

Research & Innovation

Overview of Green Gas Technologies

Published in collaboration with **C blunomy**

E

Legal information

GRDF – Public limited company with a capital of 1,835,695,000 euros Registered office: 6 rue Condorcet – 75009 Paris RCS: PARIS 444 786 511

Graphic Design: Radiographique – Léa ROLLAND and Redouan CHETUAN

First published in April 2024

Introduction

A successful energy transition requires the widespread deployment and use of Renewable Energies (RE) with low greenhouse gas emissions. Green gases are an essential component of the French energy system if we are to make the transition to carbon neutrality and greater energy independence. Green gases can be produced from a diversity of local resources and feedstocks, using various processes – anaerobic digestion, Power-to-methane, pyrogasification, hydrothermal gasification.

By 2030, green gases could account for 20% of French gas consumption; by 2050, France has the potential to cover 100% of its demand with green gases. The industry estimates that the realistic potential for renewable, low-carbon methane production by 2050 is 320 TWh. In recently published scenarios, gas demand could be between 200 TWh and 300 TWh in France by 2050.

Anaerobic digestion is currently the first renewable gas production technology that can be considered mature. In the medium and long term, new renewable, low-carbon and recovered gas production processes will be developed.

> **Latin 2018** Understand the levers and obstacles to their development and assess their maturity

Monitor innovation fronts in these sectors.

Have a comprehensive overview of green gas production technologies

For more than 10 years, the deployment of green gases has brought together an ecosystem of French organisations who are developing, industrialising and exporting technologies and project development know-how, thereby contributing to France's drive towards reindustrialisation and energy independence.

 (\mathfrak{z})

The analyses presented in this report are based on feedback from organisations who agreed to share their expertise during targeted interviews, and on the work of the bimonthly technology watch launched by GRDF at the beginning of 2023. This watch is made available to the entire ecosystem on the GRDF website (example of a newsletter [HERE](https://act4gaz.grdf.fr/la-veille-gaz-verts-enrichit-votre-rentree)). Its aim is to provide regular updates on the maturity of the various technological building blocks in the green gas sector. Each bulletin deciphers recent scientific publications on the subject, and lists the major advances in associated projects.

As a catalyst for innovation in these sectors, GRDF is providing the entire ecosystem with a reference document in the form of this inventory of green gas technologies. The aim is to enable everyone to:

' As part of my career at GRDF, I have been keen to contribute to the development of local autonomy and energy resilience. It's a little known fact that 85% of the population lives in the immediate vicinity of our distribution infrastructures. Enriching local knowledge of their potential energy resilience and decarbonisation is one of the three levers of our new corporate project, and it is naturally one of the ambitions of our 11,000 employees who serve our 11,000,000 customers on a daily basis.

Our Research, Innovation and Development budget is less than 1% of our sales, compared with ratios of around 5 to 10% across the industry. This means that we need to be agile and effective in generating and aggregating ideas, bringing together those involved and ensuring their development. Research and innovation at GRDF is above all a matter of catalysis.

Monitoring is a critical part of our Research, Innovation and Development activities, both in terms of the substance of the subjects it examines and the methodology we use to carry it out. It requires a subtle blend of curiosity, energy and open-mindedness. By offering different angles of view, monitoring allows us to share contrasting visions of the same object, making elements accessible to some that others may not perceive. It brings us back to our senses and our childlike curiosity, while forcing us to retain the objectivity and rigour of an adult. As endearing as a technology or an idea can be, we know in advance that the likelihood of it developing depends directly on how we originally thought of it.

With this in mind, GRDF and its teams have designed this ʻOverview of green gas technologies' as a travel diary for our ecosystem. We are working alongside them to accelerate the industrialisation of green gas production technologies for the benefit of our customers and their communities.

ʻTo be an adult is to rediscover the seriousness you put into your games as a child.'

This educational and accessible reference document will help everyone understand the different ways of producing green gases, identify associated technologies, and obtain the facts regarding the obstacles and levers needed to bring these new sectors to maturity.

Aware that innovation offers a destination that reveals itself step by step, we wanted this report to be renewed every year. This will enable us to track the development of these technologies, so that we can identify options that are closing and shed light on the paths that are opening up.'

Editorial

Hugues MALINAUD, Director of Research, Innovation and Development

Glossary

 $\mathcal{L}(\mathcal{L})$ and $\mathcal{L}(\mathcal{L})$

to as Oxygen)

Pyrogasification

What is Pyrogasification? Description of the Process **[Industry Dynamics](#page-49-0)** [Some Pioneering Projects for the Sector](#page-50-0) Mapping of the Main Flagship Projects **[Mapping of Gasification Technologies](#page-52-0)** [Mapping of the Production Chain](#page-53-0) Challenges and Technical Solutions for the Sector [Key Players in the Development of the Sector](#page-57-0) [Sources](#page-58-0) 2014 and 2015 and 2016 and 2017 and 201

Contents

Hydrothermal Gasification

What is Hydrothermal Gasification? Description of the Process [Some Pioneering Projects for the Sector](#page-62-0) [Mapping of the Main Flagship](#page-63-0) Projects [Mapping of the Production Chain](#page-64-0) Challenges and Technical Solutions for the Sector [Key Players in the Development of the Sector](#page-69-0) [Sources](#page-71-0) and the set of t

Emerging Technologies

The Different Emerging Technologies Description of the Electromethanogenesis Proces Description of the CO 2 Electroreduction Process [1](#page-75-0)48 Description of the CO₂ Photoreduction Process 20[15](#page-76-0) 150 Description of the Photobioreaction Process Summary of the 4 Emerging Sectors Some Pioneering Projects for the Sector [Sources](#page-80-0) and the set of t

[Contributors](#page-81-0)

[1] Power-to-methane is the production of methane by methanation of CO₂ and H₂

Each Feedstock has its Own Technological Building Block for Producing Green Gases

Emerging technologies

the energy source is renewable (other than biomass), it is renewable methane. If the energy source is renewable (other than biomass), it is renewable methane of non-biological origin.
Finally if the energy source is low-ca [2] Injected methane can be classified in several ways, depending on the energy source used to produce it. If the energy source is biogenic Finally, if the energy source is low-carbon, it is low-carbon methane.

A technological building block for the power-to-methane sector

The Different Processes for Producing Green Gases

Each process has its own specific operating conditions

Industrial Maturity of Sectors and R&D Challenges (1/3)

 $\mathcal{O}(\mathcal{O})$

The most mature sectors can still increase their competitiveness by using more optimised technologies

- +1000 installations in operation
- +10 projects in operation or under development
- Only demonstrators or pilots in operation
- Some pilot or laboratory-scale units

Number of operations worldwide

Industrial Maturity of Sectors and R&D Challenges (2/3)

The most mature sectors can still increase their competitiveness by using more optimised technologies

CAPEX/OPEX and revenues (recovered energy, mineral salts).

- +1000 installations in operation
- +10 projects in operation or under development
- Only demonstrators or pilots in operation
- Some pilot or laboratory-scale units

Number of operations worldwide

new terms of the contract of t [1] Single-chamber systems are systems in which the cathode and anode are not separated by a membrane (unlike with 2-chamber technology) – Note that in certain configurations electromethanogenesis can be installed downstream of the digester to purify the biogas into biomethane;

 $\mathcal{O}_1 \mathcal{O}_2 \mathcal{O}_1$

Industrial Maturity of Sectors and R&D Challenges (3/3)

Less mature sectors are emerging thanks to R&D work

- +1000 installations in operation
- +10 projects in operation or under development
- Only demonstrators or pilots in operation
- Some pilot or laboratory-scale units

Number of operations worldwide

Anaerobic Digestion

What is Anaerobic Digestion?

What is Anaerobic Digestion?

Anaerobic Digestion is a natural biological process whereby organic matter (animal and/or vegetable) is broken down in the absence of oxygen (anaerobic process), through the action of micro-organisms. This process produces digestate (a wet product that can be used as a liquid fertiliser and/or solid organic soil improver), and biogas (a mixture of mainly CH $_{\textrm{\tiny{4}}}$ and CO $_{\textrm{\tiny{2}}}$, and various pollutants present in small quantities). After various treatments, this biogas can be recovered by injection into the natural gas network or for other uses (heat production or cogeneration, for example).

For dry matter content in the digester of less than 15%, the ʻinfinitely mixed' process is used,

For dry matter content of between 25% and 40%, the continuous ʻdry' process is used.

and 2% of the capacity for injecting biomethane into the grid. This report will focus on anaerobic digestion for injection. 23 and the state of [1] In 2022, landfill biogas accounted for 47% of installed capacity for electricity generation from anaerobic digestion

Anaerobic digestion can be carried out either in dedicated facilities, known as digesters, or directly in the bins of non-hazardous waste storage facilities (ISDND), where the waste is stored [1].

This report focuses on digester-based anaerobic digestion, which presents specific challenges, linked in particular to the heterogeneity of the mixed waste and injection into the network.

Depending on the moisture content of the mixture in the digester, two main anaerobic digestion routes [2] (and therefore several technologies) can be envisaged:

The anaerobic digestion process enables the recovery of a variety of feedstocks [3]

Livestock effluent manure/pig and cattle slurry, poultry manure

Crop residues rape cane, maize cane, cereal straw, etc.

Intermediate energy crops

[2] Other anaerobic digestion processes exist: the discontinuous dry process, whose day-to-day operating conditions (batch anaerobic digestion) are simpler than the continuous process, is technologically mature but has not yet been deployed in France; the liquid process, which is mature, treats industrial effluent in dedicated digesters (without mixing, low volumes, short residence time because dissolved dry matter is more easily degradable, etc.); [3] Excluding landfill waste.

Green waste

grass cutting, roadside mowing, etc.

Biodegradable waste

biowaste from households or the food industry, fats and edible oils, fruit residues /vegetables, etc.

Urban and industrial WWTP sludge

Description of the Process

HYDROLYSIS consists of breaking down the complex molecules of organic matter (carbohydrates, lipids, proteins) into smaller molecules such as amino acids, fatty acids and simple sugars. This biological reaction is promoted by continuous agitation of the medium, and is optimal at a temperature of 50 to 60°C [2].

ACIDOGENESIS is the breakdown of amino acids, fatty acids and sugars into acids (Short-chain fatty acids) and alcohols (as well as a small amount of CO $_2$ and H $_2$) by bacteria.

production of acetate from $\mathsf{H}_2^{}$ and CO $_2^{}$ by homoacetogenic bacteria, and the production of acetate, ${\sf H}_{_2}$ and CO $_{_2}$ from the short-chain fatty acids produced by acidogenesis.

ACETOGENESIS leads to the

Anaerobic digestion produces a biogas made up of 50 – 60% CH $_{\textrm{\tiny 4}}$, 35 – 40% CO $_{\textrm{\tiny 2}}$ and containing water vapour and traces of H_{2} , O_{2} , NH₃ and H₂S. The residue from digestion, known as digestate, can be used as a fertiliser in agriculture, thanks in particular to its high nitrogen, ammonium, phosphorus and potassium content. Digestion is an anaerobic fermentation process, sensitive to temperature,

> 1 – Reduction of CO $_{2}$ by H $_{2}$ (produces 30% of methane).

 $CO₂ + 4H₃ \rightarrow CH₄ + 2H₃O$

pH and water content, which takes place in 4 phases.

EQT This temperature will be lower during operation to maintain the biological process in the following stages.
25 [1] A low level of dryness can be maintained if necessary by recirculating digestate;

Proportion by mass of products and by-products

Proportion by volume of gaseous products

METHANOGENESIS is the synthesis of methane and involves two simultaneous chemical reactions:

2 – Conversion of acetate (produces 70% of methane).

 $CH, COOH \rightarrow CH, + CO,$

Anaerobic Digestion, a snapshot

ENERGY EFFICIENCY[1] 10to450Nm³ /tRM

80-85%

BIOMASS - BIOGAS YIELD [2]

Anaerobic digestion produces an energy yield of between 40 and 50% for cogeneration, and as much as 80 and 85% for injection of biomethane into networks.

The biomethane yield from anaerobic digestion can be assessed using the biochemichal methane potential, which is specific to each feedstock and refers to the quantity of methane produced by one tonne of feedstock. This yield varies widely: from a few Nm³ per tonne of raw material (respectively c. 27 and 12 Nm3 /tRM for cattle manure and slurry [3], c. 75 Nm³/tRM for sugar beet pulp) to several hundred Nm3 (c. 100 Nm3 /tRM for household bio-waste, c. 405 Nm3 /tRM for maize straw).

[1] (Energy produced by biogas + heat produced + other energy production)/(energy from inputs + electricity consumption + other energy consumption);

- [2] Expressed as the biochemical methane potential;
- [3] [DIGES 2:](https://hal.inrae.fr/hal-02593780) Application for calculating greenhouse gas emissions from anaerobic digestion plants;
- [4] Figures based on feedback from the industry.

50 to 60 k€ per Nm3/h [4] **CAPEX**

0.3-1hectares per 100 Nm3 /h [4]

LAND HOLDINGS

The land required for an anaerobic digestion facility (anaerobic digestion plants and surrounding infrastructure) can vary depending on the recovery method, the feedstocks, the use of the gas produced, etc. For projects producing a few hundred Nm3 /h of biogas, the land area is a few hectares. The anaerobic digestion unit represents only a small fraction of this total surface area. When the unit is agricultural, it generally uses the land of the farmers involved in the project.

40 to 60€ per MWh [4]

ANNUAL OPEX

The CAPEX of an anaerobic digestion plant can vary greatly depending on its size and type (on-farm, industrial, local): each project is unique. The anaerobic digestion unit is by far the item with the highest CAPEX. However, when they are necessary, infrastructure for pre-treating feedstocks or storing/digestate can also account for up to a third of total CAPEX.

The annual OPEX of an anaerobic digestion plant represents 10 to 20% of the CAPEX. This expenditure mainly relates to feedstocks (between 1/3 and half of OPEX), electricity consumption, labour, maintenance and digestate treatment.

©Franck Dunouau

Industry Dynamics

Anaerobic digestion for injection has been widely deployed over the last decade, particularly in Europe

The principles of anaerobic digestion were first developed in the 1880s for the treatment of wastewater, and then on farms from the 1930s, with the first digester patented in France. Today, anaerobic digestion plants are found all over the world, in all shapes and sizes, from small-scale micro-digesters to industrial units.

