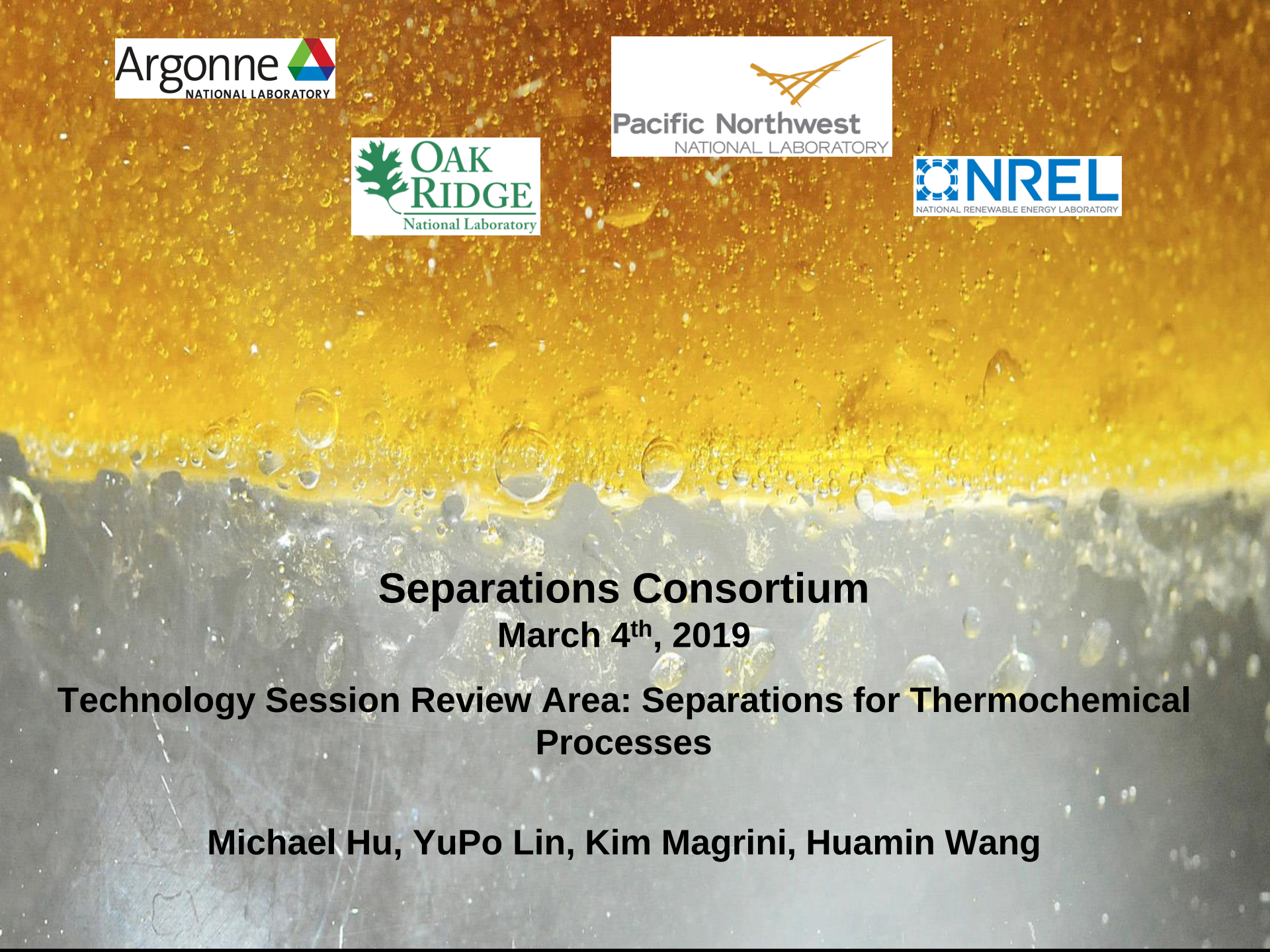


Separations Consortium

March 4th, 2019

Technology Session Review Area: Separations for Thermochemical Processes

Michael Hu, YuPo Lin, Kim Magrini, Huamin Wang

Goal Statement

Low level contaminants can be catastrophic for industrial processes

BETO analyses identified separations challenges that, if resolved, could reduce minimum fuel selling price of biofuels by up to 50%

Goal: Develop efficient separations to remove contaminants from biomass-derived feedstocks before thermochemical conversion by:

- *Removing* contaminants to *preserve* upgrading catalyst performance for CFP, HTL
- *Valorizing carbon* from HTL aqueous process streams to offset costs
- *Intensifying* separation processes to reduce process costs

Outcome: Efficient, integrated separation technologies that enable biofuels and chemicals for thermochemical conversion

Relevance to Bioenergy Industry: High C and H atom efficiencies are *essential* to achieve BETO cost target of a $3/gge MFSP and >50% GHG reduction

TCS Quad Chart Overview

Timeline

- Start Date: October 2016
- End Date: September 2019
- Percent Complete: 78%

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded				
ANL	$0.0	$100K	$ 90K	$180K
NREL	$0.0	$150K	$370K	$395K
PNNL	$0.0	$ 60K	$190K	$140K
ORNL	$0.0	$490K	$995K	$970K

Partners: ANL (9%), NREL (22%), ORNL (59%), PNNL (9%)

BETO Projects: ChemCatBio, CCPC

University of Florence

Barriers Addressed:

Ct-O. Selective Separation of Organic Species

- New separation processes for cleaning pre-conversion biomass derived vapors and liquids

Ct-P: Selective Separations of Inorganic Contaminants

- Selective removals of particulates from biomass vapor feeds

Ct-E. Improving Catalyst Lifetime

- Via upstream contaminant removal

Objective

Develop efficient thermochemical separation processes targeting significant CAPEX and OPEX cost savings (via TEA) through catalyst preservation, carbon valorization and process intensification strategies

