Resource Recovery and Environmental Protection in Wyoming's Greater Green River Basin Using Selective Nanostructured Membranes

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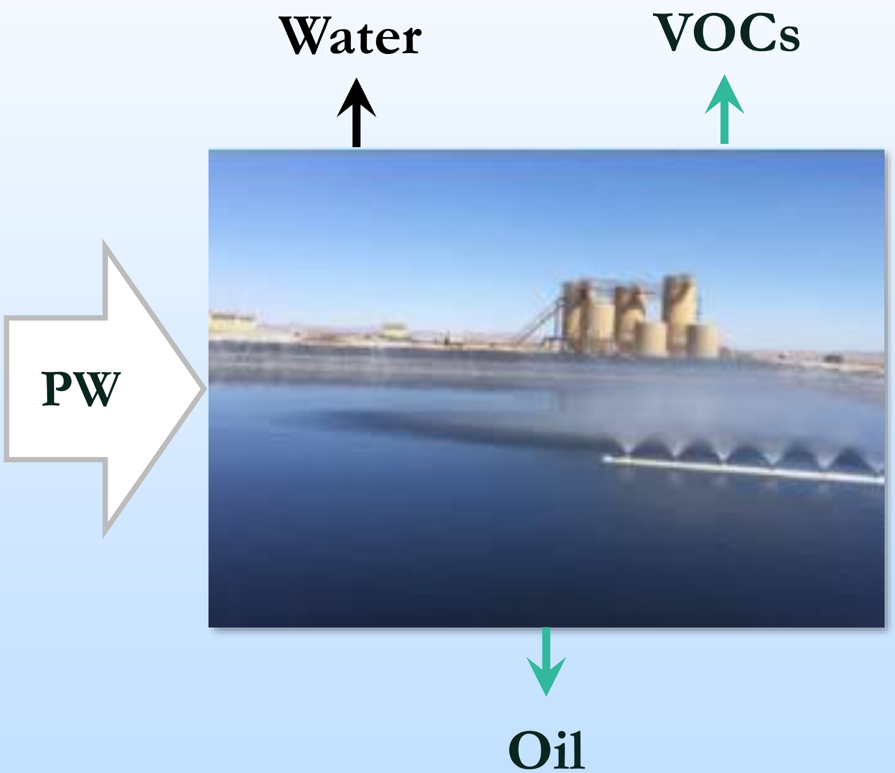
Virtual Meetings August 2 through August 31, 2021

Presentation Outline

- Project motivation and technical background
  - Treatment challenges and resource recovery
  - A "new" way to make membranes - electrospinning
- Technical status
  - Superhydrophobic & superhydrophilic membrane characteristics
  - Membrane performance & fouling
- Accomplishments & lessons learned

Motivation



- Hydrocarbon recovery via separators is incomplete leaving VOCs/free oils to persist in PWs moved to pits
  - VOC concentrations in GGRB ~ 0.06 to 5.1 lbs/bbl
- VOC emissions are problematic from an environmental perspective & BTEX/oil represents lost revenue

