Renewable Carbon Fiber Consortium (RCFC)

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

2017 DOE-BETO Project Peer Review

Biochemical Conversion Area

March 8., 2017

Adam Bratis, Ph.D

National Renewable Energy Laboratory (NREL)

Renewable Carbon Fiber Consortium
Goals/Outcome

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

Goal: Develop and demonstrate an acrylonitrile (bio-ACN) production process from biomass-derived sugars at ≤ $1/lb

- *Utilize hybrid biological/catalytic approach*
- *Leverage functionality inherent to biomass*

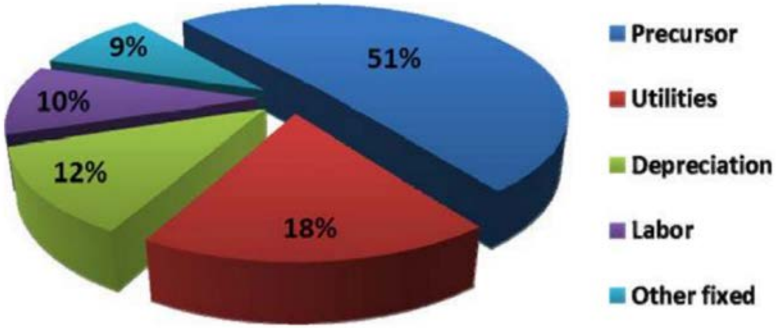
Goal: Demonstrate suitability of bio-ACN for the production of carbon fiber relative to conventional practices

- *Utilize real time / small scale carbon fiber production and testing capabilities*

Outcome: A route to affordable, high quality renewable carbon fiber

- *Initially target automotive lightweighting*
- *Wider potential applications*

Polyacrylonitrile accounts for >50% of carbon fiber production cost



Renewable Carbon Fiber Consortium
Quad Chart

Timeline

Start date: August 2015
End date: December 2018
Percent complete: 45%

Barriers

Ct-E Efficient Low T Deconstruction
Ct-H Efficient Catalytic Upgrading of Sugars to Chemicals
Ct-I Product Finishing Acceptability and Performance
Ct-J Process Integration

Budget

$K	FY15 Costs	FY16 Costs	FY17 - End
DOE Funded	353	2120	3349
Partner Cost Share	147	884	776
Total	**500**	**3004**	**4125**

DOE: ~$6M
Cost Share: ~ $2M

Partners and Collaborators

Industry partners: Biochemtex, Johnson Matthey, MATRIC, DowAksa, Ford

National laboratory collaborators: Oak Ridge National Laboratory, Idaho National Laboratory

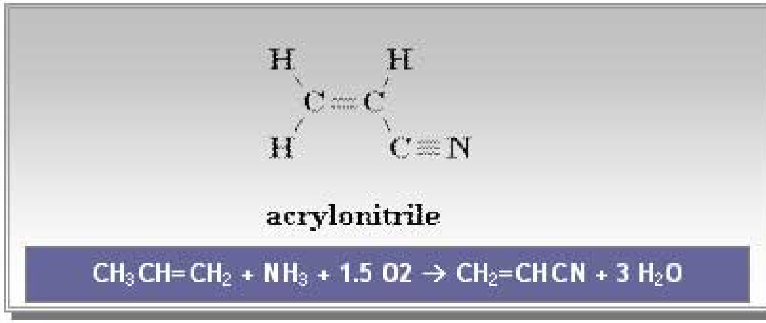
Academic collaborators: CU Boulder, Colorado School of Mines, Michigan State University

History: High quality carbon fiber is too expensive

- *Many feedstocks have been tried (e.g., lignin, pitch, rayon) but ACN is best precursor for high-quality fibers and material properties*
- *ACN price has historically been volatile and too high*

Context: ACN is currently produced via propylene ammoxidation

- *Relatively low-yield (~82%)*
- *Toxic by-product (HCN)*
- *Highly exothermic reaction (difficult to control)*
- *Complex/expensive catalysts*



Project Objectives: Demonstrate biomass based route to ACN

- *Use biology to produce and recover three targeted intermediates (PA, IPA, 3-HPA)*
- *Test catalytic conversion of each to ACN*
- *Phase I: Produce small scale bio-ACN batches to test carbon fiber properties*
- *Phase II: Scale-up a single pathway to 50 kg of ACN production and test a CF component*
- *Work with TEA and LCA team throughout to down-select to a single pathway for Phase II*

Renewable Carbon Fiber Consortium
Technical Approach

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

Aim 1: Produce ACN from biomass sugars

- *Use wheat straw and corn stover hydrolysates*
- *Microbially convert sugars to C_3 compounds*
- *Separate and upgrade C_3 compounds to ACN*

Challenges: Titer, rate, yield (TRY), hydrolysate toxicity, separations efficiency, catalyst selectivity, productivity and fouling

