Electronic Supplementary Material (ESI) for Green Chemistry.

Elucidation of Reaction Network and Kinetics between Cellulose-Derived 1,2-Propanediol and Methanol for One-Pot Biofuel Production

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SUPPLEMENTARY INFORMATION

Number of pages: 7

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Table S1. Catalyst characterization information for 20 wt% $CuMgAlO_x$ from ICP-AES[a], N_2 physisorption[b], NH_3 TPD[c], CO_2 TPD[d], and N_2O pulse chemisorption[e]. Synthesis and characterization details are described in previous work.[1, 2]

Property	Value
[a]Cu/Mg/Al ratio (mol basis)	3.5/12/5.1
[b]BET surface area (m^2 g^{-1})	173.7
[c]Acid site density (mmol g^{-1})	0.14
[d]Base site density (mmol g^{-1})	6.2
[e]Cu^0 density (mmol g^{-1})	0.40
[a,e]Cu^0 Dispersion (%)	16.2

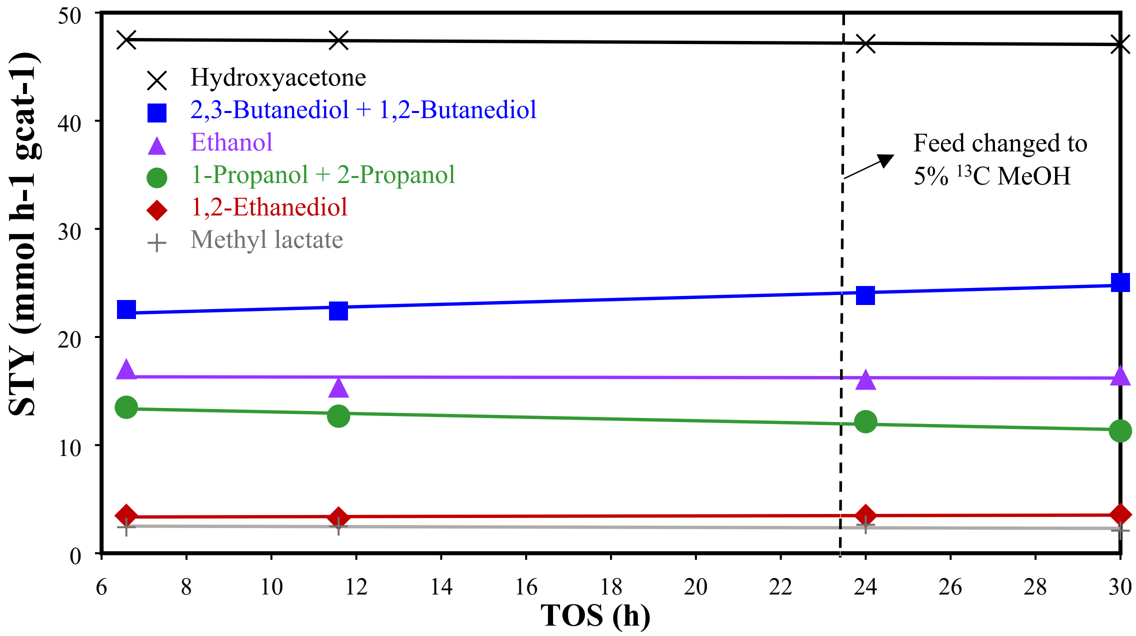

Figure S1. Product STY as a function of TOS for catalytic conversion of 1,2-PDO and MeOH during isotopic ^{13}C MeOH study from GC-FID. Reaction conditions: 300 °C, 1000 psig, 40 h^{-1} WHSV, 24 mg $CuMgAlO_x$, 0.1 mL/min feed with 10 mol% 1,2-PDO in MeOH, 102.5 mL/min H_2, 30 h. After 24 h, 5% of MeOH was replaced with ^{13}C MeOH.

