Separation challenges in the quest for sustainability

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Increasing the efficiency in the process industry

- The amount of energy used for separating chemicals is 10-15% of the world's total energy consumption

- Around 2 L crude oil/day and 30 Kg of ethylene & propylene/year are processed for each person on the planet

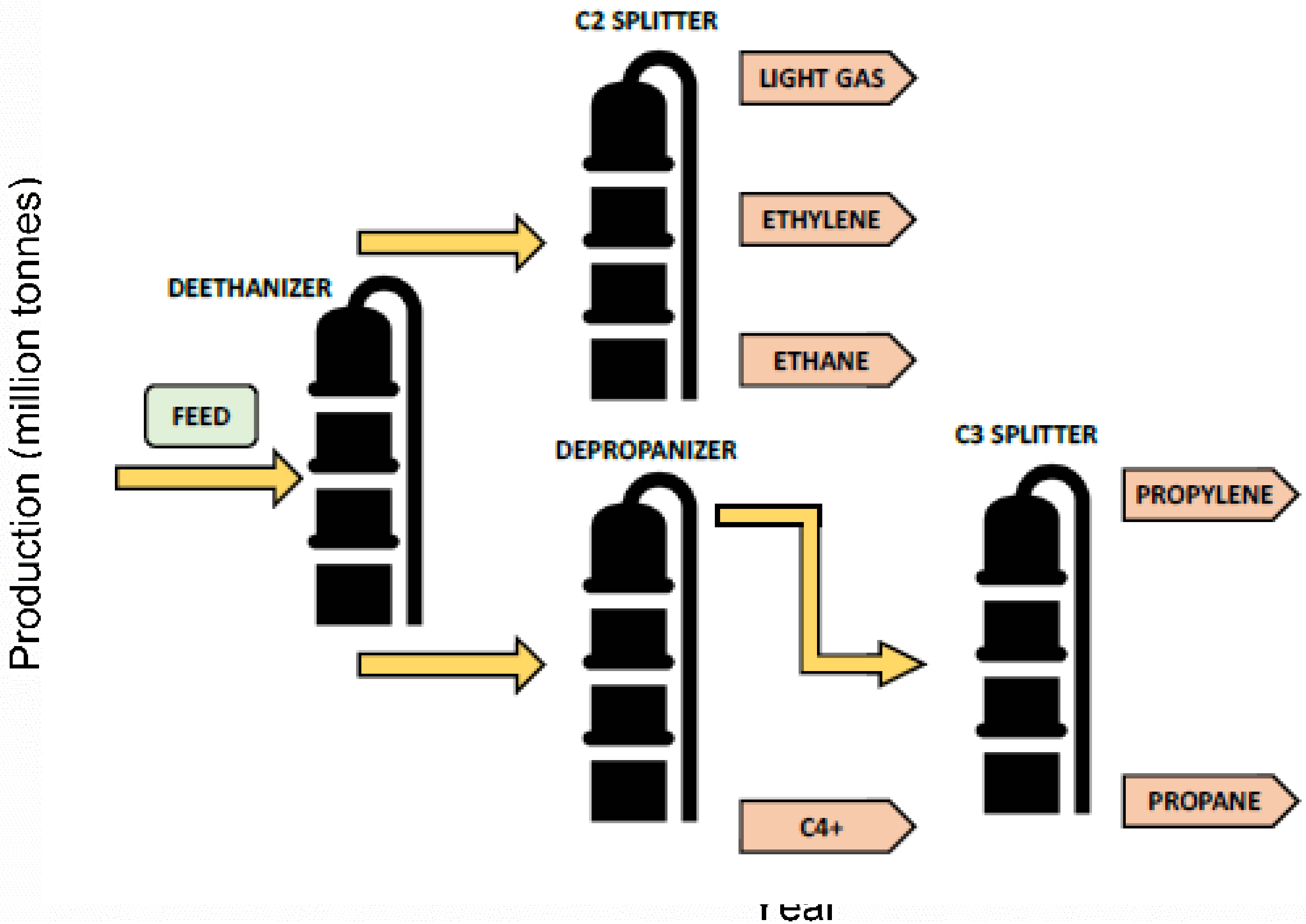
- More tan 80% of the energy associated with the separation of Chemical molecules is used in distillation and similar processes such as evaporation that rely on phase changes

Sholl & Lively Nature, 2016; Lively & Sholl Nature Mat. 2017

- **SEPARATING LIGHT OLEFINS FROM PARAFFINS**

200 million tonnes, 30 kg of ethylene and propylene per person and per year

Olefin industry

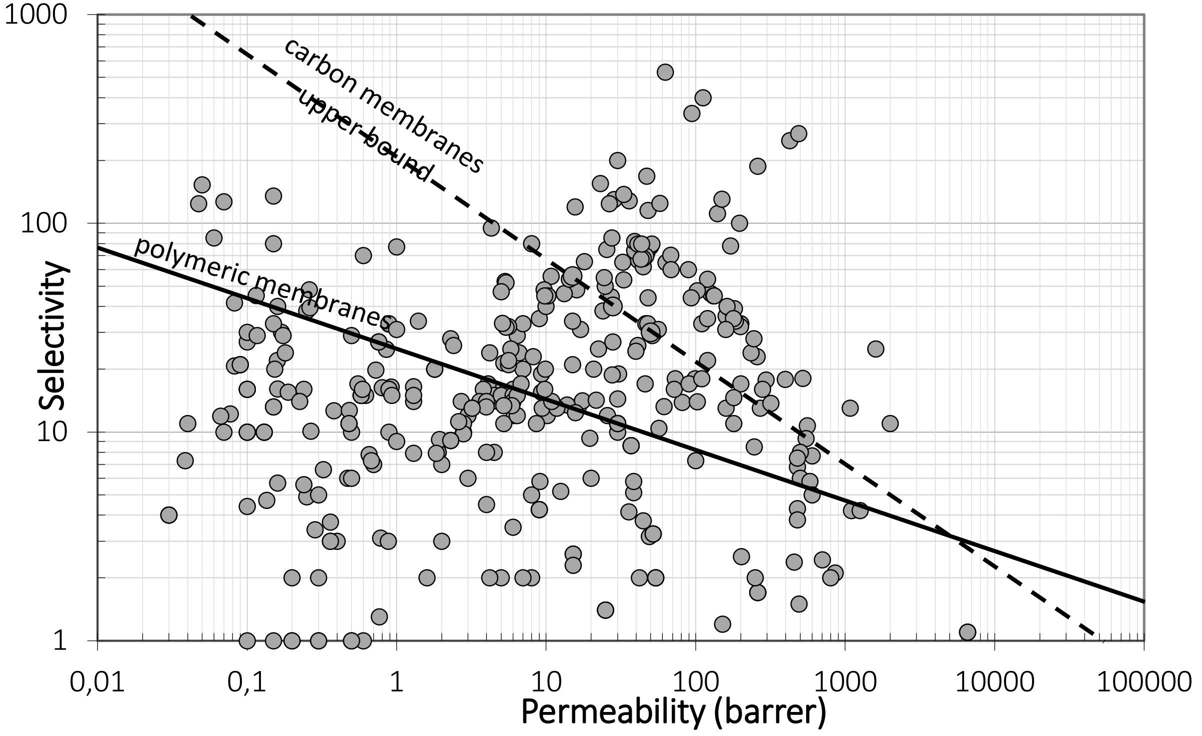


Chemical grade

Polymer grade, >99.5%

Propylene production

Membrane	C_3H_6 Permeance (GPU)	C_3H_6 Selectivity
EC	7	7
6FDA-TeMPD	37b	8.6
CMS	42	23
ZIF-8	90	50
ZIF-8/ZIF-67/ZIF-8	111	210



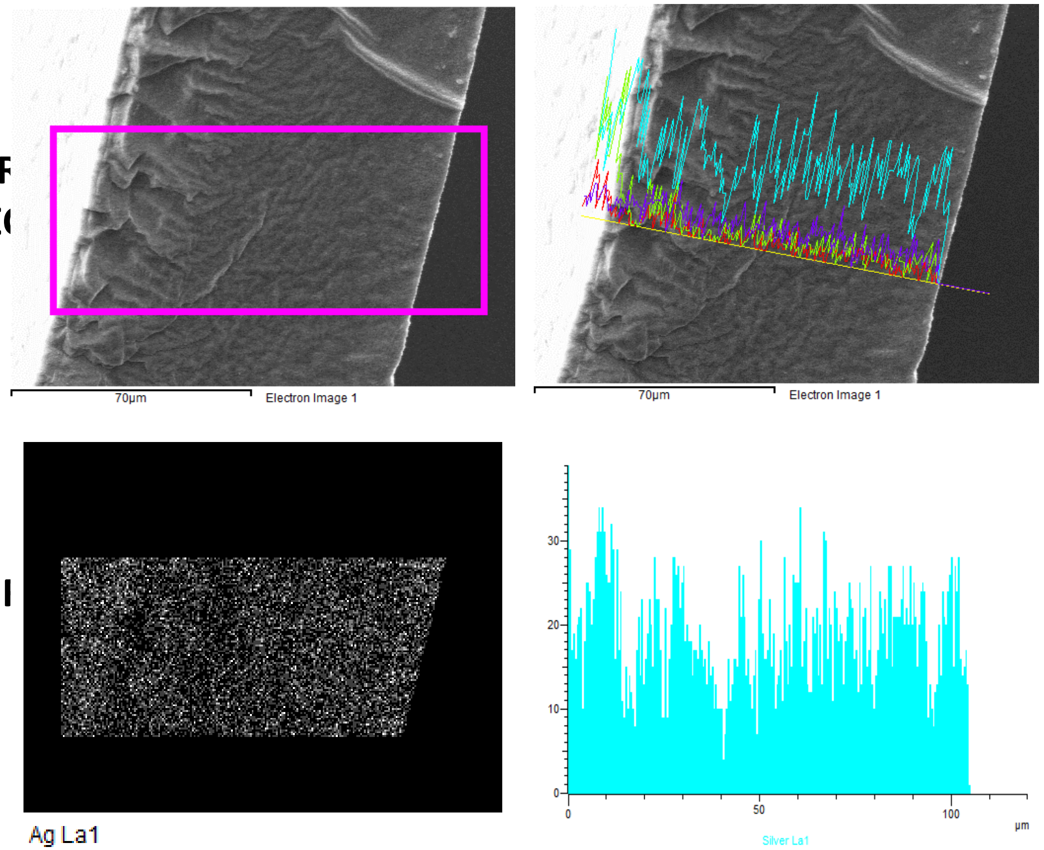
Zarca, Ortiz, Gorri, Ortiz I. J.Membr. Sci. 2018a

Zarca, Ortiz, Gorri, Ortiz I. J. Membr. Sci. 2018b

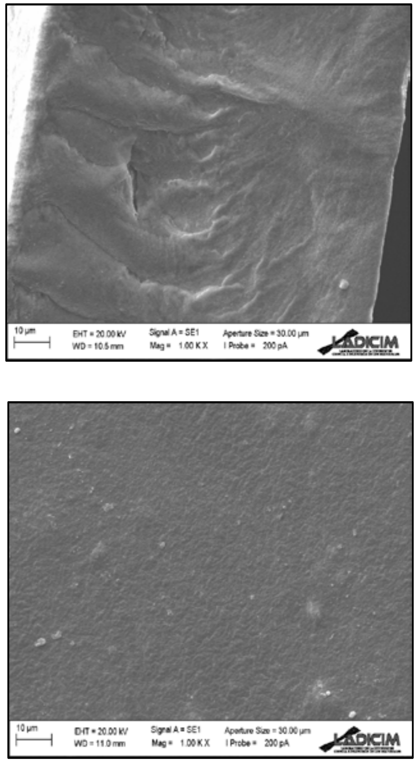
Scanning Electron Microscopy (SEM) + Energy Dispersive X-ray Spectroscopy (SEM+EDX)

