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Application of acidic resins with new formulations as catalysts in solketal synthesis

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Mathematical Modeling

**1. Copolymerization model**

Assumptions

* The sequences distributions are considered to be the same in soluble and gel polymer;
* The distribution of sequences containing only styrene units connecting the extreme groups (LAn to LEn) is considered to be the same as the distribution containing styrene and / or DVB units;
* Only mono-radicals were considered;
* Terminal model.
  1. Balance of species

Table 1 - Copolymerization steps

|  |  |  |
| --- | --- | --- |
| Reaction | Chemical equation |  |
| Initiator decomposition |  |  |
| Styrene Initiation |  |  |
| Divinylbenzene initiation |  |  |
| PDB initiation |  |  |
| Styrene propagation |  |  |
| Divinylbenzene propagation |  |  |
| PDB propagation |  |  |
| Termination |  |  |
|  |  |  |
|  |  |  |

: Initiator, : Primary radical, : Monomer of type j, : Polymeric radical, : Pendent double bond, P: Dead polymer, to : Rate constants of the reactions.

(1)

(2)

(3)

(4)

(5)

(6)

In order to estimate the content of soluble chains occluded in the polymer network, balances for linear chain were carried out as follows.

(7)

(8)

(9)

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

(10)

Where is the concentration of linear radicals and and are the concentrations of linear and total polymer chains.

* 1. Balance of sequences

Table 2 - Reactions in terms of sequences

|  |  |  |
| --- | --- | --- |
| Chemical equations | | |
|  |  |  |
|  | + |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |
|  |  |  |

: Primary radical, : Vinyl monomer (Styrene), : Divinyl monomer (Divinylbenzene – DVB), : Polymeric radical containing only styrene units, : Dead Polymer, : Polymer fragment, to : Sequences containing *r* repeating units, : cyclic chain containing r units.

(11)

(12)

(13)

(14)

(15)

(16)

(17)

(18)

(19)

(20)

(21)

Equations 1-9 and 11-21 were numerically integrated in Scilab through the algorithm ode. The concentration of crosslinked units, ; total units,; styrene units, ; and DVB units, are equated in (22), (23), (24) and (25) respectively.

(22)

(23)

(24)

(25)

The fraction of crosslinked units and the molecular weight between crosslinks are defined in equations 26 and 27.

(26)

(27)

1.3 Swelling behavior

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)1 describe a theoretical calculation for the swelling index (SI) of a resin containing occlusions, in a given solvent, based on a modification of the Flory-Rehner equation. The referred algorithm is shown in 28-31.

(28)

(29)

(30)

(31)

Where the interaction parameters can be calculated as follows.

(32)

(33)

The system was fed with the experimental value of and , provided by the copolymerization model and (dissolved polymer in the supernate was neglected). The system of non-linear equations 28-31 with four unknowns (, , and ) was solved through the function fsolve in scilab. The sulfonated polystyrene density () was calculated through the method of Sewell (1973).2 In the present work these densities of the resin () and occluded polystyenre () were calculated as a function of the Ion Exchange Capacity (IEC) of the resin, as follows.

(34)

For styrene-divinylbenzene sulfonated resin, . All terms are described in the symbology section.

The Swelling index can also be calculated for a sulfonated resin, by considering the solubility parameter of sulfonated polysterene3 in equations 32 and 33. Then the swelling index can be used to estimate the particle porosity and particle radius during the catalytic synthesis of solketal, as follows.

(35)

(36)

Where , and are the apparent density (mass of resin per volume of swollen particle), the resin density (skeletal density) and the solution density, respectively. and are the radii of dry and swollen particle, respectively.

**2. Heterogeneous catalysis model**

Hypotheses

* Homogeneous liquid phase
* Constant activity coefficients for the compounds along time and space
* Isothermal reaction

2.1 Balance equations

(37)

(38)

Boundary conditions

(39)

(40)

(41)

(42)

Discretization with 4 points along the radius were carried out to transform equation 36 into a system of ordinary differential equations (ODEs) using finite differences method. Adaptative refinement was implemented considering for the two layers adjacent to the particle surface (inner and outer), the other points were equally spaced along the particle as shown in Figure 1.

