Parameter estimation

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ABSTRACT

We consider a system of partial differential equations, $F(t, x, \dot{x}, \Theta, u) = 0$, where x denotes the state variables, Θ represents the parameters, and u is the control variables. Our focus is on the supercritical extraction process, which involves a partially filled extractor with a fixed bed that operates under constant conditions. We assume the flow is uniform across any cross-section, although the area available for the fluid phase can vary along the extractor. To model this two-dimensional case, we use the concept of quasi-one-dimensional flow. To describe the fluid-solid extraction process of caraway oil from caraway seeds with CO_2 as a solvent, we use a distributed-parameter model based on Reverchon [1]. This model requires parameters such as partition factor, internal diffusion coefficient, axial diffusion coefficient, and saturation concentration. We estimate these parameters from four experiments at different temperatures and pressures: 40°C/200 bar, 50°C/200 bar, 40°C/300 bar, and 50°C/300 bar. We obtain the parameter values using the maximum likelihood estimation method on yield data under the normal error assumption.

1. Introduction

Over the years, the extraction of natural substances from solid materials and liquids using solvents has been a topic of significant interest for research and development. Supercritical fluids are particularly useful in extraction processes due to their pressure-dependent dissolving power and ability to exhibit both gas- and liquid-like properties, such as fluid-like density and gas-like diffusivity. Of the various supercritical fluids available, supercritical CO_2 is particularly attractive due to its nontoxic, non-flammable, and non-corrosive properties. Moreover, the critical point of CO_2 is relatively low (73.8 bar and 31°C) compared to other fluids, making it an excellent alternative to traditional extraction techniques.

Different mathematical models have been proposed to describe the extraction of valuable compounds from a fixed biomass bed, as reviewed by Huang et al. [2]. However, the selection of an appropriate extraction model should be based on the knowledge of the physical phenomena taking place in the operational unit. Each model has its own set of assumptions and describes different mass transfer mechanisms and equilibrium relationships.

Based on an analogy to heat transfer, Reverchon et al. [3] proposed a hot ball model to describe an extraction process from solid particles containing small quantities of solute, where solubility is not a limiting factor. Sovova [4] presented the Broken-and-Intact Cell model, which describes a system where the outer surfaces of particles have been mechanically interrupted, allowing easy access of solvent to the solute from the broken cells. In contrast, the solute from the intact cells is less accessible due to high mass transfer resistance.

Reverchon [1] developed a model for fluid-solid extraction, where the oil is treated as a single component, and the extraction process is controlled by internal mass transfer resistance, neglecting external mass transfer. This model, however, does not consider the influence of axial dispersion or changes in density and flow rate along the bed. Our work assumes that the extraction process operates semi-continuously in a cylindrical vessel. The solvent is first brought to supercritical conditions, pumped through a fixed bed of finely chopped biomass, and the solute is extracted from the biomass. The solvent and solute are then separated in a flush drum, and the extract is collected. The feed flow rate (F_{in}) and inlet temperature (T_{in}) of the extractor can be measured and manipulated. In contrast, the vessel pressure (P) can be measured and manipulated, but the outlet temperature (T_{out}) can only be measured. Figure 1 depicts a simplified flow diagram.

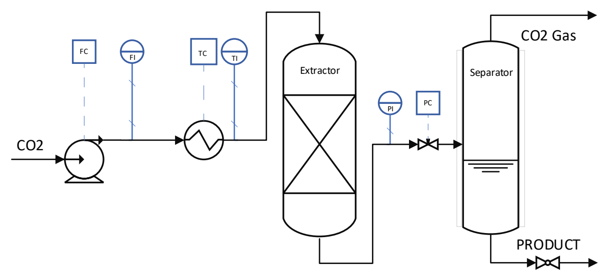

Figure 1: Process flow diagram (Font size)

2. Materials and methods

2.1. Supercritical fluids

A supercritical fluid (SCF) is a substance at a temperature and pressure above its critical point, where there are no distinct liquid and gas phases but below the pressure required to compress it into a solid. SCFs can move through porous solids like gases, which is faster than liquid transport through such materials. SCFs have a higher ability to dissolve materials like liquids or solids compared to gases. Near the

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critical point, small changes in pressure or temperature result in significant changes in density, allowing many properties of an SCF to be fine-tuned. By changing the pressure and temperature, the properties can be tuned to be more liquid-like or gas-like.

Fluid properties 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, vapour pressure, fugacity and fugacity coefficient, vapour-liquid equilibrium, and all kinds of excess properties.

Supercritical CO_2's thermodynamic properties, such as density, the local speed of sound, and specific heat capacity, vary significantly with slight changes in temperature and pressure due to real gas effects. The Peng-Robinson equation of state (P-R EOS) is used to calculate the thermodynamic properties by accounting for these real gas effects. The P-R EOS belongs to a specific class of thermodynamic models for modelling the pressure of a gas as a function of temperature and density. It can be written as a cubic function of the molar volume (of the density). Detail information about Peng-Robinson equation of state can be found in the work of Peng and Robinson [5], Elliott [6] or Pratt [7]. The P-R EOS is presented by equation 1

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

The parameters a, b, α are parameters defined as presented in the appendix A.1.1.

The properties of CO_2 are presented as a function of operating conditions (temperature and pressure) in Figure 2. At standard atmospheric pressure and temperature, CO_2 behaves as an ideal gas, and its compressibility factor equals unity. However, at high pressures and/or low temperatures, intermolecular forces between gas molecules become more significant, causing them to deviate from ideal behaviour. As a result, the compressibility factor can either be greater than or less than unity, depending on the magnitude of these forces. As presented in Figure 2a, 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 solving the polynomial form of the P-R EOS given by 2.

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

where A and B are parameters as defined in the appendix A.1.1. The roots of the polynomial can be found iteratively or by the Cardano formula. In a one-phase region, the fluid is described by one real root corresponding to the gas, liquid or supercritical phase. The gas-liquid mixture is present in the two-phase region, and two roots are found. The biggest root is assigned to the gas phase, and the smallest root corresponds to the liquid phase.

The real gas effects are also visible on the density plot presented in Figure 2b. The density calculations are based on the compressibility factor and its value depends on the operating conditions. The fluid's properties near the critical point are unique and combine gas-like and liquid-like properties. The details of calculations are explained in the appendix A.1.2.

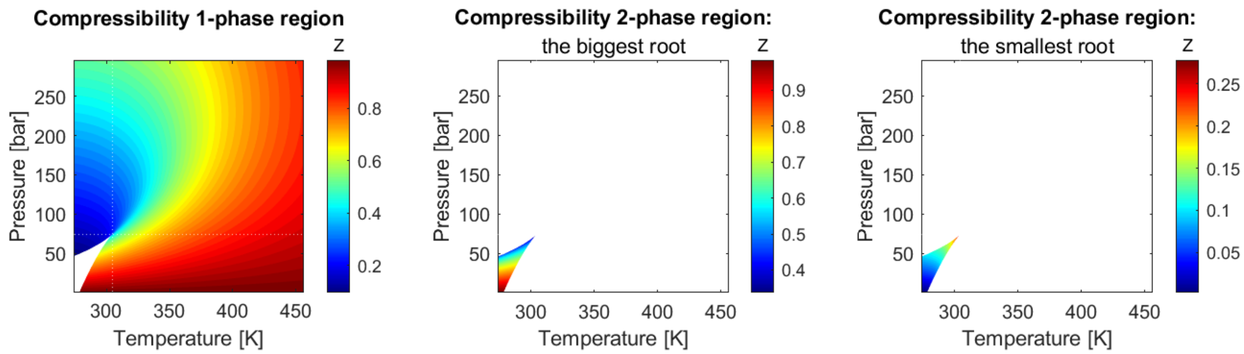
Figure 2c show the behaviour of the heat capacity of a supercritical fluid at constant pressure (C_p). The details of the calculations can be found in the appendix A.1.3. Contrary to the density, which varies monotonically, the specific heat shows very high levels in a narrow region. In the subcritical 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, which 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 (as discussed by Simeoni et al. [8] and Banuti [9]).

To determine the thermodynamic properties of a real gas, it is necessary to evaluate the departure function of the chosen equation of state for that property. As explained by Elliott [6], the departure function is the difference between the actual value of a thermodynamic property of a real gas and its value if the gas were ideal under the same temperature and pressure conditions. The ideal gas serves as a reference state to which the properties of real gases are compared. The departure function is a measure of the extent to which a real gas deviates from ideal gas behaviour. The departure functions allow for the accurate calculation of thermodynamic properties for real gases.

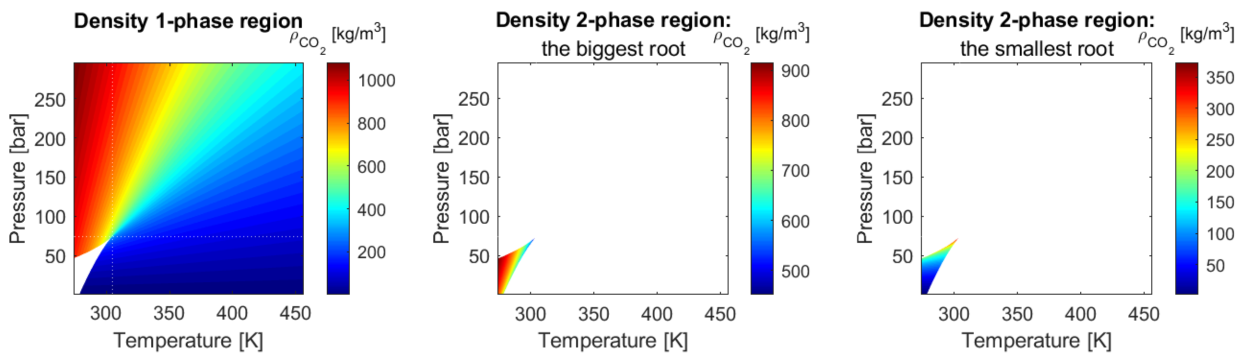
Transport properties such as viscosity and conductivity play a crucial role in engineering design for production, fluid transportation, and processing. However, as highlighted by Sheng et al. [10], developing a satisfactory theory for transport properties of real dense gases and liquids is a challenging task. This is due to the inherent difficulties involved in accurate measurements and the complexity involved in theoretical treatments.

To address this issue, the correlations of transport coefficients are either empirical or based on some theoretical foundation. Chapman-Enskog's theory (presented in Chapman and Cowling [13]) for transport properties of dense gases based on the distribution function is a popular theoretical approach. However, the Chapman-Enskog theory was developed for rigid spherical molecules and modifications are required to apply it to real gases. Many correlations have been proposed following the Chapman-Enskog theory in the form of reduced density and reduced temperature, such as those developed by Fenghour et al. [11] and Laesecke and Muzny [12] from the National Institute of Standards and Technology (NIST). A comparison of these correlations is presented in Figure 3.

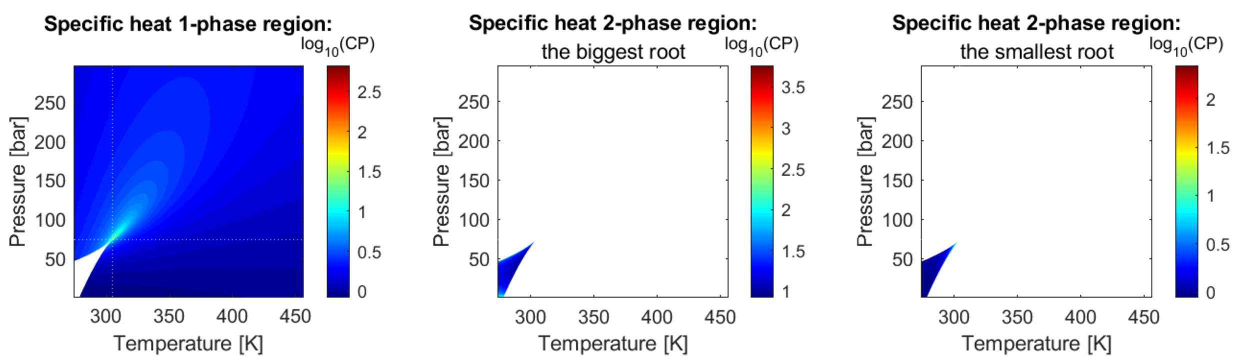
NIST has developed a viscosity formulation consisting of four contributions: (i) for the limit of zero density, (ii) for the initial density dependence, (iii) for the residual viscosity, and (iv) for the singularity of the viscosity at the critical point. The NIST correlation covers temperatures from 100 to 2000 K for gaseous CO_2, and from 220 to 700 K with



(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 2: Properties of CO_2 based on the equation of state

pressures along the melting line up to 8000 MPa for compressed and supercritical liquid states. These correlations and theories are essential in predicting transport properties for real gases and liquids and can assist in engineering design and analysis.

Similarly, several correlations for thermal conductivity of CO_2 were compared in Figure 4. The presented figures show regions around the critical point where the singularity is present. Similarities between specific heat and thermal conductivity can be observed. The NIST correlation (Huber et al. [14]) captures the singular behaviour of thermal conductivity around the critical point. The correlations are applicable for the temperature range from the triple point to 1100 K and pressures up to 200 MPa.