Europe alone accounts for more than half of the world's biogas production (ahead of China and the United States) and has more than 20,000 biogas plants, most of which are used to produce electricity and/or heat. In recent years, however, the production of biomethane for injection into the grid has accelerated and is over 40 TWh from more than 1,200 units in Europe, including nearly 500 in France.

of 2023. The most recent data on renewable heat production was published in 2022; [1] The data include the energy production of anaerobic digestion and that of ISDND facilities. They correspond mainly to data provided by the French Ministry of Energy Transition and by the Biomethane Observatory, and have been calculated for the period covering the last quarter of 2022 and the first three quarters of 2023. The most recent data on renewable heat production was published in 2022; [2] Négawatt& Solagro, [Anaerobic digestion in the energy mix.](https://negawatt.org/IMG/pdf/210621_note_la-methanisation-dans-le-mix-energetique_solagro_negawatt.pdf)

BREAKDOWN OF FEEDSTOCKS USED [2] (tonnes, 2021)

PRODUCTION [1]

TREND IN INSTALLED CAPACITY FOR INJECTING BIOMETHANE

Some Pioneering Projects for the Sector

FRANCE

The first anaerobic digestion plant to inject biomethane into the grid in France, the plant is located at the Lille metropolitan area's main organic waste treatment centre. The gas produced was initially intended for direct consumption by the city's buses. These are now supplied via the GRDF network.

Biomethane for injection into the grid

CVO LILLE

Since 2011 Lille métropole

STATUS

BRIE BIOENERGY

Since 2013 Ferme d'Arcy (Seine-et-Marne)

STATUS

PROJECT INITIATOR

Suez /ENGIE

SIZE

180 Nm^3CH_4/h

PRODUCTION

FEEDSTOCKS

Biomethane for injection

into the grid

PRODUCTION

SIZE PROJECT INITIATOR Farmers

125 Nm^3CH_4/h

PRODUCTION

Biomethane for injection into the grid

Biodegradable waste and green waste

Livestock effluents,

FEEDSTOCKS

Intermediate energy crops, food co-products, crop residues

> An anaerobic digestion unit that has installed a bioNGV unit on site, with the developer Prodeval, which can refuel eight trucks a day.

SIZE 120 Nm^3CH_4/h

FEEDSTOCKS

The first WWTP sludge anaerobic digestion unit to inject biomethane into the network in France. The project has made a major contribution to the establishment of a regulatory framework for the recovery of biogas from wastewater treatment plants.

MÉTHAMOLY

Since 2019 Monts-du-Lyonnais

STATUS

PROJECT INITIATOR

Farmers

Livestock effluent,

The first agricultural anaerobic digestion plant to inject biomethane into the grid in France. The plant also stands out for its efforts to recover anaerobic digestion by-products. This year, for example, GAZFIO installed its first bioCO $_2$ recovery unit on a anaerobic digestion unit in France.

A number of key projects have led to the gradual deployment of anaerobic digestion for injection in France over the last fifteen years. The industry is now trying to innovate with alternative anaerobic digestion methods or by better integrating the recovery of by-products.

Mapping of the Biogas Production Chain

by anaerobic digestion

Focus on the Pre-treatment Chain for Anaerobic Digestion Feedstocks

Focus on the Biogas Treatment Chain

Focus on the Digestate Treatment Chain

38 39 [1] Spreading is the process of spreading digestate on fields to take advantage of its amending and fertilising properties. A land-spreading plan, available to the environmental inspectorate, must be drawn up for all farms subject to the regulations governing installations classified for environmental protection;

[2] In the case of a cogeneration unit, drying can be carried out by recovering heat from the cogeneration unit; [3] These liquid phase treatments are rarely used; the liquid phase is generally spread directly as a fertiliser.

Challenges and Technical Solutions for the Sector

Solutions are being developed but need to demonstrate their feasibility and economic viability on a large scale

Mature solutions exist to meet this challenge, but their deployment remains limited

No solution yet in development to meet this challenge,

An important challenge

d

 \blacksquare

for the industry,

KEY

described in more detail

later in the report

JI d d

d.

Focus on an innovative

Broadening the range of of feedstocks suitable for digestion is one of the main challenges facing the industry. In particular, crop residues such as straw and dry waste are the focus of considerable research. To date, however, their incorporation into digester rations has yet to be developed, and they still need to be proven to digest well in non-laboratory facilities. One of the main obstacles is pre-conditioning and pre-treatment.

Batch dry anaerobic digestion of dry feedstocks

Alongside mechanical pretreatments [1], which are mature and widespread, other biological, thermochemical and physical pretreatments are being developed. These are not yet fully mature: they still need to be demonstrated on a large scale and their technical and economic performance improved before they can be integrated on site. For example, some thermochemical pre-treatments lead to the formation of chemical co-products that could inhibit the methanogenic organisms present in digesters; some biological treatments require very long periods of time (up to several days) and induce reactions that can compete with biogas production. However, the potential benefits are numerous: optimising gas production, reducing the energy required in the digester, etc. \rightarrow [See focus on MethaPlanet](#page-29-0).

Research into the integration of new feedstocks is looking at both the identification of the methanogenic potential of different types of biomass (e.g. studied at INSA Lyon) and pre-treatment techniques. INRAE has conducted a number of studies on the subject, both in France and abroad.

Pre-treatment of feedstocks for digestion

The ʻinfinitely mixed' process is less suitable than the dry process for anaerobic digestion of dry, fibrous or viscous feedstocks. The discontinuous dry process has developed in Europe in recent years because it better treats these feedstocks than the continuous dry process: it operates on a batch basis, requiring limited pre-treatment and mixing. However, the difficulty of managing batches and the lack of industrial feedback and technology developers have limited its deployment in France so far.

B Better treatment of microplastics

Solutions are being developed but need to demonstrate their feasibility and economic viability on a large scale

Mature solutions exist to meet this challenge, but their deployment remains limited

The proportion of municipal biowaste recovered by anaerobic digestion should increase with compulsory sorting [2]. Improved deconditioning technologies should limit the formation and leakage of microplastics into anaerobic digestion feedstocks. Otherwise, these microplastics end up in the anaerobic digestate, limiting its use as an agricultural soil improver.

Limiting the volume of microplastics in feedstocks requires the public to be made more aware of the need to sort waste and for local authorities to set up efficient waste collection systems. In addition to these efforts to raise awareness, new technological developments are needed. For example, the elimination of microplastics is a growing area of research for the anaerobic digestion sector. Over the last few years, the APESA Valorisation cluster has carried out numerous tests on the biodegradability of plastics. More recently, the METHAPLAST project, funded by ADEME and led by RITTMO, has helped the industry to integrate biodegradable plastic materials into biowaste processing. In addition, several projects have been launched in 2023 by ADEME and the OFB to gain a better understanding of the impact of microplastics on natural ecosystems. One of the keys to controlling the rate of residual inert elements in ʻsoups' after deconditioning will be to improve monitoring.

[1] Mincers, grates, recirculating mills, etc.;

No new developments to date.

R&D solutions and innovations

d

 \blacksquare

Challenges and Technical Solutions for the Sector

Technical challenges in the sector

B Integrating new digestion feedstocks

No solution yet in development to meet this challenge, or low-maturity solutions

Focus on an innovative player available later in the report

Several deoxygenation or desulphurisation technologies can be used to limit the level of O₂ in biogas and have already reached a high level of technological maturity (activated carbon, chemical absorption, adsorption, bio-washing, etc.). They are now starting to be deployed in European countries and are the subject of in-depth comparative studies (see the publications on this subject by the Danish Gas Technology Centre). However, achieving low O_2 levels often remains difficult under economic conditions that are acceptable for project development. The network operators are supporting various innovative projects in this area, which could help producers to choose the most appropriate solutions.

Biogas is made up (by volume) of around 35% CO₂, separated from CH₄ for injection, and often released directly into the atmosphere. Recovering CO_2 would not only help to limit emissions from biogas plants, but also meet demand from consumer sectors such as the food, chemical and fuel industries. Liquefaction and transport costs are currently a major obstacle to recovery. The industry needs to develop new technologies and business models over the next few years.

Biogas

Several ways of recovering CO $_{\rm 2}$ are now technologically mature (food use, injection into greenhouses, etc.) or on the way to becoming so (methanation, e-fuels). The technologies for upgrading, liquefaction, transport, etc. are known and mature; the challenge now lies above all in the industry's ability to structure itself and develop viable business models for transporting CO $_{\textrm{\tiny{2}}}$ and bringing it up to the technical specifications of the targeted uses. A [guide](https://systemesenergetiques.org/wp-content/uploads/2023/06/Guide-projet-valorisation-bioCO2-methanisation-VF-2023.05.30-1.pdf) written by the CTBM and the CSF Nouveaux Systèmes Energétiques for project developers was published this year. In 2023, GRDF also launched a number of regional calls for projects 'Valorising biogenic CO $_{\textrm{\tiny{2}}}$ from anaerobic digestion', which led to the emergence of around twenty innovative solutions: upgrading technologies (ARISTOT), methane production (éMA, ENOSIS), the creation of local recovery loops (Agroénergie Conseil, CH, process, Voltigital, Ferest Energies), concrete production, recovery from PSA vents d (Rytec GmbH), etc.

Digestate treatment Solutions are being developed but need to demonstrate their feasibility and economic viability on a large scale

Mature solutions exist to meet this challenge, but their deployment remains limited

Improving digestate recovery by concentrating it

The management of digestate, produced in large quantities, raises two questions:

• The digestate storage capacity of anaerobic digestate units is limited.

• Digestates are low-concentration fertilisers, which are more expensive to transport and spread than synthetic fertilisers. Concentrating the digestate should make it possible to reduce volumes,

make it easier to transport and increase its fertilising properties, in particular to achieve standardised characteristics.

Various concentration technologies exist and are already being used on an occasional basis: membranes, stripping, flocculation, etc. However, these technologies have proved to be very energyintensive and unsuitable for heterogeneous digestates. A great deal of R&D work on these solutions is already underway to make it easier to scale them up and improve their technical and economic performance. A number of research projects have also been launched to gain a better understanding of the agronomic impact of digestate and better define the expected specifications: the Concept-Dig project, coordinated by INRA, aims to assess the agronomic and fertilising value of digestates according to their characteristics; the Omix project, coordinated by Nereus, aims to develop a process for the complete transformation of bio-waste digestates to obtain fertilisers đ and water that can be reused in agriculture.

Challenges and Technical Solutions for the Sector

No solution yet in development to meet this challenge, or low-maturity solutions

 α

đ

player available later

in the report

Technical challenges in the sector **R&D** solutions and innovations and innovations and innovations

 \mathbf{d}

Injecting biomethane into networks requires biogas upgrading, which can be very costly for small units (up to a few dozen Nm $^3\!$ h).

Facilitating the development of anaerobic digestion for small units

The upgrading cost can account for between 15% and 25% of the CAPEX of a anaerobic digestion plant.

Deploying alternative technical solutions to the on-site integration of upgrading technologies would make it possible to increase the volume of biomethane injected and unlock the use of small local feedstock sources.

Smaller, and therefore less expensive, micro upgrading technologies are currently being developed to make biogas treatment and injection economically viable for small units (up to a few dozen Nm3 /h).

Examples include Greenmac's Bio-Up amine scrubbing technology, the PurePac Mini membrane technology developed by Bright Biomethane and the Epuragaz system under development at Toulouse Tech Transfer.

[See focus on Greenmac.](#page-60-0)

The deployment of injection on small-scale anaerobic digestion units could also be facilitated by the development of alternative upgrading/injection models. Models under study include:

• Transported biogas, which involves pooling both upgrading and injection. Transporting the biogas is both a technical challenge (compression or liquefaction without precipitation of undesirable substances) and an economic one (part of the biogas volume has no energy value). Transporting this biogas over short distances using high-density polyethylene (HDPE) networks, as with conventional gas distribution networks, could meet this challenge. This model is currently less mature than the previous one, but it is just as attractive for capturing deposits d at a competitive cost.

Optimising the energy consumption of anaerobic digestion plants is a major challenge for the industry. Exposure to fluctuations in the price of electricity, which accounts for around 10% of its gas production (around 1 kWh per Nm3 /h), is a major issue for the profitability of plants. In addition, recent regulatory changes (notably RED II) set thresholds for the energy efficiency of plants. The entire anaerobic digestion chain needs to be considered, as many mature solutions can

already be deployed: insulation of gasometers with additional membranes, heat recovery from compressors, self-consumption energy production on site self-consumption (solar photovoltaic, cogeneration, solid biomass for heating needs on plants with hygienisation, etc.). d

• Transported biomethane, which involves pooling the injection point for several units, transporting the purified biomethane mainly by truck, in compressed or liquefied form. The economic relevance of this model has yet to be demonstrated, as transporting biomethane to the injection point currently involves higher additional costs than on-site injection. However, projects are being considered.

Solutions are being developed but need to demonstrate their feasibility and economic viability on a large scale

Mature solutions exist to meet this challenge, but their deployment remains limited

Challenges and Technical Solutions for the Sector

Global integration of the technical bricks

Optimising energy consumption

No solution yet in development to meet this challenge, or low-maturity solutions

KEY

Technical challenges in the sector **R&D** solutions and innovations and innovations and innovations

The average residence time in a digester varies between 60 and 120 days depending on the feedstocks, but is rarely optimised. Reducing this residence time is a challenge for continuous improvement, enabling feedstocks to be processed more quickly, digester contents to be changed more frequently and the size of the digester to be reduced: this results in savings on land, concrete and CAPEX. A reduction in residence time could, however, be detrimental to the expression of methanogenic potential and run the risk of increasing digestate emissions.

Digestion

Responding to parameter divergence

In addition to greenhouse gas emissions (in particular CO $_2$ and CH $_4$) inherent in the anaerobic digestion process (e.g. upgrading vents), there may also be unplanned fugitive emissions. Frequent monitoring and optimisation of plant operation should help to guarantee the environmental efficiency of the units.

B Better anticipation of maintenance

Anaerobic digestion is a complex biological process in which the biological and physico-chemical parameters can diverge, leading to inhibition of the reaction and loss of yield. Predicting changes in parameters (pH, C/N ratio, fatty acid concentration, etc.) and preventing biological imbalances are key issues.

Measuring and reducing fugitive emissions

A better understanding and prediction of equipment operation in a anaerobic digestion plant could make it possible to limit breakdowns in order to optimise biogas production over the long term.

The sector could draw inspiration from fermentation processes used in other industries (pharmaceuticals, animal feed, etc.) such as the use of inoculants (e.g. fungi or bacteria). Larger-scale studies are needed to quantify the cost/benefits of these solutions from an environmental, economic and energy point of view.