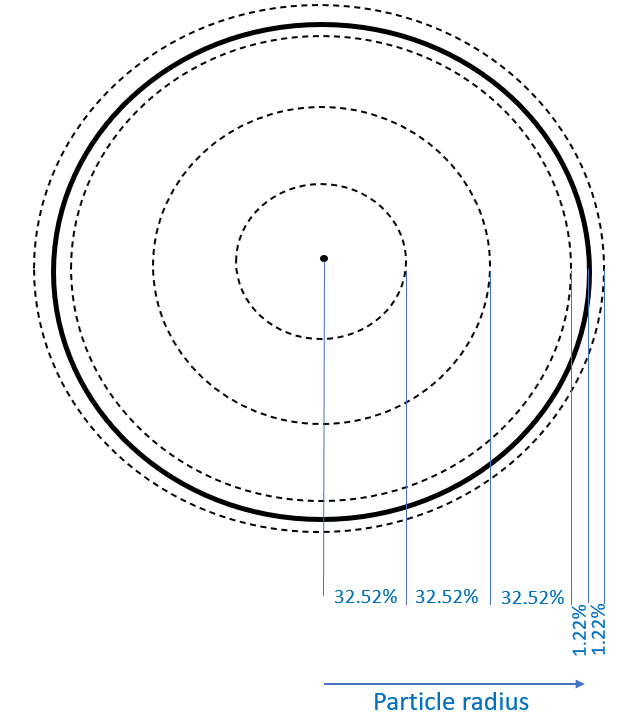


Figure 1 – Discretization with adaptative refinement.

The ODEs were numerically integrated along the reaction time through the algorithm ode in Scilab.

The effective diffusion coefficients were calculated through equation 43. Fernandez-Prini et al. (1976) described the tortuosity factor for a styrene-divinylbenzene sulfonated resin as , which was used in the present study. 4

(43)

The diffusion coefficient of the component in the mixture was calculated through the Perkins and Geankoplis correlation5 as follows.

(44)

The infinite dilution diffusivity of in is a function of temperature , viscosity of j and the molar volumes of and ( and ), and can be calculated for each pair of compounds in the mixture through equation 45.6

(45)

The reaction rate of the limiting reagent consumption was written considering the LHHW model in terms of activities as follows.

(46)

Applying the assumption of constant activity coefficient along the reaction, equation 47 can be written as:

(47)

Where:

(48)

(49)

(50)

and are the activity coefficient and concentration of the component , respectively; is the total concentration of compounds in the mixture. The activity coefficients used in equations 46 - 48 were calculated at the chemical equilibrium through UNIFAC, and the referred data are related in Appendix A.

The variation of and with temperature were considered as follows.

(51)

(52)

The reference temperature used in the present study was .

The parameter 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 () as described in equation (53).

(53)

Where is the effective ion exchange capacity, i.e., the catalytic sites content that effectively participates in the reaction. Equation 54 shows its calculation.

(54)

Where 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 . This radius of gyration of the sequences was estimated by considering the radius of a polystyrene chain in tetrahydrofuran at 25 oC, according to equation 55.7

(55)

In equation 55, is the molecular weight of the chain in g mol-1 and is the radius of gyration in nm. The comparison among molecular sizes is illustrated in Figure 2.

