

Supplementary Information

Sustainable Upgrading of Biomass: A Thermodynamic Approach to Fine-Tuning Product Selectivity for Glycerol Oxidation

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Table S1. Molecules not present in the database. Their thermodynamic properties were calculated by the GANI method.

Molecule	Formula
GLAC	$C_3H_6O_4$
TAC	$C_3H_4O_5$
HPAC	$C_3H_4O_4$
MESAC	$C_3H_2O_5$
GLYX	$C_2H_2O_3$

Table S2. Comparison between Gibbs free energy of formation and enthalpy of formation from thermodynamic model NTRL-NTH ideal gas and thermodynamic data from literature¹.

		NTRL-NTH + GANI + UNIFAC-DMD		literature	
		$\Delta_f G$ ideal	$\Delta_f H$ ideal	$\Delta_f G$ gas	$\Delta_f H$ gas
WATER	kJ/mol	-228.6	-241.8	-228.6	-241.8
CO2	kJ/mol	-394.4	-393.5	-394.4	-393.5
GLY	kJ/mol	-447.1	-577.9	not available	-578.0
FAC	kJ/mol	-351	-378.6	-315.1	-379.0
GAC	kJ/mol	-507	-585.0	-504.9	-583.0
HYDROGEN	kJ/mol	0	0.0	0	0.0
OXYGEN	kJ/mol	0	0.0	0	0.0
OXAC	kJ/mol	-662.4	-719.5	-662.7	-731.8
AcOH	kJ/mol	-374.6	-392.4	-374.2	-432.2

Table S3. Gibbs free energy of formation of the different reactants and products, using the different thermodynamic models.

		Gibbs free energy of formation				
Molecule		NTRL-NTH + GANI + UNIFAC-DMD	NTRL- HOC + GANI	NTRL- RK + GANI	UNIF-DMD + GANI	WILS- NTH + GANI
H2O	kJ/mo 1	-237	-237	-237	-237	-237
GLY	kJ/mo 1	-485	-485	-485	-485	-485
DHA	kJ/mo 1	-471	0	-471	-479	-479
GLAD	kJ/mo 1	-442	0	-446	-446	-446
LAC	kJ/mo 1	-526	-526	-526	-526	-526
GLAC	kJ/mo 1	-702	0	-702	-702	-702
HPAC	kJ/mo 1	-693	0	-693	-693	-693
TAC	kJ/mo 1	-912	0	-912	-912	-912
MESAC	kJ/mo 1	-885	0	-885	-885	-885
GCAD	kJ/mo 1	-264	-264	-264	-264	-264
AcOH	kJ/mo 1	-388	-388	-384	-384	-388
GAC	kJ/mo 1	-529	-529	-529	-529	-529
GLYX	kJ/mo 1	-489	0	-489	-489	-489
OXAC	kJ/mo 1	-689	-689	-689	-689	-689
FAC	kJ/mo 1	-358	-363	-358	-358	-358
CO2	kJ/mo 1	-385	-385	-385	-385	-385
O2	kJ/mo 1	-0.031	-0.031	-0.031	-0.031	-0.031
H2	kJ/mo 1	-0.034	-0.034	-0.034	-0.034	-0.031

Table S4. Gibbs free energy of formation at different temperatures

		$\Delta_f G$						
		25°C	30°C	40°C	50°C	60°C	70°C	80°C
H2O	kJ/mol	-237.2	-236.3	-234.7	-233.2	-231.6	-230.1	-228.5
CO2	kJ/mol	-384.9	-384.6	-384.0	-383.4	-382.8	-382.2	-381.6
GLY	kJ/mol	-485.1	-482.0	-476.0	-470.0	-464.1	-458.2	-452.4
DHA	kJ/mol	-451.2	-449.5	-446.2	-442.8	-439.3	-435.7	-432.1

FAC	kJ/mol	-358.1	-357.2	-355.3	-353.5	-351.7	-349.9	-348.1
GAC	kJ/mol	-529.2	-527.1	-522.9	-518.7	-514.6	-510.4	-506.3
GCAD	kJ/mol	-264.1	-262.4	-259.0	-255.6	-252.2	-248.9	-245.6
GLAC	kJ/mol	-702.0	-699.4	-694.1	-688.8	-683.6	-678.5	-673.3
H2	kJ/mol	-0.03	-0.03	-0.03	-0.03	-0.04	-0.04	-0.04
O2	kJ/mol	-0.03	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04
OXAC	kJ/mol	-688.9	-687.4	-684.2	-681.1	-678.1	-675.0	-672.0
LAC	kJ/mol	-526.4	-523.7	-518.3	-513.0	-507.8	-502.7	-497.6
AcOH	kJ/mol	-387.7	-386.1	-382.9	-379.8	-376.7	-373.7	-370.6
TAC	kJ/mol	-912.0	-909.4	-904.3	-899.3	-894.3	-889.3	-884.4
HPAC	kJ/mol	-692.5	-691.3	-688.8	-686.4	-684.0	-681.6	-679.3
MESAC	kJ/mol	-888.6	-886.7	-882.9	-879.1	-875.4	-871.7	-868.0
GLYX	kJ/mol	-488.6	-487.9	-486.3	-484.8	-483.4	-481.9	-480.5
GLAD	kJ/mol	-445.9	-445.2	-443.7	-442.2	-440.7	-439.3	-437.8

