

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 (L_{An} to L_{En}) is considered to be the same as the distribution containing styrene and / or DVB units;
- Only mono-radicals were considered;
- Terminal model.

1.1 Balance of species

Table 1 - Copolymerization steps

Reaction	Chemical equation
Initiator decomposition	$I \xrightarrow{k_d} 2R_0^\cdot$
Styrene Initiation	$R_0^\cdot + M_1 \xrightarrow{k_{I1}} R^\cdot$
Divinylbenzene initiation	$R_0^\cdot + M_2 \xrightarrow{k_{I2}} R^\cdot + PDB$
PDB initiation	$R_0^\cdot + PDB \xrightarrow{k_{P3}} R^\cdot$
Styrene propagation	$R^\cdot + M_1 \xrightarrow{k_{P1}} R^\cdot$

Divinylbenzene propagation	$R^\cdot + M_2 \xrightarrow{k_{P_2}} R^\cdot + PDB$
PDB propagation	$R^\cdot + PDB \xrightarrow{k_{P_3}} R^\cdot$
Termination	$R^\cdot + R^\cdot \xrightarrow{k_t} P$

I : Initiator, R_0^\cdot : Primary radical, M_j : Monomer of type j, R^\cdot : Polymeric radical, PDB : Pendent double bond,

P : Dead polymer, k_d to k_t : Rate constants of the reactions.

$$\frac{dI}{dt} = -k_d I \quad (1)$$

$$\frac{dR_0^\cdot}{dt} = 2fk_d I - k_{I_1} R_0^\cdot M_1 - k_{I_2} R_0^\cdot M_2 - k_{P_3} R_0^\cdot PDB \quad (2)$$

$$\frac{dR^\cdot}{dt} = k_{I_1} R_0^\cdot M_1 + k_{I_2} R_0^\cdot M_2 - k_t R^{\cdot 2} \quad (3)$$

$$\frac{dPDB}{dt} = k_{I_2} R_0^\cdot M_2 + k_{P_2} R^\cdot M_2 - k_{P_3} PDB (R_0^\cdot + R^\cdot) \quad (4)$$

$$\frac{dM_1}{dt} = -k_{I_1} R_0^\cdot M_1 - k_{P_1} R^\cdot M_1 \quad (5)$$

$$\frac{dM_2}{dt} = -k_{I_2} R_0^\cdot M_2 - k_{P_2} R^\cdot M_2 \quad (6)$$

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

$$\frac{dR_L^\cdot}{dt} = k_{I_1} R_0^\cdot M_1 - k_{P_2} R_L^\cdot M_2 - k_{P_3} R_L^\cdot PDB - k_t R_L^{\cdot 2} \quad (7)$$

$$\frac{dP_L}{dt} = \frac{k_t}{2} R_L^{\cdot 2} \quad (8)$$

$$\frac{dP}{dt} = \frac{k_t}{2} R^{\cdot 2} \quad (9)$$

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

$$w_p = \frac{P_L}{P} \quad (10)$$

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

1.2 Balance of sequences

Table 2 - Reactions in terms of sequences

Chemical equations		
$R_0^\cdot + M_1 \xrightarrow{k_{I1}} R_S^\cdot$	$L_{Ar} + L_{As} \xrightarrow{k_t} L_{Br+s}$	$R_S^\cdot + L_{Ar} \xrightarrow{k_t} F$
$R_S^\cdot + M_1 \xrightarrow{k_{P1}} R_S^\cdot$	$L_{Ar} + L_{Cs} \xrightarrow{k_t} L_{Dr+s}$	$R_S^\cdot + L_{Cr} \xrightarrow{k_t} F$
$R_0^\cdot + M_2 \xrightarrow{k_{I2}} L_{A0}$	$L_{Ar} + L_{As} \xrightarrow{k_{P3}} L_{Cr} + L_{C0} + L_{Ds}$	$R_S^\cdot + L_{Ar} \xrightarrow{k_{P3}} L_{Cr} + L_{C0}$
$R_S^\cdot + M_2 \xrightarrow{k_{P2}} L_{A0}$	$L_{Ar} + L_{Bs} \xrightarrow{k_{P3}} L_{Dr} + L_{Ds} + L_{C0}$	$R_S^\cdot + L_{Br} \xrightarrow{k_{P3}} L_{Dr} + L_{C0}$
$R_S^\cdot + R_S^\cdot \xrightarrow{k_t} P$	$L_{Ar} + L_{Ds} \xrightarrow{k_{P3}} L_{Dr} + L_{Es} + L_{C0}$	$R_S^\cdot + L_{Dr} \xrightarrow{k_{P3}} L_{Er} + L_{C0}$
$L_{Ar} + M_1 \xrightarrow{k_{P1}} L_{Ar+1}$	$L_{Cr} + L_{As} \xrightarrow{k_{P3}} L_{Er} + L_{Cs} + L_{C0}$	$R_0^\cdot + L_{Ar} \xrightarrow{k_{P3}} L_{Cr} + L_{C0}$
$L_{Ar} + M_2 \xrightarrow{k_{P2}} L_{Br} + L_{A0}$	$L_{Cr} + L_{Bs} \xrightarrow{k_{P3}} L_{Er} + L_{Ds} + L_{C0}$	$R_0^\cdot + L_{Br} \xrightarrow{k_{P3}} L_{Dr} + L_{C0}$
$L_{Cr} + M_1 \xrightarrow{k_{P1}} L_{Cr+1}$	$L_{Cr} + L_{Ds} \xrightarrow{k_{P3}} L_{Er} + L_{Es} + L_{C0}$	$R_0^\cdot + L_{Dr} \xrightarrow{k_{P3}} L_{Er} + L_{C0}$
$L_{Cr} + M_2 \xrightarrow{k_{P2}} L_{Dr} + L_{A0}$	$L_{Cr} + L_{Cs} \xrightarrow{k_t} L_{Er+s}$	$L_{Ar} \xrightarrow{k_{cyc}} Cy_r + L_{C0}$

