



MemCCSea

Innovative membrane systems
for CO₂ capture and storage at sea

George Skevis, Akrivi Asimakopoulou, Dimitrios Koutsonikolas

**Chemical Process & Energy Resources Institute
Centre for Research & Technology Hellas**

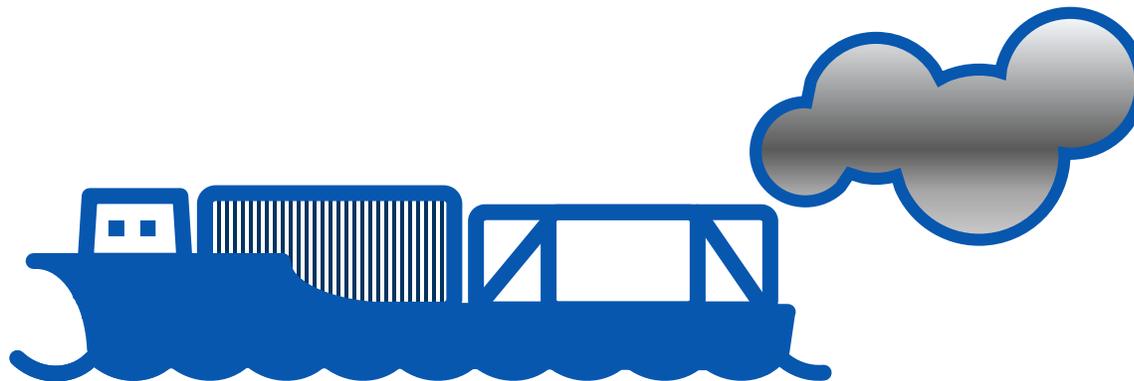


MemCCSea project is funded through the ACT programme (Accelerating CCS Technologies, Horizon2020 Project No 294766). Financial contributions made from GSRT (GR), BMWi (DE), RCN (NO) and DoE (USA) are gratefully acknowledged.

Greenhouse gas emissions from SHIPS
are currently estimated at 3% of the
total global emissions and are
expected to rise by 2050 up to **17%**



MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea

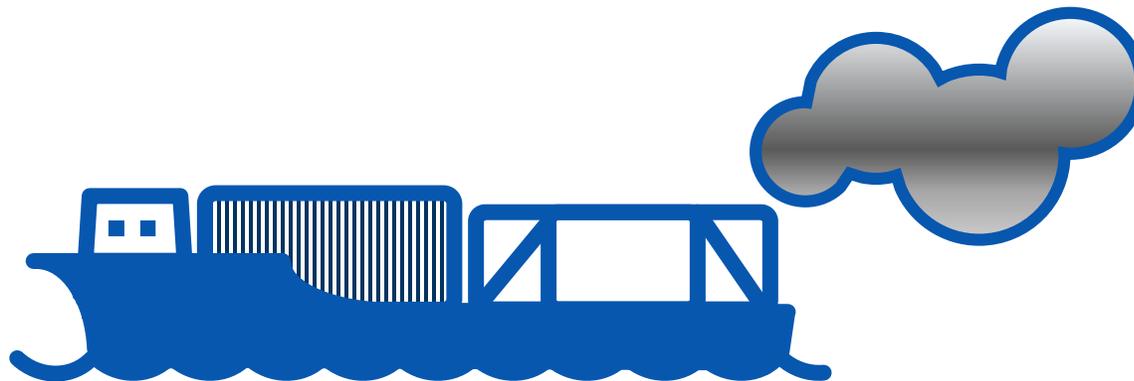


To address the Paris agreement,



MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea

has adopted an initial strategy for the reduction of GHG
emissions from ships by **50%**

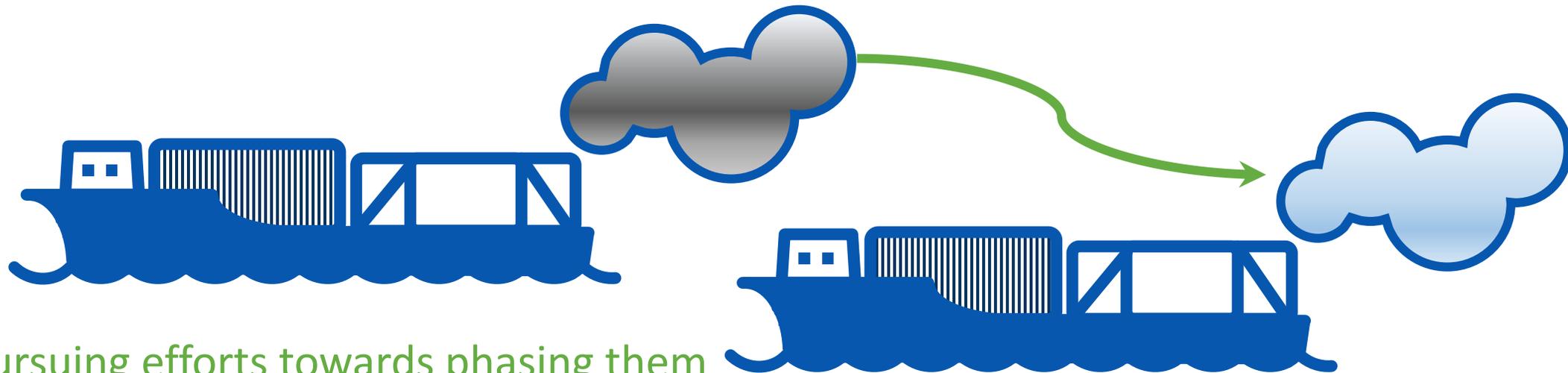


To address the Paris agreement,



MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea

has adopted an initial strategy for the reduction of GHG
emissions from ships by **50%**



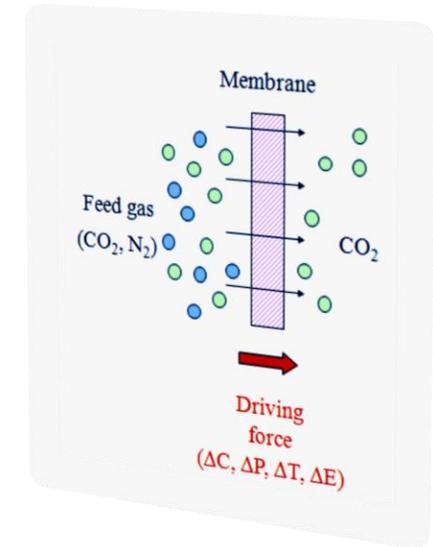
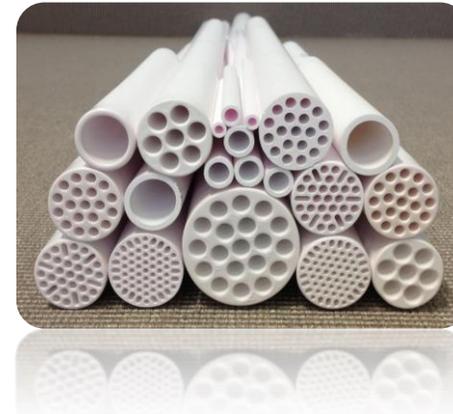
while pursuing efforts towards phasing them
out entirely

