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

March 6, 2017
Biochemical Conversion

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Consortium Steering Committee Lead
Argonne National Laboratory
Goal Statement

Goal: Move cost-effective, high-performing separations technology to market faster through coordinated separations research at the national laboratories that targets challenges relevant to BETO’s priority pathways and industry.

Outcome: Biofuels and bioproducts industries will have new, high-performing, low-cost separations technologies available to them.

Relevance to Industry: BETO industrial stakeholders have long raised separations challenges as a major barrier to cost competitive biofuels and bioproducts. BETO analyses indicate that separations steps can constitute up to 50% of processing costs.
### Quad Chart Overview

**Timeline**
- Project start date: 10/1/2016
- Project end date: 9/30/2019
- Percent complete: 8%

**Barriers**
- Ct-G: Efficient Intermediate Clean Up and Conditioning
- Ct-I: Product finishing, acceptability, and performance.
- Ct-J: Process integration

### Budget ($thousand)

<table>
<thead>
<tr>
<th>Costs</th>
<th>FY 16</th>
<th>FY 17*</th>
<th>Total Planned Funding (FY 17- End)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consortium (DOE Funded)</td>
<td>$500</td>
<td>$3,000/$2,500</td>
<td>$9,000/$7,500</td>
</tr>
<tr>
<td>Biochemical Separations</td>
<td>0</td>
<td>$800/$885</td>
<td></td>
</tr>
<tr>
<td>Thermochemical Separations</td>
<td>0</td>
<td>$800</td>
<td></td>
</tr>
<tr>
<td>Ionic Liquid Separations</td>
<td>0</td>
<td>$400/$0</td>
<td></td>
</tr>
<tr>
<td>Algal Separations: Seed</td>
<td>0</td>
<td>$200</td>
<td></td>
</tr>
<tr>
<td>Biochemical Catalyst Preservation: Seed</td>
<td>0</td>
<td>$200</td>
<td></td>
</tr>
<tr>
<td>Analysis</td>
<td>0</td>
<td>$400/$315</td>
<td></td>
</tr>
<tr>
<td>Steering Committee</td>
<td>0</td>
<td>$200/$100</td>
<td></td>
</tr>
</tbody>
</table>

*Black text indicates originally planned funding levels. Red text indicates revised funding levels to account for budget uncertainty.

**Partners**
- ANL
- INL
- LANL
- LBL
- ORNL
- NREL
- PNNL
- Sandia
1. Project Overview

Industrial stakeholder input to BETO\textsuperscript{1,2} has indicated that separations challenges impede the cost-competitive production of biofuels and bioproducts. Stakeholders identified upstream and downstream separations and purification challenges as near term barriers that could benefit from immediate attention. For example:

- Separations steps are a barrier to efficient unit operation integration
- Improved solid-liquid and liquid-liquid separations technologies are needed for bioprocessing
- Residual solids influence downstream processes and need to be removed
- Membrane fouling and poorly-understood material properties limit their effective application in bioprocessing

The Consortium addresses this stakeholder feedback, bringing together expertise and capabilities across eight national laboratories to develop new separations technologies and apply existing technologies to new bioprocessing challenges.
Separations are crucial to all biomass conversion pathways

1. Project Overview

Separations, Integration, and Enabling Technologies
1 - Project Overview: Consortium Formation

- Teams surveyed separations challenges in BETO priority pathways
- 54 separation challenges identified from seven separate pathways across the BETO algae and conversion platforms and formed the “technology map”

