

How to change the world with membrane reactors: High-purity hydrogen generation

Membrane reactors for H2 generation



Outlook

- Who we are?
- Our Mission and Vision
- When did this story begin?
- Foundation and current projects
- Future challanges

- Patented membrane technology for gas separation developed over >10 years
- Committed with net-zero emisión in 2050 thanks to Hydrogen utilisation
- We design and manufacture entire balace of plant for high purity hydrogen production from different feedstocks
- Technology based on catalytic membrane reactors thanks to long time R&D collaboration and technology transfer (Tecnalia / TUe)

What is H2SITE's technology?

Palladium-Alloy membranes that produce high purity hydrogen (99.97%)...

...to recover up to 98% of the hydrogen from wide variety of feedstocks...





...for on site generation in a reduced footprint



Hydrogen separators and purifiers



Crackers, reformers and WGS reactors

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tors for H2 generation

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Transport through hydrogen carriers can be done more easily done than gaseous or liquid hydrogen

Development of hydrogen storage strategies, is the key to the successful deployment of hydrogen, including its economic sustainability.



H2SITE MISSION & VISION

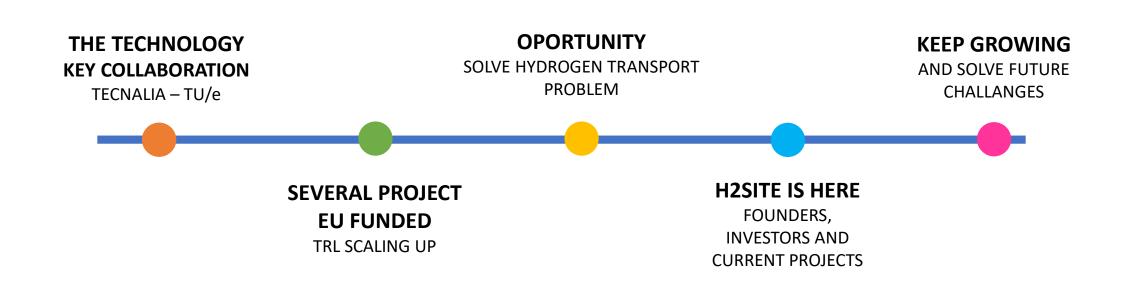
Hydrogen will be produced where it is cheaper but consumed where it is needed





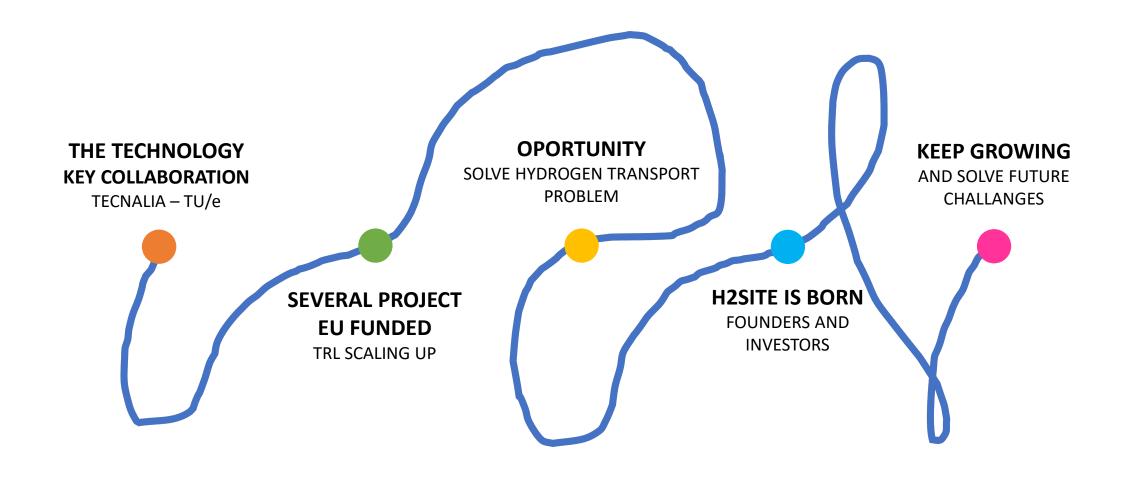
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This is our story





This is our story



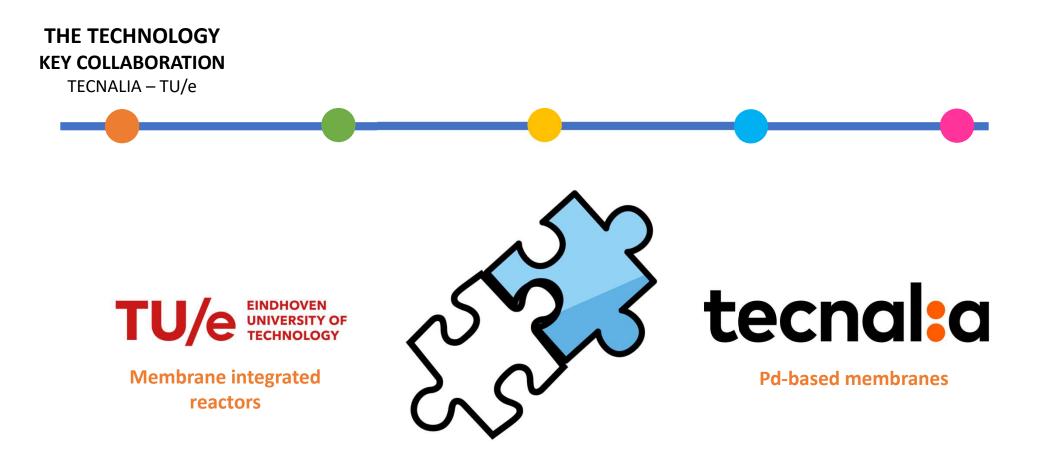
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When did this story begin?