Table S5. Reversible potential at different temperatures for the oxidation of glycerol to different products.

	E reversible						
	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
OER	1.23	1.22	1.22	1.21	1.20	1.19	1.18
CO2	0.03	0.03	0.02	0.01	0.01	0.00	-0.01
DHA	0.18	0.17	0.15	0.14	0.13	0.12	0.10
FAC	0.16	0.15	0.15	0.14	0.13	0.13	0.12
GAC	0.10	0.09	0.09	0.09	0.08	0.08	0.07
GCAD	0.46	0.46	0.45	0.45	0.44	0.44	0.44
GLAC	0.05	0.05	0.04	0.04	0.03	0.03	0.02
OXAC	0.15	0.15	0.14	0.14	0.13	0.13	0.12
LAC	-0.21	-0.22	-0.22	-0.22	-0.23	-0.23	-0.23
AcOH	-0.50	-0.50	-0.51	-0.52	-0.52	-0.53	-0.54
TAC	0.06	0.06	0.05	0.05	0.04	0.04	0.03
HPAC	0.05	0.05	0.04	0.03	0.02	0.01	0.00
MESAC	0.07	0.07	0.06	0.06	0.05	0.05	0.04
GLYX	0.14	0.14	0.13	0.12	0.11	0.10	0.10
GLAD	0.10	0.10	0.08	0.07	0.06	0.05	0.04

Table S6. Standard enthalpy of reaction.

Reactant	Product	$\Delta_R H^\circ$ (kJ/mol)
H2O	H2, O2	286
GLY	GLAD, H2	667
GLY, H2O	GLAC, H2	114
GLY, H2O	TAC, H2	197
GLY	DHA, H2	99
GLY, H2O	HPAC, H2	192
GLY, H2O	MESAC, H2	240
GLY	LAC, H2	-23
GLY, H2O	GAC, H2	202

GLY, H2O	GLYX, H2	574
GLY, H2O	OXAC, H2	649
GLY	AcOH, H2	-115
GLY, H2O	FAC, H2	329
GLY, H2O	CO2, H2	331
GLY	GCAD, H2	220

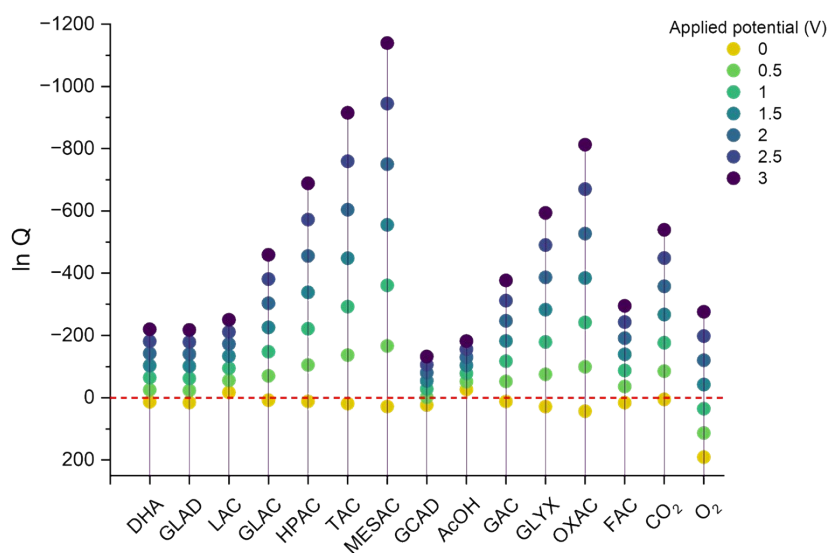


Figure S1. Natural logarithm of the reaction quotient (Q) at different applied potentials (E_{app}), determined under standard state conditions (i.e., 298.15 K and 1 bar). A more negative $\ln Q$ indicates a larger displacement of the reaction toward glycerol oxidation reaction (GOR) products. Note that at $E_{app} = 0$, $Q = K_{eq}$. Note that $\ln Q$ as a function of potential is reported in Figure S2.