R_0^\cdot : Primary radical, M_1 : Vinyl monomer (Styrene), M_2 : Divinyl monomer (Divinylbenzene – DVB), R_S^\cdot :

Polymeric radical containing only styrene units, P : Dead Polymer, F : Polymer fragment, L_{Ar} to L_{Er} :

Sequences containing r repeating units, Cy_r : cyclic chain containing r units.

$$\begin{aligned} \frac{dR_S^\cdot}{dt} = & k_{I1}R_0^\cdot M_1 - k_{P2}R_S^\cdot M_2 - k_{P3}R_S^\cdot \left(\sum_{r=0}^{n_{max}} L_{Ar} + 2 \sum_{r=0}^{n_{max}} L_{Br} + \sum_{r=0}^{n_{max}} L_{Dr} \right) - \\ & k_t R_S^\cdot \left(\sum_{r=0}^{n_{max}} L_{Ar} + \sum_{r=0}^{n_{max}} L_{Cr} \right) - k_t R_S^\cdot{}^2 \end{aligned} \quad (11)$$

$$\begin{aligned}
\frac{dL_{A_0}}{dt} = & k_{I_2} \dot{R}_0 M_2 + k_{P_2} M_2 (\sum_{r=0}^{n_{max}} L_{A_r} + \sum_{r=0}^{n_{max}} L_{C_r} + \dot{R}_S) - L_{A_0} [k_{P_1} M_1 + k_{P_2} M_2 + \\
& k_t (\sum_{r=0}^{n_{max}} L_{A_r} + \sum_{r=0}^{n_{max}} L_{C_r} + \dot{R}_0 + \dot{R}_S) + k_{P_3} (2 \sum_{r=0}^{n_{max}} L_{A_r} + 2 \sum_{r=0}^{n_{max}} L_{B_r} + \sum_{r=0}^{n_{max}} L_{C_r} + \\
& \sum_{r=0}^{n_{max}} L_{D_r} + \dot{R}_0 + \dot{R}_S)] \quad (12)
\end{aligned}$$

$$\begin{aligned}
\frac{dL_{A_r}}{dt} = & k_{P_1} M_1 L_{A_{r-1}} - k_{P_1} M_1 L_{A_r} - k_{P_2} M_2 L_{A_r} - k_t L_{A_r} (\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + \dot{R}_S) - \\
& k_{P_3} L_{A_r} (2 \sum_{s=0}^{n_{max}} L_{A_s} + 2 \sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{C_s} + \sum_{s=0}^{n_{max}} L_{D_s} + \dot{R}_S + \dot{R}_0) - k_{cyc} L_{A_r} \quad (13)
\end{aligned}$$

$$\frac{dL_{B_0}}{dt} = k_{P_2} L_{A_0} M_2 + \frac{1}{2} k_t L_{A_0}^2 - 2 k_{P_3} L_{B_0} (\sum_{r=0}^{n_{max}} L_{A_r} + \sum_{r=0}^{n_{max}} L_{C_r} + \dot{R}_0 + \dot{R}_S) \quad (14)$$

$$\begin{aligned}
\frac{dL_{B_r}}{dt} = & k_{P_2} L_{A_r} M_2 + \frac{1}{2} k_t \sum_{s=1}^r L_{A_s} L_{A_{r-s}} - 2 k_{P_3} L_{B_r} (\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + \dot{R}_0 + \dot{R}_S) \quad (15)
\end{aligned}$$

$$\begin{aligned}
\frac{dL_{C_0}}{dt} = & -k_{P_1} L_{C_0} M_1 - k_{P_2} L_{C_0} M_2 - k_t L_{C_0} (\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + \dot{R}_S) - \\
& k_{P_3} L_{C_0} (\sum_{s=0}^{n_{max}} L_{A_s} + 2 \sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{D_s}) + k_{P_3} \sum_{r=0}^{n_{max}} L_{A_r} (2 \sum_{r=0}^{n_{max}} L_{A_s} + \\
& 2 \sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{C_s} + \sum_{s=0}^{n_{max}} L_{D_s} + \dot{R}_S + \dot{R}_0) + 2 k_{P_3} \sum_{r=0}^{n_{max}} L_{B_r} (\sum_{s=0}^{n_{max}} L_{C_s} + \dot{R}_S + \\
& \dot{R}_0) + k_{P_3} \sum_{r=0}^{n_{max}} L_{D_r} (\sum_{s=0}^{n_{max}} L_{C_s} + \dot{R}_S + \dot{R}_0) + k_{cyc} \sum_{r=3}^{n_{max}} L_{A_r} \quad (16)
\end{aligned}$$

$$\begin{aligned}
\frac{dL_{C_r}}{dt} = & k_{P_1} L_{C_{r-1}} M_1 - k_{P_1} L_{C_r} M_1 - k_{P_2} L_{C_r} M_2 - k_t L_{C_r} (\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + \dot{R}_S) - \\
& k_{P_3} L_{C_r} (\sum_{s=0}^{n_{max}} L_{A_s} + 2 \sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{D_s}) + k_{P_3} L_{A_r} (\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + \dot{R}_S + \\
& \dot{R}_0) \quad (17)
\end{aligned}$$

$$\begin{aligned} \frac{dL_{D0}}{dt} = & k_{P2}M_2L_{C0} + k_tL_{A0}L_{C0} + k_{P3}L_{A0}(2\sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{D_s} + \sum_{s=0}^{n_{max}} L_{A_s}) + \\ & 2k_{P3}L_{B0}(\sum_{s=1}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + R_0 + R_S) - k_{P3}L_{D0}(\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + R_0 + R_S) \end{aligned} \quad (18)$$

$$\begin{aligned} \frac{dL_{Dr}}{dt} = & k_{P2}L_{Cr}M_2 + k_t\sum_{s=1}^r L_{A_s}L_{C_{r-s}} + k_{P3}L_{Ar}(2\sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{D_s} + \sum_{s=0}^{n_{max}} L_{A_s}) + \\ & 2k_{P3}L_{Br}(\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + R_S + R_0) - k_{P3}L_{Dr}(\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + R_S + R_0) \end{aligned} \quad (19)$$

