Catalytic Conversion of Polyolefins to Fuels, Lubricants, and Olefins

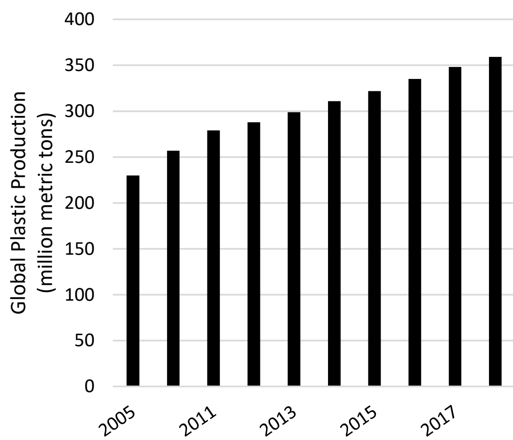
Dion Vlachos

Outline

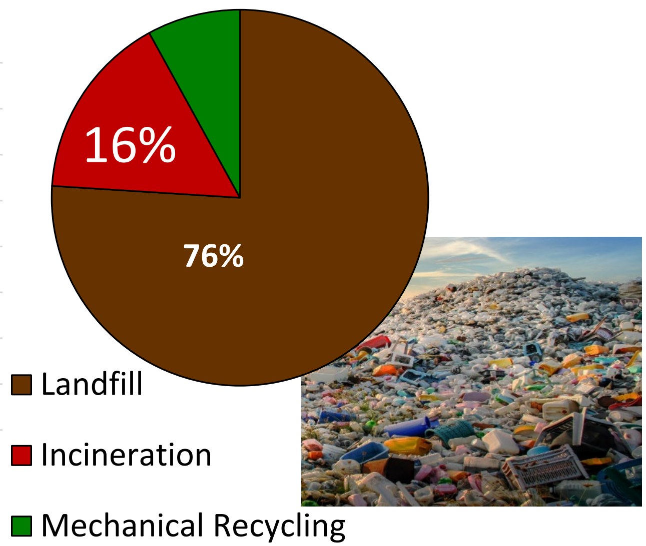
- Plastics and challenges
- Catalyst and process development: Tuning **product selectivity**
- Novel reactors: **Recycling**
- Processes and catalysts for **compositional complexity**: Additives and mixed feedstocks

The Plastics Waste Problem

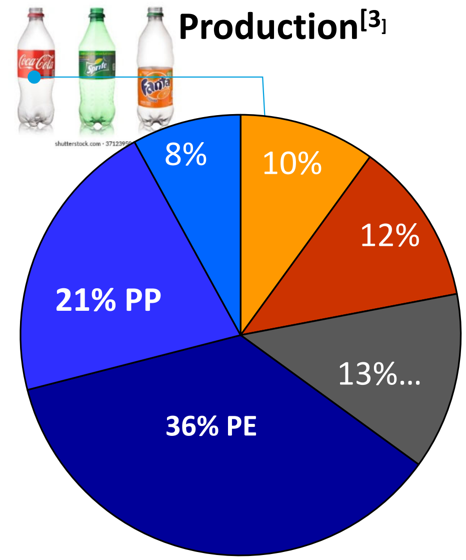
Total Global Plastic Production[1]



US Plastic Waste Management[2]



Breakdown of Global Plastic Production[3]



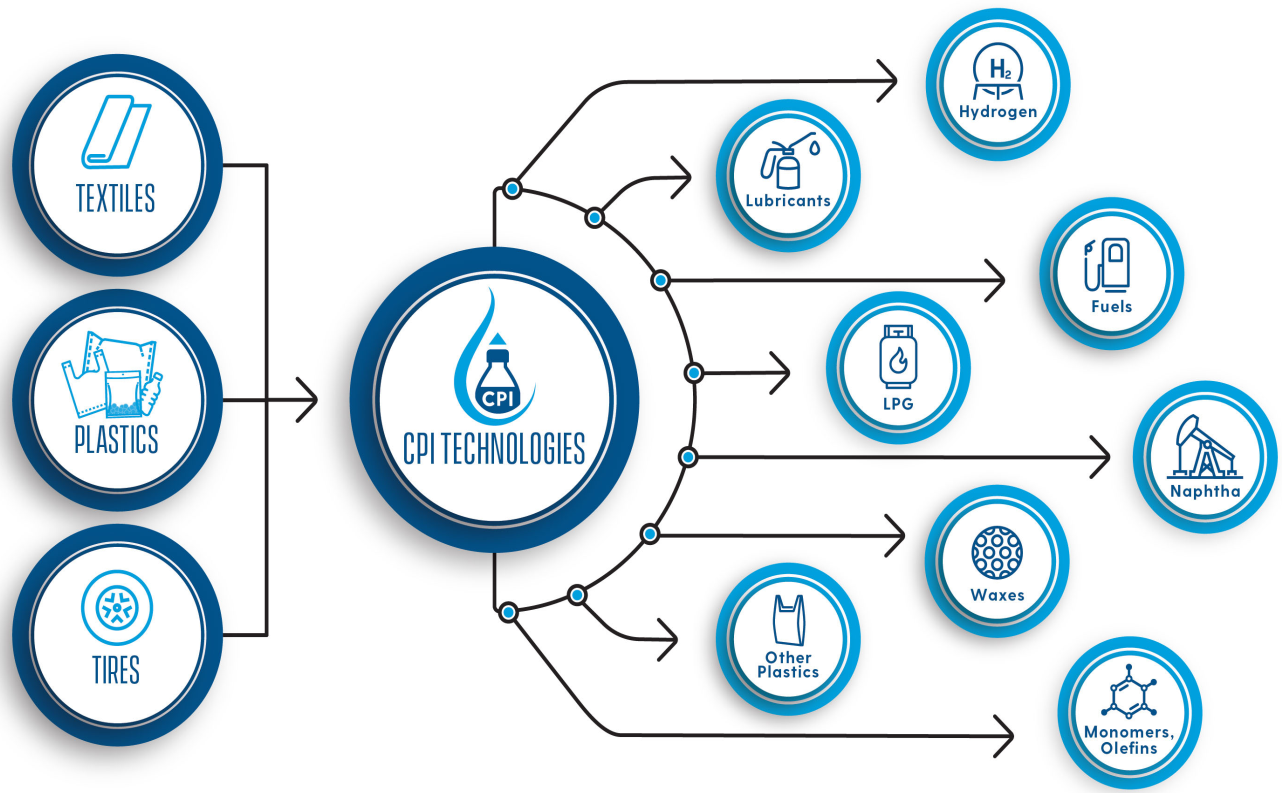
Microplastics; Additive Leaching

[1] PlasticsEurope. Plastics - the Facts 2019.; https://www.plasticseurope.org/application/files/3715/1689/8308/2015plastics_the_facts_14122015.pdf
[2] US EPA - Advancing sustainable materials management: 2017 Fact Sheet. Washington, DC 20460 22 (2019) doi:EPA530F-18-004.
[3] Geyer et al., Production, use, and fate of all plastics ever made. Sci. Adv. 3, (2017).

CENTER FOR
Plastics Innovation

Catalysis and Reaction Engineering for Chemical Recycling and Upcycling

Center's Portfolio is on Mixed Plastics, Films, Additives, and New Materials for Circularity



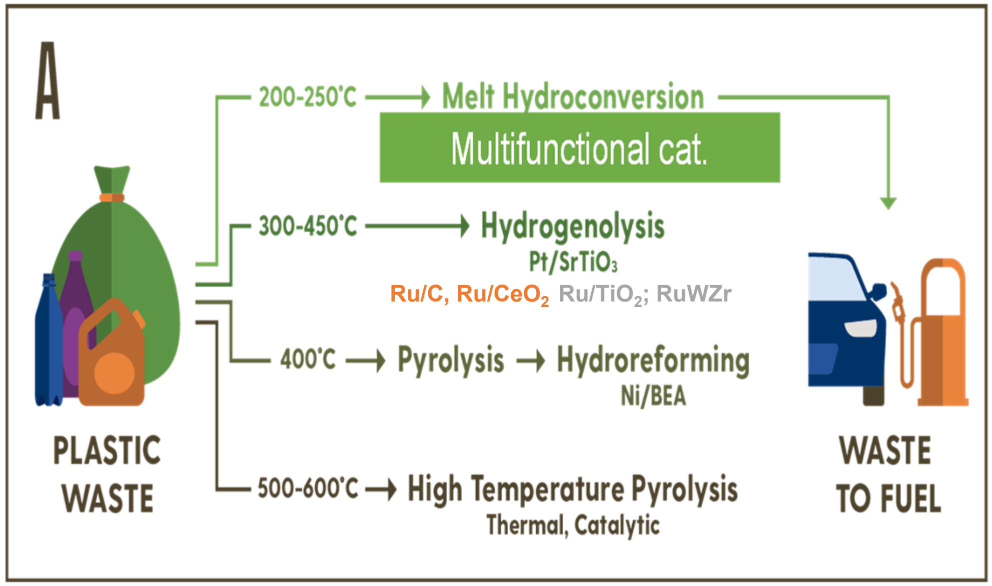
Key accomplishments

- New catalysts
- New reactor designs and processes (electrified and intensified)
- Complex feedstocks
- Scalability
- Multiscale modeling, process modeling, AI
- Mechanistic insights
- TEA/LCA

Plastics: HDPE, LDPE, LLDPE, PP, PS, PVC; PET, PEF; EVOH, EVA, PA6, P66, Elastane, etc.
Real bags, fish nets, etc.

Overview of Technologies

- **Gasification**, liquefaction
- **Pyrolysis**: energy intensive and unselective, mainly to light gases
- **Hydrogenolysis**: long processing times, low yields, linear (low value) molecules
- **Hydrocracking**: coke and gases
  - Refinery-cats are poorly performing
- **Cracking:** can this work?



Recent Hydrogenolysis Work: Sadow, Scott (iCoup); Tomishigue, Roman/Beckham, and many others

PP to Lubricants on Ru/TiO_2: Kots et al., *ACS Catal.* **11**, 8104 (2021); PE on RuWZr: Wang et al., *JACS Au* **1**, 1422 (2021).

