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The hydrogen gas bio-based economy and the production of renewable building block chemicals, food and energy

Jo De Vrieze^{a,*},¹, Kristof Verbeeck^a, Ilje Pikaar^b, Jos Boere^d, Ad Van Wijk^{c,d}, Korneel Rabaey^a, Willy Verstraete^{a,d,e}

^a Center for Microbial Ecology and Technology (CMET), Ghent University, Coupure Links 653, B-9000, Ghent, Belgium

^b The University of Queensland, The School of Civil Engineering, QLD, 4072, Australia

^c Department of Process & Energy, Faculty of Mechanical, Maritime and Materials Engineering, TU Delft, Leeghwaterstraat 39, 2628 CB, Delft, the Netherlands

^d KWR Watercycle Research Institute, PO Box 1072, the Netherlands

^e Avecom NV, Industrieweg 122P, Wondelgem, 9032, Belgium

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ABSTRACT

The carrying capacity of the planet is being exceeded, and there is an urgent need to bring forward revolutionary approaches, particularly in terms of energy supply, carbon emissions and nitrogen inputs into the biosphere. Hydrogen gas, generated by means of renewable energy through water electrolysis, can be a platform molecule to drive the future bioeconomy and electrification in the 21st century. The potential to use hydrogen gas in microbial metabolic processes is highly versatile, and this opens a broad range of opportunities for novel biotechnological developments and applications. A first approach concerns the central role of hydrogen gas in the production of bio-based building block chemicals using the methane route, thus, bypassing the inherent low economic value of methane towards higher-value products. Second, hydrogen gas can serve as a key carbon-neutral source to produce third-generation proteins, *i.e.* microbial protein for food applications, whilst simultaneously enabling carbon capture and nutrient recovery, directly at their point of emission. Combining both approaches to deal with the intermittent nature of renewable energy sources maximises the ability for efficient use of renewable resources.

Introduction

The current rate of energy, chemicals and food/feed consumption is depleting the Earth's natural resources. This is reflected in the fact that "Earth Overshoot Day" is attained earlier each year [1], which was the case on 29th July 2019 (www.overshootday.org). The resulting disturbance of the Earth's long-term carbon cycle, related to the use of fossil fuels [2], emphasizes the human influence on the climate system [3]. This can be summarised in five key Reasons For Concern (RFCs), *i.e.* risks related to unique and threatened systems (RFC1), extreme weather events (RFC2), distribution of impacts (RFC3), global aggregate impacts (RFC4), and large-scale singular events (RFC5) [4]. Equally important, albeit receiving less attention than climate change, is the unprecedented release of reactive nitrogen and phosphorus into

the environment, which has led to the planetary boundaries being exceeded to a level beyond uncertainty [5]. Hence, to sustain the ever-growing world population, while reducing the environmental footprint of humanity, alternative and more sustainable ways of providing energy, chemicals and food/feed are needed.

Second-generation biorefineries allow the production of renewable chemicals from organic waste streams, such as crop residues [6], with multiple viable full-scale systems in Denmark [7], Brazil [8], Canada [9], the USA, and China [10]. In this way, a broad range of building block chemicals, not only ethanol, but also others, such as succinic acid, lactic acid, glycerol and sorbitol [10–12], can be produced, while avoiding competition with the agricultural food supply chain [13]. Nonetheless, the biorefinery concept can be challenged on three different levels. First, the photon-to-product conversion efficiency in

Abbreviations: CAPEX, capital expenditures; CCU, carbon capture and utilization; CNG, compressed natural gas; COD, chemical oxygen demand; HOB, hydrogen oxidizing bacteria; HHV, higher heating value; MOB, methane oxidizing bacteria; P2G, power-to-gas; RFCs, Reasons For Concern; OPEX, operational expenditures

* Corresponding author at: Ghent University, Faculty of Bioscience Engineering, Center for Microbial Ecology and Technology (CMET), Coupure Links 653, B-9000, Ghent, Belgium.

E-mail addresses: Jo.DeVrieze@UGent.be (J. De Vrieze), Kristof.Verbeeck@UGent.be (K. Verbeeck), i.pikaar@uq.edu.au (I. Pikaar), jos.boere@alliedwaters.com (J. Boere), a.j.m.vanwijk@tudelft.nl (A. Van Wijk), Korneel.Rabaey@UGent.be (K. Rabaey), Willy.Verstraete@UGent.be (W. Verstraete).

