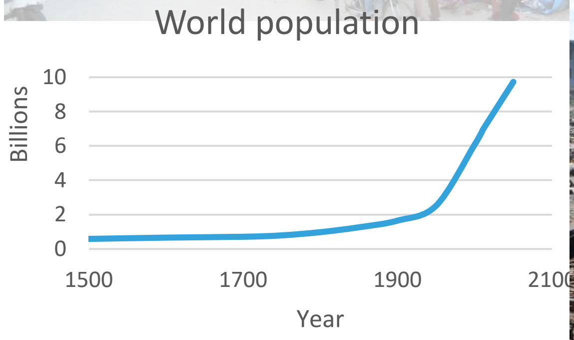
ROYAL SOCIETY OF CHEMISTRY SYMPOSIUM 2019
RE SOURCING OUR RESOURCES
REDUCING ENVIRONMENTAL IMPACT

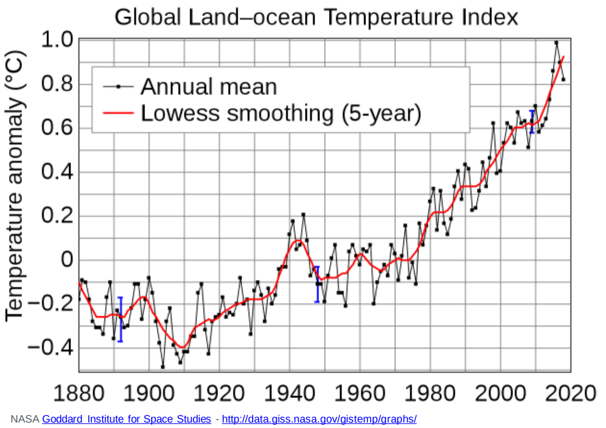
MEMBRANE ENHANCED CHEMICAL AND BIOCHEMICAL PROCESSES

The effect of nanomodification of membrane surface on process efficiencies

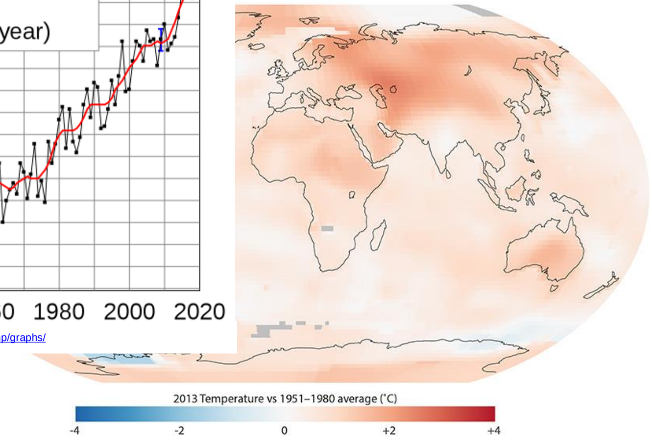
Flemish Institute of Technological Research



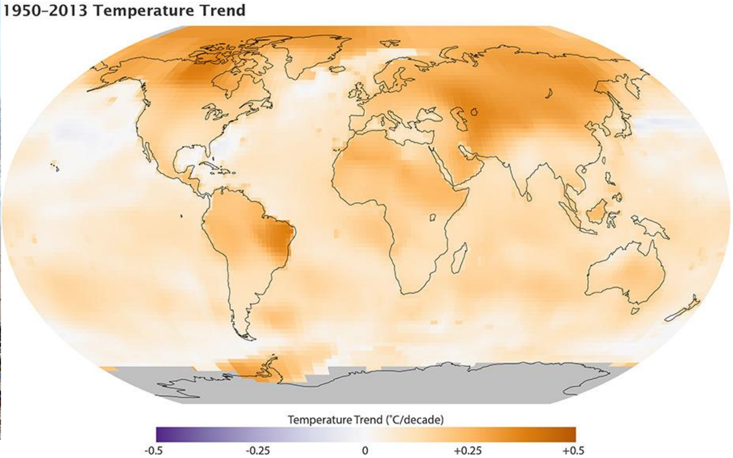
World population
Billions
10
8
6
4
2
0
1500
1700
1900
2100
Year