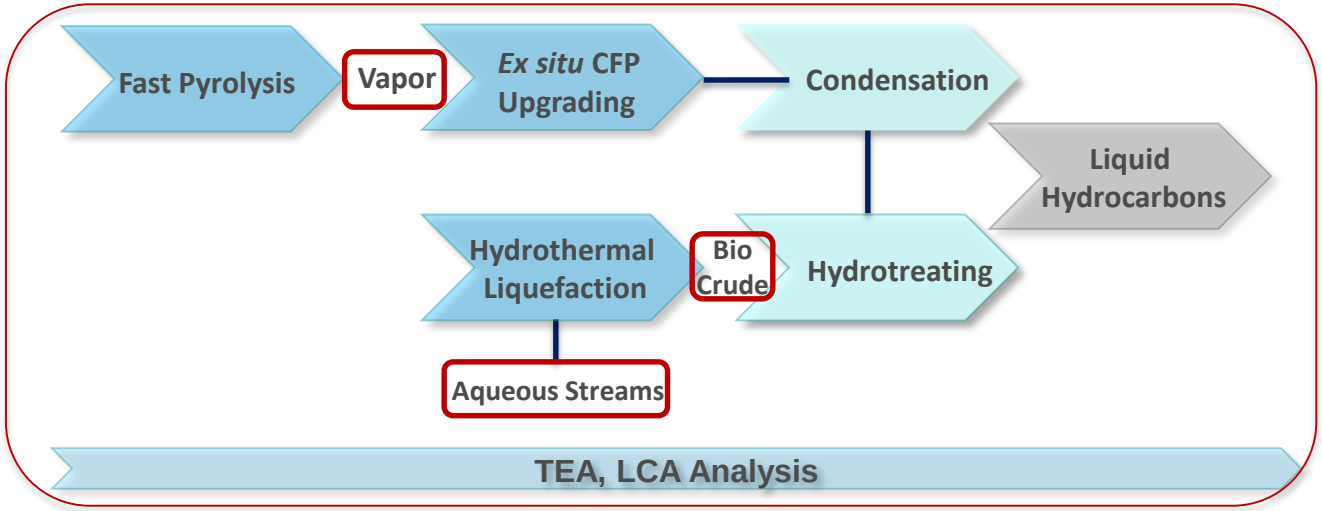
End of Project Goal

[NREL, ORNL] Demonstrate at least a 10% decrease in catalyst coking by cofeeding VGO and FP oil which has been passed over a hot gas filter and has the heavy (>300˚C), coke-precursors compounds removed using fractional condensation.

Project History/Overview

History: *Separation materials (catalysts, sorbents, membrane) longevity is a known barrier to cost-effective thermal biomass conversion.*

- New project in FY17, catalyst preservation, feed cleaning, carbon valorization are three challenges



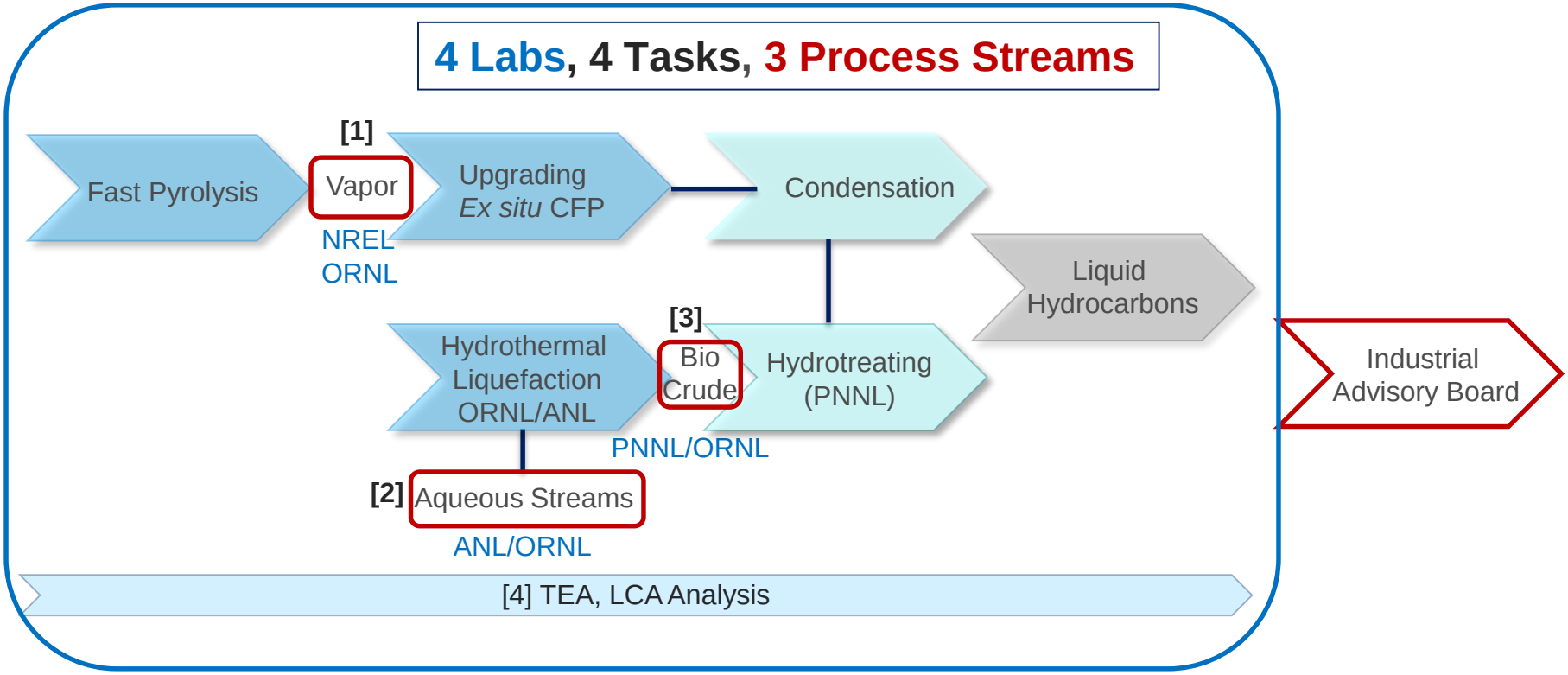
Context:

- Extending catalyst lifetime for bio oil upgrading is critical
- Valorizing carbon in bio oil/crude waste streams offsets process costs

Project Goals:

- Remove contaminants from bio-oil, bio crude feedstocks to improve upgrading catalyst lifetime
- Valorize carbon from HTL aqueous streams to offset process cost
- Use TEA and LCA to quantify impact on efficiency improvement and cost reduction

