Innovation Day Posters

September 12, 2023

Online Poster Session, 9:00 AM – 10:00 AM

In-Person Poster Session, 10:15 AM – 11:15 AM

Innovation Day 2023 features 18 posters. The themes of this year's event explore sustainability with particular focus on plastics recycling, life cycle analysis, and biomaterials and bioprocessing.

The posters in this document are organized alphabetically by poster presenter last name. For full poster citations, please contact the poster presenter(s) during Innovation Day 2023. To review poster abstracts, refer to the *Poster Session Guide* on the Innovation Day homepage.

Poster Listing in order of appearance:

1. Mohammed Abutaqiya, An Advanced Equation of State for Predictive Modeling of Molecules with Complex Energy Scales
2. Joseph Accardo, Effects of dye formulation on defect detection in waterborne barrier coated papers
3. Ashley Childress, The Power of Experimental Design in Innovation
4. Brian Edwards, Rapid Degradation of Cellulose Diacetate Materials in the Coastal Ocean
5. Erica Frankel, Towards More Sustainable Architectural Coatings: Synergistic Design of Biobased Binders for Improving the Carbon Footprint of Premium Architectural Paints
6. Adam Gross, Advanced Recycling of Polyolefins
7. Vince Herrera, From Ideas to Action: DuPont's Journey in Harnessing the Power of Generative AI
8. Natalie Kadlubowski, Vespel Enables Longer Service Life and Enhances Performance in Hydrogen Applications
9. Corey Kaminsky, Oxidative Stability of Amine-based Sorbents for CO2 Capture
10. Mu Sung (Matt) Kweon, Doing More with Less through Lightweighting: Foaming Capability of ExxonMobil High-Melt-Strength Polypropylene
11. Manjiri Moharir, Better Call SOL for FCC Operation
12. Michael Petr, Material Developments in Polyethylene Insulated Power Cables for More Sustainable Power Delivery
13. Agostino Pietrangelo, Morphology, Thermal Behavior, and Toughness of Poly(β-butyrolactone-co-β-valerolactone) Thermoplastics
14. Kara Radford, Let's Talk Trash: A Discussion on Plastic Circularity
15. Ali Slim, Next generation film design enhances process-to-application sustainability in packaging materials via innovative catalysis and formulation
16. Laurien Vandewalle, Application of Filtered Two-Fluid Models to Industrial-Scale Fluidized Beds
17. Megan Witzke, Advanced Materials for Renewable Diesel and Jet Production
18. Alex Zabula, Towards the Next Generation of General Purpose Rubbers: Polypentenamers

An Advanced Equation of State for Predictive Modeling of Molecules with Complex Energy Scales

Mohammed I. L. Abutaqiya and Bennett D. Marshall

ExxonMobil Technology and Engineering Company

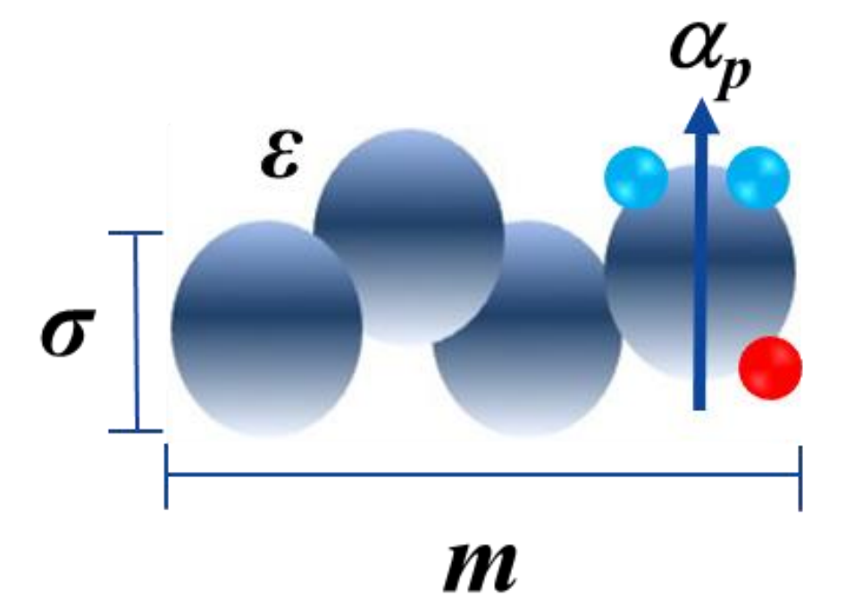
Introduction

- Significant efforts in the energy industry towards processing new feeds (e.g. renewable resources), manufacturing new specialty chemicals, and CCUS.
- Proper accounting for the thermodynamics is a key first step in **developing new technologies** or **optimizing existing technologies**.
- **Commonly used thermodynamic models:**
  - ☐ **Cubic EOS (SRK, PR)**: Empirical models. Not accurate for complex energy scales (polar, HB).
  - ☐ **Activity Coefficient Models**: Correlative and require an extensive amount of data.
- Predictive thermodynamic models that incorporate proper physics are key for success.

ExxonMobil PC-SAFT Model

EMPC-SAFT is an advanced and predictive equation of state that can handle complex **polar** and **associating** components

Molecular Description



Multiple Energy Scales

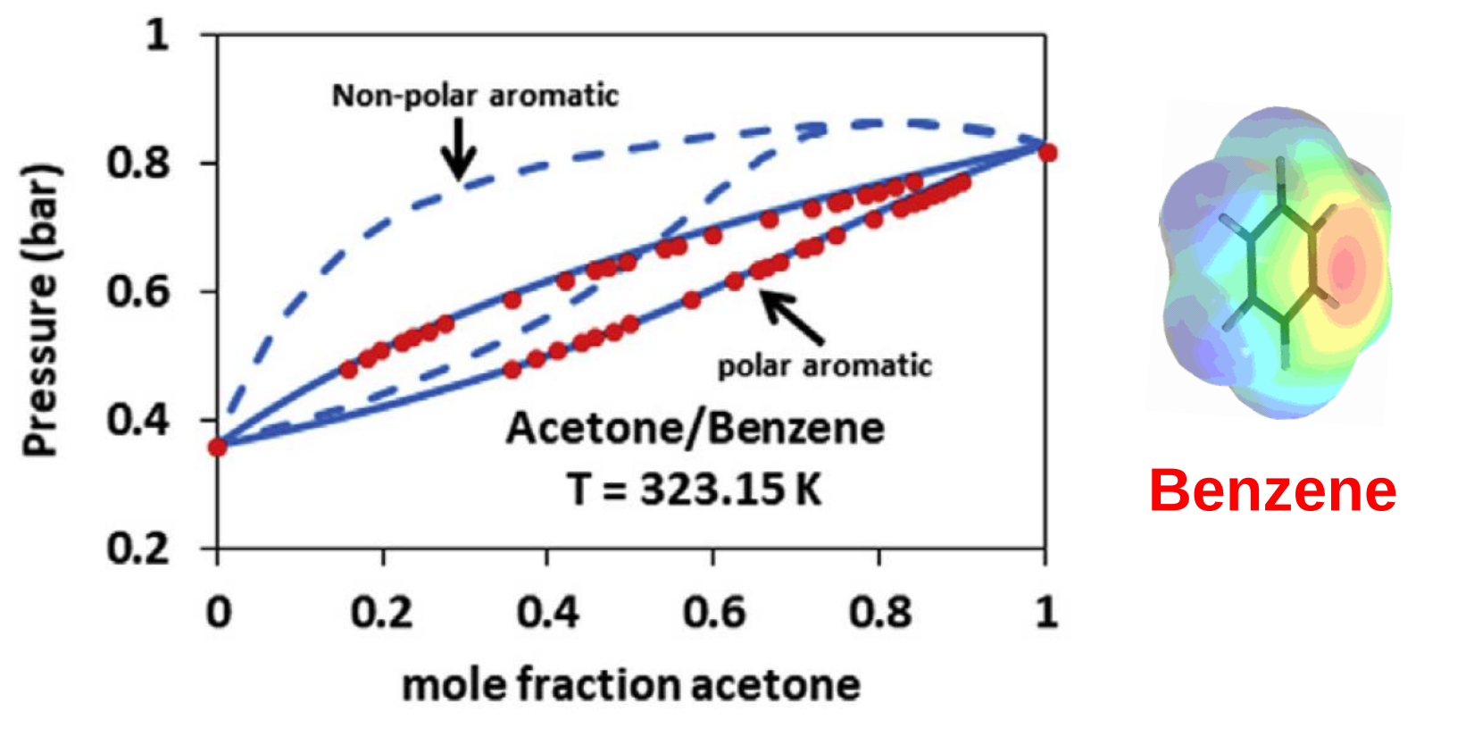
- London Dispersion (alkane-alkane)
- Dipole-Dipole (ketone-aldehyde)
- Dipole-Induced Dipole (alcohol-olefin)
- Hydrogen Bonding (alcohol-water)

$$a^{R} = a^{HC} + a^{Disp} + a^{Dipolar} + a^{Assoc}$$

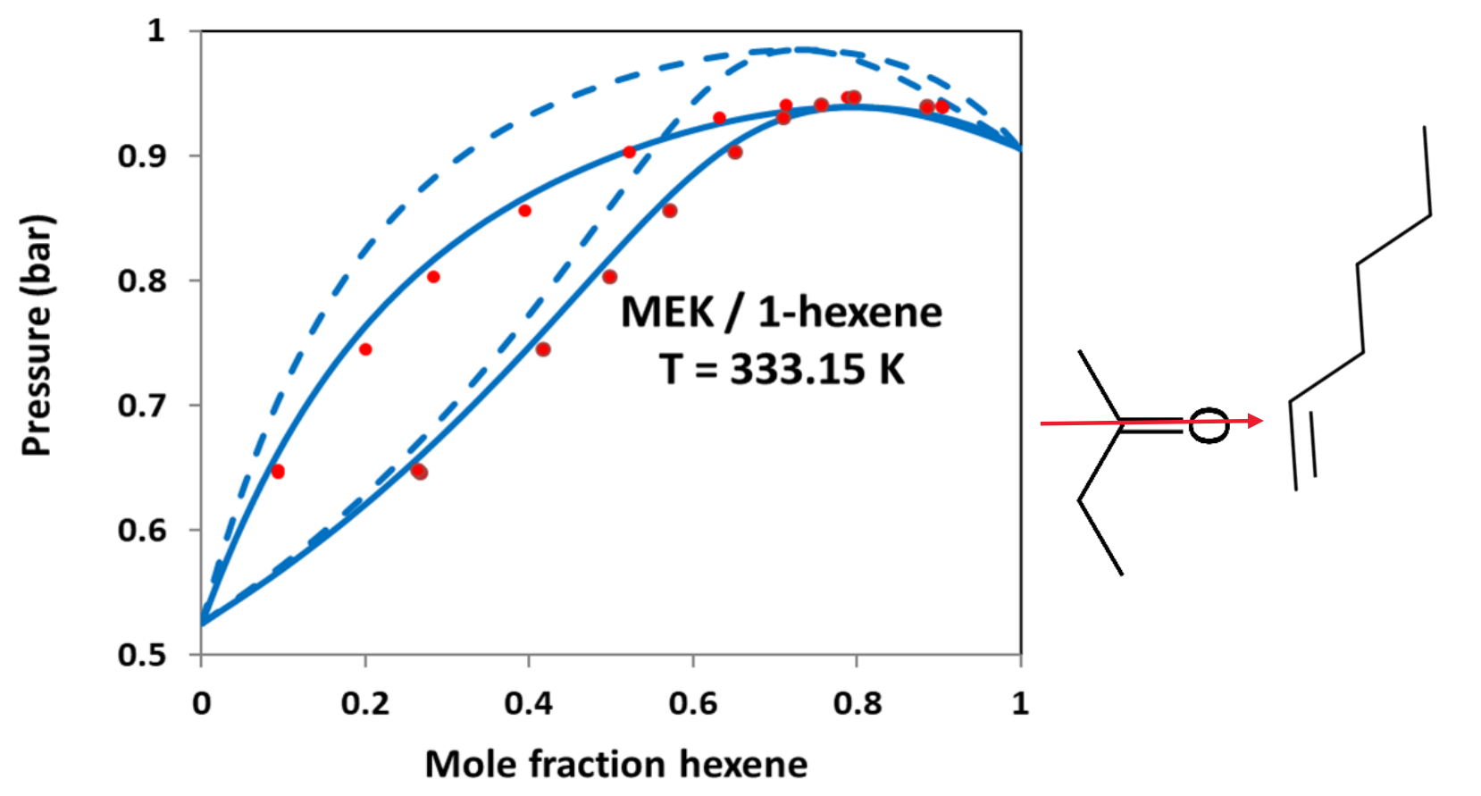
Hard Chain **Dispersion** **Dipolar** **Association (Hydrogen Bonding)**

Special Features

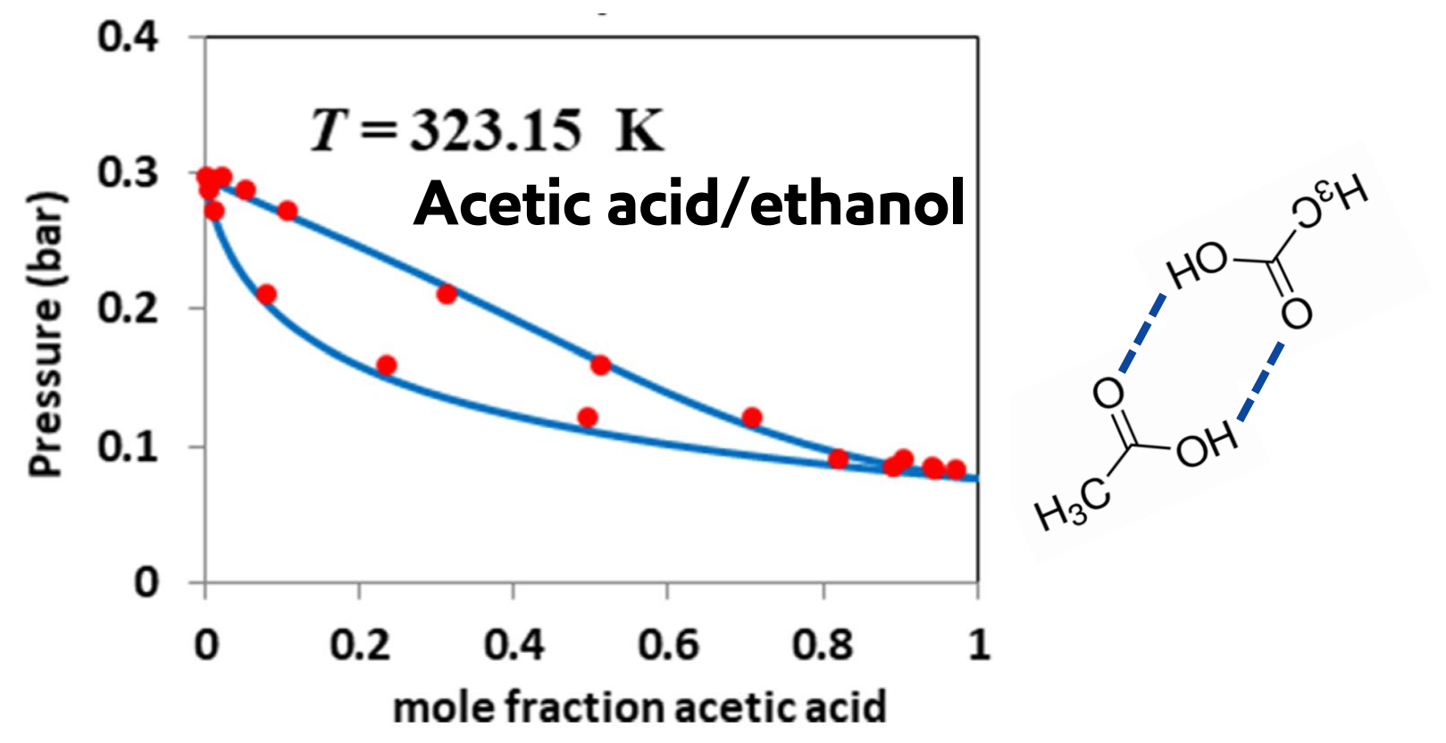
Mapping of π–π bonds in aromatics onto a dipolar free energy



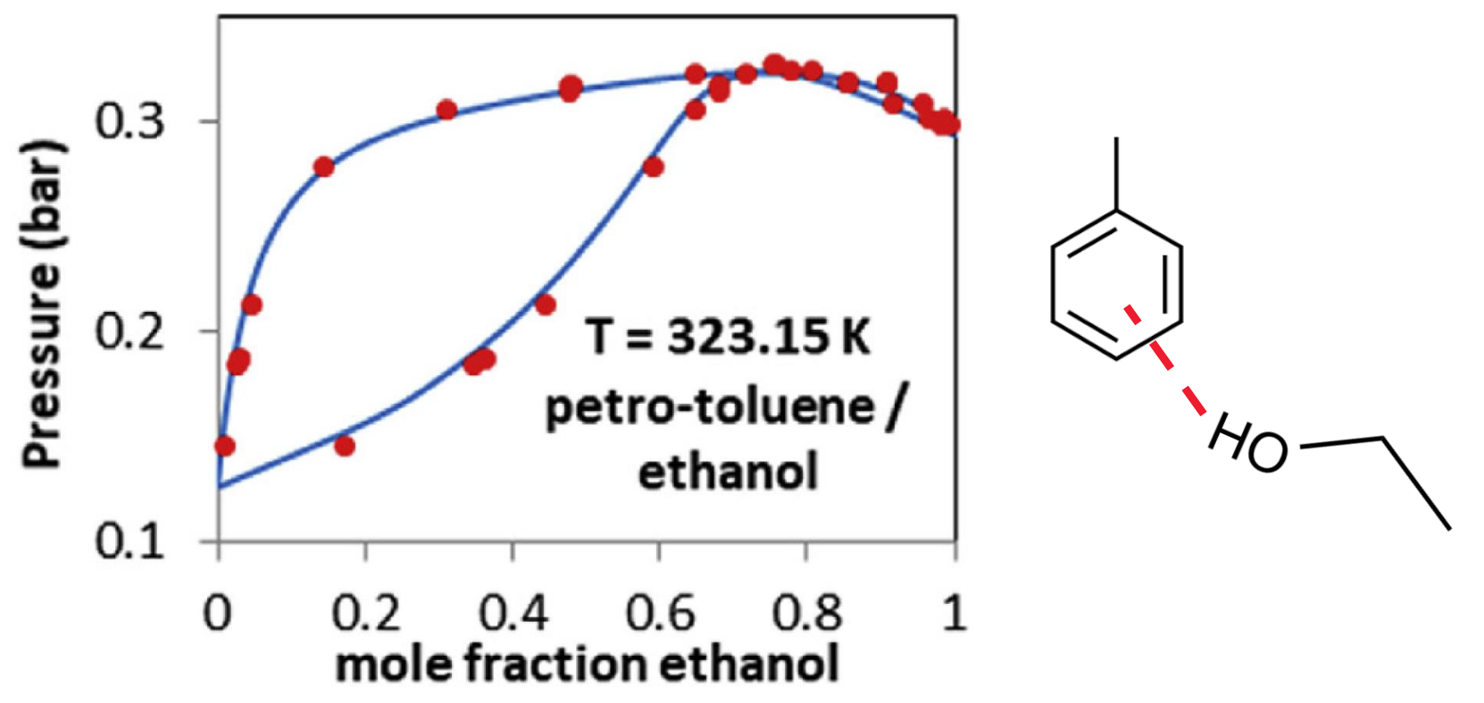
Phantom Dipole representation for induction (polarizability) effects of olefins



Incorporation of Double Bonding theory in Carboxylic Acids

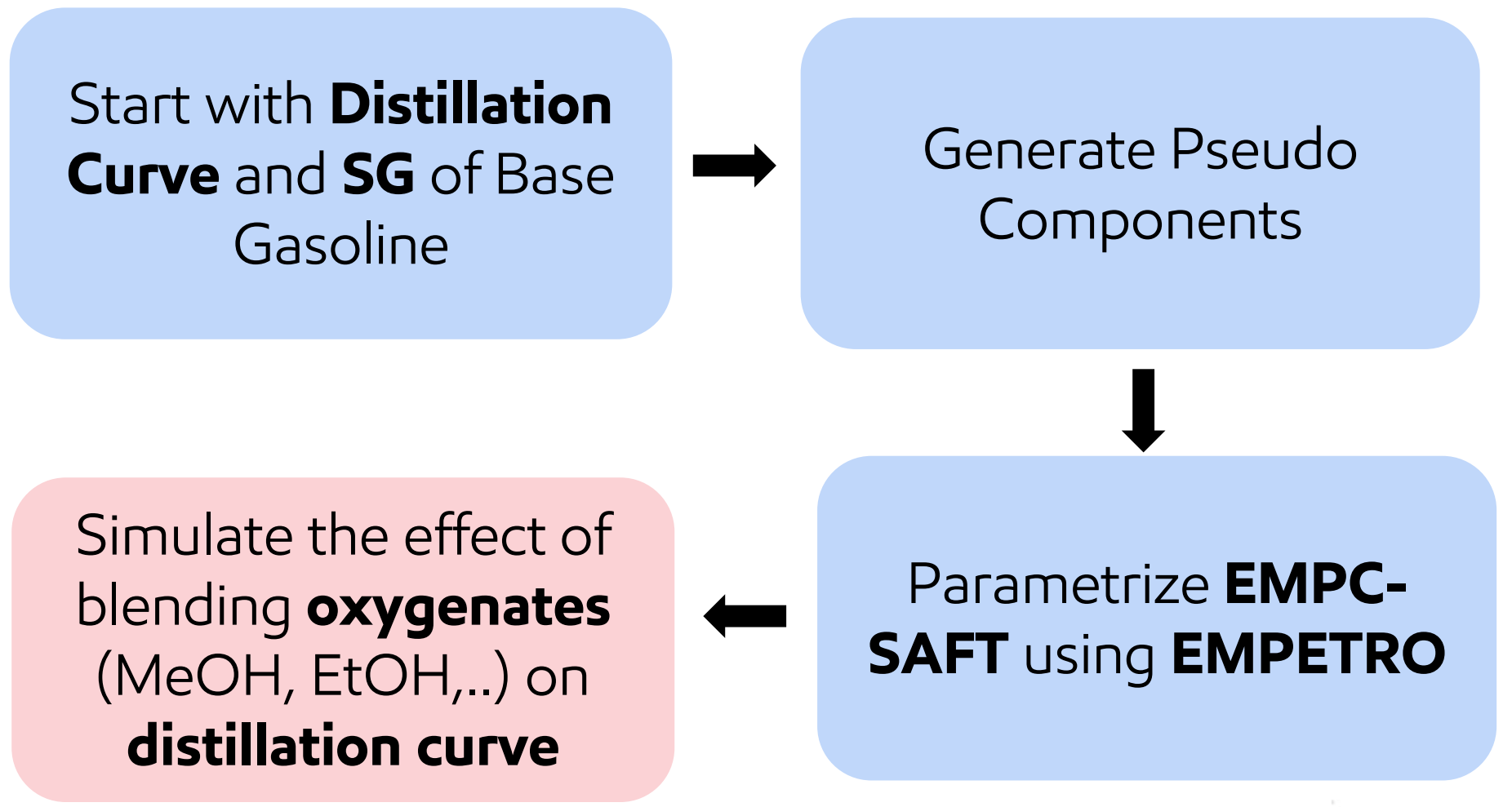


General treatment of pseudo-molecules from T_b, SG, MW using EMPETRO



Industrial Applications

Gasoline/Alcohols Blending to Reduce Harmful Emissions

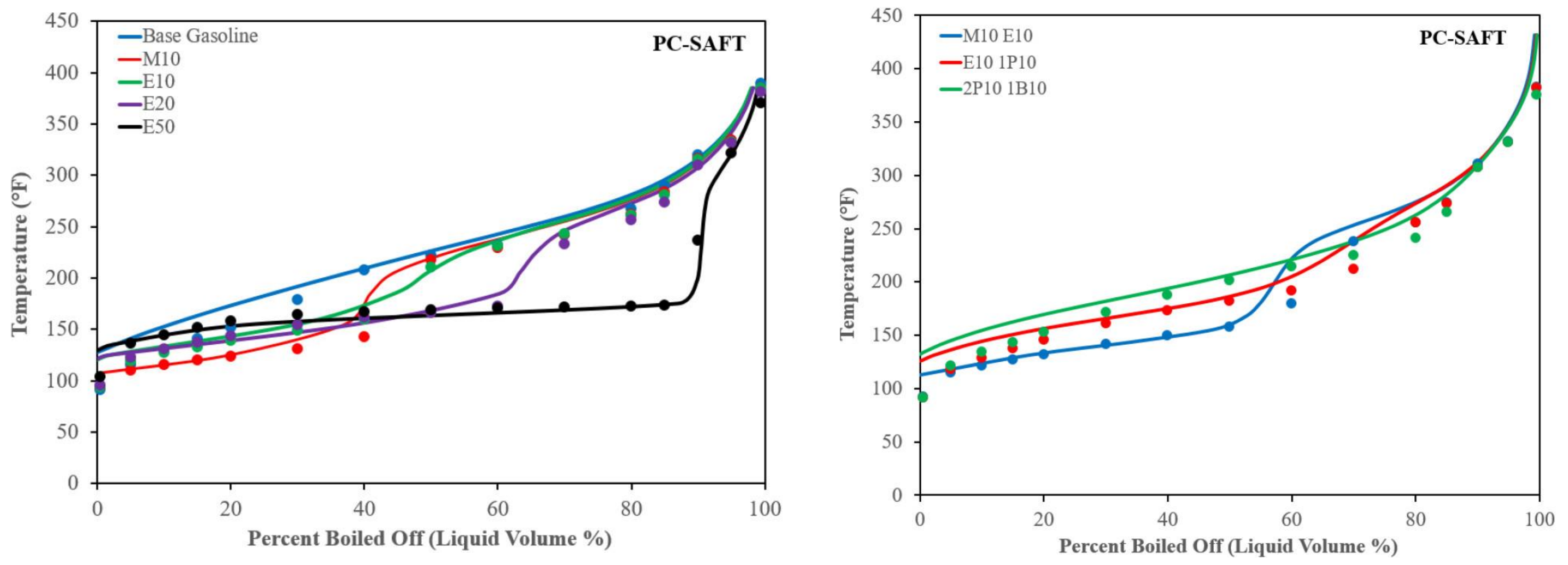


Start with **Distillation Curve** and **SG** of Base Gasoline

Generate Pseudo Components

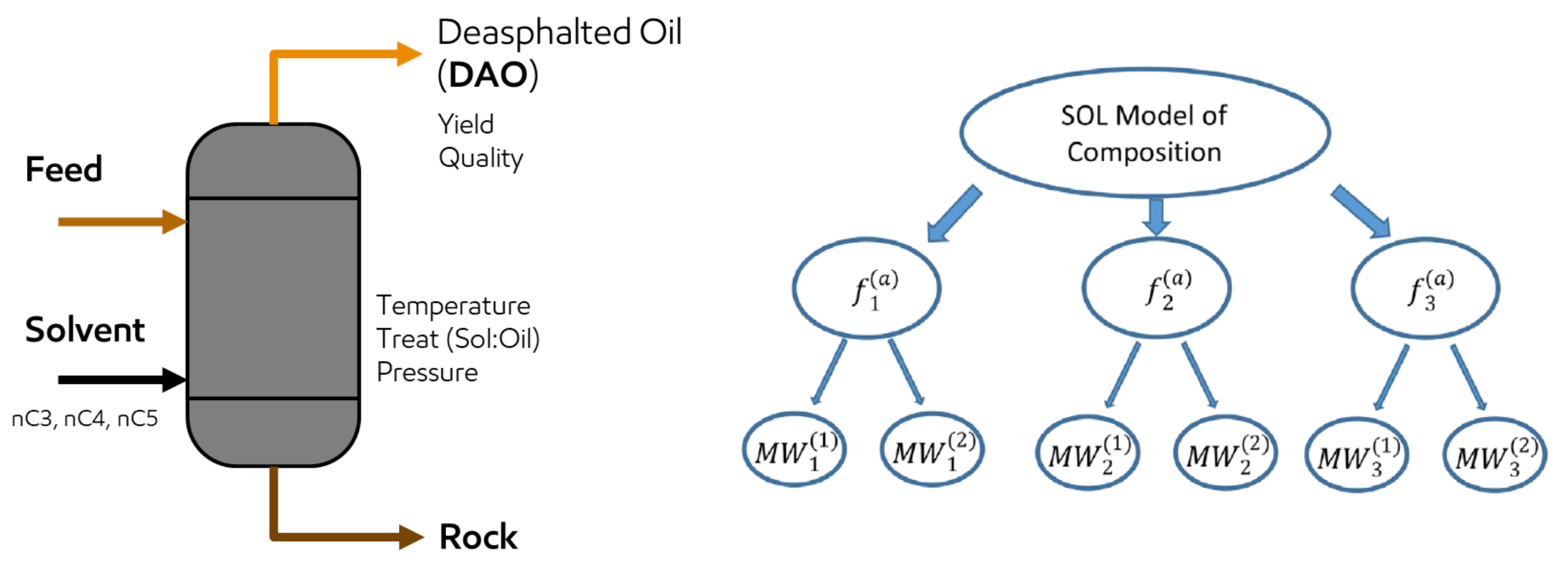
Parametrize **EMPC-SAFT** using **EMPETRO**

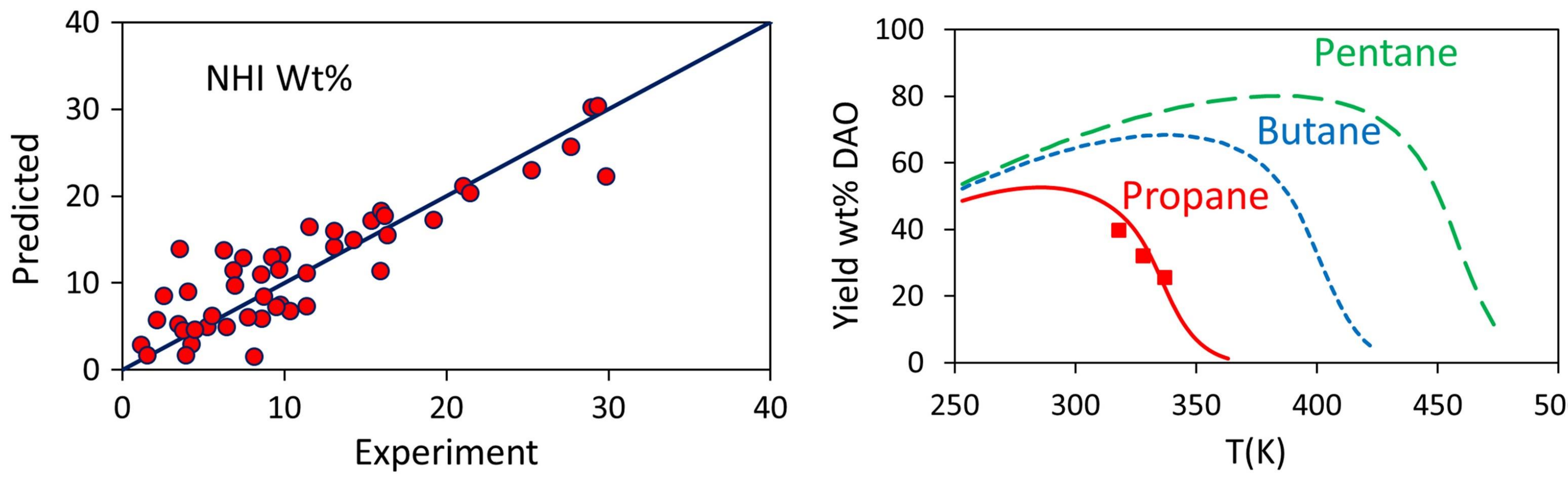
Simulate the effect of blending **oxygenates** (MeOH, EtOH,..) on **distillation curve**



✓ ***Model accurately predicts D86 distillation curves of gasoline/alcohol blends***

Modeling Solvent De-Asphalting for Resid Upgrading

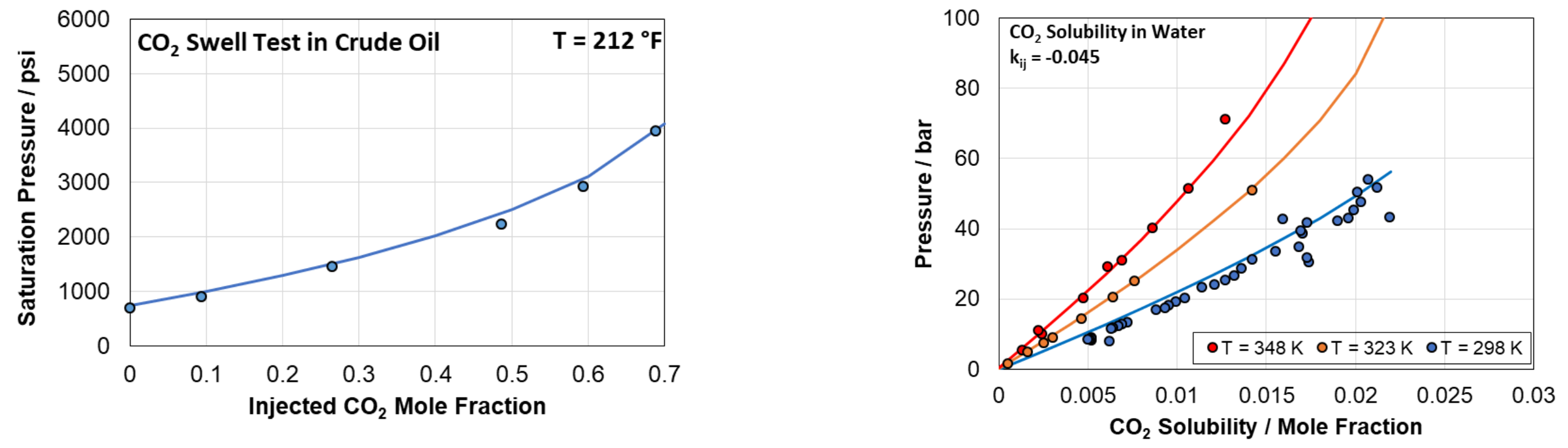




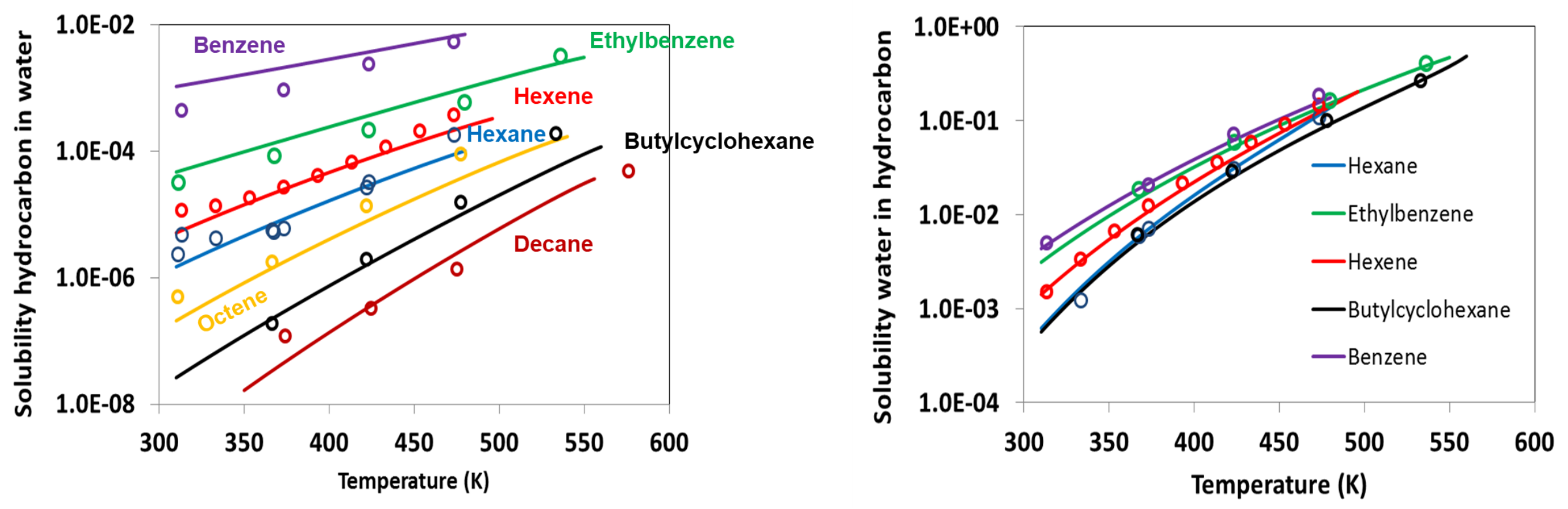
✓ ***Model accurately predicts nC_7 insolubles and deasphalted oil yield***

Upstream & CCUS Applications

Solubility of CO_2 in Crude Oil **Solubility of CO_2 in Water**



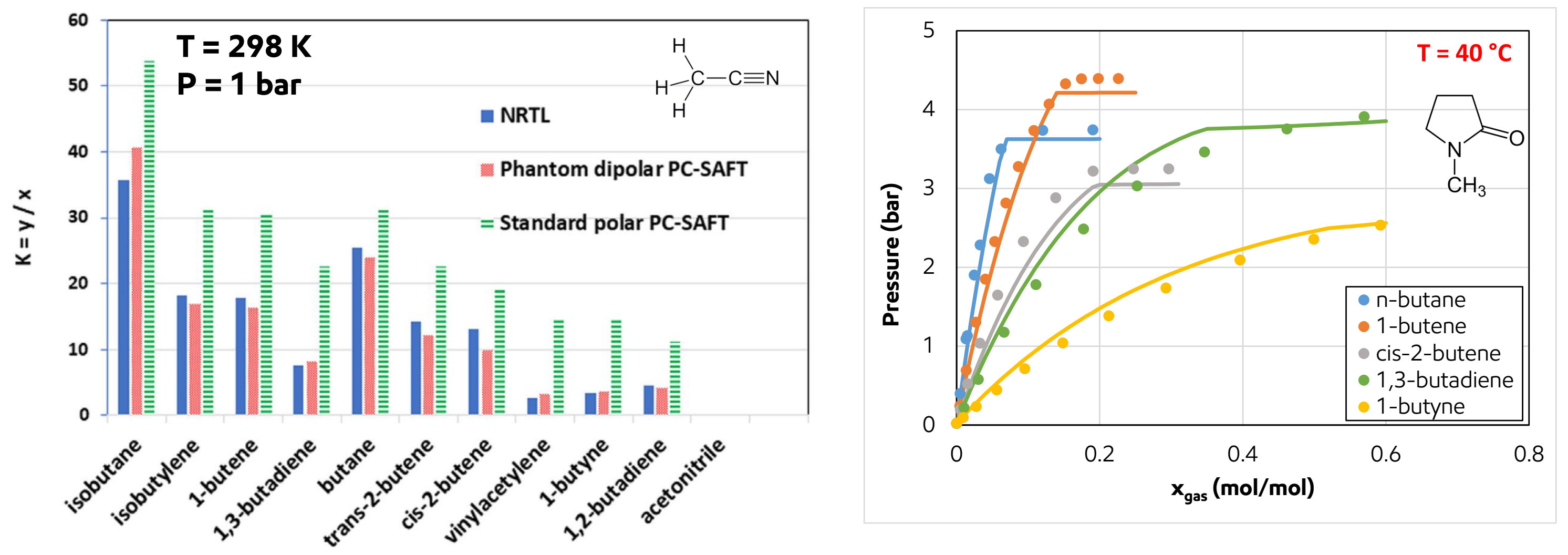
Mutual Solubility of Hydrocarbons / Water



Butadiene Extraction Using Polar Solvents

1,3-Butadiene is an important chemical for the **tire** industry. It comes out of the olefin recovery train downstream of a **steam cracker** with other C4's and is extracted using polar solvents such as **ACN** and **NMP**.

Phase Behavior C4's with ACN **Phase Behavior C4's with NMP**



✓ ***Phantom dipoles enable predictive capability for polar-olefin systems***

Conclusion & Final Remarks

- **EMPC-SAFT** is a comprehensive thermodynamic model that can be used for Upstream, Downstream, or Chemicals applications.
- A strategic implementation of the **dipolar free energy** within the EOS framework allows for excellent predictive capability of the phase behavior of **aromatics** and **unsaturated hydrocarbons** (olefins/alkynes).
- Incorporation of **advanced hydrogen bonding theory** allows for predictive capability for systems relevant to bio-feeds (alcohols, carboxylic acids, water).

Acknowledgment

The authors would like to thank ExxonMobil Technology and Engineering Company for their support and for approving the presentation of this work in SCI Innovation Day 2023.

Parameters of the dye-penetration test and influence on defect detection in waterborne barrier coated papers

Joseph Accardo[1], Rachael Smith[1], Allyson Marianelli[2], Samantha Woodfin[2], Brian Einsla[2], Melinda Einsla[1], John Roper III[2], Sharon Vuong[1]. Mary Alice Upshur[2], Betha Snow[2]

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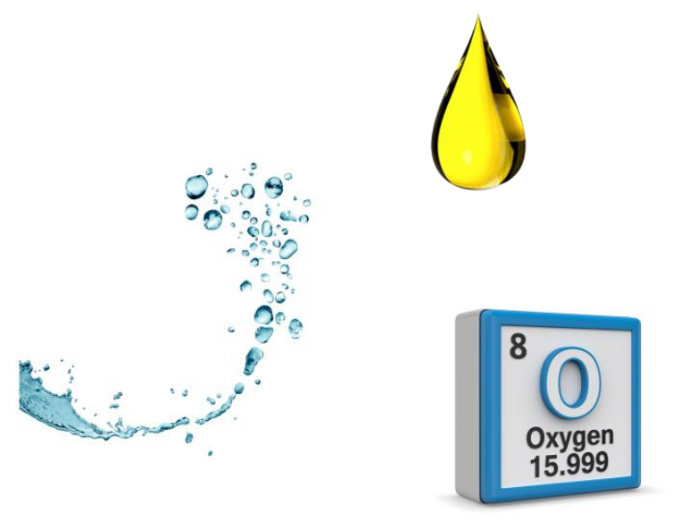
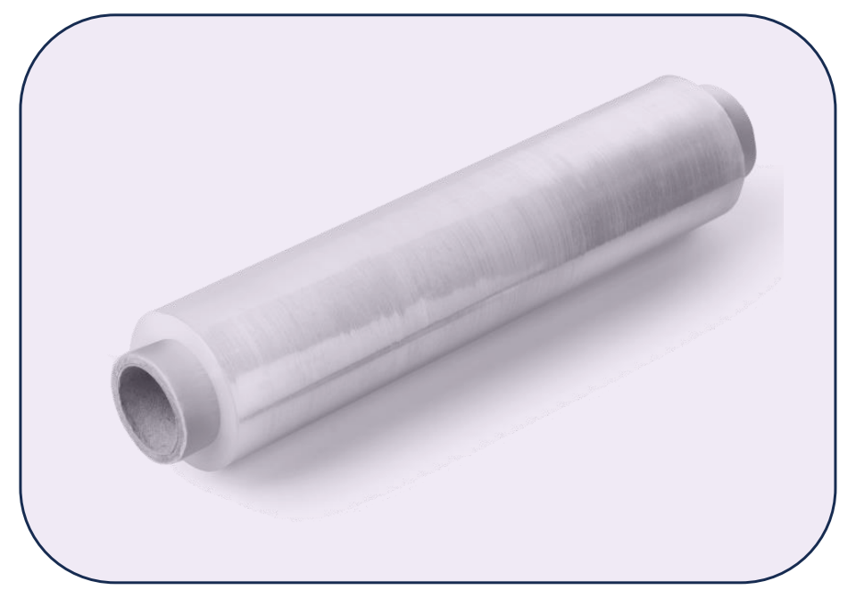
Introduction



Barriers for water, water vapor, oils, and gases play an essential role in everyday packaging

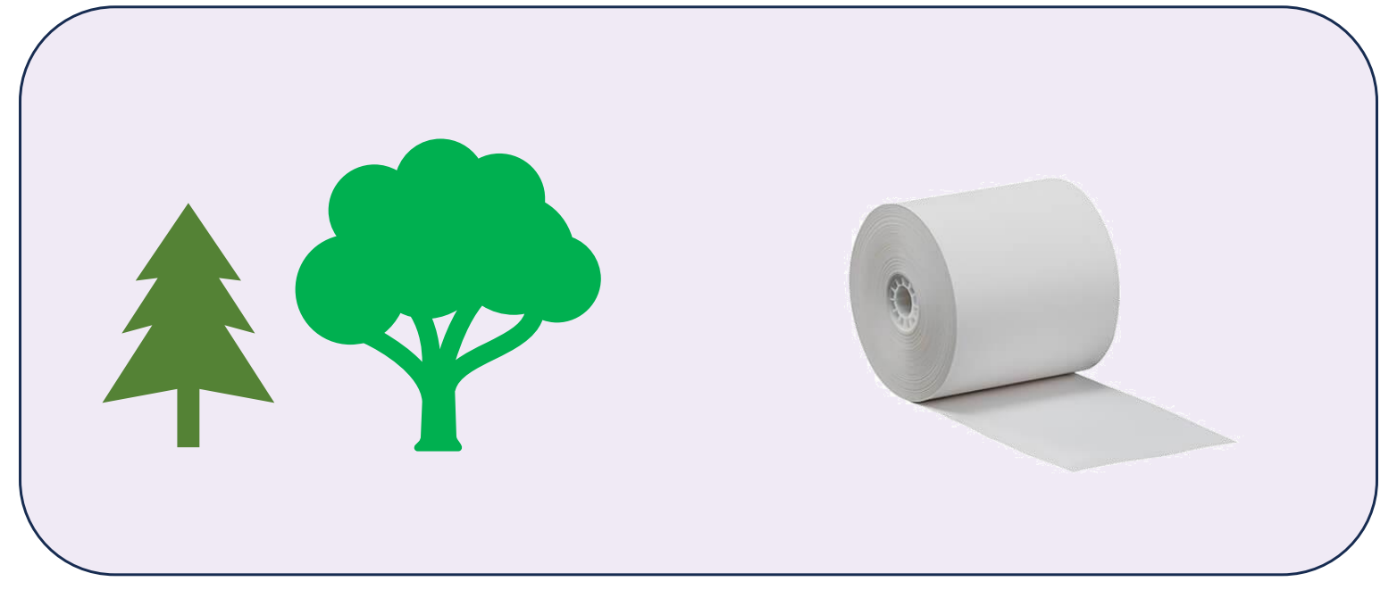
From medical supplies and food packaging to home and personal care products the goals are similar***. Keep solutes in and/or out.***

plastic packaging

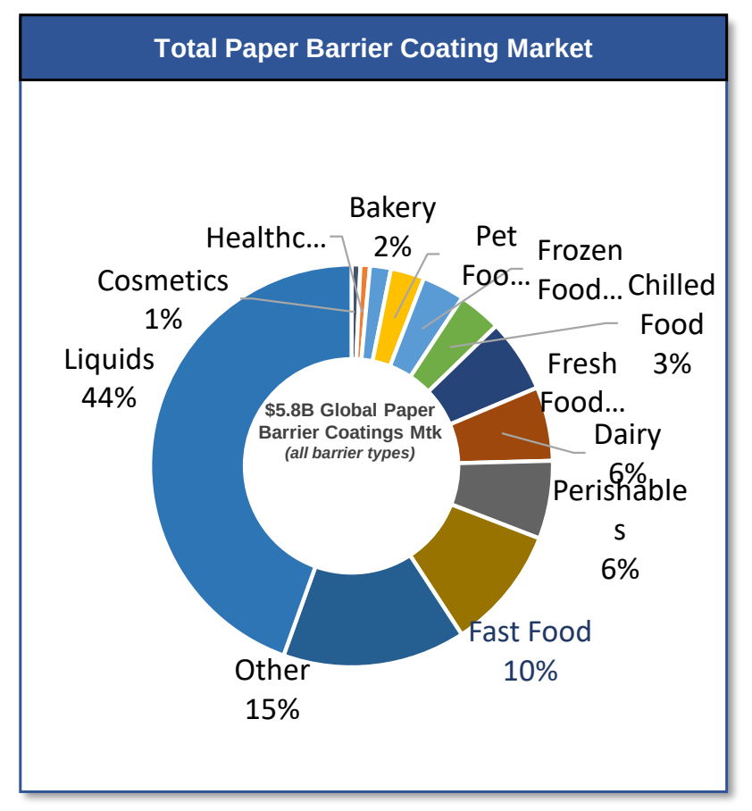


- Durable
- Long-term stability
- Inexpensive
- Intrinsic barrier properties

paper packaging

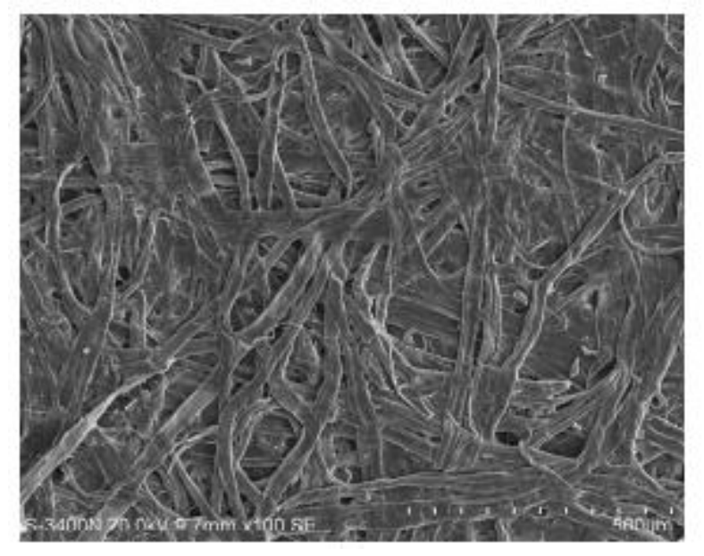


- Bioderived
- Biodegradable



Consumer demand and sustainability initiatives are a large driver for the development of paper-based packaging.

Why is this not the standard?
Paper is inherently porous and a bad barrier for a variety of substrates. To overcome this, polymeric barriers need to be applied

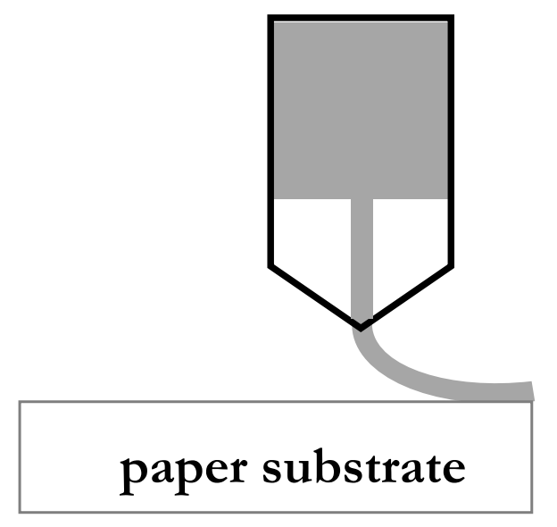


AFM of paper cross-section

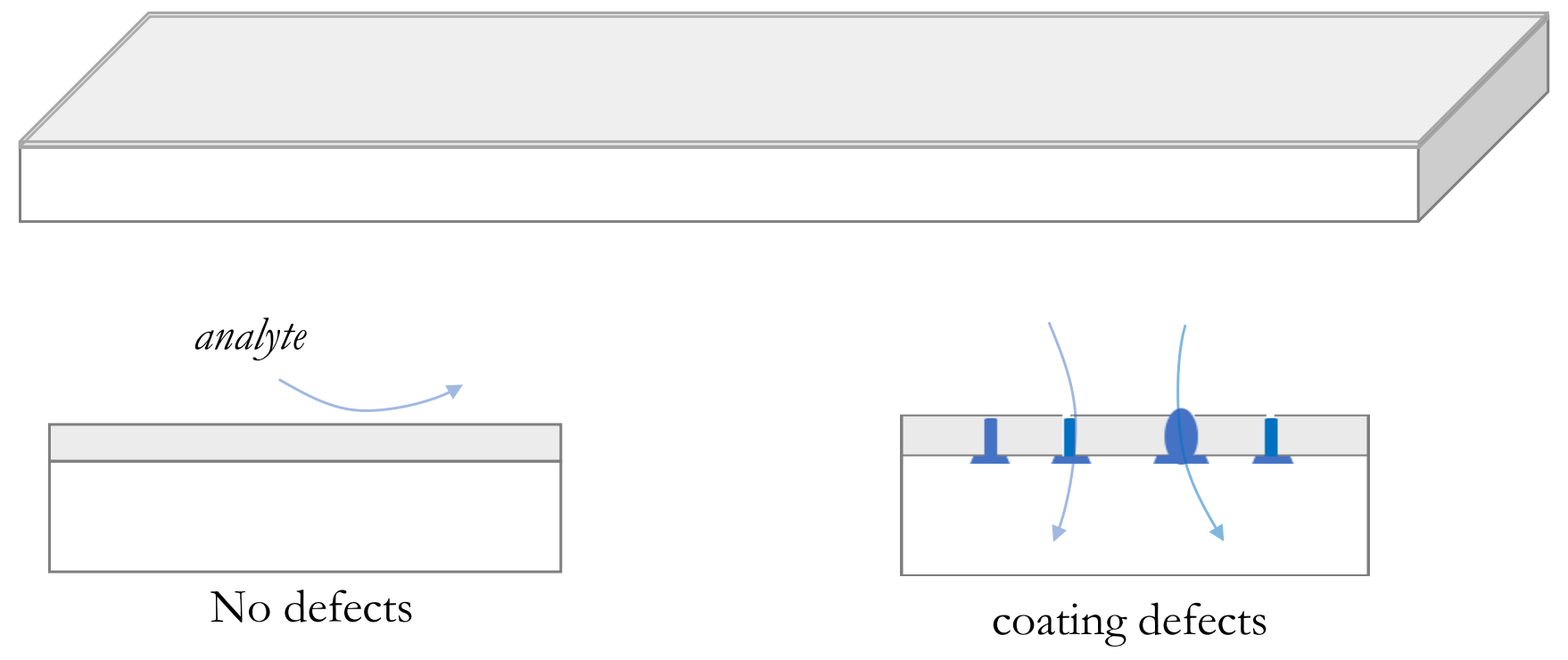
Packaging barriers play essential roles in preventing the transfer of solutes such as water, oxygen, or grease from either permeating into, *or out of*, a packaged product of interest. Commodity plastics and their coated counterparts have dominated the barrier market, though their sourcing (typically the petroleum industry) and biodegradation profiles contrast with the sustainable initiatives driving new product development. The use of paper for packaging, which is derived from a renewable resource and can be biodegradable, is a promising avenue toward greener materials. Unfortunately, the porous nature of paper makes it natural employed susceptible to solute permeation. To overcome this, the application of barrier coatings (such as of waterborne polymers) is often such that the necessary solute resistance is achieved.

The application of a coating does not guarantee a high-performance package, as microscopic structural defects, such as pinholes, cracks, and blistering can dramatically reduce the performance of the barrier coating. As these structural defects are not easily identifiable, the quality of the coating can be inferred from the coating performance tests, such as oxygen or water vapor transmission rate or oil and grease resistance. Consequently, there has been a need to develop tests which can assess the coating quality both *rapidly and reliably*. These tests can serve to screen barrier integrity before they are subject to performance studies, which typically are the bottleneck in product development. In addition to screening barrier integrity, some test results can be correlated to the barrier performance, which gives an idea of promising barriers.

