Supplementary Information (SI) for Sustainable Energy & Fuels.

Cellulose Hydrogenolysis on a Combination of Tungsten Oxide Nanorods with and without Ruthenium Loading for enhanced Ethanol Selectivity

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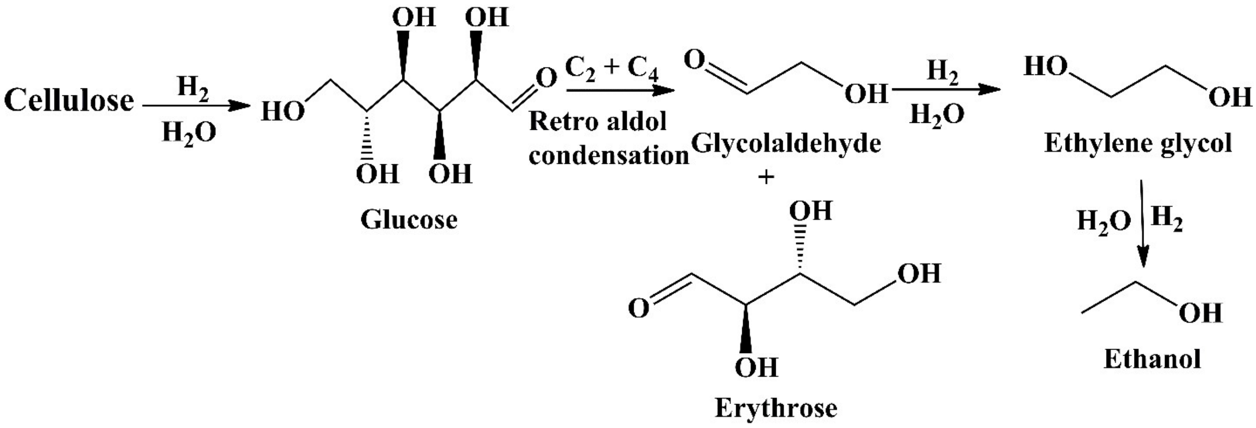


Scheme S1. Schematic representation of cellulose conversion to ethanol.

S1. Catalysts synthesis

S1.1 Synthesis of Tungsten oxide nanorods

Tungsten oxide nanorods (WO_3NRs) were synthesized in the chemical vapor deposition (CVD) reactor as reported by Sunkara and co-workers [15]. The reactor was equipped with a 0.5mm diameter coiled tungsten filament as the source. The temperature of the heating filament rises to 1950 K. The substrate, comprised of both quartz and fluorinated tin oxide (FTO)-coated quartz slides, was placed on the quartz boat employed on the wall of the quartz tube. The quartz boat also prevents direct depositions on the walls of the quartz and collects the depositions. The experiment was performed using the furnace around the quartz tube with high temperature and oxygen partial pressure of 1073 K and 0.0054 bar torr respectively. The obtained nanorods were calcined for 4 h at 923K.

S1.2 Synthesis of Ru-loaded tungsten oxide nanorods

The Ru was loaded on the surface of the as-synthesized tungsten oxide nanorods by simply performing an impregnation method. Typically, an appropriate amount of $RuCl_3.xH_2O$ is dissolved in an aqueous solution of tungsten oxide nanorods under magnetic stirring, and the mixture is stirred vigorously at a temperature of 333 K until all the water present gets evaporated. The sample was dried overnight in an oven at 353 K which was further treated at 773 K for 2h followed by a reduction in H_2 atmosphere at 873 K for 2 h with a heating rate of 273 K/min.

S2. Catalysts characterization

X-ray diffraction (XRD) was used to determine the catalysts' crystalline phase by using a Rigaku, Miniflex-300 with Cu K radiation (= 0.15418 nm), 40 kV, and 15 mA where the tube voltage and current, respectively. The range of the scanning angle (2θ) was 5 to 80°. The Raman spectra were captured using an argon laser ion and a Renishaw Micro Spectrometer. The laser's excitation wavelength was 514 nm, and its power was 2 mW. The exposure lasted for two seconds. With the aid of Agilent 7900 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) with UHMI technology, the Ru metal content over nanowire WO_3 of catalysts was determined. Utilizing AXIS SUPRA, which is equipped with a monochromatic Al K X-ray source bombarded with a beam of energy of 1486.6 eV, X-ray photoelectrons spectroscopy (XPS) analysis was performed. Using the JOEL Model JSM-7900F and the OXFORD EDS system, field emission scanning electron microscopy (FESEM) was used to examine the surface morphology of the catalysts. Before the analysis, the sample was coated in platinum and mounted on the aluminium stub. Using an FEI Tecnai TF20 operating at 200KV, high-resolution transmission electron microscopy (HRTEM) was used to gather data on the crystallographic structure of catalysts. The powdered sample was dissolved in ethanol before being dropped onto the carbon-coated copper grid for analysis.