CR
SE

SU



PVDF-HFP/BMImBF$_4$/AgBF$_4$ (5.23 mol/l

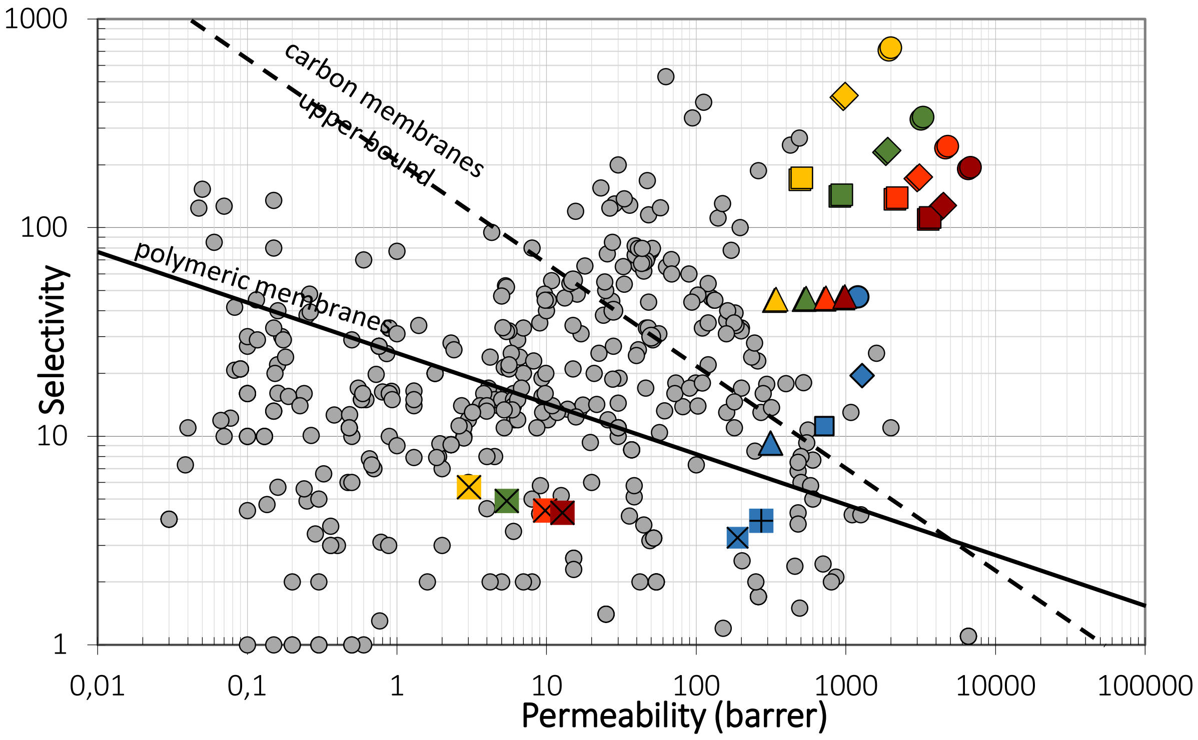


PVDF-HFP/BMImBF$_4$/AgBF$_4$ (5.23 mol/l)

UNIFORM DISTRIBUTION OF THE ELEMENT SILVER ... URES

Zarca, Ortiz, Gorri, Ortiz I. 2018 a

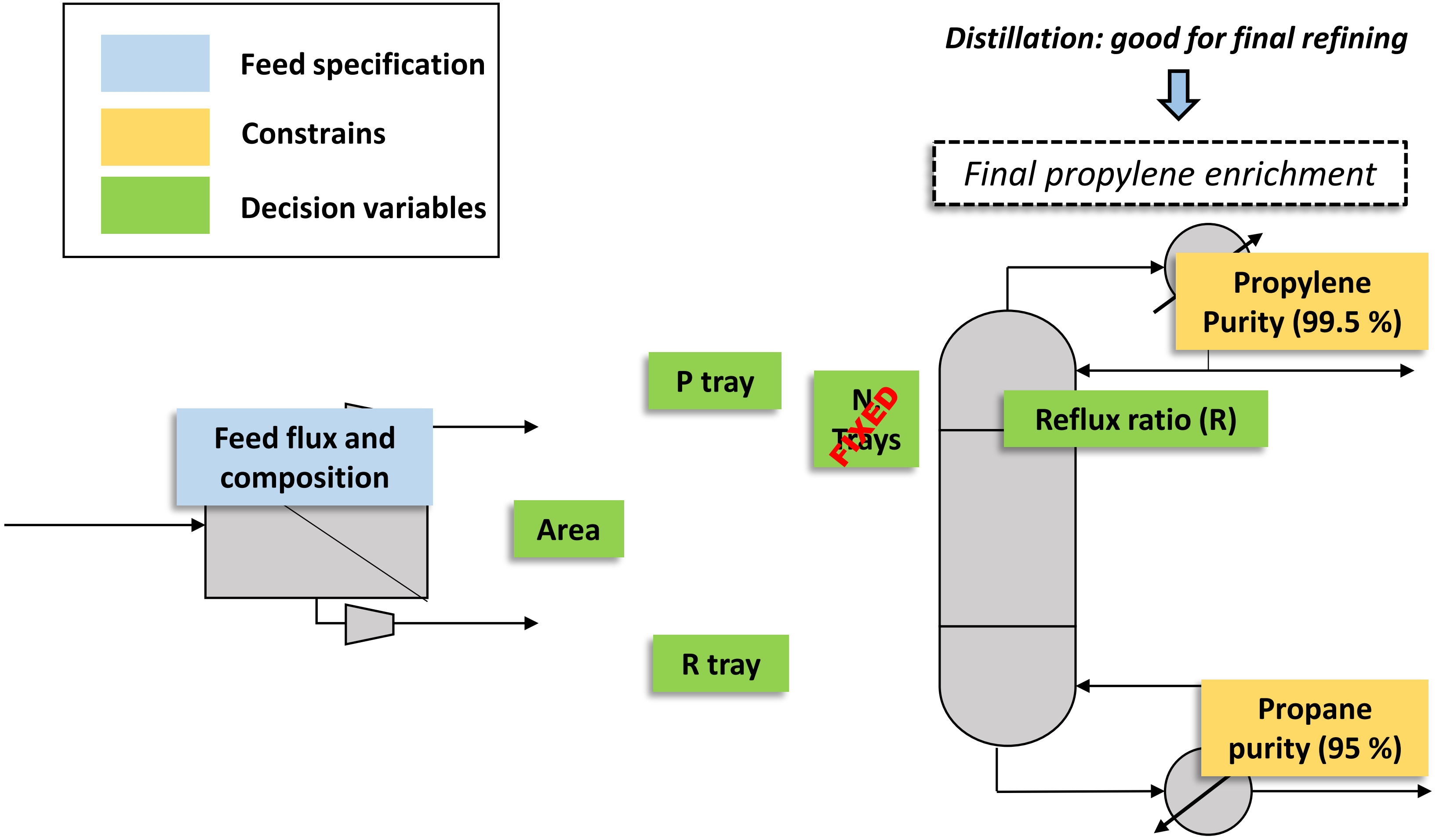
ID	Membrane	Area ($x10^3$ m^2)	Reflux	TOC Savings (%)
-	**None**	-	14.9	0
A	**ZIF8 / ZIF67/ZIF8**	2.8	4.5	56.2
B	**PVDF-HFP/$AgBF_4$/$BMImBF_4$**	7.4	5.3	50.3
C	**ZIF 8**	2.9	7.4	38.3
D	**6FDA-based polyimide CMS**	5.8	8.7	29.2
E	**6FDA-TeMPD**	5.3	10.5	17.6
F	**EC**	23.2	11.2	9.9



Zarca, Ortiz, Gorri, Ortiz I. J.Membr. Sci. 2018a

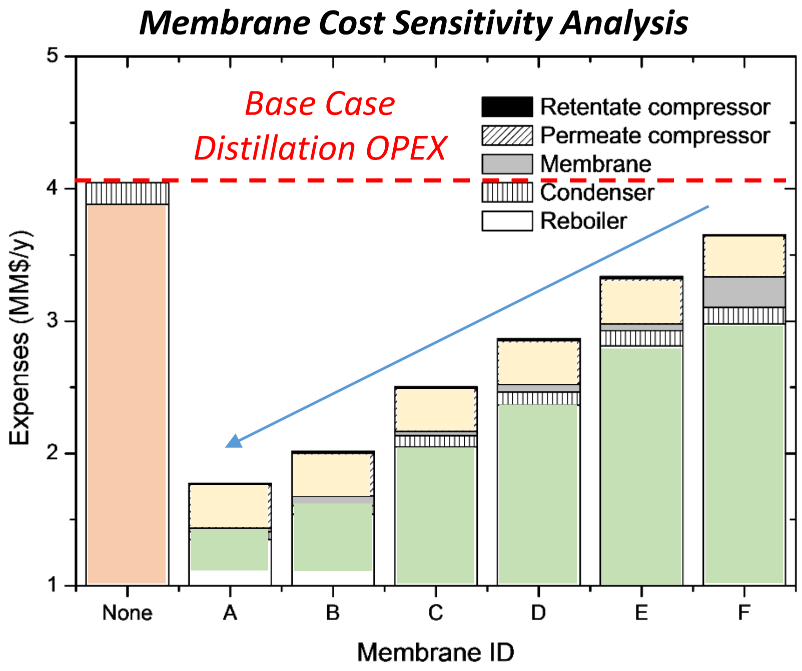
Zarca, Ortiz, Gorri, Ortiz I. J. Membr. Sci. 2018b

Optimization of a hybrid hollow fiber/distillation separation system



Sholl, Lively, 2016; Zarca, Ortiz, Gorri, Ortiz I. 2018b

TOC Reduction achieved with the studied membranes



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E	6FDA-TeMPD	5.3	10.5	17.6
F	EC	23.2	11.2	9.9

The main contribution to Base Case Distillation OPEX are the reboiler expenses

Preconcentration with membranes results in lower reflux → lower reboiler expenses

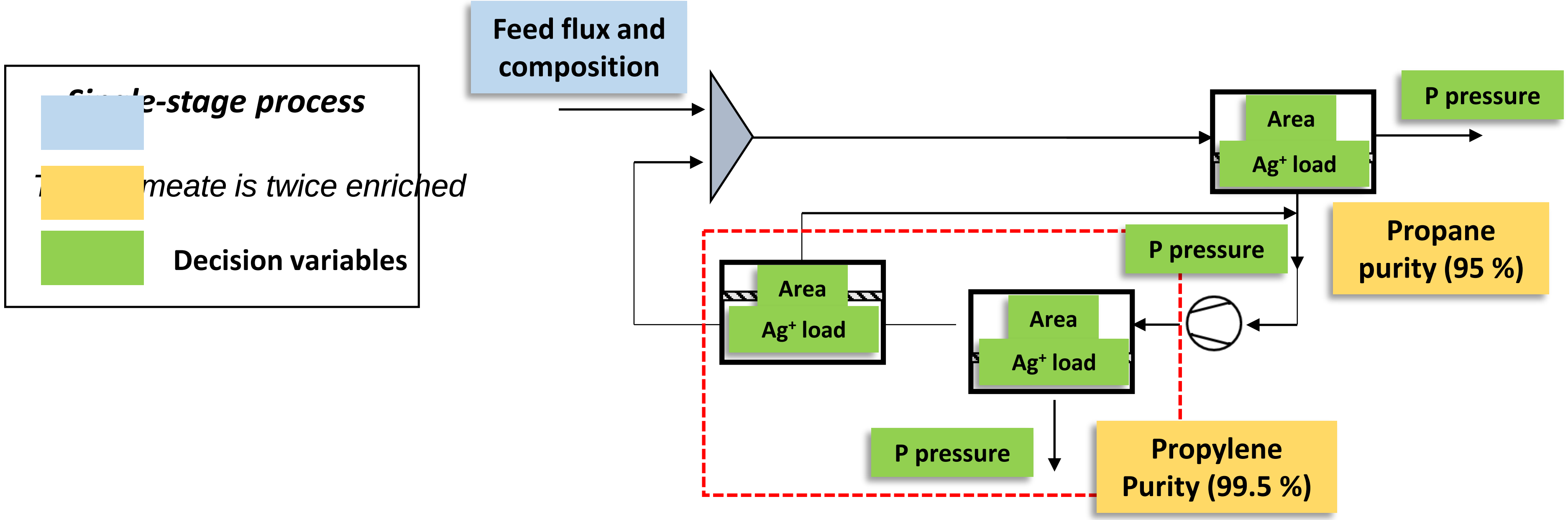
OPEX reduction is proportional to the reflux decrease