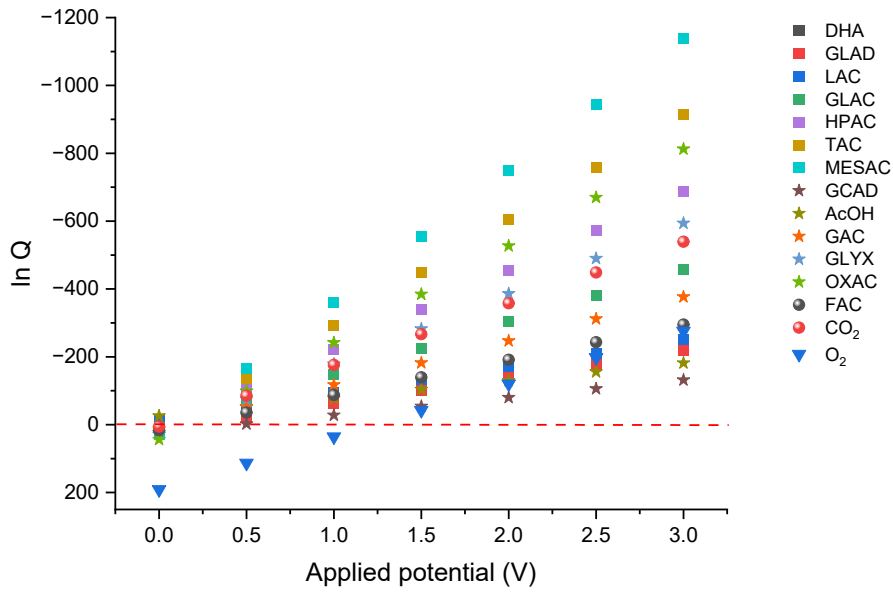


Figure S2. Natural logarithm of the reaction quotient (Q) as a function of applied potential, determined under standard state conditions (i.e., 298.15 K and 1 bar). The slope is given by $-nF/RT$ (or $-n/0.0257 \text{ V}^{-1}$) where n is the number of electrons transferred during the reaction. A more negative $\ln Q$ indicates a larger displacement of the reaction toward glycerol oxidation reaction (GOR) products, meaning that different potentials may favour the formation of one product over the others. However, because of the proximity of $\ln Q$ for the different species at different potentials, it is not possible to obtain a high selectivity towards a specific product from purely thermodynamic considerations. Hence, experimental conditions aiming at tuning the selectivity toward a desired product could be achieved by considering reaction kinetics in combination with the reported information on thermodynamics.

Supplementary note 1 - Density and viscosity

We calculated the dependence of density and viscosity of the mixture with the concentration of glycerol. To achieve this, we used the empirical models developed by Cheng et. al² (for viscosity) and Volk et. al³ (for density), valid from 0 to 100°C and a glycerol mass fraction from 0-1. The equations of the model for viscosity are:

$$\mu_w = 1.79 * \exp\left(\frac{-1230 * T - T^2}{36100 + 360T}\right) * 0.001 \quad (1)$$

$$\mu_{GLY} = 12100 * \exp\left(\frac{-1233 * T - T^2}{9900 + 70T}\right) * 0.001 \quad (2)$$

$$\mu_{mix} = \mu_{GLY} * \exp(A * \alpha) \quad (3)$$

$$A = \ln\left(\frac{\mu_w}{\mu_{GLY}}\right) \quad (4)$$

$$\alpha = 1 - w_{GLY} + \frac{a * b * w_{GLY} * (1 - w_{GLY})}{a * w_{GLY} + b * (1 - w_{GLY})} \quad (5)$$

$$a = 0.705 - 0.0017 * T \quad (6)$$

$$b = (4.9 + 0.036 * T) * a^{2.5} \quad (7)$$

Where μ_w , μ_{GLY} and μ_{mix} are the dynamic viscosities of water, glycerol and mixture in Pa*s, respectively; T corresponds to temperature in °C, A is the logarithmic ratio of the viscosities and α is a weighting factor for the contribution of glycerol viscosity on the viscosity of the solution. For the case of density, the equations are:

$$\rho_w = 1000 * \left(1 - \left|\frac{T - 3.98}{615}\right|^{1.71}\right) \quad (8)$$

$$\rho_{GLY} = 1273 - 0.612 * T \quad (9)$$

$$\rho_{mix} = \kappa * \frac{\rho_w + (\rho_{GLY} - \rho_w)}{1 + \frac{\rho_{GLY}}{\rho_w} * \frac{1}{w_{GLY} - 1}} \quad (10)$$

$$\kappa = 1 + c * \sin(w_{GLY}^{1.31} * \pi)^{0.81} \quad (11)$$

$$c = 1.41 * 10^{-2} - 1.82 * 10^{-4} * T + 1.78 * 10^{-6} * T^2 \quad (12)$$

Where ρ_w , ρ_{GLY} and ρ_{mix} are the densities of water, glycerol and mixture in kg/m³, respectively; T corresponds to temperature in °C and κ is the volume contraction. This last term is used to improve the accuracy of the model, by considering the decrease in solution volume due to interaction between the involved species³.

