Separations Consortium

Lignin Rich Stream Fractionation and Purification

March 11, 2021

Technology Area Session: Performance-Advantaged Bioproducts and Bioprocessing Separations, and Plastics

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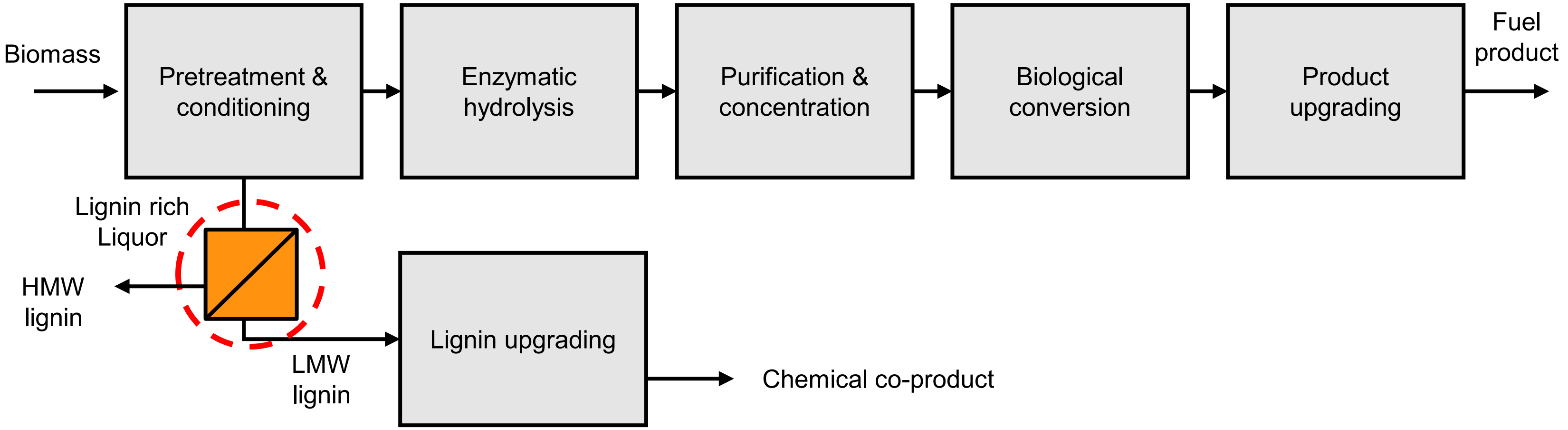
NREL, ANL, LBNL

Background

High level lignin first approach



- ***Separation challenge –*** *Recover LMW lignin from lignin first pretreatment streams for further upgrading.*
- *Includes Alkaline Pretreatment Liquor (APL), Reductive Catalytic Fractionation (RCF), and Catalytic Oxidation (CO) pretreatments*

Project Overview

- ***Context:*** Technology is needed to effectively recover LMW compounds from complex lignin-derived streams for valorization purposes.
- ***Project Goals:*** Develop filtration and electrochemical technology to recover LMW lignin from lignin derived streams APL, RCF, and catalytic oxidation oils.
- ***Heilmeier Catechism:***
  - ***What are you trying to do?*** *Recover LMW aromatics from lignin derived process streams.*
  - ***How is it done today and what are the limits?*** *To our knowledge there is no commercial process to separate lignin aromatics via membrane filtration.*
  - ***Why is it important?*** *LMW lignin needs to be isolated for downstream valorization purposes*
  - ***What are the risks?*** *Membrane filtration has been investigated in the past for LMW lignin recovery but very low fluxes and fouling have prevented industrial use. Membrane cascades, ElectroDeIonization (EDI), and dynamic filtration are explored in this project but remain unproven for lignin streams.*

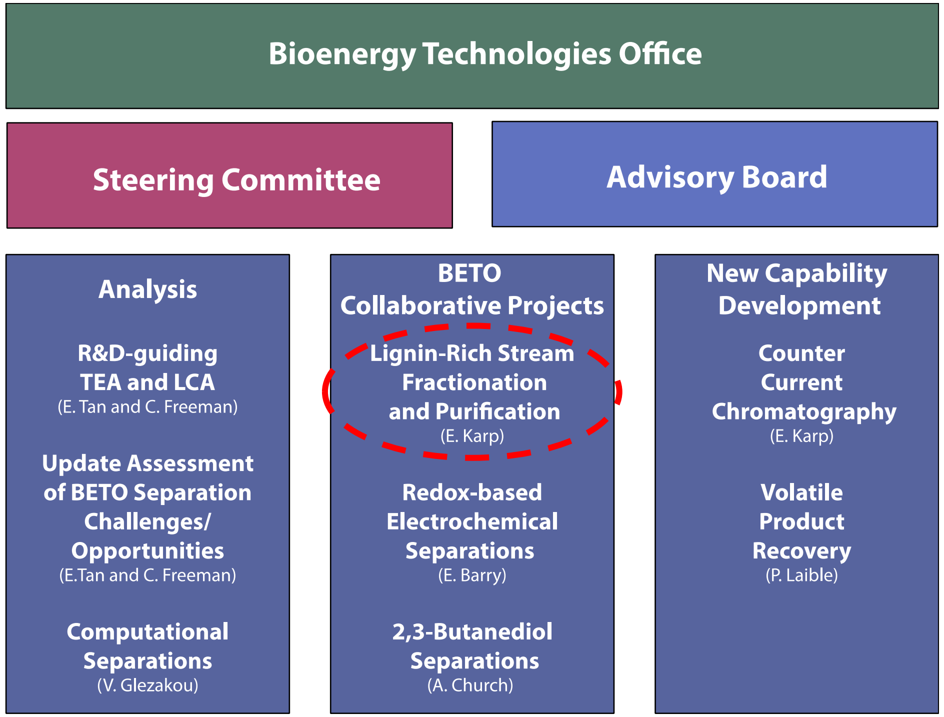
Management

1. Membrane cascades

2. Dynamic membranes

3. ElectroDeIonization (EDI)

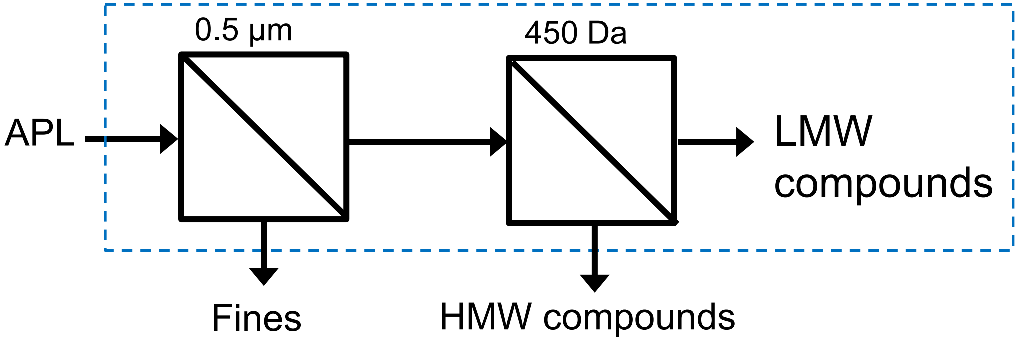
4. TEA & LCA



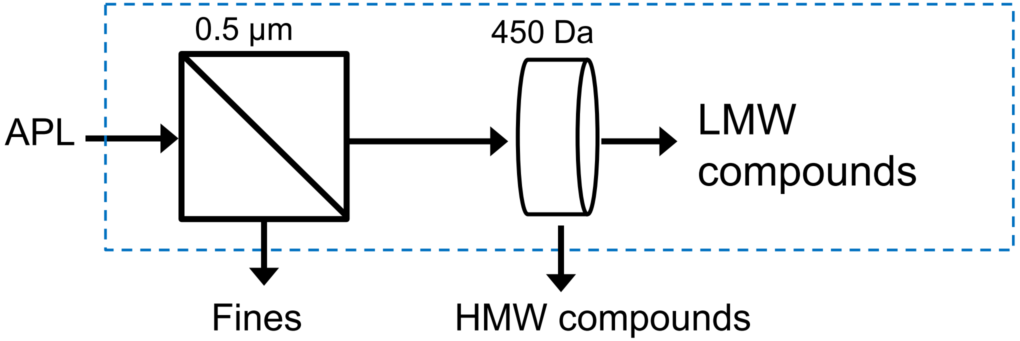
- ***Progress tracking with monthly consortium meetings***
- ***Dedicated monthly analysis meetings***
- ***Ad hoc inter-lab meetings coordinating milestones and deliverables***
- ***Publish findings and IP for new concepts***
- ***Smartsheet tool –*** used to coordinate milestones and joint work between labs. Manages risks in real time.
- ***Collaborate with other BETO projects***
  - *Biological Lignin Valorization*
  - *Lignin utilization*
  - *Performance advantaged bioproducts*

Approach

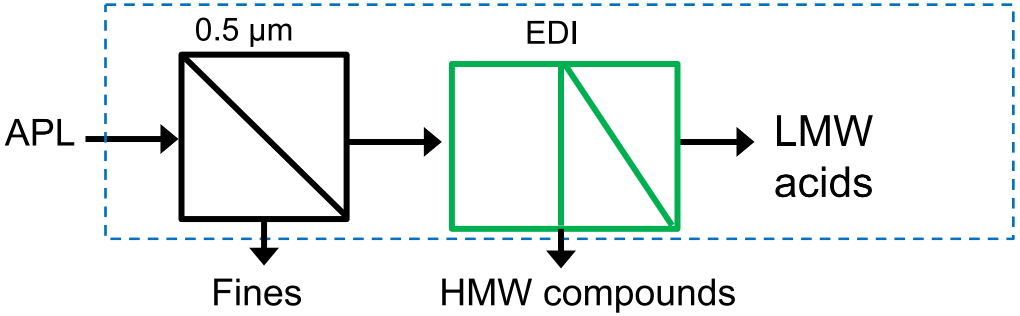
1. Two-stage membrane cascade



2. Two-stage RCD cascade



3. Two-stage EDI cascade for acids



- **3 filtration configurations (left)**
- **Lignin derived streams (APL, RCF, CO oil)**
- **Risk Mitigation –** Rotary Ceramic Disk (RCD) filtration
- **EDI to recover LMW acids & recycle caustic**
- **Challenges**
  - *Flux >1 L / hr / m^2 / bar (LMH/bar) for process (IAB input)*
  - *Filtration of fines (cascades used to address this)*
  - *Compatible materials for pilot scale (IAB input)*
- **Go /No-go**
  - >20% energy reduction with RCD compared to Tangential Flow Filtration (TFF)
- **TEA targets are**
  - ***Goal is costs of <$1.0 / kg dry LMW lignin[1]***
  - *Energy consumption*
  - *Yields (HMW rejection factors)*

