Renewable Carbon Fibers Consortium
WBS 2.3.4.102

March 5, 2019
Technology Area: Performance-Advantaged Bioproducts and Separations Consortium

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National Renewable Energy Laboratory
Goal Statement

Goal: Cost effective production of renewable carbon fibers through bio-based acrylonitrile

Highlight
- Produce 50 kg of ACN converted into a carbon fiber (CF) component for performance testing
- TEA/LCA analyzing bio-ACN to CF, detailing the process design for meeting economic and sustainability metrics

Outcome
- Demonstrated production of CF from renewable acrylonitrile (ACN) at a modeled cost of <$1/lb.
- Report on process design metrics, with documented data, assumptions, and R&D

Relevance
- Identified bioenergy product and co-product opportunities for industry evaluation with associated TEA/LCA
- Industrially relevant improvements for bio-ACN and CF production via 3-HP pathway
Quad Chart Overview
2.3.4.102

Timeline
• Project start date: 10-1-2018
• Project end date: 9-30-2020
• Percent complete: 15%

<table>
<thead>
<tr>
<th></th>
<th>Total Costs Pre FY17**</th>
<th>FY 17 Costs</th>
<th>FY 18 Costs</th>
<th>Total Planned Funding (FY 19-Project End Date)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Funded</td>
<td>$0K</td>
<td>$0K</td>
<td>$174K</td>
<td>$2,061K</td>
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- **Partners:** NREL (94%); ORNL (6%)
- **Subcontractors (no cost share):** Cargill, Mid-Atlantic Technology, Research and Innovation Center, Johnson Matthey, Fisipe, Ford

Barriers addressed
• Ct-K. Developing Methods for Co-product Production
• ADO-D. Technical Risk of Scaling

Objective
• Cost effective production of renewable carbon fibers through bio-based acrylonitrile

End of Project Goals
• Produce bio-ACN meeting performance targets and mechanical metrics
• Deliver final report detailing the process design for meeting economic and sustainability metrics
Lead: NREL

Partners: ORNL, Johnson Matthey, MATRIC, Ford, Cargill, FISIPE

Objective: Cost effective production of renewable carbon fibers through bio-based acrylonitrile

History:

- High quality carbon fiber is too expensive
- Many feedstocks have been tried (e.g., lignin, pitch, rayon) but ACN is the best precursor for high-quality fibers and material properties
- ACN price has historically been volatile and too high
- DOE FOA demonstrated biomass based routes to ACN
Advantages of Ester Nitrilation

- **Endothermic reaction**: simplifies process control
- **No toxic by-products** produced: simplifies process safety
- **Cheaper and simpler catalysts**
  - TiO₂ ~20-25 $/kg
  - State of the art ammomx cat. = 66$/$kg
- **Higher yields** than ammoxidation (90-95% ACN yield)
  - State of the art ammoxidation catalyst ~80-83%
- **Renewably sourced starting materials**

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Task 1: Demonstration scale, TEA/LCA

- Produce CF from renewable acrylonitrile (ACN) at a modeled cost of <$1/lb
- Deliver report on process design to meeting economic and sustainability metrics, documenting assumptions, data, and R&D for further improvements

**Scale-up (50 kg of bio-ACN):**

- 3-HP
- 3-HP ester
- ACN
- Renewable Carbon Fiber
- RCF Composite

**Partners:**
- Cargill (from 1G sugars)
- MATRIC (NREL, JM)
- FISIPE (ORNL)
- Ford

Task 2: Bench scale

- Improve catalyst lifetime and reduce coking using rational catalyst design
• Rigorous milestone-based timeline
• Go/No-go decision based on bio-ACN production delivery
• Project meetings, quarterly project reports, and cross-institutional team calls
**Approach- Technical (Scale up)**

Complete single carbohydrate to CF product demonstration run with industrial partners

**Cargill:** 3-HP production
Capabilities: Extensive experience in strain engineering, fermentation optimization with IP and 3-HPA

**MATRIC:** Bio-ACN Production
Capabilities: Extensive experience in development, testing and scale-up of catalytic processes and handling reactive monomers

**FISIPE:** Carbon Fiber Production
Capabilities: Extensive experience in polymerization, polymer solution preparation, acrylic fiber extrusion and carbon fiber production.

