

Parameter estimation

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ABSTRACT

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

1. Introduction

2. Materials and methods

2.1. Extraction model

The main components of the model are three one-dimensional differential equations related to mass balances (solid and fluid phase) and heat balance. As in all batch processes, our system has only one steady state. The steady-state occurs only if the solute is entirely taken out of the biomass. The extraction from a fixed bed is an unsteady process, implying that the solute concentrations in the solid and solvent phases vary over time and space. The convection and the diffusion of the mass and the heat are considered only in the axial direction. The radial distribution of such properties like a velocity is assumed to be flat in that direction. The assumption of the flat velocity profile allows considering a lack of back mixing. The pressure drop in the bed is assumed to be assumed to negligible. Under such conditions, the fluid flow can be considered a plug flow. Since the solute is assumed to be a single pseudo-component, there is only one mass balance equation for each phase (Eq. 2 and 3). On the other hand, there is only one heat balance (Eq. 8) because the presence of a single pseudo-phase is assumed. Moreover, the process model does not consider the change of particle size or the void fraction during the process. The particles are assumed to be uniformly distributed along the bed and to have the same size.

A distributed-parameter model, based on Reverchon [1], is used to describe the solid-fluid extraction process. The process model consists of three partial differential equations: two mass balance equations relative to the concentration of solute in the fixed solid phase and the mobile fluid phase, and the heat balance equation relative to the temperature of the fluid phase. The amount of solute in the solvent is considered negligible. Therefore, the fluid phase can be described as

pseudo-homogenous, and its properties are assumed to be the same as the solvent.

The movement of the mobile pseudo-homogeneous phase (Eq. 2) is considered only in the axial direction. The properties of the system in the radial direction is assumed to be uniform. In addition, it is considered that the boundary layer adjacent to the inner wall of the extractor does not exist. Therefore, the velocity profile is constant across any cross-section of the extractor perpendicular to the axial direction. As a result, the plug flow model can be introduced. The particle size distribution and the void fraction of the solid phase are assumed to be uniform in space and remain constant in time. Moreover, the pressure is considered to be constant along the fixed bed. The mass balance for the fluid phase consists of convection, diffusion, and kinetic terms.


Considering the solid phase to be fixed, the convection and diffusion terms in the corresponding mass balance are both assumed to be negligible or absent. Therefore, the mass balance for the solid phase (Eq. 3) consists of the kinetic term only.

As for the mass transfer from the solid to the fluid phase, a kinetic term based on two-film theory for the solute is considered. The mass transfer kinetic (Eq. 4) consists of the overall diffusion coefficient and the concentration gradient, which acts as a driving force for the process. A single pseudo-component is used to represent the extract collectively.

The heat balance (Eq. 8) consists of the convective and diffusive terms. It follows the assumption of a pseudo-homogeneous phase, which properties are the mean between fluid and solid phases. We consider no heat loss through the wall, and there is no heat generation in the system. Therefore, the temperature of the extractor can be changed only by manipulating the temperature of the inlet stream $T_{In}(t)$.

We assume that at a given section, where the cross-sectional area is A , the flow properties are uniform across that section. Hence, although the area of an extractor changes as a function of a distance along an extractor (e.g. if a fixed fill an extractor partially), z , and therefore in reality the

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flow field is two-dimensional (the flow varies in the two-dimensional space), we make the assumption that the flow properties vary only with z ; this is tantamount to assuming uniform properties across any given cross section. Such flow is defined as quasi-one-dimensional flow.

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

2.1.1. Continuity equation

The continuity equation for the fluid phase is given by Eq. 1. The details of derivation can be found in the appendix A.1.1

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

where u is the superficial velocity, ϵ is the bed porosity and ρ_f is the fluid density.

2.1.2. Mass balance for the fluid phase

The fluid phase is a mobile phase, which means that the fluids mass balance (Eq. 2) is made of convection, diffusion, and mass transfer kinetic terms.

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

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

2.1.3. Mass balance for the solid phase

The solid phase is a stationary phase, which indicates a lack of convection and diffusion terms in the mass balance (Eq. 3). Therefore, the only term present in this equation is the kinetic term (defined as presented in equation 4), which links solid and fluid phases.

$$\frac{\partial c_s(t, z)}{\partial t} = \underbrace{r_e(t, z)}_{\text{Kinetics}} \quad (3)$$

2.1.4. Kinetic term

As the solvent flows through the bed, it forms a film around the porous solid particle and occupies its pores: the CO_2 molecules diffuse into the pores and adsorb on the particle surface to form an external fluid film around the solid particles through the solvent–solid matrix interactions. Assuming that the mean free path of the molecule is much smaller than the pore diameter, the effect of Knudsen diffusion is small and can be neglected. In this work, the molecular diffusion is assumed. The dissolved solute diffuses from

the particle's core through the solid-fluid interface, the pore, and the film into the bulk. The graphical representation of the mass transfer mechanism is shown in Figure 1. The mean solute concentration in the solid phase is denoted as c_s . At the solid-fluid interface, the equilibrium concentrations are given as c_s^* and c_p^* , respectively for solid and fluid phases. The concentration of the solutes in the fluid phase in the centre of the pore is denoted as c_p . As the solute diffuses through the pore, its concentration changes and reaches c_{pf} at the end of the opening of the pore. The solute diffuses through the film around the particle and reaches a concentration in the bulk c_f . It can be assumed that the two-film theory describes the solid-fluid interface inside the pore. The overall mass transfer coefficient can be introduced if the relation between the solute concentration in one phase and its equilibrium concentration is known.

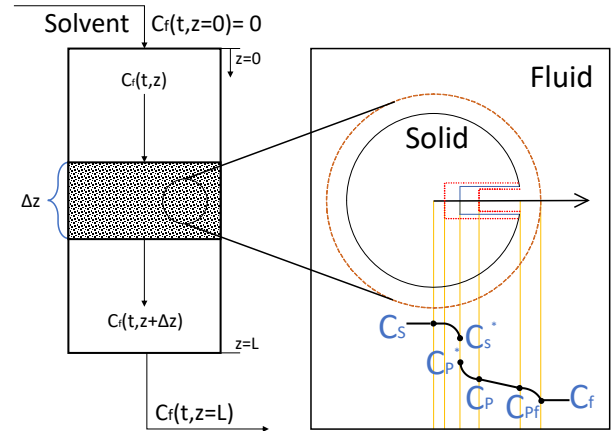


Figure 1: The extraction mechanism

Bulley et al. [2] suggest a process where the driving force for extraction is given by the difference between concentration of the solute in the bulk, c_f , and in the centre of the pore, c_p^* . The concentration c_p^* is in equilibrium with c_s according to an equilibrium relationship. The rate of extraction is thus $r_e(c_f - c_p^*(c_s))$.

On the other hand, Reverchon [1] proposes a driving force given by the difference between c_s and c_p^* . c_p^* is determined by an equilibrium relationship with c_f and the extraction rate is $r_e(c_s - c_p^*(c_f))$.

The kinetic term, denoted as equation 4, corresponds to a solute transfer rate between both phases. This term is made of the overall diffusion coefficient and the concentration gradient (between one phase and its equilibrium concentration), which acts as a driving force for the process. The mass transfer kinetic (Eq. 4) describes a diffusion rate of the solute from solid particles to the solvent. The kinetic term consists of the overall diffusion coefficient and the concentration gradient, which acts as a driving force for the process. Based on the work of Bulley et al. [2], Reverchon [1] proposed to define the kinetic terms as

$$r_e(t, z) = \frac{D_i(T(t, z))}{\mu l^2} (q(t, z) - q^*(t, z)) \quad (4)$$

where $D_i(T(t, z))$ corresponds to the overall diffusion coefficient and $q^*(t, z)$ is a concentration at the solid-fluid interface (which according to the internal resistance model is supposed to be at equilibrium with the fluid phase). $q^*(t, z)$ can be calculated based on the equilibrium relationship (Eq. 5).

