



Article A Complete Heterogeneous Model for the Production of n-Propyl Propionate Using a Simulated Moving Bed Reactor

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Abstract: n-Propyl Propionate (ProPro) is a harmless biodegradable product employed in several fields for the production of drugs, inks, coating, food, and perfume. ProPro is synthesized in an equilibrium reaction for which its yield can be enhanced by constant withdraw of the products as the reaction takes place. Simulated Moving Bed Reactor (SMBR) is a candidate for the production of ProPro with high efficiency as it is a multifunction unit able to simultaneously run reaction and separation, hence shifting the equilibrium reaction toward products. This paper proposes a complete phenomenological model for the ProPro synthesis in a Simulated Moving Bed Reactor (SMBR) packed with the heterogeneous catalyst Amberlyst 46 resin. The operating conditions are defined by the Triangle Theory to design an SMBR unit to produce ProPro efficiently and a comprehensive parameter estimation procedure is employed to obtain more representative parameters. The validated phenomenological model was applied to design an SMBR unit to produce high purity (99.28%) ProPro.

Keywords: true moving bed reactor; n-propyl propionate; process optimization; parameter performance

1. Introduction

Traditionally reaction and product purification are carried out in independent units. Multifunctional processes deal with reaction and separation in a single unit; therefore, they are more cost-effective and environmentally safe [1]. Simulated Moving Bed Reactor (SMBR) stands out among multifunctional units due to its efficiency in dealing with equilibrium-limited reactions. It has the capability of removing products from the reaction zone through selective adsorption onto porous catalyst, shifting the equilibrium toward products and, thus, increasing the yield [2–5]. Periodic switches change inlet (eluent and feed) and outlet (raffinate and extract) streams in a multicolumn system divided into four sections filled in with an adsorptive porous catalyst. The purpose of the SMBR is to simulate liquid and solid counter-current flow as in a True Moving Bed Reactor (TMBR), eliminating the solid flow since it is difficult to handle.

Figure 1 depicts the TMBR for a generic equilibrium reaction:

$$aA + bB \rightleftharpoons cC + dD \tag{1}$$

where *A* and *B* are the reactants and *B* is the eluent, *C* and *D* are the products, and *a*, *b*, *c*, and *d* are the respective stoichiometric coefficients in accordance with Figure 1. Components *A* and *B* are introduced into the system in the Eluent (E) and Feed (F) Streams, respectively, whereas the solid phase has more affinity to component *C*, which is selectively removed in the Extract (X) stream. Reaction and separation are carried out in Section II and Section III



Citation: Santos, R.; Rebello, C.; Prudente, A.; Ribeiro, A.M.; Rodrigues, A.E.; Loureiro, J.M.; Pontes, K.V.; Nogueira, I.B.R. A Complete Heterogeneous Model for the Production of n-Propyl Propionate Using a Simulated Moving Bed Reactor. *Separations* **2022**, 9, 43. https://doi.org/10.3390/ separations9020043

Academic Editor: Alberto Cavazzini

Received: 31 December 2021 Accepted: 31 January 2022 Published: 4 February 2022

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so that components C and D are removed in the Extract (X) and Raffinate (R) streams, respectively. Eluent and adsorbent are regenerated in Section Iand Section IV, respectively.

Figure 1. True Moving Bed Reactor unit representations.

n-Propyl Propionate (ProPro) is an ecofriendly product applied in drugs and ink production, polymerization reactions, coating industry, and as an additive for food and perfume [6]. The U.S. Environmental Protection Agency considers ProPro a harmless air pollutant and it is acknowledged as a biodegradable and non-toxic product. It may be used as an additive for food and perfume due to its pleasant smell and absence of toxicity [1,7,8]. ProPro can be synthesized by a heterogeneous esterification reaction of 1-propanol with propionic acid, also yielding water, as illustrated in Figure 2a. From this point on, *A* and *B* are the reactants 1-propanol and propionic acid, and *C* and *D* are the products' water and n-propyl propionate, as in (1). k_1 and k_{-1} are the kinetic constants for the formation and consumption of ProPro, respectively. 1-propanol might also undergo secondary reactions such as etherification and dehydration, producing di-n-propyl ether and propene (Figure 2b,c, respectively) [9]. These side reactions are undesired due to economic and safety issues, as propene is an easily flammable gas [7]. In order to avoid



n-Propyl Propionate

D

these side reactions, Amberlyst 46 is employed as a heterogenous catalyst due to its ester prioritization and adsorption of water that shift the equilibrium toward products [10].