**Johnson Matthey:** Catalyst production

**Ford:** Composite Manufacturing/Testing
Capabilities: Extensive experience in CF composite manufacturing and testing
## Approach - Technical (Scale up)

<table>
<thead>
<tr>
<th><strong>Cargill</strong></th>
<th><strong>MATRIC</strong></th>
<th><strong>JM</strong></th>
<th><strong>SGL GROUP</strong></th>
<th><strong>Ford</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Generate 3-HP from 1st generation sugars with existing strain</td>
<td>Receive 3-HP from Cargill and produce bio-ACN</td>
<td>Provide heterogeneous catalyst to MATRIC</td>
<td>Receive bio-ACN from MATRIC</td>
<td>Manufacture RCF composites and test relative to conventional CF composites</td>
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<tr>
<td>Demonstrate 3-HP productivity</td>
<td>Demonstrate total conversion to bio-ACN of &gt;50% relative to theoretical</td>
<td></td>
<td>Produce polyacrylonitrile</td>
<td>Manufacture an RCF automotive component</td>
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<tr>
<td>Produce and deliver bio-based 3-HP</td>
<td>Purify, stabilize and ship bio-ACN to FISIPE for carbon fiber production</td>
<td></td>
<td>Produce renewable carbon fibers (RCF)</td>
<td>Demonstrate tensile strength and modulus from RCF panel</td>
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**NREL**
Gather data and validate assumptions across each process.

**Product final report detailing the process design for meeting economic and sustainability metrics**
Critical Success Factors

• Each step in the process must produce material in sufficient quality and quantity for the subsequent step, on synchronized timelines
• TEA/LCA must have informed data to generate process models and recommend improvements
• Scaled up production run must meet the $1/lb cost targets while demonstrating an entire fiber production LCA consistent with >50% GHG reduction relative to conventional fiber production
Nitrilation Catalyst Development

- **Challenges**
  - During scale-up of nitrilation (either fluidized bed or fixed bed system), the substrate will need to be considerably more concentrated as compared to bench scale
  - This will lead to increased catalyst deactivation and increase the overall ACN selling price

- **Approach**
  - Screen multiple in-house produced and characterized acid catalysts that resist deactivation
  - Once baseline catalysts are chosen, focus on understanding how the process variables (e.g., reactant feed concentrations, temperature, etc.) affect catalyst deactivation and ACN production
  - Perform design of experiment study to determine optimal reaction conditions to mitigate deactivation rate
    - System pressure
    - Partial pressures of reactants
    - Contact time study
  - Investigate dopants to mitigate deactivation
Technical Accomplishments

- **Highlighted publications:**

- **Technical highlight:**
  - Acrylate production from lignocellulosic feedstocks
2018 R&D 100 Award

“Nitrilation to Acrylonitrile Process”

Acrylonitrile is a major commodity chemical employed in many diverse, commercial applications—from clothing to carpets to plastics to automobile components. Acrylonitrile can also be polymerized to polyacrylonitrile, which is the primary building block in carbon fiber composites. However, nearly all commercial acrylonitrile is produced today via an energy-intensive, chemically hazardous, petroleum-based process. The Nitrilation to Acrylonitrile Process provides a sustainable route to produce acrylonitrile and carbon fibers via nitrilation chemistry, offering a cost-effective alternative to the conventional petrochemical production, while also achieving even greater yields of acrylonitrile than the state-of-the-art ammoxidation process. The new, robust catalytic process has been able to achieve a 98 percent yield of acrylonitrile from 3-hydroxypropionic acid, which can be biologically produced from plant sugars, ethanol, glycerol, syngas, and other low cost renewable feedstocks.

Relevance

Goal: Cost effective production of renewable carbon fibers through bio-based acrylonitrile

- Directly supports BETO’s mission: “Develop industrially relevant, transformative, and revolutionary bioenergy technologies to enable sustainable, domestically produced biofuels, bioproducts, and biopower for a prosperous nation”

- Provides a renewable route to ACN, potentially addressing price volatility and high costs

- Project metrics and technical targets driven by technoeconomic analysis

- Relevant commercial partners actively engaged
Cost effective production of renewable carbon fibers through bio-based acrylonitrile

Future Work

Scale Up
• Demonstrate Suitability of Bio-ACN towards PAN, Fiber and CF
• Complete single carbohydrate to CF product demonstration run
• Provide report on TEA/LCA analysis of process, with relevant data and assumptions

Catalyst Development
• Improve catalyst lifetime and reduce coking rates and extents
• Pursue improved catalysts based on mechanistic insights into rate-limiting steps
• Develop more robust catalysts for ester nitrilation chemistry

ACN Polymerization to PAN:

\[
\text{N} = \text{N} \quad \rightarrow \quad \text{N} = \text{N} \quad \text{N}
\]
Future Work – Scale-up

Phase II Scale-up (50 kg of bio-ACN):

Step 1: Production of 3-HP

Cargill Led Expected Results:
- Produce and deliver 400 kg of purified bio-based 3-HP
Future Work – Scale-up

Phase II Scale-up (50 kg of bio-ACN):

Matric Led Expected Results:
- Produce, concentrate, stabilize and deliver 50 kg of bio-ACN to FISIPE
- Demonstrate total conversion to bio-ACN of >50% relative to theoretical
Future Work – Scale-up

Phase II Scale-up (50 kg of bio-ACN):