Kots, Vance, and Vlachos, Polyolefin plastic waste hydroconversion to fuels, lubricants, and waxes: A comparative study, *React. Chem. & Eng*. **7**, 41 (2022)

Hydroconversion of Plastics

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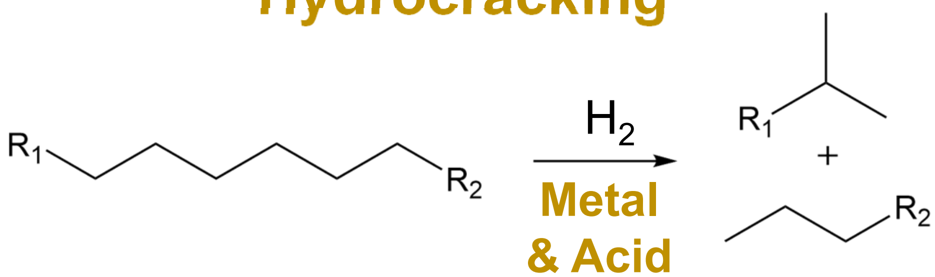
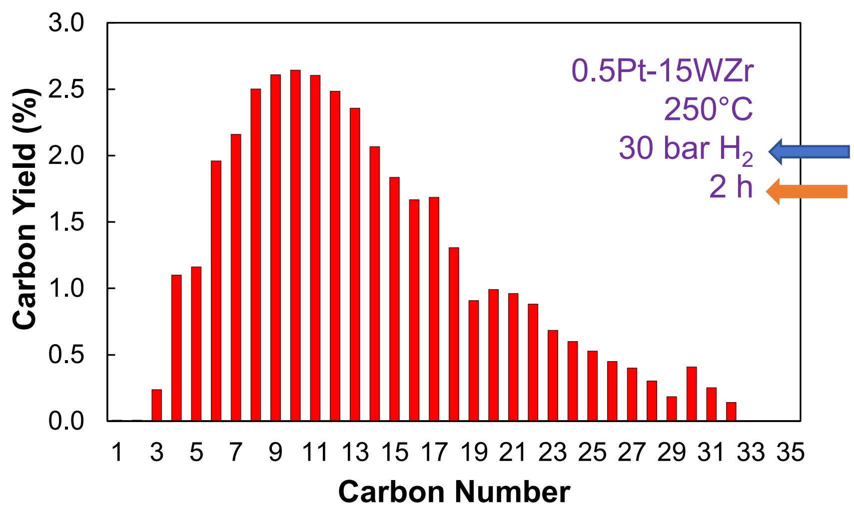
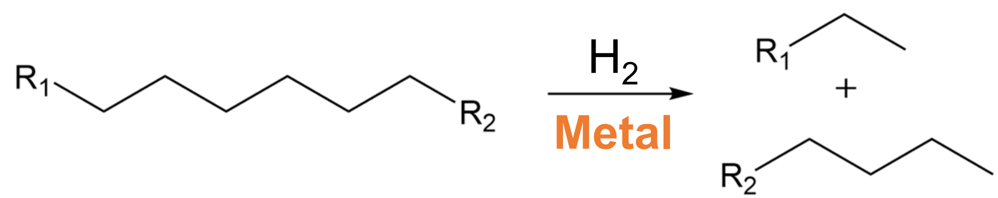
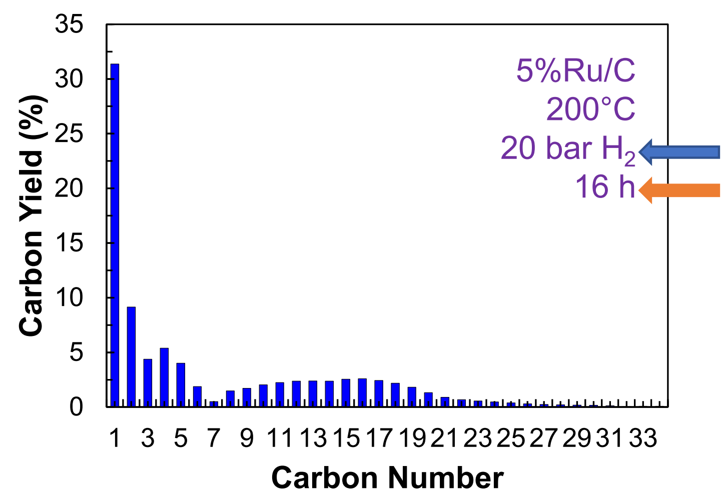
Hydrocracking





Hydrogenolysis





Liu et al. *Sci. Adv.* **7(17),** *eabf8283* (2021)

Rorrer et al. *JACS Au* (2021)

Hydrocracking using a Dual Catalyst

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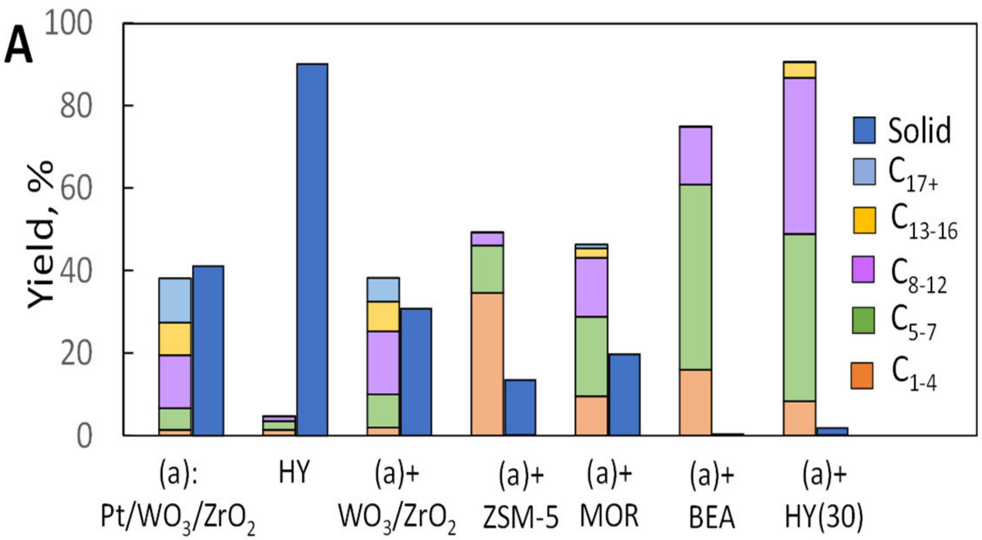
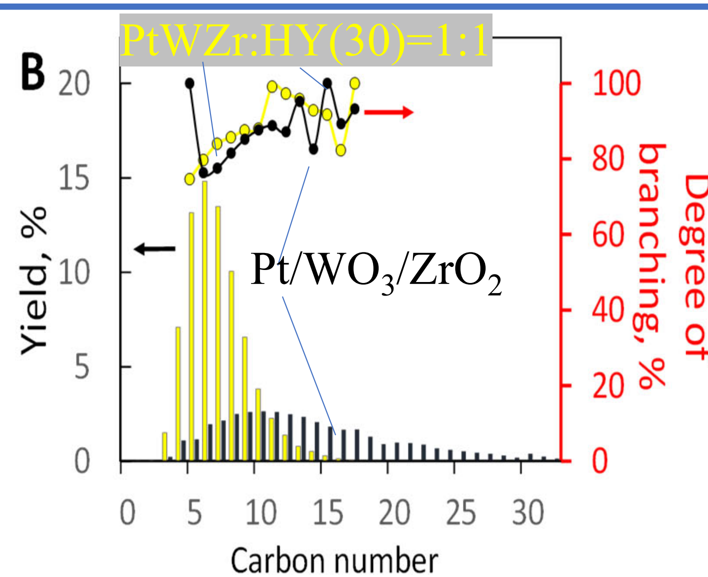
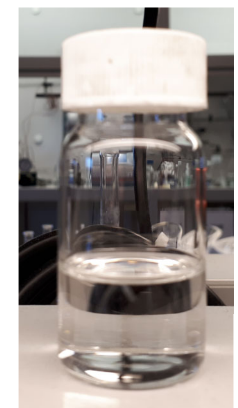






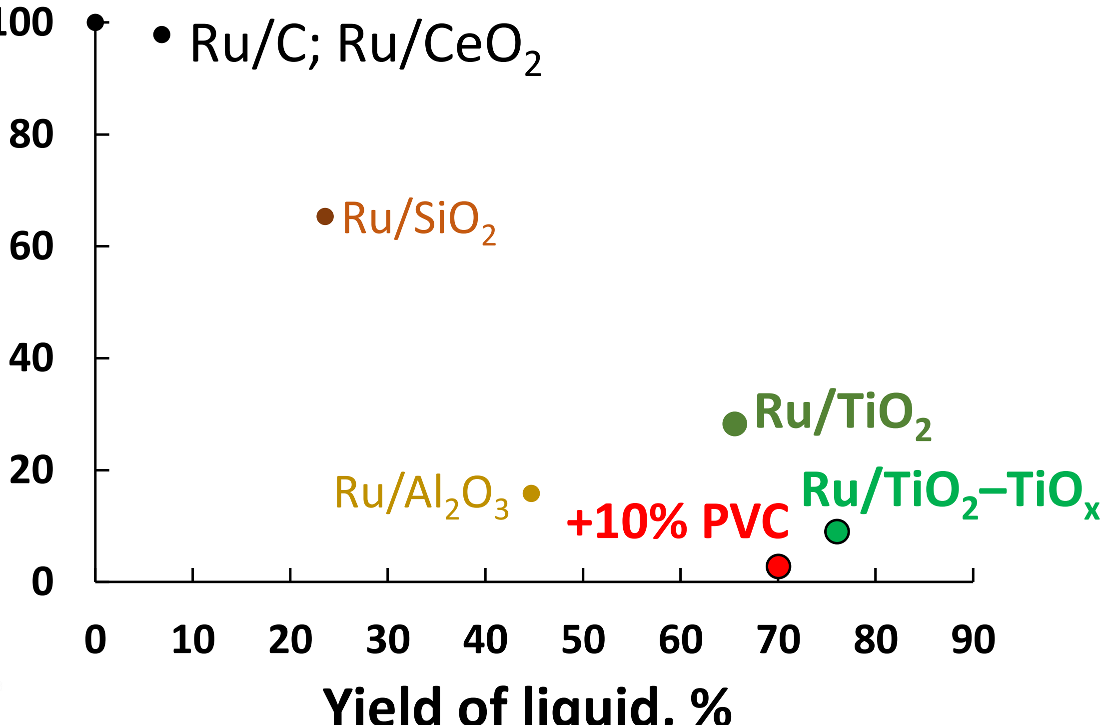
- Operation @ 250 °C (in the melt), 30 bar H_2, 2 h
- $Pt/WO_3/ZrO_2$ +FAU (HY) or BEA synergy
- Gasoline, diesel, and jet HCs: **Max liquid yield 85%; Very low light alkanes**

- **PtWZr** gives a broader distribution and drives **hydroisomerization**
- **HY** narrows distribution **cracks faster**
- **Many ways to tune the catalyst**

Liu et al. *Sci. Adv.* **7(17)**, *eabf8283* (2021)

