DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

2.5.5.100: Low-Energy Magnetic Field Separation of Hydrocarbons using Nanostructured Adsorbents

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Biochemical Conversion

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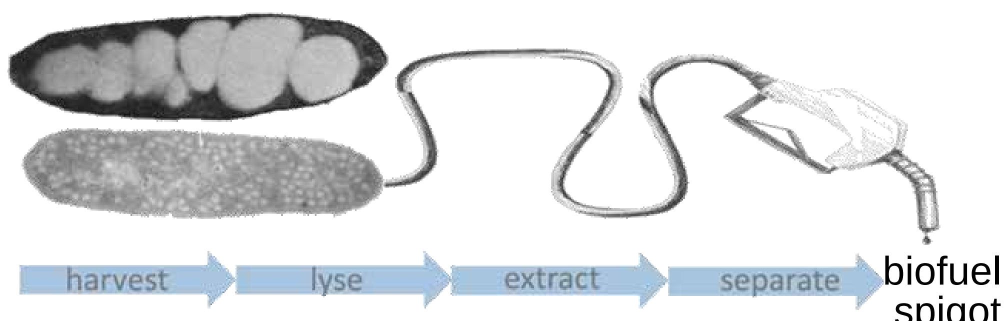
Project Goals

- 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 low-energy, magnetic field separation of hydrocarbon fuels
  - Reduces process energy use and improves process economics
  - Scale processes with industrial partner
- Enable production of biofuels from sustainable feedstocks and are cost-competitive with conventional fuels
  - Reduces dependences on foreign oil



Quad Chart Overview

Timeline

- Project start date: Oct 1, 2011
- Project end date: Sept 30, 2017
- Percent complete: 35% FY2015

Barriers

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

Budget

	Total Costs FY 10 –FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	$146,870	$182,995	$253,389	$966,746

Project Type: Existing

Partners

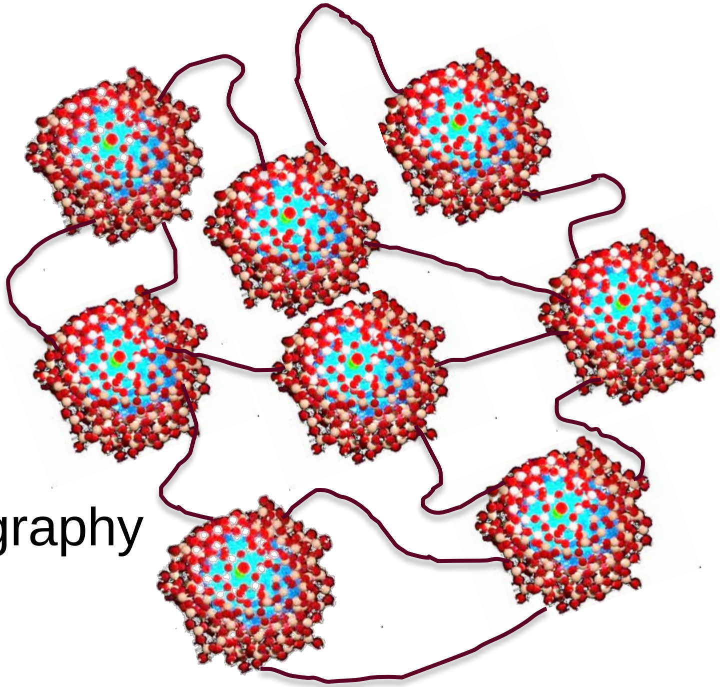
- T2M Partner: Forelight, Inc.
  - Scalable, (photo)bioreactor technology
- Leveraged activities
  - Existing ARPA-E Phase II research
  - ANL LDRD funded efforts on magnetic nanostructures

1 - Project Overview

- Leverage previous research successes
  - Cellulosic sugars dewatering/treatment pilot project (BETO)
  - Scaled surface-treatment processes from sunscreen/cosmetics industries
- Demonstrate magnetic nanoparticle adsorbent separation of fuel surrogates from biochemical processes
  - Reduce energy use and improve process economics
  - Establish and scale bioreactor-integrated separations
- Target, initially, isoprenoid-based alcohols
  - Overproduced & exported by engineered organisms
- Expand applicability to other biofuels processes
  - Other exported biofuels and bioproducts
  - Removal of toxins / minimize product inhibition

