U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Advanced Membrane Separations to Improve Efficiency of Thermochemical Conversion
(WBS2.5.5.301/2.5.5.302)

Michael Hu
Oak Ridge National Laboratory (ORNL)
Chaiwat Engtrakul
National Renewable Energy Laboratory (NREL)

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

March 8, 2017

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Goal Statement

Problem: A significant amount of biomass carbon (up to 40%) from thermochemical (TC) processes ends up in aqueous waste streams, thus wasting valuable biogenic carbon.

Project Goal: Design and develop high-flux membrane separation technologies for various TC conversion pathways to increase carbon yield of fuels and chemicals by separating water from carbon resulting in improved process economics.

Performance Targets	Values
Permeation Flux	>1 **LMH** (liter/m^2/h)
Separation Factor (SF)*	>20
Operational Stability	>8 hours

*SF for a binary mixture A and B is the ratio of the compositions of components A and B in the permeate relative to the A/B ratio in the retentate.

This project provides foundational support to BETO’s Separations Consortium -- a new “pillar” in the BETO program

Project Outcome: By September 2019, demonstrate a functional membrane separation technology that can be integrated into a TC conversion process to meet project performance targets and **achieve a >8% reduction in MFSP ($/gge).**

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Quad Chart Overview

Timeline

Project start date – Oct. 1, 2016

Project end date – Sept. 31, 2019

Percent complete – 8%

Budget

	FY 15 Costs	FY 16 Costs	Total Planned Funding FY 17
ORNL	540,742	497,348	590,000
NREL	200,000	200,000	200,000

(100% DOE BETO funding)

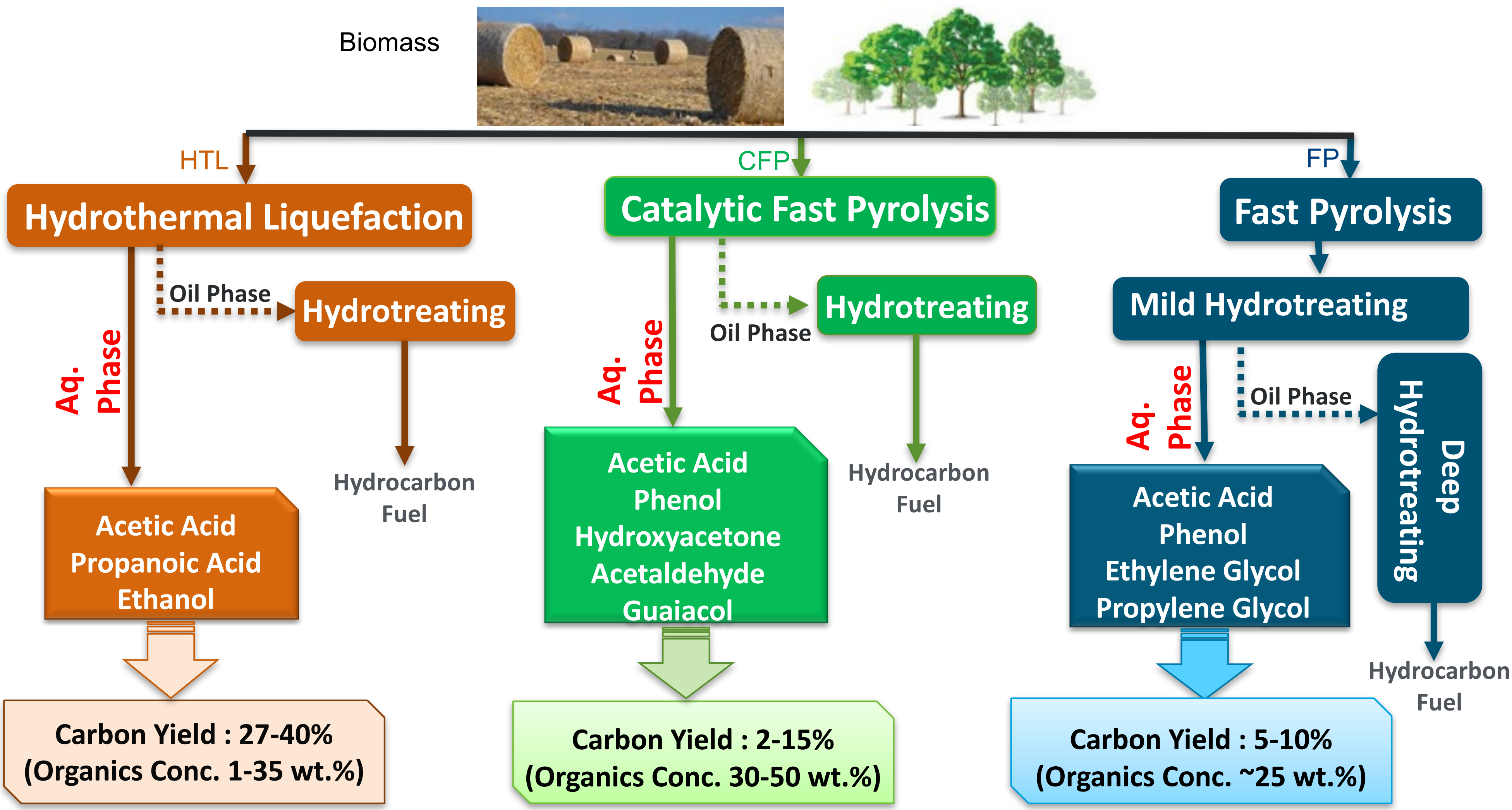
Barriers

- Ct-L. Aqueous Phase Utilization and Wastewater Treatment
- Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
- Strategy: Use advanced membranes to enhance C efficiency

Partners

- National Laboratories – ORNL (~75%) and NREL (~25%)
- Other interactions/collaborations
  - **Spin-off project sponsored by an industrial biofuel company (~$500K)**

Project Overview



Significant amounts of biogenic carbon lost to aqueous phases
Aqueous phases have diverse chemical compositions, conc. to be enriched

* Process diagram courtesy of Karl Albrecht (PNNL)

Project Overview

Objective: Improve the process carbon efficiency of TC pathways by addressing separation needs, e.g., carbon recovery from aqueous fractions, increase production of fuel and/or higher value chemicals

TEA: Aqueous-phase valorization project (WBS2.3.1.310/311)

- in-situ CFP case, 6% reduction in MFSP (due to water removal to enrich solution concentration)
- HTL case (woody biomass), 18% reduction in MFSP (due to high value products only)
- Carbon efficiency is critical to improve process economics
- Develop membrane technology that can be transferred to other TC conversion projects

High-performance architectured surface-selective (HiPAS) membranes through synergistic nano-engineering of surfaces & pores

2016 US Patent 9,308,501 B2

2014 R&D100 Award

(12) United States Patent (10) Patent No.: US 9,308,501 B2
Hu et al. (45) Date of Patent: Apr. 12, 2016

(54) SUPER-SURFACE SELECTIVE NANOMEMBRANES PROVIDING SIMULTANEOUS HIGH PERMEATION FLUX AND HIGH SELECTIVITY

(71) Applicant: UT-BATTELLE, LLC, Oak Ridge, TN (US)

(72) Inventors: Michael Z. Hu, Oak Ridge, TN (US); John T. Simpson, Oak Ridge, TN (US); Tolga Aytug, Oak Ridge, TN (US); Mariappan Parans Paranthaman, Oak Ridge, TN (US); Matthew R. Sturgeon, Golden, CO (US)

(73) Assignee: UT-BATTELLE, LLC, Oak Ridge, TN (US)

(21) Appl. No.: 13/666,217

(22) Filed: Nov. 1, 2012

(65) Prior Publication Data

(51) Int. Cl.