Water

С



Figure 2. Synthesis of n-Propyl Propionate (a) and secondary reactions (b) and (c).

ProPro synthesis in SMBR unit might be enhanced if representative models are available. Despite its importance, as far as the authors know, only Nogueira et al. (2020) approached ProPro production in SMBR, and Nogueira et al. (2019) studied a fixed bed chromatographic reactor for the production of ProPro [1,6]. These approaches, however, used a simplified model that considers the system as pseudo-homogeneous. Other works investigate the synthesis of ProPro in Reactive Distillation (RD) that presents a complex operation and not so satisfactory results, such as conversion and purities around 90%, whereas SMBR can reach over 99% [6,9,11,12]. This paper, then, proposes a rigorous phenomenological model of a TMBR for synthesizing n-propyl propionate through the esterification of 1-propanol with propionic acid catalyzed with Amberlyst 46 resin. Unlike the literature, we propose a phenomenological model that considers a heterogeneous catalyst that better describes the system's phenomenology, whereas a pseudo-homogeneous model considers a heterogeneous system as homogeneous. The TMBR model is used to design and optimize an SMBR unit to produce ProPro efficiently using the Triangle Theory.

2. Methodology

1-Propanol

А

Propionic Acid

В

As mentioned, previous studies considered a pseudo-homogeneous reaction that simplifies the model. In addition, SMBR modeling bears a high computational burden that can be prevented by substituting it by the TMBR model, which is simpler to be carried out and it is equivalent to SMBR by keeping constant the liquid velocity relative to the solid velocity in the model [13–16].

The TMBR model herein proposed considers the pilot-scale SMBR unit model LI-COSEP1 12–26 by Novasep (Porto, Porto, Portugal) packed with Amberlyst 46 located in the Laboratory of Separation and Reaction Engineering of the University of Porto in Portugal. The characteristics of the unit are shown in Table 1. This section firstly presents the TMBR model considering the heterogenous reaction, followed by its parameter estimation

and, finally, the Triangle Theory is used to define the operating conditons that provide succesful reaction and separation.

Unit Condition				
Column length	4.6 dm			
Column diameter	0.26 dm			
Temperature	313 K			
Bed porosity	0.4			
Peclet number	166			
Particle diameter	245.5 μm			
Feed composition	40% A/60% B			

Table 1. Unit conditions for simulations of the TMBR unit.

2.1. TMBR Model

A TMBR phenomenological model was developed from mass balance over a bed volume element. The model considers the following:

- A heterogeneous reaction system;
- Isothermal process;
- The bed length and porosity are constant;
- External mass transfer to the particle and internal mass transfer are negligible;
- A plug flow model with axial dispersion;
- Dispersion along radius is negligible;
- Velocity changes along the column because of composition variation and a linear driving force for the mass transfer rate.

The mass balances at the fluid phase and inside the particle are, respectively, given by the following:

$$\frac{\partial c_{i,k}}{\partial t} = D_{ax} \frac{\partial}{\partial z} \left(C_T \cdot \frac{\partial x_{i,k}}{\partial z} \right) - \frac{\partial (u_k c_{i,k})}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon} \frac{3}{R_p} K_{L,ik} \left(q_{i,k}^* - q_{i,k} \right)$$
(2)

$$\frac{\partial q_{i,k}}{\partial t} = \frac{3}{R_p} K_{L,ik} \left(q_{i,k}^* - q_{i,k} \right) + \frac{\mathbf{u}_s}{L_k} \frac{\partial q_{i,k}}{\partial z} - \vartheta_i \frac{\rho_b}{1 - \varepsilon} r_{ProPro}$$
(3)