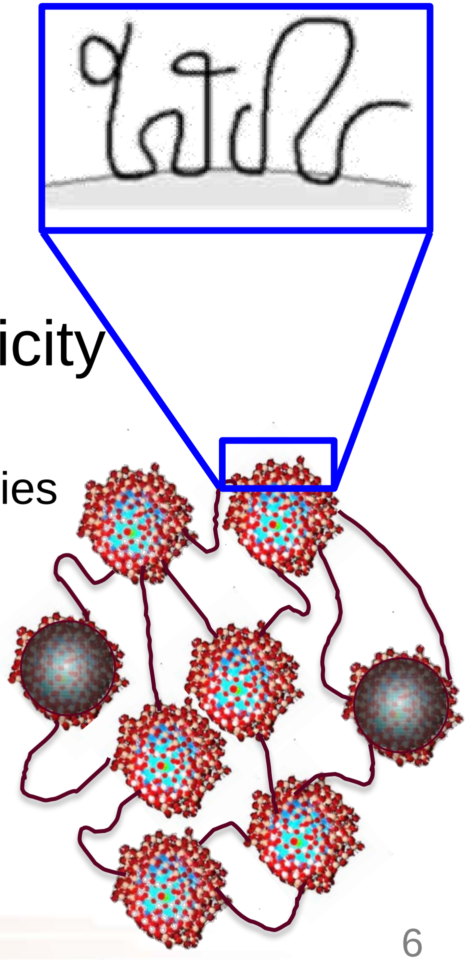
2 – Approach: Abbreviations

- HC: hydrocarbon
- NP: nanoparticle
- SN: superparamagnetic nanoparticles
- NA: nanostructured adsorbent
- IQ: installation qualification
- OQ: operation qualification
- PQ: process qualification
- TLC: thin-layer chromatography
- HPLC: high pressure liquid chromatography
- DLS: dynamic light scattering
- IR: Infrared spectroscopy



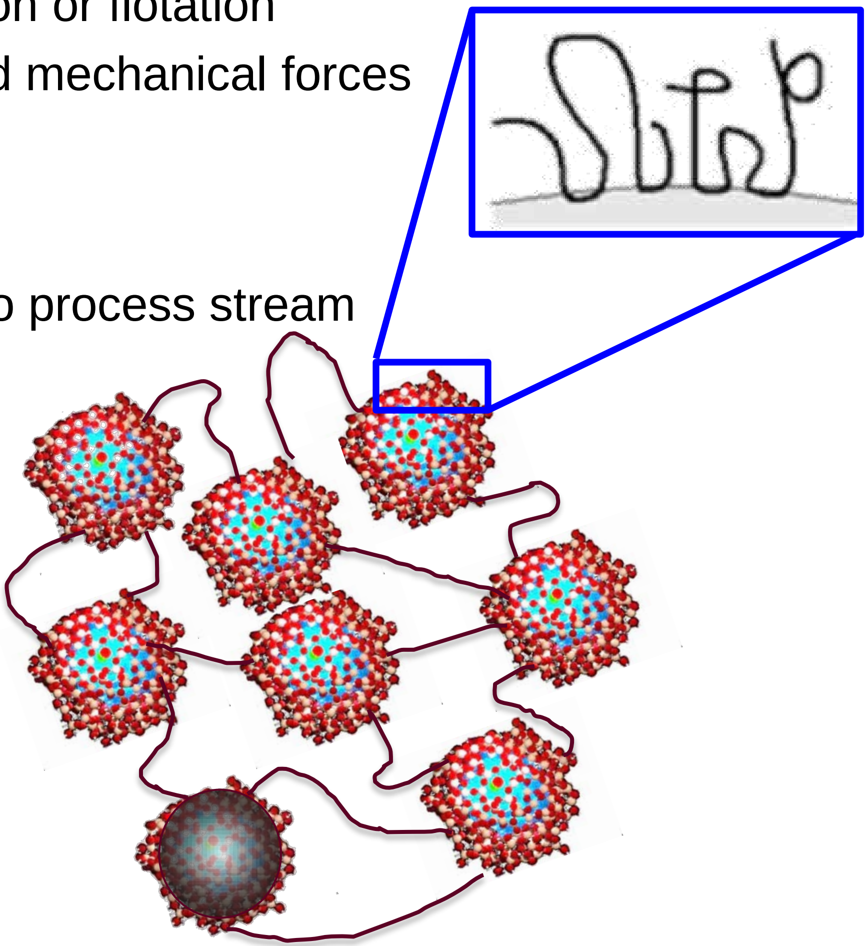
2 – Approach: NP synthesis, networking, and surface treatment