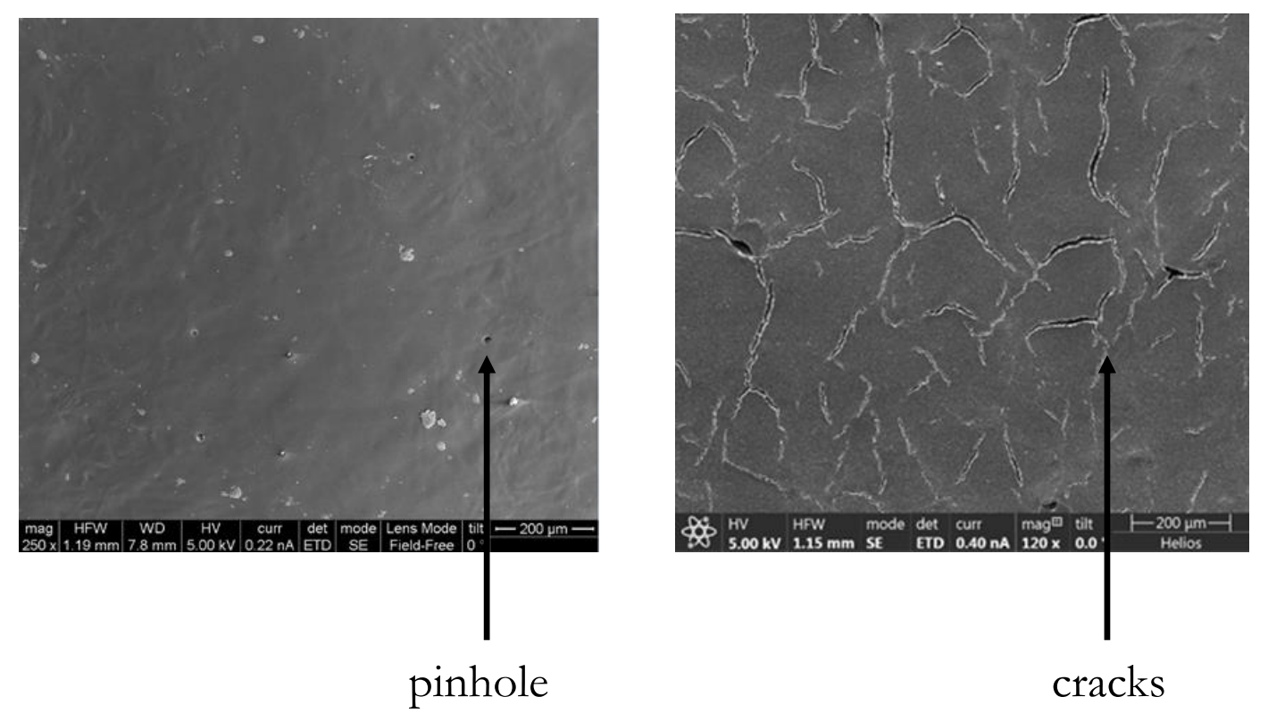
Applying waterborne coating



formulation coated paper



SEM of paper coatings with defects highlighted

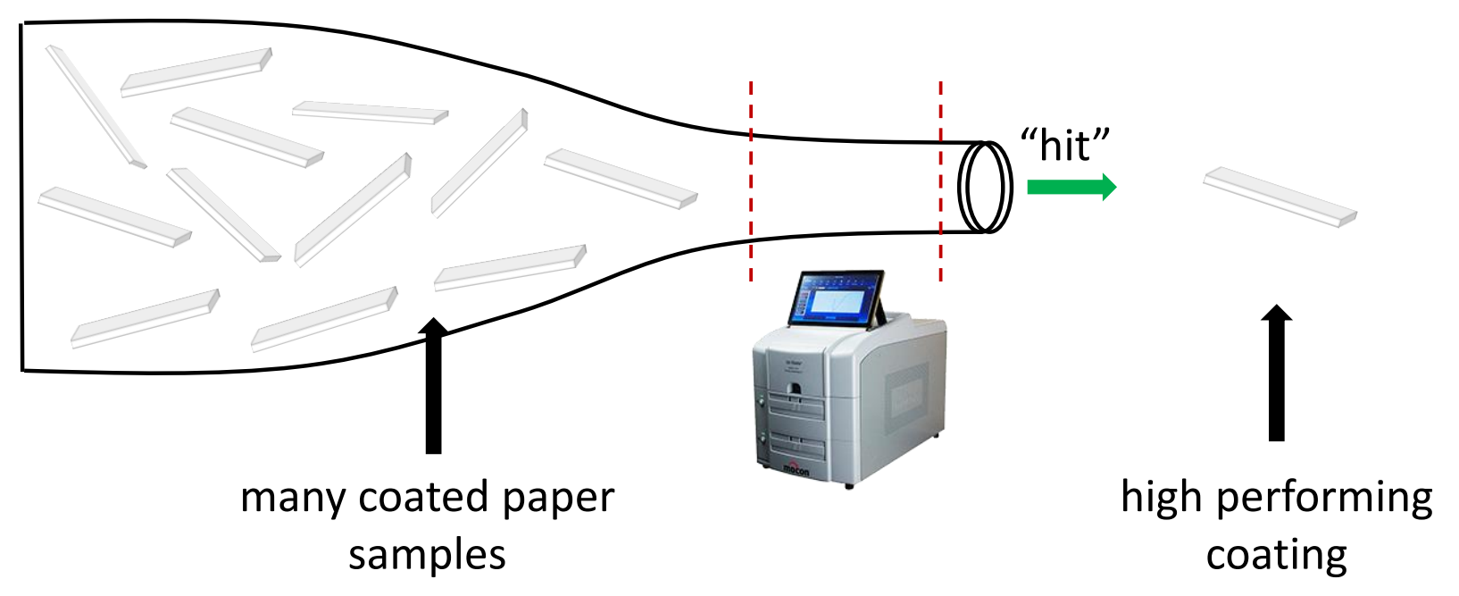


Takeaway

Defects in paper coatings will diminish the effects of the barrier.

How can we develop a tool that can be used to visualize and quantify defects?

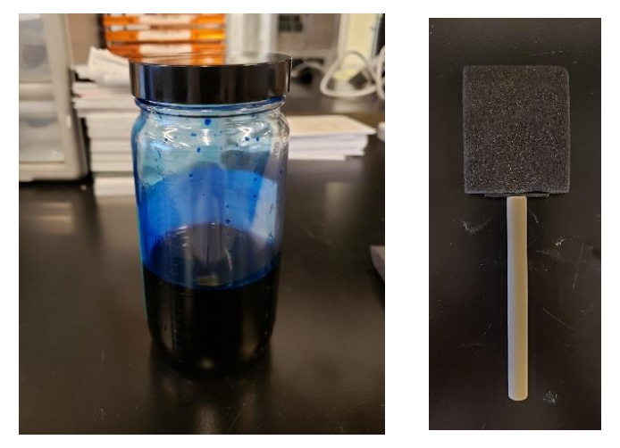
Test Method Development



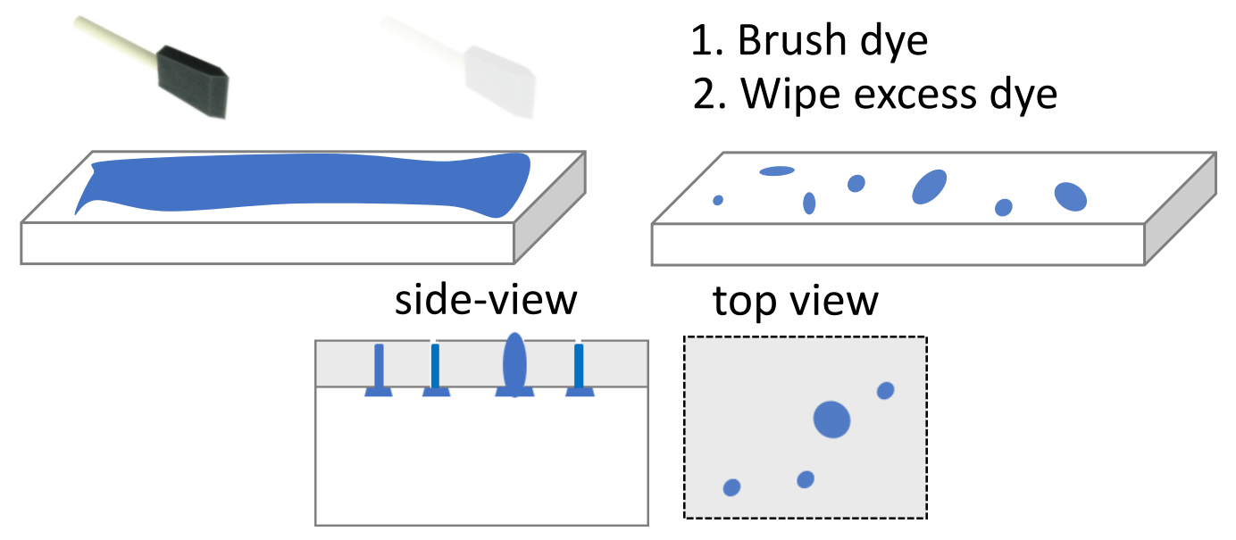
performance testing is our bottleneck

As a company we are routinely exploring new materials for barriers, and we can create materials much faster than we can test their properties, due to length testing times.

The blue dye test: *a method for rapidly visualizing defects in paper coatings*



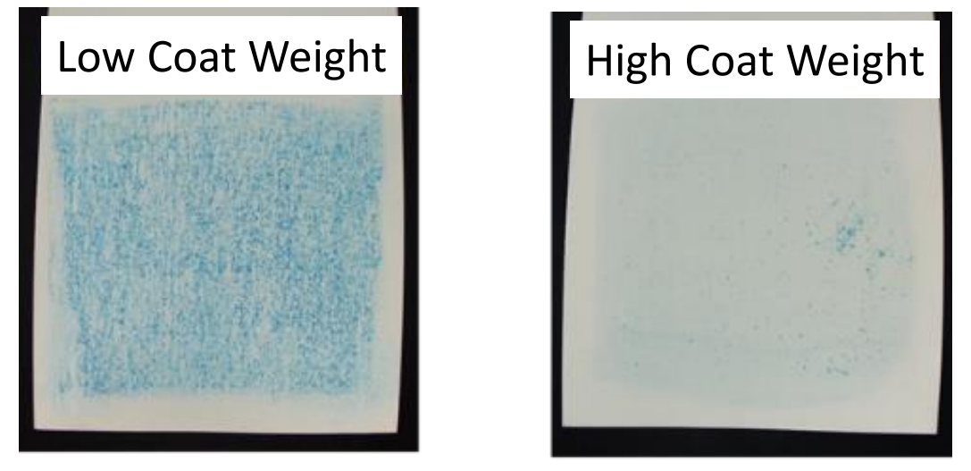
blue dye in mineral oil



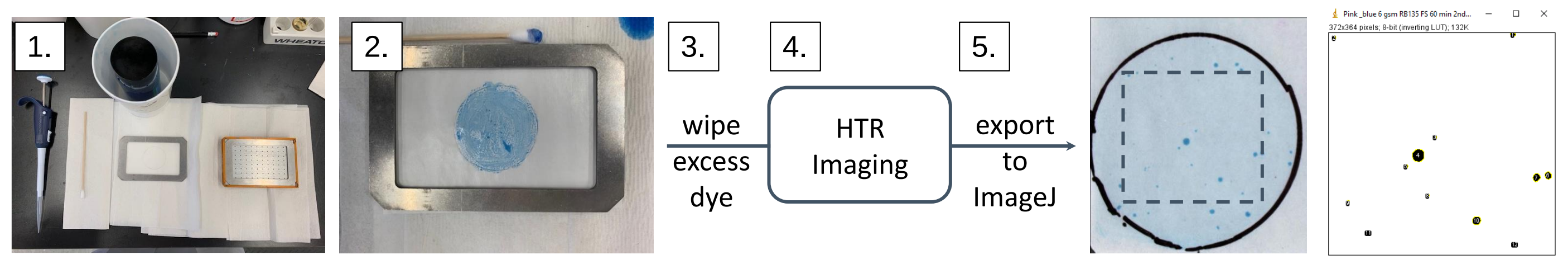
Identifies coating defects by evaluating dye transport through a coating to the substrate underneath

- Representative of liquid transport through a coating
- Analysis involves operator counting dye spots within a few minutes of wiping off the dye
- Method for prescreening defect detection for subsequent OTR and WVTR performance

Higher coat weight = more polymer coating = less defects



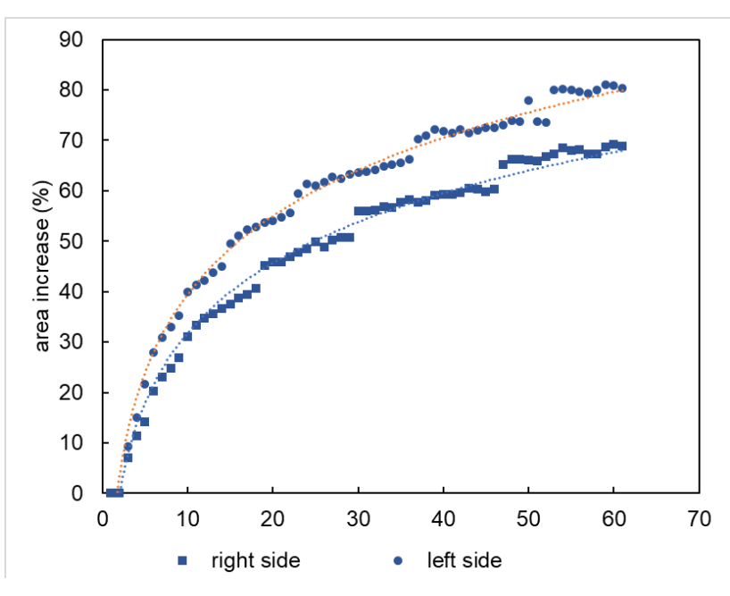
Can we reduce the number of manual steps in the process? Can the spot counting be automated? How do facts such as amount of dye and time before wiping affect the results?



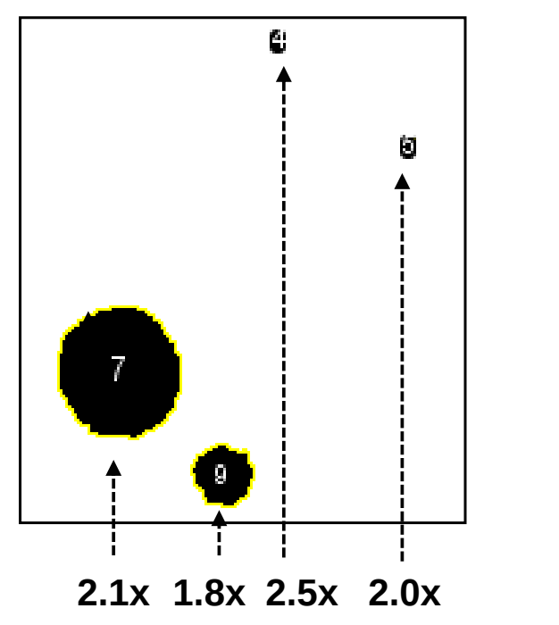
- A scaled down automated process minimizes error and acerates throughput
- Counting and quantifying dye spots is done by image analysis

data on total spots, quantity, area% of spots and average size are extracted, as well as individual spot area, are recorded

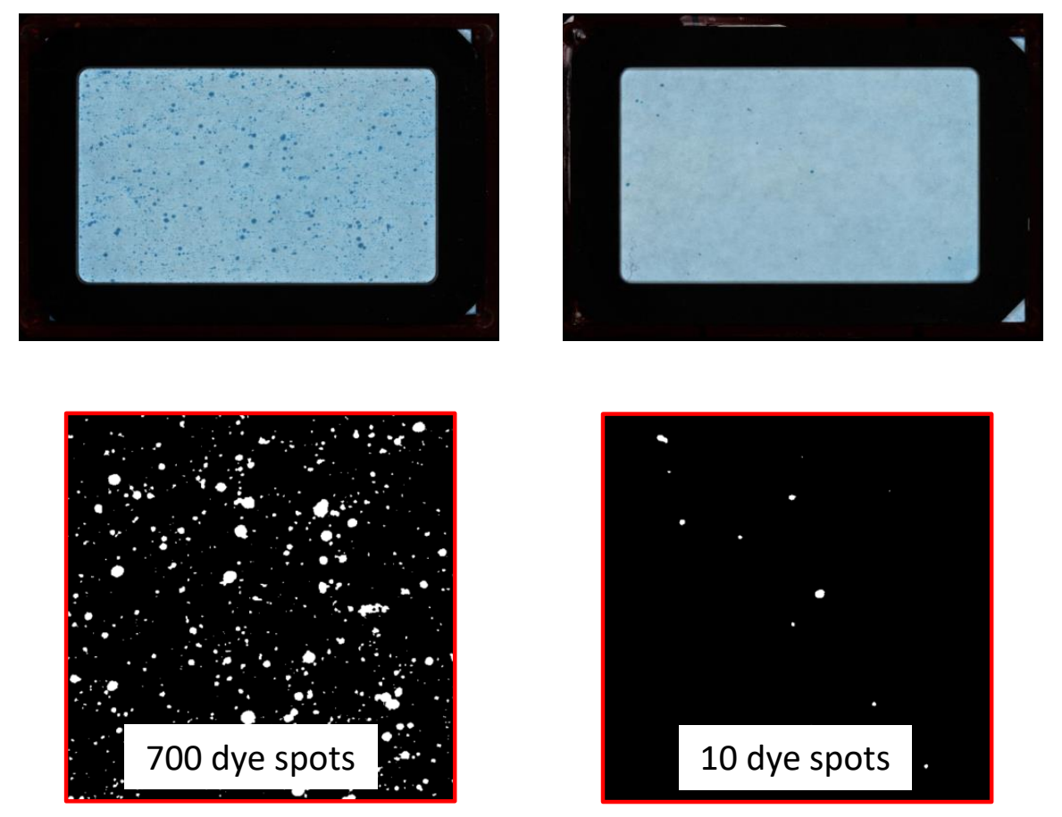
Coating 1 coated on freesheet



change in area over 3 hours



Spot area is not related to defect size

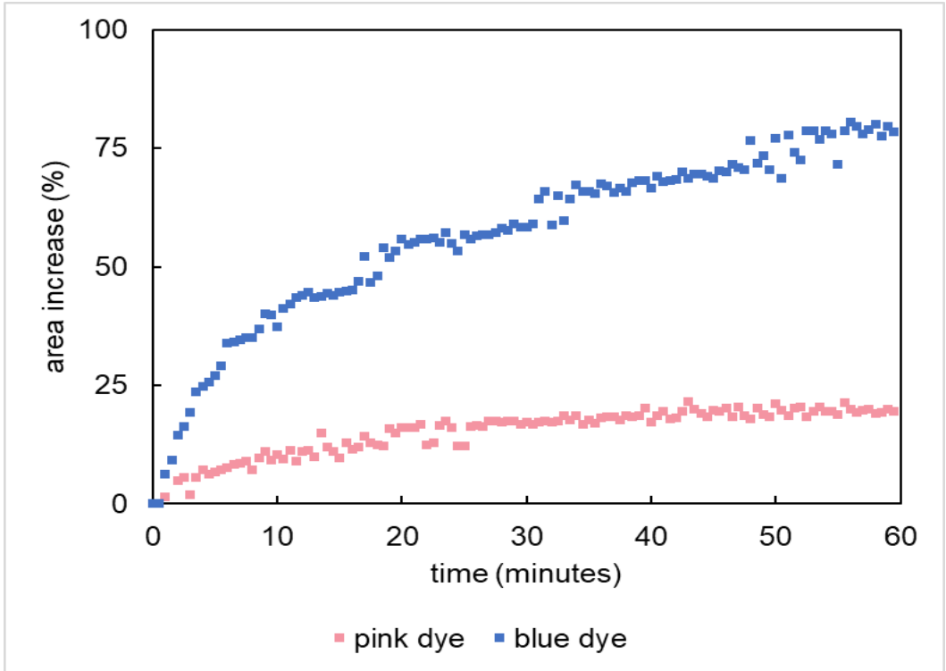


Spot count is related to coating integrity

- After dye is removed, the area of the spot increases over time
- Dye size increases independently of size

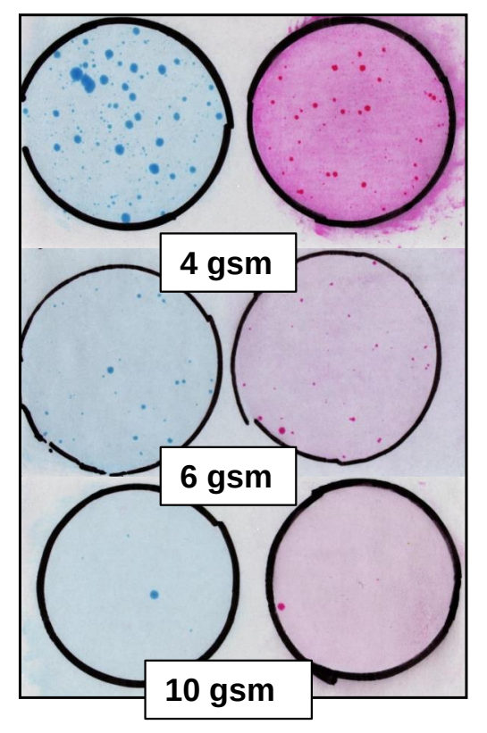
Optimization of dye test: type of dye applied

spot area vs. time for blue and pink dye



spot count vs. coat weight for blue and pink dye

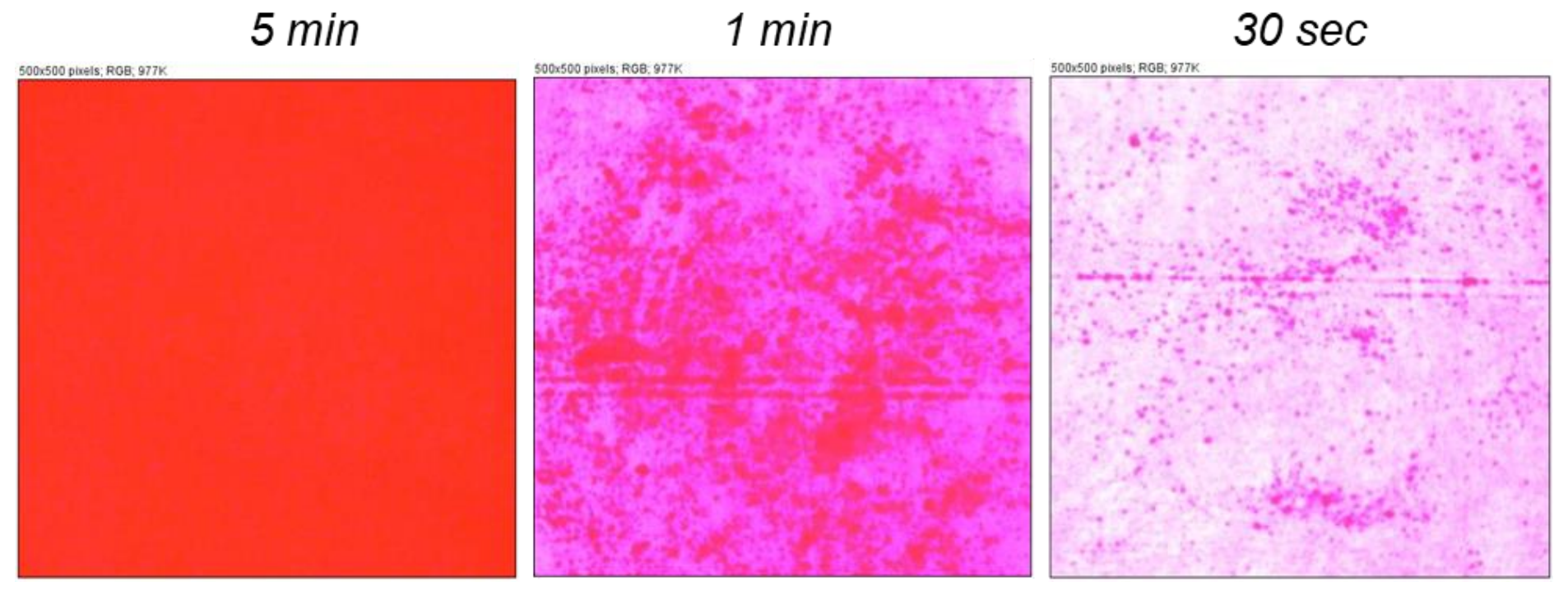
coat weight (gsm)	spots in 350x350 pixels	
	Blue dye (±)	pink dye (±)
4	42(14)	39(16)
6	15(1.5)	14(3.1)
10	<5	<5



- Changing the source of dye leads to a decrease in spreading of the spot size over time. Credit: Trinseo
- Pink and blue dye pick up similar number of defects but pink dye spreads less.
- Defect (spot) count is independent of dye color.

Choice of dye reduces error with consistent defect detection

Optimization of dye test: Dwelling time



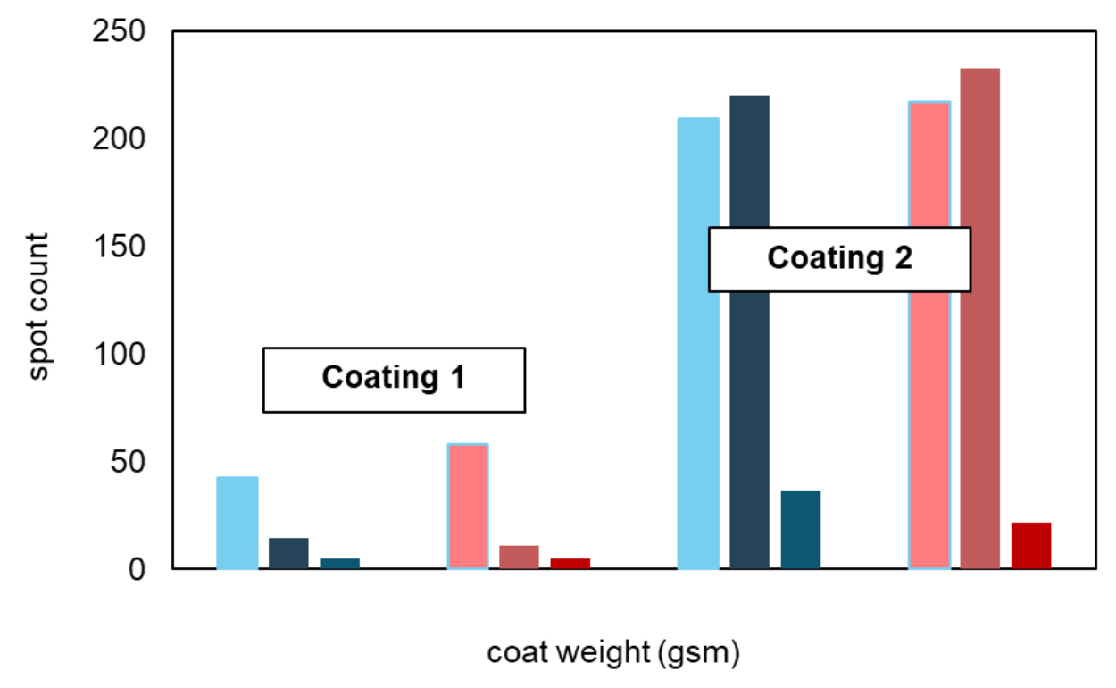
- Spot count is highly dependent upon dwelling time, especially for poor coatings
- A large quantity of defects can lead to complete staining of paper substrate, which will undercount spots
- For new barriers and coatings, dwelling time should be investigated systematically

Dwell time leads to dramatic change in spot count due to saturation

Investigation of results: area or spot count?

- Coating 1 shows a relationship between coat weight and spot count, which is not observed for coating 2
- Spot count is undercounted for coating 2 at low coat weights

For poor barriers, area of spots becomes a better parameter for defect analysis



Conclusions

Standardization of testing is crucial to performance metrics

Results of defect detest are highly dependent upon parameters. Adhering to protocol(s) is imperative for reproducibility

All samples are not the same. Adaptability is needed to perform meaningful science

The results from this work highlight multiple considerations when applying the dye-penetration test toward defect detection in waterborne paper barriers. The primary consideration is the choice of dye used in the test. Preliminary results suggest that either the viscosity or surface tension of the dye carrier reduces the dye migration rate, which comes at the expense of test speed due to prolonged dwelling times. Next, we identified photobleaching as an occurrence for blue-dye spots, which can be overcome. Preliminary observations reveal that the pink dye is more resistant to photobleaching, which is likely due to the lower energy absorbance profile and may improve the test reliability as a function of time variation prior to imaging. We demonstrated the difficulty in correlating spot count with defect count in highly defective systems due to the converge of dye and highlight the importance of recording both spot count and area as metrics of coating quality. Lastly, we note that the while the dye-penetration tests are promising tools for evaluation FS substrates, more work is needed use these tools to evaluate coatings on glassine paper. We envision that the results of this work will enable a more comprehensive understanding of optical methods for defect detection and advancement of generalizable approaches to rapidly and reliably pre-screen film quality to accelerate the development of barrier coatings for paper substrates.

REFERENCES

(1) Allyson Marianelli, B. E., Elizabeth Snow, Samantha Woodfin, Bo Shuang, Kevin Henderson, Mike Linsen, Jonathan Derocher, Shawn Oliver. Improvements in oil and grease resistance (OGR) test methodology for waterborne barrier coatings. *TAPPI Journal* **2022**, *21* (11). DOI: https://doi.org/10.32964/TJ21.11.645.
(2) Gietl, M. L.; Schmidt, H.-W.; Giesa, R.; Terrenoire, A.; Balk, R. Semiquantitative method for the evaluation of grease barrier coatings. *Progress in Organic Coatings* **2009**, *66* (2), 107-112. DOI: https://doi.org/10.1016/j.porgcoat.2009.06.009.
(3) Dustin Burton, D. V., Gregory W. Welsch. Novel test method for measuring defects in barrier coatings. *TAPPI Journal* **2022**, *21* (11). DOI: https://doi.org/10.32964/TJ21.11.625.

The Power of Experimental Design in Innovation

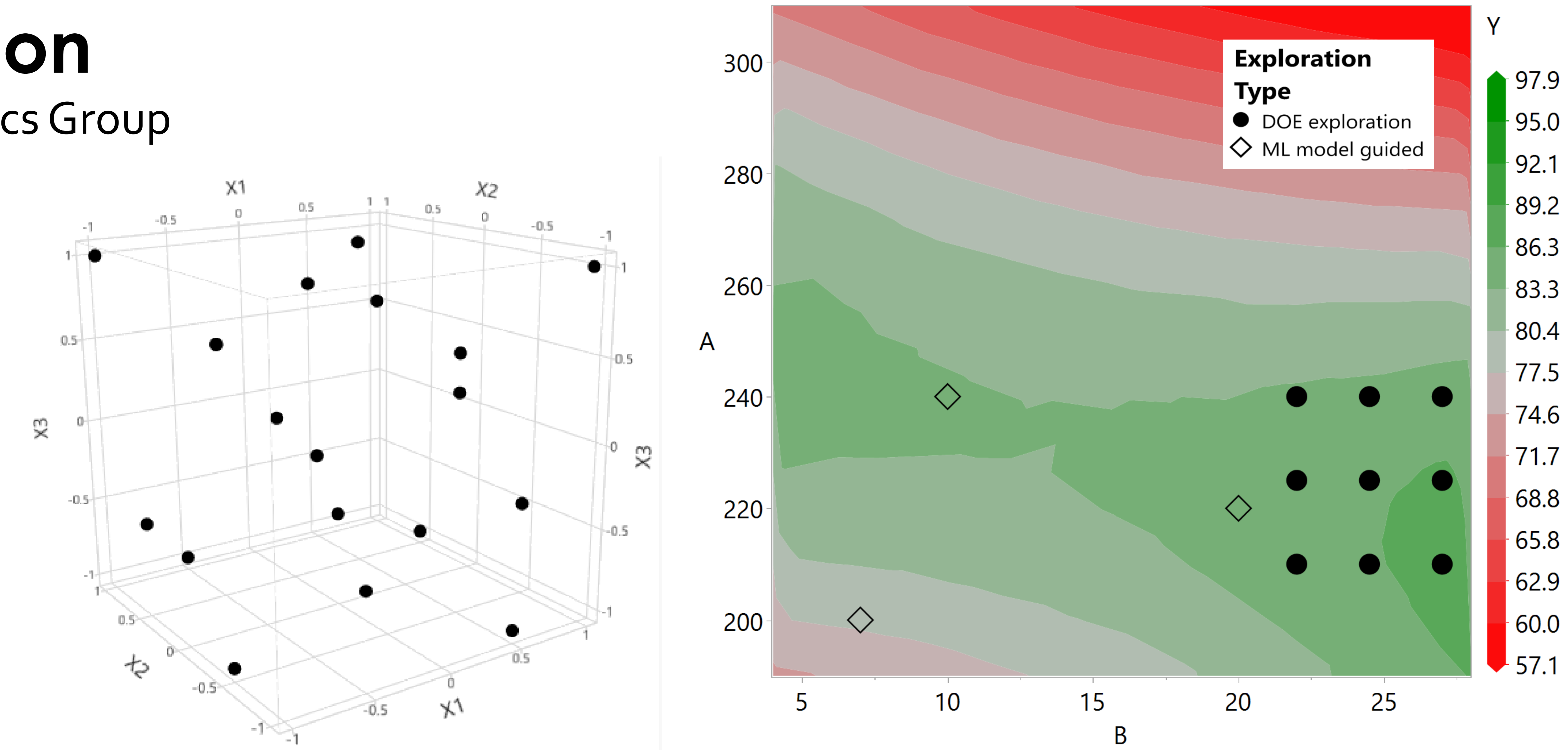
Ashley Childress – Eastman Chemical Company | Data Science | Applied Statistics Group

Applied Statistics at Eastman

Part of Eastman's Data Science organization, the Applied Statistics Group consists of statisticians who provide statistical support throughout the company, primarily working with technology and manufacturing on their top projects by providing support in experimental design and data analysis.

Our mission is to create value for Eastman through the promotion and use of statistical methods to enhance data-based decision making.

Statistically based experimental design principles provide defensible and theoretically sound data and analysis to guide scientists' research and discover innovative solutions.



Two experimental spaces are shown: the left shows a three-dimensional space with experimental combinations optimally chosen throughout the space to fit a desired model form; the right shows a contour plot of a space being searched by a ML model with a follow-up DOE at the identified optimum.

Design of Experiments (DOE)

- Innovate faster using screening techniques and sequential experimentation
- Sequential experimentation approach practically beneficial for experiments to sequentially build knowledge while conserving resources
- Develop fundamental process understanding and assist with scale-up using response surface methodology
- Discover new product formulations using mixture experiments
- Create the value story with appropriate comparisons to competitive products
- Handle process constraints and randomization restrictions using new advances in optimal design of experiments

DOE + AIML

- Application and formulation modeling can identify promising experimental spaces to explore, but cannot provide causal information, which is critical to process understanding
- Experiments can be designed to explore and understand system behavior around the identified optimum, allowing the scientist to develop key knowledge on the process or product
- DOE methods can be used to identify spatial missingness and efficiently add combinations to help fill out the training set
- Understanding prediction uncertainty is important, and statistical methodology can be used to quantify or flag areas with large amounts of error in the space
- Verification of predicted optimum is key to moving forward with product and commercialization decisions

Poster ID No.

Rapid Degradation of Cellulose Diacetate Materials in the Coastal Ocean

Collin Ward, Anna Walsh, Taylor Nelson, and Christopher Reddy – Woods Hole Oceanographic Institution
Brian Edwards, Mounir Izallalen, Sharmi Mazumder, Michael Mazzotta, and Steve Perri – Eastman

INTRODUCTION

The pervasiveness of plastic debris in the world's oceans, together with rapidly increasing consumer demand for plastics, has generated intense interest in materials with sustainable characteristics and low environmental persistence. Cellulose diacetate (CDA) (**Figure 1**) is a primarily bio-based material (derived from wood pulp) that is widely used in consumer goods and is proposed to have low persistence should leakage into the natural environment occur.

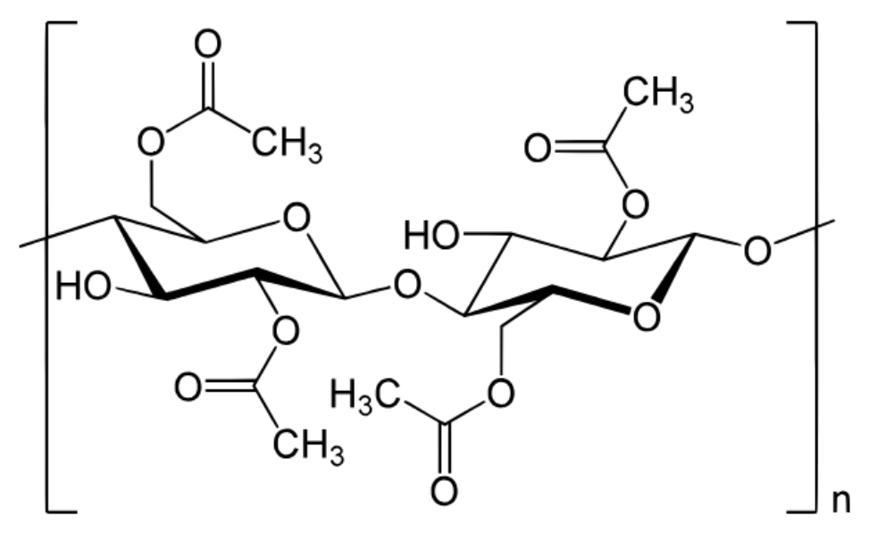


Figure 1. Molecular structure of cellulose diacetate (CDA).

Previous studies have shown that CDA is biodegradable in a variety of environmental compartments, but no peer-reviewed study had assessed the persistence of CDA-based materials in the coastal ocean. Here, we investigate the degradation of CDA-based materials by marine microbes using a continuous flow seawater mesocosm (**Figure 2**).

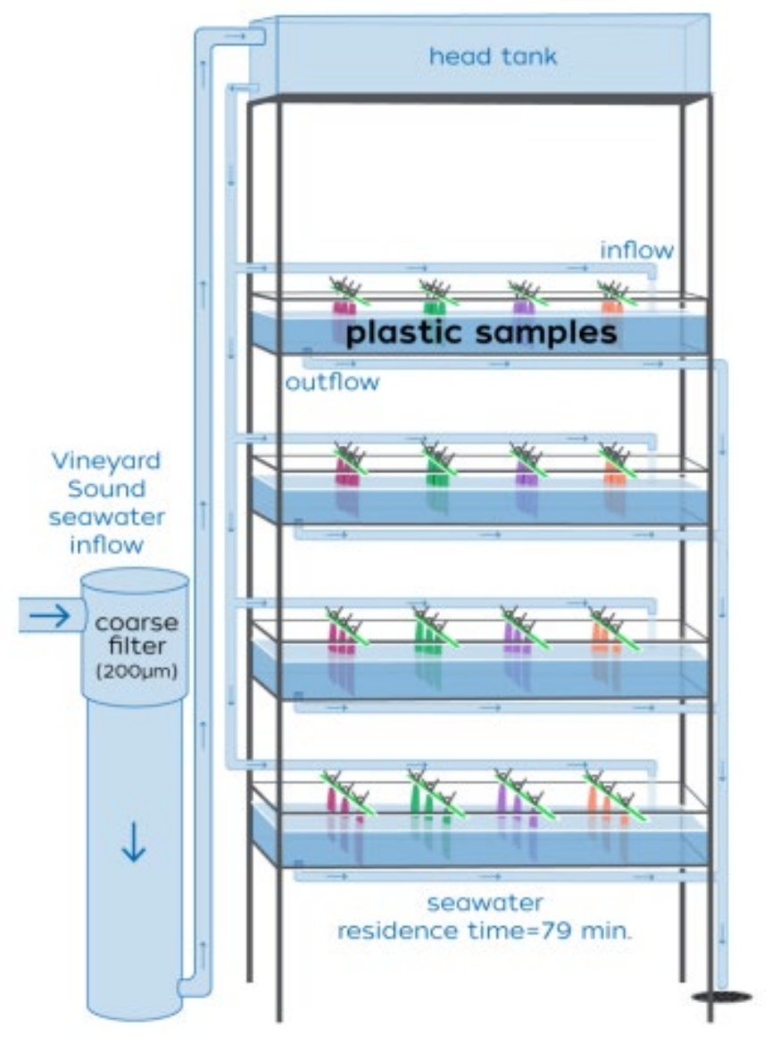
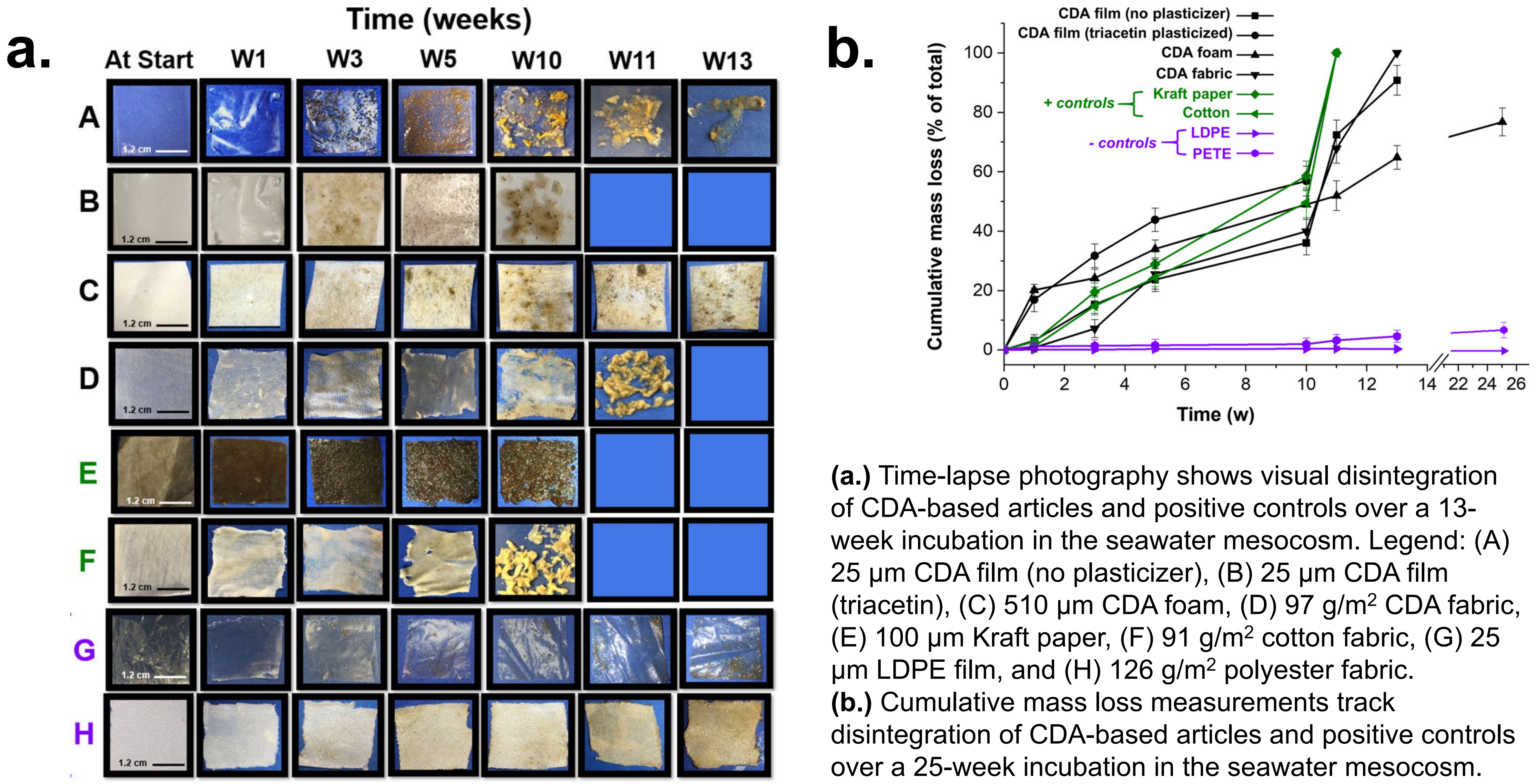


Figure 2. Coastal seawater from the Vineyard Sound (Massachusetts, US) was supplied to the mesocosm from an intake approximately 300 m offshore at an approximate depth of 4 m. The seawater contained native microbial communities and the flow was constant and equal to each rack containing specimens. (Photo credit – Natalie Renier, WHOI)

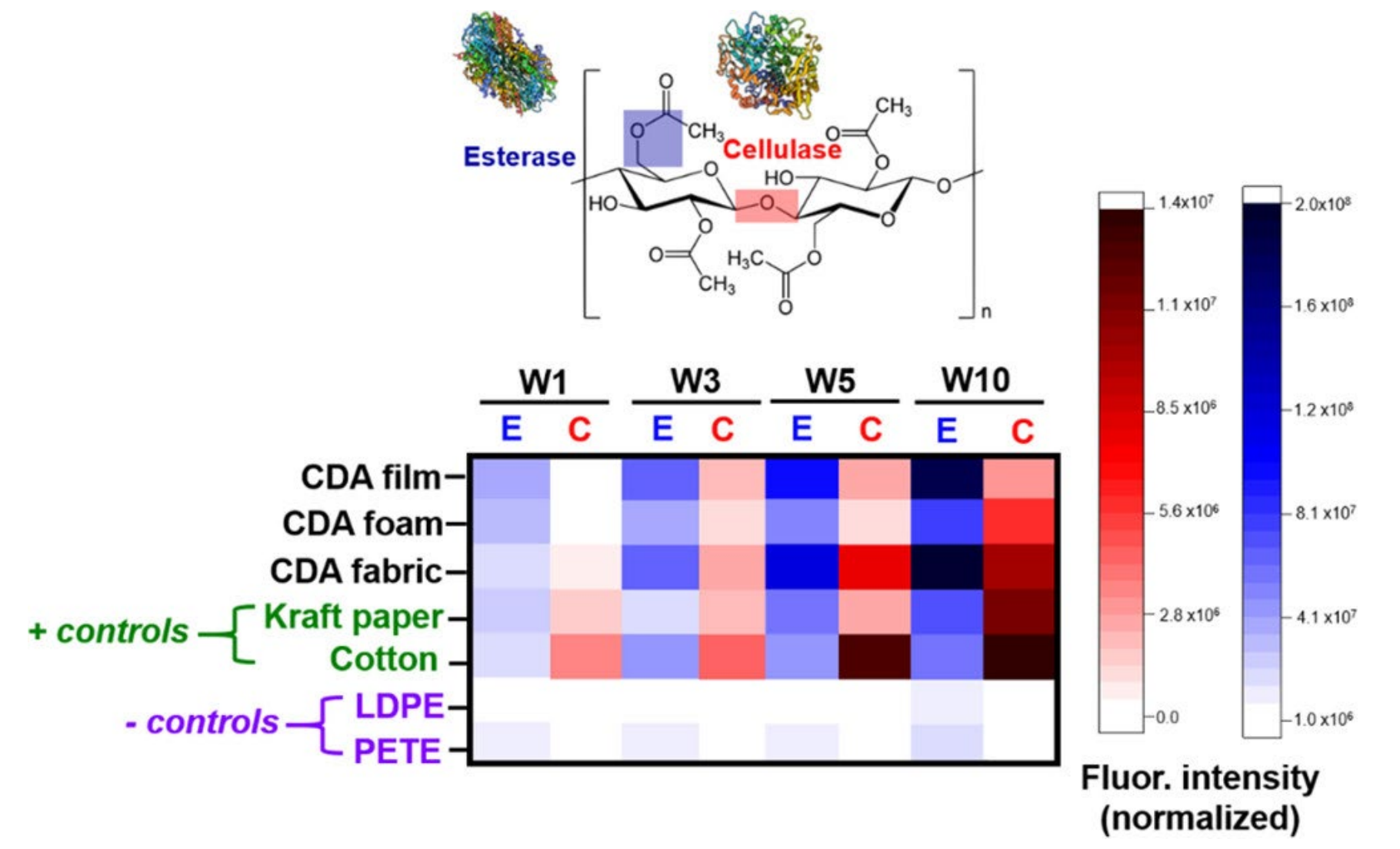
The specimens included various CDA-based materials (films, foams, and fabrics), positive controls with high degradative capacity (Kraft paper and cotton fabric), and negative controls with low degradative capacity (LDPE film and polyester fabric).

TIME-LAPSE PHOTOGRAPHY AND CUMULATIVE MASS LOSS



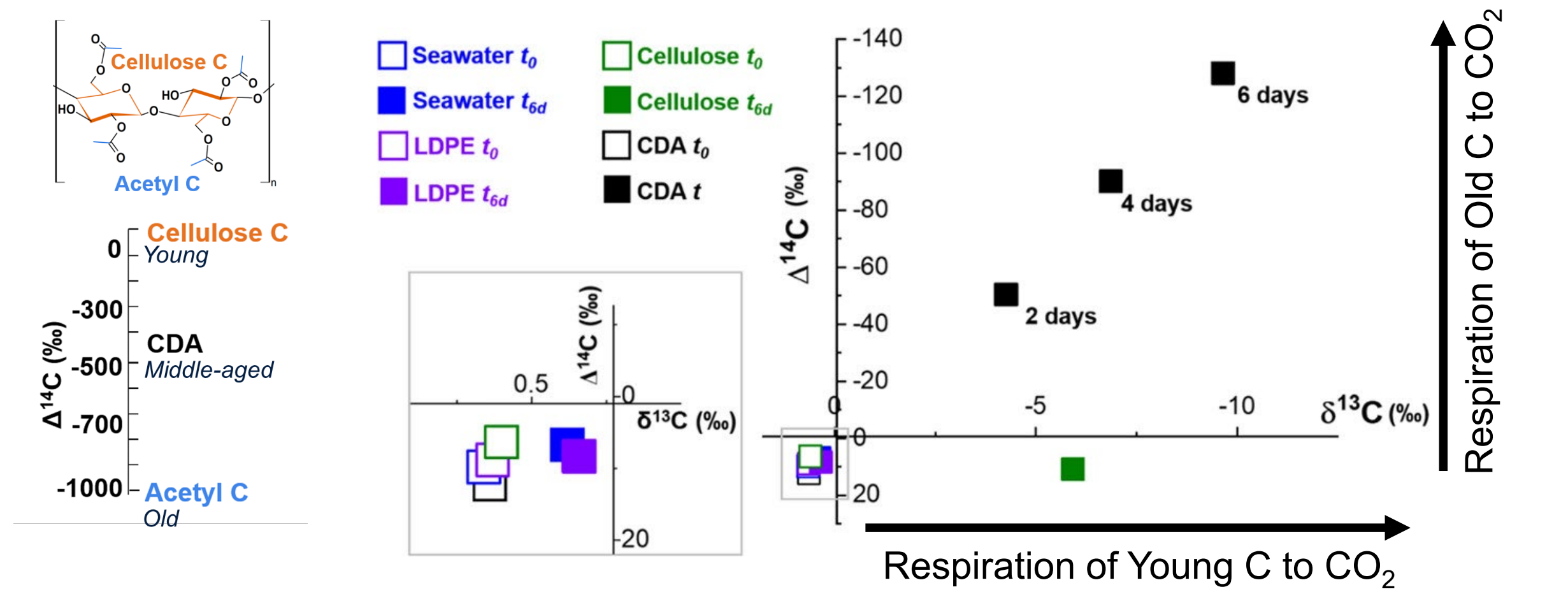
(a.) Time-lapse photography shows visual disintegration of CDA-based articles and positive controls over a 13-week incubation in the seawater mesocosm. Legend: (A) 25 µm CDA film (no plasticizer), (B) 25 µm CDA film (triacetin), (C) 510 µm CDA foam, (D) 97 g/m^2 CDA fabric, (E) 100 µm Kraft paper, (F) 91 g/m^2 cotton fabric, (G) 25 µm LDPE film, and (H) 126 g/m^2 polyester fabric.
(b.) Cumulative mass loss measurements track disintegration of CDA-based articles and positive controls over a 25-week incubation in the seawater mesocosm.

ENZYMATIC ACTIVITY



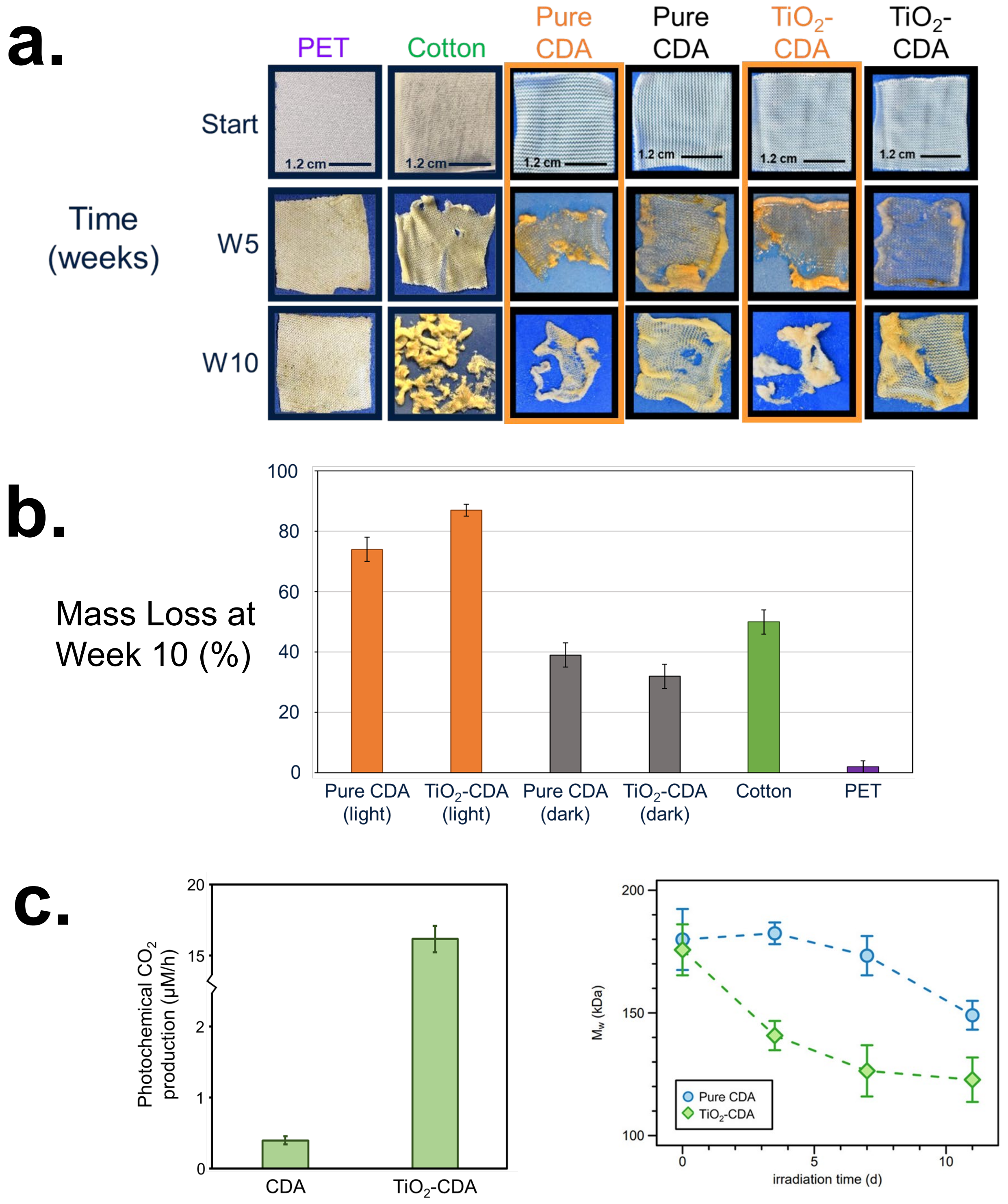
Esterase and cellulase enzymatic activity increased over a 10-week period for CDA-based articles and positive controls. For CDA, esterase activity increased before cellulase activity.

CONFIRMING BIODEGRADATION



CDA contains young cellulosic radiocarbon ($\Delta^{14}C$ = 98.0‰) and old acetyl radiocarbon ($\Delta^{14}C$ = −1000‰), providing a unique opportunity to track which C atoms are biodegraded to CO_2. Shifts in the isotopic composition of seawater dissolved inorganic carbon ($DI^{13}C$ and $DI^{14}C$) during short-term (up to 6 days) bottle incubations confirmed respiration of both the cellulosic (young) and acetyl (old) components of CDA to CO_2, with slight preferential degradation of acetyl C.

PHOTO-BIODEGRADATION



(a.) CDA fabric that was irradiated for 14 days in a solar simulator (orange column headers) disintegrated more quickly in the seawater mesocosm than dark control CDA fabrics (black column headers).
(b.) Mass loss at 10 weeks revealed that irradiated CDA fabrics (orange) disintegrated more quickly than dark control CDA fabrics (black) and cotton (green). Irradiated CDA + TiO_2 fabrics disintegrated more quickly than irradiated pure CDA fabrics, indicating that TiO_2 acts as a photocatalyst and accelerates degradation.
(c.) The susceptibility of CDA to photochemical conversion to CO_2 (left) and chain scission (right) to lower molecular weight products was greatly enhanced by TiO_2.

