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EUROMEMBRANE
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OSNF MEMBRANES ON LOW COST HIGH QUALITY CERAMIC SUPPORTS FOR HIGH TEMPERATURE APPLICATIONS

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SUSTAINABLE TECHNOLOGIES FOR INDUSTRIAL PROCESSES

PETTEN

Towards a CO_2-neutral **INDUSTRY**

GOALS 2050

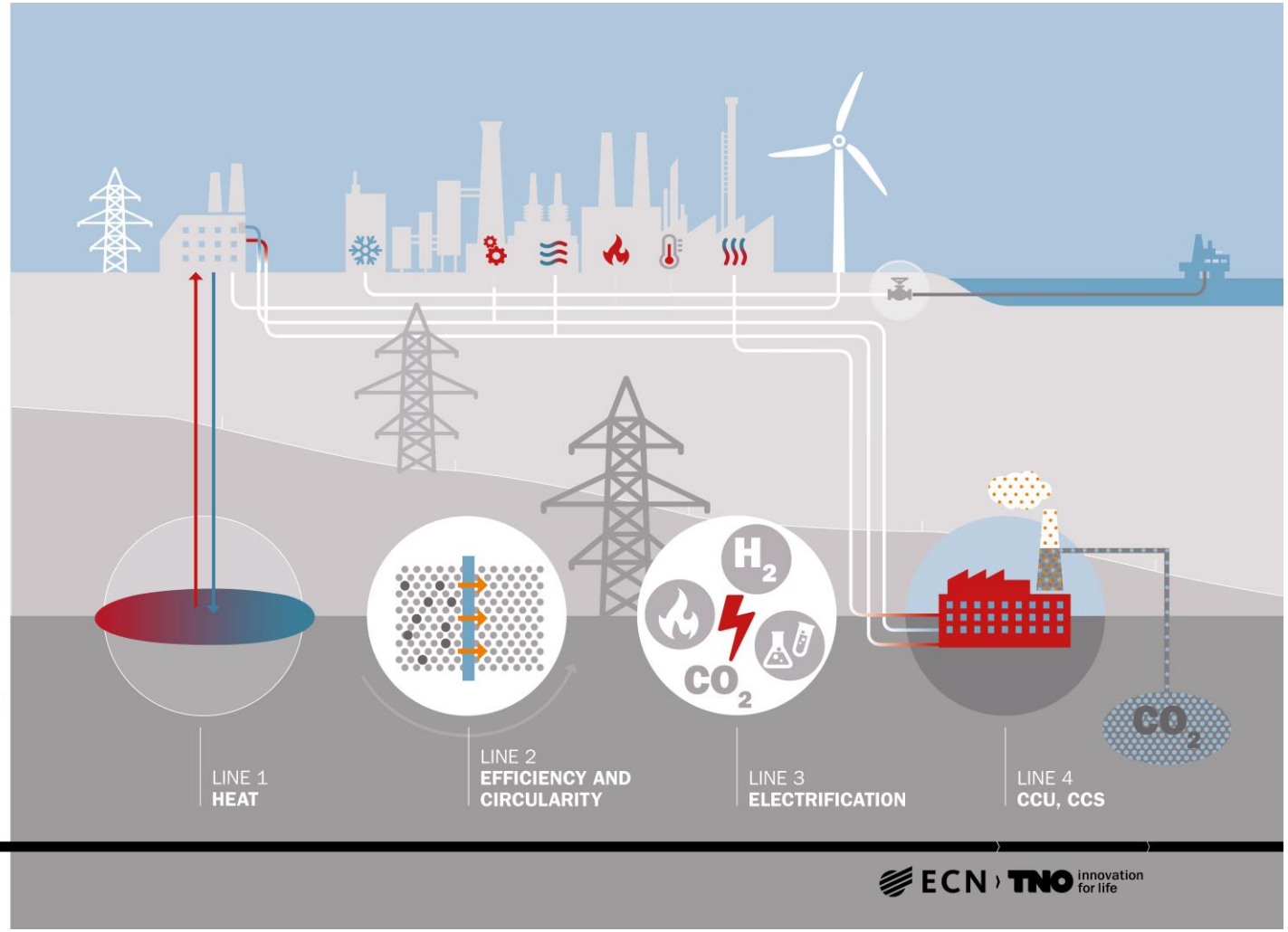
ALL INDUSTRY HAS A **ZERO NET CO_2 EMISSION**

