Highly Efficient Nanofibrous Membranes based on Hierarchical Nanofiber Structure

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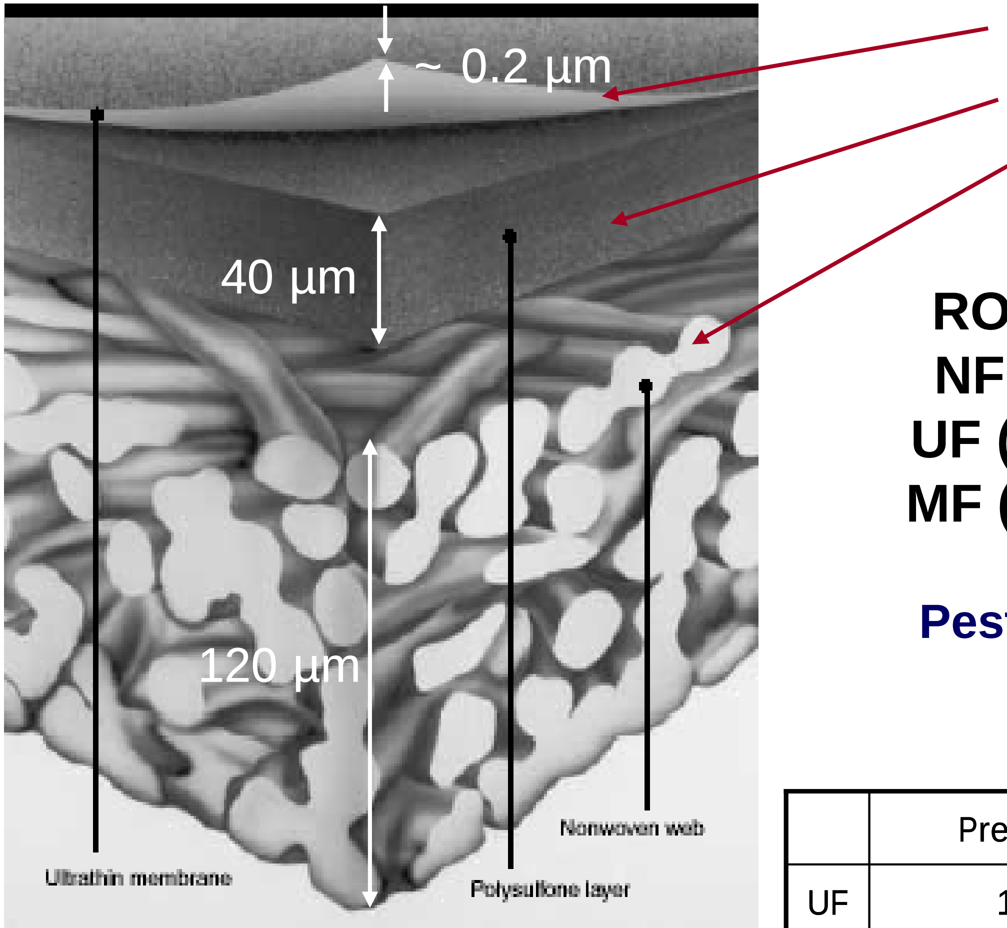
Conventional water filtration membranes (since 70's)

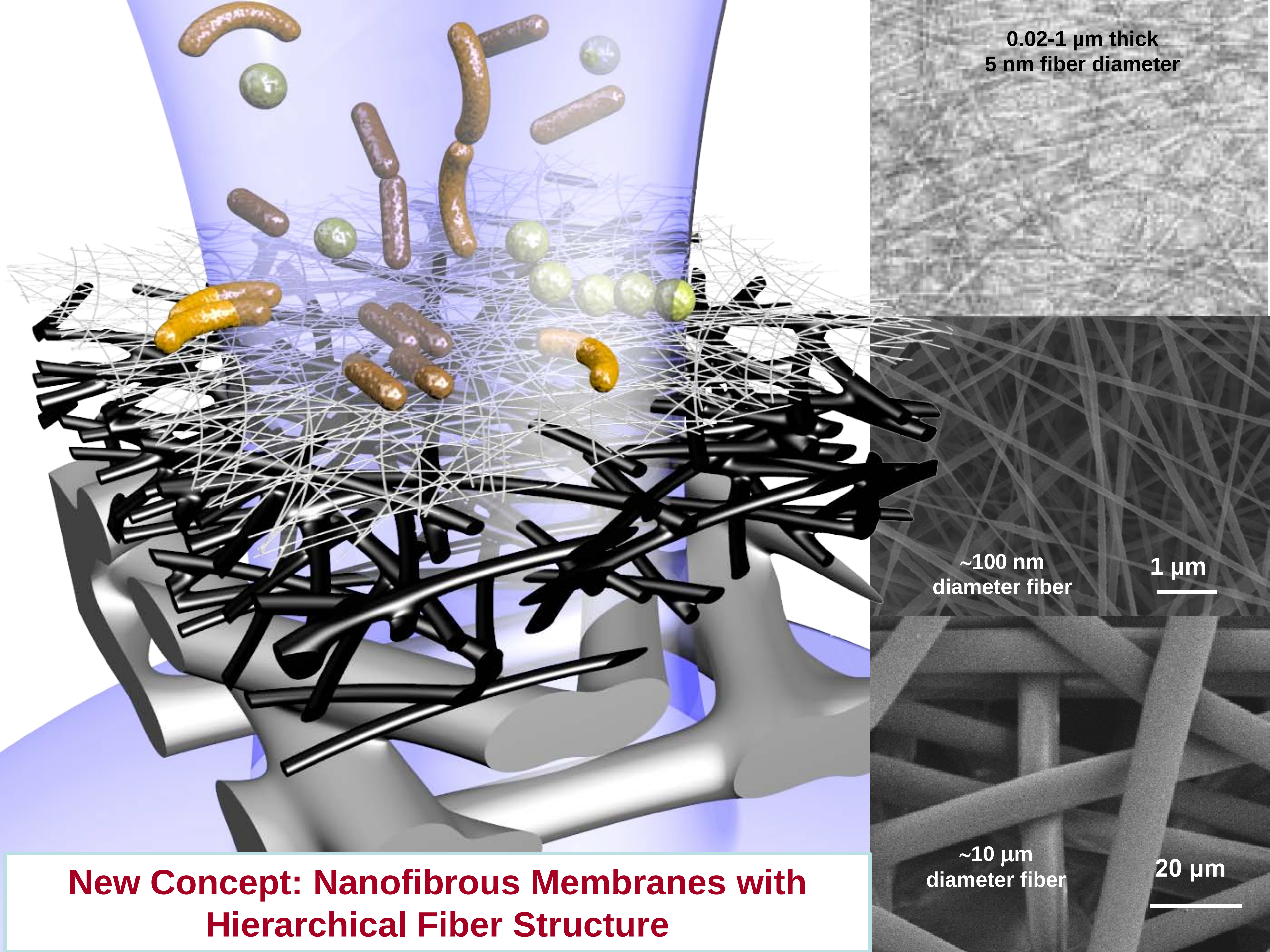


http://www.dow.com

Size exclusion range

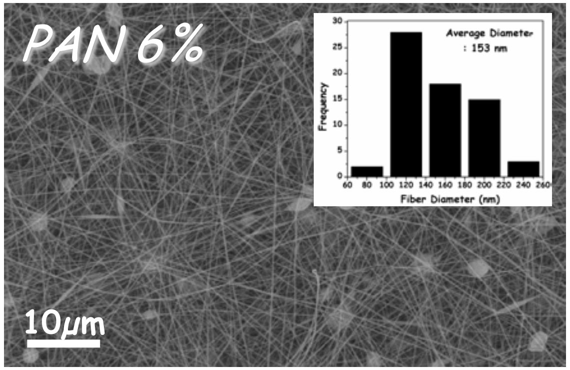
RO (Reverse Osmosis): < 1 nm
NF (Nano-Filtration): 1 – 10 nm
UF (Ultra-Filtration): 10 – 100 nm
MF (Micro-Filtration): 0.1 – 50 µm
Aqueous salts: 0.3 – 1.2 nm
Pesticides, herbicides: 0.7 – 1.2 nm
Virus: 10 – 100 nm
Bacterial: 200 nm – 30 µm

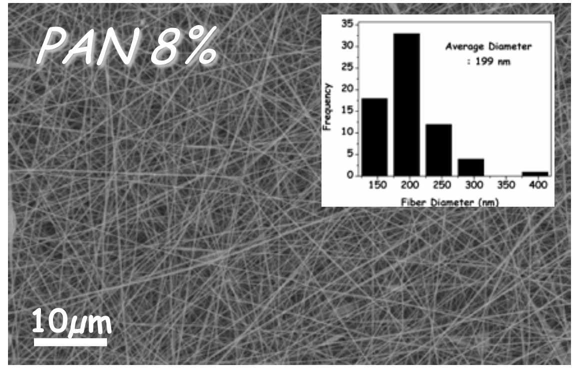
	Pressure (psi)	Flux (l/m²h)
UF	15 – 150	3 – 100 (pure water)
NF	70 - 400	0.22 – 0.66 (e.g. 2000 ppm $MgSO_4$)
RO	70 – 400 (Brackish Water) 600 – 1200 (Seawater)	0.03 – 0.40 (Brackish water : 1000 – 5000 ppm salts; Seawater : 35,000 ppm of salts)

