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Biomethane Industrial Partnership

BIOMETHANE INDUSTRIAL PARTNERSHIP

INNOVATIVE TECHNOLOGIES FOR BIOMETHANE PRODUCTION

REVIEW OF THE CURRENT STATE OF THE ART

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Review of the current state of the art in innovative technologies for biomethane production

Executive Summary

Achieving the 35 billion cubic meter (bcm) target of the RePowerEU Plan of the European Commission1 will require technological advancements in several areas, including technologies to produce biomethane. This report presents a review of the current state of the art, the technological gaps and recommendations for further research and innovation for innovative biomethane production technologies. This encompasses innovative substrate pretreatment technologies, technologies for methane production and methanation, and technologies for upgrading biogas to biomethane, through thermochemical, biochemical, and biological processes. The information presented includes technical descriptions, technological readiness level (TRL), examples of plants and—when available—costs and Green House Emissions (GHG) savings. Technologies already at a commercial stage (TRL 9) for biomethane production are not covered by the review. Data was collected from literature and through communication with experts.

This report covers innovative biomethane technologies for pretreatment, conversion, and post-conversion (Table 1). Pretreatment technologies are those that can be applied in the early steps of biogas and biomethane production to produce intermediary products that can be further processed with other technologies. Conversion technologies are technologies that can be used to produce biogas or biomethane from different forms of biomass. Post-conversion technologies include technologies for upgrading biogas to biomethane or producing biomethane from CO_2.

TABLE 1 REVIEWED TECHNOLOGIES FOR PRE-TREATMENT, CONVERSION, AND POST-CONVERSION

Pretreatment	Conversion	Post-conversion
Enzymatic hydrolysis	Biomass gasification	Biological methanation
Acid hydrolysis	Hydrothermal processes	Catalytic methanation
Lignocellulose steam explosion	Thermo-catalytic reforming	Photosynthetic upgrading
	Microbial electrolysis cell	Cryogenic upgrading
	Macroalgae fermentation	

From this review, it can be noted that there are a lot of technological tracks developing for biomethane production, some of which are close to commercialization while others are at an earlier stage of development. Pretreatment processes such as enzymatic hydrolysis, acid hydrolysis or lignocellulose steam explosion can be used to break down complex carbohydrates into digestible sugars. In addition, biomass thermo-catalytic reforming can convert biomass into

[1] EUR-Lex - 52022DC0230 - EN - EUR-Lex (europa.eu)

syngas, which can be used for biomethane production. Novel technologies to produce biogas or biomethane include biomass gasification, hydrothermal processes, microbial electrolysis cell and microalgae fermentation. Post-conversion, biogas can be upgraded to biomethane through biological or catalytic methanation or photosynthetic upgrading, converting carbon dioxide (CO_2) into methane, or by separating methane and CO_2 through cryogenic upgrading.

Many of the reviewed technologies are very promising in terms of potential economic feasibility, GHG emission savings and the ability to make use of feedstocks which are currently not used for biomethane production, such as lignocellulosic biomass. There are, however, some challenges for these technologies to their way towards commercialization, such as to improve efficiency and access to affordable and sustainable raw materials.

Hydrolysis and steam explosion have high TRL (9) for ethanol production, but are less developed when it comes to the biogas production (TRL 6). Further research is needed to reduce costs and estimate their potential.

Thermo-catalytic reforming is at TRL 6 – 7, and the main challenge is related to converting the syngas to biomethane. This requires combination with other technologies, such as biological (TRL 6 – 8) or catalytic methanation (TRL 7 – 8), which in turn need to be developed further. Apart from access to hydrogen, the mixing of hydrogen and CO_2 is a key to success for these technologies.

Gasification of lignocellulosic biomass into biomethane is at TRL 6 – 8 and requires demonstration at industrial scale and proof of reliable, continuous and long-term operation to be developed further.

Hydrothermal processes are so far at a lower status of development (TRL 5) and need more research on optimal process conditions and reactor design to reduce costs and improve performance.

Likewise, **microbial electrolysis cell based conversion** needs further process development and then demonstration at large scale (current TRL 4 – 5).

Macroalgae is at a relatively high TRL for biomass production (6 – 9) but lower for biogas (TRL 5 – 7) or biomethane production (TRL 3 – 5). One of the challenges is the variability of the feedstock, both in terms of different species of algae and seasonal fluctuations in terms of availability and growth.

Photosynthetic upgrading using microalgae is somewhat more developed when it comes to biomethane production (TRL 4 – 6). It is subject to similar challenges in terms of variability of the feedstock and the production requires larges areas of land.

Meanwhile, **cryogenic upgrading** is well developed for large capacities (TRL 6 – 9), but efficiency and smaller scale need improvement to be more compatible with biogas systems.

Innovative technologies offer an important GHG reduction opportunity and mitigating the supply risk mechanism but the price gap between biomethane and natural gas and the high capital and operational costs limit their up-scaling and deployment. Research and innovation are key to advance novel and competitive biomethane technologies from laboratory and pilot scale to full scale implementation. Upon overcoming certain technical barriers and proving the concepts at

larger scale, technologies like gasification, methanation and cryogenic upgrading have the potential to be commercialized within a couple of years, and to contribute towards the 35 bcm target and beyond.

There are also some challenges to address related to policy, for example regarding regulations on the production and use of algae. The relatively high investment and operational costs also mean that many innovative technologies will require economic support to be competitive, such as investment support, production premiums or increased taxes on fossil alternatives.

More research is needed on the integration of innovative biogas and biomethane technologies with other technologies, such as use of CO_2 from biogas upgrading and the production and use of hydrogen in relation to biomethane production. Many of the novel technologies reviewed have side streams that could be valorized in other systems or require specific external input streams such as CO_2 or hydrogen. Increased understanding through research of possible synergy effects could improve the technical conditions and resource efficiency of biogas and biomethane production.

The review illustrates that there is a diverse portfolio of technological pathways under development for biomethane production, some of which are close to commercialization while others are at an earlier stage. The table in Annex provides an overview of the reviewed technologies, their technological readiness, GHG emissions saving potential, costs, efficiencies, and industrial plant examples where available. When available, diverse technologies can mitigate the supply risk and ensure competitive production of biomethane, therefore it is worth investing in research and innovation to improve them and support a wide technology portfolio towards up-scaling. Challenges to move to full scale include reducing cost, improving efficiency, and securing access to affordable and sustainable raw materials.

Table of Contents

Executive Summary **3**

1 Pretreatment technologies **7**

1.1 Enzymatic hydrolysis 8

1.2 Acid hydrolysis 8

1.3 Lignocellulose steam explosion 9

2 Conversion technologies **11**

2.1 Biomass gasification 12

2.2 Hydrothermal processes 14

2.3 Thermo-catalytic reforming 15

2.4 Microbial electrolysis cell 16

2.5 Macroalgae fermentation 18

3 Post-conversion technologies **22**

3.1 Biological methanation 23

3.2 Catalytic methanation 24

3.3 Photosynthetic upgrading 25

3.4 Cryogenic upgrading 29

4 Conclusions and key messages **31**

References **32**

Annex Overview of the reviewed technologies **37**



1. Pretreatment technologies

In this chapter three pretreatment technologies are discussed: enzymatic hydrolysis, acid hydrolysis and lignocellulose steam explosion. For each technology the state-of-the-art, strengths and weaknesses, challenges and recommendations are described.

1.1 Enzymatic hydrolysis

State-of the-art

Enzymatic hydrolysis is a pre-treatment technology for cellulose, hemicellulose and lignocellulosic substrates to break down long carbohydrates into monomeric sugars [1]–[4]. Thereby, it has the potential to increase the methane output of anaerobic digestion and enable methane production from a wider range of substrates. Hydrolysis can also be employed as a pretreatment step in ethanol production. The efficiency of the enzymatic hydrolysis can be further improved by additional pretreatment such as milling or grinding the substrates, or through application of steam explosion prior to the process. Proteins used as enzymes include carbohydrates, proteases, and lipases. Among these, carbohydrates such as fungal enzymes are the most affordable to produce.

The operation temperature is similar to anaerobic digestion, usually around 37 – 80 °C. Compared to acid hydrolysis, it produces less substances that inhibit the AD process. While enzymatic hydrolysis can be an effective pretreatment technology for anaerobic digestion, adding enzymes directly into the digester could in fact inhibit the digestion process and reduce the methane yield [5]. In other cases, the enzymes could themselves be digested into methane, making it hard to separate the actual enzymatic effect from the effect of adding more organic matter to the process.

Strengths and weaknesses

Strengths to consider are:

- Ecological, no inorganic chemicals needed
- Operates at mild conditions
- High TRL

Weaknesses to consider are:

- Relatively high price of enzymes for a limited improvement in biogas yield – OPEX very high, overall profitability
- The process is slow – large installations required, high CAPEX

Challenges and recommendations

The costs for enzymatic hydrolysis are still high, both capital (CAPEX) and operational (OPEX) costs [4].Research on new enzymes that have lower cost and higher resistance in the fermentation media is necessary. Further development is also needed to make the process more efficient.

