Development of an innovative catalytic-based biogas-to-biomethane conversion route for industrial application

CERTH - BLAG

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innovations in the BIOMETHAne uniVERSE

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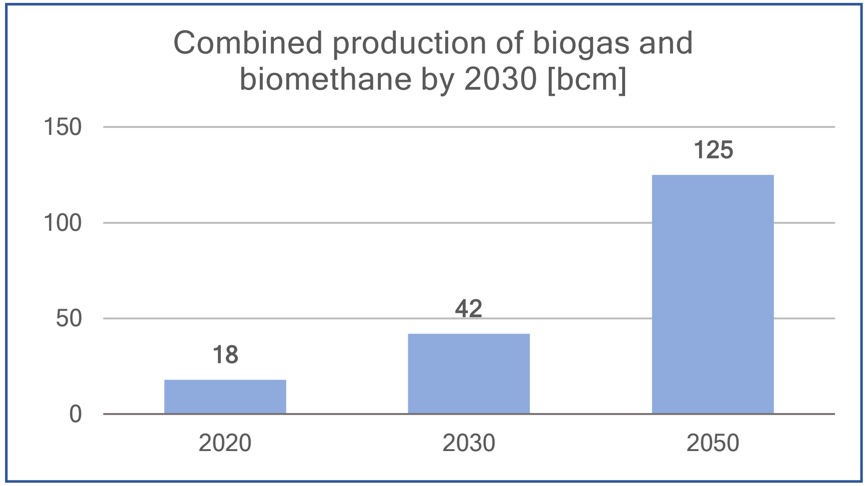
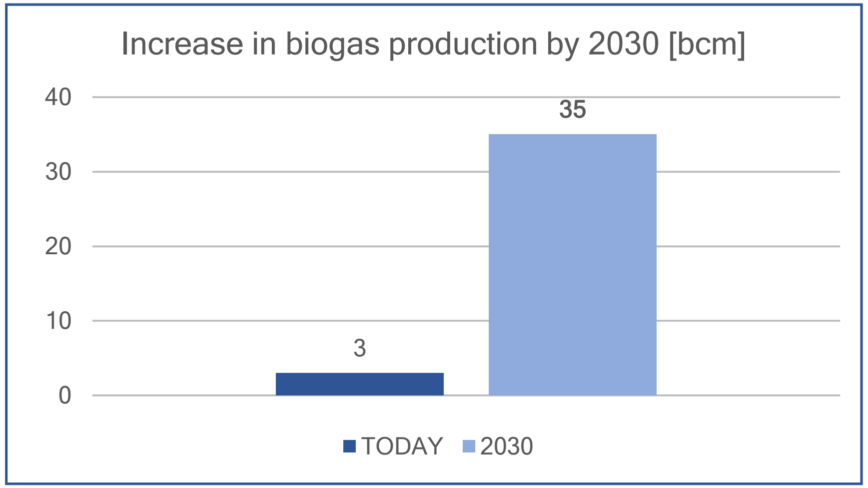
Biomethane and REPower EU: A Strategic Alliance

- ✓ **Promoting Energy Efficiency**: The EU's REPowerEU plan aims to enhance energy efficiency, diversify energy supply, and develop renewable energy sources to replace fossil fuels
- ✓ **Strategic Importance of Biomethane**: Biomethane is crucial for reducing dependence on imported fossil fuels, enhancing energy security and contributing to climate neutrality, a circular economy, and rural development
- ✓ **Diverse Sustainable Feedstock**: REPowerEU supports the use of agricultural waste, municipal sewage sludge, and industrial byproducts for biogas production to minimize waste and promote a circular economy
- ✓ **Sustainable Production Practices**: The plan sets criteria for feedstock to avoid food competition and land-use changes, and encourages life cycle assessments to ensure positive environmental impacts
- ✓ **Empowering Regions**: By promoting diverse feedstock types, REPowerEU empowers regions across the EU, fostering a geographically balanced energy landscape

