

Sensitivity Analysis

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ABSTRACT

This study aimed to investigate the supercritical extraction process of caraway oil from caraway seeds. The extraction was performed in a partially filled extractor with a fixed bed operated under multiple operating conditions. A distributed-parameter model describes the fluid-solid extraction process with CO_2 as a solvent. The concept of quasi-one-dimensional flow is applied to reduce the number of spatial dimensions. The flow is assumed to be uniform across any cross-section, although the area available for the fluid phase can vary along the extractor. The local sensitivity analysis investigates the influence of infinitely small changes in the inlet temperature, pressure, and flow rate on the extraction yield.

1. Introduction

The present study focuses on extracting essential oil from the caraway (*Carum carvi* L.) seeds with supercritical fluid extraction and modelling that process. Caraway is a biennial plant belonging to the Apiaceae family. It is widespread in Asia, Europe, and North Africa. The essential oil obtained from caraway finds its potential application as a fragrance ingredient in perfumes, liquors, and toothpaste. As presented by Hromis et al. [1], the dried caraway contains nearly 2.8–5% essential oil, from which the main compounds are carvone, pinene, camphene, limonene, and carveol.

The economic feasibility of the process is crucial when selecting the appropriate technology. Conventional processes, such as distillation and organic solvent extraction, are frequently used for essential oil extraction. The distillation process is carried out at a high temperature, which causes thermal degradation of thermolabile compounds—considering that alternative techniques like supercritical fluid extraction gained popularity for extraction. Supercritical CO_2 , in particular, is attractive due to its unique properties such as inflammable, non-toxic, low critical temperature and non-corrosive. Furthermore, its critical point is relatively low compared to other fluids, making it a suitable alternative to traditional extraction techniques. The supercritical fluids exhibit both gas- and liquid-like properties so that operating conditions can adjust pressure-dependent dissolving power.

Various mathematical models have been proposed to describe the extraction of valuable compounds from a fixed biomass bed. However, selecting an appropriate extraction model requires understanding the physical phenomena occurring in the operational unit. Each model has its own set of assumptions and describes different mass transfer mechanisms and equilibrium relationships.

One model proposed by Reverchon et al. [2] is the hot ball model, which is based on an analogy to heat transfer and describes an extraction process from solid particles

containing small quantities of solute where solubility is not a limiting factor. Another model, the Broken-and-Intact Cell model, was presented by Sovova [3]. This model 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 [4] 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. However, this model does not consider the influence of axial dispersion or changes in density and flow rate along the bed.

In this work, the fundamental governing equations are derived and combined with the kinetic model suggested by Reverchon [4] to obtain a general model for the oil extraction process from the caraway seed. This model simplifies some of the physical behaviour to obtain a control-oriented model. It is assumed 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, while the vessel pressure (P) can also be measured and manipulated. However, the outlet temperature (T_{out}) can only be measured. Figure 1 shows a simplified flow diagram.

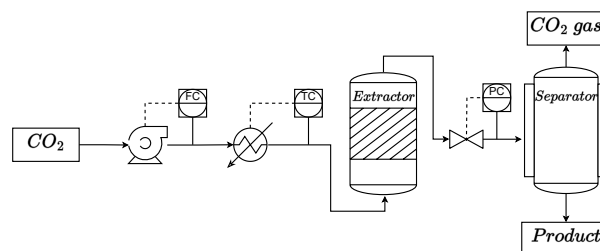


Figure 1: Process flow diagram

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This study aims to develop a process model for extracting natural substances from solid materials and liquids using supercritical fluids, specifically supercritical CO_2 . To achieve this, the model parameters are estimated based on thermodynamic relations and a set of experiments conducted at various conditions. The maximum likelihood estimator is used to solve the parameter estimation problem, and the obtained parameters are subjected to regression to derive correlations. These correlations enable the process model to be generalized across a range of temperatures (40 to 50°C) and pressures (200 to 300 bars).

The study is structured as follows: Chapter 2.1 provides a general discussion on supercritical fluids to familiarize the reader with their properties. Chapter 2.2 introduces the general balance equations derived under the Low-Mach number assumption. The simplified balance equations are combined with the extraction kinetic equation to develop the process model in Chapter 2.3. The maximum likelihood technique is presented in Chapter ?? and is then combined with the process model. The dataset obtained from laboratory experiments closes the optimization problem in Chapter ?. Finally, the parameter estimations and simulation results are discussed in Chapters 3 and 4

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 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 are presented in Appendix A.1.1. 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.

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 [5], 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 measures 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.

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 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 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 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 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 peak in the heat capacity; the highest point of this peak identifies the Widom line (as discussed by Simeoni et al. [6] and Banuti [7]).

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. [8], 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 [9]) for transport properties of dense gases based on the distribution function is a popular theoretical

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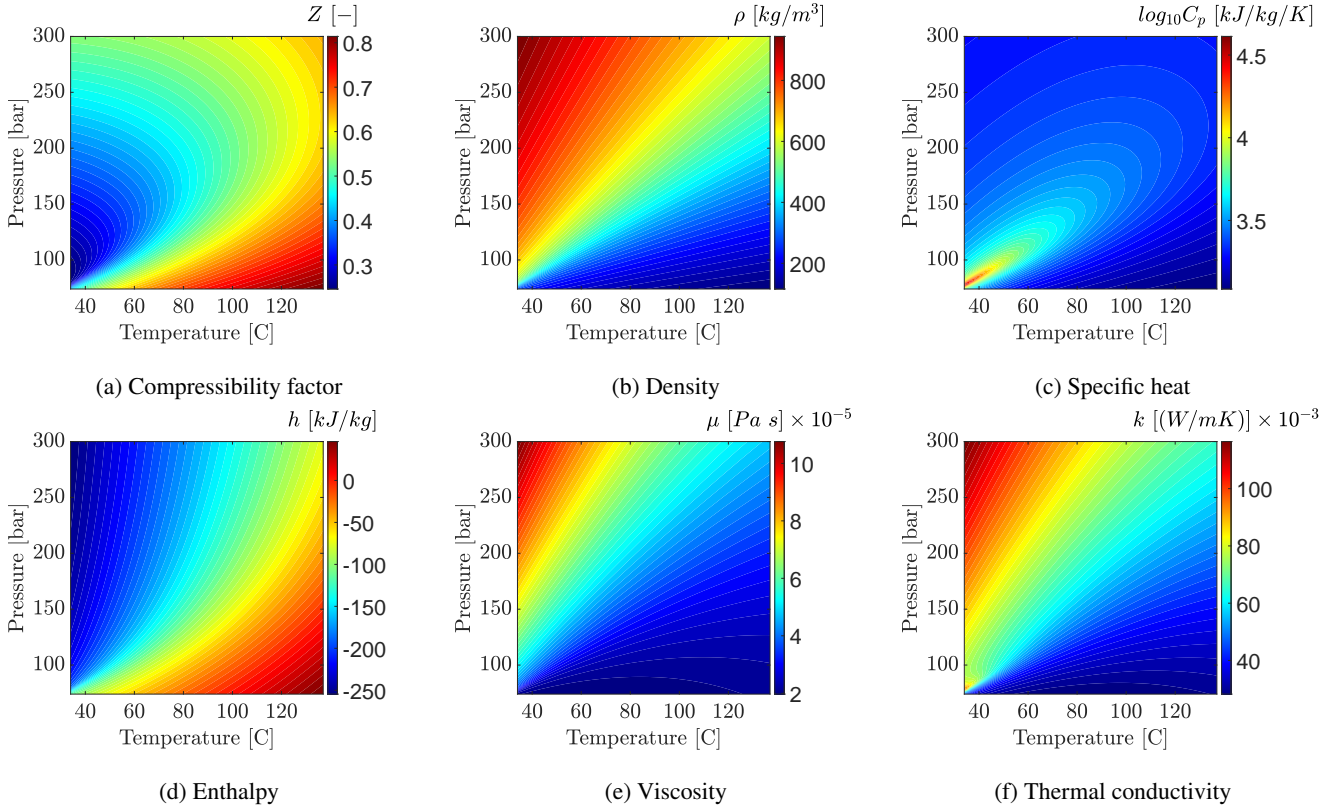


Figure 2: Properties of CO_2 based on the equation of state and correlations

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 Feghouri et al. [10], and Laesecke and Muzny [11] from the National Institute of Standards and Technology (NIST). The correlation of Laesecke and Muzny [11] is presented in Figure 2e.

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 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, the NIST developed the correlation, which describe the behaviour of thermal diffusivity of CO_2 . The work of Huber et al. [12] captures the singular behaviour of thermal conductivity around the critical point. The correlation is applicable for the temperature range from the triple point to 1100 K and pressures up to 200 MPa. Figure 2f. The presented figure show regions around the critical point where the singularity is present.

