DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Modular Catalytic Reactors for Single-Use Polyolefin Conversion to Lubricating Oils from Upcycled Plastics (LOUPs)

4 April 2023

Topic 7. Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics

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Project Overview – Motivation

- >150 million tons of the polyolefin plastics manufactured each year become waste in landfills and the environment, equivalent to ~1.3 billion barrels of oil
- Conversion of polyolefin waste into lubricants could improve the energetic, economic, and environmental impacts of plastics
- Conventional lubricant base oil manufacturing directly from petroleum also has considerable energetic, economic, and environmental impacts

Annual Polyolefin Waste

~150 M tons

~$60 B lost

Annual Lubricant Market

~40 M tons

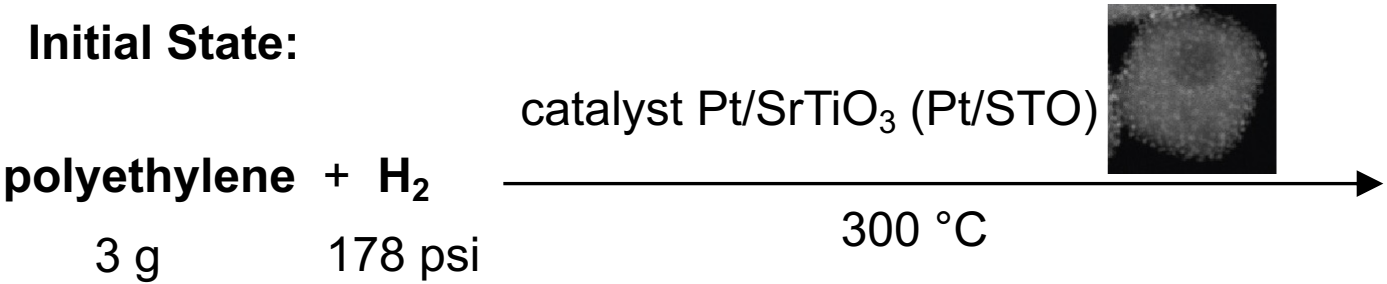
~$160 B

Can an economically and environmentally viable catalytic process be developed that provides lubricating base oils from waste polyolefins?

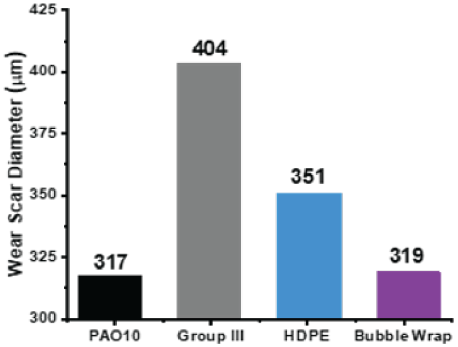
Project Overview – Goal and Background

Project Goal: Develop a modular, low-temperature (< 300 °C) and low pressure (15 bar) continuous process for the integrated catalytic conversion and distillation of single-use waste polyolefins into Lubricating Oils from Upcycled Plastics (LOUPs).