Project Management



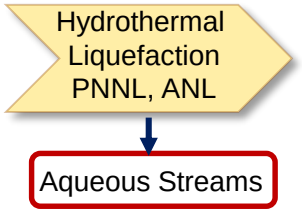
Project Management

- Monthly webinars (SepCon)
- Quarterly reports
- Bi annual meetings for progress review with IAB
- Milestones with explicit technical targets to meet

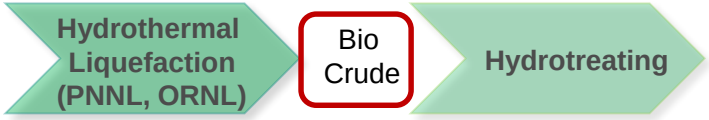
Project Management: 4 TCS Tasks

[1:] Catalytic Hot Gas Filtration for Biomass Fast Pyrolysis Vapor Chemistry Tailoring for Fuels/Chemicals

[2] Integrated Membrane Separations Technology for Carbon Recovery from Hydrothermal Liquefaction (HTL) Aqueous Streams

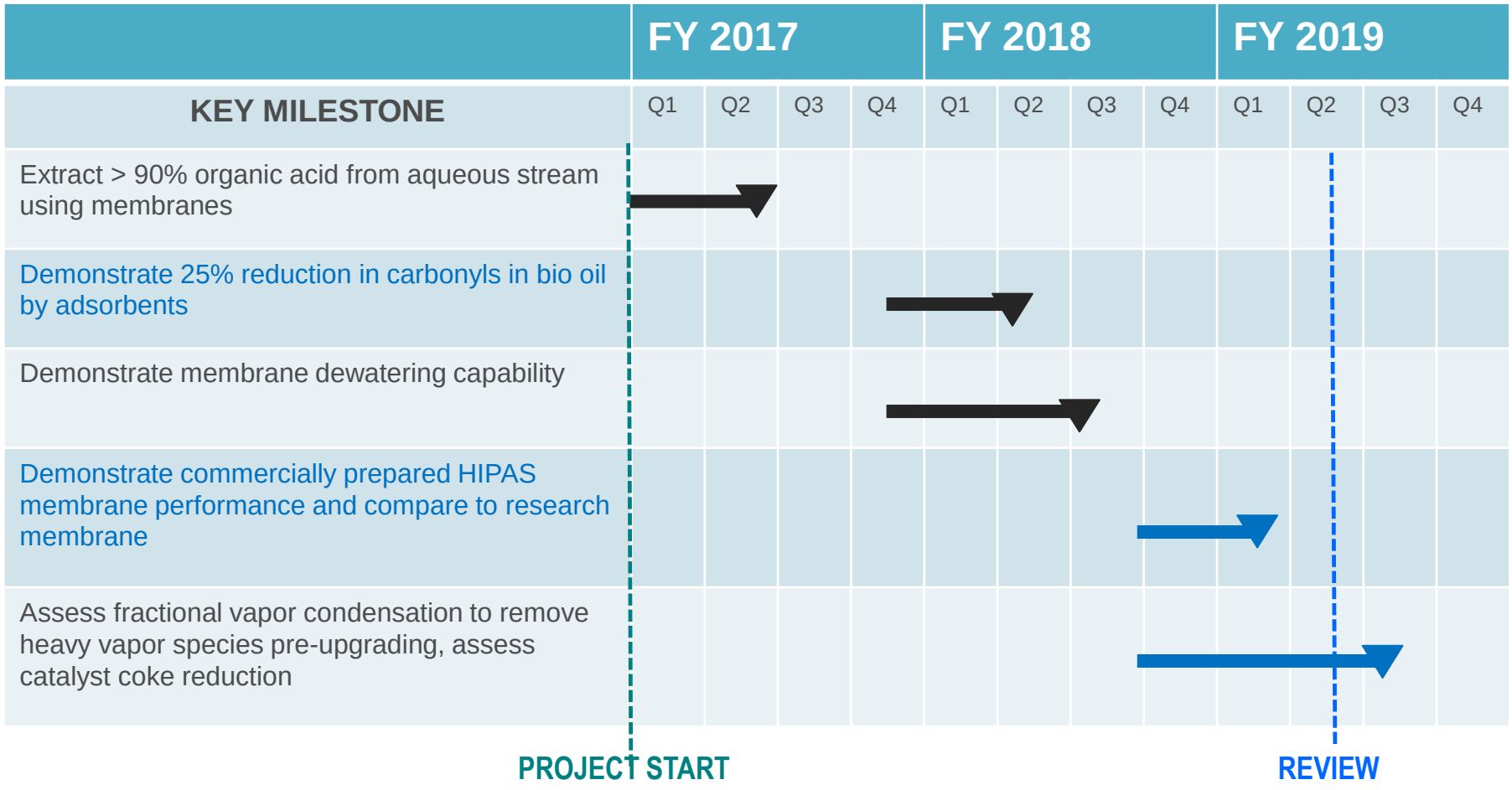


[3] Molecular Removal Technology (Adsorbents) for Pre-Processing of Liquid Bio-Oils/Bio-Crudes



[4] Integrated Process TEA and LCA

Project Milestones

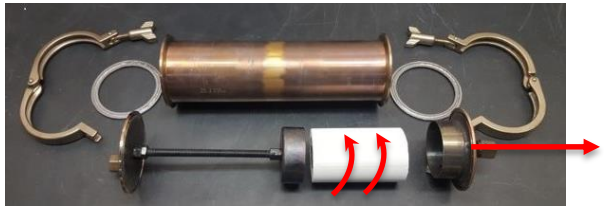


2 – Technical Approach

[1]: CHGF of Biomass Fast Pyrolysis Vapors

Approach

- Filter particulates to protect CFP upgrading catalyst performance, lifetime
- Add catalysts to convert unreactive oxygenates to upgradable components to increase carbon conversion to products
- Remove heavy vapor components to reduce carbon loss via upgrading catalyst coking



Challenges

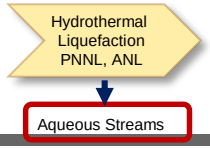
- Developing efficient catalytic filters that convert unreactive oxygenates while preserving biomass carbon (< 10% yield loss) and demonstrate extended performance (> 25 h)

Critical Success Factors/Outcome

- Demonstrated tunability of vapor chemistry (pre-upgrading)
- Enhanced CFP product (fuels, chemicals) composition post-upgrading
- Industry accepted filter and catalyst sorbent performance, lifetime and regenerability

