Chemical Upcycling of Waste Plastics

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

Chemical Upcycling of Waste Plastics (CUWP)

George W. Huber, twitter: @gwhuber2

University of Wisconsin-Madison

Department of Chemical & Biological Engineering

www.cuwp.org

CUWP by the Numbers:

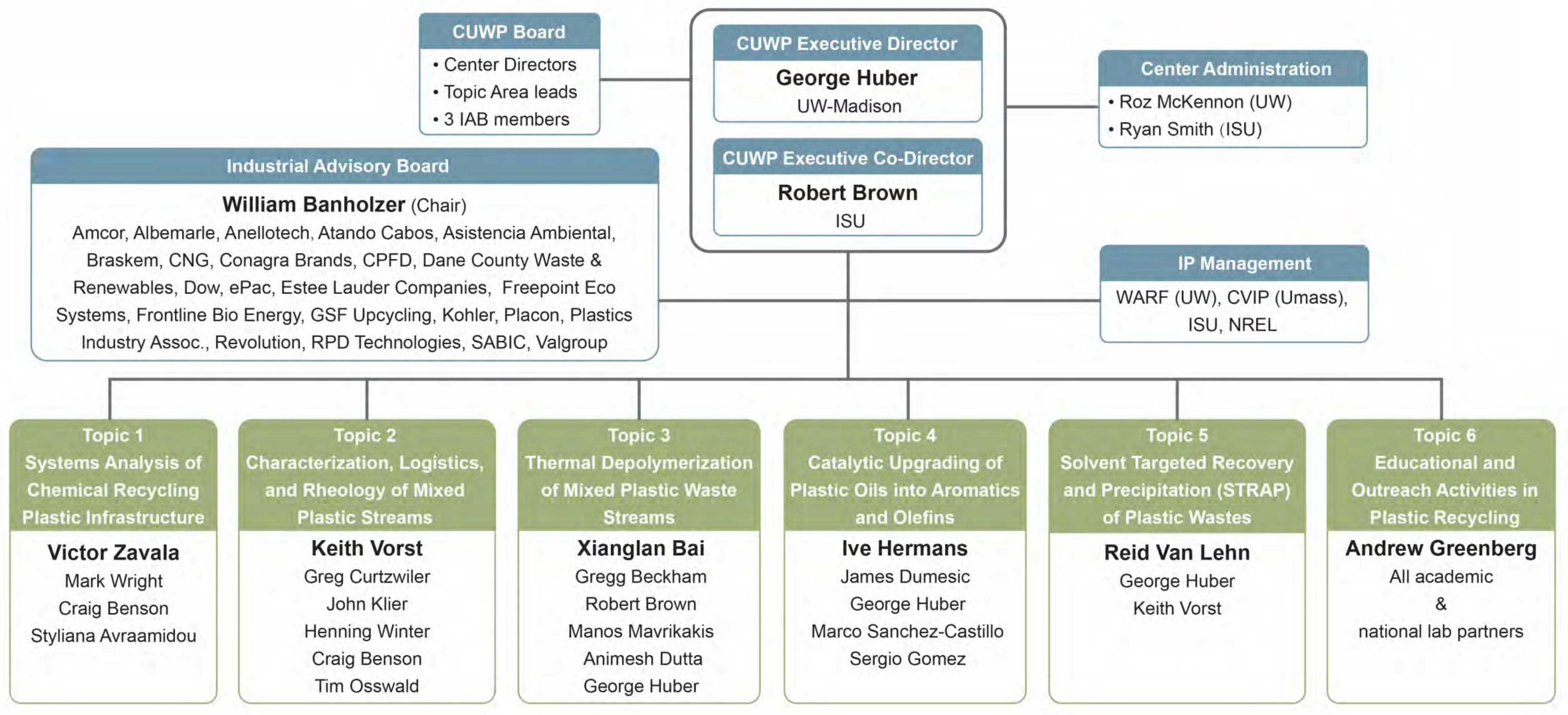
- $12.5 Million 5-year center
- 6 Universities (3 Domestic, 2 Mexico, and 1 Canada)
- 1 National Laboratory
- 23 Companies
- 2 Industry Associations

CUWP Research Team:

18 – Principal Investigators
29 Industrial Advisory Board Members
5 – Post-Doctoral Researchers
18 – Graduate Students
7+ - Undergraduate Students

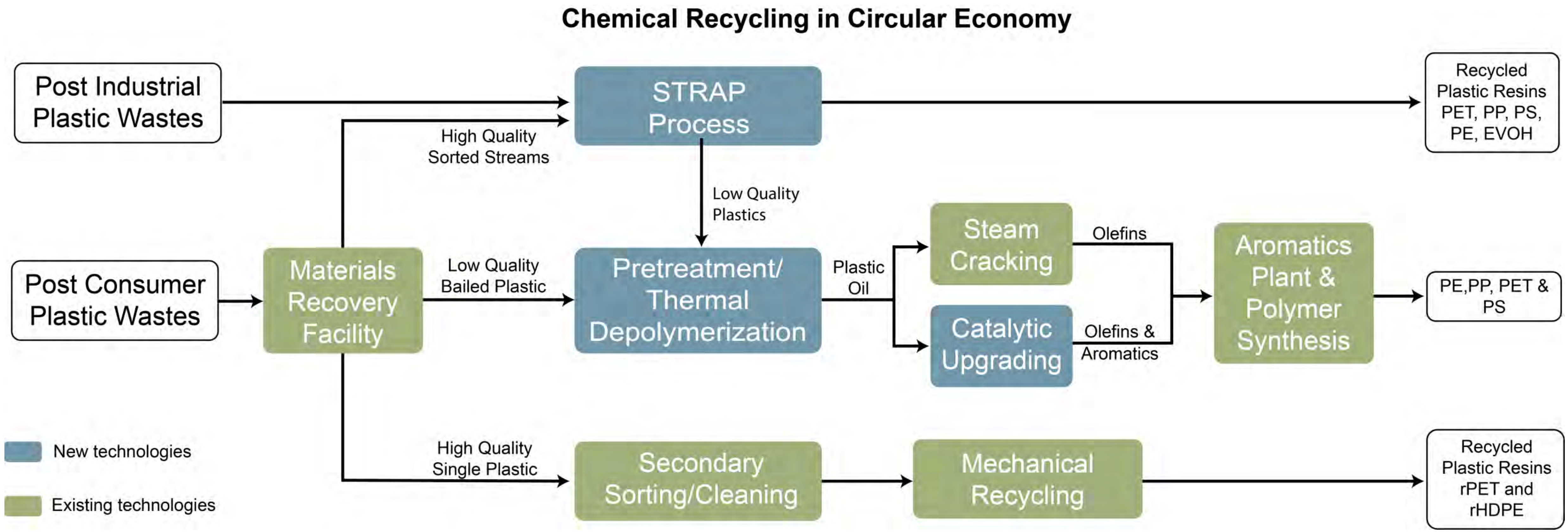
GW Huber has a financial interest in Anellotech.

Organizational Chart



CUWP supports 36 graduate students and post-doctoral researchers.

Center for Chemical Upcycling of Waste Plastics



The objective of CUWP is to develop the scientific and engineering principles that will enable the circular upcycling of plastic wastes into virgin plastic resins using chemical technology.

- Start Date: April 2021

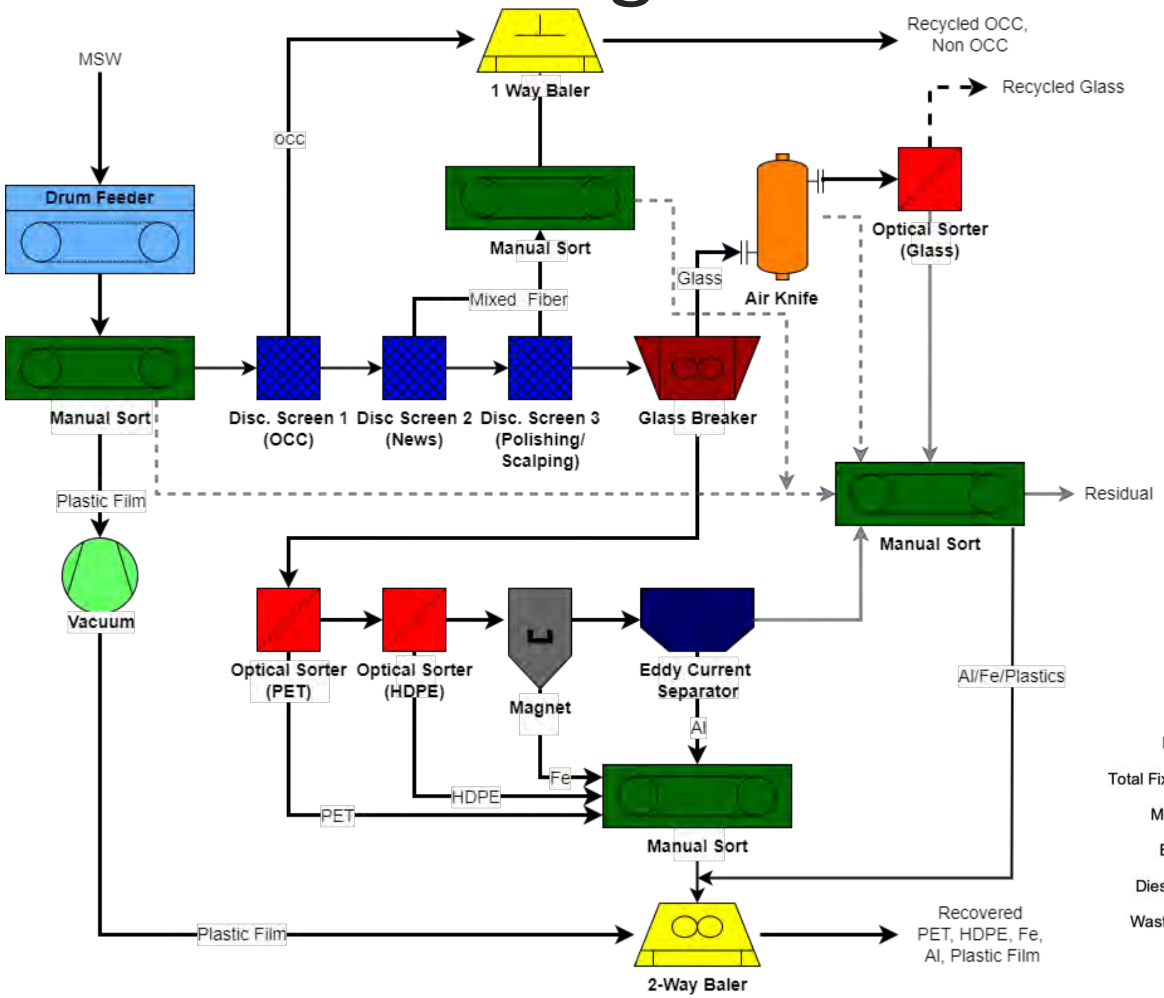

PLASTIC
SUPPLY CHAIN
Extraction Of Natural Gas & Crude Oil
Gasoline & Diesel Fuel
Landfills
Petroleum Refineries/ Steam Crackers
Waste Management Companies/MRFs
Consumers
Recyclers
Retailers
Polymer Synthesis
Brand Owners
Air
Plastic Convertors
CUWP
CUWP
OIL
OIL FACTORY

The First Step in Recycling: Material Recovery Facilities (MRF)

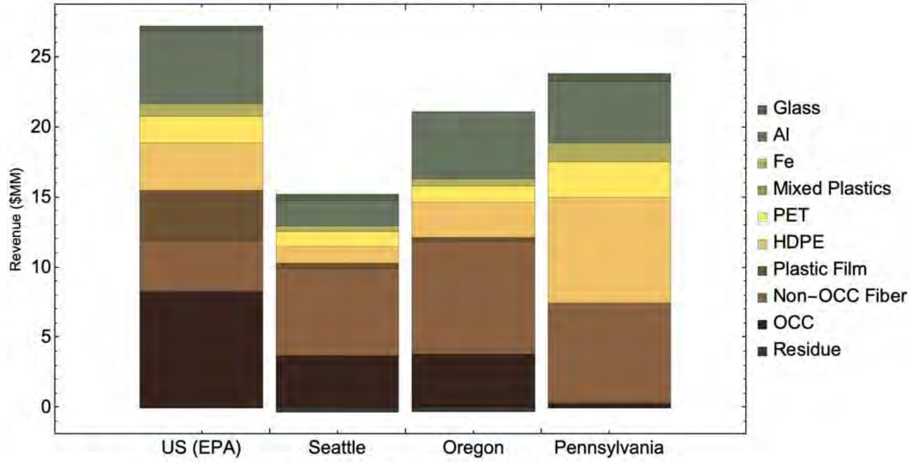
https://www.rubicon.com/blog/materials-recovery-facility/