CONCLUSIONS

- **CDA-based materials are susceptible to disintegration and biodegradation by native marine microbes on timescales of months.**
- **Marine microbes degrade both the acetyl and cellulosic components of CDA, with deacetylation appearing to be the rate limiting step.**
- **Synergistic weathering, such as photo-biodegradation, can shorten the lifetime of CDA in the ocean.**
- **Photocatalytic additives, such as TiO_2, accelerate degradation and thus reduce the environmental lifetime of CDA.**

ACKNOWLEDGEMENTS & REFERENCES

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The authors also appreciate helpful discussions and support from Bryan James, Yanchen Sun, Carol Anne Clayson, Amy Apprill, Rick Galat, Natalie Renier, Justin Ossolinski, and Dave Bailey at WHOI, and Kathy Elder, Roberta Hansman, and Josh Burton at NOSAMS.

Rapid Degradation of Cellulose Diacetate by Marine Microbes. Michael G. Mazzotta, Christopher M. Reddy, and Collin P. Ward. *Environmental Science & Technology Letters* 2022 9 (1), 37-41. DOI: 10.1021/acs.estlett.1c00843

Synergy between Sunlight, Titanium Dioxide, and Microbes Enhances Cellulose Diacetate Degradation in the Ocean. Anna N. Walsh, Michael G. Mazzotta, Taylor F. Nelson, Christopher M. Reddy, and Collin P. Ward. *Environmental Science & Technology* 2022 56 (19), 13810-13819. DOI: 10.1021/acs.est.2c04348

Towards More Sustainable Architectural Coatings

Synergistic Design of Biobased Binders and Improving the Carbon Footprint of Premium Architectural Paints

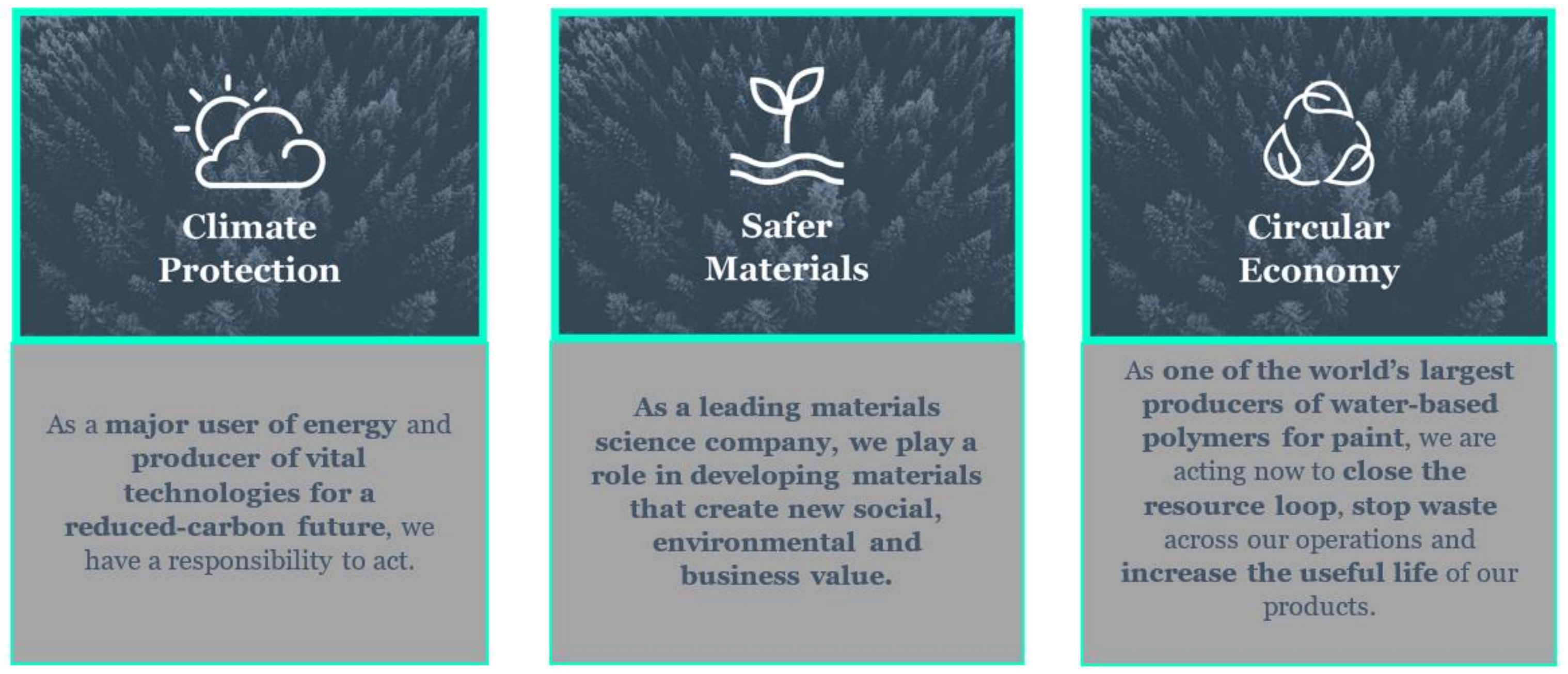
Biorenewable Team: **Erica Frankel**, Paul Doll, Gary Dombrowski, Tara Cary, Omar O'Hara, Tamara Dikic, Rebecca Zaidins, Julie Mahaffey, Pratibha Mahale, Janet Tesfai

Sustainability Focus Areas

Dow wants to be the most innovative, customer-centric, inclusive and sustainable materials science company in the world.

CORE VALUES | RESPECT FOR PEOPLE | INTEGRITY | PROTECTING OUR PLANET

To deliver a sustainable future for the world through our materials science expertise and collaboration with our partners.



Climate Protection

As a **major user of energy** and **producer of vital technologies for a reduced-carbon future**, we have a responsibility to act.

Safer Materials

As a leading materials science company, we play a role in developing materials that create new social, environmental and business value.

Circular Economy

As **one of the world's largest producers of water-based polymers for paint**, we are acting now to **close the resource loop, stop waste** across our operations and **increase the useful life** of our products.

Performance and Sustainability Trends in Coatings

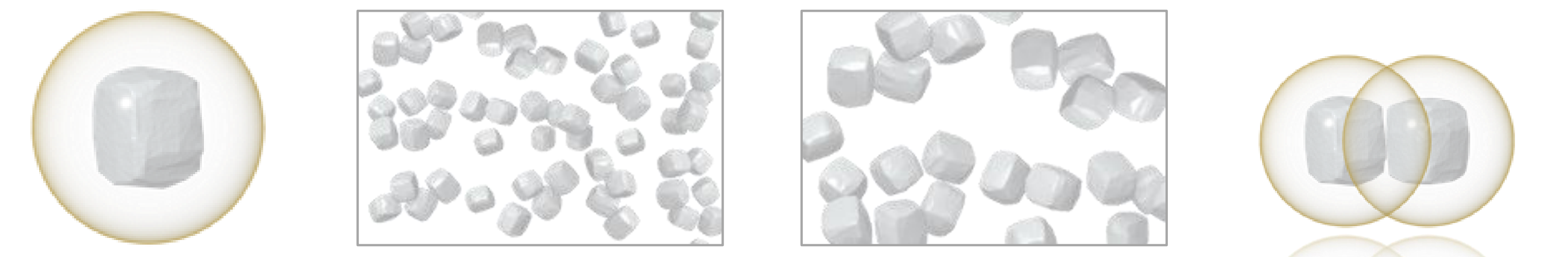
- Bio-based materials
- Pigment-free hiding
- Improved hiding technology
- Indoor air quality improvement
- APEO-free binders and additives
- Binders and additives for low VOC paints

Improved Hiding Technology

ROPAQUE™ and EVOQUE™ Polymers

TiO$_2$ is Best White Pigment for Coatings, But Deficiencies Exist

Dispersion and Agglomeration Issues



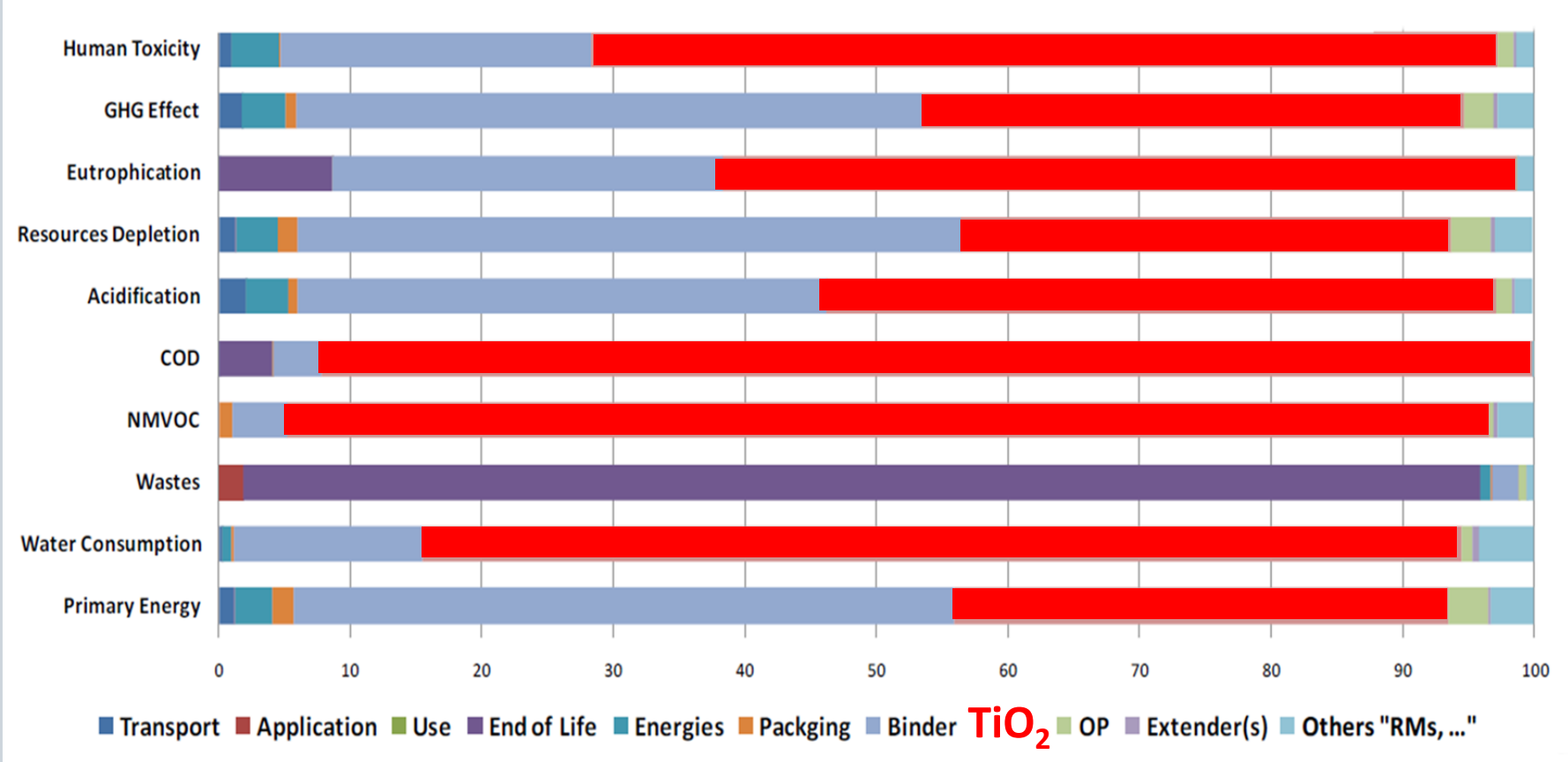
Inefficiencies of TiO$_2$

In a typical paint, TiO$_2$ distribution is worse than random.

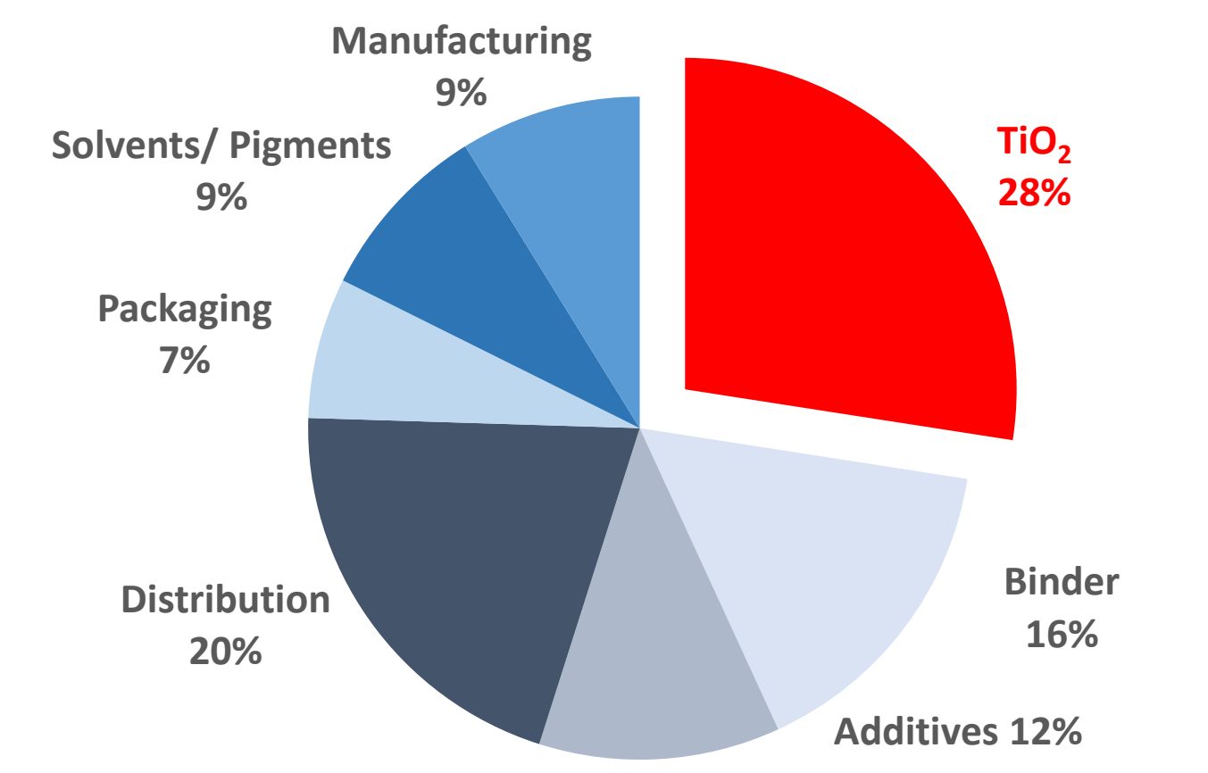
As paint film dries, crowding occurs and creates regions of high and low concentration.

In areas of high concentration, light scattering zones overlap and create inefficiency.

Environmental Impact

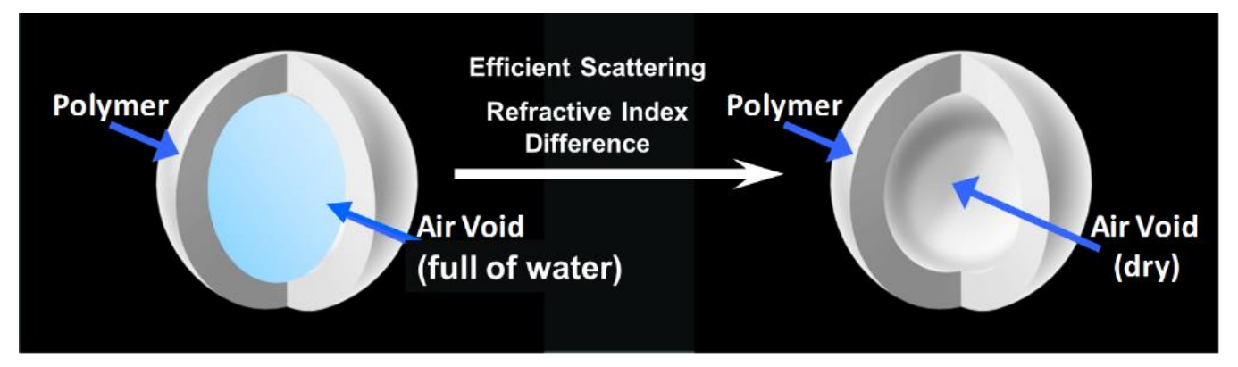


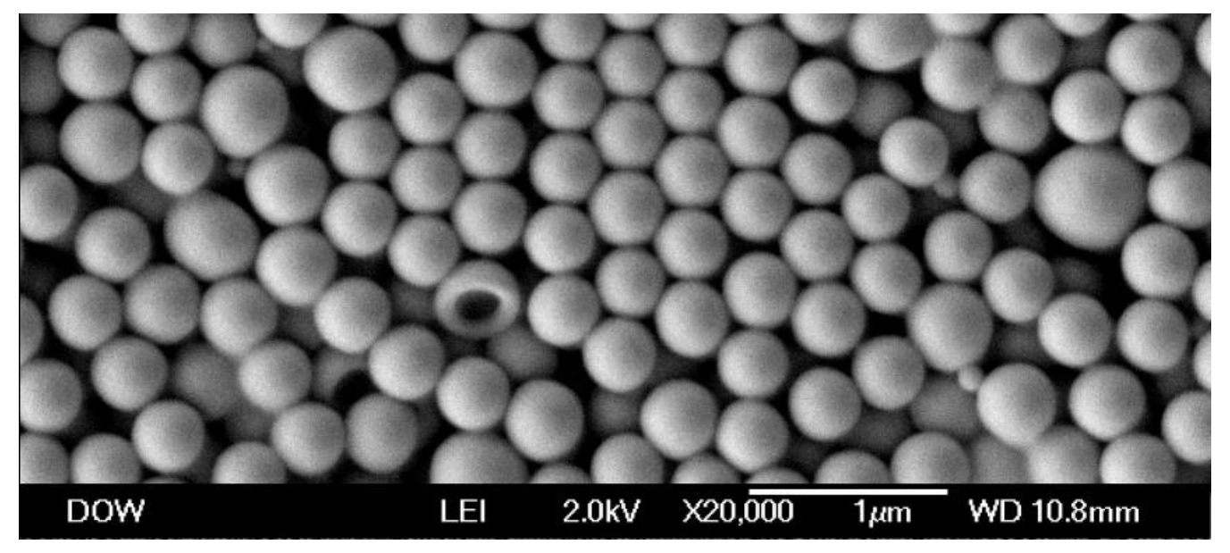
Architectural Paint Costs



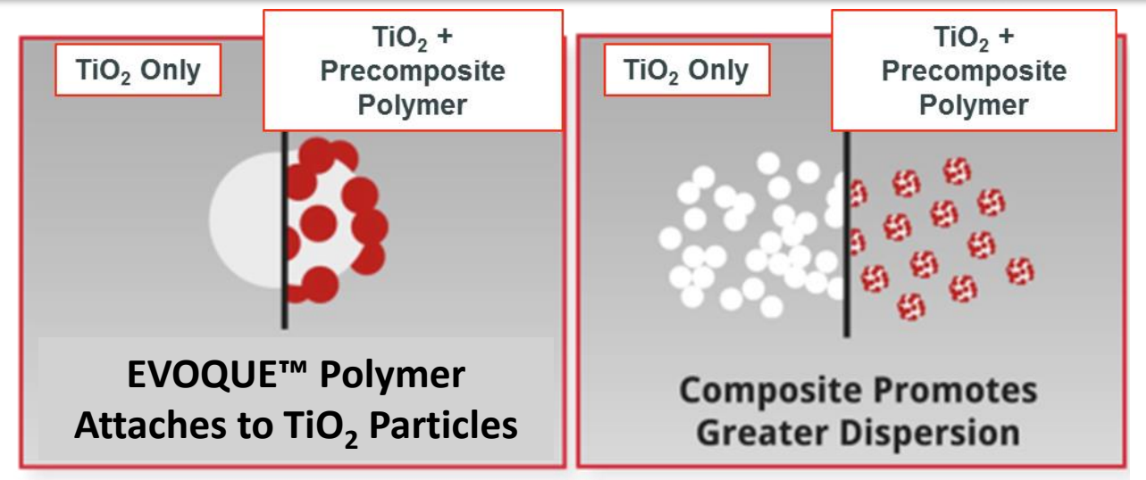
Advancing Sustainability with Polymer Technology

OPAQUE POLYMER



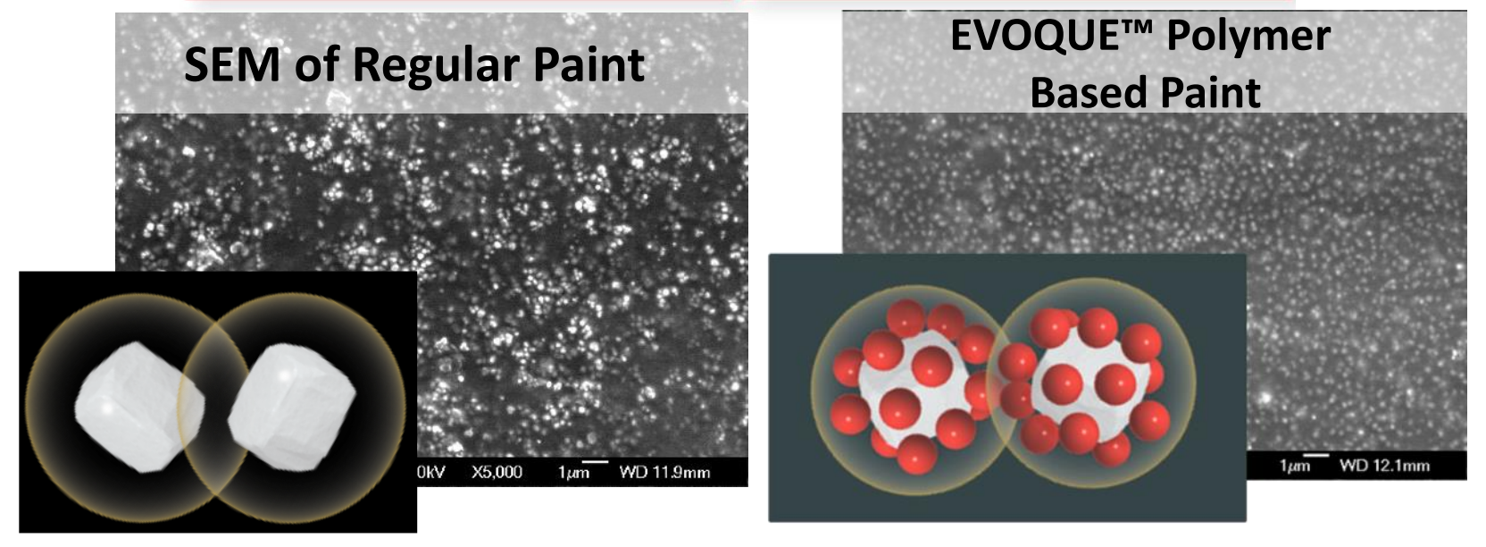


PRE-COMPOSITE POLYMER



EVOQUE™ Polymer Attaches to TiO$_2$ Particles

Composite Promotes Greater Dispersion

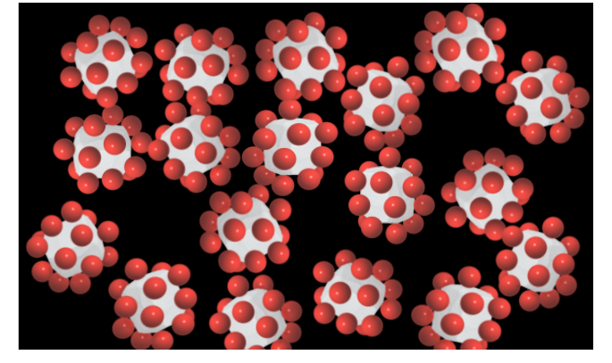


Leveraging Multiple Technologies for Broadest Impact

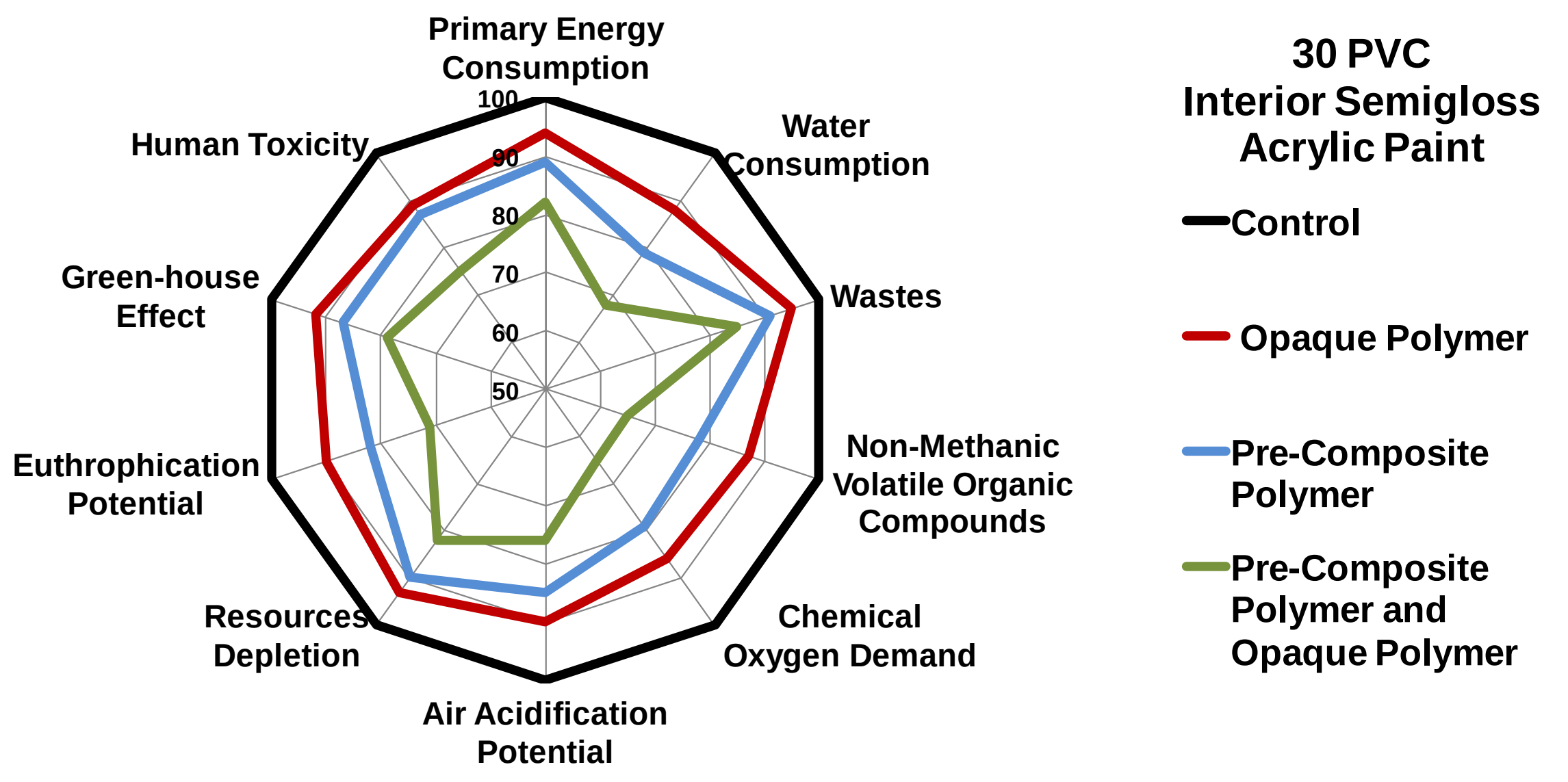
Dispersion Stability

Polymeric Pigment

Pigment Efficiency



(ISO 14040/44, Third Party Validation)

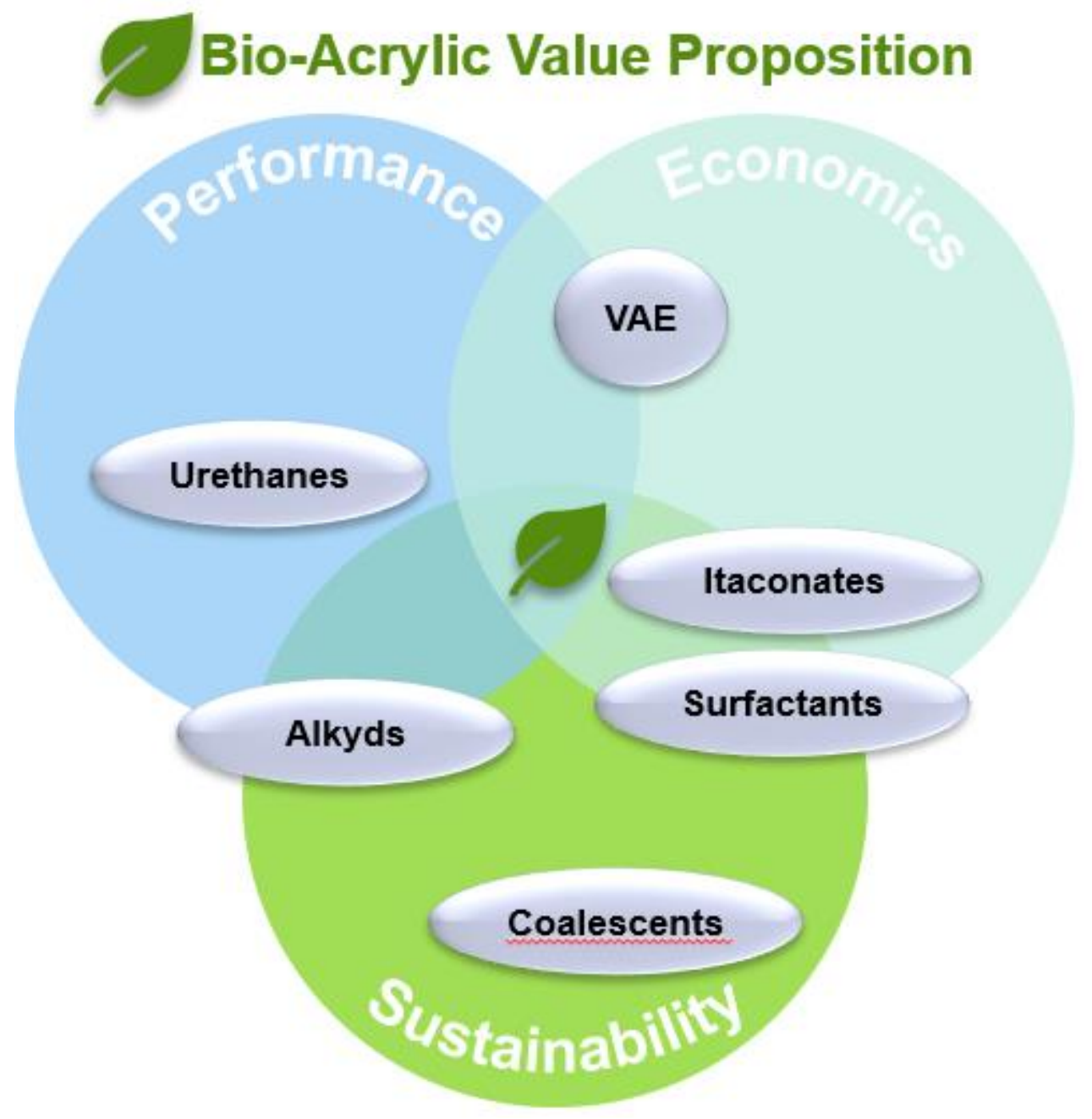


"Comparative Life Cycle Assessment (LCA) of Water-borne paints for internal and external wall decoration and protection," Presentation to Peers for Project Review, Dr. H. Kheradmand, LCA and Sustainable Development Expert, Dow Coating Materials (DCM) EMEA, September 20, 2011.
Trapani, A.; Bleuzen, M.; Kheradmand, H.; Koller, A. The Use of TiO$_2$-Polymer Composites to Lower Environmental Impact and Improve Performance of Waterborne Paints, *Paint Istanbul* **2012**, September.

Innovating Biobased Raw Materials

All-Acrylic EXP-6365 Polymer

Value Proposition for North American Market



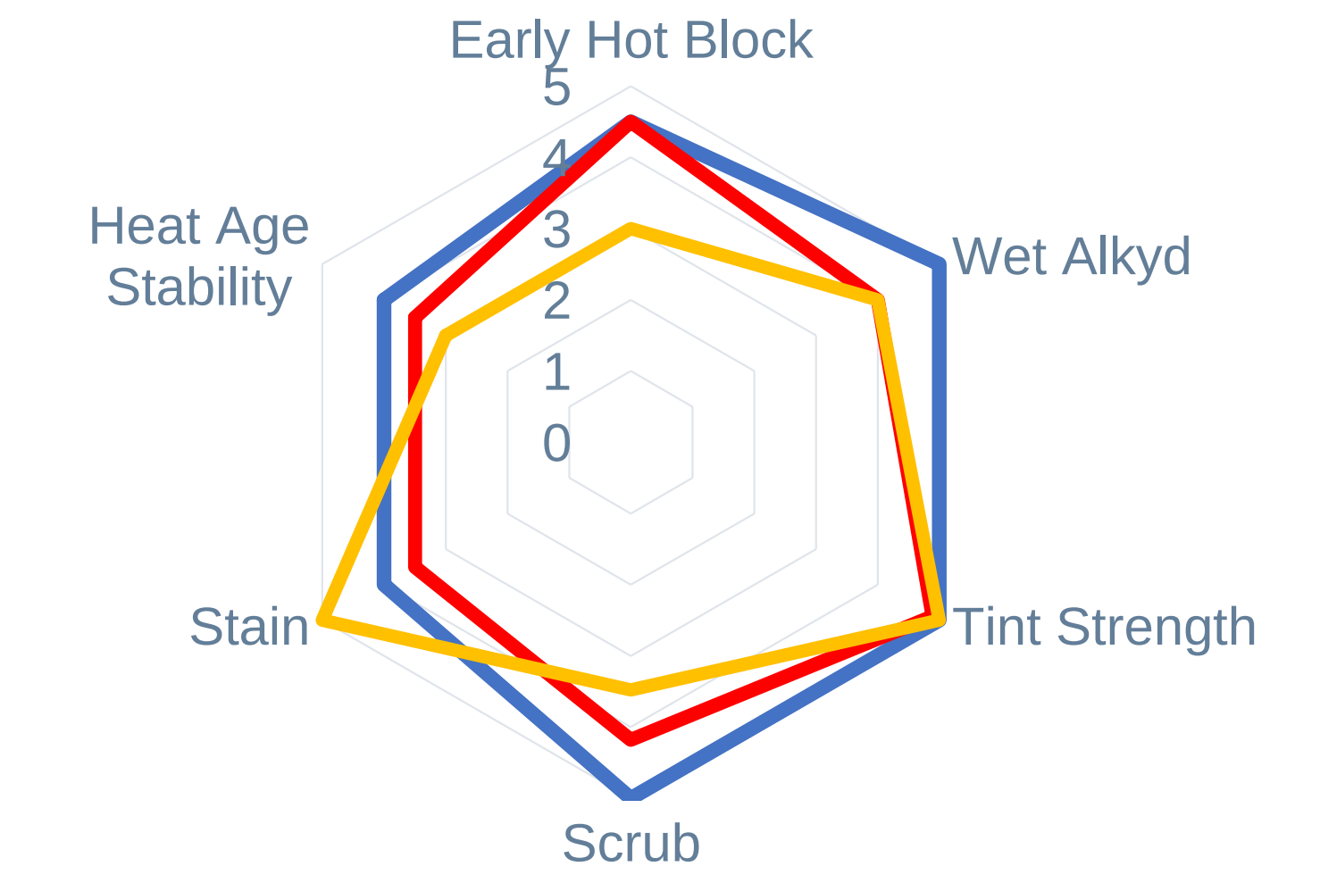
Requirements for Enabling Plant-Based Paints

- No sacrifice in premium acrylic performance
- Quantifiably sustainably advantaged
- Performance and economics that support mainstream adoption

The Binder Drives Performance And %BCC

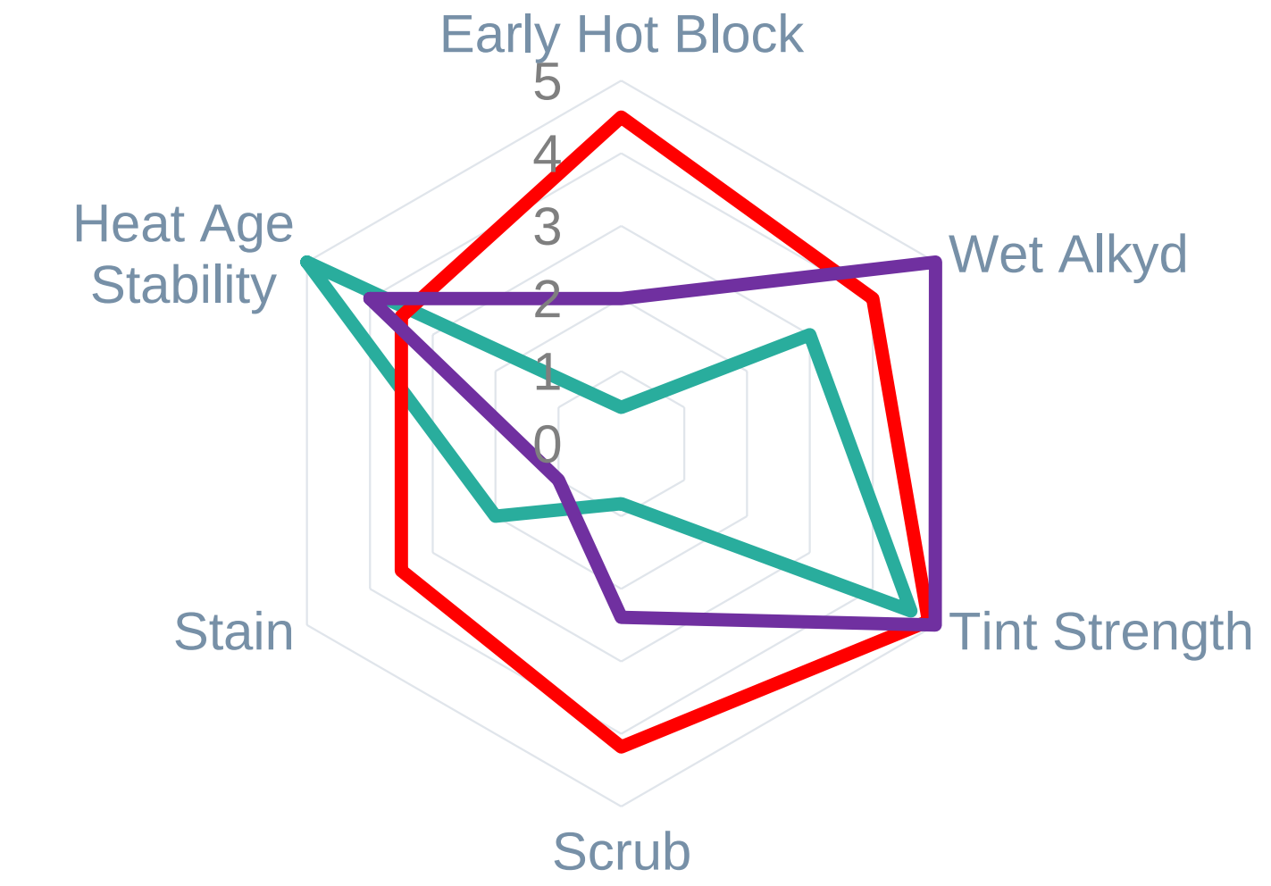
Performance Compared to Petroleum-Based Acrylic Dispersions

Performance Against All-Acrylic Emulsions



EXP-6365 Biobased Binder
RHOPLEX™ 101 Premium Acrylic Emulsion
RHOPLEX™ Basic Acrylic Emulsion

Performance Against Commercial Paint



EXP-6365 Biobased Binder
Quality All-Acrylic Paint A
Economy Paint B

*Typical values, not to be construed as specifications. Users should confirm results by their own tests.

Performance versus leading petroleum-based polymer dispersions

- Formulated into flat and semigloss interior paints
- Comparable scrub, stain, colorant compatibility, heat-age stability
- Superior block resistance

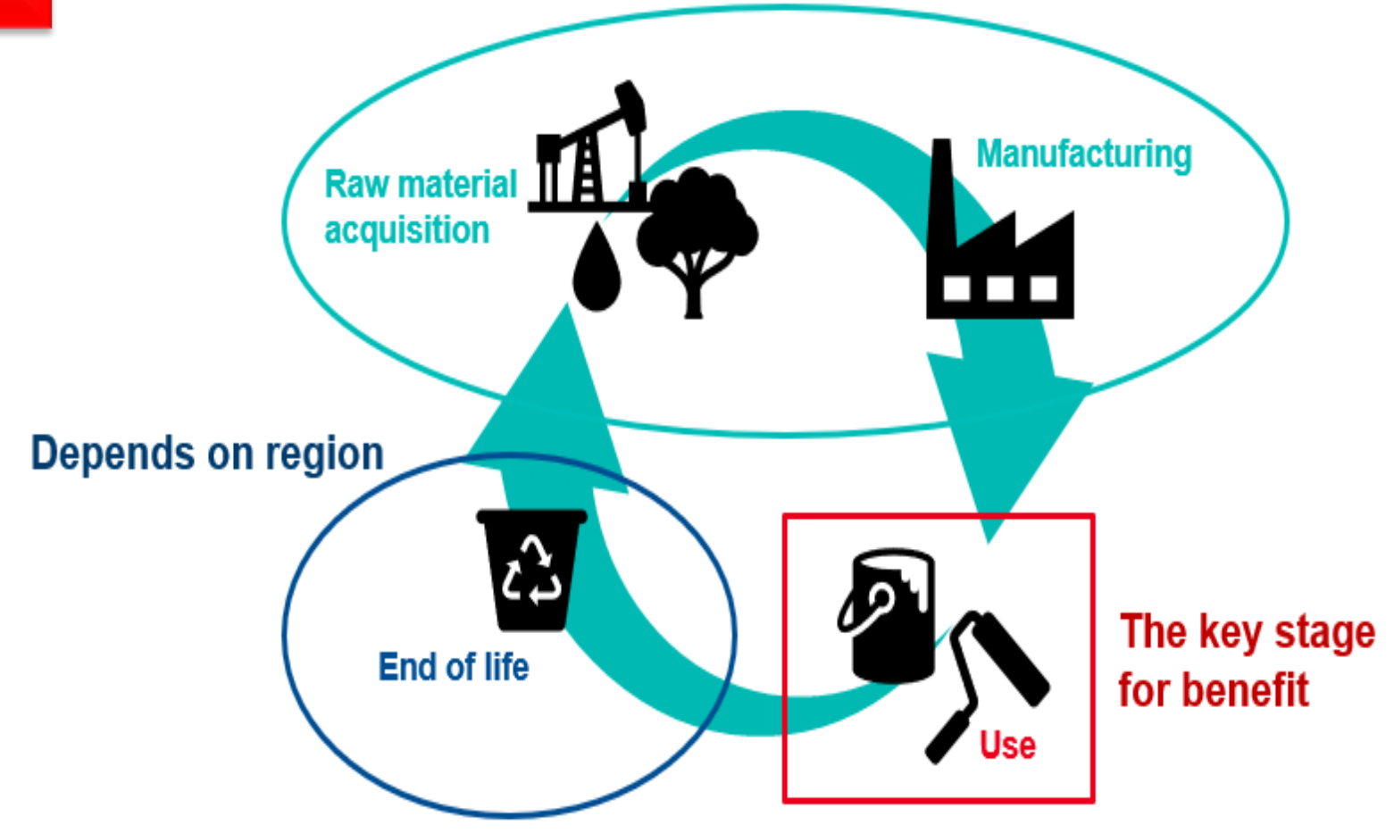
Enhancing Sustainability Through Biobased Binders

NORTH AMERICAN PROGRAM STATUS

- Biobased acrylic emulsion in final stages of development.
- LCA calculations ongoing in parallel with development.
- Next Step: Third party validation of paint LCA

✓ Incorporation of bio-feedstock into acrylic paint
✓ Quantifiable Sustainable Advantage
✓ No Sacrifice of Paints Performance
✓ Not Relegated to Niche Markets

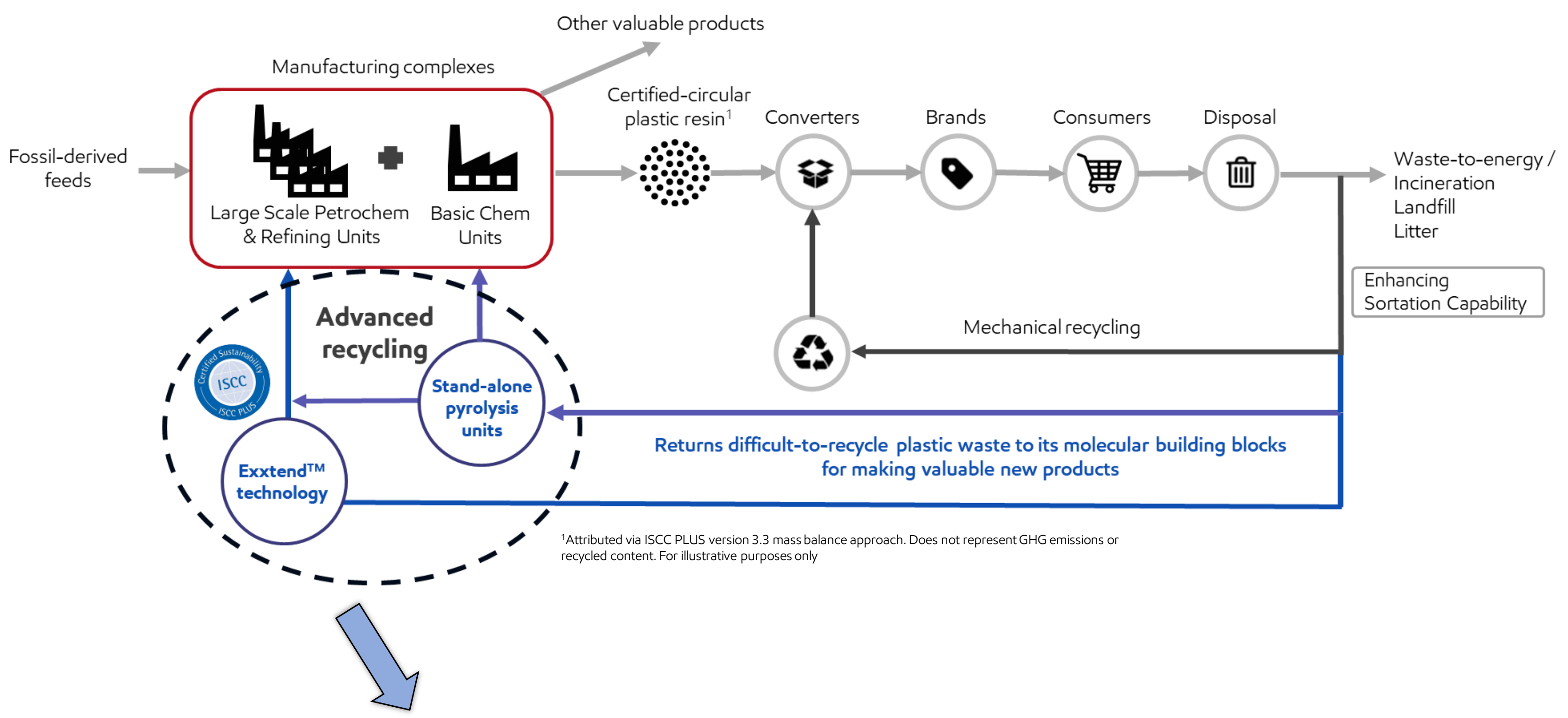
Direct Impact by Dow & Paint Manufacturers



Advanced Recycling of Polyolefins

Adam S. Gross
ExxonMobil Technology and Engineering Company
adam.s.gross@exxonmobil.com

Advanced Recycling Facilitates a More Circular Economy

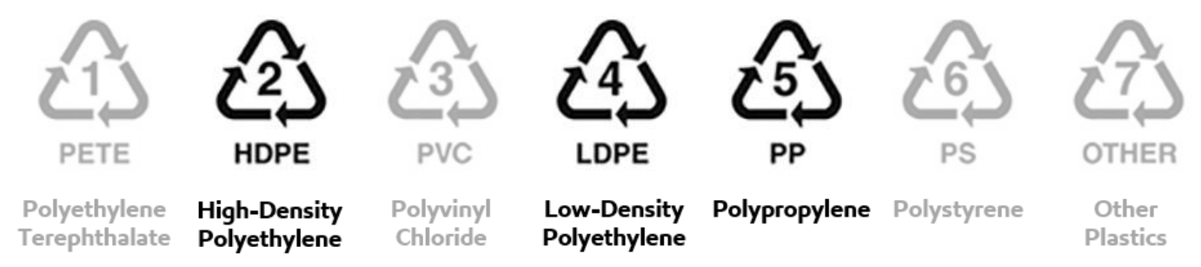


[1]Attributed via ISCC PLUS version 3.3 mass balance approach. Does not represent GHG emissions or recycled content. For illustrative purposes only

Advanced Recycling Works Together with Mechanical Recycling:

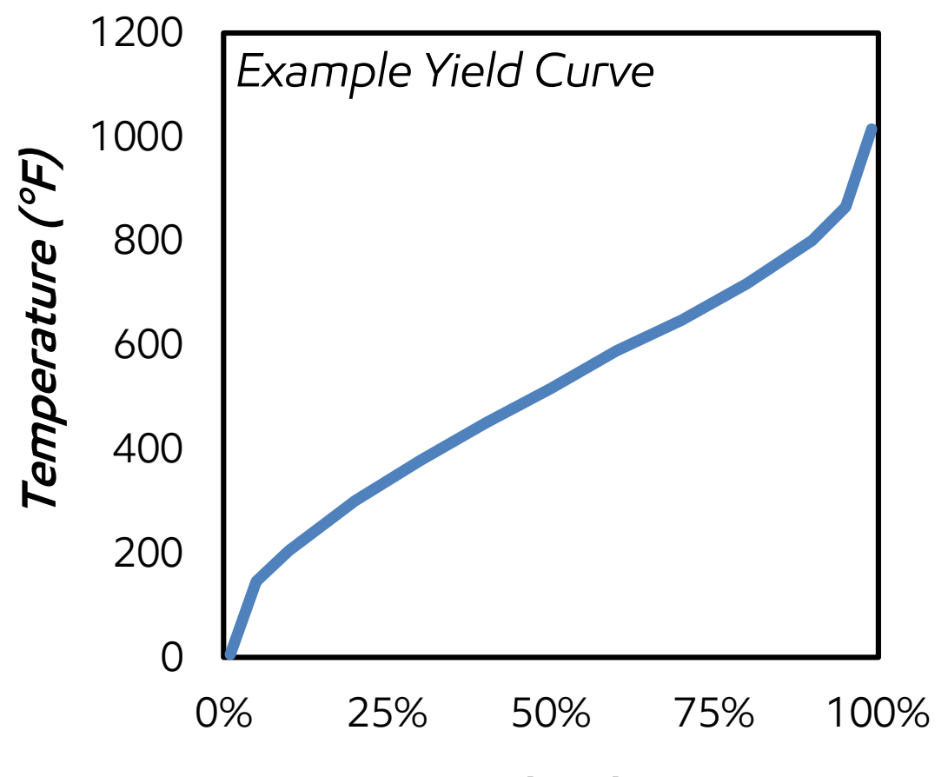
- Accepts feeds that can be difficult to mechanically recycle
- Makes products mechanical recycling cannot produce

Pyrolysis – A Route for Advanced Recycling of Polyolefins (POs)



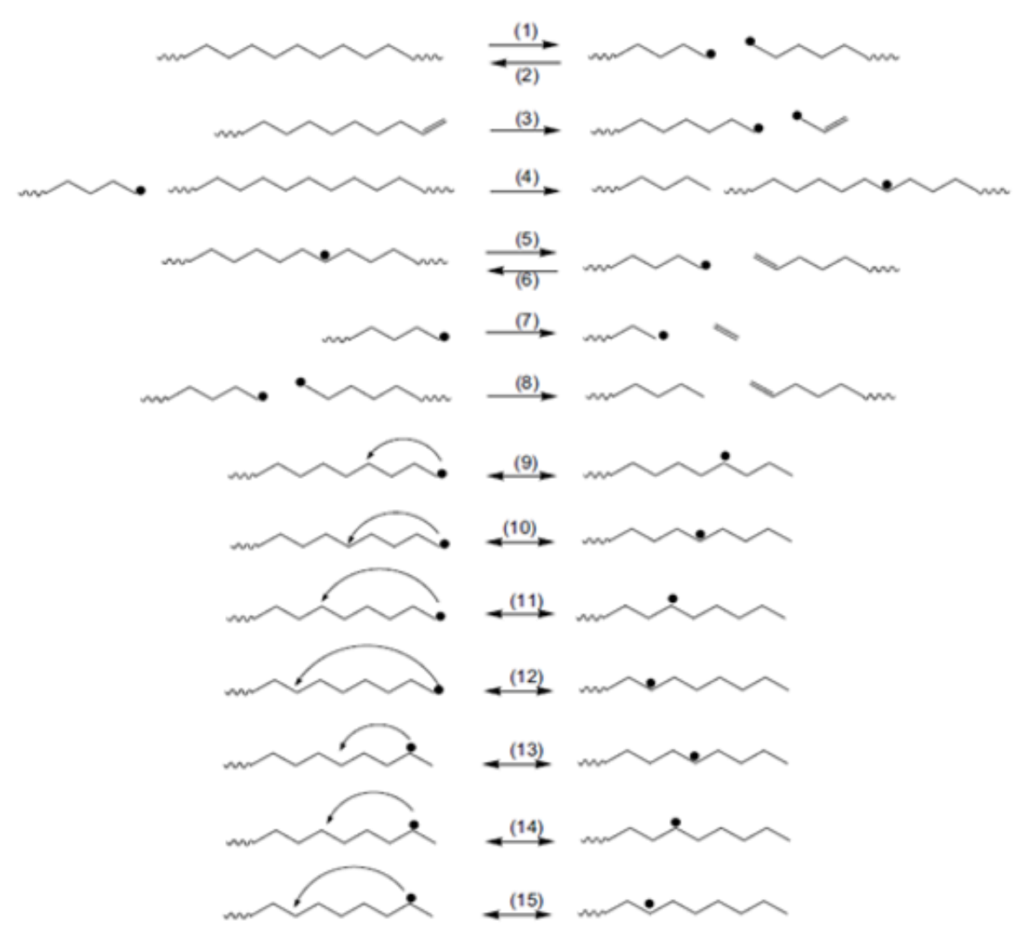
Heat → *optional catalyst*

Mix of Liquids, Gasses, & Solids



Fundamental Processes of PO Pyrolysis

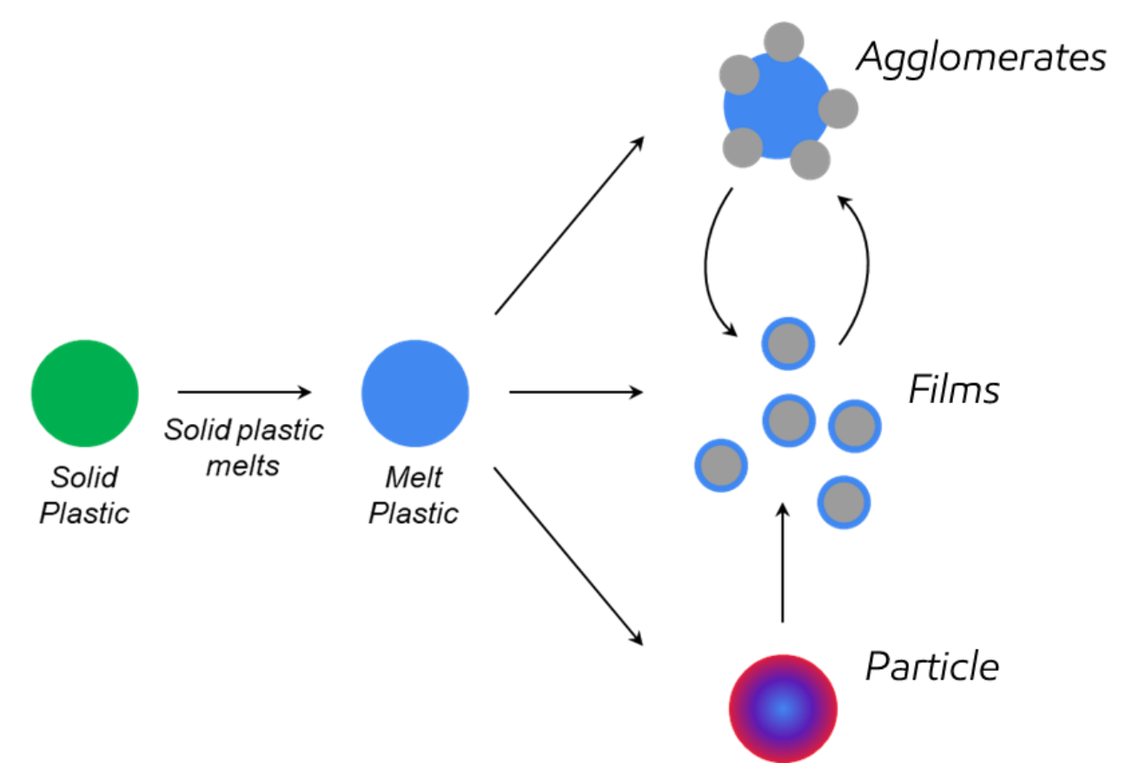
Intrinsic Chemistry[2]



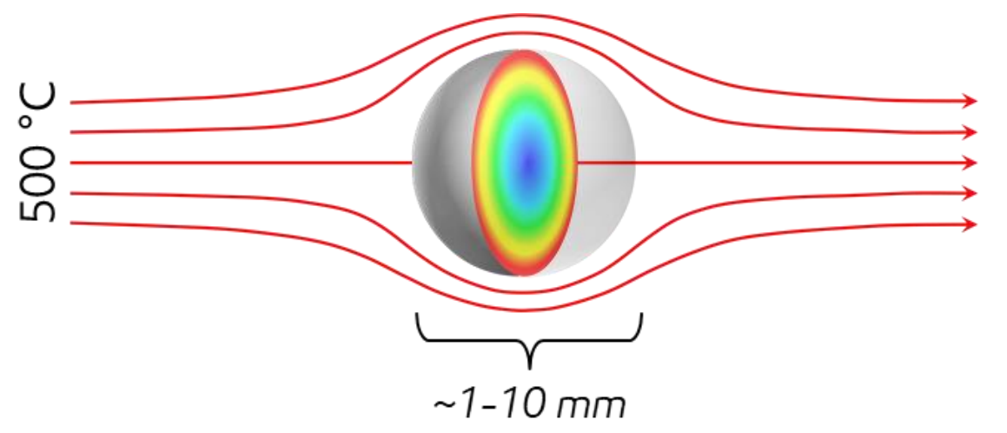
Reaction Pathways

1. Bond Fission
2. Radical Recombination
3. Allyl bond fission
4. Hydrogen Abstraction
5. Mid-chain β-scission
6. Radical Addition
7. end-chain b-scission
8. Disproportionation
9. 1,4-hydrogen shift
10. 1,5-hydrogen shift
11. 1,6-hydrogen shift
12 1,7-hydrogen shift
13 x,x + 3-hydrogen shift
14 x,x + 4-hydrogen shift
15 x,x + 5-hydrogen shift.

