2.3.1.11: Low-Energy Magnetic-Field Separation using Magnetic Nanoparticle Solid Absorbents

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DOE Biomass Platform – Bioenergy Technologies Area

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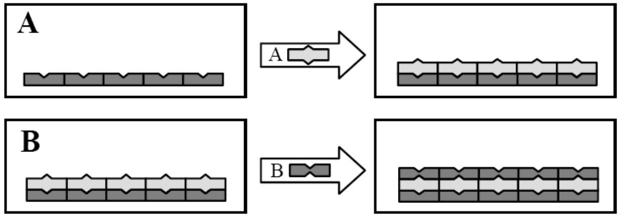
Goals

- Demonstrate low-energy, magnetic field separation of hydrocarbon fuels reduces process energy use and improves process economics
- Integrate nanostructured adsorbents into bioprocesses to establish a prototype separation process for hydrocarbon fuels
- Technology spans between biomass processes
  - Applicable to targeted products and intermediates
  - Enables investigation of quality requirements of intermediates and products

Abbreviations

- HC: hydrocarbon
- SN: superparamagnetic nanoparticles
- NP: nanoparticle
- NA: nanostructured adsorbent
- D: diameter (NP)
- ALD: Atomic Layer Deposition
- TMA: trimethyl aluminum, $Al(CH_3)_3$
- IQ: installation qualification
- OQ: operation qualification
- PQ: process qualification
- TLC: thin-layer chromatography
- HPLC: high pressure liquid chromatography

ALD



AB sequence for ALD of one monolayer. Notches represent reactive sites in substrate for reaction A. Exposing surface to reactant-A results in self-limiting chemisorption of a monolayer of A species. The resulting surface becomes the starting substrate for reaction B. Subsequent exposure to molecule B covers the surface with a monolayer of B species. Consequently, one AB cycle deposits one monolayer of compound AB and regenerates the initial surface.

Quad Chart Overview

Timeline

- Project start date: Oct 1, 2011
- Project end date: Sept 30, 2014
- Percent complete: 45% FY2013

Barriers

- Scale-up SN
- Nanostructured adsorbents
- Remove adsorbed HCs from NA

Budget

- Total project funding
  - DOE: $ 350,000
  - Contractor: $ 0
- Funding received in FY12: $ 150,000
- Funding for FY13: $ 200,000
- ARRA Funding: $ 0

Partners

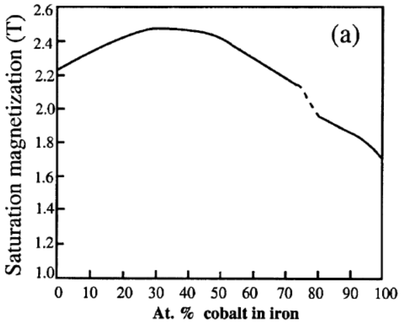
- Philip Laible – Argonne Biology
- Leveraged activities
  - BETO project to adsorb sugars
  - ARPA-E nanostructured magnets
  - LDRD magnetic nanostructures

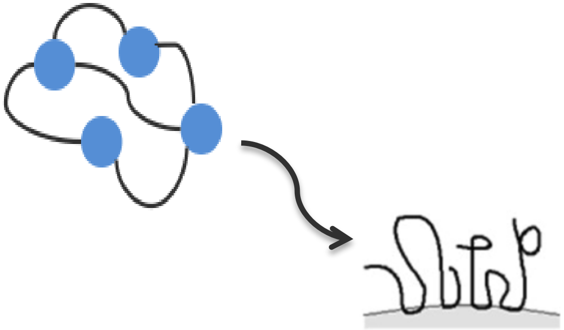
Project Overview

- Demonstrate magnetic NA separation of HC fuels from biochemical process
- Program tasks
  - Fabricate surface-treated NA (Month 3)
  - Determine hydrocarbon adsorption capacity and selectivity from mock fermentation broth (Month 6)
  - Fabricate prototype magnetic capture process system (Month 6)
  - Determine an efficient desorption process (Month 9)
  - Quantify magnetic separation (Month 12)
- Metrics
  - NA: surface-treated NP (<40-nm) covalently tethered together
  - HC adsorption capacity: extraction ratio > 1.75
  - Prototype magnetic capture process: IQ, OQ, PQ
  - Desorption target: >75% desorption
  - Determine turn-number for 10% hydrocarbon separation
  - Demonstrate NA stability and reuse