(52) U.S. Cl.

(58) Field of Classification Search
None
See application file for complete search history.

(56) References Cited

U.S. PATENT DOCUMENTS

(Continued)

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS

(Continued)

(57) ABSTRACT

Superhydrophobic membrane structures having a beneficial combination of throughput and a selectivity. The membrane structure can include a porous support substrate; and a membrane layer adherently disposed on and in contact with the porous support substrate. The membrane layer can include a nanoporous material having a superhydrophobic surface. The superhydrophobic surface can include a textured surface, and a modifying material disposed on the textured surface. Methods of making and using the membrane structures.

27 Claims, 6 Drawing Sheets

Aq. Phase Enrichment + Valorization → MFSP Reduction

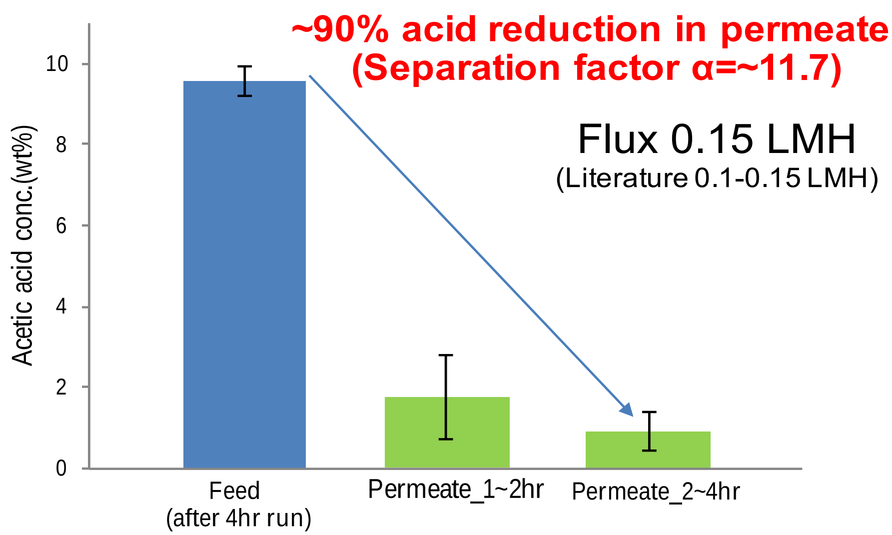
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Project Overview

- In FY17, focus on technology pathways/processes that have higher carbon losses to the aqueous phase (e.g., HTL)
- Leverage and develop tunable surface properties of membrane materials
- To achieve the cost savings associated with the recovery of carbon, a **higher membrane flux** is necessary
  - Benchmark (target) flux of 1 LMH necessary at separation factor of >12, relative to the current state-of-the-art dewatering membranes (~0.10 – 0.15 LMH)
  - No commercial membranes can meet such targets

State of Technology/Baseline (Early FY16):

Acetic acid/water membrane separation → Enrichment and recovery of carbon (acetic acid)



Tubular Membranes

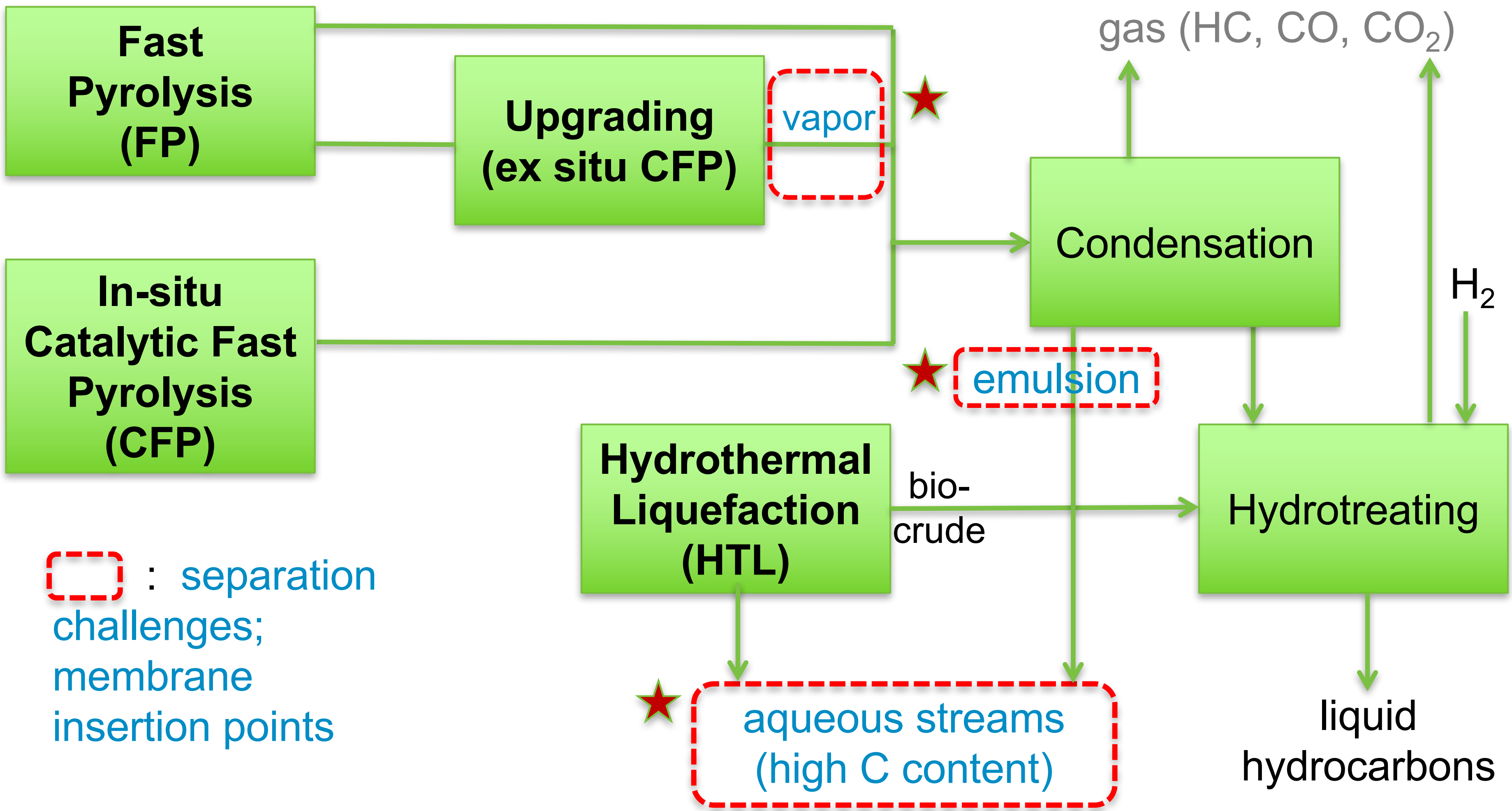
Management Approach

- **Collaborative project** (ORNL and NREL)
  - Unique membrane materials and fabrication expertise (ORNL) combined with real process evaluation capability (NREL)
  - Synthetic and real biomass-derived process streams (NREL and PNNL)

- **Synergy exists** with
  (1) an aqueous-phase valorization project at PNNL/NREL (WBS2.3.1.310/311)
  (2) BETO’s Separations Consortium

