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In Search of Resilient Chemical Technologies with Minimum Carbon Intensity

Chemical Upcycling of Lignocellulosic and Plastic Wastes

Hemant Choudhary

04/26/2022, UC Davis

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Personal Background

Research interests

- Green and Sustainable Chemistry
- Catalysis for sustainability
- Energy dense materials for fuel and propellants
- Ionic Liquids in agrochemicals and separations
- Physicochemical properties of ionic liquids
- Waste upcycling
- Surface and bulk properties and activity relationships

Contact information

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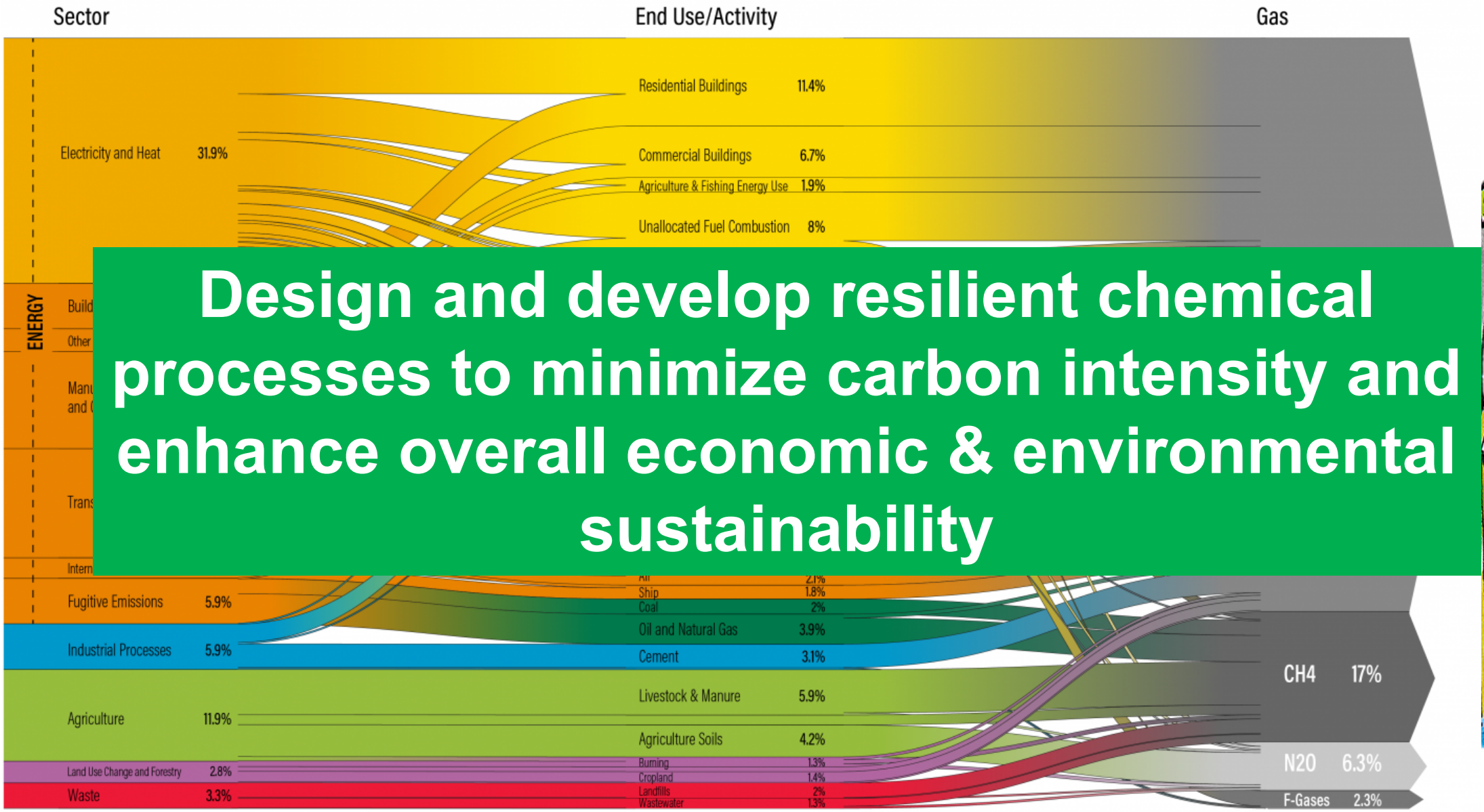
Source: Greenhouse gas emissions on Climate Watch. Available at: https://www.climatewatchdata.org

