March 5, 2019

U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Biomass conversion to Acrylonitrile monomer-precursor for the production of carbon fibers

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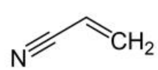
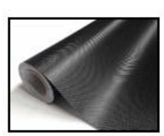
Southern Research



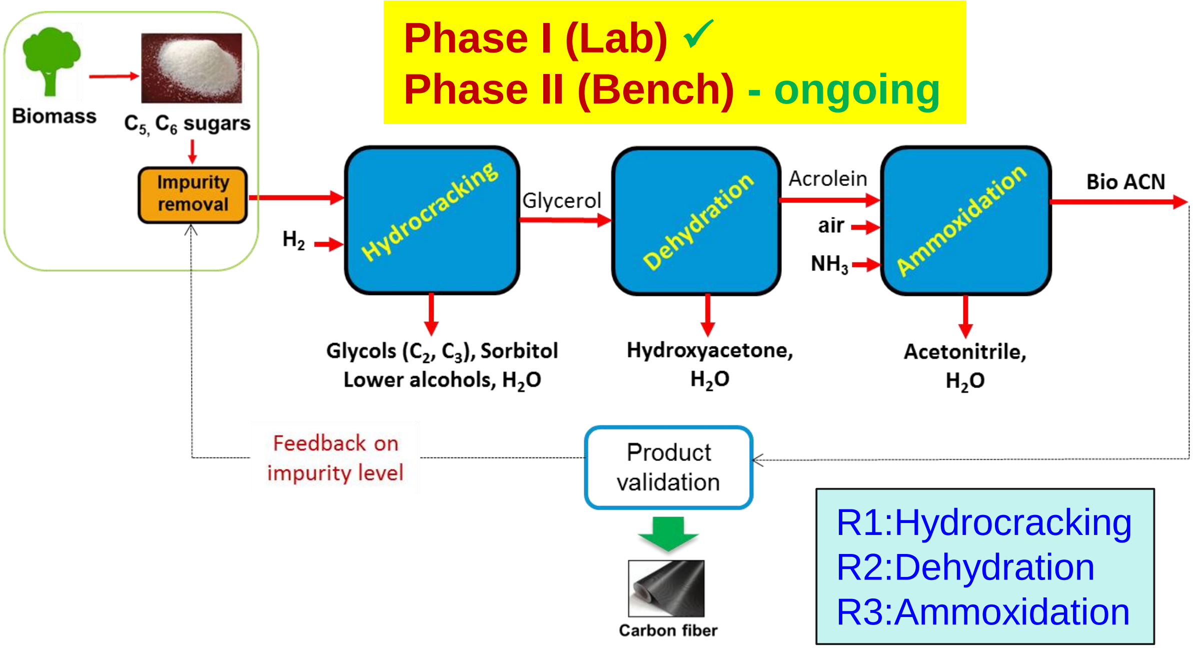


Goal Statement

Goal: Develop a novel, commercially viable, cost effective thermochemical process that enables utilization of an alternative feedstock - non-food sugars for the production of acrylonitrile (ACN) – an essential precursor for high performance carbon fiber.

Outcome:

- Novel catalyst development for multi-reaction steps
- Produce BioACN of drop-in quality
- Demonstrate catalyst and process scalability
- TEA/LCA to determine cost and GHG benefits



Relevance: Supports DOE BETO's strategic goals aimed for conversion R&D and BETO's modeled $1/lb cost goals for Bio-ACN production to reduce carbon fiber manufacturing cost to $5/lb by 2020.

Quad Chart Overview

Timeline

Phase	Start date	End date	% complete
I	02/01/2015	06/30/2017	100
II	07/01/2017	09/30/2019	60

Budget

	DOE funded	Cost share
Total Pre FY 17 costs	1,195,463	268,399
FY 17 costs	798,139	192,352
FY 18 costs	1,610,655	136,600
Total planned (FY19 – project end)	2,377,456	236,815

Partners: Southern Research (70%), Cytec-Solvay (25%), NJIT (5%), Arbiom – sugar supplier

Barriers addressed

- Ct-E Improving catalyst lifetime
- Ct-F Increasing the yield from catalytic processes
- Ct-K Developing methods for bioproduct production
- ADO-D Technology Uncertainty of integration and scaling

Objective

Demonstrate feasibility, scalability and economic merit of a new sugar to drop-in quality ACN process

End of project target

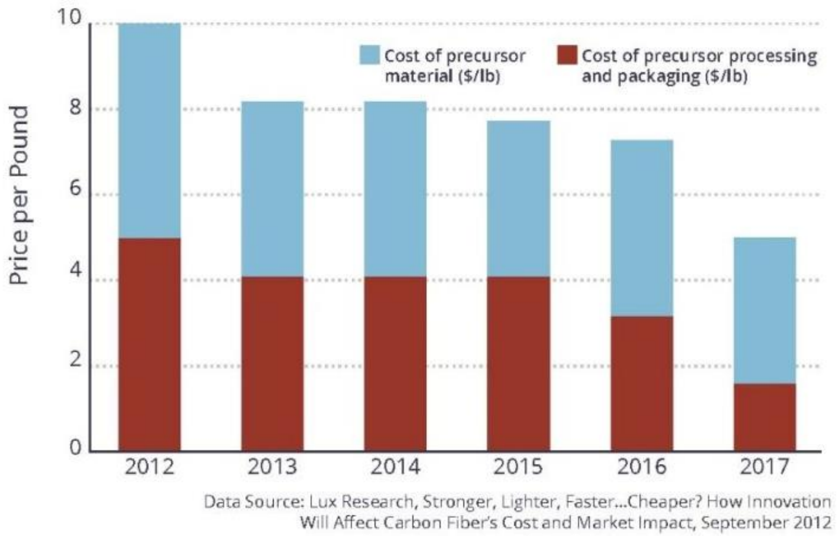
Produce 200-250kgs Bio-ACN from bench process and polymerize to PAN

SR

1 - Project Overview

Context

- Carbon fiber application critical to reach federal fuel economy standards (54.5mpg by 2025) for light duty vehicles
- Widespread use of carbon fiber restricted due to high cost of production
- Further cost reduction envisaged in precursor material (e.g., ACN) production
- DOE targets $1 per lb cost of precursor to reduce carbon fiber below $5 per lb



As the cost of precursor materials drop, the cost of carbon fiber will fall

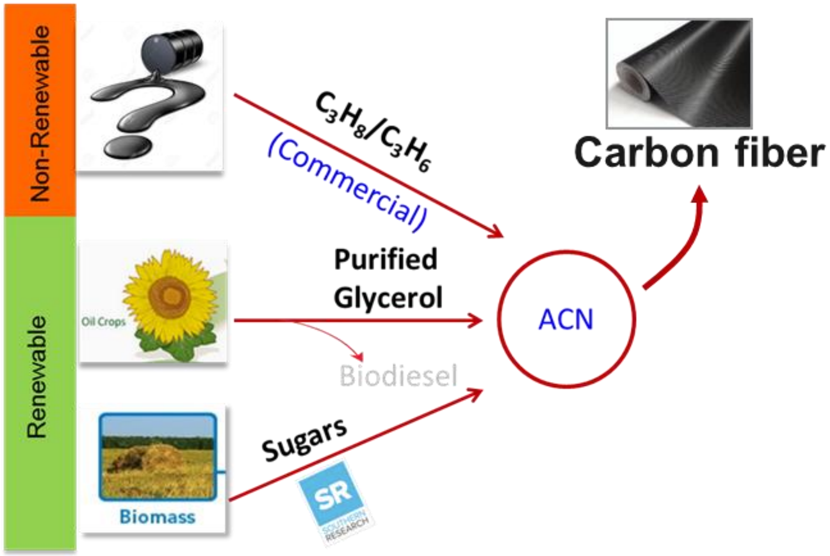
Project history

- SR received DOE award in 2014.
- Lab scale catalyst development and product validation (phase I) completed in 2017.
- Funding approved for bench scale study following stage gate review.
- Bench scale (phase II) demonstration work ongoing.

1 - Project Overview (contd)

Novelty:

Biomass derived C_5/C_6 sugar, a low cost, readily available and renewable feedstock, selectively converted to ACN in multi novel catalytic steps.