$$r_{ProPro} = \frac{K_A K_B k \left(a_A a_B - \frac{a_C a_D}{K_{eq}} \right)}{\left(1 + K_A a_A + K_B a_B + K_C a_C + K_D a_D \right)}$$
(4)

where subscripts *i* and *k* denote compounds and TMBR section, L_k is the section length, ϑ_i is the stoichiometric coefficient of component *i*, ε is the bed porosity, D_{ax} is the axial dispersion coefficient, $c_{i,k}$ is the fluid phase concentration, $q_{i,k}$ is the adsorbed phase concentration, $q_{i,k}^*$ is the adsorbed concentration of compound *i* in equilibrium with $c_{i,k}$ in section *k*, $x_{i,k}$ is the molar fraction of compound *i* in the liquid phase in section *k*, ρ_b is the bulk density, u_k is the section interstitial velocity, R_p is the particle radius, and $K_{L,ik}$ is the external mass transfer coefficient. This paper applies the Langmuir–Hinshelwood equation for reaction rate $r_{ProPro,k}$. This source term has been shown to successfully represent heterogeneous esterification reactions [17]. In Equation (4), *k* is the kinetic constant, K_{eq} is the equilibrium constant of ProPro synthesis, and K_A , K_B , K_C , and K_D are the adsorption equilibrium constants of 1-propanol, propionic acid, water, and n-propyl propionate, respectively. C_T is the total molar concentration in the liquid phase, which is related to the molar volume $V_{M,i}$ of each compound and can be found by the following.

$$C_T = \frac{1}{\sum x_{i,k} V_{M,i}} \tag{5}$$

The values of adsorption equilibrium constants for reactants and products were estimated by Nogueira et al. (2018) [18], as shown in Table 2.

Adsorption Equilibrium Constants			
$K_A/(\text{mol}\cdot\text{s}^{-1}\cdot\text{eq}^{-1})$	11.67		
K_B / (mol·s ⁻¹ ·eq ⁻¹)	9.06		
K_C / (mol·s ⁻¹ ·eq ⁻¹)	2.36		
$K_D / (\mathrm{mol} \cdot \mathrm{s}^{-1} \cdot \mathrm{eq}^{-1})$	5.1		

Table 2. Adsorption equilibrium constants for reactants and products.

The kinetic and equilibrium constants, k and K_{eq} , are related to the temperature, as expressed by the Arrhenius and Van't Hoff equations, respectively:

$$k = k_0 e^{-\frac{E}{RT}} \tag{6}$$

$$K_{eq} = K_{\infty} e^{-\frac{\Delta H}{RT}} \tag{7}$$

where k_0 is the pre-exponential factor, E is the activation energy, T is the temperature, R is the universal gas constant, K_{∞} is the pre-exponential factor for equilibrium reaction, and ΔH is the reaction enthalpy. k_0 , E, K_{∞} , and ΔH are the kinetic parameters to be estimated. a_A , a_B , a_C , and a_D are the activity:

$$a_i = \gamma_i x_i \tag{8}$$

where γ_i is the activity coefficient, obtained by a thermodynamic model. Prudente et al. (2019) studied the Liquid–Liquid Equilibrium (LLE) of the quaternary system of n-Propanol, propanoic acid, propyl propionate, and water and showed that the NRTL (Non-random two-liquid) model describes more precisely the system than the UNIQUAC (Universal Quasichemical) model [19]. The NRTL model is given by the following:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{n_c} x_j \tau_{ji} G_{ij}}{\sum_{j=1}^{n_c} x_j G_{ji}} + \sum_{j=1}^{n_c} \frac{x_j G_{ij}}{\sum_{l=1}^{n_c} x_l G_{lj}} \left(\tau_{ij} - \frac{\sum_{l=1}^{n_c} x_l \tau_{lj} G_{lj}}{\sum_{l=1}^{n_c} x_l G_{lj}}\right)$$
(9)

$$\tau_{ji} = \frac{g_{ij} - g_{ii}}{RT} = \frac{\Delta g_{ij}}{RT}$$
(10)

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ji}\right) \tag{11}$$

$$\alpha_{ij} = \alpha_{ji} \tag{12}$$

where n_c is the number of components, g_{ij} measures component *i* and *j* interactions, and α_{ij} measures the lack of randomness. The value of 0.3 is adopted for α_{ij} obtained from Samarov et al. (2016) [20], and g_{ij} are the thermodynamic parameters to be estimated.