S3. Chemicals and materials

Microcrystalline cellulose (MCC) was purchased from Spectrochem. Glucose, fructose, glycolaldehyde, ethanol, propanol, and sorbitol were purchased from Fisher Scientific. Ethylene glycol and propylene glycol from Qualigens. De-ionized water was obtained from the milli-Q system from the Instrumentation Lab of the Indian Institute of Technology Delhi (IIT Delhi).

S4. Catalytic activity testing for cellulose conversion to ethanol in a stirred batch reactor

Catalytic reactions for the conversion of cellulose to alcohols were carried out in a 100 ml HEL high-pressure slurry batch reactor operated online using WinISO software as given in Figure S1, the temperature and pressure variations are recorded every 20 seconds (step size). Typically, the reactor was fed with substrate, catalysts, and co-catalysts in an appropriate amount. Different reaction conditions were used when the three-phase slurry batch reactor was in operation. The reactor was first purged three times with N_2 gas and then pressurized with H_2 gas to 40 bar by using a mass flow controller (MFC). After attaining the steady state of the desired operating conditions, the reaction was carried out at different intervals. After the reaction was finished, the reactor was cooled. The solid residue was then separated by centrifugation, dried, and weighed to calculate the cellulose conversion by using equation S1. The liquid product was analyzed using Agilent 1260 high performance liquid chromatography (HPLC) system, equipped with an Aminex 87H column and a refractive index detector (RID) and operated at a temperature of 323K. A mobile phase consisting of 5 mM H_2SO_4 was employed, with a flow rate of 0.6 mL/min. Before analysis, the samples underwent thorough filtration using 0.20 µm syringe filters. The gaseous product was collected and quantitively analyzed using Nucon Gas Chromatography (GC) equipped with a Porapak q column and thermal conductivity detector (TCD). Moreover, the product yield and solid residue were calculated using equations (S2) and (S3) respectively.

$$Conversion\ (\%) = \frac{B_{cellulose} - A_{cellulose}}{B_{cellulose}} \times 100 \qquad \text{(S1)}$$

$$Product\ yield\ (\%) = \frac{K_i(n_i M_{cellulose})}{6(B_{cellulose} - A_{cellulose})} \times 100 \qquad \text{(S2)}$$

$$Residue\ yield\ (\%) = \frac{Mass\ of\ residue\ left}{mass\ of\ initial\ cellulose} \times 100 \qquad \text{(S3)}$$

Where $B_{Cellulose}$ is the weight of cellulose before the reaction, $A_{cellulose}$ is the weight of cellulose after the reaction.

K_i is the number of carbon in products i, n_i is the moles of product i, $M_{cellulose}$ is the molecular weight of cellulose (162 g/mol)

Figure S1. Photograph of the experimental setup of HEL high pressure slurry batch reactor

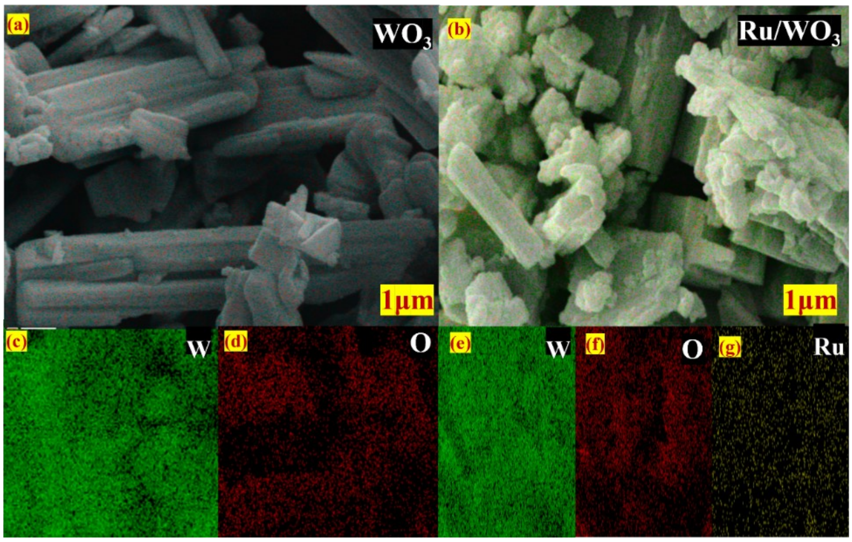


Figure S2. Elemental mapping of (a) WO_3 with elements (c) W (d) O and (b) Ru/WO_3 with elements (e) W, (f) O (g) Ru

Table S1. Elemental composition of pristine catalysts by EDX and ICP-MS analysis

	EDX analysis		**ICP-MS analysis**
Elements	**WO_3**	**Ru/WO_3**	**Ru/WO_3**
	Weight %	**Weight %**	**Weight %**

