

Demo 2 (Spain) – Production of methane from biogenic CO₂ and green hydrogen

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DEMO 2 overview

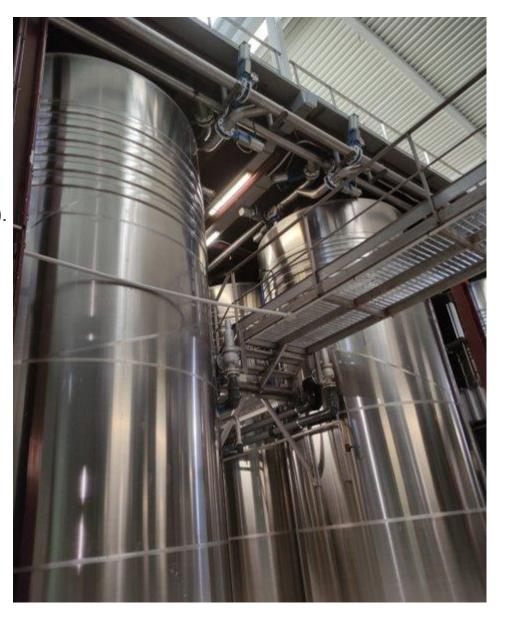
- **1.** Located in Spain (Aragon region).
- **2. Wine factory** with more of 1000 hectares of grape crops.
- DEMO will target CH₄ production (Power plant and or Road transport).
- 4. CO₂ will be taken from fermentation process.
- **5.** H_2 is currently produced by on-site **electrolyzer** (500L/h).
- **6. TRL** initial 5 Final **7**.





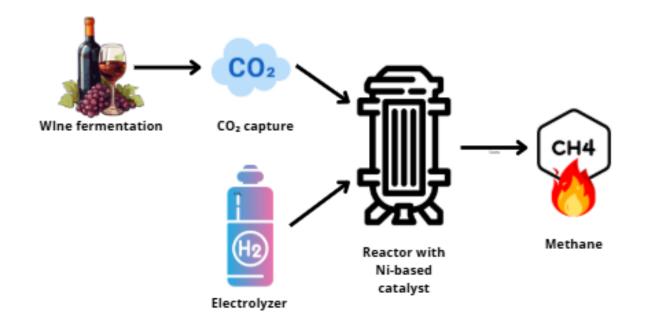






Aim of DEMO 2

- To utilize the captured CO₂ from the wine fermentation process, combined with green H₂, as feedstock for a methanation process that produces CH₄ by the Sabatier reaction.
- This is achieved using novel nickel-based catalysts.
- The CO₂ will be separated, purified from the fermentation gas, and stored for later use in the methanation process, where it will be converted into CH₄.
- The CO₂ generated during wine fermentation is carbon-neutral, matching the amount absorbed by the vines through photosynthesis.



Sabatier reaction

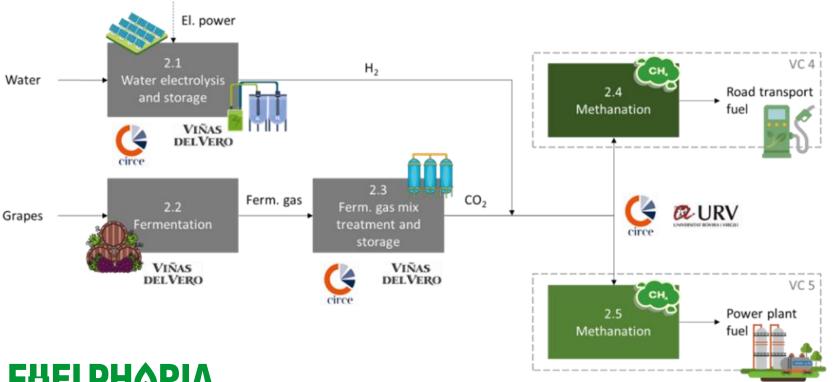
$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

 $\Delta H_r^0 = -165,1 \text{ kJ mol}^{-1}$



Project Partners and DEMO targets

- Viñas del Vero (VdV): Host site; provider of CO₂ and H₂ feedstock.
- CIRCE: Responsible for methanation process development and integration.
- URV (University Rovira i Virgili): Development of catalysts and methanation reactor.