Permeate recompression accounts for the greater contribution among the new equipment

Energy intensity can be reduced by a factor of 2 or 3

Zarca, Ortiz, Gorri, Ortiz I. 2018b

Optimization of FTM-based multistage membrane processes



Zarca, Ortiz, Gorri, Biegler, Ortiz, I. AIChE J. 2019

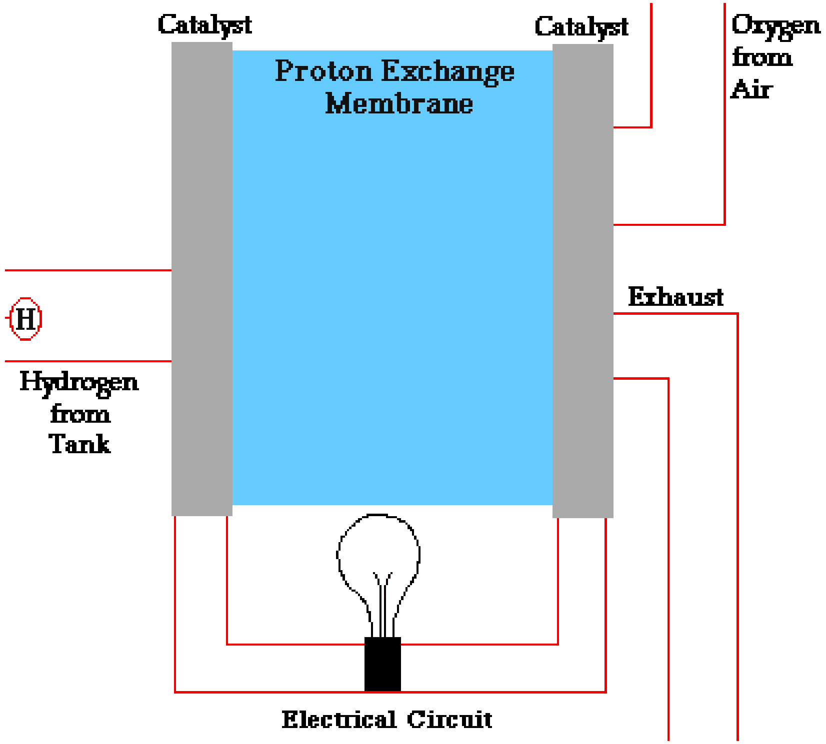
**Long term replacement of distillation columns must overcome the hurdle of membranes scaling up that requires new manufacturing methods and advances in materials' properties.*

**The use of comprehensive membrane models (structure-property links) inserted in advanced optimization software offers a very effective tool to establish the optimum process layout .*

Sholl, Lively, 2016; Zarca, Ortz, Gorri, Biegler, Ortiz I., 2019

Innovative separations for the development of renewable energy sources

PROTON EXCHANGE MEMBRANE FUEL CELLS



PEMFC

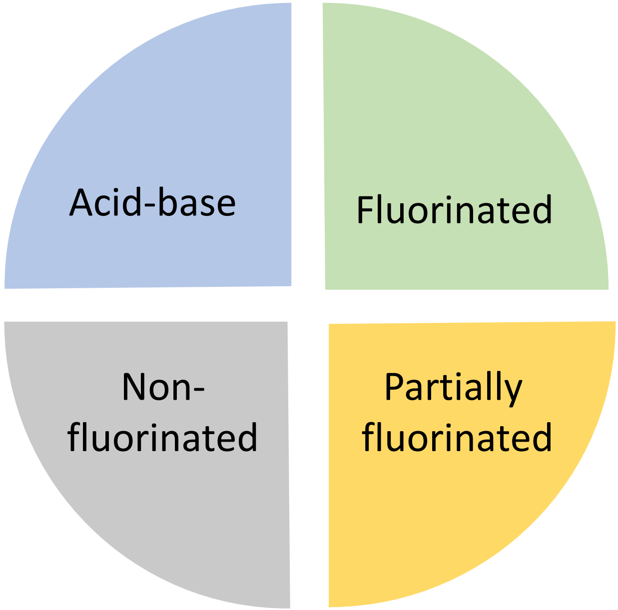
Anode: $H_2 \rightarrow 2H^+ + 2e^-$
Cathode: $\frac{1}{2} O_2 + 2e^- + 2H^+ \rightarrow H_2O$
Global: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

- H_2 oxidation at anode: formation of H^+
- O_2 reduction at cathode: O_2^-
- H^+ from anode to cathode through membrane
- Water as byproduct

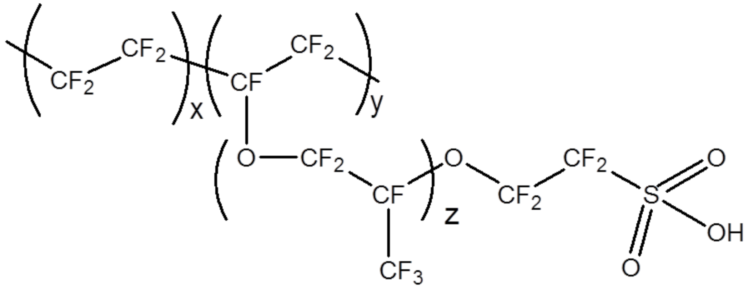
Core
Proton Exchange Membrane (PEM)

Díaz, Ortiz, Ortiz I. J. Membr. Sci. 2014

PROTON EXCHANGE MEMBRANES



Nafion membranes (PFSA) (DuPont)



High ionic conductivity

High chemical and electrochemical stability

Strong dependence of conductivity on humidity

High fuel crossover

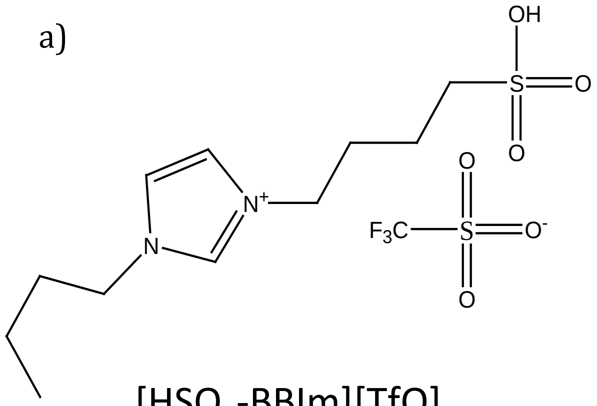
Expensive

The challenge of New proton exchange membranes

M. Díaz , Ortiz, Ortiz I. J. Membr. Sci. 2014

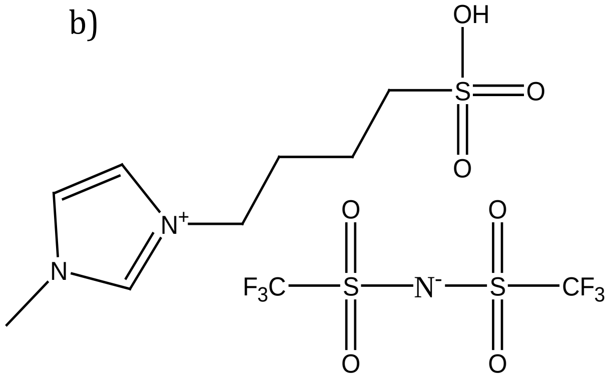
DESIGN PROTIC IONIC LIQUIDS

a)



$[HSO_3\text{-}BBIm][TfO]$

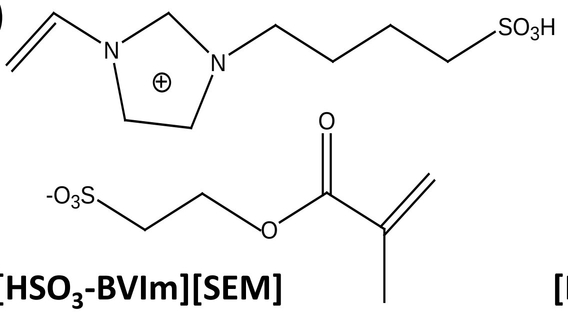
b)



$[HSO_3\text{-}BMIm][Tf_2N]$

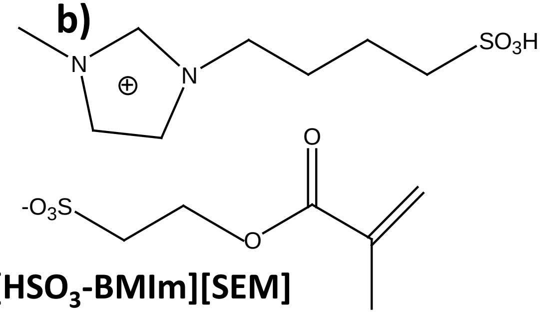
- ✓ Imidazolium high electrochemical stability
- ✓ Sulfonic groups to facilitate proton transport
- ✓ Tf_2N^- and TfO^- have high ion conductivity

Díaz, Ortiz, Vilas, Tojo, Ortiz I. , 2014 a)



[HSO$_3$-BVIm][SEM]

b)



[HSO$_3$-BMIm][SEM]

- Imidazolium high electrochemical stability
- Sulfonic groups encourage proton transport
- Methacrylate allows complex polymer

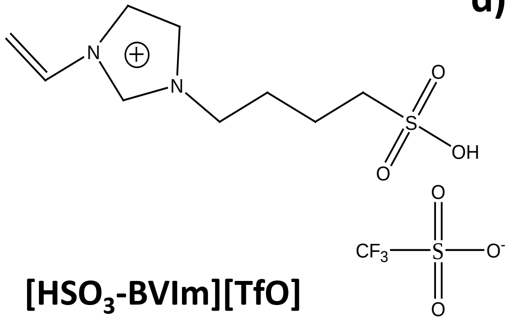
TWO POLYMERIZABLE ILs (sulfoethylmethacrylate anion)

POLYMERIZED PROTIC IONIC LIQUIDS

POLYMERIZABLE IL + NON-POLYMERIZABLE (free) IL (triflate anion)

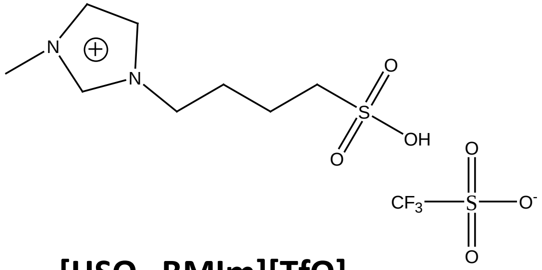
- Imidazolium high electrochemical stability
- Sulfonic groups encourage proton transport
- Triflate high conductivity

c)



[HSO$_3$-BVIm][TfO]

d)

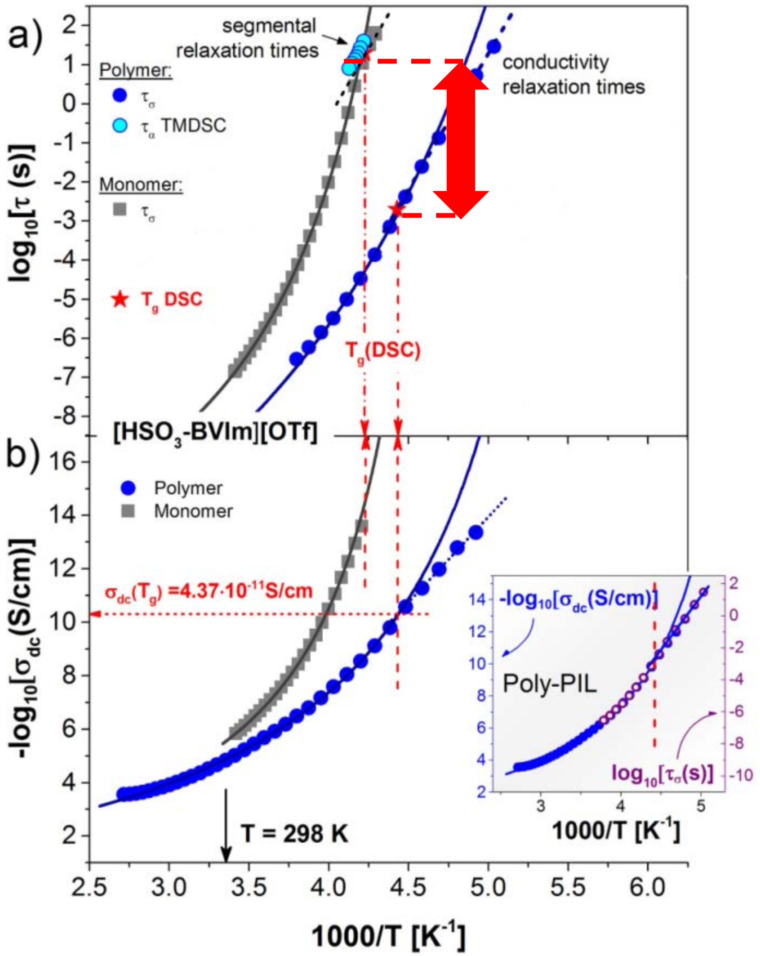


[HSO$_3$-BMIm][TfO]

