SAND2023-07780C

Sandia National Laboratories

Exceptional service in the national interest

EFFICIENT PRODUCTION OF LOW MOLECULAR WEIGHT CARBOXYLIC ACIDS VIA MILD AQUEOUS CATALYTIC OXIDATION OF LOW-DENSITY POLYETHYLENE

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

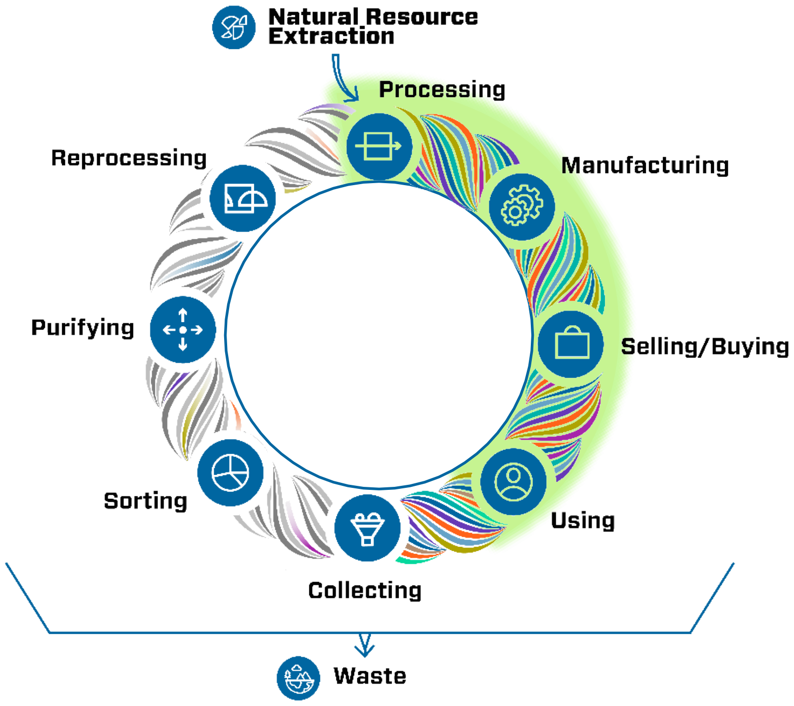
Sandia National Laboratories

August 16, 2023

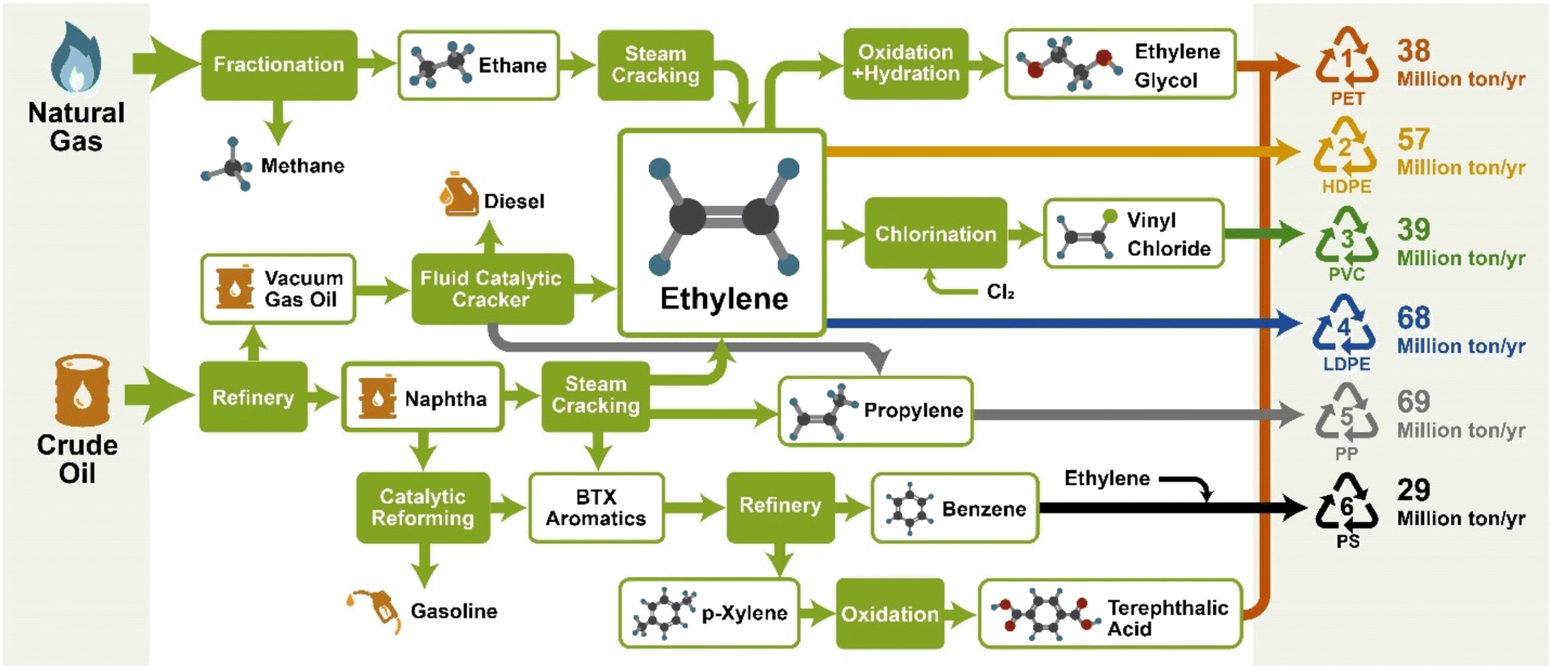
PLASTIC CIRCULAR ECONOMY

"A circular economy reduces material use, redesigns materials, products, and services to be less resource intensive, and recaptures "waste" as a resource to manufacture new materials and products." - EPA

We are great at extracting natural resources, processing, and manufacturing useful materials



NIST



Green Chem. **2022**, 24, 8899–9002.

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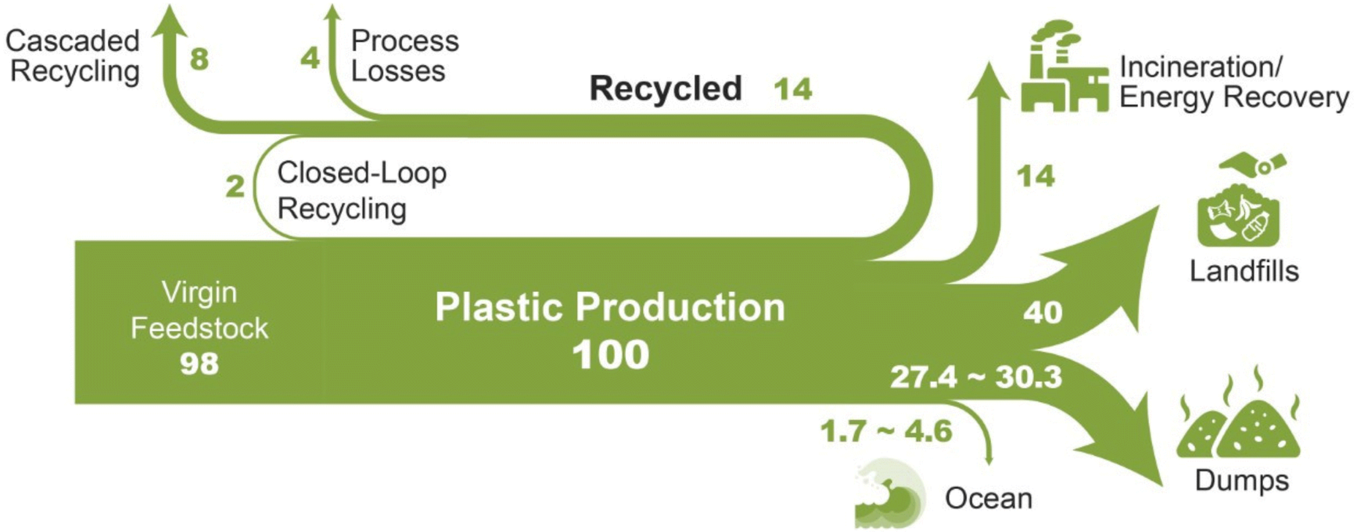

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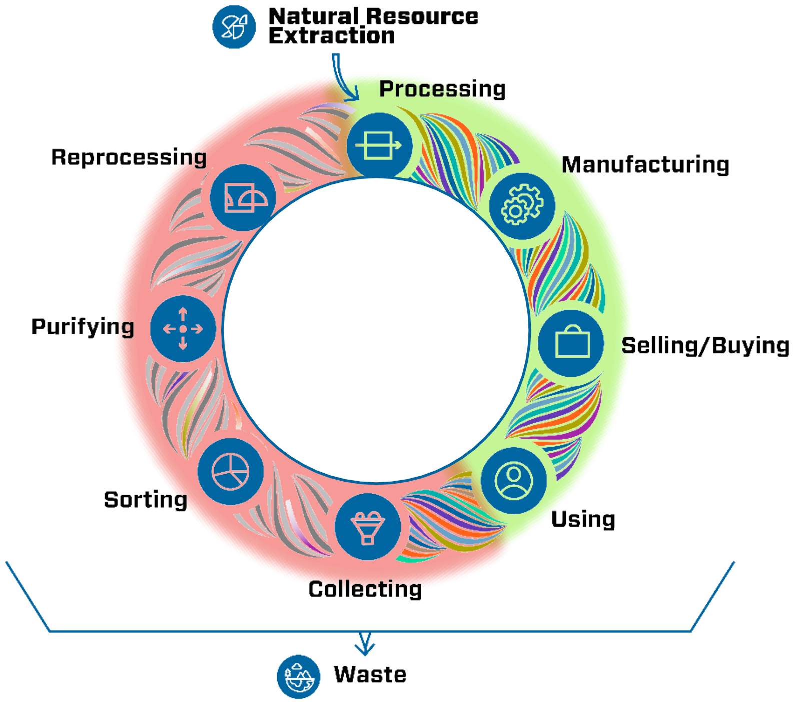

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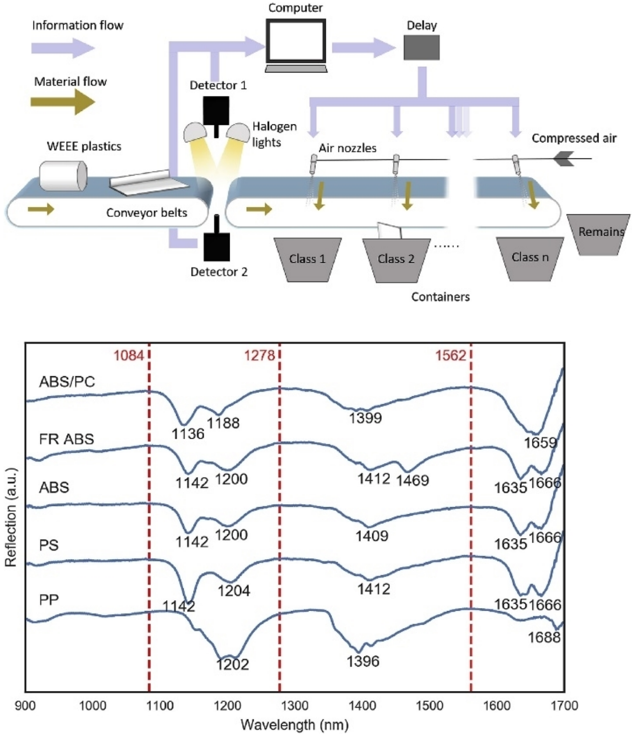
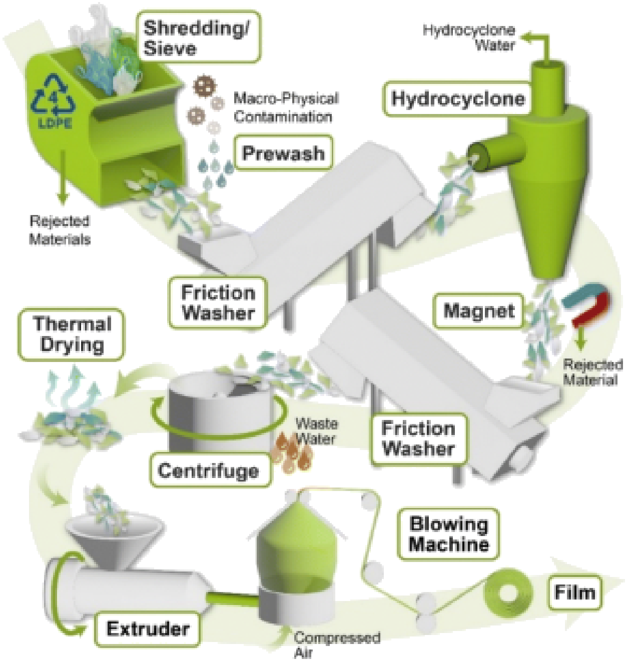
PLASTIC CIRCULAR ECONOMY



Journal of Cleaner Production *246*, **2020**, 118732.



