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

March 8, 2017
Biochemical conversion

PI: Amit Goyal
Southern Research

This presentation does not contain any proprietary, confidential, or otherwise restricted information
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.

- 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.

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**ACN production from different routes**


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**Graph**

- **Cost ($/lb ACN)**
- **GHG (kg/lb ACN)**

- Options:
  - **C₃H₆/C₃H₅** (Commercial)
  - Purified Glycerol
  - Biodiesel
  - Sugars (proposed)
Quad Chart Overview

- **Timeline**
  - Project start date: Feb 1\(^{st}\) 2015
  - Project end date: March 30\(^{th}\) 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

### Budget

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

- 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.

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Project Overview (contd)

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.

**Schematic of the proposed sugar to ACN process**

R1 = Hydrocracking, R2 = Dehydration, R3 = Ammoxidation
S-1 to S-3 = Separation trains, PG = Propylene glycol
## Activity (Phase I-Ends March 30, 2017)

<table>
<thead>
<tr>
<th>Activity</th>
<th>Task owner</th>
<th>Task</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Task 1: Micro Reactor set up</strong></td>
<td>SR</td>
<td>10, 20</td>
<td>Setup completed</td>
</tr>
<tr>
<td><strong>Task 2: Catalyst development and testing</strong></td>
<td>SR</td>
<td>10</td>
<td>At least 2 novel candidates for each of R1 and R2. R3 lit. catalyst.</td>
</tr>
<tr>
<td>Task 2.1 Develop R1 catalyst</td>
<td>SR</td>
<td>10</td>
<td>R1: S(glycerol+PG) &gt;65%, &gt;50g/l/hr</td>
</tr>
<tr>
<td>Task 2.2 Parametric study for R1</td>
<td>SR</td>
<td>10</td>
<td>R2: S(acrolein) &gt; 70%, &gt;375g/l/hr,</td>
</tr>
<tr>
<td>Task 2.3 Develop R2 catalyst</td>
<td>SR</td>
<td>10</td>
<td>R3: S(ACN) &gt; 70%, &gt;75 g/l/hr</td>
</tr>
<tr>
<td>Task 2.4 Parametric study for R2</td>
<td>SR</td>
<td>10</td>
<td>Catalyst life &gt;40h for each catalyst</td>
</tr>
<tr>
<td>Task 2.5 Optimize ACN production</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Task 2.6 Measure catalyst stability and regeneration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Task 3: Catalyst characterization</strong></td>
<td>NJIT, SR</td>
<td>10</td>
<td>Completed (fresh and used catalyst)</td>
</tr>
<tr>
<td><strong>Task 4: Bio-ACN validation</strong></td>
<td>Cytec-Solvay</td>
<td>10</td>
<td>Model impure ACN validated. 3 product samples tested.</td>
</tr>
<tr>
<td><strong>Task 5: TEA/LCA</strong></td>
<td>SR</td>
<td>10</td>
<td>Preliminary TEA completed with lab scale data. Cost &lt;$1/lb</td>
</tr>
<tr>
<td><strong>Task 6: Project Management and Reporting</strong></td>
<td>SR</td>
<td>10</td>
<td>Deliverables to DOE-EERE</td>
</tr>
</tbody>
</table>

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

Dr. Amit Goyal (PI)
Dr. Santosh Gangwal (Co-PI)
Dr. Jadid Samad (Engineer)
Lindsey Chatterton (Chemist)
Zora Govedarica (Chemist)

Dr. Zafar Iqbal
Dr. El Mostafa Benchafia

Dr. Longgui Tang
Mr. Billy Harmon
2 - Approach (Technical)

R1: Hydrocracking (Task 2,3)
- Catalyst design/synthesis
- Characterization (NJIT)
- Reaction evaluation
  - Model C₅/C₆ 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
  - O₂
  - TEA

R3: Ammoxidation (Task 2,3)
- Literature catalyst
- Characterization (NJIT)
- Reaction evaluation
  - Acrolein (AC)
- Catalyst screening
  - Performance metrics
- Parametric study
  - O₂, NH₃, 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

Reactor setup (Task 1)
- gm scale
- Meaningful scale-up
- Analytical procedure
Progress/target metrics:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Productivity (g/l/hr)</th>
<th>Desired product</th>
<th>Yield (%)</th>
<th>Catalyst life (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>&gt;50</td>
<td>Glycerol + PG</td>
<td>&gt;65</td>
<td>&gt;40</td>
</tr>
<tr>
<td>R2</td>
<td>&gt;375</td>
<td>Acrolein</td>
<td>&gt;70</td>
<td>&gt;40</td>
</tr>
<tr>
<td>R3</td>
<td>&gt;75</td>
<td>ACN</td>
<td>&gt;70</td>
<td>&gt;40</td>
</tr>
</tbody>
</table>

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

H₂, -xH₂O
P = 600-750 PSIG
170-240°C
(novel transition mixed metal catalyst)

sugar → Glycerol + Propylene Glycol (PG) + Ethylene Glycol (EG)
Products: Glycerol+PG (~1:1) and EG(<5%).