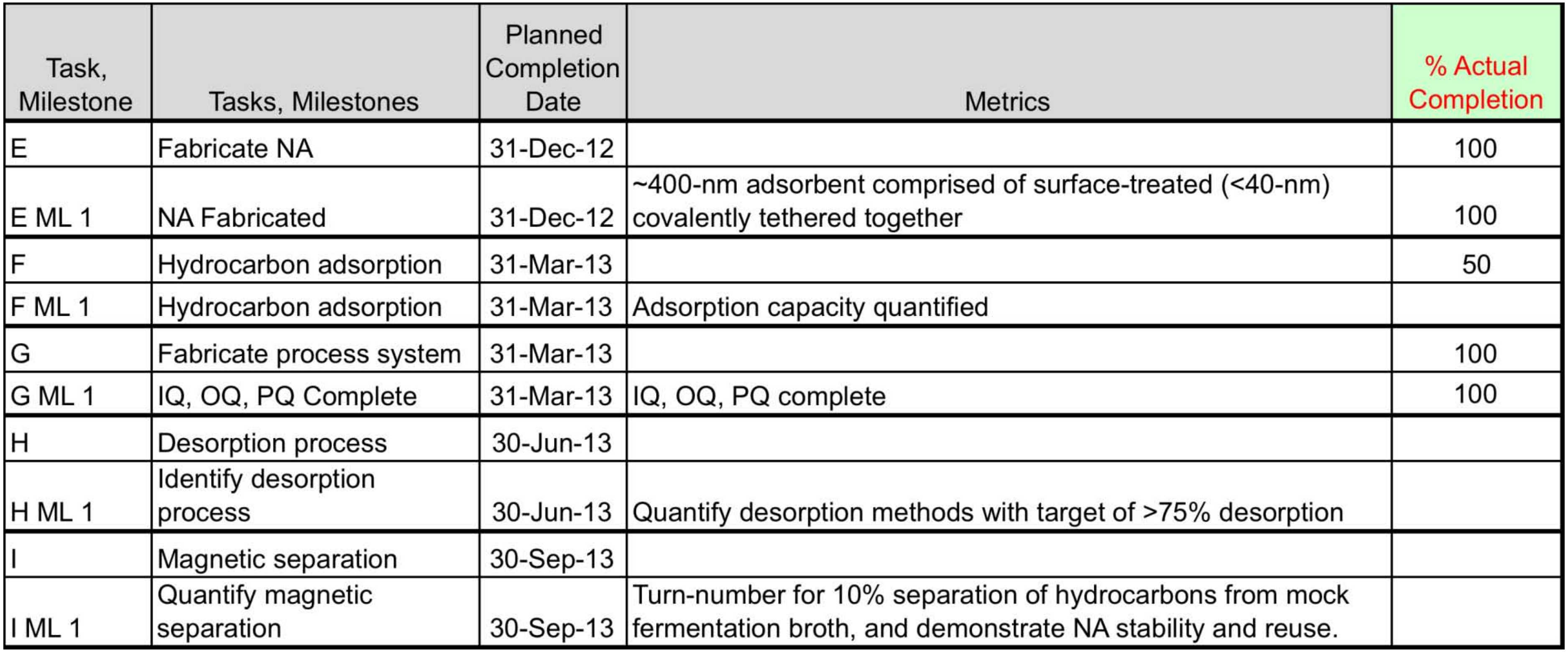
1. NA Separation Approach

- Unique synthesis process: magnetic NP
  - Fe vs. **Fe_2Co** → greater saturation magnetization and stability
  - X Colloidal method
  - Solid-state reaction
- Assembly of magnetic NP
  - Chemically bond NP using polymer chains
  - Forms elastic network – like a rubber band
- Unique: surface treatment on NP to adsorbs HC fuel
  - Heterogeneous gas phase process
  - No process solvents
- Desorption – harvest HC fuel
  - Magnetic
  - Flotation