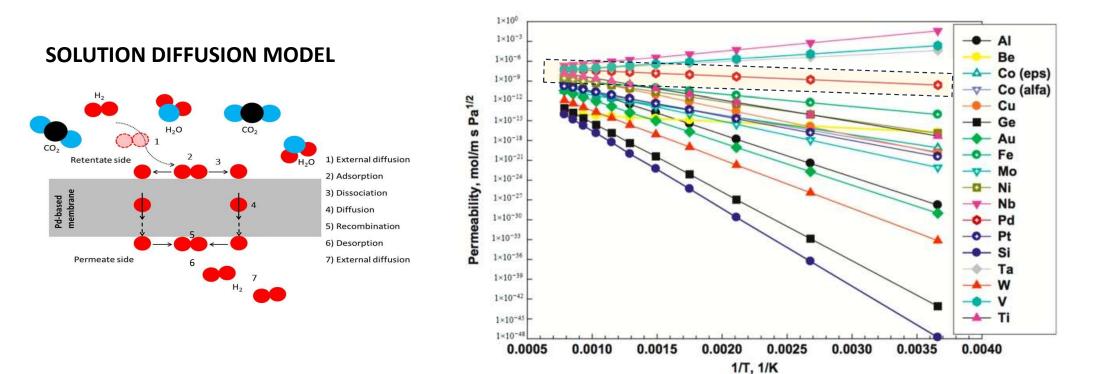


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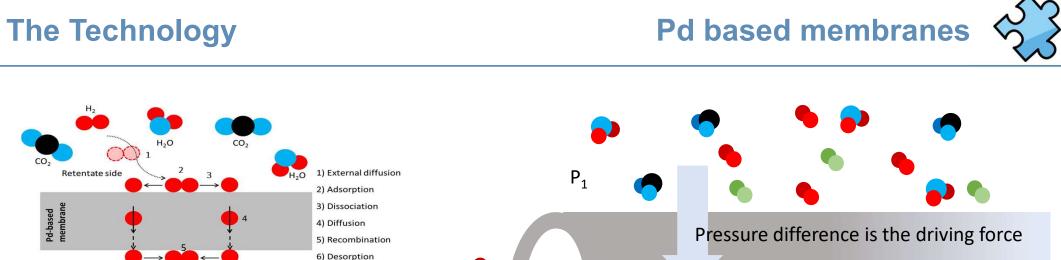
The Technology

Pd based membranes





Morreale B. et al. (2009) Gasification and Associated Degradation Mechanisms Applicable to Dense Metal Hydrogen Membranes. In: Bose A.C. (eds) Inorganic Membranes for Energy and Environmental Applications. Springer, New York, NY



P₂



High permeability, infinite selectivity and stable at high temperatures

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11

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0.0030

7) External diffusion

- AI Be

- Cu

Ge 🔶 Au

- Fe

V Mo

- Nb

O Pd

-O-Pt - Si

- Ta

- W

📥 Ti

--- V

0.0040

Morreale B. et al. (2009)

0.0035

O Ni

- Co (eps)

V Co (alfa)

Membrane re ctors for H2 generation

Permeate side

1×10⁰ 1×10-3

1×10-

1×10~

1×10⁻¹

1×10-1

1×10-1

1×10-

1×10-2

1×10-3

1×10-33

1×10-3

1×10-5

1×10~4

1×10-4 1×10-48

0.0005

0.0010

0.0015

0.0020

0.0025

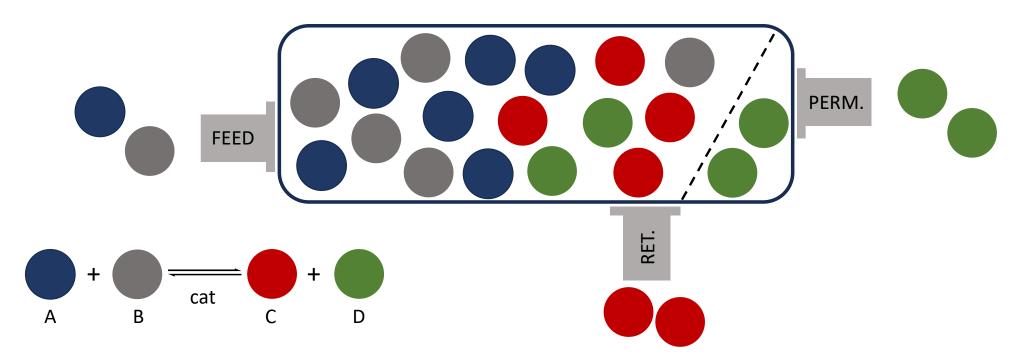
1/T, 1/K

, mol/m s Pa^{1/2}

Permeability, 1×10-2

The Technology





Conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

"When a simple system in thermodynamic equilibrium is subjected to a change in concentration, temperature, volume, or pressure, the system changes to a new equilibrium, and this change partly counteracts the applied change." Le Chatelier's principle

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The Technology



Steam Methane Reforming (SMR) reactions

Methanol decomposition

Water Gas Shift (WGS)

Ammonia decomposition

Autothermal Reforming (ATR) reactions

Methanol Steam Reforming

Conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

Ethanol reforming

"When a simple system in thermodynamic equilibrium is subjected to a change in concentration, temperature, volume, or pressure, the system changes to a new equilibrium, and this change partly counteracts the applied change." Le Chatelier's principle



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Conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

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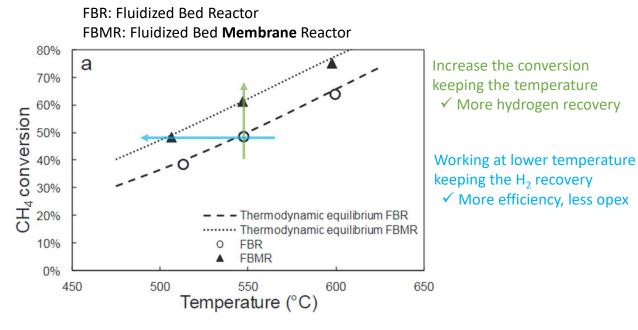


