Organic Solvent Nanofiltration
A New Technology for Molecular Separations

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Imperial College London

- OSN – An Emerging Technology
- Membrane Characterisation
- OSN Applications
- Next Generation Membranes

Also:

Managing Director

Membrane Extraction Technology Ltd

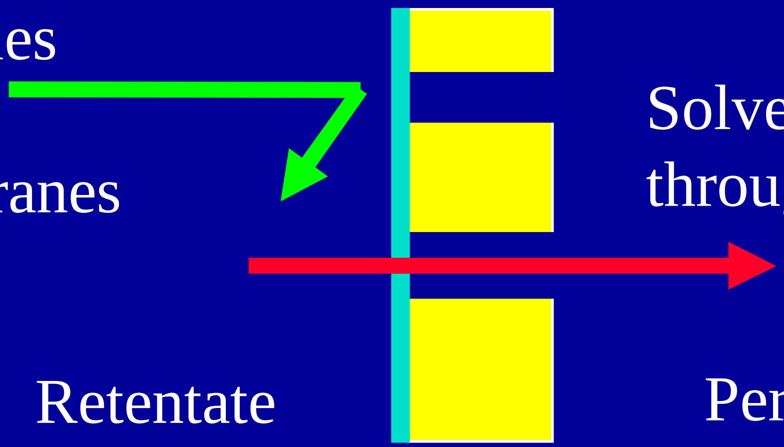
www.membrane-extraction-technology.com

MET MEMBRANE EXTRACTION TECHNOLOGY

Organic Solvent Nanofiltration
OSN –An Emerging Technology

- Nanofiltration membranes are capable of discriminating between molecules in MW range 200-1000 Da
- Applications have been based in aqueous systems
- IF nanofiltration could be applied to separations in organic liquids, could be worth billions of dollars

Larger molecules unable to pass through membranes



Solvent passes through membrane

Retentate

Permeate

Rejection $R = (1- (C_{permeate}/C_{retentate}))$

100% = perfect rejection; 0% = no separation

Organic Solvent Nanofiltration
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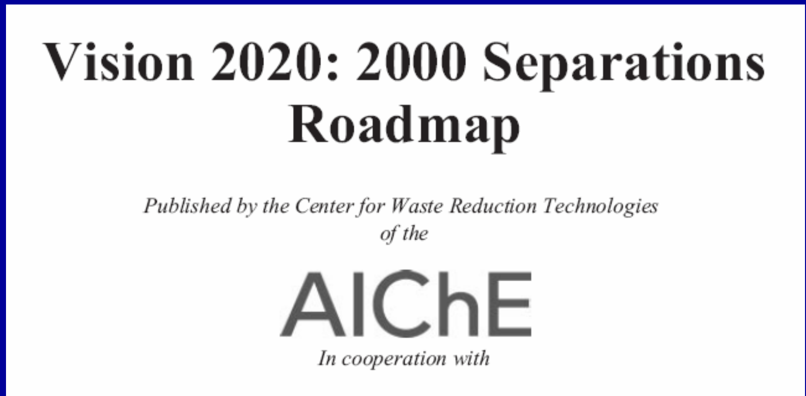

Vision 2020: 2000 Separations Roadmap

Published by the Center for Waste Reduction Technologies of the

AIChE

In cooperation with

"Separation processes account for between 40-70% of both the capital and operating costs in industry"

Consider 1m3 of a dilute solution of solute in a solvent, which needs to be concentrated 10x.

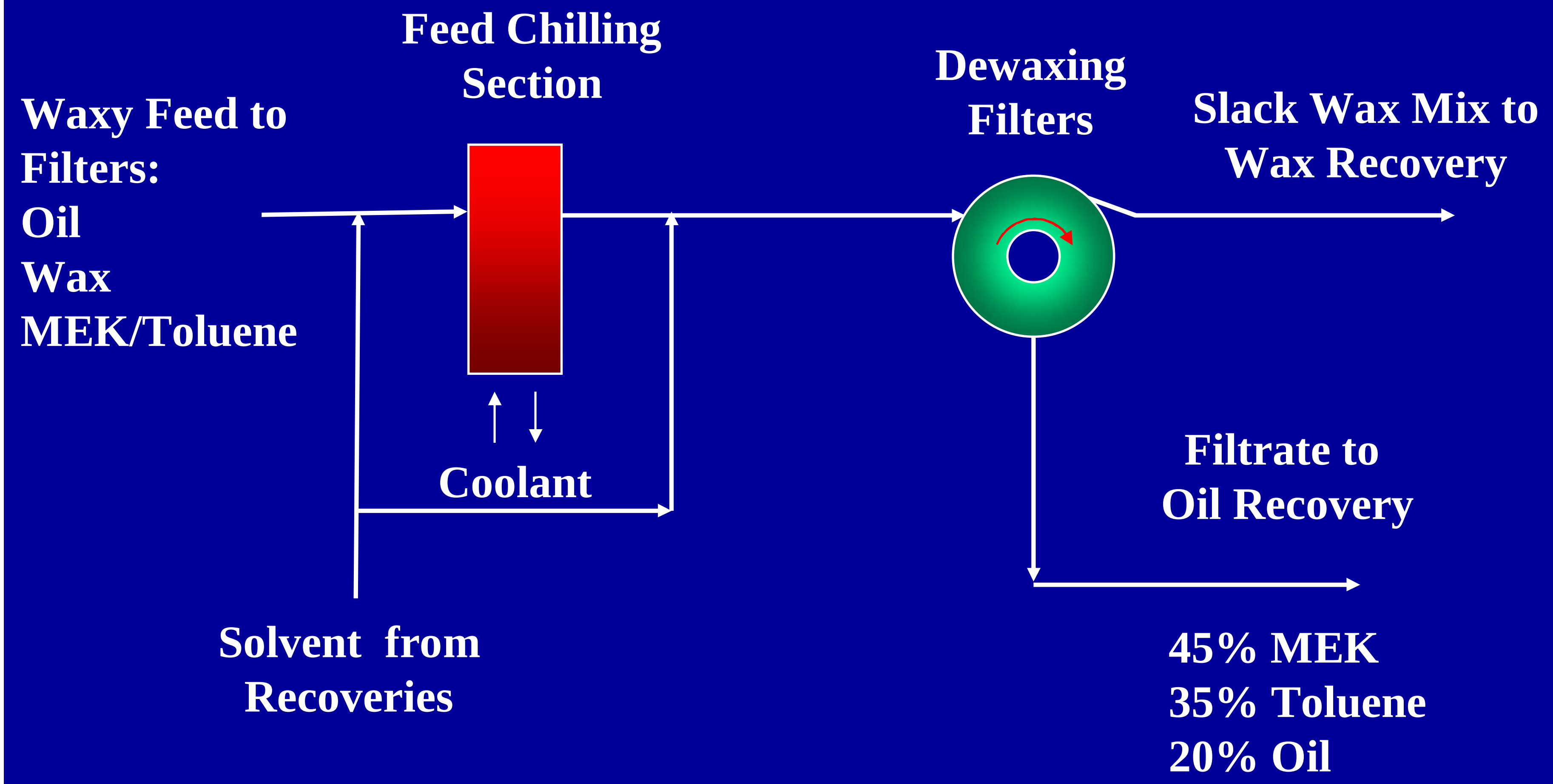
- Using distillation, ΔH_{fg} = 38 MJ kmol^{-1}, MW = 50 g mol^{-1} and ρ = 800 kg m^{-3}
  - Evaporation requires 550 MJ heating
  - Condensation requires 550 MJ cooling
- Using OSN, applied pressure = 30 bar
  - Pump energy required = 3 MJ
- Given high energy prices here to stay, massive savings possible….

Organic Solvent Nanofiltration
OSN –An Emerging Technology

- Starting in 80's and 90's, oil majors (Exxon, Shell) and chemical companies (ICI, Union Carbide) began to file patents on the use of polymeric membranes to separate molecules present in organic solutions (lube oil recovery, aromatics enrichment, homogeneous catalyst recycle). They used existing commercial (aqueous) membranes, or made their own
- In the 90's, some major membrane producers (Grace Davison, Koch, Osmonics) began serious research programmes/made acquisitions and OSN products started to appear on the market
- These have prompted a rapid rise in the number of academic publications, and in process development projects in industry
- Largest success so far industrially has been WRGrace's Max-Dewax™ process