Bailed Plastics

Modeling the Material Recovery Facility



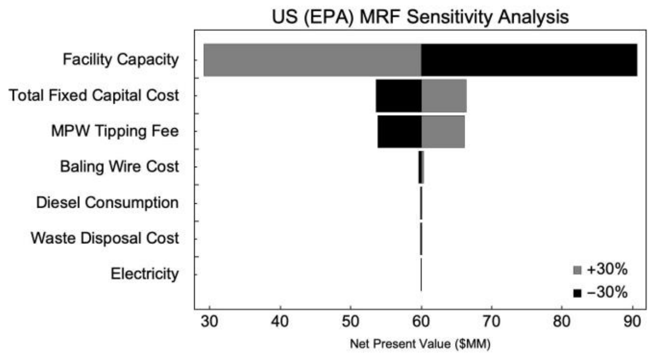
MRF Revenue by

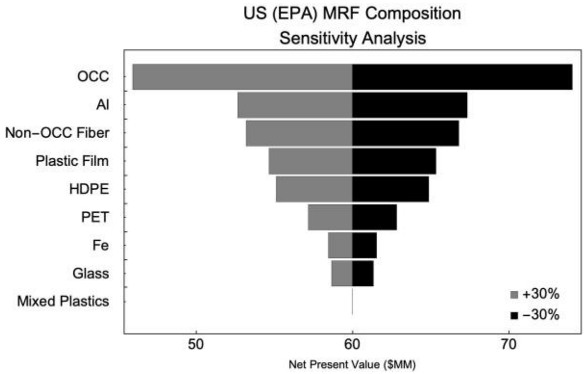


Dr. Mark Mba-Wright

Olumide Olafasakin

Techno-Economic Analysis NPV Sensitivity Analysis





Some key assumptions and results

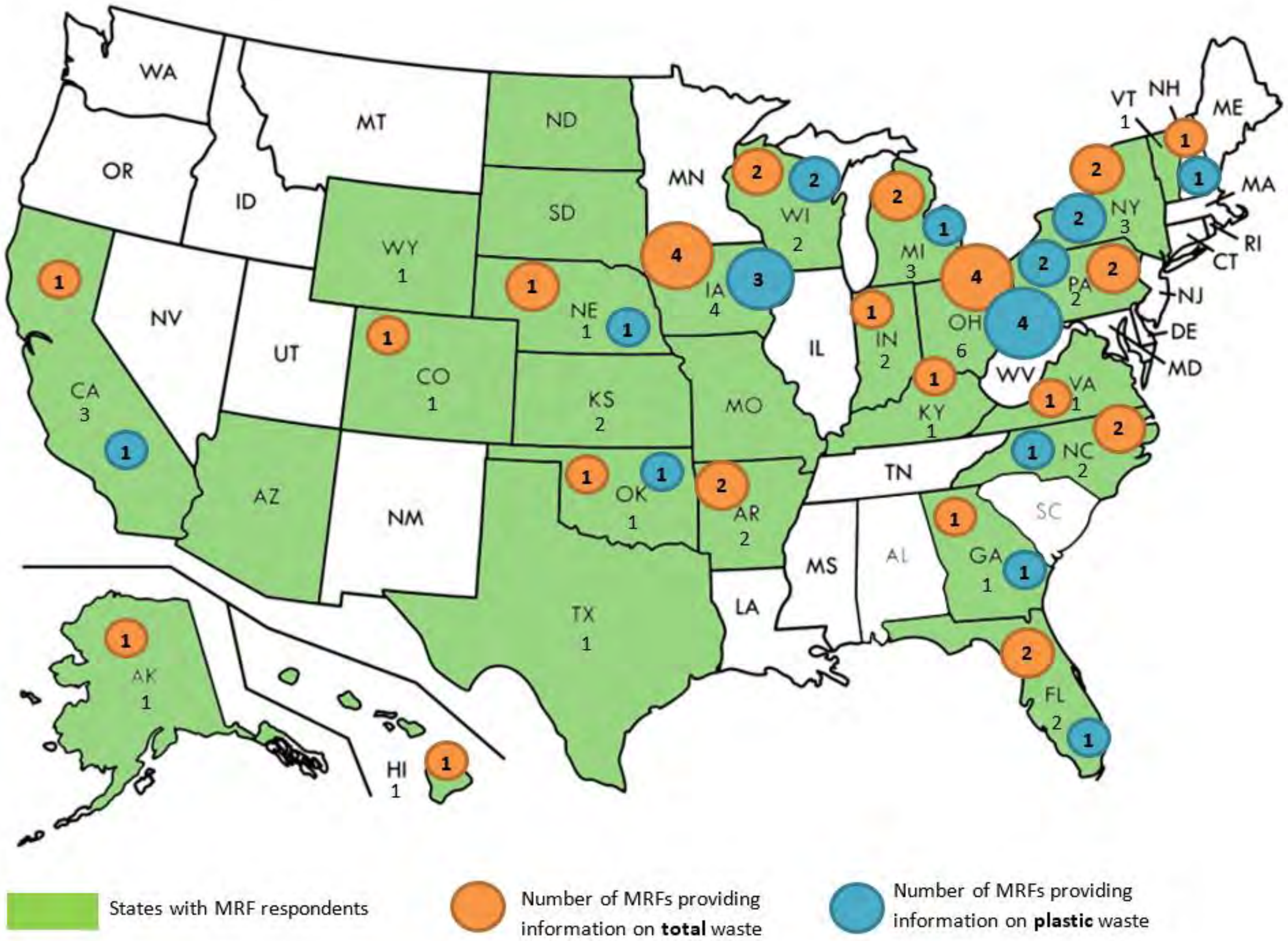
- Capacity: 120,000 MT/year
- Total Fixed Capital Cost: $5.15 MM
- Operating Cost: $Operating hours: 4160 hours/year (2 8-hours shift, 5 days a week)
- Net Present Value (NPV): 3.57 – 60 MM USD

Composition reference

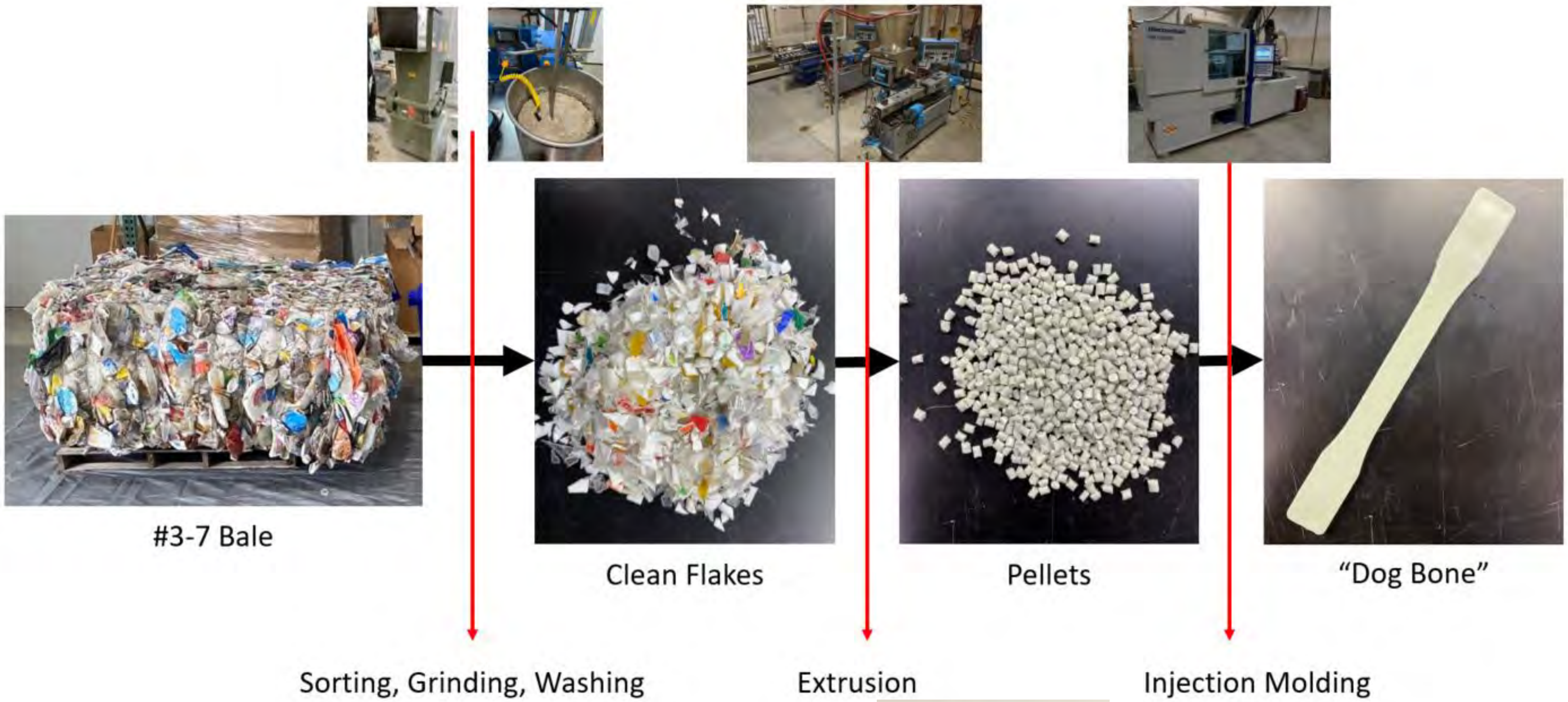
- US EPA, “Municipal Solid Waste Generation, Recycling, and Disposal in the United States Tables and Figures for 2010 https://www.epa.gov/sites/production/files/2015-09/documents/2010_msw_fs.pdf,” US Environ. Prot. Agency, no. February, p. 63, 2010.
- R.W. Beck Inc., “Pennsylvania Recovered Material Composition Study,” 2005.
- P. Spendelow, “Composition of Commingled Recyclables Before and After Processing,” no. March, 2011.
- C. C. Group, S. Public, and U. Staff, “Seattle Public Utilities Residential Waste Stream Composition Study FINAL Report,” no. November, 2007.

National MRF Survey

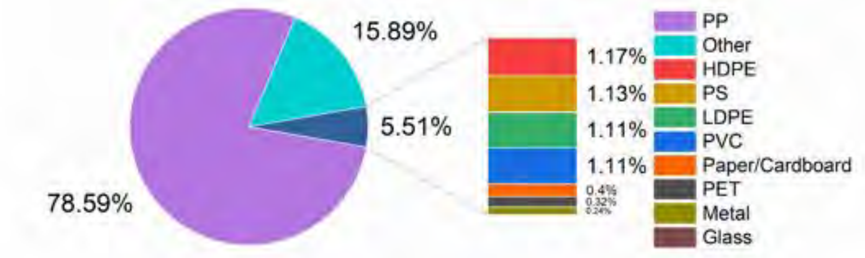
- Partnered with Environmental Research and Education Foundation.
- Questions: MRF type, waste source, handled materials (type and quantity), % revenue, type of equipment.
- 49 responses, but only 38 provided waste mass information, and 23 provided plastics information.

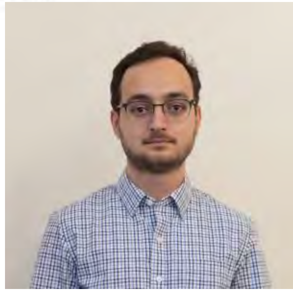
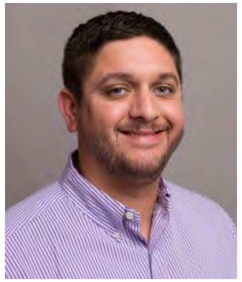


#3-7 Plastic Bale Composition from MRFs



MRF 1



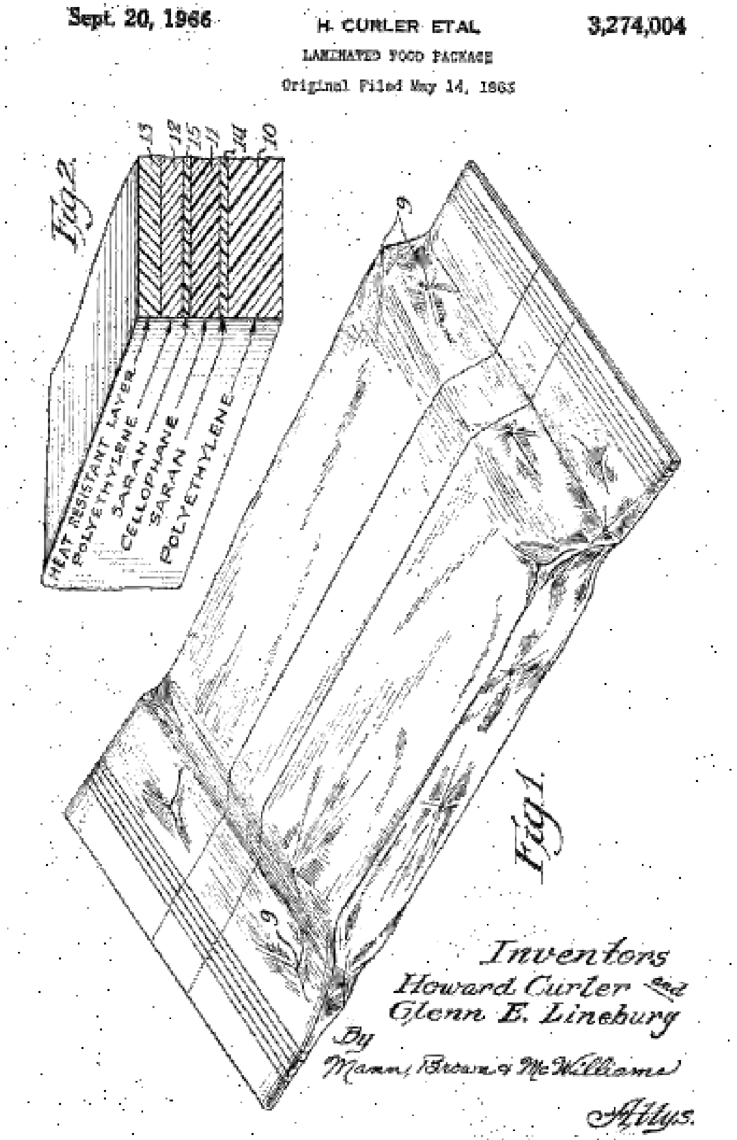




Victor Cecone Greg Curtzwiler Keith Vorst

Package Design: Natural Cheese—1966

1966

- 1.5 billion lb
  - 45% cans, boxes and rigid plastic containers
  - 35% packaged in paper and foil
  - 20% plastic film
- PVDC-coated cellophane + PE
- Polyester (PET)-PVDC-PE

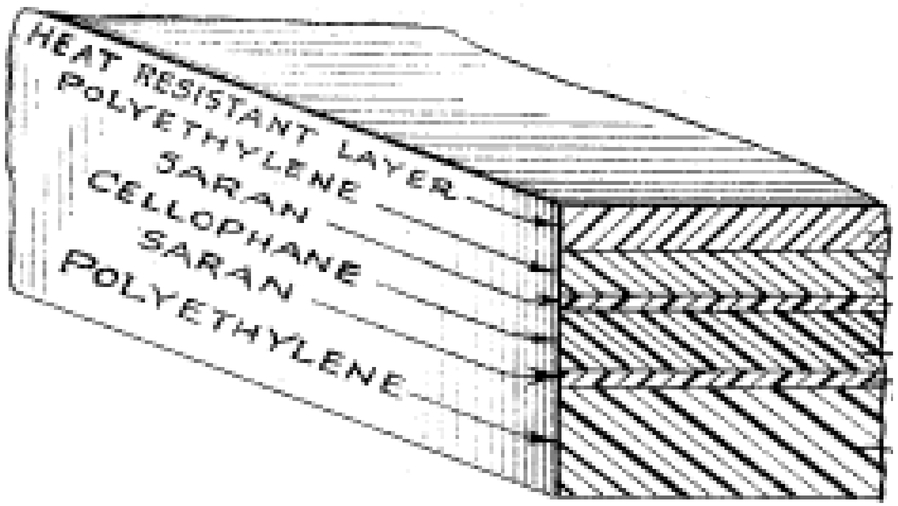


Howard Curler
UW-Madison
(1948)