1) Z. Sultan et. al.. *ChemSusChem*,, 12 (6), **2019**, 1203

Impact

- **Recovering LMW lignin is a longstanding biorefining challenge**
- **Lignin recovery can positively affect biorefinery economics**
  - ***Lignin co-products can add up to $3/GGE in revenue***
  - ***Ferulic acid and coumaric acid (Gen 1.5)***
  - ***RCF monomers for chemicals and fuel applications***
  - ***Required for BLV and PABP***
- **Disseminating results with**
  - ***Patents (see slide 17)***
  - ***Peer reviewed papers (see slide 17)***
  - ***Consortium reports[1]***
  - ***Consortium website***
  - ***Biannual IAB meetings***

Compact Membrane Systems

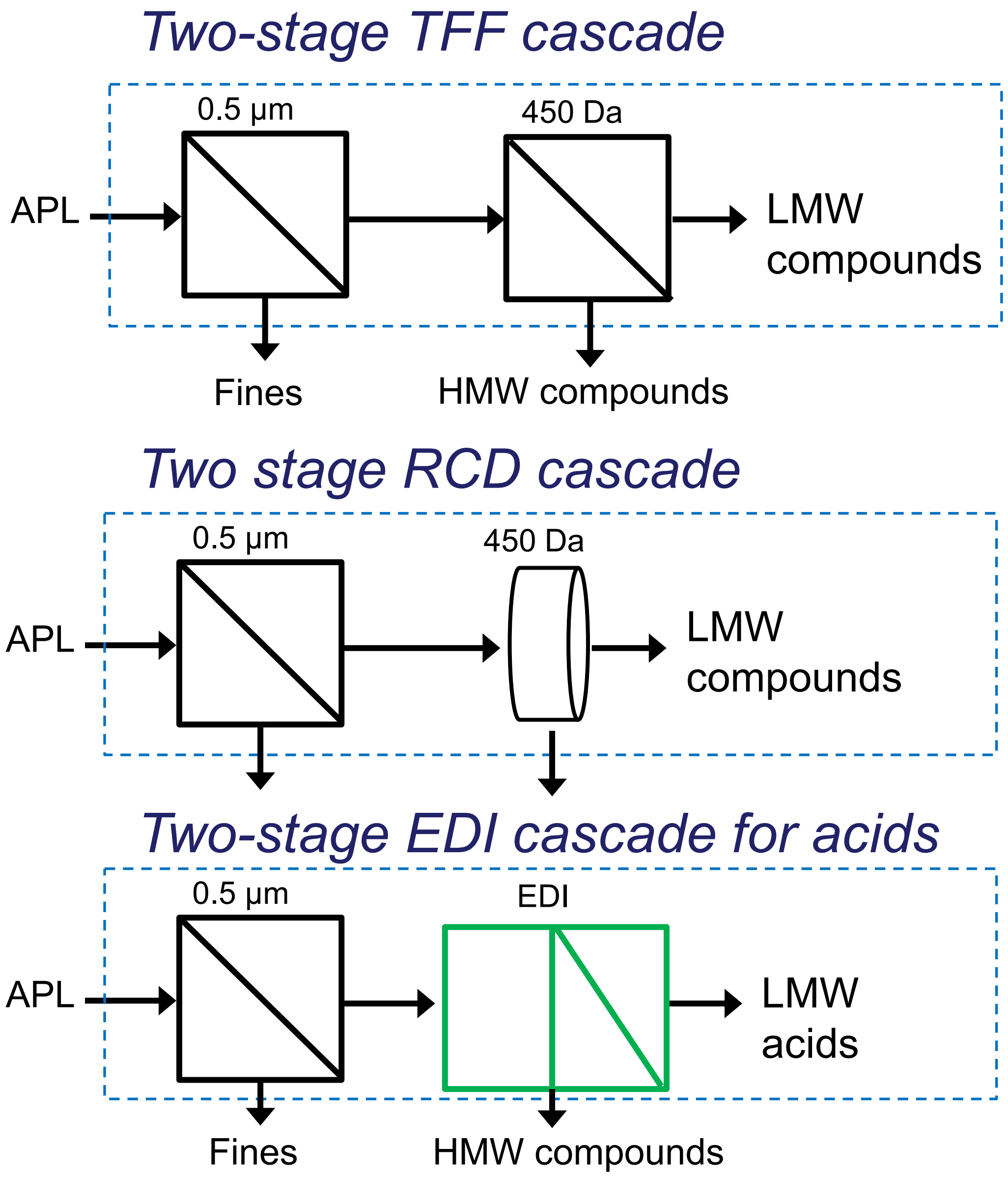
ICM

ANDRITZ

novasep
passion & smart processes

Outline of Progress and Outcomes

1. 2 stage TFF cascade
   - Discuss performance targets
   - Discuss system mass balance and analytics
2. 2 stage RCD cascade
   - Discuss system mass balance and analytics
   - Discuss performance targets relative to TFF
3. 2 stage EDI cascade for acids
   - First stage polymeric MF at 0.5 μm pore size
   - Second stage EDI for acids recovery
4. TEA of the above 3 processes



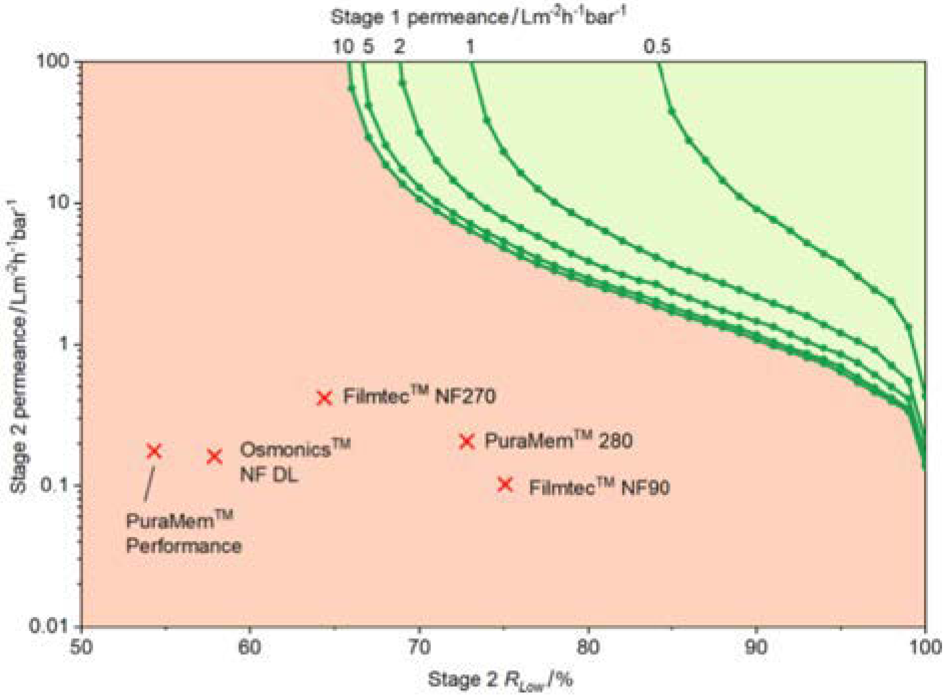
2 Stage Tangential Flow Filtartion Cascade

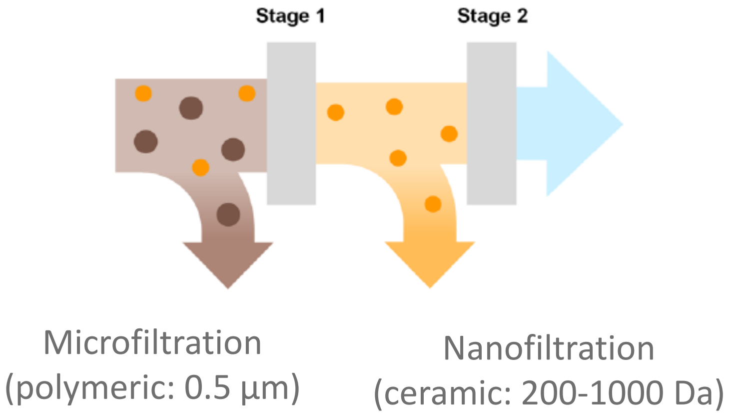
IAB Input

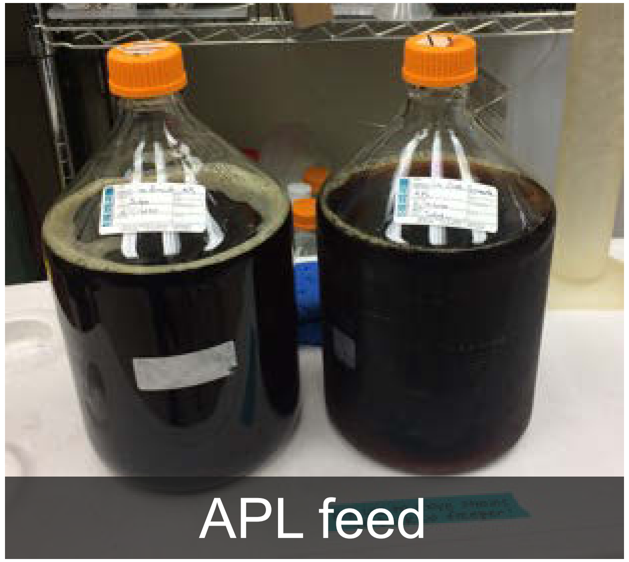
- 1st Stage CANNOT be ceramic

Goals from performance targets

- Total flux must be > 1 LMH/Bar[1]
- HMW rejections > 80 % in NF stage[1]
- > 30% volume reduction of feed stream