The mass transfer coefficient, $K_{L,ik}$, is given by the following [18,21]:

$$K_{L,ik} = \frac{1.09u_k}{\varepsilon} \left(\frac{D_{i,mix,k}}{d_p u_k}\right)^{0.67}$$
(13)

$$D_{i,mix,k}\eta_{mix}^{0.8} = \sum_{\substack{j=1\\j\neq i}}^{n_c} x_j D_{i,j}^0 \eta_j^{0.8}$$
(14)

$$D_{i,j}^{0} = \frac{8.2 \times 10^{-8} T}{\eta_{j} V_{M,i}^{1/3}} \left[1 + \left(\frac{3V_{M,j}}{V_{M,i}}\right)^{2/3} \right]$$
(15)

where d_p is the particle diameter provided by the manufacturer, $D_{i,mix,k}$ is the diffusivity coefficient of compound *i* in the mixture in section *k*, $D_{i,j}^0$ is the diffusion coefficient of component *i* diluted in component *j*, η_j is the viscosity of the pure component *j*, and η_{mix} is the mixture viscosity.

Component composition varies along the bed, therefore changing the section interstitial velocity, as given by the following:

$$\frac{\partial u_k}{\partial z} = \frac{1-\varepsilon}{\varepsilon} \frac{3}{R_p} \sum_{1=1}^{n_c} K_{L,ik} V_{M,i} \left(q_{i,k}^* - q_{i,k} \right) - \vartheta_i \frac{\rho_b}{1-\varepsilon} r_{ProPro,k}$$
(16)

for which its boundary conditions are as follows.

$$z = 0: \ \forall t \to u = u|_{z=0} \tag{17}$$

The concentration of component *i* in section *k* in the adsorbed phase, $q_{i,k}$ in equilibrium with the fluid phase concentration, $c_{i,k}$ is given by the Langmuir adsorption isotherm equation for liquid phase adsorption [18–20]:

$$q_{i,k} = \frac{Q_{max,i}K_{i}c_{i,k}}{1 + \sum_{i}^{n_{c}}K_{i}c_{i,k}}$$
(18)

where $Q_{max,i}$ and K_i are Langmuir adsorption parameters for which its values were estimated by Nogueira et al. (2019) [18].

The initial and boundary conditions for any *k* are defined as follows:

$$t = 0: \quad c_{i(i \neq eluent), j} = q_{i,k} = 0; \quad c_{i(i = eluent), k} = c_i^E; \quad q_{i(i = eluent), k} = q(c_i^E)$$
(19)

$$z = 0: \quad c_{i,k} - \frac{D_{Lk}}{u_k} C_T \frac{\partial x_{i,k}}{\partial z} = c_{i,k,0}$$
(20)

where superscript *E* regards to eluent, and $c_{i,k,0}$ is the inlet concentration of species *i* in a section *k*. At $z = L_k$, we have the following:

$$\left. \frac{\partial x_{i,k}}{\partial z} \right|_{L_k} = 0 \tag{21}$$

and the boundary conditions for the eluent (c_{i,IV,L_j}) , extract (c_{i,I,L_j}) , feed (c_{i,II,L_j}) , and raffinate (c_{i,III,L_i}) nodes are, respectively, given by the following:

$$c_{i,IV,L_k} = \frac{u_I}{u_{IV}} c_{i,I,0} \tag{22}$$

$$c_{i,I,L_k} = c_{i,II,0} \tag{23}$$

$$c_{i,II,L_k} = \frac{u_{III}}{u_{II}} c_{i,III,0} - \frac{u_F}{u_{II}} c_i^F$$
(24)

$$c_{i,III,L_k} = c_{i,IV,0} \tag{25}$$

where c_i^F is the enantiomer concentration in the feed stream. Concentrations in the adsorbed phase $(q_{i,k})$ in the beginning of a section are equal to the final concentrations of the previous ones, as shown as follows.