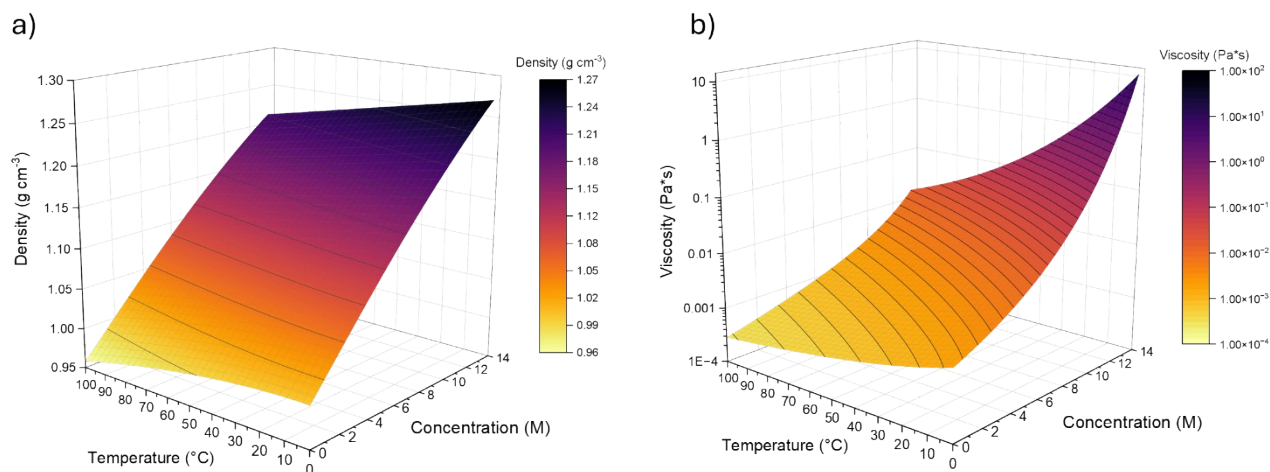


Figure S3. Density and viscosity of glycerol-water mixture as a function of glycerol concentration and temperature.