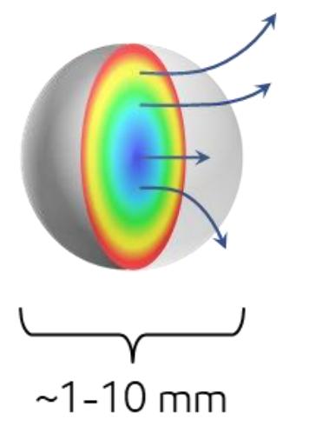
Phase Behavior and Mixing



Heat and Mass Transport



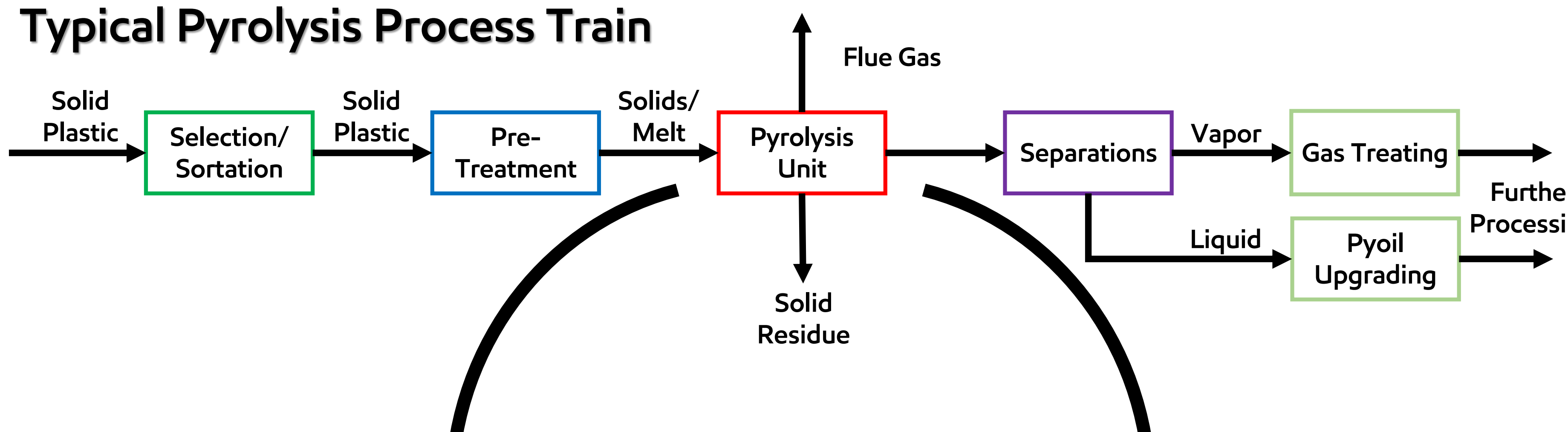
~1-10 mm
Heat transfer limitations



~1-10 mm
Mass transfer limitations

Implementing Polyolefin Pyrolysis

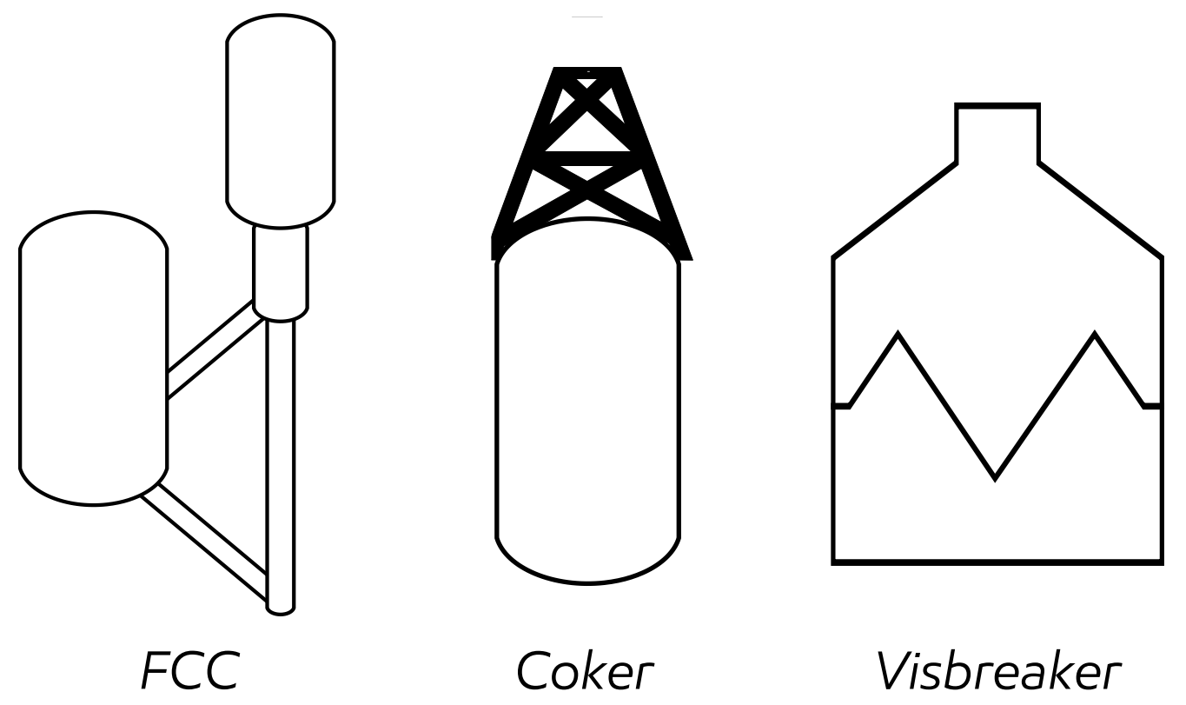
Typical Pyrolysis Process Train



Options for Pyrolysis Units

Co-Processing

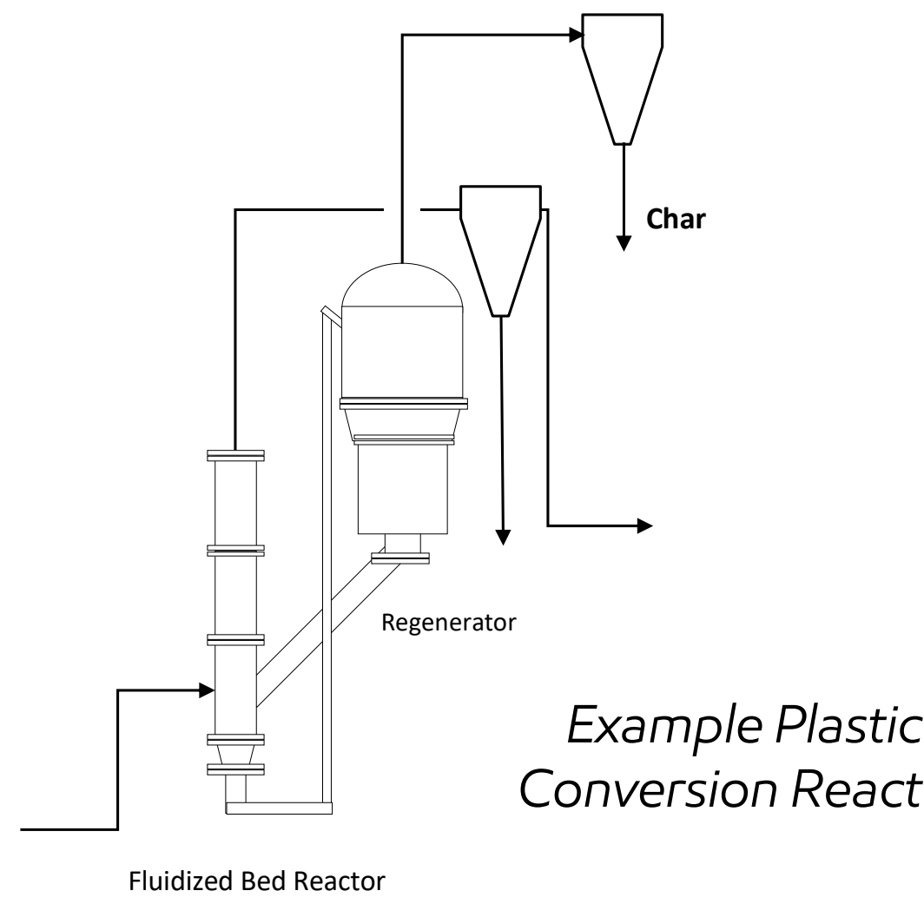
Leverage Existing Units Already Used for Pyrolysis Chemistry



- *Plastics conversion an extension of existing heavy hydrocarbon upgrading*
- *Limited to low plastic contents to maintain effective reactor performance & manage contaminants*

Grassroots

Build a new unit for on-purpose plastic pyrolysis

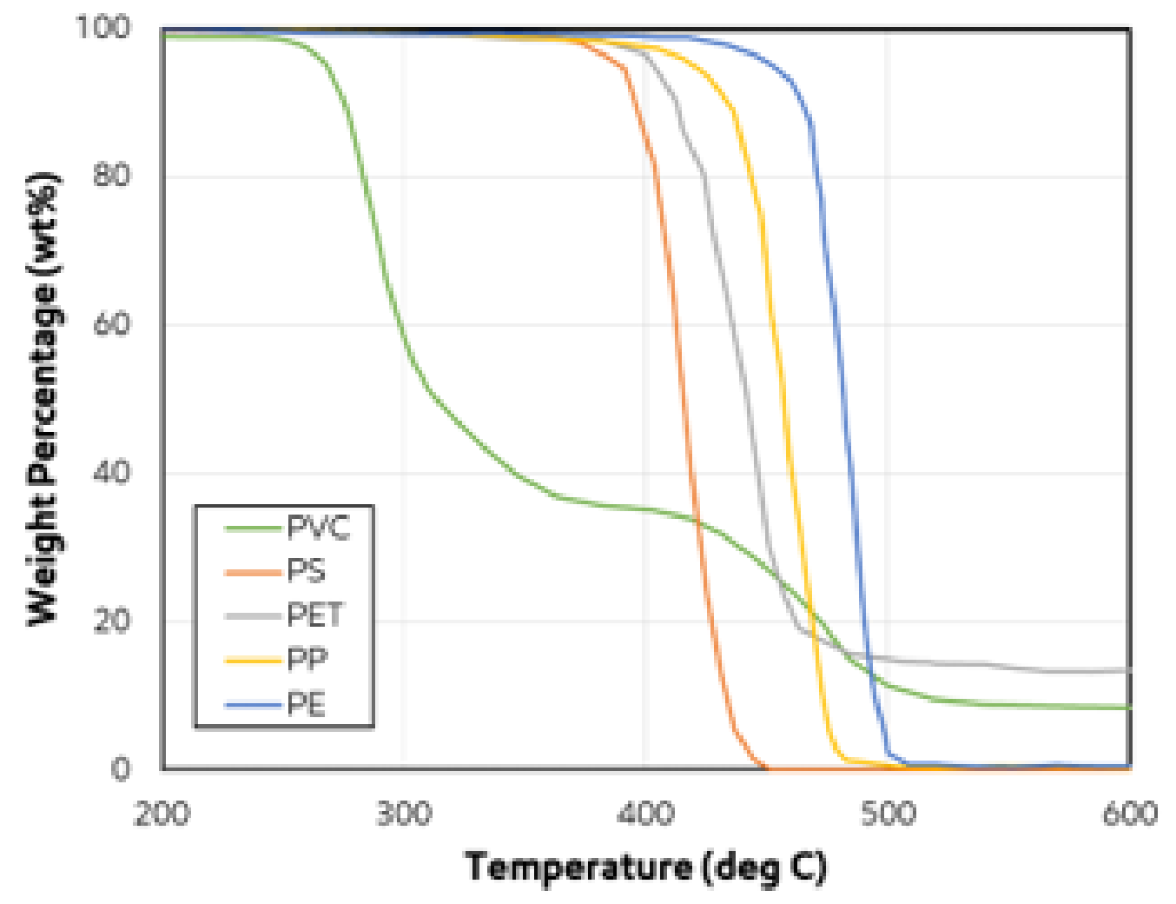


Example Plastic Conversion Reactor

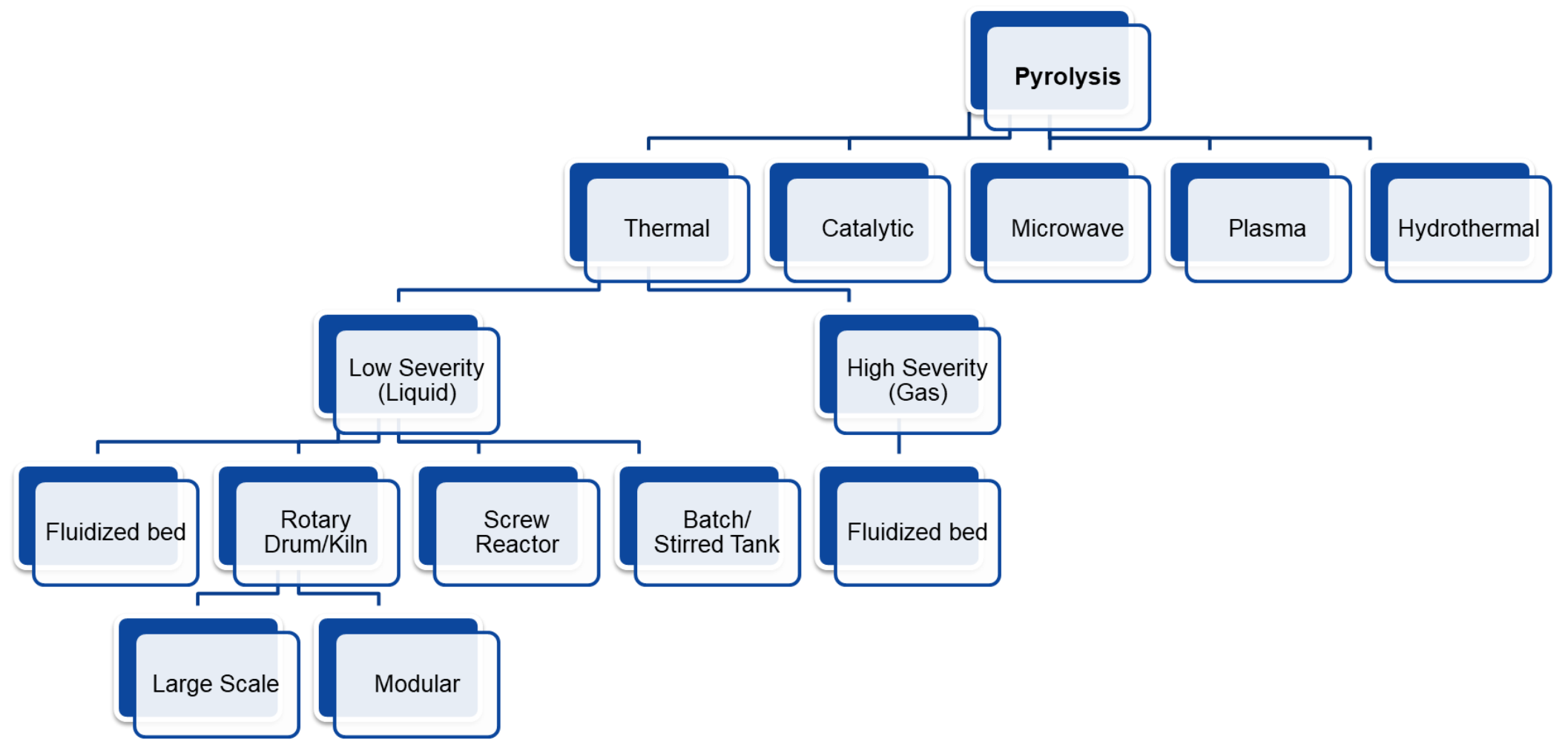
- *Requires construction of new conversion unit*
- *Flexibility in unit design for fit for purpose*
  - *~100% plastic waste in feed (excluding recycle)*
  - *Tailor design/operation for feed and product targets*

Factors Affecting Pyrolysis Process

Feed Composition[3]



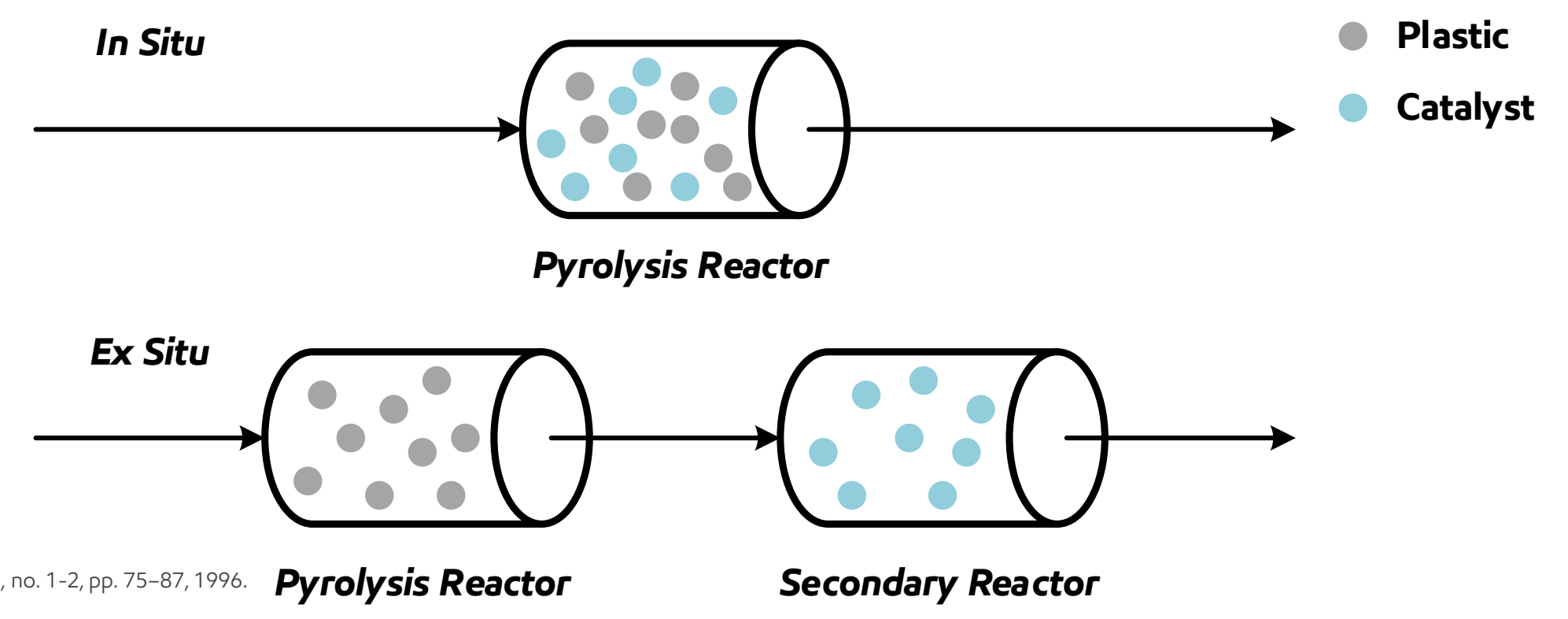
Reactor Design



Operating Conditions[4]

Temperature (°C)	605	655	700
Residence Time (s)	3.5	2.7	3.2
Gases (wt %)	30.0	68	72.0
Liquids (wt %)	70.0	31.4	27.1
Solids (wt %)	0	0.6	0.9

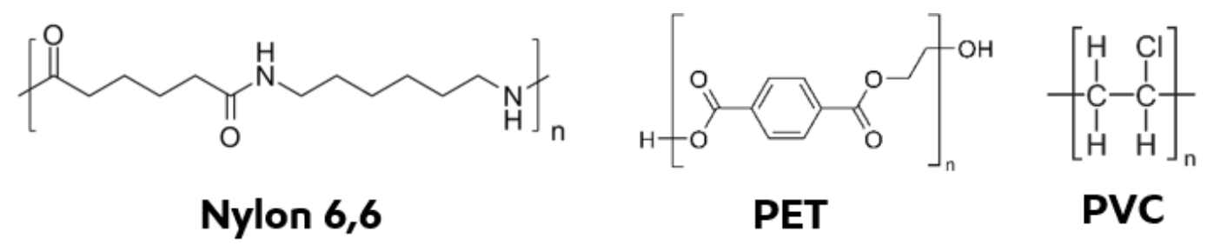
Use of Catalysts



Feed Quality Challenges & Opportunities

- *Polyolefin waste often comes with a host of different types of non-PO contaminants*
- *Managing and mitigating these contaminants is a challenge and an opportunity*
- *Ability to handle higher levels of contamination increases feed supply & lowers feed costs*

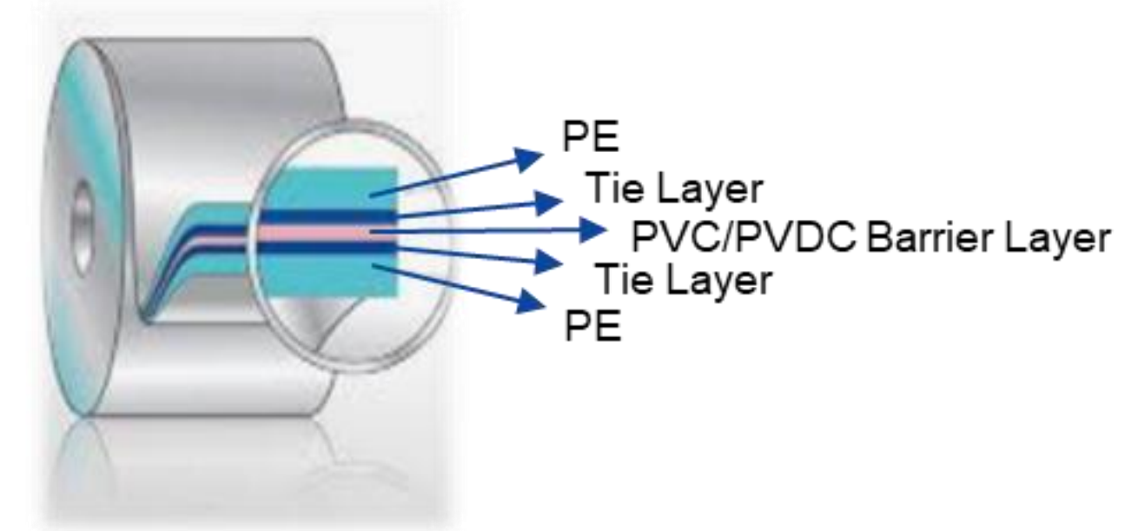
Residual Missorted Material



Many common polymers contain undesirable heteroatoms

Non-polymeric materials

Multicomponent Materials



Multilayer films typically contain non POs and heteroatoms

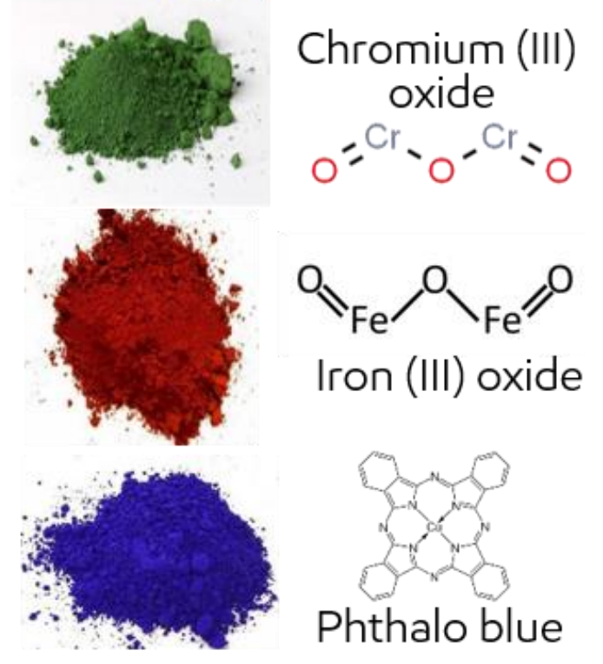
Common multilayer materials

Fillers, Additives, & Residual Processing Materials

Fillers

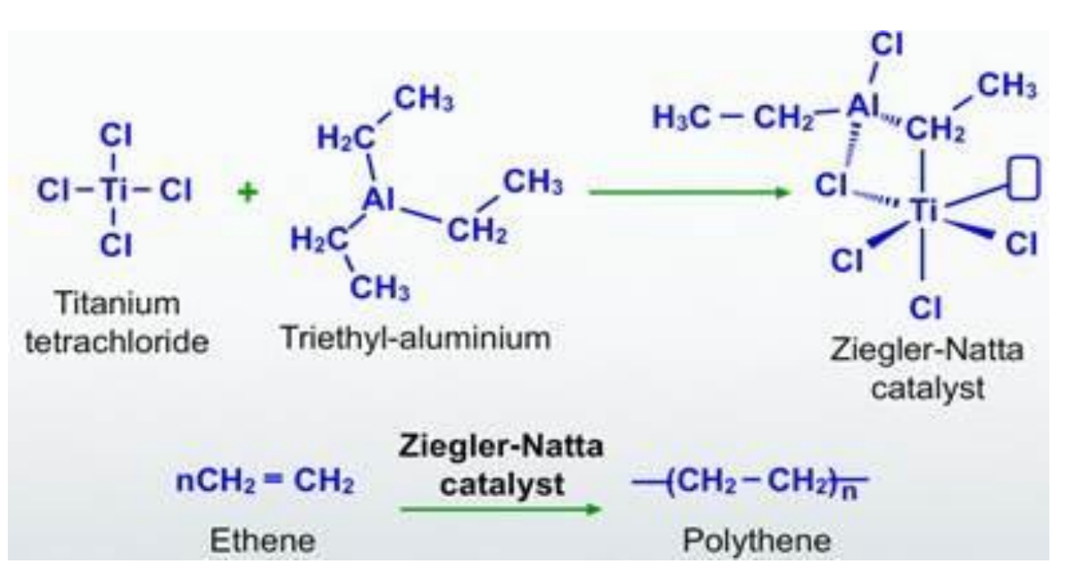
$CaCO_3$ filler, TiO_2 pigment, Talc (Mg, Si), SiO_2 particles

Pigments



Chromium (III) oxide, Iron (III) oxide, Phthalo blue

Fillers can be 10 wt % of a plastic article or more
Additives such as pigments bring a host of exotic chemistries



Example polyolefin catalyst

Surface Contamination

Environmental contamination

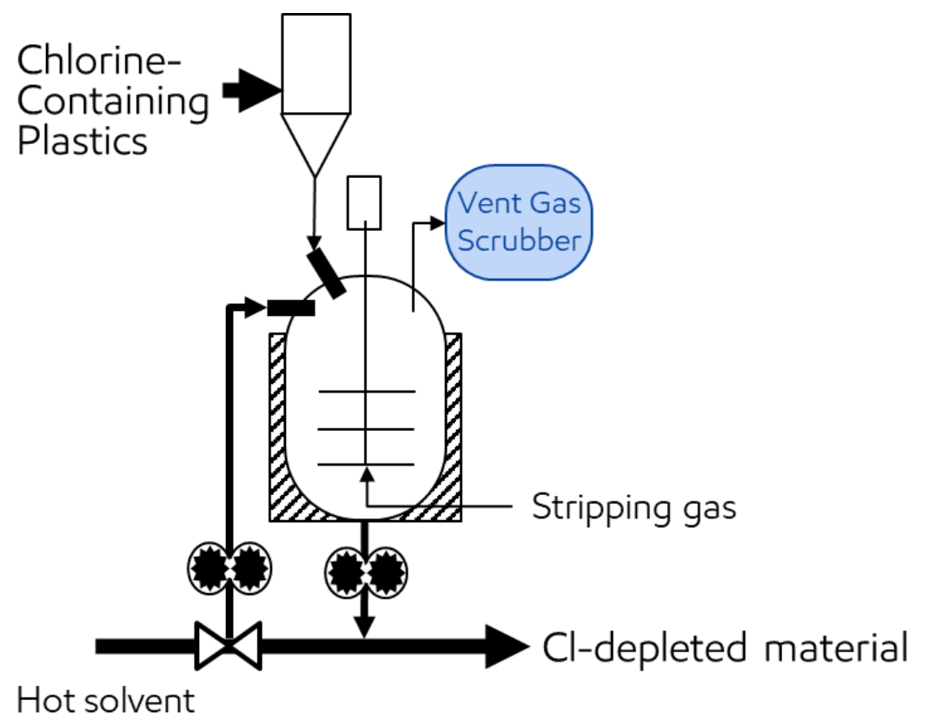
Product residues

Variations in PO Composition

Plastic Source	Plastic Hospital Bags	Mulch Bags	Bread Bags
Supplier Polymer Description	Polyethylene	Polyethylene	Polyethylene with Barrier Layer
Carbon (wt%)	74	69	80
Hydrogen (wt%)	12	11	13
Nitrogen (wt%)	0.13	0.30	0.20
Oxygen (wt%)	-	2.4	-
Chlorides (ppm)	500	400	-
Calcium (ppm)	53,000	4100	420
Sodium (ppm)	120	150	180
Iron (ppm)	210	6300	7900
Magnesium (ppm)	78	1200	80

Contaminant Management Strategies

- ***How much to remove?***
  - *Equipment safety & reliability*
  - *Product quality*
- ***Where to remove?***
  - *Pre- or post-pyrolysis*
- ***How to remove?***
  - *Mechanical or chemical*



Ex. Chemical removal of Cl from PVC

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[2]Adapted from Seth E. Levine, Linda J. Broadbelt, "Detailed mechanistic modeling of high-density polyethylene pyrolysis: Low molecular weight product evolution," Polymer Degradation and Stability, no. 94, pp. 810–822, 2009.

[3]Adapted from Yu, J., Sun, L., Ma, C., Qiao, Y., Yao, H., "Thermal degradation of PVC: A review," Waste Management, 48 (2016): 300–314.

[4]Adapted from C. Simon, W. Kaminsky, and B. Schlesselmann, "Pyrolysis of polyolefins with steam to yield olefins," Journal of Analytical and Applied Pyrolysis, vol. 38, no. 1-2, pp. 75–87, 1996.

Generative AI: An Innovative Approach for using Artificial Intelligence to Drive Productivity

Vince Herrera – Digital Product Leader
DuPont

Introduction

Generative AI (GenAI) is a powerful technology that is transforming a wide range of industries.

- Gen AI is a subfield of artificial intelligence that involves the use of algorithms to **generate new data or content**, such as images, text, video and audio.
- It involves the use of deep learning techniques such as **neural networks to learn patterns** and generate new output that is similar in style or content to existing data.

Objectives

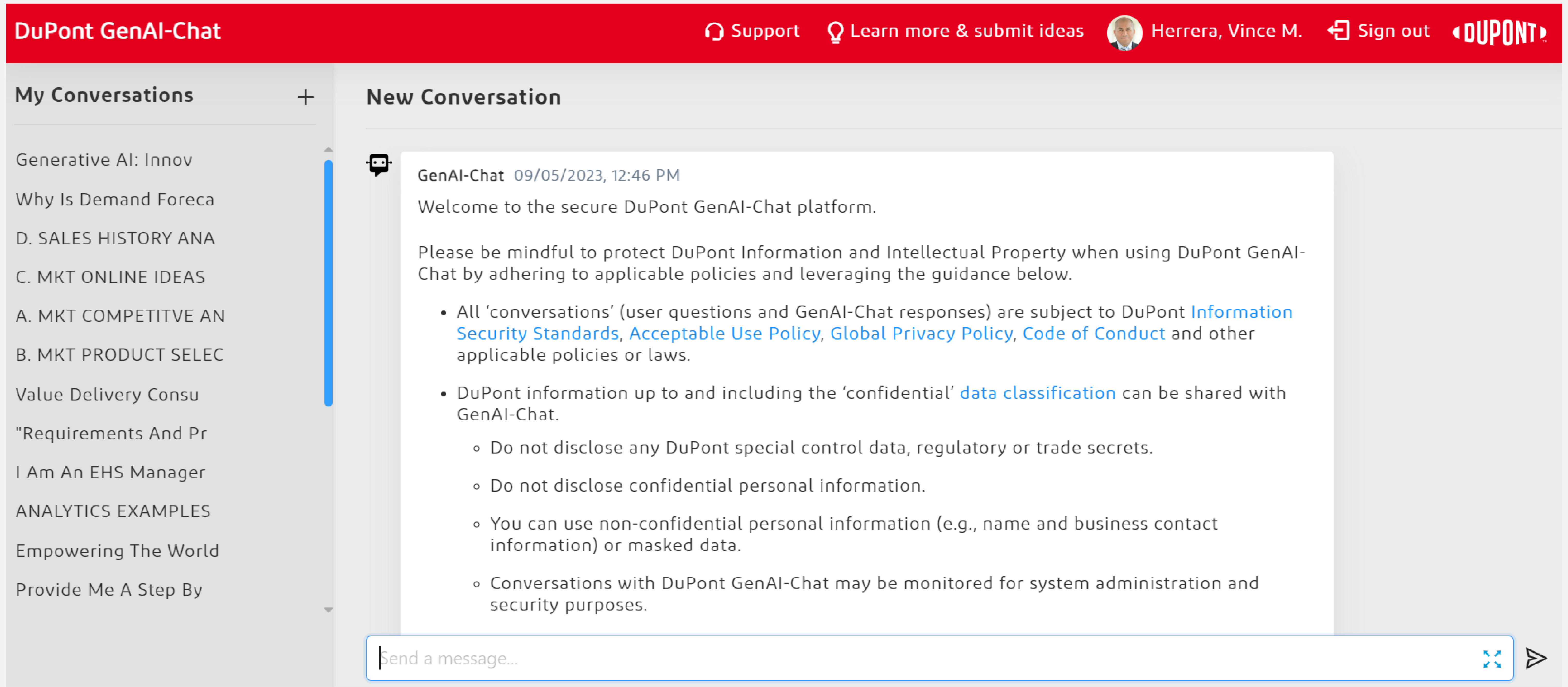
GenAI will **transform work** by automating the **generation** and **interpretation** of content

- Leverage capabilities of summarization, categorization, translation and sentiment
- Create a secure environment for employees to use GenAI to deliver **value in productivity**
- Use internal data to position GenAI as a **digital advisor** for various enterprise needs

Methods

Integration of DuPont data within a **secure** Microsoft Azure enclave using OpenAI model

Microsoft Azure
OpenAI
DUPONT

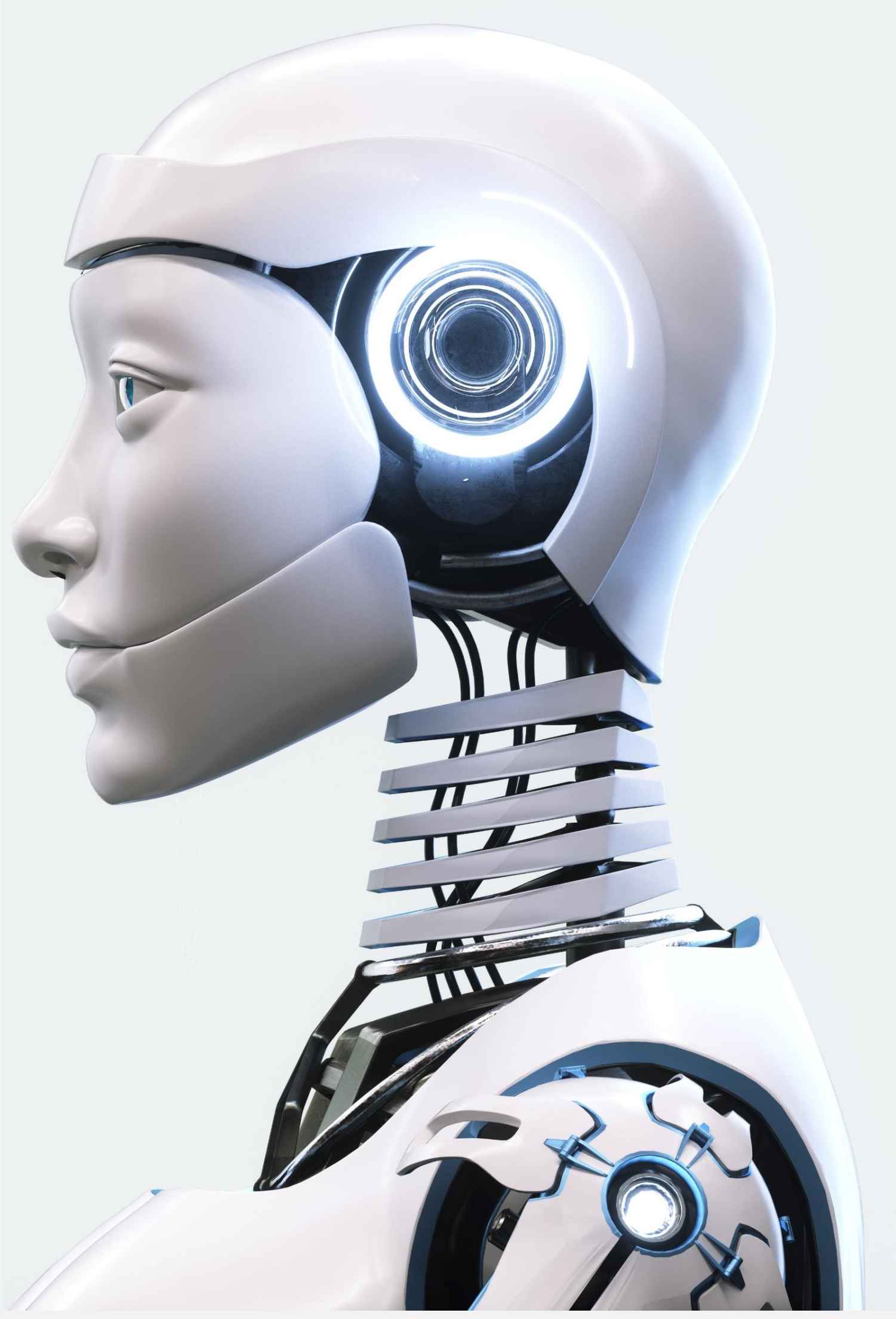


GenAI-Chat 09/05/2023, 12:46 PM

Welcome to the secure DuPont GenAI-Chat platform.

Please be mindful to protect DuPont Information and Intellectual Property when using DuPont GenAI-Chat by adhering to applicable policies and leveraging the guidance below.

- All 'conversations' (user questions and GenAI-Chat responses) are subject to DuPont Information Security Standards, Acceptable Use Policy, Global Privacy Policy, Code of Conduct and other applicable policies or laws.
- DuPont information up to and including the 'confidential' data classification can be shared with GenAI-Chat.
  - Do not disclose any DuPont special control data, regulatory or trade secrets.
  - Do not disclose confidential personal information.
  - You can use non-confidential personal information (e.g., name and business contact information) or masked data.
  - Conversations with DuPont GenAI-Chat may be monitored for system administration and security purposes.



DUPONT

Conclusion

- Accelerate R&D search to expedite development
- Streamline responses on sustainability Q&A
- Faster resolution on Information Technology inquiries and support
- General knowledge search for Marketing and Customer Service

Vespel® Enables Longer Service Life and Enhances Performance in Hydrogen Applications

Natalie Kadlubowski, Jenn Chickola, Ruth Jackowiak, Patrick Liekens, Luke Amspacher, Yuichi Maruyama

Vespel® Research & Development, Technical Service & Development

Introduction

DuPont™ Vespel® polyimides have been used for decades in the most demanding applications where **thermal and dimensional stability, soft-yet-strong mechanical properties, and strong wear and friction behavior** are required in mechanical components. With a new wave of hydrogen adoption ramping up, Vespel® polyimides have shown promise in the unique and challenging application environments inherent to **hydrogen generation, storage, and consumption.**

Problem

While hydrogen offers a carbon-free fueling solution, its **low energy density, small molecular size**, and **wide flammability range** pose processing challenges. It must be either **highly compressed** or **liquefied at extremely low temperatures** to achieve viable energy densities, the materials used for **tanks, seals, and valves must be able to prevent escape of the very small and flammable gas**, and some applications require **unlubricated systems to prevent contamination**. Because many of these requirements can overlap, it is necessary to find materials that can meet all these needs at once.

Materials and Methods

Compressive Modulus: The ratio of compressive stress to strain measures material stiffness; high values represent high resistance to deformation.

- Samples were tested per ASTM D-695 at ambient and cryogenic temperatures.

Compressive Creep: Creep indicates the deformation a material experiences over time under a constant load; higher values show higher deformation.

- Ø 8 mm x h 16 mm slugs were loaded for 600 hours, measured before and after.

Permeability: Low permeability-materials resist through-plane fluid transmission better than those with higher permeability.

- Data courtesy of Kyushu University; 1.5 mm PEEK, POM, Vespel® SP-1 and SCP-5000 films tested at 90 MPa differential pressure for permeation via GC at 30, 90 °C.

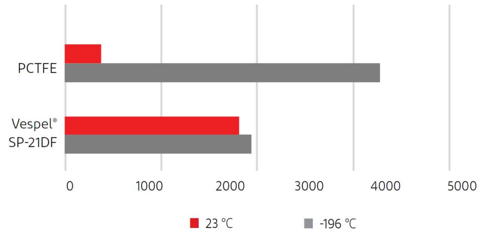
Dynamic Friction and Wear Factor: The dynamic coefficient of friction is defined as the ratio of steady-state frictional to normal force. Wear factor is defined as the volume of material lost per unit pressure and distance over the entire test.

- Data courtesy of Bundesanstalt für Materialforschung und -prüfung (BAM); Counterface AISI 304, Ra ~ 0.2 µm, v = 0.2 m/s, P = 3 MPa.

Results and Discussion

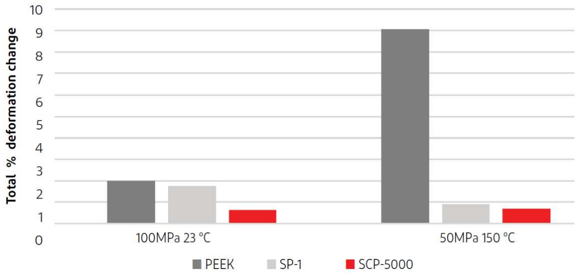
Compressive Modulus

[MPa]



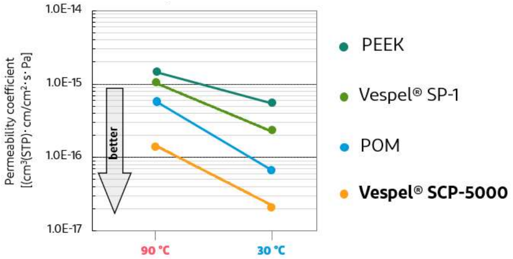
PCTFE and graphite-filled Vespel® SP-1 were compared at room and cryogenic temperatures to determine cryogenic sealing efficacy. A material with a consistent modulus over a range of temperatures will show consistent sealing performance, **enabling designs to accommodate large temperature swings**.

Compressive Creep



PEEK, Vespel® SP-1, and SCP-5000 were tested for compressive deformation over time. At both conditions, the Vespel® slugs showed lower creep, with a more pronounced difference at higher temperatures despite lower loading. Low creep can translate to **longer lifetimes for load-bearing parts**, including thrust washers or bushings.

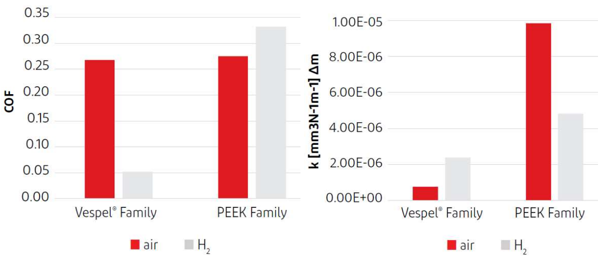
Permeability



Hydrogen permeation through PEEK and POM was compared with Vespel® SP-1 and Vespel® SCP-5000. Even at elevated temperatures, SCP-5000's permeability was a fraction of POM, the second-best sample tested. **Low permeability is critical for seals and valves** containing one of the smallest molecules in the universe; concentrations as low as 4% in air can pose a serious explosion risk.

Dynamic Friction

Wear Factor



Several Vespel® materials were compared with PEEK-based materials in a block-on-ring setup in air and gaseous hydrogen. Despite similar levels of friction in air, the Vespel® materials show *lower* friction in hydrogen, and show substantially lower wear than PEEK-based materials overall. **Lower friction and wear translate to better performance and the need for less frequent replacements** in wearing parts.

Conclusions or Future Application

Vespel® is the answer to the most stringent sealing requirements in hydrogen applications, thanks to its unique blend of thermal, mechanical, and tribological properties.

- **Low and consistent compressive moduli and creep rates**, coupled with high mechanical resistance enable exceptional sealing even at cryogenic temperatures.
- **Significantly lower permeability than materials like PEEK** prevents dangerous and costly fugitive hydrogen emissions.
- **Low friction in air and hydrogen** reduces actuation force and improves operational efficiency.
- **Low wear rates** lower component replacement frequency and maintenance downtime.

September 12, 2023

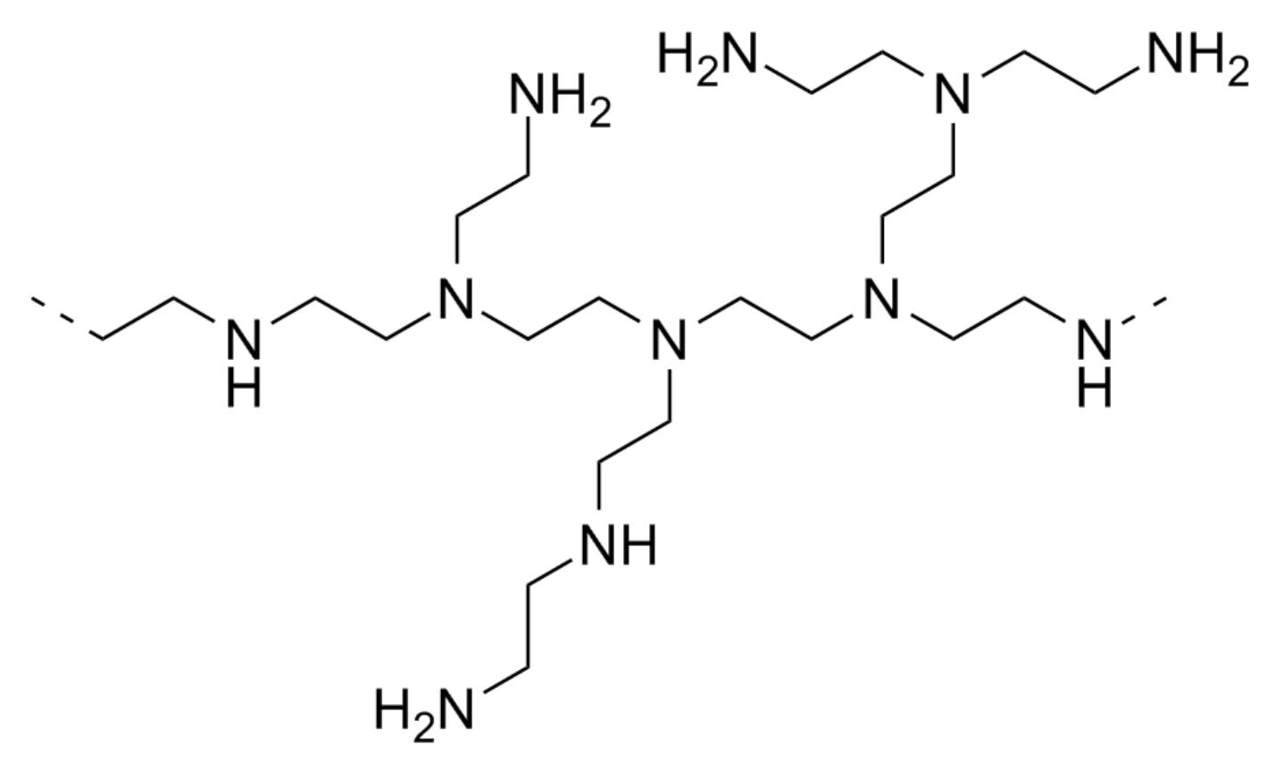
Probing Oxidation Kinetics of Amine-based Sorbents for CO_2 Capture

Shabab Abedi, Corey Kaminsky, Scott Weigel, Wes Sattler
ExxonMobil Technology & Engineering Company, Annandale, NJ

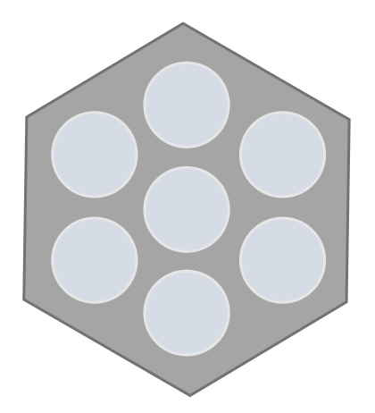
Introduction:

The development of new solid materials for CO_2 capture is challenging due to the diverse nature of CO_2 streams. These streams vary in CO_2 concentration, percent relative humidity, trace impurities such as NOx and SOx, and the concentration of O_2. While this variability suggests that different materials classes are needed for distinct CO_2 streams, in practice amines are among the most commonly examined sorbents. This poses a challenge for oxidative stability of the CO_2 sorbent since amines are prone to oxidative degradation and though the O_2 content of CO_2 streams vary, nearly all contain at least 1% O_2.

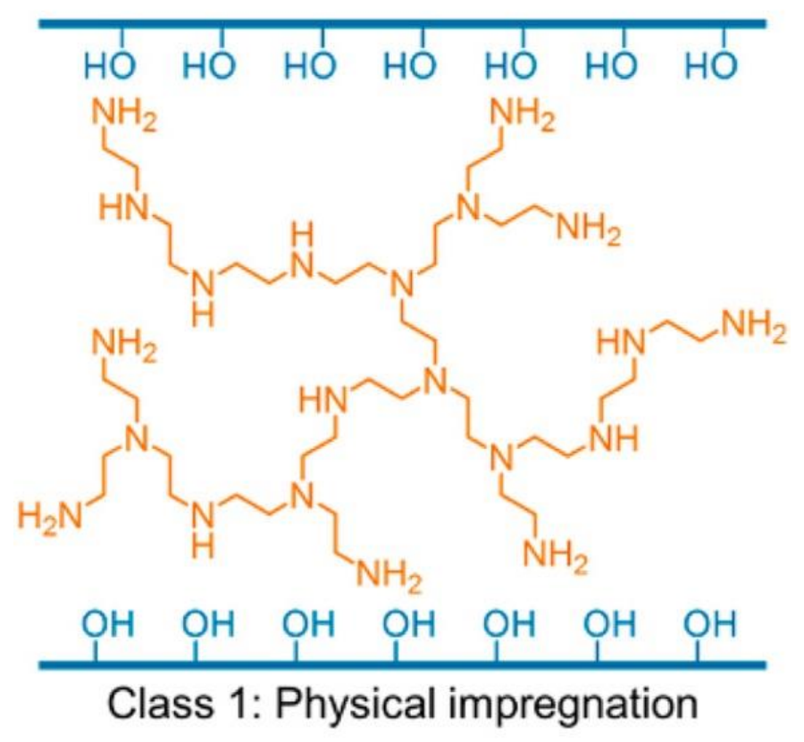
Here, we present work on understanding the oxidative stability of supported polyethylenimine (PEI). This material is widely examined in academic literature as candidate for Direct Air Capture due to its high amine density and therefore large CO_2 capacity. However, this high amine density suggests that PEI will be very sensitive to O_2-mediated degradation. To that end we are undertaking a kinetic investigation to understand if it is possible to mitigate the instability of PEI to O_2, a requirement if it is to be used for Direct Air Capture.



on



SBA-15; Al_2O_3, SiO_2
Lit supports (1, 2, 3)

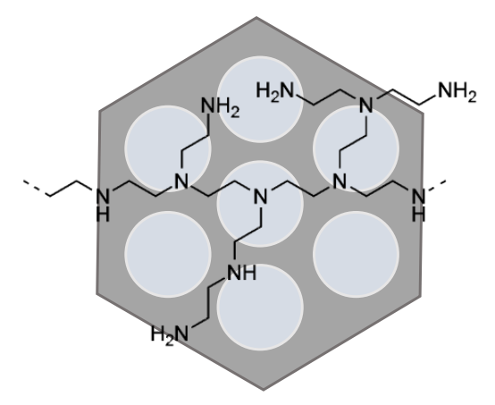


Only examined physisorbed PEI
(i.e. class 1, ref 4).