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

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

According to Bulley et al. [2], a linear equilibrium relationship (Eq. 5) can be used to find an equilibrium concentration of the solute in the fluid phase $c_f^*(t, z)$ is based on concentration of the solute in the solid phase $c_s(t, z)$

$$c(t, z) = k_p(T(t, z), P(t)) q^*(t, z) \quad (5)$$

The volumetric partition coefficient $k_p(T(t, z), P(t))$ behaves as an equilibrium constant between the solute concentration in one phase and the corresponding equilibrium concentration at the solid-fluid interphase. The $k_p(T(t, z), P(t))$ can be expressed as mass partition factor $k_m(T(t, z))$ according to Spiro and Kandiah [3]. According to Spiro and Kandiah [3], the term $k_p(T(t, z), P(t))$ can be expressed as the function of mass partition factor $k_m(T(t, z))$

$$k_m(T(t, z)) = \frac{k_p(T(t, z), P(t)) \rho_s}{\rho(T(t, z), P(t))} \quad (6)$$

Equation 7 is the full representation of the kinetic term.

$$r_e(t, z) = -\frac{D_i(T(t, z))}{\mu l^2} \left(q(t, z) - \frac{\rho_s}{k_m(T(t, z)) \rho(T(t, z), P(t))} c(t, z) \right) \quad (7)$$

2.1.5. Heat balance

The heat balance equation (Eq. 8) was developed, assuming the existence of a pseudo-homogeneous phase, which properties are the mean between fluid and solid phases (the amount of solute is considered small enough not to affect the overall heat balance). Equation 8 contains the convection and the diffusion terms. It is considered that there is no heat loss through the wall, and there is no heat generation in the system. The temperature of the extractor can be changed only by increasing the temperature of the inlet stream. The pseudo-homogeneous phase is assumed to flow only in the axial direction. The numerator of the factor in front of the convection term of the heat equation contains only the specific heat of the fluid $C_p(T(t, z), P(t))$ because

the solid phase is stationary. Therefore, this factor can be understood as the fraction of the fluid's total heat through convection. On the other hand, the axial heat diffusion is calculated based on the definition of thermal diffusivity for the fluid, as explained in the appendix.

The heat balance (Eq. 8), is based on Srinivasan and Depcik [4], and consists of convective and diffusive terms. It follows the assumption of a pseudo-homogeneous phase, which properties are the mean between fluid and solid phases. It is considered that there is no heat loss through the walls, and there is no heat generation in the system. The temperature of the extractor can be changed only by manipulating the temperature of the inlet stream $T_{Inlet}(t)$.

$$\begin{aligned} \frac{\partial T(t, z)}{\partial t} = & \underbrace{\frac{F(t) C_p(T(t, z), P(t))}{A[(1 - \epsilon) \rho(T(t, z), P(t)) C_p(T(t, z), P(t)) + \epsilon \rho_s C_{ps}]} \frac{\partial T(t, z)}{\partial z}}_{\text{Convection}} + \\ & \underbrace{D_e^T(T(t, z), P(t)) \frac{\partial^2 T(t, z)}{\partial z^2}}_{\text{Diffusion}} \end{aligned} \quad (8)$$

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

2.1.6. Extraction yield

The efficiency of the process (the yield) is calculated according to one of Eq. 9, which evaluates the mass of solute at the exit of the extraction unit and sums it. The integral form of the measurement equation can be transformed into the differential form, and augmented with model equations to be solved simultaneously.

$$y(t) [kg] = \int_{t_0}^{t_f} Q(t, z) \left[\frac{m^3}{s} \right] c_f(t, z) \Big|_{z=L} \left[\frac{kg}{m^3} \right] dt [s] \quad (9)$$

$$y(t) [kg] = \int_{t_0}^{t_f} \frac{F(t)}{\rho(t, z)} \left[\frac{kg}{s} \left(\frac{kg}{m^3} \right)^{-1} \right] c_f(t, z) \Big|_{z=L} \left[\frac{kg}{m^3} \right] dt [s] \quad (10)$$

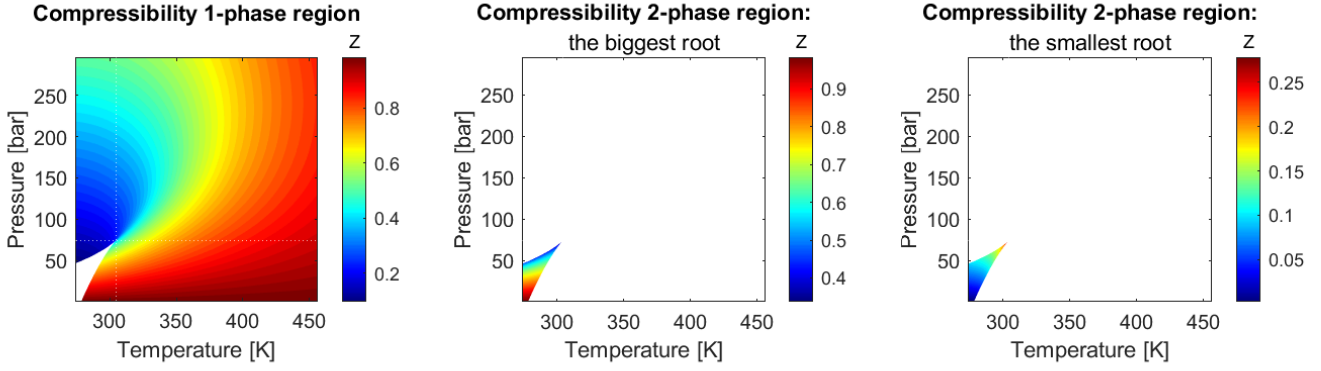
$$\frac{dy}{dt} \left[\frac{kg}{s} \right] = Q(t, z) \left[\frac{m^3}{s} \right] c_f(t, z) \Big|_{z=L} \left[\frac{kg}{m^3} \right] \quad (11)$$

$$\frac{dy}{dt} \left[\frac{kg}{s} \right] = \frac{F(t)}{\rho(t, z)} \left[\frac{kg}{s} \left(\frac{kg}{m^3} \right)^{-1} \right] c_f(t, z) \Big|_{z=L} \left[\frac{kg}{m^3} \right] \quad (12)$$