2 - Technical Approach

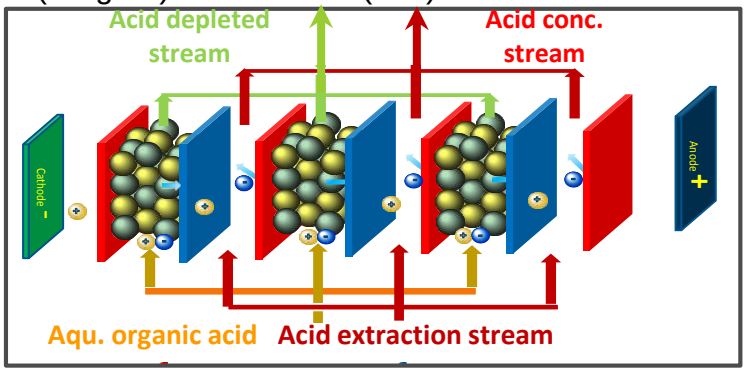
[2]: Valorizing Carbon from HTL Aqueous Streams



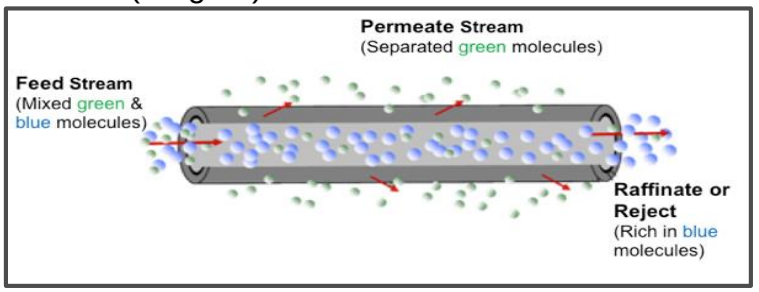
Approach: Develop membrane separations to recover/concentrate organic acids and ammonia in HTL aqueous streams:

Couple ANL's ion-exchange polymer wafer/membrane to extract carboxylic acids with ORNL's dehydration/dewatering membranes to remove water at higher acid content

(Stage-1) Resin Wafer (RW):dilute to 30 wt%



(Stage-2) HiPAS: ~30 to >50 wt% acid



Challenges

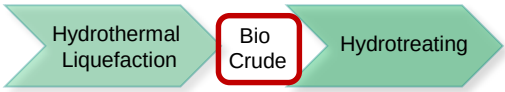
Developing efficient hybrid membranes that extract water and concentrate organic acids simultaneously in complex aqueous bio-crude streams; recover high value organic acids

Critical Success Factors

- Demonstrate extended bio-crude aqueous stream separations to reduce water and concentrate organic acids
- Industry accepted membrane performance, lifetime and regenerability
- Efficient organic acid and ammonia recovery/reuse to offset process cost

2 - Technical Approach

[3]: Cleaning Bio Oil via Sorbents



Approach

- Develop polymer and inorganic adsorbents to *remove nitrogen species* in sludge-derived HTL bio-crude and *carbonyl species* in woody bio-oil pre-HT
- Demonstrate reduced H_2 consumption and increased down stream HT throughput
- Recover high value nitrogen species (indoles, pyridines, piperidines, pyrazines, pyrroles, and pyrrolidines)

Challenges

- Developing efficient sorbent performance in complex bio-crude liquids to remove carbonyl contaminants and recover high value nitrogen species

HTL bio-crude

Critical Success Factors/Outcomes

- Extended bio-crude HT to fuels
- Industry accepted sorbent performance, lifetime and regenerability
- Efficient nitrogen product recovery to offset process cost

3 - Technical Progress

[1]: CHGF - Clean/condition Biomass FP Vapors

Hypothesis: CHGF can extend catalyst lifetime and provide low Capex bio oil stabilization

Background

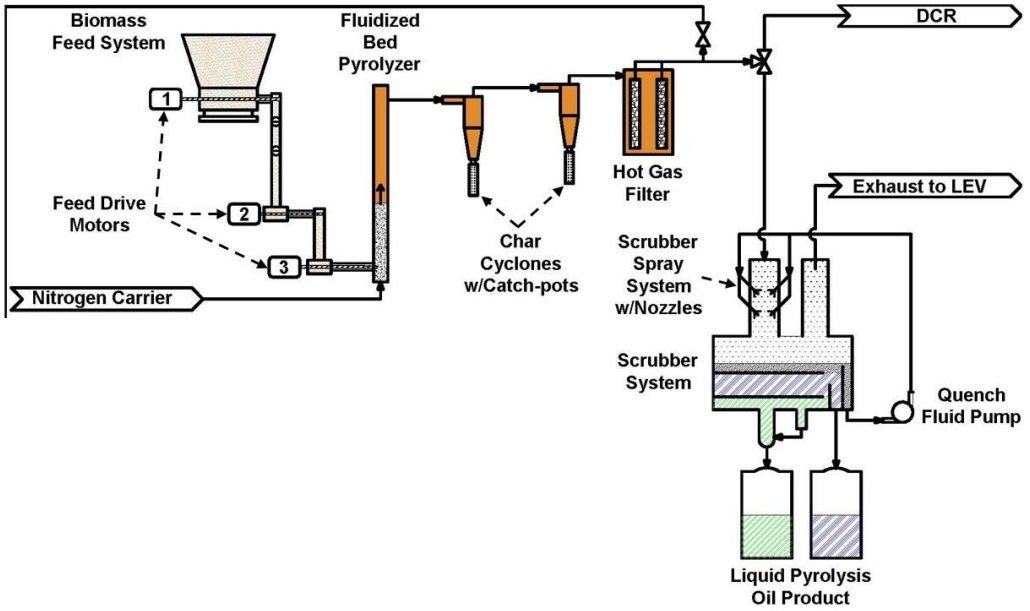
Biomass fast pyrolysis vapors contain char, alkali aerosols and carbonyls that destabilize bio oil vapor feeds and bio oils