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agriculture (photosynthesis) is, in general, very low, with values of merely 1–2% [14], although maximum values of up to 6% for C4 photosynthesis have been reported [15]. Thus, this is a rather ineffective method for active carbon capture. Secondly, the transportation of organic waste streams involves a high energy and monetary cost, ranging from €30–70 per tonne dry matter, depending on the size of, and distance to the biorefining facility [16,17]. Finally, the refining process remains energy intensive [18], which is to a large extent related to the complex nature of these second-generation feedstocks [19].

An alternative concept relies on electrification of the (bio)economy through, e.g., solar power. This involves a shortcut through which solar power can be used directly within the bio-based economy, without the need for (inefficient) biomass production. The incoming solar energy that reaches the Earth's surface averages 161 W m^{-2} [20,21]. At an approximate average of 12 h of daylight, this amounts to $705 \text{ kWh m}^{-2} \text{ year}^{-1}$, averaged over the planet. Assuming a commercially available solar panel efficiency of up to 20% [22], this is equivalent to $141 \text{ kWh m}^{-2} \text{ year}^{-1}$ or $1.41 \times 10^6 \text{ kWh ha}^{-1} \text{ year}^{-1}$. Hence, as a simplified assumption, 1 ha is sufficient to supply the electricity needs for 400 European households [23]. Considering the anticipated developments in the photovoltaics sector, these figures will increase in the coming years, but, although this contributes a partial solution to the energy demand, it cannot directly provide a renewable supply of chemicals and food/feed [24].

The energy captured from the sun in the form of electricity can be converted with high efficiency (up to 90%) into H_2 and O_2 through water electrolysis [25]. With a higher heating value (HHV) of $39.4 \text{ kWh kg}^{-1} \text{ H}_2$, this allows the annual production of 32.2 tonnes of H_2 per hectare. The current price of electricity production via photovoltaics can be estimated at $\text{€}0.05 \text{ kWh}^{-1}$, but this will reduce in the coming years to $\text{€}0.03 \text{ kWh}^{-1}$ by 2020–2025, and even down to $\text{€}0.01 \text{ kWh}^{-1}$ by 2030–2040 [26,27]. This allows H_2 production at an electricity cost of $\text{€}2.2$ down to $\text{€}1.3$ and even $\text{€}0.4 \text{ kg}^{-1} \text{ H}_2$. Taking into account also capital (CAPEX) and operational (OPEX) expenditure, the total production cost can come down below $\text{€}1.0 \text{ kg}^{-1} \text{ H}_2$ by 2030–2040 [27]. This coincides with a decarbonisation of the energy sector, leading to a strong decrease in CO_2 emissions [28]. The potential of H_2 can be extended beyond the energy sector, because it can act as a key molecule in biological and industrial biotechnological processes, related to bio-based building block chemicals and food/feed production.

The objective of this study is to provide a new vision on the full potential of H_2 in the biotechnology sector. Two different conceptual process lines, including their potential limitations, opportunities and research needs, will be discussed. The first is the role of H_2 as central molecule in the production of building block chemicals following the (bio)methane route. Secondly, the direct use of H_2 in combination with carbon capture for food/feed production through microbial protein will be examined. A temporal framework combining both process lines will be drafted in the context of the hydrogen gas bio-based economy to maximise its usage efficiency and contribution towards integrated carbon capture and resource recovery.

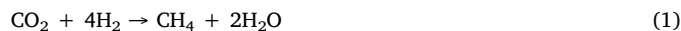
Bio-based chemical building block production: hydrogen gas as key molecule

In the carbon cycle of a CO_2 -neutral world, all anthropogenic CO_2 emissions would be captured, and converted back into fuels and chemicals with no net emission of CO_2 into the atmosphere [29]. Using concentrated CO_2 streams as carbon source in an efficient, fast, and large-scale catalytic chemical production process will require major scientific breakthroughs and technological development efforts, since today mature carbon capture and utilization (CCU) technologies are lacking [30]. Biological routes for fixation of CO_2 into valuable bio-based products, such as biomethanation, are moving from concept to reality, with various concepts demonstrated at pilot scale [31,32], and several full-scale applications for biomethanation, such as the

