SAND2023-08386C

Aqueous Catalytic Oxidative Depolymerization of LDPE film for biological conversion

Oleg Davydovich, Amit Jha, Hemant Choudhary, Alberto Rodriquez, Daniella V. Martinez, Jay E. Salinas, Estevan J. Martinez, Ryan D. Davis, Estevan J. Martinez, Michael S. Kent

Sandia National Labs, Albuquerque, NM and Livermore, CA

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 poses 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 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 mid chain length (C8-C18) diacids.[5] A panel of monocultures were tested for growth on the breakdown products as sole carbon source, with several showing strong growth. These results suggest that this method may be promising for biological conversion of polyolefins into higher value chemicals or intermediates.

Objective

Breakdown and biological conversion of LDPE film into useful fuels, chemicals, or intermediates.

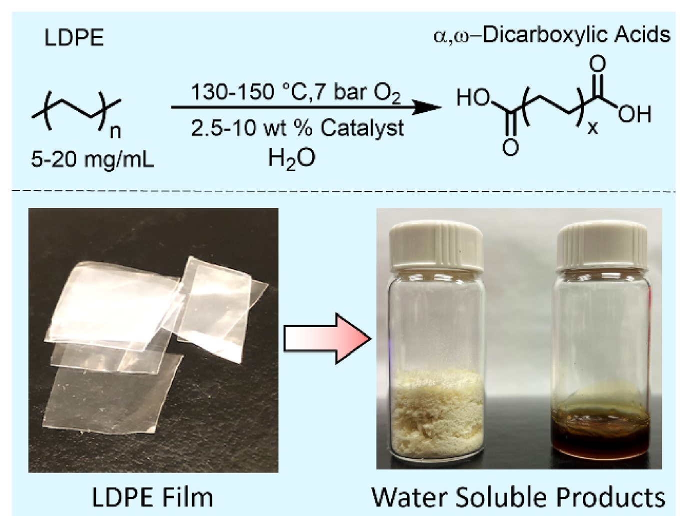
Materials and Methods

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

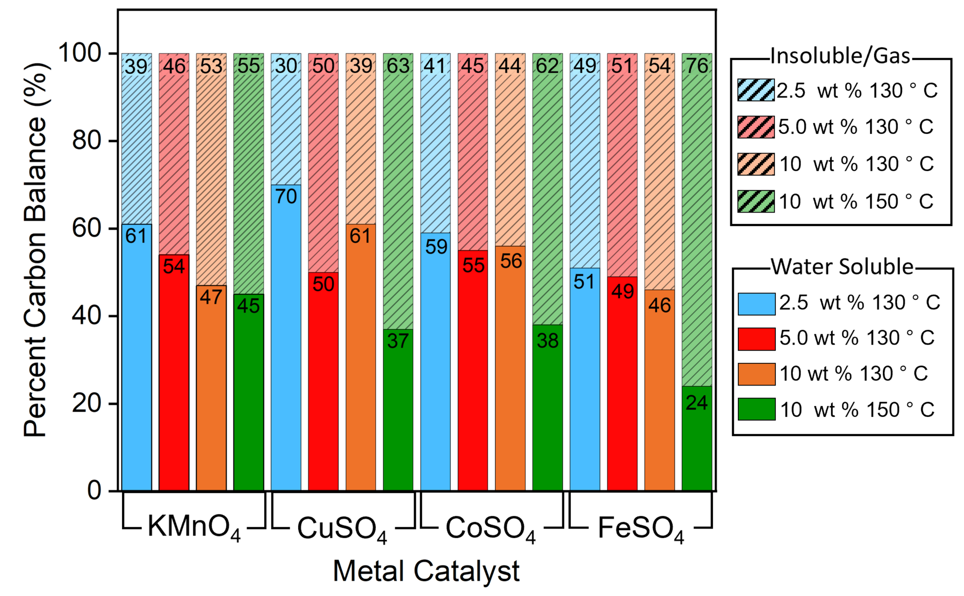
Hydrothermal Oxidation: All reactions were performed in a 4520 Reactor by Parr Instruments. The 1 L reactor was charged with 400 mL Millipore (20 MΩ) H_2O, followed by addition of catalyst ($KMnO_4$, $CuSO_4$, $FeSO_4{\bullet}7H_2O$, or $CoSO_4{\bullet}7H_2O$. The solution was stirred to dissolve the 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.