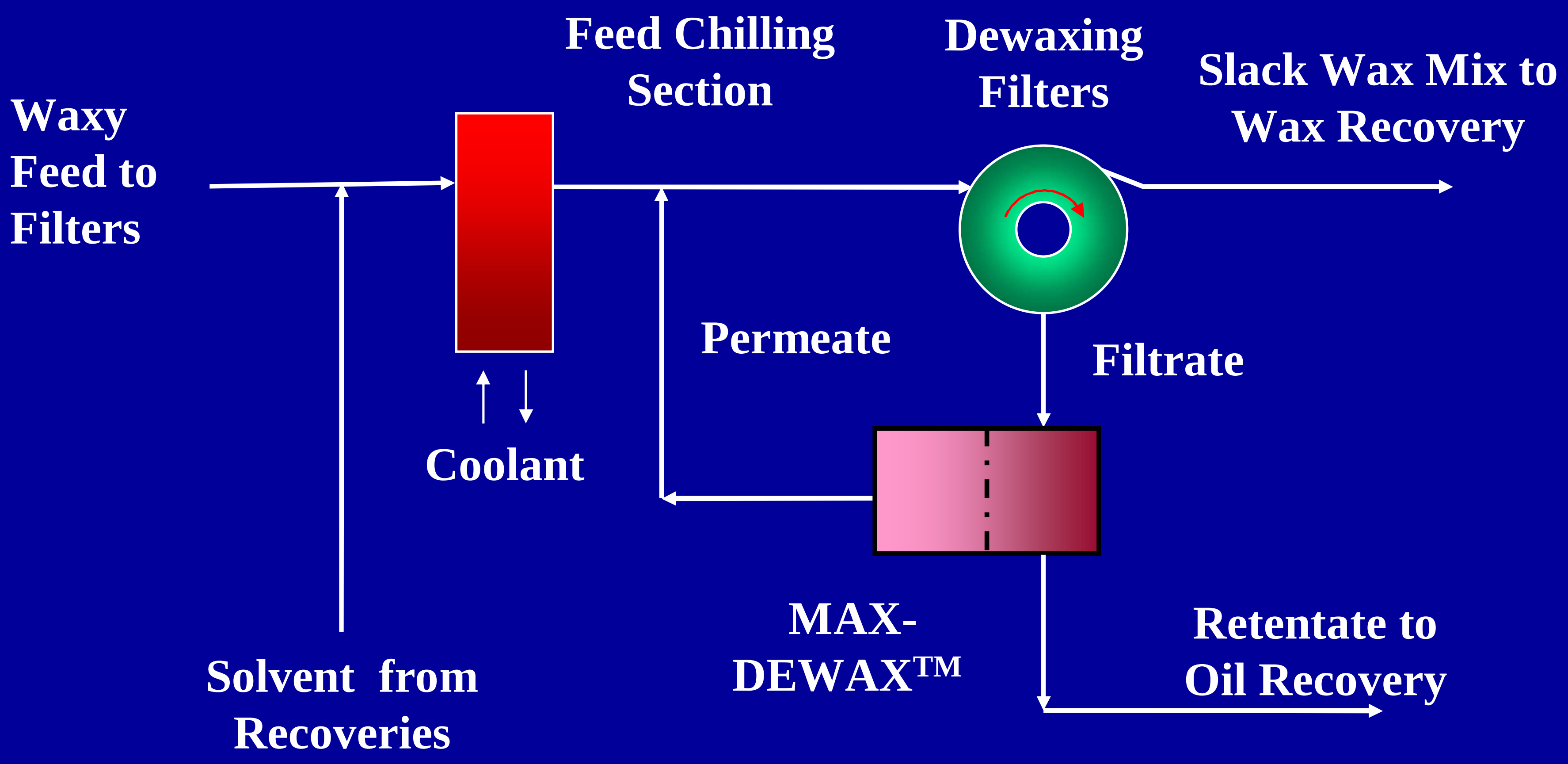
Organic Solvent Nanofiltration
OSN - An Emerging Technology

Conventional Solvent Dewaxing

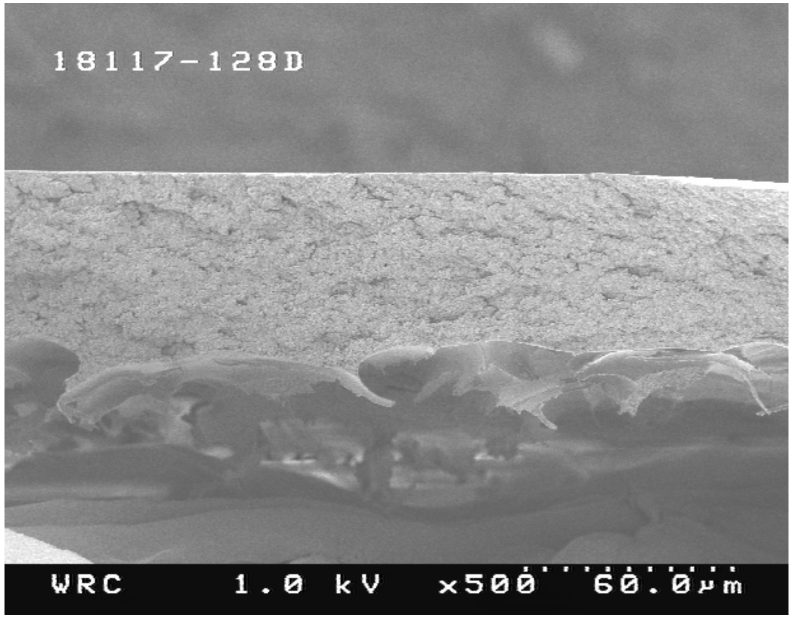


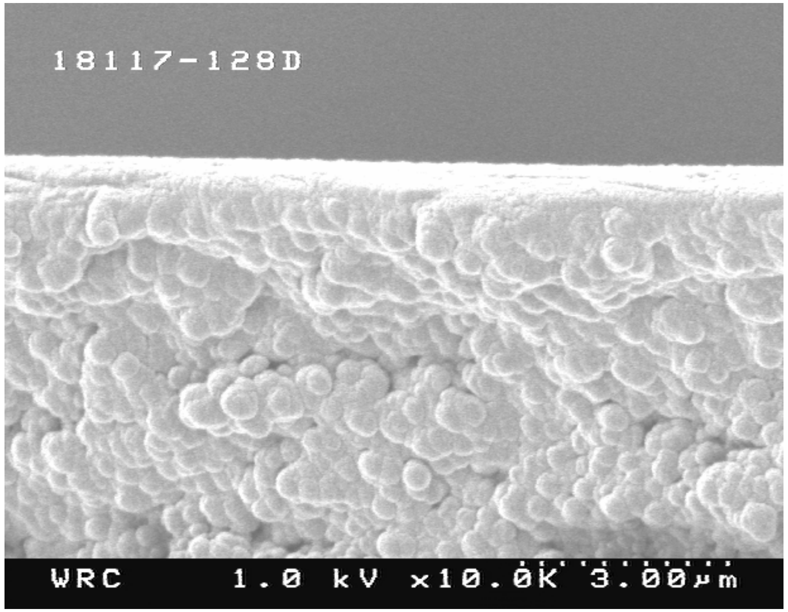
Organic Solvent Nanofiltration
OSN – An Emerging Technology

Solvent Dewaxing with Membranes – MaxDewax™



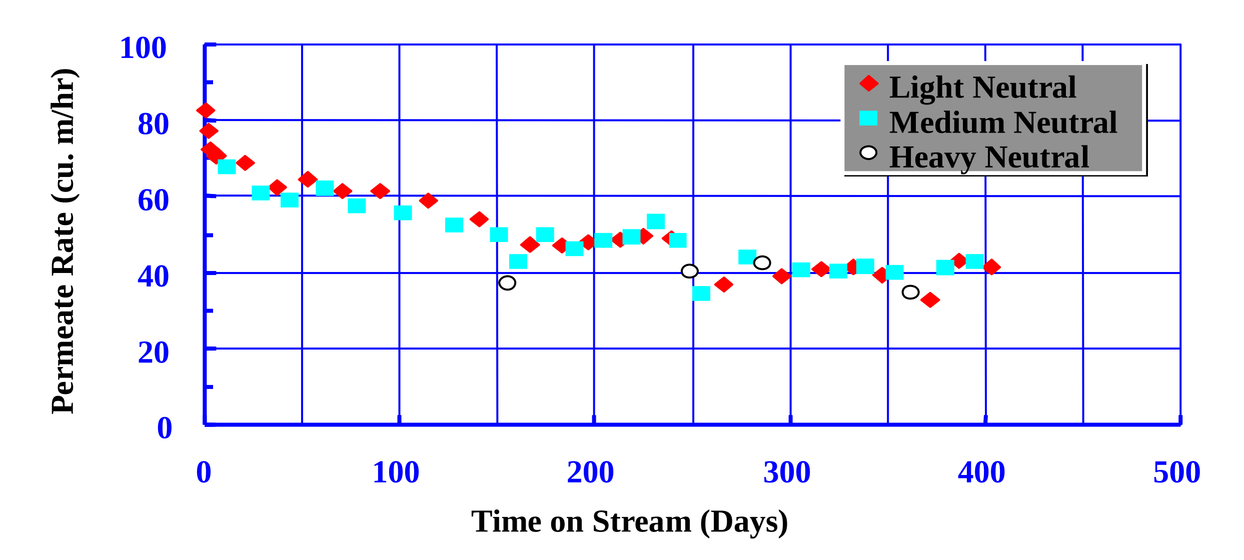
Organic Solvent Nanofiltration
OSN – An Emerging Technology



