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
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
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:
  - Activity Coefficient Models: Correlate and require an extensive amount of data.
- Predictive thermodynamic models that incorporate proper physics are key for success.

ExxonMobil PC-SAFT Model

EMPSAFT 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 (butane-alkylhydride)
- Dipole-Induced Dipole (alcohol-olefin)
- Hydrogen Bonding (Alcohol-water)

Special Features

- Incorporation of Double Bonding theory in Carboxylic Acids
- General treatment of pseudo-molecules from Tc, SG, MW using EMPETO

Gasoline/Alcohols Blending to Reduce Harmful Emissions

- Start with Distillation Curve and SG of Base Gasoline
- Generate Pseudo Components
- Simulate the effect of blending oxygenates (MeOH, ECH, 2-propanol) on distillation curve
- Parameterize EMPETO

Model accurately predicts D86 distillation curves of gasoline/alcohol blends

Upstream & CCUS Applications

- Solubility of CO2 in Crude Oil
- Solubility of CO2 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 and is extracted using polar solvents such as ACN and NMP.

Phase Behavior C4’s with ACN

- Phase Behavior C4’s with NMP

Conclusion & Final Remarks

- EMPETO 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).

Acknowledgement

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 Accardo1, Rachael Smith1, Allyson Marianelli2, Samantha Woodfin2, Brian Einsla2, Melinda Einsla1, John Roper III1, Sharon Vuong1, Mary Alice Upshur2, Betha Snow2
1Core Research and Development, Dow Inc., 400 Arcola Road, Collegeville, Pennsylvania 19426, United States. 2Dow Coating Materials, Dow Inc., 400 Arcola Road, Collegeville, Pennsylvania 19426, United States

Introduction

Dye penetration testing (DPT) is commonly used as a quality control test to determine the effectiveness of coatings. The test can also be utilized to optimize coating parameters and improve overall coating performance. However, at present, there are no industry standards or approaches used to conduct an optimal dye penetration test. In this study, we developed and implemented a new approach to dye penetration testing that consists of a dye, a substrate, a dwell time, and an automated method for evaluating the test results. The test was designed to provide a fast and accurate method for evaluating the coating effectiveness. In addition to assessing coating integrity, the test can be used to screen for defects in paper coatings and can be used as a quality control tool to evaluate the effectiveness of different coatings.

Test Method Development

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

The blue dye test

• A scaled down automated process minimizes error and accelerates throughput
• Coating and quantifying dye spots is done by image analysis
• Removes the subjective nature of visualizing dye spots

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?

SEM of paper coatings with defects highlighted

Takeaway

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

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

Optimization of dye test: type of dye applied

Optimization of dye test: Dwell time testing

Investigation of results: area or spot count?

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 detection 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 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.

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

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).
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:** Integrity, Protecting Our Planet, Innovation, Customer-Centricity, Sustainability
- **To deliver a sustainable future for the world through our materials science expertise and collaboration with our partners.**

**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**

TiO₂ is Best White Pigment for Coatings, But Deficiencies Exist

- **Dispersion and Agglomeration Issues**
  - Inefficiencies of TiO₂
  - Air-paint film stress, crowding inks and occlusion regions of high and low concentration
  - In areas of high concentration, light scattering zone emerges and creates inefficiency

- **Environmental Impact**
  - **Architectural Paint Costs**
  - **Dispersion Stability**

**Advancing Sustainability with Polymer Technology**

**OPAQUE POLYMER**

- **Pre-Composite Polymer and Opaque Polymer**

**Leveraging Multiple Technologies for Broadest Impact**

**Dispersions Stability**

- ISO 14040/44, Third Party Validation

**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

- **Performance Compared to Petroleum-Based Acrylic Dispersions**
  - Performance Against All-Acrylic Emulsions
  - Performance Against Commercial Paint

