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Resin-catalyzed reaction modeling integrating catalyst swelling and sites accessibility: Application to solketal synthesis



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Keywords: Modeling Catalysis Resin Accessibility Swelling index	A novel mathematical model for resin-catalyzed reactions, incorporating dynamic variations in the resin's swelling index, internal mass transfer resistances, non-ideal liquid mixtures, and limited site accessibility, was developed. The Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism, considering water adsorption, was used. Validation with experimental solketal synthesis data in ethanol ($R^2 = 0.96$) and solventless systems ($R^2 = 0.99$) was successful. A copolymerization model estimated the resin's swelling and accessibility features, using Karam and Tien's algorithm to obtain linear swelling data correlated with glycerol conversion ($R^2 = 0.9995$). Incorporating these linear equations into the catalysis model indicated glycerol conversion could be up to four times higher than in unswollen systems due to increased porosity and decreased tortuosity. Gibbs free energies of 4.7 ± 0.9 kJ mol ⁻¹ (solvent) and 12.1 ± 0.6 kJ mol ⁻¹ (solventless) were found, with a reaction rate constant of

 $109 \,\mathrm{s}^{-1}$ at 313 K on the catalytic sites.

1. Introduction

Among the products obtained from glycerol valorization, solketal [(2,2-Dimethyl-1,3-dioxolan-4-yl) methanol] is one of the most commonly studied compounds in the literature. Solketal has a wide range of applications, including its use in solvents, paints, and pharmaceuticals, among others (Fatimah et al., 2019). One of its key uses is as a fuel additive, as its properties can improve the octane rating of gasoline (da Silva et al., 2020a). Due to its high commercial applicability, the solketal market is projected to grow at an annual rate of 3.5 % through 2034, with revenues expected to increase from USD 80.9 million in 2024 to USD 114.2 million by 2034 (Solketal Market Outlook from, 2024).

The production of solketal typically involves various methods, including homogeneous catalysis with a solvent (e.g., petroleum ether), heterogeneous catalysis using resins or zeolites as catalysts with a solvent (e.g., ethanol), and a solventless heterogeneous catalysis route (Checa et al., 2020; Nanda et al., 2014; Chen et al., 2018; Corrêa et al., 2021). The high viscosity of glycerol poses challenges in this reaction, such as mass transfer resistance and potential phase separation, making mathematical modeling of the system complex. To address these challenges, excess acetone (da Silva et al., 2020b) or inert solvents (Deutsch

et al., 2007) are often employed. Fig. 1 shows the solketal production scheme.

The production of water during solketal synthesis is considered a drawback, as it accelerates the reversible reaction and leads to catalyst deactivation. Polymer-based catalysts offer a promising solution due to their tolerance to water (Checa et al., 2020). For instance, Rambhia et al. (2022) investigated the solventless synthesis of solketal catalyzed by the ion exchange resin Indion 225 H, achieving a glycerol conversion of 70 % at 323 K using 1 % (wt) resin and a 3:1 acetone/glycerol molar ratio (Rambhia et al., 2022). They developed a kinetic model based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism, yielding an R^2 value of approximately 0.98.

Esteban et al., 2015 also studied solketal synthesis catalyzed by an ion exchange resin, employing adsorption-reaction models and describing the system through a pseudo-homogeneous approach. They observed significant water adsorption into the catalytic sites of the resin (Esteban et al., 2015). Despite the good fit achieved with these models, phenomena such as species diffusion through catalyst particles and reaction rates in terms of activities need to be considered in mathematical modeling. A more comprehensive model for resin-catalyzed solketal synthesis was proposed by Moreira et al. (2019), incorporating diffusion coefficients based on compound viscosities and reaction rates based on

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activities using gPROMS® software. This model successfully describes the effects of temperature, particle diameter, and glycerol/acetone molar ratio on conversion, with an R^2 of 0.96 (Moreira et al., 2019). Although commercial acidic resins share the same catalytic site (sulfonic group, SO₃H), they exhibit distinct properties such as porosity, swelling index, and tortuosity. These variations among polymer resins result in different conversion profiles when they are used as catalysts. Esteban et al. (2017) observed significant differences in glycerol conversion profiles when testing various commercial resins for solventless solketal synthesis (Esteban et al., 2017). These disparities cannot solely be attributed to differences in the content of catalytic sites. Furthermore, as the reaction is diffusion-controlled, these variations in the quantity of sites do not significantly impact the outcomes (Moreira et al., 2019).

Given the aforementioned challenges, there is a clear need to investigate the behavior of these polymeric catalysts during chemical reactions. Previous studies by our group involved a copolymerization model to estimate properties of polymer networks in different sulfonated resins and their implications for reactivity and catalytic site accessibility (Aguiar et al., 2021, 2024). In this study, we enhance this model by integrating a diffusion-reaction approach to describe solketal synthesis. Compared to existing models in the literature (Rambhia et al., 2022; Esteban et al., 2015; Moreira et al., 2019), our model incorporates new features such as variations in catalyst diameter, porosity and tortuosity due to swelling/shrinkage during the reaction. Additionally, our model offers an advanced analysis of accessibility based on molecular sizes and polymer sequences, i.e., length of chain composed of n styrene units between two specific groups (cross-linker divinylbenzene, DVB, pendant double bond, PDB or radical center), along the catalytic resin. While solketal synthesis serves as a model reaction in this study, our novel theoretical framework holds promise for application in other organic reactions catalyzed by ion exchange resins.

2. Mathematical modeling

2.1. Copolymerization model

The chain densities of the different ion exchange resins are a consequence of the monomers proportion and the respective kinetics of copolymerization during their syntheses. A copolymerization model was developed in previous studies (Aguiar et al., 2021, 2024), and here it was improved with the consideration of cyclization reactions and occluded linear chains. These new features have influence on the cross-linking density and swelling behavior of the polymer matrix. The incidence of cyclization reduces the number of cross-linking points, while the consideration of occluded linear chains influences the solvent-polymer interaction during swelling (Karam and Tien, 1985). The model assumptions and an illustration of the species and sequences (Fig. 2) are shown as follows.

Assumptions:

2.1a) The sequences distributions are considered to be the same in soluble and gel polymer;

2.1b) The distribution of sequences containing only styrene units connecting the extreme groups (L_{An} to L_{En}) is considered to be the same as the distribution containing styrene and / or DVB units;

2.1c) Only mono-radicals were considered;

2.1d) Terminal model.

Assumption 2.1a is related to reducing computational effort, as it excludes the modeling of the post-gelation phase, which would significantly increase the number of calculations and the likelihood of numerical issues. Assumptions 2.1b and 2.1c address the limitation of determining the exact location of radicals and unreacted PDBs within the sequences. The terminal model (2.1d) assumes that the reaction rate constants depend solely on the functional groups involved, irrespective of chain length. The impact of these assumptions on model predictions primarily affects the sequence distribution, which may slightly deviate compared to a more rigorous model. However, for the purpose of comparing resins, as in the present study, these assumptions are considered reasonable.

2.2. Balance of species

1....

The copolymerization model was written in terms of balance of species and sequences. Table 1 shows the free-radical steps for styrenedivinylbenzene copolymerization, which is the fabrication process of most of the commercial acidic polymeric resins.

As shown in Fig. 2, the linear species $(R_{L}^{\bullet} \text{ and } P_{L})$ are formed during copolymerization. The styrene propagation step considers both linear and cross-linked radicals (R_n^{\bullet}) , similarly to the termination step, which accounts for both linear and cross-linked polymers (P).