Howard Curler
CBE
Distinguished
Chair (1997)

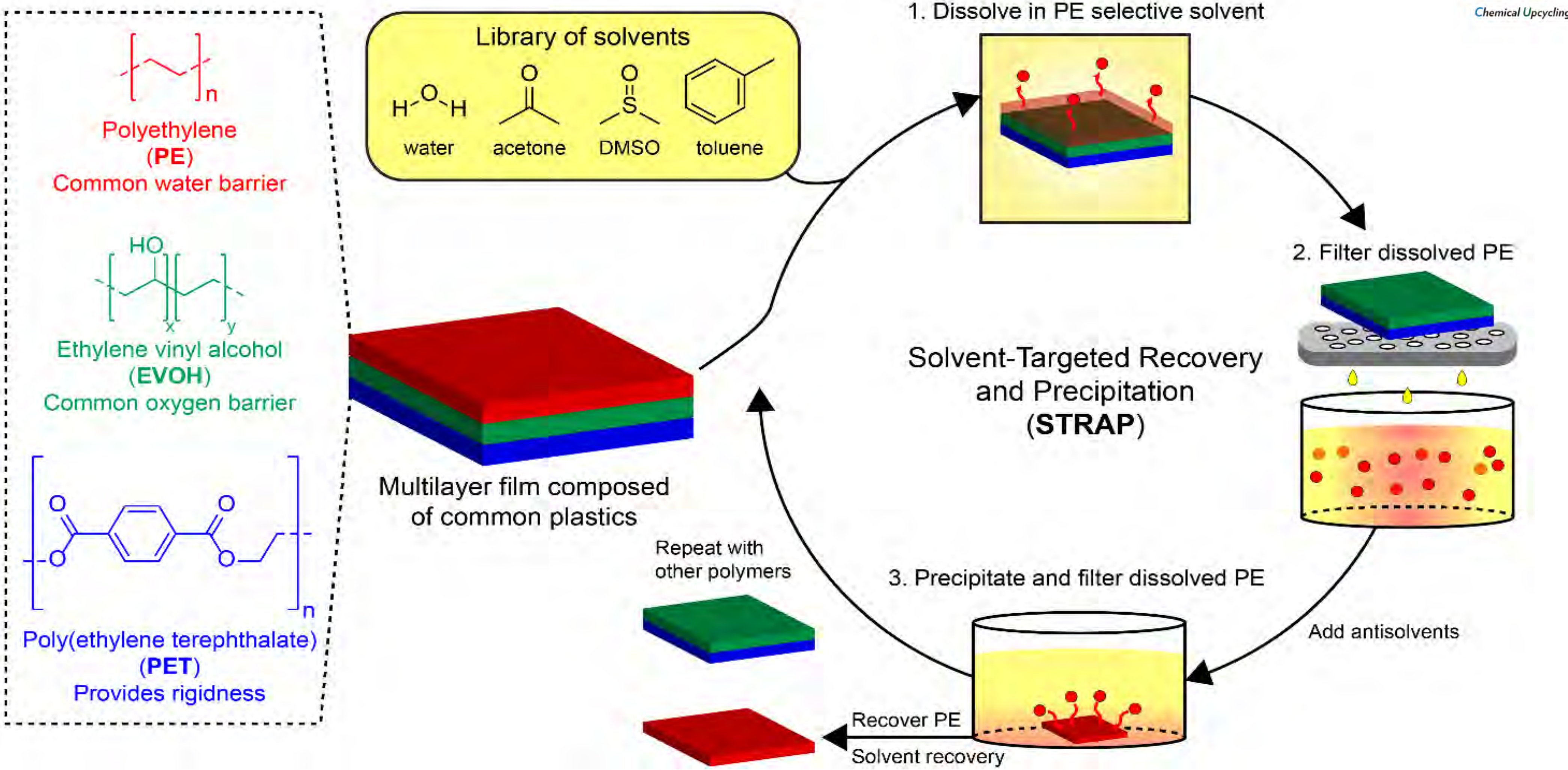
Sacharow, Stanley, and Roger C. Griffin. Food Packaging; a Guide for the Supplier, Processor, and Distributor. Westport, CT: AVI Pub., 1970.

Package Design: Natural Cheese—1966



flex fatigue resistance layer
adhesive layer
oxygen barrier layer
stiffness layer
oxygen barrier layer
seal layer

Solvent-Targeted Recovery and Precitation (STRAP) of multilayer plastic packaging



TW Walker, N Frelka, Z Shen, AK Chew, J Banick, S Grey, MS Kim, JA Dumesic, RC Van Lehn, GW Huber, Recycling of multilayer plastic packaging materials by solvent - targeted recovery and precipitation, ScienceAdvances (2020), 6, eaba7599.

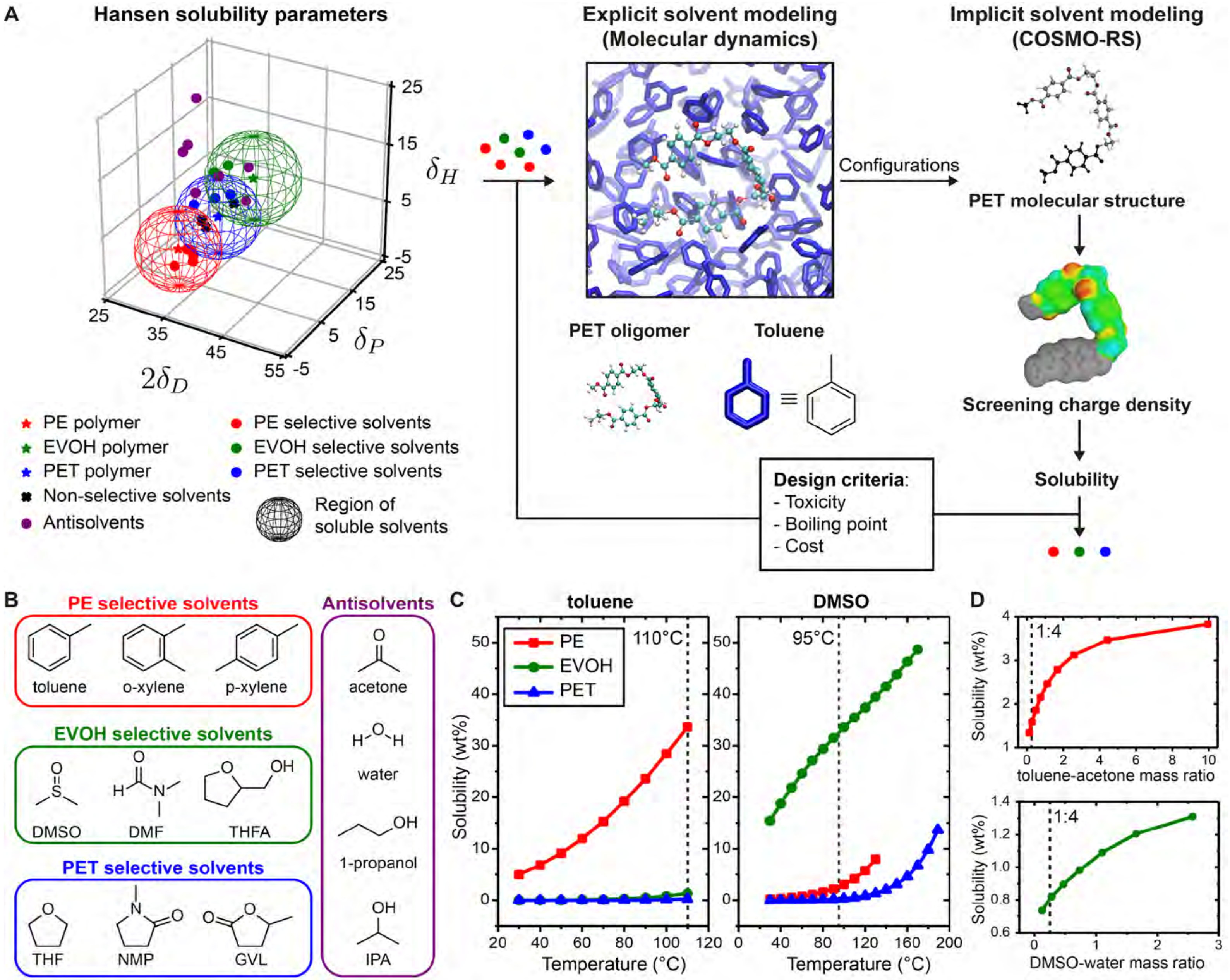
We have Processed a Large Variety of Plastics with STRAP

- Clear rigid multilayer film used in food containers
- Mixed multilayer plastic waste
- Face masks
- Printed multilayer polyester flexible films
- Printed multilayer nylon flexible films
- PVDC flexible films
- Marine plastics
- Polycarbonates (eye glass waste)
- Waste flexible PE films
- Municipal Solid Waste (MSW)

Panzheng Zhou

Thermodynamic computational tools are used to design solvents

Database of 9+ polymers in more than 1000 solvents

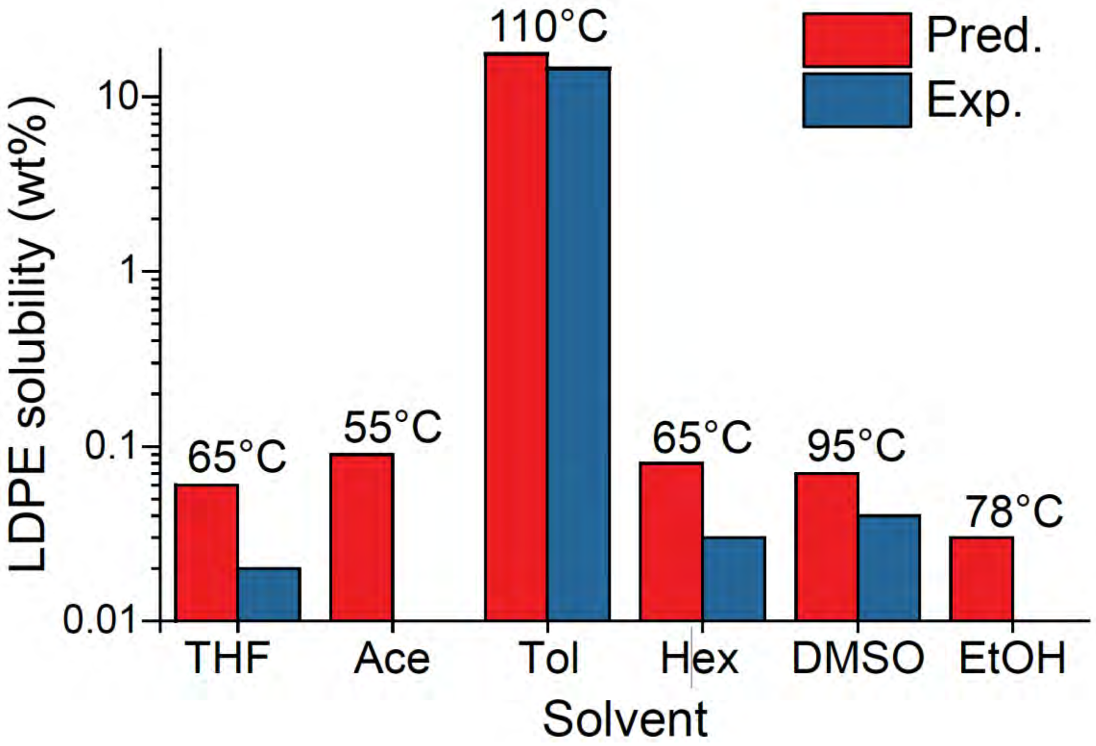


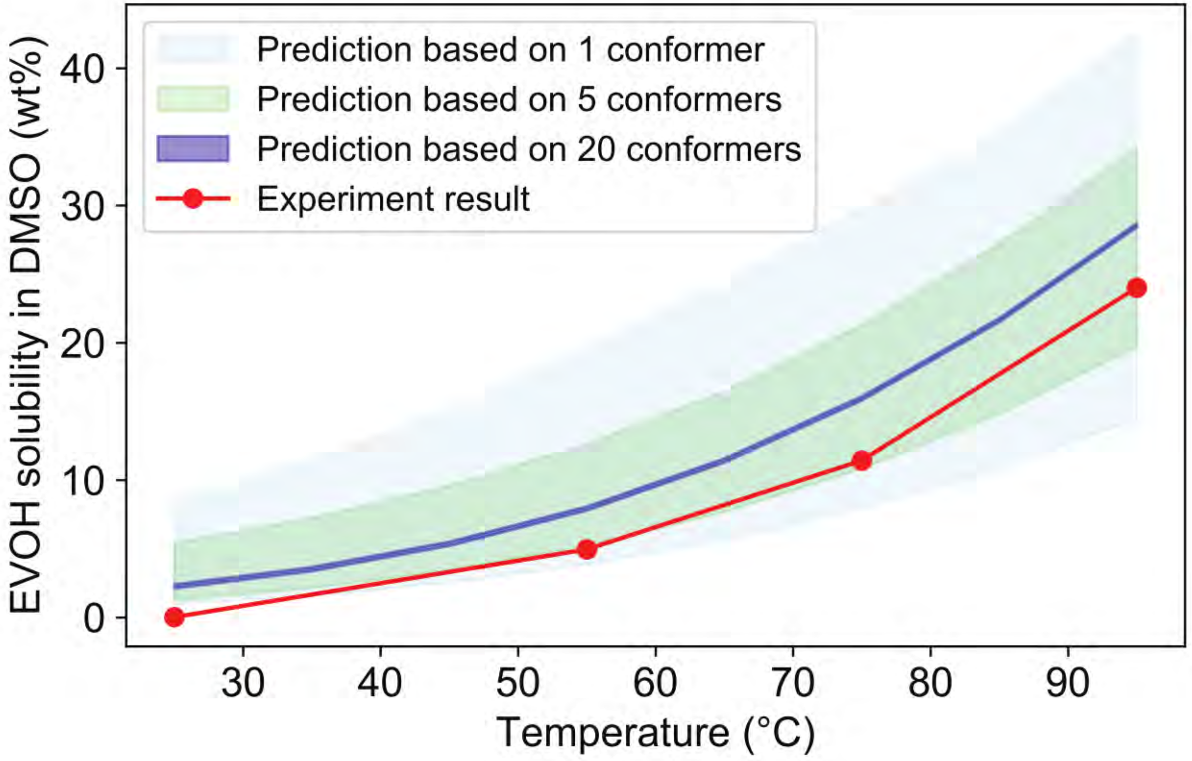
Panzheng Zhou, Kevin L Sánchez-Rivera, George W Huber, Reid C Van Lehn, Computational Approach for Rapidly Predicting Temperature-Dependent Polymer. Solubilities Using Molecular-Scale Models, (2021) ChemSusChem 14 (19), 4307-4316.