O	19.32	16.90	18.37
W	80.68	81.90	79.21
Ru	-	1.20	2.46

Table S2. Effect of various parameter on product yield

Entry No.	**Parameters**	**Product yield (%)**				
1		**Temperature of temperature**				
	Temperature (K)	**Ethylene glycol**	**Ethanol**	**Sorbitol**	**Propylene glycol**	**Propanol**
1(a)	493	10.84	15.83	13.68	2.85	8.04
1(b)	503	4.35	18.21	12.87	4.52	12.92
1(c)	513	9.79	22.40	11.82	7.30	12.59
1(d)	523	2.88	28.94	9.68	9.21	13.63
2		**Effect of time**				
	Time (h)	**Ethylene glycol**	**Ethanol**	**Sorbitol**	**Propylene glycol**	**Propanol**
2(a)	5	3.35	2.64	11.84	6.147	10.60
2(b)	7.5	7.654	12.08	10.02	7.33	11.96
2(c)	10	2.88	28.94	9.68	9.21	13.24
2(d)	12.5	0	1.78	4.30	2.21	27.93
3		**Effect of cellulose loading**				
	Cellulose loading (mg)	**Ethylene glycol**	**Ethanol**	**Sorbitol**	**Propylene glycol**	**Propanol**
3(a)	100	6.46	0	6.86	12.06	36.40
3(b)	150	7.50	18.23	8.026	10.75	25.08
3(c)	200	2.88	28.94	9.68	9.21	13.63
3(d)	250	2.874	27.93	9.32	7.91	15.62
4		**Effect of catalysts loading**				
	Catalyst loading (mg)	**Ethylene glycol**	**Ethanol**	**Sorbitol**	**Propylene glycol**	**Propanol**
4(a)	50	1.49	13.96	6.70	5.61	6.38
4(b)	100	2.88	28.94	9.68	9.21	13.63
4(c)	150	4.18	10.92	4.58	4.75	13.47

Reaction conditions: (1) 200 mg cellulose, 100 mg catalysts, 25 ml solvent, 493-523 K 10 h, 700 rpm (2) 200 mg cellulose, 100 mg catalysts, 25 ml solvent, 523 K, 5 – 12.5 h, 700 rpm (3) 100–250 mg cellulose, 100 mg catalysts, 25 ml solvent, 523 K, 10 h, 700 rpm (4) 200 mg cellulose, 50-150 mg catalysts, 25 ml solvent, 523 K, 40 bar H_2,10 h, 700 rpm

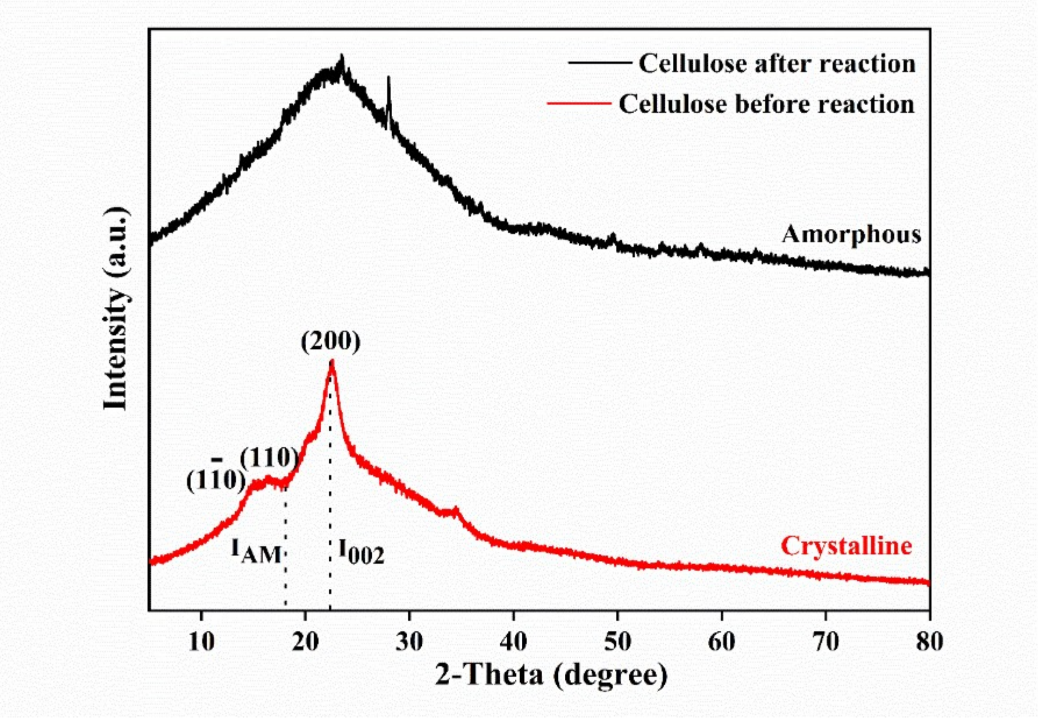


Figure S3. XRD pattern of cellulose before and after reaction

Reaction condition of blank reaction: 200 mg cellulose, 25 ml solvent, 523 K, 40 bar H_2, 10 h, 700 rpm.

