

Research & Innovation

Overview of Green Gas Technologies



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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.

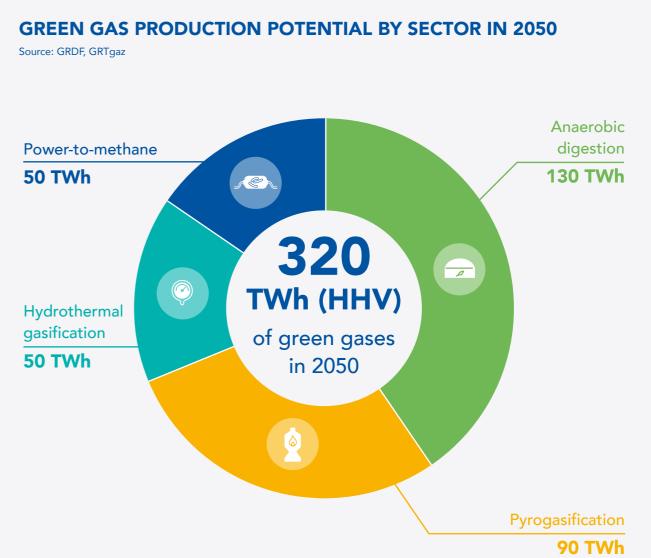
By 2030, green gases could account for 20% of French gas consumption; by 2050, France has the potential to cover 100% of its demand with green gases. The industry estimates that the realistic potential for renewable, low-carbon methane production by 2050 is 320 TWh. In recently published scenarios, gas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

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.

(?)

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). 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:

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

Editorial



Hugues MALINAUD, Director of Research, Innovation and Development

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 'Overview 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.

'To 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.'

Glossary

AD	Anaerobic Digestion	К	Potassium
ADEME	French agency for ecological transition	LNG	Liquified Natural Gas
Ag	Silver	Ν	Nitrogen
BMP	Biochemical Methane Potential	NGV	Natural Gas Vehicle
BPA	Biomethane Purchase Agreement	NH ₃	Ammonia
С	Carbon	Ni	Nickel
Ca	Calcium	O ₂	Dioxygen (commonly referred to a
CAPEX	CAPital EXpenditure	OFB	French Office For Biodiversity
CCUS	Carbon Capture, Utilisation and Storage	O&G	Oil & Gas
CEA	French atomic energy and alternative energies commission	OM	Organic Matter
CH ₄	Methane	OPEX	OPerational EXpenditure
CxHy	Hydrocarbons	ORP	Open Raceway Pond
со	Carbon monoxide	Р	Phosphorus
CO2	Carbon dioxide	PBR	PhotoBioReactor
CSF	Strategic sector commitees (part of French industry council)	рН	potential of Hydrogen
СТВМ	National technical centre for biogas and anaerobic digestion (France)	PSA	Pressure Swing Adsorption
DGEC	Directorate-General for Energy and Climate	PV	PhotoVoltaic
	(part of the French Ministry of Ecological Transition)	R&D	Research & Development
DM	Dry Matter	RDF	Refuse-Derived Fuel
EC	ElectroChemistry	RED II	Renewable Energy Directive II
EPC	Engineering Procurement & Construction	RM	Raw Matter
Fe	Iron	SAF	Sustainable Aviation Fuel
FI	Agri-Food Industry	SCFAs	Short-Chain Fatty Acids
H ₂	Dihydrogen (commonly known as Hydrogen)	SNG	Synthetic Natural Gas
ha	Hectare	VOCs	Volatile Organic Compounds
HDPE	High-Density PolyEthylene	WWTP	WasteWater Treatment Plants
H ₂ S	Hydrogen Sulfide	TRL	Technology Readiness Level
HTG	HydroThermal Gasification	tRM	tonne Raw Material
ISDND	Non-hazardous waste storage facility (French classification)	Zn	Zinc

to as Oxygen)

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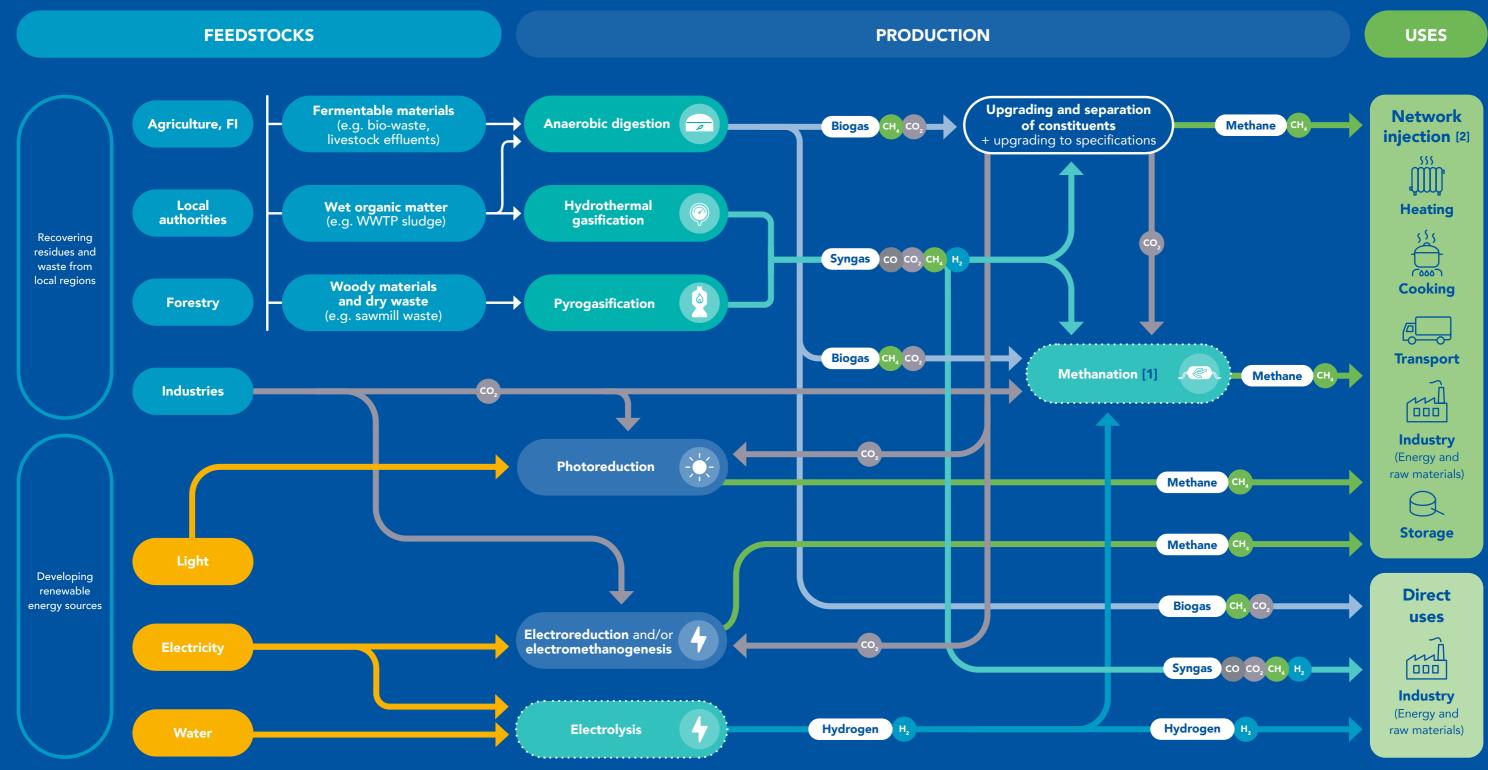
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Each Feedstock has its Own Technological Building Block for Producing Green Gases



[1] Power-to-methane is the production of methane by methanation of CO, and H, from electrolysis. It will be analysed in more detail later.

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

Emerging technologies



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

The Different Processes for Producing Green Gases

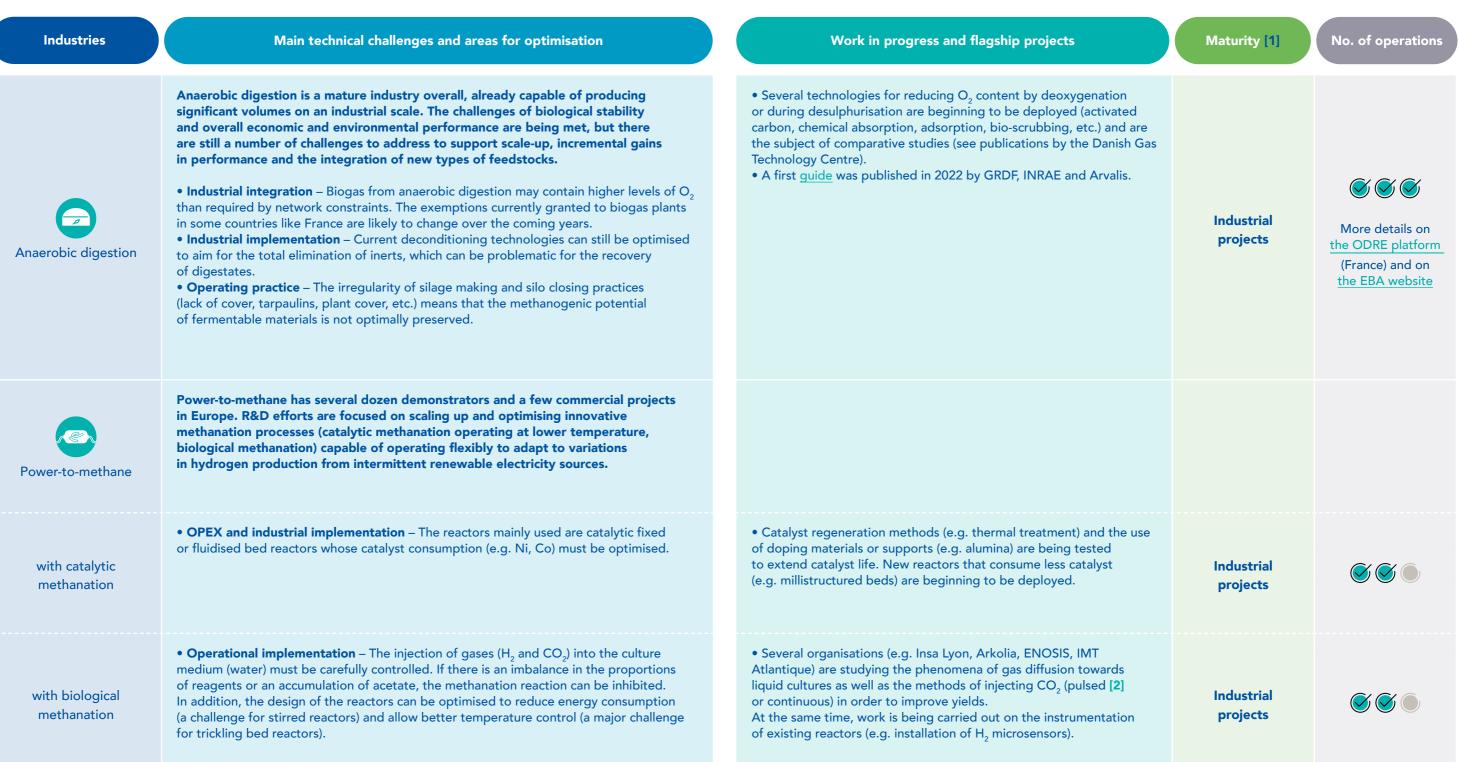
Each process has its own specific operating conditions

Industries	Main feedstocks	Description of the production process		Parameters		Other recoverable products
			Temperature (T)	Pressure (P)	Energy efficiency	
Anaerobic Digestion	Fermentable matter	Exploitation of the natural biological process of degradation of organic matter in the absence of oxygen, through the action of anaerobic organisms or methanogens, to obtain biogas and digestate inside the anaerobic digester.	35 – 60°C	<10 bar	80 – 85%	– Digestate (fertiliser) – BioCO ₂
R	Electricity, water	An electrochemical conversion chain that converts electrical energy into energy. Electricity is used to produce hydrogen (by electrolysis), which is recombined with CO ₂ to synthesise	Catalytic methanation 200 – 600°C	1 – 15 bar	<u>&</u>	– Water
Power-to-methane	and CO ₂	methane in a methanation reactor (catalytic or biological).	Biological methanation 35 - 65°C	<10 bar	50 – 65% [1]	– Heat (for catalytic methanation)
	Woody materials	and in the absence of oxygen to obtain synthesis gas (syngas), 800 – 1500°C < 10 bar			eric 25 - 65%	– Oils – Coal (especially
Pyrogasification	and dry waste (<20% moisture)		<10 bar		for pyrolysis) – Heat – (Bio)CO ₂	
(Wydrothermal gasification	Wet organic matter (>50% moisture)	High-temperature, high-pressure thermal treatment of wet materials to obtain synthesis gas and valuable by-products (mineral salts and water).	400 – 700°C	250 – 300 bar		– Mineral salts – Water – (Bio)CO ₂
C Electromethanogenesis	CO ₂ , H ₂ O, electricity	A bioelectrochemical process involving micro-organisms that reduce CO ₂ to methane by applying a low electrical voltage between two electrodes.	200 – 300°C	<10 bar	little data available	N/A
\mathbf{CO}_2 electroreduction	CO ₂ , H ₂ O, electricity	Electrochemical process for reducing CO ₂ to another carbon molecule such as methane, methanol or formic acid by applying an electric current.	200 – 300°C	<10 bar	little data available	N/A
CO ₂ photoreduction	CO ₂ , H ₂ O, light	An electrochemical process similar to electroreduction, in which the energy supplied by the electric current is replaced by sunlight.	<100°C	<10 bar	little data available	N/A



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

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



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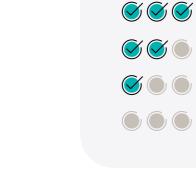
Number of operations worldwide

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

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

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

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



	Industries	Main technical challenges and areas for optimisation	Work in progress and flagship projects
F	Pyrogasification	 Pyrogasification is based on mature technology that has been tried and tested for several decades, and has traditionally been used for heating and cogeneration. Over the last ten years or so, the industry has been moving towards the production of molecules, including synthetic methane, making it necessary to carefully integrate the syngas cleaning and enrichment stages into the process chain to achieve the desired quality. With a handful of demonstrators and references already underway in Europe, the industrialisation of methane production by gasification is gathering pace, against a backdrop of decarbonisation, energy security, and better waste management. Projects are being set up to make the most of local, renewable or recovered feedstocks. Industrial use – For molecule production, it is preferable to avoid the presence of nitrogen upstream of the syngas conversion stages, in order to optimise costs by avoiding oversizing the downstream building blocks or a nitrogen separation stage. Industrial implementation – Technologies are mature, but little use has been made of syngas from biomass and waste in the grid (lack of competitiveness compared with fossil gas and lack of public support for the first industrial demonstrators). Controlling the syngas cleaning before the methanation unit is important to avoid the process on an industrial scale, it will be necessary to develop good control over the supply of feedstocks and the pre-treatments applied in order to limit variability in their quality, optimise the production of clean syngas and avoid degradation of the equipment. 	 Gasification technologies are being adapted to generate the necessary heat without injecting air directly into the gasifier (oxysteam process, plasma or electric heating, separation of the combustor from the main bed). The introduction of calls for projects in future years could lead to the development of demonstration units on an industrial scale (see mapping projects being set up in France).
	O Hydrothermal gasification	 Hydrothermal gasification is a relatively recent development in energy production technologies. It has however benefited from a significant R&D drive in Europe in recent years thanks to its ability to address (at a high temperature and high pressure) wet and polluted waste that is difficult to recycle. Several European companies, mainly in the Netherlands and Switzerland, have set up pilots and demonstrators to work on high-pressure injection, salt separation, reactor design, thermal integration and optimisation to address the main technical hurdles to the industrial emergence of the process. Industrial implementation – Pre-treatment must be controlled according to the nature of the feedstocks (grinding, adjusting the moisture content, etc.) to ensure pumpability and optimum operation of the plant. Controlling CAPEX and OPEX costs – The process requires expensive materials (high pressure combined with high temperature and corrosion issues) and can consume expensive catalysts, the life of which must be maximised. By working on the economic balance of projects, the competitiveness of the industry can be improved by optimising 	 New feedstock injection and salt separator technologies are beind developed (e.g. a new pump and separator patented by CEA as profit the Gazhyvert project that started in 2021). Existing laboratories, including PSI (Paul Scherrer Institut), PNNL (Pacific Northwest National Laboratory) and KIT (Karlsruhe Institute of Technology), are studying catalyst recycling and the efficiency of sulphur traps. The design of suitable alloys and the extension of their service life are also major areas of reset. A first industrial high-temperature hydrothermal gasification platfor injection was already put into operation in 2018 in Alkmaar, the Netherlands, by SCW Systems.

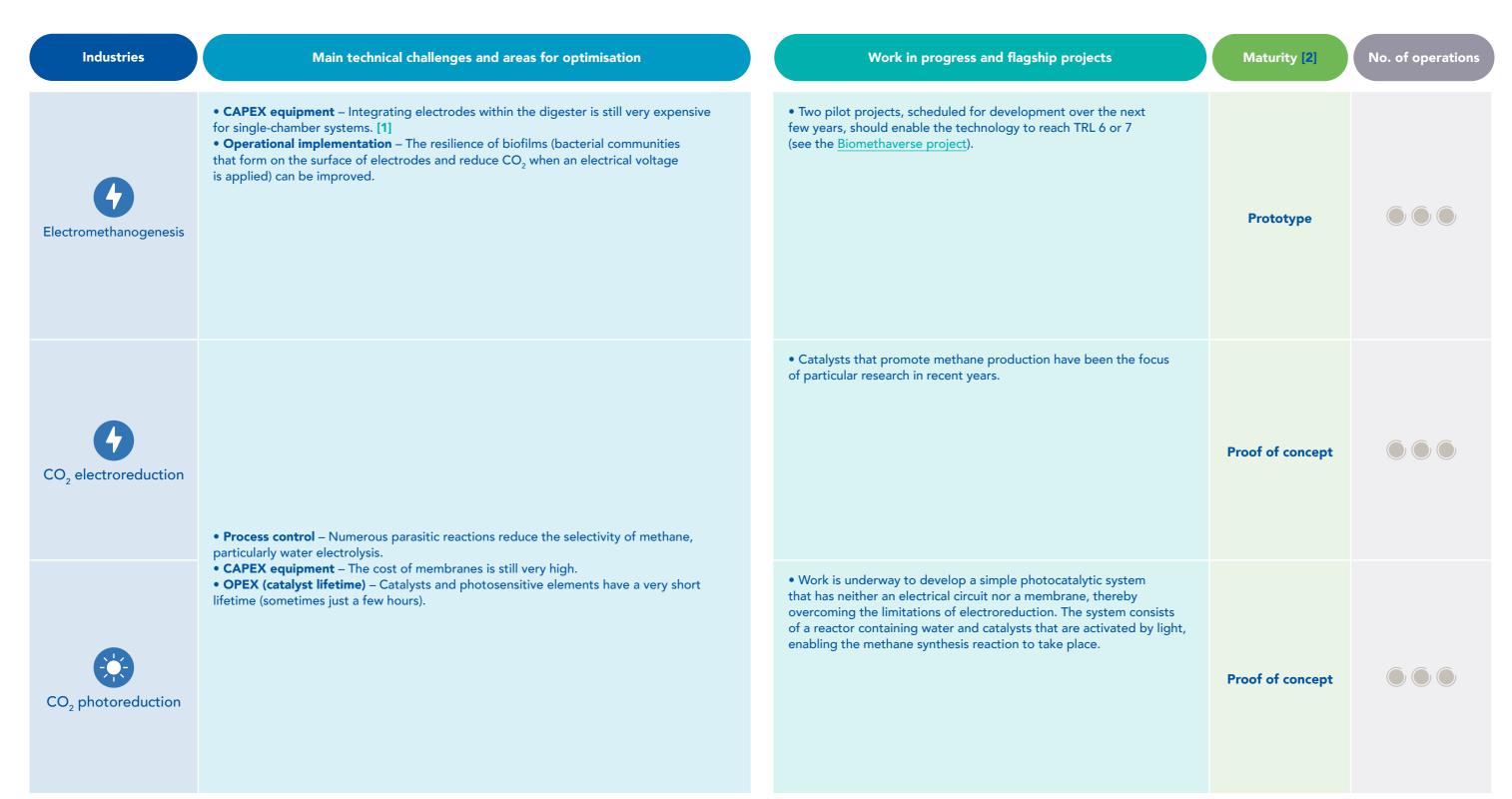
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- Only demonstrators or pilots in operation
- Some pilot or laboratory-scale units



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

Less mature sectors are emerging thanks to R&D work



[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

Number of operations worldwide

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

Anaerobic Digestion



What is Anaerobic Digestion?

