Supplementary Materials for:

Article

Crude Glycerol Hydrogenolysis to Bio-Propylene Glycol: Effect of Its Impurities on Activity, Selectivity and Stability

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Supplementary Material S1

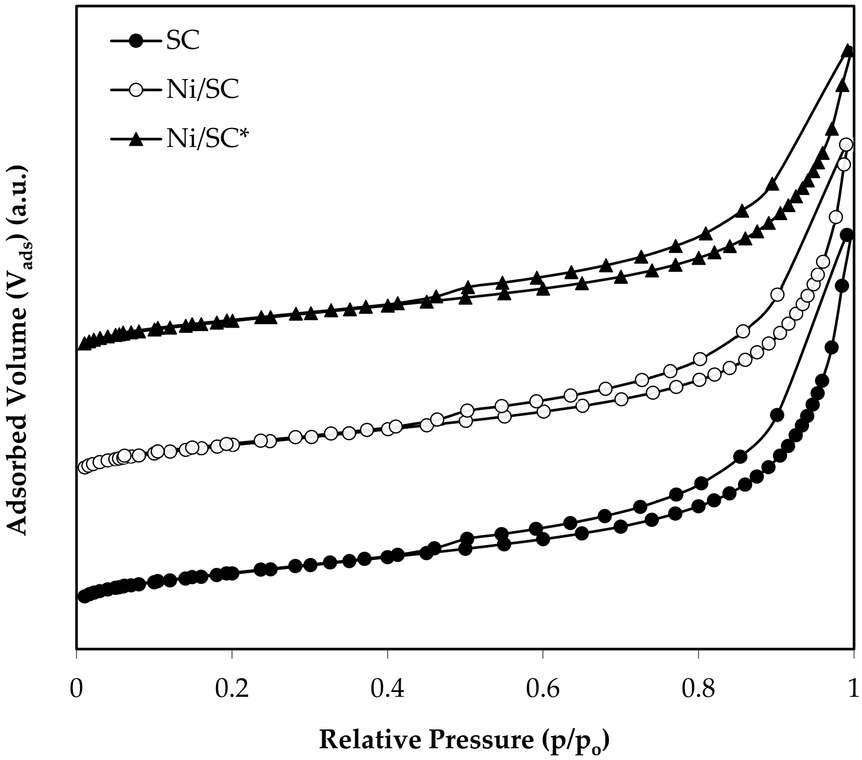


Figure S1. N_2 adsorption-desorption isotherms of SC (●), Ni/SC (○) and Ni/SC* (▲).

Supplementary Material S2

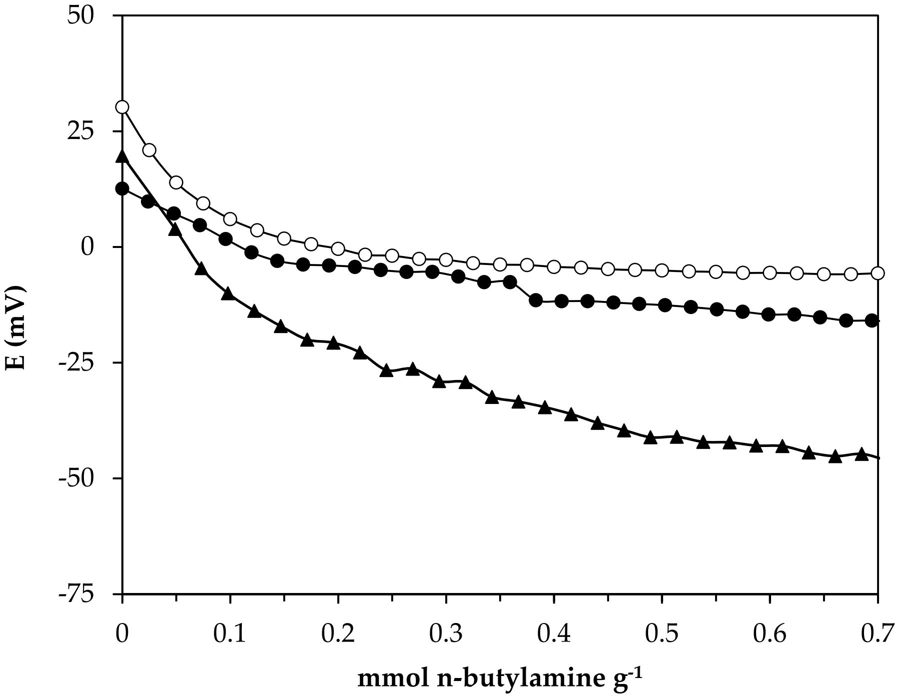


Figure S2. Potentiometric titration curves with n-butylamine in acetonitrile of SC (●), Ni/SC (○) and Ni/SC* (▲).

Supplementary Material S3

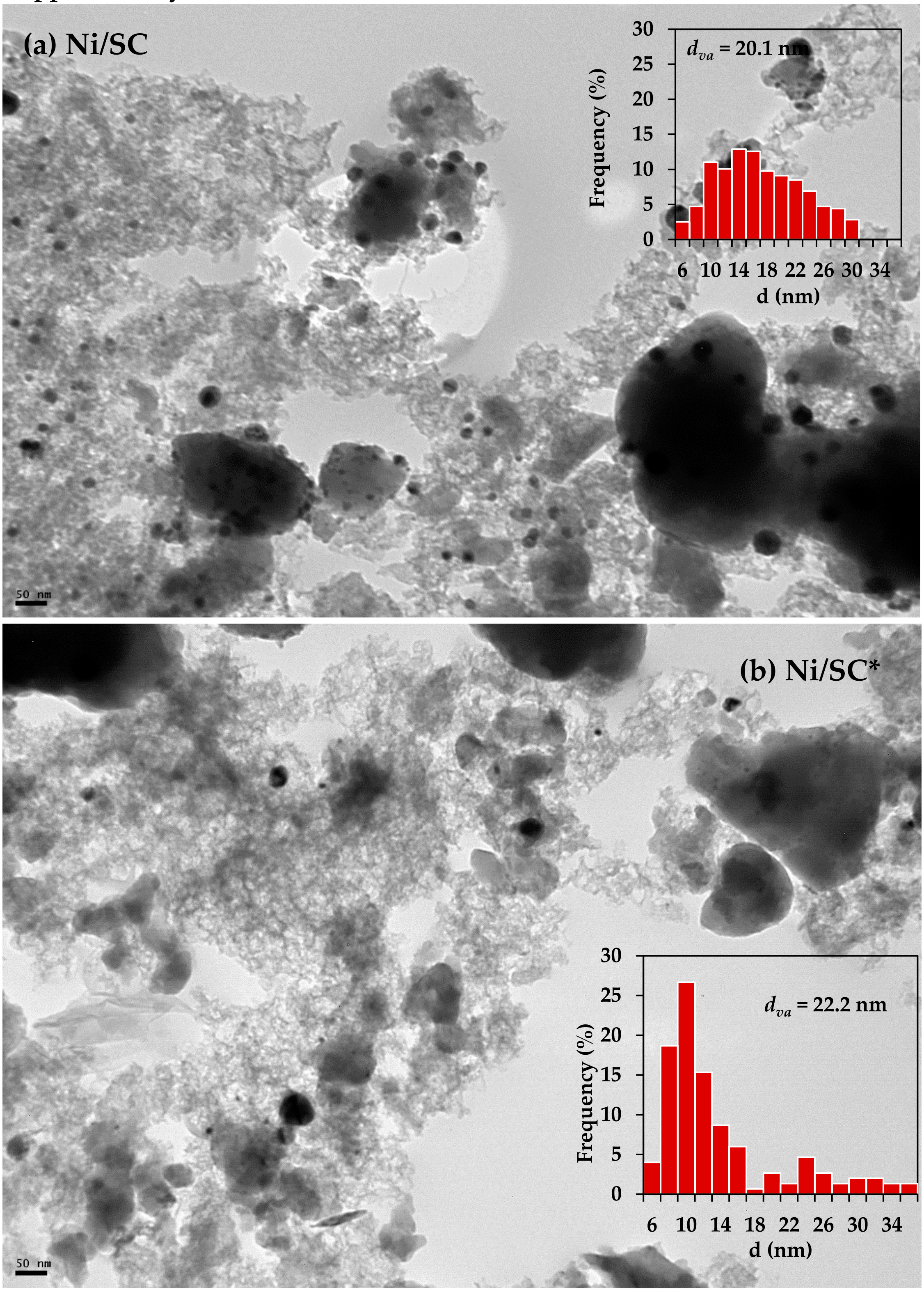


Figure S3. TEM micrographs for the reduced catalysts **(a)** fresh Ni/SC **(b)** used Ni/SC*

Supplementary Material S4

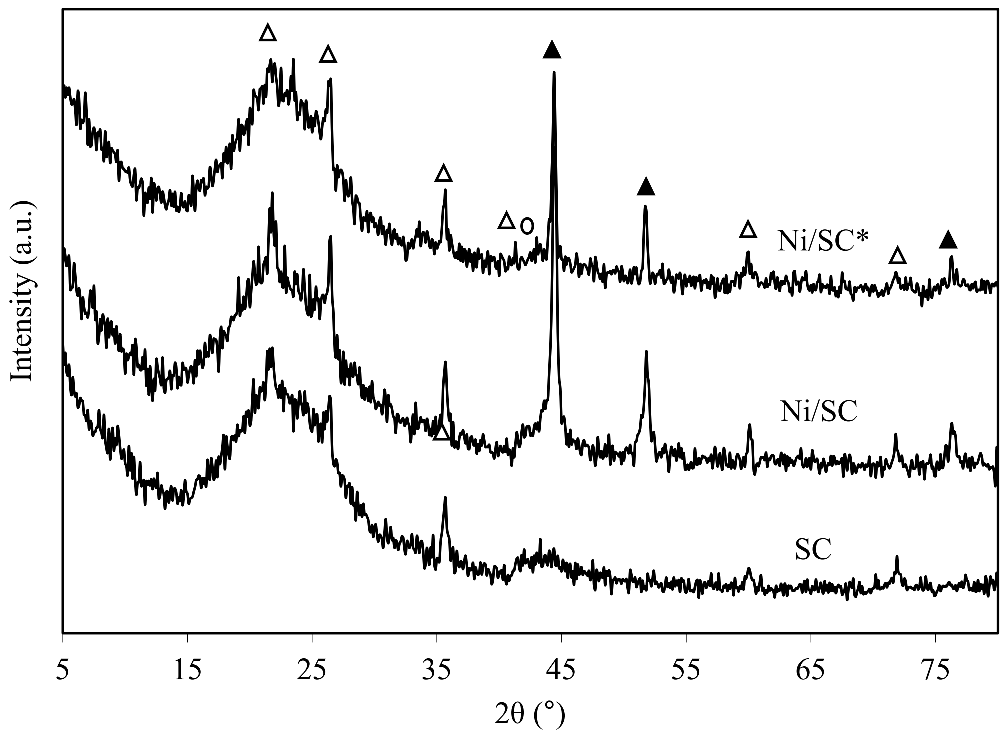


Figure S4. XRD patterns of SC, Ni/SC reduced fresh catalyst and used Ni/SC* catalyst. Symbols are referred to metallic nickel (▲), silicon carbide (Δ) and graphitic carbon (○).

