

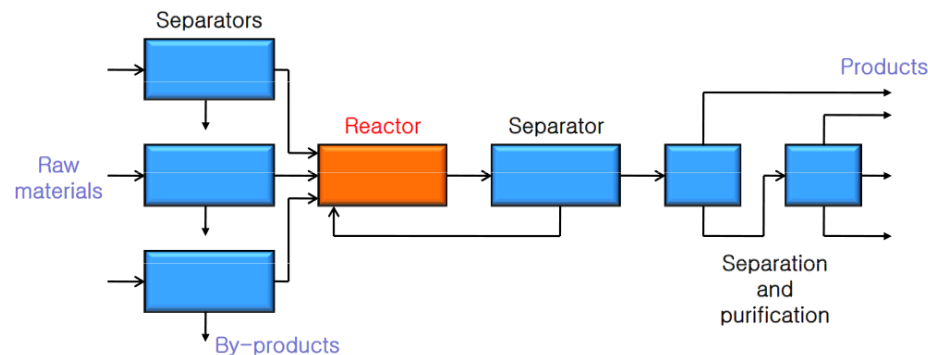
# Thin Film Composite Nanofiltration Membrane: from Aqueous to Organic Solvent Nanofiltration Application.

- Muntadher Almjibilee
- Tianjin university, [malmijbilee@tju.edu.cn](mailto:malmijbilee@tju.edu.cn)
- Nanofiltration membrane
- Organic solvent nanofiltration membrane
- Membrane synthesis
- OSN membrane high permeance



# Separation and Purification

- How much separation and purification process is important in the chemical plant?



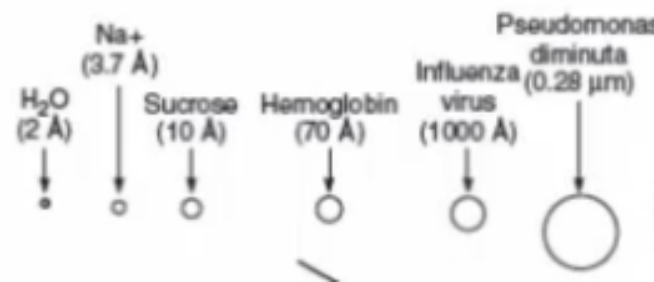
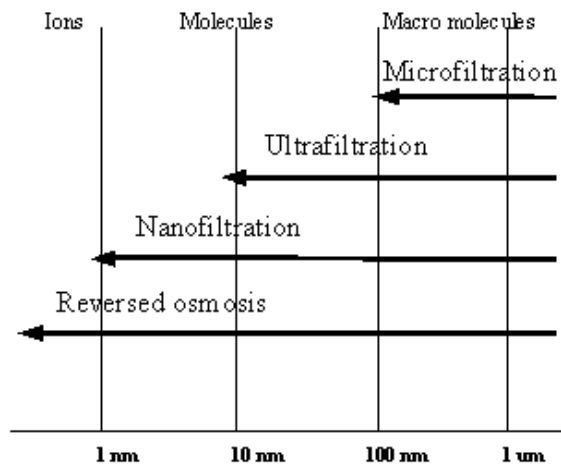
Separation processes can account for generally **40 - 70%** of chemical plant costs

S. Sholl and P. Lively, *nature* (2016) 532 pp 435-437

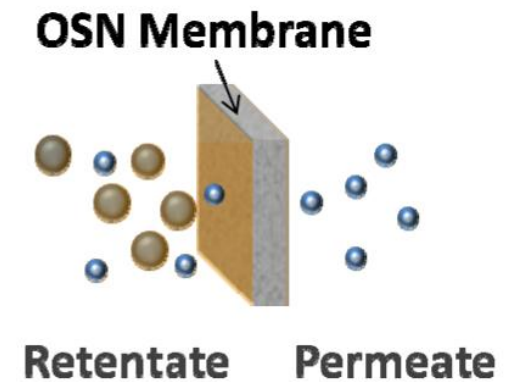
- separation and purification include distillation, crystallization, adsorption, **membrane processes**, absorption and stripping, and extraction.

# Nanofiltration definition

- Nanofiltration process involving separating a dissolved molecules in liquid
- Pressure is the most common driving force
- Molecular weigh cut off (MWCO) 200-1000 g/mol



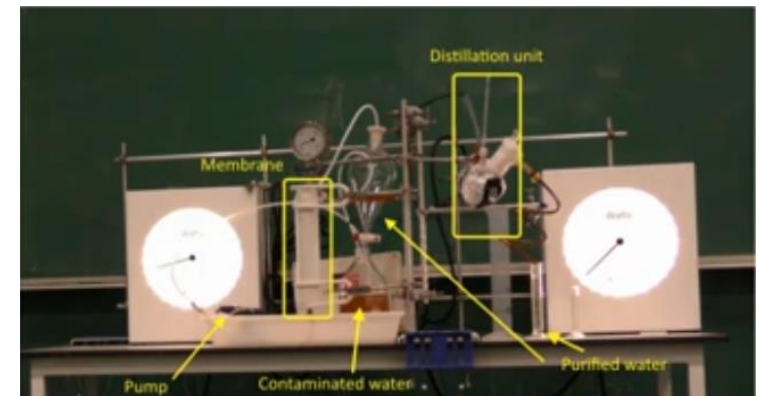
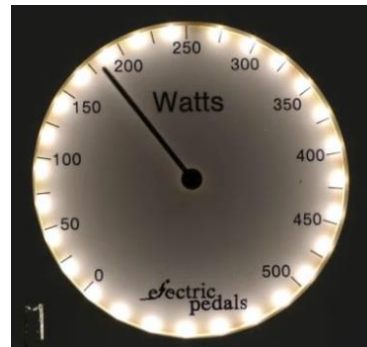
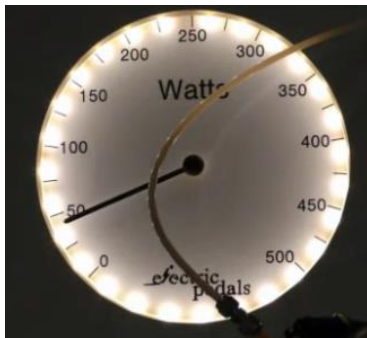
Applied Pressure