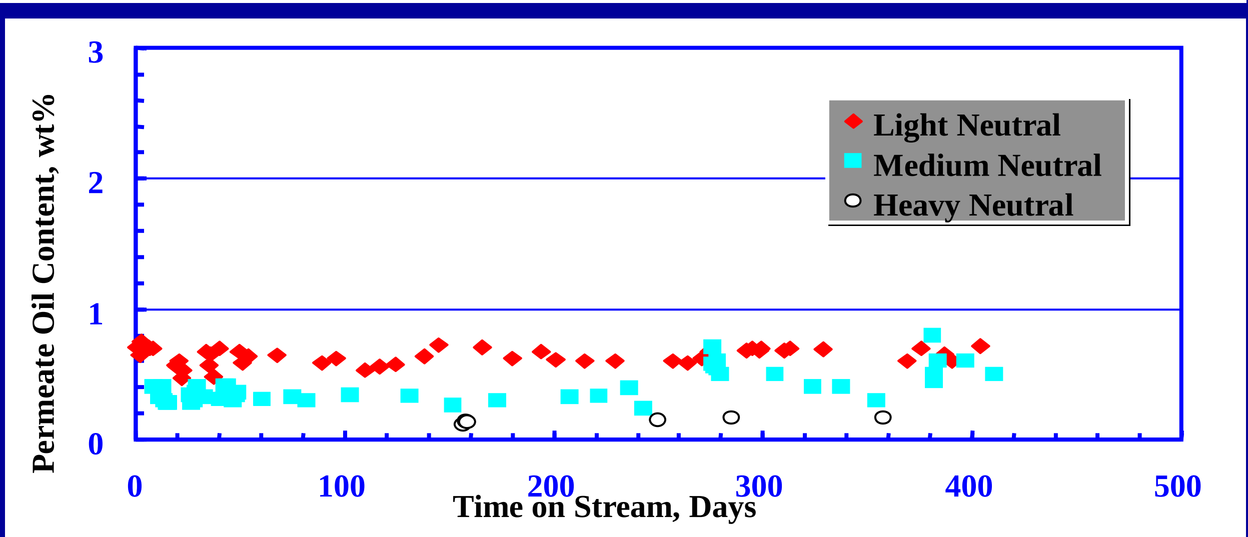


Grace Davison Membranes STARMEM^{TM} polyimide membrane at 500x and 10,000x magnification of active separation layer.

Organic Solvent Nanofiltration
OSN – An Emerging Technology



Commercial Unit
Permeate Production
Typically 60 $m^3 h^{-1}$



Commercial Unit
Permeate Purity
Feed filtrate typically
18-22wt% oil;
Oil rejection 95-99%

Organic Solvent Nanofiltration
OSN – An Emerging Technology

MaxDeWax™ Unit At
ExxonMobil Beaumont Refinery
Processes 11,000 $m^3\ d^{-1}$ solvent

10% expansion of lube and wax train
Project cost $6 million,
Net benefit $6 million per annum

Organic Solvent Nanofiltration
OSN –An Emerging Technology

RESEARCH CHALLENGES IN OSN

- How can we characterise OSN membranes?
- How should we describe transport through OSN membranes?
- Can we find further applications where OSN can provide breakthroughs over current technology?

Existing Membranes

↓

Next Generation Membranes

- How do we improve stability of membranes to apply OSN to all solvents?
- Can we engineer the nanostructure so as to engineer molecular weight cutoff/molecular discrimination?

Organic Solvent Nanofiltration
Membrane Characterisation

STRUCTURAL CHARACTERISATION

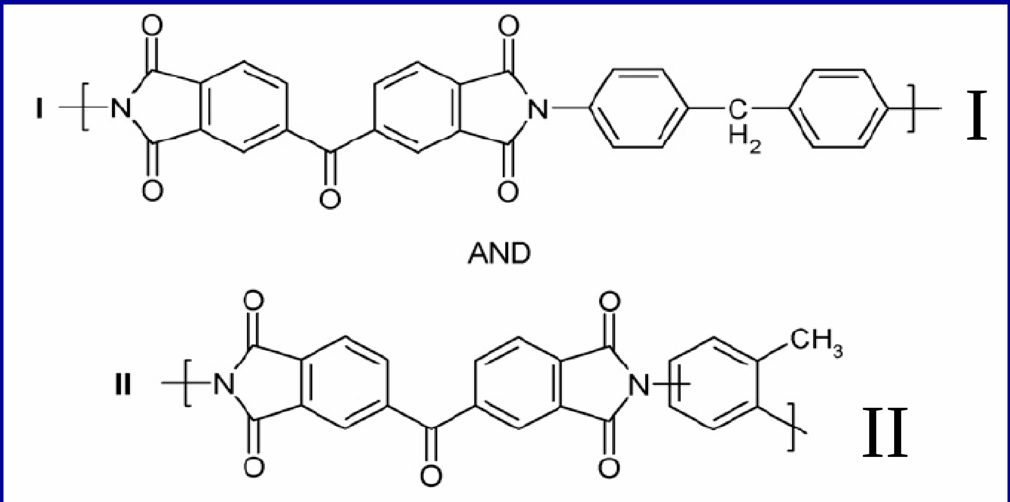
Can we relate any physically observable feature to performance ?

STRATEGY

- Form membranes by phase inversion

-Vary casting parameters to get functional performance changes

-See if observed features correlate with performance change



Lenzing P84 polyimide

20% I

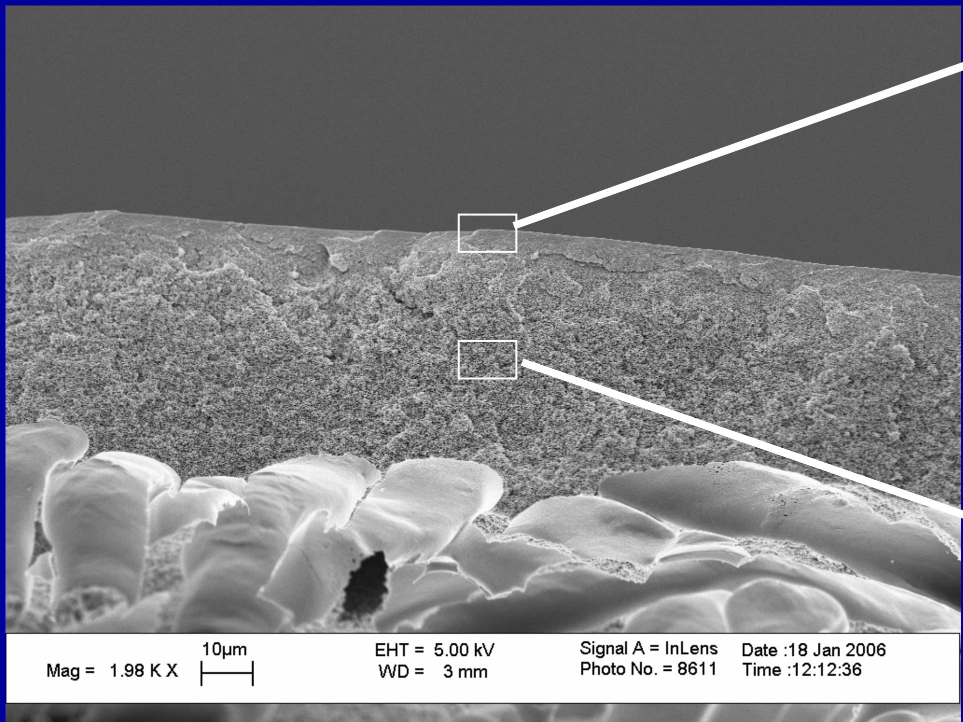
80% II

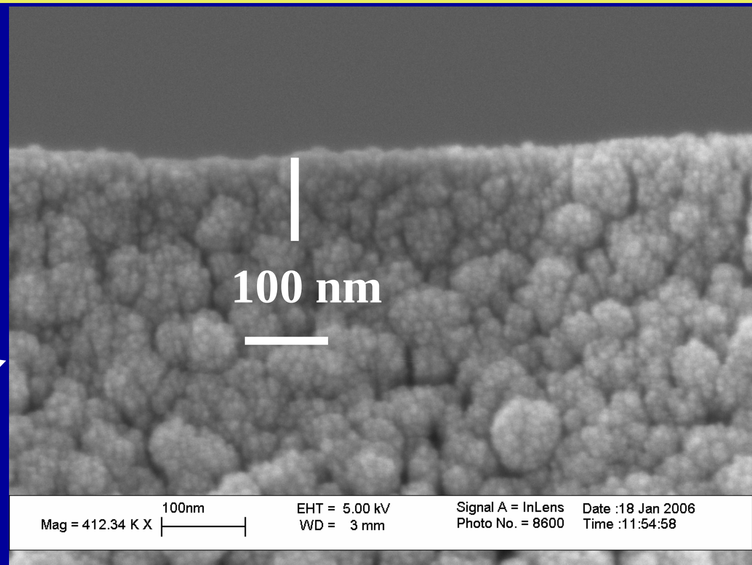
Organic Solvent Nanofiltration
Membrane Characterisation

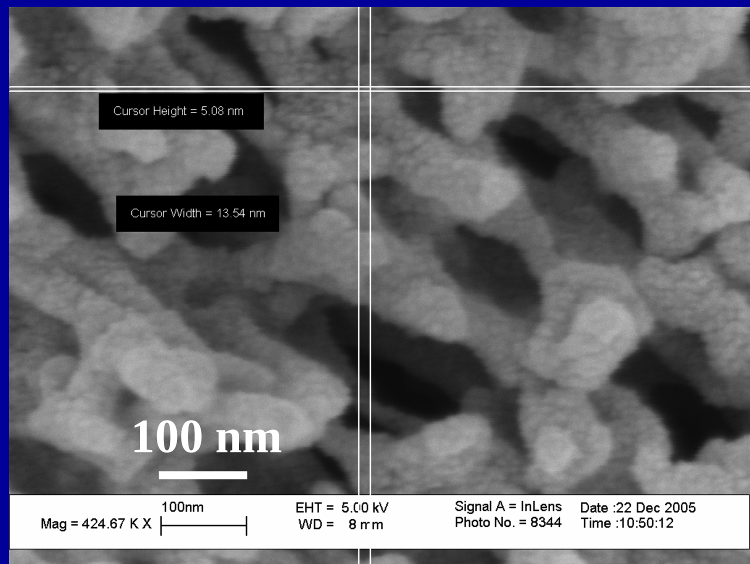
Organic Solvent Nanofiltration Membrane Characterisation

Resulting integrally skinned asymmetric membranes

Can high resolution SEM reveal structure? Do “pores” exist?