$$q_{i,k,0} = q_{i,k-1,L_k} \tag{26}$$

The global mass balance for each node considering the inlet and outlet streams for each section can be expressed as follows.

$$Fluent: u_I = u_{IV} + u_E \tag{27}$$

$$Extract: u_{II} = u_I - u_X \tag{28}$$

$$\text{Feed}: u_{III} = u_{II} + u_F \tag{29}$$

Raffinate :
$$u_{IV} = u_{III} - u_R$$
 (30)

TMBR performance is measured by purity, conversion, eluent consumption, and productivity, as given by the following:

$$Pur_X = \frac{c_D^R}{\sum_{i=1}^{n_c} c_i^R}$$
(31)

$$Pur_R = \frac{c_C^X}{\sum_{i=1}^{n_c} c_i^X}$$
(32)

$$Conv = 100 \frac{c_B{}^F u_F - (c_B{}^X u_X + c_B{}^R u_R)}{c_B{}^F u_F}$$
(33)

$$EC = \frac{c_A{}^E u_E - u_F \left(c_A{}^F - c_A{}^F \frac{Conv}{100} \right)}{c_D{}^R u_R}$$
(34)

$$Pr = \frac{c_D{}^R u_R}{V_T} \tag{35}$$

where Pur_X and Pur_R are the extract and raffinate purities, Conv is the conversion, *EC* and *Pr* denote eluent consumption and unit productivity, and V_T is the volume of the bed.

2.2. Parameter Estimations

Herein, a default PSO (Particle Swarm Optimization) from MATLAB combined with a gradient method was employed to perform the estimations of thermodynamic and kinetic parameters separately in order to find the sets of model parameters that better fit experimental results.

Kinetic experimental data were obtained from [7]. The author carried out a parameter estimation widely used in works related to ProPro synthesis in batch reactor [1,22,23]. The author employed linearization technique to adjust a set of parameters of the Arrhenius and Van't Hoff equations. This approach can mask or not cover entirely the results, since this system is non-linear. Moreover, it relies only on the R-square parameters for fitness, which can be easily biased. Herein, parameters are estimated simultaneously considering different sets of experimental data from [7] that respect its non-linearity.

Thermodynamic experimental data were obtained from Samarov et al. (2016)'s LLE at 313.15 K [20]. The authors estimated the thermodynamic parameters within a temperature range from 293.15 to 333.15. Herein, the thermodynamic parameters are estimated at 313.15 K that is the operating temperature.

2.3. Unit Design and Optimization

The optimization and design of the TMBR unit must guarantee that reaction and separation work efficiently and simultaneously. The equilibrium Triangle Theory is an approach, usually employed in TMB/SMB design and optimization, for which its goal is to determine the necessary conditions for liquid and solid regeneration in recycling stream [24,25]. It firstly sets the limits for fluid internal and solid flow rates ratio, as given by the following:

$$\gamma_I = \frac{u_I}{u_s} > \frac{(1-\varepsilon)}{\varepsilon} \frac{q_{C,I}(c_C{}^X)}{c_C{}^X} = UB = 0.9693$$
(36)

$$\gamma_{IV} = \frac{u_{IV}}{u_s} < \frac{(1-\varepsilon)}{\varepsilon} \frac{q_{D,I}(c_D{}^R)}{c_D{}^R} = LB = 0.2484$$
(37)

where u_s is the solid velocity ($u_s = L_k/t^*$). Herein, the limits for the ratios, *UB* and *LB* (Upper and Lower Bounds), were established by previous investigation by the equilibrium theory. A Safety Factor, SF, is added to *UB* and *LB* due to the mass transfer resistance in the system [6], wherein SF equals 1.7 was adopted based on previous studies. The second step in the equilibrium triangle theory is to determine a suitable switching time value by a reactive separate reactive region for a particular purity requirement. A sensitivity analysis

indicated a value of 60 min for suitable switching time. The second step in the triangle theory is carried out by process simulations and performance parameter determination with different values of γ_{II} and γ_{III} starting with low feed and extract flow rate values. The simulation is repeated with a gradual increase in the extract flow rate up to the two reactive separation region limits. Then the simulation is carried out repeatedly with an increase in the feed flow rate with different extract flow rate up to the separation region closure, i.e., maximization of the feed flow rate within purity restriction.