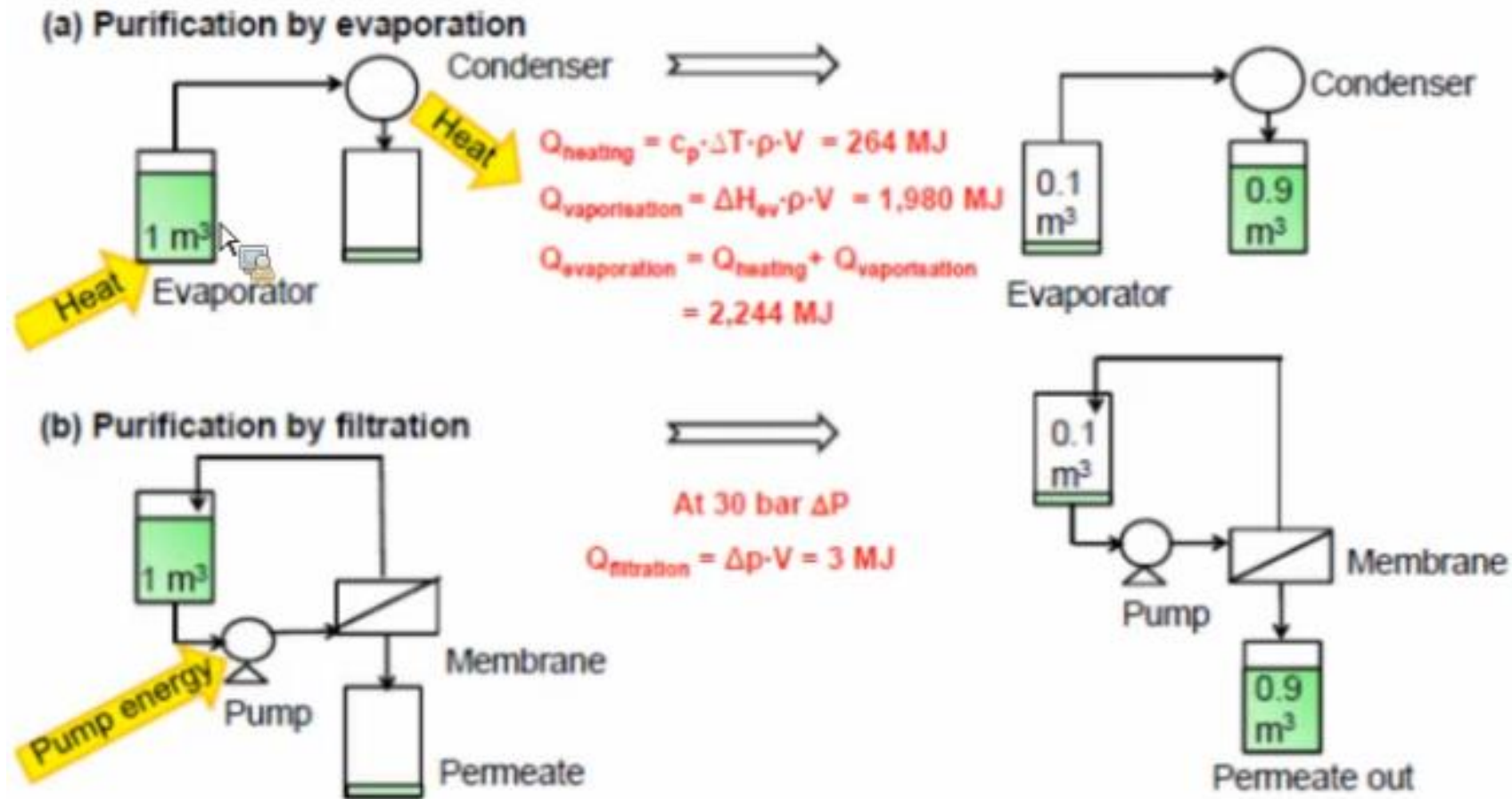
# Separation by membrane VS evaporation Energy consumption

- Membrane nanofiltration vs other separation technology; suitability, economic efficiency.

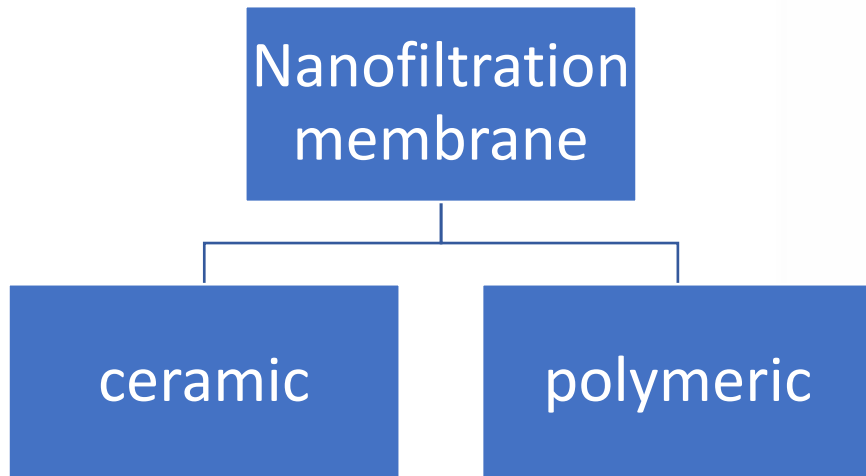
Membrane	VS traditional distillation
50 watts	200 watts
50 ml/min	2 ml/min



# Separation by membrane VS evaporation Energy consumption



# Nanofiltration membrane types

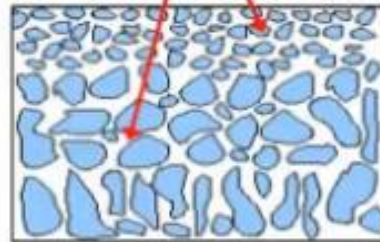


Ceramic membrane; more stable, high MWCO, Difficult to fold

Polymeric membrane; easy to fold, low MWCO, Less stable

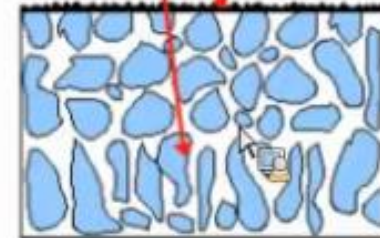
**Integrally skinned asymmetric (ISA) membrane**  
**ONE step process**

same material



**Thin Film composite (TFC) membrane**  
**MULTIPLE step process**

different material

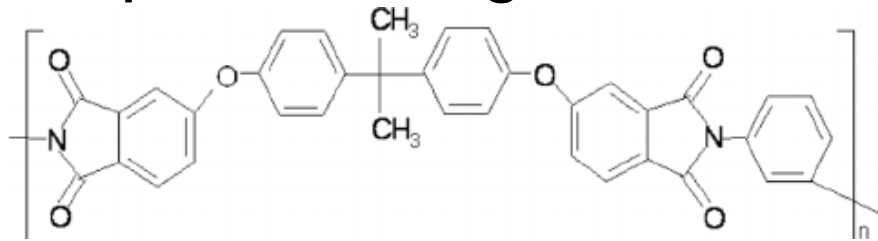




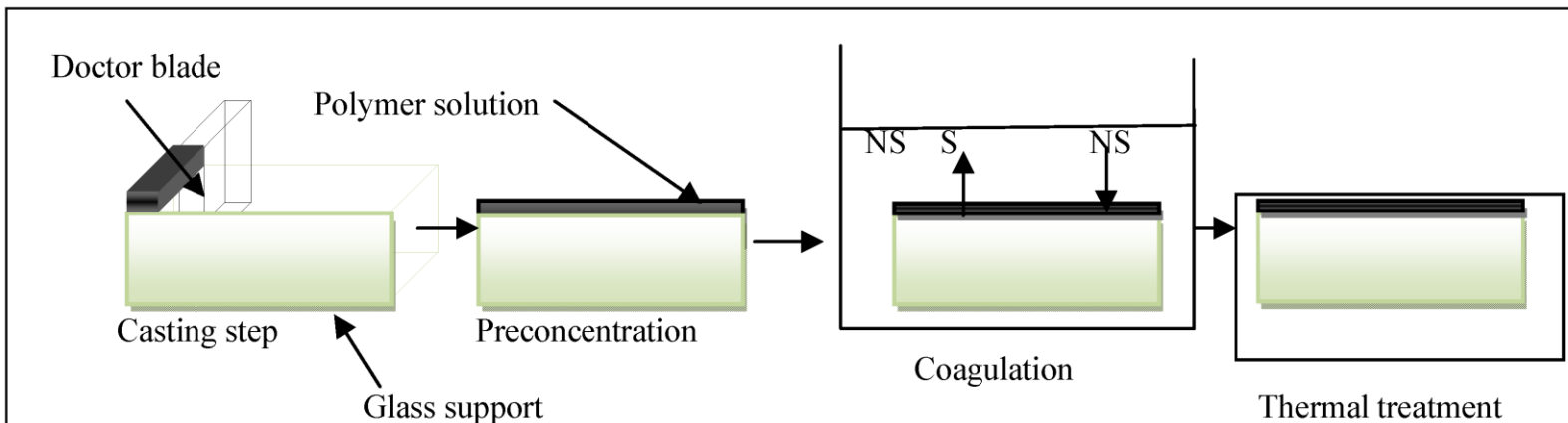
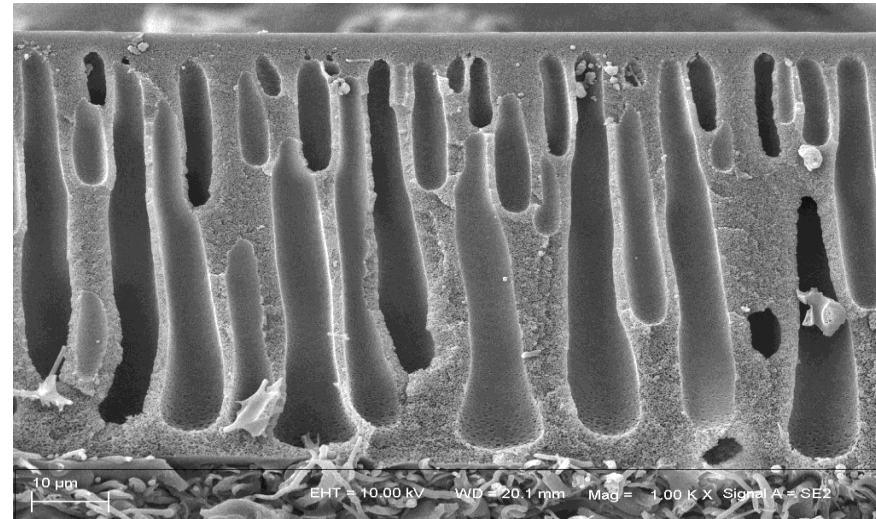
# Polymeric membrane preparation