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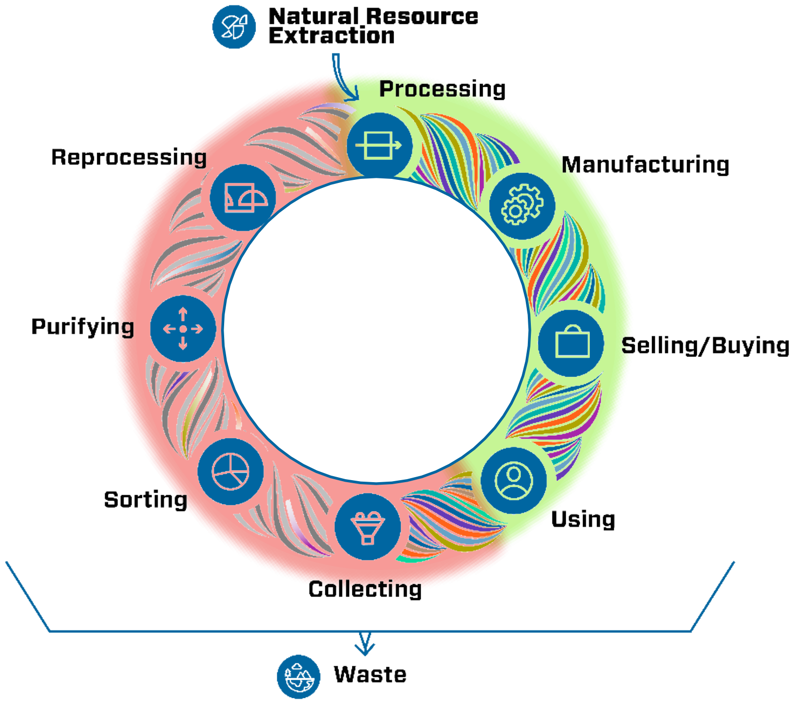
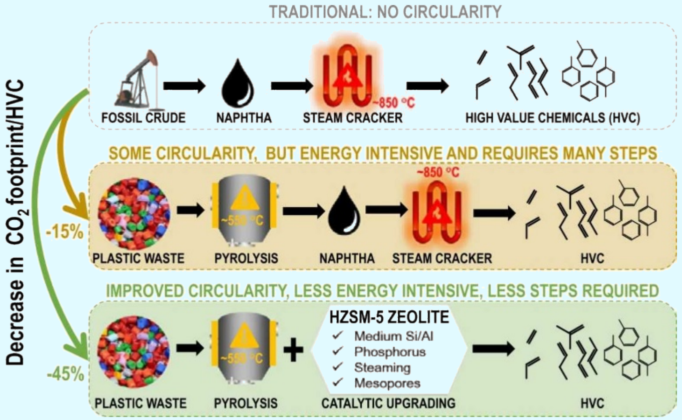


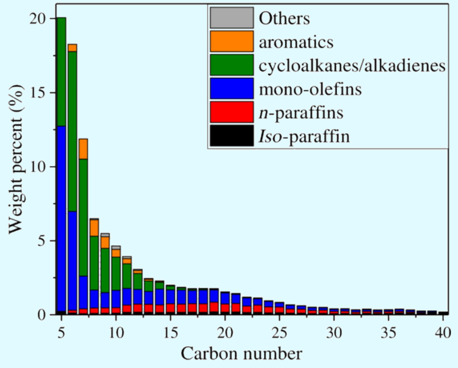
NIST

POLYOLEFIN CHEMICAL CONVERSION

Pyrolysis	Hydrogenolysis	Oxidation
Hydrocarbons including waxes, oils, gases, and fuels	Hydrocarbons including waxes, oils, gases, and fuels	Carboxylic acid and ketonated waxes, oils, and chemical feedstocks



Applied Catalysis B: Environmental 309, **2022**, 121251.



ChemSusChem, 2020, **13** , 1764 —1774.

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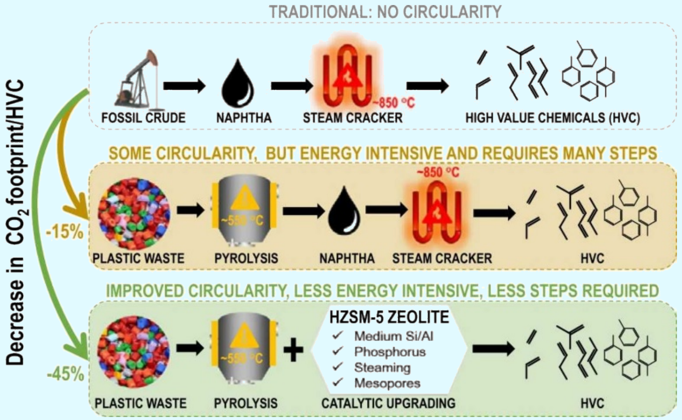

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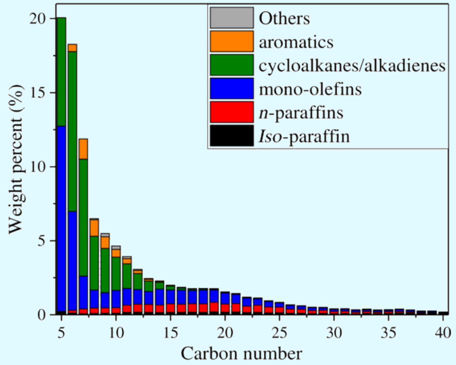

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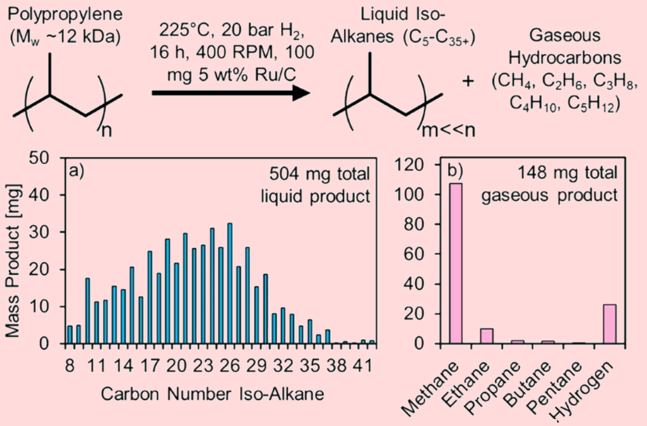
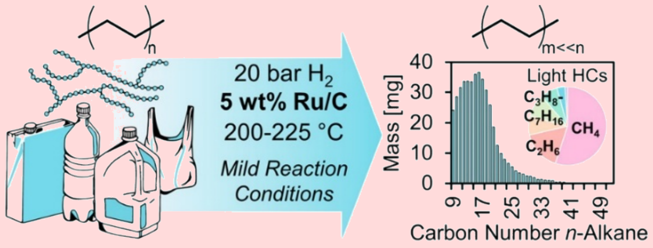


JACS Au **2022**, *2*, 10, 2259–2268.

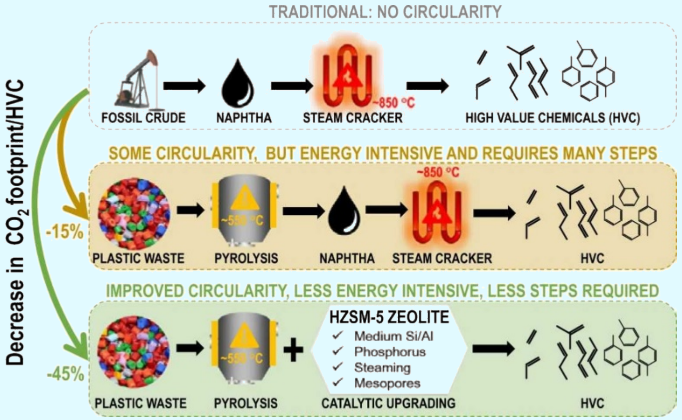


JACS Au **2021**, *1*, 1, 8–12.

POLYOLEFIN CHEMICAL CONVERSION

Pyrolysis

Hydrocarbons including waxes, oils, gases, and fuels



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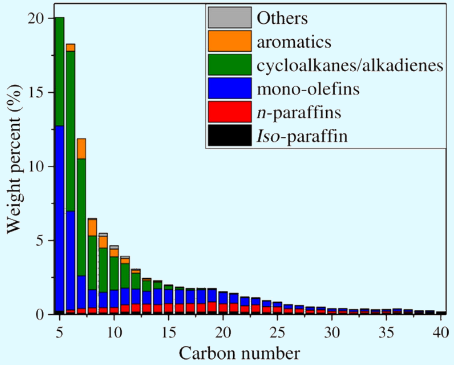

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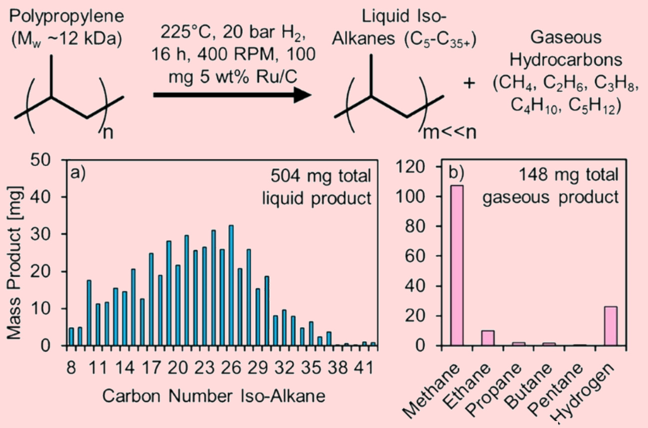
Hydrogenolysis

Hydrocarbons including waxes, oils, gases, and fuels



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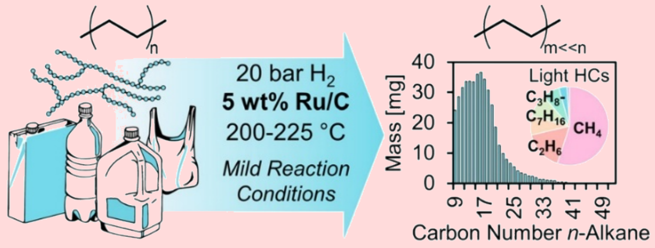

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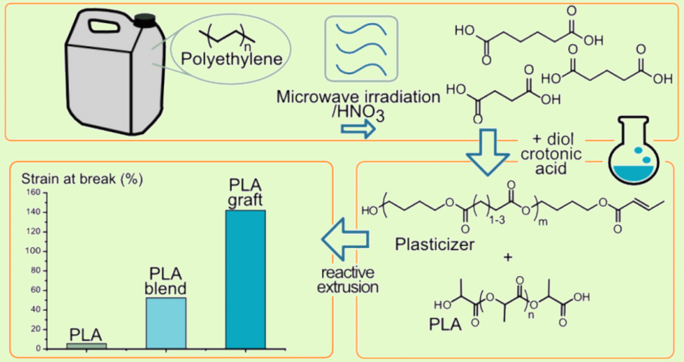
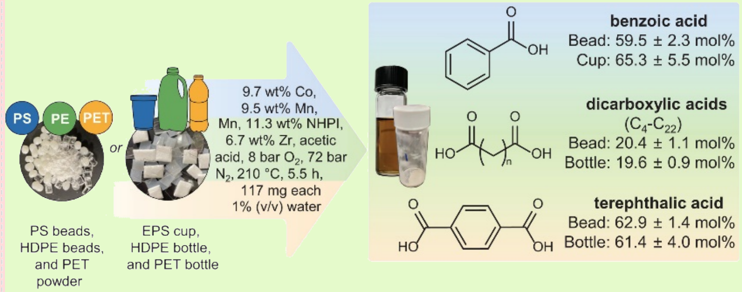
Oxidation

Carboxylic acid and ketonated waxes, oils, and chemical feedstocks



ACS Sustainable Chem. Eng. **2019**, *7*,12, 11004–11013.



Science **2022**, *378*, 207.

OUR APPROACH: GREENER OXIDATION

Our Focus

To develop an inexpensive process to break C-C bonds in polyolefins to form bioavailable compounds.

To develop a process which avoids post-processing steps prior to bioconversion.

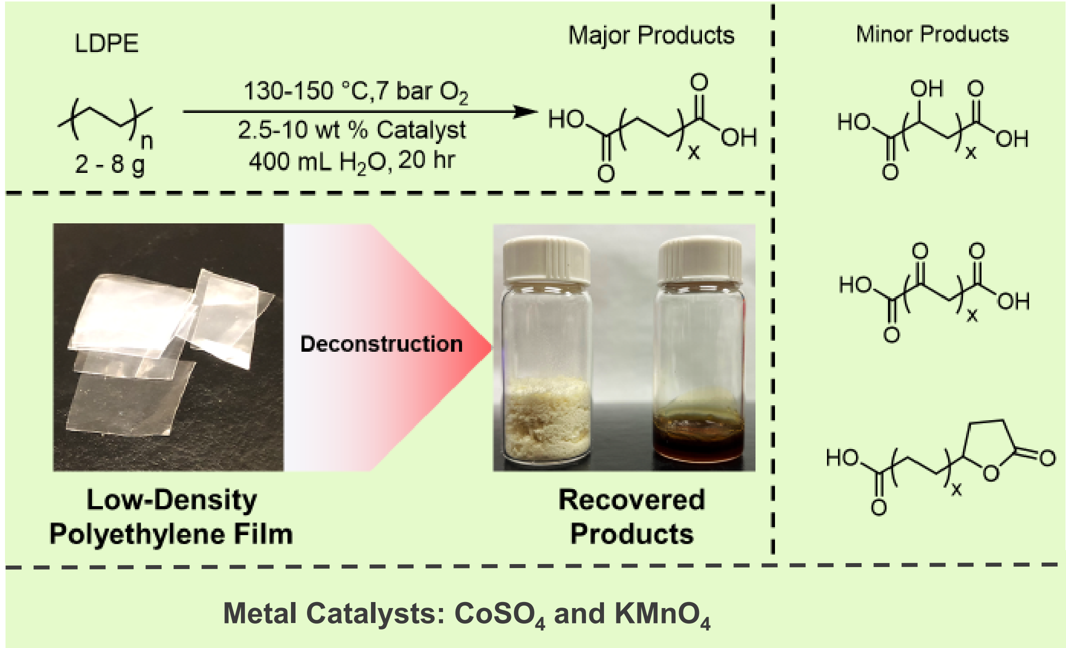
Benign metal catalysts and no toxic additives