Routes to ACN

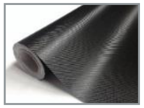
State of the art:

Affected by the volatility in price and availability (non-renewable C_3 feedstock) or high cost of purified raw materials (renewable glycerol)

Project goals:

- High performance catalyst development for multistep catalytic process
- Feedstock and product validation with commercial partners
- Process optimization and TEA to achieve <\$1/lb cost of ACN
- Performance and product validation in bench scale

2 – Approach (Technical)

 ➔ **Sugar** ➔ **Glycerol** ➔ **ACN** ➔ 

Biomass to carbon fiber pathway

Phase I (Laboratory scale):

- Process development using model as well as commercial sugar hydrolyzates
- Novel catalyst development for desired product/intermediate characteristics
- Product validation with commercial partner
- Feedstock (Sugar) optimization from product validation feedback
- Process simulation and TEA/LCA to determine cost

Phase II (Bench scale):

- Decoupled bench scale skid (R1, R2, R3) fabrication and continuous testing for > 500hrs
- Testing with commercial sugar hydrolyzate feedstock
- Up to 1000x catalyst/process scale up from phase I
- Produce and deliver drop-in quality BioACN in necessary amount for polymerization
- Feedback from impurity effect study to guide Bio-ACN purification

2 – Approach (Technical)

Challenges:

- Impact of feedstock and process derived impurities on Bio-PAN
- Catalyst scalability and stability
- Commercial viability of intermediate separation and byproduct recovery

Critical success factors:

- Producing drop-in quality ACN
- Cost of ACN production <$1/lb

Progress/target metrics:

Reaction	Productivity (g/l/hr)[a]	Desired product	Yield (%)[a]	Catalyst mass (g)[b]	Production rate (kg/h)[b]	Production Scale up in phase II
R1	>50	Glycerol	>65	200 – 300	0.2-1.0	60 – 100x
R2	>375	Acrolein	>70	200 – 300	0.65-1.0	650 - 975x
R3	>75	ACN	>70	160 - 300	0.55- 1.0	320 – 600x

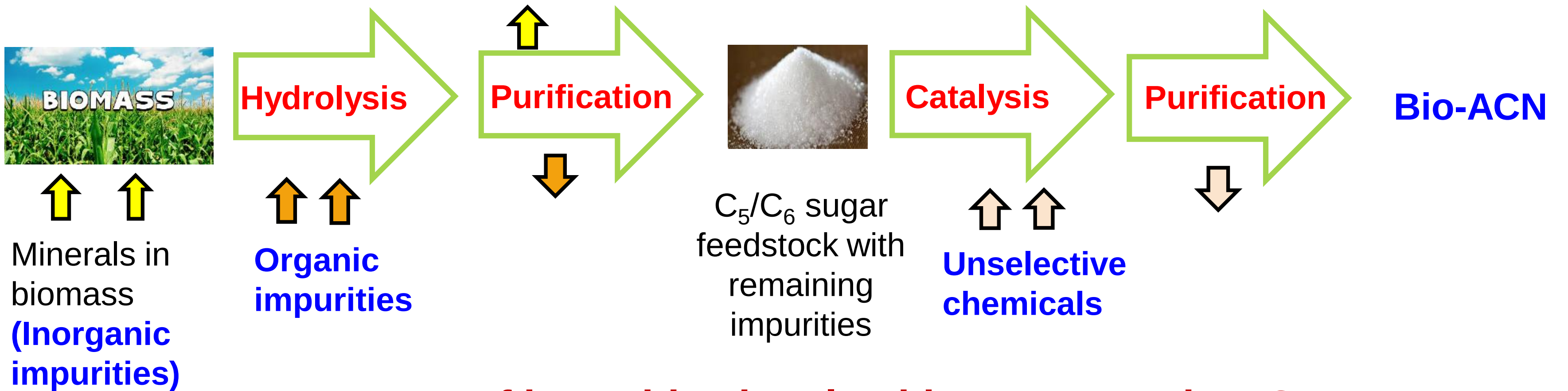
[a]Target set and achieved for Phase I, [b]Target set for Phase II

SR

2 – Approach (Technical)

Impurities are key barriers towards commercializing any chemical technology

- SR tracks an extensive list of **two** types of impurities –
  - **Feedstock impurities:** Inorganic and Organic
  - **Process impurities:** Unselective chemicals generated and carried over during sugar to ACN conversion (e.g., acrolein, acetonitrile, water and propionitrile)

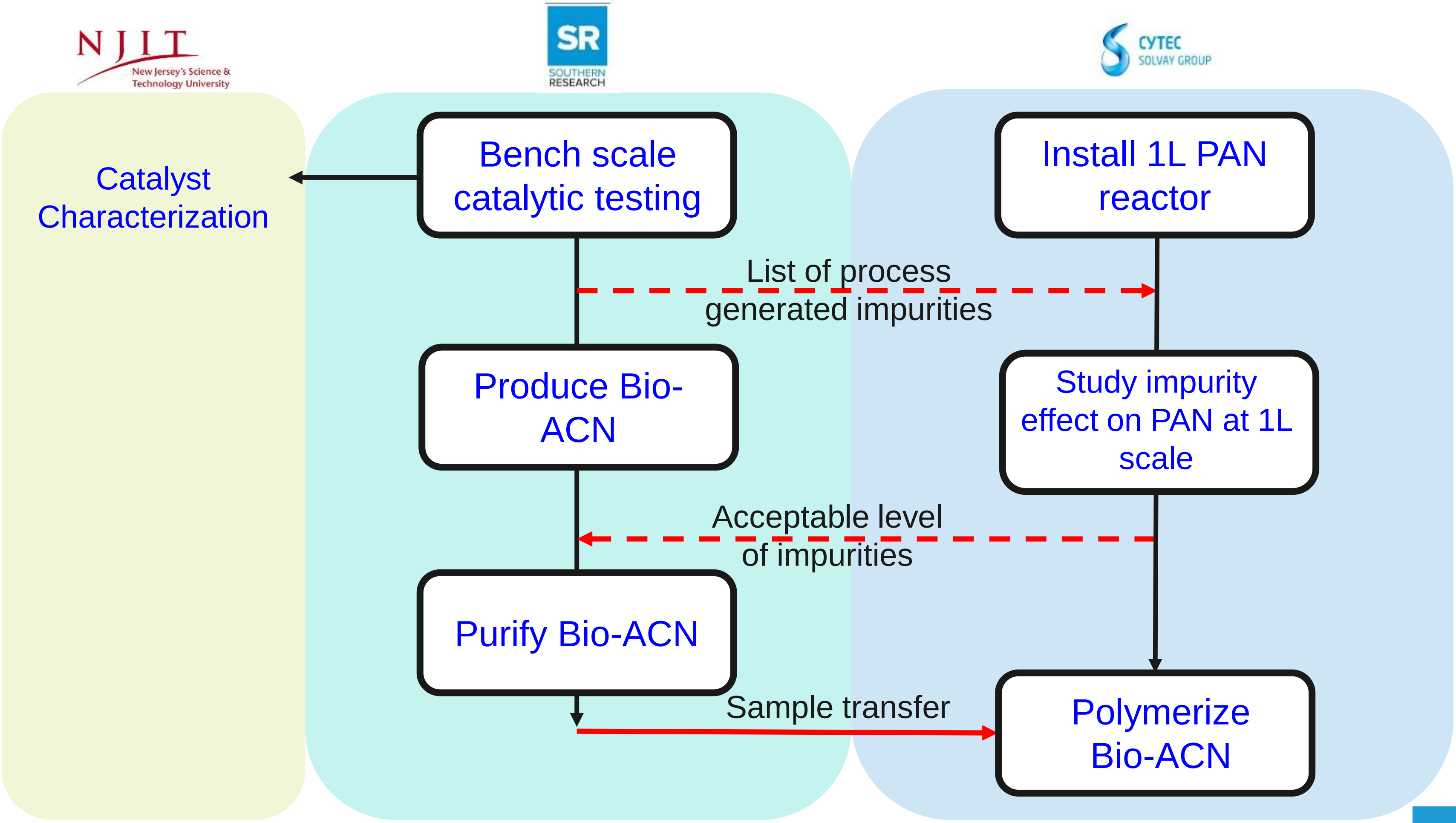


Types of impurities involved in sugar to Bio-ACN process

- Impact of impurities on **catalysis** and **final product specification** studied
- Study guides the extent of purification required on feedstock and/or product

2 – Approach (Technical)

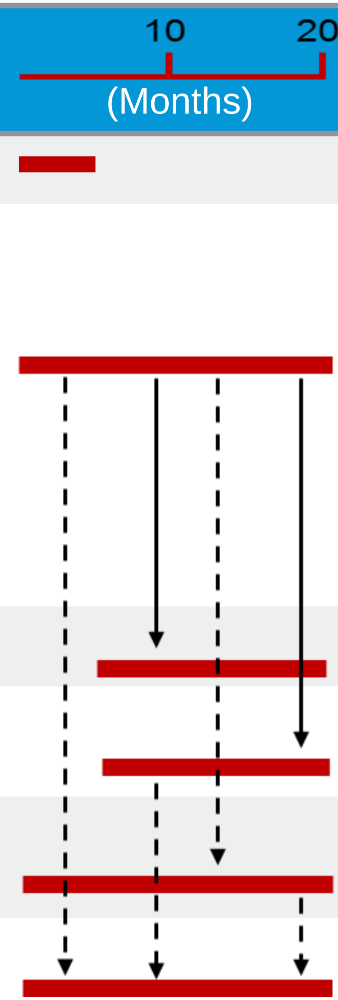
Produce, deliver and polymerize drop-in quality Bio-ACN is a key phase II target



Timely transfer of materials and information to minimize Phase II risks

2 – Approach (Management)

Activity (Phase I-completed on 03/2017)	Task owner	Status & Milestone
Task 1: Micro Reactor set up	SR	Task completed
Task 2: Catalyst development and testing Task 2.1 Develop R1 catalyst Task 2.2 Parametric study for R1 Task 2.3 Develop R2 catalyst Task 2.4 Parametric study for R2 Task 2.5 Optimize ACN production Task 2.6. Measure catalyst stability and regeneration	SR	Task completed
Task 3: Catalyst characterization	NJIT,SR	Task completed
Task 4: Bio-ACN validation	Cytec-Solvay	Task completed
Task 5: TEA/LCA	SR	Task completed
Task 6: Project Management and Reporting	SR	Task completed



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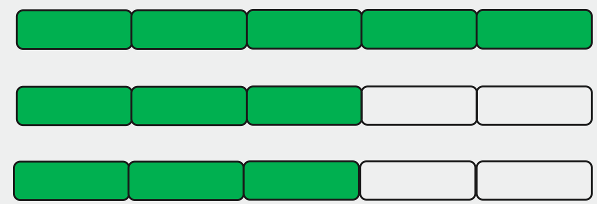
2 – Approach (Management)