Have database with 9+ polymers, 1000+ solvents

abbr	lab name	Solvent name in cosmobase	CAS numbe	BP (°C)	Th (°C)	EVOH		PE		PET		PP		PS		PVC		Nylon 6		Nylon 66	
						RT	Th	RT	Th	RT	Th	RT	Th	RT	Th	RT	Th	RT	Th	RT	Th	RT	Th
	methanol	methanol	67-56-1	64.6	63.6	0.0	0.8	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.8	0.0	0.3	0.0	0.1
DCM	dichloromethane	ch2cl2	75-09-2	40	39.0	0.0	0.0	0.0	0.1	0.3	0.8	0.2	0.5	4.6	8.5	2.7	4.6	0.9	1.7	0.2	0.5
	ethylene glycol	glycol	107-21-1	197.3	120.0	0.0	10.6	0.0	0.9	0.0	0.0	0.0	0.1	0.0	0.0	0.0	1.6	0.0	0.4	0.0	0.2
	Acetone	propanone	67-64-1	56	55.0	0.0	0.2	0.0	0.3	0.1	0.7	0.3	1.4	9.2	21.3	10.9	19.8	0.0	0.2	0.0	0.1
	Isopropanol	2-propanol	67-63-0	82.3	81.3	0.0	1.4	0.0	1.6	0.0	0.0	0.1	2.3	0.0	1.2	0.2	2.9	0.0	1.0	0.0	0.4
	1-propanol	propanol	71-23-8	97.2	96.2	0.0	4.1	0.0	4.2	0.0	0.1	0.1	4.1	0.0	2.8	0.1	5.4	0.0	2.6	0.0	1.1
	toluene	toluene	108-88-3	110.6	109.6	0.0	0.3	0.1	22.6	0.0	2.5	1.1	30.9	3.6	41.0	0.7	14.8	0.0	1.3	0.0	0.4
	chloroform	chcl3	67-66-3	61.1	60.1	0.0	0.0	0.0	0.6	0.2	1.0	0.5	3.1	2.3	9.8	1.1	4.2	4.4	6.2	1.9	2.9
THF	tetrahydrofuran	thf	109-99-9	65	64.0	0.1	0.9	0.1	1.7	0.0	0.8	2.0	10.1	14.0	31.3	8.9	19.1	0.0	0.4	0.0	0.2
THP	tetrahydropyran	thp	142-68-7	88	87.0	0.0	1.1	0.1	7.3	0.0	0.8	2.0	20.9	7.2	33.7	3.9	17.9	0.0	0.7	0.0	0.3
	cyclohexane	cyclohexane	110-82-7	80.7	79.7	0.0	0.0	0.1	6.9	0.0	0.0	4.0	24.0	0.2	4.6	0.1	1.2	0.0	0.0	0.0	0.0
	heptane	n-heptane	142-82-5	98.5	97.5	0.0	0.0	0.1	15.3	0.0	0.0	2.9	29.3	0.1	5.2	0.0	1.7	0.0	0.0	0.0	0.0
	triethylamine	triethylamine	121-44-8	89	88.0	nan	7.7	0.1	8.7	0.0	0.0	2.8	23.2	0.8	12.9	0.5	4.7	0.0	0.2	0.0	0.1
	1,2-propanediol	propyleneglycol	57-55-6	187.6	120.0	0.0	12.4	0.0	3.2	0.0	0.0	0.0	0.6	0.0	0.3	0.0	3.8	0.0	1.7	0.0	0.7
DMSO	dimethyl sulfoxide	dimethylsulfoxide	67-68-5	189	120.0	1.3	35.3	0.0	5.3	0.0	8.3	0.0	1.7	1.5	18.2	8.4	33.2	0.0	3.0	0.0	1.6
	hexane	hexane	110-54-3	68.7	67.7	0.0	0.0	0.1	3.1	0.0	0.0	3.6	16.2	0.1	1.9	0.1	0.6	0.0	0.0	0.0	0.0
	acetylacetone	acetylacetone	123-54-6	138	120.0	0.0	6.6	0.0	8.2	0.0	2.0	0.0	3.0	0.5	23.0	2.1	23.7	0.0	1.7	0.0	0.7
	tert-butanol	tert-butanol	75-65-0	82.4	81.4	0.0	0.9	0.0	2.1	0.0	0.0	0.3	3.8	0.0	2.0	0.2	3.3	0.0	0.7	0.0	0.3

Experimental validation

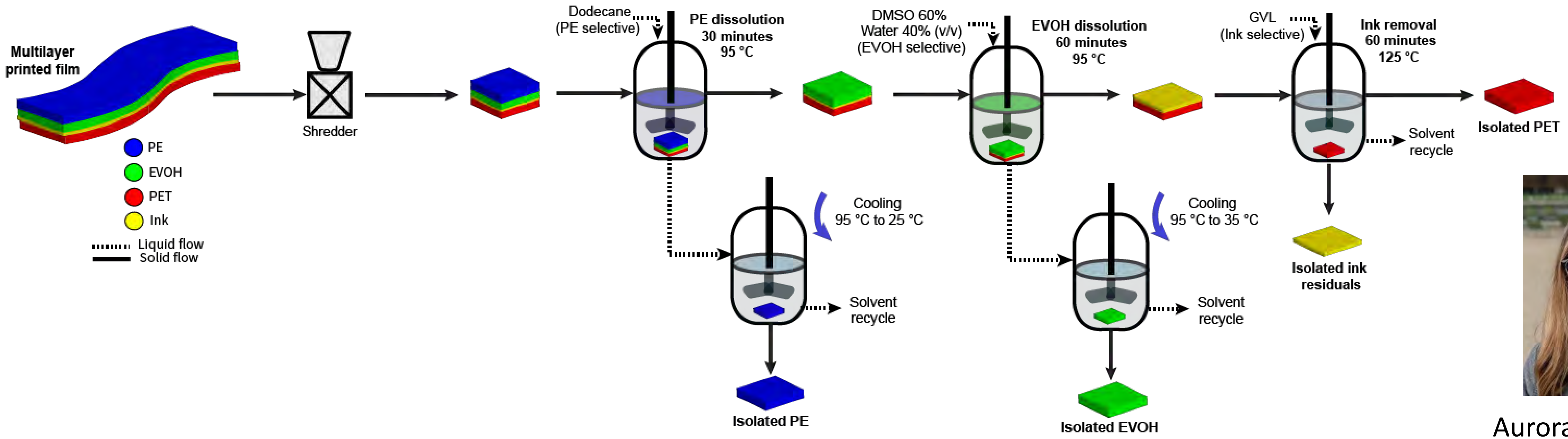


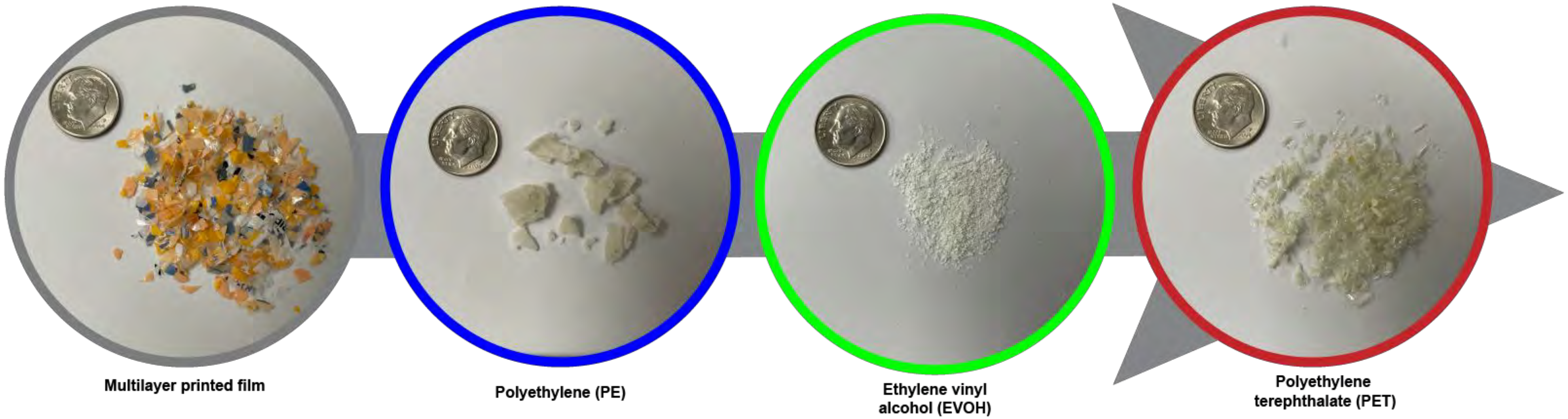


Pred. solubilities are in good agreement with expts at multiple temps!

P Zhou, KL Sanchez-Rivera, GW Huber, RC Van Lehn, *ChemSusChem* 2021; P Zhou, J Yu, KL Sanchez-Rivera, GW Huber, RC Van Lehn, *Green Chemistry*

Food Grade Resins from Reverse Laminated Printed Flexible Films



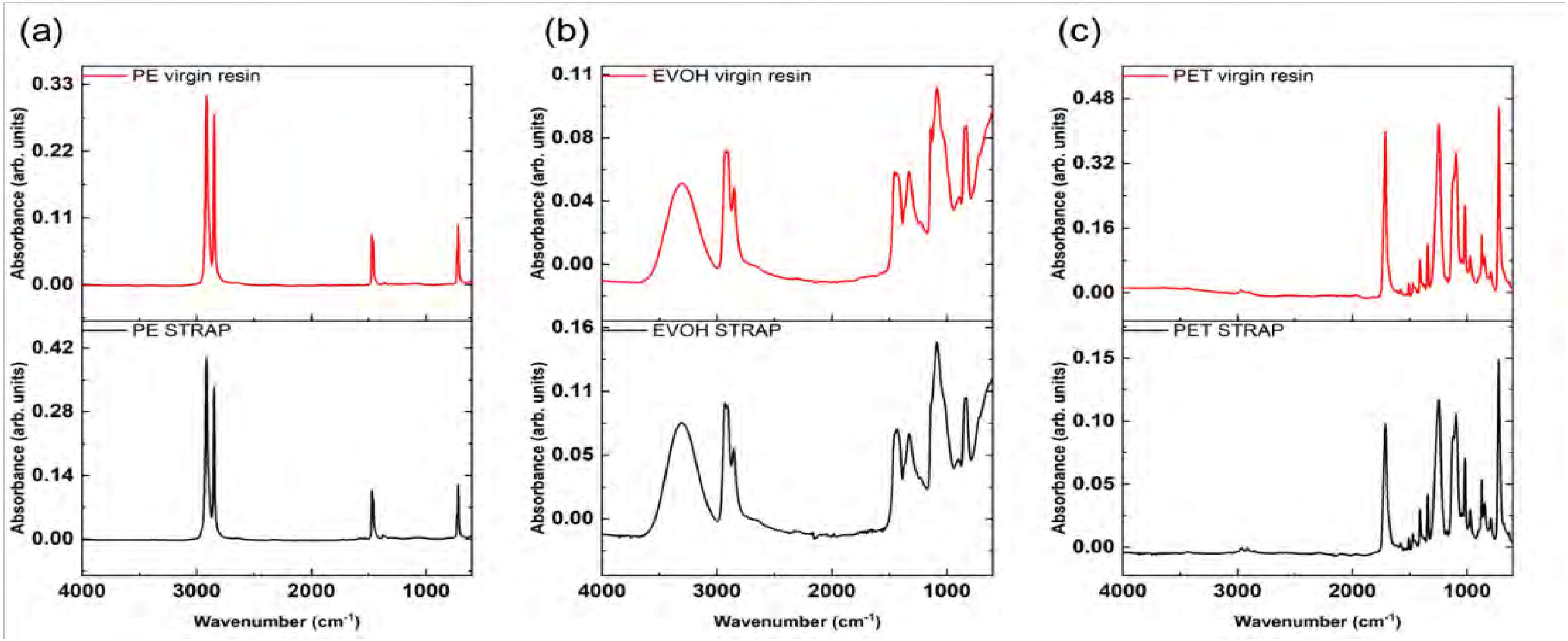


Aurora Munguia

Kevin Sánchez-Rivera

Kevin L Sánchez-Rivera, Aurora del Carmen Munguía-López, Panzheng Zhou, Victor S Cecon, Jiuling Yu, Kevin Nelson, Daniel Miller, Steve Grey, Zhuo Xu, Ezra Bar-Ziv, Keith L Vorst, Greg W Curtzwiler, Reid C Van Lehn, Victor M Zavala, George W Huber, Recycling of a post-industrial printed multilayer plastic film containing polyurethane inks by solvent-targeted recovery and precipitation, Resources, Conservation and Recycling, (2023) 197, 107086.