REPowerEU Objectives





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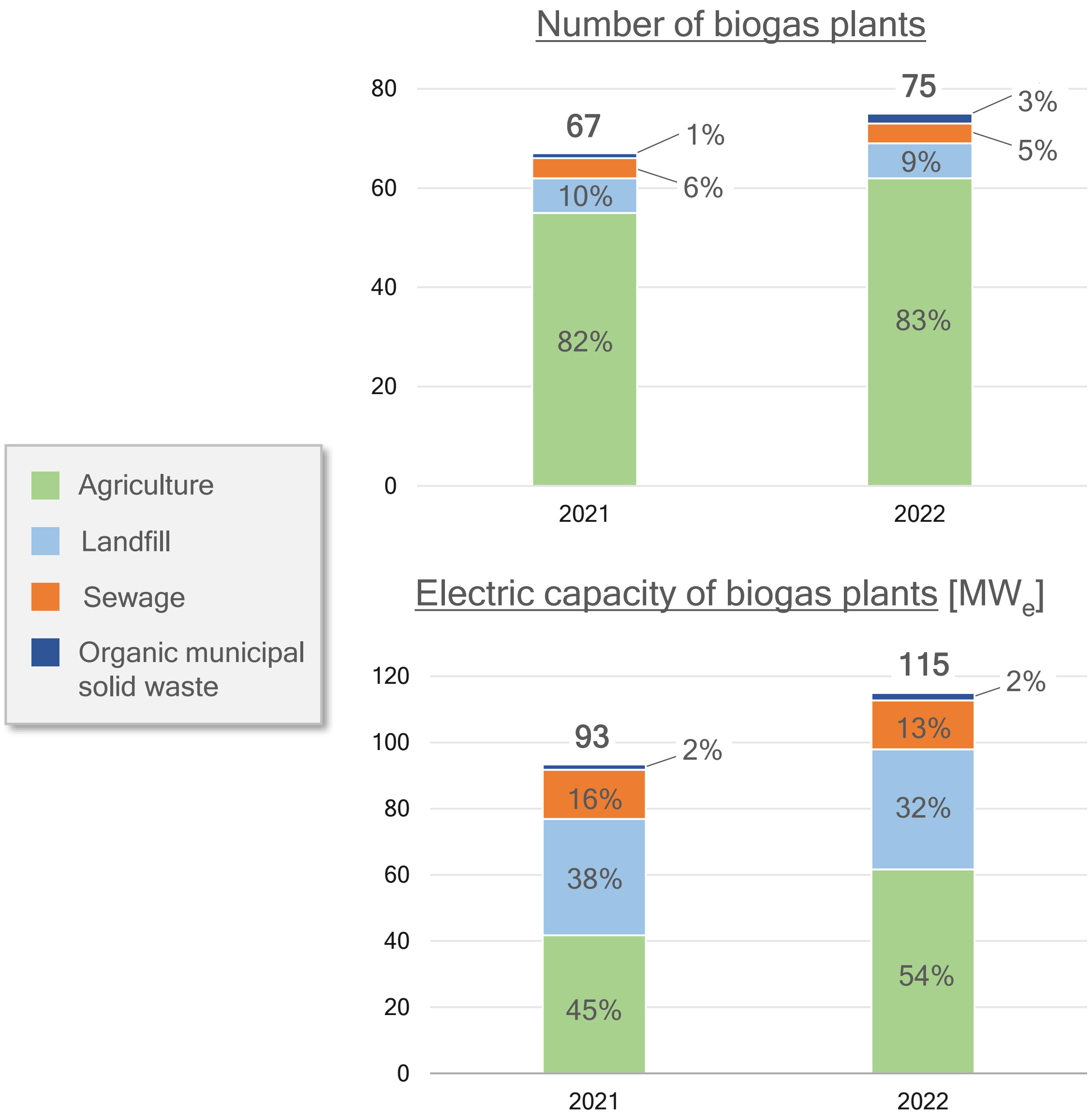
Biogas and biomethane sector in Greece

- ✓ Greece has been gradually increasing its focus on **renewable energy** (the share of energy from renewable sources has increased from **15.3%** in 2013 to **22.7%** in 2022)
- ✓ Today, **only biogas** is produced and there is **no biomethane market**. In 2022, **75 units** operated with a total capacity of 115 megawatts (the total biogas production was 1,277 GWh)
- ✓ Biomethane is produced through **mature and competitive technologies** that can help Greece in its **energy transition**
- ✓ The two defining **problems** in Greece today are the **absence of a legal framework** and the **lack of a secure supply chain of feedstock** on the other
- ✓ Greece's NECP (2020) includes targets for biomethane production, seeking to reach up to **2.1 TWh/year by 2030 and 9.7 TWh/year by 2050**
- ✓ The 2030 biomethane potential for Greece is **0.54 bcm** (*Gas for Climate, 2020*)