$$\begin{aligned} \frac{dL_{E0}}{dt} = & k_{P3}(L_{C0} + L_{D0})\sum_{s=0}^{n_{max}} L_{A_s} + k_{P3}L_{C0}(2\sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{D_s}) + \\ & k_{P3}L_{D0}(\sum_{s=1}^{n_{max}} L_{C_s} + R_0 + R_S) + \frac{1}{2}k_tL_{C0}^2 \end{aligned} \quad (20)$$

$$\begin{aligned} \frac{dL_{Er}}{dt} = & k_{P3}\sum_{s=0}^{n_{max}} L_{A_s}(L_{Cr} + L_{Dr}) + k_{P3}L_{Cr}(2\sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{D_s}) + \\ & k_{P3}L_{Dr}(\sum_{s=0}^{n_{max}} L_{C_s} + R_S + R_0) + \frac{1}{2}k_t\sum_{s=1}^r L_{C_s}L_{C_{r-s}} \end{aligned} \quad (21)$$

Equations 1-9 and 11-21 were numerically integrated in Scilab through the algorithm ode. The concentration of crosslinked units, $[CL]$; total units, $[U]$; styrene units, $[U_1]$; and DVB units, $[U_2]$ are equated in (22), (23), (24) and (25) respectively.

$$[CL] = M_{2,0} - M_2 - PDB \quad (22)$$

$$[U] = [U_1] + [U_2] \quad (23)$$

$$[U_1] = M_{1,0} - M_1 \quad (24)$$

$$[U_2] = M_{2,0} - M_2 \quad (25)$$

The fraction of crosslinked units (Y_{CL}) and the molecular weight between crosslinks (\overline{M}_C) are defined in equations 26 and 27.

$$Y_{CL} = \frac{[CL]}{[U]} \quad (26)$$

$$\overline{M}_C = \frac{\overline{M}_U}{Y_{CL}} \quad (27)$$

1.3 Swelling behavior

The swelling index (SI) 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.

$$\ln(1 - v_R) + v_R + \mu_R v_R^2 + \frac{\rho_R V_1 v_R^{\frac{1}{3}}}{\overline{M}_C K^{\frac{4}{3}}} - [\ln(1 - v_0) + v_0 + \mu_P v_0^2] = 0 \quad (28)$$

$$\ln(1 - v_R) + v_R + \mu_R v_R^2 + \frac{\rho_R V_1 v_R^{\frac{1}{3}}(1+2K^2)}{3\overline{M}_C K^{\frac{4}{3}}} + \frac{(K+1)^3+2K^3}{2[(K+1)^3-K^3]} \{ \ln(1 - v_P) + v_P + \mu_P v_P^2 - [\ln(1 - v_0) + v_0 + \mu_P v_0^2] \} \quad (29)$$

$$K = \frac{v_R}{v_P} \quad (30)$$

$$SI = 1 + \frac{\left[\frac{\rho_S w_R}{\rho_R} \left(\frac{1}{v_R} - 1 \right) + \frac{\rho_S w_P}{\rho_P} \left(\frac{1}{v_P} - 1 \right) \right]}{w_R + w_P} \quad (31)$$

$$\mu_R = 0.34 + V_1 \frac{(\delta_S - \delta_R)^2}{RT} \quad (32)$$

$$\mu_P = 0.34 + V_1 \frac{(\delta_P - \delta_S)^2}{RT} \quad (33)$$

The system was fed with the experimental value 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 equations 28-31 with four unknowns (v_R , v_P , K and SI) was solved through the function `fsolve` in `scilab`. The sulfonated polymer and resin densities (ρ_P and ρ_R) 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 polystyrene³ in equations 32 and 33. Then the swelling index (SI) can be used to estimate the particle porosity (ε_p) and particle radius (R_p) during the catalytic synthesis of solketal, as follows.

$$\varepsilon_p = \frac{\rho_R(SI-1)}{\rho_R(SI-1)+\rho_s} \quad (34)$$

$$R_p = R_{p,dry} \sqrt[3]{\frac{\rho_R}{\rho_{app}}} \quad (35)$$

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. Heterogeneous catalysis model

Hypothesis

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

2.1 Balance equations

$$\varepsilon_p \frac{\partial C_{p,i}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{eff,i} r^2 \frac{\partial C_{p,i}}{\partial r} \right) + (1 - \varepsilon_p) v_i \rho_R r_A \quad (36)$$

$$\frac{\partial C_{b,i}}{\partial t} = - \left(\frac{1-\varepsilon_b}{\varepsilon_b} \right) \frac{3}{r_p} D_{eff,i} \frac{\partial C_{p,i}}{\partial r} \Big|_{r=r_p} \quad (37)$$

Boundary conditions

$$t = 0 \quad C_{b,i} = C_{b,i0} \quad (38)$$

$$t = 0 \quad C_{p,i} = C_{p,i0} \quad (39)$$

$$r = 0 \quad \frac{\partial C_{p,i}}{\partial r} = 0 \quad (40)$$

$$r = r_p \quad C_{b,i} = C_{p,i} \Big|_{r=r_p} \quad (41)$$

The effective diffusion coefficients was calculated through equation 42. A tortuosity factor $\tau = 1.6$ was used. (REF)

$$D_{eff,i} = \frac{\varepsilon_p D_{i,m}}{\tau} \quad (42)$$

The diffusion coefficient of the component i in the mixture ($D_{i,m}$) was calculated through the Perkins and Geankoplis correlation⁴ as follows.

$$D_{i,m} = \frac{1}{\eta_m^{0.8}} \sum_{\substack{j=1 \\ j \neq i}}^{nc} x_j D_{i,j}^0 \eta_j^{0.8} \quad (43)$$