- **TEA conducted** in collaboration with the Thermochemical Platform Analysis Group (at NREL and PNNL) to identify and assess economic impact of implementing a cross-flow membrane technology in the TC pathways

Technical Approach – Membrane Insertion Points

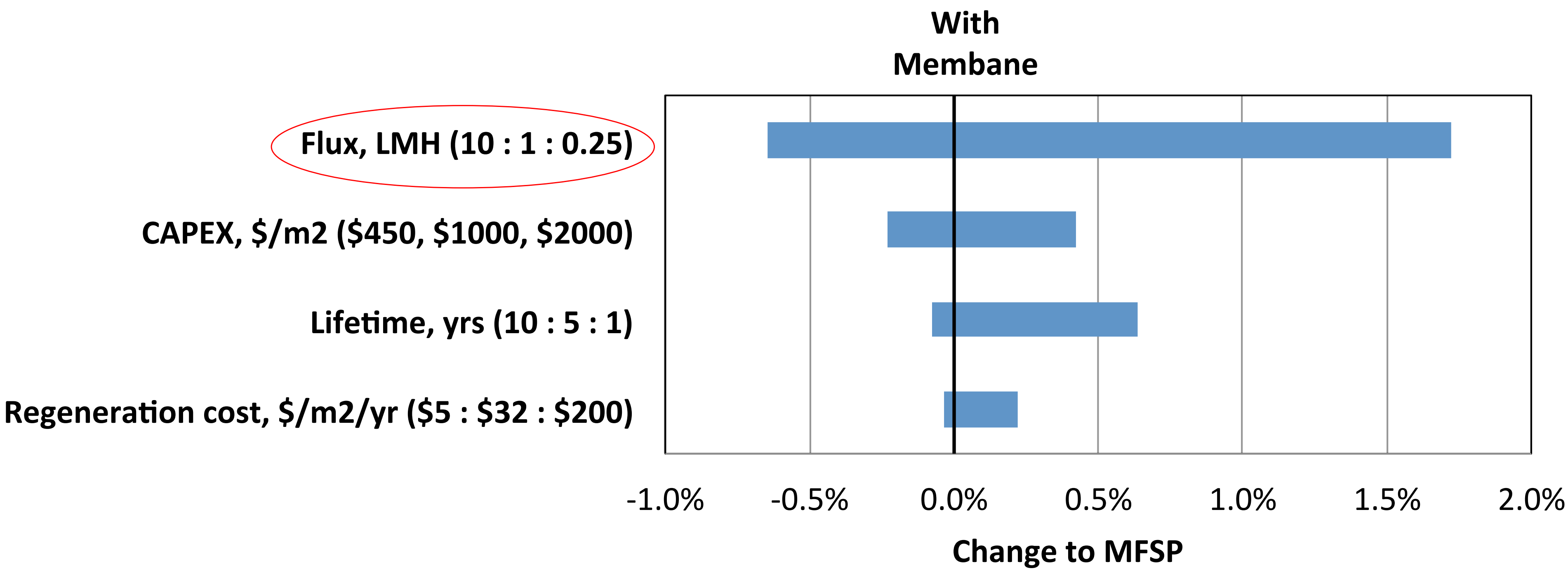


- **Membrane separation ≠ only filtration or size-exclusion**
- **TEA-driven path-forward for C recovery:** High impact for membranes able to recover carbon from aqueous waste streams

Technical Approach – TEA Guided Targets

- Utilized techno-economic analysis (TEA, FY16) to help guide decision points for membrane insertion points in TC pathways

Sensitivity Analysis: Membrane performance metrics

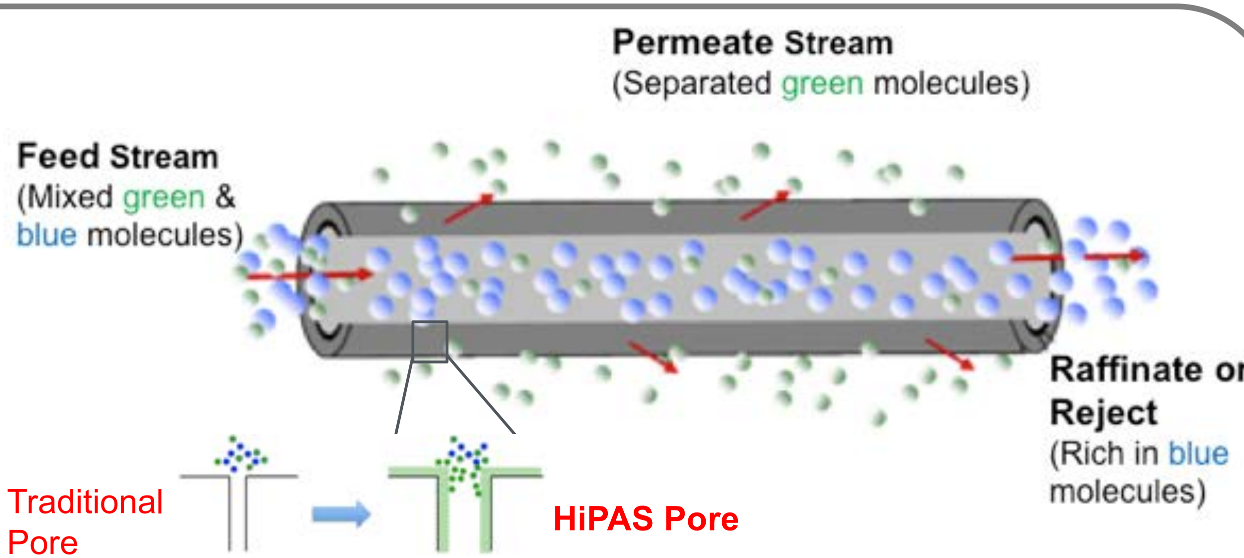


Membrane flux is the most sensitive parameter impacting MFSP

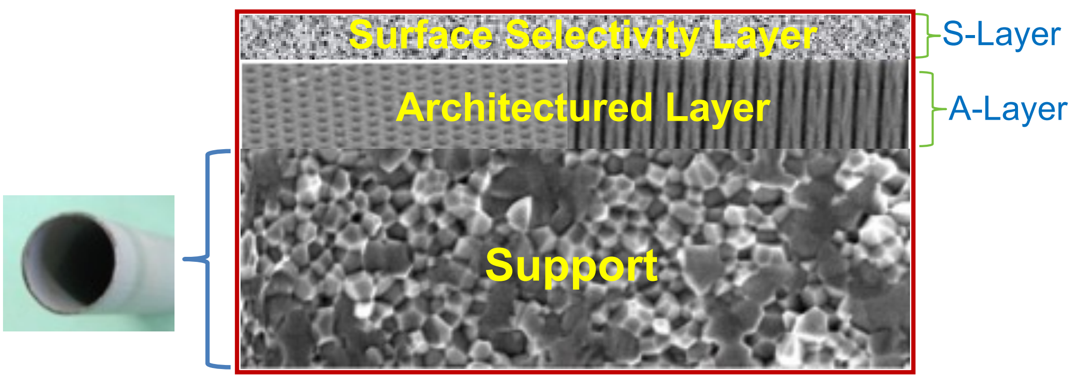
Technical Approach – Overcome Challenges

HiPAS Separation Concept:

Membranes with superhydrophilicity or superhydrophobicity coatings enhance surface selectivity, making it possible to employ larger pores in order to achieve 10-100X higher permeation flux