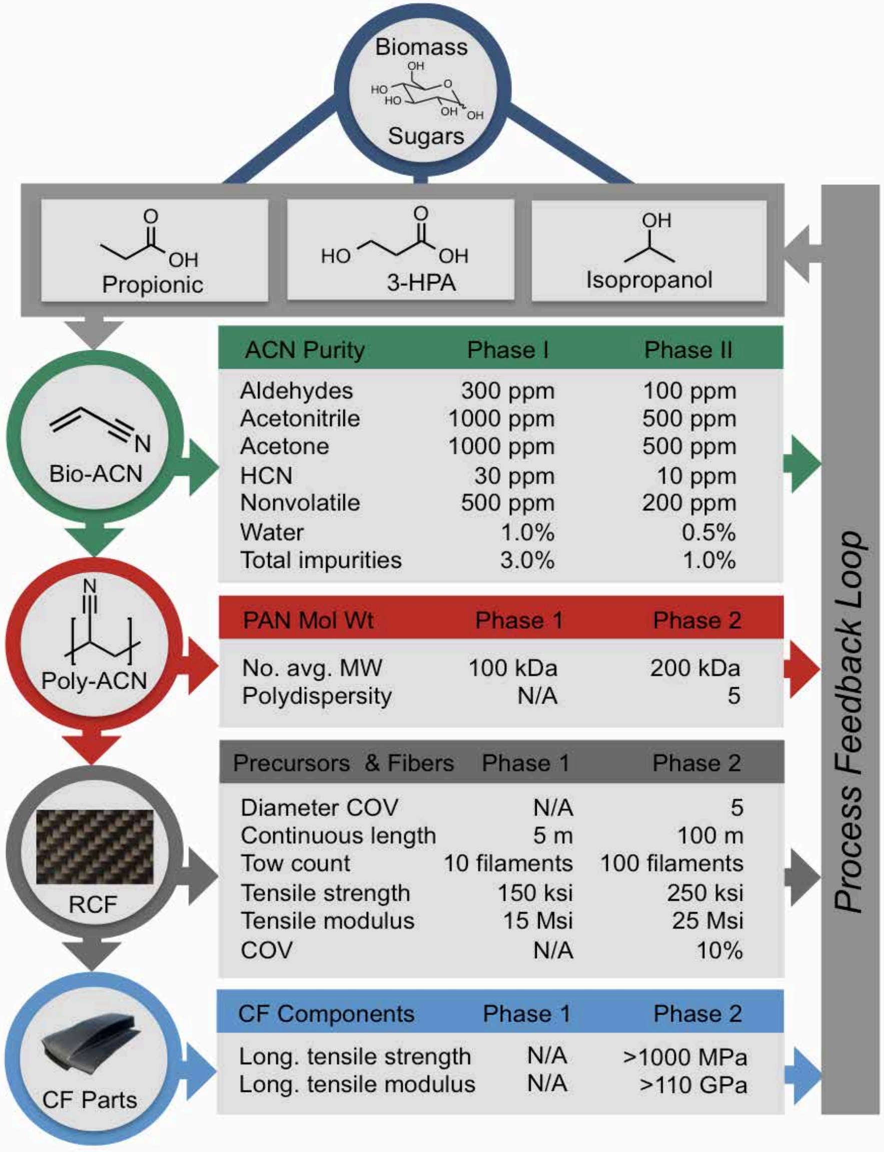
Aim 2: Produce carbon fiber from bio-ACN

- *Polymerize to PAN, spin to CF at single fiber scale (Phase I) and 50 kg scale (Phase II)*

Challenges: Biomass-derived impurities could impact polymerization and fiber properties

Critical Success Factors:

- *Develop **organism tolerance** and **engineer pathways** to produce high TRY*
- *High yield separations and catalytic processes*
- *Manage biomass specific impurities that could adversely affect fiber properties*



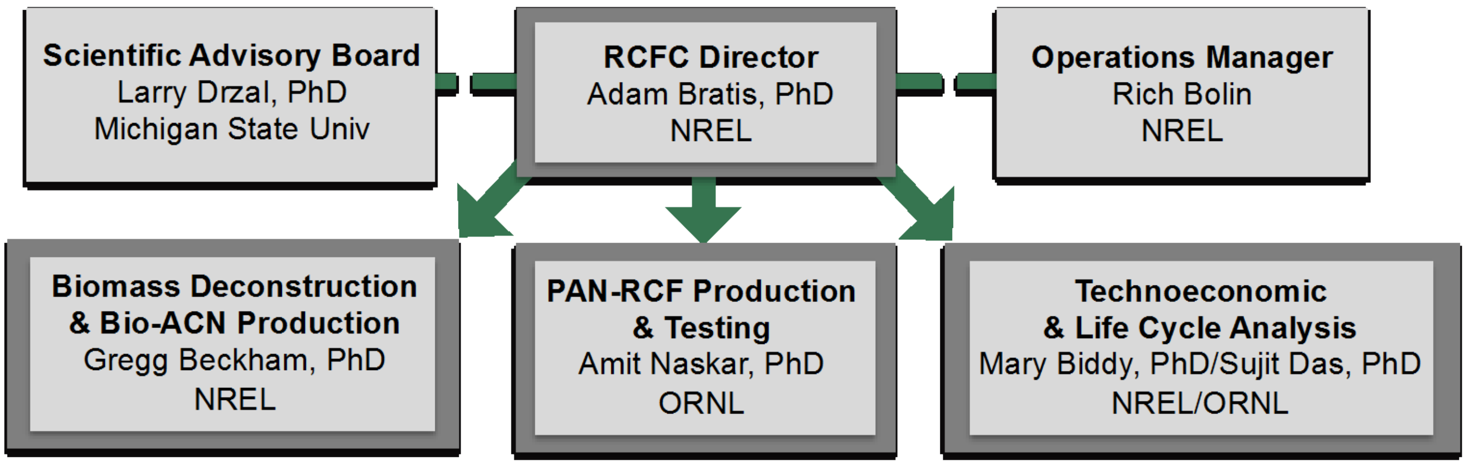
ACN Purity	Phase I	Phase II
Aldehydes	300 ppm	100 ppm
Acetonitrile	1000 ppm	500 ppm
Acetone	1000 ppm	500 ppm
HCN	30 ppm	10 ppm
Nonvolatile	500 ppm	200 ppm
Water	1.0%	0.5%
Total impurities	3.0%	1.0%