Activity (Phase II- ongoing)	Task owner	Timeline	Status & milestone
Task 7: Decoupled bench scale unit design and operation Task 7.1 Determine optimal safety and storage conditions Task 7.2 Separation methods design Task 7.3 Commissioning	SR	M21-M35	Design-Construct-Catalyst scale up-Commission-Separation **Skid 1** **Skid 2** **Skid 3** 
Task 8: Continuous operation	SR	M25-M40	**Skid 1:** > 500hrs of continuous testing completed **Skid 2, 3:** Pending
Task 9: Periodic ACN validation Install new lab hood and polymerization reactor, polymerize with impurities and their physical and chemical properties	Cytec-Solvay	M31-M40	✓ New 1L reactor installed and commissioned ✓ Impacts of major Bio-ACN impurities and their accepted levels determined
Task 10: Characterization	NJIT, SR		**Skid 1:** Completed **Skid 2, 3:** Pending
Task 11: TEA/LCA	SR	M21-M40	<$1/lb cost, <35% GHG emission
Task 12: Project Management and Reporting	SR	M21-M40	Deliverables to DOE-EERE

2 – Approach (Management)

U.S. Department of Energy – Energy Efficiency & Renewable Energy

Southern Research

Dr. Amit Goyal (PI)
Dr. Santosh Gangwal (Co-PI)
Dr. Jadid Samad (Engineer)
Dr. Swanand Tupsakhare (Separations engineer)
Zora Govedarica (Chemist)

-Quarterly report and meetings - DOE
-Bi-weekly labor hour report
-Monthly Meeting with partners
-Catalyst synthesis
-Reaction evaluation
-TEA/LCA

NJIT – New Jersey's Science & Technology University

Dr. Zafar Iqbal
Dr. El Mostafa Benchafia

- Characterization

Cytec – Solvay Group

Dr. Jeremy Moskowitz
Mr. Billy Harmon

-ACN validation

Phase I

3- TECHNICAL ACCOMPLISHMENTS/PROGRESS/RESULTS

Summary of phase I accomplishments:

Task 2: Catalyst development and testing

High performance catalysts/process developed-

- Catalyst developed and tested on formed custom tolled supports for easy scalability
- Validated using commercial sugar hydrolyzates of C_5, C_6 sugars and their mixtures
- Various sugar hydrolyzates qualified with respect to final product (ACN) specification
- Single step sugar to C_3 (glycerol and glycol) conversion
- Highly selective ACN production (No HCN, CO_2)
- Low overall H_2 demand (2% of biomass)
- Production of valuable co-products

Task 3: Catalyst characterization

Task 4: BioACN validation

- Meets required critical performance attributes (CPA)
- First sample of bio-PAN polymer produced

Task 5: TEA/LCA

- < $1/lb of ACN production cost

SR produced BioACN for phase I

Phase II

3- TECHNICAL ACCOMPLISHMENTS/PROGRESS/RESULTS

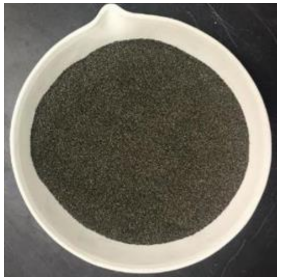
Task 7: Decoupled Bench Scale Unit design and operation

Decoupled bench scale skid specifics:

Skid ID	Type of reaction	Type of reactor	Feed	Pressure	Separation	Special safety feature in skid	Reactor size
R1	Hydro-cracking	Fixed bed	Sugar,H_2	Pressurized	Glycerol/PG -EG	H_2 recycle limits use	
R2	Dehy-dration	Fixed bed	Glycerol	Atmospheric	Acrolein/ Acetol	Inside hood. Handsfree Acrolein collection	1meter L x 1-2" OD
R3	Ammoxi-dation	Fixed bed	Acrolein, NH_3, O_2	Atmospheric	ACN/ acetonitrile	Inside hood. Handsfree ACN collection	

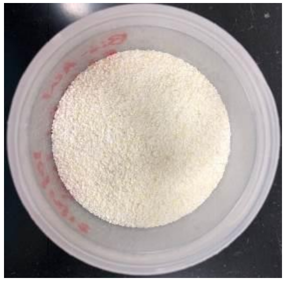
Catalyst scale up

- All <u>three</u> catalysts synthesized in 500gm batches
- Formed (industrial) custom tolled catalyst support and industrially applicable synthesis
- Catalyst characterized to ensure retention of key parameters at desired levels



R1

R2



R3

Scaled up catalysts

Task 7: Decoupled Bench Scale Unit design and operation

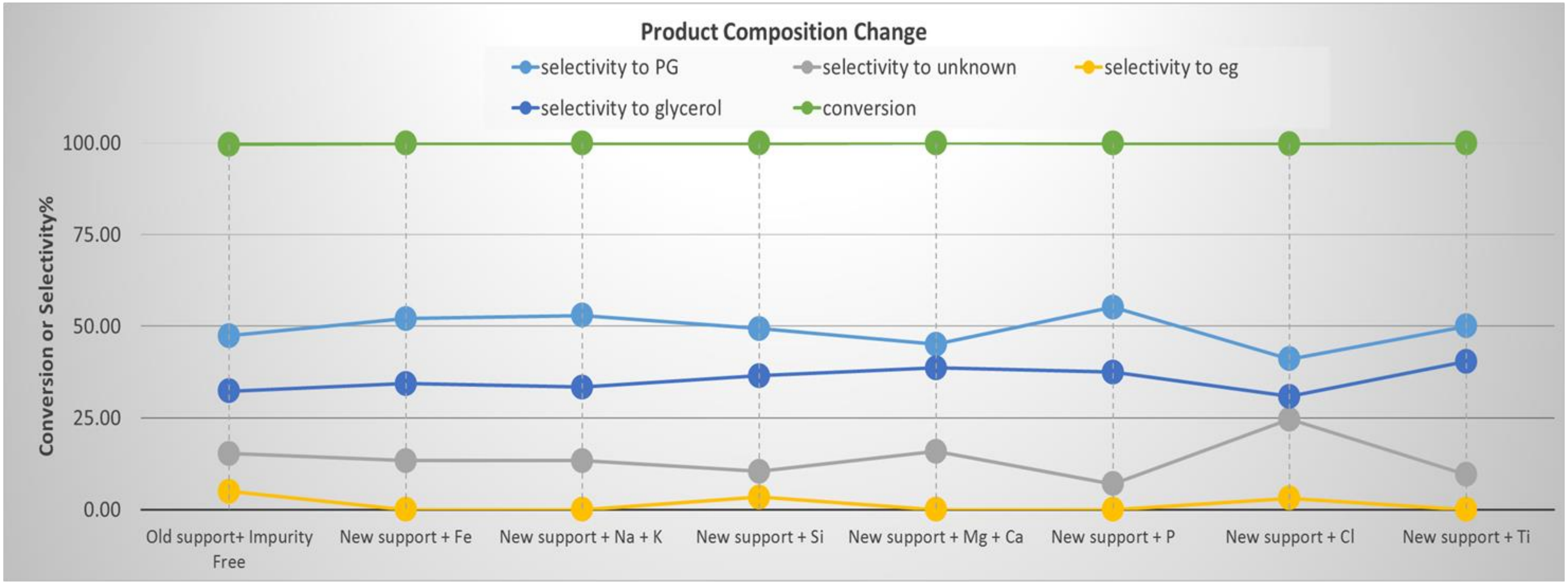
Feedstock selection via impurity assessment

- Non-food sugar feedstock procured in large batches from commercial vendor
- Feedstock carefully screened for impurity levels within the allowable limit
- Allowable levels determined based on their impact on **catalysis** and **product**
    - SR determined the levels of **nine** different inorganic (sampled from **nine** representative biomass) and **nine** organic impurities (introduced during biomass to sugar conversion) – **Feedstock impurity**
    - These impurities were traced in the process and their impacts on the first catalytic step (hydrocracking, R1) studied
    - To know the cumulative effect, SR also tested commercial sugar hydrolyzates with varying purity levels as feed

SR

Task 7: Decoupled Bench Scale Unit design and operation

Effect of inorganic impurity on R1 performance



- Dosing one inorganic impurity at a time in hydrocracking feedstock (model sugar)
- 48-96hrs continuous run data
- No distinct influence on catalyst performance from any of the impurities.

Task 7: Decoupled Bench Scale Unit design and operation

(Process simulation with reaction data to know the fate of impurities)

Feed to R1

Major Components	Composition tested		
Sugar	10%		
Water	90%		
Maximum Impurities (on dry basis - db)[*]			
Organic		Inorganic	
Impurity	ppm	Impurity	ppm
Formic Acid	30-11000	Fe	1-2100
Acetic Acid		K	
Levulinic Acid		Si	
HMF		Mg	
Furfural		Ca	
Glycolic Acid		P	
Vanilin		Cl	
Syringaldehyde		Ti	
		Na	

R1 Reactions

Reaction 1
Major Reactions:
$C_6H_{12}O_6$ (Hexose) + 2 H_2 = 2 $C_3H_8O_3$ (Glycerol)
$C_6H_{12}O_6$ + 4H_2 = 2 $C_3H_8O_2$ (Propylene glycol) + 2 H_2O
$C_6H_{12}O_6$ + 3 H_2 = 3 $C_2H_4O_2$ (Ethylene Glycol)
Other Reactions:
Formic Acid = Methanol
Levulinic Acid = γ-Valerolactone (GVL)
Glycolic Acid = Ethylene Glycol
Vanilin =Cresol

Product of R1

Major Components	Composition (db)		
Glycerol	38.5%		
Ethylene Glycol (EG)	7%		
Propylene Glycol (PG)	45.5%		
Unknowns	8.15%		
Impurities in the product (db)			
Organic		Inorganic	
Impurity	Ppm	Impurity	Ppm
Formic Acid	3-5000	Fe	0-20
Acetic Acid		K	
Levulinic Acid		Si	
HMF		Mg	
Furfural		Ca	
Glycolic Acid		P	
Vanilin		Cl	
Syringaldehyde		Ti	
Methanol[†]		Na	
GVL[†]			
EG[†]			
Cresol[†]			

Separation

Desired Product (dry basis)	
Component	**Composition**
Glycerol	**99.9%**
GVL	691 ppm
Vanilin	3 ppm
Cresol	3 ppm
Others	303 ppm

Byproducts (NOT carried forward to R2)	
Component	Component
EG + PG + Unknowns	Fe
Formic Acid	K
Acetic Acid	Si
Levulinic Acid	Mg
HMF	Ca
Furfural	P
Glycolic Acid	Cl
Syringaldehyde	Ti
Methanol[†]	Na
EG[†]	

Note: Highest values of impurities tested. The values in commercial sugars are significantly lower.