## ISA membrane

- Casting the membrane
- Aqueous coagulation



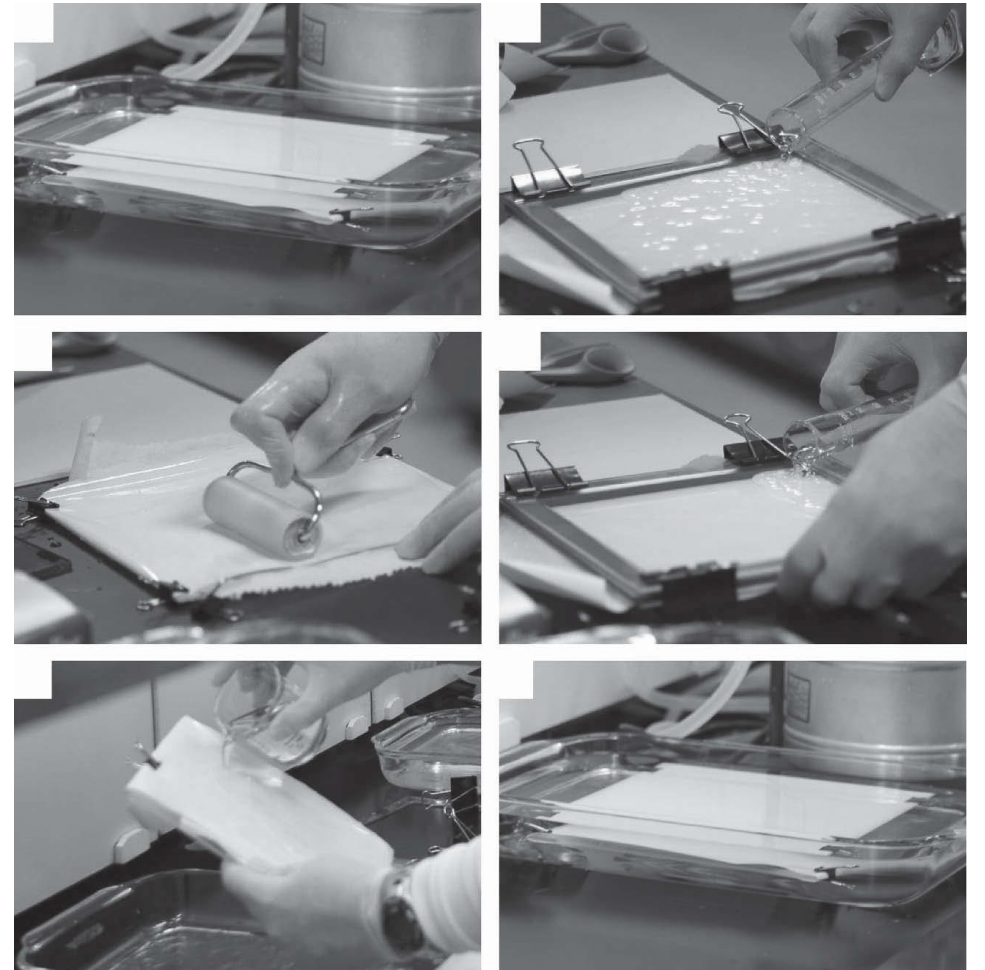
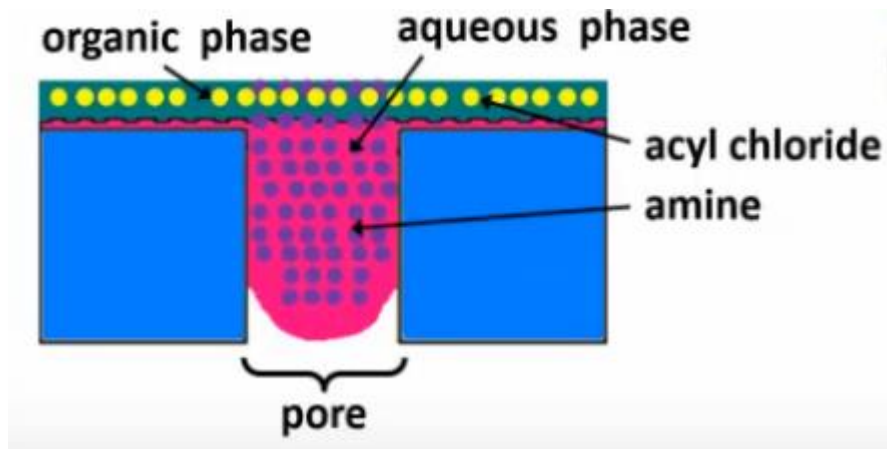
Polyetheramide PEI 23% wt/wt in DMAc



