GREEN CHEMISTRY

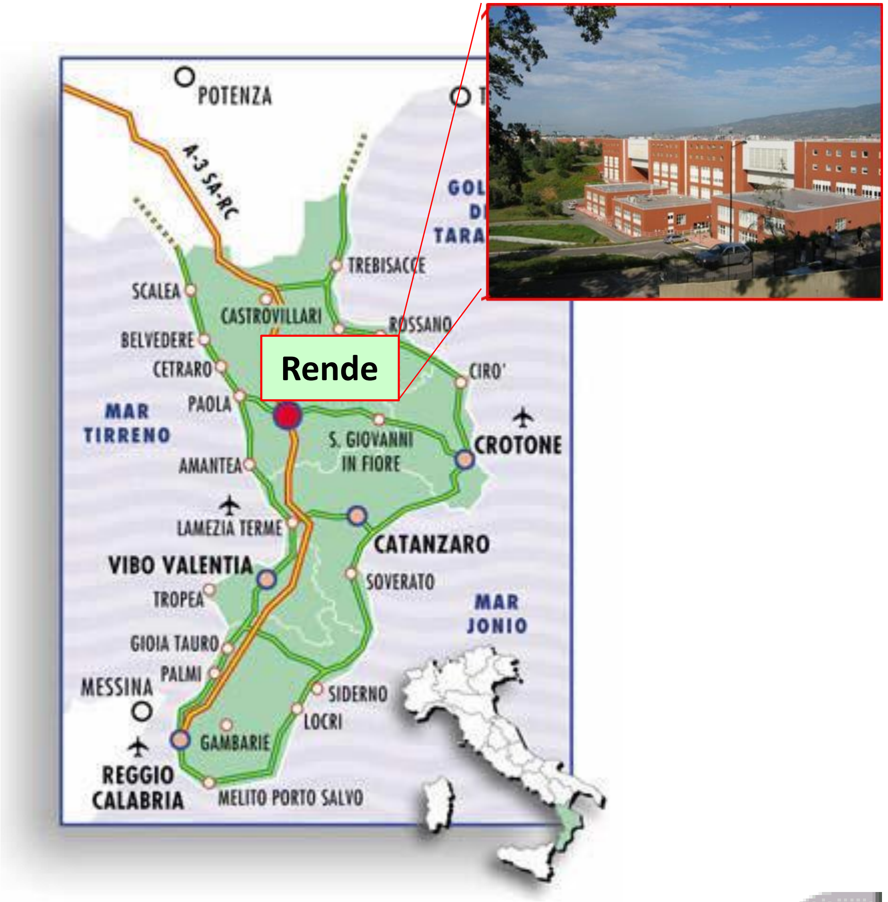
DSCTM

Dipartimento Scienze Chimiche e Tecnologie dei Materiali

Young Investigator Award 2019

Consiglio Nazionale delle Ricerche
ITM

Membranes for Green processes

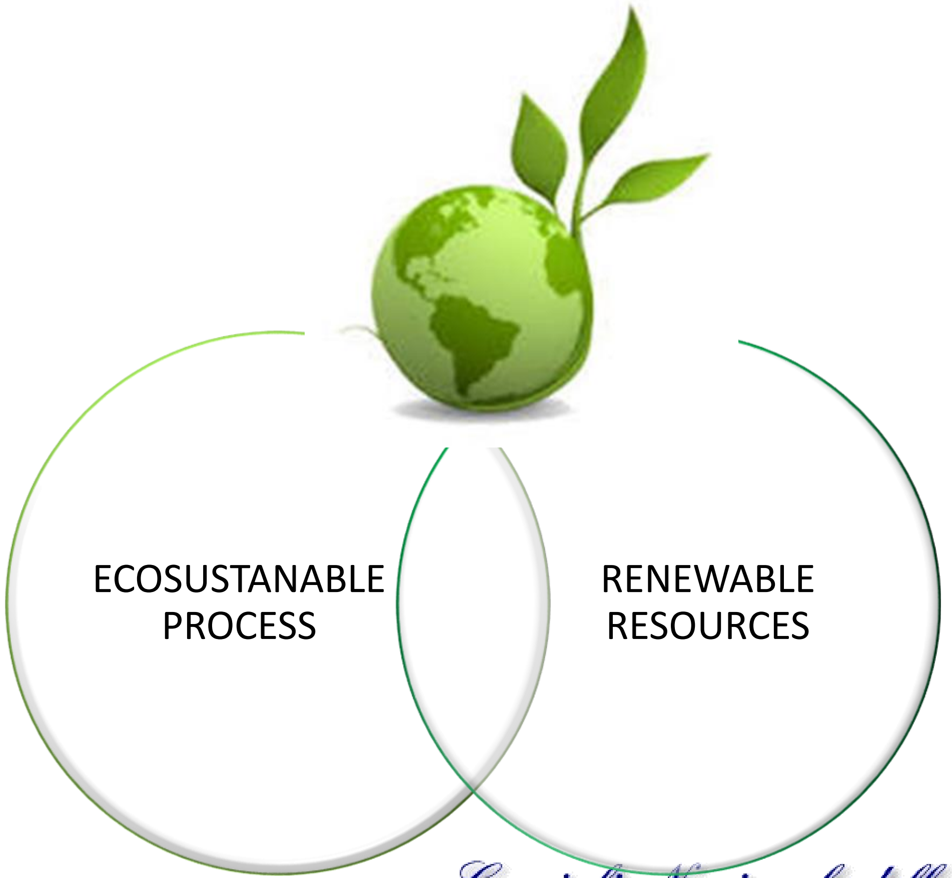


Elisa Esposito

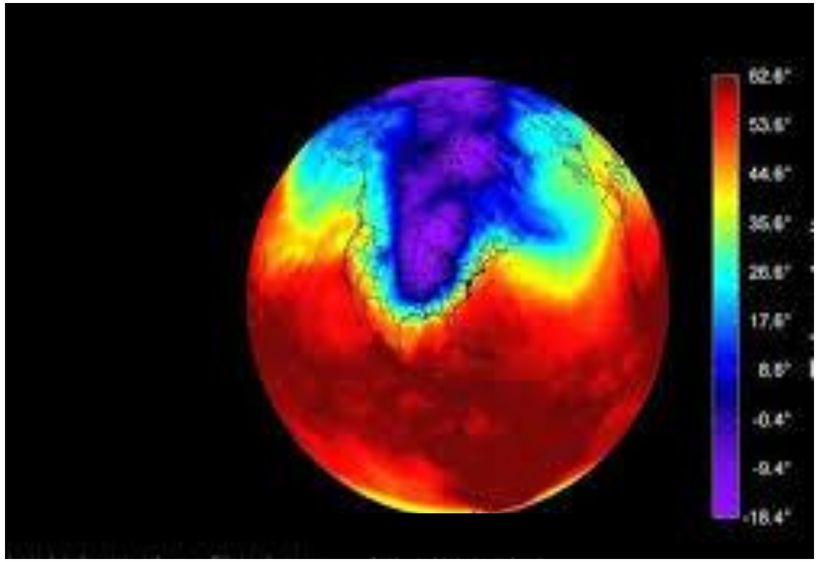
Consiglio Nazionale delle Ricerche

Green Chemestry

Green chemistry, also called **sustainable chemistry**, is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize or eliminate the use and generation of hazardous substances