Global Land–ocean Temperature Index
Temperature anomaly (°C)
1.0
0.8
0.6
0.4
0.2
0
−0.2
−0.4
Annual mean
Lowess smoothing (5-year)
1880
1900
1920
1940
1960
1980
2000
2020
NASA Goddard Institute for Space Studies - http://data.giss.nasa.gov/gistemp/graphs/



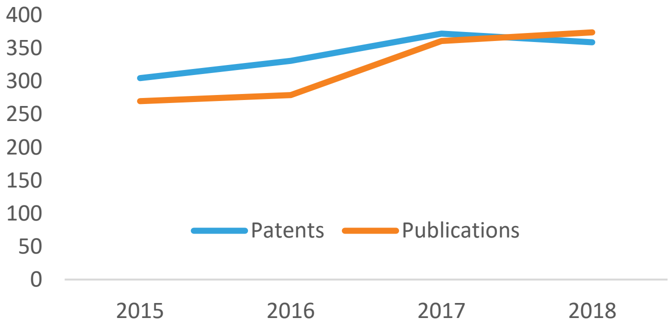
2013 Temperature vs 1951–1980 average (°C)
-4
-2
0
+2
+4

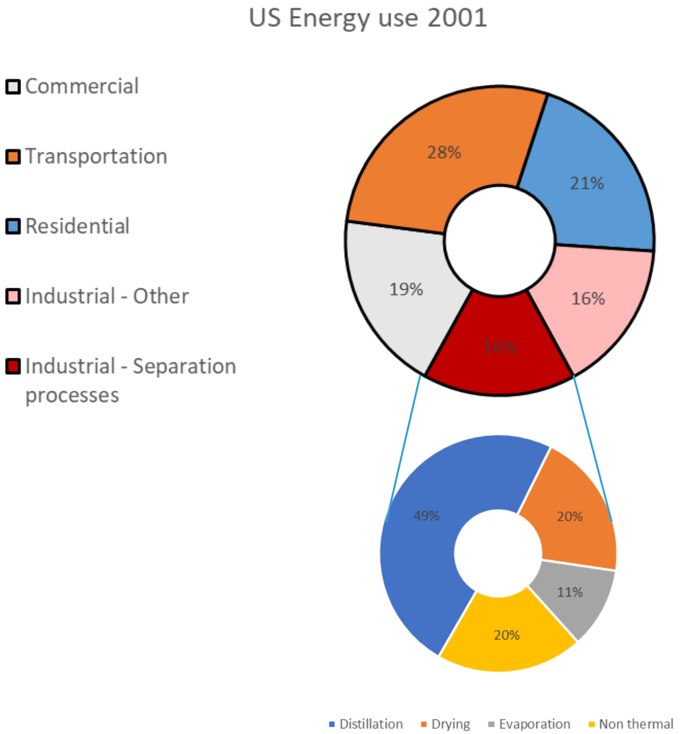


1950–2013 Temperature Trend
Temperature Trend (°C/decade)
-0.5
-0.25
0
+0.25
+0.5

PROCESS INTENSIFICATION

Since 2015 : 1284 publications and 1244 patents





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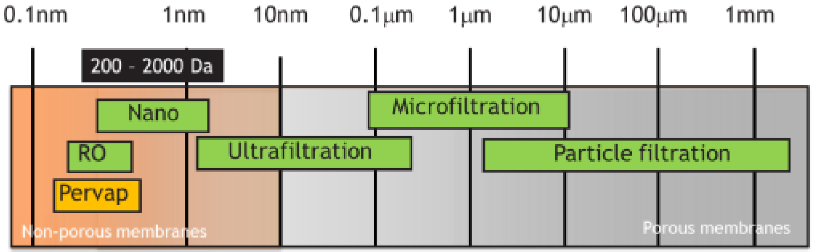
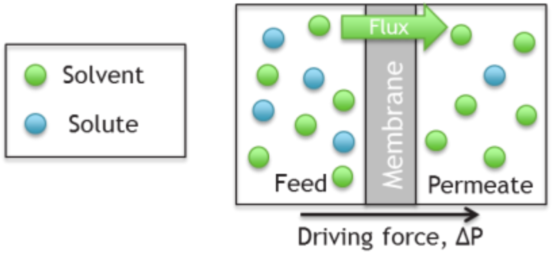
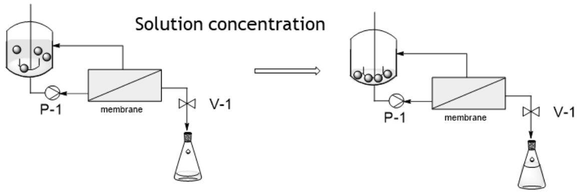
Web of science 2019/05/15;
Google scholar 2019/05/15
Nature 532 (7600), 435-438
Oak Ridge National Laboratory. *Materials for Separation Technologies: Energy and Emission Reduction Opportunities* (2005).