**Enhancing Sustainability Through Biobased Binders**

**NORTH AMERICAN PROGRAM STATUS**

- **Direct impact by Dow & Paint Manufacturers**
  - Incorporation of bio-based materials in their stages of development
  - Incorporation of bio-based materials in stages of development

- **Research**
  - First party validation of paint LCA

- **Worldwide**
  - Incorporation of bio-based binder into acrylic paints
  - Sustainability and performance advantages
  - No sacrifice of paint performance
  - No change to配方 requirements
Advanced Recycling of Polyolefins

Adam S. Gross
ExxonMobil Technology and Engineering Company
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Advanced Recycling Facilitates a More Circular Economy

Advanced Recycling Works Together with Mechanical Recycling:
- Accepts feeds that can be difficult to mechanically recycle
- Makes products mechanical recycling cannot produce

Implementing Polyolefin Pyrolysis

Typical Pyrolysis Process Train

- Solid Plastic Selection/ Isolation
- Pre-Treatment
- Pyrolysis Unit
- Separations
- Solid Residue

Options for Pyrolysis Units

- Co-Processing: Leverage Existing Units Already Used for Pyrolysis Chemistry
- Grassroots: Build a new unit for on-purpose plastic pyrolysis

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

- Plastics conversion an extension of existing heavy hydrocarbon upgrading
- Limited to low plastic contents to maintain effective reactor performance & manage contaminants
- Requires construction of new conversion unit
- Flexibility in unit design for fit for purpose
- Tailor design/operation for feed and product targets

Factors Affecting Pyrolysis Process

- Feed Composition
- Reactor Design
- Operating Conditions

Fundamental Processes of PO Pyrolysis

Intrinsic Chemistry

- Reaction Pathways
  1. Bond Fission
  2. 1,2-Hydrogen Shift
  3. 1,2-Alkene Hydrogenation
  4. 1,3-Diene Isomerization
  5. 1,3-Alkene Hydrogenation
  6. 1,3-Diene Isomerization
  7. 1,4-Alkene Hydrogenation
  8. 1,4-Diene Isomerization
  9. 1,4-Hexene Hydrogenation
  10. 1,4-Octene Hydrogenation
  11. 1,4-Decene Hydrogenation
  12. 1,4-Decene-1 Hydrogenation

Phase Behavior and Mixing

Heat and Mass Transport

Factors Affecting Pyrolysis Process

- Feed Composition
- Reactor Design
- Operating Conditions

Fundamental Processes of PO Pyrolysis

Intrinsic Chemistry

- Reaction Pathways
  1. Bond Fission
  2. 1,2-Hydrogen Shift
  3. 1,2-Alkene Hydrogenation
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  5. 1,3-Alkene Hydrogenation
  6. 1,3-Diene Isomerization
  7. 1,4-Alkene Hydrogenation
  8. 1,4-Diene Isomerization
  9. 1,4-Hexene Hydrogenation
  10. 1,4-Octene Hydrogenation
  11. 1,4-Decene Hydrogenation
  12. 1,4-Decene-1 Hydrogenation

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

Environmental contamination

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

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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

**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

September 12, 2023

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

Hydrogen permeation through PEEK and POM was compared with Vespel® SP-1 and 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.

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.
Probing Oxidation Kinetics of Amine-based Sorbents for CO₂ Capture
Shabab Abedi, Corey Kaminsky, Scott Weigel, Wes Sattler
ExxonMobil Technology & Engineering Company, Annandale, NJ

Introduction:
The development of new solid materials for CO₂ capture is challenging due to the diverse nature of CO₂ streams. These streams vary in CO₂ concentration, percent relative humidity, trace impurities such as NOx and SOx, and the concentration of O₂. While this variability suggests that different materials classes are needed for distinct CO₂ streams, in practice amines are among the most commonly examined sorbents. This poses a challenge for oxidative stability of the CO₂ sorbent since amines are prone to oxidative degradation and though the O₂ content of CO₂ streams vary, nearly all contain at least 1% O₂.