SUSTAINABLE SUPPLY AND (RE-)USE OF INDUSTRIAL HEAT

> 40% PROCESS EFFICIENCY IMPROVEMENT

COMPLETE ELECTRIFICATION

CO_2 CAPTURE CONVERSION AND STORAGE



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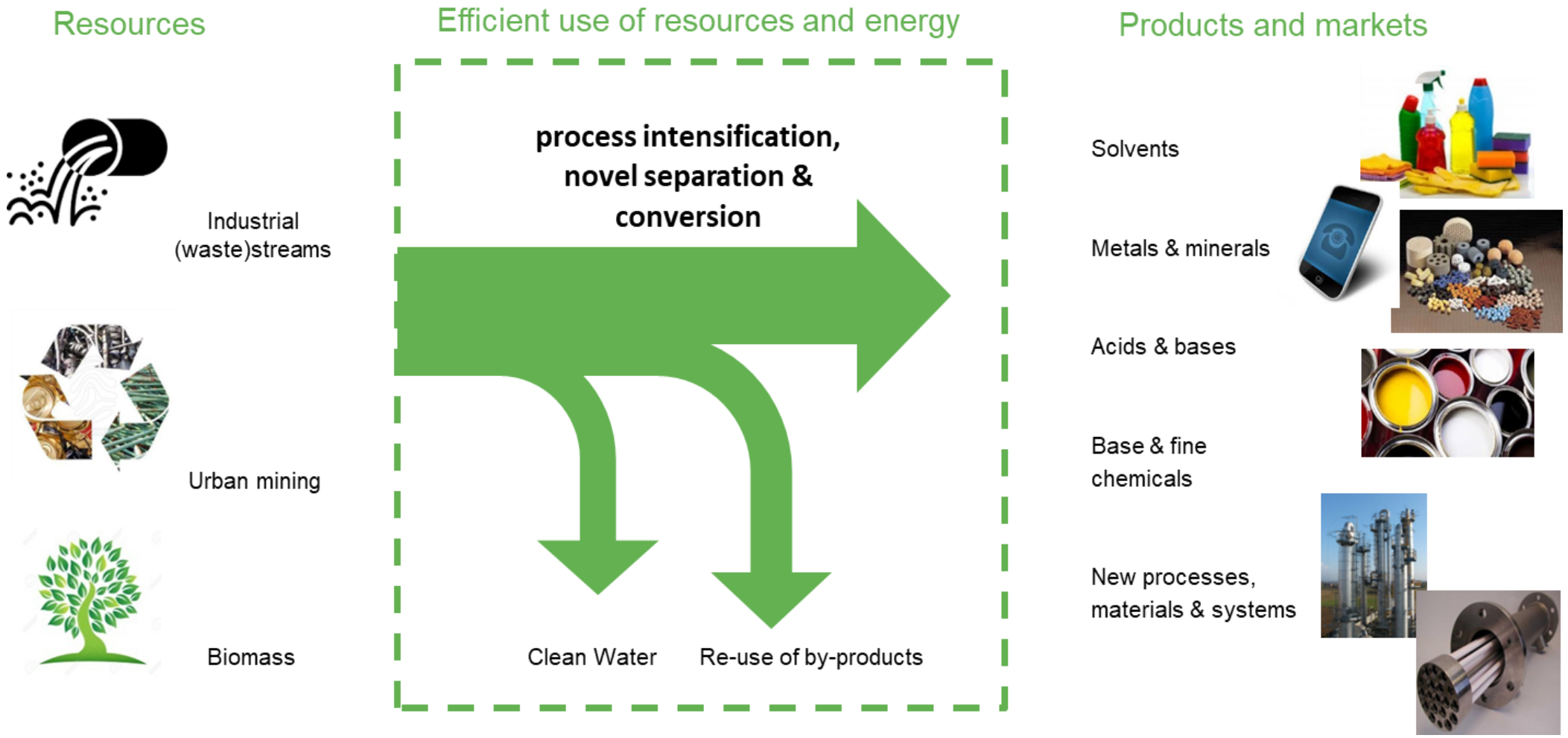
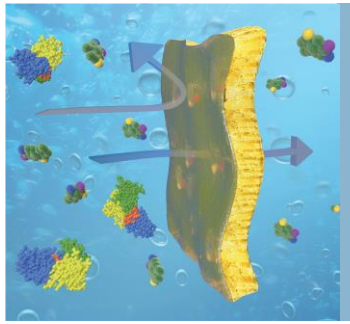
EFFICIENT SEPARATION IS KEY TO VIABLE PROCESSES

