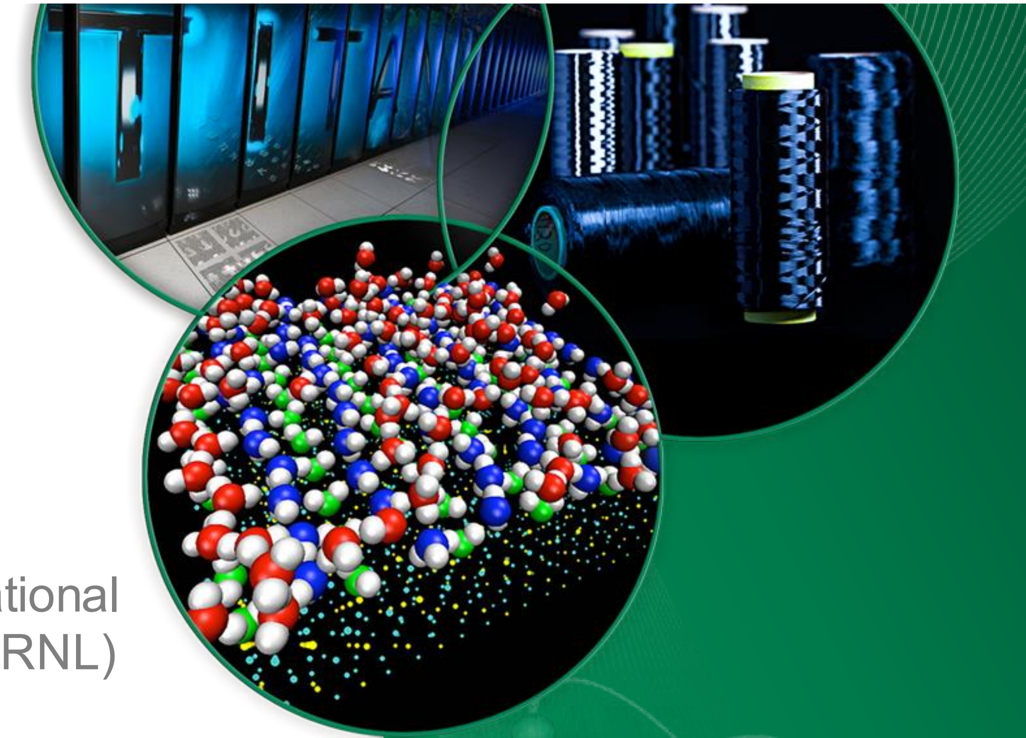
DOE Bioenergy Technologies Office (BETO)
2015 Project Peer Review

Advanced Membrane Separations to Improve Efficiency of Thermochemical Conversion



March 24, 2015
Technology Area Review

Project Team:

Michael Hu
Brian Bischoff
Oak Ridge National Laboratory (ORNL)

Chaiwat Engtrakul
Mark Davis
National Renewable Energy Laboratory (NREL)

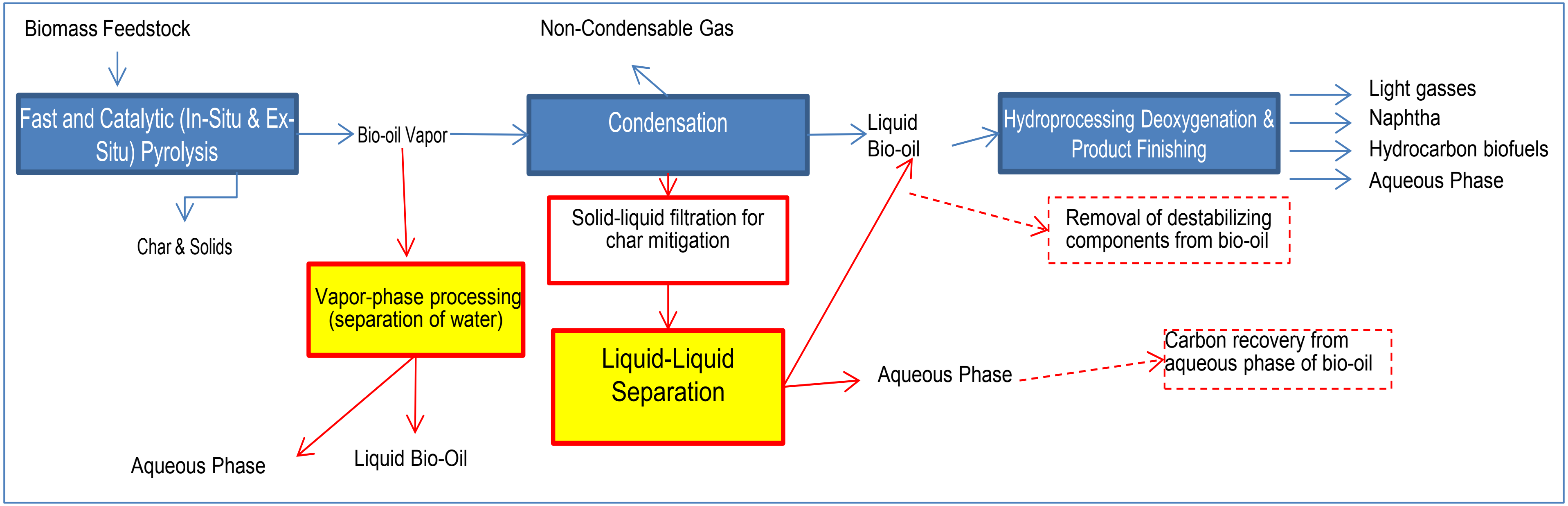
High **P**erformance **A**rchitectured **S**urface-Selective (**HiPAS**)

Goal Statement

This project seeks to develop & employ a new class of HiPAS membranes, to improve the efficiency of bio-oil processing in both vapor- and liquid-phase.

Measurable performance target: >10:1 selectivity & 100X higher flux

- **Fits with BETO Technology Areas**: Thermochemical Conversion, Integration & Intensification (Advanced Separations), Fractionation, Biochemical Conversion, etc.
- **Address multiple separation needs** in biorefinery and biofuel processing industries



Tangible outcome on economics of drop-in fuels & biofuel blends: Lower cost biofuel processing will reduce carbon emission and petro-oil dependency for the US

Quad Chart Overview: WBS 2.5.5.(301 & 302)

Timeline

- Project start date: January 2014 (Initial development)
- Renewed into FY2015 (Bench-scale development)
- Planned end date: 9/30/2017 (Long-term testing utilizing a continuous slip stream)
- Percent complete: ~25%

Barriers

Address BETO-MYPP Barriers & Technical targets:

1) Tt-O. Separations Efficiency
2) Tt-J. Catalytic Upgrading of Bio-Oil Intermediates to Fuels & Chemical
3) Bt-H. Cleanup/Separation

Conversion Cost target: $1.87/GGE (2017)

Budget

DOE Funded	Total Costs FY11-FY13	FY14 Costs ($)	Planned Funding FY15-End ($)	Project Type
ORNL	N/A	391,420.00	908,580.00	existing
NREL				

Partners

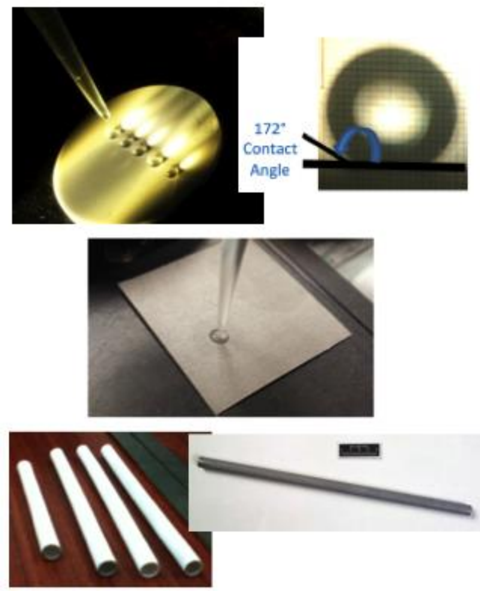
- Partners (this project)
  - **ORNL** (~75%), **NREL** (~25%)
- Also attracted industrial interests, working with others to apply HiPAS membranes for related applications
  - Amyris Inc. (signed NDA, bio conversion)
  - Verso Paper Corp. (saving 80 trillion Btu/yr)
  - NL Chemical Technology Inc. (will sign NDA)

1 – Project Overview

Objective: **To develop and employ a new class of high-flux membranes by utilizing surface-enhanced selectivity for the processing of bio-oils.**

- **FY14 (Jan):** Work initiated on membrane fabrication, surface modification, proof-of-principle selective separation with ethanol/water (liquid & vapor) system & developed initial testing of bio-oil vapors
- **FY15:**
  Engineer 1st-generation HiPAS membranes to demonstrate vapor- and liquid-phase selectivity using real bio-oils.
  - Develop membrane materials by engineering nanopore size/structure & surface nanotexture/wetting properties
  - Evaluate membranes for vapor- & liquid-phase separations
  - Work together with NREL on developing integrated membrane-catalytic upgrading system for pyrolysis bio-oil vapor processing.

New Membrane & Materials Concept



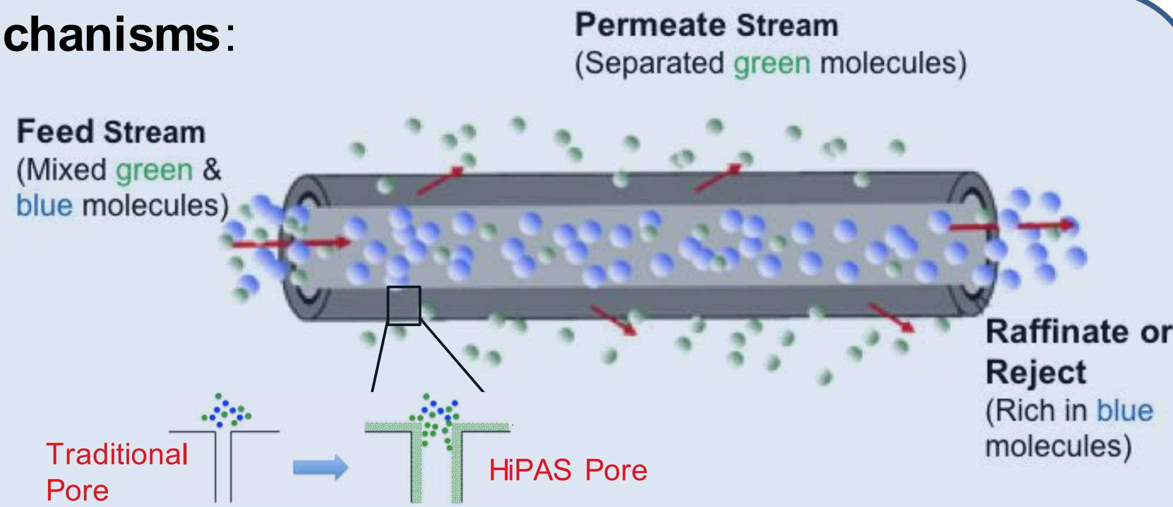
Membrane discs and tubes based on a new class of materials, with synergistic control of nano-engineered surface and pore properties

***Strategy**: High performance achieved through synergistic nano-engineering of surfaces & pores*

2 – Approach (Technical)

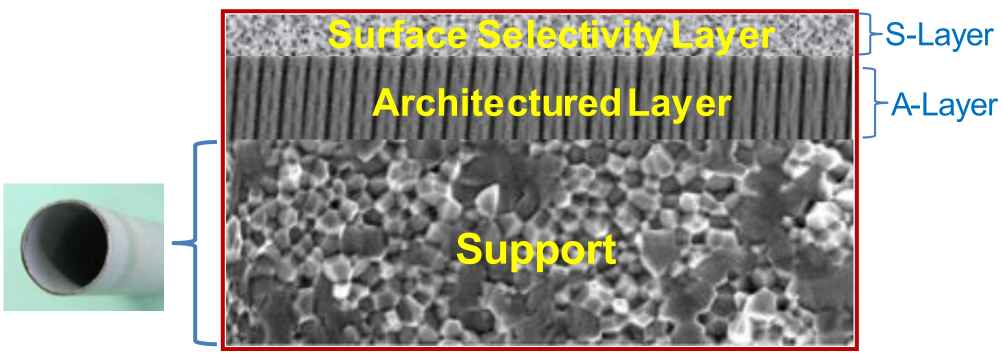
Revolutionary Separation Mechanisms:

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



Fabricate Nano-Surface HiPAS Membranes and Evaluate in Relevant Vapor- and Liquid-Phase Bio-oil Systems

US Patent 20140116944

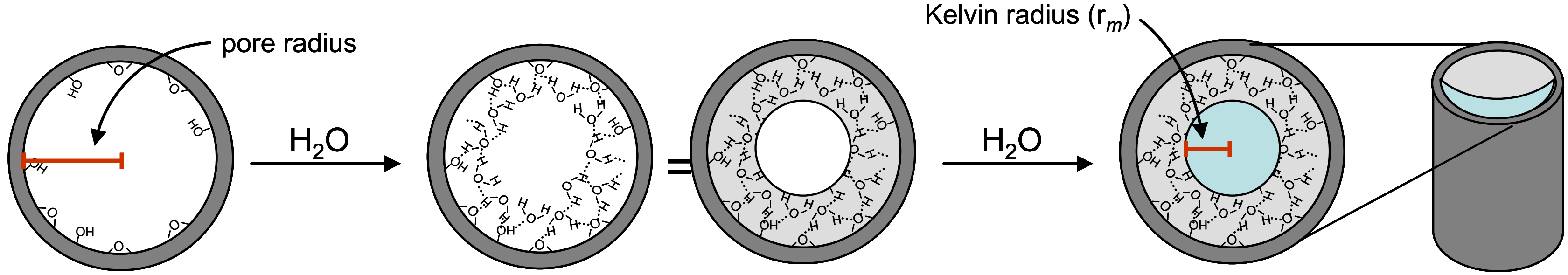


High Performance in
Selectivity, Permeability, & Stability

- Build upon a pioneering membrane & material concept
- Fabrication takes advantage of unique combination of ORNL legacy inorganic membrane support platform & new material nanotechnology
- Strong NREL/ORNL teaming to develop new processes, testing under relevant bio-oil conditions

HiPAS are unique and different from traditional membranes

Illustration of Enabling Mechanisms to Enhance Selectivity & Flux with a Superhydrophilic HiPAS Membrane for Vapor-Phase Separations



Alumina Pore | **Enhanced preferential adsorption** | **Water adsorbs to surface** | **Water condenses in pore** | **Elongated view of pore**

Capillary Condensation (Kelvin Eq.):

$$\ln\left(\frac{P}{P_{sat}}\right) = \frac{-2\gamma V_m}{r_m RT}$$

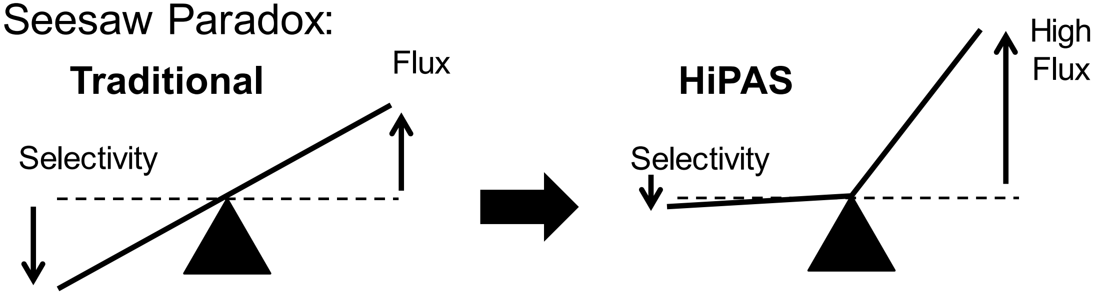
Where $\frac{P}{P_{sat}}$ is the ratio of the vapor pressure to the saturation vapor

γ is the surface tension of the fluid

V_m is the molar volume

r_m is the radius of the pore.

Seesaw Paradox:



- Nano-textured superhydrophilic surfaces increase the affinity for water vapor to adsorb and condense in nanopores
- Feed water content ~20% by weight (~50% on molar basis) in bio-oil can be lowered to 3% (molar) to achieve **greater than 90% water removal!**

2 – Approach (Management)

- **Critical Success Factors**
  - Demonstrate > 10:1 selectivity and 100X higher flux with HiPAS membranes (FY14 − FY15)
  - Demonstrate improved catalyst stability and/or yield under standard catalytic upgrading conditions, e.g., reduction in coke formation (> 20%) (FY15 − FY16)
  - Demonstrate acceptable long-term HiPAS membrane stability (> 8h) under standard fast pyrolysis and hydrotreating bio-oil conditions (FY16 − FY17)
- **Management Plan**
  - AOP development was accomplished in conjunction with BETO
  - Key project SMART milestones were developed under BETO guidance and approved
  - Developed go/no-go project decision points to guide the overall direction of the project
  - Established bi-weekly project progress meetings to coordinate efforts pertaining to the technical project tasks

2 – Approach (Challenges)

Membrane Materials Development (vapor- and liquid-phase)

- **Pore nano-engineering** [A-layer]
  - Tailored size, 5nm, 8nm, 20nm (Pore size effect on flux)
  - Pore shape & architecture
- **Surface nano-engineering** [S-layer]
  - Superhydrophilicity ←→ Superhydrophobicity
  - Enhanced selectivity by molecular affinity to surfaces
- **Chemical stability & ruggedness**
  - Corrosion resistance to maintain structural integrity and surface treatment
  - Liquid phase separation (50−70°C)
- **Thermal stability**
  - Bio-oil vapors enter membrane at 250−350°C, hydrophilic HiPAS is good

Vapor-Phase Separations Process Parameters

- **Membrane temperature (*T*)**
  - Threshold *T*, below which capillary condensation starts
- **Transmembrane pressure drop (Δ*P*)**
  - Threshold Δ*P*, above which nanopores are emptied of condensed liquid and both gases flow freely through pores
- **Feed component concentration (*C*)**
  - Minimum vapor concentration needed to condense in nanopores
- **Feed flow rate (*F*)**
- **Surface affinity** of target permeate molecule to membrane/pore surfaces
  - Significantly lowers the "critical concentration" for capillary condensation to occur

Is a benchmark selectivity of 10:1 achievable?

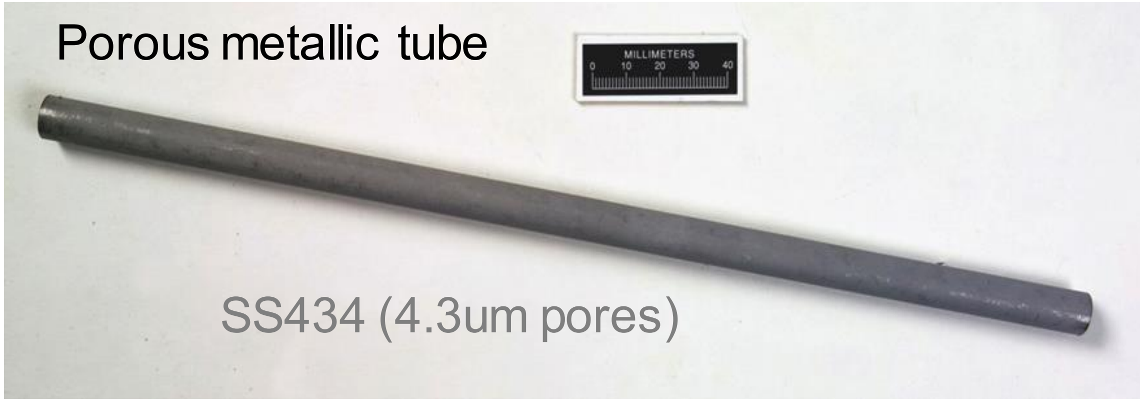
3 – Technical Accomplishments (Summary)

- **Demonstrated the new nano-surface enhanced effect for selective separation of water-hydrocarbon mixtures (both vapor- and liquid-phase)**
- **Obtained encouraging HiPAS performance data with pyrolysis/upgraded bio-oil vapors:**
  - Superhydrophilic membranes demonstrated desirable water permeation while rejecting hydrocarbon vapors. Directly relevant to dewatering applications!
  - Superhydrophobic membranes showed promising separation of hydrocarbons from water vapor; allowed preferential permeation of hydrocarbons.
  - Promising results with real bio-oil vapors: Experimentally captured the unique nano-surface enhanced "capillary condensation" separation mechanism

    Achieved water/hydrocarbon selectivity approaching benchmark 10:1
- **Successfully integrated the membrane with the catalytic upgrading reactor for testing pyrolysis bio-oil & upgraded vapors**

3 – Technical Accomplishments/Progress/Results

Over 30 tubular membranes have been fabricated for further materials development, membrane testing, and process advancement



Current

Single tube assembly, designed and established for vapor-phase studies

Established integration of HiPAS membrane (A) into membrane holder (B) with catalytic upgrading reactor (C), for monitoring performance

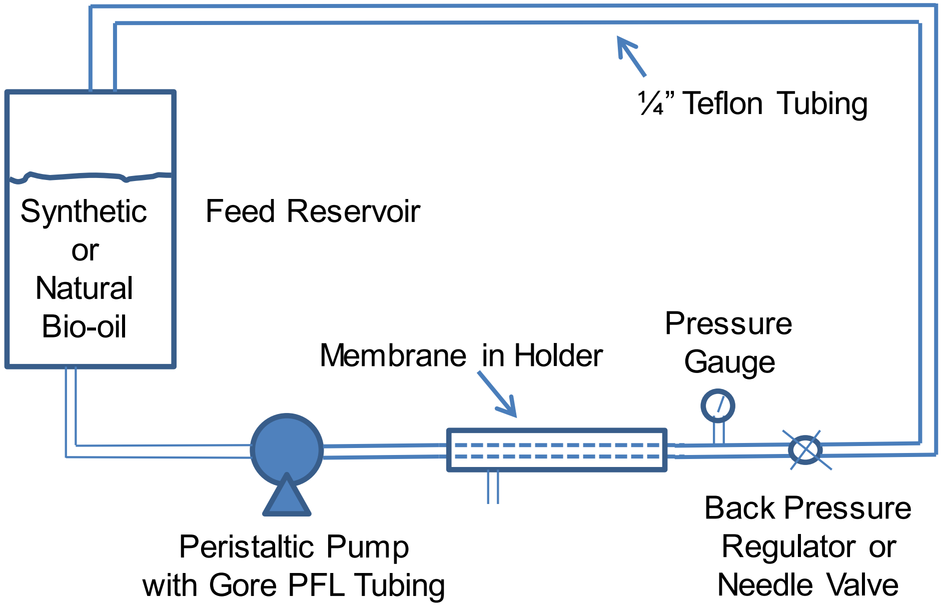
Future

Multi-tube array system, suitable for scale up processing volume throughput

3 – Technical Accomplishments/Progress/Results

Preliminary Liquid Separation Tests

- Employed a 10-component surrogate bio-oil mixture to accelerate analysis and speed up membrane property adjustments



Preliminary results show a difference in appearance between feed and permeate through superhydrophobic HiPAS membrane. Chemical analysis is pending.

Mixture Composition*

Chemical	wt %
Methanol	5%
Acetaldehyde	12%
Acetic acid	14%
Glyoxal	4%
Acetol	8%
Glucose	8%
Guaiacol	17%
Furfural	4%
Vanillin	8%
De-ionized water	20%
	100%

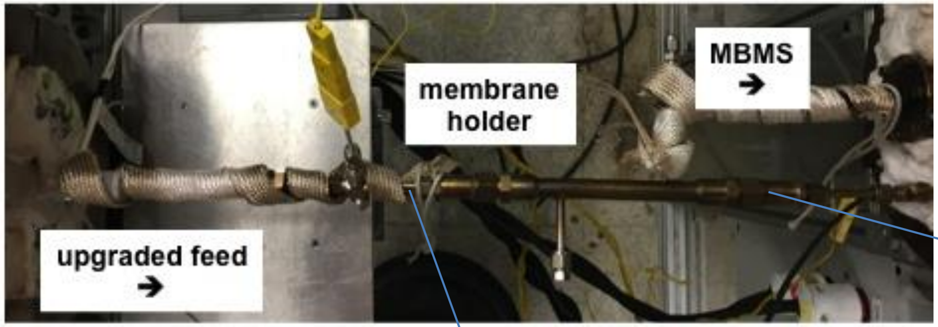
*Fisk, C.A.; et al. Applied Catalysis A: General 358 (2009) 150–156.