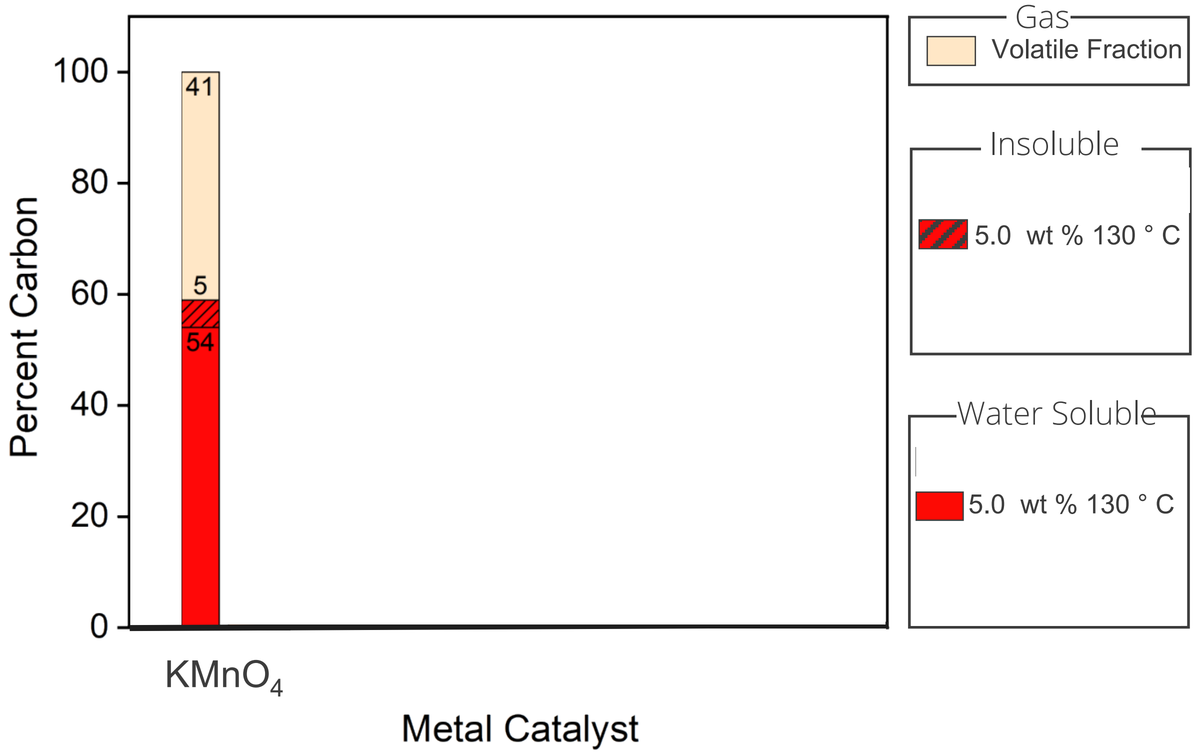
Reduce reaction temperature and minimize catalyst loading

Aqueous conditions for bio-upcycling

METAL CATALYZED OXIDATION OF LDPE FILM

- Develop a technique breaking down LDPE using a “inexpensive and greener” process
- Using aqueous conditions, earth-abundant first row transition metals and low temperatures





*Carbon Present in LDPE vs Carbon Present in Products

Patent Pending, Submitted for Review

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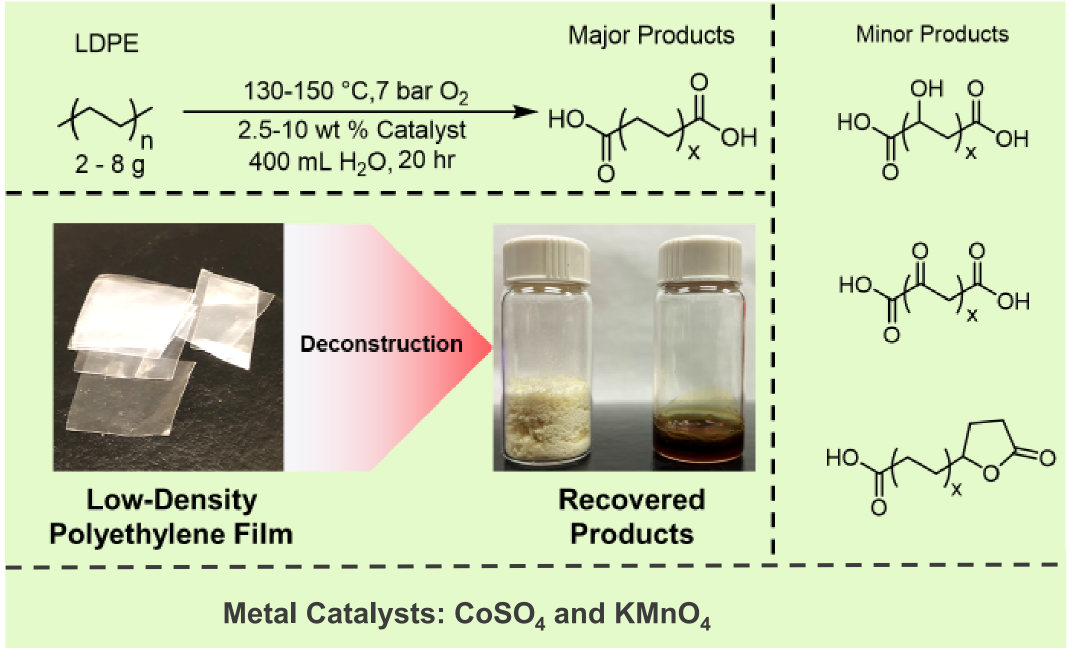

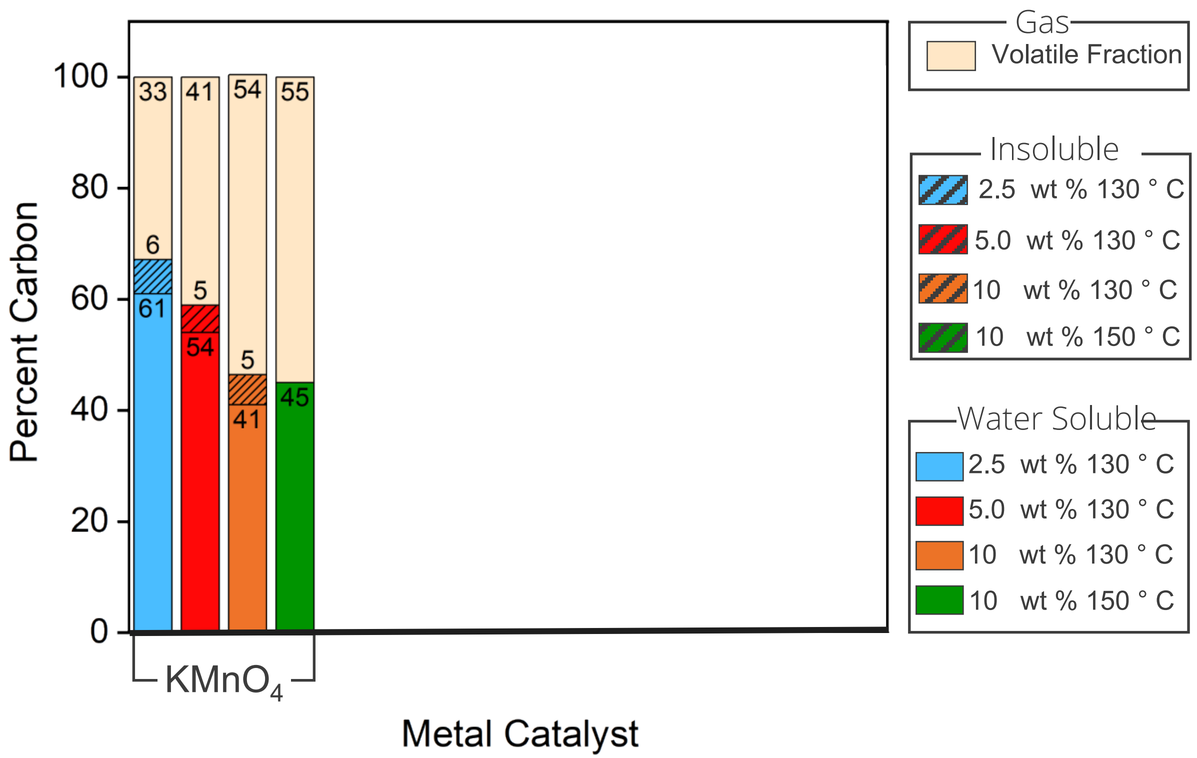

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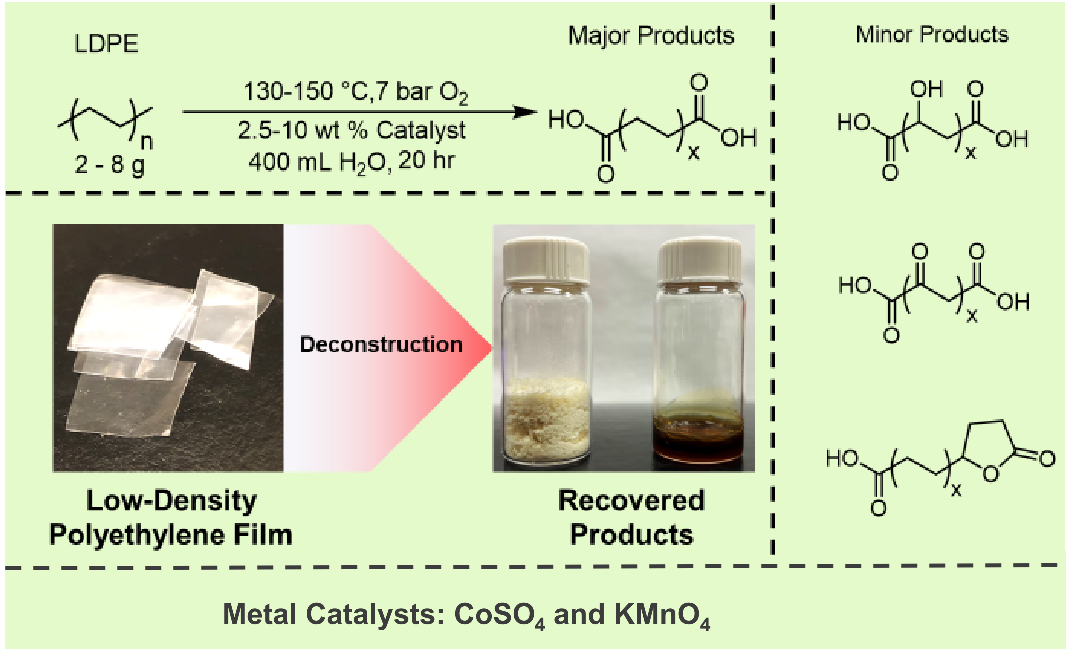
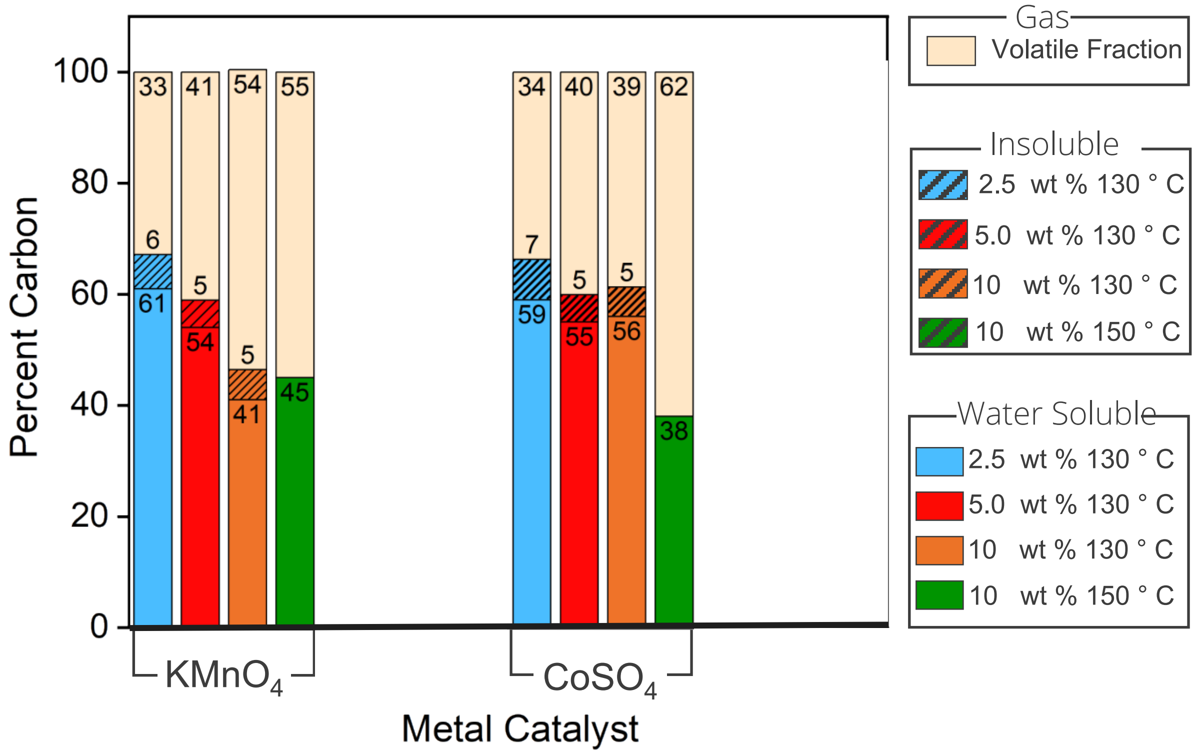


