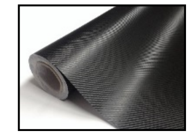
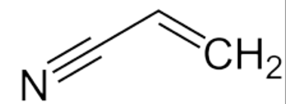
U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

WBS 2.3.1.200 - Biomass conversion to Acrylonitrile monomer-precursor for the production of carbon fibers





SOUTHERN RESEARCH

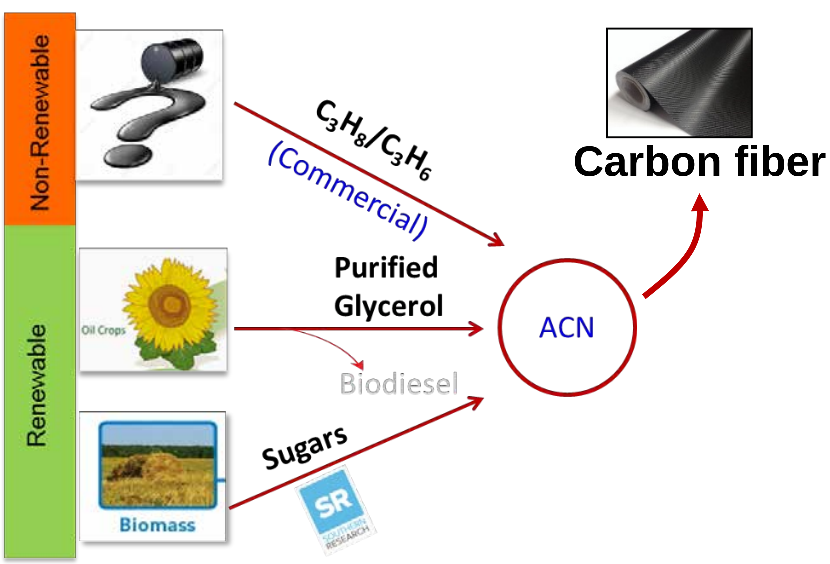
Solving the world's hardest problems.

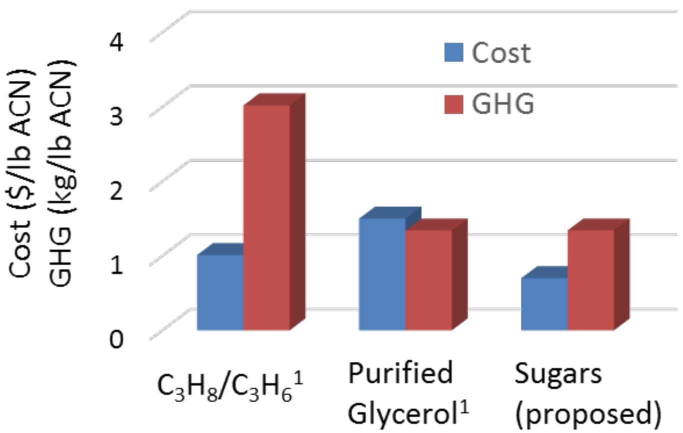
March 8, 2017
Biochemical conversion

PI: **Amit Goyal**
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.
- Laboratory (phase I, ongoing) and bench (phase II, future) scale demonstration.





ACN production from different routes

[1]Guerrero-Pérez, et al *Catalysis Today* 239 (2015): 25-30.

- 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

- Project start date: Feb 1st 2015
- Project end date: March 30th 2017
- Percent complete: 95%

Partners

- Southern Research (70%), Cytec-Solvay (25%), NJIT (5%)
- Arbiom, Renmatix and NCSU – Sugar suppliers

Barriers

- Ct-A. Feedstock Variability
- Ct-H. Efficient Catalytic Upgrading of sugars/aromatics, Gaseous and Bio-Oil Intermediates to Fuels and Chemicals
- Ct-I. Product Finishing Acceptability and Performance.

Budget

	Total Costs FY 12-14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY17 – Project End Date)
DOE Funded		$333,333	$862,130	$593,108
Project total cost share		$94,593	$173,806	$233,731
Southern Research		$93,238	$149,849	$186,523
Cytec-Solvay		$0	$23,512	$34,806
NJIT		$1,355	$445	$12,402

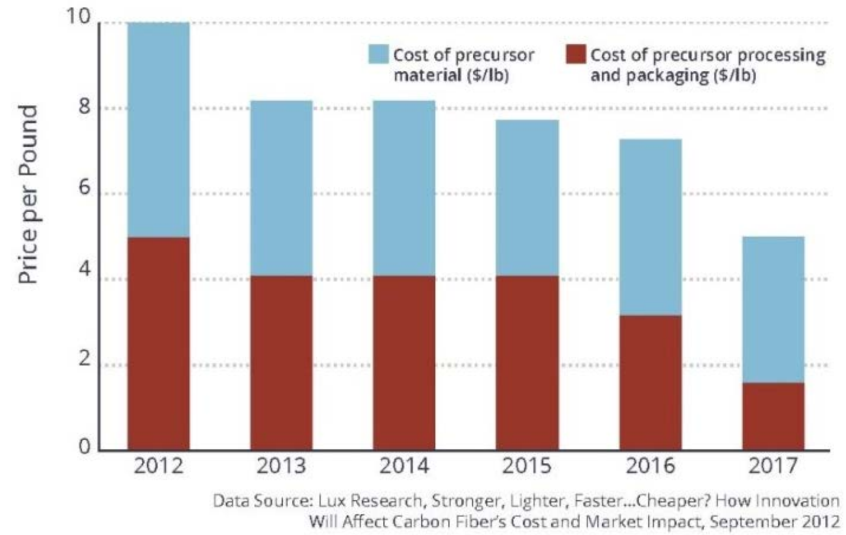
1 - Project Overview

Context

- Carbon fiber – *strength of steel, weight of plastic.*

- Widespread use of carbon fiber restricted due to high cost of production.

- Production of carbon fiber precursor chemicals e.g., ACN is a potentially viable area to reduce the cost of making carbon fibers.



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

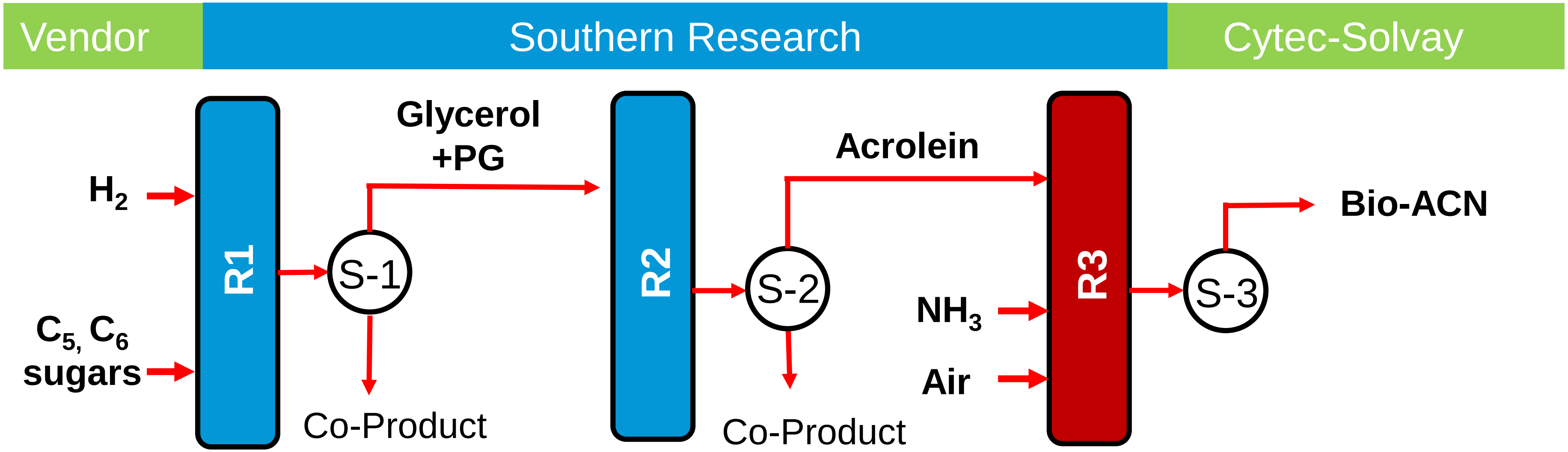
- DOE estimates carbon fiber production cost needs to be at \$5/lb equivalent to \$1/lb cost of the precursor.

