Pilot site in Greece

CERTH - BLAG

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Workshop

Thessaloniki, June 20th 2024

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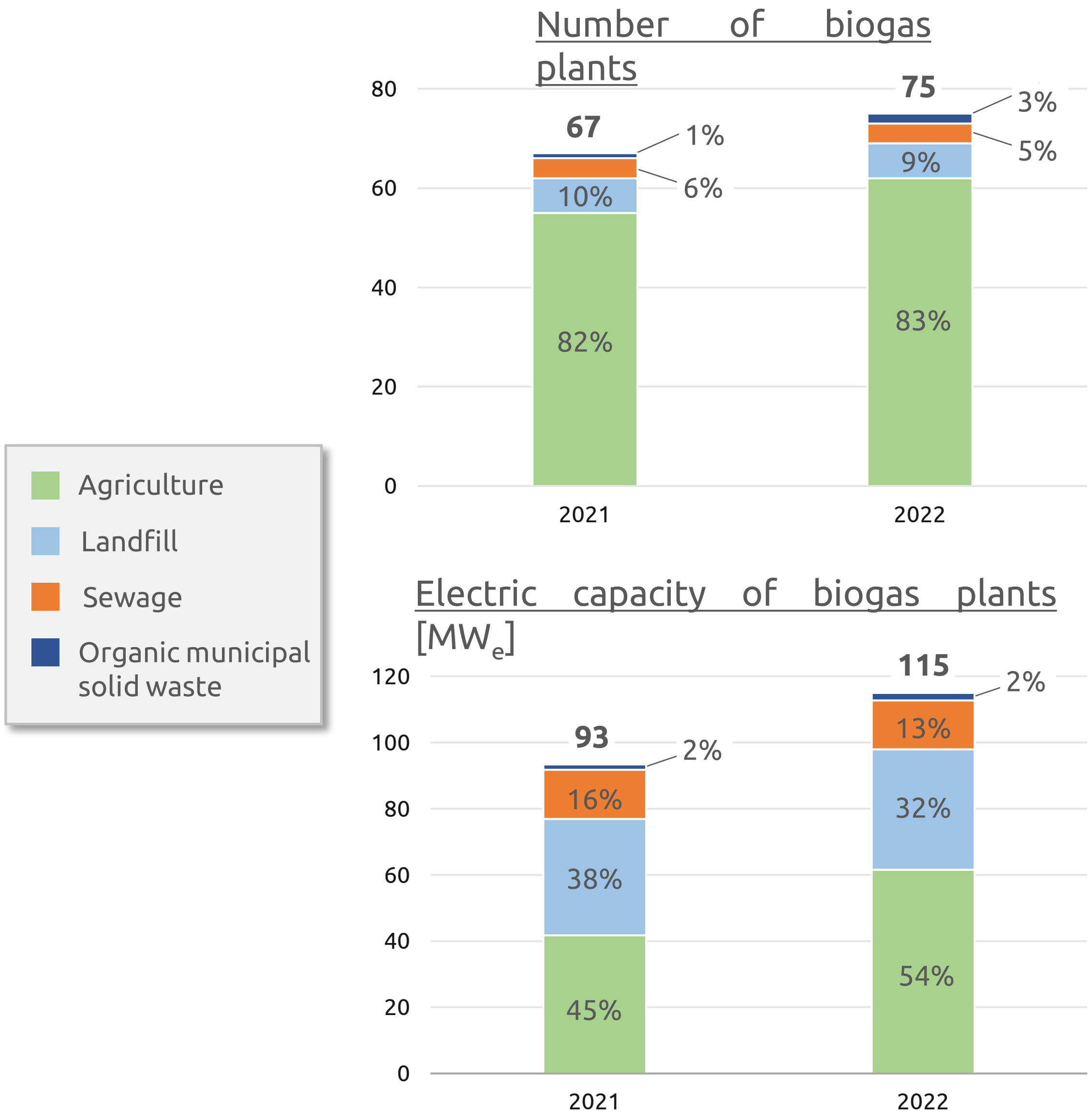
innovations in the BIOMETHAne uniVERSE