Solutions are being developed but need to demonstrate their feasibility and economic viability on a large scale

Mature solutions exist to meet this challenge, but their deployment remains limited

French researchers have produced a state-of-the-art report on the effects of adding various additives (microbes, enzymes, etc.) to anaerobic co-digestion reactors. [> Link to the GRDF watch](https://act4gaz.grdf.fr/pas-de-pause-pour-la-veille-gaz-verts)

American researchers have developed an anaerobic bioreactor incorporating an electrolysis process to maintain the bioreactor's pH stability and increase biogas production. [> Link to the GRDF watch](https://act4gaz.grdf.fr/pas-de-pause-pour-la-veille-gaz-verts)

Numerous R&D projects are studying the modelling of the digestion process, identifying the key parameters, attempting to interpret their divergence and seeking solutions. A number of service companies offer technologies for monitoring parameters: digital solutions to assist operations, laboratory analyses, etc.

The detection of fugitive emissions is already mature, based on technologies adapted from the O&G sector: used directly at source (cooled cameras, analysers, lasers, etc.) or remotely (sensors on drones or satellites). On the other hand, quantifying emissions is a major scientific challenge: at present, it remains unreliable due to the uncertainty of measurements and their limited repeatability. Methodological developments (image processing and calculation methods) and technological developments are needed.

Numerous predictive maintenance tools have been developed over the last few years to analyse the operation of a plant's equipment in real time and anticipate the need for intervention, and are beginning to be deployed on test units: Yuman.io, Ovalie Tech, Eco-Adapt.

Challenges and Technical Solutions for the Sector

Global integration of the technical bricks

No solution yet in development to meet this challenge, or low-maturity solutions

11

d

d

d

d

Technical challenges in the sector **R&D** solutions and innovations and innovations and innovations

which are forcing them to refuse these feedstocks, raising awareness of the sector upstream is an important first step towards more effective de-conditioning. However, it is still necessary to develop new tools that can be used on site to compensate for these sorting errors.

For example, many hydromechanical lines already incorporate decantation systems to separate heavy elements such as glass. As for metals, various solutions can also be envisaged, such as metal detectors and separators placed upstream of the shredder. These technologies now need to be perfected, supplemented by new systems and deployed on the units or within the facilities specialised in collection and treatment (deconditioning, shredding, hygienisation) making ʻsoups' of bio-waste available to methanisers.

Focus on Three Challenges (1/2)

Adapting deconditioning technologies

Silage is a method of preserving plant feedstocks, inspired by livestock farming practices.

The bio-waste streams used in anaerobic digestion are heterogeneous. To separate the organic content from the non-fermentable containers, the plants have to set up deconditioning lines: bag openers, sieves, separator shredders, presses, hydromechanical deconditioning, etc. However, some elements remain difficult to detect and extract: plastics, metals, glass. These can lead to soil pollution when the digestate is spread, as well as more rapid wear and tear on the anaerobic digestion equipment.

With regulations requiring local authorities to sort bio-waste at source, which came into force on January 1st, 2024, the volume and heterogeneity of incoming flows are set to increase: better deconditioning is therefore becoming a priority.

At a time when several units are reporting sorting errors in the waste streams from supermarkets and hypermarkets,

Optimising intermediate energy crop silage to preserve biochemical methane potential (BMP)

For the time being, silage-making practices in France remain highly heterogeneous from one unit to another, and do not always allow for optimum conservation of the material. On the one hand, as a [guide](https://systemesenergetiques.org/guide-pour-realiser-un-projet-de-valorisation-du-bioco2-issu-de-methanisation/) published in 2022 by GRDF, INRAE and Arvalis, the natural production of liquid effluents from plant silage can cause losses in BMP that exceed 10% of the total potential of the harvest. In addition, contact of the silage with the air leads to losses of mass and energy that can reduce the BMP by up to 30% over the entire silo.

Implementing good practice could therefore limit these losses and increase yields in the sector. The production of silage juice, for example, can be reduced by harvesting feedstocks when their dry matter content is optimal (from 25 or 30%) or by pre-drying (drying in the sun) the biomass for one or two days.

To limit the aerobic degradation of silage, silos need to be properly sized and sealed. Various covering techniques exist (tarpaulins, covering with cereal seedlings or food byproducts) but are deployed in different ways. Their implementation needs to be considered on a case-by-case basis, depending on the equipment used, the climate, the cyclical nature of the activity, etc. In addition to communication efforts, better documentation of their cost, their impact on the preservation of BMP and on the environment is becoming a priority.

reduce the O_2 content in the gas by choosing desulphurisation processes without oxygen injection. Several mature technologies are marketed in several countries, although they are not yet deployed in France: chemical absorption (proposed by AirDep, among others), adsorption (HeGo, Axens, etc.), bio-washing (Paques, EcoTec, DMT, etc.), activated carbon (Danish Gas Technology Centre, etc.). Given the size of anaerobic digestion plants in France, the associated costs are significant.

The technical and economic relevance and viability of deploying some of these solutions will have to be assessed and compared with the other innovations being studied by network operators and their partners.

The O_2 content of biomethane produced by anaerobic digestion can be exempted from the specifications for the physicochemical characteristics of natural gas. Given the expected increase in the volume of biomethane injected in the coming years, identifying and characterising the technologies that will make it possible to reduce the O₂ content of injected biomethane is becoming a priority for the development of the sector.

Focus on Three Challenges (2/2)

Reducing the oxygen content in biomethane before injection

A number of direct biogas deoxygenation processes have been developed over the last decade and are receiving increasing attention from the industry. They are, however, not yet fully technologically mature and are often associated with high costs (e.g. catalytic oxidation). Nevertheless, it is already possible to

Summary: Anaerobic Digestion

Anaerobic digestion is a mature sector whose deployment could be further accelerated by overcoming the few remaining technological challenges

Key Players in the Development of the Sector

$(1/2)$

Challenges: integrating new feedstocks and unlocking their potential through new pre-treatments

Methaplanet has developed a process for pre-treating equine manure straw to make better use of its BMP. The process transforms these feedstocks into pellets using a combination of thermal and mechanical processes. The pellets are then easier to transport and can be fed directly into the digester, giving yields 5 to 10 times higher than those obtained with raw materials, while addressing the problem of flotation.

Non-exhaustive list (which does not include plant operators [1]). All companies below are listed by ATEE in a directory available at this [LINK.](https://atee.fr/energies-renouvelables/club-biogaz/liste-des-adherents-du-club-biogaz)

The cost of biogas upgrading (representing between 15 and 25% of CAPEX according to feedback from industry players) is often prohibitive for small-scale anaerobic digestion plants.

Q

Greenmac, which specialises in biogas upgrading, has designed Bio-Up, a small-scale upgrading system (units with a flow rate of a few dozen Nm 3 /h): CO₂ is separated from CH_4 by bringing the biogas into contact with an amine solution in an absorption column.

This system offers a number of advantages (possible regeneration of the amine liquid, low energy consumption compared with large-scale scrubbers, limited land area), making it possible to reduce the CAPEX of upgrading for small units.

Other micro-purifier technologies are also available, such as the membrane micro-purifiers developed by Bright Biomethane, which recently acquired Greenmac.

Challenge: facilitate the development of anaerobic digestion for small units

Sources

The main French players in the sector are federated by the [ATEE Biogas Club](https://atee.fr/energies-renouvelables/club-biogaz).

[L'observatoire de la filière biométhane](https://odre.opendatasoft.com/pages/observatoire-biomethane-v2/implantation-des-sites#implantation-des-sites) ODRE, 2023

[Tableau de bord: biogaz pour la production d'électricité](https://www.statistiques.developpement-durable.gouv.fr/publicationweb/596) Ministry of Energy Transition, 2023

[Comment optimiser les ensilages de CIVE?](https://projet-methanisation.grdf.fr/cms-assets/2023/04/GRDF-mise-en-page-V4.pdf) GRDF & INRAE & Arvalis, 2023

[The impact of anaerobic digestate on soil life: a review](https://www.sciencedirect.com/science/article/pii/S0929139323002640)

van Midden et al., 2023

[A critical review on the techno-economic feasibility of nutrients recovery from AD](https://www.sciencedirect.com/science/article/abs/pii/S138358662202247X) Rizzioli et al., 2023

[Focus sur les intrants en méthanisation: stockage, prétraitements & optimisation](https://www.methanormandie.fr/wp-content/uploads/2023/07/Presentations-matinee-intrants-de-methanisation.pdf)

Métha'Normandie, 2023

[Les matières organiques](https://www.methafrance.fr/la-methanisation-en-france/les-matieres-organiques)

MéthaFrance, 2023

[Panorama des gaz renouvelables en 2022](https://www.syndicat-energies-renouvelables.fr/wp-content/uploads/basedoc/ser-panoramagazrenouvelables2022_web-rvb.pdf) GRDF, GRTgaz, SER, SPEGNN, Téréga, 2023

[Carte des unités de méthanisation et de biogaz](https://eci-sig.ademe.fr/adws/app/bb11ce07-5cc9-11eb-a8fe-7dd6c4f9bb1d/index.html) SINOE, 2023

[La méthanisation dans le mix énergétique](https://negawatt.org/IMG/pdf/210621_note_la-methanisation-dans-le-mix-energetique_solagro_negawatt.pdf)

Solagro & négaWatt, 2021

[Les solutions de déconditionnement des biodéchets emballés et leurs performances](https://librairie.ademe.fr/cadic/6420/1-deconditionnement-biodechets-emballes-performance-rapport.pdf) ADEME, 2021

[Desulphurisation of biogas: a systematic qualitative and economic-based quantitative review](https://www.sciencedirect.com/science/article/abs/pii/S0306261914001718) Okoro et al., 2019

[Pretreatment of agricultural biomass for AD: current state and challenges](https://www.sciencedirect.com/science/article/abs/pii/S0960852417314967)

Paudel et al., 2017

[Gestion et traitement des digestats issus de méthanisation](https://aile.asso.fr/wp-content/uploads/2020/03/Traitement-des-digestats.pdf)

IFIP, Agricultures & territoires, IDELE, Trame, 2017

[Inventaire et performances des technologies de déconditionnement des biodéchets](https://www.bioenergie-promotion.fr/wp-content/uploads/2018/01/technologies_deconditionnement_201611_rapport.pdf)

ADEME & AEFEL, 2016

[DIGES 2](https://hal.inrae.fr/hal-02593780)

Bioteau et al., 2009

©Grégory Brandel - GRDF

Power-to-methane

*A***@R** METHANATION BUILDING BLOCKS

What is Power-to-methane?

What is Power-to-methane?

– a water electrolysis stage during which electricity is consumed to produce hydrogen $\mathsf{H}_{_2}$ [1] (and oxygen O_2 as a co-product),

Power-to-methane consists of 2 stages:

– then a **methanation** stage during which the hydrogen from the electrolysis and the CO $_{\textrm{\tiny{2}}}$ from capture or purification (industrial source or anaerobic digestion) are converted into methane through a biological or chemical reaction.

> Catalytic methanation is a continuous reaction allowing the formation of CH₄ from H₂, CO $_{\rm 2}$ and/or CO thanks to the presence of a physico-chemical catalyst. It generally takes place at temperatures between 200 and 600˚C and pressures between 1 and 15 bar.

Biological methanation takes place in an anaerobic environment in the presence of H_2 and CO₂ and/or CO dissolved in an aqueous phase, and micro-organisms (mainly methanogenic archaea) at temperatures between 35 and 65°C and pressures below 10 bar. The continuous biological methanation reaction can be carried out by supplying pure fatal CO $_{\rm 2}$ (standalone) or by supplying a biogas / syngas containing CO and/or $CO₂$ (upgrade).

The methane can then be injected into the gas networks for all the usual uses of natural gas (heating, cooking, mobility, industry or storage).

Catalytic methanation

©Benoit Rouchon

[1] Hydrogen production is not covered in this report. However, it remains a key stage and is the most costly component (in terms of CAPEX and OPEX) of the power-to-methane chain.

Injected methane can be classified in several ways, depending on the energy source used to produce it. If it is of biogenic origin (biomass), it is referred to as biomethane. If the energy source is renewable (other than biomass), it is referred to as renewable methane of non-biological origin. Finally, if the source is low-carbon, the preferred term is low-carbon methane.

There are two distinct methanation technologies: catalytic methanation and biological methanation. These technological building blocks can be included in a power-to-methane system or coupled with a system for producing syngas (containing CO) after post-treatment (e.g. coupling with a pyrogasification plant or, in some cases, hydrothermal gasification). In this section, methanation technologies as a whole will first be examined. The analysis will then focus on the dynamics and issues specific to the power-to-methane sector [1].

Catalytic methanation is the hydrogenation of carbon monoxide (CO) or carbon dioxide (CO $_2$) to CH $_4$ in the presence of a physico-chemical catalyst. Methanation by hydrogenation of CO was developed in the 1970s and 80s and is already a proven process. Methanation of $CO₂$ (Sabatier's reaction, discovered in 1897) has been the subject of growing interest in recent years, thanks to the development of renewable energies, power-to-gas and CO $_{\textrm{\tiny{2}}}$ recovery issues.

 $\sqrt{\mathscr{P}}$ METHANATION BUILDING BLOCKS Γ

Description of the Catalytic Methanation **Process**

Catalytic methanation enables CO and CO₂ to be converted into CH₄ using catalysts

FEEDSTOCKS are injected at pressures of 1-15 bar [2] and in temperature ranges of 200˚C to 600˚C. If syngas is used as a feedstock, a prior pre-treatment step is required.

Methanation of CO involves the following reaction (an exothermic reaction) $CO + 3H_2 \longrightarrow CH_4 + H_2O + heat$

CO₂ ROUTE

Catalysts (mostly heterogeneous [1]) are a key element in catalytic methanation, since they increase the reaction rate and reduce the activation energy. Nickel (Ni) remains the most widely used metal catalyst, thanks to its good efficiency ratio/ cost.

Direct or indirect methanation of CO₂ involves the following reactions (exothermic reactions)

Direct methanation: $CO₂ + 4H₃ \longrightarrow CH₄ + 2H₃O + heat$

[1] The catalyst and reactants are in several phases (the catalyst is in solid form and the reactants in gaseous form): e.g. metals, ionocovalent oxides, ionic oxides;

[2] Cold plasma methanation operates at close to atmospheric pressure. Other processes still at the R&D stage could reach pressures of around 100 bar;

[3] The selectivity of a chemical reaction specifies the quantity of desired product formed (in this case $CH₄$) in relation to the number of moles consumed of the limiting reactant (in this case $CO₂$). It indicates whether several reactions are occurring in parallel, leading to unwanted co-products;

CO ROUTE

[4] In the catalytic methanation reaction, the most favourable reaction is with CO because it is direct.