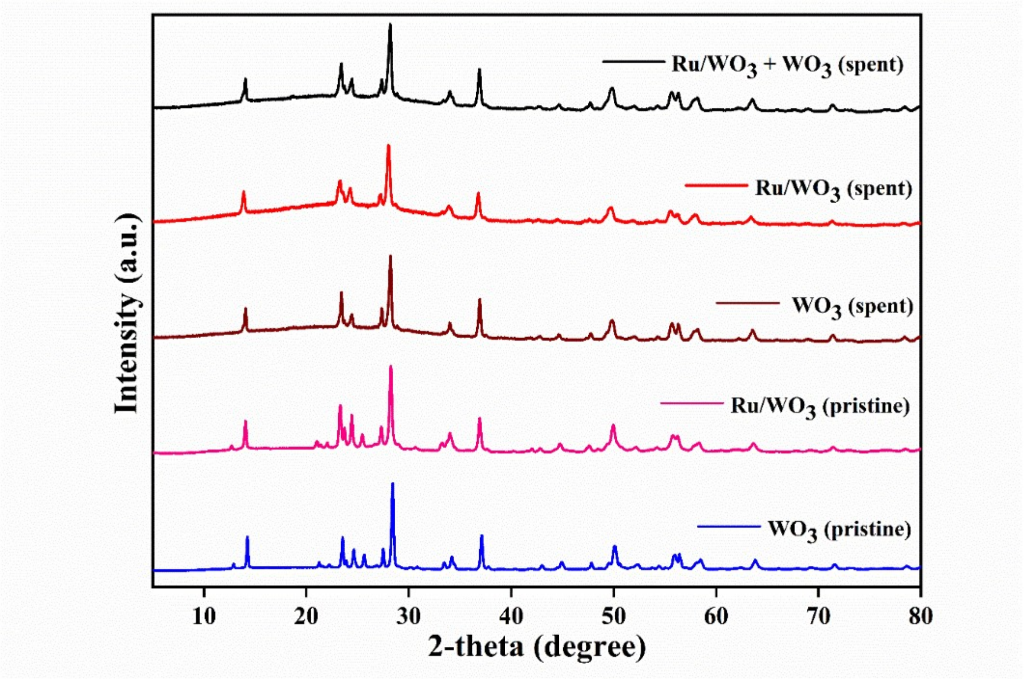


Figure S4. Comparison of XRD pattern of pristine and spent catalyst

Reaction conditions of spent catalyst: 200 mg cellulose, 100 mg Ru/WO_3, 50 mg WO_3, 25 ml solvent, 523 K, 40 bar H_2, 10 h, 700 rpm.