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**
- ✓ 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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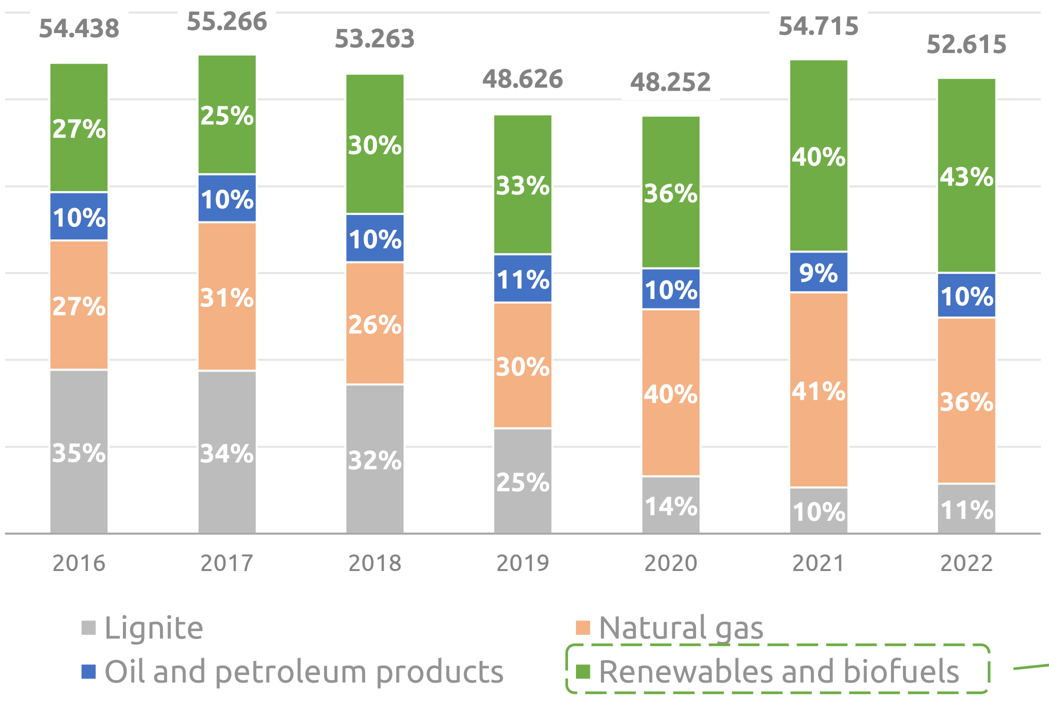
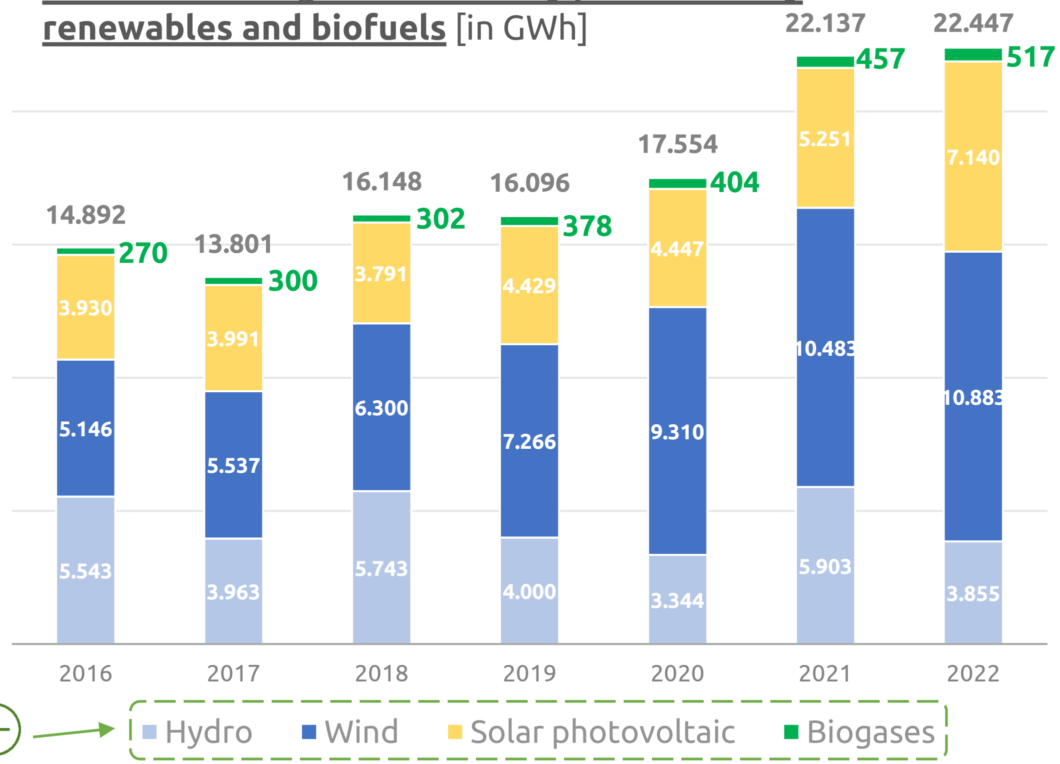
The role of renewables in the electricity mix of Greece