IMPROVING PROCESS & RESOURCE EFFICIENCY

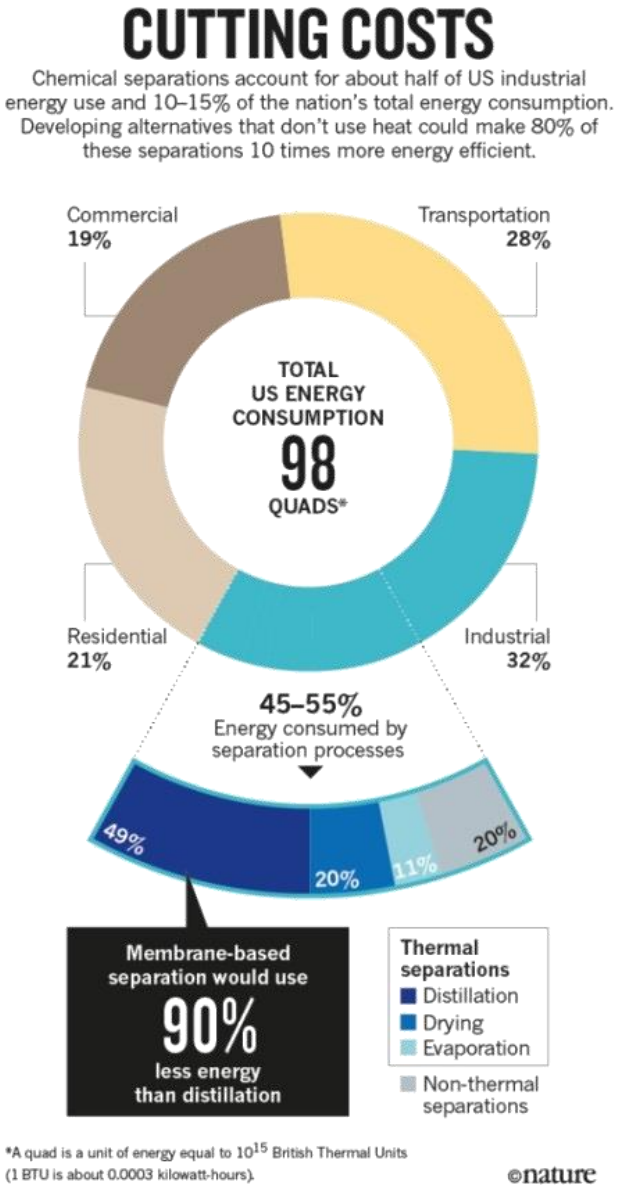


EFFICIENT SEPARATION TECHNOLOGY
USING MEMBRANES

- Within process industry >25% of the energy used for (thermal) separations
  - Mainly distillation is used (low efficiency)
- Organic solvent nanofiltration (OSNF): 40% more efficient separation processes
  - Energy saving potential of 2 - 8 PJ/year in NL
  - Application in (petro)chemical, food, biorefinery and pharma industry



OSNF: pressure driven membrane (pore size 10^{-3} µm) separation technology to separate molecules or small particles from an organic solvent.

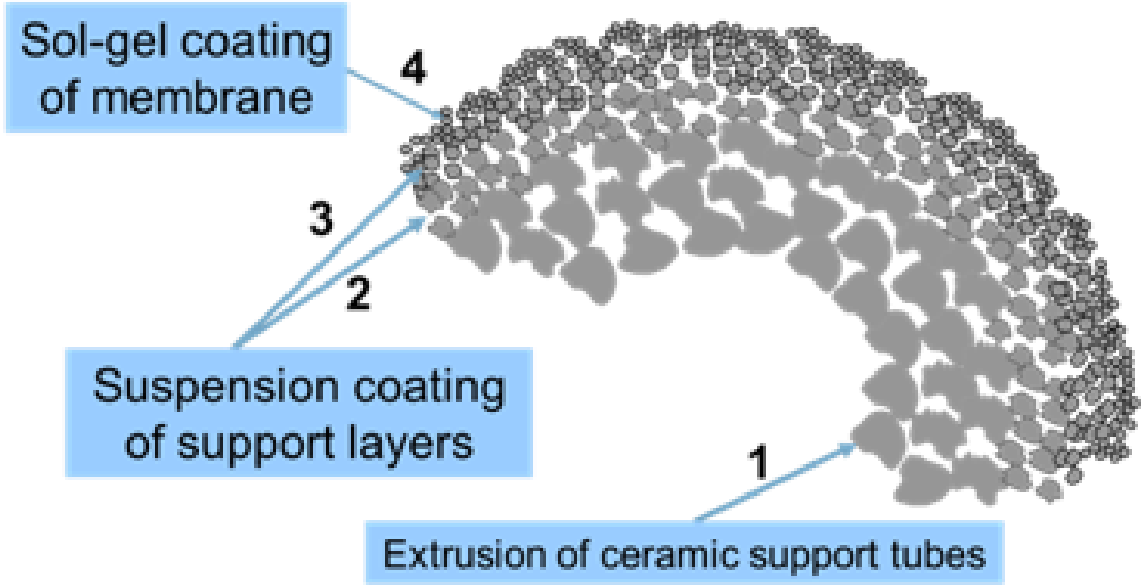


Scholl and Liverly, Nature (2016), 532,435-437

MEMBRANE TECHNOLOGY AT TNO

DEVELOPMENT OF (HYBRID) CERAMIC MEMBRANES

- Ceramic support
  - High chemical and thermal stability
  - Suspension coating between support tube and top-layer
- Top layer for selective separation:
  - Polymer coating top layer, or
  - Sol-gel (ceramic) chemistry
- Different recipes to tune properties