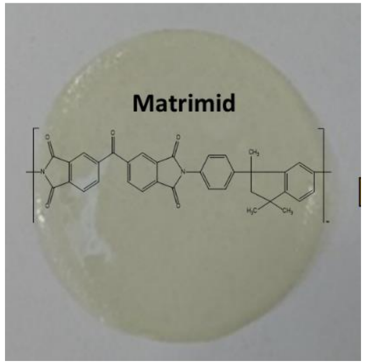


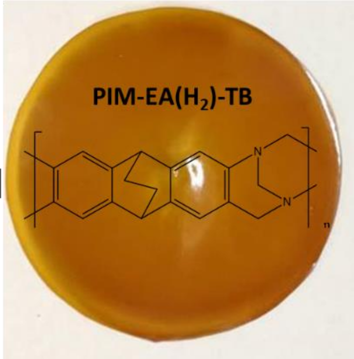
Context

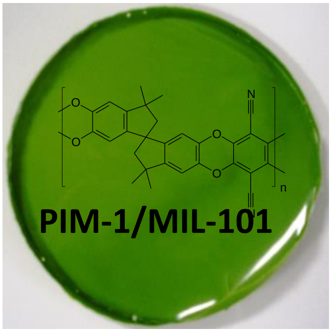


Focus of Research

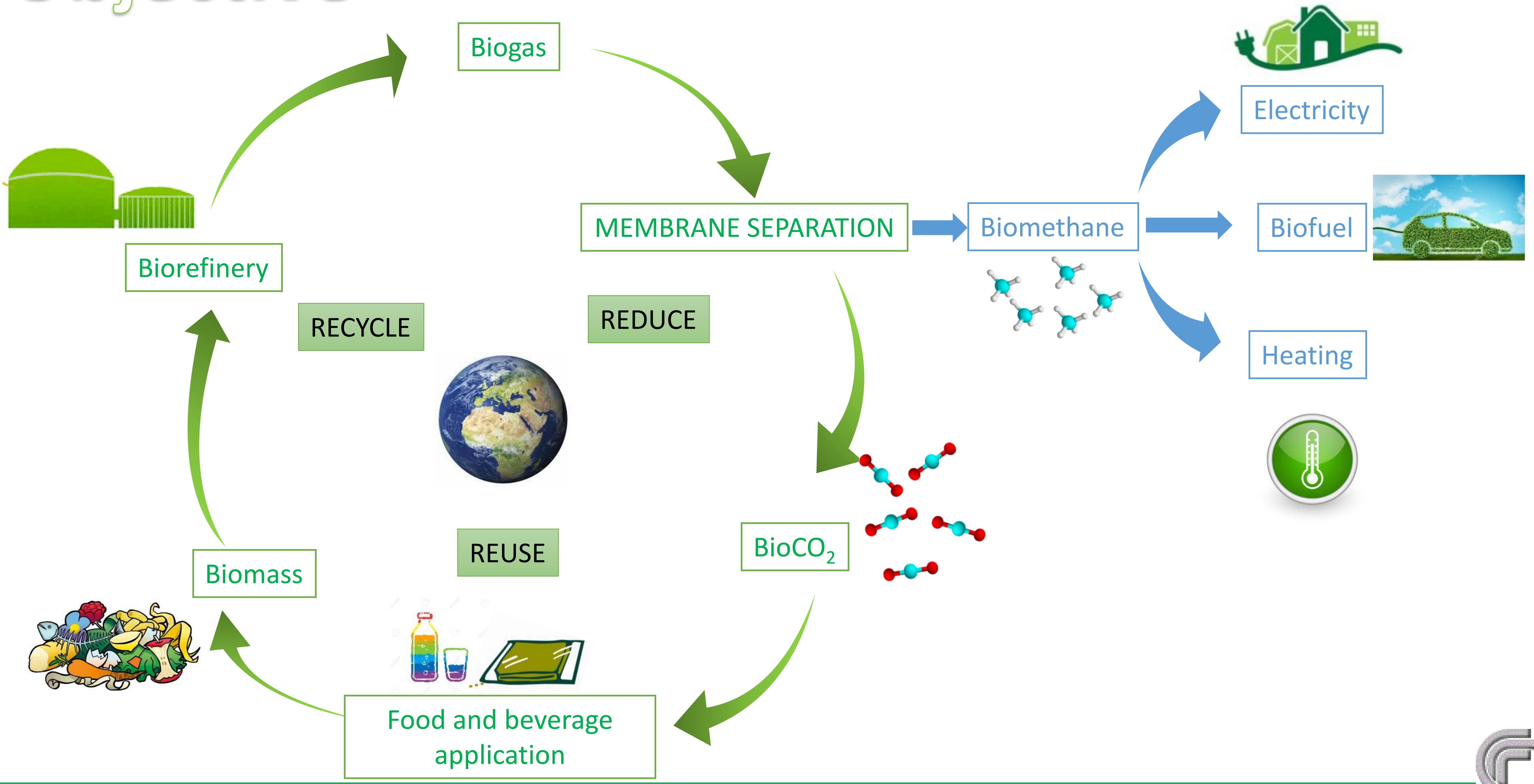
Design and development of new materials for membrane preparation







Objective

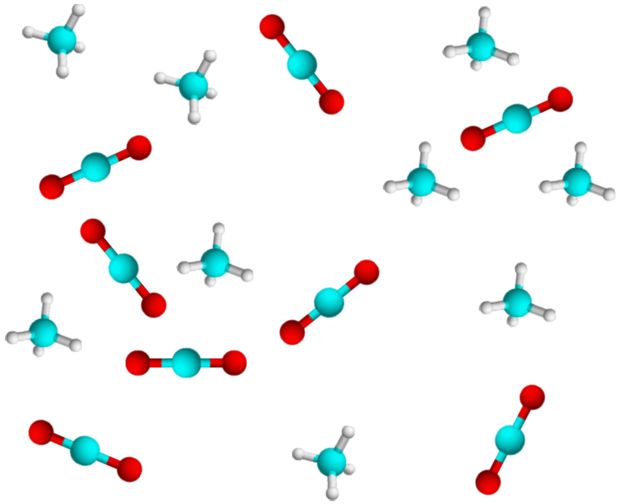

Biogas
MEMBRANE SEPARATION
Biomethane
Electricity
Biofuel
Heating
Biorefinery
RECYCLE
REDUCE
REUSE
$BioCO_2$
Biomass
Food and beverage application

Gas transport in Membrane

DSCTM

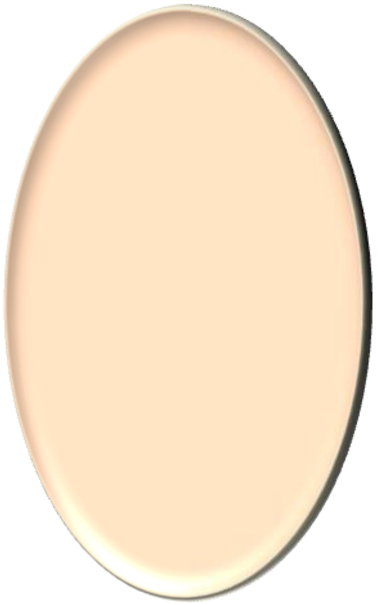
Feed mixture

e.g. CO_2/CH_4



Membrane

(selective barrier)



Retentate

Enriched in methane

CH_4 > > CO_2

$$\text{Permeability (P)} = \frac{n \cdot \ell}{t \cdot A \cdot \Delta P}$$

Permeate

Enriched in CO_2

CO_2 > > CH_4

$$\text{selectivity } (\alpha_{AB}) = \frac{P_A}{P_B}$$

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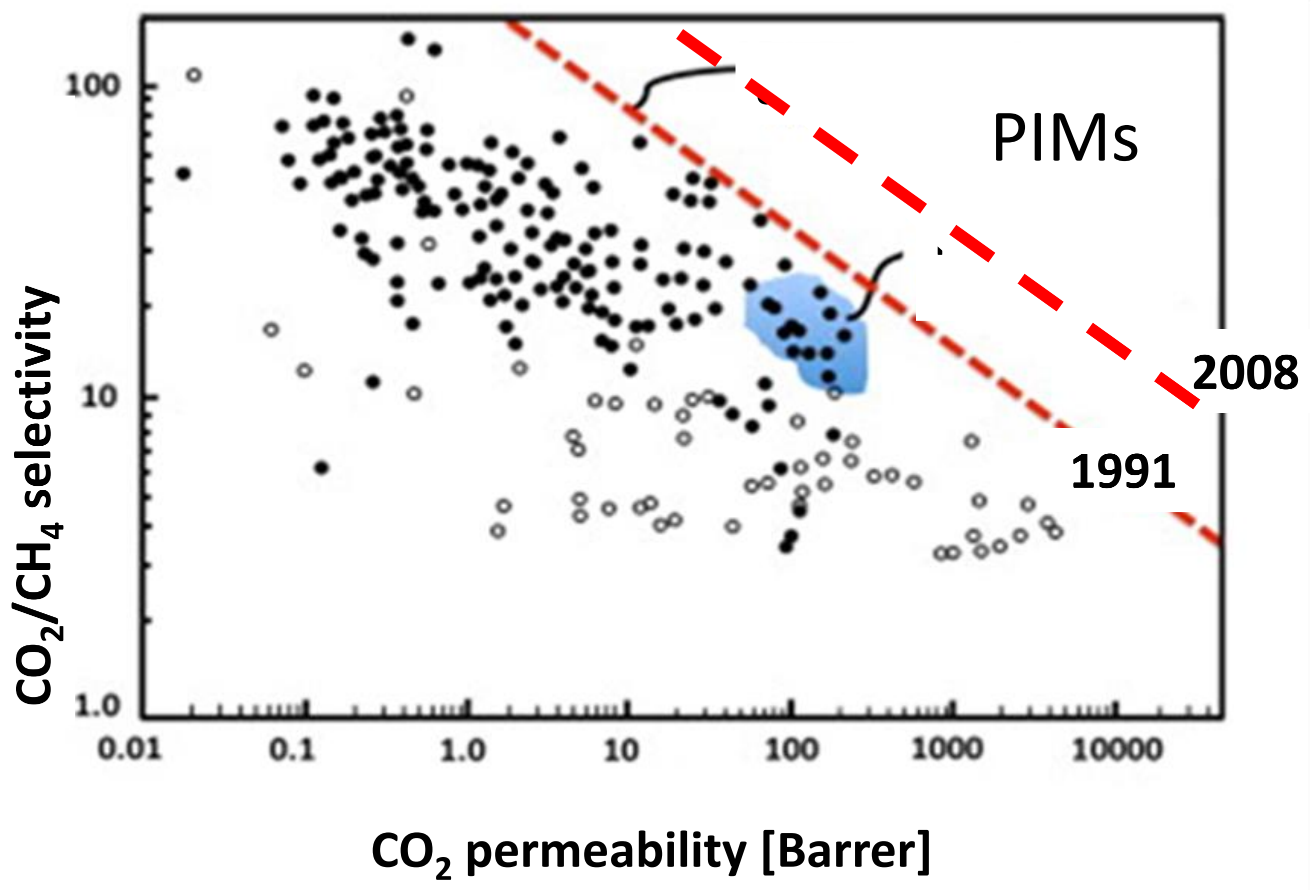
Robeson plot