In **MemCCSea**, we capture CO_2
from ships and floating vessels using

membrane technology



MemCCSea
Innovative membrane systems
for CO_2 capture and storage at sea

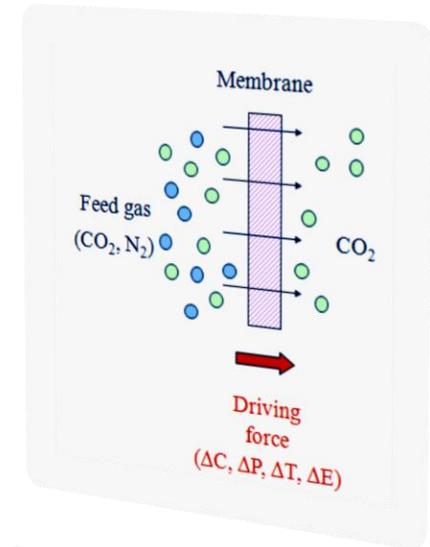


In **MemCCSea**, we capture **CO₂**
from ships and floating vessels using

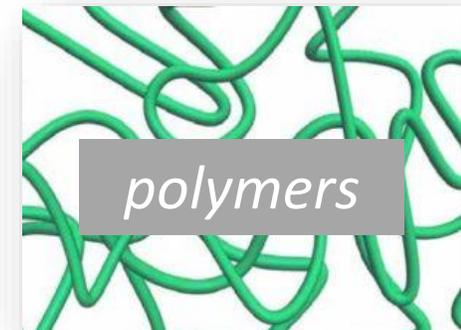
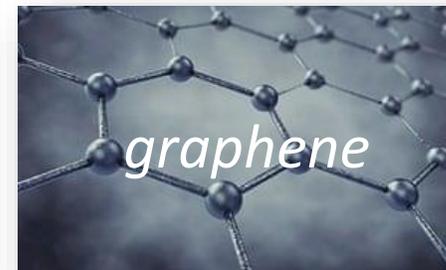
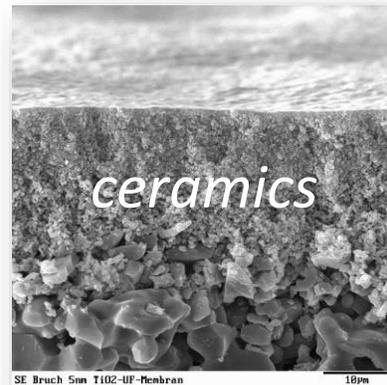
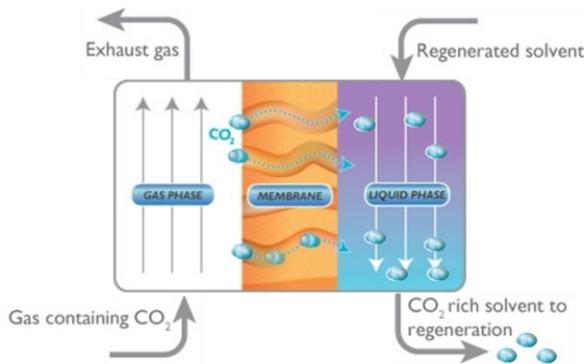


MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea

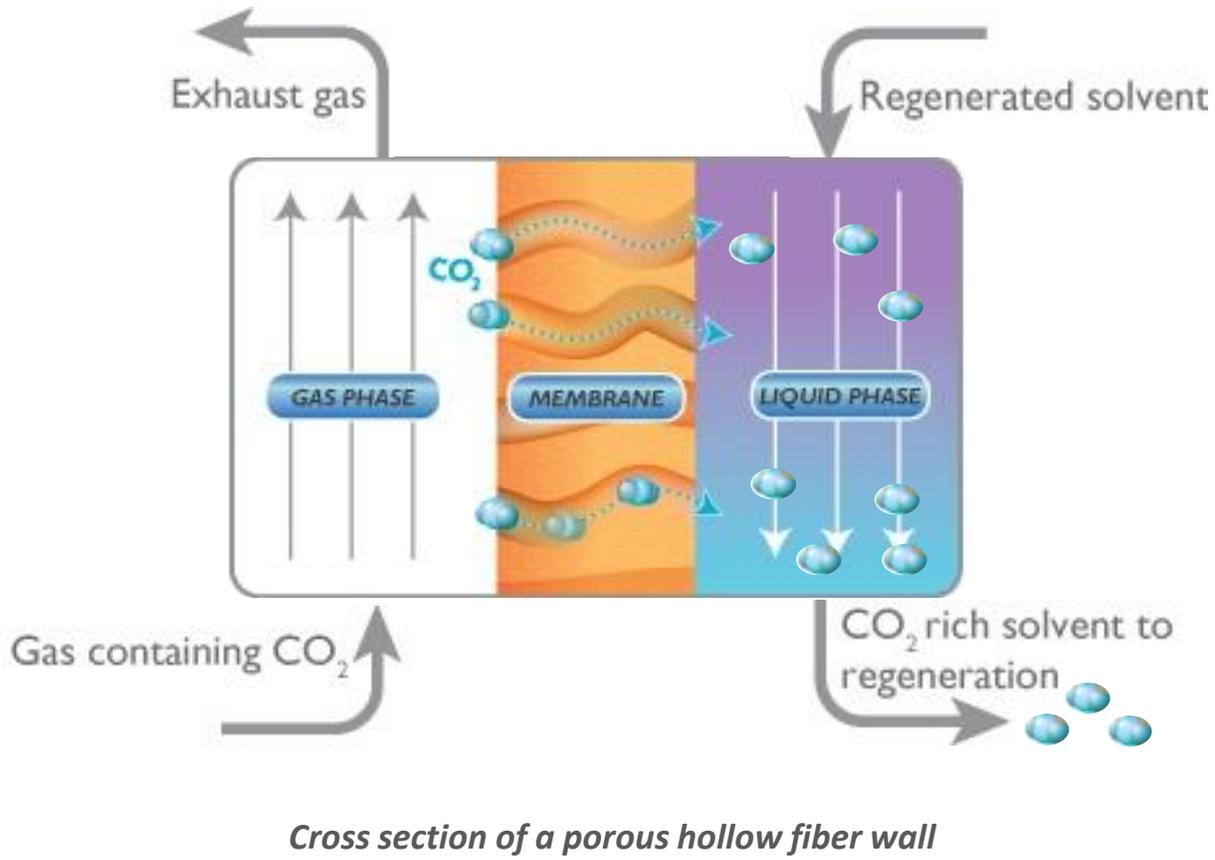
membrane technology
sea water + promoters