2.2. Governing equations

The governing equation ¹ for a quasi-one-dimensional compressible flow in Cartesian coordinates can be found in the Appendix A.2 and in the work of Anderson [13]. Quasi-one-dimensional flow is a fluid flow 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 an 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 1 to 3. The derivation of these Equations are presented in Appendix A.2.

$$\frac{\partial (\rho_f A_f(z))}{\partial t} + \frac{\partial (\rho_f A_f(z) v)}{\partial z} = 0 \quad (1)$$

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

$$\frac{\partial (\rho_f e A_f(z))}{\partial t} + \frac{\partial (\rho_f A_f(z) v e)}{\partial z} = -P \frac{\partial (A_f(z) v)}{\partial z} + \frac{\partial}{\partial z} \left(\frac{\partial T}{\partial z} \right) \quad (3)$$

where ρ_f is the density of the fluid, $A_f(z)$ is the function which describe change of the cross-section, v is the

¹For 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.

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 in Figure 3, can be analysed. The analysis follows the work of Schreier [14].

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

Figure 3: Small discontinuity in one-dimensional flow

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

$$\begin{aligned}\rho_f \delta v + v \delta \rho_f + \delta \rho_f \delta v &= 0 \\ \delta P &= \delta v \delta \rho_f\end{aligned}$$

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

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

By combining the momentum equation with the above equation, we get

$$\frac{dv}{d\rho_f} = -\frac{dv}{dP} \frac{dP}{d\rho_f} = -\frac{1}{\rho_f} \frac{dP}{dv} = -\frac{v}{\rho_f} \quad (4)$$

Suppose the flow is presumed to be isentropic, $dP/d\rho_f = c^2$, so $v^2 = c^2$, where c is the speed of sound. This can be interpreted as a small pressure wave propagating with the speed of sound relative to the flow. Moreover, if the flow velocity is relatively low, all pressure changes are hydrodynamic (due to velocity motion) rather than thermodynamic which leads to $\partial\rho_f/\partial P \approx 0$. 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 $\partial P/\partial\rho_f = \infty$ 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. The details of the Mach-number analysis are presented in Appendix A.3.

2.3. Extraction model

2.3.1. Continuity equation

The obtained above quasi-one-dimensional continuity equation (Equation 1) is further modified by specifying a function $A_f(z) = A_f\phi(z)$ to take into account the change of the cross-section available for the fluid. The cross-section change is taken into account by void fraction $\phi(z)$, which depends on the spatial dimension. The Equation 5 shows the differential form of the continuity equation:

$$\frac{\partial(\rho_f(T(t, z), P(t))\phi(z))}{\partial t} + \frac{\partial(\rho_f(T(t, z), P(t))vA\phi(z))}{\partial z} = 0 \quad (5)$$

where A is the total cross-section of the extractor.

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

$$\int \frac{\partial(\rho_f(T(t, z), P(t))vA\phi(z))}{\partial z} dz = 0 \rightarrow F = \rho_f(T(t, z), P(t))vA\phi(z) \quad (6)$$

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 $\rho_f(T(t, z), P(t))$.

$$v = \frac{F(t)}{\rho_f(T(t, z), P(t))A\phi(z)} \quad (7)$$

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 might be introduced to the model and defined as

$$u = v\phi(z) = \frac{F(t)}{\rho_f(T(t, z), P(t))A} \quad (8)$$

2.3.2. 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 pseudo-homogeneous fluid phase (Equation 9) 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.

$$\frac{\partial c_f(t, z)}{\partial t} + \frac{1}{\phi(z)} \frac{\partial (c_f(t, z)u)}{\partial z} = \frac{1 - \phi(z)}{\phi(z)} r_e(t, z) + \frac{1}{\phi(z)} \frac{\partial}{\partial z} \left(D_e^M \frac{\partial c_f(t, z)}{\partial z} \right) \quad (9)$$

Here, $c_f(t, z)$, $c_s(t, z)$, and $T(t, z)$ represent the concentration of solute in the fluid phase, the 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 and $D_e^M(T(t, z), P(t), F(t))$ is the axial mass diffusion coefficient.

(16)

Such a formulation limits the availability of the solute in the solid phase. Similarly to the BIC model, this can be explained if oil is assumed to be contained in the cells, a part of which is open because the cell walls were broken by grinding, and the rest remains intact. The diffusion of the solute from a particle's core takes more time compared to the diffusion of the solute located close to the outer surface, considering that the internal diffusion coefficient decay as the concentration of the solute in the solid decrease. As the value of the c_s decrease over time, the exponential term approach unity and $\lim_{c_s \rightarrow 0} D_i = D_i^R$. D_i^R can be interpreted as the internal diffusion coefficient at vanishing gradient.

Alternatively, the decay function γ can be consider with respect to the Shrinking Core model presented by Goto et al. [18], where the particle radius change as the amount of solute in the solid phase decrease. As the particle size decrease due to dissolution, the diffusion path increase which makes the diffusion slower and reduce the value of a diffusion coefficient. The same analogy can be apply to the Equation 15 to explain the change of the diffusion coefficient.

2.3.6. Heat balance

The heat equation was introduced in the previous chapter through Equation 3, in the appendix A.2 as well as through Equation 17

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

Following Elliott [5] or Gmehling et al. [19], a real gas internal energy definition can be obtained from the departure functions, defined through Equation 18. In thermodynamics, the departure function is a mathematical function that characterizes the deviation of a thermodynamic property of a real substance from that of an ideal gas at the same temperature and pressure. The departure function is typically defined as the difference between the value of a thermodynamic property for a real fluid and the corresponding value for an ideal gas at the same temperature and pressure. Common departure functions include those for enthalpy, entropy, and internal energy. They are typically computed by integrating a function that depends on the equation of state and its derivatives. More information on the departure functions can be found in appendix A.1.4.

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

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

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

For real gases, it is complicated to write the heat balance in terms of temperature, but it can be used directly in the form of internal energy, as it is given by Equation 3. In such a case, the temperature needs to be recovered 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 [5].

$$\frac{e(t, z) - e^{id}(t, z)}{RT(t, z)} = - \frac{A(T(t, z), P(t))}{B(T(t, z), P(t)) \sqrt{8}} \frac{\kappa \sqrt{T_c}}{\sqrt{a}} \ln \left[\frac{Z(T(t, z), P(t)) + (1 + \sqrt{2}) B(T(t, z), P(t))}{Z(T(t, z), P(t)) + (1 - \sqrt{2}) B(T(t, z), P(t))} \right] \quad (19)$$

To solve Equation 19, temperature, pressure, and density values need to be known. If an equation of state is introduced, then only two out of three variables need to be obtained as the third one can be calculated; this can be represented as follow

$$e(t, z) = e(T(t, z), P(t), \rho_f(T(t, z), P(t))) = e(T(t, z), P(t), \rho_f(T(t, z), P(t))) \quad (20)$$

If the value of internal energy $e(t, z)$ is known from the time evolution of the energy Equation 3, and pressure is known from measurement, then the temperature can be reconstructed. A rootfinder can be used to find a value of temperature, which minimizes the difference between the value of internal energy coming from the time evolution (Equation 17) 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 $h(t, z) = e(t, z) + P(t)/\rho_f(T(t, z), P(t))$. By introducing the definition of enthalpy, the energy equation becomes

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

The main advantage of this formulation is the presence of term $\partial P(t)/\partial t$, which allows it 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:

$$h(t, z) = h(T(t, z), P(t), \rho_f(T(t, z), P(t))) = h(T(t, z), P(t), \rho_f(T(t, z), P(t))) \quad (22)$$

If the value of enthalpy is known from the time evolution and pressure can be measured, then the Equation 22 can be solved for the 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. [19].

$$h(t, z) - h(t, z)^{id} = RT(t, z) \left[T_r(Z(T(t, z), P(t)) - 1) \right. \\ \left. - 2.078(1 + \kappa) \sqrt{\alpha(T(t, z)) \ln \left(\frac{Z(T(t, z), P(t)) + (1 + \sqrt{2}) B(T(t, z), P(t))}{Z(T(t, z), P(t)) + (1 - \sqrt{2}) B(T(t, z), P(t))} \right)} \right] \quad (23)$$

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

As discussed by Gmehling et al. [19], special attention should be paid to high pressures systems, so the influence of the intermolecular forces on the enthalpy is taken into account. In most cases, these forces are attractive, so additional energy is necessary to move the molecules away from each other, that is, to lower the density. If this energy is not added, the substance cools down when it is expanded.