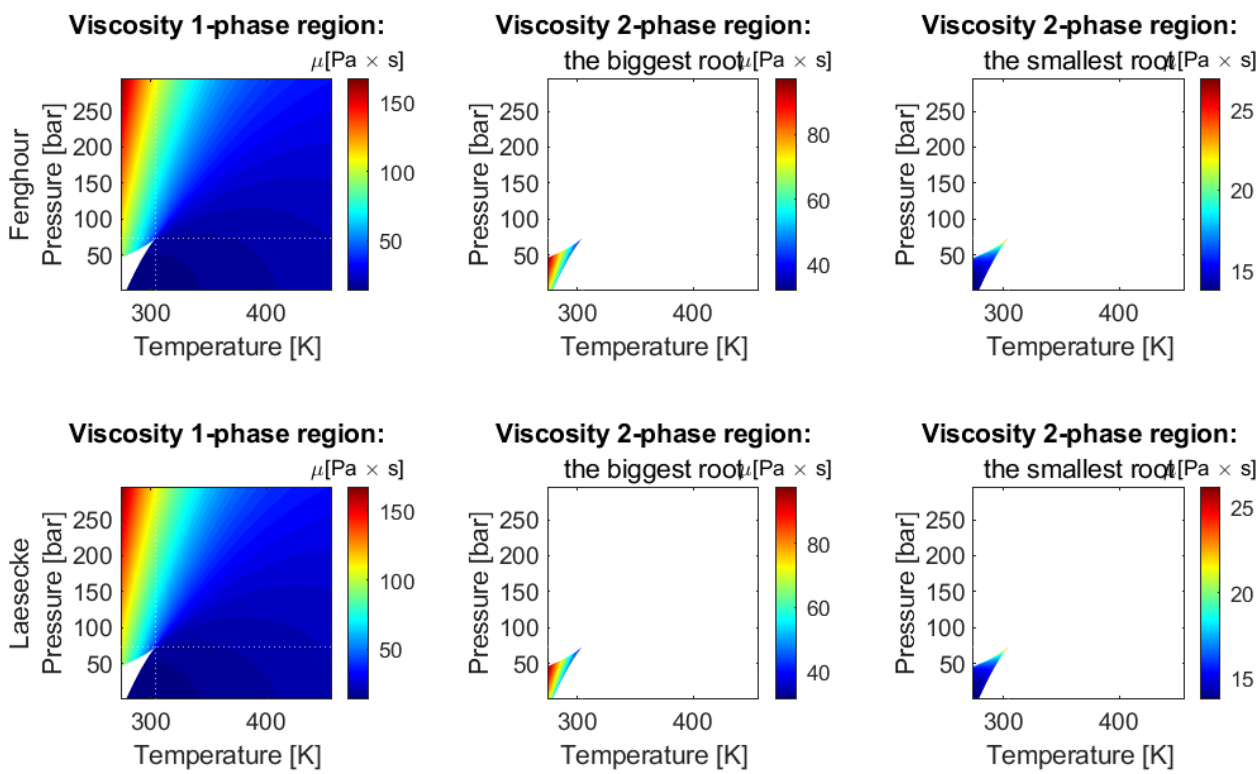


Figure 3: Viscosity obtained based on different correlations

2.2. Governing equations

The governing equation for a quasi-one-dimensional compressible flow in Cartesian coordinates can be found in the appendix A.2 and in the work of Anderson [15]. Quasi-one-dimensional flow is a type of fluid flow that is characterized by the assumption that the flow properties remain uniform across any given cross-section of the flow. This assumption is made when there is a variation in the cross-sectional area of the flow channel, such as a irregular shape or partial filling of an extractor. In such cases, the flow is considered to be quasi-one-dimensional because the velocity and other flow properties are assumed to vary only in the direction of flow.

The quasi-one-dimensional compressible Navier-Stokes equations in Cartesian coordinates are given by equations 3 to 5.

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

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

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

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.

Based on governing equations, the small discontinuity (defined as δ) in flow properties, shown on figure 5, can be analysed. The analysis follow the work of Schreier [16].

The discontinuity is presumed to be at rest relative and the balance equations become

$$\rho_f\delta v+v\delta\rho_f+\delta\rho_f\delta v=0$$
$$\delta P=\delta v\delta\rho_f$$

These relations are equally valid if the two regions are separated by a regions of finite width rather than a discontinuity.

$$\lim_{\rho_f v\to 0}\rho_f\delta v+v\delta\rho_f+\delta\rho_f\delta v=0/\delta\rho_f\rightarrow\frac{dv}{d\rho_f}=-\frac{v}{\rho_f}$$

By combining momentum equation with above equation we get

$$\frac{dv}{d\rho_f}=-\frac{dv}{dP}\frac{dP}{d\rho_f}=-\frac{1}{\rho v}\frac{dP}{d\rho_f}=-\frac{v}{\rho_f}$$

If the flow is presumed to be isentropic, $dP/d\rho=c^2$, so $v^2=c^2$, where c is the speed of sound. This can be interpreted that a small pressure wave propagates with the speed of sound relative to the flow.

2.3. Low Mach number expansion

As discussed by Lions [17], the low Mach number equations are a subset of the fully compressible equations of motion (continuity, momentum and energy). Such a

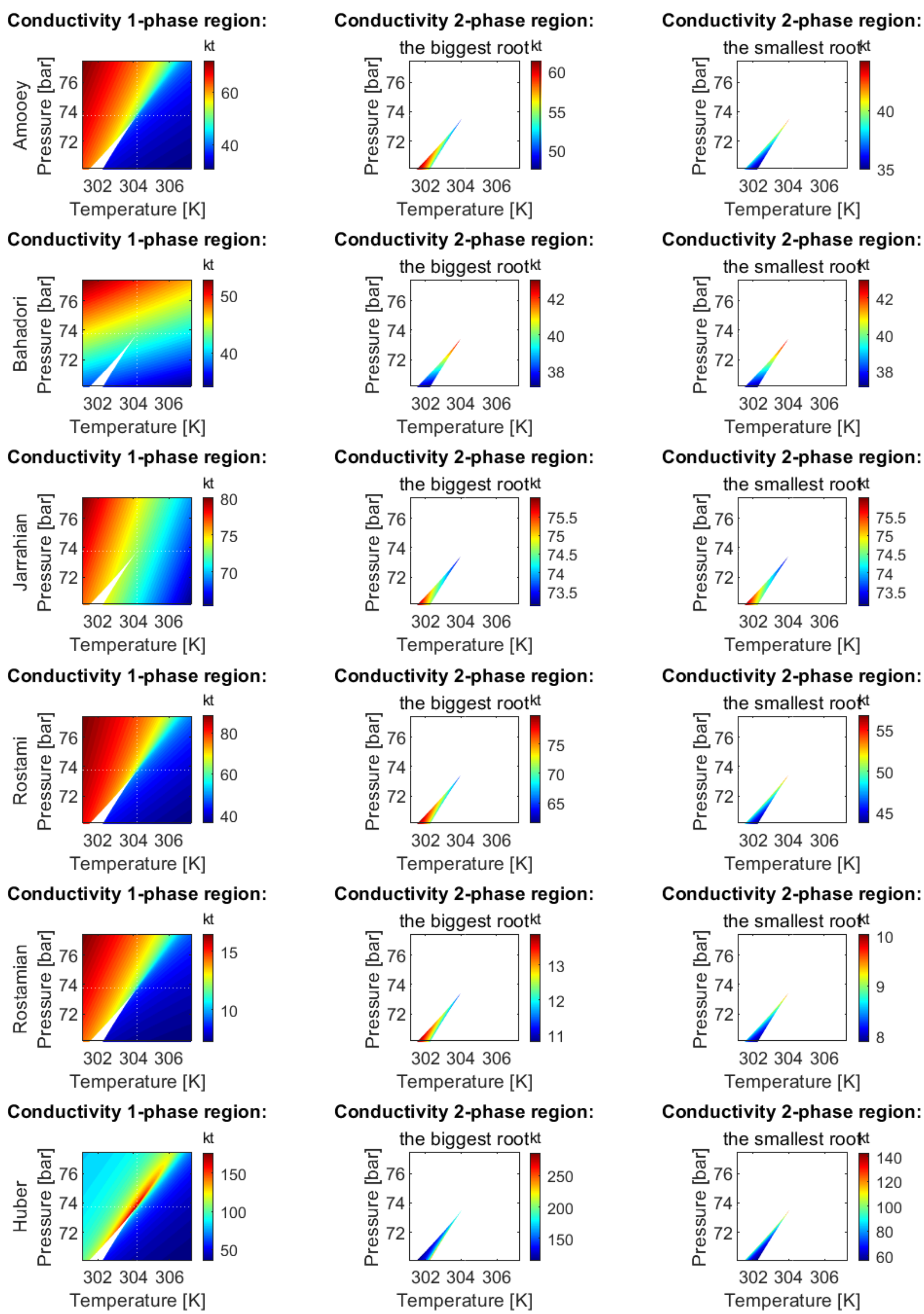


Figure 4: Thermal conductivity obtained based on different correlations

set of equations allow for large variations in gas density, but it is considered acoustically incompressible. Therefore, the low Mach number equations are preferred over the full compressible equations for low-speed flow problems $\left(M_a = \frac{|v|}{\sqrt{\partial P / \partial \rho_f}} \ll 1\right)$ to avoids the need to resolve fast-moving acoustic signals. The equations are derived from compressible equations based on the perturbation theory.

	ρ_f	$\rho_f + \delta\rho_f$	
$v \rightarrow$	P	$P + \delta P$	$v + \delta v \rightarrow$
	T	$T + \delta T$	

Figure 5: Small discontinuity in one-dimensional flow

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 3 to 4 describe the fully compressible equations of motion (respectively, the transport of mass, momentum and energy) for the quasi-one-dimensional case. We rescale the time variable, considering finally

$$\rho_\zeta = \rho\left(z, t/M_a\right), \quad v_\zeta = \frac{1}{\zeta} v\left(z, t/M_a\right)$$
$$T_\zeta = T\left(z, t/M_a\right), \quad k_\zeta = \zeta k(\rho_f, T)$$

The conservative non-dimensional equations of motion become

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

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 the square of the Mach number scales those terms. 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

$$P_\zeta = P_0 + P_1\zeta + P_2\zeta^2 + \mathcal{O}(\zeta^3)$$
$$\rho_\zeta = \rho_0 + \rho_1\zeta + \mathcal{O}(\zeta^2)$$
$$v_\zeta = v_0 + v_1\zeta + \mathcal{O}(\zeta^2)$$
$$T_\zeta = T_0 + T_1\zeta + \mathcal{O}(\zeta^2)$$
$$e_\zeta = e_0 + e_1\zeta + \mathcal{O}(\zeta^2)$$

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

$$\lim_{\zeta\to 0_+} \frac{\partial\left(\left(\rho_0 + \rho_1\zeta + \mathcal{O}(\zeta^2)\right) A_f\right)}{\partial t} + \\ + \frac{\partial\left(\left(\rho_0 + \rho_1\zeta + \mathcal{O}(\zeta^2)\right) A_f \left(v_0 + v_1\zeta + \mathcal{O}(\zeta^2)\right)\right)}{\partial z} = 0$$

The continuity equation becomes

$$\frac{\partial\left(\rho_0 A_f\right)}{\partial t} + \frac{\partial\left(\rho_0 A_f v_0\right)}{\partial z} = 0 \tag{6}$$

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 behaviour.

$$\lim_{\zeta\to 0_+} \frac{\partial\left(\left(\rho_0 + \rho_1\zeta + \mathcal{O}(\zeta^2)\right) A_f \left(v_0 + v_1\zeta + \mathcal{O}(\zeta^2)\right)\right)}{\partial t} + \\ + \frac{\partial\left(\left(\rho_0 + \rho_1\zeta + \mathcal{O}(\zeta^2)\right) A_f \left(v_0 + v_1\zeta + \mathcal{O}(\zeta^2)\right)\left(v_0 + v_1\zeta + \mathcal{O}(\zeta^2)\right)\right)}{\partial z} + \\ + A_f \frac{\partial}{\partial z}\left(\frac{P_0}{M_a^2} + \frac{P_1\zeta}{M_a^2} + \frac{P_2\zeta^2}{M_a^2} + \mathcal{O}(\zeta^3)\right)$$

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

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

The simplification of the P_0 in the momentum equation comes from the fact that P_0 is independent of z. As was presented above, the thermodynamical pressure moves with the speed of sound, and any perturbation propagates instantaneously. The term related to P_2 and higher order terms become zero at the limit of $M_a \to 0$. The momentum equation becomes

$$\frac{\partial\left(\rho_0 A_f v_0\right)}{\partial t} + \frac{\partial\left(\rho_0 v_0 A_f v_0\right)}{\partial z} + A_f \frac{\partial P_1}{\partial z} = 0$$

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

$$\lim_{\zeta\to 0_+} \frac{\partial\left(\left(\rho_0 + \rho_1\zeta + \mathcal{O}(\zeta^2)\right) A_f \left(e_0 + e_1\zeta + \mathcal{O}(\zeta^2)\right)\right)}{\partial t} + \\ + \frac{\partial\left(\left(\rho_0 + \rho_1\zeta + \mathcal{O}(\zeta^2)\right) A_f \left(v_0 + v_1\zeta + \mathcal{O}(\zeta^2)\right)\left(e_0 + e_1\zeta + \mathcal{O}(\zeta^2)\right)\right)}{\partial z} + \\ + \frac{\partial}{\partial z}\left(k\frac{\partial}{\partial z}\left(T_0 + T_1\zeta + \mathcal{O}(\zeta^2)\right)\right) + \\ - \left(P_0 + P_1\zeta + P_2\zeta^2 + \mathcal{O}(\zeta^3)\right)\frac{\partial\left(A_f\left(v_0 + v_1\zeta + \mathcal{O}(\zeta^2)\right)\right)}{\partial z} = 0$$

The form of the energy equation stays the same.

$$\frac{\partial\left(\rho_0 e_0 A_f\right)}{\partial t} + \frac{\partial\left(\rho_0 e_0 v_0 A_f\right)}{\partial z} - \frac{\partial}{\partial z}\left(k\frac{\partial T_0}{\partial z}\right) + P_0\frac{\partial\left(A_f v_0\right)}{\partial z} = 0$$

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:

$$\frac{\partial\left(\rho_f A_f\right)}{\partial t}+\frac{\partial\left(\rho_f A_f v\right)}{\partial z}=0$$
$$\frac{\partial\left(\rho_f A_f v\right)}{\partial t}+\frac{\partial\left(\rho_f v A_f v\right)}{\partial z}+A_f\frac{\partial P_1}{\partial z}=0$$
$$\frac{\partial\left(\rho_f e A_f\right)}{\partial t}+\frac{\partial\left(\rho_f e v A_f\right)}{\partial z}-\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right)+P_0\frac{\partial\left(A_f v\right)}{\partial z}=0$$

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

$$\rho A_f\left(\frac{\partial e}{\partial t}+v\frac{\partial e}{\partial z}\right)+e\underbrace{\left(\frac{\partial\left(\rho_f A_f\right)}{\partial t}+\frac{\partial\left(\rho_f v A_f\right)}{\partial z}\right)}_{Continutiy}-\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right)+P_0\frac{\partial\left(A_f v\right)}{\partial z}=0$$

The non-conservative form of the energy equation becomes

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

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

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

If an isothermal case is assumed, then the energy equation becomes

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

which leads to

$$\frac{\partial\left(A_f v\right)}{\partial z}=0 \tag{7}$$

In one-dimensional case, the equation 7 become equivalent of $\mathrm{div}(A_f v)=0$, which known as the incompressibility condition (Lions [17]).