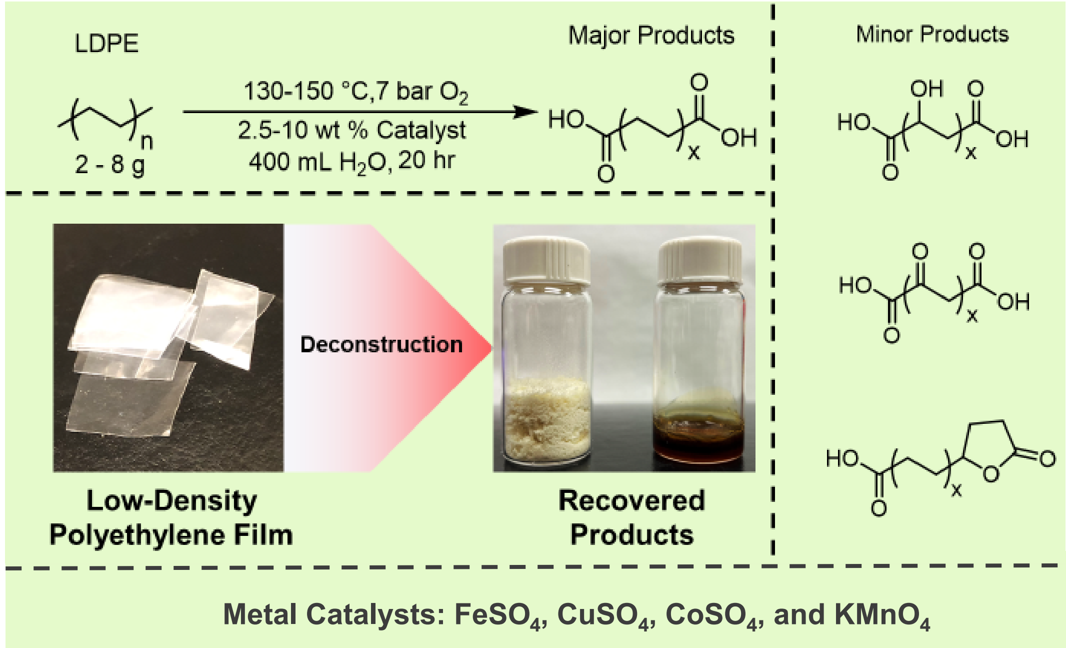


*Carbon Present in LDPE vs Carbon Present in Products

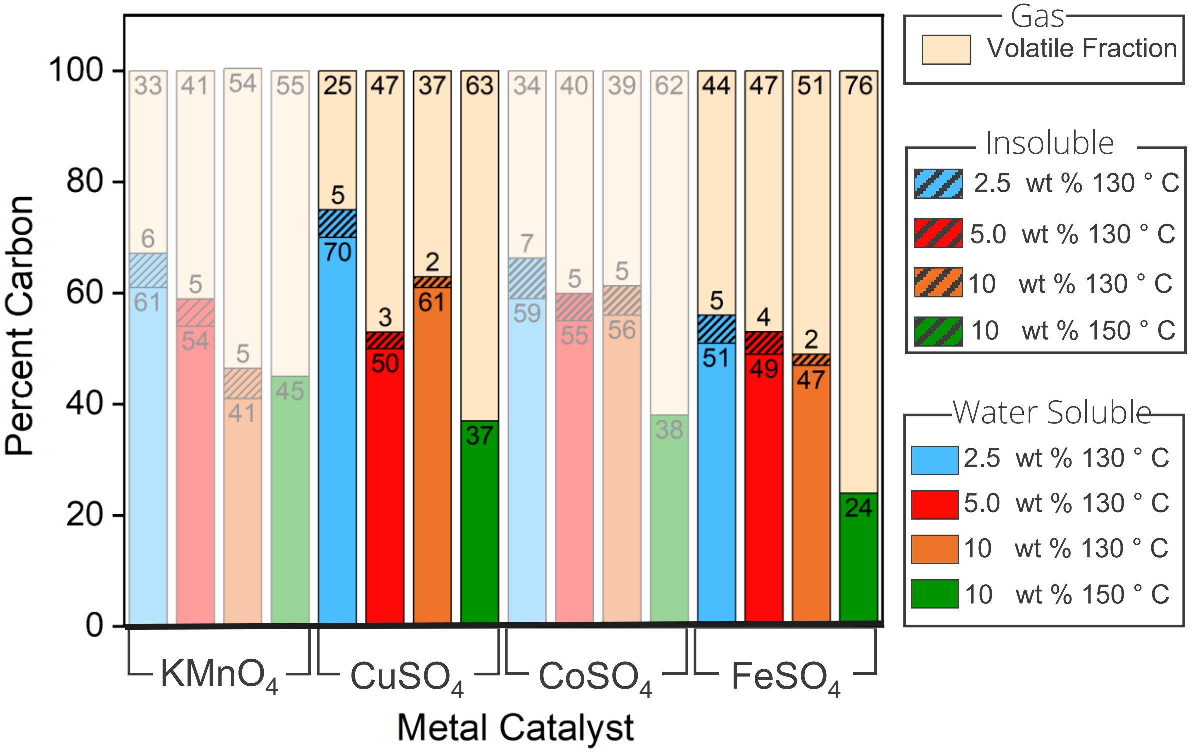
Patent Pending, Submitted for Review

METAL CATALYZED OXIDATION OF LDPE FILM

- Develop a technique breaking down LDPE using a “inexpensive and greener” process
- Using aqueous conditions, earth-abundant first row transition metals and low temperatures
- Achieving high carbon recoveries



*$FeSO_4$ and $CoSO_4$ are heptahydrate salts



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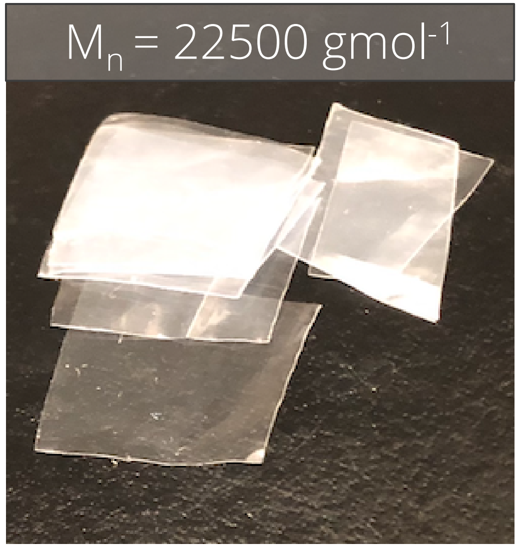
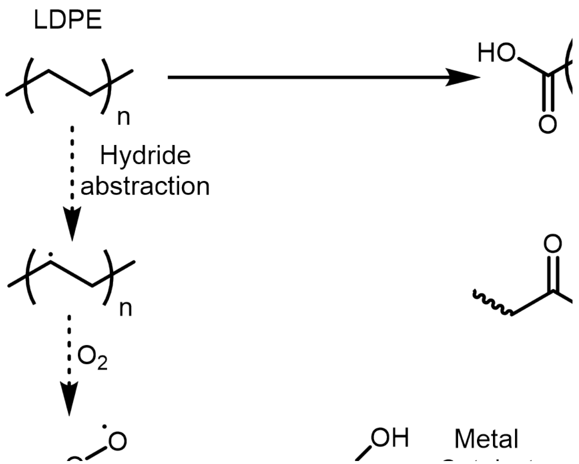
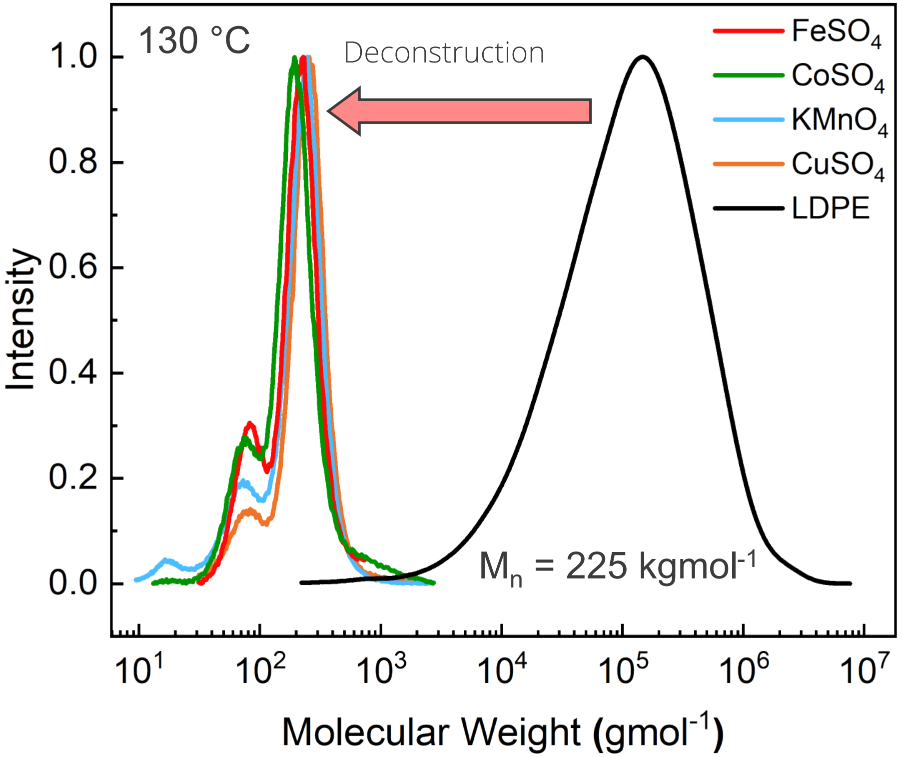
EXTENT OF LDPE DECONSTRUCTION

- Catalyzed oxidative C-C cleavage results in low molecular weight species



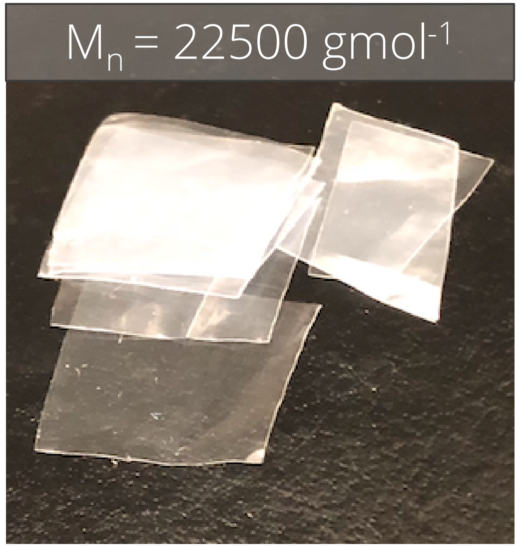


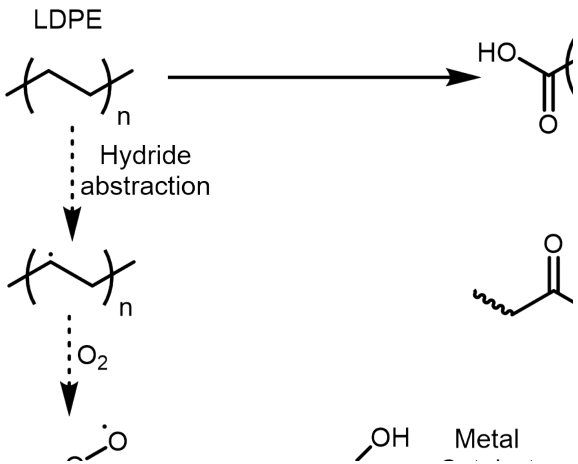


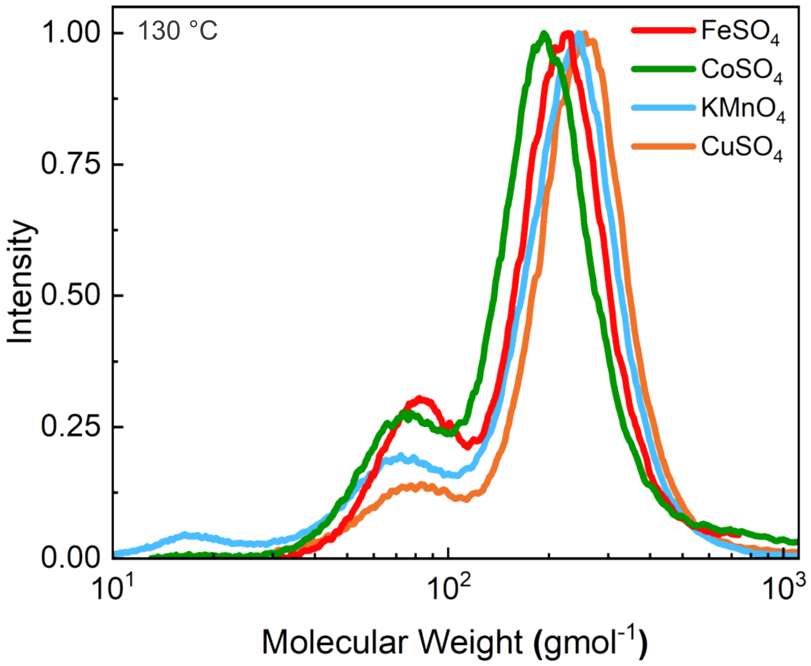
Patent Pending, Submitted for Review

EXTENT OF LDPE DECONSTRUCTION

- Catalyzed oxidative C-C cleavage results in significant depolymerization
- Water soluble low molecular weight fragments (100-500 gmol $^{-1}$)