Sources: Eurostat
Gas for Climate, 2020
EBA Statistical Report 2022
EBA Statistical Report 2023

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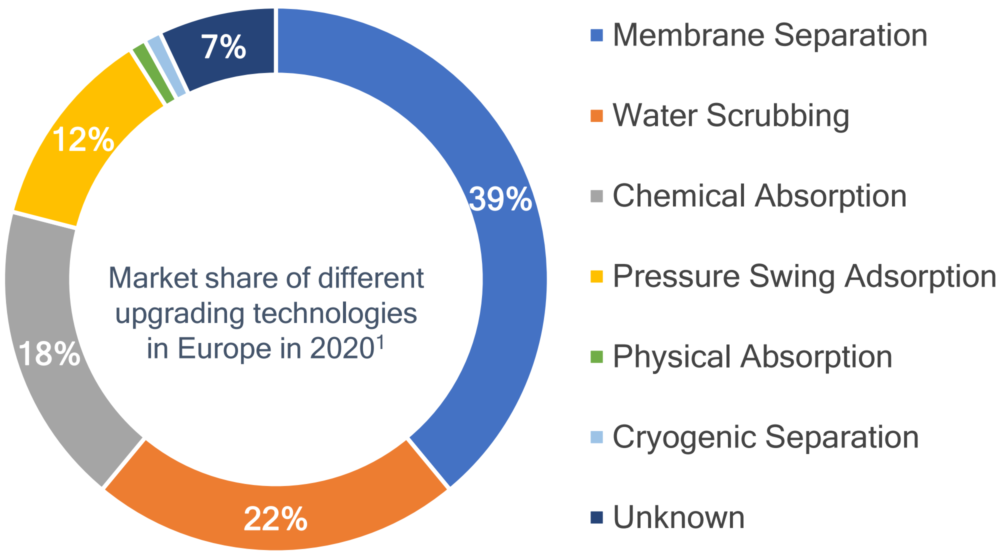
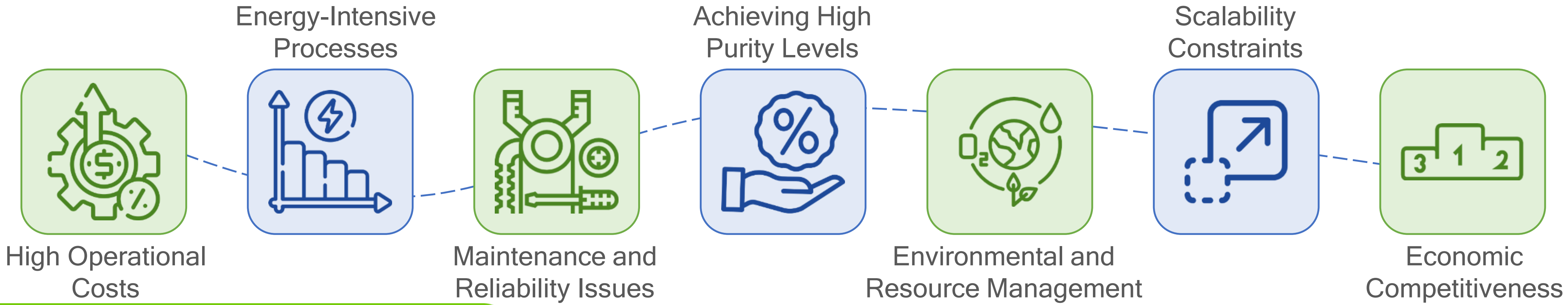
Conventional technologies for biomethane production

Biomethane production technologies

- **Membrane Separation**: semi-permeable membranes that selectively allow CH_4 to pass while retaining CO_2 and other impurities.
- **Water Scrubbing**: biogas passes through a water column where CO_2 is absorbed by the water.
- **Chemical Absorption**: use of chemical solvents to absorb CO_2 from the biogas.
- **Pressure Swing Adsorption**: use of adsorbents like zeolites to selectively adsorb contaminants under high pressure.



