Bioprocessing Separations Consortium
Volatile Product Capture

- March 11, 2021
- Technology Area Session: Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics

- Philip Laible, Eric Sundstrom, and Edward Barry
- ANL, LBNL, LANL

Project Overview: Biorefining Separations Challenge

Problem: A wide range of biosynthetically-produced molecules partition readily to fermenter off-gases and are lost; no current technologies specifically address capture and recovery of low concentration organics from off-gas streams

Goal: Alleviate losses by application of advanced materials approach; enable bio-production of volatile toxic products via in situ off-gas stripping

Current approach: Limited studies use two thermally intensive steps - condensation of humid off-gases & distillation of product from condensate

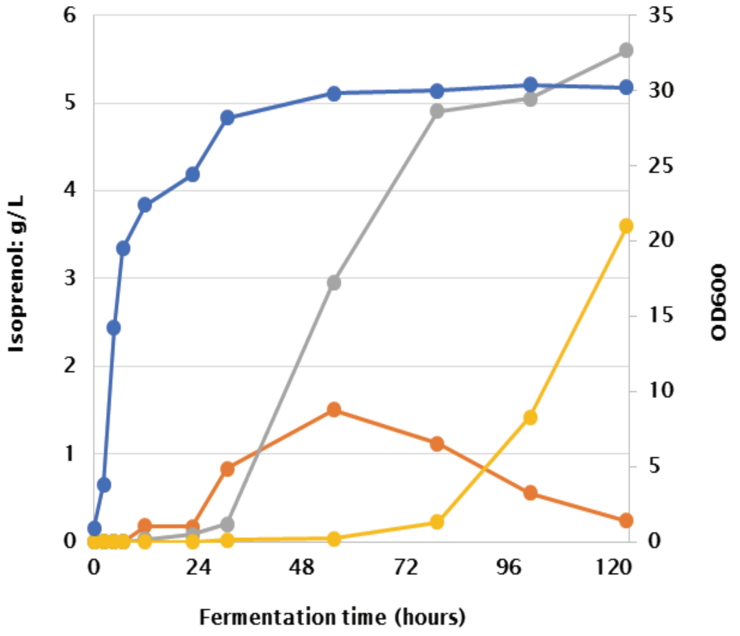
Importance: Volatile loses can be significant; without a low-cost solution many high volatility product classes may be unapproachable

Risks: Can materials be designed for high-gas flow and specificity for product; can materials syntheses and processes be successfully scaled?

Broad Applicability

Representative volatile aerobic fermentation products	
Alcohols	isoprenol, prenol isopentanol
Terpenes	Cineole, limonene, farnasene
Ketones	methyl/ethyl isopropyl (isobutyl) ketone
Aromatics	3-methyl anisole m-cresol
Olefins	isoprene

Isoprenol volatilization (typical conditions)



Origins of volatile bioproducts insights

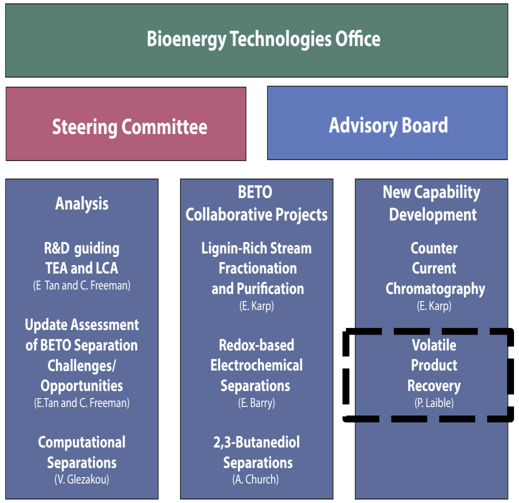
- Discussions with potential Directed Funding Opportunity partners
- Interactions with Advanced Demonstration Unit users at LBNL
- Energy I-Corps interviews with industry stakeholders
- Interactions with other BETO consortia scientists (Co-Optima, Agile BioFoundry)

1 – Management

Interacting Component	Lead(s)	Major Responsibilities
Materials design and construction	Philip Laible Edward Barry	Engineering of advanced materials for high gas flows and selective recovery of volatile bioproducts
Scaled process engineering and performance evaluation	Eric Sundstrom	Process development for scaled deployment of advanced materials and analytics in pilot plant
Computational-guided materials optimization	Vanda Glezakou	Multi-scale modeling to obtain first-principles of materials approach
Techno-economic and life-cycle evaluations	Charles Freeman Jian Liu	Evaluate cost-effectiveness of materials approach and compare to baseline case(es)

Risks: At bi-weekly coordination meetings of experimental teams, factors that impact volatile product recovery are reviewed and mitigation strategies are evaluated (for known existing risks) and/or devised (for newly discovered risks).

Communication strategy: Monthly intra-task discussions coordinate teams towards milestone goals. Inter-task meetings amongst experimental, modeling, and analysis efforts coordinate materials and process designs. Bi-annual consortium meetings, as well as constructive feedback from the Industry Advisory Board, align this task with larger goals of the Separations Consortium, BETO, and the biomanufacturing industry.



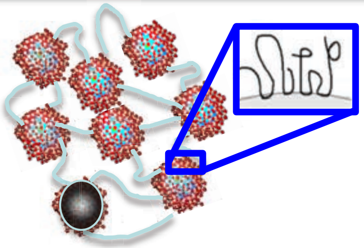
2 – Approach: Advanced Materials Application

Strategy: Reduce operating costs and complexity of volatile product recovery via highly specific and tunable gas-phase adsorbents:

- Utilize selective nanostructured adsorbents
- Passive, non-thermal, adsorptive capture
- Facile product recovery via compression
- Eliminates continuous condensation and solvent stripping
- Extracts pure product without dewatering or distillation

Xerogels

Networked Nanoparticles



Polymeric Foam

Key Challenges:

- Designing materials with high specificity for product of interest while maintaining high gas flow
- Designing scalable and economically viable processes that incorporate advanced materials capture

Key Metrics:

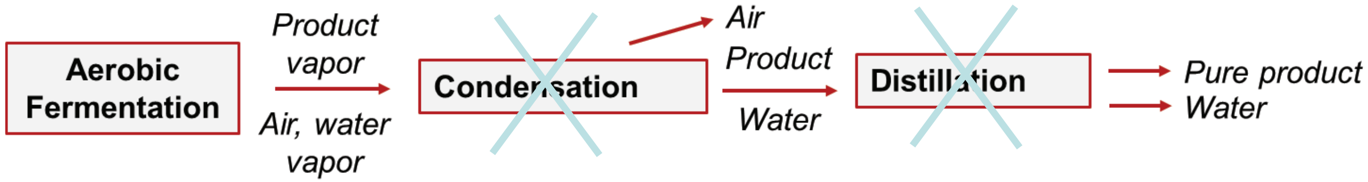
- Product capture efficiency, adsorbant capacity, product purity, and adsorbant longevity
- Process economics must demonstrate operational and capital costs less than 50% of baseline case(s)

Xerogels used as the high-surface-area materials platform for testing of processes.