Materials Matter

Hydrogenolysis: Ru/support effect



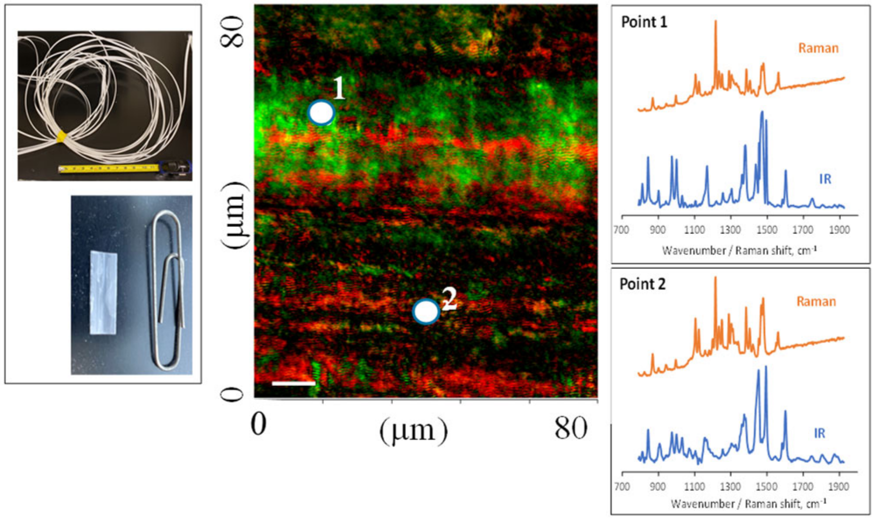
- Ru/TiO$_2$ is the best catalyst for liquids
- The support has a profound effect
- Further optimization reduces the light gas

30 bar H_2 pressure; 2 g of PP (M_w 250 kDa); 100 or 50 mg of Ru/support (4% Ru loading)

Kots et al., *Polypropylene Plastic Waste Conversion to Lubricants over Ru/TiO$_2$ Catalysts. ACS Catal.* **11**(13), 8104 (2021); Electronic modulation of metal-support interactions improves polypropylene hydrogenolysis over ruthenium catalysts. *Nat. Commun.* **13**(1), 5186 (2022). Upcycling of plastic waste severely contaminated with chlorinated compounds, *Nature Sustainability* **6**(10), 1258 (2023).

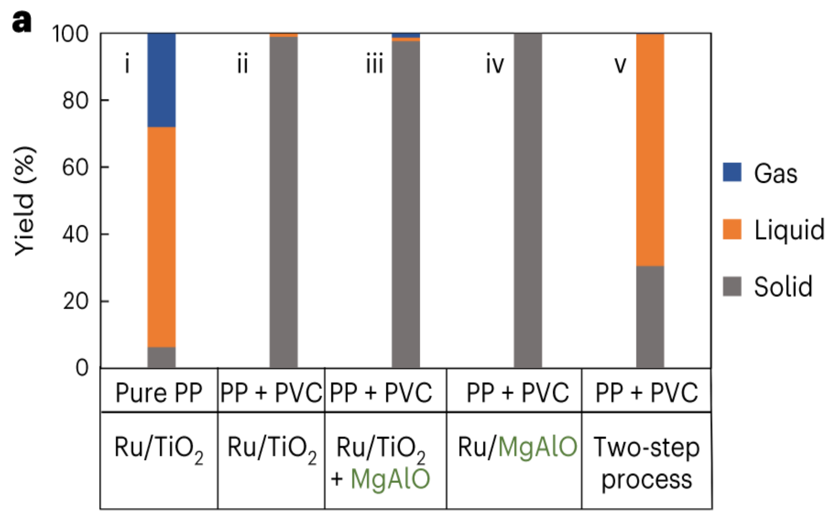
Grand Challenges

- High volume
  - **Scalability; catalyst abundance and cost**
- Feedstock complexity
  - **Mixed plastic waste**; poisons, e.g., PVC
  - **Multilayer plastics**; many functional groups
  - **Additives**: Can poison catalysts; can be carcinogenic
- The chemistry challenge
  - **C-C bond strength:** High temperatures; significant energy; mostly methane produced
  - **The nastiness of heteroatoms!!**



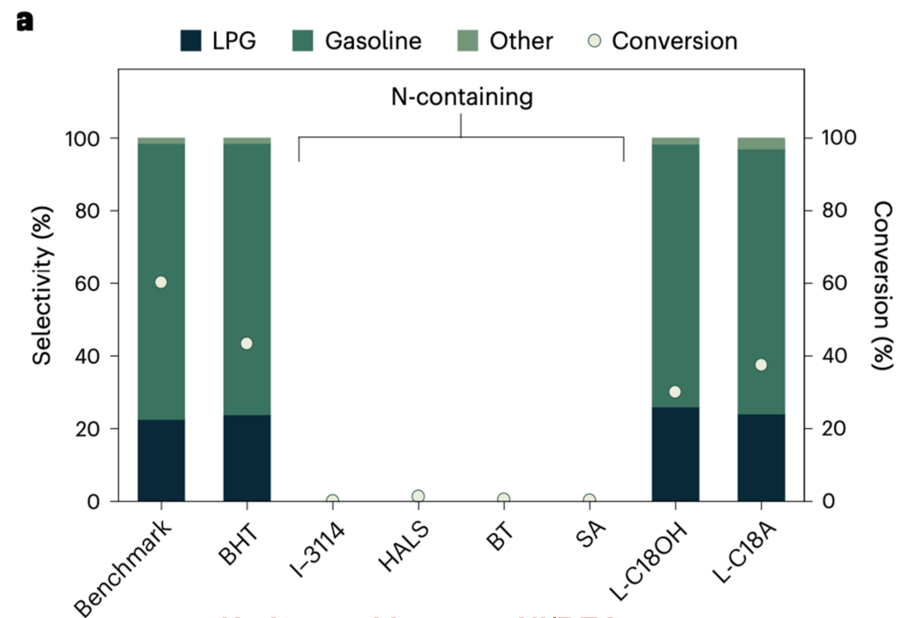
Kots, Vance, and Vlachos, Polyolefin plastic waste hydroconversion to fuels, lubricants, and waxes: A comparative study, *React. Chem. & Eng*. **7**, 41 (2022)

Hydroconversion of Additive- & Impurity-rich Polyolefins



Hydrogenolysis over Ru/TiO_2 and Hydrocracking over Pt/WO_3-ZrO_2

Kots, Pavel et al. *Nature Sustain.* **2023**, 6, 1258.



Hydrocracking over Ni/BEA

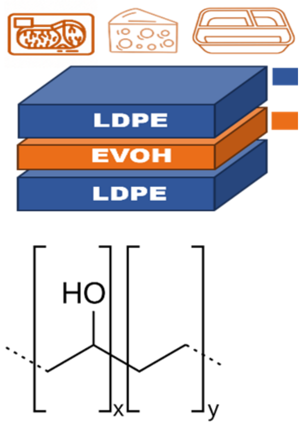
Ngu, Jackie et al. *Nature Chem. Eng.* **2025**, 2, 220

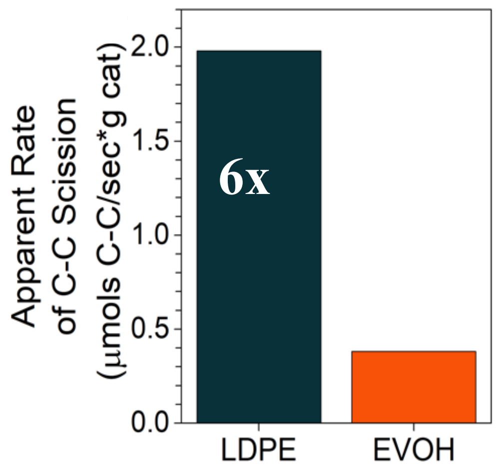
Traditional Ru, Pt, and Ni-based hydroconversion catalysts lose significant activity in the presence of small amounts of additives and other heteroatom-containing polymers such a PVC

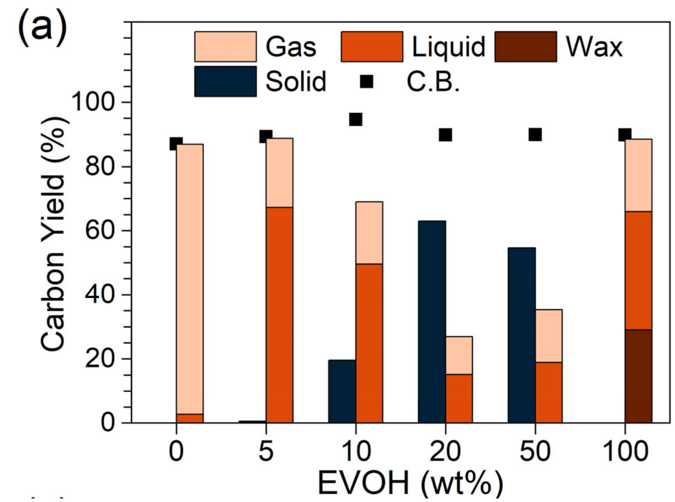
VlachosLab AT THE UNIVERSITY OF DELAWARE

LDPE + Ethylene Vinyl Alcohol (EVOH)

Reactivity





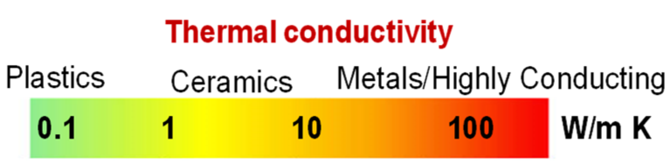


- EVOH reacts more slowly than LDPE even though it contains active OH groups!
- EVOH retards LDPE's reactivity despite not interacting strongly with the catalyst
- **EVOH and EVA from aromatics or polyenes that deactivate the catalyst**

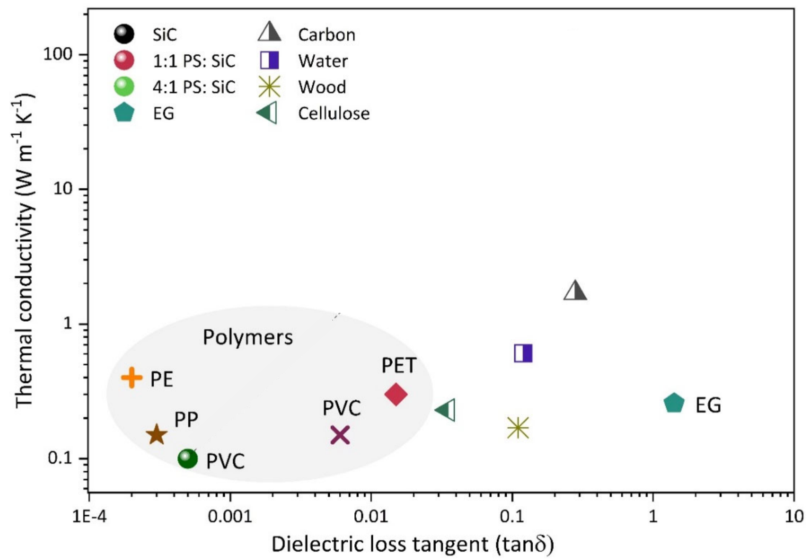
Oberhausen, Christine et al., Hydrogenolysis of Poly(Ethylene-co-Vinyl Alcohol) and Related Polymer Blends over Ruthenium Heterogeneous Catalysts. *ChemSusChem* e202400238 (2024).