2.3.7. Pressure term

The pressure term in the energy equation, given by Equation 21, describes the change of the thermodynamic pressure with respect to time. As explained in Chapters A.2 and A.3, at low-Mach number conditions, the thermodynamic pressure is nearly constant in space due to the small pressure wave propagation that occurs at the speed of sound. Under such conditions, the term $\partial P / \partial t$ can be approximated by an ordinary differential equation, which describes the instantaneous change of pressure in the system. The pressure in the system is considered a state variable, while the pressure in the new time-step is considered a control variable.

$$\frac{\partial P(t)}{\partial t} \approx \frac{P(t) - P_{in}(t)}{\Delta t} \quad (24)$$

Such a simplified equation takes into account the pressure change in the energy balance, but the dynamics are simplified and do not consider the effects of pressure losses. In a real system, the dynamics of pressure change would depend on a pump used in an extraction system, as well as a back-pressure regulator used to control an outlet valve.

2.3.8. Extraction yield

The efficiency of the process (the yield) is calculated according to Equation 25 as presented by Sovova et al. [20]. The measurement equation evaluate the mass of solute at the outlet of the extraction unit and sums it. The integral form of the measurement equation (25) can be transformed into the differential form (26) and augmented with the process model.

$$y(t) = \int_{t_0}^{t_f} \frac{F(t)}{\rho_f(T(t, z), P(t))} c_f(t, z) \Big|_{z=L} dt \quad (25)$$

$$\frac{dy(t)}{dt} = \frac{F(t)}{\rho_f(T(t, z), P(t))} c_f(t, z) \Big|_{z=L} \quad (26)$$

2.3.9. Initial and boundary conditions

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 c_{s0} . On the other hand, the solute concentration in the fluid phase should not follow the same assumption as the solid phase. Every SFE system needs some time to reach the desired operating conditions

but the solute diffuses from solid phase to the fluid phase already at the preparation stage. For instance, a pump introduce more and more fluid to the extractor to increase the pressure, which makes the fluid present already in that vessel to moves internally hence the solute in the fluid phase is non-uniformly distributed. Some conclusions can be drawn from the analysis of the initial part of each yield curve obtained from the laboratory (Figure ??). It can be noticed that each curve at the beginning has a curvature, which is not linear. Generally, a quadratic function could approximate the initial part of each extraction curve. A function that, after integration, gives a quadratic-like result is a straight line. Based on that observation, the solute concentration in the fluid phase is assumed to be linearly distributed. The solute concentration is assumed to be zero at the outlet and reach the maximum at the beginning of the fixed bed. The details on the calculation are given in Appendix A.6. The linear distribution $H(z)$ can be defined if the total mass of solute m_{total} and initial mass ratio between solid and fluid phases τ are known. Moreover, it is considered that the initial temperature of the extractor in every place is the same and described by h_0 . Therefore, the initial conditions employed in the simulation are:

$$c_f(t = 0, z) = H(z)$$

$$c_s(t = 0, z) = c_{s0}$$

$$h(t = 0, z) = h_0$$

2.3.10. State-space representation

The process model can be written in a general form:

$$\begin{bmatrix} \frac{\partial c_f(t, z)}{\partial t} \\ \frac{\partial c_s(t, z)}{\partial t} \\ \frac{\partial h(t, z)}{\partial t} \\ \frac{\partial P(t, z)}{\partial t} \\ \frac{\partial y(t)}{\partial t} \end{bmatrix} = \begin{bmatrix} \bar{\phi}_1(c_f(t, z), c_s(t, z), h(t, z); \Theta) \\ \bar{\phi}_2(c_f(t, z), c_s(t, z), h(t, z); \Theta) \\ \bar{\phi}_3(c_f(t, z), c_s(t, z), h(t, z); \Theta) \\ \bar{\phi}_4(c_f(t, z), c_s(t, z), h(t, z); \Theta) \\ \bar{\phi}_5(c_f(t, z), c_s(t, z), h(t, z); \Theta) \end{bmatrix} = \bar{\phi}(t, z; \Theta) = \frac{\partial \chi(t, z)}{\partial t} \quad (28)$$

where Θ is a parameter space consisting of model parameters θ and controls u , $\bar{\phi}$ is a set of functions that correspond to state equations of the model, and χ is the state-space model.

Each function $\bar{\phi}_i$ 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 $\dot{x}(t)$.

$$\dot{\mathbf{x}}(t) = \frac{d\mathbf{x}(t)}{dt} = \begin{bmatrix} \frac{dc_{f,1}(t)}{dt} \\ \vdots \\ \frac{dc_{f,N_z}(t)}{dt} \\ \frac{dc_{s,1}(t)}{dt} \\ \vdots \\ \frac{dc_{s,N_z}(t)}{dt} \\ \frac{dh_1(t)}{dt} \\ \vdots \\ \frac{dh_{N_z}(t)}{dt} \\ \frac{dP(t)}{dt} \\ \frac{dy(t)}{dt} \end{bmatrix} = \begin{bmatrix} \mathbf{G}_1(c_f(t), c_s(t), h(t); \Theta) \\ \vdots \\ \mathbf{G}_{N_z}(c_f(t), c_s(t), h(t); \Theta) \\ \mathbf{G}_{N_z+1}(c_f(t), c_s(t), h(t); \Theta) \\ \vdots \\ \mathbf{G}_{2N_z}(c_f(t), c_s(t), h(t); \Theta) \\ \mathbf{G}_{2N_z+1}(c_f(t), c_s(t), h(t); \Theta) \\ \vdots \\ \mathbf{G}_{3N_z}(c_f(t), c_s(t), h(t); \Theta) \\ \mathbf{G}_{3N_z+1}(c_f(t), c_s(t), h(t); \Theta) \\ \underbrace{\mathbf{G}_{3N_z+2}(c_f(t), c_s(t), h(t); \Theta)}_{\mathbf{G}(\mathbf{x}(t); \Theta)} \end{bmatrix}$$

where $\mathbf{x} \in \mathbb{R}^{N_x=3N_z}$ and $\Theta \in \mathbb{R}^{N_\Theta=N_\theta+N_u}$, 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 ($c_f(t, z)$ and $c_s(t, z)$, respectively), and the local enthalpy of the pseudo-homogeneous phase ($h(t, z)$). The controllable input variables are the mass flow-rate and temperature of the solvent in the feed and the pressure in the extractor. Additionally, the pressure change is augmented with the state-space and denoted as $P(t)$. The system state-space is extended by assuming 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 (enthalpy) of CO_2 in the feed, and the pressure in the extractor.

2.3.11. Discretization methods

The method of lines is used to transform the process model equations into a set of ODEs denoted as $\mathbf{G}(\mathbf{x}(t); \Theta)$. 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 the first-order derivative, while the central difference scheme is used to approximate the second-order derivative. The length of the fixed bed is divided into N_z equally distributed points in z-direction.

As presented in Appendix A.2, all the governing can be written in the integral form using the Divergence Theorem. The integral equation states that the change rate of the integral of any quantity over an arbitrary control volume is given by the flux through the boundary of the control volume, with being the outer surface normal through the

boundary. That quantity is neither produced nor consumed inside of the control volume and is hence conserved. For a derivative to be conservative, it must form a telescoping series. In other words, after the addition of all terms coming from the discretization over a grid, only the boundary terms should remain and the artificial interior points should cancel out. To ensure the mass conservation, the discretization is applied on the conservative form of the process model.

2.4. Sensitivity Analysis

Local derivative-based methods involve taking the partial derivative of the output with respect to an input parameter. This set of derivatives is known as sensitivity equations, and it is solved simultaneously with the process model. The purpose of the sensitivity analysis is to investigate how responsive the solution is for the perturbation of the parameter p . According to Dickinson and Gelinas [21], the sensitivity analysis can be used to determine the influence of the uncertainty on the solution of the original system. Another purpose is to distinguish sensitive parameters from insensitive ones, which might be helpful for model reduction. Finally, from a control engineering point of view, the sensitivity analysis allows to sort the control variables with respect to the level of effort required to change the model's output.