Electrochaea and ETOGAS approaches [33]. We envision H_2 as a key molecule in a future CCU-based bioeconomy, since (1) an extensive variety of microorganisms with a wide plethora of end-product metabolites can use this electron source for bioproduction, and (2) its carbon-free production via water electrolysis enables a CO_2 -neutral carbon/energy cycle to be achieved. The use of microorganisms as biocatalysts to metabolize CO_2 and H_2 (and CO) into organic compounds has several advantages over chemical catalytic conversion processes, including higher specificity, lower energy costs (mild operational conditions) and greater resistance to poisoning by e.g., tars, sulphur compounds or chlorine [34–36]. In our opinion, the transition from a fossil carbon-based to a CO_2 -neutral world economy can only be achieved if a massive amount of sustainable (low-carbon or carbon free) energy is available to electrify the production of chemicals and fuels. It is estimated that about 1200 TWh green electrical power would be needed per year as the resource base in a decarbonized basic material industry, based on the values of the 28 European Union (EU) countries in 2010 [37]. Assuming that this energy would be generated with solar technology at a solar panel efficiency of 20%, 8500 km^2 of installed photovoltaic panels would be needed (0.19% of the EU land area). Low-value land areas for installing the panels are available worldwide (e.g., arid zones). It can be estimated that, with a global total energy consumption of $1.64 \times 10^{14} \text{ kWh}$ in 2017 [38], about 13% of the Sahara desert surface area can suffice to empower the entire planet. Hence, these values indicate a huge need for increased production capacity of photovoltaic panels.

Hydrogenotrophic biomethanation: why (not)?

The hydrogenotrophic methanogens are the main representatives in the archaeal domain that can use molecular H_2 as electron donor to produce methane (CH_4) (Eq. (1)) [39,40].



This group of chemoautotrophic biocatalysts presents the opportunity of producing an attractive renewable energy carrier with well-established facilities in terms of distribution (e.g., the existing natural gas grid) and use (e.g., road transportation, power, heat or chemical production) [41]. Hydrogenotrophic biomethanation is often discussed in the context of power-to-gas (P2G) technology. The P2G concept links the power grid with the gas grid by converting intermittent or off-peak power into methane through electrolytic H_2 production and subsequent CO_2/H_2 conversion via (bio)methanation [33] (Fig. 1). This has recently gained interest as a scalable option for long-term and large-capacity storage of surplus renewable electrical power within the existing natural gas distribution grid [32]. The P2G technology could address the issue of an existing electricity transmission infrastructure that is found inadequate in transmitting large volumes of renewable power from wind and solar farms to the end users. As the share of renewable energy sources in the electricity mix is increasing rapidly, the need for efficient power balancing technologies becomes more important [42].

Large stationary point sources of CO_2 (such as power plants, (bio-)refineries, steel and cement industries) are often put forward as top candidates for methanation, but relatively small biogas plants can also suit the P2G process. In this proposal, the biomethanation process is used as an alternative strategy for CO_2 removal from biogas [43]. The P2G can be used as a biogas upgrading process unit that results in an increase in the total production of CH_4 from an organic feedstock [44].

Since the first description of the P2G technology, major developments have been achieved that resulted in rapid scale-up and industrialization of various methanation concepts. Two configurations for the conversion of CO_2 from biogas with H_2 have been proposed: (1) H_2 injection inside the anaerobic digester to stimulate the autochthonous hydrogenotrophic archaea (*in-situ* biomethanation) [45,46], and (2) H_2 and biogas injection in an external anaerobic reactor containing a pure