# Polymeric membrane preparation

## TFC membrane

- Interfacial polymerization (IP)
- Aqueous phase
- Organic phase

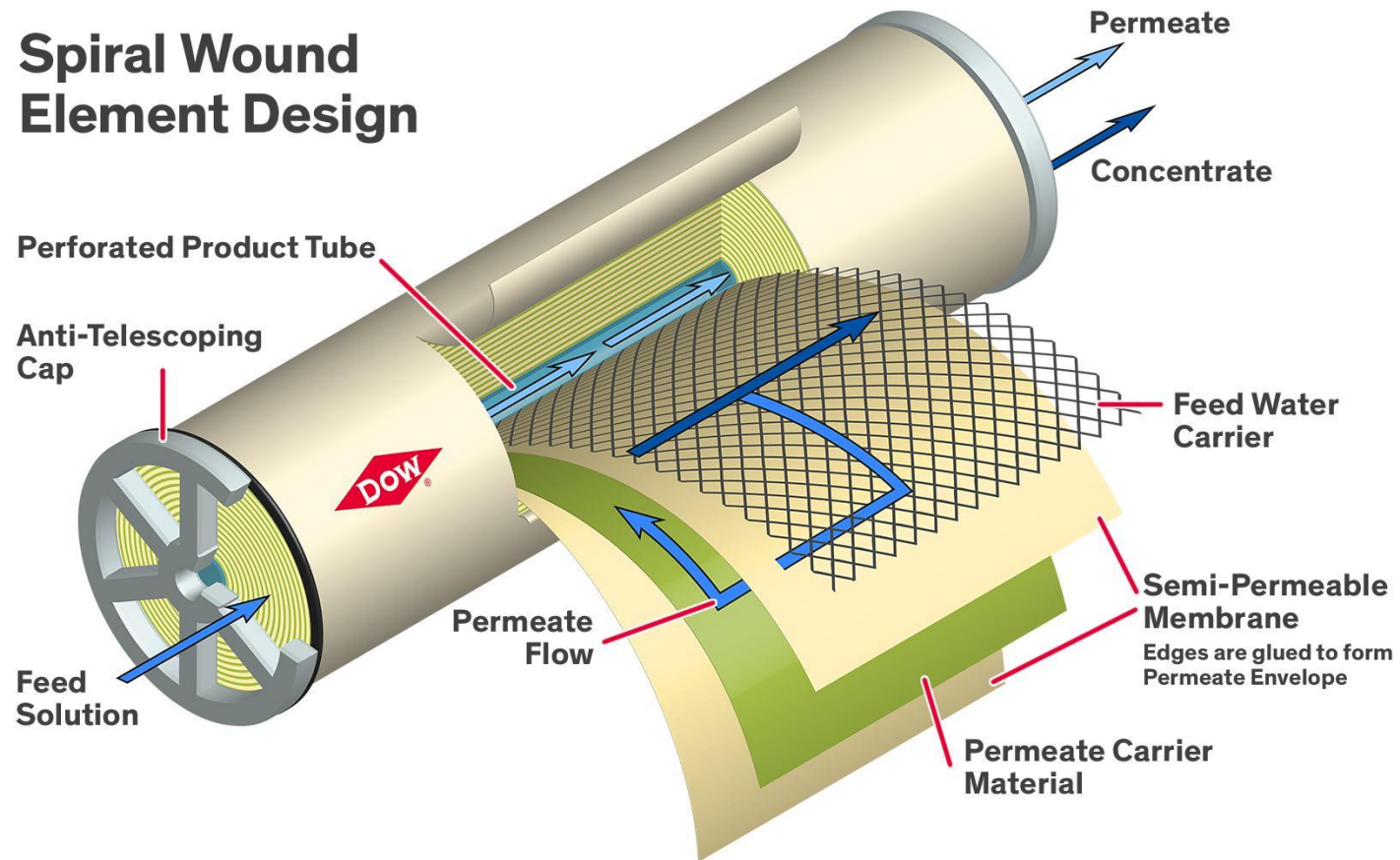




# Prepare the membrane for application

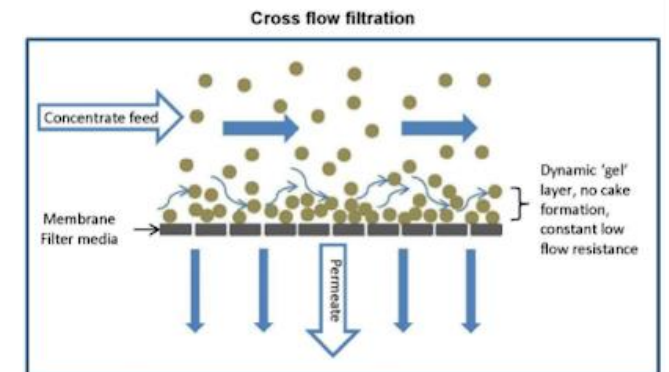
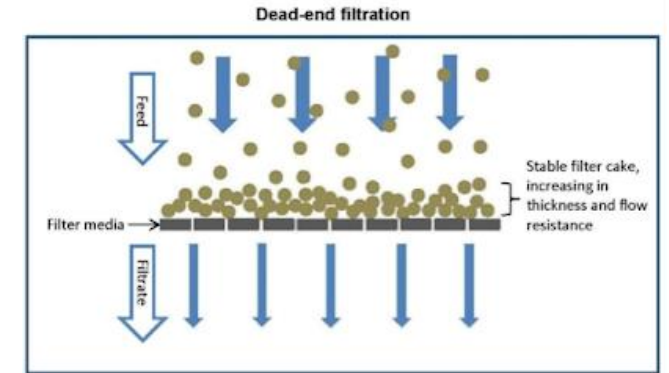
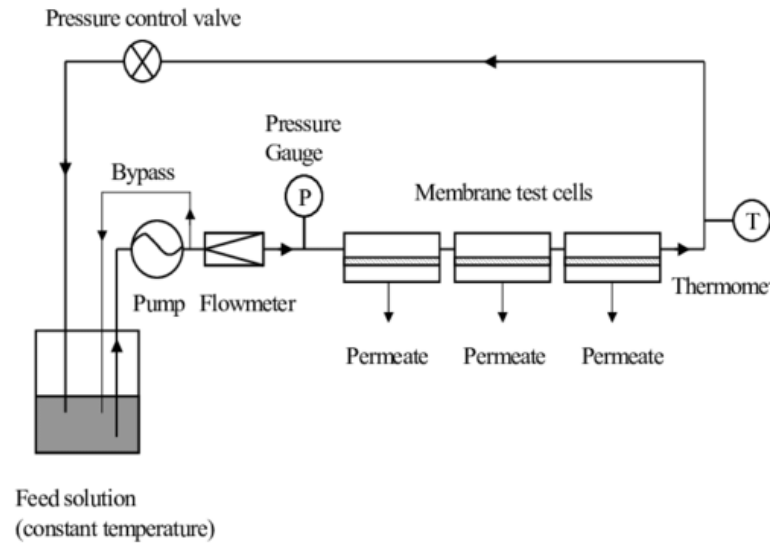
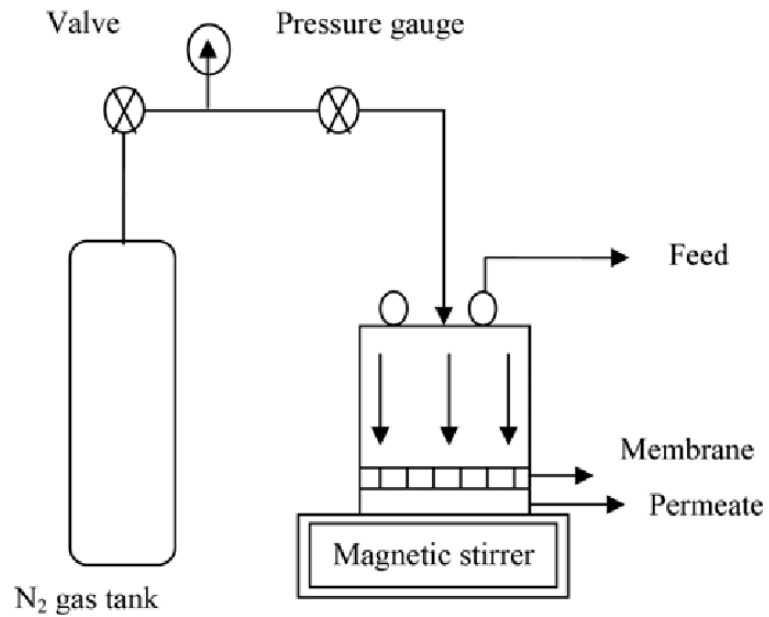
## Module the membrane

- Module the membrane sheet to spiral module



# Nanofiltration evaluation

## Dead-end VS cross-flow

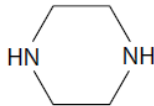
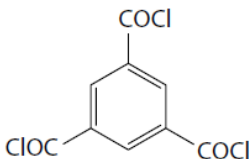
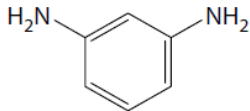
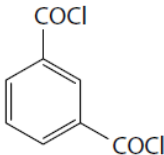
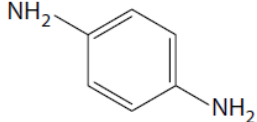
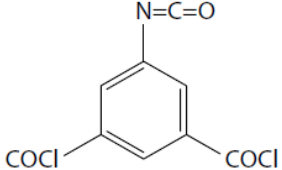