Supplementary Material S5

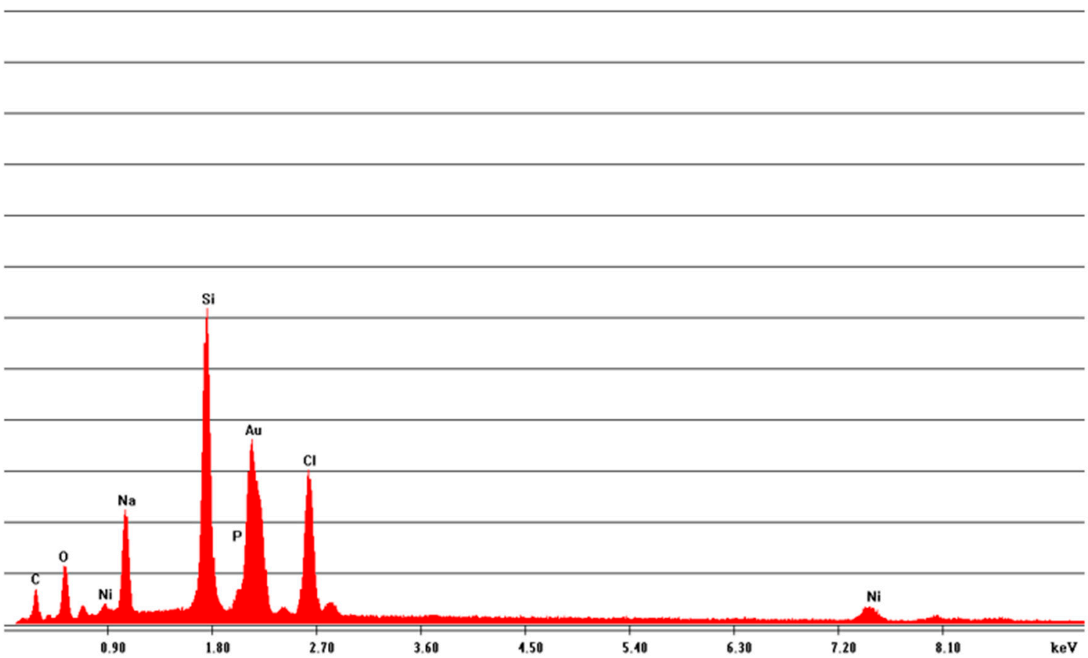


Figure S5. Analysis of elements by SEM-EDAX for the used catalyst after three reaction cycles in the presence of the crude glycerol sample D. Reaction conditions: 30 wt.% aqueous glycerol solution, 260 °C, 2 MPa, 2 h, m_c/m_{gly} = 0.24 (mass ratio).

Supplementary Material S6

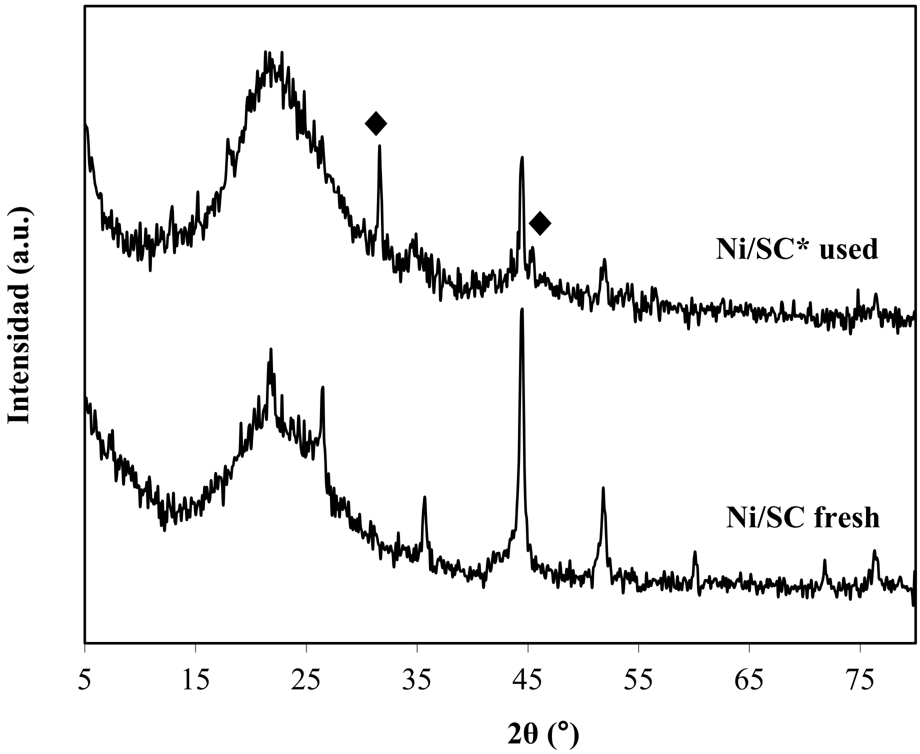


Figure S6. XRD patterns of Ni/SC reduced fresh catalyst and used Ni/SC* catalyst. Symbols are referred to planes (2 0 0) at 31.69° and (2 2 0) at 45.45° of crystalline cubic NaCl (♦) (JCPDS 05-0628).

Supplementary Material S7

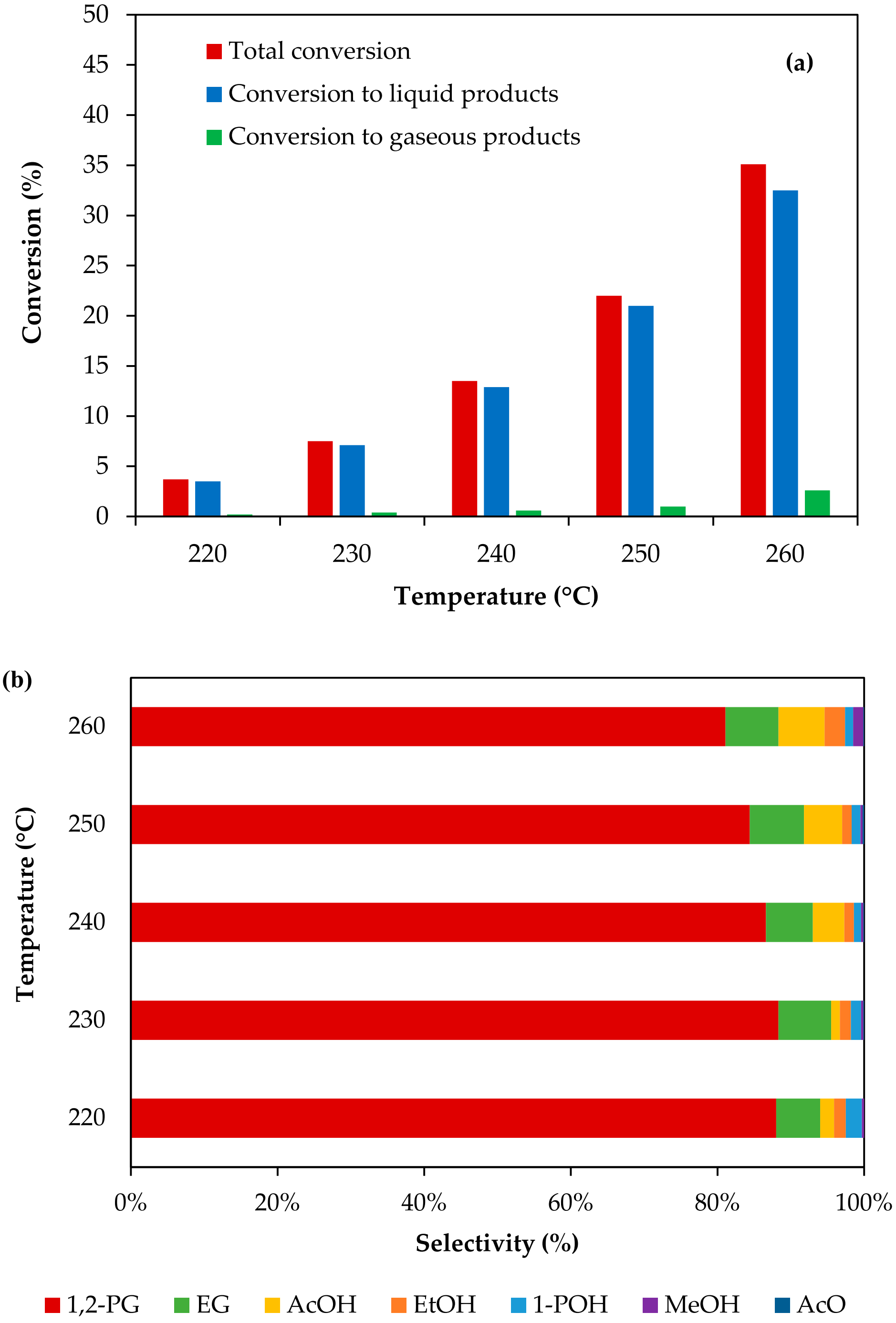


Figure S7. (a) Glycerol conversion vs temperature **(b)** Selectivity to liquid products vs temperature. Reaction conditions: 30 wt.% aqueous glycerol solution, 2 h, 2 MPa H_2, $m_c/m_{gly} = 0.24$ (mass ratio).