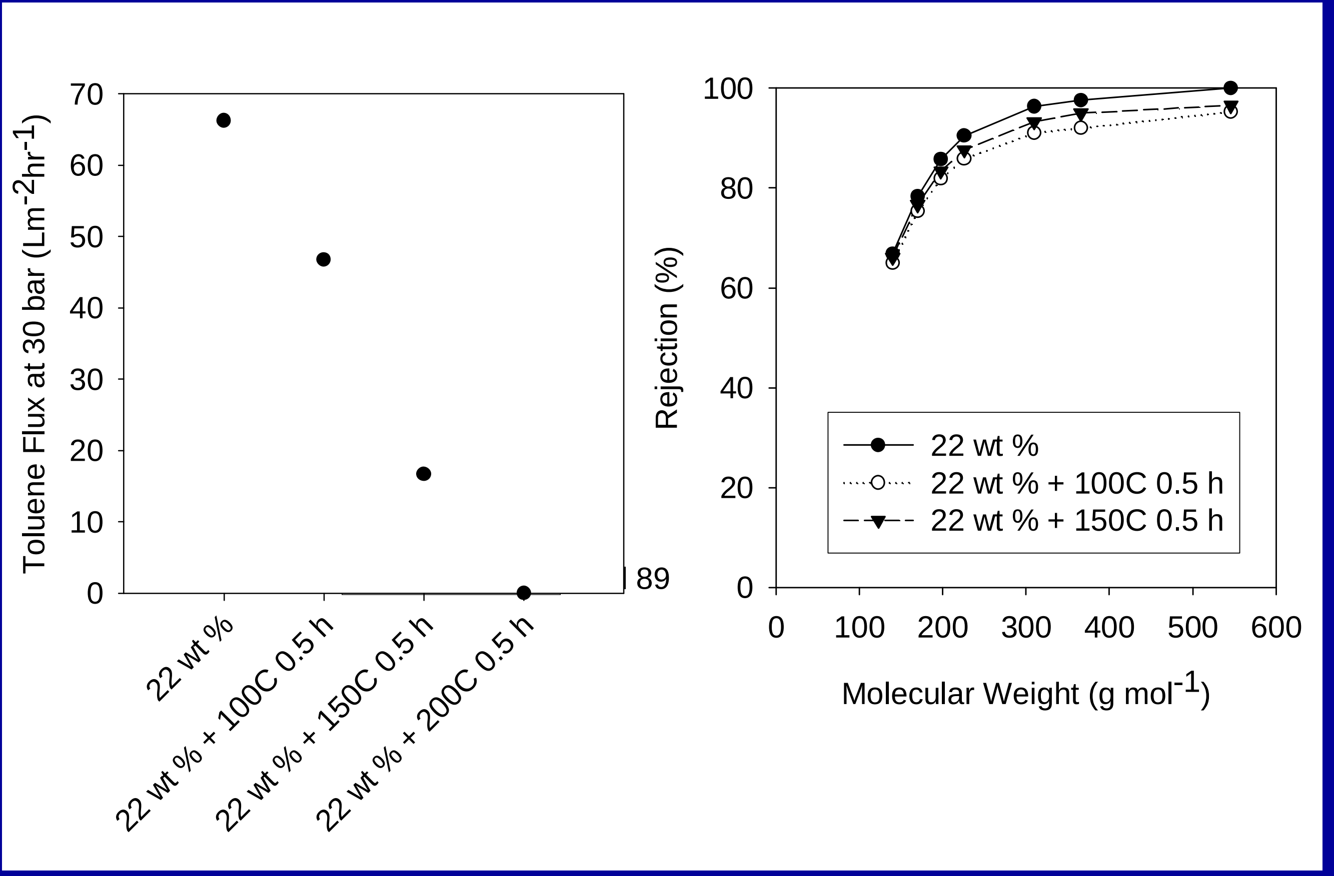




Organic Solvent Nanofiltration Membrane Characterisation

Is the nodular structure viewed under SEM only an artefact of the SEM technique?

Effect of thermal annealing on flux……



Flux and rejection of 22 wt % membranes at different thermal annealing temperatures.

Organic Solvent Nanofiltration Membrane Characterisation

Shows that nodular structure disappears with annealing.

So can see gross changes. Nodular structure exists….

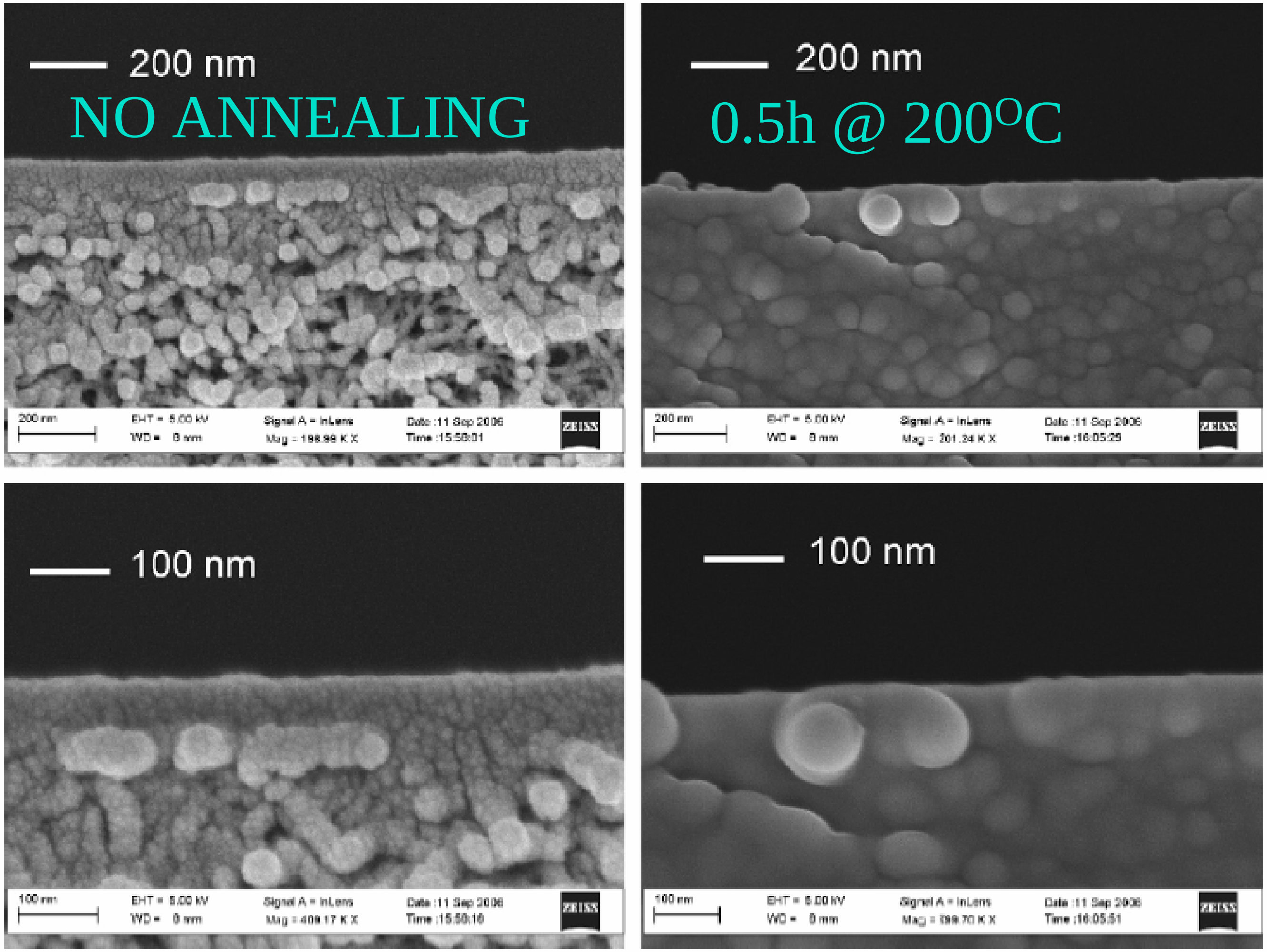
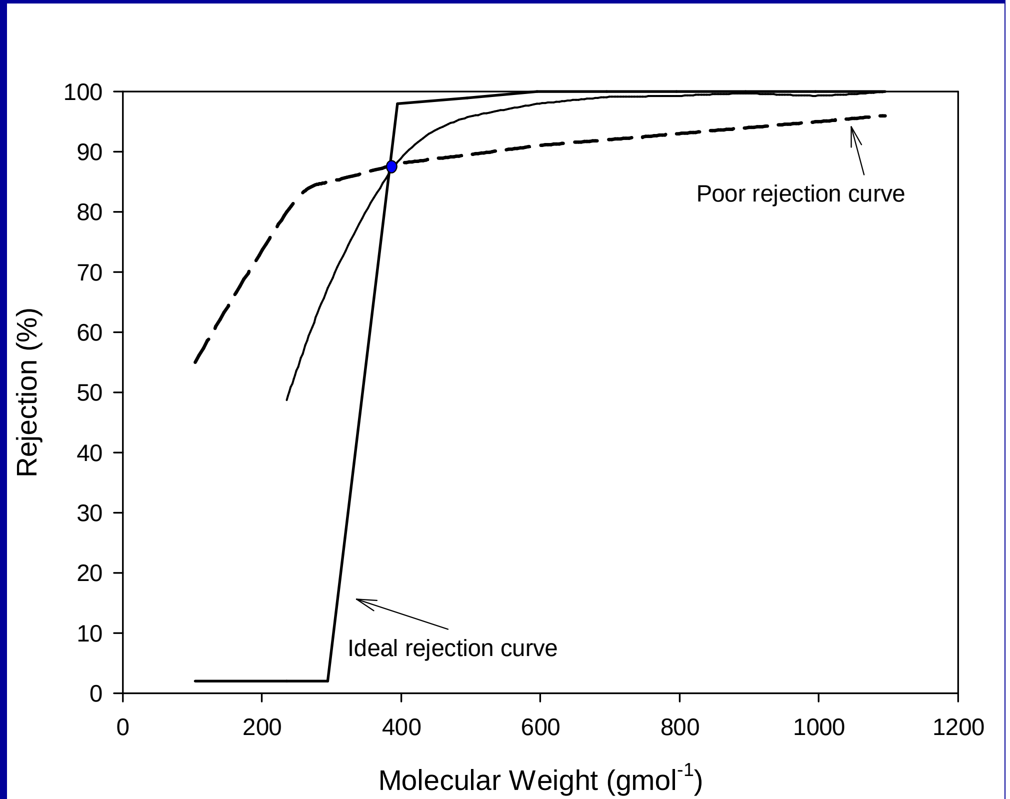


