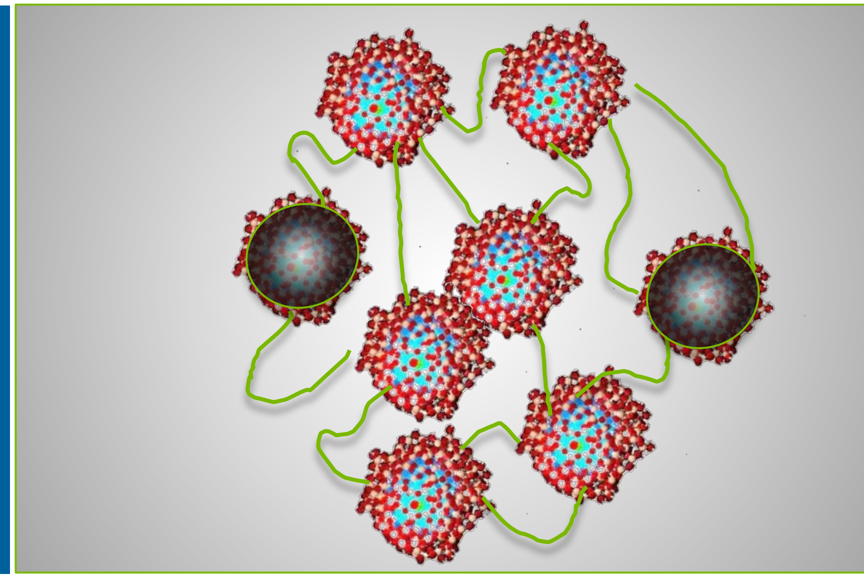
U.S. DEPARTMENT OF ENERGY (DOE)
BIOENERGY TECHNOLOGIES OFFICE (BETO)
2017 PROJECT PEER REVIEW

Low-Energy Magnetic Field Separation of Hydrocarbons using Nanostructured Adsorbents



PHILIP D. LAIBLE
Biophysicist
Argonne National Laboratory

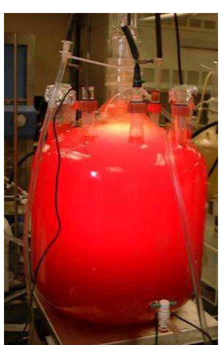
March 8, 2017 (2:00 – 2:30)
Denver, Colorado

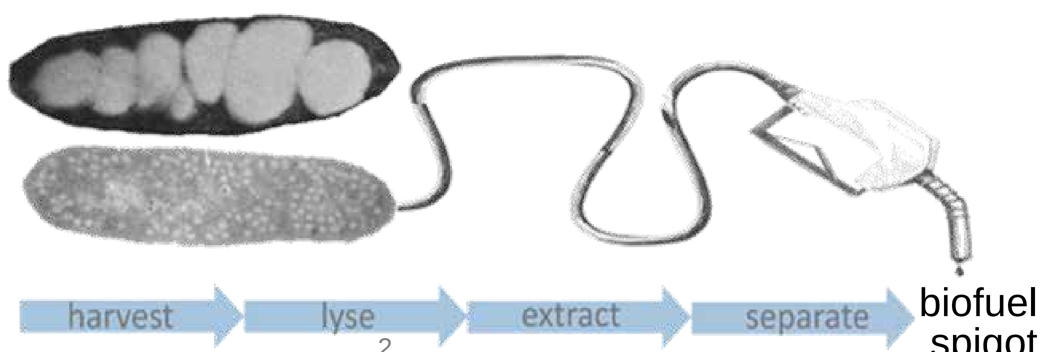
PROJECT GOALS

Develop novel materials by chemically modifying and linking high-surface-area nanoparticles to specifically remove biofuels and bioproducts from fermentation streams

Specific outcomes:

- Improve biochemical conversion process through integration of nanostructured adsorbents as separations agents in fermentation
  - Allows for continuous fermentation
  - Limit difficulties with toxins or product inhibition
- Demonstrate and scale low-energy, adsorbent-based separation of biofuels
  - Reduces process energy use and improves process economics
  - Establish syntheses compatible with activities of industrial partners
- Enable biofuels production from sustainable feedstocks that are cost-competitive with conventional fuels by reducing costs to separate fermentation end-products





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QUAD CHART OVERVIEW

Timeline

- Project start date: Oct 1, 2014
- Project end date: Sept 30, 2017
- Percent complete: 75% current cycle

