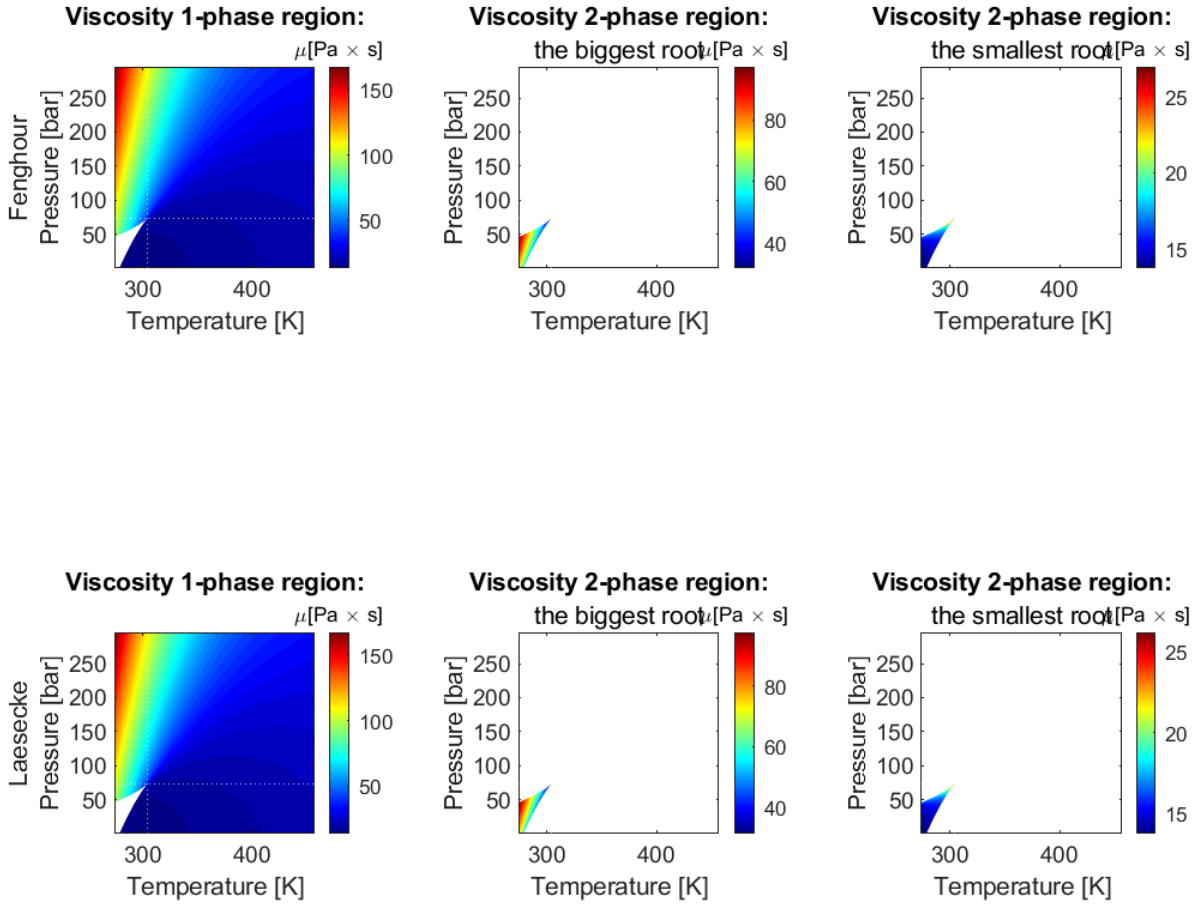


Figure 2: Viscosity obtained based on different correlations

The form of the continuity equation stays the same. Considering the momentum equation, it can be seen that the inverse of Mach number squared remains which suggests singular behavior.

$$\lim_{\zeta \rightarrow 0_+} \frac{\partial \left((\rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2)) A_f (V_0 + V_1 \zeta + \mathcal{O}(\zeta^2)) \right)}{\partial t} + \frac{\partial \left((\rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2)) A_f (V_0 + V_1 \zeta + \mathcal{O}(\zeta^2)) (V_0 + V_1 \zeta + \mathcal{O}(\zeta^2)) \right)}{\partial z} + A_f \frac{\partial}{\partial z} \left(\frac{P_0}{M_a^2} + \frac{P_1 \zeta}{M_a^2} + \frac{P_2 \zeta^2}{M_a^2} + \mathcal{O}(\zeta^3) \right)$$