PAN Mol Wt	Phase 1	Phase 2
No. avg. MW	100 kDa	200 kDa
Polydispersity	N/A	5

Precursors & Fibers	Phase 1	Phase 2
Diameter COV	N/A	5
Continuous length	5 m	100 m
Tow count	10 filaments	100 filaments
Tensile strength	150 ksi	250 ksi
Tensile modulus	15 Msi	25 Msi
COV	N/A	10%

CF Components	Phase 1	Phase 2
Long. tensile strength	N/A	>1000 MPa
Long. tensile modulus	N/A	>110 GPa

Management Approach



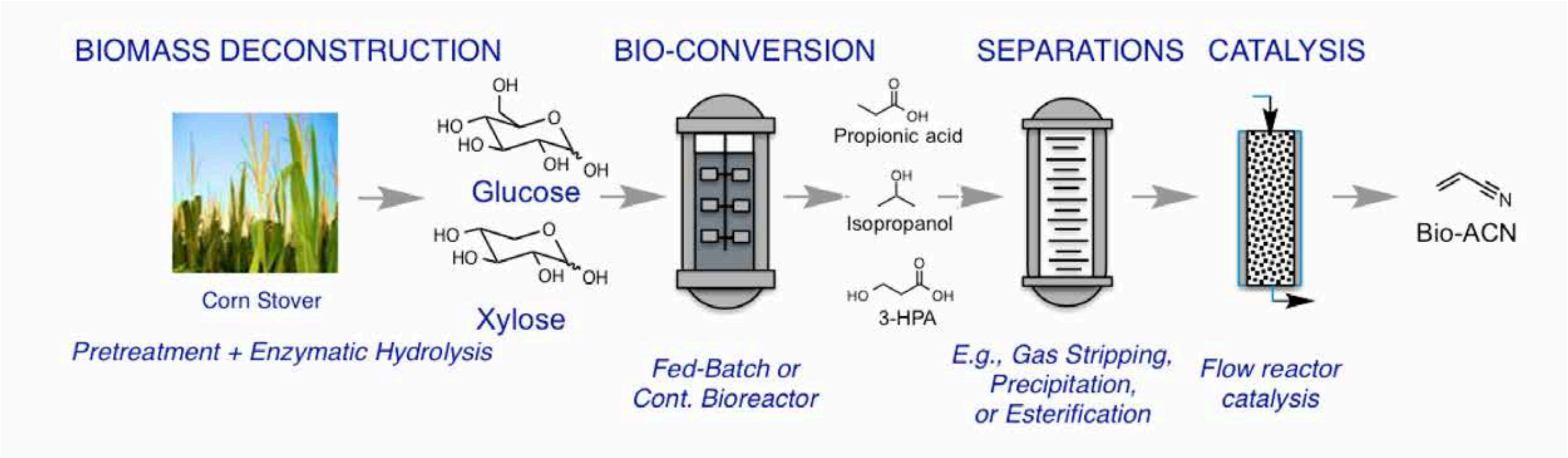
Assembled team of industrial, academic, and nat'l lab experts across the relevant R&D space

- Metabolic engineering and fermentation
- Separations and catalysis
- Carbon fiber production
- Techno-economic and life-cycle analysis
- Process Integration and scale-up

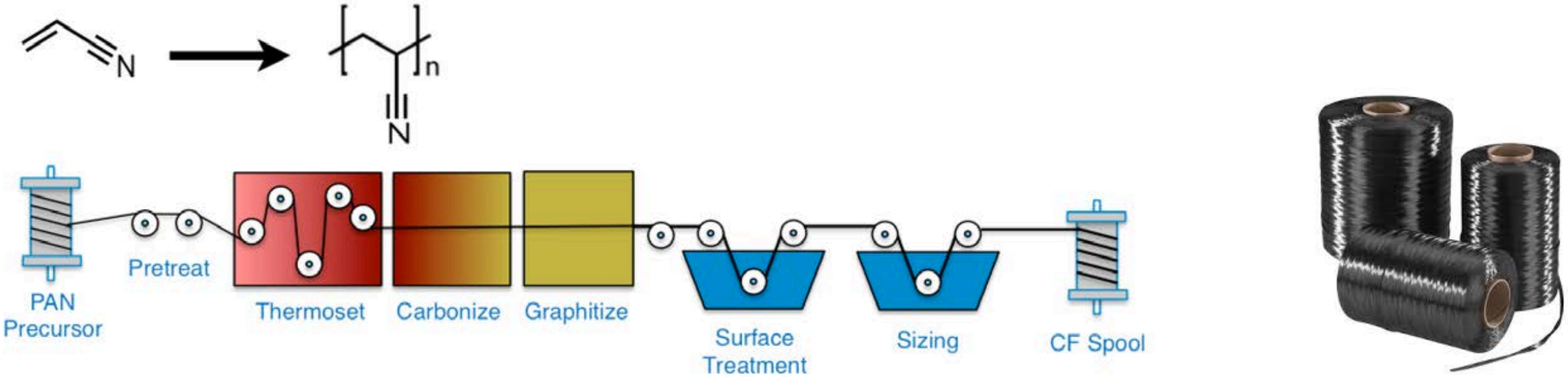
Developed a rigorous milestone-based timeline for Phase I and II of the project