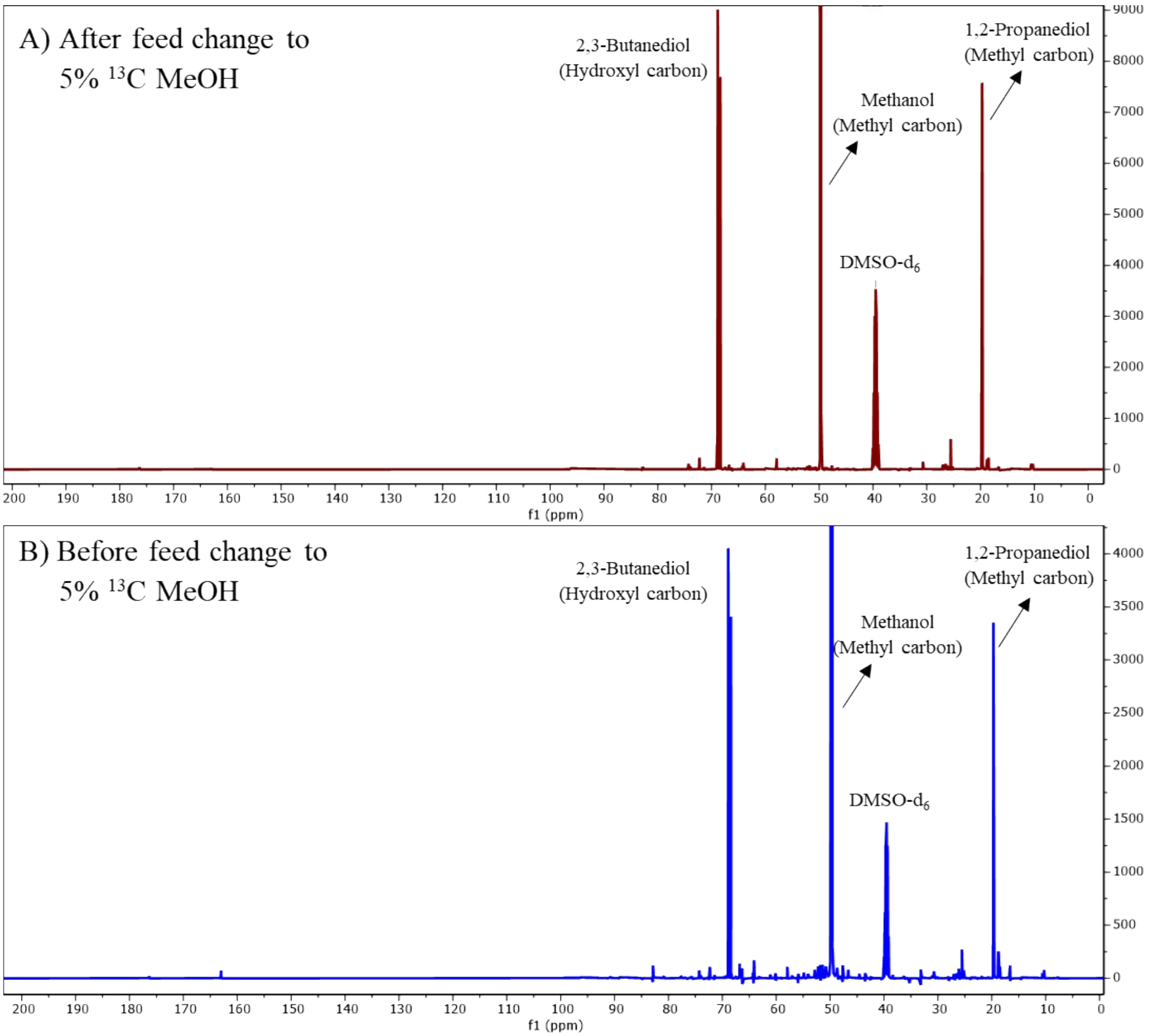

Figure S2. Quantitative ^{13}C NMR spectra for sample: A) after 5% of feed MeOH was replaced with ^{13}C MeOH; and B) before feed switch (natural abundance of ^{13}C). Reaction conditions: 300 °C, 1000 psig, 40 h^{-1} WHSV, 24 mg $CuMgAlO_x$, 0.1 mL/min feed with 10 mol% 1,2-PDO in MeOH, 102.5 mL/min H_2, 30 h, feed switched to 5% ^{13}C MeOH after 24 h.