Barriers

- Bt-H. Cleanup/Separation
- Bt-J. Biochemical Conversion Process Integration

Budget

	Total Costs FY 12 – FY 14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY 17-Project End Date
DOE Funded	$583,245	$339,351	$274,800	$352,595

Project Type: Sunsetting

Partners

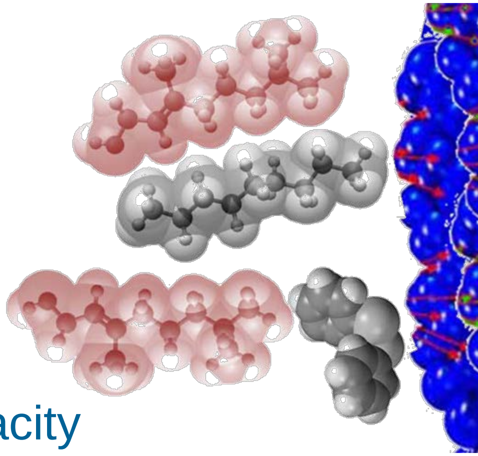
- Potential Tech-Maturation
  - Nanophase Technologies (Lemont, IL)
- Leveraged activities
  - Existing ARPA-E Phase II research
  - ANL LDRD-funded efforts on magnetic nanostructures

1 - PROJECT OVERVIEW

- Leverage previous research successes
  - Cellulosic sugars dewatering/treatment pilot project (BETO)
  - Scaled surface-treatment process from sunscreen/cosmetics industries
- Demonstrate nanoparticle-based adsorbent separation of fuel surrogates from biochemical processes
  - Low-cost, scalable syntheses
  - Novel materials with high binding capacity and molecular selectivity
  - Low-energy recovery of product
  - Reusable materials
- Demonstrate materials integration into bioreactor environment
  - Limit materials interference to bioconversion process
  - Limit biological interference on separations approach
- Expand applicability to other biofuels processes
  - Target, initially, isoprenoid-based alcohols
  - Other exported biofuels and bioproducts
  - Removal of toxins / minimize product inhibition

2 – APPROACH (MANAGEMENT)

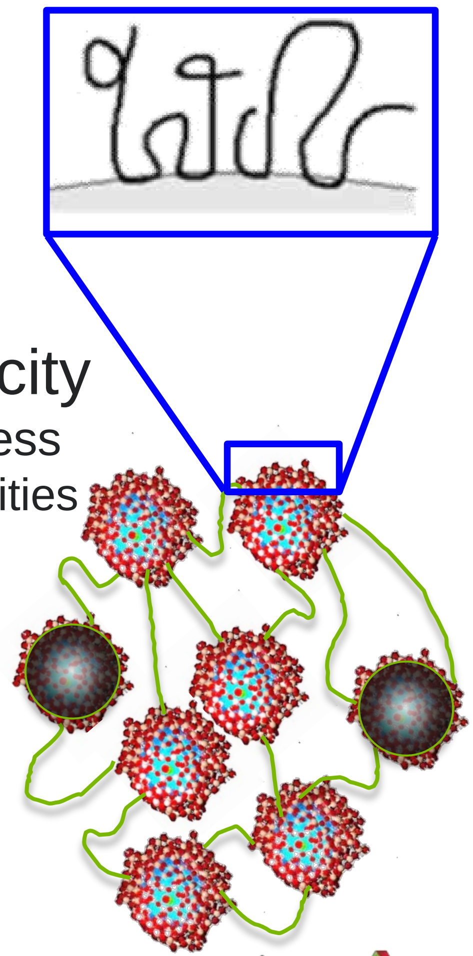
- Interdisciplinary Team Organization (less than 1 FTE in total)
  - PI: Philip Laible (microbial biofuels production; metabolic engineering)
  - Materials Specialists: Xing Chen, Patricia Ignacio-de Leon (postdoc), and Emily Rabe
  - Technical support: Deborah Hanson and Claire Kohout
  - Industrial outreach