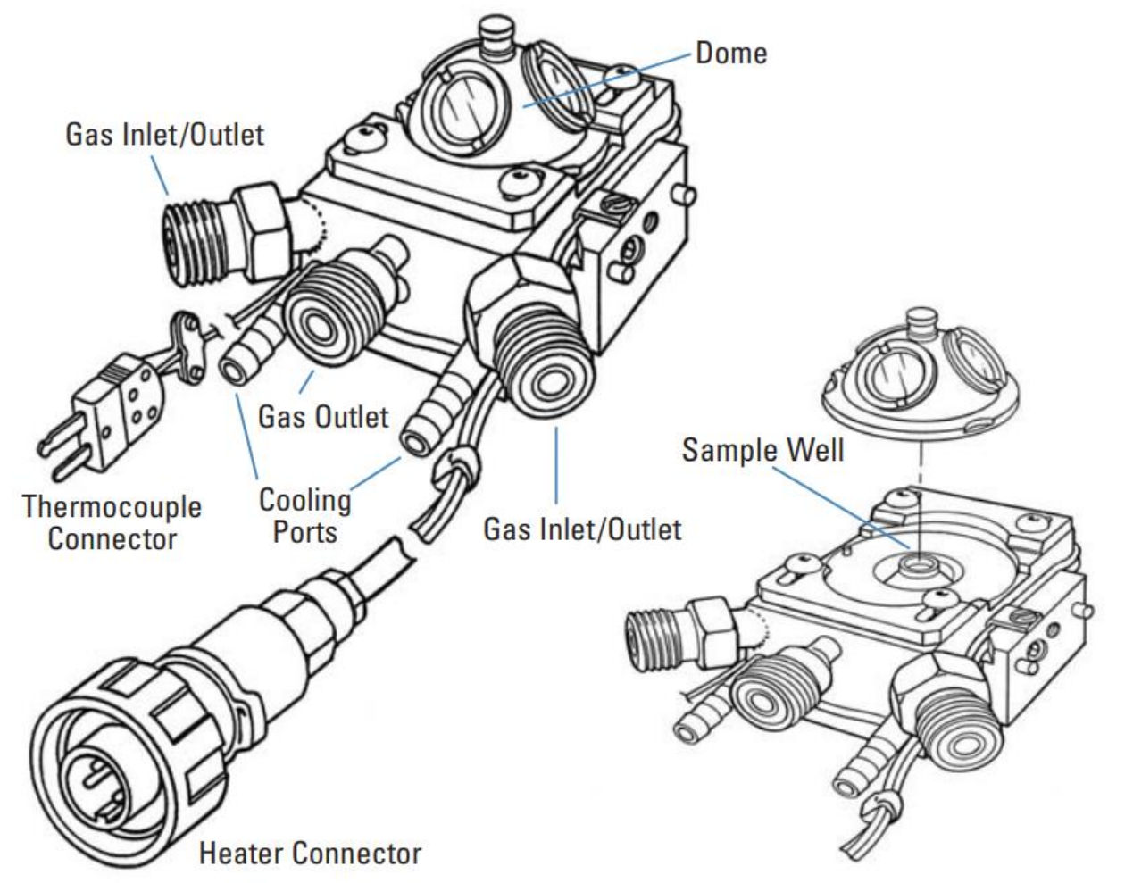
Approach:

We combined spectroscopic techniques such as NMR and FT-IR to probe the degradation as a function of oxidation time. The rate of decomposition of PEI with two different supports and with or without addition of a stabilizer was examined.

FT-IR:

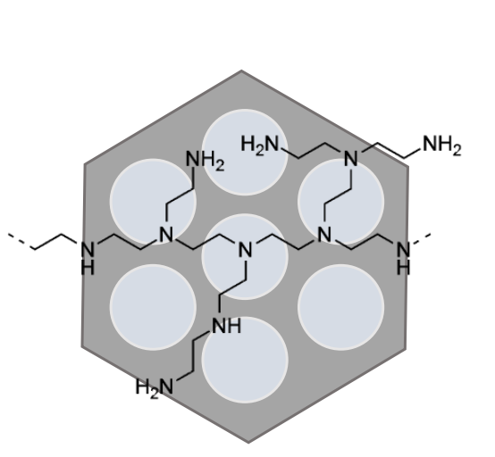


1) Dilute with KBr
2) Press into environmental cell (ref 5)

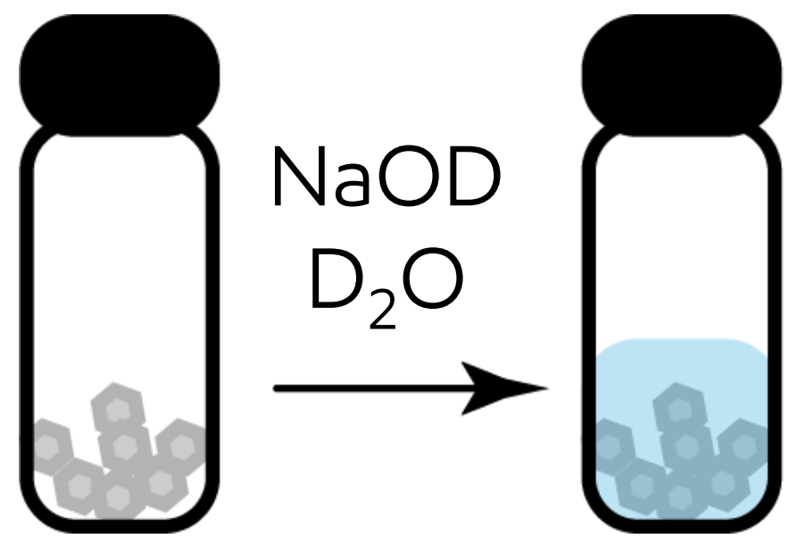


3) Pre-treatment under N_2 and heating to 120 C.
4) Bring to T of interest, switch to reaction gas
5) Collect spectra

NMR:



1) Weigh out ~10 mg samples into vials (1 per time point)
2) Heat at temperature of interest in air

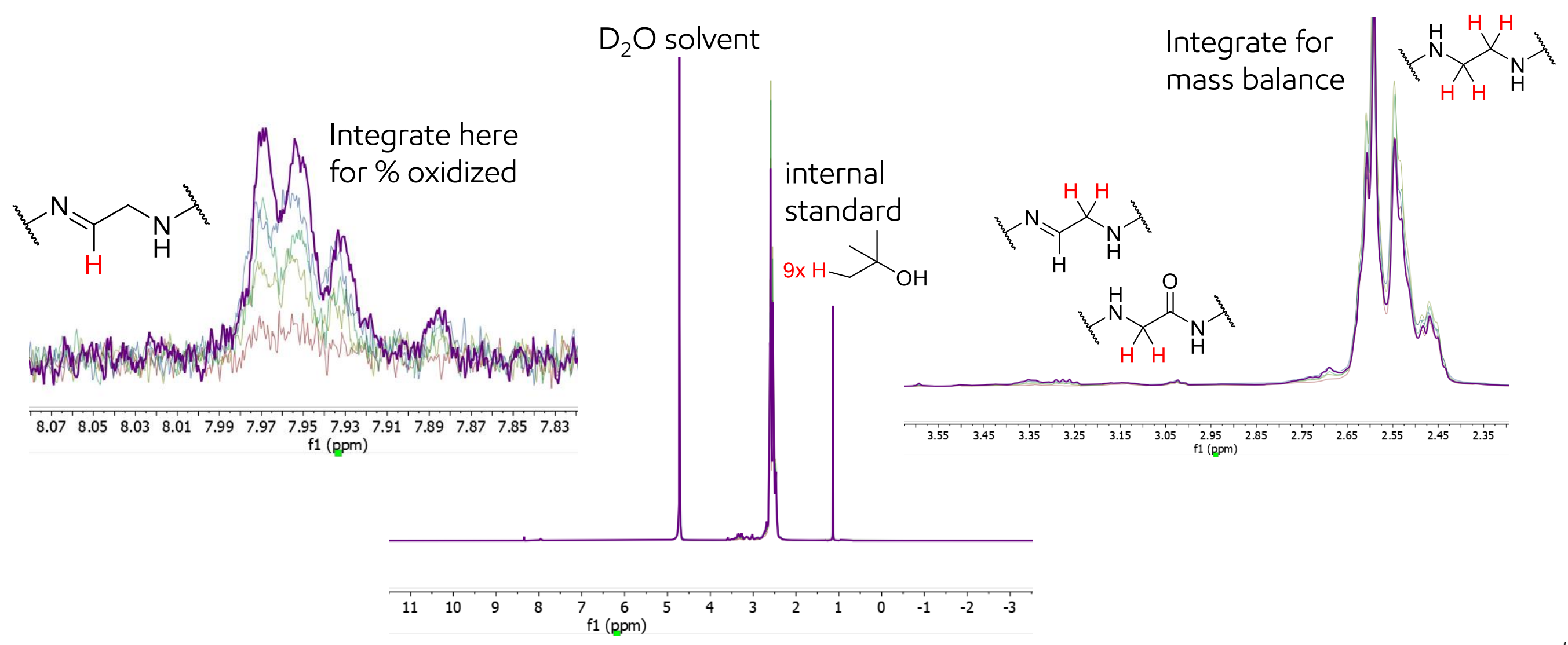


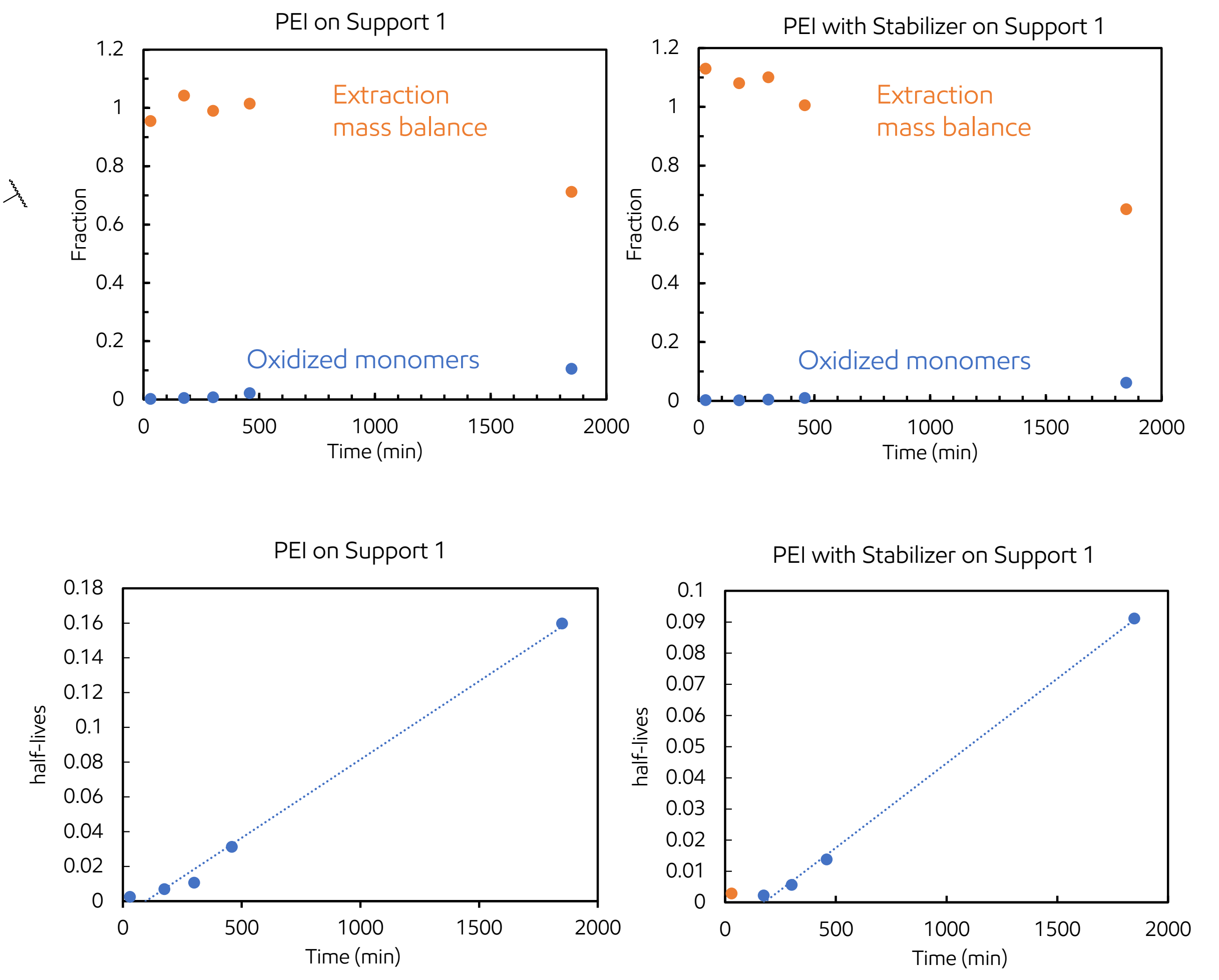
3) Extract sample using NMR solvent
4) Collect spectra for each time point

Results:

NMR:

Typical spectra of PEI at different time points
Air, 133 °C, Support 1

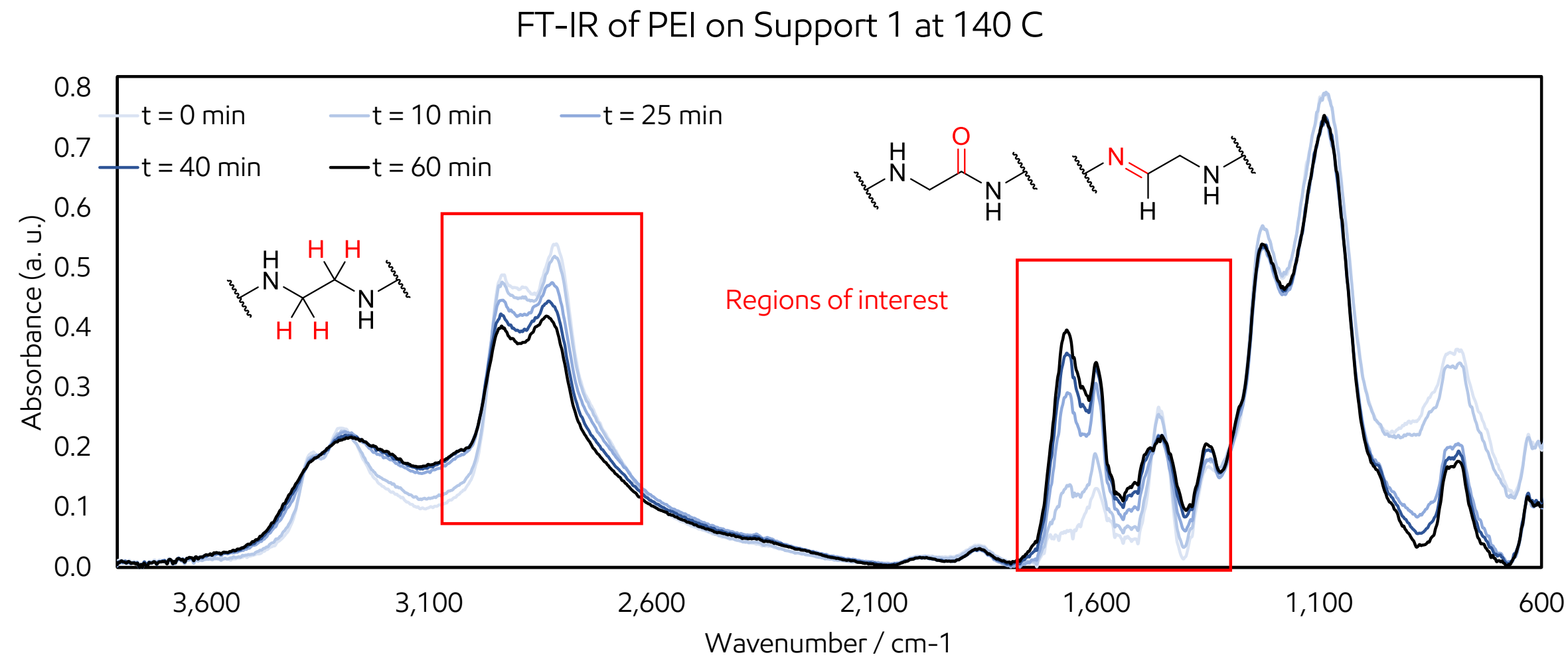




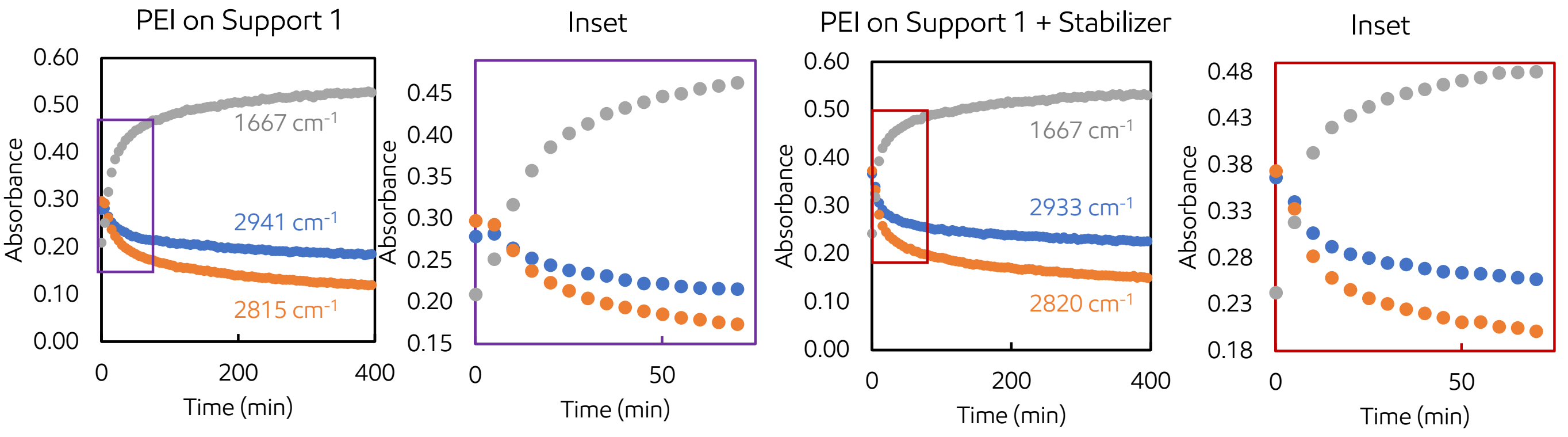
Comparison of NMR oxidation data with different supports, both with and without stabilizer, reveals that the support has minimal impact on stability. The slight differences are likely within the error of the measurements. Addition of stabilizer decreases the rate of oxidation by ~2-fold.

	Support 1	Support 1 + Stabilizer	Support 2	Support 2 + Stabilizer
k_{obs} (min^{-1})	6.3 x 10^{-5}	3.8 x 10^{-5}	8.1 x 10^{-5}	4.2 x 10^{-5}
$t_{1/2}$ (min)	11000	18400	8500	16300

FT-IR:

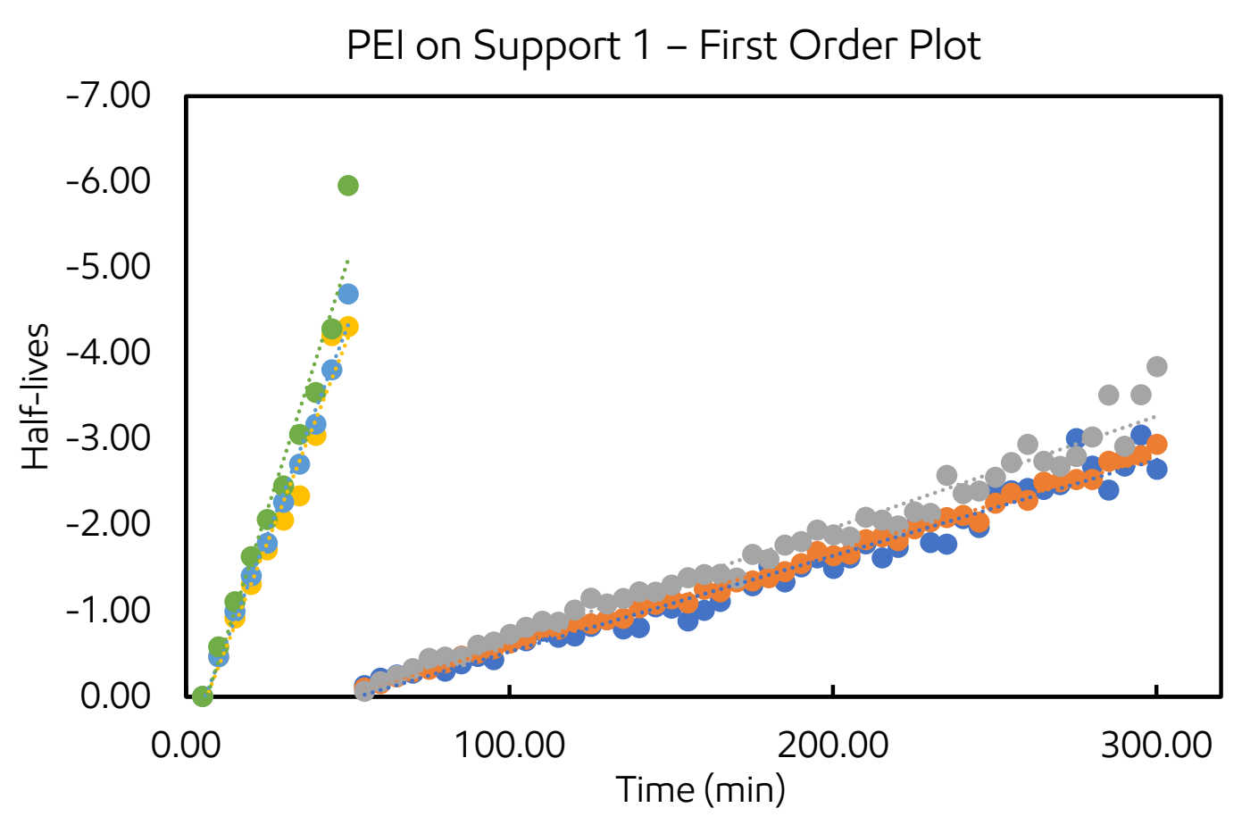


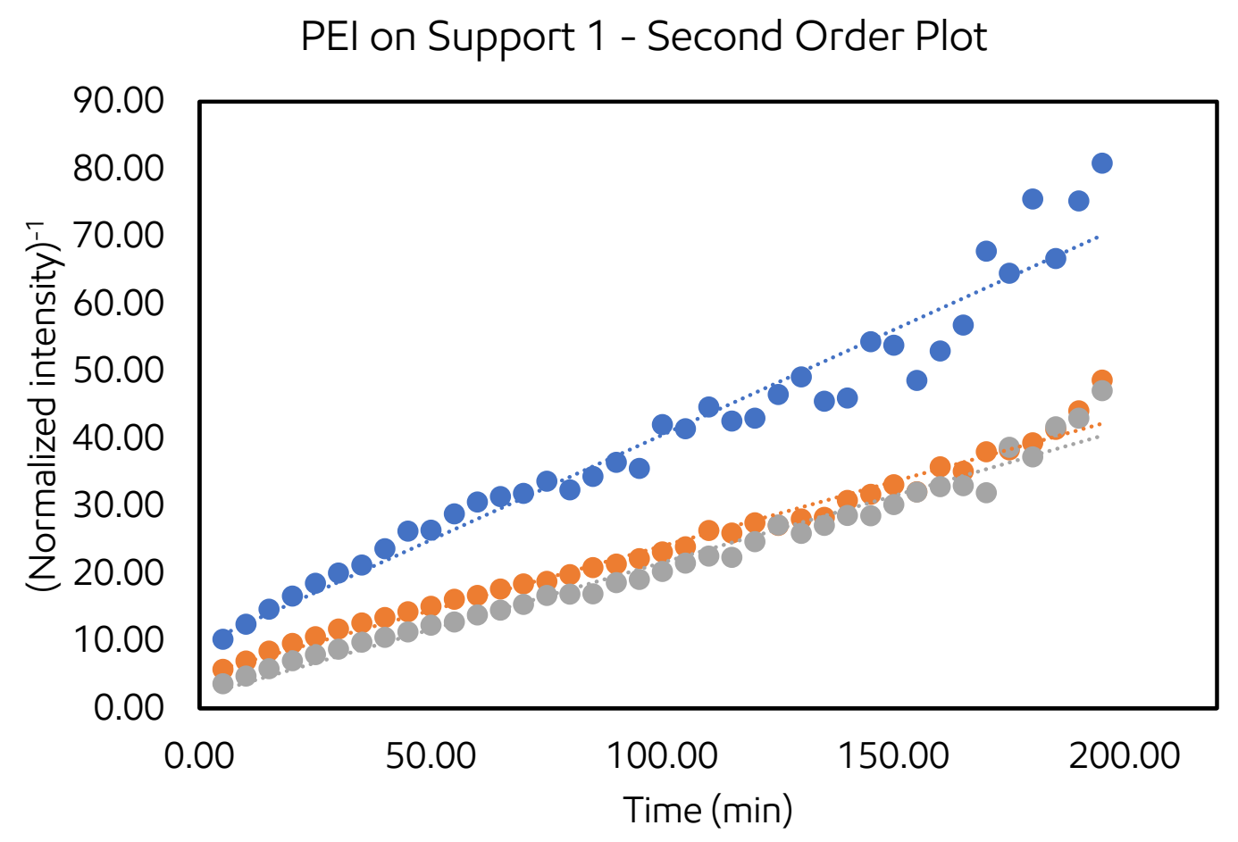
Time traces of PEI oxidation with 30 sccm dry, simulated air (20% O_2 in N_2) at 140 °C.



Does this oxidation proceed by a series of first order reactions or a single overall second order reaction?
PEI is a very complex molecule and it is easy to envision two different amine sites reacting at very different time scales but it is also easy to envision an overall second order process for this reaction.

Determined at 1667 cm^{-1}:	Support 1	Support 1 + Stabilizer
1st order fast k_{obs}	0.0710	0.0569
1st order slow k_{obs}	0.0082	0.0081
Second order k_{obs}	0.2383	0.2049





In contrast to the NMR data, the FT-IR kinetics reveal no enhanced oxidative stability upon addition of stabilizer.
This discrepancy likely arises because these techniques do not probe the exact same species.

Citations: 1 – *Angew. Chem. Int. Ed.* **2023**, *62*, e202302887. 2 – *J. Am. Chem. Soc.* **2022**, *144*, 11664. 3 – *Ind. Eng. Chem. Res.* **2017**, *56*, 13766. 4 – *Acc. Chem. Res.* **2015**, *48*, 2680. 5 – Sold by Harrick, image from: https://tools.thermofisher.com/content/sfs/brochures/PS51812-Praying-Mantis.pdf.

Doing More with Less through Lightweighting:

Foaming Capability of ExxonMobil High-Melt-Strength Polypropylene

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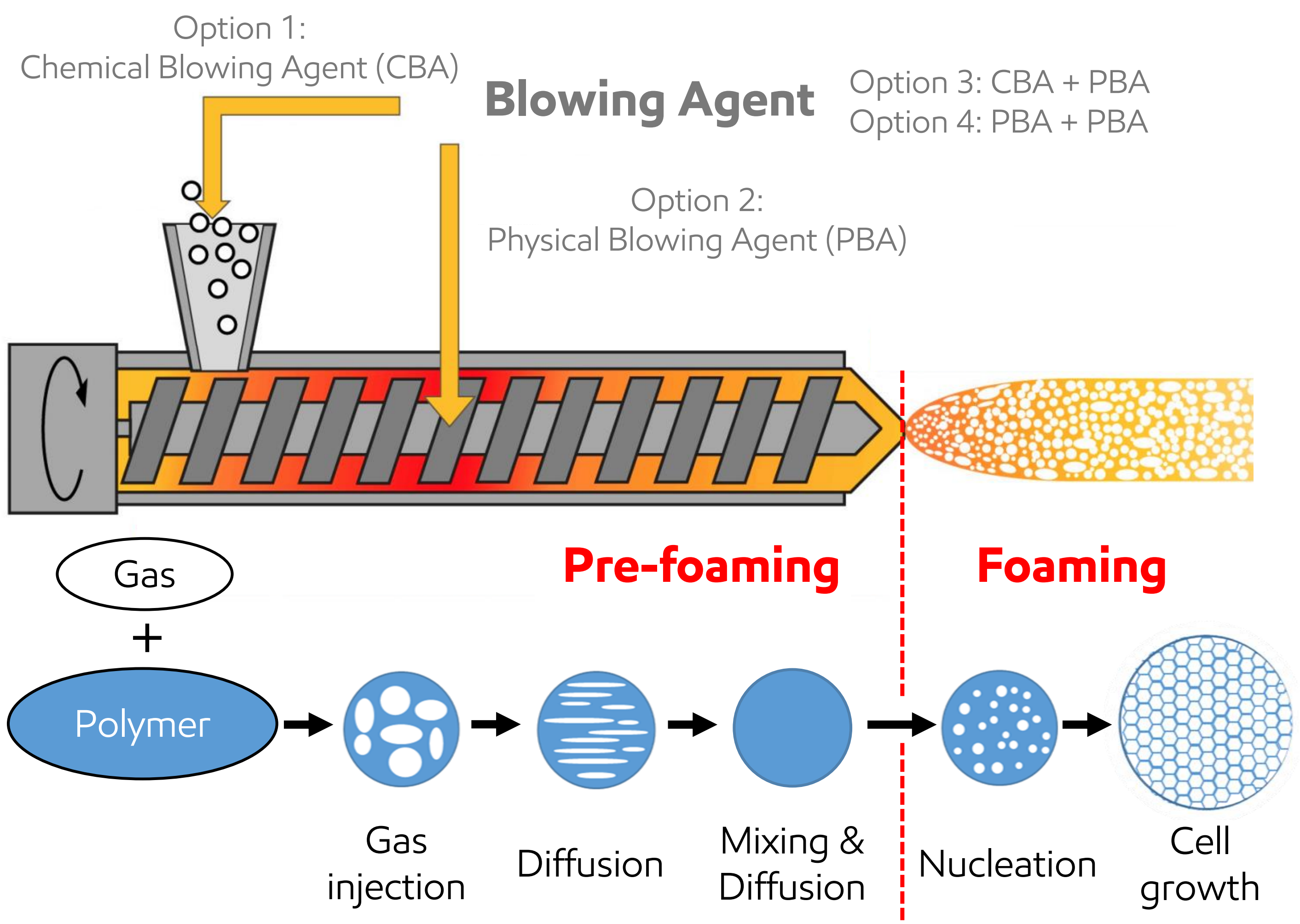
UNIVERSITY OF TORONTO

ExxonMobil

Abstract

The pursuit of materials that can offer sustainability benefits has become a major focus in various industries to help address value chain sustainability commitments. Among these materials, polypropylene (PP) stands out as an ideal candidate for a wide variety of applications. A prime example of how PP can offer sustainability benefits is its use in plastics foaming. The lightweight nature of PP foams can translate into lower material consumption and the potential for reduced transportation energy, and enhanced fuel efficiency – thus potentially offering carbon footprint benefits in automotive and packaging applications. In addition, the strong chemical resistance and excellent insulation properties of PP foams can result in durable products with long lifespans that can offer energy efficiency benefits in construction applications. However, PP typically possesses low melt strength and produces low-quality foams with poor cell structure, limiting its use in high-density foams. To help address these drawbacks, ExxonMobil has developed high-melt-strength (HMS) PP grades that can deliver significant weight reduction while maintaining the desirable attributes after foaming. In this work, we examined the foamability of these HMS PP materials under conditions relevant to foam manufacturing processes to demonstrate the use of PP foams in various applications.

Foaming Background[1,2]



Option 1:
Chemical Blowing Agent (CBA)

Blowing Agent

Option 3: CBA + PBA
Option 4: PBA + PBA

Option 2:
Physical Blowing Agent (PBA)

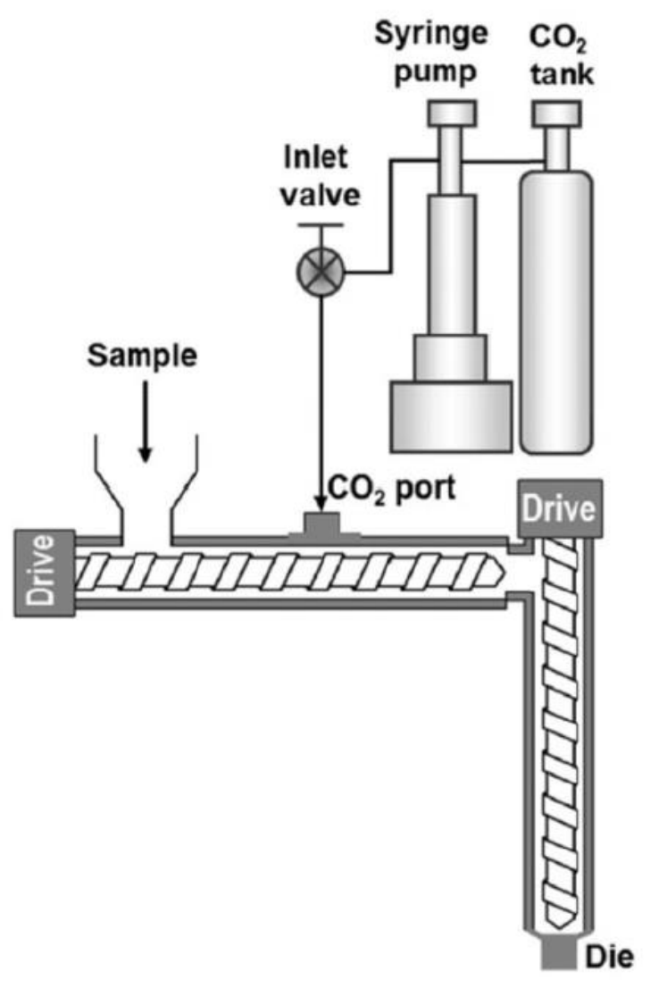
Pre-foaming

Foaming

Gas
+
Polymer

Gas injection → Diffusion → Mixing & Diffusion → Nucleation → Cell growth

Extrusion Foaming:
Effect of processing condition on PP foamability[3]



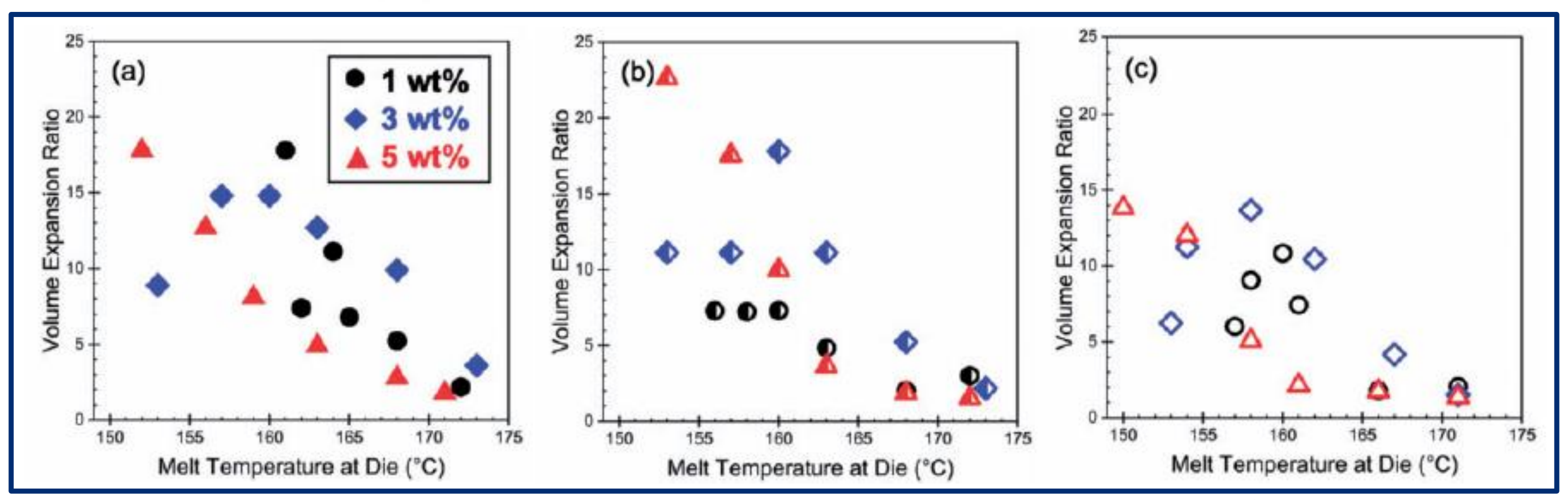
Materials

Polymer: long-chain branched HMS PP (PDH025, ExxonMobil)
Physical blowing agent: CO_2
Cell nucleating agent: talc

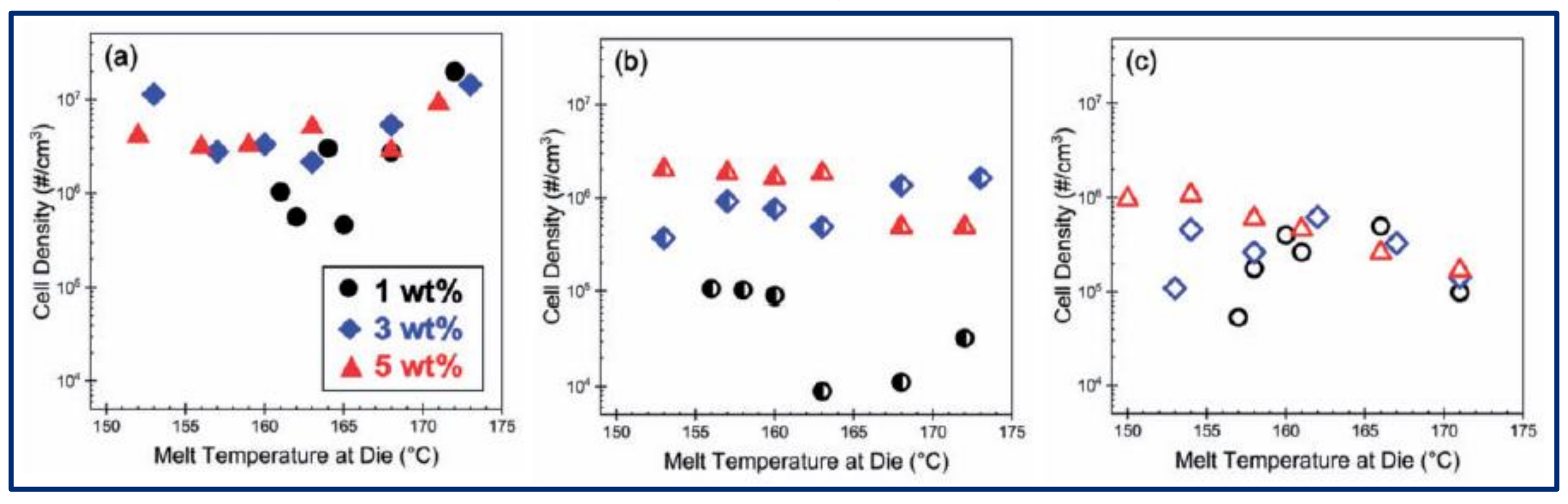
MFR 230°C/2.16kg [dg/min]	Density [g/cm³]	T_m [°C]	T_c [°C]	M_w [g/mol]	M_w/M_n
1.9	0.9	165.2	126.8	424,500	12.1

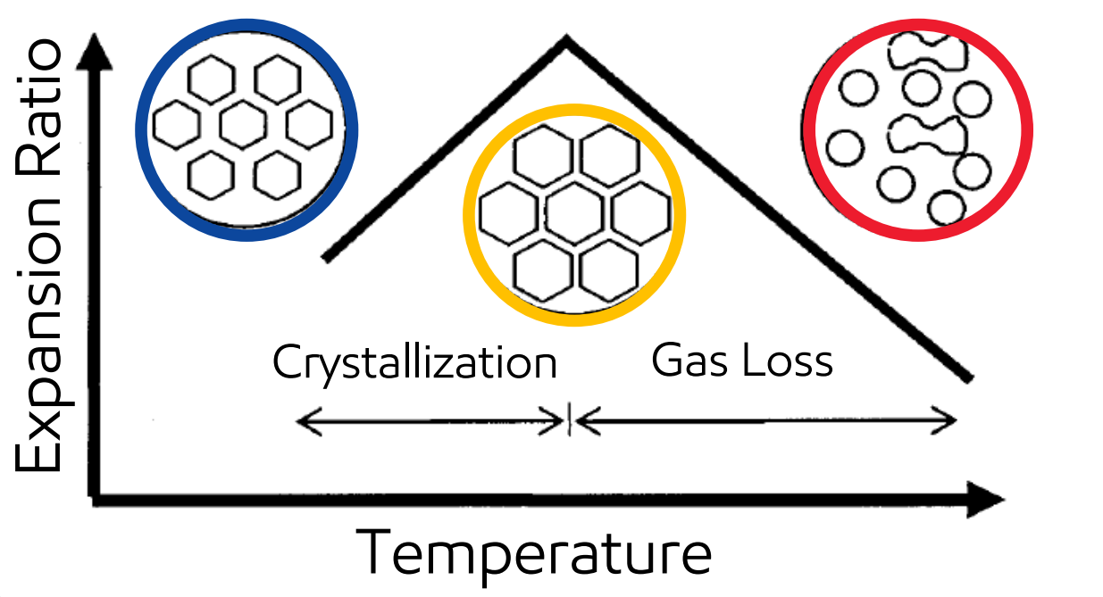
Processing Condition:

Die pressure drop rates (dP/dt) explored: 280, 60, 21 MPa/s
CO_2 loading: 1, 3, 5 wt%



Decreasing dP/dt



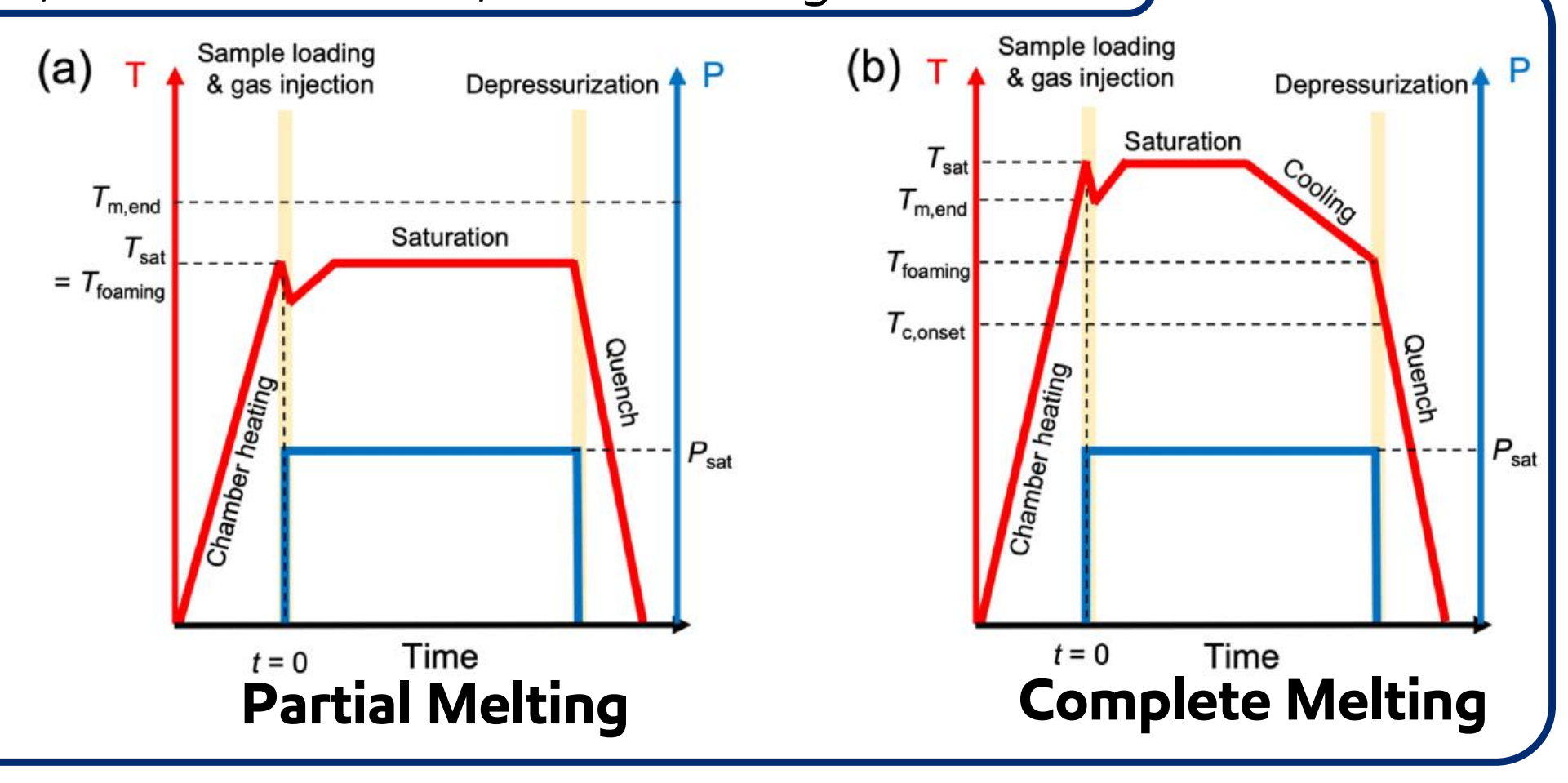


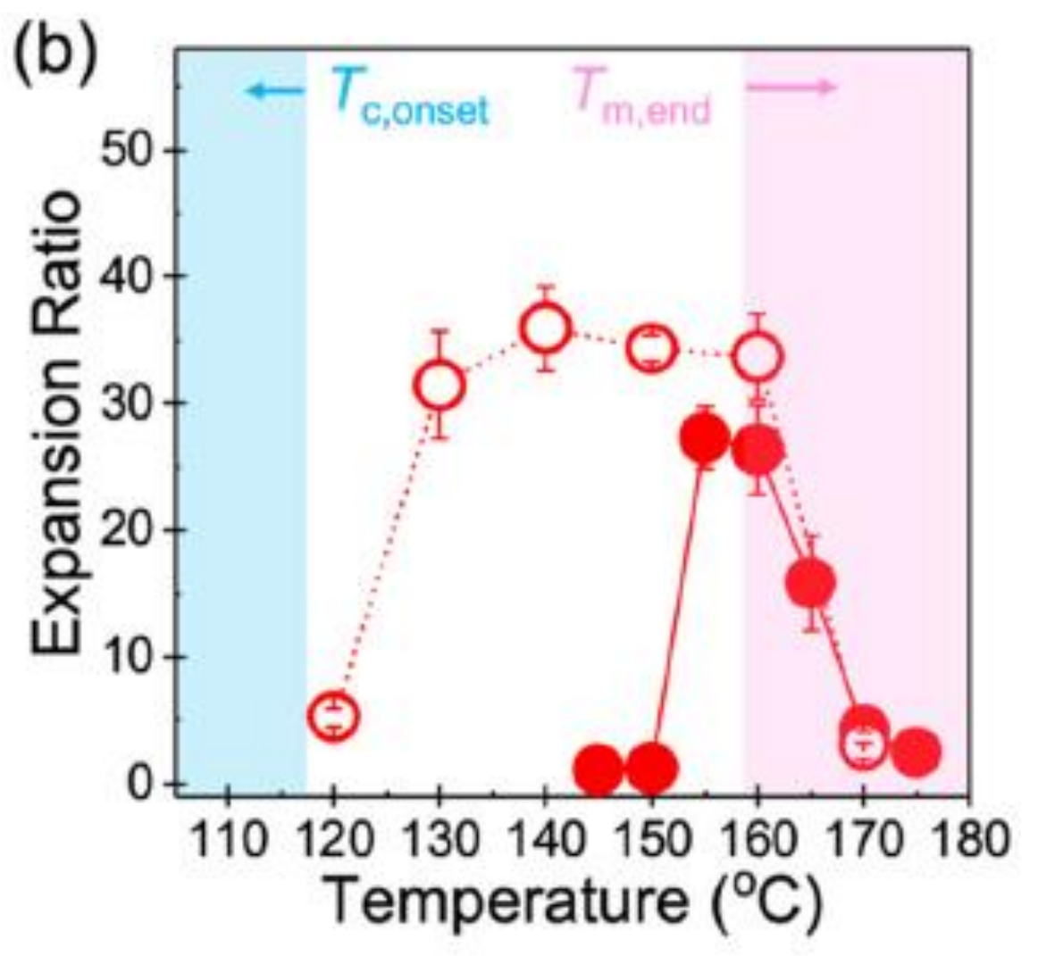
Representative SEM images from low dP/dt die at 3 wt% CO2 loading

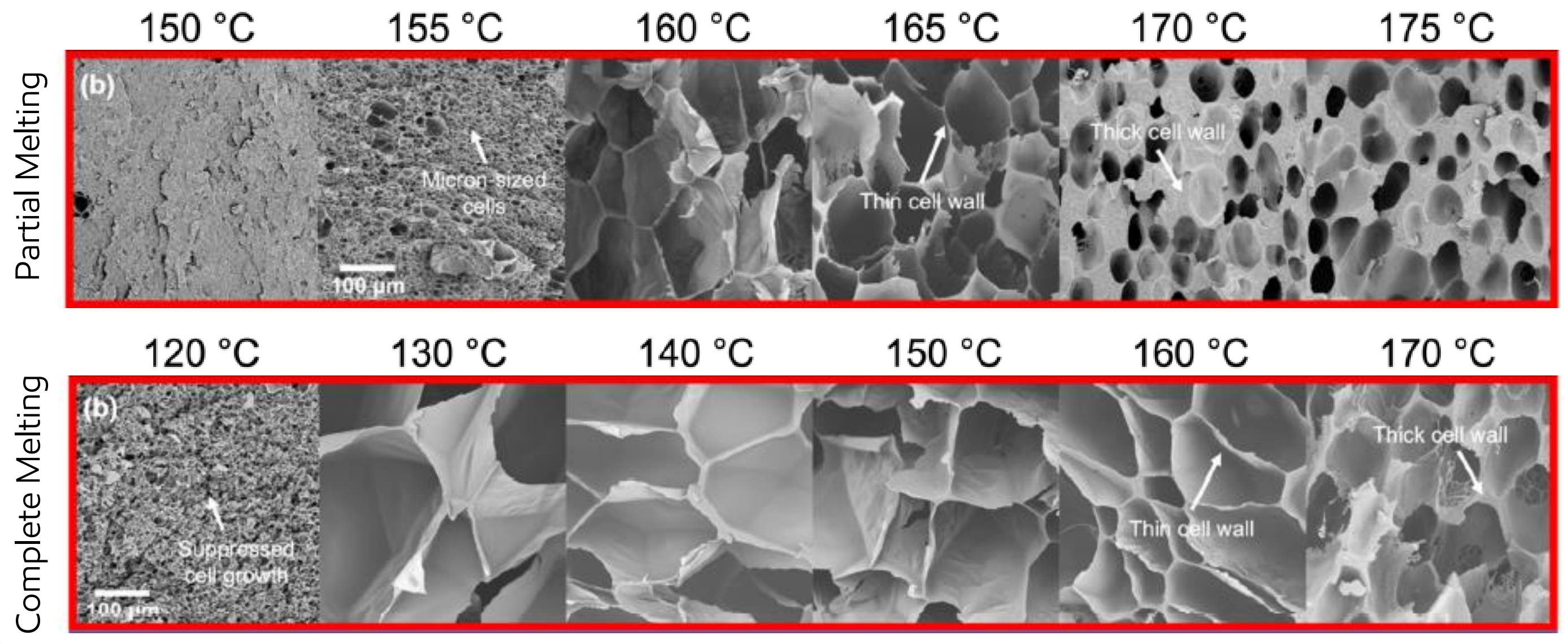
Batch Foaming:
Effect of partial vs complete melting on foam expansion and morphology[4]

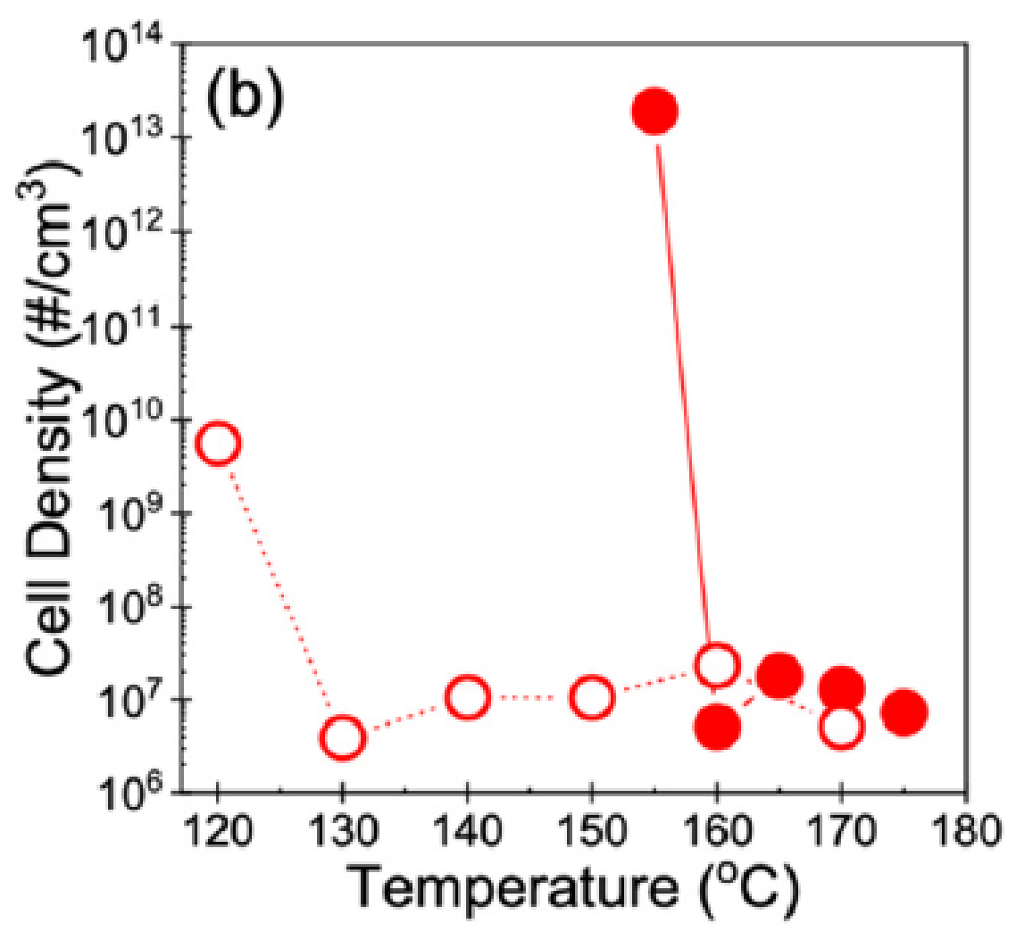
Materials, Test Parameters, and Foaming Protocol

Material	HMS long-chain branched PP
Melt Strength	45 cN
M_w	541,000 g/mol
M_w/M_n	13
PBA	CO_2
Saturation Pressure	2000 psi