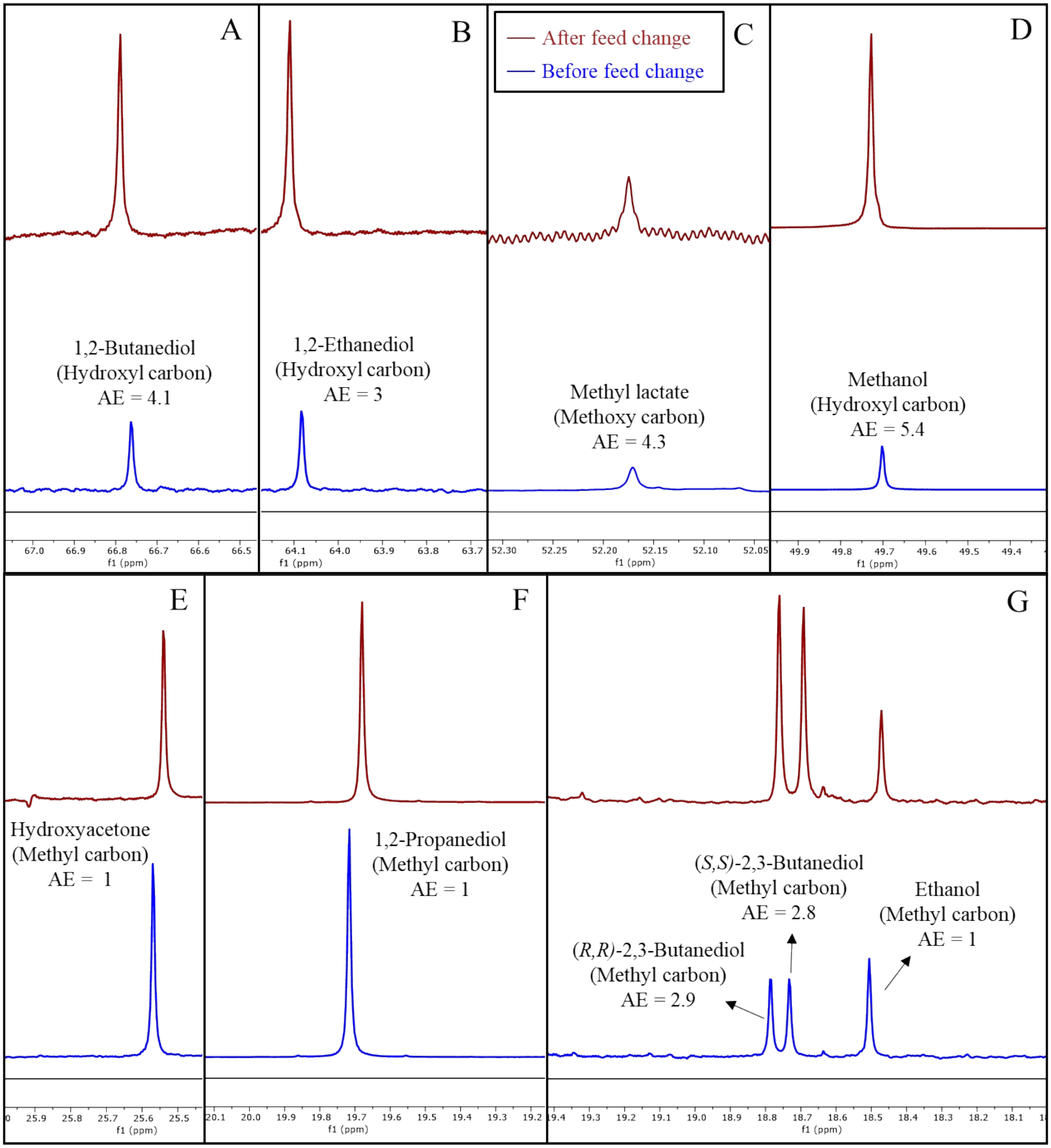

Figure S3. Quantitative ^{13}C NMR spectrum from isotopic ^{13}C MeOH study with Area Enhancement (AE) for: A) 1,2-Butanediol; B) 1,2-Ethanediol; C) Methyl lactate; D) Methanol; E) Hydroxyacetone; F) 1,2-Propanediol; G) 2,3-Butanediol and Ethanol. Reaction conditions: 300 °C, 1000 psig, 40 h^{-1} WHSV, 24 mg CuMgAlO$_x$, 0.1 mL/min feed with 10 mol% 1,2-PDO in MeOH, 102.5 mL/min H_2, 30 h, feed switched to 5% ^{13}C MeOH after 24 h.

Table S2. Enthalpy, Gibbs free energy, and entropy of dehydrogenation, esterification, C-C coupling, C-O scission, direct C-C scission, and retro aldol condensation reactions at 300 °C and 1000 psig from Aspen Plus.