Polymer Characterization



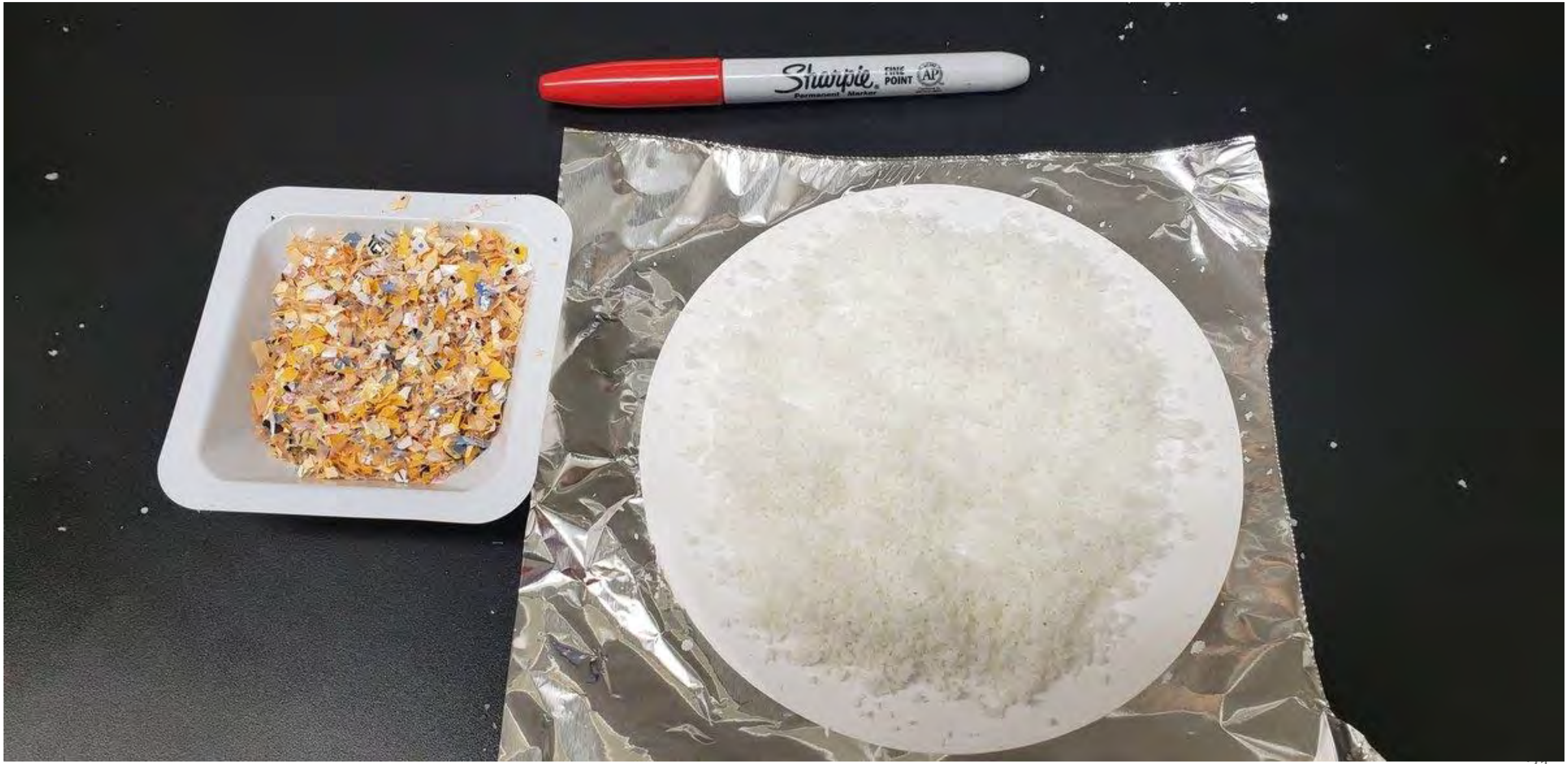
Thermal Properties do not Change During STRAP

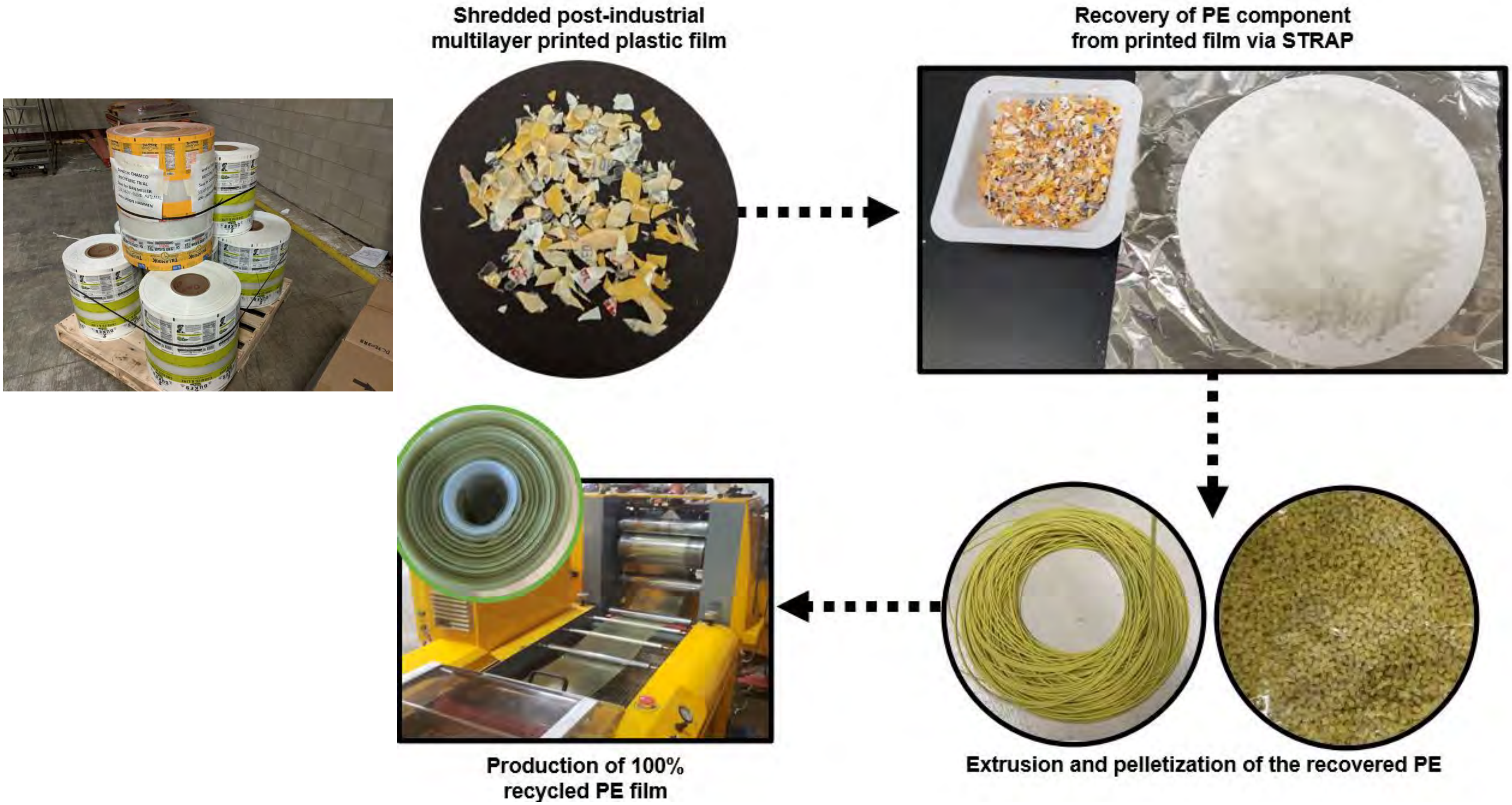
Thermal and molecular parameters for virgin resins and polymers recovered from the printed multilayer film by STRAP.					
Resin	**T_c (° C)**	**$T_{m,2}$ (° C)**	**ΔH_c (J/g)**	**$\Delta H_{m,2}$ (J/g)**	**Crystallinity**
PE STRAP	**105.0**	**119.7**	**76.0**	**82.3**	**28.38%**
LDPE Virgin	**98.3**	**112.0**	**84.8**	**86.1**	**29.69%**
LLDPE Virgin 45G	**106.1**	**122.4**	**83.3**	**85.5**	**29.48%**
LLDPE Virgin 47N	**107.0**	**122.2**	**70.2**	**73.3**	**25.28%**
EVOH STRAP	**150.4**	**175.7**	**41.8**	**37.4**	**17.17%**
EVOH Virgin	**147.8**	**176.4**	**54.2**	**54.3**	**24.93%**
PET STRAP	**209.6**	**246.0**	**41.7**	**22.7**	**16.21%**
PET Virgin	**169.2**	**244.6**	**30.0**	**38.5**	**27.50%**

- Melt temperature ($T_{m,2}$) of recovered resins (printed film) were comparable to original
- Differences were some samples of PET & EVOH are due to residuals
- Additional ink/other-resin removal to ensure PET is free of any contaminants

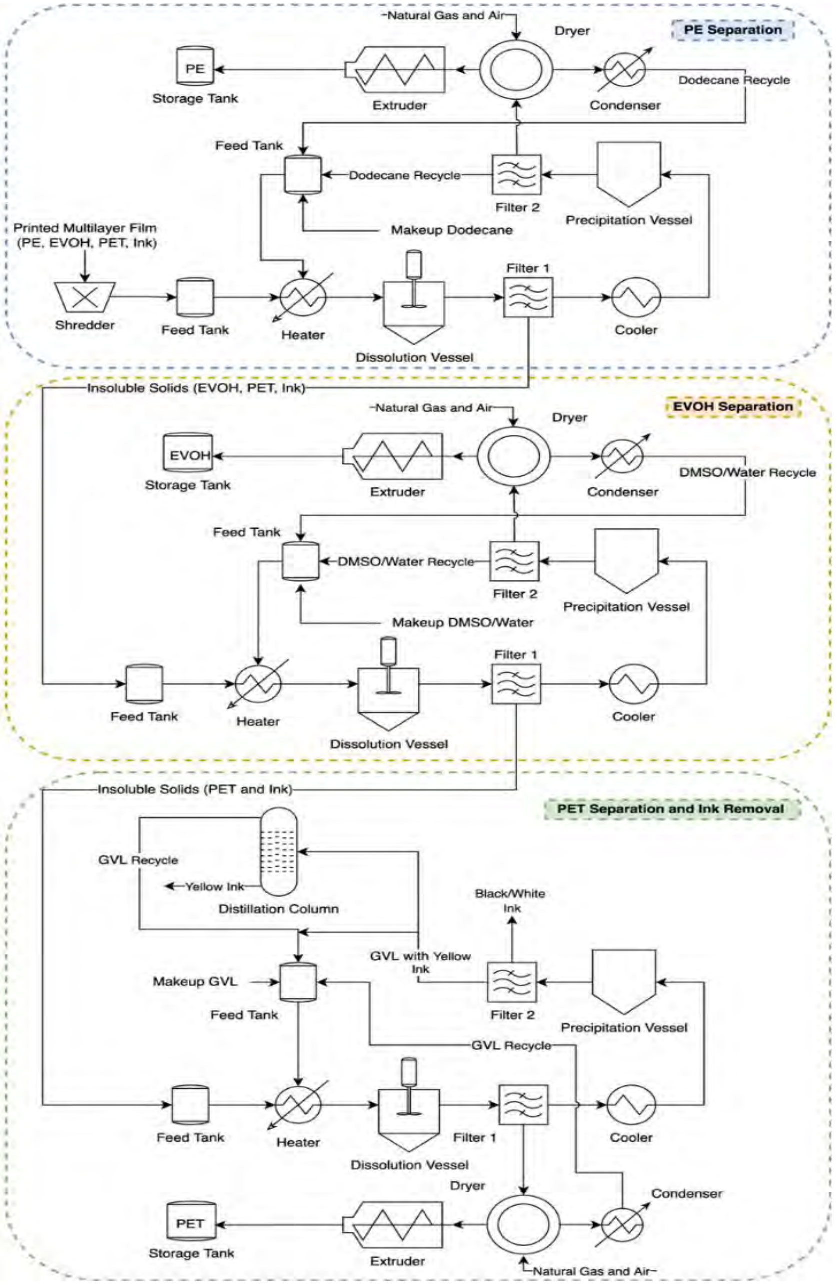
Cecon, V., Da Silva, P.F., Vorst, K., Curtzwiler, G.W., The effect of post-consumer recycled polyethylene (PCRPE) on the properties of polyethylene blends of different densities. Polymer Deg. and Stability, 190, 2021.

Printed Flexible Film to High Quality PE

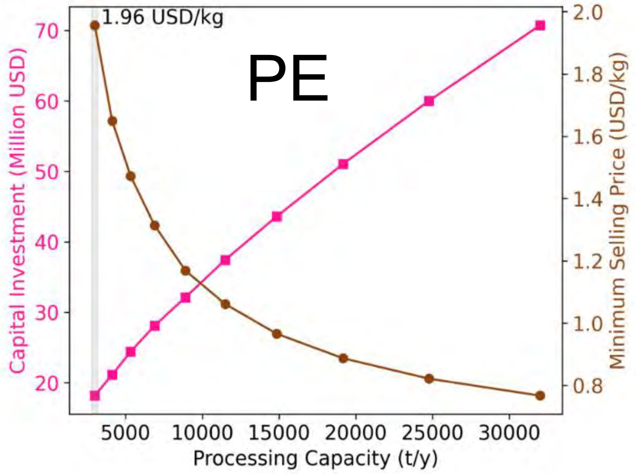



Shredded post-industrial
multilayer printed plastic film
Recovery of PE component
from printed film via STRAP
Extrusion and pelletization of the recovered PE
Production of 100%
recycled PE film

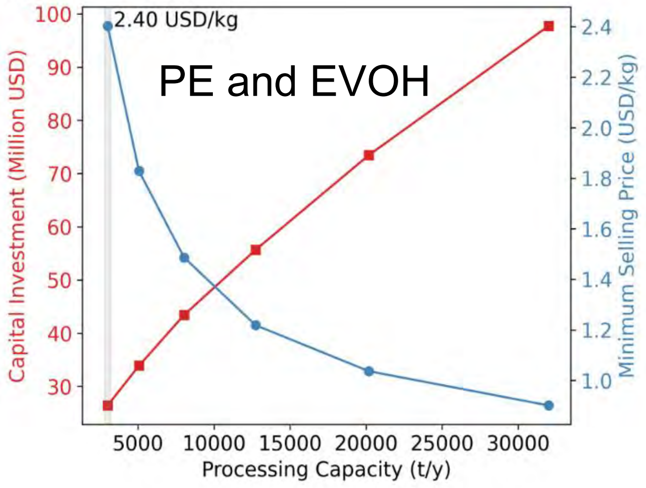
Process model from laboratory Data for STRAP films



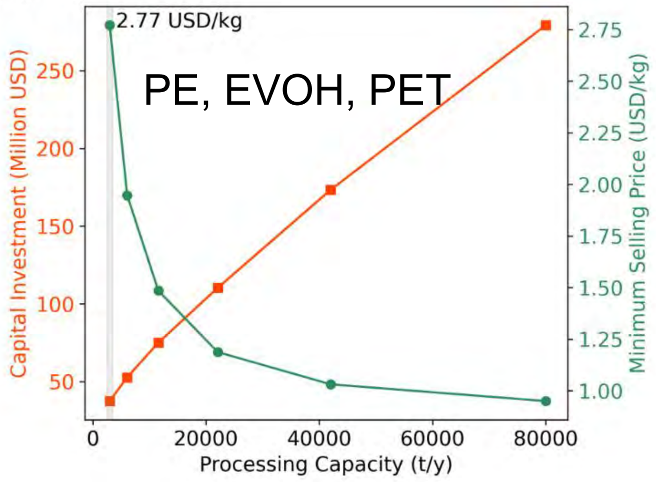
(a)

