

AUGUST 22, 2024

PLASTIC UPCYCLING: TURNING PLASTIC WASTE INTO VALUABLE INDUSTRIAL PRODUCTS



MAX DELFERRO

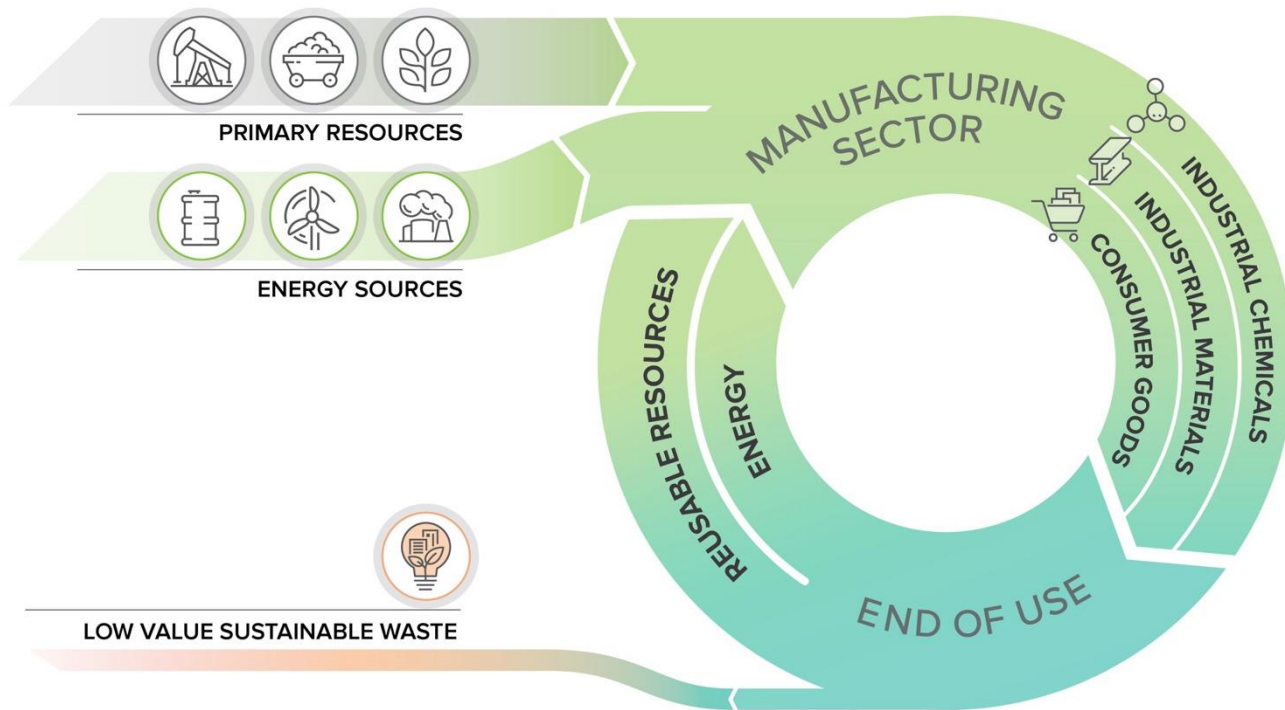
Group Leader Catalysis Science
Chemical Sciences And Engineering Division
Argonne National Laboratory



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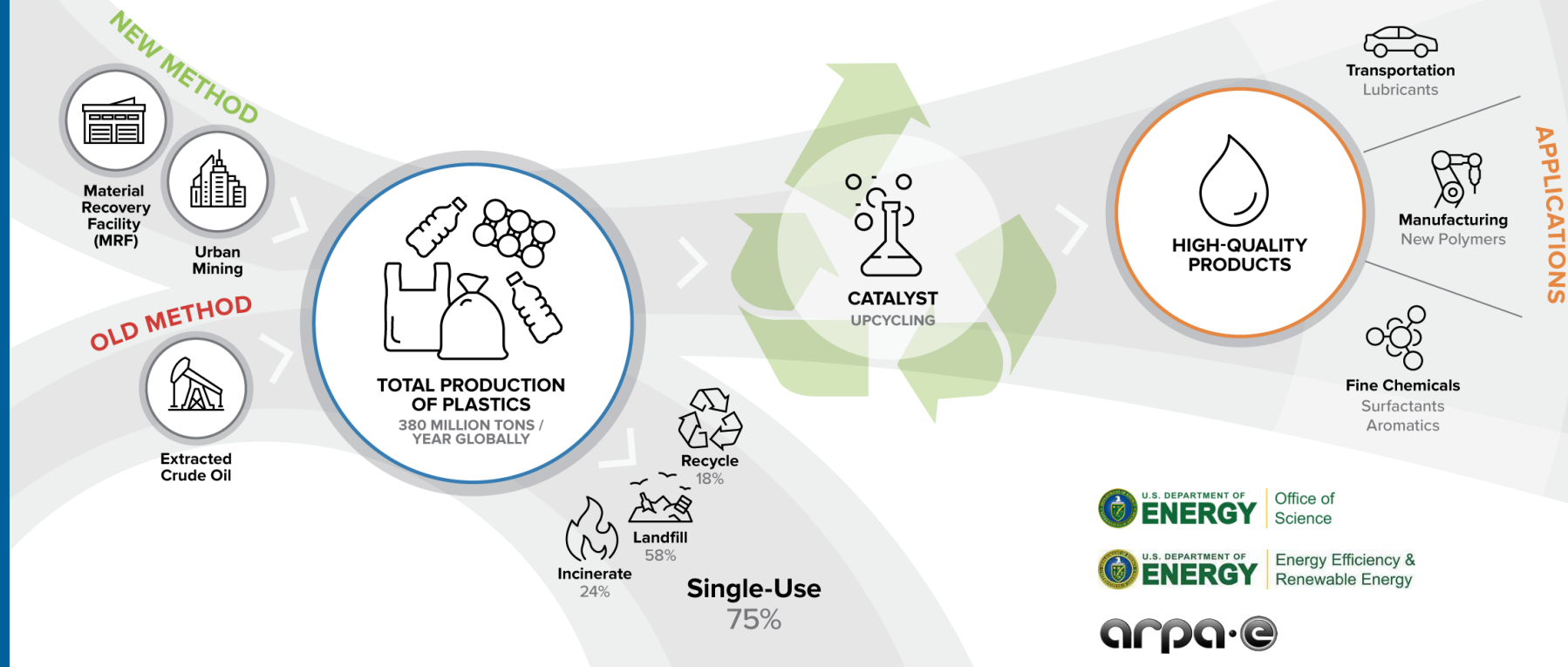
MATERIALS AND CHEMISTRY IN A CIRCULAR ECONOMY