Supplementary Material S8

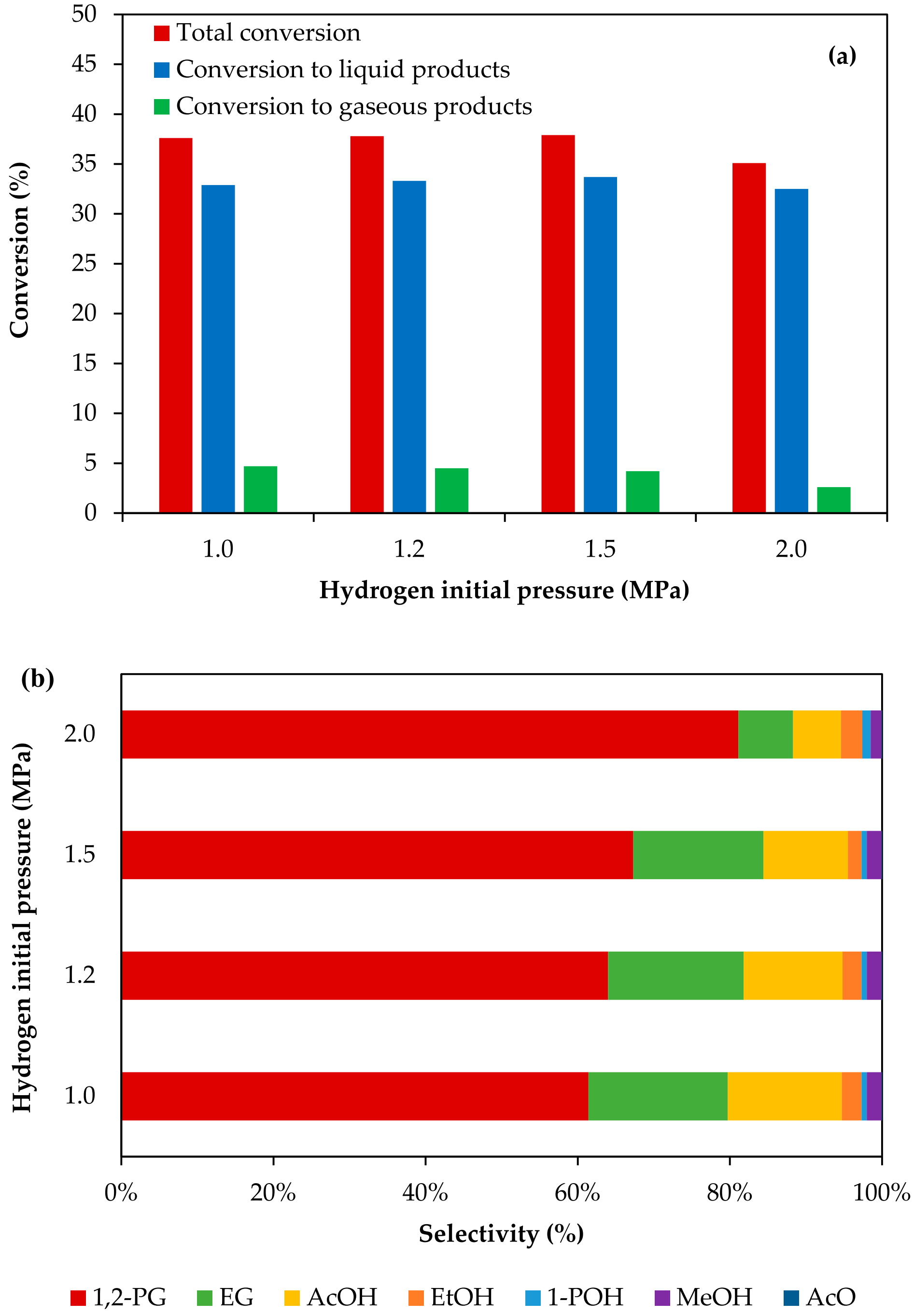


Figure S8. (a) Glycerol conversion vs partial pressure of H_2 **(b)** Selectivity to liquid products vs partial pressure of H_2. Reaction conditions: 30 wt.% aqueous glycerol solution, 260 °C, 2 h, m_c/m_{gly} = 0.24 (mass ratio).

Supplementary Material S9

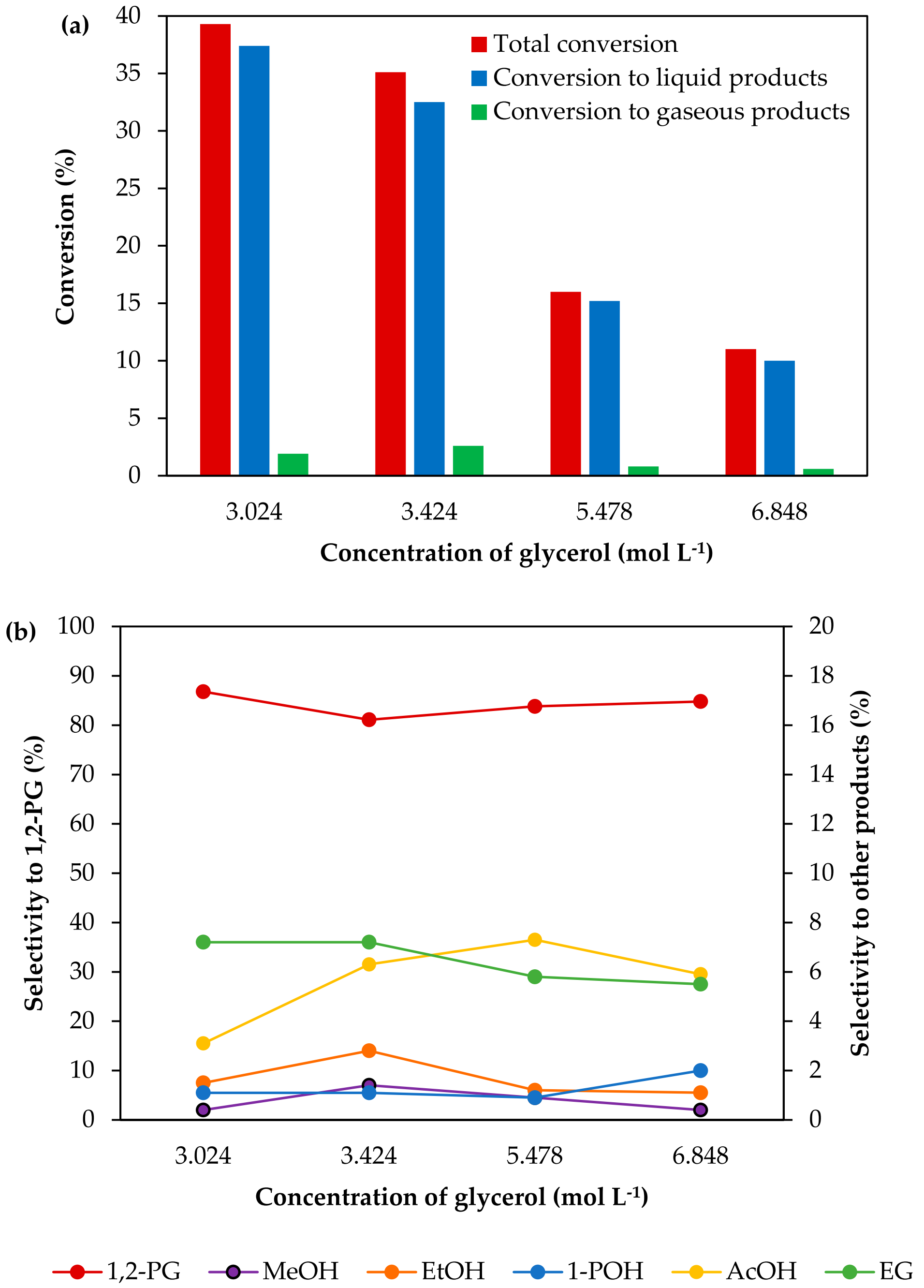
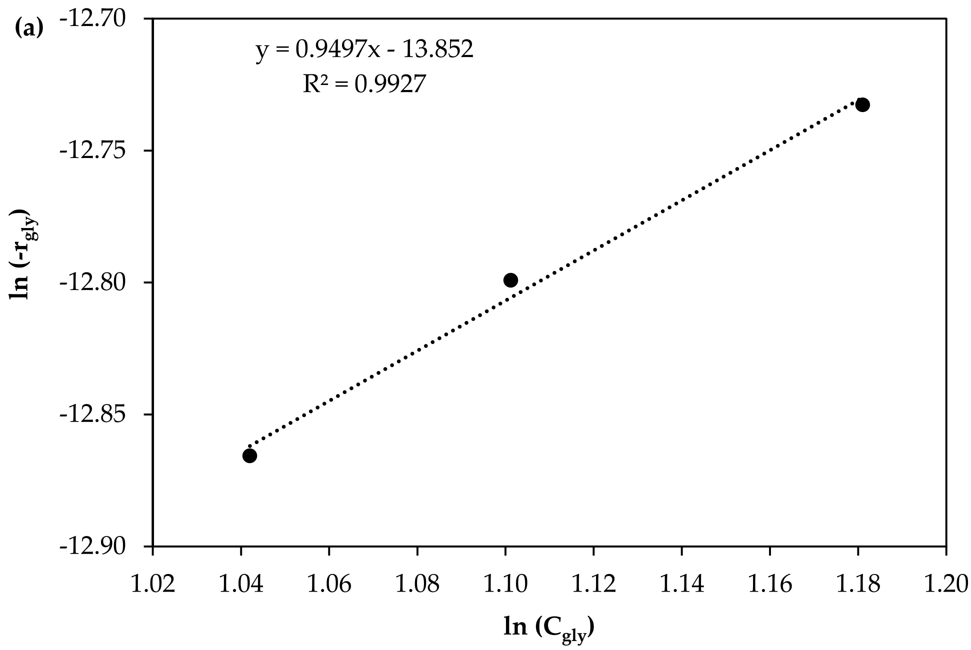
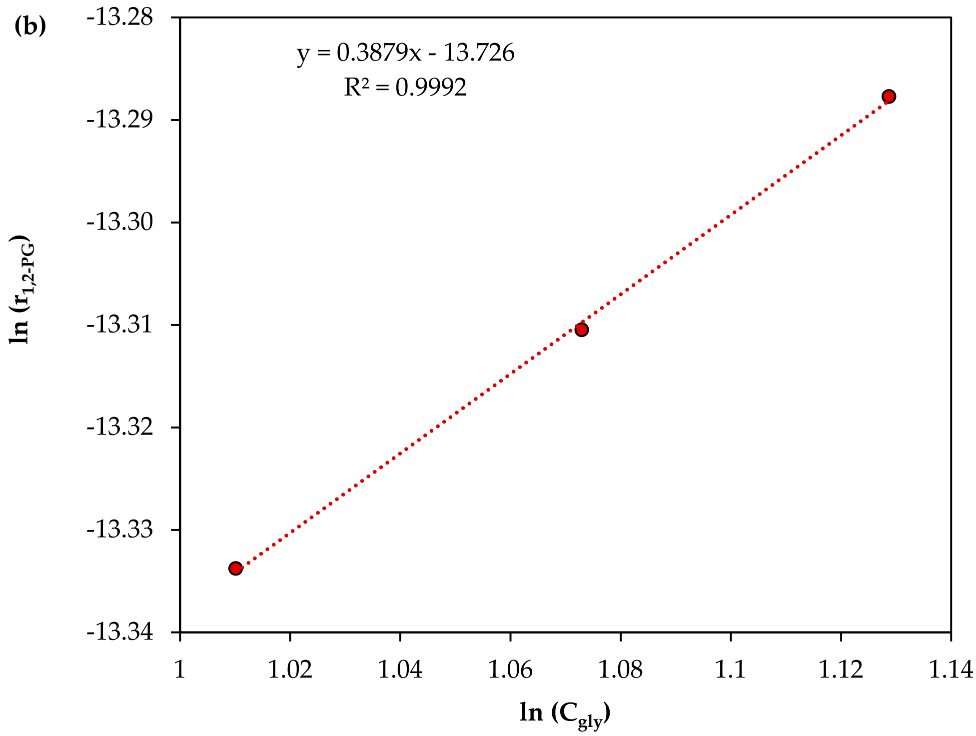
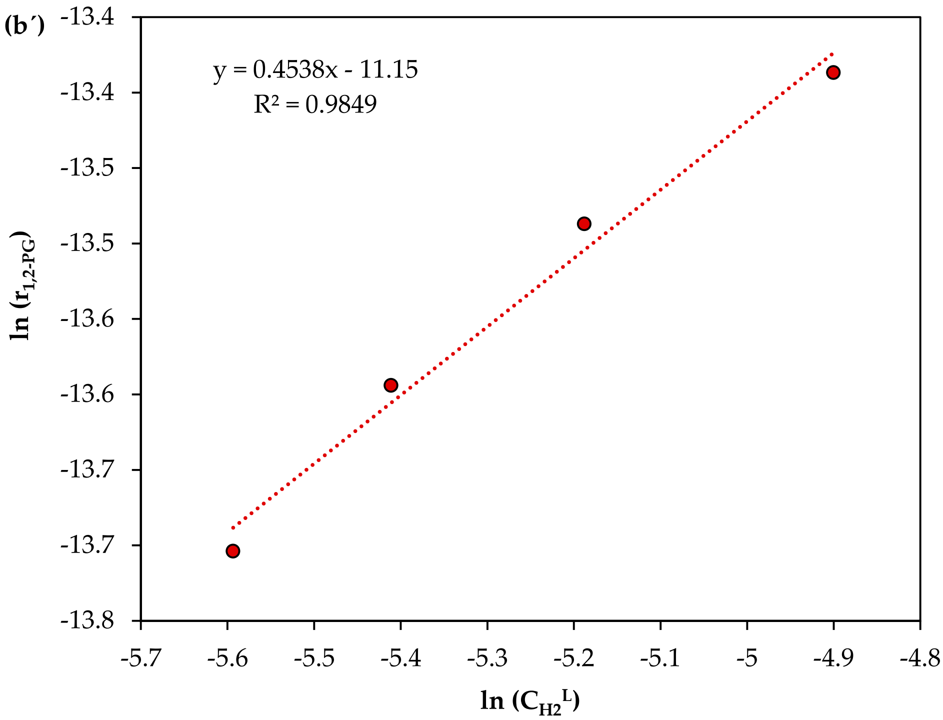


