ARTICLE

Autocatalyzed and heterogeneously catalysed esterification kinetics of glycolic acid with ethanol

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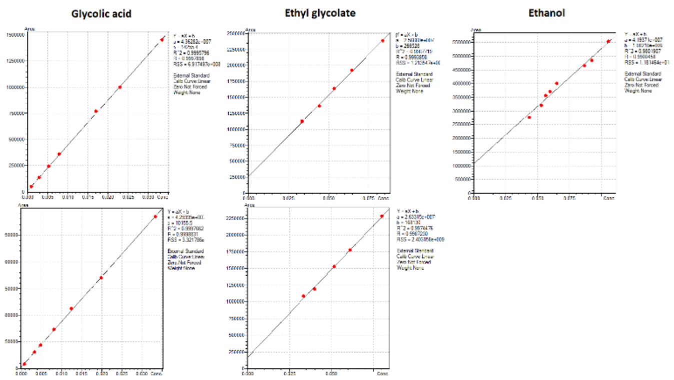
Supplementary Information

HPLC quantification



Plots of area and concentration correlations for compounds quantified by HPLC

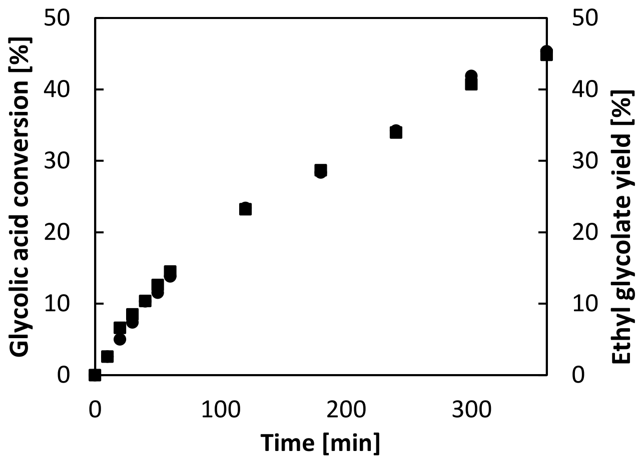


Figure S2. Example representation of glycolic acid conversion and ethyl glycolate yield Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm, 75°C. Yield (●); Conversion (■).

Carbon balance

Table S1. Example of the carbon balance, conversion and yield for a reaction Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm. ,75°C.

Reaction time (min)	Carbon balance (%)	Conversion (%)	Yield (%)
0	0.00	0.00	0.00
10	-0.56	2.59	2.59
20	-2.44	6.61	4.98
30	0.99	8.48	7.36
40	-5.22	10.38	10.31
50	-2.52	12.59	11.52
60	-4.93	14.47	13.82
120	-2.51	23.23	23.40
180	0.67	28.69	28.35
240	-3.36	33.97	34.23
300	-4.89	40.69	41.87
360	-3.49	44.82	45.34

Reproducibility of experiments

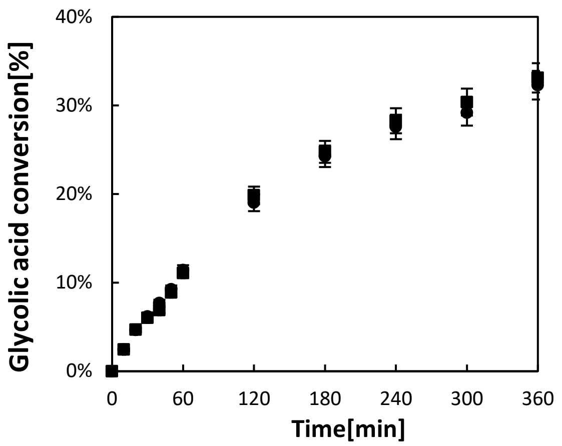


Figure S3 Test of glycolic acid esterification with ethanol. Conditions: 60°C, Acid/Alcohol 1/3 [mol/mol]. (●) test 1; (■) test2

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Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

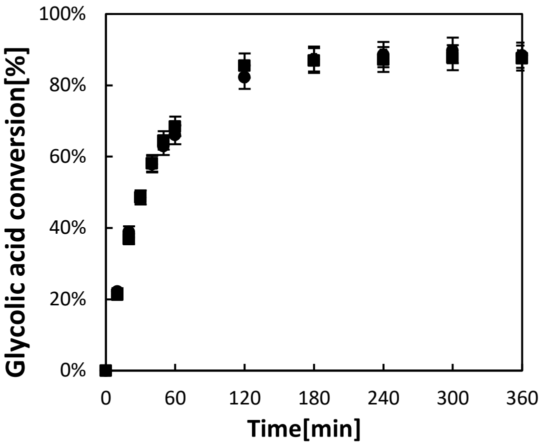

Figure S4 Test of glycolic acid esterification with ethanol. Conditions: 70°C, Acid/Alcohol 1/4 [mol/mol] , Amberlyst 2 wt%. (●) test 1; (■) test2.