- ACN production from non-petroleum feedstock is limited to purified glycerol available at high cost[1].

- Petroleum based processes are affected by volatile propylene price and shortage most recently due to preference for low cost ethane.

[1]Guerrero-Pérez, et al *Catalysis Today* 239 (2015): 25-30.

1 - Project Overview (contd)



R1 = Hydrocracking, **R2** = Dehydration, **R3**=Ammoxidation
S-1 to S-3 = Separation trains, **PG =** Propylene glycol

Schematic of the proposed sugar to ACN process

Project goals/objective:

- Multistep catalytic (R1-R3) ACN production at **<$1/lb**.
- Development of 2 novel (R1 & R2) and 1 known (R3) catalysts to meet target.
- Process intensification via novel one step sugar to Glycerol and PG conversion.
- Use of known technologies to separate undesirables, main and co-products.

2 – Approach (Management)

Activity (Phase I-Ends March 30,2017)	Task owner	10 20 (Months)	Milestone
Task 1: Micro Reactor set up	SR		Setup 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		At least 2 novel candidates for each of R1 and R2. R3 lit. catalyst. **R1:** S(glycerol+PG) >65%, >50g/l/hr **R2:** S(acrolein) > 70%, >375g/l/hr, **R3:** S(ACN) > 70%, >75 g/l/hr Catalyst life >40h for each catalyst
Task 3: Catalyst characterization	NJIT,SR		Completed (fresh and used catalyst)
Task 4: Bio-ACN validation	Cytec-Solvay		Model impure ACN validated. 3 product samples tested.
Task 5: TEA/LCA	SR		Preliminary TEA completed with lab scale data. Cost <$1/lb
Task 6: Project Management and Reporting	SR		Deliverables to DOE-EERE

-----> Data transfer ——> Material transfer

Activity (Phase II- Future)	Task owner	20 30 40 (Months)	Milestone
Task 7: Bench scale unit Task 7.1 Optimal safety and storage conditions Task 7.2 Separation methods design Task 7.3 Commissioning	SR		Complete design specs and transfer to EPC. Commission units and complete preliminary readiness test
Task 8: Continuous operation	SR		500hrs of operation. 500kgs of ACN.
Task 9: Periodic ACN validation	NJIT,SR		ACN validation every 40hr.
Task 10: Characterization	Cytec-Solvay		To determine regeneration, if required.
Task 11: TEA/LCA	SR		<$1/lb cost, <35% GHG emission
Task 12: Project Management and Reporting	SR		Deliverables to DOE-EERE

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

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CYTEC SOLVAY GROUP
Dr. Longgui Tang
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2 – Approach (Technical)

Reactor setup (Task 1)

- gm scale
- Meaningful scale-up
- Analytical procedure

R1: Hydrocracking (Task 2,3)

- Catalyst design/synthesis
- Characterization **(NJIT)**
- Reaction evaluation
  - Model C_5/C_6 sugar
  - Sugar with impurities
- Catalyst screening
  - Performance metrics
- Parametric study
  - T, P, impurity
- TEA

R2: Dehydration (Task 2,3)

- Catalyst design/synthesis
- Characterization **(NJIT)**
- Reaction evaluation
  - Glycerol, PG
- Catalyst screening
  - Performance metrics
- Parametric study
  - O_2
  - TEA

R3: Ammoxidation (Task 2,3)

- Literature catalyst
- Characterization **(NJIT)**
- Reaction evaluation
  - Acrolein (AC)
- Catalyst screening
  - Performance metrics
- Parametric study
  - O_2, NH_3, AC conc. %
- 50g ACN
- TEA

ACN validation (Task 4)

- ACN baseline with impurity **(Cytec)**
- Product ACN **(Cytec)**

Phase II: Bench scale (Future)

- 500 kg ACN
- Continuous operation
- Final TEA/LCA

2 – Approach (Technical)

Progress/target metrics:

Reaction	Productivity (g/l/hr)	Desired product	Yield (%)	Catalyst life (hr)
R1	>50	Glycerol + PG	>65	>40
R2	>375	Acrolein	>70	>40
R3	>75	ACN	>70	>40

Challenges:

- Final product specification at different sugar impurity levels.
- Catalyst deactivation.
- Extent of separation required prior to each reaction step.

Critical success factors (Go/No Go decision points):

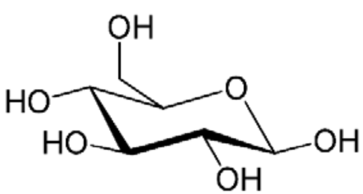
- Cost of production <$1/lb.
- 1kg of recoverable product per 3.34 kg non-food sugar (~30% mass recovery).
- Validity of purified Bio-ACN as a carbon fiber ready monomer.

3- Technical accomplishments/progress/results

- **Task 2: Catalyst development & testing**
  - **Catalyst development:** At least two novel catalysts for each of R1 and R2 developed that fully meet performance target for sugar to polyols and Glycerol to acrolein.
  - **Catalyst testing:**
    - – Single step with mild operating conditions (T,P) used. (R1)
    - – Model and commercial (with impurities) sugar feeds from two different vendors tested. (R1)
    - – Product specification tested with varying degrees of feed impurities. (R1)
    - – Glycerol and PG to acrolein conversion tested on same catalysts. (R2)
    - – Alternative pathway proposed using PG as co-product. (R2)
    - – Catalyst lifetime verified and regeneration method established with long term testing. (R1-R3)
- **Task 4: ACN validation**
  - Optimized performance and product validation completed.
- **Task 5: TEA/ LCA**
  - Preliminary cost analysis and separation simulation conducted.
  - Cost distribution and sensitivity analysis with respect to raw material price reveals extent of risk