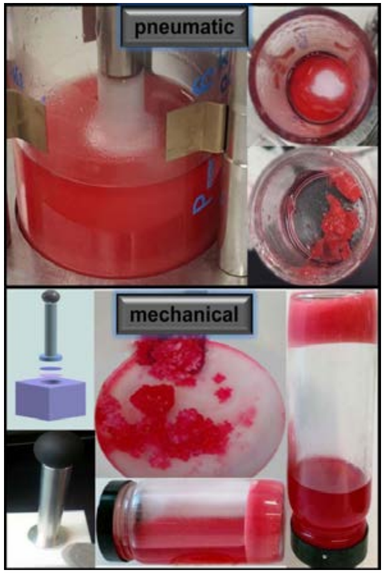
- Structure of approach
  - Challenging SMART, quantifiable milestones
  - Key go/no-go decision points
- Distributed project tasks
  - Fabricate nanoparticle aggregates at competitive costs
  - Adsorb fermentation products with high specificity and capacity
  - Determine low-energy processes for recovery of biofuels
  - Demonstrate cycling of NA to maximize cost benefits
- Potential challenges to be overcome for success
  - Process integration
    - Are the NA approach and fermentation processes compatible?
    - Does either process interfere with the other?
  - Costs must be well below traditional separation techniques
    - Comparison to L-L extraction and distillation

2 – APPROACH: NA SYNTHESIS, NETWORKING, AND SURFACE TREATMENT

- Synthesis of magnetic nanoparticles (Fe_2Co)
  - Utilize scaled solid-state reaction process
  - 250X less expensive than colloidal Fe_2Co materials
- Assembly of nanoparticles into aggregates
  - Chemically bind particles using polymer chains
  - Forms elastic network (similar to porous rubber bands)
- Surface treatments allow for adsorption specificity
  - Modify particle surface via heterogeneous gas-phase process
    - Flexible process allowing for variety of surface functionalities
    - No process solvents necessary
- Performance metrics
  - Adsorption capacity and specificity
  - Mechanical pressures needed for desorption
  - Ability to reuse by adsorbing and desorbing multiple times (cycle)

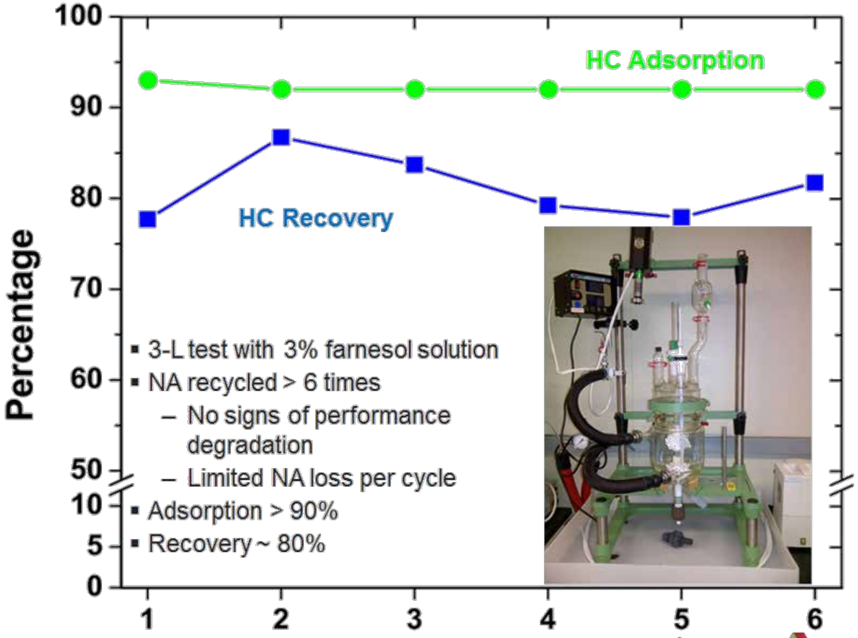


2 – APPROACH: HC RECOVERY AND NA REUSE



<u>Critical Success Factors</u>

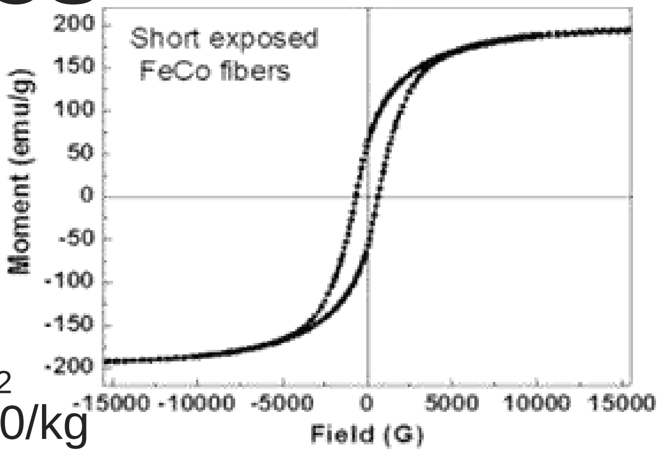
- Recovery of HC fuel
  - Isolation by magnetic separation or flotation
  - Desorption using magnetic and mechanical forces
- Reuse of NA
  - Return desorbed adsorbents to process stream
- Performance metrics
  - HC recovery
  - NA loss
  - Adsorption capabilities of recycled NA
- Cost/Performance comparison (compared to traditional approaches)
  - Must perform as well
  - Process costs < 30%