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 CO₂ capacity. However, this high amine density suggests that PEI will be very sensitive to O₂-mediated degradation. To that end we are undertaking a kinetic investigation to understand if it is possible to mitigate the instability of PEI to O₂, a requirement if it is to be used for Direct Air Capture.

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 N₂ 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:

**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.**

**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.**

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.
Doing More with Less through Lightweighting: Foaming Capability of ExxonMobil High-Melt-Strength Polypropylene

Mu Sung (Matt) Kweon,1 Mahmoud Embabi,2 Steven Mendoza-Cedeno,2 Eric S. Kim,2 Patrick C. Lee,2 Anvit Gupta,1 Maksim E. Shvilkhin,1 George Pehlert1

1. ExxonMobil Technology and Engineering Company, 5200 Bayway Drive, Baytown, TX 77520
2. Multifunctional Composites Manufacturing Laboratory, Department of Mechanical and Industrial Engineering, University of Toronto, 5 King’s College Road, Toronto, ON M5S 3G8, Canada

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

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

- Materials, Test Parameters, and Foaming Protocol
- Pre-foaming
- Foaming

Extrusion Foaming:
Effect of processing condition on PP foamability

- Materials
- Processing Condition
- Potential Benefits Summary

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

- Sample
- Melt Strength
- Melt Strength

Potential Benefits Summary
- Extrusion Foaming
- Batch Foaming

Mold-Opening Foam Injection Molding
- Higher molecular weight PP is 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 2018–05888)
- Collaborative Research and Development grant (ORIPDU 543896–19) of the Natural Sciences and Engineering Research Council of Canada

References

Foaming Capability of ExxonMobil High-Melt-Strength Polypropylene

1. ExxonMobil Technology and Engineering Company, 5200 Bayway Drive, Baytown, TX 77520
2. Multifunctional Composites Manufacturing Laboratory, Department of Mechanical and Industrial Engineering, University of Toronto, 5 King’s College Road, Toronto, ON M5S 3G8, Canada
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

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

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
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
  
<table>
<thead>
<tr>
<th>Year</th>
<th>Factor</th>
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<tbody>
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<td>2030</td>
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<td></td>
<td>1.3 X</td>
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<td>1.5 X</td>
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<td>2 X</td>
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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

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

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 XLPE based on coagent technology:

- Achieves excellent cure performance
- Increased dielectric loss
- Improved conductivity/space charge

Technology need exists to minimize byproducts (reduce DCP initiator)

<table>
<thead>
<tr>
<th>Byproduct</th>
<th>Application</th>
<th>Negative Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>AC / DC</td>
<td>Vaults: Explosive Mixture Joints: Internal Pressure/Reliability</td>
</tr>
<tr>
<td>Polar “Heavies”</td>
<td>AC / DC</td>
<td>Quality Test: mask void detection by partial discharge testing</td>
</tr>
<tr>
<td>Polar “Heavies”</td>
<td>AC DC</td>
<td>Increased dielectric loss, Increased conductivity/space charge</td>
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</tbody>
</table>

Conventional XLPE

Novel XLPE

- Lab scorch test (140 °C, min)
- Hot Set (%)
- Tensile strength (psi)
- Elongation (%)
- Retention (%) – after 14 days at 150 °C

<table>
<thead>
<tr>
<th>Property</th>
<th>Conventional XLPE</th>
<th>Novel XLPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab scorch test (140 °C, min)</td>
<td>50</td>
<td>72</td>
</tr>
<tr>
<td>Hot Set (%) (20 N/cm², 200 °C)</td>
<td>77 ± 7</td>
<td>81 ± 9</td>
</tr>
<tr>
<td>Tensile strength (psi)</td>
<td>2944 ± 203</td>
<td>2770 ± 203</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>547 ± 27</td>
<td>516 ± 31</td>
</tr>
<tr>
<td>Retention (%) – after 14 days at 150 °C</td>
<td>≥ 98</td>
<td>≥ 85</td>
</tr>
</tbody>
</table>

