

## Mathematical Modeling

### 1. Copolymerization model

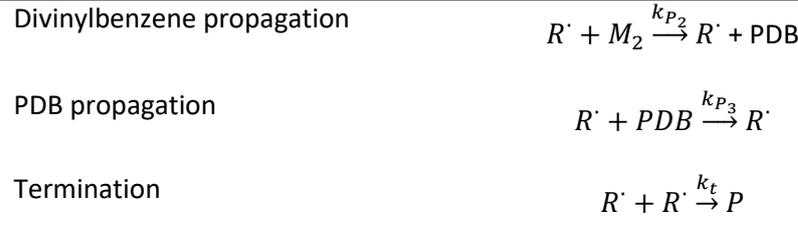
#### Assumptions

- 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	$R^{\cdot} + M_1 \xrightarrow{k_{P1}} R^{\cdot}$



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

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

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.

$$\frac{dR_S}{dt} = k_{I1}R_0M_1 - k_{P2}R_SM_2 - k_{P3}R_S(\sum_{r=0}^{n_{max}} L_{Ar} + 2\sum_{r=0}^{n_{max}} L_{Br} + \sum_{r=0}^{n_{max}} L_{Dr}) - k_tR_S(\sum_{r=0}^{n_{max}} L_{Ar} + \sum_{r=0}^{n_{max}} L_{Cr}) - k_tR_S^2 \quad (11)$$

$$\begin{aligned}
\frac{dL_{A_0}}{dt} &= k_{I_2}R_0M_2 + k_{P_2}M_2(\sum_{r=0}^{n_{max}} L_{A_r} + \sum_{r=0}^{n_{max}} L_{C_r} + R_S) - L_{A_0}[k_{P_1}M_1 + k_{P_2}M_2 + \\
&k_t(\sum_{r=0}^{n_{max}} L_{A_r} + \sum_{r=0}^{n_{max}} L_{C_r} + R_0 + R_S) + k_{P_3}(2\sum_{r=0}^{n_{max}} L_{A_r} + 2\sum_{r=0}^{n_{max}} L_{B_r} + \sum_{r=0}^{n_{max}} L_{C_r} + \\
&\sum_{r=0}^{n_{max}} L_{D_r} + R_0 + R_S)] \tag{12}
\end{aligned}$$

$$\begin{aligned}
\frac{dL_{A_r}}{dt} &= k_{P_1}M_1L_{A_{r-1}} - k_{P_1}M_1L_{A_r} - k_{P_2}M_2L_{A_r} - k_tL_{A_r}(\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + R_S) - \\
&k_{P_3}L_{A_r}(2\sum_{s=0}^{n_{max}} L_{A_s} + 2\sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{C_s} + \sum_{s=0}^{n_{max}} L_{D_s} + R_S + R_0) - k_{cyc}L_{A_r} \tag{13}
\end{aligned}$$

$$\frac{dL_{B_0}}{dt} = k_{P_2}L_{A_0}M_2 + \frac{1}{2}k_tL_{A_0}^2 - 2k_{P_3}L_{B_0}(\sum_{r=0}^{n_{max}} L_{A_r} + \sum_{r=0}^{n_{max}} L_{C_r} + R_0 + R_S) \tag{14}$$

$$\frac{dL_{B_r}}{dt} = k_{P_2}L_{A_r}M_2 + \frac{1}{2}k_t\sum_{s=1}^r L_{A_s}L_{A_{r-s}} - 2k_{P_3}L_{B_r}(\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + R_0 + R_S) \tag{15}$$