Culture conditions. All strains were cultured in tryptic soy broth seed medium for 1 day to regenerate the microbes. For growth analysis in the presence of depolymerized LDPE, the strains were cultured on a minimal production medium (MM) containing (per liter) 0.05 g yeast extract, 0.5 g KH_2PO_4, 0.5 g K_2HPO_4, 2.5 g $(NH_4)_2SO_4$, 0.1 g NaCl, 0.01 g $FeSO_4 \cdot 7H_2O$, 0.004 g $MnSO_4 \cdot H_2O$, 0.6 g $MgSO_4 \cdot 7H2O$, and 0.02 g $CaCl_2 \cdot 2H2O$. For each strain 0.3 ml of the seed medium was inoculated in 3 ml of either MM alone of MM with 5% of depolymerized LDPE in a total volume of 3 ml in 15 ml plastic tubes and grown at 30°C on a rotary shaker at 250 rpm for 5 days. Samples were collected each day from all tubes and analyzed for growth by OD_{600} measurement.

Reaction Conditions

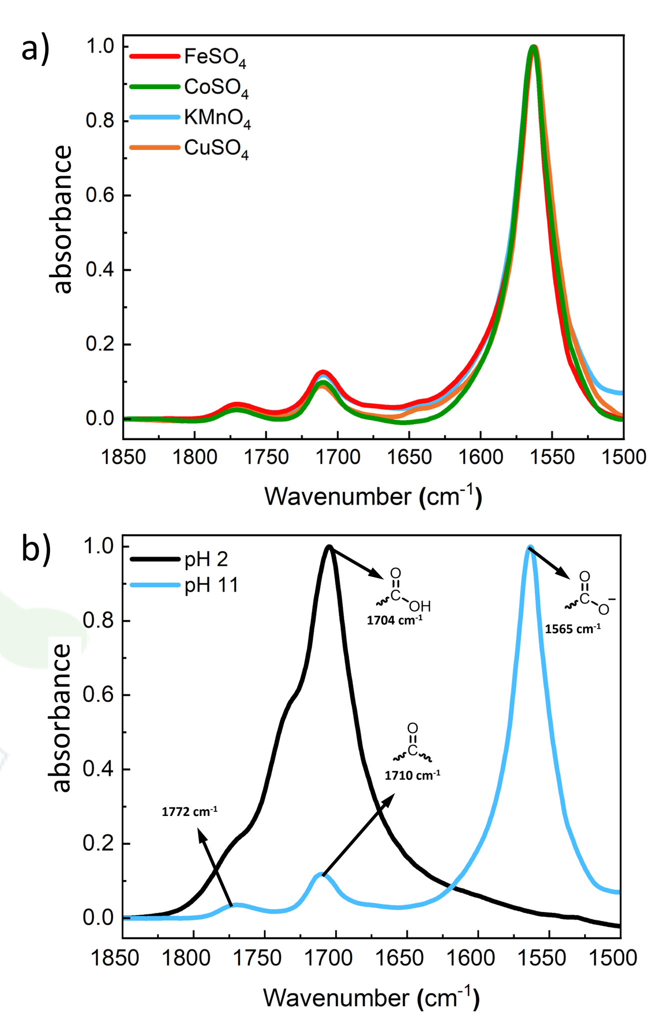


Carbon Yield



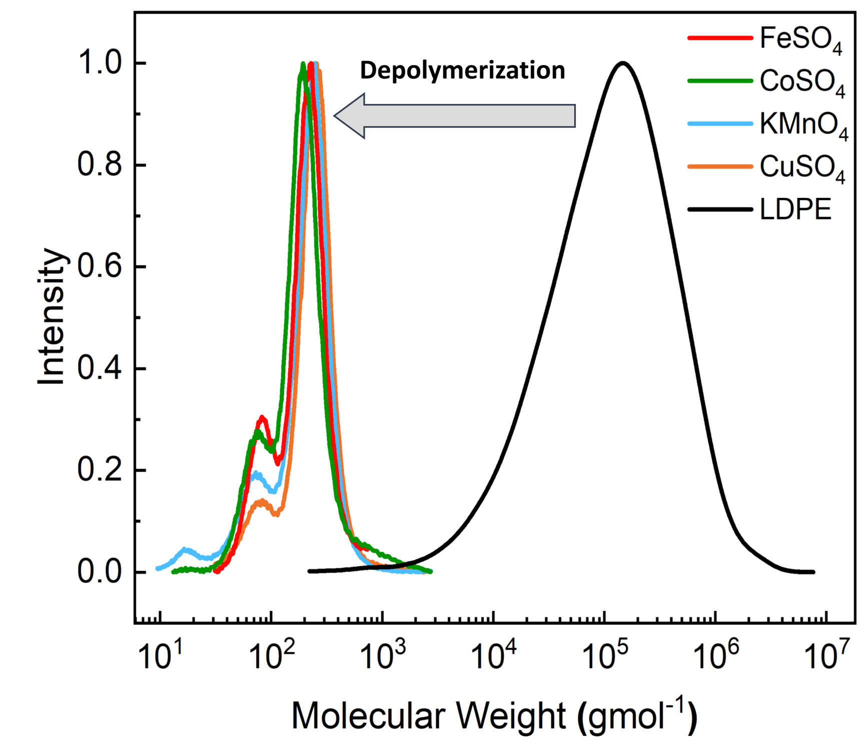
Carbon balance after LDPE oxidation using various catalyst concentrations and reaction temperatures. Using elemental analysis, percent carbon was determined by comparing carbon recovered in the water-soluble products with the carbon content of the initial LDPE film. The percent carbon present in insoluble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

FTIR



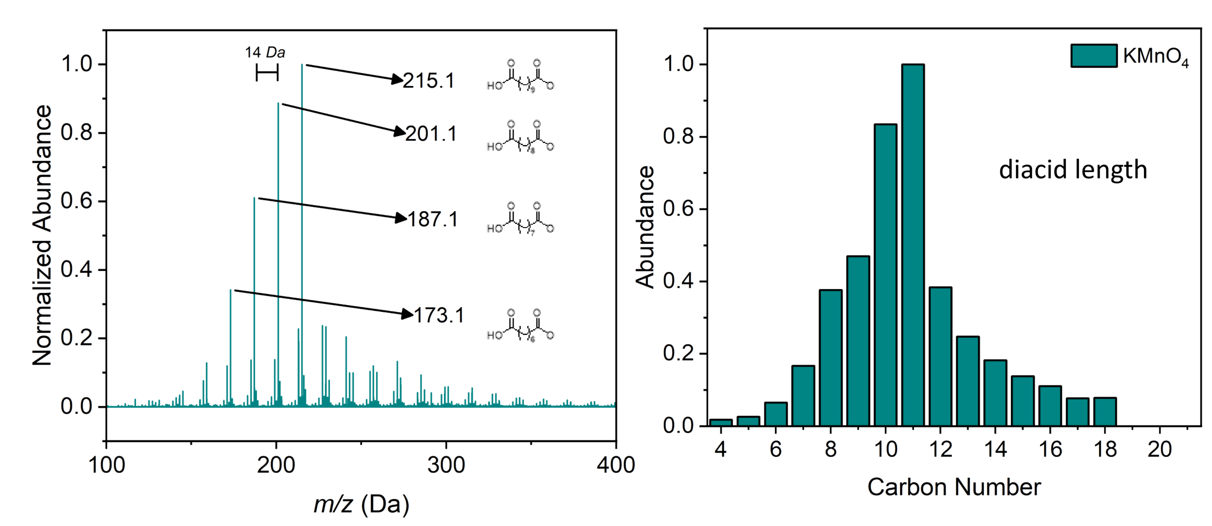
a). Representative FTIR spectra for the water-soluble oxidized products at pH 11. Reactions were run using 10 wt % catalyst, 130 °C, and an initial oxygen pressure of 7 bar. b). FTIR spectra for the water-soluble oxidized products of the reaction with $KMnO_4$ at pH 2 and pH 11.