Novel crosslinked polyethylene technology:

- Increases in run length
- Reduction in degassing time and GHG emission
- Reduction in scrap per CV line, equivalent to 32.4MT CO2 saving/year

- Conventional XLPE
- Novel XLPE

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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 13C 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

<table>
<thead>
<tr>
<th>Entry</th>
<th>B:V (mol%)</th>
<th>P(B/V vac)</th>
<th>Td (°C)</th>
<th>X° (°C)</th>
<th>g° (°C)</th>
<th>X°%</th>
<th>T°C</th>
<th>T°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100:0</td>
<td>P(B)</td>
<td>87</td>
<td>21</td>
<td>1.55</td>
<td>3.3</td>
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</tr>
<tr>
<td>2</td>
<td>90:10</td>
<td>P(B)0.9V0.1</td>
<td>86</td>
<td>10</td>
<td>1.24</td>
<td>1.6</td>
<td>87</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>79:21</td>
<td>P(B)0.2V0.8</td>
<td>84</td>
<td>8</td>
<td>1.17</td>
<td>1.3</td>
<td>87</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>60:40</td>
<td>P(B)0.02V0.98</td>
<td>86</td>
<td>11</td>
<td>1.31</td>
<td>1.2</td>
<td>87</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>40:60</td>
<td>P(B)0.02V0.98</td>
<td>86</td>
<td>11</td>
<td>1.31</td>
<td>1.2</td>
<td>87</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>20:80</td>
<td>P(B)0.02V0.98</td>
<td>87</td>
<td>13</td>
<td>1.33</td>
<td>1.4</td>
<td>87</td>
<td>-</td>
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<tr>
<td>7</td>
<td>0:100</td>
<td>P(V)</td>
<td>41</td>
<td>18</td>
<td>1.46</td>
<td>1.3</td>
<td>87</td>
<td>-</td>
</tr>
</tbody>
</table>

* All reactions were performed at 25 °C for ca. 18 h in anhydrous toluene. 
** Deconvoluted (co)polymer compositions. 
*** GPC measurements were performed with multiple detectors in CHCl₃ solvent at 60 °C. 
** Measured by DSC. 
* Calculated using equation 3.

Morphology

- POM micrographs of (P-V) copolymers measured after two hours of isothermal crystallization at 20 °C.
- X-ray analysis of (P-V) copolymers measured after two hours of isothermal crystallization at 20 °C. (a) Concentrated SAXS/WAXS profiles. (b) WAXS diffraction peaks. (c) 2D fiber diffraction of the 58% V copolymer.
- Long period and crystal thickness, (a) lattice parameters, and (f) lattice volume as a function of comonomer content.
- Photographs of (a) dumbbell specimens. (b) tensile (g) holders mounted on the RSA-G2, and (c) tensile (g) holder mounted on the Linkam tensile stage.
- Crystallinity and enthalpy of fusion as a function of composition for (P-V) copolymers measured after two hours of isothermal crystallization at 20 °C. Inset: Parametric plot of enthalpy versus crystallinity.

Mechanical Properties

- Tensile properties of B:V copolymers. (a) and (b) stress-strain curves measured at 22 °C. (b) DSC of the elastic regime. (c) Tensile properties as a function of composition.
- Deconvoluted 13C NMR spectrum of the carbonyl region of P(B,V cop). Experimental data (black line), deconvoluted peaks (blue line), sum of deconvoluted peaks (magenta line), and residue (red line). (b) Ml fraction of peaks B and D (vs V mol%). (c) Ml fraction of peaks J, K, O, and G vs V (mol%). (d) Ml fraction of peaks L, N, and P vs V (mol%).
- Stacked bar chart (P-V) illustrating compositional tetrad compositions.
- Gray bar aligned to tactic enriched tetrad.