Grand Challenges (Cont.)

- **Solids' handling**: low contact area
- Macromolecular chemistry of **melts on surfaces and in pores** is poorly understood
- **Transport effects** are important



Conventional heating



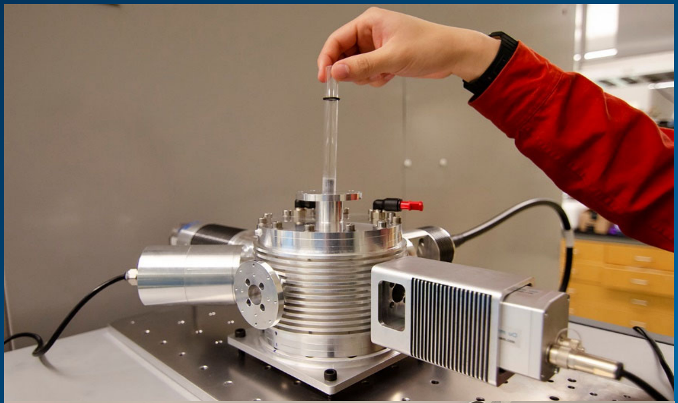
Microwave heating

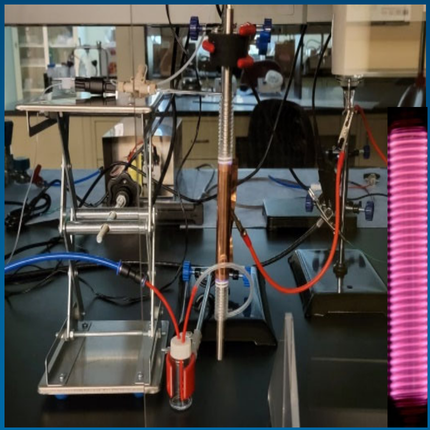
Novel reactors

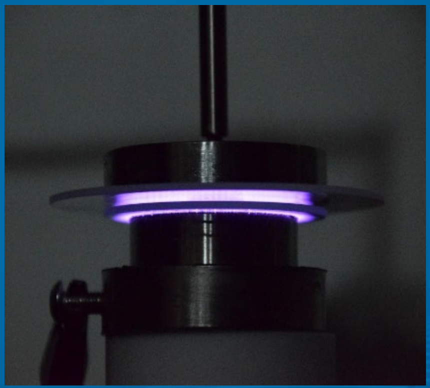
Esun Selvam, Jacqueline Ngu, Dionisios G. Vlachos

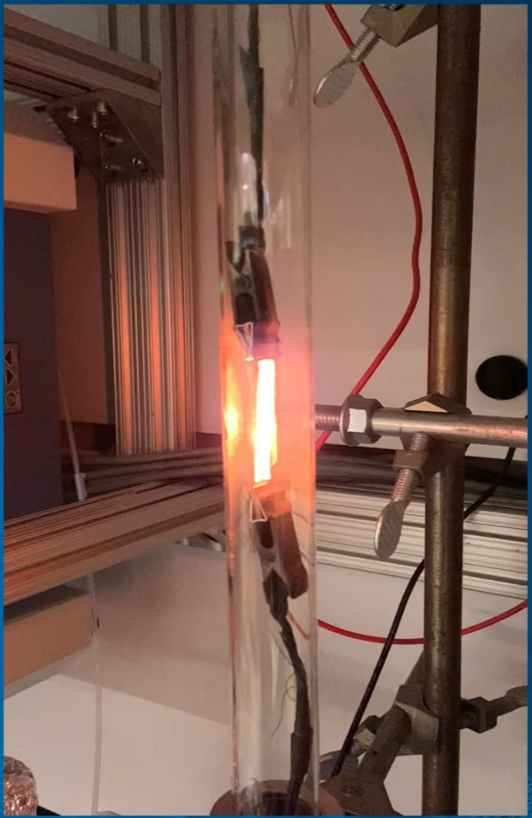
Process Intensification and Electrification:

MWs, Joule, Plasmas



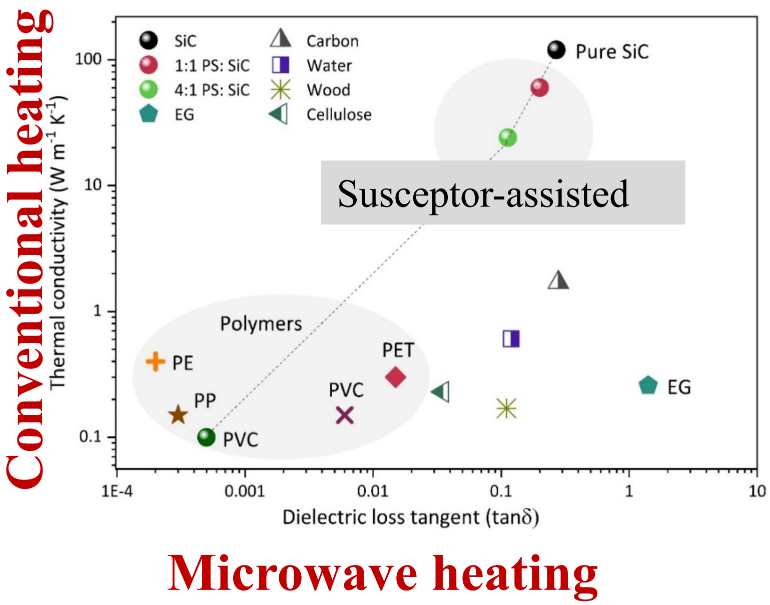


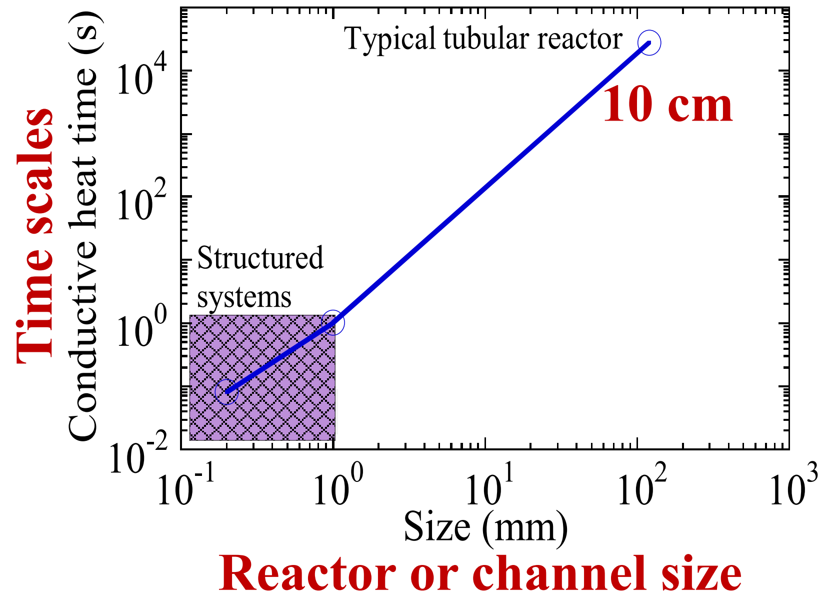




Grand Challenges

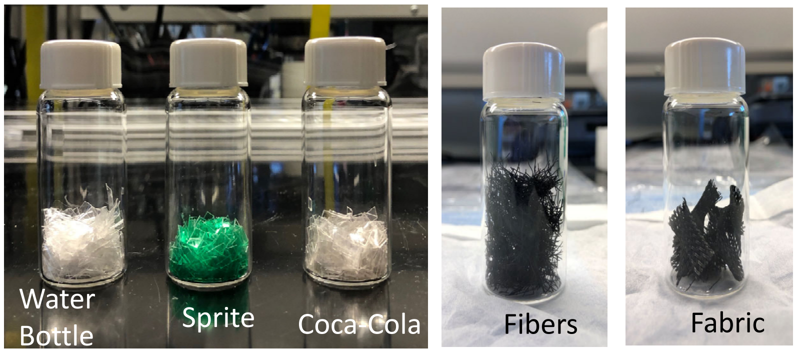
Transport Limitations

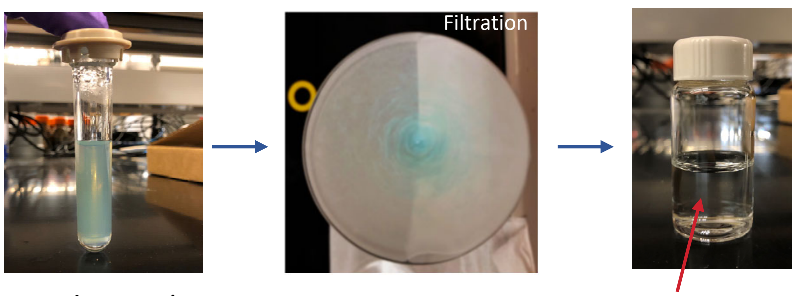




Property calculation: Goyal and Vlachos, Multiscale modeling of microwave-heated multiphase systems. *Chem. Eng. J.* **397**, 125262 (2020).