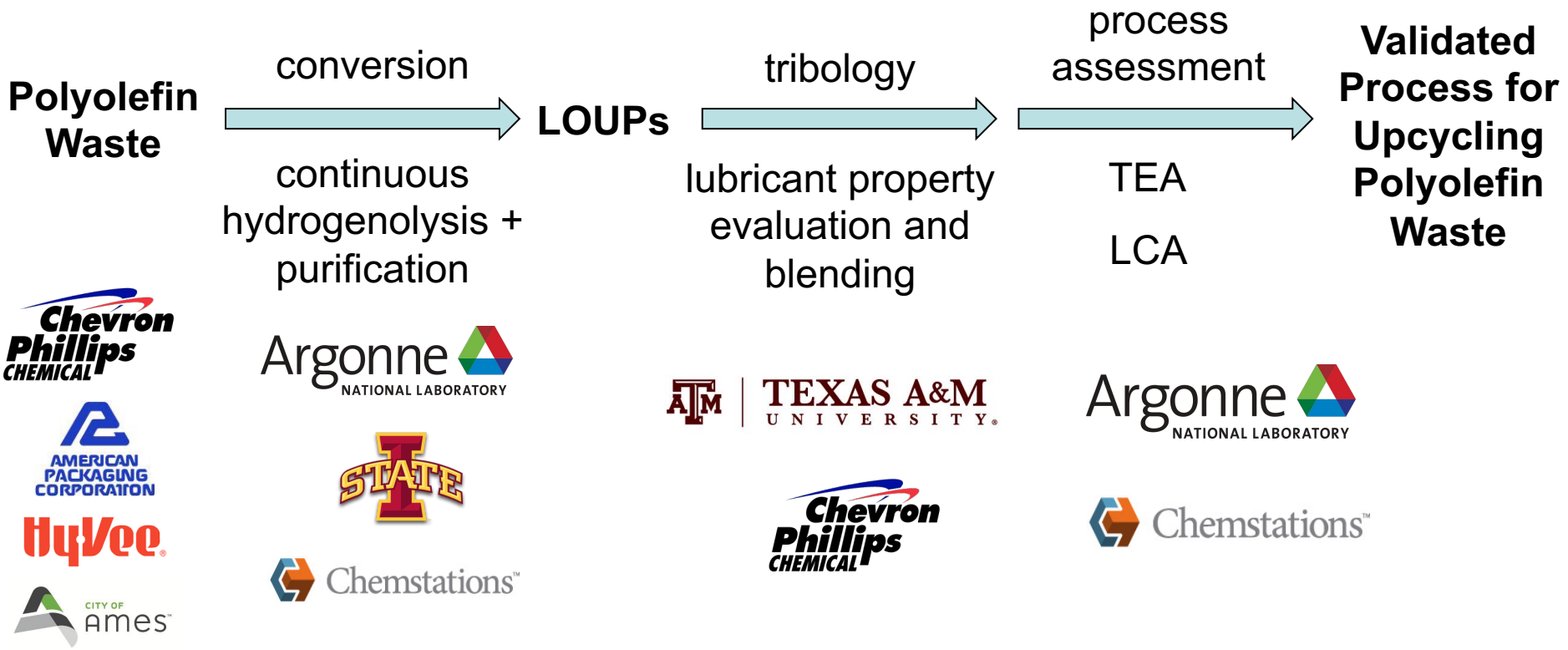
Initial State:



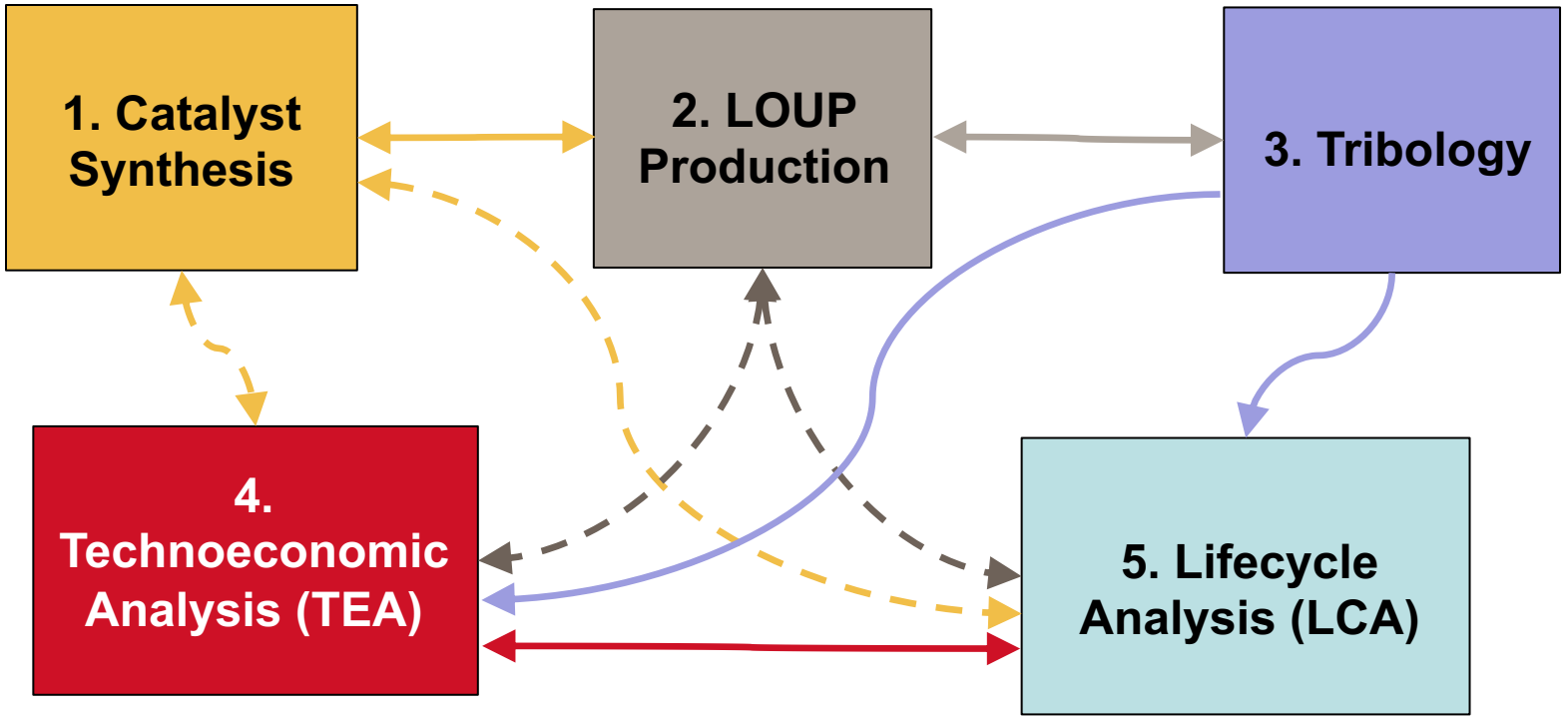
promising lubricating properties:



1 – Approach, Overview and Expertise



1 – Technical Approach and Challenges: Objectives



1 – Approach – Go/No-Go and Management

BP 1 Go/No-Go DP: Produce LOUPs in >35% yield from PE waste (3 g/batch) using Pt/STO in batch reactor.

BP 2 Go/No-Go DP: At least 1 catalyst preparation method and reaction conditions identified as feasible via TEA and meeting performance targets that yield products that provide adequate tribology properties (20% improvement)

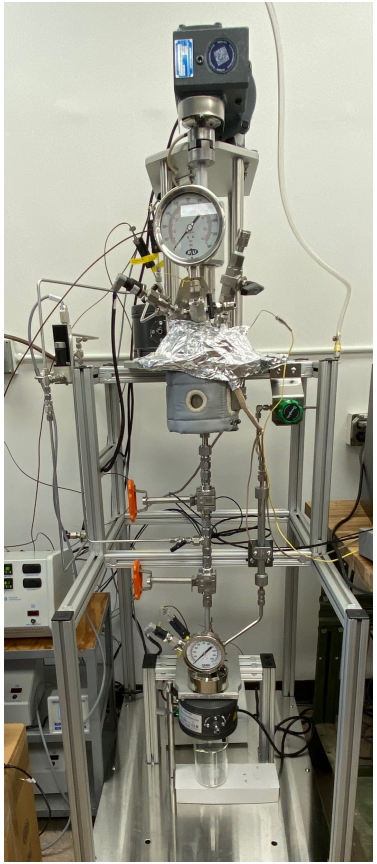
Risk mitigation: catalyst synthetic methods, polymer samples, reactor configuration and conditions investigated to understand variables affecting LOUP tribology, techno-economic and lifecycle outcomes

Bi-Monthly Whole Team Meetings:

- Presentations by researchers' reporting results and progress toward milestones
- Opportunity to discuss challenges and make corrections
- All team members have an equal opportunity to make their voices heard

2 – Progress and Outcomes – Objectives 1-2

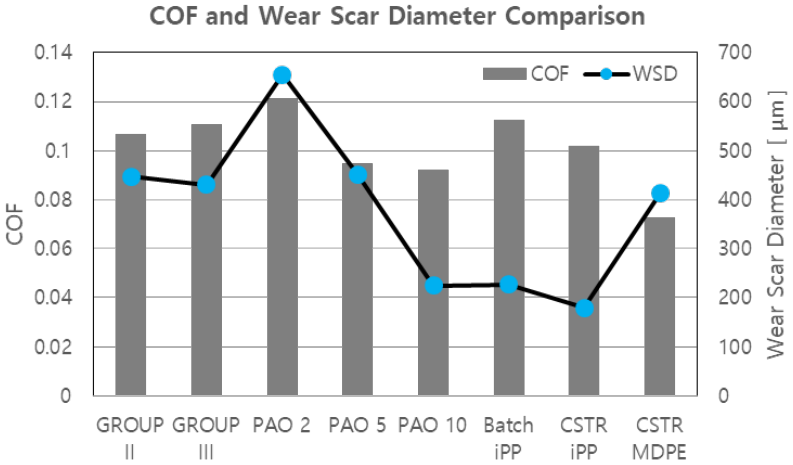
1. **Catalyst Synthesis**
   - STO cuboid synthesis on >20 g/batch in 4 L reactor and on >40 g in a microwave
   - Solution-phase Pt deposition using simple precursor affords >20 g Pt/STO
2. **LOUP Production**
   - Pt/STO from solution-phase large scale synthesis produces LOUPs from polypropylene, medium density polyethylene, and linear low-density polyethylene
   - Reactor design and construction
   - 200 g polypropylene converted to LOUPs in a 1 L reactor and separated from Pt catalyst