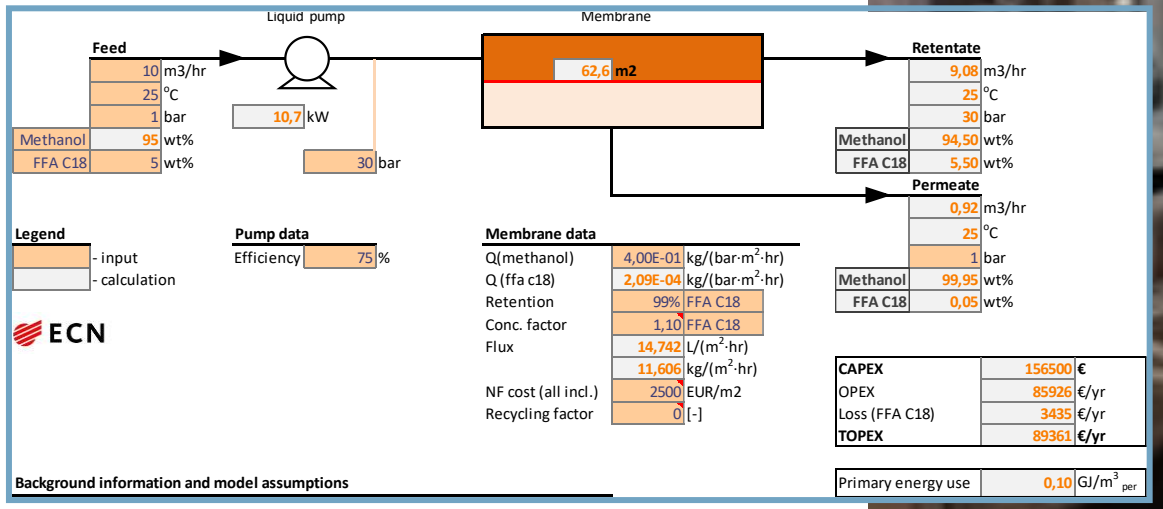


MEMBRANE TECHNOLOGY AT TNO

TESTING AND IMPLEMENTATION OF MEMBRANES

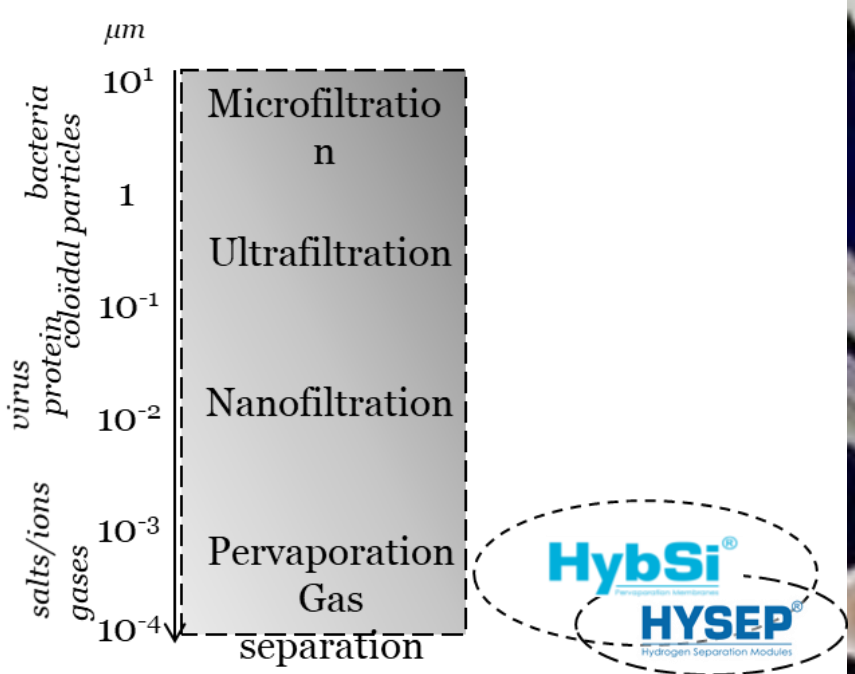
- Testing and evaluating in selected processes:
  - Pore size, affinity, layer thickness, etc.
  - Fluxes and retentions with PEG model system (→ MWCO)
  - Evaluation in defined model mixtures
  - Testing in real industrial mixtures at partners

- Techno-economic evaluations
  - Model for calculating membrane area, OPEX and CAPEx
  - Comparison to conventional process costs and performance



MEMBRANE TECHNOLOGY AT TNO
TYPES OF SEPARATION

- Pervaporation (vapour permeation)
  - HybSi®
- Gas separation
  - E.g. separation enhanced MeOH synthesis (CONVERGE project)
  - 30/11 10:30 - 11:00: Marija Saric (Harlekin)
- Organic solvent nanofiltration (OSNF)



Pervaporation
= permeation + evaporation
= selective evaporation of liquids via a membrane
= much more energy efficient than distillation

SCALE-UP & REDUCING COSTS MEMBRANES
THE COSMOS PROJECT

- Scale-up hybrid silica (HybSi) and polymer based OSNF membranes using low cost, high quality (hollow fiber and multi-channel) ceramic supports for 2 applications (TRL 4 → 6):
  - Polycyclic aromatics (PCA) removal from waxy hydrocarbon stream : retention of 200 Dalton (T≤140°C)
  - Edible oils from acetone: retention of 800 Dalton
- Target permeance (solvent) ≥ 1 L/m^{2}hbar
- Inexpensive membranes
  - Hollow fibers and multi-channel (coating on inside)
  - Reduce cost by reducing layers