Polyesters Depolymerization using Microwaves





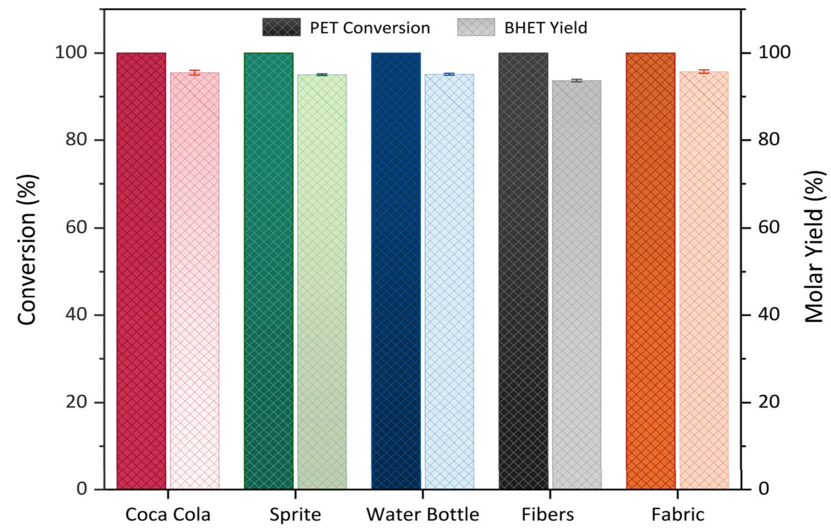
Product Solution

After Filtration - BHET in Water

Microwave reactor

ZnO heterogeneous catalyst

EG as a solvent, a nucleophile, and MW media

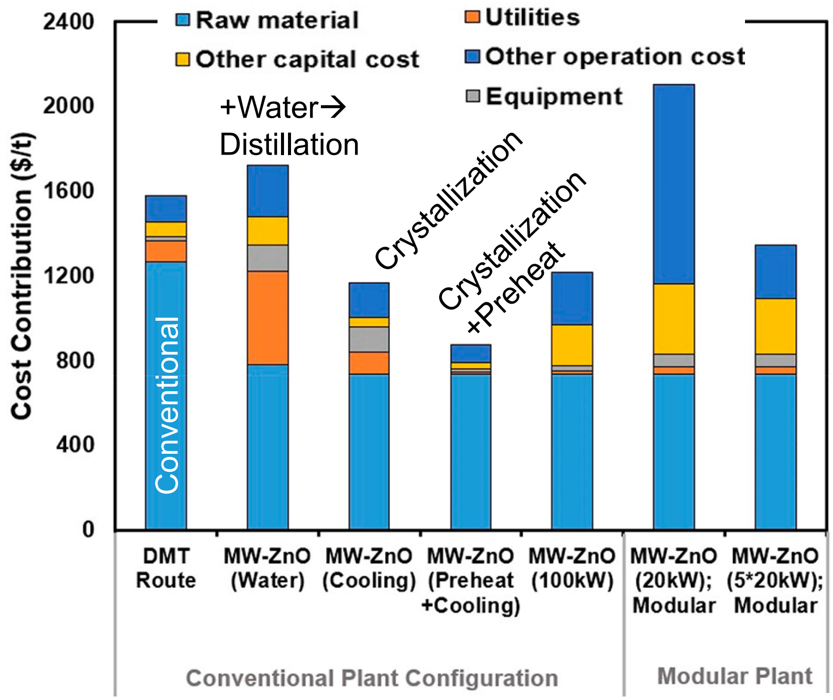


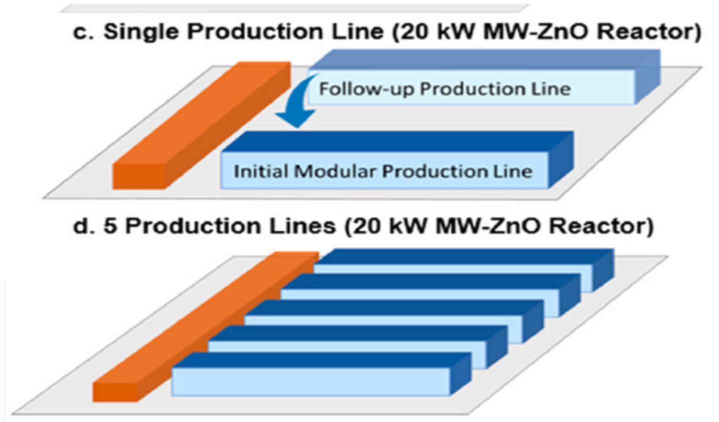
100% conversion; 95% BHET yield

210 °C; Reaction time ~**5 min**

Selvam et al., Microwave-assisted depolymerization of PET over heterogeneous catalysts. *Catal. Today* **418**, 114124 (2023); Luo et al., Economic and Environmental Benefits of Modular Microwave-Assisted Polyethylene Terephthalate Depolymerization. *ACS Sustain. Chem. Eng.* **11**, 4209 (2023).

TEA of MW-assisted PET Glycolysis



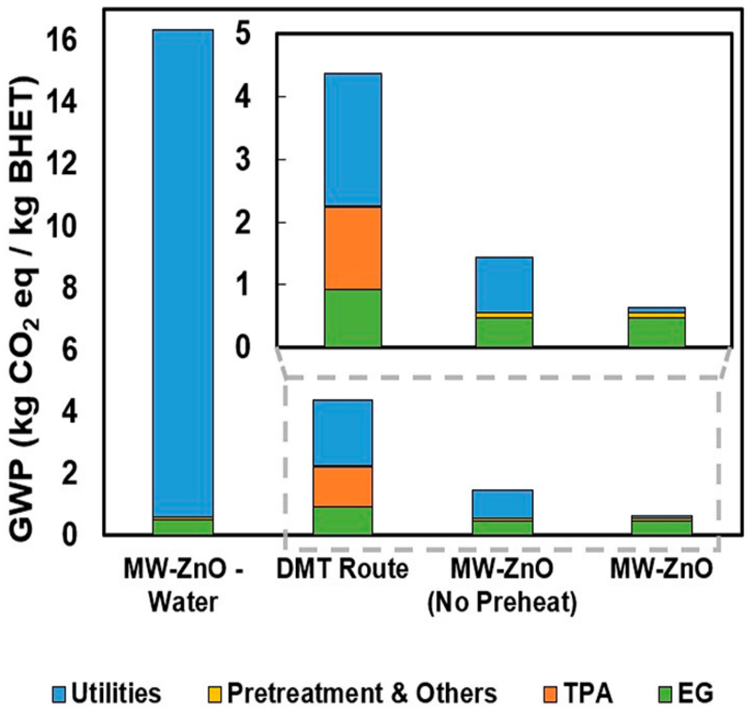


- The efficient MW-ZnO process demonstrates a lower production cost at a much smaller scale

Conventional Plant: 14,600 kg BHET/h | Modular plant: 20 kW, 132 kg PET/h, 0.4 m^3 (~1 kta)
115 kta

Luo, Selvam, et al. *ACS Sustainable Chemistry & Engineering* **2023** *11* (10), 4209-4218

Life Cycle Assessment



- Energy-intensive separation to separate EG and water results in high GWP in the dissolution-crystallization pathway
- **Crystallization and pre-heat (heat recuperation) are essential**

Global Warming Potential

MW-Glycolysis < CH-Glycolysis << DMT Route

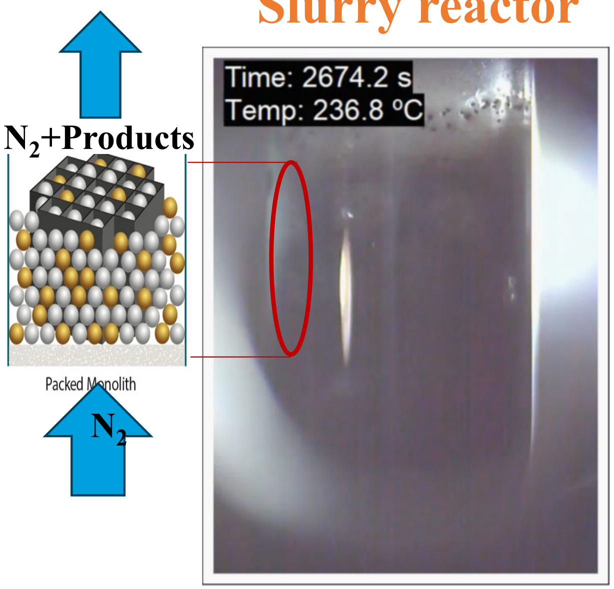
Luo, Selvam, et al. *ACS Sustainable Chemistry & Engineering* **2023** *11* (10), 4209-4218

Polyolefin Depolymerization

MW Slurry Reactor

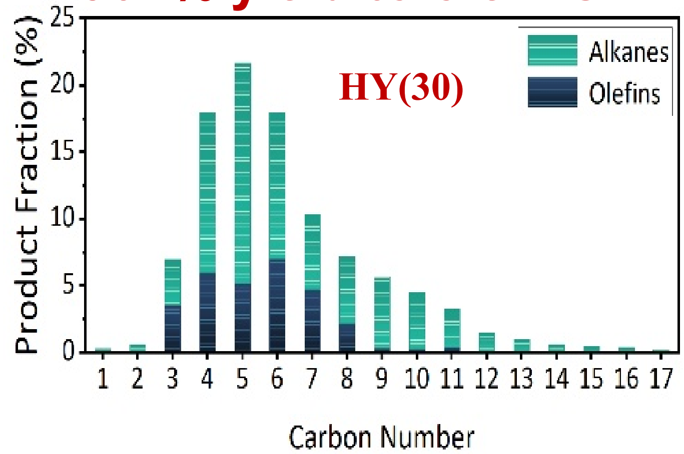
- **Reaction in Seconds!!**
- **No External H_2 Use!!**

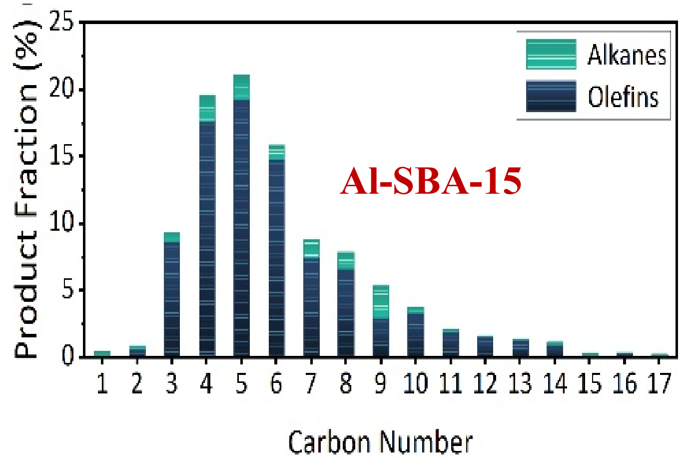
Slurry reactor



Selvam et al., Plastic waste upgrade to olefins via mild slurry microwave pyrolysis over solid acids. *Chem. Eng. J.* **454**(Part 3), 140332 (2023).