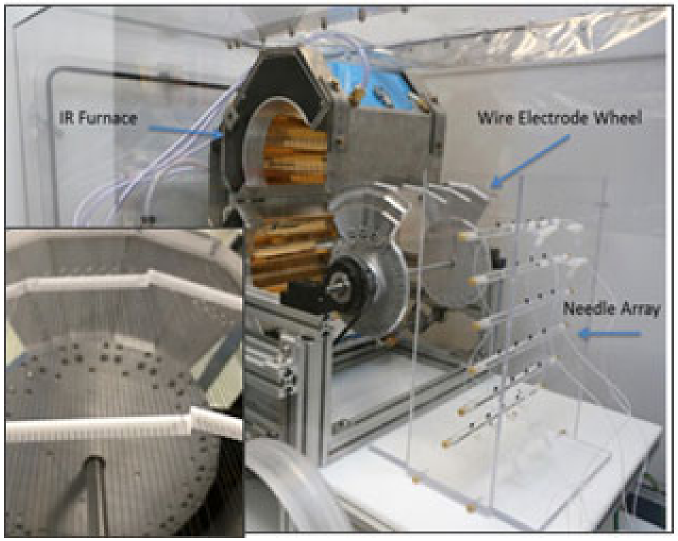
3 – TECHNICAL ACCOMPLISHMENTS

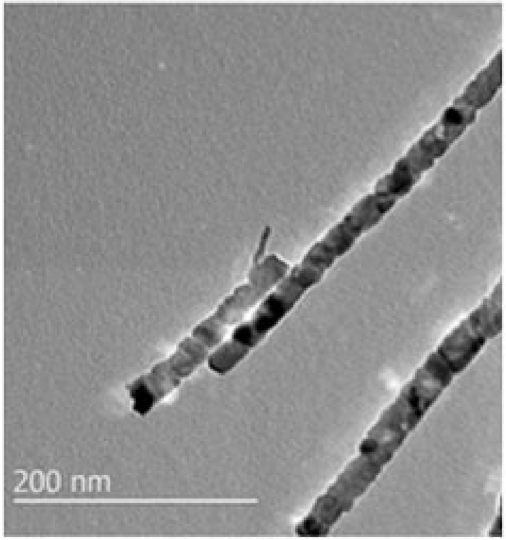
Task/Milestone	Planned Completion	Metrics	% Completion
Recycling of NA	30-Sep-2015	Number of cycles > 5	100
Scale lab synthesis to > 10L; evaluate properties	31-Dec-2015	Adsorption >80% product; desorb > 60%; >10 cycles	100
Integrate NA approach into bioreactor	31-Mar-2016	Sterile introduction into reactors; limited cell binding	100
On multi-L scale, evaluate costs	30-Jun-2016	NA process costs <40% of conventional approaches	100
Establish commercial specification sheet	30-Sep-2016	Quantify production, capac-ity and specificity metrics	100
Scale NA synthesis	15-Dec-2016	Commercial scale conserved performance	paused
Evaluate large-scale cost/performance	31-Mar-2017	NA process costs <30% of conventional separations	
Quantify biological interference	30-Jun-2017	Growth rates and production >80% without NA in process	
Test recovered product quality; NA reuse	30-Jun-2017	Recovered product > 90% pure; NA cycled 100s times	

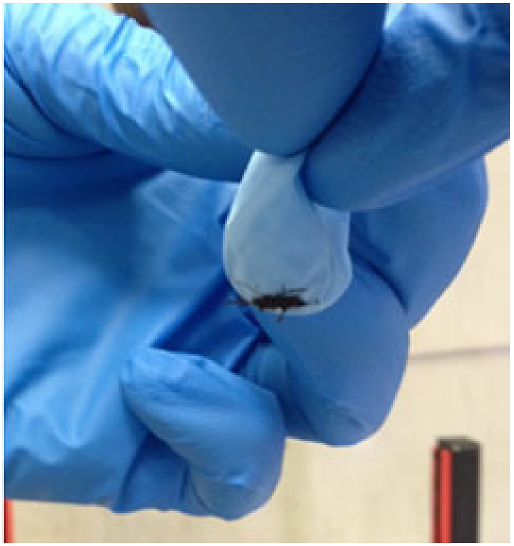
3 – TECHNICAL: NA SYNTHESIS INCORPORATING MAGNETICS