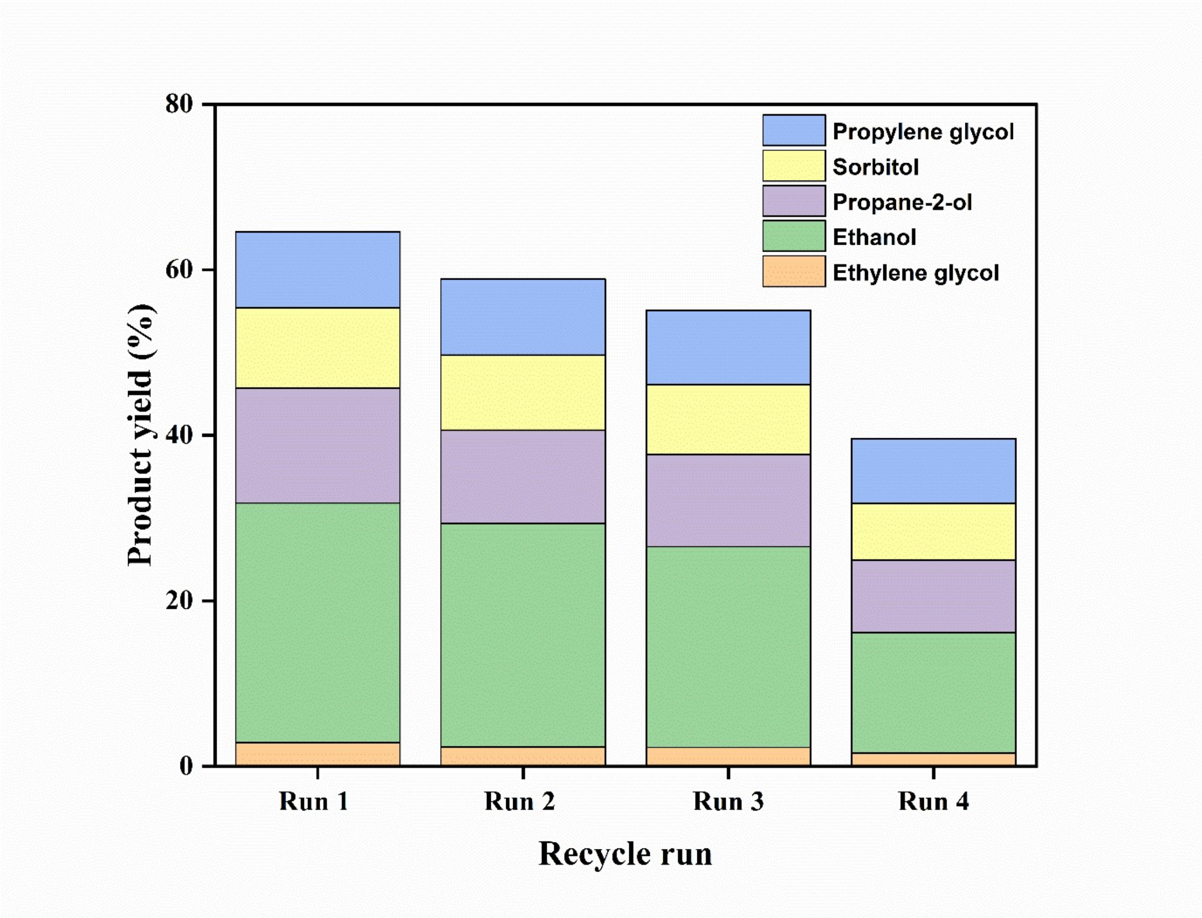


Figure S5. Recycling experiments for the catalytic conversion of cellulose to ethanol using Ru/WO_3

Reaction condition: 200 mg reactant, 100 mg catalysts, 25ml of water, 523 K, 40 bar H_2, 10h and 700 rpm.

Table S3. ICP-MS analysis of Ru species in Ru/WO_3 of spent catalyst

Runs	**Ru (wt.%)**	**Ru Leaching (wt.%)**
Fresh	2.46	-
Run 1	2.40	0.06
Run 2	2.38	0.08
Run 3	2.29	0.17
Run 4	1.98	0.56

Table S4. Product Distribution over Ru/WO_3 under optimized reaction conditions

Reactant	**Product yields (%)**					
	Conversion (%)	**Ethylene glycol**	**Ethanol**	**Propanol**	**Propylene glycol**	**Sorbitol**
Cellulose	98.5	2.88	28.94	13.88	9.21	9.68
Glucose	100	4.17	7.86	2.91	4.34	20.42
Fructose	100	0	0	38.44	7.28	32.22
Glycolaldehyde	100	51.47	35.61	0	0	0
Ethylene glycol	70	0	66.97	0	0	0

Reaction conditions: 200 mg reactant, 100 mg catalyst Ru/WO_3, 25 ml of water, 523K, 40 bar H_2, 10 h, and 700 rpm.