3 – Technical Accomplishments/Progress/Results

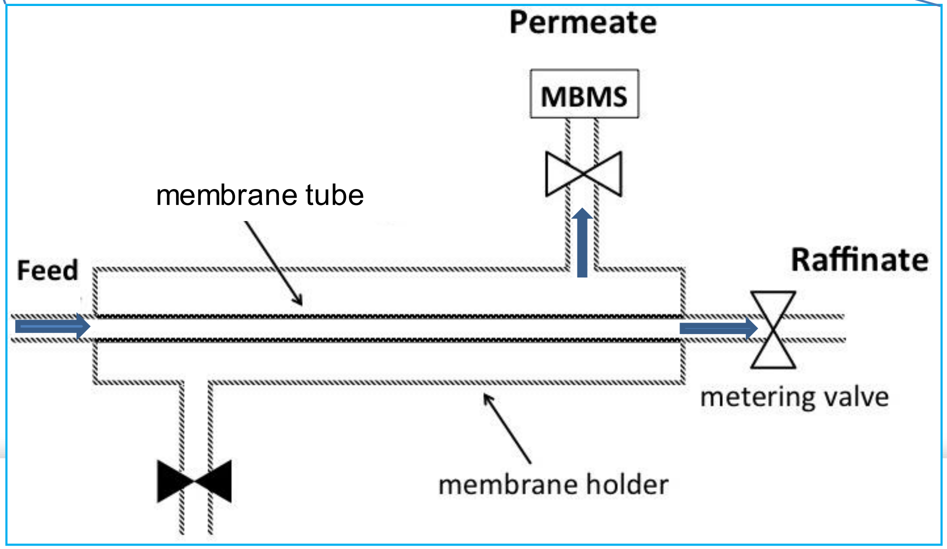
Developed real biomass vapor membrane test configurations with in-situ, real-time monitoring of performance using Molecular Beam Mass Spectrometry (MBMS)

Integrated horizontal quartz reactor / membrane / MBMS system

Initial Permeate Test Configuration



Pine pyrolysis vapors analyzed with or without a catalyst upgrading bed



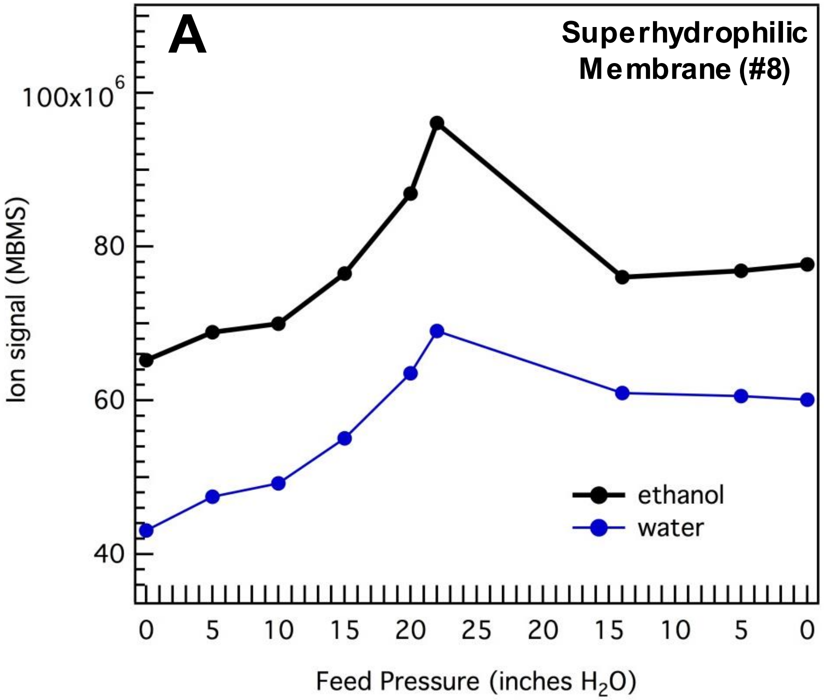
A – a typical membrane tube with seals at ends

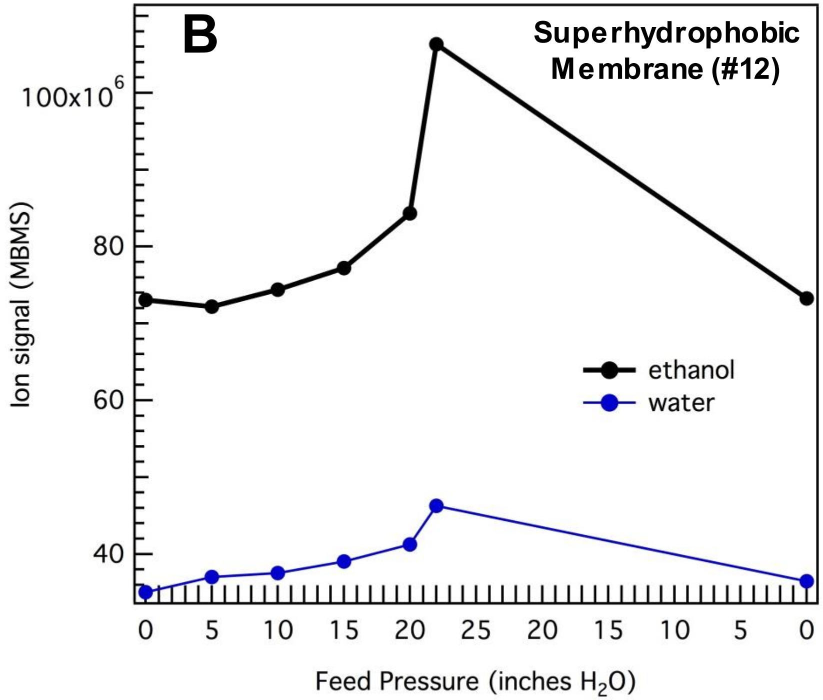
B – assembly holder with a membrane tube inside

3 – Technical Accomplishments/Progress/Results

<u>EtOH-Water Vapor Separation Data</u>: Superhydrophilic membrane showed enhanced water vapor permeability, while superhydrophobic membrane inhibited water permeation!

Permeate as a function of feed pressure



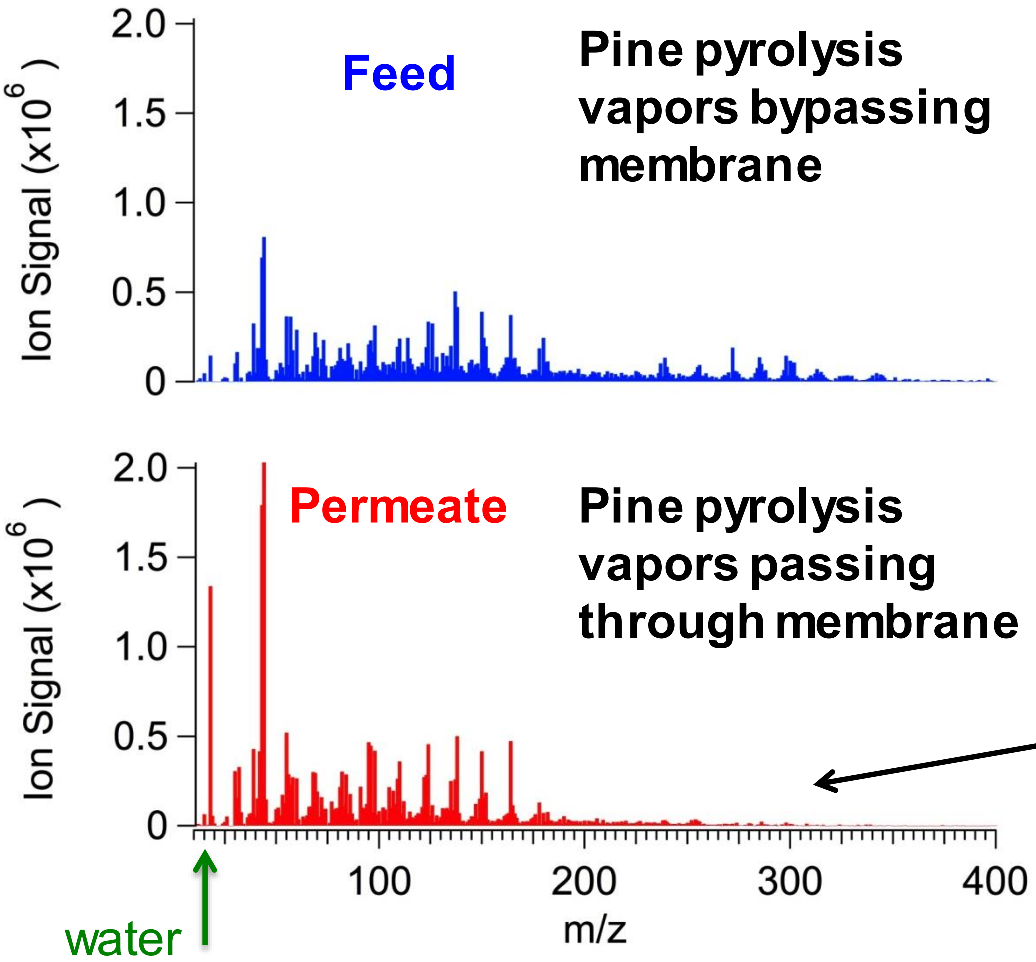


- Demonstrated that a **superhydrophilic** treatment enabled a strong preference for water in a HiPAS membrane when exposed to a mixture of water and ethanol vapor
- Demonstrated improved selectivity for ethanol vapor when using a **superhydrophobic** HiPAS membrane

Impact: At this stage of development, HiPAS membranes were strong candidates for the separation of vapor-phase products

3 – Technical Accomplishments/Progress/Results

MBMS efficiently evaluated membrane using pine pyrolysis vapors (including water, sugars, and oxygenated hydrocarbons)

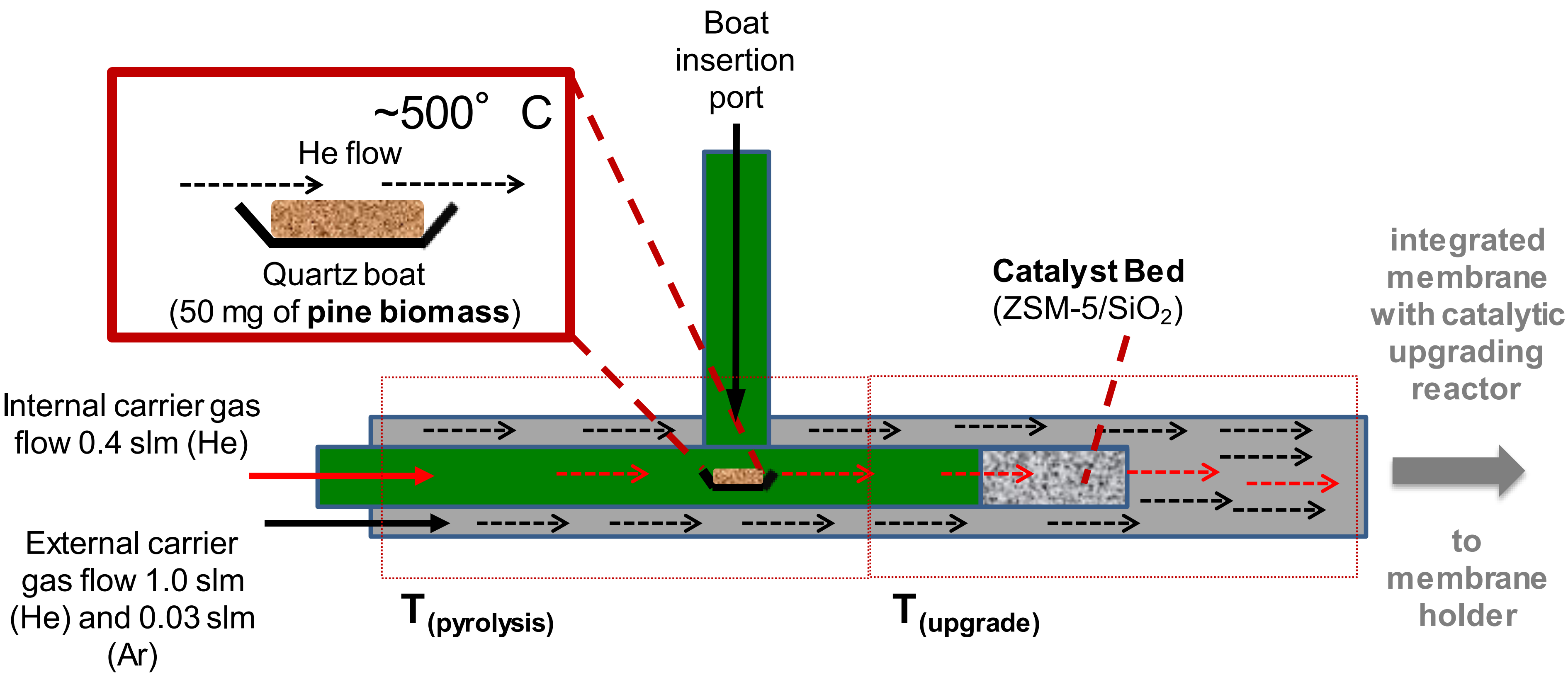


Pine pyrolysis vapors were able to pass through a HiPAS membrane and were detected by MBMS successfully. Signals for water and light gas products (permeate) were enhanced!