The first two terms stays the same, but the third one become different in structure. By further investigation of the pressure term in the momentum equation it can be observed

$$\begin{aligned} \lim_{\zeta \rightarrow 0_+} \frac{\partial}{\partial z} \left(\frac{P_0}{M_a^2} + \frac{P_1 \zeta}{M_a^2} + \frac{P_2 \zeta^2}{M_a^2} + \mathcal{O}(\zeta^3) \right) &= \\ &= \lim_{\zeta \rightarrow 0_+} \frac{\partial}{\partial z} \left(\frac{P_0}{M_a^2} \right) + \frac{\partial}{\partial z} \left(\frac{P_1 \zeta^2}{M_a^2} \right) + \frac{\partial}{\partial z} \left(\frac{P_2 \zeta^2}{M_a^2} \right) \\ &= \lim_{\zeta = M_a^2 \rightarrow 0_+} \frac{\partial}{\partial z} \left(\frac{P_0}{M_a^2} \right) + \frac{\partial}{\partial z} \left(\frac{P_1 M_a^2}{M_a^2} \right) + \frac{\partial}{\partial z} \left(\frac{P_2 M_a^4}{M_a^2} \right) \\ &= \lim_{\zeta = M_a^2 \rightarrow 0_+} 0 + \frac{\partial P_1}{\partial z} + 0 \end{aligned}$$

The simplification of the P_0 in the momentum equation comes from the fact that P_0 is independent of z . The term related to P_2 and higher order terms become zero at the limit of $M_a \rightarrow 0$. The momentum equation become

$$\frac{\partial (\rho_0 A_f V_0)}{\partial t} + \frac{\partial (\rho_0 V_0 A_f V_0)}{\partial z} + A_f \frac{\partial P_1}{\partial z} = 0$$

By expanding performing power expansion on the energy equation and taking the limit of ζ from the positive side we get

$$\begin{aligned} \lim_{\zeta \rightarrow 0_+} \frac{\partial \left((\rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2)) A_f (e_0 + e_1 \zeta + \mathcal{O}(\zeta^2)) \right)}{\partial t} &+ \\ &+ \frac{\partial \left((\rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2)) A_f (V_0 + V_1 \zeta + \mathcal{O}(\zeta^2)) (e_0 + e_1 \zeta + \mathcal{O}(\zeta^2)) \right)}{\partial z} \\ &+ \frac{\partial}{\partial z} \left(k \frac{\partial}{\partial z} (T_0 + T_1 \zeta + \mathcal{O}(\zeta^2)) \right) + \\ &- (P_0 + P_1 \zeta + P_2 \zeta^2 + \mathcal{O}(\zeta^3)) \frac{\partial (A_f (V_0 + V_1 \zeta + \mathcal{O}(\zeta^2)))}{\partial z} = 0 \end{aligned}$$

The form of the energy equation stays the same.

$$\frac{\partial (\rho_0 e_0 A_f)}{\partial t} + \frac{\partial (\rho_0 e_0 V_0 A_f)}{\partial z} - \frac{\partial}{\partial z} \left(k \frac{\partial T_0}{\partial z} \right) + P_0 \frac{\partial A_f V_0}{\partial z} = 0$$