Díaz, Ortiz, Isik, Mecerreyes, Ortiz I. 2014

Ion dynamics studies

TRIFLATE ANION-BASED MEMBRANES



POLYMER

Shift from non-Arrhenius to Arrhenius behavior at τ_σ faster than 10^2 s

Decoupling between τ_σ and τ_α at Tg

Grotthuss mechanism
Ions movements are still fast when structural relaxation becomes frozen

Conductivity of polymer is higher

2 different proton transport mechanisms

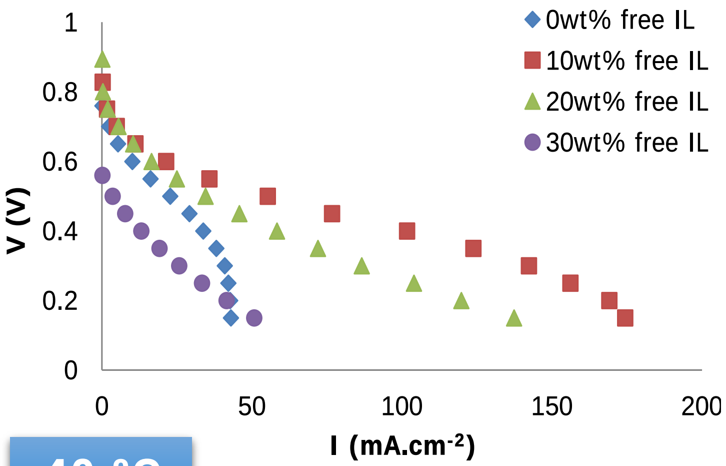
Monomer: Vehicular ⟷ Polymer: Grotthuss

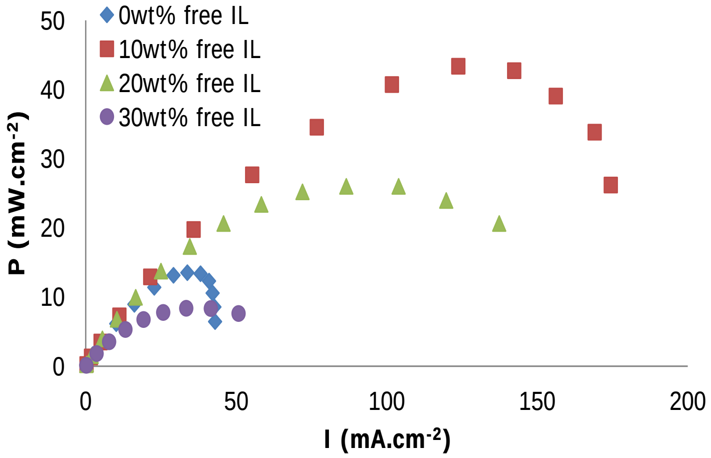
Z. Wojnarowska, J. Knapik, M. Diaz, A. Ortiz, I. Ortiz, Ma. Paluch., 2014; Z.Wojnarowska, H. Feng, M. Diaz, A.Ortiz, I. Ortiz. 2017

ECCE 12
ECAB 5

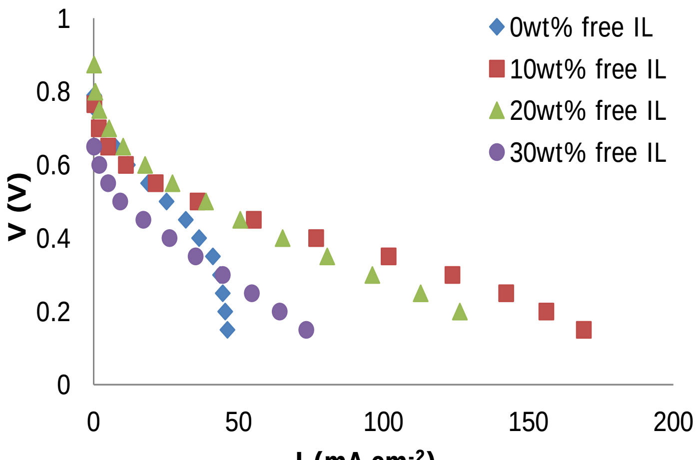
Fuel cell performance. Triflate anion-based membranes

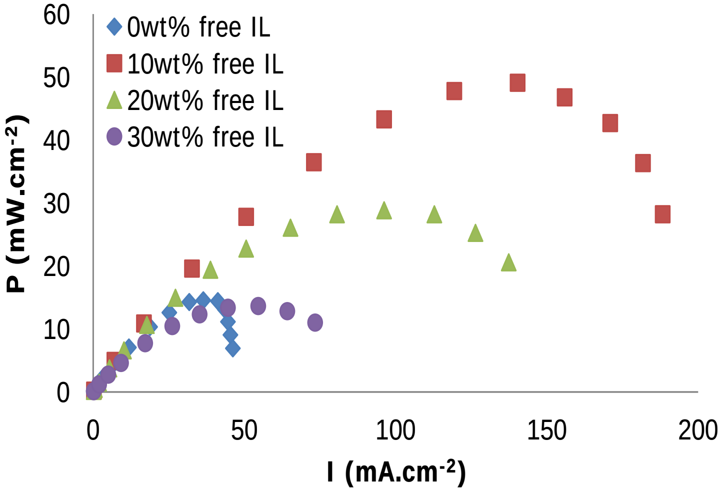
25 °C





40 °C





Tª improves FC performance

+ 30 wt% IL

22 $mA.cm^{-2}$ (0.15 V)

5.3 $mW.cm^{-2}$

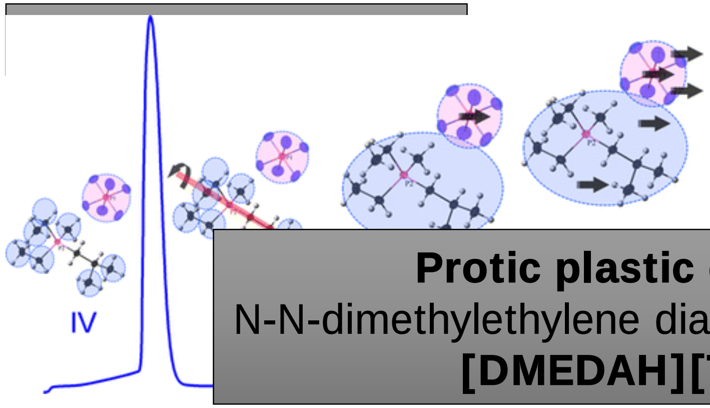
Lower free IL: effect of temperature is less pronounced

Mechanical stability compromises high temperatures

M. Dıaz, A. Ortiz, M. Vilas, E. Tojo, **I. Ortiz**, 2014

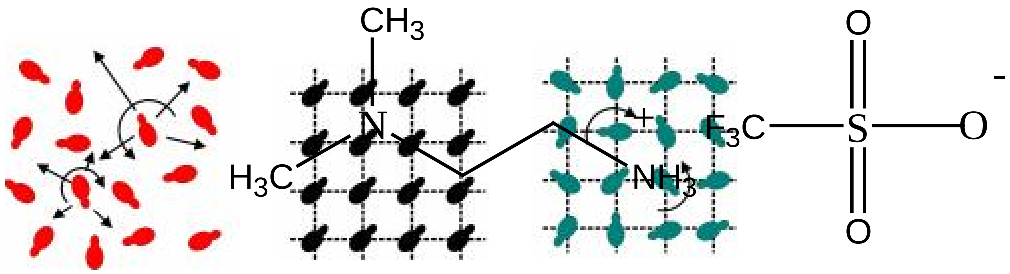
* Better understanding of the role of the components of polymerized ILs on charge transport and membrane performance

* Solid Electrolytes: Protic plastic crystals

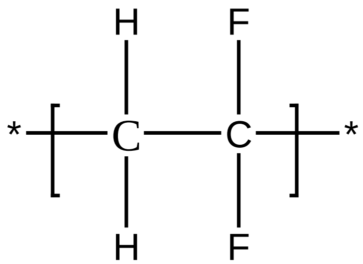


Protic plastic crystal
N-N-dimethylethylene diammonium triflate
[DMEDAH][TFO]

Polymer
Electrospun poly(vinylidene fluoride) nanofibers
PVDF



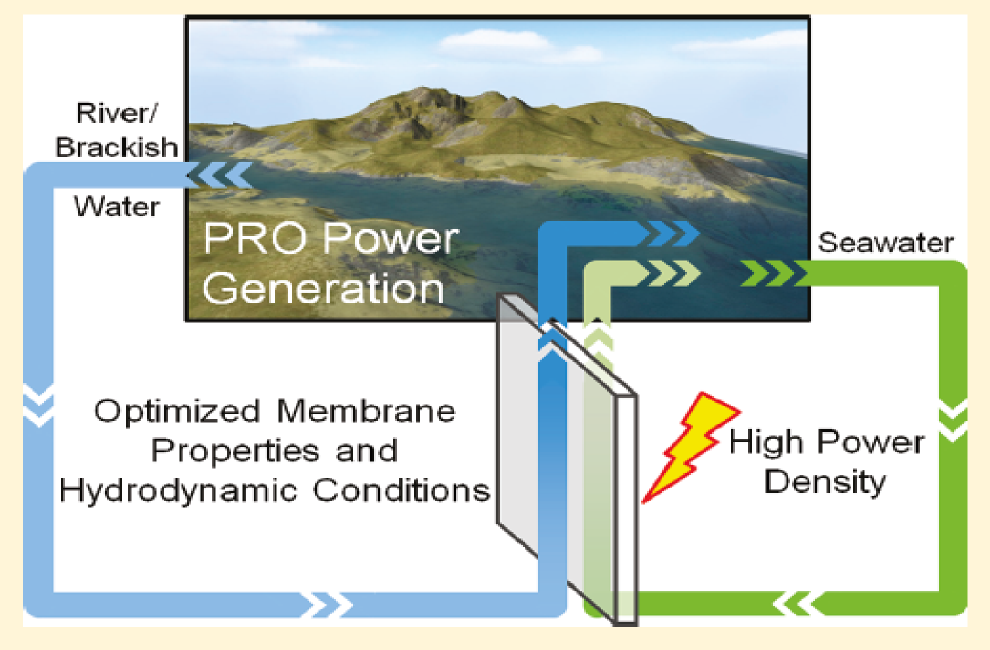
Liquid **Ordered crystal** **Plastic crystal**



Phys.Chem.Chem.Phys., 2013

- **SALINE GRADIENT**

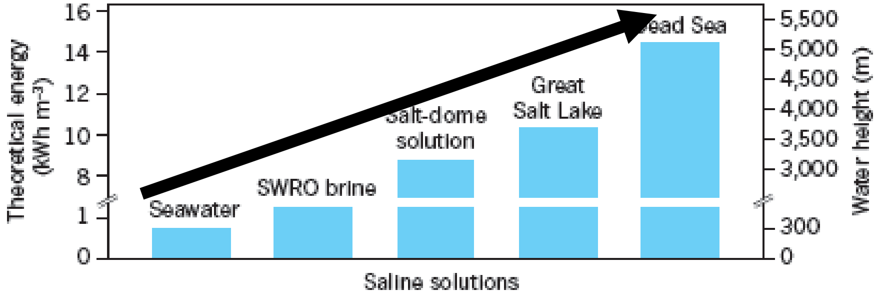
0.8 kW/m^3



Equivalent to the energy generated from water falling over a dam more than 280 meters high