As presented by Elliott [6], a general formulation of 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 $v_m=1/\rho_f$. 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

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

Assuming constant temperature and pressure along space and in time:

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

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

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

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

From the incompressibility conditions, we can deduce that

$$\frac{\partial\left(A_f v\right)}{\partial z}=0\rightarrow A_f\frac{\partial v}{\partial z}=-v\frac{\partial A_f}{\partial z}$$

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 superficial velocity $u_s=A_f v$

$$\int\frac{\rho_f v^2}{A_f}\frac{\partial A_f}{\partial z}dz=\int\frac{\rho_f v^2}{A_f}\frac{A_f^2}{A_f^2}\frac{\partial A_f}{\partial z}dz$$
$$=\rho_f u_s^2\int\frac{1}{A_f^3}\frac{\partial A_f}{\partial z}dz=-\frac{\rho_f u_s^2}{2\Delta A_f^2}=-\frac{\rho_f\Delta v^2}{2}$$
$$\int\frac{\partial\hat{P}}{\partial z}dz=\Delta\hat{P}$$

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

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

Bernoulli's principle can be used to find the hydrodynamic pressure caused by varying cross-sections at steady-state. Moreover, if the flow velocity is relatively low, 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 since they are both connected through the equation of state.

2.4. Extraction model

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 derived in Appendix A.2. When the cross-sectional area of the channel A_f is specified as a function of the void fraction $\phi(z)$ (where ϕ is the void fraction of the bed and A is the cross-section of the empty extractor), the continuity equation takes the form:

assign color to v and u

$$\frac{\partial(\rho_f(T(t,z),P(t))\phi)}{\partial t} + \frac{\partial(\rho_f(T(t,z),P(t))vA\phi)}{\partial z} = 0$$

Assuming that the mass flow rate is constant in time, the temporal derivative becomes zero, and the spatial derivative can be integrated along z as

$$\int \frac{\partial(\rho_f(T(t,z),P(t))vA\phi)}{\partial z} dz = 0 \rightarrow F = \rho_f(T(t,z),P(t))vA\phi \quad (8)$$

Here, F is a constant obtained from the integration and is understood as the mass flux per unit area, which is assumed to be constant along z. To simplify the dynamics of the system, it is assumed that $F = F(t)$ is a control variable and affects the whole system instantaneously. This assumption allows for finding the velocity profile that satisfies mass continuity based on $F(t)$, $\phi(z)$, and $\rho_f(T(t,z),P(t))$.

$$v = \frac{F(t)}{\rho_f(T(t,z),P(t))A\phi} \quad (9)$$

The fluid density $\rho_f(T(t,z),P(t))$ can be obtained from an equation of state if temperature and the thermodynamic pressure (assumed $P(t)$ to be constant along z due to the low-Mach number condition) are known. The variation in density may be caused by the fluid accumulation in the system (equivalent to pressure change), which occurs instantaneously along z or by a temperature change.

Analogously, the superficial velocity mught be introduced to the model and defined as

$$u = v\phi = \frac{F(t)}{\rho_f(T(t,z),P(t))A} \quad (10)$$

2.4.2. Mass balance for the fluid phase

The detailed derivation of the mass balance equation for the fluid phase can be found in the appendix (A.2). The movement of the mobile pseudo-homogeneous phase (equation 11) is considered only in the axial direction, while the properties of the system in the radial direction are assumed to be uniform. Additionally, the boundary layer adjacent to the inner wall of the extractor is neglected, resulting in a constant velocity profile across any cross-section of the extractor perpendicular to the axial direction. Although the particle size distribution and void fraction of the solid phase may change along the extractor, they are assumed to remain constant in time. Furthermore, the thermodynamic pressure is assumed to be constant along the device due to the Low-Mach number condition, as previously discussed. The amount of solute in the solvent is considered negligible, resulting in the fluid phase being described as pseudo-homogeneous, and its properties are assumed to be the same as the solvent. The mass balance equation for the fluid phase includes convection, diffusion, and kinetic terms.

$$\frac{\partial c_f(t,z)}{\partial t} + \frac{1}{\phi}\frac{\partial\left(c_f(t,z)u\right)}{\partial z} = \frac{1-\phi}{\phi} r_e(t,z) + \frac{1}{\phi}\frac{\partial}{\partial z}\left(D_e^M \frac{\partial c_f(t,z)}{\partial z}\right) \quad (11)$$

Here, $c_f(t,z)$, $c_s(t,z)$, and $T(t,z)$ represent the concentration of solute in the fluid phase, concentration of solute in the solid phase, and 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, $\rho_f(T(t,z),P(t))$ is the fluid density, ρ_s is the solids density, $D_e^M(T(t,z),P(t),F(t))$ is the axial mass diffusion coefficient, and u is the superficial velocity.

2.4.3. Mass balance for the solid phase

The solid phase is considered to be stationary, with negligible convection and diffusion terms in the mass balance equation (equation 12). Therefore, the only significant term in this equation is the kinetic term (as defined in equation 13), which connects the solid and fluid phases. The extract is represented by a single pseudo-component to simplify the analysis.

$$\frac{\partial c_s(t,z)}{\partial t} = \underbrace{r_e(t,z)}_{\text{Kinetics}} \quad (12)$$

2.4.4. Kinetic term

The kinetic term in this study is based on the two-film theory proposed by Reverchon [1] and the mass transfer kinetic is given by equation 13. This equation takes into account the overall diffusion coefficient and the concentration gradient, which acts as the driving force for the process.

As the solvent flows through the bed, CO_2 molecules diffuse into the pores and adsorb on the particle surface to form an external fluid film around the solid particles due to the solvent-solid matrix interactions. The effect of Knudsen diffusion is negligible in this process, as the mean free path of the molecule is much smaller than the pore diameter. The dissolved solute diffuses from the particle's core through the solid-fluid interface, the pore, and the film into the bulk. Figure 6 illustrates the mass transfer mechanism, where the mean solute concentration in the solid phase is denoted as c_s and the equilibrium concentrations at the solid-fluid interface are denoted 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 opening of the pore. The solute then diffuses through the film around the particle and reaches a concentration in the bulk c_f. The two-film theory describes the solid-fluid interface inside the pore. The overall mass transfer coefficient can be determined if the relation between the solute concentration in one phase and its equilibrium concentration is known.

Bulley et al. [18] 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 $r_e\left(c_f - c_P^*(c_s)\right)$.

On the other hand, Reverchon [1] proposes a driving force given by the difference between c_s and c_P^*. c_P^* is

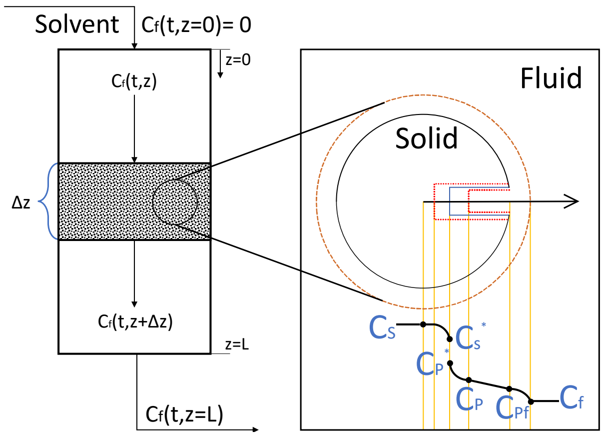


Figure 6: The extraction mechanism

determined by an equilibrium relationship with c_f and the extraction rate is $r_e\left(c_s - c_P^*(c_f)\right)$ or more precisely

$$r_e(t,z) = \frac{D_i(T(t,z),P(t))}{\mu l^2}\left(c_s(t,z) - c_P^*(t,z)\right) \tag{13}$$

where μ is sphericity, l a characteristic dimension of particles and can be defined as $l = r/3$, r is the mean particle radius, ρ_s is the solid density, $D_i(T(t,z))$ corresponds to the overall diffusion coefficient and $c_P^*(t,z)$ 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).

According to Bulley et al. [18], a linear equilibrium relationship (equation 14) 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 $c_s(t,z)$

$$c(t,z) = k_p(T(t,z),P(t))q^*(t,z) \tag{14}$$

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. According to Spiro and Kandiah [19], the term $k_p(T(t,z),P(t))$ can be expressed as the function of mass partition factor $k_m(T(t,z))$.

$$k_m(T(t,z)) = \frac{k_p(T(t,z),P(t))\rho_s}{\rho(T(t,z),P(t))} \tag{15}$$

Equation 16 represents of the kinetic term according to Reverchon [1]

$$r_e(t,z) = -\frac{D_i(T(t,z),P(t))}{\mu l^2}\left(c_s(t,z) - \frac{\rho_s}{k_m(T(t,z))\rho_f(T(t,z),P(t))}c_f(t,z)\right) \tag{16}$$

2.4.5. *Heat balance*

The heat equation was introduced in the previous chapter through equation 5 and in the appendix A.2

$$\frac{\partial\left(\rho_f(T(t,z),P(t))e(t,z)A_f\right)}{\partial t} + \frac{\partial\left(\rho_f(T(t,z),P(t))A_f v e(t,z)\right)}{\partial z} = -P(t)\frac{\left(A_f v\right)}{\partial z} + \frac{\partial}{\partial z}\left(\frac{\partial T(t,z)}{\partial z}\right) \tag{17}$$

Following Elliott [6] or Gmehling et al. [20], a real gases internal energy definition can be obtained from the departure functions:

$$de(t,z) = C_v dT - \left[P(t) - T(t,z)\left(\frac{\partial P(t)}{\partial T(t,z)}\right)_{v_m}\right]dv_m \tag{18}$$

where $e^{id}(t,z)$ is the internal energy of perfect gas.

If a gas is consider to be perfectly caloric ($e(t,z) = C_v T(t,z)$), then the energy equation can be written in form of temperature. The perfectly caloric gas can be seen as the special case of a real gas, where the second term of the equation 18 goes to zero.

For real gases it is complicated to write the heat balance in terms of temperature, but it be can used directly in the form of internal energy, as it is given by equation 5. In such a case, the temperature (which is used as the input to some other functions) needs to be recover from the internal energy. A relation for the internal energy can be obtained from an equation of state. For Peng-Robinson, such a relation is given by equation 19 as presented by Elliott [6].

$$\frac{e(t,z) - e^{id}(t,z)}{RT(t,z)} = -\frac{A}{B\sqrt{8}}\frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}}\ln\left[\frac{Z + \left(1+\sqrt{2}\right)B}{Z + \left(1+\sqrt{2}\right)B}\right] \tag{19}$$

To solve equation 19, values of temperature, pressure and density needs to be know. If an equation of state is introduce, then only two out three variables needs to be know as the third one can be calculated, this can be represented as follow

$$e(t,z) = e(T(t,z),P(t),\rho_f(T(t,z),P(t))) = e(T(t,z),P(t),\rho(T(t,z),P(t))) \tag{20}$$

If the value of internal energy $e(t,z)$ is know from time evolution of the energy equation (5), and pressure is know from measurement, then the temperature can be reconstructed. A rootfinder can be used to find a value of temperature, which minimize the difference between value of internal energy coming from the time evolution and the output from equation 19. Such a procedure allow to find local temperature along spatial direction z and needs to be repeated every time-step.