- Superparamagnetic Fe_2Co
  - Colloidal Fe_2Co:[1]
    - $15,000/kg
  - Solid-state reaction of $Fe(NO_3)_3$ and $Co(NO_3)_2$
    - Oxidize nitrates, fracture, reduction – $350/kg
    - Leverage advances from a Phase II ARPA-E project

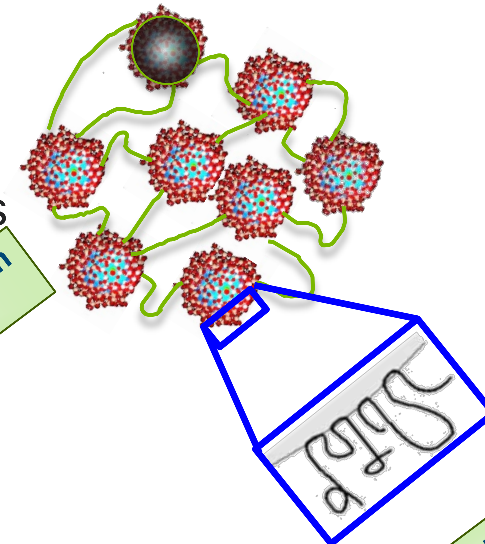






[1] *Adv. Mater.* (2006) **18**: 3154-3159.

3 – TECHNICAL: NA NETWORK AND SURFACE TREATMENT



- NA Network
  - Chemically bond nanoparticles using polymer chains
    - bi-functional coupling
    - 1,8-bis(triethoxysilyl)octane
    - bis(3-triethoxysilylpropyl)poly-ethylene oxide
  - Forms elastic network

ease in manipulation and reuse

- Surface Treatment
  - Heterogeneous vapor-phase polymerization – hydrocarbon adsorption
  - Hydrophobic: octyl (C_8), octadecyl (C_{18}), phenyl ($-C_6H_5$)
  - Hydrophilic: hydroxyl (-OH), amino ($-NH_2$), carboxyl (-COOH)
  - Characterized by swelling, TGA, IR

binding capacity / target molecule specificity

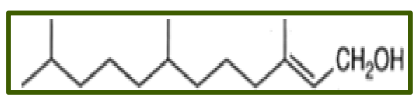
- Scalable Chemistries
  - Analogous reactions for other applications routine
  - Experience with scaling similar industrial processes

keeping costs of scaled syntheses low / favorable TEA

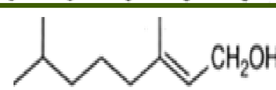
3 – TECHNICAL: NEXT-GENERATION-BIOFUEL TESTBED

- Adsorb isoprenols from doped fermentation broth
- Tune NA specificity to minimize broth-component interference
  - Minimal medium (restrictive approach; reduced chance of interference)
  - Rich medium (broad feedstock choices; increased chance of interference)
- Tailor surface-treatment affinities for branched fuel surrogates with varied chain length
  - Phytol (C_{20}; diesel)

  - Farnesol (C_{15}; diesel/ jet)

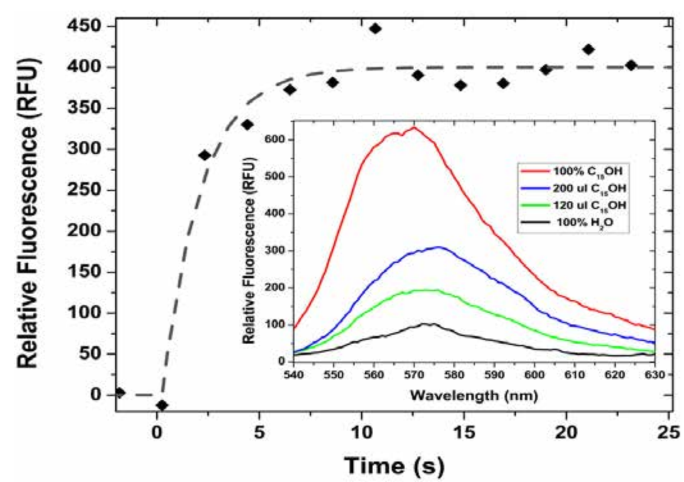


  - Geraniol (C_{10}; gas/jet)