3 – Impact: Relevance to Industry

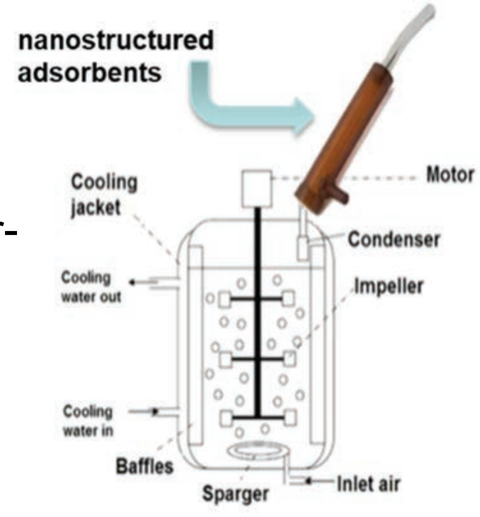
Classical condensation approach:

- High aeration and low product concentrations often necessitate condensation at -20C to -30C
- 70-85% recovery typical[1] – can necessitate further polishing via solvent stripping and distillation



Advanced materials approach:

- Condense selectively onto materials
- Utilize highly scalable synthetic processes
- Desorption with pressure/temperature swings
- Eliminate energy intensive steps
- Enhance recovery
- Enable production of toxic and/or high-vapor-pressure, low-titer bioproducts
- Broad applicability



Dissemination: Task C.2 work will be propagated to the biomanufacturing community as integrated result packages combining materials engineering, process design, computational insights, and techno-economic and life-cycle considerations. Primary routes for results dissemination are:

- Presentation at scientific meetings
- Publication in high-impact journals, and
- Protection by invention reports, leading to patent applications
- Direct engagement with industry partners and stakeholders

Facile vapor phase recovery would broaden the suite of product classes available for biomanufacturing

Biomanufacturing interest:

DMC
VISOLIS CARBON NEGATIVE MATERIALS
iMiCROBES
RHO Renewables, Inc.
amyris
DUPONT

1. F. Khan and A. Ghoshal, Journal of Loss Prevention in the Process Industries, 2000, 13:527

4 – Progress and Outcomes

Target prioritization:

Systematic down-selection from 15 candidate molecules with known strains based on:

- Chemical properties
- Physical properties
- Commercial Value
- Literature/patent info
- Strain availability
- Industrial interest
- BETO relevance
- Safety
- Commercial availability

Volatile aerobic fermentation products considered	
Alcohols	isoprenol, prenol isopentanol
Terpenes	Cineole, limonene, farnasene
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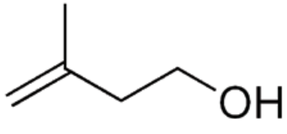
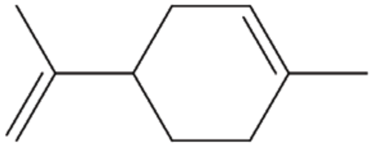
Aromatics	3-methyl anisole m-cresol
Olefins	isoprene

Initial target molecules prioritized:



Isoprenol



Limonene

Most product candidates are toxic to biocatalysts – offgas capture can double as *in situ* product removal

Strains sourced for biological testing:

Initial targets

DMC — *Farnesol, Limonene*

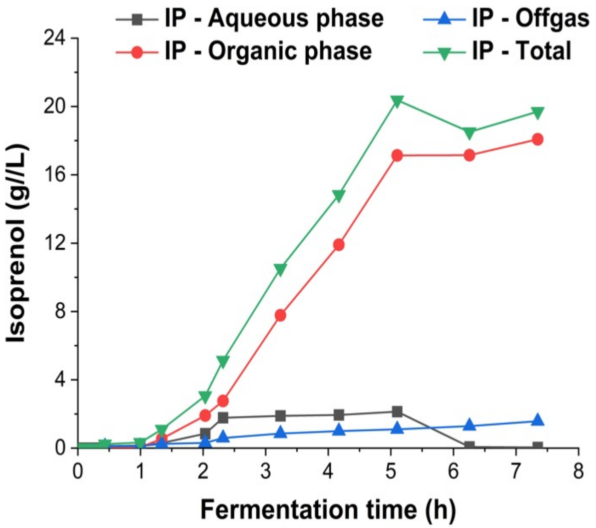
JBEI Joint BioEnergy Institute — *Isoprenol*

Potential future targets

RHO Renewables, Inc. — *3-methyl anisole*

VISOLIS Carbon Negative Materials — *Isoprene*

Agile BioFoundry — *Cineole*

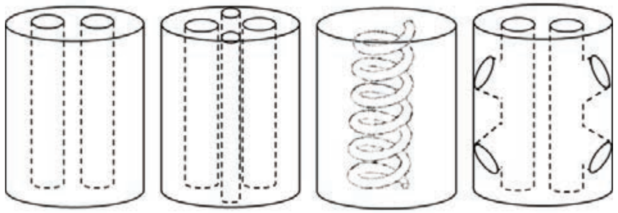


Priority strains and processes are successfully transferred for future off-gas capture studies