**WHERE THERE
IS WASTE,
THERE IS
OPPORTUNITY.**

UPCYCLING PLASTICS INTO NEW MATERIALS



ENERGY, ENVIRONMENT, AND ECONOMY



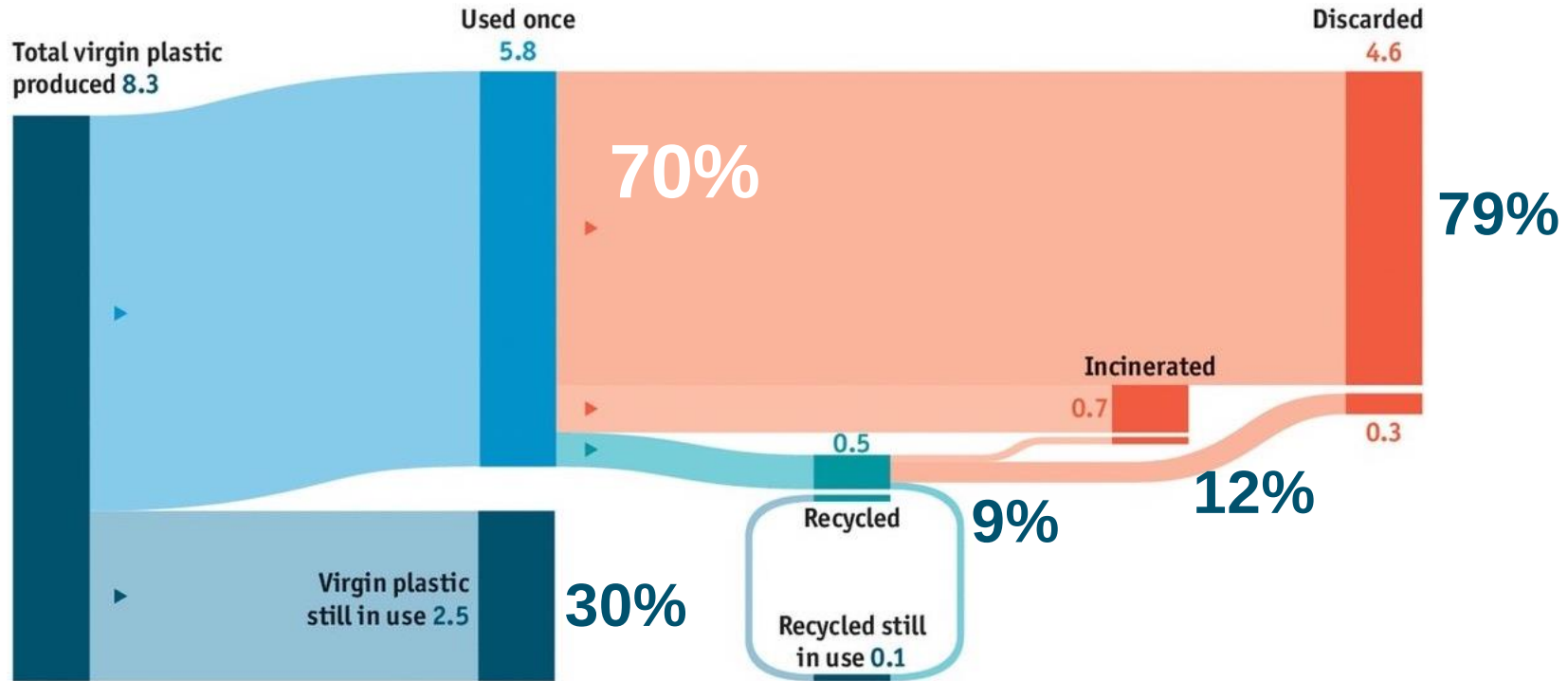
8.3B

**Tons of
plastics**

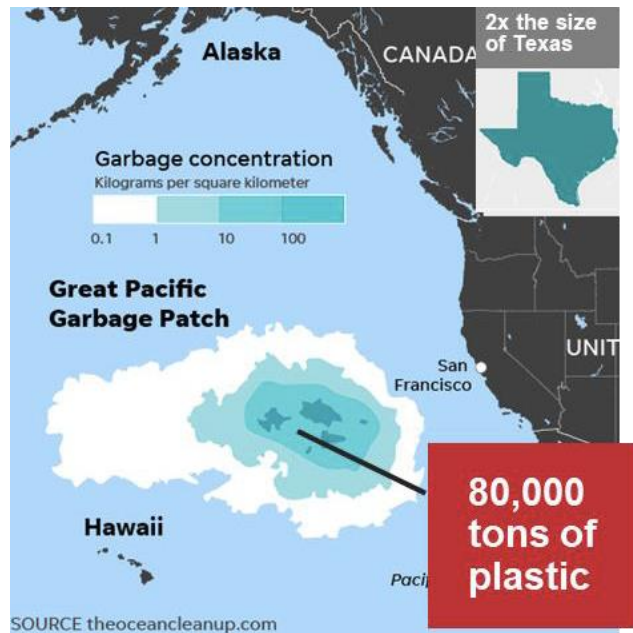
- **6–8%** worldwide petroleum and LNG consumed
- **350–400** million tons of new plastics
- **75% (300 million tons)** discarded annually
- **10%** of US municipal solid waste
- About **55%** of manufactured plastics are hydrocarbons only
- Annual polyolefin waste equivalent to **1.3 billion barrels of oil**
 - 20% of yearly US petroleum consumption
 - 2x ~ the US strategic petroleum reserve

Source: Borrel le, S. B. et. al Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. *Science* **2020**, 369, 1515.