  - Isoprenol (C_5; gas)

Kinetics of Binding of Farnesol



Adsorption at 5x weight of material complete in less than 30 seconds

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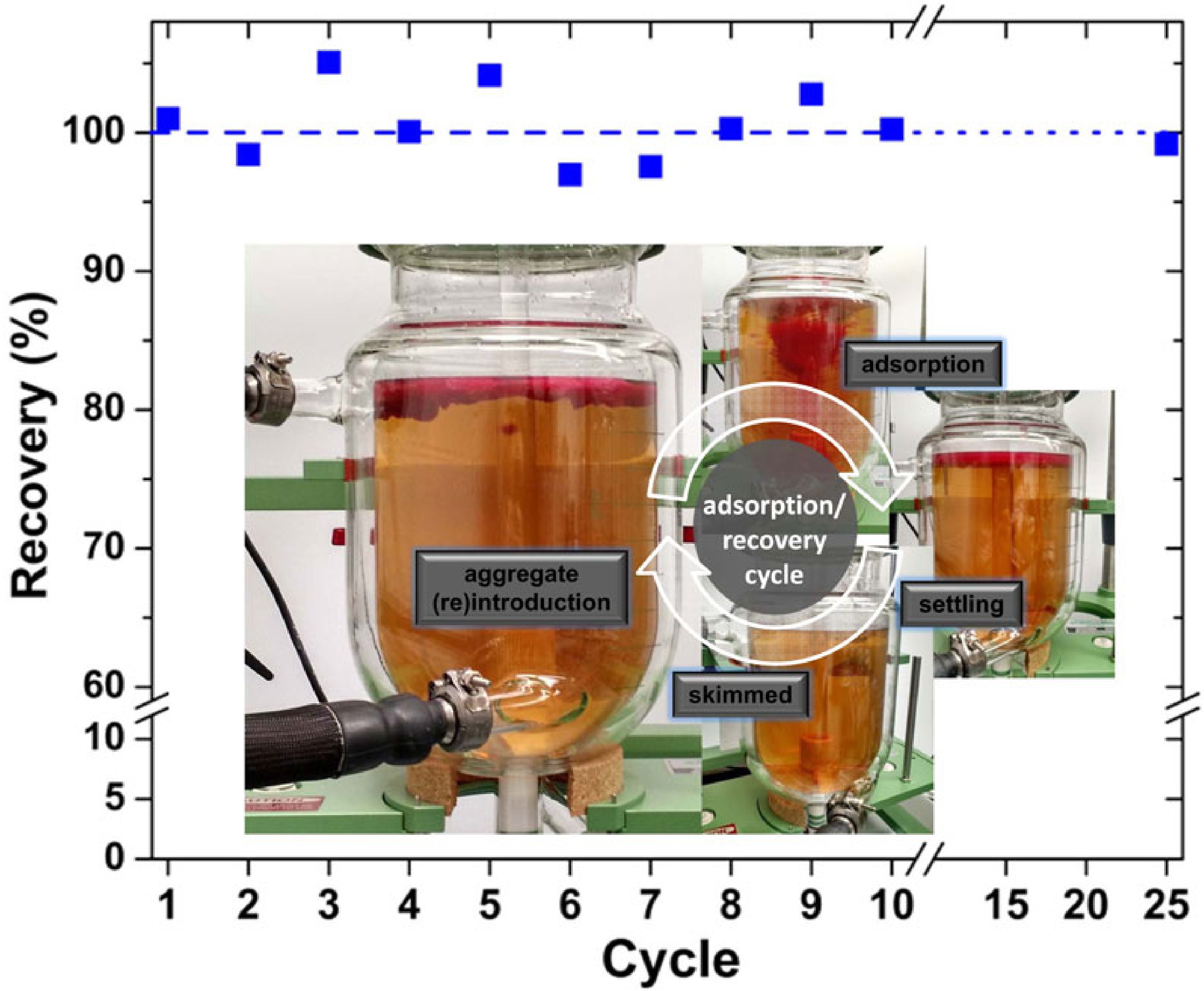
3 – TECHNICAL: SCALED NA PROCESS PERFORMANCE



- 10-L experiments
- 3% farnesol
- Adsorption > 95%
- Recovery > 95%
- NA recycled > 25 times
  - No performance degradation
  - Limited NA loss per cycle