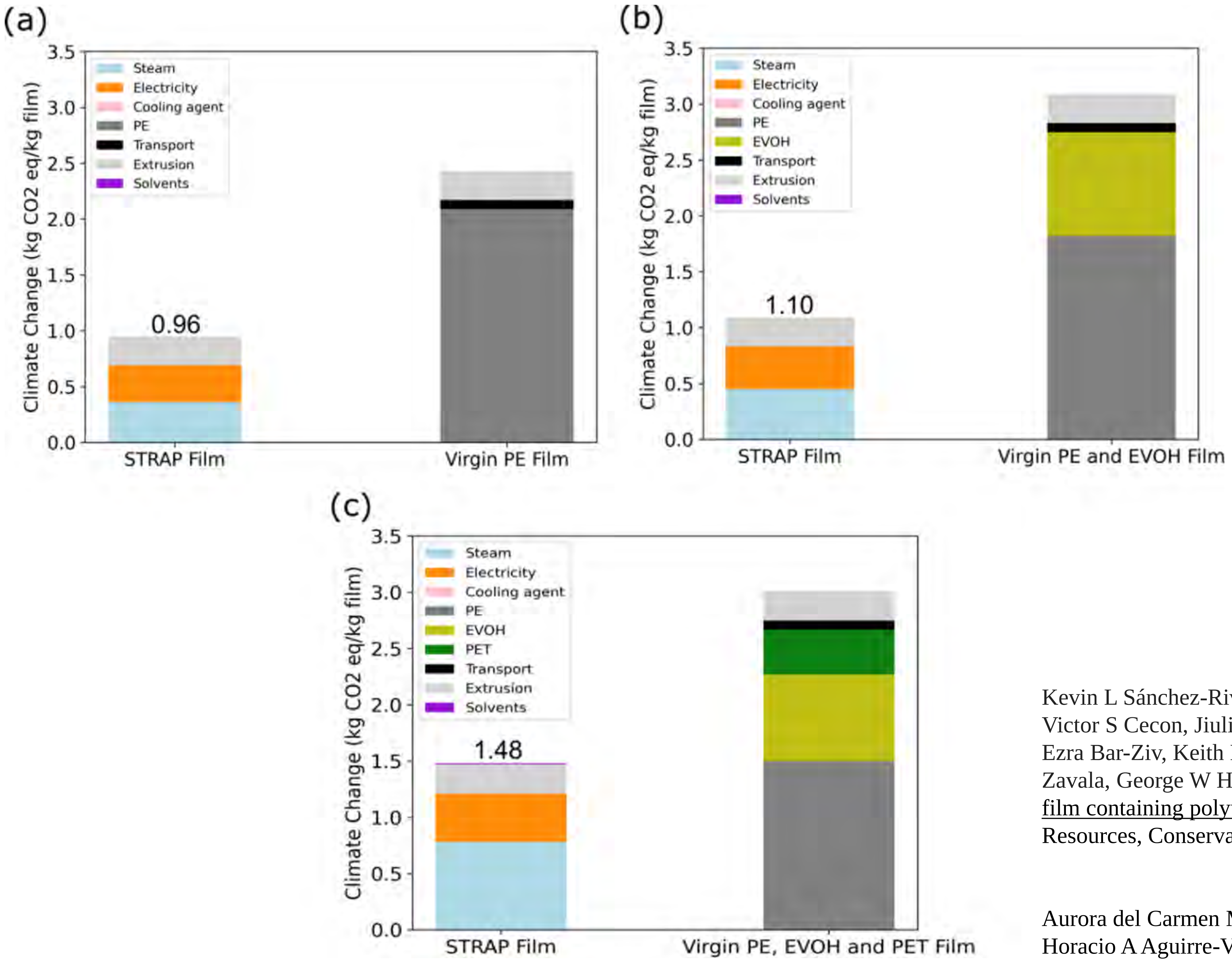


(b)



(c)





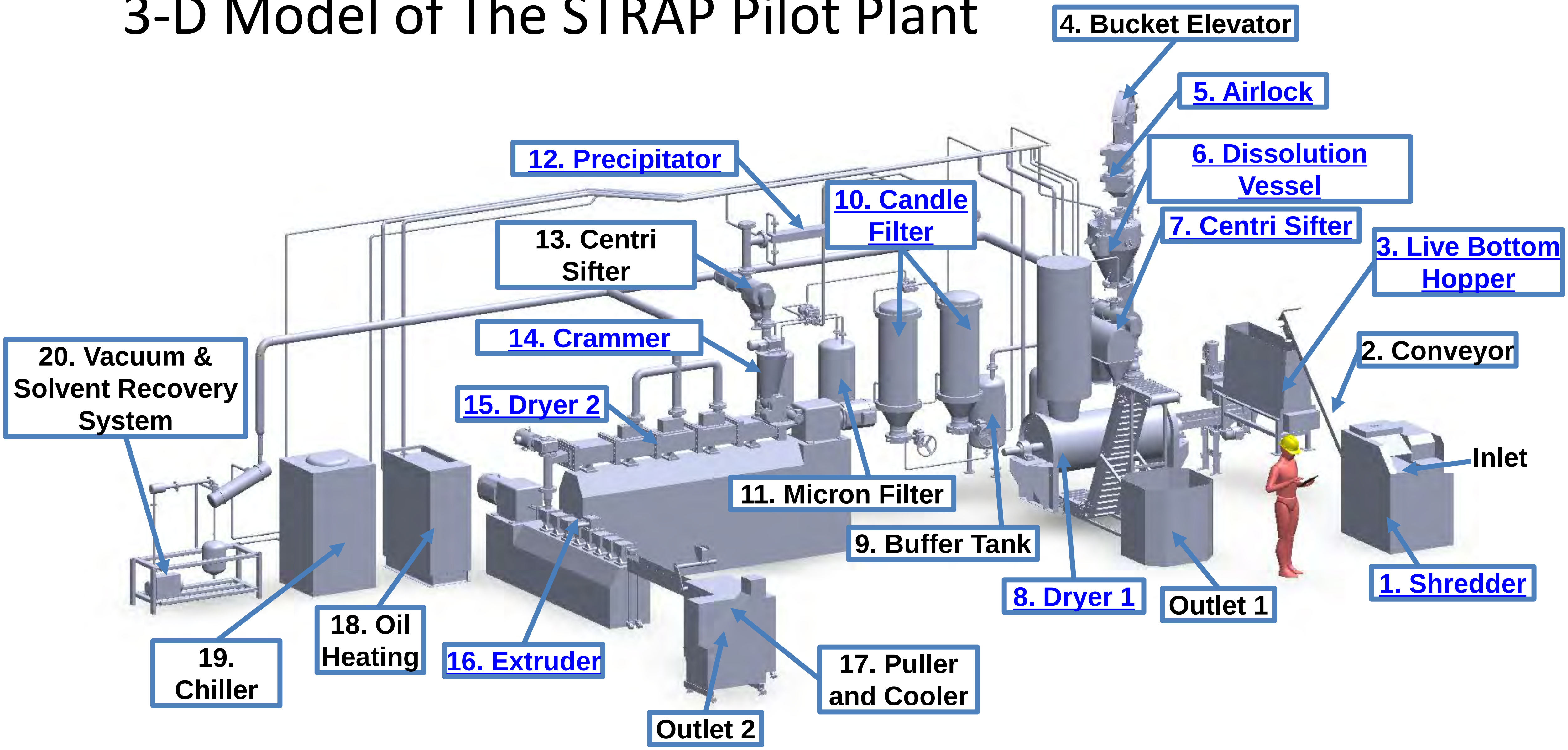
STRAP has 60-70% lower greenhouse gas emissions than the Virgin Resins production process.

Aurora Munguia

Kevin L Sánchez-Rivera, Aurora del Carmen Munguía-López, Panzheng Zhou, Victor S Cecon, Jiuling Yu, Kevin Nelson, Daniel Miller, Steve Grey, Zhuo Xu, Ezra Bar-Ziv, Keith L Vorst, Greg W Curtzwiler, Reid C Van Lehn, Victor M Zavala, George W Huber, Recycling of a post-industrial printed multilayer plastic film containing polyurethane inks by solvent-targeted recovery and precipitation, Resources, Conservation and Recycling, (2023) 197, 107086.

Aurora del Carmen Munguía-López, Dilara Göreke, Kevin L Sánchez-Rivera, Horacio A Aguirre-Villegas, Styliani Avraamidou, George W Huber, Victor M Zavala, Quantifying the Environmental Benefits of a Solvent-Based Separation Process for Multilayer Plastic Films, Green Chemistry, (2023) 25, 4, 1611-1625

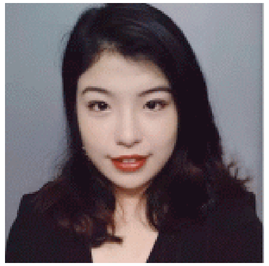
3-D Model of The STRAP Pilot Plant



STRAP is moving towards commercialization

- Successfully demonstrated STRAP technology with a range of post-industrial and post-consumer plastic materials
- Generated laboratory scale high quality resins for food packaging applications
- Designed (and are building) a 25 kg/hr STRAP system at Michigan Tech University (with Ezra Bar-Ziv)
- Identified location to build first commercial STRAP system at Convergen Energy in Green Bay, WI
- Looking for partners who want to help us commercialize or implement STRAP technology

Pyrolysis/Liquefaction of Plastics produces a Plastic Oil



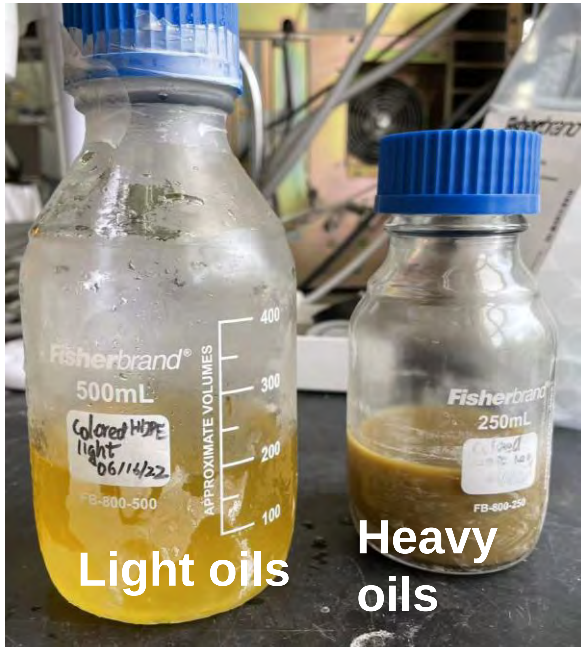
Jiayang Wu

Mixing Colored HDPE (PCR)

→

Fluidized bed reactor
at University of Wisconsin-Madison

→



Distilled Plastic oil at 165 ºC
Light oil: 50 wt%
Heavy oil: 18 wt%

Pyrolysis is not burning plastics

Plastic combustion products are CO_2, H_2O, and heat

Combustion = Burning = Incineration

Plastic Pyrolysis products are an oil and light gases

Pyrolysis or thermal depolymerization (also liquefaction)

1. Pyrolysis of plastic has a significantly lower carbon footprint compared to incineration
   GHG emission of pyrolyzing one tonne of plastic waste is 500-1000kg CO_2e.[a]
   GHG emission of combusting one tonne of plastic waste is 2200-3000kg/CO_2e.[b]
2. Pyrolysis enables a circular economy for plastic

a. RTI International. (2012). Environmental and Economic Analysis of Emerging Plastics Conversion Technologies.
b. Rudolph, N., Kiesel, R., & Aumnate, C. (2020). Understanding plastics recycling: Economic, ecological, and technical aspects of plastic waste handling.

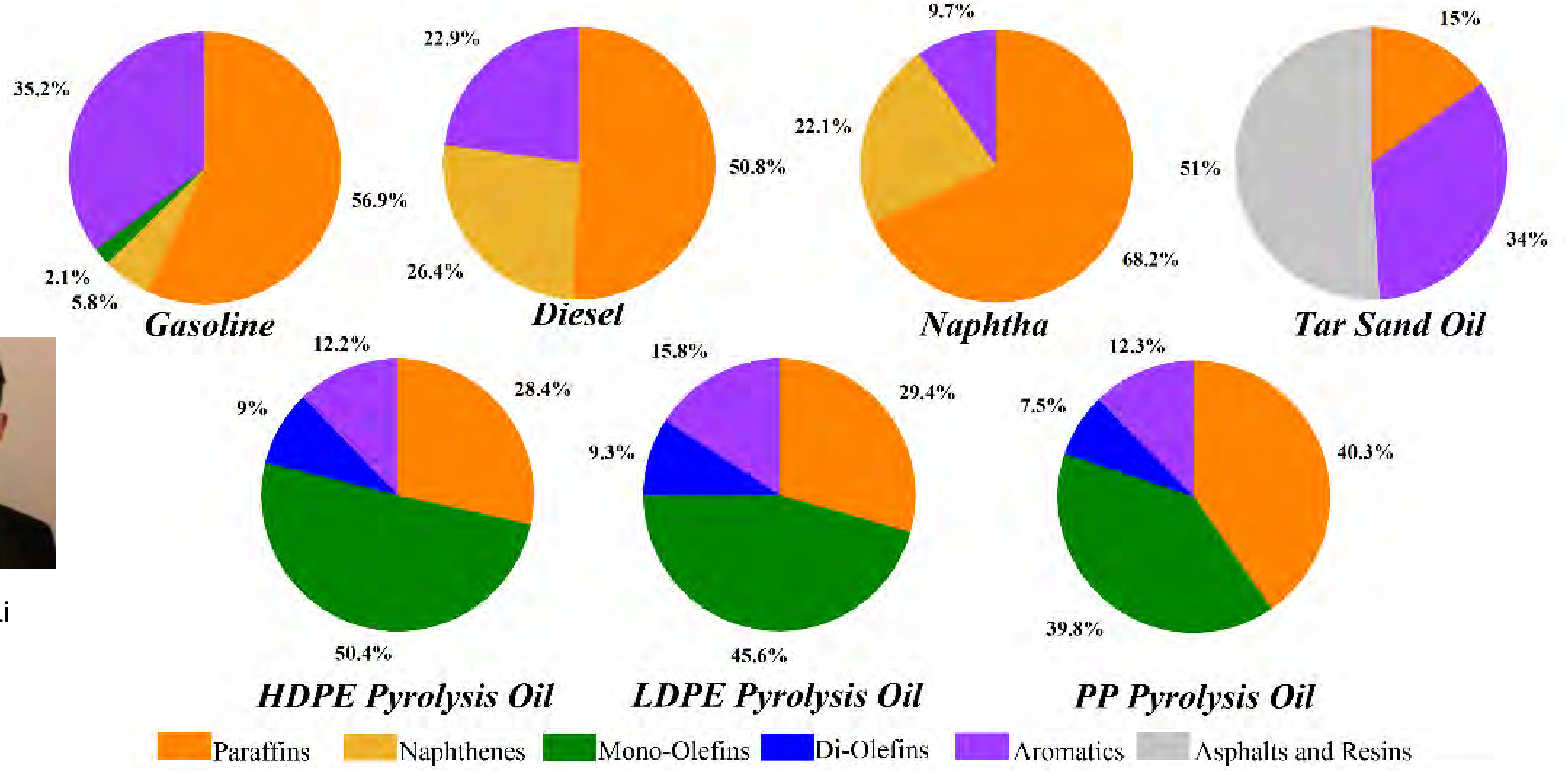
8 Companies have made Announcement on Plastic Pyrolysis/thermal depolymerization Commercial Facilities

