

Optimization of the Particle Diameter Profile in a Fixed Bed for Separation of γ -Valerolactone

Thatyana N. Soeiro^a Melissa A. G. Vieira, Reginaldo Guirardello^{*}

School of Chemical Engineering, University of Campinas (Unicamp), Av. Albert Einstein 500, 13083-852, Campinas-SP, Brazil
guira@feq.unicamp.br

Conversion of polysaccharides – cellulose and hemicellulose – into fermentable sugars is one of the factors that makes the production of lignocellulosic ethanol more complex in relation to ethanol produced from feedstock containing sugars or starch. The use of γ -valerolactone (GVL) solvent was recently indicated as an alternative to improve the conversion of these biomass polysaccharides. However, GVL removal before fermentation is an essential step, because its presence has negative effects on the metabolism of sugars by microorganisms. The extraction technique using subcritical CO₂ is able to separate a large amount of GVL. Nonetheless, a complementary method is still required to separate small quantities of GVL remaining in the sugar solution, which can be efficiently performed by fixed bed adsorption. In this process the size of the adsorbent particles plays an important role, because it influences both the mass transfer and the pressure drop in the column. While small diameters favour mass transfer rate, but increase pressure drop, the opposite effect is observed for larger particle sizes. Hence, the aim of this study was to optimize the particle diameter profile of a fixed bed column to perform the separation of γ -valerolactone from a sugar solution with minimum pressure drop and a satisfactory mass transfer coefficient. The optimization problem was formulated as a nonlinear programming and solved by means of the General Algebraic Modeling System (GAMS) software and the IPOPT (Interior Point OPTimizer) solver.

1. Introduction

The production of lignocellulosic ethanol is a complex and expensive process, due to the hydrolysis stage of the lignocellulosic biomass (Bastos, 2007), in which cellulose and hemicellulose are converted into monosaccharides (sugars), which in turn can be transformed into fuels. The use of the γ -valerolactone (GVL) solvent in the conversion of the lignocellulosic biomass has shown some advantages over the application of water alone as solvent (Mellmer et al., 2014), such as increased catalytic activity (Alonso et al., 2013) and the selectivity and efficiency of the reaction (Luterbacher et al., 2014).

A step of GVL separation after hydrolysis is required, due to the fact that the high concentration of this solvent is harmful to the fermentation stage, since it is toxic to the microorganisms that metabolize the sugar to produce ethanol. An extraction method using subcritical CO₂ was able to decrease the concentration of GVL. However, a further separation step was still necessary in order to remove an amount of GVL which still remained in the sugar solution (Luterbacher et al. 2014).

Fixed bed adsorption is a separation process that has demonstrated efficiency as a complementary step for the removal of solvent GVL, and it has been utilized to obtain a higher concentration of sugars in solution (Trindade, 2015a; Trindade et al., 2015b). Trindade (2015a) evaluated the use of four adsorbents in the removal of GVL, and the resin Seapabeads SP 850 was found to be the most efficient.

The efficiency of the adsorption process and pressure drop in the bed is influenced by the size of the adsorbent particle diameters, and so the determination of an optimum particle diameter aims to achieve adequate mass transfer, while at the same time presenting an acceptable pressure drop (Gamarrá, 1994; Cussler, 2007).

Therefore, the objective of this work was to optimize the profile of particle diameters in a fixed bed, for the adsorption of γ -valerolactone (GVL) from an aqueous solution containing GVL, glucose and xylose, in order to meet the requirements of a suitable pressure drop and output concentration of the GVL for the process.

2. Methodology

The problem of optimization of the particle diameter profile was formulated as a nonlinear program and for the development of the mathematical model the following equations were used:

- Material balance inside the particles and in the mobile phase;
- Adsorption isotherm;
- Momentum balance.