1.2 Acid hydrolysis

State-of-the-art

Acid hydrolysis is another technology for pretreatment of cellulose and other polymeric carbohydrates to obtain more accessible sugar molecules [4], [6], [7]. While the process is faster and more efficient than enzymatic hydrolysis, the use of acids such as sulfuric acid can damage the equipment and disrupt the methanation process if brought into the AD reactor. The acid can be either concentrated or diluted, where diluted acid hydrolysis has better selectivity and

produces less degradation products. Still, sulfuric acid is the most common agent used, because of its low cost and good availability. The process temperature for diluted acid hydrolysis is around 160 °C, and the pressure around 10 bar. Diluted acid hydrolysis is more developed (TRL 5-7) than concentrated acid hydrolysis (TRL 4-5).

Strengths and weaknesses

Strengths to consider are:

- Relatively fast and efficient process

Weaknesses to consider are:

- High CAPEX cost
- Equipment with high resistance to corrosion is needed because of the corrosive properties of the acid
- The system produces toxic substances
- The process releases inhibitory compounds – low AD process yield

Challenges and recommendations

Acid hydrolysis has some technical challenges as mentioned above, including the high use of chemicals, corrosion, toxicity and inhibitory byproducts. Improvements could be made in terms of chemicals recovery and reuse and using microorganisms that are less sensitive to the inhibitors created [4].

1.3 Lignocellulose steam explosion

State-of-the-art

Lignocellulosic material can be converted to sugars through pre-treatment, as described in the Clean Energy Technology Observatory report on advanced biofuels in the EU [8]. Its conversion requires: a) pre-treatment, usually thermal or thermochemical, to disrupt the cellular structure and facilitate access to enzymes; b) enzymatic hydrolysis, to break the large carbohydrates (cellulose and hemicellulose) down into monomeric C5-C6 sugars; and c) fermentation of the sugars to alcohol using yeasts, other species of fungi or bacteria. Pre-treatment converts biomass into a more accessible form for hydrolysis through mechanical, physical-chemical, chemical and biological methods. Several processes can be used, including physical processes (steam explosion, thermohydrolysis), chemical (acid hydrolysis, alkaline hydrolysis, organic solvolysis or biologic) and combined (catalyzed steam explosion, ammonia or CO_2 explosion). Steam explosion is the most widely used pre-treatment technology, involving high-pressure steam at high temperature for a short time, followed by rapidly depressurization. The next step, which is also part of the pre-treatment, consists of lignin removal and hydrolysis of the hemicellulose. However, the process needs a lot of energy and leads to the creation of by-products that inhibit downstream fermentation [4]. Other pre-treatment options include acid or alkali treatment, or solubilization with solvents, e.g., organic solvolysis. Overall, this makes the use of special steels.

Strengths and weaknesses

Strengths to consider are:

- Degrades hemicellulose and softens the lignin: softens or breaks lignin microstructure, the plasticity of lignin should be taken into consideration.
- Economical: using digestate as energy for steam make it even more economical.
- Low CAPEX.
- Low energy use (internal energy production).
- It has little or no effects on the environment: positive impact if the digestate is used for nutrient recycling, soil improvement and carbon farming, capture and utilization.
- Lignocellulosic digestate considered organically inactive, to be used as carbon sink.

Weaknesses to consider are:

- The process destructs a certain percentage of xylan.
- The debasement of lignin-carbohydrate matrix is not complete, probably related to the crystalline cellulose structure of softwood.
- Certain compounds that hinder the microorganisms are released. This is partially related to the process parameters; furfural creation is depending on the process parameters and duration.
- Not effective for softwood treatment (crystalline cellulose is a challenge). Softwood (with crystalline cellulose) is about 10% of available feedstock in EU 54 Mton/y vs. 600 Mton/y mixed wood (soft/hard) gives high yields.

Challenges and recommendations

- Effectiveness of steam explosion related to available different relevant feedstock, estimated by available feedstock (in EU Straw 430 Mton/y, softwood residues 54 Mton/y, hard wood residues 36 Mton/y, dry manure 80 Mton/y). Further improvement on effectiveness and on the feedstock mobilization as the feedstock needed for the 35 bcm at a production rate of 300 m^3 CH_4/ton of volatile solids equals roughly 120 Mton (e.g., hardwood).
- Feedstock availability and mobilization study (from largest supply to the smallest).

2. Conversion technologies

In this chapter five conversion technologies are discussed: biomass gasification, hydrothermal processes, thermo-catalytic reforming, microbial electrolysis cell, and macroalgae fermentation. For each technology the state-of-the-art, strengths and weaknesses, challenges and recommendations are described.



2.1 Biomass gasification

State-of-the-art

Gasification is a thermo-chemical conversion process of biomass into a fuel gas (syngas), at high temperature (700 – 1500 °C), by partial oxidation with limited oxygen [29]. The syngas is a gas mixture of carbon monoxide, hydrogen, methane and carbon dioxide as well as light hydrocarbons (ethane and propane), traces of ammonia, hydrogen sulphide, and hydrogen halides, condensable gas (tar and water vapors) and particulate matter (char and ash).

The gasification process includes the following steps: i) preheating and drying; ii) thermal decomposition; iii) partial combustion of some gases and char; iv) gasification of char and gaseous components [30]. Direct gasification utilizes the exothermic oxidation reactions from thermally degrading biomass inside the reactor while indirect gasification requires an external source of energy. At indirect gasification, the heat source can be ensured through the separation of the gasification and combustion processes in different reactors, or by a novel technology, microwave heating instead of traditional heating methods, ensuring better heating rates compared to the conventional process. Indirect gasification allows the production of a N_2-free gas without the need for an air separation unit, making it suitable for synthesis applications.

Gasification is a highly versatile process, being able to convert any biomass feedstock into fuel gas. There is a wide range of possible configurations for biomass gasification, depending on the oxidation agent (air, oxygen or steam), process heating (direct or indirect), pressure level (atmospheric pressure or elevated pressure), or reactor type (moving bed, fluidized bed or entrained flow, up-draught and down-draught reactors). The selection of the most appropriate gasification process depends on the properties of the feedstock used, the final applications of gas and other factors.

Fluidized bed gasifiers are more tolerant to feedstock properties and require less pre-treatment than entrained flow gasifiers, but produce more tars, and light hydrocarbon gases, which need more complex gas purification systems [31]. Fluidized-bed gasifiers typically operate in the temperature range of 800 – 1000 °C. Entrained-flow gasifiers typically operate at 1400 °C and high pressure (20 – 70 bar), using oxygen as the most common gasification medium. Extremely high temperatures (≈ 4000 °C) during plasma gasification allow the complete dissociation of the feedstock into syngas and complete breakdown of tars and other gas contaminants. Plasma promotes the decomposition of hydrocarbons and tars and enhances the formation of combustible gases such as hydrogen and carbon monoxide. This technology is particularly promising for waste gasification (industrial or municipal waste, hazardous wastes, tires etc.) producing a chemically inert slag itself that is safe to handle. The application of catalytic gasification has shown promising results in tar mitigation in syngas as well as enhanced high hydrogen and syngas production compared to without catalyst.

The composition of the gas produced in a gasifier depends on the gasification agent, temperature, pressure, heating rate and feedstock characteristics (composition, water content, particle size) and the gasifying agent used. Oxygen gasification offers a product gas with the highest heating value (12 – 28 MJ/m^3) and increased carbon-based compounds such as CO and CO_2 in the product gas. Air-based gasifiers typically produce a gas with lowest heating value (due

to the dilution), a high nitrogen content and a low energy content (4 – 7 MJ/m³). Steam gasifiers produce a product gas with higher hydrogen concentration and higher energy content (10 – 18 MJ/m³) due to water gas shift reaction [32]–[34]. Biomass gasification produces a syngas that can be used to produce heat and power directly in internal combustion engines, boilers and fuel cells, synthetic natural gas (SNG) or to be used for the production of methanol or and other chemicals, or the synthesis of Fischer-Tropsch hydrocarbons. Nowadays, biomass gasification is mainly used for heat and power production at small- and medium-scale plants. Syngas in engines operating at electrical conversion efficiencies between 30 – 35%, in gas turbines (up to 40% efficiency), in gas and steam turbine combined cycles (up to 42%), or in fuel cells (50 – 55%) (IEA Bioenergy, 2009).

Typical gasification plant capacities range from a few tens to a few hundred MW for biomethane production, with a typical commercial capacity of 200 MW When operating as a biomethane production plant efficiency from biomass input to methane up to 70% is possible, depending on technology choice. Although several projects are implemented worldwide, biomass gasification is still at demonstration stage, reaching TRL 6 – 8. Further technology development requires demonstration at scale and proof of reliable, continuous and long-term operation.

Strengths and weaknesses

Strengths to consider are:

- Rather fuel agnostic, wide variety of fuels possible
- Large facilities possible, scale needed
- Continuous process, high efficiency possible

Weaknesses to consider are:

- High costs (60 – 105 €/MWh)
- Mismatch in scale between gasification/biomass supply (suitable in 1 – 50 MW) and methanation (expensive < 50 MW)
- Lack of technology providers (large scale)

Challenges and recommendations

Biomass gasification of woody residues to different synthetic fuels has been discussed for a long time. A challenge is the rather long value chain, which is difficult to develop fully in smaller scale, when the technology as such is suitable for large scale. Exploring the energy densification of the raw material to intermediate biomass carriers (e.g., torrefied bio-pellets, pyrolysis bio-oils) at decentralized units and converting them in centralized facilities could improve the economics but support of further research and innovation is needed. Another challenge is the choice of different synthesis routes – biomethane, bio-DME, biomethanol with different market challenges. Technically, a major challenge is the cleaning of tars and for pressurized gasification also fuel feeding and which requires further research.