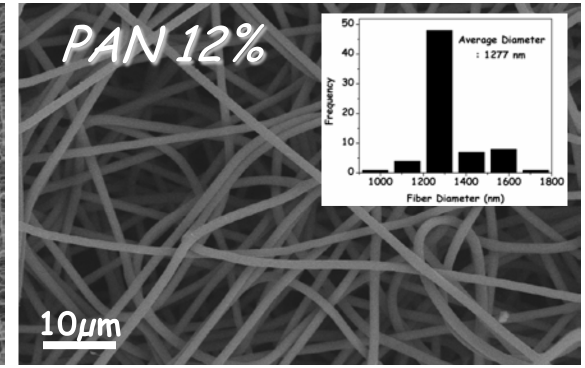


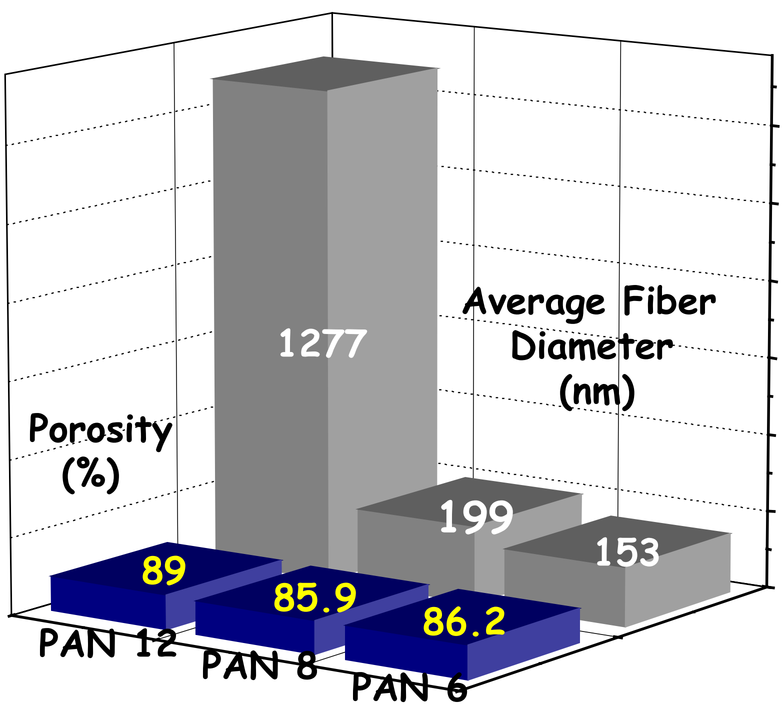
New Concept: Nanofibrous Membranes with Hierarchical Fiber Structure

Fiber diameter has little effect on porosity









- **Electro-spinning Conditions**

  - Flow rate : 20 μl/min
  - Electric Field Strength : 1.0 ~ 2.5 kV/cm

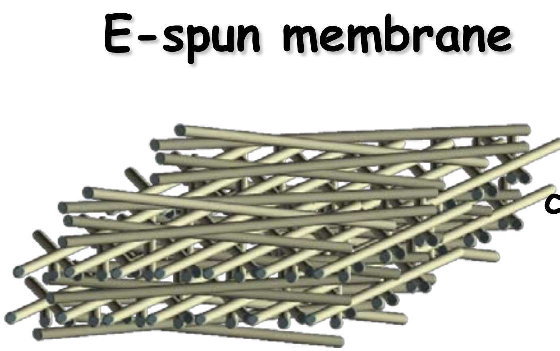
- **Porosity Measurements**

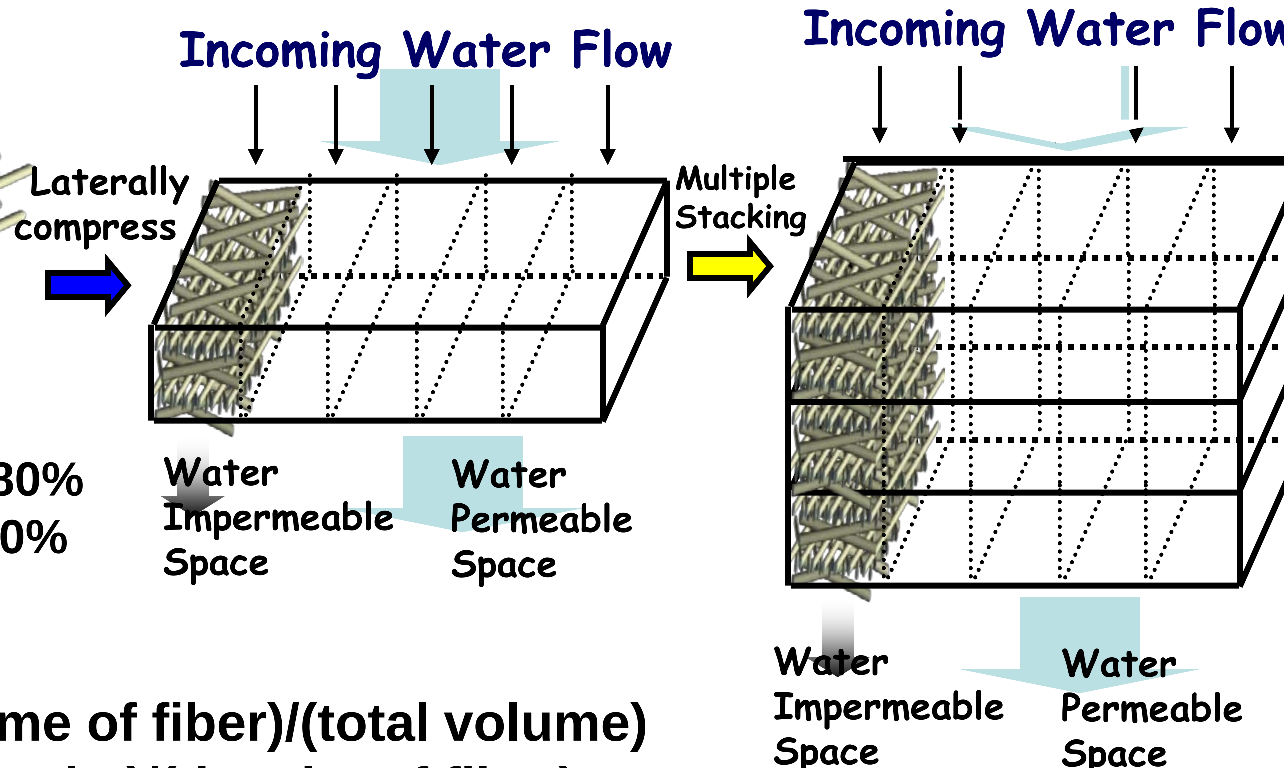
  - Porosity (%) = $(1 - \rho_{es}/\rho_p) \times 100$

  (ρ_{es} : electrospun membrane density
  ρ_p : polymer density)

✓ **porosity change (3%) << fiber diameter change by a factor of > 8**

Thickness of nanofibrous scaffold and porosity





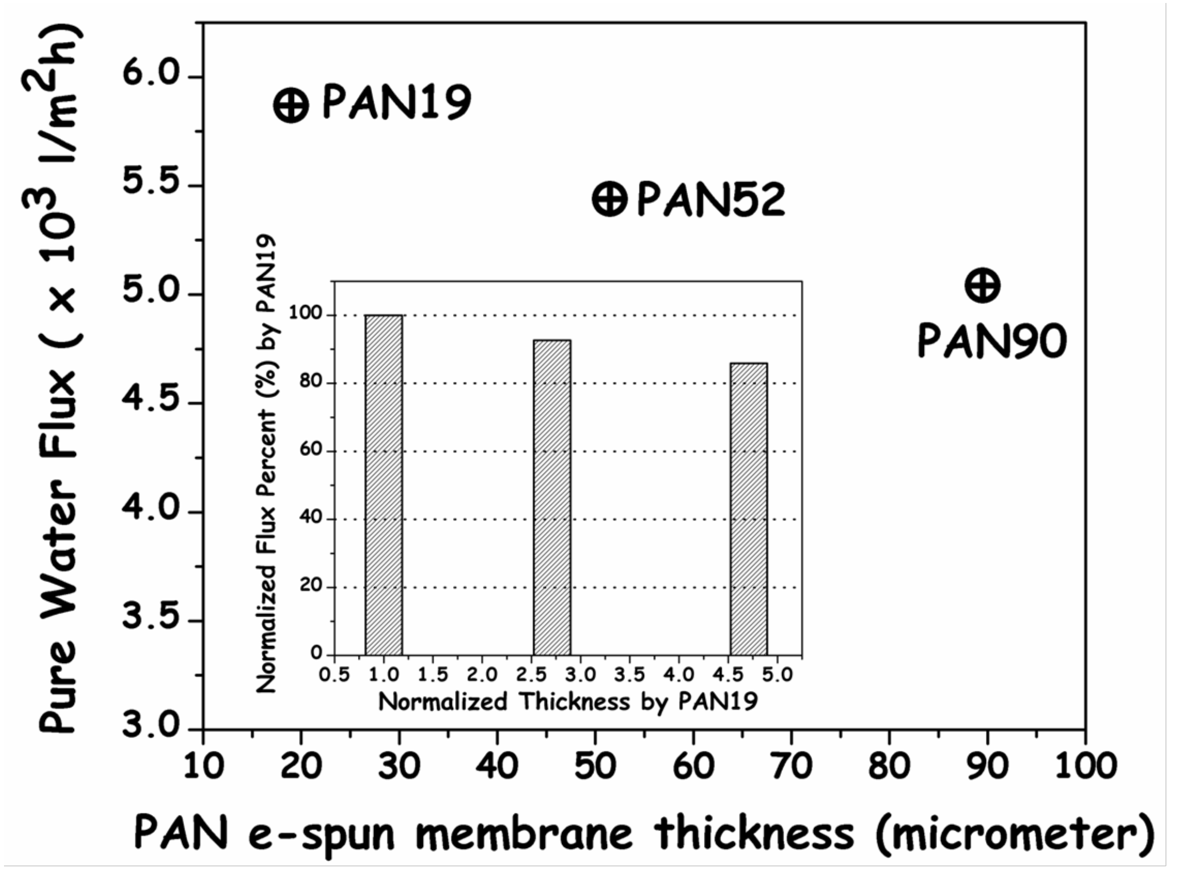
volume fraction (%): ~ 80%
- fibrous materials : ~ 20%

Porosity = 1- (volume of fiber)/(total volume)
= 1 – (mat density)/(density of fiber)

Essentially little effect of fiber diameter on porosity.