Another way to express the energy equation is to introduce enthalpy $h(t,z) = e(t,z) + P(t)/\rho$. By introducing the definition of enthalpy, the energy equation becomes

$$\frac{\partial\left(\rho_f(T(t,z),P(t))h(t,z)A_f\right)}{\partial t} - \frac{\partial\left(P(t)A_f\right)}{\partial t} + \frac{\partial\left(\rho_f(T(t,z),P(t))h(t,z)A_f v\right)}{\partial z} - \frac{\partial}{\partial z}\left(k\frac{\partial T(t,z)}{\partial z}\right) \tag{21}$$

The main advantage of this formulation is the presence of term $\partial P(t)/\partial t$, which allow to directly affect the system through the change of thermodynamic pressure (which is a control variable). If an equation of state is known, the temperature can to be recovered from the enthalpy. The enthalpy is related to the pressure and temperature through the following equation:

"For high pressures, the influence of the intermolecular forces on the enthalpy has to be taken into account, usually by applying a cubic equation of state. In most cases, these forces are attractive, so

$$h(t,z) = h(T(t,z),P(t),\rho_f(T(t,z),P(t))) = h(T(t,z),P(t),\rho(T(t,z),P(t)))$$

(22)

If the value of enthalpy is know from the time evolution and pressure can be measured, then the equation 22 can be solved for temperature to recover the temperature profile. By applying the departure functions to Peng-Robinson equation of state, the relation 22 can be expressed directly through equation 23 as presented in A.1.4 or given by Gmehling et al. [20].

$$h(t,z)-h(t,z)^{id} = RT(t,z)\left[T_r(Z-1) - 2.078(1+\kappa)\sqrt{\alpha}\ln\left(\frac{Z+2.414B}{Z-0.414B}\right)\right] \quad (23)$$

The equation 23 requires an reference sate, which in this case is assumed to be $T_{ref} = 298.15\ [K]$ and $P_{ref} = 1.01325\ [bar]$.

Add short section about boundary conditions and comment on the used numerical methods

Give reference for measurement function

2.4.6. Extraction yield

The efficiency of the process (the yield) is calculated according to equations 24 to 25, which evaluate 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.

$$y(t) = \int_{t_0}^{t_f} \frac{F(t)}{\rho_f(T(t,z), P(t))} c_f(t,z)\Big|_{z=L} dt \quad (24)$$

$$\frac{dy}{dt} = \frac{F(t)}{\rho_f(T(t,z), P(t))} c_f(t,z)\Big|_{z=L} \quad (25)$$

2.5. Parameter estimation

The goal of parameter estimation is to obtain the "best" estimate of parameter set θ (which is a subset of the parameter space Θ containing all parameters of a model) based on the continuous observations $Y(t)$ or the discrete observations $Y(t_i)$. Conceptually, the unobservable error $\epsilon(t)$ is added to the deterministic model output, $y(t)$ (equation 24), to give the observable dependent variable $Y(t)$ (for example results of an experiments). For discrete observations, this can be expressed as:

$$Y(t_i) = y(\theta, t_i) + \epsilon(t_i)$$

For continuous variables, the equation is:

$$Y(t) = y(\theta, t) + \epsilon(t)$$

However, obtaining analytical solutions for a deterministic process model can be challenging, so experiments are often conducted where the vector of derivatives $dY(t_i)/dt$ is measured instead of $Y(t_i)$ itself. In such cases, it is assumed that the unobservable error is added to the deterministic derivative $dy(\theta, t_i)/dt$ (as shown in equation 25) as follows:

$$\frac{dY(t_i)}{dt} = \frac{dy(\theta, t_i)}{dt} + \epsilon(t_i)$$

In the case where the error in the first observation is denoted as ϵ_1, the error in the second observation ϵ_2' incorporates ϵ_1 as well as an independent random component, given by $\epsilon_2' = \epsilon_1 + \epsilon_2$. Similarly, the error in the third observation is $\epsilon_3' = \epsilon_1 + \epsilon_2 + \epsilon_3$, and so on. Mandel [21] made a distinction between the typically assumed independent measurement error in the dependent variable and a "cumulative" or interval error, in which each new observation encompasses the error of the previous ones. Cumulative errors arise from fluctuations in the process itself due to small variations in operating conditions and are not independent; only the differences in measurement from one period to the next are independent.

2.5.1. Least squares estimation

In statistics, least squares parameter estimation is a method used to estimate the parameters of a linear regression model. One of the benefits of this method is that it does not require any prior knowledge about the distribution of unobservable errors. Additionally, it yields unbiased estimates and results in the minimum variance among all linear unbiased estimators.

If the model responses, represented by Y, are continuous functions of time from $t = 0$ to $t = t_f$, the Markov criterion, also known as "rigorous least squares," is used to minimize the integral squared error γ. This is achieved by minimizing the following expression:

$$\gamma = \frac{1}{2}\int_0^{t_f} \left[Y(t) - y(\theta,t)\right]^T \Gamma^{-1} \left[Y(t) - y(\theta,t)\right] dt \quad (26)$$

$$\hat{\theta} = \arg\min_{\theta\in\Theta} \gamma \quad (27)$$

Here, Γ represents the covariance matrix or a matrix of appropriate weights, $\hat{\theta}$ is the parameter estimate, Θ is the parameter space, and γ is the time-integrated value of the error squared.

Alternatively, if the observations are made at discrete time intervals t_i, where $i = 1, 2, \dots, n$, the Markov criterion is to minimize the sum of squared errors, which is given by:

$$\gamma = \frac{1}{2}\sum_{i=1}^{n} \left[Y(t_i) - y(\theta,t_i)\right]^T \Gamma^{-1} \left[Y(t_i) - y(\theta,t_i)\right] \quad (28)$$

$$\hat{\theta} = \arg\min_{\theta\in\Theta} \gamma \quad (29)$$

The parameter estimate, $\hat{\theta}$, is obtained by minimizing γ over the parameter space Θ.

If the covariance matrix, Γ, is a diagonal matrix, the Markov criterion becomes a "weighted least squares" criterion. If $\Gamma = \sigma^2\mathbf{I}$, where σ is a standard deviation and $\mathbf{I}$ is the identity matrix, the Markov criterion becomes the "ordinary least squares" criterion.

2.5.2. Maximum likelihood estimation

Maximum likelihood estimation (MLE) is a method of estimating the parameters of an assumed probability distribution, given some observed data. This is achieved by maximizing a likelihood function so that, under the assumed statistical model, the observed data is most probable. The MLE has the desirable characteristics of asymptotic efficiency and normality. Each time it has been associated with the (joint) normal distribution because of mathematical convenience. Consider the joint probability density function (the likelihood function) $p\left(\theta | y(t_1), y(t_2), ..., y(t_n)\right)$ for parameter θ. If a maximum of this function over all choices of θ can be found, the estimates so obtained are maximum likelihood estimates. The conditions at the maximum can be evolved incorporating prior information as follows.

The posterior probability density $p(\theta|y)$ can be expressed as the ratio of two probability densities if we make use of the analogue for continuous variables of Equation 110:

$$p\left(\theta|y(t_n),...,y(t_1)\right) = \frac{p\left(\theta, y(t_n),...,y(t_1)\right)}{p\left(y(t_n),...,y(t_1)\right)} \tag{30}$$

Notation is a bit unclear

The numerator of the right-hand side od Equation 30 using Equation 111a becomes

$$\begin{aligned} p\left(\theta, y(t_n),...,y(t_1)\right) &= p\left(y(t_n)|\theta, y(t_{n-1}),...,y(t_1)\right) \\ &\cdot p\left(\theta, y(t_{n-1}),...,y(t_1)\right) \end{aligned} \tag{31}$$

These operations can be continued repetitively until we get

$$p\left(\theta, y(t_n),...,y(t_1)\right) = p(\theta)\prod_{i=1}^{n} p\left(y(t_i)|\theta, y(t_{i-1}),...,y(t_1)\right) \tag{32}$$

Examination of Equation **??** shows that $Y(t_i)$ depends only on t_i, θ and $\epsilon(t_i)$ and is not conditioned by any previous measurement. Consequently, we can write

$$p\left(y(t_i)|\theta, y(t_{i-1}),...,y(t_1)\right) = p\left(y(t_i)|\theta\right) \tag{33}$$

provided Equation **??** is observed as a constraint. The desired joint conditional probability function is thus

$$p\left(\theta|y(t_n),...,y(t_1)\right) = \frac{p(\theta)\prod_{i=1}^{n} p\left(y(t_i)|\theta\right)}{p\left(y(t_n),...,y(t_1)\right)} \tag{34}$$

We can get rid of the evidence term $p\left(y(t_n),...,y(t_1)\right)$ because it's constant with respect to the maximization. Moreover, if we are lacking a prior distribution over the quantity we want to estimate, then $p(\theta)$ can be omitted. In such a case:

$$p\left(\theta|y(t_n),...,y(t_1)\right) = \prod_{i=1}^{n} p\left(y(t_i)|\theta\right) = \prod_{i=1}^{n} L\left(\theta|y(t_i)\right) \tag{35}$$

By collecting a values of y and selecting the values of θ that maximize the likelihood function $L(\theta|y)$, a function described in chapter A.3 in connection with Bayes' theorem. Such estimators, $\hat{\theta}$, are known as maximum likelihood estimators. In effect, the methods selects those values of θ that are at least as likely to generate the observed sample as any other set of values of the parameters if the probability density of y were to be extensively simulated through use of the probability density $p(y|\theta)$. In making a maximum likelihood estimate, we assume the form of the probability density and that all possible values of θ are equally likely before experimentation.

Is the reference it previous chapter needed?

Needed?

The likelihood function for the parameters based on several observations is the product of the individual functions if the observations are independent.

$$\begin{aligned} L\left(\theta|y(t_n),...,y(t_1)\right) &= \prod_{i=1}^{n} L\left(\theta|y(t_i)\right) \\ &= p\left(y(t_1)|\theta\right) p\left(y(t_2)|\theta\right) ...p\left(y(t_n)|\theta\right) \end{aligned} \tag{36}$$

In choosing as estimates of θ the values that maximize L for the given values $\left(y(t_i)\right)$, it turns out that it is more convenient to work with the ln L than with L itself:

$$\ln L = \ln p\left(y(t_1)|\theta\right) + \ln p\left(y(t_2)|\theta\right) + ... + \ln p\left(y(t_n)|\theta\right) = \sum_{i=1}^{n} \ln p\left(y(t_i);\theta\right) \tag{37}$$

By assuming that the conditional distribution of $\bar{Y}_i$, given y_i, is normal, then we form the likelihood function based on the probability density:

$$\begin{aligned} p\left(\theta, \sigma|y(t_n),...,y(t_1)\right) &= \prod_{i=1}^{n} \frac{1}{\sqrt{2\pi\sigma}} \exp\left[\frac{1}{2\sigma}\left(Y(t_i) - y(\theta, t_i)\right)^2\right] \\ L\left(\theta, \sigma|y(t_n),...,y(t_1)\right) &= \prod_{i=1}^{n} \frac{1}{\sqrt{2\pi\sigma}} \exp\left[\frac{1}{2\sigma}\left(Y(t_i) - y(\theta, t_i)\right)^2\right] \end{aligned} \tag{38}$$

where σ is the variance

By taking the natural logarithm of the Equation 38, the final form of the objective function can be obtained:

$$\ln L = -\frac{n}{2}\left(\ln\sqrt{2\pi} + \ln\sigma^2\right) - \frac{\sum_{i=1}^{n}\left[Y(t_i) - y(\theta, t_i)\right]^2}{2\sigma^2} \tag{39}$$

The parameter estimation problem can be formulated as follow:

$$\begin{aligned} \hat{\theta}_{MLE} \quad &= \arg\max_{\sigma,\theta\in\Theta} \ln L = \arg\max_{\sigma,\theta\in\Theta} p(\theta|y) \\ \text{subject to} \quad & \dot{x} = f(t, x, \theta) \\ & \dot{\theta} = 0 \\ & y = y(x) \end{aligned} \tag{40}$$

x has not been defined

Based on the first order optimality condition, the ln L can be maximized with respect to the vector θ by equating to zero the partial derivatives of ln L with respect to each of the parameters:

$$\frac{\partial \ln L}{\partial\theta} = \frac{\partial \sum_{i=1}^{n} \ln p\left(y(t_i)|\theta\right)}{\partial\theta} = 0 \tag{41}$$

Solution of Equations 41 yield the desired estimates $\hat{\theta}$. For some models, these equations can be explicitly solved for $\hat{\theta}$ but in general no closed-form solution to the maximization problem is known or available, and an MLE can only be found via numerical optimization.

2.6. Experimental work

The close the optimization problem given by set of equations 40, it is require to know the dataset $Y(t)$. In this case, the dataset have been obtained by performing extraction of caraway oil from caraway seeds. The caraway seeds have been obtained from the company Caraway Finland during 2022 growing season. The caraway seeds have been pre-treated with Retsch SM 300 cutting mill to decrease the particle size to 1mm and break the outer shell of the seeds. Later, the moisture content was analysed to ensure that it does not have a negative effect on the extraction process. An Infrared Moisture Analyser was used to investigate the sample. The moisture content after grinding was 4.83%. The grind material density was measured by pyncometery and its result can be found in appendix A.5

Should be mentioned?

The unit used for the experimental work is 10 litre extractor with inner diameter around 15 cm and 60 cm height . Four experiments have been performed in that unit at following operating conditions: 40°C/200 bar, 50°C/200 bar, 40°C/300 bar and 50°C/300 bar. 1 kg of grind material

Should Biorukki be mentioned?