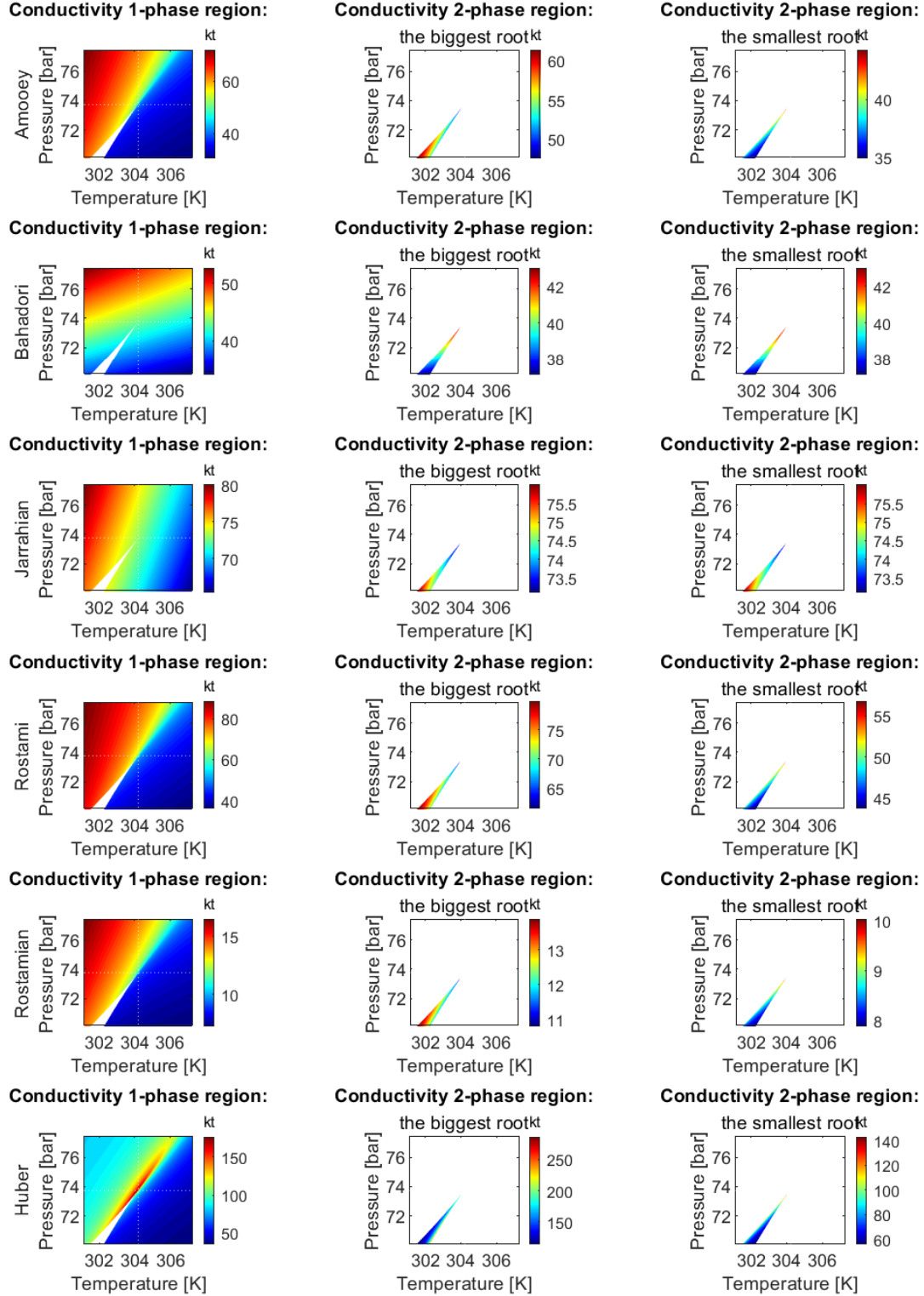


Figure 3: Thermal conductivity obtained based on different correlations

where $e_0 = e(\rho_0, T_0)$ and $k = k(\rho_0, T_0)$.

The expansion results in two different types of pressure and they are considered to be split into a thermodynamic

component (P_0) and a dynamic component (P_1). The thermodynamic pressure is constant in space, but can change in time. The thermodynamic pressure is used in the equation of

state. The dynamic pressure only arises as a gradient term in the momentum equation and acts to enforce continuity.

The resulting unscaled low Mach number equations are:

$$\begin{aligned}\frac{\partial(\rho_f A_f)}{\partial t} + \frac{\partial(\rho_f A_f V)}{\partial z} &= 0 \\ \frac{\partial(\rho_f A_f V)}{\partial t} + \frac{\partial(\rho_f V A_f V)}{\partial z} + A_f \frac{\partial P_1}{\partial z} &= 0 \\ \frac{\partial(\rho_f e A_f)}{\partial t} + \frac{\partial(\rho_f e V A_f)}{\partial z} - \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + P_0 \frac{\partial A_f V}{\partial z} &= 0\end{aligned}$$

The energy equation can be expanded through the chain rule to obtain

$$\rho A_f \left(\frac{\partial e}{\partial t} + V \frac{\partial e}{\partial z} \right) + e \underbrace{\left(\frac{\partial(\rho_f A_f)}{\partial t} + \frac{\partial(\rho_f V A_f)}{\partial z} \right)}_{\text{Continuity}} - \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + P_0 \frac{\partial A_f V}{\partial z} = 0 \quad \text{that}$$

The non-conservative form of the energy equation become

$$\rho A_f \left(\frac{\partial e}{\partial t} + V \frac{\partial e}{\partial z} \right) - \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + P_0 \frac{\partial A_f V}{\partial z} = 0$$

If the calorically perfect gas is assumed then $e = C_v T$, where C_v is the constant specific heat. The energy equation can derived in terms of temperature T

$$\rho A_f C_v \left(\frac{\partial T}{\partial t} + V \frac{\partial T}{\partial z} \right) - \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + P_0 \frac{\partial A_f V}{\partial z} = 0$$

If isothermal case is assumed then, the energy equation becomes

$$\lim_{\Delta T \rightarrow 0^+} \rho A_f C_v \left(\frac{\partial T}{\partial t} + V \frac{\partial T}{\partial z} \right) - \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + P_0 \frac{\partial A_f V}{\partial z} = 0$$

which leads to

$$\frac{\partial A_f V}{\partial z} = 0 \quad (7)$$

In one-dimensional case, the equation 7 become equivalent of $\text{div}(A_f V) = 0$, which known as the incompressibility condition (Lions [1]).

A general formulation the internal energy for a real gas is:

$$de = C_v dT - \left[P - T \left(\frac{\partial P}{\partial T} \right)_{v_m} \right] dv_m$$

where v_m is the molar volume.