- Down-select to a single pathway in Phase I
- Reallocate project responsibilities to scale up and demonstration in Phase II
- Hold annual project meeting, quarterly project reviews and monthly cross-institutional team meetings
- Setup a scientific advisory board led by expert in carbon fiber, Professor Larry Drzal of MSU

Aim 1: Produce ACN from biomass sugars



Aim 2: Produce carbon fiber from bio-ACN



Sugar Production from Biomass

Goal: Production of biomass derived sugars from wheat straw (Biochemtex) and corn stover (NREL/INL)

Metric: Suitable for downstream conversion operations @ $0.10-0.15 per lb

Status

- *>10 kg hydrolyzate delivered to ACN production team from both NREL and BioChemtex pilot plants*
- *Performance very good on both sugar streams during fermentation*
- *Subsequent batches have been produced for studies at higher sugar concentrations and with different fermentation strategies*

Pretreatment and Enzymatic Hydrolysis sections in the BioChemtex PROESA™ pilot plant

NREL's Integrated BioRefinery Research Facility (Pilot Scale)

Propionic Acid (PA) Pathway to ACN

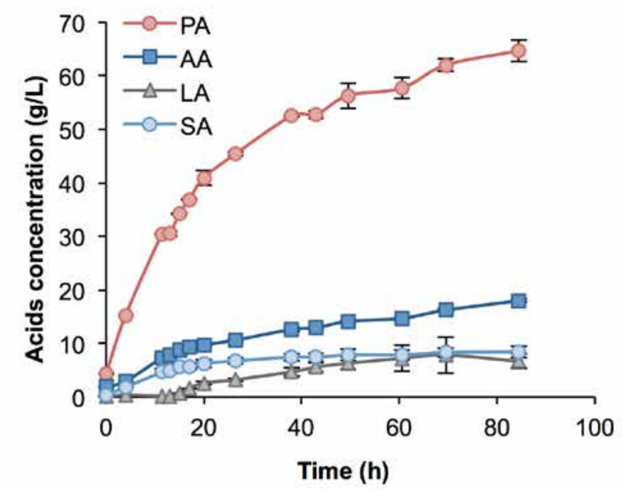
Goal: Production of PA from fermentation of biomass derived sugars with subsequent upgrading to bio-ACN

Metrics: Phase I PA productivity (0.5 g/L/hr) and overall ACN yield (20%) with a "path forward" to $1/lb

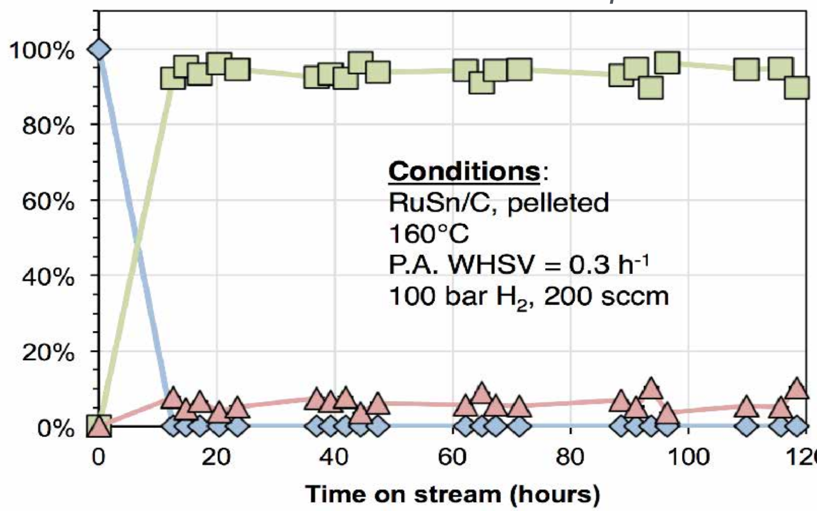
Status:

- *Near complete utilization of all sugars*
- *Titer=65 g/L, yield=0.5 g/g; productivity=0.8 g/L/hr*
- *Separations ~82% yield and near quantitative catalytic conversion to propylene*
- *Propylene ammoxidation commercial, but demonstrated yields of bio-ACN consistent with commercial practices*
- *Delivered several batches of ACN to carbon fiber production team for polymerization experiments*
- *Provided initial bench scale data to TEA/LCA team*