and advanced materials

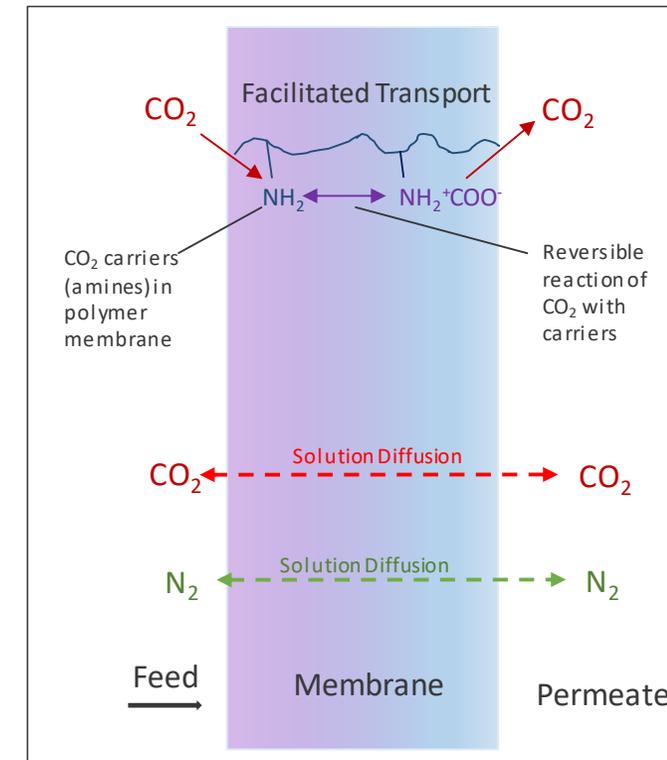
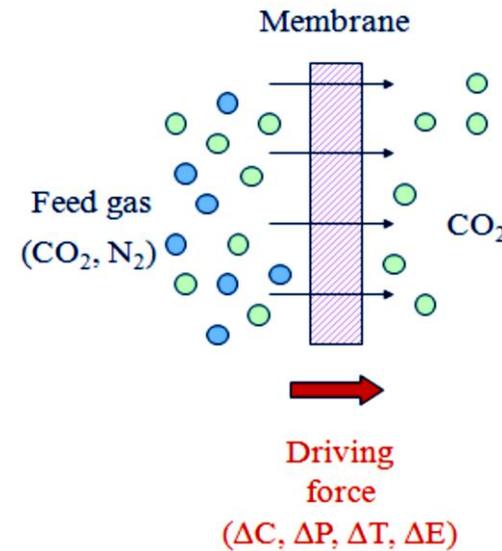


Membrane Technology | Gas-Liquid Contactors



MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea

Membrane Technology | Permeators



Ceramic membranes (e.g. TiO_2 , Al_2O_3)

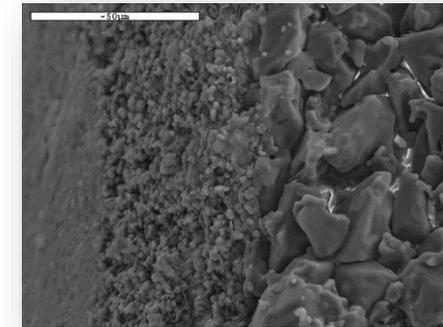


of various pore sizes
(1-1,000 nm)

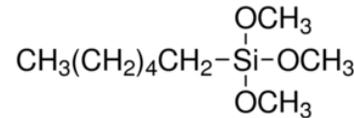


MemCCSea

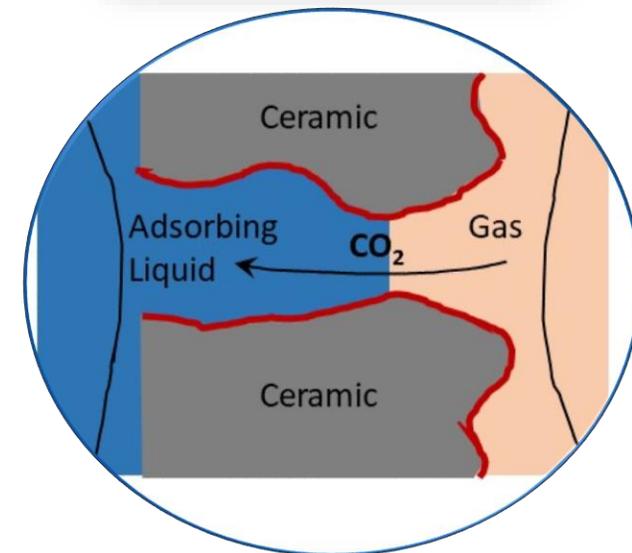
Innovative membrane systems
for CO_2 capture and storage at sea



are properly coated with hydrophobic precursors
(e.g. carbon, organosilanes)



to prevent the entry of liquid into the gas phase for
efficient contactor mode of operation in gas-liquid
membrane process.

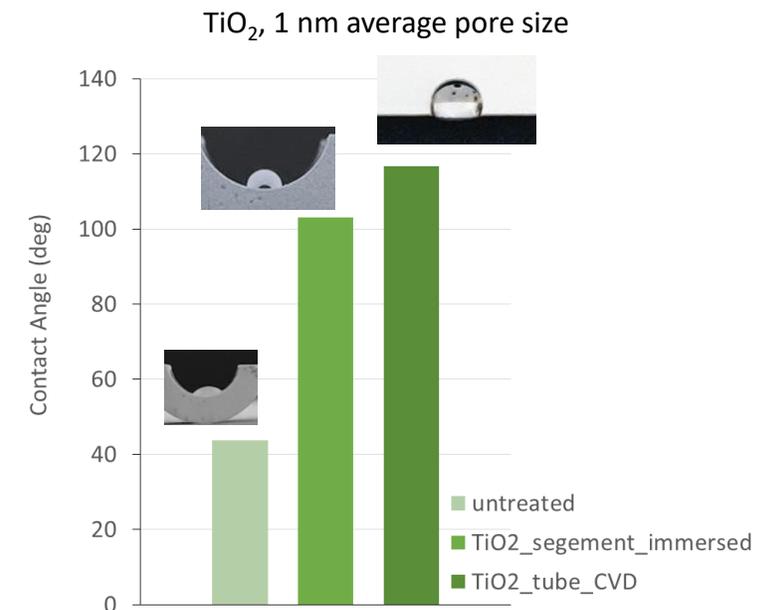
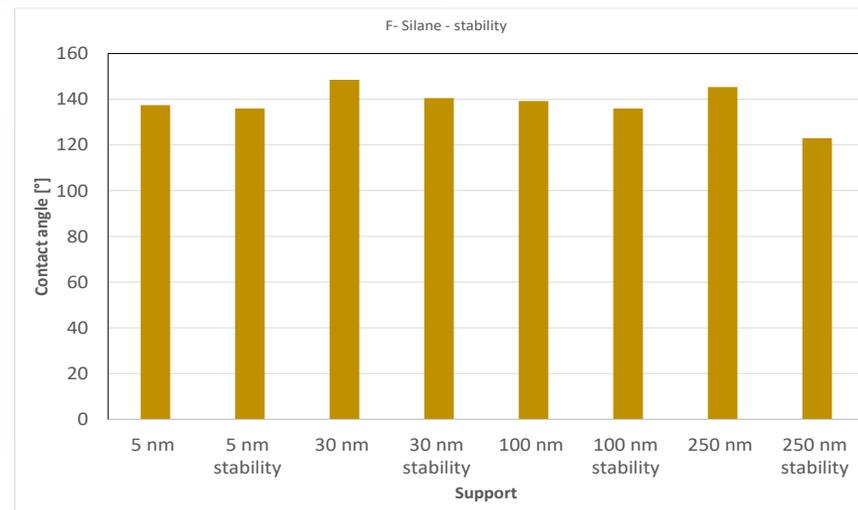
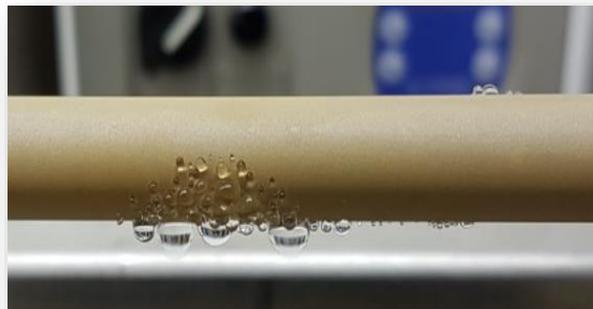
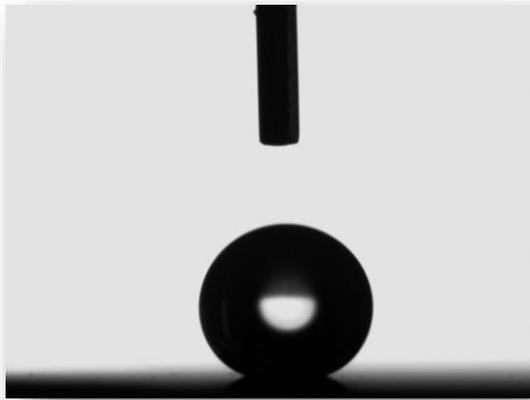