Disappearance of the large lignin dimer peaks was due to a size exclusion process

3 – Technical Accomplishments/Progress/Results

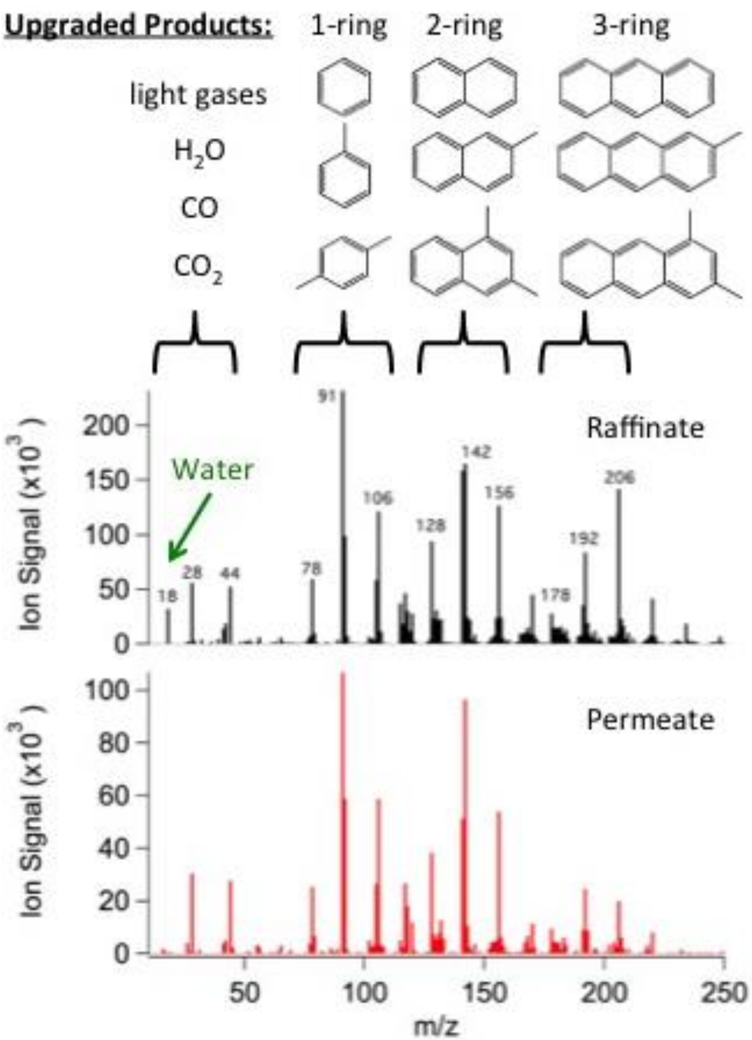
Utilized a custom-built quartz reactor at NREL to generate "crude" vapor-phase pine pyrolysis or upgraded products

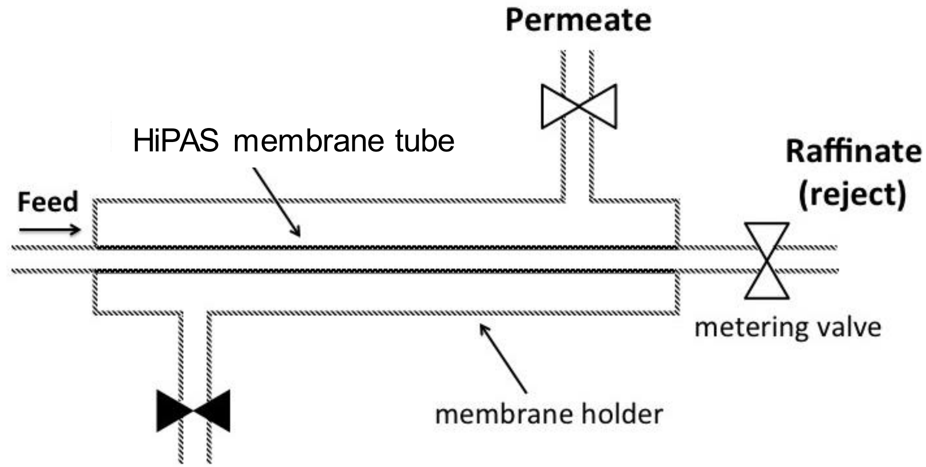


Impact: (1) enabled evaluation with real bio-oil vapors
(2) enabled membrane integration into bio-oil process system

3 – Technical Accomplishments/Progress/Results

Encouraging results were obtained for water separation from upgraded vapors by a superhydrophobic HiPAS membrane



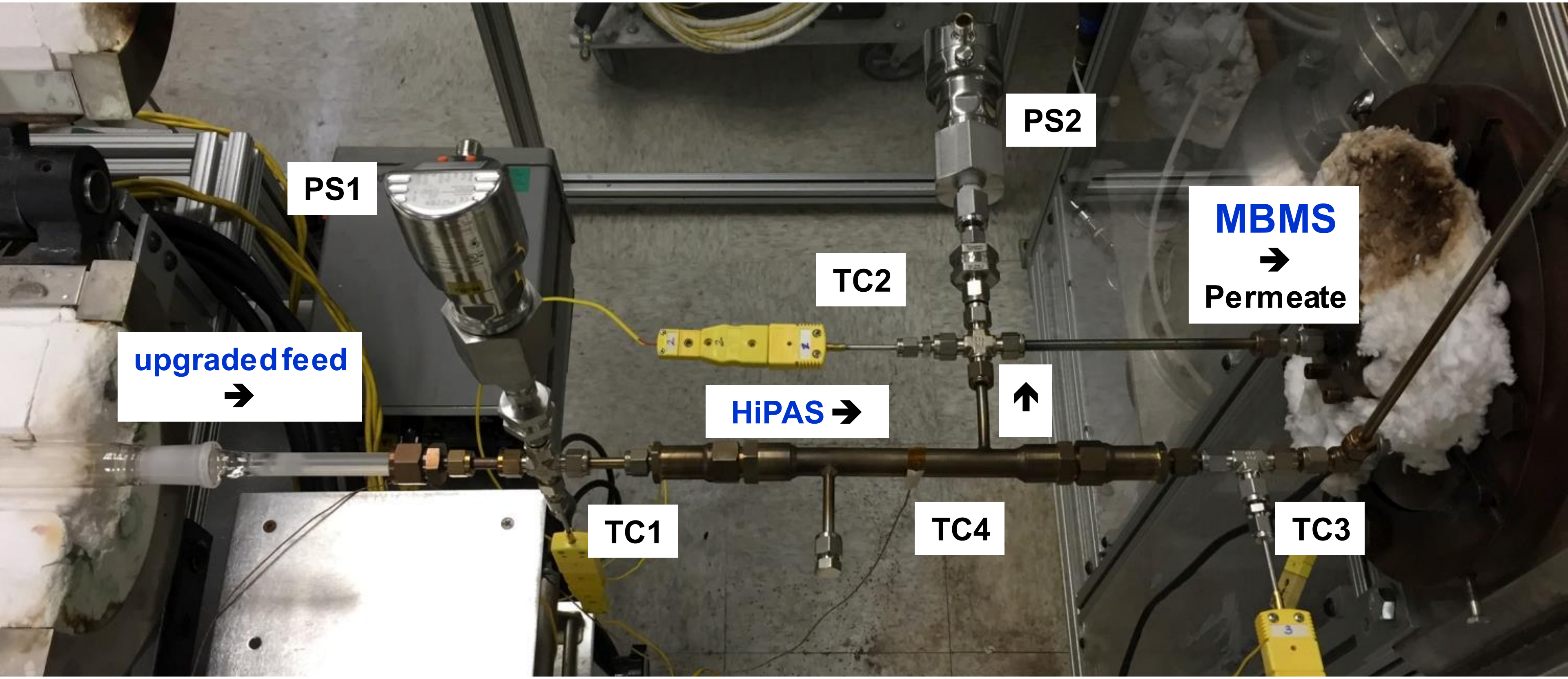


- Superhydrophobic membrane effectively separated water from upgraded pine pyrolysis vapor products
- Membrane showed strong preference selectivity for hydrocarbons at 300°C

Based on encouraging preliminary results a decision was made for further investigation in FY15

3 – Technical Accomplishments/Progress/Results

Refined membrane evaluation setup by incorporating better control and monitoring of process parameters



PS1: feed-side pressure
PS2: permeate-side pressure

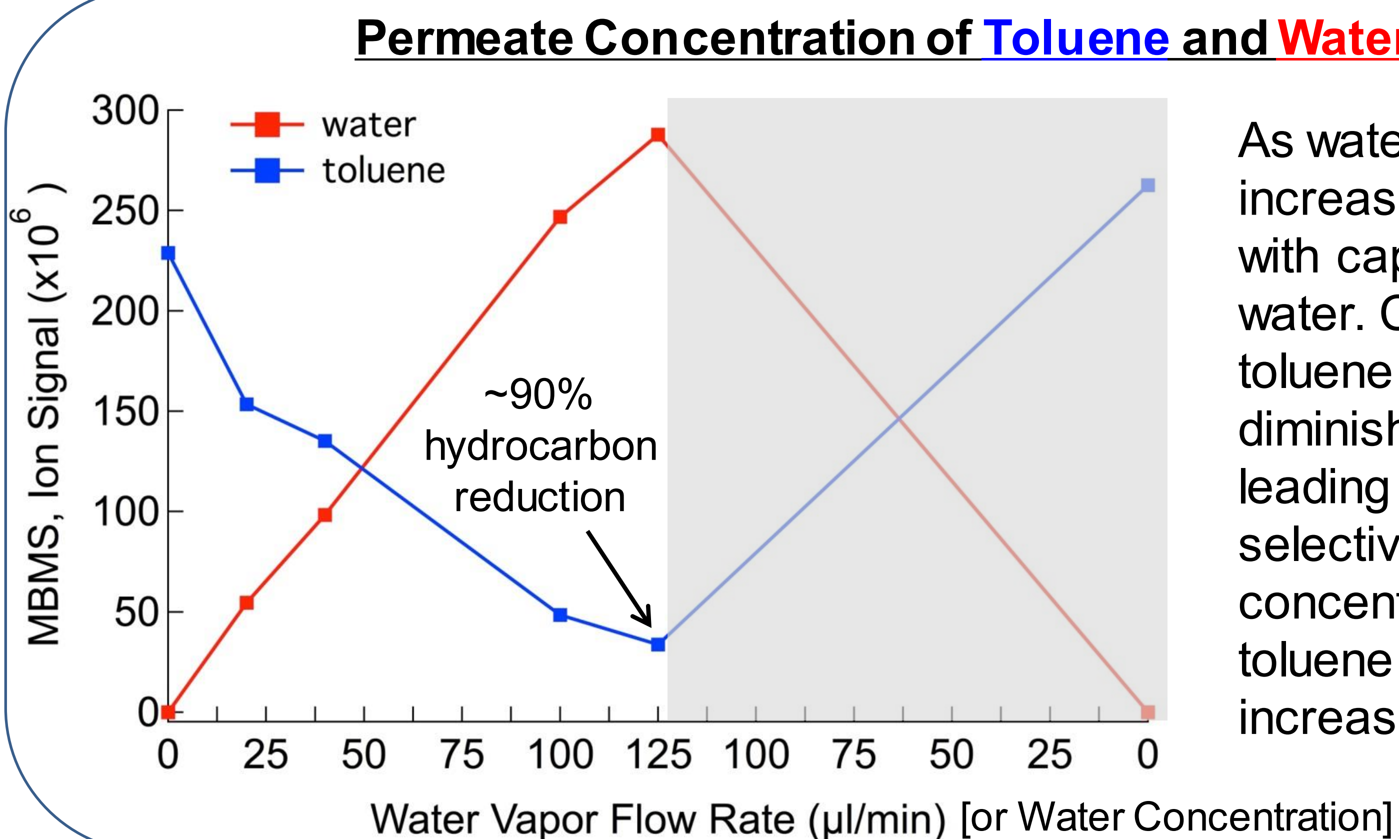
TC1: feed-side temperature
TC2: permeate-side temperature

TC3: reject-side temperature
TC4: outside membrane holder temperature

New test configuration enabled direct monitoring of the adsorption and capillary condensation phenomena occurring in the pores of the HiPAS membranes which is necessary for high selectivity.