$$\begin{aligned}
\frac{dL_{C_0}}{dt} &= -k_{P_1}L_{C_0}M_1 - k_{P_2}L_{C_0}M_2 - k_tL_{C_0}(\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + R_S) - \\
&k_{P_3}L_{C_0}(\sum_{s=0}^{n_{max}} L_{A_s} + 2\sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{D_s}) + k_{P_3}\sum_{r=0}^{n_{max}} L_{A_r}(2\sum_{r=0}^{n_{max}} L_{A_s} + \\
&2\sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{C_s} + \sum_{s=0}^{n_{max}} L_{D_s} + R_S + R_0) + 2k_{P_3}\sum_{r=0}^{n_{max}} L_{B_r}(\sum_{s=0}^{n_{max}} L_{C_s} + R_S + \\
&R_0) + k_{P_3}\sum_{r=0}^{n_{max}} L_{D_r}(\sum_{s=0}^{n_{max}} L_{C_s} + R_S + R_0) + k_{cyc}\sum_{r=3}^{n_{max}} L_{A_r} \tag{16}
\end{aligned}$$

$$\begin{aligned}
\frac{dL_{C_r}}{dt} &= k_{P_1}L_{C_{r-1}}M_1 - k_{P_1}L_{C_r}M_1 - k_{P_2}L_{C_r}M_2 - k_tL_{C_r}(\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + R_S) - \\
&k_{P_3}L_{C_r}(\sum_{s=0}^{n_{max}} L_{A_s} + 2\sum_{s=0}^{n_{max}} L_{B_s} + \sum_{s=0}^{n_{max}} L_{D_s}) + k_{P_3}L_{A_r}(\sum_{s=0}^{n_{max}} L_{A_s} + \sum_{s=0}^{n_{max}} L_{C_s} + R_S + \\
&R_0) \tag{17}
\end{aligned}$$

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

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

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

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

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)<sup>1</sup>, 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 ( $\rho_p$  and  $\rho_R$ ) were calculated through the method of Sewell (1973).<sup>2</sup> 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 polystyrene<sup>3</sup> in equations 32 and 33. Then the swelling index ( $SI$ ) can be used to estimate the particle porosity ( $\varepsilon_p$ ) 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  $\rho_{app}$ ,  $\rho_R$  and  $\rho_s$  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

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

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

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 correlation<sup>4</sup> 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  $j$  ( $\eta_j$ ) 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.<sup>5</sup>

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

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:

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

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

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

$\gamma_i$  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.

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

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

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:  $T= 303$  K

Molar ratio acetone/glycerol:  $MR= 1$

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

Catalyst percentage:  $Cat= 0.5\%$

Swelling index:  $SI= 1.2$

Tortuosity factor:  $\tau= 1.6$

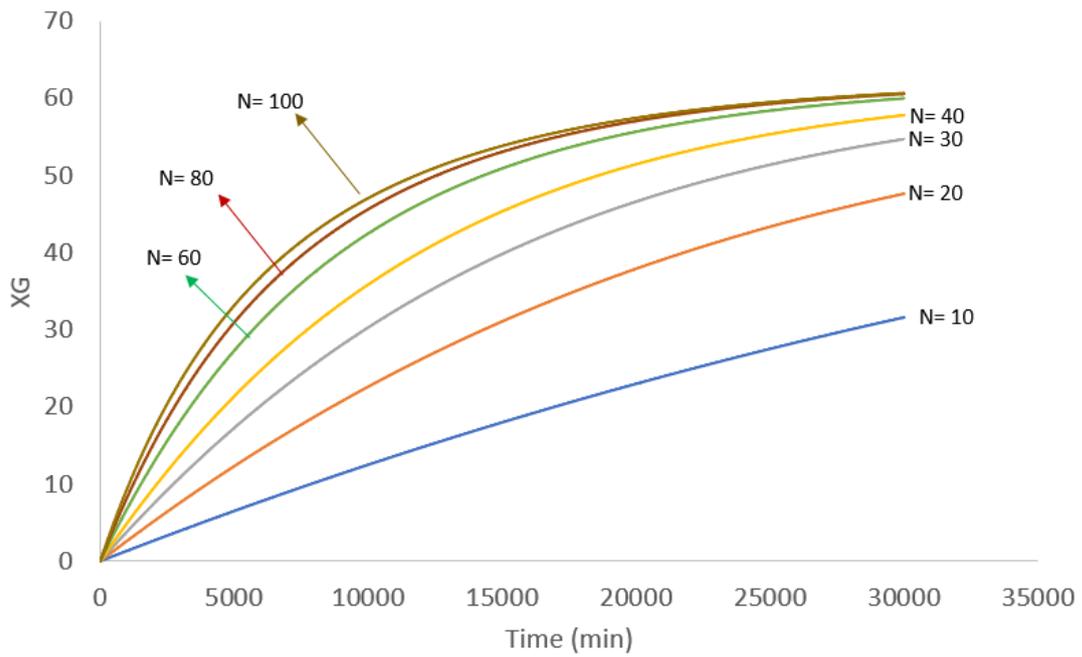
Rate constant at 313K:  $k_{C_0}= 492$  mol  $kg^{-1} s^{-1}$