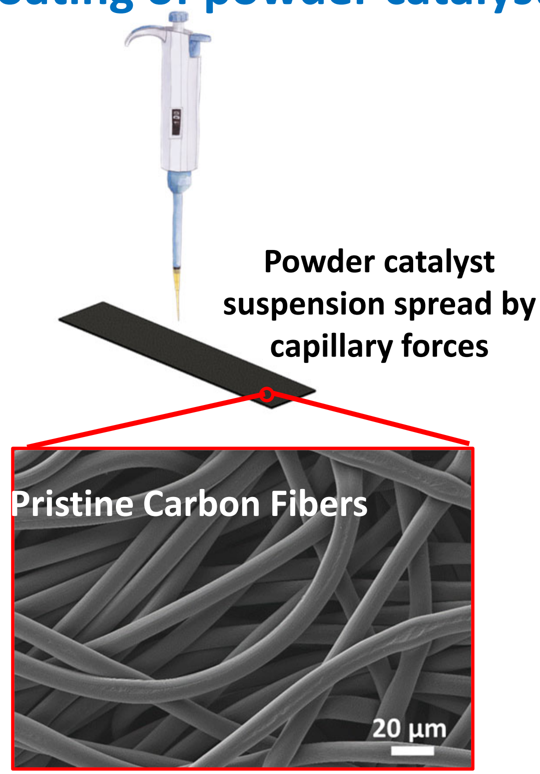
90+% yield to olefins

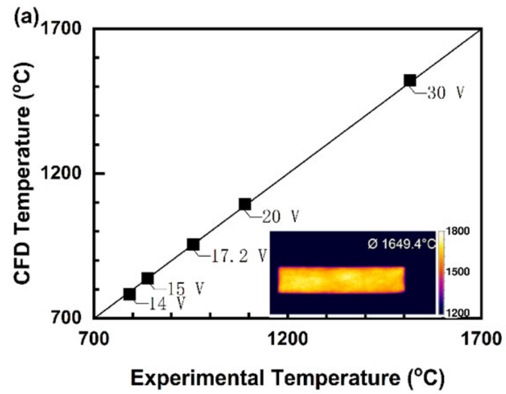


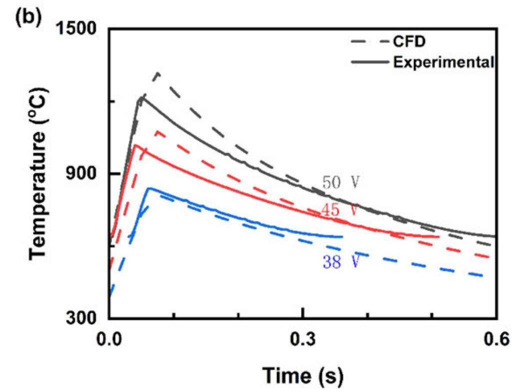


Catalyst Coating & Temperature Uniformity

Drip coating of powder catalysts

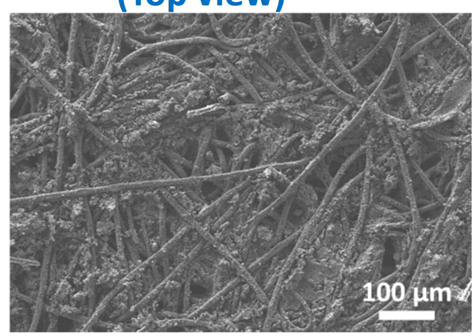




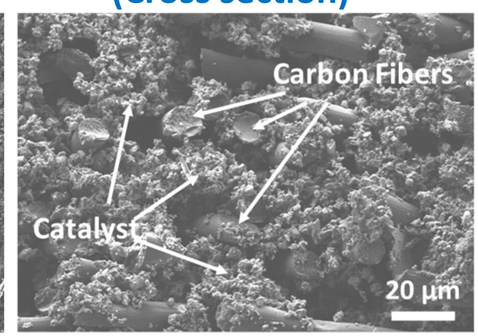


Catalyst-coated tape

(Top view)



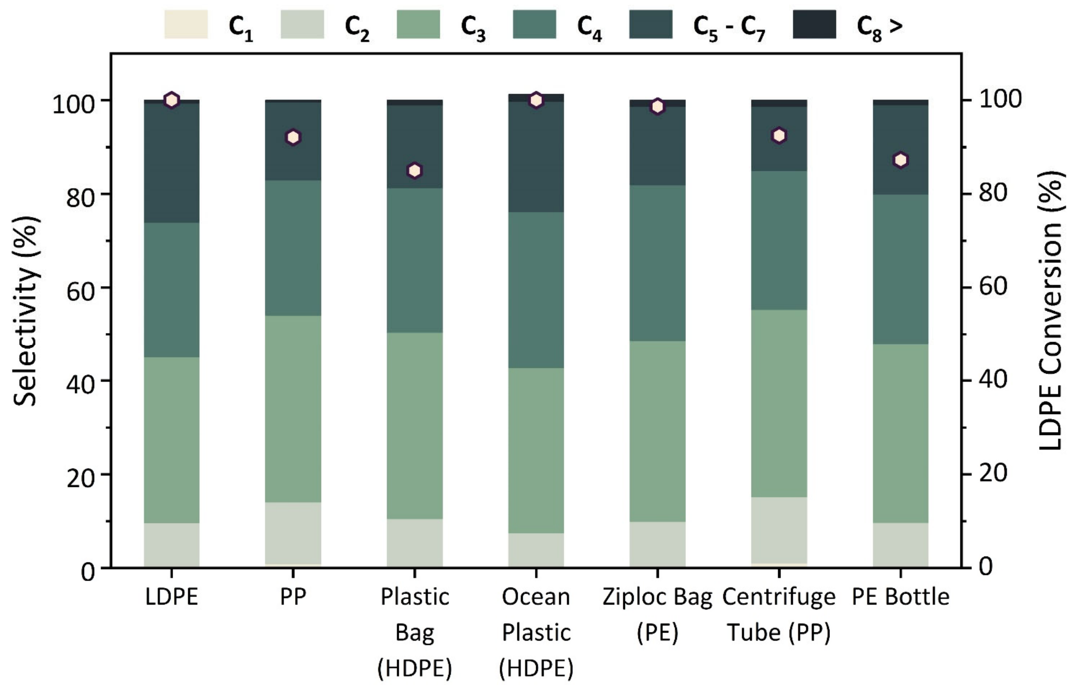
(Cross section)



Vast catalyst inventory for coating

K. Yu, C. Wang, W. Zheng, and D. G. Vlachos, Dynamic Electrification of Dry Reforming of Methane with In Situ Catalyst Regeneration. *ACS Energy Letters*, 1050-1057 (2023).

Tuning Further to Reach Contact Times of <100 ms; Joule Rxtr



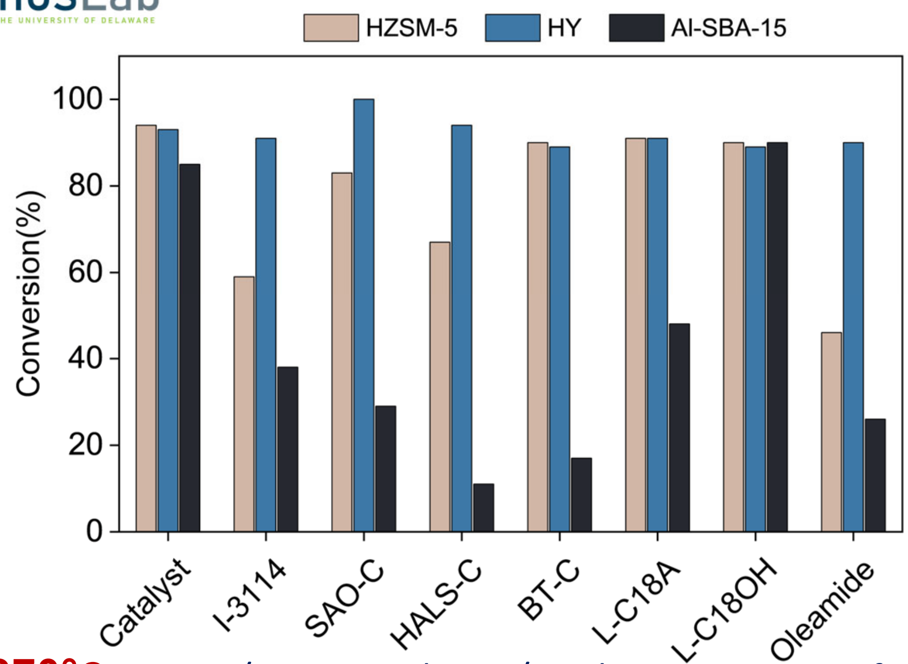
Esun Selvam, Recycling polyolefin plastic waste at short contact times via rapid heating. *Nat. Commun.* **15**, 5662 (2024).

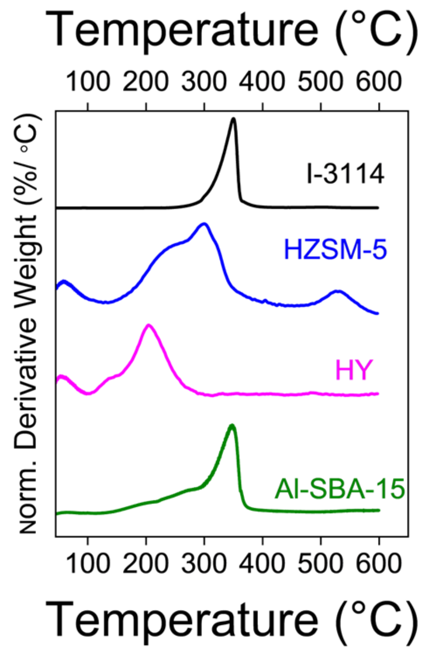
- We can selectively produce light olefins by tuning catalyst and reactor
- **No change in performance with various real-life plastic feeds**

Cat deconstruction of organic additive-containing and mixed plastics

Jacqueline Ngu, Sean Najmi, Esun Selvam, Brandon Vance,
Piaoping Yang & Dionisios G. Vlachos

