Supporting Information

# High Yield Production of Levulinic Acid by Catalytic Partial Oxidation of Cellulose in Aqueous Media

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## Experimental

### Materials

The following reagents and products were used as received for the experiments: Cellulose Microcrystalline, average particle size 50 μm, D(+)- Glucose Reagent ACS Grade, and D(+)-Cellobiose, 98%, were purchased from Acros Organics. For chemical analysis and derivatization, the following reagents and products were used as received: glacial acetic acid, acrylic acid 99% inhibited with 200 ppm MEHQ (monomethyl ether hydroquinone), BSTFA (N,O-bis(trimethylsilyl) trifluoroacetamide) + TMCS (trimethylchlorosilane) 99:1, butyl alcohol 99%, butly lactate 98%, butyl acetate > 99%, citric acid 99%, D-(+)- Glyceraldehyde >98%, hydrochloric acid 37% ACS grade, L-(+)- lactic acid 98%, DL-malic acid > 99%, oxalic acid +99%, propionic acid > 99.5%, pyridine anhydrous 99.8%, pyruvaldehyde 40 wt% solution in water, sulfuric acid ACS reagent

95%, and trifluouroacetic acid (TFA) 99%, were purchased from Sigma Aldrich. Formic acid 98%, was purchased from Fluka. The following zeolites and metal oxides were used for catalysts: aluminium oxide, Zeolite-β, Zeolite-Y, ZSM-5, and zirconium oxide were purchased from Alfa Aesar; hydrotalcite was purchased from Sigma Aldrich. Water used during catalyst preparation and testing and chemical analysis is ultra-pure water (18.2 MΩ·cm at 25 °C, Millipore)

## Catalyst preparation

Zirconia (Alfa Aesar) was ground and calcined in air at 250 °C for three hours before using as the catalyst. Sulfated zirconia and sodium hydroxide passivated zirconia were prepared by wet impregnation. A solution of 0.87 M sulphuric acid was used for wet impregnation of zirconia. The wetted zirconia was dried at 100 $^{o}$C for overnight, and then calcined in air in a box furnace at 550 $^{o}$C, with a 5 $^{o}$C/min heating ramp, for five hours. To impregnate zirconia with sodium hydroxide, the zirconia pellets were immersed in a solution of 0.1 M NaOH and then transferred into the round bottom flask of a rotovap. The pellets were dried under vacuum and at 100 $^{o}$C in the rotovap for twelve hours. The NaOH impregnated $ZrO_2$ pellets were washed with water until the pH of wash water was 7, then dried at 100 $^{o}$C overnight, and calcined in air at 250 °C for three hours

## Catalyst testing

All reactions were carried out in a 100 mL stirred Parr microreactor. In each reaction, a glass liner was used to prevent the reactants from contacting the metal reactor walls. The appropriate amounts of catalysts and biomass were added into 20 mL water in the glass liner. The reactor was then sealed, purged with high purity nitrogen, and then charged with the reactive gas to the set pressure. The reactor was heated at a ramp rate of 10 °C/min until the desired set temperature was reached. During the reaction, mixing was achieved through an internal propeller operating at 1200 RPM. Once the set temperature was attained, the reactor was held at the set temperature for 20 minutes and then quenched in an ice bath to quickly lower the temperature. The reactor was cooled until approximately 25 °C, and then the gas pressure was recorded and vented. The reactor was

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immediately broken down and the solid residue remaining on the propeller and reactor head was recovered and dried for the calculation of mass conversion. The liner was removed and the aqueous and solid fractions were separated using a centrifuge. The liquid portion weight was recorded and the solid residues were dried overnight at 110 °C. The water lost through drying was calculated through subtraction of pre- and post- drying weights.

Mass conversion of cellulose to liquid and gas products was calculated using the following equation:

$$\text{Mass Conversion} = 1 - \frac{\text{Mass of dried solid residue} - \text{Mass of dried catalyst}}{\text{Initial mass of cellulosic biomass}}$$

Since organic compounds in the aqueous phase products were the desired chemicals in the catalytic APPO process, the total organic carbon (TOC) yield was used to assess the percentage of the TOC content of the aqueous phase products in the TOC of the initial cellulosic biomass:

$$\text{TOC Yield} = \frac{\text{Total organic carbon content of the aqueous phase products}}{\text{Total carbon content of the cellulosic biomass}}$$

## Chemical analysis

After the reaction, the resultant aqueous phase product samples were prepared for TOC, high performance liquid chromatography (HPLC), and gas chromatography coupling with mass spectrometer (GC/MS) analysis. The gaseous products were analysed using a gas chromatogram equipped with thermal conductivity detector (GC/TCD).