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

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.

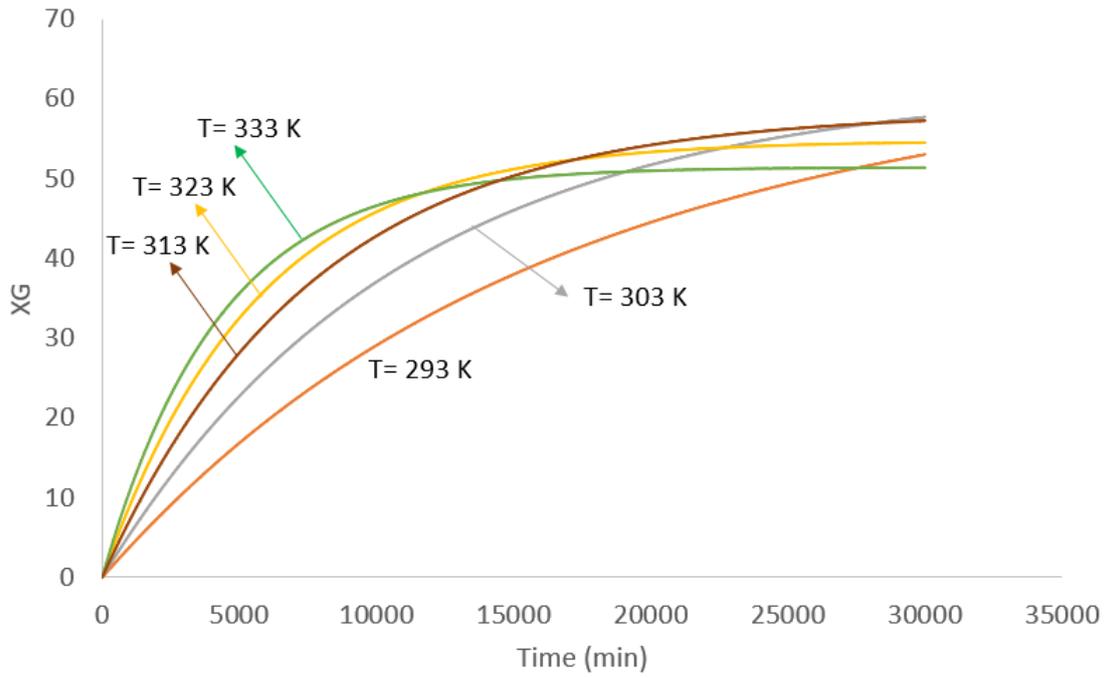