Double check dimension

Time min	$40°C/200$ bar Mass g	$50°C/200$ bar Mass g	$40°C/300$ bar Mass g	$50°C/300$ bar Mass g
0	0.0	0.0	0.0	0.0
5	1.7	1.8	1.1	1.2
10	5.7	4.7	4.7	4.5
15	10.9	9.5	10.8	11.3
20	17.8	15.1	20.6	20.6
25	24.9	21.3	32.1	30.6
30	30.3	26.4	40.5	37.8
35	34.0	29.8	46.7	43.3
40	37.5	33.1	50.5	47.5
45	40.1	35.6	53.1	50.8
50	43.3	38.7	55.5	53.7
55	45.5	41.5	57.6	56.5
60	47.6	43.5	59.3	58.1
65	49.2	45.9	60.9	59.6
70	50.8	48.3	62.2	61.1
75	52.6	50.8	63.7	62.7
80	54.2	52.9	64.9	64.4
85	55.1	55.3	66.6	65.8
90	56.2	57.2	67.6	66.7
95	57.3	58.3	68.9	67.4
100	58.3	59.4	69.7	68.2
105	59.4	60.4	70.6	69.1
110	60.2	61.6	71.2	70.1
115	61.4	62.7	71.9	70.9
120	62.5	63.9	72.3	71.6
125	63.3	64.7	72.8	72.3
130	64.0	65.4	73.2	72.9
135	64.8	65.9	73.6	73.5
140	65.5	66.4	74	74
145	66.2	67.1	74.3	74.5
150	66.8	67.7	74.6	74.9

Table 1
Yield data

was weighted and placed in the extraction chamber. Due to some technical limitations, the amount of solid material fro extraction was selected to be 1 kg per batch, which is not sufficient to fill the whole chamber.

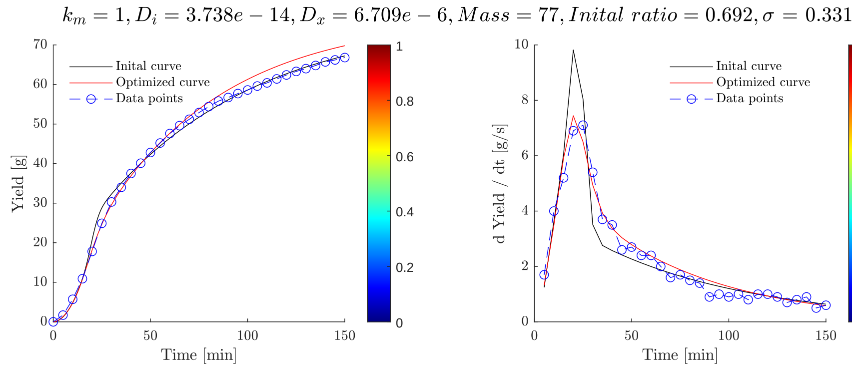
After the material was loaded into chamber, the extractor is pre-heated to desired temperature. The next step is to close the outlet line coming out of the extractor and fill the extraction chamber with CO_2. The CO_2 is pumped and compressed until the operating pressure is achieved. When the operating temperature and pressure are obtained, the outlet in is open to allow the solvent flow through the system. The solvent extract essential oils from the fixed bed of solid material and the mixture CO_2-oil flow from the extractor to separator. The separator was operating at $50°C$ and 50 bar. At this condition the CO_2 is gasified and leave from the top, while oil stays in the liquid form and it is collected at the bottom of separator. Every 5 minutes, the oil is drained from the separator and its weight is measured. The amount of oil collect during a batch is an output of the experiment and it is used as data for parameter estimation. The extraction time for each batch was 150 minutes, counted from the opening of the extractor outlet port.

The result of the experiment are presented in the table 1.

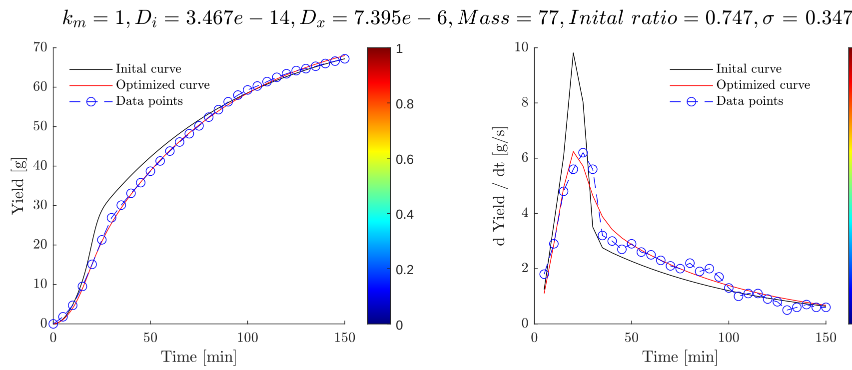
3. Results

Some results of the parameter estimations

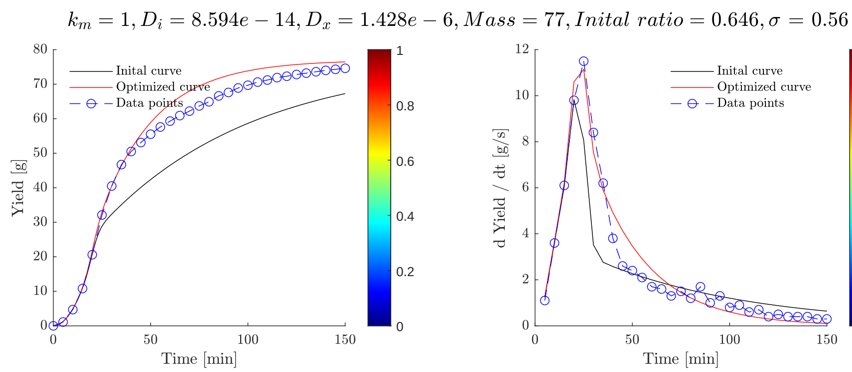
4. Conclusions



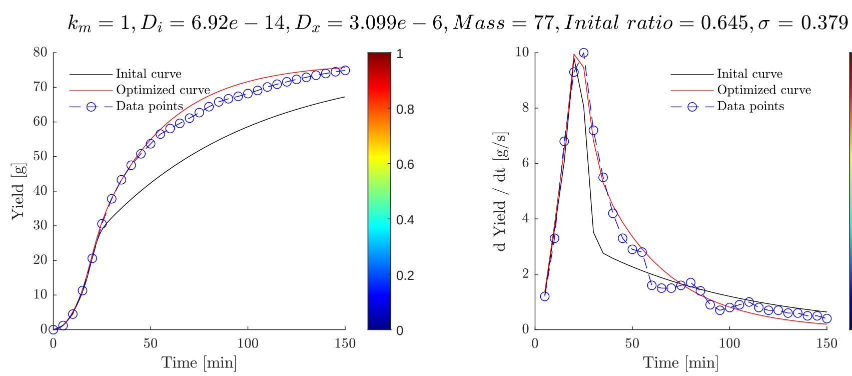
(a) Experiment at 40°C and 200 bar



(b) Experiment at 50°C and 200 bar

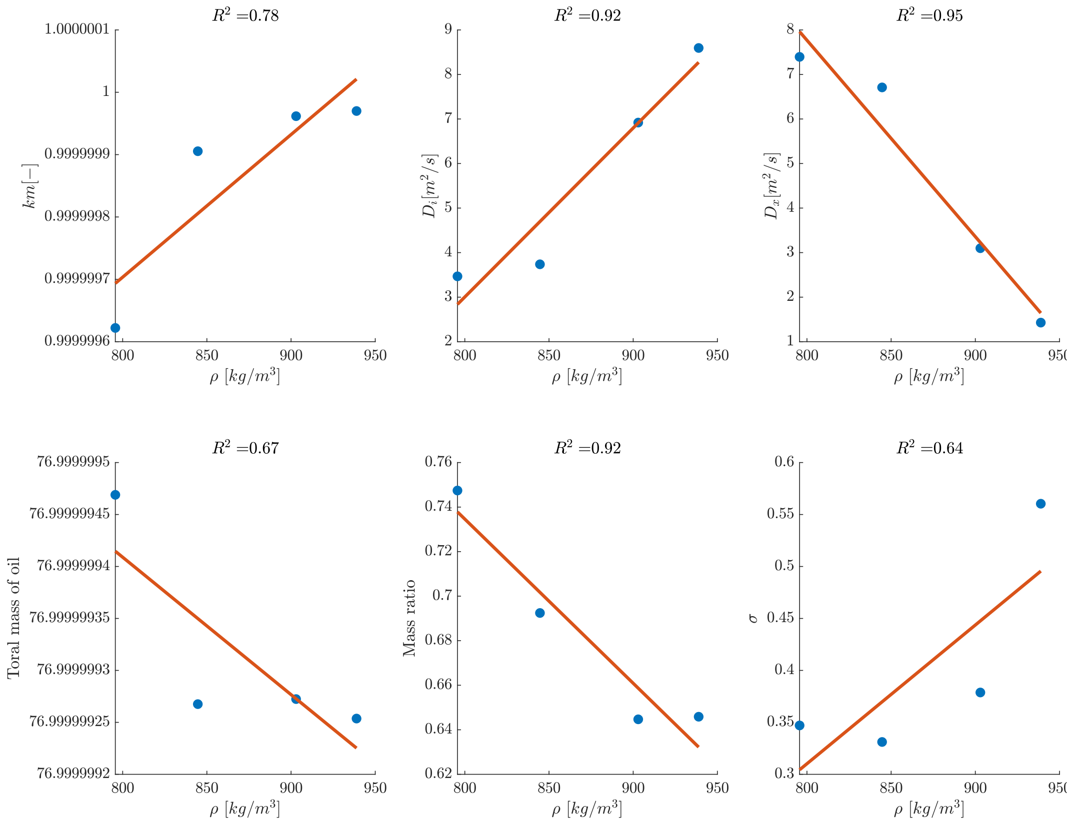


(c) Experiment at 40°C and 300 bar

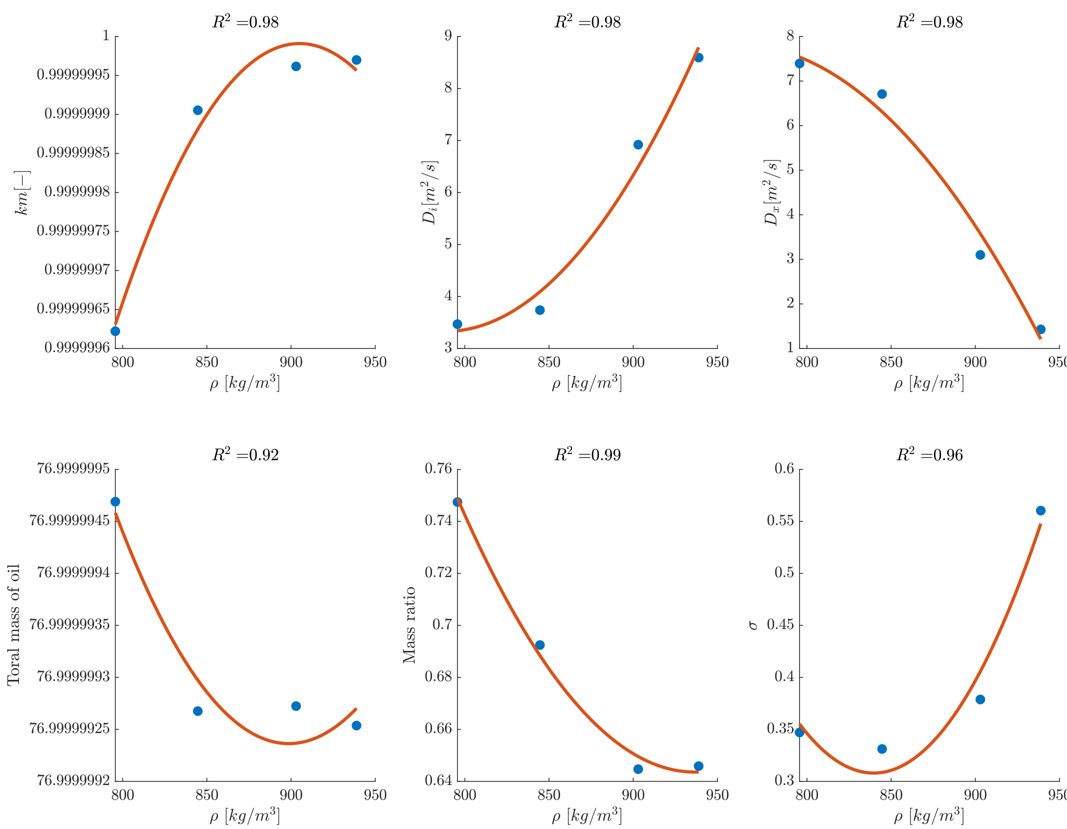


(d) Experiment at 50°C and 300 bar

Figure 7: Results of parameter fitting, with estimation of the initial state



(a) First order polynomial regression of fitted parameters as a function of fluid density ρ_f



(b) Second order polynomial regression of fitted parameters as a function of fluid density ρ_f

Figure 8: Results of parameter fitting, with estimation of the initial state

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A. Appendix

A.1. Thermodynamic

A.1.1. *Equation of state and properties of the fluid phase*

We consider equations of state in the general form $P(t)v_m[T(t,z),P(t)] = ZRT(t,z)$, where v_m denotes the molar volume of CO_2, Z represents its compressibility factor, and R is the universal gas constant. More specifically, we are interested in these equations because of the possibility to express the compressibility Z as an explicit function of temperature and pressure. This is the case when Z is obtained as one of the physically meaningful roots of a polynomial equation, like the Peng-Robinson's and stuff with REFS to equations of state.