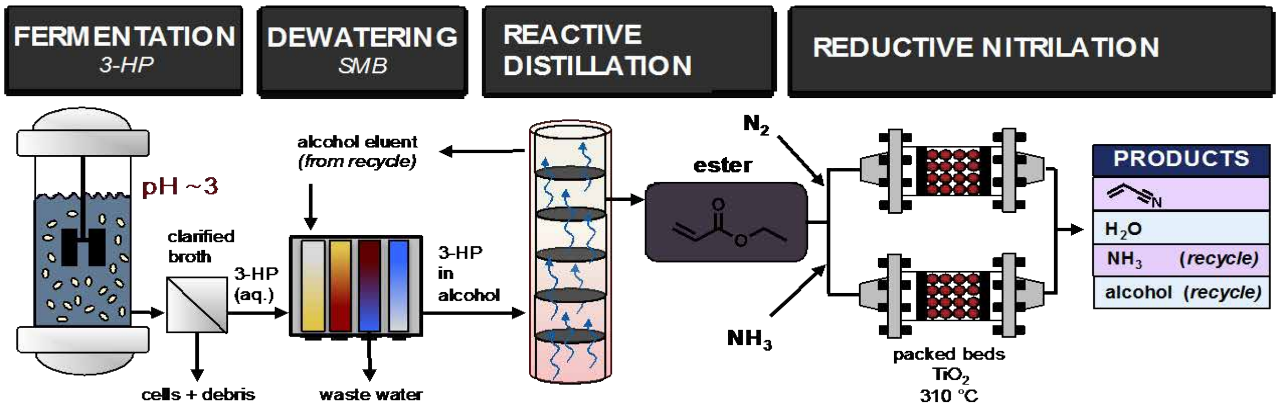
Fermentation of biomass sugars to PA



Conversion of PA to 1-Propanol

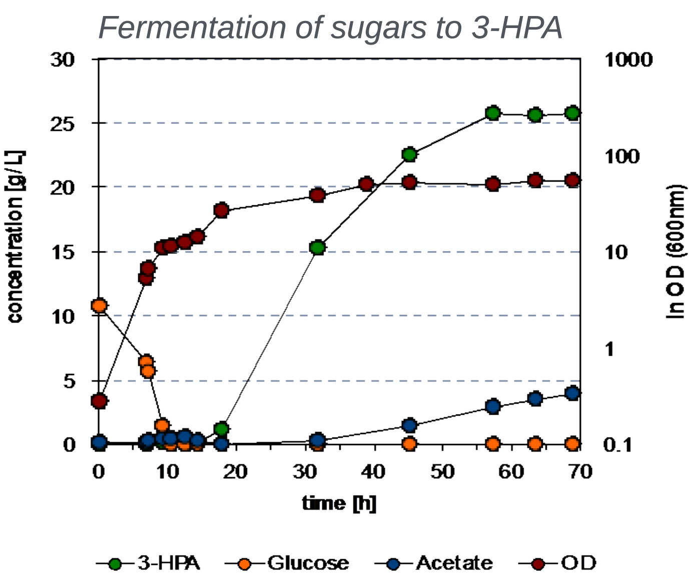


3-HPA Pathway to ACN



Goal: Production of 3-HPA from fermentation of biomass derived sugars

Metric: : Phase I PA productivity (0.5 g/L/hr)



Status

- *Engineered pathway to 3HPA utilizing glucose and xylose*
- *25.7 g/L titer; 0.44 g/L productivity; 0.23g/g glucose yield*
- *In discussions with industrial partners to obtain high-performing industrial strains*
- *Bench scale separations ~80% yield, large scale would benefit from low pH strain*

3-HPA Pathway to ACN

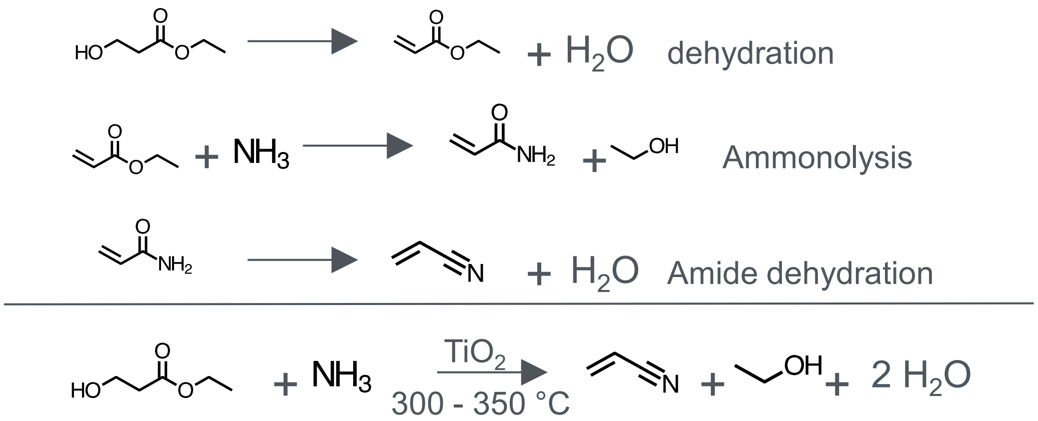
Goal: Production of Acrylonitrile (ACN) from biomass derived 3-HPA