As presented in the work of Maly and Petzold [22], the sensitivity analysis equations (\mathbf{Z}) are developed by taking the total derivative of the original system $\mathbf{F}(\mathbf{x}(t); p)$ with respect to p .

$$\mathbf{Z}(\mathbf{x}(t); p) = \frac{\partial \mathbf{x}(t)}{\partial p} \quad (29)$$

As the process model depends on time t , parameters p and initial conditions, each parameter's sensitivity also depend on time t . Therefore, the new system of equations can be obtained by taking derivatives with respect to time t and applying the chain rule.

$$\dot{\mathbf{Z}}(\mathbf{x}(t); p) = \frac{d\mathbf{Z}(\mathbf{x}(t); p)}{dt} = \frac{\partial}{\partial t} \left(\frac{\partial \mathbf{x}(t)}{\partial p} \right) = \frac{\partial}{\partial p} \left(\frac{\partial \mathbf{x}(t)}{\partial t} \right) = \frac{d\mathbf{F}(\mathbf{x}(t); p)}{dp} \quad (30)$$

By applying the definition of the total derivative to the equation 30, the sensitivity equation can be obtained.

$$\frac{d\mathbf{F}(\mathbf{x}(t); p)}{dp} = \underbrace{\frac{\partial \mathbf{F}(\mathbf{x}(t); p)}{\partial \mathbf{x}(t)}}_{\mathbf{J}_x(\mathbf{x}(t); p)} \underbrace{\frac{\partial \mathbf{x}(t)}{\partial p}}_{\mathbf{S}(\mathbf{x}(t); p)} + \underbrace{\frac{\partial \mathbf{F}(\mathbf{x}(t); p)}{\partial p}}_{\mathbf{J}_p(\mathbf{x}(t); p)} \quad (31)$$

The sensitivity equation 31 is solved simultaneously with the original system. This equation is made of three terms: jacobian $\mathbf{J}_x(\mathbf{x}(t); p)$, sensitivity matrix $\mathbf{S}(\mathbf{x}(t); p)$ and jacobian $\mathbf{J}_p(\mathbf{x}(t); p)$. The jacobian $\mathbf{J}_x(\mathbf{x}(t); p)$ represents the matrix of equations of size $N_x \times N_x$, where each equation $\mathbf{J}_{x_{n_x}}(n_x, n_x)$ is the derivative of process model equations $\mathbf{F}_{n_x}(\mathbf{x}(t); p)$ with respect to the state variable x_{n_p} .

$$J_x(x(t); p) = \begin{pmatrix} \frac{\partial F_1(x(t); p)}{\partial x_1(t)} & \frac{\partial F_1(x(t); p)}{\partial x_2(t)} & \dots & \frac{\partial F_1(x(t); p)}{\partial x_{N_x}(t)} \\ \frac{\partial F_2(x(t); p)}{\partial x_1(t)} & \frac{\partial F_2(x(t); p)}{\partial x_2(t)} & \dots & \frac{\partial F_2(x(t); p)}{\partial x_{N_x}(t)} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial F_{N_x}(x(t); p)}{\partial x_1(t)} & \frac{\partial F_{N_x}(x(t); p)}{\partial x_2(t)} & \dots & \frac{\partial F_{N_x}(x(t); p)}{\partial x_{N_x}(t)} \end{pmatrix} \quad (32)$$

The sensitivity matrix $S(x(t); p)$ represents the matrix of equations of size $N_x \times N_p$, where each equation $S(n_x, n_p)$ is the derivative of the state variable x_{n_x} with respect to the parameter p_{n_p} .

$$S(x(t); p) = \begin{pmatrix} s_{(1,1)} & s_{(1,2)} & \dots & s_{(1,N_p)} \\ s_{(2,1)} & s_{(2,2)} & \dots & s_{(2,N_p)} \\ \vdots & \vdots & \ddots & \vdots \\ s_{(N_x,1)} & s_{(N_x,2)} & \dots & s_{(N_x,N_p)} \end{pmatrix} = \begin{pmatrix} \frac{dx_1(t)}{dp_1} & \frac{dx_1(t)}{dp_2} & \dots & \frac{dx_1(t)}{dp_{N_p}} \\ \frac{dx_2(t)}{dp_1} & \frac{dx_2(t)}{dp_2} & \dots & \frac{dx_2(t)}{dp_{N_p}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{dx_{N_x}(t)}{dp_1} & \frac{dx_{N_x}(t)}{dp_2} & \dots & \frac{dx_{N_x}(t)}{dp_{N_p}} \end{pmatrix} \quad (33)$$

The jacobian $J_p(x(t); p)$ represents the matrix of equations of size $N_x \times N_p$, where each equation $J_p(n_x, n_p)$ is the direct derivative of the process model equation F_{n_x} with respect to the parameter p_{n_p} .

$$J_p(x(t); p) = \begin{pmatrix} \frac{\partial F_1(x(t); p)}{\partial p_1} & \frac{\partial F_1(x(t); p)}{\partial p_2} & \dots & \frac{\partial F_1(x(t); p)}{\partial p_{N_p}} \\ \frac{\partial F_2(x(t); p)}{\partial p_1} & \frac{\partial F_2(x(t); p)}{\partial p_2} & \dots & \frac{\partial F_2(x(t); p)}{\partial p_{N_p}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial F_{N_x}(x(t); p)}{\partial p_1} & \frac{\partial F_{N_x}(x(t); p)}{\partial p_2} & \dots & \frac{\partial F_{N_x}(x(t); p)}{\partial p_{N_p}} \end{pmatrix} \quad (34)$$

The combined system containing the original set of equations $F(x(t); p)$ and sensitivity equations can be formulated as $\mathbf{F}(x(t); p)$. The size of $\mathbf{F}(x(t); p)$ is equal to $N_s = N_x(N_p + 1)$.

$$\mathbf{F}(x(t); p) = \begin{bmatrix} F(x(t); p) \\ J_x(x(t); p)S(x(t); p) + J_p(x(t); p) \end{bmatrix} \quad (35)$$

The initial conditions are described as

$$\mathbf{F}(x(t_0); p) = \begin{bmatrix} x(t_0) & \frac{dx(t_0)}{dp_1} & \dots & \frac{dx(t_0)}{dp_{N_p}} \end{bmatrix}^T \quad (36)$$

In a similar way, the sensitivity analysis of the output function can be performed with respect to parameters p . The output function $g(x(t))$ returns $y(t)$. By taking a total derivative of $y(t)$ with respect to p , the new sensitivity equation can be found.

$$\frac{dy(t)}{dp} = \frac{dg(x(t))}{dp} = \frac{\partial g(x(t))}{\partial x(t)} \frac{dx(t)}{dp} + \frac{\partial g(x(t))}{\partial p} \quad (37)$$

The $g(x(t))$ itself is independent of the parameters, but it depends on $x(t)$, which is the function of p . In such a case the sensitivity equation for the output becomes

$$\frac{dg(x(t))}{dp} = \frac{\partial g(x(t))}{\partial x(t)} \frac{dx(t)}{dp} + 0 = \frac{\partial g(x(t))}{\partial x(t)} S(x(t); p) = \begin{pmatrix} \frac{\partial g_1(x(t))}{\partial x_1} & \frac{\partial g_1(x(t))}{\partial x_2} & \dots & \frac{\partial g_1(x(t))}{\partial x_{N_x}} \\ \frac{\partial g_2(x(t))}{\partial x_1} & \frac{\partial g_2(x(t))}{\partial x_2} & \dots & \frac{\partial g_2(x(t))}{\partial x_{N_x}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial g_{N_g}(x(t))}{\partial x_1} & \frac{\partial g_{N_g}(x(t))}{\partial x_2} & \dots & \frac{\partial g_{N_g}(x(t))}{\partial x_{N_x}} \end{pmatrix} \begin{pmatrix} s_{(1,1)} & s_{(1,2)} & \dots & s_{(1,N_p)} \\ s_{(2,1)} & s_{(2,2)} & \dots & s_{(2,N_p)} \\ \vdots & \vdots & \ddots & \vdots \\ s_{(N_x,1)} & s_{(N_x,2)} & \dots & s_{(N_x,N_p)} \end{pmatrix} \quad (38)$$

3. Results

The sensitivity equations were solved simultaneously with the original process model. The focus of this work is to investigate the influence of inlet temperature, pressure and mass flow-rate on the state-space as well as on the extraction yield.

The increase of the mass-flow rate affects the whole system simultaneously in the spatial direction. The change in mass flow-rate makes the fluid moves faster, but its thermodynamic state is not affected. As the result, the Figure 5 show no change in pressure during the simulation.

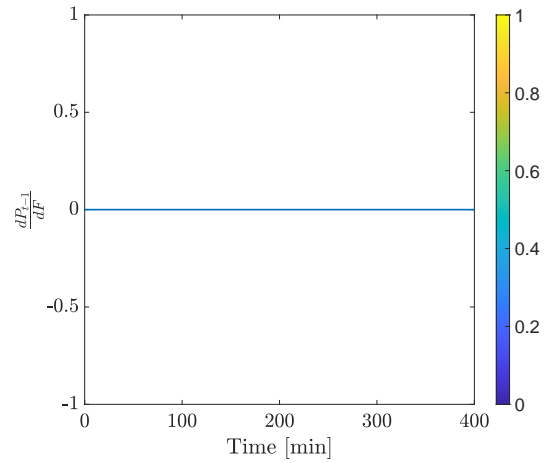


Figure 5: The effect of F change on P

Similarly, the energy in the system (defined as $\rho \times h$) is not affected as presented on Figure 6.