# Polyamide TFC membrane

## The used monomers

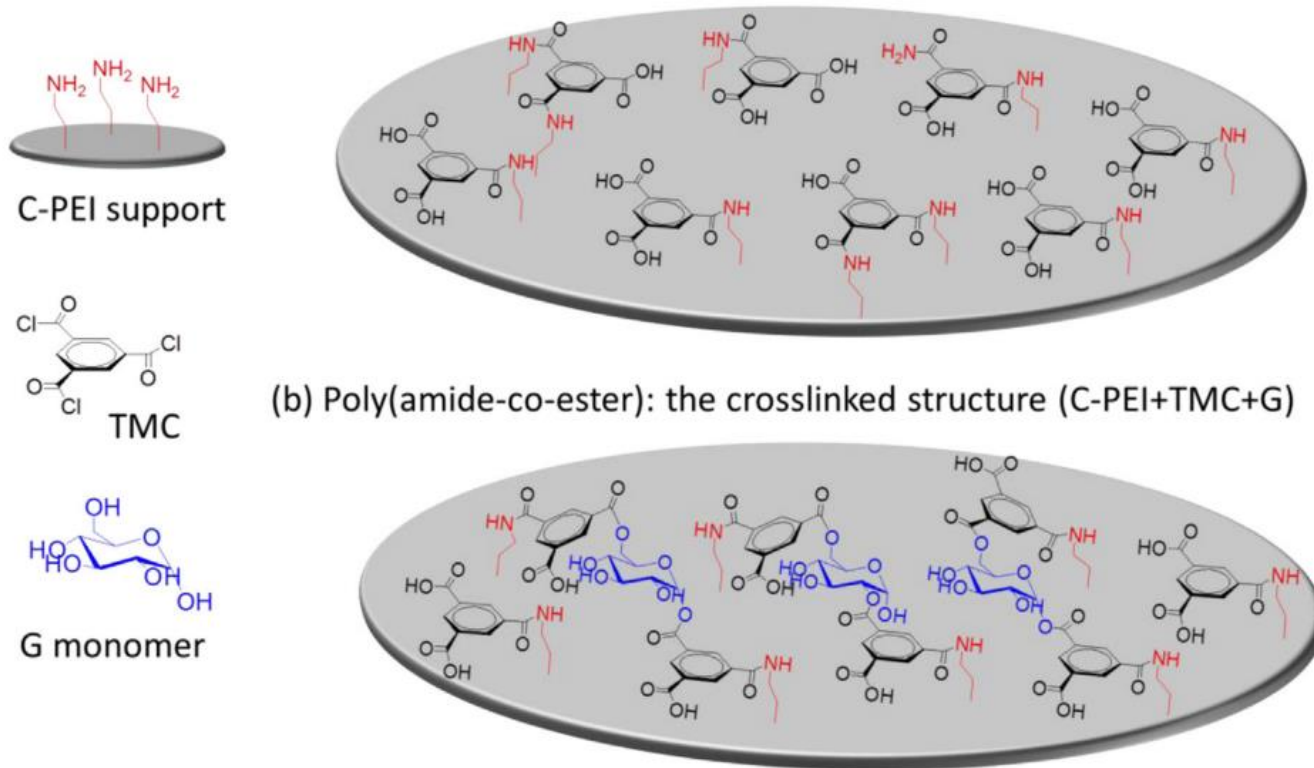
- The aqueous phase contains a diamine monomer
- The organic phase contains an acid chloride

Organic Structure of Commonly Used Monomers for PA Thin Layer Synthesis Together with Their Respective MW

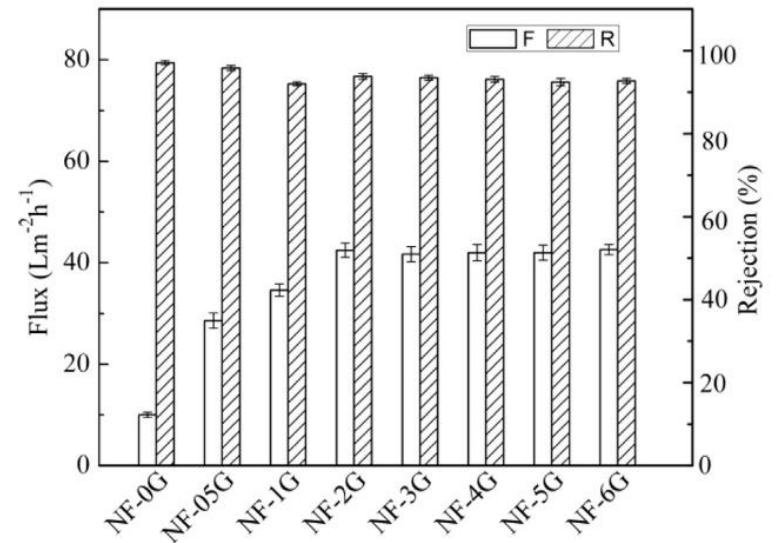
Amine Monomer (Abbreviation)	Chemical Structure	Molecular Weight (g mol <sup>-1</sup> )	Acyl Chloride Monomer (Abbreviation)	Chemical Structure	Molecular Weight (g mol <sup>-1</sup> )
Piperazine (PIP)		86.14	Trimesoyl chloride (TMC)		265.48
<i>m</i> -Phenylenediamine (MPD)		108.10	Isophthaloyl chloride (IPC)		203.02
<i>p</i> -phenylenediamine (PPD)		108.10	5-isocyanato-isophthaloyl chloride (ICIC)		243.04

# poly(amide-co-ester) nanofiltration membrane

## Hydrophilic membrane

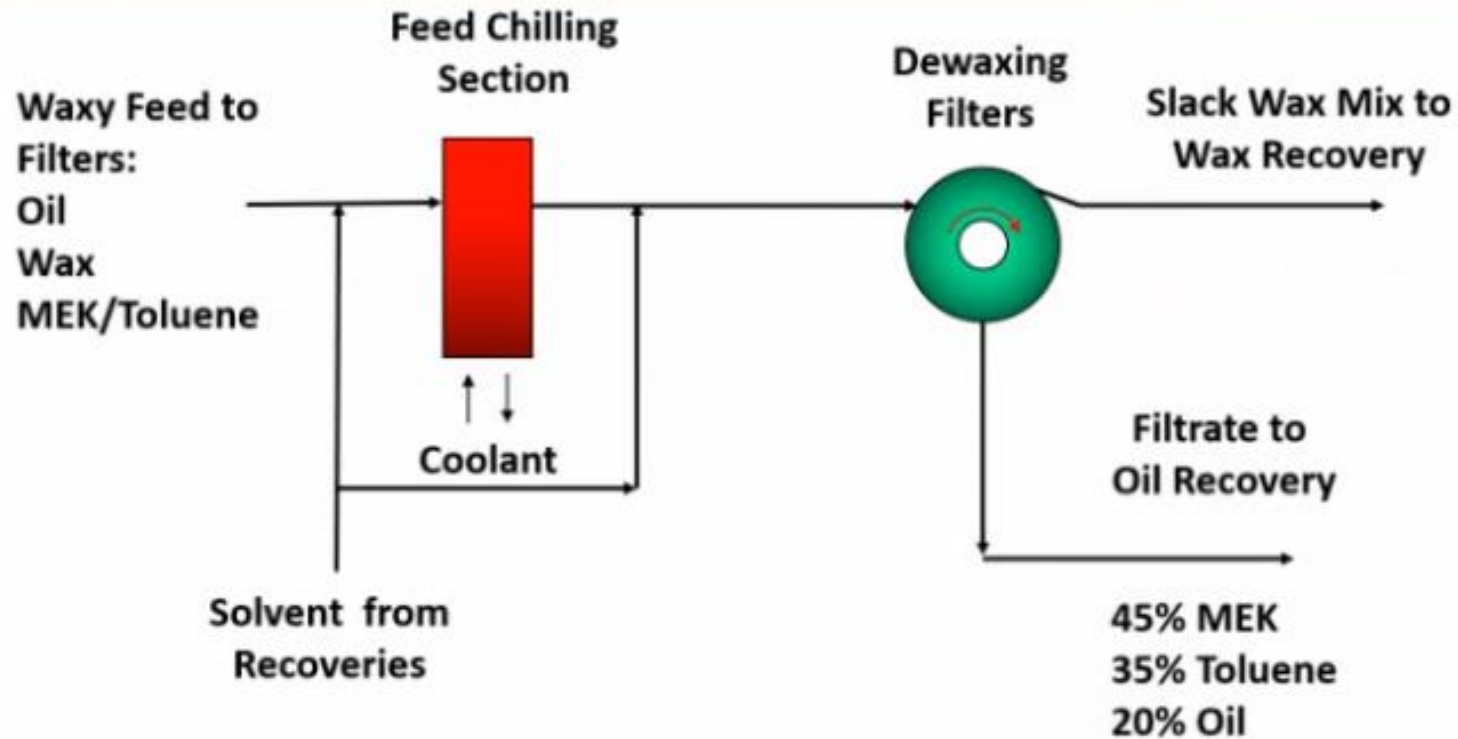


Membrane	Contact angles (deg)
NF-0G	$40.7 \pm 2.8$
NF-1G	$30.6 \pm 1.6$
NF-2G	$29.1 \pm 0.9$
NF-4G	$26.5 \pm 0.5$