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Membrane Type 1 (Liquid Phase)</th>
<th>Membrane Type 2 (Vapor Phase)</th>
<th>LLE 1 (Liquid-liquid equilibrium separations, no solvent used)</th>
<th>LLE 2 (liquids extraction into a solvent immiscible with process liquid)</th>
<th>Low Frequency Sonication</th>
<th>High Frequency Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Challenges</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y - possible to extract some</td>
<td>N</td>
<td>Y - temp dependent</td>
</tr>
<tr>
<td>Pyrolysis and Upgrading (In-Situ/Ex-Situ) Fuel Production</td>
<td>YY</td>
<td>YY</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Separate liquid organic and aqueous phases</td>
<td>YY</td>
<td>YY</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Separate oxygenates from hydrocarbon in intermediate upgraded bio-oils; separation of aqueous phase becomes easier with more deoxygenation; removal residual hydrocarbons from aqueous phase</td>
<td>YY</td>
<td>Y</td>
<td>Y - separation easier with more deoxygenation</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
</tbody>
</table>
Many possible projects identified; the following questions used to select first portfolio and organize the consortium into teams.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Does the project address a technical challenge facing one of the priority pathways?</td>
<td>• Can check technology map or with the author(s) of the relevant design reports</td>
</tr>
<tr>
<td>Does the challenge have a large impact on process economics for the relevant pathway(s)? (e.g., potential to reduce modeled costs)</td>
<td>• Can check technology map or with the author(s) of the relevant design reports</td>
</tr>
<tr>
<td>Is this project similar to or a continuation of a project within BETO’s portfolio?</td>
<td>• Check technology map and with the steering committee</td>
</tr>
<tr>
<td>Is there any indication that this project has been addressed by external work?</td>
<td>• Brief literature/patent search</td>
</tr>
<tr>
<td>Do the labs have existing capital equipment and personnel with the necessary technical knowledge to carry out the project?</td>
<td>• Check with team members/LRM/steering committee</td>
</tr>
<tr>
<td>Potential annual cost of project (($ - &lt;$250k, $$ - $250-$500k, $$$ - $500k-$1MM, $$$$ - &gt; $1MM)</td>
<td>• Estimate based on staff needs, operating costs, etc. No major capital costs should be expected</td>
</tr>
<tr>
<td>What other projects would benefit if this project were successful?</td>
<td>• For example, maybe a catalysis project will no longer be impacted by a certain inhibitor or perhaps a fermentation will have a higher yield because an inhibitor will no longer be present</td>
</tr>
<tr>
<td>Who (specifically) are potential industrial and academic partners</td>
<td>• Synergistic projects list is <a href="#">here</a></td>
</tr>
</tbody>
</table>
2. Approach (Management)

**Bioenergy Technologies Office:** Nichole Fitzgerald

**Steering Committee:**
- Jennifer Dunn (Argonne)
- Taraka Dale (LANL)
- Todd Pray (LBL)

**Advisory Board**

**Crosscutting Analysis:**
- Mary Biddy (NREL)
- Sue Jones (PNNL)
- Jennifer Dunn (Argonne)

**Biochemical:**
- Gregg Beckham (NREL)
- YuPo Lin (Argonne)

**Thermochemical:**
- Jae-Soon Choi (ORNL)
- Bob Baldwin (NREL)

**Ionic Liquid:**
- Ning Sun (LBL)
- Aaron Wilson (INL)
- Seema Singh (Sandia)

**Biocatalyst Preservation (Seed):**
- Phil Laible (ANL)

**Algae (Seed):**
- Jim Coons (LANL)
- Brian Bischoff (ORNL)
Investigator Roster

**Biochemical Separations:**
- Gregg Beckham (NREL)
- David Brandner (NREL)
- Jim Coons (LANL)
- Robin Cywar (NREL)
- Eric Karp (NREL)
- YuPo Lin (ANL)
- Lorenz Manker (NREL)
- Michelle Reed (NREL)
- Patrick Saboe (NREL)

**Thermochemical Separations:**
- Robert Baldwin (NREL)
- Justin Billing (PNNL)
- Jae-Soon Choi (ORNL)
- Chai Engkatrul (NREL)
- Michael Hu (ORNL)
- Mark Jarvis (NREL)
- Sue Jones (PNNL)
- YuPo Lin (ANL)
- Aimee Lu (ORNL)
- Kim Magrini (NREL)
- Asange Padmaperuma (PNNL)
- Andrew Schmidt (PNNL)
- Tim Theiss (ORNL)
- Huamin Wang (PNNL)

**Algae Processing Separations:**
- Brian Bischoff (ORNL)
- Jim Coons (LANL)
- Tao Dong (NREL)
- Phil Pienkos (NREL)
- Nicholas Sweeney (NREL)
- Ben Yap (LANL)

**Biochemical Catalyst Preservation:**
- Seth Darling (ANL)
- Deborah Hanson (ANL)
- Patricia Ignacio de Leon (ANL)
- Phil Laible (ANL)

**Cross-Cutting Analysis:**
- Mary Biddy (NREL)
- Jennifer Dunn (ANL)
- Sue Jones (PNNL)

**Ionic Liquid Separations:**
- Seema Singh (SNL)
- Ning Sun (LBL)
- Aaron Wilson (INL)

**Steering Committee:**
- Taraka Dale (LANL)
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- Todd Pray (LBL)
2- Approach (Management)

Consortium Management

• Monthly full-consortium calls to update on business and technical accomplishments; each team has regularly scheduled calls
• **Cross-team interactions** leverage results and information
• **Cross-cutting analysis team** engages with each R&D team to inform technical targets, economic impact of projects
• Stream stewards produce commonly-used, **exemplary streams** for separations experiments within different teams
• Internal sharepoint for file management
• **External website** established to disseminate information about the consortium and provide stakeholders information about current project portfolio and how to interact with the consortium.