For TOC analysis, the resultant aqueous phase was filtered through a 0.45 micron syringe filter and then diluted ~200 times with ultra-pure water. TOC was measured by a Shimadzu Total Organic Carbon Analyser model TOC-V. The aqueous products were analysed by using a Shimadzu high performance liquid chromatography (HPLC). HPLC analysis was performed using a Shimadzu HPLC system equipped with a UV-VIS Detector (Shimadzu SPD 10-AV) and Refractive Index Detector (Shimadzu RID-6A). For analysis of organic acids and reaction intermediates, the samples were separated in an Aminex 87-H column from Bio-Rad, using 5 mM $H_2SO_4$ as the mobile phase, 0.7 mL/min flow, at a column temperature of 55 °C. For quantitative identification and results, the dual UV-VIS detectors were utilized at 208 nm and 290 nm.

Derivatization of the polar components was performed in order to perform qualitative GC/MS analysis and identification of unknown components in the aqueous phase. BSFTA with TMCS (99:1) was used as the reagent for trimethylsilylation of alcohols, carboxylic acids, and phenols. The method for derivatization was taken from the literature. 1 mL samples of the resultant aqueous phase were dried overnight in deactivated 1.5 mL Waters Maximum recovery vials. To the dried solids, 50 µL acetonitrile was added and ultrasonicated for 1 hour to allow the solids to dissolve. After ultrasonication, 50 µL pyridine and 150 µL BSFTA with TMCS (99:1, Sigma-Aldrich) were added and the vials were capped. The capped vials were placed in a sand bath maintained at 65 °C for 2 hours to allow complete silylation. After silylation, the samples were cooled for 2 hours and 5 µL silylation mixture was diluted with 1.5 mL acetonitrile. The samples were injected in an Agilent 6890 series GC/MS with an equipped with an Agilent DB5-SMS Column and Agilent 5973 Mass Selective Detector (TIC detector). The column temperature was maintained at 70 °C for 5 minutes then ramped at 5 °C/ min to 300 °C and held at 300 °C for 2 minutes.

After the reaction, the gaseous products were collected in a Tedlar gas bag and analyzed using a SRI 8610C gas chromatogram equipped with 0.5 mL gas sampling loop and thermal conductivity detector (TCD). A Haysep D packed column was employed (6 ft. 1/8 in) with a flow rate of 11 mL/min helium. The heating profile employed allowed separation of $H_2$, $N_2$, CO, $CH_4$ and $CO_2$. The column temperature was initially held at 40 °C then increased to 200 °C at a heat rate of 50 °C/min.

The post-reaction aqueous phase supernatant was filtered, and then diluted with water for ~200 times for elemental analysis, which was performed using a Varian Vista PRO Inductively Coupled Plasma Optical Emission Sectrometry (ICP-OES). A $HNO_3$ solution containing 0.5 ppm $Y^{3+}$ and 1500 ppm $Ce^{2+}$ was added into the sample for internal standardization and ioniziation buffer.

## Materials characterization

The surface morphology of catalysts was characterized by a Hitachi S-4700 scanning electron microscopy (SEM). The powder X-Ray Diffraction (XRD) analysis of the samples was carried out with a Bruker AXS D8 Discover diffractometer with GADDS (General Area Detector Diffraction System) operating with a Cu-Ka radiation source filtered with a graphite monochromator ($\lambda$ = 1.5406 Å). Data were collected in a range of 5 to 80$^{o}$. Brunauer−Emmett−Teller (BET) was used to measure the specific surface area of the samples. BET adsorption and desorption isotherms were obtained using a surface area analyzer (NOVA 1000 Series, Quantachrome). The solid sample to be analyzed was weighed and placed inside the sample holder cell of a known volume. The used refrigerant was liquid nitrogen placed in a vacuum Dewar at about 77 K and the carrier gas was $N_2$ (ultra high purity grade, Airgas).

