Supporting Information

Bio-additives from glycerol acetylation with acetic acid: Chemical Equilibrium Model

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Table S1. Functional groups and group additivity values from Domalski and Hearing database (Domalski and Hearing 1993) at standard conditions (T=298.15 K and 101.325 Pa). $\Delta h^{s}_{f,j}$ = molar enthalpy of formation of group j; $s^{s}_{f,j}$ = absolute molar entropy of formation of group j; $\Delta h^{S}_{f,i}$ = molar enthalpy of formation of compound i and $s^{S}_{f,i}$ =molar entropy of formation of compound i.

Compound	Group	n_i	$\Delta h^{s}_{f,j}$ [kJ mol^{-1}]	$s^{s}_{f,j}$ [kJ mol^{-1} K^{-1}]	$\Delta h^{s}_{f,i}$ [kJ mol^{-1}]	$s^{s}_{f,i}$ [kJ mol^{-1} K^{-1}]
Glycerol (G)	C-$(H)_2$(O)(C)	2	-35.8	0.03259	-673.7	0.16702
	C-(H)(O)$(C)_2$ (Alcohols, peroxides)	1	-27.6	-0.02983		
	O-(H)(C)	3	-191.5	0.04389		
Acetic Acid (AA)	C-$(H)_3$(CO)	1	-47.61	0.0833	-482.6	0.1543
	CO-(C)(O)	1	-149.37	0.03272		
	O-(CO)(H)	1	-285.64	0.03828		
1-monoacetyl glycerol (1-MAG)	O-(H)(C)	2	-191.5	0.04389	-875.2	0.27743
	C-$(H)_2$(O)(C)	2	-35.8	0.03259		
	C-(H)(O)$(C)_2$ (Alcohols, peroxides)	1	-27.6	-0.02983		
	CO-(C)(O)	1	-149.37	0.03272		
	O-(CO)(C)	1	-196.02	0.03828		
	C-$(H)_3$(CO)	1	-47.61	0.0833		
2-monoacetyl glycerol (2-MAG)	O-(H)(C)	2	-191.5	0.04389	-868.6	0.28195
	C-$(H)_2$(O)(C)	2	-35.8	0.03259		
	C-$(H)_3$(CO)	1	-47.61	0.0833		
	CO-(C)(O)	1	-149.37	0.03272		
	O-(CO)(C)	1	-196.02	0.03828		
	C-(H)(O)$(C)_2$ (Ethers, esters)	1	-21	-0.02531		
1,3-diacetyl glycerol (1,3-DAG)	O-(H)(C)	1	-191.5	0.04389	-1077	0.38784
	C-$(H)_2$(O)(C)	2	-35.8	0.03259		
	C-$(H)_3$(CO)	2	-47,61	0.0833		
	CO-(C)(O)	2	-149.37	0.03272		
	O-(CO)(C)	2	-196.02	0.03828		
	C-(H)(O)$(C)_2$ (Alcohols, peroxides)	1	-27.6	-0.02983		
1,2-diacetyl glycerol (1,2-DAG)	O-(H)(C)	1	-191.5	0.04389	-1070	0.39236
	C-$(H)_2$(O)(C)	2	-35.8	0.03259		
	C-$(H)_3$(CO)	2	-47.61	0.0833		
	CO-(C)(O)	2	-149.37	0.03272		
	O-(CO)(C)	2	-196.02	0.03828		

	C-(H)(O)$(C)_2$ (Ethers, esters)	1	-21	-0.02531		
Triacetyl glycerol (TAG)	C-$(H)_3$(CO)	3	-47.61	0.0833	-1272	0.50277
	CO-(C)(O)	3	-149.37	0.03272		
	O-(CO)(C)	3	-196.02	0.03828		
	C-(H)2(O)(C)	2	-35.8	0.03259		
	C-(H)(O)$(C)_2$ (Ethers, esters)	1	-21	-0.02531		

Table S2. Parameters b_j, d_j y e_j from Poling-Prausnitz-O'Connell for the specific heat calculus (Poling et al. 2001).