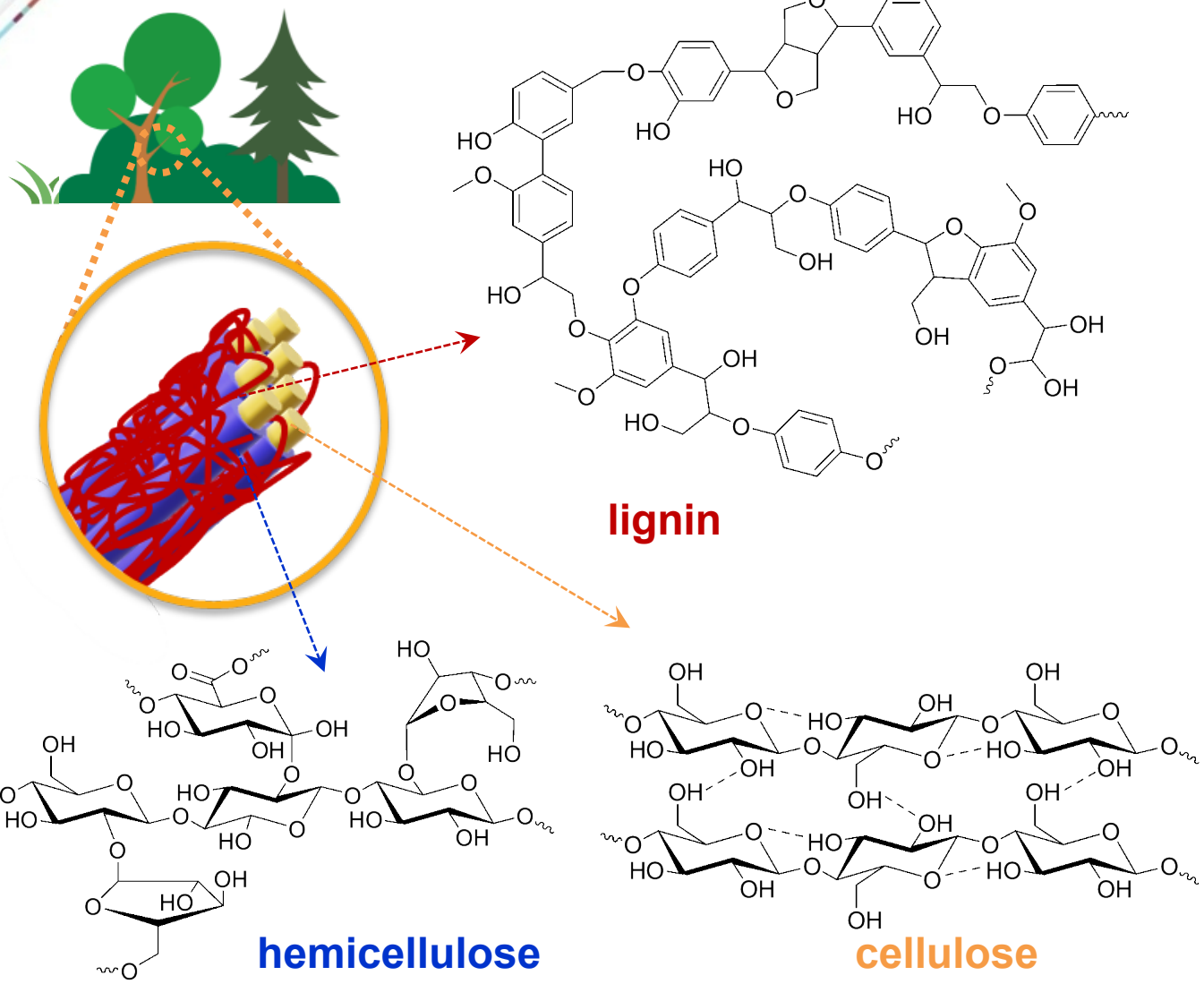
WORLD RESOURCES INSTITUTE

Inspiration and Motivations



Design and develop resilient chemical processes to minimize carbon intensity and enhance overall economic & environmental sustainability