The balance of species is described as follows (see symbology section for variables definition).

$$\frac{dI}{dt} = -k_d I \tag{1}$$

$$\frac{dR_0}{dt} = 2fk_dI - k_{I1}R_0^{\bullet}M_1 - k_{I2}R_0^{\bullet}M_2 - k_{P3}R_0^{\bullet}PDB - k_tR_0^{\bullet}(R_0^{\bullet} + R^{\bullet})$$
(2)

$$\frac{dR^{\bullet}}{dt} = k_{I2}R_0^{\bullet}M_2 + k_{P3}R_0^{\bullet}PDB - k_tR^{\bullet 2} - k_tR_L^{\bullet}R_n$$
(3)

$$\frac{dPDB}{dt} = k_{I2}R_0^{\bullet}M_2 + k_{P2}R^{\bullet}M_2 - k_{P3}PDB(R_0^{\bullet} + R^{\bullet}) - \sum_{r=3}^{n_{\text{max}}} k_{cyc}L_{Ar}$$
(4)

$$\frac{dM_1}{dt} = -k_{I1}R_0^{\bullet}M_1 - k_{P1}R^{\bullet}M_1$$
(5)

$$\frac{dM_2}{dt} = -k_{I2}R_0^{\bullet}M_2 - k_{P2}R^{\bullet}M_2 \tag{6}$$

$$\frac{dP}{dt} = \frac{k_t}{2} R^{\bullet 2} + k_t R_0^{\bullet} R^{\bullet} + \frac{k_t}{2} R_0^{\bullet 2}$$
(7)

where f is the initiator efficiency, taking into account the cage effect in the initiator decomposition step, and R^{\bullet} is the concentration of all polymer radicals.

In order to estimate the content of soluble chains occluded in the polymer network, balances for linear chains (R_I^{\bullet} and P_L) were carried out as follows.



Glycerol

Fig. 1. - Solketal production reaction scheme.



Fig. 2. – Elements of the copolymerization model. L_{An} : Sequence connecting a PDB to a radical center through n units; L_{Bn} : Sequence connecting two PDBs through n units; L_{Cn} : Sequence connecting a CLP to a radical center through n units; L_{En} : Sequence connecting a CLP to a radical center through n units; L_{En} : Sequence connecting a CLP to a radical center through n units; L_{En} : Sequence connecting a CLP to a radical center through n units; L_{En} : Sequence connecting two CLPs through n units; R_L^{\bullet} : Linear radical; P_L : Linear polymer entrapped in the polymer network; PDB: Pendant double bond; CLP: Cross-linking point (Aguiar et al., 2021, 2024).

Table 1 –

Styrene-divinylbenzene copolymerization steps.

Reaction	Chemical equation
Initiator decomposition	$I \longrightarrow^{k_d} 2R_0^{\bullet}$
Styrene Initiation	$R_0^ullet + M_1 \longrightarrow^{k_{I_1}} R_{L1}^ullet$
Divinylbenzene initiation	$R_0^{ullet} + M_2 \longrightarrow^{k_{I_2}} R_n^{ullet} + PDB$
PDB initiation	$R_0^{\bullet} + PDB \longrightarrow^{k_{P_3}} R_n^{\bullet}$
Styrene propagation*	$R_n^{ullet} + M_1 \longrightarrow^{k_{P_1}} R_{n+1}^{ullet}$
Divinylbenzene propagation*	$R_n^{ullet} + M_2 \longrightarrow^{k_{P_2}} R_{n+1}^{ullet} + PDB$
PDB propagation*	$R_n^{\bullet} + PDB \longrightarrow^{k_{P_3}} R_{n+1}^{\bullet}$
Termination*	$R^ullet_m+R^ullet_n{ ightarrow}^{k_t}P_{n+m}$
	$R_0^{ullet} + R^{ullet} ightarrow ^{k_t} P$
	$B^{\bullet} + B^{\bullet} \rightarrow k_t P$

I: Initiator, R_0^{\bullet} : Primary radical, M_j : Monomer of type j, R_n^{\bullet} : Polymeric radical containing n units (R_n^{\bullet} can be cross-linked or linear (R_L^{\bullet}) radicals), *PDB*: Pendant double bond, P: Dead polymer, k_d to k_t : Rate constants of the reactions (the numerical values used can be found in a previous work) (Aguiar et al., 2021).

$$\frac{dR_L^{\bullet}}{dt} = k_{I1}R_0^{\bullet}M_1 - k_{P2}R_L^{\bullet}M_2 - k_{P3}R_L^{\bullet}PDB - k_tR_L^{\bullet\,2} - k_tR_L^{\bullet}(R_0^{\bullet} + R^{\bullet})$$
(8)

$$\frac{dP_L}{dt} = \frac{k_t}{2} R_L^{\bullet 2} + \frac{k_t}{2} R_L^{\bullet} R_0^{\bullet}$$
(9)

The fraction of occluded soluble chains can be calculated through Eq. 10.

$$w_p = \frac{P_L}{P} \tag{10}$$

where R_L^i is the concentration of linear radicals and P_L and P are the concentrations of linear and total polymer chains. The copolymerization rate constants were collected from literature (Aguiar et al., 2014).

The differential equations were numerically integrated in Scilab through the algorithm ode. The concentration of cross-linked units, [CL]; total units, [U]; styrene units, $[U_1]$; and DVB units, $[U_2]$ are equated in (11), (12), (13) and (14) respectively.

$$[CL] = M_{2,0} - M_2 - PDB \tag{11}$$

 $[U] = [U_1] + [U_2] \tag{12}$

 $[U_1] = M_{1,0} - M_1 \tag{13}$

 $[U_2] = M_{2,0} - M_2 \tag{14}$

The fraction of cross-linked units (Y_{CL}) and the molecular weight between crosslinks $(\overline{M_C})$ are defined in Eqs. 15 and 16.

$$Y_{CL} = \frac{[CL]}{[U]} \tag{15}$$

$$\overline{M_C} = -\frac{\overline{M_U}}{Y_{CL}}$$
(16)

2.3. Heterogeneous catalysis model

Within this study, we elucidated the heterogeneous catalysis involved in solketal synthesis, considering the swelling of the resin (catalyst) throughout the reaction. The Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach was used to describe the reaction rate law. Water adsorption was incorporated into the LHHW model, as supported by the literature (Moreira et al., 2019), since water is one of the products in the system. The assumptions for this model are shown below.

Assumptions:

2.2a) Homogeneous liquid phase;

2.2b) Constant activity coefficients for the compounds along time and space;

2.2c) Isothermal reaction.

Assumption 2.2a is reasonable for solketal synthesis in the presence of a solvent (e.g., ethanol), where only a single phase is observed. However, this assumption introduces a limitation for solventless systems, where two liquid phases are present (Esteban et al., 2015). In such cases, a correction must be incorporated into the model, as discussed in Section 3.3.

The activity coefficients were assumed to be constant throughout the reaction, using their equilibrium values, determined by fitting the equilibrium plateau of the model to the final experimental point of glycerol conversion for each case studied. This is because they do not significantly influence the reaction rate in a diffusion-controlled process, and this assumption helps to reduce the simulation time. The predictions provided by Eqs. 10 and 16 for w_p and $\overline{M_c}$, respectively, play a crucial role in determining the catalyst's swelling index in the reaction medium, as detailed in the subsequent section.

2.4. Swelling behavior

The swelling of resins occurs due to the affinity of their structure for the reaction medium (solvent). According to literature, as the crosslinking percentage decreases, the flexibility of the resin increases (Bringué et al., 2019). Therefore, understanding the swelling behavior of resins during the reaction is an important factor to analyze, since as the resins swells, its diameter increases, which consequently enlarges the contact area between the catalytic sites and the reaction medium, leading to improved catalytic performance (Ramírez et al., 2021). It is understood that the swelling of resins depends on its interaction with the solvent, cross-link density, among other variables. Karam and Tien (1985) (Karam and Tien, 1985) describe a theoretical calculation for the swelling index (Sw) of a resin containing occlusions, in a given solvent, based on a modification of the Flory-Rehner equation. The referred algorithm is shown in 17–20.