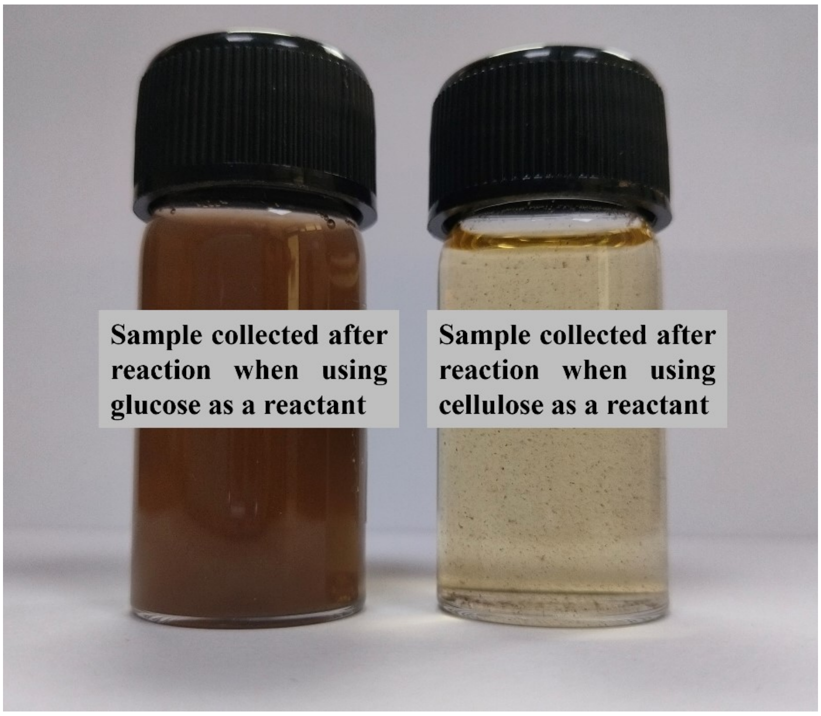
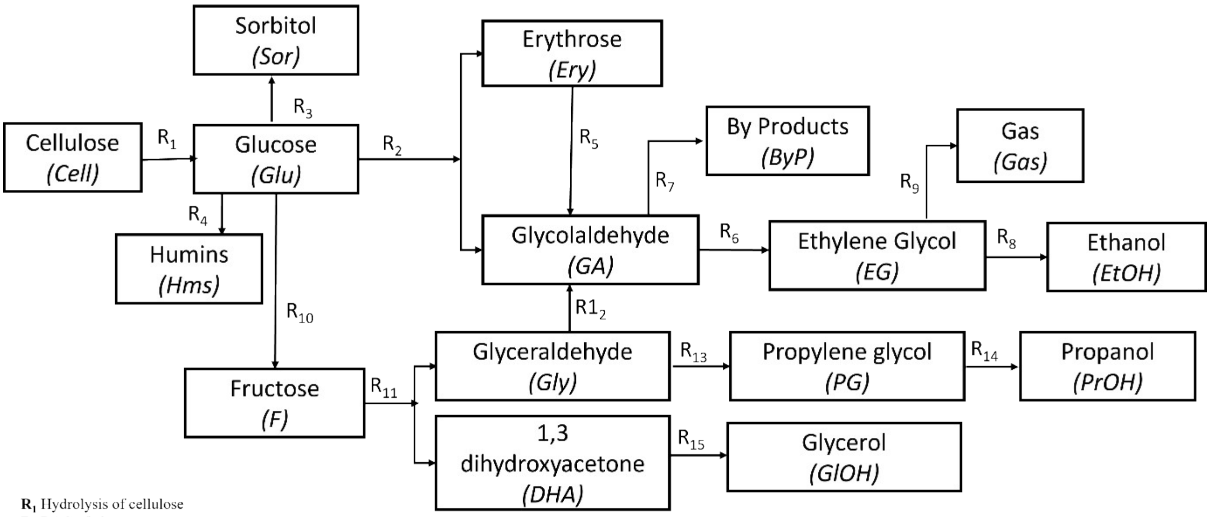


Figure S6. Sample collected after the reaction with different substrate under same reaction condition



R_1 Hydrolysis of cellulose
R_2 RAC of glucose
R_3 Hydrogenation of glucose
R_4 Oligomerization to humins
R_5 RAC of erythrose
R_6 Hydrogenation of glycolaldehyde
R_7 Thermal side reaction of glycolaldehyde
R_8 Hydrogenation of ethylene glycol
R_9 Hydrogenolysis of ethylene glycol
R_{10} Isomerization reaction of glucose
R_{11} RAC of fructose
R_{12} RAC of glyceraldehyde
R_{13} Hydrogenation of Glyceraldehyde
R_{14} Hydrogenation of Propylene glycol
R_{15} Hydrogenation of 1,3 dihydroxyacetone

Figure S7. Possible overall reaction network for cellulose conversion to ethanol and propanol