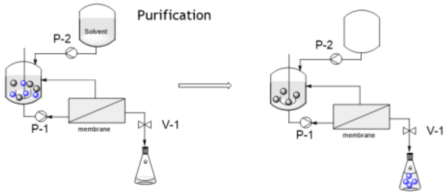
MEMBRANE TECHNOLOGY

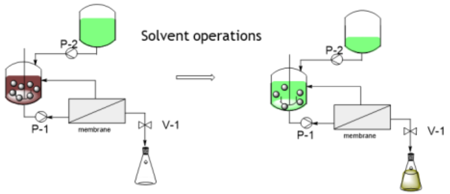
Membrane technology is today an additional tool for process chemist, offering alternative and more efficient solutions to existing challenges.

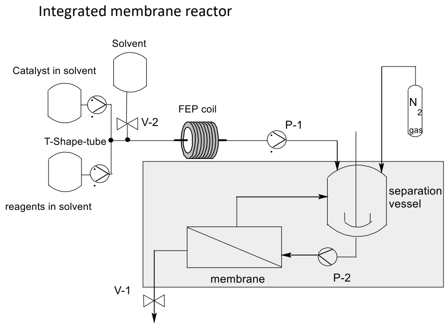






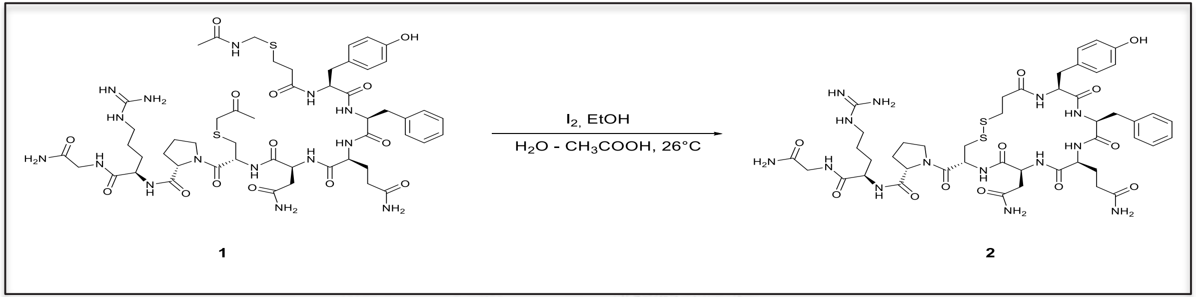


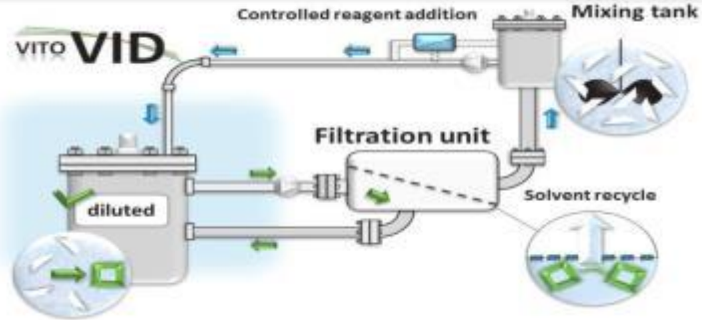




CHEMICAL PROCESSES REQUIRING HIGH DILUTION

Proof of Concept: Peptide Cyclisation

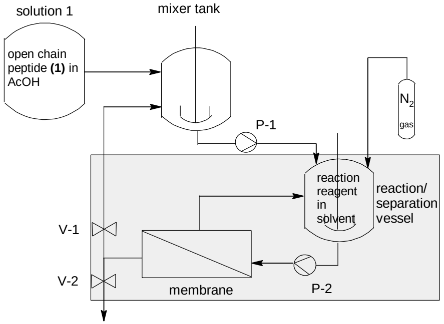


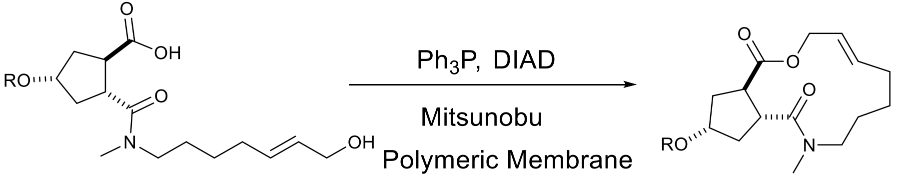


Benifits

- Yield: 71% ➔ 95%
- Conversion: 84% ➔ 100%
- Product purity ⬆
- Solvent use: ⬇ -85%
- PMI ⬇: 1700 ➔ 300
- Production price ⬇

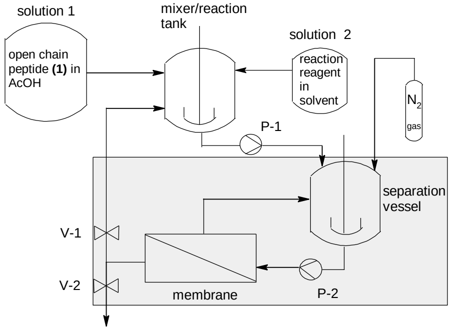
CHEMICAL PROCESSES REQUIRING HIGH DILUTION