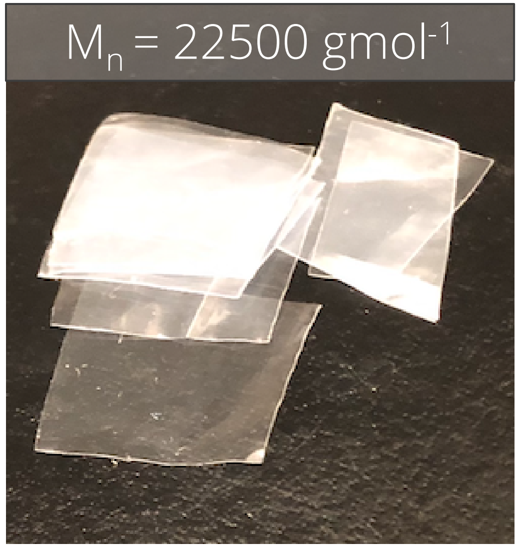


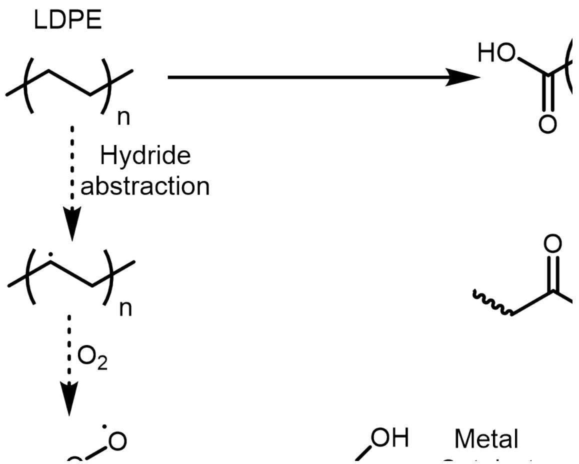


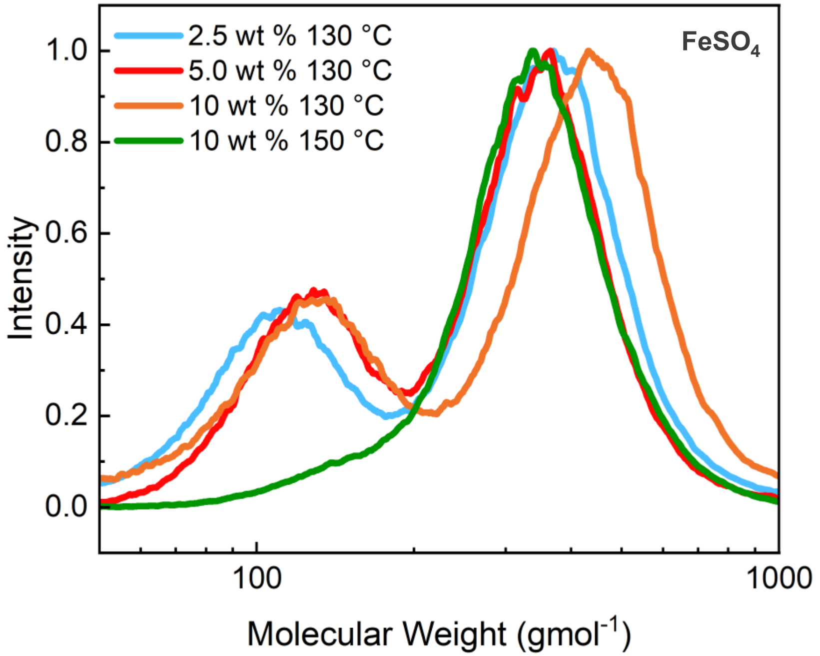


EXTENT OF LDPE DECONSTRUCTION

- Catalyzed oxidative C-C cleavage results in significant depolymerization
- Water soluble low molecular weight fragments (100-500 gmol $^{-1}$)
- No significant effect from catalyst loading and higher temperatures





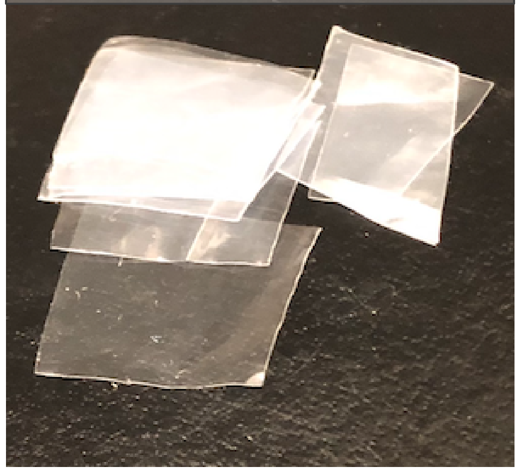


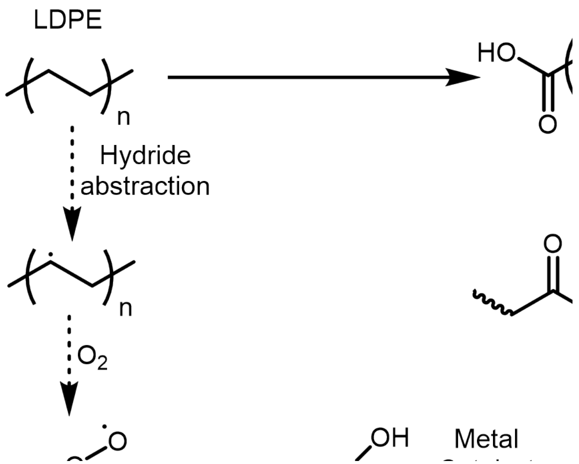
Patent Pending, Submitted for Review

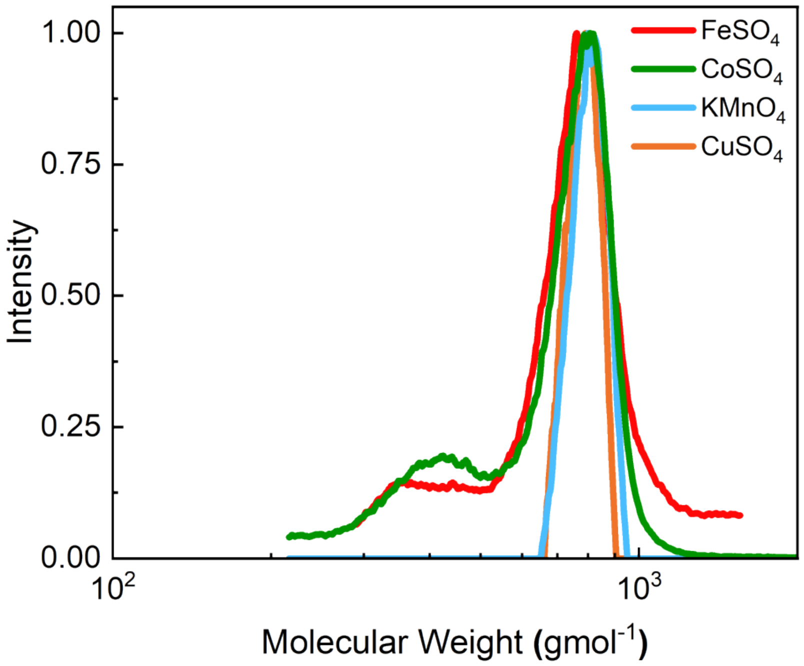
EXTENT OF LDPE DECONSTRUCTION

- Catalyzed oxidative C-C cleavage results in significant depolymerization
- Water soluble low molecular weight fragments (200-300 $gmol^{-1}$)
- No significant effect at higher temperatures
- Water insoluble species are partly depolymerized (600-1200 $gmol^{-1}$)

M_n = 22500 $gmol^{-1}$







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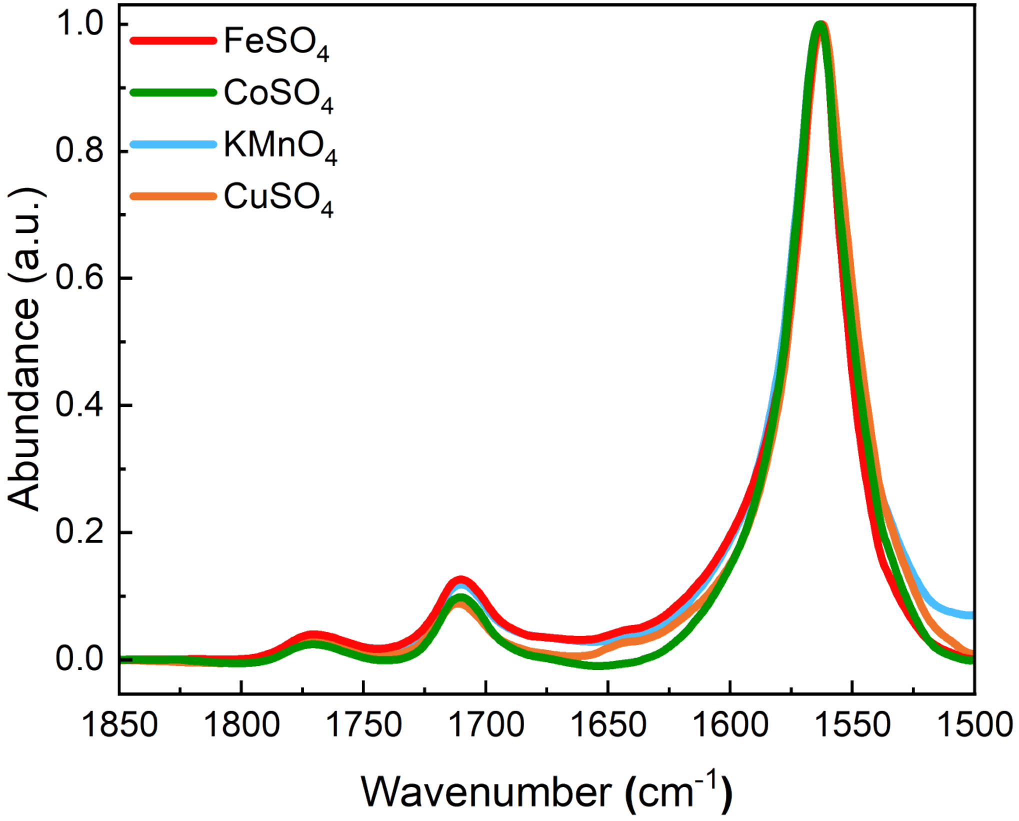
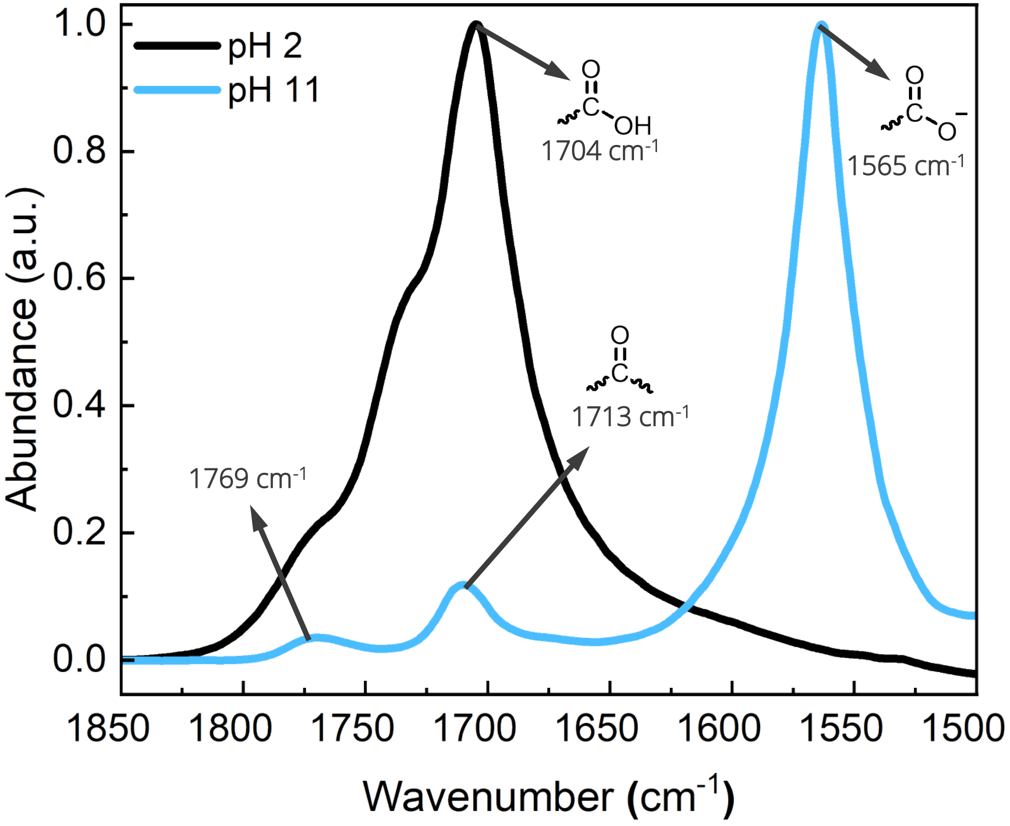
CHEMICAL COMPOSITION OF PRODUCTS

- Carboxylate and carboxylic acid functionalities
- Small amounts of γ-lactone and carbonyl (aldehyde or ketone species)



2.5 % wt Catalyst



2.5 % wt $KMnO_4$

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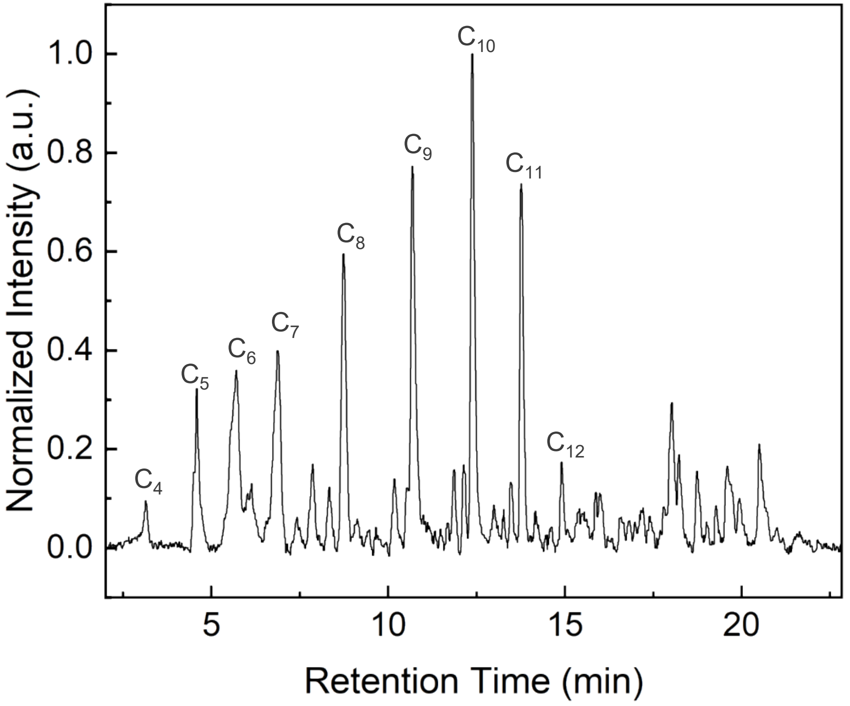
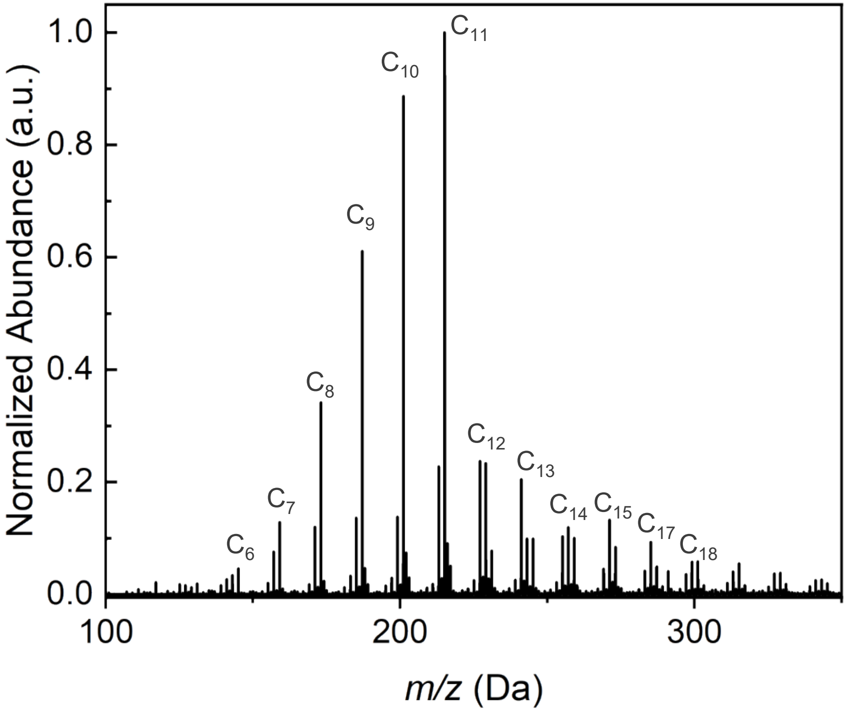
WATER-SOLUBLE PRODUCTS CHEMICAL COMPOSITION