Challenges of conventional technologies



[1]C. Soto, L. Palacio, R. Muñoz, P. Prádanos, and A. Hernandez "Recent Advances in Membrane-Based Biogas and Biohydrogen Upgrading"

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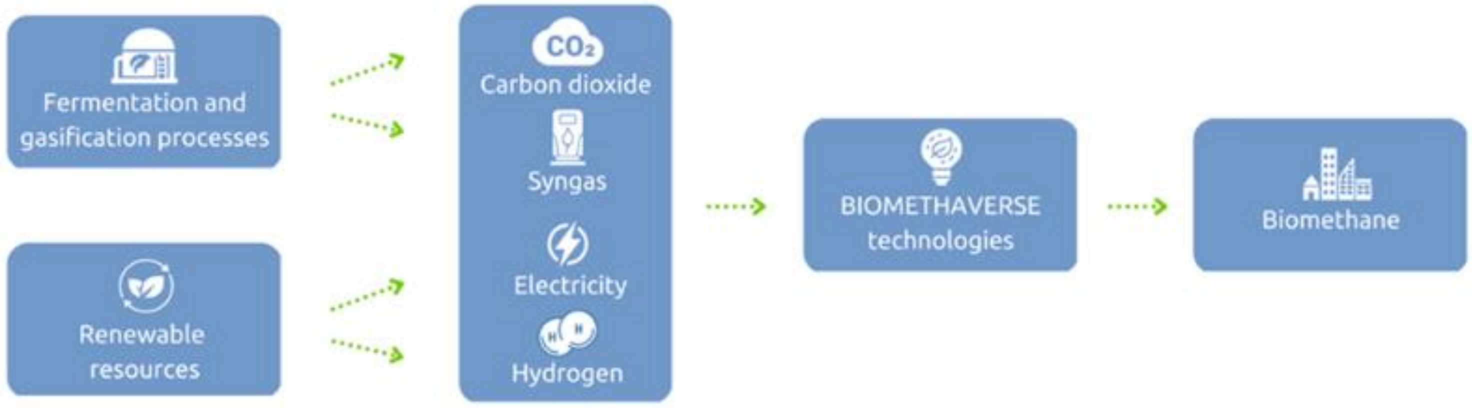
The BIOMETHAVERSE project

Demonstrating and Connecting Production Innovations in the BIOMETHAne uniVERSE

Main objectives of the project

- to diversify the **technology basis** for biomethane production in Europe
- to increase its **cost-effectiveness**
- contribute to the uptake of **biomethane technologies**
- contribute to the priorities of the **SET Plan Action 8**



5 innovative biomethane production **pathways** in 5 European **countries**

- **France**: In-Situ and Ex-Situ Electromethanogenesis (EMG)
- **Italy**: Ex-Situ Biological Methanation (EBM)
- **Sweden**: Ex-Situ Syngas Biological methanation (ESB)
- **Ukraine**: In-Situ Biological Methanation (IBM)
- **Greece**: Ex-Situ Thermochemical/ Catalytic Methanation (ETM)

For more info, please visit the official website of the project:
https://www.biomethaverse.eu/

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Stakeholders for the Greek pilot unit

Centre for Research & Technology Hellas (CERTH)

Key role in BIOMETHAVERSE

- ✓ Leader of the demonstrator in Greece
- ✓ Technical, policy & communication expertise
- ✓ Solid background on biogas/biomethane market
- ✓ Support on the design of the biomethane plant based on the specifications of the biogas plant
- ✓ Support on the construction and operation of the pilot plant

Main fields of research

- Circular Economy
- Biomass/waste treatment and utilization
- Alternative (renewable) fuels/e-fuels and renewable gases
- Bioplastics/Biochemicals
- CO_2 capture and utilization
- Integrated energy production and storage systems
- Smart Grids
- Fertilizer production
- Recycling/Upcycling/Recovery of materials

Biogas Lagada (BLAG)

Key role in BIOMETHAVERSE

- ✓ Biogas plant owner
- ✓ Technical expertise
- ✓ Demo site for the implementation of ETM technology
- ✓ Design of the biomethane plant based on the specifications of the biogas plant
- ✓ Construction and operation of the pilot plant

BLAG at a glance

- Located in Lagadas, in Central Macedonia Region
- Established in 2011 and operates since 2016
- 2 fermenters with 4,000 m^3 volume each
- Exploitation of around 70,000 tons of livestock and agro-industrial waste per year
- Production of 4.2 million m^3 of biogas annually
- Production of 8,400 MWh of electricity per year
- Production of 75,000 tons of digestate (organic soil improver for 2,000 ha of agricultural land)
- The capacity of the CHP generator is 1 MW_e