High selectivity at different feed types and C5/C6 ratios.

Sugar type

<table>
<thead>
<tr>
<th>Sugar type</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model feed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose (G)</td>
<td>100</td>
<td>81</td>
</tr>
<tr>
<td>Xylose (X)</td>
<td>100</td>
<td>95</td>
</tr>
<tr>
<td>G 25%-X 75%</td>
<td>100</td>
<td>96</td>
</tr>
<tr>
<td>G 50%-X 50%</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>G 75%-X 25%</td>
<td>100</td>
<td>81</td>
</tr>
<tr>
<td>Impure feed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrolyzate</td>
<td>100</td>
<td>76</td>
</tr>
<tr>
<td>Bagasse</td>
<td>100</td>
<td>76</td>
</tr>
<tr>
<td>Pure Hydrolyzate</td>
<td>100</td>
<td>79</td>
</tr>
</tbody>
</table>

Catalyst stable at high temperature in aqueous phase

Catalyst life: > 100hr

Low H₂ requirement (~0.04-0.05kg H₂/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).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Method 1</th>
<th>Method 1</th>
<th>Method 2</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrolysis method</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sugar type</strong></td>
<td>Oligomer</td>
<td>Oligomer</td>
<td>Monomer</td>
<td>Monomer</td>
</tr>
<tr>
<td><strong>Metal/ion impurities [mg/kg]</strong></td>
<td>4532</td>
<td>84</td>
<td>2270</td>
<td>129</td>
</tr>
<tr>
<td><strong>Organic impurities [g/kg]</strong></td>
<td>23</td>
<td>28</td>
<td>10</td>
<td>82</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>3.3</td>
<td>2.9</td>
<td>higher</td>
<td>3.3</td>
</tr>
</tbody>
</table>

**Hydrocracking Results: Hydrolyzate conversion to polyols**

<table>
<thead>
<tr>
<th></th>
<th>Hydrolyzate Conv. [%]</th>
<th>Overall selectivity [%]</th>
<th>Performance stability</th>
<th>Meets product specs?</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>47</td>
<td>79</td>
<td>44 hrs</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>85</td>
<td>&gt; 48 hrs</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>70</td>
<td>&gt; 32 hrs</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>81</td>
<td>&gt; 120 hrs</td>
<td>Yes</td>
</tr>
</tbody>
</table>
3 – Technical Accomplishments/Progress/Results

R2: Dehydration

Glycerol (B.P. 290°C)

Propylene glycol (PG) (B.P. 188.2°C)

Acrolein (B.P. 52.6°C)

Mixed metal oxide

-S2H2O

-H2O, -H2
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.
3 – Technical Accomplishments/Progress/Results

R3: Ammoxidation

Acrolein $\xleftarrow{400-450^\circ\text{C}, \text{NH}_3, 0.5 \text{ O}_2}$ Bi-Mo/Silica $\rightarrow$ Acrylonitrile
- 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).

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$^{-1}$
# ACN validation

<table>
<thead>
<tr>
<th>Bio-mass ACN sample</th>
<th>Sample-1</th>
<th>Sample-2</th>
<th>Sample-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Clear</td>
<td>Slightly pink</td>
<td>Clear</td>
</tr>
<tr>
<td><strong>Product composition (wt%)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basis</td>
<td>Wet</td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>Actual ACN /wt%</td>
<td>1.69</td>
<td>15.9</td>
<td>4.31</td>
</tr>
<tr>
<td>Water/wt%</td>
<td>~89</td>
<td>-</td>
<td>~95</td>
</tr>
<tr>
<td><strong>Impurities</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone /wt%</td>
<td>0.01</td>
<td>0.01</td>
<td>/</td>
</tr>
<tr>
<td>Acrolein /wt%</td>
<td>7.84</td>
<td>73.75</td>
<td>/</td>
</tr>
<tr>
<td>Acetonitrile /wt%</td>
<td>0.13</td>
<td>1.25</td>
<td>0.74</td>
</tr>
<tr>
<td>Propionitrile/ wt%</td>
<td>0.96</td>
<td>9.02</td>
<td>/</td>
</tr>
</tbody>
</table>

- Very low impurity level. Excess water due to use of acetic acid solution to neutralize excess NH₃.
3 – Technical Accomplishments/Progress/Results

TEA/LCA
## Preliminary TEA

Comparison between originally proposed and alternative process.

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

- 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.
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 H₂ and NH₃ requirement as raw materials.