Background – Lignocellulosic Biopolymers

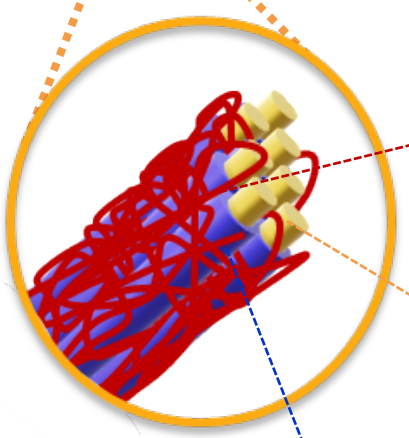


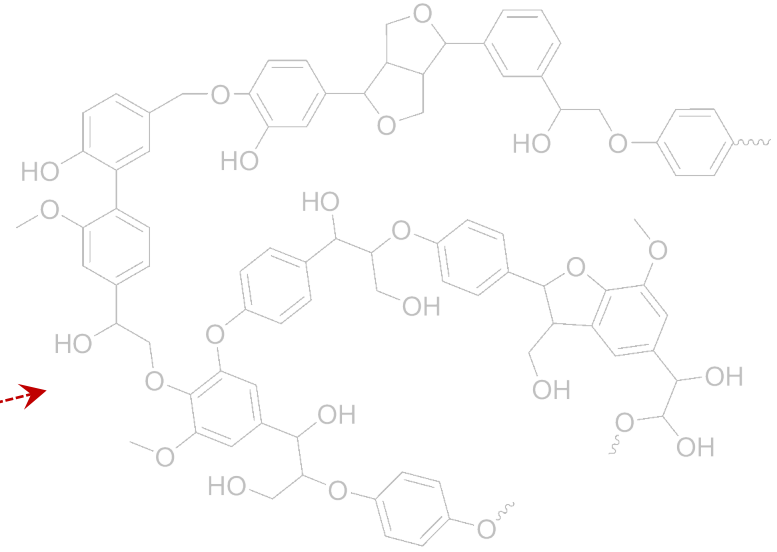
Challenges and Gaps:

- High environmental impact and carbon intensity
- Limited utilization – “either” and “or”
- Non-biocompatible
- Limited efficiency for mixed biomass and/or waste streams

Zhou et al, *Biotechnol. Bioeng.* **2018**, *115*, 2683; Kumar et al, *Fuel Process. Technol.* **2020**, *199*, 106244; Torr et al, *Biotechnol. Bioeng.* **2016**, *113*, 540; Cheng et al, *Biomacromolecules* **2011**, *12*, 933; Doherty et al, *Green Chem.* **2010**, *12*, 1967; Fu et al, *J. Agr. Food. Chem.* **2010**, *58*, 2915; Li et al, *Bioresour. Technol.* **2011**, *102*, 4518; Sun et al, *Green Chem.* **2009**, *11*, 646; Yuan et al, *Biotechnol. Bioeng.* **2013**, *110*, 729.