- ✓ The share of **renewables** in the electricity mix of the country has increased significantly (**27%** in 2016 → **43%** in 2022)
- ✓ However, the **contribution of biogas** still remains low (only 2% of total renewables and biofuels) as other forms of renewables (mostly wind and solar) were mainly promoted during the last decade
- ✓ **Biogas and Biomethane sectors** are expected to rise drastically in the next few years

Gross electricity production by type of fuel [Total in GWh and fuel shares in %]



Drill down into gross electricity production by renewables and biofuels [in GWh]



Source: Eurostat

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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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The Ex-situ Thermochemical/catalytic Methanation (ETM)

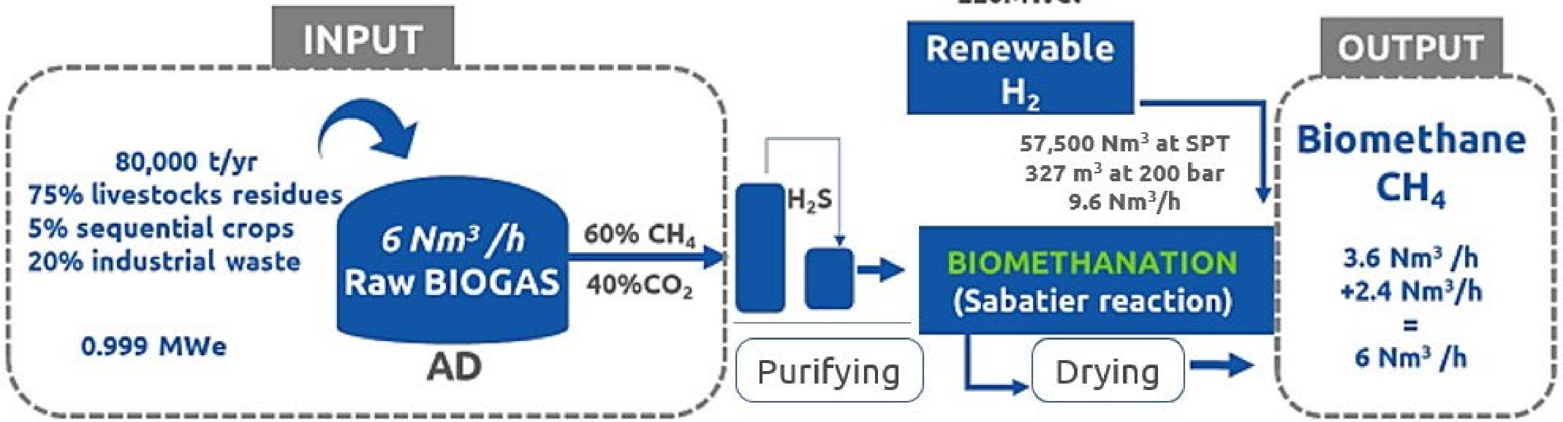
The technology is based on the Sabatier reaction: $CO_2 + 4H_2 \xrightarrow{pressure + catalyst} CH_4 + 2H_2O \quad (\Delta H = -165\ kJ/kmol)$