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 equation 44.⁵

$$D_{i,j}^0 = \frac{8.2 \times 10^{-8} T}{\eta_j V_{M,i}^{\frac{1}{3}}} \left[1 + \left(\frac{3V_{M,j}}{V_{M,i}} \right)^{\frac{2}{3}} \right] \quad (44)$$

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

$$r_A = \frac{k_c \left(a_{Ac} a_{Gly} - \frac{a_{Sol} k_{eq}}{K_{eq}} \right)}{(1 + K_{S,W} a_w)^2} \quad (45)$$

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

$$r_A = \frac{k'_c \left(C_{Ac} C_{Gly} - \frac{C_{Sol} k_{eq}}{K'_{eq}} \right)}{(1 + K'_{S,W} C_w)^2} \quad (46)$$

Where:

$$k'_c = k_c \frac{\gamma_{Ac} \gamma_{Gly}}{C_T^2} \quad (47)$$

$$K'_{eq} = \frac{\gamma_{Ac} \gamma_{Gly}}{\gamma_{Sol} \gamma_w} K_{eq} \quad (48)$$

$$K'_{S,W} = \frac{K_{S,W} \gamma_w}{C_T} \quad (49)$$

γ_i and C_i are the activity coefficient and concentration of the component i , respectively; C_T 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 k_c and K_{eq} with temperature were considered as follows.

$$k_c = k_{c0} \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (50)$$

$$K_{eq} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \quad (51)$$

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

Discretization with 80 points along the radius r 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: $T = 303 \text{ K}$

Molar ratio acetone/glycerol: $MR = 1$

Content of ethanol: $x_{\text{eth}} = 50 \text{ \% (mol)}$

Catalyst percentage: $\text{Cat} = 0.5\%$

Swelling index: $SI = 1.2$

Tortuosity factor: $\tau = 1.6$

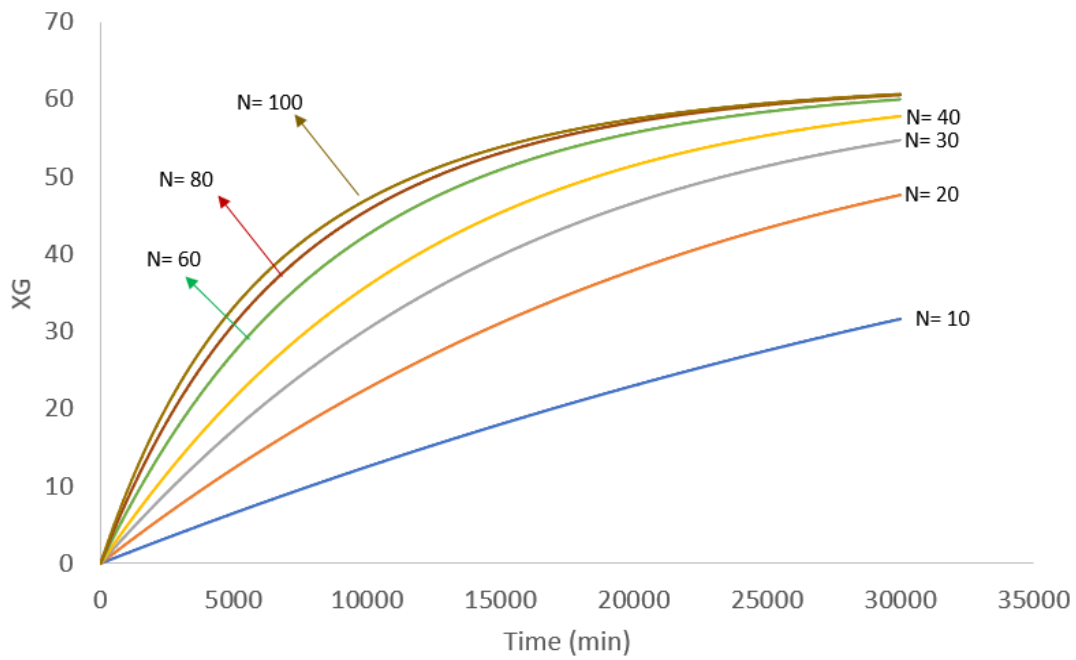
Rate constant at 313K: $k_{C0} = 492 \text{ mol kg}^{-1} \text{ s}^{-1}$

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.