http://bioesep.org/
2- Approach (management)

• Industrial Advisory Board Interactions
  • Held first face-to-face with IAB on December 1, 2016
  • Preparing document to address comments from IAB at face-to-face
  • IAB interactions will be quarterly, two face-to-face meetings per year

• Industrial Advisory Board Charter
  – Help the consortium maintain an industry-relevant focus and knowledge of recent technology advances and challenges.
  – Provide advice, review results and progress in comparison with work plans, provide feedback regarding prioritization of research projects (experimental and analytical), and inform development of the consortium’s strategy for out years.
Cross Cutting Analysis Team

Analysis Team plays a critical role in the consortium

• Completed Assessment of BETO Priority Conversion Routes
  • Identified separations challenges with potential to reduce biofuel production costs
  • Quantified $/gge that these separation challenges are posing

• Analysis Team Consortium Goals
  • Work closely with each technical team
    • Estimate potential cost reductions for proposed projects
    • Enable teams to generate appropriate data for TEA analyses
    • Help set technical targets and direct research towards greatest impact
    • Track technical progress towards targets
  • Compare proposed technologies to baseline technologies
    • Understand potential for improving costs,
    • Assess sustainability footprint (such as fossil/water/electricity usage)
    • Evaluate reliability of proposed strategies
  • Integrate life-cycle analysis into portfolio for projects that achieve a certain threshold (e.g., pass go/no-go)
Assessed BETO Priority Conversion Routes:

- Fast pyrolysis and upgrading
- Combined algal processing
- Ex Situ catalytic fast pyrolysis
- Hydrothermal liquefaction
- Indirect liquefaction
- Biological conversion of sugars
- Catalytic conversion of sugars
- Algae production
- Ex Situ catalytic fast pyrolysis
- Indirect liquefaction
- Algae production

Example: *Biochemical Conversion of Sugars*

**Low cost separation strategies needed**

**Challenge:** continuous fermentation product removal

**Challenge:** fines removal, catalyst recovery, dewatering

**Challenge:** separations for lignin valorization

**Challenge:** toxins and inhibitors removal
Example: Biological Conversion of Sugars
Assessing Costs and Strategies

Significant Cost Reductions needed between now and 2022 – mostly related to lignin usage

R&D Strategies

- Develop on-stream data with recyclable materials to mitigate toxins and inhibitors for fermentation
- Electrochemical membrane separation technology to extract/concentrate lignin depolymerization catalysts and low molecular weight aromatic acids from alkaline pretreated liquor (APL)
3- Accomplishments

- Establishment of industrial advisory board and charter, first face-to-face meeting
- Launched website
- Early technical accomplishments within the Consortium’s first quarter of work summarized by team in future work section
4-Relevance to Biofuels and Bioproducts Industries

• BETO stakeholders in the biofuels and bioproducts industries have flagged separations challenges as ripe for near- and mid-term research. The consortium addresses this input.
• The consortium is actively engaging with industry through its advisory board, seeking input regarding current and future research portfolios.
• Further biofuel and bioproduct industry input will be sought in a listending day scheduled for May 2017.
4-Relevance to BETO’s Strategic Plan and the MYPP

• One strategy to enhance bioenergy’s value proposition is to reduce cost and improve performance. This strategy has a substrategy of Improving Process Performance through Improved Catalysts and Separations, which states:
  – Currently, separations costs can represent up to 50% of processing costs for biofuels and bioproducts. Carbon not contained in the biofuel or bioproduct is usually used for power generation—a low-value use. **It is imperative to move cost-effective, high-performing separations technologies to market faster to enable cost-competitive biofuels production. BETO will ... optimize separations technologies to use biomass feedstocks efficiently.**

• The Separations Consortium directly addresses this substrategy.

• The Consortium addresses the following MYPP goals and barriers
  – Separations and cleanup are overarching issues in conversion
  – Cost-effective routes to eliminating impurities in intermediates that inhibit chemical and biological catalysts
  – BETO is targeting improved separations processes to increase yields and purity including solid-gas (e.g., hot gas filtration), solid-liquid, gas-liquid, and liquid-liquid separations.
4-Relevance to other BETO projects

- The Separations Consortium is integrated with the overall BETO conversion platform
- Project metrics, technical targets, and newly proposed projects driven by TEA and LCA
- Through regular Conversion Team conference calls, the Consortium provides updates regarding project progress and learns about separations challenges faced in other conversion projects or ways in which consortium learnings could be applied to other projects.
- Addressing challenges associated with biochemical (e.g., enzymes, microorganisms) and thermochemical (e.g., hydrotreating) catalysts.
- Separations Consortium projects are largely designed around challenges faced in BETO’s priority pathways and are therefore directly applicable to the overall work of the Conversion platform.
Section 5: Future Work

