

Supporting Information for:

**Mild Aqueous Metal Catalyzed Oxidative Conversion of Low-Density Polyethylene to Low Molecular Weight Aliphatic Carboxylic Acids**

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## Materials:

Commercial low-density polyethylene (LDPE) film (0.030 mm thickness) was purchased from Goodfellow Corporation. Chemicals were purchased from Sigma Aldrich and used without further purification. Deuterated aliphatic dicarboxylic acid internal standards adipic acid 3,3,4,4,-D<sub>4</sub>, and suberic acid 2,2,7,7-D<sub>4</sub> were purchased from Cambridge Isotopes Laboratories. FeSO<sub>4</sub> and CoSO<sub>4</sub> are both heptahydrate salts. The commercial products used were a Ziploc bag, Thermo Fisher Scientific packaging film, and the connector ring for a six pack of soft drink.

## Methods:

*Oxidation Reactions:* All reactions were performed in a 4520 Reactor by Parr Instruments. The T316 stainless steel 1 L reactor (equipped with a T316 stainless steel impeller) was charged with 400 mL Millipore (20 MΩ) H<sub>2</sub>O, followed by addition of catalyst (KMnO<sub>4</sub>, CuSO<sub>4</sub>, FeSO<sub>4</sub>•7H<sub>2</sub>O, or CoSO<sub>4</sub>•7H<sub>2</sub>O ranging from 20-200 mg). The solution was stirred (350 rpm) to dissolve the catalyst and then 2g of low-density polyethylene film (cut into 1 in. by 1 in. squares) was added. The reactor was then sealed and purged with oxygen three times, followed by charging the reactor with oxygen ranging from 30-100 (2.1 - 6.9 bar) PSI. For reactions with 20 mg/mL LDPE (8 grams of LDPE was added to the solution), the oxygen pressure was held constant at 100 PSI during the reaction. The reactor was then heated to either 130 or 150 °C and stirred for 20-24 hours. The pressure in the reactor was not controlled and increased during the heating process. The reactor was then cooled using an ice bath and depressurized. Control reactions without metal catalyst were run using 130 °C, 100 PSI oxygen, 24 h of reaction time and 5mg/ml loading of LDPE film which are shown in **Figure S21**.

*Oxidation Reactions with Post-Consumer Commercial Films:* Three consumer plastics were chosen, a six-pack ring holder holding vitamin water listed as LDPE, a Ziploc bag, and a LDPE Thermo Fisher Scientific packaging film for Nalgene filters. Note that the Thermo Fisher Scientific packaging material contained some black ink on the packaging. The materials were oxidized using 5 wt % FeSO<sub>4</sub>•7H<sub>2</sub>O, 130 °C, 100 PSI oxygen for 20 h.

*Post-Processing of Oxidized Species:* The solution of oxidized products was first centrifuged at 10000 rpm for 20 minutes to remove the insoluble species. The insoluble species were collected, and characterized with size exclusion chromatography. Either Amberlite HPR1100 or Lewatit TP 207 cation exchange resins were added to the remaining water solution to remove free metal cations and stirred overnight. The solutions were then filtered over a 0.2 μm filter and freeze dried to generate resinous or powdery materials. The cation exchange resins made the resulting freeze-dried material easier to handle and removed the majority of the metal catalyst as shown in ICP-OES data for several samples in **Table S2**. The solids recovered after freeze drying consisted of powders or resinous materials. The differences were the type of cation exchange resin that was used and the type of metal catalyst used in the reaction. Typically, for reactions

run with  $\text{CuSO}_4$  and  $\text{KMnO}_4$  the resulting freeze-dried solids were powder-like, whereas for  $\text{FeSO}_4$  and  $\text{CoSO}_4$  the products had a more resinous texture.

*Size exclusion chromatography (SEC)*: The molecular weight distributions of the water-soluble products were determined using an Agilent 1260 HPLC system with PL Aquagel-PH30 and PL Aquagel-OH50 columns in series at a temperature of 30 °C. The HPLC system was equipped with UV detectors at 210 nm and 270 nm, an evaporative light scattering detector (ELSD), and a refractive index detector (RID). Samples were filtered using a 0.2-micron filter prior to injection into the HPLC systems and the HPLC system contained an in-line filter in front of the guard column. Samples from the reactions were run directly, without dilution or concentration. **Figures S2-S6** show the SEC data using ELSD. The eluent was 1 mM ammonium bicarbonate buffer at pH 9. Polystyrene sulfonate standards with molecular weights ( $M_p$ ) of 246, 1690, 5180, 7540, 16000, 29000, 67000  $\text{gmol}^{-1}$ . Deconstructed aqueous samples were fit with the calibration samples and used to determine the molecular range distribution (100-600  $\text{gmol}^{-1}$ ).

SEC of water-insoluble species were determined using an Agilent 1260 HPLC system with 2 PLgel MIXED-D columns in series equipped with an ELSD. HPLC grade Toluene was used as the eluent. Polystyrene standards with molecular weights ( $M_p$ ) of 370, 580, 855, 1920, 2970, 4900, 9960, 19920, 30230, 45120  $\text{gmol}^{-1}$  were used for calibration.

SEC of the native LDPE was determined by SGS Polymer Solutions Inc. using trichlorobenzene as an eluent at 130 °C and polystyrene standards for molecular weight calibration.

*Fourier-transform infrared spectroscopy (FTIR)*: Samples for FTIR analysis were prepared by evaporating 50 mL of reaction liquid onto Teflon substrates and drying them in a vacuum oven. IR spectra were collected with a Bruker LUMOS ATR-FTIR microscope using a germanium probe tip contacting the residue left over from evaporation. Each spectrum consisted of 16 averaged scans at a resolution of 4  $\text{cm}^{-1}$  and an atmospheric correction was applied to remove vapor contributions from water and  $\text{CO}_2$ . The spectra were then transferred into OriginLab and the spectra were baseline-corrected and normalized. **Figures S7-S10** and **Figure S18** show the FTIR spectra of each reaction.

*Elemental analysis*: Native LDPE film and water-soluble oxidized products (freeze-dried) were sent to ALS Environmental for CHN analysis. Samples were analyzed with a Perkin Elmer Series II 2400 CHNS/O Analyzer on CHN mode. Combustion of the samples occurs at 950 °C and reduction of gases at 640 °C. The instrument uses IR cells to detect the gases. The instrument was calibrated on Acetanilide OAS (Elemental Microanalysis; B2000). Before analysis the calibration was verified with Acetanilide OAS and EDTA (Alpha Resources; AR2092) and verified again with Acetanilide after analysis. The percent carbon recovered was determined from comparing the amount of carbon in the original LDPE film to the amount of carbon present in the degraded products. The raw data is shown in **Table S2** and **Table S3** and associated calculations are shown in Equations 1 and 2.

Total Organic Carbon (TOC) Analysis: Samples were submitted to Hall Environmental Analysis Laboratory Inc. (Eurofins Environment Testing South Central, LLC).

*Aliphatic Dicarboxylic Acid Spiking Experiments:* A sample was oxidized with 10 wt%  $\text{KMnO}_4$  at a reaction temperature of 130 °C. A stock solution of that sample (1 mg/mL) in 50:50 (v/v) water methanol solution was prepared along with stock solutions of dicarboxylic acid standards (100  $\mu\text{g/mL}$ ) in THF. Samples were diluted to 100  $\mu\text{g/mL}$  and spiked with 10  $\mu\text{g/mL}$  of each aliphatic dicarboxylic acid standards (C4-C12). The final solution solvent composition was 10:45:45 (v/v) THF: water: methanol. The data are shown in **Figure S12**.

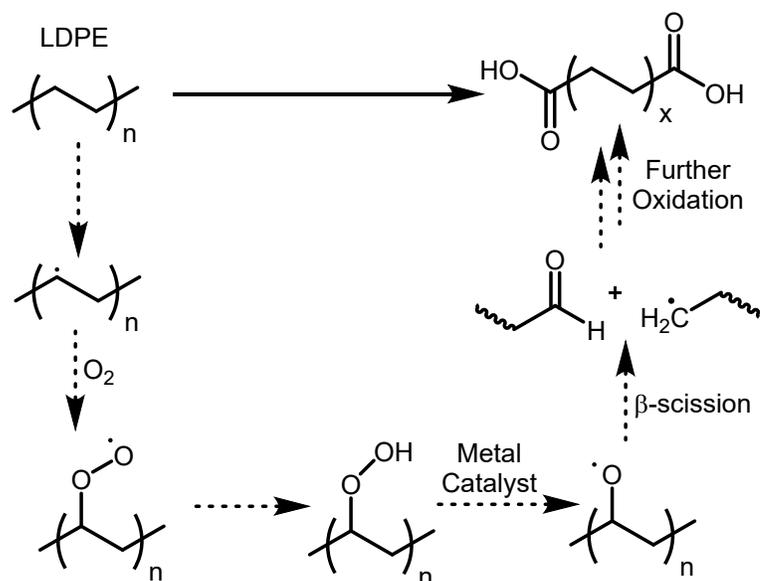
*Aliphatic Dicarboxylic Acid Calibration Curve Preparation:* A stock solution of aliphatic dicarboxylic acid standards ranging of C4-C12 was prepared at a 1 mg/mL in a 10:45:45 (v/v) THF: water: methanol solution. This mixture of solvents was used to ensure carboxylic acid solubility and remove possible matrix effects across all samples. Several deuterated internal standards including succinic acid-2,2,3,3,- $\text{D}_4$ , adipic acid 3,3,4,4,- $\text{D}_4$ , and suberic acid 2,2,7,7,- $\text{D}_4$  were combined to generate 250  $\mu\text{g/mL}$  solution in 10:45:45 (v/v) THF: water: methanol to ensure solubility. The solutions were combined to generate a 100, 50, 25, 12.5, 6.25, and 3.125  $\mu\text{g/mL}$  solution of C4-C12 aliphatic dicarboxylic acid standards and 5  $\mu\text{g/mL}$  of deuterated internal standards. The samples were analyzed with HPLC-MS to generate a calibration curve for each aliphatic dicarboxylic acid standard by plotting the ratio of signal of standards versus internal standards as a function of concentration as shown in **Figure S24**.

*Aliphatic Dicarboxylic Acid Quantification:* A 1.9 mL 10:45:45 (v/v) THF: water: methanol solution containing 5  $\mu\text{g/mL}$  of deuterated internal standards. 100  $\mu\text{L}$  of each sample was added and analyzed using HPLC-MS. Quantification of each aliphatic dicarboxylic acid was performed using the calibration curves generated of diacid standards (**Figure S24**).