14 kWh/m^3

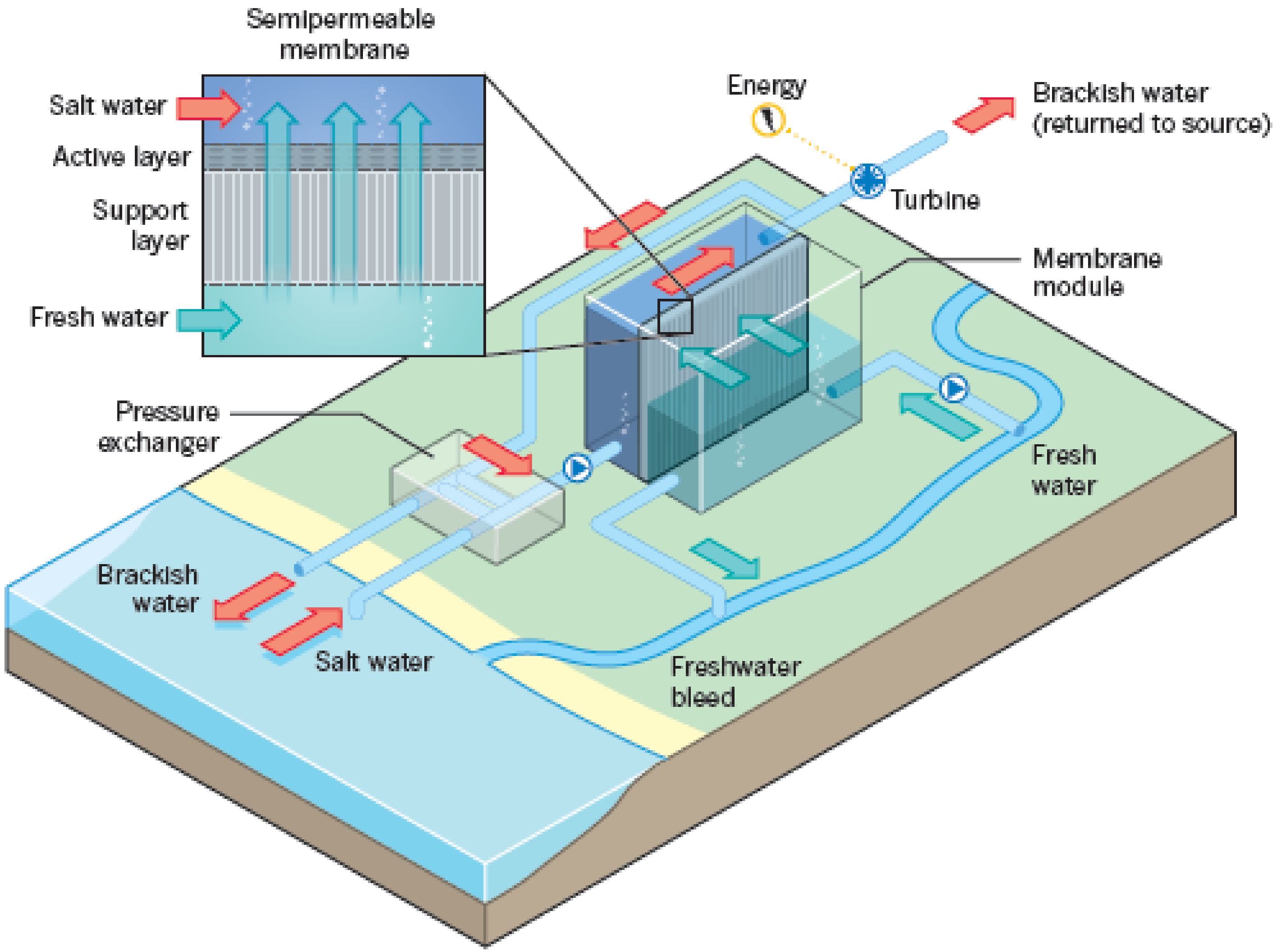
0.8 kWh/m^3



About 2 terawatts (1 TW is equal to 1000 gigawatts) is available globally from rivers flowing into the sea, of which perhaps 980 GW could be harnessed. In addition, wastewater release into the ocean could provide another 18 GW of salinity-gradient power.

Pattle 1954 *Yip & Elimelech 2011* *Logan & Elimelech 2012*

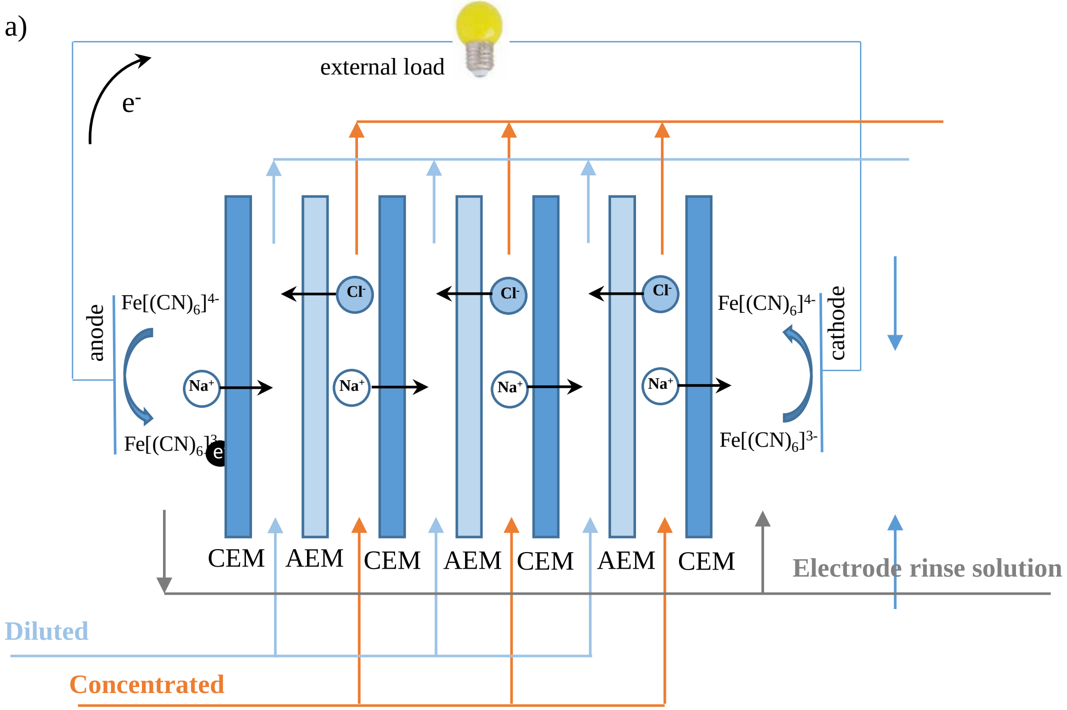
Harnessing energy by PRO

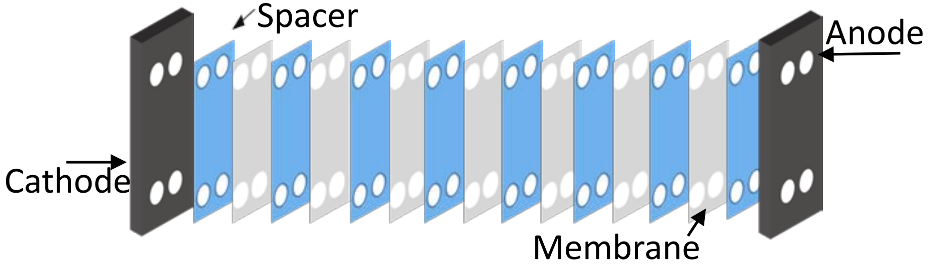


Logan & Elimelech, 2012

The plant ran from 2009 to 2012 at 10kW capacity with an initial membrane energy density of 1 W/m^2

Reverse Electrodialysis

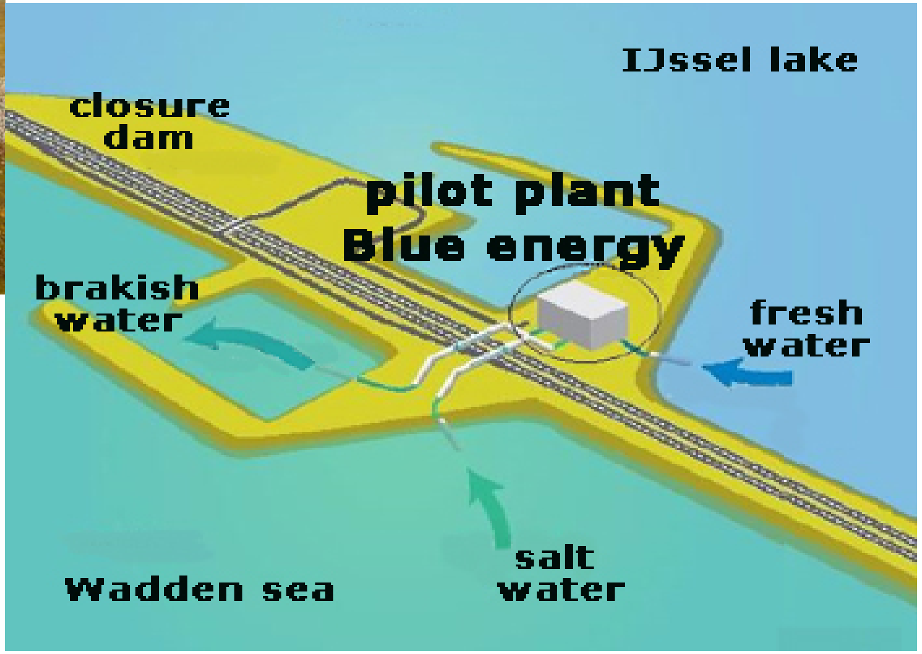




Ortiz R. …Ortiz, I. 2019

Afsluitdijk (Harlingen, The Netherlands)

Start , May 2008-2010
Target power: 5kW
Sea water and lake water
Extension in 2013 to 50kW
Target power 200MW (2020)



Sea water				Lake water			
Cations	meq/L	Anions	meq/L	Cations	meq/L	Anions	meq/L
Na^+	405	Cl^-	482	Na^+	2	Cl^-	3
Mg^{2+}	83	SO_4^{2-}	19	Mg^{2+}	1	SO_4^{2-}	1
Ca^{2+}	3	Br^-	1	Ca^{2+}	3	Br^-	0
K^+	9	HCO_3^-	1	K^+	0	HCO_3^-	3
Total	500	Total	503	Total	7	Total	7

Marsala (Sicily, Italy)