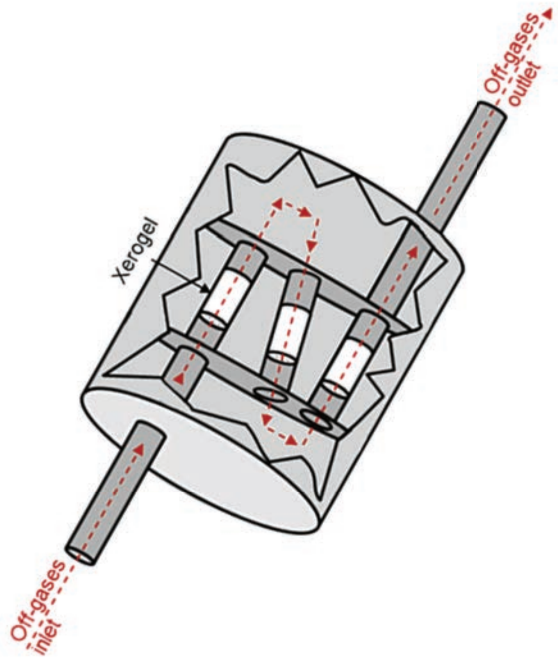
4 – Progress and Outcomes:

Facile materials synthesis strategies:

- Xerogel-based high surface area designs
- Macroporous structure incorporated facilitating airflow
- Tuned surfaces for selectivity in product recovery by leveraging earlier work on liquid-liquid extraction



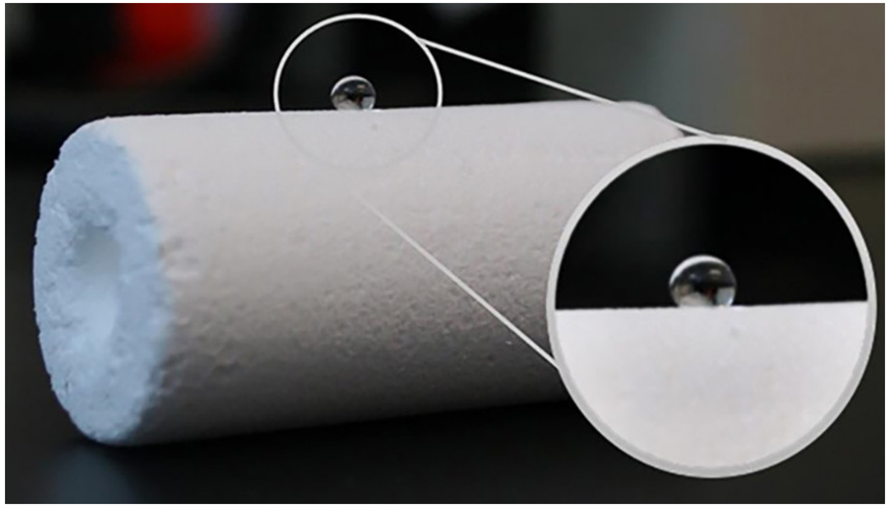
Additional macroporous structures under evaluation



High specificity for bioproduct in the presence of humid air:

Experimental conditions:

- 3 VVM agitation airflow
- 37ºC temperature
- 4 hours of exposure
- Test water co-recovery and binding capacity for product (before and after)



Engineered advanced materials for high gas flows and bioproduct recovery

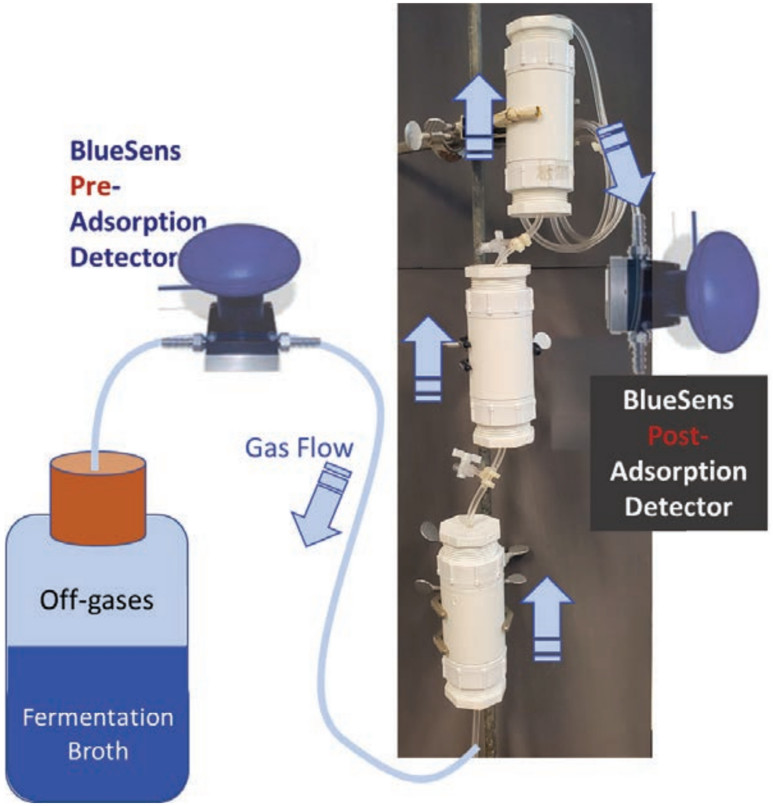
- Capacity for volatile product recovery unaffected by the presence of water vapor
- Water recovery insignificant

4 – Progress and Outcomes: Volatile capture cartridge design

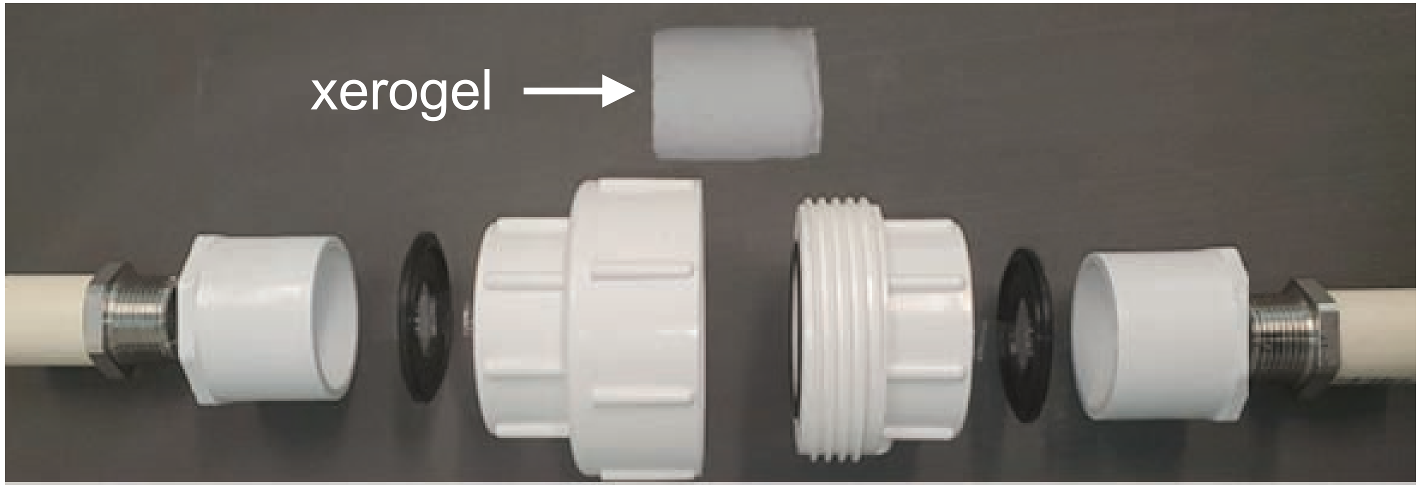
Cartridge Goals:
1. Affordable, easy-to-use adsorption system
2. Scalable design
3. Airtight design with limited opportunity for non-xerogel condensation