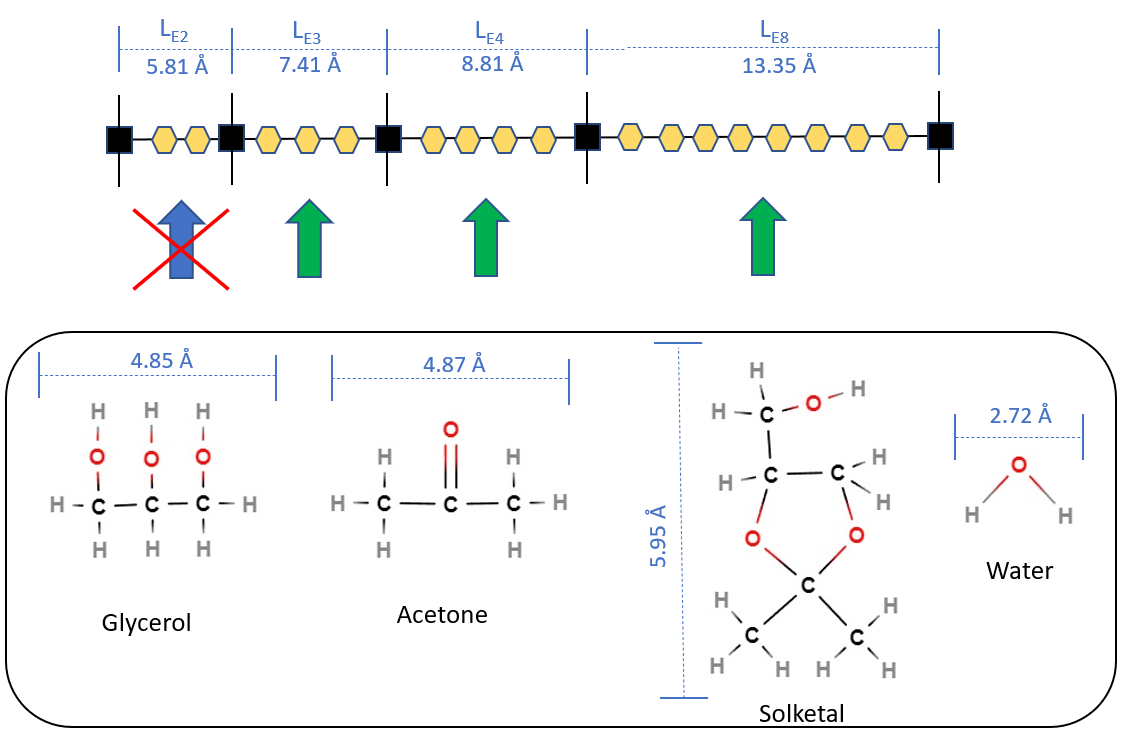


Figure 2 – Comparison among sequences and compounds molecular diameters.

In Figure 2, the molecular sizes of the compounds were estimated through Kim’s expression, as described in equation 56.8

(56)

Where is the molecular diameter in nm, and is the molar volume in cm3 mol-1. This simplified analysis suggests that LEn sequences with n ≤ 2 might be inaccessible due to hindering effects caused by the adjacent chains passing through the cross-linkages. The hindering effects can also be evaluated at free catalytic sites surrounded by occupied sites, as depicted in Figure 3.

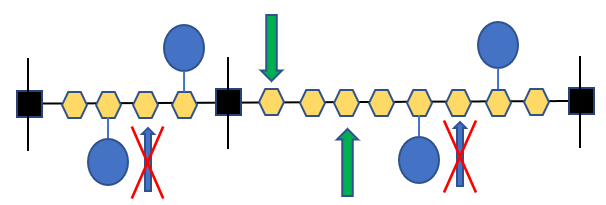


Figure 3 – Hindering effects caused by the occupied catalytic sites.

Considering that adjacent catalytic sites can not be occupied simultaneously (based on the molecular dimensions shown in Figure 2), the fraction of inaccessible sites can be estimated as follows.

Where accounts for the sequences containing 3 or more units, and is the fraction of hindered units during the adsorption of molecules on the catalytic sites.

If then

If then

**3. Results and discussion**

3.1 Sensitivity analysis

Simulations were carried out considering the following data (unless otherwise stated):

Table 3 – Simulation data

|  |  |
| --- | --- |
| Variable | Value |
| Number of discretization points (N) | 4 |
| Temperature | 303 K |
| Molar ration acetone / glycerol | 1 |
| Ethanol percentage | 50 % (mol) |
| Catalyst percentage | 0.5 % (weight) |
| Particle diameter | 412 μm |

Thermodynamic data used in the model were collected from Moreira et al (2019).9 ; ; . Hindering effects due to the sites’ occupation were neglected ().

In order to conduct a sensitivity analysis for the model reaction variables and resin characteristics were studied as follows.

3.1 Effect of the resin characteristics

Firstly, simulations were carried considering constant and variable swelling indexes. The swelling index has a direct effect on the particle radius (RP) and on its porosity (ɛP). The Figure 4 illustrates the results.

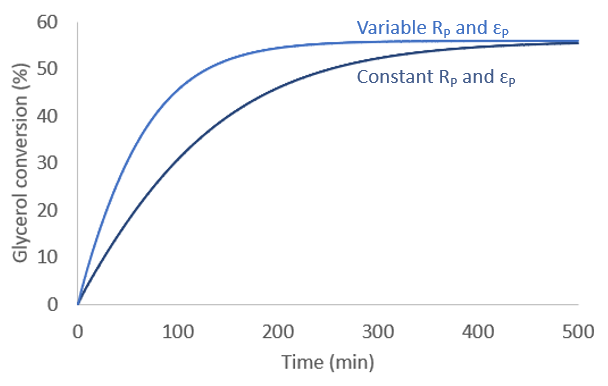


Figure 4 – Effect of the swelling index variation during the reaction.

