REPORT 12/2023 – 02/2024

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

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Mathematical Modeling

**1. Compolymerization model**

Assumptions

* The sequences distributions are considered to be the same in soluble and gel polymer (gelation was not modeled);
* 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 |  |
| 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

The swelling index of the simulated polymer network in a given medium was estimated through the algorithm of Karam and Tien (1985)1, and the referred equations are shown in 28-31.

(28)

(29)

(30)

(31)

(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 polymer and resin densities ( and ) were calculated through the method of Sewell (1973).2 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.

(34)

(35)

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

Hypothesis

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

2.1 Balance equations

(36)

(37)

Boundary conditions

(38)

(39)

(40)

(41)

The effective diffusion coefficients was calculated through equation 42. A tortuosity factor was used.(REF)

(42)

The diffusion coefficient of the component in the mixture was calculated through the Perkins and Geankoplis correlation4 as follows.

(43)

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 44.5

(44)

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

(45)

Applying the assumption of constant activity coefficient along the reaction, equation 45 can be written as:

(46)

Where:

(47)

(48)

(49)

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.

(50)

(51)

The reference temperature used in the present study was .

Discretization with 80 points along the radius were carried out to transform equation 35 into a system of ordinary differential equations (ODEs) using finite differences method. The ODEs were numerically integrated along the reaction time through the algorithm ode (stiff) in Scilab.

3. Results and discussion

Simulations were carried out considering the following data:

Number of discretization points: N= 80

Temperature: T= 303 K

Molar ratio acetone/glycerol: MR= 1

Content of ethanol: xeth= 50 % (mol)

Catalyst percentage: Cat= 0.5%

Swelling index: SI= 1.2

Tortuosity factor: τ= 1.6

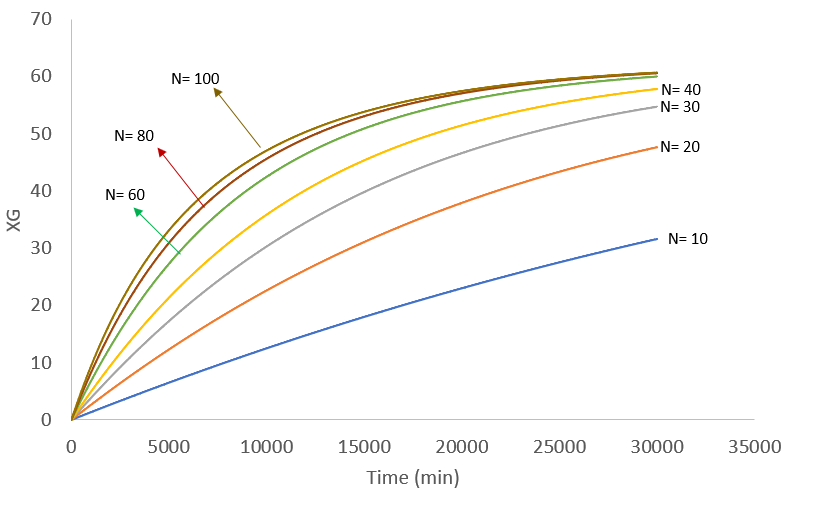
Rate constant at 313K: kc0= 492 mol kg-1 s-1

Thermodynamic data used in the model were collected from Moreira et al (2019).6

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

Firstly, the number of discretization points (N) were varied, as shown in Figure 1.

Figure 1 – Effect of the number of discretization points.



3.1 Effect of reaction variables

The effects of temperature (T), acetone/glycerol molar ratio (MR) and catalyst content are illustrated in Figures 2, 3 and 4 respectively.

Figure 2 – Effect of Temperature.