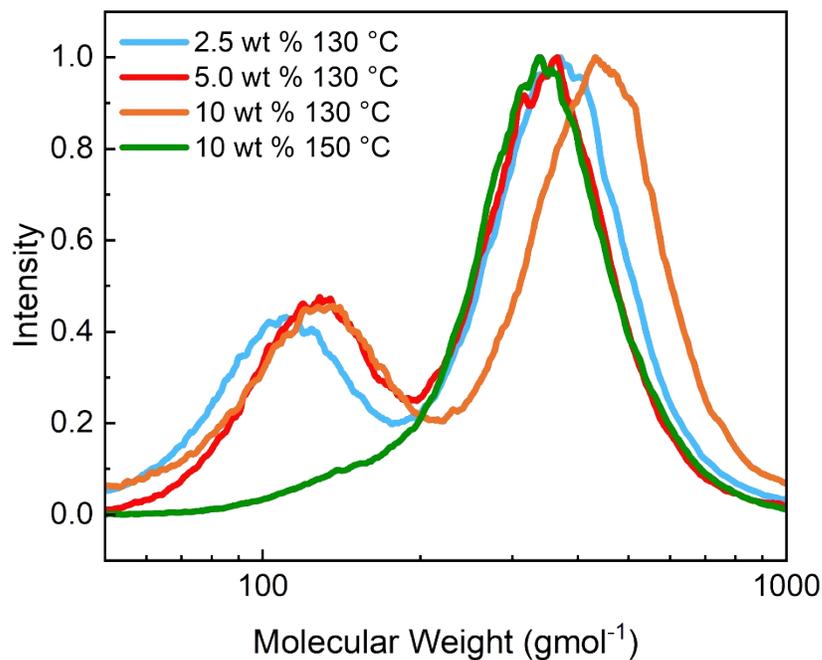
*High-Performance Liquid Chromatography Mass Spectrometry (HPLC-MS):* Characterization was performed with a Waters Acquity UPLC system with an Acquity C18 column (1.7  $\mu\text{m}$ , 2.1 x 100 mm) at a constant flow rate of 0.3 mL/min, and injection volume of 10  $\mu\text{L}$ , and a column oven temperature of 25 °C. The mobile phase solvents consisted of (A) water containing 0.1 wt % of formic acid and (B) methanol containing 0.1 wt % of formic acid. The solvent conditions for separation were: 0-1 min hold at 95 % A, 1-4 min linear ramp to 45 % A, 4-20 min linear ramp to 1 % A and a 3 min hold. Compounds were ionized by electrospray ionization in negative mode using a 2.1 kV spray voltage on a Waters Xevo TQ-S micro mass spectrometer. The desolvation and source temperatures were set to 450 °C and 150 °C, respectively. Ions were scanned between a  $m/z$  range of 30-650. Nitrogen gas was used for desolvation and for cone gas at 500 L/hr and 1 L/hr, respectively. The cone voltage was -25 V.

*Direct Injection Electrospray Ionization Mass Spectrometry (ESI-MS):* Direct injection ESI-MS was performed using a Waters Xevo G2-S on water soluble oxidized products at a 0.1 mg/mL concentration. The ESI were performed in both negative with settings comprised an ionization voltage of 2.0 kV, source temperature of 120 °C, acquisition mass range of 50-500 Da, scan time of 0.5 s and centroid data format. MassLynx software version 4.0 (Waters, USA) was used to control the instrument and for data processing.

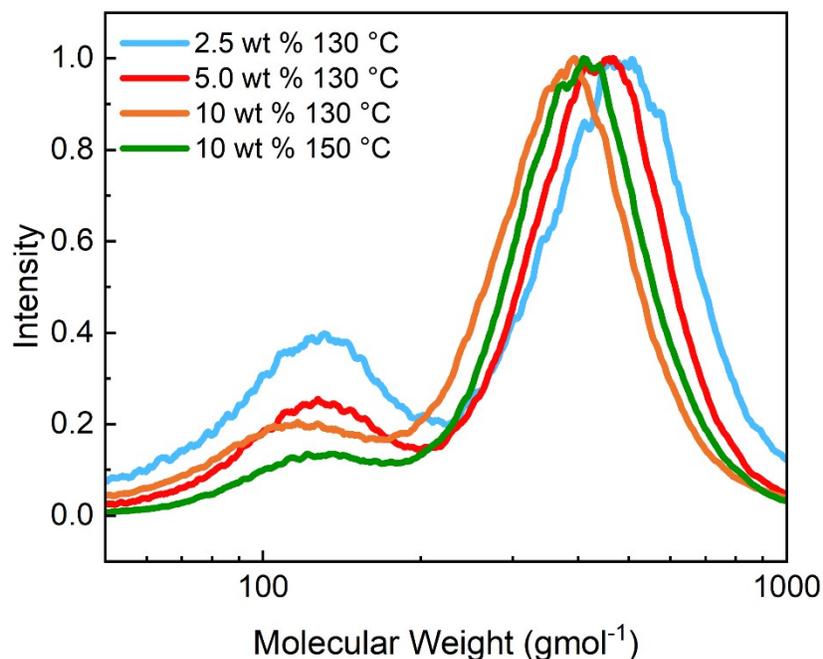
*Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES):* Samples were water soluble and therefore were simply dissolved in 25 mL of water, followed by dilution up to 50 mL with 2% nitric acid. Elemental analysis of the six samples was carried out using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer Avio 500, Groton, CT). ICP-OES background-corrected emission lines were chosen for evaluation by their optimal performance for each element. Samples were analyzed along with standard elemental reference materials (Inorganic Ventures, prepared in 1% nitric acid). Replicates were performed for each sample set. The data are shown in **Table S1**.



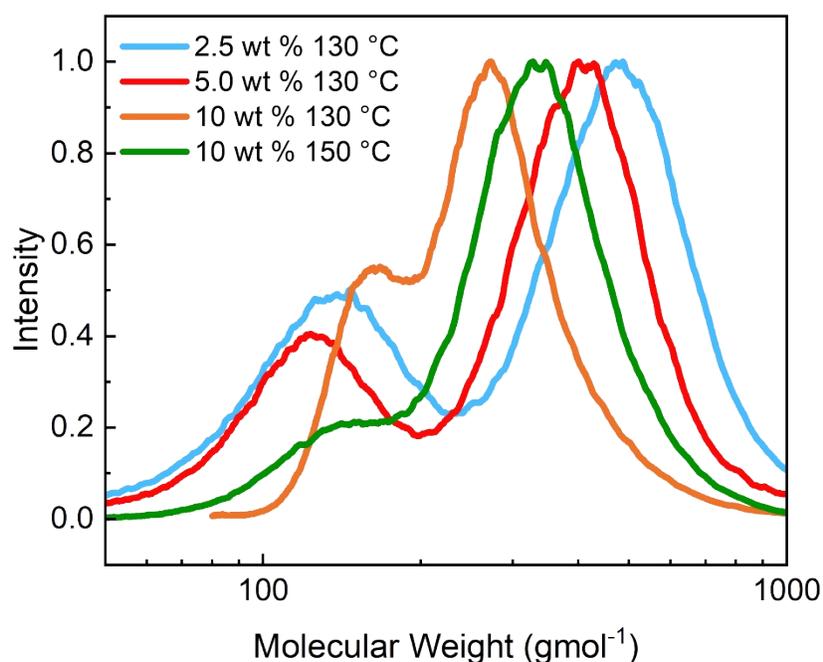
**Figure S1:** Generalized reaction mechanism of metal catalyzed polyethylene autoxidation. Note that this mechanism is a simplified and other mechanisms exist.<sup>1-4</sup>



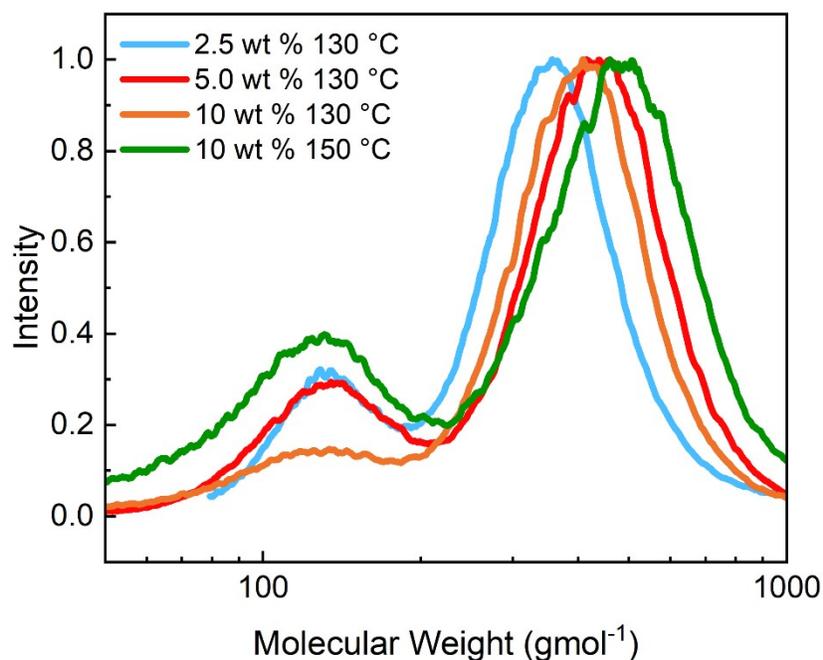
**Figure S2:** Size exclusion chromatograms of water-soluble oxidized products using an ELSD for  $FeSO_4 \cdot 7H_2O$  as the metal catalyst. Reaction conditions: initial oxygen pressure of 100 PSI and 20 h reaction time.



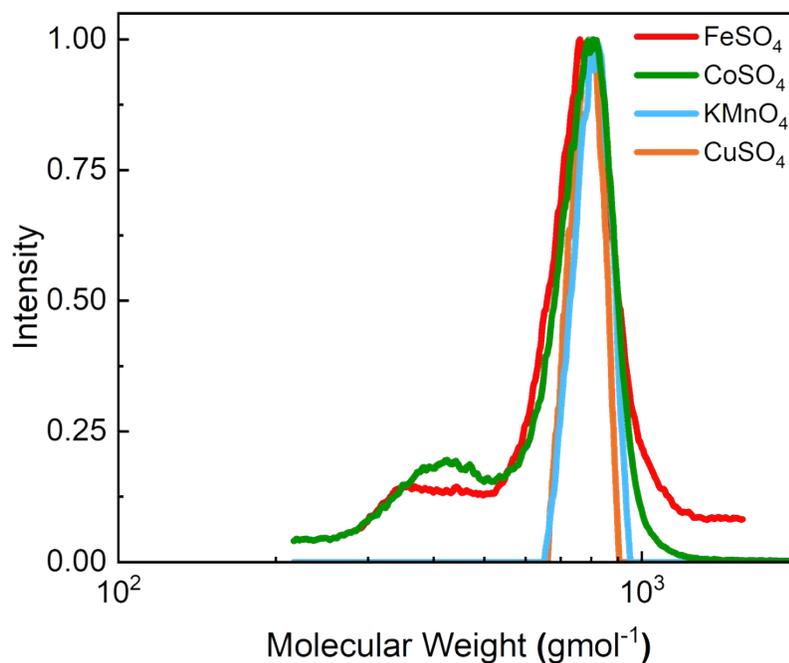
**Figure S3:** Size exclusion chromatograms of water-soluble oxidized products using an ELSD for  $\text{KMnO}_4$  as the metal catalyst. Reaction conditions: initial oxygen pressure of 100 PSI and 20 h reaction time.