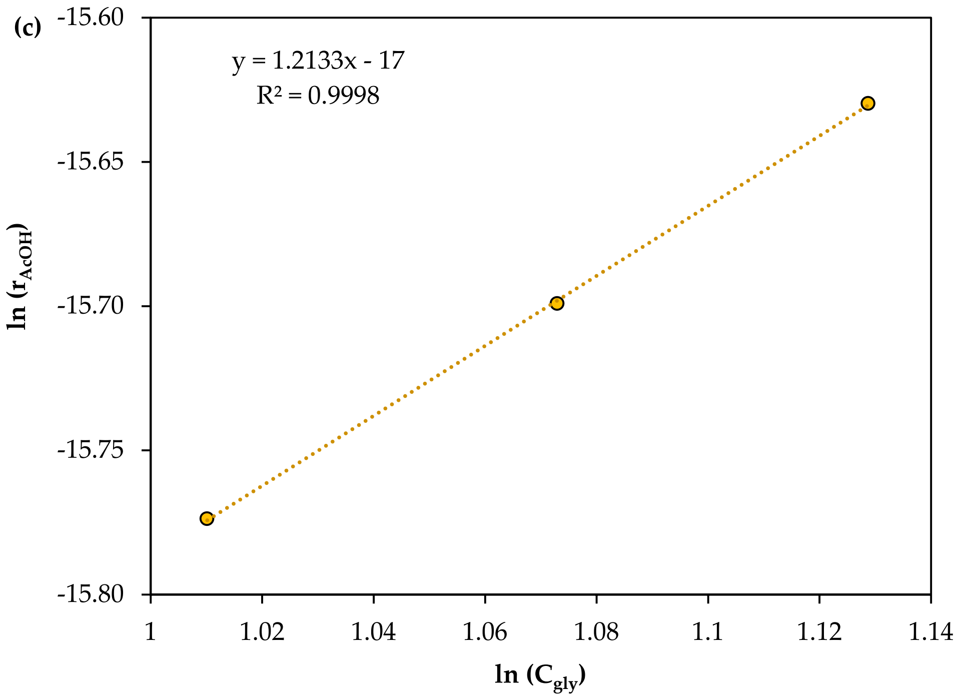
Figure S9. (a) Glycerol conversion vs glycerol initial concentration **(b)** Selectivity to liquid products vs initial glycerol concentration. Reaction conditions: 30-80 wt.% aqueous glycerol solutions, 260 °C, 2 MPa de H_2, 2 h, m_c/m_{gly} = 0.08-0.24 (mass ratio).