Metric: Phase I overall ACN yield (20%) with a "path forward" to $1/lb

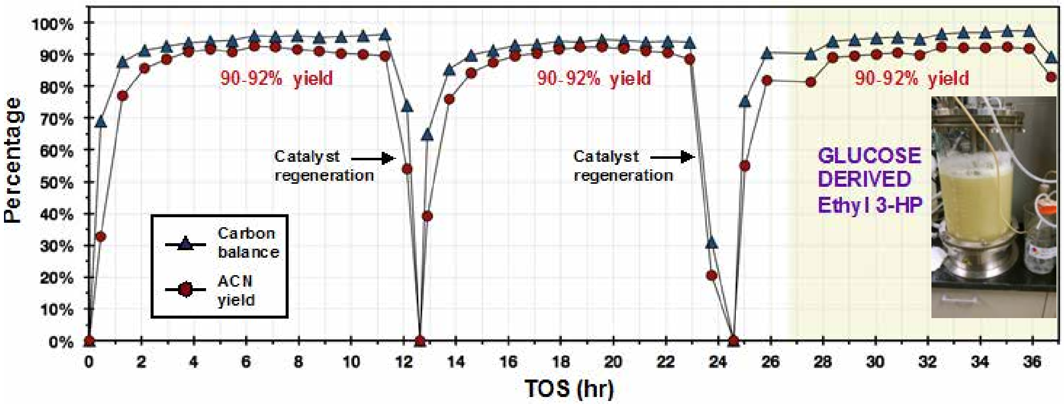
Status

- ***Yield of >90% bio-ACN from 3HPA***
- *Endothermic reaction, no toxic by-products, cheaper/simpler catalysts, renewable feedstock*
- *Delivered 50g batch of ACN to carbon fiber production team for polymerization experiments*
- *Provided initial bench scale data to TEA/LCA team*

Mechanistic Conversion of 3HPA ester to Acrylonitrile



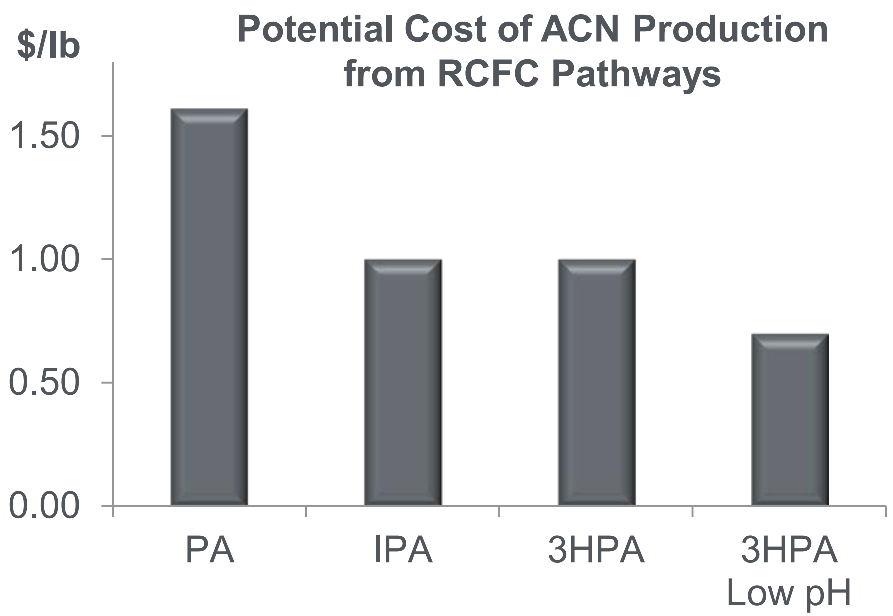
Experimental Conversion of 3HPA ester to Acrylonitrile



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

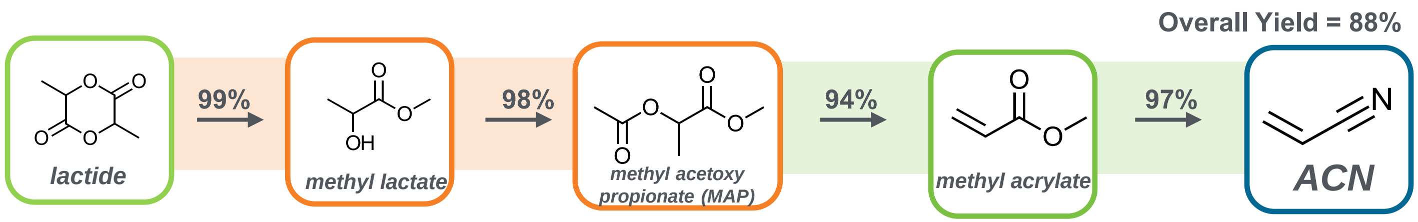
Preliminary TEA shows a pathway to ≤$1/lb ACN