THE CATALYTIC METHANATION OF CO₂ IS ENHANCED AT LOW TEMPERATURE (<300°C) OR AT HIGH TEMPERATURE AND HIGH PRESSURE

Indirect methanation:

 (1) CO₂ + H₂ \rightarrow CO₊ H₂O (Reverse Water-Gas-Shift) (2) CO + 3H₂ \rightarrow CH₄ + H₂O + heat

R&D efforts to operate at low pressure and low temperature (less restrictive and costly conditions) are underway (e.g. development of millistructured or cold plasma reactors) [4].

Biological methanation produces methane, via micro-organisms, which will be able to be put to specifications for injection into the gas network or use in NGV stations. Micro-organisms are present in an aqueous phase and a combination of two or three types of micro-organisms (co-culture or triculture) can be used to improve reaction yields.

 $\sqrt{\mathscr{P}}$ methanation building blocks $\sqrt{\mathscr{P}}$

Description of the Biological Methanation **Process**

Biological methanation can be carried out *ex situ* (in a dedicated reactor, leading to the formation of CH $_{\tiny 4}$ from gaseous feedstocks: pure CO $_{\rm 2^{\prime}}$ biogas or syngas) or *in situ* (directly in an anaerobic digester, for example, by adding ${\sf H}_{_2}$ to the substrates that supply the carbonaceous matter and micro-organisms).

FEEDSTOCKS are injected at

METHANATION BY THE INDIRECT ROUTE

Homoacetogenesis: $2CO₂ + 4H₂ \longrightarrow CH₂COOH + 2H₂O$

Methanogenesis with acetic acid: $CH_{2}COOH \rightarrow CH_{1} + CO_{2}$

DIRECT METHANATION takes place in thermophilic conditions $(>45^{\circ}C)$

Water-Gas-Shift: $CO + H₂O \rightarrow CO₂ + H₂$

Methanogenesis with carbon dioxide: $CO₂ + 4H₂ \longrightarrow CH₄ + 2H₂O$

Biological methanation produces methane in the presence of micro-organisms

pressures below 10 bar in gaseous form into the reactor under anaerobic conditions (without O_2). If syngas is used as a feedstock, pollutants such as nitrates, sulphates and tars are eliminated beforehand. Inside the reactor, the micro-organisms are contained in a liquid phase.

Direct methanation of CO₂ is simpler and better controlled.

takes place under mesophilic conditions (between 20 and 45˚C).

Carboxydotrophic acetogenesis:

 $4CO + 2H₂O \rightarrow CH₃COOH + 2CO₂$

- Impurity resistance
- Productivity
- Ability to favour one reaction over another
- Flexibility depending on the feedstock
- Ability to pre-treat the feedstock
- Robustness
- Examples: Eubacteria, Archaea

Carboxydotrophic **Homoacetogenesis Methanogenesis** with acetic acid **INDIRECT ROUTE** DIRECT ROUTE Acetic acid (CH₂COOH) methane methane **Feedstocks** purified syngas

THERE ARE SEVERAL CRITERIA TO CONSIDER WHEN CHOOSING MICRO-ORGANISMS

CO (especially at high levels, >50%) inhibits the action of micro-organisms, which is why the indirect route is less effective than the direct route.
Mapping of Methanation **Technologies**

70 71 Note: This is a non-exhaustive list of the most commonly used technologies [1] Examples of suppliers – non-exhaustive list.

Fixed-bed methanation is the most mature methanation technology, capable of handling large gas flows. Other solutions that are more compact (e.g. millistructured reactors) or operate under less restrictive operating conditions (temperature or pressure) like biological systems are currently being deployed.

Methanation bricks are used in many power-to-methane and syngas projects, with a trend towards increasing injection capacity [1]

METHANATION BUILDING BLOCKS

Mapping of the Main Flagship Projects

Project status **Existing**

WUpcoming

Q FOCUS ON POWER-TO-METHANE SECTOR

Some Pioneering Projects for the Sector

Numerous power-to-methane projects have recently been launched, involving both catalytic and biological methanation

With growing targets for biomethane, the sector is developing mainly in Europe, but there is also growing interest internationally.

GERMANY

H SWITZERLAND

Industrial methanation unit consisting of a cooled fixed-bed isothermal reactor. The CO $_{\textrm{\tiny{2}}}$ used for methanation comes from a biogas plant operating with residual matter and waste. The methanation reactor can produce 325 Nm3 /h of methane (i.e. 1,000 tonnes) per year.

AUDI E-GAS PROJECT

2013 | Werlte Man EnergySolutions | 325 Nm³/h

The climate policy of some Swiss cities with respect to biological power-to-methane projects is ambitious, with targets such as carbon neutrality by 2040 (e.g. Winterthur).

In France, the prospects for the development of power-to-methane are significant, with a potential estimated by the gas industry at 50 TWh between now and 2050. Several equipment manufacturers are positioned in biological and catalytic methanation, and a number of pilot projects are already in operation.

2020 | Fos-sur-mer Khimod | 25 Nm³/h

2022︱Dietikon Hitachi Zosen Inova | 250 Nm³/h

Catalytic **Disk and Science and Science and Science and Science and Science and Science and Catalytic Biological**

Denmark has ambitious targets: 100% biomethane in the gas network by 2030. In addition, annual calls for projects to produce biomethane and feed-in tariffs are in place. National universities are at the forefront of research (e.g. Aarhus and DTU).

Specific to catalytic Catalytic peting to catalytic methanation technology

Germany has high biomethane production targets (8.4 GW by 2030). It is the most advanced country in the industrialisation of power-to-methane, with several mature equipment manufacturers and numerous pilot projects already in operation.

> First industrial power-to-methane installation in Switzerland (2.5 MW) by Hitachi Zosen Inova. Since 2022, it has been possible to inject 18 GWh/per year of renewable methane. The electricity is generated by a municipal solid waste incineration plant, and the CO $_{\textrm{\tiny{2}}}$ comes from the purification gases from a wastewater treatment plant.

The world's largest power-to-methane plant has been commissioned in Glansager, Denmark. This facility uses renewable electricity for electrolysis and CO₂ from a biogas plant to produce methane.

Power-to-gas industrial demonstration project with expected methane production of 25 Nm 3 /h from CO $_2$ from plants in the Fos-sur-Mer industrial port zone and hydrogen (1MWe) for injection into the grid.

LIMECO PROJECT

JUPITER1000 PROJECT GLANSAGER PROJECT

2023 | Glansager Nature Energy | 380 Nm³/h

Specific to biological methanation technology

Biological

In the United States, this is a major area of research for many laboratories, but there is only one recent pilot project in deployment.

O JAPAN

Japan has ambitious targets: ~90% of synthetic methane in the future residential gas mix by 2050.

Demonstration unit using $CO₂$ as a feedstock 2 shows a discussed and $2\frac{1}{2}$ as a reseased that will inject biomethane into the residential gas network in 2025. The project aims to develop a 400 Nm 3 /h unit.

A project to demonstrate biomethanation (using $\mathsf{CO}_2^{}$ captured from biogas production) on an industrial scale for injection has been under development in Colorado (collaboration between NREL and Electrochaea) since 2019.

2019 | Colorado, US | Electrochaea 600 MWh of methane per MWh e

Biological Catalytic Catalytic

2025︱Nagaoka INPEX | 400 Nm³/h

Catalytic

Feasibility study underway to produce methane using blue hydrogen (with CCS) and CO $_{\textrm{\tiny{2}}}$ captured from a bioethanol refinery. The unit will produce 200 kT/year by 2030, and the use of green hydrogen is currently being studied.

GREEN PLAINS PROJECT

from 2024 | Midwest, US GreenPlains | 55 Nm³/h

SOCALGAS PROJECT

INPEX PROJECT

UNITED STATES

Mapping of the Methane Production Chain

of the contract of the contrac [1] Produced by electrolysis; [2] Can come from several sources: biogas, industry, etc. Biogas can also be treated directly by methanation.

Catalysts are often subject to deactivation phenomena that reduce their efficiency: poisoning, carbon deposits and sintering [2].

In addition, many French laboratories (e.g. Université de Strasbourg, ICPEES, Université du Littoral Côte d'Opale) are studying these phenomena within different reactors \Box Use of critical minerals

The catalyst is the key element in catalytic methanation. It is possible to increase its activity, stability and selectivity, and to reduce deactivation and sintering phenomena, in particular by reducing the size of the metal particles in the catalyst, adding dopants or using supports (often alumina (Al2O3) or ceramic) for the catalyst. Another solution is to reduce the speed at which the catalyst circulates.

In fixed-bed reactors, it is impossible to replace the catalyst during the reaction and temperature control is difficult.

In **fluidised bed reactors**, the catalyst wears out quickly and energy costs are also high.

Cobalt, which is sometimes used as a catalyst, is considered a ʻcritical raw material [3]' by the European Commission. Nickel could become a critical resource as electric mobility becomes more widespread. That's why regenerating catalysts, to limit their replacement and therefore maintenance, is a key challenge.

Reactor design

Methane production

> New reactor designs (e.g. millistructured, such as Khimod, or cold plasma, such as Energo) consume 10 to 100 times less catalyst than existing reactors and the catalyst can be regenerated *in situ*.

Millistructured fixed-bed reactors [4] are complex to manufacture.

Gas quality for injection

80 as the 'electrolysis' brick has not been studied in this report; **Exercity and intervents allow** exchanges to be intensified by reducing the size of the reactor and multiplying the number of channels. **81** [3] Critical raw materials are raw materials of great economic importance to the EU and which present a high risk of supply disruption due to the concentration of their sources and the absence of quality and affordable substitutes;

[2] Migration, growth and accumulation of metal particles reducing the active surface of the catalyst;

Gas quality measurement and control equipment is available, and methane recirculation solutions can reduce the proportion of residual H_{2} .

The performance of fixed and fluidised bed reactors continues to be improved (see example below). Manufacturing methods for millistructured reactors (which are less technologically mature) should be rationalised as orders increase. These systems are more compact and easier to control. They therefore enable an optimised reaction and ensure a longer catalyst life.

Specific to catalytic Catalytic reforms to datalytic research methanation technology

Feedstock pre-treatment [1]

Post-treatment

Global integration of the technical bricks [1]

Catalyst deactivation

[1] No specific issues relating to power-to-methane have been examined in this report. The issues of syngas pre-treatment are to be found in the post-treatment part of the pyrogasification and hydrothermal gasification process. Integration issues have not been addressed, as the ʻelectrolysis' brick has not been studied in this report;

Technical challenges in the sector **R&D** solutions and innovations and innovations and innovations

Mature technologies are already in operation on projects. R&D is focusing on optimising catalyst consumption and scaling up innovative processes

A team of Egyptian researchers has demonstrated that using cerium (Ce) or lanthanum oxide (La $_{\textrm{2}}\textrm{O}_{\textrm{3}}$) with zirconia (ZrO $_{\textrm{2}}$) as a support, coupled with Ni as a catalyst, increases the rate of CO $_{\textrm{\tiny{2}}}$ conversion. [> Link to the GRDF watch](https://act4gaz.grdf.fr/la-veille-gaz-verts-enrichit-votre-rentree)

Challenges and Technical Solutions for the Sector Catalytic

In accordance with European legislation, the concentration of hydrogen must be less than 2% (by volume) downstream of the post-treatment process.

Specific to biological methanation technology

FOCUS ON POWER-TO-METHANE SECTOR

Diffusion of gas into the liquid phase

The gas diffusion stage towards the liquid culture is limiting for methane conversion. If the injection of gases (H₂ and CO₂) is poorly controlled or if there is an accumulation of acetate, the methanation reaction may be inhibited.

Reactor design

In-situ reactors would reduce the cost, but there are issues of competition between reactions within the reactor (parasitic reactions).

Gas quality for injection

Several reactor technologies and designs exist today, but still need to be optimised.

For stirred reactors, the yield is still fairly low, mainly because power consumption increases with stirring.

For trickle-bed reactors, temperature control is complex, there is a risk of clogging the linings and CAPEX remains high.

82 83 addressed, as the ʻelectrolysis' brick has not been studied in this report. [1] No specific issues relating to power-to-methane have been examined in this report. The issues of syngas pre-treatment are to be found in the post-treatment part of the pyrogasification and hydrothermal gasification process. Integration issues have not been

appropriate for continuous operation).

Gas quality measurement and control equipment is available, and methane recirculation solutions can reduce the proportion of residual H_{2} .

Methane production Specific to catalytic methanation technology

R&D activities (modelling, temperature control, productivity, etc.) are underway at equipment manufacturers and research centres (cf. [mapping of methanation technologies page 71](#page-36-0)). The conclusions of these studies will enable a better choice to be made of the technologies Different flow rates and injection methods (pulsed or continuous) for $\mathsf{CO}_2^{}$ have been studied. When CO $_{\textrm{\tiny{2}}}$ is injected in a pulsed manner, methane yields can be increased. [> Link to the GRDF watch](https://act4gaz.grdf.fr/la-veille-gaz-verts-enrichit-votre-rentree)

Challenges and Technical Solutions for the Sector

Biological

Biological systems can also be used to produce methane. Several models are currently available and can be optimised to reduce costs and increase yields

Technical challenges in the sector **R&D** solutions and innovations and innovations and innovations

Several possibilities for optimising Trickle Bed Reactors (TBRs) have been identified: on liquid flow and biofilm formation, in particular. [> Link to the GRDF watch](https://act4gaz.grdf.fr/la-veille-gaz-verts-enrichit-votre-rentree)

A new approach to monitoring the internal dynamics of Trickle Bed Reactors (TBRs) has been investigated by installing multiple H_2 microsensors along the vertical axis to improve reactor performance.

In accordance with European legislation, the concentration of hydrogen must be less than 2% (by volume) downstream of the post-treatment process.

FOCUS ON POWER-TO-METHANE SECTOR

Feedstock pre-treatment [1]

Post-treatment

Specific to biological methanation technology

Global integration of the technical bricks [1]

Khimod has also participated in a number of EU-funded projects, including: METHAMOD (production of 8,000 Nm³/year of synthetic methane per year), STORE&GO (LNG production of 33,000 kWh) and Jupiter 1000 (expected methane production of 25 Nm3 /h).