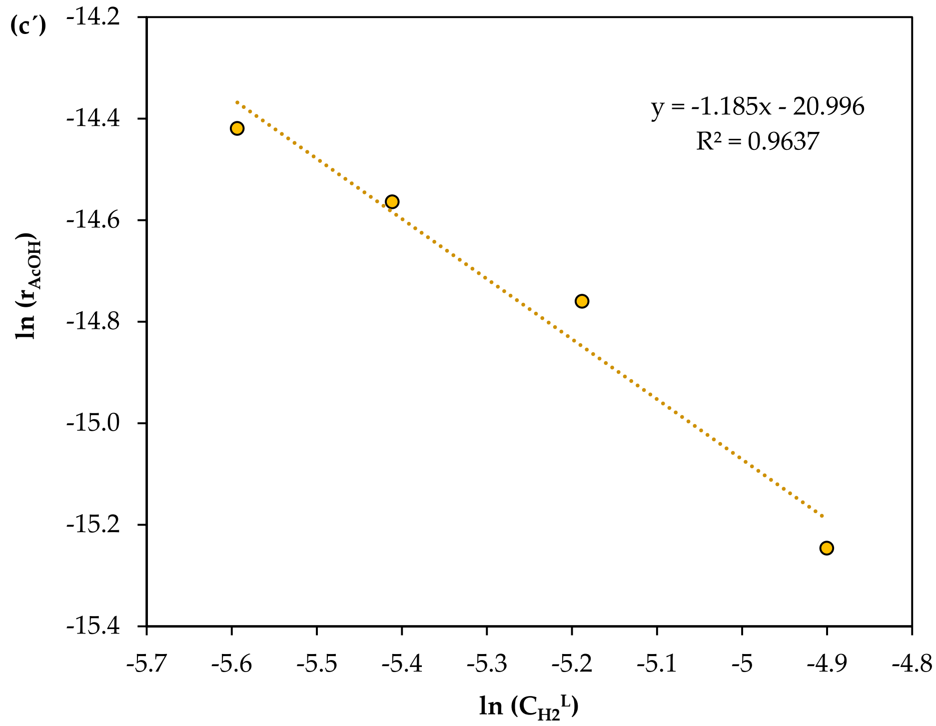
Supplementary Material S10

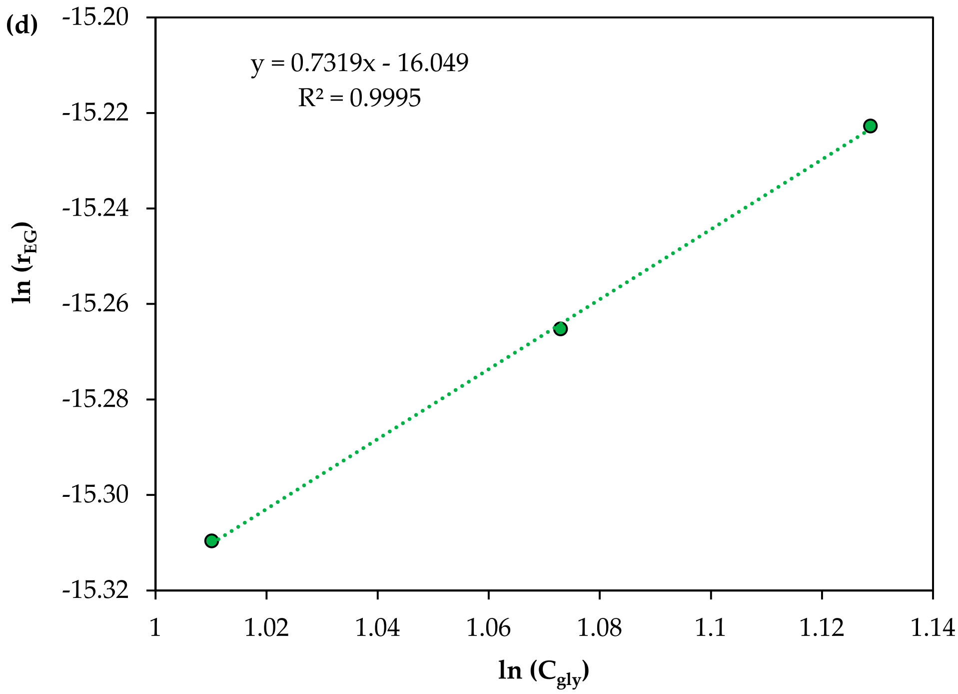




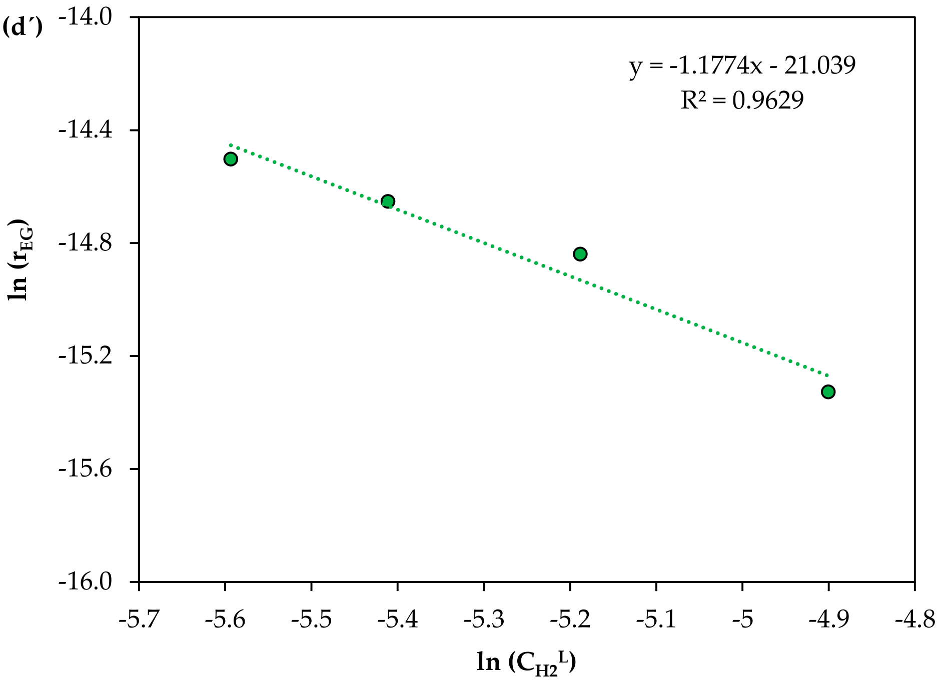

(b´)
y = 0.4538x - 11.15
R² = 0.9849
-13.4
-13.4
-13.5
-13.5
-13.6
-13.6
-13.7
-13.7
-13.8
ln (r1,2-PG)
-5.7
-5.6
-5.5
-5.4
-5.3
-5.2
-5.1
-5
-4.9
-4.8
ln (CH2L)


(c)
y = 1.2133x - 17
R² = 0.9998
-15.60
-15.65
-15.70
-15.75
-15.80
ln (rAcOH)
1
1.02
1.04
1.06
1.08
1.1
1.12
1.14
ln (Cgly)

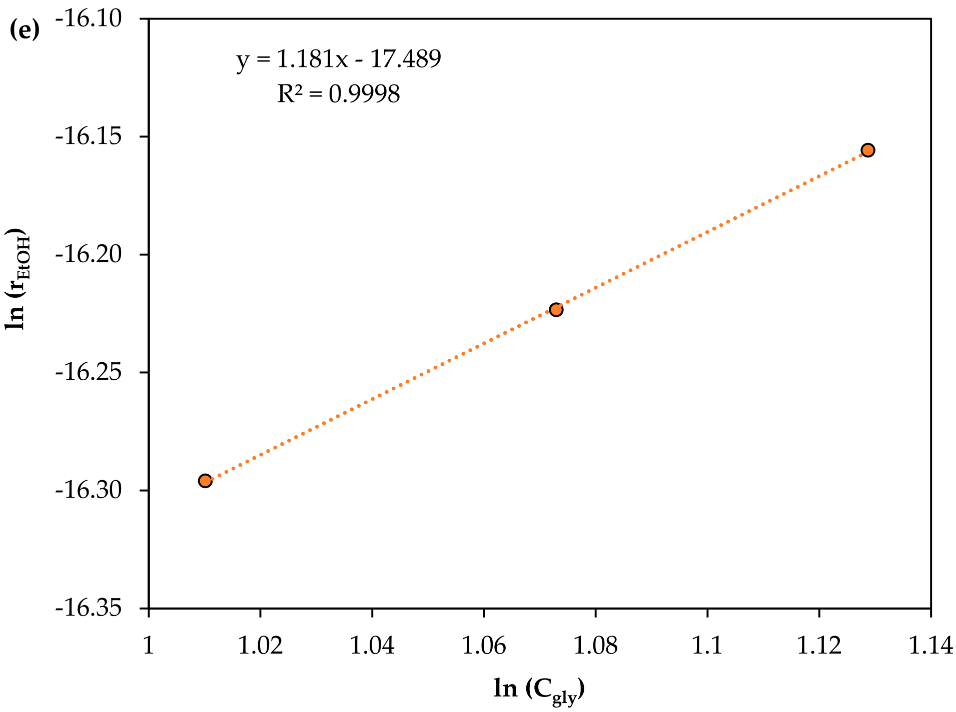

(c′)
y = -1.185x - 20.996
R² = 0.9637
ln (r_AcOH)
ln (C_H2^L)
-14.2
-14.4
-14.6
-14.8
-15.0
-15.2
-15.4
-5.7
-5.6
-5.5
-5.4
-5.3
-5.2
-5.1
-5
-4.9
-4.8

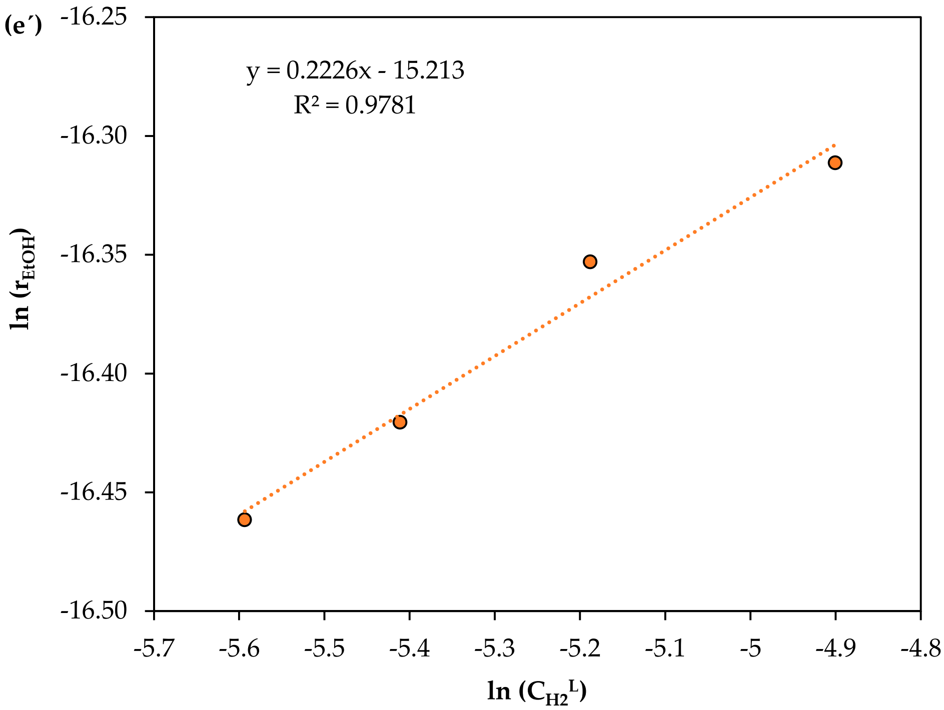

(d)
y = 0.7319x - 16.049
R² = 0.9995
ln (r_EG)
ln (C_gly)
-15.20
-15.22
-15.24
-15.26
-15.28
-15.30
-15.32
1
1.02
1.04
1.06
1.08
1.1
1.12
1.14

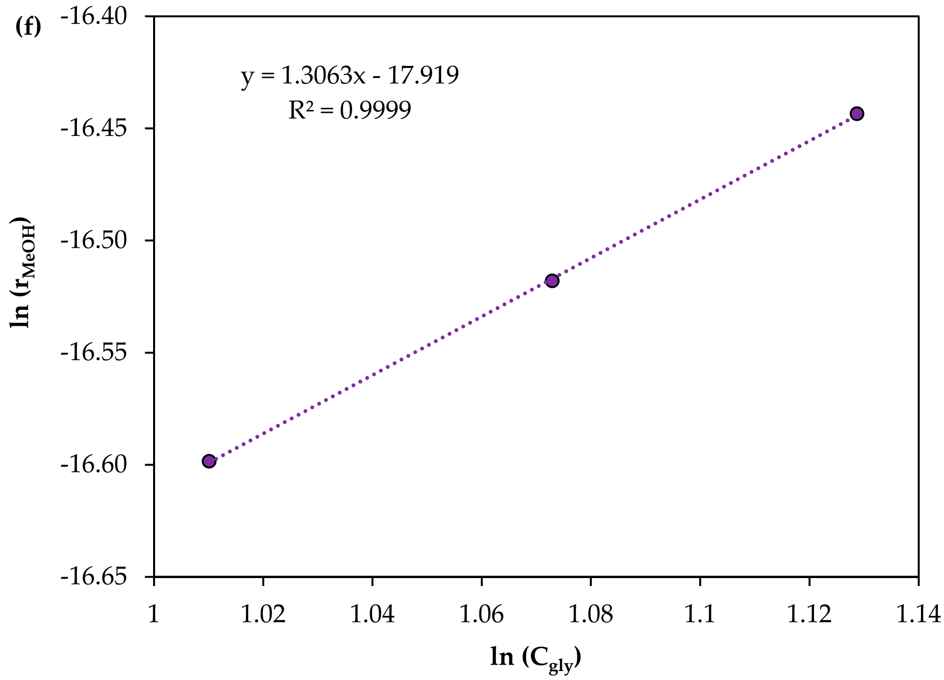
(d′)