Compound	Group	n_i	b_i	d_i	e_i	B	D	E
Glycerol (G)	O- (C, H)	3	12.952	-10.145	2.6261	43.996	-28.939	8.0306
	C-(2H, C, O)	2	1.4596	1.4657	-0.2714			
	C-(H,2C, O) Alcohol	1	2.2209	-1.435	0.69508			
Acetic Acid (AA)	C-(3H, C)	1	3.8452	-0.33997	0.19489	5.504	2.9213	0.0470
	O-(H, CO)	1	-27.587	-0.16485	2.7483			
	CO-(C, O)	1	29.246	3.4261	-2.8962			
1-monoacetyl glycerol (1-MAG)	C-(3H,C)	1	3.8452	-0.33997	0.19489	42.701	-19.7239	5.7563
	O-(C,H)	2	12.952	-10.145	2.6261			
	C-(2H,C,O)	2	1.4596	1.4657	-0.2714			
	C-(H,2C,O) Alcohol	1	2.2209	-1.435	0.69508			
	O-(C,CO)	1	-21.434	-4.0164	3.0531			
	CO-(C,O)	1	29.246	3.4261	-2.8962			
2-monoacetyl glycerol (2-MAG)	C-(3H,C)	1	3.8452	-0.33997	0.19489	41.468	-17.8948	5.0451
	O-(C,H)	2	12.952	-10.145	2.6261			
	C-(2H,C,O)	2	1.4596	1.4657	-0.2714			
	C-(H,2C,O) Ether-Ester	1	0.9879	0.39403	-0.01612			
	O-(C,CO)	1	-21.434	-4.0164	3.0531			
	CO-(C,O)	1	29.246	3.4261	-2.8962			

1,3-diacetyl glycerol (1,3-DAG)	C-(3H,C)	2	3.8452	-0.33997	0.19489	41.407	-10.5091	3.4820
	O-(C,H)	1	12.952	-10.145	2.6261			
	C-(2H,C,O)	2	1.4596	1.4657	-0.2714			
	C-(H,2C,O) Alcohol	1	2.2209	-1.435	0.69508			
	O-(C,CO)	2	-21.434	-4.0164	3.0531			
	CO-(C,O)	2	29.246	3.4261	-2.8962			
1,2-diacetyl glycerol (1,2-DAG)	C-(3H,C)	2	3.8452	-0.33997	0.19489	40.174	-8.6801	2.7708
	O-(C,H)	1	12.952	-10.145	2.6261			
	C-(2H,C,O)	2	1.4596	1.4657	-0.2714			
	C-(H,2C,O) Ether-Ester	1	0.9879	0.39403	-0.01612			
	O-(C,CO)	2	-21.434	-4.0164	3.0531			
	CO-(C,O)	2	29.246	3.4261	-2.8962			
Triacetyl glycerol (TAG)	C-(3H,C)	3	3.8452	-0.33997	0.19489	38.879	0.5346	0.4964
	O-(C,H)	0	12.952	-10.145	2.6261			
	C-(2H,C,O)	2	1.4596	1.4657	-0.2714			
	C-(H,2C,O) Ether-Ester	1	0.9879	0.39403	-0.01612			
	O-(C,CO)	3	-21.434	-4.0164	3.0531			
	CO-(C,O)	3	29.246	3.4261	-2.8962			

Table S3. Heat capacity of chemical species (H_2, O_2 and C) and water.

$$c_{p,m}^{0}(T) = A + B \cdot T + C \cdot T^{2} + D \cdot T^{3} + E \cdot T^{4} + F \cdot T^{-2}$$ **[J mol^{-1} K^{-1}]**

Compound	A	B	C (x10^{-5})	D(x10^{-9})	E (x10^{-9})	F
H_2 [a]	33.06618	-0.01136	1.14	-2.8	0	-158558
O_2 [a]	31.32234	-0.02024	5.79	-37	0	-7374
C [a]	8.1	0	0	0	0	0
Water [b]	276.37	-2.0901	821.5	-14110	9.37	0

[a] From literature (NIST)

[b] From literature (Perry 2008)

Table S4. Groups and group parameters of the UNIFAC method employed in the determination of the activity coefficients (Prausnitz et al. 1975).