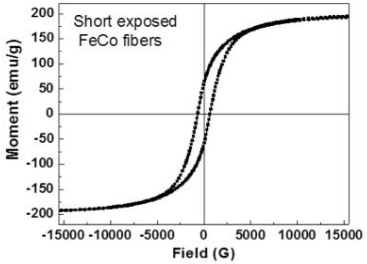
2. Technical Progress: Schedule

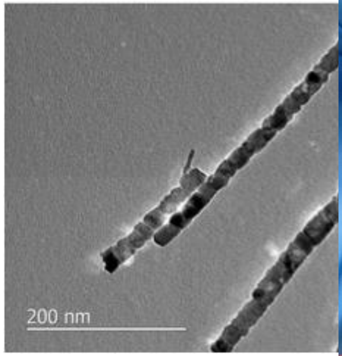


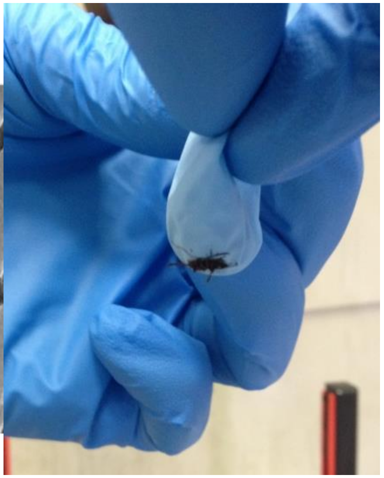
Task, Milestone	Tasks, Milestones	Planned Completion Date	Metrics	% Actual Completion
E	Fabricate NA	31-Dec-12		100
E ML 1	NA Fabricated	31-Dec-12	~400-nm adsorbent comprised of surface-treated (<40-nm) covalently tethered together	100
F	Hydrocarbon adsorption	31-Mar-13		50
F ML 1	Hydrocarbon adsorption	31-Mar-13	Adsorption capacity quantified	
G	Fabricate process system	31-Mar-13		100
G ML 1	IQ, OQ, PQ Complete	31-Mar-13	IQ, OQ, PQ complete	100
H	Desorption process	30-Jun-13		
H ML 1	Identify desorption process	30-Jun-13	Quantify desorption methods with target of >75% desorption	
I	Magnetic separation	30-Sep-13		
I ML 1	Quantify magnetic separation	30-Sep-13	Turn-number for 10% separation of hydrocarbons from mock fermentation broth, and demonstrate NA stability and reuse.	

2.E.1 NP Synthesis

- Superparamagnetic Fe_2Co
  - X Colloidal Fe_2Co:[1]
    - D ~10-nm; iron chloride and cobalt acetate by polyol reduction at 130°C in ethylene glycol using sodium hydroxide and $H_2PtCl_6 \bullet 6H_2O$ (~ 2.4×10-5 mol/L) \$15,000/kg
  - – Solid-state reaction of $Fe(NO_3)_3$ and $Co(NO_3)_2$
    - Fe_2Co metal alloy cylinders (D ~10-nm, L ~30-nm)[2]
    - Oxidize nitrates, fracture, reduction – \$350/kg
- Passivate surface
  - Al_2O_3
  - ALD: TMA/H_2O







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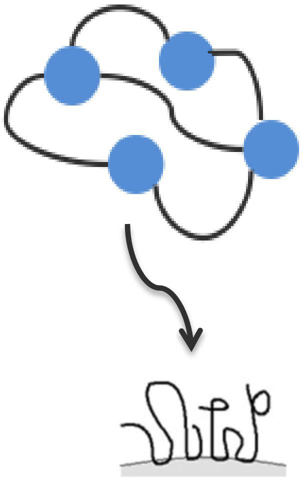
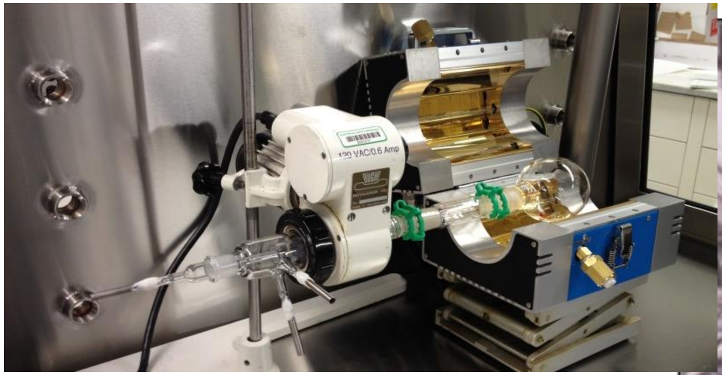
[1] *Adv. Mater.* (2006) **18**: 3154-3159.