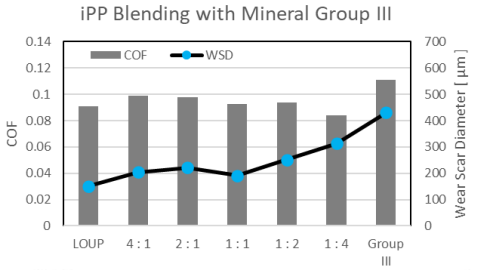


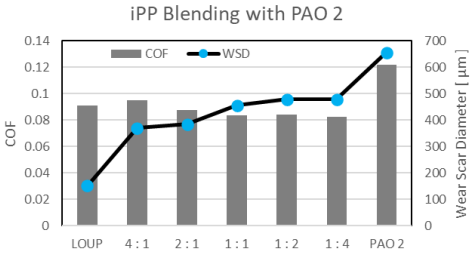
2 – Progress and Outcomes – Objective 3

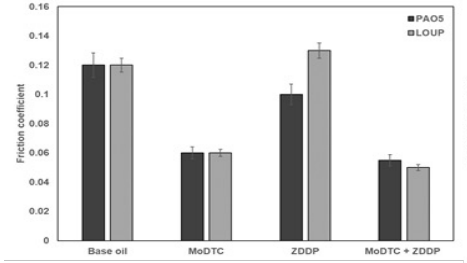
3. Tribology

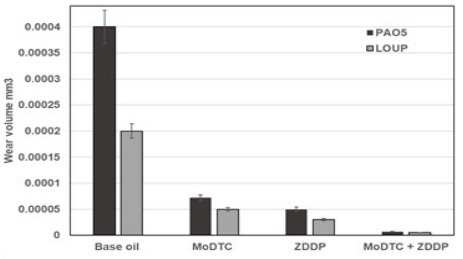
- Polypropylene LOUPs (Batch & CSTR) give low wear-scar
- Base oils show reduction in friction and wear with increasing LOUPs ratio
- An excellent synergy was observed between LOUPs and anti-friction and – wear additives: MoDTC & ZDDP leading to significantly lower friction and wear











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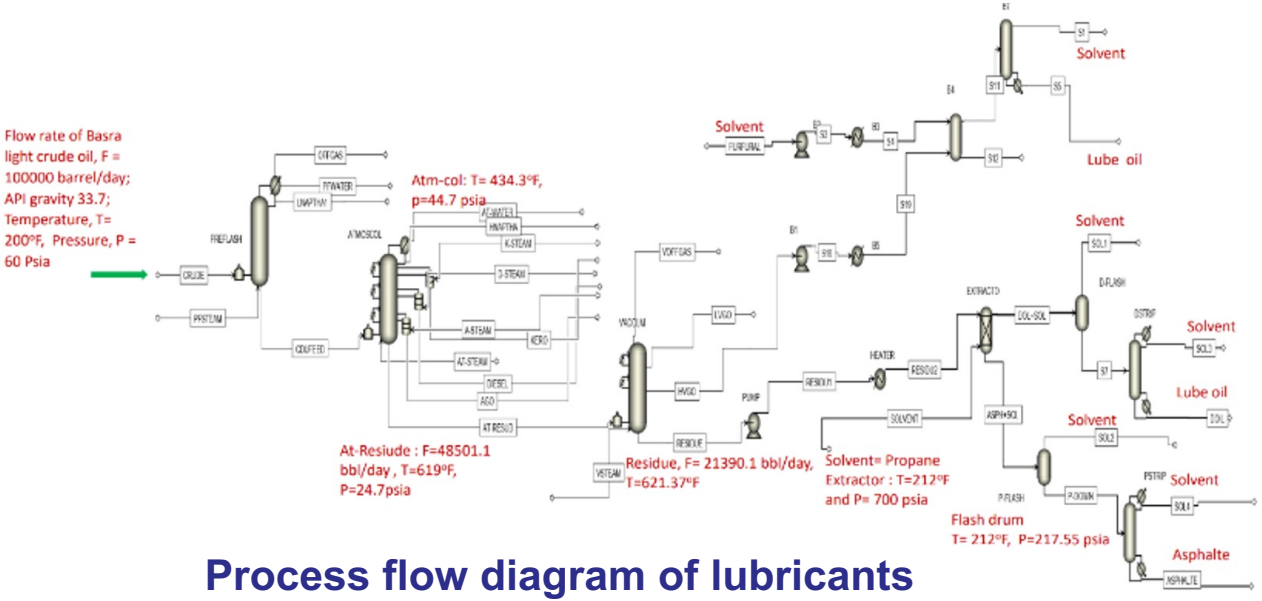
2 – Progress and Outcomes – Objective 4