# Nanofiltration for organic system

## Lube oil extraction



lab scale 1993

Large scale 1999

Capacity 11,000 m<sup>3</sup>/day solvent

Project cost \$6 million in 2000

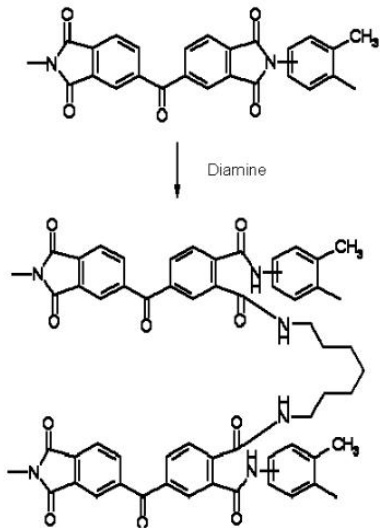
Net benefits \$6 million per year



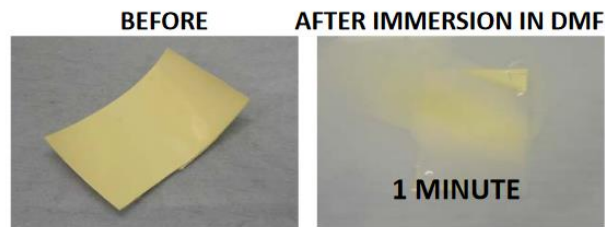
# From aqueous to organic solvent applications

## Organic solvent nanofiltration (OSN) membranes

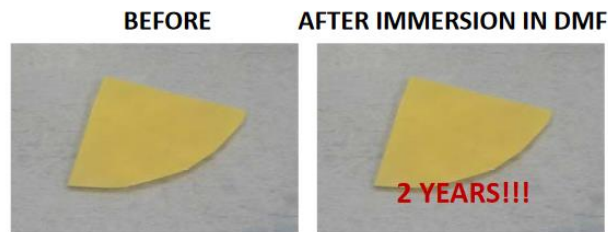
- Membrane solvent resistant
- Crosslinking the membrane



Non-crosslinked P84



Crosslinked P84

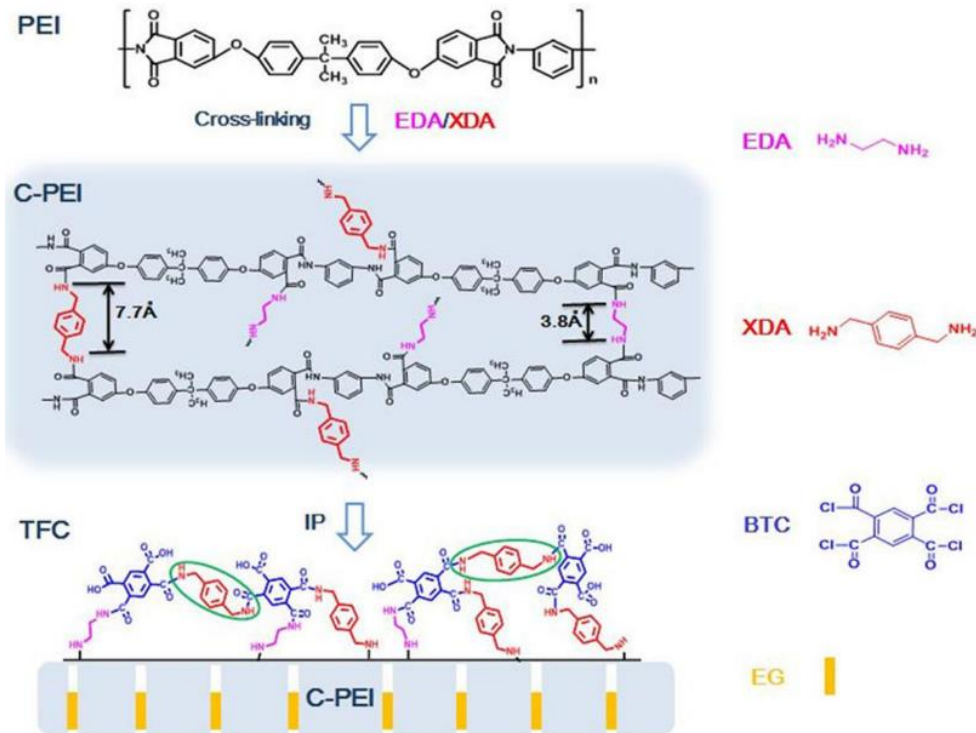


Membrane Extraction Technology (MET), Imperial Spin-out company, licensed OSN technology from Imperial College and developed the **DuraMem™** range

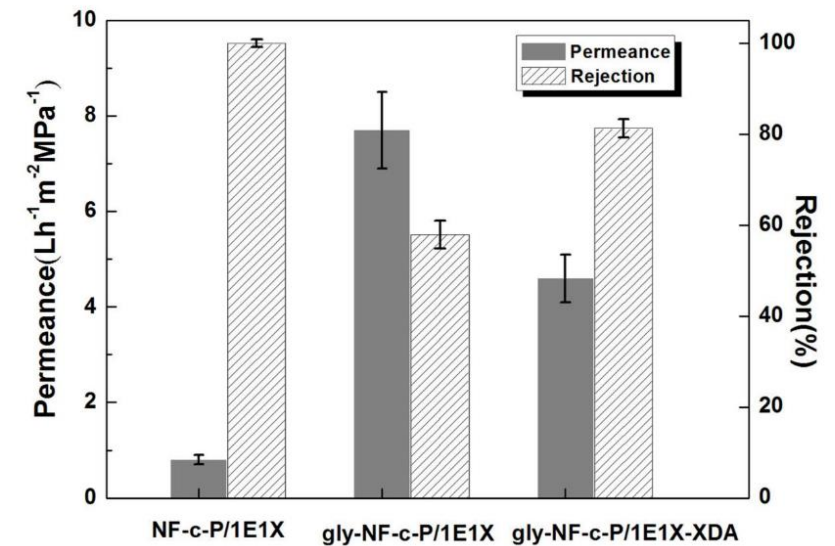




# Polyamide OSN membrane one step IP with different crosslinkers



Ethylene glycol filling inside the intermediate pores.

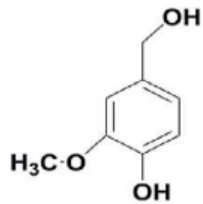


The permeance and rejection of modified NF membranes of gly-NF-c-P/1E1X and gly-NF-c-P/1E1X-XDA versus NF-c-P/1E1X for RB DMF solution.