2.2 Hydrothermal processes

State-of-the-art

Hydrothermal processes (HTP) are thermochemical processes that involve thermal degradation of wet biomass at low temperature and high pressure using liquid water as conversion medium and is described in the Clean Energy Technology Observatory report on bioenergy in the EU [29]. The process converts biomass into a solid (hydrochar), a liquid (bio-oil or bio-crude), or a gas (e.g., hydrogen, biomethane), depending on the process parameters. Hydrothermal processing is a greatly flexible process because it can use both dry and mainly wet biomass, requiring no feedstock drying. Different hydrothermal processes depend on pressure, temperature and residence time: hydrothermal carbonization (HTC, 160 – 250 °C, 10 – 30 bar, 1 – 72 h) to produce hydrochar, hydrothermal liquefaction (HTL, 180 – 400 °C, 40 – 200 bar, 10 – 240 min) to produce bio-oil and hydrothermal gasification (HTG, catalytic/low-temperature 350-450 °C 250 – 400 bar to produce biomethane, or non-catalytic/high-temperature >500 °C 250 – 400 bar to produce hydrogen) [35]. HTP is a promising technology platform for processing wet biomass and residues in which the type and yield of products depend on the catalyst, feedstock, and process conditions (temperature, pressure).

HTG is a process for the production of syngas by treating biomass in liquid water at high temperature (> 350 °C) and high pressure (250 – 400 bar). The gas produced is rich in hydrogen or methane, depending on the reaction conditions. Temperature has a high influence on the nature and type of reaction while pressure has only minor direct influence. HTG can be conducted in subcritical or supercritical water conditions. Subcritical gasification typically requires the use of a catalyst (nickel, palladium, platinum, rhodium, ruthenium, etc.). Catalytic gasification of biomass occurs at 350 – 450 °C and produces methane and carbon dioxide in the presence of a catalyst promoting CO2 hydrogenation (methanation) to methane. Gasification at a lower temperature carried out by catalyst offers higher energy efficiency and improves the yield and quality of the output. Supercritical water gasification (SCWG) uses water at a supercritical state in the range of 600 – 700 °C to generate mainly hydrogen and carbon dioxide with/without a catalyst. The gases resulting from hydrothermal gasification include H2, CO, CH4 and CO2, with small amounts of ethylene C2H4 and ethane C2H6 [35], [36].

Strengths and weaknesses

In comparison to conventional thermal gasification, supercritical water gasification has higher thermal efficiency for very wet biomass, production of a hydrogen-rich gas with low CO and low tar in one step [30]. In the case of sewage sludge conversion, near-competitive production costs with fossil fuels and greenhouse gas reductions of more than 80 % can be achieved.

Challenges and recommendations

Hydrothermal processing is progressing from lab-pilot scale (TRL 4 – 5) to pilot-industrial scale (TRL 5 – 6) with some projects closer to demonstration. There is a wide range of potential process designs and there are several technological gaps for the commercialization of hydrothermal processing such as the lack of understanding well the chemical mechanisms, the need for advanced materials due to corrosion in the extreme reaction conditions, the need for more performing and low cost catalyst and catalytic systems, the need to establish the optimal process parameters, as well as the need for reactor design, process development and optimization and

reducing of the high-capital costs. In addition, further research of HTG to reduce the cost of biomethane production and increase the sustainability through higher GHG emission savings in the conversion step(s) and even negative emissions through utilizing or storing carbon from the production process in the soil should be pursued.

2.3 Thermo-catalytic reforming

State-of-the-art

Thermo-catalytic reforming (TCR) is a technology developed by Fraunhofer UMSICHT [8]. The technology combines intermediate pyrolysis of biomass with post catalytic reforming of the pyrolysis products in the absence of oxygen with the char produced acting as a catalyst. The TCR technology combined with hydrogen separation through pressure swing adsorption (PSA) and hydrotreatment (HDO) to produce green hydrogen, renewable gasoline and diesel has been demonstrated at TRL 7 (Hohenburg, Germany, in the EU project To-Syn-Fuel) [85] and is ready to be upscaled at precommercial scale (TRL 9). TCR produces hydrogen-rich syngas, bio-oil with improved physical and chemical properties and bio-char. The catalytic reforming of pyrolysis products is the key difference from other existing technologies. The TCR technology consists of a two-stage reactor system. Intermediate pyrolysis takes place in the first reactor stage, the Auger reactor, at a temperature around 400 °C, and it converts the feed to char and vapor. Catalytic reforming process takes place at high temperatures (600 – 750 °C) in the second stage reactor, which is the post-reformer, where char acts as a catalyst. Bio-oil production is thus possible without the need of extensive pre-treatment steps or expensive metals catalysts or zeolites [86] and has the quality for further downstream synthesis into liquid fuels [87]. The product syngas coming from the TCR-500 system contains CO, CO2, CH4, N2 and up to 45%vol H_2 which can be separated from the produced syngas and used together with bio-oil in the HDO step to produce a hydrotreated bio-oil. The hydrotreatment process is carried out at a temperature of around 260 – 400 °C and up to 200 bar pressure where the TCR-oil is upgraded using the hydrogen from the plant process through the removal of Sulphur, nitrogen and oxygen. The hydrotreated TCR bio-oil has a LHV of 42 MJ/kg and can be separated by distillation to produce gasoline and diesel fractions. Nevertheless, the off-gas coming out from the TCR-500 reactor could be further upgraded to biomethane, using (instead of separating) the hydrogen.

Strengths and weaknesses

The production costs for the alternative fuel could be comparable to those of fossil fuels [88], depending on the size of the production plant, the type of end-product and taxation. They would thus be above biofuels and biogas from energy crops, but below other alternative fuels, for example from power-to-x processes. Unlike conventional biofuels and biogases, they do not compete with food production. The CO_2 footprint per kilometer driven is reduced by over 85%, while if the solid carbon (biochar) is also produced in the manufacturing process and stored, as a soil amendment for example to enhance soil organic carbon content in soils with less than 1.5% soil carbon, CO_2-negative liquid and gaseous fuels can be produced.

Challenges and recommendations

More research is necessary for the off-gas upgrading to biomethane utilizing the rich hydrogen component in this gas. This would include catalytic, electrochemical or biological upgrading and the development of the appropriate catalysts and catalytic systems, besides possibly suitable separation technologies. Upgrading the off-gas from TCR to biomethane could be an effective way of using low-grade and abundant organic feedstock, such as sewage, utilizing most of the carbon and hydrogen contained in it to produce lower cost biomethane. In addition, further research to reduce the cost of biomethane production and increase the sustainability through higher GHG emission savings in the conversion step(s) and even negative emissions through utilizing CO_2 from the production process should be pursued.

2.4 Microbial electrolysis cell

State-of-the-art

A microbial electrolysis cell (MEC) is an electrochemical system where microorganisms catalyze the cathodic or the anodic redox reactions settling on electrically polarized electrodes (cathode or anode), as described in the Clean Energy Technology Observatory report on RFNBO in the EU [37]. The bacteria enhance electron-transfer from the anode to the cathode while protons are released to the solution balancing the charge exchange. In order to produce hydrogen at the cathode, MEC reactors require an energy input (0.2 – 0.8 V) that is relatively lower compared to typical abiotic water electrolysis (1.23 – 1.8 V) under biologically assisted condition (pH = 7, temperature about 30 °C) [38].

MEC can operate at the nexus of microbiology and electrochemistry to reduce CO_2 to different value-added products [39]. Electricity provides the reducing power in this case. The electroactive microbes, specifically electroautotrophs, can directly utilize electrons from the cathode, or the process can be mediated by hydrogen (H_2) or other energy carriers [40].

The reduction of CO_2 in the form of methane via microbial electrolysis is the most important process concerning bioelectrochemical systems [41]. It is a valuable alternative to both biochemical methanogenesis and thermochemical methanation from the Sabatier process [42]. Among the innovative technologies for energy conversion, the peculiarity of this bioelectrochemical process is to address the need of storing the energy produced from unprogrammable sources in renewable fuel (hydrogen or methane), in a power-to-gas concept. Although such processes address marginal energy resources, their study finds valuable meaning in promoting a green circular economy by producing new biomethane or upgrading biomethane and CO_2 from anaerobic digestion (AD) in the already operating biogas plants.

Another electricity-driven biotechnology that is gaining ground alongside MEC is electrofermentation (EF). It has the potential to modulate the fermentation process to overcome the metabolic constraints of unbalanced reactions. EF integrates the concepts of microbial fermentation processes with electrochemistry to advance the bioconversion processes for converting organic matter or wastes into value-added products. It does so by restricting the thermodynamic limitations of a conventional fermentation process [39]. Polarized electrodes are used as electron sink or source to facilitate the production of a broad spectrum of products via

anodic or cathodic EF. Electricity is required to modulate the oxidation-reduction potential (ORP) and the NAD þ/NADH ratio to influence the metabolic fluxes in the case of EF [43].

Strengths and weaknesses

Microbial electrochemical technologies provide a promising futuristic approach to valorize CO_2 and organic wastes into valuable products with the help of green energy. To accomplish a sustainable and environment-friendly economy, industrialization of such technologies is earnestly required. Some efforts have been made to improve materials for electrodes, reactor designs, anodic reaction optimization, product optimization, and the production rate during the last two years. Further advancements will be required for improving mass transfer, energetic efficiencies, and product extraction strategies, along with scale-up studies with renewable energy sources to achieve the goal of transferring these technologies from lab to industry.