FISIPE Led Expected Results:
- Produce >200 kDa PAN & 100 filament tow w/ <5 PDI and < 10% COV for fiber diameter
- Produce RCF w/1.7 GPa tensile strength, 170 GPa modulus and <10% COV
Future Work – Scale-up

Phase II Scale-up (50 kg of bio-ACN):

Ford Led Expected Results:
- Demonstrate 300 mPa tensile strength and 30 GPa modulus from RCF panel

Step 4: Production of RCF Composite
Future Work – Catalyst Development

Mitigating catalyst deactivation

Catalyst screened during phase I
- All catalysts tested showed some deactivation
- Heating in air at 550 °C restored activity
- Increased partial pressure of NH3 slowed catalyst deactivation
- Weak solid acids deactivated slower

Slower deactivation is needed!
- We currently use a riser reactor with 30 second recycle time
- IF we can use a packed bed reactor this would save ~0.07 / lb AN
- Catalyst must last at least 10 bed masses of product to before regeneration to use a packed bed.
- Our TiO₂ catalyst currently lasts 2.5 bed masses before needing regeneration
Future Work – Catalyst Development

Understanding the deactivation mechanism

How is deactivation occurring?

- Hypothesize that this is similar to olefin coking reactions
- DFT studies to determine mechanism
- Deactivation rate measurements
- Does it occur from methyl acrylate or acrylamide?

1. C.H. Bartholomew, R.J. Farrauto, Fundamentals of Industrial Catalytic Processes. 2006,
Future Work – Catalyst Development

Building longer lasting catalysts

What makes a longer lasting catalyst?

- Weaker acids deactivate slower.
  - $\text{TiO}_2 < \text{ZrO}_2 < \text{NbO}_2 < \text{Al}_2\text{O}_3 < \text{phosphated oxides}$

- Can we find a weaker solid acid than TiO$_2$?

- Is surface acrylate proximity the issue?

- Can we island oxides on an inert support (carbon, Au)?
Future Work – Catalyst Development

Summary of Work Plans

**Fundamental work**
- Understand deactivation mechanism through low conversion studies on TiO2
- Catalyst autopsy post deactivation
- Use DFT study in parallel to model the deactivation mechanism.

**Reaction Engineering**
- Design of experiment study to determine optimal reaction conditions to mitigate deactivation rate
  - System pressure
  - Partial pressures of reactants
  - Contact time study

**Catalyst Engineering**
- Synthesize weaker solid acids and compare their deactivation rates.
- Synthesize islanded oxides on inert supports and compare deactivation rates.
- Use parallel DFT study to predict ideal oxide materials.
**Summary**

**Overview**
- Objective: Cost effective production of renewable CF through bio-based acrylonitrile
- Scale up: Produce CF from renewable acrylonitrile (ACN) at a modeled cost of <$1/lb
- TEA/LCA: Deliver report on process design to meeting economic and sustainability metrics
- Bench scale: Improve catalyst lifetime and reduce coking using rational catalyst design

**Approach**
- Scale up: Complete single carbohydrate to CF product demonstration run with industrial partners
  - 3-HP production $\rightarrow$ Bio-ACN production $\rightarrow$ Carbon fiber production $\rightarrow$ CF product manufacture
- TEA/LCA: Gather data across production process and report process design
- Bench scale: Understand catalyst deactivation and take steps to mitigate deactivation

**Technical Accomplishments/Progress/Results**
- Largely limited in this new start project to knowledge leveraged from previous FOA work

**Relevance**
- Directly supports BETO’s mission: “Develop industrially relevant. . .bioenergy technologies to enable sustainable, domestically produced. . .bioproducts. . .”
- Provides a renewable route to ACN, potentially addressing price volatility and high costs
- Project metrics and technical targets driven by technoeconomic analysis
- Relevant commercial partners actively engaged

**Future work**
- Complete single carbohydrate to CF product demonstration run
- Provide report on TEA/LCA analysis of process, with relevant data and assumptions
- Develop more robust catalysts for ester nitrilation chemistry
Acknowledgements

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Additional Slides
This is a new project. *There were no reviewer comments from 2017.*
• G. T. Beckham, “Hybrid biological and catalytic processes to manufacture and recycle plastics”, USC, January 14th, 2019
• G. T. Beckham, “Hybrid biological and catalytic processes to manufacture and recycle plastics”, Princeton University, November 28th, 2018
• G. T. Beckham, “Hybrid biological and catalytic processes to manufacture and recycle plastics,” IBM Almaden, September 12th, 2018
• G. T. Beckham, “Hybrid biological and catalytic processes to manufacture and recycle plastics,” University of British Columbia, June 20th, 2018
• G. T. Beckham, “Developing new processes to valorize lignin and sugars to building-block chemicals and materials,” RWTH Aachen University, May 28th, 2018