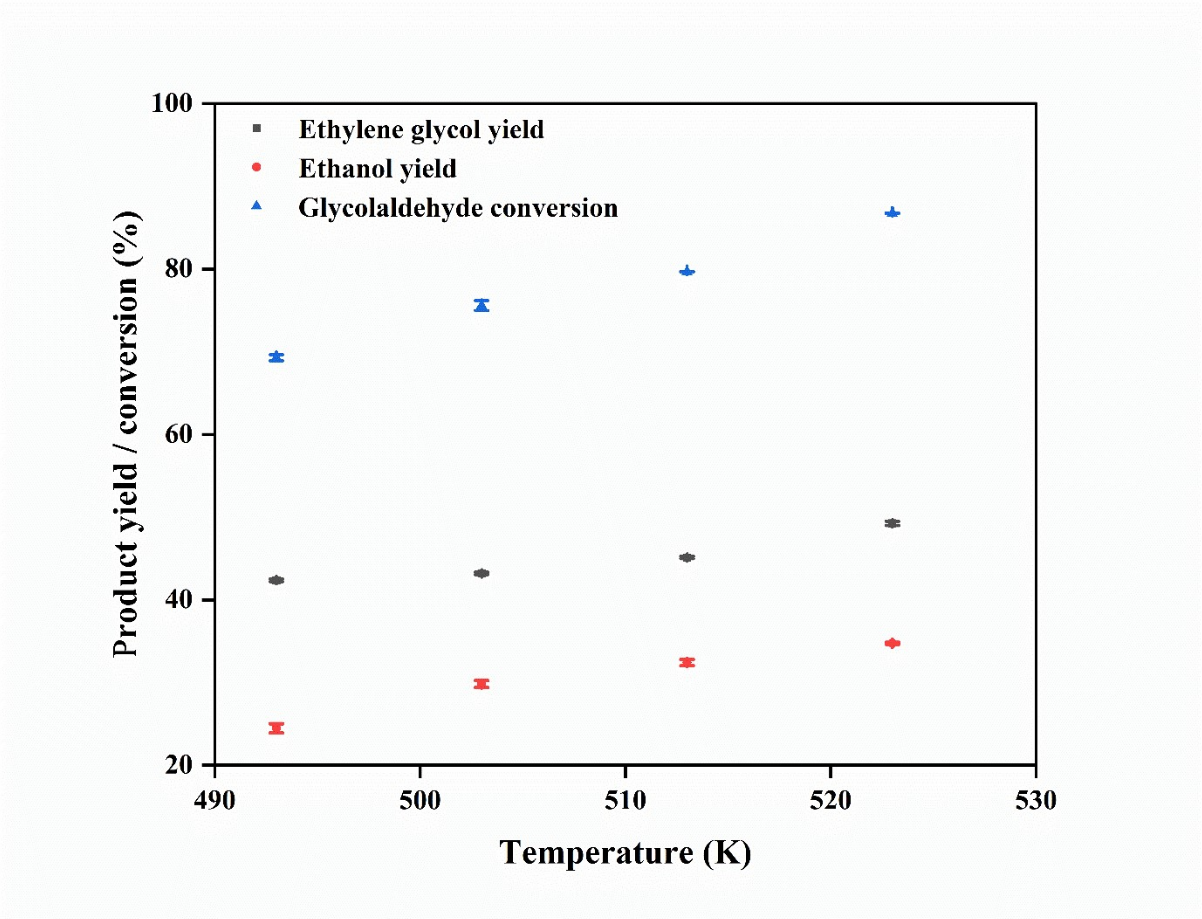


Figure S8. Reaction performed with glycolaldehyde as a reactant

Reaction conditions: 200 mg glycolaldehyde, 100 mg Ru/WO_3, 50 mg WO_3, 25 ml solvent, 493-523 K 10 h, 40 bar H_2, 700 rpm.

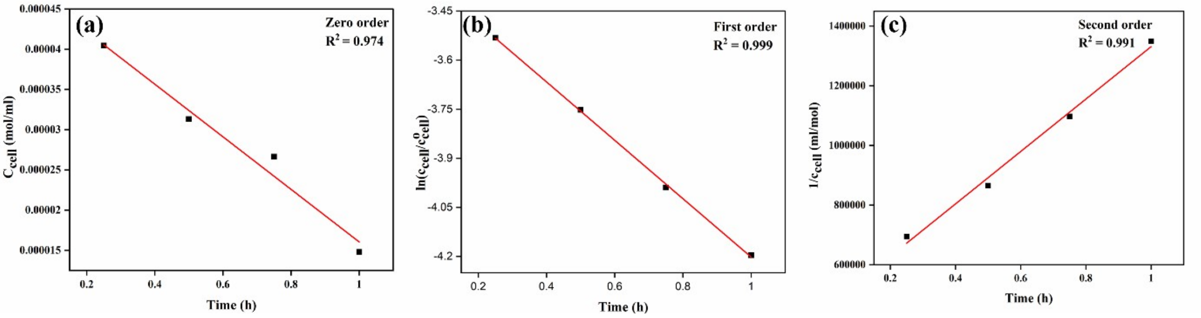


Figure S9. Concentration-time plot for (a) zero order (b) first order (c) second order of reaction R_1

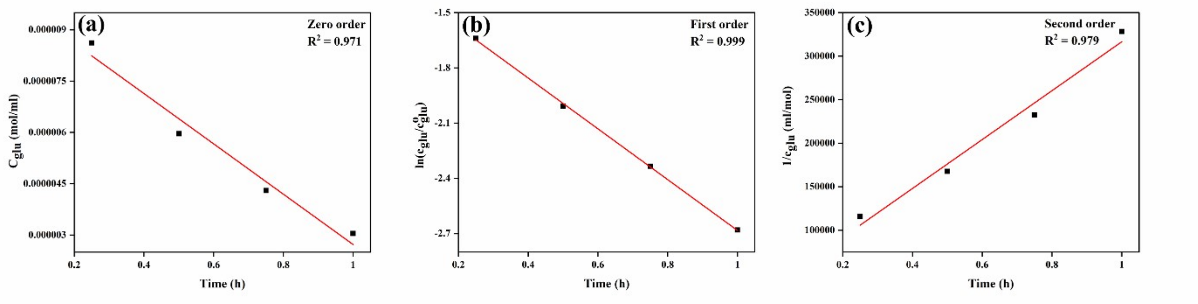


Figure S10. Concentration-time plot for (a) zero order (b) first order (c) second order of reaction R_2