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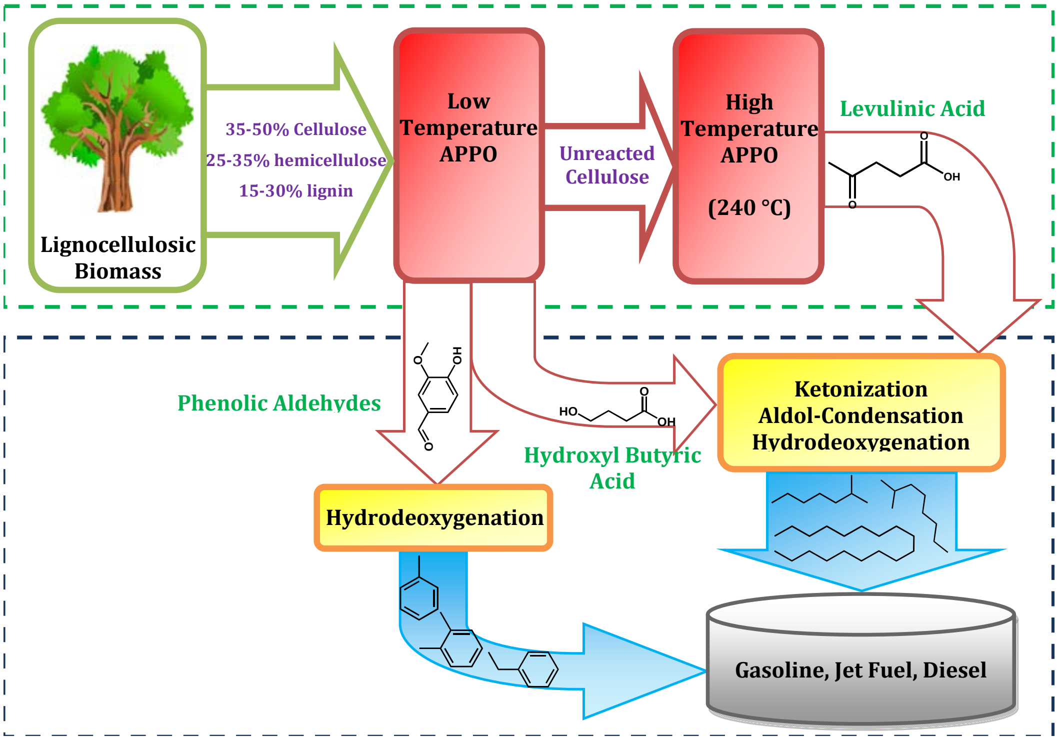

**Scheme S1**. Illustration of an integrated biorefinery based on the concept of the aqueous phase partial oxidation of lignocellulosic biomass. Cellulose and hemicellulose are converted into carboxylic acids such as levulinic acid and hydroxybutyric acid; lignin is converted into phenolic aldehydes or acids such as vanillin. The carbohydrate derived carboxylic acids are further upgraded into paraffinic hydrocarbons through ketonization, aldol-condensation, and hydrodeoxygenation. The lignin derived phenolic compounds were converted into aromatic hydrocarbons by hydrodeoxygenation.