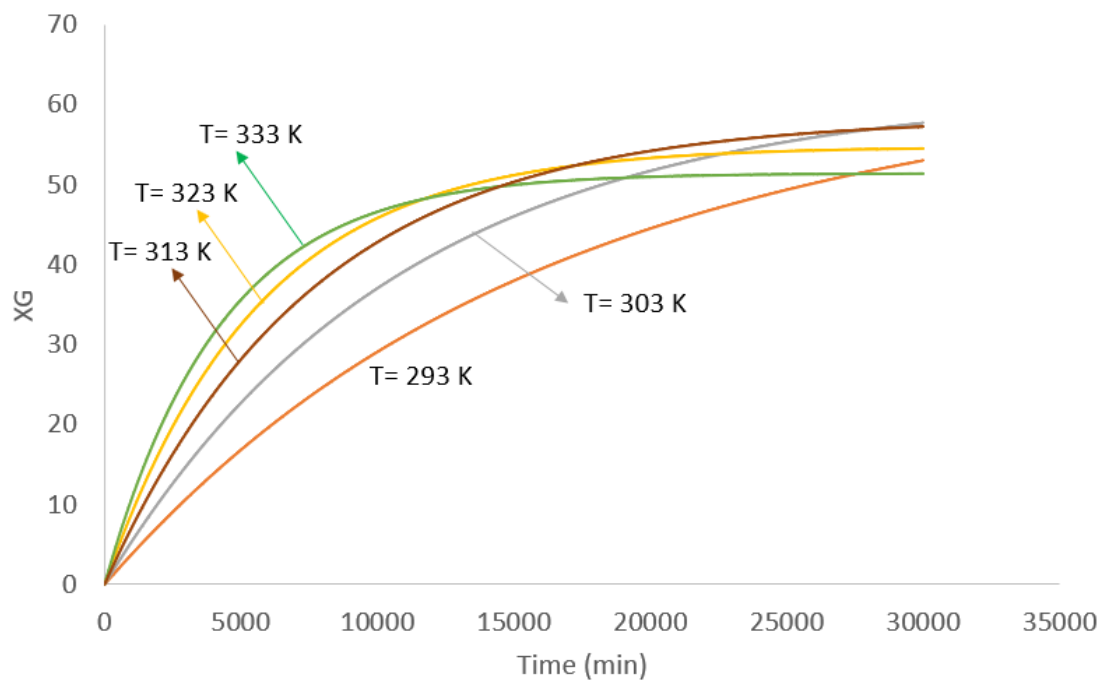


Figure 3 – Effect of acetone/glycerol molar ratio

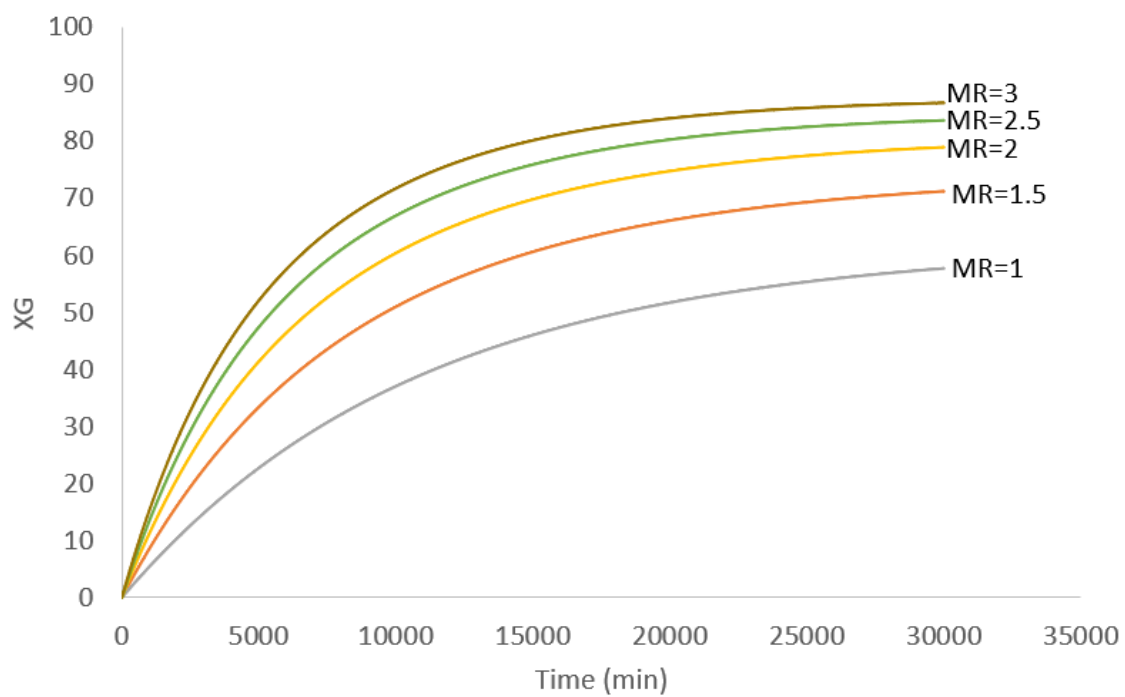
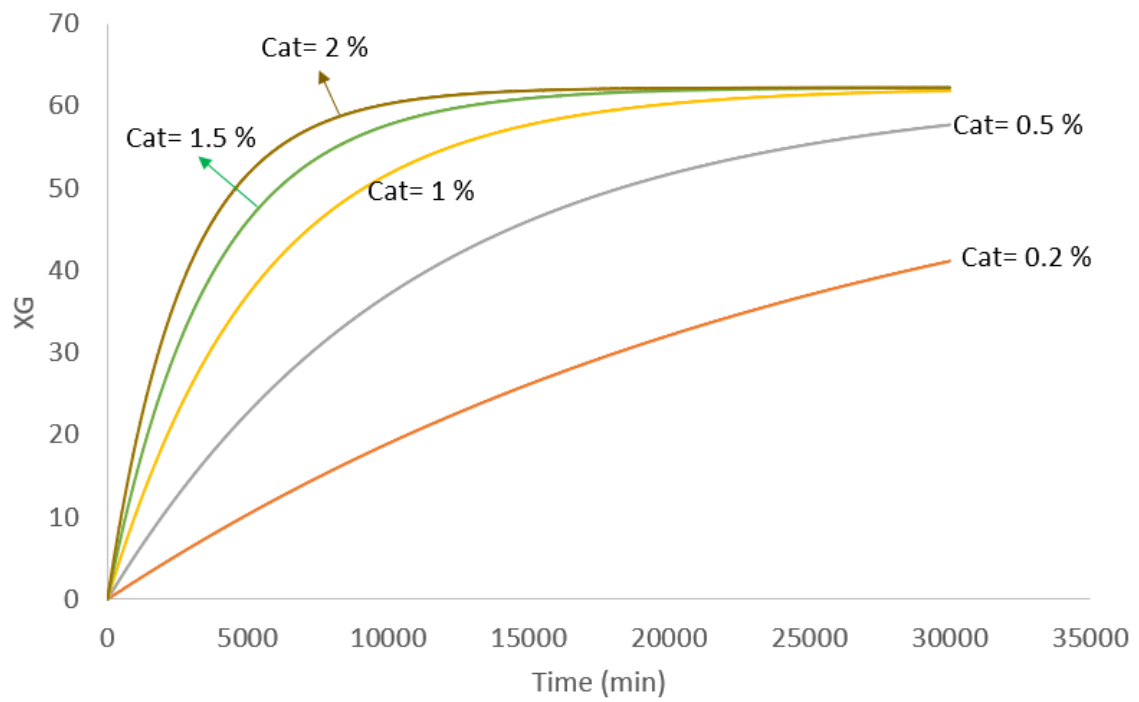