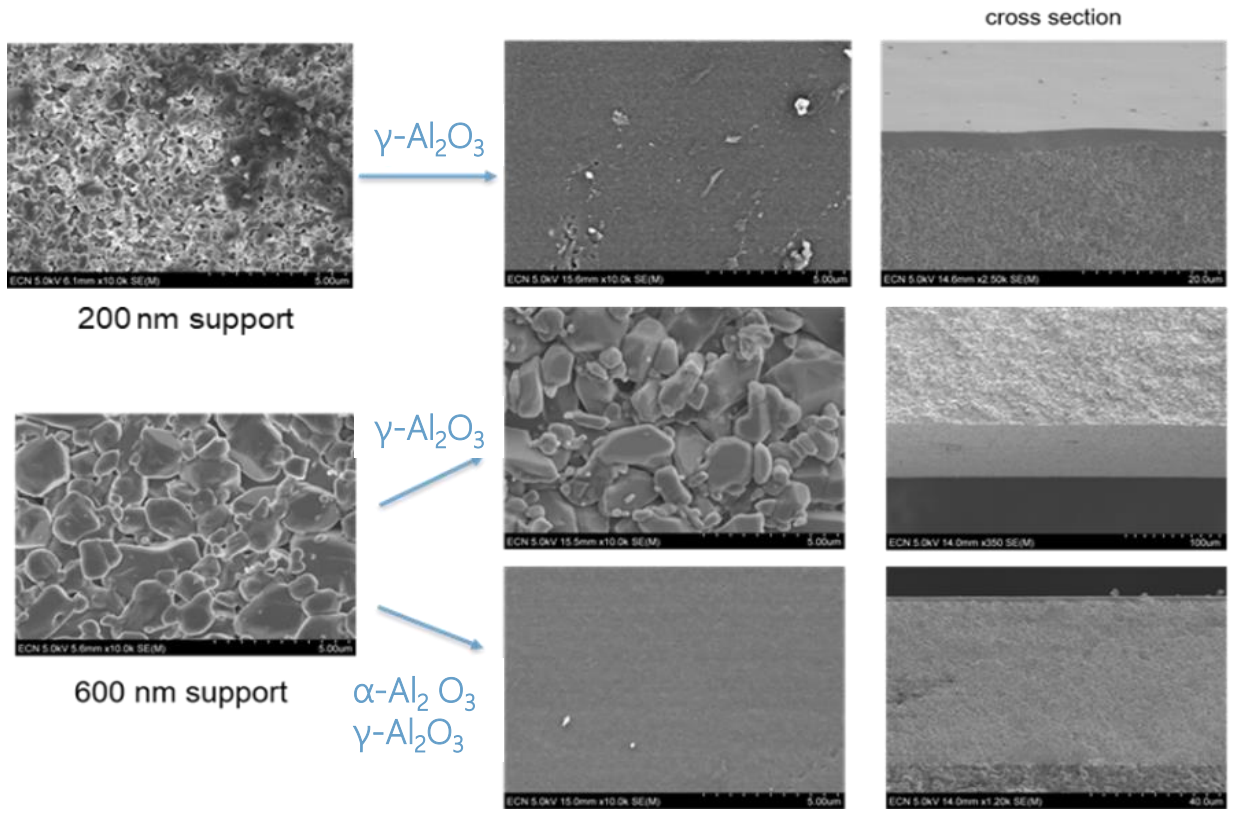
Organic solvent nanofiltration membranes on low cost ceramic supports (COSMOS)

UNIVERSITY OF TWENTE. CoorsTek Institute for Sustainable Process Technology TNO

SUPPORT & MEMBRANE DEVELOPMENT
INTERMEDIATE LAYERS COATING

- Supports with pore sizes of 0.2 and 0.6 µm were selected & improved (membrane strength & flow behaviour)
- Intermediate layers with good quality applied
  - Characterized by SEM, Helium test, bubble point
- To allow for scale-up coating on inside

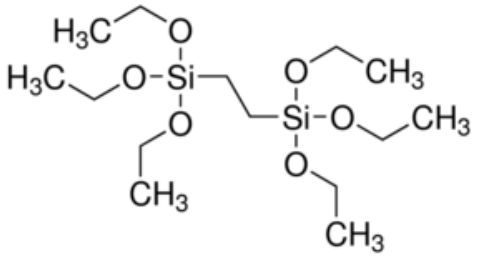
Mass production of ceramic tubes



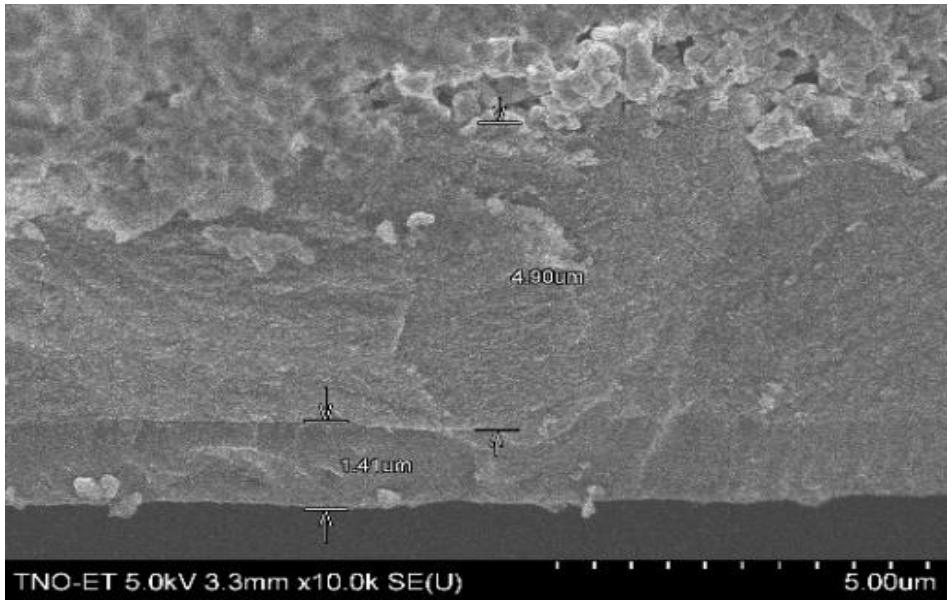
SUPPORT & MEMBRANE DEVELOPMENT

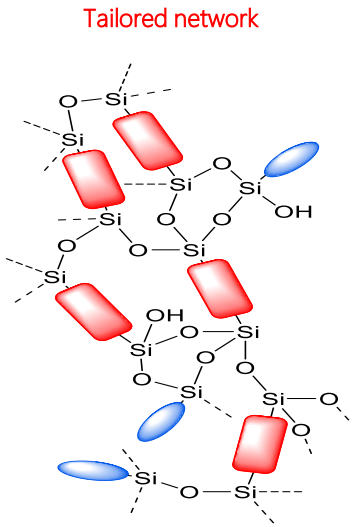
TOP-LAYERS HYBRID SILICA

- Hybrid silica (BTESE) top layer:
  - CTAB as templating agent to enlarge the pores
  - Selective layer succesfully applied on inside 200 nm support + γ-Al_2O_3
  - Characterized by SEM, Helium test, bubble point