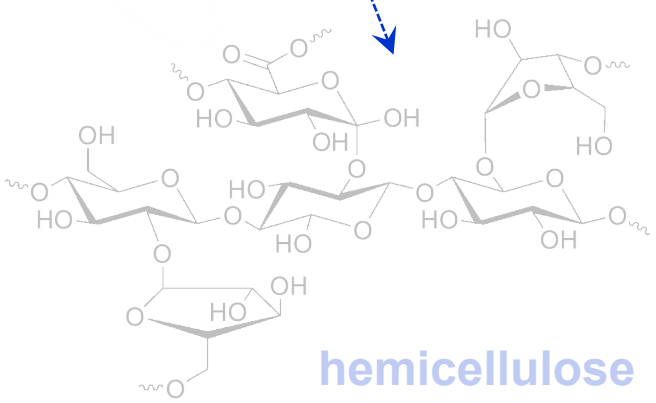
Upcycling of Biopolymers



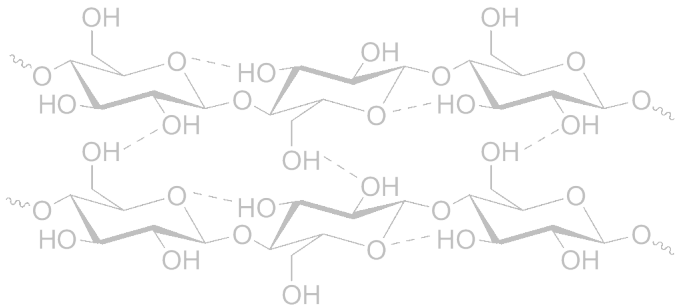


lignin

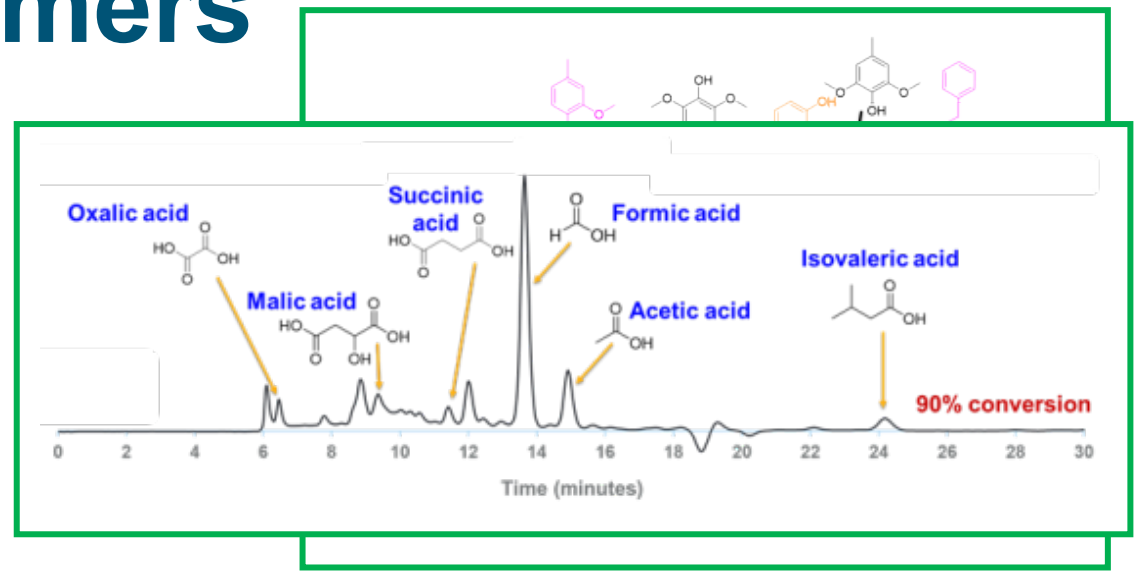
“One-Pot” Approach

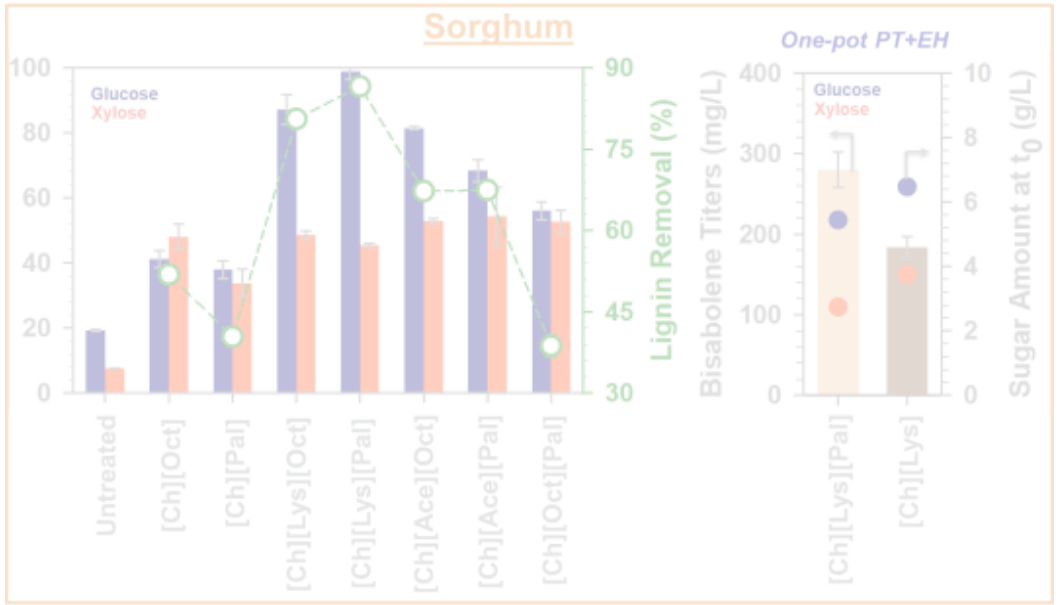


hemicellulose



cellulose

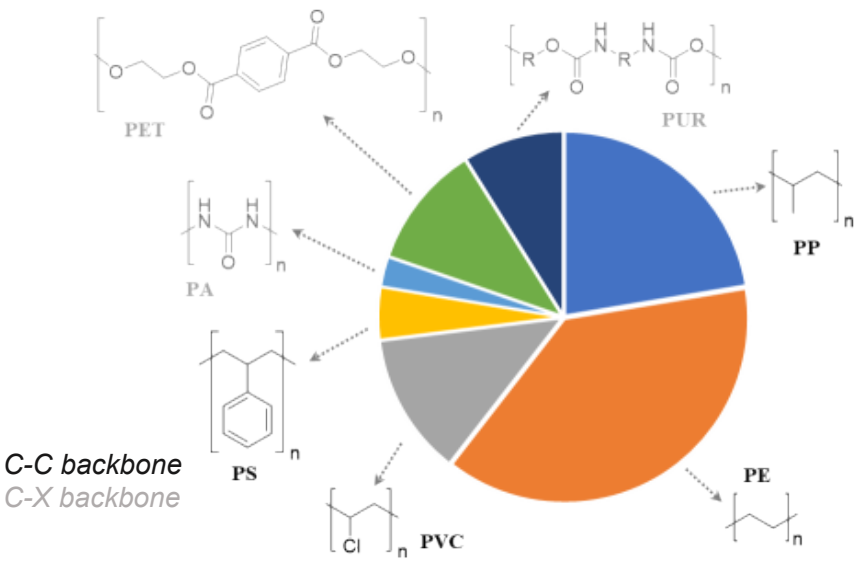




Further reads: *ACS Sustainable Chemistry & Engineering*, **2021**, *9*, 4371; *ACS Sustainable Chemistry & Engineering*, **2021**, *9*, 4422; *Green Chemistry*, **2021**, *23*, 7269; *Green Chemistry*, **2021**, *23*, 6020; *Front. Energy Res.* **2022**, *10*, 868181; US Pat. Appl. 17//560,051; US Pat. Appl. 17/547,134; *ROI 2020-145, 2020-148, 2020-155, 2021-171*