Group i	CH_3	CH_2	CH	CH_3COO	H_2O	OH	COOH
ν_i^{Gly}	0	2	1	0	0	3	0
ν_i^{Acet}	1	0	0	1	0	0	0
$\nu_i^{1\text{-}MAG}$	0	2	1	1	0	2	0
$\nu_i^{2\text{-}MAG}$	0	2	1	1	0	2	0
$\nu_i^{1,3\text{-}DAG}$	0	2	1	2	0	1	0
$\nu_i^{1,2\text{-}DAG}$	0	2	1	2	0	1	0
ν_i^{TAG}	0	2	1	3	0	0	0
ν_i^{Water}	0	0	0	0	1	0	0
R_k	0.9011	0.6744	0.4469	1.9031	0.92	1	1.3013
Q_k	0.848	0.54	0.228	1.728	1.4	1.2	1.224

Table S5. Group contribution values (t_{cj}, p_{cj} and v_{cj}) of the Joback method for the critical properties (T_{ci}, P_{ci}, v_{ci}) (Joback and Reid 1987).

Compound	Group	n_i	t_{ci}	p_{ci}	v_{ci}
1-monoacetyl glycerol (1-MAG)	-CH3	1	0.0141	-0.0012	65
	-CH2-	2	0.0189	0.0000	56
	-CH-	1	0.0164	0.0020	41
	-OH	2	0.0741	0.0112	28
	-COO-	1	0.0481	0.0005	82
2-monoacetyl glycerol (2-MAG)	-CH3	1	0.0141	-0.0012	65

	-CH2-	2	0.0189	0.0000	56
	-CH-	1	0.0164	0.0020	41
	-OH	2	0.0741	0.0112	28
	-COO-	1	0.0481	0.0005	82
1,3-diacetyl glycerol (1,3-DAG)	-CH3	2	0.0141	-0.0012	65
	-CH2-	2	0.0189	0.0000	56
	-CH-	1	0.0164	0.0020	41
	-OH	1	0.0741	0.0112	28
	-COO-	2	0.0168	0.0015	18
1,2-diacetyl glycerol (1,2-DAG)	-CH3	2	0.0141	-0.0012	65
	-CH2-	2	0.0189	0.0000	56
	-CH-	1	0.0164	0.0020	41
	-OH	1	0.0741	0.0112	28
	-COO-	2	0.0168	0.0015	18
Triacetyl glycerol (TAG)	-CH3	3	0.0141	-0.0012	65
	-CH2-	2	0.0189	0.0000	56
	-CH-	1	0.0164	0.0020	41
	-COO-	3	0.0168	0.0015	18

Table S6. Group contribution values for boiling temperature calculus (Nannoolal et al. 2004).

Compound	Group	n_i	Value C_i
1-monoacetyl glycerol (1-MAG)	CH_3-(ne)	1	177.3066
	> C(c) < (e)	3	266.8769
	HO-(C,Si) long	1	443.8712
	HO-(C,Si) sec	1	390.2446
	(c)-COO-(C)	1	636.2020
	Corrections		
	-OH/-OH	1	291.7985
	-OH/-COOC-	2	211.6814
2-monoacetyl glycerol (2-MAG)	CH_3-(ne)	1	177.3066
	(c)-COO-(C)	1	636.2020
	HO-(C,Si) long	2	443.8712
	> C(c) < (e)	3	266.8769
	Corrections		
	-OH/-OH	1	291.7985
	-OH/-COOC-	2	211.6814
1,3-diacetyl glycerol (1,3-DAG)	CH_3-(ne)	2	177.3066
	(c)-COO-(C)	2	636.2020
	> C(c) < (e)	3	266.8769
	HO-(C,Si) long	1	443.8712
	Corrections		
	-OH/-COOC-	2	211.6814
1,2-diacetyl glycerol (1,2-DAG)	CH_3-(ne)	2	177.3066
	(c)-COO-(C)	2	636.2020
	> C(c) < (e)	3	266.8769
	HO-(C,Si) long	1	443.8712
	Corrections		
	-OH/-COOC-	2	211.6814
Triacetyl glycerol (TAG)	CH_3-(ne)	3	177.3066
	(c)-COO-(C)	3	636.2020
	> C(c) < (e)	3	266.8769
	Corrections		
	-COOC-/-COOC-	2	431.0990

Table S7. Physicochemical properties of reagents and products.