Reactions	**ΔH (kJ/mol)**	**ΔG (kJ/mol)**	**ΔS (J/mol K)**
Dehydrogenation			
1,2-Propanediol → Hydroxyacetone + H_2	-1.1	-23.3	-14.2
Esterification			
1,2-Propanediol + Methanol → Methyl lactate + $2H_2$	-15.2	-32.2	-56.1
Hydroxyacetone + Methanol → Methyl lactate + H_2	-14.1	-8.9	-41.8
C-C coupling			
1,2-Propanediol + Methanol → 2,3-Butanediol + H_2O	-11.8	-148.4	62.0
1,2-Propanediol + Methanol → 1,2-Butanediol + H_2O	-17.0	-99.6	12.1
C-O scission			
1,2-Propanediol + H_2 → 1-Propanol + H_2O	-1.7	-119.4	66.7
1,2-Propanediol + H_2 → 2-Propanol + H_2O	-5.7	-132.8	65.2
Direct C-C scission			
1,2-Propanediol + H_2 → Ethanol + Methanol	15.4	-61.9	72.2
Retro aldol condensation			
1,2-Propanediol + Methanol → Ethanol + 1,2-Ethanediol	13.3	-56.1	68.8

Table S3. Major products (with corresponding STYs in parentheses) from reaction of MeOH with vicinal diols (1,2-butanediol and 2,3-butanediol) and terminal diols (1,3-propanediol and 1,4-butanediol) using GC-FID. Reaction conditions: 300 °C, 1000 psig, CuMgAlO$_x$, 120 h^{-1} WHSV, 0.1 mL/min feed with 10 mol% diol in MeOH, 102.5 mL/min H$_2$, 24 h. For reaction of 1,2-PDO with MeOH, see **Table S4**.

Feed diol	**1,2-Butanediol**	**2,3-Butanediol**	**1,3-Propanediol**	**1,4-Butanediol**
Dehydrogenation	1-Hydroxy-2-butanone (100)	3-Hydroxy-2-butanone (41)	0	2-Hydroxy-THF (4)
C-C coupling with MeOH	2,3-Pentanediol (23); 1,2-Pentanediol (13)	2,3-Pentanediol (2.6)	0	0
Retro aldol condensation	1,2-Ethanediol (6)	1,3-Propanediol (3.6)	0	0
C-O scission	2-Butanol (12); 1-Butanol (10)	2-Butanol (3)	1-Propanol (48); Propanal (8)	1-Butanol (32)
Direct C-C scission	1-Propanol (18)	Ethanol (3.7)	Ethanol (16)	Ethanol (5)
Others	Methyl butanoate (2)	N/A	1,3-Dioxane (24)	THF (7.5)
Conversion of diol (%)	7.5	3.5	5.8	2.8

Table S4. Major products (with corresponding STYs in parentheses) from reaction of 1,2-PDO with primary monoalcohols (MeOH, ethanol and 1-propanol) and secondary monoalcohols (2-propanol) using GC-FID. Reaction conditions: 300 °C, 1000 psig, CuMgAlO$_x$, 120 h^{-1} WHSV, 0.1 mL/min feed with 10 mol% 1,2-PDO in monoalcohol, 102.5 mL/min H$_2$, 24 h.

Feed monoalcohol	**Methanol**	**Ethanol**	**1-Propanol**	**2-Propanol**
Hydroxyacetone	131	37	80	70
C-C coupling with 1,2-PDO	2,3-Butanediol (40); 1,2-Butanediol (18)	2,3-Pentanediol (1.4); 1,2-Pentanediol (1)	1,2-Hexanediol (4)	0
Retro aldol condensation	1,2-Ethanediol (8)	0	0	0
C-O scission	1-Propanol (11.6); 2-Propanol (12.3)	1-Propanol (2.4); 2-Propanol (1.9)	*Feed* 2-Propanol (9)	1-Propanol (11) *Feed*
Direct C-C scission	*Feed* Ethanol (40)	Methanol (13) *Feed*	Methanol (24); Ethanol (25)	Methanol (22); Ethanol (20)
Others	Methyl lactate (8)	Ethyl acetate (0.7)	Propyl propanoate (12)	Isopropyl lactate (0.6)
Conversion of 1,2-PDO (%)	11.8	4.3	7.5	0.05

References:

1. Galebach, P. H.; McClelland, D. J.; Eagan, N. M.; Wittrig, A. M.; Buchanan, J. S.; Dumesic, J. A.; Huber, G. W., Production of Alcohols from Cellulose by Supercritical Methanol Depolymerization and Hydrodeoxygenation. *ACS Sustainable Chemistry & Engineering* **2018,** *6* (3), 4330-4344.
2. Galebach, P. H.; Thompson, S.; Wittrig, A. M.; Buchanan, J. S.; Huber, G. W., Investigation of the Reaction Pathways of Biomass-Derived Oxygenate Conversion into Monoalcohols in Supercritical Methanol with CuMgAl-Mixed-Metal Oxide. *ChemSusChem* **2018,** *11* (23), 4007-4017.