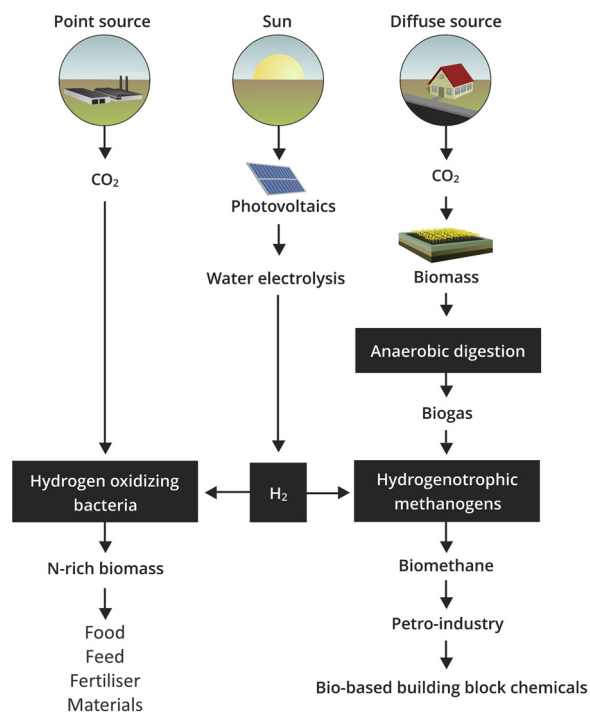


Fig. 1. Schematic overview of how H_2 can play a central role in the bio-based economy in the context of power-to-gas (P2G) approach.

or mixed hydrogenotrophic culture (*ex-situ* biomethantion) [47,48]. Current volumetric methane production rates of both concepts are still low compared to industrially established biogas formation in anaerobic digestion plants [49]. As recently reviewed, *in-situ* biomethanation is, at present, not considered a suitable option for industrial biomethanation, due to various operational challenges, such as pH control [43,44]. For both strategies, the key limitation of methanogenesis is the H_2 gas-to-liquid mass transfer. This limitation is typically addressed by (1) vigorous mixing, gas recirculation or fine-bubble gas distributors that increase the volumetric mass transfer coefficient ($k_L a$), and (2) enhancing the solubility of H_2 by increasing the partial pressure of H_2 (p_{H_2}) through an elevated headspace pressure [48,50]. Recently, the direct introduction of an electrode into the biomethanation reactor was proposed to increase production rates, and lower the power input for biomethanation *via* the *in-situ* supply of electrons or H_2 from the (microbially catalysed) cathode to the biocatalysts [51]. This strategy that enables the conversion of electrical current into methane is often referred to as electromethanogenesis [52], and although it is an intriguing concept, several challenges, such as uncontrollable side reactions and overall system complexity, hamper its further development.

Assuming a current H_2 production electricity cost of $\text{€}2.2 \text{ kg}^{-1} H_2$, and a hydrogen-to-methane efficiency of 90%, hydrogenotrophic biomethanation allows CH_4 production at $\sim \text{€}1.2 \text{ kg}^{-1} CH_4$. Because the current wholesale price of natural gas is below $\text{€}0.25 \text{ kg}^{-1}$, methane from biomethanation, at present, cannot compete with inexpensive fossil methane. These estimates highlight that the process would hold economic potential at a projected electricity cost for H_2 production of $\text{€}0.4 \text{ kg}^{-1} H_2$ by 2030–2040. Increasing power production from intermittent renewable sources can lead to temporarily low electricity prices, offering an opportunity for the application of biomethanation for energy storage.

Biomethane as origin for the bio-based petroleum industry

Grid injected biomethane could play a major role in the decarbonisation of the flexible energy system of the future. In particular, the ability to transport gas to be used elsewhere adds flexibility to the system, as not only the share of renewables in the transport and the heating sectors can be increased, but potentially also chemical production can be supplied with renewable (“green”) methane produced through anaerobic digestion or biomethanation. The prospect of using biomethane as carbon and energy source for chemical production initiates new utilization options for biogas, *i.e.*, not just for heat and power production or as fuel for vehicle use (compressed natural gas, CNG) [53,54], but also as a feedstock to produce bio-based commodity chemicals. Different biomethane utilization routes for production of platform chemicals are being proposed, starting from “green” C1 based products with subsequent (bio)catalytic synthesis [55,56]. For example, the upgrading of biogas to biomethane *via* different possible routes [57], subsequent conversion to syngas through steam reforming [55,56] and methanol production from syngas allows the production of dimethyl ether [58], which is an example of a bio-based commodity chemical. Hence, the notion of producing platform chemicals, conventionally derived from natural gas, from biomethane instead opens a path to a plethora of molecules that can be generated in a carbon-neutral way [59].