The Technology

^m

Why integrate membranes inside the reactor

Example of impact of equilibrium shifting on methane reforming and ammonia cracking reactions



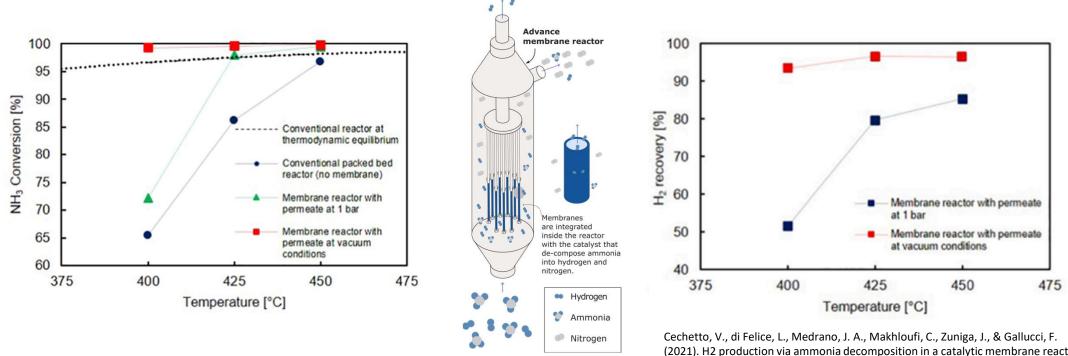
Medrano, J. A., Fernandez, E., Melendez, J., Parco, M., Tanaka, D. A. P., van Sint Annaland, M., & Gallucci, F. (2016). Pd-based metallic supported membranes: Hightemperature stability and fluidized bed reactor testing. *International Journal of Hydrogen Energy*, 41(20), 8706–8718. <u>https://doi.org/10.1016/j.ijhydene.2015.10.094</u>



tors for H2 generation

Why integrate membranes inside the reactor

Example of impact of equilibrium shifting on methane reforming and ammonia cracking reactions



(2021). H2 production via ammonia decomposition in a catalytic membrane reactor. Fuel Processing Technology, 216. https://doi.org/10.1016/j.fuproc.2021.106772

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Membrane rea

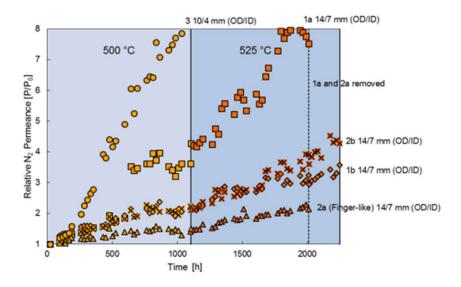
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The Technology – Double skin membranes

The long-term stability of the membranes in fluidized bed membrane reactors at high temperatures (> 400 °C) might be a problem:

- defects due to the mobility of the atoms present in the selective layer or
- consequence of the attrition by the fluidized particles.



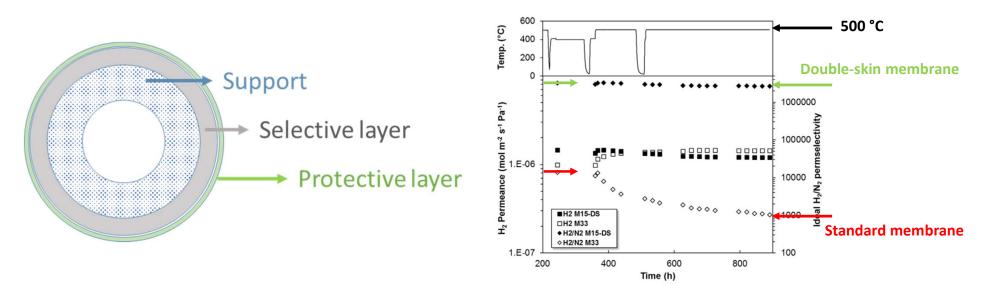
Nooijer, N.d.; Arratibel Plazaola, A.; Meléndez Rey, J.; Fernandez, E.; Pacheco Tanaka, D.A.; Sint Annaland, M.v.; Gallucci, F. Long-Term Stability of Thin-Film Pd-Based Supported Membranes. *Processes* **2019**, *7*, 106.



The Technology – Double skin membranes

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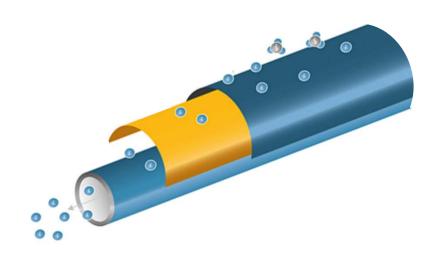
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Arratibel.A, Medrano.J, Melendez.J, Pacheco Tanaka.D.A, van Sint Annaland.M, Gallucci.F, Attrition-resistant membranes for fluidized-bed membrane reactors: Double-skin membranes, Journal of Membrane Science, Volume 563,2018, Pages 419-426,

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Outstanding H2SITE membranes

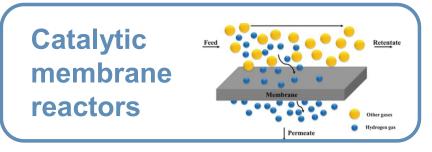


- Thin selective layer
- Porous supported membranes
- Protection against attrition which means we can target H₂ generation (unique)
- Very high reported H₂ flux ^(a)
 - Up to 2.2 10⁻⁶ mol s⁻¹ m⁻² Pa⁻¹ at 450 °C
- Purities of 99.98% achieved in ammonia cracking application ^(b)