Only limited feedstock impurities at ppm levels are carried over to the next step

SR

Task 7: Decoupled Bench Scale Unit design and operation

Common skid design objectives:

- Process calculation for size/capacity/range of process units
- Automated control on critical units for safe and stable operation
- Provisions for system wash/purge and periodic as well as bulk product collection

Skid specific design attributes:

Hydrocracking (R1)

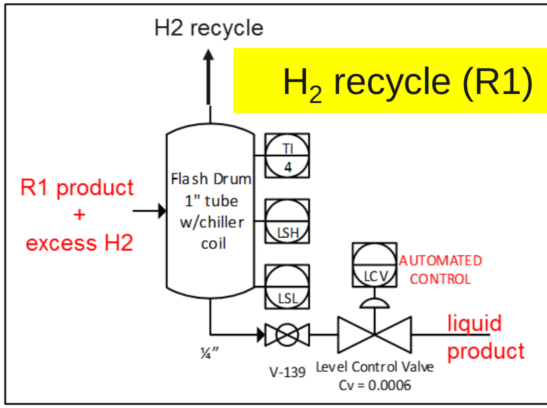
- Sophisticated automated control for H_2 recycle

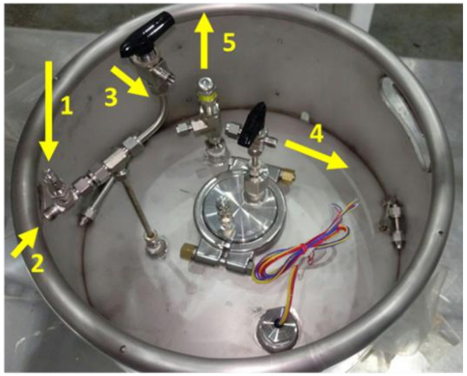
Dehydration (R2)

- Enclosed in 14' x 12 x 5' fume hood
- Hands-free storage and automated discharge (waste or distillation column) of hazardous product (acrolein) in two 56-L hazardous product vessels

Ammoxidation (R3)

- Enclosed in 14' x 12' 5' fume hood
- Process calculation to operate outside of flammability limit (exothermic reaction)
- Hands-free safe acrolein feeding system
- Hands-free storage of product containing ACN in hazardous vessel and automated discharge (similar to R2)





Custom installed ports on hazardous product vessels for R2 & R3: 1.liquid in, 2. N_2 in (for liquid discharge), 3. Gas vent, 4. Liquid discharge (dip tube), 5. PRV

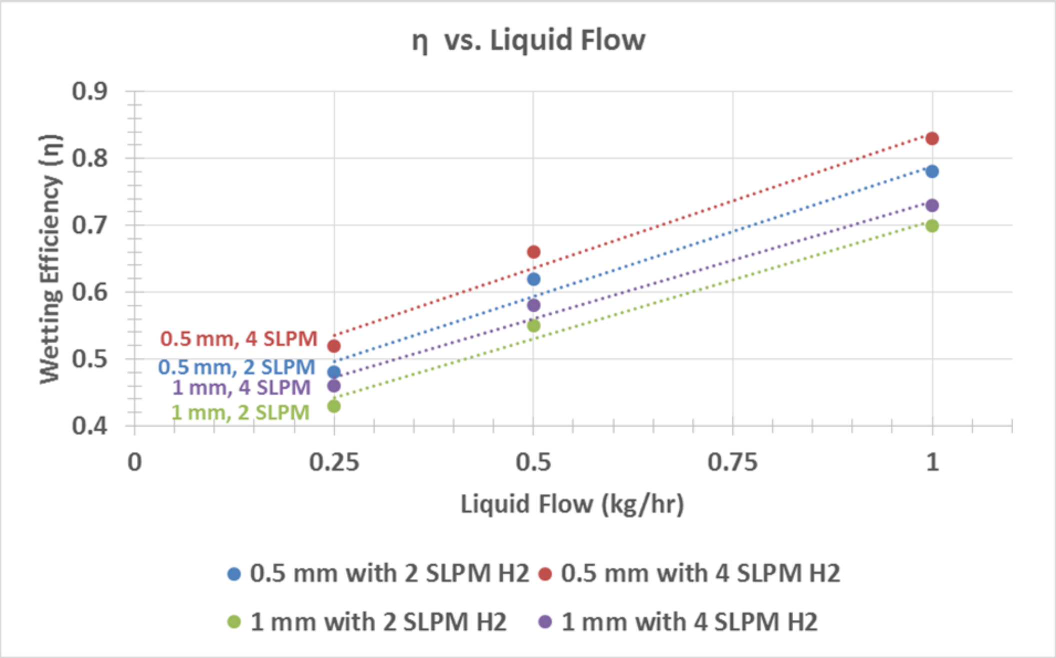
Task 7: Decoupled Bench Scale Unit design and operation

(Skid footprint)

BioACN bench scale (phase II) footprint

Task 8: Continuous operation (R1: Hydrocracking)

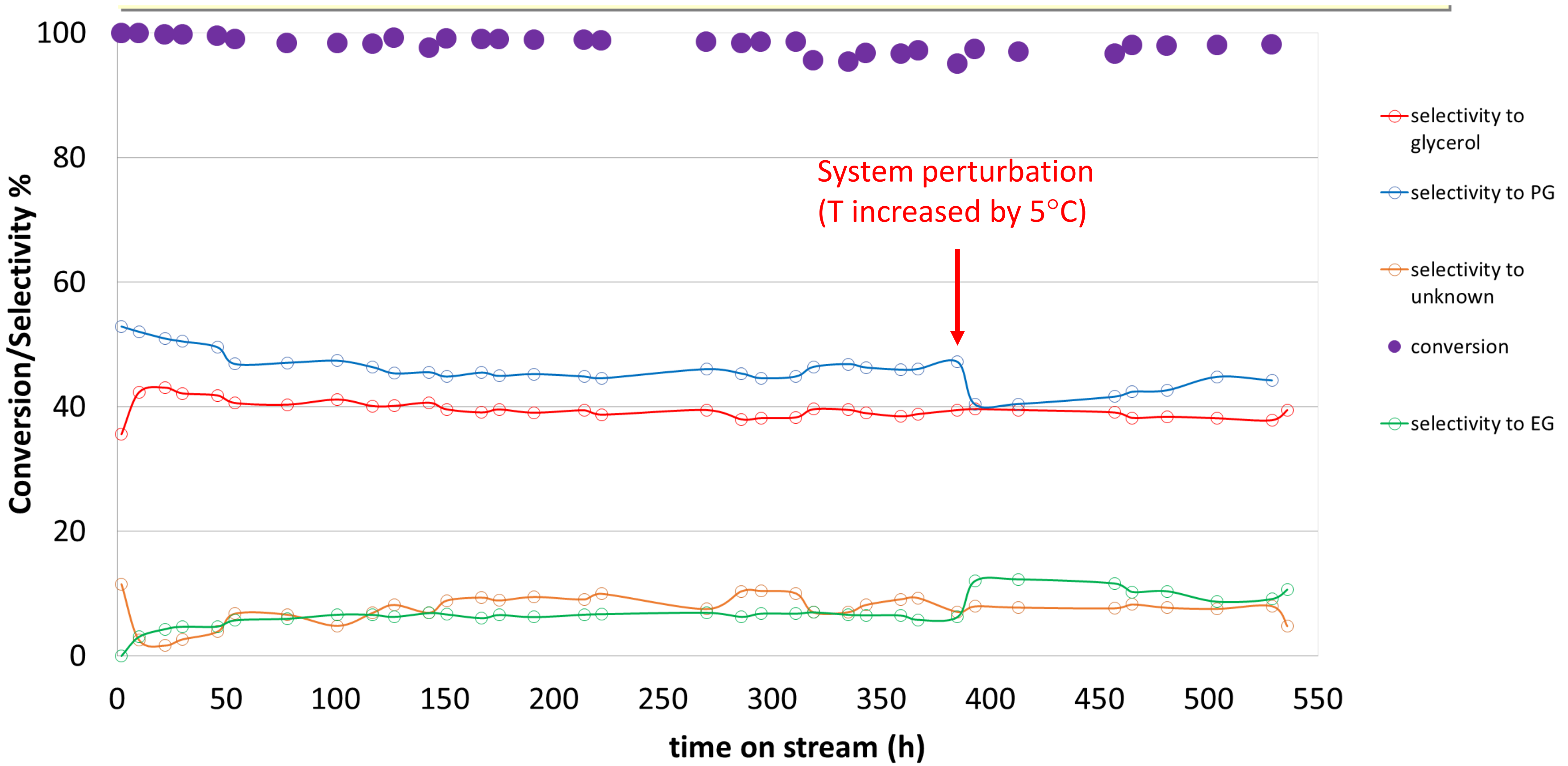
- Optimum size of catalyst particles determined from correlation and used to maximize catalyst wetting efficiency