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 Nm³/h (60% CH_4 and 40% CO_2)
- CH_4 in biogas → 60% x 6 = **3.6** Nm³/h
- Conversion of the CO_2 into the biogas stream → Additional **2.4** Nm³/h CH_4



Operation targets

- Production of a total of **15,000 m³** 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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A simplified flowchart of our pilot unit

Raw biogas → **Section A**: Pretreatment unit → *Purified biogas* → **Section B**: Mixing of gases (+ *Renewable hydrogen*) → **Section C**: Methanation → **Section D**: Final treatment

Section A – Pretreatment unit

The raw biogas enters the **purification unit**: Removal of H_2S, S-containing compounds and other impurities

Section B – Mixing of gases

Pressure regulation, **mixing** of hydrogen and purified biogas and heating of the gases stream

Section C – Methanation

The stream enters the primary unit for a **three-step methanation**: 3 sets of fixed bed reactors and condensers are used to achieve the desired biomethane composition

Section D – Final treatment

Residual H_2 and CO_2 are removed from the final stream through a **Pressure Swing Adsorption (PSA)** process to obtain biomethane meeting pipeline quality gas standards (**96-98 vol-% CH_4**).

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A deep dive in the purification unit of the pilot plant

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

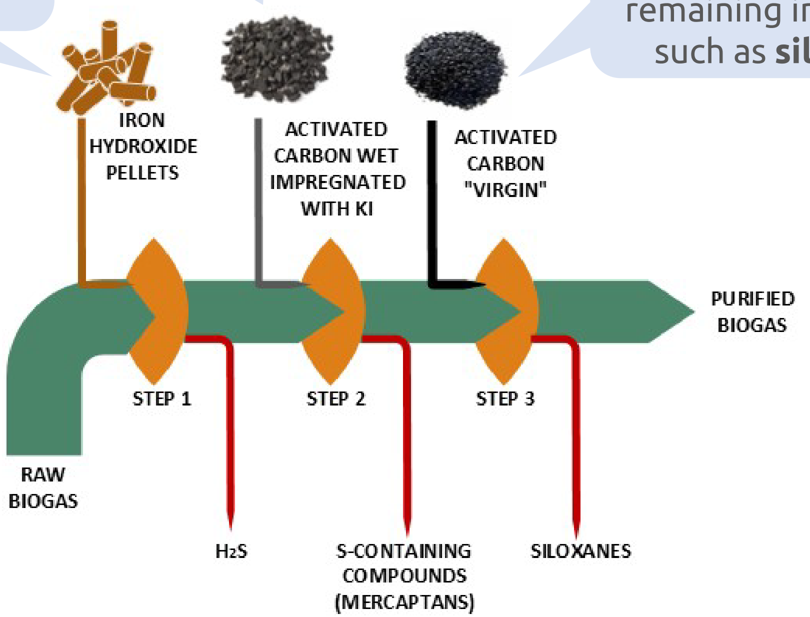
- H_2S < **1 ppm**
- Removal of other **S-containing compounds** (e.g. mercaptans)
- Siloxanes < **1 ppm**

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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Why 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**