3. Results

The Triangle Theory is applied to define operating conditions (Table 3) that enable reaction and separation with a purity of above 90%.

Operating Conditions				
$Q_F / (ml/min)$	0.14			
Q_E / (ml/min)	2.56			
Q_{IV} / (ml/min)	0.12			
$Q_X / (ml/min)$	0.90			
$Q_{\rm S}$ / (ml/min)	2.45			

Table 3. Operation conditions.

The TMBR model relies on thermodynamic and kinetic parameters that need to be estimated. Experimental data were obtained from literature, and parameters were estimated by PSO combined with a gradient method. Results are shown in Tables 4 and 5 together with parameters estimated in the literature. Table 6 presents the Root-Mean Square Deviation (RMDS) between the experimental data from the literature and simulation results obtained with the heterogeneous model using, respectively, the kinetic and thermodynamic parameters estimated in this study and the ones from the literature. It provides a comparison between the parameters estimated here and the literature.

Table 4. Kinetic parameters for heterogeneous and pseudo-homogeneous.

Kinetic Parameter	Estimated	Literature
$k_0 \neq (\text{mol} \cdot \text{s}^{-1} \cdot \text{eq}^{-1})$	$5.8 imes10^5$	$6.9 imes10^7$
$E / (J \cdot mol^{-1})$	$5.3 imes10^4$	$5.9 imes 10^4$
K_{∞}	$8.0 imes10^3$	7.5
$\Delta H / (J \cdot mol^{-1})$	$1.9 imes10^4$	$4.2 imes 10^3$

Table 5. NRTL thermodynamic parameters Δg_{ij} for heterogeneous and pseudo-homogeneous at 313.15 K.

j	I	A	I	B	(2	Ι)
i	Estimated	Literature	Estimated	Literature	Estimated	Literature	Estimated	Literature
А	0.0	0.0	674.9	1754.0	704.0	1744.7	391.7	566.0
В	-712.0	1120.8	0.0	0.0	672.6	1 631.9	384.5	590.0
С	766.6	-93.5	4 244.0	-182.3	0.0	0.0	3 302.4	1 142.5
D	-677.4	236.9	224.6	32.1	2 237.8	3 505.0	0.0	0.0

Table 6. RMDS between experimental results and simulations results using the parameters estimated in this work and parameters from literature.

Parameter	Estimated	Literature
Kinetic	6.7%	20.3%
Thermodynamic	0.2%	2.9%

As shown in Table 6, the RMDS value for parameters estimated in the present work is significantly smaller than the parameter from the literature. Therefore, the estimated parameters for the heterogeneous model are more suitable to be used in the present context. As Amberlyst 46 is a heterogeneous catalyst, the Langmuir–Hinshelwood equation employment suits the system better.

Appling the operating conditions from Table 3 and the estimated parameters, the performance parameters were calculated from Equations (31)–(35). The equilibrium conversion of 99.28% was observed. The possibility of removing products from the reaction medium is a benefit of moving bed reactors that enable higher conversion percentages, as evidenced in Table 7.

Table 7. TMBR Performance parameters.

Performance Parameters		
Pur_R (%)	98.30	
Pur_X (%)	98.90	
Conv (%)	99.28	
Pr(mol/d)	18.88	
<i>EC</i> (1/g)	10.40	

The results obtained for the optimal point are presented in Figure 3. It shows the concentration profiles along the columns and sections for propanoic acid, n-propyl propionate, and water singly in 3D graphics. In turn, Figure 4 shows the concentration profiles along the sections for the reactants and products together in a 2D graphic. It is worth observing that 1-propanol is the eluent and is not presented in Figures 3 and 4. Its concentration is higher than the others and virtually does not change over time and sections. As it is possible observe from the concentration profiles that the unit can promote the separation of the product water from the reaction area (Section II), shifting the equilibrium to yield more n-propyl propionate. Therefore, this results in a reaction conversion close to 100%. Moreover, it is possible to observe that the ProPro is collected at the end of Section III with high purity, which agrees with Table 7.