3 – Technical Accomplishments/ Progress/Results

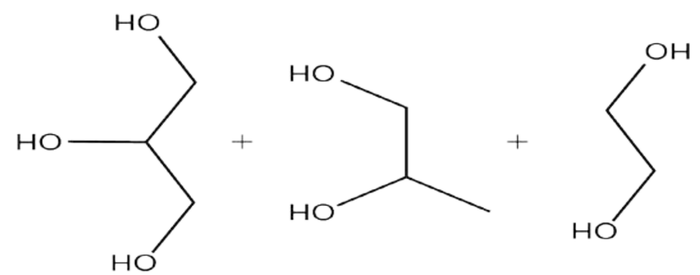
R1:Hydrocracking



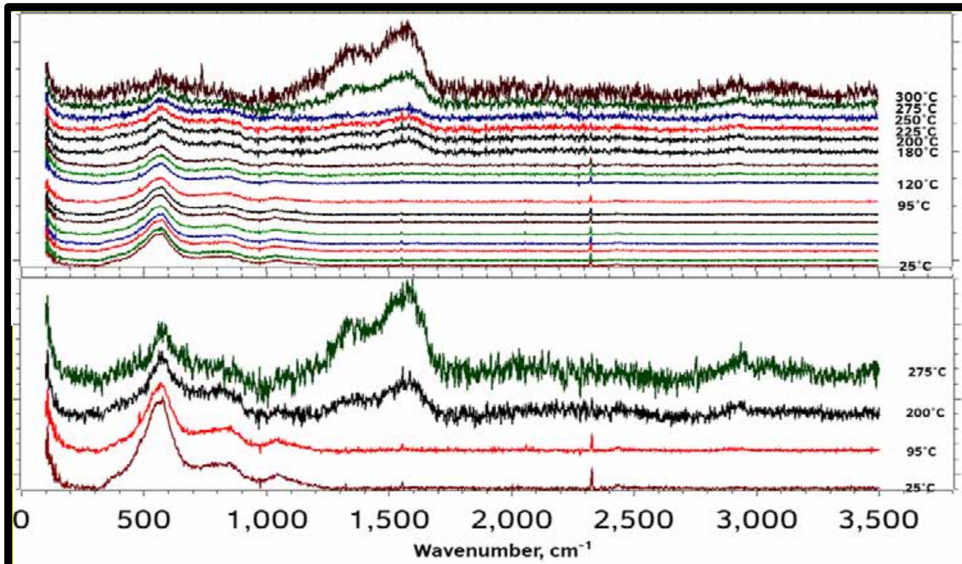
sugar

H_2, -xH_2O

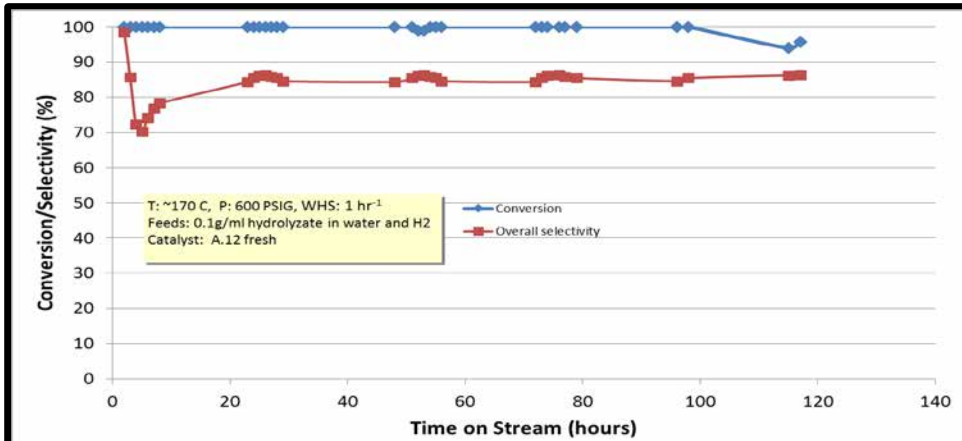
P = 600-750 PSIG
170-240°C
(novel transition mixed metal catalyst)



Glycerol **Propylene Glycol (PG)** **Ethylene Glycol (EG)**



Catalyst stable at high temperature in aqueous phase



➢ **Catalyst life:** > 100hr

Sugar type	**Conv. (%)**	**Yield (%)**
Model feed		
Glucose (G)	100	81
Xylose (X)	100	95
G 25%-X 75%	100	96
G 50%-X 50%	100	83
G 75%-X 25%	100	81
Impure feed		
Hydrolyzate	100	76
Bagasse	100	76
Pure Hydrolyzate	100	79

- **Products:** Glycerol+PG (~1:1) and EG(<5%).
- High selectivity at different feed types and C_5/C_6 ratios.

Low H_2 requirement (~0.04-0.05kg H_2/kg sugar); Productivity – 50 g/l/hr

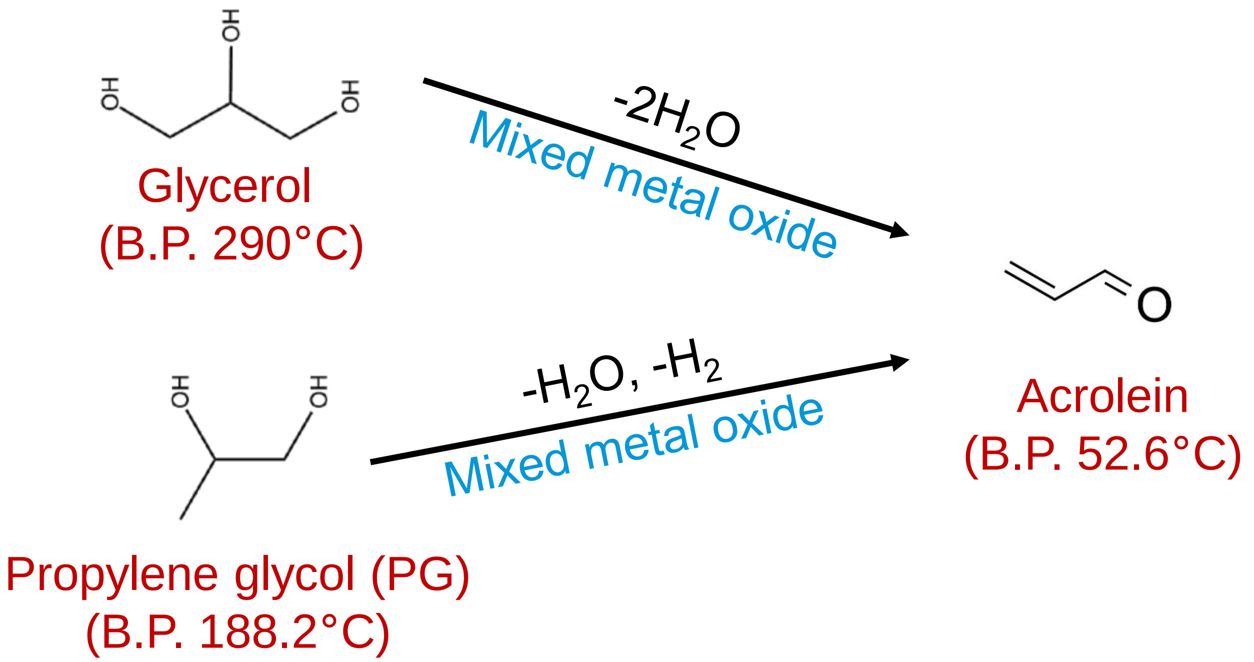
Effect of sugar impurities:

- Catalytic runs using sugars from commercial vendors.
- Different levels of metallic as well as organic impurities.
- High levels of impurity negatively affected catalyst activity and more importantly, final product specification (Purification necessary).