Fabricate HiPAS Membranes and Evaluate Under Relevant Processing Conditions



High Performance in Permeability, Selectivity, & Stability

HiPAS membranes take advantage of

- Robust and scalable inorganic membrane support tube platform
- Enhanced surface selectivity concept to overcome limitations of current polymer/zeolite based membranes

Technical Approach – Key Research Challenges

- **High flux at desirable separation factor**
  - Surface affinity of HiPAS to target permeate molecule to membrane/pore surfaces
- **Chemical stability & ruggedness**
  - Corrosion resistance to maintain structural integrity and surface coating
- **Thermal stability; membrane operating temperature**
  - Bio-oil vapors enter membrane at 250−450°C
  - Liquid phase pervaporation at 50−70°C
- **Fouling Resistance**
  - Prevents irreversible adsorption on surface or in pores
- **Engineering process controllability and scalability**
  - Feed flow rate (re-circulate vs. single pass) and transmembrane pressure drop (ΔP) with time
  - Module design and fabrication to maximize Area/Volume (productivity)

<u>Critical Success Factor</u>

- Demonstrate separations at high flux (>1 LMH) under relevant TC conditions

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

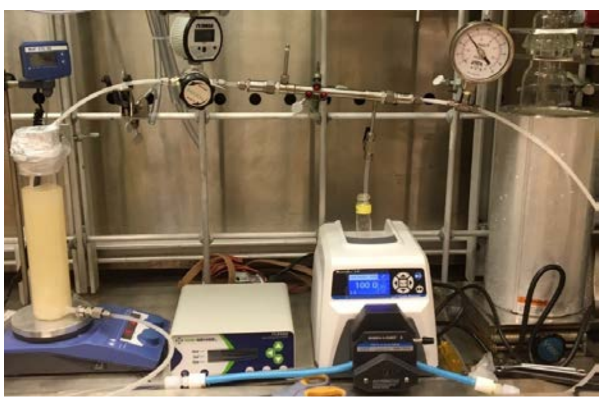
Technical Approach – Tasks

Task 1:
Membrane materials development, synthesis, and fabrication (ORNL)

Task 2:
Liquid-phase separation process development (ORNL/NREL)

Task 3:
Vapor-phase separation process development (NREL/ORNL)

Recovery of carbon from emulsions



Recovery of soluble carbon from aqueous streams

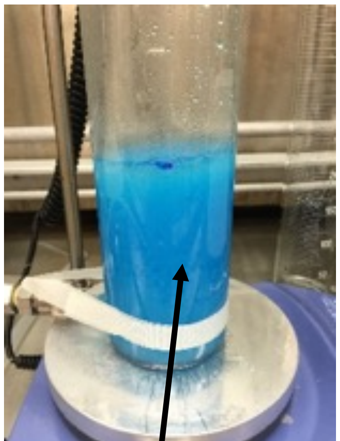
Vapor-phase dewatering

Technical Accomplishments

Recovery of Carbon from Emulsions

Large-pore (4-μm) HiPAS membrane can separate oil from water because of superhydrophobic surface

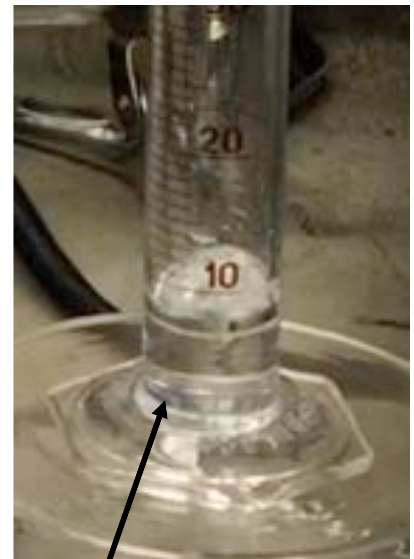
Emulsion Feed



Oil-in-Water
(water soluble color indicator added for visual effect)

HiPAS membrane operates at >10x higher break-through pressure (P_B), resulting in 2-3 orders of magnitude **higher flux** at ~100% selectivity (relative to the un-coated membrane).

Permeate (Pure Oil)



Clear oil ~100% selectivity
(No blue water phase)

- Aqueous phase composition is complex: emulsions and oxygenated hydrocarbons
- HiPAS membrane efficiently recovers the dispersed oil droplets

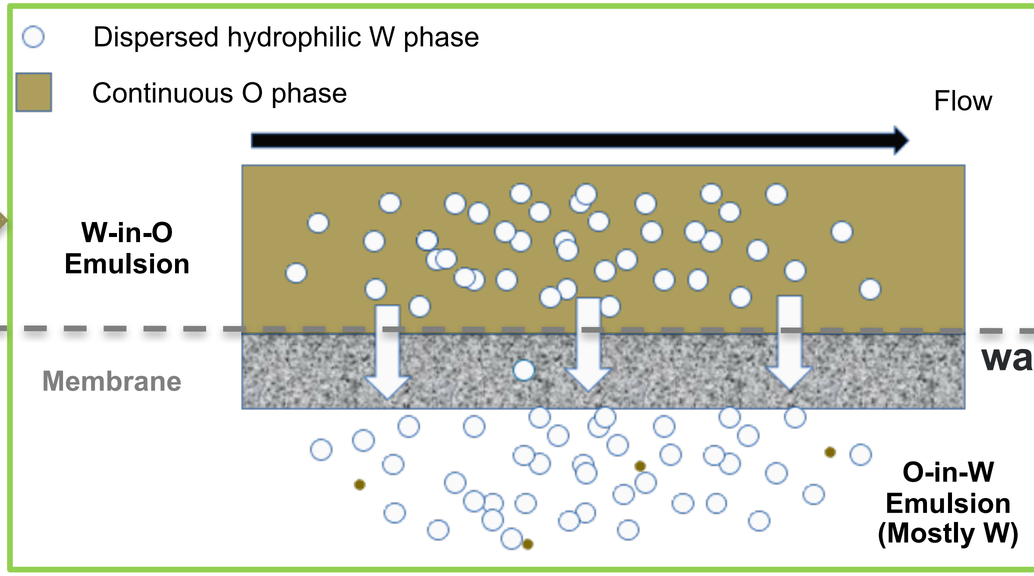
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Technical Accomplishments

Recovery of Carbon from an Industrially Relevant Biofuel Emulsion

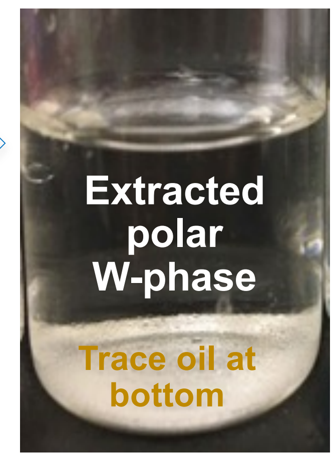
HiPAS Hydrophilic Membrane (6 nm)

Water-in-Oil Emulsion in Feed Tank



Enriched hydrocarbon stream (for higher reaction yield for biofuel)

Cross-flow water permeation



- Demonstrated a high selectivity for water phase extraction; permeate water have shown near 99 vol.% purity
- Cross-flow permeation significantly reduced membrane fouling by oil compared to dead-end filtration
- **This work has led to an industry funded commercialization project**