$$\ln(1-\nu_R) + \nu_R + \mu_R \nu_R^2 + \frac{\rho_R V_1 \nu_R^{\frac{1}{3}}}{\overline{M_C} K^{\frac{4}{3}}} - \left[\ln(1-\nu_0) + \nu_0 + \mu_P \nu_0^2\right] = 0$$
(17)

$$\ln(1 - \nu_{R}) + \nu_{R} + \mu_{R}\nu_{R}^{2} + \frac{\rho_{R}V_{1}\nu_{R}^{\frac{1}{3}}(1 + 2K^{2})}{3\overline{M_{C}}K^{\frac{4}{3}}} + \frac{(K+1)^{3} + 2K^{3}}{2\left[(K+1)^{3} - K^{3}\right]} \left\{ \ln(1 - \nu_{P}) + \nu_{P} + \mu_{P}\nu_{P}^{2} - \left[\ln(1 - \nu_{0}) + \nu_{0} + \mu_{P}\nu_{0}^{2}\right] \right\}$$

$$(18)$$

$$K = \frac{\nu_R}{\nu_P} \tag{19}$$

$$Sw = 1 + \frac{\left[\frac{\rho_s}{\rho_R} w_R\left(\frac{1}{\nu_R} - 1\right) + \frac{\rho_s}{\rho_P} w_P\left(\frac{1}{\nu_P} - 1\right)\right]}{w_R + w_P}$$
(20)

where the interaction parameters can be calculated as follows (Blanks and Prausnitz, 1964).

$$\mu_R = \mu_P = 0.34 + V_1 \frac{A_{12}}{RT} \tag{21}$$

$$A_{12} = \left(\delta_s - \delta_R\right)^2 \tag{22}$$

The system was fed with the values of $\overline{M_c}$ and w_p , provided by the copolymerization model and $v_0 = 0$ (dissolved polymer in the supernate was neglected). The system of non-linear Eqs. 17–20 with four unknowns (v_R , v_P , K and Sw) was solved through the function follow in scilab.

According to Blanks and Prausnitz (1964), the Eq. 22 is only valid for apolar-apolar solvent-polymer interaction. For polar-apolar and polarpolar interactions, the term A_{12} presents different equations (Blanks and Prausnitz, 1964). Since the synthesis of solketal produces water, a sharp variation in polarity may happen during the reaction, depending on its conversion degree. For this reason, rather than collecting/fitting the solubility parameters (δ), the parameter A_{12} was directly fitted to experimental data of swelling in isolate compounds (of the solketal synthesis) and also mixtures, as shown in the Results and discussion section.

The sulfonated polystyrene density (ρ_{PSS}) was calculated through the method of (Sewell, 1973). In the present work these densities of the resin (ρ_R) and occluded polystyrene (ρ_P) were calculated as a function of the Ion Exchange Capacity (IEC) of the resin, as follows.

$$\rho_R = \rho_P = \frac{[IEC]}{[IEC]_{\max}} \rho_{PSS} + \left(1 - \frac{[IEC]}{[IEC]_{\max}}\right) \rho_{PS}$$
(23)

For styrene-divinylbenzene sulfonated resin, $[IEC]_{max} = 5.43 \text{ mmolg}^{-1}$ (considering that all aromatic rings contain a single SO₃H).

The swelling index (Sw) can be used to calculate the particle porosity (ϵ_p) and particle radius (R_p) during the catalytic synthesis of solketal, as follows.

$$\varepsilon_p = \frac{\rho_R(Sw - 1)}{\rho_R(Sw - 1) + \rho_s} \tag{24}$$

$$R_p = R_{p,dry} \sqrt[3]{\frac{\rho_R}{\rho_{app}}}$$
(25)

where ρ_{app} , ρ_R and ρ_s are the apparent density (mass of resin per volume of swollen particle), the resin density (skeletal density) and the solution density, respectively. $R_{p,dry}$ and R_p are the radii of dry and swollen particle, respectively.

2.5. Mass Balance equations for species i in the resin particle and bulk fluid

The mass balance was based on the species involved in the entire reaction system, including concentrations within the particles $(C_{p,i})$ and in the bulk $(C_{b,i})$. Fig. 3 provides an illustration of the reaction system.

Eqs. 26 and 27 represent the concentrations of reactions species "i", in the particle $(C_{p,i})$ and bulk $(C_{b,i})$.

$$\varepsilon_p \frac{\partial C_{p,i}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{eff,i} r^2 \frac{\partial C_{p,i}}{\partial r} \right) + (1 - \varepsilon_p) \nu_i \rho_R \Re$$
(26)

$$\frac{\partial C_{b,i}}{\partial t} = -\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right) \frac{3}{r_p} D_{eff,i} \frac{\partial C_{p,i}}{\partial r}\Big|_{r=r_p}$$
(27)

Boundary conditions:

$$t = 0C_{b,i} = C_{b,i0}$$
(28)

$$t = 0C_{p,i} = C_{p,i0}$$
(29)

$$r = 0 \frac{\partial C_{p,i}}{\partial r} = 0 \tag{30}$$

$$\mathbf{r} = \mathbf{r}_p C_{b,i} = C_{p,i} \big|_{\mathbf{r} = \mathbf{r}_p} \tag{31}$$

Discretization with 4 points (N= 4) along the radius *r* were carried out to transform Eq. 26 into a system of ordinary differential equations (ODEs) using finite difference method (FDM). The discretization points range from h = 1 (r = 0) to h = N ($r = r_p$). The finite difference equations are described in 32 and 33 (Li and Zeng, 2012).

$$\left. \frac{\partial C_{p,i}}{\partial r} \right|_{h} = \frac{C_{p,i_{h+1}} - C_{p,i_{h-1}}}{2\Delta r}$$
(32)

$$\left. \frac{\partial^2 C_{p,i}}{\partial r^2} \right|_h = \frac{C_{p,i_{h+1}} - C_{p,i_h} + C_{p,i_{h-1}}}{2\Delta r}$$
(33)

where:

 C_{p,i_h} is the concentration of i inside the particle at the point h; Δr is the distance between discretization points.

A singularity problem arises $\begin{pmatrix} 0\\0 \end{pmatrix}$ when applying FDM to Eq. 26. This issue was resolved by applying the L'Hopital's rule to the terms where r = 0, as shown in Eq. 34.

$$\frac{2}{r}\frac{\partial C_{p,i}}{\partial r}\Big|_{r=0} = 2\frac{\partial^2 C_{p,i}}{\partial r^2}\Big|_{r=0}$$
(34)

The application of the finite difference method also requires addressing the term $C_{p,i_{N+1}}$, when h = N in Eqs. 32 and 33. This is handled using the boundary condition 31, i.e., $C_{p,i_{N+1}} = C_{p,i}|_{r=r_p} = C_{b,i}$. Anyway, this term appears in (32) and (33) when h = N. Therefore, for mathematical consistency, a layer between N and N+1 must be considered to close the method, as illustrated in Fig. 4. This approach does not interfere with the actual value of the particle radius r_p , as the



Fig. 3. - Illustration of the reactor, particles, and reaction medium.



Fig. 4. - Discretization with adaptative refinement.

additional layer is purely a numerical artifact to ensure the stability of the finite difference scheme.

As a first approach, the aforementioned traditional finite difference method was applied. However, the required number of points to ensure accurate results was high (around 80), leading to considerably long simulation times (~ 30 min per case). To address this, adaptive refinement was implemented using four discretization points, corresponding to five layers ($\Delta r_1 to \Delta r_5$), as illustrated in Fig. 4. In this approach, the two layers adjacent to the particle surface (inner and outer) were adjusted according to the studied system (with or without solvent). Adaptive refinement led to a significant improvement, reducing simulation times to approximately 0.2 minutes per case, making the optimization procedure more viable by enabling a quicker maximization of the R² value between the model and experimental data. It is important to note that the computer used for the simulations has the following specifications: Windows 10 Enterprise (version 22H2), Processor Intel® Core™2 Quad CPU Q9500 @ 2.83 GHz, and 10.0 GB of RAM. The numerical data for the thicknesses of the layers along the radial direction of the particles for each system are provided in the Results and discussion section.