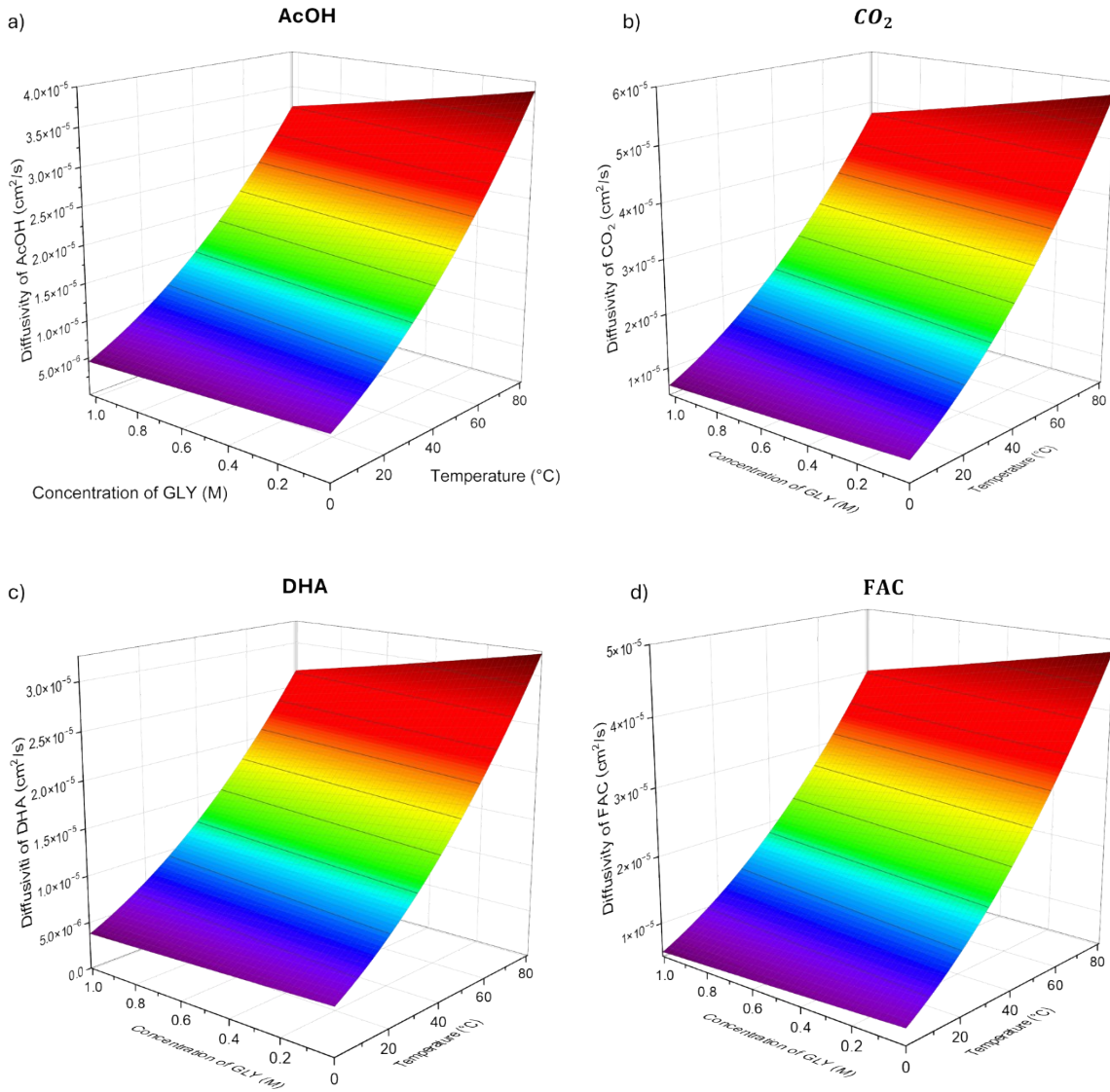
Supplementary note 2 - Diffusivity

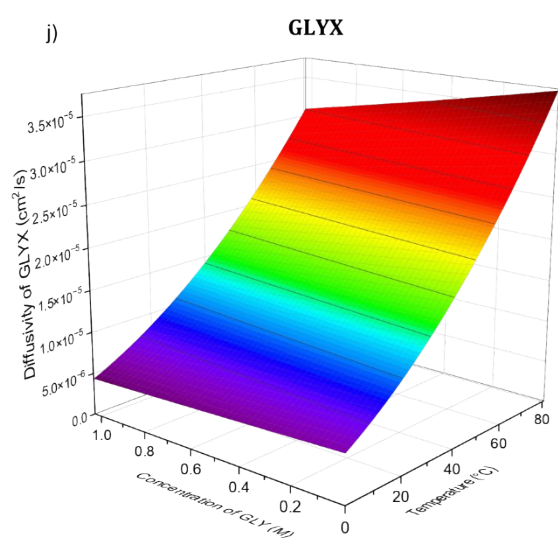
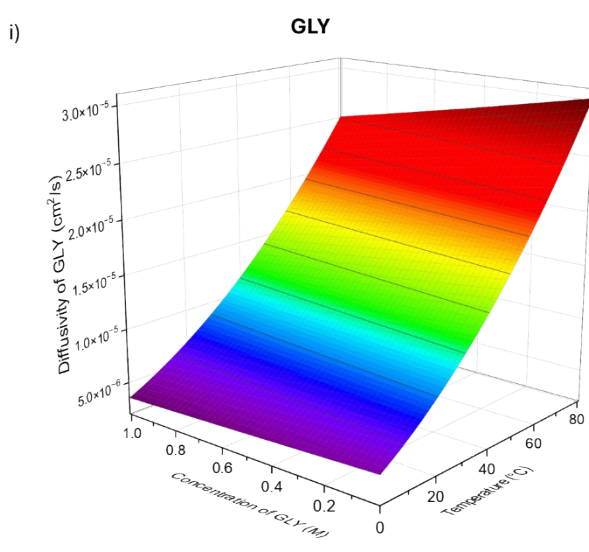
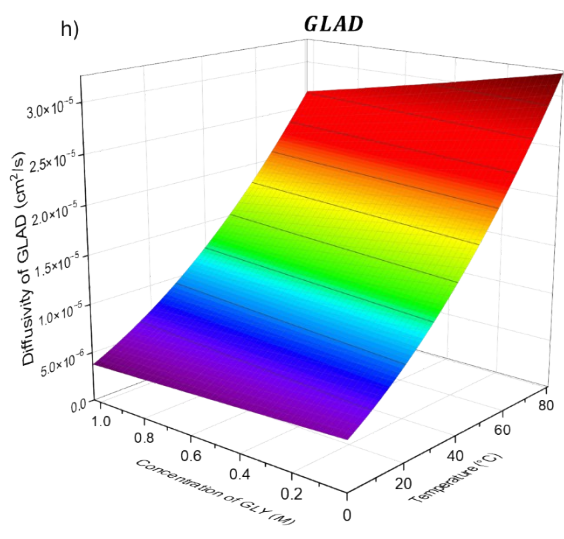
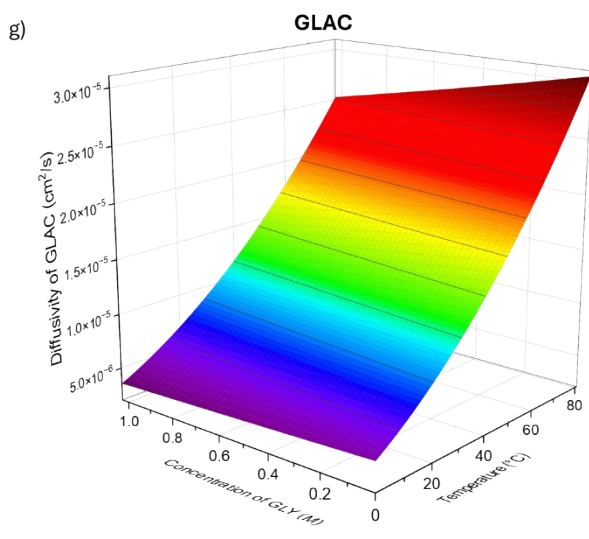
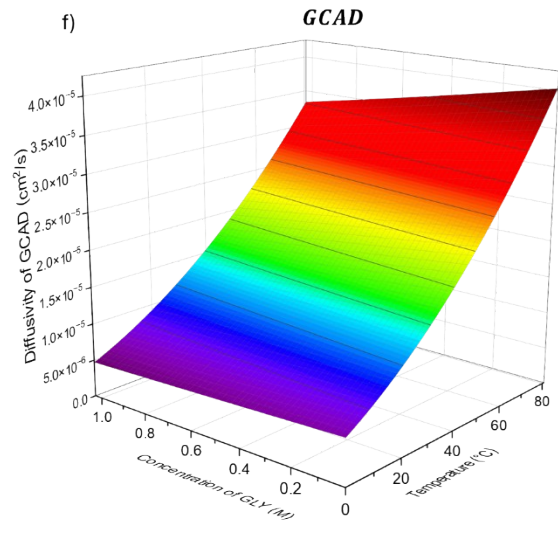
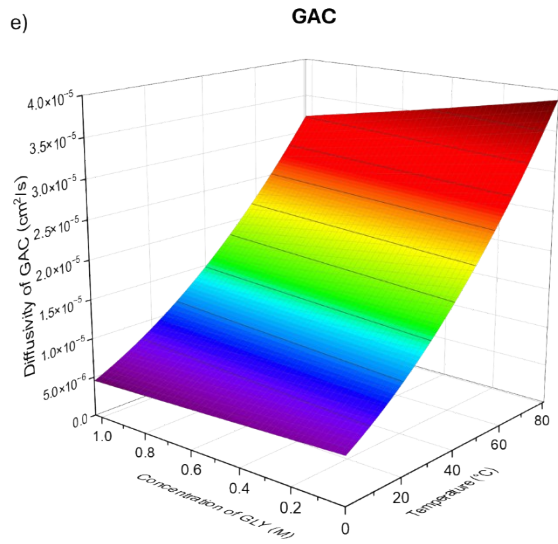
The diffusion coefficient of the different products was calculated using the semi empirical Wilke-Chang equation (Eq. 13)⁴. This model predicts the diffusion coefficients of solute (2) in solvent (1), neglecting solute-solute molecular interactions (i.e. infinite dilution). In our model, to partially include contributions from solute-solute interaction and the effect of temperature, we used the previously calculated viscosity at each temperature and concentration. To stay within the limits of the high dilution approximation, we used a concentration from 0 to 1M.