Rubbery Polymers

Permeability

Selectivity

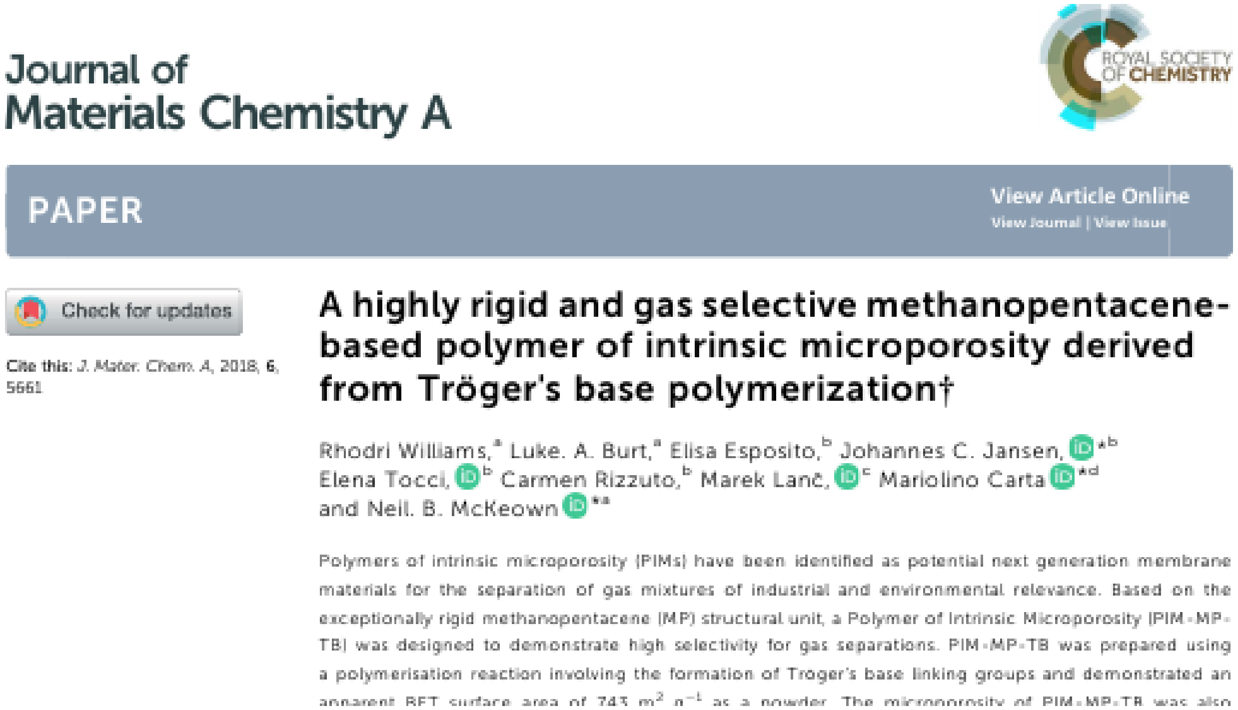
Glassy polymers

Permeability

Selectivity

B.D. Freeman, Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes, Macromolecules. 32 (1999) 375–380

L.M. Robeson, The upper bound revisited, J. Memb. Sci. 320 (2008) 390–400.



Journal of Materials Chemistry A

ROYAL SOCIETY OF CHEMISTRY

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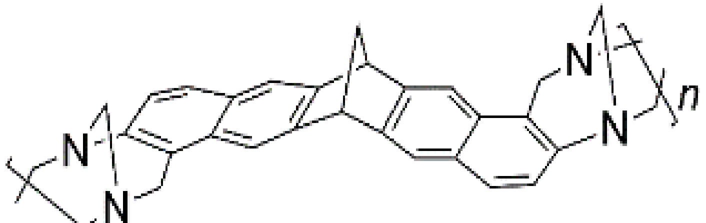
Cite this: J. Mater. Chem. A, 2018, 6, 5661

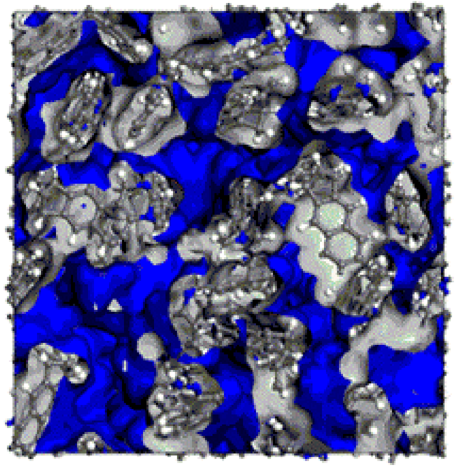
A highly rigid and gas selective methanopentacene-based polymer of intrinsic microporosity derived from Tröger's base polymerization†

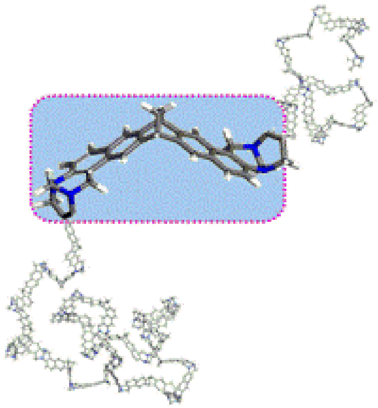
Rhodri Williams,[a] Luke. A. Burt,[a] Elisa Esposito,[b] Johannes C. Jansen,[*b] Elena Tocci,[b] Carmen Rizzuto,[b] Marek Lanč,[c] Mariolino Carta[*d] and Neil. B. McKeown[*a]

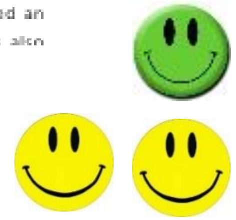
Polymers of intrinsic microporosity (PIMs) have been identified as potential next generation membrane materials for the separation of gas mixtures of industrial and environmental relevance. Based on the exceptionally rigid methanopentacene (MP) structural unit, a Polymer of Intrinsic Microporosity (PIM-MP-TB) was designed to demonstrate high selectivity for gas separations. PIM-MP-TB was prepared using a polymerisation reaction involving the formation of Troger's base linking groups and demonstrated an apparent BET surface area of 743 m^2 g^{-1} as a powder. The microporosity of PIM-MP-TB was also