Water flows only into empty space
- Minimum flux reduction by thickness increase

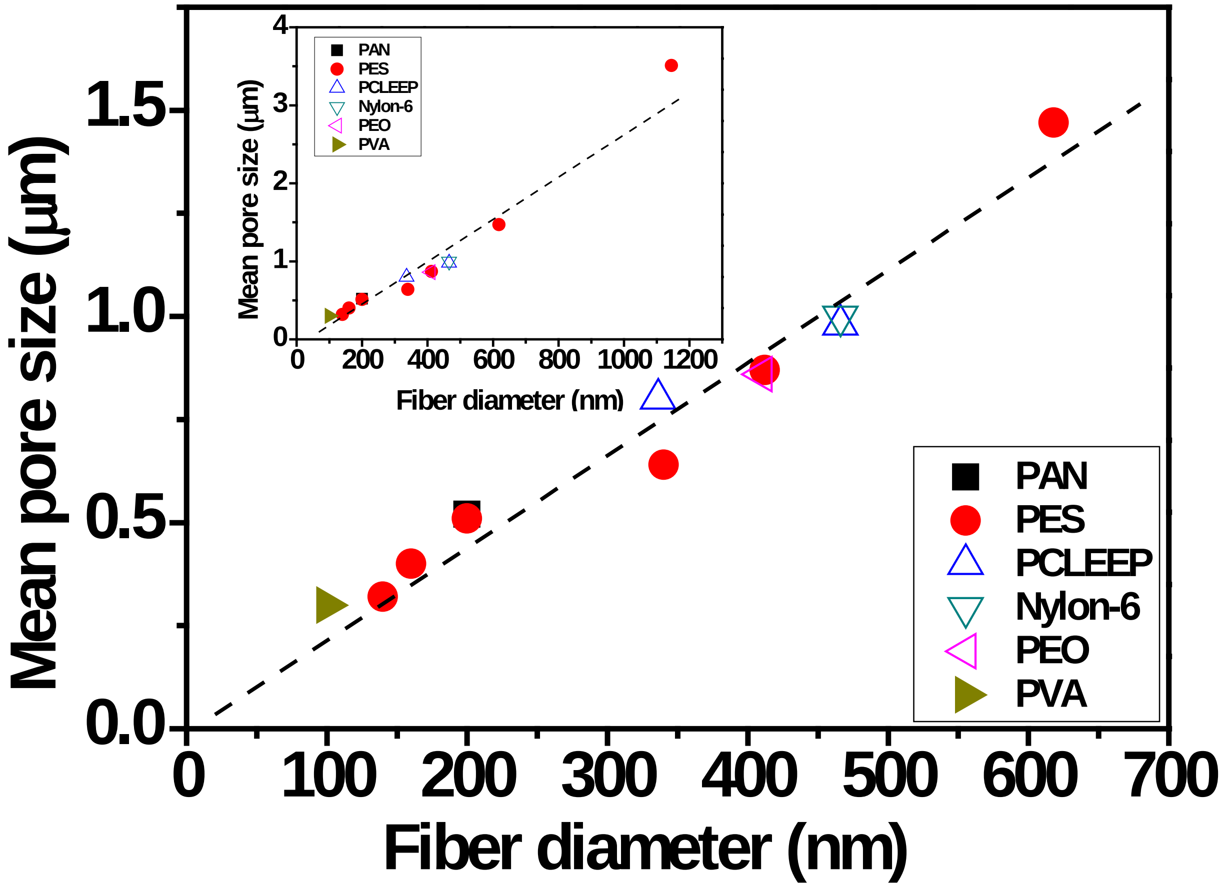
Low hydraulic resistance for nanofibrous support



Condition :
20 psi inlet pressure,
30 ~ 32 °C
Cross-flow

✓ **Low hydraulic resistance :**
Only 14% flux decrease by a factor of 5 in the thickness increase
✓ **Pure water fluxes for PAN e-spun membrane (5~6 x 10^3 l/m^{2}h) is 10 times higher than commercial PAN UF membranes (100 ~ 800 l/m^{2}h)**

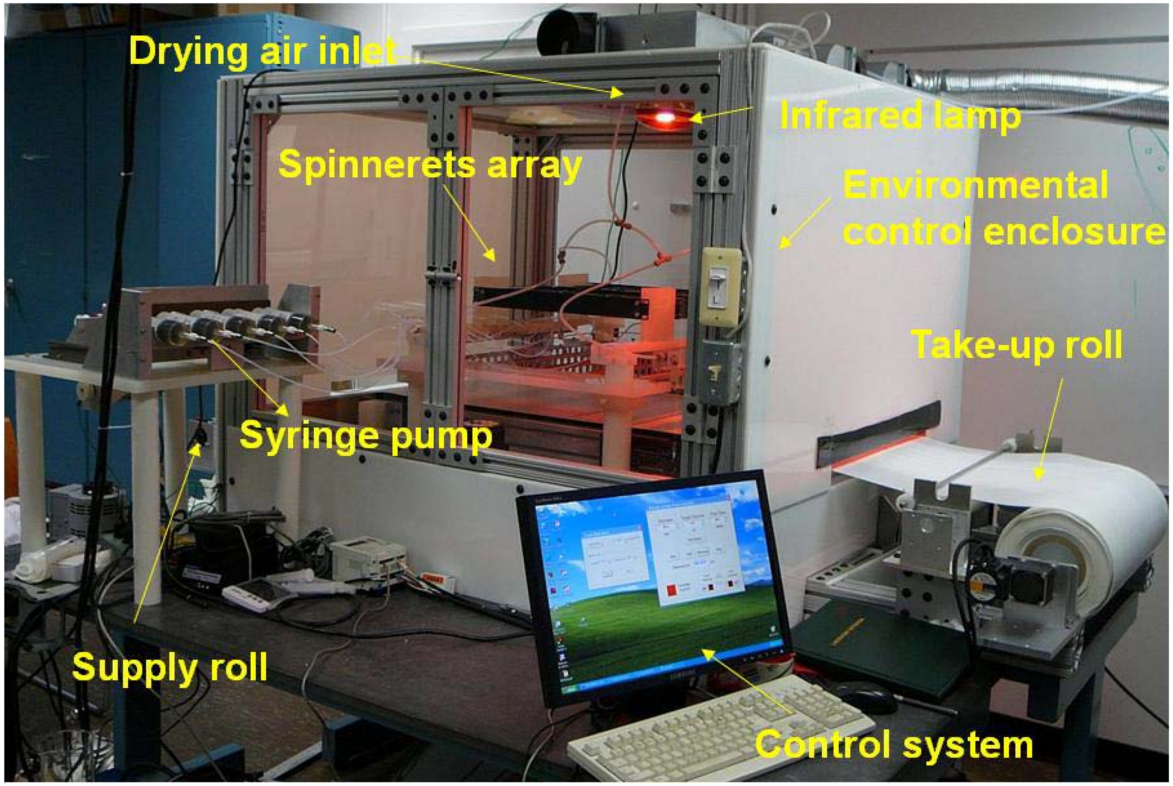
Relationship between pore size and fiber diameter



- ✓ All solid points were obtained from Stonybrook Group, hollow points were from literatures
- ✓ Pore size is about 3 times of the fiber diameter

•Lin K, Chua KN, Christopherson GT, Lim S, Mao, HQ. *Polymer* 2007; 48:6384-6394
•Jin HJ, Fridrikh SV et al. *Biomacromolecules* 2002; 3: 1233-1239
•Ryu YJ, Kim HY et al. *European Polymer Journal 2003;*39: 1883–1889