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

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_4 and CO_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).

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:

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

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



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.

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



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

Anaerobic digestion produces a biogas made up of 50 – 60% CH_{4} , 35 – 40% CO_{2} and containing water vapour and traces of H_2 , O_2 , NH_3 and H_2S . 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, pH and water content, which takes place in 4 phases.

Proportion by mass of the mixture Dry route

btw. 25% and 40% btw. 60% and 75% dry matter H,O Infinitely mixed route [1] over 85% less than 15% dry matter H,O

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 CO₂ and H₂) by bacteria.

ACETOGENESIS leads to the production of acetate from H₂ and CO₂ by homoacetogenic bacteria, and the production of acetate, H₂ and CO₂ from the short-chain fatty acids produced by acidogenesis.

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

 $1 - \text{Reduction of CO}_2$ by H₂ (produces 30% of methane).

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

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

 $CH_{COOH} \rightarrow CH_{A} + CO_{2}$

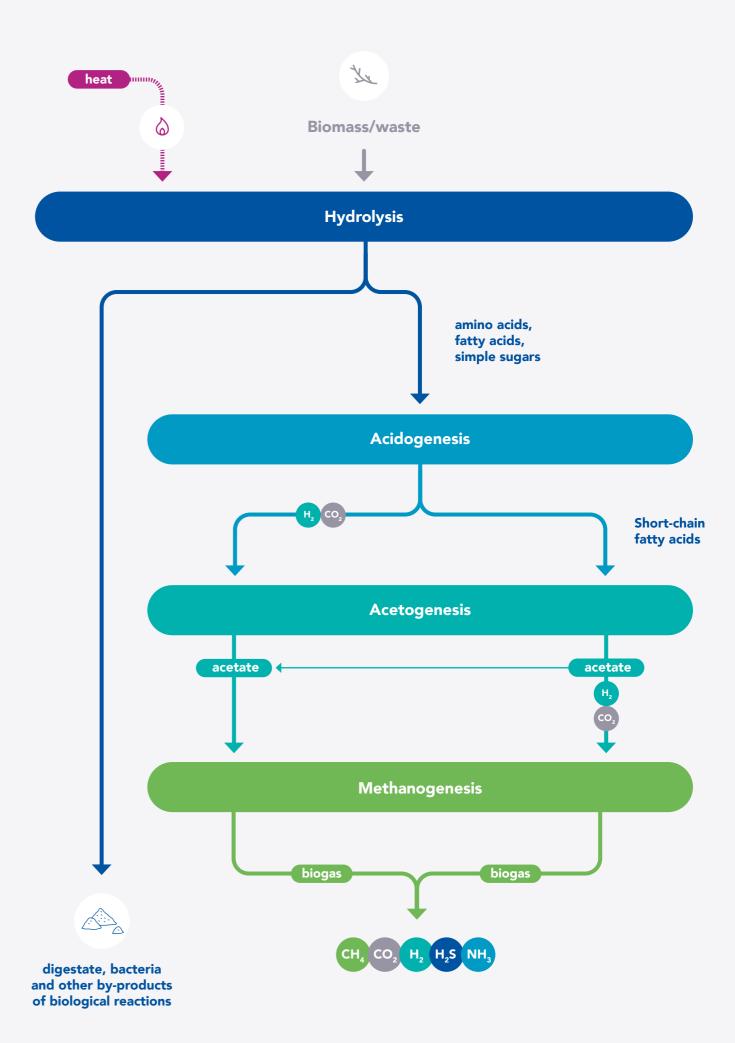
Proportion by mass of products and by-products



6% CO.

Proportion by volume of gaseous products

60%		35%	
CH ₄ (gas)		CO ₂ (gas)	
	5% H _{2'}	H ₂ S, H ₂ O, NH ₃	(gas)



[1] A low level of dryness can be maintained if necessary by recirculating digestate; [2] This temperature will be lower during operation to maintain the biological process in the following stages.

Anaerobic Digestion, a snapshot

80-85% **ENERGY EFFICIENCY**[1]

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.



10 to **450** Nm³ /tRM

BIOMASS - BIOGAS YIELD [2]

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: Application for calculating greenhouse gas emissions from anaerobic digestion plants;
- [4] Figures based on feedback from the industry.

0.3-1 hectares 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 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.

50 to 60 k€ per Nm³/h [4] CAPEX

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.



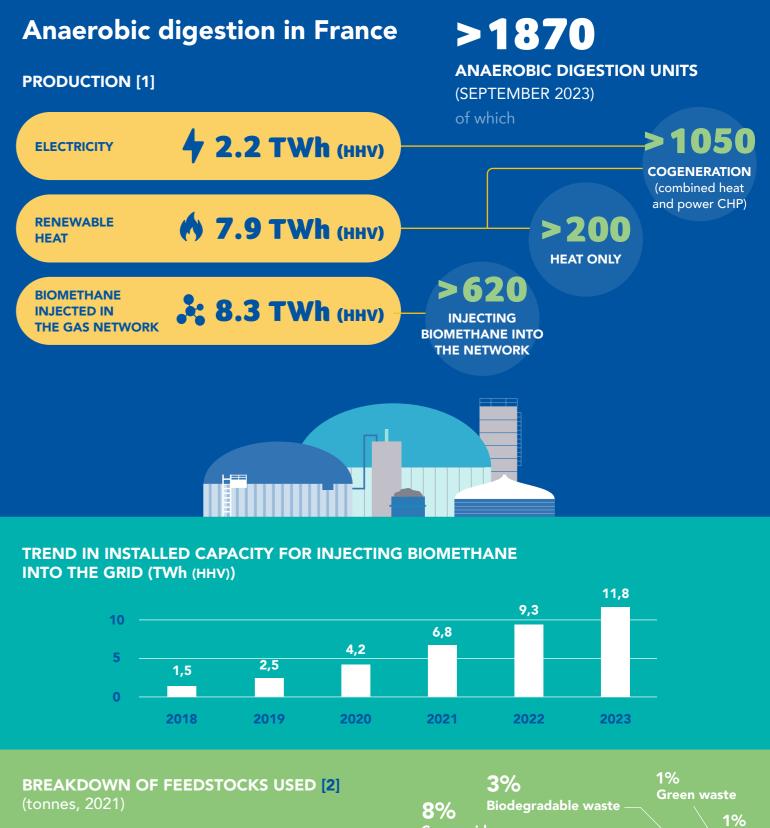
Industry Dynamics

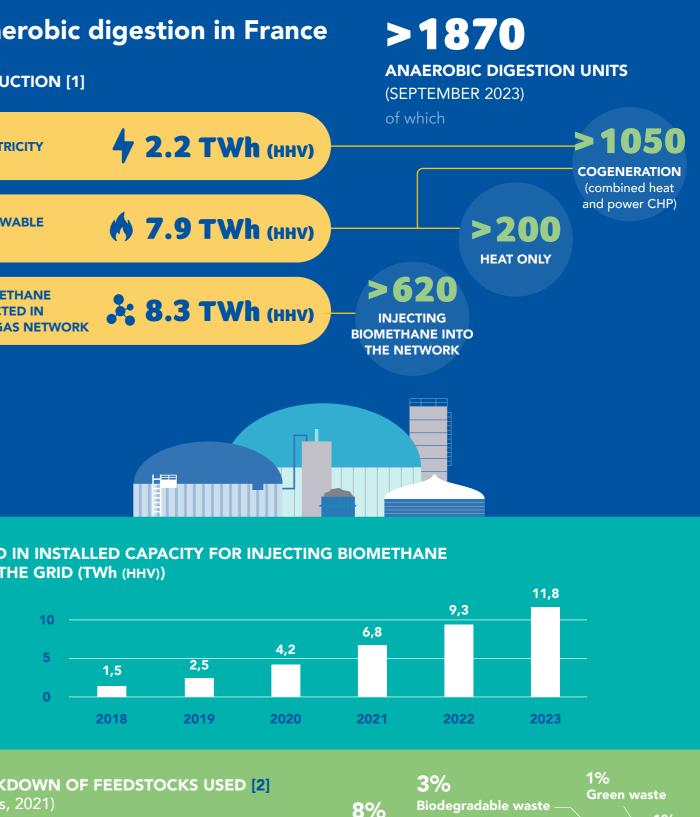
Anaerobic digestion for injection has been widely deployed over the last decade, particularly in Europe

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.









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;
 Négawatt& Solagro, <u>Anaerobic digestion in the energy mix</u>.

Crop residue

13%

WWTP sludge and

co-products of agro-industries

Others

Some Pioneering Projects for the Sector

FRANCE

CVO LILLE

Since 2011 Lille métropole

STATUS

Operating

PROJECT INITIATOR Suez/ENGIE

SIZE

180 Nm³CH₄/h

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.

FEEDSTOCKS

PRODUCTION

into the grid

Biodegradable waste

Biomethane for injection

and green waste



BRIE BIOENERGY

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

STATUS

Operating

PROJECT INITIATOR Farmers SIZE

125 Nm³CH₄/h

PRODUCTION Biomethane for injection into the grid

crops, food co-products,

FEEDSTOCKS

crop residues

Livestock effluents,

Intermediate energy

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 bioCO₂ 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.

BIOVALSAN Since 2015 Strasbourg	
STATUS	FEEDSTOCKS
Operating	Sewage sludge
PROJECT INITIATOR	PRODUCTION
GDS/Suez	Biomethane
SIZE	for injection
200 Nm ³ CH ₄ /h	into the grid

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

Operating

PROJECT INITIATOR

Farmers

SIZE 120 Nm³CH₄/h

FEEDSTOCKS

Livestock effluent, biodegradable waste

PRODUCTION

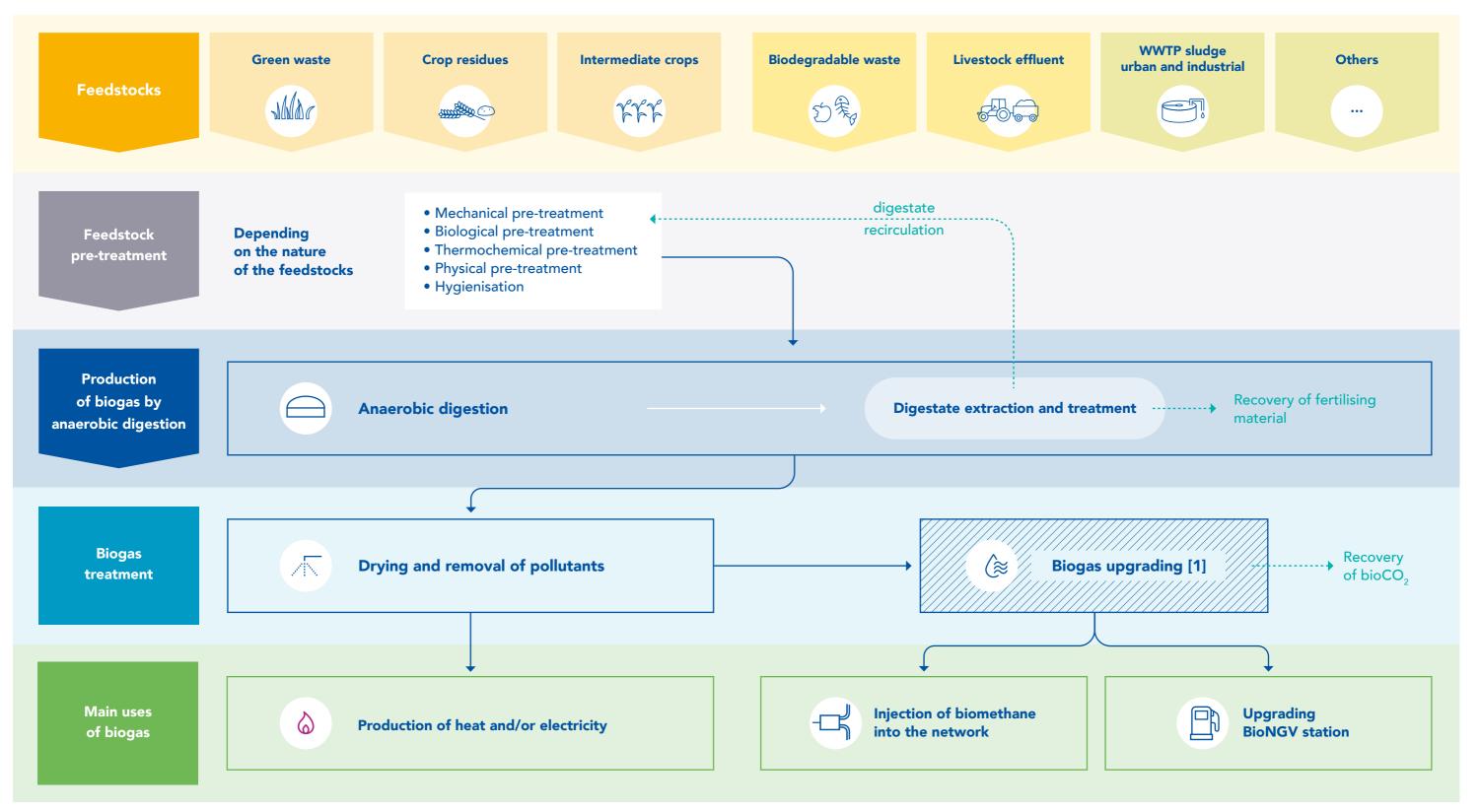
Biomethane for injection into the grid

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



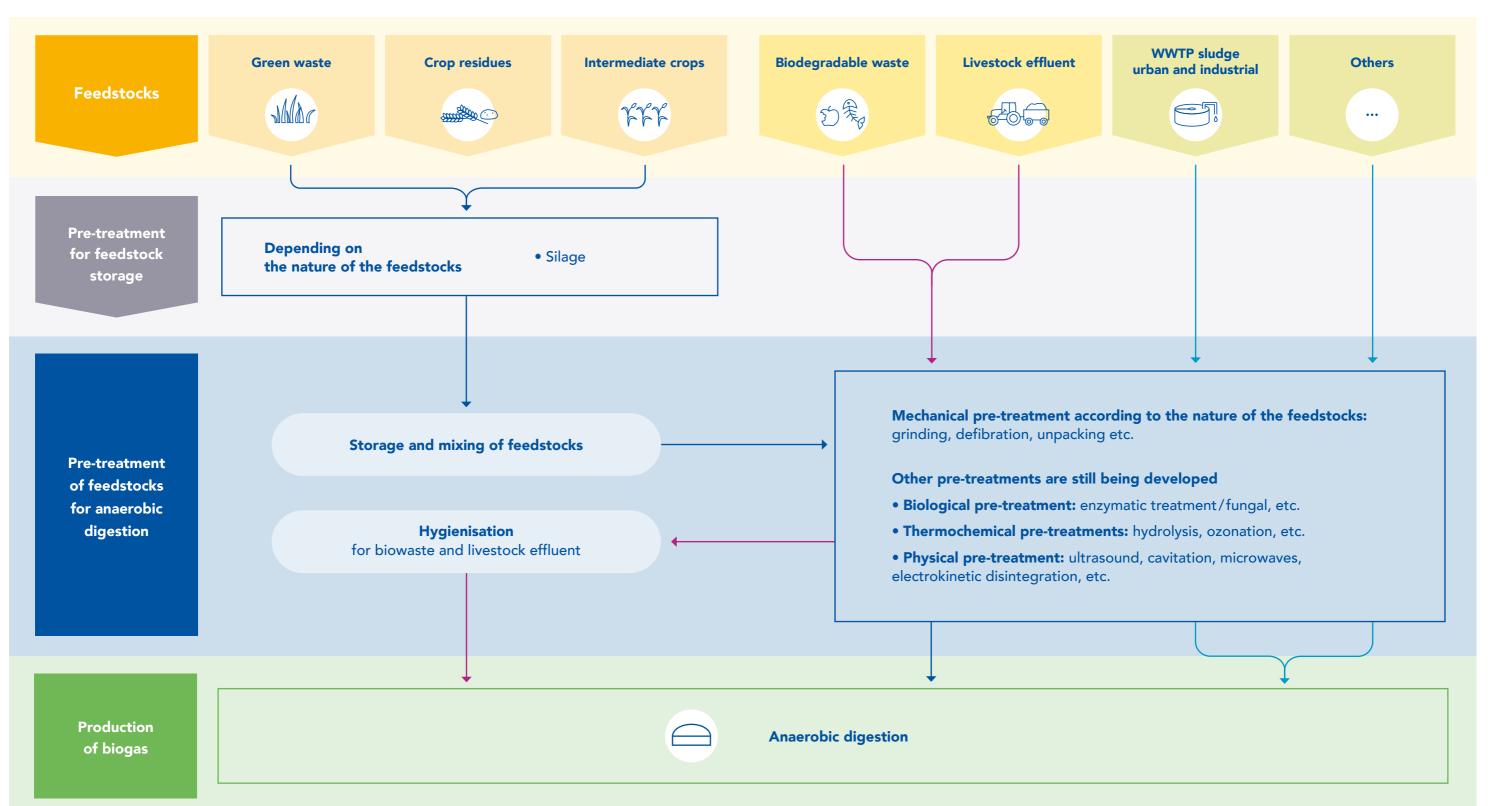
Mapping of the Biogas Production Chain by anaerobic digestion