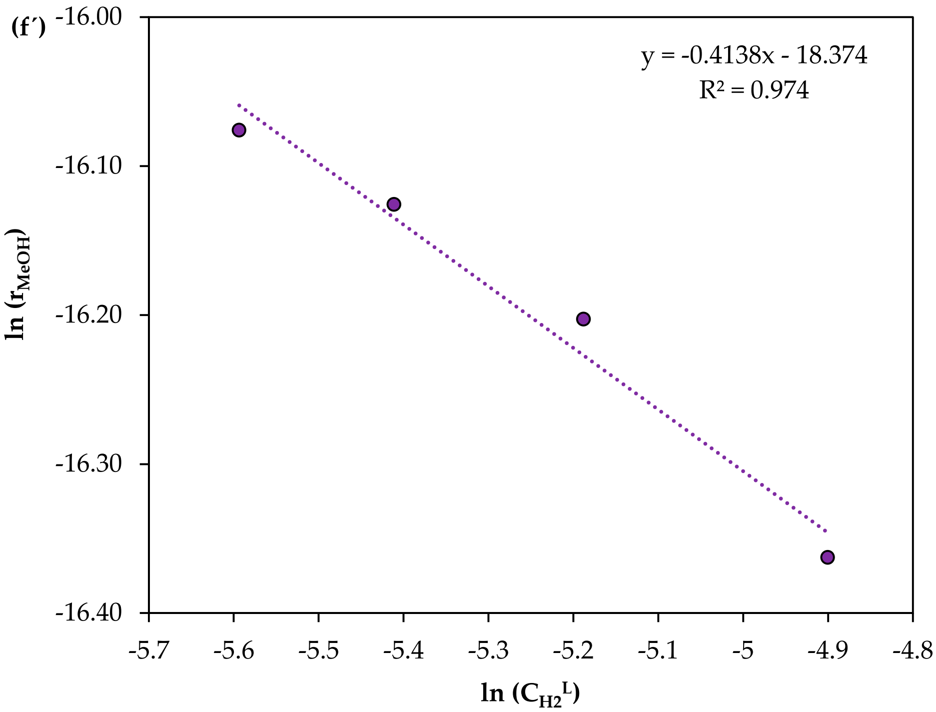

-14.0
-14.4
-14.8
-15.2
-15.6
-16.0
y = -1.1774x - 21.039
R² = 0.9629
ln (r_EG)
-5.7
-5.6
-5.5
-5.4
-5.3
-5.2
-5.1
-5
-4.9
-4.8
ln (C_H2^L)

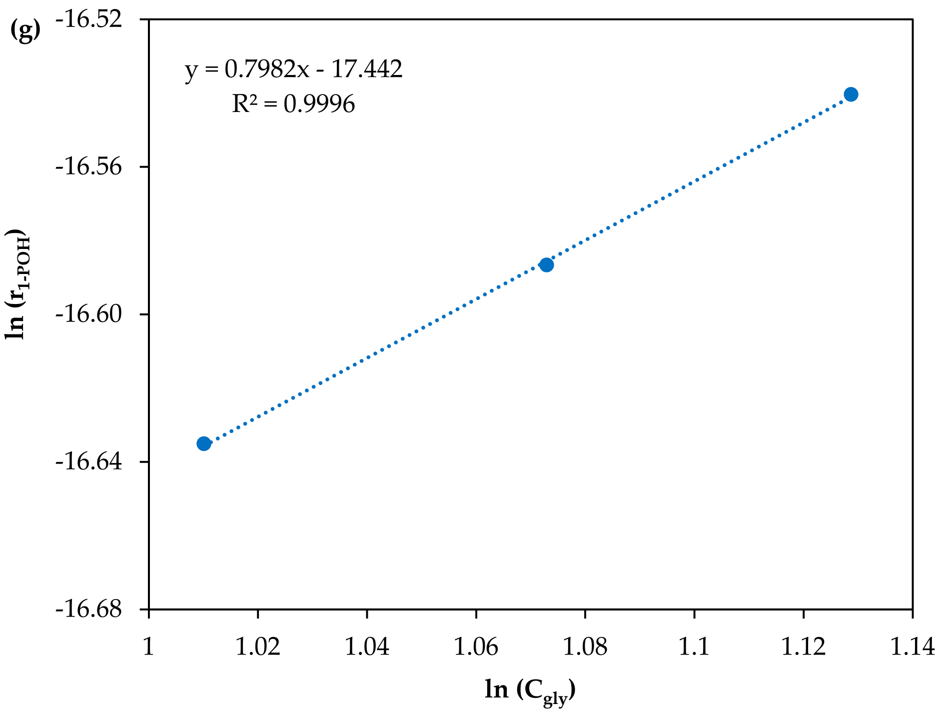
(e)


-16.10
-16.15
-16.20
-16.25
-16.30
-16.35
y = 1.181x - 17.489
R² = 0.9998
ln (r_EtOH)
1
1.02
1.04
1.06
1.08
1.1
1.12
1.14
ln (C_gly)


(e´)
y = 0.2226x - 15.213
R² = 0.9781
-16.25
-16.30
-16.35
-16.40
-16.45
-16.50
ln (r_{EtOH})
-5.7
-5.6
-5.5
-5.4
-5.3
-5.2
-5.1
-5
-4.9
-4.8
ln (C_{H2}^{L})


(f)
y = 1.3063x - 17.919
R² = 0.9999
-16.40
-16.45
-16.50
-16.55
-16.60
-16.65
ln (r_{MeOH})
1
1.02
1.04
1.06
1.08
1.1
1.12
1.14
ln (C_{gly})


(f′)
y = -0.4138x - 18.374
R^2 = 0.974
-16.00
-16.10
-16.20
-16.30
-16.40
ln (r_{MeOH})
-5.7
-5.6
-5.5
-5.4
-5.3
-5.2
-5.1
-5
-4.9
-4.8
ln (C_{H2}^{L})


(g)
y = 0.7982x - 17.442
R^2 = 0.9996
-16.52
-16.56
-16.60
-16.64
-16.68
ln ($r_{1\text{-}POH}$)
1
1.02
1.04
1.06
1.08
1.1
1.12
1.14
ln (C_{gly})

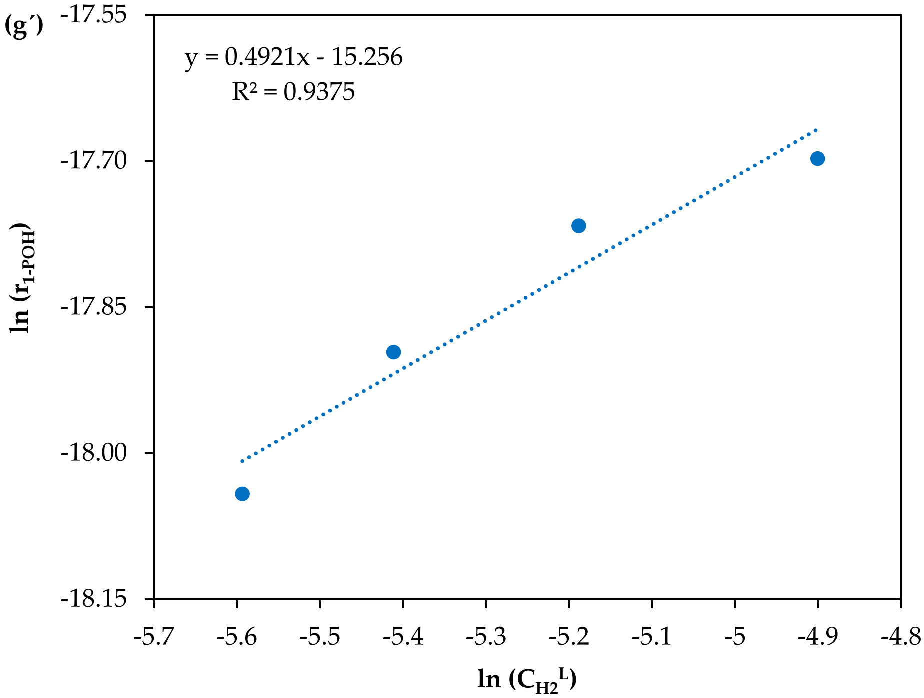
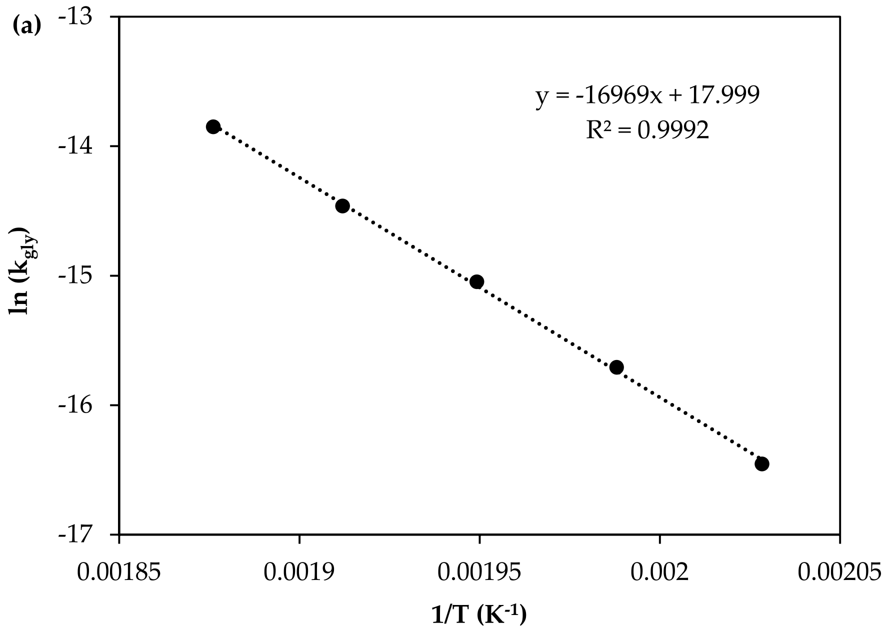
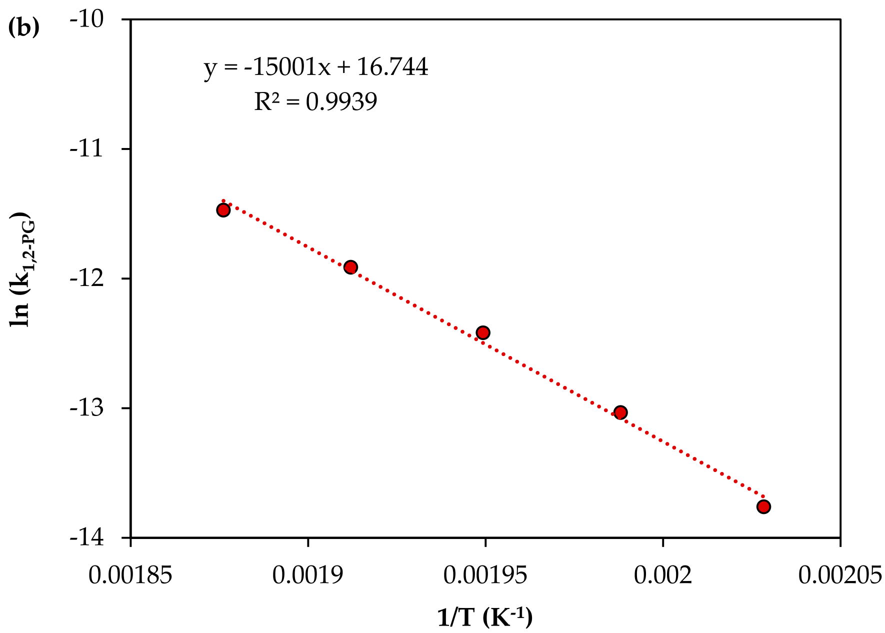