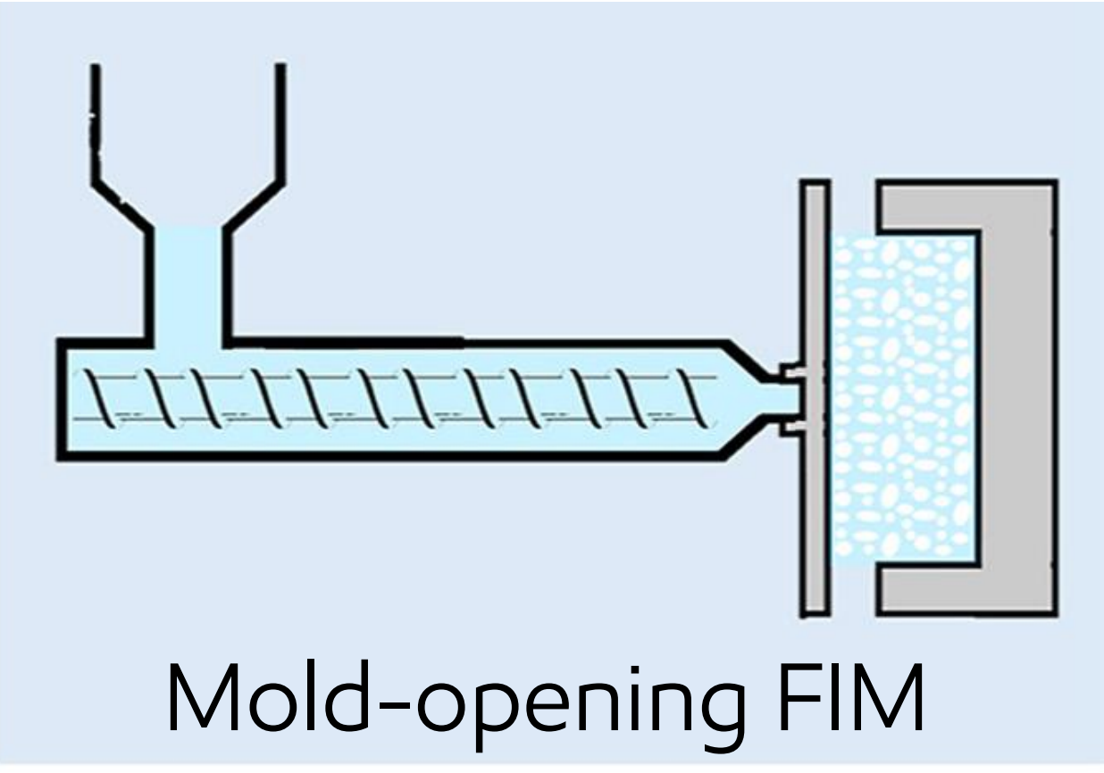






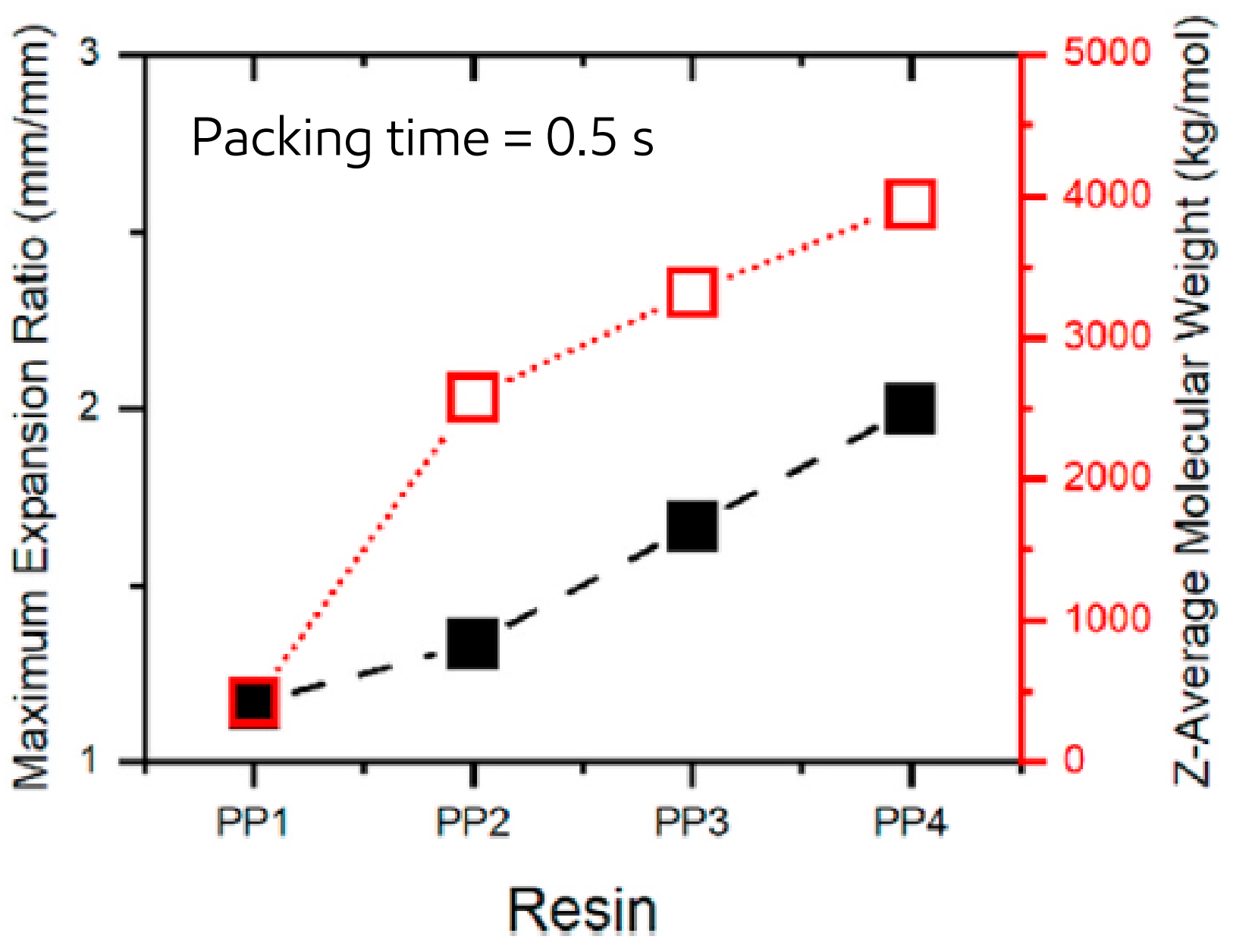


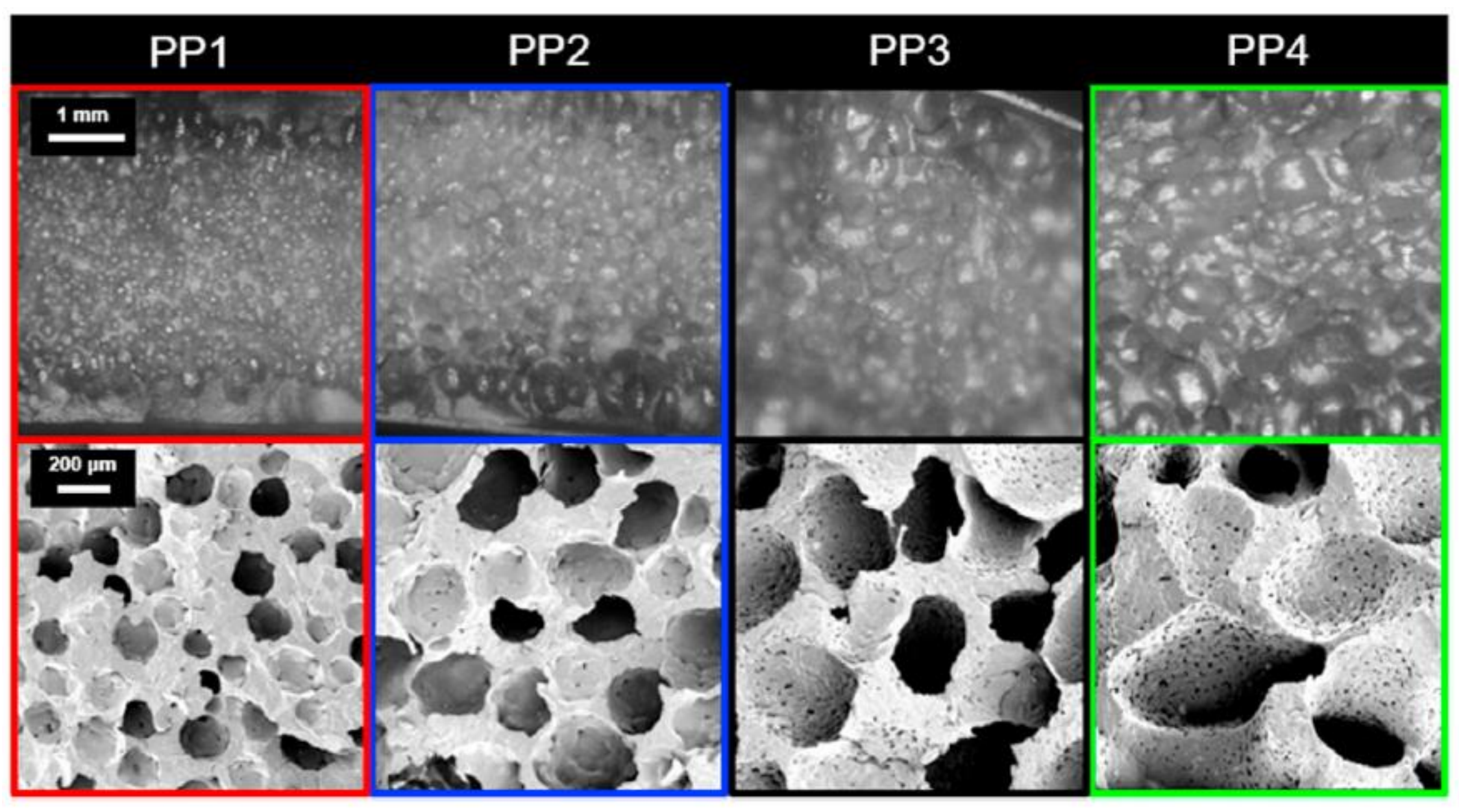
Foam Injection Molding (FIM):
Influence of molecular weight during high-expansion FIM[5]



Mold-opening FIM

Sample	MFR 230°C/2.16kg [dg/min]	M_w [g/mol]	M_w/M_n	M_z [g/mol]	Melt Strength [cN]
PP1	36	182,000	3.7	423,000	-
PP2	30	303,000	18	2,580,000	3
PP3	37	312,000	13	3,320,000	5
PP4	34	373,000	28	3,950,000	11





Packing time = 0.5 s; optical microscopy (top) & SEM (bottom)

Potential Benefits Summary

Extrusion Foaming
- Higher dP/dt leads to greater density reduction; higher CO_2 content widens the foaming temperature window
- Higher dP/dt and CO_2 content contribute to higher cell density

Batch Foaming
- Foaming temperature range can be widened by >20°C via complete melting (compared to partial melting) without compromising the density reduction capability and cell morphology

Mold-Opening Foam Injection Molding
- Higher molecular weight PP are able to achieve higher expansion due to higher crystallization temperatures and improved extensional rheology that contribute to improved cell structure stability

Acknowledgments

Funding

- ExxonMobil Technology and Engineering Company (research project 2018–0588)
- Collaborative Research and Development grant (CRDPJ 543896–19) of the Natural Sciences and Engineering Research Council of Canada

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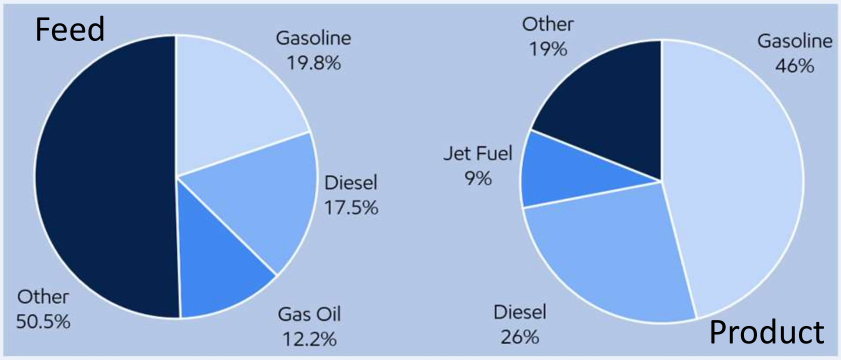
BETTER CALL SOL FOR FCC OPERATION

Manjiri Moharir, Scott Horton, Ashish Mhadeshwar, Aaron Sattler, Daniel Bilbao

The What



Fluidized Catalytic Cracker (FCC)
Cracks heavy feed molecules into smaller product molecules

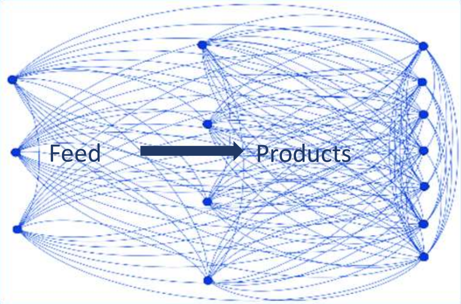
Structure Oriented Lumping (SOL)

- In-house proprietary technology
- Rigorous, robust model
- High compositional detail
- High model fidelity

The Why

FCC Units

- Feed contains lower fractions of fuel grade material
- Cracking yields higher fractions of fuel grade material
- FCC units upgrade the feed into profitable products
- Integral to the energy industry for decades

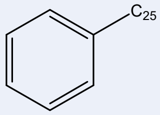


SOL Model

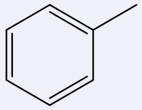
- FCC chemistry is complex
- Hundreds of thousands of species and reactions
- Models required for safe and optimized operations
- SOL enables complex chemistries to be captured in tractable models

The How

SOL Representation



A6	A5	A2	N6	N5	N4	N3	N2	N1	R	br	me	H	AA	S	RS	AN	NN	RN	O	RO	O=	Ni	V
1	0	0	0	0	0	0	0	0	25	0	0	0	0	0	0	0	0	0	0	0	0	0	0



A6	A5	A2	N6	N5	N4	N3	N2	N1	R	br	me	H	AA	S	RS	AN	NN	RN	O	RO	O=	Ni	V
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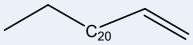


A6	A5	A2	N6	N5	N4	N3	N2	N1	R	br	me	H	AA	S	RS	AN	NN	RN	O	RO	O=	Ni	V
0	0	0	0	0	0	0	0	0	24	0	0	0	0	0	0	0	0	0	0	0	0	0	0

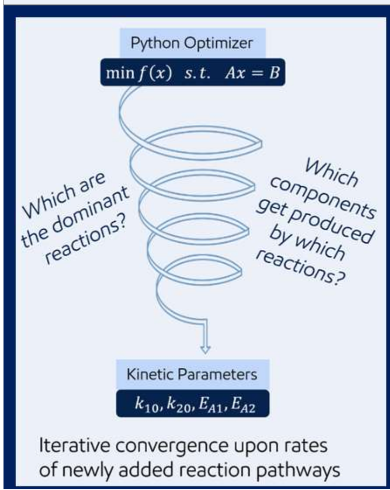
Reaction Network

Select reactants: A_6 >1 & R > 2
Create products:
Product 1 = Reactant 1; R = 1
Product 2 = Reactant 1; $A_6 = 0$*; R = R-1*

Model Details

- Fluidized bed, regenerator, simplified fractionator
- ~10,000 species and reactions
- Model condensed to ordinary differential equations
- Parameter estimation using lab, pilot, commercial data
- Thermodynamics input using group additivity methods

Next Up



Iterative convergence upon rates of newly added reaction pathways

Next Generation FCC SOL Model:

- Addition of new chemistry
  - Improved predictions
  - Overcome limitations of current model
  - Guided by data and literature
- Updates in kinetics, thermodynamics
  - ~500 new components
  - ~5000 new reactions

Major changes/challenges:

- Assessing relevant chemistry
- Impact of new reaction pathways on FCC SOL products, downstream unit models
- Estimation of unknown kinetic parameters
- Thermodynamics of new products/byproducts

MATERIAL DEVELOPMENTS IN POLYETHYLENE INSULATED POWER CABLES FOR MORE SUSTAINABLE POWER DELIVERY

STACEY SABA, ROSHAN AARONS, SAURAV SENGUPTA, JEFFREY COGEN, YABIN SUN, EDIT BERCZI
WIRE AND CABLE R&D AND TS&D, DOW

Global Megatrends in Energy Demand

- **Increases in population growth, urbanization, and renewables require increased energy demand**
  - **Connecting energy generation sources to the grid**
  - **Increasing transmission voltage**
  - **Insulation solution enables reduced emissions**

2030

1.2 X

1.3 X

1.5 X

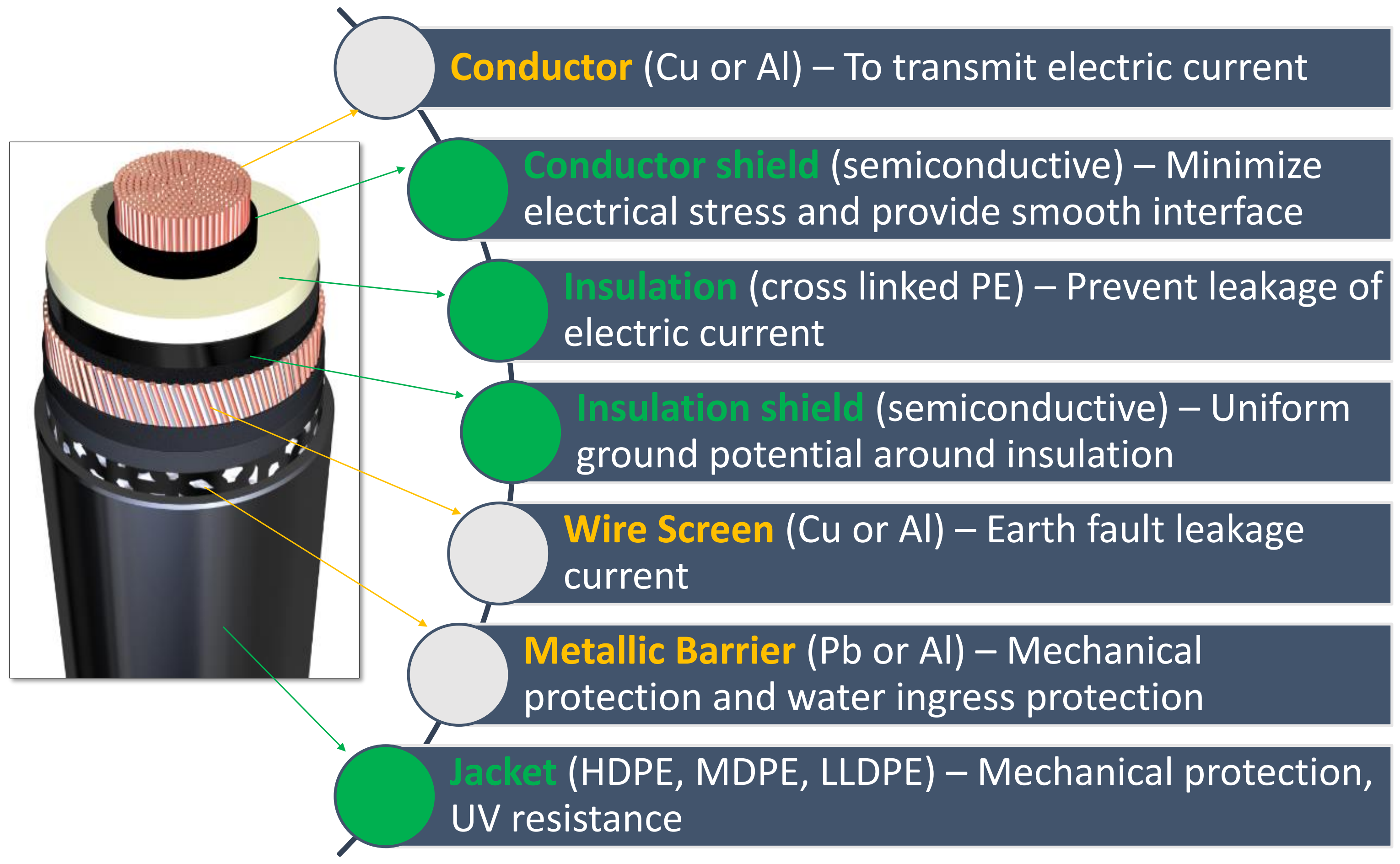
2 X

High & Extra High Voltage

The world requires a grid that is high performing, reliable, and resilient

Crosslinked Polyethylene Insulated Cables

- **Cables are coated with polymeric materials because of good mechanical and electrical properties**
- **Crosslinked polyethylene (XLPE) is widely used as insulation for MV/HV/EHV cables**
  - **Low permittivity, low loss**
  - **High dielectric strength**
  - **High toughness, low temperature flexibility**
  - **Crosslinking increases conductor operating temperature**



Conductor (Cu or Al) – To transmit electric current

Conductor shield (semiconductive) – Minimize electrical stress and provide smooth interface

Insulation (cross linked PE) – Prevent leakage of electric current

Insulation shield (semiconductive) – Uniform ground potential around insulation

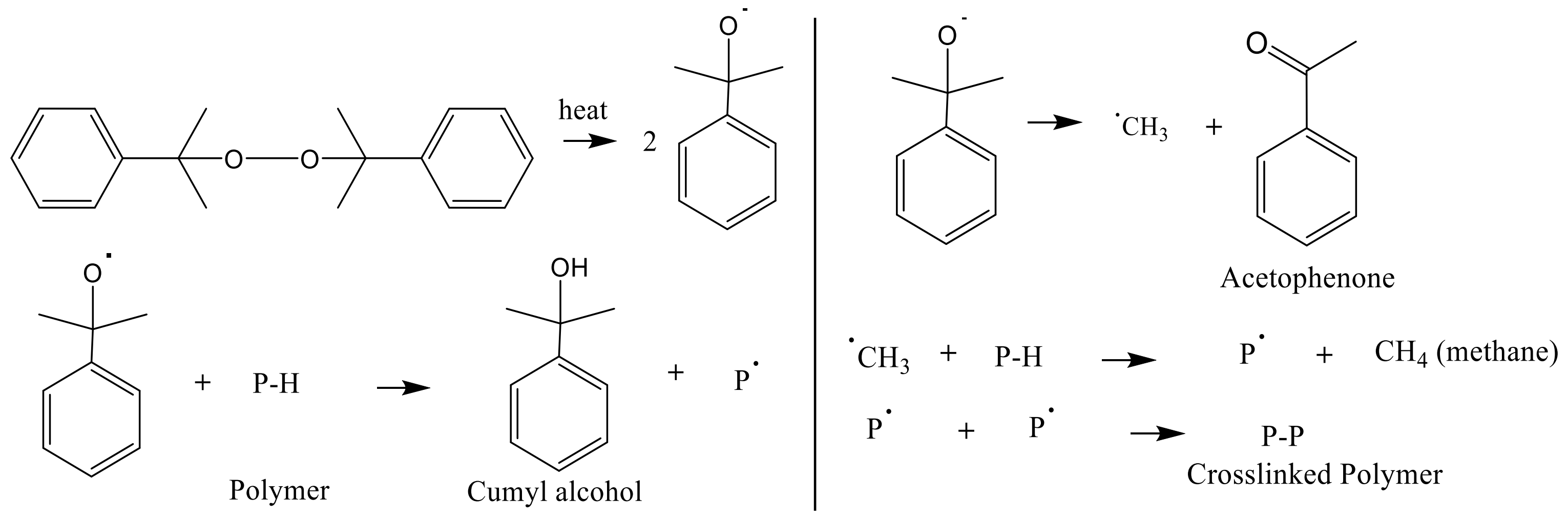
Wire Screen (Cu or Al) – Earth fault leakage current

Metallic Barrier (Pb or Al) – Mechanical protection and water ingress protection

Jacket (HDPE, MDPE, LLDPE) – Mechanical protection, UV resistance

Coagent-Enabled Advances in Crosslinking Technology

- **Dicumyl peroxide (DCP) is a widely used peroxide initiator for crosslinking**
- **Compatible with cable manufacturing process**
- **Peroxide crosslinking byproducts are undesirable and need to be removed which adds time and cost to cable manufacture**



Why Are Byproducts Removed?

Byproduct	Application	Negative Impact
Methane	AC / DC	Vaults: Explosive Mixture Joints: Internal Pressure/Reliability
Polar "Heavies"	AC / DC	Quality Test: mask void detection by partial discharge testing
Polar "Heavies"	AC DC	Increased dielectric loss Increased conductivity/space charge

Technology need exists to minimize byproducts (reduce DCP initiator)

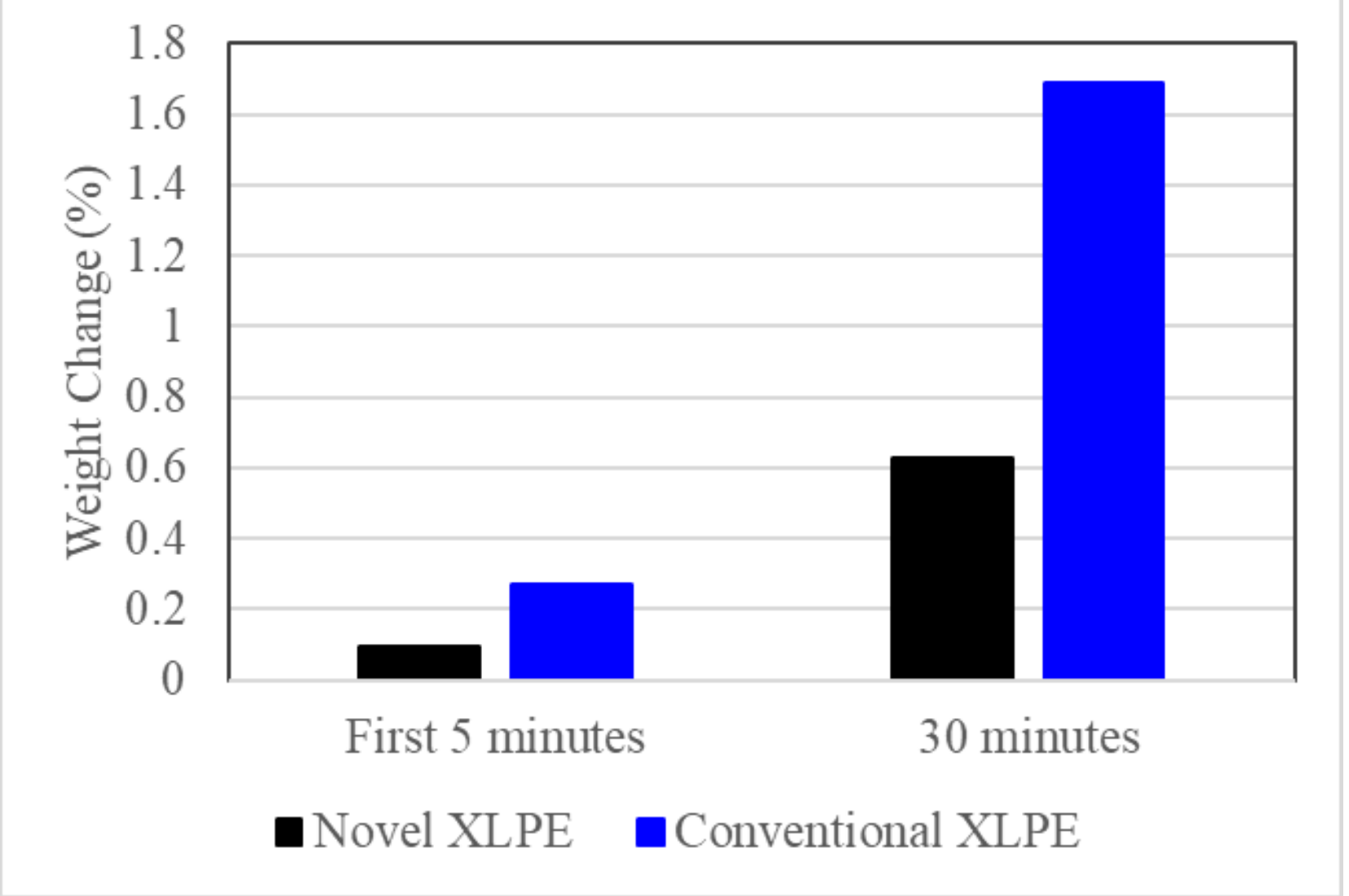
Scorch retardant + crosslinking coagent

Novel XLPE based on coagent technology achieves excellent cure performance, improved scorch (premature cure) resistance

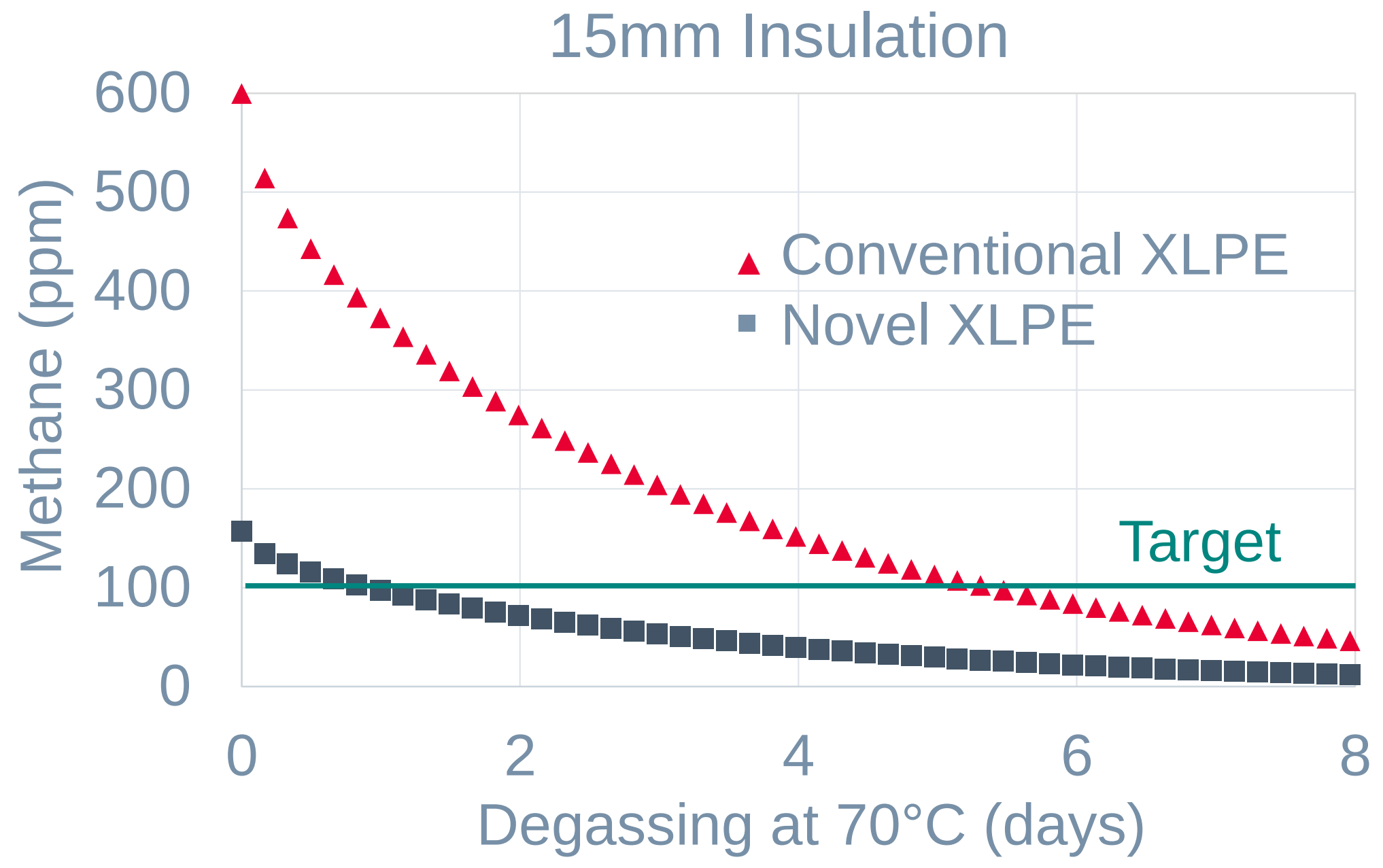
Property	Conventional XLPE	Novel XLPE
Lab scorch test (140 °C, min)	50	72
Hot Set (%) (20 N/cm^2, 200 °C)	77 ± 7	81 ± 9
Tensile strength (psi)	2944 ± 203	2770 ± 203
Elongation (%)	547 ± 27	516 ± 31
Retention (%) – after 14 days at 150 °C	≥ 98	≥ 85

Reduction in Crosslinking Byproducts and Computational Degassing Prediction Model

- **Thermogravimetric analysis screening shows novel XLPE has a lower byproduct concentration in a cable**



- **Diffusion model based on Fick's law was developed for a cable to predict methane removal at 70 °C**
- **Methane target of < 100 ppm achieved in 1 day**



Conclusions

- **Increasing need for higher performing materials to meet energy demands**
- **Conventional crosslinked polyethylene technology is susceptible to scorch and long degassing times**

Novel crosslinked polyethylene technology:

>100% Increase in run length

80% Reduction in degassing time and GHG emission

18MT Reduction in scrap per CV line, equivalent to 32.4MT CO2 saving/year

Thermal Behavior, Morphology, and Mechanical Properties of Poly(β-butyrolactone-co-β-valerolactone)

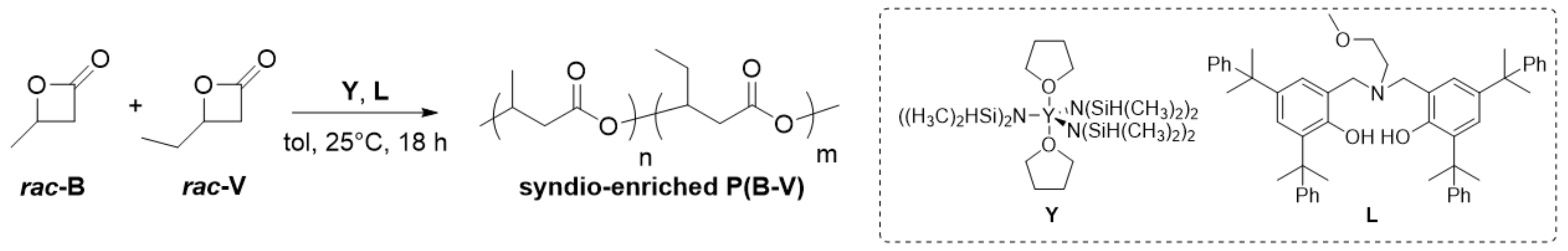
Agostino Pietrangelo*, Carlos R. López-Barrón*, Matthew T. DeRocco, Shuhui Kang, Sarah J. Mattler, Pamela J. Wright

ExxonMobil Technology and Engineering Company

Abstract

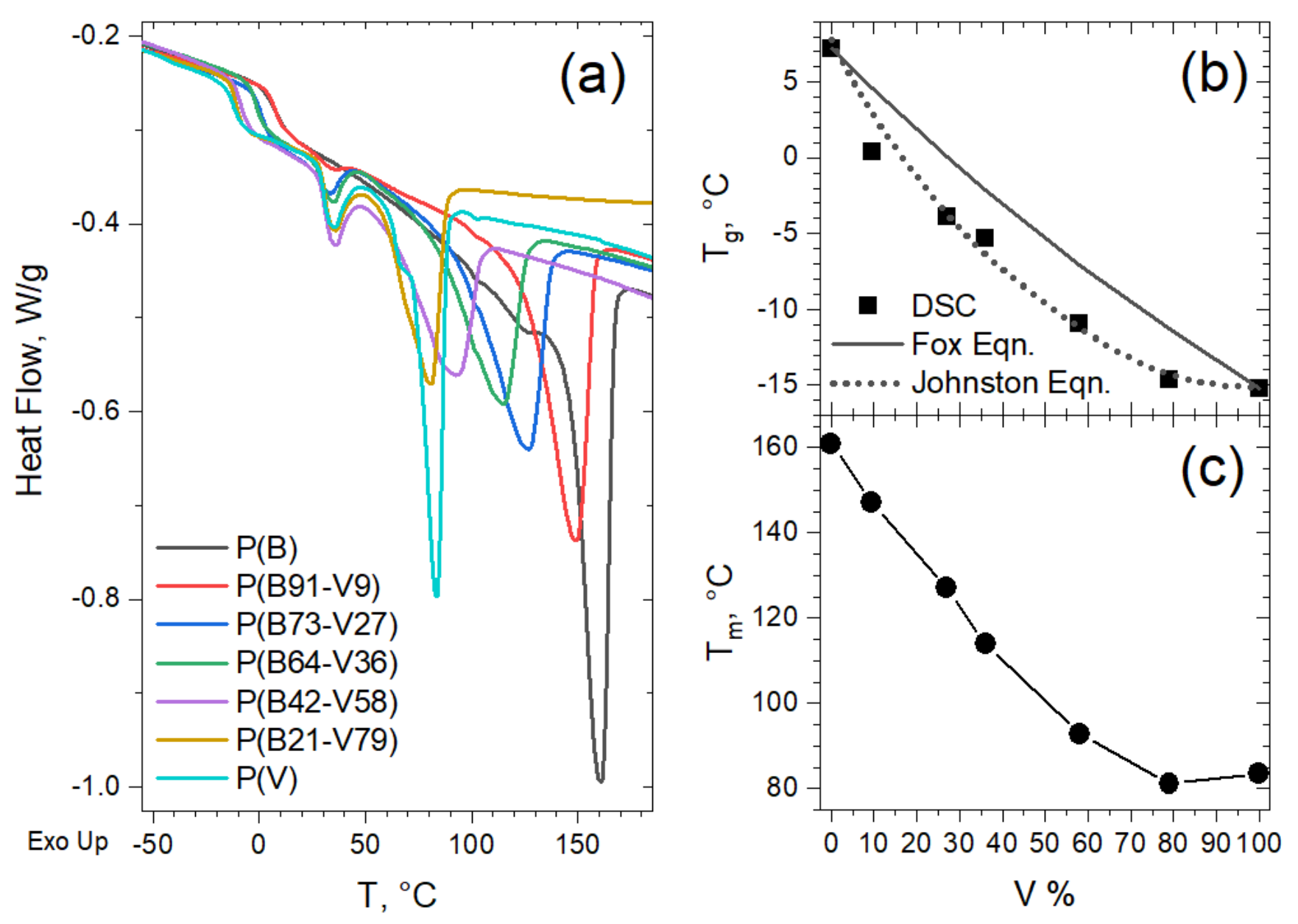
Racemic β-butyrolactone (B) and β-valerolactone (V) are polymerized by ring-opening to afford a series of syndio-enriched (co)polymers that cover the entire compositional range. The effect of copolymer composition on the thermal properties, crystallinity, morphology, and mechanical properties is presented. A monotonic decrease in elastic modulus with increasing V content is observed, with melt transitions following a similar functional form. Tensile properties, including toughness and tensile strength, show sharp transitions at a V content of 36%, coinciding with changes in crystallinity and crystal structure at the same composition. Copolymer microstructure was investigated using ^{13}C NMR spectroscopy enabling a partial assignment of resonances at the tetrad level. The results of this study show that at 27% V content, nearly 50% of the copolymer is comprised of syndiotactic tetrads that have at least three B units. At 36% V content, a significant compositional shift is observed whereby the majority of tetrads are syndiotactic with at least two V units or are iso-enriched.

Thermal Behavior

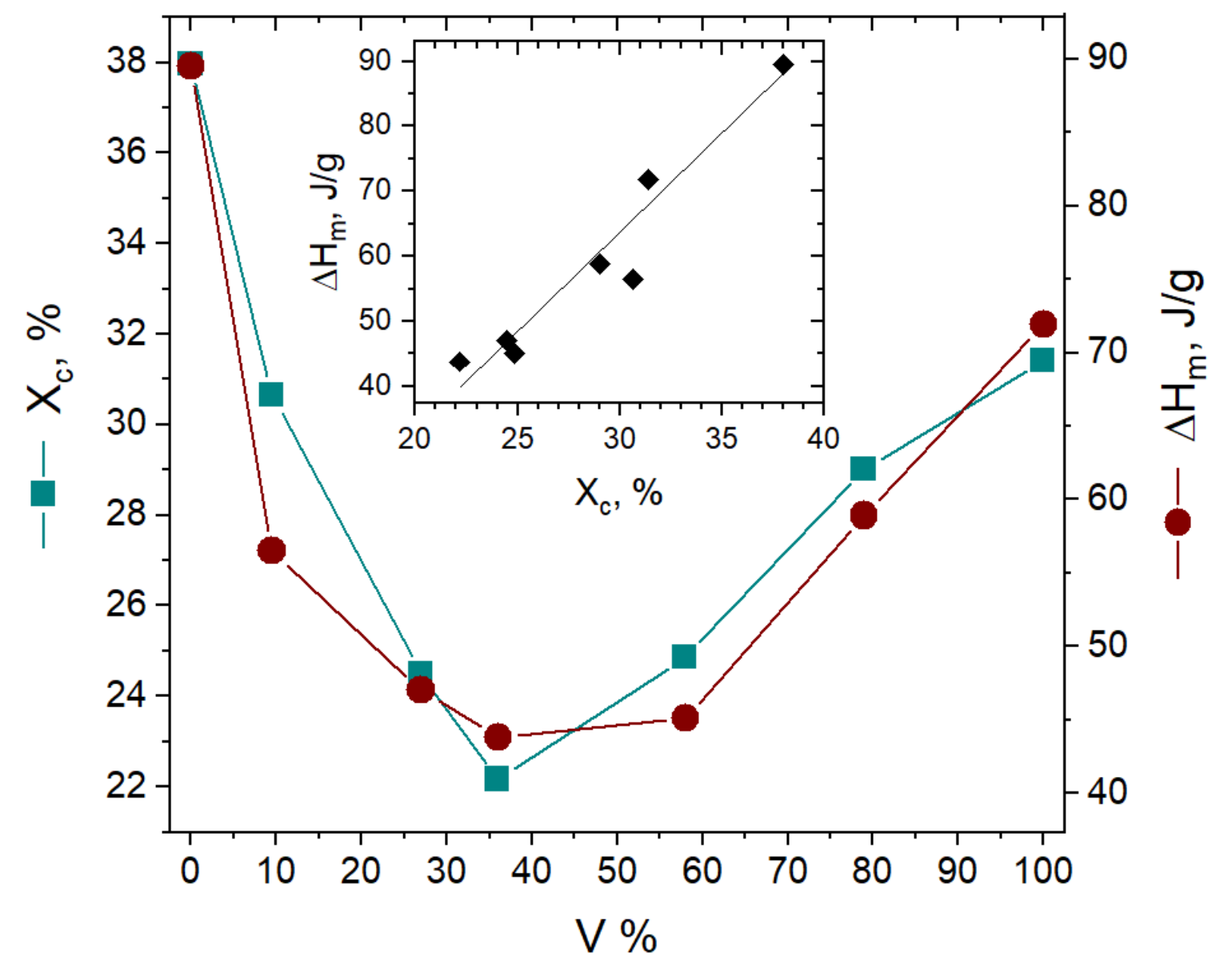


Entry	B:V (feed) (mol%:mol%)	$P(B_n\text{-}V_m)$ n(mol%)/m(mol%)	Yield (%)	M_w[b] (kg/mol)	Đ[b]	T_g[c] (°C)	T_m[c] (°C)	ΔH_m[c] (J/g)	X_c[d] (%)	r_1r_2[e]
1	100:0	P(B)	95	42	1.87	7	161	90	38	-
2	90:10	$P(B_{91}\text{-}V_9)$	95	60	1.53	0	147	57	30	3.3
3	70:30	$P(B_{73}\text{-}V_{27})$	86	83	1.24	-4	127	47	24	1.8
4	60:40	$P(B_{64}\text{-}V_{36})$	84	86	1.17	-5	114	44	22	1.5
5	40:60	$P(B_{42}\text{-}V_{58})$	86	114	1.31	-11	93	45	25	1.90
6	20:80	$P(B_{21}\text{-}V_{79})$	87	179	1.53	-15	81	59	29	1.4
7	0:100	P(V)	41	180	1.46	-15	72	72	30	-

[a] All reactions were performed at 25 °C for ca.18 h in anhydrous toluene. $[Lactone]_0$ = 2.43 M. $[Lactone]_0$:[Y]:[L] = 600:1:1. [b] GPC measurements were performed with multiple detectors in $CHCl_3$ solvent at 40 °C. [c] Measured by DSC. [d] Measured by WAXS. [e] Calculated using equation 3.



- (a) DSC thermograms of P(B-V) copolymers measured showing heating temperature scans performed after two hours of isothermal crystallization at 20 °C. (b) Glass transition temperature and (c) melting temperature as a function of V mole%. Solid and dotted lines in (b) are calculated using the Fox and Johnston equations, respectively.

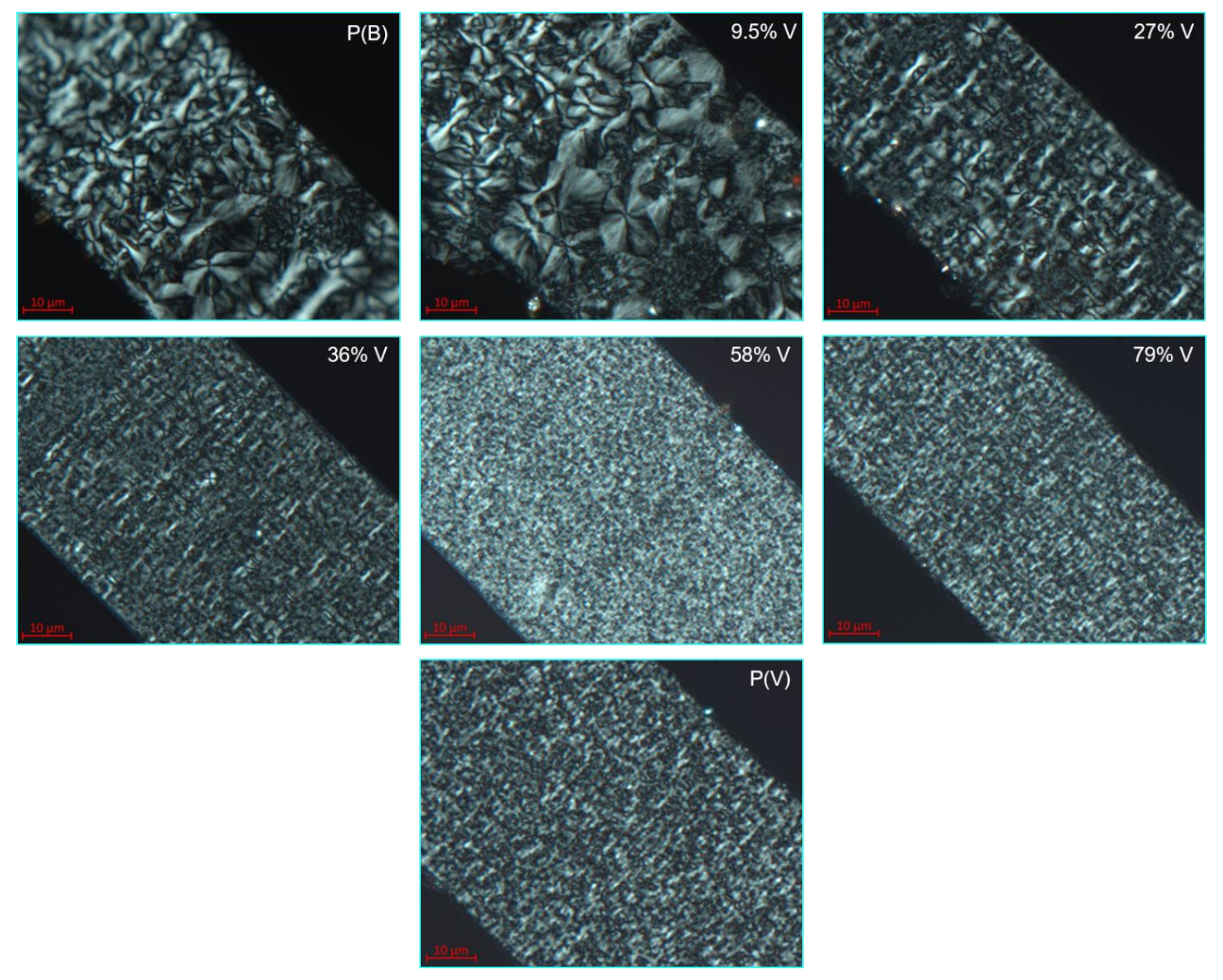


- Crystallinity and enthalpy of fusion as a function of composition for P(B-V) copolymers measured after two hours of isothermal crystallization at 20 °C. Inset: Parametric plot of enthalpy versus crystallinity.

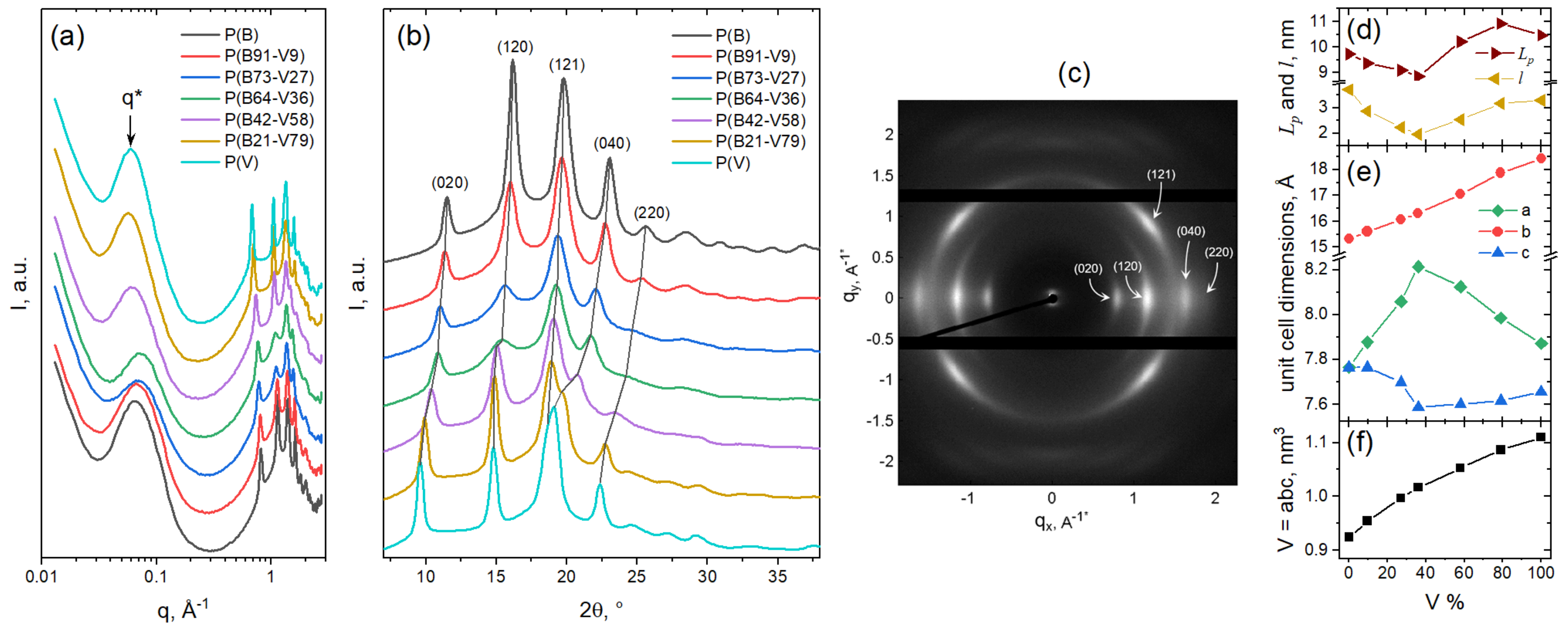
Key Learnings

- **Comonomer feed ≈ copolymer composition**
- **Dyad distribution effect (BB, VB, BV, VV, accounted for in Johnston eqn) describes deviation from Fox eqn**
- **The crystallinity of P(V) is significantly lower than that of P(B)**
- **The presence of B or V hinders the formation of P(B) and P (V) crystals**
- **Enthalpy of fusion ΔH_m mirrors the compositional dependence of crystallinity**

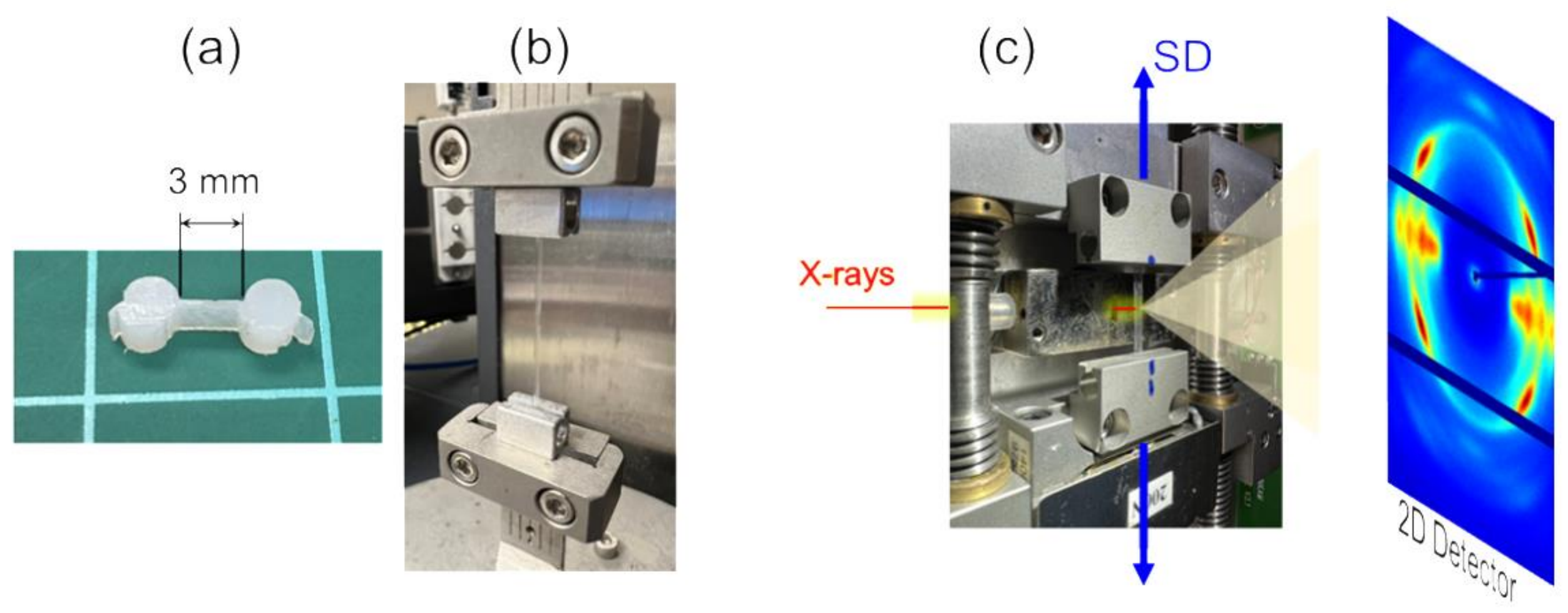
Morphology



- POM micrographs of P(B-V) copolymers measured after two hours of isothermal crystallization at 20 °C.



- X-ray analysis of P(B-V) copolymers measured after two hours of isothermal crystallization at 20 °C. (a) Combined SAXS-WAXS profiles. (b) WAXS diffractograms. (c) 2D fiber diffraction of the 58% V copolymer content. (d) Long period and crystal thickness, (e) lattice parameters, and (f) lattice volume as a function of comonomer content.

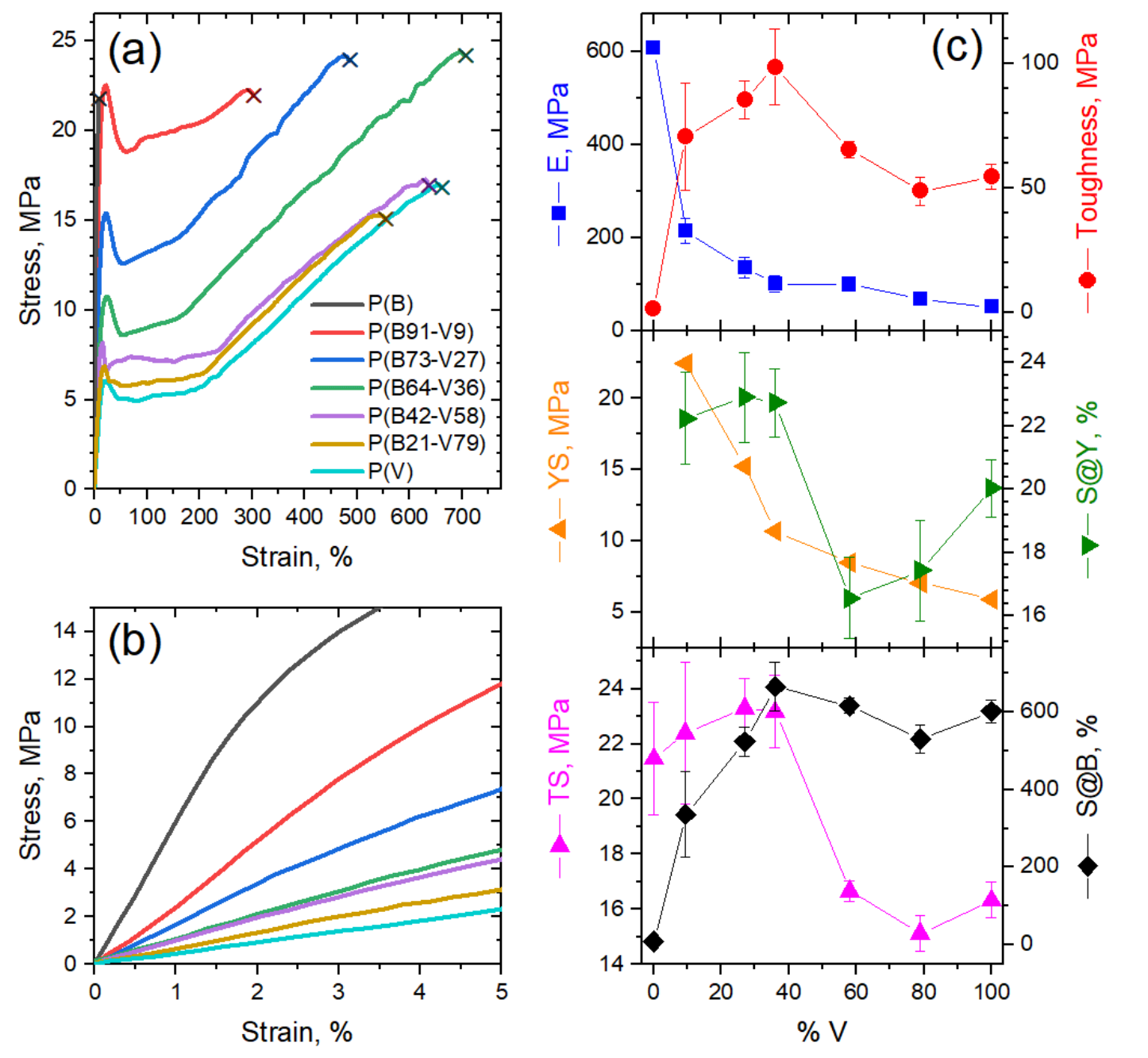


- Photographs of (a) dumbbell specimens, (b) tensile jig holders mounted on the RSA-G2, and (c) tensile jig holder mounted on the Linkam tensile stage.