# Polyarylester OSN nanofiltration membrane

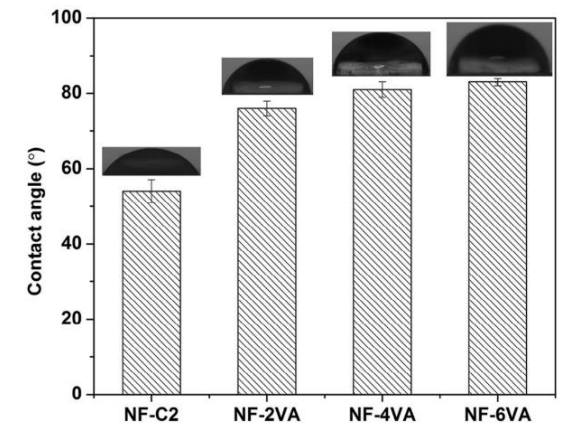
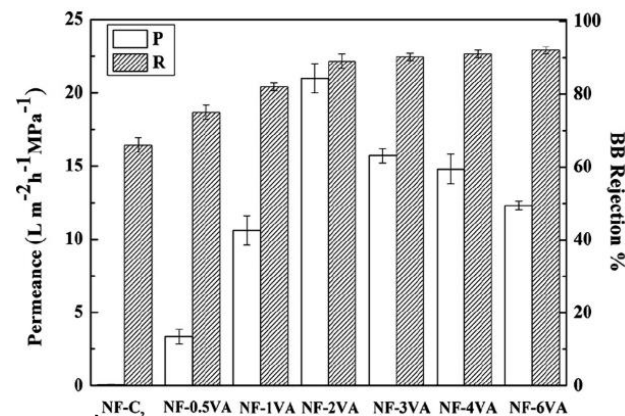
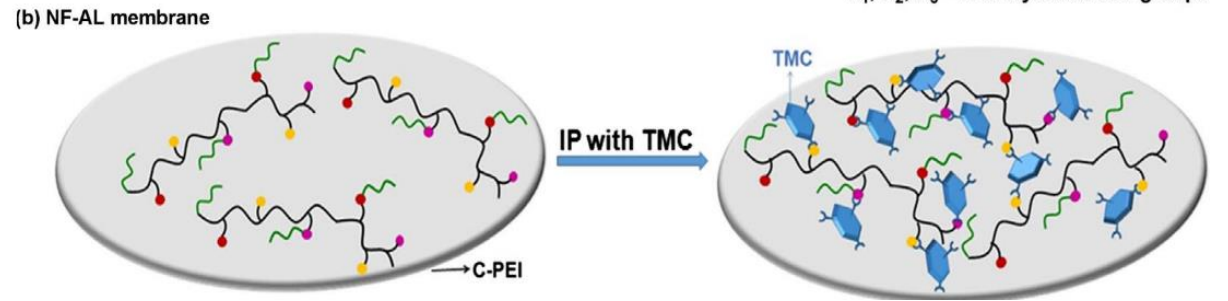
## High DMSO permeance

vanillic alcohol was adopted  
 high DMSO permeance  
 21 Lm<sup>-2</sup> h<sup>-1</sup> MPa<sup>-1</sup>



vanillic alcohol

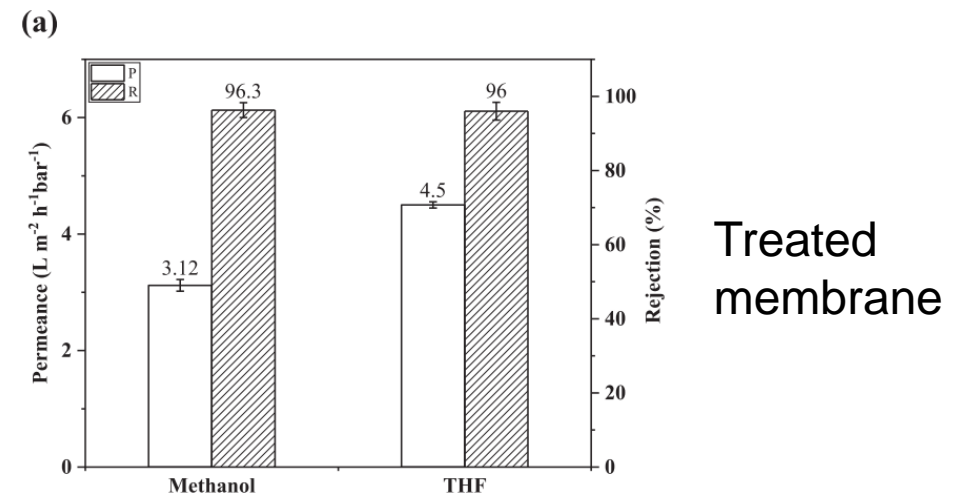
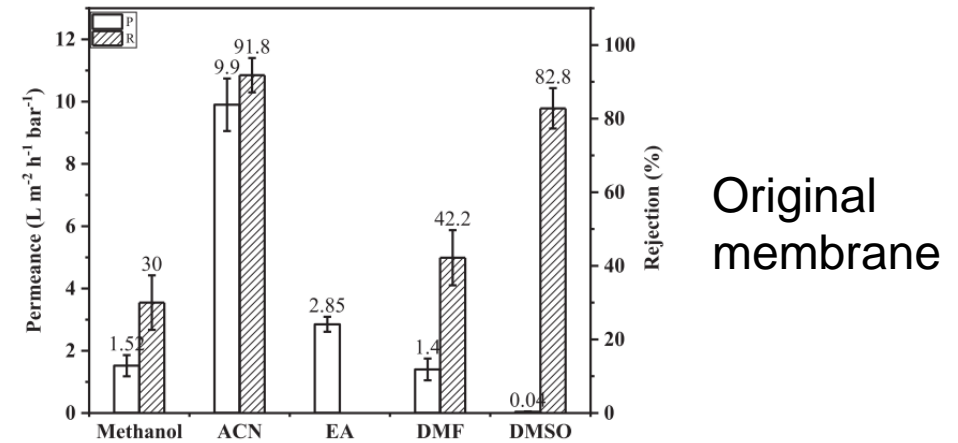
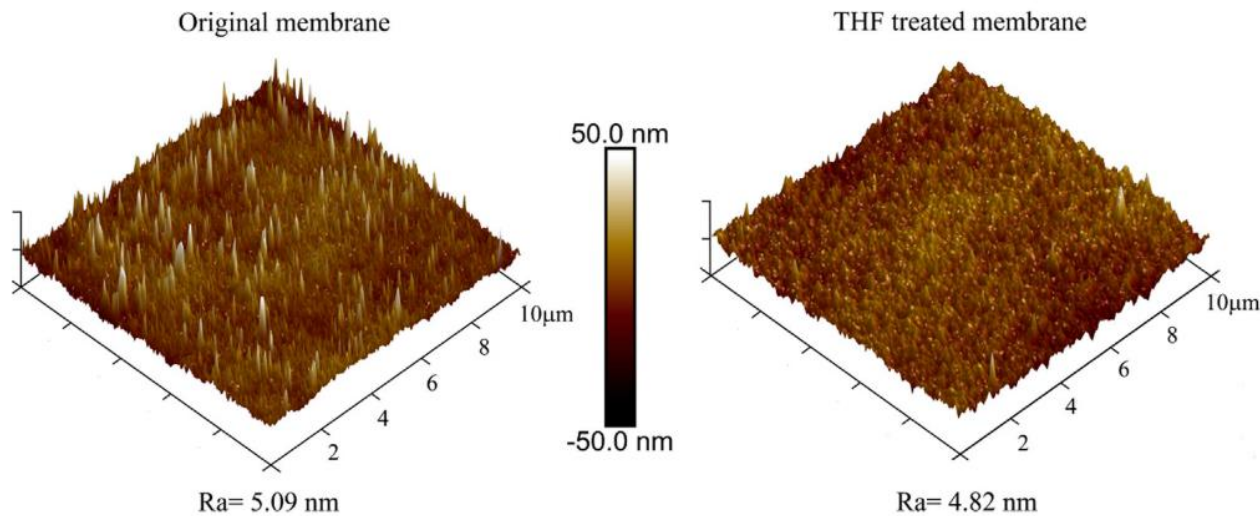
The performance of NF membranes with different VA concentrations (0, 0.5%, 1%, 2%, 3%, 4%, 6% (w/v)) for a 0.01 g L<sup>-1</sup> BB DMSO solution.