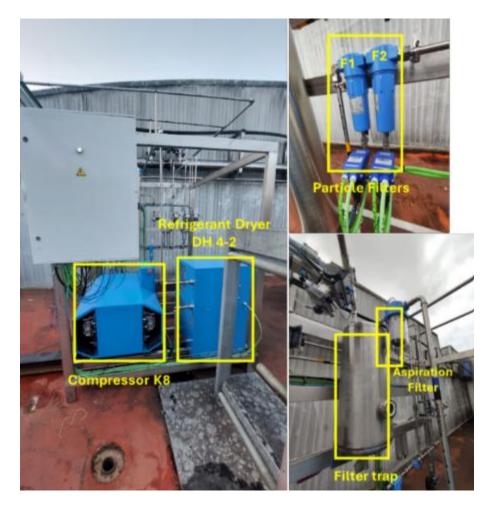


DEMO TARGETS

- H₂ production: 500 L/h, 99.94% purity, 30 bar pressure.
- CH₄ production: 2.2 kg/day → 780 kg/year.
- CO₂ utilization: 0.4% of winery's annual emissions.



CO₂ capture unit







Captured CO₂

The captured CO₂ in this harvesting period (from the 20th of August to the 9th of September) has been 17 Tm. From this, only 800 kg are going to be used for potential methanation.

- 99.95 % of purity.
- CO, hydrocarbons, ethanol and water are the main "impurities".
- Sulphur is below the food grade level. No risks for the catalysts.

SC CO2 EL GRADO, SLU

L86.01.01 / Rev:0

Certificado de Análisis CO2

Linea n*: 12 Fecha: 06/09/2024 Batch n*: 8317 Hora: 14:09:33

Nº de LOTE: 24/01/D/000 Nº de albarán: 24/01/A/000

PRECINTOS: BOTELLA CO2-VIÑAS DEL VERO

Pureza	Resultados Análisis				Especificaciones		
CO2	>-	99.95	16	>	99.99	96	
Impurezas	Resultados Análisis				Especificaciones		
CO		66.55	ppm	≤	10.00	ppm	
CH4	45	0.10	ppm	S	30.00	ppm	
THC		124.81	ppm	5	20.00	ppm	
O6H6	40	0.01	ppm	5	0.02	ppm	
C7H8	<	0.01	ppm	S	0.02	ppm	
pm-C8H10	40	0.01	ppm	S	0.02	ppm	
o-C8H10	<.	0.01	ppm	S	0.02	ppm	
C2H4O		27.94	ppm	5	0.20	ppm	
CH3OH		2.93	ppm	≤	10.00	ppm	
C2H5OH	40	0.10	ppm	≤	1.00	ppm	
TS		0.01	ppm	5	0.10	ppm	
O2		96.80	ppm	- 55	20.00	ppm	
NH3	40	0.20	ppm	≤	2.50	ppm	
NO		0.75	ppm	≤	2.50	ppm	
NO2		0.80	ppm	S	2.50	ppm	
NOX		1.54	ppm	-5	2.50	ppm	
H2O		103.77	ppm	S	20.00	ppm	
Sabor		Característico			Característico		
Olor		Característico			Característico		
Aspecto		Ausencia			Ausencia		
TOTAL	<	424.70	ppm				



Catalyst tests and first results

Base:

Synthesized Ni-based catalyst (Ni-based) – 100-200 µm particles.

Promoted catalysts:

- Promoter 1 → Ni-Prom1
- Promoter 2 → Ni-Prom2
- Promoter 3 → Ni-Prom3

Goal:

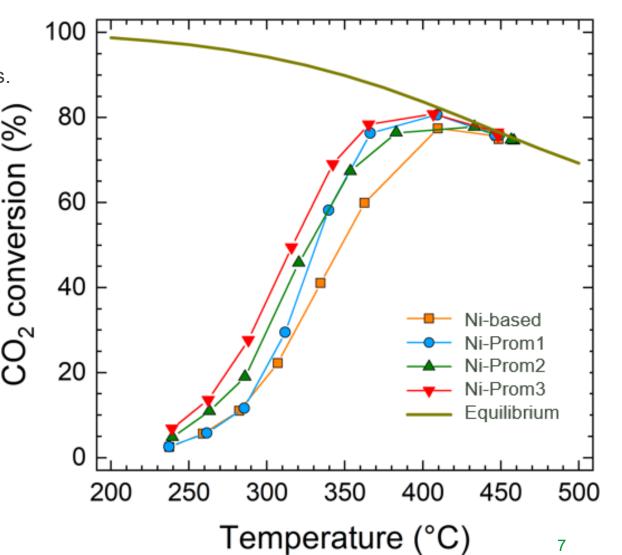
Increase stability and resistance to sintering and coking.