The internal energy is a function of two intensive properties, in this case T and V . But, in the case of an ideal gas, the equation of state is such that the second term in this equation is identically equal to zero. So the ideal gas is a special case in which the molar internal energy is a function only of temperature. For Peng-Robinson equation of state, the internal energy is defined as

$$e = C_v T + \frac{a \left(\alpha - T \frac{da}{dT} \right)}{2\sqrt{2}b} \ln \left[\frac{1+b(1-\sqrt{2}\rho)}{1+b(1+\sqrt{2}\rho)} \right]$$

Assuming constant temperature and pressure along space and in time:

$$\lim_{\Delta T, \Delta P \rightarrow 0^+} \rho A_f \left(\frac{\partial e}{\partial t} + V \frac{\partial e}{\partial z} \right) - \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + P_0 \frac{\partial A_f V}{\partial z} = 0 \rightarrow \frac{\partial A_f V}{\partial z} = 0$$

It can be deduce that the continuity equation becomes $\frac{\partial \rho_f}{\partial t} = 0$ at constant temperature and pressure. Moreover, the incompressibility condition $\text{div}(A_f V) = 0$ is obtained.

Assuming an arbitrary function \hat{P} , which describe the total pressure, the dimensional momentum equation can be written as

$$V \underbrace{\left(\frac{\partial \rho_f A_f}{\partial t} + \frac{\partial \rho_f V A_f}{\partial z} \right)}_{\text{Continuity equation}} + \rho_f A_f \frac{\partial V}{\partial t} + \rho_f V A_f \frac{\partial V}{\partial z} = -A_f \frac{\partial \hat{P}}{\partial z}$$

From the incompressibility conditions we can deduce that

$$\frac{\partial A_f V}{\partial z} = 0 \rightarrow A_f \frac{\partial V}{\partial z} = -V \frac{\partial A_f}{\partial z}$$

By combining both above equations, assuming that $\partial V / \partial t = 0$:

$$\frac{\rho_f V^2}{A_f} \frac{\partial A_f}{\partial z} = \frac{\partial \hat{P}}{\partial z} \rightarrow \int \frac{\rho_f V^2}{A_f} \frac{\partial A_f}{\partial z} dz = \int \frac{\partial \hat{P}}{\partial z} dz$$

The l.h.s integral can be solved by assuming ρ_f is constant and introducing $u = A_f V$

$$\begin{aligned}\int \frac{\rho_f V^2}{A_f} \frac{\partial A_f}{\partial z} dz &= \int \frac{\rho_f V^2}{A_f} \frac{A_f^2}{A_f^2} \frac{\partial A_f}{\partial z} dz \\ &= \rho_f u^2 \int \frac{1}{A_f^3} \frac{\partial A_f}{\partial z} dz = -\frac{\rho_f u^2}{2\Delta A_f^2} = -\frac{\rho_f \Delta V^2}{2} \\ \int \frac{\partial \hat{P}}{\partial z} dz &= \Delta \hat{P}\end{aligned}$$

The final form of the momentum equation corresponds to the Bernoulli's principle

$$\Delta \hat{P} = -\frac{\rho_f \Delta V^2}{2} \xrightarrow{P_0 = \text{const}} \Delta M_a^2 P_1 = -\frac{\rho_f \Delta V^2}{2}$$

The Bernoulli's principle can be used to find the hydrodynamic pressure caused by varying cross-section at steady-state. Moreover, if the flow velocity is relatively low and so all pressure changes are hydrodynamic (due to velocity motion) rather than thermodynamic. The effect of this is that $\partial \rho / \partial p = 0$. In other words, the small changes in pressure due to flow velocity changes do not change the density. This has a secondary effect – the speed of sound in the fluid is $\partial p / \partial \rho = \infty$ in this instance. So there is an infinite speed of sound, which makes the equations elliptic in nature. It can be deduced that at the isothermal conditions the density in the system propagates with the same speed as pressure due to the fact that they are both connected through the equation of state.

2.4. Extraction model

A distributed-parameter model, based on Reverchon [2], is used to describe the solid-fluid extraction process. The process model consists of three partial differential equations: two mass balance equations relative to the concentration of solute in the fixed solid phase and the mobile fluid phase, and

the heat balance equation relative to the temperature of the fluid phase. The amount of solute in the solvent is considered negligible. Therefore, the fluid phase can be described as pseudo-homogeneous, and its properties are assumed to be the same as the solvent.

The movement of the mobile pseudo-homogeneous phase (Eq. 9) is considered only in the axial direction. The properties of the system in the radial direction is assumed to be uniform. In addition, it is considered that the boundary layer adjacent to the inner wall of the extractor does not exist. Therefore, the velocity profile is constant across any cross-section of the extractor perpendicular to the axial direction. As a result, the plug flow model can be introduced. The particle size distribution and the void fraction of the solid phase are assumed to be uniform in space and remain constant in time. Moreover, the pressure is considered to be constant along the fixed bed. The mass balance for the fluid phase consists of convection, diffusion, and kinetic terms.