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**

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

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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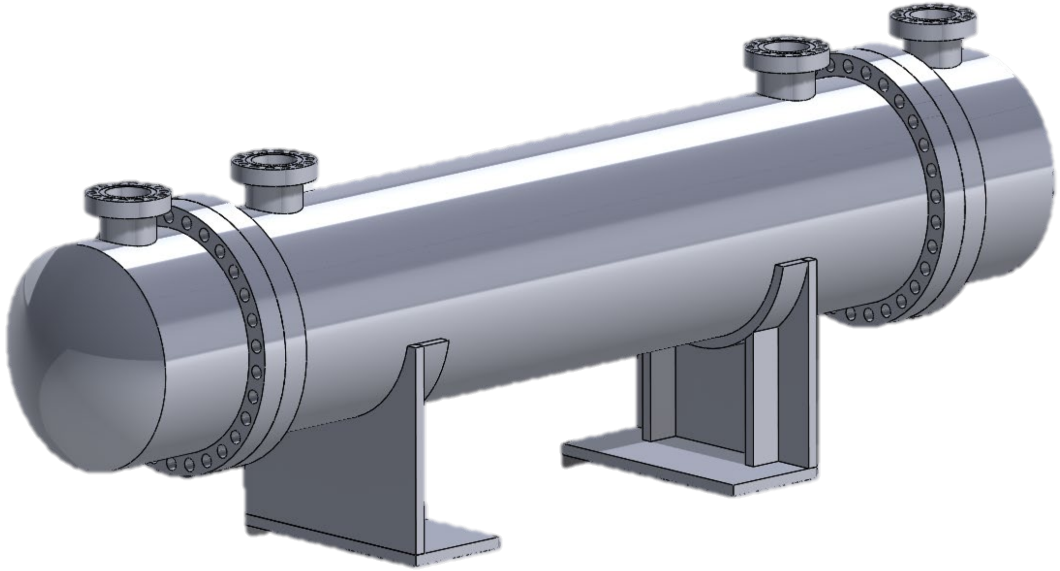
A more detailed view of the cooled fixed bed reactor

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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The challenges we face…

Essential aspects which must be considered for the Greek demo site include:

Catalyst deterioration and contamination	The catalyst has been extensively studied regarding the characterization of its **composition** and the optimal **conditions** for the process performance
Safe **distribution of H_2** to the pilot unit, **storage** and replenishment	**Safety study** for the hydrogen storage at biogas plant facilities, distribution through piping system to the pilot unit based on dangerous goods legislation and safety standards regarding compressed gases
Appropriate **automation** with the respective controller unit	Key operation parameters, such as **temperature**, **pressure** and biogas **composition** will be controlled at specific points during the demo activities
Successful **operation** of the catalyst	The process will be evaluated during the demo activities so as to **recognize any deviations** (lower biomethane yield, lack of H_2, no ideal conditions for the catalyst)

During the BIOMETHAVERSE project, **all the aforementioned measures will be investigated** to identify possible edge effects at **pilot scale** for the **transition of the biogas Lagada** plant to a **full scale** biomethane production plant.

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Further exploitation of the pilot project

Exploitation steps

- Basic **design of the biomethane plant** with necessary engineering and operational specifications
- **Construction and full integration** of the pilot plant into biogas industrial plant
- Conduction of **Factory Acceptance Test (FAT)** and **Site Acceptance Test (SAT)**
- Further commercial exploitation by BLAG and policy exploitation by CERTH

Policy perspective

- Contribution to the **biomethane penetration** and the establishment of a **legislative framework** for biomethane production in Greece.
- Policy working groups with key stakeholders (Ministry, HABIO, gas distribution network operator, gas transmission operator)
- **Location planning and dimensioning of new biomethane plants**, including the BIOMETHAVERSE technologies
- Technical specifications for the integration of the project results within existing plants in Greece

Business perspective

- **Scale-up studies** based on the pilot campaigns results (different composition of biogas, range of feedstock, catalysts)
- Promotion of a relevant legislative framework to provide **financial initiatives** for relevant activities
- BLAG stakeholders are also interested to proceed to **similar retrofitting activities in Nigrita biogas plant**

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