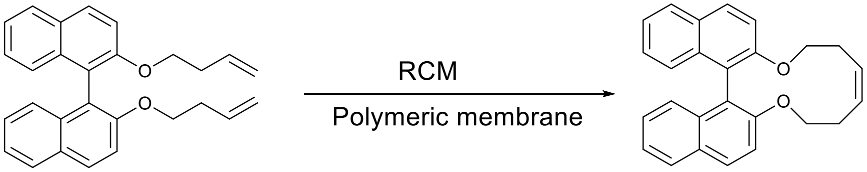




Head to tail cyclisation

PMI ↓: 45%



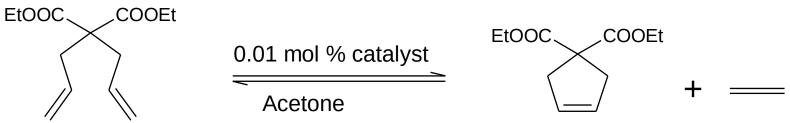


Metathesis cyclisation

PMI ↓: 75%

RE USE AND RECYCLE OF VALUABLE HOMOGENEOUS CATALYSTS

Reaction :



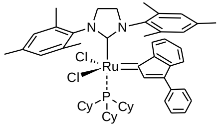
$C_{13}H_{20}O_4$
240.29

DEDAM

$C_{11}H_{16}O_4$
212.24

Ru Catalyst : Pre-catalyst :

$C_{54}H_{69}Cl_2N_2PRu$
949.09
M2

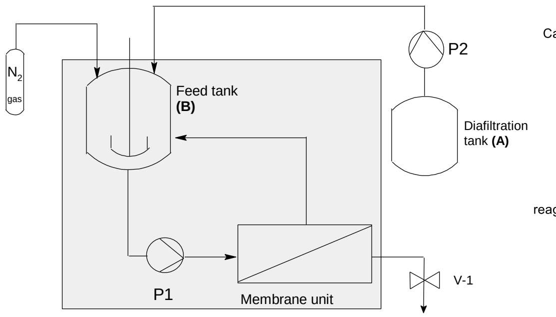


Peformance on Funmem membrane + benchmark :

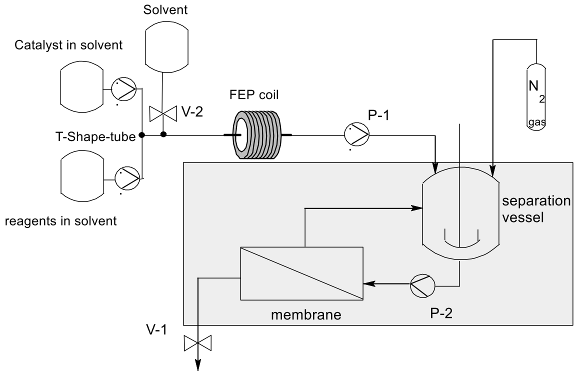
Membrane	Permeability	Catalyst retention	Product retention
Funmem®	6 $lm^{-2}h^{-1}bar^{-1}$	87 %	35 %
0,9 nm TiO_2	0.3 $lm^{-2}h^{-1}bar^{-1}$	96 %	60 %
Polymeric OSN	0.8 $lm^{-2}h^{-1}bar^{-1}$	91 %	97 %