Fig. 12. Membrane morphology before (M2 left) and after annealing (M11) at 200 °C for 0.5 h.

Organic Solvent Nanofiltration Membrane Characterisation

FUNCTIONAL CHARACTERISATION

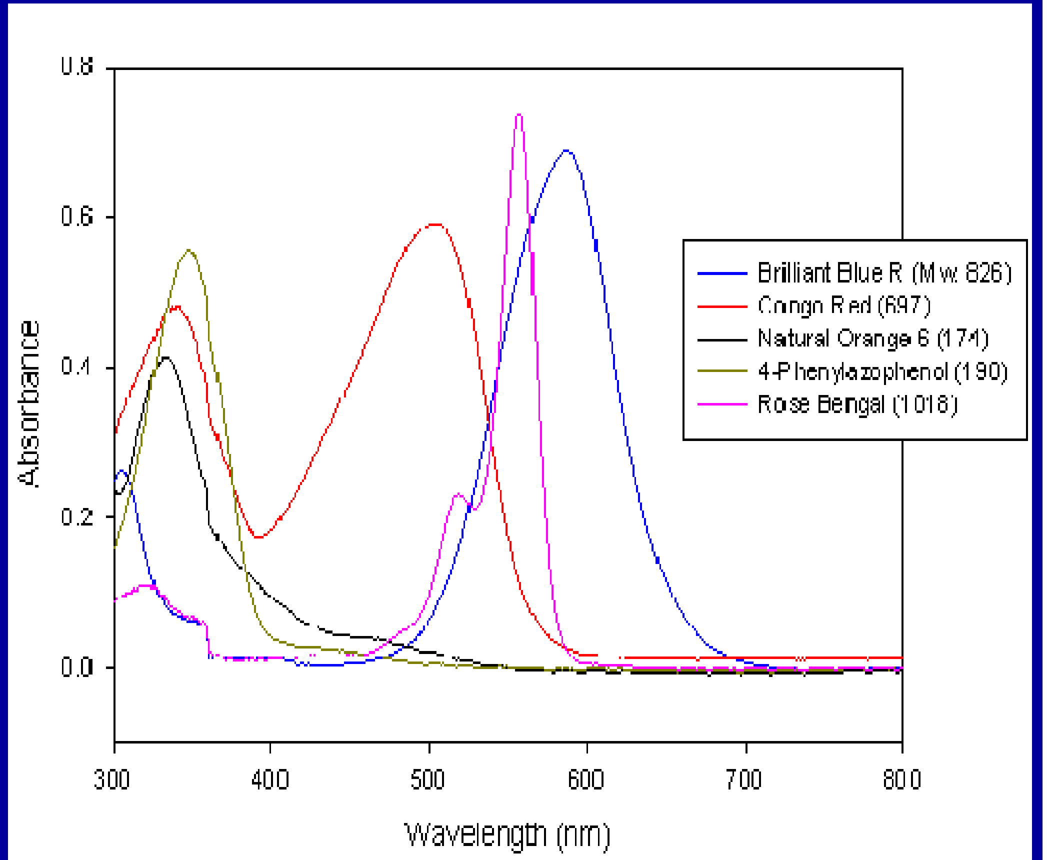
- Many different solvent/solute combinations are used
- Most methods only provide a few or even just one point in the nanofiltration range 200 – 1000 $gmol^{-1}$
- Alkanes, organic dyes, polymers, etc.



Organic Solvent Nanofiltration Membrane Characterisation

DYES

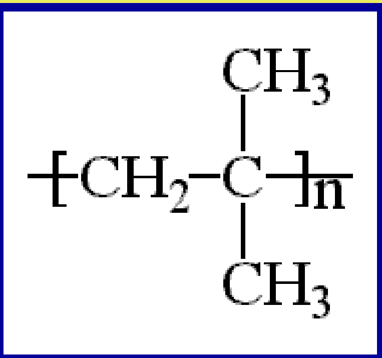
- Quick analysis using UV spectrophotometer
- Changes in concentration clearly visible
- Many dyes are charged or acidic
- Various non-uniform structures
- Spectrum overlap



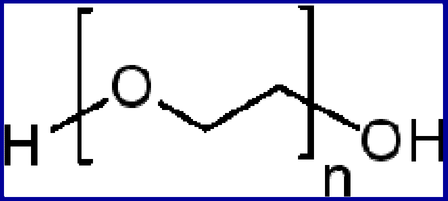
UV spectrum for dyes with various MW

Organic Solvent Nanofiltration Membrane Characterisation

- Homologous polymers with steadily increasing MW
- eg: polyisobutylene, polyethylene glycol, sugars etc.
- Analysis with size exclusion chromatography requires de-convolution of overlapping peaks