So, KER 2.1 – Hydrophobic coating on porous ceramic membranes has already been achieved



MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea

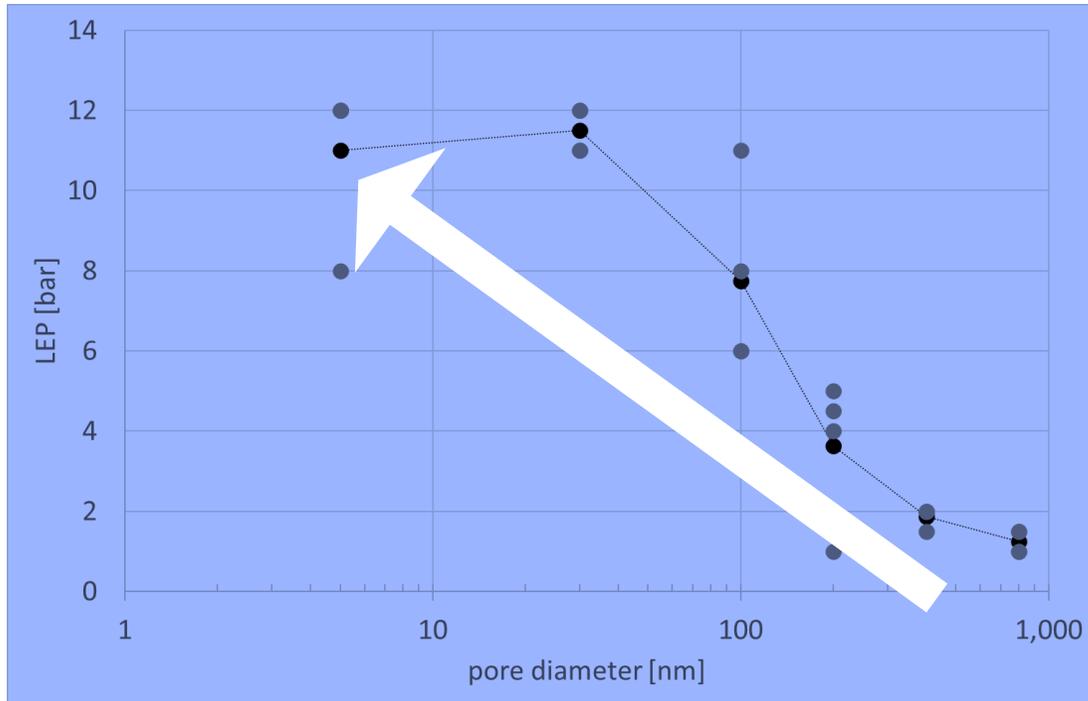
... and clear hydrophobic behavior is obtained even in initially really hydrophilic materials



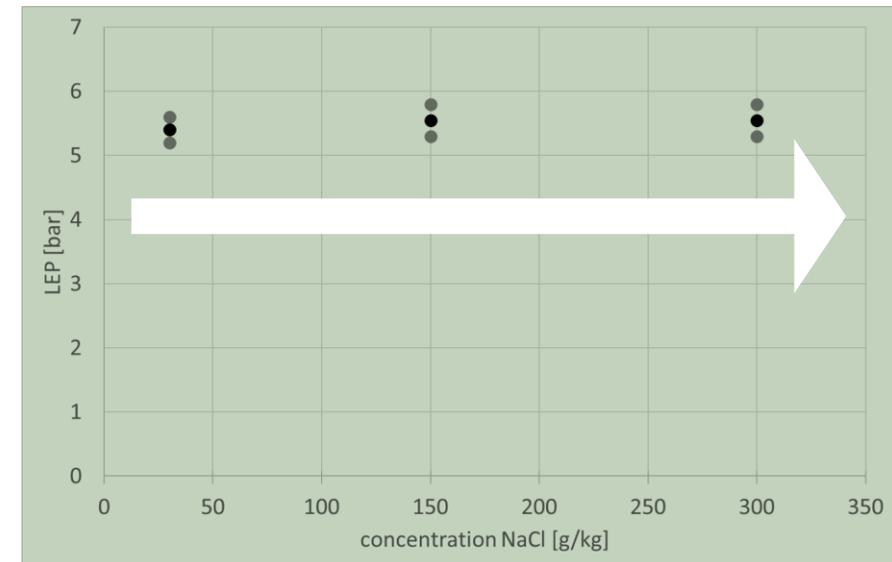
Further optimization with decreasing pore size from 1000nm to 5nm, LEP becomes higher than 10bar



MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea



Sodium chloride is added in the absorption solvent to simulate sea-water based solvents (~35g/kg). Further increase of LEP is achieved!