The effective diffusion coefficients were calculated through Eq. 35. Fernandez-Prini and Philipp (1976) described the tortuosity factor for a styrene-divinylbenzene sulfonated resin as $\tau = \frac{(2-\varepsilon_p)^2}{\varepsilon_p}$, which was used in the present study Fernandez-Prini and Philipp (1976). Effects that were not theorized in the model, such as the possibility of phase separation occurring in specific compositions, were taken into account through the correction factor φ_C .

$$D_{eff,i} = \frac{\varepsilon_p D_{i,m}}{\varphi_c \tau} \tag{35}$$

The diffusion coefficient of the component *i* in the mixture $(D_{i,m})$ was calculated through the Perkins and Geankoplis correlation (Perkins and Geankoplis,) as follows.

$$D_{i,m} = \frac{1}{\eta_m^{0.8}} \sum_{\substack{j=1\\j\neq i}}^{nc} x_j D_{ij}^0 \eta_j^{0.8}$$
(36)

The infinite dilution diffusivity of *i* in *j* is a function of temperature (*T*), viscosity of j (η_j) and the molar volumes of *i* and *j* ($V_{M,i}$ and $V_{M,j}$), and can be calculated for each pair of compounds in the mixture through Eq. 37 (Andreas, 1952).

$$D_{i,j}^{0} = \frac{8.2 \times 10^{-8} T}{\eta_{j} V_{M,i}^{\frac{1}{3}}} \left[1 + \left(\frac{3V_{M,j}}{V_{M,i}} \right)^{\frac{2}{3}} \right]$$
(37)

The viscosities of solketal and the other reaction compounds were collected from literature (Esteban et al., 2016; Carl, 1999). The reaction rate (\Re) was written considering the LHHW model in terms of activities as follows.

$$\mathfrak{R} = \frac{k_c \left(a_A a_G - \frac{a_S a_w}{\kappa_{eq}}\right)}{\left(1 + K_{S,W} a_w\right)^2}$$
(38)

Applying the assumption of constant activity coefficient along the reaction, Eq. 39 can be written as:

$$\mathfrak{R} = \frac{k_c' \left(C_A C_G - \frac{C_S C_w}{K_{eq}} \right)}{\left(1 + K_{S,W}' C_w \right)^2}$$
(39)

where:

$$k'_c = k_c \frac{\gamma_A \gamma_G}{C_r^2} \tag{40}$$

$$K_{eq}' = \frac{\gamma_A \gamma_G}{\gamma_S \gamma_w} K_{eq}$$
(41)

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$$K_{S,W}' = \frac{K_{S,W}\gamma_{W}}{C_{T}}$$
(42)

 γ_i and C_i are the activity coefficient and concentration of the component *i* (A: Acetone, G: Glycerol, S: Solketal, W: Water), respectively; C_T is the total concentration of compounds in the mixture. The activity coefficients used in Eqs. 40 - 42 were calculated at the chemical equilibrium through modified UNIFAC (Jakob et al., 2006), and the referred data are related in Supplementary Information (S1).

The variation of k_c and K_{eq} with temperature were considered as follows.

$$k_c = k_{c0} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$
(43)

$$K_{eq} = \exp\left(-\frac{\Delta G^o}{RT}\right) \tag{44}$$

The reference temperature used in the present study was $T_{ref} = 313K$.

The parameter k_{c0} is the rate constant of the reaction catalyzed by a give resin at the reference temperature. This parameter can be correlated with the rate constant of the reaction at the catalytic site (k_{c0}^{s}) as described in Eq. (45).

$$k_{c0} = k_{c0}^{s} [IEC]_{eff} \tag{45}$$

where $[IEC]_{eff}$ is the effective ion exchange capacity, i.e., the catalytic sites content that effectively participates in the reaction. Eq. 46 shows its calculation.

$$[IEC]_{eff} = Y_{AS}[IEC] \tag{46}$$

where Y_{AS} is the fraction of accessible sites in the resin. The accessibility to catalytic sites was assessed based on the molecular size of the compounds in the reaction medium and the radius of gyration of the sequences L_{En} . This radius of gyration of the sequences was estimated by considering the radius of a polystyrene chain in tetrahydrofuran (THF) at 25 °C, according to Eq. 47 (Terao and Mays, 2004).

$$R_{g} = 0.0118 M_{w}^{0.6} \tag{47}$$

In Eq. 47, M_w is the molecular weight of the chain in g mol⁻¹ and R_g is

the radius of gyration in nm. The comparison among molecular sizes is illustrated in Fig. 5.

Since the kinetics of swelling from the dry resin were not studied in this work, the simulations were conducted under the assumption that the catalyst was pre-swollen in the reaction medium. This is a reasonable assumption, as all resins studied here are porous, allowing relatively easy penetration of the reaction medium. To the best of our knowledge, no data on the radius of gyration of polystyrene in the solketal reaction system is available. Therefore, the radius of gyration of polystyrene solvated in THF was used as an approximation (Eq. 47). Nonetheless, the impact of variables related to the reaction rate (e.g., k_{c0}^s , Y_{AS}) is less pronounced than the effects of diffusion, as will be discussed in Section 3.3.

In Fig. 5, the molecular sizes of the compounds were estimated through Kim's expression, as described in Eq. 48 (Marcus, 2003).

$$\sigma = 0.1363 V_M^{\frac{1}{3}} - 0.085 \tag{48}$$

where σ is the molecular diameter in nm, and V_M is the molar volume in cm³ mol⁻¹. This analysis suggests that L_{En} sequences with $n \leq 2$ might be inaccessible due to hindering effects caused by the adjacent chains passing through the cross-linkages. Hence, the fraction of accessible sites can be estimated as follows.

$$Y_{AS} = \frac{\sum_{n=3}^{n_{max}} nL_{En}}{\sum_{n=1}^{n_{max}} nL_{En}}$$
(49)

where L_{En} is the sequence containing n styrene units connecting two crosslinking points. The reactions in terms of sequences and the respective molar balances are detailed in Supplementary Information S2. Background information on the concept of sequences can be found elsewhere (Aguiar et al., 2021). The differential-algebraic system of equations described in this section was solved in Scilab. For solventless reaction simulations, the 'stiff' argument was used with the ode algorithm, whereas for reactions with solvent, the 'stiff' argument was not used.



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Fig. 5. - Comparison among sequences and compounds molecular diameters.

3. Results and discussion

3.1. Resin characteristics

An estimation of the main parameters of the polymer network of the resins was carried out with the copolymerization model described in the in Section 2.1. Since the formulation of commercial resins is classified information, the synthesis conditions used in the simulations were collected from the literature. Coutinho et al. (2006) synthesized a variety of sulfonated styrene-DVB particles with characteristics resembling those of commercial resins, and these synthesis conditions were considered in the present simulations (Coutinho et al., 2006).

The distribution of sequences between cross-links (L_{En}) and the data of the resins studied herein are presented in Fig. 6 and Table 2, respectively.

Based on the experimental results found in the studies of Esteban et al., the highest performance was obtained for the resin GF 101 (among the resins studied), which indicates that this resin has lower cross-linking degree (better swelling and accessibility) (Esteban et al., 2015, 2017). For this reason, the present copolymerization simulations were carried out setting the DVB percentage at 8 % for the resin GF 101, which is a cross-linker content commonly found in commercial resins (Tejero et al., 2016). It can be observed that the copolymerization model provides coherent predictions of $\overline{M_{C}}$, i.e., longer sequences between cross-links for lower DVB percentages. The properties w_P and Y_{AS} also increases with the decreasing of DVB percentage as expected, which is corroborated by the curves in Fig. 6. The simulated data presented in Table 2 were used to predict the swelling behavior of the resins during the catalytic runs as described in the following section.

3.2. Swelling Index results

The solubility term A_{12} used to calculate the interaction parameters (Eq. 22) was estimated as an average considering the contribution of each component in the mixture, as follows.

$$A_{12} = \emptyset_G A_{12G} + \emptyset_A A_{12A} + \emptyset_S A_{12S} + \emptyset_W A_{12W} + \emptyset_E A_{12E}$$
(50)

where \emptyset_i is the volume fraction of the component i in the mixture, and A_{12i} is the solubility term for the resin swollen in the pure component i. In this study, it was assumed that all the resins have similar chemical characteristics, as they share the same chemical composition, consisting of styrene-divinylbenzene copolymers containing sulfonic groups (SO₃H). Hence, the term A_{12i} refers to the interaction between the component i and the referred resins (with i= A, G, S, W, E).