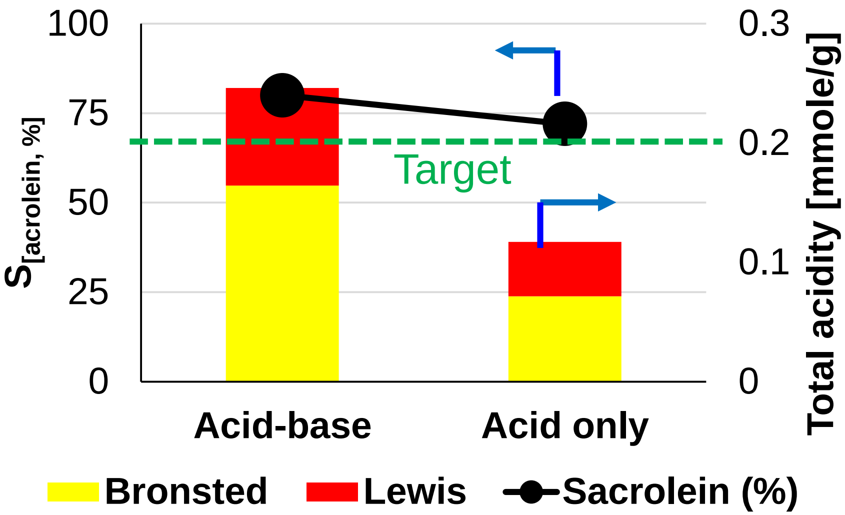
Characteristics				
Hydrolysis method	Method 1	Method 1	Method 2	Method 2
Sugar type	Oligomer	Oligomer	Monomer	Monomer
Metal/ion impurities[mg/kg]	4532	84	2270	129
Organic impurities [g/kg]	23	28	10	82
pH	3.3	2.9	higher	3.3
Hydrocracking Results: Hydrolyzate conversion to polyols				
Hydrolyzate Conv.[%]	47	75	100	100
Overall selectivity [%]	79	85	70	81
Performance stability	44 hrs	> 48 hrs	> 32 hrs	>120 hrs
Meets product specs?	No	Yes	No	Yes

3 – Technical Accomplishments/ Progress/Results

R2:Dehydration

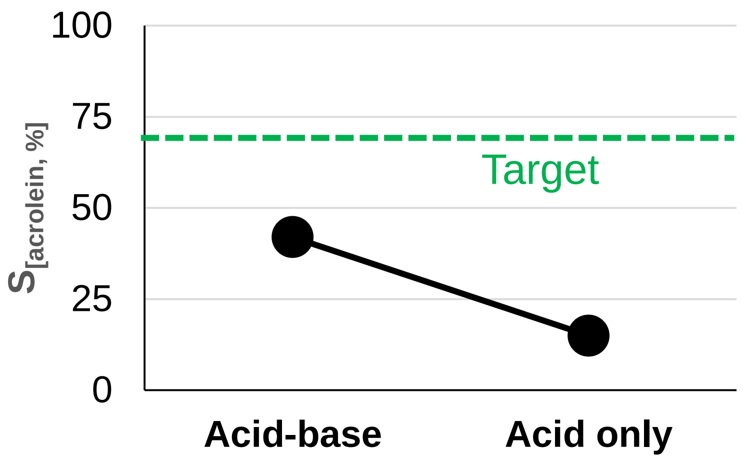


Feed: Glycerol



- Conversion = 100%.
- Catalyst life up to 51 hrs.
- Selectivity improves with B/L ratio.
- Productivity > 350 g/l/hr.
- Performance meets target.
- Acetol (hydroxyacetone) main by-product.

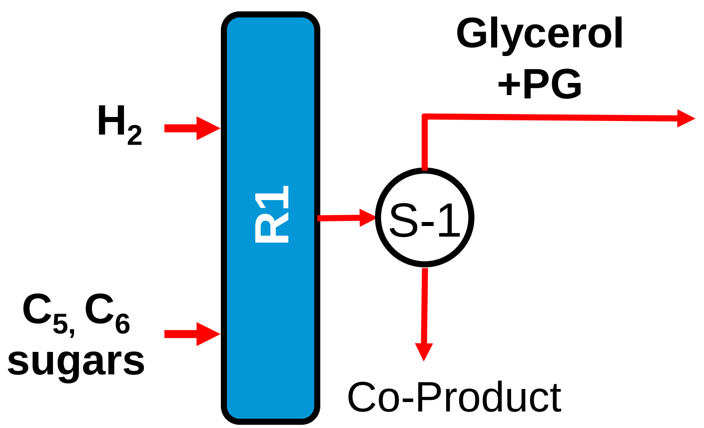
Feed: Propylene Glycol (PG)



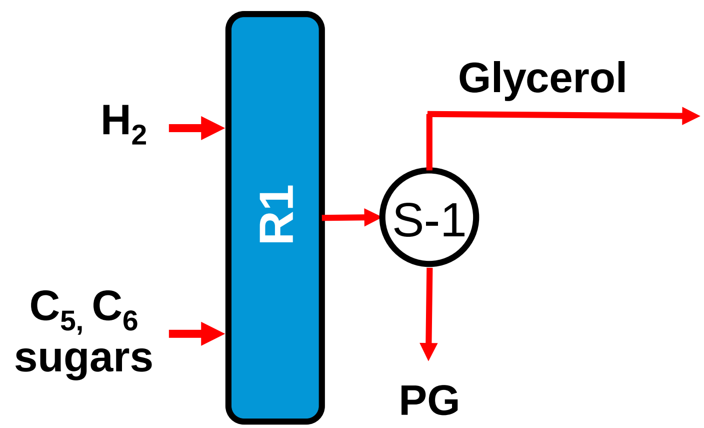
- Conversion = 100%, decreases with time (short catalyst life)
- Performance does not meet target.
- Propanal main by-product.

Moving forward with PG: Alternative Approach

- Poor acrolein yield from PG (42% max).
- Higher selectivity (>50%) to propionaldehyde – complex separation from acrolein due to similar boiling points (49°C vs. 52.6°C for acrolein).
- An alternative approach could be to separate PG from Glycerol prior to dehydration reaction and use it (PG) as a high value co-product.



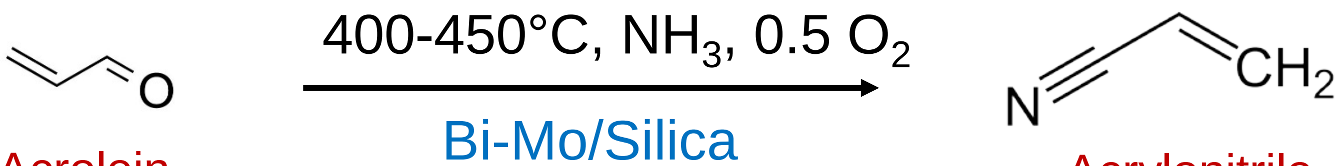
Originally proposed



Alternative approach

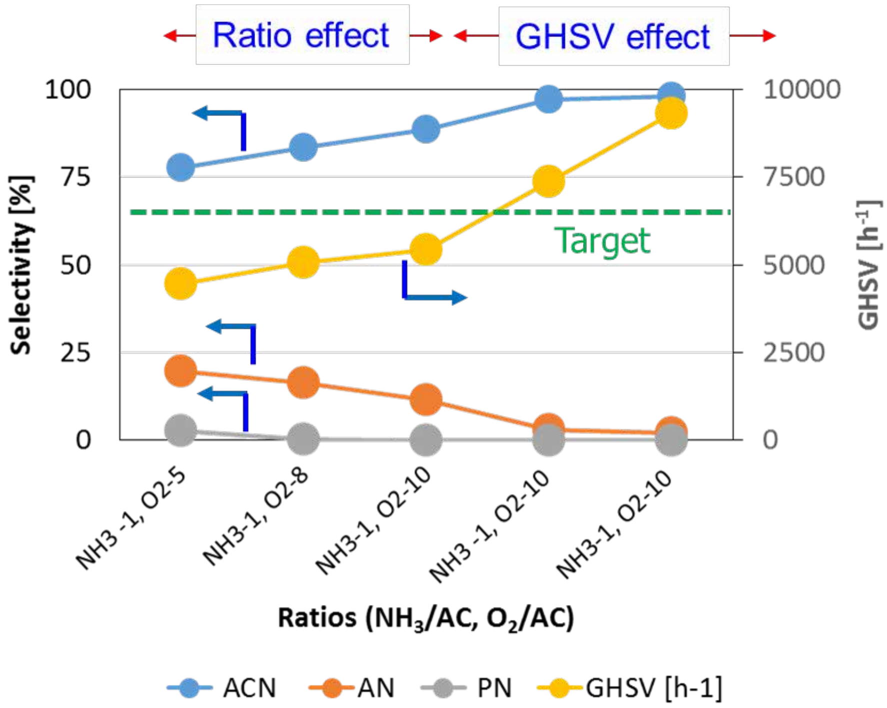
3 – Technical Accomplishments/ Progress/Results