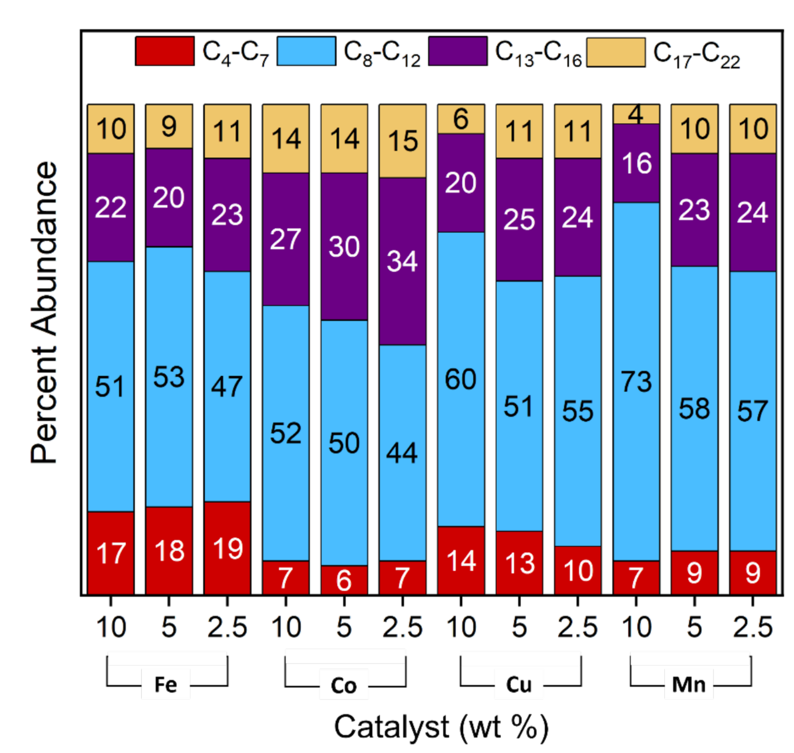
SEC



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: 10 wt % catalyst loading, 130 °C, and an initial oxygen pressure of 7 bar.

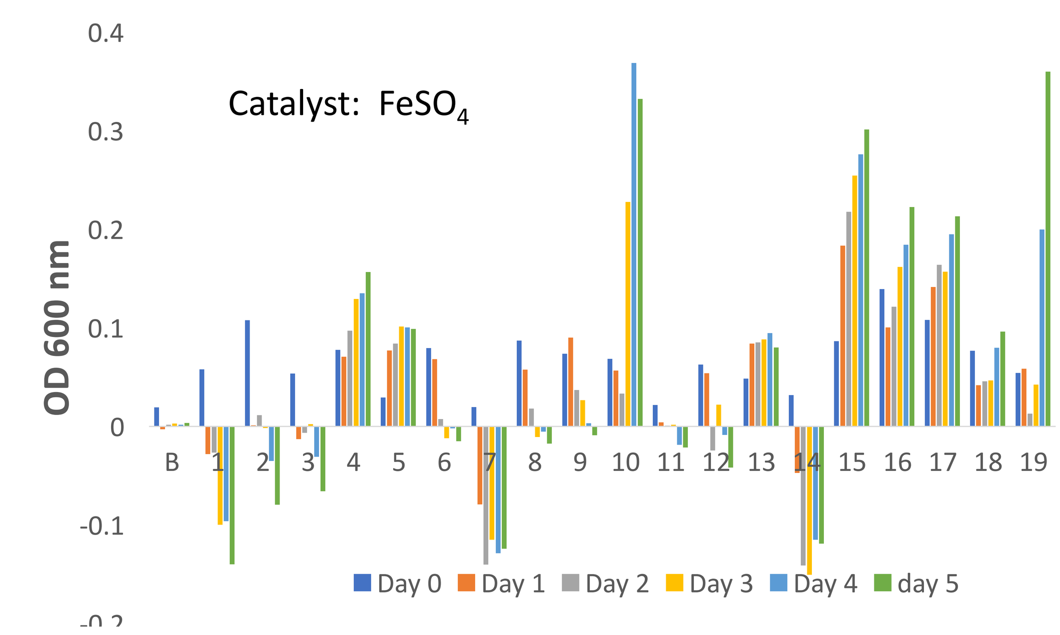
Mass Spectrometry





Electrospray ionization mass spectrometry results for water-soluble oxidized products at various catalyst concentrations at 130 °C. Columns represent the percent abundance of carbon chain lengths of aliphatic dicarboxylic acids.