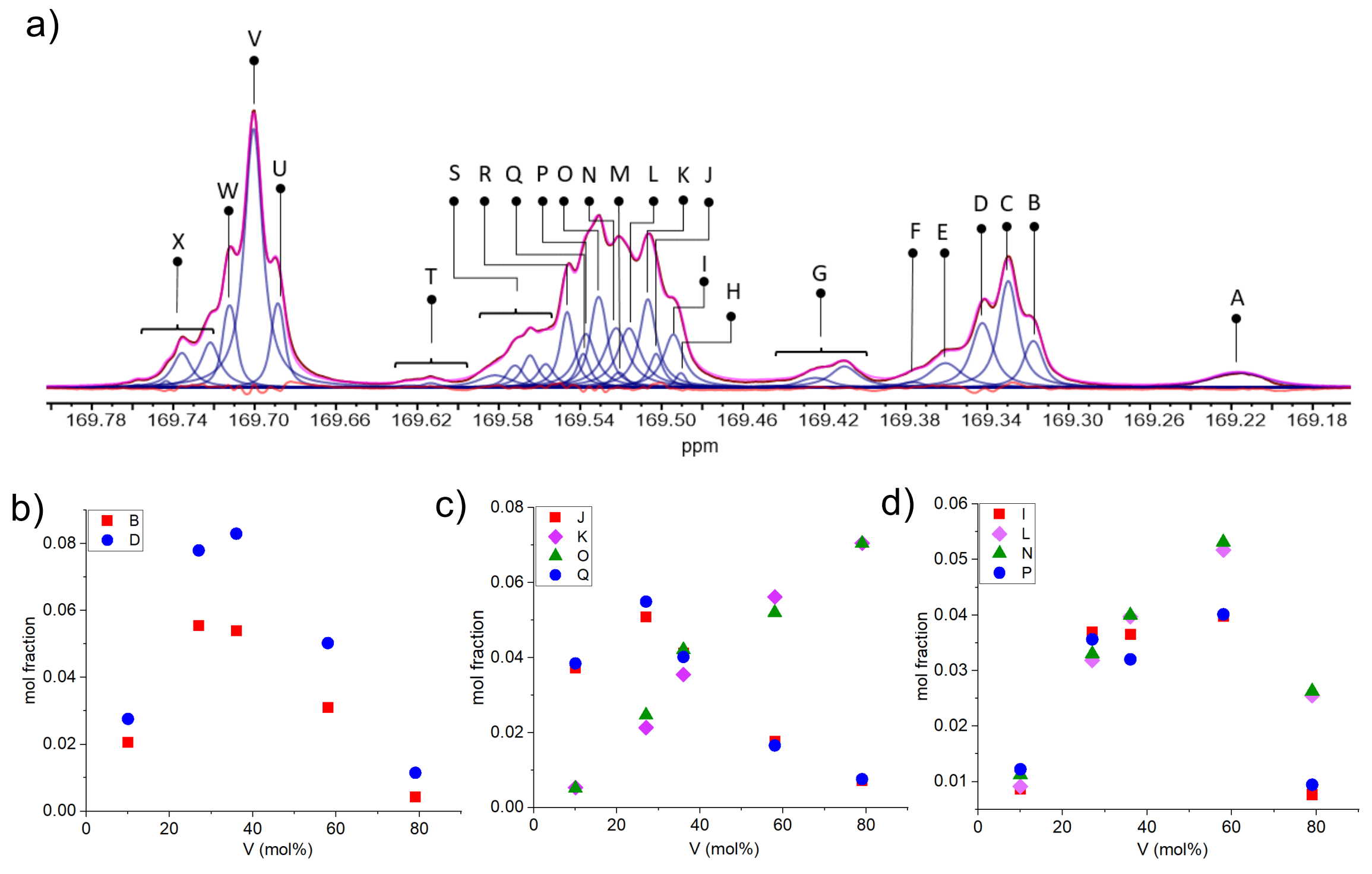
Key Learnings

- **Large spherulites (> 10μm) are only observed in P(B) and 9.5% V copolymer**
- **As V content ↑s, there is a shift from nucleation-limited crystallization to growth-limited crystallization**
- **All samples crystallize into an orthorhombic unit cell**
- **Increasing the V content results in an overall swelling of the unit cell**
- **Length of *b* increases monotonically with V% while *a* and *c* vary with composition**

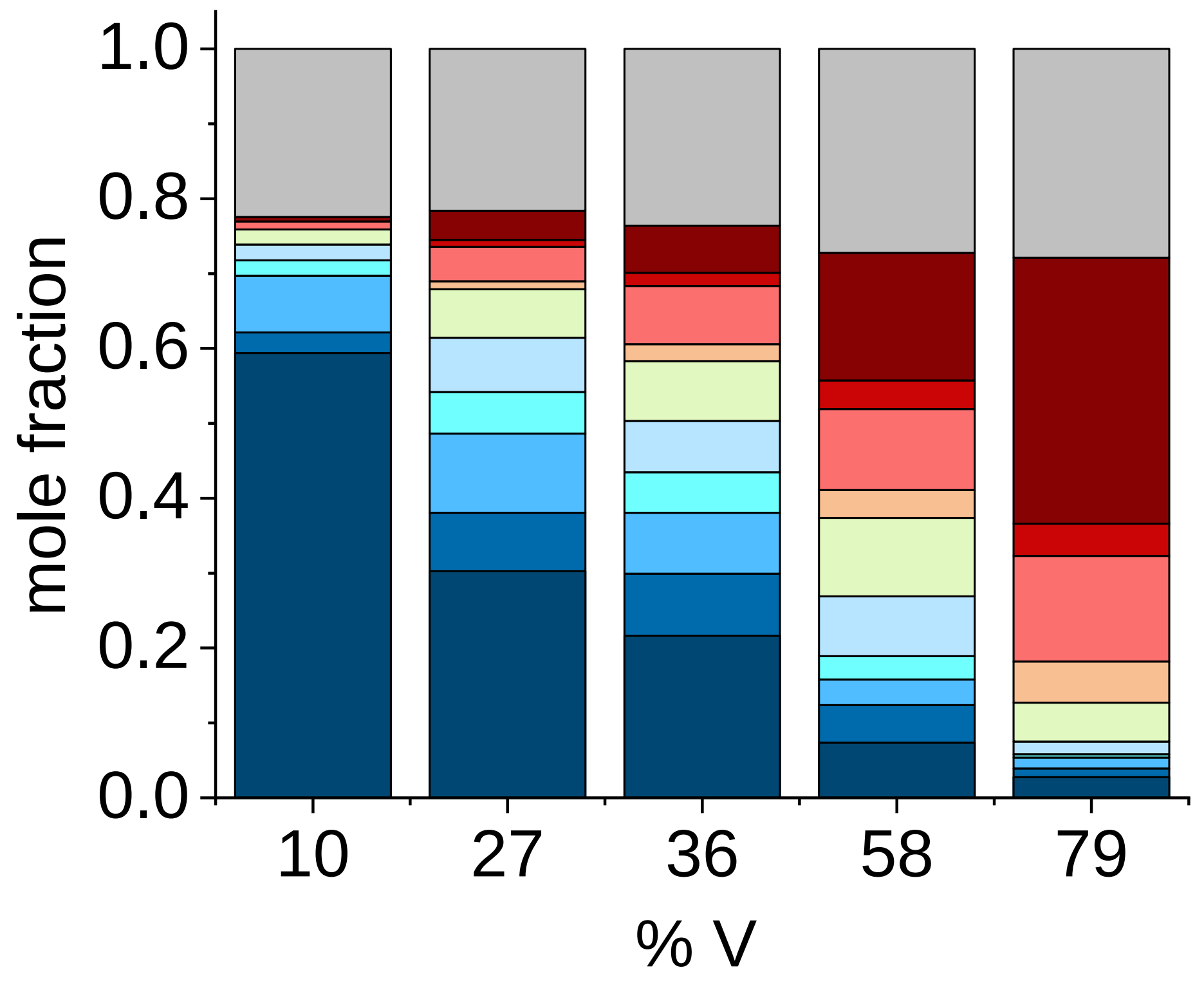
Mechanical Properties



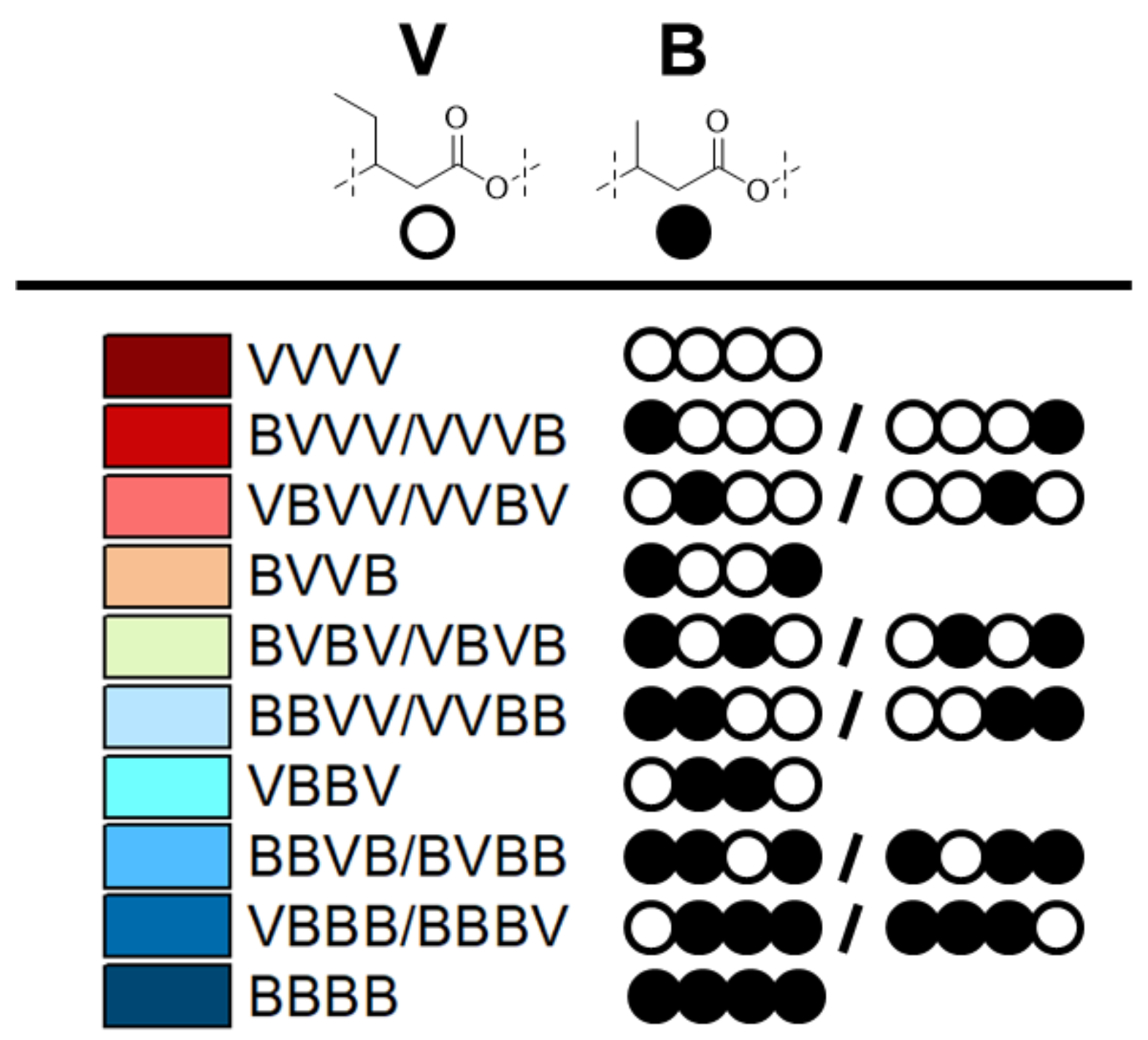
- Tensile properties of P(B-V) copolymers. (a and b) stress-strain curves measures at 22 °C. (b) Detail of the elastic regime. (c) Tensile properties as a function of comonomer content.



- Deconvoluted ^{13}C NMR spectrum of the carbonyl region of $P(B_{42}\text{-}V_{58})$. Experimental data (black line), deconvoluted peaks (blue line), sum of deconvoluted peaks (magenta line), and residue (red line). b) Mol fraction of peaks **B** and **D** vs V (mol%). c) Mole fraction of peaks **J**, **K**, **O**, and **Q** vs V (mol%). d) Mole fraction of peaks **I**, **L**, **N**, and **P** vs V (mol%).



- Stacked bar chart P(B-V) illustrating compositional tetrad compositions



- Gray bar assigned to isotactic enriched tetrads

Key Learnings

- **Elastic modulus (E) ↓s with V content**
- **Sharp transitions in toughness, yield strength (YS), strain at yield (S@Y), ultimate tensile strength (UTS), and strain at break (S@B) at 36% V composition**
- **Partial tetrad resolution observed in ^{13}C NMR spectra**
- **At 27% V content, nearly 50% of P(B-V) copolymer is comprised of syndiotactic tetrads with at least three B units**
- **At 36% V content, the majority of the tetrads (*ca.* 62%) are syndiotactic and comprised of at least two V units or are iso-enriched**

Pietrangelo, A.*; López-Barrón, C. R.*; DeRocco, M. T.; Kang, S.; Mattler, S. J.; Wright, P. J. *Macromolecules*, **2023,** 56, 5588-5598

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Let's Talk Trash: A Discussion on Plastic Circularity

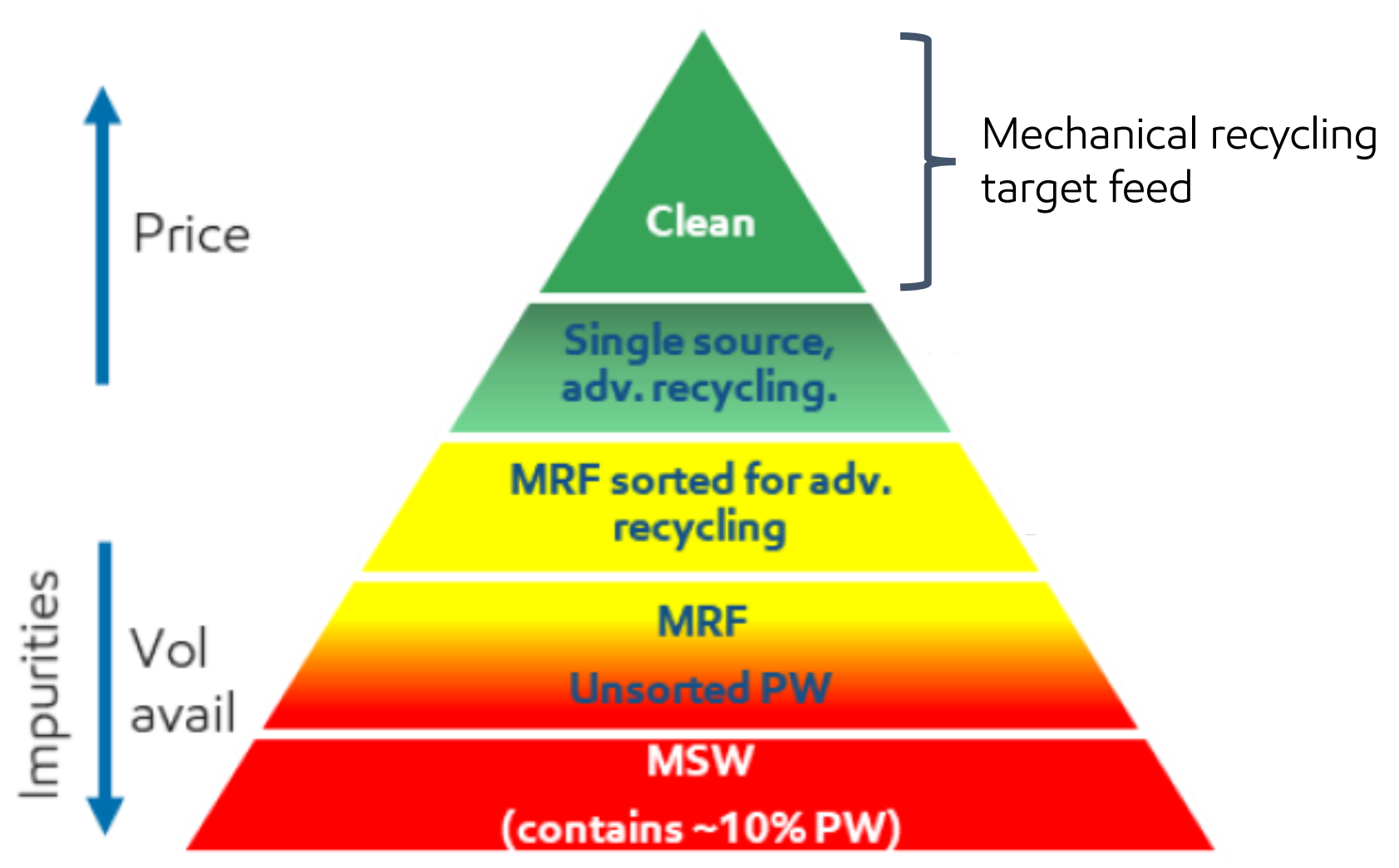
SCI Innovation Day, 12 September 2023

What happens when you put plastic in your recycling bin?

- It is estimated that only 9% of plastics worldwide are recycled, highlighting the urgent need to find ways to recycle more plastic[1]
- In the U.S. about 9% of plastic in MSW is recycled, about 76% is sent to landfill, and about 16% is combusted for energy recovery[2]
- Current sorting technology is not effective at handing approximately 30% of plastic packaging[3]
- Chemical recycling provides a pathway to take plastic wastes and break them down to molecules indistinguishable from their virgin counterparts[4]

1. OECD Global Plastics Outlook (https://www.oecd-ilibrary.org/environment/data/global-plastic-outlook_c0821f81-en)
2. EPA, National Overview: Facts and Figures on Materials, Wastes, and Recycling, 3 December 2022 (https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/national-overview-facts-and-figures-materials#Recycling/Composting)
3. McKinsey & Company, Accelerating plastic recovery in the United States, December 20, 2019 (https://www.mckinsey.com/industries/chemicals/our-insights/accelerating-plastic-recovery-in-the-united-states)
4. Ellen MacArthur Foundation, Enabling a Circular Economy for Chemicals with the Mass Balance Approach a White Paper from Co.Project Mass Balance, p. 4 (https://emf.thirdlight.com/link/f1phopemqs36-8xgjzx/@/preview/1?o)

Understanding the post-Consumer Landscape



- Advanced recycling target feedstocks Single Source & MRF Sorted to manage impurity content
- Driving for innovation to push AR feedstock lower in the pyramid

Estimates based on internal ExxonMobil analysis

ExxonMobil Advanced Recycling Projected Capacity

Certification through the International Sustainability and Carbon Certification (ISCC) PLUS process.
Numbers based on year-end capacity.
Planning basis subject to final investment decisions.

U.S. National Challenges

- Limited access to recycling programs
- Lack of standards and fragmentation across current programs
- Films, flexibles, and other mixed-polymer feedstock not accepted
- Lack of sorting capacity
- Confusing consumer education

Meeting ExxonMobil's Advanced Recycling Capacity Ambitions

Scaling technology demonstrated in Baytown, Texas

- *Baytown advanced recycling facility started up in December 2022*
- *Since the start of pilot operations, ExxonMobil has already processed 11,700 metric tons of plastic waste (more than 25 million pounds!) as of 8/8/2023*

- Large-scale advanced recycling facility by ExxonMobil
- Advanced recycling facility in development with 3rd party, Plastic Energy; ExxonMobil TACOIL offtake agreement
- ExxonMobil sites under assessment for advanced recycling
- MoUs to assess collaboration on advanced recycling

Planning basis subject to final investment decisions

Widening the Range of Recyclable Plastics[1]

Material type		Single-stream plastics recovered for mechanical recycling[2,3]		Mixed-plastics desirable for Exxtend™ technology[4]
1 PET	🟢	•Monomaterial, easy to sort •Polymer properties amenable to M/R and food contact qualification	🟡	•Acceptable in quantities up to oxygen contaminant limit
2 HDPE	🟢	•Monomaterial, single source more common •Polymer properties amenable to M/R	🟢	
3 PVC	⚫	•Limited single source collection •Lack of monomaterial (additives)	⚫	•Capable of taking small amounts
4 LDPE	⚫	•Film collection & sortation more challenged •Polymer properties not amenable to M/R	🟢	
5 PP	🟡	•Sortation improving •Polymer properties less amenable to M/R	🟢	
6 PS	⚫	•Expanded PS foam collection, cleaning, densification is challenged	🟡	•Acceptable in quantities up to contaminant limits
7	⚫	•Not a monomaterial	🟡	•Acceptable in quantities up to contaminant limits (e.g., high nitrogen content from nylon and polyamides)

🟢 Target
🟡 Tolerated in feed mix
⚫ Challenge

[1] In communities with programs and facilities in place that collect and recycle the resulting product.
[2] Plastics Recyclers Europe: PET Market in Europe: State of Play – Production, Collection and Recycling Data 2018 (https://743c8380-22c6-4457-9895-11872f2a708a.filesusr.com/ugd/dda42a_e0c40c546a7446daa7ba5e0bedd67cca.pdf)
[3] Prepared for ACC by More Recycling, US PCR 2020 (https://www.plasticsmarkets.org/jsfcontent/Non-BottleReport18_jsf_1.pdf)
[4] Internal ExxonMobil Analysis

Exxtend™ Complements Mechanical Recycling

	Mechanical recycling	Exxtend™ technology
Feed	Typically limited to cleaner single-polymer feeds	Can accept mixed-polymer, that are difficult to mechanically recycle[1]
Polymer performance	Degraded quality with each cycle	Virgin polymer performance and processability
Greenhouse gas	Often provides a GHG emission advantage compared to production of virgin plastics	Sphera carbon footprint assessment (ISO 14067) Feedstock Study*
Scaleability	Leverages new regional-scale infrastructure	Leverages existing world-scale infrastructure

[1] For example, mixed polyolefins with limited amounts of PET or PS

**Every 1,000 tons of waste plastics processed results in 185-525 tons CO2e (19-49%) lower GHG emissions than processing the same amount of fossil-based feedstock.*
https://www.exxonmobilchemical.com/en/exxonmobil-chemical/sustainability/advanced-recycling-technology/carbon

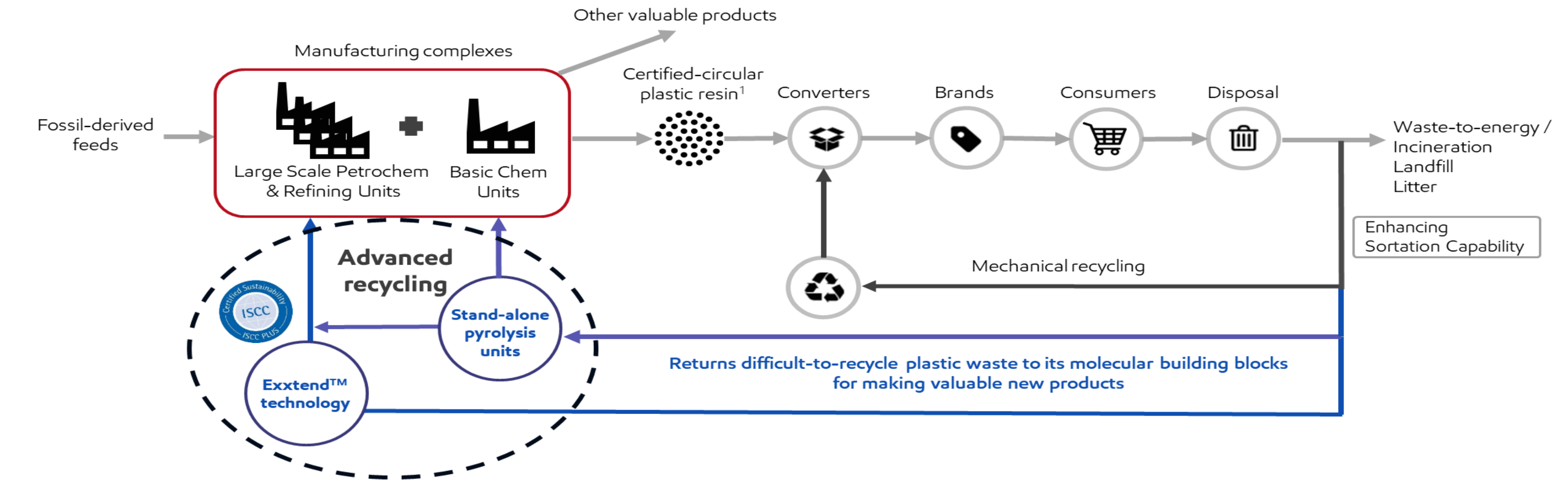
What does plastic waste look like?


Mixed Plastic Waste


PEX Tubing


Pharmacy Pill Bottles

Exxtend™ aims to accelerate progress towards a more circular plastic economy



[1] Attributed via ISCC PLUS version 3.3 mass balance approach.

Does not represent GHG emissions or recycled content. For illustrative purposes only.

Does not represent GHG emissions or recycled content.

Collaborating to collect & sort difficult-to-recycle plastics

HOUSTON RECYCLING COLLABORATION
ExxonMobil · lyondellbasell Advancing Possible · cyclyx · FCC Environmental Services

- Collaborating to increase collection & sortation of plastic waste in Houston
- Collecting films at ExxonMobil Houston Campus
- Collecting Mobil1 bottles at auto stores
- Collaborating with TenCate to recycle end-of-life artificial turf

Next Generation Film Design for Product-to-Application Sustainability Enhancement

Ali H. Slim*, Matthew W. Holtcamp, Irene C. Cai

Materials Innovation, Novel Products Research, ExxonMobil Technology and Engineering Company

Polyethylene Applications

The polyethylene world is a complex and rewarding field with everlasting challenges. The nature of these polymers makes them suitable for a wide range of applications ranging from films to molding.

Packaging

Adhesion

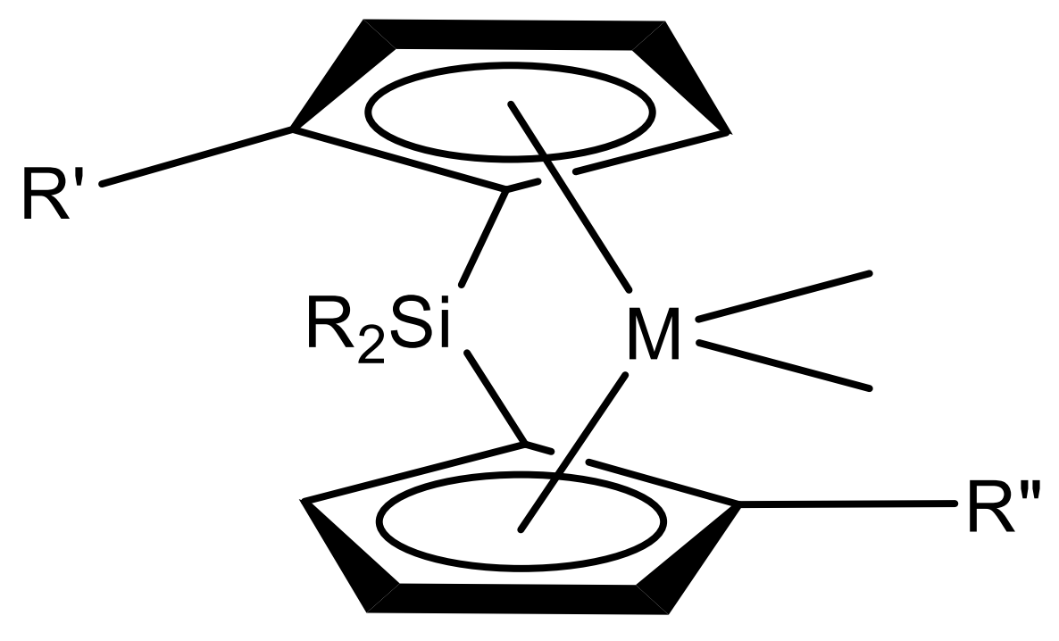
Molding

Product to Application Overview

- The properties of the resin dictate the potential attributes of the film including mechanical, processing, and optical properties
- Resin design highly influences the processability of the films with easiness of processing desired to minimize energy consumption
- Advanced resin and processability properties in return enhance the film durability and shelf life of products which reduces waste
- Better overall performance leads to a higher conversion efficiency of films and increases yield per product

Catalyst Design

- Single site novel catalyst allows for tailoring to desired product attributes:
  - R substituents enhance ability to control comonomer incorporation, activity, and molecular weight capability
- Innovative design and structure provide sustainability benefits:
  - Less energy: Low impurity contents including ash and residue enable keeping catalyst in the final product resin
  - Resource reduction: Smaller material needs due to high catalyst activity and single sourcing approach



Generic Metallocene type catalyst structure

Resin Properties and Attributes

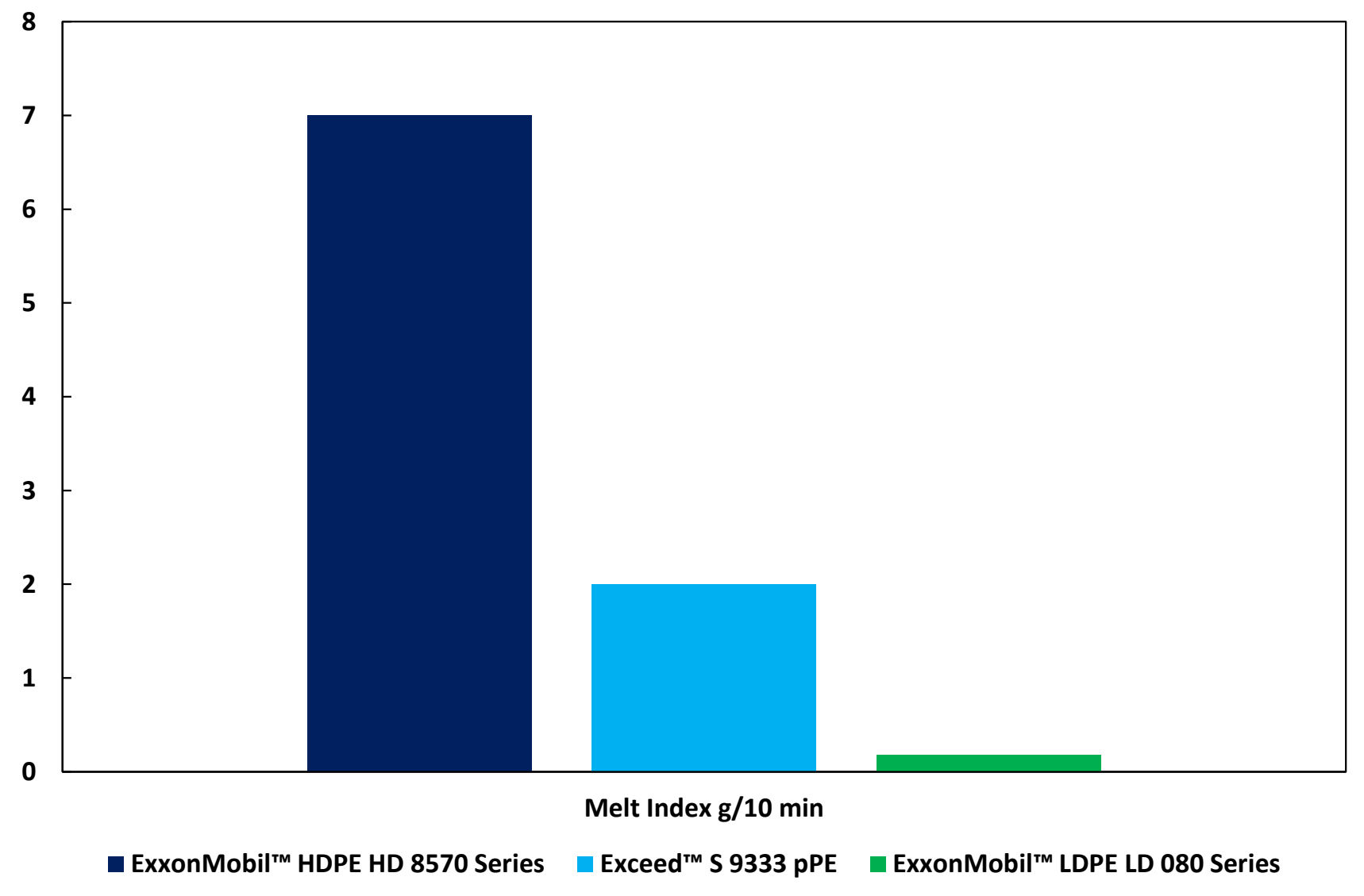
- The resin properties influence the end-to-end behavior of the polymers
  - Structural and morphological changes in polymer chains alter the processability, stiffness, strength, and durability of the resulting film products
  - Minor changes in molecular weight or comonomer content can alter the polymer chain properties and significantly impact the film design and handling

Attribute	Exceed™ S 9333 pPE	ExxonMobil™ LDPE LD 080 Series
Density, g/cm^3	0.925	0.92
Puncture Energy, in·lb	24	6.9
Puncture Force, lbf	9	12

- Performance polymer products focus on capturing the best of both world by having high stiffness and toughness while maintaining good processability
- Exceed™ S performance PE presents innovative film converters with solutions to deliver high performance durable packaging with sustainability benefits that help reduce food waste and raw material needs for processing

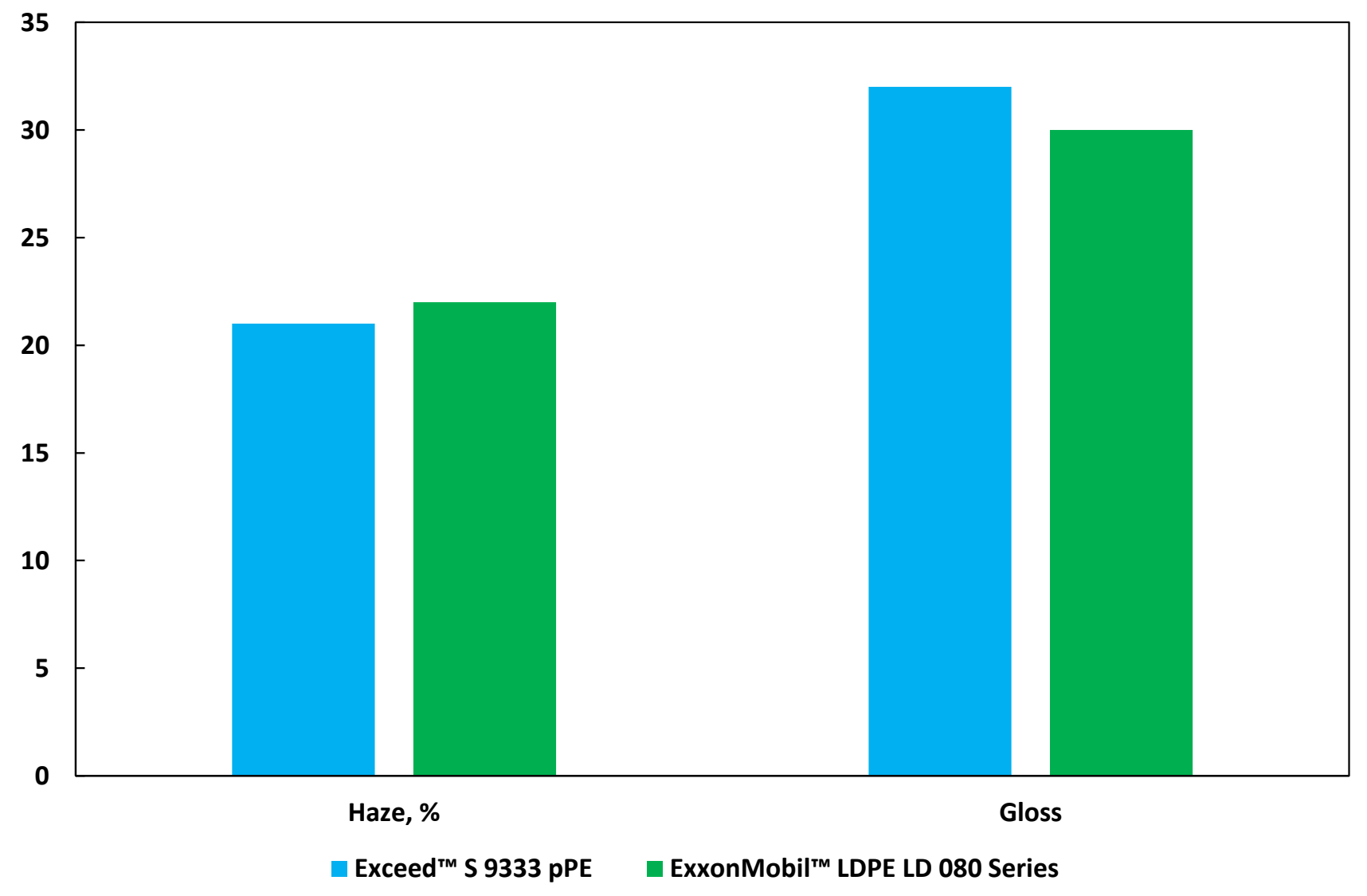
Formulation Capability

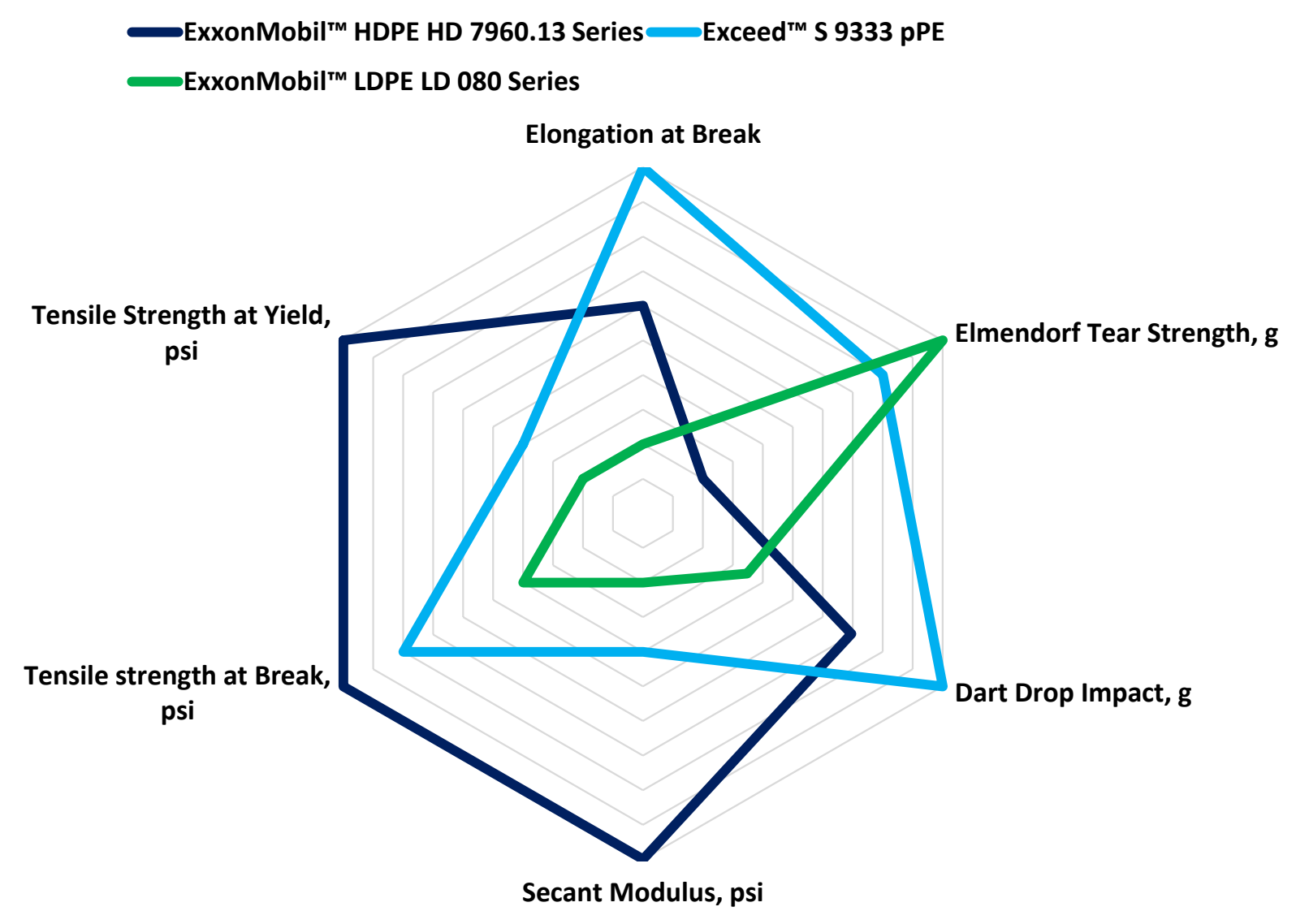
- Reducing the need to add high density polyethylene for stiffness and low density polyethylene for better processability via a one resin solution
- Exceed™ S performance PE balances the processability capability with mechanical properties to reduce the need of pre-processing formulation



Film Optics and Performance

- New generation of performance polyethylene products are capable of capturing a wide-range of the property spectrum while maintaining the processability and optics of LDPE grades and performance of their HDPE counterparts





Benefits in Packaging Applications

- Exceed™ S performance polyethylene delivers industry-leading combinations of stiffness and toughness while being easy to process

- Performance resins simplify the film processing steps thus minimizing inefficiencies, human mistakes, and scrap
- Exceed™ S performance PE allows converters to rethink film design by:
  - Leveraging increased performance to help facilitate solutions with sustainability benefits
  - Reducing the need to add HDPE for stiffness or LDPE for processing

Takeaways and Future Considerations

- Polyethylene products have a versatile set of applications due to the ability to tailor them to specific properties and needs
- The properties of the product resin dictate the formulation of the film to ensure good processability while maintaining the desired performance of such films in applications
- Performance polyethylene grades capture the delicate balance between performance and processability which helps enhancing film durability and shelf life of products
- The advancement in polymer science technology has led to major sustainability advantages including reduction of waste material and processing energy consumption, while maintaining high performance standards in a wide range of consumer applications

References

1. “ExxonMobil Introduces New Exceed™ S Performance Polyethylene, Enabling Converters to Rethink Film Design for Simpler Solutions” ExxonMobil Corporation, *Press Release*, April 11, 2022.
2. Polyethylene Products, Digital Product Selector; https://www.exxonmobilchemical.com/en/products/polyethylene/productselector#/datatable/landing.

Acknowledgement

Application of Filtered Two-Fluid Models to Industrial-Scale Fluidized Beds

Laurien A. Vandewalle, Kevin E. Buettner, Timothy M. Healy
ExxonMobil Technology and Engineering Company, Spring (TX), USA

Motivation

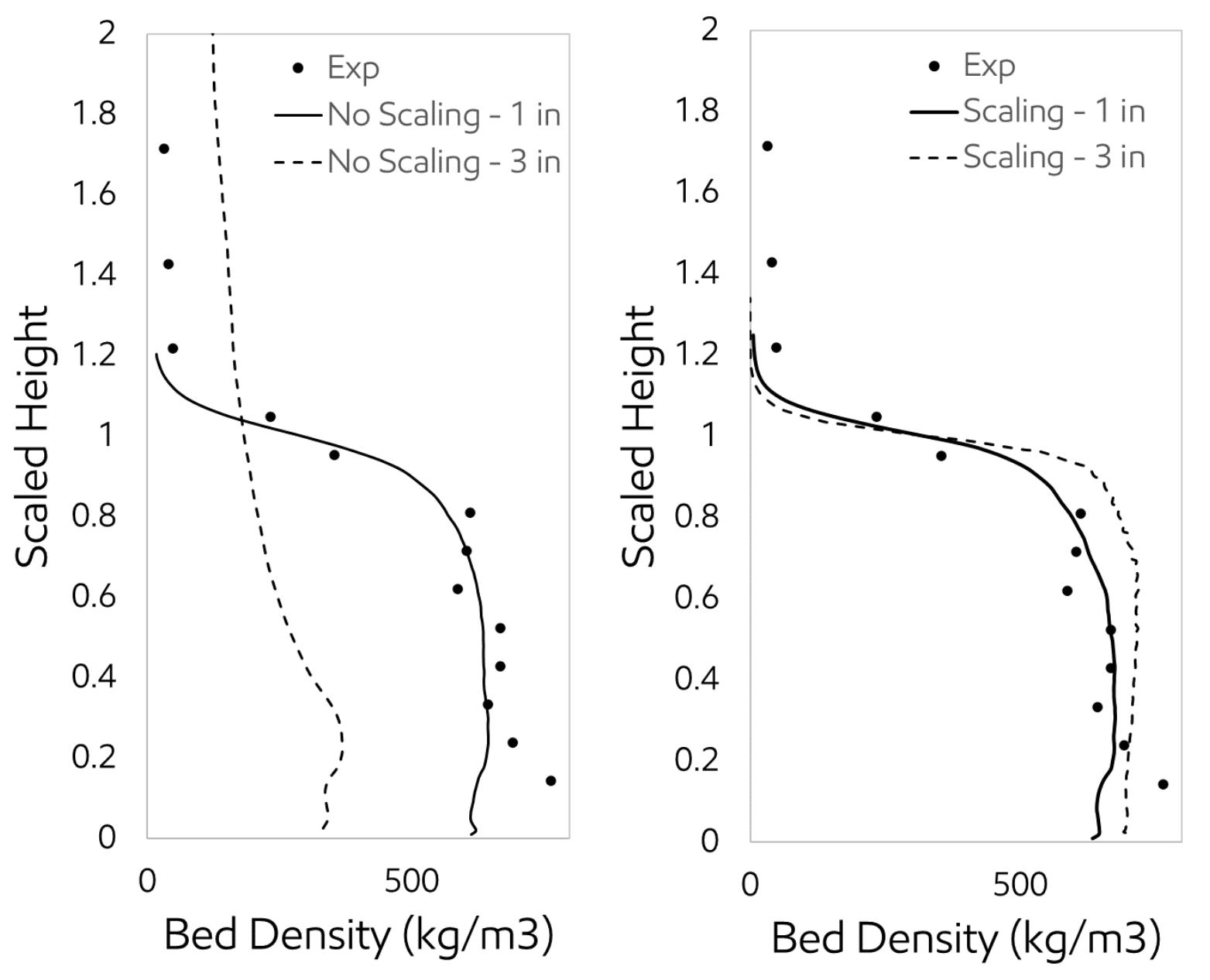
- Enhanced heat and mass transfer characteristics make gas-solid fluidized the preferred reactor choice for many industrial processes
- EMTEC uses **computational fluid dynamics (CFD)** to study, debottleneck and improve existing commercial units (e.g., FCC), as well as for the **design and scale-up** of many novel gas-solid fluidized bed processes
- **Validated** CFD models can increase confidence when scaling-up from smaller-scale, often cold-flow, experimental studies:
  - Physical basis to bridge gap in scales
  - Insight into commercial operation via **fully coupled process physics**
- But, CFD simulation of commercial-scale fluidized beds is **problematic**:
  - Most widely adopted existing methodologies require very fine grids
  - Commercial urgency usually necessitates fastest-possible turnaround
- Industrial application of CFD to fluidized beds **requires alteration of current methods**, to adequately capture the physics while keeping the simulation size **tractable**.