By using Karam and Tien's algorithm (Eqs. 17–20), A_{12i} was found for each component by fitting with experimental data collected in the present work. Table 3 and the bars graph in Fig. 7 show the results.



Fig. 6. – Distribution of sequences L_{En} along the resin. Y_{nLE} is the fraction of monomer units in chains containing n units among all the monomer units in the resin (equation S12).

 Table 2 –

 Nominal and simulated data for the resins.

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		Nominal data (Esteban et al., 2017)			Simulated dat study)	a (present		
	Resin	% DVB	R _{P,dry} (μm)	<i>IEC</i> (mol kg ⁻¹)	$\overline{M_C}$ (g mol ⁻¹)	WP	Y_{AS}	
	CT276	17	190	4.90	3561	0.0087	0.89	
	A15	20	190	4.81	2935	0.0056	0.86	
	A35	20	190	5.25	2935	0.0056	0.86	
	A36	12	190	5.42	5454	0.0211	0.94	
	CT275	12	190	4.98	5454	0.0211	0.94	
	GF101	N/A	190	5.11	9191	0.0518	0.97	

 $R_{P,dry}$: radius of the dry resin, *IEC*: ion exchange capacity, $\overline{M_C}$: Average molecular weight between cross-links, w_P : fraction of occluded linear chains in the resin Y_{AS} : fraction of accessible sites. N/A: Not available.

 Table 3 –

 Swelling experiments and interaction data.

Exp	ØG	ØA	Øs	Øw	ØE
Ι	0.50	0.00	0.00	0.50	0.00
II	0.00	1.00	0.00	0.00	0.00
III	0.00	0.00	1.00	0.00	0.00
IV	0.00	0.00	0.00	1.00	0.00
V	0.00	0.00	0.00	0.00	1.00
VI	0.10	0.10	0.31	0.05	0.44
VII	0.07	0.70	0.20	0.03	0.00
$A_{12G} = 20$	$0.25 A_{12A} =$	10.55 A ₁₂₅	$= 6.78 A_{12W}$	$= 49.46 A_{1}$	$_{12E} = 12.33$

G: Glycerol, A: Acetone, S: Solketal, W: Water, E: Ethanol. Swelling experiments conducted in this work with the resin Amberlyst 15 through gravimetry (Godoy et al., 2022). VI and VII represent chemical equilibrium compositions for solvent and solventless systems, respectively.

In order to avoid numerical issues and long simulation times for the catalytic process, the system of Eqs. 17-20 was replaced by linear equations of *Sw* as a function of the glycerol conversion (*X_G*), as follows.

$$Sw = a_{sw}X_G + b_{sw} \tag{51}$$

Eq. 51 was fitted to each reaction condition obtained from literature. The experimental conditions and the respective fitted parameters a_{sw} and b_{sw} are related in Table 4. The fitting results provided an average R² of 0.9995 and are illustrated in Fig. 7.

The swelling data presented in Fig. 7 was obtained using Karan and Tien's algorithm, which was supplied with $\overline{M_C}$ and w_P data from the copolymerization model. Despite the different values of these variables for each resin, the algorithm produced linear swelling profiles as a function of glycerol conversion in all cases.

On one hand, the particle radius grows with conversion, which enhances the mass transfer barrier. On the other hand, the effective diffusion coefficient rises due to the increasing porosity throughout the reaction. Further discussions are provided in the next section.

3.3. Catalysis model results

A preliminary evaluation of the heterogeneous catalysis model developed for solketal synthesis was conducted to verify the accuracy of the discretization approach (variation of N) and the impact of the reaction rate on the results (variation of k_{c0}^s). The corresponding results are presented in Fig. 8.

Fig. 8a shows that, despite the small number of discretization points, made possible by adaptive refinement (unequal point spacing), N=4 is sufficient to yield accurate results. For higher values of N, the results remain practically unchanged.

The discretization data were defined differently for each system, as mentioned in the model description. For the system with ethanol as solvent, it was defined $\Delta r_i = 0.00732R_P$ for the two outer layers of the



Fig. 7. – Swelling index study. Bars graph: fitting of Karam and Tien's algorithm to experimental data (fitting A_{12i} for each component i). The dots represent the swelling data obtained with Karam and Tien's algorithm for different compositions (as a function of X_G), using the A_{12i} previously obtained for each component.

 Table 4 –

 Experimental conditions and resins data.

Run	Resin	T (K)	MR	%Е	%Cat	a _{sw}	b _{sw}
E1	CT276	313	4.5	0	0.50	0.1117	1.6999
E2	A15	313	4.5	0	0.50	0.1025	1.6723
E3	A35	313	4.5	0	0.50	0.1025	1.6723
E4	A36	313	4.5	0	0.50	0.1373	1.7732
E5	CT275	313	4.5	0	0.50	0.1373	1.7732
E6	GF101	313	4.5	0	0.50	0.1698	1.8510
M1	A35	323	1.0	50	0.50	0.1626	1.7429
M2	A35	313	1.0	50	0.50	0.1594	1.7142
M3	A35	303	1.0	50	0.50	0.1560	1.6851
M4	A35	303	2.0	50	0.50	0.1064	1.7086
M5	A35	303	1.0	70	0.50	0.1560	1.6851
M6	A35	323	1.0	50	0.25	0.1626	1.7429
M7	A35	323	1.0	50	0.25	0.1626	1.7429

T: Temperature, MR: Molar ratio acetone:glycerol, %E: molar percentage of solvent (Ethanol), %Cat: weight percentage of catalyst, a_{sw} and b_{sw} : coefficients of linear swelling. Runs E1-E6 from Esteban et al (Esteban et al., 2017). and M1-M7 from Moreira et al (Moreira et al., 2019).

catalyst (i = 4 and 5), and $\Delta r_i = 0.32845R_P$ for the 3 inner layers (i = 1–3). On the other hand, for the solventless system, it was possible to work with $\Delta r_i = 0.2R_P$ for all layers. This difference in discretization is related to the steep slope observed in the solvent system, as depicted in Fig. 8. Due to rapid changes occurring early in the reaction, the model can only achieve experimental conversions with very narrow boundary layers for the system operated with ethanol.

Fig. 8b evaluates the effect of the rate constant k_{c0}^s on the conversion curve. It can be observed that large changes in k_{c0}^s lead to only small variations in the conversion profile. This behavior suggests a diffusion-controlled process, which is discussed in detail later in this section.

The heterogeneous catalysis model developed for the synthesis of solketal was validated using experimental data from the literature (Moreira et al., 2019). The reactions were conducted over 8 hours at a pressure of 8 bars, with stirring at 750 rpm. The molar ratio of acetone to glycerol, temperature, solvent percentage, and catalyst loading were varied across multiple experiments, as shown in Table 4. The model was validated for both solvent and solventless systems, as illustrated in Figs. 9 and 10, respectively

Fig. 9 demonstrates the ability of the present model to represent the exothermal character of the reaction, correctly predicting the equilibrium plateau for each temperature, i.e., the equilibrium conversion



Fig. 8. – Preliminary simulations under the conditions of experiment M1. Variation of glycerol conversion with the number of discretization points (a) and with k_{c0}^{s} (b).



Fig. 9. – Glycerol conversion along the reaction time for the solketal synthesis in presence of ethanol as solvent. Mod: model results, Exp: Experimental data (Moreira et al., 2019a).



Fig. 10. – Glycerol conversion along the reaction time for the solventless solketal synthesis. (a) Resins CT276, A15 and A35, (b) Resins A36, CT275 and GF101 Mod: model results, Exp: Experimental data (Esteban et al., 2017).

decreases as the temperature increases from 303 to 323 K (a). The effects of the acetone: glycerol molar ratio (c) and particle diameter (d) were also well predicted by the model. The equilibrium conversions for different dilution degrees (50 % and 70 %, Fig. 9b) were similar, and the model accurately captured this behavior. The results shown in Fig. 9 yielded an R^2 of 0.96.