THE FATE OF PLASTIC WASTE



PLASTIC WASTE IS A GLOBAL ISSUE



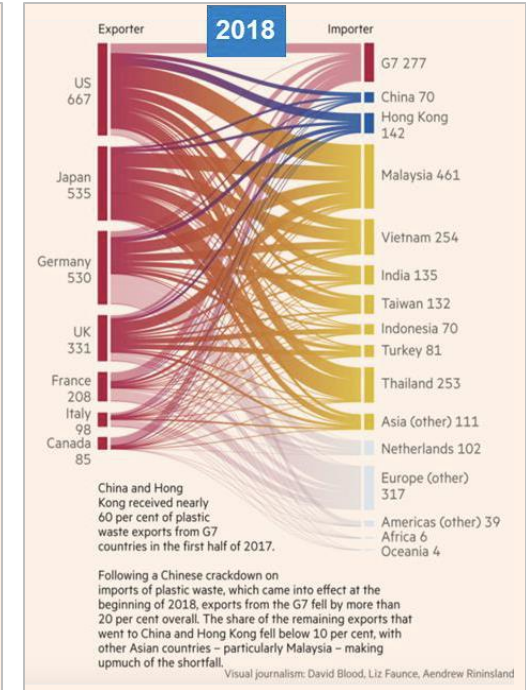
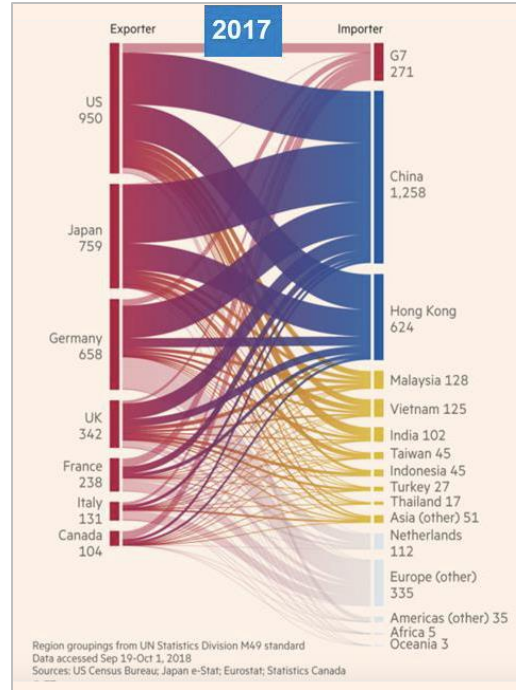
U.S. DEPARTMENT OF
ENERGY

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NATIONAL LABORATORY

POLICIES MAKE A DIFFERENCE

China's plastic trash ban has big impacts. It creates scientific and economic opportunities.



Source: <https://www.ft.com/content/360e2524-d71a-11e8-a854-33d6f82e62f8>

In '000 tonnes

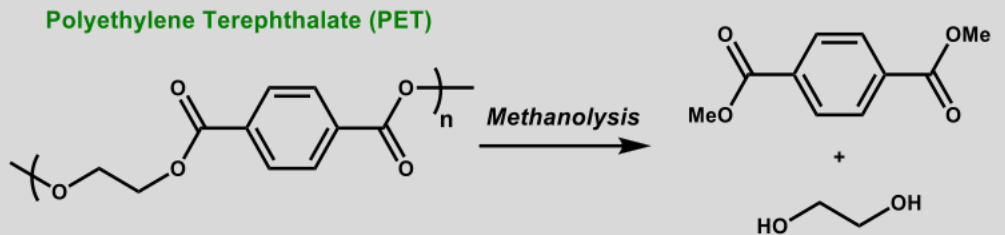
CHEMICAL AND MECHANICAL RECYCLING OF PLASTIC WASTE

Plastics by the Numbers

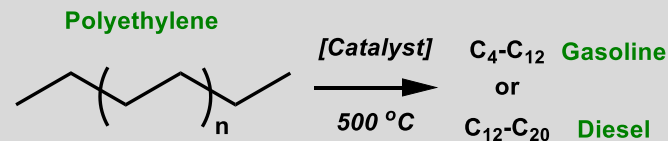
NO.	FULL NAME	RECYCLABLE	RECOVERY RATE	USES
	Polyethylene terephthalate	Yes	19.5%	Disposable bottles and many other consumer products
	High-density Polyethylene	Yes	10%	More durable containers (detergent, shampoo)
	Polyvinyl Chloride	No	0%	Piping, cables, fencing, furniture, carpet backing
	Low-density polyethylene	Mostly no	5%	Plastic bags, wrapping films, trays, computer parts
	Polypropylene	Sometimes	1%	Bottle caps, reusable food containers, car parts
	Polystyrene	Sometimes	1%	Plastic utensils, packaging peanuts, Styrofoam
	Others (polycarbonate, polymethyl methacrylate)	No	Very low	Multilayer barrier films, toothbrushes, some food containers, CDs, DVDs

STATE-OF-THE-ART CHEMICAL RECYCLING (AT SCALE) OF PET, PS, AND POS

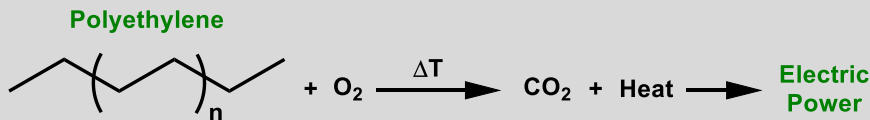
Depolymerization-to-monomer



Pyrolysis of plastic waste to oils



Waste-to-energy

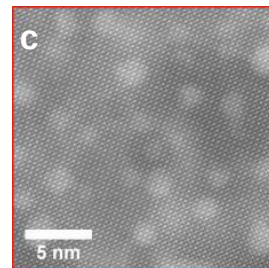
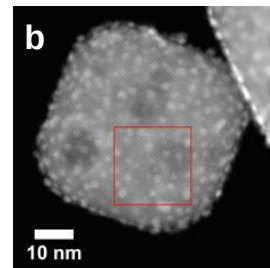
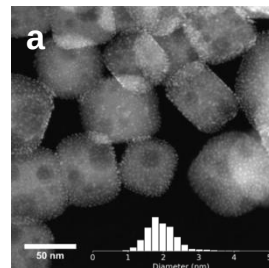


UPCYCLING SINGLE-USE POLYETHYLENE INTO HIGH-QUALITY LIQUID PRODUCTS

Platinum@Perovskite Catalyst

Superior Catalyst Performances

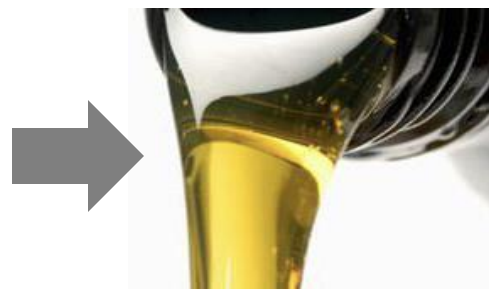
- Two properties (epitaxy and non-porosity) make this catalyst highly selective vs. other available materials
- Preference for narrow distribution of products makes processing easier
- The ANL catalyst has the capability to meet the needs of the market



Pt nanoparticles on SrTiO₃ with a narrow size distribution (2.0 ± 0.5 nm)



Plastic Waste



Lubricant Oil

Sources:

<https://www.howitworksdaily.com/wp-content/uploads/2015/09/plastic-bottles-1024x698.jpg>

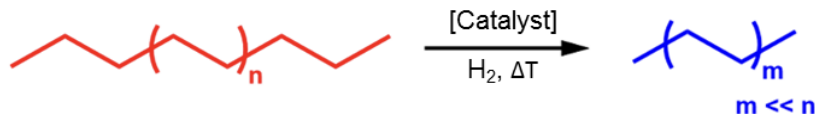
<https://cdn.hswstatic.com/gif/synthetic-conventional-motor-oil0-1.jpg>