In Peng-Robinson's equation, the compressibility $\overline{Z}[T(t,z),P(t)]$ solves the third-order polynomial equation

reference to Cardano formula

$$\begin{aligned} &Z^3 - [1 - B[T(t,z),P(t)]]Z^2 \\ &+ \left[A[T(t,z),P(t)] - 2B[T(t,z),P(t)] - 3B[T(t,z),P(t)]^2\right]Z = 0 \end{aligned} \tag{42}$$

where $A[T(t,z),P(t)]$ and $B[T(t,z),P(t)]$ are functions of time and space defined on the attraction parameter, $a[T(t,z)] = a^c_{CO_2}\alpha[T(t,z)]$ with $a^c_{CO_2} \approx 0.45724 R^2 {T^c_{CO_2}}^2 / P^c_{CO_2}$, and the repulsion parameter, $b_{CO_2} \approx 0.07780 RT^c_{CO_2}/P^c_{CO_2}$, both functions of the critical temperature $T^c_{CO_2}$ and pressure $P^c_{CO_2}$. Specifically, we have

$$A[T(t,z),P(t)] = \frac{\alpha[T(t,z)]\, a^c_{CO_2} P(t)}{R^2 T^2(t,z)}; \tag{43a}$$

$$B[T(t,z),P(t)] = \frac{b_{CO_2} P(t)}{RT(t,z)}. \tag{43b}$$

The quantity $\alpha[T(t,z)] = \left[1 + \kappa_{CO_2}\left[1 - \sqrt{T(t,z)/T^c_{CO_2}}\right]\right]^2$, with constant $\kappa_{CO_2} = 0.37464 + 1.54226\omega_{CO_2} - 0.26992{\omega_{CO_2}}^2$, is a dimensionless correction term defined on the acentric factor $\omega_{CO_2} = 0.239$ of CO_2 molecules.

By denoting the physical constants as $\varphi_Z = \left(R, T^c_{CO_2}, P^c_{CO_2}, \kappa_{CO_2}\right)$, we obtain a spatio-temporal representation of the compressibility $\overline{Z}\left[T(t,z),P(t) \mid \varphi_Z\right]$ with its complete set of functional dependencies and parameters.

A.1.2. *Density of the fluid phase*

The density ρ_F of the fluid phase is assumed to be equal to the density of solvent, at given temperature and pressure. Because temperature $T(t,z)$ of the fluid phase is a modelled variable, we allow for the density to vary along the bed and in time. From an equation of state of the form $P(t)v_m[T(t,z),P(t)] = ZRT(t,z)$, we get

$$\rho_F\left[T(t,z),P(t) \mid \varphi_{\rho_F}\right] = \frac{P(t)M_{CO_2}}{RT(t,z)\overline{Z}\left[T(t,z),P(t) \mid \varphi_Z\right]}, \tag{44}$$

where M_{CO_2} denotes the molar mass of CO_2 and $\overline{Z}[T(t,z),P(t)]$ is the compressibility factor that solves Eq. (42). The density of the fluid is thus a function of space and time, due to its dependence on temperature and pressure, and it is expressed in terms of the set of physical constants $\varphi_{\rho_F} = \left(R, M_{CO_2}, T^c_{CO_2}, P^c_{CO_2}, \omega_{CO_2}\right)$.

A.1.3. *Heat capacity of the fluid phase*

The specific heat C^F_p can be calculated from the equation of state, again under the assumption that the fluid phase consists of pure carbon dioxide and that the specific heat of real fluids can be calculated from an ideal contribution plus a residual term REF. In the following, we report only the main steps in the derivation of $C^{CO_2}_p[T(t,z),P(t)]$: Step-by-step derivations using the Peng-Robinson's equation are given.

Add step-by-step derivation

At given temperature and pressure, for CO_2 we have

$$C^{CO_2}_v[T(t,z),P(t)] = C^I_v[T(t,z),P(t)] + C^R_v[T(t,z),P(t)]; \tag{45a}$$

$$C^{CO_2}_p[T(t,z),P(t)] = \underbrace{C^I_p[T(t,z),P(t)]}_{\text{Eq. (46)}} + \underbrace{C^R_p[T(t,z),P(t)]}_{\text{Eq. (47)}}. \tag{45b}$$

$C^{CO_2}_v[T(t,z),P(t)]$ and $C^{CO_2}_p[T(t,z),P(t)]$ are the specific heat of CO_2 at constant volume and pressure, respectively. $C^I_v[T(t,z),P(t)]$ and $C^I_p[T(t,z),P(t)]$, with $C^I_p(T(t,z)) - C^I_v(T(t,z)) = R$, are the specific heat of an ideal gas at constant volume and pressure. $C^R_v[T(t,z),P(t)]$ and $C^R_p(T(t,z),P(t))$ are the correction terms.

Add REF

For CO_2 (), we have the ideal gas contribution to the specific heat at constant $P(t)$, as function of $T(t,z)$,

$$C^I_p[T(t,z),P(t)] = C_{P0} + C_{P1}T(t,z) + C_{P2}T^2(t,z) + C_{P3}T^3(t,z) \tag{46}$$

where the coefficients of the expansion are $C_{P0} = 4.728$, $C_{P1} = 1.75 \times 10^{-3}$, $C_{P2} = -1.34 \times 10^{-5}$, and $C_{P3} = 4.10 \times 10^{-9}$. For the correction term $C^R_p[T(t,z)P(t)]$ at constant pressure $P(t)$, we have

$$\begin{aligned} C^R_p[T(t,z),P(t)] = &\underbrace{C^R_v[T(t,z),P(t)]}_{\text{Eq. (51)}} \\ &+ T(t,z)\underbrace{\left(\frac{\partial P(t)}{\partial T}\right)_{v_m(t,z)}}_{\text{Eq. (50)}}\underbrace{\left(\frac{\partial v_m[T(t,z),P(t)]}{\partial T}\right)_{P(t)}}_{\text{Eq. (48)}} - R. \end{aligned} \tag{47}$$

The braced terms are obtained from the chosen equation of state $P(t)V[T(t,z),P(t)] = Z[T(t,z),P(t)]RT(t,z)$.

For the partial derivative of the volume with respect to temperature T at constant pressure $P(t)$, we have

$$\left(\frac{\partial v_m[T(t,z),P(t)]}{\partial T}\right)_{P(t)} = \frac{Z[T(t,z),P(t)]R}{P(t)} + \frac{RT(t,z)}{P(t)}\underbrace{\left(\frac{\partial Z[T(t,z),P(t)]}{\partial T}\right)_{P(t)}}_{\text{Eq. (49)}} \tag{48}$$

with partial derivative of the compressibility factor with respect to temperature T at constant pressure $P(t)$

$$\left(\frac{\partial Z\left[T(t,z), P(t)\right]}{\partial T}\right)_{P(t)} = \left(\frac{\partial \dfrac{P(t) v_m\left[T(t,z), P(t)\right]}{RT(t,z)}}{\partial T}\right)_{P(t)} \tag{49}$$

Similarly, for the partial derivative of the pressure with respect to temperature at constant volume, we have

$$\left(\frac{\partial P(t)}{\partial T}\right)_{v_m(t,z)} = \left(\frac{\partial \dfrac{Z\,RT(t,z)}{v_m\left[T(t,z), P(t)\right]}}{\partial T}\right)_{V(t,z)} \tag{50}$$

The residual specific heat at constant volume is obtained, by definition, by using the residual internal energy

$$C_v^{\mathrm{R}}\left[T(t,z), P(t)\right] = \left(\frac{\partial U^{\mathrm{R}}\left[T(t,z), P(t)\right]}{\partial T}\right)_{V(t,z)}. \tag{51}$$

By denoting the physical constants as $\varphi_{C_p^{\mathrm{F}}} = \left(R, M_{\mathrm{CO_2}}, T^c_{\mathrm{CO_2}}, P^c_{\mathrm{CO_2}}, \omega_{\mathrm{CO_2}}\right)$, we get the spatio-temporal representation $C_p^{\mathrm{F}}\left[T(t,z), P(t) \mid \varphi_{C_p^{\mathrm{F}}}\right]$ of the specific heat of the fluid phase.

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A.1.4. Departure functions for enthalpy calculations

In thermodynamics, a departure function is defined for any thermodynamic property as the difference between the property as computed for an ideal gas and the property of the species as it exists in the real world, for a specified temperature T and pressure P. Common departure functions include those for enthalpy, entropy, and internal energy.

Departure functions are used to calculate real fluid extensive properties (i.e. properties which are computed as a difference between two states). A departure function gives the difference between the real state, at a finite volume or non-zero pressure and temperature, and the ideal state, usually at zero pressure or infinite volume and temperature.

For example, to evaluate enthalpy change between two points $h(V_1, T_1)$ and $h(V_2, T_2)$ we first compute the enthalpy departure function between volume V_1 and infinite volume at $T = T_1$, then add to that the ideal gas enthalpy change due to the temperature change from T_1 to T_2, then subtract the departure function value between V_2 and infinite volume.

Departure functions are computed by integrating a function which depends on an equation of state and its derivative. The general form the enthalpy equation is given by

$$\frac{h^{id} - h}{RT} = \int_{v_m}^{\infty}\left[T\left(\frac{\partial Z}{\partial T}\right)_{v_m}\right]\frac{dv_m}{v_m} + 1 - Z \tag{52}$$

The Peng–Robinson equation of state relates the three interdependent state properties pressure P, temperature T, and molar volume v_m. From the state properties (P, v_m, T), one may compute the departure function for enthalpy per mole (denoted h) as presented by Gmehling et al. [20] or Elliott [6]:

$$h - h^{\mathrm{id}} = RT\left[T_r(Z-1) - 2.078(1+\kappa)\sqrt{\alpha}\ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right)\right] \tag{53}$$

A.2. Governing equations

A.2.1. Mass continuity

Following the work of Anderson [15], the governing equations for compressible fluid with non-uniform cross-section can be obtained. Let's assume that any properties of the flow are uniform across any given cross-section of an extractor. The variation of the cross-section might be an result of partial filling of an extractor or its irregular shape. In reality, such a flow is two-dimensional, because with the area changing as a function of z, in actuality there will be flow-field variations in both directions. The assumption of quasi-one-dimensional flow dictates that the flow properties are function of z only. The equations described by quasi-one-dimensional assumption hold: (1) mass conservation, (2) Newton's second law, and (3) energy conservation. To ensure that these physical principles are satisfied the modified governing equation can be derived. Let's start with the integral form of the continuity equation:

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f} \rho_f\, d\mathcal{V}_f + \iint_S \rho_f \mathbf{V}\cdot\mathbf{dS} = 0 \tag{54}$$

We apply this equation to the shaded control volume shown in Fig. 9.

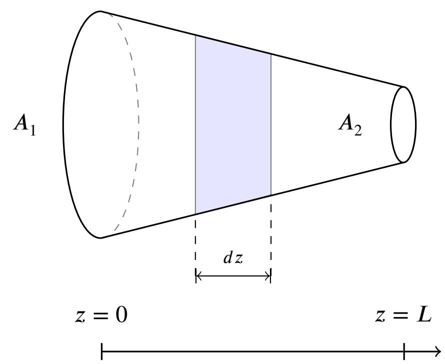

Figure 9: Control volume for deriving partial differential equation for unsteady, quasi-one-dimensional flow

This control volume is a slice of an extractor, where the infinitesimal thickens of the slice is dz. On the left side of the control volume, consistent with the quasi-one-dimensional assumptions, the density, velocity, pressure and internal energy denoted by ρ_f, V, P, and e, respectively, are uniform over the are A. Similarly, on the right side of the control volume, the density, velocity, pressure, and internal energy $\rho_f + d\rho_f$, $V + dV$, $P + dP$, and $e + de$, respectively, are uniform over the area available for fluid phase $A_f + dA_f$. Applied to the control volume in Fig. 9, the volume integral in Eq. 54 becomes, in the limit as dz becomes very small,

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f} \rho_f\, d\mathcal{V}_f = \frac{\partial}{\partial t}\left(\rho_f A_f dz\right) \tag{55}$$

where $A\,dz$ is the volume of the control volume in the limit of dz becoming vanishingly small. The surface integral in Eq. 54 becomes

$$\iint_S \rho_f \mathbf{V}\cdot\mathbf{dS} = -\rho_f V A_f + (\rho_f + d\rho_f)(V + dV)(A_f + dA_f) \tag{56}$$

where the minus sign on the leading term on the right-hand side is due to the vectors $\mathbf{V}$ and $\mathbf{dS}$ pointing in opposite directions over the left of the control volume, and hence the dot product is negative. Expending the triple product term

$$\iint_S \rho_f \mathbf{V}\cdot\mathbf{dS} = -\rho_f V A_f + \rho_f V A_f + \rho_f V dA_f + \rho_f A_f dV$$

$$+\rho_f dV dA_f + VA_f d\rho_f + Vd\rho_f dA + A_f d\rho_f dV + d\rho_f dV dA_f \tag{57}$$

In the limit as dz becomes very small, the terms involving products of the differential in Eq. 57, sych as $\rho_f dV dA_f$, $d\rho_f dV dA_f$, go to zero much faster than those terms involving only one differential. Hence, all terms involving products of differentials can be dropped, yielding in the limit as dz becomes very small

$$\iint_S \rho_f \mathbf{V}\cdot \mathbf{dS} = \rho_f V dA_f + \rho_f A_f dV + VA_f d\rho_f \tag{58}$$

Substituting Eqs. 55 and 58 into 54, we have

$$\frac{\partial\left(\rho_f A_f\right)}{\partial t} + \frac{\partial\left(\rho_f A_f V\right)}{\partial z} = 0 \tag{59}$$

Above partial differential equation form of the continuity equation suitable for unsteady, quasi-one-dimensional flow. It ensures that mass is conserved for this mode of the flow. The $A_f(z)$ is an arbitrary function, which describe change of the cross-section of an extractor. The function $A_f(z)$ can be defined as $A_f(z) = \mathbf{A}\phi(z)$, where ϕ is the bed porosity and $\mathbf{A}$ is the cross-section of an empty extractor.

$$\frac{\partial\left(\rho_f \mathbf{A}\phi(z)\right)}{\partial t} + \frac{\partial\left(\rho_f \mathbf{A}\phi(z) V\right)}{\partial z} = 0 \tag{60}$$

The equation can be simplified by cancel out a constant $\mathbf{A}$

$$\frac{\partial\left(\rho_f \phi(z)\right)}{\partial t} + \frac{\partial\left(\rho_f \phi(z) V\right)}{\partial z} = 0 \tag{61}$$

If so called superficial velocity is defined $u = \phi V$, the mass continuity becomes

$$\frac{\partial\left(\rho_f \phi(z)\right)}{\partial t} + \frac{\partial\left(\rho_f u\right)}{\partial z} = 0 \tag{62}$$

A.2.2. Transport of a species

The transport of a chemical species, in this case a solute, can be described by analogous equation to the Eq. 54 with additional terms on the right-hand side. The first term on the right-hand side describes that a substance goes from high density regions to low density regions and is based on the Fick's law $\left(J_{diff} = D_e^M \frac{\partial c_f}{\partial z}\right)$. The other term correspond for the mass transfer between solid and fluid phases, which is treated as a source term.