For the sake of performance assessment, changes in the operating condition were performed to analyze the process behavior, as shown in Figure 5. As observed, the extract and raffinate purities (Pur_X and Pur_R) are very sensitive to flow rate variations, except for variations on the feed flow rate. Pur_X decreases with the increase in feed (Q_F) and recycle (Q_{IV}) flow rates, whereas increases in extract (Q_X) and solid (Q_S) flow rates yield an increase in extract purity followed by a further decrease. Conversion (Conv) and productivity (Pr) do not change as much. As expected, productivity shows a significant increase as the feed flow rate increases and a drop as the solid flow rate increases.

The behavior of Figures 3 and 4 is explained by the analysis of the concentration profiles. Thus, the evaluation of the concentration profiles was also carried out with variations of the operating conditions, as shown in Figure 6. Reactants are fed between Section II and Section III, which justifies the higher concentration of propionate acid in Section II in Figure 6a–d. Pure water and ProPro must be removed, respectively, at the end of Section I and Section III. Any other compounds in these nodes means contamination in the extract and raffinate streams. Contamination of ProPro in the extract product can be observed in Figure 6a with the increase in extract flow rate. In other words, as the extract flow rate increases, the fluid flow rate in Section III and Section II decreases; therefore, not only water is carried with the solid toward the extract but also ProPro and the acid, and the reaction conversion is further reduced. An increase in feed flow rates in Figure 6b yields a higher concentration of products. Therefore, higher productivity. However, the water front starts to contaminate the raffinate stream. With the increase in solid flow rates in Figure 6c, the solid is not fully regenerated. Thus, the column is contaminated with the water dragged by the solid. In addition, the lighter components are also dragged by the solid. In turn, an increase in the recycle flow rates in Figure 6d does not affect the internal



profile, which indicates that Section IV of the TMBR is more than enough to regenerate the eluent in the range studied.

Figure 3. Cont.



Figure 3. TMBR concentration profile along sections and time for (**a**) propanoic acid, (**b**) n-propyl propionate, and (**c**) water in a transient evolution.



Figure 4. TMBR concentration profile for propanoic acid, n-propyl propionate and water along sections in the cyclic steady state.





Figure 5. Cont.



Figure 5. Performance parameter behaviors with variations of (**a**) feed (Q_F), (**b**) extract (Q_X), (**c**) solid (Q_S), and (**d**) recycle (Q_{IV}) flow rates.



Figure 6. Cont.



Figure 6. Concentration behaviors with variations of (**a**) feed (Q_F), (**b**) extract (Q_X), (**c**) solid (Q_S), and (**d**) recycle (Q_{IV}) flow rates.

4. Conclusions

This article proposes a phenomenological model for the production of n-Propyl Propionate in a Simulated Moving Bed Reactor (SMBR) packed with a heterogeneous adsorptive catalyst, Amberlyst 46 resin. A comprehensive methodology to estimate the thermodynamic and kinetic parameters was presented. Experimental data from the literature were used to estimate the parameters yielding a validated model with experimental data in its fundamental levels. This paper proposes a novel heterogeneous model for producing n-Propyl Propionate in SMBR. The results demonstrated that it is possible to achieve conversions and purities higher than 98% in this process. Therefore, providing the literature with solid evidence that the SMBR can be a reliable, efficient, and environmentally friendly route for ProPro production.

The results also show that it is possible to produce a 99.28% conversion of n-Propyl Propionate with 98.30% and 98.90% of purity in the raffinate and extract, respectively, as well as a productivity of 18.88 mol/d with an eluent consumption of 10.40 l/g. This result points out that the production of n-Propyl Propionate from an SMBR is feasible, as long as economic and scale factors are taken in consideration in future studies.