Conditions:

P = 1 atm

 $H_2:CO_2$ molar ratio = 4

 CO_2 weight hourly space velocity (WHSV) = 0.54 $mol_{CO2} \cdot g_{cat}^{-1} \cdot h^{-1}$





Testing modified NiProm3 catalyst

An additional catalyst was prepared and tested by adding another material as a second promoter to the Ni-Prom3 catalyst (NiProm3-Modified).

Conditions:

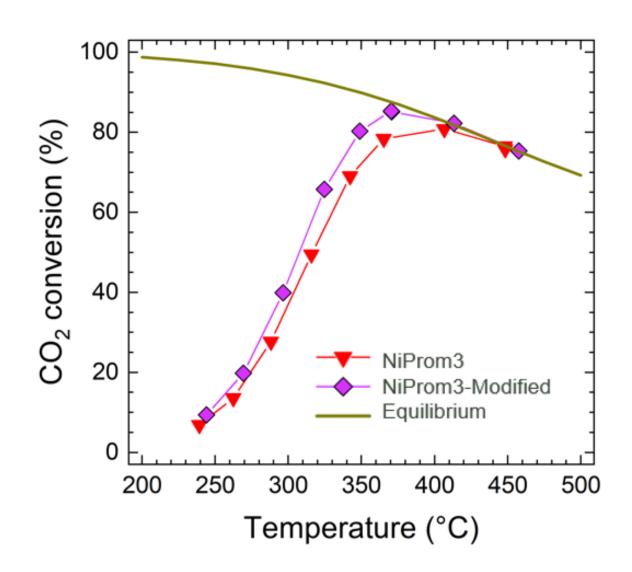
P = 1 atm

 $H_2:CO_2$ molar ratio = 4

WHSV = $0.54 \text{ mol}_{CO2} \cdot g_{cat}^{-1} \cdot h^{-1}$

Results

- Slight improvement, mainly above 300 °C.
- No significant advantage and more complex → Not selected.





Lifetime Test with Real Winery CO₂

Extended evaluation for the **NiProm3** for matching real reaction conditions.

Conditions:

P = 1 atm

T = 300 °C

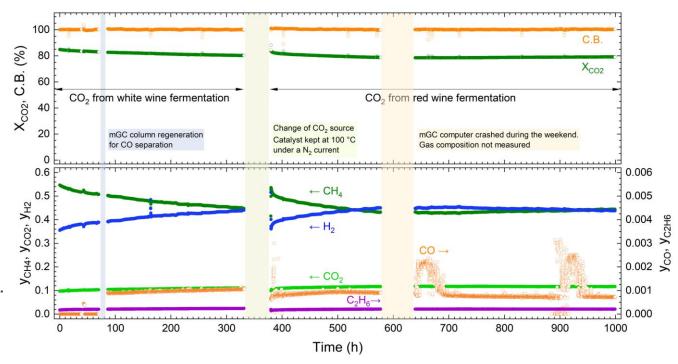
 H_2 : CO_2 molar ratio = 4

WHSV = 0.18 $mol_{CO2} \cdot g_{cat}^{-1} \cdot h^{-1}$

Feed = CO_2 from white and red wine fermentation.

Results:

- Initial conversion ≈ 85 %, stabilized at 80 % after 250 h.
- Total time on stream = 1000 h (≈ 41 days)
- High stability and CH₄ selectivity.
- Performance was similar when switching from white to red wine CO₂, demonstrating robustness to feedstock variations.



NiProm3 confirmed as DEMO 2 catalyst



From Powder to Reactor Pellets

Coprecipitation method produces fine powder (<1 mm) → Unsuitable for fixed-bed reactor.