Figure 4 – Effect of catalyst content



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

Figure 5 – Effect of swelling index

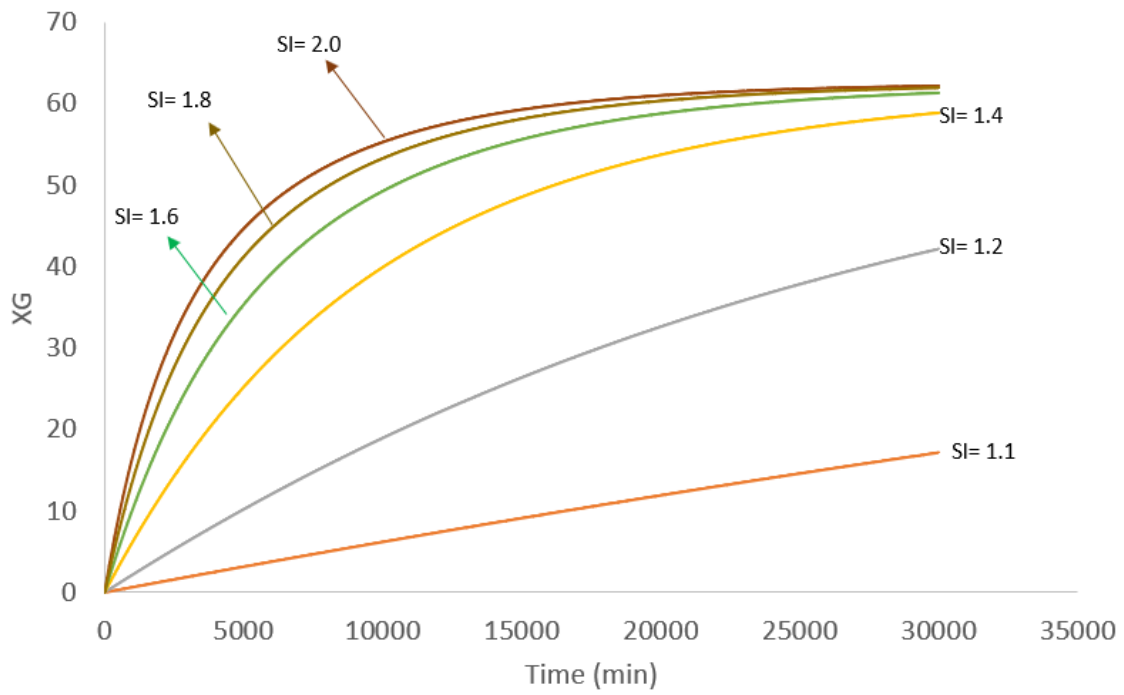


Figure 6 – Effect of tortuosity factor

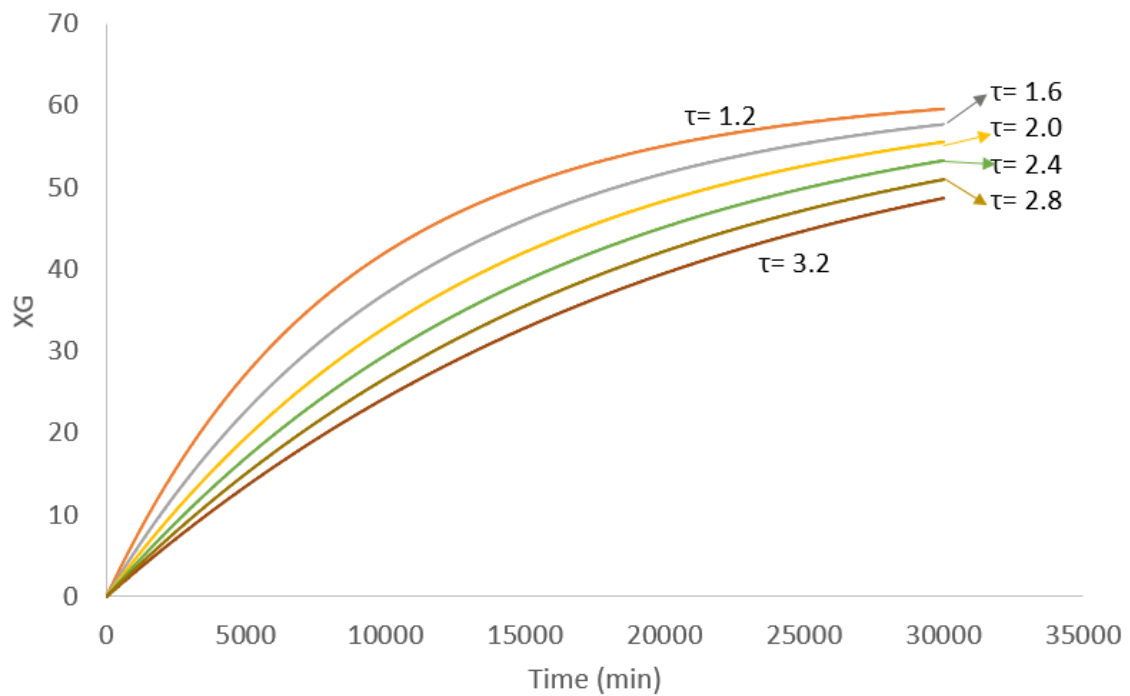
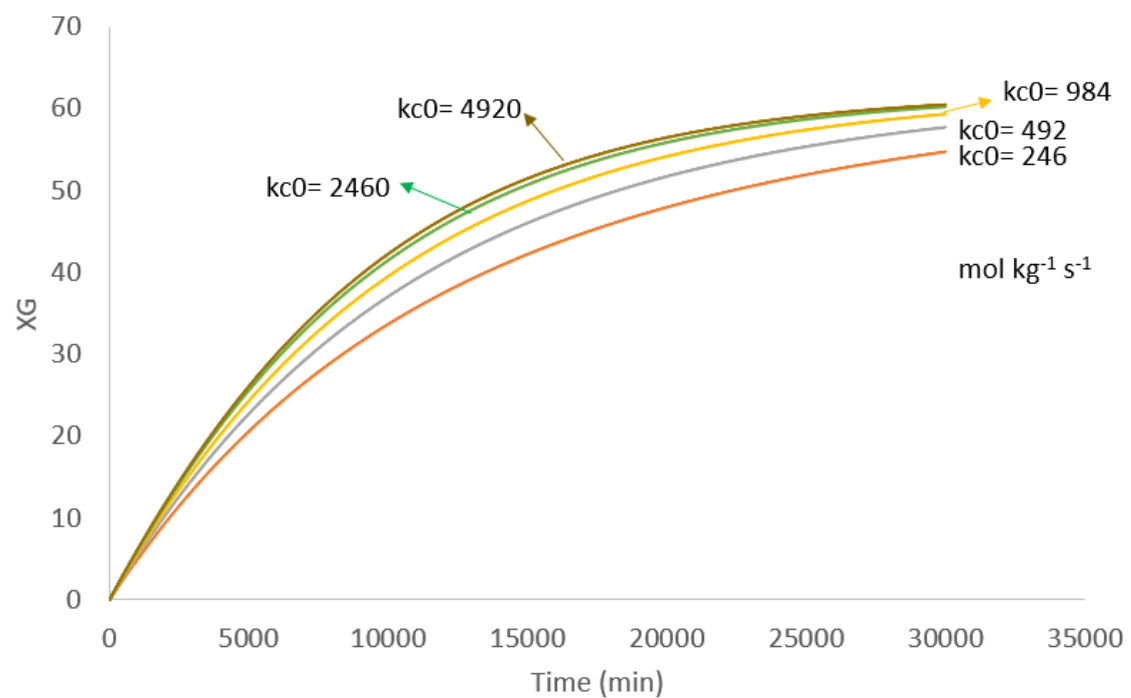


