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AQUEOUS CATALYTIC OXIDATIVE DECONSTRUCTION OF LDPE FILM

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Abstract

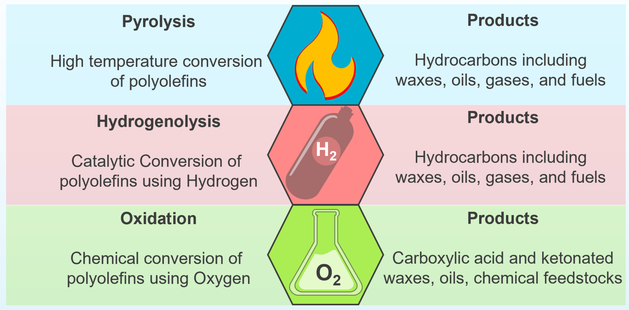
Massively accumulating plastic waste is a danger to terrestrial and aquatic ecosystems, as only about 9% is recycled.[1,2] In addition, since a significant fraction of fossil fuels are devoted to plastic production, single-use petroleum-based plastics pose a direct threat to the climate. Recycling or upcycling of these carbon-based materials is imperative to preserve the environment and to reduce energy consumption and associated CO_2 emissions.[3] Polyolefin films are particularly difficult to recycle as these can damage recycling equipment. Upcycling polyolefins is challenging due to the need to cleave C-C bonds in the backbones of these polymers.[4] In this work aqueous oxidative depolymerization of low-density polyethylene (LDPE) film for biological conversion was explored for various metal catalysts under different conditions. The catalysts included $CuSO_4$, $FeSO_4$, $CoSO_4$, and $KMnO_4$. The products were characterized by FTIR, SEC, and mass spectrometry. The extent of depolymerization and the product distribution were a strong function of temperature, with depolymerization in high yield occurring only at or above the melting temperature. Favorable conditions resulted in a high yield of C4-C12 aliphatic diacids.[5]

Materials and Methods

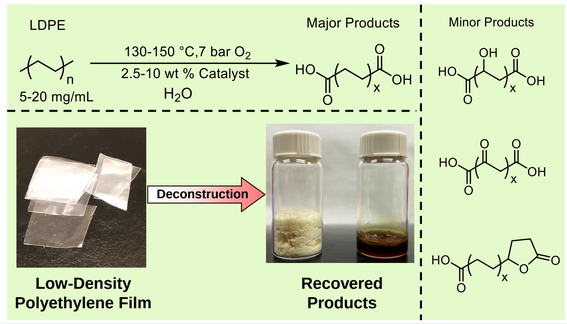
LDPE film was purchased from Goodfellow (30 μm). All other chemicals were purchased from Sigma Aldrich and used without further purification.

***Hydrothermal Oxidation*:** All reactions were performed in a 4520 Reactor by Parr Instruments. The 1 L reactor was charged with 400 mL Millipore (20 MΩ) H_2O, followed by addition of catalyst ($KMnO_4$, $CuSO_4$, $FeSO_4$•$7H_2O$, or $CoSO_4$•$7H_2O$). The solution was stirred to dissolve the catalyst and then 2-20g of low-density polyethylene film (cut into 1 in. by 1 in. squares) was added. The reactor was then sealed and purged with oxygen several times, followed by charging with oxygen to 7 bar. For reactions with 20 mg/mL LDPE, the oxygen pressure was held constant at 7 bar during the reaction. The reactor was then heated to either 130 or 150 °C and stirred for 20-24 hours.