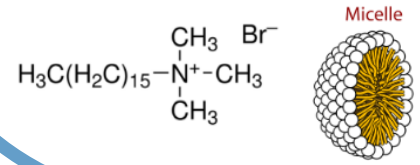


BTESE





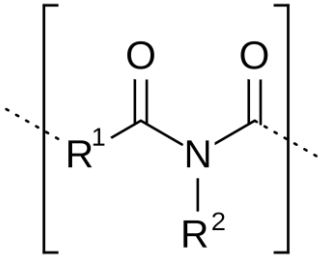
Tune pore size (selecticity and permeance), e.g. with CTAB



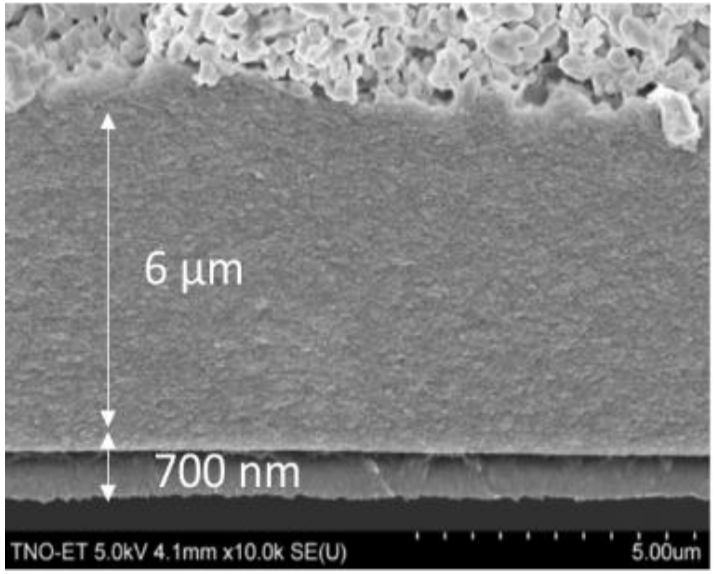
SUPPORT & MEMBRANE DEVELOPMENT

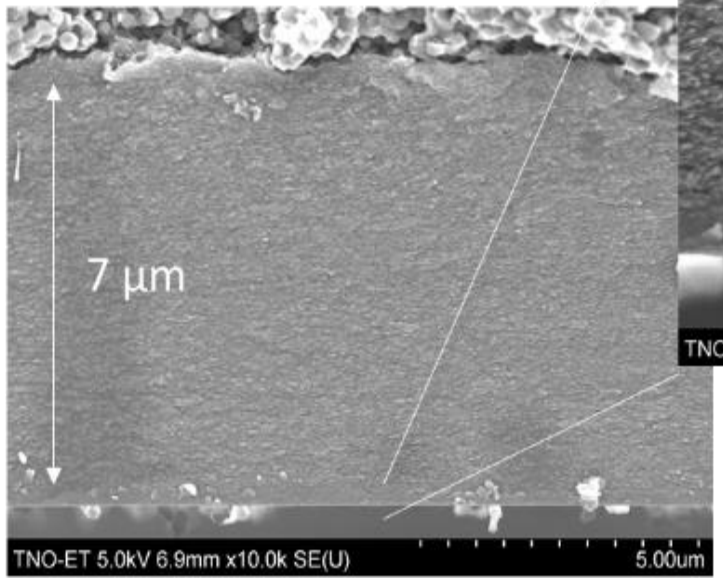
POLYMERIC TOP-LAYERS

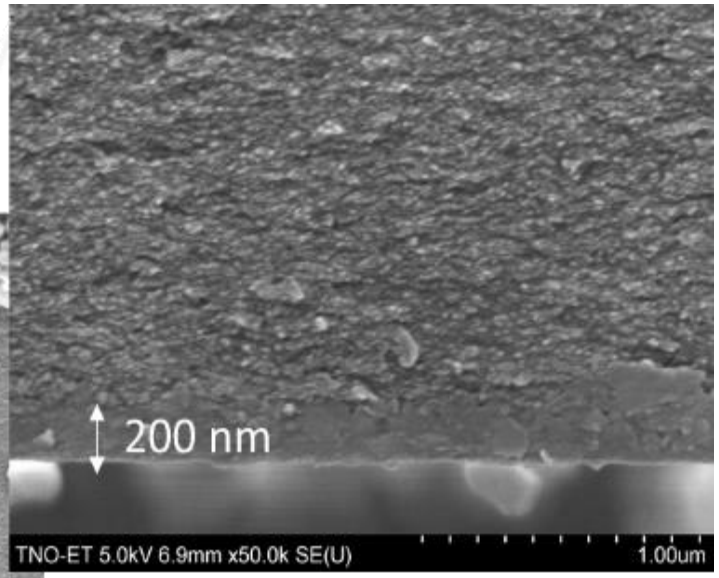
- Selective layer succesfully applied on inside 200 nm support + γ-Al_2O_3
  - 1 wt% PI
  - 2 wt% PI
  - Characterized by SEM, Helium test, bubble point