Company name	Plant location	Scale (kton/year)	Status	Reactor type	Feedstocks	Product	Collaborators
Agilyx	Tigard	3	Operational since 2018	Stirred tank reactor	PS	Styrene monomer	Toyo, ExxonMobil, Braskem, AmSty, Lucite, and NextChem
QuantaFuel	Skive	20	Operational since 2017	Fluidized bed reactor	HDPE, LDPE, PP, PS, and PET	Liquid oil, non-condensable gas, and carbon rich ash	BASF, VITOL, and VITTI
	Amsterdam	100	2023-2024				
	Sunderland	100	2024				
Pryme	Rotterdam	40-60	Plan to start up in 2022	Stirred tank reactor	PS, PE, and PP	Kerosine, naphtha, and wax	Shell
Brightmark	Asheley	100	Not reported	Auger Rector	PET, HDPE, PVC, LDPE, PP, and PS	Ultra-low sulfur diesel, naphtha and wax	BP, Chevron, Clean fuel Partners, and Northeast Indiana Solid Waste Management District
Plastic Energy	Seville	5	Operational since 2017	Stirred tank reactor	LDPE, HDPE, PP, PS	Diesel and Naphtha	SABIC, ExxonMobil, and Freepoint Eco-Systems
	Le Havre	25	Design phase planned to start up in 2023				
	Almeria	Not reported	Operational since 2014				
Freepoint Eco-Systems	Houston	33	Start up in Mid-2024	Not reported	LDPE, HDPE, PP, PS	Synthetic oil	Plastic Energy, and TotalEnergies
	Obetz	90	Start up in 2023				
Shell	Pulau Bukom	50	2022	Not reported	Not reported	Not reported	Pryme
ExxonMobil	Baytown	30	Start up in End 2022	Fluidized Bed Reactor	Not reported	Not reported	Cyclyx, Agilyx, and Plastic Energy

H Li, HA Aguirre-Villegas, RD Allen, X Bai, CH Benson, GT Beckham, SL Bradshaw, JL Brown, RC Brown, MA Sanchez Castillo, VS Cecon, JB Curley, GW Curtzwiler, S Dong, S Gaddameedi, JE Garcia, I Hermans, MSKim, J Ma, LO Mark, M Mavrikakis, OO Olafasakin, TA Osswald, KG Papanikolaou, H Radhakrishnan, KL Sánchez-Rivera, KN Tumu, RC Van Lehn, KL Vorst, MM Wright, J Wu, VMZavala, P Zhou, GW Huber, Expanding Plastics Recycling Technologies: Chemical Aspects, Technology Status and Challenges, Green Chemistry, (2022) 4/18

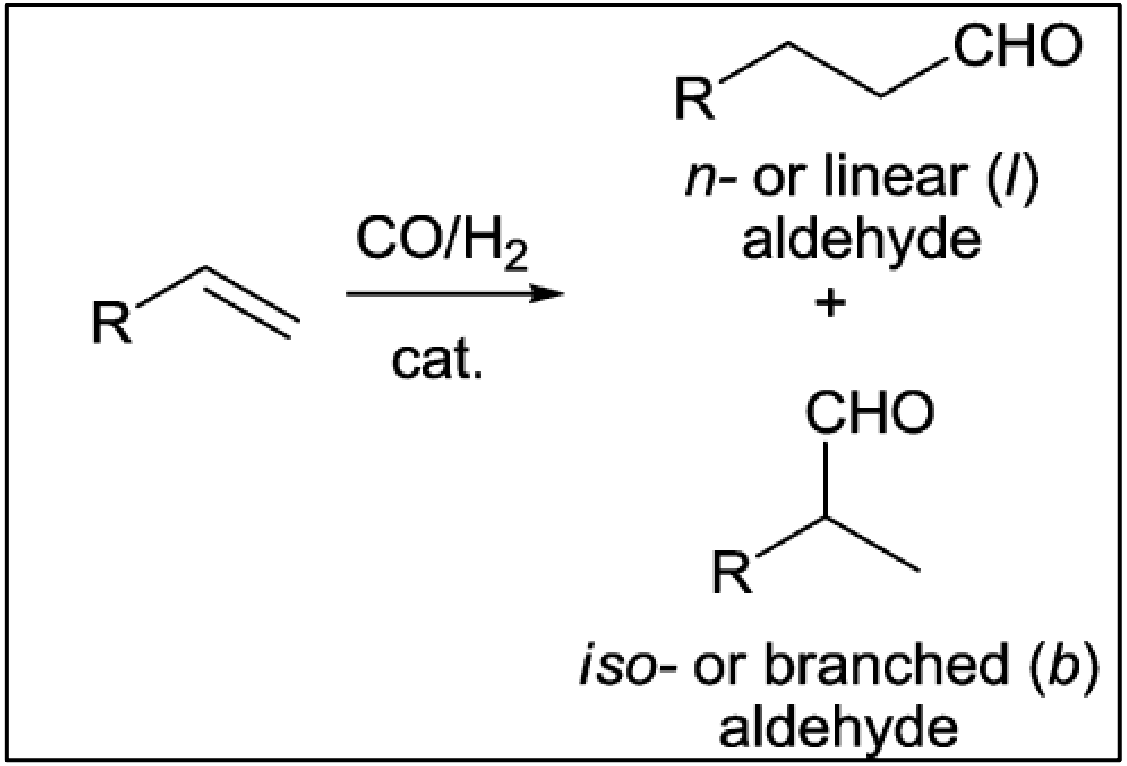
Plastic Pyrolysis Oil Contain High Amount of Olefins

Dr Houqian Li



H. Li, J. Wu, Z. Jiang, J. Ma, VM Zavala, CR Landis, M Mavrikakis, GW Huber, (2023). Hydroformylation of pyrolysis oils to aldehydes and alcohols from polyolefin waste. Science, 381(6658), 660-666.

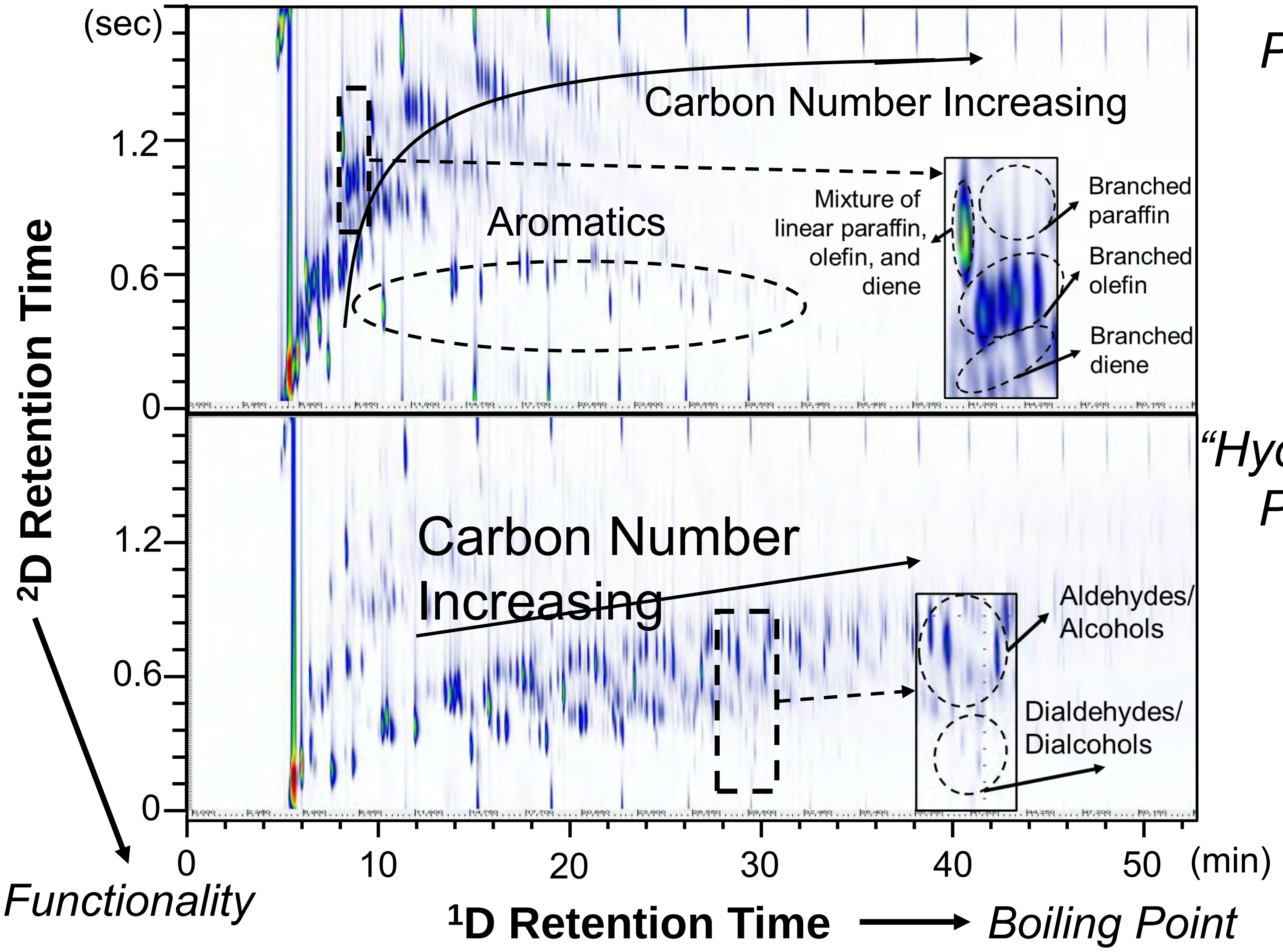
An array of chemicals can be produced from aldehydes by Hydroformylation



- ***Does the chemistry work for waste plastic pyrolysis oil?***
- ***High-purity products?***

Franke, Robert, et al. Chemical Reviews 112.11 (2012): 5675-5732.
Liu, Dupeng, Bala Subramaniam et al. React. Chem. & Eng. 3.3 (2018): 344-352.

Down shifting of the blobs suggests the formation of aldehydes



Pyrolysis Oil

C: 86% H: 14%

CHNOS Analysis

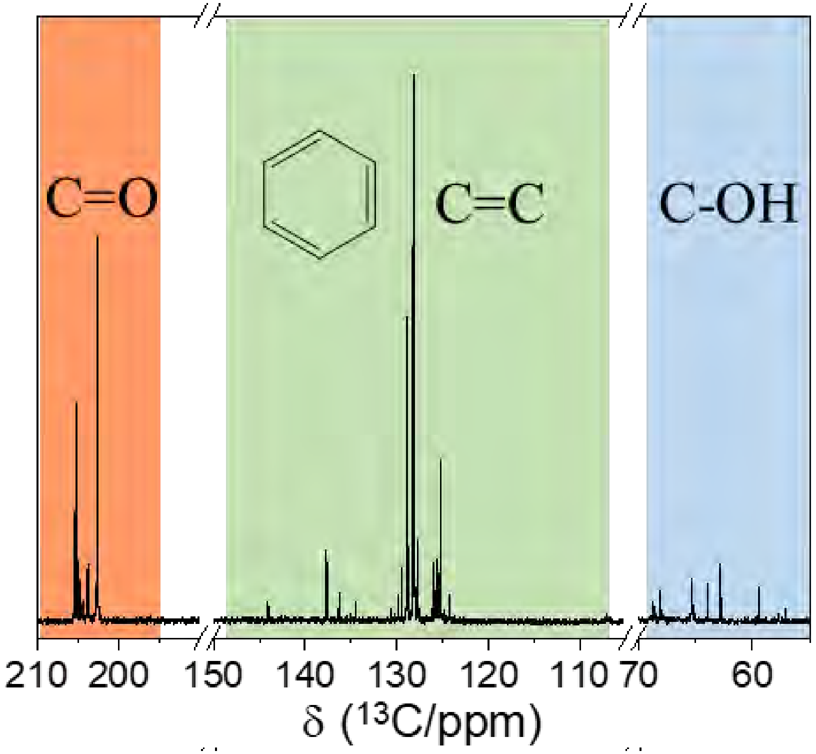
"Hydroformylated" Pyrolysis Oil

C:75%, H:11%, O:14%

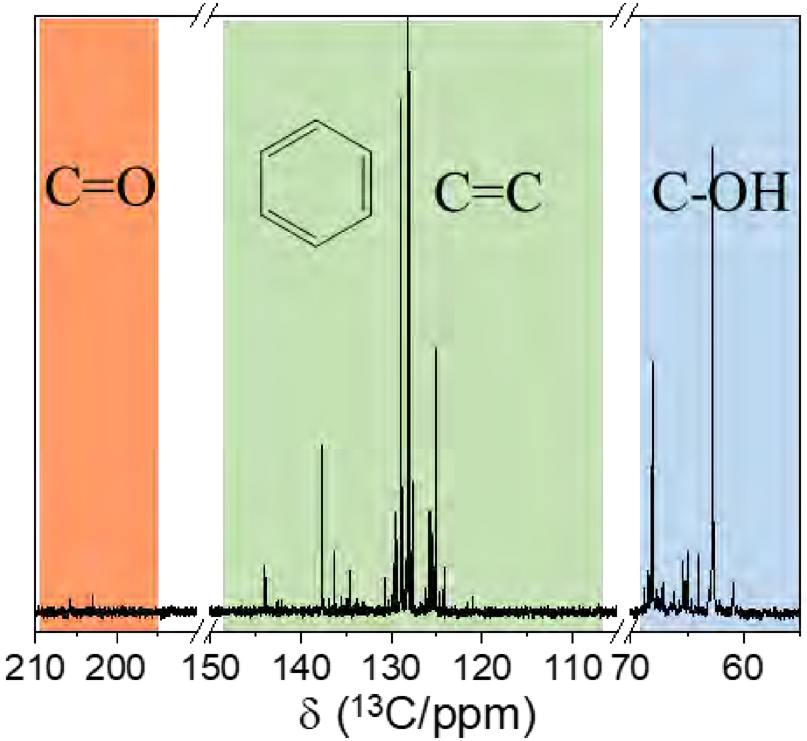
CHNOS Analysis

H. Li, J. Wu, Z. Jiang, J. Ma, VM Zavala, CR Landis, M Mavrikakis, GW Huber, (2023). Hydroformylation of pyrolysis oils to aldehydes and alcohols from polyolefin waste. Science, 381(6658), 660-666.