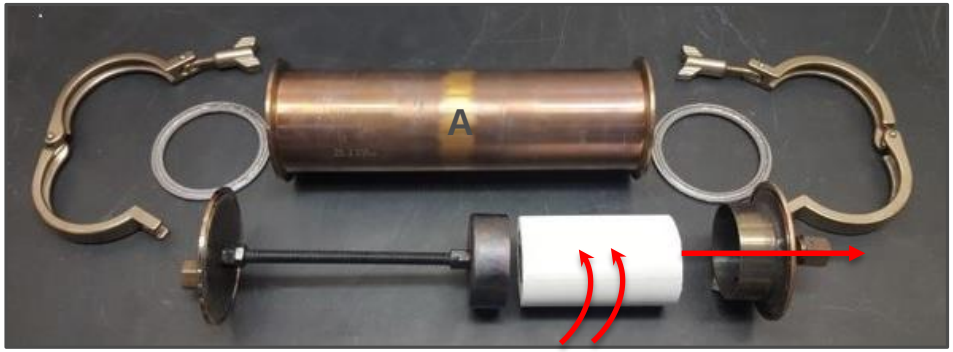
Results

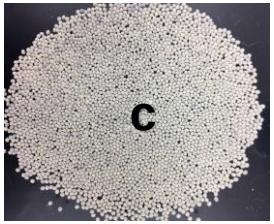
- Ceramic filter removes > 99% char and alkali from FP vapor
- CeO_2 catalysts convert acetic acid to ketones
- HPA catalysts deoxygenate, alkylate vapor feedstocks (pre-CFP)

Outcomes

- HGF provides particulate-free vapors for catalytic upgrading
- CHGF converts unreactive oxygenates to upgradeable species - enhances C conversion to product







A) Filter housing, B) catalyst coated on filter or C) packed in filter interior

Technical Progress

[1]: Feedstock and Catalyst Impact on CHGF

Hypothesis

Feedstock and catalyst may impact CHGF vapor composition, downstream catalyst lifetime and oil stability

Background

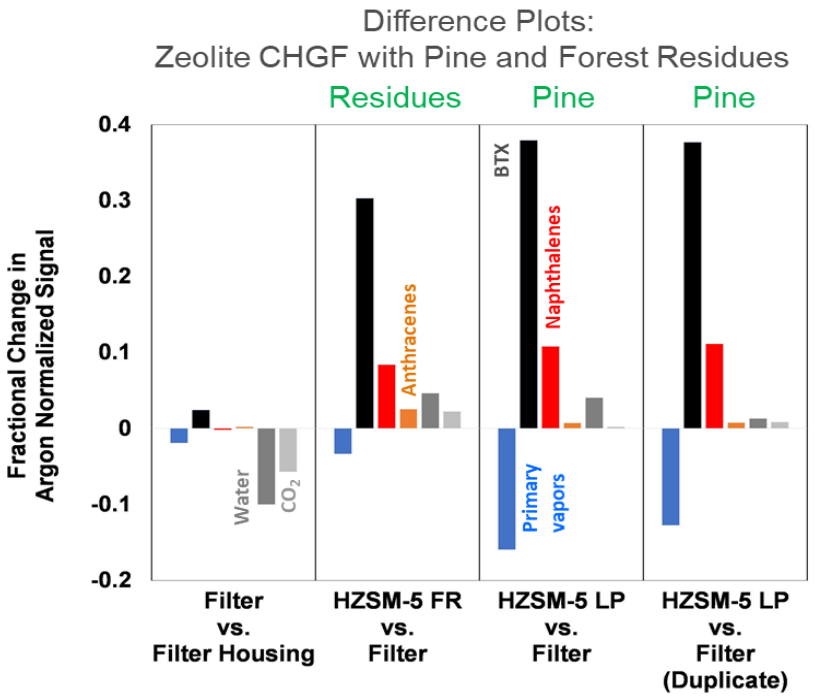
Determining biomass feedstock and catalyst impact on vapor feed is required for CHGF development

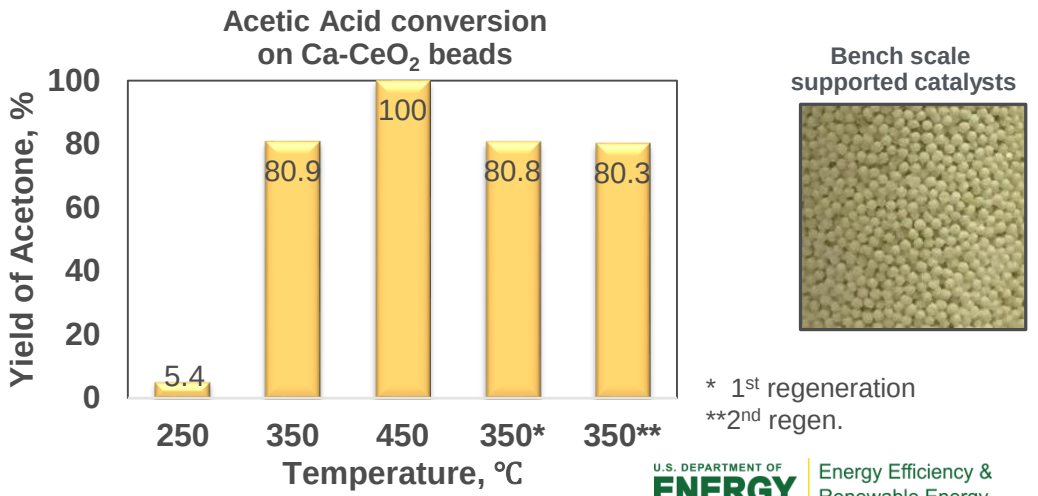
Results

- Pine and pine residues exhibit similar conversion with zeolites (BTX)
- CeO_2 converts acetic acid to more upgradable acetone

Outcomes

- REO_2 catalysts candidates for ketonizing carboxylic acids
- CHGF is feedstock agnostic





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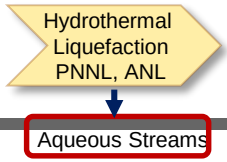
Technical Progress