Evaluation at increasing scale provides valuable metrics for cost/performance calculations/comparisons

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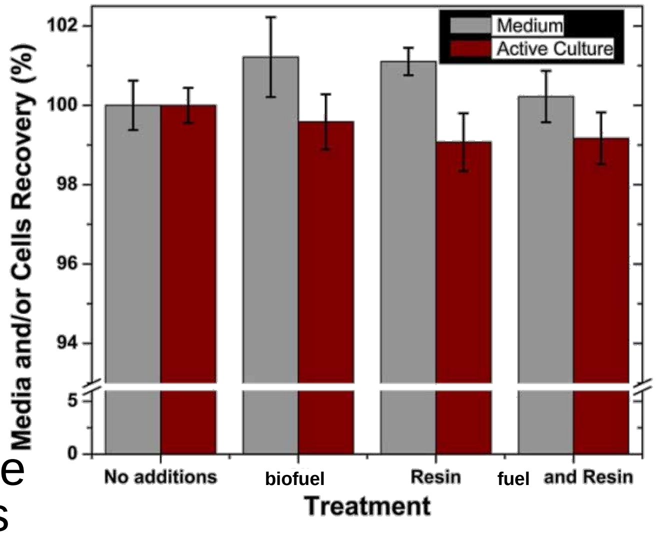
3 – TECHNICAL: INTERFERENCE STUDIES

- Study binding capacity and selectivity in fermentation conditions
  - Quantify biofuel purity
    - Can fuels directly meet production specifications without further purification?
- Are production strategies influenced by presence of adsorbents?
  - Monitor cell densities and doubling times
  - Compile list of reactor parameters than may be affected by integrated process

Integrated process results

- Biofuels recovered with high purity
- Production strains active in presence of adsorbents
  - Doubling times marginally increased
  - Notable variation in aeration of the cultures will be important parameter to control in scaled activities



Treatment	Cells Only	Cells plus NA	Cells plus NA plus biofuel
Doubling Time (hours)	16.3 ± 1.6	19.7 ± 2.1	20.6 ± 3.4

3 – TECHNICAL: COST COMPARISONS

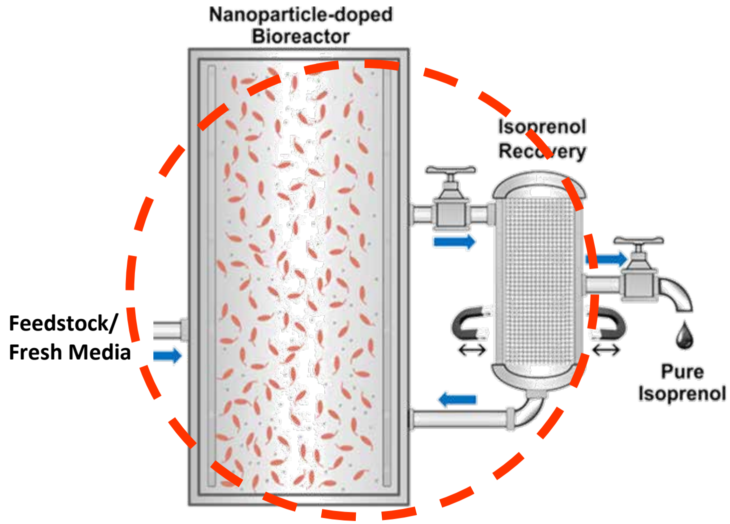
- Conventional solvent extraction/distillation costs evaluated
  - calculations strongly dependent upon the costs of solvents employed
    - e.g., large-laboratory or US-spot-commercial pricing
- On 10-L scale, NA processes found to be ≤65% cost of solvent methods
  - Leverage synthesis estimates obtained from cosmetic and sunscreen industries
  - Surface treatment modified to bind target product at 7X weight of materials
  - Additional cost reductions depend upon ability to further reuse materials
  - Cross-portfolio analyses possibly through Separations Consortium activities

Process	Operational Costs* ($GGE)
Conventional	8.41
Nanostructured Adsorbents	2.98

*Inclusion of CapEx in calculations – as difficult as it may be to estimate – would only further differentially raise the cost of the conventional approach. We note that the magnitude of OpEx above strongly depends on final titers/yields. These calculations based upon process with 3% biofuels yield. NA process expected to improve production parameters.

Bottom line: Even with the cheapest of solvents and limited NA reuse, the **NA approach appears exceedingly cost competitive**.