Motivation

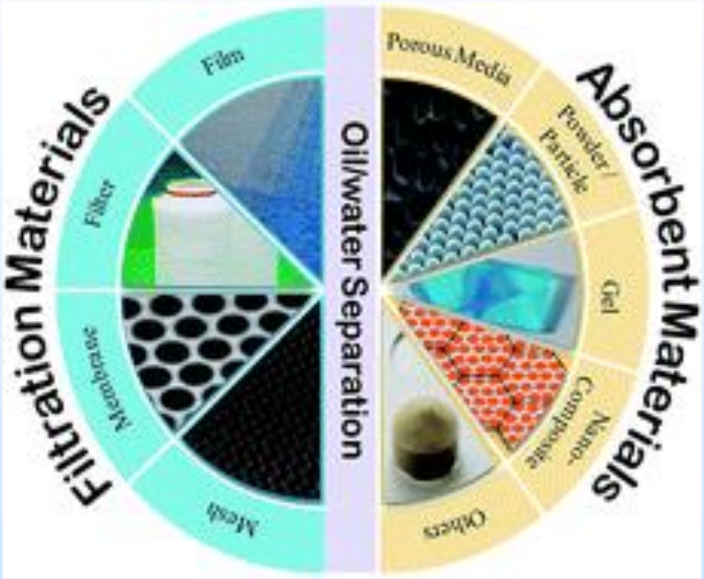
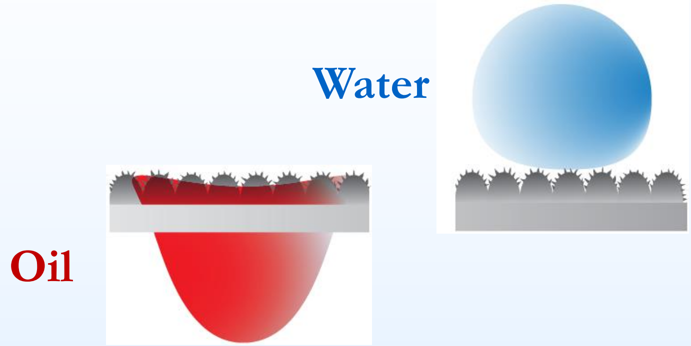
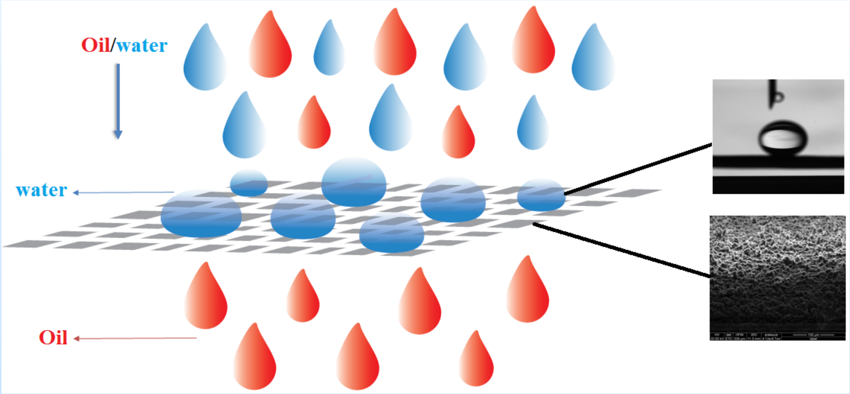


***Image Credit**: Gupta et al. 2017

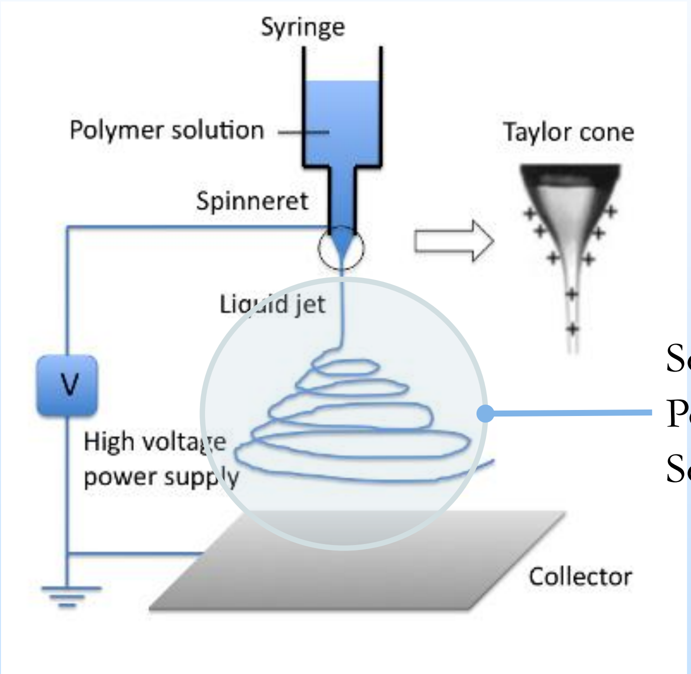
Conventional separations plagued by inefficiencies related to non-selectivity and inability to target dispersed fractions.