Saltwork Brine and brackish water

Lab-scale stack (0.5m2) 2012

Power: 1.09W

Large lab-scale stack(5m2) 2013

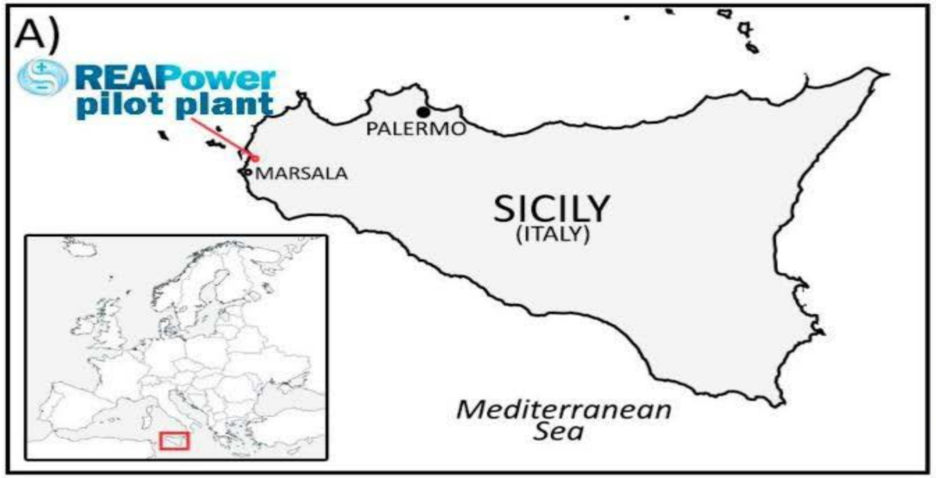
Power: 11.25W

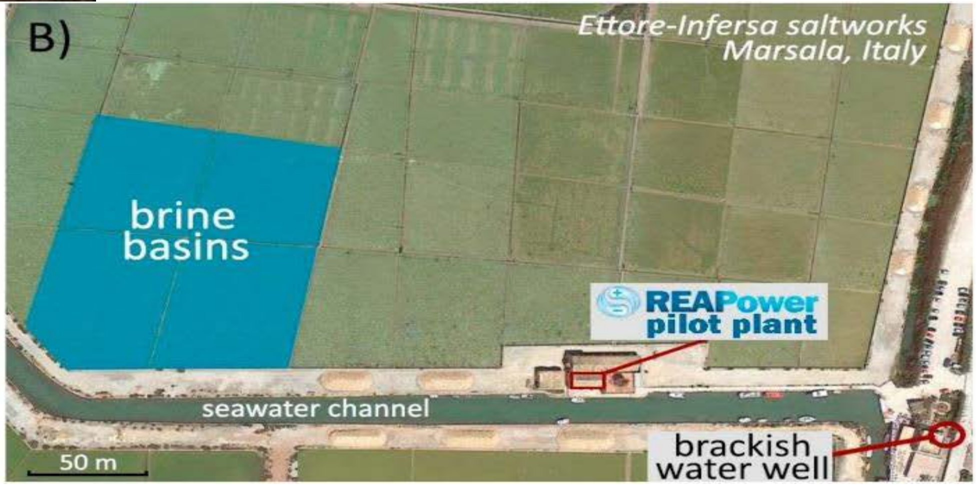
Small prototype2014

Power: 38.4W

Large prototype 2015

Power: 350W





Brine				Brackish water			
Cations	meq/L	Anions	meq/L	Cations	meq/L	Anions	meq/L
Na^+	2782	Cl^-	5408	Na^+	18	Cl^-	34
Mg^{2+}	3704	SO_4^{2-}	812	Mg^{2+}	7	SO_4^{2-}	2
Ca^{2+}	20	-		Ca^{2+}	14	-	
K^+	282	-		K^+	0.5	-	
Total	6788	Total	6220	Total	39.5	Total	36

- **Improving the stack components and design: cost-effective and high performance membranes, optimal fluid dynamics etc**

- **Advancing comprehensive models and optimum design tools**

Yañez, Brunaud, Ortiz A, Grossmann, Ortiz, I., . 2018; Ortiz-Imedio R. …Ortiz, I. 2019

Innovative separations under magnetic field: Challenges in Bio-medicine

Magnetic micro and nano-materials

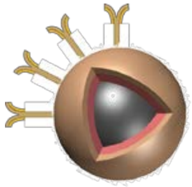
High surface area to volume ratio

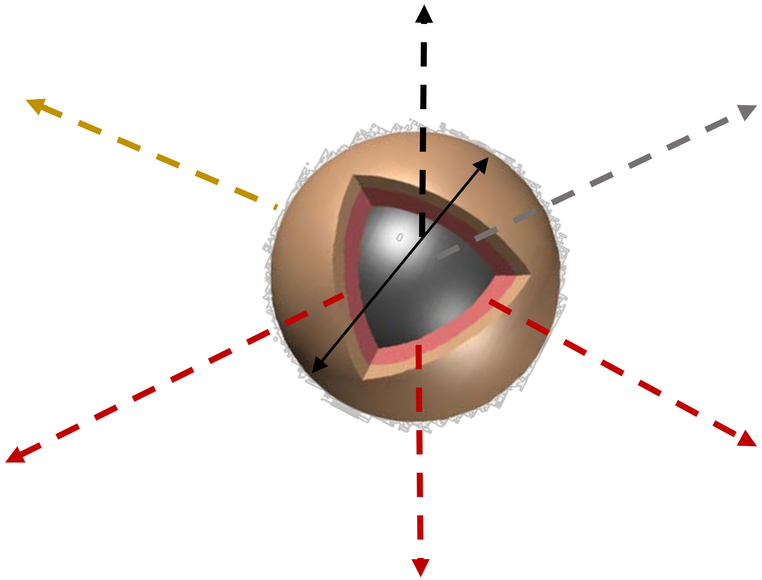
Nanometer to micrometer size

Superparamagnetic characteristics

Fe, Ni, Co, Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$

Functionalizable surface





Biocompatibility

Stability against corrosion and oxidation

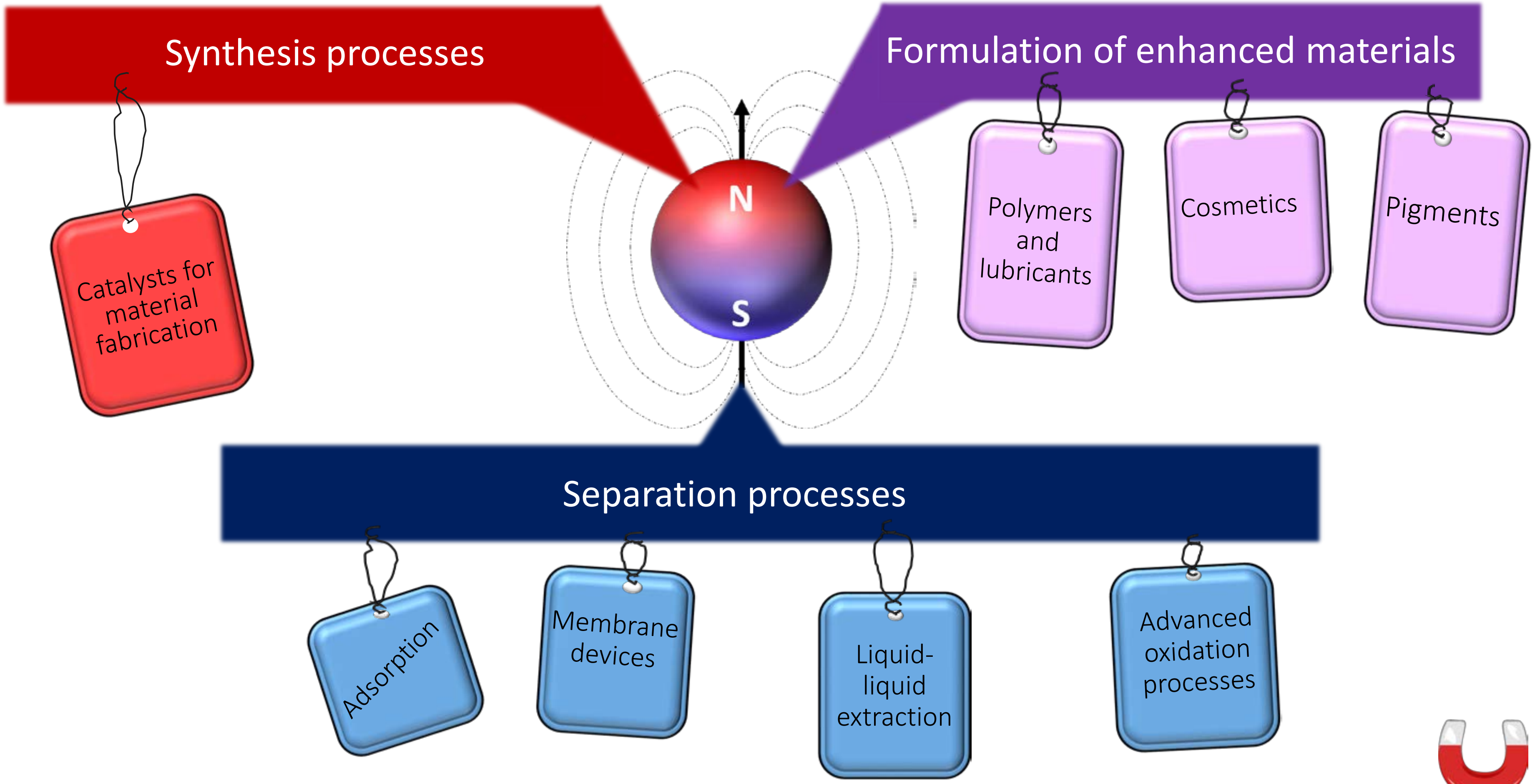
Physicochemical stability

Polymers (dextran, chitosan, PEG), SiO_2

Gomez, Bringas, Ortiz, I. 2014

Applications in chemical and biomolecular engineering

Chemical engineering



Magnetic separation

Benefits

Efficient

Selective

Fast

Non-invasive

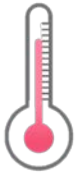
Not affected by solution parameters

Energetically more efficient than conventional processes

Allows the separation of magnetic materials from non-magnetic solids

Faster than conventional methods (filtration and centrifugation)