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f} c_f d\mathcal{V}_f + \iint_S c_f \mathbf{V}\cdot\mathbf{dS} = \iint_S J_{diff}\cdot\mathbf{n}\,\mathbf{dS} + \frac{\partial}{\partial t}\iiint_{\mathcal{V}_s} c_s d\mathcal{V}_s \tag{63}$$

Similarly to the continuity equation, in the limit as dz becomes very small

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f} c_f d\mathcal{V}_f = \frac{\partial}{\partial t}\left(c_f A_f dz\right) \tag{64}$$

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_s} c_s d\mathcal{V}_s = \frac{\partial}{\partial t}\left(c_s A_s dz\right) \tag{65}$$

The surface integrals in the limit of dz becomes

$$\iint_S c_f \mathbf{V}\cdot\mathbf{dS} = c_f V dA_f + c_f A_f dV + VA_f dc_f \tag{66}$$

From the Divergence theorem in multi-variable calculus, we have

$$\iint_S J_{diff}\cdot\mathbf{n}\,\mathbf{dS} = \iiint_{\mathcal{V}_f} \nabla J_{diff} dV_f = \nabla \iiint_{\mathcal{V}_f} J_{diff} dV_f = \nabla\left(J_{diff} A_f dz\right) \tag{67}$$

By substituting the equations derived above into Eq. 63 we obtain

$$\frac{\partial\left(c_f A_f\right)}{\partial t} + \frac{\partial\left(c_f A_f V\right)}{\partial z} = \frac{\partial\left(c_s A_s\right)}{\partial t} + \frac{\partial\left(J_{diff} A_f\right)}{\partial z} \tag{68}$$

By defining $A_f = A\cdot\phi$, $A_s = A\cdot(1-\phi)$ and $u = V\cdot\phi$, and assuming that A is constant, the above equation becomes

$$\frac{\partial\left(c_f\phi\right)}{\partial t} + \frac{\partial\left(c_f u\right)}{\partial z} = \frac{\partial\left(c_s(1-\phi)\right)}{\partial t} + \frac{\partial\left(J_{diff}\phi\right)}{\partial z} \tag{69}$$

By assuming that $\frac{\partial\phi}{\partial t} = 0$ and expanding J_{diff}, we get

$$\frac{\partial c_f}{\partial t} + \frac{1}{\phi}\frac{\partial\left(c_f u\right)}{\partial z} = \frac{(1-\phi)}{\phi}\frac{\partial c_s}{\partial t} + \frac{1}{\phi}\frac{\partial}{\partial z}\left(D_e^M\frac{\partial c_f}{\partial z}\right) \tag{70}$$

The equation can be further simplified if $\frac{\partial u}{\partial z} = \frac{\partial\phi}{\partial z} = D_e^M = 0$, which corresponds to the assumptions of constant velocity along the bed(which might be a case of isothermal and low-mach number flow), constant porosity(which comes from the assumption of constant area for both solid and fluid phase) and no radial diffusion.

$$\frac{\partial c_f}{\partial t} + \frac{u}{\phi}\frac{\partial c_f}{\partial z} = \frac{1-\phi}{\phi}\frac{\partial c_s}{\partial t} \tag{71}$$

The Eq. 71 is equivalent to the equation presented by Reverchon [1].

A.2.3. Momentum conservation

Similarly to the mass conservation, the momentum conservation is derived for inviscid fluid with no body forces

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f}\left(\rho_f V_z\right) d\mathcal{V}_f + \iint_S\left(\rho_f V_z \mathbf{V}\right)\mathbf{dS} = \iint_S (PdS)_z \tag{72}$$

where V_z is the z component of the velocity.

We the momentum conservation to the shaded control volume in Fig. 9, the integrals on the left side are evaluated in the same manner as discussed above in the regard to the continuity equation. That is,

$$\frac{\partial}{\partial t}\iiint_{\mathcal{V}_f}\left(\rho_f V_z\right) d\mathcal{V}_f = \frac{\partial}{\partial t}\left(\rho_f V A_f dz\right) \tag{73}$$

equation

and

$$\iint_S\left(\rho_f V_z \mathbf{V}\right) dS = -\rho_f V^2 + \left(\rho_f + d\rho_f\right)(V+dV)^2 (A+dA) \tag{74}$$

The evaluation of the pressure force term on the right side of Eq. 72 can be understood based on the Fig. 10. Here, the z components of the vector PdS are shown on all four side of the control volume. Remember that $\mathbf{dS}$ is assumed to points away from the control volume; hence any z component $(PdS)_z$ that acts toward the left (in the negative z direction) is a negative quantity, and any z component that acts toward the right (in the positive z direction) is a positive quantity. Also note that the z component of $P\mathbf{dS}$ acting on the top and the bottom inclined faces of the control volume in Fig. 10 can be expressed as the pressure P acting on the component of the inclined are projected perpendicular to the

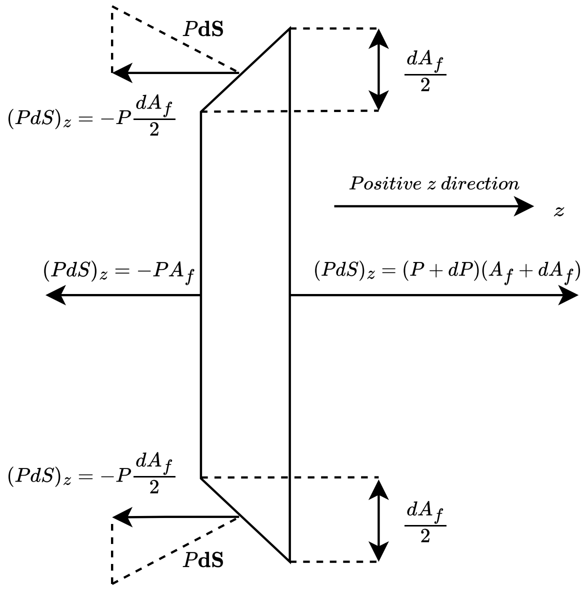

Figure 10: The forces in the z direction acting on the control volume

z direction, $dA_f/2$; hence, the contribution of each inclined face (top or bottom) to the pressure integral in Eq. 72 is $-P(dA_f/2)$. All together, the right-hand side of Eq. 72 is expressed as follows:

$$\iint (PdS)_z = -PA_f + (P+dP)(A+dA_f) - 2P\frac{dA_f}{2} \tag{75}$$

Substituting Eqs. 73 to 75 into Eq. 72, we have

$$\begin{aligned}&\frac{\partial}{\partial t}\left(\rho_f V A_f dz\right) - \rho_f V^2 A_f + (\rho_f + d\rho_f)(V+dV)^2(A_f+dA_f)\\ &= PA_f - (P+dP)(A+dA_f) + PdA_f\end{aligned} \tag{76}$$

Cancelling like terms and ignoring products of differentials, equation above becomes in the limit dz becoming very small

$$\frac{\partial}{\partial t}\left(\rho_f V A_f dz\right) + d\left(\rho_f V^2 A_f\right) = -AdP \tag{77}$$

Dividing above equation by dz and taking the limit as dz goes to zero, we obtain

$$\frac{\partial\left(\rho_f V A_f\right)}{\partial t} + \frac{\partial\left(\rho_f V^2 A_f\right)}{\partial z} = -A_f\frac{\partial P}{\partial z} \tag{78}$$

The Eq. 78 can be expanded further by assuming that $A_f = \mathbf{A}\phi$

$$\frac{\partial\left(\rho_f V \mathbf{A}\phi\right)}{\partial t} + \frac{\partial\left(\rho_f V^2 \mathbf{A}\phi\right)}{\partial z} = -\mathbf{A}\phi\frac{\partial P}{\partial t} \tag{79}$$

The equation can be further simplified by assuming that the cross-section of an extractor $\mathbf{A}$ is constant and cancel out

$$\frac{\partial\left(\rho_f V \phi\right)}{\partial t} + \frac{\partial\left(\rho_f V^2 \phi\right)}{\partial z} = -\phi\frac{\partial P}{\partial t} \tag{80}$$

If the superficial velocity $u = \phi V$ is introduced, then the momentum conservation becomes

$$\frac{\partial\left(\rho_f u\right)}{\partial z} + \frac{\partial\left(\rho_f u^2/\phi\right)}{\partial z} = -\phi\frac{\partial P}{\partial z} \tag{81}$$

Eq. 78 represents the conservative form of the momentum equation for the quasi-one-dimensional flow. The equivalent non-conservative form can be obtained by multiplying the continuity equation by V and subtracting it from Eq. 78

$$\frac{\partial\left(\rho_f V A_f\right)}{\partial t} - V\frac{\partial\left(\rho_f A_f\right)}{\partial t} + \frac{\left(\rho_f V^2 A_f\right)}{\partial z} - V\frac{\left(\rho_f V A_f\right)}{\partial z} = -A_f\frac{\partial P}{\partial z} \tag{82}$$

Expanding the derivatives on the left-hand size of above equation and cancelling like terms, gives

$$\rho_f A_f\frac{\partial V}{\partial t} + \rho_f A_f V\frac{\partial V}{\partial z} = -A_f\frac{\partial P}{\partial z} \tag{83}$$

Dividing above equation by A_f the non-conservative form of the momentum can be obtained

$$\rho_f\frac{\partial V}{\partial t} + \rho_f V\frac{\partial V}{\partial z} = -\frac{\partial P}{\partial z} \tag{84}$$

The Eq. 84 is stylistically the same as the general momentum conservation for one-dimensional flow with no-body forces. The momentum equation can be expressed in terms of superficial velocity $u = V\phi$.

$$\rho_f\frac{\partial\left(u/\phi\right)}{\partial t} + \rho_f\frac{u}{\phi}\frac{\partial\left(u/\phi\right)}{\partial z} = -\frac{\partial P}{\partial z} \tag{85}$$

By expanding all the terms of equation above, we get

$$\frac{\rho_f}{\phi}\frac{\partial u}{\partial t} + \rho_f u\frac{\partial\phi^{-1}}{\partial t} + \rho_f\frac{u}{\phi}\frac{1}{\phi}\frac{\partial u}{\partial z} + \rho_f\frac{u}{\phi}u\frac{\partial\phi^{-1}}{\partial z} = -\frac{\partial P}{\partial z} \tag{86}$$

If the bed is not compressible and doesn't change its properties during the batch, then $\dfrac{\partial\phi}{\partial t} = 0$

$$\frac{\rho_f}{\phi}\left(\frac{\partial u}{\partial t} + \frac{u}{\phi}\frac{\partial u}{\partial z} + u^2\frac{\partial\phi^{-1}}{\partial z}\right) = -\frac{\partial P}{\partial z} \tag{87}$$

If the porosity is constant along an extractor, then the momentum conservation equation becomes

$$\frac{\rho_f}{\phi}\left(\frac{\partial u}{\partial t} + \frac{u}{\phi}\frac{\partial u}{\partial z}\right) = -\frac{\partial P}{\partial z} \tag{88}$$

The Eq. 88 represents non-conservative form of the momentum equation for quasi-one-dimensional flow with no body forces and constant porosity.