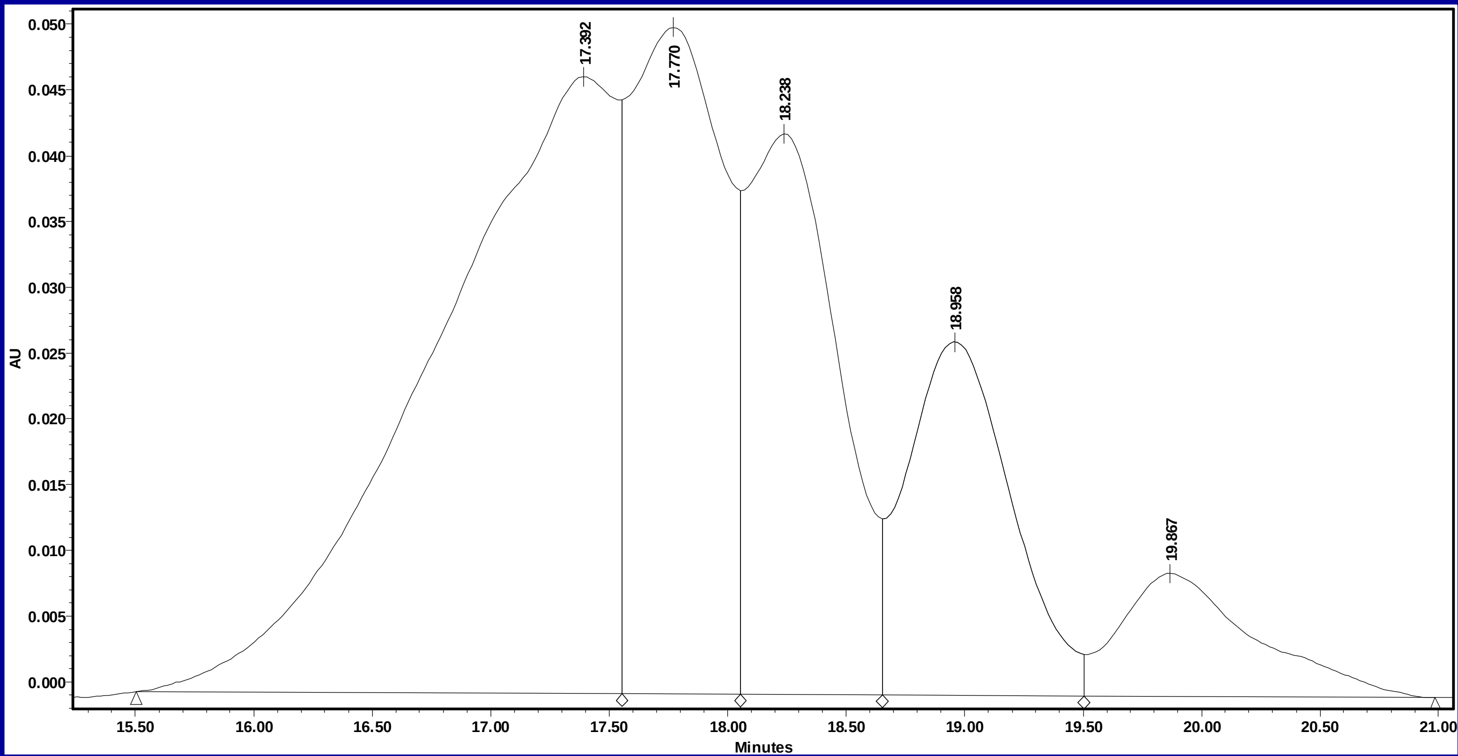
Polyisobutylene



Polyethylene glycol

Organic Solvent Nanofiltration Membrane Characterisation

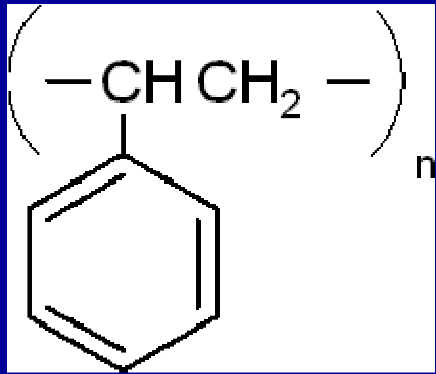
- Typical size exclusion chromatography trace of polystyrene



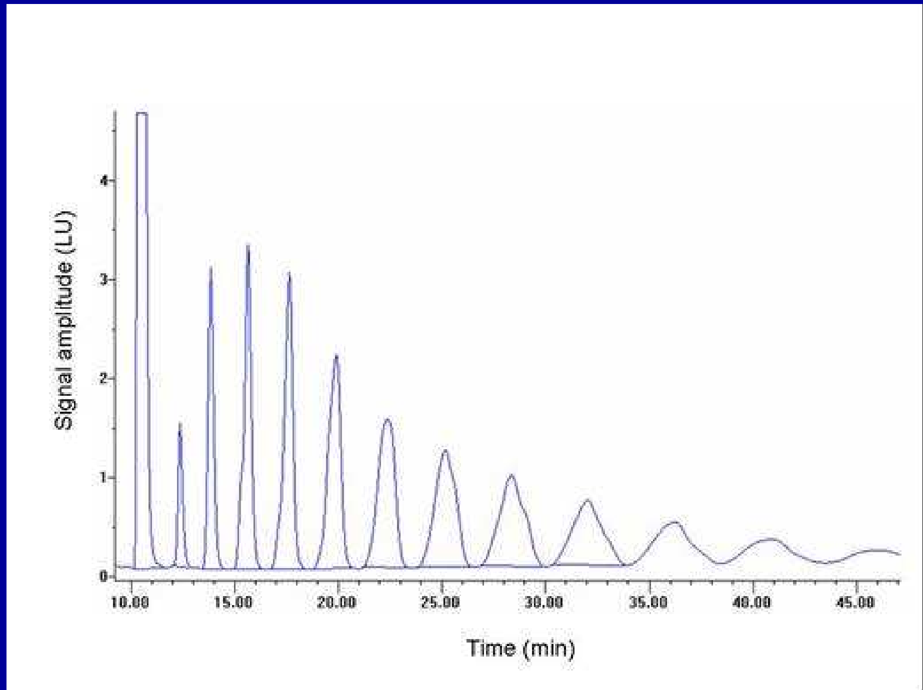
- Overlapping peaks require complex calculations to separate each species

Organic Solvent Nanofiltration Membrane Characterisation

- We have developed a simple and reliable method using styrene oligomers obtained from Polymer Labs, UK
- Styrene oligomers easily detected using UV-vis at a wavelength of 264 nm

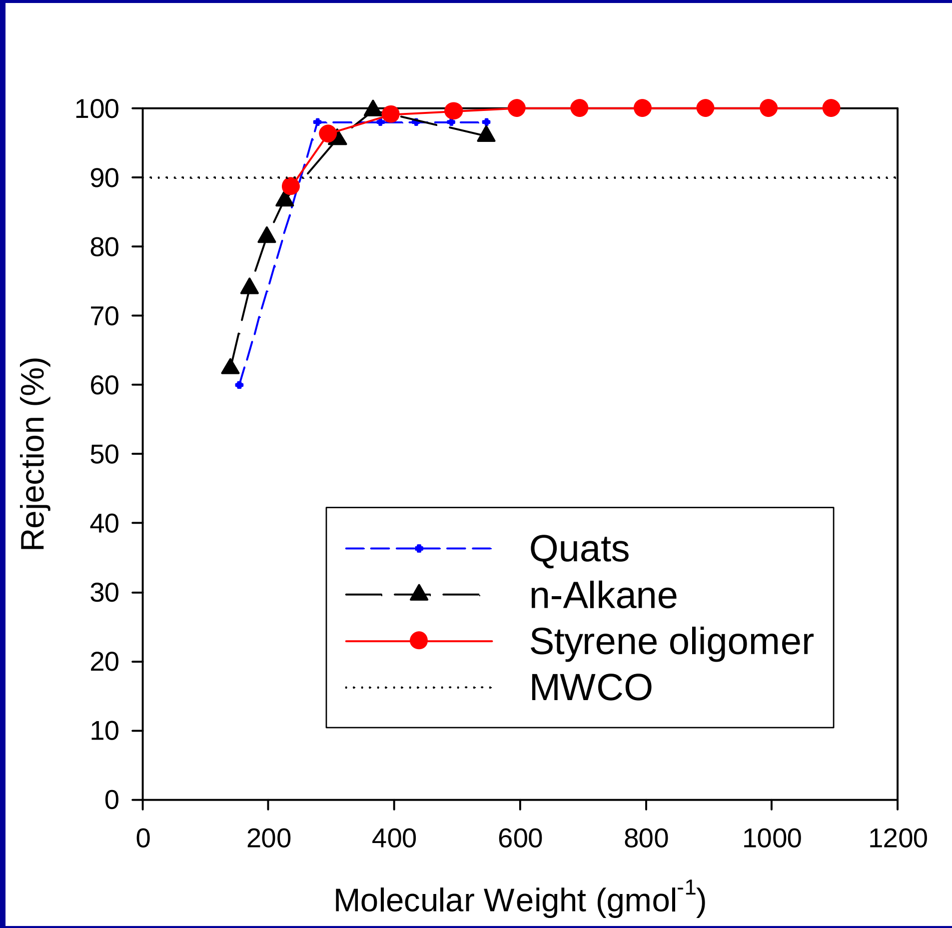


- Separation of test species achieved using liquid chromatography employing a conventional reverse phase C18 column
- Mobile phase H_2O to tetrahydrofuran 35:65 by volume



Organic Solvent Nanofiltration Membrane Characterisation

- Validation of oligostyrene test comparing to other established methods and results
- Filtrations performed in toluene @ 30 bar pressure
- STARMEM™122 has been characterised across the entire nanofiltration range