Carboxylic acids and alcohols as alternatives to methane

Not only methanogens, but also acetogenic bacteria are well-known for their ability to fix CO_2 with electrons from H_2 and produce acetate, ethanol, butyrate, butanol and 2,3-butanediol as natural end-products under chemolithoautotrophic growth [60]. Acetogenic gas fermentation is a novel and rapidly growing platform for bioproduction from industrial off-gases [61]. Its feasibility has been demonstrated at pilot scale [36,62], with the production of ethanol from CO -rich waste streams currently being scaled up to a commercial scale [61]. Key to the further development of this microbial production platform is the establishment of more efficient metabolic pathways from CO_2 . Most studies on CO_2/H_2 fermentations report acetate as sole product, with only traces of other higher-value organics, such as formate, butyrate or caproate [60,63]. Hence, higher-value products should be targeted at high rates to evolve towards economically feasible technologies. To achieve this, research is warranted to overcome the energetic limitations, related to thermodynamic constraints, by optimising gas composition and other operational parameters [64].

Microbial protein production driven by solar power coupled with carbon capture

The ability of different micro-organisms to use H_2 as electron donor transcends the different domains of life. Under anaerobic conditions, H_2 can be used by sulphate reducing [65] and homoacetogenic [66] bacteria. Under aerobic conditions, *e.g.*, hydrogen oxidising bacteria (HOB) *via* the Knallgas reaction [67] and cyanobacteria [68] can use H_2 as electron donor. In contrast to the hydrogenotrophic methanogens of the archaea domain, the aerobic HOB (Knallgas bacteria), so far, received little attention in the framework of engineering applications. Their ability to use H_2 as electron donor and O_2 as electron acceptor with the formation of H_2O , whilst simultaneously incorporating CO_2 autotrophically for biomass production and utilizing recovered nutrients can empower them with an important role in the bio-based economy. The idea of using HOB to produce microbial biomass rich in protein for food/feed applications originates from the 1970s [69]. This can be done either with pure cultures of *e.g.*, *Cupriavidus necator*, or mixed populations enriched on H_2 . This perception recently gained renewed interest [70], mainly related to the pressing need for alternative protein sources, surpassing first (animal meat) and second (soy) generation

proteins [71]. As both animal meat and soy production require considerable energetic and high inorganic fertiliser inputs, and have a high land footprint, the need for a transition to a more renewable protein source is apparent.

Microbial protein production through hydrogen oxidizing bacteria

The first key advantage of HOB lies in their ability to use H_2 as single electron donor. One kilogram of H_2 is equivalent to 8 kg of chemical oxygen demand (COD), derived from the fact that the Knallgas reaction requires 0.5 mol (16 g) O_2 per mole (2 g) H_2 (Eq. (2)). In contrast, 1 kg glucose, for example, coincides with 1.06 kg COD (Eq. (3)).



As the total production cost is expected to come down below a value of $\text{€}1.0 \text{ kg}^{-1} H_2$ by 2030–2040, it can compete with inexpensive carbon sources, such as methanol ($\text{€}0.8 \text{ kg}^{-1}$) and starch ($\text{€}0.3\text{--}0.5 \text{ kg}^{-1}$), due to the high COD content of H_2 , relative to organic carbon sources [10]. Considering a minimum safe protein intake of 60 g per person per day [72], and taking into account a world population of 7.2 billion in 2018, this amounts to an annual protein consumption of $1.6 \times 10^{11} \text{ kg}$ protein in the world. Based on a 75% protein content per gram cell dry weight for microbial protein [73] and a yield of 2.4 kg cell dry weight per kg of H_2 supplied [74], this leads to an annual H_2 consumption of $8.8 \times 10^{10} \text{ kg}$. Based on the HHV of $39.4 \text{ kWh kg}^{-1} H_2$ and a 90% efficiency for water electrolysis [25], this amounts to $3.8 \times 10^{12} \text{ kWh year}^{-1}$, which reflects 2.3% of global total energy consumption in the year 2017 [38].