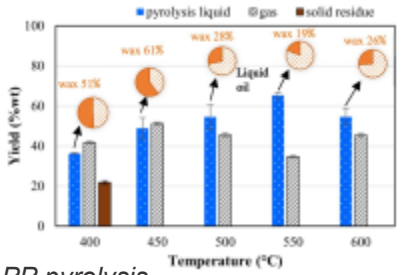
Background - Synthetic Polymers

Plastic Production Distribution, 2016

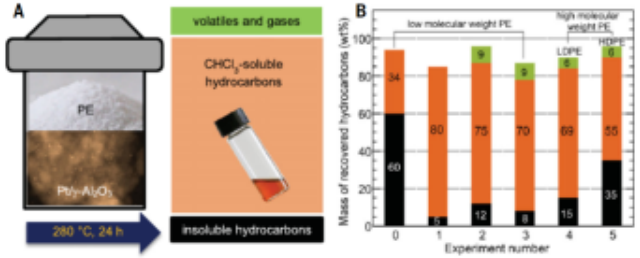


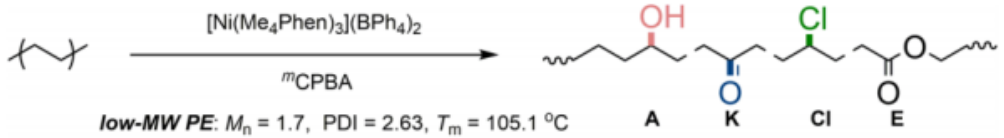
❑ Chemical recycling approaches for **polyolefins**

- **high temperature pyrolysis** or **non-economical hydrogenolysis** to low-value alkanes



PP pyrolysis





low-MW PE: M_n = 1.7, PDI = 2.63, T_m = 105.1 °C
LDPE: M_n = 10.1, PDI = 8.65, T_m = 108.8 °C
HDPE: M_n = 10.3, PDI = 11.2, T_m = 127.4 °C
LLDPE: M_n = 23.6, PDI = 5.2, T_m = 122.3 °C

Past and Present Solutions: Plastic recycling!

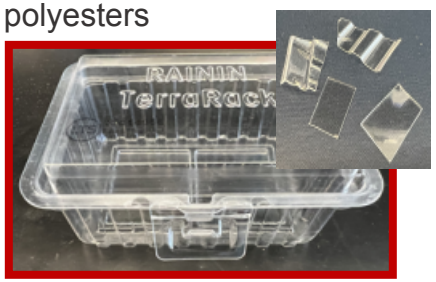
❑ Only **5% to 9%** of the global produce is recycled
❑ **~22%** of globally produced C-X backbone plastics recycled (mechanical recycling mostly)
❑ C-C backbone plastics such as polyolefins forms **>75% waste** (by mass)
❑ Polyolefins are not recycled mechanically

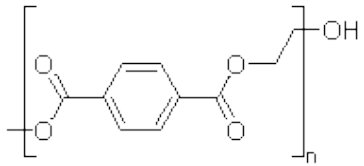
Limitations of current chemical recycling approaches:
● halogenated or organic solvents ● non-reusable homogeneous metal catalysts ● low-value products ● energy-intensive ● carbonaceous deposits ● deactivation of catalyst

https://www.plasticsinsight.com/world-plastics-production/ (last retrieved on 09-07-2021); *Sci. Adv.* **2017**, *3*, e1700782; *Renewable Sustainable Energy Rev.* **2016**, *54*, 421; *Science* **2020**, *370*, 437; *ACS Cent. Sci.* **2017**, *3*, 895; WO 2019/204687 A1; *Waste Manage.* **2021**, *127*, 101.