Bioavailability

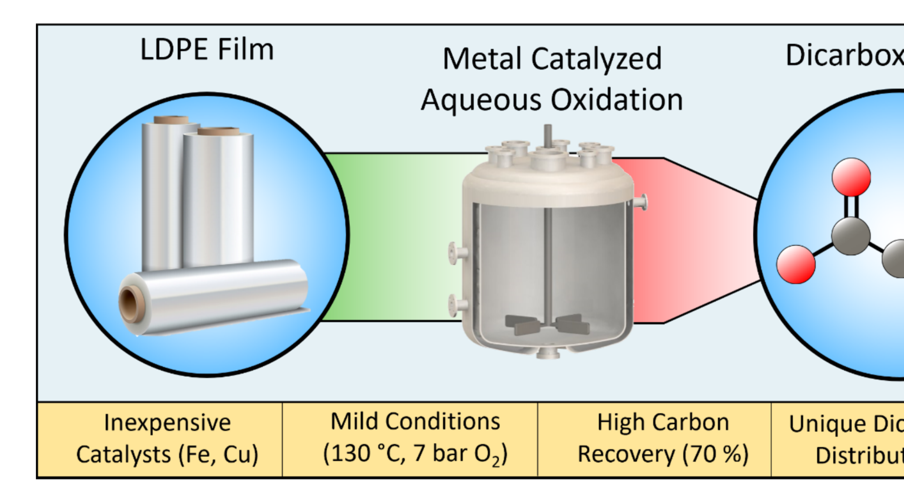


Organisms that grow well:

- 4 - *Delftia acidovorans*
- 5 - *Pseudomonas stutzeri*
- 10 - *Yarrowia lipolytica*
- 13 - *Sphingopyxis witflariensis*
- 15 - *Pseudomonas sp. Rh926*
- 16 - *Brevundimonas vesicularis*
- 17 - *Bacillus megaterium*
- 18 - *Sphingomonas sp.* PWE1
- 19 - *Candida maltosa*

1 - *Exophiala alcalophila*, 2 - *Bacillus subtilis*, 3 - *Corynebacterium glutamicum*, 4 - *Delftia acidovorans*, 5 - *Pseudomonas stutzeri*, 6 - *Rhodococcus opacus*, 7 - *Rhodococcus ruber* , 8 - *Pseudomonas putida*, 9 - *Rhodococcus jostii*, 10 - *Yarrowia lipolytical*, 11 - *Yarrowia lipolytica*, 12 - *Rhodococcus rhodochrous*, 13 - *Sphingopyxis witflariensis*, 14 - *Streptomyces venezuelae*, 15 - *Pseudomonas sp. Rh926*, 16 - *Brevundimonas vesicularis*, 17 - *Bacillus megaterium*, 18 - *Sphingomonas sp.* PWE1, 19 - *Candida maltosa*

Conclusions



- A mild aqueous oxidation process cleaves C-C bonds in LDPE to generate mid chain length diacids
- With $FeSO_4$ as catalyst, the breakdown solution can be used directly for bioconversion without further processing
- A number of organisms grow on this substrate as sole carbon source, including *Yarrowia lipolytica*, several *Pseudomonas* stains, *Brevundimonas vesicularis*, *Bacillus megaterium*, *Sphingomonas*, and *Candida maltosa.*
- This a promising approach for upcycling LDPE into higher value chemicals or intermediates.

References

1. Miao, Y. et al., Current Technologies in Depolymerization Process and the Road Ahead, *Polymers* **2021**, *13*, 449.
2. Brooks, A. L. et al., The Chinese import ban and its impact on global plastic waste trade, *Science Advances* **2018**, *4*, eaat0131.
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)

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
SAND No. ____________

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.