PIM-MP-TB

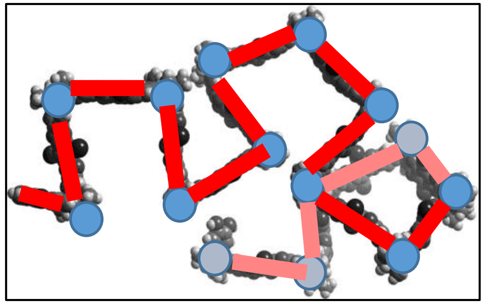


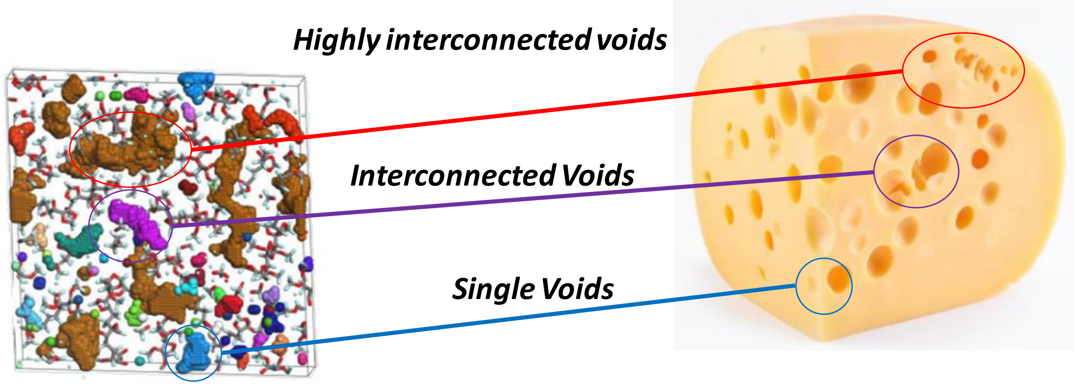




Permeability

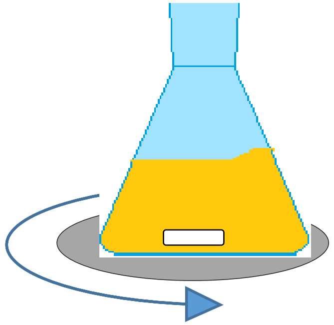
Selectivity



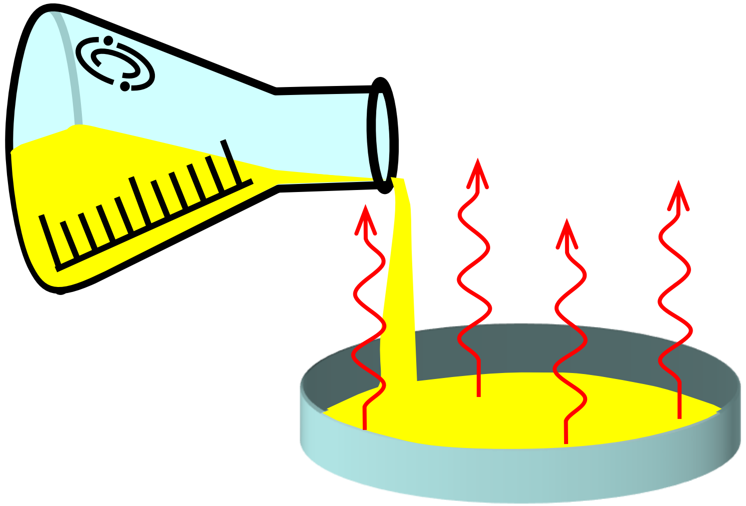


Membrane preparation

PIM-MP-TB polymer solution

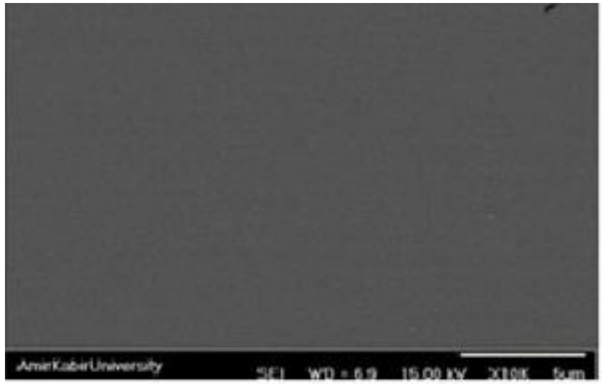


Mechanical stirring



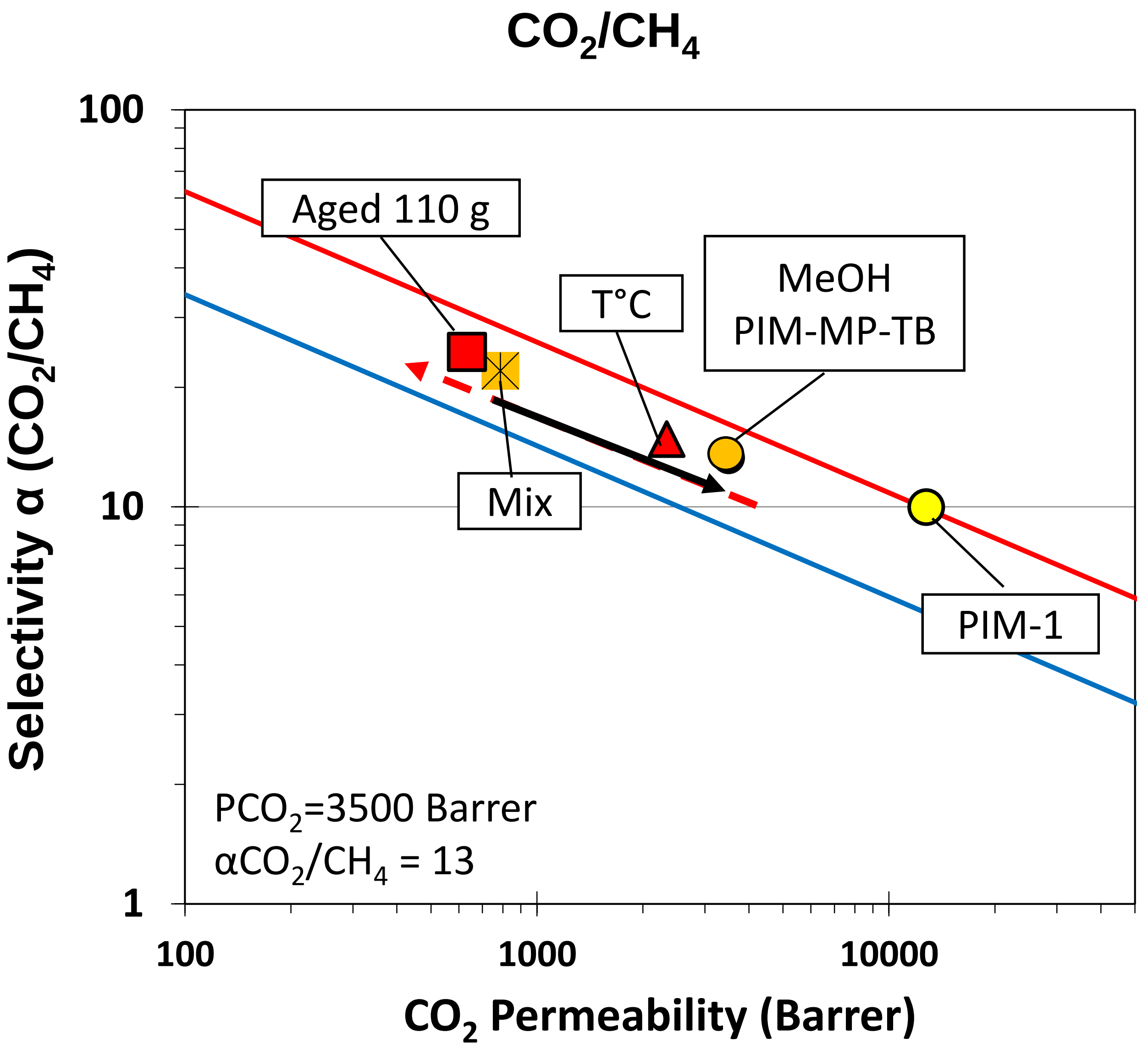
Slow solvent evaporation

SEM image



Dense and homogenous membrane

Mixed gas permeation test



Separation and Purification Technology 212 (2019) 545–554

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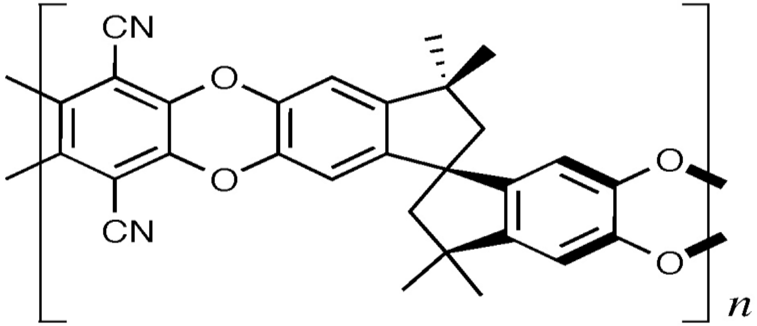
Separation and Purification Technology

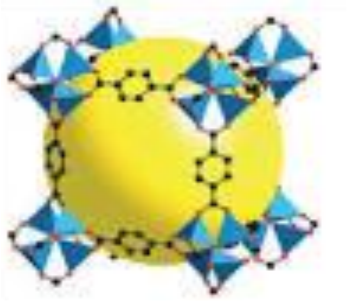
journal homepage: www.elsevier.com/locate/seppur

Mixed matrix membranes based on MIL-101 metal–organic frameworks in polymer of intrinsic microporosity PIM-1

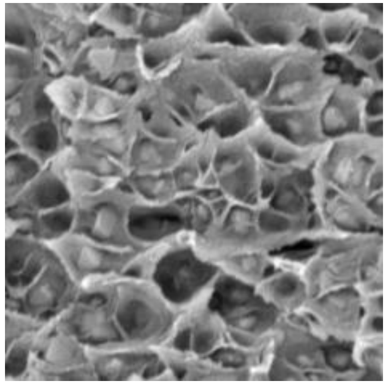
Muhanned Khdhayyer[a], Alexandra F. Bushell[a], Peter M. Budd[a], Martin P. Attfield[a,*], Dongmei Jiang[b], Andrew D. Burrows[b] Elisa Esposito[c,*],, Paola Bernardo[c], Marcello Monteleone[c], Alessio Fuoco[c], Gabriele Clarizia[c], Fabio Bazzarelli[c], Amalia Gordano[c], Johannes C. Jansen[c]