RE USE AND RECYCLE OF VALUABLE HOMOGENEOUS CATALYSTS

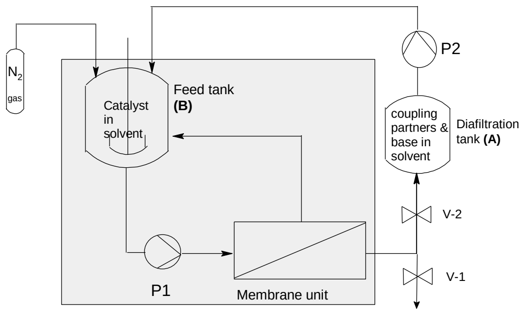
Off-line processing



At-line processing



On-line processing



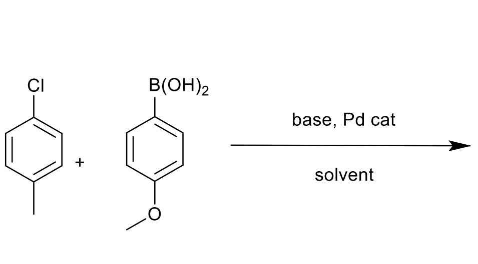
With **all processing methods** rejection of Pd species > 99 %

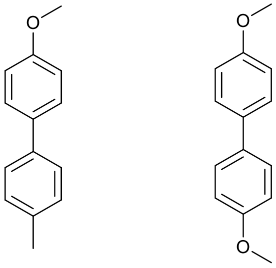
Reaction Pd content (ppm)	Membrane	Pd in product (ppm)
8700	1 nm $C_8 - TiO_2$	67
	0.9 nm TiO_2	7
	0.9 nm $C_8H_4F_{13} - TiO_2$	6
	0.9 nm $C_8H_4F_{13} - TiO_2$*	3

*PEPPSI catalyst , other CX-31

INCREASING CATALYST TON

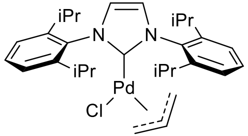
Catalyst performance in (semi)continuous reaction



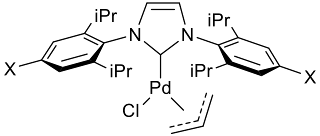


1 2 3 4

homocoupling product

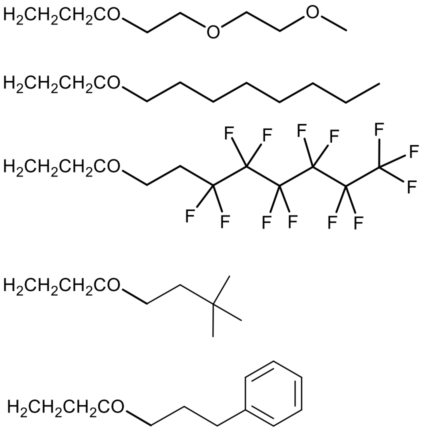


CX-21



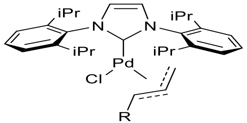
6 a-e

X = **a**, **b**, **c**, **d**, **e**

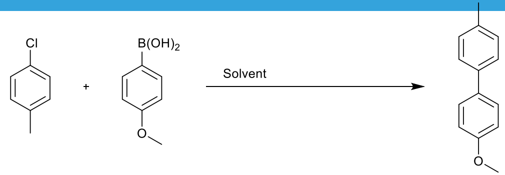


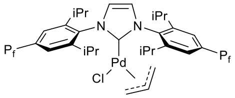
Tail in catalyst designed for rejection and impedes cluster formation

INCREASING CATALYST TON



CX-31





6 c

Literature example	
Yield (%)	93
Substrate -catalyst ratio	50
Pre-catalyst load (ppm)	20000
Catalyst retention (24°C)	/
Av. Process permeance ($Lm^{-2}h^{-1}bar^{-1}$)	/
Isolated product metal contamination (ppm)	/
Mass intensity (reaction)	/
Mass intensity (reaction & product isolation	500
solvent	1,4-dioxane
Organometallics	Not recovered