- Mass Spectrometry of water soluble products
- Water soluble products spiked with dicarboxylic acid standards





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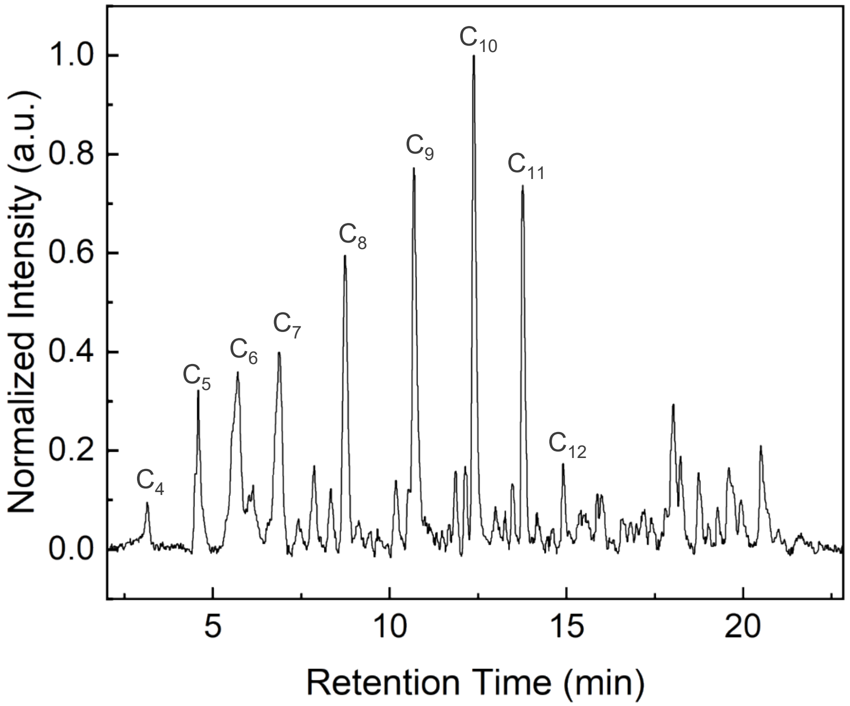
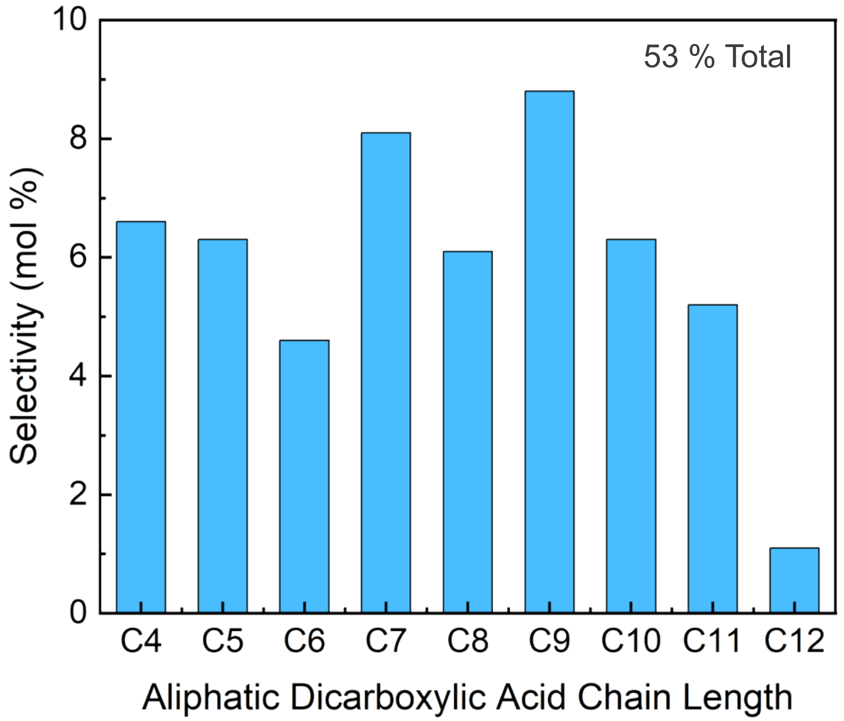
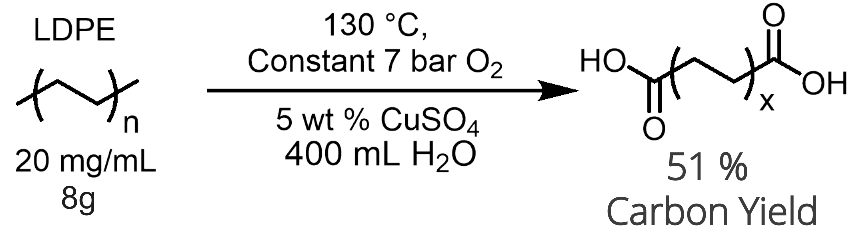


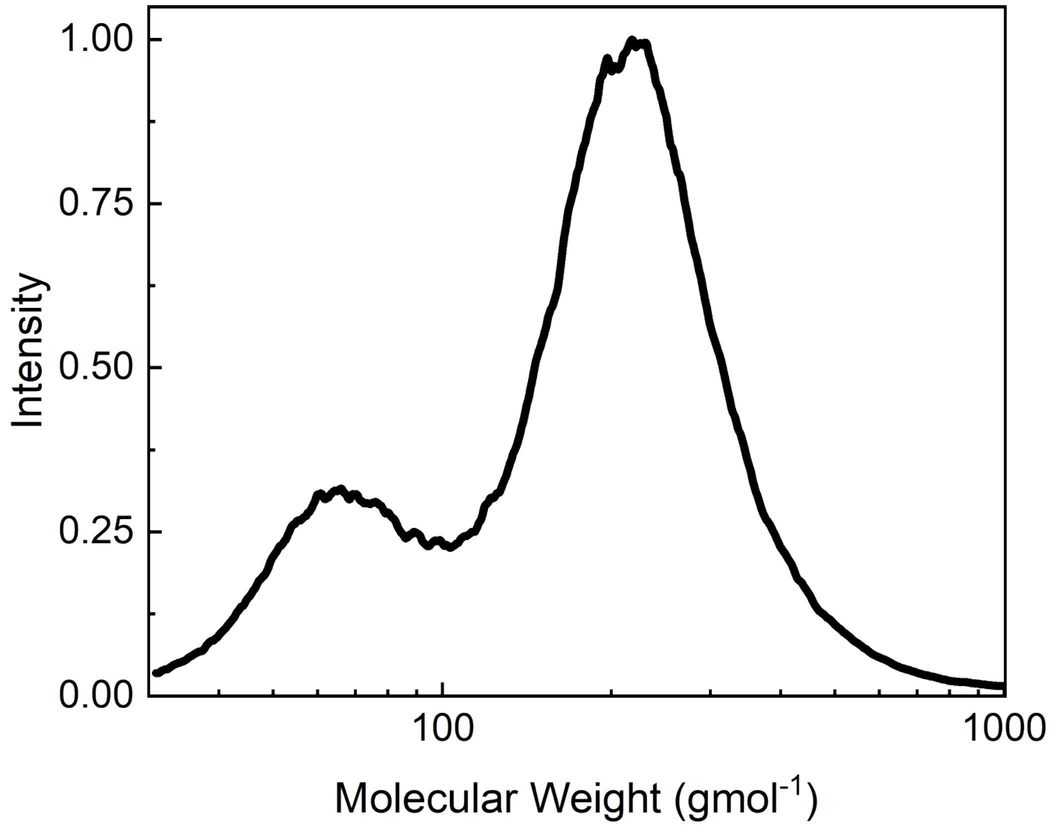


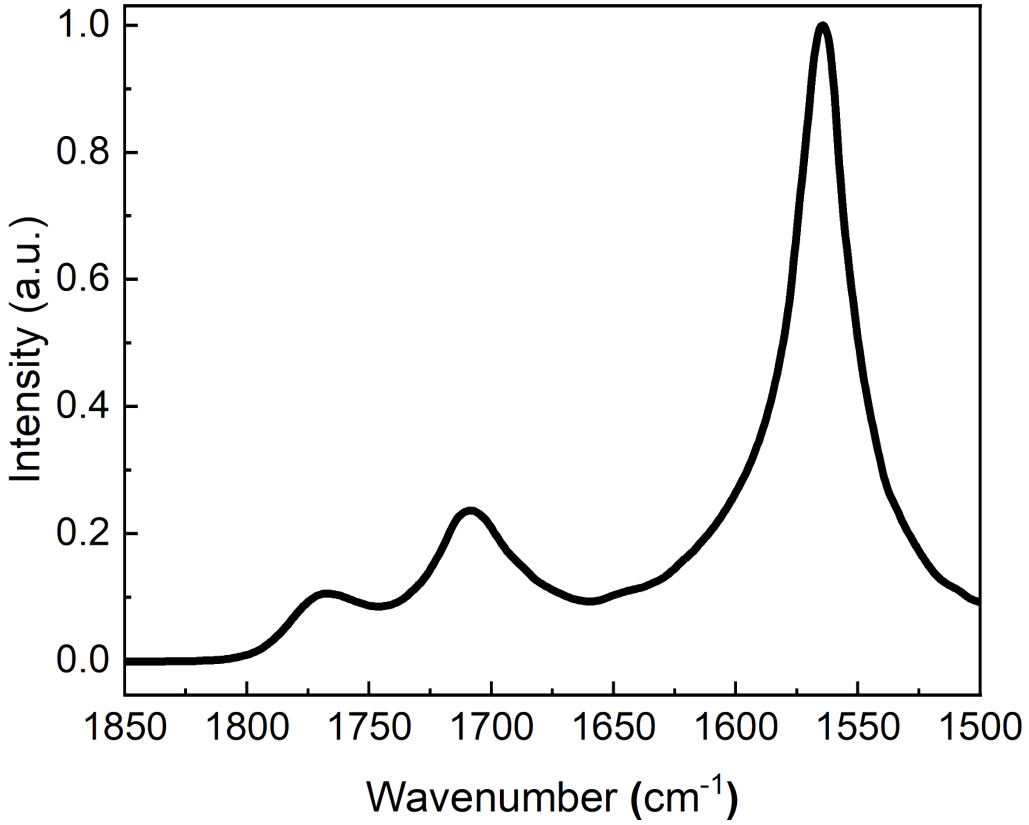
Patent Pending, Submitted for Review

LARGE SCALE REACTION SHOWS SIMILAR PROPERTIES

- Significant effect on yield (unoptimized)
- Extent of depolymerization (100-500 $gmol^{-1}$)
- Similar dicarboxylic acid products