For more info, please visit the official websites of CERTH and BLAG:
https://www.certh.gr/root.en.aspx
https://www.biogaslagada.gr/

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Ex-situ Thermochemical/catalytic Methanation (ETM)

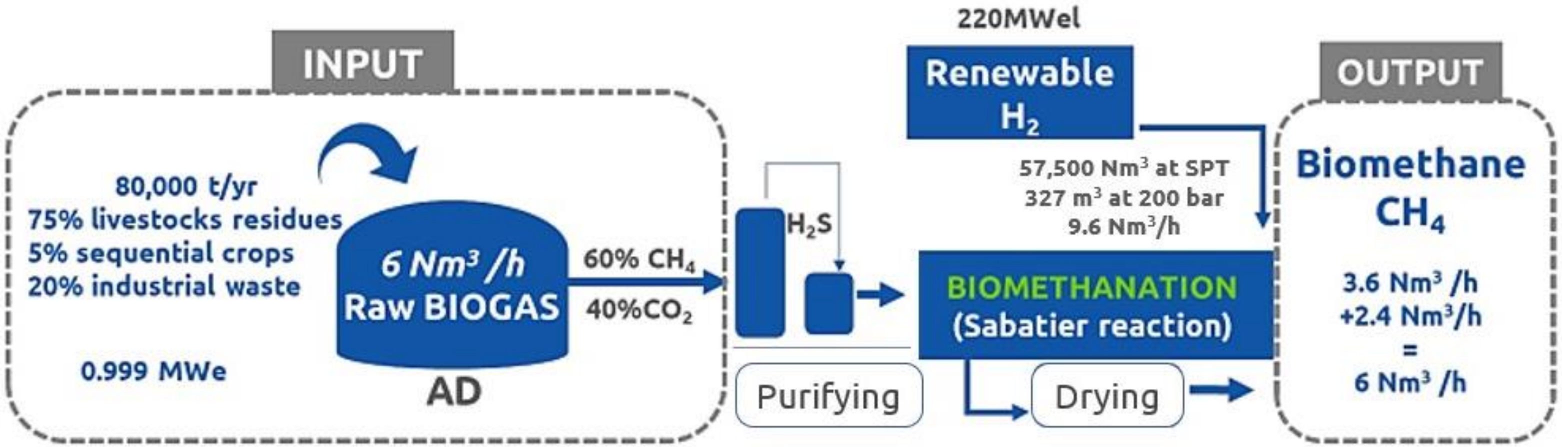
The technology is based on the Sabatier reaction: $CO_2 + 4H_2 \xrightarrow{pressure + catalyst} CH_4 + 2H_2O \quad (\Delta H = -165\ kJ/kmol)$

The CO_2 contained in the biogas is converted to biomethane through its reaction with **renewable H_2**

The catalytic reaction takes place at high **pressure** (8 - 10 bar) and **temperature** (200 - 550 °C)

The final product is biomethane already reaching pipeline quality gas standards (**96-98 vol% CH_4**)

- Input biogas flow → 6 Nm^3/h (60% CH_4 and 40% CO_2)
- CH_4 in biogas → 60% x 6 = **3.6** Nm^3/h
- Conversion of the CO_2 into the biogas stream → Additional **2.4** Nm^3/h CH_4



Operation targets

- Production of a total of **15,000 m^3** of biomethane.
- Operation of the pilot plant for a total of **6,000 hours**.
- The target for the total energy efficiency of the process is set to **61%**[1]

[1] Defined as the energy content of the biomethane divided by the electricity consumption for renewable hydrogen production

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Key benefits of the demonstrated technology

- The catalytic reactor can handle a mixture of CH_4 and CO_2 → **No separation** of biogas is required before conversion
- The technology is based on **well-proven equipment**, i.e., fixed bed reactors and tube heat exchangers.
- Conversion of all the CO_2 in the biogas so the output flow of CH_4 rises → the **productivity** increases by about **66%**
- The CH_4 content will be increased from **60%** in the input stream towards more than **95%** in the output stream
- The final product is biomethane already reaching **pipeline quality** gas standards → No further upgrading is necessary
- Expected **reduction in production** costs by approximately **20%** compared to conventional technologies
- Potential **replicability** of the demonstrated technology to other biogas plants