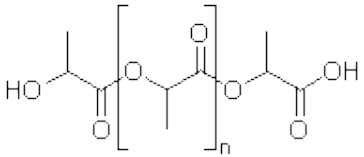
Upcycling of Synthetic Polymers

polyesters



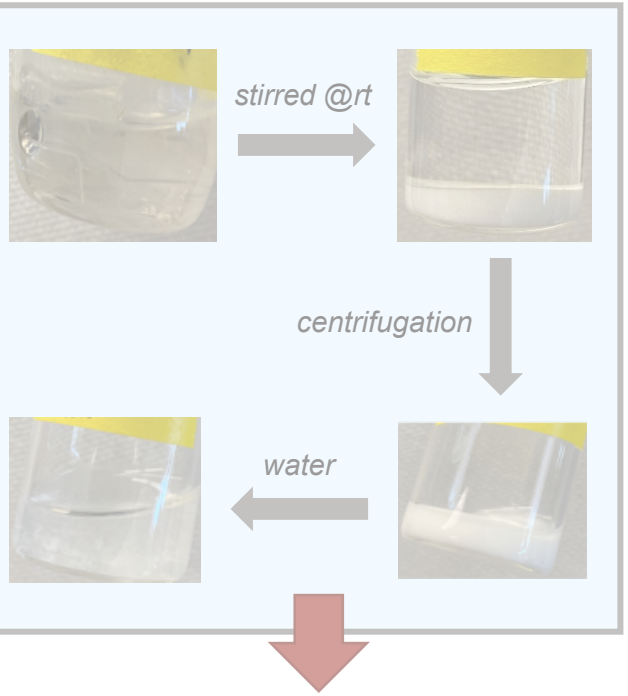


PET

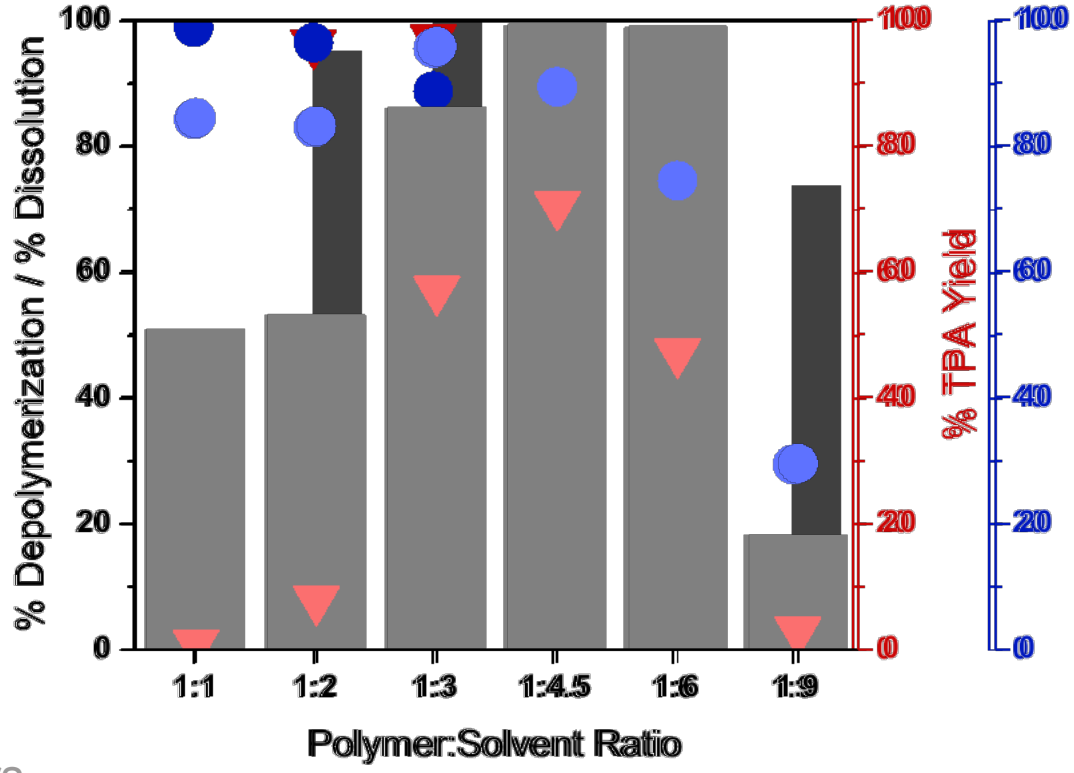


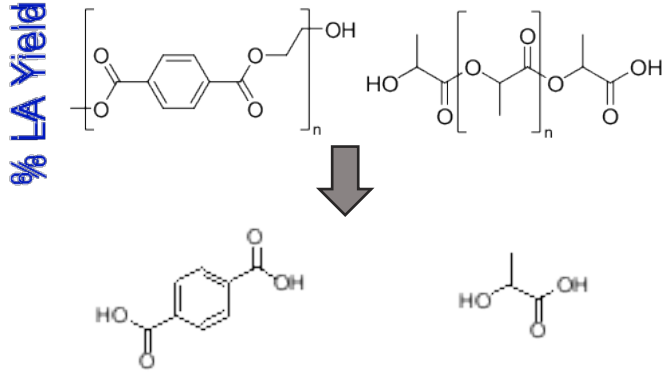
PLA

%Conversion	%Yield
92-95% (at room temperature)	**86-92%** (at room temperature)