Sensor Goals:
1. Ensure the continuous quantification of volatiles
2. Understand in real-time levels of captured volatiles

Conceptual Multi-stage Designs



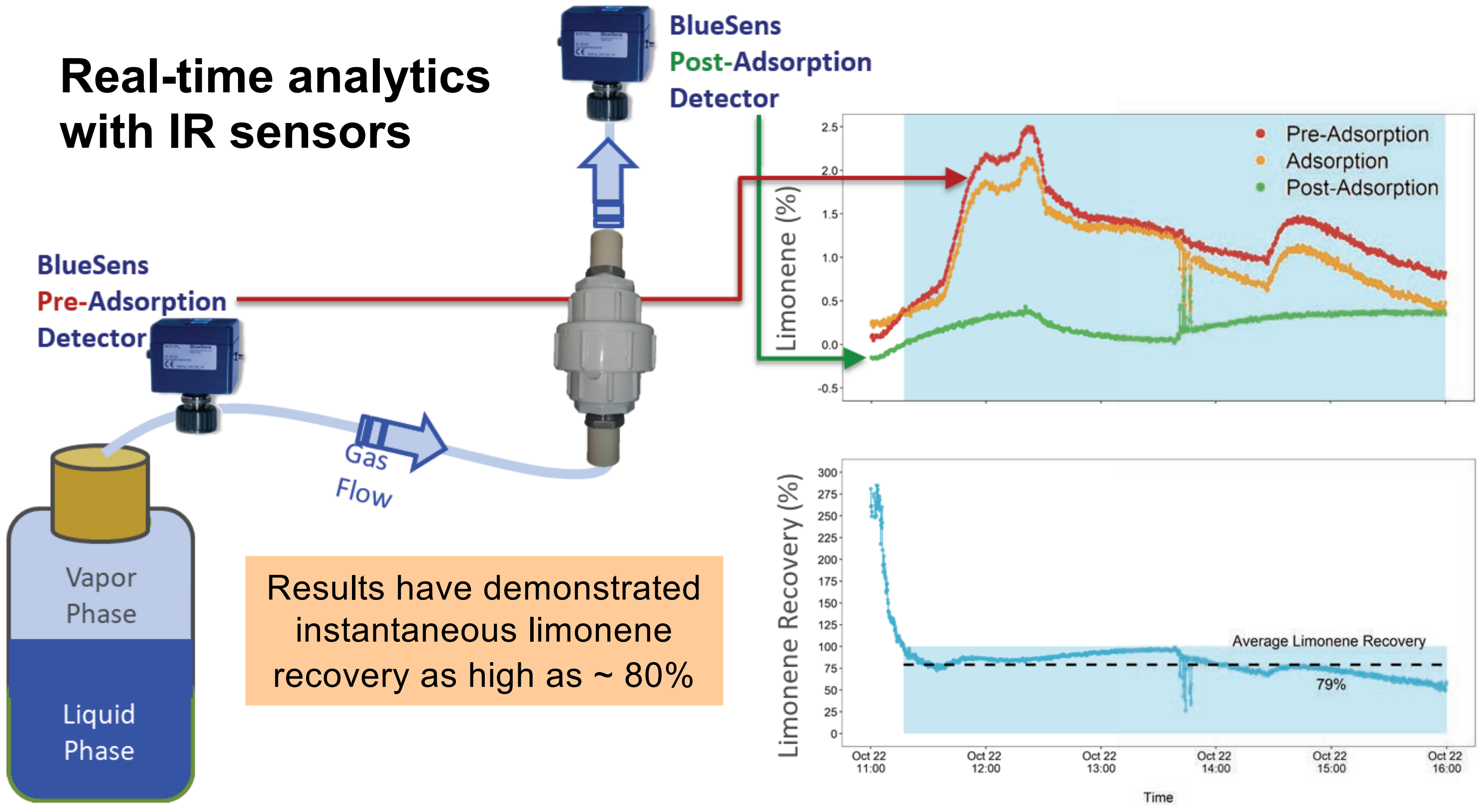
Initial prototype used in testing



PVC-based cartridge prototype and in-line sensor systems ready for use in materials evaluation and process scaling.

4 – Progress and Outcomes: Limonene adsorption testing

Real-time analytics with IR sensors



Results have demonstrated instantaneous limonene recovery as high as ~ 80%

Instantaneous measurements of recovery provides means to test larger number of materials and processes in less time.