The tortuosity in particulate systems can be a constant value or a function of the particle porosity. Figure 5 shows a comparison among the different approaches for tortuosity.

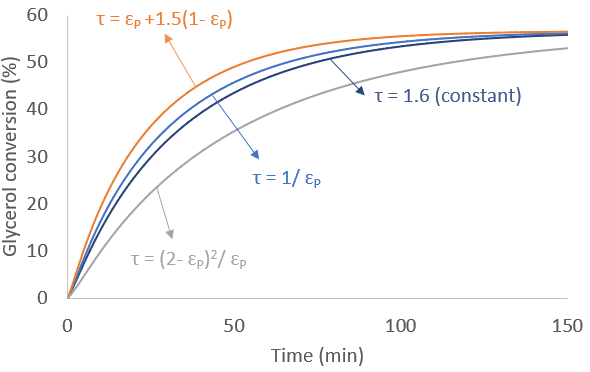


Figure 5 – Effect of Tortuosity.4,10

Figure 6 shows the effect of the particle size on the glycerol conversion.

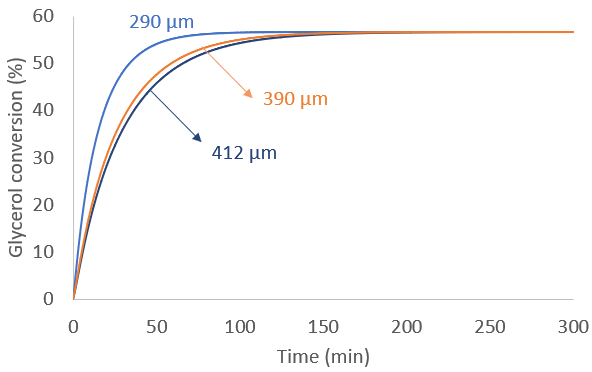


Figure 6 – Effect of particle size

3.2 Effect of reaction variables

The effects of temperature (T), acetone/glycerol molar ratio (MR) and catalyst content are illustrated in Figures 7, 8 and 9 respectively.

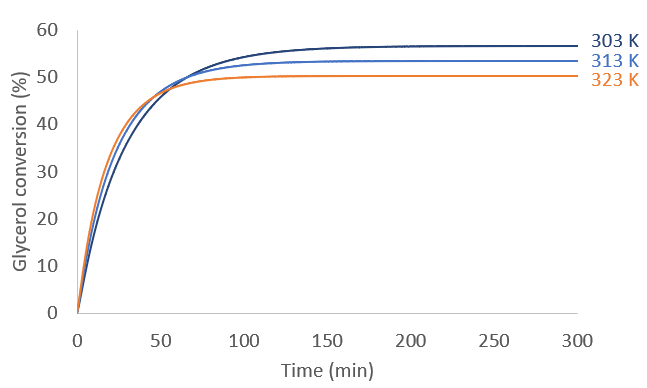


Figure 7 – Effect of temperature

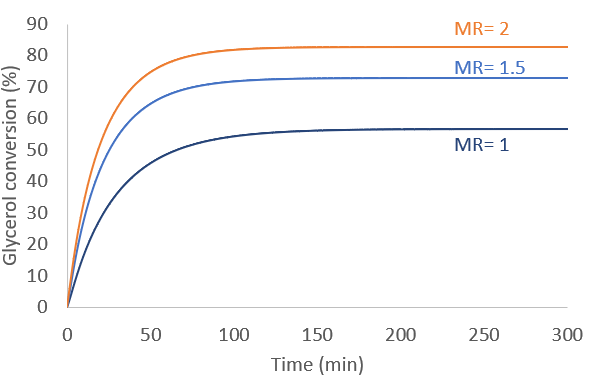


Figure 8 - Effect of acetone/glycerol molar ratio (MR).

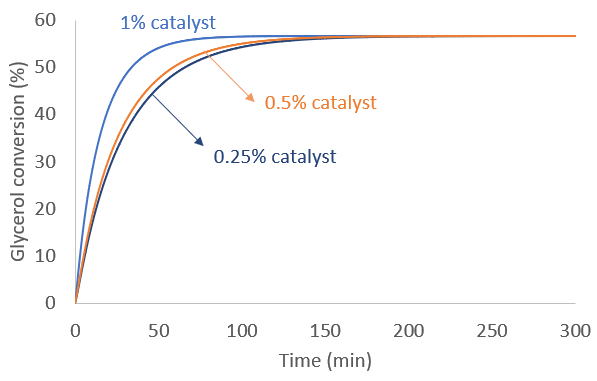


Figure 9 – Effect of catalyst content

Figures 10 and 11 illustrate the effect of dilution and initial loading of the particles on the conversion results.