Author Contributions: Conceptualization, I.B.R.N. and R.S.; methodology, I.B.R.N., R.S. and A.P.; writing—original draft preparation, I.B.R.N., R.S., A.P. and C.R.; writing—review and editing, I.B.R.N., R.S., J.M.L., A.P., C.R. and A.E.R.; supervision, I.B.R.N., K.V.P., A.E.R., A.N.R. and J.M.L. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES)—Finance Code 001. This work was also financially supported by Base Funding UIDB/50020/2020 of the Associate Laboratory LSRE-LCM funded by national funds through FCT/MCTES (PIDDAC); FCT—Fundação para a Ciência e Tecnologia under CEEC Institutional program.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

- *a* Activity (dimensionless)/ 1-propanol stoichiometric coefficient
- A Reactant 1-propanol
- *b* Propionic acid stoichiometric coefficient
- *B* Reactant propionic acid
- *c* Fluid phase concentration $(mol \cdot l^{-1})$ / Water stoichiometric coefficient
- *C* Product water
- C_T Total molar concentration in the fluid phase (mol·l⁻¹)
- *Conv* Conversion (%)
- *d* n-propyl propionate stoichiometric coefficient
- *D* Diffusivity coefficient (dm^2/min)
- d_p Particle diameter (**dm**)
- D_{ax} Axial dispersion coefficient ($dm^2 \cdot min^{-1}$)
- *E* Activation energy ($\mathbf{J} \cdot \mathbf{mol}^{-1}$)
- *EC* Eluent consumption $(\mathbf{l} \cdot \mathbf{g}^{-1})$
- *g* Thermodynamic parameter ($\mathbf{J} \cdot \mathbf{mol}^{-1}$)
- *G* NRTL model parameter (dimensionless)
- *H* Reaction enthalpy ($\mathbf{J} \cdot \mathbf{mol}^{-1}$)
- **k** Kinetic constants ($mol \cdot s^{-1} \cdot eq^{-1}$)
- *K* Langmuir adsorption parameter $(\mathbf{l} \cdot \mathbf{mol}^{-1})$ /Adsorption equilibrium constants $(\mathbf{mol} \cdot \mathbf{s}^{-1} \cdot \mathbf{eq}^{-1})$
- k_0 Pre-exponential factor (mol·s⁻¹·eq⁻¹)
- *K_{eq}* Equilibrium constant (dimensionless)
- $K_{L,ik}$ External mass transfer coefficient (**dm**·min⁻¹)
- K_{∞} Pre-exponential factor for equilibrium reaction (dimensionless)
- *L* Length (**dm**)
- *LB* Lower bound (dimensionless)
- *n_c* Number of components
- Pur Purity (%)
- *Pr* Productivity (mol·d⁻¹·l⁻¹)
- *q* Adsorbed phase concentration (**mol**· l^{-1})
- q^* Adsorbed phase concentration in equilibrium with c (mol·l⁻¹)
- ProPro n-Propyl Propionate

- **Q** Flow rate ($\mathbf{ml} \cdot \mathbf{min}^{-1}$)
- *Q_{Max}* Langmuir adsorption parameter (mol/l)
- *r* Reaction rate (**mol**·**l**⁻¹·**min**⁻¹)
- **R** Universal gas constant ($\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1}$)
- R_p Particle radius (dm)
- T Temperature (K)
- t Time (min)
- *u* Velocity ($dm \cdot min^{-1}$)
- *UB* Upper bound (dimensionless)
- ϑ Stoichiometric coefficient
- V_M Molar volume ($\mathbf{l} \cdot \mathbf{mol}^{-1}$)
- V_T Volume of the bed (l)
- *x* Dimensionless axial position in the bed / Molar fraction (Dimensionless)
- *z* Axial position in the bed (**dm**)

Subscripts and Superscripts

- A Reactant 1-propanol
- B Reactant propionic acid
- C Product water
- D Product n-propyl propionate
- *E* Eluent stream
- *F* Feed stream
- *i* Component
- I Section 1
- II Section 2
- III Section 3
- IV Section 4
- j Component
- k TMBR section
- *mix* Mixture
- **R** Raffinate stream
- S Solid
- *X* Extract stream
- ⁰ Diluted component

Greek Symbols

- *α* Number of non-randomness in the systems (dimensionless)
- ε Bed porosity (dimensionless)
- γ Activity coefficients (dimensionless)
- η Fluid viscosity (**cP**)
- ρ_b Bulk density ($eq \cdot l^{-1}$)
- τ NRTL model parameter (dimensionless)

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