Figure 7 shows the effect of the rate constant k_{c0} on the glycerol conversion

Figure 7 – Effect of k_{c0} on the conversion results.



3. Further studies

- Swelling studies: Validate Karam and Tien method for sulfonated resins;
- Hindering effects: Calculate radius of gyration of L_E 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
C_i	Concentration of the component i	mol L^{-1}
C_{i0}	Initial concentration of the component i	mol L^{-1}
C_p	Reactivity correlation parameter	Dimensionless
$[CL]$	Crosslinked units concentration	mol L^{-1}
f	Initiator efficiency	Dimensionless
I	Initiator concentration	mol L^{-1}
IEC	Ion exchange capacity	meq g^{-1}
IEC_{eff}	Effective ion exchange capacity	meq g^{-1}
k_c	Rate constant of reaction	$\text{mol kg}^{-1} \text{s}^{-1}$
k'_c	Apparent rate constant of reaction	$\text{L}^2 \text{mol}^{-1} \text{kg}^{-1} \text{s}^{-1}$
k_{c0}	Rate constant for the reference temperature	$\text{mol kg}^{-1} \text{s}^{-1}$
K	Ratio $\frac{v_R}{v_P}$	Dimensionless
k_d	Initiator decomposition constant	s^{-1}
K_{eq}	Equilibrium constant of the reaction	Dimensionless
K'_{eq}	Apparent equilibrium constant	Dimensionless
k_{I1}	Styrene initiation constant	$\text{L mol}^{-1} \text{s}^{-1}$
k_{I2}	DVB initiation constant	$\text{L mol}^{-1} \text{s}^{-1}$
k_{p1}	Styrene propagation constant	$\text{L mol}^{-1} \text{s}^{-1}$
k_{p2}	DVB propagation constant	$\text{L mol}^{-1} \text{s}^{-1}$
k_{p3}	PDB propagation constant	$\text{L mol}^{-1} \text{s}^{-1}$
$K_{S,w}$	Adsorption equilibrium constant for water	Dimensionless
$K'_{S,w}$	Apparent adsorption equilibrium constant	L mol^{-1}
k_t	Termination constant	$\text{L mol}^{-1} \text{s}^{-1}$

L_{Ar}	Concentrations of sequences containing r styrene units connecting a PDB to a radical center	mol L^{-1}
L_{Br}	Concentration of sequences containing r styrene units connecting two PDBs	mol L^{-1}
L_{Cr}	Concentration of sequences containing r styrene units connecting a crosslinked unit to a radical center	mol L^{-1}
L_{Dr}	Concentration of sequences containing r styrene units connecting a PDB to a crosslinked unit	mol L^{-1}
L_{Er}	Concentration of sequences containing r styrene units connecting two crosslinked units	mol L^{-1}
M_1	Styrene concentration	mol L^{-1}
$M_{1,0}$	Initial styrene concentration	mol L^{-1}
M_2	DVB concentration	mol L^{-1}
$M_{2,0}$	Initial DVB concentration	mol L^{-1}
\overline{M}_C	Average molecular weight between CLs	g mol^{-1}
\overline{M}_U	Average molecular weight of polymerized units	g mol^{-1}
n	Number of units between CLs	r.u.
n_{max}	Maximum n considered in the copolymerization modeling	r.u.
PDB	Pendant double bonds concentration	mol L^{-1}
R^\cdot	Total radicals' concentration	mol L^{-1}
R_0^\cdot	Primary radicals' concentration	mol L^{-1}
r_A	Rate of reaction for the limiting reagent	$\text{mol L}^{-1} \text{min}^{-1}$
R_p	Radius of swollen particle	dm
$R_{p,dry}$	Radius of dry particle	dm
R_S^\cdot	Concentration of radicals containing only styrene units	mol L^{-1}
SI	Swelling Index	Dimensionless