[2]: Valorizing Carbon from HTL Aqueous Streams



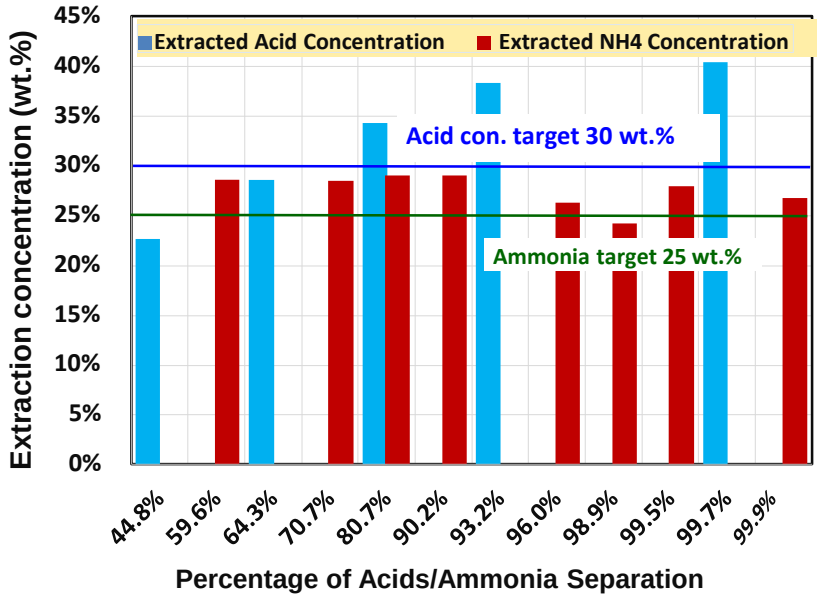
Hypothesis: Selectivity and material stability to handle concentrated organic acids can be developed

Background: Organic acid concentration >50 wt% is required to be economical

Results: (>25 wt.% ammonia from algae HTL aqueous phase) and >50 wt.% acids captured separately for FY2018 Go/No Go milestone

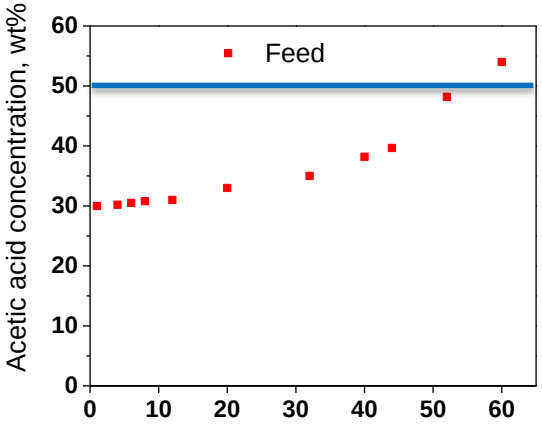
Outcomes

- Demonstrated polymer wafer extraction of acids/ammonia from dilute aqueous streams (Stage 1)
- Developed strongly adhered, chemically stable HIPAS membranes for dewatering (Stage 2)
- Conducting TEA for cost assessment
- Develop new adsorbent in wafer membrane to capture individual acid and ammonia species



FY18 annual milestone met:

Capture > 50wt% acetic acid using the HIPAS membrane



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Technical Progress

[3]: Cleaning Bio Oil and Bio Crude via Sorbents

Hypothesis: Carbonyl reduction >25% in pine FP bio oils is possible using selective sorbents

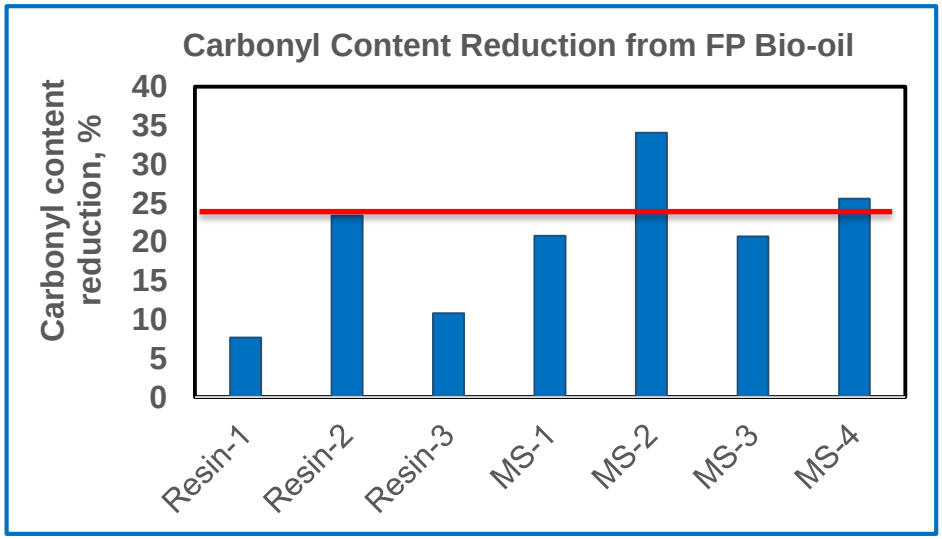
Background: FP bio oil has carbonyl content of 4.5 mmol/g; sludge HTL crude has ~5 wt% N; these contaminants impact downstream HT catalysts

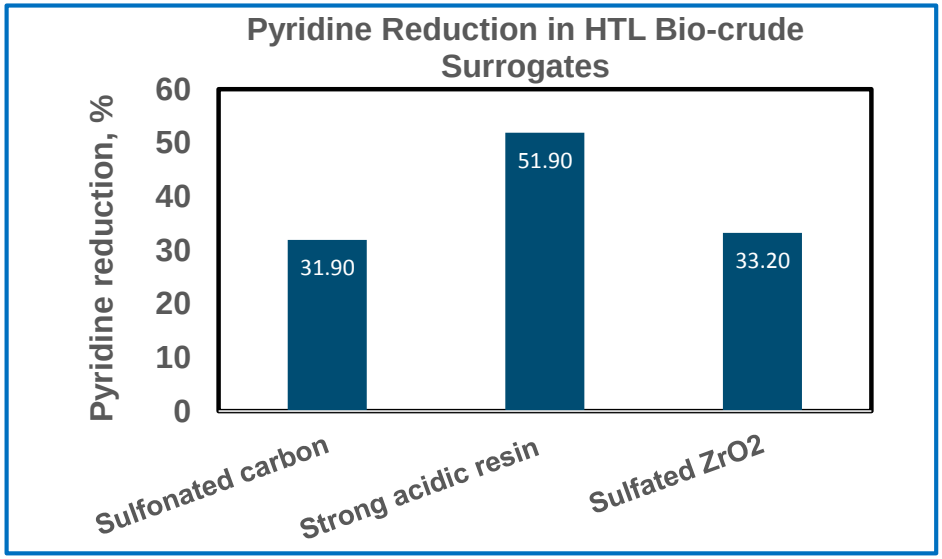
Results: Demonstrated 34% removal of carbonyl contaminants