The increase in the mass flow-rate affects the concentration gradient and accelerate the extraction kinetic. The acceleration

4. Conclusions

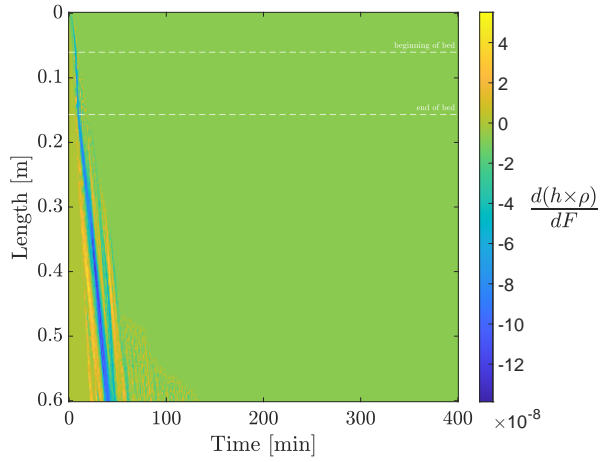


Figure 6: The effect of F change on $\rho \times h$

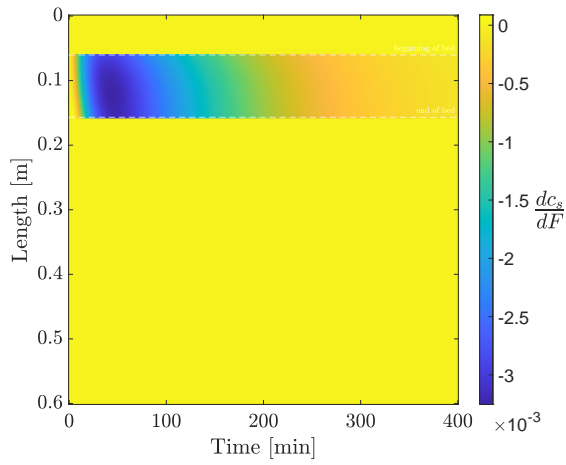


Figure 7: The effect of F change on C_s

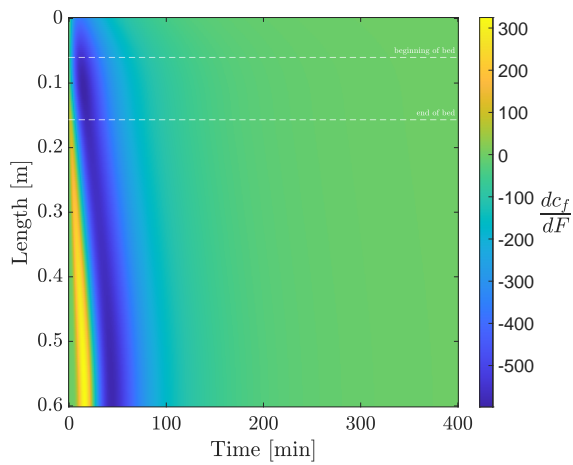


Figure 8: The effect of F change on C_f

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A. Appendix

A.1. Thermodynamic

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

In this study, the influence of real gas effects are introduced through $P(t)v_m(T(t, z), P(t)) = Z(T(t, z), P(t))RT(t, z)$, where v_m represents the molar volume of CO_2 , $Z(T(t, z), P(t))$ denotes its compressibility factor, and R is the universal gas constant. The main advantage of using compressibility in calculations is to express it as an explicit function of temperature and pressure. 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 [26], Elliott [5] or Pratt [27]. The P-R EOS is presented by Equation 40.

$$P(t) = \frac{RT(t, z)}{v_m(T(t, z), P(t)) - b} - \frac{a^c \alpha(T(t, z))}{v_m(T(t, z), P(t))^2 + 2bv_m(T(t, z), P(t)) - b^2} \quad (40)$$

The Equation 40 can be also written as the third-order given by Equation 41. Numerical methods such as Newton-Raphson can be used to solve the polynomial equation to obtain the compressibility $Z(T(t, z), P(t))$ at given temperature and pressure. Alternatively, the Cardano formula can be used to get the closed form solution of the Equation 41. Further details regarding the Cardano formula can be found in Appendix A.5.

$$Z^3 - (1 - B(T(t, z), P(t)))Z^2 + (A(T(t, z), P(t)) - 2B(T(t, z), P(t)) - 3B(T(t, z), P(t))^2)Z = 0 \quad (41)$$

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, $a(T(t, z)) = a^c \alpha(T(t, z))$ with $a^c \approx 0.45724R^2T_c^2/P_c$, and the repulsion parameter, $b \approx 0.07780RT_c/P_c$, both functions of the critical temperature T_c and pressure P_c .

$$A(T(t, z), P(t)) = \frac{\alpha(T(t, z)) a^c P(t)}{R^2 T^2(t, z)}; \quad (42a)$$

$$B(T(t, z), P(t)) = \frac{bP(t)}{RT(t, z)}. \quad (42b)$$

The quantity $\alpha(T(t, z))$ is a dimensionless correction term that depends on the temperature $T(t, z)$ and a constant κ . The constant κ is given by the formula $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$, where ω is the acentric factor of CO_2 molecules and is equal to 0.239.

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.

A.1.2. Density of the fluid phase

The density of the fluid phase, denoted by ρ_f , is assumed to be equal to the density of the solvent at a given temperature and pressure. Since the temperature $T(t, z)$ of the fluid phase is a modelled variable, the density can vary both along the bed and in time. Using the definition of

compressibility, the following expression for the density can be obtained:

$$\rho_f(T(t, z), P(t)) = \frac{P(t)M_{CO_2}}{RT(t, z)Z(T(t, z), P(t))}, \quad (43)$$

where M_{CO_2} denotes the molar mass of CO_2 , and $Z(T(t, z), P(t))$ is the compressibility factor that solves Eq. (41). This means that the density of the fluid depends on both space and time, due to its dependence on temperature and pressure.

A.1.3. Heat capacity of the fluid phase

Following the work of Pratt [27], it is assumed that the specific heat can be obtained as a sum of ideal gas contribution and a residual correction for non-ideal behaviour, as given by Equations 44a and 44b.

$$C_v(T(t, z), P(t)) = C_v^I(T(t, z), P(t)) + C_v^R(T(t, z), P(t)); \quad (44a)$$

$$C_p(T(t, z), P(t)) = C_p^I(T(t, z), P(t)) + C_p^R(T(t, z), P(t)). \quad (44b)$$

Eq. (45) Eq. (46)

$C_v(T(t, z), P(t))$ and $C_p(T(t, z), P(t))$ are the specific heat of CO_2 at constant volume and pressure, respectively.

The ideal-gas contribution $C_v^I(T(t, z), P(t))$ and $C_p^I(T(t, z), P(t))$, can be obtained based on heat-capacity data applicable to gases at low pressure. For CO_2 , the ideal gas contribution to the specific heat at constant $P(t)$, as function of $T(t, z)$ is given by,

$$C_p^I(T(t, z), P(t)) = C_{P0} + C_{P1}T(t, z) + C_{P2}T^2(t, z) + C_{P3}T^3(t, z) \quad (45)$$

where the coefficients (REF) of the expansion are $C_{P0} = 4.728$, $C_{P1} = 1.75 \times 10^{-3}$, $C_{P2} = -1.34 \times 10^{-5}$, and $C_{P3} = 4.10 \times 10^{-9}$.

The correction term $C_p^R(T(t, z), P(t))$ at constant pressure $P(t)$, can be defined by introducing $C_p^I(T(t, z)) - C_v^I(T(t, z)) = R$ and using the definition of $C_v^R(T(t, z), P(t))$. The general form of the correction term is given by Equation 46

$$C_p^R(T(t, z), P(t)) = \underbrace{C_v^R(T(t, z), P(t))}_{\text{Eq. (50)}} + \underbrace{T(t, z) \left(\frac{\partial P(t)}{\partial T} \right)_{v_m(t, z)}}_{\text{Eq. (49)}} \underbrace{\left(\frac{\partial v_m(T(t, z), P(t))}{\partial T} \right)_{P(t)}}_{\text{Eq. (47)}} - R. \quad (46)$$

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

$$\left(\frac{\partial v_m(T(t, z), P(t))}{\partial T} \right)_{P(t)} = \frac{Z(T(t, z), P(t))R}{P(t)} + \frac{RT(t, z)}{P(t)} \underbrace{\left(\frac{\partial Z(T(t, z), P(t))}{\partial T} \right)_{P(t)}}_{\text{Eq. (48)}} \quad (47)$$

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

$$\left(\frac{\partial Z(T(t, z), P(t))}{\partial T} \right)_{P(t)} = \left(\frac{\frac{P(t)v_m(T(t, z), P(t))}{RT(t, z)}}{\frac{\partial T}{\partial T}} \right)_{P(t)} \quad (48)$$

Similarly, for the partial derivative of the pressure with respect to temperature at constant volume is :

$$\left(\frac{\partial P(t)}{\partial T} \right)_{v_m(t,z)} = \left(\frac{\partial \frac{ZRT(t,z)}{v_m(T(t,z), P(t))}}{\partial T} \right)_{v_m(t,z)} \quad (49)$$

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

$$C_v^R(T(t,z), P(t)) = \left(\frac{\partial U^R(T(t,z), P(t))}{\partial T} \right)_{v_m(t,z)} \quad (50)$$

A.1.4. Departure functions for enthalpy calculations

In thermodynamics, a departure function is a concept used to calculate the difference between a real fluid's thermodynamic properties and those of an ideal gas, given a specific temperature and pressure. Common departure functions include those for enthalpy, entropy, and internal energy. These functions are used to calculate extensive properties, which are properties computed as a difference between two states.