Membrane assisted (commercial catalysts)	
Yield (%)	92
Substrate -catalyst ratio	100
Pre-catalyst load (ppm)	10000
Catalyst retention (24°C)	50
Av. Process permeance ($Lm^{-2}h^{-1}bar^{-1}$)	6
Isolated product metal contamination (ppm)	/
Mass intensity (reaction)	/
Mass intensity (reaction & product isolation	780
solvent	Ethanol
Organometallics	(Partially) recovered

Membrane assisted (tailed catalysts)	
Yield (%)	88
Substrate -catalyst ratio	2000
Pre-catalyst load (ppm)	500
Catalyst retention (24°C)	96
Av. Process permeance ($Lm^{-2}h^{-1}bar^{-1}$)	1
Isolated product metal contamination (ppm)	16
Mass intensity (reaction)	51
Mass intensity (reaction & product isolation	167
solvent	Ethanol
Organometallics	Recovered

CONTINUOUS FERMENTATION PROCESSES

Challenges in traditional fermentation

Product toxicity:

- Low product concentrations
- Low productivity

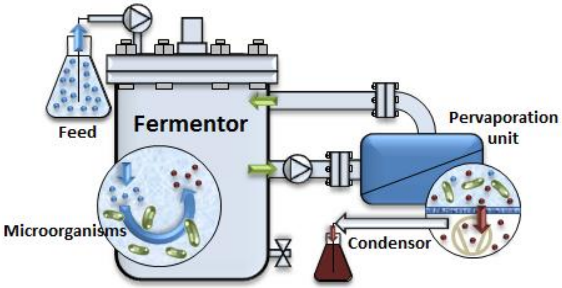
→ High purification costs
→ High waste water volumes
→ Energy-intensive separation
→ Cost of substrate

Integration with pervaporation

Integration of

- Organophilic pervaporation and
- two-stage clostridial fermentation
- using a membrane-based in situ product recovery technique (ISPR)

→ Continuous, selective product withdrawal from reaction medium

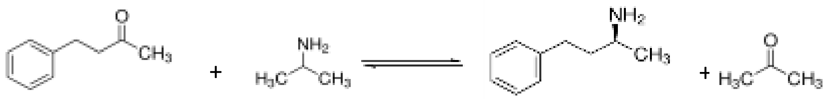


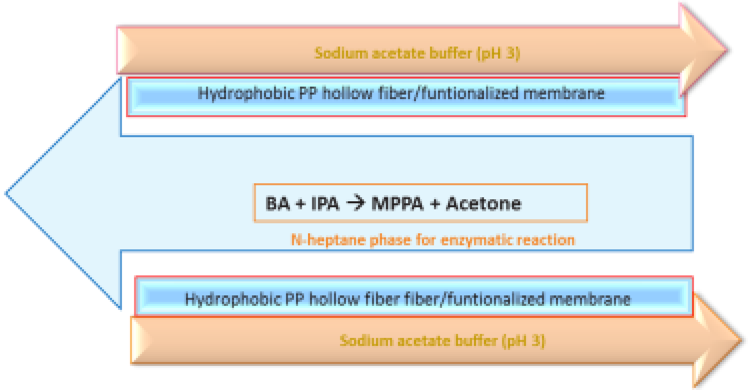
Benefits

- 2,5 x production increase by removal of product inhibition
- Fermentor cost ↓
- Water footprint -50%
- Steam consumption -50%
- Applicable to batch & continuous processes
- Production price -10%

ENZYMATIC SYNTHESIS OF CHIRAL AMINES

Chiral amines in enantiopure forms are important chemical building blocks in pharmaceutical and agrochemical industries





Background

- Chemical synthesis of chiral amines still remains a challenge because it requires high chemo-, regio-, diastereo-, and enantio-control
- ω-transaminase is a promising catalyst which produces chiral amines with exquisite enantioselectivity

Limits in aqueous phase:

- Low substrate solubility (BA): only 1,48 g/L (or 10 mM)
- Severe product inhibition by (S)-MPPA

Targets:

- To establish the enzymatic reaction in solvent phase (n-heptane in preliminary tests) to increase substrate concentration
- In-situ product recovery by MPPA extraction into an aqueous phase by use of a membrane contactor using an aqueous phase as extractant

Results

- ☑ Higher substrate conversion
- ☑ Co-extraction of substrate amine (IPA) solved with NF

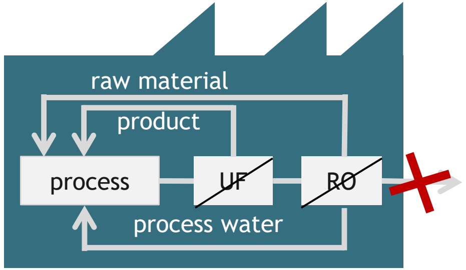
Next steps

- ☐ Increase the specific productivity
- ☐ NF optimization
- ☐ Strategies to retain the donor amine selectively in the reactor

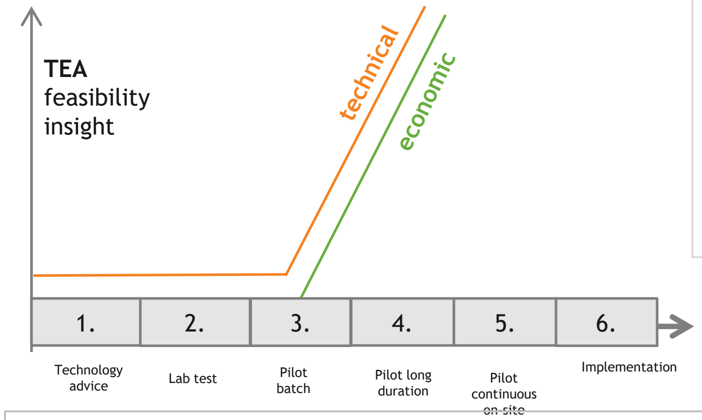
PRODUCT & RAW MATERIALS RECOVERY

- Product / raw materials in waste stream
- Inhibiting biological waste water plant
- End-of-pipe treatment required

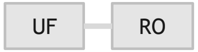
- In-process membrane technology



Assessment



@ 20.000 m^3/year



- CAPEX : 453 kEUR
- OPEX: 46 kEUR/year
- Return: 437 kEUR/year

IMPACT

Recovery/year
- 33.3 ton product (3 EUR/kg)
- 105 ton raw material

Production process water/year
- 14.450 m^3 (1.5 EUR/m^3)

No waste treatment cost

Pay back time ~1 year

PRODUCT & RAW MATERIALS RECOVERY

Challenge

Rinsing water

- Contains high concentration of detergent
- External treatment → high incineration cost

Testing

Assessment

Screening tubular membranes

UF

NF

PCI pilot tests

Lab testing

RO

SUCCESS

Industrial implementation

Collaboration with PCI

- Test assistance
- Pilot PCI available

Time-lapse 2 years

IMPACT

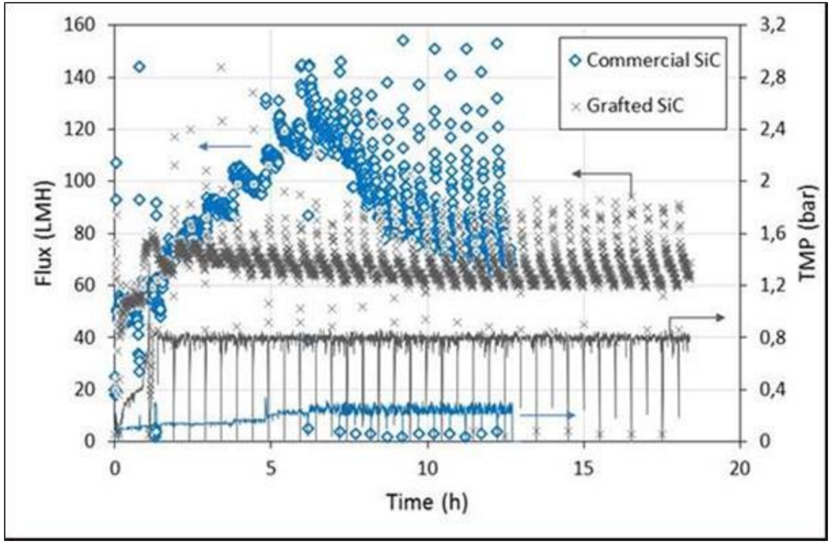
- Reuse detergent stream
- Reuse waste water
- No waste incineration cost