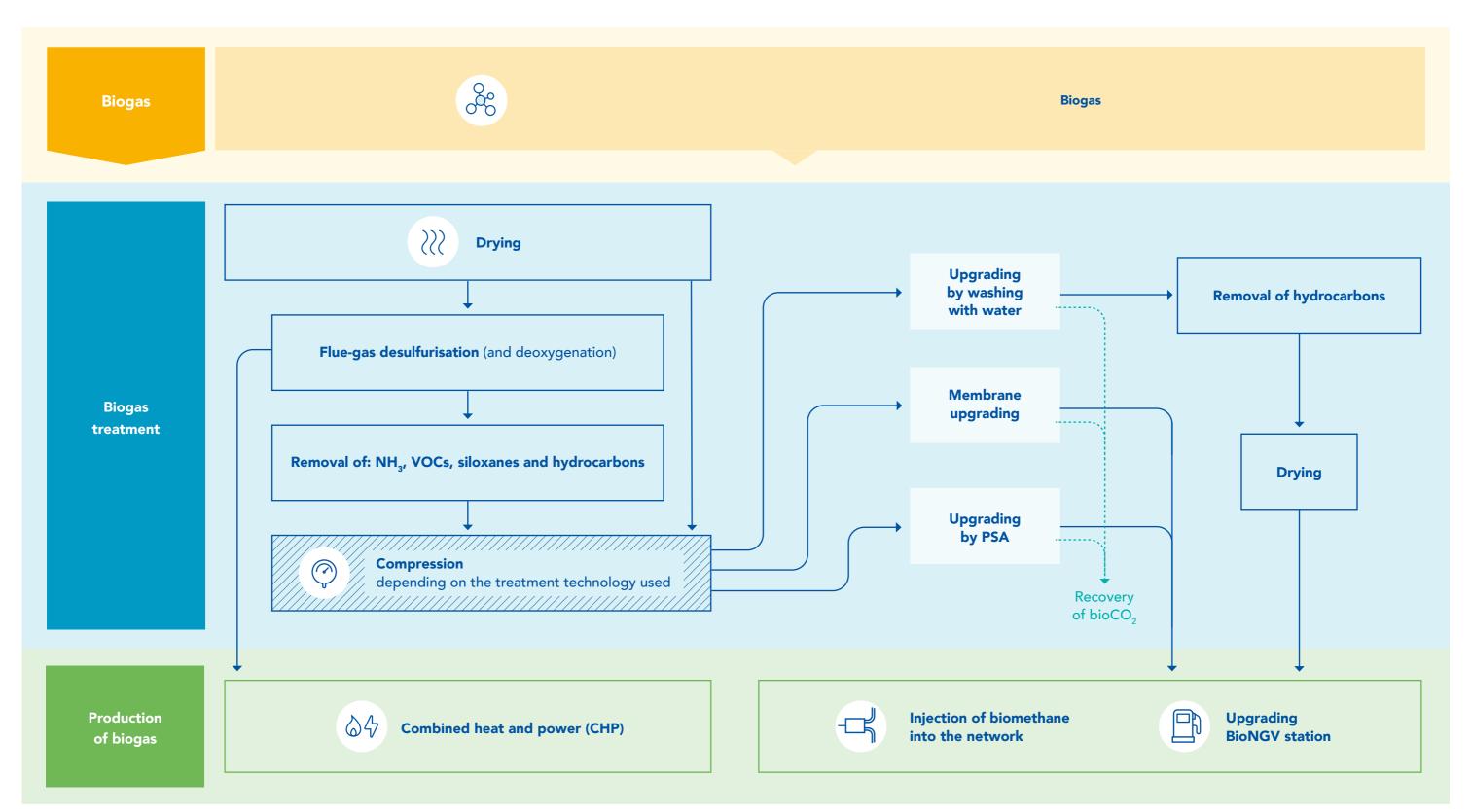
Focus on the Pre-treatment Chain for Anaerobic Digestion Feedstocks





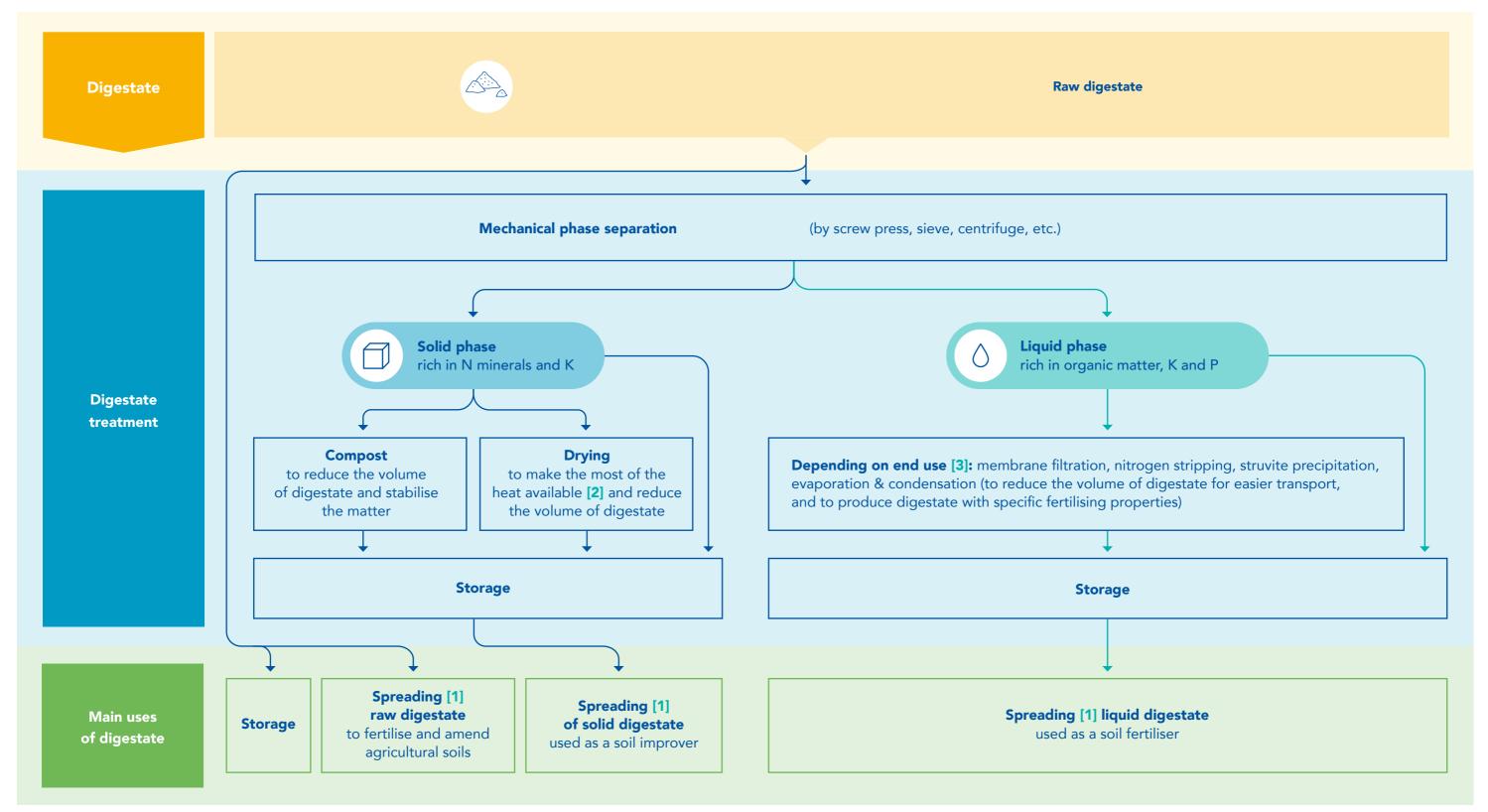
Focus on the Biogas Treatment Chain





Focus on the Digestate Treatment Chain





[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.



KEY

An important challenge

described in more detail

for the industry,

later in the report

1

for/before storage

of feedstocks

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

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

No solution yet in development to meet this challenge,

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R&D s

Technical challenges in the sector

Integrating new digestion feedstocks

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

Pre-treatment of feedstocks for digestion The 'infinitely 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.

Better treatment of microplastics

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. 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.

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. → <u>See focus on MethaPlanet</u>.

No new developments to date.

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 'soups' after deconditioning will be to improve monitoring.

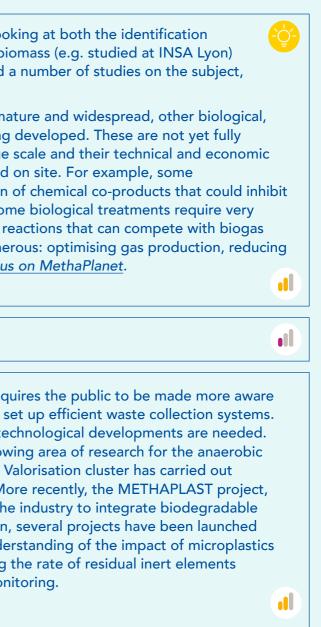
[1] Mincers, grates, recirculating mills, etc.;

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

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

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

R&D solutions and innovations





Technical challenges in the sector



In some countries like France, the O₂ content of biomethane produced by anaerobic digestion can currently be exempted from network specifications for the physico-chemical characteristics of natural gas. Given the expected increase in the volume of biomethane injected in the coming years, identifying and characterising the technologies that can reduce the O₂ content of injected biomethane is becoming a priority for the development of the sector.



R&D solutions and innovations

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 O₂ 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.

Several ways of recovering CO₂ 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 CO₂ and bringing it up to the technical specifications of the targeted uses. A guide 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, 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 1 (Rytec GmbH), etc.

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 . and water that can be reused in agriculture.

Biogas treatment

Digestate

treatment

P Recovering biogenic CO, from anaerobic digestion

Biogas is made up (by volume) of around 35% CO₂, separated from CH₄ for injection, and often released directly into the atmosphere. Recovering CO₂ 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.

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.

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

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

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

Q



Technical challenges in the sector

P Facilitating the development of anaerobic digestion for small units

Injecting biomethane into networks requires biogas upgrading, which can be very costly for small units (up to a few dozen Nm³/h).

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.

Global integration of the technical bricks

Optimising energy consumption

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.

R&D solutions and innovations

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 Nm^{3}/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.

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 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.

• 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 1 at a competitive cost.

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.). 1

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

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

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



Technical challenges in the sector

© Optimising plant size by reducing residence time

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

P Responding to parameter divergence

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.

B Measuring and reducing fugitive emissions

In addition to greenhouse gas emissions (in particular CO₂ and CH₄) 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.

Better anticipation of maintenance

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.

R&D solutions and innovations

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.

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

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.

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

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.

Global integration of the technical bricks

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

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

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

1

11

Focus on Three Challenges (1/2)

Adapting deconditioning technologies

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, 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 'soups' of bio-waste available to methanisers.



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



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

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 <u>guide</u> 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.

Focus on Three Challenges (2/2)

Reducing the oxygen content in biomethane before injection

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 O_2 content of injected biomethane is becoming a priority for the development of the sector.

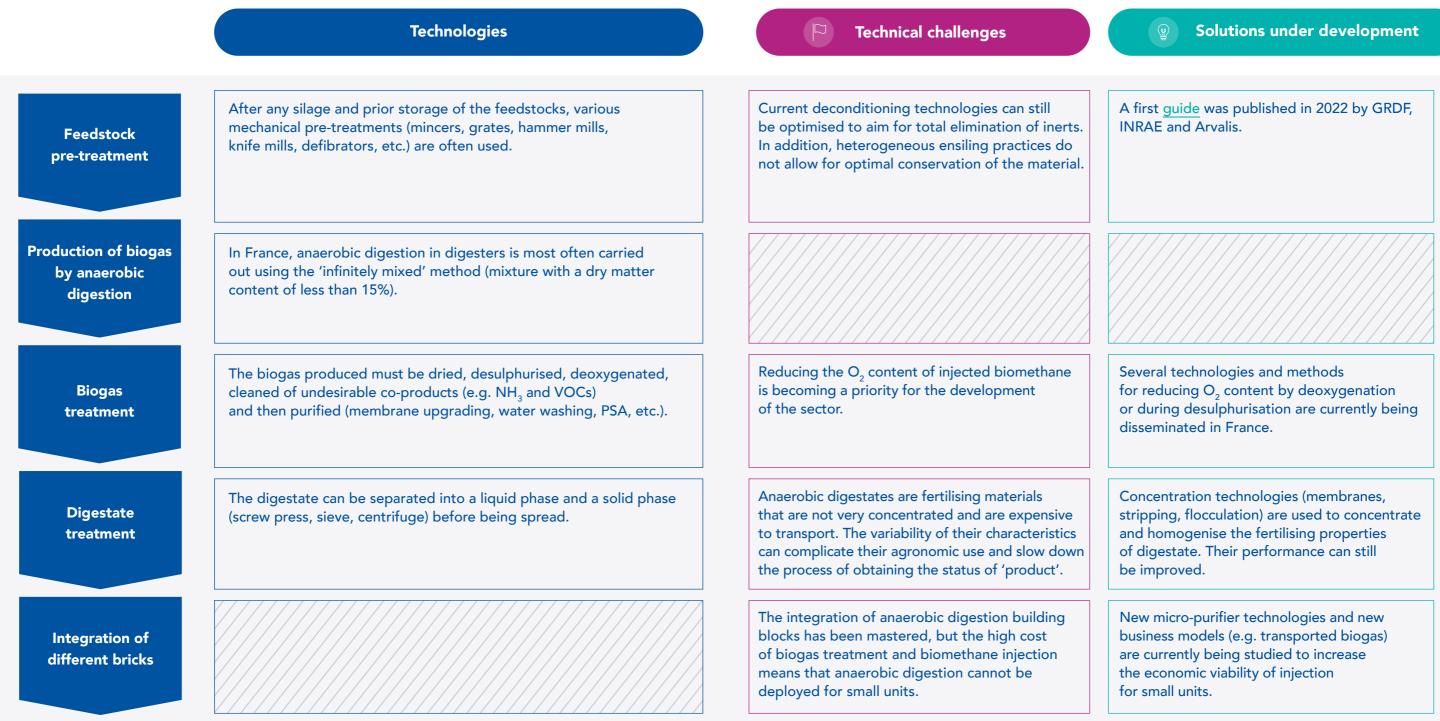
A number of direct biogas deoxygenation processes have been developed over the last decade and are receiving increasing attention from the industry. They are, however, not yet fully technologically mature and are often associated with high costs (e.g. catalytic oxidation). Nevertheless, it is already possible to reduce the O₂ 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.



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)

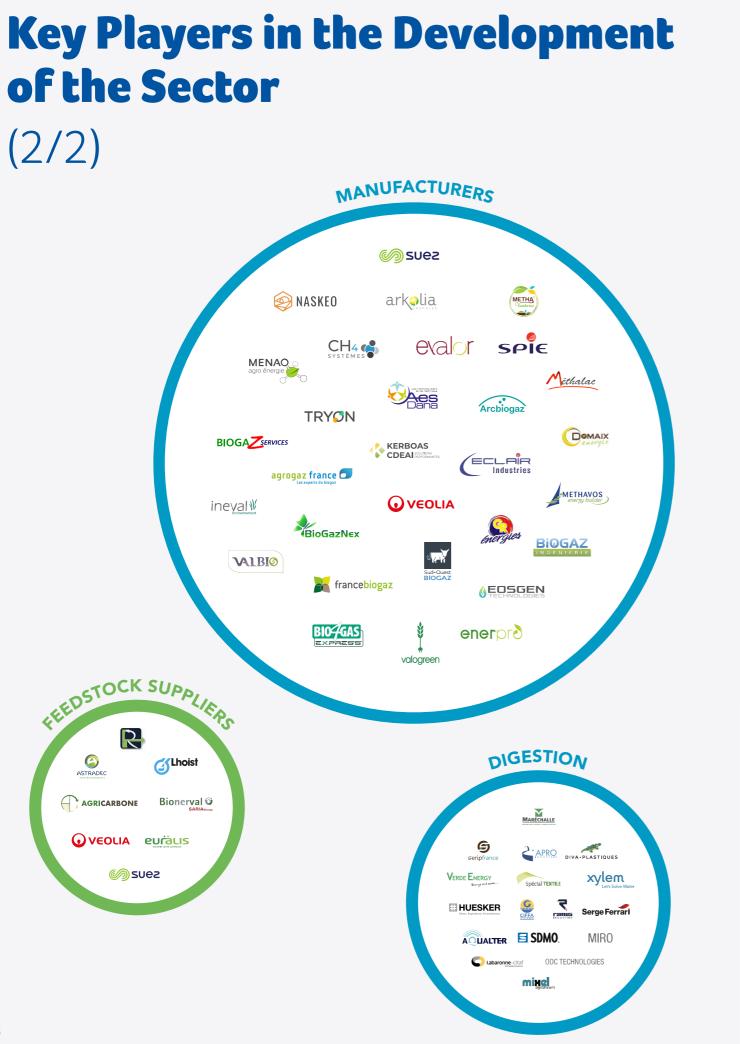
Non-exhaustive list (which does not include plant operators [1]). All companies below are listed by ATEE in a directory available at this LINK.



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.



Challenges: integrating new feedstocks and unlocking





Challenge: facilitate the development of anaerobic digestion for small units

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.

Greenmac, which specialises in biogas upgrading, has designed Bio-Up, a small-scale upgrading system (units with a flow rate of a few dozen Nm³/h): CO₂ is separated from CH₄ 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.

Sources

The main French players in the sector are federated by the ATEE Biogas Club.



L'observatoire de la filière biométhane ODRE, 2023

Tableau de bord: biogaz pour la production d'électricité Ministry of Energy Transition, 2023

Comment optimiser les ensilages de CIVE? GRDF & INRAE & Arvalis, 2023

The impact of anaerobic digestate on soil life: a review

van Midden et al., 2023

A critical review on the techno-economic feasibility of nutrients recovery from AD

Rizzioli et al., 2023

<u>Focus sur les intrants en méthanisation: stockage, prétraitements & optimisation</u> Métha'Normandie, 2023

Les matières organiques

MéthaFrance, 2023

Panorama des gaz renouvelables en 2022

GRDF, GRTgaz, SER, SPEGNN, Téréga, 2023

Carte des unités de méthanisation et de biogaz SINOE, 2023

La méthanisation dans le mix énergétique

Solagro & négaWatt, 2021

Les solutions de déconditionnement des biodéchets emballés et leurs performances ADEME, 2021

Desulphurisation of biogas: a systematic qualitative and economic-based quantitative review Okoro et al., 2019

Pretreatment of agricultural biomass for AD: current state and challenges Paudel et al., 2017

Gestion et traitement des digestats issus de méthanisation

IFIP, Agricultures & territoires, IDELE, Trame, 2017

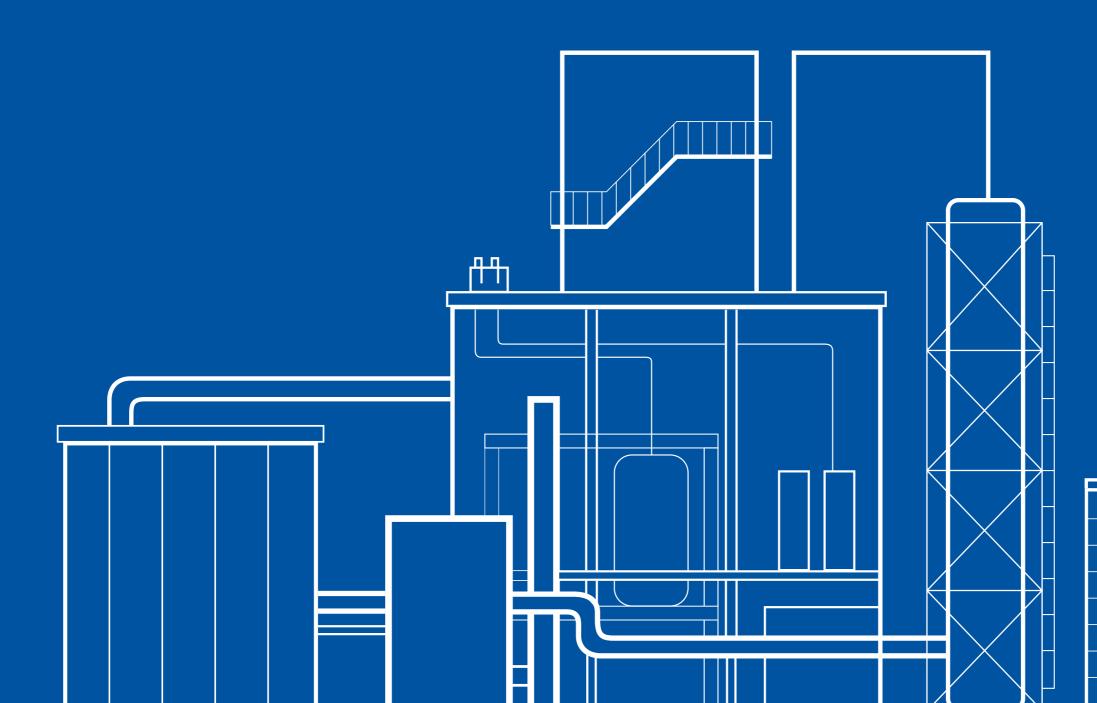
Inventaire et performances des technologies de déconditionnement des biodéchets ADEME & AEFEL, 2016

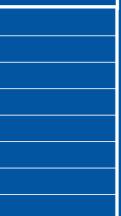
DIGES 2

Bioteau et al., 2009



Power-to-methane







METHANATION BUILDING BLOCKS

What is Power-to-methane?