Compound	T_B (K)	T_c (K)	P_c (bar)	v_c ($cm^3\,mol^{-1}$)	ω	v^L ($m^3\,mol^{-1}$) [d]
Glycerol (G)[a]	563.0	850.0	66.87	255.0	0.52	0.00007482
Acetic acid (AA)[b]	391.2	591.9	57.86	177.9	0.46	0.00006866
1-monoacetyl glycerol (1-MAG)	510.3	663.3	44.39	373.5	1.40	0.00004611
2-monoacetyl glycerol (2-MAG)	519.3	675.0	44.39	373.5	1.40	0.00004662
1,3-diacetyl glycerol (1,3-DAG)	510.5	698.1	32.28	364.5	0.76	0.00011204
1,2-diacetyl glycerol (1,2-DAG)	510.5	698.1	32.28	364.5	0.76	0.00011204

Triacetyl glycerol (TAG)	520.2	738.4	24.29	419.5	0.41	0.00019784
Water (W)[c]	373.1	647.1	220.64	55.9	0.33	0.00002071

[a,b,c] From literature (NIST)

[d] Calculated at 298 K

Table S8. Molar enthalpy of formation (Δh_f^0) of all the compounds involved in the reaction as a function of temperature, in kJ mol^{-1}.

T (°C)	G	AA	1-MAG	2-MAG	1,2-DAG	1,3-DAG	TAG	W
298.15	-673.7	-482.6	-875.2	-868.6	-1070.1	-1076.7	-1271.6	-285.8
303.15	-673.4	-482.5	-874.9	-868.4	-1070.0	-1076.5	-1271.5	-285.7
313.15	-672.6	-482.3	-874.3	-868.0	-1069.7	-1076.0	-1271.4	-285.3
323.15	-6717	-482.1	-873.6	-867.5	-1069.4	-1075.5	-1271.3	-285.0
333.15	-670.6	-481.8	-872.7	-866.9	-1069.0	-1074.8	-1271.1	-284.7
343.15	-669.3	-481.5	-871.7	-866.1	-1068.5	-1074.1	-1270.9	-284.4
353.15	-667.8	-481.2	-870.5	-865.2	-1067.9	-1073.2	-1270.7	-284.1
373.15	-664.0	-480.5	-867.6	-862.9	-1066.5	-1071.2	-1270.1	-283.5
393.15	-659.3	-479.7	-863.9	-860.1	-1064.8	-1068.6	-1269.4	-282.8
413.15	-653.4	-478.8	-859.4	-856.5	-1062.5	-1065.5	-1268.6	-282.1
433.15	-646.2	-477.8	-854.0	-852.1	-1059.9	-1061.8	-1267.7	-281.5
453.15	-637.8	-476.7	-847.6	-846.9	-1056.7	-1057.5	-1266.6	-280.8
473.15	-627.8	-475.5	-840.1	-840.7	-1053.0	-1052.4	-1265.3	-280.1
493.15	-616.3	-474.1	-831.5	-833.6	-1048.7	-1046.7	-1263.9	-279.4

Table S9. Molar entropy of formation (Δs_f^0) of all the compounds involved in the reaction as a function of temperature, in kJ K^{-1} mol^{-1}.

T (°C)	G	AA	1-MAG	2-MAG	1,2-DAG	1,3-DAG	TAG	W
298.15	-0.641	-0.324	-0.815	-0.810	-0.945	-0.949	-1.079	-0.163
303.15	-0.640	-0.323	-0.814	-0.810	-0.944	-0.949	-1.079	-0.163
313.15	-0.638	-0.323	-0.812	-0.809	-0.944	-0.947	-1.079	-0.162
323.15	-0.635	-0.322	-0.810	-0.807	-0.942	-0.945	-1.078	-0.161
333.15	-0.632	-0.321	-0.807	-0.805	-0.941	-0.943	-1.077	-0.160
343.15	-0.628	-0.320	-0.804	-0.803	-0.940	-0.941	-1.077	-0.159
353.15	-0.623	-0.319	-0.801	-0.800	-0.938	-0.939	-1.076	-0.158