PLASTIC UPCYCLING PATENT PORTFOLIO

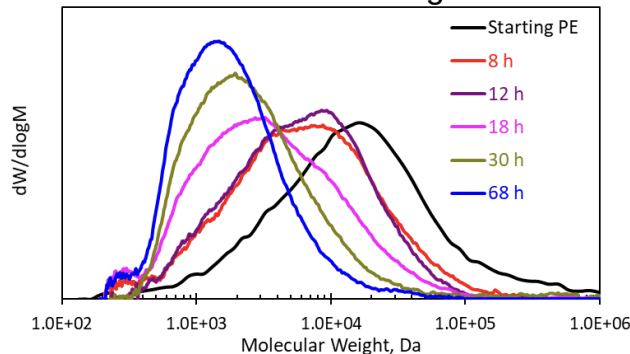
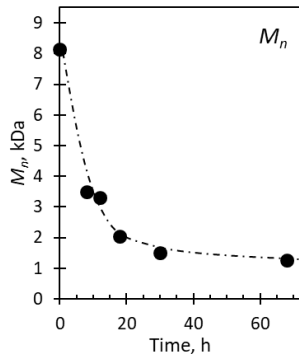
PATENT NO.	DESCRIPTION
US 11,596,935	Catalytic hydrogenolysis for converting plastics into other hydrocarbon products.
US 11,780,985	Catalyst and process of upcycling polymers to useful hydrocarbon materials.
US 11,499,110	Catalyst and process for selectively converting plastics into lubricant products.
Pending	Process for converting plastic waste to a lubricants.
Pending	Multi-metallic catalysts for plastic waste recycling.

Source : <https://www.anl.gov/partnerships/collaborative-partnerships>

POLYMER UPCYCLING: CATALYTIC HYDROGENOLYSIS USING Pt/SrTiO₃



<1% light alkanes



Starting Material → **High-Quality Liquid Product**

8K Mn, PDI 2.2 PE

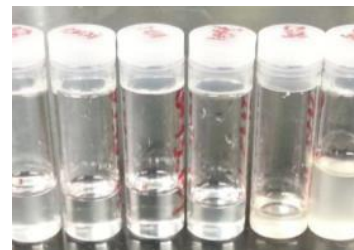
600 Mn, PDI 1.1 HQL

- Motor oil
- Advanced tribology/Wind Turbines
- Wax/White oils

Catalytic Reaction Conditions

2nm Pt/SrTiO₃, 170 psi H₂, 300 °C, melted polyolefin, solvent-free

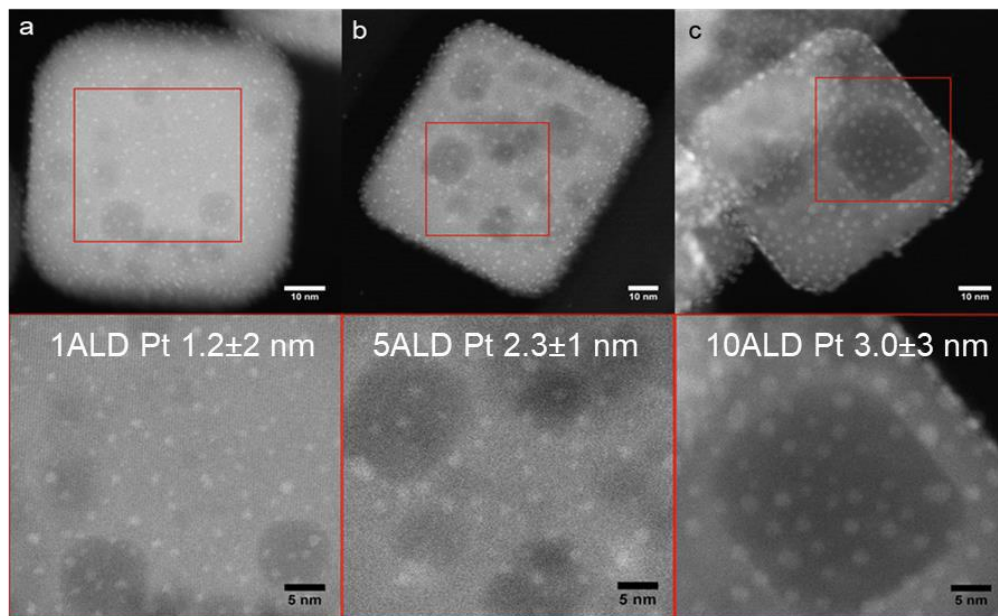
Entry	M _n , HQL	Đ
PE M _n = 8,150	590	1.1
PE M _n = 15,400	660	1.1
PE M _n = 64,300	800	1.1
PE M _n = 158,000	820	1.2
Plastic Bag M _n = 33,000	990	1.3



¹H, ¹³C NMR,
MALDI, FTIR,
UV-Vis, Br₂:
No olefins,
No aromatics

STRUCTURE SENSITIVITY OF PE HYDROGENOLYSIS

Catalytic Activity Comparison at Equal Pt Surface Area (2,000 cm²)

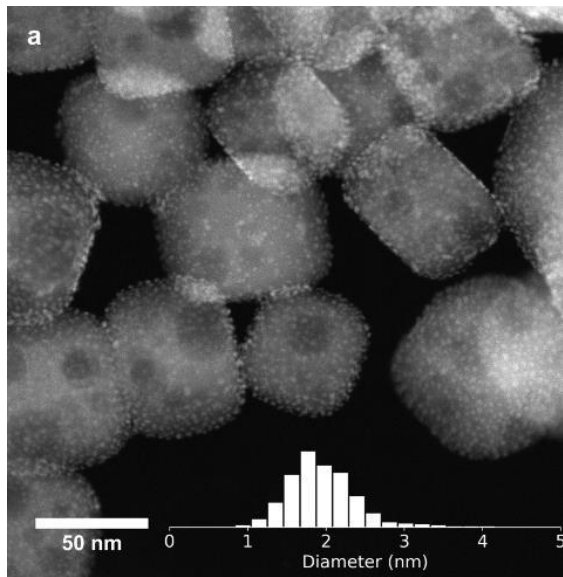


Catalysts	Average Pt edge (nm) to face (nm ²) ratio ^c	M _n , Da	Đ
1c-Pt/SrTiO ₃	0.265	<100	
5c-Pt/SrTiO ₃	0.138	600	1.1
10c-Pt/SrTiO ₃	0.109	750	1.1