3 – Technical Accomplishments/Progress/Results

Captured actual capillary condensation with a superhydrophilic HiPAS



As water vapor concentration increased, pores start to fill with capillary-condensed water. Correspondingly, toluene vapor in permeate diminished almost completely, leading to high water/toluene selectivity. As water vapor concentration decreased, toluene vapor permeation increased.

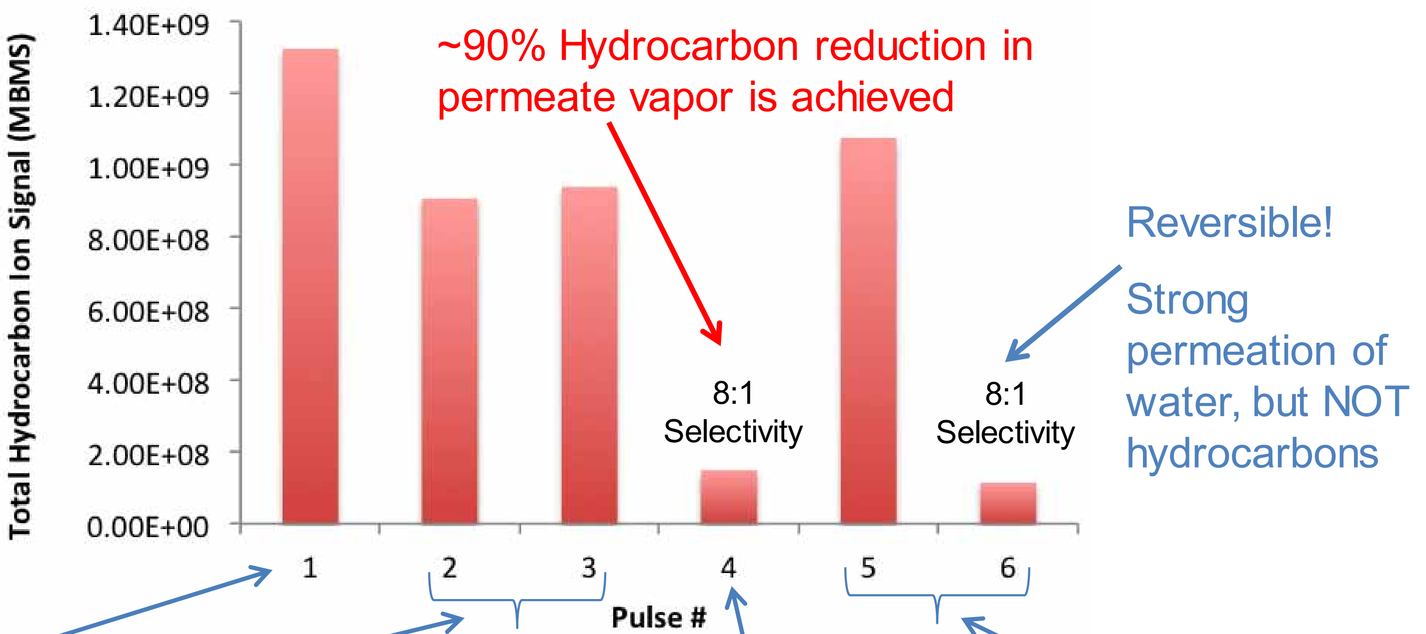
- **Demonstrated that superhydrophilic nano-surfaces enabled an enhanced water vapor adsorption/condensation processes, which induce membrane selectivity**

Does this work for separation of real pyrolysis bio-oil vapors?

3 – Technical Accomplishments/Progress/Results

Successfully observed desirable capillary condensation phenomenon in superhydrophilic HiPAS membrane with real upgraded pyrolysis vapor !

Hydrocarbons in Permeate Stream
[Total Ion Signals for Mass Spectral Peaks (m/z 78, 91, 106, 128, 142)]



Vapor-phase upgraded components in permeate, NO additional water vapor (pulse 1)

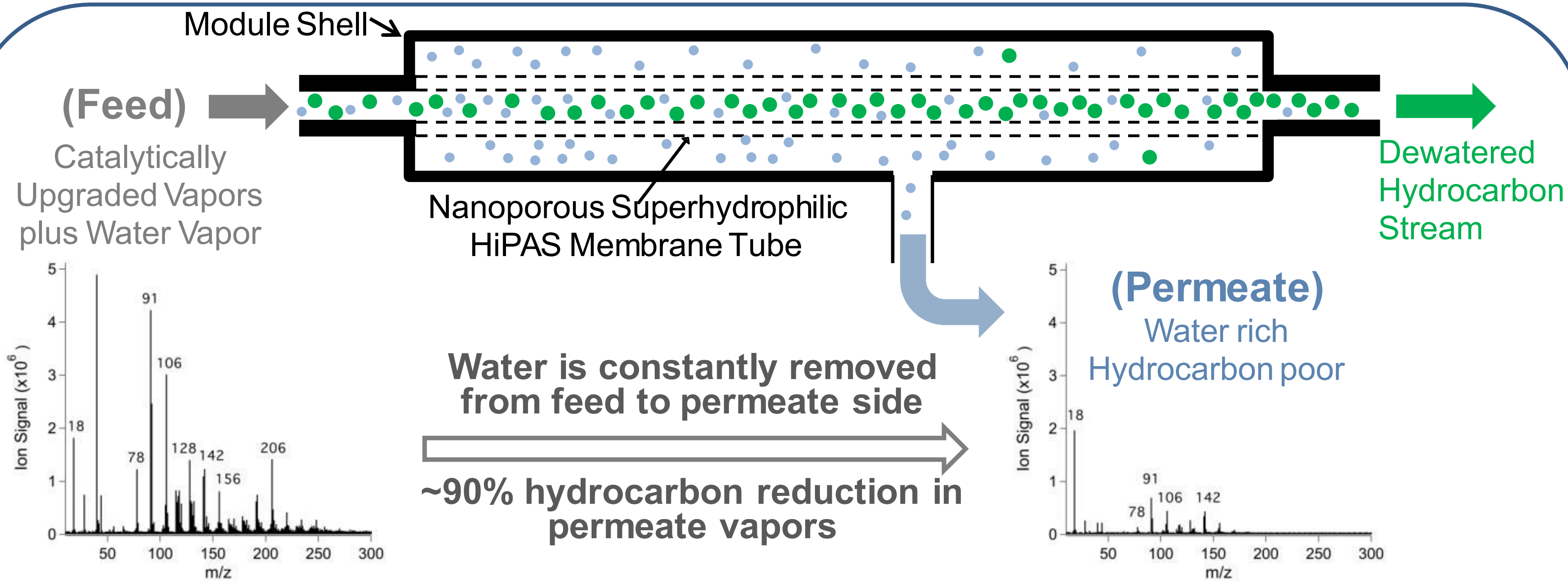
As adsorption and capillary condensation of water vapor occurs in the pores, the total hydrocarbon signal begins to decrease (pulses 2 & 3)

When more complete pore filling is achieved, condensed water blocks flow of hydrocarbons resulting in lower concentration as observed (pulse 4)

Evacuation and re-filling of pores is reversible (pulse 5 and 6)

3 – Technical Accomplishments/Progress/Results

Nano-enhanced surface effect & augmented capillary condensation phenomenon was demonstrated experimentally to enable high water/hydrocarbon selectivity, promising for dewatering technology



- **Superhydrophilic HiPAS can selectively remove water from upgraded hydrocarbon/water vapor mixture**
- **Could be applied as efficient dewatering membrane**

Impact: Attained precedent for future development of highly selective super-hydro-tunable HiPAS membranes, which could improve vapor-phase processing operations.

4 – Relevance

- **This project contributes to the Thermochemical Conversion platform goals & objectives of BETO Multi-Year Program Plan**
  - Addresses barriers in Process Integration & Intensification, Advanced Separations, and Selective Fractionation.
- **Tangible outcome & impact**
  - HiPAS provides dewatering potential for typical pyrolysis bio-oil vapors (~50 mol% reduced to ~3 mol% is possible)
  - The project will advance the state of membrane separation technology with orders-of-magnitudes higher processing productivity, which potentially impacts the commercial viability of biomass and/or biofuels
  - In the emerging bioenergy industry, HiPAS membrane separations could be integrated before or after the pyrolysis/upgrading reactors
    - Enabling higher process efficiency and fractionation product quality
    - Impact downstream processing including catalyst life/yield/cost and reactor capital
- **Tech transfer/marketability**
  HiPAS has attracted interest from multiple industrial companies:
  - **Amyris Inc**. (NDA in place, Jan. 2015, WFO for industrial biochemical conversion application)
  - **Verso Paper Corp**. (considering WFO spin-off application, for potential energy saving 80 trillion Btu/year)
  - **NL Chemical Technology Inc**. (N. Lee, will sign a NDA, high-temp separations)

5 – Future Work

Remainder of FY2015 (Q3 & Q4): 1st-Generation Membranes & Single Tube Efforts

ORNL Development

- ✓ **Deliverable Q1**: Engineering nanopores and structures (starting with ~5nm synthesis). Fabrication of over 30 membrane tubes (completed)
- ✓ **Deliverable Q2**: Membrane surface engineering (starting with PDTMS modification). Delivered both superhydrophilic and superhydrophobic membrane tubes to NREL for performance evaluation and process integration studies.

Continue materials & process development:

Deliverable Q3: Thermal/chemical stability study & separation process evaluation and development
Measure: identify stable nano-textured coating, organic ligand, binder

Milestone Q4 (go/no-go): Integrated pyrolyzer-upgrader-membrane system & liquid-phase testing (single-tube module)
Milestone measure: must show stable, water/hydrocarbon selectivity (> 10:1).

NREL Process Testing

- ✓ **Deliverable Q1:** Complete construction of two configurations for incorporating a membrane unit in a small-scale laboratory reactor that will enable extended membrane testing under standard pyrolysis and upgraded vapor flow conditions.
- ✓ **Deliverable Q2:** Report on the performance of at least two membranes for vapor-phase separations. Complete membrane testing as a function of temperature, feed concentration, and flow rate conditions.

Deliverable Q3: Down-select to the most promising HiPAS membranes for additional development for processing pyrolysis and upgraded vapor streams. Provide a status update of possible pathways that improve the quality of the pyrolysis and upgraded vapor streams.

Milestone Q4 (go/no-go): 1st-generation HiPAS membranes must demonstrate improved vapor-phase selectivity (> 10:1) that translates to reductions in coke formation (> 20%).