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Basic design of the biogas purification unit

Typical composition of biogas

• CH_4	55 - 60%
• CO_2	40 - 45%
• O_2	0.2 - 0.8%
• N_2	0.8 - 3.0%
• H_2S	1 - 200 ppm

The biogas is obtained from **anaerobic digestion** at BLAG plant site, currently yielding 500 m^3 biogas per hour from livestock and agro-industrial waste

Purification Requirements

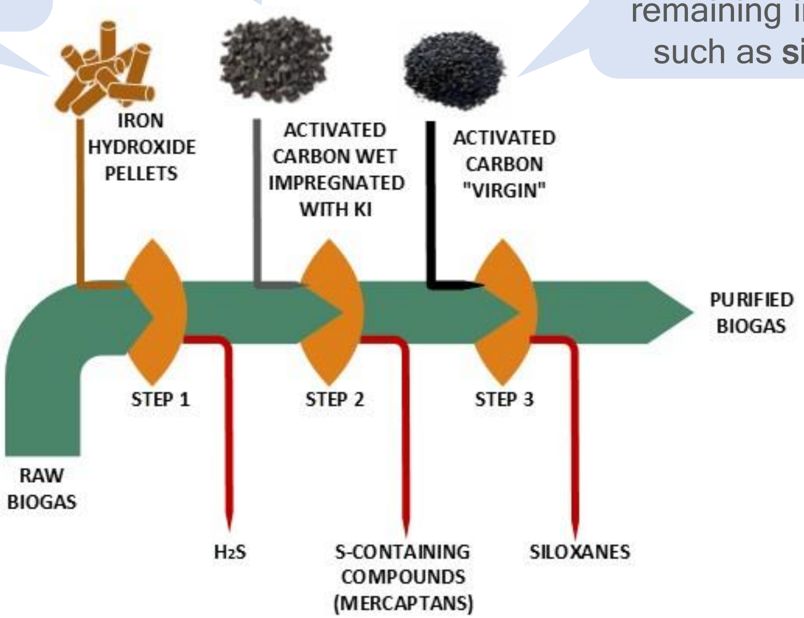
- H_2S < **1 ppm**
- Removal of other **S-containing compounds** (e.g. mercaptans)
- Siloxanes < **1 ppm**

A multi-stage pre-treatment process is crucial for optimizing the performance and reliability of subsequent processing steps in biogas utilization.

Iron hydroxide pellets are employed to effectively remove a substantial portion of H_2S

Activated carbon (AC) wet impregnated with **potassium iodide** is utilized to capture **sulfur-containing compounds**

Non-impregnated AC is employed to cleanse the remaining impurities, such as **siloxanes**



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Selection of Ni-based methanation catalysts

Selection of Ni catalysts:

- **Ni** is the most **selective** methanation catalyst
- Ni-based catalysts have been widely used due to their good catalytic **performance** and **cost-effectiveness**

Attention points:

- Carbon build-up
- Particle sintering
- Formation of $Ni(CO)_4$
- Severe sulfur poisoning during the production of SNG at high temperatures
- Insufficient stability of the catalyst, leading to a brief lifespan and limited ability to be reused

Methods to achieve high CO_2 conversion and CH_4 selectivity at low temperatures:

- incorporating a second metal or promoter into the matrix
- adjusting the synthesis method and parameters

Altering the synthesis method aims to generate catalysts with a **high surface area** and **small particle size**

Benefits from Ni supporting:

- enhanced dispersion
- diminishment of Ni particle sintering
- enhanced CO_2 methanation by leveraging synergistic effects
- enhanced capacity to resist carbon deposition

NiO / Al_2O_3 catalysts of a **40 / 60** ratio have shown best results, with recovery of approximately **90% CH_4** at a temperature of **300°C - 400°C** for syngas

Relative literature:
- N.D.M. Ridzuan, M. S. Shaharun, M. A. Anawar, I. Ud-Din, Ni-Based Catalyst for Carbon Dioxide Methanation: A Review on Performance and Progress, Catalysts, 12 (2022) 469
- S. Danaci. Optimisation and integration of catalytic porous structures into structured reactors for CO conversion to methane. Catalysis. Université Grenoble Alpes, 2017.