- Synthesis of magnetic nanoparticles (Fe_2Co)
  - Utilize scaled solid-state reaction process
  - 250X less expensive than colloidal Fe_2Co materials
- Assembly of NP into aggregates
  - Chemically bind NP using polymer chains
  - Forms elastic network (rubber band)
- Surface treatments allow for adsorption specificity
  - Modify NP surface via heterogeneous gas-phase process
    - Flexible process allowing for variety of surface functionalities
    - No process solvents necessary
- Performance metrics
  - Adsorption capacity and specificity



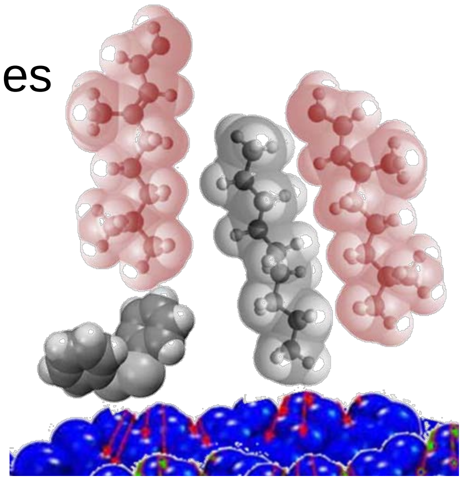
2 – Approach: HC recovery and NA reuse

- Recovery of HC fuel
  - Isolation by magnetic separation or flotation
  - Desorption using magnetic and mechanical forces
- Reuse of NA
  - Return desorbed aggregates to process stream
- Performance metrics
  - HC recovery
  - NA loss
  - Adsorption capabilities of recycled NA



2 – Approach (Management)

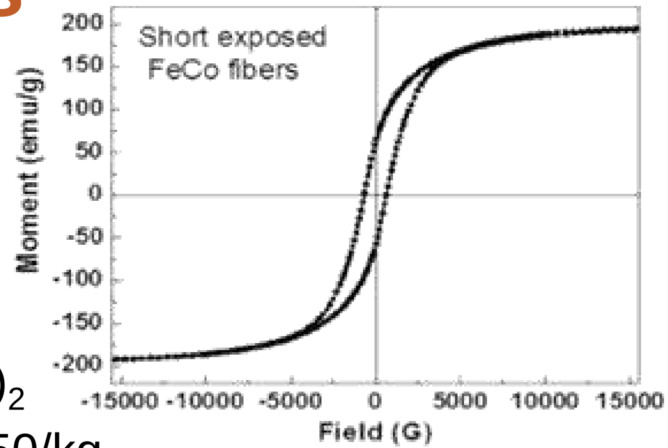
- Critical success factors
  - Fabricate nanoparticle aggregates at reasonable costs
  - Adsorb fermentation products with high specificity and capacity
  - Determine low-energy processes for recovery of biofuels
    - Also applicable to other fermentation products or bioproduct precursors
  - Best process economics result from maximum cycling of NA
- 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
- Structure of approach
  - Challenging milestones
  - Key go/no-go decision points