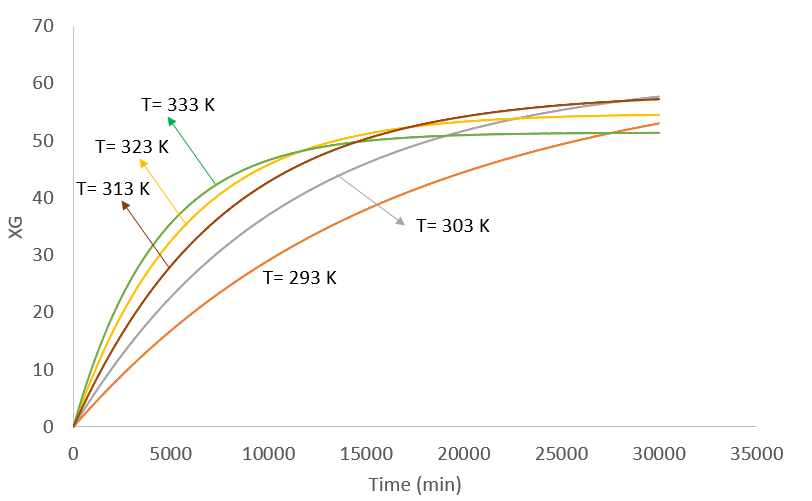


Figure 3 – Effect of acetone/glycerol molar ratio

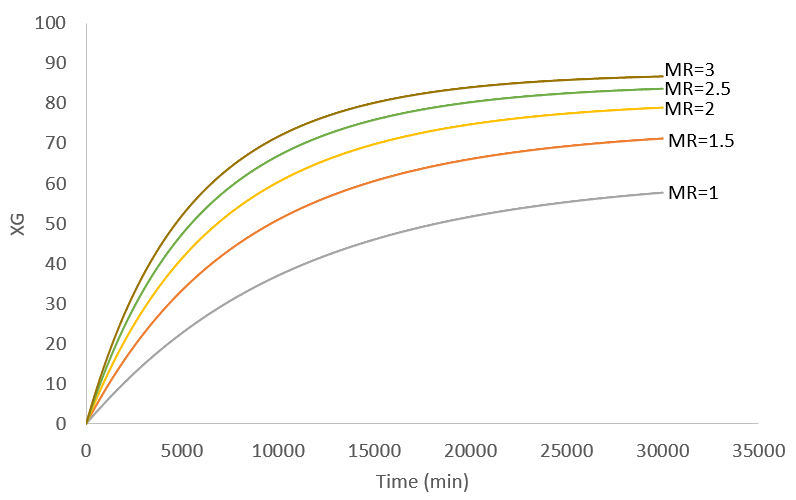
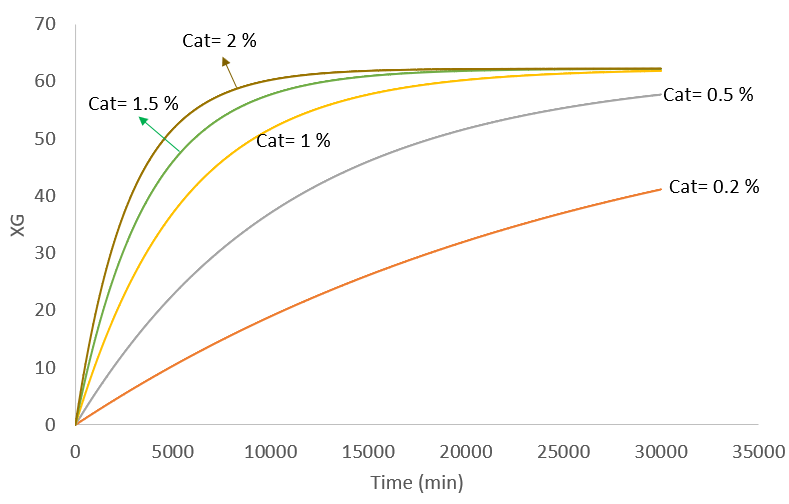


Figure 4 – Effect of catalyst content



Figures 5 and 6 show the effects of swelling index and tortuosity factor on the glycerol conversion.