373.15	-0.613	-0.318	-0.793	-0.794	-0.934	-0.933	-1.075	-0.156
393.15	-0.601	-0.315	-0.783	-0.786	-0.930	-0.926	-1.073	-0.155
413.15	-0.586	-0.313	-0.772	-0.778	-0.924	-0.919	-1.071	-0.153
433.15	-0.569	-0.311	-0.759	-0.767	-0.918	-0.910	-1.069	-0.151
453.15	-0.550	-0.308	-0.745	-0.755	-0.911	-0.900	-1.066	-0.150
473.15	-0.529	-0.306	-0.729	-0.742	-0.903	-0.889	-1.063	-0.148
493.15	-0.505	-0.303	-0.711	-0.727	-0.894	-0.877	-1.061	-0.147

Table S10. Molar Gibbs free energy of formation (Δg_f^0) of all the compounds involved in the reaction as a function of temperature, in kJ mol^{-1}.

T (°C)	G	AA	1-MAG	2-MAG	1,2-DAG	1,3-DAG	TAG	W
298.15	-482.5	-386.1	-632.2	-627.0	-788.4	-793.7	-949.9	-237.1
303.15	-479.3	-384.5	-628.1	-622.9	-783.7	-788.9	-944.5	-236.3
313.15	-472.9	-381.3	-620.0	-614.8	-774.3	-779.4	-933.7	-234.7
323.15	-466.5	-378.0	-611.9	-606.7	-764.8	-770.0	-922.0	-233.1
333.15	-460.2	-374.8	-603.8	-598.7	-755.4	-760.5	-912.1	-231.5
343.15	-453.9	-371.6	-595.8	-590.6	-746.0	-751.1	-901.4	-230.0
353.15	-447.6	-368.4	-587.7	-582.6	-736.6	-741.7	-890.6	-228.3
373.15	-435.3	-362.0	-571.8	-566.7	-717.9	-723.0	-869.1	-225.2
393.15	-423.1	-355.7	-556.0	-550.9	-699.2	-704.4	-847.6	-222.0
413.15	-411.2	-349.4	-540.5	-535.2	-680.7	-685.9	-826.1	-219.0
433.15	-399.7	-343.2	-525.2	-519.8	-662.3	-667.6	-804.8	-215.9
453.15	-388.5	-337.0	-510.1	-504.6	-644.0	-649.5	-783.4	-212.9
473.15	-377.7	-330.9	-495.4	-489.6	-625.9	-631.6	-762.1	-209.9
493.15	-367.4	-324.8	-481.0	-474.9	-607.9	-614.0	-740.9	-207.0