Regarding the adsorbent used for adsorption of GVL, the resin Seapabeads SP 850 was considered. According to Trindade (2015a), it has proven to be more efficient in the removal of GVL from the solution compared to the other adsorbents tested. In relation to the adsorption of Glucose (GL), Seapabeads SP 850 was also found to be the best adsorbent, because it removed only a small amount of GL (Trindade, 2015a). According to Sigma Aldrich, producer of Seapabeads SP 850, this resin is a polyaromatic adsorbent, which adsorbs hydrophobic compounds, such as organic species, so it has a favorable property for the system. In addition, the producer also provides a resin granulometry, which is in the range 0.025 - 0.085 cm.

Table 1 presents data obtained from Trindade (2015a), which were used as parameters for the values of the model equations. Table 2 shows the fixed bed operational conditions that were considered for an industrial scale fixed bed column and later used as parameters for the values of the model equations.

Table 1: Specifications of Fixed bed

Parameters	Nomenclature	Value	Unit
Initial concentration	Ce	0.0257	g/cm ³
Adsorption constant	k _p	10.2	cm ³ /g

Table 2: Fixed bed operating conditions

Parameters	Nomenclature	Value	Unit
Flow rate	Q	5000	cm ³ /s
Bed Length	L	1000	cm
Inner Diameter of bed	D	200	cm

2.1 Adsorption Isotherm

The equilibrium was described by Henry linear isotherm, for low solute concentration, following Trindade (2015a), and is described by Eq(1):

$$q = k_p \cdot c \quad (1)$$

where c is the concentration in the particle pores and q is the amount adsorbed in the particle solid phase.

2.2 Material Balance

The equations of the material balance in the mobile phase and inside the particles are described by differential equations, based on the work of Cremasco et al. (2004).

- Column concentration profile, mobile phase:

$$-D_L \cdot \varepsilon_b \cdot \frac{\partial^2 C}{\partial z^2} + \frac{Q}{A} \cdot \frac{\partial C}{\partial z} + \varepsilon_b \cdot \frac{\partial C}{\partial t} + R_a = 0 \quad (2)$$

where:

$$R_a = (1 - \varepsilon_b) \cdot \frac{\partial}{\partial t} [\varepsilon_p \cdot c + (1 - \varepsilon_p) \cdot q] \quad (3)$$

where D_L is the effective pore diffusion coefficient, ε_b is the bed porosity, C is the solute concentration in the fluid phase (mobile phase), z is the axial position, Q is the flow rate, A is the cross-sectional area of the column and t is the time.

- Concentration profile inside the particle:

$$k_f \cdot A_s \cdot (C - c) = \frac{\partial}{\partial t} [V_p \cdot [\varepsilon_p \cdot c + (1 - \varepsilon_p) \cdot q]] \quad (4)$$

$$A_s = 4\pi \cdot \left(\frac{d_p}{2}\right)^2 \quad (5)$$

$$V_p = \frac{4}{3}\pi \cdot \left(\frac{d_p}{2}\right)^3 \quad (6)$$

where k_f is the mass transfer coefficient, c is the solute concentration inside the particle, ε_p is the particle porosity, A_s is the surface area of the particle and V_p is the volume of the particle.

- Boundary conditions:

$$C = C_0 \quad z = 0 \quad t > 0 \quad (7)$$

$$-A_s \cdot D_L \cdot \varepsilon_b \cdot \frac{\partial C}{\partial z} = 0 \quad z = L \quad t > 0 \quad (8)$$

- Initial conditions:

$$C = 0 \quad t = 0 \quad 0 \leq z \leq L \quad (9)$$

$$c = 0 \quad t = 0 \quad 0 \leq z \leq L \quad (10)$$

The coefficient of axial dispersion (D_L) used in the equations of the material balance was calculated through Eq(11) suggested by Wakao (Ruthven, 1984):

$$D_L = \frac{20}{\varepsilon_b} \cdot D_m + \frac{1}{2} \cdot v \cdot d_p \quad (11)$$

where v is the interstitial fluid velocity (cm/s) and D_m is the mass diffusion coefficient (cm²/s).