Technical Accomplishments

Recovery of soluble carbon from aqueous streams: Improved flux and selectivity

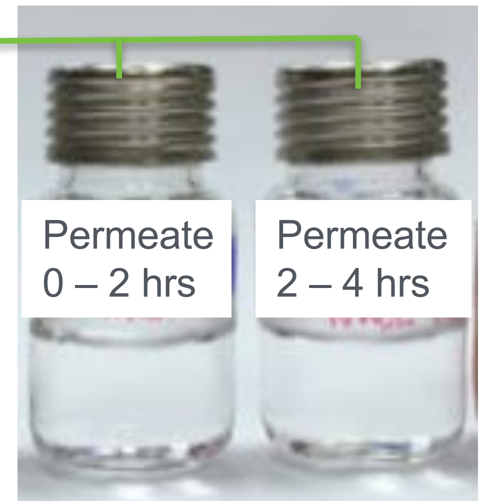
Feed mixture: Aqueous bio-oil fraction

- Represents a high carbon containing HTL aqueous phase fractions (organic content ~18 wt.%)

single tube 4-h run membrane separation

Processed feed:
Carbon conc. is enriched by ~16%

Permeate samples:
>97% reduction in the carbon concentration



- Contains levoglucosan, acetic acid, hydroxyacetone, 2-furanone, furfural, 5-methylfurfural

Demonstrated excellent carbon recovery performance with a representative HTL aqueous bio-oil solution as feed

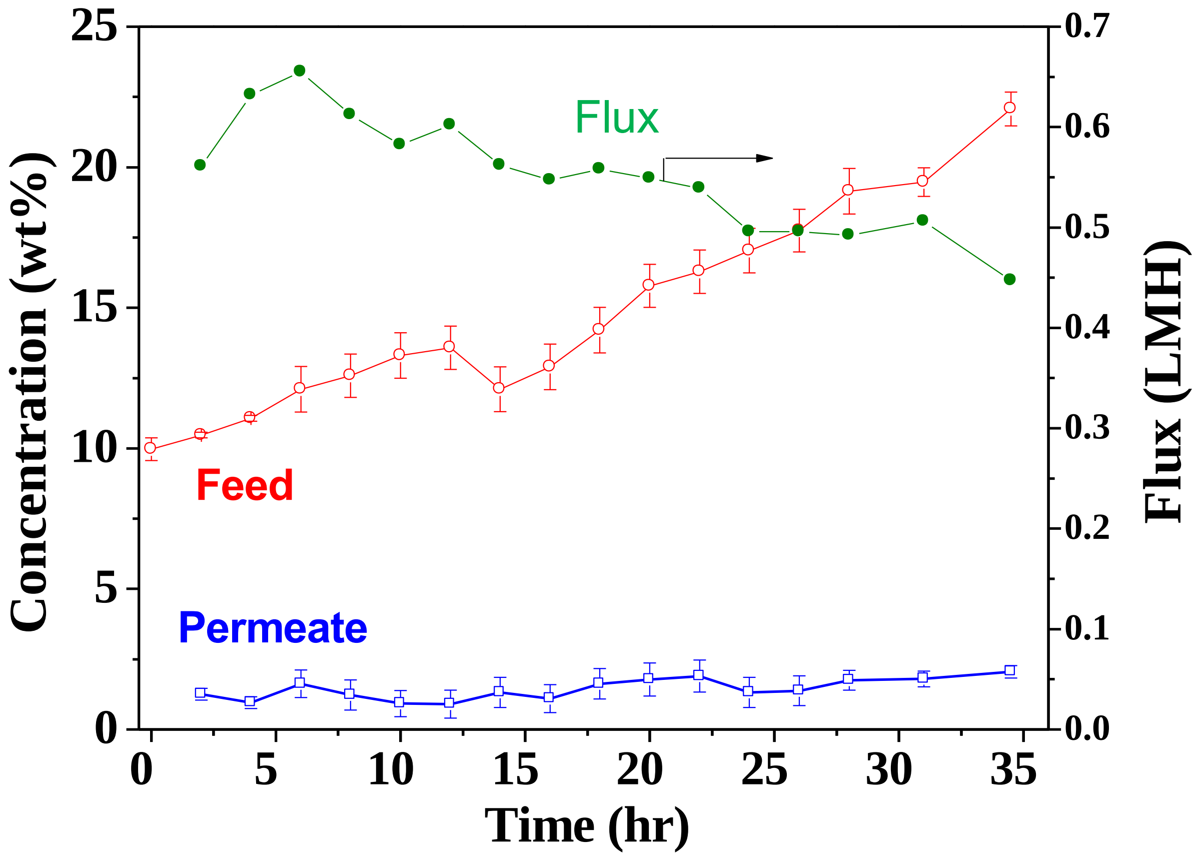
- **Achieved**: water selective permeation flux of 0.63 LMH and separation factor of 57 for our new superhydrophilic membrane
- **Baseline (early FY16)**: flux of 0.1 LMH, separation factor of 12

We are developing chemically stable materials for the fabrication of membrane modules with maximized surface/volume design to increase productivity

Technical Accomplishments

Long-Term Continuous Membrane Water Removal Studies (for Carbon Recovery and Enrichment)

- Feed: 10 wt.% acetic acid solution
- Superhydrophilic **composite coatings** were more chemically stable
- Multi-tube **membrane module** will further improve productivity

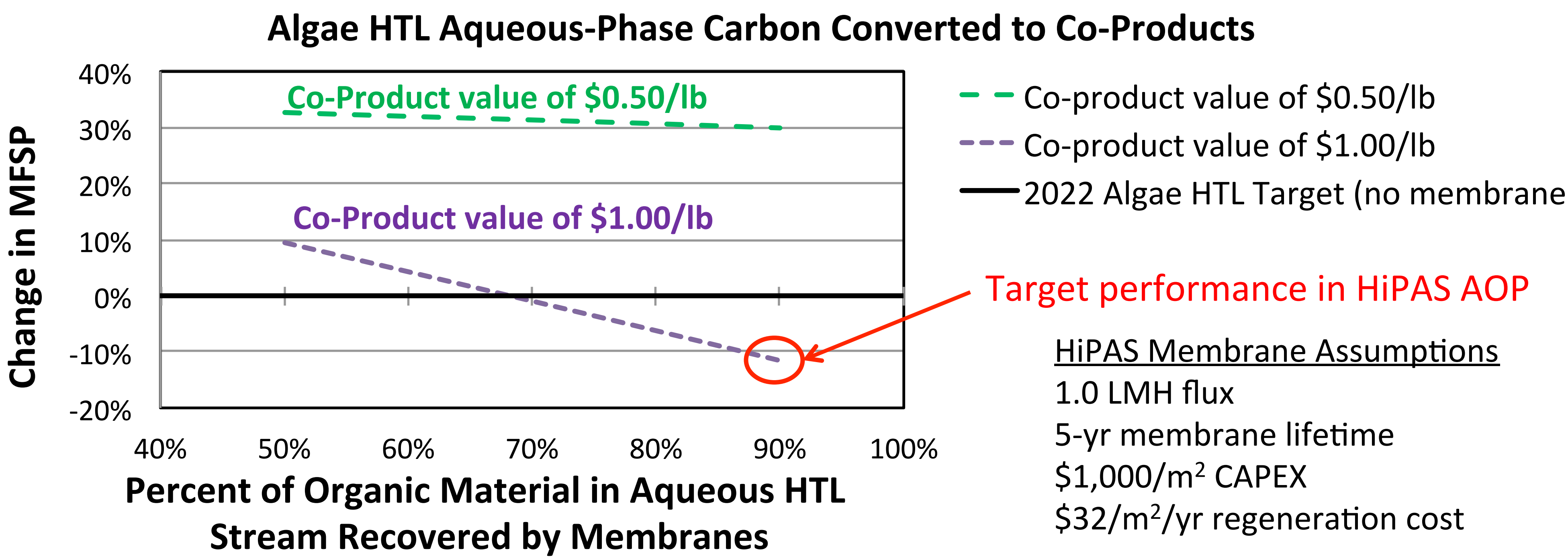


Acetic acid concentration in the feed tank was enriched by factor >2 after processing in continuous water removal runs (studies with HTL aqueous phase are planned)