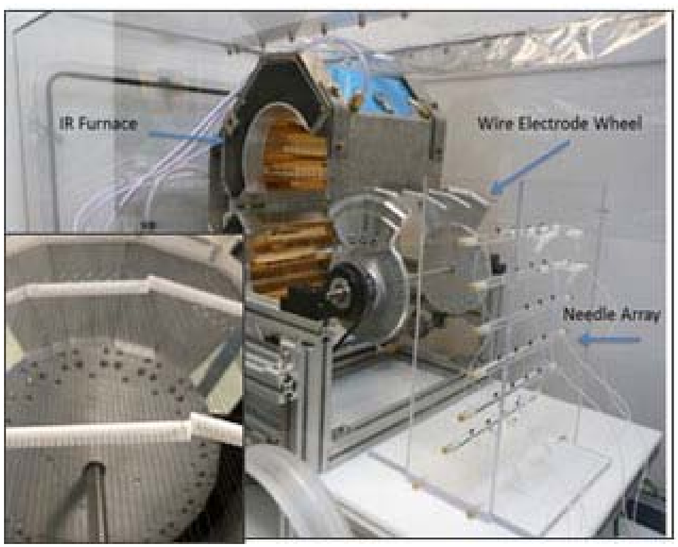
3 – Technical Accomplishments

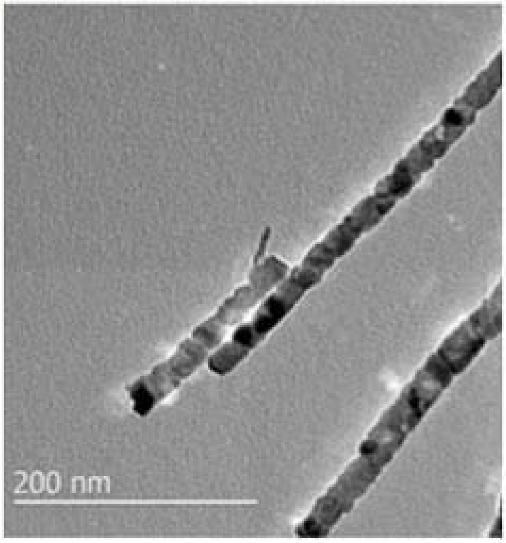
Task/Milestone	Planned Completion	Metrics	% Completion
Desorption process	30-Sep-2013	IQ, OQ, PQ complete	100
Quantify separations	31-Dec-2013	Methods established; > 60% desorption	100
Separation process for NA from Bioreactor	31-Mar-2014	IQ, OQ, PQ complete	100
Recycling of NA	30-Jun-2014	Number of cycles > 5	100
Initial cost/performance	30-Sep-2014	NA process < 75 % traditional approaches	100
Scale NA process	15-Dec-2014	Separation and NA reuse at 3-L scale	100
NA adsorption metrics	31-Mar-2015	Adsorption rate > production rate	
NA adsorption specificity	30-Jun-2015	Target HC bound > 2X other products	
Determine large scale cost/performance	30-Sep-2015	NA process < 65% traditional, at scale	

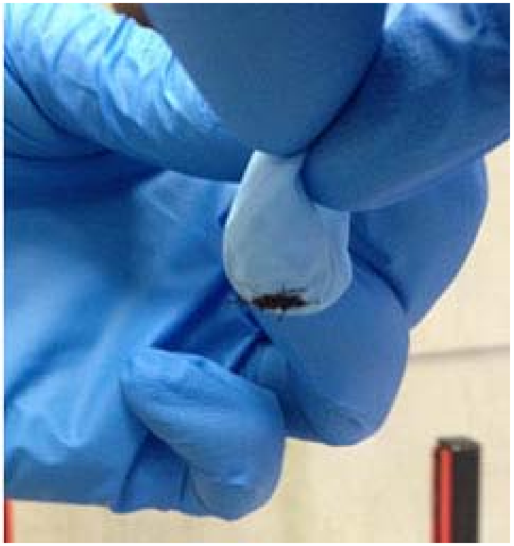
3 – Technical: NP Synthesis



- 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



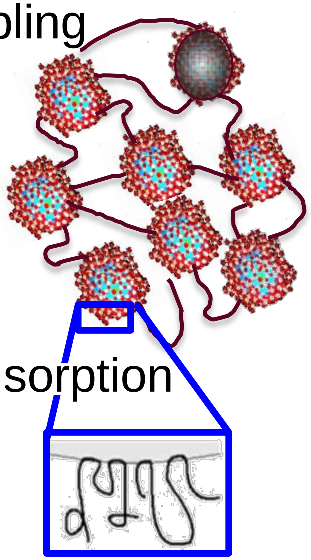




[1] *Adv. Mater.* (2006) **18**: 3154-3159.