Challenges and recommendations

The choice of a more cost-effective material for electrodes particularly drove recent research. Carbon based materials, and biochar (of biological origin), is generally preferred. This is because pyrolyzed carbon assure high porosity, good conductivity, high biocompatibility, acceptable mechanical strength, and resilience [44]–[46]. Carbon can also be suitably functionalized with cost-effective alternative to Pt group elements (Fe, Mn etc.) [47].

The reactor design for scaling up these technologies is not specific. With large-scale reactors, the ohmic losses will also get higher, which will reduce the overall efficiency. For example, the area-specific ohmic resistance for most bioelectrochemical reactors used for MEC is generally higher than 100 Ω cm2. The ionic conductivity is also considerably low (around 10 mS cm-1) in these systems compared to that of a commercial electrolyzer (> 200 mS cm-1) [48]. Hence, small-size stackable reactors may be considered for scaling up where a much lower area-specific ohmic resistance (e.g., < 10 Ω cm2) can be achieved. To ensure higher conductivity conditions and minimize ohmic losses, using saline electrolytes (> 50 mS cm-1) with microbial catalysts adapted to such conditions is a promising option.

The source of electricity is crucial for the practical applications of MEC and EF. Though it is always claimed that it could be obtained from renewable sources, such as solar or wind, they also bring costs. The availability of such energy sources at the application site is another issue as is their intermittent nature since the bacterial process cannot be switched off and on at will depending on the availability of renewable electricity. Therefore, implementing the integration of renewable energy and MEC/EF should be considered now, instead of leaving that to occur in the future.

The production rates and efficiencies of the main products (i.e., acetate and CH4 for MEC) have increased considerably but are still low compared to commercially available technologies. If this issue is not addressed, both MEC and EF will be far from commercialization [49]. In most of the studies, the energetic efficiencies are not calculated. Though some studies reported the energy costs, the overall costs, including operating and capital costs, should also be considered. Energetic efficiency is a very crucial parameter when aiming for the scaling up of the system. Therefore, with every advancement, energetic efficiencies should also be reported to understand the overall energy expenditure of the system. In order to bridge the gap between lab and industry, an energetic efficiency of >50% and a current density of >100 mA cm-2 are required. Currently, the

range of current density reported for these systems is within 20 mA cm-2, far from the desired values [50].

Although some studies reported the energy costs, the overall costs, including operating, capital, and downstream costs, should also be considered. It has merely been discussed in most of the studies. With the current technology status, the overall production cost is way higher (e.g., for acetic acid, it is 1.66 €/kg, compared to the market value of 0.56 €/kg) [51]. In the current scenario, the molar output of acetic acid via MEC needs to be improved 267,000 times (4,550 mol/day) to enter the global market.

Only a few attempts have been made for the scaling up of these technologies [52]. For a better understanding of practical feasibility and challenges associated with scaling up, more research is desired in this direction. Some of the key bottlenecks for field scale applications for these systems are high capital cost, low current density, high ohmic resistance, low yield, and low energetic efficiency [48]. Apart from these, membrane fouling in long-term operation is another hurdle on the path which can be addressed by physical or chemical methods [53]. Though effective electrode materials and membranes have been demonstrated in lab-scale studies, their practical and long-term feasibility on a larger scale remains to be tested [54]. The reactor handling and operational issues also require attention in the scale-up studies.

At last, the environmental loads associated with the scaling up of this technology are still not explored well. A cradle-to-gate life cycle assessment for MEC has been performed recently for formic acid [55] and acetic acid [56]. For acetic acid production, MEC is far from industrialization. On the other hand, formic acid has a lower environmental impact. Although formic acid has a good market opportunity, its production is not that promising through these technologies thus far. Economic viability and life cycle evaluation should be included in future studies.

2.5 Macroalgae fermentation

State-of-the-art

Macroalgae, commonly known as seaweeds, comprise a vast array of species and are known for their rapid growth, high biomass production, and ability to thrive in diverse marine environments. These unique characteristics make them an ideal feedstock for fermentation, as they can be used to produce a wide range of bioactive compounds, biofuels, food and feed ingredients, and other valuable products. The process of seaweed fermentation involves the breakdown of complex carbohydrates, proteins and lipids in seaweed biomass by microorganisms, such as bacteria, fungi, and yeasts, into simpler compounds through various enzymatic reactions. These compounds can then be further converted into desired products using different fermentation techniques, including aerobic, anaerobic, and solid-state fermentation.

Brown seaweeds dominate the harvest with twice the volume of red seaweeds. Green seaweeds are less valuable and are not harvested in significant quantities [57]. The latest estimates (for 2013) indicate that globally 26 Mt (wet weight) of farmed aquatic plants (predominately seaweed) were produced, an increase of 129% in seaweed harvested in 13 years. This may be compared with the fish harvest, which was 158 Mt in 2012 [58]. China harvested 13.5 Mt of seaweed in 2013. In a European

context, Norway and France have the biggest harvests: Norway harvests 120,000 tonnes of Laminaria annually and France 50,000 – 70,000 tonnes per year [59]. Traditionally in Ireland, cast seaweed (including for Laminaria spp., Fucus spp. and Ascophyllum spp.) was collected and used primarily as a fertilizer, but also for cattle fodder, human consumption and medical applications [57]. Approximately 30,000 tonnes of A. nodosom is harvested each year in Ireland at a cost of € 330/t [60].

Growing and harvesting of macroalgae removes nutrients from water and therefore can be used to reduce eutrophication [61]. U. lactuca can have a sulphur content of up to 5%. This leads to significant levels of hydrogen sulphide (H_2S) in anaerobic digestion. In long shallow coastal estuaries suffering from eutrophication and associated algae blooms, the "rotten egg" smell of H_2S is apparent at low tide when the bloom is deposited on the bay.

The methane fermentation process is suitable for converting seaweeds into gaseous fuel in view of a high (about 90%$_{wt}$) water concentration. The plant consists of four processing units, namely pre-treatment, fermentation, biogas storage, and generation, as shown schematically in Figure 1. In the pre-treatment stage, seaweed test materials are cut after removing foreign objects such as shells. Then, the seaweeds are further cut down to several mm^2 pieces and diluted with water. Finally, they are sent to a receiver tank as the slurry state for ease of handling. The fermentation stage is divided into pre-fermentation and methane fermentation for achieving higher fermentation efficiency. Seaweed slurry is treated by pre-fermentation (acid production) and used in methane fermentation as a substrate. Biogas is produced in the methane fermentation process. Inside the methane fermentation tank, porous matrices are held for immobilizing bacterial cells to minimize washout of bacteria. Since biogas contains trace amounts of H_2S, it is refined using a de-sulphur agent. Purified biogas is stored in a gasholder, which is made of rubber. A residue of methane fermentation is dehydrated and used as fertilizer.

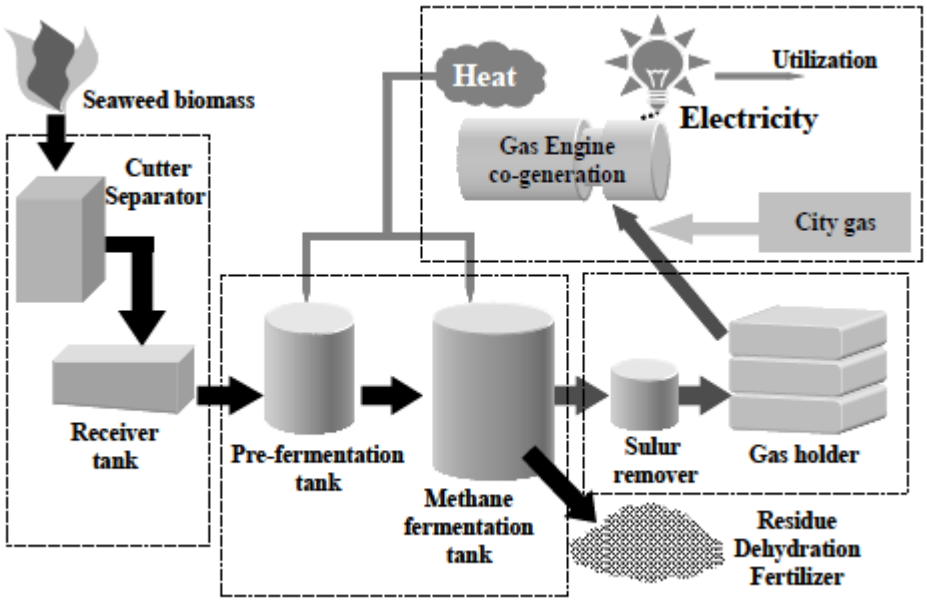

FIGURE 1. SCHEMATIC DIAGRAM OF A SEAWEED FERMENTATION PLANT

Strengths and weaknesses

There are several advantages of producing biogas from macroalgae. Some of the main advantages include:

- Sustainable: Seaweed is a renewable resource that can be harvested multiple times a year, making it a potentially sustainable source of biogas. It does not compete with food crops for land and resources.
- Fast growth rate: Seaweed has a high growth rate and can reach maturity within a few months. This means that it can be harvested more frequently than other biomass sources such as trees.
- High energy content: Seaweed has a high energy content, which makes it a valuable source of biogas. It contains high levels of carbohydrates and other organic compounds that can be converted into biogas through anaerobic digestion.
- Nutrient recycling: Seaweed cultivation can help recycle nutrients in the water, which can improve water quality and reduce the risk of harmful algal blooms.