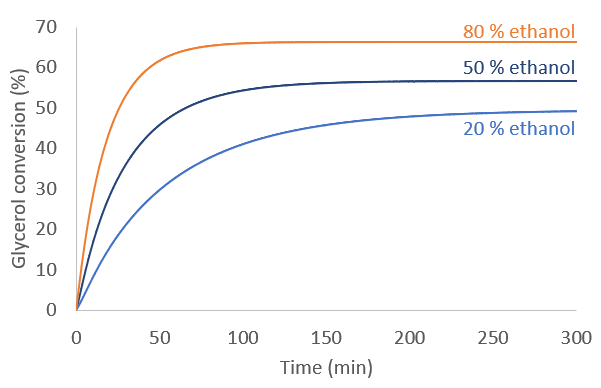


Figure 10 – Effect of dilution.

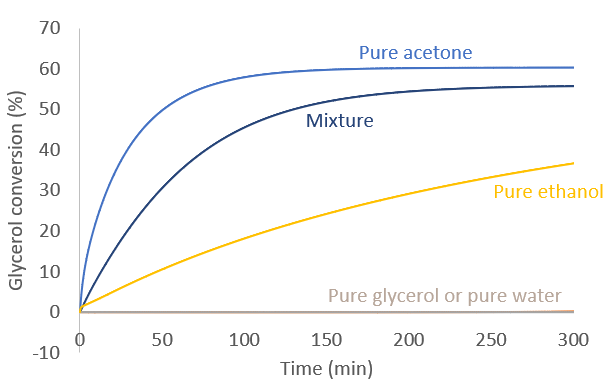


Figure 11 – Effect of initial particle loading

It is observed that considering particle swelling as described in section 2 has a considerable effect on the glycerol conversion curve compared to considering constant radius and porosity (as considered in literature studies) 11,12. It is possible to notice that the tortuosity of sulfonated resin particles is higher compared to other tortuosity approaches, resulting in lower conversion over time. In Figure 11, the model prediction indicates that the initial loading of catalyst particles with acetone favors conversion. This behavior is associated with the acetone solubility parameter, which provides greater swelling, increasing the porosity of the particles. The model was also able to represent the decrease in reaction rate with increasing particle diameter, as expected for a diffusion-controlled process. Figures 7-9 present typical results of an exothermic reversible reaction (equilibrium conversion increases with decreasing temperature). Figure 10 indicates a strong effect of compound activity on conversion curves, prevailing over the effect of compound concentrations (see equations 47-50).

3.2 Model validation

The model was tested using experimental data from Moreira et al. (2019)11, and the adjustments are illustrated in Figure 12.