Key Learnings

- Comonomer feed a 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 \( \Delta H_m \) mirrors the compositional dependence of crystallinity

- Large spherulites ( > 10μm) are only observed in P(B) and 8.5% V copolymer
- As V content increases, 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

- Elastic modulus (E) increases 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 13C NMR spectra
- At 27% V content, nearly 50% of P(B-V) copolymer is comprised of syndiotactic tetrad 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
**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.
- 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.
- Current sorting technology is not effective at handling approximately 30% of plastic packaging.
- Chemical recycling provides a pathway to take plastic wastes and break them down to molecules indistinguishable from their virgin counterparts.

**Advanced recycling targets feedstocks to recycle end-of-life artificial turf**

**Meeting ExxonMobil’s Advanced Recycling Capacity Ambitions**

**U.S. National Challenges**

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

**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

**ExxonMobil Advanced Recycling Projected Capacity**

**Material type** | **Single-stream plastics recovered for mechanical recycling** | **Mixed-plastics desirable for Exxon™ technology**
--- | --- | ---
PET | Monomaterial, easy to sort | Acceptable in quantities up to oxygen contaminant limit
HDPE | Monomaterial, single source more common | Acceptable in quantities up to oxygen contaminant limit
PVC | Limited single source collection | Capable of taking small amounts
LDPE | Lack of monomaterial (additives) | Tolerated in feed mix
PP | Film collection & sorting more challenged | Challenging
PS | Sorption improving | Challenging
PS foam collection, cleaning, densification is challenged | Acceptable in quantities up to contaminant limits
Not a monomaterial | Acceptable in quantities up to contaminant limits

**Exxon™ Complements Mechanical Recycling**

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

**What does plastic waste look like?**

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

**Collaborating to collect & sort difficult-to-recycle plastics**

- Collecting plastic waste in Houston
- Collecting Mobil1 bottles at auto stores
- Collaborating with TenCate to recycle end-of-life artificial turf

**Widening the range of recyclable plastics**

- In communities with programs and facilities in place that collect and recycle the resulting product.

**ExxonMobil’s latest report on Form 10-K**

**Extended FXE Emtech report.** This information is not representative of ExxonMobil Corporation's performance. For illustrative purposes only.
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

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

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Exceed™ S 9333 pPE</th>
<th>ExxonMobil™ LDPE LD 080 Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>0.925</td>
<td>0.92</td>
</tr>
<tr>
<td>Puncture Energy, in-lb</td>
<td>24</td>
<td>6.9</td>
</tr>
<tr>
<td>Puncture Force, lb</td>
<td>9</td>
<td>12</td>
</tr>
</tbody>
</table>

- 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 single 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

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

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


Acknowledgement

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

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

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

ExxonMobil
**Motivation**

- Enhanced heat and mass transfer characteristics make gas-solid fluidized beds preferred for many industrial processes.
- EMTEC uses computational fluid dynamics (CFD) to study, debottleneck, and improve commercial units (e.g., FCC), as well as for design and scale-up of novel gas-solid fluidized beds.
- 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.

**Filtered two-fluid models**

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

- **Macro-scale (kinetic theory):**
  - particle-particle interactions
- **Meso-scale (10d, mesh):**
  - particle clustering and fine flow structures
- **Macro-scale for integral-scale bed fluid dynamics**

**Timely commercial-scale simulations require 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

**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

**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.

**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

---

**Example #1**

- 36” column (no internals)
- FCC particles: 70 µm, 1500 kg/m³
- 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

---

**Model validation**

**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.
Advantaged Materials for Renewable Diesel and Jet Production

Chuansheng Bai, Majosefina Cunningham, Mark Deimund, Jason Golas, 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

Advancing Technologies to Enable Renewable Fuels

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

- **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

Aviation Fuel Demand, GHG Emissions, and Revenue

<table>
<thead>
<tr>
<th>Year</th>
<th>Aviation Fuel Demand</th>
<th>Aviation CO₂ Emissions</th>
<th>Global Airlines Revenue</th>
</tr>
</thead>
<tbody>
<tr>
<td>2018</td>
<td>918 MBillion</td>
<td>2.4% of global emissions</td>
<td></td>
</tr>
</tbody>
</table>

SAF at $300/MT CO₂ implies a cost of $300 billion/year to avoid ~1 billion MT/year of CO₂ 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.