PI

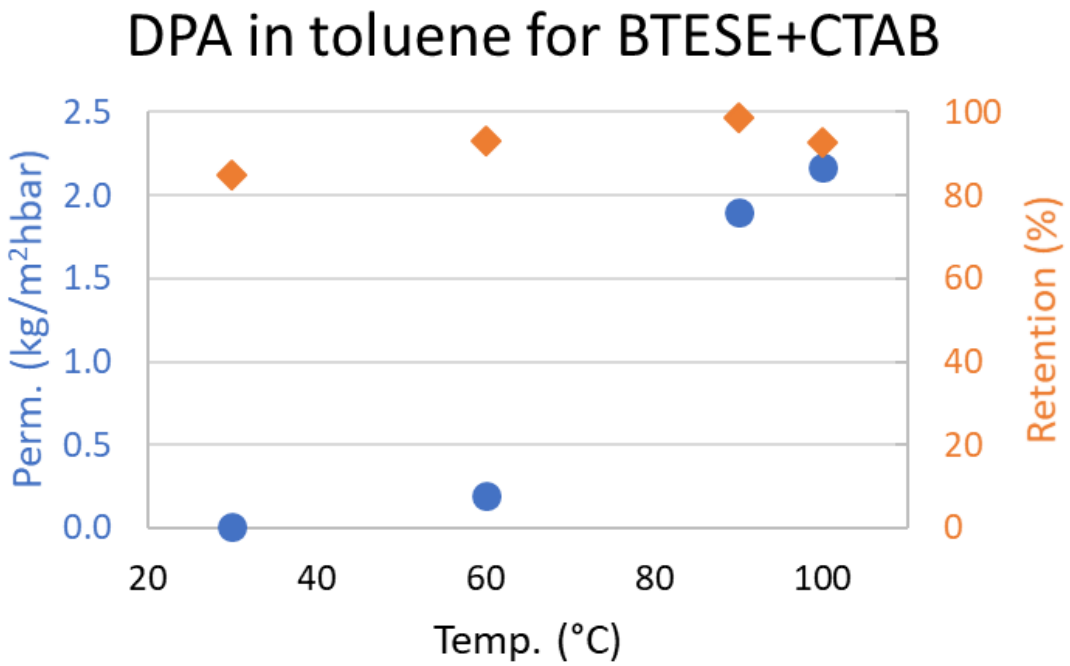




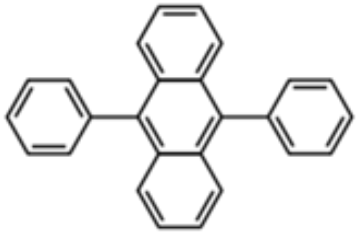


HIGH TEMPERATURE MEMBRANE TESTING
MODEL MIXTURE AROMATICS-ALIPHATICS

- Feed = 100 ppm of 9,10 diphenyl anthracene (DPA, 330 g/mol) in toluene



TEA: PCA removal from waxy hydrocarbon stream economically feasible with high concentration factor!



DPA, mw = 330 Da

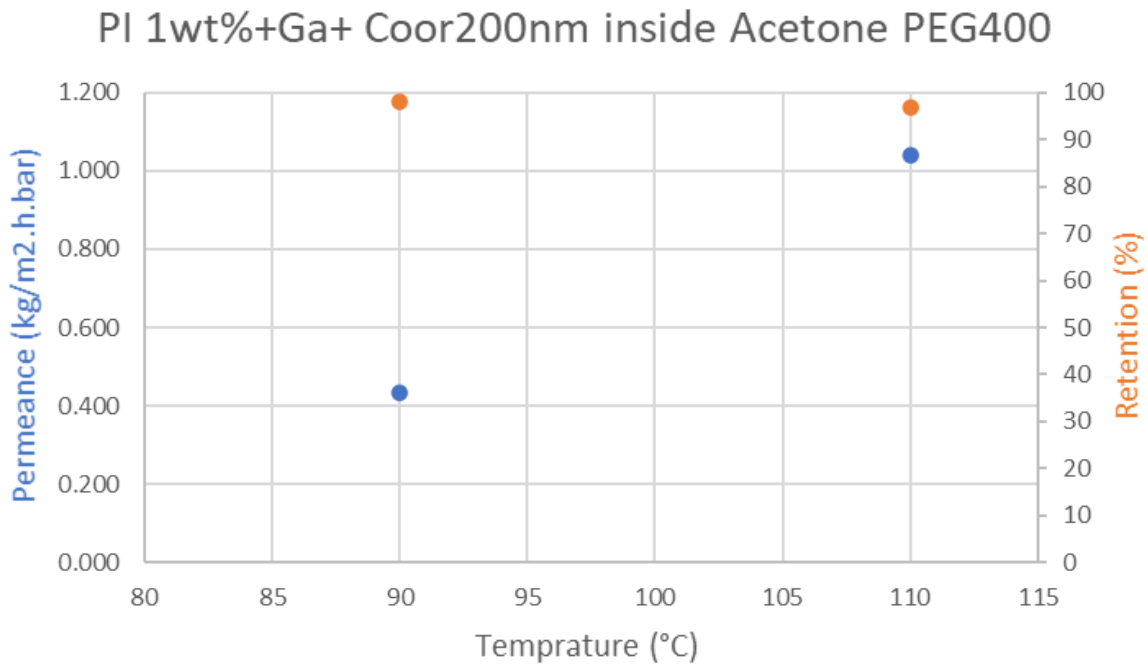
- The permeance strongly increases with elevated temperatures at 100 °C (retention > 95% for DPA).
  - Reproducibility needs to be improved.
  - The permeance change vs. temperature is reversible (tested for toluene & acetone)