(a) https://doi.org/10.1016/j.ijhydene.2022.04.240 (b) https://doi.org/10.1016/j.fuproc.2021.106772



We are not alone in the market







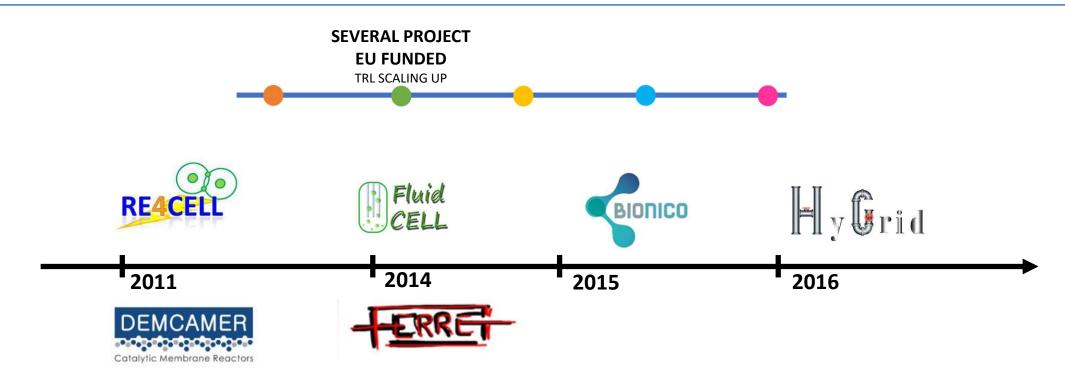
Pressure Swing Adsorption



- CMR capable of solving hydrogen transport problem
- CMR are capable of separation when %H₂ is low (<20%)
- CMR can resist some pollutants than others (EHC) don't
- CMR can be scalable (tons/day) in a compact solution with a reduced footprint
- Recovery is not hampered by reaching higher purity for CMR in the same way as PSA does
- CMR needs lower maintenance in continuous operation (unlike PSA)

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Everything started long time ago...



- Fluidized/Packbed configuration
- Scaling up of reactors and H₂ production
- Different feedstocks (mainly methane but also bio-ethanol and biogas)
- Boost Pd membrane properties

Membrane re

ctors for H2 generation

- Authothermal reforming
- Targeting high H₂ purities
- Not only H2 generation (separation from the grid)
- LCA and techno-economic analysis

Being in the right place at the right time



- Existing technology for H₂ production in a compact and more efficient solution
- H₂ transport not been solved yet (although it is considered as a key enabler for the energy transition)
 - Transport cost adds 80% 300% to the H₂ generation cost and
 - Inefficient: leaks of >10% H2



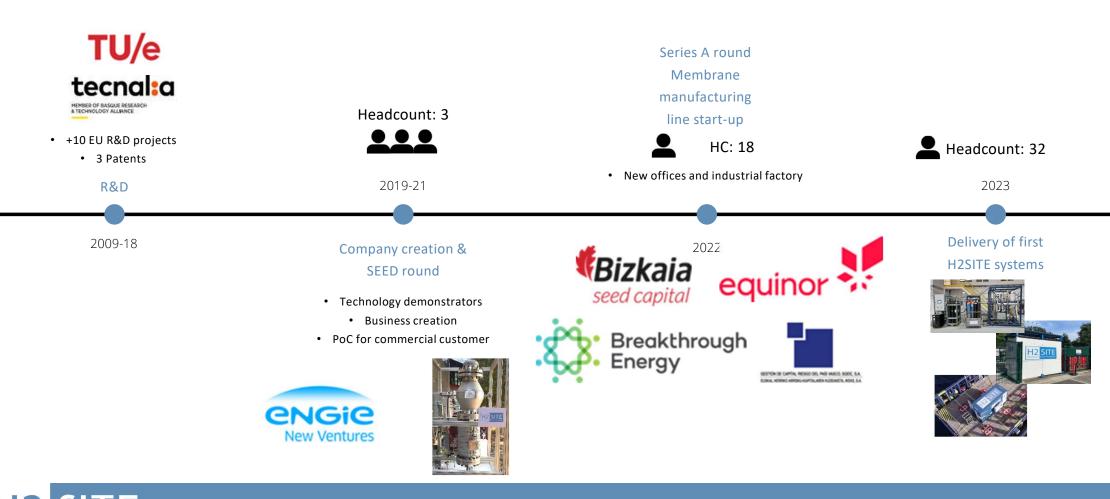
H2SITE is here





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Founders and investors



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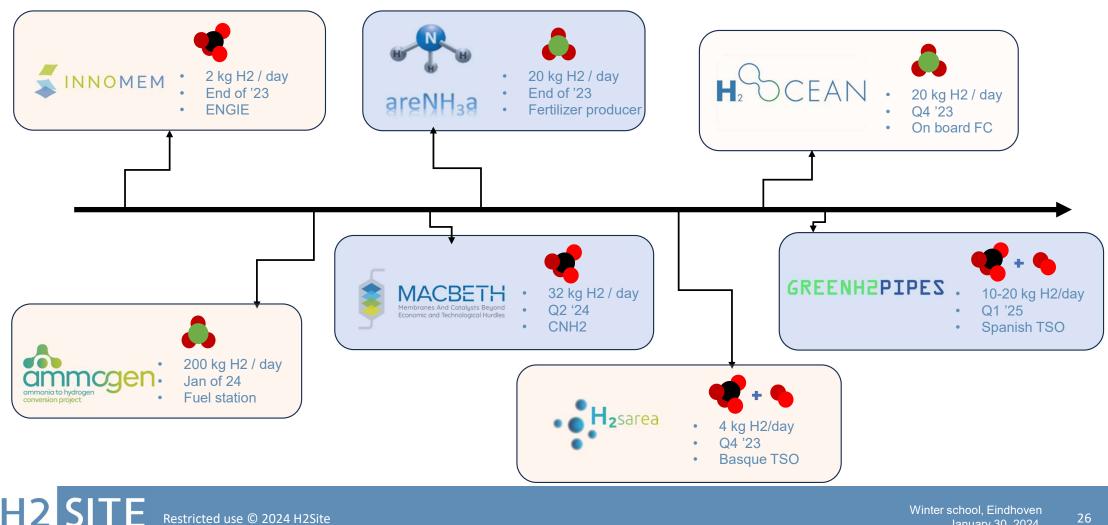
Membrane Manufacturing Line