Key Players in the Development of the Sector

Catalytic

High-performance catalytic methanation

Khimod is a French technology developer for the production of synthetic methane (as well as paraffin, methanol, olefins, etc.) from CO $_{\textrm{\tiny{2}}}$, based on innovative millistructured heat exchanger-reactors, the result of a research partnership with the CEA.

has a high performance for catalytic reactions: **TRL of the technology** \blacksquare **7-8** The millistructured heat exchanger-reactor high CO $_2$ to CH $_4$ conversion rate, high energy efficiency, uses low quantities of catalysts, and with a lifetime in excess of 20 years. Thanks to its technology, KHIMOD can work on projects of different sizes (CO $_{\textrm{\tiny{2}}}$ flow rates ranging from 1.2 to 768 Nm^3).

EtoGas offers 3 main solutions: Power-to-Hydrogen (electrolysis), Hydrogen-to-SNG (methanation) and the combination of the two above-mentioned solutions within a complete Power-to-SNG chain. The methanation system (Hydrogen-to-SNG) is an innovative concept using fixed-bed plate reactors (patented) andmembranes to convert hydrogen-containing gases into SNG (synthesis gas with up to 99% CH, output).

Etogas already has several projects in operation: Audi e-gas plant (Power-to-SNG, 325 Nm3 /h of synthetic methane), design of the first Power-to-SNG system in Switzerland for Hochschule Rapperswil (25 kWe), and a Power-to-SNG pilot project in Stuttgart (250 kWel).

TRL of the technology

Industrial unit in operation and several under construction

Specific to biological methanation technology Specific to catalytic Catalytic rethanation technology

Hitachi Zosen Inova (HZI) EtoGas is a pioneer in power-to-gas, with experience in the planning and delivery of complete turnkey facilities, as well as in the maintenance and operation of these facilities.

> *Hitachi Zosen Inova is also active in biological methanation, with an industrial project (Limeco) in operation since 2022.*

Biological methanation for injection successfully tested

Electrochaea, a German developer of powerto-gas technologies, has developed an archaea micro-organism and a process for producing synthetic methane for injection. The process includes the production of H_2 by electrolysis (using renewable electricity) and the biological methanation of CO₂ from the micro-organism.

The process can be used as a CCUS solution for industrial facilities that emit CO_2 . Electrochaea offers to support these installations in the design of the solution, project management and commissioning.

In 2019, its two pilot projects BioCat and STORE&GO injected methane into the commercial gas networks of Denmark and Switzerland respectively.

The ready-to-market solution has received support from the European Innovation Council to speed up the commercial development of large-scale units (10 to 75 MWe). An initial 10 MWe plant to convert 5,700 $\mathsf{Mt}_{\mathsf{CO}_2}$ /year and produce 2.8 Nm³/year of synthetic methane is currently under construction.

TRL of the technology \blacksquare 8-9

Biological

Key players in the Development of the Sector

FOCUS SUR LA FILIÈRE POWER-TO-METHANE

The main French players in the field are federated by the <u>ATEE's Power to Gas Club</u>.

[Techno-Economic Evaluation of Biological and Fluidised-Bed Based Methanation Process](https://www.frontiersin.org/articles/10.3389/fenrg.2021.775259/full) [Chains for Grid-Ready Biomethane Production](https://www.frontiersin.org/articles/10.3389/fenrg.2021.775259/full)

Gantenbein et al., 2022

[Biological Aspects, Advancements and Techno-Economical Evaluation of Biological](https://www.mdpi.com/1996-1073/15/11/4064) <u>[Methanation for the Recycling and Valorization of CO](https://www.mdpi.com/1996-1073/15/11/4064)₂</u> Bellini et al., 2022

[Techno-economic analysis of Power-to-gas plants in a gas and electricity distribution network](https://www.sciencedirect.com/science/article/abs/pii/S0306261922001994) [system with high renewable energy penetration](https://www.sciencedirect.com/science/article/abs/pii/S0306261922001994)

[Compréhension et modélisation des mécanismes de désactivation d'un catalyseur](https://theses.hal.science/tel-03009134v1/file/Champon_Isabelle_2019_ED222.pdf) <u>de méthanation de CO₂ [au sein d'un réacteur-échangeur milli-structuré à lit fixe](https://theses.hal.science/tel-03009134v1/file/Champon_Isabelle_2019_ED222.pdf)</u>

Fambri et al., 2022

[European Biomethane Benchmark](https://www.sia-partners.com/system/files/document_download/file/2022-05/Sia%20Partners%20Benchmark%20Europe%20Biomethane.pdf)

Sia Partners, May 2022

[BIOMÉTHANATION DU SYNGAS: Étude cinétique et mise en œuvre à l'échelle pilote](https://hal.science/hal-03369567) Figueras et al., 2021

[Production d'un syngaz par pyrogazéification de biomasse en vue d'une](https://theses.hal.science/tel-03326017) biométhanation Tchini Séverin Tanoh, 2021

<u>[Plasma catalytic process for CO](https://theses.hal.science/tel-01612734/document)₂ methanation</u> Magdalena Nizio, 2016

[La méthanation biologique](https://atee.fr/system/files/2021-03/METHANATION%20BIOLOGIQUE_Claire%20Dumas_14122020.pdf)

ATEE, December 2020

[Biométhanation par injection de dihydrogène état de l'art et potentiel d'émergence](https://record-net.org/storage/etudes/19-0419-1A/synthese/Synth_record19-0419_1A.pdf) Voltigital /Enerka /IMT Atlantique, October 2020

Biological CO 2 [–Methanation: An Approach to Standardization](https://www.mdpi.com/1996-1073/12/9/1670) Thema et al., 2019

Isabelle Champon, 2019

[Valorisation énergétique de CO via la méthanation par voie catalytique](https://www.researchgate.net/publication/333015328_Valorisation_energetique_de_CO_via_la_methanation_par_voie_catalytique) Nathalie Elia, 2019

[Statu quo sur la méthanation du dioxyde de carbone: une revue de la littérature](https://www.sciencedirect.com/science/article/pii/S1631074817301571) Ducamp et al., 2018

[Report on the costs involved with PtG technologies and their potentials across the EU](https://erig.eu/wp-content/uploads/2023/02/20180424_STOREandGO_D8.3_RUG_accepted.pdf) Van Leeuwen, 2018

Sources

Pyrogasification

What is Pyrogasification?

What is Pyrogasification?

Pyrogasification combines two processes, pyrolysis and gasification. These processes involve the thermochemical treatment of dry carbonaceous materials (biomass or waste) at high temperature (between 800 and 1500 ˚C), in the absence or lack of oxygen. These two processes transform organic matter into synthesis gas (or ʻsyngas'), oil and/or coal.

Pyrolysis mainly leads to the formation of (bio)char, as well as oil and gas that can be used to produce heat and combined heat and power, or to produce fuels.

The Gasification generally follows a pyrolysis stage. The aim is to convert as much of the solid carbon and pyrolysis oil as possible into syngas, in particular for fuel production and injection into the grid.

However, the proportions of each of these compounds and their potential use depend on the route chosen:

forestry wood, wood industry by-products, cork residues, wood waste in SSD [1], etc.

 $\frac{1}{2}$ authorities) with a view to its re-use. [1] Waste has a specific legal status governed by environmental and health regulations. However, a waste holder can implement a procedure for removing waste status, known as SSD (specified on a case-by-case basis and validated by the competent authorities) with a view to its re-use.

The pyrogasification process can be used to recover a variety of dry feedstocks

Non-waste wood

Lignocellulosic crop residues

straws, canes, vine shoots, etc.

Non-recyclable waste

non-recyclable plastics, used tyres, etc.

Green waste branches, prunings, woody fraction

Non-hazardous wood waste

wood/end-of-life packaging, pallets, furniture waste, etc.

Refuse-derived fuel (RDF)

sorting refusals: wood, cardboard, plastics, etc.

Description of the Process

Pyrolysis and gasification produce different products depending on the reaction conditions

Pyrolysis produces gases, tars/oils and solid coal, which can mainly be used to produce heat. To increase the proportion of gas, the initial pyrolysis can be followed by a gasification stage. A subsequent methanation stage is also added when the desired gaseous product is CH $_{\scriptscriptstyle 4}$, for example for injection into the grid.

Dry feedstocks \longrightarrow CO₂ + H₂O + CH₄ $+ CO + coal(s) + tar(g) + minerals$ and metals

The **OXIDATION** of the volatile matter produced during pyrolysis, by adding an oxidising agent (air, ${\sf H}_{\sf z}$ O vapour or O_2), provides the heat required for the other stages of pyrolysis and gasification.

 $CO + H₂O \rightarrow CO₂ + H₂$ $CO + \frac{1}{2}O_2 \rightarrow CO_2$ $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

GASIFICATION leads to the formation of syngas rich in CO and $\mathsf{H}_2^{}$ through the chemical reduction of solid coal [1]. This phase requires external energy, supplied by the exothermic oxidation reaction.

 $C + H_2O \rightarrow CO + H_2$ $C + CO₂ \longrightarrow 2CO$

 $c.55 - 75$ ENERGY EFFICIENCY

Indicative proportion of products:

a ratio of 3:1 by means of an intermediate Water-Gas-Shift reaction: $CO + H_2O \longrightarrow CO_2 + H_2$. [1] In the syngas produced, the H₂/CO ratio is close to 1. To encourage the production of methane through a subsequent methanation stage (see <u>presentation of the methanation building blocks</u> in the Power-to-methane section), the proportion of H₂ can be increased to

Pyrogasification produces syngas with an energy efficiency of around 80%.

With subsequent washing and methanation (cf. methanation process), the energy efficiency is closer to 55-65% when methane alone is taken into account, and more than 75% if the recoverable waste heat is taken into account.

> 90%

FEEDSTOCK CONVERSION RATE

The conversion of biomass into gas is almost complete during gasification.

PYROLYSIS consists of breaking down the molecules of organic matter into smaller, more thermally stable molecules (CO, CO₂, H₂) under the effect of heat (high temperature) in the absence of O_{2} .

Industry dynamics

Pyrogasification plants in operation around the world are mainly used for combined heat and power (CHP)

The principles of pyrolysis and gasification have been used for several centuries: as far back as antiquity, wood was pyrolysed to produce coal; since the 19th century, coal has been gasified to produce gas for lighting and town gas. More recently, these processes have been widely used to produce heat and cogeneration (CHP) from biomass: there are several hundred industrial units in Germany, Italy and the United States.

In recent years, the growing need for carbon-free energy has led to gasification being increasingly considered as a way of producing biomethane that can be injected into networks to replace natural gas.

> [1] CEI: Call for Expressions of Interest. [AMI pyrogazéification pour injection - Webinaire de restitution](https://www.grtgaz.com/sites/default/files/2022-06/GRTgaz-AMI-pyrogazeification-webinaire-de-restitution-21062022.pdf), NSE/GRTgaz, 2022; [2] Data for non-waste wood or green waste feedstocks;

[3] The ratio of CH_4 production to incoming tonnage remains broadly the same whatever the size of the plant.

The gradual change in use cases (lighting, cogeneration, production of molecules) and the growing complexity of feedstocks (forestry residues, waste wood, RDF) are continually imposing new technical and economic challenges on the industry. Injection requires quality conditions that are not met by raw syngas produced by simple gasification: a reduction in contaminants and $\mathsf{CH}_{_4}$ enrichment (methanation) are required, which have yet to be deployed on an industrial scale.

A non-exhaustive map of pyrolysis and gasification projects around the world is available at: https://www.ieabioenergy.com/installations/

Generic equivalent of feedstock tonnage/ CH_4 production

A map of projects under development in France is available at: https://odre.opendatasoft.com/explore/dataset/projet-commerciaux-et-demonstrateurs-enfrance-de-pyrogazeification/information/?disjunctive.statut&disjunctive.nom_region

MAIN FEEDSTOCKS FOR CEI PROJECTS [1]

Historically, pyrogasification of biomass and waste has mainly been used for heat production and cogeneration. In recent years, however, there has been an acceleration in the development of pyrogasification for the injection of biomethane into the grid.

In 2022, in France, GRTgaz led a call for expressions of interest (CEI) that identified 49 projects with a potential injection capacity of 4.1 TWh (HHV)/ year or 51,000 Nm3 /h [1].

1.3 million tonnes / year

Production of biomethane for injection

Some commercial demonstrators in Europe

PYROGASIFICATION PROJECTS

Units are moving towards sizes that enable waste to be processed on a regional scale.

non-hazardous

Non-waste wood, green waste and crop residues

RDF

甲

Mix of non-hazardous wood waste and RDF

8%

8%

Mix of non-hazardous and non-waste wood waste, green waste and crop residues

CAPACITY OF CEI PROJECTS

Some Pioneering Projects for the Sector

In recent years, a number of countries and a few demonstration projects have made progress towards pyrogasification for injection into the grid

FIFCB Güssing

2001-2015 | Güssing

Closed **Stopped Stopped**

One of the first commercial demonstrators of biomass gasification, supplying the town of Güssing with electricity and heat. In 2009, the unit was upgraded for almost a year to produce biomethane. Other gasification demonstrators have since been installed in the region.

The first biomass gasification demonstrator for injection into the grid. Due to a lack of profitability, the development of a commercial unit that was initially planned did not take place in the end.

PROJECT INITIATOR

Güssing Renewable Energy PRODUCTION Combined heat and power

Operating Mon-waste wood, Constructed Under development Non-waste wood, green waste, RDF

FEEDSTOCKS

Production of biomethane and CO₂

Ongoing development of the first commercial gasification demonstrator for injection, using wood waste as the feedstock, thanks to the integration of a methanation module. The first Nm³ of clean syngas were produced in early 2024.

Semi-industrial R&D demonstrator, designed to demonstrate the technical and economic feasibility of methane production by gasification/methanation. The world's first m3 of grid-quality gas obtained from RDF

gasification was produced in 2020.

PROJECT INITIATOR Engie and consortium PRODUCTION Wood waste and non-renewable waste

Production of noninjected biomethane

 0.6 MW $_{\rm th}$ (50 Nm $^3_{\rm CH_{\rm 4}}$ /h)

PROJECT INITIATOR

Advanced Biofuels Solutions Ltd

PROJECT INITIATOR

Séché, Enosis, GRTgaz, EQTec and consortium

FEEDSTOCKS

Local wood waste and non-hazardous waste (8,000 tonnes/ year)

PRODUCTION

PRODUCTION

Production of biomethane

Plainergie

2019 | Plaine de l'Ain

STATUT

Operating

SIZE

 3.4 MW_{th} $(300 \text{ Nm}^3_{\text{CH}_4} / \text{h})$

FEEDSTOCKS

SIZE

 0.1 MW $_{\rm th}$ (10 Nm $^3_{\rm CH_{\rm 4}}$ /h)

SIZE

8 MW $_{\text{th}}$ and 2 MW $_{\text{e}}$

SIZE

STATUT FEEDSTOCKS STATUT

Development of a European demonstrator for converting unused waste into injectable methane, by combining pyrogasification and biological methanation.