**Crosscutting Analysis:**
- Mary Biddy (NREL)
- Sue Jones (PNNL)
- Jennifer Dunn (Argonne)

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- Nichole Fitzgerald

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Cross Cutting Analysis Team

Using TEA and LCA to support FY18 Go/No-Go decisions

On-going integration of TEA, LCA and R&D:
- Example template shown below
  - Outlines data needs for R&D to develop TEAs
  - At least 3 separations strategies to be assessed at the Go/No-Go

<table>
<thead>
<tr>
<th>Key Process Step</th>
<th>Brief Design Description</th>
<th>Based on Biomass Feedstock/Model Compounds/Other?</th>
<th>Experimental Scale (lab/bench/pilot/literature)</th>
<th>Experiment Consistent with Design (yes/no), explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Key process parameters</th>
<th>Key results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Closure (%)</td>
<td></td>
</tr>
<tr>
<td>Carbon Balance (%)</td>
<td></td>
</tr>
<tr>
<td>Number of times experi-</td>
<td></td>
</tr>
<tr>
<td>ment repeated</td>
<td></td>
</tr>
<tr>
<td>Time on stream (hrs)</td>
<td></td>
</tr>
<tr>
<td>Temp (°C)</td>
<td></td>
</tr>
<tr>
<td>Press (psi)</td>
<td></td>
</tr>
<tr>
<td>Residence Time (hr)</td>
<td></td>
</tr>
<tr>
<td>Efficiency (wt%)</td>
<td></td>
</tr>
<tr>
<td>Selectivity (wt%)</td>
<td></td>
</tr>
<tr>
<td>Yield (g/g)</td>
<td></td>
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</table>
Goal Statement – Biochem. Conversion Separations

Two aims and associated outcomes:

• Enable cost effective separations relevant to lignin valorization
• Enable cost effective recovery of target products from fermentation

Relevance to Conversion Platform, BETO, and industry:

• Lignin valorization is essential for BETO cost targets of a $3/gge MFSP – many separations challenges exist
• Recovery of intermediates from fermentation often accounts for ≥ 50% of MSP of a fuel or chemical produced via biological cultivation

Team from 4 national labs:
**Technical Approach (and Future Work) – Lignin Separations**

**Approach:** examine homogenous & heterogeneous catalytic lignin depolym.
- S/L separation (fines or catalysts)
- MW fractionation
- Dewatering
- Catalyst recovery

**Challenges and Critical Success Factors**
- Developing **scalable** separations processes
- “Too many pots and pans”
- Catalyst recovery is critical for lignin valorization (both NaOH or solid catalyst)

Working towards **quantitative separations targets** based on TEA
- Applying technical approaches to **exemplary** lignin streams mainly from NREL pilot plant
- Common problems for lignin valorization: results will be applicable to many lignin streams
Approach: Homogeneous depolymerization

HOMOGENEOUS LIGNIN DEPOLYMERIZATION

Biomass

NaOH + H₂O → Lignin Depolym. → Fines separation → Sep. challenge #1

pH 10-12

Residual solids

MW separation

HMW lignin

Neutralization NaOH recovery → Sep. challenge #3

NaOH recovery / recycle

dewatering → Sep. challenge #4

Valorization

H₂O

Fines separations

- Alkaline pretreated liquor from stover – a BETO process-relevant stream for lignin processing
- APL contains significant amount of fines from biomass processing
- Ultrasonic separation: can result in particle aggregation at low energy inputs

Karp et al. ACS SusChemEng 2014; Karp et al. ACS SusChemEng 2015
Approach: Homogeneous depolymerization

HOMOGENEOUS LIGNIN DEPOLYMERIZATION

MW separations
- Membrane filtration
- Chromatographic approaches (simulated moving bed)
- Membranes with targeted MW sizes
- APL contains significant amount of high MW species from biomass processing
- Very common, general problem in lignin processing

Linger, Vardon, Guarnieri, Karp *et al.* PNAS 2014
Approach: Homogeneous depolymerization

**HOMOGENEOUS LIGNIN DEPOLYMERIZATION**

```
Biomass

NaOH + H₂O → Lignin Depolym. → Fines separation → MW separation → Neutralization NaOH recovery → dewatering
```

**Residual solids**

**Value Propositions**

- Homogeneous catalyst recovery
  - Electrochemical membrane technology for continuous separation
  - Ion exchange resin assisted capture
  - Selective separation process to recycle homogeneous catalyst and capture aromatic acids in a single device
  - Can greatly reduce the salt and wastewater burden on the biorefinery
Approach: Homogeneous depolymerization