Towards scaled demo

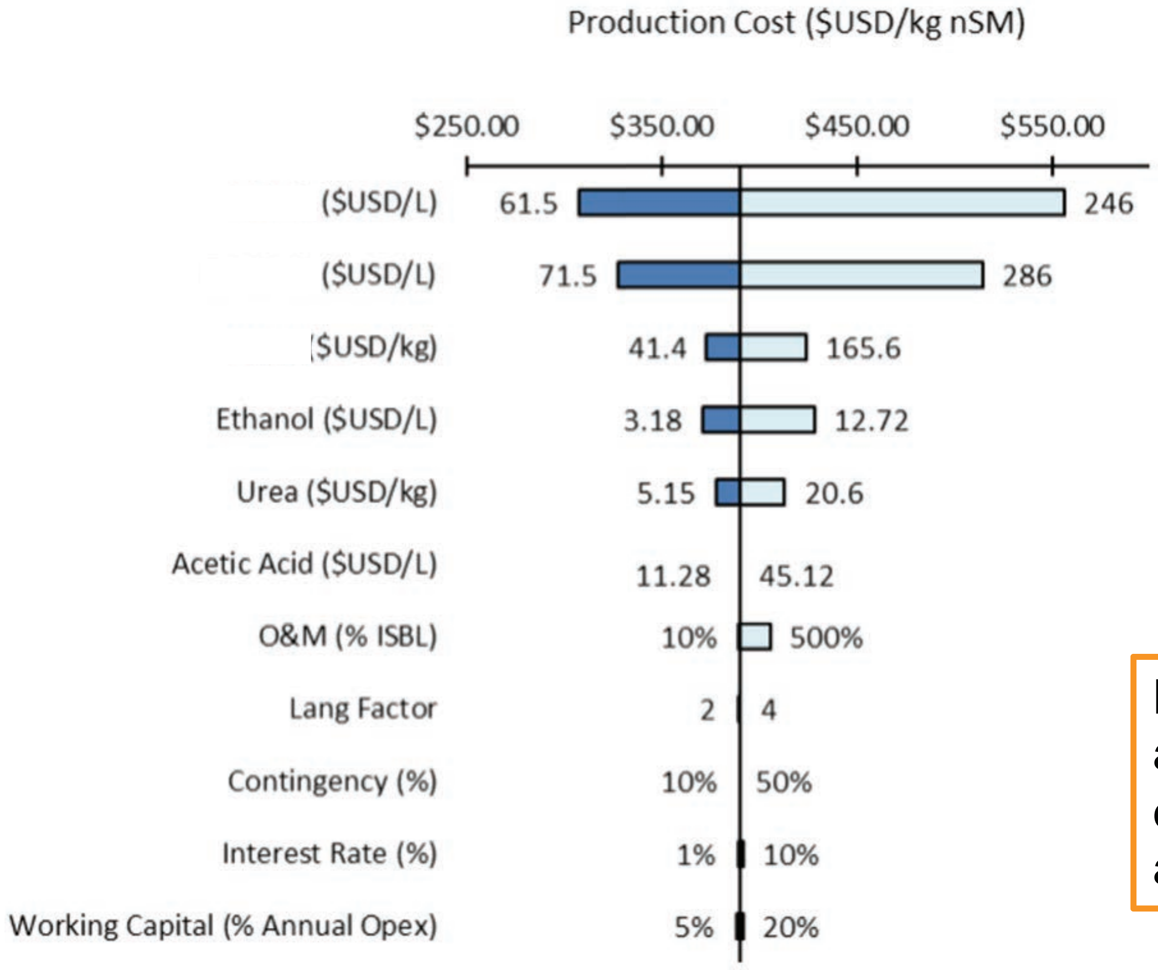
- 1L Scale – 1% limonene
- batch addition
- 2 VVM airflow

Results

- Volatilization complete (~5.5 hr)
- Adsorption onto xerogel: 48%
- Total recovery of system: 59%

Advanced-materials cartridge performed well in recovery of limonene. Tests with isoprene and modified designs ongoing. Recovery cartridges delivered to ABPDU for validation and scaled evaluation.

4 – Progress and Outcomes: Materials costs at scale



Working extensively with inCTRL Solutions to model and estimate materials costs at scale

- Assembled nanoscale materials production model
- Collected technical specifications and cost data from publicly available sources and subject experts
- Calculated costs estimates
- Identified cost drivers and evaluated sensitivities

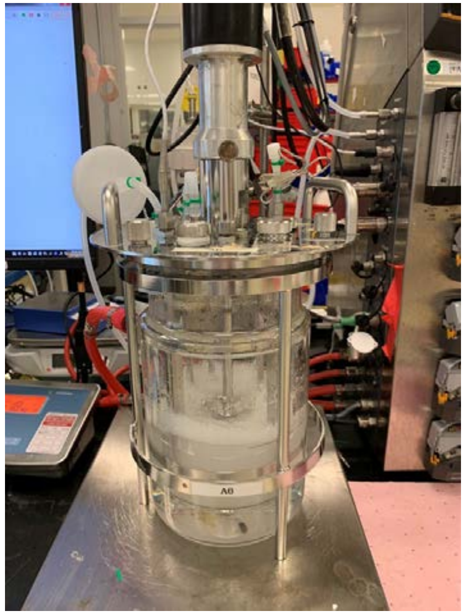
Conclusion:
scaled cost $0.39/g xerogel

Materials synthesis costs dominated by costs of polymerizing agents. The analysis suggests materials approach will be economic at scale, assisted by synthesis costs being amortized over many adsorption/desorption cycles.

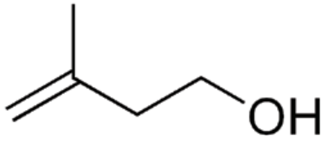
4 – Progress and Outcomes

Mock fermentation systems established

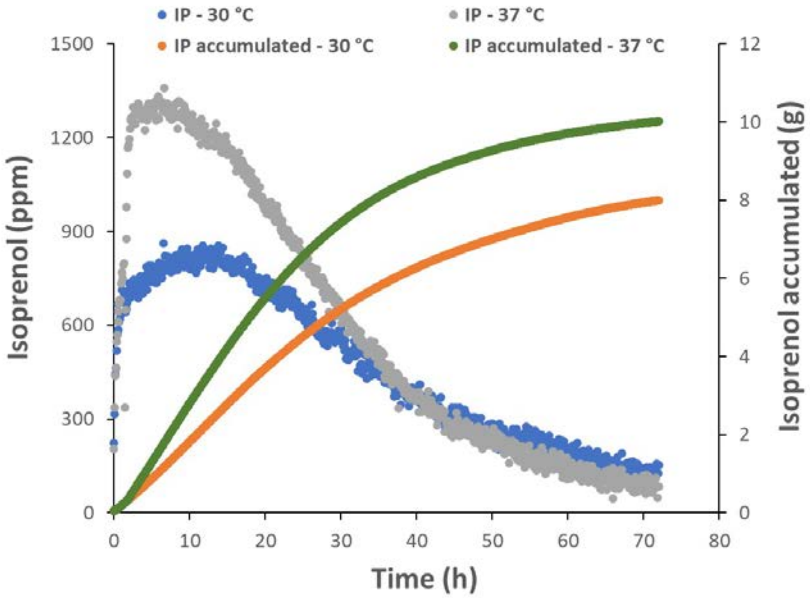
- Replicable test platform to evaluate adsorbents
- Validate offgas analysis and close mass balance
- Evaluate temperature and aeration effects
- Provide real-world offgas data to analytical team

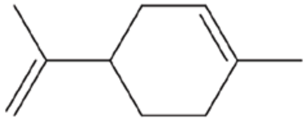


Mock fermentations inform and validate Aspen modeling efforts.