Figure 3 – Effect of acetone/glycerol molar ratio

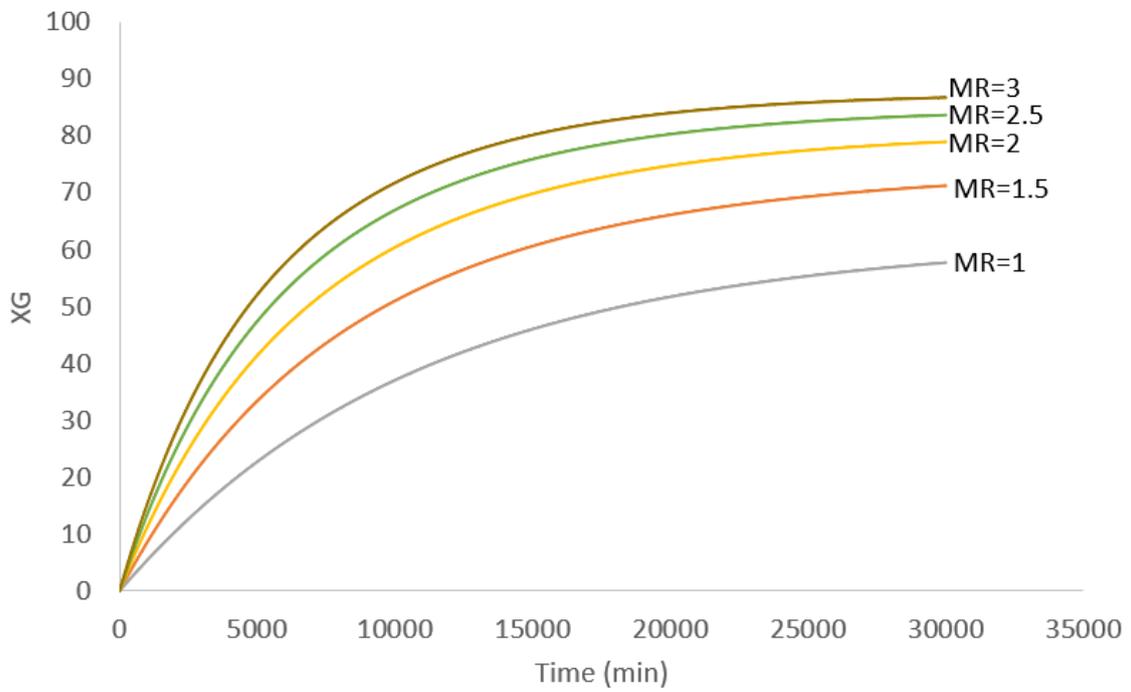
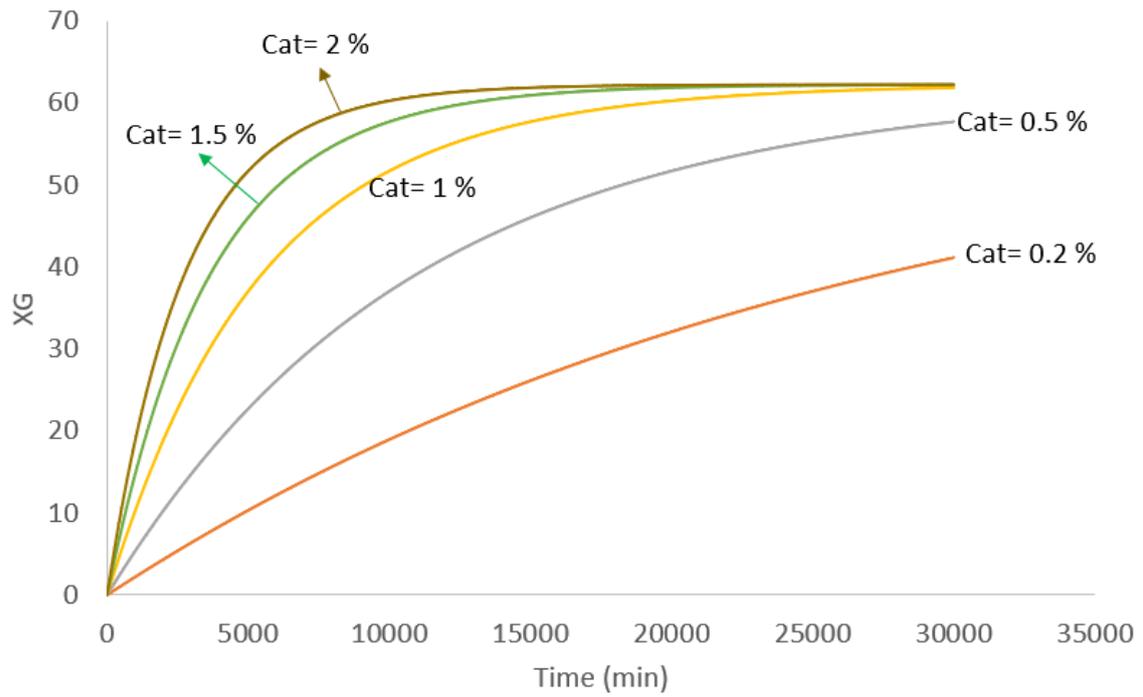