- Improved catalyst wetting efficiency led to **3x** increase **(50 g/l/hr → 150 g/l/hr)** in productivity from hydrocracking (R1) step in phase II

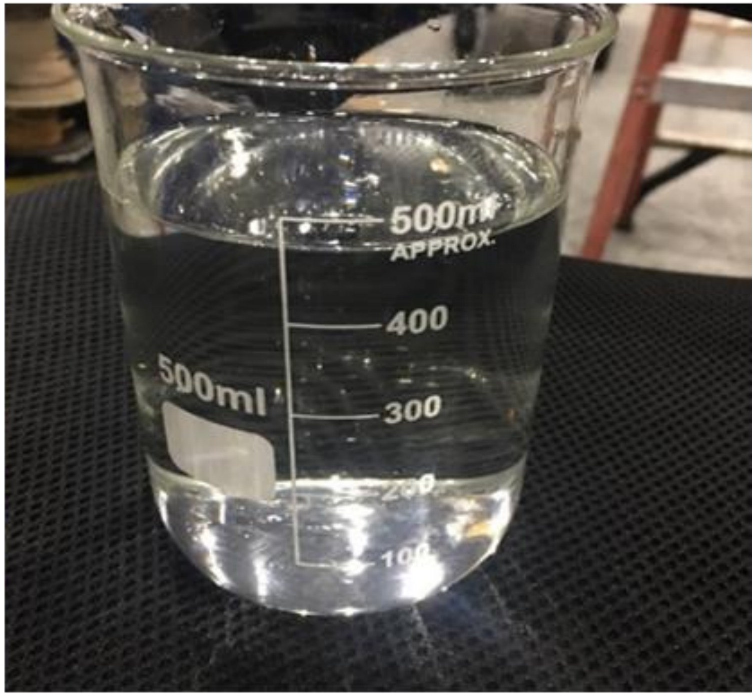
Task 8: Continuous operation
(R1: Hydrocracking)

Pilot Scale Results – All impurities present in the sugar hydrolyzate



Stable catalyst operation continuously up to 550hrs (overall 1000 hrs.)

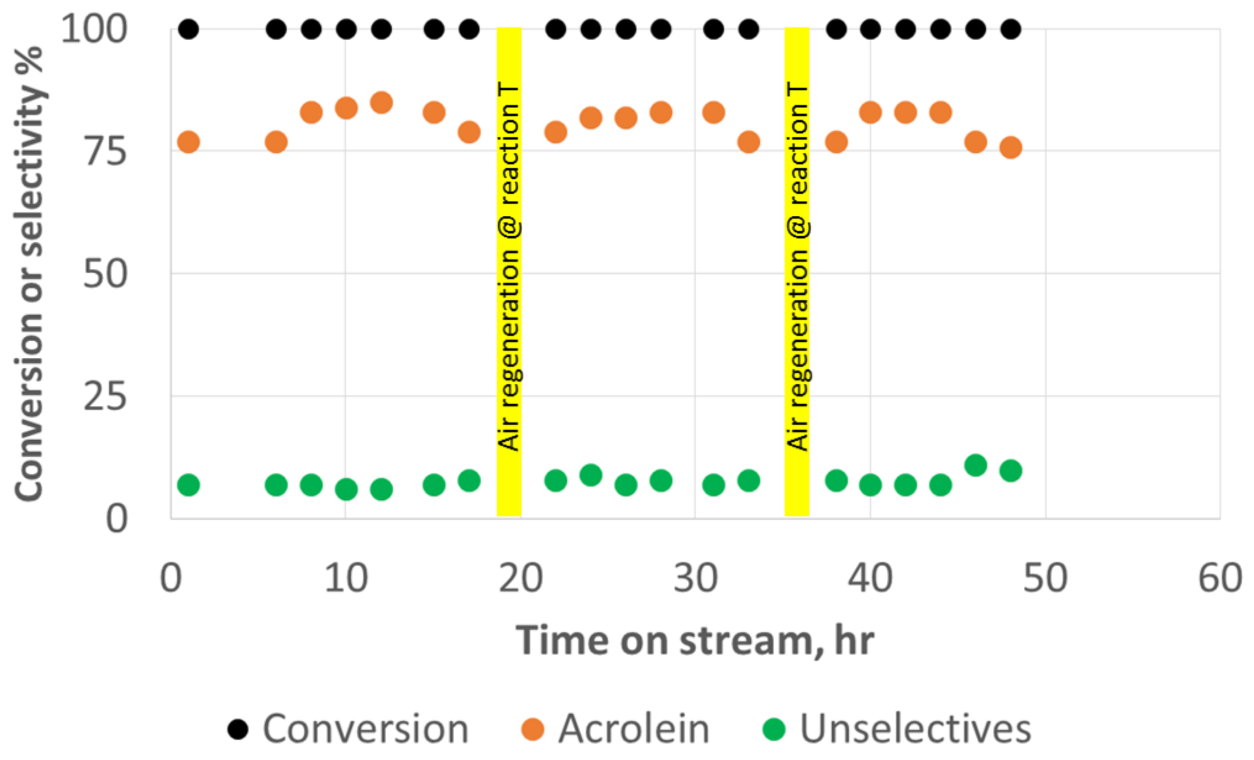
Task 8: Continuous operation
(R1: Hydrocracking)



Collected product from continuous hydrocracking (R1) pilot operation

Task 8: Continuous operation
(R2: Dehydration)

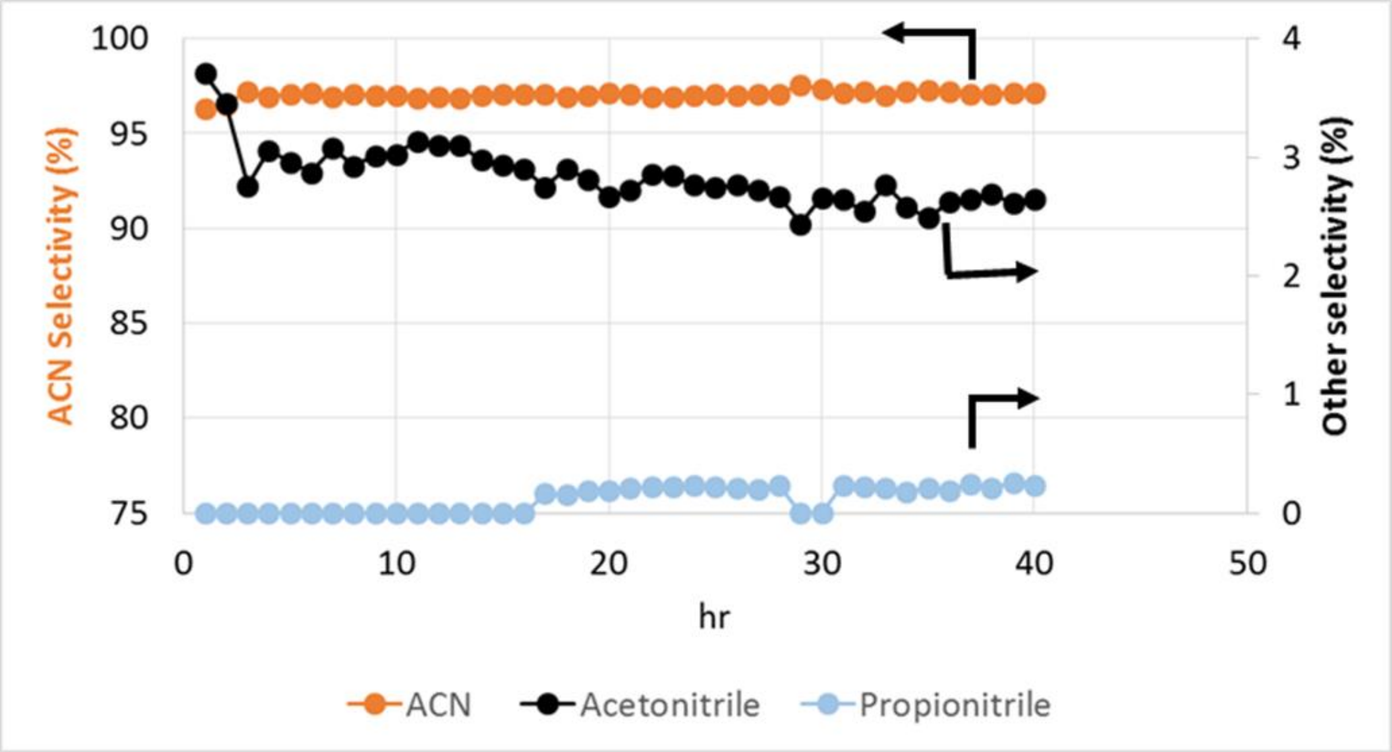
- More soluble salt for major catalyst component identified which drastically reduces required solvent volume during catalyst scale up



- Catalyst life improved by systematic regeneration at reaction temperature
- Bench scale continuous 500hr run pending

Task 8: Continuous operation
(R3: Ammoxidation)

- High performance catalyst and process parameters identified to selectively produce ACN with no detectable HCN or CO_2 formation