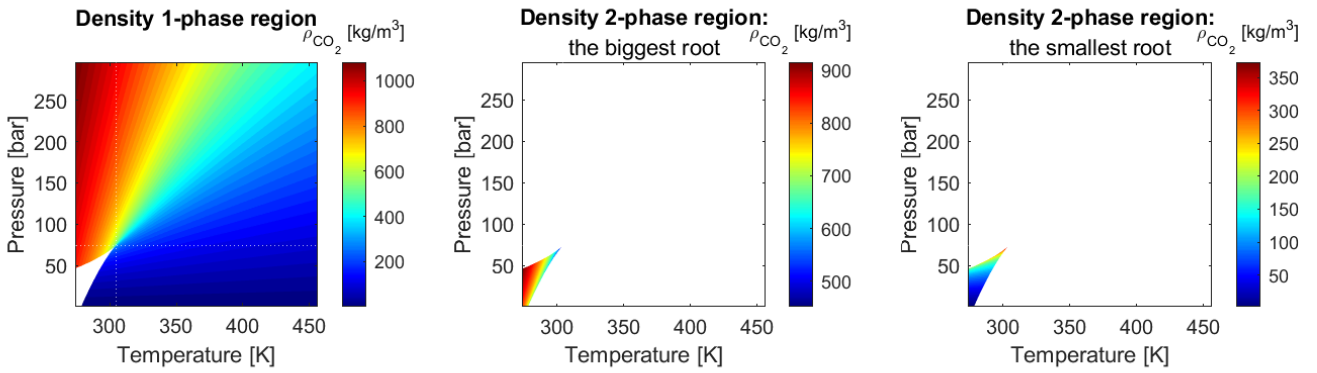
2.1.7. Thermodynamic

At standard atmospheric pressure and temperature, the CO_2 behaves as an ideal gas, and its compressibility factor equals to unity. However, at high temperature and pressure, the compressibility factor varies from unity, due to real gas effects. In order to predict this real gas effects, the Peng-Robinson equation of state (P-R EOS) is used to compute properties of CO_2 . As the density is obtained from the continuity equation, the P-R EOS can be used to evaluate: compressibility, density and specific heat. The properties of the CO_2 computed as a function of operating conditions (temperature and pressure) are presented on fig. 2

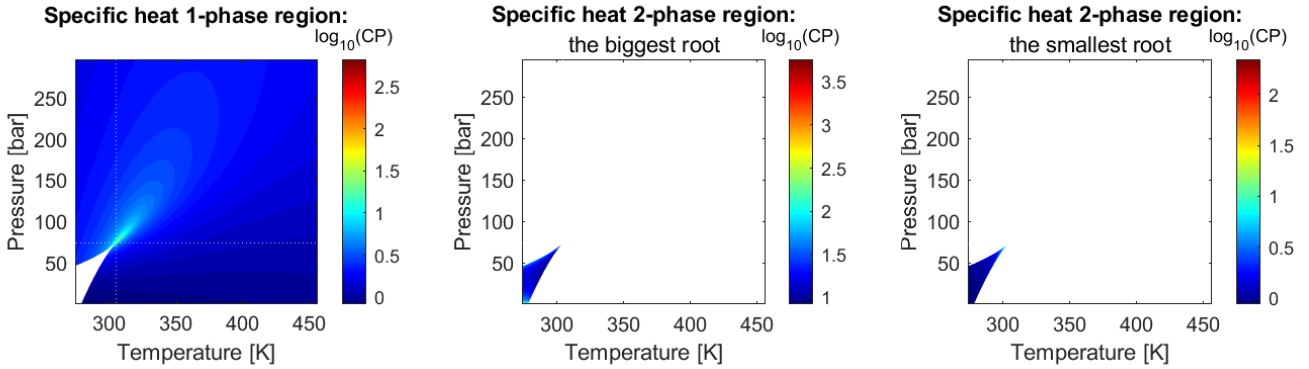
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(a) The compressibility factor based on the Peng-Robinson equation of state



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



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

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

2.1.8. Dependencies

TODO:

1. Viscosity
2. Thermal conductivity
3. Internal diffusion

4. Partition factor

2.1.9. State-space representation

It is assumed that the solvent is free of solute at the entrance of the extractor and that all the solid particles have the same initial solute content q_0 . Moreover, it is considered that the initial temperature of the extractor in every place is

equal to T_0 . Therefore, the initial conditions employed in the simulation are:

$$\begin{aligned} c(t=0, z) &= 0 \\ q(t=0, z) &= q_0 \\ T(t=0, z) &= T_0 \end{aligned}$$

The process model can be written in a general form:

$$\begin{bmatrix} \frac{\partial c(t, z)}{\partial t} \\ \frac{\partial q(t, z)}{\partial t} \\ \frac{\partial T(t, z)}{\partial t} \end{bmatrix} = \begin{bmatrix} \phi_1(c(t, z), q(t, z), T(t, z); \theta) \\ \phi_2(c(t, z), q(t, z), T(t, z); \theta) \\ \phi_3(c(t, z), q(t, z), T(t, z); \theta) \end{bmatrix} = \phi(t, z; \theta) = \frac{\partial \chi(t, z)}{\partial t} \quad (14)$$

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

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

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

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

In a state-space sense, the state variables of the system are the local concentrations of solute in the fluid and solid phases ($c(t, z)$ and $q(t, z)$, respectively), and the local temperature of the pseudo-homogeneous phase ($T(t, z)$). The controllable input variables are the mass flow-rate and temperature of the solvent in the feed ($F_{in}(t) = F(t)$ and $T_{in}(t) = T(t, z = 0)$, respectively) and the pressure in the

extractor ($P(t, z) = P(t)$). We also assume that extraction yield can be modelled as a function of a known initial mass of solute in the solid phase and it can be measured after the separator ($Y(t)$). The system is controllable by manipulating the flow-rate and temperature of CO₂ in the feed, and the pressure in the extractor.

2.2. Low Mach number expansion

As discussed by Lions [5], the low Mach number equations are a subset of the fully compressible equations of motion (continuity, momentum and energy). Such a set of equations allow for large variations in gas density but it is consider to be acoustically incompressible. The low Mach number equations are preferred over the full compressible equations for low speed flow problems

$$\left(M_a = \frac{|V|}{\sqrt{\partial P / \partial \rho}} \ll 1 \right)$$

to avoids the need to resolve fast-moving acoustic signals. The equations are derived from the compressible equations based on the perturbation theory. The perturbation theory develops an expression for the desired solution in terms of a formal power series known as a perturbation series in some "small" parameter ζ , that quantifies the deviation from the exactly solvable problem. The leading term in this power series is the solution of the exactly solvable problem, while further terms describe the deviation in the solution, due to the deviation from the initial problem.

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

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

The conservative non-dimensional equations of motion becomes

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

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

$$\begin{aligned} P_\zeta &= P_0 + P_1 \zeta + P_2 \zeta^2 + \mathcal{O}(\zeta^3) \\ \rho_\zeta &= \rho_0 + \rho_1 \zeta + \mathcal{O}(\zeta^2) \\ V_\zeta &= V_0 + V_1 \zeta + \mathcal{O}(\zeta^2) \\ T_\zeta &= T_0 + T_1 \zeta + \mathcal{O}(\zeta^2) \\ e_\zeta &= e_0 + e_1 \zeta + \mathcal{O}(\zeta^2) \end{aligned}$$

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

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

The continuity equation become

$$\frac{\partial (\rho_0 A_f)}{\partial t} + \frac{\partial (\rho_0 A_f V_0)}{\partial z} = 0 \quad (15)$$

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

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

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

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

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

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

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

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

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

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

The non-conservative form of the energy equation become

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

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

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

If isothermal case is assumed then, the energy equation becomes

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

which leads to

$$\frac{\partial A_f V}{\partial z} = 0 \quad (16)$$

In one-dimensional case, the equation 16 become equivalent of $\text{div}(A_f V) = 0$, which known as the incompressibility condition (Lions [5]).