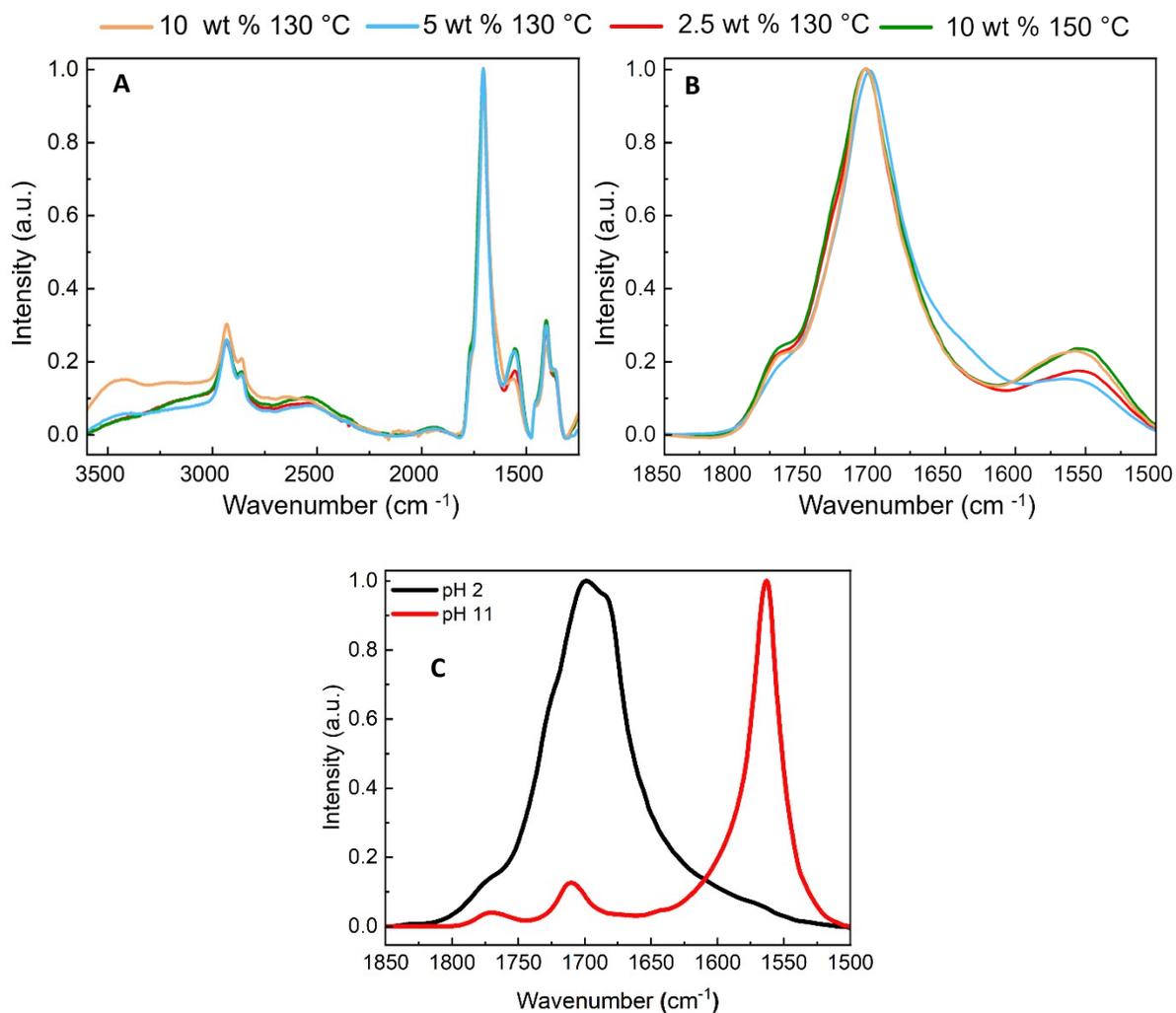
**Figure S4:** Size exclusion chromatograms of water-soluble oxidized products using an ELSD for  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  as the metal catalyst. Reaction conditions: initial oxygen pressure of 100 PSI and 20 h reaction time.



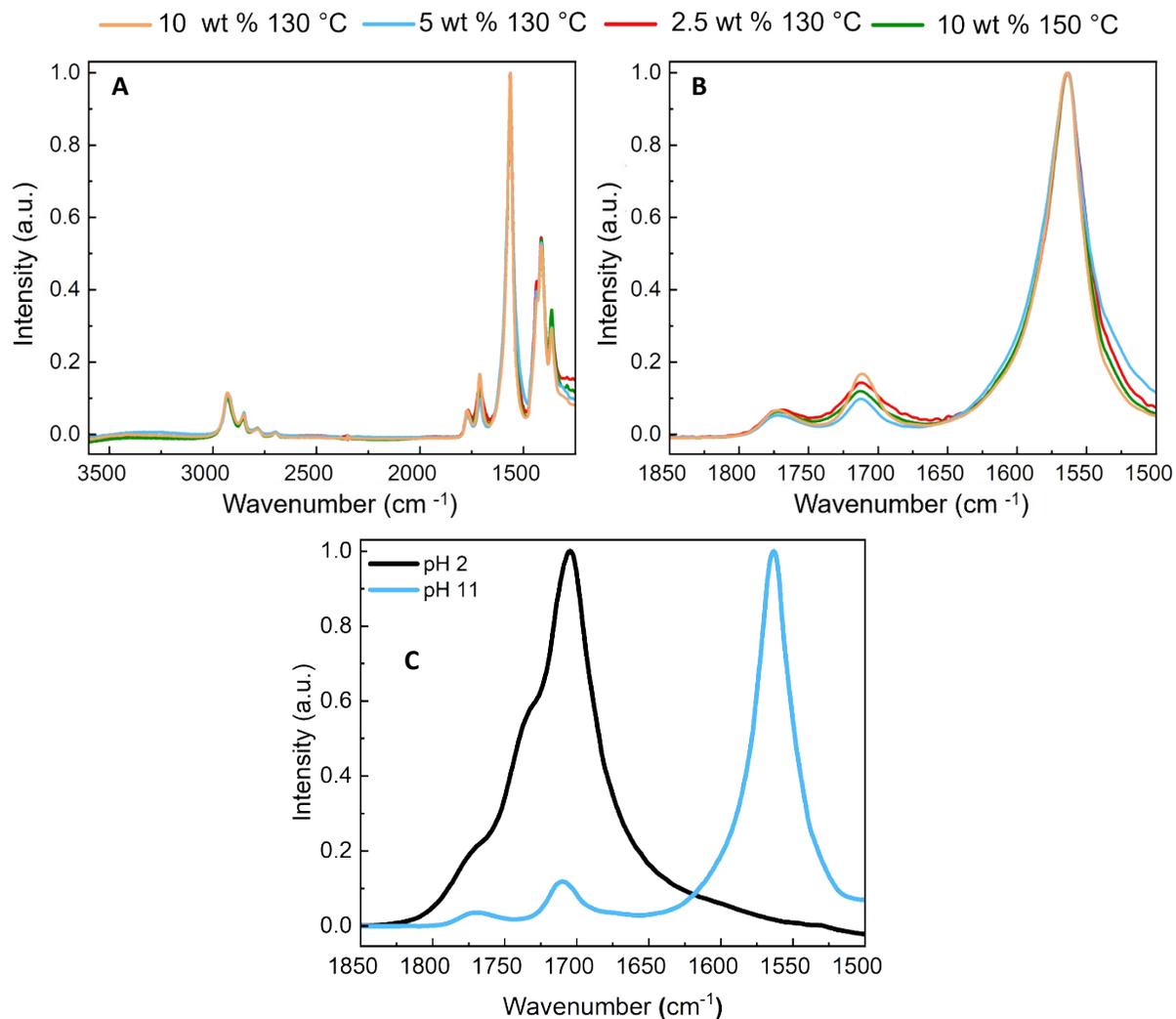
**Figure S5:** Size exclusion chromatograms of oxidized water-soluble LDPE products using an ELSD for  $\text{CuSO}_4$  as the metal catalyst, initial oxygen pressure of 100 PSI and 20 h reaction time.



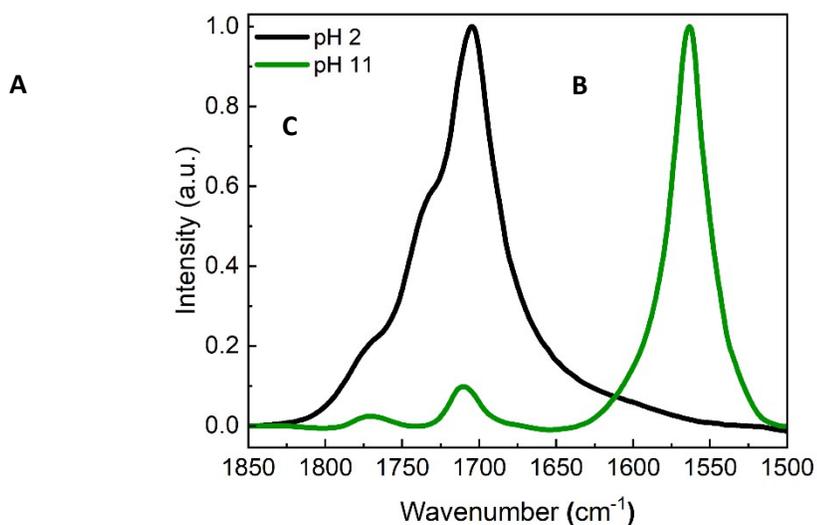
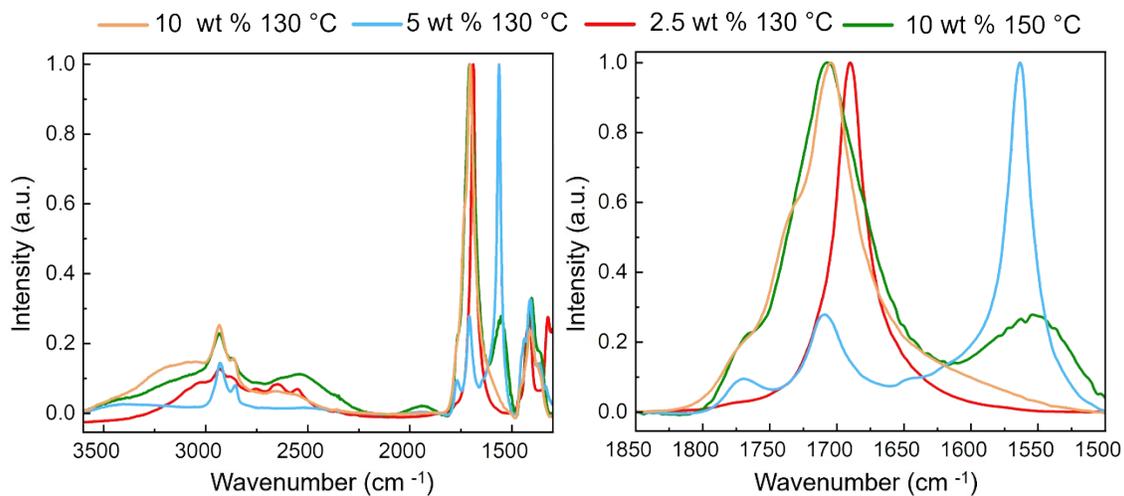
**Figure S6:** Size exclusion chromatograms of oxidized toluene-soluble LDPE products using an ELSD for various metal catalysts at 5 wt % catalyst loadings and a reaction temperature of 130 °C, initial oxygen pressure of 100 PSI and 20 h reaction time.