The mass transfer coefficient (k_f) was calculated through Eq(12) (Ruthven, 1984):

$$k_f = \frac{Sh \cdot D_m}{d_p} \quad (12)$$

The Sherwood number (Sh) was calculated through the correlation suggested by Wilson and Geankoplis, represented by Eq(13) (Ruthven, 1984):

$$Sh = \frac{1.09}{\varepsilon_b} \cdot Sc^{0.33} \cdot Re^{0.33} \quad 0.0015 < Re < 55 \quad (13)$$

where Sh is the Schmidt number and Re is the particle Reynolds number.

2.3 Momentum Balance

The pressure variation along the bed length is given by the momentum balance, which is represented by the Ergun equation:

$$-\frac{dP}{dz} = 150 \cdot \frac{(1-\varepsilon_b)^2}{\varepsilon_b^3} \cdot \frac{\mu \cdot u}{(d_p \cdot \varphi)^2} + 1.75 \cdot \frac{(1-\varepsilon_b)}{\varepsilon_b^3} \cdot \frac{\rho \cdot u^2}{(d_p \cdot \varphi)} \quad (14)$$

where ε_b is the porosity of the bed, μ is the viscosity of the fluid, d_p is the diameter of the particle, φ is the sphericity of the Particle and ρ is the fluid density.

The surface velocity is given by $u = Q/A$ and $d_p = 2 \cdot R$ is the diameter of adsorbent particles in the fixed bed. For this work, it was considered that the diameter of these particles is a function of the axial coordinate, which is, $d_p = d_p(z)$.

The total pressure drop in the bed is given by the integration of Eq(14):

$$-\Delta P = \int_0^L -\frac{dP}{dz} \cdot dz \quad (15)$$

2.4 Optimization of the particle diameter profile

Since the model described requires solving partial differential equations, a discretization method was used. The continuous concentration profiles $C(t, z)$ and $c(t, z)$ were replaced by the discrete profiles $C_{i,j}$ and $c_{i,j}$, at time t_i and position z_j . Eq(15) was solved by the trapezoidal rule. The partial derivatives were calculated by the finite differences method. The advection-diffusion equation given by Eq(2) was solved by the Method of Characteristics.

Rearranging Equations (1) and (4) and applying the implicit Euler method, the result is given by Eq(16):

$$C_{i+1,j+1} = \frac{c_{i,j+1} + \gamma \cdot \Delta t \cdot C_{i+1,j+1}}{1 + \gamma \cdot \Delta t} \quad (16)$$

$$\gamma = \frac{6 \cdot k_f}{d_p \cdot [\varepsilon_p + (1 - \varepsilon_p) \cdot k_p]} \quad (17)$$

In order to apply the Method of Characteristics, Equations (1)-(4) were rearranged to give:

$$-D_L \cdot \frac{\partial^2 C}{\partial z^2} + v \cdot \frac{\partial C}{\partial z} + \alpha \cdot \frac{\partial C}{\partial t} - \frac{(\alpha-1)}{\gamma} \cdot \frac{\partial^2 c}{\partial t^2} = 0 \quad (18)$$

$$v = \frac{Q}{\varepsilon_b \cdot A} \quad (19)$$

$$\alpha = 1 + \frac{(1-\varepsilon_b)}{\varepsilon_b} \cdot [\varepsilon_p + (1-\varepsilon_p) \cdot k_p] \quad (20)$$

The Method of Characteristics, which combines implicit and explicit Euler methods for the first derivatives in position and time, requires that $\Delta t = \Delta z \cdot \alpha / v$.

For the terms with second-order derivatives, finite central differences were applied, both for position and time. The result is then given by Eq(21):

$$C_{i+j,j+1} = \frac{C_{i,j} + \beta \cdot (C_{i+j,j+2} + C_{i+1,j}) + \omega \cdot (c_{i+2,j+1} - 2 \cdot c_{i+1,j+1} + c_{i,j+1})}{1 + 2 \cdot \beta} \quad (21)$$

$$\beta = \frac{D_L}{v \cdot \Delta z} \quad (22)$$

$$\omega = \frac{(\alpha - 1)}{\alpha \cdot \gamma \cdot \Delta t} \quad (23)$$

The optimization of the particle diameter profile in a fixed bed then was formulated as a nonlinear programming model, with the previous equations inserted as restrictions. It must be observed that Equations (11) and (12) were also used, since they depend on $d_p(z_j)$, which is a variable in the model.