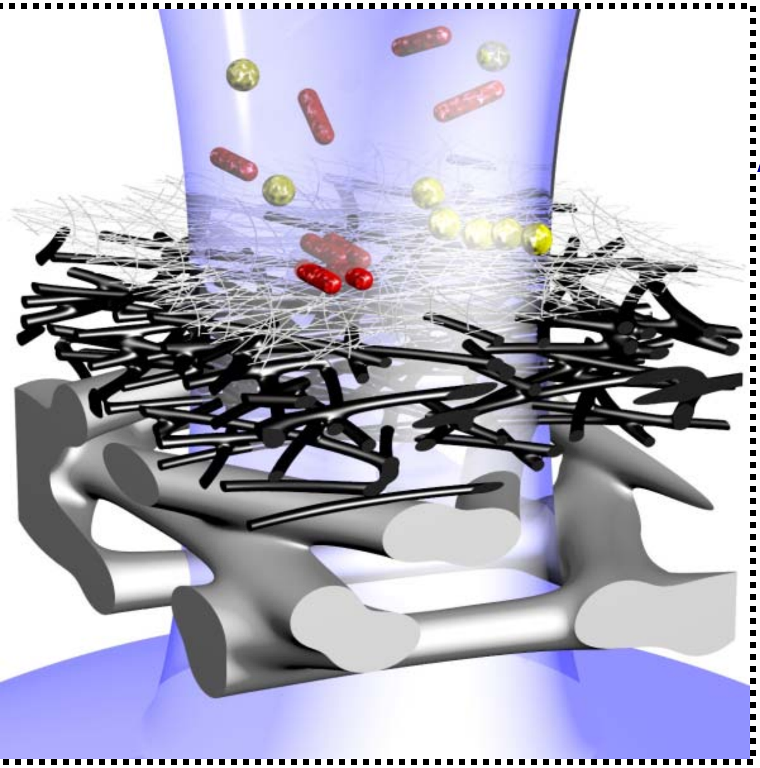
Stony Brook's precision multi-jet electrospinning process to fabricate nanofibrous membranes for liquid filtration



- Instrumentation scalable to large production
- Controlled environmental conditions (e.g. humidity, temperature) to fabricate high quality nanofibrous scaffolds
- Platform scaffolds suitable for MF, UF, NF, RO and FO

Microfiltration to eliminate water borne diseases

Water with bacteria



Water without bacteria

Bacteria sizes of most common water-borne diseases

Dysentery

(0.4-0.6) µm X (1-3) µm

Cholera

(0.5-0.8) µm X (1-3) µm

Typhoid

~3.5 μm^2 longitudinal area of rod x (0.7-1.5) µm

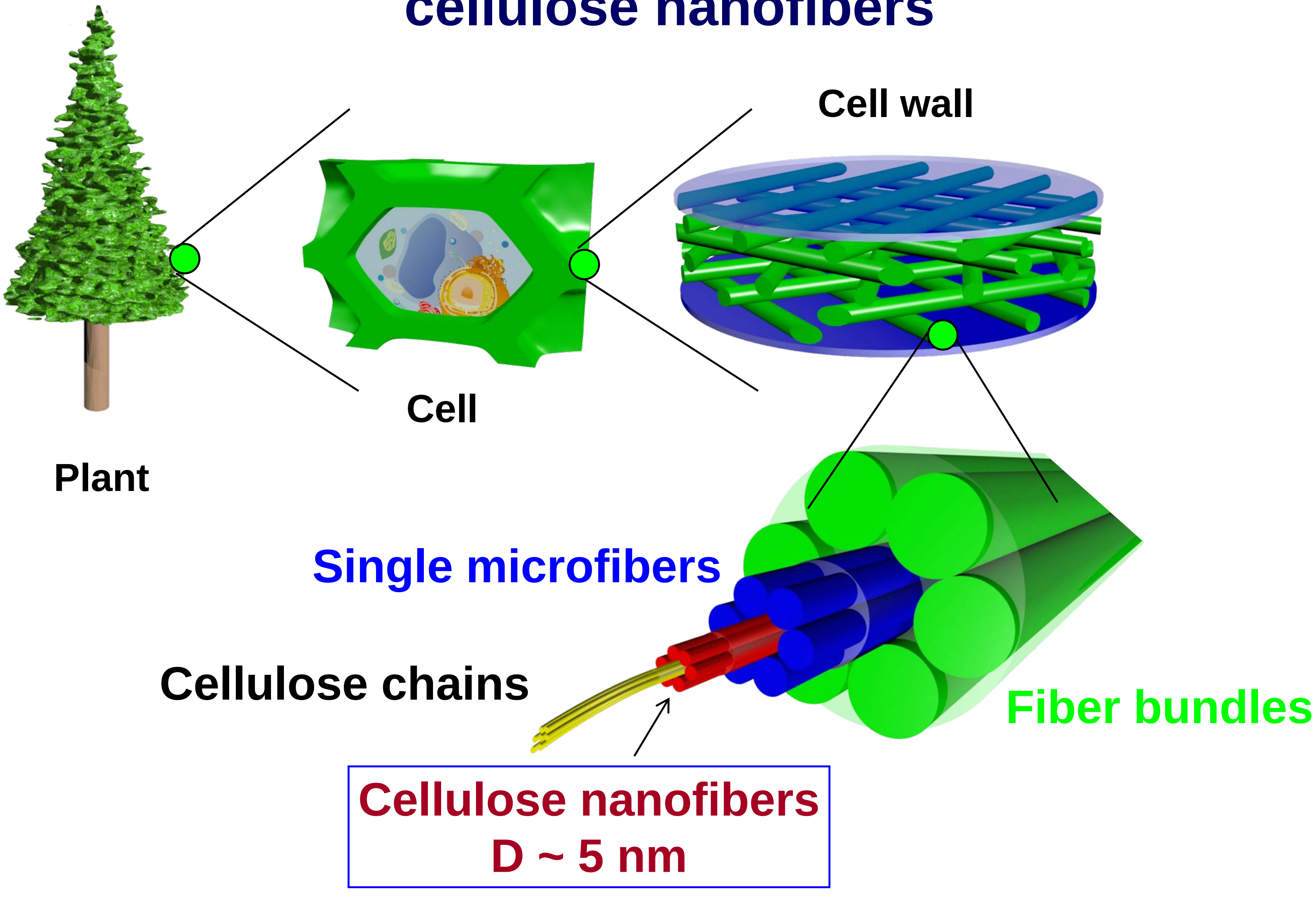
- **Pore size ~ 300 nm; pore volume ~ 85%**
- **Mechanically strong with nano-trusses**

Microfiltration performance

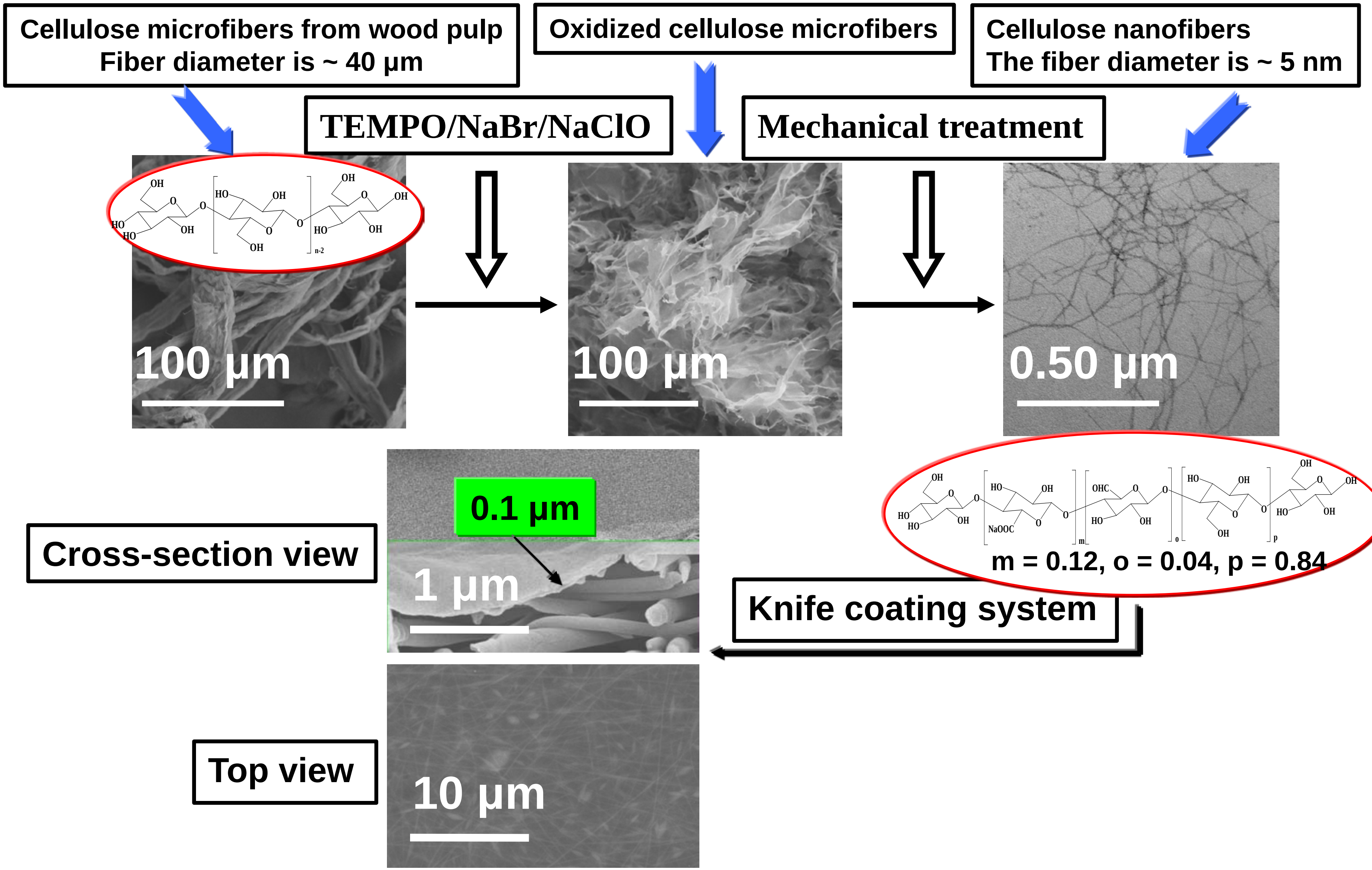
Name	Total thickness (μm)	Ave. flux (1000L/m^2h)	Max. pore size (μm)	Ave. pore size (μm)
E-spun PES/Coffee Filter Paper	130	16.6	2.5	0.8
	140	13.4	1.7	0.6
	155	11.7	1.2	0.4
E-spun PVA/nonwoven PET	**160**	**5.5**	**0.6**	**0.2**
Millipore GS 0.22 μm	**175**	**0.39**	**0.6**	**0.2**
Millipore RA 1.20 μm	145	2.0	4.4	1.5

* All the above test were processed on the dead-end flow system at 2.28 psi by gravity.