WW TREATMENT

Fouling solution :
real foam - produced water (NL)
~700 ppm oil

Foulants :
oil droplets in O/W emulsions

18h filtration in cross-flow, recovery 50% + use 100ppm de-oiler



Oil content in the permeate

MGR 100 ppm de-oiler	**21 ppm**
MGR no de-oiler	**66 ppm**
Native no de-oiler	**250 ppm**

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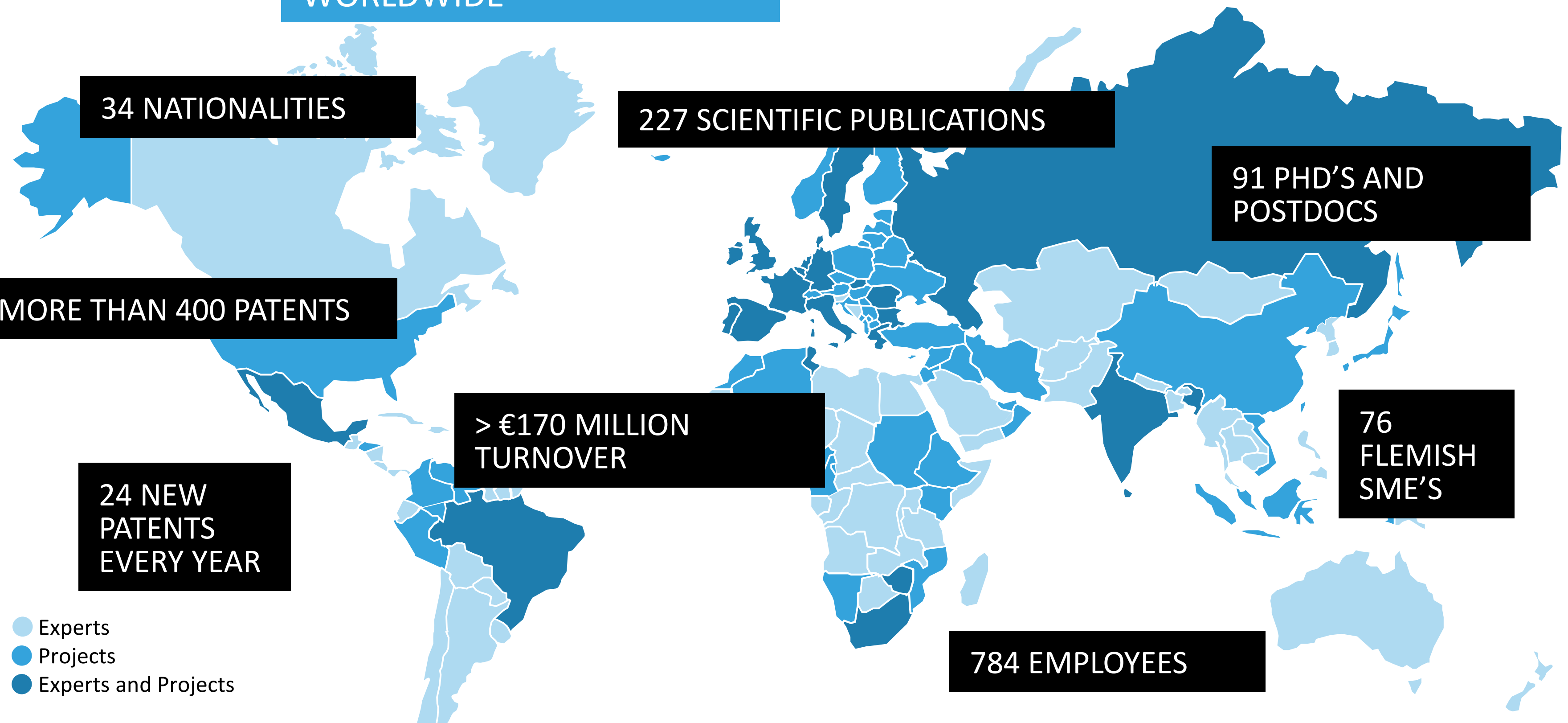

SUSTAINABLE ENTREPRENEURIAL INSPIRING CREATIVE

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