Considering the solid phase to be fixed, the convection and diffusion terms in the corresponding mass balance are both assumed to be negligible or absent. Therefore, the mass balance for the solid phase (Eq. 10) consists of the kinetic term only.

As for the mass transfer from the solid to the fluid phase, a kinetic term based on two-film theory for the solute is considered. The mass transfer kinetic (Eq. 11) consists of the overall diffusion coefficient and the concentration gradient, which acts as a driving force for the process. A single pseudo-component is used to represent the extract collectively.

The heat balance (Eq. 15) 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 no heat loss through the wall, and there is no heat generation in the system. Therefore, the temperature of the extractor can be changed only by manipulating the temperature of the inlet stream $T_{In}(t)$.

We assume that at a given section, where the cross-sectional area is A , the flow properties are uniform across that section. Hence, although the area of an extractor changes as a function of a distance along an extractor (e.g. if a fixed fill an extractor partially), z , and therefore in reality the flow field is two-dimensional (the flow varies in the two-dimensional space), we make the assumption that the flow properties vary only with z ; this is tantamount to assuming uniform properties across any given cross section. Such flow is defined as quasi-one-dimensional flow.

For the sake of clarity of the process model, different colors have been used in the equations to indicate: **control variables**, **state variables**, **variables** and **parameters**.

2.4.1. Continuity equation

The continuity equation for the fluid phase is given by Eq. 8. The details of derivation can be found in the appendix ??

$$\frac{\partial (\rho_f A_f)}{\partial t} + \frac{\partial (\rho_f v A_f)}{\partial z} = 0 \quad (8)$$

Considering the mass flow-rate which is constant in time, the temporal derivative become zero and the spacial derivative can be integrated along z .

$$\int \frac{\partial (\rho_f v A_f)}{\partial z} dz = 0 \rightarrow F = \rho_f v A_f$$

where F is a constant obtained from the integration. The constant F can be understood as the mass flux per unit area which is assumed to be constant along z . F can be treated as a control variable, which can change in time but it is constant in space. Such a assumption allows to find the velocity profile which satisfy the mass continuity based on F , A_f and ρ_f . The fluid density ρ_f density is connected through equation of state with thermodynamical pressure, which is assumed to be constant along z (due to the low-Mach number) and temperature. The variation in density might be caused by the accumulation of the fluid in the system (which happen instantaneously along z) or by temperature change. To simplify the dynamic of the system, it is assumed that $F = F(t)$ is a control variable and affects the whole system instantaneously.

2.4.2. Mass balance for the fluid phase

The fluid phase is a mobile phase, which means that the fluids mass balance (Eq. 9) is made of convection, diffusion, and mass transfer kinetic terms.

$$\begin{aligned} \frac{\partial c_f(t, z)}{\partial t} = & \underbrace{-\frac{u}{\epsilon} \frac{\partial c_f(t, z)}{\partial z}}_{\text{Convective term}} - \underbrace{\frac{c_f(t, z)}{\epsilon} \frac{\partial u(t, z)}{\partial z}}_{\text{Convective term}} \\ & + \underbrace{\frac{D_e^M}{\epsilon} [T(t, z), P(t), F(t)] \frac{\partial^2 c_f(t, z)}{\partial z^2}}_{\text{Diffusive term}} + \underbrace{\frac{1 - \epsilon}{\epsilon} r_e(t, z)}_{\text{Kinetic term}} \quad (9) \end{aligned}$$

where $c_f(t, z)$, $c_s(t, z)$, $T(t, z)$ correspond to concentration of solute in the fluid phase, concentration of solute in the solid phase and the temperature, respectively. $r_e(t, z)$ is a mass transfer kinetic term. $F(t)$ is the mass flow rate, $P(t)$ is the pressure, ϵ is the void fraction of the bed, A is the extractor's cross section, $\rho(T(t, z), P(t))$ is the fluid's density, ρ_s is the solids density, $D_e^M(T(t, z), P(t), F(t))$ is the axial mass diffusion coefficient.

2.4.3. Mass balance for the solid phase

The solid phase is a stationary phase, which indicates a lack of convection and diffusion terms in the mass balance (Eq. 10). Therefore, the only term present in this equation is the kinetic term (defined as presented in equation 11), which links solid and fluid phases.

$$\frac{\partial c_s(t, z)}{\partial t} = \underbrace{r_e(t, z)}_{\text{Kinetics}} \quad (10)$$

2.4.4. Kinetic term

As the solvent flows through the bed, it forms a film around the porous solid particle and occupies its pores. the CO_2 molecules diffuse into the pores and adsorb on the particle surface to form an external fluid film around the solid particles through the solvent-solid matrix interactions.