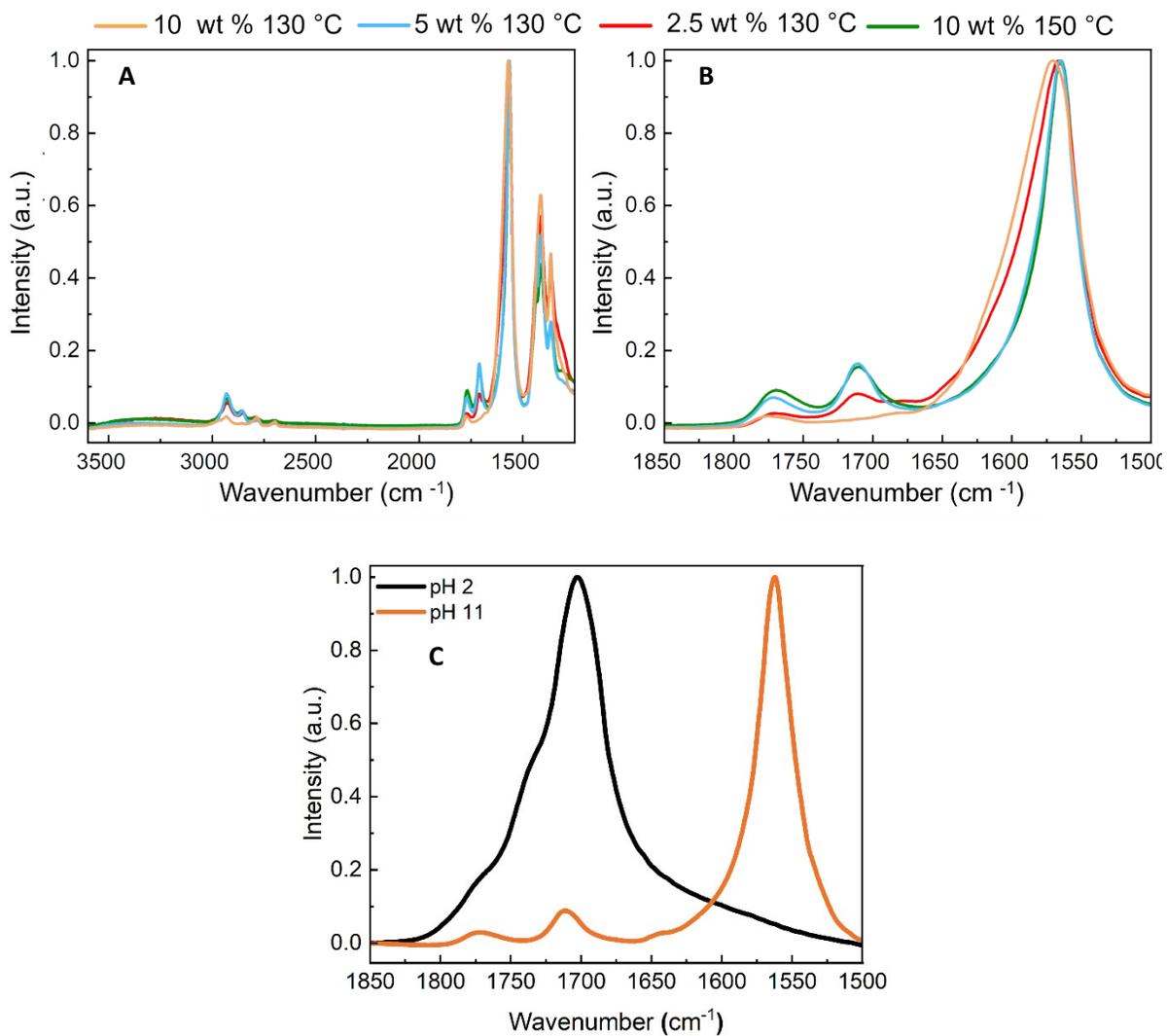
**Figure S7:** A) FTIR spectra for water-soluble oxidized products for  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . B) Expanded view of the carbonyl region. C) Spectra for the water-soluble oxidized products at pH 2 and pH 11. Reaction conditions: Initial oxygen pressure of 100 PSI and 20 h reaction time.



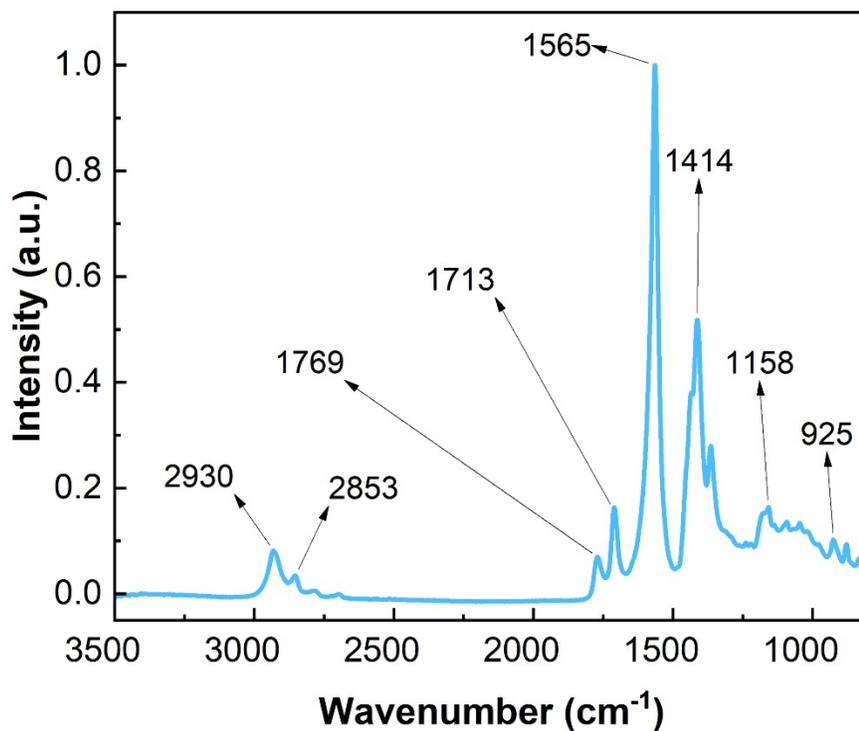
**Figure S8:** A) FTIR spectra for water-soluble oxidized products for  $\text{KMnO}_4$ . B) Expanded view of the carbonyl region. C) Spectra for the water-soluble oxidized products at pH 2 and pH 11. Reaction conditions: Initial oxygen pressure of 100 PSI and 20 h reaction time.



**Figure S9:** A) FTIR spectra for water-soluble oxidized products for  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  B) Expanded view of the carbonyl region. C) Spectra for the water-soluble oxidized products at pH 2 and pH 11. Reaction conditions: Initial oxygen pressure of 100 PSI and 20 h reaction time.

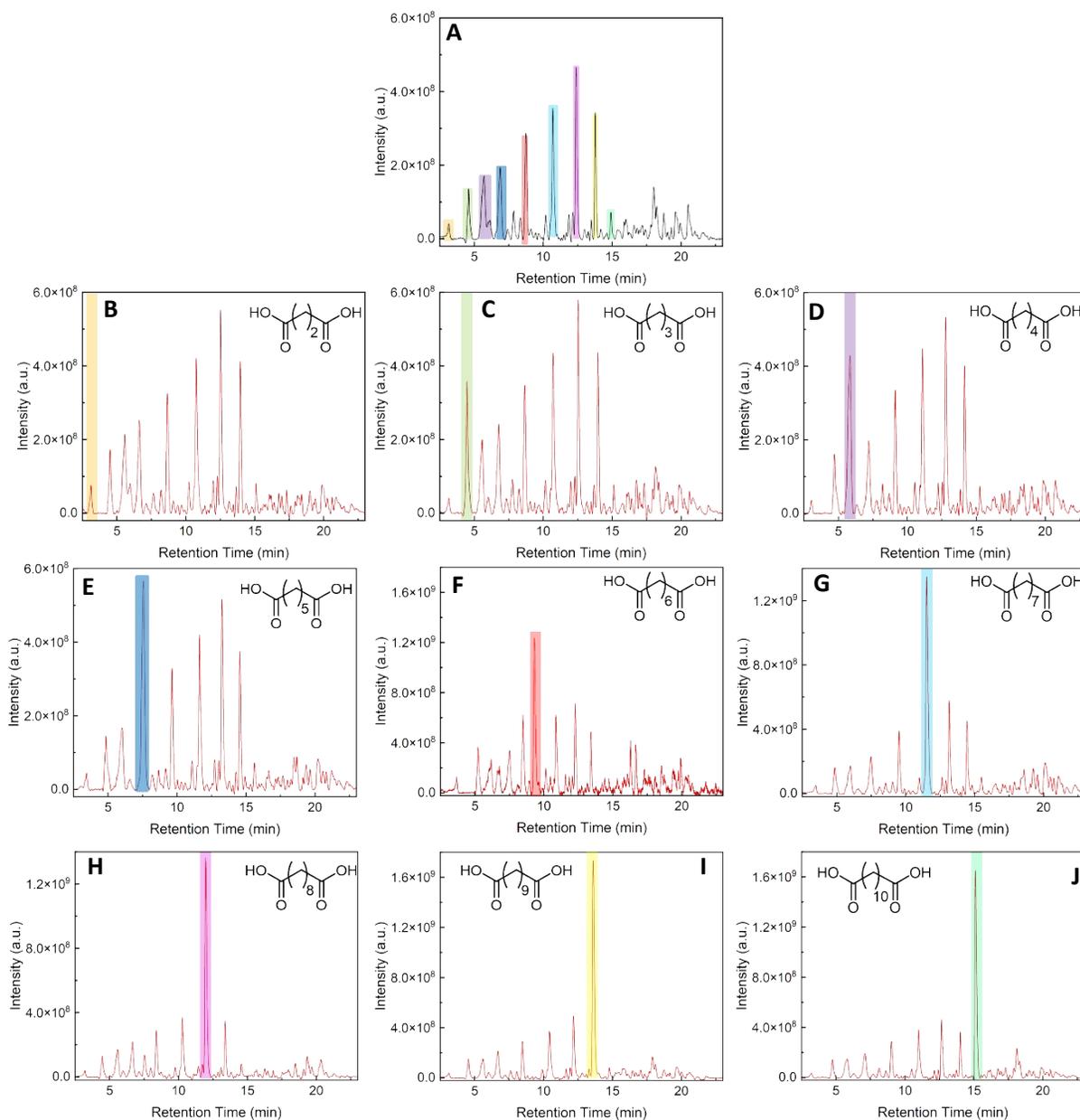


**Figure S10:** A) FTIR spectra for water-soluble oxidized products for CuSO<sub>4</sub>. D) Expanded view of the carbonyl region. C) Spectra for the water-soluble oxidized products at pH 2 and pH 11. Reaction conditions: Initial oxygen pressure of 100 PSI and 20 h reaction time.