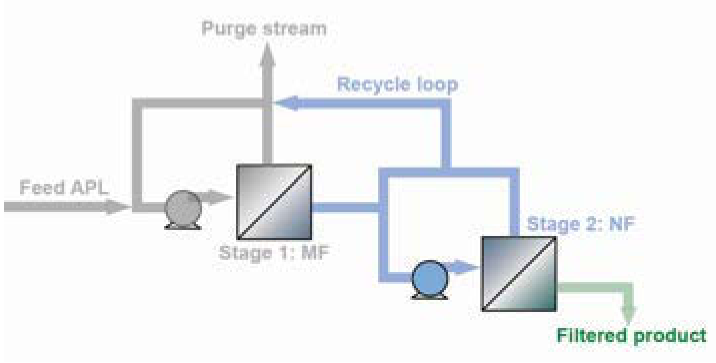






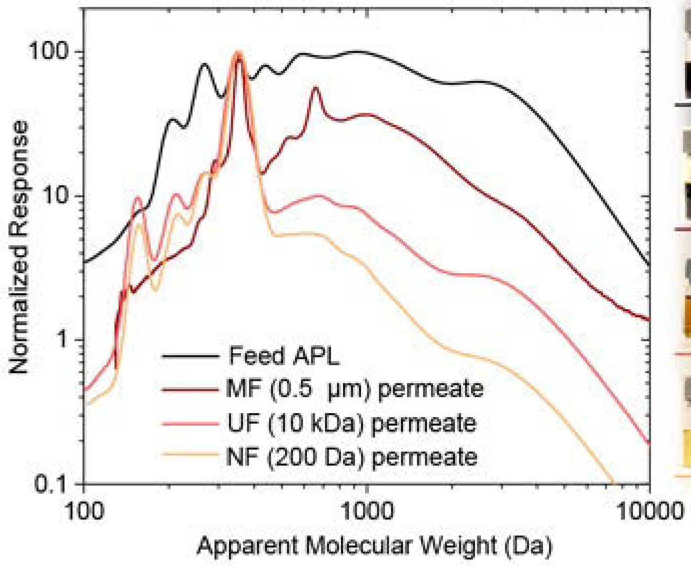
1) Z. Sultan et. al.. *ChemSusChem,*, 12 (6), **2019**, 1203

2-Stage TFF Cascade Analytics



NF permeate streams

200 Da 450 Da 600 Da 1 kDa



Dried LMW lignin

Recovery of aromatic monomers in permeate

Membrane	p-Coumaric Acid	Ferulic Acid	Vanillin	4-Hydroxybenzaldehyde
0.5 um	100%	100%	100%	100%
1 kDa	67%	66%	100%	95%
600 Da	76%	73%	100%	100%
450 Da	82%	75%	95%	92%
200 Da	60%	46%	81%	87%

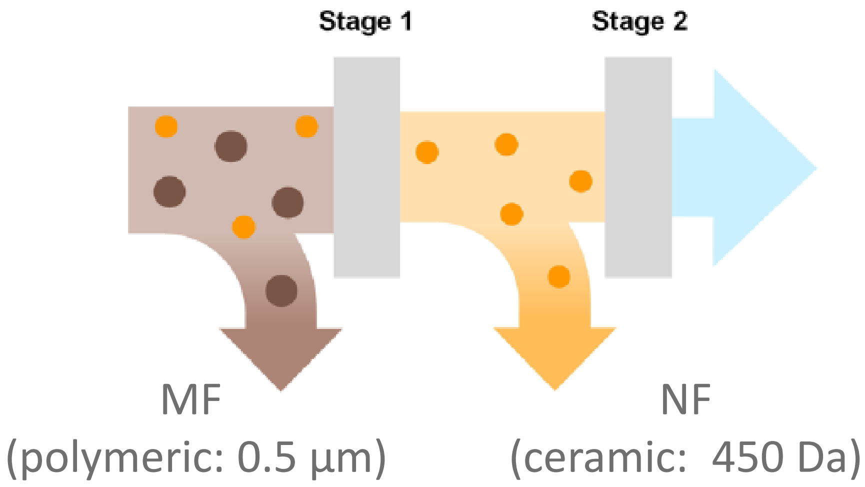
Analytics of 2-stage TFF cascade

- GPC analysis of permeates confirms HMW rejection
- Compositional analysis on permeates indicates 450 Da is ideal for high yield recovery with > 70% HMW rejection
- Dried solids given to BLV for conversion
- IAB indicates 200 Da needed for natural products
- ***However for 450 Da is ideal for chemical products based on yield***

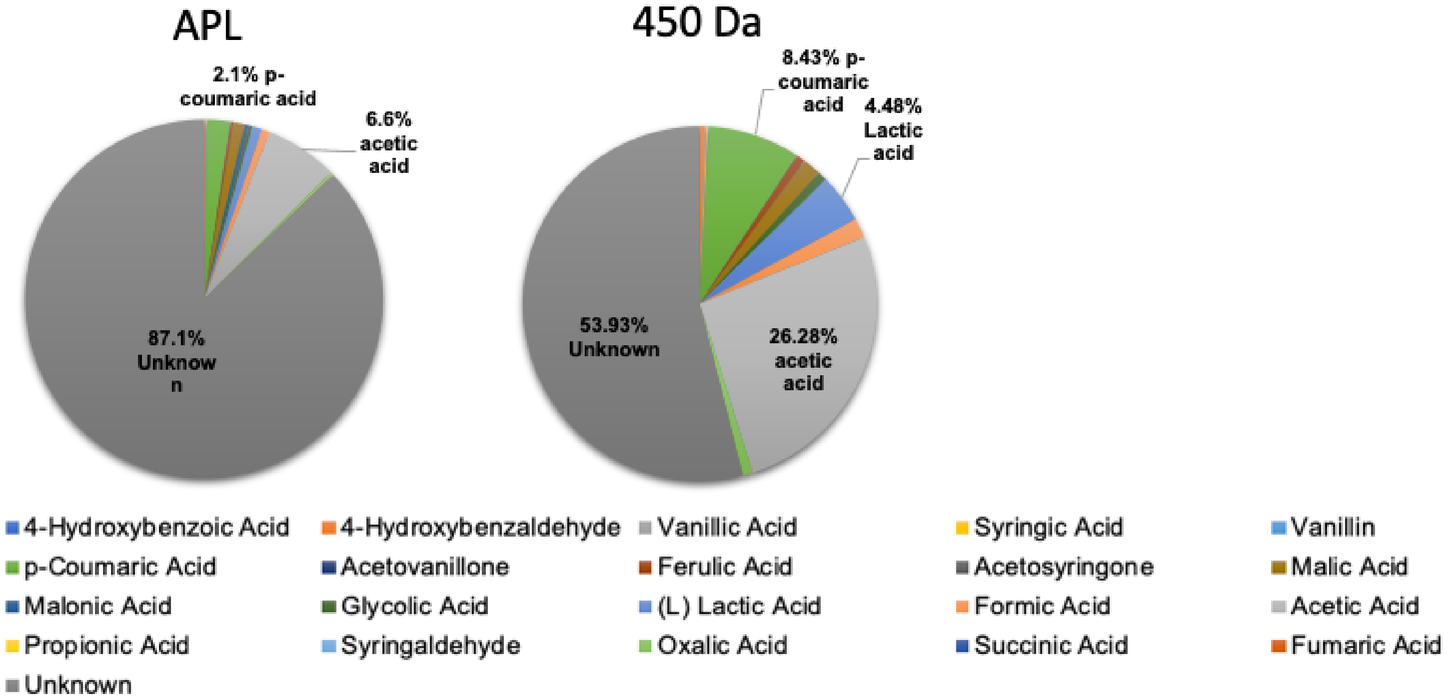
2-stage TFF Cascade Analytics

Analytics of 2-stage TFF cascade

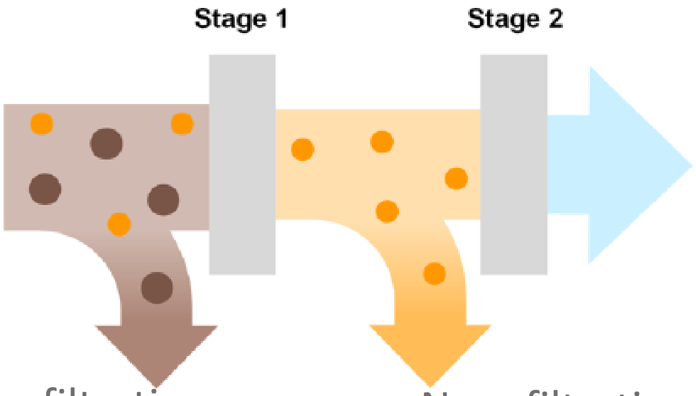
- ~46% by weight identified
- Unknowns are likely dimers
- Analytical challenge
- Collaborating with Lignin tasks for additional analytics to close unknown section
- ***2-stage cascade is effective***
- ***BUT what about flux targets?***