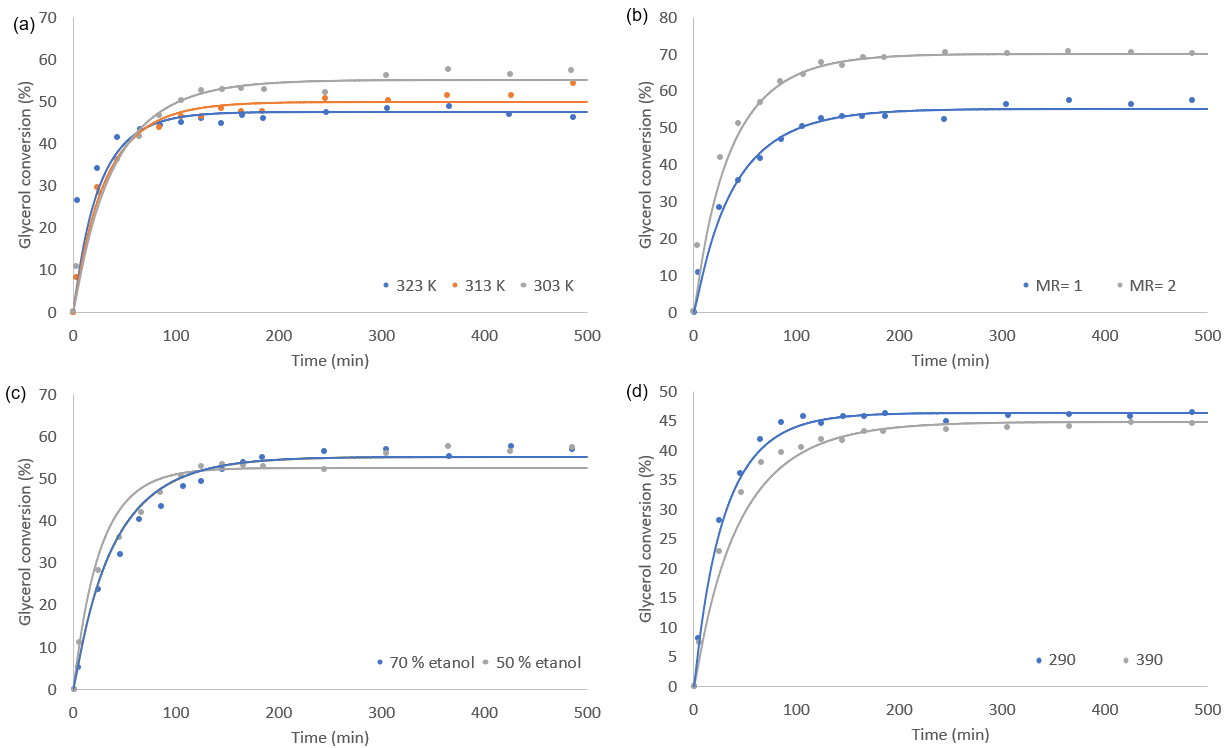


Figure 12 - Model fitting to experimental data from the literature.11 (a) Temperature, (b) Acetone / glycerol molar ratio, (c) Ethanol percentage, (d) Particle diameter (μm).

It is observed in Figure 2.4 that the model generally represents the experimental profiles well. The optimal fit was obtained by minimizing the squared residuals, yielding an R2 of 0.96. Table 4 presents the parameters used in this simulation and their differences from the literature values.

Table 4 - Parameters used in model validation.

|  |  |  |
| --- | --- | --- |
| Parameter | This study | Moreira et al. (2019)11 |
|  | -25.53 ± 0.6 | -20.10 ± 1.1 |
|  | 4.80 ± 0.9 | 1.40 ± 0.1 |
|  | 0.96 | 0.96 |

Os parâmetros cinéticos utilizados são os mesmos do modelo LHHW de Moreira et al. (2019)11 ; ; . Hindering effects due to the sites’ occupation were neglected ().

The discrepancies observed in Table 4 may be primarily associated with the differences between the methods used in the models. The present work used finite differences and modified UNIFAC, while the work of Moreira et al. (2019) used orthogonal collocation and the original UNIFAC method. It is worth noting that the present model also takes into account particle swelling during the process.

**4. Conclusion**

Copolymerization modeling was carried out for the synthesis of the catalyst support through species and sequence balances, considering cyclization reactions and distinguishing between linear and crosslinked chains. Information provided by this model, such as the average molecular weight between cross-links and the fraction of soluble chains, were used to predict the swelling variation of the resin during its application. It is concluded from the simulations that considering the variation in particle size and porosity due to catalyst swelling produces the expected effect on simulated glycerol conversions. The adjustments with experimental data revealed an R2 of 0.96, and the thermodynamic parameters found were close to literature values. Furthermore, the copolymerization model provides an indication of chain density through sequence size distributions, which will allow, in future studies, the evaluation of accessibility to catalytic sites as a function of resin synthesis conditions.