[2] Fridrikh, S.V., et al., *Physical Review Letters* (2003) **90**(14): p. 144502.

2.E.2 NA Network and Surface Treatment

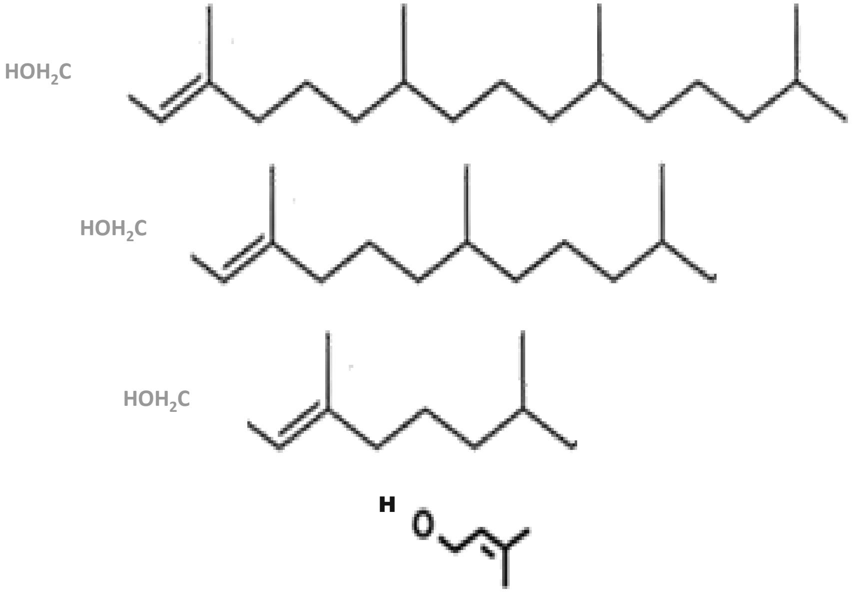


- NA Network
  - Chemically bond NP using polymer chains – bi-functional coupling
    - 1,8-bis(triethoxysilyl)octane
    - bis(3-triethoxysilylpropyl)poly-ethylene oxide.
  - Forms elastic network – junction functionality ~ 2.2 to 2.5
- NP Surface Treatment
  - Heterogeneous vapor-phase polymerization – hydrocarbon adsorption
  - Lyophilic: octyl (C_8), octadecyl (C_{18}), phenyl ($-C_6H_5$)
  - Hydrophilic: hydroxyl (-OH), amino ($-NH_2$), carboxyl (-COOH)
  - ST characterized by swelling, TGA, MAS, and CP MAS solid-state NMR techniques
- Process



2.F.1 Bioenergy System and Hydrocarbon Fuels

- Adsorb Isoprenols from doped fermentation broth
- Richness of the medium
  - Minimal (mimicking selective fermentation schemes required for some autotrophic or phototrophic conversion processes)
  - Rich (more realistic cultures that may result from growth on cellulosic hydrolysates and more versatile heterotrophic production schemes)
- Length of fuel carbon chain
  - Phytol (C_{20}; diesel)
  - Farnesol (C_{15}; diesel/ jet)
  - Geraniol (C_{10}; gas/jet)
  - Isoprenol (C_5; gas)



2.F.2 Monitor and Quantify Fuel Recovery

- TLC with iodine staining
  - Rapid and efficient recovery methods
  - Generic hydrocarbon identification
  - Impurities identified as media composition / relevant controls initially well defined
- HPLC and GCMS available
- Growth (impairment) of bacterial strains in presence of NA monitored by final cell densities and growth rates
- C_{20} and C_{15} adsorption ongoing from minimal and rich media