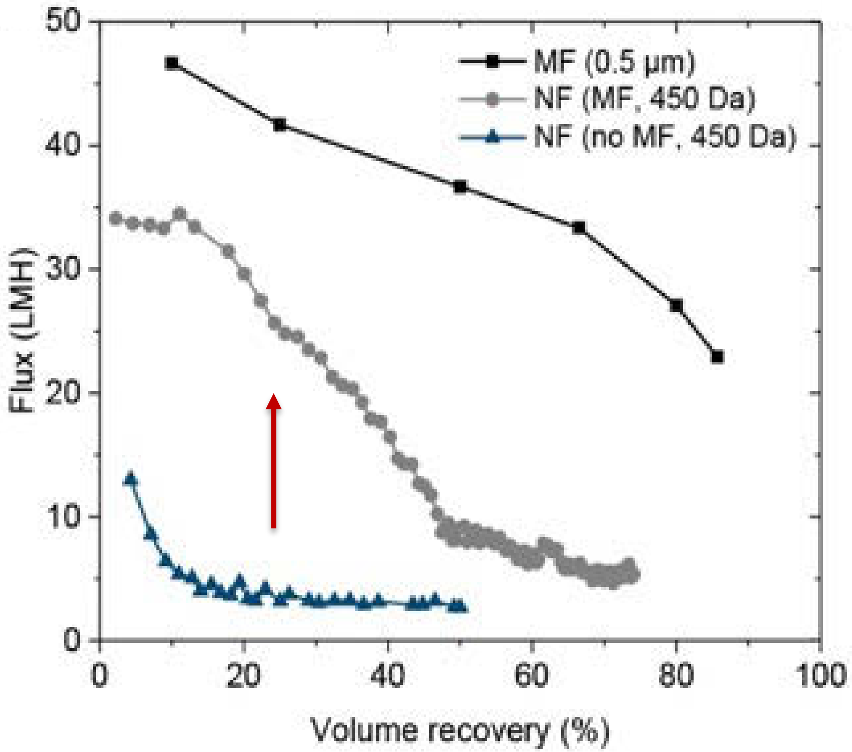



Dried LMW lignin



2-Stage Tangential Flow Filtration Cascade Flux





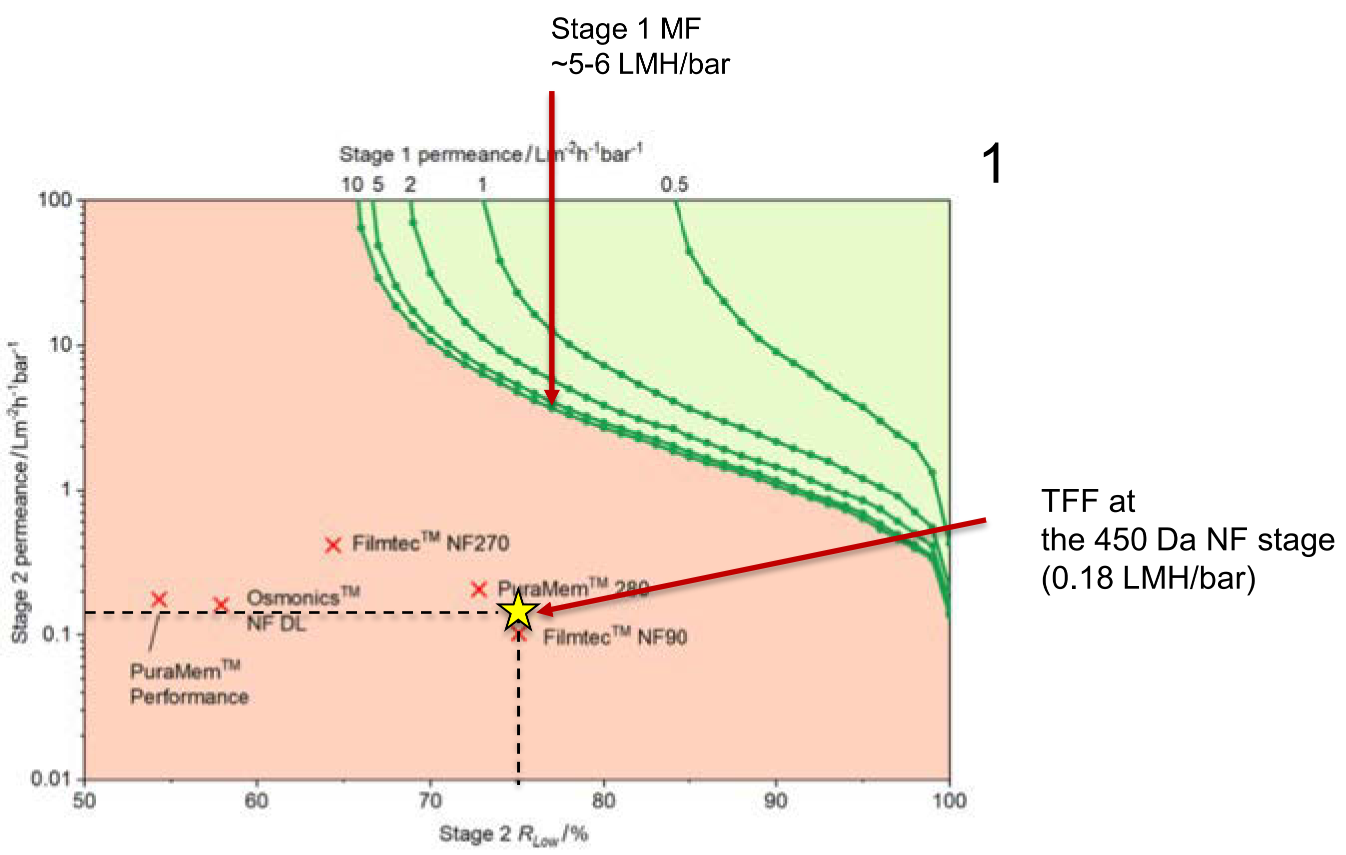
2-stage cascade flux for APL

- Target > 1 LMH/bar
- Identified a 0.5 µm 1st stage and 450 Da 2nd stage
- 1st stage polymeric to avoid shattering during operation, cleaning, and general plant operation
- 1st stage removes fines and permeance of ~5-6 LMH/bar
- **2nd stage 2 LMH/bar below 20% volume reduction, > 70% volume reduction < 0.1 LMH/bar NOT MEETING TARGET**

Flux Targets for Tangential Flow Filtration Cascade

<u>Flux is not meeting industry targets</u>

- Need to increase flux at the 450 Da NF stage
- Challenge within the field of membrane science is high flux at the NF level
- ***Moved to dynamic filtration to increase NF stage flux to > 1 LMH/bar***



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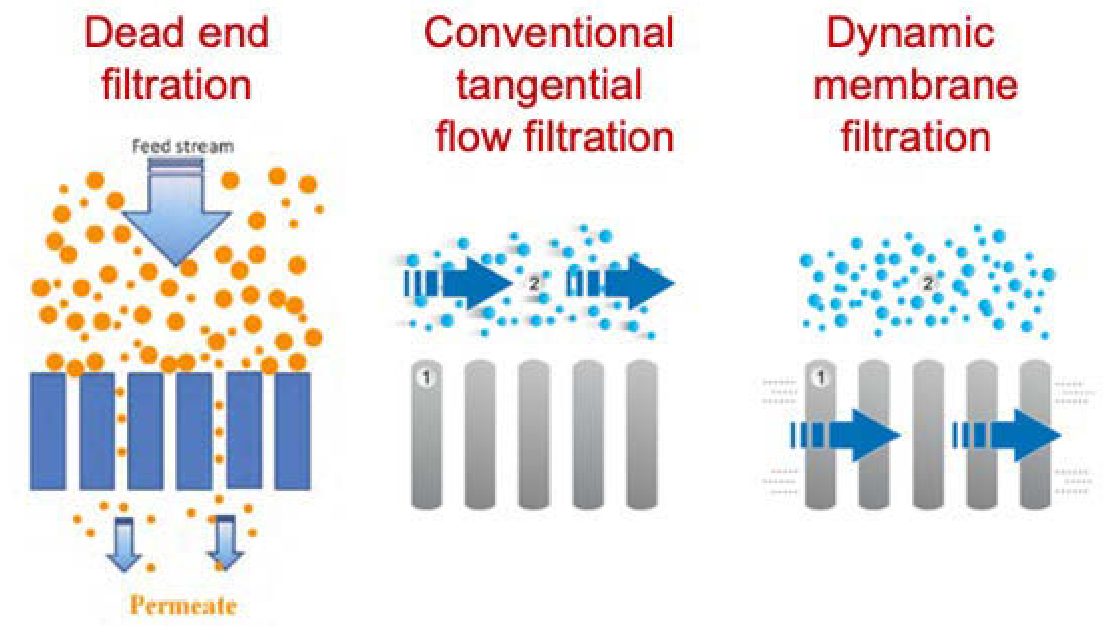
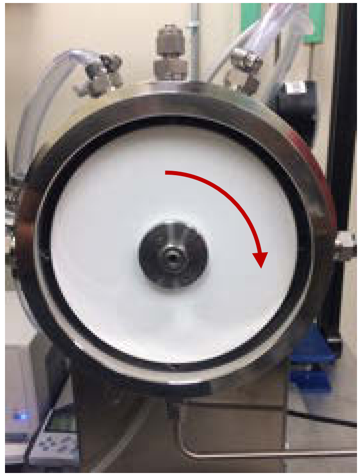
Dynamic Filtration

Dynamic filtration with Rotary Ceramic Disk (RCD) filter

- Flux is proportional to shear force at surface
- Can generate much larger shear forces by moving the membrane rather than pumping the fluid
- More energy efficient than pumping large volumes of fluid
- Collaborated with Fraunhofer IKTS Germany to coat Disk membranes and reduce pore size to the NF range

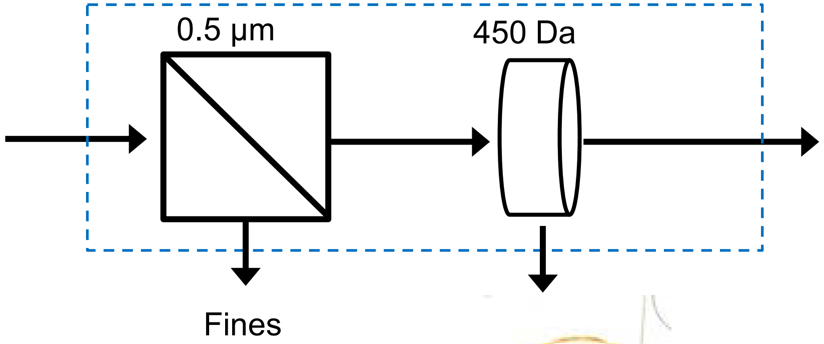


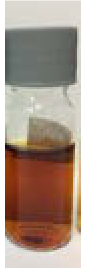


RCD NF unit (450 Da cutoff)

Dynamic Filtration at 450 Da

Two stage RCD cascade



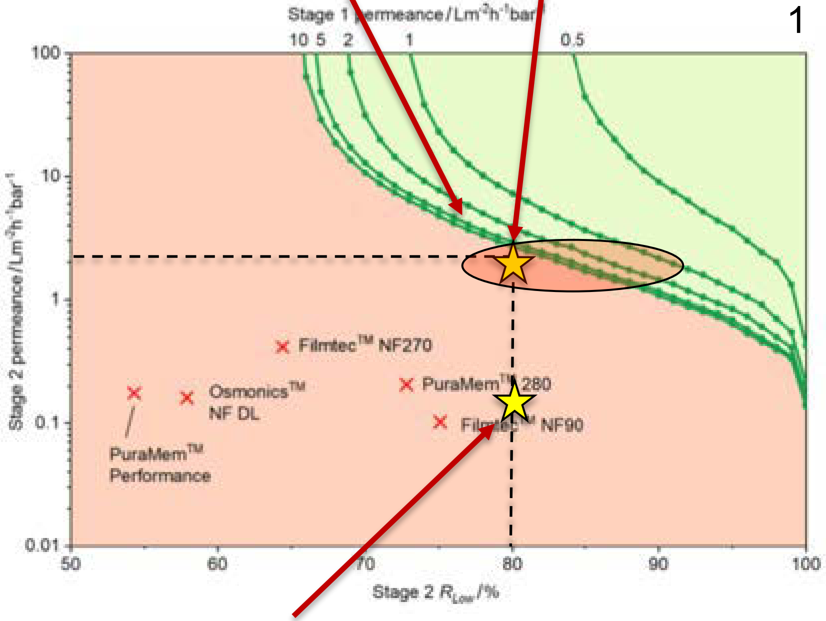


Water removal

retentate
(viscosity of 2000 cP!
~ like honey)