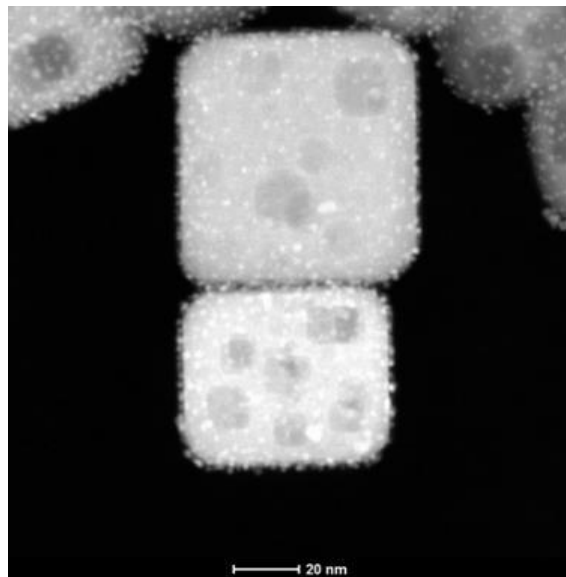
Reaction Conditions: 300 °C, 170 psi H₂, 3 g of PE (8K Mn), 1.1 mg [Cat], 96 h

STABILIZATION OF PLATINUM NANOPARTICLES

The epitaxy growth on the {100} facet of SrTiO_3 stabilizes Pt nanoparticles versus other oxide supports

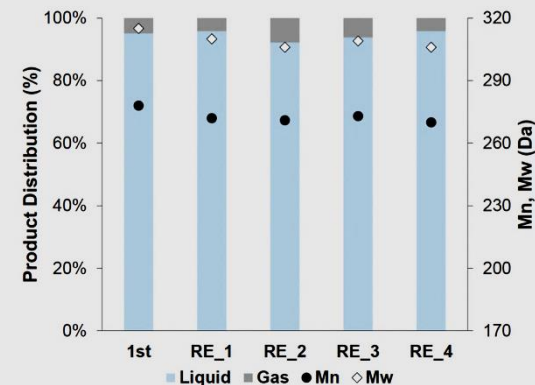


Pre-reaction : 2.0 ± 0.5 nm



Post-reaction : 2.1 ± 0.5 nm

Recycle Experiments, no reactivation needed



2nm Pt/ SrTiO_3 , 170 psi H_2 , 300 °C,
melted polyolefin, solvent-free

SCALE UP CATALYST SYNTHESIS

SrTiO₃ via hydrothermal synthesis: Scale-Up at MERF

1 Bimetallic Precursor Sol $\text{Sr}^{2+}_{(\text{aq})} + \text{Ti}^{4+}_{(\text{aq})}$

Ethanol, Acetic Acid
pH = 1

2 Co-Precipitation

Viscous Suspension
pH = 14

3 Hydrothermal Treatment

10M NaOH_(aq)
Add bimetallic sol
to base sol

Sr-TiO_x(OH)_y

180–240 °C
12–36 h
< 20 atm

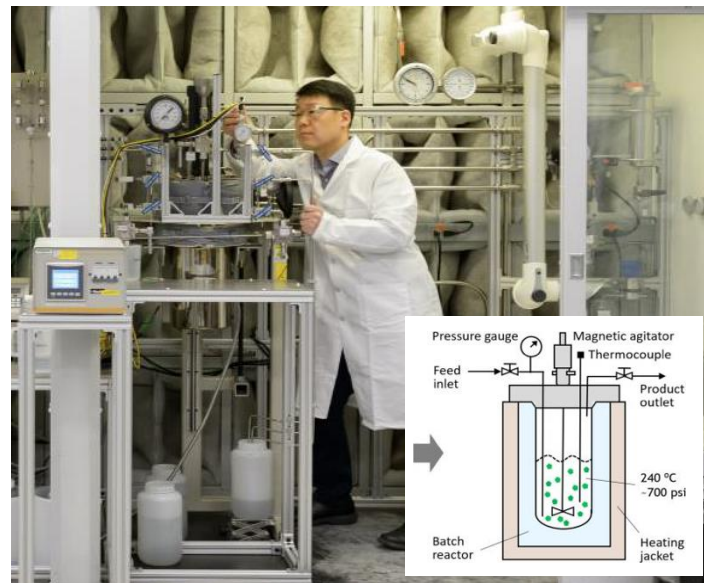
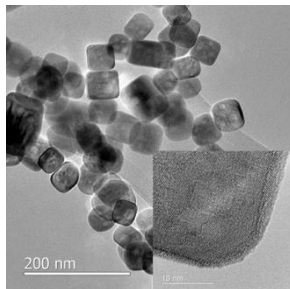
SrTiO₃ (s)