- *Current ACN price is ~$1.25/lb*
- *PA pathway mature, but too many steps and requires ammoxidation*
- *IPA fewer steps, potential for lower cost, but less mature from fermentation perspective*
- *3-HPA has potential to meet and exceed cost target*
    - *For 1st gen sugars, industrially relevant strains exist with these TRYs at low pH for 3-HPA*
    - *For 2nd gen sugars, strains would need to be engineered*
- *Lactic Acid (LA) appealing because biology more efficient and works on 2nd gen sugars*

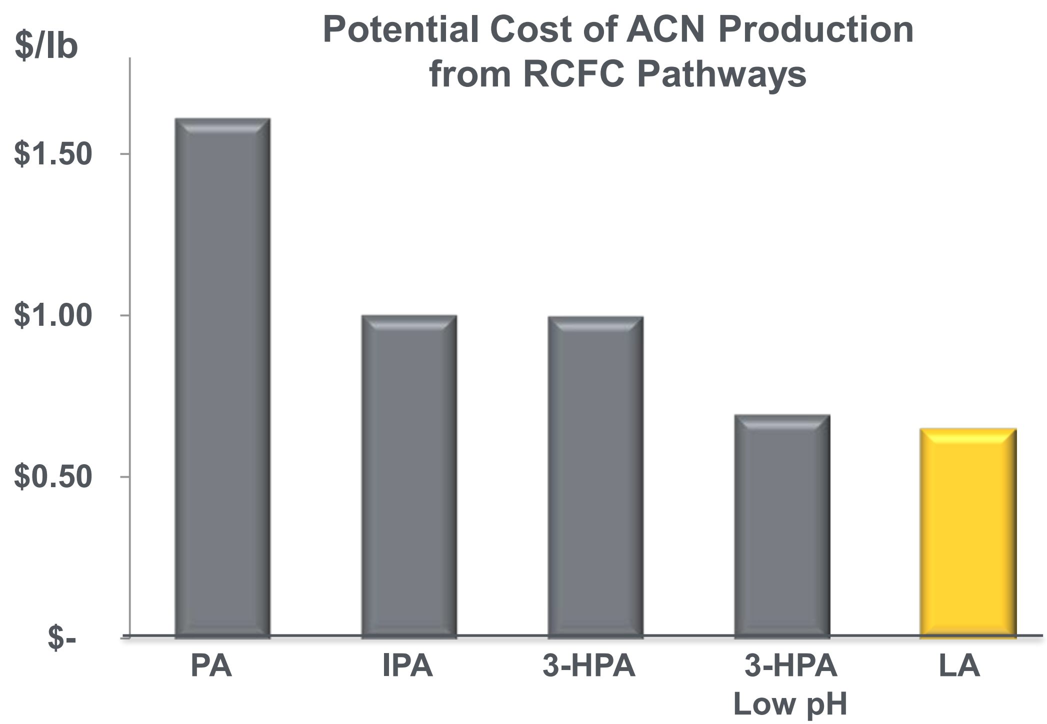


LA Pathway to ACN

Goal: Production of Acrylonitrile (ACN) from biomass derived LA



Metric: : Phase I overall ACN yield (20%) with a "path forward" to $1/lb



Status

- *Biology higher carbon efficiency and more amenable to 2nd gen sugars than 3HPA*
- *Chemistry multiple steps, but all very high yield*
- *TEA shows comparability to 3HPA case*
- *Potential for further cost improvements through process intensification of catalysis*

Polyacrylonitrile (PAN) Production and Spinning

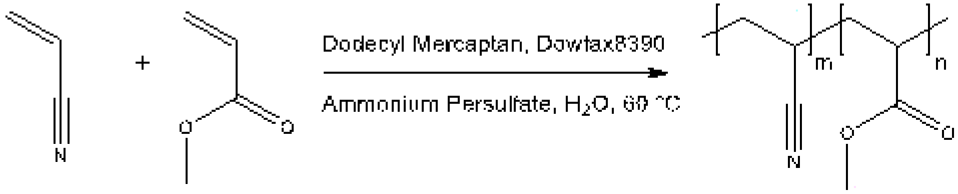
Goal: Production of poly-acrylonitrile (PAN) powder and fibers from bio-ACN

Metric: Phase I MWw > 100,000 Da and Phase II Polydispersity Index (PDI) <5

Status

- *ACN purification strategies being pursued*
- *Model ACN polymerization promising (97% yield, <2 PDI, 108,000 MWw)*
- *Bio-ACN samples polymerized to PAN with MWw >100,000 Da*
- *Single fiber spinning and testing underway*