Stage 1 MF
~5-6 LMH/bar

RCD at
the NF stage
(2 LMH/bar)



[1]

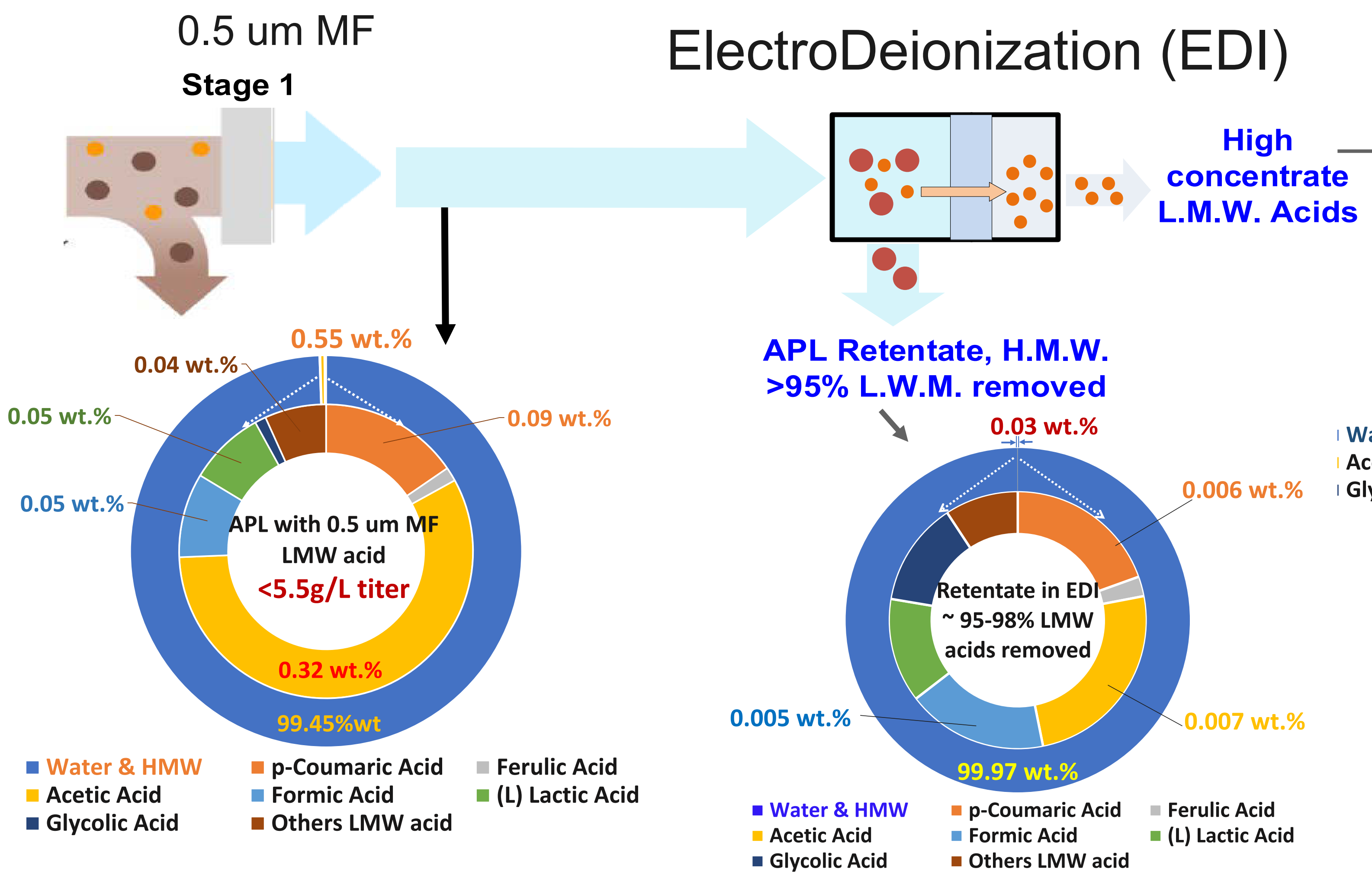
TFF at
the 450 Da NF stage
(0.18 LMH/bar)

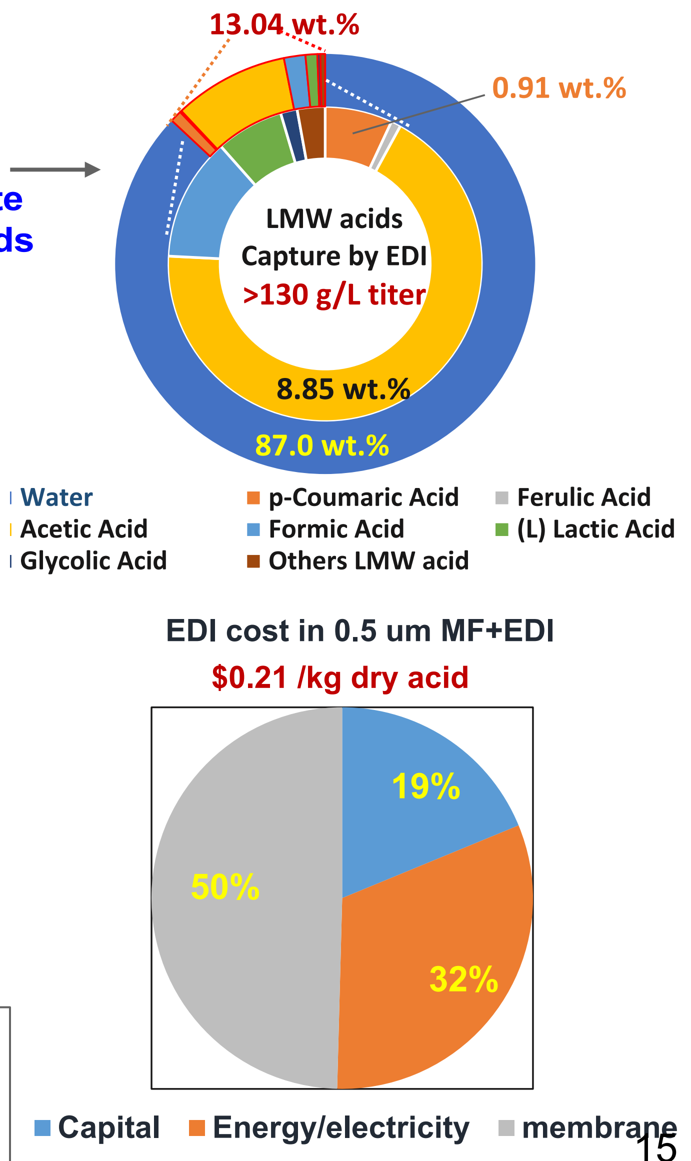
Preparative scale filtration

- Running at 90% volume reduction!
- Flux is right at the edge of where literature predicts economic viability
- >50g LMW product recovered
- Future work optimizing energy consumption and volume reduction

1) Z. Sultan et. al.. *ChemSusChem*,, 12 (6), **2019**, 1203

Progress and Outcomes

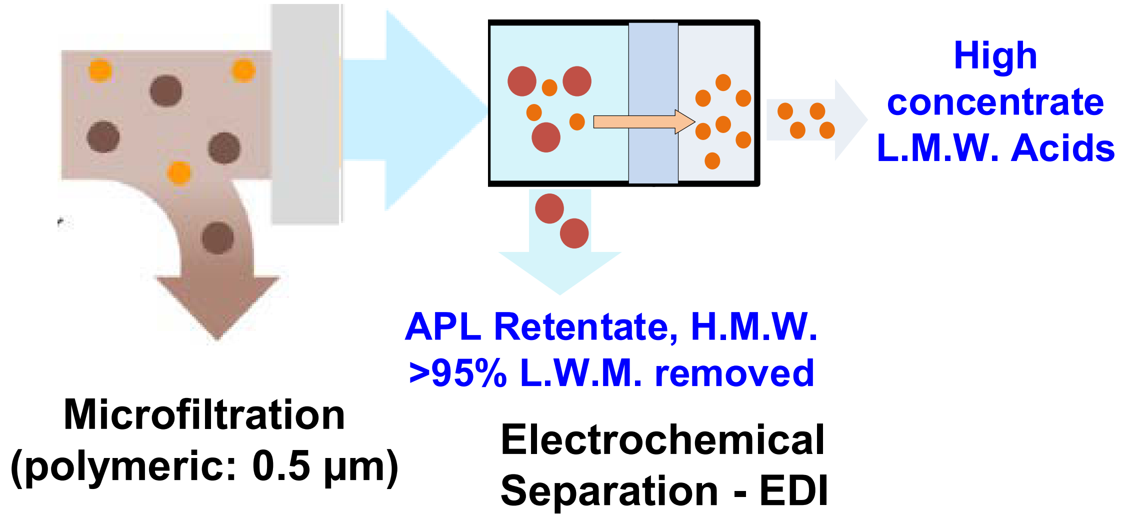




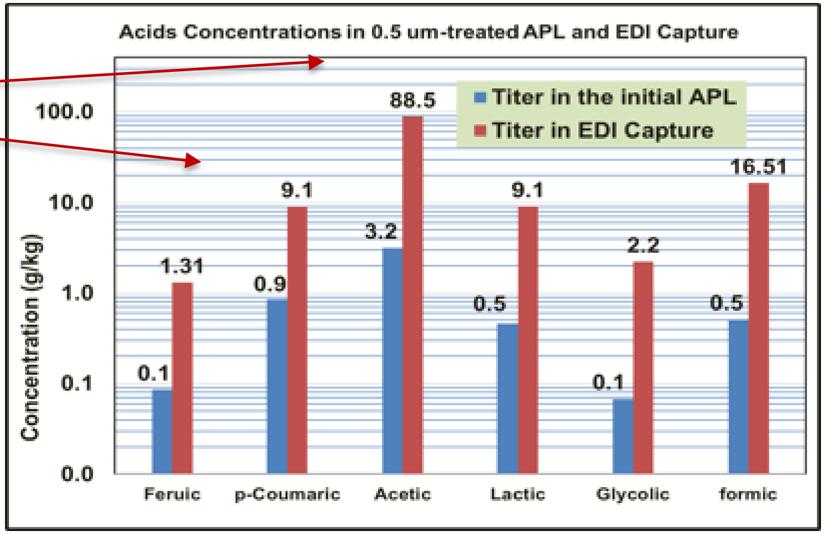
- Enable to capture >98% LMW acids from APL
- One-step capture and concentrate >25 X acids titer from the APL
- High energy efficiency and low processing cost