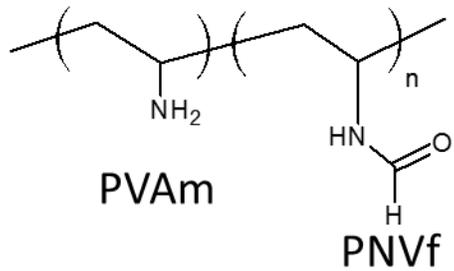


Polymeric & Mixed Matrix Membranes through the synthesis of novel functionalized graphene

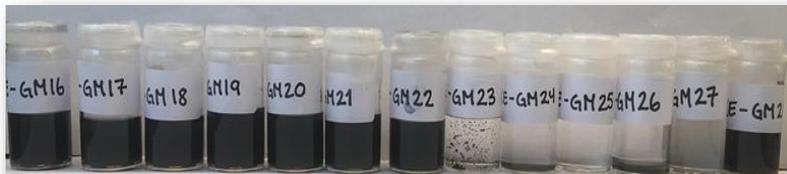
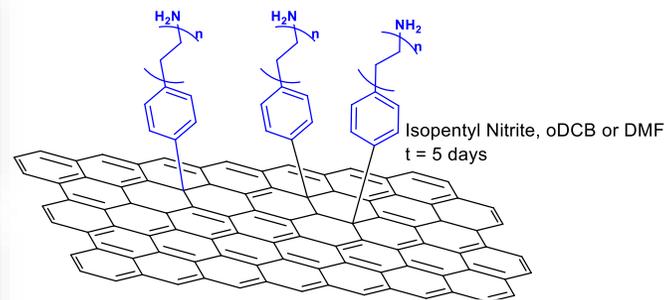
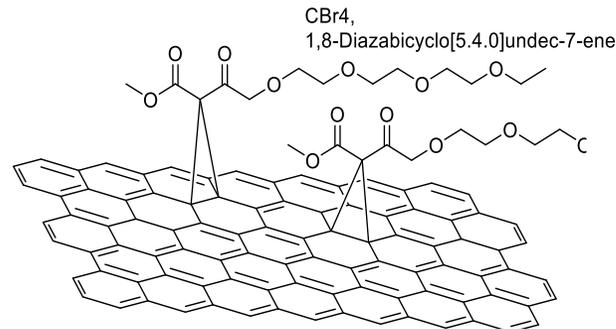


MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea

Polyvinylamine



Graphene



Graphene in benzyl alcohol
Suspension stable upon standing
overnight

Polymeric & Mixed Matrix Membranes



PVAm/graphene solution



Cast membrane film

PVAm/graphene solution (2 wt% graphene) is cast in mold and dried in vacuum oven.

Next steps: Test two more PVAm/graphene films Thin film composites (TFC) of sub-micron

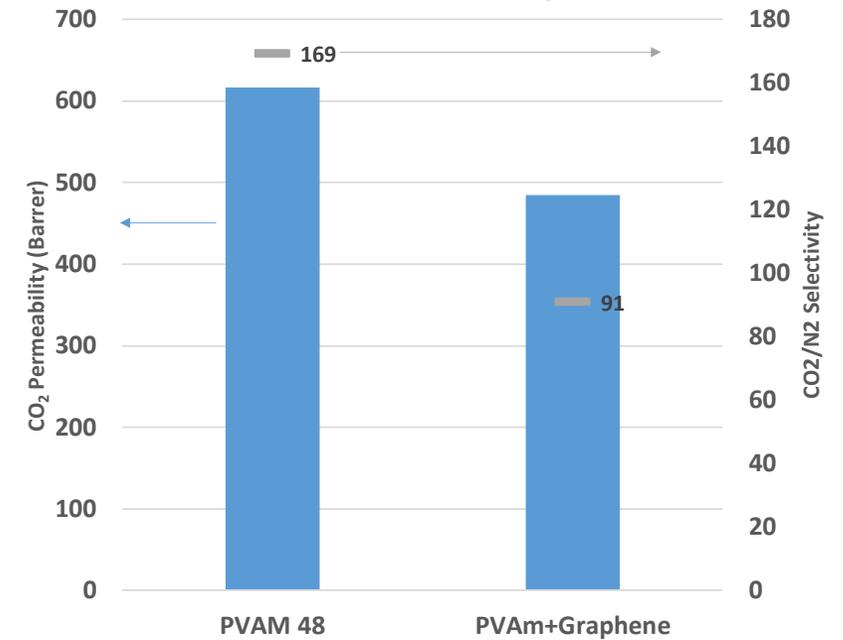
PVAm/graphene/graphene oxide on porous supports



MemCCSea

Innovative membrane systems for CO₂ capture and storage at sea

Membrane gas permeability and selectivity



Permeation testing conditions:

60 °C, 95% relative humidity (feed and sweep), 14/86 CO₂/N₂ mixed feed gas at 1.36 atm, Air sweep gas at 1.22 atm, p_{CO_2} 0.19 atm

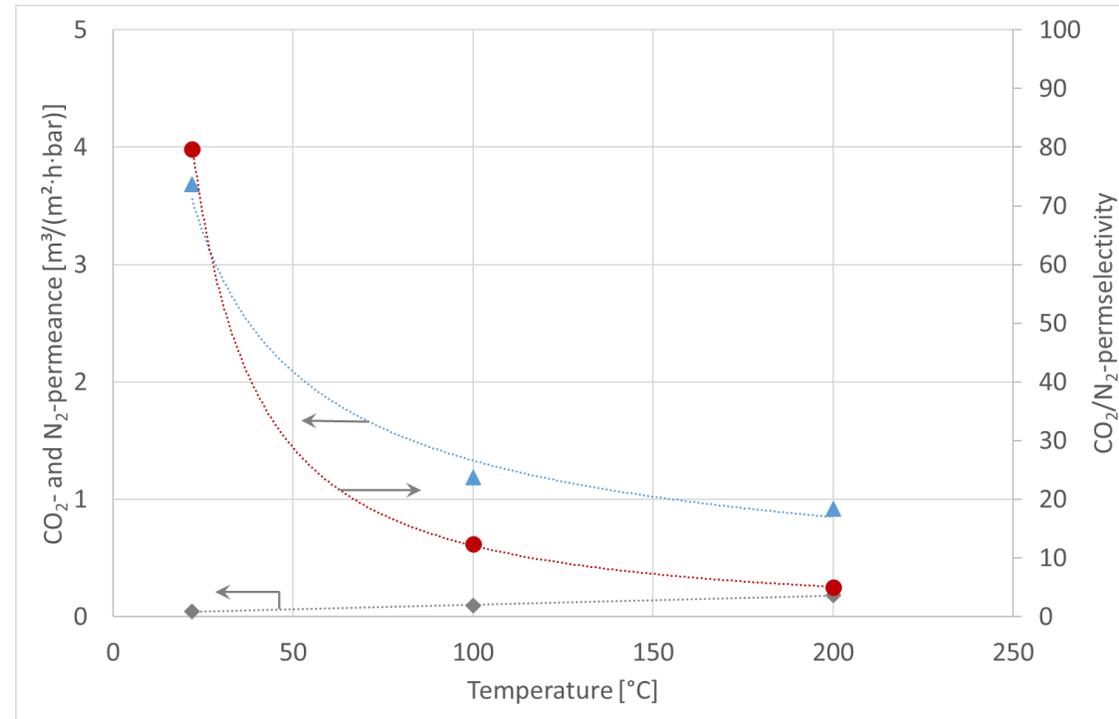
Evaluation of the developed materials as permeators



MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea



Carbon membranes for permeators



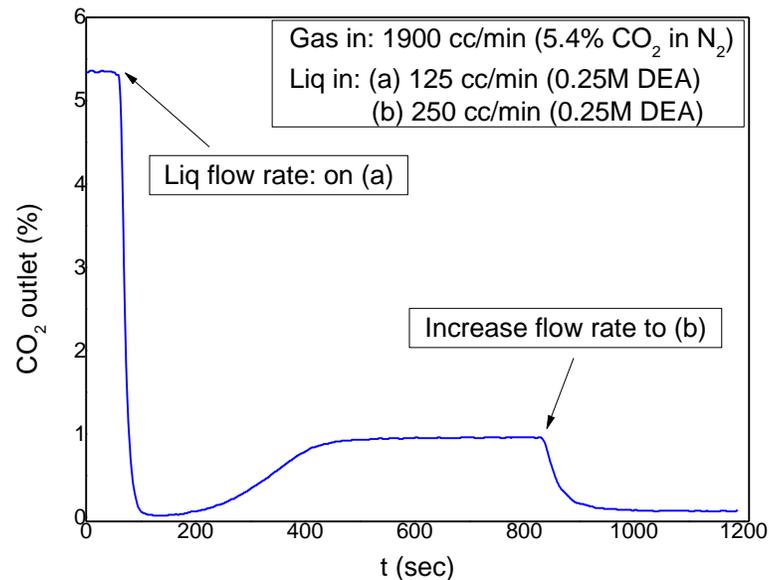
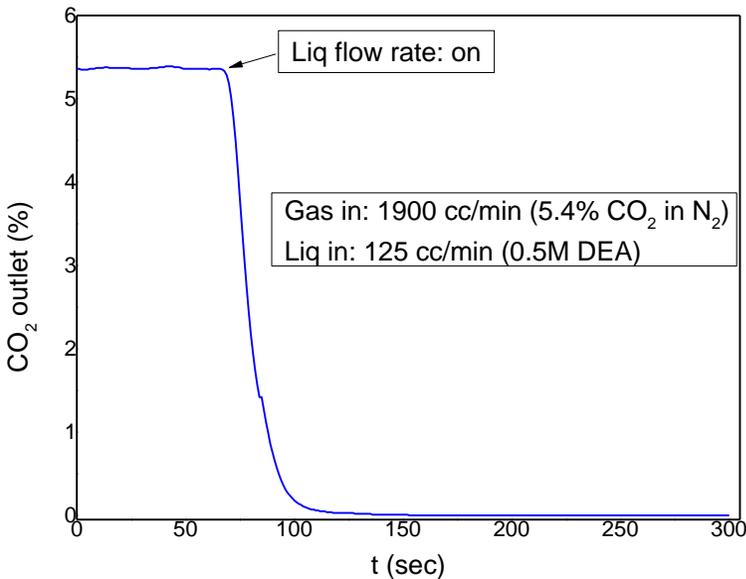
Highest CO₂/N₂-selectivity up to 80

Increasing of CO₂/N₂-selectivity with decreasing temperature

Evaluation of the developed materials as contactors

5.4% CO₂ in N₂ represents flue gas composition

Amine based solvent (DEA) | long-term working performance | no wetting | no efficiency loss



MemCCSea

Innovative membrane systems
for CO₂ capture and storage at sea

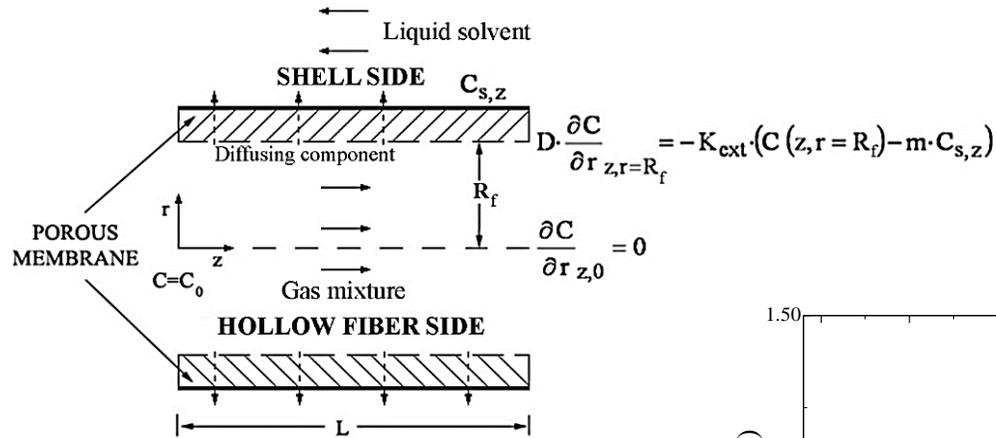


Even very low DEA concentrations are adequate for complete CO₂ capture at high G/L ratios

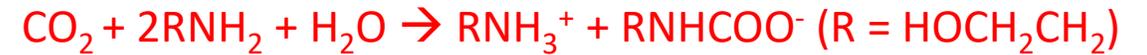
Online CO₂ analysis | Quick response | Quick steady-state development

We want to simulate the mass transfer phenomena and predict what happens in the lab....

Gas-liquid membrane contactor model



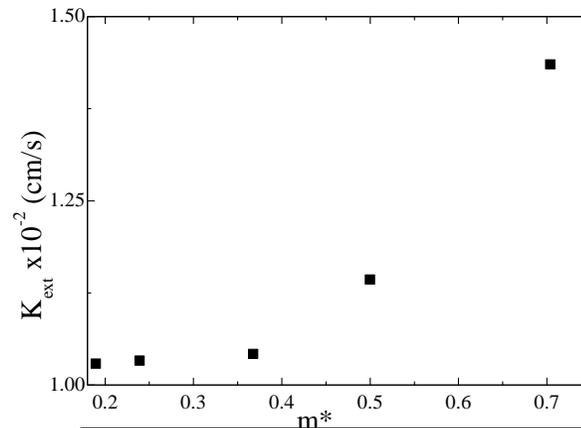
Coupled membrane process with solution thermodynamics



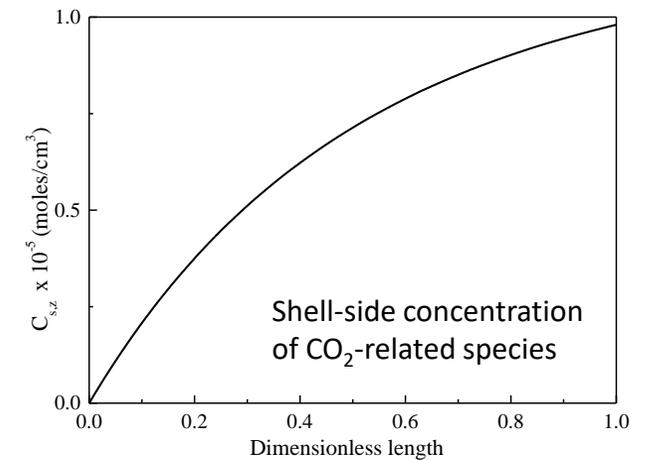
Steady-state, isothermal, 2D laminar flow (CO_2/N_2 mixture) in the fibre side (lumen)

Reaction in the shell side with the liquid solvent

Predict combined mass transfer resistance (K_{ext}) based on experiments



No.	E	K_{ext} (cm/s)	Sh_w	M	m^*	H_{CO_2} (mol/cm ³) [*]	z^*
1	0.09788	0.01029	1.600×10^{-3}	0.12094	0.18945	3.582×10^{-5}	222.
2	0.19334	0.01033	1.615×10^{-3}	0.23519	0.23922	3.648×10^{-5}	544.
3	0.18207	0.01042	1.620×10^{-3}	0.22498	0.36774	3.582×10^{-5}	567.
4	0.09559	0.01143	1.786×10^{-3}	0.11628	0.49979	3.648×10^{-5}	214.
5	0.06827	0.01435	2.242×10^{-3}	0.08305	0.70390	3.648×10^{-5}	109.