Figure 4 – Effect of catalyst content



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

Figure 5 – Effect of swelling index

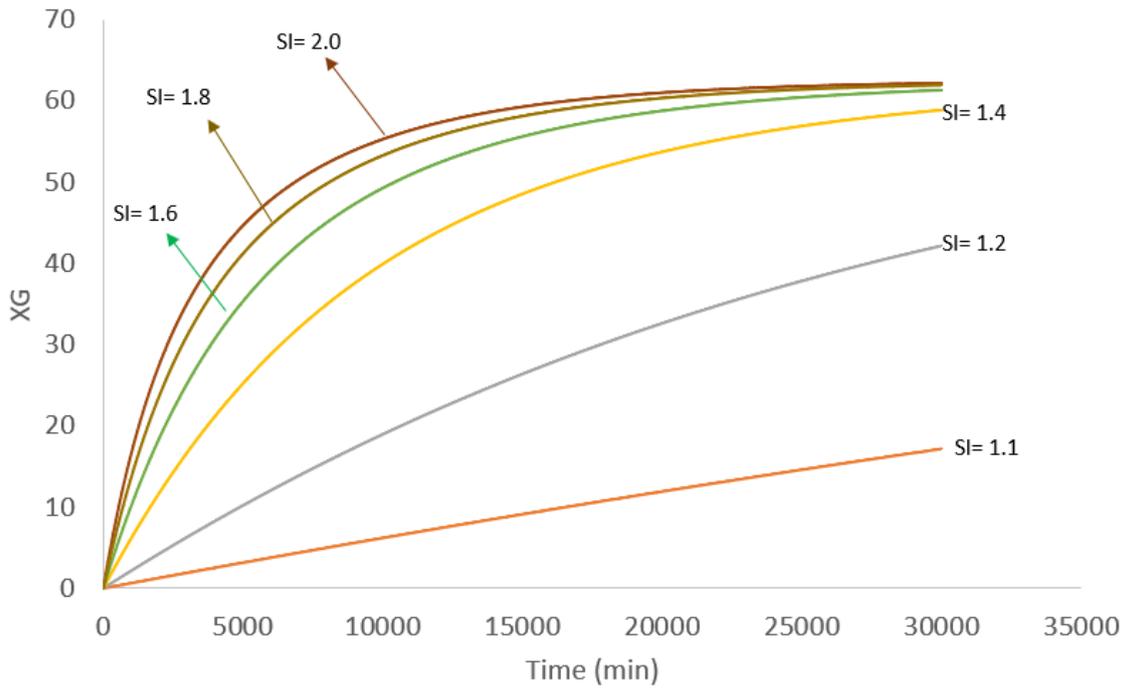


Figure 6 – Effect of tortuosity factor

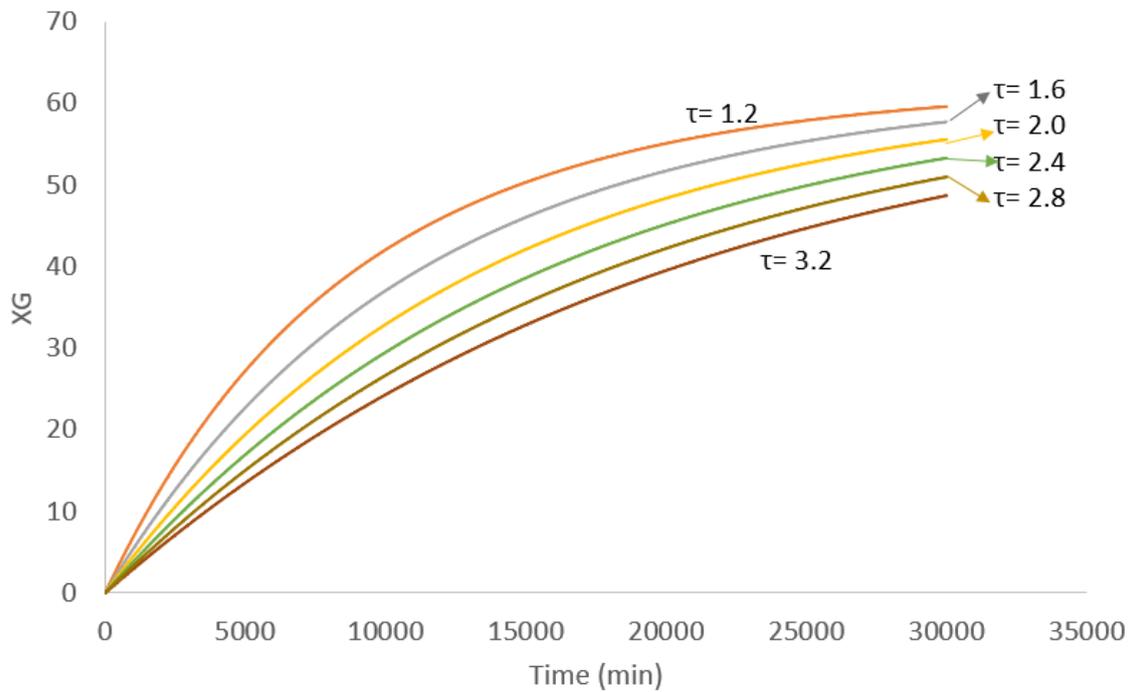
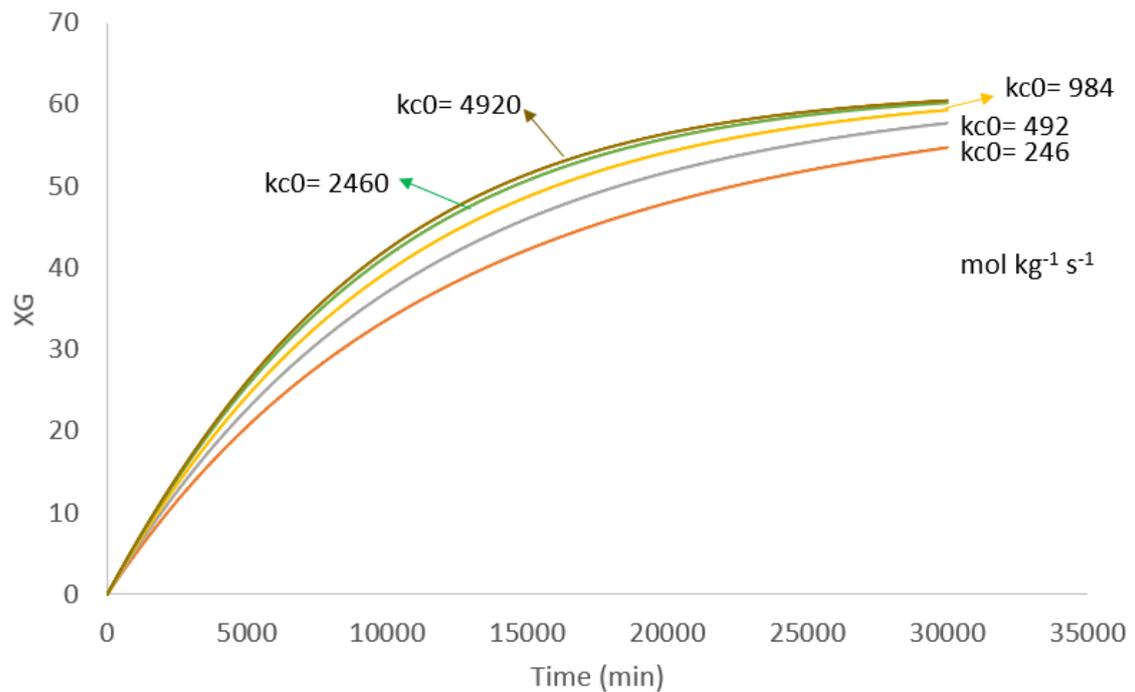