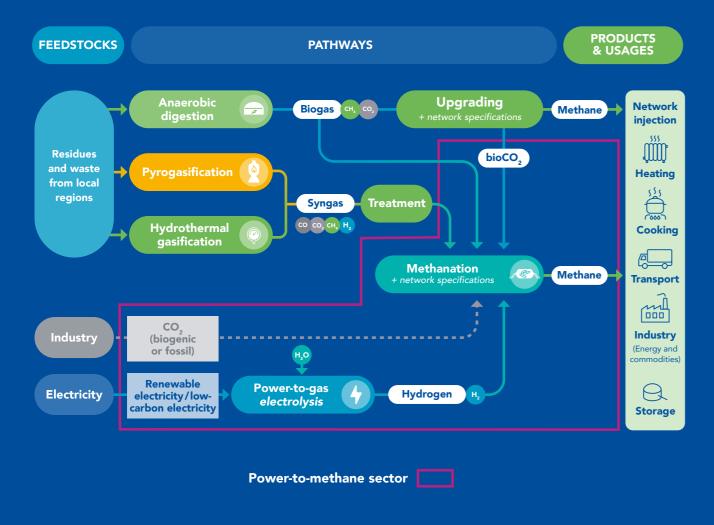
What is Power-to-methane?

Power-to-methane consists of 2 stages:

- a water electrolysis stage during which electricity is consumed to produce hydrogen H_2 [1] (and oxygen O_2 as a co-product),

- then a methanation stage during which the hydrogen from the electrolysis and the CO₂ from capture or purification (industrial source or anaerobic digestion) are converted into methane through a biological or chemical reaction.

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



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].

Å **Catalytic methanation**

Catalytic methanation is a continuous reaction allowing the formation of CH₄ from H₂, CO₂ 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

Biological methanation takes place in an anaerobic environment in the presence of H₂ 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 CO₂ (standalone) or by supplying a biogas/syngas containing CO and/or CO₂ (upgrade).

[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.



METHANATION BUILDING BLOCKS

Description of the Catalytic Methanation Process

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

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 CO_2 (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_2 recovery issues.

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. **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.

CO ROUTE

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

CO₂ ROUTE

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

Direct methanation: CO₂ + 4H₂ \rightarrow CH₄ + 2H₂O + heat

Indirect methanation:

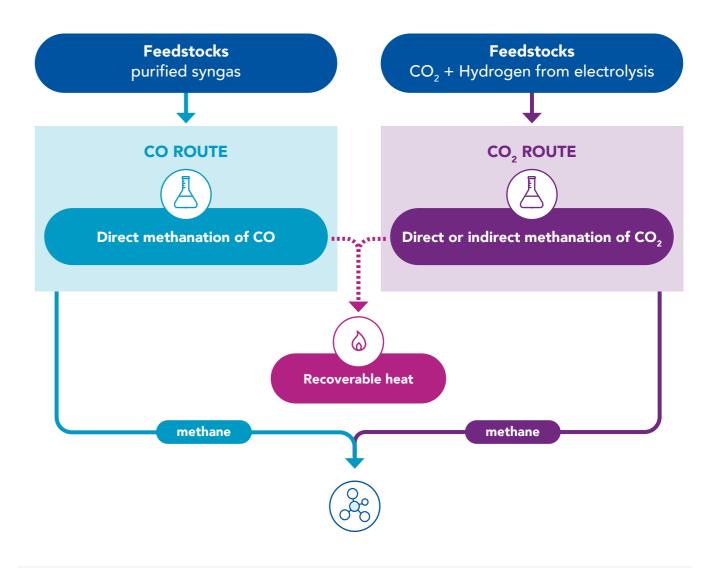
(1) $CO_2 + H_2 \longrightarrow CO + H_2O$ (Reverse Water-Gas-Shift) (2) $CO + 3H_2 \longrightarrow CH_4 + H_2O + heat$

[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;

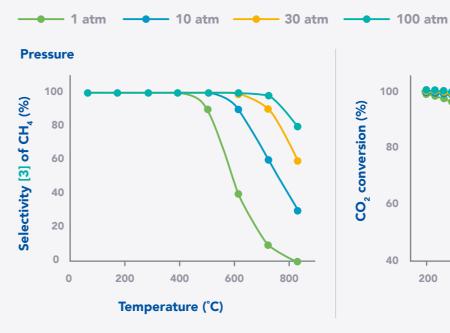
[3] The selectivity of a chemical reaction specifies the quantity of desired product formed (in this case CH_4) in relation to the number of moles consumed of the limiting reactant (in this case CO_2). It indicates whether several reactions are occurring in parallel, leading to unwanted co-products;

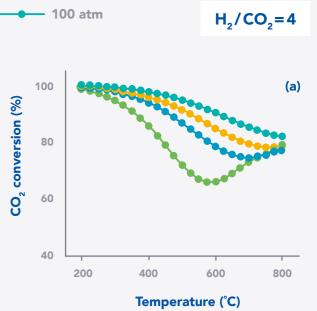
[4] In the catalytic methanation reaction, the most favourable reaction is with CO because it is direct.



THE CATALYTIC METHANATION OF CO $_{\rm 2}$ IS ENHANCED AT LOW TEMPERATURE (<300°C) OR AT HIGH TEMPERATURE AND HIGH PRESSURE

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].





METHANATION BUILDING BLOCKS

Description of the Biological **Methanation** Process

Biological methanation produces methane in the presence of micro-organisms

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.

Biological methanation can be carried out ex situ (in a dedicated reactor, leading to the formation of CH₄ from gaseous feedstocks: pure CO₂, biogas or syngas) or in situ (directly in an anaerobic digester, for example, by adding H₂ to the substrates that supply the carbonaceous matter and micro-organisms).

FEEDSTOCKS are injected at

pressures below 10 bar in gaseous form into the reactor under anaerobic conditions (without O₂). 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.

METHANATION BY THE INDIRECT ROUTE

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

Carboxydotrophic acetogenesis:

 $4CO + 2H_{2}O \rightarrow CH_{3}COOH + 2CO_{2}$

Homoacetogenesis: $2CO_2 + 4H_2 \rightarrow CH_2COOH + 2H_2O$

Methanogenesis with acetic acid: $CH_3COOH \rightarrow CH_4 + CO_2$

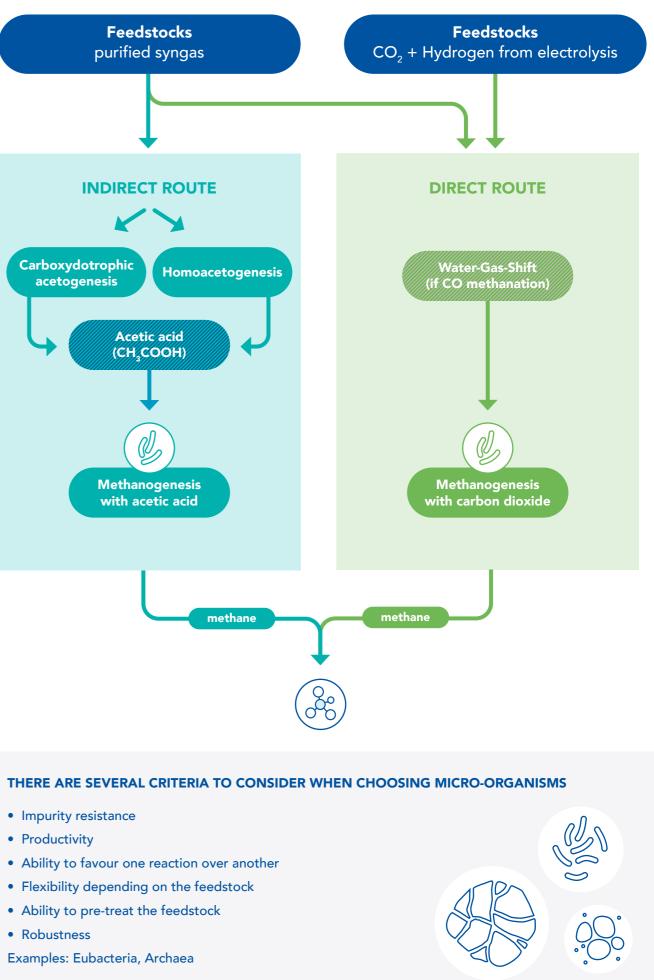
DIRECT METHANATION takes place in thermophilic conditions (>45°C)

Water-Gas-Shift: $CO + H_{2}O \rightarrow CO_{2} + H_{2}$

Methanogenesis with carbon dioxide: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

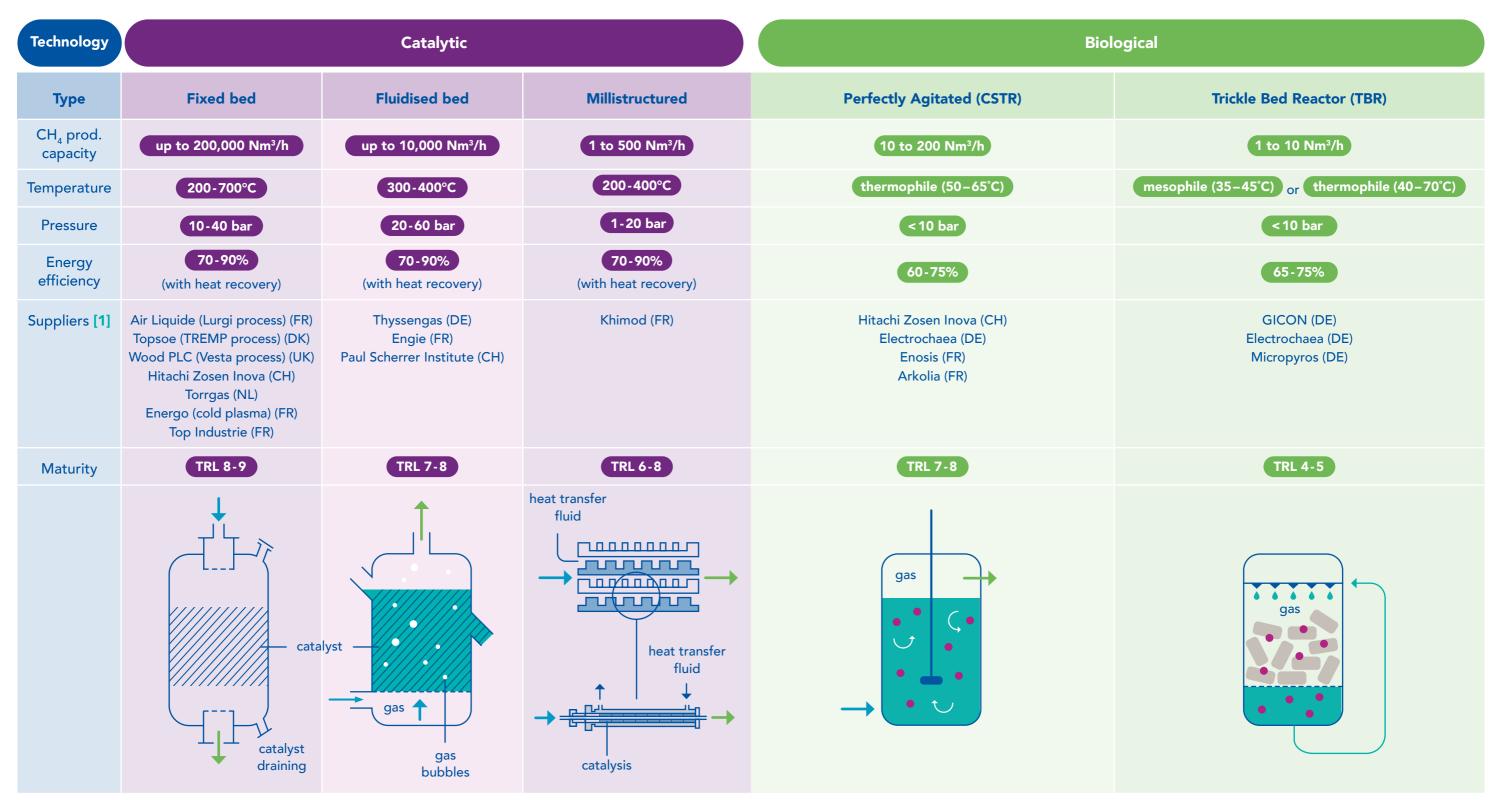
CO (especially at high levels, > 50%) inhibits the action of micro-organisms, which is why the indirect route is less effective than the direct route.

Direct methanation of CO, is simpler and better controlled.

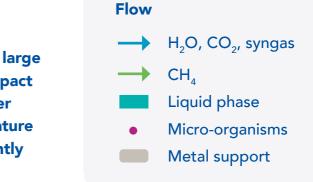


Mapping of Methanation Technologies

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.



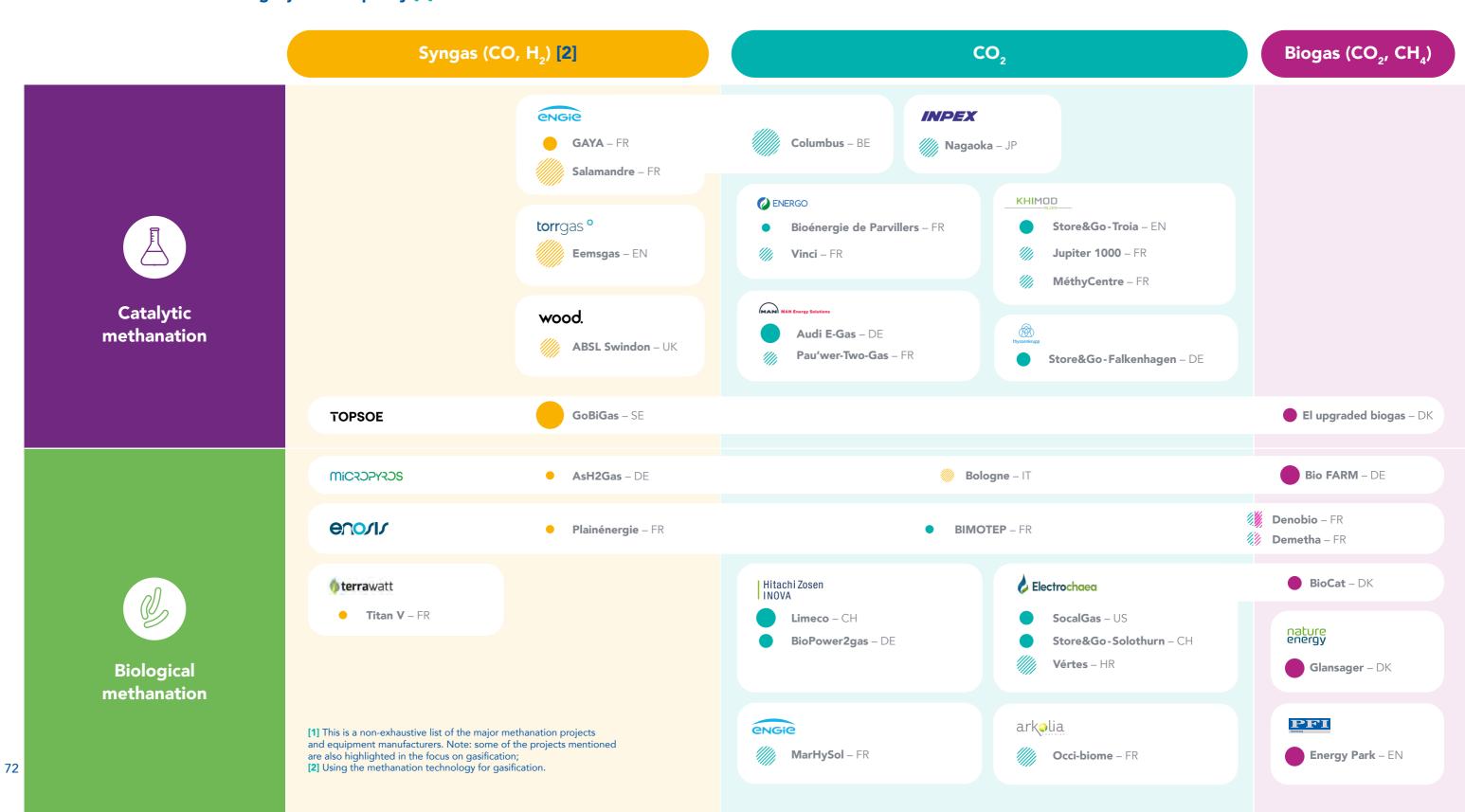
Note: This is a non-exhaustive list of the most commonly used technologies [1] Examples of suppliers – non-exhaustive list.



METHANATION BUILDING BLOCKS

Mapping of the Main Flagship Projects

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



Project status

Existing
Upcoming





 \bigcirc 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

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.

AUDI E-GAS PROJECT 2013 | Werlte

Man EnergySolutions | 325 Nm³/h

Catalytic

Industrial methanation unit consisting of a cooled fixed-bed isothermal reactor. The CO_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.



+ SWITZERLAND

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).

LIMECO PROJECT

2022 | Dietikon Hitachi Zosen Inova | 250 Nm³/h

Biological

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_2 comes from the purification gases from a wastewater treatment plant.



FRANCE

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.