Fig. 10 shows the validation of the model with experimental data of a solventless system of solketal synthesis. Different resins were tested in this set of experiments, namely those related in Table 2. These fitting results specifically validate the ability of the model to account for the properties of the resin, such as swelling behavior and accessibility to acidic sites. Despite the similar reaction times and temperatures compared to cases M1-M7, the equilibrium plateau is less pronounced in Fig. 10, underscoring the importance of the solvent in this reaction. The simulated data for resin characteristics presented in Tables 2 and 4 are responsible for distinguishing the catalytic performance of each resin, as the reaction conditions were the same for runs E1 to E6. The results shown in Fig. 10 yielded an R^2 of 0.99.

Table 5 relates the parameters used in the simulations.

The kinetic parameters k_{c0}^s , E_a and $K_{S,W}$ agree with those found by (Moreira et al., 2019). Simulations revealed internal effectiveness factors below 1, as illustrated in Fig. 11a.

Fig. 11a shows that the process is diffusion-controlled under the studied conditions, as evidenced by the small effectiveness factor values

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Model parameters for the solketal synth	esis.

System	ΔG° (kJ mol ⁻¹)	φ_C	$k_{c0}^{s}(s^{-1})^{a}$	$E_a(kJ mol^{-1})^b$	$K_{S,W}^{b}$
With ethanol (Moreira et al., 2019)	$\textbf{4.7}\pm\textbf{0.9}$	1.0	109	69	14.4
Solventless (Esteban et al., 2017)	12.1 ± 0.6	5.1 ± 0.2	109	69	14.4

^a Obtained for T = 313 K, ^b collected from reference (Moreira et al., 2019)

for experiments M3-M5. Notably, glycerol exhibits very high viscosity, exceeding 500 cP under certain conditions simulated in this work. According to Eqs. 35–37, such high viscosities reduce the effective diffusion coefficients, particularly when calculating the diffusion coefficient of binary mixtures containing glycerol (Eq. 37). Consequently, the diffusion rate is significantly lowered, which explains the relatively low values of the effectiveness factor. Nevertheless, the values obtained for the effectiveness factor (< 0.1) are consistent with those reported in a previous study (Moreira et al., 2019). Eq. 52 provides the calculation of the effectiveness factor (EF):

$$EF = \frac{\overline{\Re}}{\overline{\Re}_{S}}$$
(52)



Fig. 11. - Effectiveness factor over time for cases M3-M5 (a) and average effectiveness factors for different dry particle radius considering conditions of case M3 (b).

where:

 $\overline{\mathfrak{R}}$: Average reaction rate within the particle (mol Kg⁻¹ s⁻¹);

 \Re_{S} : Reaction rate at the surface of the particle (mol $Kg^{-1}\ s^{-1}$).

To determine the particle radius at which intraparticle diffusion limitations become negligible, simulations with varying particle radius were performed (Fig. 11b). For the simulated conditions of experiment M3, it was observed that for dry particle radii of 3 μ m or smaller, the average effectiveness factor approaches 1. This indicates that for dry particles with a radius smaller than 3 μ m, under the mentioned conditions, the process is no longer purely diffusion-limited, and the reaction rate becomes the controlling mechanism. Based on this finding, further studies can be conducted using the aforementioned radius magnitude to isolate the effect of the reaction rate. This will enable a reevaluation of parameters such as activation energy and pre-exponential factor, considering the accessibility concepts described herein.

While variations in the number of discretization points starting from N = 4 have a negligible effect on the conversion profiles (see Fig. 8), they do show some impact on the effectiveness factor in the cases studied, likely due to the adaptative refinement. Therefore, the simulations in Fig. 11 were conducted with N = 30.

In the study of (Moreira et al., 2019), the authors considered the nonideal behavior of the reaction medium and found $\Delta G^{\circ} = 1.4$ + 0.1 kJ mol⁻¹, which contrast with the negative value found by Nanda et al. ($\Delta G^{\circ} = -2.1 \pm 0.1 \text{ kJ mol}^{-1}$) (Nanda et al., 2014), where the nonideal behavior of the reaction medium was neglected. In the present study, nonideal homogeneous liquid mixture was considered, and the activities of the compounds were calculated through modified UNIFAC, making use of current parameters (see Supplementary Information S1). Furthermore, Nanda et al. presented a purely kinetic model that does not account for intraparticle diffusion resistance, which is a relevant factor in justifying the differences in ΔG° values. With the present update, ΔG° is still positive but higher than the previously reported value (see Table 5). The ΔG° and φ_{C} values were obtained by curve fitting (Figs. 9 and 10) by maximizing the R^2 , achieving values of 0.96 and above, as previously mentioned. The system with ethanol was accurately described by the model without any need for correction ($\varphi_C = 1.0$), indicating that this enhanced mathematical model effectively accounted for most phenomena.

Conversely, the solventless system involve additional phenomena, such as phase separation due to the limited miscibility between glycerol and acetone (Esteban et al., 2015), mainly in the initial stages of the reaction. Since the complexity of the model would increase considerably for a multiphase system, the same model was applied to the solventless system, yielding an apparent ΔG° of 12.1 ± 0.6 kJ mol-1. The transport phenomena could not be properly described by the present model with $\varphi_C = 1$ for the solventless system. Instead, φ_C was found to be 5.1 ± 0.2 , indicating slower diffusion compared to the medium diluted in ethanol. This correction factor is likely necessary due to segregation in the liquid phase, which was not accounted for in the model. Under this assumption, the glycerol-rich phase would diffuse more slowly into the particle than predicted by the model using $\varphi_C = 1$.

The novelty of the present approach lies in considering a swollen

resin (catalyst) and the variation of its properties during the reaction as a function of the medium composition. In this sense, the particle radius is directly impacted by the swelling index, which varies during catalysis. Consequently, the porosity of the particle also changes throughout the reaction, as depicted in Fig. 12.

Despite the increase in swelling index over reaction time, the porosity of the particle also depends on the average density of the medium (ρ_s), as shown in Eq. 24. For this reason, a competition of effects is observed in Fig. 12, where ε_p reaches a maximum in the first minutes of the reaction (due to the sharp increase in conversion) and then decreases slightly. Similarly, the particle radius (R_p) depends on the apparent density (Eq. 25) which is a function of the particle porosity: $\rho_{app} = \rho_R (1 - \varepsilon_p)$, presenting the same profile shape. It is important to highlight that the higher cross-linking density of A35 (20 % DVB) leads to smaller porosities and radius in comparison with A36, which contains 12 % DVB.

The current state of the art in modeling resin-catalyzed reactions includes studies that often overlook the behavior of the resin and its consequent effect on catalytic performance. Research on solketal synthesis ^{(Fukumura et al., 2023; Trisnantari et al., 2024), as well as other} reactions catalyzed by commercial resins (Sánchez-Correa et al., 2023; Melfi et al., 2021; Orabona et al., 2024; Badia et al., 2021), typically does not consider the swelling of the catalyst during the process. A significant discrepancy in reaction variables is observed when comparing simulations with and without the swelling of the resin, as shown in Fig. 13. For the simulation without swelling, the porosity was set constant at 0.22, which is the porosity of the dry resin (A36). In the case of the simulation with resin swelling, however, the porosity was allowed to vary according to Eq. 24. As mentioned in Section 2.2, the simulations were conducted under the condition of pre-swollen resin in the reaction medium at time zero. Consequently, the porosity of 0.22 for dry resin does not align with the initial porosity values shown in Fig. 12.

The tortuosity factor is considerably reduced when the resin is swollen in the reaction medium, as can be observed in Fig. 13. A surge of



Fig. 12. – Predictions of particle radius and porosity along the reaction time for resins Amberlyst 35 (E3) and Amberlyst 36 (E4).



Fig. 13. – Comparison between simulations considering constant porosity ($\varepsilon_p = 0.22$) and variable porosity (Eq. 24). Resin Amberlyst 36 and conditions of Run E4.

approximately 4 times is observed in the conversion results when comparing these two cases. The tortuosities in Fig. 13 do not begin at the same value due to the previously mentioned pre-swollen conditions of the resins. This effect also influences the concentration gradient along the particle radius, leading to a faster progression towards concentration uniformity within the particle in the case of variable porosity, as expected (Fig. 14).