Two routes explored to increase particle size:

1. Impregnation on commercial particles

2. Pelletization by cold pressing the NiProm3 precursor







Impregnation on commercial particles

Two samples were synthesized:

- Ni-based-pellet
- NiProm3-pellet

Conditions:

P = 1 atm

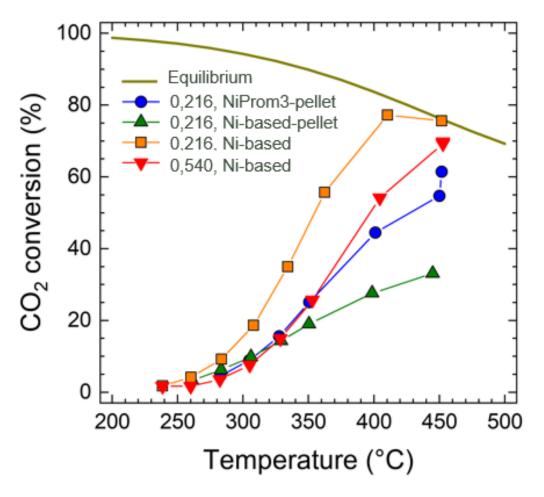
 $H_2:CO_2$ molar ratio = 4

WHSV = 0.216 $\text{mol}_{\text{CO2}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$

Results:

- Large particles (1/8") limited by diffusion → Lower conversion.
- The NiProm3-pellet catalyst showed deactivation above 400 °C.

This is not the optimal solution for the DEMO reactor.





Pelletized Catalyst Performance

Pellets of cold **NiProm3**: cylindrical 3 mm × 2.5 mm.

Good mechanical integrity after calcination.

Conditions:

P = 1 atm

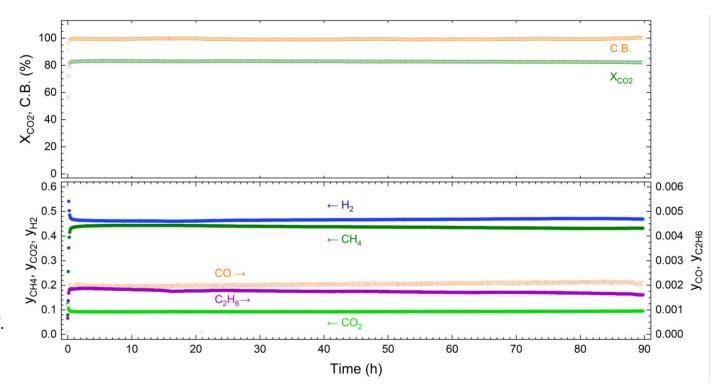
T = 360 °C

 H_2 : CO_2 molar ratio = 4

WHSV = $0.027 \text{ mol}_{CO2} \cdot g_{cat}^{-1} \cdot h^{-1}$

Results:

- 82 % conversion, stable after 90 h (almost 4 days).
- High CH₄ selectivity → Suitable for DEMO 2 reactor.