ACN Polymerization to PAN



Isolated PAN

Small scale fiber production

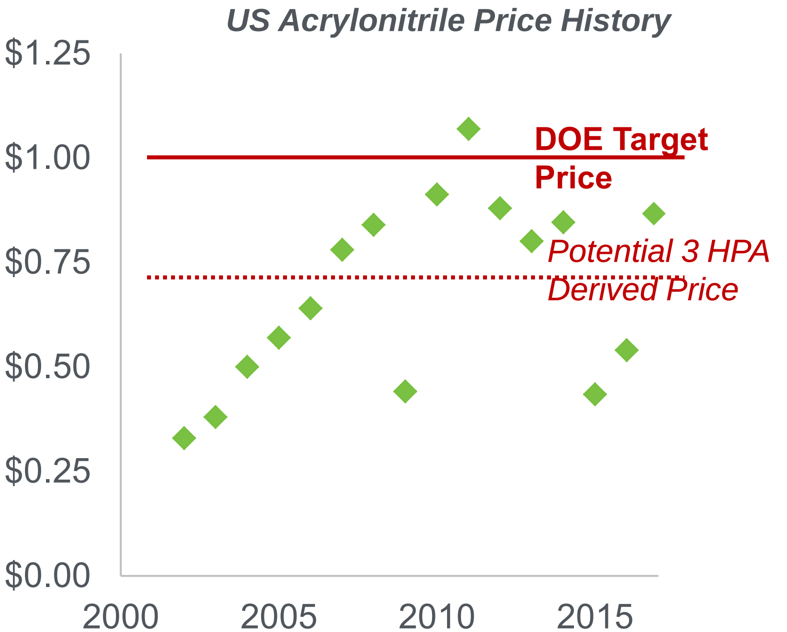
Large scale fiber production

Renewable Carbon Fiber Consortium
Relevance

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

Goal: Produce Bio-ACN that is suitable for carbon fiber production at <$1/lb

- *Directly supports BETO mission:* "Transform our renewable biomass resources into commercially viable, high performance biofuels and chemicals"
- *Provides a renewable route to ACN that addresses price and volatility*
- *Project metrics and technical targets driven by techno-economic analysis*
- *Suitability of ACN for downstream polymerization evaluated throughout process*
- *Relevant commercial partners actively engaged*
- *If successful, leverages other massive DOE investments for carbon fiber production cost reductions (NNMI)*
- *Nitrilation chemistry applications potentially much broader than just ACN production*



"US ACN market price history (average of spot and contract prices). Reproduced with permission from IHS."

Communicate Results to Stage Gate Review Team

- *Show technical and economic results from all 3 pathways*
- *Show novelty and superiority of nitrilation chemistry*
- *Show we met all technical targets laid out in the FOA for Stage I*
- *Show appropriate team capabilities to perform Stage II scale-up*

Demonstrate Suitability of "Bio-ACN" towards PAN, Fiber and CF

- *Translate model ACN results to Bio-ACN and transition to CF composites*

Finalize Stage II Plan with DOE and RCFC Team (and then execute)

- *Definitely want to utilize novel nitrilation technology*
- *Balance what is more commercially ready biologically (lactic acid) vs what has been more thoroughly demonstrated catalytically to date in the project (3-HPA)*
- *Balance industry (e.g. 1st gen sugars) with DOE objectives (e.g. 2nd gen sugars)*
- *Incorporate right mix of downstream CF viability studies (DOE originally only asked for ACN production)*

Renewable Carbon Fiber Consortium
Summary

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

Approach

- *Produce bio-derived ACN via three different biologically-derived intermediates (PA, IPA, and 3-HPA)*
- *Develop separations and catalytic processing to make ACN, conduct small-scale PAN synthesis and CF testing in Phase I; scale up in Phase II and add CF composite testing*
- *Strong team of targeted partners from academia, national lab and industry*

Technical accomplishments

- *Demonstrated ACN production from all 3 pathways*
- *Developed novel ester nitrilation chemistry as an alternative to propylene ammoxidation*
- *Demonstrating small-scale PAN and carbon fiber testing results for small scale ACN batches*

Relevance

- *Affordable, renewably-sourced ACN could enable significant new investment in carbon fiber composites for light-duty vehicle manufacturing and other large-market light-weighting applications*
- *Leverages other downstream carbon fiber cost reduction efforts*

Critical success factors and challenges

- *High titers, rates, and yields in biological steps, facile and cheap separations solutions, active, selective, and stable catalysts, effects of biomass impurities on PAN and carbon fiber properties*

Future work

- *Communicate results to stage gate review team and jointly with DOE develop stage II strategy*

Technology transfer

- *Working with relevant **industry partners** to demonstrate commercial viability at every stage of process*

Renewable Carbon Fiber Consortium

Acknowledgements

Project Contributors

- Robert Baldwin
- Gregg Beckham
- Patrick Blanchard
- Mary Biddy
- Rich Bolin
- Lara Bozzini
- Brenna Black
- David Brandner
- Jae-Soon Choi
- Robin Cywar
- Sujit Das
- John Dorgan
- Larry Drzal
- Todd Eaton
- Cliff Eberle
- Stan Fruchey
- Michelle Gilhespy
- Ryan Gill
- Prasad Gupta
- Andrew Heavers
- Eric Karp
- Jeff Lacey
- Andrew Lepore
- Liya Liang
- Rongming Liu
- Lorenz Manker
- Kelly Meek
- Bill Michener
- Chaitanya Narula
- Amit Naskar
- Stephania Pescarolo
- Valeria Rasetto
- Nicholas Rorrer
- Davinia Salvachua
- Violeta Sanchez i Nogue
- Zinovia Skoufa
- Tim Theiss
- Cynthia Tyler
- Derek Vardon
- Vassili Vorotnikov
- Xiaoqing Wang
- Mike Watson
- Joyce Yang
- Haibo Zhao

Project Team