Secondly, while carbon sources, such as methanol and sugar, are partially converted to CO_2 through a heterotrophic metabolism, the autotrophic HOB allow CO_2 capture from industrial point sources, based on renewable H_2 as energy source. Assuming a heterotrophic biomass yield of 0.4 kg biomass dry weight per kg organic substrate (e.g., sugar), 1 kg of dry biomass, containing on average about 50% carbon corresponds to 2.75 kg CO_2 produced. In contrast, 1 kg of autotrophic dry biomass corresponds with about 1.83 kg of CO_2 fixated. The current CO_2 market price is, however, reaching a historic low, with values not exceeding $\text{€}10 \text{ ton}^{-1}$ in the years 2014 to 2018, related to the imbalanced emission trading in the framework of the economic downturn of 2009, though a steady increase was observed in the second half of 2018 [75]. With the anticipated economic revival, the CO_2 market price is predicted to increase to $\text{€}30\text{--}50 \text{ ton}^{-1}$ by 2030 [76,77]. With a market price of $\text{€}50 \text{ ton}^{-1} CO_2$, the CO_2 fixating HOB could yield a revenue of $\text{€}0.23 \text{ kg}$ dry biomass in carbon credits, compared to CO_2 producing heterotrophs.

Third, the ability to use recovered nutrients, with nitrogen (N) and phosphorus (P) as the most relevant in terms of recovery potential, can be considered an important advantage of microbial protein production through HOB [73]. Different “waste” streams can act as a source of N, such as anaerobic digestate, source-separated urine and fresh animal manure, as each can contain over 4 g of total ammonia nitrogen per litre [78–80]. Nitrogen recovery from each of these waste streams can take place through different techniques of which ammonia stripping [81–83], electrochemical extraction [84] or a combination thereof [85,86] are the most promising approaches. An excellent example of such an integrated approach is reflected in the direct coupling of microbial protein production through HOB by directly introducing recovered ammonia from urine, combined with electrochemically produced H_2 [87]. Such an integrated electrochemical approach allows combining N recovery with H_2 production to increase the efficiency of the system. Although N is ubiquitous in the atmosphere, its recovery preserves energy needed for (1) fixation by the Haber-Bosch process ($10\text{--}12 \text{ kWh kg}^{-1} N$), and (2) removal through nitrification/denitrification ($2.8 \text{ kWh kg}^{-1} N$) or partial nitrification/anammox (1.4 kWh

$\text{kg}^{-1} N$) [80,88]. This would justify a N recovery cost of up to $15 \text{ kWh kg}^{-1} N$, due to the energy savings for N fixation and removal. This value can be obtained by most recovery technologies [84,87,89], although their transition from lab-scale proof-of-concepts to full-scale applications requires validation.

The recovery of P commonly takes place from the same waste streams through struvite precipitation, often combined with electrochemical systems [90–93]. The economic potential of P recovery, like N, will depend strongly on the market price of P, which reached a value of $\text{€}1.6 \text{ kg}^{-1} P$ (triple super phosphate) in 2018 [94]. This market price, in contrast to N, relates strongly with geopolitical constraints, due to the global disparity in phosphate rock reserves [95]. The low market value of recovered P, e.g., $\text{€}0.38\text{--}0.46 \text{ kg}^{-1} P$ for struvite [96], in addition to the total costs for P recovery, which are often a factor 5–10 higher than the recovered product market value [88,95], make P recovery from waste streams, at present, economically infeasible.

Microbial protein: challenges and application

Although the production of microbial protein appears to be very promising as a third-generation protein product, several challenges need to be addressed to evolve towards full-scale applications. First, the low solubility of H_2 (1.6 mg L^{-1}) is an important issue that needs to be addressed to increase efficiency of H_2 usage. Different strategies can be used to maximise H_2 availability to the HOB, as discussed above. Second, the availability of suitable concentrated gaseous CO_2 streams is essential to provide sufficient CO_2 to the HOB. Key candidate gas streams are biogas from anaerobic digestion or other large industrial stationary point sources. The anaerobic digestion plant can act as provider of recovered nutrients, renewable energy for electricity production through the combined heat and power unit, and CO_2 . Because biogas, next to CH_4 and CO_2 as main components, also contains H_2S and NH_3 , the potential toxicity, especially of H_2S , to the HOB requires special attention. The presence of H_2S in the biogas can also be advantageous, as a valuable source of sulphur for protein production. The use of biogas as source of CO_2 also opens the potential to consider a combined supply of CH_4 and H_2 to create a system that relies on methane oxidizing bacteria (MOB) and HOB for microbial protein production. This suggests novel possibilities for the combined use of H_2 and CH_4 as source for food/feed [97,98]. An interesting aspect that warrants further research is tuning the CH_4/H_2 ratio to modify the microbial composition and, ultimately, the quality of the final product in terms of protein quality (amino acid composition) and quantity, as well as digestibility. Incineration and steel plant off-gases may provoke similar issues as biogas, due to the presence of nitrogen oxides, carbon monoxide or other components, which may inhibit the HOB.