JUPITER1000 PROJECT

2020 | Fos-sur-mer Khimod | 25 Nm³/h

Catalytic

Power-to-gas industrial demonstration project with expected methane production of 25 Nm³/h from CO₂ from plants in the Fos-sur-Mer industrial port zone and hydrogen (1MWe) for injection into the grid.





Biological

Specific to catalytic methanation technology Specific to biological methanation technology



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).

GLANSAGER PROJECT

2023 | Glansager Nature Energy | 380 Nm³/h

Biological

The world's largest power-to-methane plant has been commissioned in Glansager, Denmark. This facility uses renewable electricity for electrolysis and CO_2 from a biogas plant to produce methane.



JAPAN

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

INPEX PROJECT

2025 | Nagaoka INPEX | 400 Nm³/h

Catalytic

Demonstration unit using CO_2 as a feedstock that will inject biomethane into the residential gas network in 2025. The project aims to develop a 400 Nm³/h unit.



UNITED STATES

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

SOCALGAS PROJECT

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

Biological

A project to demonstrate biomethanation (using 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.



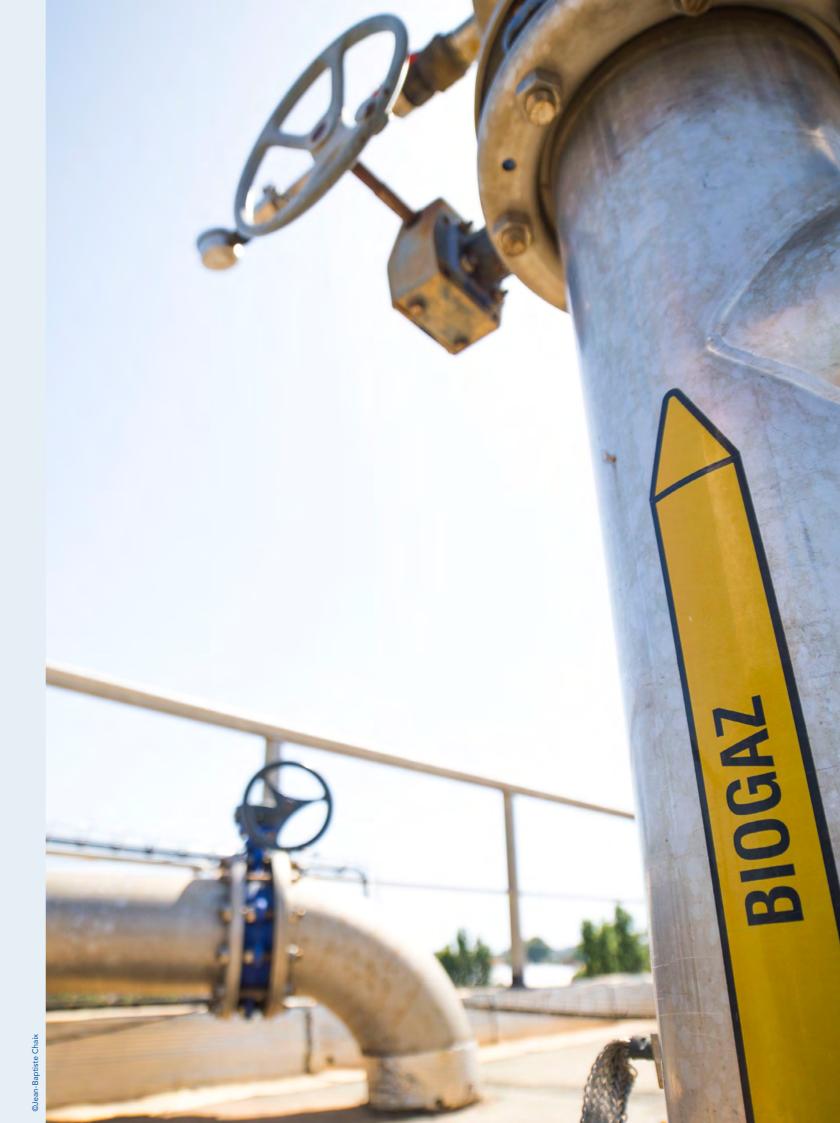
GREEN PLAINS PROJECT

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

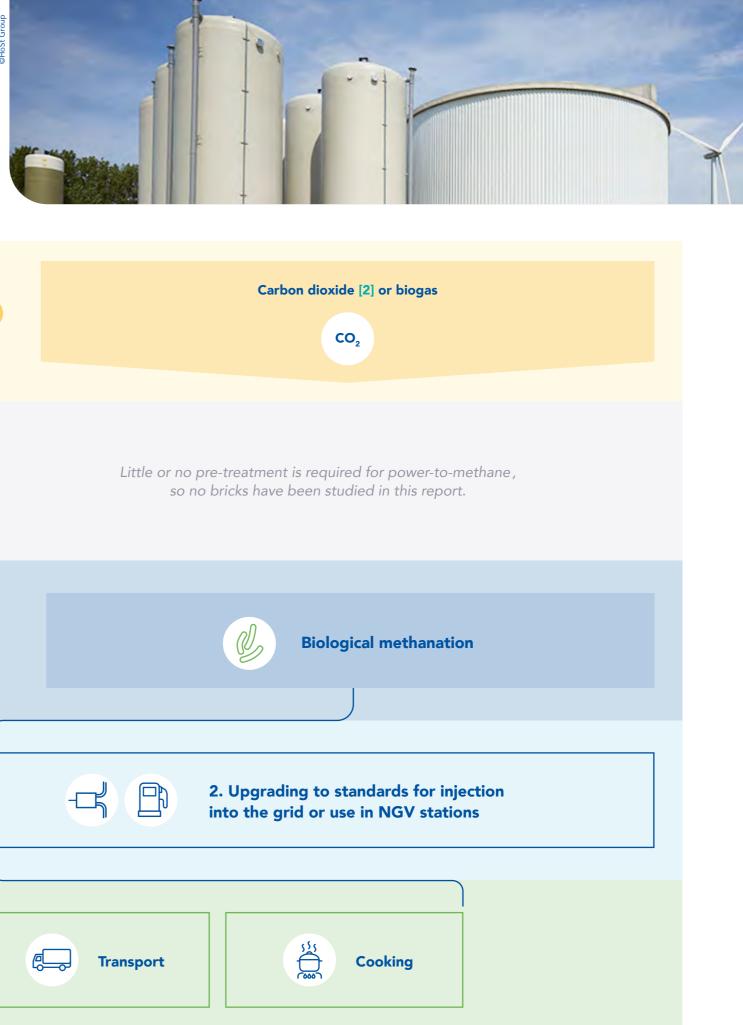
Catalytic

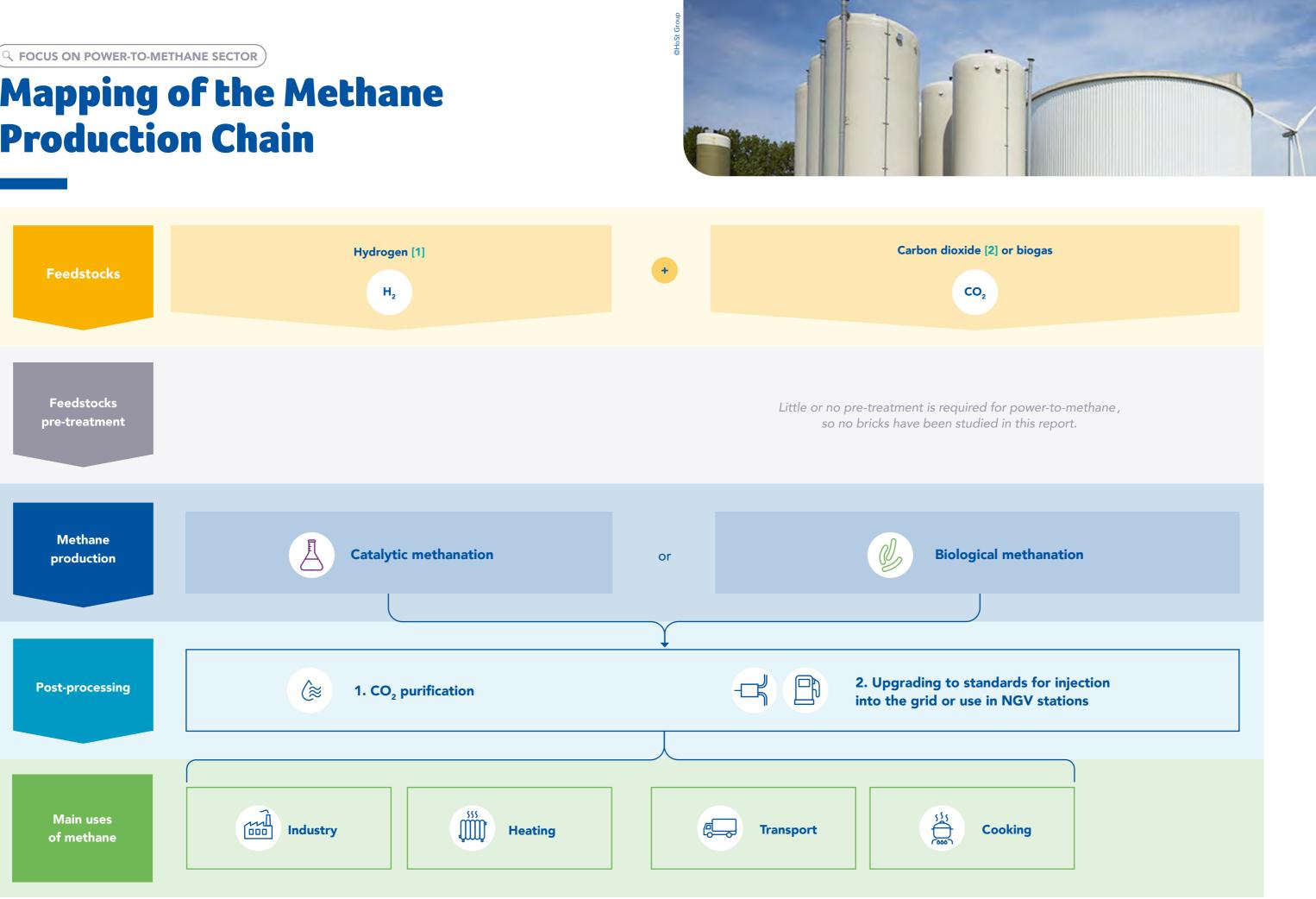
Feasibility study underway to produce methane using blue hydrogen (with CCS) and CO_2 captured from a bioethanol refinery. The unit will produce 200 kT/year by 2030, and the use of green hydrogen is currently being studied.





Mapping of the Methane Production Chain





[1] Produced by electrolysis;



 \bigcirc FOCUS ON POWER-TO-METHANE SECTOR

Challenges and Technical Solutions for the Sector Catalytic

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

Technical challenges in the sector

Feedstock pre-treatment [1]

> Methane production

Post-treatment

Global integration of the technical bricks [1]

Catalyst deactivation

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

Use of critical minerals

Cobalt, which is sometimes used as a catalyst, is considered a 'critical 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

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.

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

Gas quality for injection

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

[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 'electrolysis' brick has not been studied in this report;

R&D solutions and innovations

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 addition, many French laboratories (e.g. Université de Strasbourg, ICPEES, Université du Littoral Côte d'Opale) are studying these phenomena within different reactors (e.g. fixed bed, millistructured reactor-exchanger).

A team of Egyptian researchers has demonstrated that using cerium (Ce) or lanthanum oxide (La_2O_3) with zirconia (ZrO_2) as a support, coupled with Ni as a catalyst, increases the rate of CO₂ conversion. > Link to the GRDF watch

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*.

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.

Gas quality measurement and control equipment is available, and methane recirculation solutions can reduce the proportion of residual H_2 .

[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;[4] These reactors allow exchanges to be intensified by reducing the size of the reactor and multiplying the number of channels.

80 as the 'electrolysis' brick has not been studied in this report;
 [2] Migration, growth and accumulation of metal particles reducing the active surface of the catalyst;



Specific to catalytic methanation technology

Specific to biological methanation technology

○ FOCUS ON POWER-TO-METHANE SECTOR

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

Feedstock pre-treatment [1]

> Methane production

Post-treatment

Global integration of the technical bricks [1]

82

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

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.

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

Gas quality for injection

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

[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 'electrolysis' brick has not been studied in this report.

are looking at this issue in order to accelerate the diffusion of gas in biological methanation. Different flow rates and injection methods (pulsed or continuous) for CO₂ have been

studied. When CO₂ is injected in a pulsed manner, methane yields can be increased. > Link to the GRDF watch

R&D activities (modelling, temperature control, productivity, etc.) are underway at equipment manufacturers and research centres (cf. mapping of methanation technologies page 71). The conclusions of these studies will enable a better choice to be made of the technologies to be integrated depending on the reactor's operating mode (e.g. bubble columns are not appropriate for continuous operation).

Several possibilities for optimising Trickle Bed Reactors (TBRs) have been identified: on liquid flow and biofilm formation, in particular. > Link to the GRDF watch

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

Gas quality measurement and control equipment is available, and methane recirculation solutions can reduce the proportion of residual H₂.



Specific to catalytic methanation technology

Specific to biological methanation technology

R&D solutions and innovations



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 CO₂, based on innovative millistructured heat exchanger-reactors, the result of a research partnership with the CEA.

The millistructured heat exchanger-reactor has a high performance for catalytic reactions: TRL of the technology 7-8 high CO₂ to CH₄ 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 (CO₂ flow rates ranging from 1.2 to 768 Nm³).

Khimod has also participated in a number of EU-funded projects, including: MÉTHAMOD (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).





Catalytic

Industrial unit in operation and several under construction



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.

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) and membranes 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



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



Specific to catalytic methanation technology Specific to biological methanation technology

Sur la filière power-to-methane

Key players in the Development of the Sector

Biological

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 CO_2 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 Mt_{CO_2} /year and produce 2.8 Nm³/year of synthetic methane is currently under construction.

TRL of the technology



Sources

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 Chains for Grid-Ready Biomethane Production

Gantenbein et al., 2022

Biological Aspects, Advancements and Techno-Economical Evaluation of Biological Methanation for the Recycling and Valorization of CO₂ Bellini et al., 2022

Techno-economic analysis of Power-to-gas plants in a gas and electricity distribution network system with high renewable energy penetration Fambri et al., 2022

European Biomethane Benchmark

Sia Partners, May 2022

BIOMÉTHANATION DU SYNGAS: Étude cinétique et mise en œuvre à l'échelle pilote Figueras et al., 2021

<u>Production d'un syngaz par pyrogazéification de biomasse en vue d'une biométhanation</u> Tchini Séverin Tanoh, 2021

La méthanation biologique

ATEE, December 2020

Biométhanation par injection de dihydrogène état de l'art et potentiel d'émergence Voltigital/Enerka/IMT Atlantique, October 2020

Biological CO₂–Methanation: An Approach to Standardization Thema et al., 2019

Compréhension et modélisation des mécanismes de désactivation d'un catalyseur de méthanation de CO_2 au sein d'un réacteur-échangeur milli-structuré à lit fixe Isabelle Champon, 2019

Valorisation énergétique de CO via la méthanation par voie catalytique Nathalie Elia, 2019

<u>Statu quo sur la méthanation du dioxyde de carbone: une revue de la littérature</u> Ducamp et al., 2018

Report on the costs involved with PtG technologies and their potentials across the EU Van Leeuwen, 2018

Plasma catalytic process for CO₂ methanation Magdalena Nizio, 2016





Pyrogasification



What is Pyrogasification?

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



Non-waste wood

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



Lignocellulosic crop residues

straws, canes, vine shoots, etc.



Non-recyclable waste

non-recyclable plastics, used tyres, etc.

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 'syngas'), oil and/or coal.

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

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.

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.

[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.



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_{λ} , for example for injection into the grid.

c. 55-75% ENERGY EFFICIENCY

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 pyrogasification.

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} .

Dry feedstocks \rightarrow CO₂ + H₂O + CH₄ + CO + coal(s) + tar(q) + mineralsand metals

Indicative proportion of products:

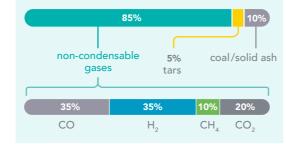


The **OXIDATION** of the volatile matter produced during pyrolysis, by adding an oxidising agent (air, H₂O vapour or O_2), provides the heat required for the other stages of pyrolysis and gasification.

 $CO + H_{,O} \rightarrow CO_{,} + H_{,}$ $CO + \frac{1}{2}O_{2} \rightarrow CO_{2}$ $H_{2} + \frac{1}{2}O_{2} \rightarrow H_{2}O_{2}$

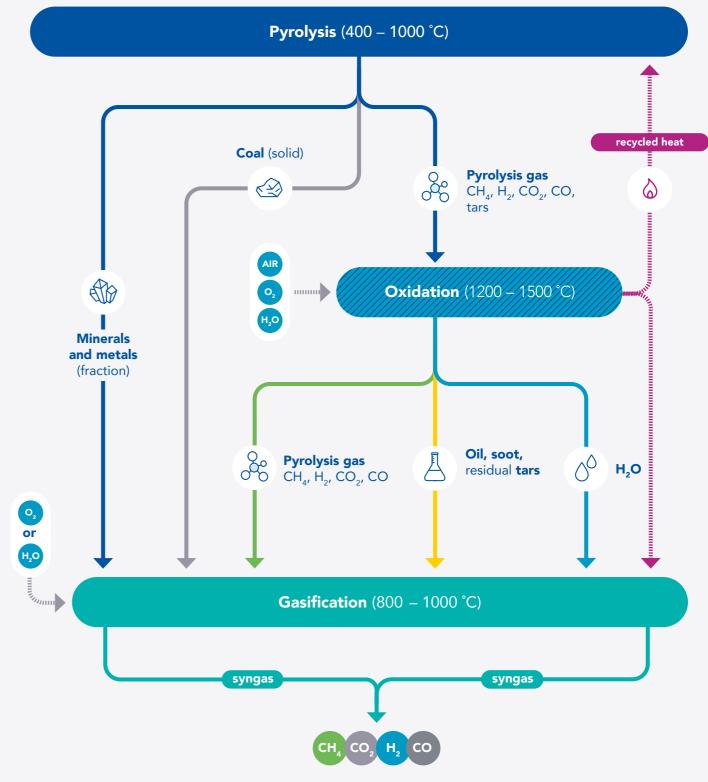
GASIFICATION leads to the formation of syngas rich in CO and H₂ through the chemical reduction of solid coal [1]. This phase requires external energy, supplied by the exothermic oxidation reaction.

 $C + H_0 \rightarrow CO + H_0$ $C + CO_2 \rightarrow 2CO$









[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 presentation of the methanation building blocks in the Power-to-methane section), the proportion of H_a can be increased to a ratio of 3:1 by means of an intermediate Water-Gas-Shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$.

Industry dynamics

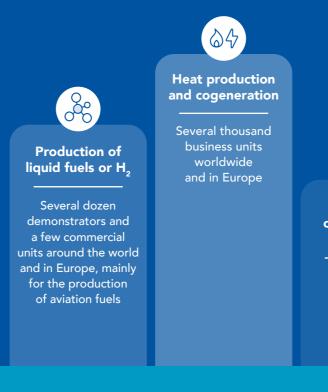
Pyrogasification plants in operation around the world are mainly used for combined heat and power (CHP)

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.