3 – Technical: NA Network and Surface Treatment

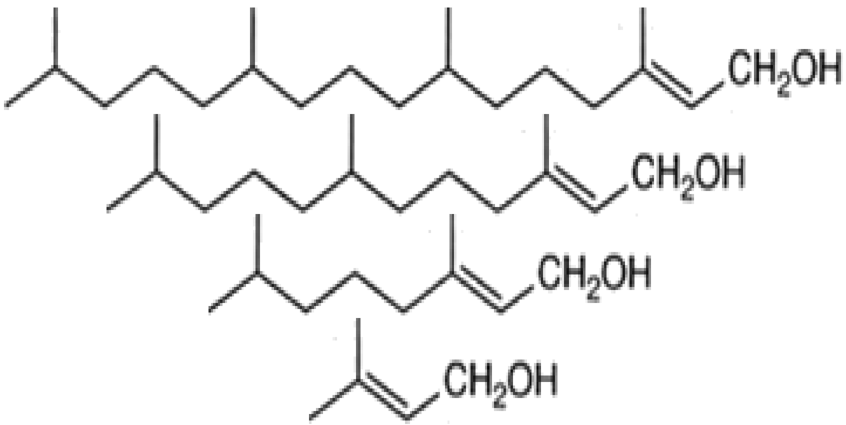
- NA Network
  - Chemically bond NP using polymer chains – bi-functional coupling
    - 1,8-bis(triethoxysilyl)octane
    - bis(3-triethoxysilylpropyl)poly-ethylene oxide
  - Forms elastic network



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

3 – Technical: Next-generation-Biofuel Testbed

- Adsorb isoprenols from doped fermentation broth
- Tune NA specificity to minimize culture medium 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)



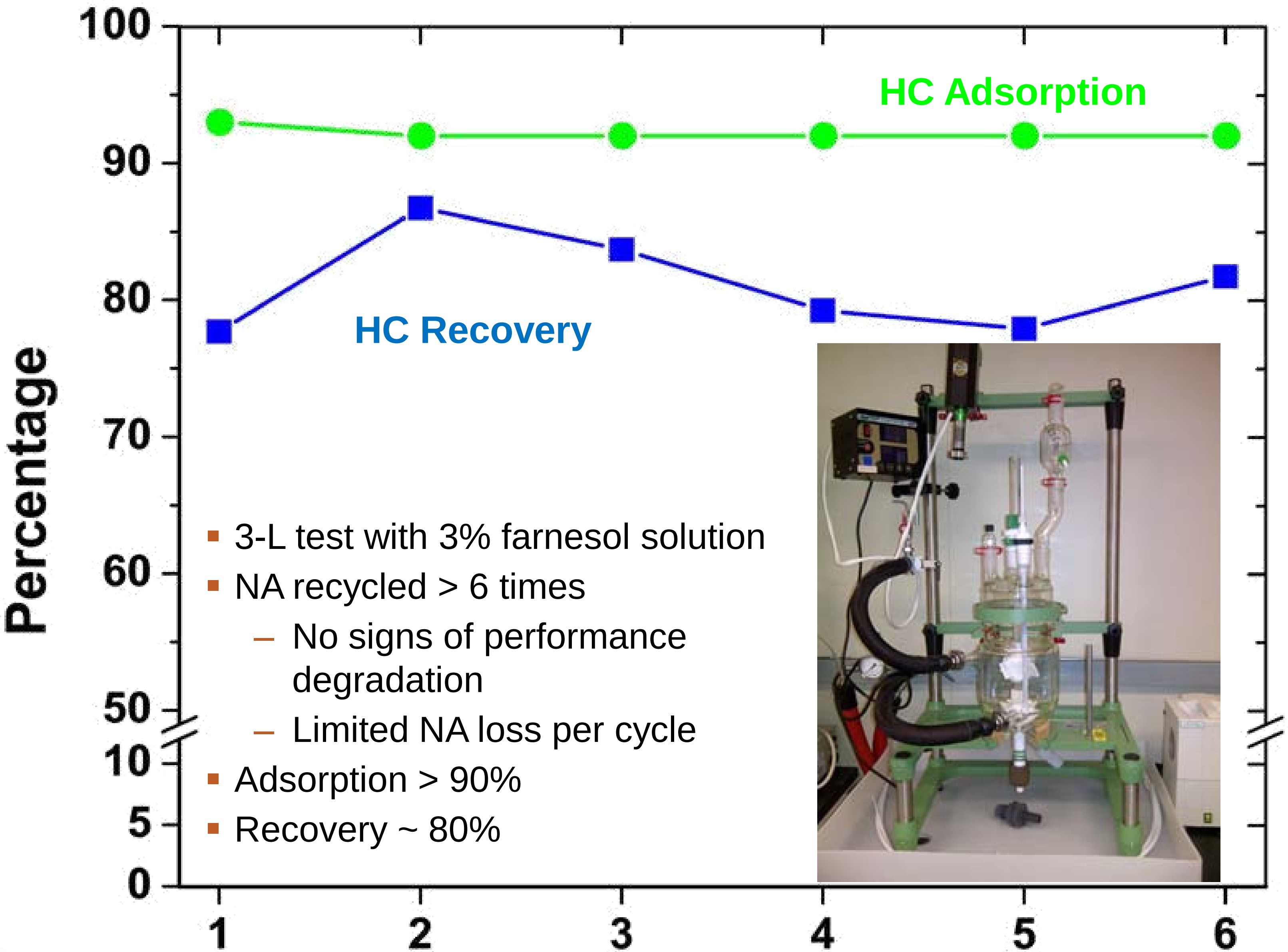
3 – Technical: Binding capacity and conditional properties