Relevance

Process	Carbon Loss to Aqueous Phase	Potential Reduction in MFSP
PNNL Algae HTL	10-30%	12%

* Preliminary HTL analysis completed by Sue Jones (PNNL)



HiPAS Membrane Assumptions
1.0 LMH flux
5-yr membrane lifetime
$1,000/m² CAPEX
$32/m²/yr regeneration cost

- Examples of higher-value co-products include phenolic resins, cyclopentanone, methyl tetrahydrofuran (in collaboration with aqueous-phase valorization project).
- Of the scenarios evaluated; algae HTL offers the greatest potential impact. A sensitivity analysis will be conducted.

Planned Future Work

FY 17

- Evaluate membrane flux and fouling during long-term continuous operation with HTL aqueous bio-oil solutions
- Improve permeation flux through polymer-graphene coated membrane
  - Increase pressure differential across membrane
  - Thinner coating processes will be developed
- Develop chemically stable coating materials to enable processing of high organic acid solutions

FY 18

- Explore hydrophobic membranes to reduce the total membrane surface area required (leading to lower membrane capital costs)
- Continuous process development, scalability, and module A/V optimization (investigate re-circulated vs. one-pass flow mode)

Go/No-Go (March 2018): Meet or exceed technical separation targets: separation factor >10 and permeation flux >0.40 LMH (Note: this value is greater than the state-of-the-art literature value of 0.15 LMH).

Summary

Overview: Design and develop versatile high-flux membrane separation technologies that are applicable for multiple thermochemical conversion pathways to increase carbon yield of fuels and chemicals by separating water from carbon (water management) resulting in improved process economics.

Relevance: Technology pathways/processes that suffer from high carbon losses offer more potential for cost reduction (e.g., 12% reduction in MFSP for HTL).

Approach:

- Membrane concept (applicable in multiple processing areas):
  - Rugged inorganic supports and surface enhanced selectivity enabling high flux separations
- Combined expertise in biomass and separations (NREL and ORNL)

Technical Accomplishments/Progress/Results:

- Demonstrated that HiPAS membranes are promising dewatering technologies for integration into TC pathways
- Improved flux and increased water/hydrocarbon selectivity in liquid separations
- Continue to improve material properties and understand process parameters on performance
- Developed a path forward to module design and scale up
- This work has led to an industry funded commercialization project

Acknowledgements

Brian Bischoff
Gyoung Jang
Marissa Morales
Timothy Theiss

Chris Kinchin
Braden Peterson
Steve Deutch
Joshua Schaidle

Additional Slides

Technical Accomplishments

Publications (3 published, 2 submitted):

1. M.Z. Hu*, C. Engtrakul*, B.L. Bischoff, G.G. Jang, T.J. Theiss, M.F. Davis (2016). “Superhydrophobic and Superhydrophilic Surface-Enhanced Separation Performance of Porous Inorganic Membranes for Biomass-to-Biofuel Conversion Applications.” *Separation Science and Technology*, pp. 1-16, http://dx.doi.org/10.1080/01496395.2016.1260144.
2. C. Engtrakul*, M.Z. Hu*, B.L. Bischoff, G.G. Jang (2016). “Surface-Enhanced Separation of Water from Hydrocarbons: Potential Dewatering Membranes for the Catalytic Fast Pyrolysis of Pine Biomass.” *Energy & Fuels*, 30, pp. 8343-8348.
3. M.Z. Hu*, C. Engtrakul, B. L. Bischoff, M. Alemseghed (2017). “Surface-Engineered Inorganic Porous Membranes for Vapor and Pervaporative Separations of Water-Ethanol Mixtures.” *Separation Science and Technology*, submitted.
4. M. Z. Hu* and M.R. Sturgeon (2017). “Architectured Nanomembranes,” invited contribution to a book chapter for book *Shape Selective/Anisotropic Nanomaterials*, submitted.
5. G.G. Jang, B. Song, L. Li, J.K. Keum, Y. Jiang, A. Hunt, K.S. Moon, C.P. Wong, and M. Z. Hu* (2017). “Microscopic Vertical Alignment of Nano-Interspaced Graphene Architectures in Deposit Films as Electrodes for Enhanced Supercapacitor Performance,” *NanoEnergy* 32, 88-95.

Patents:

1. U.S. Provisional-Patent Application (on January 25, 2016), Application No. 62/286,65; Title: Integrated Membrane-Pyrolysis-Catalytic Upgrading Systems; Inventors: Michael Hu (ORNL), Brian Bischoff (ORNL), Chaiwat Engtrakul (NREL), Mark Davis (NREL).

   - 2 new invention disclosures were submitted but have not been filed.

Presentations (2 invited talks):

1. (Invited talk) Michael Hu, Chaiwat Engtrakul, Brian Bischoff, and Gyoung Jang; “Surface-Enhanced Separation Performance of Porous Inorganic Membranes.” Advanced Membrane Technology VII (ECI); Cork, Ireland; September 2016.
2. (Invited talk) Michael Hu, Chaiwat Engtrakul, Brian Bischoff, and Gyoung Jang; “Superhydrophobic and Superhydrophilic Surface-Enhanced Separation Performance of Porous Inorganic Membranes for Biomass-to-Biofuel Conversion Applications.” 19th Symposium on Separation Science and Technology for Energy Application; Gatlinburg, TN; October 2016.
3. Michael Hu, Chaiwat Engtrakul, and Brian Bischoff; “Membrane Separations for Thermochemical Conversion of Biofuels.” TCS 2016; Chapel Hill, NC; November 2016.

Previous (Year 2015) Reviewers' Comments

Reviewer Comment: Not clear that the membrane would have economic impact, even if successful. Simply removing water in one step would not necessarily help the process. The project needs a prompt, basic TEA to show how the work could potentially impact process economics. Not clear that the nano-pore structure will be effective with real bio-oil. Fouling is a major potential problem and does not appear to be adequately addressed.

Reviewer Comment: Techno-economic analysis needs to be done quickly to set meaningful targets!

Reviewer Comment: Not evident why separating water before the hydrotreater is advantageous. Also, performance of membrane for fouling and selectivity for a range of oxygenates represents a huge challenge. How much carbon will be lost to the water and what will be its fate? What will be the economic impact if the project is wildly successful?