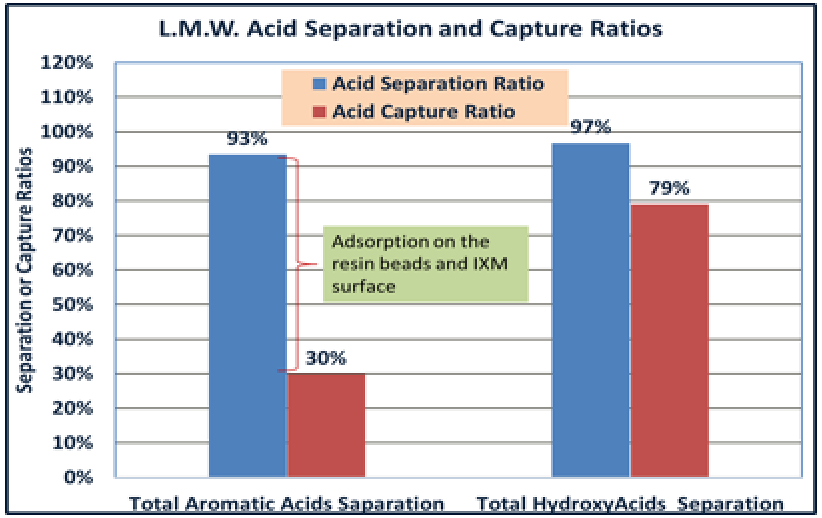
EDI yields and analytics

Stage 1



10-35 X concentrated titers in the capture stream



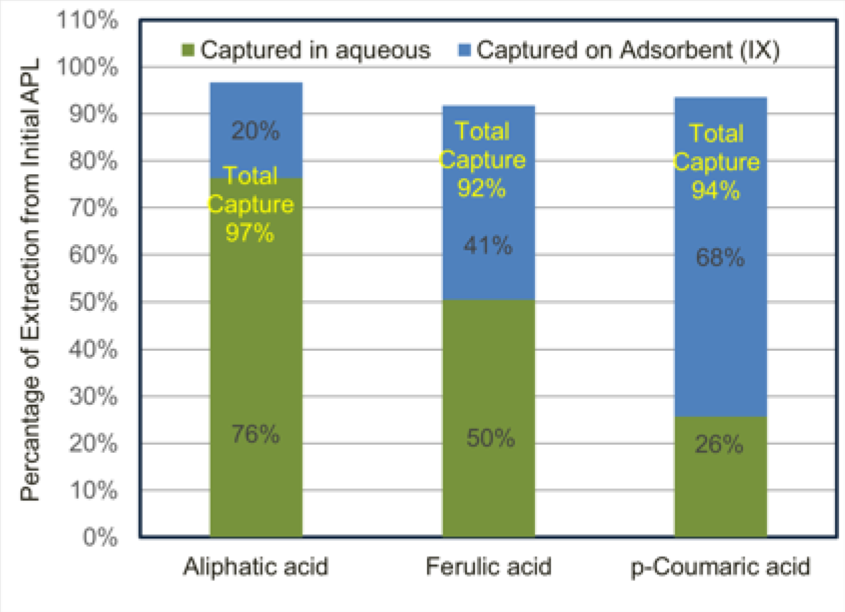


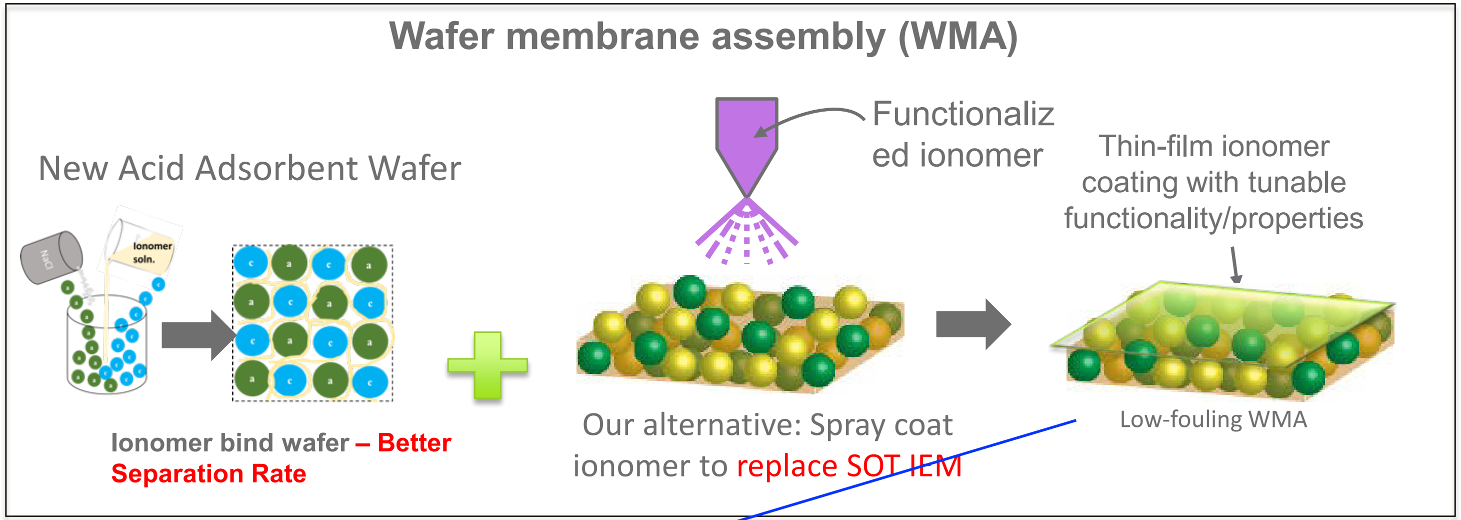
- >93% aromatic acid, >97% hydroxyacid acid and 35% TOC were captured,
- 10-35 X increases of the acid titer in the capture stream
- Reasonable processing cost and energy consumption, ~$0.2/kg dry acid and 15 kWh/ton APL in >95% L.M.W. acid capture

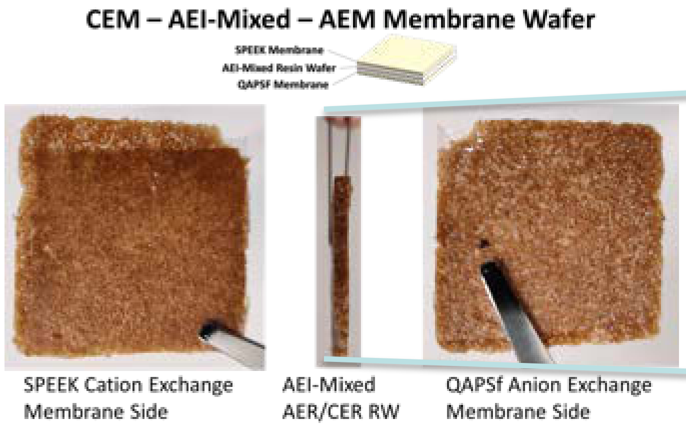
Future work will enhance the extraction of aromatic acid in the capture product stream by material innovation on

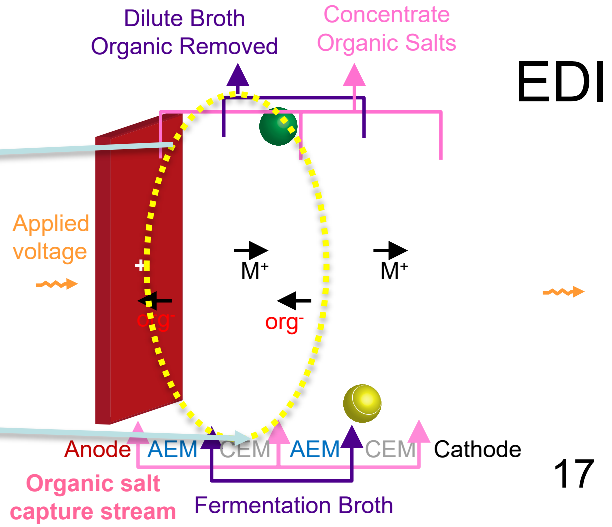
- Integrated assembly of new ion-selective thin film and new acid adsorbent for fast capture and no/or low fouling to extract and concentrate L.M.W. acids.