**HOMOGENEOUS LIGNIN DEPOLYMERIZATION**

- **NaOH + H₂O** → Lignin Depolym. → Sep. challenge #1 (Fines separation) → Sep. challenge #2 (MW separation) → Sep. challenge #3 (Neutralization NaOH recovery) → Sep. challenge #4 (dewatering) → Valorization

- **Biomass** → Residual solids

**Dewatering**
- Resin testing and design
- Electrochemical membrane separation platform technology
- Target 10-100x lignin-derived aromatics concentration increase
- Generalizable well beyond APL

**Polyvinylpyridine (PVP)**
**Polybenzimidazole (PBI)**
**Approach: Heterogeneous depolymerization**

**HETEROGENEOUS LIGNIN DEPOLYMERIZATION**

**Solid catalyst recovery**
- Filtration
- Batch reactions with metal and metal oxides as example solid catalysts

**MW separations**
- Membrane filtration
- Chromatographic approaches (simulated moving bed)
- Membranes with targeted MW sizes
- Common problem in lignin processing

**Dewatering**
- Resin testing and design
- Electrochemical membrane separation platform technology
- Require high concentrations of aromatic compounds for bioreactor feed or direct use in valorization stream
- Generalizable for most lignin streams
Technical Approach (and Future Work) – Fermentation Sep.

**Approach:** examine recovery of challenging fermentation intermediates

- Carboxylic acids as intermediates (often most expensive and challenging products to remove)
- Common problem in biorefining given many value-added chemicals from biomass are acids
- Determine if extraction is a scalable separations solution

**Challenges and Critical Success Factors**

- Developing scalable, cost-effective extraction processes – two processes
  - Solvent recycle and recovery or
  - Resin wafer separation for direct acid capture from ferment. broth
- Membrane fouling
- Minimization of salt generation
- Produce **acids**, not carboxylates

**Working towards quantitative separations targets** based on TEA

- Applying technical approaches to exemplary lignin streams mainly from NREL pilot plant
- Common problems for lignin valorization: results will be applicable to many lignin streams
Approach: Fermentation separations

Developing more efficient methods for extractive fermentation

- Using **TOPO** as extractant for online extraction
- Enables recovery of carboxylates in protonated form
- Using ion-exchange **resin-wafer electrodeionization** to selective separate organic acid
- Enable direct capture and concentration of carboxylates in the acid form
- Simplifies downstream processing
Biochem- Relevance, Current Progress, and Impact

**Relevance:** Develop new separation strategies that will improve the efficiency and costs of lignin valorization and ease recovery of fermentation products and intermediates.

**Progress to Date:**

**Lignin Separations**
- Developed baseline protocol to produce lignin streams for distribution to partners
- Screened ion-exchange resin wafer compositions for ability to capture the targeted aromatic acids vanillic, perulic and coumaric acids
- Began measurements of particle size distribution in alkaline pretreated liquor

**Fermentation Separations**
- Identify optimal resin wafer compositions to effectively ionize carboxylic acids and succinic acids in the aqueous phase. These compositions will be used in an electrochemical membrane separation system to extract organic acids from fermentation broth.
- Began working with TOPO and other novel extraction agents to understand carboxylate removal from fermentation.

**Impact:** Biochemical conversion routes will become more cost competitive because a low molecular weight aromatic acid stream – a valuable co-product - will be cost effectively produced from biomass and costs to recover intermediates and final products from fermentation broth will decline.
Increase catalyst lifetime & renewable carbon efficiency to fuels and reduce need for external non-renewable hydrogen through the use of enhanced separations

Relevance to Conversion Platform, BETO, and industry:
• High C and H atom efficiencies are essential to achieve BETO cost target of a $3/gge MFSP and >50% GHG reduction
• Frequent catalyst replacement and maintenance currently represent a major cost in thermochemical conversion processes

Team from 4 national labs:

Argonne

NREL

Oak Ridge

Pacific Northwest
**Overall Technical Approach – Thermochemical Separations**

**Approach:** examine separation methods & their integration for enhanced C & H atom efficiency & hydrotreating catalyst durability

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**Working towards quantitative sep. targets based on TEA**
- Using exemplary thermochem. streams from NREL & PNNL pilots
- Addressing common problems: results will be applicable to many other bio-oil and aqueous streams

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- **Fast Pyrolysis**
  - vapor

- **Catalytic Fast Pyrolysis**

- **Upgrading (ex situ CFP)**

- **Condensation**

- **Hydrothermal Liquefaction**

- **Hydrotreating**

- **gas (HC, CO, CO₂)**

- **H₂**

- **bio-oil**

- **liquid hydrocarbons**

- **aqueous streams**
Approach – Catalytic Hot Gas Filtration

**Approach**: filter-based upgrading of hot pyrolysis vapors to remove char and alkali metals

- Optimize HGF filtration performance
- **Add catalysts** to HGF to **pre-deoxygenate** vapors for downstream upgrading
- Condensed oils will be hydrotreated at PNNL
- Conduct TEA for cost impact assessment