We want to simulate the mass transfer phenomena and predict what happens in the lab....

Membrane permeator model

Molecular Diffusion/Fick's Law Model (FLM)

$$\vec{J}_i = -\frac{D_i}{RT} c_i \frac{\partial \mu}{\partial x} \quad (i = 1, \dots, n)$$

$$\mu = \mu_o + RT \ln c_i$$

Fick's First Law

Chemical Potential

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} \quad (i = 1, \dots, n)$$

Fick's Second Law

FLM is (a) appropriate only for molecular diffusion of **binary mixtures**
 (b) can accommodate Knudsen Diffusivity for binary mixtures

Mass Transfer Coefficient (MTC)

$$|\vec{J}| = MTC * \Delta c = \frac{1}{R_{MT}} \Delta c$$

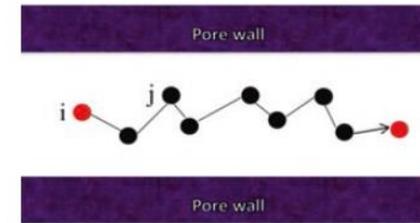
Description of flux through MTC



MemCCSea

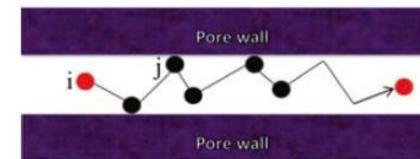
Innovative membrane systems
for CO₂ capture and storage at sea

Pure molecular diffusion



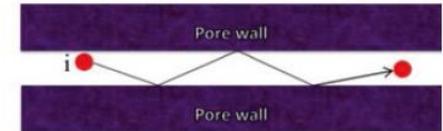
$$D_{ij} = \frac{0.00186T^{\frac{3}{2}}}{p\sigma_{ij}^2\Omega} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{\frac{1}{2}}$$

Knudsen + molecular diffusion



$$\frac{1}{D'_i} \cong \frac{1}{D_{ij}} + \frac{1}{D_{iK}}$$

Pure Knudsen diffusion



$$D_{iK} = \frac{d_p}{3} a \sqrt{\frac{8RT}{\pi M_i}}$$

Random porous material



$$D_i^{eff} = \frac{\phi}{\tau} D'_i$$

...and optimize what happens on board!



Specs that affect membrane system

Exhaust Gas					
Gas flow	kg/h	85471	87477	45858	27186
Gaseous Emission Data					
CO concentration (Dry)	ppm	119.0	58.5	55.5	48.0
CO2 concentration (Dry)	%	5.24	4.82	4.89	4.30
HC concentration (Wet)	ppmC	59.5	54.0	58.5	49.5
O2 concentration (Dry)	%	13.78	14.43	14.25	14.23
NOx concentration (Dry)	ppm	794.0	1038.0	1374.0	1404.0
NOx humidity/temp. correction factor	-	1.016	1.022	1.001	0.998
Dry / Wet correction factor	-	0.949	0.954	0.955	0.981
NOx mass flow	kg/h	103.84	108.30	95.53	58.02
NOx specific	g/kWh	8.64	12.01	15.90	19.31
Test Cycle (E3)	g/kWh	11.85			

* The IMO NOx value is based on reference scavenge air temperature, but not corrected reference Pmax.



MemCCSea
Innovative membrane systems for CO₂ capture and storage at sea

Case study definition

Vessel type

- Tanker

Trade route

- Modes of operation

Laden: Arab gulf → Singapore: 23 days
Ballast: Singapore → Arab Gulf: 19 days

Trips per year

- Fuel and emissions per trip & year

Per trip: ~1400 tons fuel → 4360 tons CO₂
Per year: ~15500 tons fuel → 48267 tons CO₂

Fuel type

- LSHFO
- **LNG**

Machinery in operation

- Main engine
- Auxiliary engines
- Auxiliary boiler

Onboard space capacity

- Machinery
- Deck

Safety aspects

- Materials
- Consumables

Techno-economics

- CAPEX
- CO₂ price



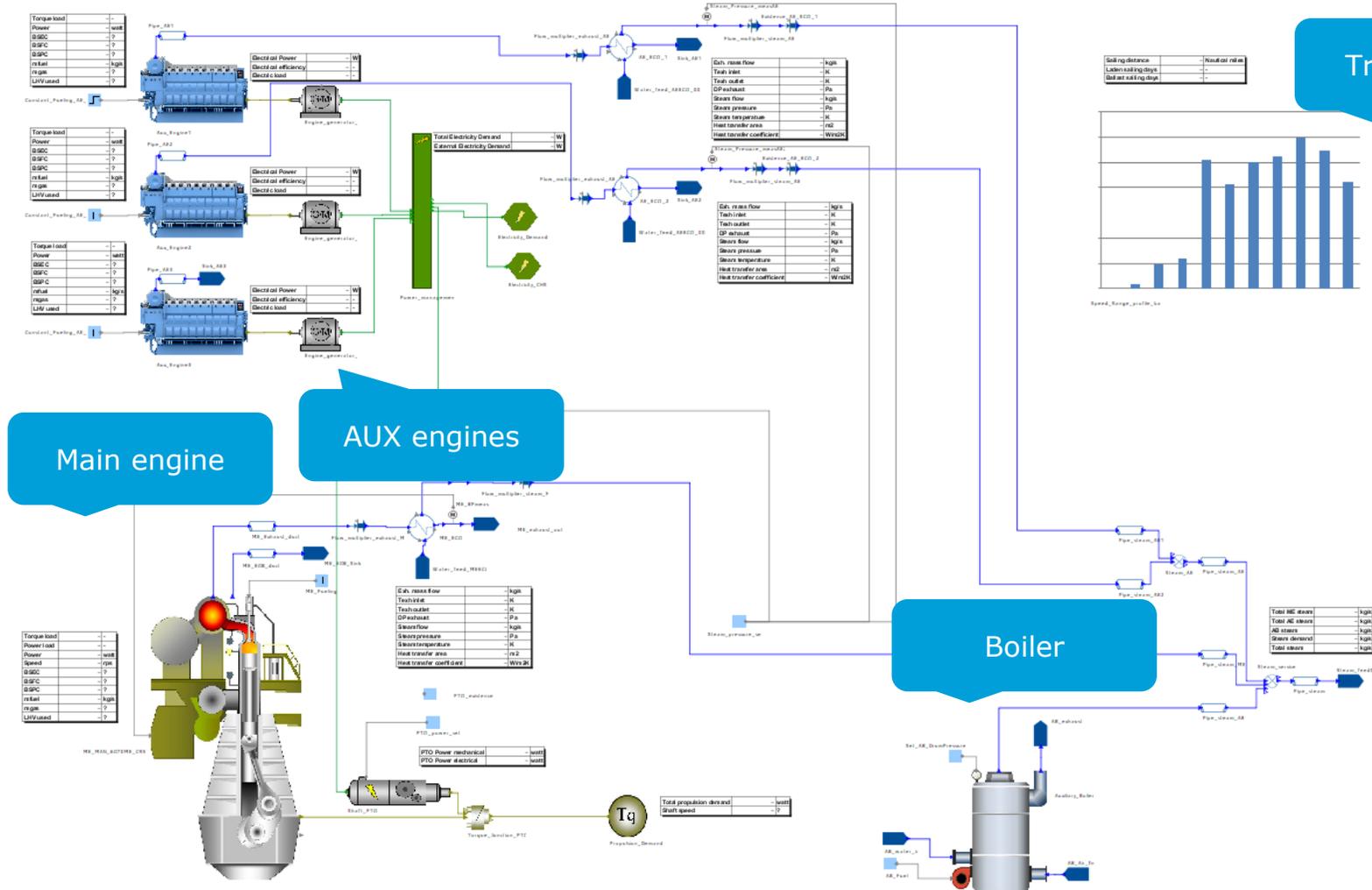
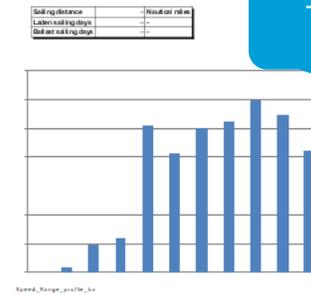
...and optimize what happens on board!