Molecular weight cutoff curve for ST 122

Organic Solvent Nanofiltration
OSN Applications

"The best way to have a good idea is to have a lot of ideas" – Linus Pauling

Potential Applications of OSN

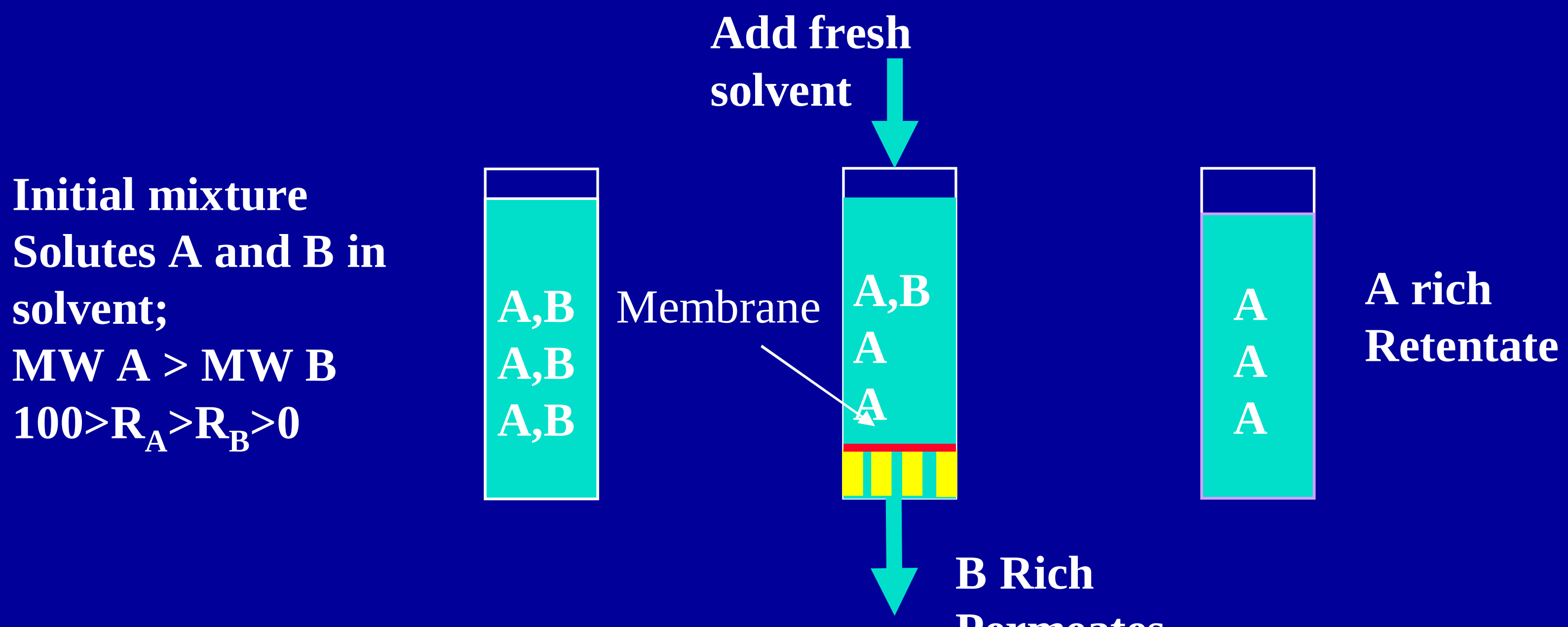
- Concentration of Solutes in Solvents
- Solvent Exchanges (high-boiling solvent to a low boiling solvent)
- Purifications – separation of high and medium MW species in solvent
- Catalyst Recycle and Re-Use
  - Phase transfer catalysts (re–use catalysts, separate catalysts from products)
  - Organometallic catalysts recovery and reuse (re-use ligands, avoid metal contamination of product)
  - Ionic Liquid Mediated Catalytic Reactions
- Dynamic Kinetic Resolution (separated catalyst systems)
- Chiral separations (host-guest interactions)
- Biotransformations
- Natural Oils Processing

Organic Solvent Nanofiltration in Chemical Processes
OSN Applications

Constant Volume Membrane Purification

Solute (API) is added as a batch at start of process

Solvent is added continuously to make up for solvent permeating across the membrane – therefore volume in system stays constant



Organic Solvent Nanofiltration
OSN Applications

Constant Volume Diafiltration to separate model active pharmaceutical ingredient (API -Yellow) from model large impurity ie dimer/trimer (Blue). Solvent is Methanol

FEED – mixture of blue and yellow dyes

Organic Solvent Nanofiltration
OSN Applications

- Example – Separation of coloured impurity from API at Astra Zeneca by OSN (The Chemical Engineer, August 2006)
  - 3(a) Starting material containing high MW colour compound
  - 3 (b) Downstream issues caused by impurities
  - Nanofilter solution so that API passes through membrane with solvent, impurity is retained
  - 3 (c) Product after OSN purification – nice white powder!

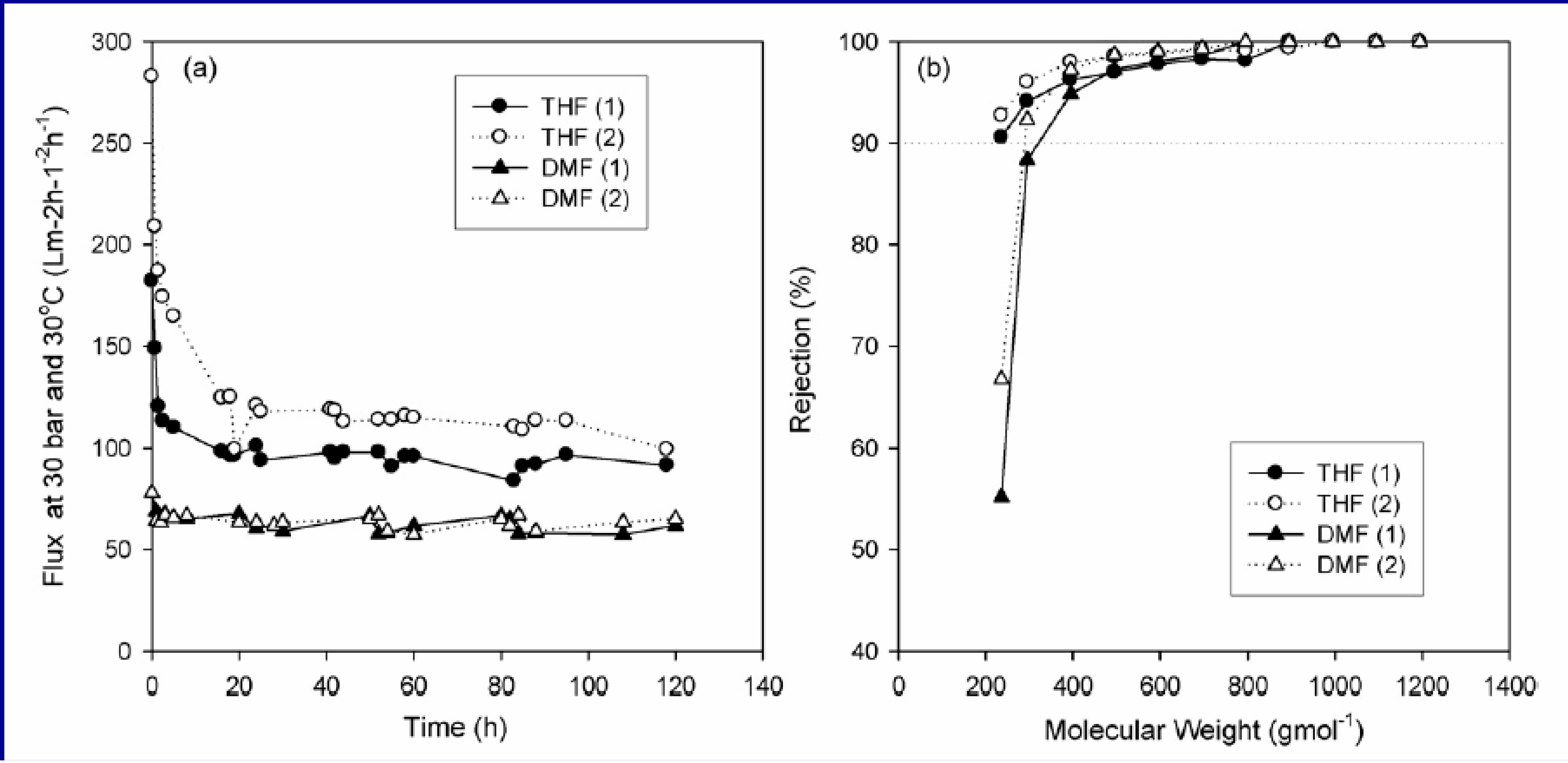
Organic Solvent Nanofiltration
Next Generation Membranes

Challenges for new membranes

- Membranes Stable in “tough” solvents eg acetone, DCM, DMF, THF, NMP
- Tunable molecular weight cutoff profiles