Figure from ELPAIS

- First Pd-membrane industrial plant
- To feed our own H_2 production commercial systems
- Working with several batches at different stages
- Membrane production equivalent to 9000 tons H₂/year (ammonia application)
- Traceability and quality is essential to ensure later performance
- We do not sell membranes separately!

Current projects...

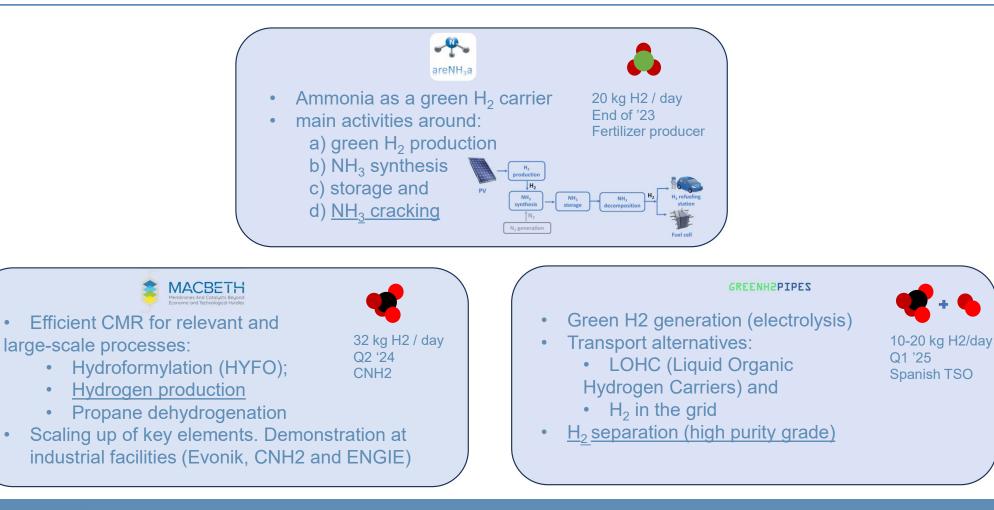


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Currents projects...



Membrane re

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INNOMEM



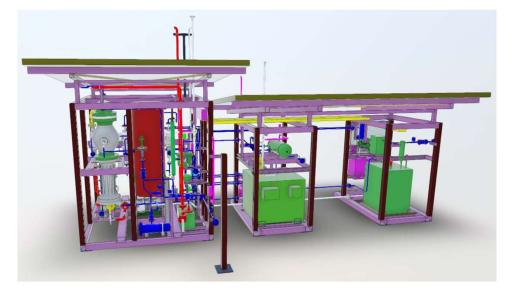


Figure from H2SITE

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 862330 (INNOMEM project).

- 32 partners in project. Develop and organize a sustainable Open Innovation Test Bed (OITB) and membranes for different applications.
 - Key for membrane development
- H₂ from biogas at 450-500 °C
- First H2SITE's prototype system delivered
- Performance targets:
 - > 99,9 % H₂ purity
 - 100 hours continuous running
 - 2 Nm3/h H₂ production (≈ 4 Kg H₂/day)

INNOMEM

ors for H2 generation





Figure from H2SITE

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 862330 (INNOMEM project).

- Biogas naturally generated from the decomposing of the organic matter by anaerobic bacteria.
- Biogas is susceptible for energy production
 - Depending of source, biogas ranges from 45% to 70% CH₄ and from 30% to 45% CO₂ ^[2]
- In 2019 there were over 18,943 biogas plants in Europe, with an installed capacity of 193 TWh ^[3]
- BG offers several advantages;
 - bio-renewable fuel, easily generated from local agricultural wastes
 - converting BG into H2 via SMR; less CO₂/kg H₂
 - 5.6 kg CO_2 /kg H_2 vs 11-13.5 kg CO_2 /kg H_2 ^[4]

[2] Gioele Di Marcoberardino et al; Potentiality of a biogas membrane reformer for decentralized hydrogen production, Chemical Engineering and Processing - Process Intensification, Volume 129, 2018, Pages 131-141,
[3] European Biogas Association. EBA Annual Report 2020; European Biogas Association: Brussels, Belgium, 2020
[4] Noureddine Hajjaji et al. Life cycle assessment of hydrogen production from biogas reforming, International Journal of Hydrogen Energy, Volume 41, Issue 14, 2016, Pages 6064-6075

INNOMEM







Figures from H2SITE

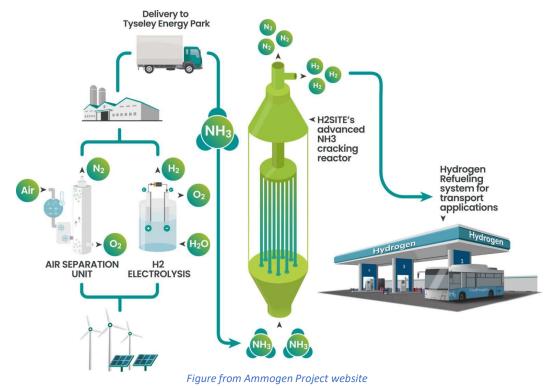
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Main outcomes:

- KPI's achieved:
 - 100 hours (five days and nights) of continuous operation without any technical or safety issue
 - High-purity hydrogen obtained \rightarrow 99,95 % H₂
 - 75% of H₂ h production capacity achieved
- Optimizing design, procurement, construction, operation and maintenance

Ammogen



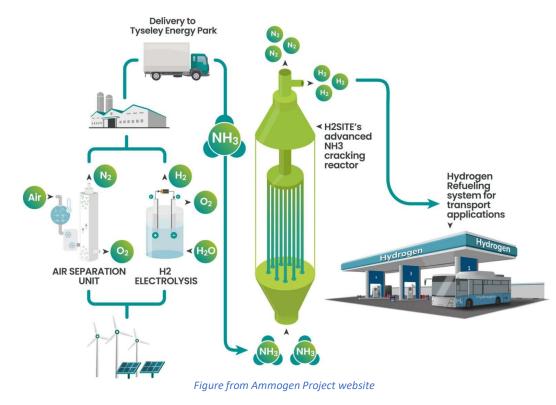


- Project is part of UK's BEIS low carbon H2 competition (Business, Energy & Industrial Strategy) launched in 2021.
- Demonstrator of the use of ammonia as an energy carrier
 - transport larger amounts of energy in less space (more energy-efficient)
- H2SITE's technology will be used to produce H₂ for the bus fleet of the city of Birmingham.
 - Ammonia cracker will deliver 200kg/day of transport-grade H₂

tors for H2 generation

Ammogen





- Ammonia cracker will fit in a 20-ft container to be delivered Jan'24
- To an existing and co-located hydrogen refuelling station at Tyseley Energy Park
 - Purity target: ISO 14687-2:2021
- Partners within the value chain of ammonia as Hydrogen Carrier (i.e YARA)

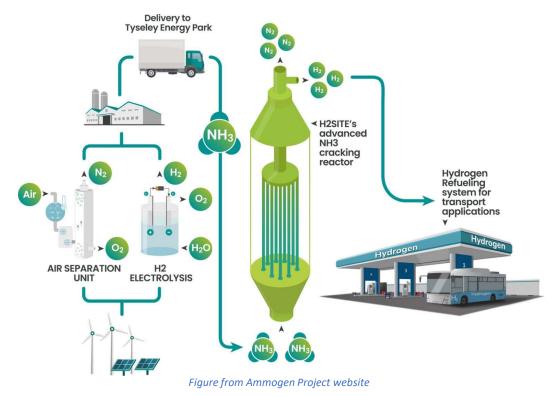


Membrane re

ctors for H2 generatior

Ammogen





Main outcomes:

- Biggest ammonia cracking membrane reactor for mobility solutions
 - Improvement in reactor heat integration and membrane installation
- Compact and commercial housing
 - Container / plug and play
- It matches three main players in the green hydrogen economy:
 - Feed supplier
 - Technology enabler
 - End-user (mobility sector)

Membrane re

ctors for H2 generation

H2SAREA





Validation of entire ecosystem for a CH_4 grid with (up to) 20% of H_2 .

Figure from ELPAIS

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H2SAREA

Membrane re

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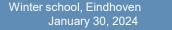
- "European Hydrogen Backbone EHB"
- Accelerate Europe's decarbonisation journey based on existing and new pipelines



- 75% of the infraestruture could be used for H₂ transport
 - Efficient, safe and cost-effective
- Materials, compounds and systems must be developed.

Figure from El

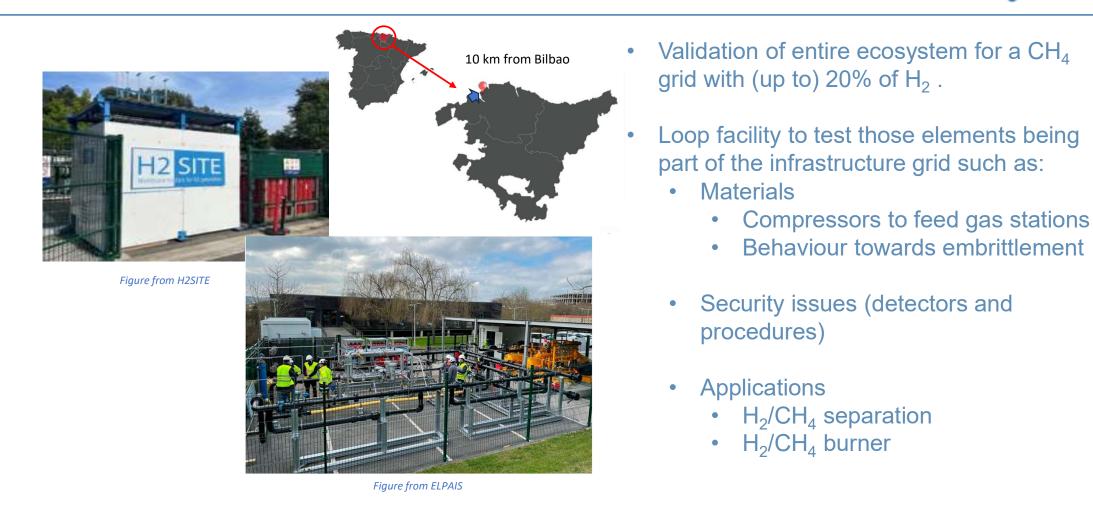
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H2SAREA

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H2SAREA





Figure from ELPAIS

- H2SITE deblender will deliver up to 4 kg H_2 /day of pure hydrogen
- % H_2 can be tunned (5 20%) in the feed
- System already in TSO facilities since Sep '23
- Commissioning ongoing (more than 20 hours running). Recovery >95%, H_2 < 2% and H_2 purity: fuel cell

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H2SAREA

ctors for H2 generation



Figure from ELPAIS

Main outcomes:

- First industrial deblending plant in Spain
 from NG + H2 mix
- Working in a closed loop feed with actual NG from the grid and operating conditions similar.
- Scaling system towards higher pressures (80 bar) and bigger systems (100 kg H₂/day) will come next



H2OCEAN

tors for H2 generation





Figure from Ammogen Project website

- Local project
- Demonstrator of the use of ammonia in onboard generation
- H2SITE's technology used to produce H₂ for fuel cell and make boat work
 - 20kg/day of transport-grade H₂

H2OCEAN



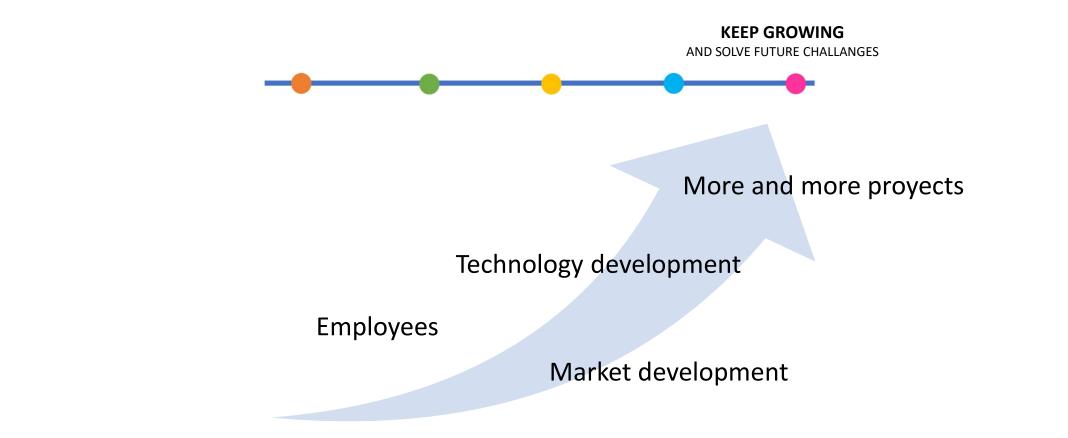


Figure from Ammogen Project website

- Boat trip of \approx 20 km
- Hydrogen production from ammonia the entire trip
- 1 kg H₂/hour produced during several hours, able to feed 20 kW fuel cell (not linked to critical engine parts)



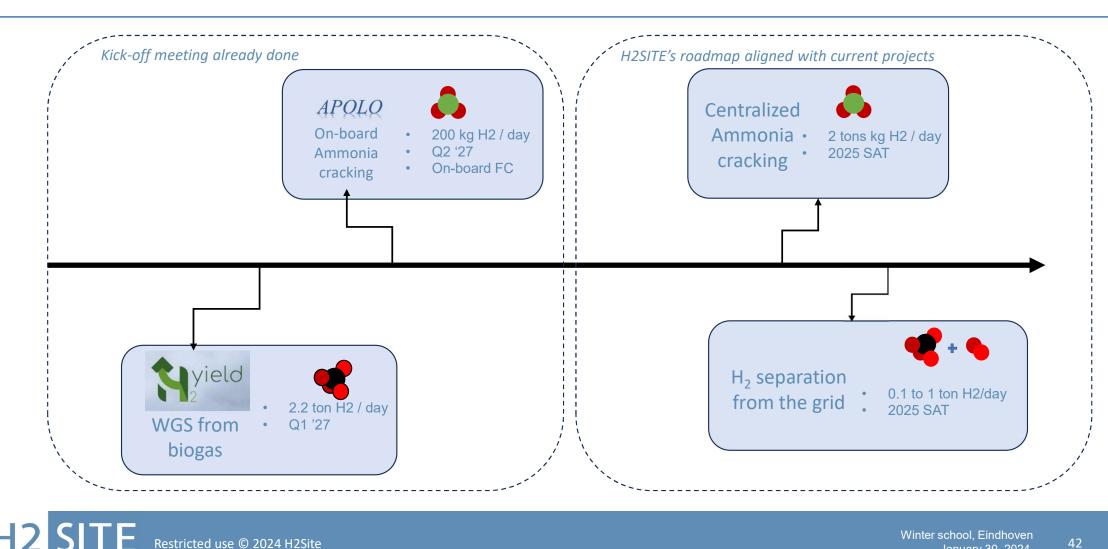
...and what comes next?





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Future projects



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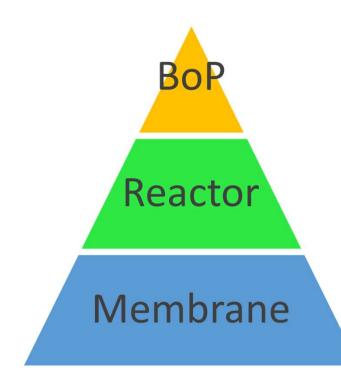
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H2SITE wants to enable (and lead) the Hydrogen economy in the future

...thanks to cost, efficiency and footprint...



to achieve more competitive solutions

.. in bigger and more efficient reactors...

Making productive membranes...

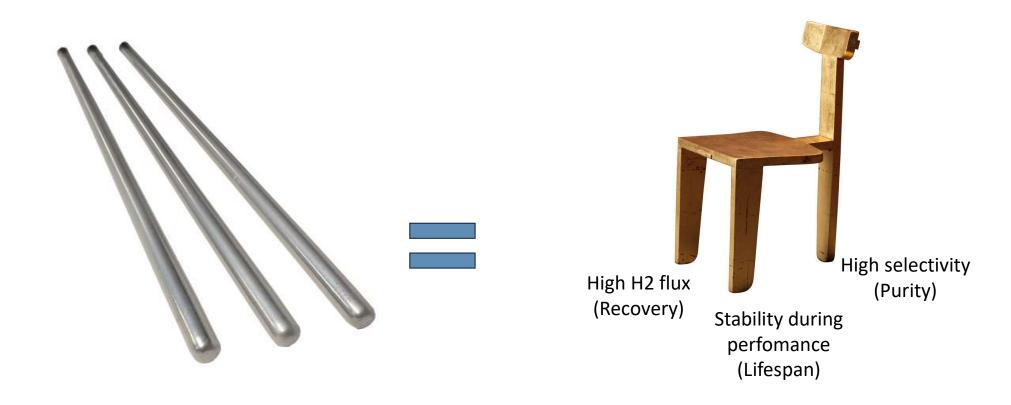


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Which is the way to achive the best H₂ selective membrane?