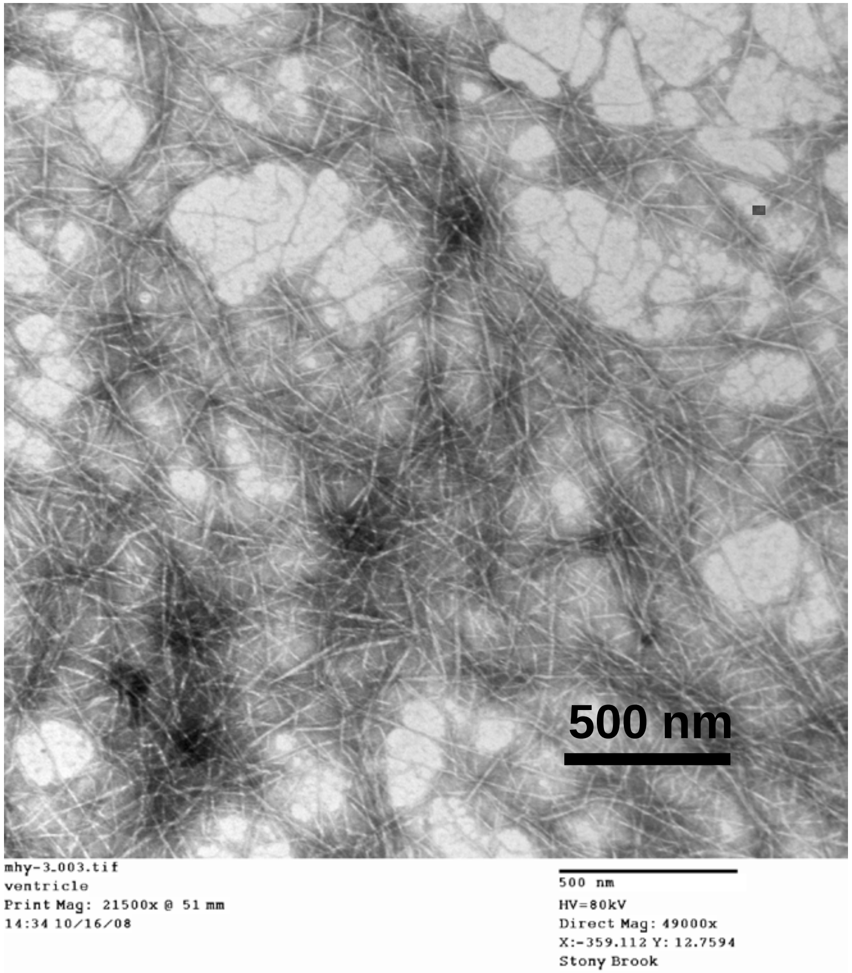
Cost-effective green approach to prepare cellulose nanofibers



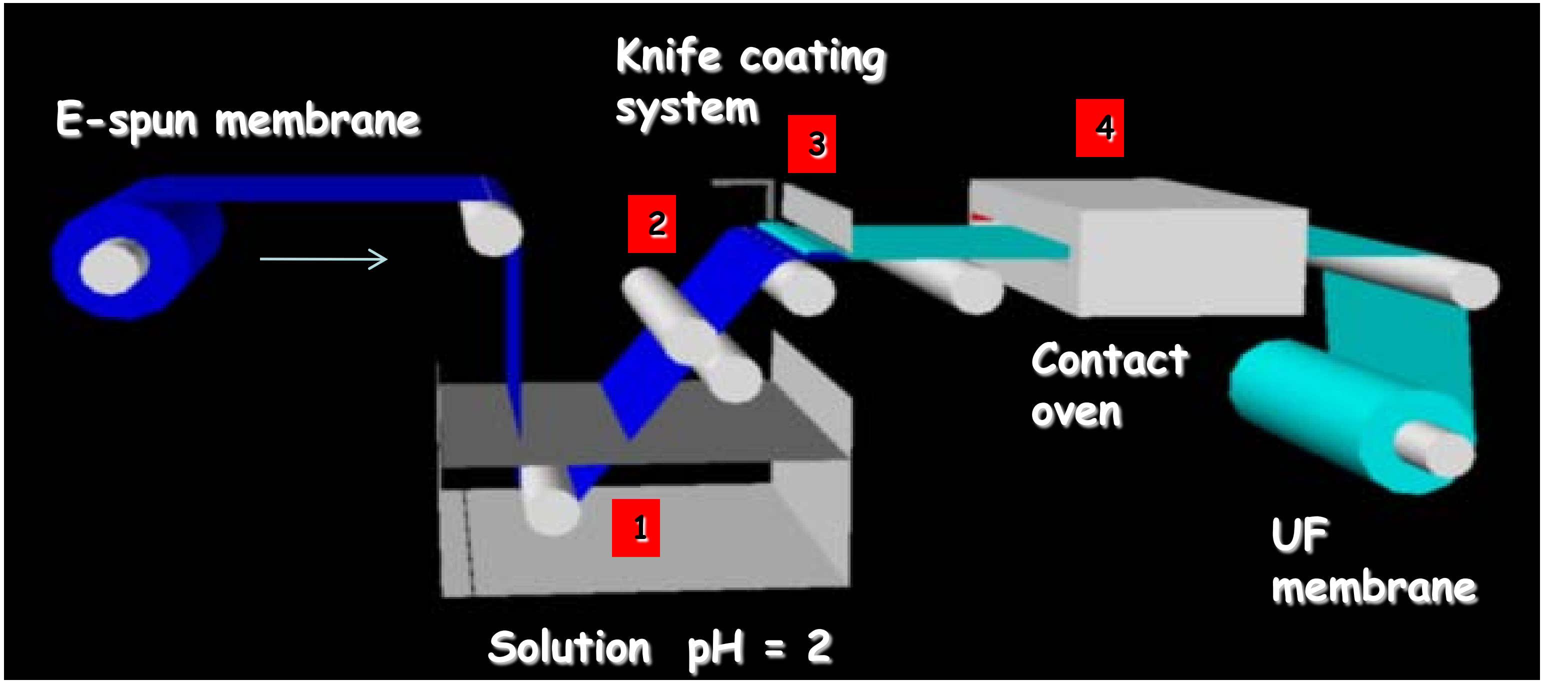
Demonstrated chemical scheme to prepare cellulose nanofiber scaffold (d~ 5nm)