Figure 7 shows the effect of the rate constant  $k_{c0}$  on the glycerol conversion

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	$\text{mol L}^{-1}$
$C_{i0}$	Initial concentration of the component i	$\text{mol L}^{-1}$
$C_p$	Reactivity correlation parameter	Dimensionless
$[CL]$	Crosslinked units concentration	$\text{mol L}^{-1}$
$f$	Initiator efficiency	Dimensionless
$I$	Initiator concentration	$\text{mol L}^{-1}$
$IEC$	Ion exchange capacity	$\text{meq g}^{-1}$
$IEC_{eff}$	Effective ion exchange capacity	$\text{meq g}^{-1}$
$k_c$	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	$\text{s}^{-1}$
$K_{eq}$	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	$\text{L mol}^{-1}$
$k_t$	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	$\text{mol L}^{-1}$
$L_{Br}$	Concentration of sequences containing r styrene units connecting two PDBs	$\text{mol L}^{-1}$
$L_{Cr}$	Concentration of sequences containing r styrene units connecting a crosslinked unit to a radical center	$\text{mol L}^{-1}$
$L_{Dr}$	Concentration of sequences containing r styrene units connecting a PDB to a crosslinked unit	$\text{mol L}^{-1}$
$L_{Er}$	Concentration of sequences containing r styrene units connecting two crosslinked units	$\text{mol L}^{-1}$
$M_1$	Styrene concentration	$\text{mol L}^{-1}$
$M_{1,0}$	Initial styrene concentration	$\text{mol L}^{-1}$
$M_2$	DVB concentration	$\text{mol L}^{-1}$
$M_{2,0}$	Initial DVB concentration	$\text{mol L}^{-1}$
$\overline{M}_C$	Average molecular weight between CLs	$\text{g mol}^{-1}$
$\overline{M}_U$	Average molecular weight of polymerized units	$\text{g mol}^{-1}$
$n$	Number of units between CLs	r.u.
$n_{max}$	Maximum n considered in the copolymerization modeling	r.u.
$PDB$	Pendant double bonds concentration	$\text{mol L}^{-1}$
$R^{\cdot}$	Total radicals' concentration	$\text{mol L}^{-1}$
$R_0^{\cdot}$	Primary radicals' concentration	$\text{mol L}^{-1}$
$r_A$	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	$\text{mol L}^{-1}$
$SI$	Swelling Index	Dimensionless

$[SU]$	Concentration of sulfonated units	$\text{mol L}^{-1}$
$[U]$	Concentration of total polymerized units	$\text{mol L}^{-1}$
$[U_1]$	Concentration of Styrene units	$\text{mol L}^{-1}$
$[U_2]$	Concentration of DVB units	$\text{mol L}^{-1}$
$v_0$	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 $L_E$	$\text{mol } L_{E,n} (\text{mol total } L_E)^{-1}$
$\mu_R$	Rubber-solvent interaction factor	Dimensionless
$\mu_P$	Polystyrene-solvent interaction factor	Dimensionless
$\rho_i$	Density of $i$	$\text{kg dm}^{-3}$