GAYA

Since 2017 | Saint-Fons

GoBiGas

2014-2018 | Gothenburg

Swindon Advanced Biofuels

2023 | Swindon

Mapping of the Main Flagship Projects

With the exception of Enerkem's project, most pyrogasification projects for the production of molecules are still under development

Project status

Existing

Incoming power

Increasing quality of syngas needed to address usage

Mapping of Pyrogasification **Technologies**

[1] Reactor with rotating drum, screw, etc. Heat can be supplied by an electrical thermal resistor.

The scale of production and the nature of the feedstocks determine the choice of gasification reactor

Up until now, fixed-bed reactors have been widely used for small-scale applications. The development of the industry towards larger units and more complex processing of gases for injection should lead to more frequent use of fluidised beds and entrained beds.

Mapping of the Production Chain

Pre-treatment of waste feedstocks is currently usually carried out by suppliers, who have the necessary skills and technologies. To roll out the process on an industrial scale, it will be necessary to ensure good control over the supply of feedstocks and the pre-treatments applied, in order to limit their heterogeneity and the variability in their quality, which can lead to lower yields and equipment deterioration.

Feedstock pre-treatment

> In conventional gasification technologies, the oxidation of pyrolysis gases using air injection provides the heat required for the other stages of the process. However, because it increases the N₂ content of the gas, air injection presents a twofold constraint for reactors:

 \bullet The presence of N_2 reduces the energy efficiency of the process,

• Its elimination requires complex treatment of syngas before methanation and oversizing of the treatment bricks.

Challenges and Technical Solutions for the Sector

The development of new gasifiers (or the adaptation of existing ones) using oxidising agents other than air is one of the major technological challenges facing the industry

Production of syngas by pyrogasification

> Syngas treatment

R&D solutions and innovations

P Production of clean syngas from heterogeneous waste products

Integrating the pre-treatment stages on site (usually shredding and drying to homogenise the feedstocks, and pelletising to increase their density) gives greater control over the quality of the feedstocks. This integration can lead to constraints in terms of investment and skills development, but also to opportunities (on-site processing can be a source of additional income).

Conventional gasification technologies are being adapted to generate the necessary heat without injecting air directly into the gasifier. Some technology developers are opting to replace the air with another oxidising agent, such as pure oxygen or an oxygen/steam mixture (ʻoxysteam' process). This is the case, for example, with ABSL, KEW Technology and EQTEC. Other developers are choosing to supply the necessary heat in other ways: by electricity, like Clean Carbon Conversion or ETIA, or by plasma, like Solena. Finally, some players are developing reactors in which the main bed is separate from the combustor (Engie, Milena). In addition, a number of laboratories, including ENEA Trisaia (Italy) and the ʻEnergy Technology' section at TU Delft (Netherlands), have for several years been paying particular attention to the impact of the choice of oxidant on the gasification reaction and its products.

Heterogeneous feedstocks can lead to lower yields (load variations) and equipment degradation. Ongoing optimisation of conventional gasifiers is needed to produce clean syngas with a good yield from heterogeneous waste, such as non-recyclable waste and RDF.

E Oxidation with limited air injection

Several research centres are particularly interested in these issues: modelling reaction mechanisms (CIRAD-BioWooEB or LRGP Lorraine in France), technical and economic optimisation of existing processes (SFC in Sweden, LERMAB or CEA in France, or Danish Technological Institute in Denmark), scaling up technologies to industrial scale (SFC), etc. A number of developers (ABSL, Clean Carbon Conversion, EQTEC, etc.) are already proposing technologies for recovering RDF that can be gradually incorporated into commercial projects (e.g. the Salamandre project currently under development).

Global integration of the technical bricks

E Controlling pre-treatment

The formation of tars during gasification is one of the major challenges facing the industry. On the one hand, reducing the presence of tars (which contain 5 to 15% of the energy produced during the process) makes it possible to increase the energy efficiency of the process. Secondly, eliminating the tars formed is necessary to prevent clogging and damage to downstream equipment, particularly methanation reactors.

Challenges and Technical Solutions for the Sector

The integration of syngas production and methanation systems has already been successfully achieved in demonstrators. Their coupling can be further optimised by improving syngas treatment processes (1/2)

Technical challenges in the sector **Technical challenges in the sector** R&D solutions and innovations

D Optimising tar cracking

There are two main types of sulphur removal unit:

• Mature absorption systems (often using water washing), for which optimisation of energy consumption is still necessary,

• Adsorption systems (often on activated carbon beds), which are less mature, and for which the treatment of solid residues downstream still needs to be improved.

• It can take place directly *inside the gasifier:* by choosing optimum reaction conditions (e.g. reactors that play on temperature variations, such as those developed by Clean Carbon Conversion), by new reactor designs (e.g. plasma reactors, multi-stage gasifiers, etc.), or by introducing catalysts (e.g. catalytic candle filter reactors developed by the European UNIFHY project);

• Tars can also be eliminated at the gasifier outlet (filters, scrubbers, chemical cracking, thermal cracking by partial oxidation in a second reactor as developed by KEW Technology and EQTEC, etc.)

Several research centres are looking at these issues, particularly modelling (University of Liège in Belgium, University of Quebec in Canada, University of Lorraine in France) and optimising the energy and environmental performance of absorption columns (Mines ParisTech in France).

In addition, the conversion of tars for the production of renewable hydrocarbons is one of the most widely studied areas of gasification research: by SFC (Sweden), RAPSODEE (France), CIRAD-BioWooEB (France), LRGP (France), Danish Technological Institute (Denmark) and many other laboratories in France and abroad.

Several R&D strategies have been adopted in recent years to improve tar elimination:

In-situ elimination strategies are now increasingly mature and effective, but they still do not achieve total elimination of tars. Combining them with *ex-situ* strategies may therefore be necessary to achieve elimination rates in excess of 90-95%, but the scaling-up of the corresponding technologies has yet to be demonstrated.

Feedstock pre-treatment

> Syngas treatment

Global integration of the technical bricks [1]

Elimination of sulphide and chloride

Production of syngas by pyrogasification

Challenges and Technical Solutions for the Sector

The integration of syngas production and methanation systems has already

been successfully achieved in demonstrators. Their coupling can be further optimised by improving syngas treatment processes (2/2)

At the same time, the elimination of hydrogen sulphide and VOCs by biofiltration is being looked at closely, for example by KRONOS ecochem in Germany and INSA Lyon in France. However, a feasibility/compatibility test between the micro-organism and the feedstock is still

[1] H₂S - Hydrogen sulphide; VOC - Volatile Organic Compounds (e.g.: benzene, toluene);

[2] Methanation and syngas production are the two main building blocks of the pyrogasification process. Other systems can complete

 110 this technological chain, such as CO₂ recovery systems. 111

Focus on coupling gasification and biological methanation

solid waste into biomethane that can be injected into the grid. Swindon is due to start injecting biomethane into the UK grid in the coming months (end of 2023-2024).

Supplied with local organic waste, Swindon will theoretically be able to produce up to 1,500 tonnes of SNG (c. 22 GWh) and 500 tonnes of H_2 /year. What's more, recovering the co-produced $\mathsf{CO}_2^{}$ for food use will avoid on-site gas emissions.

TRL of the technology \sim 8-9

Key players in the Development of the Sector

Europe's first commercial wood waste injection unit

Advanced Biofuel Solutions Ltd. (ABSL), a British technology and project developer, has for several years been developing a fluidised bed gasification reactor (RadGas), based on oxidation with oxygen and steam rather than air, with plasma cracking of the tars in a second reactor.

The technology is designed to work with a wide variety of feedstocks: municipal solid waste, dried biomass residues, wood, shredder residues, used cooking oil, etc.

To date, RadGas has been demonstrated in pilot units, accumulating more than 3,500 hours of operation. For several months now, the technology has been integrated into the industrial production unit at Swindon, the first unit in the world to convert municipal

Development of a gasification plant for injection in France

EQTEC is an Irish gasification technology developer, involved in the development of the sector through its various projects in Europe (Greece, Italy, Spain, etc.) and the United States.

Drawing on decades of R&D experience in gasification, EQTEC now offers a bubbling fluidised-bed gasifier technology that operates with a variety of feedstocks, including forestry wood and industrial and municipal waste.

In France, EQTEC has recently been selected, alongside the IDEX group, to develop a gasification plant for the Limoges local authority. The unit will process 40,000 tonnes of wood residues and waste per year, producing up to 100 GWh of synthetic methane to supply local homes and industry.

TRL of the technology $7 - 8$

Since 2014, Enosis has developed several biological methanation prototypes (the Bimotep mobile unit and the Demetha pre-industrial unit coupled to methanation) and participated in a number of projects coupling gasification and biological methanation (e.g. the Plainergie European demonstrator).

The technology developed by Enosis is based on a co-culture of micro-organisms to allow great flexibility with regard to feedstocks.

Biological methanation combined with gasification

Enosis, a French technology and project developer, is developing biological methanation systems using from CO_{2^I} syngas from gasification or biogas from anaerobic digestion, to produce methane or hydrogen.

Sources

The main French players in the field are federated by the [Club Pyrogazéification de l'ATEE](https://atee.fr/energies-renouvelables/club-pyrogazeification) .

[Global biomass conversion facilities](https://www.ieabioenergy.com/installations/) IEA Bioenergy, 2023

[gazéification.info](https://www.gazeification.info/) S3D, 2023

[A comprehensive review of primary strategies for tar removal in biomass gasification](https://www.sciencedirect.com/science/article/pii/S0196890422012742)

Cortazar et al., 2023

[Gasification of municipal solid waste: progress, challenges, and prospects](https://www.sciencedirect.com/science/article/abs/pii/S1364032122006980) Sajid et al., 2022

[AMI pyrogazéification pour injection - Webinaire de restitution](https://www.grtgaz.com/sites/default/files/2022-06/GRTgaz-AMI-pyrogazeification-webinaire-de-restitution-21062022.pdf) NSE/GRTgaz, 2022

[Projets de production de gaz renouvelable et bas carbone par pyrogazéification](https://odre.opendatasoft.com/explore/dataset/projet-commerciaux-et-demonstrateurs-en-france-de-pyrogazeification/information/?disjunctive.statut&disjunctive.nom_region) pour [injection dans les réseaux gaziers](https://odre.opendatasoft.com/explore/dataset/projet-commerciaux-et-demonstrateurs-en-france-de-pyrogazeification/information/?disjunctive.statut&disjunctive.nom_region)

ODRÉ, September 2022

[Filières gazéification: analyses des états de l'art et recommandation](https://librairie.ademe.fr/cadic/6763/filieres_gazeification_etat_art_et_recommandation_2022-synthese.pdf) ADEME, 2022

[Biométhanation du syngas: Etude cinétique et mise en oeuvre à l'échelle pilote](https://hal.science/hal-03369567) Figueras et al., 2021

[Benchmarking et selection des technologies de pyrolyse et de gazéification adaptées](https://hal.science/hal-03192601/document) à la [valorisation des CSR et du Bois-B sous forme du gaz](https://hal.science/hal-03192601/document) Iwunze, 2021

[Production of syngas by gasification of biomass with a view to biomethanation](https://www.sciencedirect.com/science/article/pii/S1631074817301571) Tchini Séverin Tanoh, 2021

[Craquage thermique des vapeurs de pyrolyse-gazéification de la biomasse en réacteur](https://hal.univ-lorraine.fr/tel-01752750/document) [parfaitement auto-agité par jets gazeux](https://hal.univ-lorraine.fr/tel-01752750/document) Baumlin, 2018

[Pyrolyse, liquéfaction et gazéification de la biomasse](https://www.asprom.com/biotech/dufour.pdf) Dufour et al., 2018

[Pyrolyse et gazéification, une filière complémentaire pour la transition énergétique](https://www.green-news-techno.net/fichiers/201602021004_GNT_588.pdf) et le [développement de l'économie circulaire](https://www.green-news-techno.net/fichiers/201602021004_GNT_588.pdf) French National Industry Council, 2015

Hydrothermal Gasification

What is Hydrothermal Gasification?

What is Hydrothermal Gasification?

Hydrothermal gasification (HTG) is a thermochemical process involving the treatment of wet (about 80%) or water-miscible organic matter (biomass or waste), at high temperature (400 – 700˚C) and high pressure (250 – 300 bar). The reaction medium is the water contained in the feedstock in its supercritical state [1].

This process transforms carbonaceous matter into synthesis gas (or ʻsyngas') and recovers mineral salts and water present in the feedstock. As the gas leaving the plant is under high pressure, it is worth injecting it into the network.

Hydrothermal gasification is a cost-effective alternative to incineration, landfill and return to landfill, because it enables the treatment of waste that cannot be recycled in any other way and reduces atmospheric pollution.

Be pumpable, which often means a dry matter (DM) to gross matter (GM) ratio of around 20%.

The highest possible proportion of organic matter (OM) in dry matter (DM). A ratio of OM to DM of at least 50% is generally sought.

There are currently two operating conditions: hydrothermal gasification with a catalyst, to lower the conversion temperature, and hydrothermal gasification at a higher temperature, without a catalyst.

> **Digestate** from anaerobic digestion not suitable for land application

[1] Supercritical fluid: fluid heated above its critical temperature and compressed above its critical pressure without becoming a solid (for water >374°C and >221 bar).

Sludge from urban and industrial wastewater treatment plants

Dredging sludge

Agricultural waste and effluents molasses, vinasses, etc.

Industrial residues

agri-food (dairy by-products, sugar production, fruit and vegetables, etc.) and pharmaceutical residues

Biodegradable waste

Feedstocks must meet certain technical characteristics to ensure the plant performs well:

Hydrothermal gasification (HTG) produces high-pressure gases that can be injected into the gas network or used directly in NGV stations or in industry, and co-products such as mineral salts and water, which can be used mainly to produce fertilisers and clear water [1] (for drinking or irrigation).

Description of the Process

Depending on the operating conditions (retention time, temperature, pressure, DM rate, etc.) for hydrothermal gasification, the amount of $CH₄$ in the syngas can vary between 20 and 70%

The **FEEDSTOCK** passes through a stage of elimination of certain major undesirable elements (e.g. sand, threads) and a preparation stage (possible grinding, concentration or dilution and pre-heating) and homogenisation. It is then compressed.