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 CH₄ enrichment (methanation) are required, which have yet to be deployed on an industrial scale.

PYROGASIFICATION PROJECTS



CAPACITY OF CEI PROJECTS

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



Generic equivalent of feedstock tonnage/ CH, production

MAIN FEEDSTOCKS FOR CEI PROJECTS [1]

1.3 million tonnes / year



23%

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

(?)

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

[1] CEI: Call for Expressions of Interest. AMI pyrogazéification pour injection - Webinaire de restitution, NSE/GRTgaz, 2022; [2] Data for non-waste wood or green waste feedstocks;

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

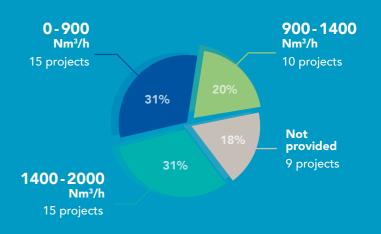
Historically, pyrogasification of biomass and waste has mainly been used for heat production and cogeneration. In recent years, however, there has been an acceleration in the development of pyrogasification for the injection of biomethane into the grid.

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].



Production of biomethane for injection

Some commercial demonstrators in Europe





8%

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

8% Mix of non-hazardous wood waste and RDF



Non-waste wood, green waste and crop residues

E S 12% RDF

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

PROJECT INITIATOR

Güssing Renewable Energy PRODUCTION Combined heat and power

Forestry wood

FEEDSTOCKS

SIZE

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

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.



GoBiGas

2014-2018 | Gothenburg

STATUT	FEEDSTOCKS
Stopped	Non-waste wood
PROJECT INITIATOR	PRODUCTION
Göteborg Energi AB	Biomethane production
SIZE	production
20 MW _{th} (1800 Nm ³ _{CH} /h)	

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.



Plainergie

2019 | Plaine de l'Ain



GAYA

Since 2017 | Saint-Fons

STATUT

Operating

SIZE

FEEDSTOCKS

Non-waste wood, green waste, RDF

PROJECT INITIATOR Engie and consortium

PRODUCTION Production of noninjected biomethane

0.6 MW_{th} (50 Nm³_{CH}/h)

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.



STATUT

Operating

PROJECT INITIATOR

Séché, Enosis, GRTgaz, EQTec and consortium

FEEDSTOCKS

Wood waste and non-renewable waste

PRODUCTION

Production of biomethane

0.1 MW_{th} (10 Nm³_{CH}/h)

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

Swindon Advanced Biofuels

2023 | Swindon

STATUT

Under development

PROJECT INITIATOR

Advanced Biofuels Solutions Ltd

SIZE

3.4 MW_{th} (300 Nm³_{CH}/h)

FEEDSTOCKS

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

PRODUCTION

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.

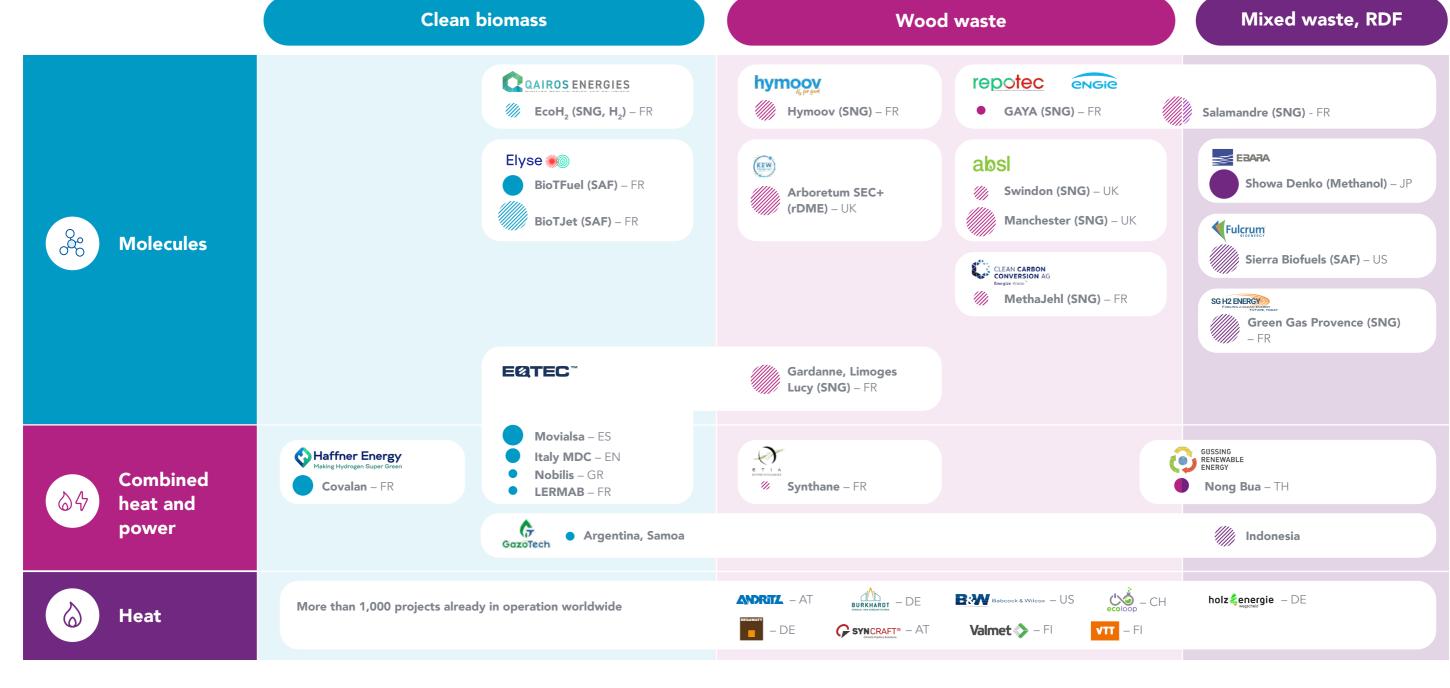


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Mapping of the Main Flagship Projects

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

Increasing complexity of feedstocks



Increasing quality of syngas needed to address usage

Incoming power

Project status

Existing

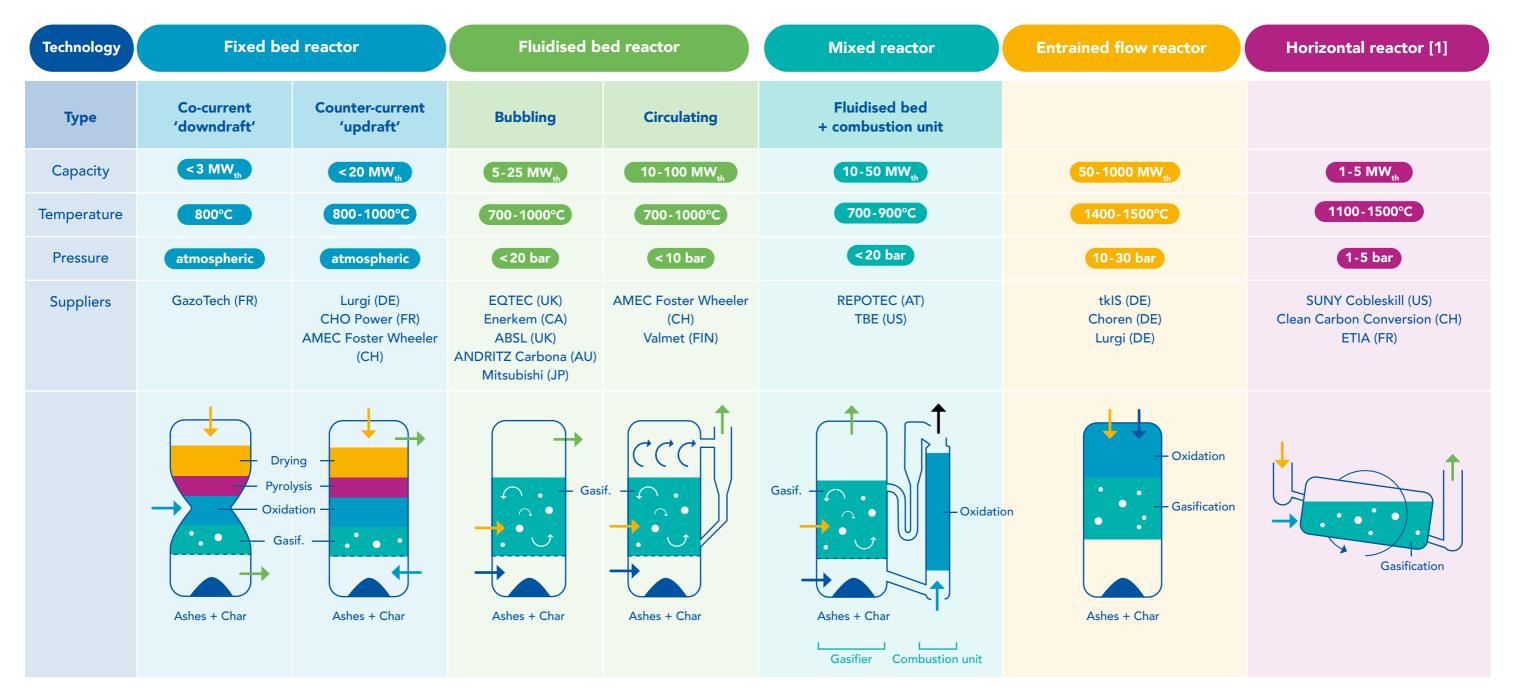
Upcoming

● ≤1 MW_{+h} ~ 0.25t/h 5 MW_{th} ~ 1.25t/h 10 MW_{th} ~ 2.5t/h ≥20 MW_{th} ~ 5t/h

Mapping of Pyrogasification Technologies

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.

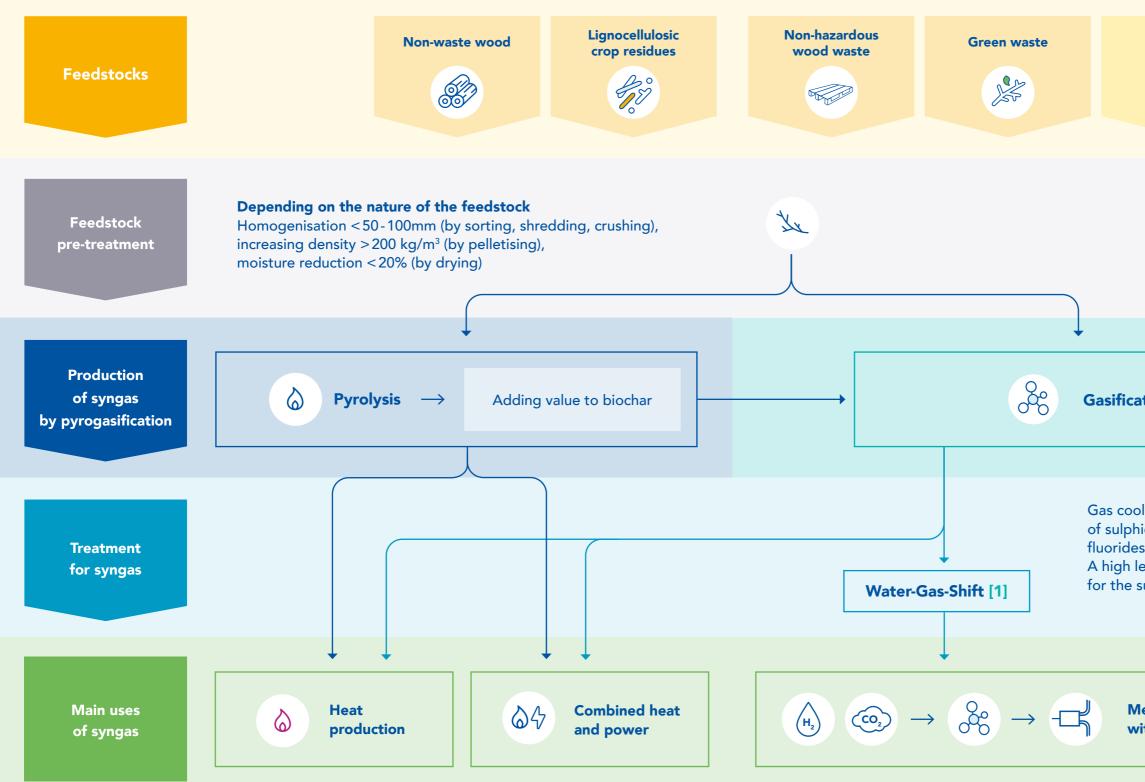


[1] Reactor with rotating drum, screw, etc. Heat can be supplied by an electrical thermal resistor.



Mapping of the Production Chain





RDF	Non-recyclable waste	
æ₽	60	
ation		
bling, elimination of water vapour, removal nides, nitrogenous species, chlorides, s, bromides, heavy metals and alkalis, etc. evel of syngas purity is required, particularly subsequent catalytic stages.		
lethanation followe ith standards for inj	d by compliance jection into the grid	

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



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.

Production of clean syngas from heterogeneous waste 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.

Oxidation with limited air injection

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 N_2 content of the gas, air injection presents a twofold constraint for reactors:

• The presence of N₂ reduces the energy efficiency of the process,

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

R&D solutions and innovations

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).

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).

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 ('oxysteam' 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 'Energy 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.

Production of syngas

by pyrogasification

Syngas treatment

Global integration

of the technical

bricks

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

Optimising tar cracking

Feedstock pre-treatment

Production of syngas by pyrogasification

> **Syngas** treatment

Global integration of the technical bricks [1]

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Elimination of sulphide and chloride

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,

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.

• 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.

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

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.

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 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).



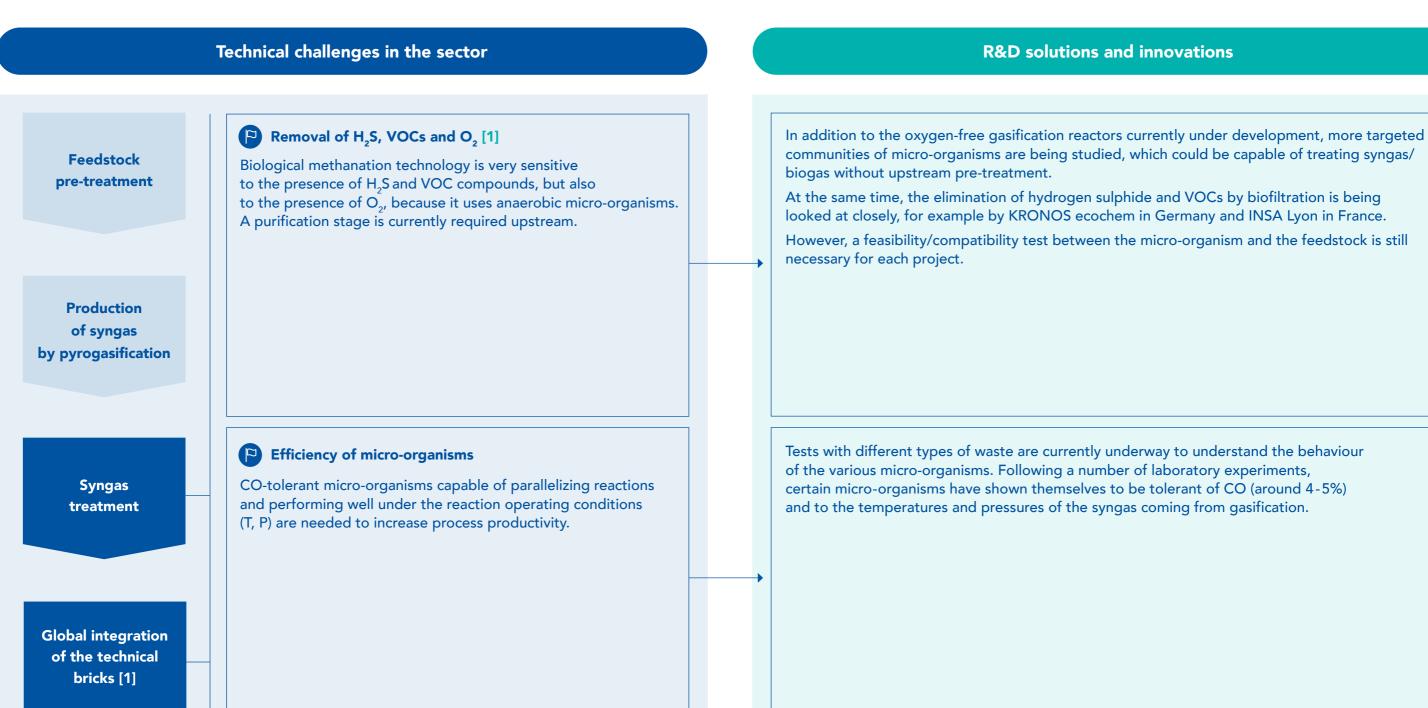
Focus on coupling gasification and catalytic methanation

R&D solutions and innovations

Solutions for the Sector The integration of syngas production and methanation systems has already been successfully achieved in demonstrators. Their coupling can be further

Challenges and Technical

optimised by improving syngas treatment processes (2/2)



[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. Focus on coupling gasification and biological methanation

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 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 CO_2 for food use will avoid on-site gas emissions.

TRL of the technology 8-9



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.

Biological methanation combined with gasification

Enosis, a French technology and project developer, is developing biological methanation systems using from CO₂, syngas from gasification or biogas from anaerobic digestion, to produce methane or hydrogen.



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.



Sources

The main French players in the field are federated by the <u>Club Pyrogazéification de l'ATEE</u>.