# TFC membrane post treatment

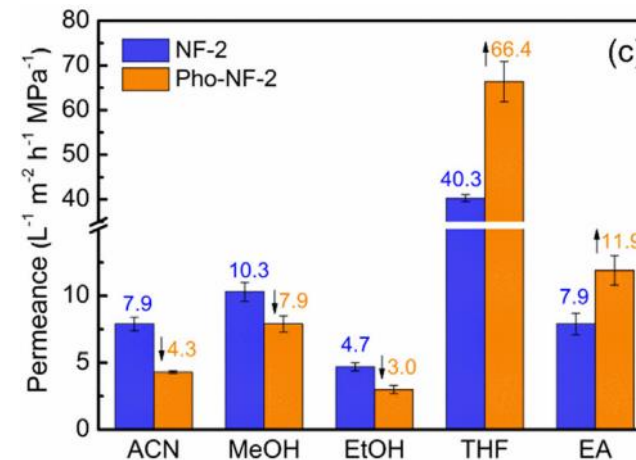
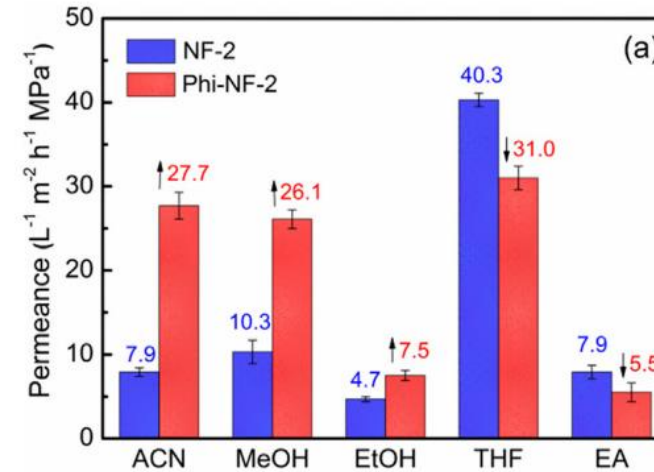
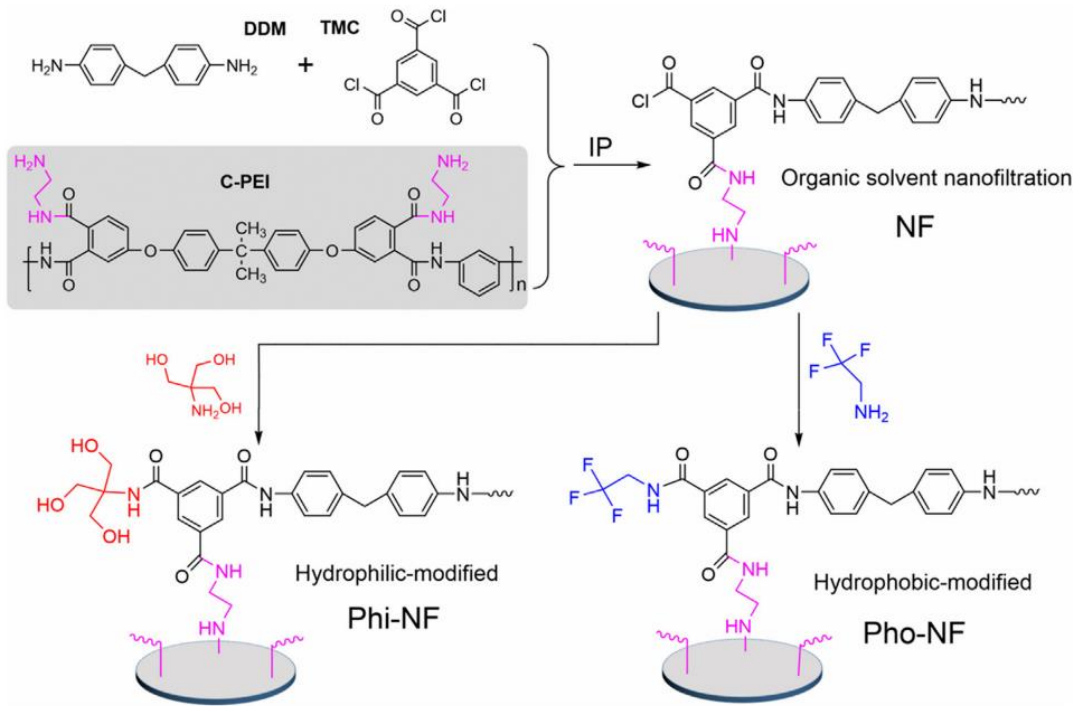
## Solvent activation

Polyetheramide membrane  
24 h-THF immersion



# Surface hydrophobicity effect Modulate hydrophobicity polyamide OSN membrane surface

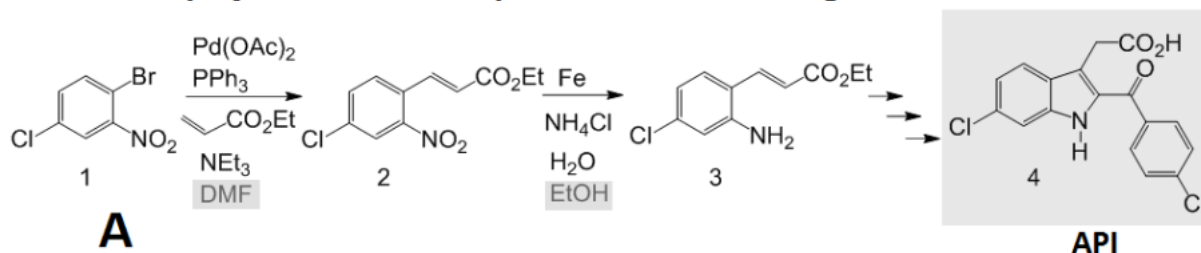
Hydrophobic- High THF permeance



# OSN applications to Sequential Reactions pharmaceutical applications

## Synthesis route for a COX-2 inhibitor candidate drug published by Pfizer

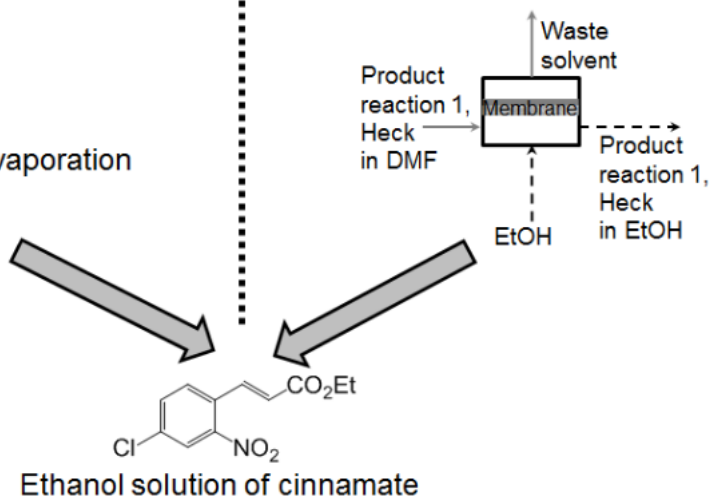
### Multi-step synthesis that require solvent exchange – DMF to Ethanol



### Published procedure for solvent exchange | Membrane cascade solvent exchange

1. Extraction with toluene
2. Wash with 1 N HCl
3. Wash with water
4. Wash with water
5. Concentration to oil via evaporation
6. Crystallisation in hexane
7. Dissolution in ethanol

**B**





# OSN applications in food industries

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- Concentrated the **fruit juices** without losing the color and taste
- Milk industries **protein valorization** between (200–1000 Da)
- Recovery of **lactic acids (LA) and amino acids**
- Vegetable oil processing, the molecular weight of triglycerides and phospholipids are roughly in the range of 900 and 800 Da
- Flavonoids, protein, and other natural products extraction



# Concluding

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- Extraction by membranes save massive amounts of energy over alternatives such as evaporation
- Nanofiltration in organic solvents is still in its infancy relative to RO, but will also lead to massive energy savings
- Understanding membrane formation and function can lead to fundamental insights which catalyze process improvements
- Most important membrane improvements are likely to be improving stability and chemical resistance, and selectivity

# Acknowledgements....

- Al-qasim green university-college of food science
- Lec. Haitham Alsharifi
- Dr. Ali Raad
- Chemical Process Intensification (*CPI*) team



.....and to you for listening