Free of fluid heating issues if permanent magnets are used

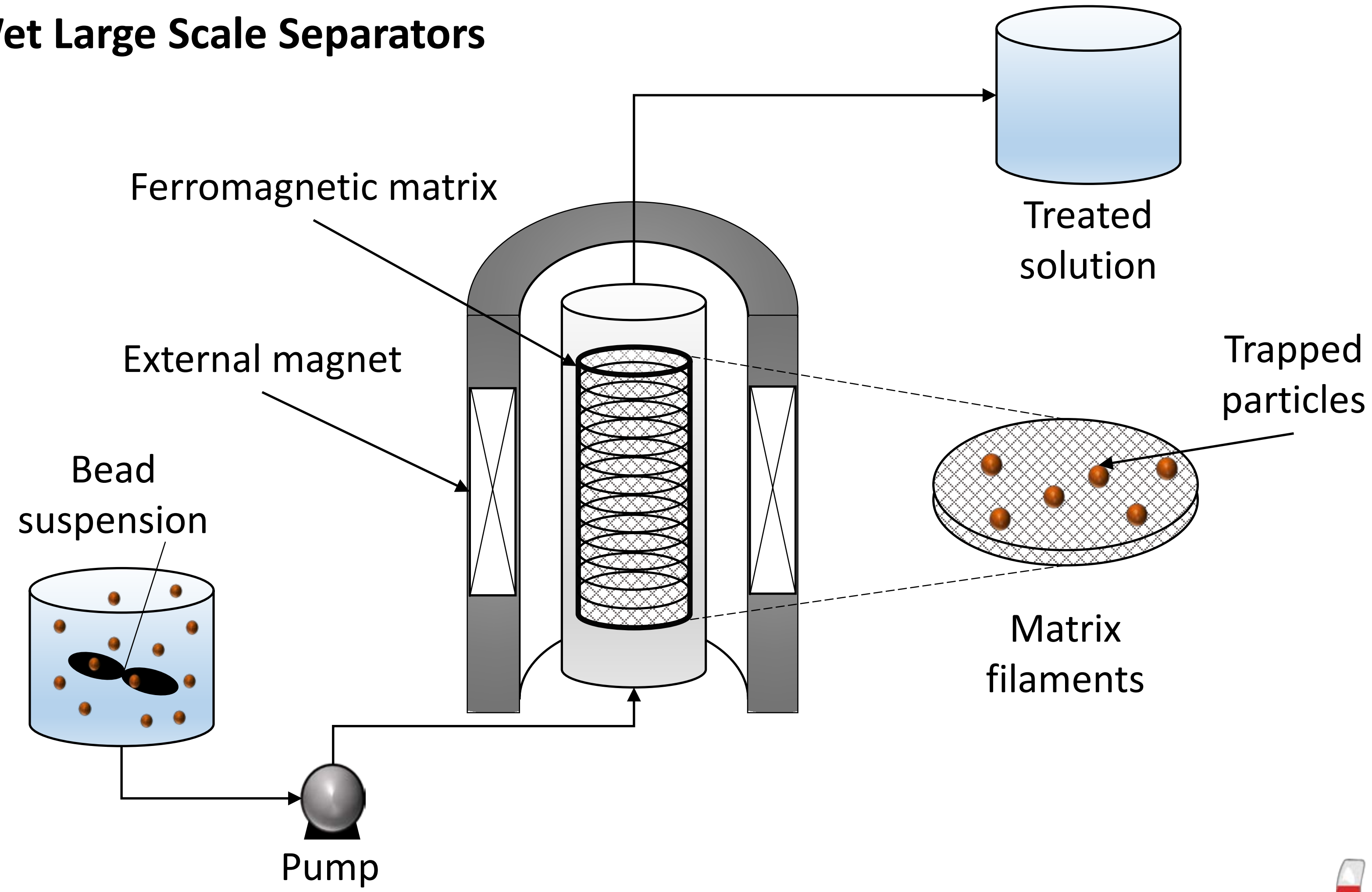


Not sensitive to pH, temperature or ionic concentration

Gómez, Domínguez, Bringas, Rivero, Ortiz,I., Dionysiou, 2017

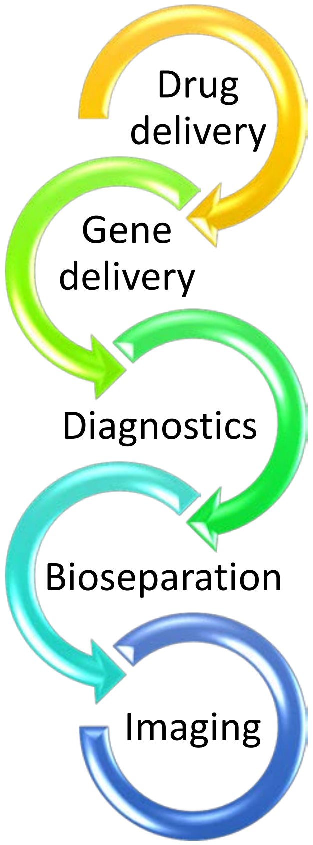
Magnetic separation

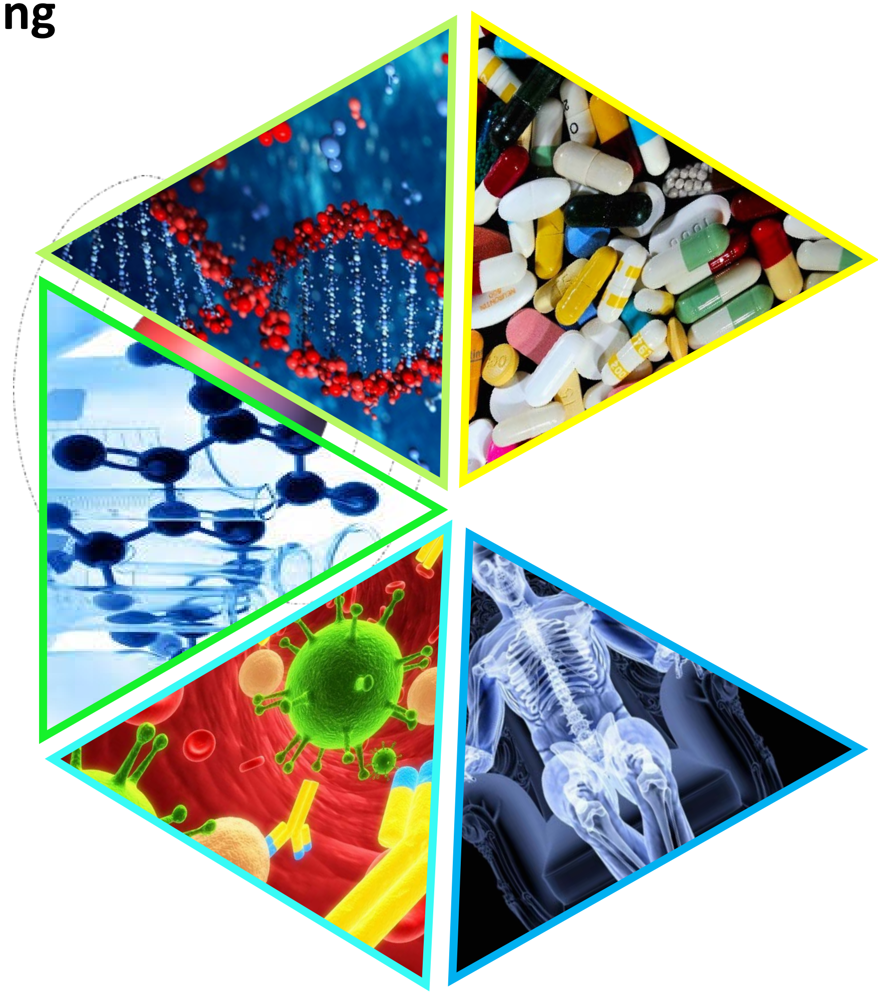
Wet Large Scale Separators



Applications in chemical and biomolecular engineering

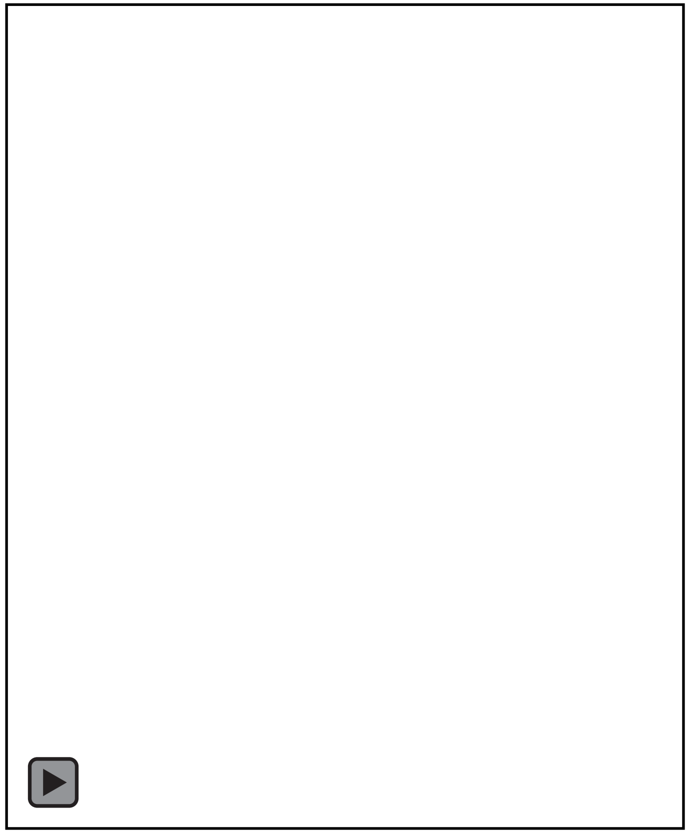
Biomolecular engineering





Significant progress to separation in the analytical or biomedical fields has come from the advantageous characteristics of microfluidics

micro-devices provide for significant enhancement in heat and mass transfer and due to the small diffusion path lengths they gather characteristics that make of them ideal candidates in the design of more sustainable units.



Passive mixing

In continuous-flow microdevices multiple liquids flow side-by-side in a stable manner

Mixing occurs by diffusion

Possibility to control their diffusive interface

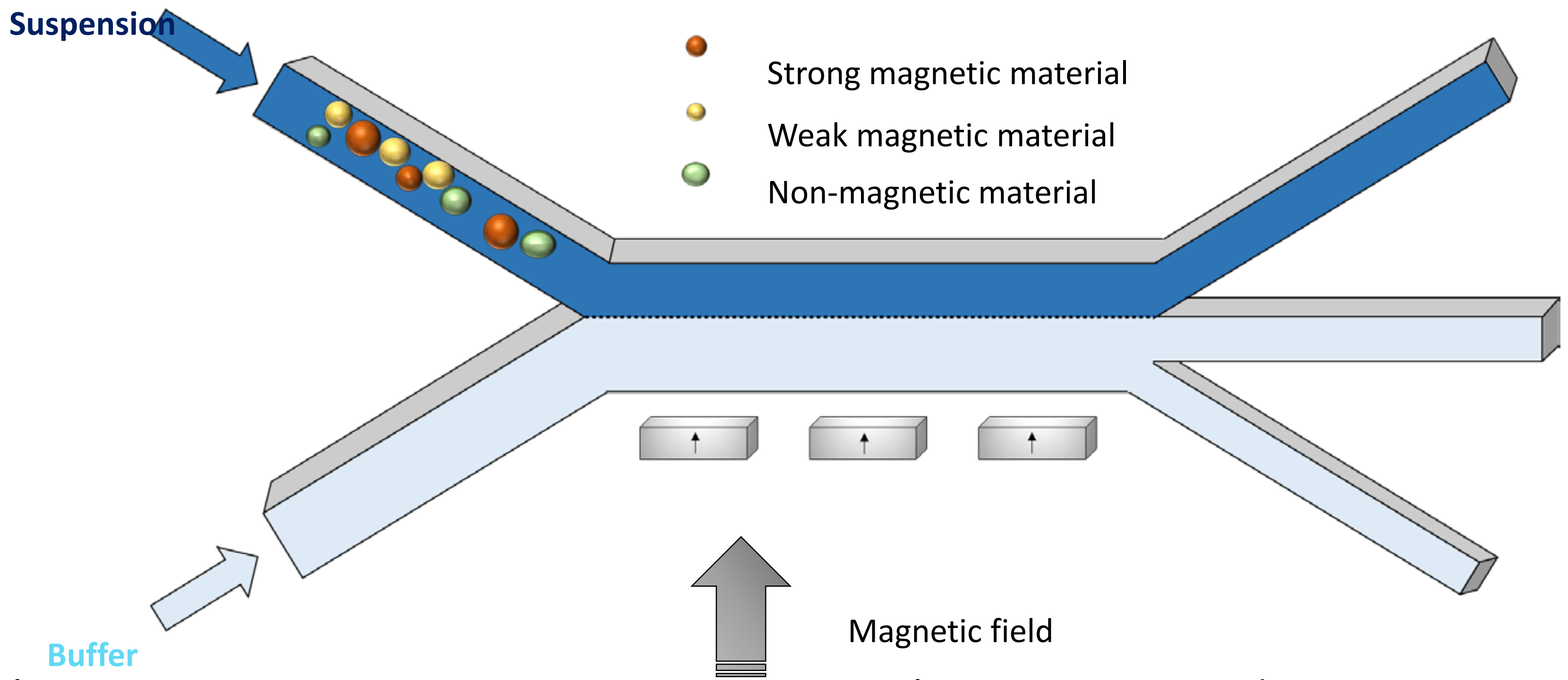
Understanding of the fluid dynamics of the flowing fluids and mass transfer kinetics of the solutes contained in the fluids

Gómez, Basauri, Fallanza, Bringas, Ortiz, I. . 2018

Micro-magnetoforetic separation

Microfluidic devices

Microfluidics is an emerging state-of-the-art technology that handles small volumes of liquids (10^{-9} to 10^{-18} L) within an area with dimensions of tens to hundreds of µm

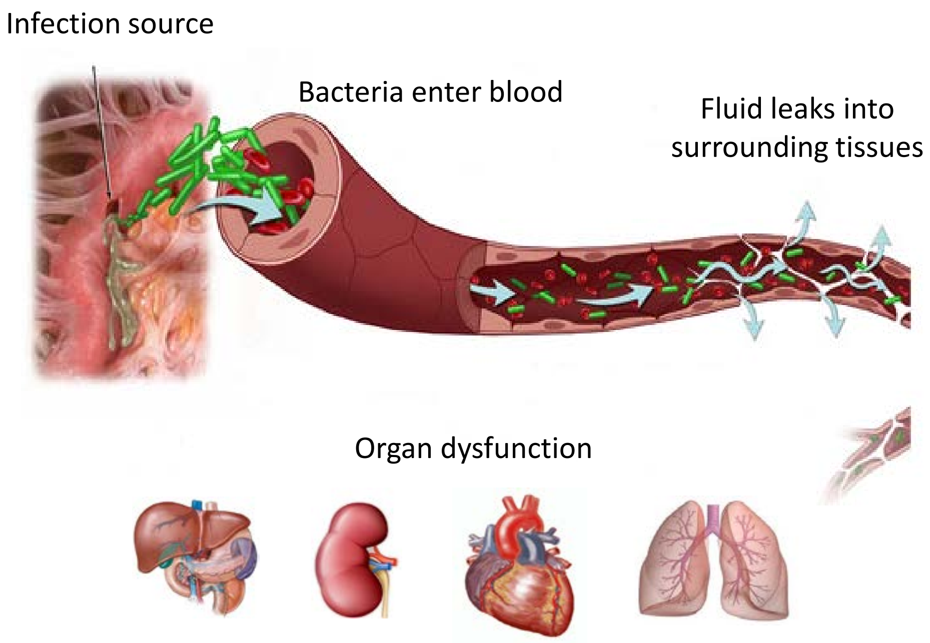


Alorabi, Tarn, Gómez-Pastora, Bringas, Ortiz, I, Pamme 2017, J. Gómez, XueKarampelas, Bringas, PFurlani, **I. Ortiz, 2016**