- Exceeds the target (carbonyl reduction >25%)
- Carboxylic and phenolic acids were also reduced

Outcomes:

- Carbonyl removal correlates with adsorbent basic sites measured with CO_2 adsorption studies
- Strong acidic sorbents can remove 52% pyridine in complex HTL crude surrogates





4 - Relevance

Develop critical and efficient thermochemical separation processes to remove process contaminants before upgrading through catalyst preservation, carbon valorization and process intensification strategies

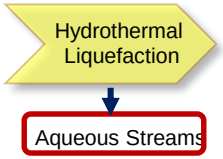
- Project directly supports BETO's mission: transform biomass into commercially viable, refinery integrable biofuels
- Efficient thermochemical separations are consistent with BETO's goal of a < $3/GGE range fuel production cost
- Project addresses a critical need for separations enabling technology development (catalysts, sorbents, membranes) that enable bio oil/crude conversion to fuels and chemicals
- Project metrics and technical targets are vetted by the IAB
- Reduce separations costs by:
  - Protecting downstream upgrading catalysts (↑ lifetime, ↓ losses)
  - Valorizing carbon from aqueous process streams
  - Producing more upgradeable bio oils for upgrading

5 - Future Work (Plan)

[1]: Catalytic Hot Gas Filtration of FP Vapors

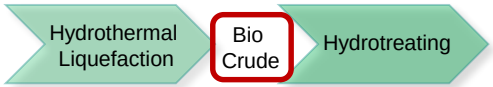
- Assess rare earth oxide catalysts for ketonizing acids, carbonyls to more easily upgraded ketones
- Optimize HPA catalyst/support for coupling FP vapor oxygenates pre-upgrading
- Assess heavy species removal via fractional vapor condensation on bio oil
- Update process TEA to determine impact on fuel MFSP

[2] Integrated Membranes for C Valorization of Aqueous Streams



- Design/understand membrane chemistry for acid capture in aqueous streams
- Introduce ultrafast molecule-transport interfaces – to enhance H_2O transport in membranes
- Evaluate sulfonated poly ether ketone as binder in resin wafers for acid capture

[3] Sorbents for Bio Oil/Crude Cleaning



- Develop sorbents with strong acidity and high site density for bio crude cleaning
- Understand oxygenate impact on adsorbents (with CCPC modeling task)
- Assess selected sorbents for denitrogenating actual sludge HTL bio-crude

5 - Future Work (Milestones)

[1]: due 6.30.2019: CHGF Improvement via Fractional Vapor Condensation

[NREL, ORNL] Demonstrate decreased coking when cofeeding VGO and fast pyrolysis oil (NREL and ORNL). Demonstrate at least a 10% decrease in catalyst coking at bench-scale by cofeeding VGO and FP oil which has been passed over a hot gas filter and has the heavy (>300°C), coke-precursors compounds removed using fractional condensation

Progress: on target for completion

[3]: due 3.31.2019: Membrane Performance

[ORNL] Demonstrate commercial large-dimension dip coater-assisted ceramic tube-supported HiPAS membranes exhibit equivalent or better performance compared to that of existing research-grade membrane coatings (i.e., state-of-art performance: exceeding 0.1-0.25 LMH at separation factor of >10)

Progress: on target for completion

Summary

Overview

Project develops efficient thermochemical separation processes to remove bio oil feed contaminants before upgrading to fuels and chemicals and capture/valorize carbon in biomass-derived aqueous streams.

Approach

Develop catalysts, membranes and adsorbents to 1) clean/separate contaminants in bio oil feeds from FP, CFP and HTL pre-upgrading to fuels and chemicals and 2) capture valuable carbon in process streams for co-products

Technical Progress

[1]: Catalytic Hot Gas Filtration

Met the 2018 CHGF performance metrics with Mo-HPA/TiO_2 catalyst: 26% reduction in summed oxygenates, 17% increase in summed alkylated species including methylated naphthalenes, <10% oil yield loss to the filter

[2]: Integrated Membranes

Met the 2018 annual milestone demonstrating the capability of HIPAS membrane to concentrate acetic acid feed to > 50 wt%

[3]: Selective Sorbents

Found that nitrogen-fatty acid complexation hinders pyridine adsorption in HTL biocrude

Summary

Relevance

This project develops critical and efficient thermochemical separation processes to remove process feedstock contaminants before upgrading through catalyst preservation, carbon valorization and process intensification strategies

Future Work

[1]: Catalytic Hot Gas Filtration

- Develop catalysts for tailoring FP vapors to produce enhanced and stable CFP oils (carbonyl conversion, carbon coupling, heavy species removal)
- Assess process costs via TEA to determine impact on fuel MFSP

[2]: Integrated Membranes

- Design/understand membrane chemistry for acid capture in aqueous streams
- Develop enhanced H_2O transport and PEK binders in membranes for acid capture

[3]: Selective Sorbents

- Develop sorbents for HTL feedstock and bio crude cleaning
- Understand oxygenate impact on adsorbents (with CCPC modeling task)

Acknowledgements

BETO: Nichole Fitzgerald

Steering Committee: Jennifer Dunn, Taraka Dale, Todd Pray

TEA/LCA SepCon Team: Mary Biddy, Sue Jones

PNNL	ORNL	ANL	NREL
Huamin Wang	Michael Hu	YuPo Lin	Steve Deutch
Corinne Drennan	Mi Lu	Lauren Valentino	Chai Engtrakul
Suh-Jane Lee	Zhenglong Li	Louis Edano	Stefano Dell'Orco
Jian Liu	Tim Theiss		Brady Peterson
Marie Swita	Ting Wu		Mike Sprague
Asanga Padmaperuma			Nolan Wilson
			David Chiaramonte

Mike Watson: (JM)

JM Johnson Matthey

Argonne NATIONAL LABORATORY

Pacific Northwest NATIONAL LABORATORY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

OAK RIDGE National Laboratory

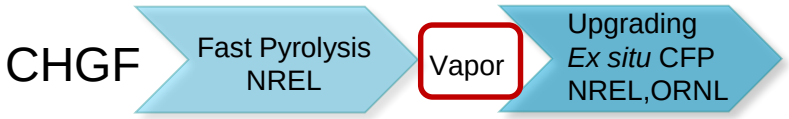
Additional Slides

Acronyms and Pathways
Publications
Patents
Presentations
Awards

Project Acronyms and Pathways

CFP: catalytic fast pyrolysis
CHGF: catalytic hot gas filtration
CO: carbonyl
CAN: carboxylic acid number
FP: fast pyrolysis
HT: hydrotreating
HTL: hydrothermal liquefaction
LCA: lifecycle analysis
TCS: thermochemical separations
TEA: technoeconomic analysis

Separations Tasks



Publications, Patents, Presentations, Awards, and Commercialization

Publications

B. Peterson, C. Engtrakul, K. Magrini, Assessing Catalytic Hot Gas Filters for Biomass Fast Pyrolysis Vapor Cleaning and Deoxygenation, in review Green Chemistry, February 2019.