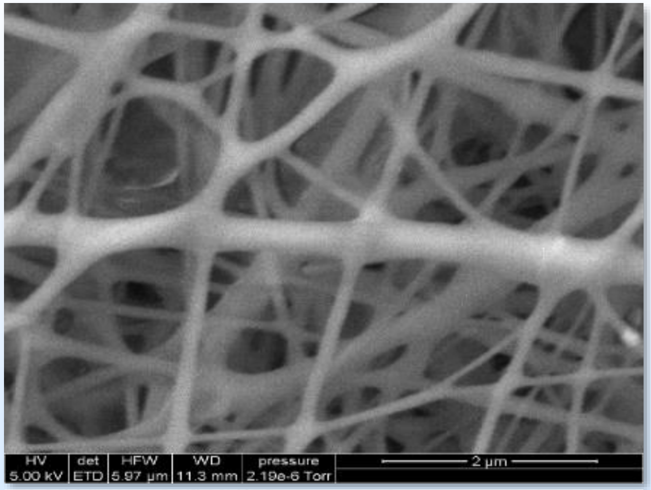


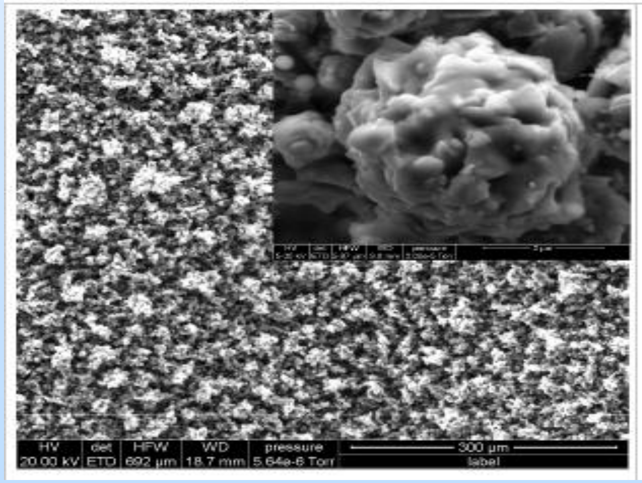
Development of "smart" membrane materials reduces fouling and achieves high selectivity for target phase.

Electrospinning



Solvent, NP,
Polymer
Solution





Using interfacial chemistry, the selectivity of the membrane is tailored through selection of appropriate nano-surface coating(s).

Technical Status

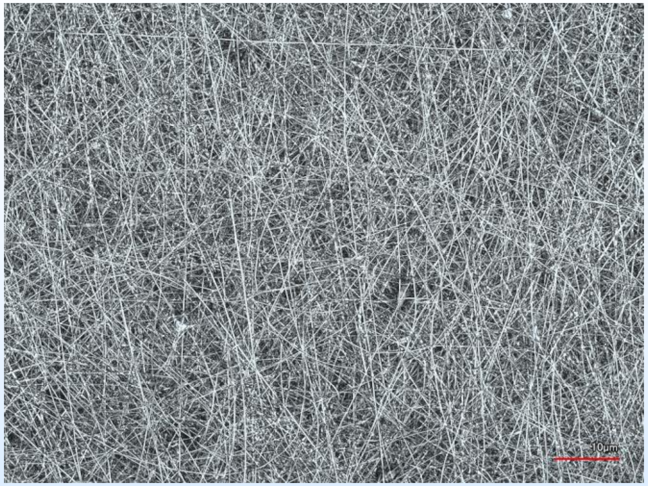
Produced water samples collected throughout the GGRB

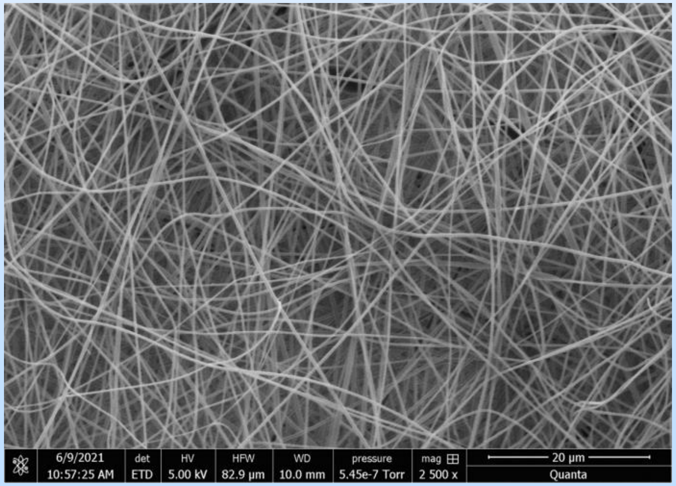
- Samples collected at both impoundments and prior to blending at wellheads
- Variability in total O&G (concentration effects in impoundments, unique formation characteristics)