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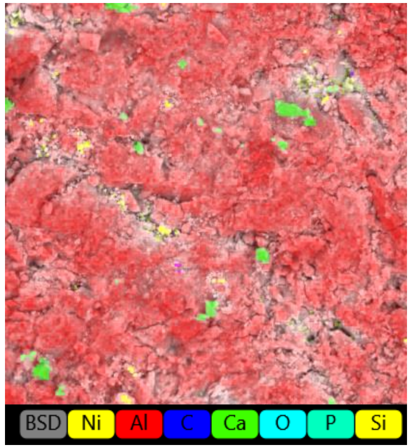
Execution of lab-scale experiments

Experiments were carried out to evaluate the main characteristics for the methanation process and achieve **high CO_2 conversion and CH_4 selectivity**.

- Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) → Verification of the **composition and morphology** of catalysts
- The selected catalyst exhibits a **well-dispersed configuration** of **Al_2O_3** within the **NiO** matrix
- Experiments were performed at different space velocities → The **catalyst activity** decreases with an increase in velocity (reduced residence time)
- The catalytic activity was examined at different **temperatures**: from 200 to 400 °C → At **T > 300 °C**, chemical equilibrium is nearly achieved for each velocity
- Inflow and outflow **volumetric flow rates** and the **carbon and hydrogen mass balance** were extracted → CO not detectable indicating very high selectivity towards CH_4
- The same sample showed **excellent stability** for over 70 hours

Selected catalyst in a sphere form



Approximately **23% Ni** and **54% Al**

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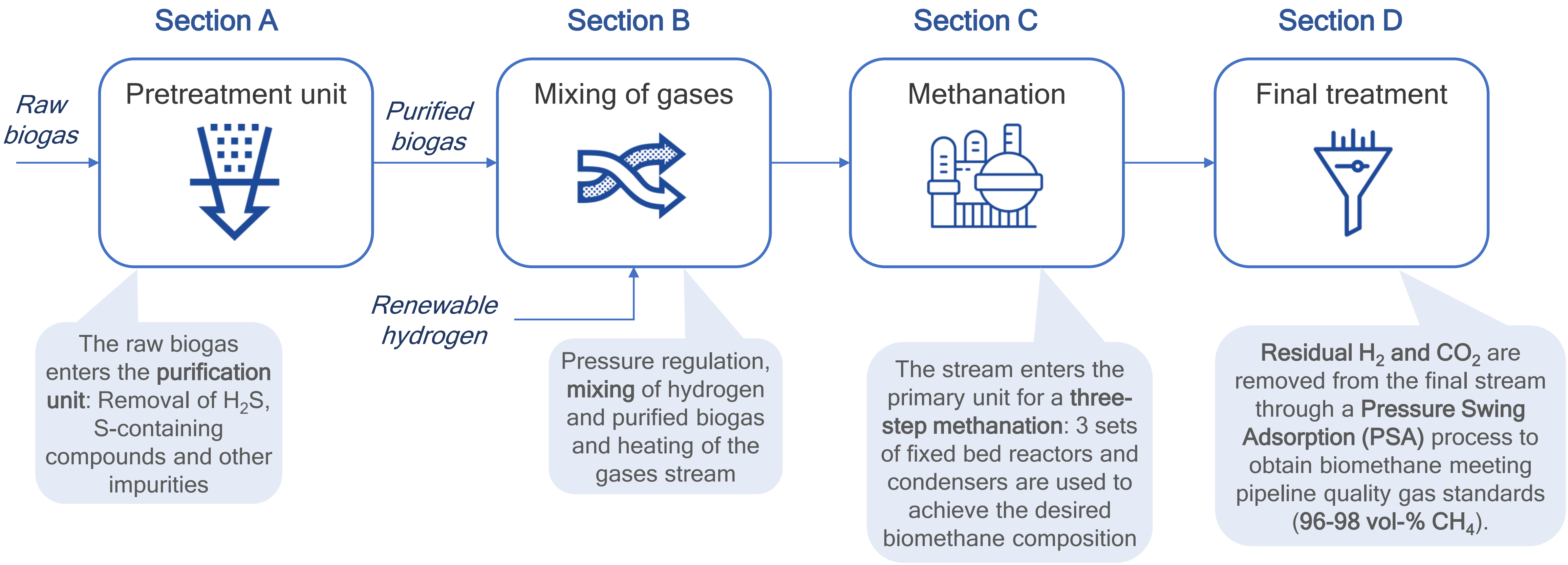
A simplified flowchart of the pilot unit