HC capacity of NA with various surface treatments			
Sample	Ref #	Structure of Surface Treatment	HC (g) : NA (g)
phenyl – diphenyl	57	20% phenyl 80% diphenyl loops	3:1 Floats
phenyl – diphenyl – methyl – di-hydroxyl	78	15% phenyl 85% diphenyl – methyl – di-hydroxyl loops	3:1 Sinks
octyl – diphenyl	87	16.7% octyl 83.3% diphenyl loops	3:1 Floats
octadecyl – diphenyl	88	16.6% octadecyl 83.4% diphenyl loops	3:1 Sinks

Surface-treated NA exhibit a range of physical properties with HC adsorbed

- Binding capacity can exceed 5-10x weight of NA
- Process development has focused on NA that float when HC adsorbed

3 – Technical: Scaled NA process performance



- 3-L test with 3% farnesol solution
- NA recycled > 6 times
  - No signs of performance degradation
  - Limited NA loss per cycle
- Adsorption > 90%
- Recovery ~ 80%

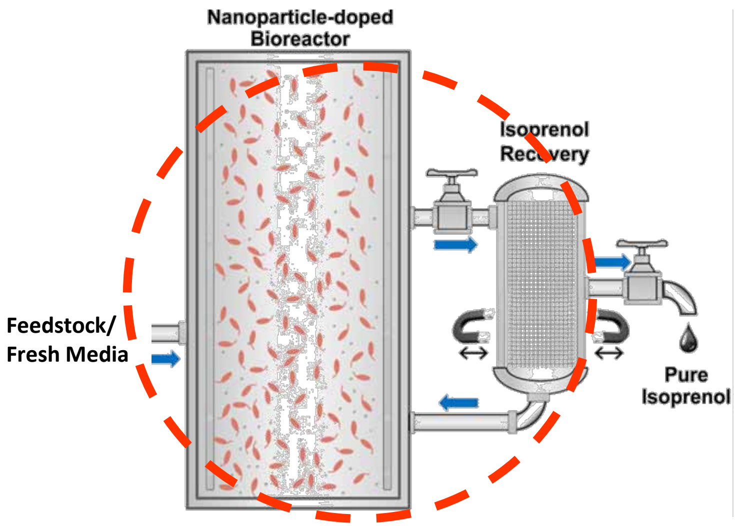
3 – Technical: Cost comparisons

- Conventional solvent extraction/distillation costs evaluated
  - Ranged between $22.54 and $1.52, depending upon solvent costs employed, for processing 2L of a 3% HC-containing fermentation stream (large laboratory or US-spot-commercial scales, respectively)
- NA processes found to be <75% cost of conventional methods
  - Identified path to achieve <50% cost
  - Future cost reductions depend upon ability to increase recycling success