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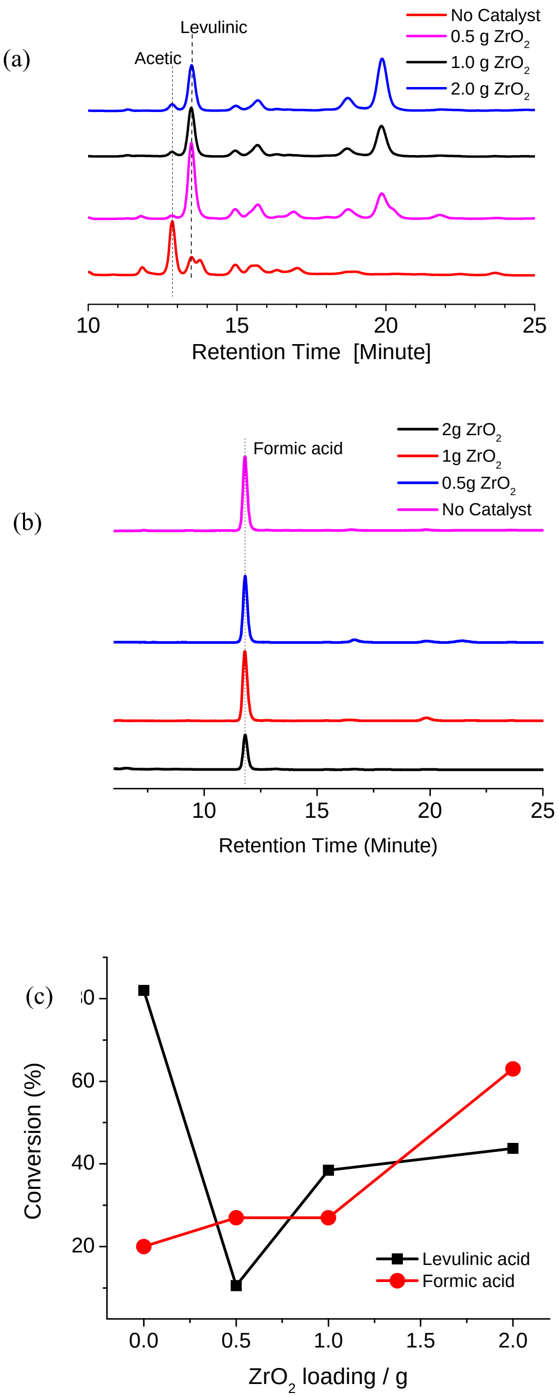

**Figure S1**. HPLC spectra of (a) levulinic acid (LA) and the derived oxidation products and (b) formica acid with and without adding the $ZrO_2$ catalyst. (c) The conversions of levulinic acid and formic acid with different $ZrO_2$ catalyst loadings. Reaction conditions: 240 ºC, lean air with 2.8% $O_2$, 400 psi initial pressure, 25 minute reaction time, 1.5 wt% LA loading. The initial concentrations of LA and formic acid were the same: 0.129M. Zirconia stablizes LA under the APPO environment. 82% LA was converted with no added catalyst, while only 11% LA was degraded with 0.5 g $ZrO_2$ catalyst. However, further increasing the catalyst loading to 1.0 g and 2.0 g, 42% and 44% LA were converted, respectively. Formic acid is relatively stable without catalyst or with 0.5g $ZrO_2$ but decomposes to a large extent at higher $ZrO_2$ loadings.

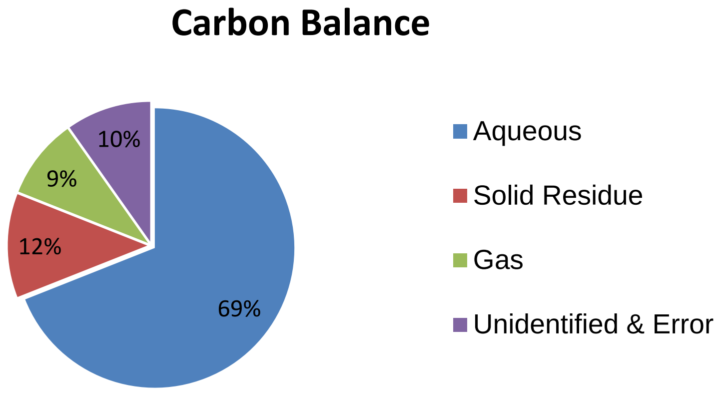

**Figure S2.** Distribution of carbon balance of the reaction products of the APPO of cellulose over $ZrO_2$. Reaction conditions: 240 ºC, lean air with 2.8% $O_2$, 400 psi initial pressure, 25 minute reaction time, 9.1 wt% biomass loading, and 1:2 catalyst to biomass mass ratio. The catalyt is the monolinic $ZrO_2$ with a surface area of 108 $m^2/g$.