High-Resolution TEM Images of Ultra-Fine Cellulose Nanofiber



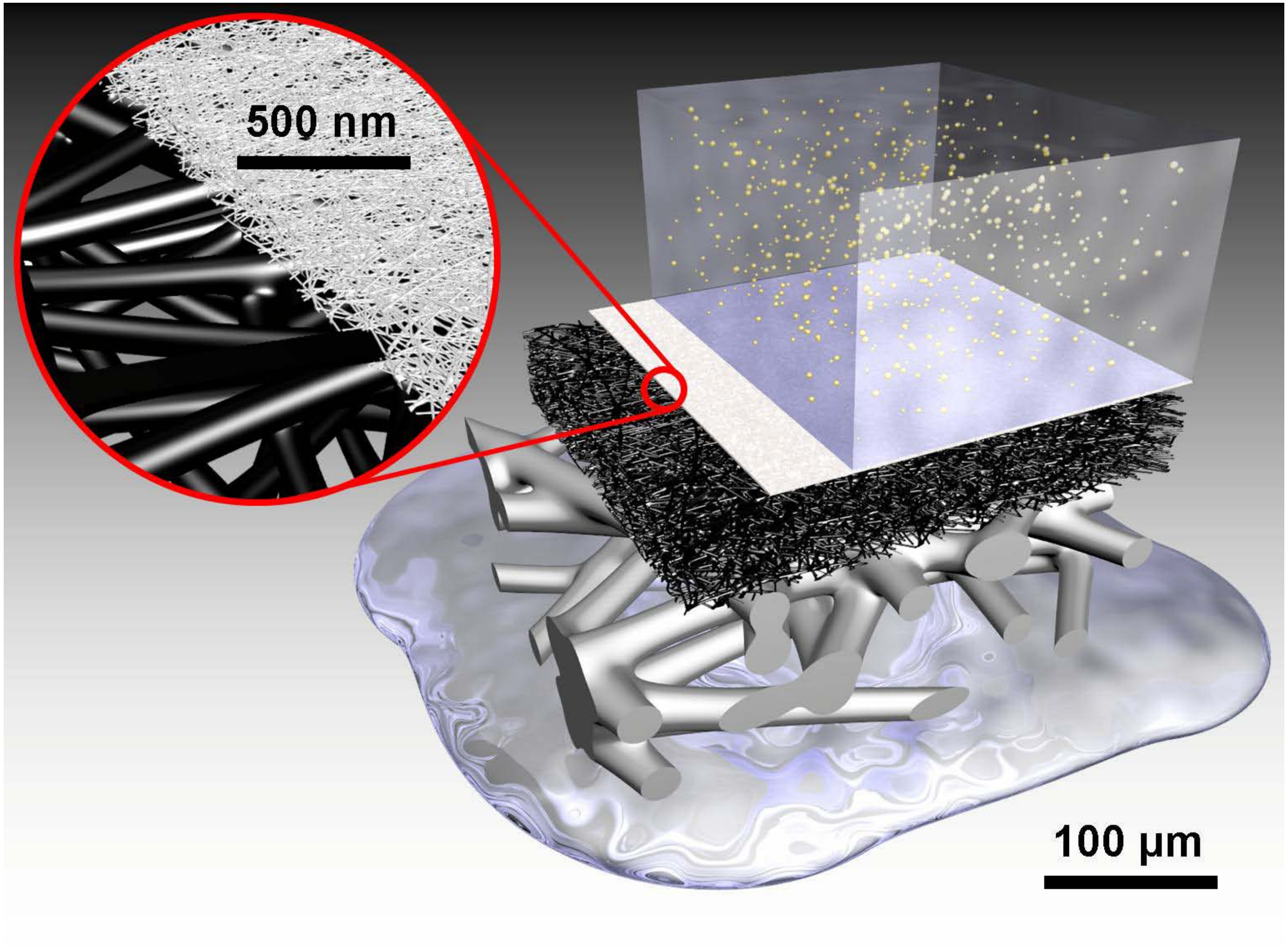
Stony Brook coating process to cast ultra-fine cellulose nanofiber barrier layer



<u>Process :</u>

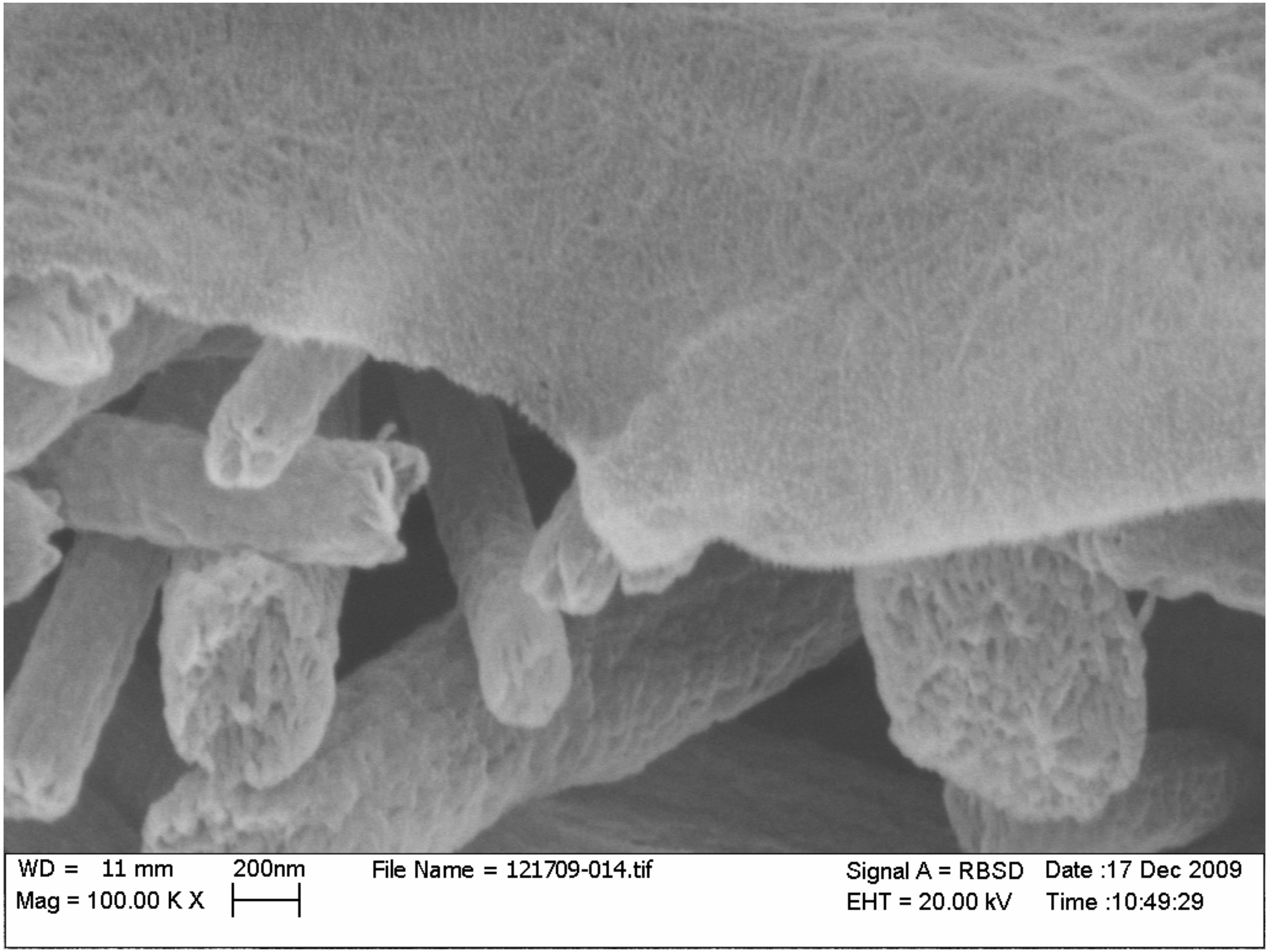
1. Soak nanofibrous scaffold in HCl solution (pH = 2)
2. Drain out excess solution
3. Cast cellulose nanofiber solution (0.05-0.10 wt%) with knife coating system
4. Dry in 100 ^oC contact oven

High-Flux Nanofibrous Membranes for UF Applications

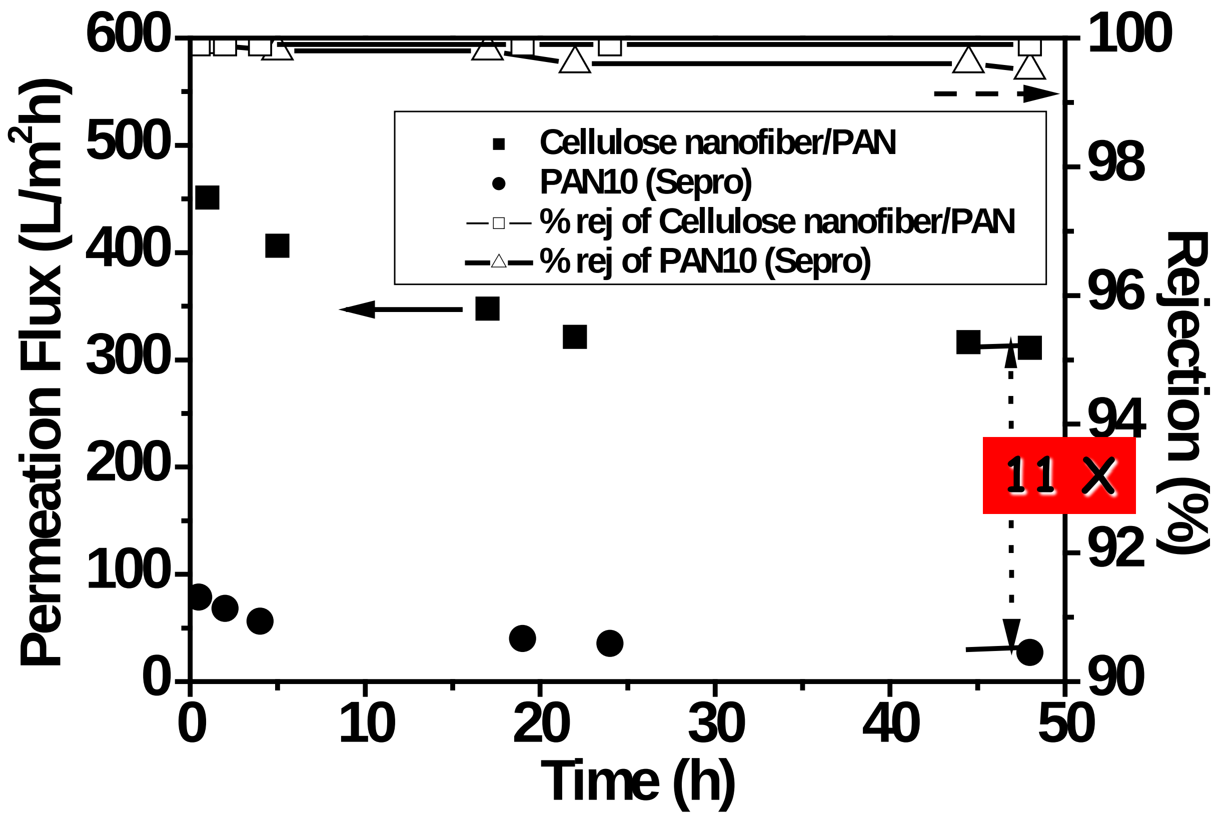


High Resolution SEM Image of Cellulose Nanofiber Barrier Layer

Mean pore size about 20 nm



UF performance of cellulose-based TFNC membrane for oil and water separation



Filtration conditions

- **Feed solution: soybean oil -1350 ppm, DC 193 surfactant – 150 ppm**
- **Cross-flow mode at 30 psi, filter area : 65.15 cm^2, temperature ~ 35 ˚C**
- **The thickness of barrier layer: ~ 0.1 μm**

Advantages of high-flux TFNC membranes

What a substantial increase in efficiency will do?