PIM-1

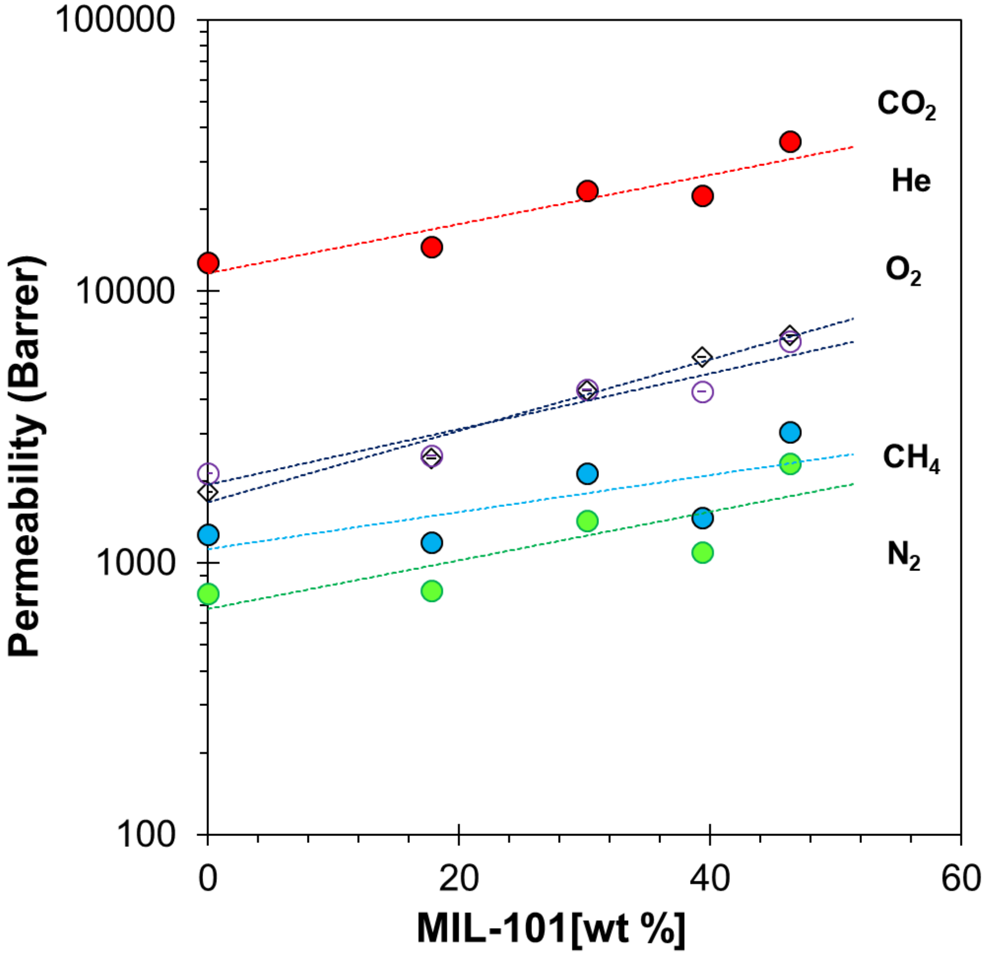


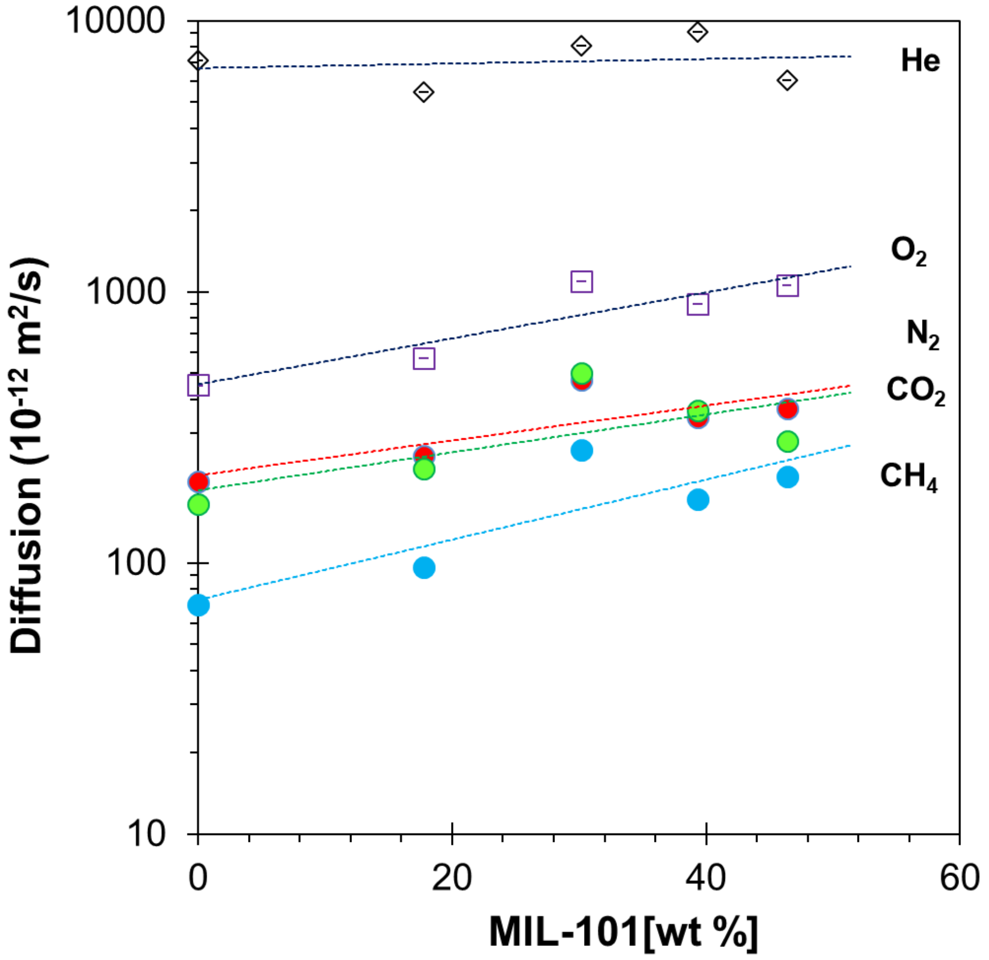
MOF
MIL-101

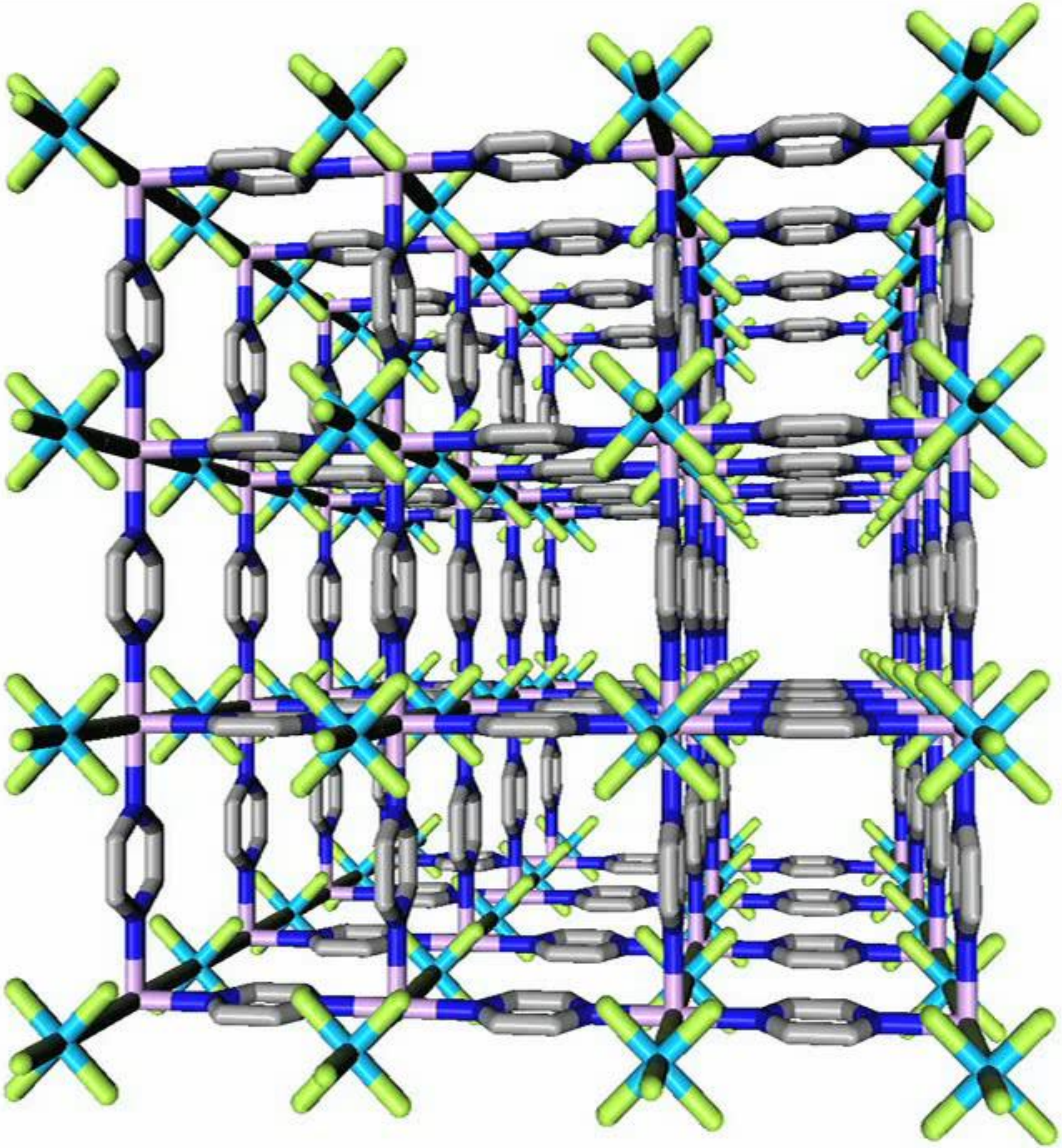


Mixed Matrix membranes

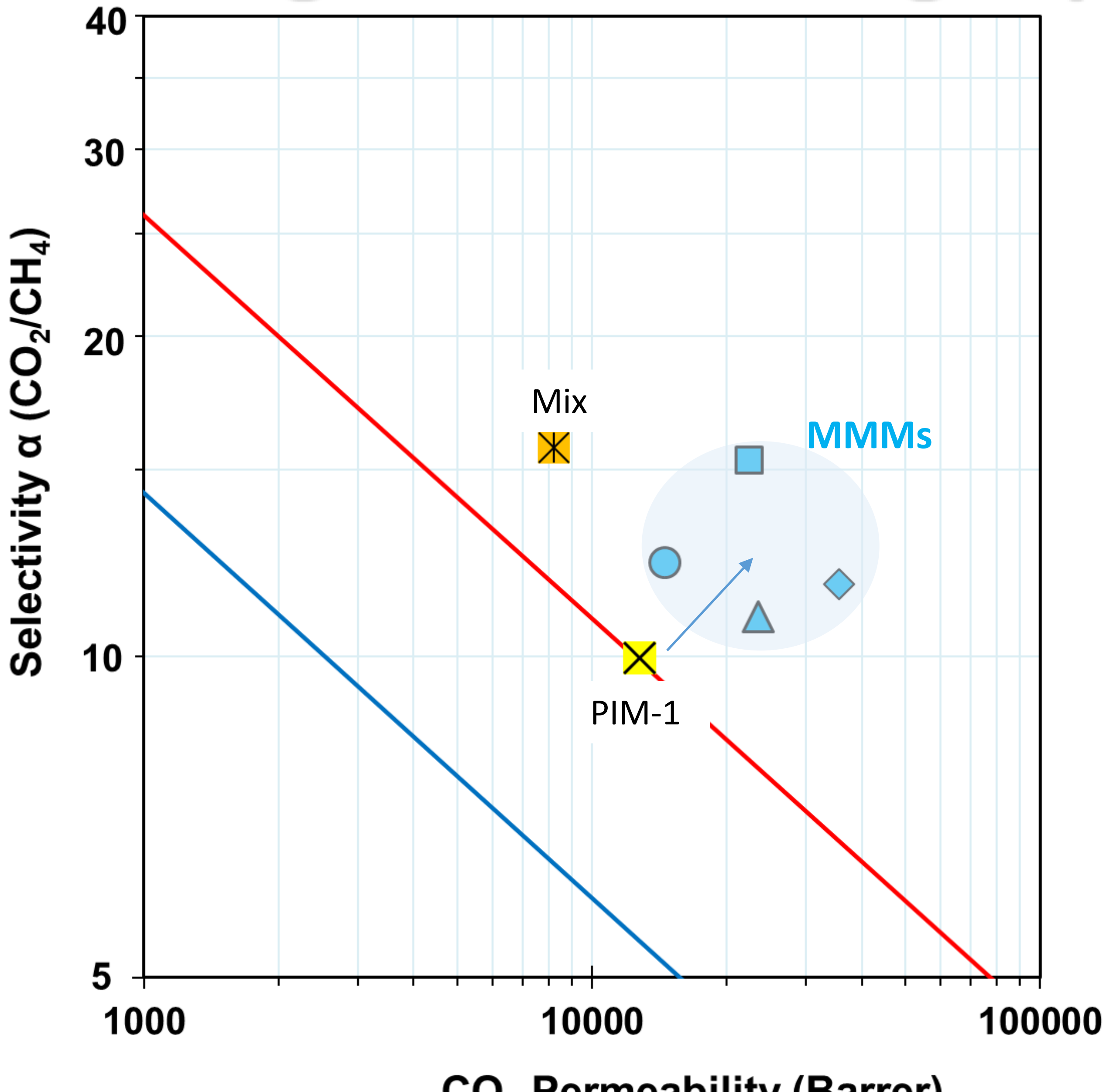
Single gas permeation test







Overview of Single and Mixed gas performance



Scale-up

Laboratory scale

Large-scale

Industrial-scale

Energy & Environmental Science