2.3. Parameter estimation

Conceptually, the unobservable error $\epsilon(t)$ is added to the deterministic model output, $y(t)$, to give the observable dependent variable $Y(t)$, for example the experimental process output. For discrete observations:

$$Y(t_i) = y(t_i) + \epsilon(t_i) \quad (17)$$

and for continuous variables:

$$Y(t) = y(t) + \epsilon(t) \quad (18)$$

The objective in parameter estimation is to obtain the "best" estimate of θ based on the continuous observations $Y(t)$ or the discrete observations $Y(t_i)$. We assume that $x(t)$ is given a priori (for example as a solution of process model) but θ is to be estimated over the time interval $0 \leq t \leq t_n$ from discrete observation described by the following relation:

$$Y(t_i) = \mathbf{h}(t_i)y(t_i) + \epsilon(t_i) \quad 1 \leq i \leq n \quad (19)$$

where $Y(t_i)$ is an $n \times 1$ column vector, $\mathbf{h}(t_i)$ is an $n \times v$ matrix given a priori, and $\epsilon(t_i)$ is an $n \times 1$ column vector ("noise" vector) whose elements are the unobservable errors. The above equation can be written in general form as:

$$Y(t_i) = y(\theta, t_i) + \epsilon(t_i) \quad (20)$$

where y is the output model, which is a function of θ and time t_i .

Because of the difficulty of obtaining analytical solutions to the deterministic process model, experiments have been arranged whereby the vector of derivatives $dY(t_i)/dt$ is measured rather than $Y(t_i)$ itself. In such cases, it is assumed that the unobservable error is added to the deterministic derivative $dy(\theta, t_i)/dt$ as follows:

$$\frac{dY(t_i)}{dt} = \frac{dy(\theta, t_i)}{dt} + \epsilon(t_i) \quad (21)$$

2.4. Least squares estimation

A least squares parameter estimation does not require prior knowledge of the distribution of unobservable errors, yield unbiased estimates, that is, $\mathbb{E}\{\hat{Y}(t) - y(t)\} = 0$, and results in the minimum variance among all linear unbiased estimators. If the observations Y for the model responses are continuous functions of time from $t = 0$ to $t = t_f$, the Markov (or "rigorous least squares") criterion is to minimize:

$$\phi = \frac{1}{2} \int_0^{t_f} [Y(t) - y(\theta, t)]^T \Gamma^{-1} [Y(t) - y(\theta, t)] dt \quad (22)$$

$$\hat{\theta} = \arg \min_{\theta \in \Theta} \phi \quad (23)$$

where Γ is the covariance matrix (or perhaps a matrix of appropriate weights), $\hat{\theta}$ is the parameter estimate, Θ is the parameter space, and ϕ is the time integrated value of the error squared ("integral squared error"). If the observations are made at discrete instants of time, t_i , $i = 1, 2, \dots, n$, the Markov criterion is to minimize:

$$\phi = \frac{1}{2} \sum_{i=1}^n [Y(t_i) - y(\theta, t_i)]^T \Gamma^{-1} [Y(t_i) - y(\theta, t_i)] \quad (24)$$

$$\hat{\theta} = \arg \min_{\theta \in \Theta} \phi \quad (25)$$

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

2.5. Weighted sum of squares - Cumulative data

One characteristic feature of certain special experiments is the use of the same batch of materials for the entire series of measurements. If unobservable error in the first observation is designated as ϵ_1 , the second error observation ϵ'_2 includes ϵ_1 plus a random component introduced side from ϵ_1 , or $\epsilon'_2 = \epsilon_1 + \epsilon_2$. The error in the third observation is $\epsilon'_3 = \epsilon_1 + \epsilon_2 + \epsilon_3$, and so forth. Mandel [6] distinguished between the usually assumed type of independent measuring error in the dependent variable and a 'cumulative' or interval error in which each new observation includes the error of the previous observations. Cumulative errors, arising because of the fluctuations as a function of time in the process itself due to small changes in operating, are not independent - only the differences in measurement from one period to the next are independent. Thus, if we consider two model:

Model A - independent error:

$$Y(t_i) = y(\theta, t_i) + \epsilon_i \quad i = 1, 2, \dots, n$$

Model B - cumulative data:

$$Y(t_j) - Y(t_{j-1}) = y(\theta, t_j) - y(\theta, t_{j-1}) + \epsilon_j, \quad j = 1, 2, \dots, n$$

or

$$Y(t_i) = \sum_{j=1}^i (Y(t_j) - Y(t_{j-1})) = \sum_{j=1}^i (y(\theta, t_j) - y(\theta, t_{j-1})) + \sum_{j=1}^i \epsilon_j$$

in which ϵ_i are independent random variables with $\mathbb{E}\{\epsilon_i\} = 0$ and $\text{Var}\{\epsilon_i\} = \sigma_1^2$, a constant. The ϵ_j are also random independent variables because they represent differences such as $\epsilon'_3 - \epsilon'_2 = (\epsilon_1 + \epsilon_2 + \epsilon_3) - (\epsilon_1 + \epsilon_2) = \epsilon_3$. We assume that $\mathbb{E}\{\epsilon_j\} = 0$ and $\text{Var}\{\epsilon_j\} = \sigma_1^2 (y_j - y_{j-1})$; i.e., the variance of ϵ_j can be a function of the test interval. The experimental point tend to stay on one side of the regression line of the best fit for Model B.

The best unbiased estimate of the Model B is obtained by minimizing the weighted sum of squares:

$$\hat{\theta} = \arg \min_{\theta \in \Theta} \sum_{j=1}^n \frac{[(Y(t_j) - Y(t_{j-1})) - (y(\theta, t_j) - y(\theta, t_{j-1}))]^2}{y(\theta, t_j) - y(\theta, t_{j-1})}$$

2.6. Maximum likelihood estimation

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

The posterior probability density $p(\theta|y)$ can be expressed as the ratio of two probability densities if we make use of the analogue for continuous variables of Equation 94:

$$p(\theta|y(t_n), \dots, y(t_1)) = \frac{p(\theta, y(t_n), \dots, y(t_1))}{p(y(t_n), \dots, y(t_1))} \quad (26)$$

The numerator of the right-hand side of Equation 26 using Equation 95a becomes

$$p(\theta, y(t_n), \dots, y(t_1)) = p(y(t_n)|\theta, y(t_{n-1}), \dots, y(t_1)) \cdot p(\theta, y(t_{n-1}), \dots, y(t_1)) \quad (27)$$

These operations can be continued repetitively until we get

$$p(\theta, y(t_n), \dots, y(t_1)) = p(\theta) \prod_{i=1}^n p(y(t_i)|\theta, y(t_{i-1}), \dots, y(t_1)) \quad (28)$$

Examination of Equation 20 shows that $Y(t_i)$ depends only on t_i , θ and $\epsilon(t_i)$ and is not conditioned by any previous measurement. Consequently, we can write

$$p(y(t_i)|\theta, y(t_{i-1}), \dots, y(t_1)) = p(y(t_i)|\theta) \quad (29)$$

provided Equation 20 is observed as a constraint. The desired joint conditional probability function is thus

$$p(\theta|y(t_n), \dots, y(t_1)) = \frac{p(\theta) \prod_{i=1}^n p(y(t_i)|\theta)}{p(y(t_n), \dots, y(t_1))} \quad (30)$$

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

$$p(\theta|y(t_n), \dots, y(t_1)) = \prod_{i=1}^n p(y(t_i)|\theta) = \prod_{i=1}^n L(\theta|y(t_i)) \quad (31)$$

By collecting a random sample of values of the random variable y and selecting the values of θ that maximize the likelihood function $L(\theta|y)$, a function described in chapter A.2 in connection with Bayes' theorem. Such estimators, $\hat{\theta}$, are known as maximum likelihood estimators. In effect, the methods selects those values of θ that are at least as likely to generate the observed sample as any other set of values of the parameters if the probability density of the random variable y were to be extensively simulated through use of the probability density $p(y|\theta)$. In making a maximum likelihood estimate, we assume that the form of the probability density (only the θ need be determined) and that all possible values of θ are equally likely before experimentation.