Varada M. Palakkal, Lauren D. Valentino, Yupo J. Lin, Christopher G. Arges,"Highly conductive ion-exchange resin wafer wafers produced from ionomer binders for electrochemical separations", to be submitted to ACS Sustainable Chemistry & Engineering, 2019.

Michael Z. Hu*, Chaiwat Engtrakul, Brian L. Bischoff, Mussie Alemseghed, and Mi Lu, "Surface-Engineered Inorganic Nanoporous Membranes for Vapor and Pervaporative Separations of Water-Ethanol Mixtures", Membranes 8, 95 (2018). doi:10.3390/membranes8040095. Resolution ID: 110238

Michael Z. Hu*, and Marissa Morales, "Super-hydrophobic and super-hydrophillic surface functionalized porous inorganic (ceramic or metallic) membranes for oil-water microemulsion separations," Invited contribution to special issue of I&EC, August (2018).

Shenjie Xu, Feng Li, Baowei Su*, Michael Z. Hu*, Xueli Gao, and Congjie Gao, "Novel graphene quantum dots (GQDs)-incorporated thin film composite (TFC) membranes for forward osmosis (FO) desalination," Desalination, accepted, April (2018). Resolution Pub ID: 110764

Mi Lu, Andrew Lepore, Jae-Soon Choi, Felipe Poli Garzon, Zili Wu, Kim Margrini, Mark Javis, and Michael Z. Hu* "Carbide catalysts for catalytic hot gas filtration to tailor vapor chemistry of fast pyrolysis process," catalysts 8, 643 (2018).

Michael Z. Hu, "Nanostructured Polymer-Graphene Hybrid Coatings for Membrane Separations and Energy Applications," Proceeding book for 2nd International Conference on Membrane Science and Technology, Sept13-14, 2018, London, UK. Resolution Pub ID: 117946. DOI: 10.4172/2155-9589-C1-004

Patents

Hu, M.Z.; Engtrakul, C.; Bischoff, B.L.; Davis, M.F. Integrated Membrane-Pyrolysis-Catalytic Upgrading Systems, ORNL/NREL Invention Disclosure ID 201503495, DOE S-138,126 (2017); US Patent US10,118,124B2 (Nov. 6, 2018).

Hu, Michael Z. et al. "Super-surface selective nanomembranes providing simultaneous high permeation flux and high selectivity", US Patent 9,308,501 B2 (August, 2018).

Provisional patent filing for Invention Disclosure 201704036. "Fast-Permeating Graphene-Polymer Hybrid Membranes for Dewatering, Desalination and Water/Ion Separations." Inventor: Michael Z. Hu.

Provisional patent filing discussion for Invention Disclosure 201503616. "External Field Aligned Graphene Sheets Particulate Deposit Films/Electrodes" Inventor: Michael Z. Hu

NREL Invention Disclosure K. Magrini, B. Peterson, C. Engtrakul, "Catalytic Hot Gas Filtration System: Filters and Catalysts for Catalysts for Alkylating Biomass Vapors for Fuel Production", NREL Record of Invention filed October 4, 2018.

Invention Disclosure 201804070. "Separations of Bio-Derived 2,3-Butanediol (BDO) for Enhanced Thermal Catalytic Upgrading." Inventors: Michael Z. Hu and Zhenglong Li.

Invention Disclosure 201704043. "Catalysts for Catalytic Hot Gas Filtration to Tailor Vapor Chemistry of Fast Pyrolysis Bio-Oils." Inventors: Michael Z. Hu, Mi Lu.

Invention Disclosure 201704033. "Sorbent Selective Removal/Reduction of Carbonyls and Carboxylic Acids for Bio-Oil Stabilization and Down-Stream Catalyst Preservation." Inventors: Michael Z. Hu, Mi Lu.

Awards

2018 Best Paper/Presentation Award from American Chemical Society (ACS), for paper I&EC 144 (Surface functionalized nanomaterials for separation processing of crude and aqueous streams of biooils) that Hu presented at the 255th ACS National Meeting in New Orleans in March 2018

2018 Certificate of Recognition, honored by Editors of Journal of Membrane Science & Technology, for Hu's phenomenal and worthy Keynote presentation on "Nanostructured Polymer-Graphene Hybrid Coatings for Membrane Separations and Energy Applications," at the 2nd International Conference on Membrane Science and Technology, September 13-14, 2018, London (UK).

Publications, Patents, Presentations, Awards, and Commercialization

Awards cont.

Year 2017 Outstanding Alumni Contribution Award: On Nov. 26, Dr. Michael Hu has received 2017 Alumni Award (certificate and trophy) from Nanjing University of Technology.

2017 July DOE/EERE Success Story: for recognition of Dr. Hu's team research work on HiPAS nano-membrane development for improved separation processing of biofuels and bioproducts.

Presentations

Braden Peterson, Chaiwat Engtrakul, Nolan Wilson, Stefano Dell'Orco, Jessica Olstad, Yves Parent, Kim Magrini, "Conditioning of Pyrolysis Vapors via Catalytic Hot-Gas Filtration for Enhancement of the Ex-Situ Catalytic Fast-Pyrolysis Process", poster presentation accepted to TCS 2018, October 8-10, 2018, Auburn, AL.

K. Magrini, B. Peterson, N. Wilson, C. Engtrakul, Separations Consortium Update: Task C3: Catalytic Hot Gas Filtration", BETO Conversion Update, September 28, 2018.

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Technology transfer or commercialization efforts

Milestone Reports

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