Chemical equation for hydrothermal gasification:

Wet matter (C_xH_yO_z + H₂O) \rightarrow Synthesis gas (CH $_{_4}$, H $_{_2}$, CO $_{_2}$, C $_{_\mathrm{x}}$ H $_{_\mathrm{y}}$) + mineral salts + liquid phase (H₂O, NH₄+)

In the case of a process with a catalyst [2] integrated into the gasifier, sulphur capture is necessary upstream to protect the catalyst and maximise its life. The gasification stage then leads to the formation of a syngas that is richer in methane and contains less H_2 .

A SALT SEPARATOR is used to recover the mineral salts that can be recycled and avoid clogging the gasifier.

Dry matter around ~20%, the key factor being that the feedstock is pumpable

HIGH-TEMPERATURE HTG

In the case of a higher temperature process without a catalyst, the organic part of the feedstocks can be directly gasified. The syngas obtained contains a higher proportion of hydrogen and hydrocarbons.

Low-temperature waste heat (<150°C) can also be recovered.

>75% **ENERGY EFFICIENCY**

HTG WITH CATALYST

Indicative proportion of feedstocks:

The process generates three co-products. Mineral salts are obtained upstream of gasification, during salt separation, while nitrogenous water and synthesis gas are obtained at the gasifier outlet.

Indicative proportion of products:

[1] After post-processing;

[2] Catalysts can be homogeneous (e.g. metals, ionocovalent oxides, ionic oxides) or heterogeneous (e.g. hydroxides and carbonates). [Link to watch;](https://act4gaz.grdf.fr/system/files/document_download/file/2023-09/Veille%20technologique%20gaz%20verts%20-%20septembre%202023%20-%20vF.pdf)

Entry of the solid components may also be precipitated at high pressure. The solid components may also be precipitated at high pressure.

(with heat recovery)

> 85% FEEDSTOCK CONVERSION RATE

The conversion rate can be close to 100% when inorganic solvents are used.

Some Pioneering Projects for the Sector

A number of key projects for the development of the Hydrothermal Gasification sector have been launched in recent years

With only one industrial unit in the world, located in the Netherlands, and a number of R&D and equipment manufacturers, this promising sector still has a long way to go to reach maturity. Over the last few years, however several projects around the world over the past few years, enabling us to benefit from new feedback of experience with this technology and illustrating the growing interest of industrial players in this field for this high-potential sector.

GERMANY UNITED STATES NETHERLANDS SWITZERLAND

FRANCE

GHAMA PROJECT

Leroux & Lotz Technologies | 2t/h Planned for 2026 | Montoir-de-Bretagne

Germany pioneered hydrothermal gasification in Europe with the VERENA project at the Karlsruhe Institute of Technology (KIT), which was a success and inspired other European developers.

The United States was one of the first countries to take an interest in hydrothermal processes: it was at MIT (Massachusetts Institute of Technology) that the first experiment was reported. It was also in the United States, at PNNL (Pacific Northwest National Laboratory), that hydrothermal gasification with catalysis was first introduced.

Since 2004 | Karlsruhe Karlsruhe Institute of Technology︱100kg/h Genifuel︱500kg/h SCWSystems︱2 to 4 t/h per module

High-temperature HTG **HTG HTG** with catalyst

The Netherlands is a world leader in hydrothermal gasification technology, with strong public support. This technology, which is included in the country's energy roadmap, is considered to be the preferred method of producing renewable gas (with 11.2 TWh, equivalent to 57% of renewable gas production in 2030).

Since 2017 │NorthAmerica Since 2018 │ Since 2018 │ Alkmaar Since 2017 │ Since 2020 │ Villigen

High-temperature HTG

The GHAMa project is the first $2 t/h$ (2 MW_{th}) demonstration project to be announced in France. However, its implementation depends on the public support framework that will be available to it in the meantime.

[1] WWTP: WasteWater Treatment Plants.

Switzerland has strongly supported the development of hydrothermal gasification since the 2000s. Its main motivation is to find an alternative solution to the incineration of sludge and digestate from WWTP sludge [1] (land application banned since 2006; obligation to recover phosphorus from sludge and digestate from 2026).

VERENA PROJECT **ALKWAAR PROJECT ALKWAAR PROJECT ALKWAAR PROJECT** ALKWAAR PROJECT ALKWAAR PROJECT ALKWAAR PROJECT

TreaTech/PSI | 110kg/h

HTG with catalyst

In France, there are few active projects at the moment, but a working group on the sector is supporting a number of projects in development since 2021. To date, there is only one test facility at CEA LITEN (10 kg/h); other projects are expected to come on stream by the end of 2024.

The VERENA project was the world's first pre-industrial hydrothermal gasification pilot plant (100 kg/h).

The Genifuel project has several facilities quasi-industrial demonstration projects currently underway (0.5 t/h). Using a mobile unit, various feedstocks are tested: algae and sewage sludge [1].

The Alkmaar project, led by SCW Systems, is the world's first industrial hydrothermal gasification plant for injection into the grid (~20 MW_{SNG} with 4 modules of 4 t/h). An extension of 2 other units of 40 MW_{SNG} each is planned.

After two prototype gasifiers with catalysts, a 110 kg/h pilot plant has been brought into operation. It treats sludge and digestate from WWTP sludge. Industrial units are expected to be up and running by 2025.

High-temperature HTG

Mapping of the Main Flagship Projects

High-temperature waste-to-energy plants are being developed primarily to recover waste-to-energy sludge, which is available in large quantities and difficult to recover using other energy sources. With the largest unit in operation, high-temperature HTG is the most advanced

Feedstock flow rate

1-100 kgRM/h \bullet 100-1000 kgRM/h 1000-4000 kgRM/h >4000 kgRM/h

124 125 Note: Non-exhaustive representation -listing major projects [1] Absence of salts and inorganic elements.

Mapping of the Production Chain

126 127 [1] Now made up by default of ruthenium, a rare metal; [2] Methane production can be maximised by co-injecting hydrogen into the gasifier.

Challenges and Technical Solutions for the Sector

The injection of feedstocks, their characterisation and the separation of salts are three major obstacles linked to the raw materials pre-treatment phase

130 131

of the reactor.

Challenges and Technical Solutions for the Sector

Syngas production is mature; efforts are focused on reducing costs and improving energy yields and carbon conversion rates

There is still room for improvement in the carbon conversion rate. On the one hand, part of the carbon stream is lost in the salt separators. On the other hand, the reaction kinetics remain poorly understood and the residence time of the species in the reactor is short. The result is incomplete conversion of the feedstock carbon content. For gasifiers with catalysts, the sulphur trap and the catalyst are consumed continuously and generate significant costs. At high temperatures, the energy and gas/water treatment OPEX are higher. Specific expensive alloys are required for the reactor to withstand Improving the efficiency of the heat exchanger, while optimising the other parameters (DM rate, residence time, pressure, temperature, etc.), is a key factor in increasing plant profitability. In the presence of inorganic elements that can precipitate, a salt separator is essential to separate the mineral salts from the fluid upstream of the reactor. The design of separators must continue to be optimised, both to improve their efficiency in continuous operation and to manage the removal of brine in all circumstances. **B** Improving energy efficiency **Design and efficiency of salt separators O** Optimising carbon conversion **Optimisation of consumables O** Cost control To increase the CH $_{\scriptscriptstyle 4}$ content, H $_{\scriptscriptstyle 2}$ can be injected upstream or a methanation stage can be added downstream. To limit losses, high-pressure recycling devices are planned to reinject the carbon downstream of the pump. Experiments to gain a better understanding of the reaction kinetics are also under way. The economic benefits of implementing these solutions will need to be precisely quantified. R&D is improving the recycling of high-temperature heat for both types of HTG. Initiatives are also underway to recover low-temperature heat [1] for use in heating networks or industrial sites. Finally, researchers are looking into the possibility of improving yields by increasing the DM content, which poses pumping problems above certain thresholds (>30%). Separator performance is the subject of R&D work and studies on separation efficiency are still required. Institutes (e.g. PSI, CEA Liten) and specialist technology developers (e.g. TreaTech) are very active in this field. Existing laboratories, including PSI (Paul Scherrer Institut), PNNL (Pacific Northwest National Laboratory) and KIT (Karlsruhe Institute of Technology), are taking a keen interest in catalyst recycling and the effectiveness of sulphur traps. Existing suppliers (see technology mapping) are studying the lifespan of alloys. Modular installations (2 to 6 t/h) are needed to take account of mechanical constraints (thickness of steel linked to pressure), Technical challenges in the sector **R&D** solutions and innovations and innovations and innovations Feedstock pre-treatment Syngas production by hydrothermal gasification **Product** post-treatment Global integration of the technical bricks

the high pressures and temperatures, prevent $\mathsf{H}_2^{}$ filtration and corrosion

enabling different throughputs to be covered, and would be less expensive.

Syngas: The syngas output is the main product, but additional steps are needed to recover the methane, particularly by injection. Two methods are generally used. The first is to upgrade the syngas (generally by membrane separation). The second involves using a methanation brick. Given the limited experience of this process and the high operating conditions (T, P), the integration of this brick has yet to be demonstrated.

Water: The water remaining after post-treatment could also be used for irrigation, for example. The nitrogen recovered could also be recycled.

 CO_2 : The significant proportion of CO_2 remaining in syngas (20 to 35%) could be recovered for use by consumer sectors such as the food industry, chemicals and fuels.

Mineral salts: Technologies for treating brine leaving the salt separator must be optimised to recover recoverable elements (e.g. phosphorus, representing 10 to 15% of salts for WWTP sludge).

H₂: Technical and economic studies could be carried out to determine whether it is attractive to recover the hydrogen present in the gas (0-50%). Given the marginal share of $\mathsf{H}_{\mathsf{2}'}$ the recovery bricks need to be adapted and optimised.

Water: The quality of the water leaving the process requires more in-depth studies, for each technology (high temperature and catalytic), in order to identify any post-treatment needs.

 $CO₂$: There are several mature ways of recovering $CO₂$ (see description in the anaerobic digestion section). The challenge now lies above all in the industry's ability to structure itself and develop viable business models for the units.

H₂: No major solution under consideration identified.

Challenges and Technical Solutions for the Sector

Several ways of optimising the recovery of co-products are currently being studied

Technical challenges in the sector **R&D** solutions and innovations and innovations and innovations

Recycling and recovery of products P) and co-products

Promising technologies are currently being developed.

Syngas: The growing number of projects involving pyrogasification for injection (see [dedicated](#page-51-0) map) should provide useful feedback on methods for coupling a syngas production unit and a methanation unit.

Mineral salts: For the recovery of salts, chemical treatment, a multi-stage salt separator or upstream cyclone separation are being studied. Phosphorus recovery requires R&D efforts, as the process is not yet known.

Feedstock pre-treatment

Product post-treatment

Syngas production by hydrothermal gasification

Global integration of the technical bricks

Challenges and Technical Solutions for the Sector

Tests on industrial units will be key to validating the proper integration of all the technological building blocks making up the system

Key Players in the Development of the Sector

High-temperature hydrothermal gasification without catalysts is more mature and the capacities developed are greater

> SCW Systems is also focusing on the mineralisation of excess CO $_2^{\vphantom{\dagger}}$. The company has developed and patented a process capable of transforming $\mathsf{CO}_2^{}$ into carbon powder, which is also eligible for carbon credits.

TRL of the technology \sim 8-9

High-temperature hydrothermal gasification on an industrial scale

With its demonstrator, in 2018, several types of feedstock were tested as well as materials for the plant's robustness.

Its first prototype in 2014 encountered a major obstacle concerning the evacuation of inorganic compounds from the plant. SCW Systems has filed several private patents that have overcome this obstacle.

SCW Systems, a Dutch technology and project developer, is the most advanced HTG company in the world, with a 2 MW industrial installation commissioned in 2021, and a scale-up to around 20 MW completed in 2023. SCW Systems is aiming to massmarket its installations: by 2030, 10 TWh/year in the Netherlands and 40 TWh/year in Europe.

French pioneer in high-temperature hydrothermal gasification

Thanks to the GHAMa demonstration project, Leroux & Lotz will be able to market its own high-temperature hydrothermal gasification technology from 2025/2026. The plants will range in size from 4 to 8 t/h, and will be capable of processing industrial, municipal and agricultural waste.

TRL of the technology \blacksquare 5-6

Leroux & Lotz Technologies, a French equipment supplier since 1946 and part of the Altawest group, is developing the most advanced hydrothermal gasification project in France. It involves high-temperature hydrothermal gasification, without catalyst, based on the process initially developed by the Karlsruhe Institute of Technology (KIT).

The GHAMa project aims to treat 2 t/h $(2 MW_u)$ of waste, in particular WWTP sludge. Its implementation, scheduled for the end of 2026, depends on the public support framework that will be available by then.

Key Players in the Development of the Sector

Hydrothermal gasification with a catalyst is at the demonstration stage, but the aim is to bring it to market in the next few years

Hydrothermal gasification with catalysis to recover syngas, water and mineral salts

TreaTech, a Swiss developer of project technologies since 2015, is focusing on hydrothermal gasification with catalysis. This technology produces syngas with a high methane content (70%) at a lower temperature of 400°C.

Working with the Paul Scherrer Institut (PSI), the company has developed a quasi-industrial unit that treats 110 kg/h of waste. TreaTech also has a salt separator technology optimised for the treatment of WWTP sludge.

Driven by national bans on the spreading of sludge and the requirement for maximum recovery of phosphorus from sludge, TreaTech and PSI are working on an industrialisable process for reclaiming phosphorus.

TreaTech is targeting operational units from 2025 to treat WWTP sludge and industrial organic waste (capacity of 2 to 4 t/h). Since 2023, it has pilot plant that can be mobilised on customer premises.

TRL of the technology \sim 7-8

Hydrothermal liquefaction and gasification with catalyst in series

Genifuel, an American technology developer since 2006, has the only commercial mobile unit in the world with a hydrothermal gasification technology with catalyst patented in collaboration with PNNL (Pacific Northwest National Laboratory). The process operates at 350°C and 200 bar.

More than 100 types of feedstocks have been tested, and since 2017 Genifuel has been commissioning several demonstrators that will enable different feedstocks to be tested on a near-industrial scale: algae and WWTP sludge in Vancouver and Florida.

The systems developed by Genifuel can operate in hydrothermal liquefaction mode, catalytic hydrothermal gasification mode or both at the same time (in series). In series mode, the system can convert more than 85% of the carbon in the feedstocks into syngas.