- **High flux membrane is analog to faster CPU**
- **TFNC membrane can be a platform technology to MF, UF, NF, and RO**
- **Enabling new system design with small foot print, less component and less energy consumption**
  - **Much more cost effective**
  - **Low pressure systems**
  - **Manual operation**
- **Broad range of other applications, including (osmotic) energy generation**

Nanofibrous Membranes for Ethanol-Water Separation via Pervaporation Method

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Benjamin Chu, SBU
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Objectives:

- A unique class of high-flux nanofibrous membrane has been demonstrated for water purification
- The new membrane format will be tested for energy efficient pervaporation of separating ethanol and water

Introduction: Ethanol consumption is growing

Reason

~ 10 wt. % of ethanol in petro; present engine structure does not need to be modified. ⇨ Ethanol consumption grows every year.

Currently

Compare 2002 with 2009, ethanol consumption growth is up to 440%

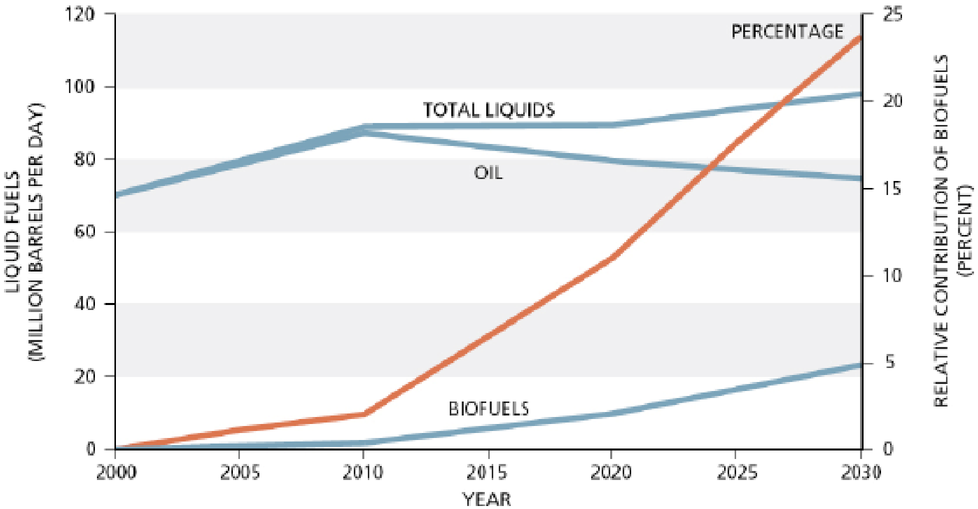
Year	Ethanol Consumption (Billion Gallon)	Production (Billion Gallon)
2002	2.0	2.1
2003	2.8	2.8
2005	3.9	4.0
2007	6.9	6.5
2008	9.6	9.3
2009	10.8	10.7

US Energy Information Administration (EIA),2010

Future

For US, 1/3 oil displacement by 2025

By 2012, US ethanol production is estimated at 15.2 billion gallons per year



National Petroleum Council, July 2007.

Approach:
Energy Saving Refined Process

Center for BioEnergy Research and Development

CBERD

A Multi-University/Industry Initiative Spanning North America

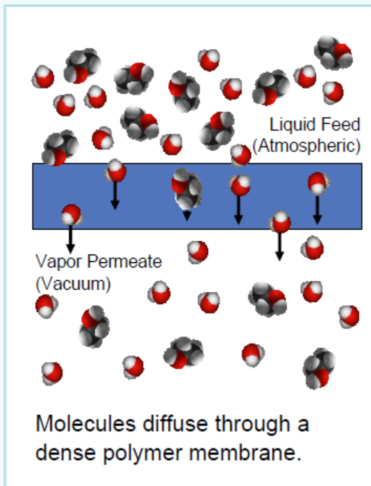
- Bio-ethanol as fuel level should be dehydrated.
- Refined process is needed due to azeotrop in water-ethanol mixture.

Components	Boiling Point (°C)	Azeotrope B.P (°C)	Composition of Azeotrope (wt%)
Water	100.0	78.15	4.4
Ethanol	78.3		95.6

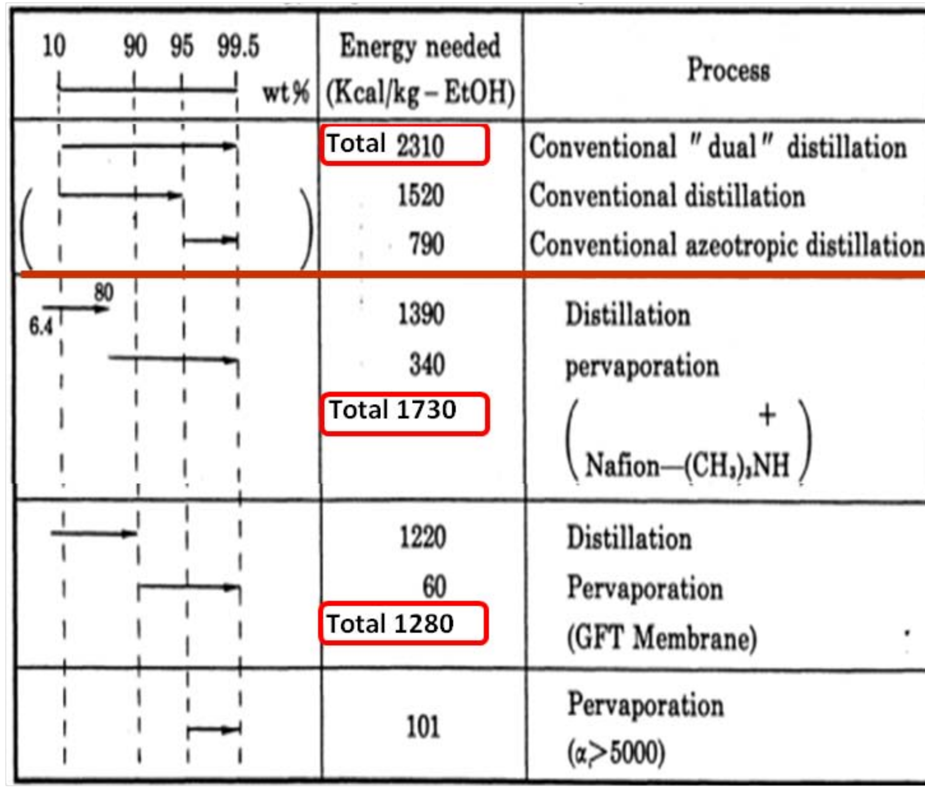
Distillation

- Higher energy waste in production
- Exhaust emission problem

Pervaporation



- Lower energy waste
- Clean process, no emission problem



10 90 95 99.5 wt%	Energy needed (Kcal/kg – EtOH)	Process
	Total 2310	Conventional "dual" distillation
	1520	Conventional distillation
	790	Conventional azeotropic distillation
6.4 → 80	1390	Distillation
	340	pervaporation
	Total 1730	(Nafion—$(CH_3)_3NH^+$)
	1220	Distillation
	60	Pervaporation
	Total 1280	(GFT Membrane)
	101	Pervaporation ($\alpha > 5000$)

K.R. ,Lee, J.Y. Lai, "Pervaporation", .J. of the Chinese Institute of Chemical Engineers,1998