In the optimization, two cases were tested, each with a different objective function:

- First Case: The minimization of the pressure drop given by Eq(15) was used as objective function, by calculating the optimum particle diameter profile $d_p(z)$, such that $-\Delta P$ is a minimum, satisfying the equations of the model given by Eq (11), (12), (16), (17), (21), (22), and (23), as well as its boundary conditions and initial conditions, and the output restriction condition given by Eq(24):

$$C(L, t) \leq C_{\text{Limit}} \quad (24)$$

- Second Case: The minimization of the output GVL concentration, given by $C_{i,j}$ at $z = L$, was used as objective function, by calculating the optimum particle diameter profile $d_p(z)$, satisfying the equations of the model given by Eq (11), (12), (16), (17), (21), (22), and (23), as well as its boundary conditions and initial conditions, and the restriction condition for the pressure drop given by Eq(25):

$$-\Delta P \leq -\Delta P_{\text{Limit}} \quad (25)$$

The optimization of this problem was solved using GAMS software and IPOPT (Interior Point OPTimizer) solver.

3. Results e Discussion

The mathematical model was implemented in GAMS, with the previously described equations, and solved as a nonlinear programming model, where the variables are $d_p(z_j)$ and all quantities that depend on $d_p(z_j)$, and the concentration profiles $C_{i,j}$ and $c_{i,j}$. The discretization intervals were $\Delta z = 50$ cm and $\Delta t = 1160$ s, with an operating time equal to 6.44 hours. For the first and second case, Tables 3 and 4 were generated, respectively.

Several restrictions were tested for both cases; in other words, various output concentrations were considered for the first case, and various pressure drop values for the second case. Tests for all restrictions indicated that the optimal diameter profile is practically constant. In this way, particles of the same diameter can be used along the bed length to achieve a certain output concentration and pressure drop suitable for the process.

In an analysis of Table 3, it can be seen that the particle diameter and output concentration are directly related; in which the smaller is the particle diameter, lower will be the output concentration, despite a greater pressure drop.

Table 3: Results of the first case.

Output concentration (g/cm ³)	dp optimum (cm)	Pressure drop (atm)
0.0050	0.080	0.34
0.0045	0.078	0.36
0.0040	0.069	0.44
0.0035	0.062	0.54
0.0030	0.055	0.70
0.0025	0.048	0.90

These same effects can be observed in Table 4. This shows that the model is useful both to minimize the pressure drop and the output concentrations, simply by using the appropriate objective function and restraint

condition for each case. For a size of about 0.047 cm, a solution with 0.0020 g/cm³ of GVL and a pressure drop of 0.95 atm can be obtained. On the other hand, a larger size (0.08 cm) offers an output concentration of 0.005 g / cm³ and a pressure drop of 0.34 atm.

It is also possible to note that a smaller output concentration leads to a greater pressure drop.

Table 4: Results of the second case.

Pressure drop (atm)	dp optimum (cm)	Output concentration (g/cm ³)
0.34	0.080	0.005
0.40	0.073	0.004
0.45	0.068	0.004
0.60	0.059	0.003
0.70	0.055	0.003
0,95	0,047	0,002

4. Conclusions

The mathematical modeling was presented in two ways, each one with a different objective function: the minimization of the pressure drop, and the minimization of the output concentration. The results of both cases have shown that the optimum diameter profile is practically constant and that also the particle diameter has different effects on the pressure drop and the efficiency of the adsorption. Thus, from these results one can define the optimum diameter of the particle in fixed bed, according to the pressure drop and an acceptable output concentration for the process.

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