PI TOP-LAYERS

PI FOR EDIBLE OIL AND PCA REMOVAL APPLICATION

- Good retention for PEG1000 & 400 in acetone at higher temperature
- High permeance of 1 kg m^{-2} h^{-1} bar^{-1} in acetone at 110°C

- Good retention for DPA (85%) in Toluene at higher temperature, but low permeance of 0,06 kg m^{-2} h^{-1} bar^{-1} in Toluene at 130 °C



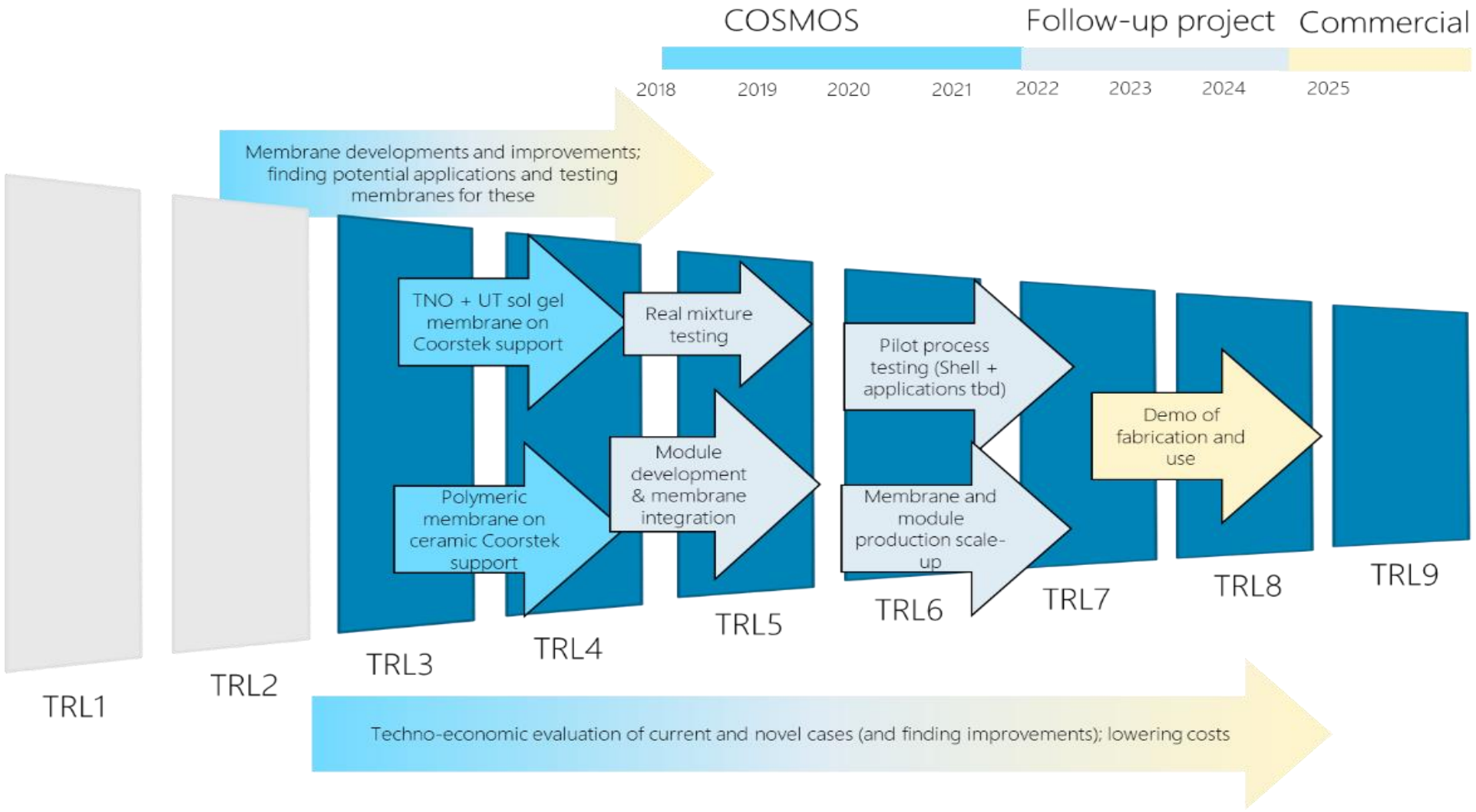
SUMMARY & CONCLUSION
TOWARDS HIGH QUALITY LOW COST OSNF MEMBRANES

- Membrane development
  - (Few) intermediate layers lead to good support
  - Prepared for scale-up (multichannel/hollow fiber)
- Testing of membranes
  - HybSi: low MWCO, promising candidate for PCA removal
  - PI: promising membrane for high temperature separations (MWCO ~400).
- Techno-economic evaluation
  - Positive business case for PCA removal from waxy hydrocarbon stream

The combination of high quality low cost supports and different recipes to tune the membrane performance will lead to low cost, tunable, high temperature solvent stable membranes for significant energy savings in industry.

GENERAL OUTLOOK

TOWARDS HIGH TEMP & QUALITY LOW COST OSNF MEMBRANES



THANK YOU FOR ATTENTION

QUESTIONS?

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