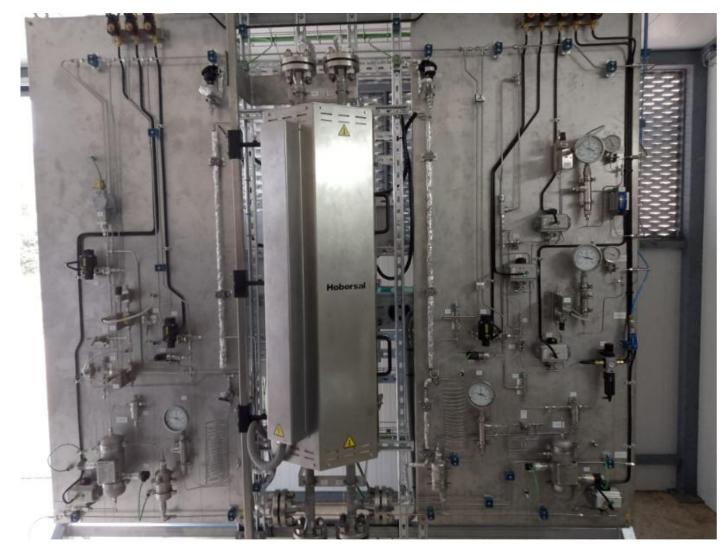




Methanation unit - Overview

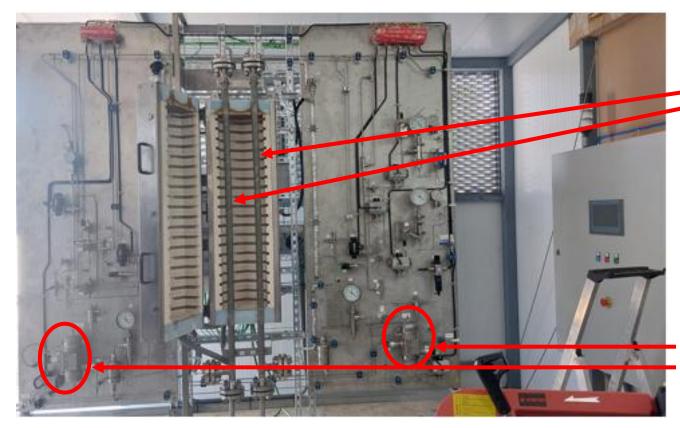
Reactor prototype commissioned for DEMO 2

- Leak-tightness of the full line successfully verified
- Catalyst activation performed during the initial heat-up phase
- System start-up completed under controlled pressure and temperature
- First temperature and conversion profiles obtained using real winery CO₂



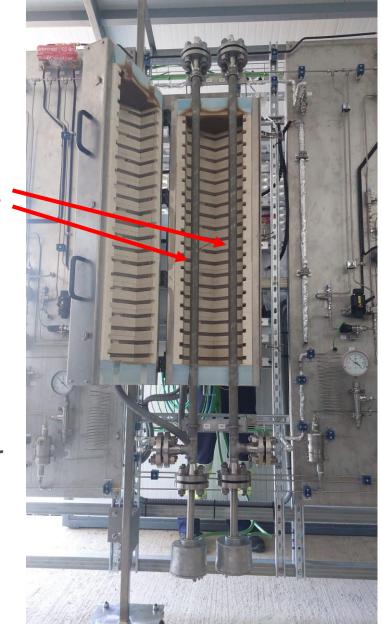


Methanation unit - Overview



Reactors







First test during start-up

Conditions

Feed

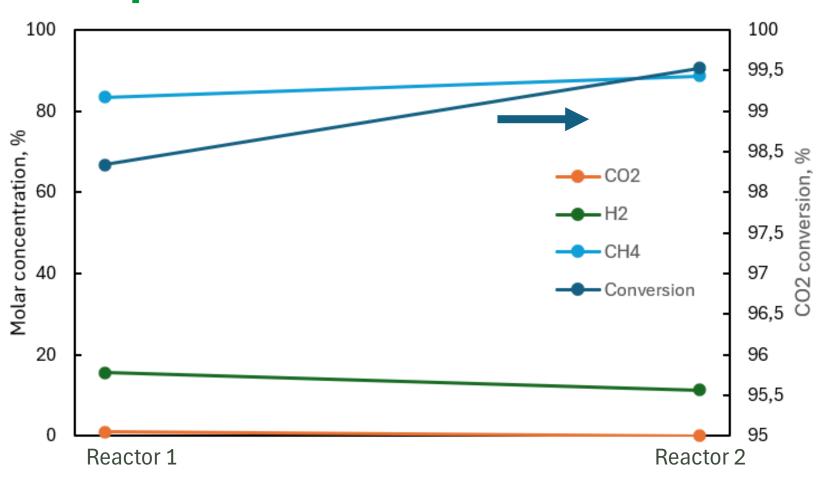
 H_2 flowrate = 0.027 kg/h CO_2 flowrate = 0.130 kg/h H_2/CO_2 = 4.57

Temperature

T_{Furnace} = 200 °C

Pressure

P = 7 bar





Next steps and improvements

- The demo aims to perform long-term lifetime tests of the catalyst under industrial conditions. The system will operate with a stoichiometric CO₂/H₂ feed, maintaining temperatures below 500 °C and working pressures between 5 and 10 bar.
- Further optimization of the reactor thermal control to ensure a more uniform temperature distribution during long-term operation.
- Validation of the numerical reactor model by comparing predicted and measured temperature and composition profiles in upcoming test campaigns.



About FUELPHORIA

FUELPHORIA is an EU-funded Innovation Action project working to establish sustainable, competitive, and secure value chains for advanced biofuels and renewable fuels of non-biological origin.

Coordinated by CERTH, the project will set up and test a portfolio of 9 complete value chains in Belgium, Greece, and Spain.

Project partners will also evaluate the environmental performance of the FUELPHORIA renewable fuels, design innovative business models to prepare their market entry, and explore their export potential through collaboration with Africa

Get in touch

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Thank you for your attention