Figure 5 – Effect of swelling index

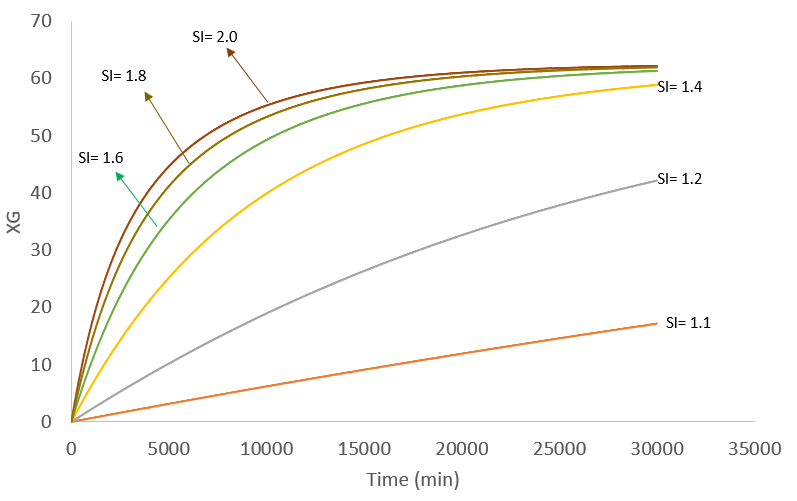


Figure 6 – Effect of tortuosity factor

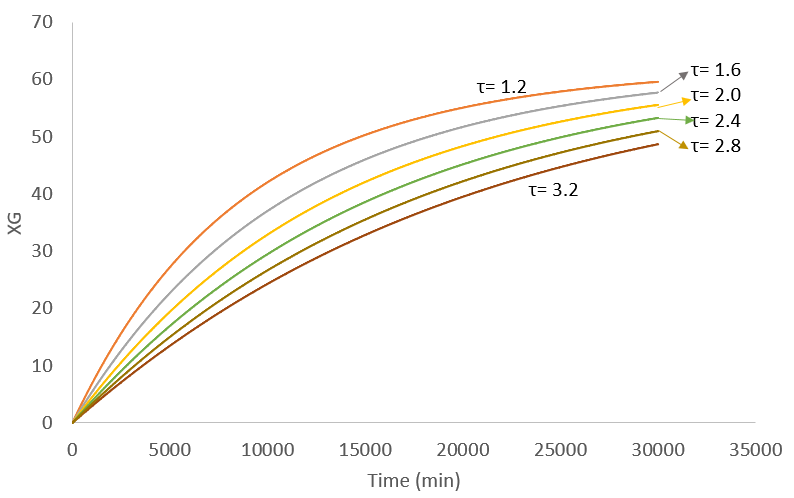
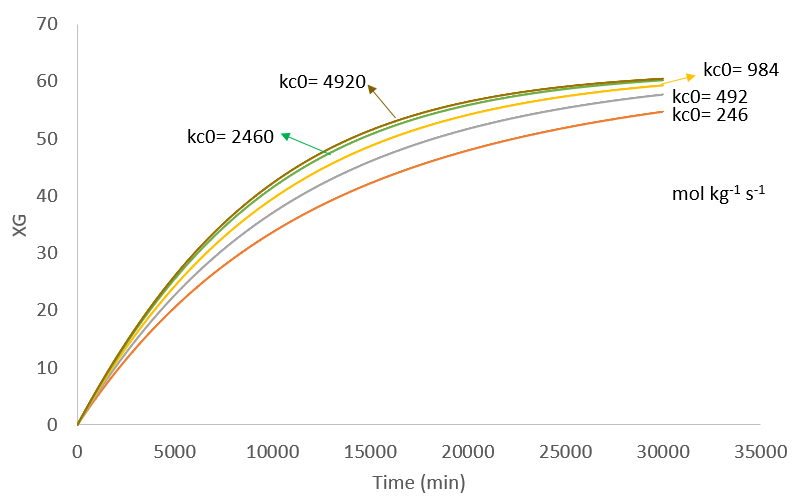


Figure 7 shows the effect of the rate constant kc0 on the glycerol conversion

Figure 7 – Effect of kc0 on the conversion results.



3. Further studies

- Swelling studies: Validate Karam and Tien method for sulfonated resins;

- Hindering effects: Calculate radius of gyration of LE sequences and compare to reagents molecular size to estimate the fraction of inaccessible catalytic sites;

- Catalytic tests: Assess the effect of mass transfer, adsorption, crosslinking degree with synthesized resins.

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 |

References

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APPENDIX A

The activity coefficients of the compounds in the reaction mixture were calculated through the modified UNIFAC model.7 The groups used in the calculation are depicted in Figure A1.

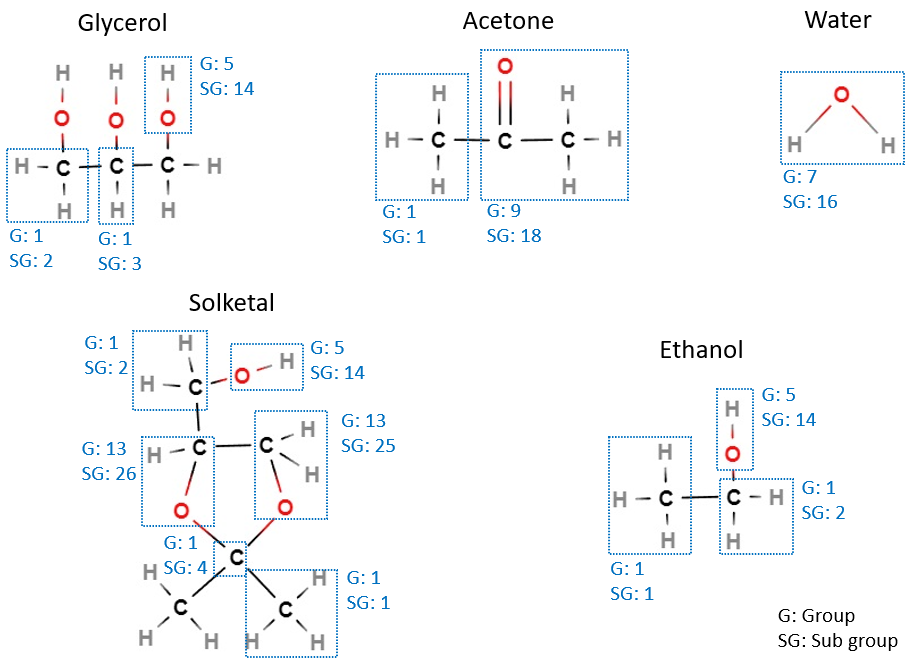


Figure A1 – Groups used in the calculation of activity coefficients.

The UNIFAC parameters were collected from Dortmund Data Bank8 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 |