Response to Previous Reviewers' Comments

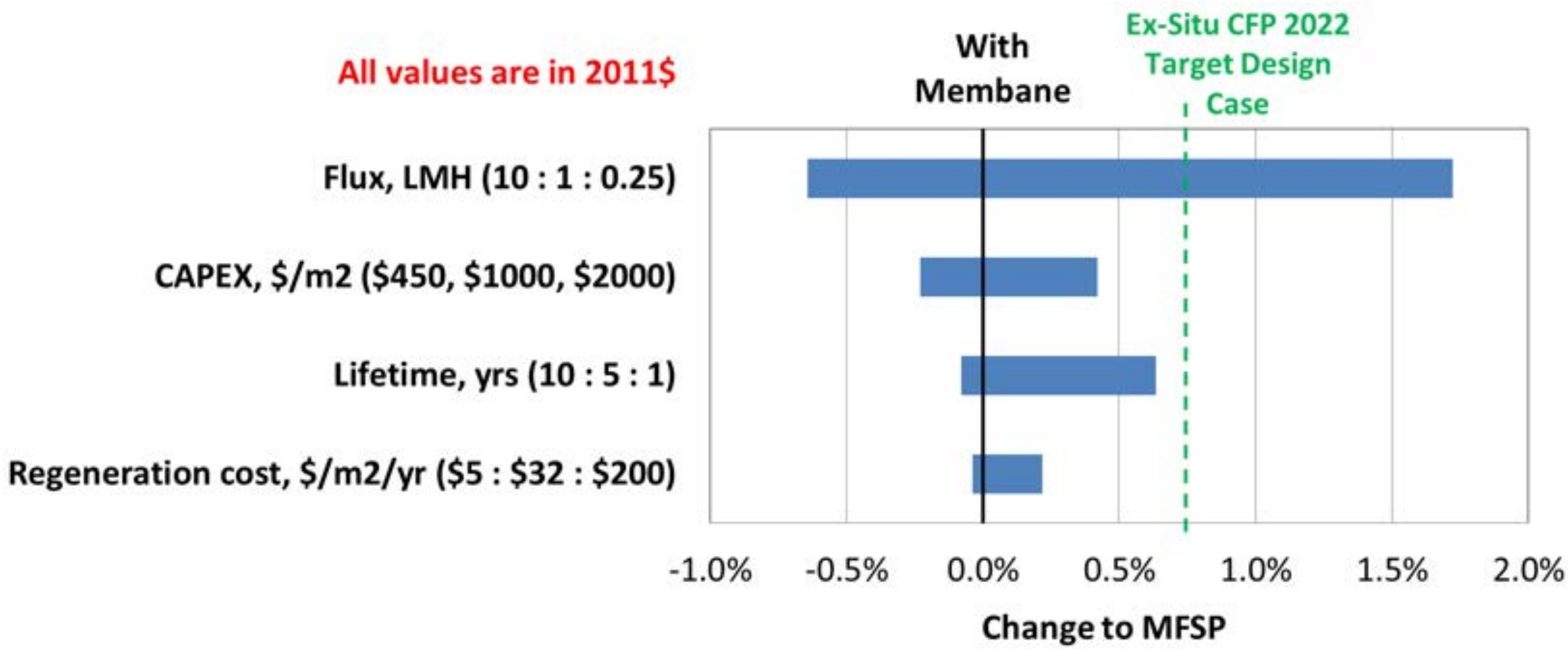
Response: A TEA study conducted by NREL (FY16) based on the ex situ CFP design report,[1] suggested that membrane separation technologies could have a significant economic impact on TC conversion pathways by improving carbon recovery and converting the carbon to fuel. Even with the low carbon loss design case (i.e., 1.3% of the carbon ends up in the aqueous wastewater stream),[1] the TEA demonstrated an ~1% reduction in the minimum fuel selling price (MFSP) ($/gge). For TC conversion pathways, the carbon loss to wastewater is significantly larger. These pathways produce aqueous bio-oil fractions and wastewater streams with much higher organic fractions of the biomass carbon. For example, the wastewater stream in the in situ CFP case contains 2.1% of the biomass carbon.[1] Aqueous-phase wastewater in VTT's CFP design contains 15% of the biomass carbon,[2] and according to RTI's CFP pilot-scale operations report, 18% of the biomass carbon ends up in the aqueous phase.[3] Hydrothermal liquefaction (HTL) models report 40% biomass carbon goes to the aqueous fraction; most of it, however, is recovered for use elsewhere in the facility, and the wastewater stream contains 9% of the biomass carbon.[4] In summary, a significant economic benefit (*up to an est.* 8% reduction in MFSP, $/gge) can be realized if the advanced membrane technology is applied to pathways that lose carbon to wastewater. Moreover, the planned TEA in this project will evaluate additional cost savings and profits by converting recovered organics to higher-value chemical co-products rather than fuels.

References:

1.Dutta et al. NREL Technical Report NREL/TP-5100-62455. March 2015.
2.Paasikallio et al. *Green Chem.* **2014**, 16, 3549.
3.Dayton et al. *Green Chem.* **2015**, 17, 4680.
4.Zhu et al. *Appl. Energ.* **2014**, 129, 384.

Relevance: Response to Previous Reviewers' Comments

TEA for Recovering Carbon from ex-situ CFP Wastewater



- HiPAS membranes have the potential to reduce MFSP of some technology pathways if flux is improved to at least 1.0 LMH.
- Membrane lifetimes greater that 5 years and membrane capital costs below $1,000/m^2 are necessary to reduce MFSP. Current estimates for longevity and capital cost of membranes are speculative, but are based on literature values for similar applications.
- Applications that eliminate downstream equipment (e.g., RTO) can potentially reduce MFSP.

Technical Approach − Tasks

Task 1: Membrane materials development, synthesis, and fabrication (ORNL)

- Identify HiPAS membrane materials that enable permeation of either polar species (e.g., water or oxygenates) or less-polar species (e.g., organic acids or hydrocarbons)
- Modify pore structure (size) and membrane surface to control flux and surface properties (superhydrophilic to superhydrophobic), respectively
- Add surface texturing and/or polymer/ligand functionalities to understand the effectiveness of tuning surfaces to improve selectivity and flux

Task 2: Liquid-phase separation process development (ORNL/NREL)

- Evaluate HiPAS membranes using TC wastewater streams with high amounts of biomass carbon to recover (> 5 wt.%)

Task 3: Vapor-phase separation process development (NREL/ORNL)

- Evaluate HiPAS membranes under constant TC processing conditions. Possible insertion point will be after the upgrading vapor-phase reactor (e.g., two fixed-bed ex situ catalytic fast pyrolysis pathway)

Technical Accomplishments – Highlights

FY 15 − 16:

- For liquid-phase separations, developed superhydrophobic and superhydrophilic HiPAS membranes to separate oil-in-water and water-in-oil emulsions. Oil or water permeation with high selectivity was achieved with high flux and less oil fouling.
- A new polymer-coated membrane was identified as a potential dehydration membrane for recovering carbon from aq. fractions. Initial success was achieved in separating water from oxygenated hydrocarbon feed solutions.
- Pore size of superhydrophilic membrane was increased by a factor of two and high selectivity was achieved in a vapor-phase separation process (1-ring hydrocarbons vs. water) by employing a surface-enhanced capillary condensation mechanism.

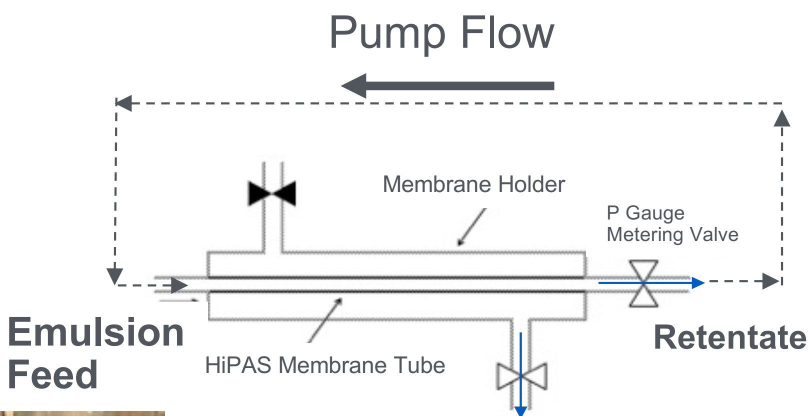
FY 17 (Q1):

- Two new polymer and polymer/graphene composite coated membranes demonstrated excellent dewatering performance with an aqueous bio-oil feed and acidic acid solutions (e.g., separation factor of 57 and water selective permeation flux of 0.63 LMH).
- Initial tests demonstrated that up to ~50% of the water can be removed from the water vapor feed under constant process conditions of the continuous feed reactor (concentration and flow conditions).