Organic Solvent Nanofiltration
Next Generation Membranes

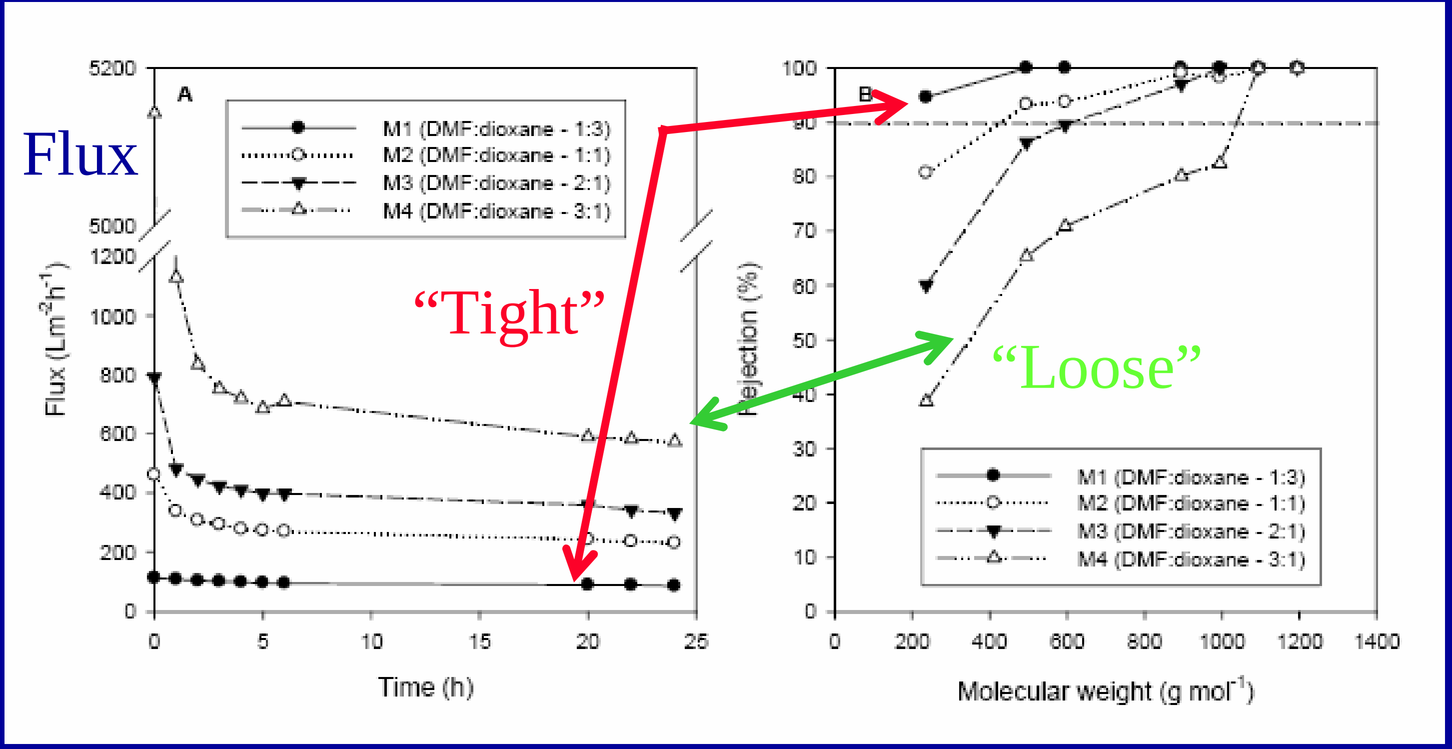
Post-formation cross-linking of polyimide membranes Resulting membranes have excellent stability and flux in "tough" solvents such as DMF! (data below collected at 30 bar, 30^{o}C)



Organic Solvent Nanofiltration
Next Generation Membranes

Tunable Molecular Weight Cutoff Profile

- Found that the main variable which could provide significant changes in the profile was the solvent/volatile co-solvent ratio
- Using P84 and DMF (solvent) Dioxane (co-solvent)



Organic Solvent Nanofiltration Technology Transfer

SO WHAT?

Economist.com

May 24th-30th 1997 Economics Focus

Playing godmother to invention

"Many countries spend heavily to foster research and development. But inventing new technology is less important than using it effectively."

USE IT – OR LOSE IT!

US005585004A

United States Patent [19] | [11] **Patent Number:** **5,585,004**

Livingston | [45] **Date of Patent:** **Dec. 17, 1996**

.... 210/656
.... 568/454

[73] Assignee: **Imperial College of Science Technology & Medicine**, London, Great Britain

[21] Appl. No.: **211,159**

[22] PCT Filed: **Sep. 18, 1992**

[86] PCT No.: **PCT/GB92/01719**

§ 371 Date: **Jun. 10, 1994**

§ 102(e) Date: **Jun. 10, 1994**

[87] PCT Pub. No.: **WO93/06045**

PCT Pub. Date: **Apr. 1, 1993**

[30] **Foreign Application Priority Data**

Sep. 18, 1991 [GB] United Kingdom 9119955

[51] **Int. Cl.**[6] **B01D 61/00**; B01D 63/02

[52] **U.S. Cl.** **210/651**; 210/321.27; 210/500.21; 210/500.23; 210/909

[58] **Field of Search** 210/321.87, 500.21, 210/615, 651, 909, 500.23

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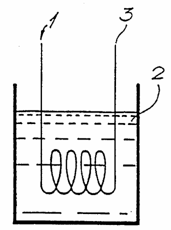
Primary Examiner—Robert A. Dawson
Assistant Examiner—Kenneth M. Jones
Attorney, Agent, or Firm—Fay, Sharpe, Beall, Fagan, Minnich & McKee

[57] **ABSTRACT**

A method of reducing the concentration of at least one organic compound present in an aqueous feedstock, wherein said feedstock is supplied to one side of a substantially water-insoluble selectively permeable polymeric sheet or tubular membrane whose permeability to the or each said organic compound exceeds its permeability to chloride ion whilst simultaneously maintaining in contact with the other side of said membrane an aqueous reaction medium containing biologically active reaction means capable of reacting with said at least one compound after it permeates through the wall of the tubular membrane. Apparatus, preferably enclosed, for carrying into effect the method is also disclosed and permits treatment of waste waters containing volatile organic compounds. Modular bioreactor apparatus in the form of a cartridge containing a bundle of polymeric membrane tubes is also disclosed.

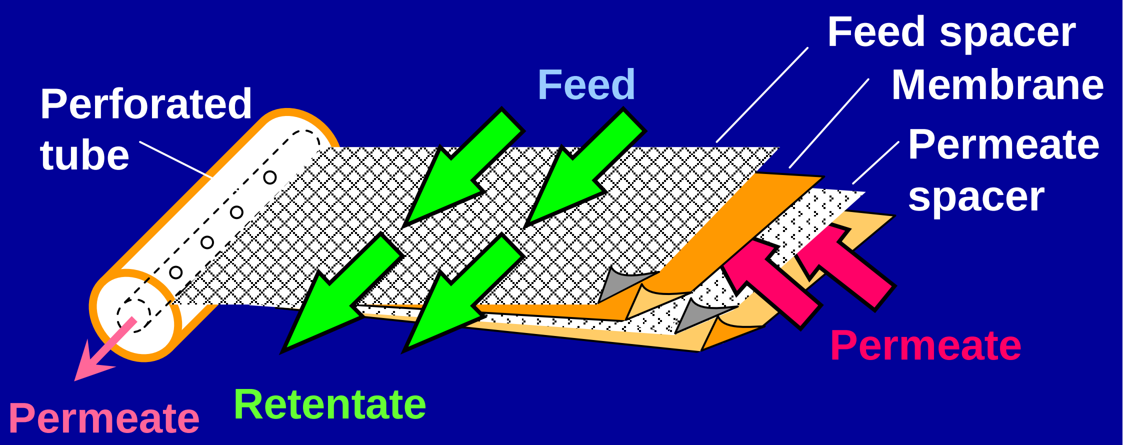
36 Claims, 6 Drawing Sheets



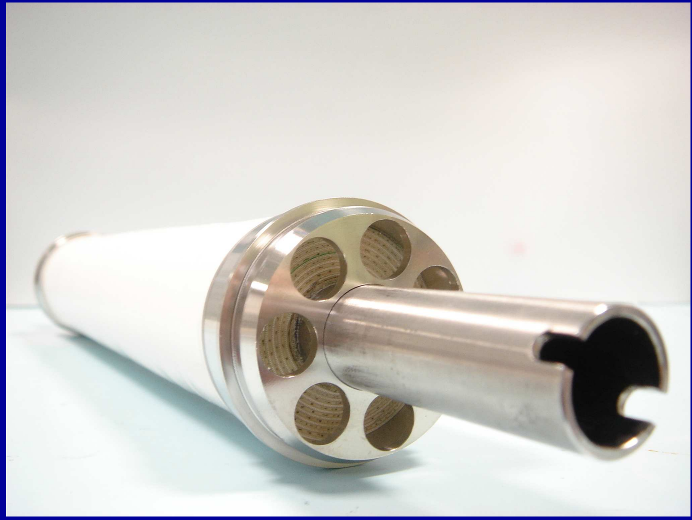
Organic Solvent Nanofiltration OSN Commercial

- Membrane Extraction Technology – started as Spin Out Company from Imperial College in 1996, now based in West London
- MET delivers “innovation to operation” on new separation technologies (equipment, process development, membranes)
- Technology Platforms
  - Selective extraction of organics from aqueous streams
  - Molecular separation in organic solvents (Organic Solvent Nanofiltration, OSN)
- MET provide WR Grace STARMEM^{TM} series of polyimide OSN membranes to chemical and pharmaceutical industry
- Crosslinked membranes licensed to MET for commercialisation

Organic Solvent Nanofiltration
OSN Commercial



- Scale up membrane formation and develop appropriate spiral module fabrication
- DuraMem™ range of highly stable OSN membranes launched by MET in 2008
- First installation made at process scale in "large pharma" plant April 2008



Organic Solvent Nanofiltration
SUMMARY

- Organic solvent nanofiltration (OSN) has already reached large scale in refining operations
- Major challenges remain for technology to make paradigm shift
- We are still seeking ways to observe the detailed physical nanoscale structure of separating layer
- Transport mechanisms still under investigation
- A new generation of highly stable membranes with tuneable molecular weight cutoff curves – DuraMem™ - has been created

Organic Solvent Nanofiltration Acknowledgements

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- Lloyd S. White W.R.Grace and Co, MD, USA; Craig Wildemuth Grace Davison Membranes, CO, USA
- UK Engineering and Physical Sciences Research Council, European Commission