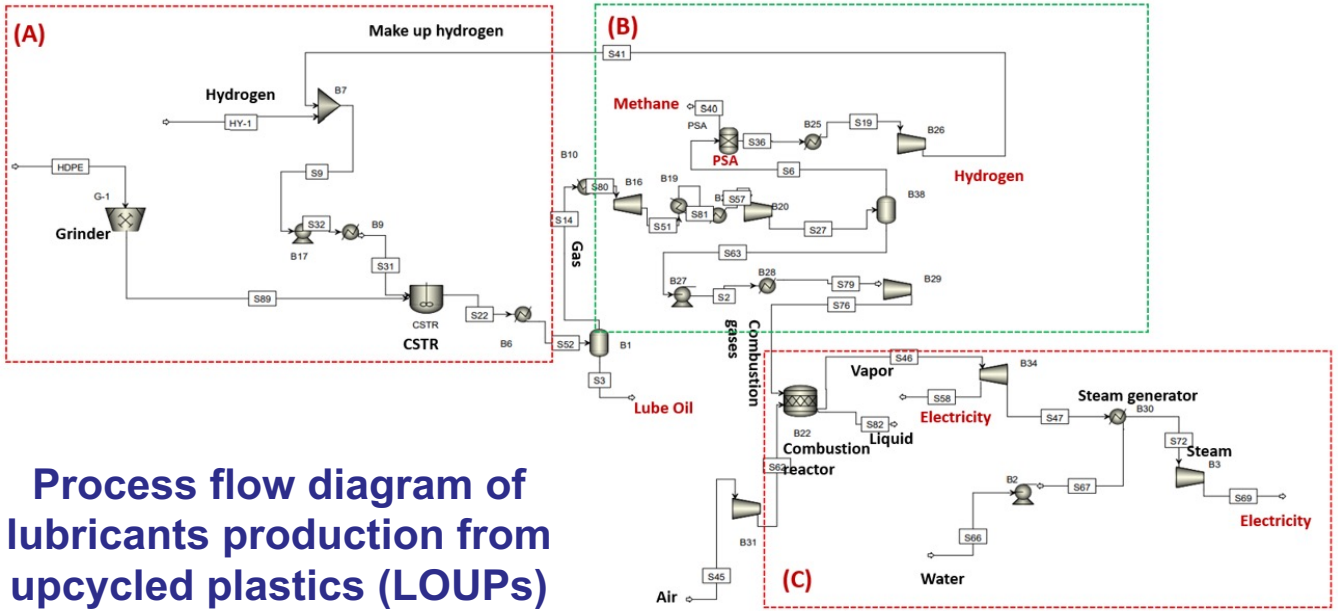
- PAO Material Flow Analysis completed and results published in a book chapter
- TEA framework for conventional lubricant oil production from crude oil completed for group I, group II, and group III oils (base case)



Process flow diagram of lubricants production from crude oil

2 – Progress and Outcomes – Objective 4

- The initial framework of catalyst cost production was completed using CatCost software (NREL)- the catalyst cost is estimated as $585/kg
- Completed the framework for producing lubricants from post-use HDPE

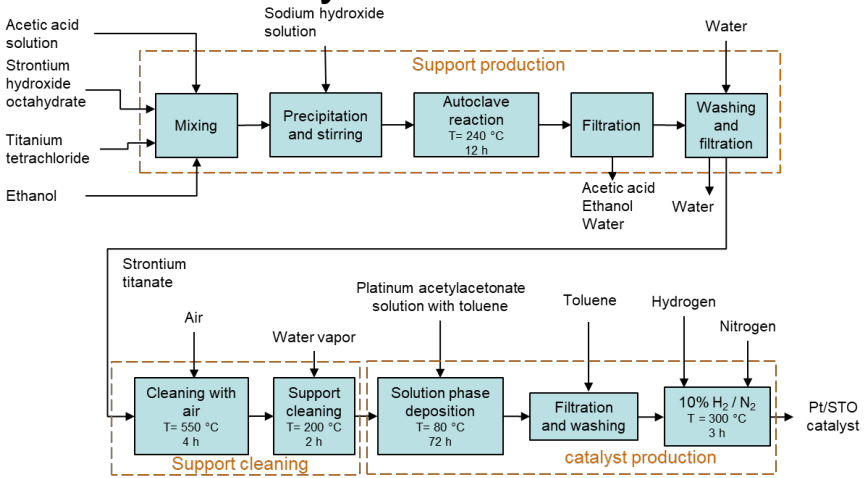


Process flow diagram of lubricants production from upcycled plastics (LOUPs)