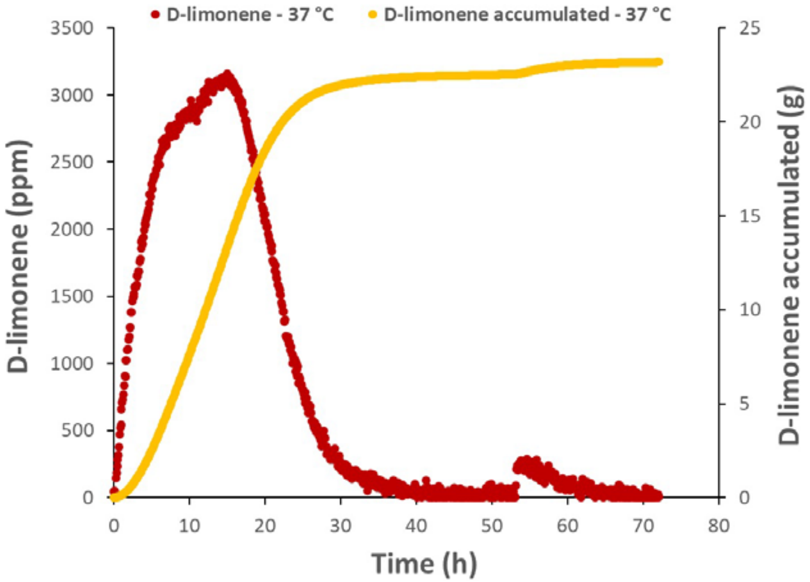


Isoprenol (IP)





Limonene



4 – Progress and Outcomes

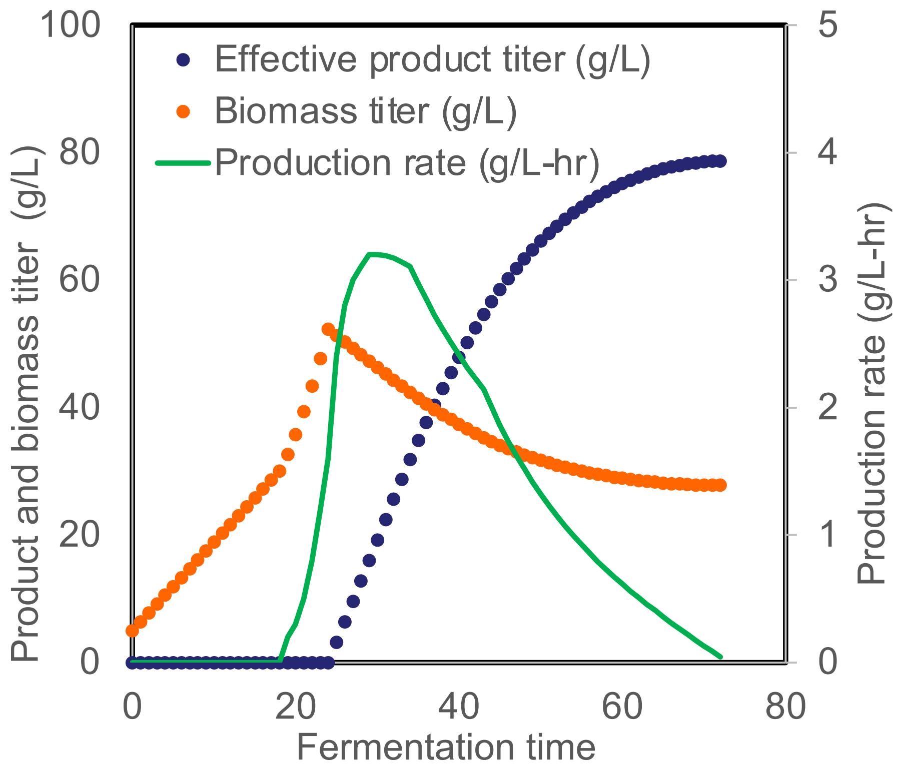
Metrics established for standardized offgas streams

- **Goal:** establish offgas characteristics representative of commercial streams for use in analytical modeling and adsorbent testing
- **Initial model:** steady state, production matches volatilization

Parameter	Value	Unit
Oxygen uptake rate	120	mmol/L-hr
Reaction quotient	1.4	mol CO2/mol O2
CO_2 emission rate	168	mmol/L-hr
Production rate	1	g/L-hr
Air flow	1	L/L-min
Air outflow temp	310	Kelvin

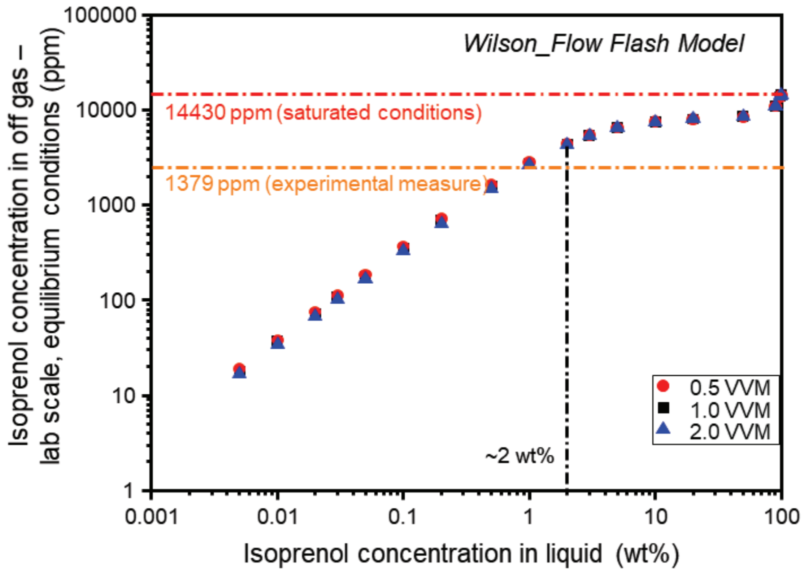
Standard offgas characteristics	
Total offgas flow	2.7 mol/L-hr
N_2	71.8 %
O_2	14.9 %
CO_2	6.2 %
H_2O	6.2 %
Isoprenol	0.4 %