Assuming that the mean free path of the molecule is much smaller than the pore diameter, the effect of Knudsen diffusion is small and can be neglected. In this work, the molecular diffusion is assumed. The dissolved solute diffuses from the particle's core through the solid-fluid interface, the pore, and the film into the bulk. The graphical representation of the mass transfer mechanism is shown in Figure 4. The mean solute concentration in the solid phase is denoted as c_s . At the solid-fluid interface, the equilibrium concentrations are given as c_s^* and c_p^* , respectively for solid and fluid phases. The concentration of the solutes in the fluid phase in the centre of the pore is denoted as c_p . As the solute diffuses through the pore, its concentration changes and reaches c_{pf} at the end the opening of the pore. The solute diffuses through the film around the particle and reaches a concentration in the bulk c_f . It can be assumed that the two-film theory describes the solid-fluid interface inside the pore. The overall mass transfer coefficient can be introduced if the relation between the solute concentration in one phase and its equilibrium concentration is known.

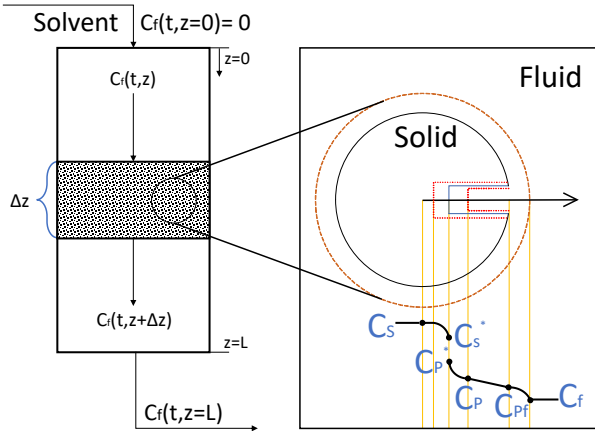


Figure 4: The extraction mechanism

Bulley et al. [3] suggest a process where the driving force for extraction is given by the difference between concentration of the solute in the bulk, c_f , and in the centre of the pore, c_p^* . The concentration c_p^* is in equilibrium with c_s according to an equilibrium relationship. The rate of extraction is thus $r_e(c_f - c_p^*(c_s))$.

On the other hand, Reverchon [2] proposes a driving force given by the difference between c_s and c_p^* . c_p^* is determined by an equilibrium relationship with c_f and the extraction rate is $r_e(c_s - c_p^*(c_f))$.

The kinetic term, denoted as equation 11, corresponds to a solute transfer rate between both phases. This term is made of the overall diffusion coefficient and the concentration gradient (between one phase and its equilibrium concentration), which acts as a driving force for the process. The mass transfer kinetic (Eq. 11) describes 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. Based on the work of Bulley et al. [3], Reverchon [2] proposed to define the kinetic terms as

$$r_e(t, z) = \frac{D_i(T(t, z))}{\mu l^2} (q(t, z) - q^*(t, z)) \quad (11)$$

where $D_i(T(t, z))$ corresponds to the overall diffusion coefficient and $q^*(t, z)$ is a concentration at the solid-fluid interface (which according to the internal resistance model is supposed to be at equilibrium with the fluid phase). $q^*(t, z)$ can be calculated based on the equilibrium relationship (Eq. 12).

The kinetic term of the model takes into account the properties of the biomass like a sphericity (through the shape coefficient μ equal to 1/3 for slabs and 3/5 for spheres), a characteristic dimension of particles (through the parameter $l = r/3$ where r is the mean particle radius), and the solid density ρ_s . The fixed bed is characterized by a void fraction ϵ .

The kinetic term of the model takes into account properties of the solid particles like a sphericity (through the shape coefficient μ), a characteristic dimension of particles (through the parameter $l = r/3$ where r is the mean particle radius), and the bulk density ρ_s . The fixed bed is characterized by a void fraction ϵ .

According to Bulley et al. [3], a linear equilibrium relationship (Eq. 12) can be used to find an equilibrium concentration of the solute in the fluid phase $c_f^*(t, z)$ is based on concentration of the solute in the solid phase $c_s(t, z)$

$$c(t, z) = k_p(T(t, z), P(t)) q^*(t, z) \quad (12)$$

The volumetric partition coefficient $k_p(T(t, z), P(t))$ behaves as an equilibrium constant between the solute concentration in one phase and the corresponding equilibrium concentration at the solid-fluid interphase. The $k_p(T(t, z), P(t))$ can be expressed as mass partition factor $k_m(T(t, z))$ according to Spiro and Kandiah [4]. According to Spiro and Kandiah [4], the term $k_p(T(t, z), P(t))$ can be expressed as the function of mass partition factor $k_m(T(t, z))$

$$k_m(T(t, z)) = \frac{k_p(T(t, z), P(t)) \rho_s}{\rho(T(t, z), P(t))} \quad (13)$$