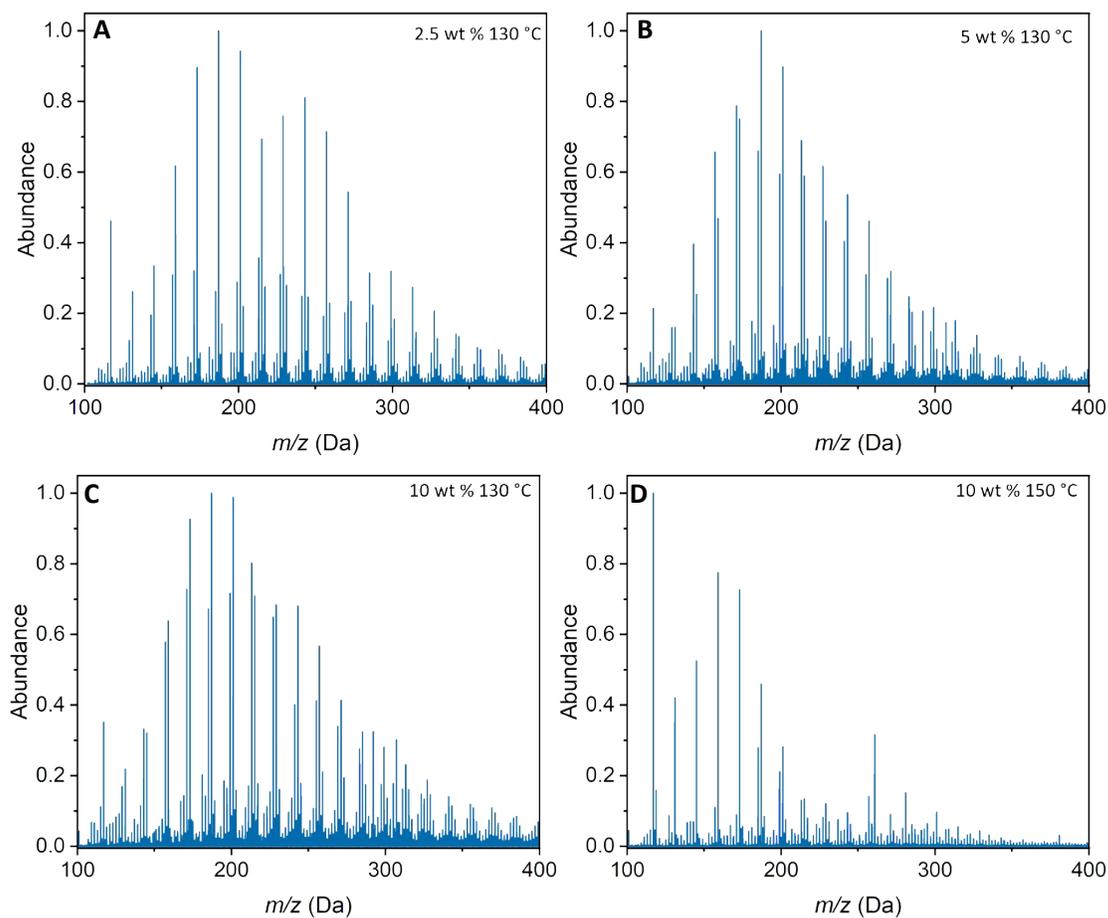


Peak (cm <sup>-1</sup> )	Functional Group
925	O-H Bending
1158	C-O stretching vibration
1414	CO <sub>2</sub> <sup>-</sup> symmetric stretching vibration
1565	CO <sub>2</sub> <sup>-</sup> asymmetric stretching vibration
1713	C=O stretching vibration of ketone
1769	C=O stretching vibration of $\gamma$ -lactone
2853	C-H stretching (symmetric)
2930	C-H stretching (asymmetric)

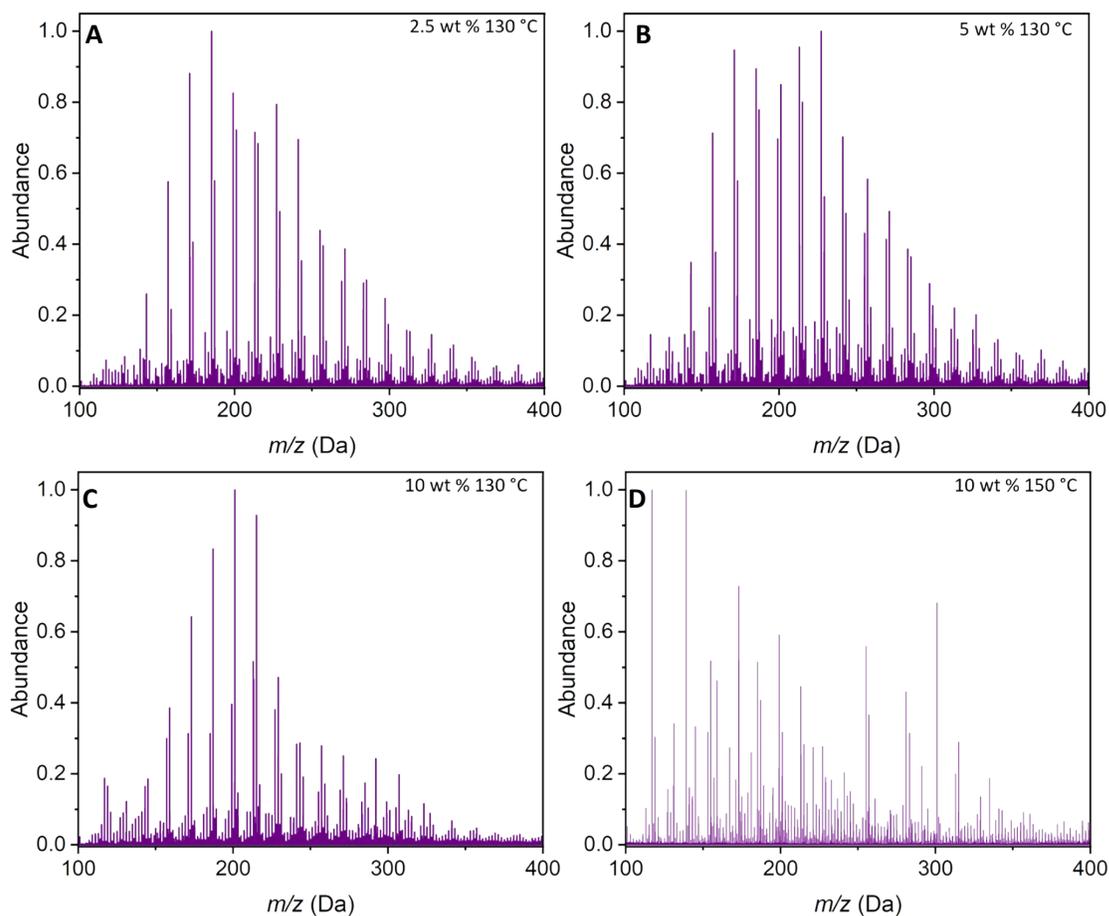
**Figure S11:** Representative FTIR spectra of oxidized products generated using 5 wt % CuSO<sub>4</sub> at 130 °C labeled with relevant peaks. Reaction conditions: Initial oxygen pressure of 100 PSI and 20 h reaction time.



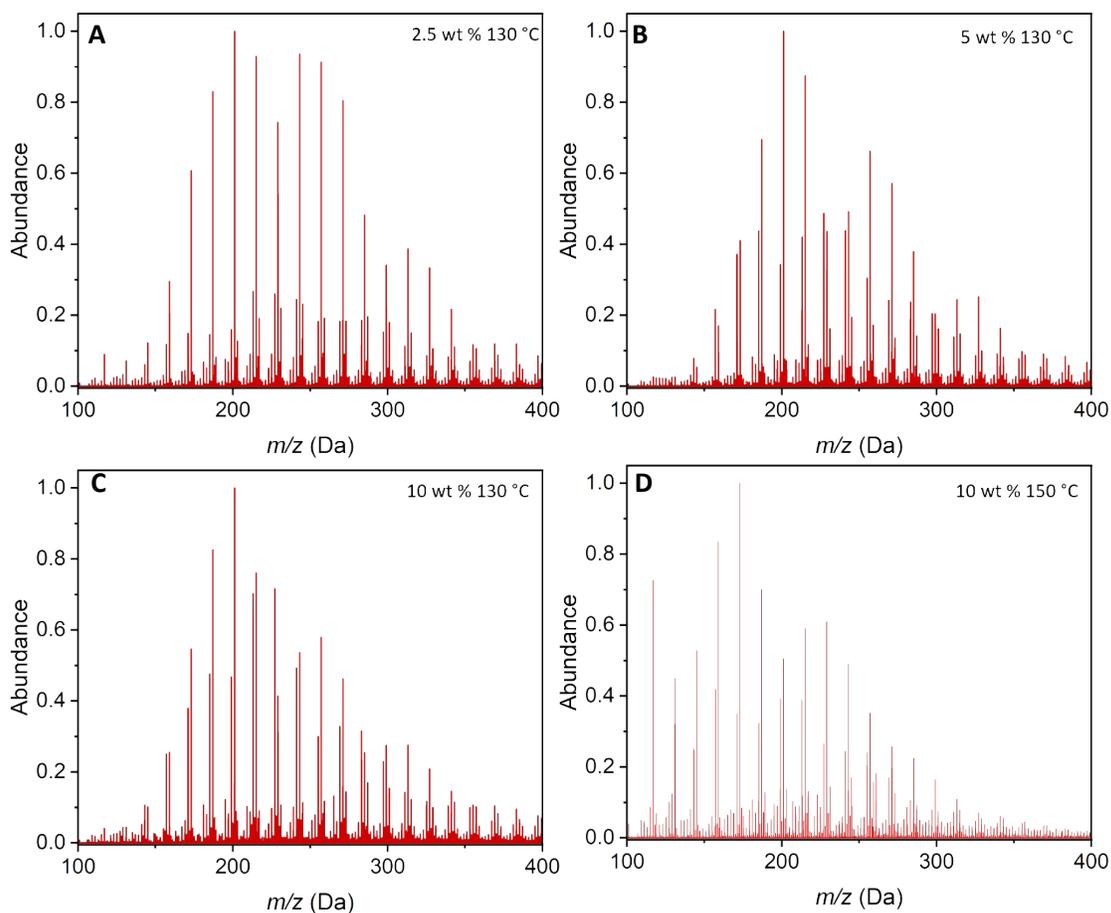
**Figure S12:** Spiking experiments of high-performance liquid chromatography mass spectrometry. (A) Sample chromatogram. (B) Sample spiked with succinic acid. (C) Sample spiked with glutaric acid. (D) Sample spiked with adipic acid. (E) Sample spiked with pimelic acid. (F) Sample spiked with suberic acid (G) Sample spiked with azelaic acid. (H) Sample spiked with sebacic acid. (I) Sample spiked with undecanedioic acid. (J) Sample spiked with dodecanedioic acid. Solutions contained 100  $\mu\text{g/mL}$  of oxidized sample and spiked samples contained 10  $\mu\text{g/mL}$  of standard.