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**Challenges and Critical Success Factors**

- **Challenge**: filter plugging and deactivation => consider dual beds swing operation, as pressure drops to maintain performance
- **Targets for upgraded bio oil**:
  - Reduce metals and char to < 0.01%
  - De-oxygenate vapors to <30% oxygen content (water-free basis)
**Approach: Integration of solvent extraction, adsorbents & membranes for selective separation of catalyst foulants (carbonyls, carboxylic acids)**

- Develop efficient solvent extraction methods to concentrate foulant molecules
- Selective adsorptive removal of reactive carbonyl and carboxylic acid molecules
- Pre-processed oils will be hydrotreated at PNNL
- Conduct TEA for cost impact assessment

**FPBO:** Fast Pyrolysis Bio-Oil  
**WSBO:** Water Soluble Bio-Oil  
**WIBO:** Water Insoluble Bio-Oil  
**PUBO:** Partially Upgraded Bio-Oil

**Challenges and Critical Success Factors**

- Developing scalable & regenerable adsorption processes
- Targets
  - Foulant concentration in stabilized bio-oil >90% less than in raw bio-oil
  - >200% catalyst lifetime enhancement & >25% conversion cost reduction
Approach – Carbon Recovery from Aqueous Streams

**Approach:** Integration of ANL polymer wafers (extraction) with ORNL advanced membranes (dewatering) to obtain concentrated acids

**Selective Separations-Dewatering**

- Wafer-Membrane selective separations of mixed organic acids in APBO into pure organic acid streams
- Effective water removal membrane separation to concentrate organic acids
- Conduct TEA for cost impact assessment

**Challenges and Critical Success Factors**

- Challenge: selectivity and material stability to handle concentrated organic acids
- Targets:
  - Organic acid concentration >60 wt%
  - 90% acid capture and <$0.25/lb acid
Relevance: Use advanced separations technology to improve carbon efficiency and operability of downstream upgrading unit operations by reducing catalyst poisons, removing acids, and recovering lost carbon from aqueous streams.

Progress to Date:

*Catalytic Hot Gas Filtration*
- Fabricated and tested filter holder assembly and pyrolyzer slipstream reactor
- Characterized Pall ceramic filters for surface area, porosity, fluid uptake (wettability), metal content, pressure drop
- Conducted slipstream testing of uncoated and 1% NiO coated ceramic filters
- Completed preliminary TEA

*Molecular Removal Pre-Processing of Liquid Bio-oils*
- Began screening of adsorbents (e.g., molecular sieves and resins) for extraction of carbonyl and acid components from bio-oil with and without water induced phase separation
- Analysis of dozen extraction samples completed (e.g., TAN, CAN, carbonyl content)

*Carbon Recovery from Aqueous Streams*
- Conducted screening of resin wafer composition for acid extraction
- Resin wafer membrane selective separation increased concentration of 1 wt% acetic acid solution in water to ~15-20wt.% (separation factor = 20)

Impact: If successful, this project will lead to dramatically enhanced catalyst lifetime and C/H atom efficiency of TC intermediates upgrading and monetization of aqueous stream molecules.
Goal Statement – Ionic Liquid (IL) Separations

Development of ionic liquid recycling technologies to enable cost-effective biomass processing

Relevance to Conversion Platform, BETO, and industry:

• Enable innovative biomass deconstruction approaches to improve yields and lower the cost of fermentable sugars
• IL recycling is essential to enable cost-effective IL deconstruction technologies (IL process TEAs assume >95% IL recycling)
Technical Approach—Overall process

Team will evaluate different ILs’ recyclability and identify potential links with other SepCon teams (e.g. biochemical team-lignin recovery, biocatalyst preservation, etc.)


Technical Approach-PV, FO, WFE

• Challenges of IL/H₂O separation using current methods
  o Conventional Distillation: High energy cost, low selectivity
  o Extraction: Low recovery rate, multi-step, waste stream
  o Electrodialysis: High IL loss, limited concentration ranges

• Approach I: pervaporation (PV)
  o Low operation temperature
  o Excellent resistance of IL permeation (IL recovery >99.9%)
  o High separation selectivity for azeotrope

• Approach II: forward osmosis (FO)
  o Addresses high concentration solutions
  o Low operation temperature (70-80 °C)
  o High energy efficiency
  o Better fouling resistance

• Approach III: wiped film evaporation (WFE)
  o High efficiency to remove water to ppm level
  o Industrial relevant process used for IL production
  o Easily scalable
Ionic Liquid Separations - Relevance, Current Progress, and Impact

Relevance: Development of ionic liquid (IL) recycling technologies is necessary to enable IL-based biomass deconstruction approaches to improve yields and lower the cost of fermentable sugars.