Equation 14 is the full representation of the kinetic term.

$$r_e(t, z) = - \frac{D_i(T(t, z))}{\mu l^2} \left(q(t, z) - \frac{\rho_s}{k_m(T(t, z)) \rho(T(t, z), P(t))} c(t, z) \right) \quad (14)$$

2.4.5. Heat balance

The heat balance equation (Eq. 15) was developed, assuming the existence of a pseudo-homogeneous phase, which properties are the mean between fluid and solid phases (the amount of solute is considered small enough not to affect the overall heat balance). Equation 15 contains the convection and the diffusion terms. It is considered 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 increasing the temperature of the

inlet stream. The pseudo-homogenous phase is assumed to flow only in the axial direction. The numerator of the factor in front of the convection term of the heat equation contains only the specific heat of the fluid $C_p(T(t, z), P(t))$ because the solid phase is stationary. Therefore, this factor can be understood as the fraction of the fluid's total heat through convection. On the other hand, the axial heat diffusion is calculated based on the definition of thermal diffusivity for the fluid, as explained in the appendix.

The heat balance (Eq. 15), is based on Srinivasan and Depcik [5], and consists of convective and diffusive terms. It follows the assumption of a pseudo-homogeneous phase, which properties are the mean between fluid and solid phases. It is considered that there is no heat loss through the walls, 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 $T_{Inlet}(t)$.

$$\frac{\partial T(t, z)}{\partial t} = \underbrace{\frac{F(t)C_p(T(t, z), P(t))}{A[(1-\epsilon)\rho(T(t, z), P(t))C_p(T(t, z), P(t)) + \epsilon\rho_s C_{ps}]} \frac{\partial T(t, z)}{\partial z}}_{\text{Convection}} + \underbrace{D_e^T(T(t, z), P(t)) \frac{\partial^2 T(t, z)}{\partial z^2}}_{\text{Diffusion}} \quad (15)$$

where $D_e^M(T(t, z), P(t), F(t))$ is the axial mass diffusion coefficient, $C_p(T(t, z), P(t))$ is the fluid's specific heat, C_{ps} is the specific heat of the solid phase, $D_e^T(T(t, z), P(t), F(t))$ is the axial heat diffusion coefficient.

2.4.6. Extraction yield

The efficiency of the process (the yield) is calculated according to one of Eq. 16, which evaluates the mass of solute at the exit of the extraction unit and sums it. The integral form of the measurement equation can be transformed into the differential form, and augmented with model equations to be solved simultaneously.

$$y(t) [kg] = \int_{t_0}^{t_f} Q(t, z) \left[\frac{m^3}{s} \right] c_f(t, z) \Big|_{z=L} \left[\frac{kg}{m^3} \right] dt [s] \quad (16)$$

$$y(t) [kg] = \int_{t_0}^{t_f} \frac{F(t)}{\rho(t, z)} \left[\frac{kg}{s} \left(\frac{kg}{m^3} \right)^{-1} \right] c_f(t, z) \Big|_{z=L} \left[\frac{kg}{m^3} \right] dt [s] \quad (17)$$

$$\frac{dy}{dt} \left[\frac{kg}{s} \right] = Q(t, z) \left[\frac{m^3}{s} \right] c_f(t, z) \Big|_{z=L} \left[\frac{kg}{m^3} \right] \quad (18)$$

$$\frac{dy}{dt} \left[\frac{kg}{s} \right] = \frac{F(t)}{\rho(t, z)} \left[\frac{kg}{s} \left(\frac{kg}{m^3} \right)^{-1} \right] c_f(t, z) \Big|_{z=L} \left[\frac{kg}{m^3} \right] \quad (19)$$

2.4.7. State-space representation

It is assumed that the solvent is free of solute at the entrance of the extractor and that all the solid particles have the same initial solute content q_0 . Moreover, it is considered that the initial temperature of the extractor in every place is equal to T_0 . Therefore, the initial conditions employed in the simulation are:

$$c(t = 0, z) = 0$$

$$q(t = 0, z) = q_0$$

$$T(t = 0, z) = T_0$$

The process model can be written in a general form:

$$\begin{bmatrix} \frac{\partial c(t, z)}{\partial t} \\ \frac{\partial q(t, z)}{\partial t} \\ \frac{\partial T(t, z)}{\partial t} \end{bmatrix} = \begin{bmatrix} \phi_1(c(t, z), q(t, z), T(t, z); \theta) \\ \phi_2(c(t, z), q(t, z), T(t, z); \theta) \\ \phi_3(c(t, z), q(t, z), T(t, z); \theta) \end{bmatrix} = \phi(t, z; \theta) = \frac{\partial \chi(t, z)}{\partial t} \quad (21)$$