Experimental thermodynamic equilibrium

It was considered that the equilibrium was reached for all temperatures after a period of 3h of reaction

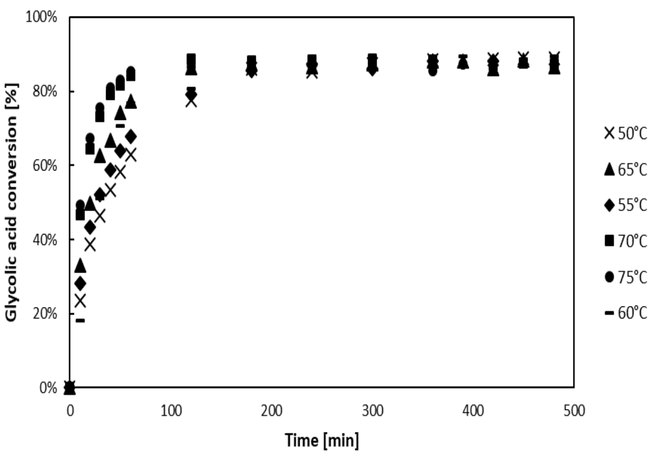

Figure S5. Experimental profiles of glycolic acid conversion in presence of sulfuric acid Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm, H_2SO_4 0.3 w%.

Experimental fitting for autocatalyzed reactions

Table S2. Correlation coefficients matrix for pseudo homogeneous, autocatalysis promoted by solvated protons and molecular glycolic acid respectively

1	0.277
0.277	1
1	-0.394
-0.394	1
1	-0.558
-0.558	1

Heterogeneously catalysts

Table S3. Main properties of the commercial heterogeneous catalysts tested

	Si/Al Mole Ratio	Surface Area [m².g⁻¹]	Main pore opening [Å]	Membered rings
Faujasite[1]	40.0[1]	780[1]	7.4 × 7.4[1]	12[1]
Faujasite [2]	2.5[2]	730[2]	7.4 × 7.4[2]	12[2]
ZSM-5 [3]	40.0 [3]	425 [3]	5.1 × 5.5 [3]	10[3]
ZSM-5 [4]	11.5[4]	425[4]	5.1 × 5.5[4]	10[4]
Mordenite [5]	10.0 [5]	500 [5]	6.5 × 7 [5]	12 [5]
	Physical form	**Surface Area [m².g⁻¹]**	**Ave Pore diameter [Å]**	**Total pore vol [mL.g¹]**
Amberlyst 15 [6]	Beads	53[6]	300[6]	0.4[6]
Amberlyst 36 [7]	Beads	33[7]	240[7]	0.2[7]
Amberlyst 70 [8]	Beads	36 [8]	220 [8]	0.15[8]
Dowex 50XW8-100[9]	Powder		100-200[9]	0.33[9]
Nafion NR50 [10]	Beads			
	Crystalline phase	**Surface Area [m².g⁻¹]**	**Av Pore diameter [Å]**	**Total pore volume [mL.g⁻¹]**
TiO_2 [11]	Anatase	150 [11]	140 [11]	0.388 [11]

Table S4. Acid sites for the acid solids tested in the catalyst screening

	Strong	Medium	Weak	Total	Bibliographic reference
FAU 2.51	0	449	1149	1598	1900[12]
MOR 10.1	616	245	159	1020	950[12]
MFI 11.5	797	180	158	1134	1320[13]
MFI 40.1	143	117	380	640	610[13]
FAU 40.1	348	69	122	540	530[12]
Amberlyst15	3995	0	0	3995	4700[6]
Amberlyst36	4890	0	0	4890	5400[7]
Amberlyst70	2615	0	0	2615	2650[8]
Dowex50XW8-100	4218	0	0	4218	4700[9]
Nafion NR50	880	0	0	880	900[10]
TiO_2	163	89	171	423	430[14]

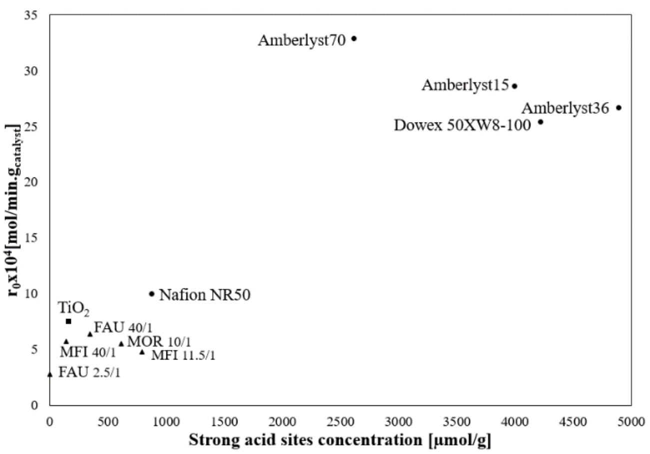

Figure S6. Influence of strong acid sites concentration over the initial reaction rate. Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm, 70°C, Catalyst 2% [g/g sln]. Catalyst (●) Ion exchange resin; (■) Oxide; (▲) Zeolite