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

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

$$\frac{h^{id} - h}{RT} = \int_{v_m}^{\infty} \left(T \left(\frac{\partial Z}{\partial T} \right)_{v_m} \right) \frac{dv_m}{v_m} + 1 - Z \quad (51)$$

Here, h^{id} represents the enthalpy of an ideal gas, h is the enthalpy of a real fluid, R is the universal gas constant, T is temperature, v_m is the molar volume, and Z is the compressibility factor.

The integral in the equation is evaluated over the range of molar volumes from v_m to infinity. The integral includes a term that depends on the derivative of the compressibility factor with respect to temperature, evaluated at the molar volume v_m . Finally, the term $1 - Z$ is added to account for the deviation of the fluid's properties from those of an ideal gas.

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. [19] or Elliott [5]:

$$h - h^{id} = RT \left(T_r(Z - 1) - 2.078(1 + \kappa)\sqrt{\alpha} \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \right) \quad (52)$$

A.2. Governing equations

A.2.1. Mass continuity

Following the work of Anderson [13], 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 result from the partial filling of an extractor or its irregular shape. In reality, such a flow is two-dimensional because the area changes as a function of z , and there is a flow-field variation in both directions. The assumption of quasi-one-dimensional flow dictates that the flow properties are a 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. The modified governing equation can be derived to ensure that these physical principles are satisfied. Let's start with the integral form of the continuity equation:

$$\frac{\partial}{\partial t} \iiint_{V_f} \rho_f dV_f + \iint_S \rho_f \mathbf{V} \cdot d\mathbf{S} = 0 \quad (53)$$

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

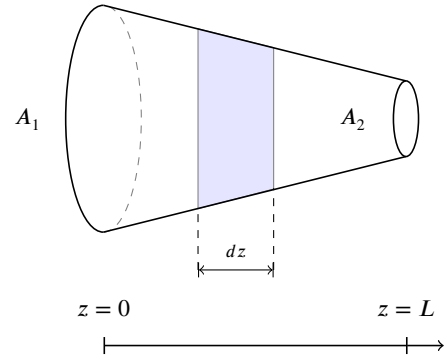


Figure 9: Control volume for deriving the partial differential equation for unsteady, quasi-one-dimensional flow

This control volume is a slice of an extractor, where the infinitesimal thickness 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 area 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. 53 becomes, in the limit as dz becomes very small,

$$\frac{\partial}{\partial t} \iiint_{V_f} \rho_f dV_f = \frac{\partial}{\partial t} (\rho_f A_f dz) \quad (54)$$

where $A dz$ is the volume of the control volume in the limit of dz becoming vanishingly small. The surface integral in Eq. 53 becomes

$$\iint_S \rho_f \mathbf{V} \cdot d\mathbf{S} = -\rho_f v A_f + (\rho_f + d\rho_f)(v + dv)(A_f + dA_f) \quad (55)$$

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

$$\iint_S \rho_f \mathbf{V} \cdot d\mathbf{S} = -\rho_f v A_f + \rho_f v A_f + \rho_f v dA_f + \rho_f A_f dv$$

$$+ \rho_f d v d A_f + v A_f d \rho_f + v d \rho_f d A + A_f d \rho_f d v + d \rho_f d v d A_f \quad (56)$$

In the limit as dz becomes very small, the terms involving products of the differential in Eq. 56, such as $\rho_f d v d A_f$, $d \rho_f d v d A_f$, 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

$$\iint_S \rho_f \mathbf{V} \cdot d\mathbf{S} = \rho_f v d A_f + \rho_f A_f d v + v A_f d \rho_f \quad (57)$$

Substituting Eqs. 54 and 57 into 53, we have

$$\frac{\partial (\rho_f A_f)}{\partial t} + \frac{\partial (\rho_f A_f v)}{\partial z} = 0 \quad (58)$$

The above partial differential equation form of the continuity equation is suitable for unsteady, quasi-one-dimensional flow. It ensures that mass is conserved for this mode of flow. The $A_f(z)$ is an arbitrary function that describes a change in 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.

$$\frac{\partial (\rho_f \mathbf{A}\phi(z))}{\partial t} + \frac{\partial (\rho_f \mathbf{A}\phi(z)v)}{\partial z} = 0 \quad (59)$$

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

$$\frac{\partial (\rho_f \phi(z))}{\partial t} + \frac{\partial (\rho_f \phi(z)v)}{\partial z} = 0 \quad (60)$$

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

$$\frac{\partial (\rho_f \phi(z))}{\partial t} + \frac{\partial (\rho_f u)}{\partial z} = 0 \quad (61)$$

A.2.2. Transport of a species

The transport of a chemical species, in this case, a solute, can be described by an analogous equation to the Eq. 53 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 ($J_{diff} = D_e^M \frac{\partial c_f}{\partial z}$). The other term corresponds to the mass transfer between solid and fluid phases, which is treated as a source term.

$$\frac{\partial}{\partial t} \iiint_{V_f} c_f dV_f + \iint_S c_f \mathbf{V} \cdot d\mathbf{S} = \iint_S J_{diff} \cdot \mathbf{n} dS + \frac{\partial}{\partial t} \iiint_{V_s} c_s dV_s \quad (62)$$

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

$$\frac{\partial}{\partial t} \iint_{V_f} c_f dV_f = \frac{\partial}{\partial t} (c_f A_f dz) \quad (63)$$

$$\frac{\partial}{\partial t} \iint_{V_s} c_s dV_s = \frac{\partial}{\partial t} (c_s A_s dz) \quad (64)$$

The surface integrals in the limit of dz become

$$\iint_S c_f \mathbf{V} \cdot d\mathbf{S} = c_f v d A_f + c_f A_f d v + v A_f d c_f \quad (65)$$

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

$$\iint_S J_{diff} \cdot \mathbf{n} dS = \iiint_{V_f} \nabla J_{diff} dV_f = \nabla \cdot \iiint_{V_f} J_{diff} dV_f = \nabla \cdot (J_{diff} A_f dz) \quad (66)$$

By substituting the equations derived above into Eq. 62 we obtain

$$\frac{\partial (c_f A_f)}{\partial t} + \frac{\partial (c_f A_f v)}{\partial z} = \frac{\partial (c_s A_s)}{\partial t} + \frac{\partial (J_{diff} A_f)}{\partial z} \quad (67)$$

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

$$\frac{\partial (c_f \phi)}{\partial t} + \frac{\partial (c_f u)}{\partial z} = \frac{\partial (c_s (1 - \phi))}{\partial t} + \frac{\partial (J_{diff} \phi)}{\partial z} \quad (68)$$

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

$$\frac{\partial c_f}{\partial t} + \frac{1}{\phi} \frac{\partial (c_f u)}{\partial z} = \frac{(1 - \phi) \partial c_s}{\phi \partial t} + \frac{1}{\phi} \frac{\partial}{\partial z} \left(D_e^M \frac{\partial c_f}{\partial z} \right) \quad (69)$$

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.

$$\frac{\partial c_f}{\partial t} + \frac{u}{\phi} \frac{\partial c_f}{\partial z} = \frac{1 - \phi}{\phi} \frac{\partial c_s}{\partial t} \quad (70)$$

The Eq. 70 is equivalent to the equation presented by Reverchon [4].