R3:Ammoxidation

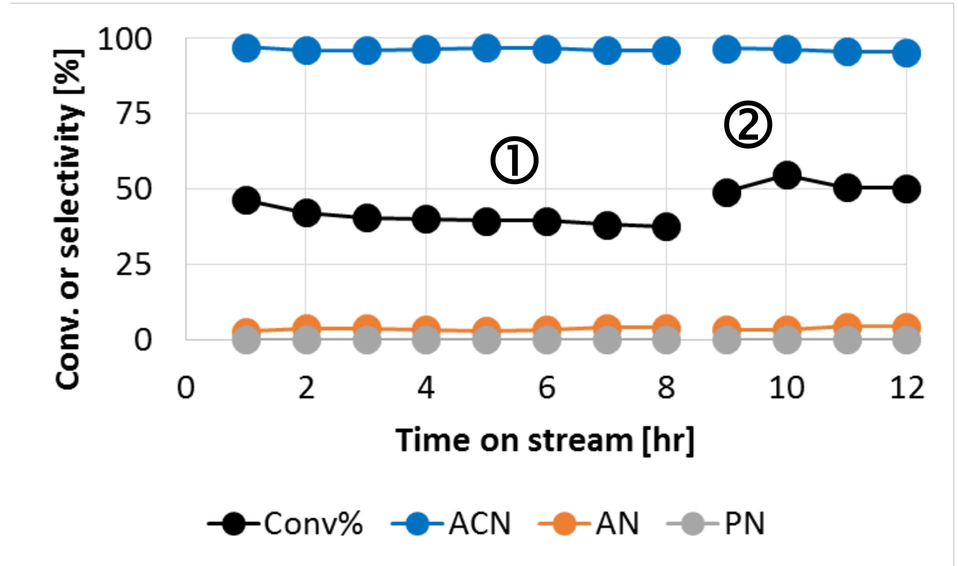


Acrolein

Acrylonitrile



Catalyst optimization
(Parametric study)



Long term run at optimized conditions:
NH_3/AC = 1.0, O_2/AC=10 for
① GHSV=9675h^{-1} and ② GHSV = 7661h^{-1}

- BiMo/silica catalyst. Acrolein (AC) evaporated from 90% pure feed.
- High selectivity (>90%) to Acrylonitrile (ACN).
- Other by-products are acetonitrile (AN) and propionitrile (PN).

ACN validation

Bio-mass ACN sample	Sample-1		Sample-2		Sample-3	
Appearance	Clear		Slightly pink		Clear	
Product composition (wt%)						
Basis →	Wet	Dry	Wet	Dry	Wet	Dry
Actual ACN /wt%	1.69	15.9	4.31	85.28	5.11	98.3
Water/wt%	~89	-	~95	-	~95	
Impurities						
Acetone /wt%	0.01	0.01	/	0	0	0
Acrolein /wt%	7.84	73.75	/	0	0	0
Acetonitrile /wt%	0.13	1.25	0.74	14.7	0.10	0.02
Propionitrile/ wt%	0.96	9.02	/	0	0	0

- Very low impurity level. Excess water due to use of acetic acid solution to neutralize excess NH_3.

3 – Technical Accomplishments/ Progress/Results

TEA/LCA

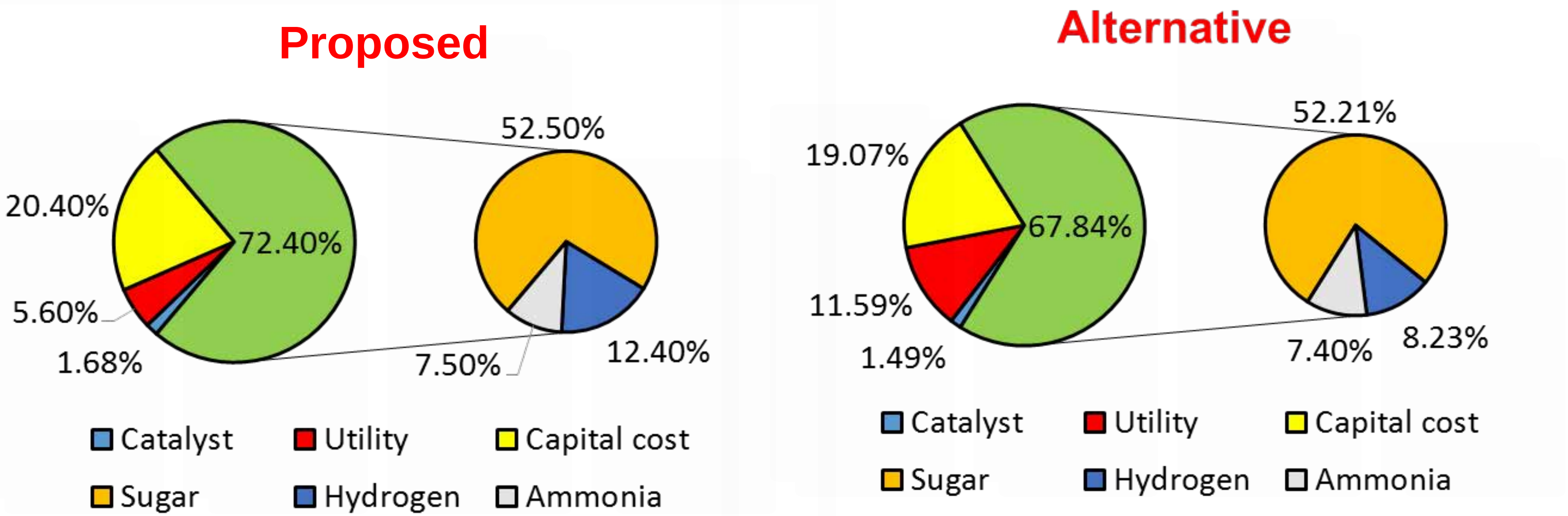
➢ Preliminary TEA

Comparison between originally proposed and alternative process.

Category	Proposed	Alternative
Separation of Glycerol/PG	No	Yes
ACN yield, wt%	27	20
Recoverable product yield, wt%	~34	~40
Co-product	Acetol	PG, Acetol
Co-product, lb/lb ACN	0.25 (Acetol)	1.6 (PG); 0.25 (Acetol)
Overall carbon efficiency, %	60	80
ACN production cost ($/lb ACN)	0.78	0.73

- Higher ACN yield from proposed route as both Glycerol and PG used for ACN production.
- Separating PG (alternative process) improves carbon efficiency.
- ACN production cost calculated based on 5,000 MT/year production capacity.
- More efficient co-product recovery makes the alternative process more economic.