Membranes are like a three-legged chair



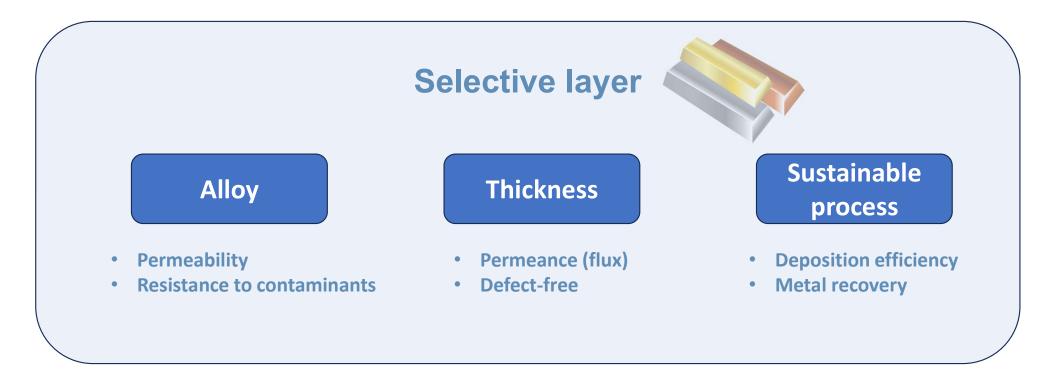
What is H2SITE caring about and how we could collaborate?

Cost of membranes is obviously something everybody cares, but we pay attention to...



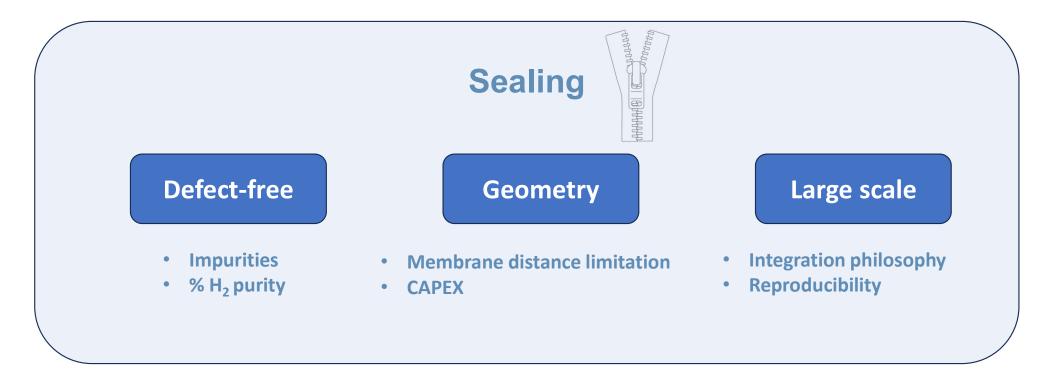
What is H2SITE caring about to have the best H₂ selective membrane?

Cost of membranes is obviously something everybody cares, but we pay attention to...



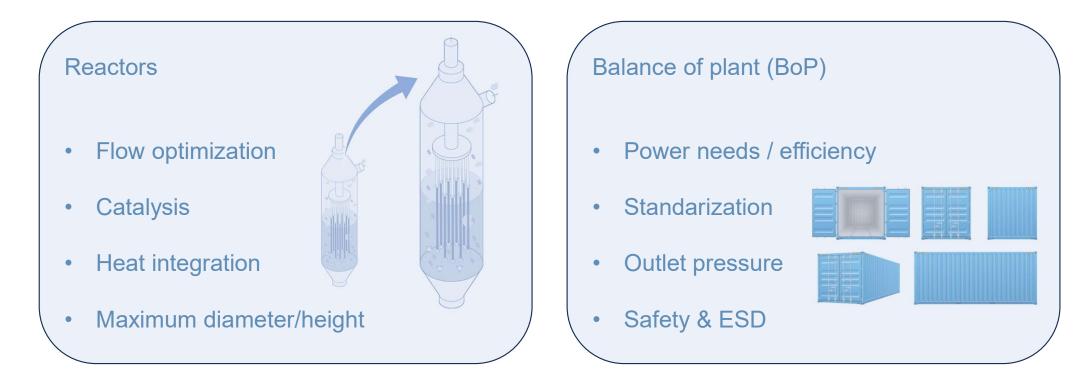
What is H2SITE caring about to have the best H₂ selective membrane?

Cost of membranes is obviously something everybody cares, but we pay attention to...



What is H2SITE caring about to have the best H₂ selective membrane?

Not only about membranes but also about...



Main outcomes

- \approx 300 kg H₂ /day in 7 systems from 3 different feedstocks, right now.
- Demonstrated of first on-board ammonia cracking producing H₂ continuously
- Up coming project including a 2.2 ton H_2 / day to be delivered in '27
- Short-term future will demand a huge effort in terms of development at three levels:
 - Membrane, Reactor and BoP to gain in cost reduction, efficiency and footprint
- H2SITE's technology shows great performance (HRF and purity) and can be competitive compared with PSA and EHC
- Small scale separation molecules will lead H2SITE to have big impact in the world
 - Think about hydrogen molecule size and the change in energy economy we want to lead

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H2 SITE

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Thanks for your attention jon.melendez@h2site.eu