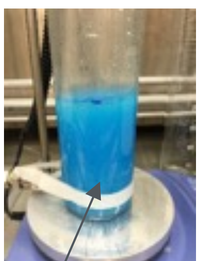
Technical Accomplishments

Continuous Engineering Process for Carbon Recovery from Emulsions

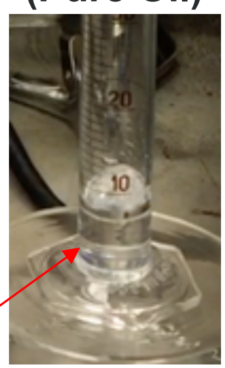
Hydrophobic large-pore (4-µm) HiPAS membrane



Permeate (Pure Oil)



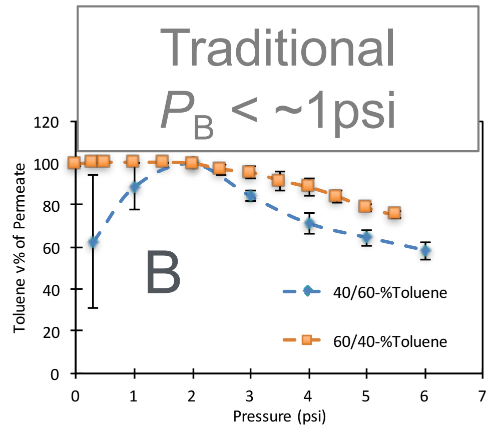
Oil-in-Water
Emulsion Feed Tank



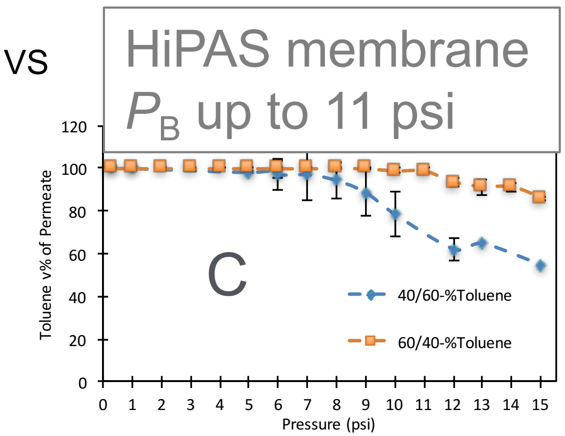
Continuous harvest **clear oil** phase with ~100% selectivity!

- Separation performance comparison, demonstrating surface enabled separation efficiency.

HiPAS membrane can operate at >10x higher break-through pressure (P_B) conditions, resulting in 2-3 orders of magnitude higher flux at 100% selectivity



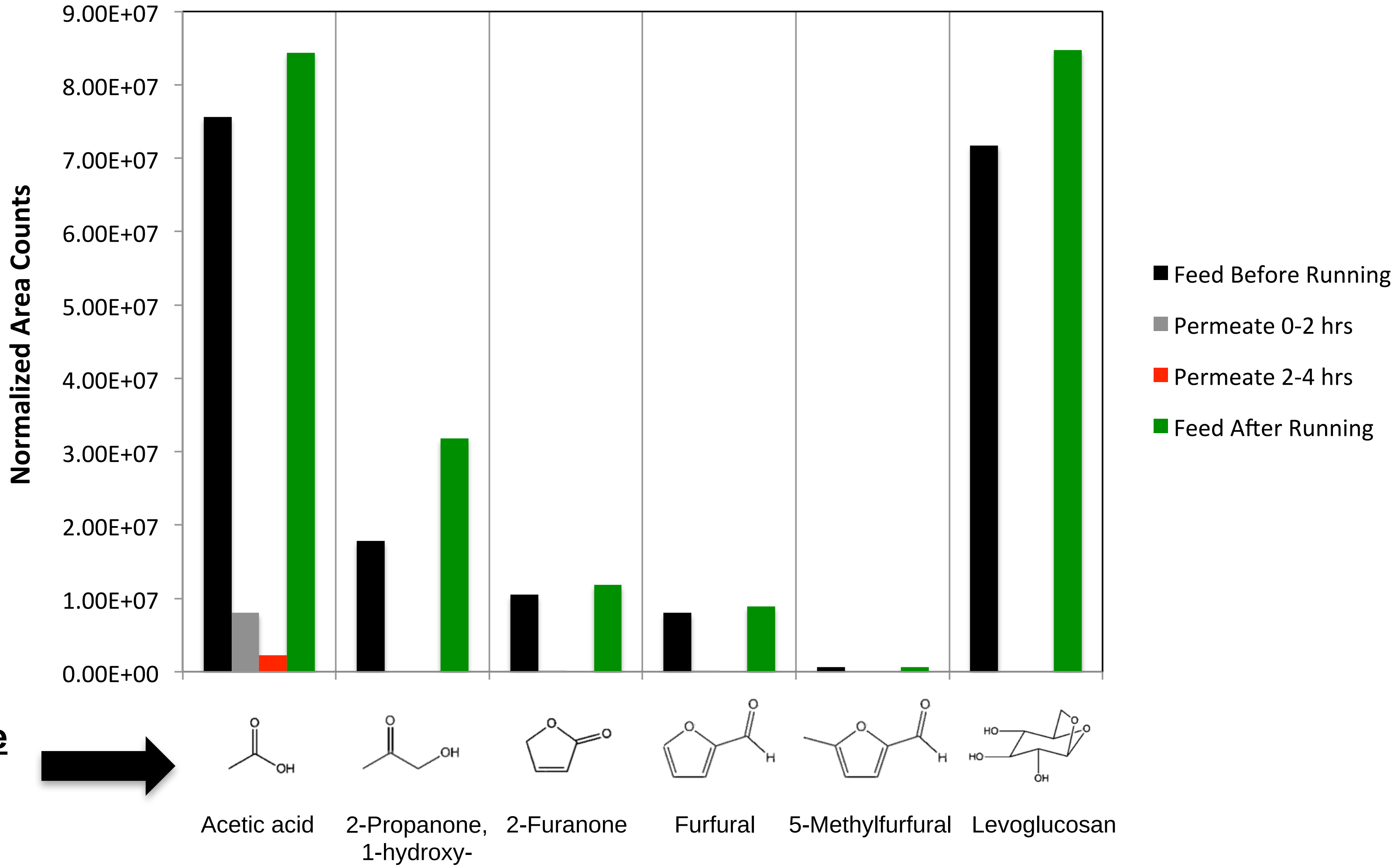
vs



Technical Accomplishments

2D-GCMS Analysis of the Membrane Processed Aqueous Bio-oil Samples

Water-Soluble Organics:



- Significant reduction in the hydrocarbons permeating through the membrane
- Trace amount of component in permeate is mainly acetic acid