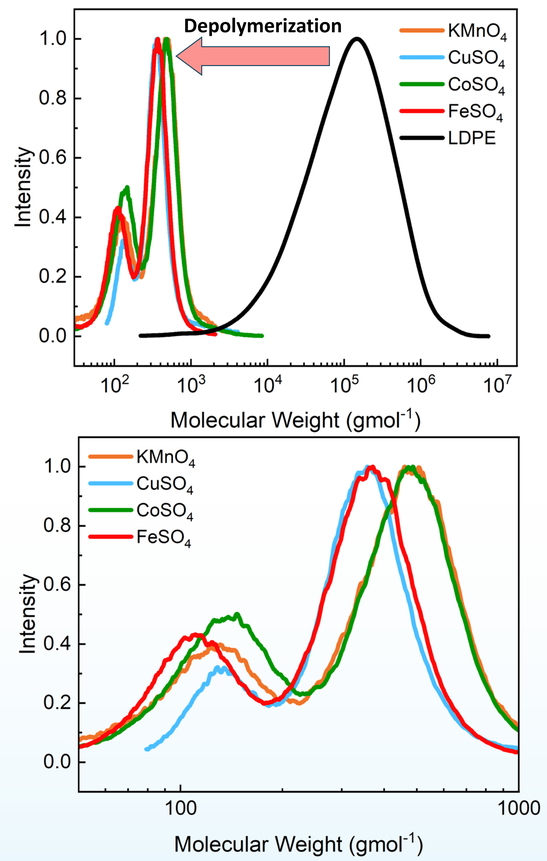
Polyolefin Deconstruction Techniques



Oxidative Reaction Conditions

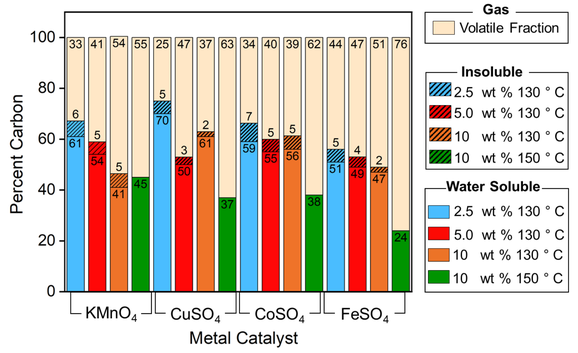


Size Exclusion Chromatography



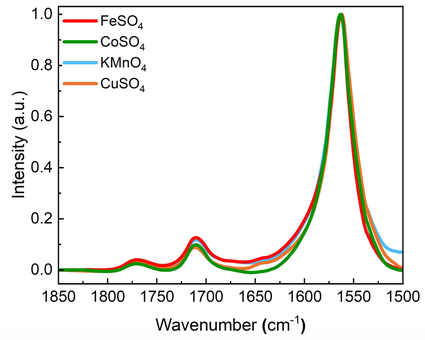
Molecular weights by size exclusion chromatography of oxidized water-soluble products (aqueous) compared to that of the original film (trichlorobenzene). The following reaction conditions were used: 2.5 wt % catalyst loading, 130 °C, and an initial oxygen pressure of 7 bar.

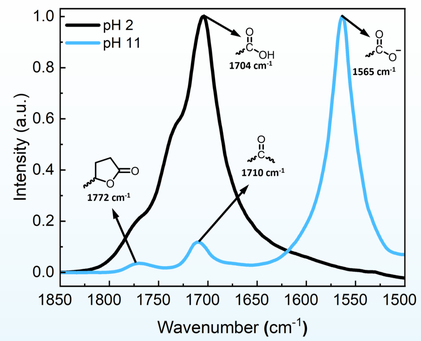
Carbon Yield



Carbon balance after LDPE oxidation using various catalyst concentrations and reaction temperatures. Using elemental analysis, percent carbon was determined by comparing carbon recovered in the water-soluble products with the carbon content of the initial LDPE film. The percent carbon present in volatile compounds was determined as the difference between the carbon of the initial LDPE film and that recovered in water soluble and insoluble products.

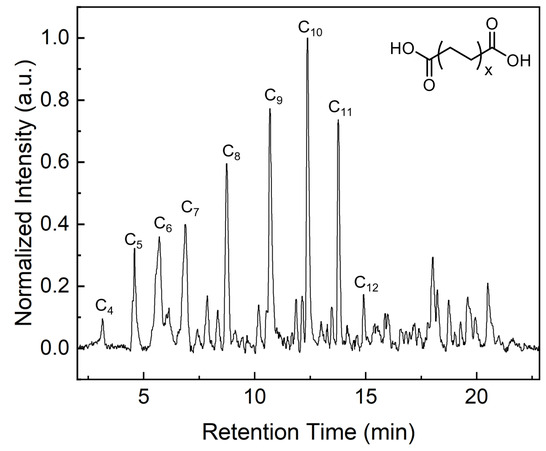
FTIR of Deconstructed Products





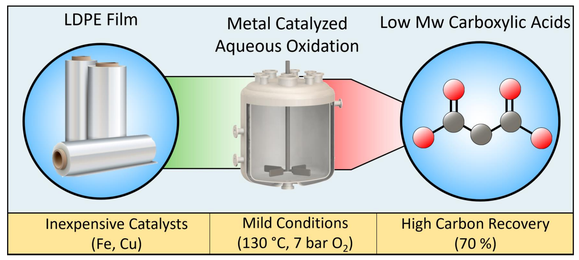
Top: Representative FTIR spectra for the water-soluble oxidized products at pH 11. Reactions were run using 2.5 wt % catalyst, 130 °C, and an initial oxygen pressure of 7 bar. **Bottom:** FTIR spectra for the water-soluble oxidized products of the reaction with $KMnO_4$ at pH 2 and pH 11.

Mass Spectrometry



Representative High Performance Liquid Chromatography Mass spectrometry results for water-soluble oxidized products using 10 wt % KMnO4 at 130 °C. Highlighted peaks correspond to aliphatic dicarboxylic acids

Conclusions



- A mild aqueous oxidation process cleaves C-C bonds in LDPE to generate low molecular weight aliphatic diacids
- With $FeSO_4$ as catalyst, the breakdown solution can be used directly for bioconversion without further processing
- This a promising approach for upcycling LDPE into higher value chemicals

References

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3. Chamas, A. et al., Degradation Rates of Plastics in the Environment, *ACS Sustainable Chem. Eng.* **2020**, *8*, 3494.
4. Sullivan, K. P. et al., Mixed Plastic Waste Valorization though Tandem Chemical Oxidation and Biological Funneling, *Science* **2022**, *378*, 207.
5. Davydovich, O. Efficient Production of Aliphatic α,ω-Dicarboxylic Acids Using Mild Aqueous Catalytic Oxidation of Low-Density Polyethylene (in review)

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