5 – Future Work

FY2016: **2nd-Genearation Membranes and Tube Array Module System Efforts**

ORNL

Materials Development:

- Improve the degree of superhydrophilicity or superhydrophobicity, and stability
- Increase useable pore size (5nm → upper threshold 50nm?) while maintaining desirable separation selectivity (10:1)

Milestone: Demonstrate single-tube selectivity of 10:1 and measured flux > 100X of baseline membrane

Process design and development:

- Processing volume scale-up with multi-tube module system

Milestone: Demonstrate scalability using multi-tube module system

NREL

- Work with ORNL to integrate HiPAS membrane technologies into the in-situ catalytic fast pyrolysis technology pathway
- Continuous flow reactor (pyrolysis and upgraded vapors)
- Membrane productivity (permeation flux) will be a major thrust area in FY16
- Continue testing next-generation HiPAS membranes from ORNL under standard pyrolysis and upgraded vapor flow conditions

Summary

Overview: Developing a new class of HiPAS membranes with tunable material properties depending on the target separation need (vapor- or liquid-phase)

Relevance: BETO mission to improve biofuel processing productivity through separation-enabled process intensification & integration; lower cost for thermochemical or biochemical conversions

Approach:

Pioneering membrane concept:

- Rugged inorganic based, nano-surface enhanced, larger mesopore enabling strategy

Strong Teaming (ORNL and NREL):

- Real bio-oil process evaluation capability combines with unique membrane materials expertise

Technical Accomplishments/Progress/Results:

We have demonstrated that superhydrophilic HiPAS membranes are promising for future dewatering technology development

- FY2015 – Obtained promising results with 1st-generation HiPAS membranes (~5nm pores) and upgraded pyrolysis vapors
- Identified a pathway toward higher water/hydrocarbon separation selectivity
- Will continue improve material properties and understand process parameters

End

Additional Slides

Advanced Membrane Separations to Improve Efficiency of Thermochemical Conversion [WBS 2.5.5.(301 & 302)]

Team Members:

Michael Hu
Brian Bischoff
Oak Ridge National Laboratory (ORNL)

Chaiwat Engtrakul
Mark Davis
National Renewable Energy Laboratory (NREL)

Note: The additional slides are for the use of the Peer Reviewers only – it is not to be presented as part of oral presentation.
These Additional Slides will be included in the copy of the presentation that will be made available to the Reviewers.

Responses to Previous Reviewers' Comments

- **N/A to this project**

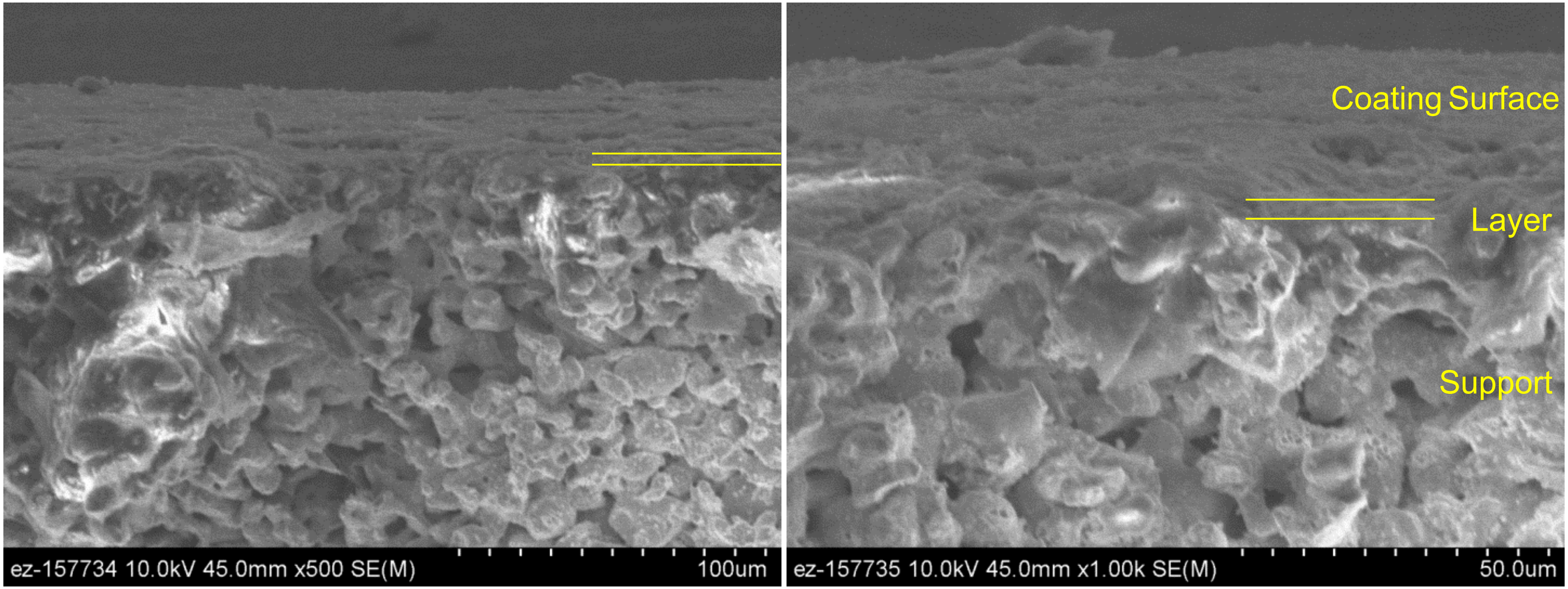
  This project started on January 2014 and has NOT been reviewed previously

Publications, Patents, Presentations, Awards, and Commercialization

- Publications: (Since project start Jan. 2014)
  - A paper abstract was published in the proceeding book for *Advanced Membrane Technology VI, Feb 8-13, 2015.*
  - A proceeding paper abstract discussing nanomaterials for energy applications (including membranes for biofuel processing and separations) were published in the meeting book of *Energy Materials Nanotechnologies*, Jan 11-15, 2014.
  - An written document titled "Super-hydro-tunable HiPAS Membranes" were prepared, submitted, and has won the 2014 *R&D100 Award*, press release date July 11, 2014. (There were multiple news media articles generated for the award technology)
  - Michael Z. Hu, Donglu Shi, and Douglas A. Blom, *Journal of Nanomaterials*, Article ID 932160 (8 pages), March (2014).
- Patents: (1 patent, relevant to the 2014 R&D100 Award for HiPAS membranes)
  - Second invention filed 3/2015, "Integrated Membrane/Catalytic Biofuel Upgrading System"
- Awards:
  - 2014 R&D100 Award
  - 2014-2015 UT-Battelle Technology Commercialization Award
- Presentations:
  - March 4, 2015, invited "ORICL lecture" for the R&D100 award-winning membrane work.
  - Feb. 12, 2015, invited talk "Super-hydro-tunable Membranes for Advanced Separations and Processing of Biofuels", *Adv. Membrane Technology VI*
  - October 28, 2014, invited talk entitled "High-Performance Super-hydro-tunable Membranes for Advanced Separations in Biofuel Processing," at the *18th Symposium on Separation Science and Technology For Energy Applications*
  - March 30-31 2014. invited by Honeywell Engineering Solutions to visit and deliver a presentation, part of which is on membrane separations.
  - On Feb 27 2014, Dr. Michael Hu of ORNL had the honor to participate in the face-to-face roundtable discussion with the US Senator Sheldon Whitehouse and the US Congressman Henry Waxman et al., on the topic of clean energy and climate change.
  - Aug. 21, 2014, a poster presentation was given to BETO director Jonathan Male
- Status of any technology transfer or commercialization efforts
  - Superhydrophobic coating patent, licensed to Dry Surface Coatings LLC.
  - NDA signed with Amyris Inc. for integrating HiPAS membranes in biodiesel production process
  - A prelim testing done for Verso Paper Corp. for energy-saving dewatering applications
  - NL Chemical Technology Inc. has requested NDA and will visit ORNL to discuss future commercialization collaboration
  - Honeywell Engineering Solutions, invited the PI for an on-site discussion of potential membrane processing of natural gas and petro-oils

3 – Technical Accomplishments/Progress/Results

A-layer: Pore Size Control in Nanoporous Alumina by Sol-Gel Coating (uniform pore size: ~ 7nm)

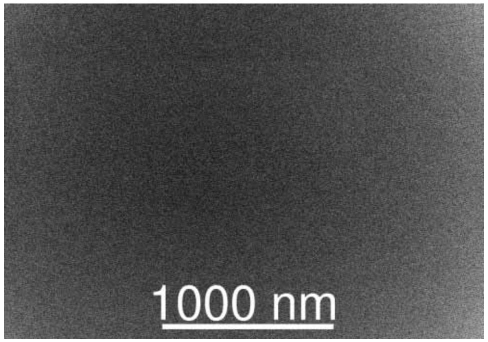


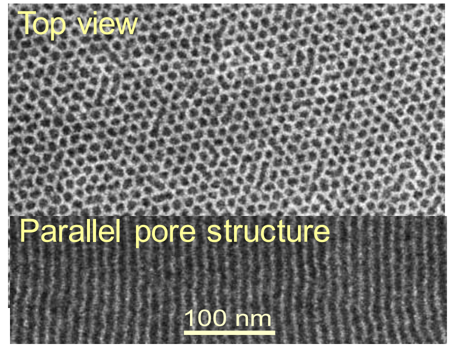
Cross section of fractured membrane shows thin separation layer on inside surface of tubular metallic support structure.

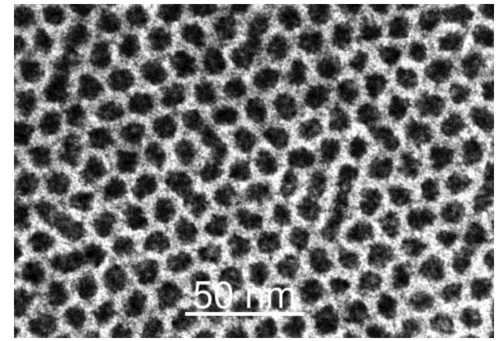
- Lower section in micrographs shows macroporous stainless support with pore-size of approximately 4 microns.
- Gamma alumina top layer has nanopore-size of approximately 7nm (determined by permeance measurement). Layer is approximately 5 microns in thickness.

Besides Pore Size, Engineered Assembly Approach Could Control <u>Uniformity</u>, <u>Orientation</u>, and <u>Ordering</u> of Mesopores in A-Layer or S-Layer

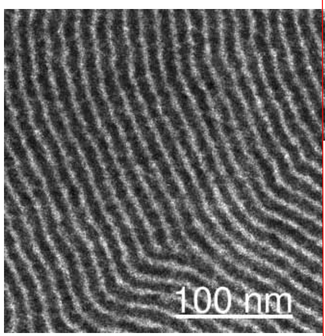
•Vertical Oxide Mesostructure: (Pore diam. 7.5 nm; hexagonally arranged)

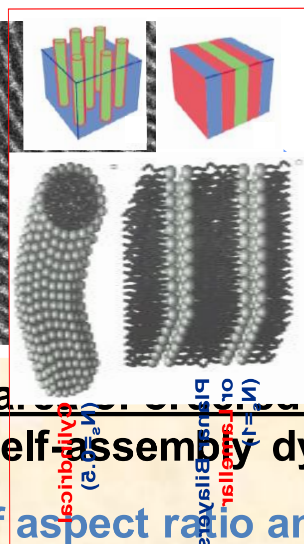


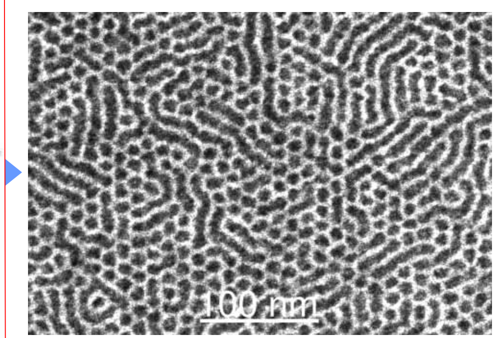


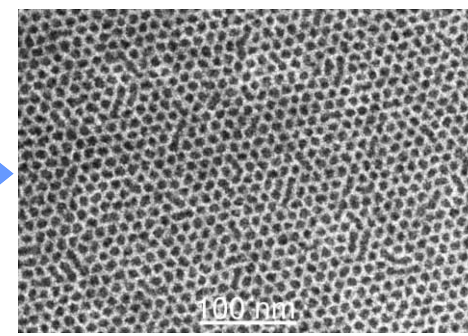


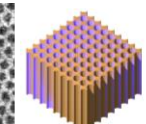
•Transition of Mesostructure: L → H phase transformation mechanism