Overall, producing biogas from seaweed has the potential to be a sustainable, low-carbon alternative to fossil fuels that can help address climate change and promote environmental sustainability.

Weaknesses to consider are:

- The production of biogas from seaweed can be costly due to the expenses associated with seaweed cultivation, harvesting, transportation, and processing. The cost-effectiveness of this technology is still being studied.
- Technical challenges associated with the production of biogas from seaweed.
- The cultivation and harvesting of seaweed can have environmental impacts.
- Seaweed growth and production can be affected by seasonal variability.
- While seaweed cultivation does not require land, it does require access to coastal waters.

Overall, while producing biogas from seaweed has several potential benefits, there are also some significant challenges and potential drawbacks that need to be carefully considered and managed.

Challenges and recommendations

Seaweed cultivation is still in its early stages of development, and large-scale, reliable seaweed supply chains are yet to be established. The variability in seaweed biomass composition, including differences in species, growth conditions, and seasonal fluctuations, can also impact the quality and consistency of fermentation processes and product outcomes. Standardization of seaweed biomass, including the development of seaweed breeding programs and cultivation techniques, could help ensure a reliable and sustainable supply of high-quality seaweed biomass for fermentation.

Identification and optimization of appropriate microorganisms and fermentation conditions. Seaweed-associated microorganisms are highly diverse and complex, and their interactions with seaweed biomass and fermentation processes are not fully understood. Dynamic control systems might be needed to maintain optimal process conditions [62].

The enzymatic and metabolic pathways involved in seaweed fermentation are still being elucidated, and there is a need for further research to identify and characterize key microorganisms, enzymes, and metabolic pathways that can efficiently convert seaweed biomass into desired products. The optimization of fermentation conditions, such as temperature, pH, nutrient availability, and oxygen levels, is also crucial for achieving high product yields and quality.

The scale-up of seaweed fermentation from laboratory to commercial production presents technical and economic challenges. Fermenting large volumes of seaweed biomass requires efficient mixing, aeration, and temperature control to ensure uniform fermentation and prevent the growth of undesirable microorganisms. The development of cost-effective and scalable fermentation systems, such as bioreactors or fermentation tanks, for seaweed biomass is an area that requires further research and innovation.

The regulatory framework for seaweed cultivation, processing, and product development varies across countries and regions, and there is a need for harmonized regulations that promote the safe and sustainable use of seaweed biomass for fermentation.



3. Post-conversion technologies

In this chapter four post-conversion technologies are discussed: Biological methanation, catalytic methanation, photosynthetic upgrading, and cryogenic upgrading. For each technology the state-of-the-art, strengths and weaknesses, challenges and recommendations are described.

3.1 Biological methanation

State-of-the-art

Biological methanation, or methanogenesis, is the conversion of carbon dioxide and hydrogen into methane and water (Eq. 1), using hydrogenotrophic methanogenic archaea as catalysts. The optimal working temperature of these bacteria is mostly within the range 55 – 65 °C, making the process temperature considerably lower than for catalytic methanation. Both biological and catalytic methanation are exothermic reactions, producing substantial amounts of excess heat, which needs to be cooled off and can be used in other processes.

Biological methanation, where CO2 is used as the feedstock for microorganisms is suitable for small plants as waste heat can be used to supply the process. This biological process presents several advantages over catalytic methanation, such as the use of inexpensive biocatalysts, milder operation conditions, higher tolerance to the impurities of syngas and higher product selectivity. Therefore, the gas cleaning process can be simplified. As opposed to the catalytic methanation process, the biological process is not sensitive to the ratio of C/H. Both biological and catalytic methanation make use of the Sabatier reaction:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H0 = -165\ MJ/kmol \quad (1)$$

Biological methanation can be done either in-situ, through injection of hydrogen into an AD reactor, or ex-situ, in a separate reactor containing the methanogenic bacteria and nutrients [9], [10], mixing CO_2 from biogas upgrading with hydrogen at a stoichiometric ratio of 1 to 4. Biological methanation is not as developed as catalytic methanation; still a TRL of 7 and 8 has been achieved for in-situ and ex-situ setups, respectively. Regarding in-situ methanation, reactor designs such as stirred bubble column (TRL 7) are more proven than trickle bed reactor (TRL 6,7), which has mainly been tested at pilot scale [11]. The mixing that occurs in a stirred bubble column or a continuous stirred tank improves the conditions for the microorganisms in terms of heat distribution and facilitates the contact between the gaseous hydrogen and the CO_2, which can be partly dissolved in water [12], [13]. A trickle bed reactor instead aims to achieve mixing through counter-current flow, thus reducing the electricity consumption otherwise required for stirring the tank.

Strengths and weaknesses

The conversion efficiency of CO_2 to methane can be close to 100% under the right conditions, leaving only small amounts of unreacted CO_2 and hydrogen in the product gas [14]. Methanation of biogas can be seen as a form of upgrading, increasing the methane content from around 50 – 70% to nearly 100%. In fact, in-situ methanation can be used to replace conventional upgrading. The gas retention time to reach full conversion ranges from around 45 minutes to a couple of hours. Ex-situ methanation is more flexible in the sense that it can utilize any CO_2 stream.

The biomethanation of syngas comprises a complex network of biochemical reactions mainly based on the water-gas shift reaction, acetogenesis, hydrogenotrophic methanation, carboxydotrophic methanation and acetoclastic methanation [15]. The pH value should be in the same range as for AD, although the methanogenic archaea can also tolerate somewhat higher pH as well. If the environment gets too alkaline, the hydrogen injection can be reduced to allow increased formation of carbonic acid [16]. Impurities and trace compounds such as hydrogen

sulphide are no more problematic in biological methanation than in AD but can be tolerated to a relatively high degree.

Challenges and recommendations

There are still several challenges to be addressed in order to reach a commercial stage [17]–[21]. Hydrogen is the main bottleneck for this technology, both in terms of continuous access and in terms of making it react with CO_2, since hydrogen has poor solubility in water. The tank layout is therefore important to successfully mix gas and fluid. Hydrogen is also expensive to produce, both in terms of electrolyzer CAPEX and operational costs. For the methanation process, CAPEX is around 20-200 €/MWh [22] and OPEX 13 €/MWh (0.4 kWh electricity/Nm^3 biogas) [23].

From the perspective of the biogas plant, methanation should be operated continuously at its nominal output. However, hydrogen from renewable, intermittent sources will not be produced continuously, which means that a large storage for biogas or CO_2 would be needed. The low cell growth rate of anaerobic microorganisms is another limiting factor since the low cell productivities of continuous processes result in low volumetric productivities of CH_4. The overall energy efficiency of converting electricity to methane via hydrogen is around 50 – 60%. This cannot be increased much due to the reaction stoichiometric maximum efficiency (78%) and typical electrolyzer efficiencies (70%).

Recommendations for the further development include intensification of the reactor to reduce its volume, optimization of biogas storage size, H_2 storage, electrolyzer sizing and matching of excess renewable electricity with H_2 production, and valorization of waste heat from electrolysis and methanation.

3.2 Catalytic methanation

State-of-the-art

Catalytic methanation produces methane and water from CO_2 and H_2 (just as biological methanation, equation 1) or from CO and H_2 (equation 2). Compared to biological methanation, it uses a metal catalyst instead of microorganisms and at higher temperature and pressure [24]–[27]. The most common catalyst is nickel, because of its suitable properties and relatively low cost. Other metals that can be used as catalysts in this process include iron, cobalt, molybdenum, ruthenium, rhodium, palladium and platinum. The catalytic methanation process operates at around 250 – 400 °C and 20 bar pressure. It is therefore best employed ex-situ, after upgrading of the biogas, as the anaerobic digestion works at much lower temperature and pressure. Furthermore, a proper separation of all impurities is required before inserting the CO_2 for methanation, particularly H_2S, which can reduce the reactivity and the conversion of CO_2 into methane [11]. On the other hand, ex-situ offers the flexibility of allowing the use of CO_2 from any source, not only biogas.

$3H_2 + CO \rightarrow CH_4 + H_2O$ $\Delta H0 = -206$ MJ/kmol (2)

Various technical innovations have been tested to improve the performance of the process. One such solution is to combine different catalysts, for example to add a small amount of iron to a nickel catalyst, which can increase the methane conversion. Another concept is sorption-enhanced methanation (SEM), where a sorption material is introduced to remove the water from

the reaction (see equation 1) and enable full methanation at a reduced pressure. This is commonly done with zeolites, which can adsorb and release water depending on variations in temperature and pressure.

Strengths and weaknesses

Methanation of syngas can be a short-term solution for synthetic natural gas (SNG) production. Although methanation of gas from coal gasification has been demonstrated at large scale, biomass syngas methanation is challenging. In order to produce SNG in a reliable manner, gasification process conditions can be designed to optimize the syngas quality. The use of air as a gasification agent is not favorable due to the resulting high N_2 content in the syngas and thus, pressurized oxygen or indirect gasification are usually used. Just as with methanation of CO_2 from biogas, syngas methanation is very sensitive to impurities and requires an intensive gas cleaning process to remove for example tars, ammonia, chlorine, sulphur compounds and particles, that cause poisoning and deactivation. The use of biocatalysts in syngas biomethanation is investigated as they show a higher tolerance to the impurities of syngas and operate at mild temperatures.