Sample	EC (mS/cm)	Turbidity (NTU)	Total O&G mg/L	TSS (mg/L)	TDS (mg/L)
Canyon Creek	33.6	153	4,100	128	26,192
Trail	28.9	130	800	154	28,440
Kinney	119.0	49	2,400	658	103,482
Powder Wash	62.0	27	3,200	296	54,066
Church Buttes	23.8	>1,000	5,200	2,768	22,996

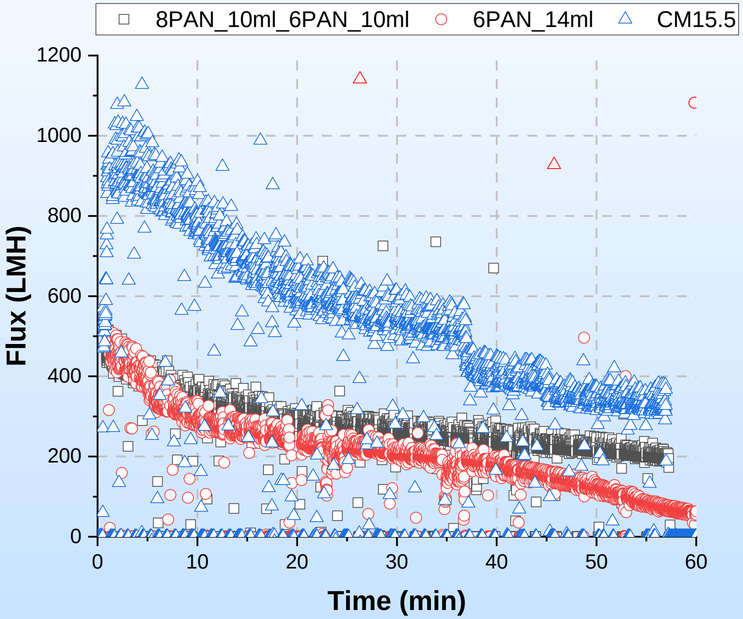
Technical Status

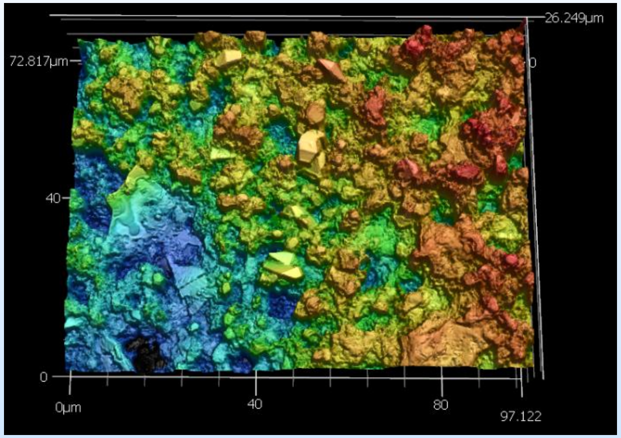
- Superhydrophilic PAN membranes
  - Water filtration
  - Prevent O&G fouling of membrane
- Synthesis conditions & characteristics
  - Baseline Conditions: 6%PAN in DMF feed solution for top coat
    - 8%PAN in DMF feed solution for base coat
  - Pore size: ~0.45μm
  - Fiber diameter: ~200 nm
  - Membrane thickness: ~200 μm
  - Water contact angle = 0°





Technical Status





6% PAN Membrane after fouling test. O&G adhesion prevalent due to high flux (permeate drag forces). Must reduce permeability!

Nanofibers prevented pore throat construction/plugging by O&G.