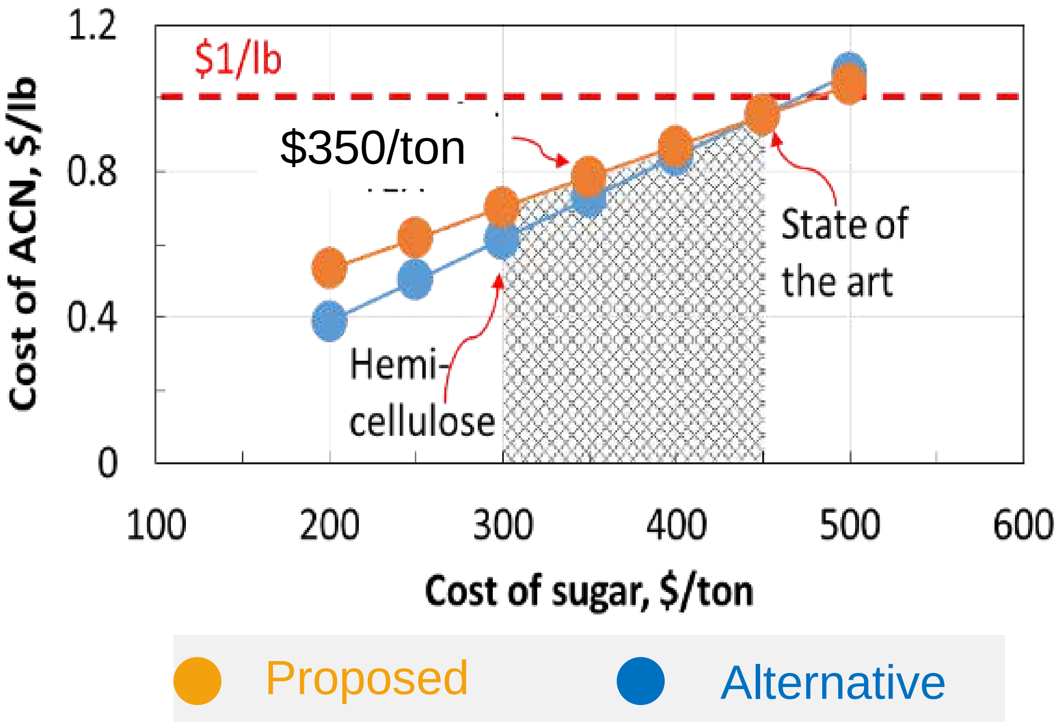
Cost distribution pie charts



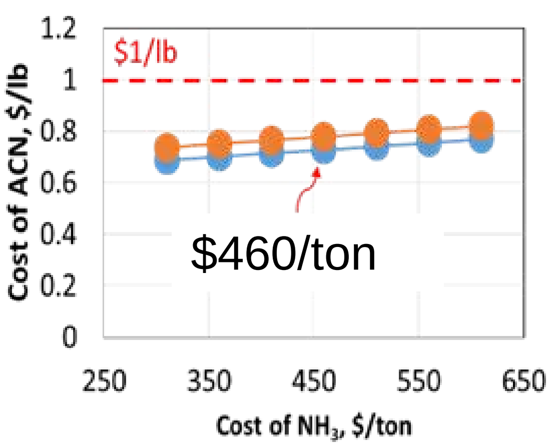
Distribution of cost in ACN production

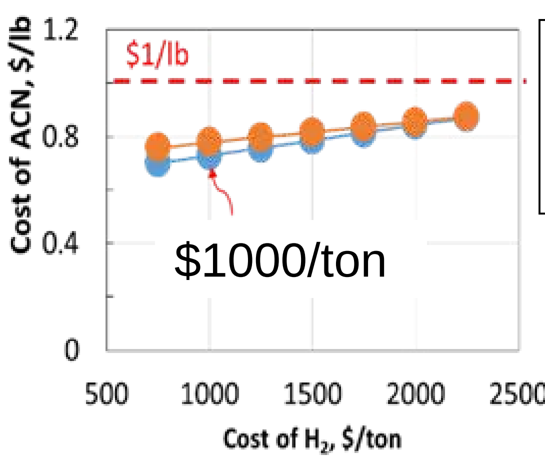
- Catalyst price contributes small fraction of the cost due to use of non-precious metal catalysts.
- Maximum cost contribution from raw materials, in particularly, sugar.
- Overall low H_2 and NH_3 requirement as raw materials.
- Sensitivity analysis of ACN production cost with respect to raw materials price essential.

Sensitivity analysis



- ACN production cost shows high sensitivity to sugar price.
- <$1/lb within $300-$450/ton sugar price.





- ACN production cost nearly insensitive to H_2 and NH_3 price change.

Preliminary LCA

Petroleum based ACN	kg GHG/ kg ACN
Crude to Propylene	0.16
Propylene to ACN	2.86
Total	**3.02**

Biomass to ACN	kg GHG/ kg ACN
Sugars to polyols (R1,S1)	0.91
Polyols to Acrolein (R2,S2)	0.42
Acrolein to ACN (R3,S3)	0.56
Total	**1.92**

- ~37% reduction in greenhouse gas emissions compared to conventional petroleum based processes.

Technical progress summary

Tasks	Milestone	Achievements	Meet target?
2.1-2.2 (R1)	≥ 2 novel candidates Selec.(di-,triols) >65%, Productivity >50g/l/hr	3 novel candidates Selec.(di-,triols) >75%, Productivity >50g/l/hr	☑
2.3-2.4 (R2)	≥ 2 novel candidates Selec.(acrolein)> 70%, Productivity >375g/l/hr,	2 novel candidates Selec.(acrolein) 72-80% (Glycerol feed) and <50% (PG feed), Productivity >375g/l/hr	☑ Glycerol ☒ PG
2.5 (R3)	Selec. (ACN) > 70%, Productivity >75 g/l/hr	Selec. (ACN) 90-98% Productivity>75 g/l/hr	☑
2.6	Catalyst life > 40h	>120h (R1), ~51h (R2), >40h (R3)	☑
4	ACN validation	Product ACN validated	Ongoing
5	<$1/lb	$0.73-0.78/lb	Ongoing
6	Project reporting	Reports delivered regularly to DOE	Ongoing

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.
  - **Plant scale:** Relatively small scale (5000 MT/Year) ACN plants needed to feed Carbon fiber lines (2 lines or 1000 MT/year).

4 – Relevance

➢ **Technology Transfer - Initiatives**

Acrylonitrile Manufacturers	**Catalyst Manufacturers**	**Investor Groups**	**Sugar Suppliers**
Three companies interested – USA, Japan and India 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 two commercial vendors – Arbiom and Renmatix – for sugar supplies for Phase I and Phase II

5 – Future Work

- **For ongoing Phase I (ending on March 2017)**
  - Produce 50 grams of ACN
  - ACN product validation
  - Update TEA/LCA
  - Phase I final report and deliverables

Stage Gate Review – Phase I – After March 30th 2017

- **Phase II – Validating prototype system**
  - Continuous bench scale unit design for kgs/hr production
  - Integrated and slip stream separations to achieve product/by-product purities
  - Continuous 1000 hr operation for the production of up to 500kg ACN.
  - Product stabilization and safe operations for hazardous products
  - Finalize TEA/LCA
  - Continue discussion with potential partners.
  - Complete final project report

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:** Scale up to bench scale. Detail TEA/LCA. Product validation.