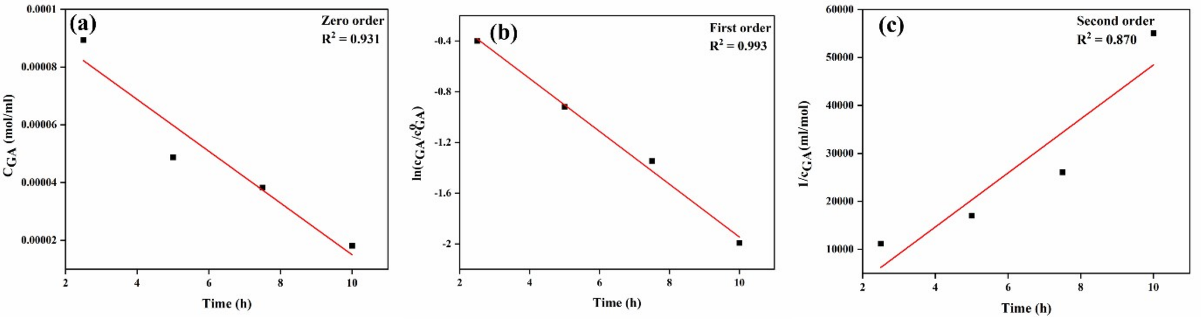


Figure S11. Concentration-time plot for (a) zero order (b) first order (c) second order of reaction R_6

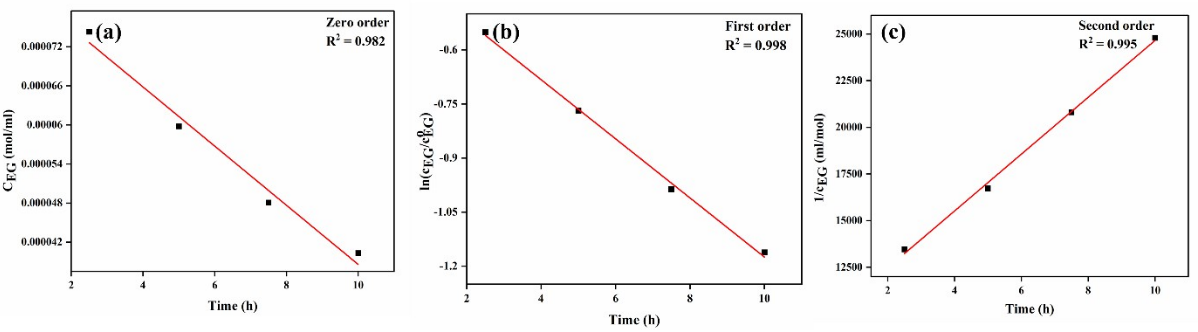


Figure S12. Concentration-time plot for (a) zero order (b) first order (c) second order of reaction R_8

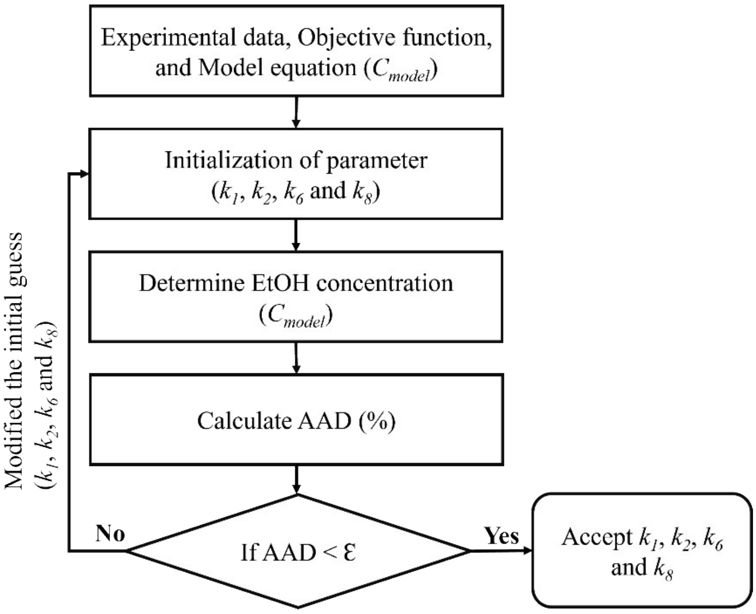


Figure S13. Proposed methodology for estimation of kinetic parameters