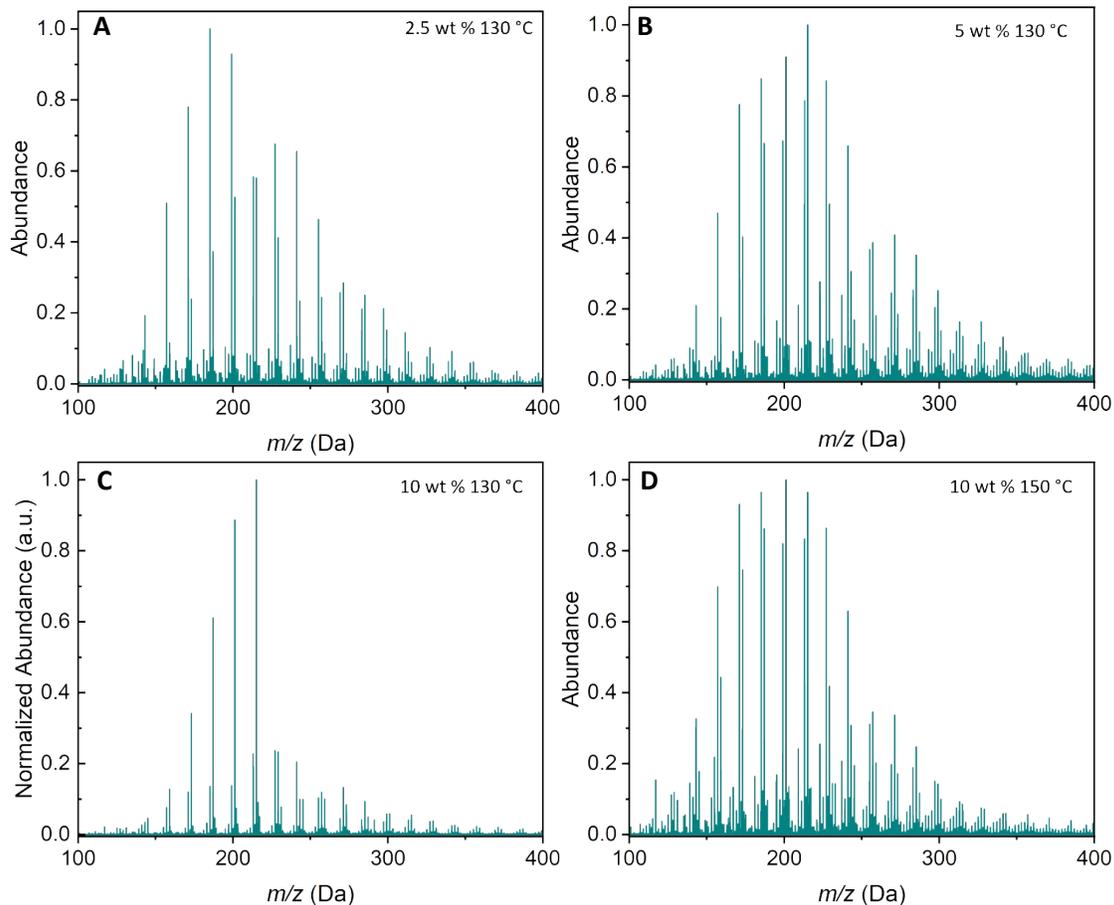
**Figure S13:** Direct injection electrospray ionization mass spectrometry results for water-soluble products using  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  using various conditions. A) 2.5 wt % catalyst loading and 130 °C. B) 5.0 wt % catalyst loading and 130 °C. C) 10 wt % catalyst loading and 130 °C. D) 10 wt % catalyst loading and 150 °C. Reaction conditions: Initial oxygen pressure of 100 PSI and 20 h reaction time.



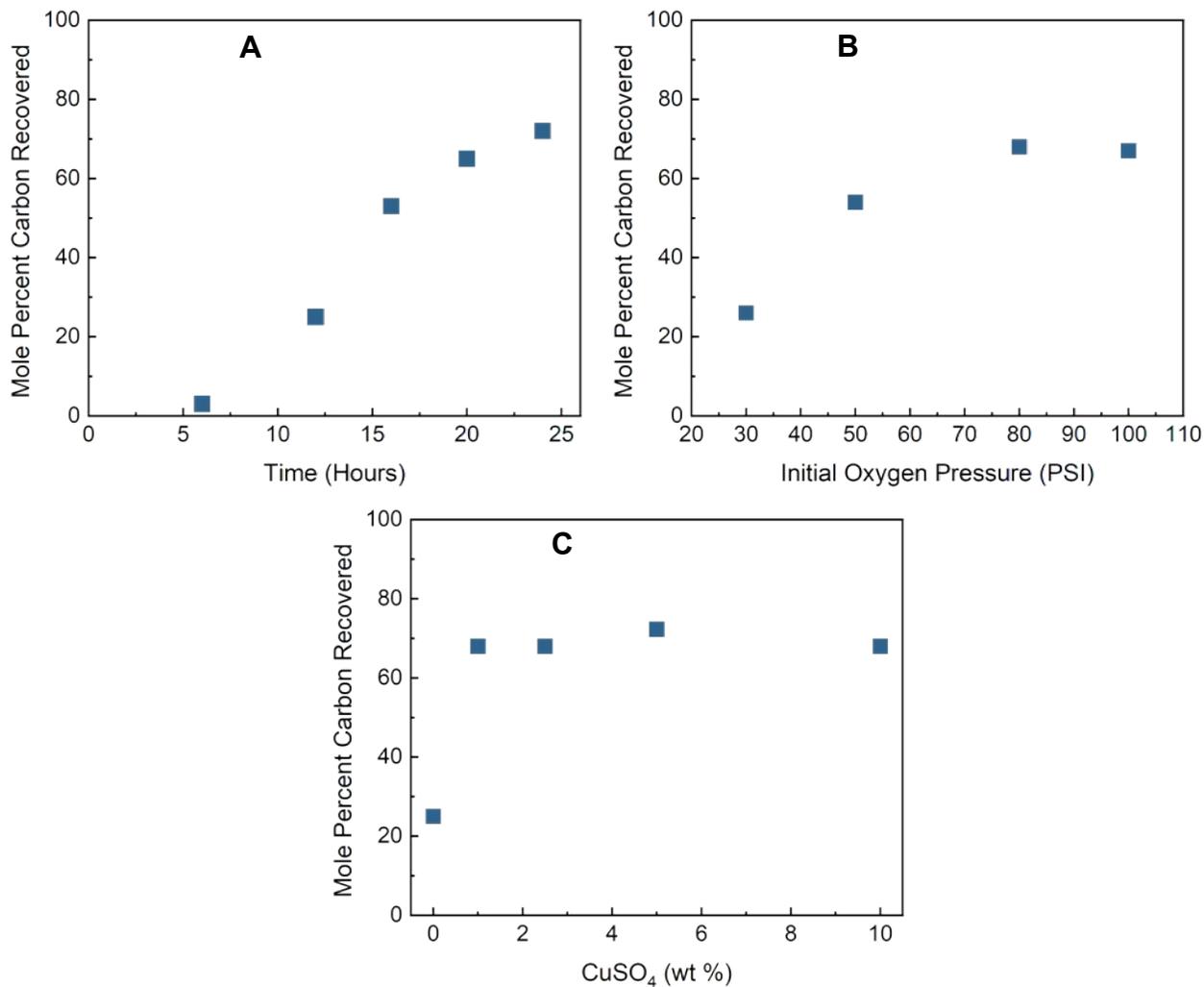
**Figure S14:** Direct injection electrospray ionization mass spectrometry results for water-soluble products using  $\text{CuSO}_4$  using various conditions. A) 2.5 wt % catalyst loading and 130 °C. B) 5.0 wt % catalyst loading and 130 °C. C) Reaction at 10 wt % catalyst loading and 130 °C. D) 10 wt % catalyst loading and 150 °C. Reaction conditions: Initial oxygen pressure of 100 PSI and 20 h reaction time.



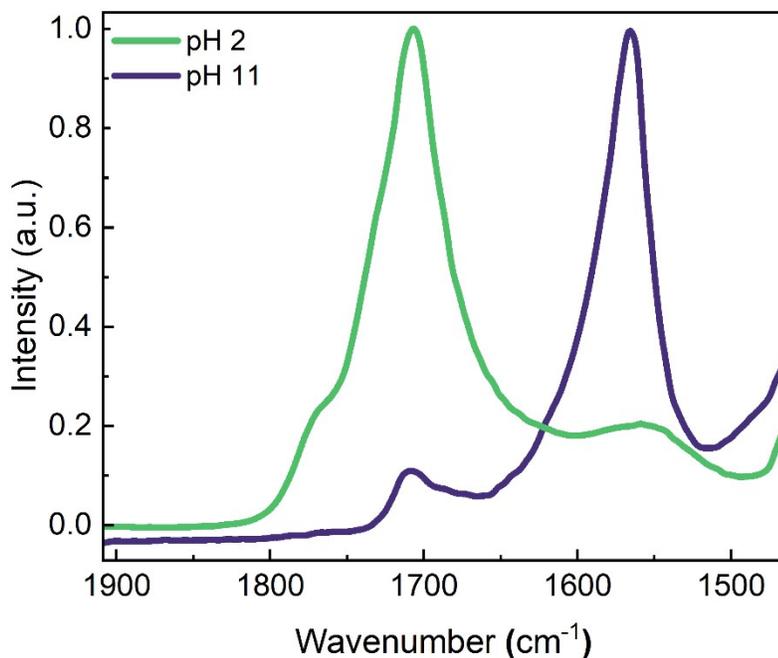
**Figure S15:** Direct injection electrospray ionization mass spectrometry results for water-soluble products using  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  using various conditions. A) 2.5 wt % catalyst loading and 130 °C. B) 5.0 wt % catalyst loading and 130 °C. C) 10 wt % catalyst loading and 130 °C. D) 10 wt % catalyst loading and 150 °C. Reaction conditions: Initial oxygen pressure of 100 PSI and 20 h reaction time.



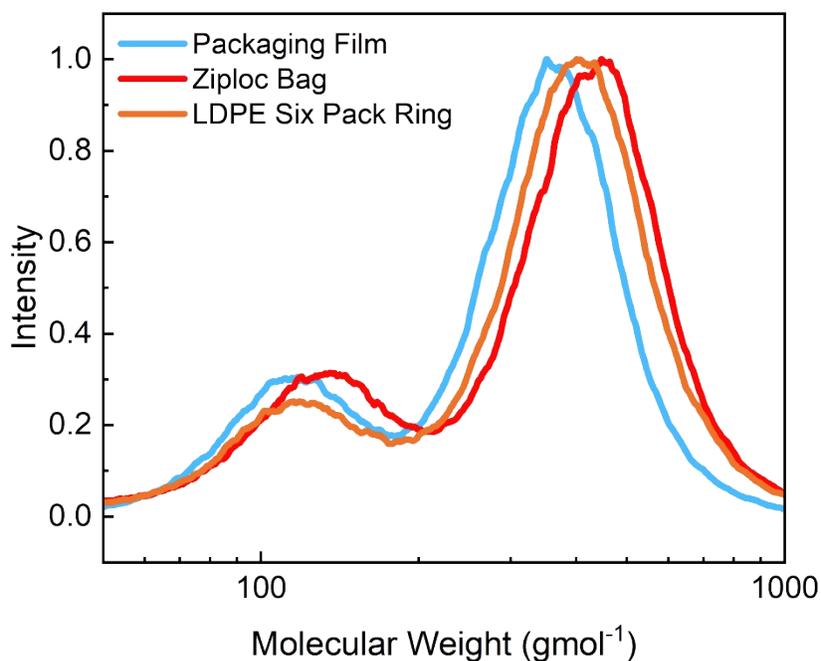
**Figure S16:** Direct injection electrospray ionization mass spectrometry results for water-soluble products using  $\text{KMnO}_4$  using various conditions. A) 2.5 wt % catalyst loading and 130 °C. B) 5.0 wt % catalyst loading and 130 °C. C) 10 wt % catalyst loading and 130 °C. D) 10 wt % catalyst loading and 150 °C. Reaction conditions: Initial oxygen pressure of 100 PSI and 20 h reaction time.