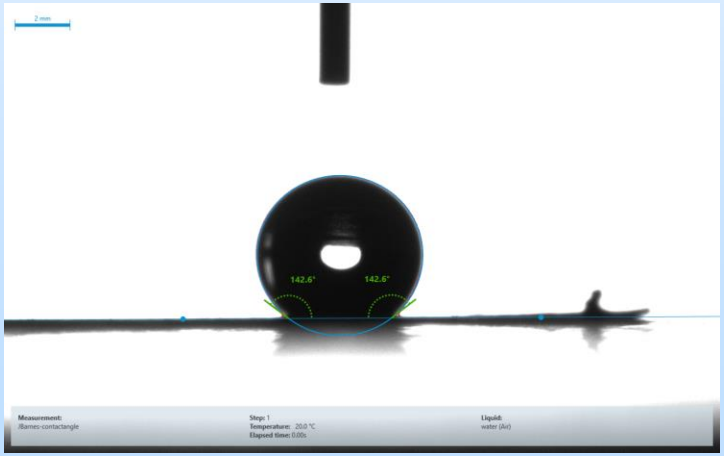
Technical Status

Superhydrophobic PDMS/PVDF membranes

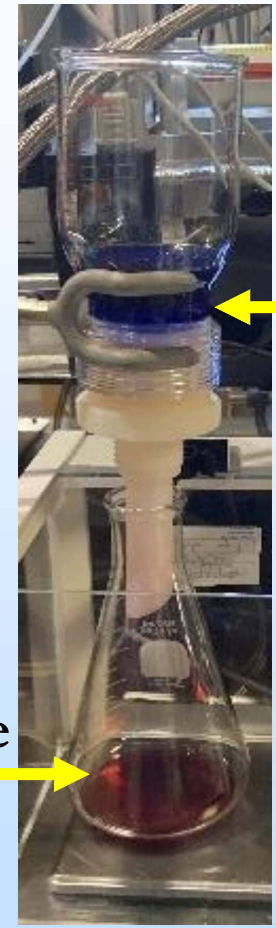
- Selective hydrocarbon recovery

Synthesis conditions & characteristics

- Baseline Conditions: 12% PDMS and 8% PVDF in 1:1 DMF/THF feed solution
- Pore size: ~ 0.46 μm ± 0.08 μm
- Membrane thickness: ~120 μm
- Water contact angle = 142.6° ± 0.1°



Technical Status



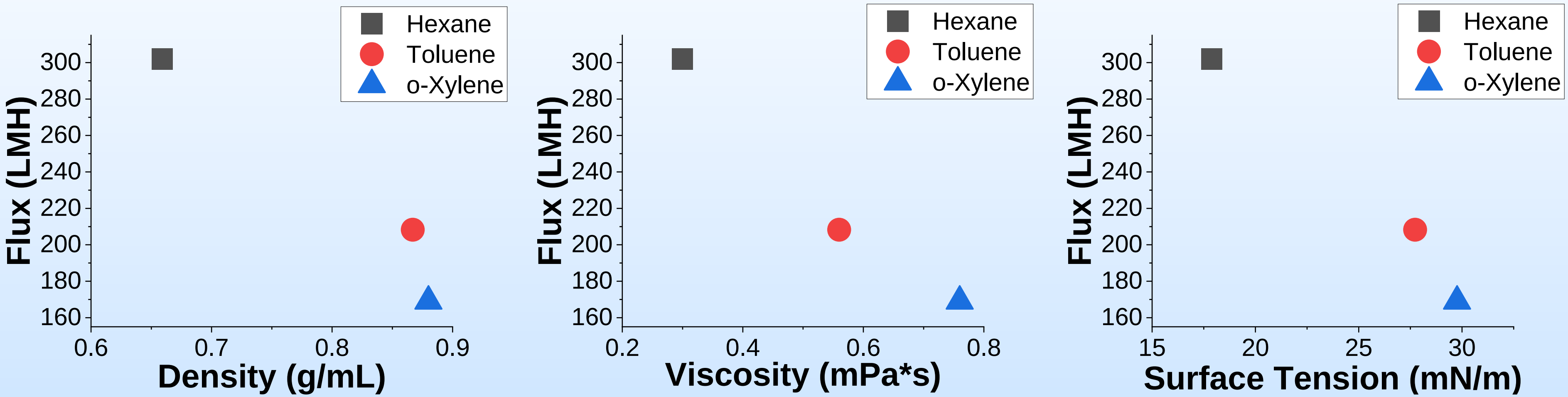
Water

Dichloromethane

~99% selective

Technical Status

- Tested flux of hexane, toluene, and *o*-xylene



- Flux tended to decrease with higher solvent properties

Accomplishments to Date

- CFD model developed for describing mixed 2-phase behavior (water & hydrocarbons) in membrane flow channels as a function of spacer geometry
- TEA completed for filtered water production and hydrocarbon recovery using selective membranes in GGRB
- Polymer solution chemistry and electrospinning conditions established for creating superhydrophilic PAN and superhydrophobic PVDF membranes for produced water applications
- Mobile water filtration / hydrocarbon recovery prototype design completed