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

$$L(\theta|y(t_n), \dots, y(t_1)) = \prod_{i=1}^n L(\theta|y(t_i)) = p(y(t_1)|\theta) p(y(t_2)|\theta) \dots p(y(t_n)|\theta) \quad (32)$$

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

$$\ln L = \ln p(y(t_1)|\theta) + \ln p(y(t_2)|\theta) + \dots + \ln p(y(t_n)|\theta) = \sum_{i=1}^n \ln p(y(t_i); \theta) \quad (33)$$

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

$$p(\theta, \sigma|y(t_n), \dots, y(t_1)) = \prod_{i=1}^n \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{1}{2\sigma^2} (Y(t_i) - y(\theta, t_i))^2 \right] \\ L(\theta, \sigma|y(t_n), \dots, y(t_1)) = \prod_{i=1}^n \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{1}{2\sigma^2} (Y(t_i) - y(\theta, t_i))^2 \right] \quad (34)$$

where σ is the variance

By taking the natural logarithm of the Equation 34, the final form of the objective function can be obtained:

$$\ln L = -n \ln \sqrt{2\pi} - \frac{n}{2} \ln \sigma - \frac{\sum_{i=1}^n [Y(t_i) - y(\theta, t_i)]^2}{2\sigma^2} \quad (35)$$

The parameter estimation problem can be formulated as follow:

$$\begin{aligned} \hat{\theta}_{MLE} &= \arg \max_{\sigma, \theta \in \Theta} \ln L = \arg \max_{\sigma, \theta \in \Theta} p(\theta|y) \\ \text{subject to} & \quad \dot{x} = f(t, x, \theta) \\ & \quad \dot{\theta} = 0 \\ & \quad y = y(x) \end{aligned} \quad (36)$$

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

$$\frac{\partial \ln L}{\partial \theta} = \frac{\partial \sum_{i=1}^n \ln p(y(t_i)|\theta)}{\partial \theta} = 0 \quad (37)$$

Solution of Equations 37 yield the desired estimates $\hat{\theta}$. For some models, these equations can be explicitly solved for $\hat{\theta}$ but in general no closed-form solution to the maximization problem is known or available, and an MLE can only be found via numerical optimization.

By carrying out this operation, under fairly unrestrictive conditions, it can be shown that as n approaches infinity the maximum likelihood estimates have the desirable asymptotic properties:

- (1) $\lim_{n \rightarrow \infty} \mathbb{E}\{\hat{\theta}\} = \theta$
- (2) $\left[\sqrt{n}(\hat{\theta} - \theta) \right]$ is normally distributed

and for the case of two parameters:

$$(3) \lim_{n \rightarrow \infty} \text{Var}\{\hat{\theta}\} = \frac{1}{n} \left[\mathbb{E} \left\{ \left(\frac{\partial \ln p}{\partial \theta} \right)^2 \right\} \right]^{-1} \frac{1}{1 - \rho_{\hat{\theta}}^2}$$

where $\rho_{\hat{\theta}}^2$ is the matrix of correlation coefficients.

Maximum likelihood estimates are not necessarily unbiased. Maximum likelihood estimates, however are efficient and, hence, consistent estimates. Furthermore, where a sufficient estimate can be obtained, the maximum likelihood method will obtain it. Finally, if $\hat{\theta}$ is a maximum likelihood estimator of θ , the $f(\hat{\theta})$ is a maximum likelihood estimator of $f(\theta)$, a function of θ .