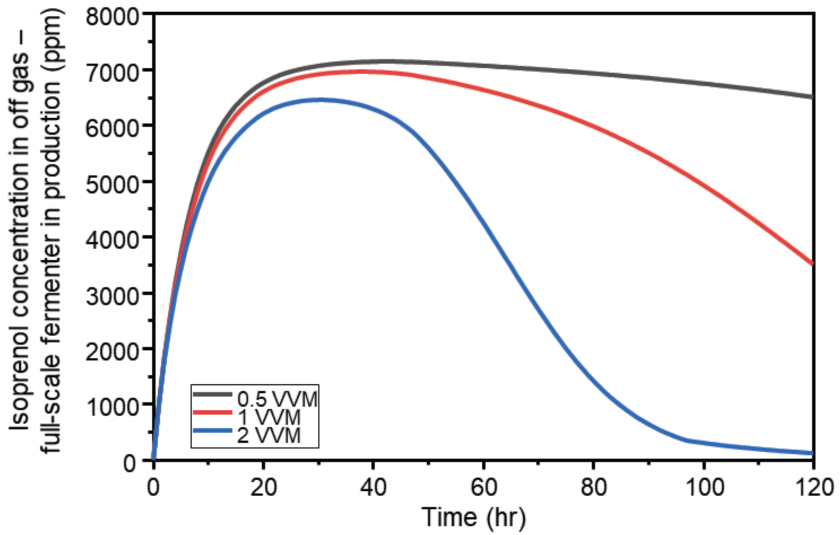
- **Updated model:** dynamic production conditions, tunable fermentation kinetics, wide range of offgas concentrations



Validated understanding of system allows for realistic predictions of product concentration in off-gas streams and effects of process modifications.

4 – Progress and Outcomes





Model Predictions of Product Losses to Off Gas

- Laboratory off-gas loss measurements used to fit model thermodynamic properties.
- Full-scale aerobic fermenter model developed: 250,000 liters, typical fermentation rates/ profiles
- Significant losses to off gas predicted for both isoprenol and limonene. Isoprenol estimates:
  - 100% after 120 hours at 2 VVM
  - 87% after 120 hours at 1 VVM
  - 50% after 120 hours at 0.5 VVM (68% after 168 hours)

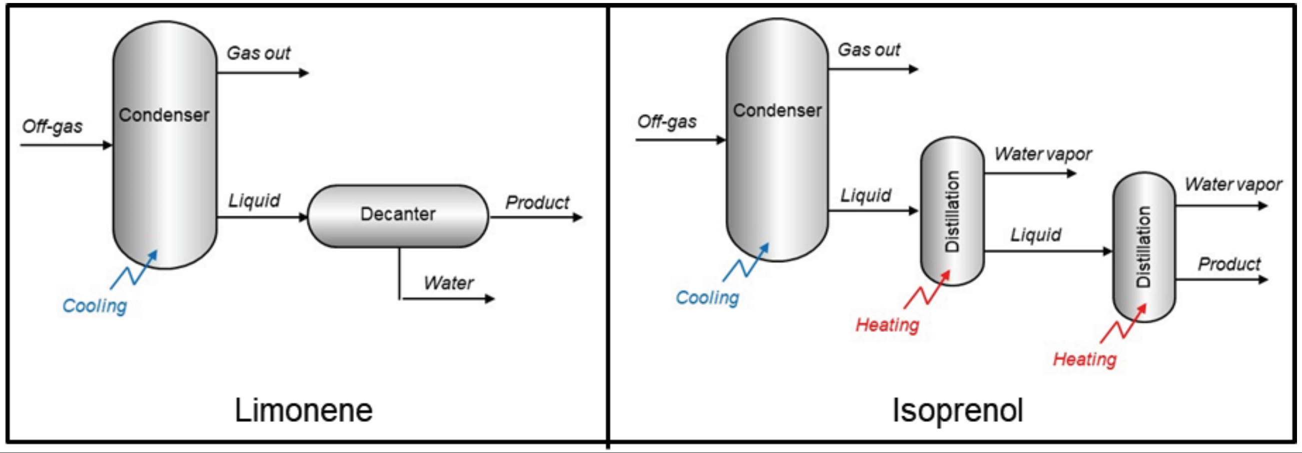
Data supports option for full volatilization via full product recovery from off gas, versus the broth.

4 – Progress and Outcomes

- Condenser-based recovery configurations developed and modeled for full-scale aerobic fermenter (250,000 liters, typical fermentation rates/ profiles).

- Limonene and isoprenol recovery yields estimated theoretically to be <90% and <82%, respectively. Adsorption technology aimed at higher product captures.

- Data analyses/ cost projections underway for new adsorbent technology, along with total cost (full plant) estimates.



Product	Limonene	Isoprenol
Estimated Average Flowrate of Product in Off-gas (kg/day)	9,403	7,488
Estimated Recovery from Off-gas using Condensation	<90%	<82%
Estimated Electricity Cost using Condensation (kWh/kg)	0.7	1.4
Estimated Capital Cost of Condenser Technology ($MM)	0.34	1.12