Fig. 14 shows that the concentration gradients of solketal and glycerol evolve more rapidly in the variable porosity case, indicating that the reaction is facilitated compared to the constant porosity case.

The reaction rate along the time is also well represented by the model, which captures the effect of excess acetone and different dilution degrees, as shown in Fig. 15.

4. Conclusion

Properties of commercial resins that directly affect their performance as catalysts were estimated through an improved copolymerization model developed herein. For resins with 8–20 % DVB, the molecular



Fig. 15. - Simulation of reaction rates along time for runs M3, M4 and M5.

weight between cross-links was found to be in the range of $2935 - 9191 \text{ g mol}^{-1}$, and the fraction of accessible acidic sites was in the range of 0.86 - 0.97. These properties were useful for calculating the Swelling Index of each resin for components of the solketal synthesis through the Karam and Tien's algorithm, which fairly represented the experimental swelling results. The swelling index predictions during the reaction could be approximated as a linear function of the glycerol conversion, with an average R^2 of 0.9995.

In the solketal synthesis, the effects of temperature, acetone/glycerol molar ratio, dilution degree, particle size, and type of resin were well predicted by the present model, yielding $R^2 = 0.96$ for the system with ethanol as solvent and $R^2 = 0.99$ for the solventless system. Gibbs free energies of 4.7 ± 0.9 kJ mol⁻¹ and 12.1 ± 0.6 kJ mol⁻¹ were found for solvent and solventless systems, respectively. Furthermore, φ_C was found to be 1 for the solvent system and 5.1 ± 0.2 for the solventless system. These differences in parameters for each system may be attributed to the multiple liquid phases that occur in the solventless system.

The difference in catalytic efficiency is remarkable when simulations are conducted with and without considering a swollen resin. When the swollen resin is considered, the reaction can reach a conversion approximately four times higher than that achieved with the unswollen



Fig. 14. – Intraparticle profiles considering constant porosity ($\varepsilon_p = 0.22$) and variable porosity (Eq. 24). Resin Amberlyst 36 and conditions of Run E4. C_s: Solketal concentration, C_G: Glycerol concentration, r / R_p: Normalized radial coordinate.

resin, according to the developed model. Hence, the deterministic model developed herein is able to encompass a multitude of phenomena in resin-catalyzed reactions, proving to be more comprehensive and with feasible parameters compared to current literature. Additionally, this approach can be applied to other reactions catalyzed by polymer-supported materials, allowing for the assessment of catalyst behavior and providing more realistic predictions

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Symbology

Symbol	Description	Unit
A_{12}	Solubility term	MPa
a_i	Activity of component i	Dimensionless
% Cat	Catalyst percentage	%
$C_{b,i}$	Concentration of component i in bulk	$mol L^{-1}$
C_i	Concentration of the component i	$mol L^{-1}$
C_{i0}	Initial concentration of the component i	$mol L^{-1}$
CLP	Crosslinking points	Dimensionless
C_P	Reactivity correlation parameter	Dimensionless
$C_{p,i}$	Concentration of component i in the particle	$mol L^{-1}$
Cnib	Concentration of i inside the particle at the point h	$mol L^{-1}$
C _s	Solketal concentration	$mol L^{-1}$
C_T	Total concentration of the components in the	mol L ⁻¹
- 1	mixture	
[CL]	Crosslinked units concentration	$mol L^{-1}$
Dim	Diffusion coefficient of component i in the mixture	$dm^2 s^{-1}$
D.a.	Effective diffusion coefficient	$dm^2 s^{-1}$
E ejj i	Reaction activation energy	k I mol ⁻¹
0%E	Molar percentage of ethanol	N5 11101 0/2
FE	Effectiveness factor	Dimensionless
f	Initiator efficiency	Dimensionless
J h	Discretization point inside the particle	Dimensionless
11	Initiation concentration	mal I ⁻¹
I IEC		mod a^{-1}
IEC	Effective in eveloped consists	med g
IEC _{eff}	Elective ion exchange capacity	11 - 1 - 1
κ _c	Rate constant of reaction	mol kg $\frac{1}{5}$ s $\frac{1}{-1}$
k _c	Apparent rate constant of reaction	L ² mol ⁻ kg ⁻ s ⁻
k_{c0}	Rate constant for the reference temperature	$mol \ kg^{-1} \ s^{-1}$
k_{c0}^{s}	Rate constant of the reaction at the catalytic site	s ⁻¹
k _{cyc}	Cyclization constant	s^{-1}
Κ	Ratio $\frac{\nu_R}{m}$	Dimensionless
	v_P	
k_d	v_P Initiator decomposition constant	s^{-1}
k _d K _{eq}	v_p Initiator decomposition constant Equilibrium constant of the reaction	s ⁻¹ Dimensionless
$egin{array}{c} k_d \ K_{eq} \ K'_{eq} \end{array}$	v_p Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant	s ⁻¹ Dimensionless Dimensionless
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$egin{aligned} k_d \ K_{eq} \ K'_{eq} \ k_{I1} \ k_{I2} \ k_{R}. \end{aligned}$	v_p Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant Styrene propagation constant	s^{-1} Dimensionless Dimensionless L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1}
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k_d K_{eq} K_{lq} k_{l1} k_{l2} k_{p1} k_{p2} k_{P3} K_{eq}	v_p Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant Styrene propagation constant DVB propagation constant PDB propagation constant PDB propagation constant Adsorption equilibrium constant for water	s^{-1} Dimensionless Dimensionless L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1}
k_d K_{eq} k_{I1} k_{I2} k_{P1} k_{P2} k_{P3} $K_{S,W}$	v_p Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant Styrene propagation constant DVB propagation constant PDB propagation constant Adsorption equilibrium constant for water	s^{-1} Dimensionless Dimensionless L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} Dimensionless L mol ⁻¹
k_d K_{eq} k_{I1} k_{I2} k_{P1} k_{P2} $K_{S,W}$ $K'_{S,W}$	v_p Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant DVB propagation constant DVB propagation constant PDB propagation constant Adsorption equilibrium constant for water Apparent adsorption equilibrium constant	s^{-1} Dimensionless Dimensionless L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} L mol ⁻¹ s^{-1} Dimensionless L mol ⁻¹
k_{d} K_{eq} k_{I1} k_{I2} k_{P1} k_{P2} k_{P3} $K_{S,W}$ $K'_{S,W}$ k_{t}	v_p Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant Styrene propagation constant DVB propagation constant PDB propagation constant Adsorption equilibrium constant for water Apparent adsorption equilibrium constant Termination constant	s^{-1} Dimensionless Dimensionless L mol ⁻¹ s ⁻¹ L mol ⁻¹ s ⁻¹ L mol ⁻¹ s ⁻¹ L mol ⁻¹ s ⁻¹ Dimensionless L mol ⁻¹ s ⁻¹
k_{d} K_{eq} k_{I1} k_{I2} k_{P1} k_{P2} k_{P3} $K_{S,W}$ $K'_{S,W}$ k_{t} L_{An}	 V_P V_P Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant Styrene propagation constant DVB propagation constant PDB propagation constant PDB propagation constant Adsorption equilibrium constant for water Apparent adsorption equilibrium constant Termination constant Concentrations of sequences containing n styrene 	$\begin{array}{c} {\rm s}^{-1} \\ {\rm Dimensionless} \\ {\rm Dimensionless} \\ {\rm L} \ {\rm mol}^{-1} \ {\rm s}^{-1} \\ {\rm L} \ {\rm mol}^{-1} \ {\rm s}^{-1} \\ {\rm L} \ {\rm mol}^{-1} \ {\rm s}^{-1} \\ {\rm L} \ {\rm mol}^{-1} \ {\rm s}^{-1} \\ {\rm L} \ {\rm mol}^{-1} \ {\rm s}^{-1} \\ {\rm L} \ {\rm mol}^{-1} \ {\rm s}^{-1} \\ {\rm Dimensionless} \\ {\rm L} \ {\rm mol}^{-1} \\ {\rm L} \ {\rm mol}^{-1} \ {\rm s}^{-1} \\ {\rm mol} \ {\rm L}^{-1} \end{array}$
k_d K_{eq} k_{11} k_{12} k_{p1} k_{p2} $k_{S,W}$ $K_{S,W}$ k_t L_{An}	 V_P V_P Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant DVB propagation constant DVB propagation constant PDB propagation constant Adsorption equilibrium constant for water Apparent adsorption equilibrium constant Termination constant Concentrations of sequences containing n styrene units connecting a PDB to a radical center 	s^{-1} Dimensionless Dimensionless L mol ⁻¹ s ⁻¹ L mol ⁻¹ s ⁻¹ L mol ⁻¹ s ⁻¹ L mol ⁻¹ s ⁻¹ Dimensionless L mol ⁻¹ L mol ⁻¹ s ⁻¹
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k_d K_{eq} k_{f1} k_{f2} k_{p1} k_{p2} k_{p3} $K_{S,W}$ $K'_{S,W}$ k_t L_{Bn} L_{Cn}	 Vp Vp Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant DVB propagation constant DVB propagation constant PDB propagation constant PDB propagation constant Adsorption equilibrium constant for water Apparent adsorption equilibrium constant Termination constant Concentrations of sequences containing n styrene units connecting two PDBs Concentration of sequences containing n styrene 	$ s^{-1} Dimensionless Dimensionless L mol^{-1} s^{-1} Dimensionless L mol^{-1} s^{-1} mol L^{-1} mol L^{-1} $
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k_d K_{eq} k_{eq} k_{11} k_{12} k_{p1} k_{p2} k_{P3} $K_{S,W}$ $K_{S,W}$ $K_{S,W}$ k_t L_{Bn} L_{Cn}	 V_P V_P Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant DVB propagation constant DVB propagation constant PDB propagation constant PDB propagation constant Adsorption equilibrium constant for water Apparent adsorption equilibrium constant Termination constant Concentrations of sequences containing n styrene units connecting a PDB to a radical center Concentration of sequences containing n styrene units connecting two PDBs Concentration of sequences containing n styrene units connecting a crosslinked unit to a radical center 	s^{-1} Dimensionless Dimensionless L mol ⁻¹ s ⁻¹ L mol ⁻¹ s ⁻¹ L mol ⁻¹ s ⁻¹ L mol ⁻¹ s ⁻¹ Dimensionless L mol ⁻¹ L mol ⁻¹ s ⁻¹ mol L ⁻¹ mol L ⁻¹
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$ \begin{array}{l} k_{d} \\ K_{eq} \\ K_{eq} \\ k_{l1} \\ k_{l2} \\ k_{p1} \\ k_{p2} \\ k_{P3} \\ K_{S,W} \\ k_{t} \\ L_{An} \\ L_{Bn} \\ L_{Cn} \\ L_{Dn} \\ L_{En} \\ \\ M_{1,0} \\ M_{2} \\ M_{2,0} \\ \overline{M_{C}} \end{array} $	 Vp Initiator decomposition constant Equilibrium constant of the reaction Apparent equilibrium constant Styrene initiation constant DVB initiation constant DVB propagation constant DVB propagation constant DVB propagation constant PDB propagation constant PDB propagation constant Adsorption equilibrium constant for water Apparent adsorption equilibrium constant Termination constant Concentrations of sequences containing n styrene units connecting a PDB to a radical center Concentration of sequences containing n styrene units connecting two PDBs Concentration of sequences containing n styrene units connecting a crosslinked unit to a radical center Concentration of sequences containing n styrene units connecting a PDB to a crosslinked unit Concentration of sequences containing n styrene units connecting a PDB to a crosslinked unit Concentration of sequences containing n styrene units connecting a PDB to a crosslinked unit Concentration of sequences containing n styrene units connecting two crosslinked units Styrene concentration Initial styrene concentration DVB concentration DVB concentration Average molecular weight between CLs 	
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(continued)