Model validation

Example #1

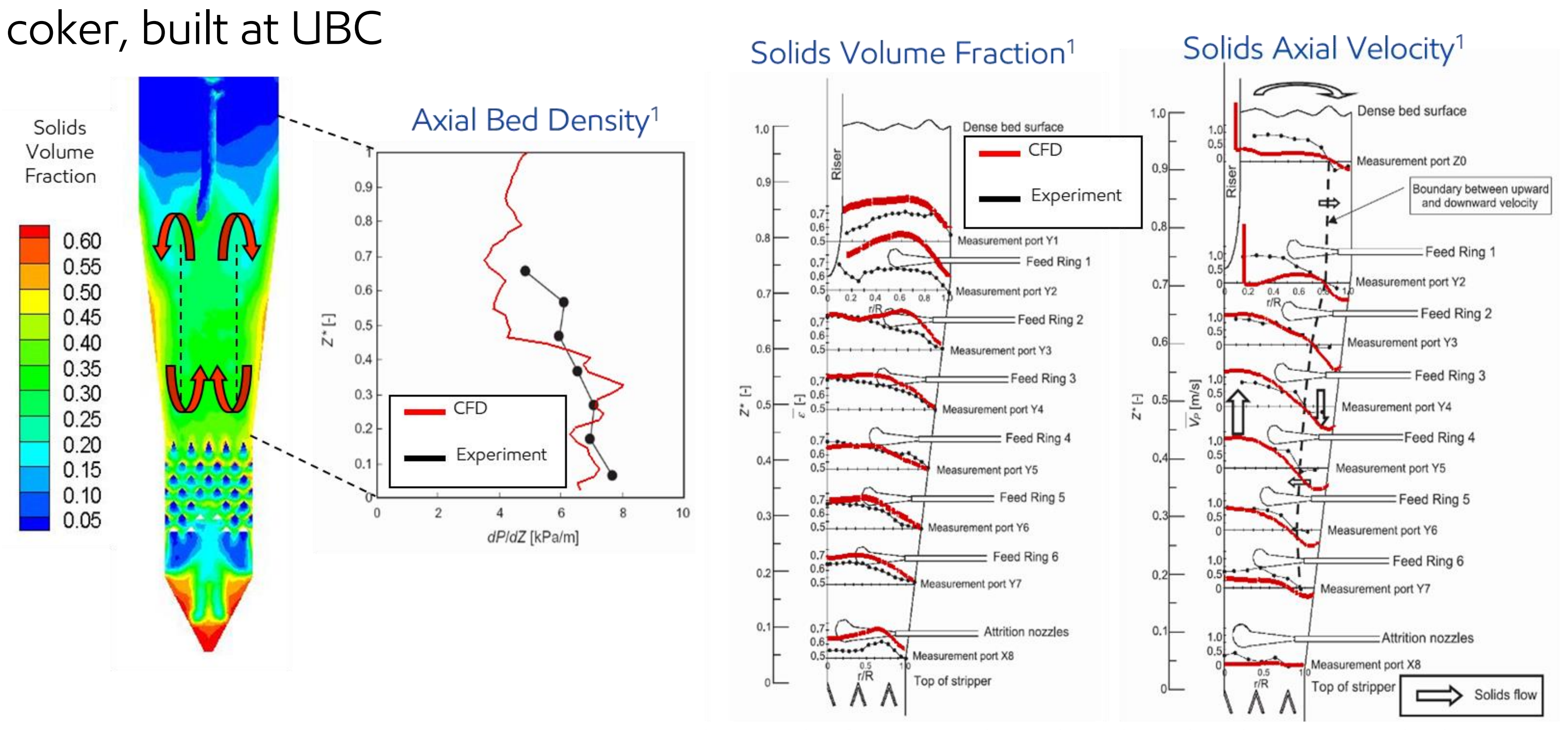
- 36″ column (no internals)
- FCC particles: 70 µm, 1500 kg/m^3
- Ambient air at various flow rates

Validation by comparison with experimental bed density profiles, for grids with two different cell sizes



Example #2

Air and FCC particle system in a 1/19th scale cold-flow twin of an actual fluid coker, built at UBC



[1]Figures taken from Song et al., *Powder Tech*, **147** (2004) 126-136 – Used with permission

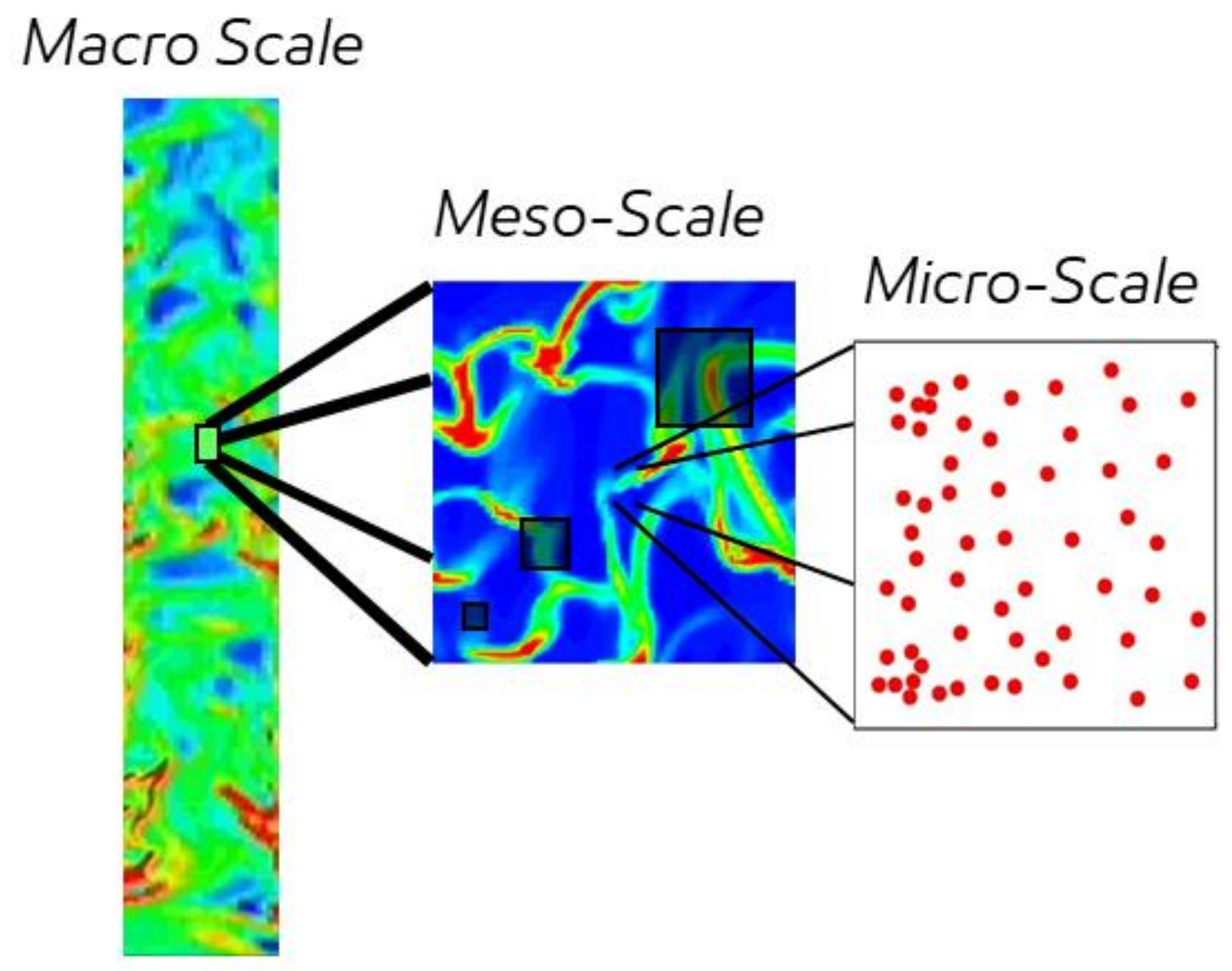
Filtered two-fluid models

CFD simulations of fluidized beds require an understanding at **multiple flow scales**

Micro-scale (**kinetic theory**): particle-particle interactions

Meso-scale (**10d$_p$ mesh**): particle clustering and fine flow structures

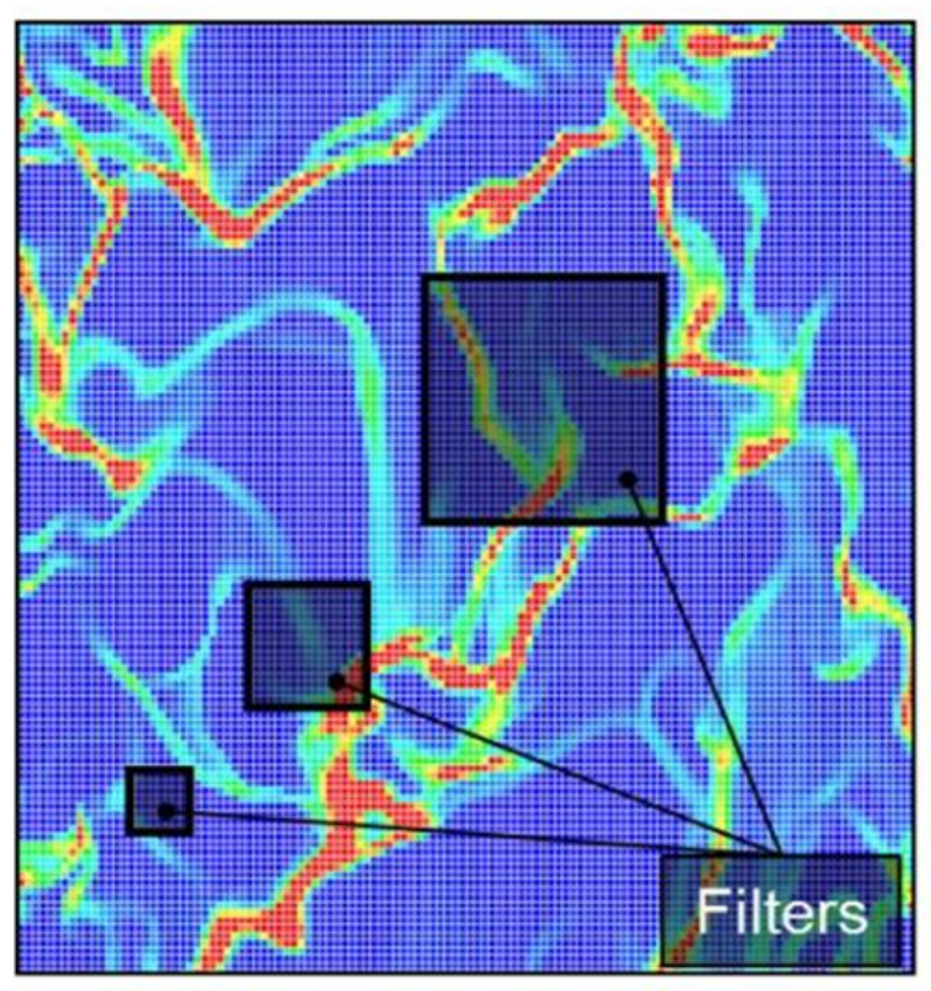
Macro-scale for integral-scale bed fluid dynamics



Timely commercial-scale simulations requires avoidance of the meso-scale resolution

➔ **Filtering approach models sub-macro-scale**

➔ **Filtered model allows simulation of commercial-scale fluidized beds using large computational cell-sizes**

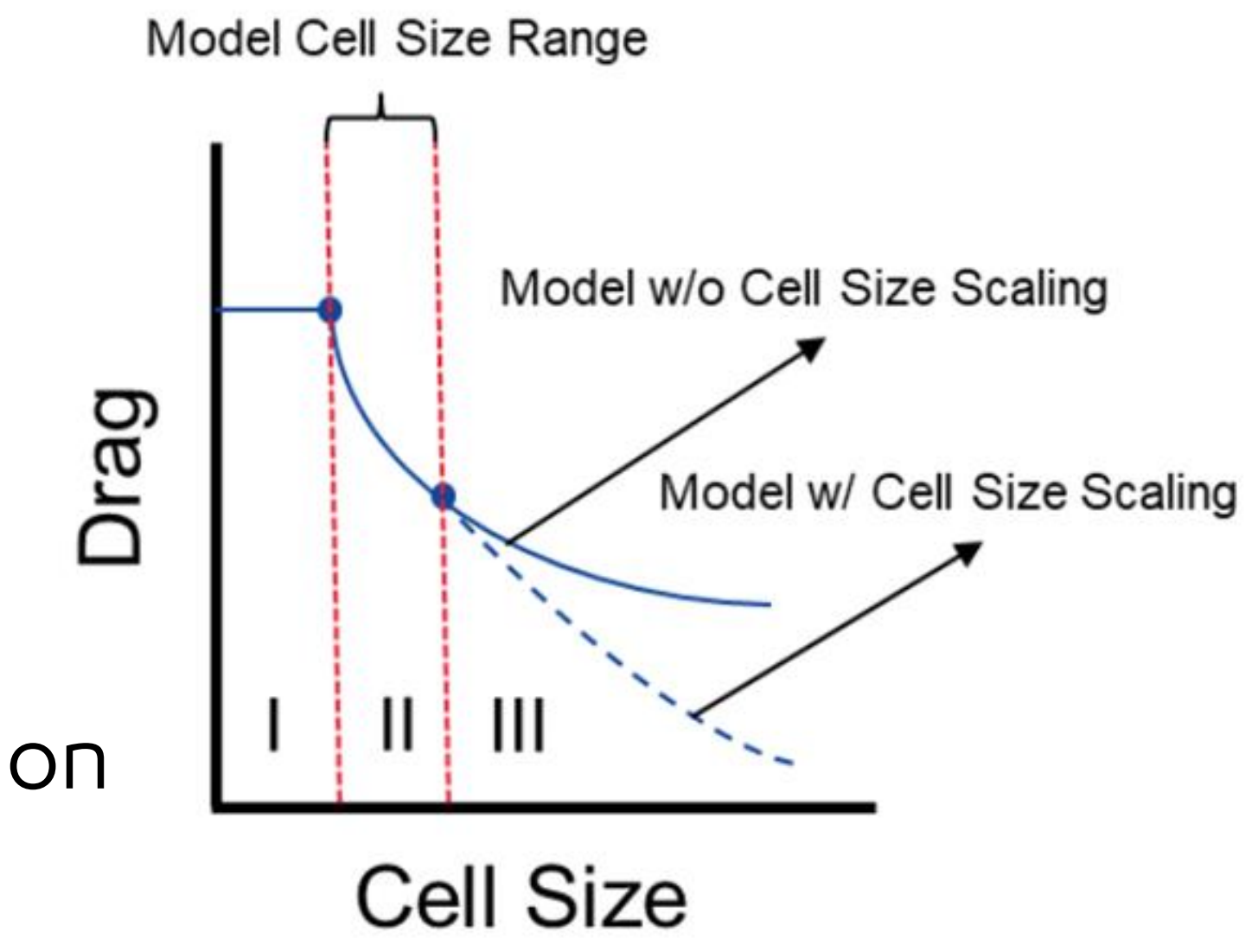


Blue: Low solids volume fraction
Red: High solids volume fraction

Filtering methodology

- Fine mesh simulations (for various domain-averaged solids volume fractions) in periodic domain resolves detailed flow structures
- Various filter sizes used to determine region-averaged quantities
- Regression across filter sizes, initial solids volume fractions results in closures for two-fluid model, mesh size and filter size related

Filtered model enhancements



\+ Extrapolation to very large grid sizes
Cascading vs. use of scaling relations

\+ Application to reacting gas-particle flows
Filtered reaction rate and species dispersion
Cluster-scale effectiveness factor

\+ High-slip velocity processes require transition from one-marker (function of voidage) to two-marker (function of voidage and Reynolds number / slip velocity) filtered drag models

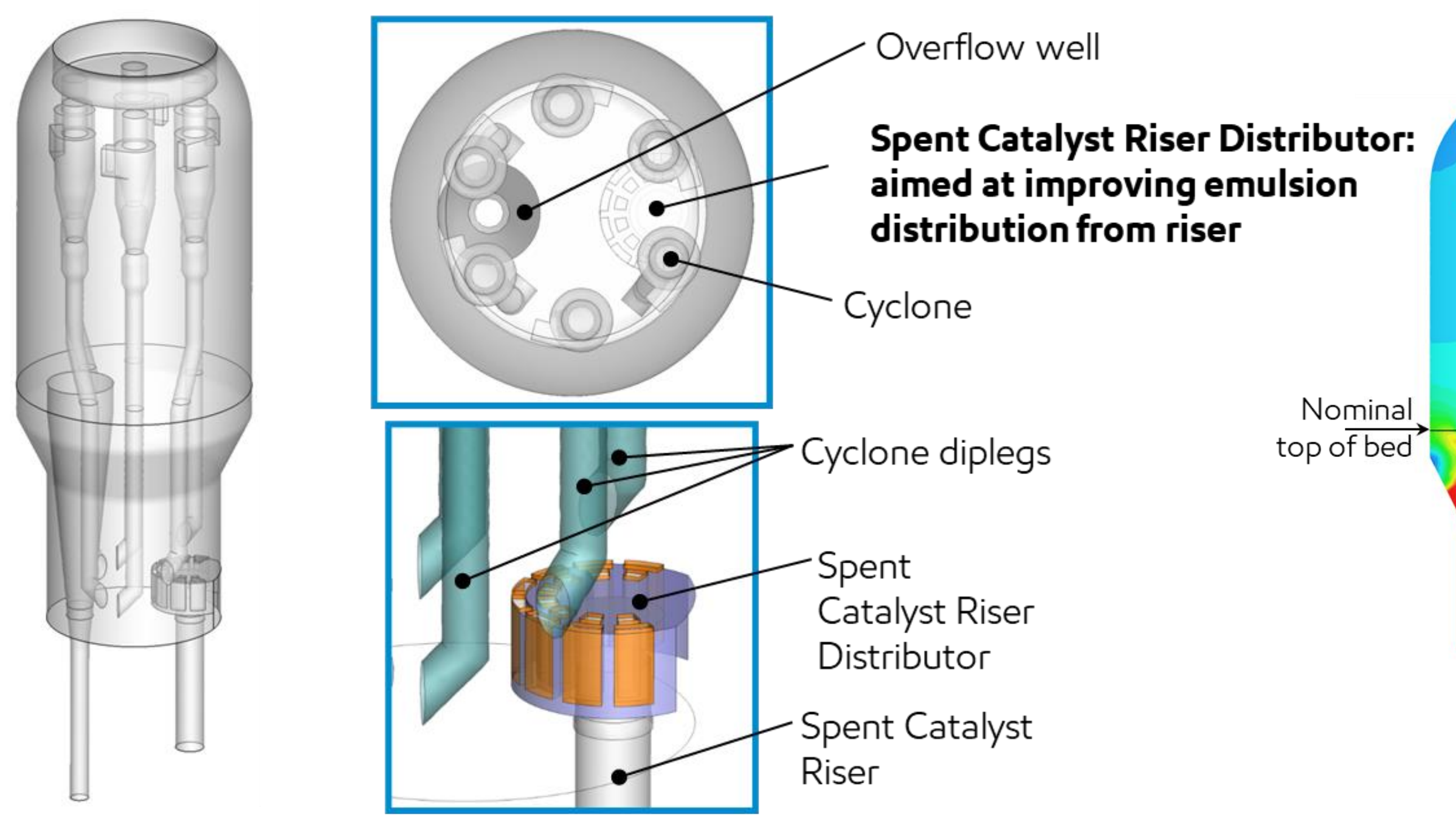
EMTEC developed and applied this methodology to their fluid catalytic cracking (FCC) and fluid coking processes. Nowadays, this methodology is continuously applied to and further improved for the design and scale-up of novel gas-solid fluidized processes.

Application to industrial-scale fluidized beds

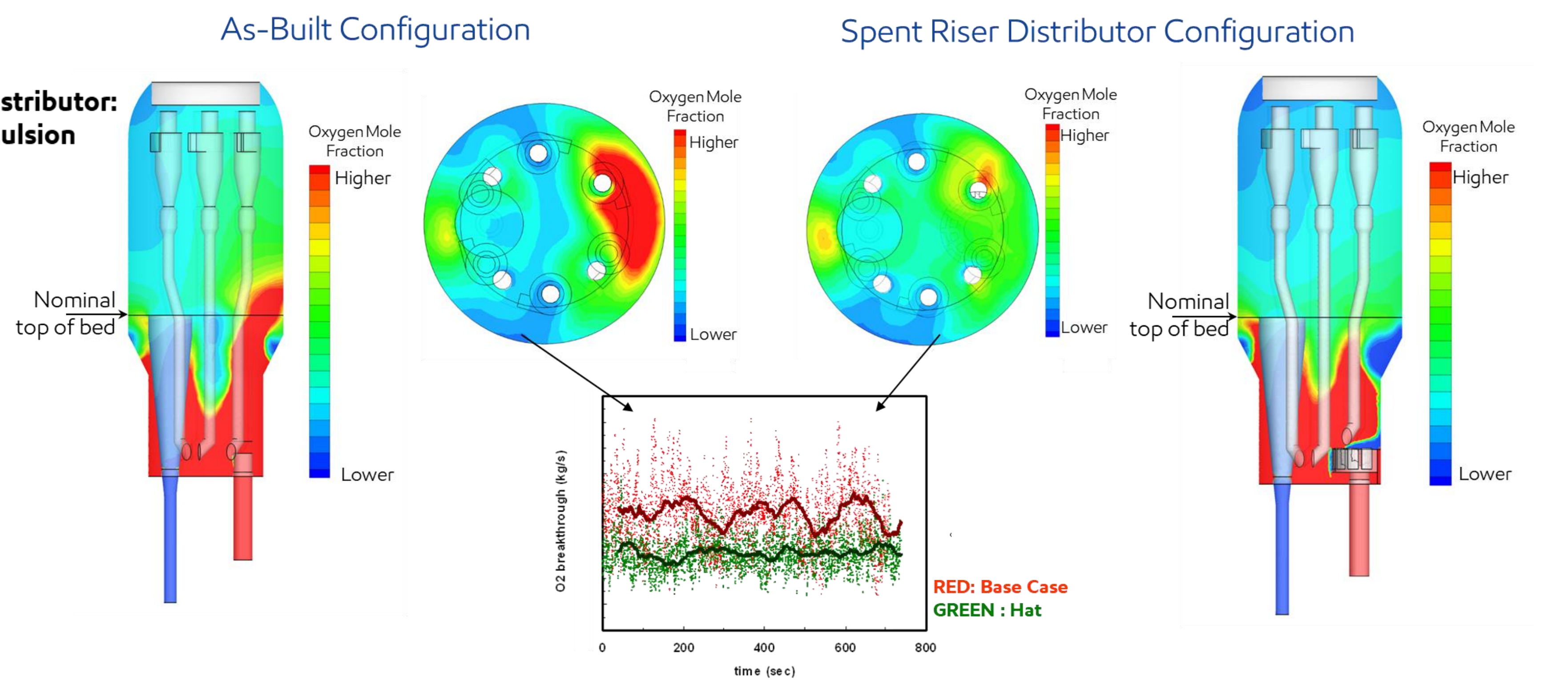
Improving the regenerator for Fluid Catalytic Cracking (FCC): spent catalyst riser distributor

FCC is an important process for gasoline manufacturing, comprising of several process vessels: reactor, stripper, regenerator.

CFD was used to study flow instabilities and non-uniformities which drive air bypassing in the regenerator. CFD model incorporates custom burn kinetics and the filtered gas-solid flow model



Spent Catalyst Riser Distributor: aimed at improving emulsion distribution from riser



From CFD to reality

Distributor fabricated and installed in commercial FCC regenerator

- ✓ Solid circulation, feed restored to pre-installation rates
- ✓ Lower afterburn following installation
- ✓ Higher dense bed temperature allowing higher conversion at constant circulation rate

US Patent: 8,728,302

SCI Innovation Day 2023
September 12, 2023, Philadelphia (PA)

Advantaged Materials for Renewable Diesel and Jet Production

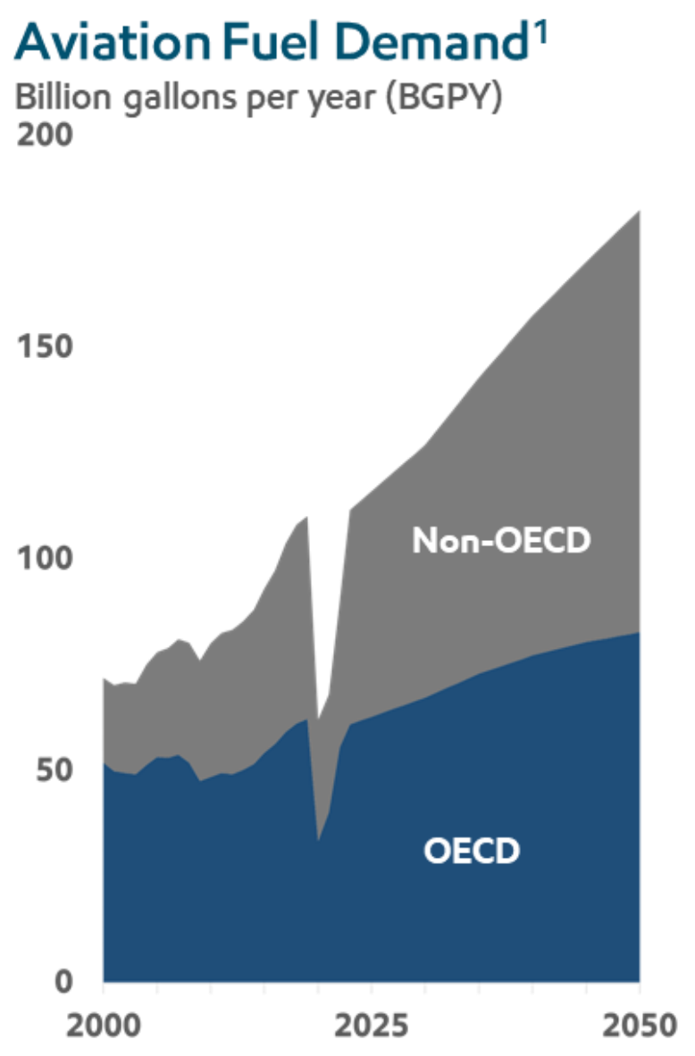
Chuansheng Bai, Majosefina Cunningham, Mark Deimund, Jason Golias, Rishi Gupta, Kelsey McNeely, Randy Smiley, Megan Witzke, Sara Yacob

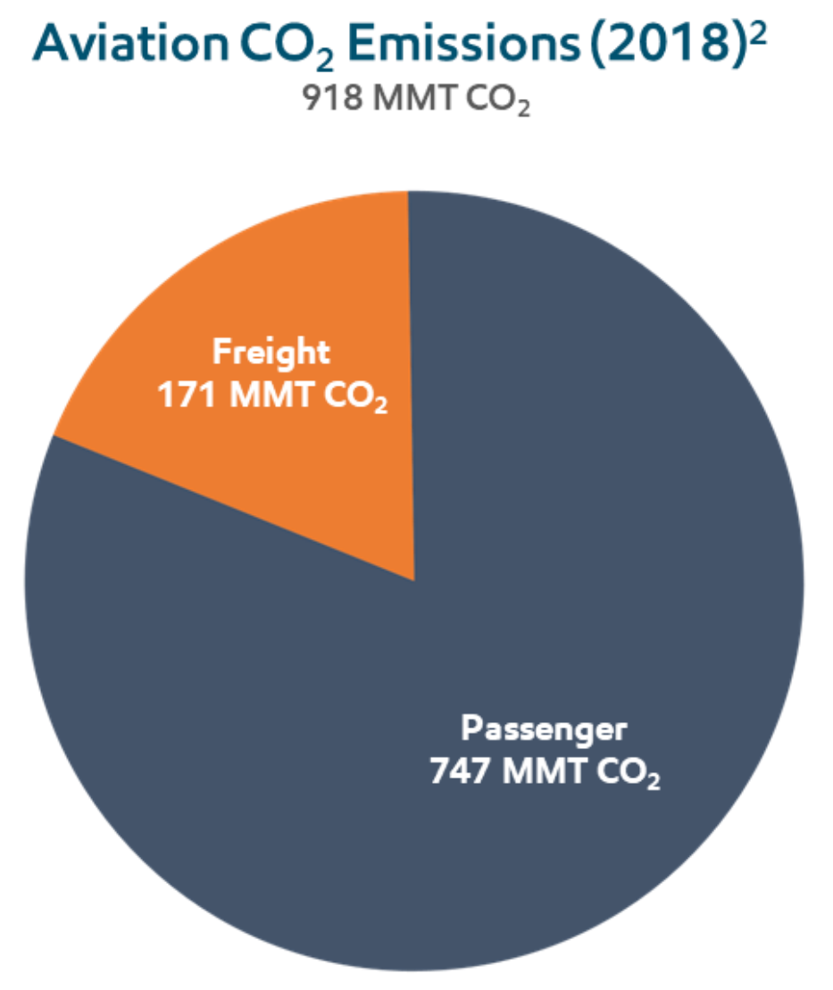
ExxonMobil Technology and Engineering Company, ExxonMobil Catalysts and Licensing

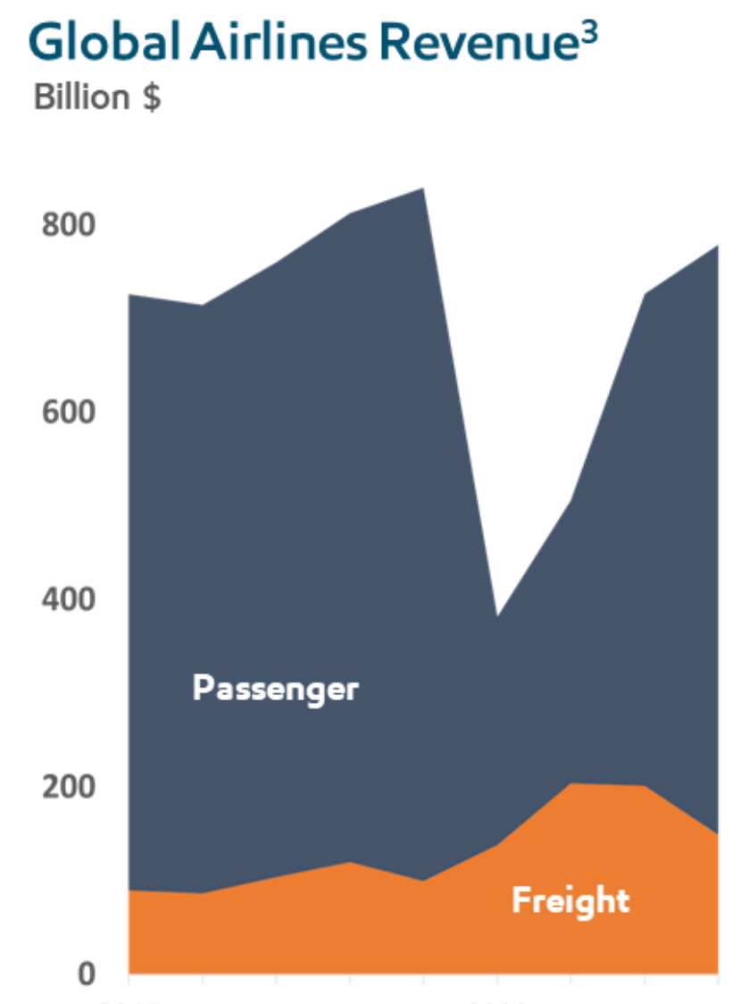
SCI America Innovation Day 2023 Science History Institute Philadelphia, PA

Aviation Fuel Demand, GHG Emissions, and Revenue

2018 aviation emissions were 918 million MT or 2.4% of global emissions


Aviation Fuel Demand[1]
Billion gallons per year (BGPY)

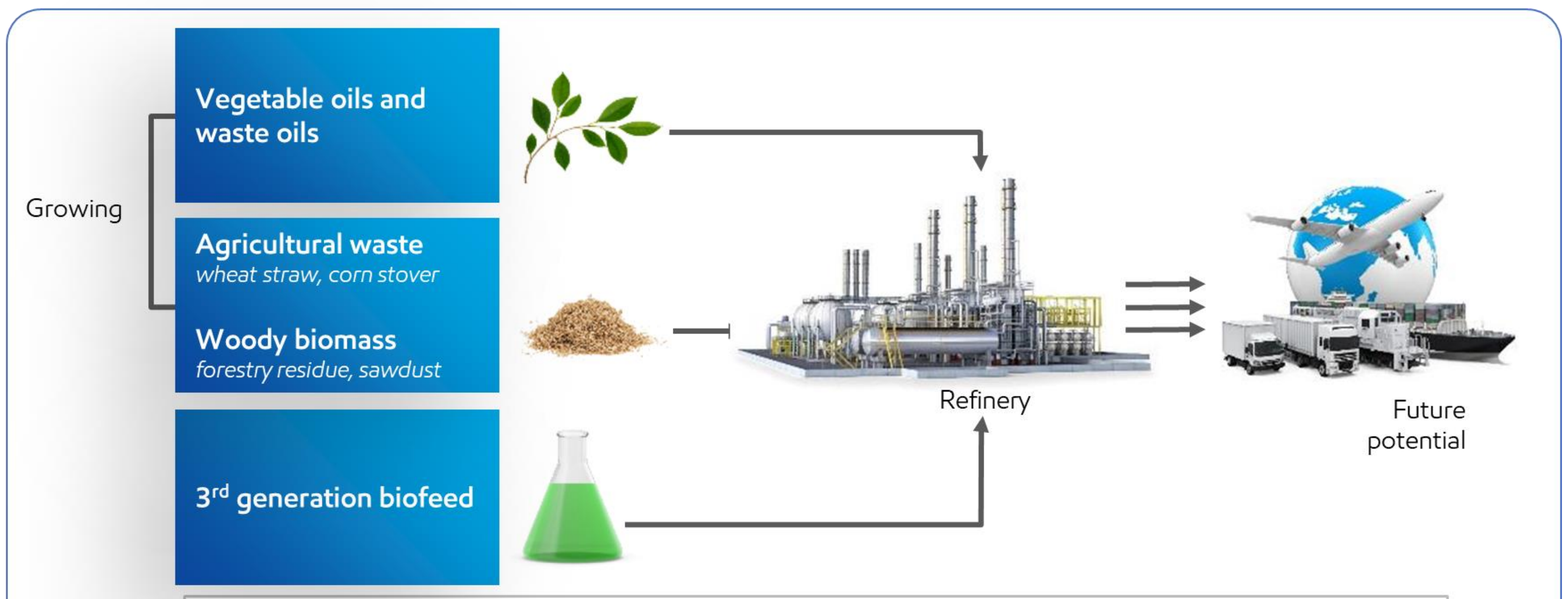

Aviation CO_2 Emissions (2018)[2]
918 MMT CO_2


Global Airlines Revenue[3]
Billion $

SAF at \$300/MT CO_2 implies a cost of \$300 billion/yr to avoid ~1 billion MT/yr of CO_2 vs. typical airline revenues of ~\$800 billion (25% fuel cost)

Several Routes to Upgrade to Biofuels

Replacing crude oil with biofeeds to produce lower-emission transportation fuels



Near-term projects focused on Canada, Europe and California, where regulations support attractive returns

BIOFUELS POTENTIAL \$1 TRILLION MARKET SIZE BY 2050†

Advancing Technologies to Enable Renewable Fuels

ExxonMobil is advancing the development and use of technologies for lower-emission fuels

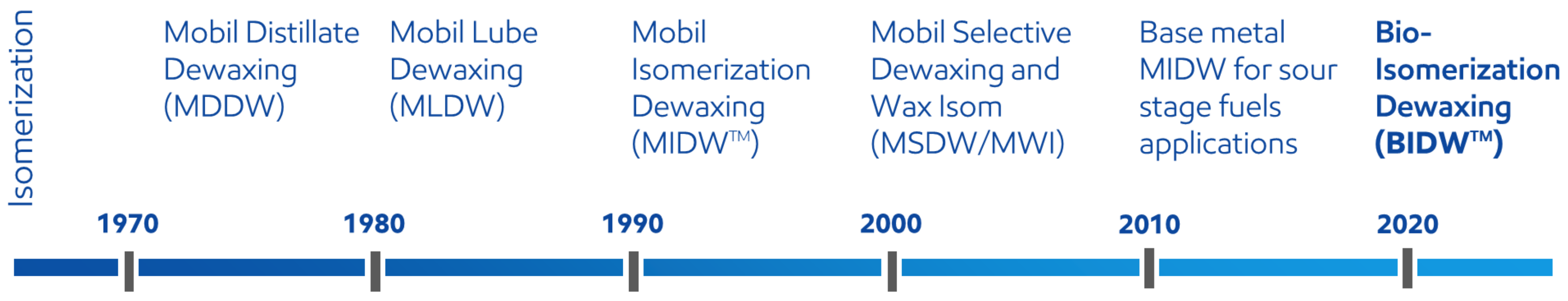
ExxonMobil Catalysts & Licensing (C&L)

Renewable Distillate Fuel Technologies:
- Bio-Isomerization Dewaxing (BIDW™) catalysts
- ExxonMobil Renewable Diesel Process (EMRD™)
- Flexibility to tailor the amount of jet fuel vs. diesel

Renewable Methanol Technologies:
- Methanol to Gasoline
- Methanol to Jet

Technology Leader and Operating Excellence in Isomerization Catalysis

Proven track record of deploying technologies and integrating into ExxonMobil business plans and facilities

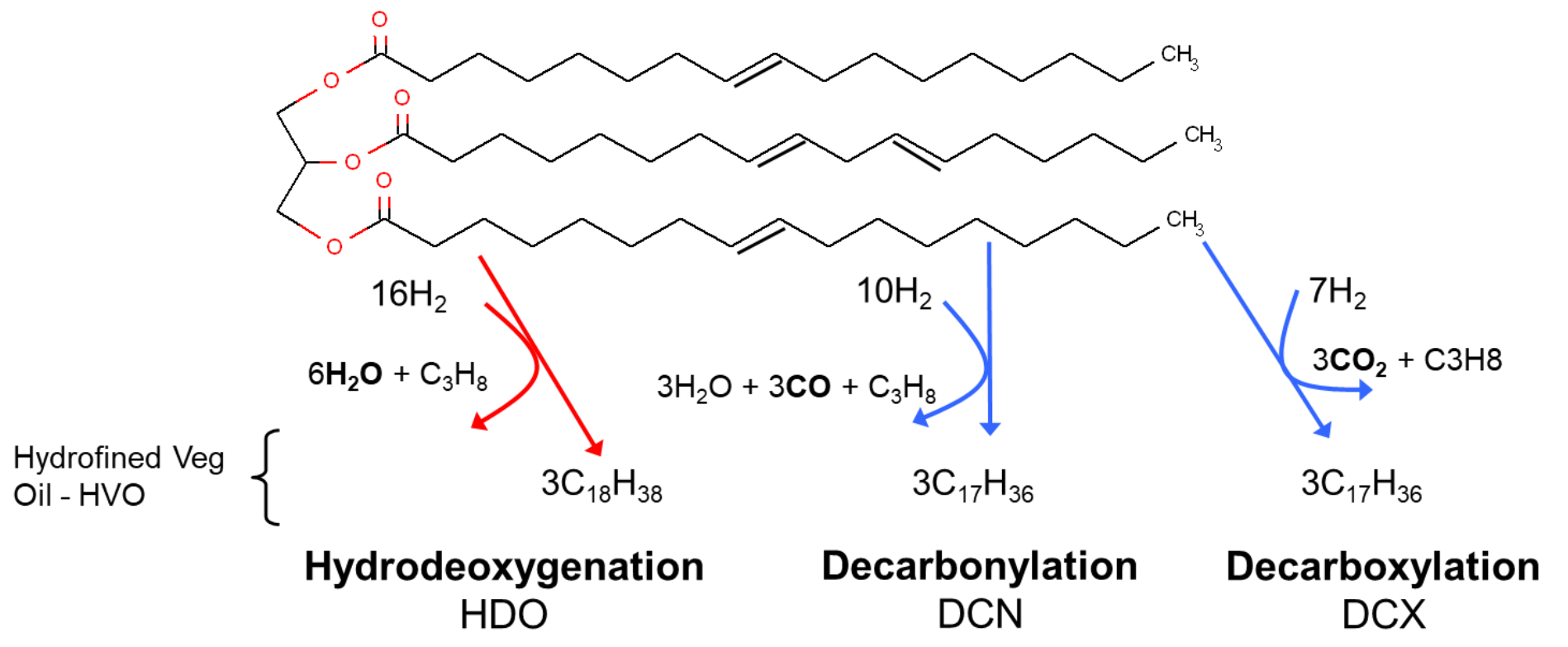


ExxonMobil Renewable Diesel (EMRD™) process with BIDW™

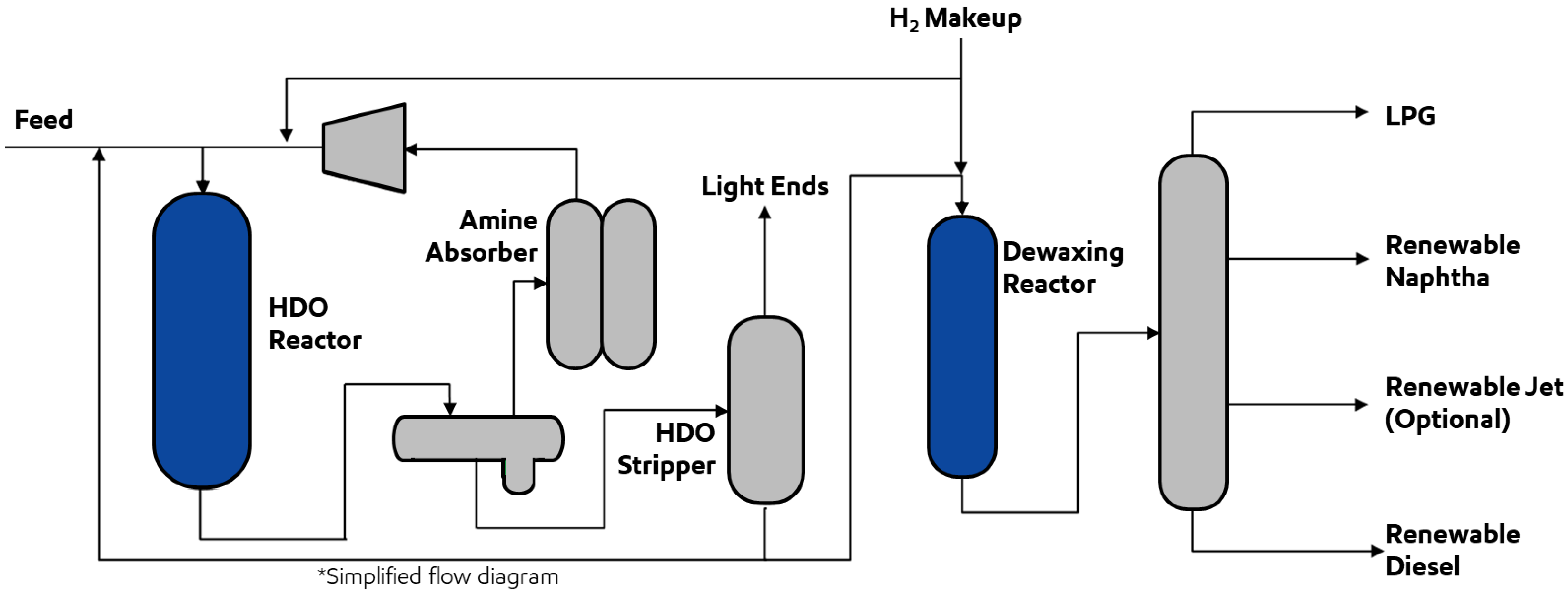
ExxonMobil is an **industry leader** in design and operation of hydroprocessing units and **advantaged dewaxing technology**, and is utilizing this expertise to provide an integrated renewable fuels technology package


Example Feed
Unconverted Cooking Oil

Triglyceride Deoxygenation Pathways

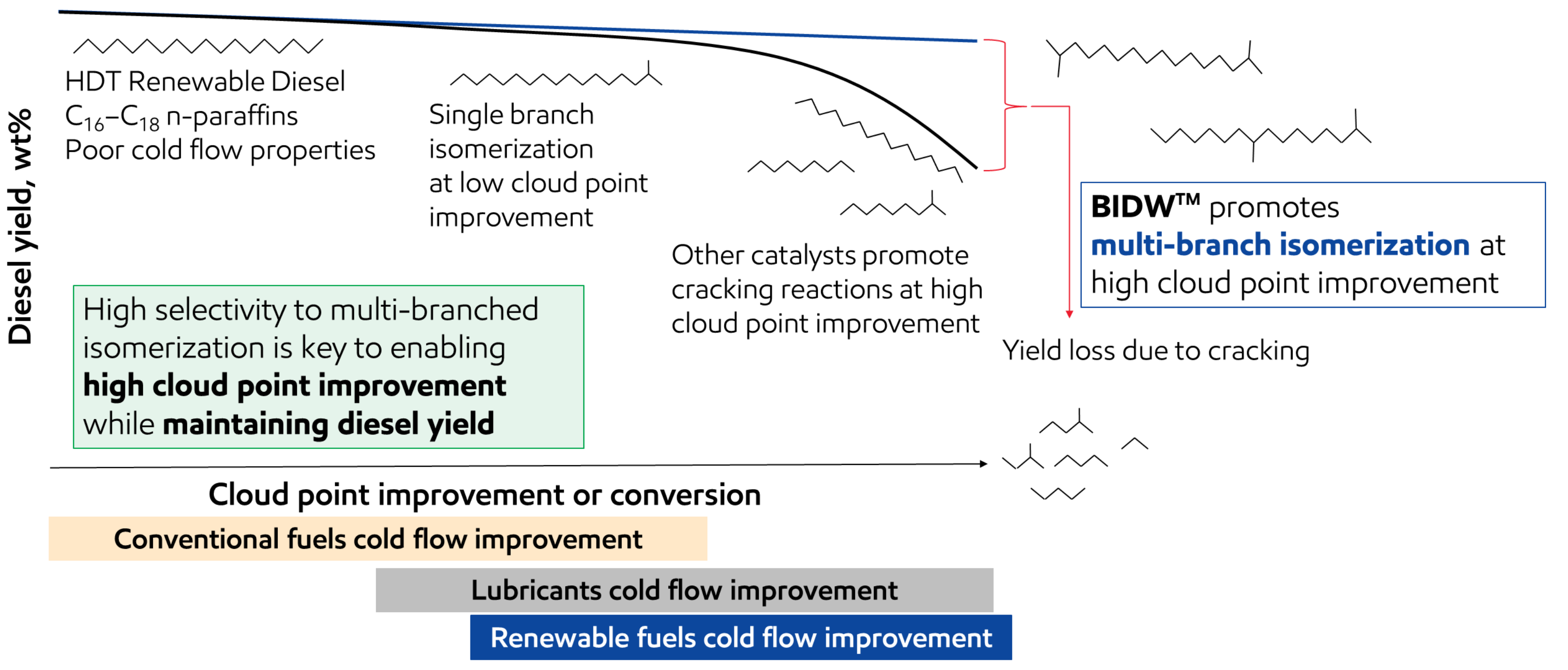


Hydrodeoxygenation HDO — Highest diesel yield
Decarbonylation DCN
Decarboxylation DCX



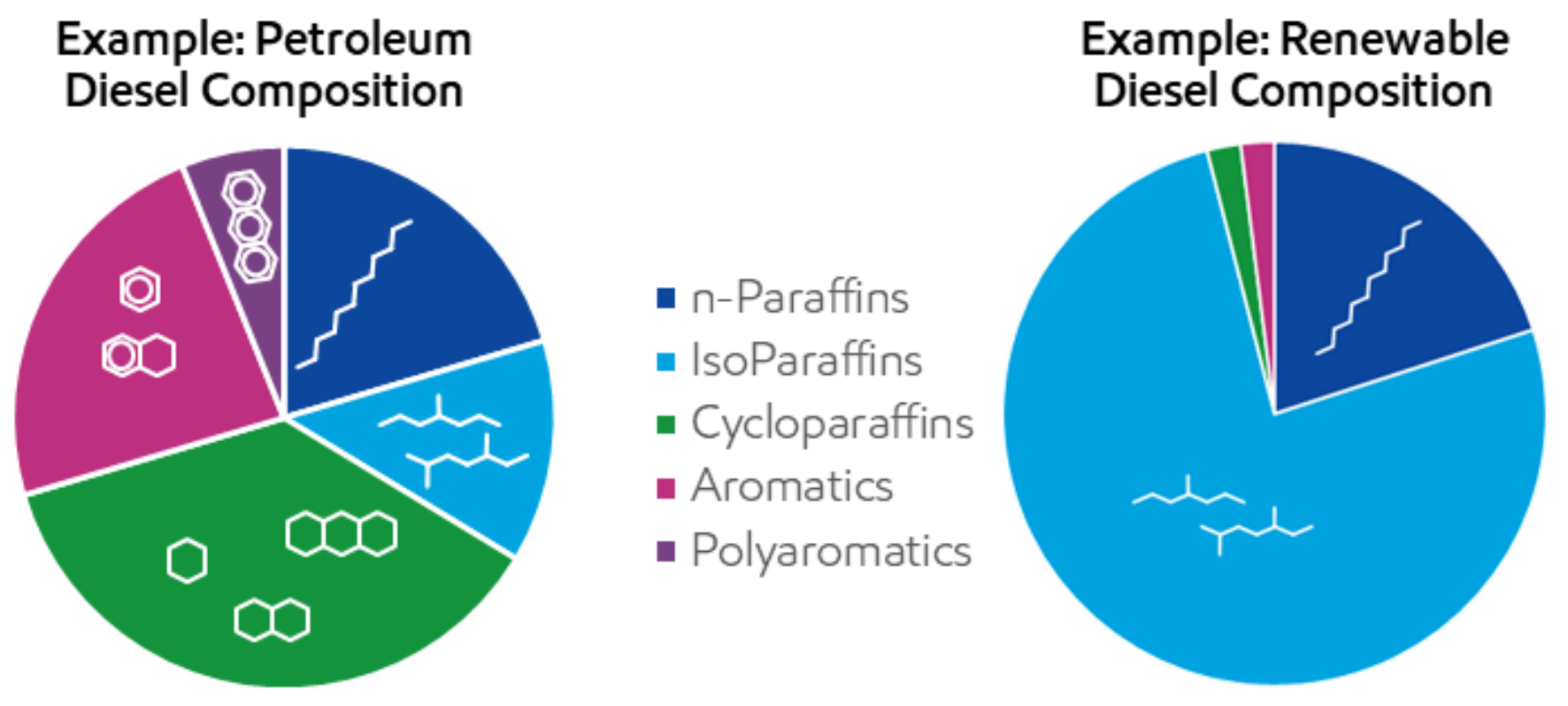
*Simplified flow diagram

Maintaining high diesel yield at high cloud point improvement



BIDW™ promotes **multi-branch isomerization** at high cloud point improvement

High selectivity to multi-branched isomerization is key to enabling **high cloud point improvement** while **maintaining diesel yield**


Example: Petroleum Diesel Composition

Example: Renewable Diesel Composition

	Units	Petroleum Based Diesel	Case 1: Soybean Typical Product	Case 2: Soybean Arctic Diesel
Hydrotreated Product Cloud Point*	°C	0 to 5	25	25
Diesel Product Cloud Point Target	°C	-5	-5	-35
Required Cloud Point Improvement	°C	5 to 10	30	60

*Feed quality & cutpoint dependent

Renewable fuels using bio-feedstocks

ExxonMobil Renewable Diesel Process, EMRD™ technology

New process technology converts bio-feedstocks into renewable diesel:

- Vegetable oils
- Unconverted cooking oil
- Animal fats

~90% — Bio-feed utilization drives competitiveness ~90%[4] production cost

EMRD enabled by BIDW™ catalyst, provides higher yield[5]

H_2 — Lower hydrogen use[5]

EMRD VS. ALTERNATIVES[5]

		Base 30 C dCP		Arctic diesel	
	units	NBA	EMRD	NBA	EMRD
Delta cloud point (dCP)	°C	30	30	60	60
Hydrotreated Veg Oil Cloud Point	°C	25	25	25	25
Renewable Diesel Cloud Point	°C	-5	-5	-35	-35
Delta yield	Wt%		+1.0 to +2.0		+6.0 to + 8.0
Delta diesel on ***10 kbd*** bio feed rate	Bpd		+90 to +190		+570 to +770
Incremental margin estimates	M$/yr		+7 to +14		+43 to +55

Notes: Cutpoint between naphtha and diesel assumed at 280°F, actual operations will set absolute diesel yields. Margin credit assumes ~200 \$/bbl value on renewable diesel.

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†ExxonMobil analysis of Integrated Assessment Modeling Consortium (IAMC) 1.5 scenario explorer and data on Lower 2°C scenarios. Volumes and prices in 2050 in the Lower 2°C scenarios were used, where available, to calculate an estimate of the market revenue.

Sources

1. ExxonMobil Energy Outlook (2022)
2. ICCT (2018) (combustion only emissions not full lifecycle)
3. IATA (2022)
4. IHS Markit "Second Generation Biofuels" PEP Report 278A December 2020
5. ExxonMobil data

Towards the Next Generation of General Purpose Rubbers: Polypentenamers

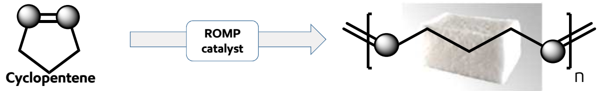
Alexander V. Zabula,[1] Carlos R. Lopez-Barron,[2] Lubin Luo,[1] Robert Halbach[1]

[1]Organometallic Catalysis (OMC), EMTEC
[2]Product Innovation, EMTEC

Abstract

Controlled ring opening metathesis polymerization (ROMP) for cyclic olefins is a powerful platform for the development of new types of elastomers with improved properties including polymer-to-monomer circularity. This work discloses controlled ROMP of cyclopentene (CP) alone, or with dicyclopentadiene (DCPD) for the production of long chain branched polypentenamers. The variation of ligands at the metal catalytic center was used to control *cis/trans* ratio, molecular weight and molecular weight distribution of the resulting polymers. This invention paves the way to the development of entirely new GPRs with controlled architecture and remarkably improved attributes (e.g. melt strength, shear thinning, and tensile strength) which brings value for various tire applications. Finally, the resulting elastomers exhibit potential for selective conversion back to monomer under mild conditions using Ru-based catalysts in the yields above 90%.

Introduction

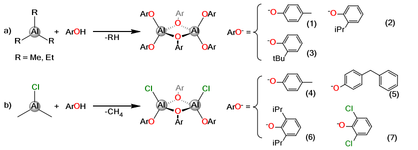


Cyclopentene-based rubber (CPR)

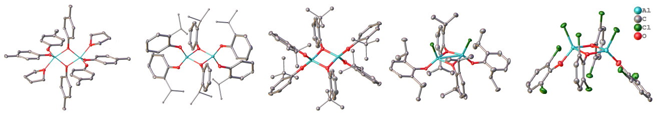
- Obtained by Ring-Opening Metathesis Polymerization (ROMP) of cyclopentene
- Renewed interest in CPR as a recyclable elastomer
- Potentially valuable elastomer for tire industry

J. Mol. Cat. **1980,** 8, 227; . *J. Macromol. Sci. Part C* **1972,** 7, 105; *ACS Sustain. Chem. & Eng.* **2016,** 4, 6090; *ACS Macro Letters* **2019,** 8, 46.

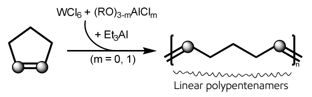
Polymerization



- ✓Cheap Al-aryloxides
- ✓Co-catalysts for ROMP
- ✓High M_w polymers
- ✓*Cis/trans* control

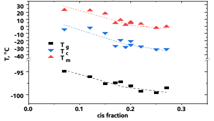


New active pre-catalysts prepared



Linear polypentenamers

Thermal Properties of CPR



Polymerization Results for Cyclopentene Using Pre-catalysts **1-7**[a]

Entry	Pre-catalyst	W:Al$_{aryloxide}$	M:cC$_5$	Yield (%)[b]	TON[c]	M_w, kDa	Đ	cis/trans[d]
1	1	1.33	1941	22	427	709	2.11	24/76
2	2	1.33	1941	82	1592	389	2.07	12/88
3	3	1.33	2000	38	760	276	1.91	9/91
4	4	2.00	1941	91	1766	315	1.80	17/83
5	4	2.00	3000	74	2220	412	2.21	18/82
6	4	2.00	4000	66	2640	490	2.02	20/80
7	4	1.00	4000	8	320	383	1.64	24/76
8	4	2.00	10000	16	1600	464	3.41	25/75
9	5	2.00	4000	90	3600	515	1.82	15/85
10	5	2.00	10000	56	5600	563	2.02	19/81
11	6	2.00	1941	23	446	268	1.98	22/78
12	7	2.00	10000	44	4400	946	1.32	20/80
13	Schrock catalyst[e]	N/A	20000	41	8200	69	1.59	14/86

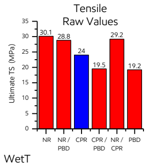
[a]General conditions for entries 1-14: 2L jacketed reactor; W:AlEt$_3$ = 1:2; 0 °C; 3h; solution of cyclopentene in toluene (20 wt%). [b]Based on isolated polymer product. [c]TON = $n_{(reacted\ cyclopentene)}/n_{(W)}$. [d]Estimated based on ^{13}C NMR spectroscopy. [e]2,6-Diisopropylphenylimidoneophylidene molybdenum(VI) bis(hexafluoro-t-butoxide).

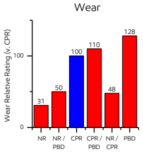
Organometallics **2022**, 41, 17, 2425; WO2020/061271; WO2021/188335

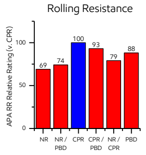
High Mw products, controlled cis/trans ratio

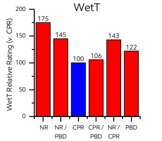
Tire Performance of CPR

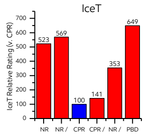
Comparisons: Normalized to CPR (80% trans), Higher is Better









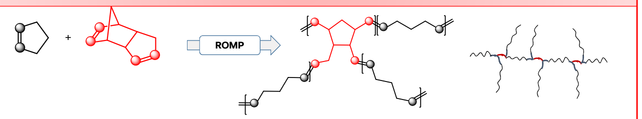


Property	Correlator
Tensile	Ultimate TS
Wear	DIN
Rolling Resistance	Tan(δ) at 60°C
Wet Traction	Tan(δ) at 0°C
"Ice" Traction	G′ at -20°C

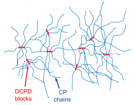
Nomenclature:
XX/YY
XX = 70 phr
YY = 30 phr
e.g., NR/PBD = 70/30

- Improved tire tread properties
- Good rolling resistance (RR) and wear

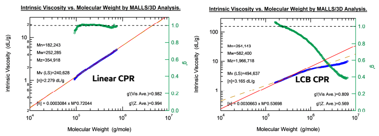
Long-chain Branching



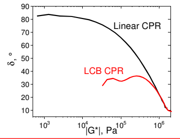
- **Fundamental challenge:**
  - Reactivity of DCPD >> CP
    ➔ Blocky structure, gelation
- **New method for LCB:**
  - Very low DCPD/CP ratio
  - Slow addition of DCPD
  - No gelation
- **New LCB CPR:**
  - Improved melt strength and shear-thinning
  - Significantly larger tensile strength



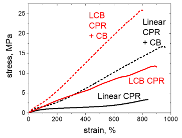
GPC and rheological evidence of LCB



Enhanced processability for LCB

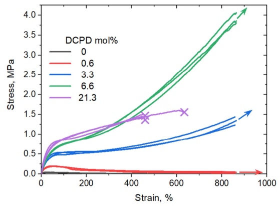


Superior mechanical properties

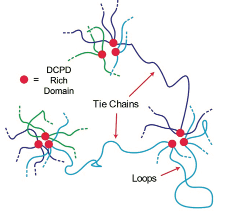


Improved properties for LCB CPR

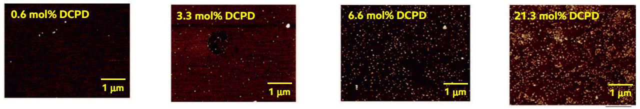
Stress–strain curves



Predicted morphology of CP/DCPD branching units



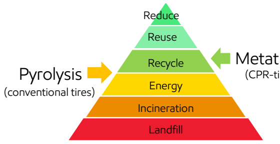
AFM images of hard nanodomains in polypentenamer matrix

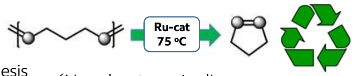


ACS Appl. Polym. Mater. **2021**, 3, 5, 2498; *Macromolecules* **2020**, *53*, 4, 1356

Stiffer behavior of branched PPR is caused by a reduction in the chain mobility

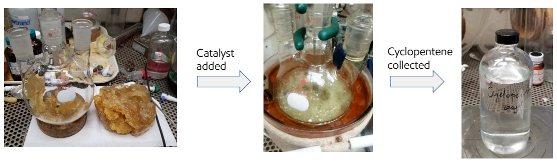
Potential Circularity for CPR



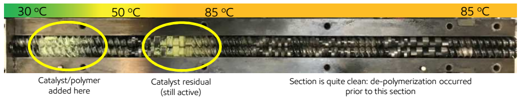


- ✓No solvent required!
- ✓> 90% of monomer recycled (>99% purity)!
- ✓Works for fully formulated CPR!

Attractive recyclability for polypentenamers



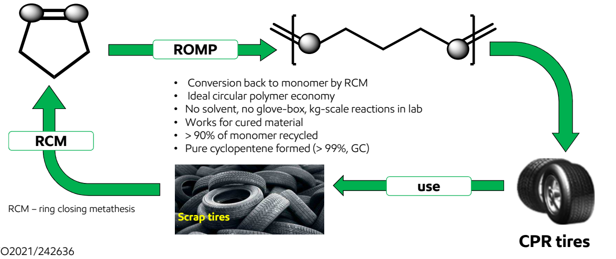
Continuous Depolymerization in Reactive Extruder



Properties of polypentenamers obtained from recycled and commercial CP using Ru-catalyst

	Ru:monomer	Yield, %	Mw, kDa	PDI	Cat efficiency, kg$_{product}$/g$_{cat}$
Recycled	1:100 000	90-94	**471-539**	1.69-1.82	6.0-6.7
Commercial	1:100 000	74	**72**	1.83	5.2

Conditions: Neat, -35-0 °C



- Conversion back to monomer by RCM
- Ideal circular polymer economy
- No solvent, no glove-box, kg-scale reactions in lab
- Works for cured material
- > 90% of monomer recycled
- Pure cyclopentene formed (> 99%, GC)

RCM – ring closing metathesis

WO2021/242636

Summary and Acknowledgements

- New catalysts for ROMP of cyclopentene
  - Ability to control stereochemistry and M_w's of polymers
- Potentially improved Wear and Rolling Resistance
- Long-chain branched polypentenamers for improved properties
- Highly selective depolymerization for CPR products under industrially relevant conditions
  - Potentially attractive circularity for CPR-based tires

Acknowledgments:

- Organometallic Catalysis Group (ExxonMobil)
- Brian Rohde, Torin Dupper, Rainer Kolb (ExxonMobil)