Teflon-Lined Autoclave



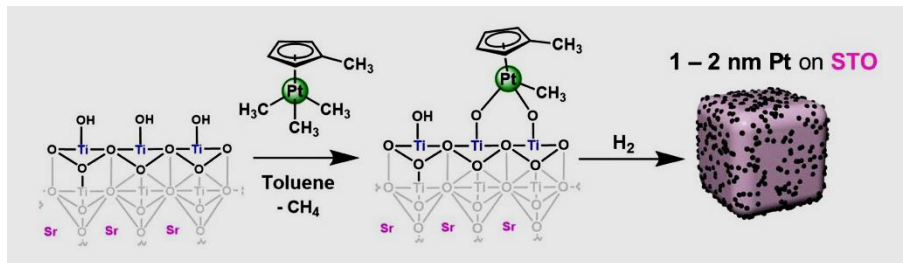
SrTiO₃ in liner
post-synthesis



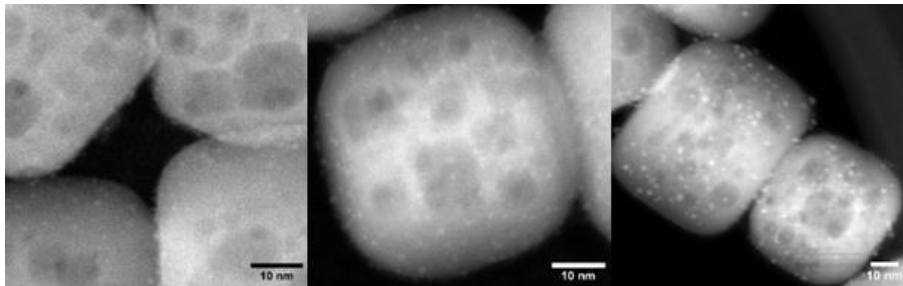
From mg to kg

SCALE UP CATALYST SYNTHESIS

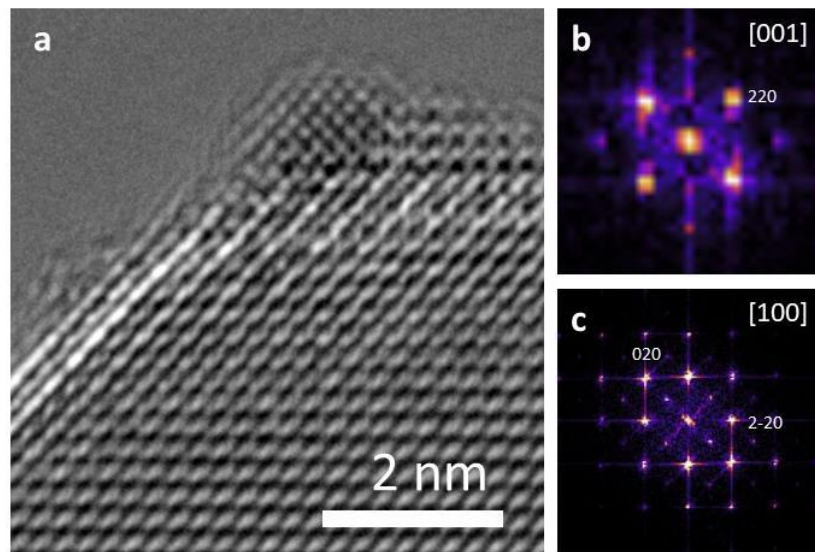
Pt Deposition via Surface Organometallic Chemistry



SS NMR (¹H, ¹⁷O, and ¹⁹⁵Pt), XAS, STEM HAADF



Cube-on-cube epitaxial growth



McCullough, K. E. et al. 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, 1216-1231.

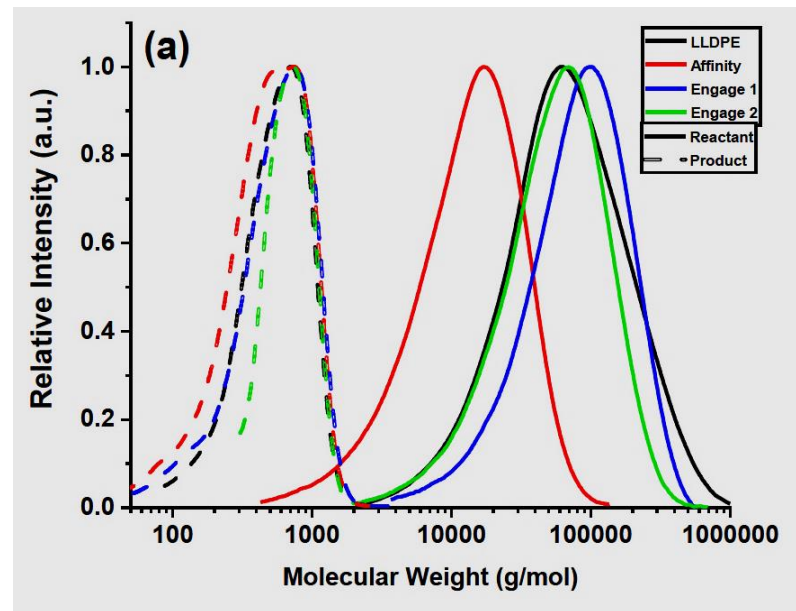
EXPLORATION OF HYDROGENOLYSIS CONDITIONS

Polymer structure/branching

Reaction conditions:

- 170 psi H₂
- 300 mg Pt/STO (1% Pt)
- 1.5 g HDPE or LLDPE
- 700 rpm stirring

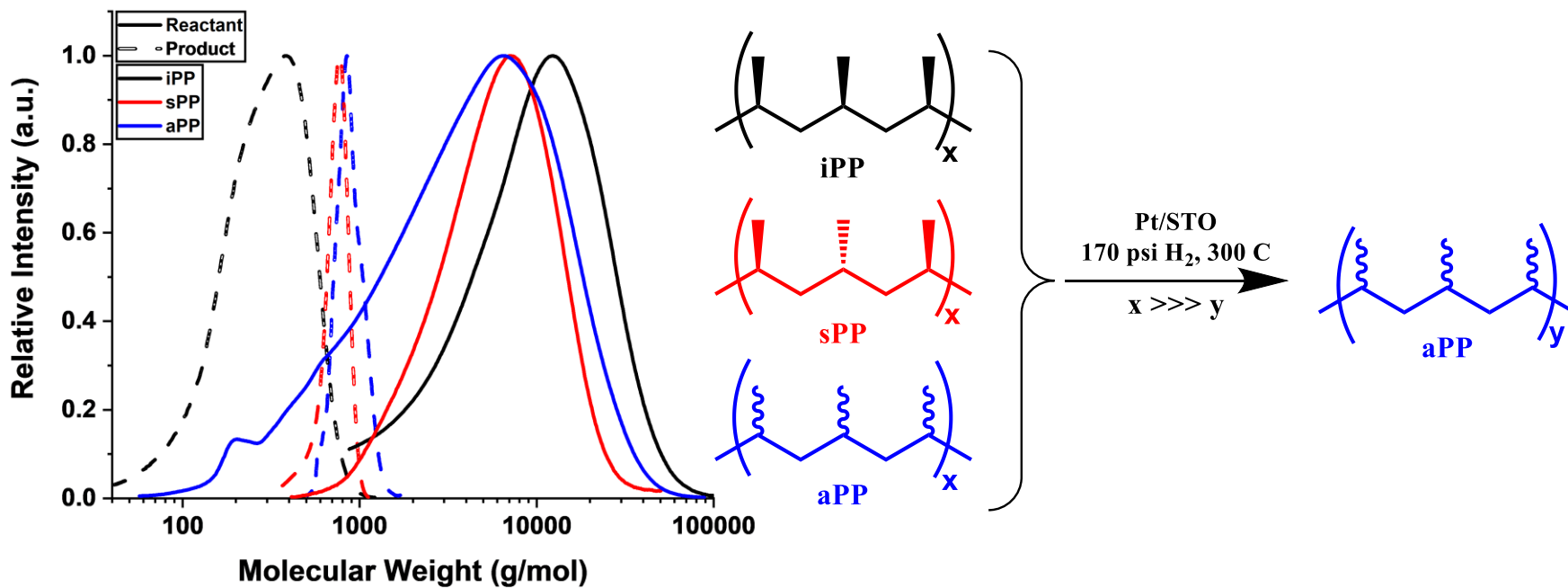
Polyolefins	M _n	Đ
LLDPE (M _w = 899K, 4%)	430	1.4
Engage 8003 (M _w = 115K, 9%)	450	1.4
Engage 8100 (M _w = 115K, 13%)	500	1.1
Affinity GA 1875 (M _w = 15K, 13%)	440	1.6



LLDPE was a generous gift from Dow Chemical

EXPLORATION OF HYDROGENOLYSIS CONDITIONS

Polypropylene Stereoisomers



Hackler, R. et al Effect of Macro- and Microstructures on Catalytic Hydrogenolysis of Polyolefins
Macromolecules 2022, 55, 6801–6810