- Bench scale continuous 500hr run pending

Task 9: Periodic ACN validation

Item	Success Criterion*	SR specs.
Acetone, ppm by weight	75 maximum	Not detected
Acetonitrile, ppm by weight	300 maximum	3000
Appearance	Clear liquid, free from suspended matter	Clear liquid, free from suspended matter
Color (APHA)	5 maximum	
Acrolein, ppm by weight	1 maximum	Not detected
Oxazole, ppm by weight	10 maximum	Not detected
Hydrocyanic acid, ppm by weight	5 maximum	Not detected
Inhibitor, MEHQ, ppm by weight	35 minimum/45 maximum	35-45
Peroxides, as H2O2, ppm by weight	0.2 maximum	Not detected
Water, % by weight	0.2 minimum/ 0.5 maximum	0.3

*Non-proprietary publicly available information shown here for comparison

Task 9: Periodic ACN validation

Summary: Impact of impurities

Water	Propionitrile	Acetonitrile	Acrolein
High Concern	Low Concern	Insignificant	Insignificant
Conversion	Conversion	Conversion	Conversion
Polymer Concentration	Polymer Concentration	Polymer Concentration	Polymer Concentration
Molecular Weight	Molecular Weight	Molecular Weight	Molecular Weight
Polydispersity	Polydispersity	Polydispersity	Polydispersity
Rheology	Rheology	Rheology	Rheology

- Detrimental: Causes significant deviation from baseline process*
- High Concern: Causes some deviation from some baseline properties*
- Low Concern: May cause minor deviation from baseline properties*
- Insignificant: No deviation from baseline properties can be detected*

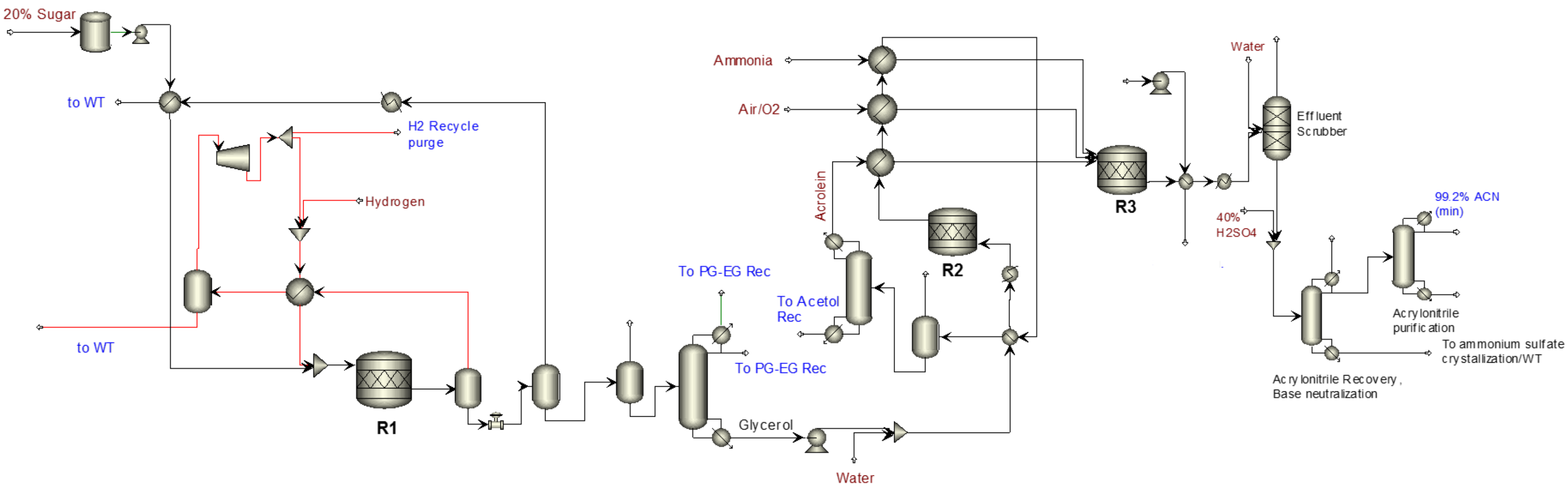
*Above undisclosed concentrations

SR

Task 10: Characterization

- All catalysts have been extensively characterized during phase I catalyst development study using-
  - BET, NH_3 TPD, Raman, IR, EDX and XRD
- For phase II, samples from scaled up catalysts are characterized for consistency and reproducibility of key characteristics of catalysts
- Used catalysts following 500 hr continuous run are characterized

Task 11: TEA/LCA



Sugar to BioACN process simulation (Aspen Plus)

Task 11: TEA/LCA

Process mass balance:

(mass rates in metric tons/year)

Rxn step	Feed	Recovered Product[1]	Other recoverable product[2]
R1	27,000 (sugar), 1090 (H_2)	7,000 (PG)	2,000 (PG), 1,340 (EG)
R2	-	-	1760 (Acetol)
R3	1996 (O_2) 2300 (NH_3)	5000 (ACN)	-
Total mass	**32,386**	**12,000**	**5100**
% mass recovery		37%	16%
C efficiency %		62%	21%

[1]Considered in TEA, [2]Not considered in TEA.

Mass recovery 53%, C efficiency 83%

1 kg Sugar → 0.63 kg total recoverable product

Task 11: TEA/LCA

TEA assumptions:

- ACN production capacity 5000 MT/year
- Only **propylene glycol (PG)** co-production credit considered
- Catalyst life 3 years

Total capital investment $ 15 – 19 million (verified by independent contractor)

Annualized cost for 5000 MT/year ACN production	$/year
Utility (Steam, CW, Electricity)	1,346,928
Raw materials (sugar, hydrogen, ammonia, sulfuric acid)	12,188,346
Annualized catalyst	557,272
Operation labor (16-member staff at average $80,000/year)	1,280,000
Maintenance (5% of Fixed capital investment)	875,000
Total recurring cost without depreciation	**16,247,547**
Annual depreciation on capital cost (10-year straight)	**1,750,000**
Credit from co-product (PG) sale	- 10,028,200
Annualized cost of production w/co-product credit	**7,969,347**

Production cost of ACN = $0.72 / lb

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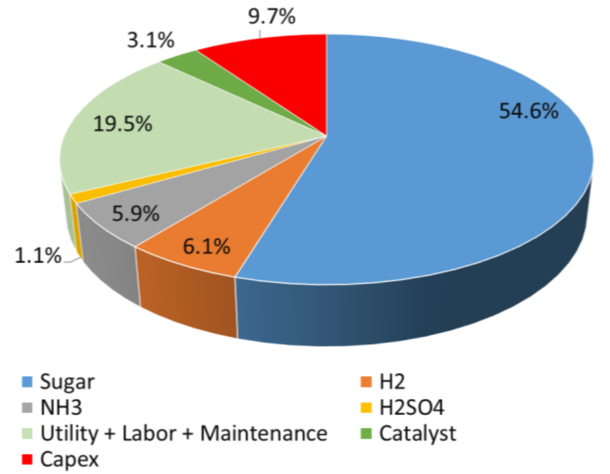
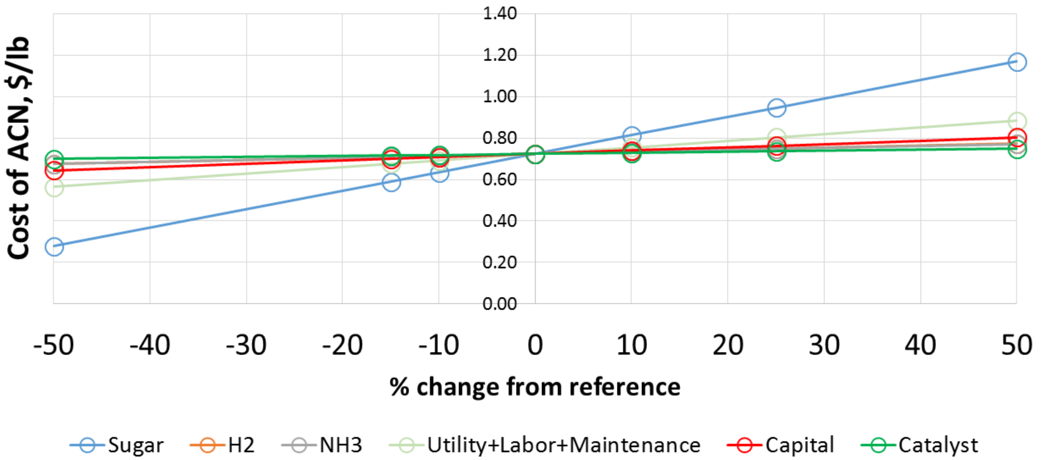
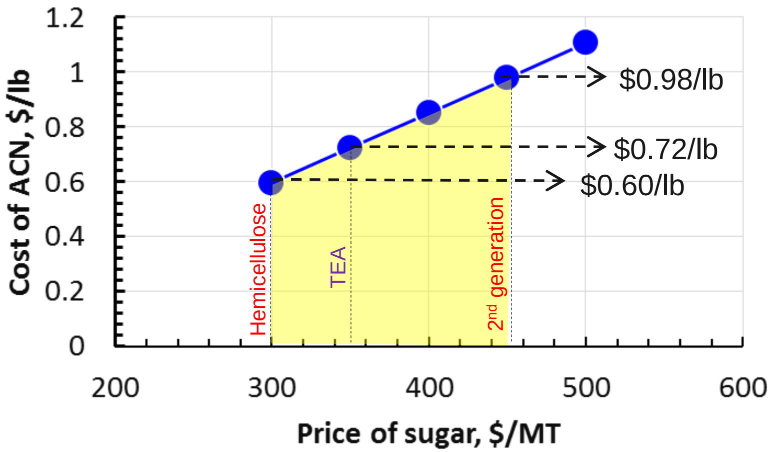
Task 11: TEA/LCA