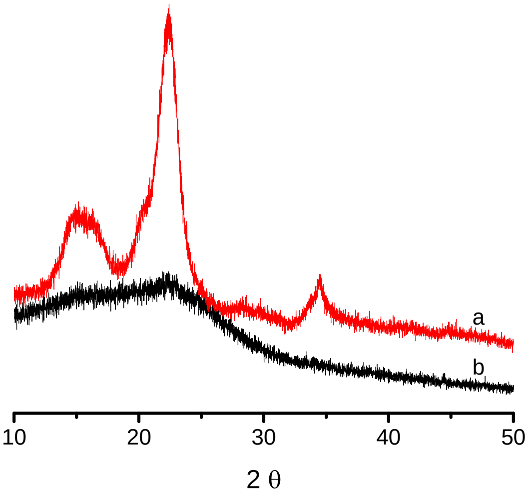

**Figure S3.** X-ray diffraction patterns of solid residue samples receovered from the APPO of cellulose. (a) Pure cellulose; (b) after the APPO reaction. Reaction conditions: 240 ºC, lean air with 2.8% $O_2$, 400 psi initial pressure, 25 minute reaction time, 9.1 wt% cellulose loading, and 1:2 catalyst to cellulose ratio.

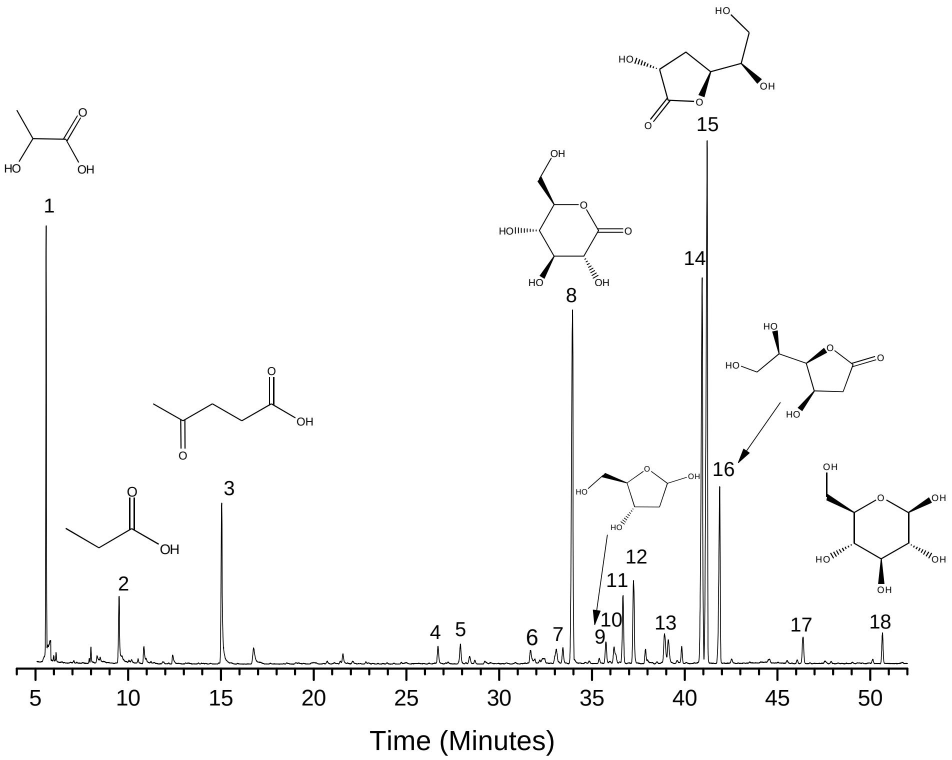

**Figure S4**. The GC/MS spectra of the aqueous phase products by the APPO of cellulose. Reaction conditions: 240 ºC, lean air with 2.8% $O_2$, 400 psi initial pressure, 25 minute reaction time, 9.1 wt% biomass loading, and 1:2 catalyst to biomass mass ratio. The quantitative amount of LA was obtained from both HPLC and GC/MS analysis. The results by the two analytical methods were close. Other peaks in the GC/MS spectra were not calibrated and only qualitative information is given:

| **Peak Number** | **Retention Time (min)** | **Relative Area (%)** | **Compound Name** |
|---|---|---|---|
| **1** | 5.583 | 8.60 | Lactic Acid |
| **2** | 9.5139 | 2.17 | Proponic Acid |
| **3** | 15.0396 | 6.49 | Levulinic Acid |
| **4** | 26.7077 | 0.71 | 2-Methyl-butane-1,3-diol |
| **5** | 27.9054 | 0.94 | Butane-2,3-diol |
| **6** | 31.6999 | 0.70 | 2-Hydroxy-3-methyl-butyric acid |
| **7** | 33.0813 | 0.91 | 2-(2-Hydroxy-ethoxy)-ethanol |
| **8** | 33.9469 | 15.14 | 2-methyl-2,3,4,5-Tetrahydroxy-D-Ribonolactone |
| **9** | 35.7434 | 0.97 | D-Erythro Pentofuranose, 2-deoxy |
| **10** | 36.194 | 1.12 | D- threo Pentofuranose, 2-deoxy |
| **11** | 36.6802 | 2.73 | D-Erythro Pentonic acid, 3-deoxy |
| **12** | 37.2434 | 3.34 | D-threo-Pentonic acid, 3-deoxy |
| **13** | 38.9094 | 1.50 | 2-Dihydroxymethyl-butyric acid |
| **14** | 40.943 | 17.64 | 3-deoxy-D-Ribo Hexonic Acid γ-Lactone |
| **15** | 41.2099 | 23.06 | 3-deoxy-D-Arabino Hexonic Acid γ-Lactone |
| **16** | 41.8798 | 7.18 | 5-(1,2-Dihydroxy-ethyl)-4-hydroxy-dihydro-furan-2-one |
| **17** | 46.3799 | 1.15 | D-Glucopyranose |
| **18** | 50.6605 | 1.22 | β-D-Glucopyranose |

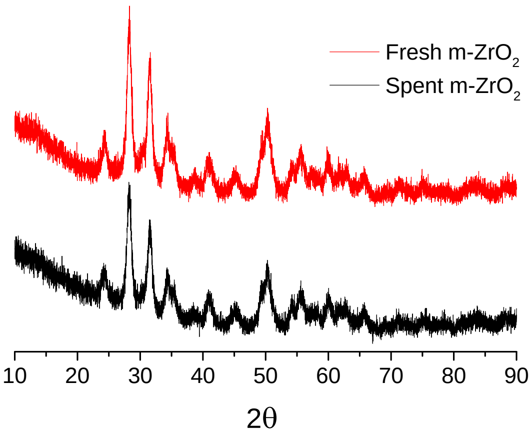

**Figure S5.** X-ray diffraction pattern of fresh and spent monoclinic $ZrO_2$ catalysts. Reaction conditions: 240 ºC, lean air with 2.8% $O_2$, 400 psi initial pressure, 25 minute reaction time, 9.1wt% cellulose loading. Monoclinic crystalline struture was preserved after the APPO of cellulose.

**Table S1.** Product yields of carboxylic acids and HMF by converting cellulose in the APPO process with $ZrO_2$ catalysts and modified $ZrO_2$ catalysts. (The initial materials loading in the 100 mL Parr reactor: 2 grams cellulose, 20 grams water, and 1 gram catalyst. Other reaction conditions: 240 °C, 2.8% $O_2$, 20 min)

| Entry | Catalyst | Mass Conversion | TOC Yield | Product Yield (carbon mol) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Formic | Acetic | Glycolic | Lactic | Levulinic | HMF |
| 1 | ZrO2 | 81% | 61% | 2.9% | 1.5% | 3.6% | 8.3% | 42.0% | 1.3% |
| 2 | $Na^+$/ZrO2 | 78% | 64% | 0.0% | 2.5% | 4.5% | 8.1% | 37.8% | 1.8% |
| 3 | $SO_4^{2-}$/ZrO2 | 74% | 52% | 4.5% | 0.0% | 2.0% | 3.8% | 27.2% | 3.0% |