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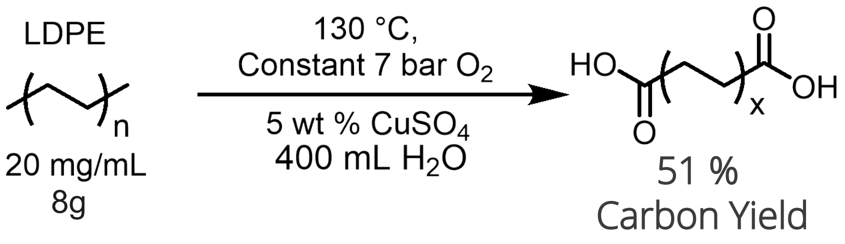
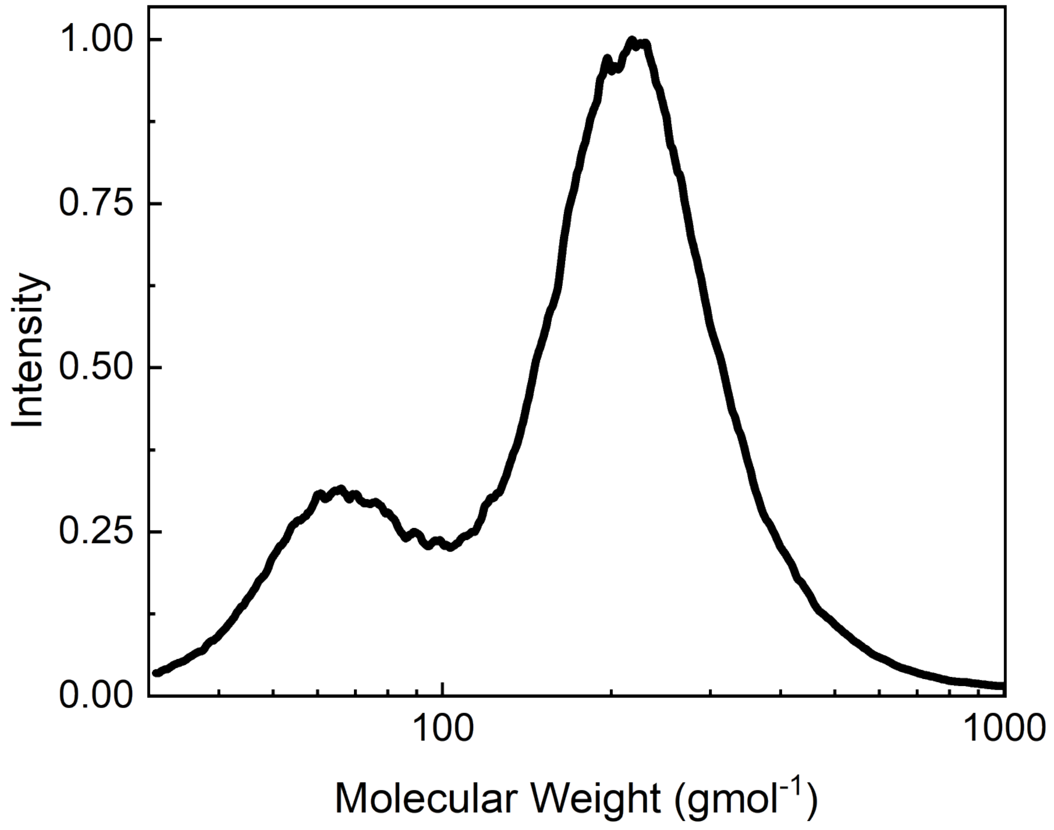
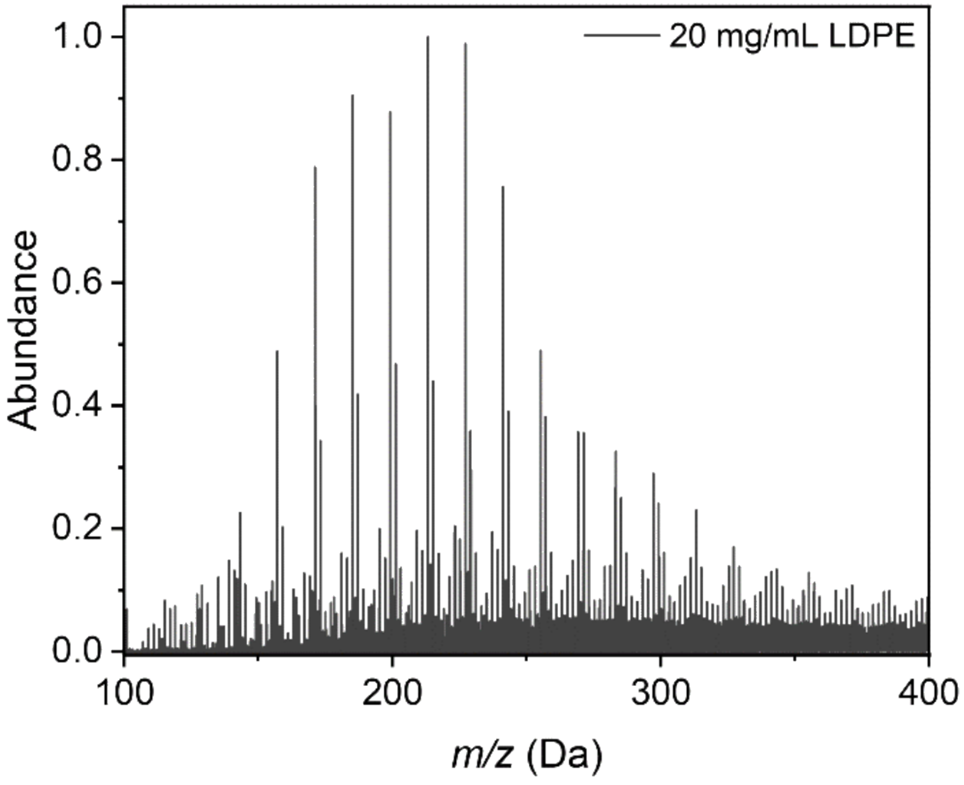
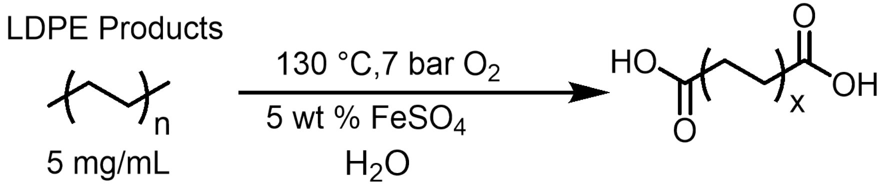






CHEMICAL CONVERSION OF COMMERCIAL PRODUCTS

- Yield was significantly effected with Sandwich Bag and Six Pack Holder

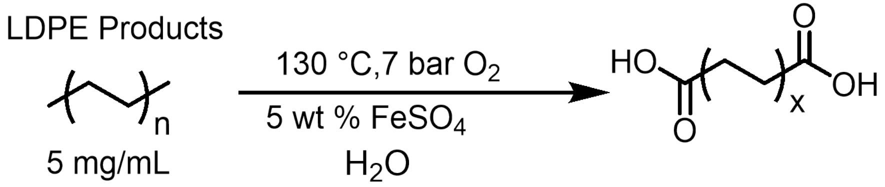


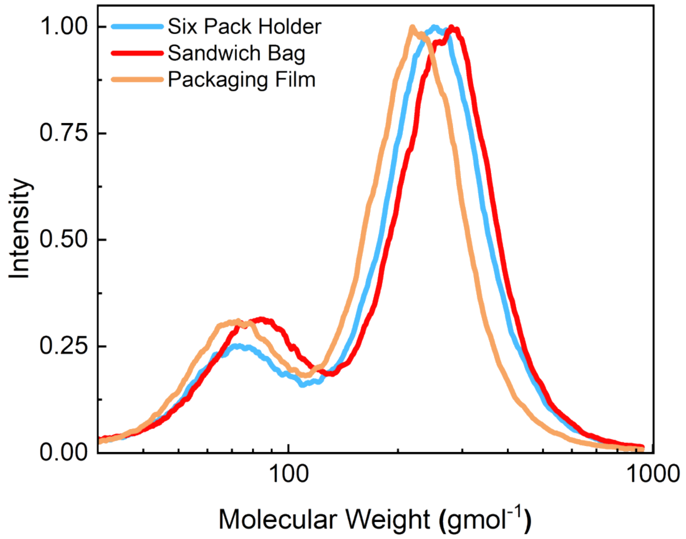
Thermo Scientific Packaging Film	Ziploc Bag	LDPE Six Pack Ring
		
46 Carbon % Yield	24 % Carbon Yield	26 % Carbon Yield

Patent Pending, Submitted for Review

CHEMICAL CONVERSION OF COMMERCIAL PRODUCTS

- Yield was significantly effected with Sandwich Bag and Six Pack Holder
- Extent of depolymerization is similar (100-500 $gmol^{-1}$)





Thermo Scientific Packaging Film

46 Carbon % Yield

Ziploc Bag

24 % Carbon Yield

LDPE Six Pack Ring

26 % Carbon Yield

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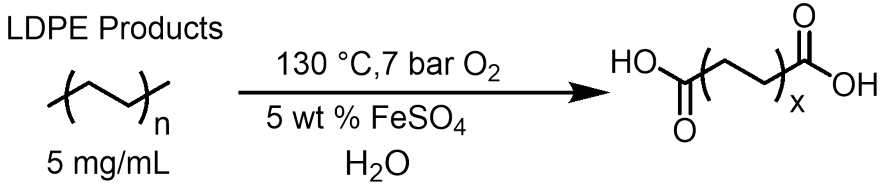
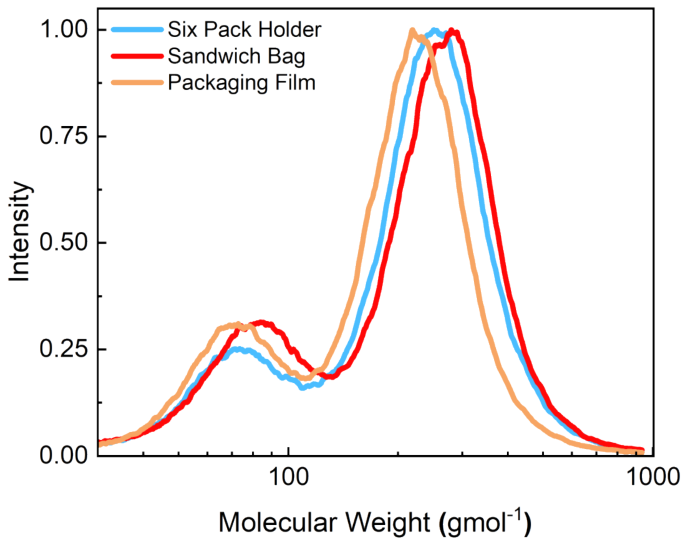
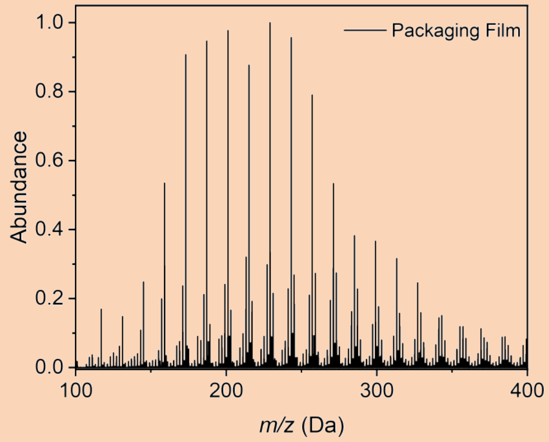
CHEMICAL CONVERSION OF COMMERCIAL PRODUCTS

- Yield was significantly effected with Sandwich Bag and Six Pack Holder
- Extent of depolymerization is similar (100-500 $gmol^{-1}$)
- Slight differences in dicarboxylic acid products







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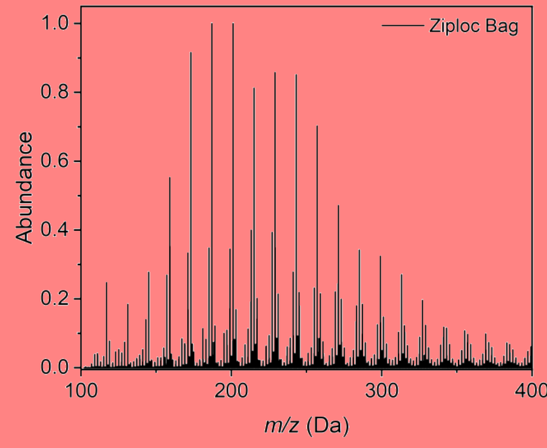
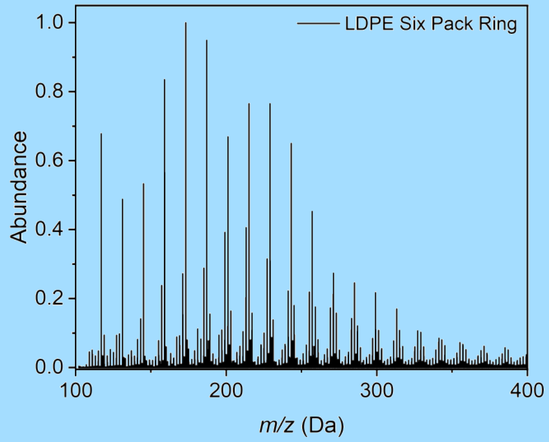
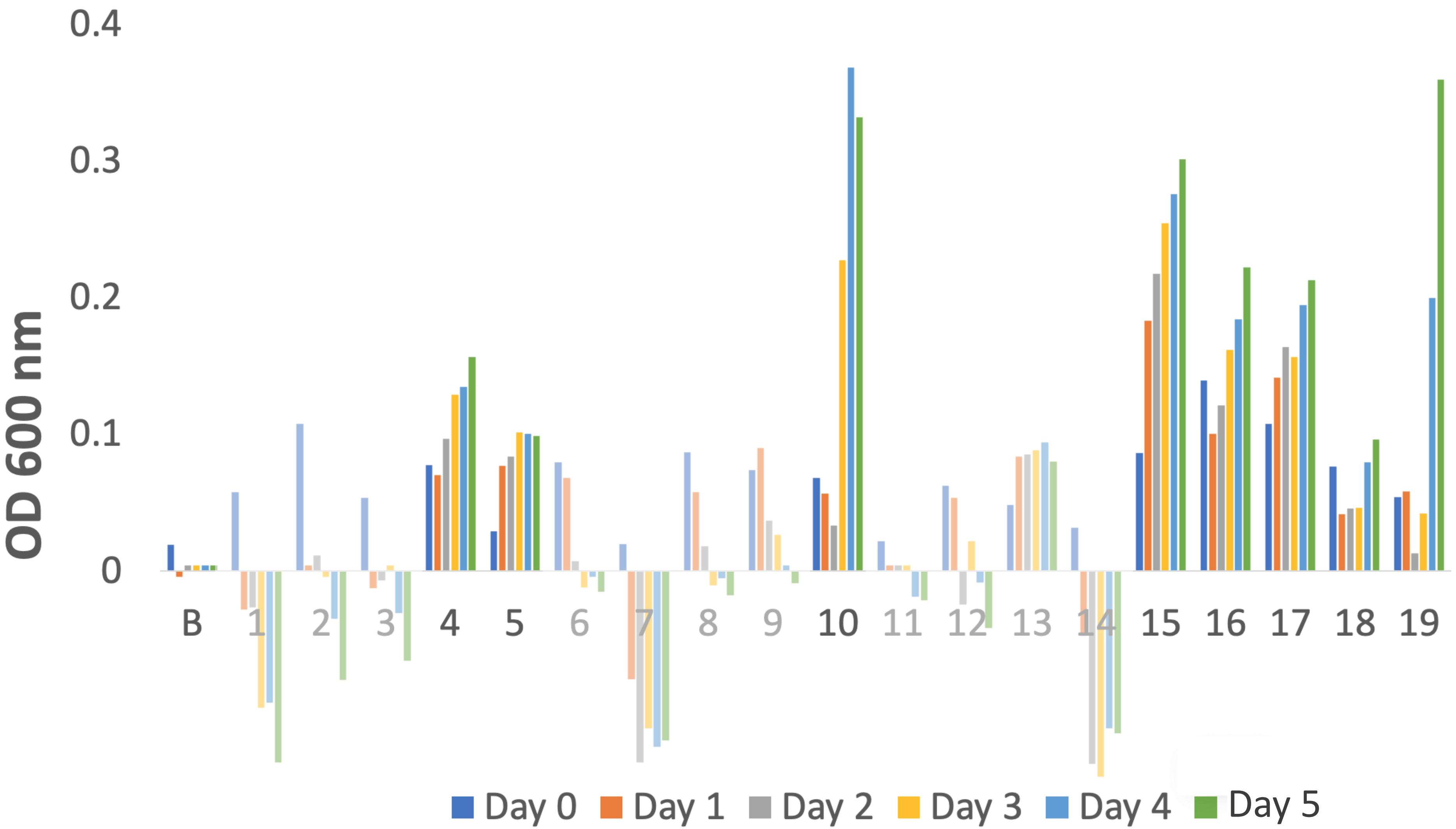