Acknowledgements

U S Department of Energy

BETO Project officer: Prasad Gupte
Project Coordinator: Cynthia Tyler

Partners

SOUTHERN RESEARCH

CYTEC SOLVAY GROUP

NJIT New Jersey's Science & Technology University

Sugar Suppliers

ARBIOM

Renmatix

NC STATE UNIVERSITY

Southern Research

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Jadid Samad
Lindsey Chatterton
Govedarica Zora

Cytec Solvay

Longgui Tang (Lead)
Billy Harmon

NJIT

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El Mostafa Benchafia

ARBIOM

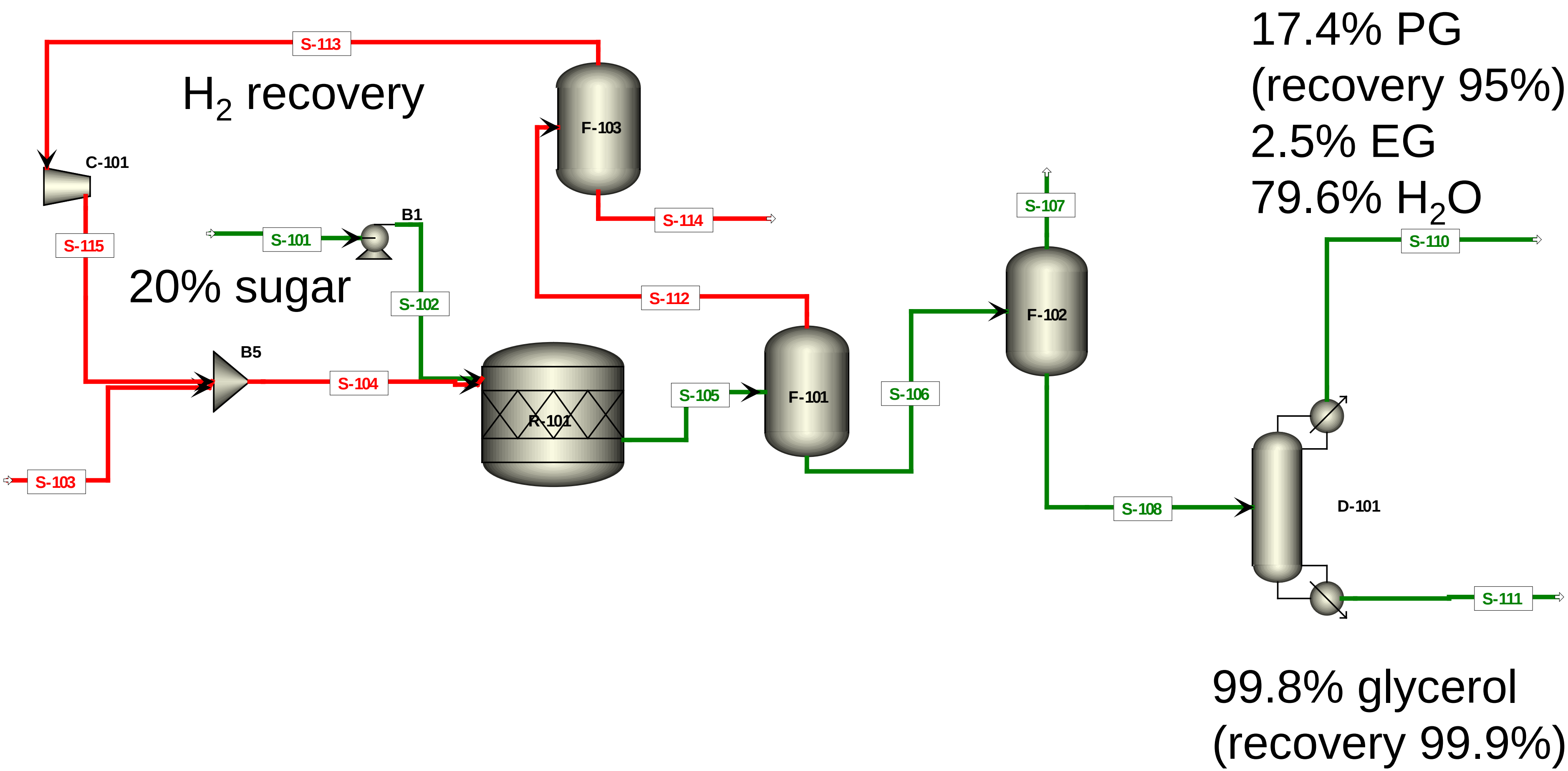
Lisette Tenlep
Bill McDonald

Renmatix

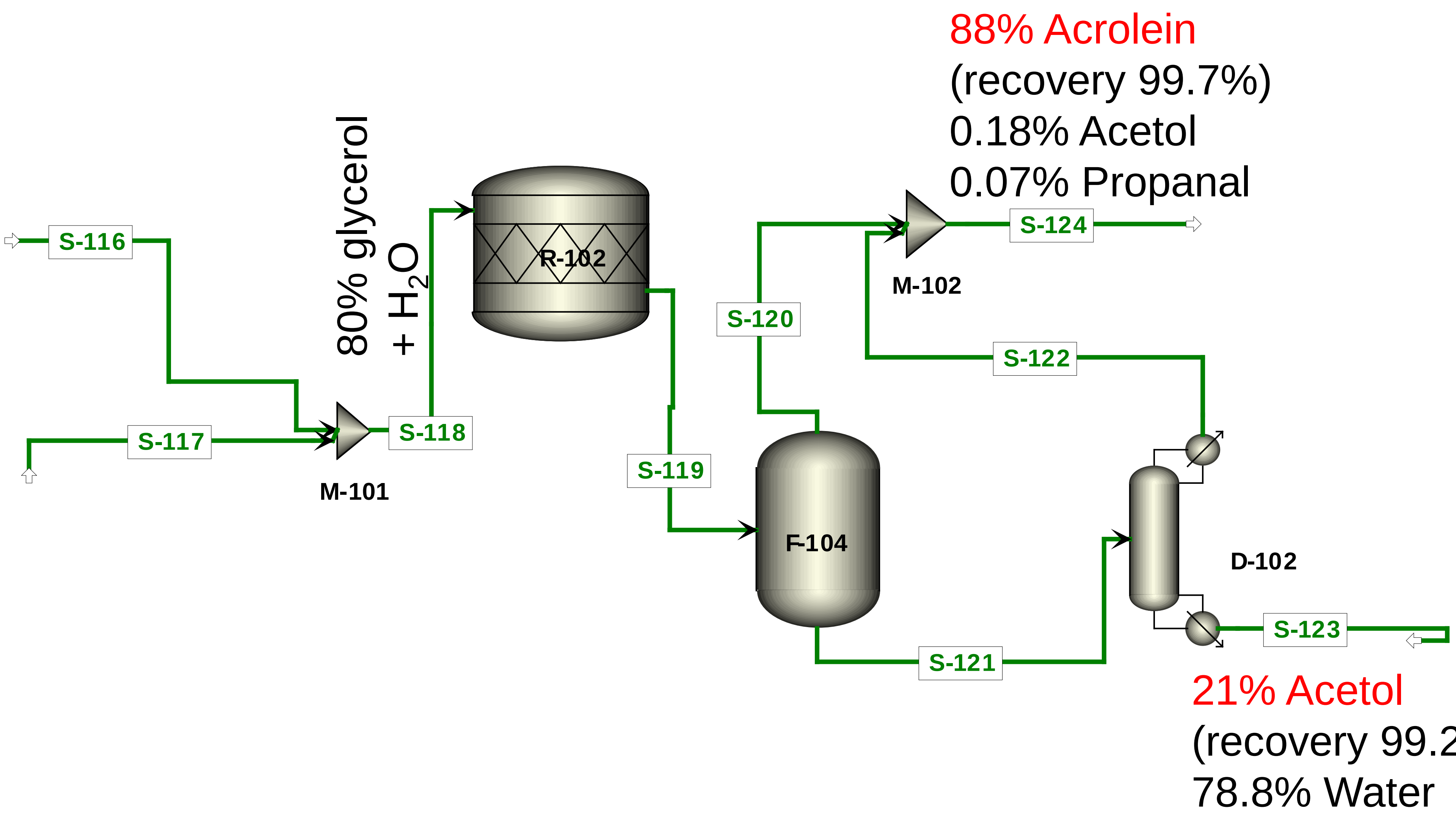
Dan Beacom
Jeremy Austin

Additional Slides

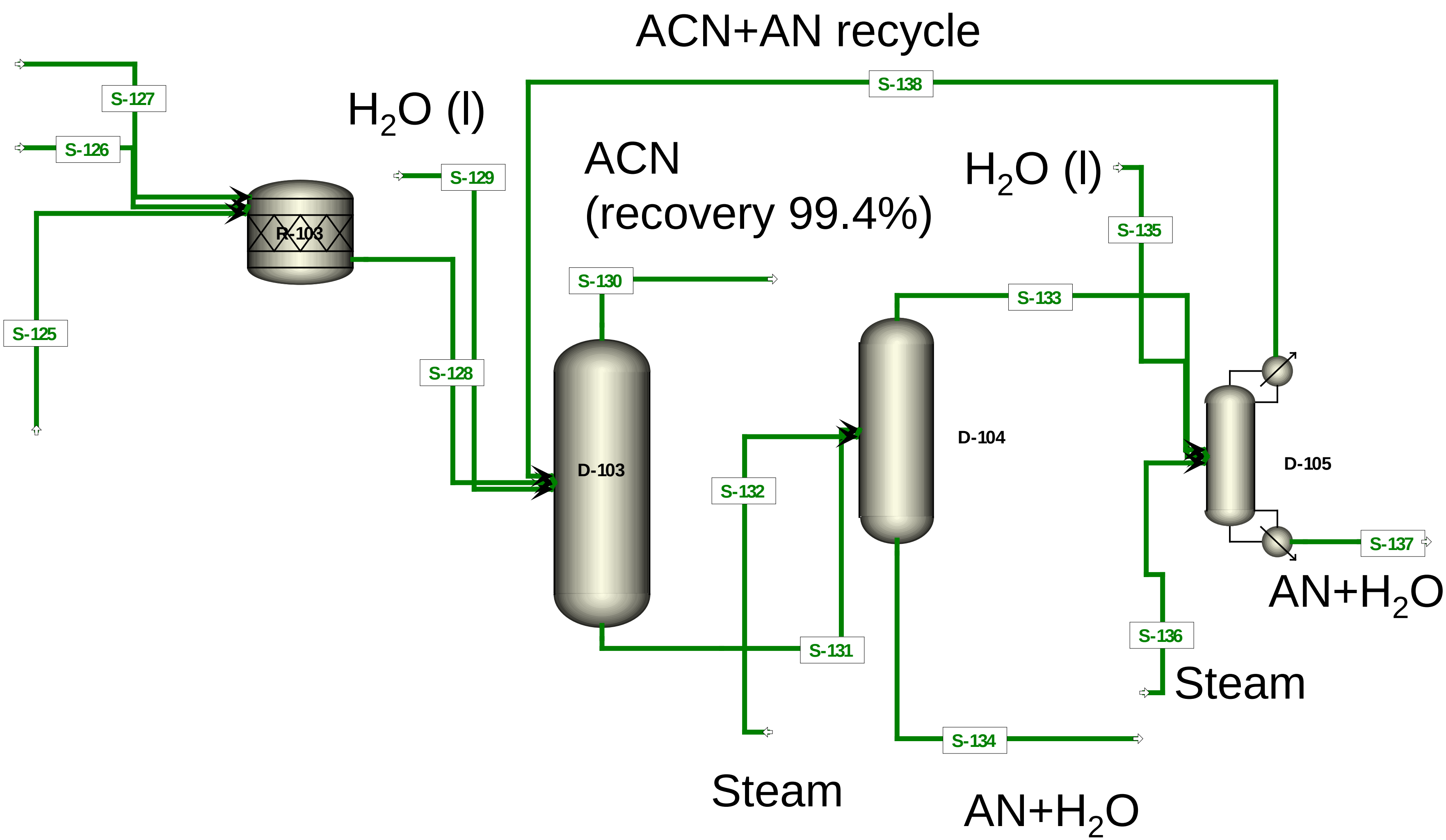
S-1


S-113
H_2 recovery
F-103
C-101
S-114
S-107
S-115
S-101
B1
S-110
20% sugar
S-112
S-102
F-102
B5
S-104
S-105
S-106
F-101
R-101
S-103
S-108
D-101
S-111
17.4% PG
(recovery 95%)
2.5% EG
79.6% H_2O
99.8% glycerol
(recovery 99.9%)

S-2


88% Acrolein
(recovery 99.7%)
0.18% Acetol
0.07% Propanal
80% glycerol
+ H2O
S-116
S-117
S-118
M-101
R-102
S-119
S-120
F-104
S-121
S-122
M-102
S-124
D-102
S-123
21% Acetol
(recovery 99.2
78.8% Water

S-3



ACN+AN recycle
S-138
S-127
S-126
H_2O (l)
S-129
ACN
(recovery 99.4%)
H_2O (l)
S-135
R-103
S-130
S-133
S-125
S-128
D-104
D-103
D-105
S-132
S-137
AN+H_2O
S-136
S-131
Steam
S-134
Steam
AN+H_2O

Publications, Patents, Presentations, Awards, and Commercialization

Publications/Presentations:

- Amit Goyal and Santosh Gangwal, *Biomass Conversion to Acrylonitrile Monomer-Precursor for Production of Carbon Fibers*, Poster Presentation at Bio Pacific Rim Summit, Dec 6 to 9, 2015 San Diego, CA.
- Project Fact Sheet for BioEnergy Summit, June 23rd – June 24th, 2015 Washington DC.
- Amit Goyal and Santosh Gangwal, *Process for Biomass Conversion to Acrylonitrile- Precursor for Production of Carbon Fibers*, Oral Presentation at Bio World Congress July19th - 22nd, Montreal, Canada. Invited talk in Breakout Panel Session: Clustered Research and Development of Ag-Based BioProducts.