Lessons Learned

- Research gaps, challenges, and difficulties
  - Complex chemistry of produced waters in GGRB challenges predictive models in terms of interfacial membrane interactions
  - Changes in polymer solution stability must be accounted for when scaling up electrospinning process
  - Adhesion of nanofibers to support substrate must be studied in more depth as commonly employed techniques (heat pressing) are not feasible for larger scale production
- Technical disappointments
  - Scale-up of single needle to multi-needle electrospinning is challenged by emitter plugging
  - Nano-carbon black became an infeasible surface coating agent for superhydrophobic membranes due to plugging of emitters

Project Summary

- Key research findings
  - Separation of free/dispersed hydrocarbons from mixed aqueous phases is possible and determined by collision efficiency with membrane surface (selectivity ≥ 95%)
  - High aqueous permeability of electrospun superhydrophilic membranes must be balanced against drag forces acting on free/dispersed phases to control fouling
- Next research steps
  - Model membrane fouling for optimization of flow conditions and final election of pretreatment requirements for prototype
  - Use developed CFD model to guide the manufacturing of 3D printed membrane spacers to control O&G deposition on PAN membranes
  - Modify polymer doping solution chemistry to prevent emitter plugging during large-scale production of membranes for prototype construction
  - Create membrane envelopes for integration into spiral wound element configuration

Appendix

Benefit to the Program

- The following program goals are being addressed in this work:
  - Development of treatment technologies/approaches for significantly reducing the quantity of produced water going to deep, underground injection well facilities.
  - Development of cost-effective treatment technologies for removing non-TDS produced water constituents that are especially resistant to removal using current practices.
- The water filtration/hydrocarbon separation technology reduces the volume of water requiring disposal, recovers resources of value (hydrocarbons) from produced water creating economic benefits for treatment, and improves the quality for downstream treatment, like desalination, for creating higher quality water for reuse.

Project Overview

Goals and Objectives

- Describe the project goals and objectives in the Statement of Project Objectives.
  - How the project goals and objectives relate to the program goals and objectives.
  - Identify the success criteria for determining if a goal or objective has been met. These generally are discrete metrics to assess the progress of the project and used as decision points throughout the project.

Project Overview

Task/ Subtask	Milestone Title & Description	Completion	Verification Method
2.2, 2.3, 3.1	M4 – Water samples collected & characterized from 4 distinct stations in GGRB (70% of total sites)	09/01/2020	UW summarizes and reports PW WQ data to H2O/Triton for TEA & use in initial phase membrane performance analyses
	M5 – Continuation Application	09/01/2020	Continuation Application is received by the DOE Project Manager
2.1	M6 – Design of superhydrophobic & superhydrophilic membranes is complete	12/31/2020	UW reports bench-scale performance and characterization analysis data on membranes (final design and iterations) to match with prototype requirements
2.4	M7 – Completion of CFD modelling for membrane spacers & channel height	04/01/21	Dimensions (AUTOCAD files) and geometry of spacers/flow channel reported to PI and Triton
3.1	M8 – TEA of BTEX/oil recovery process complete	12/31/2021	H2O/Triton reports TEA to UW/DOE
3.2	M9 – Membrane prototype design and construction complete	12/31/2021	UW presents prototype design and performance specs to DOE Project Manager