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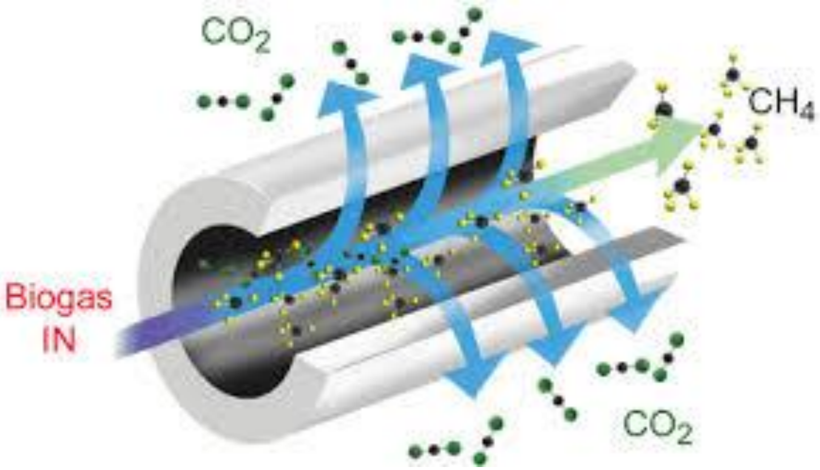
Cite this: *Energy Environ. Sci.*, 2019, **12**, 281

Impact factor: 33

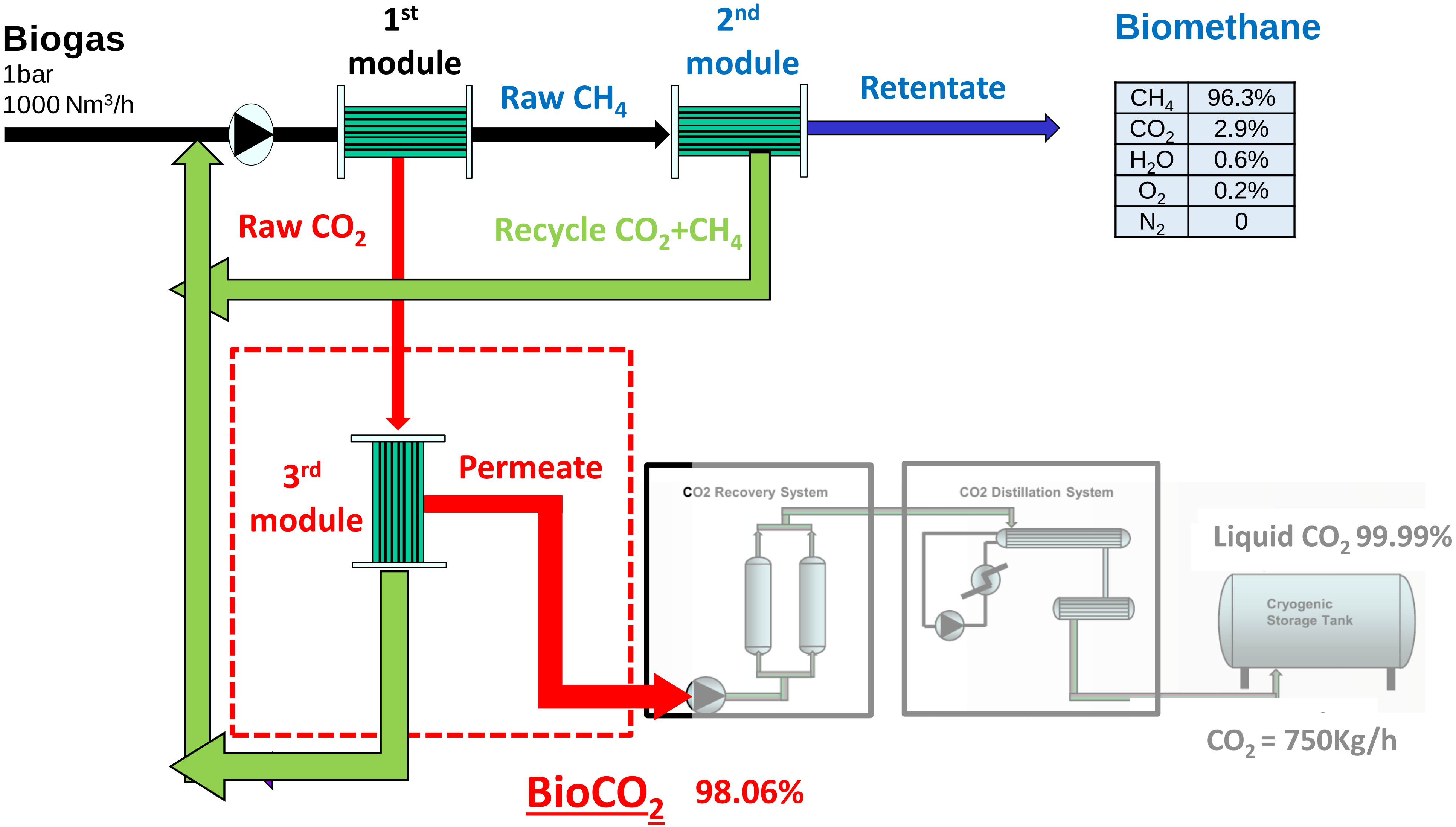
Simultaneous production of biomethane and food grade CO_2 from biogas: an industrial case study†

Elisa Esposito,[*a] Loredana Dellamuzia,[b] Ugo Moretti,[b] Alessio Fuoco,[a] Lidietta Giorno[a] and Johannes C. Jansen[*a]