Catalytic Cracking with Additives



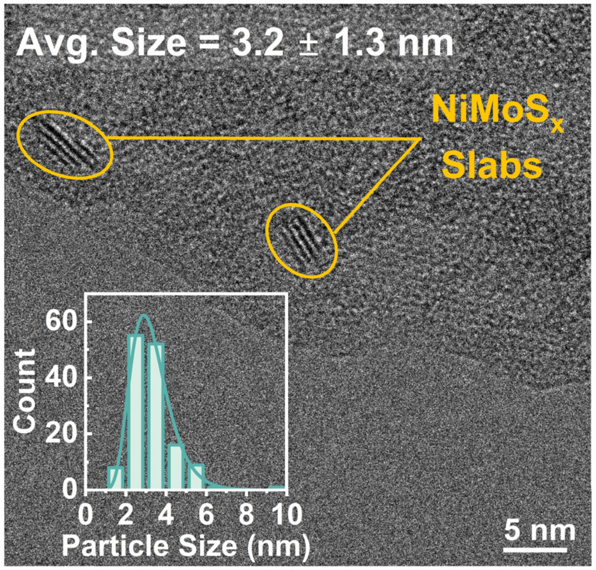


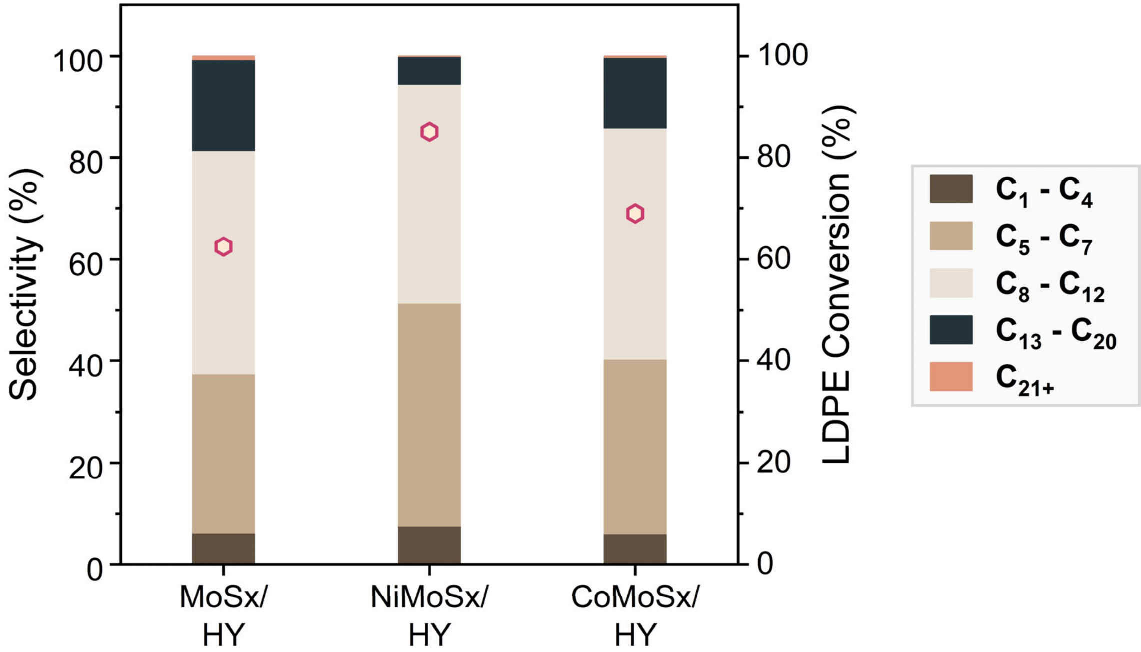
370°C 100 mL/min N_2, polymer/catalyst = 10, 2wt% of additive, **200 seconds**

- HY (mesoporous) is resistant to most additives
- HZSM-5's decrease in conversion is due to the lack of mesopores
- Al-SBA-15's lower acidity makes it susceptible to poisoning

Hydrocracking of Complex Wastes over $NiMoS_x$/Zeolite

Temperature = 300 °C, time = 2 h



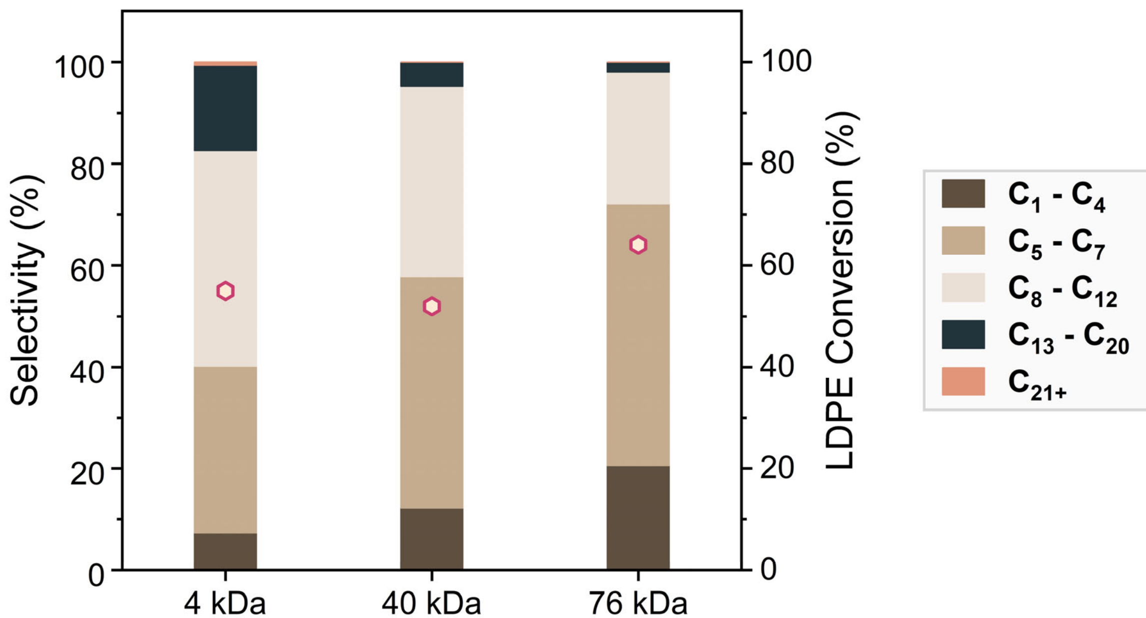


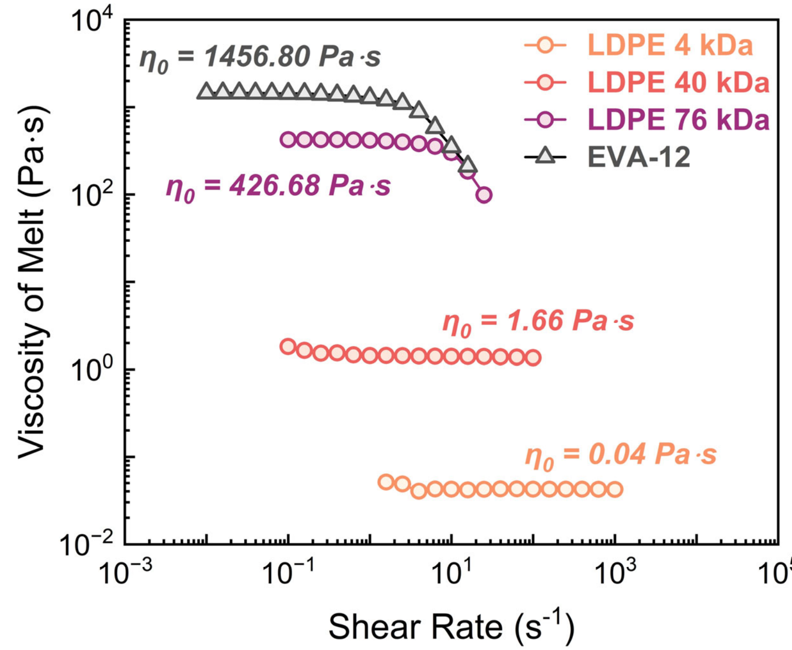
Ni outperforms **MoS_x** and **Co-promoted MoS_x** supported on HY

Selvam, Esun et al., *JACS*, 2025, 47, 11227.

Impact of Polymer Rheology on Hydrocracking

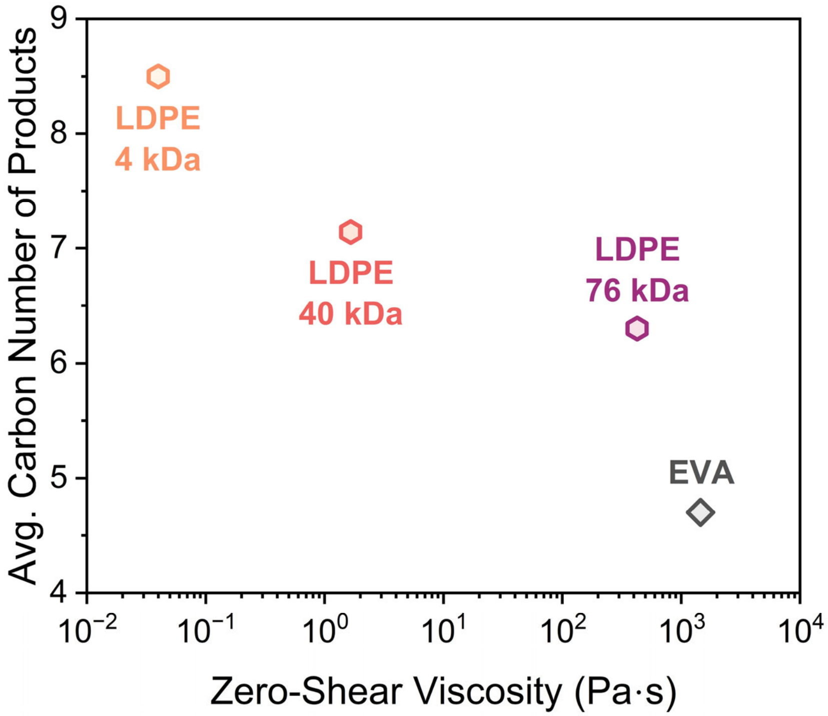
Temperature = 300 °C

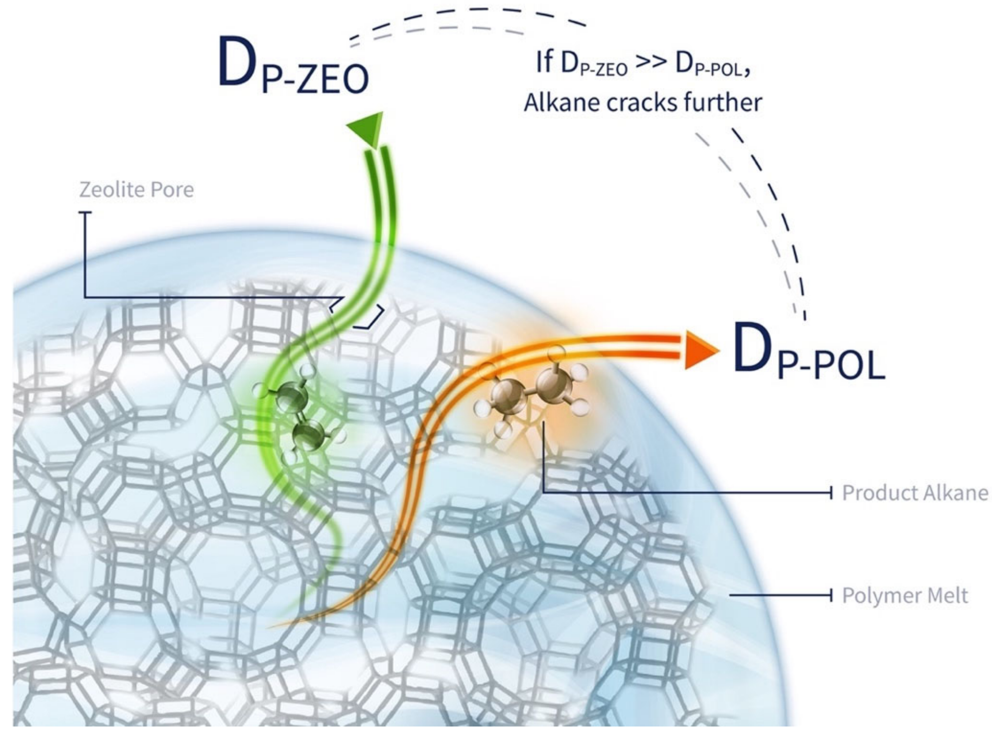




- Varying MWs (with comparable branch densities): $\mathbf{C_{avg\text{-}4\,kDa}} > \mathbf{C_{avg\text{-}40\,kDa}} > \mathbf{C_{avg\text{-}76\,kDa}}$
- Zero-Shear Viscosity: **LDPE 4 kDa < LDPE 40 kDa < LDPE 76 kDa < EVA-12**