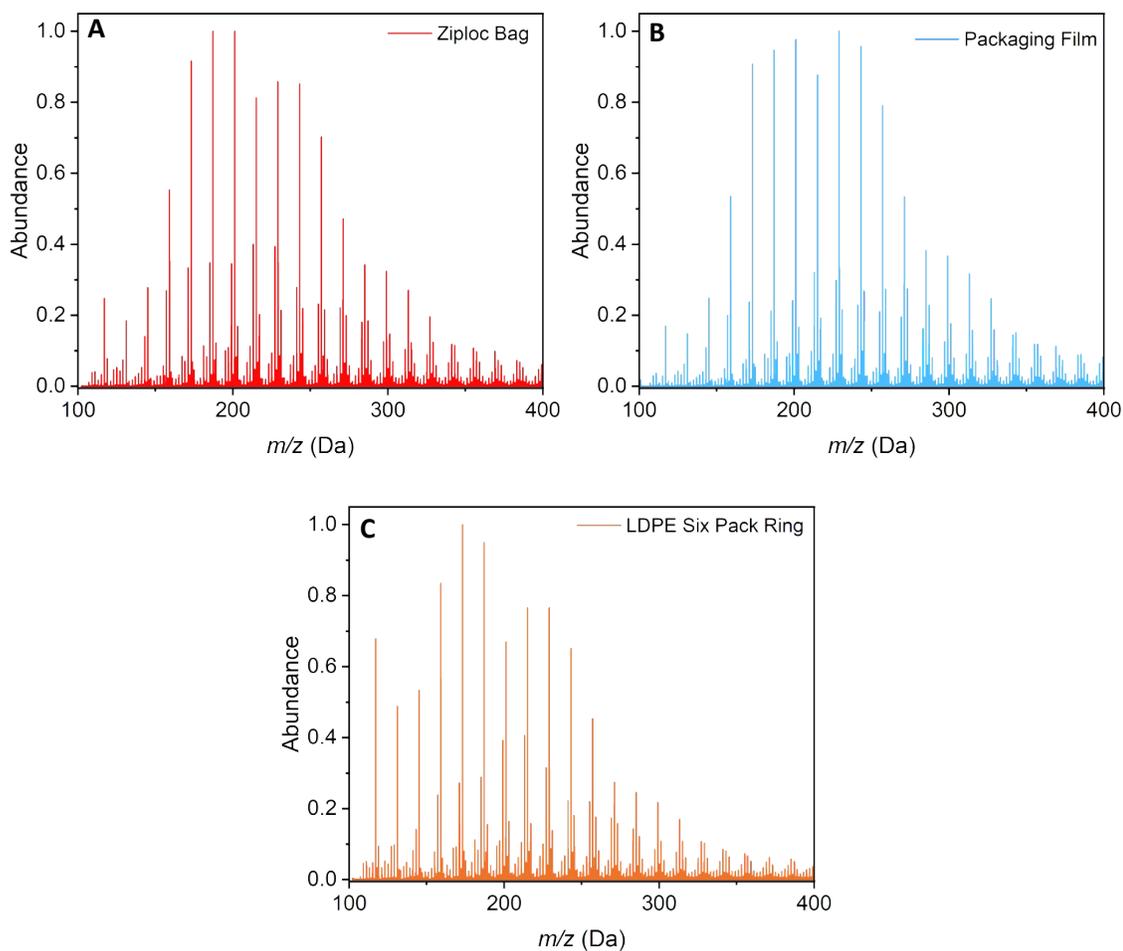
**Figure S17:** Carbon yield as soluble species during CuSO<sub>4</sub> catalyzed reactions. A) Reaction time variation using 2.5 wt % CuSO<sub>4</sub> with 100 PSI Oxygen. B) Oxygen content variation using 2.5 wt % CuSO<sub>4</sub> for 20 h. C) CuSO<sub>4</sub> concentration variation with 100 PSI oxygen for 20 h. CuSO<sub>4</sub> loading is determined as weight percent versus LDPE substrate. Mole percent carbon recovered is determined by comparing the initial carbon content in LDPE films versus the total organic carbon content measurements from water soluble products. All reactions were run at a constant temperature of 130 °C.



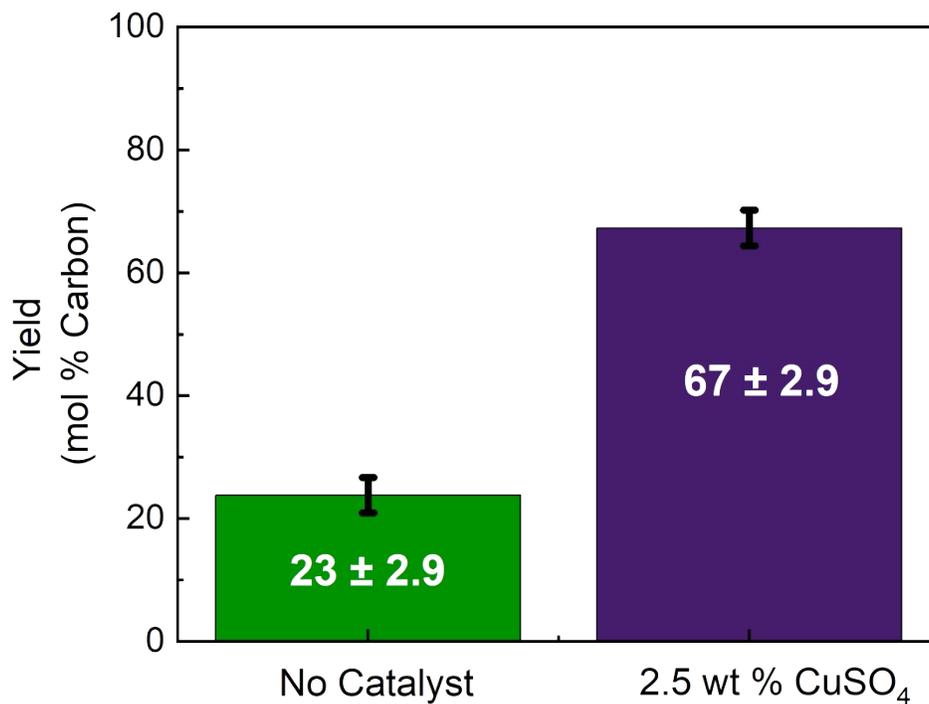
**Figure S18:** Representative FTIR spectrum for  $\text{CuSO}_4$  catalyzed oxidation reactions of LDPE. pH was shifted to show the shift for the carboxylic acid peak and to show the presence of other carbonyl groups.



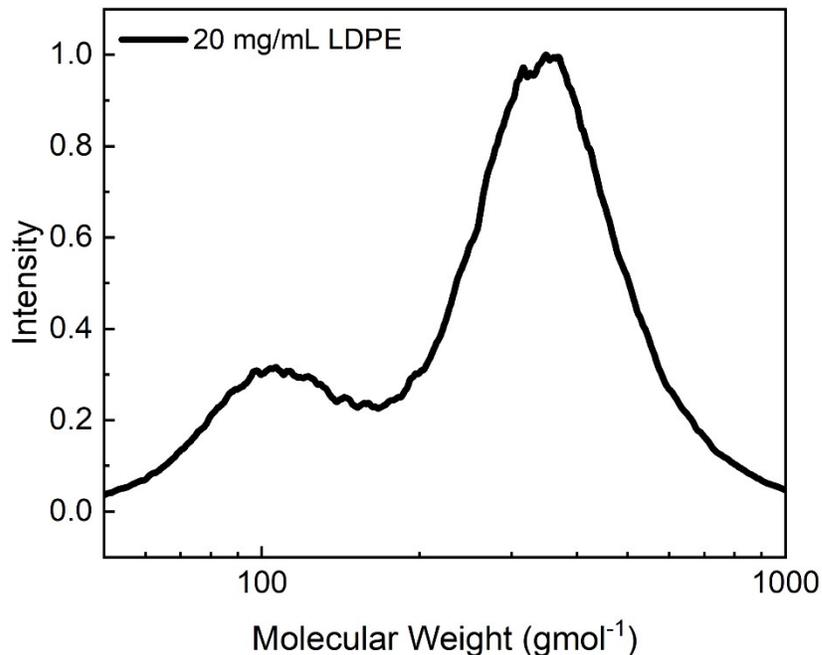
**Figure S19:** Size exclusion chromatogram of water-soluble oxidized LDPE commercial products using an ELSD. Reaction was run using the following conditions: 5 wt %  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  loading and a reaction temperature of 130 °C, initial oxygen pressure of 100 PSI and 20 h reaction time.



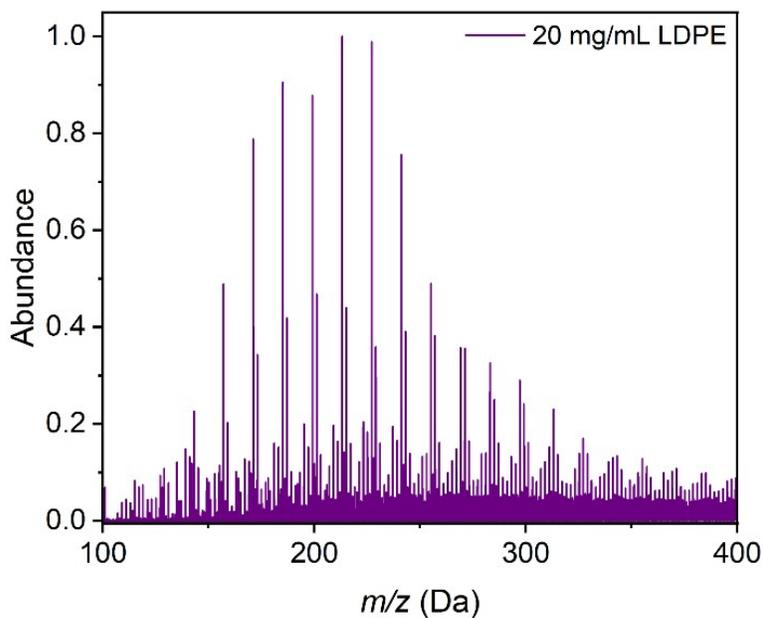
**Figure S20:** Direct injection electrospray ionization mass spectrometry results for oxidized LDPE commercial products using  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . (A) Ziploc bag (B) Packaging film (C) LDPE six pack ring. Reactions were run at 5 mg/ml LDPE product, 5 weight %  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and 130 °C with an initial pressure of 100 PSI Oxygen for 20 h.