2 – Progress and Outcomes – Objective 5: LCA

Pt/STO Catalyst Production

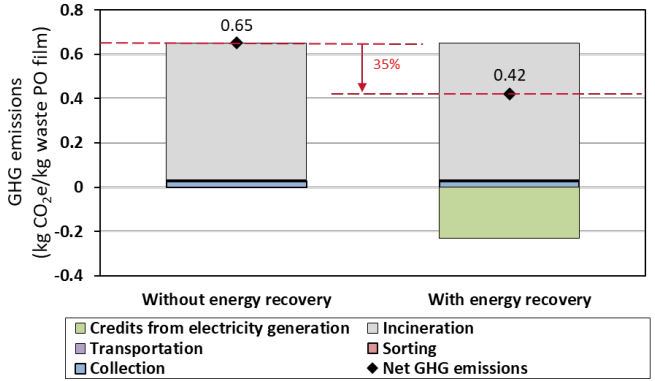
- ✓ Process flow diagram assessed material and energy inputs
- ✓ 56 $kgCO_2e/kg$ estimated GHG emissions
- ✓ Solvent recovery will lower GHG emission



Process flow diagram

Defined LOUPs System Boundary and Comparisons

- ✓ Landfill and incineration (with energy recovery reduces emissions 35%)
- ✓ Base oils production



GHG emissions of conventional waste management of PO films

2 – Progress and Outcomes – Management

Catalyst Scale-up: Preparations achieved target (produce 100 g); success informed by LOUP production and tribology.

- next steps: catalyst synthesis optimizations informed by TEA and LCA

LOUPs production: Catalyst, reactor configuration, and polymer sample studies informed for 1L reactor design, now validated for *i*PP conversion (produce 100 mL)

- next steps: produce iPP and LDPE LOUPs for large volume property study, 1L-conversion metrics inform for TEA and LCA

Tribology: Measurements identified improvements to comparable conventional base oils, synergy in blends and from additives

- next steps: relate physical properties and chemical composition to improve lubricant performance in scaled up samples

Technoeconomic Analysis: Completed the PAO material flow analysis and TEA framework for conventional lubricant oil production

- next steps: finalize the TEA framework for high-performance oil production from plastic waste streams and catalyst production; prepare a manuscript for publication

Lifecycle Analysis: Defined LCA system boundary for catalyst, conventional based oils, HDPE waste management and LOUPs, estimated catalyst GHG emissions

- next steps: build LCA model for base oils and LOUPs and evaluate environmental impact

3 – Impact

- Published solution-phase, scaled synthesis of Pt/STO and its catalytic hydrogenolysis of plastic waste
- Tribology society (STLE)-recognized impact of plastic waste-to-lubricant approach with Platinum Poster Award
- Contributed a book chapter assessing plastics waste material flow analysis in a lubricant production case study
- Spin-off startup company Aeternal is pursuing commercialization of polyolefin upcycling to lubricants based on Pt/STO
- Developed technology enabling plastic waste valorization, supporting the DOE Strategy for Plastics Innovation and BETO goals to reduce plastic waste in oceans and landfills

From the journal:
Journal of Materials Chemistry A

Synthesis of platinum nanoparticles on strontium titanate nanocuboids *via* surface organometallic grafting for the catalytic hydrogenolysis of plastic waste†

Check for updates

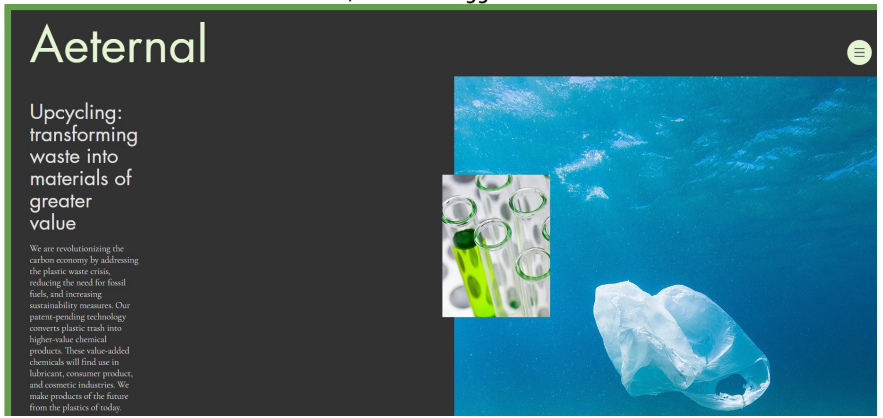
Katherine E. McCullough, Ian L. Peczak, Robert M. Kennedy, Yi-Yu Wang, James Lin, Xun Wu, Alexander L. Paterson, Frédéric A. Perras, Jacklyn Hall, A. Jeremy Kropf, Ryan A. Hackler, Youngho Shin, Jens Niklas, Oleg G. Poluektov, Jianguo Wen, Wenyu Huang, Aaron D. Sadow, Kenneth R. Poeppelmeier, Massimiliano Delferro and Magali S. Ferrandon