TRL of the technology $7 - 8$

Sources

[Gazéification hydrothermale](https://www.grtgaz.com/medias/communiques-de-presse/livre-blanc-gazeification-hydrothermale) White Paper, National Hydrothermal Gasification Working Group, January 2023

[La Gazéification Hydrothermale: solution d'avenir pour la valorisation des](https://aqua-valley.com/wp-content/uploads/2022/06/8-Tristan-RIGOU-GRDF_compressed.pdf) effluents liquides GRDF, June 2022

[La Gazéification Hydrothermale](https://atee.fr/system/files/2022-05/10_D%C3%A9carboner%20le%20mix%20gazier_GRTgaz_RobertMuhlke.pdf) GRTgaz, May 2022

[Potentiel de la Gazéification Hydrothermale en France](https://www.grtgaz.com/sites/default/files/2021-01/03102019-Note-de-synthese-Etude-de-potentiel-GH-GRTgaz.pdf) GRTgaz, October 2019

Emerging Technologies

The electromethanogenesis process involves micro-organisms that convert $\mathsf{CO}_2^{}$ into methane when an electric current is applied between two electrodes.

Photoreduction involves the same reactions as electroreduction, but differs in that it is more sustainable. The energy required to reduce the CO_2 comes solely from sunlight.

Electromethanogenesis

Photobioreaction $-\sum_{n=1}^{n}$

Aqueous solution with sensitiser (semiconductor or organic molecule)

 CO_2 electroreduction is an electrochemical technique that transforms $\mathsf{CO}_2^{}$ into carbon molecules such as methane. The process requires electricity to oxidise the water. This reaction releases oxygen, electrons and protons, which are used to break the C=O bond and form hydrogenated compounds.

The Different Emerging **Technologies**

Photobioreaction is the process of growing algae in photobioreactors. Microalgae are very small aquatic organisms that grow by absorbing CO₂ and converting it into oxygen through photosynthesis. They can then be used to produce biogas, as they are a particularly suitable source of biomass for anaerobic digestion.

CO₂ electroreduction

4 emerging green gas production pathways have been identified. What are they?

CO₂ photoreduction $-\sum_{i=1}^{n}$

in a photobioreactor

Harvesting micro-algae

Anaerobic digestion

Electromethanogenesis can significantly increase the quantity of biogas and its methane concentration [1]

Electromethanogenesis is at the frontier between electrolysis (production of H₂ in situ) and biological methanation (conversion of ${\sf H}_{_2}$ and $\mathsf{CO}_{_2}$ into $\mathsf{CH}_{_4}$).

The electromethanogenesis process involves micro-organisms that convert $\mathsf{CO}_2^{}$ into methane when an electric current is applied between two electrodes (an anode and a biocathode). When voltage is applied, the activity of the micro-organisms in the biofilm attached to the electrodes is stimulated, increasing the production and/or quality of the biogas.

For anaerobic digestion units, electromethanogenesis represents an opportunity to to increase biogas production from 50% to 70% and methane concentration from 20% to 30% [1].

Many researchers are interested in this emerging sector

This sector could emerge rapidly over the next few years, given the advantages and challenges still to be overcome

2-chamber reactor: Biogas recovery towards a high percentage of CH₄

The first scientific paper

on electromethanogenesis was published in 2009 by MIT. Since then, interest in this sector has continued to grow.

There are currently two challenges to deploying the technology in a largerscale chamber: the cost of integrating the electrodes into the digestate is high and the resilience of the biofilms over time could be improved.

The advantages of this method are the increased production of biogas and biomethane and the stability of this production, even if the composition of the digestate changes.

TRL of the technology $\sqrt{4}$

Single chamber reactor: Increased biogas production

 $CO₂ + 8H⁺ + 8e⁻$ *electricity* $CH₂ + 2H₂O$ $2H⁺ + 2e⁻$ *electricity* $H₂$

The number of scientific papers on bioelectrochemical systems has grown exponentially in recent years.

Description of the Electromethanogenesis Process

Electromethanogenesis is an emerging process that uses micro-organisms to promote methane production

> Number of scientific papers published per year on bioelectrochemical systems

HCO3 - + H2 + 7H+ electricity CH4 + 3H2O

Hydrogen-trophic micro-organisms

Selective production of methane by electroreduction is possible, but complex

Electroreduction requires the application of a current between two electrodes. When the difference in electrical potential is sufficiently great, oxidation of the water is observed at the anode, releasing oxygen, electrons and protons. The electrons released at the cathode will be used to reduce the CO $_{\textrm{\tiny{2}}}$ and the protons will be used to form hydrogen compounds.

The process of reducing CO $_{\textrm{\tiny{2}}}$ to methane gives rise to numerous parasitic reactions due to the application of a high potential. The electrolysis of water to form hydrogen is the reaction that most interferes with the formation of methane. By choosing catalysts and potentials that are very specific to methane, we aim to avoid water electrolysis in order to obtain greater methane selectivity.

It is therefore possible to produce methane selectively from CO $_{2'}$ but the reaction that produces this hydrocarbon directly is complex to implement. A number of parasitic reactions reduce the selectivity [1] of methane.

CO₂ + 8H⁺ + 8e⁻ electricity_b</sub> CH₄ + 2H₂O

Description of the CO₂ Electroreduction Process

The electroreduction of $CO₂$ is a complex chemical reaction that produces methane

CO₂ electroreduction is not yet a mature technology, and a number of technological hurdles still need to be overcome

However, experimentally this selectivity does not exceed 40%. What's more, applying a high potential requires a lot of energy.

The very high cost of membranes could act as a brake on the development of this sector.

TRL of the technology \sim 3

Only protons (H⁺) can pass through this membrane. In the anode compartment, oxidation of the water forms protons which pass through the membrane to reduce the CO $_2^{\vphantom{\dagger}}$. This membrane has the advantage of being durable over time. However, as water forms in the cathode compartment, the application of a current gives rise to a parasitic reaction that forms hydrogen. This drastically reduces the selectivity of the methane.

Only anions can pass through (OH⁻). The advantage of this membrane is that water is consumed in the cathode compartment. As a result, there is much less electrolysis of water and little parasitic hydrogen production. However, these membranes are only very rarely available on the market, and face obstruction problems linked to the formation of crystals in the membrane.

In an electrochemical cell, there are two components of interest: the electrodes and the membrane.

The electrodes are the conductive materials through which the electric current flows. By choosing copper as the material and a suitable catalyst, the application of a sufficiently high potential can achieve Faraday efficiency [2] of the order of 50%.

[1] The selectivity of a reaction is the ratio of the quantity of reactant consumed leading to the desired product to the total quantity of reactant consumed; [2] The Faraday efficiency of an electrolysis is the ratio of the number of moles of the desired product actually obtained to the number of moles of the desired product that would ideally be obtained. This yield may be less than 1

when an undesirable product has been formed.

1

2

The proton membrane:

The anion membrane:

The membrane separates the anode compartment from the cathode compartment. There are currently two types of membrane, each with its own distinct characteristics.

Photoreduction enables methane to be produced from CO₂ using only solar energy

Photoreduction involves the same equations as electroreduction, but differs in its durability. In electroreduction, a current flows between an anode and a cathode, allowing the reduction to take place. In photoreduction, the energy required for the reduction to take place comes solely from sunlight. In order to convert $\mathsf{CO}_2^{}$ into another carbon compound, a catalyst is required.

Description of the **CO₂ Photoreduction Process**

Photoreduction is a reaction that uses sunlight to convert $CO₂$ into methane

The most widely developed photoreduction technology is the coupled photovoltaic-electrochemical system. The energy required for the reaction is supplied by the photovoltaic cell. However, the electrochemical cell presents the same

Some are more selective than others, so a suitable catalyst must be chosen to promote the eight-electron reduction of CO $_2$ to methane. The selectivity of a process that reduces $\mathsf{CO}_2^{}$ and then CO to produce methane can theoretically reach 82%.

 $CO_2 + 8H^+ + 8e^-$ *light* \rightarrow *CH₄* + 2H₂O

challenges as for electroreduction, and only achieves TRL 2. Other systems without solar panels are also being studied, but their maturity is even lower.

There are still too many challenges surrounding photoreduction to envisage rapid development of this sector in the next few years

Description of the Photobioreaction Process

Micro-algae culture enables significant recovery of CO₂

Photobioreaction can be implemented in different types of reactors whose productivity and cost can vary significantly

Microalgae develop through photosynthesis. Since solar energy is the basis of photosynthesis, microalgae can be used to recycle CO₂ in a sustainable way.

 $CO_2 + H_2O$ *light* \rightarrow (CH₂O) + O₂

Thanks to this balance, the consumption of 1 kg of CO $_{\textrm{\tiny{2}}}$ enables the production of 0.6kg of biomass.

A wide variety of technological systems can be used to grow algae, with different characteristics and performance levels to suit different uses.

Some technical and economic data relating to these cultures

The rate at which sunlight is converted into chemical energy through photosynthesis can reach

To produce biogas, micro-algae are placed in a digester, where they ferment without oxygen. This produces biogas, which consists of

9%

Yields

Copyright photo PBR in plastic bag ©Phytolutions

.
opyright photo PBR in plastic bag ©Phytolutions:
ubular PBR, flat and open panels ©Ashley Roulst

Tubular PBR, flat and open panels ©Ashley Roulston - Industrial Plankton

Solutions under development

A major area of research involves increasing the size of electromethanogenesis cells. The planned development of 2 pilots over the next few years should enable the technology to reach TRL 6-7 (see the Biomethaverse project).

\mathbb{Q}

Developing a simple photocatalytic system in which there is neither an electrical circuit nor a membrane to overcome the limitations of electroreduction.

Summary of the 4 Emerging Sectors

Improving light diffusion in closed reactors.

Imperial College London

HyMAP project – Funded by the EU,

the project is developing new

that convert $\mathsf{CO}_2^{}$ into fuels.

<u>wimdea</u> energía

 $-\bigcirc$

 \bullet

materials and hybrid photocatalysts

THEIA project – Funded by the EU, this project is working on the development of new classes of photocatalysts. The project is scheduled

Robinson project – The main aim of the project is to develop an integrated energy system to help decarbonise islands. As part of this project, Leitat is developing a 1 $m³$ demonstrator.

M. n.

Biomethaverse project – Funded by the EU, the project brings together 22 partners from 9 European countries, including France. The ultimate aim is to increase biomethane production in Europe by 66%. In France, Engie is aiming to develop 2 pilots of $1m³$.

for completion in 2025.

Some Pioneering Projects for the Sector

Electromethanogenesis

LEITEIT

Photobioreaction

Advanced Algal Systems – Developinga longterm R&D strategy to reduce the cost of producing biofuels

from macro-algae.

O ENERGY

engicipin

Engicoin – Development, from TRL 3 to TRL 5, of three new microbial plants, integrated into an anaerobic digestion platform for organic waste.

CEA – Catalysts Ni/Fe bio-inspired by hydrogenase enzymes

Carboneo – Electrodes operating with catalysts abundant on the Earth's surface.

Sources

[Emerging sustainable technologies](https://innovation.engie.com/en/emerging-sustainable-technologies-2023) Gaspard Bouteau ENGIE, 2023

[Techno-Economic Analysis for the Production of Algal Biomass via Closed](https://www.nrel.gov/docs/fy19osti/72716.pdf) [Photobioreactors: Future Cost Potential Evaluated Across a Range of Cultivation](https://www.nrel.gov/docs/fy19osti/72716.pdf) System [Designs](https://www.nrel.gov/docs/fy19osti/72716.pdf) NREL, 2019

<u>Visible-light-driven methane formation from CO₂ with a molecular iron catalyst</u> Rao H., Schmidt L., Bonin J., Juin 2017

<u>Du CO₂ [aux hydrocarbures, un renversement salutaire](https://www.college-de-france.fr/fr/agenda/cours/du-co2-aux-hydrocarbures-un-renversement-salutaire)</u> Marc Fontecave Collège de France, 2014

Comparison of commonly used technologies for the cultivation of algae Schott, 2016

[Étude de catalyseurs à base de cuivre dérivés d'oxyde pour la conversion électrochimique](https://espace.inrs.ca/id/eprint/2768/) du CO et du CO₂ Claudie Roy, May 2015

[Microalgal bioreactors: Challenges and opportunities](https://www.researchgate.net/publication/227877162_Microalgal_Bioreactors_Challenges_and_Opportunities) Ling Xu, Pamela J. Weathers, Xue-Rong Xiong, Chun-Zhao Liu, Juillet 2009

[Direct biological conversion of electrical current into methane by electromethanogenesis](https://pubs.acs.org/doi/10.1021/es803531g) Bruce Logan, 2009

Anaerobic digestion

Sylvaine Berger – Solagro – Head of bioeconomy activity Ivan Desneulin – Solagro – Anaerobic digestion project manager Cristina Ferreira – TotalEnergies – Head of Biogas Department Alice L'Hostis – ATEE – Director of the CTBM Yves Le Roux – ENSAIA – Professor at the University of Lorraine-ENSAIA, holder of the Agrométha Industrial Chair Thierry Ribeiro – Institut Polytechnique UniLaSalle – Lecturer and researcher in Bioprocessing and Anaerobic digestion, holder of the Agricultural Anaerobic digestion and Transitions Chair Jean-Philippe Steyer – INRAE – Research Director

Power-to-methane

Gianfranco De Feo – MicroPyros – CEO Vincent Guerré – Enosis – Chairman Marion Guillevic – Energo – Business Development Director Tahar Melliti – Khimod – Member of the Executive Board Vincent Piepiora – Energo – CEO

Pyrogasification

Ammar Bensakhria – UTC – Lecturer and researcher Anthony Kerihuel – S3D Ingénierie – CEO Chourouk Nait Saidi – ATEE – Club pyrogazéification General Delegate

Hydrothermal gasification

Sebastien Quenard – CEA – R&D engineer – Technological Research Division Joël Tanguy – Nevezus – Chairman and Founder

Photobioreaction, electromethanogenesis and other emerging processes

Gaspard Bouteau – Engie – Lab Crigen – Green gas research engineer Isabelle Rougeaux – CEA – Research engineer at CEA LITEN/LVME

Editorial team

Garazi Alcalde, Laurent Blaisonneau, Thomas Deronzier, Aurélie Dhavernas, Albain Ferchal, Bertille Guénégo, Timothé Husser, Baptiste Kas, Hélène Stéphan, Salma Zouari

Process expertise

Laetitia Aubeut Chojnacki, Leo Benichou, Luc Budin, Gaëtan Courtecuisse, Eric Feuillet, Toinou Frezouls, Sami Ghardaddou, Étienne Goudal, Alice L'Hostis, Vincent Jean-Baptiste, Cédric Jolivet, Malika Madoui-Barmasse, Chourouk Nait Saidi, Étienne Philippe, Bastien Praz, Tristan Rigou, Amélie Sanz

Contributors