Enhanced materials



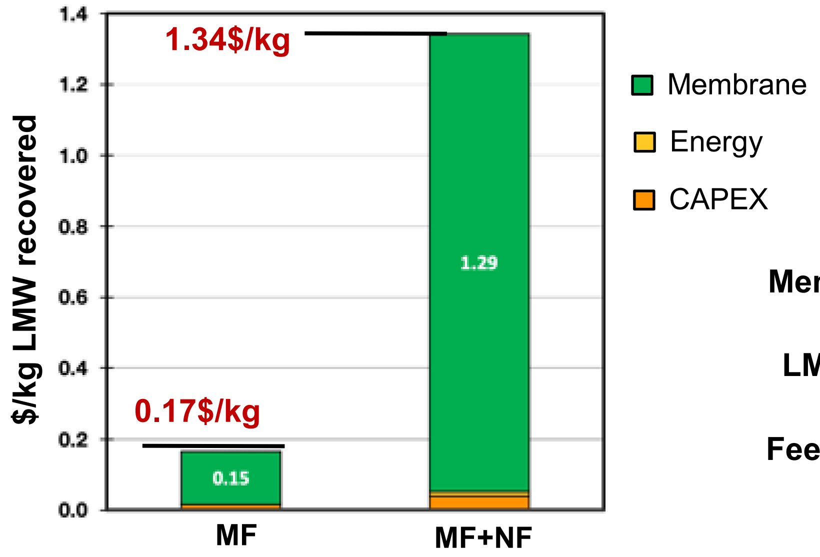


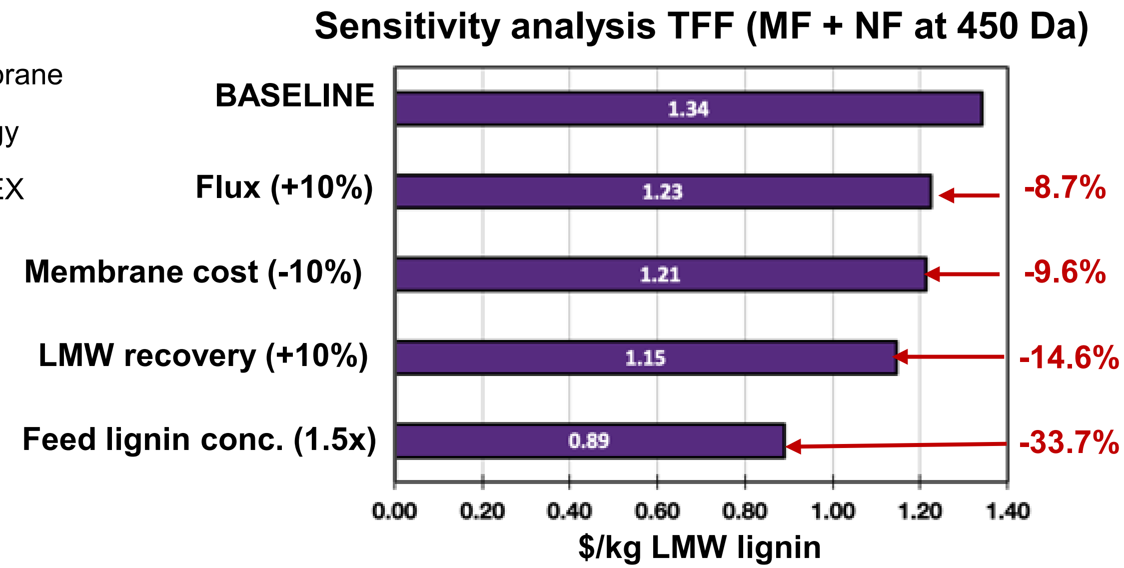


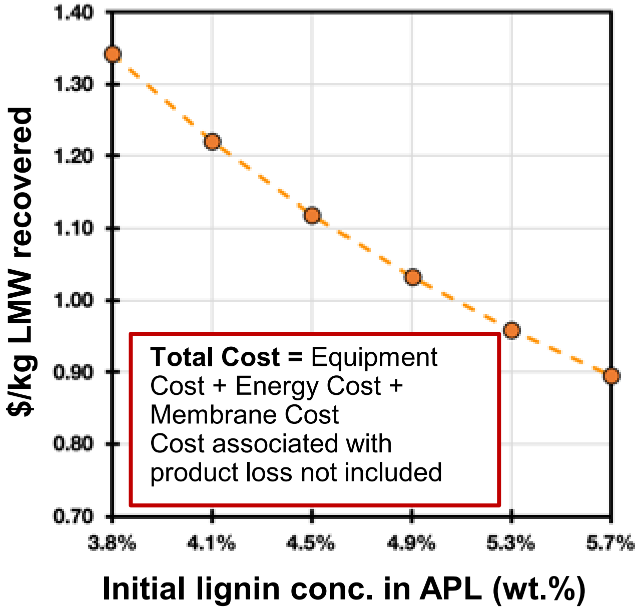


- Only 30% captured aromatic acids was transported into the capture stream, 70% still adsorbed in IX resin
- Wafer membrane assembly - new adsorption material and ion-exchange thin film coating
- Enhance aromatic acid transport rate and better antifouling

TEA (TFF system)



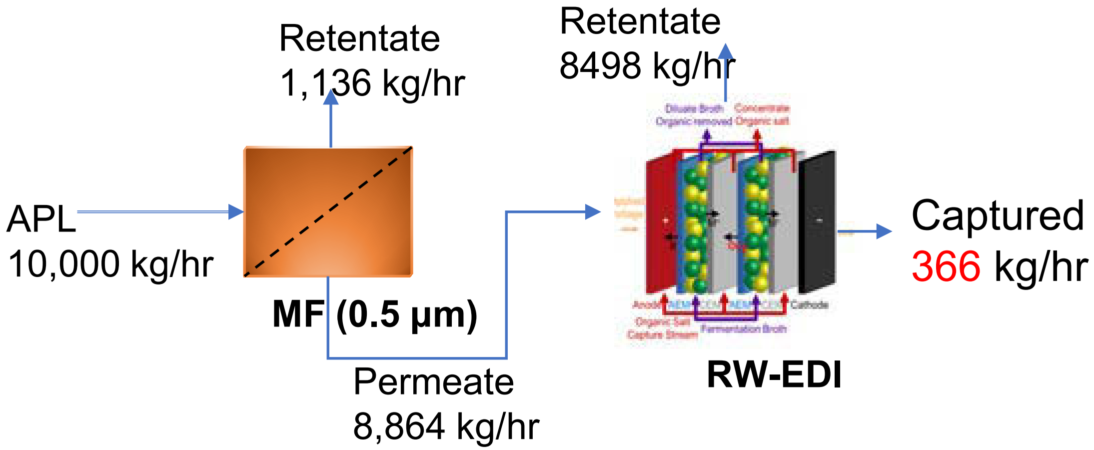




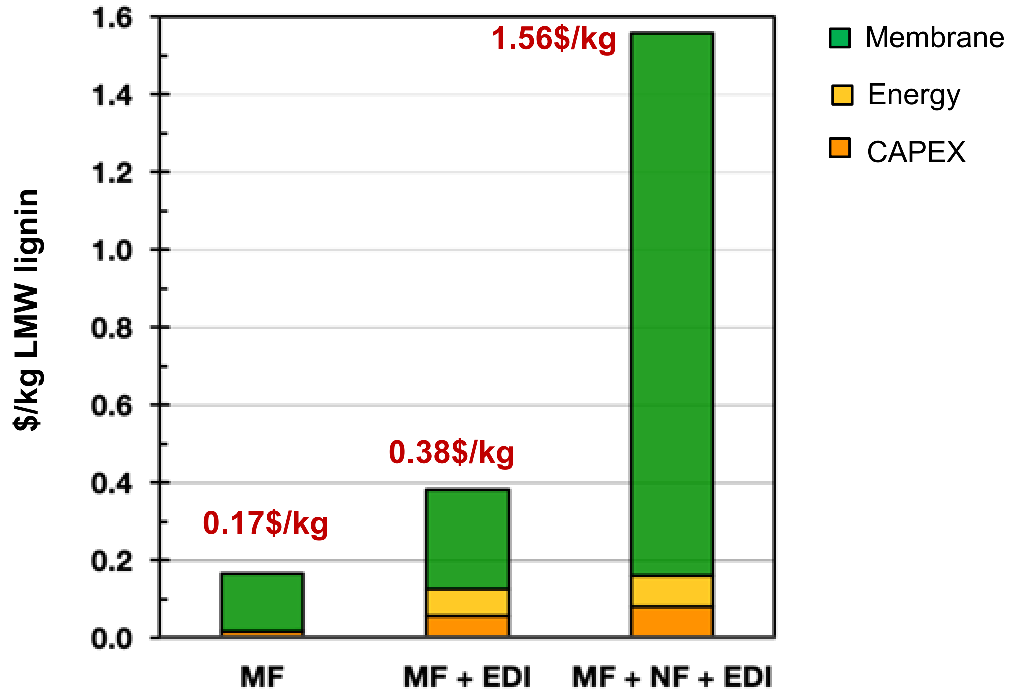
Economic analysis demonstrates sensitivity to APL starting concentration

- More concentrated starting material reduces membrane costs
- If APL is > 4.9 wt.% in starting solution and > 1 LMH/bar throughput is achieved the cost of LMW lignin from APL is < $1 / kg
- APL is currently at 3.8 wt.% at ~10 wt.% solids in pretreatment
- Upstream pretreatment could be run at 18 - 20 wt.%

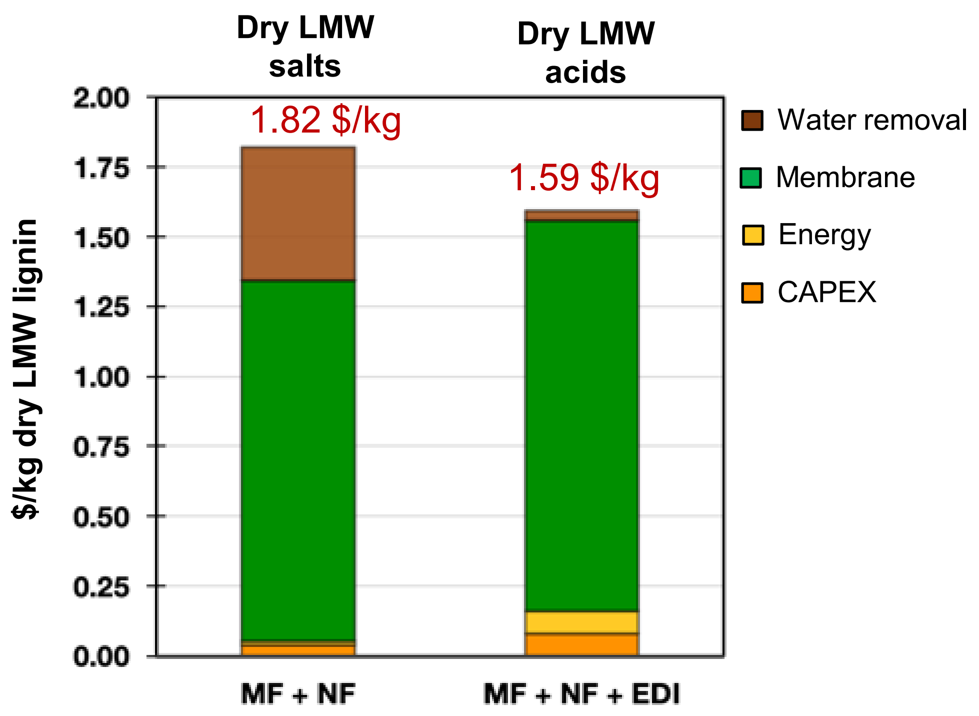
TEA (EDI)



	Microfiltration MF (0.5 µm)	Extraction RW-EDI
Performance		
% HMW Lignin Removed	54.4%	N/A (No HMW)
% Aromatic Monomers & Hydroxyacids Recovery	90.0%	71.1%
Membrane Sizing		
Flux, $L/m^2/hr$	30	9
Membrane Area, m^2	296	985
Membrane Cost Assumptions		
Membrane Cost, $\$/m^2$	500	132
Membrane lifetime, yr	2	1