**Table S2.** Product yields of carboxylic acids by using gluconic acid or 5-HMF as the probe reactants, respectively. A high production of levulinic acid was obtained with gluconic acid as the reactant and $ZrO_2$ as the catalyst. In contrast, $ZrO_2$ appears to suppress the LA formation with 5-HMF as the reactant. The lower concentration of the gluconic acid leads to the higher yield of levulinic acid. (The initial materials loading in the 100 mL Parr reactor: 20 grams water and 350 psi gas mixture of $N_2$ and $O_2$. Reaction time: 25 min)

| Entry | Temp (ºC) | Probe Reactant | Initial Concentration (mol/L) | $ZrO_2$ (g) | $O_2$ partial pressure | TOC Yield | Product Yield (carbon mol%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Acetic | Glycolic | Lactic | Succinic | Levulinic |
| 1 | 220 | GA | 0.0255 | 0.10 | 2.8% | 80% | 3.7% | 9.2% | 0.0% | 1.8% | 41.4% |
| 2 | 240 | GA | 0.0255 | 0.10 | 2.8% | 74% | 6.4% | 10.2% | 0.0% | 1.5% | 19.2% |
| 3 | 260 | GA | 0.0255 | 0.10 | 2.8% | 67% | 0.0% | 2.0% | 3.4% | 0.0% | 16.8% |
| 4 | 220 | GA | 0.1275 | 0.25 | 2.8% | 79% | 6.4% | 11.1% | 5.8% | 6.6% | 33.6% |
| 5 | 240 | GA | 0.1275 | 0.25 | 2.8% | 66% | 1.3% | 4.3% | 3.0% | 0.6% | 13.0% |
| 6 | 240 | GA | 0.1275 | 0.25 | 0.0% | 80% | 1.5% | 1.8% | 1.5% | 0.0% | 11.6% |
| 8 | 220 | HMF | 0.0255 | 0.10 | 2.8% | 32% | 0.0% | 0.0% | 0.0% | 0.0% | 0.1% |
| 9 | 220 | HMF | 0.0255 | - | 2.8% | 37% | 0.4% | 0.0% | 0.0% | 0.4% | 7.1% |
| 10 | 240 | HMF | 0.0255 | 0.10 | 2.8% | 24% | 0.0% | 0.0% | 0.0% | 0.0% | 1.3% |
| 11 | 220 | HMF | 0.1275 | 0.25 | 2.8% | 66% | 0.4% | 0.0% | 0.0% | 0.3% | 0.0% |
| 12 | 240 | HMF | 0.1275 | 0.25 | 2.8% | 46% | 0.5% | 3.5% | 0.0% | 0.3% | 0.1% |
| 13 | 240 | HMF | 0.1275 | 0.25 | 0.0% | 17% | 0.0% | 0.0% | 0.0% | 0.0% | 0.1% |

**Table S3** Comparison of the mass conversions, the TOC yields, and the carbon molar yields of major carboxylic acids of the APPO of cellulose with and without catalysts. (100mL Parr reactor; 2.0g cellulose, 20.0g water, and 1.0g catalyst; initially charged with 350psi 97.2%$N_2$ + 2.8%$O_2$; reaction time was 25 min). The mass balances were in the range of 98-101%.

| **Entry** | **Catalyst** | **Temp.** (ºC) | **Mass Conversion** | **TOC Yield** | **Carbon Yields of Aqueous Products** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Formic | Acetic | Glycolic | Lactic | Levulinic | Others |
| 1 | No catalyst | 260 | 59% | 28% | 1.8% | 1.2% | 1.3% | 0.0% | 10.6% | 14.2% |
| 2 | γ- $Al_2O_3$ | 260 | 69% | 41% | 1.4% | 1.7% | 1.4% | 5.8% | 10.2% | 21.9% |
| 3 | $TiO_2$ | 260 | 68% | 25% | 1.5% | 5.7% | 6.2% | 0.0% | 9.4% | 3.7% |
| 4 | $ZrO_2$ | 260 | 80% | 55% | 2.2% | 1.4% | 2.0% | 8.1% | 27.8% | 13.5% |
| 5 | Zeolite β | 260 | 74% | 44% | 3.4% | 1.2% | 2.4% | 0.8% | 16.9% | 22.7% |
| 6 | ZSM-5 | 260 | 72% | 39% | 2.6% | 1.6% | 1.3% | 0.3% | 13.2% | 18.8% |
| 7 | Zeolite Y | 260 | 70% | 43% | 2.2% | 1.5% | 2.2% | 3.6% | 15.9% | 19.8% |
| 8 | Hydrotalcite | 260 | 78% | 57% | 3.2% | 2.5% | 2.8% | 7.3% | 0.0% | 44.4% |