Symbology

|  |  |  |
| --- | --- | --- |
| Symbol | Description | Unit |
|  | Concentration of the component i | mol L-1 |
|  | Initial concentration of the component i | mol L-1 |
|  | Reactivity correlation parameter | Dimensionless |
|  | Crosslinked units concentration | mol L-1 |
|  | Initiator efficiency | Dimensionless |
|  | Initiator concentration | mol L-1 |
|  | Ion exchange capacity | meq g-1 |
|  | Effective ion exchange capacity | meq g-1 |
|  | Rate constant of reaction | mol kg-1 s-1 |
|  | Apparent rate constant of reaction | L2 mol-1 kg-1 s-1 |
|  | Rate constant for the reference temperature | mol kg-1 s-1 |
|  | Ratio | Dimensionless |
|  | Initiator decomposition constant | s-1 |
|  | Equilibrium constant of the reaction | Dimensionless |
|  | Apparent equilibrium constant | Dimensionless |
|  | Styrene initiation constant | L mol-1 s-1 |
|  | DVB initiation constant | L mol-1 s-1 |
|  | Styrene propagation constant | L mol-1 s-1 |
|  | DVB propagation constant | L mol-1 s-1 |
|  | PDB propagation constant | L mol-1 s-1 |
|  | Adsorption equilibrium constant for water | Dimensionless |
|  | Apparent adsorption equilibrium constant | L mol-1 |
|  | Termination constant | L mol-1 s-1 |
|  | Concentrations of sequences containing r styrene units connecting a PDB to a radical center | mol L-1 |
|  | Concentration of sequences containing r styrene units connecting two PDBs | mol L-1 |
|  | Concentration of sequences containing r styrene units connecting a crosslinked unit to a radical center | mol L-1 |
|  | Concentration of sequences containing r styrene units connecting a PDB to a crosslinked unit | mol L-1 |
|  | Concentration of sequences containing r styrene units connecting two crosslinked units | mol L-1 |
|  | Styrene concentration | mol L-1 |
|  | Initial styrene concentration | mol L-1 |
|  | DVB concentration | mol L-1 |
|  | Initial DVB concentration | mol L-1 |
|  | Average molecular weight between CLs | g mol-1 |
|  | Average molecular weight of polymerized units | g mol-1 |
|  | Number of units between CLs | r.u. |
|  | Maximum n considered in the copolymerization modeling | r.u. |
|  | Pendant double bonds concentration | mol L-1 |
|  | Total radicals’ concentration | mol L-1 |
|  | Primary radicals’ concentration | mol L-1 |
|  | Rate of reaction for the limiting reagent | mol L-1 min-1 |
|  | Radius of swollen particle | dm |
|  | Radius of dry particle | dm |
|  | Concentration of radicals containing only styrene units | mol L-1 |
|  | Swelling Index | Dimensionless |
|  | Concentration of sulfonated units | mol L-1 |
|  | Concentration of total polymerized units | mol L-1 |
|  | Concentration of Styrene units | mol L-1 |
|  | Concentration of DVB units | mol L-1 |
|  | Volume fraction of dissolved polymer in the supernate | Dimensionless |
|  | Molar volume of solvent | cm³ mol-1 |
|  | Volume fraction of polystyrene in the swollen occluded polystyrene | Dimensionless |
|  | Volume fraction of rubber in the swollen rubber network | Dimensionless |
|  | Weight fraction of occluded polystyrene in the gel | Dimensionless |
|  | Weight fraction of rubber in the gel | Dimensionless |
|  | Glycerol conversion | Dimensionless |
|  | Fraction of crosslinked units | mol CL (mol U)-1 |
|  | Fraction of among all | mol (mol total )-1 |
|  | Rubber-solvent interaction factor | Dimensionless |
|  | Polystyrene-solvent interaction factor | Dimensionless |
|  | Density of | kg dm-3 |

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APPENDIX A

The activity coefficients of the compounds in the reaction mixture were calculated through the modified UNIFAC model.13 The groups used in the calculation are depicted in Figure A1.