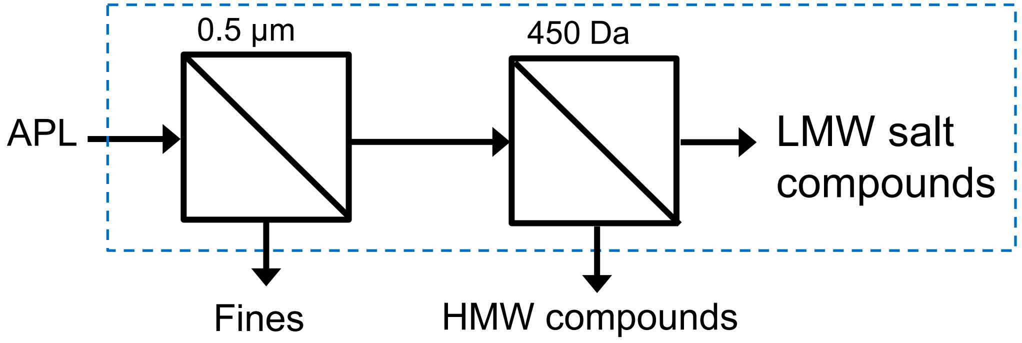
TEA (dried LMW products)



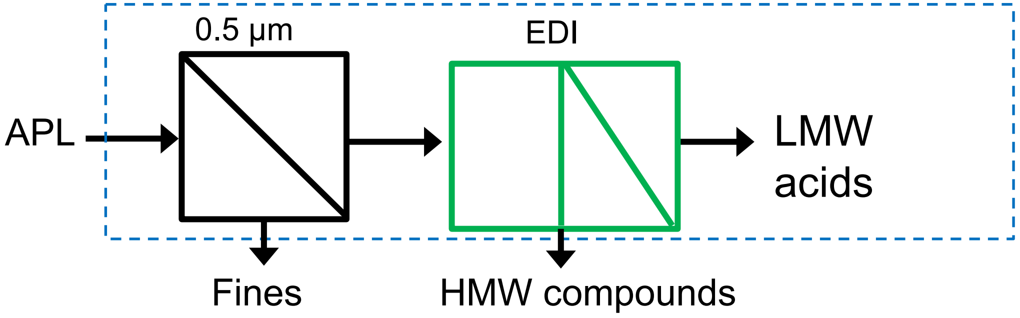
Salt recovery and EDI driven acid recovery

- EDI case exhibits higher capital and energy costs
- Reduce significant downstream process volume and water removal with EDI post-treatment
- TFF only has larger mass flow (~16x)
- TEA for RCD unit is future work

Two-stage membrane cascade



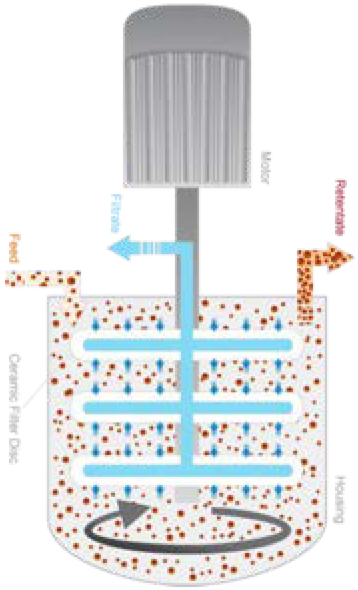
Two-stage EDI cascade for acids



Summary

Key points

1. 2 stage cascade is required for APL filtration to achieve a flux > 1 LMH/bar and costs < 1$/kg MW lignin
2. However, the NF stage is only 0.1 LMH/bar below 1 LMH/bar target
3. Dynamic membranes for the NF is 2 LM/bar and meets flux target. This is an advance over the SOT.
4. APL is too dilute from the pretreatment stream. >5.3 wt.% lignin in stream is needed.
5. >95% of phenolic acids can be recovered with EDI
6. EDI reduces the water removal costs and recycles caustic
7. EDI may enable a cost effective process to capture LMW organic acids by direct capture of L.M.W. acids from crude APL if NF stage is not required.



Future work

1. Mathematical models being developed for energy consumption of RCD compared to TFF
2. These models will be publicly available
3. TEA of RCD is ongoing
4. Deliver more material to BLV
5. TEA for credit of caustic recycle is ongoing
6. Same framework for RCF oil

Publications

Publications

1. Recovery of LMW compounds from APL via nanofiltration – LBNL, NREL (September / October 2021)
2. Energy consumption of rotary disk nanofiltration - NREL (December 2021)
3. Extraction of organic acids from APL using WMA EDI – ANL, LBNL, NREL (October/November 2022)

4. Recovery of LMW compounds from RCF oil via nanofiltration – LBNL, NREL (September 2022)

Patents

1. Rotary ceramic disk methods for nanofiltration of lignin streams (end of FY21) (September 2021)

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Quad Chart Overview - Analysis

Timeline
- 10/1/2020
- 9/30/2023

	FY20	Active Project
DOE Funding	(10/01/2019 – 9/30/2022)	*$1,500,000* *ANL: $450,000* *LBNL: $450,000* *NREL: $600,000*

Project Partners*
- ANL
- LBNL
- NREL

Barriers addressed
Ot-B: Cost of production

Ct-O: Selective separations of organic species

Ct-D: Advanced bioprocess development

Project Goal
Develop filtration and electrochemical technology to recover LMW lignin from lignin derived streams APL, RCF, and catalytic oxidation oils. These technologies must meet the 1 LMH/bar industrial target for flux.

End of Project Milestone
Filtration: Deliver > 50g of purified APL monomers to PABP at recovery yields > 80%. Report the chemical composition, carbon balance, and closure obtained in analysis of this purified stream.

EDI: Demonstrate a prototype PFG device to assist nano-filtration. Feasibility to extend effective operation period of nano-filtration of APL for LMW aromatic acid recovery.

Funding Mechanism
Merit reviewed AOP-based consortium

Separations Consortium

Lignin Rich Stream Fractionation and Purification

Additional Slides

Abbreviations

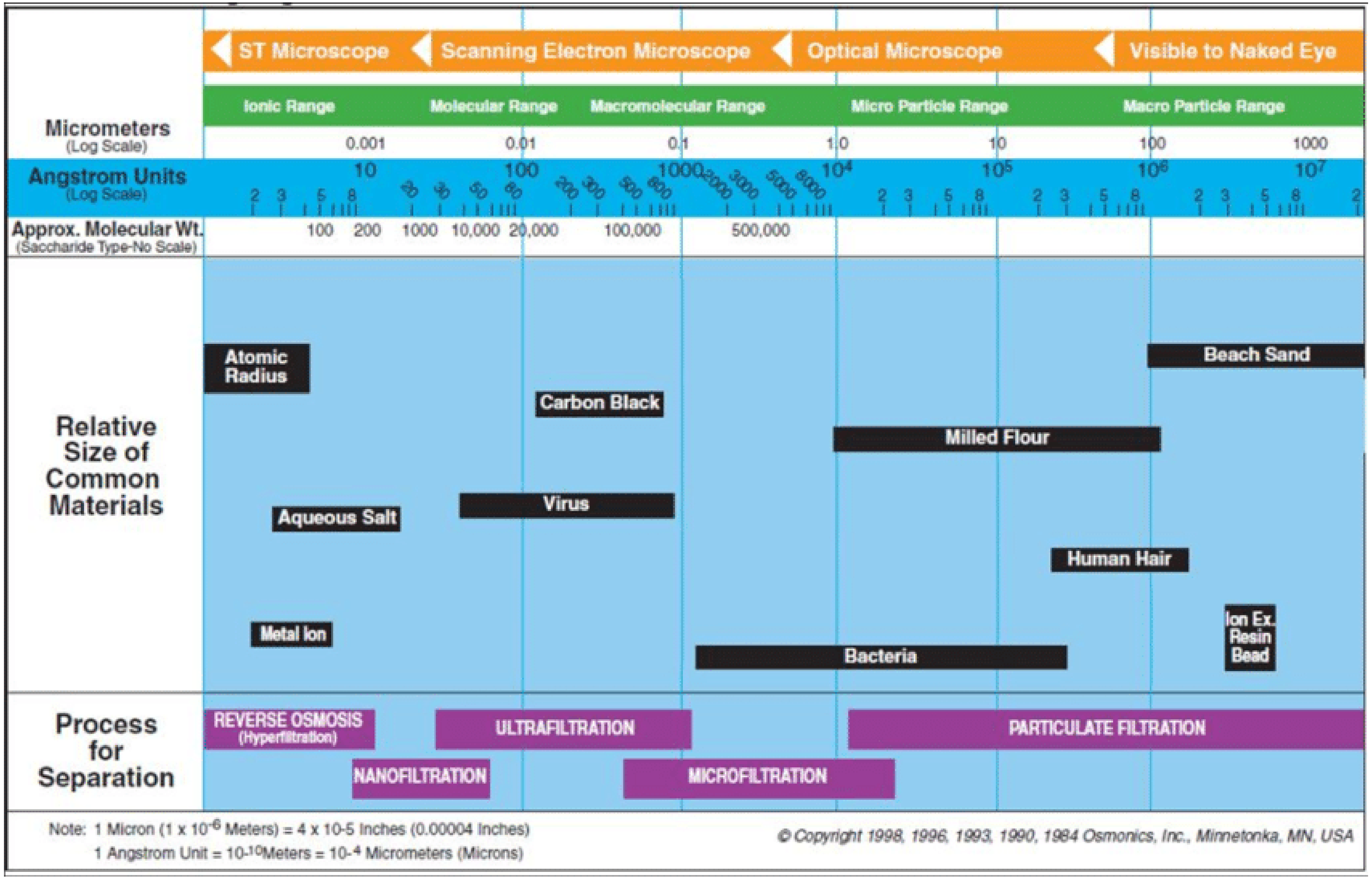
1. APL – Alkaline Pretreatment Liquor
2. BLV – Biological Lignin Valorization
3. DFO – Directed Funding Opportunity
4. EDI – ElectroDeIonization
5. IAB – Industrial Advising Board
6. LMW – Low Molecular Weight
7. MF – Microfiltration
8. NF – Nanofiltration
9. RCD – Rotating Ceramic Disk filter
10. RCF – Reductive Catalytic Fractionation
11. SepCon – Separations Consortium

Dynamic membrane scalability

Very large units available

- Andritz, Spintek, Kerafol, etc.
- Disk overlap increases CIP, flux, and uptime before cleaning needed

Membrane pore size chart



Response to reviewer comments