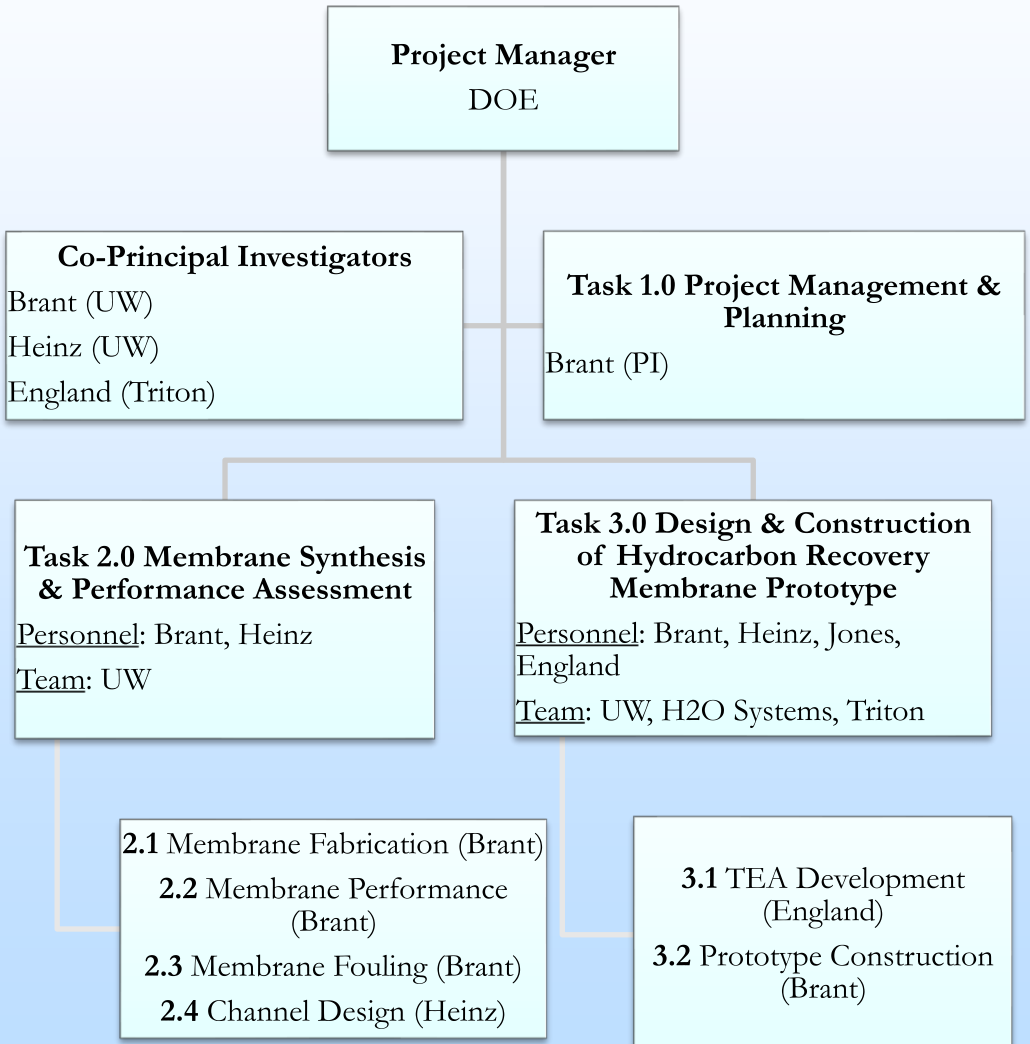
Project Overview

Goals and Objectives

Overall project objective is to generate superhydrophilic/oleophobic and superhydrophobic/oleophilic membrane module prototypes for selectively concentrating and then separating benzene, toluene, ethylbenzene and xylene (BTEX) compounds and oil and grease (O&G) from produced water originating from the Greater Green River Basin (GGRB).

- Aim #1 – Material optimization and performance evaluation of superhydrophilic/oleophobic and superhydrophobic/oleophilic membranes made using electrospinning/spraying.
- Aim #2 – Design and construction of crossflow membrane modules for selectively concentrating and then separating BTEX/oil from GGRB produced water.
- Aim #3 – Techno-economic assessment of BTEX/oil recovery, and clean water production, using superhydrophilic/oleophobic and superhydrophobic/oleophilic membrane separation for GGRB produced water.

Organization Chart



Gantt Chart

ACTIVITY	PLAN START	% COMPLETE
Task 1: Project Management & Planning	1	
ST 1.1: Project Management Plan	1	
ST 1.2: Technology Maturation Plan	2	
ST 1.3: Data Management Plan	1	
Task 2: Membrane Synthesis & Performance Assessment	4	
ST 2.1: Superhydrophobic & Superhydrophilic Membrane Fabrication	4	
ST 2.2: Membrane Performance Assessment	5	
ST 2.3: Membrane Fouling Assessment	5	
ST 2.4: Optimization of Membrane Feed & Permeate Channel Geometries	5	
Task 3: Design & Construction of Hydrocarbon Recovery Membrane Prototype	6	
ST 3.1: TEA of Water and BTEX/Oil Recovery in GGRB	6	
ST 3.2: Membrane Prototype Design & Construction	7	

Quarters: Start January 1, 2020 End December 31, 2021