Impact of Polymer Rheology on Hydrocracking

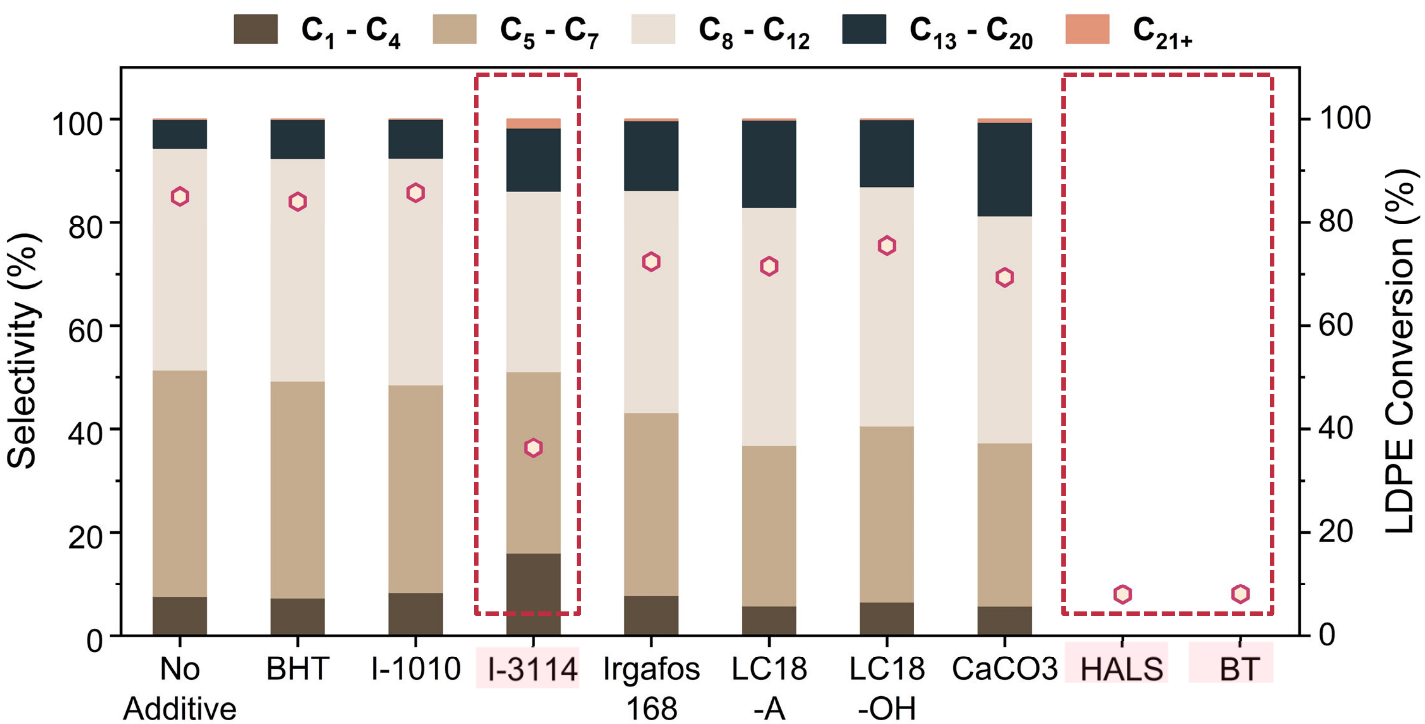




Selvam, Esun et al., *JACS*, 2025, 47, 11227.

Hydrocracking of Additive-containing Polyolefins

$NiMoS_x$/HY

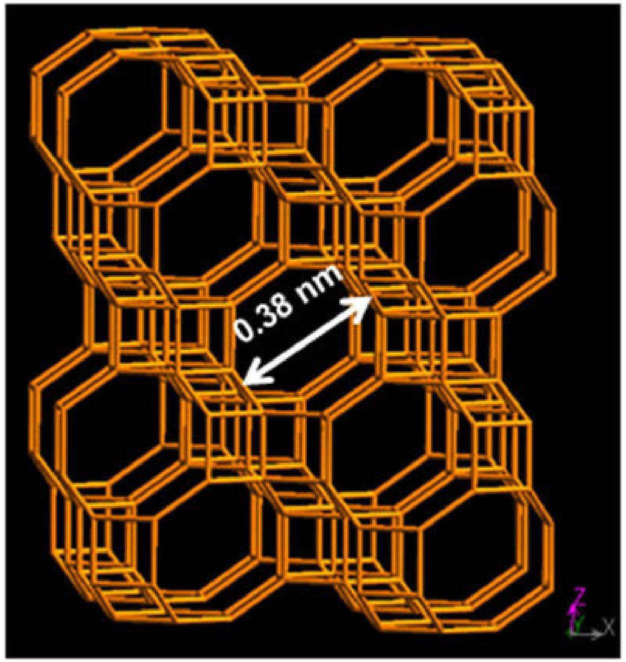


Additive Concentration = 2 wt.% (10 wt.% for $CaCO_3$)
300 °C, 2 h, polymer:catalyst ratio = 20:1

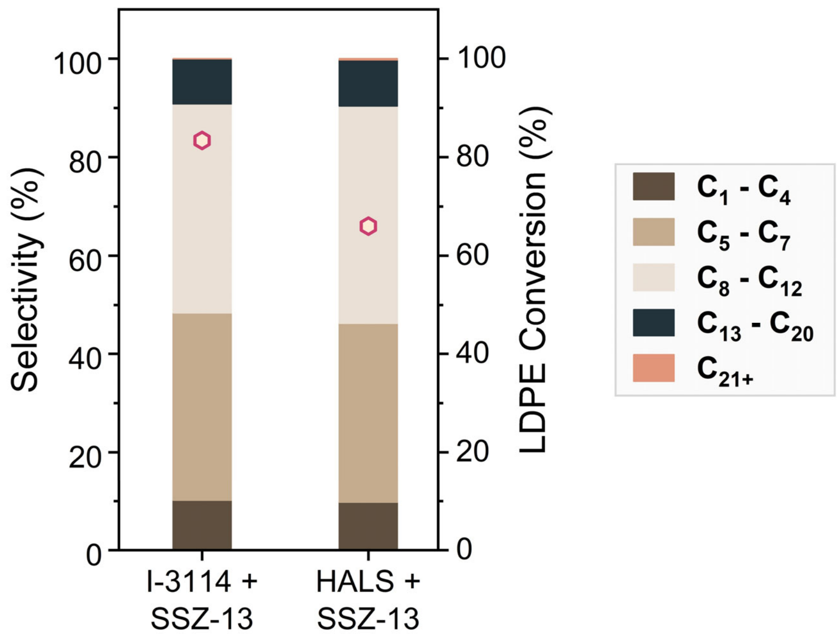
NiMoSx/HY can handle most additives with exception of N-containing additives

Selvam, Esun et al., *JACS*, 2025, 47, 11227.

Can NH_3 be Selectively Captured to Prevent Poisoning?

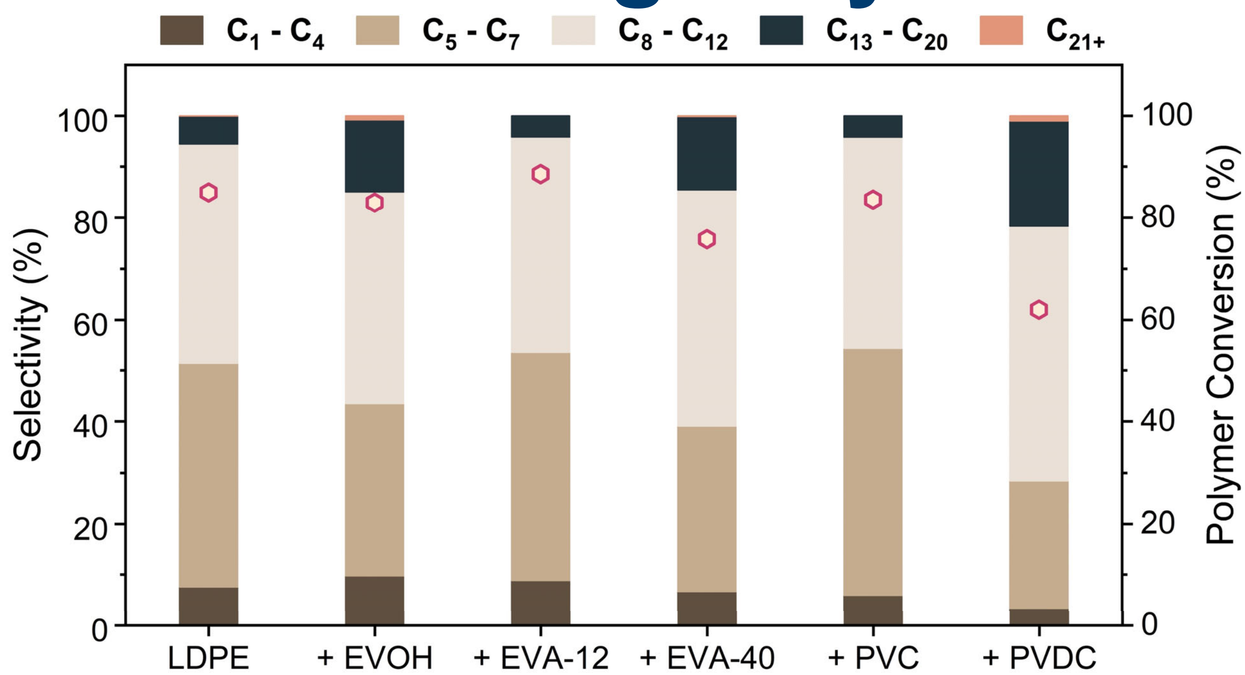


Chabazite (Small pore zeolite)



Product distribution remains unchanged ⇒ CHA acts purely as an NH_3 scavenger

Hydrocracking of Heteroatom-containing Polymer Blends



Heteroatom-containing Polymer Concentration = 10 wt.%

NiMoSx/HY catalysts can tolerate high-concentrations of heteroatom impurities during hydrocracking of polymer blends

Selvam, Esun et al., *JACS*, 2025, 47, 11227.

Summary

- Plastic recycling is a problem of huge scale
  - Abundant and cheap catalysts are needed
  - Reactor design is crucial
- Its complex composition (mixed plastics and additives) can be a major problem
  - Suitable catalysts and processing conditions can alleviate these problems
- Transport effects are of paramount importance
  - Plenty of room for novel reactors