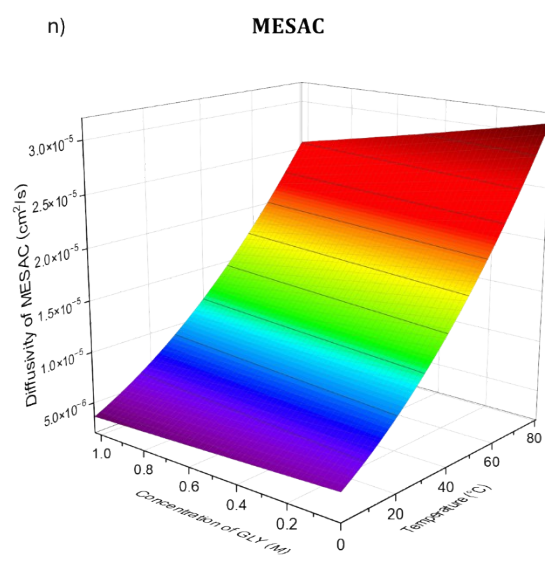
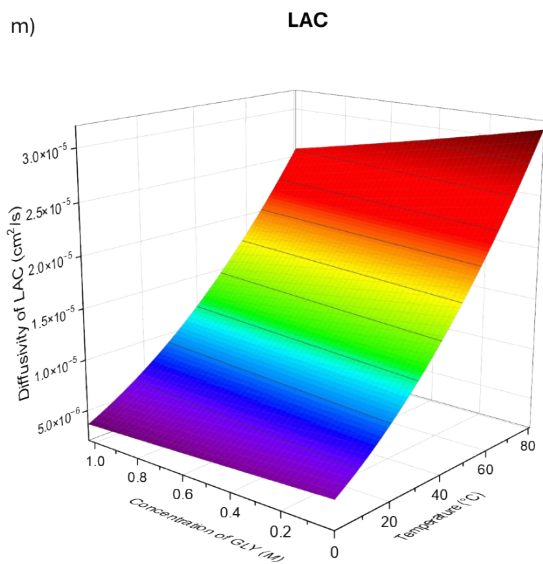
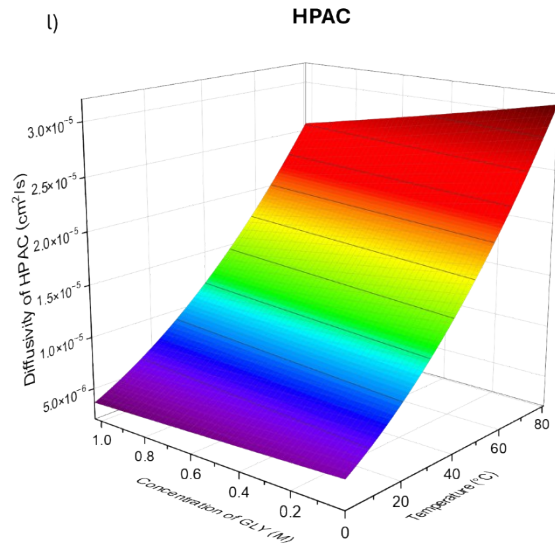
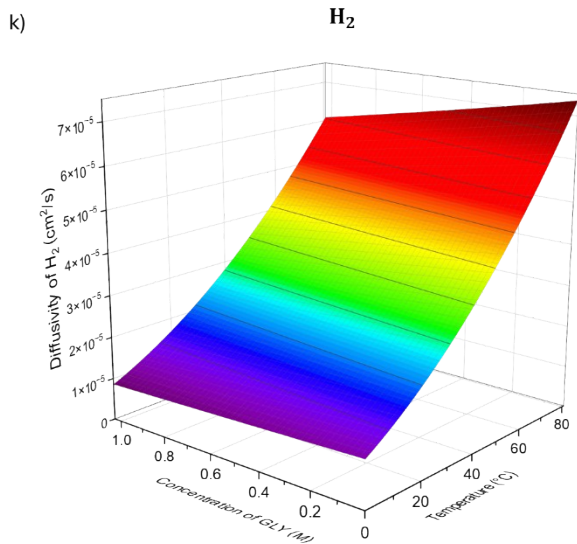
$$D_{12} = 7.4 * 10^{-8} * \frac{(\phi * M_1)^{0.5} T}{\mu_1 (V_{Tc,2})^{0.6}} \quad (13)$$

$$V_{Tc,2} = 0.285 * V_{c,2}^{1.048} \quad (14)$$

Where D_{12} is the binary diffusivity of 1 (solute) in 2 (the solvent) in cm^2/s , ϕ is the association factor of the solvent (dimensionless, 2.26 for water), M_1 is the molar mass of the solvent in g/mol , T is the temperature in K , μ_1 is the solvent viscosity in cP and $V_{Tc,2}$ is the volume at normal boiling point temperature in cm^3/mol . To calculate $V_{Tc,2}$, Eq 14 was used. Here, $V_{c,2}$ corresponds to the solute critical volume in cm^3/mol , which was obtained from the thermodynamic simulations in ASPEN Plus.