Micro-magnetophoretic separations

- **Magnetophoresis is a contactless method for manipulation of particles**
- **It does not affect the properties of the sample solution, pH, ion concentration, Surface charge, Temperature**
- **Easy operation, low cost, simple design**
- **Permanent magnets suitable for portable point-of-care applications**
- **Separations based on particle size and magnetic susceptibility**
- **Cell separations after labelling with magnetic particles, eg circulating tumor cells, CTCs**

Detoxification of biofluids-Sepsis



SEPSIS IN NUMBERS

11^{th} cause of death and 7^{th} cause of infant mortality

18 million people/year (35% ICU patients)

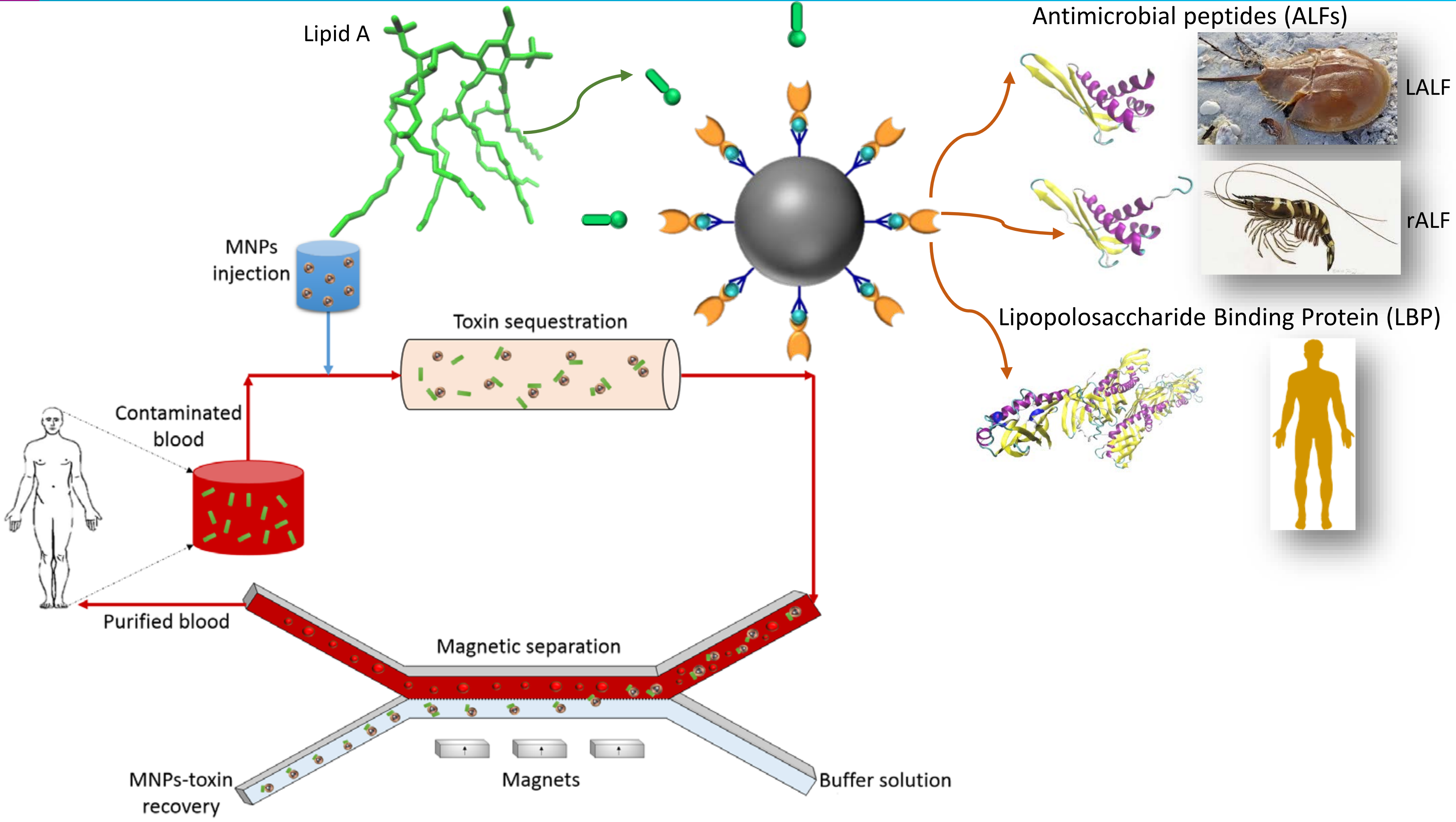
200.000 deaths in the US

Treatment costs ≈ $15 billion in the US

CONVENTIONAL TREATMENT METHODS

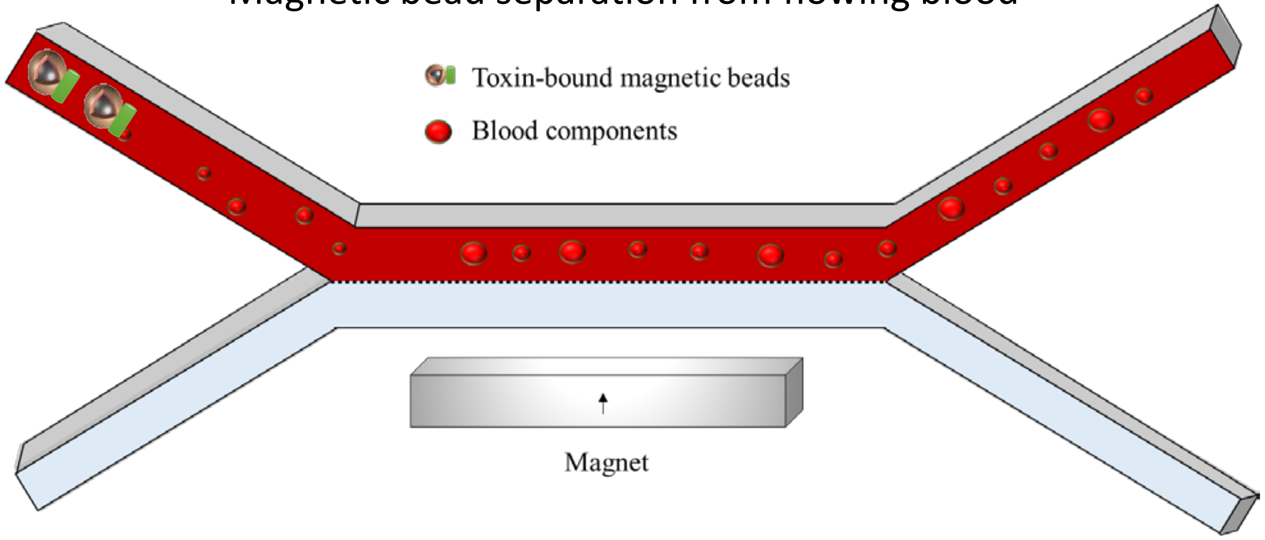
Antibiotics	✔ Broad-spectrum	✘ Takes days, blood cultures negatives, antibiotic-resistant bacteria
Hemofiltration	✔ Bacteria & toxins	✘ Non-specific, alters critical blood components

Extracorporeal blood cleansing devices



Particle magnetophoresis – Detoxification of biofluids

Magnetic bead separation from flowing blood



ADVANTAGES

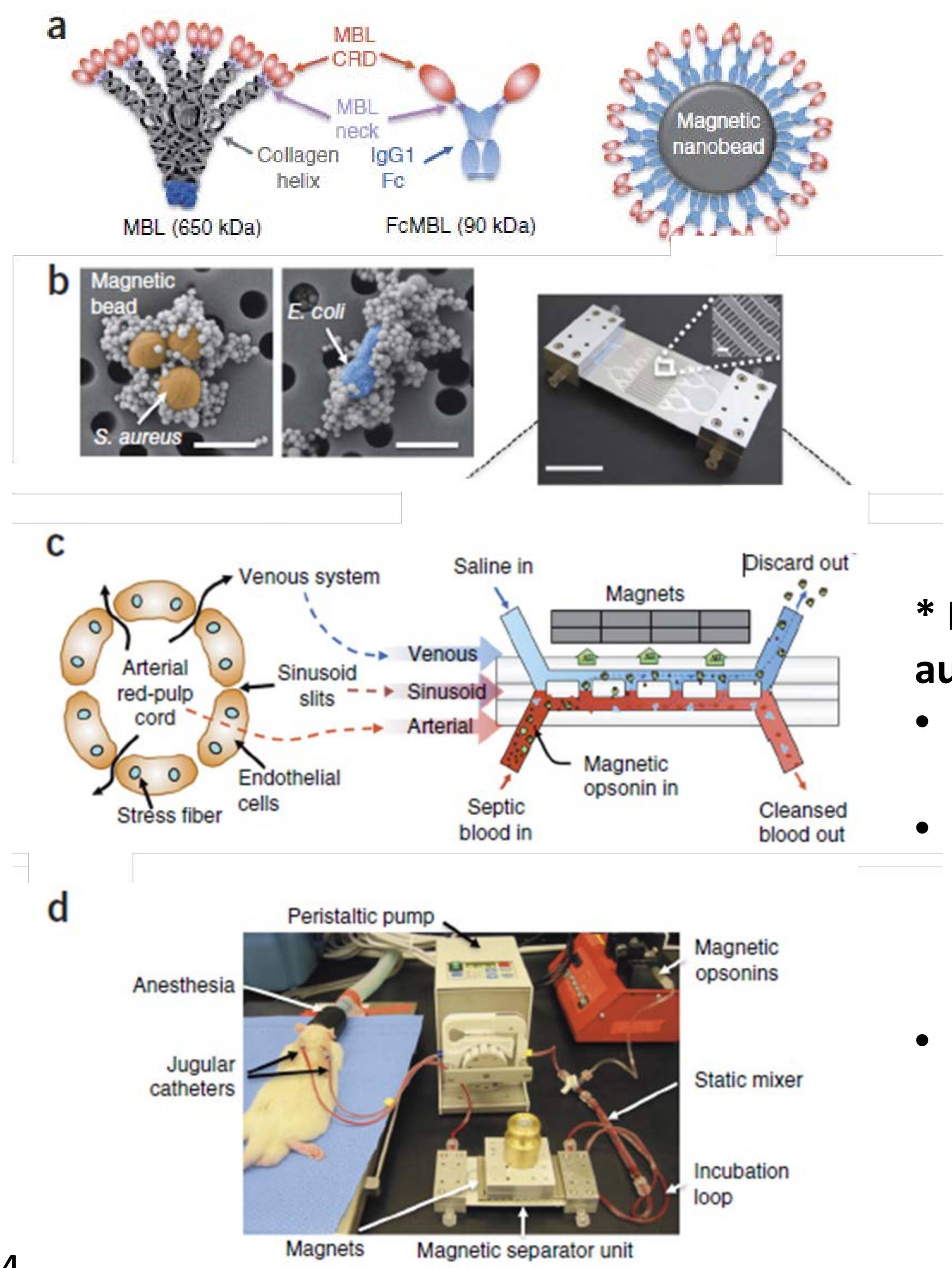
- No flow restriction
- Continuous mode

DESIGN CHALLENGES

- Independent flow of colaminar streams
- Complete magnetic bead recovery
- Minimized bead-fluid interactions
- Minimized diffusion

Advancing this technology requires the reliable removal of the magnetic beads by studied magnetic fields and the independent flow of both solutions

LOC 2017Gómez-Pastora[1,a].......l. **Ortiz,** 2017



*** Rats infected with Staphylococcus aureous or Escherichia coli**

- **> 90% bacteria were cleared from blood**
- **Reduced pathogen and immune cell infiltration in multiple organs and decreased inflammatory cytokine levels.**
- **The rat survival rate increased after 5-h treatment.**

Kang……Ingber, .Nature Med. 2014

- **Understanding the phenomena involved with the aid of molecular dynamics simulation coupled to process design tools**

- **Scale up of the separation devices coupled to in vivo and long term assessment**


go raibh maith agat
malondo asante
koszonom
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mochchakkeram
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dank je
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謝謝
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