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gazéification.info S3D, 2023

A comprehensive review of primary strategies for tar removal in biomass gasification Cortazar et al., 2023

Gasification of municipal solid waste: progress, challenges, and prospects Sajid et al., 2022

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Biométhanation du syngas: Etude cinétique et mise en oeuvre à l'échelle pilote Figueras et al., 2021

Benchmarking et selection des technologies de pyrolyse et de gazéification adaptées à la valorisation des CSR et du Bois-B sous forme du gaz Iwunze, 2021

<u>Production of syngas by gasification of biomass with a view to biomethanation</u> Tchini Séverin Tanoh, 2021

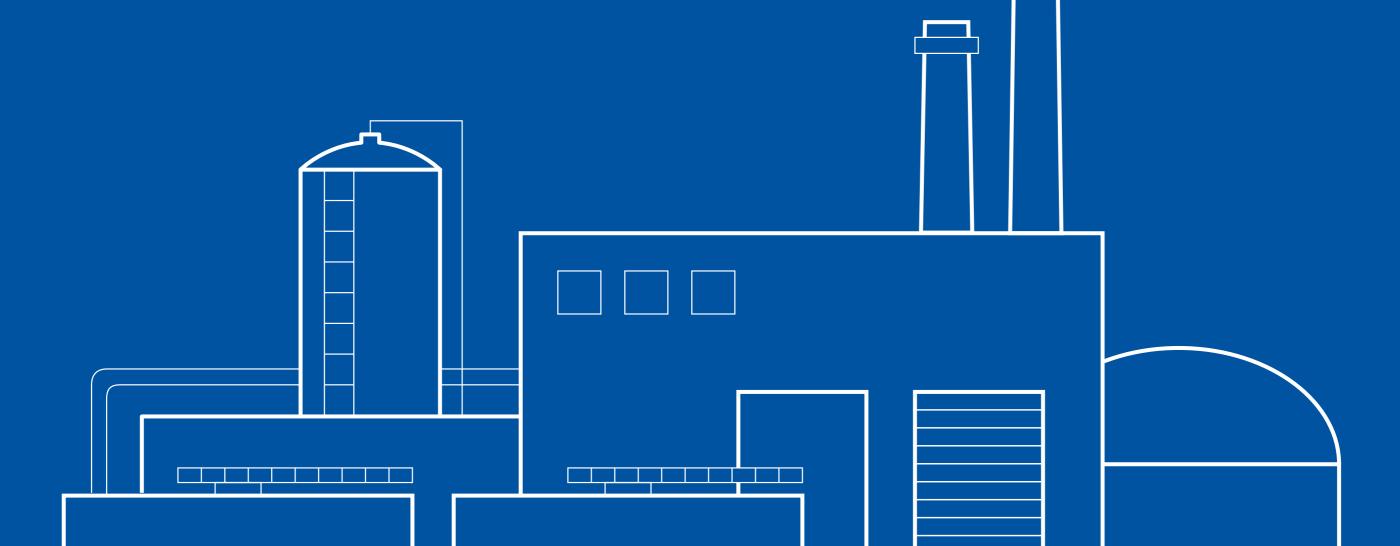
Craquage thermique des vapeurs de pyrolyse-gazéification de la biomasse en réacteur parfaitement auto-agité par jets gazeux Baumlin, 2018

Pyrolyse, liquéfaction et gazéification de la biomasse Dufour et al., 2018

Pyrolyse et gazéification, une filière complémentaire pour la transition énergétique et le développement de l'économie circulaire 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 $(400 - 700^{\circ}C)$ 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 'syngas') 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.

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.

Hydrothermal gasification enables wet feedstocks to be recycled

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

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.



Sludge from urban and industrial wastewater treatment plants



Dredging sludge



Agricultural waste and effluents molasses, vinasses, etc.

[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).



Industrial residues

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



Biodegradable waste



Digestate from anaerobic digestion not suitable for land application

Description of the Process

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

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).

>75% ENERGY EFFICIENCY

(with heat recovery)

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

FEEDSTOCK CONVERSION RATE

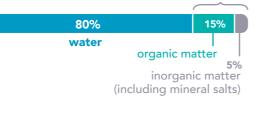
The conversion rate can be close to 100% when inorganic solvents are used.

Chemical equation for hydrothermal gasification:

Wet matter (C $H_0O_1 + H_2O_2$) \rightarrow Synthesis gas $(CH_4, H_2, CO_2, C_H) + mineral salts$ + liquid phase (H_2O , NH_4 +)

Indicative proportion of feedstocks:

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



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.

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

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.

HTG WITH CATALYST

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 .

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:

80%	15%
water and nitrogen	synthetic gas 5%
nitrogen	mineral salts

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	Syngas	Water and
	CO ₂ CH ₄ H ₂ C _x H _y	H₂O

[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;

[3] Metals or other solid components may also be precipitated at high pressure.

ly 20% dry)
250–300 bar)
aration
of HTG
HTG with catalyst
Sulphur capture
↓ ↓
А
Gasification with catalyst (400 − 450 °C)
Syngas composed of:
сн, 60 to 70%
H2 0 to 10% CO2 20 to 35%
)
nitrogen Mineral salts [3]
N Р К Са

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 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.

UNITED STATES

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.

VERENA PROJECT

Since 2004 | Karlsruhe Karlsruhe Institute of Technology | 100kg/h

High-temperature HTG

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



GENIFUEL PROJECT

Since 2017 | NorthAmerica Genifuel | 500kg/h

HTG with catalyst

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].





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.

GHAMA PROJECT

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

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.

NETHERLANDS

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).

ALKMAAR PROJECT

Since 2018 | Alkmaar SCWSystems | 2 to 4 t/h per module

High-temperature HTG

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.



[1] WWTP: WasteWater Treatment Plants.





SWITZERLAND

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).

HYDROPILOT PROJECT

Since 2020 | Villigen TreaTech/PSI | 110kg/h

HTG with catalyst

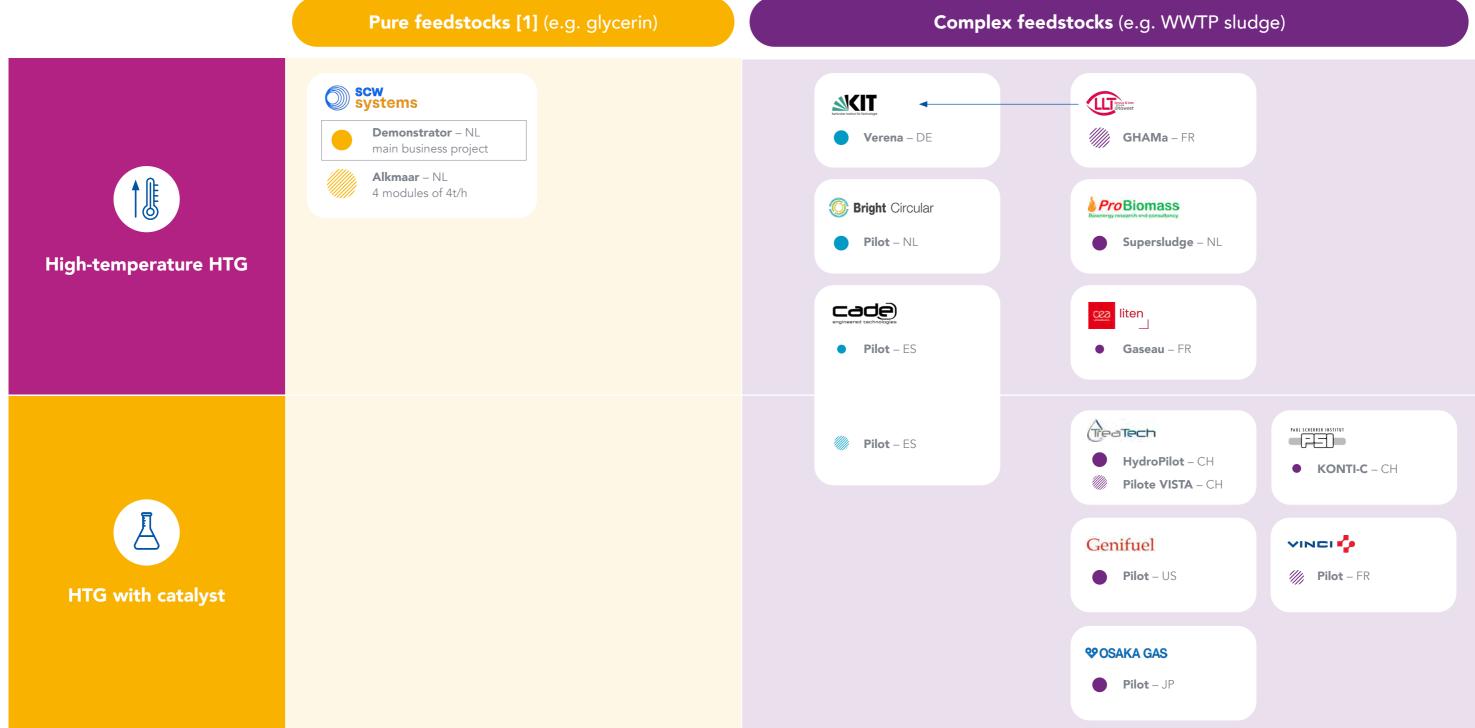
After two prototype gasifiers with catalysts, a 110 kg/h pilot plant has been brought into operation. It treats sludge and digestate from WWTP sludge. Industrial units are expected to be up and running by 2025.



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



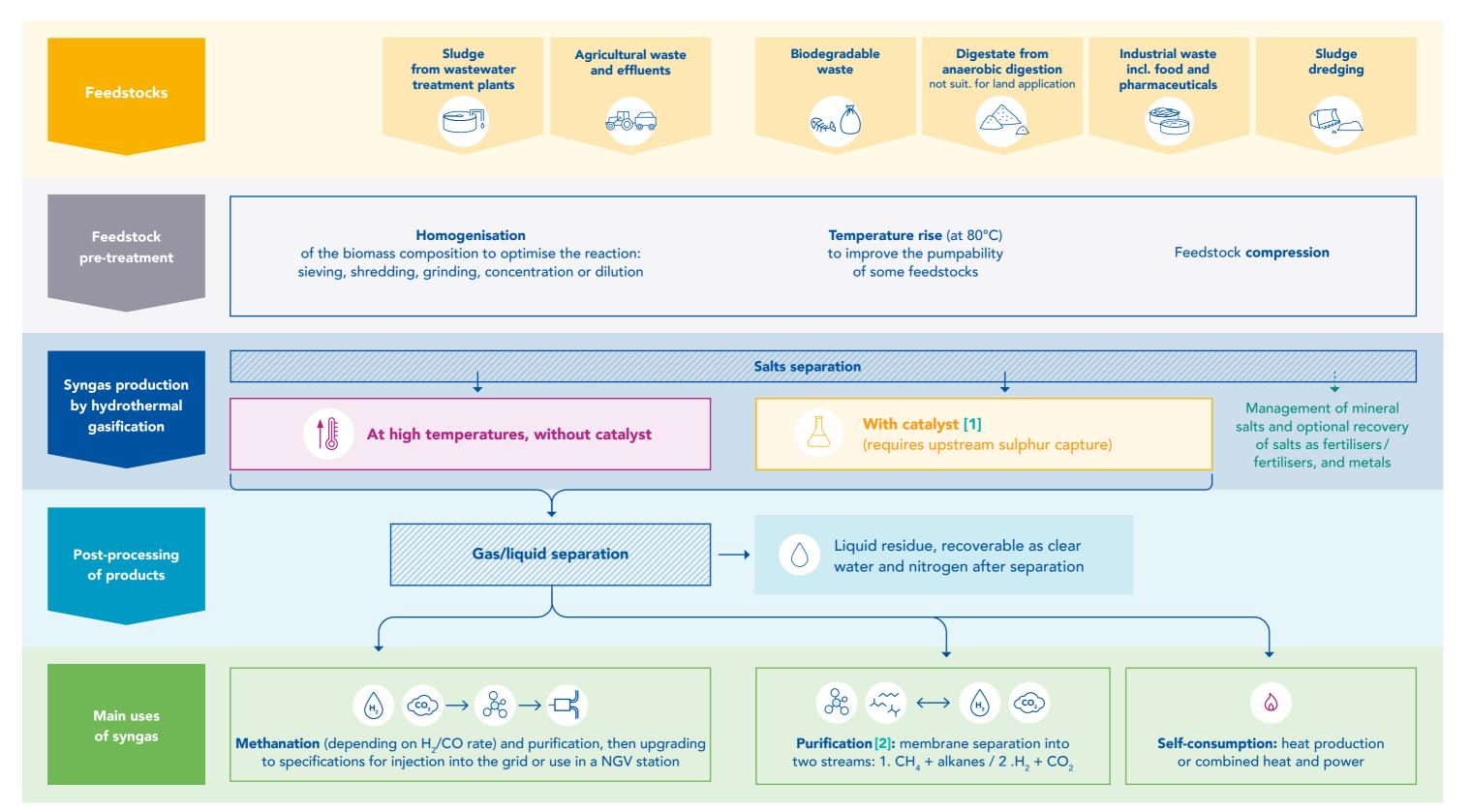


Note: Non-exhaustive representation - listing major projects [1] Absence of salts and inorganic elements.

Feedstock flow rate

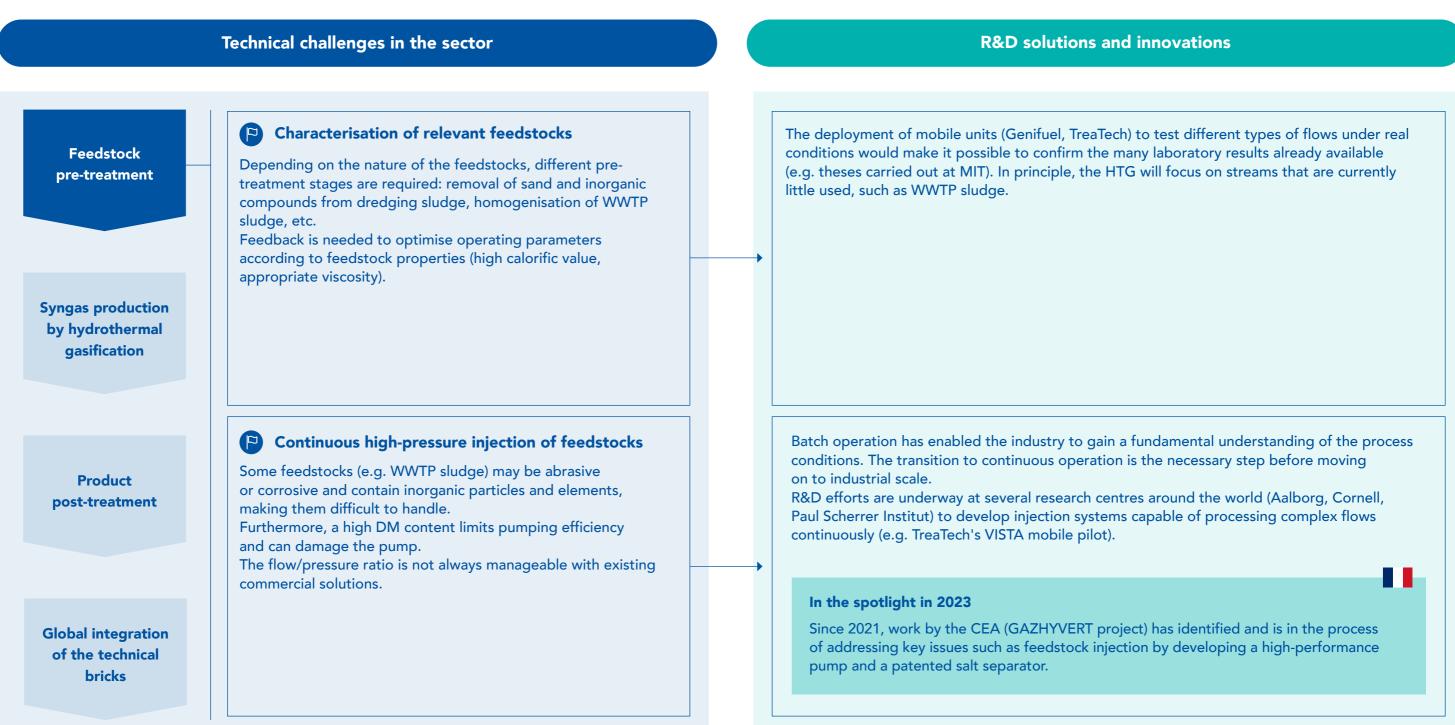
1-100 kgRM/h 100-1000 kgRM/h 1000-4000 kgRM/h >4000 kgRM/h

Mapping of the Production Chain



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

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



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

Technical challenges in the sector **R&D** solutions and innovations Design and efficiency of salt separators 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 the presence of inorganic elements that can precipitate, a salt Feedstock separator is essential to separate the mineral salts from the fluid upstream in this field. pre-treatment 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. Optimising carbon conversion To increase the CH, content, H₂ can be injected upstream or a methanation stage can be added There is still room for improvement in the carbon conversion rate. downstream. To limit losses, high-pressure recycling devices are planned to reinject the carbon On the one hand, part of the carbon stream is lost in the salt separators. downstream of the pump. Experiments to gain a better understanding of the reaction kinetics are also Syngas production On the other hand, the reaction kinetics remain poorly understood under way. The economic benefits of implementing these solutions will need to be precisely quantified. by hydrothermal and the residence time of the species in the reactor is short. The result gasification is incomplete conversion of the feedstock carbon content. Improving energy efficiency R&D is improving the recycling of high-temperature heat for both types of HTG. Initiatives are Improving the efficiency of the heat exchanger, while optimising the other also underway to recover low-temperature heat [1] for use in heating networks or industrial sites. parameters (DM rate, residence time, pressure, temperature, etc.), Finally, researchers are looking into the possibility of improving yields by increasing the DM content, is a key factor in increasing plant profitability. which poses pumping problems above certain thresholds (> 30%). Product post-treatment Optimisation of consumables 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 For gasifiers with catalysts, the sulphur trap and the catalyst are and the effectiveness of sulphur traps. consumed continuously and generate significant costs. At high temperatures, the energy and gas/water treatment OPEX are higher. **Global integration** Cost control

> Specific expensive alloys are required for the reactor to withstand the high pressures and temperatures, prevent H₂ filtration and corrosion of the reactor.

of the technical

bricks

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

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

Technical challenges in the sector

Feedstock pre-treatment

Syngas production by hydrothermal gasification

Product post-treatment

Global integration of the technical bricks

Recycling and recovery of products and co-products

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.

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).

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

CO₂: The significant proportion of CO₂ remaining in syngas (20 to 35%) could be recovered for use by consumer sectors such as the food industry, chemicals and fuels.

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 H_{2} , the recovery bricks need to be adapted and optimised.

R&D solutions and innovations

Promising technologies are currently being developed.

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

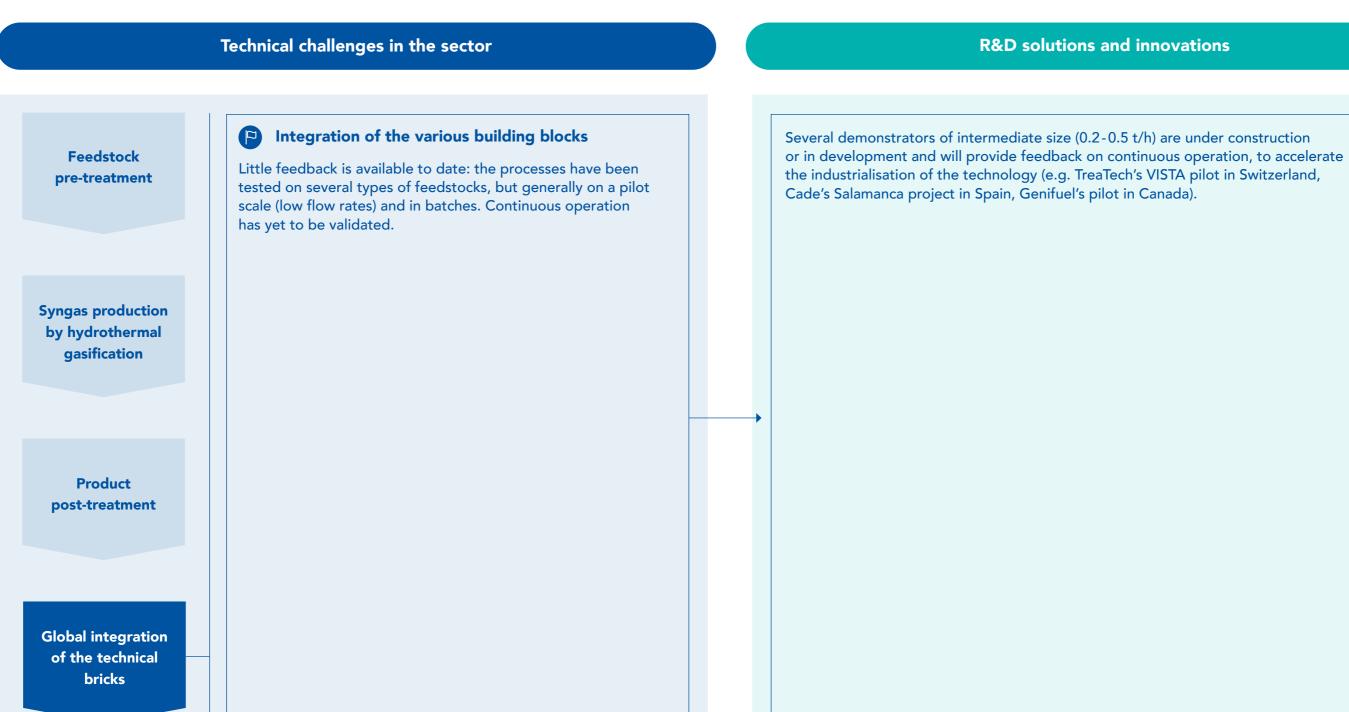
Mineral salts: For the recovery of salts, chemical treatment, a multi-stage salt separator or upstream cyclone separation are being studied. Phosphorus recovery requires R&D efforts, as the process is not yet known.