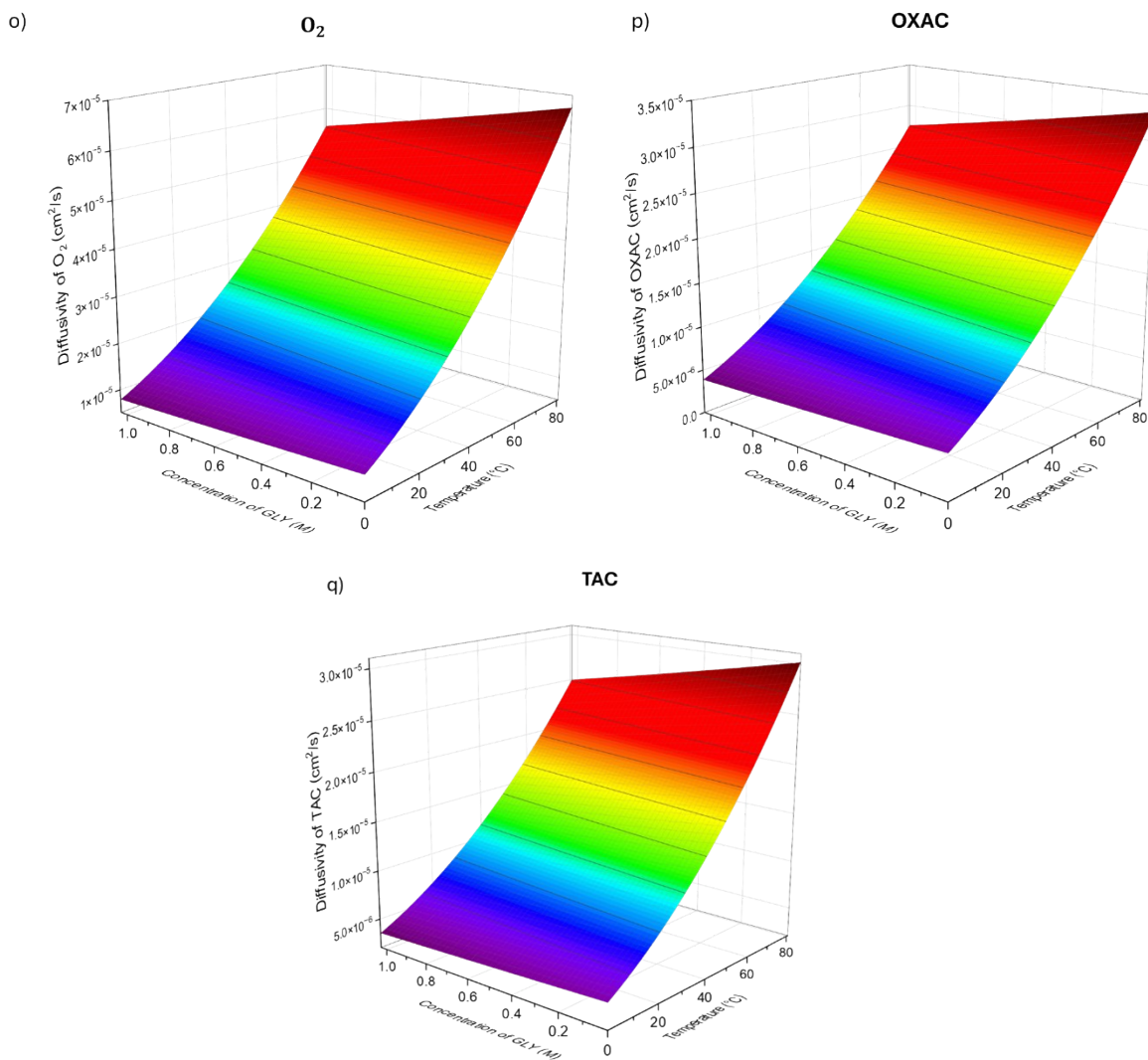


Figure S4. Diffusivity coefficients of GOR and water splitting products from 0 to 1 M, and 0 to 80°C. a) AcOH, b) CO₂, c) DHA, d) FAC, e) GAC, f) GCAD, g) GLAC, h) GLAD, i) GLY, j) GLYX, k) H₂, l) HPAC, m) LAC, n) MESAC, o) O₂, p) OXAC, q) TAC.

References:

- 1 W. M. Haynes, Ed., in *CRC Handbook of Chemistry and Physics*, CRC Press, 95th edn., 2014.
- 2 N.-S. Cheng, *Ind. Eng. Chem. Res.*, 2008, **47**, 3285–3288.
- 3 A. Volk and C. J. Kähler, *Exp. Fluids*, 2018, **59**, 75.
- 4 C. R. Wilke and P. Chang, *AIChE J.*, 1955, **1**, 264–270.