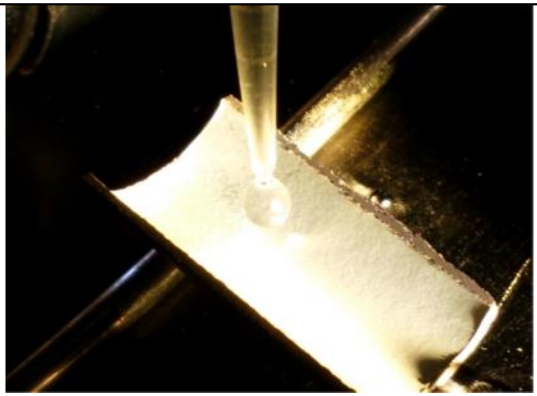


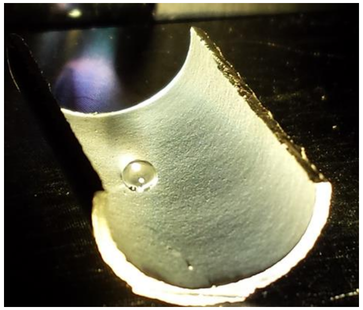
- **<u>Key for large area of ordered orientation</u>: match the mass transfer rate with the reaction kinetics and self-assembly dynamics, in combination of confinement effect.**
- **The control of aspect ratio and pore connectivity, other oxides, other block-copolymers/surfactants, etc., needs to be further developed to make A-Layer.**

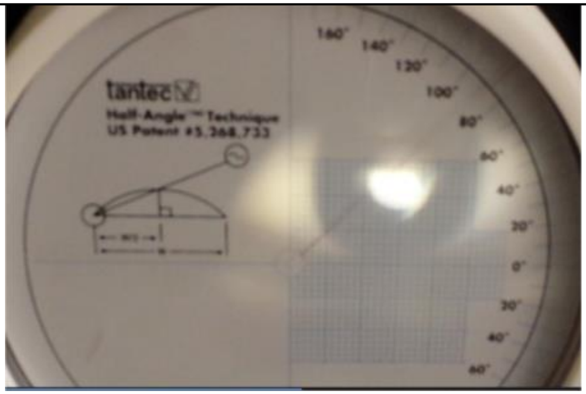
3 – Technical Accomplishments/Progress/Results

S-Layer: Snapshots and Contact Angles (CAs), demonstrating the tunability of the inner wall surface of membrane tubes to be either superhydrophobic or superhydrophilic

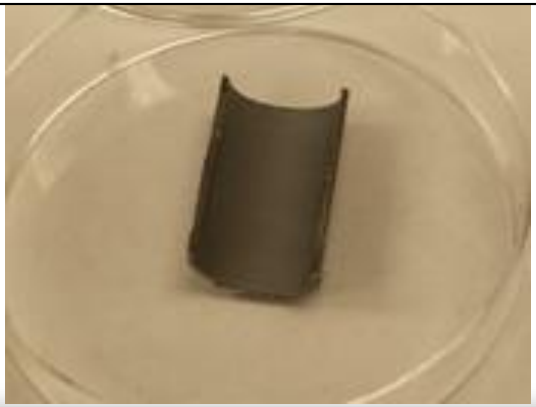
On the **superhydrophobic surface**, water simply beads up and rolls off the inner wall surface	The water droplet does not stick to the surface, thus a ~ 172-176° contact angles are achieved.

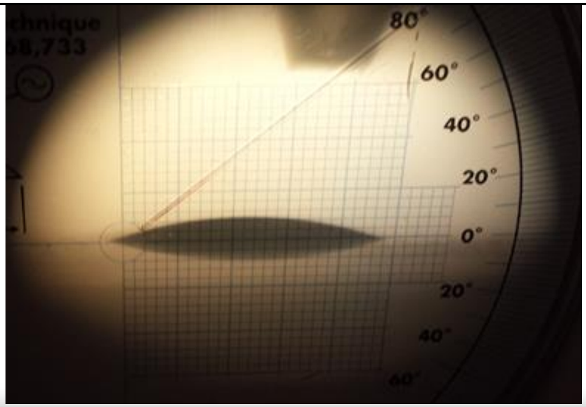




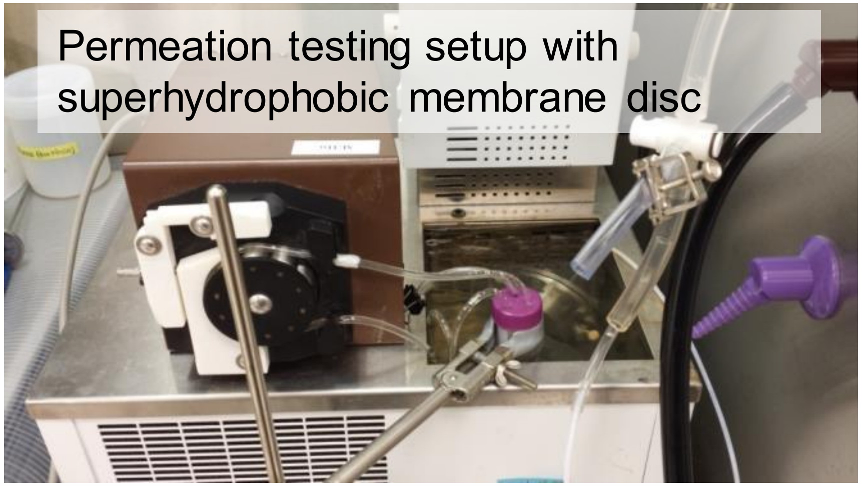


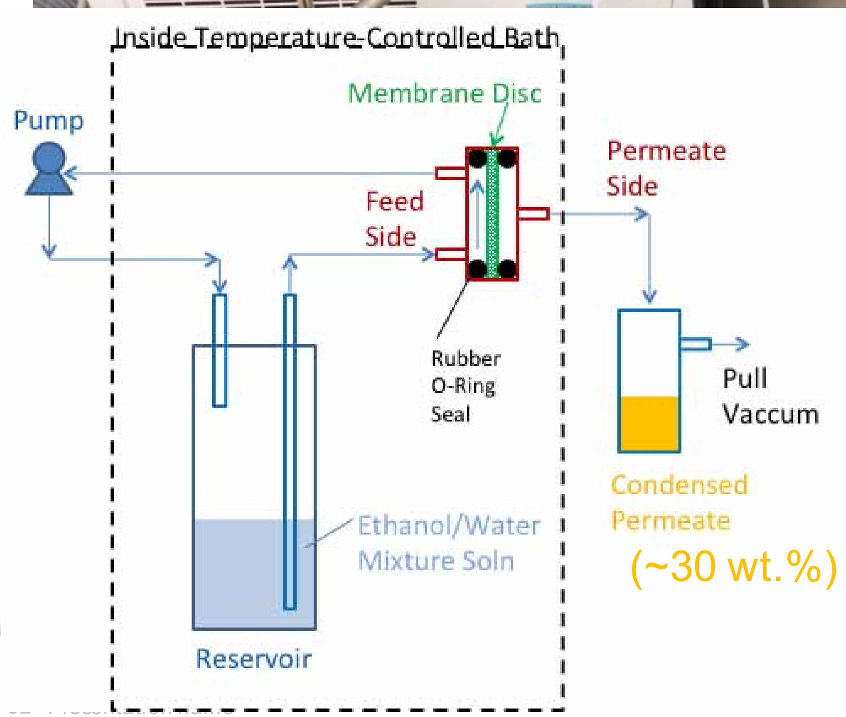
A **superhydrophilic surface** on the inner wall of a tube membrane.	A water droplet wets and penetrates quickly into the superhydrophilic surface.



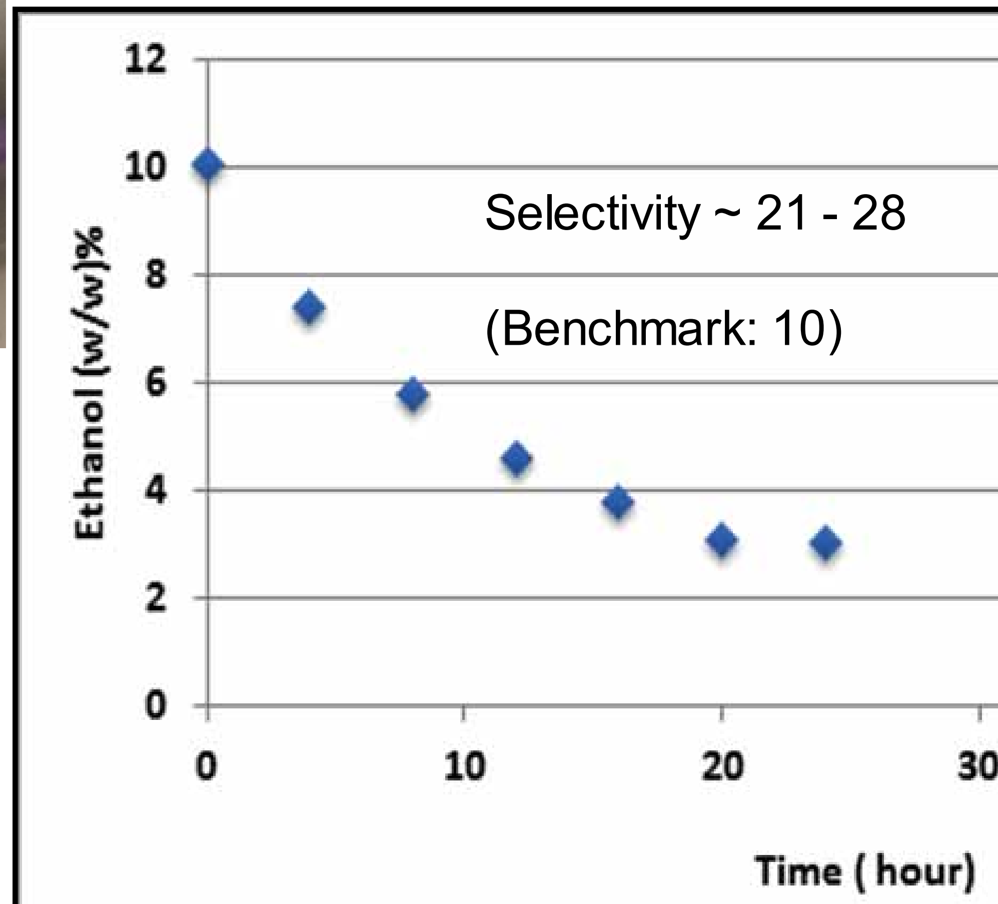


Previously Demonstrated Selective Molecular Separation of Liquid Mixture of Ethanol and Water (Internal ORNL Funded Project)