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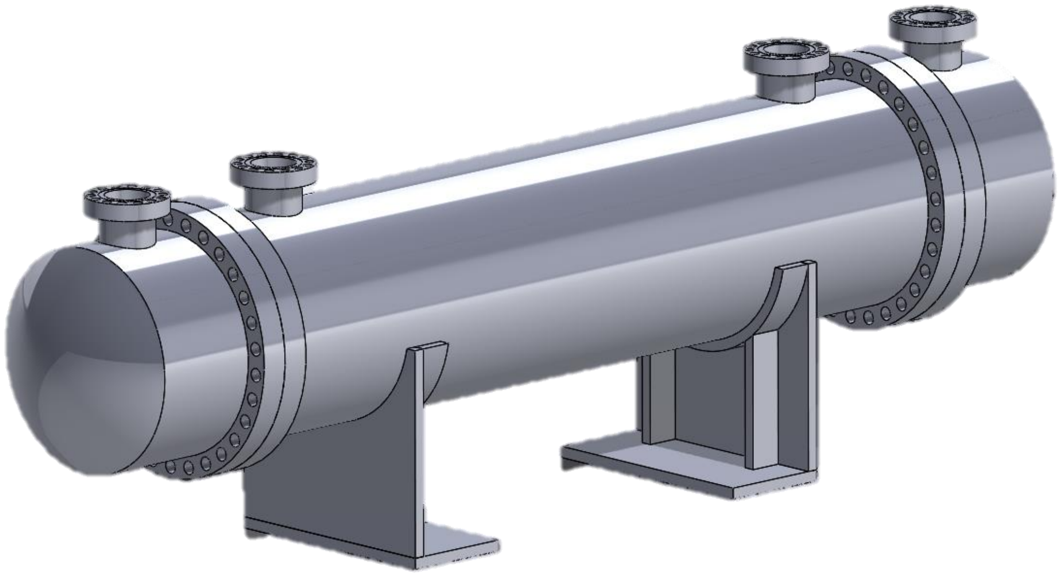
A more detailed view of the cooled fixed bed reactor

The design of the pilot-scale reactor is based on:

1. Implementation of an **optimized set of operating conditions** derived from the experimental campaign
2. Utilization of **control strategies** that ensure precise, rapid, and user-friendly management of internal reactor conditions
3. Incorporation of technology to minimize the **risk of gas leakage**
4. Emphasis on **scalability** through a modular approach, steering away from merely increasing vessel volumes
5. Focus on facilitating easy and cost-effective **maintenance** procedures



3D model of the cooled fixed bed reactor

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Policy Actions for Developing the Biomethane Market in Greece

Financial Incentives

- **Subsidies and Grants:** Provide subsidies or grants to reduce the initial capital investment
- **Financial support:** Provide support for connection or logistics-related expenses for biomethane supply

Regulatory Framework

- **Streamlined Processes:** Simplify the permitting process for biomethane projects
- **Mandatory Blending:** Introduce regulations mandating a certain percentage of biomethane blending in natural gas grid

Market Development

- **Guaranteed Feed-In Tariffs:** Establish guaranteed feed-in tariffs for biomethane producers
- **Long-Term Purchase Agreements:** Encourage long-term agreements between biomethane producers and utility companies

Infrastructure Investment

- **Pipeline Expansion:** Expansion and upgrading of natural gas biogas infrastructure
- **Storage Facilities:** Develop dedicated storage facilities to manage supply and demand fluctuations

Research and Development

- **Innovation Funding:** Allocate funds for R&D to production efficiency and reduce costs
- **Pilot Projects:** Support pilot projects to demonstrate the viability and benefits of advanced technologies

International Collaboration

- **Knowledge Sharing:** Facilitate best practice exchanges with countries with advanced biomethane markets.
- **EU Funding Programs:** Leverage EU initiatives to support the growth of the biomethane sector in Greece

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Innovative Biomethane Production Pathways in Europe

Workshop in the context of the 4th General Assembly of the BIOMETHAVERSE project

Thessaloniki, Greece

20th June, 2024

Porto Palace Hotel

10:00 - 16:00

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Thank you!

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