A.2.3. Momentum conservation

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

$$\frac{\partial}{\partial t} \iiint_{V_f} (\rho_f v_z) dV_f + \iint_S (\rho_f v_z \mathbf{V}) \cdot d\mathbf{S} = \iint_S (P dS)_z \quad (71)$$

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,

$$\frac{\partial}{\partial t} \iiint_{V_f} (\rho_f v_z) dV_f = \frac{\partial}{\partial t} (\rho_f v A_f dz) \quad (72)$$

equation
and

$$\iint_S (\rho_f v_z \mathbf{V}) \cdot d\mathbf{S} = -\rho_f v^2 + (\rho_f + d \rho_f) (v + dv)^2 (A + dA) \quad (73)$$

The evaluation of the pressure force term on the right side of Eq. 71 can be understood based on the Fig. 10. Here, the z components of the vector $P dS$ are shown on all four sides of the control volume. Remember that $d\mathbf{S}$ is assumed to point away from the control volume; hence any z component ($P dS)_z$ that acts toward the left (in the negative z direction) is a negative quantity. Any z component that acts toward the right (in the positive z direction) is a positive quantity. Also note that the z component of $P d\mathbf{S}$ 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 is projected perpendicular to the z direction,

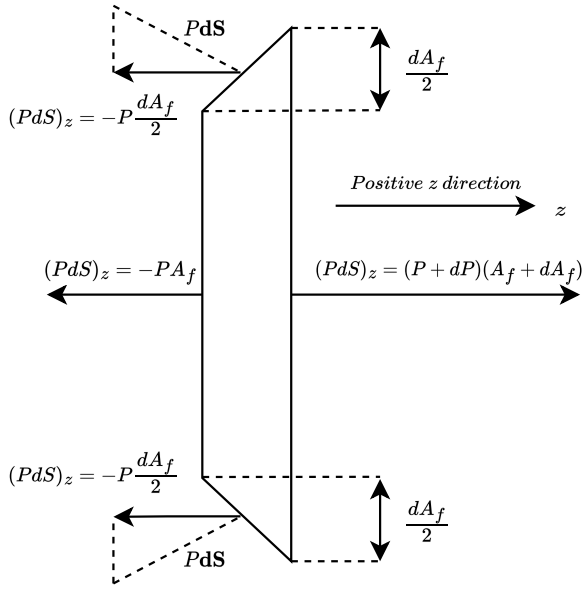


Figure 10: The forces in the z direction acting on the control volume

$dA_f/2$; hence, the contribution of each inclined face (top or bottom) to the pressure integral in Eq. 71 is $-P(dA_f/2)$. All together, the right-hand side of Eq. 71 is expressed as follows:

$$\iint (PdS)_z = -PA_f + (P + dP)(A + dA_f) - 2P \frac{dA_f}{2} \quad (74)$$

Substituting Eqs. 72 to 74 into Eq. 71, we have

$$\begin{aligned} \frac{\partial}{\partial t} (\rho_f v A_f dz) - \rho_f v^2 A_f + (\rho_f + d\rho_f)(v + dv)^2 (A_f + dA_f) \\ = PA_f - (P + dP)(A + dA_f) + PdA_f \end{aligned} \quad (75)$$

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

$$\frac{\partial}{\partial t} (\rho_f v A_f dz) + d(\rho_f v^2 A_f) = -AdP \quad (76)$$

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

$$\frac{\partial (\rho_f v A_f)}{\partial t} + \frac{\partial (\rho_f v^2 A_f)}{\partial z} = -A_f \frac{\partial P}{\partial z} \quad (77)$$

The Eq. 77 can be expanded further by assuming that $A_f = A\phi$

$$\frac{\partial (\rho_f v A\phi)}{\partial t} + \frac{\partial (\rho_f v^2 A\phi)}{\partial z} = -A\phi \frac{\partial P}{\partial t} \quad (78)$$

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

$$\frac{\partial (\rho_f v \phi)}{\partial t} + \frac{\partial (\rho_f v^2 \phi)}{\partial z} = -\phi \frac{\partial P}{\partial t} \quad (79)$$

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

$$\frac{\partial (\rho_f u)}{\partial z} + \frac{\partial (\rho_f u^2 / \phi)}{\partial z} = -\phi \frac{\partial P}{\partial z} \quad (80)$$

Eq. 77 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. 77

$$\frac{\partial (\rho_f v A_f)}{\partial t} - v \frac{\partial (\rho_f A_f)}{\partial t} + \frac{(\rho_f v^2 A_f)}{\partial z} - v \frac{(\rho_f v A_f)}{\partial z} = -A_f \frac{\partial P}{\partial z} \quad (81)$$

Expanding the derivatives on the left-hand side of the above equation and canceling like terms, gives

$$\rho_f A_f \frac{\partial v}{\partial t} + \rho_f A_f v \frac{\partial v}{\partial z} = -A_f \frac{\partial P}{\partial z} \quad (82)$$

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

$$\rho_f \frac{\partial v}{\partial t} + \rho_f v \frac{\partial v}{\partial z} = -\frac{\partial P}{\partial z} \quad (83)$$

The Eq. 83 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 $u = v\phi$.

$$\rho_f \frac{\partial (u/\phi)}{\partial t} + \rho_f \frac{u}{\phi} \frac{\partial (u/\phi)}{\partial z} = -\frac{\partial P}{\partial z} \quad (84)$$

By expanding all the terms of the equation above, we get

$$\frac{\rho_f}{\phi} \frac{\partial u}{\partial t} + \rho_f u \frac{\partial \phi^{-1}}{\partial t} + \rho_f \frac{u}{\phi} \frac{\partial u}{\partial z} + \rho_f \frac{u}{\phi} \frac{\partial \phi^{-1}}{\partial z} = -\frac{\partial P}{\partial z} \quad (85)$$

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

$$\frac{\rho_f}{\phi} \left(\frac{\partial u}{\partial t} + \frac{u}{\phi} \frac{\partial u}{\partial z} + u^2 \frac{\partial \phi^{-1}}{\partial z} \right) = -\frac{\partial P}{\partial z} \quad (86)$$

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

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

The Eq. 87 represents the 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

$$\frac{\partial}{\partial t} \iiint_{V_f} \rho_f \left(e_f + \frac{v^2}{2} \right) dV_f + \iint_S \rho_f \left(e_f + \frac{v^2}{2} \right) \mathbf{v} \cdot d\mathbf{S} = - \iint_S (P\mathbf{V}) \cdot d\mathbf{S} \quad (88)$$

Applied to the shaded control volume in Fig. 9, and keeping in mind the pressure forces shown in Fig. 10, Eq. 88 becomes

$$\begin{aligned} \frac{\partial}{\partial t} \left[\rho_f \left(e_f + \frac{v^2}{2} \right) A_f dz \right] - \rho_f \left(e_f + \frac{v^2}{2} \right) v A_f \\ + (\rho_f + d\rho_f) \left[e_f + de_f + \frac{(v + dv)^2}{2} \right] (V + dV) (A_f + dA_f) \\ = - \left[-PvA_f + (P + dP)(v + dv)(A_f + dA_f) - 2 \left(Pv \frac{dA_f}{2} \right) \right] \end{aligned} \quad (89)$$

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

$$\frac{\partial}{\partial t} \left[\rho_f \left(e_f + \frac{v^2}{2} \right) A_f dz \right] + d \left(\rho_f r_f A_f \right) + \frac{(\rho_f v^3 A_f)}{2} = -d(P A_f v) \quad (90)$$

or

$$\frac{\partial}{\partial t} \left[\rho_f \left(e_f + \frac{v^2}{2} \right) A_f dz \right] + d \left[\rho_f \left(e_f \frac{v^2}{2} \right) v A_f \right] = -d(P A_f v) \quad (91)$$

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

$$\frac{\partial [\rho_f (e_f + v^2/2) A]}{\partial t} + \frac{\partial \rho_f (e_f + v^2/2) v A_f}{\partial z} = -\frac{\partial (P A_f v)}{\partial z} \quad (92)$$

Equation 92 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. 77 is multiplied by v and then subtracted from Eq. 92

$$\frac{\partial (\rho_f e_f A_f)}{\partial t} + \frac{\partial (\rho_f e_f v A_f)}{\partial z} = -P \frac{\partial A_f v}{\partial z} \quad (93)$$

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 58, by e_f and subtracting it from 93, yielding

$$\rho_f A_f \frac{\partial e_f}{\partial t} + \rho_f A_f v \frac{\partial e_f}{\partial z} = -P \frac{\partial (A_f v)}{\partial z} \quad (94)$$

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

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

or

$$\rho_f \frac{\partial e_f}{\partial t} + \rho_f v \frac{\partial e_f}{\partial z} = -P \frac{\partial v}{\partial z} - PV \frac{\partial (\ln A_f)}{\partial z} \quad (96)$$

Equation 96 is the non-conservative form of the energy equation expressed in terms of internal energy, appropriate to unsteady quasi-one-dimensional flow. The reason for obtaining the energy equation in the form of Eq. 96 is that, for a calorically perfect gas, it leads directly to a form of the energy equation in terms of temperature T .

A.3. Low Mach number expansion

As discussed by Lions [28], 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 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 avoid the need to resolve fast-moving acoustic signals. The equations are derived from

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 1 to 2 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

$$\rho_\zeta = \rho(z, t/M_a), \quad v_\zeta = \frac{1}{\zeta} v(z, t/M_a)$$

$$T_\zeta = T(z, t/M_a), \quad k_\zeta = \zeta k(\rho_f, T)$$

The conservative non-dimensional equations of motion become

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

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 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

$$\begin{aligned} \lim_{\zeta \rightarrow 0^+} \frac{\partial ((\rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2)) A_f)}{\partial t} + \\ + \frac{\partial ((\rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2)) A_f (v_0 + v_1 \zeta + \mathcal{O}(\zeta^2)))}{\partial z} &= 0 \end{aligned}$$

The continuity equation becomes

$$\frac{\partial (\rho_0 A_f)}{\partial t} + \frac{\partial (\rho_0 A_f v_0)}{\partial z} = 0 \quad (97)$$

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.