Progress to Date:
- Selected ILs and IL concentration ranges to be evaluated with proposed dewatering technologies.
- Measured the water concentration-dependent osmotic pressure of one selected IL.
- Started to establish high-performance liquid chromatography and conductivity methods to assess IL concentration, titration-based methods to quantify trace water.

Impact: If this team is successful, the underlying assumption of 95-99% IL recycle in the techno-economic analysis of conversion processes with IL-based deconstruction will be validated, improving techno-economic evaluation of these processes as an element of BETO’s research and development portfolio.
Goal Statement – Algae Separations Seed Project

Two aims and associated outcomes:
• Enable cost and energy effective algae dewatering
• Enable cost effective lipid recovery from disrupted algae with little or no toxic solvents

Relevance to Conversion Platform, BETO, and industry:
• TEA results indicate reducing cost of algae dewatering is essential to reducing cost of algae platforms.
• Lipid separation accounts for 12% of biofuel cost ($0.523/gge)
• Solution must be scalable and commercially viable

Team from 3 national labs:
Algae Seed Project – Separation challenges targeted

Algae Feedstock Harvesting

- Algae Growth
- CO₂
- Makeup water
- Recycle water
- Makeup nutrients

Combined Algal Processing

- Product Purification
- Raw Oil
- Upgrading (Hydrotreater)
- Ethanol or Hydrocarbons
- Hydrogen
- Offgas
- Naphtha
- Diesel

Algae Dewatering

- Challenge: At a minimum, dewatering accounts for 10% of feedstock costs for “well-behaving” types of algae
- Dewatering solution is applicable for a broad range of algae species and platforms

Lipid Recovery

Combined Algal Processing (CAP)

- SOT lipid separation accounts for 12% of biofuel cost ($0.523/gge)
- Reduce costs by using less or eliminating solvent
Ultrasonics have the potential to reduce 1\textsuperscript{st} stage harvesting energy requirements and costs by more than a factor of 10.

- Ultrasonics moves particles to nearby nodes to make big particles easier to separate.
- Removes 99% of the water before filtration.
- Employs robust fouling-resistant membranes.
- Use recyclable flocculants to reduce flocculant costs by 85% and recover more biomass.

Applicable to \textit{any} microalgae feedstock pathway!
Algae Seed Project – Role of each lab

- Stream steward
- Whole microalgae
- Acid-disrupted algae

- Separations-relevant properties
- Ultrasonic separations

- Membrane separations
- Use surface enhanced robust inorganic membranes to minimize fouling
- Test cleanability of membranes
Our technology moves tiny particles (algae, lipids, etc) a short distance for aggregation and dewatering, generating less volume of material to filter, and requires >10 times less energy than conventional separation technologies.

Progress to date (LANL):

Ultrasonic removal tests in combination with passivity measurements (not shown) will determine dewatering costs using ultrasound. Passivity is a property proportional to the energy required for removal by ultrasound.

Impact:

If this project is successful, energy consumption and algae dewatering costs will be up to 90% less for all algae strains and toxic solvent use in lipid recovery will be reduced.

Progress to date (ORNL):

Superhydrophilic membranes and a crossflow membrane test system have been fabricated for algae tests.
Goal Statement – Biocatalysts Preservation Seed Project

Two aims and associated outcomes:
• Enable cost-effective synthesis of advanced materials for separations
• Improve bioconversion efficiency by extending lifetimes of enzymes and fermenting microorganisms by removing toxins and inhibitors from bioreactor feed and fermentation broth

Relevance to Conversion Platform, BETO, and industry:
• Distinct molecular contaminants from bioreactor feed and metabolic intermediates in conversion deter the cost-effective production of biofuels/products by biocatalytic routes
• Targeted removal of toxins and inhibitors will increase production rates, extend biochemical catalyst lifetimes, enable reactor-integrated separations and process intensification.