- Vegetable oils and waste oils
- Agricultural waste and crop corn
- Woody biomass
- Algae

3rd generation biofuel

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

**BIOFUELS POTENTIAL $3 TRILLION MARKET SIZE BY 2050**

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 hydrotreating units and advantaged dewaxing technology, and is utilizing this expertise to provide an integrated renewable fuels technology package.

Maintaining high diesel yield at high cloud point improvement

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

ExxonMobil Renewable Diesel Process, EMRD™ technology

- New process technology converts bio-feedstocks into renewable diesel
- Yield loss due to cracking
- H₂ Makeup

Renewable fuels using bio-feedstocks

<table>
<thead>
<tr>
<th>EMRDS vs. ALTERNATIVES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base M&quot;C-ACP</td>
</tr>
<tr>
<td>馏分点 (API)</td>
</tr>
<tr>
<td>Vegetable oils</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td></td>
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</tr>
</tbody>
</table>

Notes:
1. ExxonMobil Renewable Diesel (EMRD™) is an industry leader in design and operation of hydrotreatment units and advantaged dewaxing technology.
2. ExxonMobil is an industry leader in design and operation of hydrotreatment units and advantaged dewaxing technology.

**Units**
- Petroleum | Typical Product | Arctic Diesel |
- Btu/MBillion | Btu/MBillion | Btu/MBillion |
- **Hydrotreated Product** Cloud Point°C | 5 to 10 | 30 | 60 |
- Diesel Product Cloud Point Target°C | -5 | -5 | -35 |
- Required Cloud Point Improvement°C | 5 to 10 | 30 | 60 |

*Feed quality & cutpoint dependent
Towards the Next Generation of General Purpose Rubbers: Polypentenamers

Alexander V. Zabula,1 Carlos R. Lopez-Barron,2 Lubin Luo,1 Robert Halbach1
1Organometallic Catalysis (OMC), EMTEC
2Product 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 diisopentene (DP), 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 thickening, 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

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

Polymerization

- New active pre-catalysts prepared
- Novel properties of CPR
- Improved properties for LCB CPR

Thermal Properties of CPR

<table>
<thead>
<tr>
<th>Property</th>
<th>1°C/min</th>
<th>2°C/min</th>
<th>5°C/min</th>
<th>10°C/min</th>
<th>20°C/min</th>
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<tbody>
<tr>
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<td>4.9E+05</td>
<td>4.9E+05</td>
<td>4.9E+05</td>
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</tr>
<tr>
<td>Mn (g/mol)</td>
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<td>2.6E+05</td>
<td>2.6E+05</td>
<td>2.6E+05</td>
<td>2.6E+05</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>118</td>
<td>118</td>
<td>118</td>
<td>118</td>
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<tr>
<td>DSC</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Polymization Results for Cyclopentene Using Pre-catalyst 1-1

| Entry | Pre-catalyst | Wt% (catalyst) | Mw, Mnc (g/mol) | Tg (°C) | DSC (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>50</td>
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<tr>
<td>3</td>
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<td>50</td>
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<tr>
<td>4</td>
<td>1-1</td>
<td>0.4</td>
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<td>118</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>1-1</td>
<td>0.5</td>
<td>2.6E+05</td>
<td>118</td>
<td>50</td>
</tr>
</tbody>
</table>

New active pre-catalysts prepared

Summary and Acknowledgements

- New catalysts for ROMP of cyclopentene
  - Ability to control stereochemistry and Mn,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)

CPR tire manufacturing processes

High Mw products, controlled cis/trans ratio

Potential Circularity for CPR

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