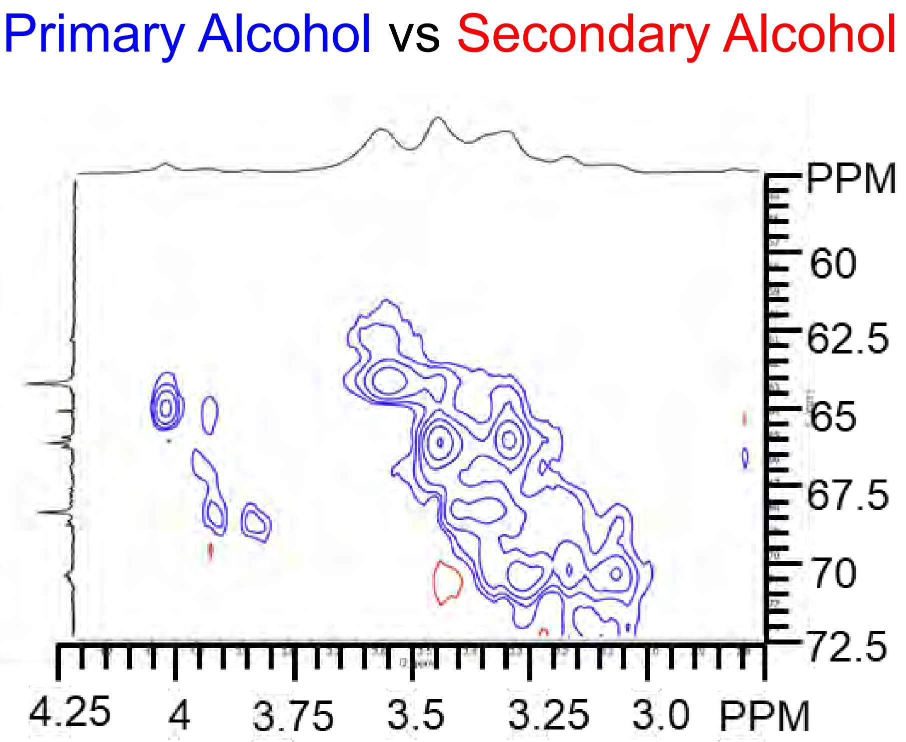
High conversion (>90%) of aldehydes was achieved



"Hydroformylated Oil"



Hydrogenated Oil

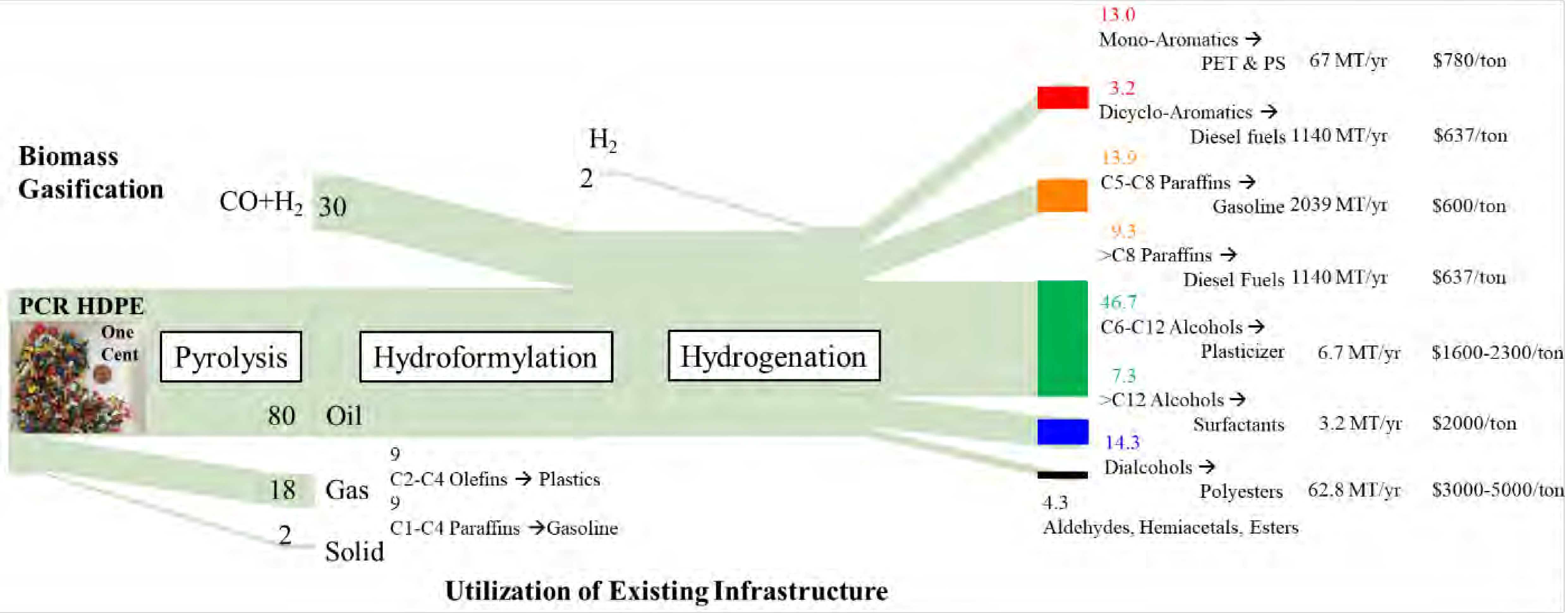


Hydrogenated Oil

Hydrogenation: 100 ° C, H_2=78 Bar, 20wt%Ni/SiO_2, WHSV=1 hr^{-1},
TOS=5 h, Co catalyst Removal, Continuous Flow Reactor

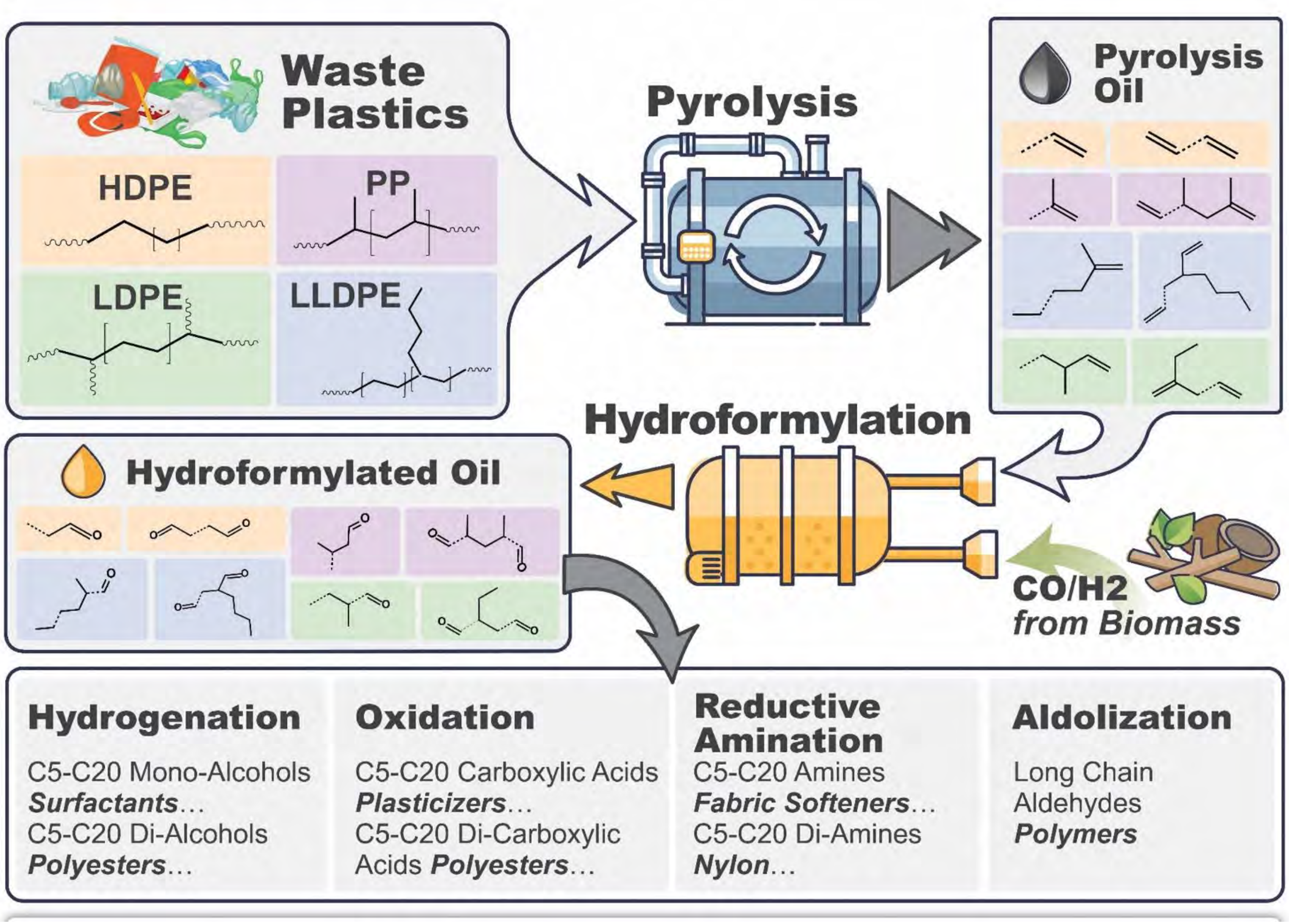
H. Li, J. Wu, Z. Jiang, J. Ma, VM Zavala, CR Landis, M Mavrikakis, GW Huber, (2023). Hydroformylation of pyrolysis oils to aldehydes and alcohols from polyolefin waste. Science, 381(6658), 660-666.

We can apply hydroformylation chemistry to upgrade waste pyrolysis oils



H. Li, J. Wu, Z. Jiang, J. Ma, VM Zavala, CR Landis, M Mavrikakis, GW Huber, (2023). Hydroformylation of pyrolysis oils to aldehydes and alcohols from polyolefin waste. Science, 381(6658), 660-666.

Combination of pyrolysis and hydroformylation is a ***platform technology*** to recycle/upcycle waste plastics, thus enables ***carbon circularity***



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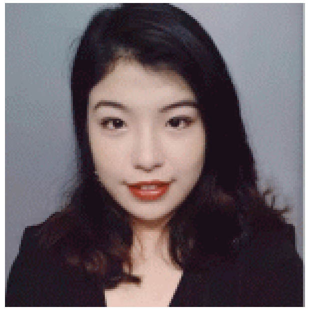
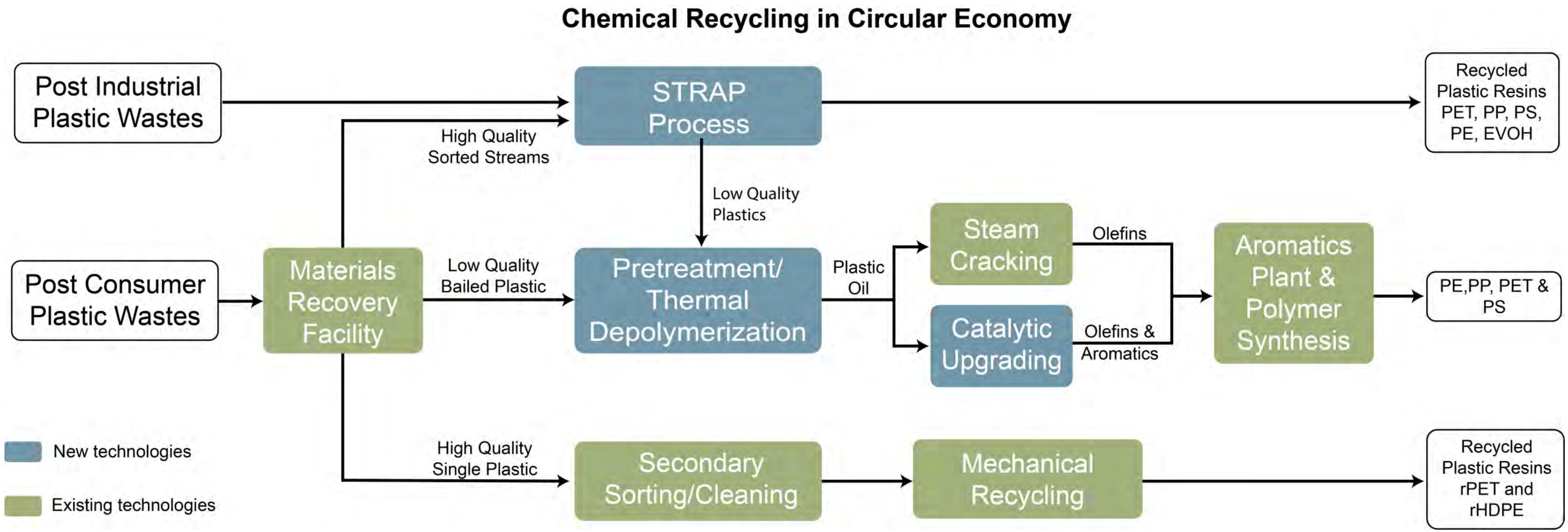


Jiayang Wu

Chemical Upcycling of Waste Plastics

Center for Chemical Upcycling of Waste Plastics



The objective of CUWP is to develop the scientific and engineering principles that will enable the circular upcycling of plastic wastes into virgin plastic resins using chemical technology.

- Start Date: April 2021

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UNIVERSITY OF WISCONSIN–MADISON