3. Results

4. Conclusions

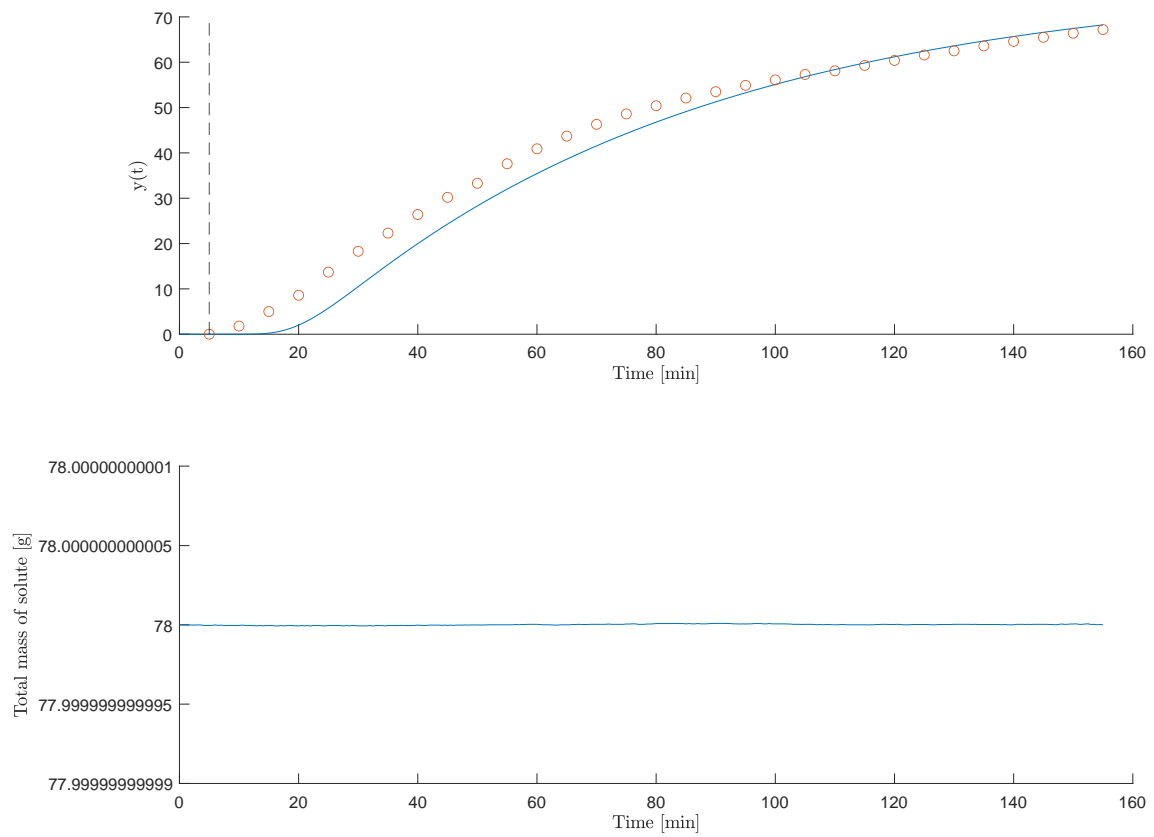


Figure 3: The yield curve vs dataset

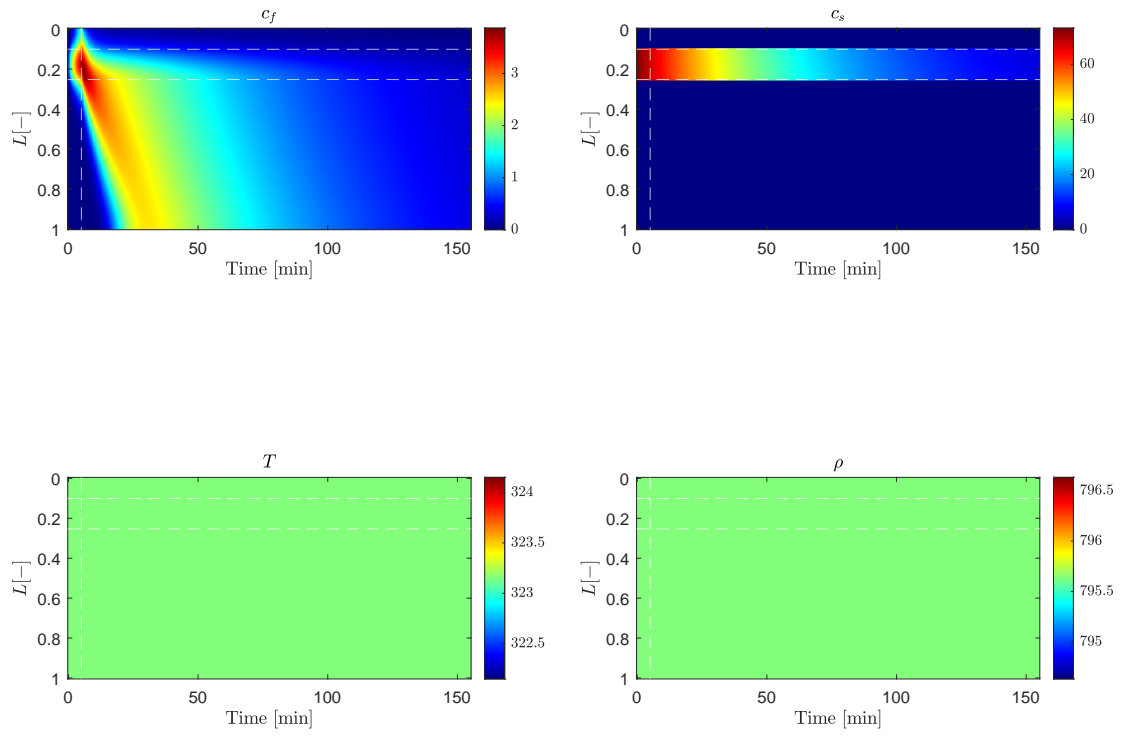


Figure 4: The fluid density based on the Peng-Robinson equation of state

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A. Appendix

A.1. Governing equations

A.1.1. Mass continuity

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

$$\frac{\partial}{\partial t} \iiint_{V_f} \rho_f dV_f + \iint_S \rho_f \mathbf{V} \cdot d\mathbf{S} = 0 \quad (38)$$

We apply this equation to the shaded control volume shown in Fig. 5.

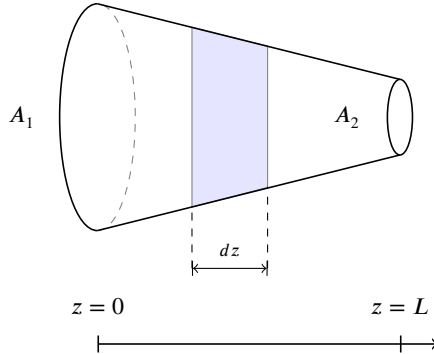


Figure 5: Control volume for deriving partial differential equation for unsteady, quasi-one-dimensional flow

This control volume is a slice of an extractor, where the infinitesimal 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. 5, the volume integral in Eq. 38 becomes, in the limit as dz becomes very small,

$$\frac{\partial}{\partial t} \iiint_{V_f} \rho_f dV_f = \frac{\partial}{\partial t} (\rho_f A_f dz) \quad (39)$$

where $A dz$ is the volume of the control volume in the limit of dz becoming vanishingly small. The surface integral in Eq. 38 becomes

$$\iint_S \rho_f \mathbf{V} \cdot d\mathbf{S} = -\rho_f V A_f + (\rho_f + d\rho_f)(V + dV)(A_f + dA_f) \quad (40)$$

where 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

$$\begin{aligned} \iint_S \rho_f \mathbf{V} \cdot d\mathbf{S} = & -\rho_f V A_f + \rho_f V A_f + \rho_f V dA_f + \rho_f A_f dV \\ & + \rho_f dV dA_f + V A_f d\rho_f + V d\rho_f dA_f + A_f d\rho_f dV + d\rho_f dV dA_f \end{aligned} \quad (41)$$

In the limit as dz becomes very small, the terms involving products of the differential in Eq. 41, such as $\rho_f dV dA_f$, $d\rho_f dV dA_f$, go to zero much faster than those terms involving only one differential. Hence, all terms involving products of differentials can be dropped, yielding in the limit as dz becomes very small

$$\iint_S \rho_f \mathbf{V} \cdot d\mathbf{S} = \rho_f V dA_f + \rho_f A_f dV + V A_f d\rho_f \quad (42)$$

Substituting Eqs. 39 and 42 into 38, we have

$$\frac{\partial (\rho_f A_f)}{\partial t} + \frac{\partial (\rho_f A_f V)}{\partial z} = 0 \quad (43)$$

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

$$\frac{\partial (\rho_f A\epsilon(z))}{\partial t} + \frac{\partial (\rho_f A\epsilon(z)V)}{\partial z} = 0 \quad (44)$$

The equation can be simplified by cancel out a constant A

$$\frac{\partial (\rho_f \epsilon(z))}{\partial t} + \frac{\partial (\rho_f \epsilon(z)V)}{\partial z} = 0 \quad (45)$$

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

$$\frac{\partial (\rho_f \epsilon(z))}{\partial t} + \frac{\partial (\rho_f u)}{\partial z} = 0 \quad (46)$$

A.1.2. Transport of a species

The transport of a chemical species, in this case a solute, can be described by analogous equation to the Eq. 38 with additional terms on the right-hand side. The first term on the right-hand side describes that a substance goes from high density regions to low density regions and is based on the Fick's law $\left(J_{diff} = D \frac{\partial C_f}{\partial z} \right)$. The other term corresponds for the mass transfer between solid and fluid phases, which is treated as a source term.

$$\frac{\partial}{\partial t} \iiint_{V_f} C_f dV_f + \iint_S C_f \mathbf{V} \cdot d\mathbf{S} = \iint_S J_{diff} \cdot \mathbf{n} d\mathbf{S} + \frac{\partial}{\partial t} \iiint_{V_s} C_s dV_s \quad (47)$$

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

$$\frac{\partial}{\partial t} \iiint_{V_f} C_f dV_f = \frac{\partial}{\partial t} (C_f A_f dz) \quad (48)$$

$$\frac{\partial}{\partial t} \iiint_{V_s} C_s dV_s = \frac{\partial}{\partial t} (C_s A_s dz) \quad (49)$$

The surface integrals in the limit of dz becomes

$$\iint_S C_f \mathbf{V} \cdot d\mathbf{S} = C_f V dA_f + C_f A_f dV + V A_f dC_f \quad (50)$$

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

$$\iint_S J_{diff} \mathbf{n} \cdot d\mathbf{S} = \iiint_{V_f} \nabla J_{diff} dV_f = \nabla \cdot \iiint_{V_f} J_{diff} dV_f = \nabla \cdot (J_{diff} A_f dz) \quad (51)$$

By substituting the equations derived above into Eq. 47 we obtain

$$\frac{\partial (C_f A_f)}{\partial t} + \frac{\partial (C_f A_f V)}{\partial x} = \frac{\partial (C_s A_s)}{\partial t} + \frac{\partial (J_{diff} A_f)}{\partial z} \quad (52)$$

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

$$\frac{\partial (C_f \epsilon)}{\partial t} + \frac{\partial (C_f u)}{\partial x} = \frac{\partial (C_s (1 - \epsilon))}{\partial t} + \frac{\partial (J_{diff} \epsilon)}{\partial z} \quad (53)$$

By expanding above equation, splitting variable and assuming that $\frac{\partial \epsilon}{\partial t} = 0$ we get

$$\frac{\partial C_f}{\partial t} + \frac{u}{\epsilon} \frac{\partial C_f}{\partial z} + \frac{C_f}{\epsilon} \frac{\partial u}{\partial z} = \frac{1 - \epsilon}{\epsilon} \frac{\partial C_s}{\partial t} + \frac{D}{\epsilon} \frac{\partial C_f}{\partial z} \frac{\partial \epsilon}{\partial z} + \frac{\partial}{\partial z} \left(D \frac{\partial C_f}{\partial z} \right) \quad (54)$$

The equation can be further simplified if $\frac{\partial u}{\partial z} = \frac{\partial \epsilon}{\partial z} = D = 0$, 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.

$$\frac{\partial C_f}{\partial t} + \frac{u}{\epsilon} \frac{\partial C_f}{\partial z} = \frac{1 - \epsilon}{\epsilon} \frac{\partial C_s}{\partial t} \quad (55)$$

The Eq. 55 is equivalent to the equation presented by Reverchon [1].