$[SU]$	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_0	Volume fraction of dissolved polymer in the supernate	Dimensionless
V_1	Molar volume of solvent	$\text{cm}^3 \text{mol}^{-1}$
v_P	Volume fraction of polystyrene in the swollen occluded polystyrene	Dimensionless
v_R	Volume fraction of rubber in the swollen rubber network	Dimensionless
w_P	Weight fraction of occluded polystyrene in the gel	Dimensionless
w_R	Weight fraction of rubber in the gel	Dimensionless
X_G	Glycerol conversion	Dimensionless
Y_{CL}	Fraction of crosslinked units	$\text{mol CL} (\text{mol U})^{-1}$
$Y_{LE,n}$	Fraction of L_{E_n} among all L_E	$\text{mol } L_{E_n} (\text{mol total } L_E)^{-1}$
μ_R	Rubber-solvent interaction factor	Dimensionless
μ_P	Polystyrene-solvent interaction factor	Dimensionless
ρ_i	Density of i	kg dm^{-3}

References

1. Karam, H. J. & Tien, L. Analysis of swelling of crosslinked rubber gel with occlusions. *J Appl Polym Sci* **30**, 1969–1988 (1985).
2. Sewell, J. H. *A Method of Calculating Densities of Polymers*. *JOURNAL OF APPLIED POLYMER SCIENCE* vol. 17 (1973).
3. Ferrell, W. H., Kushner, D. I. & Hickner, M. A. Investigation of polymer–solvent interactions in poly(styrene sulfonate) thin films. *J Polym Sci B Polym Phys* **55**, 1365–1372 (2017).
4. Perkins, L. R. & Geankoplis, C. J. *Molecular Diffusion in a Ternary Liquid System with the Diffusing Component Dilute*. *Chemical Engineering Science*, 1959 vol. 24.
5. Andreas, J. A., Hauser & Tucker. *Fundamental Research on Occurrence and Recovery of Petroleum*. *Polytechnic Inst. Brooklyn, Tech. Rcpt* vol. 44 (1952).
6. Moreira, M. N., Faria, R. P. V., Ribeiro, A. M. & Rodrigues, A. E. Solketal Production from Glycerol Ketalization with Acetone: Catalyst Selection and Thermodynamic and Kinetic Reaction Study. *Ind Eng Chem Res* **58**, 17746–17759 (2019).
7. Jakob, A., Grensemann, H., Lohmann, J. & Gmehling, J. Further development of modified UNIFAC (Dortmund): Revision and extension 5. *Ind Eng Chem Res* **45**, 7924–7933 (2006).
8. DDBST GmbH. Parameters of the Modified UNIFAC (Dortmund) Model. <https://www.ddbst.com/PublishedParametersUNIFACDO.html>. Accessed in January, 10 (2024).

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.

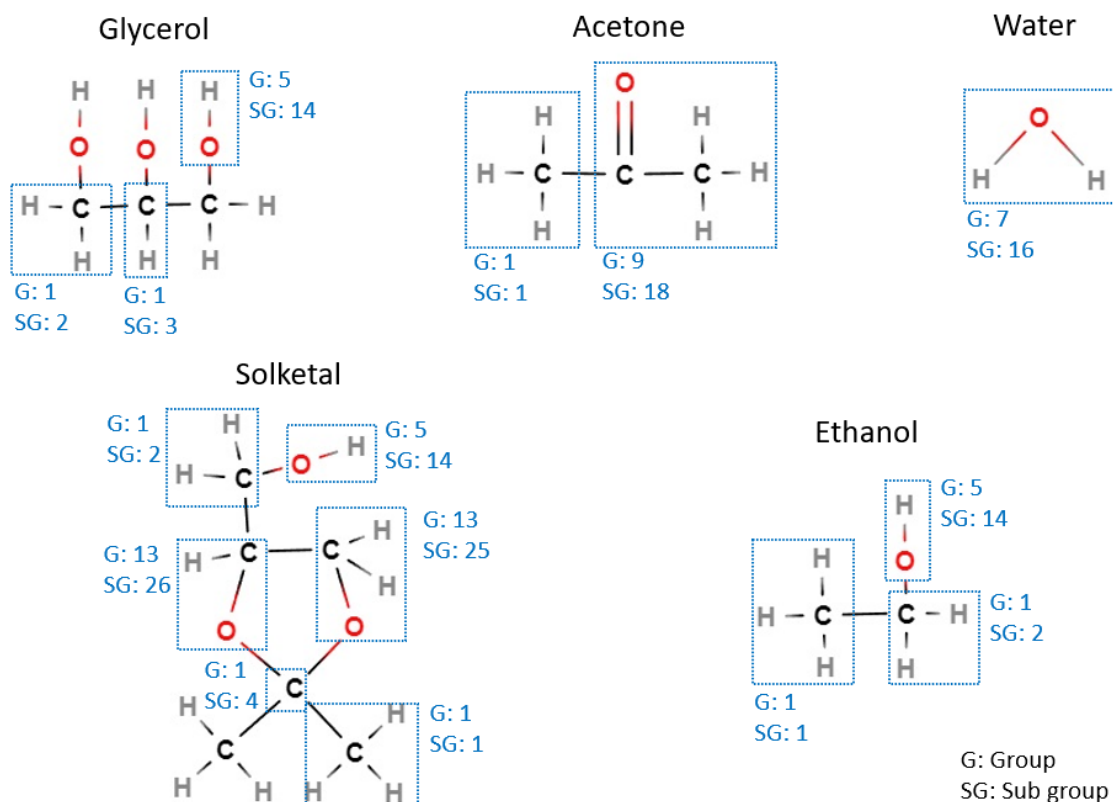


Figure A1 – Groups used in the calculation of activity coefficients.

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 $a_{n,m}$

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 $b_{n,m}$

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 $c_{n,m}$

Group	1	5	9	13	7
1	0	1.55×10^{-3}	0	0	1.144×10^{-3}
5	9.181×10^{-4}	0	6.022×10^{-3}	6.065×10^{-3}	-7.514×10^{-3}
9	0	9.54×10^{-4}	0	0	3.252×10^{-3}
13	0	8.15×10^{-4}	-2.462×10^{-3}	0	9.14×10^{-4}
7	9.021×10^{-4}	0.01641	8.838×10^{-3}	0.010763	0