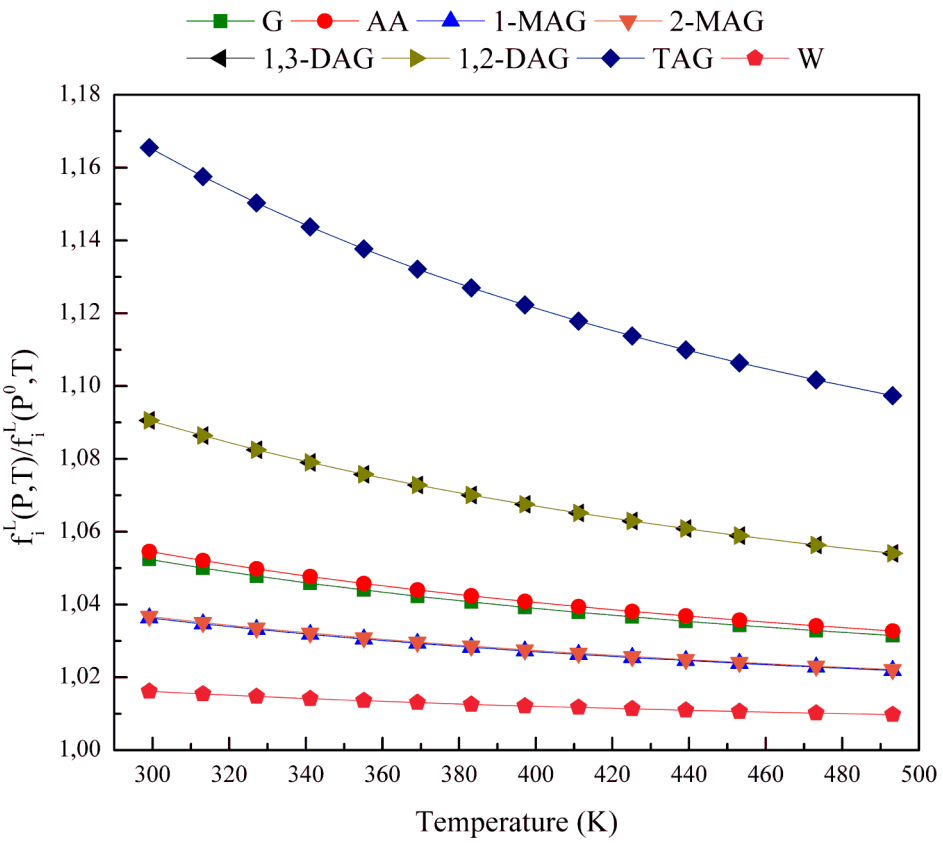

Figure S1. Quotient of $fi^L(P,))/fi^L(P^0,T)$ as function of temperature (350-500 K) for all the chemical species.

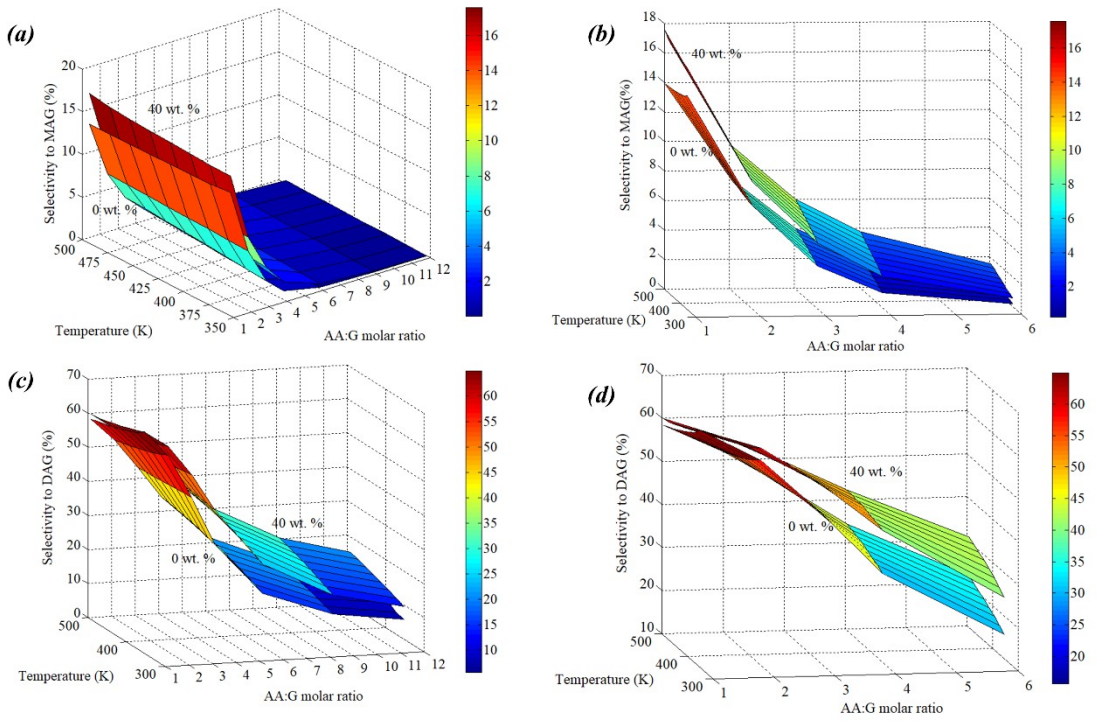

Figure S2. Results of the Gibbs free energy minimization, considering the effect of the water initial content as a function of temperature and AA:G molar ratio. (a) Selectivity to MAG; (b) Selectivity to MAG: enlargement of the AA:G region between 1 and 6. (c) Selectivity to DAG and (d) Selectivity to DAG: enlargement of the AA:G region between 1 and 6. P=2 MPa