Cost distribution pie chart



Sensitivity



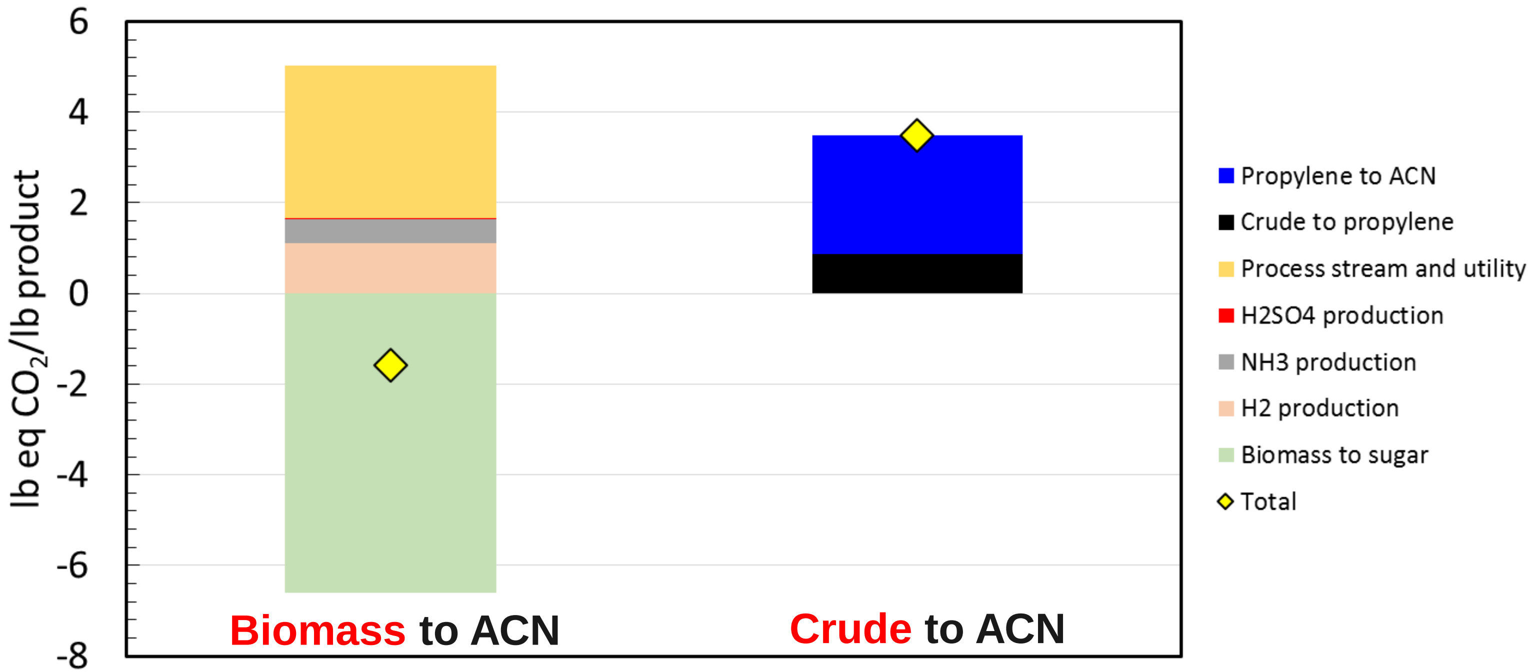
Sensitivity with respect to sugar

Sugar price is the key economic driver

Task 11: TEA/LCA

LCA Assumptions:

- Biomass source: Corn Stover with 20% bulk moisture content [1]
- Biomass to sugar yield: 1 kg sugar (C_5+C_6) produced from 2.35 kg biomass [1]



Biomass to ACN results in significantly less CO_2 footprint than **Crude to ACN** (-1.57 versus 3.5 lb eq. CO_2/ lb of product)

[1]Humbird et al. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover. NREL, 2011; [2]Mehmeti, Andi, Athanasios Angelis-Dimakis, George Arampatzis, Stephen J. McPhail, and Sergio Ulgiati. "Life Cycle Assessment and Water Footprint of Hydrogen Production Methods: From Conventional to Emerging Technologies." *Environments* 5, no. 2 (2018): 24.; [3] https://ammoniaindustry.com/ammonia-production-causes-1-percent-of-total-global-ghg-emissions/; [4] Althaus, H. -J, M. Chudatcoff, R. Hischier, N. Jungbluth, M. Osess, and A. Primas. 2007. "Life Cycle Inventories of Chemicals." *Ecoinvent Report no. 8, V2.0.*. [5]Imported from Aspen plus simulation

4 – Relevance

- Supports BETO's strategic goal of thermochemical conversion R&D: *"Develop commercially viable technologies for converting biomass into energy dense, fungible, finished liquid fuels, such as renewable gasoline, jet, and diesel, as well as biochemicals and biopower."*
- Contributes to overcoming the technical challenges and barriers in this area by:
  - Design and discovery of new low-cost catalysts for biomass conversion.
  - Process intensification via single step sugar conversion.
- **Relevance to industry and market place:**
  - **Alternative low cost feedstock:** Price and supply of propylene volatile. Biomass is abundant and the price of derived sugar is more stable.
  - **H_2 requirement and C efficiency:** Less H_2 use but high C efficiency (80%).
  - **Heat management:** Lower heat capacity of acrolein than glycerol. Requires less energy to heat acrolein than glycerol (advantage over direct ammoxidation of glycerol).
  - **Process integration:** Integrable to commercial ACN production processes.
  - **Low cost production:** Production of ACN at <$1/lb paves way for reducing cost of carbon fiber production
  - **Co-production of PG/acetol:** Alternative, low cost pathway for the production of high value chemicals and their use as co-products.

4 – Relevance

➤ Technology Transfer - Initiatives

Acrylonitrile User or Manufacturers	Catalyst Manufacturers	Investor Groups	Sugar Suppliers
Three companies interested – Europe, Japan, USA and partner Cytec-Solvay	Working with a major catalyst manufacturer to scale-up and toll-produce kilogram quantities of catalyst for Phase II	Working with a group of investor with experience in development of early stage chemicals technology – for joint development and to accelerate phase II research with further interest in funding first commercial plant	Working with commercial vendor – Arbiom – for sugar supplies for Phase I and Phase II

5 – Future Work

- Phase II – Validating prototype system
  - Continuous 500hr run using dehydration (R2) and ammoxidation (R3) skid
  - Produce acrylonitrile using skid in necessary amount for polymerization
  - Perform 1L reactor runs with BioACN
  - Complete analysis of Biomass AN polymers prepared by solution polymerization (including ICP analysis for inorganic impurities)
  - Anticipate 4 gallon reactor runs and prepare for spin run
  - Complete TEA/LCA with phase II data

Summary

- **Overview:** Novel thermocatalytic and economically viable process for the conversion of biomass derived non-food sugars to acrylonitrile.
- **Approach:** Novel, inexpensive, stable catalyst development, mild operating conditions, separation of co-products and undesirables, scalability, TEA/LCA and sensitivity analysis.
- **Technical progress:** Process flexible to sugar types. High performance catalysts meet target for sugar to oxygenates, glycerol to acrolein and acrolein to ACN conversion. Requires less H_2 and NH_3 as raw materials. Production of high value PG and acetol as co-products. Economics favorable (<$1/lb) at wide range of sugar price.
- **Challenges:** PG conversion to acrolein, meeting product specifications at different sugar impurity levels.
- **Relevance:** Supports BETO’s conversion R&D strategic goal.
- **Future work:** Complete bench scale run and TEA/LCA. BioACN polymerization and product validation.

SR

Publications, Patents, Presentations, Awards, and Commercialization

Publications/Presentations:

- Progress of this project has been presented in following conferences:
  - Poster at Bio Pacific Rim Summit, 2015 (San Diego, CA)
  - Project fact sheet at Bio Energy Summit, 2015 (Washington, DC)
  - Oral presentation at Bio World Congress (Montreal, Canada)
  - DOE site visit, 2015 (Durham, NC)
  - Invited talk at Department of Materials Science at University of Alabama, Birmingham, 2015
  - Oral/poster presentation at AIChE 2015, 2016, 2017, 2018
  - Oral presentation as Panel speaker at World Congress on Industrial Biotechnology Breakout Session: Process Improvement for Biobased Materials
  - Oral presentation and winner of Shark Tank Pitch contest at World BioMarkets, Amsterdam 2016
  - Oral presentation at TCS, 2016 (Chapel Hill, NC)

Patents:

- *Compositions and methods related to the production of acrylonitrile. US Patent 9708249*
- *Compositions and methods related to the production of acrylonitrile. United States Patent Application* 15/950788

Acknowledgements

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Partners

Sugar Suppliers

BETO Project officer: Mark Shmorhun
Project Coordinator: Robert Natelson

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Jeremy Moskowitz (Technical Lead)
Billy Harmon

NJIT

Zafar Iqbal (Lead)
El Mostafa Benchafia

ARBIOM

Lisette Tenlep

ADDITIONAL SLIDES

Task 7: Decoupled Bench Scale Unit design and operation

(Process simulation with reaction data to know the fate of impurities)

Feed to R2

Major Components	
Component	**Composition**
Glycerol (99.9% pure)	20%
Water	80%
Impurities	
Impurity	**ppm**
GVL	691
Vanilin	3
Cresol	3
Others	303