A.2.4. Energy conservation

Let's consider the integral form of the energy equation for adiabatic flow with no body forces and no viscous effects

$$\frac{\partial}{\partial}\iiint_{\mathcal{V}_f}\rho_f\left(e_f + \frac{V^2}{2}\right)d\mathcal{V}_f + \iint_S\rho_f\left(e_f + \frac{V^2}{2}\right)\mathbf{V}\cdot\mathbf{dS} = -\iint_S(P\mathbf{V})\cdot\mathbf{dS} \tag{89}$$

Applied to the shaded control volume in Fig. 9, and keeping in mind the pressure forces shown in Fig. 10, Eq. 89 becomes

$$\begin{aligned}&\frac{\partial}{\partial t}\left[\rho_f\left(e_f + \frac{V^2}{2}\right)A_f dz\right] - \rho_f\left(e_f + \frac{V^2}{2}\right)VA_f\\ &+ \left(\rho_f + d\rho_f\right)\left[e_f + de_f + \frac{(V+dV)^2}{2}\right](V+fV)\left(A_f + dA_f\right)\\ &= -\left[-PVA_f + (P+dP)(V+dV)\left(A_f+dA_f\right) - 2\left(PV\frac{dA_f}{2}\right)\right]\end{aligned} \tag{90}$$

Neglecting products of differential and cancelling like terms, the above equation becomes

$$\frac{\partial}{\partial t}\left[\rho_f\left(e_f+\frac{V^2}{2}\right)A_f dz\right]+d\left(\rho_f r_f A_f\right)+\frac{\left(\rho_f V^3 A_f\right)}{2}=-d\left(PA_f V\right) \tag{91}$$

or

$$\frac{\partial}{\partial t}\left[\rho_f\left(e_f+\frac{V^2}{2}\right)A_f dz\right]+d\left[\rho_f\left(e_f\frac{V^2}{2}\right)VA_f\right]=-d\left(PA_f V\right) \tag{92}$$

Taking the limit as dz approaches zero, the equation above becomes the following partial differential equation

$$\frac{\partial\left[\rho_f\left(e_f+V^2/2\right)A\right]}{\partial t}+\frac{\partial\rho_f\left(e_f+V^2/2\right)VA_f}{\partial z}=-\frac{\partial\left(PA_f V\right)}{\partial z} \tag{93}$$

Equation 93 is the conservation form of the energy expressed in terms of the total energy $e+V^2/2$, appropriate for unsteady, quasi-one-dimensional flow. The energy equation can be expressed in terms of internal energy if Eq. 78 is multiplicated by V and then subtracted from Eq. 93

$$\frac{\partial\left(\rho_f e_f A_f\right)}{\partial t}+\frac{\partial\left(\rho_f e_f VA_f\right)}{\partial z}=-P\frac{\partial A_f V}{\partial z} \tag{94}$$

The equation above is the conservation form of the energy equation expressed in terms of internal energy e_f suitable for quasi-one-dimensional flow. The non-conservative for is then obtained by multiplying the continuity equation 59, by e_f and substructing it from 94, yielding

$$\rho_f A_f\frac{\partial e_f}{\partial t}+\rho_f A_f V\frac{\partial e_f}{\partial z}=-P\frac{\partial(A_f V)}{\partial z} \tag{95}$$

Expanding right-hand side and dividing by A_f, the above equation becomes

$$\rho_f\frac{\partial e_f}{\partial t}+\rho_f V\frac{\partial e_f}{\partial z}=-P\frac{V}{A_f}\frac{\partial A_f}{\partial z} \tag{96}$$

or

$$\rho_f\frac{\partial e_f}{\partial t}+\rho_f V\frac{\partial e_f}{\partial z}=-P\frac{\partial V}{\partial z}-PV\frac{\partial(ln\ A_f)}{\partial z} \tag{97}$$

Equation 97 is the non-conservative for of the energy equation expressed in therms of internal energy, appropriate to unsteady quasi-one-dimensional flow. The reason for obtaining the energy equation in the form of Eq. 97 is that, for a calorically perfect gas, it leads directly to a form of the energy equation in therms of temperature T. For calorically perfect gas $e_f = C_v T$

$$\frac{\partial\left(\rho_f e_f A_f\right)}{\partial t}+\frac{\partial\left(\rho_f e_f VA_f\right)}{\partial z}=-P\frac{\partial A_f V}{\partial z}+\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right) \tag{98}$$

A.3. Bayes theorem

As discussed by Himmelblau [22], the Bayesian approach to estimation make use of prior information. Such prior knowledge can come from theoretical considerations, from the results of previous experiments, or from assumptions by the experimenter. Typically, a Bayesian approach assumes a prior probability distribution of an unknown parameter θ in some parameter space $\boldsymbol{\theta}$. The distribution is updated by using Bayes' rule to obtain the posterior probability distribution.

Consider a set of events or outcomes, $A_1, A_2, ..., A_n$, and some other event B. Bayes' theorem states that the probability that event A_i will occur, given that event B has already occured, which will denoted by $P\{A_i|B\}$, is equal to the product of the probability that A_i will occur regardless of whether B will take place and the probability that B will occur, given that A_i has already taken place, divided by the probability of the occurrence of B:

$$P\{A_i|B\}=\frac{P\{B|A_i\}P\{A_i\}}{P\{B\}} \tag{99}$$

Further, if all events comprising the set $\{A_i\}$ are included in $A_1, A_2, ..., A_n$, then

$$P\{A_i|B\}=\frac{P\{B|A_i\}P\{A_i\}}{\sum_{i=1}^{n}P\{B|A_i\}P\{A_i\}} \tag{100}$$

We can interpret these symbols as follows:

1. $P\{A_i\}$ is a measure of our degree of belief that event A_i will occur or that hypothesis A_i is true prior to the acquisition of additional evidence that may alter the measure. $P\{A_i\}$ is denoted the *prior probability*.

2. $P\{A_i|B\}$ is a measure of our degree of belief that event A_i will occur or that hypothesis A_i is true, given additional evidence B pertinent to the hypothesis. $P\{A_i|B\}$ is termed the *posterior probability*.

3. $P\{B|A_i\}$ denotes the likelihood that event B will occur, given that event A_i is true. $P\{B|A_i\}$ is a conditional probability, interpreted in the Bayesian framework as a likelihood, $L(A_i|B)$.

For continuous variable, Bayes' theorem can be more conveniently expressed in terms of the probability density function rather than the probabilities themselves. Equation 100 can be expressed in terms of a set of observed values of the random variable X, the experimental data $\mathbf{x}$ and unknown parameter θ as

$$p(\theta|X=\mathbf{x})=p(\theta|\mathbf{x})=\frac{L(\theta|\mathbf{x})\,p(\theta)}{\int_{-\infty}^{+\infty}L(\theta|\mathbf{x})\,p(\theta)d\theta} \tag{101}$$

where

$p(\theta|\mathbf{x}) =$ the posterior probability density function for θ; it includes knowledge of the possible values of θ gained from the experimental data $\mathbf{x}$

$p(\theta) =$ the prior probability density function for θ (before the experiment in which $\mathbf{x}$ was observed)

$L(\theta|\mathbf{x}) = p(\mathbf{x}|\theta) =$ the probability density function termed the likelihood function of θ given $\mathbf{x}$

The denominator in Equation 101 is a normalizing factor chosen so that the integration of the posterior distribution is unit, i.e., $\int_{-\infty}^{+\infty}p(\theta|\mathbf{x})=1$. By taking into account the law of total probability, the denominator can be written as

$$\int_{-\infty}^{+\infty}p(\mathbf{x}|\theta)\,p(\theta)d\theta=p(\mathbf{x}) \tag{102}$$

If the prior distribution is a uniform distribution, that is the prior distribution is a constant, the Equation 101 reduces to

$$p(\theta|\mathbf{x}) = \frac{L(\theta|\mathbf{x})}{\int_{-\infty}^{+\infty} L(\theta|\mathbf{x})\, d\theta} \tag{103}$$

If the prior knowledge concerning a postulated event or hypothesis is poor, the posterior probability is largely or entirely determined by the likelihood function, that is, by the additional accumulated evidence for which the likelihood function acts as a mathematical expression. If prior knowledge outweighs recent evidence, however, then the posterior probability is determined almost solely by the prior probability.

In the application of tests and the design of experiments, certain definitions and rules concerning probability are needed and are listed below.

1. It follows from the frequency theory of probability that: $0 \leq P \leq 1$

2. If the probability of occurrence of one event A depends on whether or not event B has occurred, the two events are termed *dependent*; if the probability of occurrence of event A does not depend on the occurrence of B, or the reverse, the two events are *independent*.

3. **Addition Rule** If $A_1, A_2, ..., A_n$ are mutually exclusive events, i.e., cannot occur at the same time, the probability of occurrence of just one of the events is equal to the sum of the probabilities of each A_i:

$$P\left(A_1 \text{or } A_2 ... \text{or } A_n\right) = \sum_{i=1}^{n} P\left(A_i\right) \tag{104}$$

Very often we let

$$\sum_{i=1}^{n} P\left(A_i\right) = 1 \tag{105}$$

Also, if each event is equi-probable so that $P(A_i) = q$,

$$\sum_{i=1}^{n} q = nq = 1 \qquad \text{or} \qquad q = \frac{1}{n} = P\left(A_i\right) \tag{106}$$

In set theory, mutually exclusive event have no points in common. The union of the sets which represents the set of all elements that belong to

$$P\left(A_1 \cup A_2 \cup ... \cup A_n\right) = P(A_1) + P(A_2) + ... + P(A_n) \tag{107}$$

4. **Multiplication Rule** If A and B are *independent* event

$$P(A \text{ and } B) = P(A)P(B) \tag{108}$$

In set theory the intersection of A and B is the set of all elements that belong to A and B:

$$P(A \cap B) = P(A)P(B) \tag{109}$$

If the A and B are *dependet* events,

$$P(A|B) = \frac{P(A \cap B)}{P(B)} \tag{110}$$

where the symbol $P(A|B)$ means "probability of A given B". As a corollary,

$$P(A \cap B) = P(B)P(A|B) \tag{111a}$$

$$= P(A)P(B|A) \tag{111b}$$

Two kind of probabilities enter Equation 111a (or Equation 111b): the absolute probability of event B (or A) irrespective of whether or not A (or B) has occurred, and that the conditional probability of event A (or B) computed on the assumption that B (or B) has occurred. Equation 109 or 110 is special case of Equation 111a or 111b, because if the event are independent $P(A|B) = P(A)$. For the case of many event, Equation 109 can be expanded to

$$P(A_1 \text{ and } A_2 \text{ and } ... \text{ and } A_n) = P(A_1) \cdot P(A_2) \cdot ... \cdot P(A_n) = \prod_{i=1}^{n} P(A_i) \tag{112}$$

5. Another useful relationship for event which are not mutually exclusive is

$$P(A) + P(B) - P(A \cap B) = P(A \cup B) \tag{113}$$

A.4. Cardano's Formula

Following the work of Gmehling et al. [20], a cubic equation of state can be written a following form

$$Z^3 + UZ^2 + SZ + T = 0 \tag{114}$$

with Z as the compressibility factor. Using Cardano's formula, this type of equation can be solved analytically. With the abbreviations

$$P = \frac{3S - U^2}{3} \qquad Q = \frac{2U^3}{27} - \frac{US}{3} + T$$

the discriminant can be determined to be

$$D = \left(\frac{P}{3}\right)^3 + \left(\frac{Q}{2}\right)^2 \tag{115}$$

For $D > 0$, the equation of state has one real solution:

$$Z = \left[\sqrt{D} - \frac{Q}{2}\right]^{1/3} - \frac{P}{3\left[\sqrt{D} - \frac{Q}{2}\right]^{1/3}} - \frac{U}{3} \tag{116}$$

For $D < 0$, there are three real solutions. With the abbreviations

$$\Theta = \sqrt{-\frac{P^3}{27}} \qquad \Phi = \arccos\left(\frac{-Q}{2\Theta}\right)$$

they can be written as

$$Z_1 = 2\Theta^(1/3) \cos\left(\frac{\Phi}{3}\right) - \frac{U}{3} \tag{117}$$

$$Z_2 = 2\Theta^(1/3) \cos\left(\frac{\Phi}{3} + \frac{2\pi}{3}\right) - \frac{U}{3} \tag{118}$$

$$Z_3 = 2\Theta^(1/3) \cos\left(\frac{\Phi}{3} + \frac{4\pi}{3}\right) - \frac{U}{3} \tag{119}$$

The largest and the smallest of the three values correspond to the vapor and to the liquid solutions, respectively. The middle one has no physical meaning.

A.5. Solid density measurement

QUANTACHROME CORPORATION
Upyc 1200e V5.05
Analysis Report

Tue Oct 11 15:10:37 2022
User ID: OLIW

Sample Parameters
- Sample ID: T5
- Weight: 55.5411 g
- Description: coal
- Comment: Powder

Analysis Parameters
- Cell Size - Large
- V Added - Large: 80.8546 cc
- V Cell: 149.7915 cc
- Analysis Temperature: 27.9 C
- Target Pressure: 131.0 kPa
- Type of gas used: Helium
- Equilibration Time: Auto
- Flow Purge: 1.0 min.
- Maximum Runs: 5
- Number Of Runs Averaged: 5
- Deviation Requested: 0.0050 %

Analysis Results
- Deviation Achieved: 0.1135 %
- Average Volume: 44.1994 cc
- Volume Std. Dev.: 0.0542 cc
- Average Density: 1.2566 g/cc
- Density Std. Dev.: 0.0015 g/cc
- Coefficient of Variation: 0.1227 %

Run Data

RUN	VOLUME (cc)	DENSITY (g/cc)
1	44.1311	1.2585
2	44.1423	1.2582
3	44.2163	1.2561
4	44.2709	1.2546
5	44.2365	1.2555

Figure 11: The result of solid density measurement