4 – RELEVANCE



- Decreased costs for biofuels production strategies
  - separations can account for as much as 50% of costs
- Improved biochemical conversion
  - Process integration and reduced separations expenses aid in meeting cost targets for conversion pathways
- Industrial Applications
  - Provides initial data sets on the feasibility of NA process(es) in separating products from bioprocesses
  - Directly approaches reaction-integrated separations: biofuel production and recovery in concert
  - Redirection could target and remove toxins from active production cultures
  - Intensified recovery to limit product inhibition and increase titers
- Direct involvement of Technology-to-Market partners
  - Early engagement of start-ups/industry working to bring forth innovation in scalable synthesis and NA-friendly bioreactor designs

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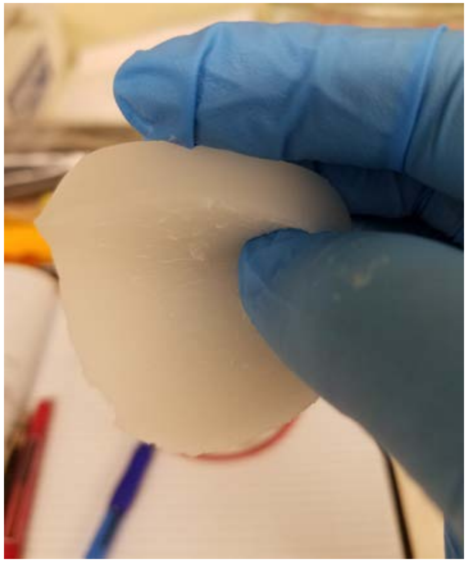
5 – FUTURE WORK



- Future FY17 Activities
  - Scale synthesis in commercial setting with attention to process economics
    - Confirm performance of scale materials
      - Binding capacity
      - Binding specificity
      - Desorption efficiency
  - Establish standardized, product-recovery processes for bioreactor-integrated operations
  - Demonstrate, at the 10s of gallons scale, that NA process costs are < 30% of conventional solvent extraction/distillation costs
  - Expand target sets: Join BETO Separations Consortium to leverage approach with targets exhibiting hydrophillic character that act as toxins or inhibitors in bioconversion processes
  - Survey BETO portfolio for applicable processes: identify projects producing biofuels or bioproducts that could be separated by these same or similar adsorbents (expanded process validation)

SUMMARY

- NA-based technologies are relevant to BETO's Bioenergy Technology Area and are proving feasible as a unique system for reactor-integrated separations
- The approach can be tailored for use in a wide separation process space; currently applied to hydrocarbon fuel recovery
- Low-cost synthesis, tunable surface treatments, flexible hybrid magnetic/compression recovery processes make NA approach attractive and competitive
- Cleared benchmarks at 10L scale and tests using commercially synthesized materials are underway
- The work leverages technology from ARPA-E, Argonne LDRD, and other BETO programs
- Technology transfer plans have been an integral component since project inception
- Expanded applications of approach to new classes of targets and additional fermentation platforms are logical next steps

EXTRA SLIDES

Publications, Patents, Presentations, Awards, and Commercialization

- Leveraged ANL Patent Applications / Awards
  - Chen X, Ziyao Zhou. USPTO 20170025729. Application number 15/082901. MAGNETIC NANOFIBER COMPOSITE MATERIALS AND DEVICES USING SAME. Filed March 28, 2016.
  - Yupo J Lin, Richard W Brotzman, Seth W Snyder. USPTO 20150041400. Application number 13/962480. COMPOSITIONS AND METHODS FOR DIRECT CAPTURE OF ORGANIC MATERIALS FROM PROCESS STREAMS. Filed August 12, 2013. Published February 12, 2015.
  - Laible, Philip D, Seth W Snyder. USPTO 20110302830. Application number 13/159340. ENGINEERED PHOTOSYNTHETIC BACTERIA, METHOD OF MANUFACTURE OF BIOFUELS. Filed June 11, 2010. Awarded September 13, 2016.

- Presentations
  - Laible, Philip D. and Emily J. Rabe. Materials Science & Technology 2015. “Nanostructured adsorbents as separating agents in integrated bioreactor processing.” within special symposium on Nanotechnology for Energy, Environment, Electronics, and Industry. October 6, 2015. Columbus, OH.

- Publications
  - Ignacio-de Leon, P.A., C. Kohout, E.J. Rabe, M. Puga, G.L. Grocke, P.D. Laible. Nanostructured adsorbents as separating agents for integrated bioreactor processing. ACS Nano. Submitted.