A.1.3. Momentum conservation

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

$$\frac{\partial}{\partial t} \iiint_{V_f} (\rho_f V_z) dV_f + \iint_S (\rho_f V_z \mathbf{v}) \cdot d\mathbf{S} = \iint_S (PdS)_z \quad (56)$$

where V_z is the z component of the velocity.

We the momentum conservation to the shaded control volume in Fig. 5, the integrals on the left side are evaluated in the same manner as discussed above in the regard to the continuity equation. That is,

$$\frac{\partial}{\partial t} \iiint_{V_f} (\rho_f V_z) dV_f = \frac{\partial}{\partial t} (\rho_f V A_f dz) \quad (57)$$

equation
and

$$\iint_S (\rho_f V_z \mathbf{v}) \cdot d\mathbf{S} = -\rho_f V^2 + (\rho_f + d\rho_f) (V + dV)^2 (A + dA) \quad (58)$$

The evaluation of the pressure force term on the right side of Eq. 56 can be understood based on the Fig. 6. Here, the z components of the vector $Pd\mathbf{S}$ are shown on all four side of the control volume. Remember that $d\mathbf{S}$ is

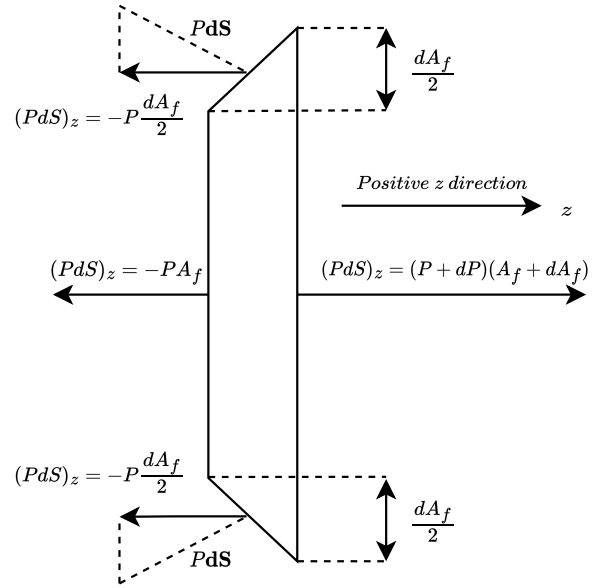


Figure 6: The forces in the z direction acting on the control volume

assumed to points away from the control volume; hence any z component $(PdS)_z$ that acts toward the left (in the negative z direction) is a negative quantity, and any z component that acts toward the right (in the positive z direction) is a positive quantity. Also note that the z component of $Pd\mathbf{S}$ acting on the top and the bottom inclined faces of the control volume in Fig. 6 can be expressed as the pressure P acting on the component of the inclined are projected perpendicular to the z direction, $dA_f/2$; hence, the contribution of each inclined face (top or bottom) to the pressure integral in Eq. 56 is $-P(dA_f/2)$. All together, the right-hand side of Eq. 56 is expressed as follows:

$$\iint (PdS)_z = -PA_f + (P + dP)(A + dA_f) - 2P \frac{dA_f}{2} \quad (59)$$

Substituting Eqs. 57 to 59 into Eq. 56, we have

$$\begin{aligned} \frac{\partial}{\partial t} (\rho_f V A_f dz) - \rho_f V^2 A_f + (\rho_f + d\rho_f)(V + dV)^2 (A_f + dA_f) \\ = PA_f - (P + dP)(A + dA_f) + PdA_f \end{aligned} \quad (60)$$

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

$$\frac{\partial}{\partial t} (\rho_f V A_f dz) + d(\rho_f V^2 A_f) = -AdP \quad (61)$$

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

$$\frac{\partial (\rho_f V A_f)}{\partial t} + \frac{\partial (\rho_f V^2 A_f)}{\partial z} = -A_f \frac{\partial P}{\partial z} \quad (62)$$

The Eq. 62 can be expanded further by assuming that $A_f = A\epsilon$

$$\frac{\partial (\rho_f V A \epsilon)}{\partial t} + \frac{\partial (\rho_f V^2 A \epsilon)}{\partial z} = -A \epsilon \frac{\partial P}{\partial t} \quad (63)$$

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

$$\frac{\partial(\rho_f V \epsilon)}{\partial t} + \frac{\partial(\rho_f V^2 \epsilon)}{\partial z} = -\epsilon \frac{\partial P}{\partial t} \quad (64)$$

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

$$\frac{\partial(\rho_f u)}{\partial z} + \frac{\partial(\rho_f u^2/\epsilon)}{\partial z} = -\epsilon \frac{\partial P}{\partial z} \quad (65)$$

Eq. 62 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. 62

$$\frac{\partial(\rho_f V A_f)}{\partial t} - V \frac{\partial(\rho_f A_f)}{\partial t} + \frac{\partial(\rho_f V^2 A_f)}{\partial z} - V \frac{\partial(\rho_f V A_f)}{\partial z} = -A_f \frac{\partial P}{\partial z} \quad (66)$$

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

$$\rho_f A_f \frac{\partial V}{\partial t} + \rho_f A_f V \frac{\partial V}{\partial z} = -A_f \frac{\partial P}{\partial z} \quad (67)$$

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

$$\rho_f \frac{\partial V}{\partial t} + \rho_f V \frac{\partial V}{\partial z} = -\frac{\partial P}{\partial z} \quad (68)$$

The Eq. 68 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 $u = V\epsilon$.

$$\rho_f \frac{\partial(u/\epsilon)}{\partial t} + \rho_f \frac{u}{\epsilon} \frac{\partial(u/\epsilon)}{\partial z} = -\frac{\partial P}{\partial z} \quad (69)$$

By expanding all the terms of equation above, we get

$$\frac{\rho_f}{\epsilon} \frac{\partial u}{\partial t} + \rho_f u \frac{\partial \epsilon^{-1}}{\partial t} + \rho_f \frac{u}{\epsilon} \frac{\partial u}{\partial z} + \rho_f \frac{u}{\epsilon} \frac{\partial \epsilon^{-1}}{\partial z} = -\frac{\partial P}{\partial z} \quad (70)$$

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

$$\frac{\rho_f}{\epsilon} \left(\frac{\partial u}{\partial t} + \frac{u}{\epsilon} \frac{\partial u}{\partial z} + u^2 \frac{\partial \epsilon^{-1}}{\partial z} \right) = -\frac{\partial P}{\partial z} \quad (71)$$

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

$$\frac{\rho_f}{\epsilon} \left(\frac{\partial u}{\partial t} + \frac{u}{\epsilon} \frac{\partial u}{\partial z} \right) = -\frac{\partial P}{\partial z} \quad (72)$$

The Eq. 72 represents non-conservative form of the momentum equation for quasi-one-dimensional flow with no body forces and constant porosity.