The molar ratio between hydrogen and carbon is adjusted using a WGS reaction before the first step of methanation. This reduces the overall efficiency of the process while increasing the complexity and the cost of operation. Complete conversion of the carbon stock in the product gas (CO and CO_2) can be achieved in case enough hydrogen can be supplied. The gas produced by methanation is a mixture of methane, carbon dioxide and water, with remaining traces of nitrogen, hydrogen and carbon monoxide. The remaining CO_2 in the gas is removed. ECN developed a pilot technology for producing SNG from biomass gasification that uses the conversion of hydrocarbons from the producer gas. The GoBiGas is a first-of-its-kind plant with production of SNG from woody biomass. Compared to biological methanation, the CAPEX is relatively low, 35 – 70 €/MWh [28].

Challenges and recommendations

Access to hydrogen, tolerance for impurities and finding local recipients for excess heat are challenges that need to be addressed for catalytic methanation in addition to improved catalytic material and systems.

3.3 Photosynthetic upgrading

State-of-the-art

Photosynthetic biogas upgrading (PBU) is a way of sequestering CO_2 from biogas with microalgae, which can further be used for producing industrial commodities such as health, medical, pharmaceutical, food, and energy compounds [63], [64]. This innovative approach has gained significant attention in recent years due to its potential to address two major challenges of modern society: renewable energy production and GHG mitigation.

The PBU technology relies on the heuristics of CO_2 fixation by solar-driven photosynthesis coupled with bacterial-based oxidation of H_2S to SO_4^{2-} with the utilization of photosynthetically produced O_2 [65]. An ideal PBU integrated wastewater treatment and biomass production comprising a two-step process with a separate biomass harvesting step is shown in Figure 2. The first step of the integrated process aims to upgrade biogas to biomethane by removing the CO_2. The second step

takes care of CO_2 sequestration through the fixation of captured CO_2 by microalgae. The final step is microalgal biomass production and harvesting for utilization in biochemicals and biofuels production. The PBU can obtain better results with the selection of better microalgae species with specific properties and the optimization of system parameters [66].

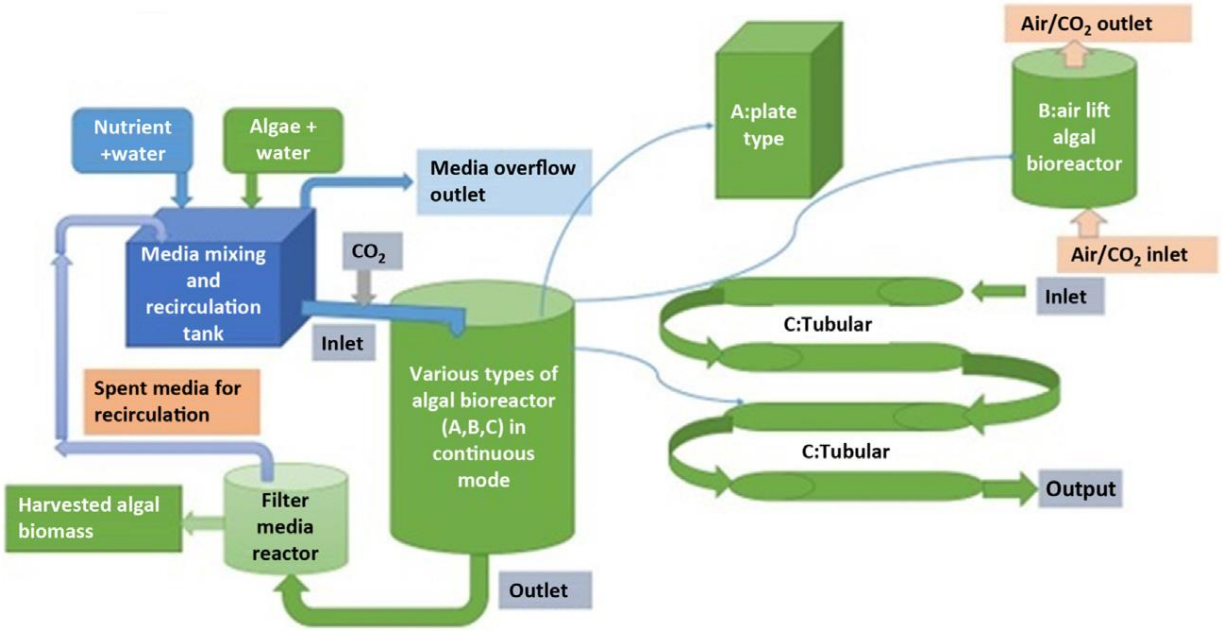

FIGURE 2 SIMPLISTIC SCHEMATIC REPRESENTATION OF CLOSED PHOTOBIOREACTORS IN CONTINUOUS OPERATION MODE (A) PLATE-TYPE; (B) AIR LIFT (BUBBLE COLUMN) ALGAL BIOREACTOR; (C) TUBULAR TYPE ALGAL PHOTOBIOREACTOR.

The positive attributes of microalgae include its fast growth rate and its adaptability to harsh process conditions [67]. The biofuel products of algal biomass include biodiesel through produced lipids transesterification [68], [69], bioethanol (through fermentation of carbohydrates) [70], and more biogas through AD of leftover algal biomass [71]. PBU also efficiently removes the CO_2 (through CO_2 sequestration) and H_2S (through oxidation of H_2S to SO/SO_4^{2-}, by synergistic association with sulfur-oxidizing bacteria) and is considered as a low-cost sustainable biogas upgrading approach [72]. The overall advantage of microalgal-based biogas upgrading mainly lies in converting CO_2 to energy and high-value industrial commodities using milder reaction conditions and subsequently developing a sustainable circular bioeconomy [73]. The ideal characteristic of microalgae utilized for PBU includes its tolerance to methane and H_2S in raw biogas to remove the CO_2 [74]. The tolerance can be achieved by developing mutant strains (*Chlorella* MM-2 and *Chlorella* sp. MB-9) through random or direct mutagenesis, which can tolerate up to 80% methane and 100 ppm of H_2S in the biogas stream [75]. The developed mutant strains enhance the biogas upgrading potential with moderate methane levels [76]. The microalgal species of *Chlorella*, *Spirulina*, *Nannochloropsis*, *Scenedesmus*, and *Chlorococcum* are ideal species for PBU due to their rapid growth and high tolerance to stress factors.

Several key factors influence the performance of PBU using microalgae, including microalgal species, bioreactor design, environmental conditions, and biogas composition [77], [78]. The selection of appropriate microalgal species is crucial, as it determines the biomass productivity, nutrient utilization efficiency, and biomass composition. Different microalgal species have varying growth rates, biomass yields, and lipid content, which can affect the overall process efficiency and economics. Therefore, the choice of microalgal species should be based on their suitability for the specific biogas composition and desired biomethane production.

Bubbling biogas in an absorption (bubble) column connected to a photobioreactor with circulating algal solution has been established as an effective configuration to optimize biogas upgrading using microalgae [66], [79]. In this process, CO_2 is first absorbed by an alkaline solution with carbonate medium (94% CO_2 removal at pH 9.5), which also ensures total H_2S removal [80], [81].

Strengths and weaknesses

Strengths to consider are:

- Negative carbon footprint process
- High-added value by-products

Weaknesses to consider are:

- High production costs
- Technical challenges to improve the process
- Land and water use
- Competition with food production
- Scale-up challenges

The cost of producing biomethane from microalgae is higher than producing biomethane from other sources. This is due to the high cost of cultivating and harvesting microalgae, as well as the energy-intensive process of converting the algae into biomethane. There are technical challenges involved in the cultivation and processing of microalgae for biomethane production. These include optimizing growth conditions, developing efficient harvesting methods, and optimizing conversion processes. While microalgae require less land than other crops, they still require significant amounts of water and nutrients to grow. This can have environmental impacts, particularly if large-scale cultivation is pursued. There is a risk that the cultivation of microalgae for biomethane production could compete with food production for land and water resources, potentially exacerbating food insecurity. Currently, most biomethane production from microalgae occurs on a small scale. Scaling up production to meet significant energy demands would require significant investment and infrastructure development.

Challenges and recommendations

Some of the challenges with photosynthetic biogas upgrading to biomethane are:

- Large land surface area needed for photobioreactor deployment.
- Development of more effective methods for CO_2 absorption and thermal energy valorization.
- Limited number of technology suppliers and track record.
- Oxygen generated during photosynthesis, leading to elevated levels of O_2 (> 0.5%) in the upgraded biomethane is a major challenge to meet gas grid specifications using this process. Additional issues including: 1) low CO_2 mass transfer; 2) effective control of process parameters e.g., gas and liquid flow rates; 3) diurnal variability in operation due to photo-autotrophy; and 4) fluctuating seasonal operation affecting microalgae growth must be overcome to commercialize the technology [66].
- Low methane content in biogas, which may require additional processing steps to achieve the desired biomethane purity [82].