MemCCSea

Innovative membrane systems for CO₂ capture and storage at sea

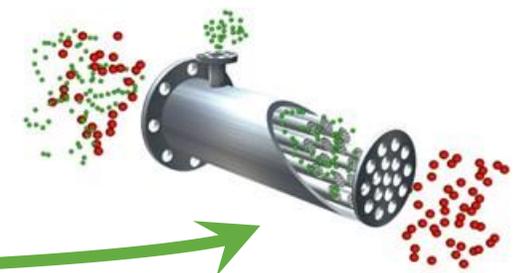
Trade route



Our goal is to create a system

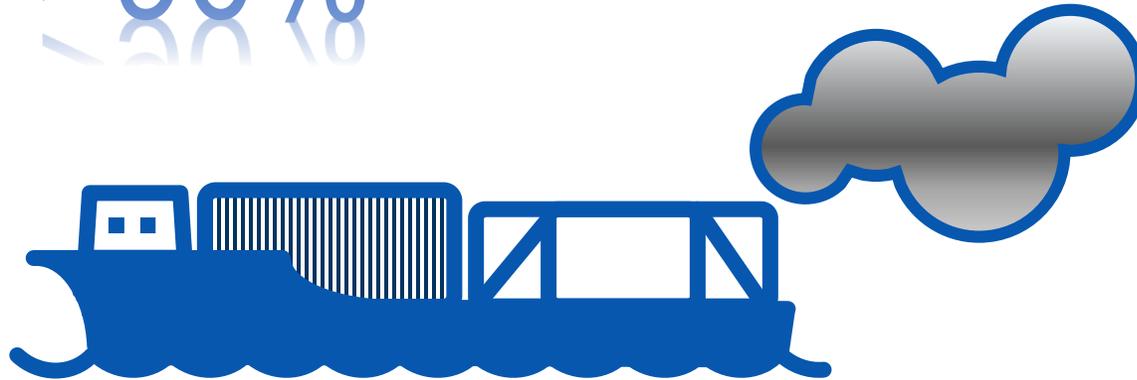


MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea



...and reduce the main
ship engine CO₂
emissions by more
than

>90%



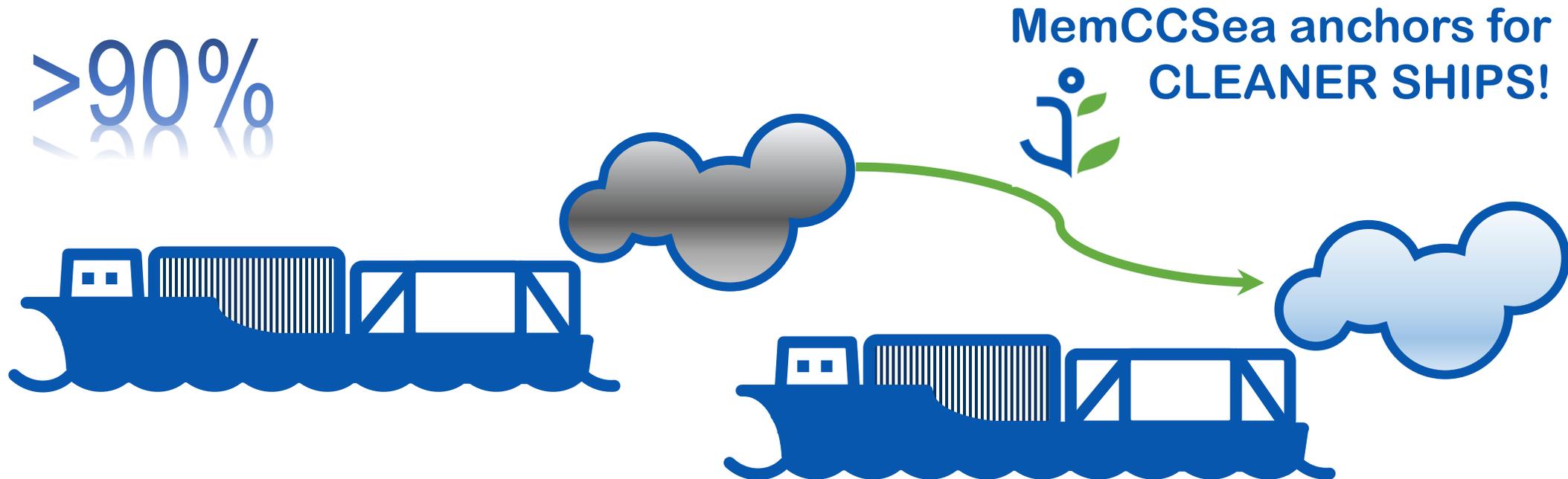
MemCCSea

Innovative membrane systems
for CO₂ capture and storage at sea

...and reduce the main
ship engine CO₂
emissions by more
than **>90%**



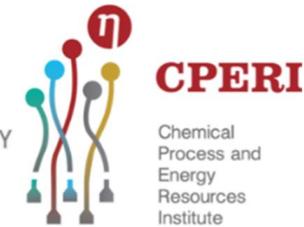
MemCCSea
Innovative membrane systems
for CO₂ capture and storage at sea





MemCCSea

Innovative membrane systems
for CO₂ capture and storage at sea



Thank you!



MemCCSea