Internal diffusion limitations

Procedure and equations employed for the by the Weisz-Prater criterion

$$\varphi = \frac{r_{0cat}\cdot \rho_{Cat}\cdot(d_P/6)^2}{D_{Eff}\cdot C_{GA}} \quad \text{(I)}$$

With r_{0cat} the observed reaction rate for the heterogeneously catalyzed reaction, ρ_{Cat} and d_P the density and particle of diameter of the catalyst, D_{Eff} the effective diffusivity of glycolic acid in the particle and C_{GA} the glycolic acid molar concentration in the solution. The first term r_{0cat} was calculated as

$$r_{0cat} = \frac{r_0}{w_{cat}.\rho_{sln}} \quad \text{(II)}$$

In which r_0 is the reaction rate by unit of volume of the reacting media, $w_{cat.}$ the catalyst loading by mass of reacting media and ρ_{sln} the density of the reacting media.

Considering that in the liquid phase the catalyst presents an homogeneous swelling, the particle swelled dimeter was calculated by equation (III) in which d_{Pdry}, V_{Pdry} are the dry diameter and volume and V_{Pdry} the swollen volume.

$$d_P = d_{Pdry}\sqrt[3]{\frac{Vpswollen}{Vpdry}} \quad \text{(III)}$$

For Amberlyst 70 the swelling ratio $(Vpswollen/Vpdry)$ had been reported to be between 2[43]-2.34[15] for short chain alcohols (C1-C4). The resin employed in this study presents an average dry diameter of 300 µm and so the calculated swelled dimeter is 398 µm.

The effective diffusivity of glycolic the value was obtained from the expression (IV), which requires the diffusion coefficient (D_{GA}), for glycolic acid, the porosity $(\mathcal{E})$ and tortuosity (τ) of the corresponding catalyst.

$$D_{Eff} = D_{GA}\left(\frac{\mathcal{E}}{\tau}\right) \quad \text{(IV)}$$

Different correlations had been proposed for the evaluation of the diffusion coefficient, however the most widely employed is the Wilke-Chang equation (V).[16]

$$D_m = \frac{7.4x10^8\, T\, \sqrt{a_s M_s}}{\mu_s V_a^{0.6}} \quad \text{(V)}$$

In which (T) represents the temperature, (M_s) (a_s) (μ_s) the molecular weigth, association coefficient and viscosity of the solvent, ethanol in this case, and V_a the molar volume at the normal boiling point. The molar volume at normal boiling point of glycolic acid in this case was calculated by group/atom contribution Le bas Method[17]

The estimated value for the diffusion coefficient was later multiplied by the correlation of porosity $(\mathcal{E})$ and tortuosity (τ) extracted from the literature for a similar resin (Amberlyst 15) considering than latter can be approximated to the inverse of the former.[18,19]

$$D_{Eff} = D_{GA}\,\mathcal{E}^2 \quad \text{(VI)}$$

Impact of acid concentration in heterogeneous tests

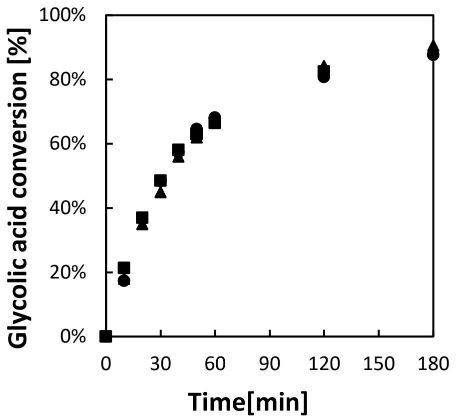

Figure S7 Influence of the concentration of glycolic acid in the initial solution over the reaction catalyzed by Amberlyst 70. Conditions: 70°C, Catalyst 2 wt%. Acid/Alcohol 1/3 [mol/mol] (●) Acid/Alcohol 1/4 [mol/mol], (■) Acid/Alcohol 1/6 [mol/mol](▲) .

Experimental fitting for reactions in presence of Amberlyst 70

Table S5. Correlation coefficients matrix for PH, ER and LH molecular glycolic acid respectively

1	-0.762
-0.762	1

1	-0.627	0.439	0.0697
-0.627	1	-0.753	-0.253
0.439	-0.753	1	0.207
0.0697	-0.253	0.207	1

1	-0.712	-0.306	0.102	0.512	-0.170
-0.712	1	0.467	0.067	-0.675	0.131
-0.306	0.467	1	-0.316	-0.651	-0.081
0.102	0.067	-0.316	1	0.010	0.502
0.512	-0.675	-0.651	0.010	1	-0.018
-0.170	0.131	-0.081	0.502	-0.018	1

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