Sensitivity analysis of ACN production cost with respect to raw materials price essential.
ACN production cost shows high sensitivity to sugar price. <$1/lb within $300-$450/ton sugar price.

ACN production cost nearly insensitive to H₂ and NH₃ price change.
## Preliminary LCA

<table>
<thead>
<tr>
<th>Petroleum based ACN</th>
<th>kg GHG/ kg ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude to Propylene</td>
<td>0.16</td>
</tr>
<tr>
<td>Propylene to ACN</td>
<td>2.86</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>3.02</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Biomass to ACN</th>
<th>kg GHG/ kg ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugars to polyols (R1,S1)</td>
<td>0.91</td>
</tr>
<tr>
<td>Polyols to Acrolein (R2,S2)</td>
<td>0.42</td>
</tr>
<tr>
<td>Acrolein to ACN (R3,S3)</td>
<td>0.56</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1.92</strong></td>
</tr>
</tbody>
</table>

~37% reduction in greenhouse gas emissions compared to conventional petroleum based processes.
## Technical progress summary

<table>
<thead>
<tr>
<th>Tasks</th>
<th>Milestone</th>
<th>Achievements</th>
<th>Meet target?</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1-2.2 (R1)</td>
<td>≥ 2 novel candidates Selecr.(di-,triols) &gt;65%, Productivity &gt;50g/l/hr</td>
<td>3 novel candidates Selecr.(di-,triols) &gt;75%, Productivity &gt;50g/l/hr</td>
<td>✓</td>
</tr>
<tr>
<td>2.3-2.4 (R2)</td>
<td>≥ 2 novel candidates Selecr.(acrolein)&gt; 70%, Productivity &gt;375g/l/hr,</td>
<td>2 novel candidates Selecr.(acrolein) 72-80% (Glycerol feed) and &lt;50% (PG feed), Productivity &gt;375g/l/hr</td>
<td>✓ Glycerol  ❌ PG</td>
</tr>
<tr>
<td>2.5 (R3)</td>
<td>Selecr. (ACN) &gt; 70%, Productivity &gt;75 g/l/hr</td>
<td>Selecr. (ACN) 90-98% Productivity&gt;75 g/l/hr</td>
<td>✓</td>
</tr>
<tr>
<td>2.6</td>
<td>Catalyst life &gt; 40h</td>
<td>&gt;120h (R1), ~51h (R2), &gt;40h (R3)</td>
<td>✓</td>
</tr>
<tr>
<td>4</td>
<td>ACN validation</td>
<td>Product ACN validated</td>
<td>Ongoing</td>
</tr>
<tr>
<td>5</td>
<td>&lt;$1/lb</td>
<td>$0.73-0.78/lb</td>
<td>Ongoing</td>
</tr>
<tr>
<td>6</td>
<td>Project reporting</td>
<td>Reports delivered regularly to DOE</td>
<td>Ongoing</td>
</tr>
</tbody>
</table>
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.
- **H₂ requirement and C efficiency:** Less H₂ 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

<table>
<thead>
<tr>
<th>Acrylonitrile Manufacturers</th>
<th>Catalyst Manufacturers</th>
<th>Investor Groups</th>
<th>Sugar Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three companies interested – USA, Japan and India and partner Cytec-Solvay</td>
<td>Working with a major catalyst manufacturer to scale-up and toll-produce kilogram quantities of catalyst for Phase II</td>
<td>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</td>
<td>Working with two commercial vendors – Arbiom and Renmatix – for sugar supplies for Phase I and Phase II</td>
</tr>
</tbody>
</table>
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 H₂ and NH₃ 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

**US Department of Energy**

**Partners**

**Southern Research**
Amit Goyal (PI)
Santosh Gangwal (Co-PI)
Jadid Samad
Lindsey Chatterton
Govedarica Zora

**Cytec Solvay**
Longgui Tang (Lead)
Billy Harmon

**NJIT**
Zafar Iqbal (Lead)
El Mostafa Benchafia

**Sugar Suppliers**

**ARBIOM**
Lisette Tenlep
Bill McDonald

**Renmatix**
Dan Beacom
Jeremy Austin
Additional Slides
H₂ recovery

20% sugar

17.4% PG (recovery 95%)
2.5% EG
79.6% H₂O

99.8% glycerol (recovery 99.9%)
88% Acrolein (recovery 99.7%)
0.18% Acetol
0.07% Propanal

21% Acetol (recovery 99.2%)
78.8% Water

80% glycerol + H₂O

M-101
S-118
S-119
S-120
S-122
S-123
S-124
R-102
F-104
D-102

S-116
S-117
ACN+AN recycle

H₂O (l)

ACN (recovery 99.4%)

H₂O (l)

Steam

AN+H₂O

Steam

AN+H₂O
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).


• 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.


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