Monomers for
impact & heat resistant polymers





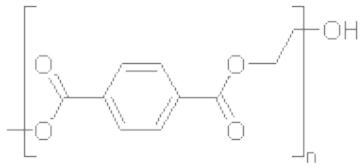
terephthalic acid (TPA)

lactic acid (LA)

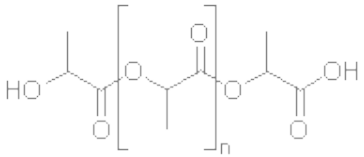
Further reads:
ROI 2021-169, 2021-186, 2021-190
Patent pending; Manuscript in preparation

Upcycling of Synthetic Polymers

polyesters

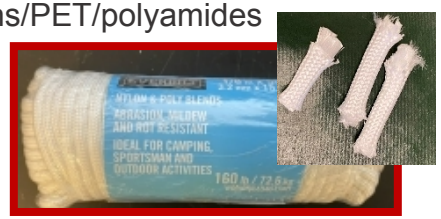


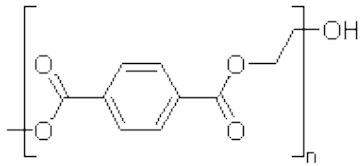
PET



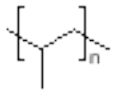
PLA

Polyolefins/PET/polyamides

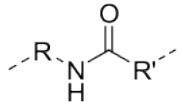




PET

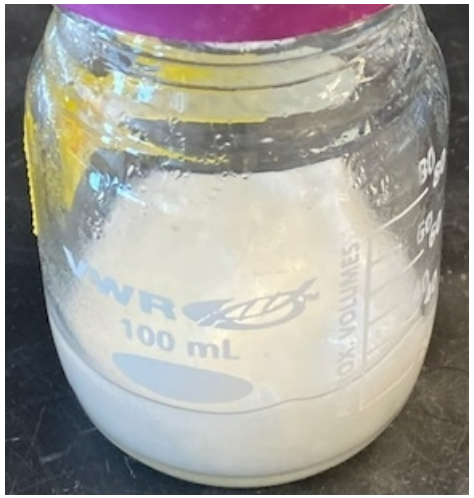


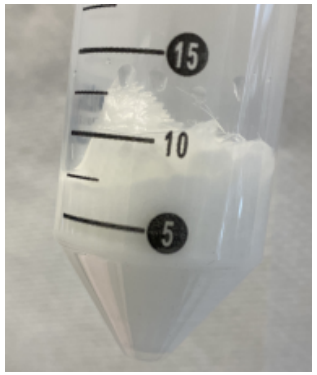
polyolefins



polyamides

%Conversion	%Yield
92-95% (at room temperature)	86-92% (at room temperature)
~99% (at elevated temperature; mix polyester stream)	~98% (at elevated temperature; mix polyester stream)
~40%	~35%





- selective dissolution and depolymerization of polyesters
- little to no impact on polyamides and polyolefins under these conditions
- ***opportunity to sort and depolymerize mixed plastic stream***

Further reads:
ROI 2021-169, 2021-186, 2021-190
Patent pending; Manuscript in preparation

Path forward / Ways to Collaborate

- Potential partnerships / collaborations for the dissolution and depolymerization of bio- and synthetic polymers
  - Ionic solvent based for biomass and plastics processing
    - High-throughput characterization / analysis of product stream
    - Solvent recycling
    - Upgrading of monomers to “new” or “ existing” polymers
    - Rheology of “new” polymers
    - TEA / LCA
  - Transition-metal catalyzed lignin depolymerization
    - Upgrading of monomers to “new” or “ existing” polymers
    - Rheology of “new” polymers
  - Precisely designed transition metal nanoparticle catalysts for polyolefins upcycling
    - High-throughput screening and analysis of product stream
    - Upgrading of monomers to “new” or “ existing” polymers
    - Rheology of “new” polymers
    - TEA / LCA

Thank you!

Imagination is more important than knowledge.

- Albert Einstien