Some of the recommendations with photosynthetic biogas upgrading to biomethane are:

- Optimization of the photosynthetic process to achieve higher yields of biomethane/biomass production.
- Larger infrastructure needs to be tested for upgrading 500 m^3/h of biogas to biomethane.
- Cost-effective strategies for implementation of PBU on a commercial scale.
- Integration with other technologies (cascading biorefinery approach).
- New products development (feed additives, antioxidants, pigments, lipids and other high added value products).
- The optimization of the operational parameters, such as the reactor size and residence time, can reduce the capital and operational costs of the process [83]. Additionally, the development of policies and incentives to promote the use of renewable energy sources and reduce greenhouse gas emissions can create a favorable market for PBU.
- The use of membrane technology, such as membrane bioreactors and gas permeable membranes, can improve the mass transfer and reduce the inhibition of microorganisms [84]. Additionally, the integration of PBU with other renewable energy technologies, such as solar panels and wind turbines, can enhance the sustainability and energy efficiency of the process.
- Depending on the end-use application of biomethane, such as injection into the natural gas grid or use as a vehicle fuel, certain gas quality requirements need to be met, including methane content, impurity levels, and odorants. Therefore, upgrading biogas to biomethane with the desired gas quality can require additional treatment steps, such as gas separation, purification, and compression.

3.4 Cryogenic upgrading

State-of-the-art

Cryogenic technology can be used for:

- Upgrading of biogas to high-purity biomethane
- Polishing of biomethane to high-purity biomethane
- Liquefaction of high-purity biomethane to bio-LNG

Biomethane typically has a CO_2 content of 0.5 – 3%. High-purity biomethane typically has a CO_2 content below 50 – 100 ppm, which is required for liquefaction to avoid dry ice on the equipment. As the name implies it uses different cooling technologies to achieve upgrading, polishing and liquefaction. Several cooling technologies are used or in development based on liquid nitrogen, mixed refrigerant or Stirling cycles [89].

Cryogenic upgrading of biogas to biomethane

Cryogenic upgrading is a method used to upgrade biogas to biomethane by removing impurities and separating the methane gas from (primarily) CO_2. After removing impurities with different filtering techniques, the cryogenic upgrading process involves cooling the biogas to very low temperatures, which causes CO_2 to freeze, allowing it to be separated from the gaseous methane. The frozen CO_2 is then evacuated as gas or liquid in a system working in sequences.

In general, cryogenic upgrading is a highly effective method for producing high-purity biomethane with CO_2 levels below 50 – 100 ppm. This is especially interesting when immediate liquefaction of the biomethane to Bio-LNG is performed as higher concentrations of CO_2 in the biomethane will cause problems in the liquefaction with solid state CO_2 clogging valves and other process equipment [90]–[93].

Cryogenic upgrading is best suited for small and medium capacity biogas streams as other conventional techniques generally scale well up to higher capacities. It is a promising technology for producing renewable high-purity biomethane from biogas, and further research and development is expected to lead to higher capacity plants and more cost-effective cryogenic upgrading processes in the future.

Cryogenic polishing and liquefaction of biomethane to bio-LNG

The high-purity biomethane can be liquefied to bio-LNG through further cooling for transportation and storage. Cryogenic liquefaction of biomethane to produce bio-LNG involves cooling the high-purity biomethane to temperatures below -160 °C (at atmospheric pressure), at which point it liquefies and can be stored and transported as a liquid biofuel. This requires that the CO_2 content in the biomethane is less than 50 – 100 ppm. Conventional upgrading technologies such as membrane, PSA, water scrubber etc. normally result in a CO_2 content in the biomethane of 0.5 – 3% and in order to liquefy the biomethane different type of polishing techniques is required where cryogenic polishing can be one alternative. It is worth mentioning that biomethane can be liquefied under higher pressures, allowing for more CO_2 than 50 – 100 ppm to be dissolved as liquid. This can be useful for intermediate storage and later released to gas again for e.g., CNG fuel or injection to gas grids.

Strengths and weaknesses

Strengths to consider are:

- Promising technology to achieve high-purity biomethane to allow immediate liquefaction to bio-LNG.
- One advantage with cryogenic upgrading and liquefaction is that they can be integrated and performed in sequence. The combination of upgrading and liquefaction in the same unit facilitates installation and operation.
- Cryogenic polishing is a cost effective and attractive solution to polish biomethane having been upgraded with other upgrading technologies to achieve purity required for liquefaction.
- Moreover, the upgrading process generates pure, liquid CO_2, which can be distributed for use or storage at another site. The CO_2 quality level needs further investigations on usability in different applications.

Weaknesses to consider are:

- Limited number of suppliers.
- Limited number of plants in operation.
- The cryogenic upgrading technology is still in early stage of market adaption and technology sub-suppliers are limited. Critical components, such as cryogenic compressors for small and medium scale solutions are limited as the volumes are small.

Challenges and recommendations

Some of the challenges with cryogenic upgrading to biomethane are:

- Improving the energy efficiency of the liquefaction process, especially for smaller capacity systems.
- The cost for building large capacity solutions, as other conventional techniques, is well developed for large capacities.
- Development of more effective methods for capturing and reusing waste heat.
- Limited number of technology suppliers and track record.

Some recommendations are as follows:

- Further test plants to be implemented within the applications of:
    - Integrated cryogenic upgrading and liquefaction.
    - Cryogenic polishing and liquefaction together with other upgrading techniques.
- Further expand the availability in critical subcomponents for small and medium scale systems such as cryogenic compressors.
- Further research in the area of the valorization of the CO_2 and its quality.

4 Conclusions and key messages

Innovative technologies for biomethane production can provide new opportunities for developing the sector and facilitate reaching the 35 bcm target and beyond. There is also a large potential in GHG reduction, as well as diversifying the supply chain with new feedstock and production technologies.

Going from laboratory test and pilot projects to implementation of these technologies at full scale will require further research and innovation, as they are currently limited by process efficiency and economic feasibility. Research on conversion materials, equipment and systems is necessary. However, some technologies—like gasification, methanation and cryogenic upgrading—are quite far advanced and have the potential to be commercialized within a couple of years.

When it comes to policy, there are some regulatory gaps regarding the production and use of algae that would need to be addressed to enable them as a feedstock in biomethane production. Overall, many innovative technologies will also require economic support to be competitive against the current pricing of fossil fuels, either through subsidies for biogas and biomethane production or taxation of fossil alternatives.

Besides, more research is needed towards the integration of biogas and biomethane production with other technologies, such as use of CO_2 from biogas upgrading and the production and use of hydrogen in relation to biomethane production. As many of the reviewed innovative technologies either require or produce CO_2 or hydrogen, understanding possible synergy effects is key to improving the technical conditions and the resource efficiency of these systems.

There is a need for making available a diverse and performing portfolio of technologies for innovative biomethane production beyond those based on anaerobic digestion. If available, it can mitigate the supply risk as it enlarges the feedstock basis that can be converted to biomethane, secures raw material supply at a feasible demand rate, and ensures cost competitive production of biomethane. This signals out that more efforts in research and innovation are necessary to make many technologies available, improve these and the existing ones and support them towards up-scaling.

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Annex Overview of the reviewed technologies

Enzymatic hydrolysis	
Inputs	Biomass (cellulose, hemicellulose, lignocellulose), enzymes (proteins)
Outputs	Sugars
Process conditions	Mesophilic or thermophilic (depending on the enzymes used) low pressure
TRL	6 – 9
Plant example	Used in bioethanol plants
GHG emission saving	N.D./depending on sources
Costs	CAPEX: 140 – 400 €/MWh; OPEX ≈ 13% of CAPEX
Challenges and recommendations	The costs for enzymatic hydrolysis are still high, both CAPEX and OPEX. Further development is also needed to make the process more efficient.

Acid hydrolysis	
Inputs	Biomass (cellulose, hemicellulose, lignocellulose), acid, water
Outputs	Sugars
Process conditions	160 °C, 10 bar
TRL	6 – 9
Plant example	Used in bioethanol plants
GHG emission saving	N.D./depending on sources
Costs	N.D./depending on sources
Challenges and recommendations	High use of chemicals, corrosion, toxicity and inhibitory byproducts. Improvements could be made in terms of chemicals recovery and reuse and using microorganisms that are less sensitive to the inhibitors created.

Lignocellulose steam explosion	
Inputs	Lignocellulosic biomass (cellulose, hemicellulose, lignin), industrial steam
Outputs	Hydrolysed hydrocarbons (sugars)
Process conditions	Industrial steam (200 °C, 16 bar)
TRL	6 (steam explosion for biogas) to 9 (steam explosion for ethanol, pulp & paper, energy (black pellets)
Plant example	FICAP (black pellets), Finrenes BioFuelFab for biomethane (TRL 6), Zorg Teofipol UA (biogas), Life Steam
GHG emission saving	For one 4 Mcm biomethane, BioFuelFab using 20 kton of dry mass hardwood feedstock: • CO_2 savings from replacing fossil natural gas with biomethane 14,520 t/y • CO_2 capture by digestate 12,065 t/y

	• Total CO_2 savings 26,585 t/y
Costs	CAPEX 200 - 250 €/MWh for a complete 4 M cm lignocellulosic biomethane plant OPEX is mainly feedstock costs, OPEX for biomethane without feedstock cost is about 16-20 €/MWh.
Challenges and recommendations	Effectiveness related to different relevant feedstock, estimated by available feedstock (in EU: straw 430 Mton/y, softwood residues 54 Mton/y, hard wood residues 36 Mton/y, dry manure 80 Mton/y). Feedstock need for 35 bcm at 300 m³ CH/t VS equals roughly 120 Mton feedstock (as hardwood) Feedstock availability study (from largest supply to the smallest).