EtOH conc left in the liquid reservoir



3 – Technical Accomplishments/Progress/Results

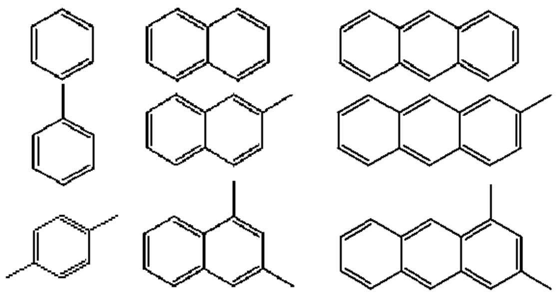
Upgraded Products: 1-ring 2-ring 3-ring

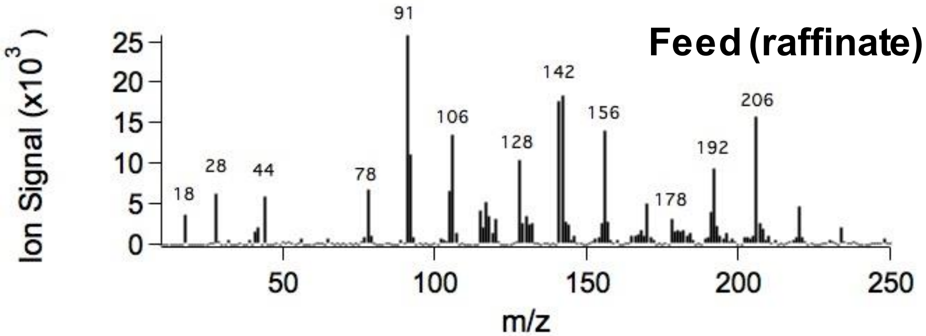
light gases

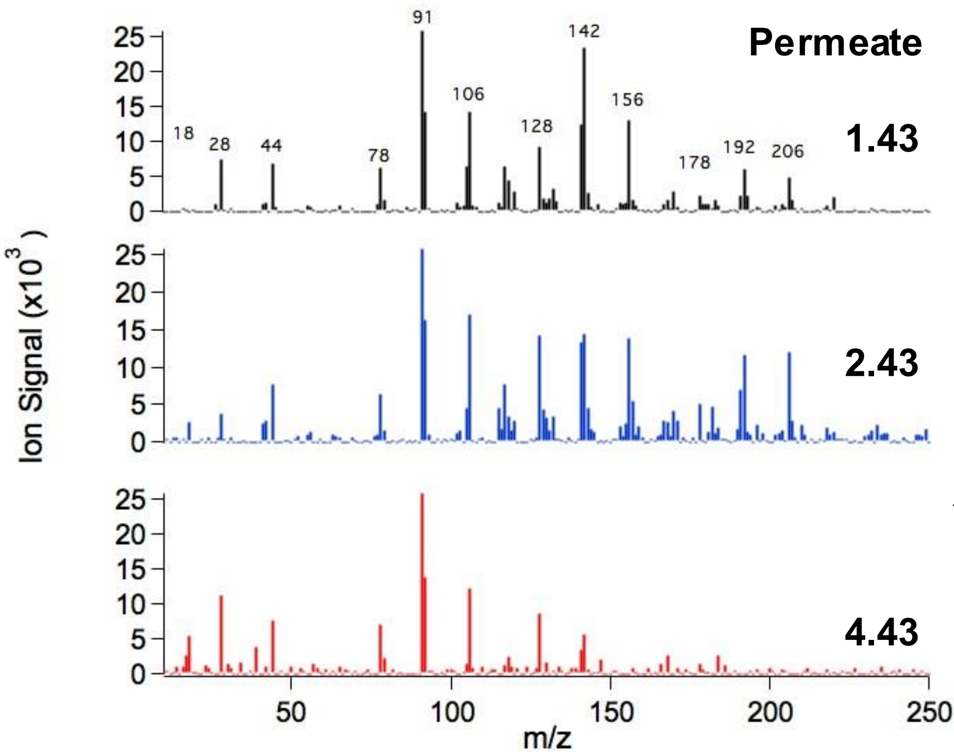
H_2O (16)

CO (28)

CO_2 (44)





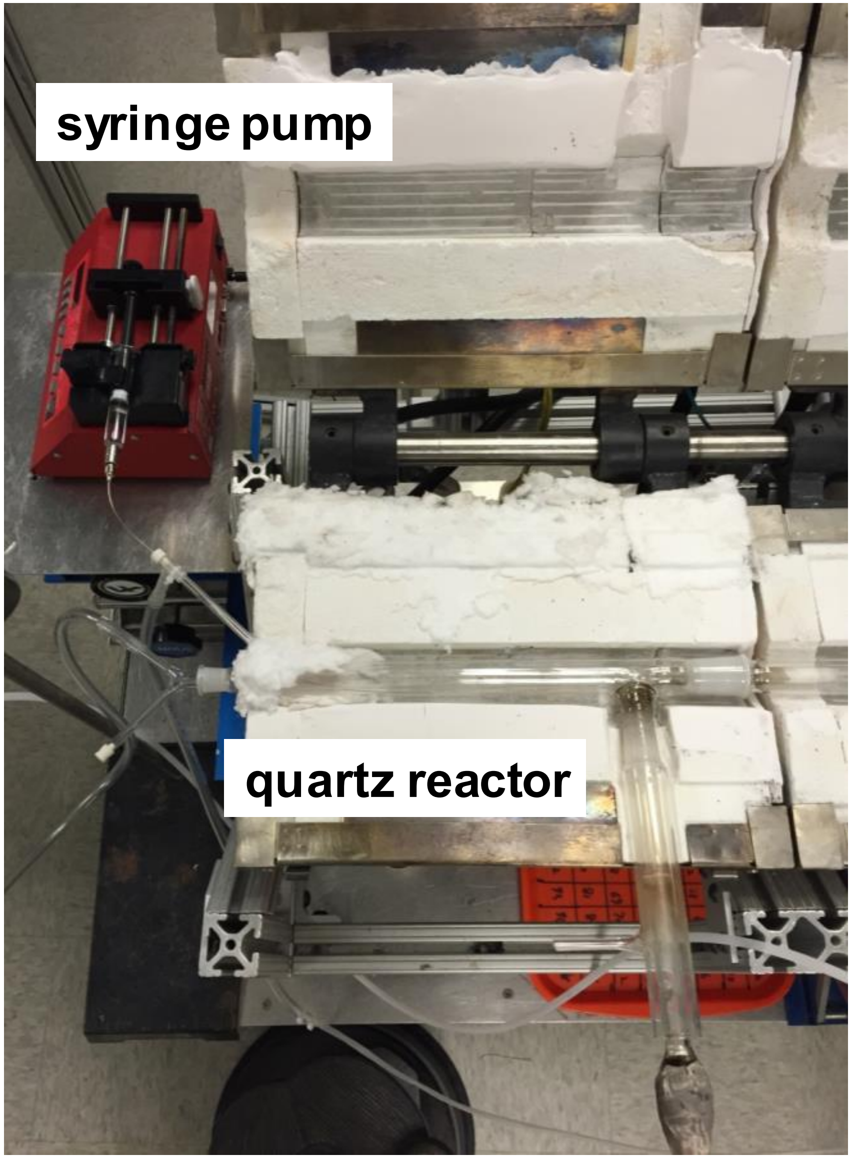


- Superhydrophobic membrane (5.2 nm pores) enabled a strong preference (selectivity) for hydrocarbons at 300° C
- Membrane based size exclusion achieved (e.g., mono- vs. di-substituted 3-ring upgraded products)

Permeate as a function of total flow rate (slm)

3 – Technical Accomplishments/Progress/Results

- Complete adsorption and capillary condensation may not occur in the porous membrane due to short pulse duration of upgraded vapors
- To increase the ability to wet the surfaces of the porous membrane and ultimately fill the pores, a syringe pump was connected to the outer flow tube of the reactor to introduce additional vapor-phase components (e.g., water, toluene, or xylene)
- Outer flow tube does not interfere with the catalytic upgrading process

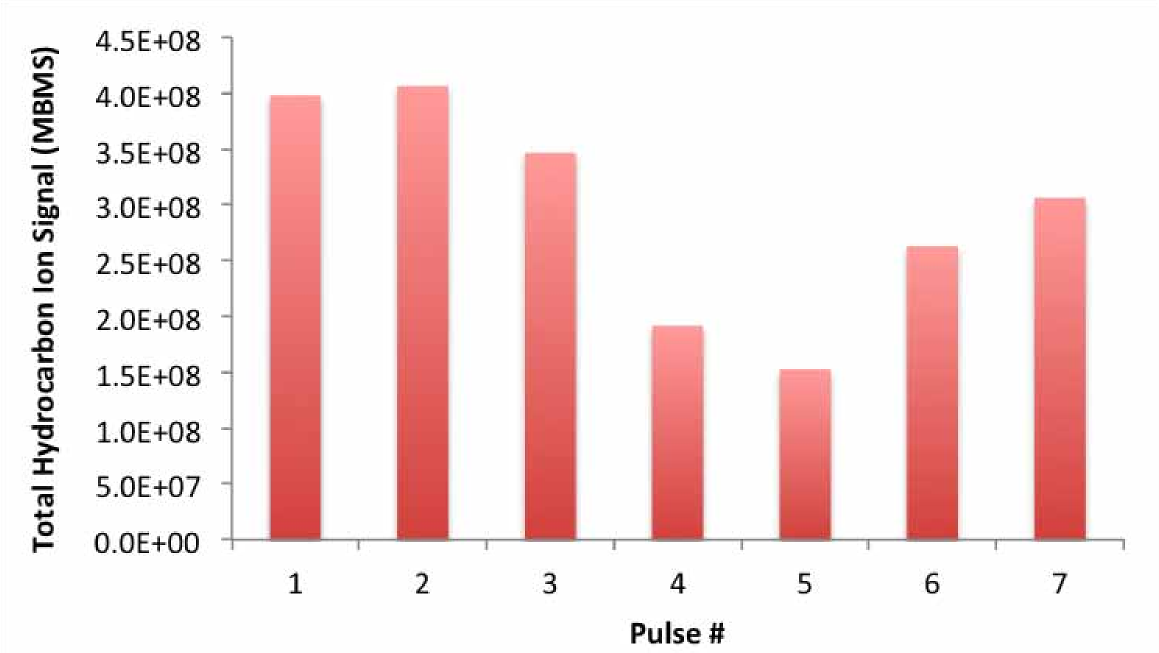


Impact: Successful in demonstrating efficient mixing of pulses of catalytically upgraded pyrolysis vapor with either water or toluene vapors delivered via syringe pump. This will ensure proper operating conditions that will enhance the selectivity of the membrane.

3 – Technical Accomplishments/Progress/Results

Tunable Selectivity with Superhydrophilic HiPAS Membrane (large pores)

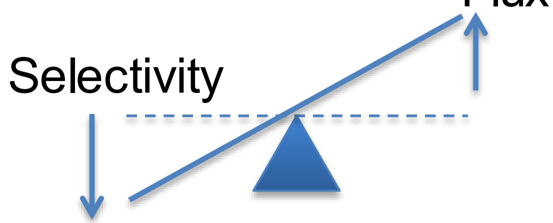
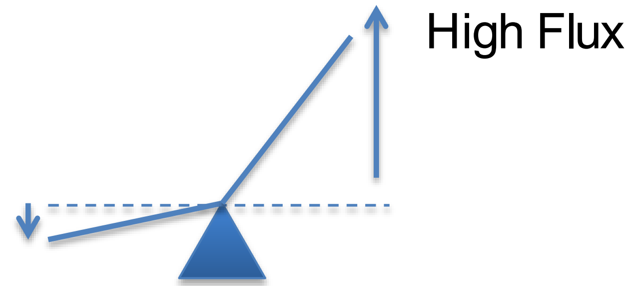
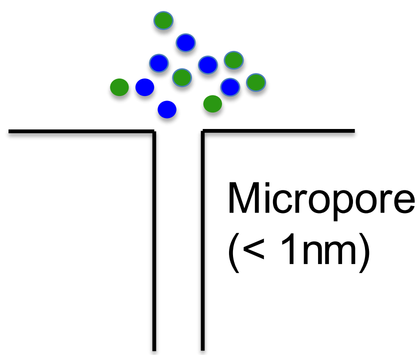
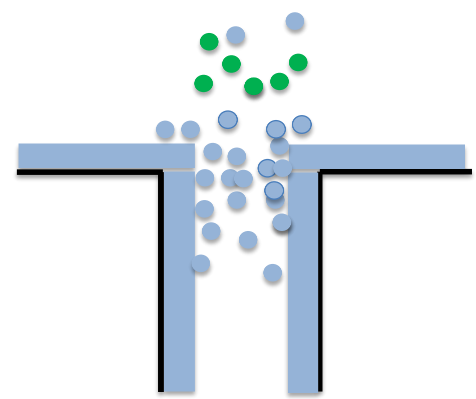
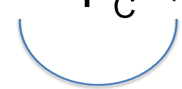
Total Ion Signals for Hydrocarbon Mass Spectral Peaks (m/z 78, 91, 106, 128, 142)



- As adsorption and capillary condensation of water vapor occurs in the pores the total hydrocarbon signal decreases (pulses 2-5)
- As water is removed from pores (pulses 6 and 7) the total hydrocarbon signal recovers

Upgraded hydrocarbon products in permeate stream are reduced by 62%

Impact: Demonstrated a strong preference (selectivity) for water relative to hydrocarbons using a superhydrophilic HiPAS membrane and detected the uptake and onset of capillary condensation in the porous membrane.

	Traditional Membranes	HiPAS Membranes
Seesaw Paradox		
Useable Pore Size		 Enlarged mesopore (2-50nm) due to nano-surface enhanced selectivity & transport
Vapor Pressure	Vapor Pressure P_B Flat Surface in Bulk Water	$P_C << P_B$, much dryer  Curved Water Surface in Capillary