A.1.4. Energy conservation

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

$$\frac{\partial}{\partial t} \iiint_{V_f} \rho_f \left(e_f + \frac{V^2}{2} \right) dV_f + \iint_S \rho_f \left(e_f + \frac{V^2}{2} \right) \mathbf{v} \cdot d\mathbf{S} = - \iint_S (P\mathbf{V}) \cdot d\mathbf{S} \quad (73)$$

Applied to the shaded control volume in Fig. 5, and keeping in mind the pressure forces shown in Fig. 6, Eq. 73 becomes

$$\frac{\partial}{\partial t} \left[\rho_f \left(e_f + \frac{V^2}{2} \right) A_f dz \right] - \rho_f \left(e_f + \frac{V^2}{2} \right) V A_f$$

$$+ (\rho_f + d\rho_f) \left[e_f + de_f + \frac{(V + dV)^2}{2} \right] (V + fV) (A_f + dA_f) \\ = - \left[-PV A_f + (P + dP)(V + dV)(A_f + dA_f) - 2 \left(PV \frac{dA_f}{2} \right) \right] \quad (74)$$

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

$$\frac{\partial}{\partial t} \left[\rho_f \left(e_f + \frac{V^2}{2} \right) A_f dz \right] + d(\rho_f r_f A_f) + \frac{(\rho_f V^3 A_f)}{2} = -d(P A_f V) \quad (75)$$

or

$$\frac{\partial}{\partial t} \left[\rho_f \left(e_f + \frac{V^2}{2} \right) A_f dz \right] + d \left[\rho_f \left(e_f + \frac{V^2}{2} \right) V A_f \right] = -d(P A_f V) \quad (76)$$

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

$$\frac{\partial [\rho_f (e_f + V^2/2) A]}{\partial t} + \frac{\partial \rho_f (e_f + V^2/2) V A_f}{\partial z} = -\frac{\partial (P A_f V)}{\partial z} \quad (77)$$

Equation 77 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. 62 is multiplied by V and then subtracted from Eq. 77

$$\frac{\partial(\rho_f e_f A_f)}{\partial t} + \frac{\partial(\rho_f e_f V A_f)}{\partial z} = -P \frac{\partial A_f V}{\partial z} \quad (78)$$

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 43, by e_f and subtracting it from 78, yielding

$$\rho_f A_f \frac{\partial e_f}{\partial t} + \rho_f A_f V \frac{\partial e_f}{\partial z} = -P \frac{\partial(A_f V)}{\partial z} \quad (79)$$

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

$$\rho_f \frac{\partial e_f}{\partial t} + \rho_f V \frac{\partial e_f}{\partial z} = -P \frac{V}{A_f} \frac{\partial A_f}{\partial z} \quad (80)$$

or

$$\rho_f \frac{\partial e_f}{\partial t} + \rho_f V \frac{\partial e_f}{\partial z} = -P \frac{\partial V}{\partial z} - PV \frac{\partial(\ln A_f)}{\partial z} \quad (81)$$

Equation 81 is the non-conservative for 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. 81 is that, for a calorically perfect gas, it leads directly to a form of the energy equation in terms of temperature T . For calorically perfect gas $e_f = C_v T$

$$\frac{\partial(\rho_f e_f A_f)}{\partial t} + \frac{\partial(\rho_f e_f V A_f)}{\partial z} = -P \frac{\partial A_f V}{\partial z} + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) \quad (82)$$

TODO: finish derivation of energy equation for real gas and introduce homogenous version of the energy equation

A.2. Bayes theorem

As discussed by Himmelblau [7], the Bayesian approach to estimation make use of prior information. Such prior knowledge can come from theoretical considerations, from the results of previous experiments, or from assumptions by the experimenter. Typically, a Bayesian approach assumes a prior probability distribution of an unknown parameter θ in some parameter space 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 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 :

$$P\{A_i|B\} = \frac{P\{B|A_i\}P\{A_i\}}{P\{B\}} \quad (83)$$

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

$$P\{A_i|B\} = \frac{P\{B|A_i\}P\{A_i\}}{\sum_{i=1}^n P\{B|A_i\}P\{A_i\}} \quad (84)$$

We can interpret these symbols as follows:

1. $P\{A_i\}$ is a measure of our degree of belief that event A_i will occur or that hypothesis A_i is true prior to the acquisition of additional evidence that may alter the measure. $P\{A_i\}$ is denoted the *prior probability*.
2. $P\{A_i|B\}$ is a measure of our degree of belief that event A_i will occur or that hypothesis A_i is true, given additional evidence B pertinent to the hypothesis. $P\{A_i|B\}$ is termed the *posterior probability*.
3. $P\{B|A_i\}$ denotes the likelihood that event B will occur, given that event A_i is true. $P\{B|A_i\}$ is a conditional probability, interpreted in the Bayesian framework as a likelihood, $L(A_i|B)$.

For continuous variable, Bayes' theorem can be more conveniently expressed in terms of the probability density function rather than the probabilities themselves. Equation 84 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

$$p(\theta|X = \mathbf{x}) = p(\theta|\mathbf{x}) = \frac{L(\theta|\mathbf{x})p(\theta)}{\int_{-\infty}^{+\infty} L(\theta|\mathbf{x})p(\theta)d\theta} \quad (85)$$

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

$$\int_{-\infty}^{+\infty} p(\mathbf{x}|\theta)p(\theta)d\theta = p(\mathbf{x}) \quad (86)$$

If the prior distribution is a uniform distribution, that is the prior distribution is a constant, the Equation 85 reduces to

$$p(\theta|\mathbf{x}) = \frac{L(\theta|\mathbf{x})}{\int_{-\infty}^{+\infty} L(\theta|\mathbf{x})d\theta} \quad (87)$$

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 :

$$P(A_1 \text{ or } A_2 \dots \text{ or } A_n) = \sum_{i=1}^n P(A_i) \quad (88)$$

Very often we let

$$\sum_{i=1}^n P(A_i) = 1 \quad (89)$$

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

$$\sum_{i=1}^n q = nq = 1 \quad \text{or} \quad q = \frac{1}{n} = P(A_i) \quad (90)$$

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

$$P(A_1 \cup A_2 \cup \dots \cup A_n) = P(A_1) + P(A_2) + \dots + P(A_n) \quad (91)$$

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

$$P(A \text{ and } B) = P(A)P(B) \quad (92)$$

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

$$P(A \cap B) = P(A)P(B) \quad (93)$$

If the A and B are *dependet* events,

$$P(A|B) = \frac{P(A \cap B)}{P(B)} \quad (94)$$

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

$$P(A \cap B) = P(B)P(A|B) \quad (95a)$$

$$= P(A)P(B|A) \quad (95b)$$

Two kind of probabilities enter Equation 95a (or Equation 95b): 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 93 or 94 is special case of Equation 95a or 95b, because if the event are independent $P(A|B) = P(A)$. For the case of many event, Equation 93 can be expanded to

$$\begin{aligned} P(A_1 \text{ and } A_2 \text{ and } \dots \text{ and } A_n) &= P(A_1) \cdot P(A_2) \cdot \dots \cdot P(A_n) \\ &= \prod_{i=1}^n P(A_i) \end{aligned} \quad (96)$$

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

$$P(A) + P(B) - P(A \cap B) = P(A \cup B) \quad (97)$$

Table 1
Notation

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