Author af

CHAPTER EIGHT

Systemic approaches to model plastics circularity

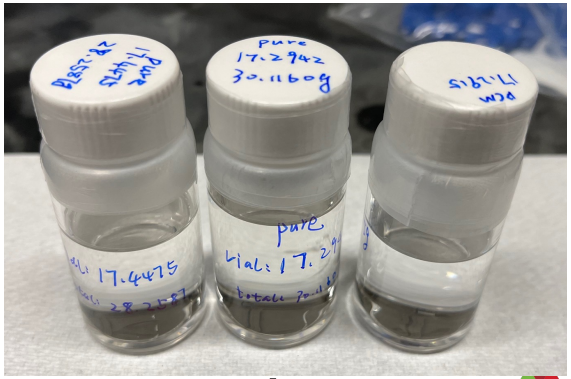
Meltem Urgun-Demirtas, Pahola Thathiana Benavides, Ulises R. Gracida-Alvarez, and Sean Riggio



3 – Impact

- LCA and TEA results that help identify process stages in catalyst production with the potential to reduce costs and environmental impacts

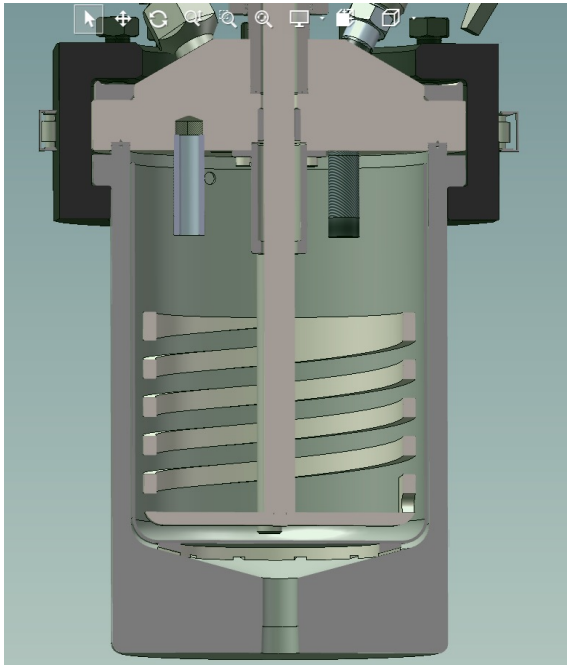
- Scaled up catalyst and LOUP production provide iPP-LOUP samples to share with partners



Summary

Catalytic hydrogenolysis of polyolefins provides oils that synergistically provide superior lubricating properties in small scale tribology tests

- Pt/STO is scalable, and gives a catalyst that is selective for LOUPs
- TEA and LCA of Pt/STO synthesis identify pressure points to improve efficiency
- 1-L CSTR achieves reactive separation of LOUPs from catalyst
- LOUPs have comparable tribological properties to base oils, and synergistically improve base oil properties upon blending and with additives
- LOUPs TEA and LCA benchmarked to conventional base oils with comparable physical properties



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Quad Chart Overview

Timeline

- *Project Start: 1 May 2021*
- *Project End: 30 April 2024*

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)*	*$318,745.72*
Project Cost Share *	*(10/01/2021 – 9/30/2022)*	$170,336

Project Goal:
Develop a process for conversion of single-use waste polyolefins at <300 °C and <15 bar, integrated with separation, to produce lubricating base oils.

End of Project Milestone:
Develop a modular scalable process that produces LOUPs from waste at >40% energy savings and >35% chemical recyclability with a cost of production of $4.19/gal (current avg. $9.00/gal)

Funding Mechanism: DE-FOA-0002245, Topic Area 2: Novel Methods for Deconstructing and Upcycling Existing Plastics, 2020

TRL at Project Start: 2
TRL at Project End: 4

Project Partners
Iowa State University
Argonne National Lab
Texas A&M
Chevron Phillips Chem
Chemstations
American Packaging
City of Ames
Hy-Vee

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- P. Thathiana Benavides
- Sultana Ferdous
- Ulises Gracida
- Magali Ferrandon
- Ian Peczak (Grad)
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- Ali Erdemir
- Pushkar Deshpande
- Seungjoo Lee

- Wendy Young
- Yurika Diaz

- William Schmitt

- Joey Hayes

- Ken Hope

- Thomas Marsch

- Kate Peretti
- Eric Peterson
- Gibson Asuquo
- Michelle Seitz

Publications

- Urgum- Demirtas M., Benavides PT., Gracida U., Riggio S. Systemic Approached to Model Plastic Circularity. Book Chapter Eight. Advances in Chemical Engineering. Toward Circular Economic: Closing the Loop with Chemical Recycling of solid Plastic Waste. Vol 60. Elsivier. https://www.elsevier.com/books/towards-circular-economy-closing-the-loop-with-chemical-recycling-of-solid-plastic-waste/moscatelli/978-0-323-95770-0