MARKET ANALYSIS AND BUSINESS CASE

PRODUCT	PRICE (\$/ton)
Paraffin wax	1,500–2,000
Lubricant base-oil	2,000–3,000
Viscosity modifier	>3,000
Pyrolysis Oils	500–700
Fuel	600–1,200

\$57B

Global Base-oils,
Waxes,
Viscosity modifiers

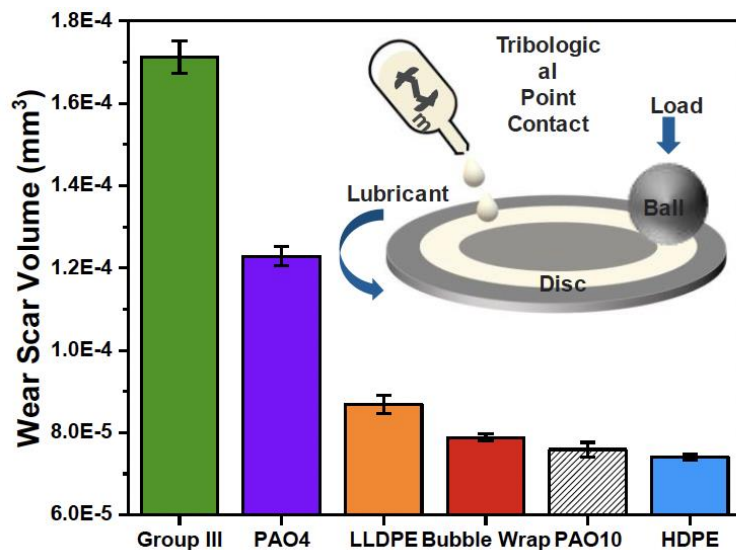
\$20B

US Group III-IV
Base-Oils,
Paraffin Waxes,
Synthetic Waxes

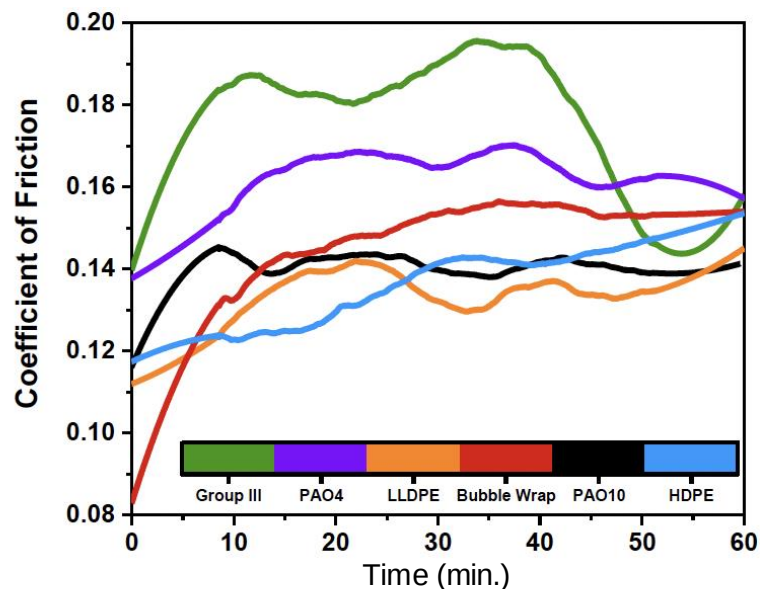
Source: Investment Banking Services and Securities offered through Independent Investment Bankers Corp. a broker-dealer, Member FINRA/SIPC. Aulos Capital, LLC is not affiliated with Independent Investment Bankers Corp