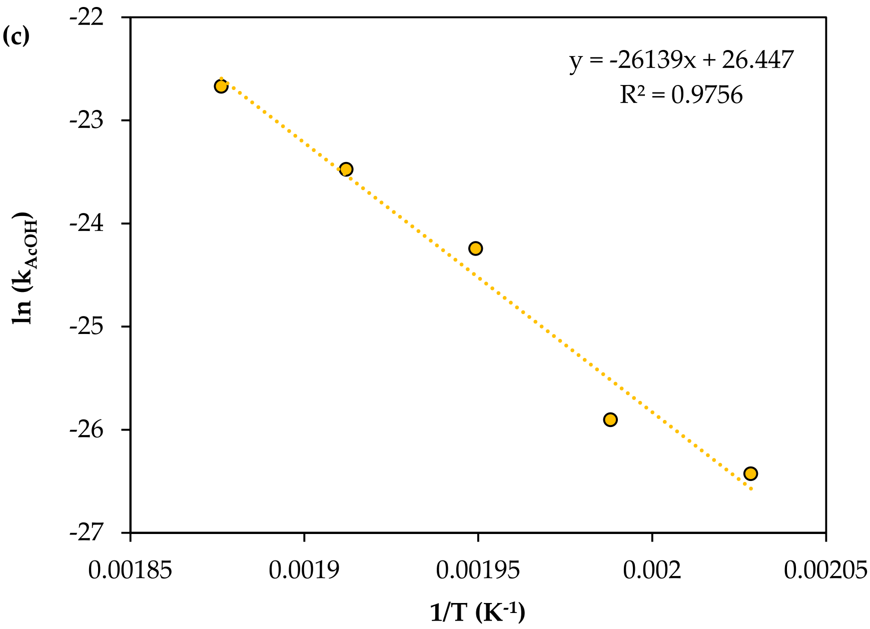
Figure S10. Fitting of experimental data by linear regression to obtain the reaction orders with respect to glycerol and hydrogen for **(a)** Gly **(b, b′)** 1,2-PG **(c, c′)** AcOH **(d, d′)** EG **(e, e′)** MeOH **(f, f′)** EtOH **(g, g′)** 1-POH. Reaction conditions: 30 wt.% aqueous glycerol solution, 260 °C, 1-2 MPa H_2, 0.5-1 h, m_c/m_{gly} = 0.24 (mass ratio).

Supplementary Material S11



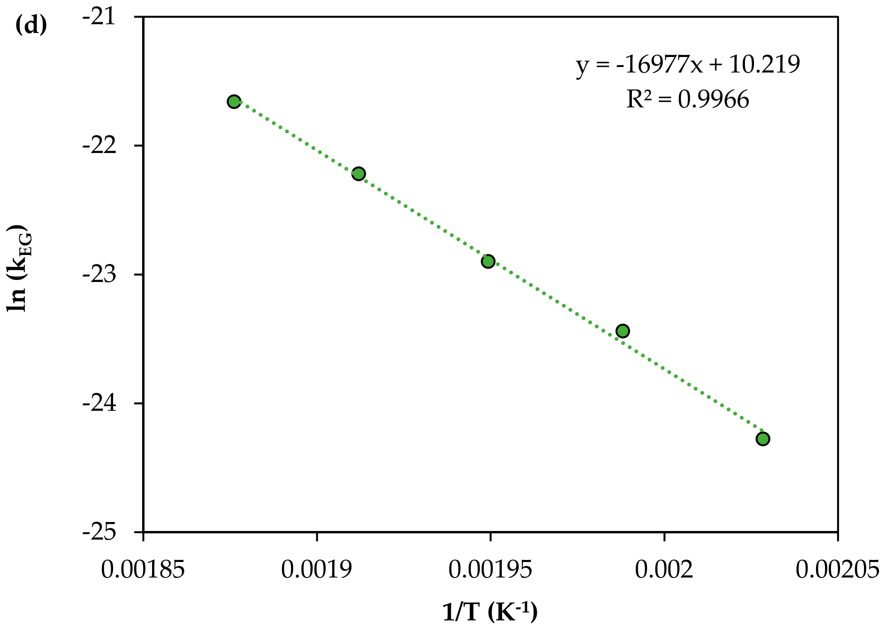


(c)



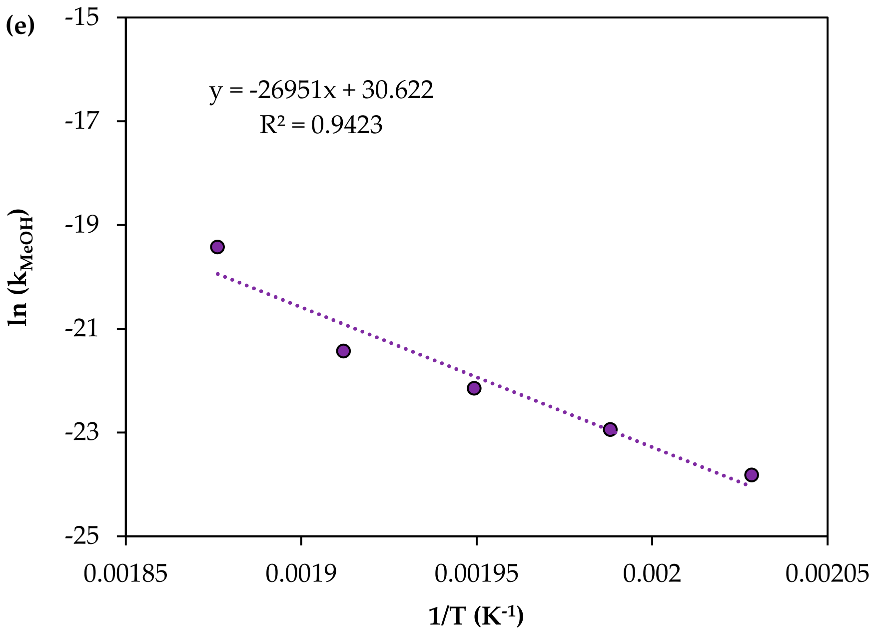
-22
-23
-24
-25
-26
-27
y = -26139x + 26.447
R² = 0.9756
ln (k_AcOH)
0.00185
0.0019
0.00195
0.002
0.00205
1/T (K-1)

(d)

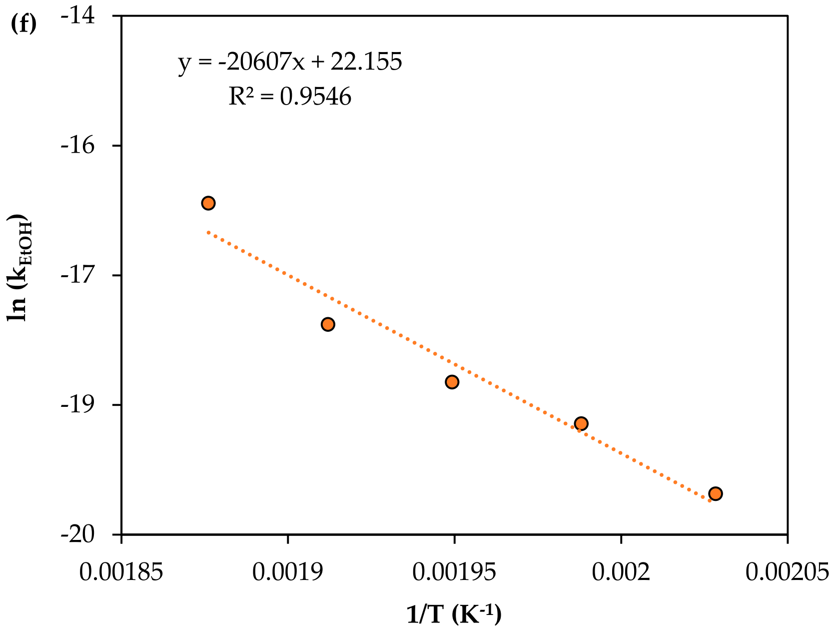


-21
-22
-23
-24
-25
y = -16977x + 10.219
R² = 0.9966
ln (k_EG)
0.00185
0.0019
0.00195
0.002
0.00205
1/T (K-1)

(e)