R2 Reactions

Reaction 2
Major Reactions: $C_3H_8O_3$ (Glycerol) = C_3H_4O (Acrolein) + $2H_2O$ $C_3H_8O_3$ (Glycerol) = $C_3H_6O_2$ (Hydroxyacetone) + H_2O

Product of R2

Major Components	Composition
Glycerol	0%
Acrolein	≥80% (db)
Hydroxyacetone + Unselective	≤20% (db)
% of feed impurity in the product	
Impurity	**ppm**
GVL	691
Vanilin	3
Cresol	3

Separation

Desired Product	
Component	**Composition**
Acrolein	88.4%
Water	11.3%
Hydroxyacetone	0.0045 %

Byproducts (db)	
Component	**Composition**
Hydroxyacetone+ Unselective	99.93%
GVL	691 ppm
Vanilin	3 ppm
Cresol	3 ppm

The carried over feedstock impurities are separated here and do not carry over in the next step

SR

Task 7: Decoupled Bench Scale Unit design and operation

(Process simulation with reaction data to know the fate of impurities)

Feed to R3

Major Components	
Component	Composition
Acrolein	≥88% (db)
Water	Balance
Hydroxyacetone	

R3 Reactions

Reaction 3
Major Reactions: $C_3H_4O + 0.5\ O_2 + NH_3 = C_3H_3N$ (ACN) + 2 H_2O $2C_3H_4O + O_2 + 3NH_3 = 3C_2H_3N$ (Acetonitrile) + 4 H_2O

Product of R3

Major Components	Composition
ACN	92%
AN	8%

Separation

Desired Product	
Component	Composition
Acrylonitrile	≥99.2%
Acetonitrile	Balance
Propionitrile	
Water	
Metals	ND

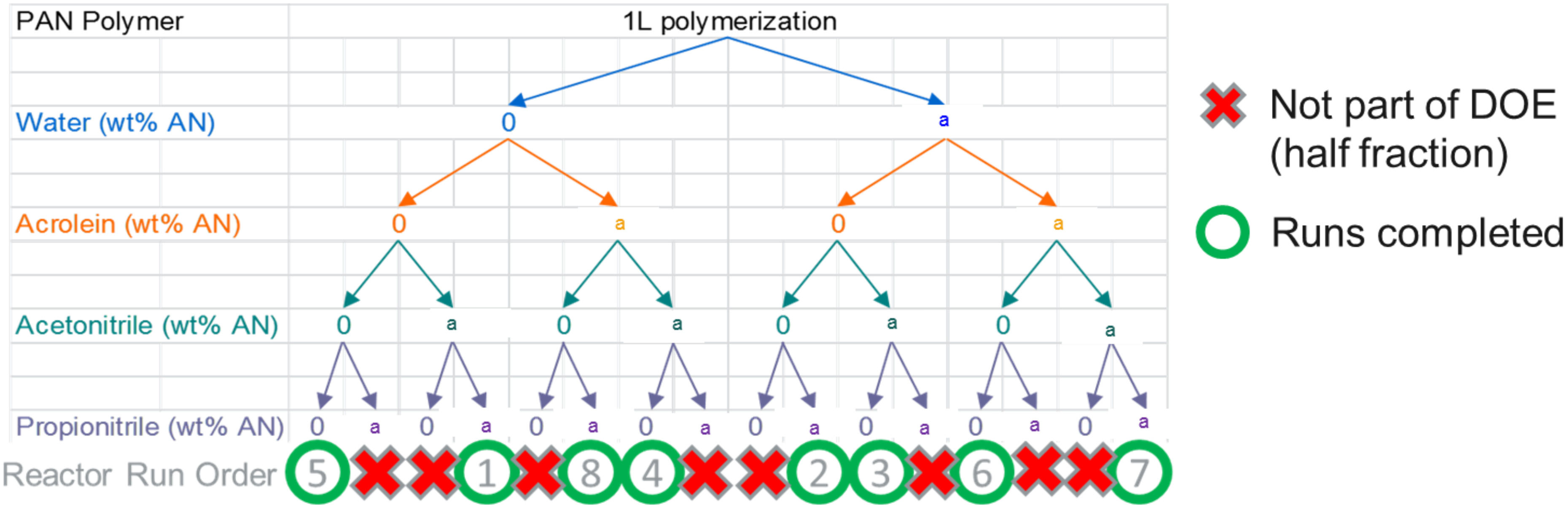
Byproducts	
Component	Composition
Acetonitrile + Propionitrile + others	~100%

Minimum 99.2% purity of final product with balance acetonitrile, propionitrile and water

Task 9: Periodic ACN validation

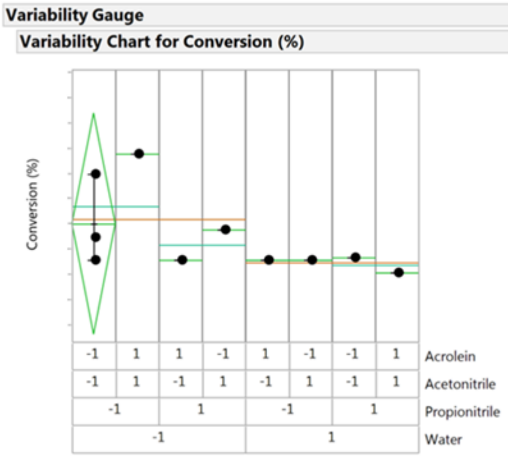
Half fraction design of experiments (DOE, 8 runs):

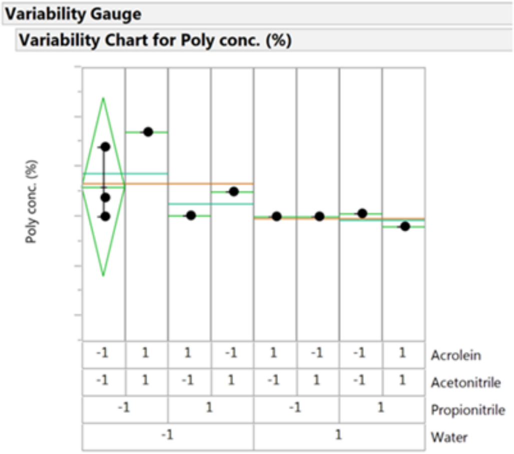
- One 1L polymerization reactor installed
- Polymerization study with process derived (unselectives) impurities to determine-
  - Physical and chemical properties of polymers
  - Maximum allowable impurity levels for drop-in quality

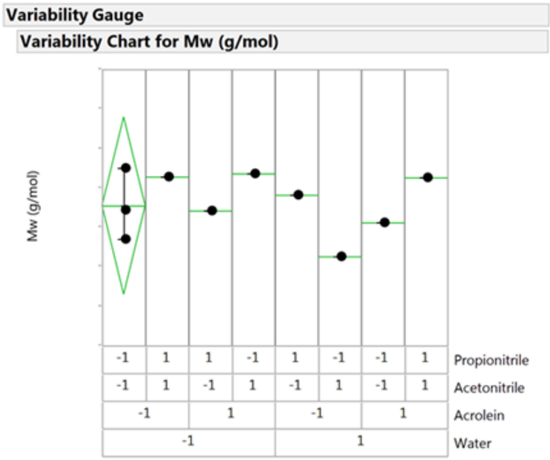


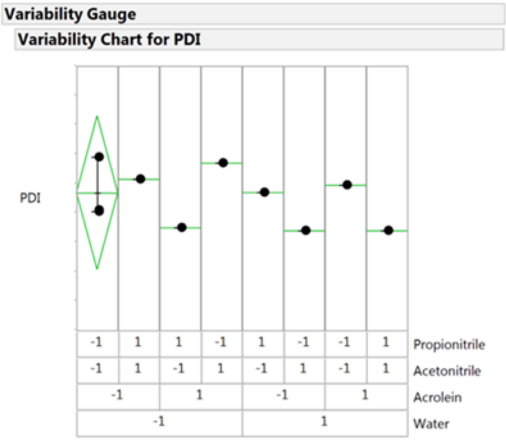
Task 9: Periodic ACN validation

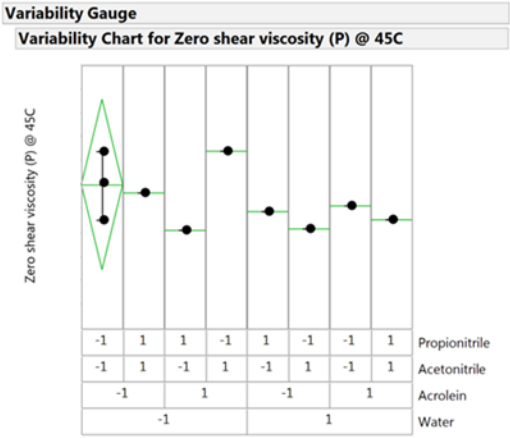
Variability metrics versus impurities











Most significant trends are identified in conversion and polymer concentration

Task 11: TEA/LCA

Raw materials	**Price**
Sugar, $/lb	0.16
Hydrogen, $/lb	0.45
Ammonia, $/lb	0.21
Sulfuric acid, $/lb	0.07

Products	**Price**
Acrylonitrile (ACN), $/lb	-
Propylene glycol (PG), $/lb	0.65
Hydroxyacetone (acetol), $/lb	0.0
Ethylene glycol (EG), $/lb	0.0
Light alcohols, $/lb	0.0

Utility	**Cost**
Cooling water ($/MJ)	0.000212
Steam ($/MJ)	0.00339
Electricity ($/kWh)	0.0692
Natural gas ($/MJ)	0.005

Catalyst	**Cost**
Reactor 1 catalyst ($/kg)	160
Reactor 2 catalyst ($/kg)	80
Reactor 3 catalyst ($/kg)	80