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

The method of lines is used to transform the process model equations into a set of ODEs denoted as $G(x(t); p)$. 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 derivative, while the central difference scheme is used to approximate second-order derivative. The length of the fixed bed is divided into N_z equally distributed points in z -direction. Each function ϕ_i is transformed to a corresponding set of N_z discretized equations denoted as $G_{i \times N_z + 1}$ to $G_{(i+1) \times N_z}$, where i corresponds to the process model equation. The state-space model $\chi(t, z)$ after the discretization is represented by $\dot{x}(t)$ (Eq. ??).

$$\dot{x}(t) = \frac{dx(t)}{dt} = \begin{bmatrix} \frac{dc_{f,1}(t)}{dt} \\ \vdots \\ \frac{dc_{f,N_z}(t)}{dt} \\ \frac{dc_{s,1}(t)}{dt} \\ \vdots \\ \frac{dc_{s,N_z}(t)}{dt} \\ \frac{dT_1(t)}{dt} \\ \vdots \\ \frac{dT_{N_z}(t)}{dt} \end{bmatrix} = \begin{bmatrix} G_1(x(t), q(t), T(t); p) \\ \vdots \\ G_{N_z}(c(t), q(t), T(t); p) \\ G_{N_z+1}(c(t), q(t), T(t); p) \\ \vdots \\ G_{2N_z}(c(t), q(t), T(t); p) \\ G_{2N_z+1}(c(t), q(t), T(t); p) \\ \vdots \\ G_{3N_z}(c(t), q(t), T(t); p) \end{bmatrix} = \underbrace{G(x(t); p)}_{G(x(t); p)}$$

where $x \in \mathbb{R}^{N_x=3N_z}$ and $p \in \mathbb{R}^{N_p=N_\theta+N_u}$, N_θ is the number of model parameters, N_u is the number of control variables.

In a state-space sense, the state variables of the system are the local concentrations of solute in the fluid and solid phases ($c(t, z)$ and $q(t, z)$, respectively), and the local temperature of the pseudo-homogeneous phase ($T(t, z)$). The controllable input variables are the mass flow-rate and temperature of the solvent in the feed ($F_{in}(t) = F(t)$ and $T_{in}(t) = T(t, z = 0)$, respectively) and the pressure in the extractor ($P(t, z) = P(t)$). We also assume that extraction yield can be modelled as a function of a known initial mass of solute in the solid phase and it can be measured after the

separator ($Y(t)$). The system is controllable by manipulating the flow-rate and temperature of CO₂ in the feed, and the pressure in the extractor.

2.5. Parameter estimation

3. Results

4. Conclusions

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A. Appendix

A.1. Governing equations

A.2. Bayes theorem

Table 1
Notation

Symbol	Description	Unit
A	cross-section	m^2
c	concentration in fluid phase	$kg\ m^{-3}$
Cp	specific heat of the fluid	$J\ mol^{-1}\ K^{-1}$
Cp_s	specific heat of the solid	$J\ mol^{-1}\ K^{-1}$
D_e^M	axial mass diffusion coefficient	$m^2\ s^{-1}$
D_e^T	axial heat diffusion coefficient	$m^2\ s^{-1}$
Di	internal diffusion coefficient	$m^2\ s^{-1}$
dp	particle diameter	m
$F(t)$	mass flow-rate	$kg\ s^{-1}$
km	partition coefficient	$[-]$
k^T	thermal conductivity	$W\ m^{-1}\ K^{-1}$
l	characteristic dimension	m
L	total length of the bed	m
m	mass of the oil in solid phase	kg
m_0	initial mass of the oil in solid phase	kg
M_{CO_2}	molecular mass of CO2	$mol\ kg^{-1}$
Np	number of model parameters and control variables	$[-]$
N_θ	number of model parameters	$[-]$
Nu	number of control variables	$[-]$
Nz	number of grid points in z-direction	$[-]$
p	vector of model parameters and control variables	$[-]$
$P(t)$	pressure	bar
Pe	Peclet's number	$[-]$
q	concentration in solid phase	$kg\ m^{-3}$
R	gas constant	$J\ K^{-1}\ mol^{-1}$
Re	Reynolds number	$[-]$
t	time	s
T	temperature	K
T_0	initial temperature	K
V	volume of the extractor	m^3
y	yield	$[-]$
z	length	m
Z	compressibility factor	$[-]$
ϵ	void fraction	$[-]$
ρ	density of the fluid	$kg\ m^{-3}$
ρ_s	solid density	$kg\ m^{-3}$
μ	shape coefficient	$[-]$
θ	vector of model parameters	$[-]$
η	viscosity	cP
Subscript		
0	initial conditions	$[-]$
*	equilibrium conditions	$[-]$