2.G Fabricate Process System

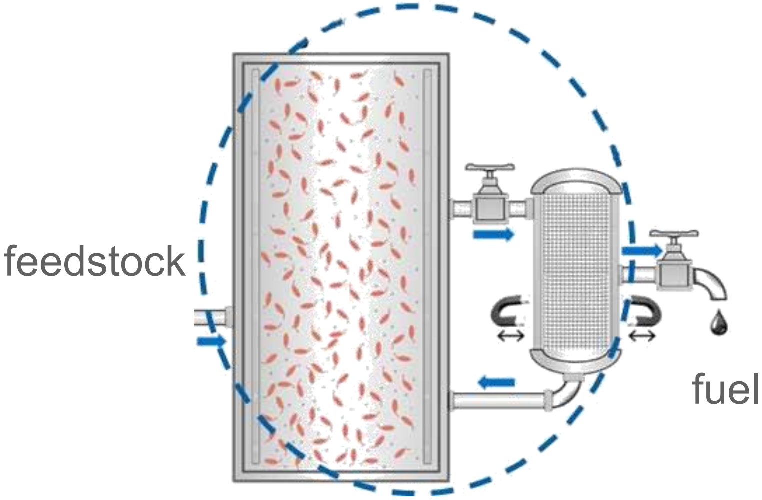
- 3-liter scale prototype magnetic capture process
- IQ, OQ, and PQ complete

- Next tasks
  - Complete adsorption of fuel from fermentation broth
  - Optimize NA
  - Identify desorption process
    - Magnetic pulse
    - Mechanical
    - Recovery fluid pH flux
  - Quantify magnetic separation
    - Flotation

Prototype magnetic separation process

3. Relevance

- Biochemical Conversion
  - Bt-I Cleanup/Separation
  - Bt-K Biological process integration
- Applications of expected outputs
  - Provides initial data sets on the feasibility of using NP to separate HC from bioprocesses
  - Develops schemes to integrate HC fuel separation and recovery into bioprocesses
  - Reactor-integrated separations: HC fuel production and recovery in concert
    - Maximize production levels
    - Reduce produce toxicity/poisoning
    - Continuous culture approaches



4. Critical Success (Risk) Factors

Risk	Mitigation Approach
Separation of NA from growth medium	• Magnetic capture of NA from process flow stream • Flotation of NA followed by magnetic capture • Hydrocyclone separation
NA become entangled with biological organism	• Disentangle under turbulent mixing • Increase residence time in bioreactor to effect flotation separation
NA stability and reuse	• Reformulate NA • Mix bioreactor during adsorption • Flotation
HC recovery is low	• Stationary NA with mechanical recovery • Multistage recovery – magnetic flux with mechanical recovery • Recovery fluid pH flux

Future Work

- Through September 30, 2013
  - Complete HC adsorption
  - Evaluate ease of NA separation from biochemical reactor
  - Evaluate ease of HC recovery from NA
  - Evaluate strategies to recover > 10% total HC fuel
- Through September 30, 2014
  - Integrate 2013 HC fuel separation performance with LCA to establish cost/performance goals
  - Evaluate separations in bioprocesses that make a distribution of hydrocarbons, and investigate the quality requirements of hydrocarbon intermediates and products
  - Leverage magnetic nanostructure programs to determine adsorbent scale-up metrics
  - Go/No-Go: cost/performance of NA versus conventional HC separation and recovery processes

Summary

- The objectives are relevant to BETO’s Bioenergy Technology Area and will provide initial data sets on the feasibility of using NP to separate HC from bioprocesses
- The approach is effective by accessing a large HC adsorption separation process space and will be coupled with HC fuel recovery
- The work has many technical accomplishments – NP synthesis, NP surface treatment, adsorbent network formation, HC adsorption, and prototype magnetic capture process
- The work has leveraged technology from ARPA-E, Argonne LDRD, and BETO programs
- Success (risk) factors were identified along with mitigation strategies
- Scale-up processing methodologies identified