Thermo-catalytic reforming	
Inputs	Lignocellulosic biomass to bio-oil and syngas
Outputs	Renewable gasoline and diesel, biomethane or hydrogen
Process conditions	Medium temperatures and high pressure with catalysts
TRL	6 – 7
Plant example	To-Syn-Fuel Hohenburg, Germany
GHG emission saving	Above 85% and >100% with the production of biochar with environmental co-benefits.
Costs	Biomethane: Comparable to AD biomethane (40 – 120 €/MWh) but no food competition and could be reduced with innovative upgrading of the off-gas.
Challenges and recommendations	More research is necessary for the off-gas upgrading to biomethane utilizing the rich hydrogen component in this gas. This would include catalytic, electrochemical or biological upgrading and the development of the appropriate catalysts and catalytic systems, besides possibly suitable separation technologies. Upgrading the off-gas from TCR to biomethane could be an effective way of using low-grade and abundant organic feedstock, such as sewage, utilizing most of the carbon and hydrogen contained in it to produce lower cost biomethane. In addition, further research to reduce the cost of biomethane production and increase the sustainability through higher GHG emission savings in the conversion step(s) and even negative emissions through storing carbon from the production process in the soil should be pursued.

Biomass gasification	
Inputs	Lignocellulosic biomass (woody residues)
Outputs	Biomethane
Process conditions	700 – 1500 °C, 1 – 20 bar
TRL	6 – 8
Plant example	GoBiGas plant in Gothenburg, Sweden (32 MW)
GHG emission saving	90% and upwards using domestic residues.

Costs	60 – 105 €/MWh
Challenges and recommendations	A challenge is the rather long value chain, which is difficult to develop fully in smaller scale, when the technology as such is suitable for large scale. Another challenge is the choice of different synthesis routes – biomethane, bio-DME, biomethanol with different market challenges. Technically, a major challenge is the cleaning of tars and for pressurized gasification also fuel feeding.

Hydrothermal processes	
Inputs	Wet biomass to syngas
Outputs	Biomethane or hydrogen depending on reaction conditions
Process conditions	Medium temperatures and high pressure with catalysts
TRL	4 – 6
Plant example	HyFlexFuel
GHG emission saving	Above 80% and >100% with the production of biochar with environmental co-benefits.
Costs	Comparable to AD biomethane (40 – 120 €/MWh) but no food competition and could be reduced with innovative upgrading of the bio-syngas
Challenges and recommendations	There is a wide range of potential process designs and there are several technological gaps for the commercialization of hydrothermal processing, such as: • Lack of understanding the chemical mechanisms • Advanced materials (due to corrosion in the extreme reaction conditions) • High performing and low cost catalyst and catalytic systems • Establish the optimal process parameters • Reactor design, process development and optimization • Reducing CAPEX In addition, further research of HTG to reduce the cost of biomethane production and increase the sustainability through higher GHG emission savings in the conversion step(s) should be pursued.

Microbial electrolysis cell	
Inputs	CO_2 and organic waste
Outputs	Biomethane
Process conditions	Near neutral pH, continuous electric power supply, maintenance of anaerobic conditions in the reactor.
TRL	4 – 5
Plant example	Denmark (University of South Denmark)
GHG emission saving	N.D./depending on sources
Costs	110 €/MWh
Challenges and recommendations	Some efforts have been made to improve reactor designs, anodic reaction optimization, product optimization, and the production rate during the last two years. Further advancements will be required for

	improving mass transfer, energetic efficiencies, and product extraction strategies, along with scale-up studies with renewable energy sources to achieve the goal of transferring these technologies from lab to industry.

Macroalgae fermentation	
Inputs	CO_2, nutrients (e.g., nitrogen, phosphorus etc.), water, light (natural or artificial illumination)
Outputs	Biomethane 90 – 97%, CO_2 < 3%, O_2 < 1%, N_2 < 3%
Process conditions	Temperature: 20 – 40 °C (depending on species), ambient pressure (P_a < 1 bar)
TRL	Biogas production: 5 – 7 Biogas upgrading: 3 – 5 Biomass production: 6 – 9
Plant example	There are no pilot units yet (only lab scale test units)
GHG emission saving	N.D./depending on sources
Costs	60 – 180 €/MWh (rough estimation)
Challenges and recommendations	Variability in feedstock (different species, growth conditions, seasonal fluctuations), optimization of process conditions, non-harmonized regulatory framework for cultivating and processing seaweed

Biological methanation	
Inputs	CO_2, H_2, microorganisms (hydrogenotrophic methanogenic archaea), nutrients
Outputs	CH_4, water, heat
Process conditions	Mesophilic to thermophilic (depending on the microorganisms used) low pressure
TRL	6 – 8
Plant example	BIOMETHAVERSE project pilot plants in Italy, Sweden and Ukraine, TRL advance: 4 → 6 – 7. www.biomethaverse.eu Sempre-Bio project pilot plants in Spain and France, TRL advance: 5 → 7. https://betatechcenter.com/projects/sempre-bio/
GHG emission saving	N.D./depending on biogas feedstock and H_2 sources
Costs	CAPEX: 20 – 200 €/MWh, OPEX: 13 €/MWh (0.4 kWh electricity/Nm^3 biogas)
Challenges and recommendations	Hydrogen is the main bottleneck for this technology, both in terms of continuous access and in terms of making it react with CO_2, since hydrogen has poor solubility in water. The tank layout is therefore important to successfully mix gas and fluid. The low cell growth rate of anaerobic microorganisms is another limiting factor since the low cell productivities of continuous processes result in low volumetric productivities of CH_4. Biological methanation remains in the laboratory and demonstration stage, and further development is required to reach the commercial stage.

Catalytic methanation	
Inputs	CO_2 or CO, H_2, metallic catalyst
Outputs	CH_4, water, heat
Process conditions	250 – 400 °C, ≈ 20 bar
TRL	7 – 8
Plant example	GoBiGas plant in Gothenburg, Sweden
GHG emission saving	N.D./depending on sources
Costs	CAPEX: 35 – 70 €/MWh
Challenges and recommendations	Access to hydrogen, tolerance for impurities and finding local recipients for excess heat are challenges that need to be addressed for catalytic methanation.

Photosynthetic upgrading	
Inputs	CO_2, nutrients (e.g., nitrogen, phosphorus etc.), water, light (natural or artificial illumination)
Outputs	Biomethane 90 – 97%, CO_2 < 3%, O_2 < 1%, N_2 < 3%
Process conditions	Temperature: 20 – 40 °C (depending on species), ambient pressure (P_a < 1 bar)
TRL	Biogas production: 7 – 9 Biogas upgrading: 4 – 6 Biomass production: 6 – 9
Plant example	University College of Cork, Ireland Bubble column photobioreactor (CO_2 absorption unit Height: 2 m, Diameter: 24 mm Valladolid University, Spain Bubble column photobioreactor (CO_2 absorption unit) Height: 1.8 m, Volume: 20 L
GHG emission saving	N.D./depending on sources
Costs	N.D./depending on sources
Challenges and recommendations	Some of the challenges with photosynthetic biogas upgrading to biomethane are: • Large land surface area needed for photobioreactor deployment • Development of more effective methods for CO_2 absorption and thermal energy valorization • Limited number of technology suppliers and track record Oxygen generated during photosynthesis, leading to elevated levels of O_2 (> 0.5%) in the upgraded biomethane is a major challenge to meet gas grid specifications using this process. Additional issues including: 1) low CO_2 mass transfer; 2) effective control of process parameters e.g., gas and liquid flow rates; 3) diurnal variability in operation due to photo-autotrophy; and 4) fluctuating seasonal operation affecting microalgae growth must be overcome to commercialize the technology.

	Recommendations are: • Optimization of the photosynthetic process to achieve higher yields of biomethane/biomass production. • Scaling up of production. Larger infrastructure needs to be tested for upgrading 500 m^3/h of biogas to biomethane. • Integration with other technologies (cascading biorefinery approach). • New products development (feed additives, antioxidants, pigments, lipids and other high added value products). • Cost reduction. Design of process and bioreactors for inexpensive solutions in cultivation, harvesting, extraction and gas separation.

Cryogenic upgrading	
Inputs	Upgrading: Biogas Polishing: Biomethane Liquefaction: High-purity biomethane
Outputs	Upgrading: Biomethane, CO_2 Polishing: High-purity methane Liquefaction: Bio-LNG
Process conditions	Cryogenic temperatures (down to -162 °C)
TRL	6 – 9
Plant example	*Cryogenic Biogas upgrading & liquefaction* *Greenville, Northern Ireland* *Sempre-Bio project: AD biogas cryogenic separation in Belgium*
GHG emission saving	Approx 33 kg CO_{2eq} saved per invested € on a 10 GWh plant
Costs	Upgrading + liquefaction CAPEX: > 70 €/MWh OPEX: > 11 €/MWh (0.8 kWh/kg methane) Service & maintenance costs: 2.5 – 5% of CAPEX per year

Challenges and recommendations	Challenges:
	• Improving the energy efficiency of the liquefaction process, especially for smaller capacity systems.
	• The cost for building large capacity solutions, as other conventional techniques, is well developed for large capacities.
	• Development of more effective methods for capturing and reusing waste heat.
	• Limited number of technology suppliers and track record.
	Recommendations:
	• Further test plants to be implemented within the applications of:
	  ○ Integrated cryogenic upgrading and liquefaction.
	  ○ Cryogenic polishing and liquefaction together with other upgrading techniques.
	• Further expand the availability in critical subcomponents for small and medium scale systems such as cryogenic compressors.
	• Further research in the area of valorization of the CO_2 and its quality.



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