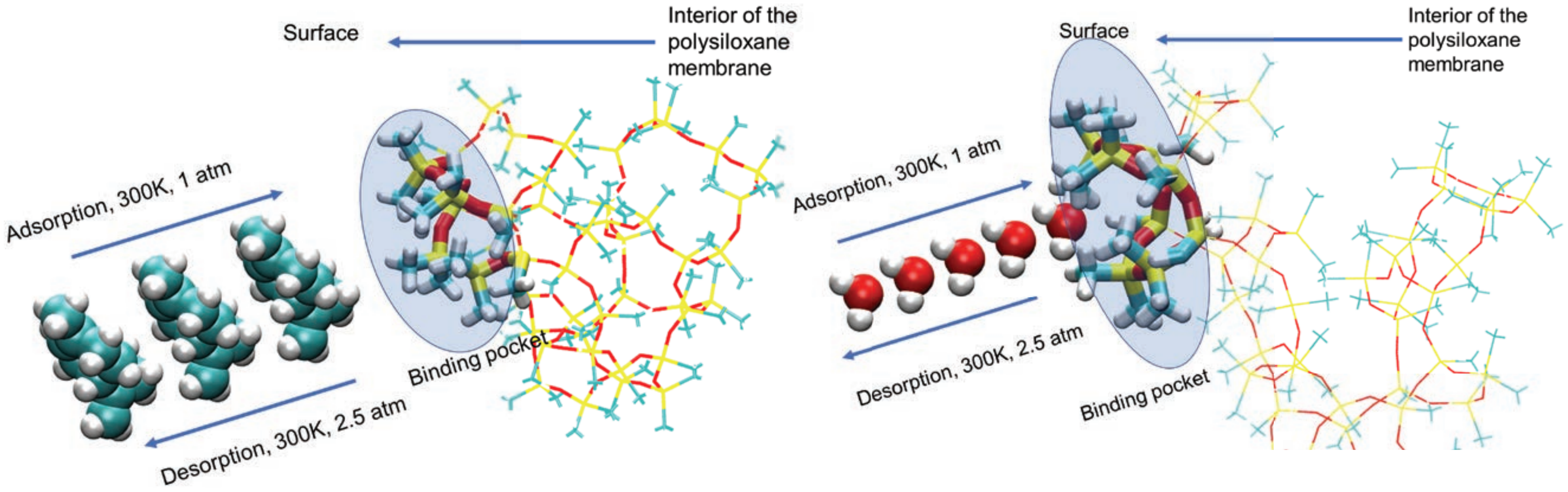
250,000 liter fermenter assumed.
Condenser temperatures set at 4°C and air flow rates at 1 VVM.

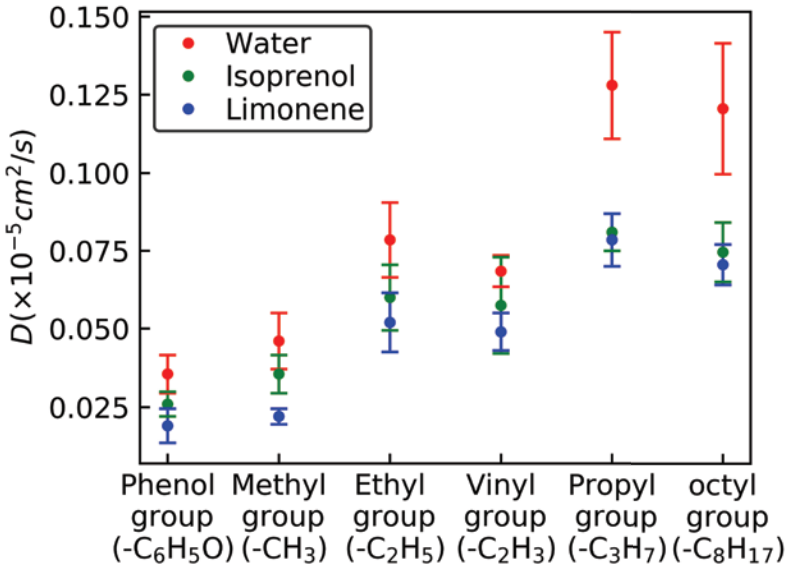
Baseline condenser/distillation case model nearly complete with TEA predictions of product recovery from fermenter off gases.

4 – Progress and Outcomes

Computation provides mechanistic insights to optimize volatile product recovery processes

- Quantify diffusion to drive enhanced binding of various volatiles
- Model selectivity of surface properties for product classes
- Uncover strategies to minimize co-recovery of water





Diffusion coefficients of VOCs and water

Key findings: Long-chain surface substituents bind limonene more selectively; Higher pressure superior to higher temperature as a driver for desorption.

Computational work leading to understanding of surface properties and predictions for improved product capture.

Summary

Management	Frequent interactions and coordination enable interdisciplinary team to achieve our goals.
Technical Approach	Generated advanced materials with varied macroporous designs that enable commercially viable recovery of the majority of volatile bioproducts from aerobic fermentation processes.
Impact	Knowledge and tools that mitigate the risks posed by production of volatiles by aerobic (or anaerobic bioconversion processes – minimizing product losses and reducing the costs of recovery of this important and growing class of bioproducts for the biomanufacturing industry – condensing and concentrating product rapidly minimizing flammability risks
Progress	Demonstration of scaled production and performance of advanced materials that tolerate high flows of humid fermenter off-gas streams that selectively recovery volatile bioproducts – validation and performance (capture of >50% of volatile products with < 20% co-recovery of water/impurities) at pilot (≥ 50 L bioreactor) scale – computation-guided design initiated for next-generation materials – established initial materials costs estimates and baseline process comparisons

Quad Chart Overview

Timeline
- October 1, 2019
- September 30, 2022

	FY20	Active Project
DOE Funding	(10/01/2019 – 9/30/2020)	$500K

Project Partners*
- SepCon Task D.2
- SepCon Task D.3

Barriers addressed
Ct-O – need for separation of organic species in biomass processes for upgrading to final fuel products

Ct-K – need for separations processes for bioproducts spec'd for the chemicals market

Project Goal
Develop scalable and economic processes based upon advanced materials –designed for high gas flows from aerobic fermenters – for selective recovery of volatile bioproducts in high yield

End of Project Milestone
On the 2-L or larger scale, demonstrate recovery of ≥ 75% of total product and recovery/release of at least 50% of product with < 30% water using advanced materials approach. Process should demonstrate 50% cost savings over condensation/distillation approaches.

Funding Mechanism
Specify lab call topic and year, if applicable.

*Only fill out if applicable.

Additional Slides

Responses to Previous Reviewers' Comments

- This project is a new start. As such, we have no responses to comments and questions from past reviews.

Publications, Patents, Presentations, Awards, and Commercialization

- The earliest studies of baseline technology applied to the isoprenol case is nearing completion and will form a stand-alone publication. The materials approach will be published after optimized recovery and scaled validation (experiments that are currently underway at ANL and LBNL).
- A utility patent to the use of xerogels in bioproduct recovery has been filed.
  - P. Ignacio-deLeon and P.D. Laible. SURFACTANT-TEMPLATED SYNTHESIS OF NANOSTRUCTURED XEROGEL ADSORBENT. USPTO serial # 16/228,593. Filed December 20, 2018.
- An invention report on volatile product recovery using an adsorbent-based cartridge has been submitted.
  - P.D. Laible and N.P. Dylla. ANL IN-20-152. Adsorbent system design for capture of volatile products in biomanufacturing. November 30, 2020.