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

The first two terms 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.

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

The simplification of the P_0 in the momentum equation comes from the fact that P_0 is independent of z . 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 $M_a \rightarrow 0$. The momentum equation becomes

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

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.

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

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

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

The non-conservative form of the energy equation becomes

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

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

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

If an 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

$$\frac{\partial (A_f v)}{\partial z} = 0 \quad (98)$$

In one-dimensional case, the Equation 98 become equivalent of $\text{div}(A_f v) = 0$, which known as the incompressibility condition (Lions [28]).

As presented by Elliott [5], 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

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

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 deduced 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 describes the total pressure, the dimensional momentum equation can be written as

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

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 $\partial v / \partial t = 0$:

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

The l.h.s integral can be solved by assuming ρ_f is constant and introducing superficial velocity $u_s = A_f v$

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

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.

A.4. Bayes theorem

As discussed by Himmelblau [29], the Bayesian approach to estimation makes 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 Θ . 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, \dots, 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 occurred, which will be 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 :

$$P\{A_i|B\} = \frac{P\{B|A_i\}P\{A_i\}}{P\{B\}} \quad (99)$$

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

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

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 a continuous variables, 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

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

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

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

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

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

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, \dots, 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 :

$$P(A_1 \text{ or } A_2 \dots \text{ or } A_n) = \sum_{i=1}^n P(A_i) \quad (104)$$

Very often we let

$$\sum_{i=1}^n P(A_i) = 1 \quad (105)$$

Also, if each event is equiprobable so that $P(A_i) = q$,

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

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

$$P(A_1 \cup A_2 \cup \dots \cup A_n) = P(A_1) + P(A_2) + \dots + P(A_n) \quad (107)$$

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

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

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

$$P(A \cap B) = P(A)P(B) \quad (109)$$

If the A and B are *dependent* events,

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

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

$$P(A \cap B) = P(B)P(A|B) \quad (111a)$$

$$= P(A)P(B|A) \quad (111b)$$

Two kinds 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

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

5. Another useful relationship for events that are not mutually exclusive is

$$P(A) + P(B) - P(A \cap B) = P(A \cup B) \quad (113)$$

A.5. Cardano's Formula

Following the work of Gmehling et al. [19], a cubic equation of state can be written a following form

$$Z^3 + UZ^2 + SZ + T = 0 \quad (114)$$

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

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

the discriminant can be determined to be

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

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

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

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

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

they can be written as

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

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

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

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.6. Initial and boundary conditions

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 c_s^0 . It is considered that the initial temperature of the extractor in every place is the same and described by h^0 .

During the preparation period, when the operating conditions are achieved, the solute diffuses to the fluid phase in contact with the solid particles. Later, the solute in the fluid phase is partially moved (if the pressure increase in the system, the pump cause the movement of the fluid, even if the outlet valve is closed) to the region where there is no solid phase. As a result, the distribution of solutes mass in the fluid phase is assumed to not be uniform, and described by an arbitrary function $H = H(z)$. Some conclusions can be drawn from the analysis of the initial part of each yield curve. It can be noticed that each curve at the beginning has a curvature, which is not linear. In a general sense, it can be said that a quadratic function could approximate the initial part of each extraction curve. A function that, after integration, gives a quadratic-like result is a straight line. Based on that observation, the solute concentration in the fluid phase is assumed to be linearly distributed. The solute concentration is assumed to be zero at the outlet and reach the maximum at the beginning of the fixed bed. The graphical representation of the solute concentration in the fluid phase is shown in Figure 11.

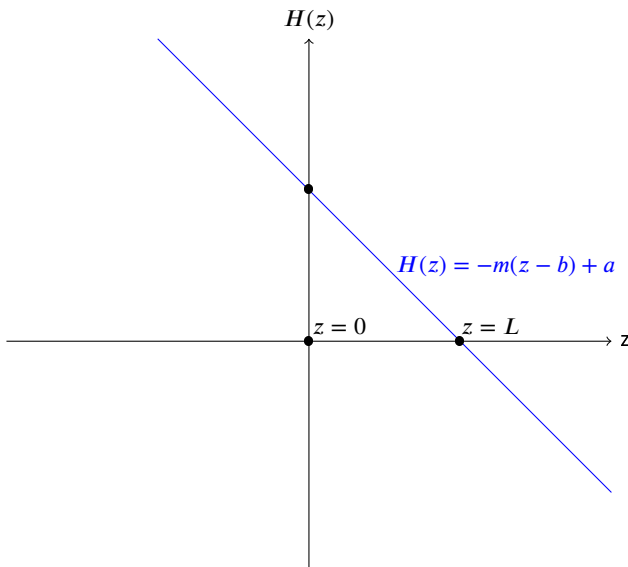


Figure 11: The linear distribution of the solute concentration in the fluid phase

As presented in Figure 11, the function H is defined as

$$H(z) = -m(z - b) + a \quad (120)$$

The function H can be integrated over the integral from a to b to describe the total amount of solute in the fluid phase (S) in that interval.

$$\int_a^b H(z) dz = S \quad (121)$$

If parameter a describe the beginning of the fixed bed, then $a = 0$. Similarly, b can be defined as the end of the fixed bed, then $b = L$. On range from $a = 0$ to $b = L$ the result of this integral is know, and it is equal to

$$S = m_{fluid}^0 = \int_{a=0}^{b=L} -m(x - L) dz \quad (122)$$

where m_{fluid}^0 is the total mass of solute in the fluid phase and N is the number of intervals between a and b . The right-hand side of the above equation can be evaluated

$$\begin{aligned} \int_{a=0}^{b=L} -m(x - L) dz &= -m \left(\int_{a=0}^{b=L} z dz - \int_{a=0}^{b=L} L dz \right) \\ &= -m \left(\frac{z^2}{2} \Big|_0^L - Lz \Big|_0^L \right) \\ &= -m \left(\frac{L^2}{2} - L^2 \right) \\ &= m \frac{L^2}{2} \end{aligned} \quad (123)$$

The parameter m can be obtained by equating the left-hand side of Equation 122 and the right-hand side of Equation 123

$$m_{fluid}^0 = m \frac{L^2}{2} \rightarrow m = \frac{2m_{fluid}^0}{L^2} \quad (124)$$

As can be seen from the above equation, the linearly distributed concentration of solute in the fluid phase can be fully determined if parameters a , b and m_{fluid}^0 are know. m_{fluid}^0 can be obtained from the total mass of the solute in the system at the initial time m_{total}^0 and the initial mass ratio τ .

$$\tau = \frac{\text{total mass of solute in the fluid phase}}{\text{total mass of solute in the system}} = \frac{m_{fluid}^0}{m_{total}^0}$$

The initial conditions can be summarized as

$$\begin{aligned} c_f(t = 0, z) &= H(z) \\ c_s(t = 0, z) &= c_{s0} \\ h(t = 0, z) &= h_0 \end{aligned}$$

A.7. Solid density measurement

$$\rho_s^{ave} = \frac{1.2585 + 1.2582 + 1.2561 + 1.2546 + 1.2555}{5} = 1.25658 [\text{g/cc}]$$

A.8. Porosity Calculations

To calculate the porosity of the solid particles ϕ , we can use the following formula:

$$\phi = \frac{\text{Volume with pores} - \text{Volume without pores}}{\text{Volume with pores}} \quad (126)$$

We can first calculate the volume, excluding the pore space, using the true density of the material:

$$\text{Volume excluding pores} = \frac{\text{mass}}{\text{true density}} = \frac{1 \text{ kg}}{1256.58 \text{ kg/m}^3} = 0.0007958 \text{ m}^3 \quad (127)$$

We can then use the volume of the solid particles, including the pore space and the volume excluding the pore space, to calculate the porosity:

$$\phi = \frac{\text{Volume with pores} - \text{Volume without pores}}{\text{Volume with pores}} \quad (128)$$



QUANTACHROME CORPORATION
Upsc 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 12: The result of solid density measurement

Since 1 kg of solid particles occupies 1.6 L, which is equivalent to 0.0016 m³, we have:

$$\phi = \frac{0.0016 \text{ m}^3 - 0.0007958 \text{ m}^3}{0.0016 \text{ m}^3} = 0.5026 \quad (129)$$

Therefore, the porosity of the solid particles is 0.5026 or 50.26%. This means that half of the total volume of the solid particles is made up of pore space.