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## APPENDIX A

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

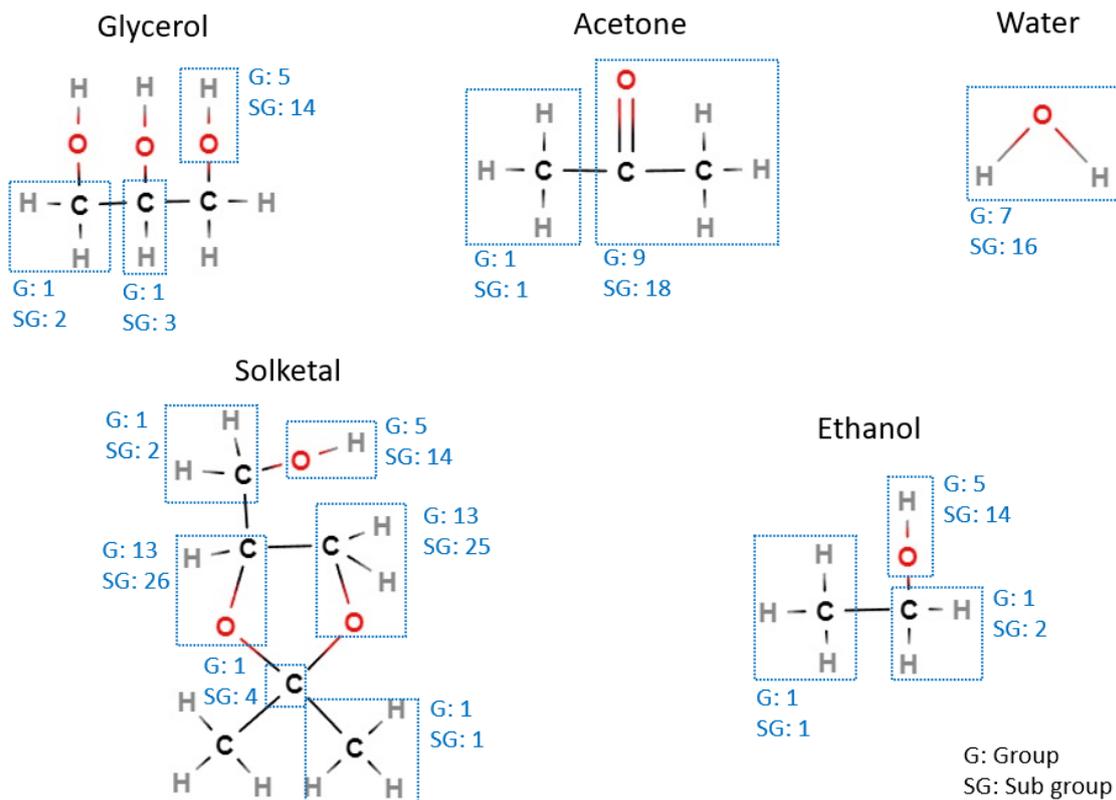


Figure A1 – Groups used in the calculation of activity coefficients.

The UNIFAC parameters were collected from Dortmund Data Bank<sup>8</sup> 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
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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	$1.55 \times 10^{-3}$	0	0	$1.144 \times 10^{-3}$
5	$9.181 \times 10^{-4}$	0	$6.022 \times 10^{-3}$	$6.065 \times 10^{-3}$	$-7.514 \times 10^{-3}$
9	0	$9.54 \times 10^{-4}$	0	0	$3.252 \times 10^{-3}$
13	0	$8.15 \times 10^{-4}$	$-2.462 \times 10^{-3}$	0	$9.14 \times 10^{-4}$
7	$9.021 \times 10^{-4}$	0.01641	$8.838 \times 10^{-3}$	0.010763	0