24 % Carbon Yield



26 % Carbon Yield

BIOLOGICAL AVAILABILITY OF THE BREAKDOWN PRODUCTS



Organisms that grow well:

4 - *Delftia acidovorans*

5 - *Pseudomonas stutzeri*

10 - *Yarrowia lipolytica MYA 2613*

13 - *Sphingopyxis witflariensis*

15 - *Pseudomonas sp. Rh926*

16 - *Brevundimonas vesicularis*

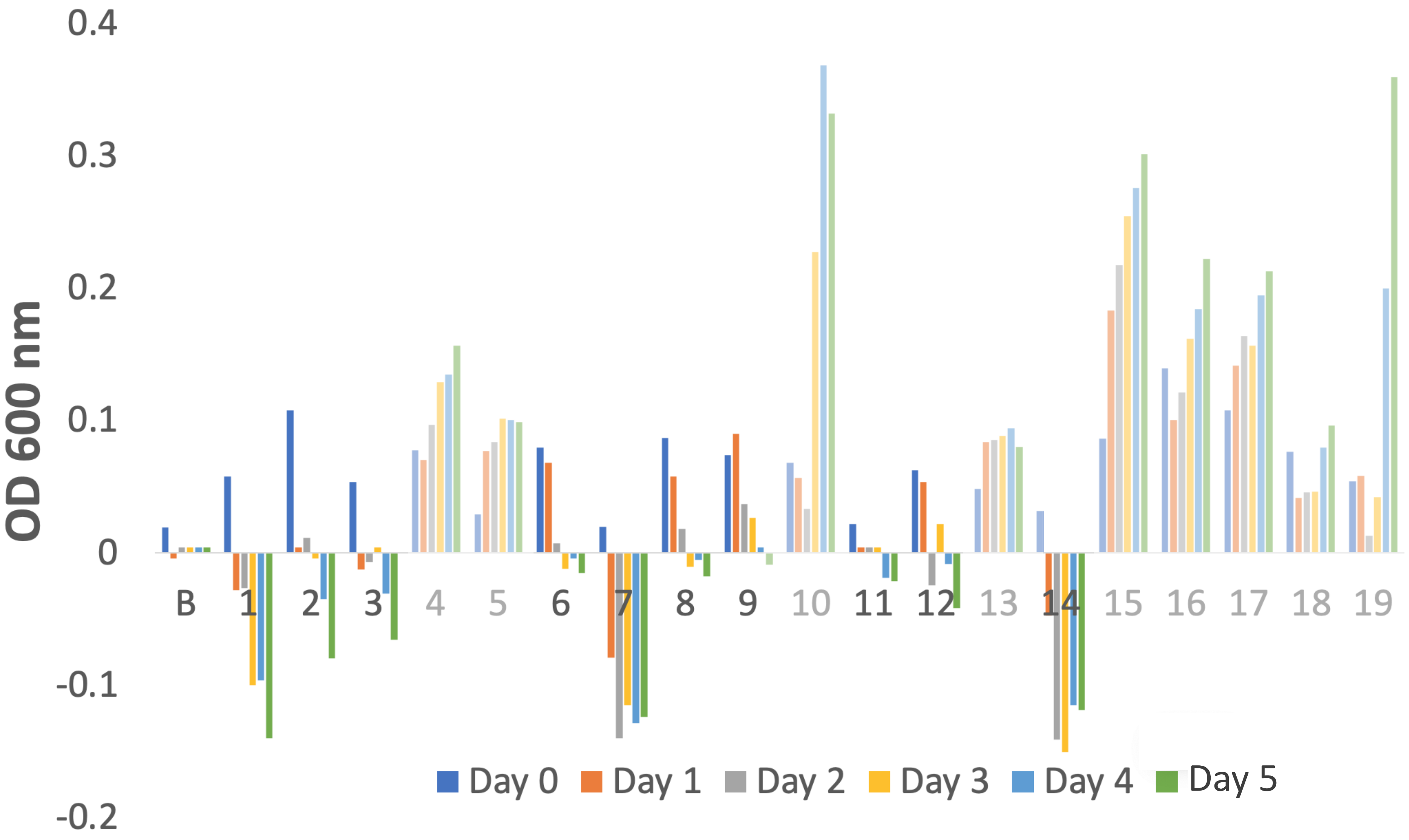
17 - *Bacillus megaterium*

18 - *Sphingomonas sp.* PWE1

19 - *Candida maltosa*

Minimal media
pH 4.5

BIOLOGICAL AVAILABILITY OF THE BREAKDOWN PRODUCTS



Organisms that do not grow well:

1 - *Exophiala alcalophila*

2 - *Bacillus subtilis*

3 - *Corynebacterium glutamicum*

6 - *Rhodococcus opacus*

7 - *Rhodococcus ruber*

8 - *Pseudomonas putida*

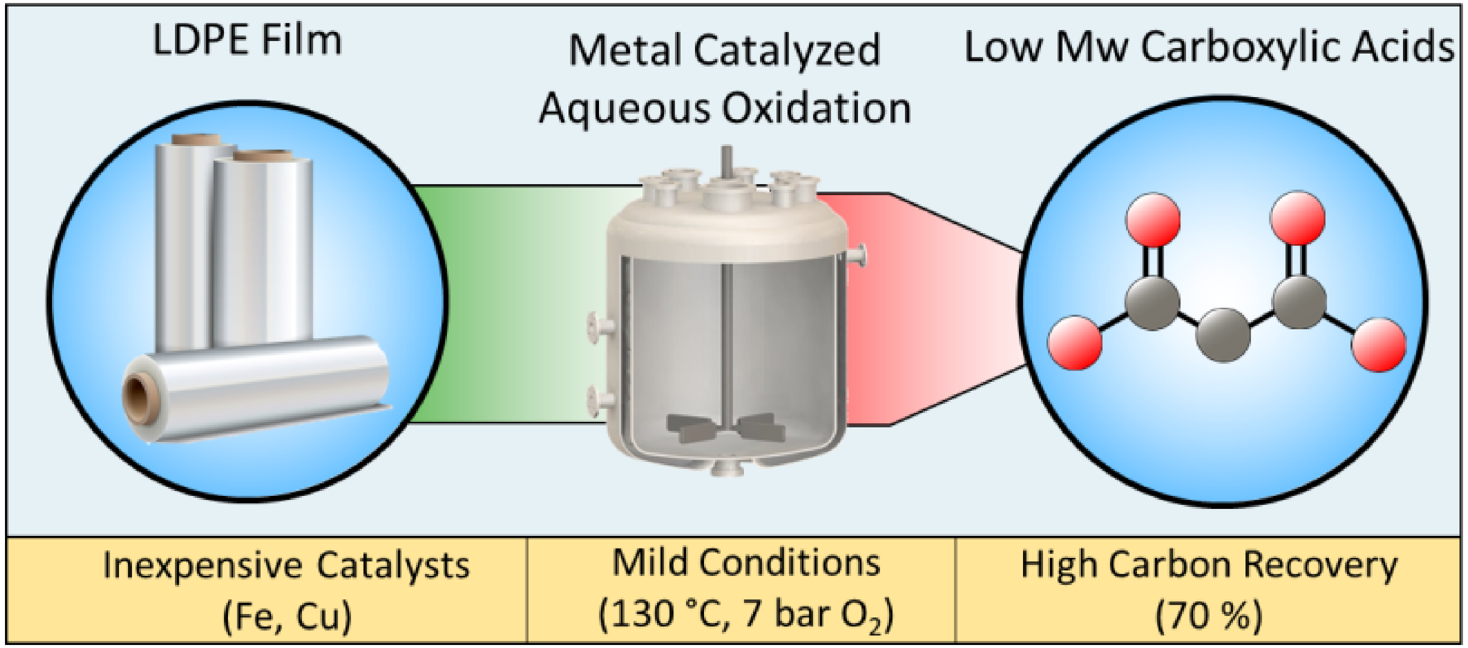
9 - *Rhodococcus jostii*

11 - *Yarrowia lipolytica ATCC 20460*

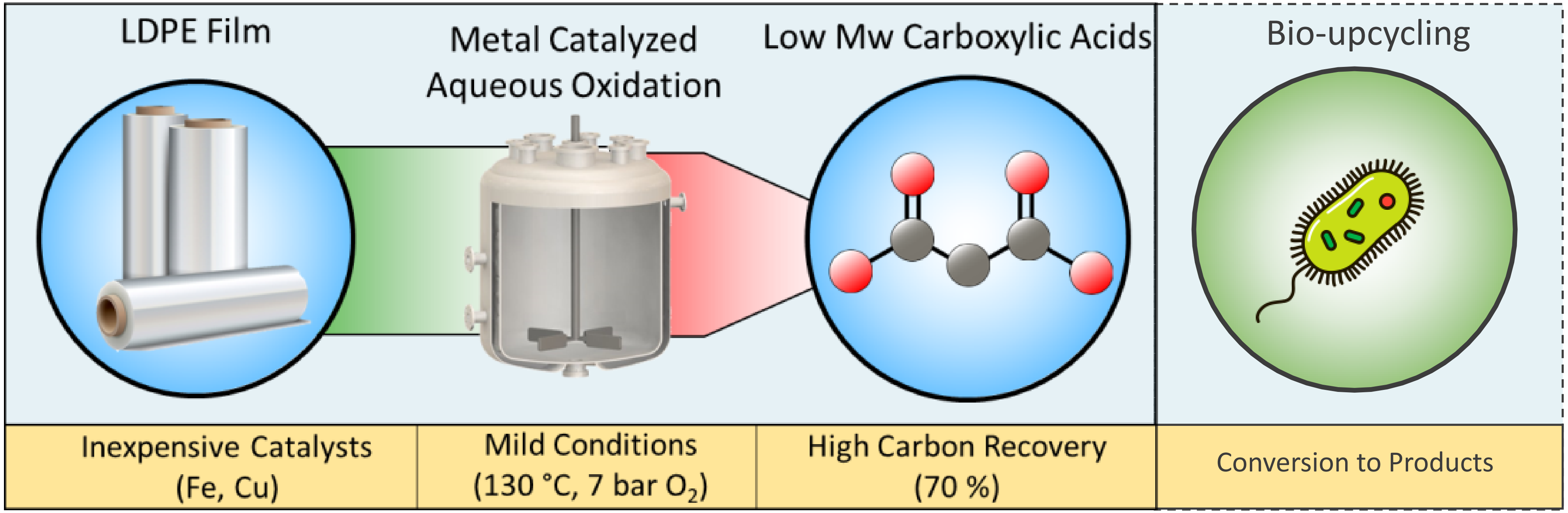
12 - *Rhodococcus rhodochrous*

14 - *Streptomyces venezuelae*

CONCLUSION

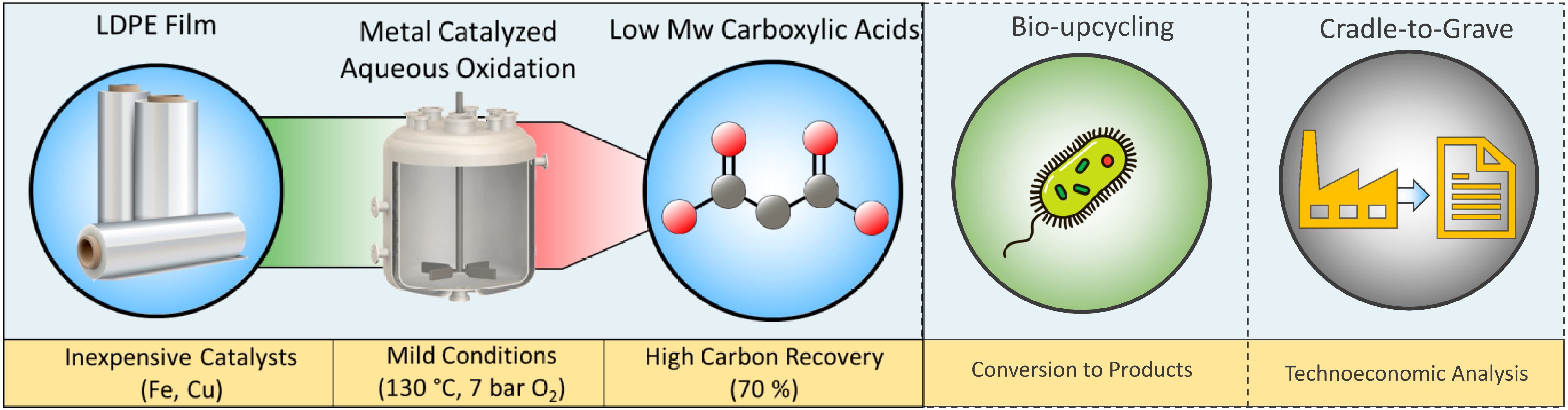

LDPE Film
Metal Catalyzed Aqueous Oxidation
Low Mw Carboxylic Acids
Inexpensive Catalysts (Fe, Cu)
Mild Conditions (130 °C, 7 bar O_2)
High Carbon Recovery (70 %)

CONCLUSION



Patent Pending, Submitted for Review

CONCLUSION



Patent Pending, Submitted for Review

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Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.