Technology development:
Technical Approach (and Future Work) – Materials Synthesis

**Approach:** examine the utility of two varieties of solid, high-surface-area adsorbents

- Surface-treated, nanostructured polymeric networks
- Reusable, environmentally benign adsorbent foams

**Challenges and Critical Success Factors**

- Developing scalable, cost-effective syntheses
- Designing surface treatments with high capacity and selectivity
- Understanding factors which allow for materials reuse
- Minimizing materials and biological interferences

**Working towards quantitative separations targets** based on TEA

- Realistic projections for materials production costs at scale will be needed
- Demonstrated reuse (100X) within a bioreactor will be key for low-cost deployment
Technical Approach (and Future Work) – Targets and Costs

**Approach:**
- Target toxins from bioreactor feed and inhibitors from fermentation
- Develop economically-favorable, bioreactor-integrated processes

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**Challenges and Critical Success Factors**
- Selecting targets of greatest impact that are amenable to materials approach
- Developing bioreactor-compatible separations processes
- Increase titer, rate, and yield for bioreactor integration

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Working towards **quantitative separations targets** based on TEA
- Binding affinities/specificities may prove more important than materials reuse
- Indirect impacts: favorable TEA depends upon appreciating influences on other processes

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*Impurities and inhibitors can be removed in multiple stages of process to raise product titers and increase production rates*
Relevance: Develop novel materials for separations to specifically remove toxins and inhibitors from bioreactor inputs and fermentation processes

Progress to Date:
- Identified sets of target compounds
  - approachable with materials platform
  - many known to deter efficiency of bioconversion strategies using cellulosics
- Preparing process energy and material use data for cross-cutting analysis team
- Designing surface treatments for selective adsorption

Impact: Substantially improve titers, rates and yields and approach continuous fermentation to reduce costs of bioconversion of cellulosics to fuels and products

<table>
<thead>
<tr>
<th>Target Number</th>
<th>Toxin or inhibitory species</th>
<th>Bioreactor feed</th>
<th>Fermentation Broth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Furfural / methyl furfural</td>
<td>Butyraldehyde</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ferulic acid</td>
<td>Malondialdehyde</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Benzoic acid</td>
<td>Succindialdehyde</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Coumaric acid</td>
<td>Tolualdehyde</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Phenyl acetate</td>
<td>Isoprenoid species</td>
<td></td>
</tr>
</tbody>
</table>

Targets to be used to test the molecular recognition approaches used within the Biocatalyst Preservation Seed Project
Move cost-effective, high-performing separations technology to market faster, targeting challenges relevant to BETO’s priority pathways and industry.

Harness expertise across eight national labs to undertake research projects informed by their influence on process economics. Concentrate efforts in biochemical, thermochemical, algal, ionic liquid separations.

Technical work commenced. Industrial advisory board engaged and listening day scheduled. Cross-cutting analysis team engaging with teams to advise regarding technology influence on process economics.

The consortium addresses separations challenges identified in the MYPP, strategic plan and by industry that are a significant contributor to biofuel and bioproduct production costs.

Informed through techno-economic and life cycle analyses & industry engagement, the consortium will carry out a portfolio of research covering biochemical, thermochemical, algal, and ionic-liquid based processes.
QUESTIONS?
ADDITIONAL SLIDES
The Bioprocessing Separations (BioESep) Consortium Industry Advisory Board (IAB) will represent experts from industry and other entities in bioenergy, biomanufacturing, industrial biotechnology, and related fields. The IAB will help the consortium maintain an industry-relevant focus and knowledge of recent technology advances and challenges. BioESep anticipates that the IAB will be comprised of 7-9 members on a 3-year rotation, with the ability to continue beyond should the interaction be mutually valuable.

The board will meet with the steering committee and team leads quarterly, with two meetings in person per year. The board will provide advice to the steering committee and team leads, review results and progress in comparison with work plans, provide feedback regarding prioritization of research projects (experimental and analytical), and inform development of the consortium’s strategy for out years. Furthermore, the IAB will help in planning an industry workshop within the first year of BioESep insofar as providing feedback regarding the agenda and identifying relevant invitees.
Relevance to MYPP goals and barriers

<table>
<thead>
<tr>
<th>MYPP Goals and Barriers</th>
<th>Consortium Approach to Addressing</th>
<th>MYPP citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separations and cleanup are overarching issues in conversion</td>
<td>The consortium was created to address this key challenge.</td>
<td>2-67</td>
</tr>
<tr>
<td>Cost-effective routes to eliminating impurities in intermediates that inhibit chemical and biological catalysts</td>
<td>The Biochemical Separations and Biochemical Catalyst Preservation Teams both address this barrier.</td>
<td>2-68, 2-73</td>
</tr>
<tr>
<td>BETO is targeting improved separations processes to increase yields and purity including solid-gas (e.g., hot gas filtration), solid-liquid, gas-liquid, and liquid-liquid separations.</td>
<td>The Thermochemical Separations team’s catalytic hot gas filtration project addresses this barrier whereas the overall consortium addresses many of these areas of interest.</td>
<td>2-76</td>
</tr>
</tbody>
</table>