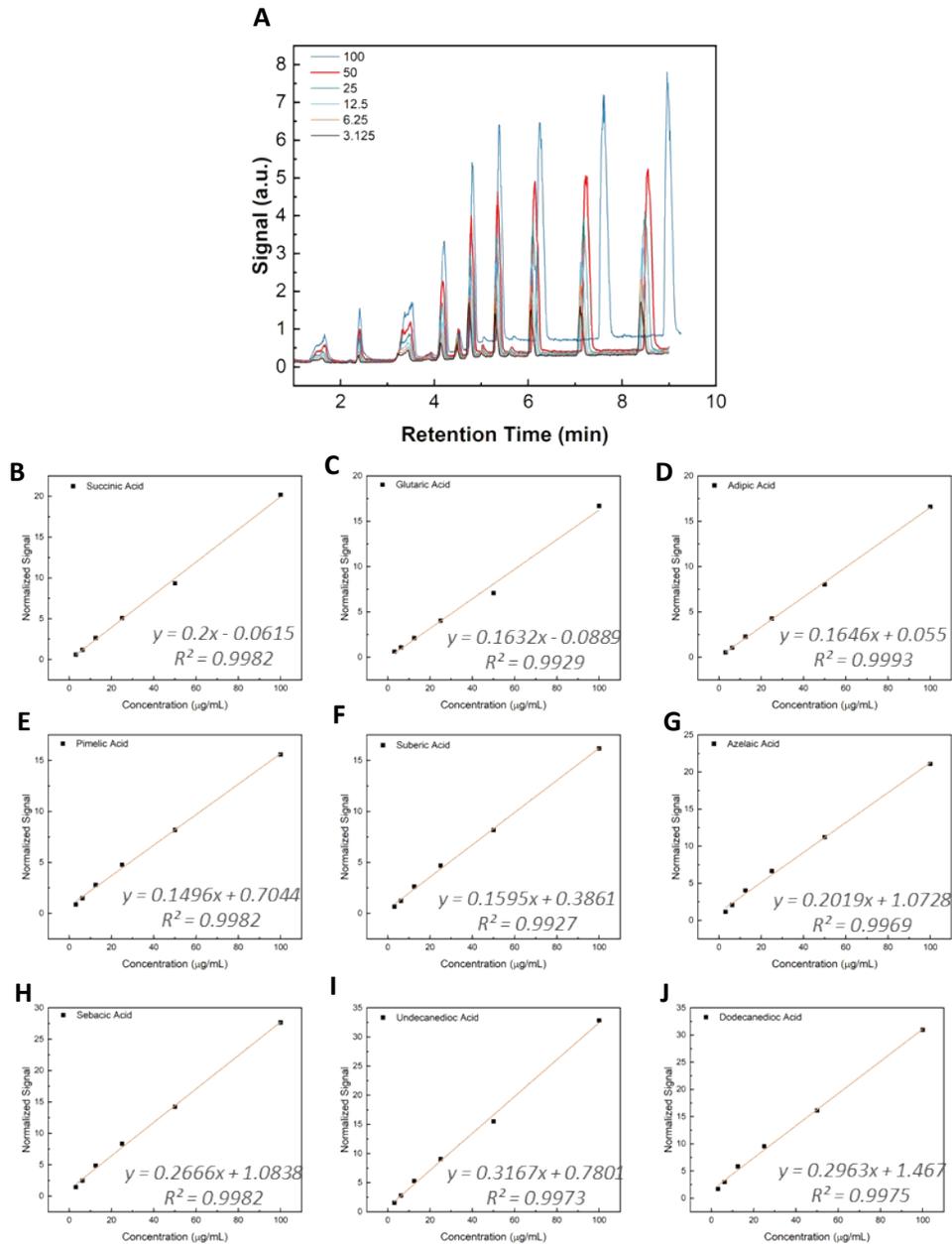
**Figure S21:** Carbon yield reproducibility in reactions without catalyst and with 2.5 wt % CuSO<sub>4</sub>. Reaction conditions: Initial oxygen pressure of 100 PSI, 20 h and at a constant temperature of 130 °C. Mole percent carbon recovered is determined by comparing the initial carbon content in LDPE films versus the total organic carbon content measurements from water soluble products. Error bars are standard deviations across three trials.



**Figure S22:** Size exclusion chromatograms of oxidized water-soluble oxidized products using an ELSD for 2.5 wt % of  $\text{CuSO}_4$ . Reaction was run at 130 °C with constant oxygen pressure of 100 PSI and 20 h reaction time.



**Figure S23:** Direct injection electrospray ionization mass spectrometry results for water-soluble products using  $\text{CuSO}_4$ . Reaction was run at 20 mg/ml LDPE loading, 2.5 weight %  $\text{CuSO}_4$ , and 130 °C with a constant pressure of 100 PSI Oxygen for 20 h.



**Figure S24:** Aliphatic Dicarboxylic acid standards calibration curve via LCMS. A) LCMS chromatogram with various concentration of standards overlaid (concentrations range from 3.125 -100 µg/ml. B) Calibration curve for succinic acid. C) Calibration curve for glutaric acid. D) Calibration curve for adipic acid. E) Calibration curve for pimelic acid. F) Calibration curve for suberic acid. G) Calibration curve for azelaic acid. H) Calibration curve for sebacic acid. I) Calibration curve for undecanedioic acid. J) Calibration curve for dodecanedioic acid.

**Table S1: Inductively Coupled Plasma Optical Emission Spectroscopy Data**

Catalyst	Reaction Conditions	Concentration (ppm)
FeSO <sub>4</sub>	5 wt % 130 °C	24.6 ± 5.8
FeSO <sub>4</sub>	10 wt % 130 °C	2.84 ± 0.1
CuSO <sub>4</sub>	5 wt % 130 °C	0.6 ± .1
CuSO <sub>4</sub>	10 wt % 130 °C	0.9 ± 0.0

**Table S2: Yield of reaction at varying conditions**

Polyolefin	Catalyst	Conditions (wt %)	Temperature (°C)	Mass Initial (g)	Mass Soluble (g)	Mass Insoluble (g)	Water Soluble (%C)	Water Insoluble (%C)
LDPE Film	FeSO <sub>4</sub>	2.5	130	1.9501	1.70	0.1231	48.99	63.9
		5	130	1.977	1.71	0.105	47.16	67.8
		10	130	2.033	1.65	0.056	48.53	66.6
		10	150	1.968	1.05	0	38	0
	KMnO <sub>4</sub>	2.5	130	2.03	2.40	0.17	43.34	61.4
		5	130	2.031	2.31	0.128	39.82	66
		10	130	2.023	1.48	0.144	46.68	63.9
		10	150	2.06	2.016	0	38.28	67.5
	CoSO <sub>4</sub>	2.5	130	1.997	1.88	0.19	52.71	64.42
		5	130	1.9955	2.19	0.128	41.89	64.6
		10	130	2.035	1.7581	0.137	54.1	66.5
	CuSO <sub>4</sub>	10	150	2.004	1.51	0	42.5	0
		2.5	130	1.9767	2.91	0.13	39.89	63.7
		5	130	1.9901	2.1936	0.072	38.18	68.7
		10	130	2.009	3.357	0.05	30.77	65.7
			10	150	2.08	2.51	0	25.6
Packaging Film	FeSO <sub>4</sub>	10	130	2.06	1.59	0.07	49.56	65.4
Sandwich Bag	FeSO <sub>4</sub>	10	130	1.9929	1.04	0.04	38.96	66.3
LDPE Six Pack Ring	FeSO <sub>4</sub>	10	130	2.07	0.997	0.065	46.18	64.9
LDPE Film (20 mg/mL)	CuSO <sub>4</sub>	2.5	130	8.023	6.64	0.4	51.95	58.2

**Table S3: Carbon Efficiency measurements at varying conditions**

Polyolefin	Catalyst	Conditions (wt %)	Temperature (°C)	Recovered Soluble %C	Recovered Insoluble %C	Volatile %C
LDPE Film	FeSO <sub>4</sub>	2.5	130	51	5	44
		5	130	49	4	47
		10	130	47	2	51
		10	150	24	0	76
	KMnO <sub>4</sub>	2.5	130	61	6	33
		5	130	54	5	41
		10	130	41	5	54
		10	150	45	0	55
	CoSO <sub>4</sub>	2.5	130	59	7	34
		5	130	55	5	40
		10	130	56	5	39
		10	150	38	0	62
	CuSO <sub>4</sub>	2.5	130	70	5	25
		5	130	50	3	47
		10	130	61	2	37
		10	150	37	0	63
Packaging Film	FeSO <sub>4</sub>	10	130	46	3	52
Sandwich Bag	FeSO <sub>4</sub>	10	130	24	2	74
LDPE Six Pack Ring	FeSO <sub>4</sub>	10	130	26	2	71
LDPE Film (20 mg/mL)	CuSO <sub>4</sub>	2.5	130	51	3	45

\* Using table S3 the recovered soluble and insoluble % C is determined using equation 1. % C lost to volatilization is determined using equation 2. LDPE Film contains 84 % C, Packaging film contained 86 % C, Sandwich bag contained 87 % C, and Six Pack Ring contained 86 % C.

(1)

$$\frac{\text{Mass of recovered products} \times \text{Water (in)soluble \% C}}{\text{Mass Film} \times 84 \% \text{ C in LDPE Film}} \times 100 = \text{Recovered \% C}$$

(2)  $100 - \text{Recovered \% C Water soluble} - \text{Recovered \% C insoluble} = \text{Volatile \% C}$

<b>CuSO<sub>4</sub> Catalyst Concentration</b>						
wt % CuSO <sub>4</sub>	TOC (g/L)	Total Volume	Mass Film	Mass Carbon in LDPE	Mass Water Soluble Carbon	Conversion
0	0.99	400	1.999	1.67916	0.396	23.58
1	2.87	400	2.001	1.68084	1.148	68.30
2.5	2.87	400	2.034	1.70856	1.148	67.19
5	3.03	400	1.995	1.6758	1.212	72.32
10	2.93	400	2.042	1.71528	1.172	68.33
<b>Reaction Time Variation</b>						
Time (h)	TOC (g/L)	Total Volume	Mass Film	Mass Carbon in LDPE	Mass Water Soluble Carbon	Conversion
6	0.14	400	2.031	1.70604	0.056	3.28
12	1.13	400	2.035	1.7094	0.452	26.44
16	2.27	400	2.033	1.70772	0.908	53.17
20	2.87	400	2.034	1.70856	1.148	67.19
24	3.13	400	2.005	1.6842	1.252	74.34
<b>Oxygen Content Variation</b>						
Oxygen Pressure	TOC (g/L)	Total Volume	Mass Film	Mass Carbon in LDPE	Mass Water Soluble Carbon	Conversion
30	1.13	400	2.003	1.68252	0.452	26.86
50	2.37	400	2.035	1.7094	0.948	55.46
80	2.93	400	1.995	1.6758	1.172	69.94
100	2.87	400	2.034	1.70856	1.148	67.19
<b>No Catalyst Reproducibility Studies</b>						
Sample	TOC (g/L)	Total Volume	Mass Film	Mass Carbon in LDPE	Mass Water Soluble Carbon	Conversion
1	0.99	400	1.999	1.67916	0.396	23.58
2	0.96	400	2.018	1.69512	0.384	22.65
3	1.2	400	1.993	1.67412	0.48	28.67
4	0.9	400	2.018	1.69512	0.36	21.24
<b>2.5 wt % CuSO<sub>4</sub> Reproducibility Studies</b>						
Sample	TOC (g/L)	Total Volume	Mass Film	Mass Carbon in LDPE	Mass Water Soluble Carbon	Conversion
1	2.87	400	2.034	1.70856	1.148	67.19
2	2.73	400	2.041	1.71444	1.092	63.69
3	3	400	2.015	1.6926	1.2	70.90

**Table S4:** Carbon Recovered of CuSO<sub>4</sub> catalyzed reactions determined via TOC

Unless noted otherwise, reaction conditions include 2.5 wt % CuSO<sub>4</sub>, 100 PSI initial oxygen pressure, 20 h of reaction time and a constant temperature of 130 °C.

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