-15
-17
-19
-21
-23
-25
y = -26951x + 30.622
R² = 0.9423
ln (kMeOH)
0.00185
0.0019
0.00195
0.002
0.00205
1/T (K-1)

(f)


-14
-16
-17
-19
-20
y = -20607x + 22.155
R² = 0.9546
ln (kEtOH)
0.00185
0.0019
0.00195
0.002
0.00205
1/T (K-1)

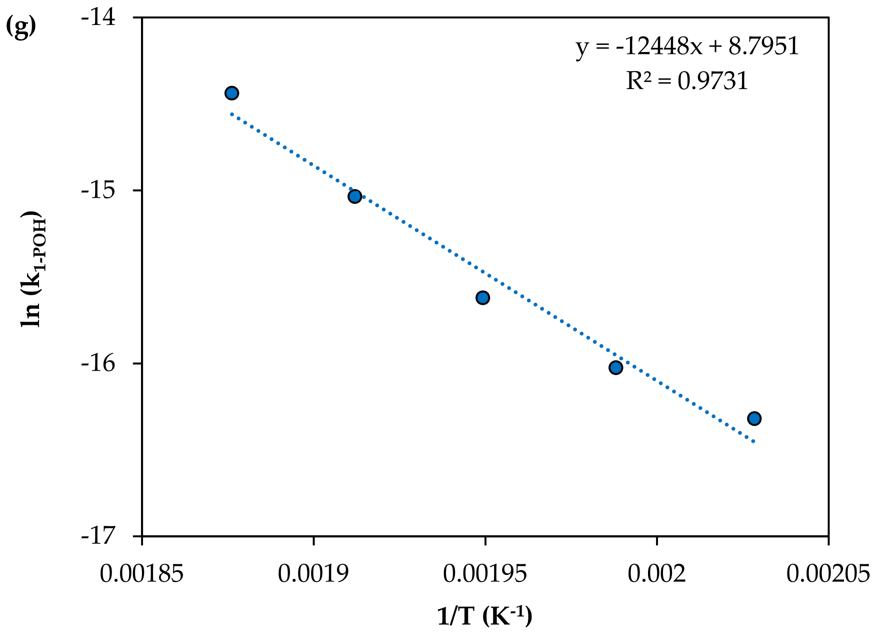
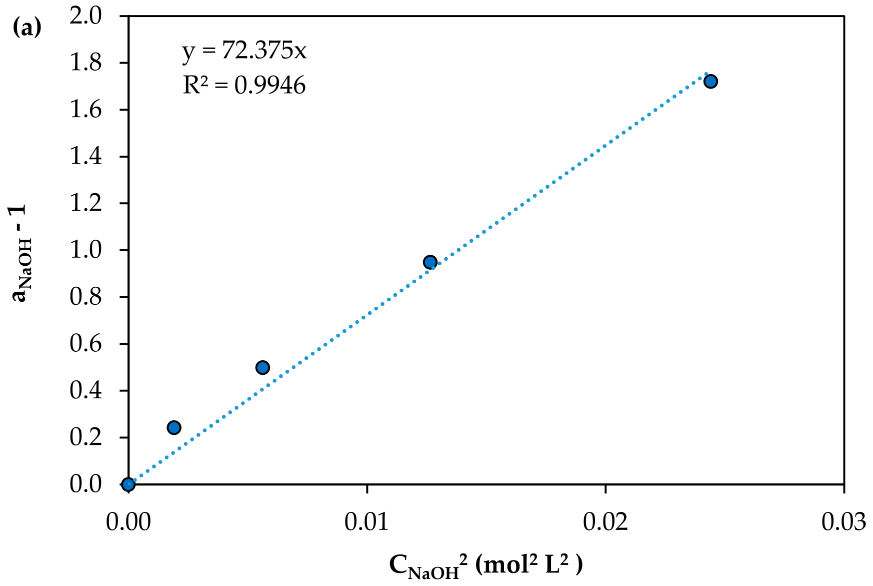
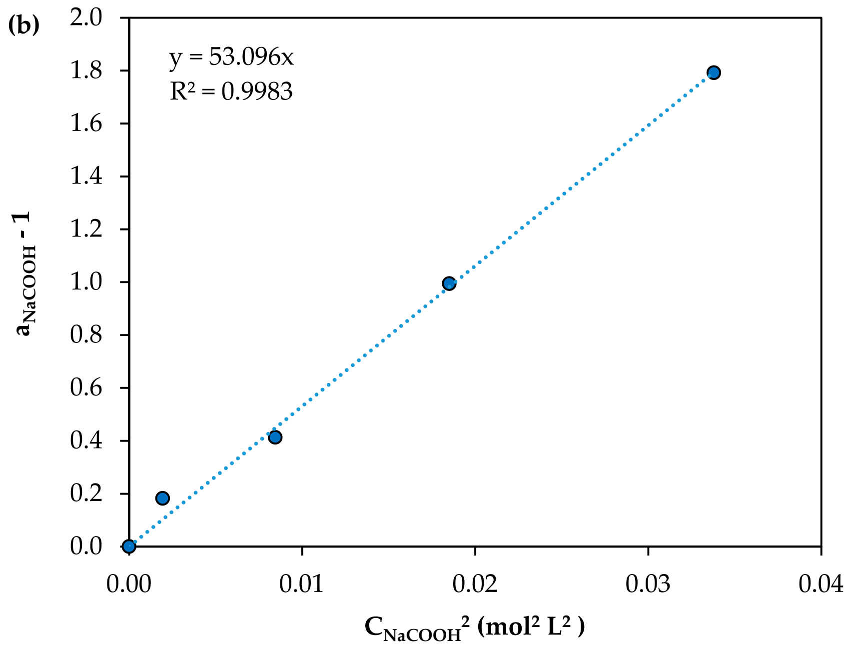
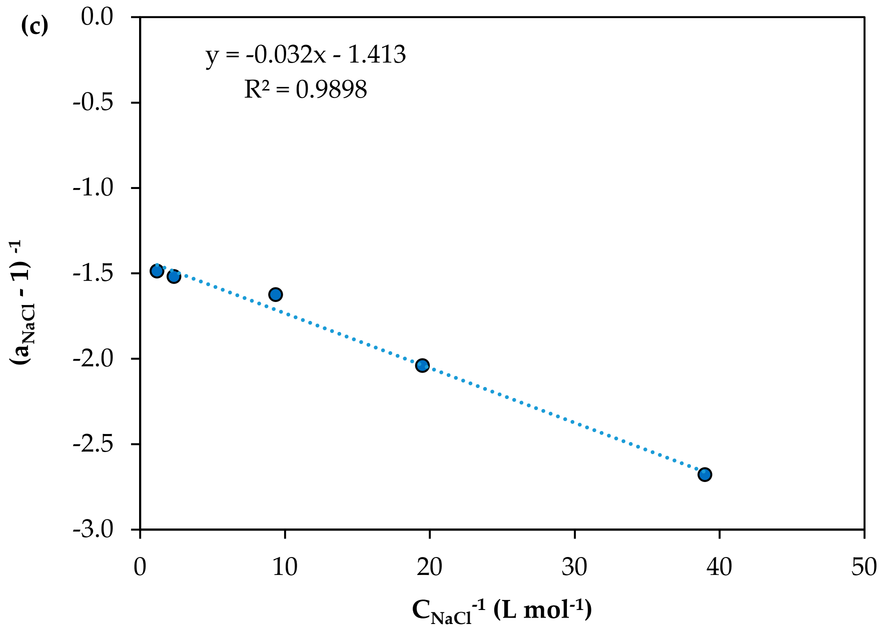


Figure S11. Fitting of experimental data by linear regression to obtain ln (k_{oj}) y Ea_j **(a)** Gly **(b)** 1,2-PG **(c)** AcOH **(d)** EG **(e)** MeOH **(f)** EtOH **(g)** 1-POH. Reaction conditions: 30 wt.% aqueous glycerol solution, 220-260 °C, 2 MPa H_2, 2 h, m_c/m_{gly} = 0.24 (mass ratio).

Supplementary Material S12







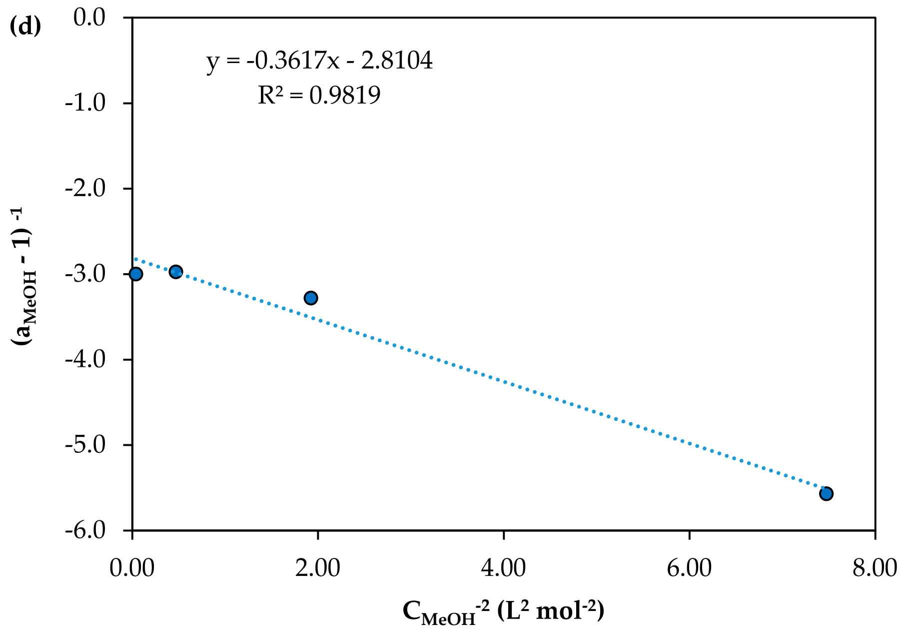


Figure S12. Fitting of experimental data by linear regression to obtain the individual activity factors (a_i) for **(a)** NaOH **(b)** NaCOOH **(c)** NaCl **(d)** MeOH. Reaction conditions: 30 wt.% aqueous glycerol solution, 260 °C, 2 MPa H_2, 2 h, m_c/m_{gly} = 0.24 (mass ratio).