TRIBOLOGY PROPERTIES OF HQL FROM SINGLE-USE POLYOLEFINS WASTE

Tribological Measurements Across Various Lubricants



Room temperature pin-on-disk tribometer

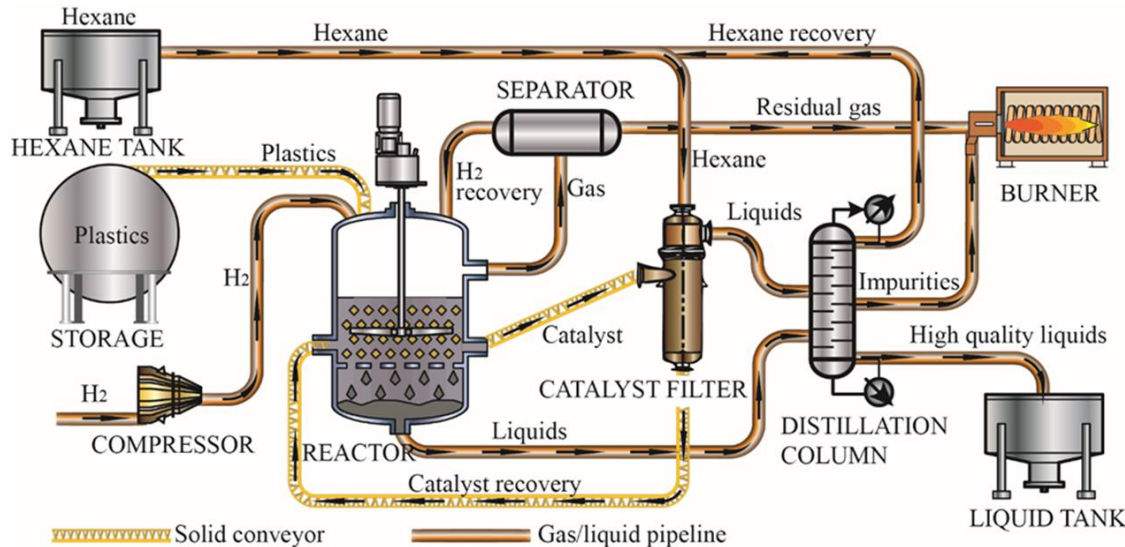


Based oils from CPChem



PROCESS DESIGN

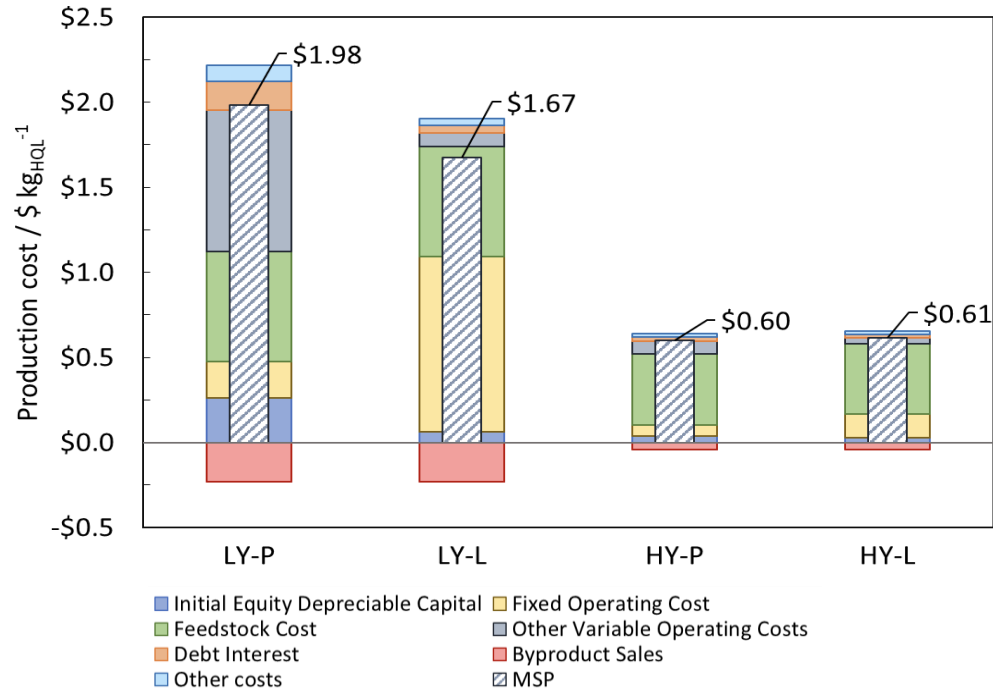
Techno-Economic Analysis (TEA) and Life-Cycle Assessment (LCA)



- 250 MT x day
- Semi-batch process
- Post consumer Polyethylene waste (HDPE, LDPE, LLDPE, PP)
- Aspen Plus v12
- Case study:
 - Low Yield (LY) = 60% liquid
 - High Yield (HY) = 90% liquid

Cappello V. et al. Conversion of plastic waste into high-value lubricants: techno-economic analysis and life cycle assessment. *Green Chem.* 2022, 24, 6306.

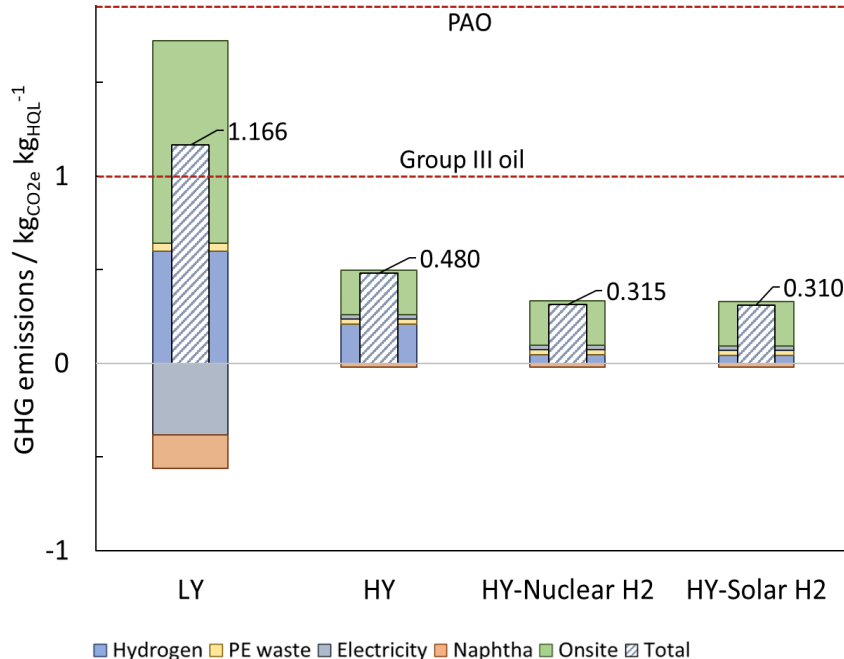
TECHNO-ECONOMIC ANALYSIS (TEA)



- HQL production cost in the range \$0.6–\$2/kg (i.e. \$1.8–\$6.0/gal)
- Leasing of catalyst (L) can be more advantageous than purchasing (P) at lower yields
- High economic potential given the market price of conventional lubricant oils with similar properties (i.e. ~\$6–\$10/gal)¹

¹EIA, Table F10: Lubricants consumption, price, and expenditure estimates, 2019, https://www.eia.gov/state/seds/data.php?incfile=/state/seds/sep_fuel/html/fuel_lu.html&sid=US

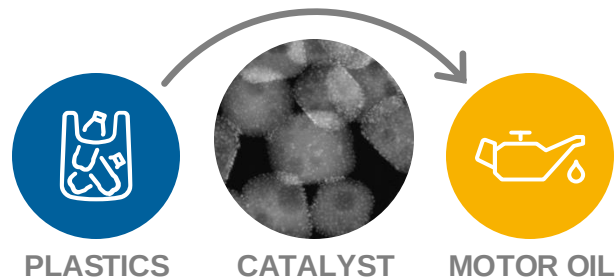
LIFE-CYCLE ASSESSMENT (LCA)



- GHG emissions trend
 - Low yield (LY) > High yield (HY) > High yield – nuclear H₂ (HY-Nuclear H₂) > High yield – solar H₂ (HY-Solar H₂)
- Emissions credit for by-product electricity the LY case
- Emissions credit for by-product naphtha for all the cases
- All HY cases reduce GHG emissions by over **50%** and **70%** when compared to emissions associated with conventional production pathways for Group III oil and PAO, respectively

CONCLUSIONS

- Catalysis enables the valorization of waste POs into valuable products to mitigate adverse impacts of the plastic pollution
- Pt NPs supported on SrTiO_3 nanocuboids convert PE (ranging from M_n of 8,000 – 158,000 Da and Mw of 17,200 – 420,000 Da) into narrowly distributed liquid products
- Catalyst – PE Interactions
 - more favorable adsorption of PE on Pt sites than on the SrTiO_3 support
 - preferential binding of high molecular weight PE on the Pt NPs surface
 - electronic and geometric properties of Pt NPs on SrTiO_3
- Reduction in friction and wear when using PAO10 blended with HQLs under automobile operating Temp.
- Synthetic lubricants (PAO) are priced at \$9/gal which is considerably higher than Crude oil (\$1.18/gal), fuels (gasoline, diesel; \$1.30 – 1.75/gal), and BTX (\$2.0 – 3.2/gal)
- US market value ~\$20 billion with an expected growth of 40 – 50% by 2035



ACKNOWLEDGEMENTS



PARTNERSHIP OPPORTUNITIES

- Collaborative research to further develop technologies
- Technology licensing
- anl.gov/partners