TECNO PROJECT INDUSTRIALE
SIAD Group



Three-stage membrane separation



CH_4	96.3%
CO_2	2.9%
H_2O	0.6%
O_2	0.2%
N_2	0

Recycle 2nd permeate and 3rd retentate→ **minimum CH_4 loss**

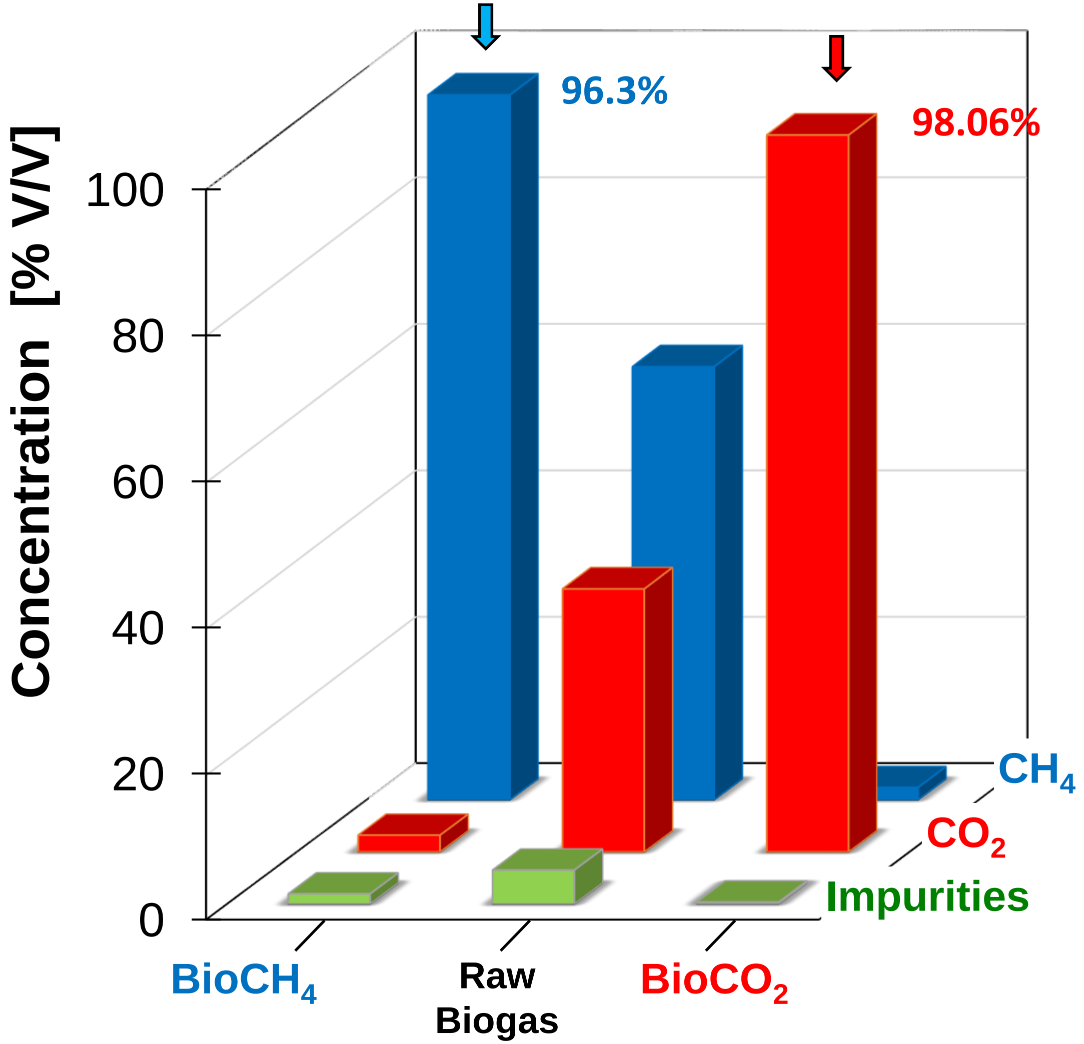
Composition of Biomethane and BioCO_2 after membrane separation

→ Biomethane suitable for injection into the natural gas grid

Parameter	Limits allowed	Biomethane Membrane stage
Purity	>80%	**96.3%**
Wobbe Index (MJ/Sm³)	47.31-52.33	**50.02**
Density (g/cm³)	0.5548-0.8	**0.56**
Heating value (MJ/Sm³)	34.95-45.28	**37.48**

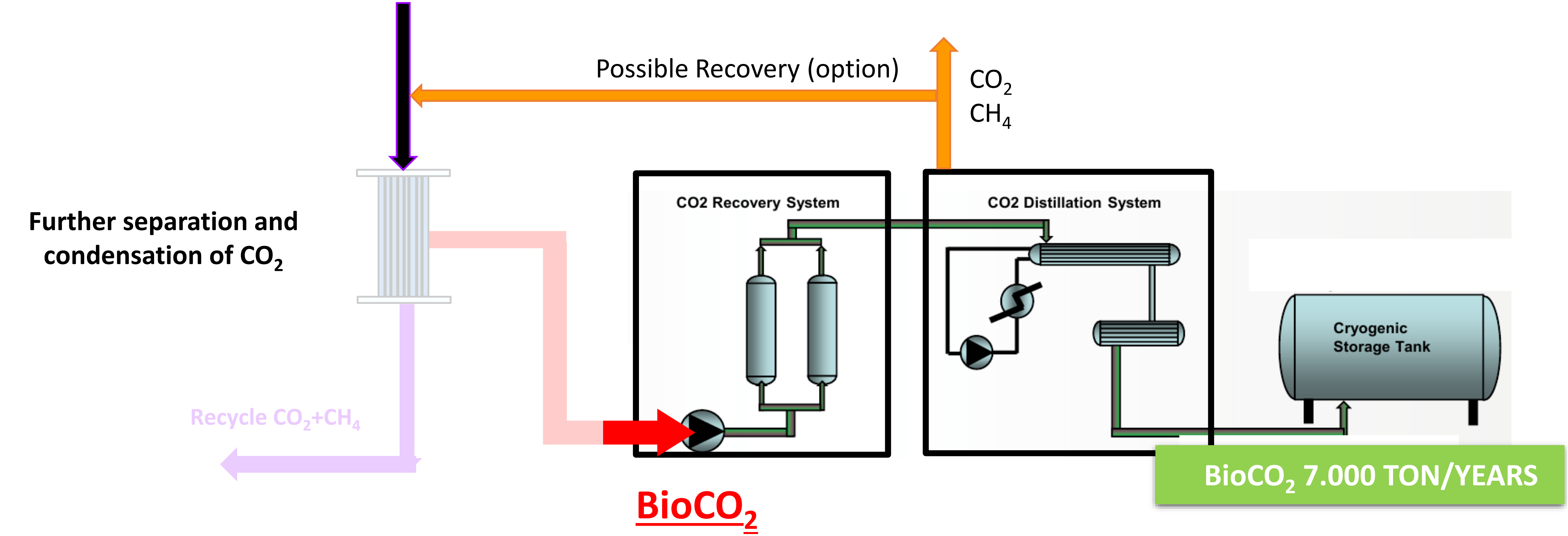
→ Further removal of trace impurities from CO_2 needed

Parameter	Limits EIGA/ISBT	CO_2 Membrane stage	Liquefied CO_2
	Threshold	*Measured values*	*Measured values*
Purity	99.9% v/v max	98.06 v/v max	99.998% v/v
humidity	20 ppm v/v max	120 ppm v/v	-
acidity	comply with the test	comply with the test	comply with the test
Oxygen	30 ppm v/v max	200 ppm v/v	1.9 ppm v/v



CO_2 recovery unit

Final CO_2 liquefying step



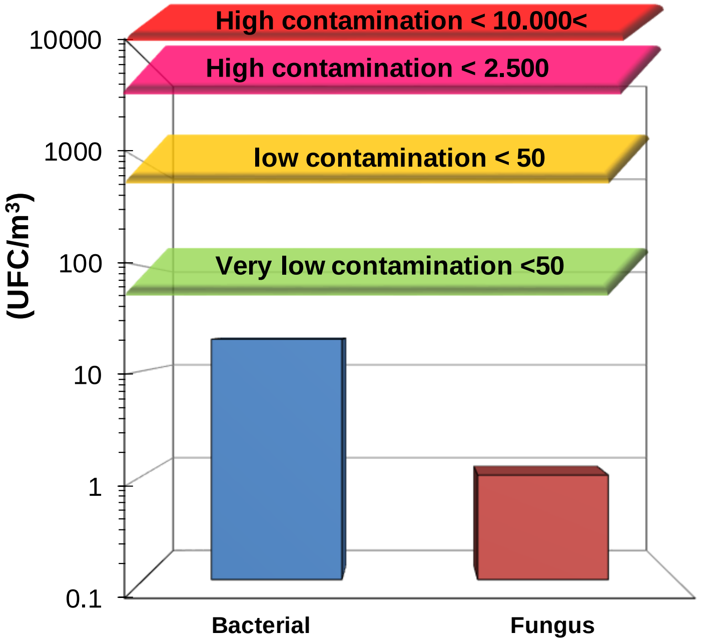
Additional advantage:

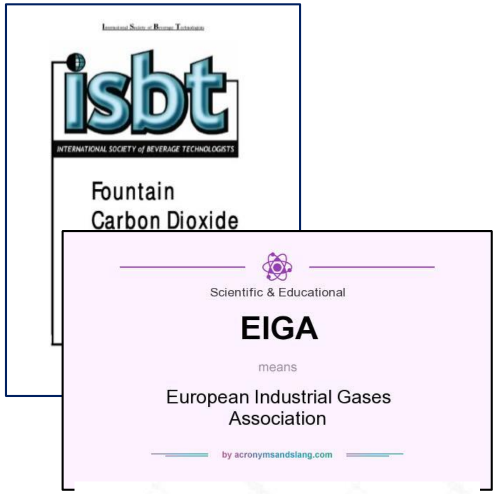
CH_4 recycle from this step back to the membrane separation unit leads to **100% CH_4 recovery** and **zero CH_4 emission**

Food grade BioCO_2

The final liquefied CO_2 is chemically and microbiologically pure, respecting the limits of **food grade quality** proposed by the EIGA/ISBT

BIOLOGICAL ANALYSIS





CHEMICAL ANALYSIS

Parameter	Limits EIGA/ISBT	CO_2 Membrane stage	Liquefied CO_2
	Threshold	*Measured values*	*Measured values*
Purity	99.9% v/v max	98.06 v/v max	99.998% v/v
humidity	20 ppm v/v max	120 ppm v/v	-
acidity	comply with the test	comply with the test	comply with the test
Oxygen	30 ppm v/v max	200 ppm v/v	1.9 ppm v/v

Conclusions

Membrane processes produces simultaneously renewable energy and re-cycle of CO_2

The energy cost of CO_2/CH_4 membrane separation (0.3 kWh/m^3) is lower compared to that the traditional separation techniques (0.6 kWh/m^3).