MR	Molar ratio	Dimensionless
n	Number of units between CLs	r.u.
Ν	Number of layers in the catalyst	Dimensionless
n _{max}	Maximum n considered in the copolymerization	r.u.
	modeling	
Р	Dead polymer	$mol L^{-1}$
PDB	Pendant double bonds concentration	$mol L^{-1}$
P_L	Concentration of linear polymer chain	$mol L^{-1}$
R	Reaction rate	mol Kg $^{-1}$ s $^{-1}$
$\overline{\mathfrak{R}}$	Average reaction rate within the particle	$mol Kg^{-1} s^{-1}$
ℜ _s	Reaction rate at the surface of the particle	$mol Kg^{-1} s^{-1}$
R^{\bullet}	Total radicals' concentration	$mol L^{-1}$
R_0^{\bullet}	Primary radicals' concentration	$mol L^{-1}$
r	Particle radial coordinate	dm
r_A	Rate of reaction for the limiting reagent	$mol L^{-1} min^{-1}$
r_p	Particle radius	dm
Rg	Radius of gyration	nm
R_L^{\bullet}	Concentration of linear radicals	$mol L^{-1}$
R_P	Radius of swollen particle	dm
$R_{P,dry}$	Radius of dry particle	dm
R_S^{\bullet}	Concentration of radicals containing only styrene	$mol L^{-1}$
	units	
Sw	Swelling Index	Dimensionless
Т	Temperature	K
T_{ref}	Reference temperature	K
[SU]	Concentration of sulfonated units	$mol L^{-1}$
[U]	Concentration of total polymerized units	$mol L^{-1}$
$[U_1]$	Concentration of Styrene units	$mol L^{-1}$
$[U_2]$	Concentration of DVB units	$mol L^{-1}$
V_1	Molar volume of solvent	$\rm cm^3~mol^{-1}$
w_P	Weight fraction of occluded polystyrene in the gel	Dimensionless
W _R	Weight fraction of rubber in the gel	Dimensionless
x_i	Molar fraction of the component j	Dimensionless
X_G	Glycerol conversion	Dimensionless
Y_{AS}	Fraction of accessible sites in the resin	Dimensionless
Y_{CL}	Fraction of crosslinked units	mol CL (mol U) $^{-1}$
$Y_{LE,n}$	Fraction of L_{En} among all L_E	mol L_{En} (mol total
		$L_E)^{-1}$

Greek	Letters	Unit
γ_i	Activity coefficient of the component i	Dimensionless
ΔG^o	Gibbs free energy	$kJ mol^{-1}$
Δr	Catalyst layer	dm
δ_R	Solubility parameter of the resin	MPa ^{0.5}
δ_s	Solubility parameter of the solution	MPa ^{0.5}
ε_b	Bulk porosity	Dimensionless
ε_p	Particle porosity	Dimensionless
η_j	Viscosity	${\rm g}~{\rm dm}^{-1}~{\rm s}^{-1}$
μ_{P}	Polystyrene-solvent interaction factor	Dimensionless
μ_R	Rubber-solvent interaction factor	Dimensionless
ρ_{app}	Apparent density	$\rm kg~dm^{-3}$
ρ_P	Occluded polystyrene density	kg dm $^{-3}$
ρ_{PSS}	Sulfonated polystyrene density	kg dm^{-3}
ρ_R	Resin density	kg dm^{-3}
ρ_s	Solution density	kg dm ⁻³
σ	Molecular diameter	nm
τ	Tortuosity factor	Dimensionless
v_0	Volume fraction of dissolved polymer in the supernate	Dimensionless
v_P	Volume fraction of polystyrene in the swollen occluded	Dimensionless
	polystyrene	
v_R	Volume fraction of rubber in the swollen rubber network	Dimensionless
Øi	Volume fraction of the component i in the mixture	Dimensionless
φ_C	Correction factor	Dimensionless

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Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT in order to improve the readability and language of the manuscript. After using the ChatGPT, the authors reviewed and edited the content as needed and takes full responsibility for the content of the published paper.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests

Leandro Aguiar reports financial support was provided by State of Sao Paulo Research Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cherd.2024.10.016.

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