Cost of NA separation and recovery process					
NA Process	Bulk Cost ($/kg)	Operation cost at 2-L scale (calculations use 60 g NA in process)			
		1 cycle	2 cycles	5 cycles	100 cycles
Production	40.00	2.40	2.40	2.40	2.40
Surface treatment	2.00	0.12	0.12	0.12	0.12
Recovery	4.00	0.24	0.48	1.20	24.00
Total	--	2.76	3.00	3.72	26.52
Cost per cycle	--	2.76	1.50	0.74	0.27

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

4 – Relevance



- Biochemical Conversion
  - Process integration will aid in meeting cost targets for conversion pathways
- Applications of expected outputs
  - 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
  - Analysis of approach to remove toxins from active production cultures
  - Intensified recovery to limit product inhibition and increase titers
  - Decrease costs for biofuels productions strategies as separations can account for as much as 50% of costs
- Direct involvement of Technology-to-Market partners
  - Early engagement of start-ups working to bring forth innovation in scalable bioreactor designs

5 – Future Work

- Upcoming Activities
  - Q2, FY15: Assess rate of HC adsorption relative to production
    - Analyze unbound HC concentration for given injection rate
  - Q3, FY15: NA specificity
    - Affinity for HC double that of other bioreactor products
    - Utilize TLC and HPLC for analysis
    - Impact on choice of fermentation broth (i.e., minimal vs. rich)
  - Q4, FY15: Cost/Performance analysis
    - At larger scale, compare costs to conventional methods
    - Determine maximum recycling as integral component in calculations
  - Mid FY16 **(Go/No-Go)**: At 3-L scale, NA process cost < 65% of conventional solvent extraction/distillation
  - FY16 and FY17: Scale processes, expand collaborations to other biofuels production processes, and transfer technology

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 HC fuel recovery
- Many technical accomplishments – NA synthesis, NA surface treatment, HC adsorption, and hybrid magnetic/compression recovery process – make its use attractive and competitive
- Scale-up plans with revised methodologies are underway
- The work leverages technology from ARPA-E, Argonne LDRD, and other BETO programs
- Success (risk) factors were identified along with mitigation strategies
- Technology transfer plans have been integrated since inception

Additional Slides

(Not a template slide - for information purposes only)

- *The following slides are to be included in your submission for Peer Evaluation purposes, but <u>will **not** be part of your oral presentation</u> –*
- *You may refer to them during the Q&A period if they are helpful to you in explaining certain points.*

Responses to Previous Reviewers' Comments

- **It is hard to imagine that this will be pragmatic. It is interesting science. What are they using as a benchmark technology? What metrics are being used? This project is better as a polishing step. It needs to start with a very simple system!**
  - Subsequent experimentation included qualifying studies that focused on simple aqueous/HC systems as outlined in the previous slides
- **If the economics of this technology look reasonable at all, this process could be applied in many ways, including removing toxic products to ultimately increase the titers in the fermentation. This could make the difference in making or breaking some types of fermentations/technologies.**
  - We agree. This exact approach is part of our follow-on studies with bioreactor-integrated separations. MANY uses (not just the primary HC)
  - Preliminary cost/performance analyses have been conducted and found purposed methods to be <75% conventional ones (and <50% with additional recycling/extended reuse of NA)
- **……………..useful for toxic molecules in a continued mode**
  - See comments above
- **……………..spend more time on basic characterization**
  - We have stepped back and completed additional characterization of system as suggested, while continuing to meet aggressive milestones

Publications, Patents, Presentations, Awards, and Commercialization

- Patent Application:
  - 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.