3000 m^3/h of Biomethane from organic waste that can be fed directly into the natural gas grid.

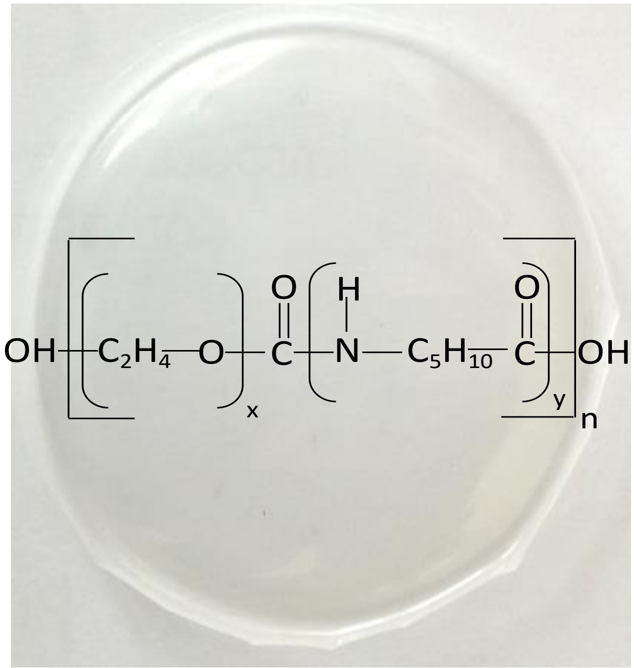
32.000 tonnes/year of CO_2 from a useless by-product to a food-grade quality gas for food and beverage industry

No CO_2 and CH_4 are released into the atmosphere and organic waste is consumed: first “carbon negative” plant in Italy

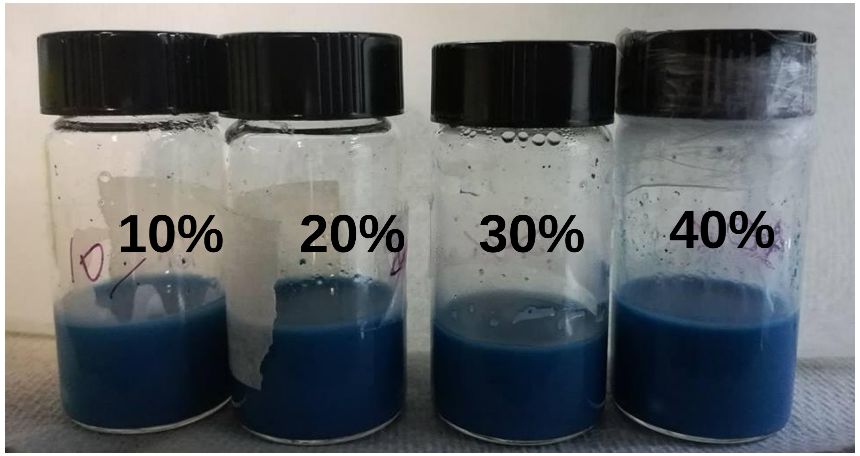
Future challenges

Future challenges:

To green materials

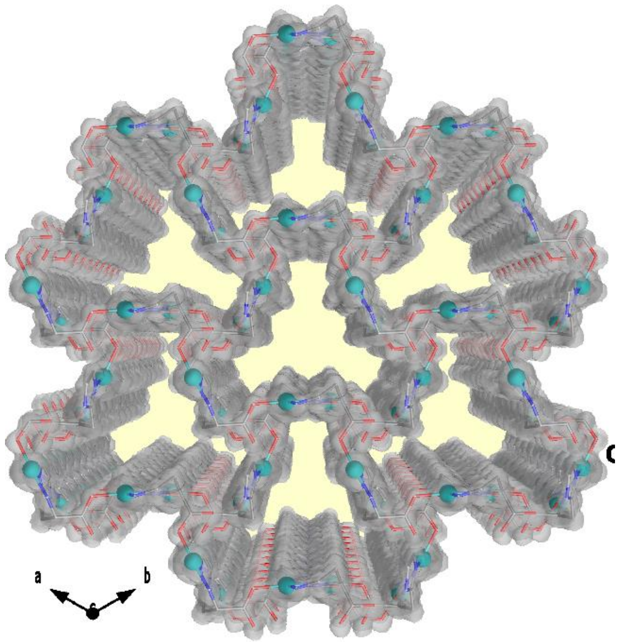


Pebax® membrane

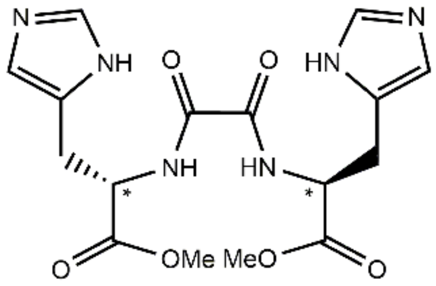


Green solvent: mixture of EtOH/H_2O 70/30 vol%

Bio-MOF



Hismox-MOF

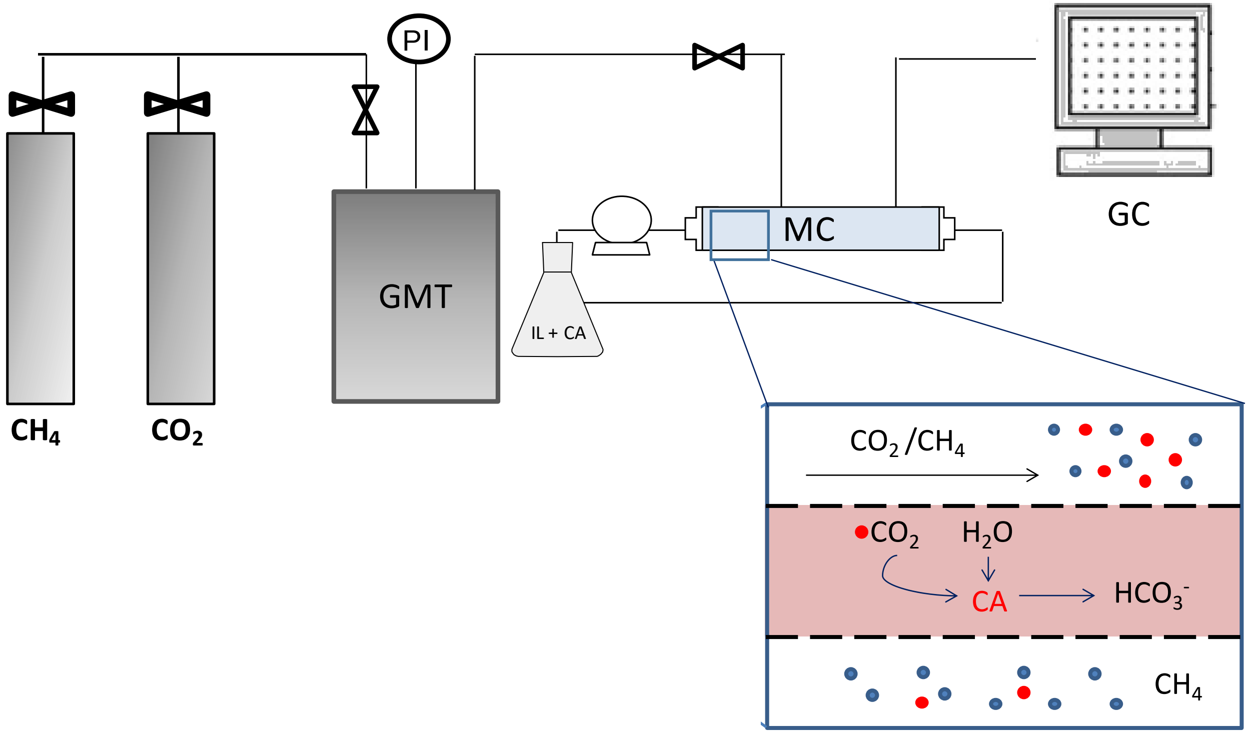


Histidin amino acid linker

Future challenges

To Bio-process

Potential use of membrane contactors for CO_2/CH_4 separation by facilitated CO_2 transport in Hollo fiber membranes

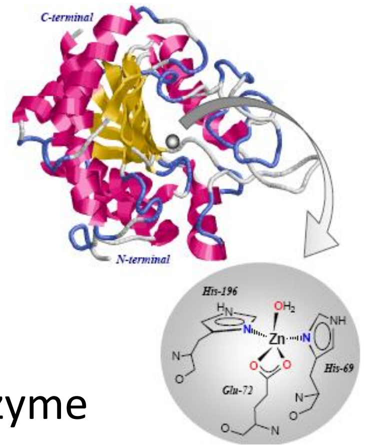


Facilitated membrane transport

The basic idea is to mimic the reaction that takes place inside the erythrocytes

RESEARCH ABROAD

UNIVERSIDADE NOVA DE LISBOA



Enzyme

Carbonic anhydrase

-Metal protein

-Zinc functional group

-Catalyzes hydration of carbon dioxide

Hydration of carbon dioxide

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+.$$

Thank you for your attention