- McCullough, K. E., Peczak, I. L., Kennedy, R. M., Wang, Y.-Y., Lin, J., Wu, X., Paterson, A. L., Perras, F. A., Hall, J., Kropf, A. J., Hackler, R. A., Shin, Y., Niklas, J., Poluektov, O. G., Wen, J., Huang, W., Sadow, A. D., Poeppelmeier, K. R., Delferro, M., Ferrandon, M. S., Synthesis of platinum nanoparticles on strontium titanate nanocuboids via surface organometallic grafting for the catalytic hydrogenolysis of plastic waste. *J. Mater. Chem. A* **2023**, *11* (3), 1216-1231. DOI: 10.1039/d2ta08133d

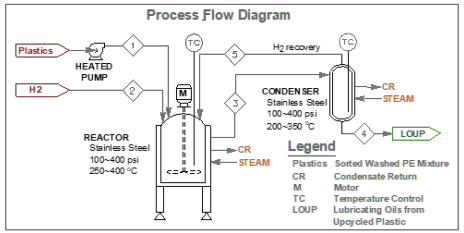
  https://pubs.rsc.org/en/content/articlepdf/2023/ta/d2ta08133d

Presentations (selected)

- Urgum-Demirtas M., Delferro M., Sadow A.D., Benavides PT., Gracida U. An integrated techno-economic and life cycle assessment of lubricant production from polyolefin waste streams. **Conference presentation**. ACS Fall Annual meeting. August 2022. Chicago Il.
- Hackler, R.; Kennedy, R. M; Peczak, I.; Kanbur, U.; Ferrandon, M.; Cappello, V.; Kumar, S.; Sun, P.; Sadow, A. D.; Poeppelmeier, K. R.; Delferro, M. Circular carbon economy by converting plastic trash into lubricants and other higher value products **Conference presentation**. ACS Fall Annual meeting. August 2022. Chicago Il.
- Benavides PT, Ferdous S. Gracida U., Urgum Demirtas. Life Cycle and Technoeconomic Analyses of Catalyst used in the Conversion of waste plastic to Lubricate Oils from Upcycled Plastics (LOUPs). **Conference Presentation**. AIChE Midwest meeting. April 17. Chicago IL.
- Sadow, A.D. Upcycling Polyolefins via Selective Catalytic Conversions. **Conference presentation.** Midwest Regional Meeting of the American Chemical Society, Iowa City IA, 19 October 2022.
- Sadow, A.D. Upcycling Polyolefins via Selective Catalytic Conversions. **Conference presentation.** 2022 NSF Nanoscale Science and Engineering Grantees Conference. Internet Meeting. 7-8 December 2022.
- Erdemir A., Lee S., Heckler R., Delferro M. , Wang Y., Behera R., Huang W., Sadow A.D. Synthetic Lubricants Derived from Plastic Waste and their Tribological Performance. **Conference presentation.** 77th Annual Meeting of the Society of Tribologists and Lubrication Engineers, Orlando, FL, May 14-19, 2022
- Lee S., Erdemir A. Lubricating Oils from Upcycled Plastics (LOUPs): A tribological and surface analytical study of their lubrication mechanisms. **Conference poster.** 77th Annual Meeting of the Society of Tribologists and Lubrication Engineers, Orlando, FL, May 14-19, 2022
- Peczak I. L. , Kennedy R.M. , Hackler R.A. , Delferro M., Poeppelmeier K.R. Synthesis of $Pt/SrTiO_3$ upcycling catalysts with controlled support shape, particle size, and catalyst dispersion. **Conference presentation**. ACS Fall Annual meeting. August 2022. Chicago Il.

TEA/LCA Integrated analysis approach

1) Create conceptual process based on current research. Determine system boundary and process flow diagram



2) Design and model individual unit operations based on experimental data. Process model outputs are used to size and cost equipment. Determine material and energy balance to LCA

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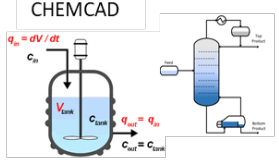

3) Conduct TEA, calculate minimum selling price (MSP). Identify cost drivers from the economic model.

4) Conduct LCA with material and Energy balance from process modeling. Identify the sustainability drivers.

Argonne GREET LIFE-CYCLE MODEL

5) Generate and understand the results and provide feedback to the team. Report MSP, GHG emissions, energy use, water use.