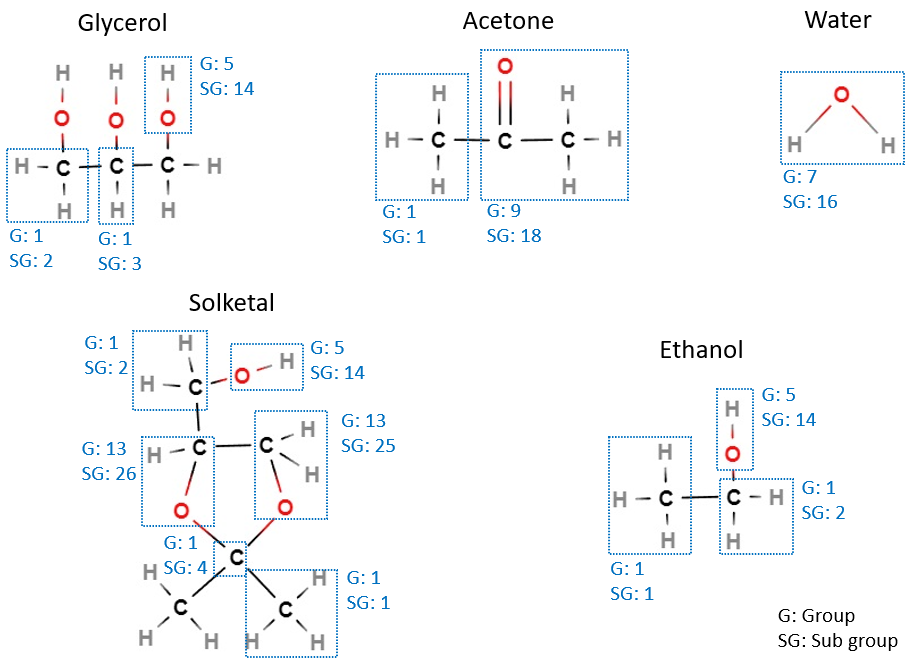


Figure A1 – Groups used in the calculation of activity coefficients.

The UNIFAC parameters were collected from Dortmund Data Bank14 and are related in Tables A1-A4.

Table A1 – UNIFAC Structural groups

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Group | Sub Group | Symbol | R | Q |
| 1 | 1 | CH3 | 0.6325 | 1.0608 |
| 1 | 2 | CH2 | 0.6325 | 0.7081 |
| 1 | 3 | CH | 0.6325 | 0.3554 |
| 1 | 4 | C | 0.6325 | 0.0000 |
| 5 | 15 | OH | 1.2302 | 0.8927 |
| 9 | 18 | CH3CO | 1.7048 | 1.6700 |
| 13 | 25 | CH2O | 1.1434 | 1.2495 |
| 13 | 26 | CHO | 1.1434 | 0.8968 |
| 7 | 16 | H2O | 1.7334 | 2.4561 |

Table A2 – UNIFAC energy interaction parameter an,m

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Group | 1 | 5 | 9 | 13 | 7 |
| 1 | 0 | 2777 | 433.6 | 233.1 | 1391.3 |
| 5 | 1606 | 0 | -250 | 816.7 | -801.9 |
| 9 | 199 | 653.3 | 0 | 3645 | 770.6 |
| 13 | -9.654 | 650.9 | 695.8 | 0 | 433.207 |
| 7 | -17.253 | 1460 | 190.5 | 177.665 | 0 |

Table A3 – UNIFAC energy interaction parameter bn,m

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Group | 1 | 5 | 9 | 13 | 7 |
| 1 | 0 | -4.674 | 0.1473 | -0.3155 | -3.6156 |
| 5 | -4.746 | 0 | 2.857 | -5.092 | 3.824 |
| 9 | -0.8709 | -1.412 | 0 | -26.91 | -0.5873 |
| 13 | -0.03242 | -0.7132 | -0.9619 | 0 | -0.6053 |
| 7 | 0.8389 | -8.673 | -3.669 | -3.7291 | 0 |

Table A4 – UNIFAC energy interaction parameter cn,m

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Group | 1 | 5 | 9 | 13 | 7 |
| 1 | 0 | 1.55x10-3 | 0 | 0 | 1.144x10-3 |
| 5 | 9.181x10-4 | 0 | 6.022x10-3 | 6.065x10-3 | -7.514x10-3 |
| 9 | 0 | 9.54x10-4 | 0 | 0 | -3.252x10-3 |
| 13 | 0 | 8.15x10-4 | -2.462x10-3 | 0 | -9.14x10-4 |
| 7 | 9.021x10-4 | 0.01641 | 8.838x10-3 | 0.010763 | 0 |

Table A5 – Activity coefficients along the reaction.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |
| 0.1 | 2.93 | 4.55 | 0.77 | 0.73 | 1.19 |
| 0.2 | 2.95 | 4.37 | 0.85 | 0.95 | 1.18 |
| 0.3 | 2.95 | 4.14 | 0.92 | 1.18 | 1.16 |
| 0.4 | 2.94 | 3.90 | 0.99 | 1.42 | 1.13 |
| 0.5 | 2.92 | 3.64 | 1.04 | 1.65 | 1.10 |
| 0.6 | 2.88 | 3.38 | 1.08 | 1.88 | 1.07 |
| 0.7 | 2.84 | 3.13 | 1.12 | 2.10 | 1.04 |
| 0.8 | 2.80 | 2.89 | 1.15 | 2.30 | 1.01 |

: glycerol conversion, : Activity coefficient of i.