- DOE Site Visit – 15th September 2015. Results for overall progress presented to Program manager and coordinator at Durham, NC.
- Amit Goyal, *Process for Biomass Conversion to Acrylonitrile- Precursor for Production of Carbon Fibers*, October 5th 2015, Invited Talk at Department of Materials Science at University of Alabama, Birmingham.
- Amit Goyal, Jiajia Meng, Jonathan P. Carroll, and Santosh K. Gangwal, *Biomass Conversion to Acrylonitrile Monomer-Precursor for Production of Carbon Fibers,* Oral Presentation at AICHE Fall 2015 meeting (579b).
- Amit Goyal, Zora Govedarica, Lindsey Chatterton, and Santosh K. Gangwal, *Acrylonitrile production from non-food biomass derived sugars for synthesis of carbon fibers*, Oral Presentation as a Panel Speaker for World Congress on Industrial Biotechnology Breakout Session: Process Improvement for Biobased Materials.
- Jadid E. Samad and Amit Goyal, *Non-food biomass to acrylonitrile: A cheaper and greener route to automotive grade carbon fibers*, Poster presentation at BioEnergy Summit, July 12-14, Washington DC
- Jadid E Samad, Lindsey Chatterton, Zora Govedarica, Amit Goyal, *Thermocatalytic Process for Biomass Conversion to Acrylonitrile for Production of Carbon Fibers*. Oral presentation at TCS 2016, Chapel Hill, NC.
- Amit Goyal, Longgui Tang and Billy Harmon, Renewable Acrylonitrile for Carbon Fiber Production, Oral Presentation at Carbon Fiber 2016, Scottsdale, AZ
- Jadid E. Samad, Lindsey Chatterton, Zora Govedarica and Amit Goyal, *Biomass Conversion to Acrylonitrile Monomer-Precursor for Production of Carbon Fibers*. AICHE, November 13-18, 2016. San Francisco, CA

Patents:

- **US Application # 20160368861: Compositions and methods related to the production of acrylonitrile**
- **US Application # 15/245,835: Compositions and methods related to the production of acrylonitrile**