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.

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



High-temperature hydrothermal gasification on an industrial scale



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.

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.

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

SCW Systems is also focusing on the mineralisation of excess CO₂. The company has developed and patented a process capable of transforming CO₂ into carbon powder, which is also eligible for carbon credits.

TRL of the technology 8-9



French pioneer in high-temperature hydrothermal gasification



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₊₊) 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.

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.

5-6

TRL of the technology

137

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 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



Sources

Gazéification hydrothermale White Paper, National Hydrothermal Gasification Working Group, January 2023

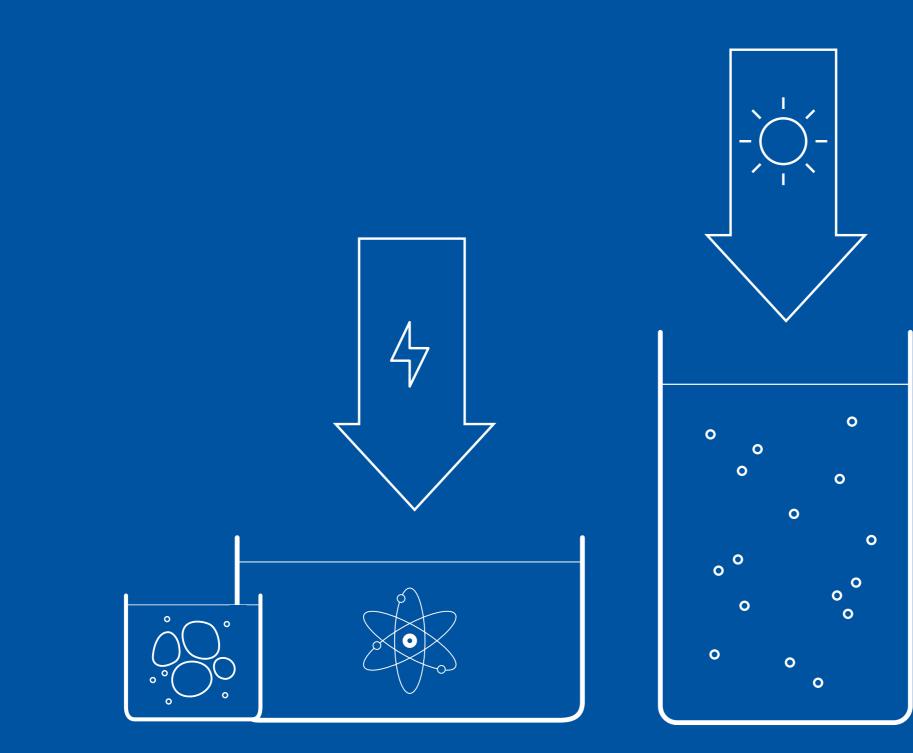
La Gazéification Hydrothermale: solution d'avenir pour la valorisation des effluents liquides GRDF, June 2022

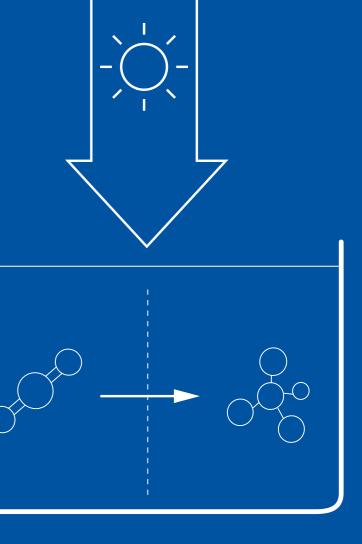
La Gazéification Hydrothermale GRTgaz, May 2022

Potentiel de la Gazéification Hydrothermale en France GRTgaz, October 2019



Emerging Technologies





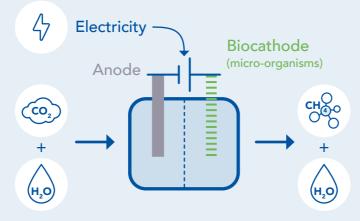
The Different Emerging Technologies

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



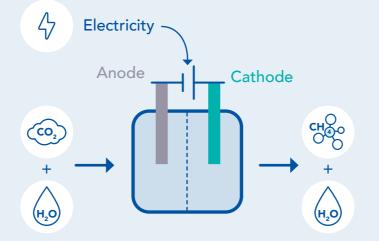
Electromethanogenesis

The electromethanogenesis process involves micro-organisms that convert CO₂ into methane when an electric current is applied between two electrodes.



CO, electroreduction

CO₂ electroreduction is an electrochemical technique that transforms CO₂ 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.



CO₂ photoreduction -Ò-

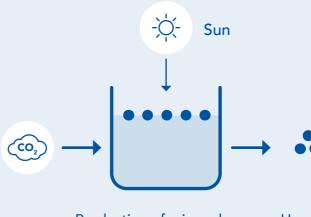
Photoreduction involves the same reactions as electroreduction, but differs in that it is more sustainable. The energy required to reduce the CO₂ comes solely from sunlight.



Photobioreaction

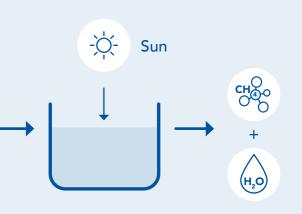
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Photobioreaction is the process of growing algae in photobioreactors. Microalgae are very small aquatic organisms that grow by absorbing CO₂ and converting it into oxygen through photosynthesis. They can then be used to produce biogas, as they are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



Production of micro-algae in a photobioreactor

Harvesting micro-algae



Aqueous solution with sensitiser (semiconductor or organic molecule)



Anaerobic digestion

Description of the Electromethanogenesis Process

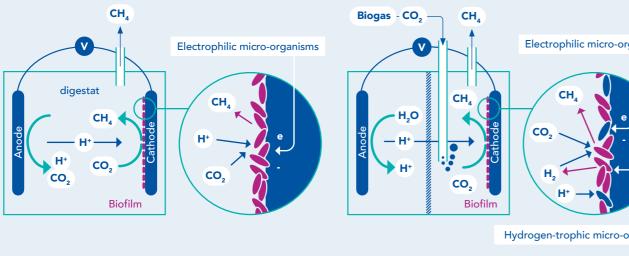
Electromethanogenesis is an emerging process that uses micro-organisms to promote methane production

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

The electromethanogenesis process involves micro-organisms that convert CO₂ 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.

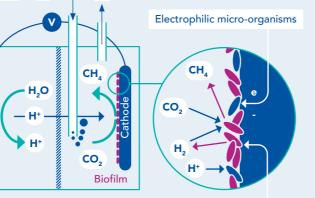
Electromethanogenesis is at the frontier between electrolysis (production of H₂) in situ) and biological methanation (conversion of H_2 and CO_2 into CH_4).

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].



Single chamber reactor: Increased biogas production

CO, + 8H⁺ + 8e⁻ electricity</sup> CH, + 2H,O



Hydrogen-trophic micro-organisms

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

2H⁺ + 2e⁻ electricity</sup> H₂

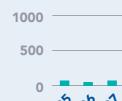
 $HCO_{2}^{-} + H_{2} + 7H^{+} \xrightarrow{\text{electricity}} CH_{2} + 3H_{2}O$

Many researchers are interested in this emerging sector

The first scientific paper

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

Number of scientific papers published per year on bioelectrochemical systems



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

There are currently two challenges This technology is currently TRL 4, to deploying the technology in a largerbut the ambition is to take it to TRL 5 scale chamber: the cost of integrating in the next 2 years by increasing the size the electrodes into the digestate is high of the electromethanogenesis cells. and the resilience of the biofilms over time The development of the various pilots could be improved. detailed on the previous page should enable this technology to reach TRL 6 or 7 in the coming years.

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.

[1] Compared to a standard anaerobic digestion unit.

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



TRL of the technology

Description of the CO, Electroreduction Process

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

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 CO₂ and the protons will be used to form hydrogen compounds.

It is therefore possible to produce methane selectively from CO₂, but the reaction that produces this hydrocarbon directly is complex to implement. A number of parasitic reactions reduce the selectivity [1] of methane.

CO, + 8H⁺ + 8e⁻ electricity</sup> CH, + 2H,O

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

The process of reducing CO₂ 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.

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



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%.

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

when an undesirable product has been formed.

2

[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



The proton membrane:

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 . 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.



The anion membrane:

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.

Description of the CO, **Photoreduction Process**

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

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 CO₂ into another carbon compound, a catalyst is required.

Some are more selective than others, so a suitable catalyst must be chosen to promote the eight-electron reduction of CO₂ to methane. The selectivity of a process that reduces CO₂ and then CO to produce methane can theoretically reach 82%.

 $CO_2 + 8H^+ + 8e^- \xrightarrow{light} CH_4 + 2H_2O$

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

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

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





	Photovoltaic panel 2 O ₂ + 8 H ⁺ CH ₄ + 2H ₂ O 4 H ₂ O CO ₂	Potoethode 4H2O	$2 O_2 + 8 H^* CH_4 + 2H_2O$ $4H_2O CO_2$
	PhotoVoltaic- ElectroChemical system (PV-EC)	PhotoElectroChemical system (PEC)	Photocatalytic Particle system (PC)
Maturity	In advanced development	Under development	Innovation
Operation	The PV device absorbs the photons and generates energy, which is transmitted to the EC cell [1], where the electrodes carry out a redox reaction [2].	The system contains one or two photoelectrodes. Light absorption and redox reactions therefore occur in the same place.	A photocatalyst is directly present in the solution and enables the oxidation- reduction reaction to take place.
Benefits	PV is a relatively mature technology The light absorber can be located outside the aqueous solution: no problem with photo-corrosion PV and EC systems can be freely modulated	As the process of solar capture and chemical reaction is a one-step process, the need for raw materials is reduced 2-compartment cell for easy chemical separation PV and EC systems can be freely modulated	The system is simple, with no electrical circuit or electrolyte Both the reduction and oxidation reactions take place on the surface of the particles, so the distance between the two sites is very small, which boosts efficiency and means that no additional electrolyte is required

Description of the Photobioreaction Process

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

Micro-algae culture enables significant recovery of CO₂

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

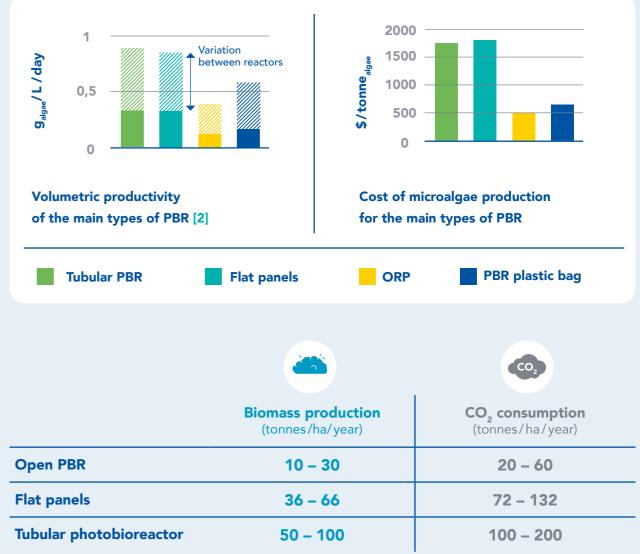
 $CO_2 + H_2O \xrightarrow{\text{light}} (CH_2O) + O_2$

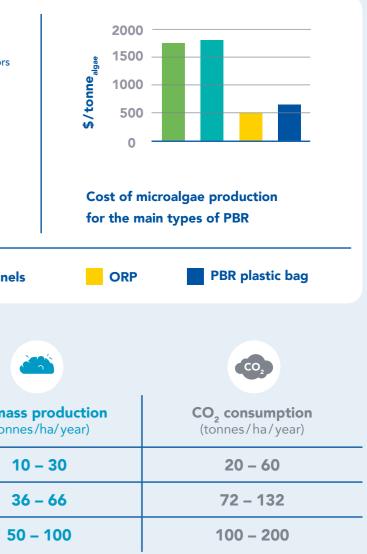
Thanks to this balance, the consumption of 1 kg of CO₂ enables the production of 0.6 kg of biomass.

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

	Benefits	Inconvénients
PBR [1] tubular (closed)	 Simple to implement Large lighting surface area and high productivity 	 Fairly large land footprint Strong pH, CO₂ and O₂ gradients High CAPEX and OPEX Energy consumption
PBR with flat panels (closed)	 Large lighting surface area and high productivity Easy maintenance Easy temperature control 	High CAPEX and OPEXScaling complexityEnergy consumption
PBR in plastic bags (closed)	Low CAPEXLimited land footprint	 Fragile, short lifespan Low homogeneity Inhomogeneous light contribution Energy consumption
Open PBR	 Easy maintenance Low energy consumption Low CAPEX and OPEX 	 High land footprint Low productivity Low homogeneity Risk of contamination

Some technical and economic data relating to these cultures





Open PBR	10 -
Flat panels	36 -
Tubular photobioreactor	50 -

Yields

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

9%

[1] PhotoBioReactor;

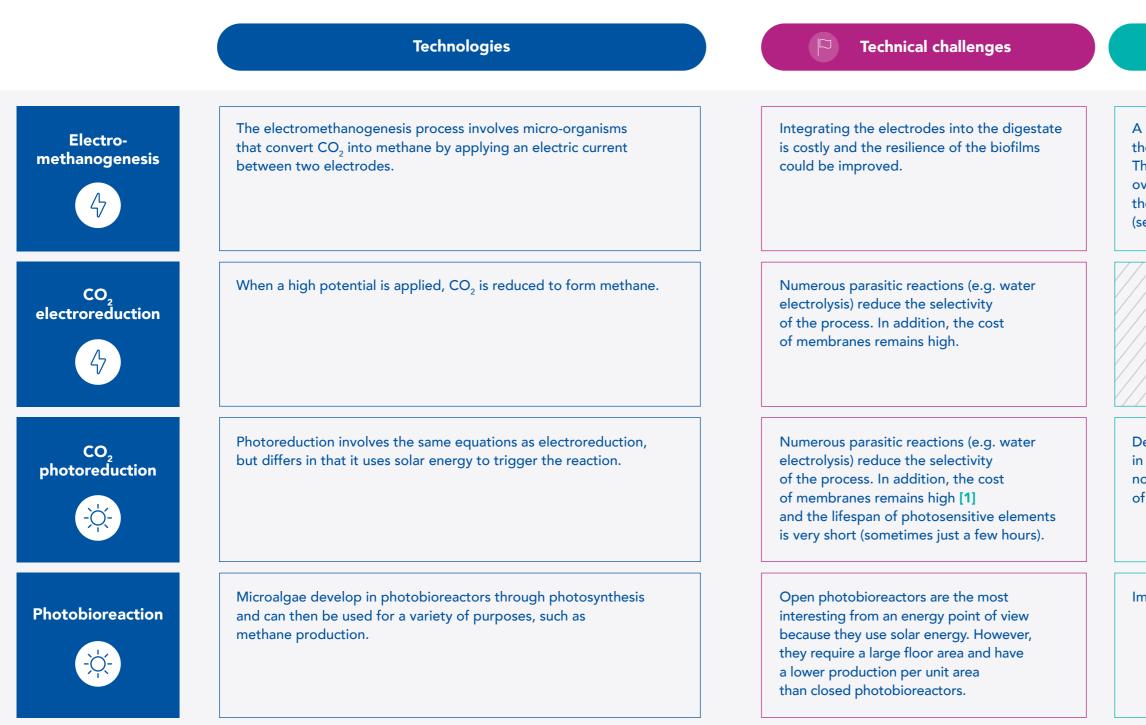


Copyright photo PBR in plastic bag ©Phytolution: Tubular PBR, flat and open panels ©Ashley Roulst

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



Summary of the 4 Emerging Sectors



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).

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

Improving light diffusion in closed reactors.

Some Pioneering Projects for the Sector

Electromethanogenesis

LEIT

Robinson project – The main aim

energy system to help decarbonise

is developing a 1m³ demonstrator.

islands. As part of this project, Leitat

of the project is to develop an integrated



wi dea energía

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.

HyMAP project – Funded by the EU, the project is developing new materials and hybrid photocatalysts that convert CO₂ into fuels.



Photobioreaction

Advanced

Algal Systems -

Developinga long-

term R&D strategy

to reduce the cost

from macro-algae.

of producing biofuels

engicoin

Engicoin -

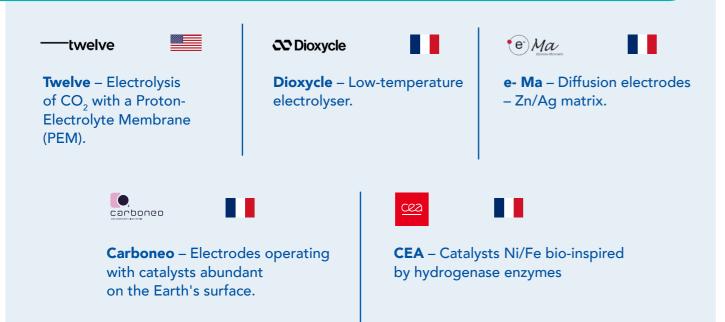
of three new

an anaerobic

for organic waste.

Development, from TRL 3 to TRL 5, microbial plants, integrated into digestion platform





engie

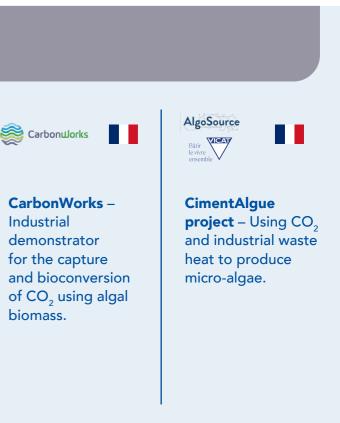
The list of projects and players is not exhaustive.





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

for completion in 2025.



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