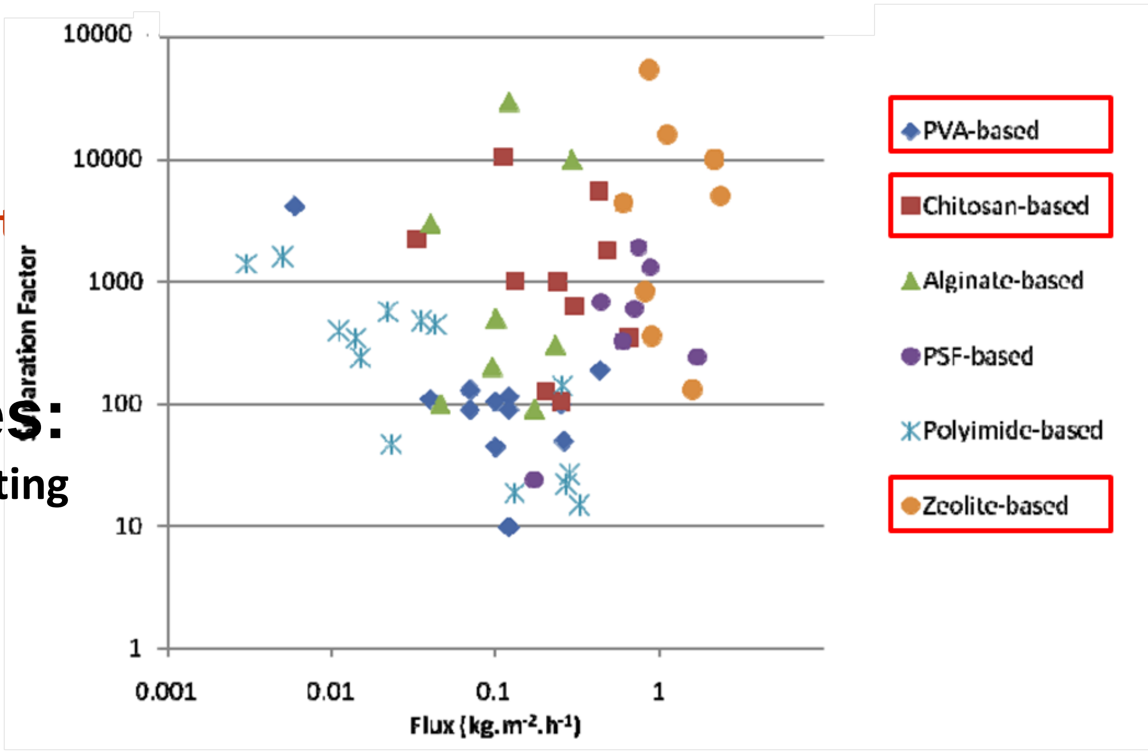
State-of-the-art of Membranes for Pervaporation

Polymeric Membranes

- Lower cost
- Simpler processing
- Good mechanical stability
- Lower selectivity and permeat flux

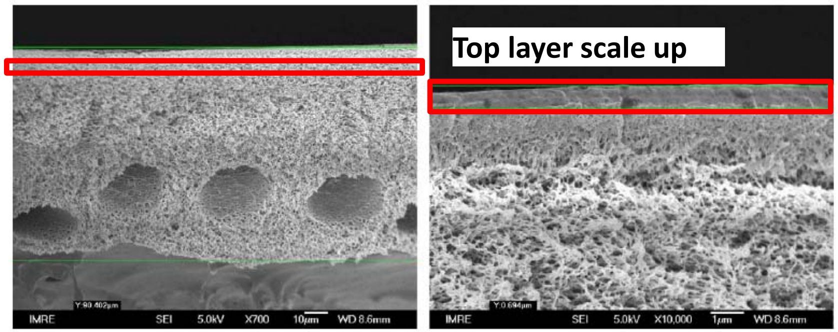
Inorganic Membranes:

- Higher selectivity and permeating flux
- Good thermal and chemical stability
- Higher cost
- Difficult to process for large scale plants



P.D. Chapman , J. Membr. Sci., vol. 218, pp. 5-37, 2008.

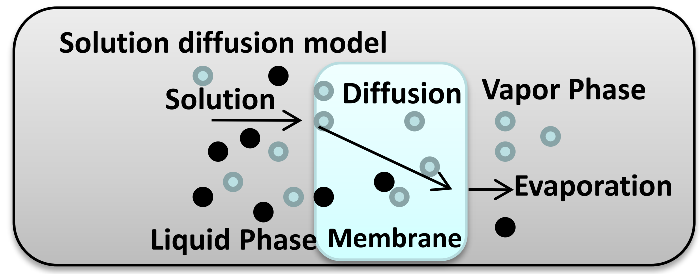
Current Status of Pervaporation Membranes

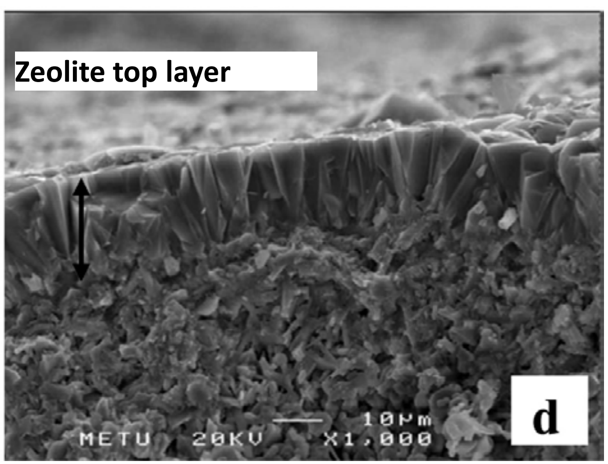


X. Qiao, J. Membr. Sci., 2005

PVA based mixed matrix membranes

- Solution diffusion type membrane
- Based on hydrophilic poly vinyl alcohol (PVA)
- (PVA) selective layer on polyacrylonitrile (PAN) porous membrane and non-woven fabric
- Annealed/cross-linked structure

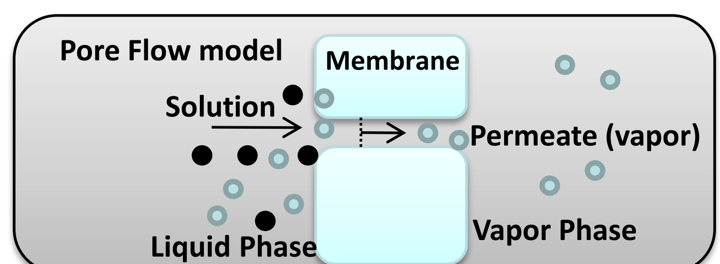




B. Soydas, Middle East Technical Univ., Ankara, Turkey, 2009

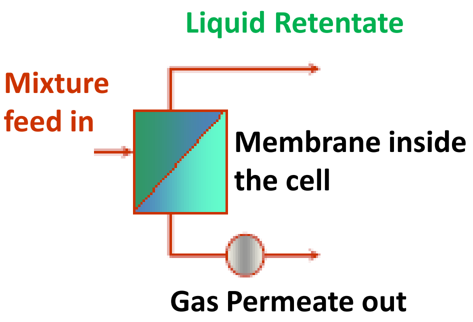
Type A zeolite membrane

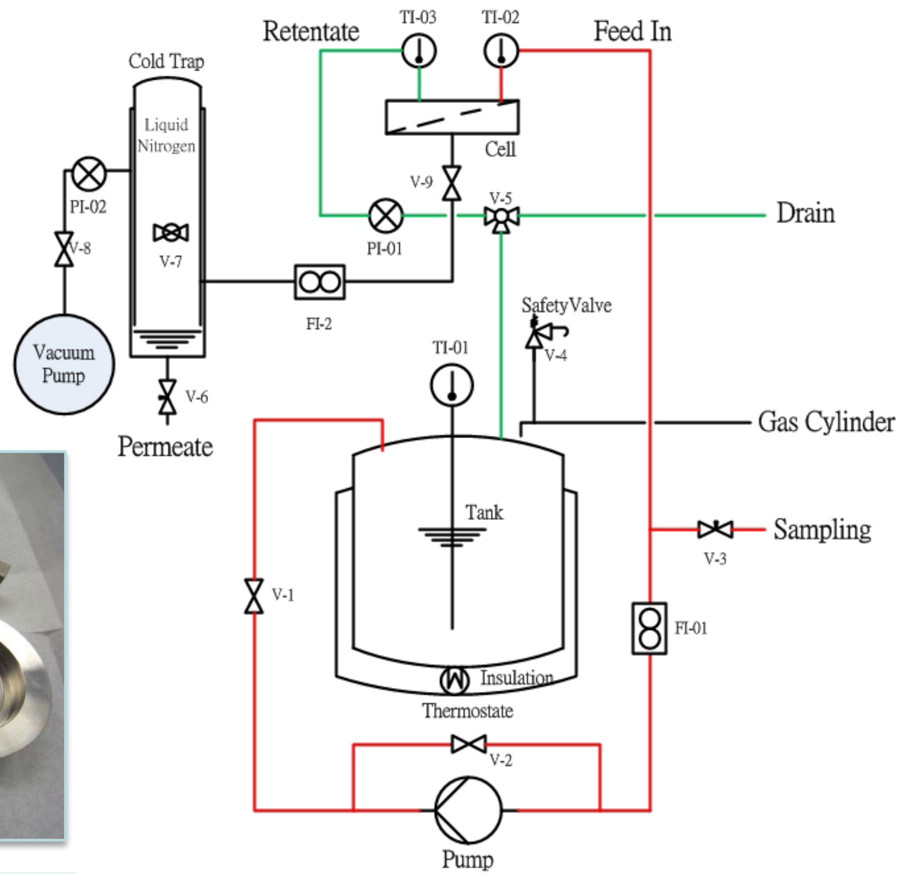
- Zeolites are crystalline micro porous aluminosilicates
- A pore flow type membrane (adsorption)
- Pore diameter ~ 0.4 nm, H_2O = 0.296 nm, EtOH = 0.43



Pervaporation Instrumentation

Pervaporation = Permeate + Evaporation





Custom cell by Sulzer Chemtech

Driving Force:

Pressure difference between feed and product , and difference of chemical potential to the membrane.

Pervaporation unit performance

Pressurized feed tank (1 gallon) Test cell (Diameter 3.15 inch)

Recycling pump (34 L/hr) Temperature (20℃~90℃)

Vacuum pump (2×10^{-3}mbar)

Anticipated Results

- Understand the structure/property relationships in pervaporation membranes
- Control and design appropriate membrane structure
- Higher flux (more energy efficient) pervaporation performance

Chu-Hsiao Group

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