The targeted application of the microbial protein will determine strongly the required quality in terms of amino acid composition, presence of trace contaminants and microbial safety. Market prices of high-quality protein are variable, ranging from $\text{€}1.0\text{--}2.0 \text{ kg}^{-1}$ protein active substance [99]. Currently, microbial protein can be produced at competitive prices, but much depends on factors relating to the quality of the inputs, the downstream processing facilities and the quantity and quality demands imposed on the final product. Quality requirements for microbial protein for feed, and especially food applications, will be stringent [71], requiring considerable developments and research needs. The presence of potential opportunistic pathogens, antibiotic resistance genes and high concentrations of nucleic acids warrants thorough evaluation. The application of microbial protein as a slow-release organic fertiliser [74] will not put high demands on protein quality or microbial safety; the main requirement will be the slow-release character that better matches the release of N with plant uptake requirements to replace Haber-Bosch based inorganic fertilisers. Microbial protein can also be formulated in certain packaging and construction materials, noting the current demands for biodegradability and pressing issues concerning plastic debris in the environment

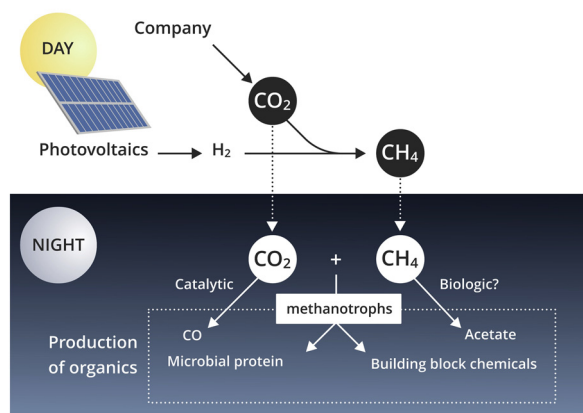


Fig. 2. Temporal equilibration in function of the available power supply of carbon fixation towards different end products.

[100,101].

Overall, microbial protein as a third-generation high-quality protein product for food and feed applications, as slow-release fertilizer or as renewable resource for other applications can be produced using H_2 as key compound together with CO_2 capture. The ability to use recovered nutrients and the need for point sources of CO_2 allow a combination with existing full-scale technologies, such as anaerobic digestion (Fig. 1), to make the transition from a “waste-to-energy” towards a “waste-to-food/feed” cyclic bio-based economy.

Temporal equilibration of power usage and CO_2 fixation

Many industries rely on continuous operation, which implies continuous CO_2 emission. Carbon capture and utilization strategies rely heavily on sustainable sources of reducing power, such as photovoltaics. The weather-related and diurnal discontinuity (in case of photovoltaics) of these energy sources in relation to the constant production of CO_2 , and the practical difficulties and economic constraints of temporarily storing large amounts of CO_2 under a pressurized form [102] may require different modes of action towards CO_2 CCU. Current proposals typically involve large-scale generation of H_2 via electrolysis, and its subsequent use to produce power, low and high temperature heat or products. In this area, microbial technologies are considered an interesting and attractive solution.

During periods of high renewable power supply, e.g., sunny and windy days, electricity can be coupled to CO_2 conversion to form an intermediate that can be used to support a diverse array of production processes (Fig. 2). A first option is the production of CH_4 . Processes to achieve this are already at demonstration scale, and production rates of $21\text{ m}^3\text{ CH}_4\text{ m}^{-3}\text{ reactor d}^{-1}$ have been obtained [47]. The concern with such P2G schemes is the low market value of CH_4 . An important point is that CH_4 not only stores electrons (8), but also CO_2 . It can also be compressed and liquefied reasonably easily, and additional supply is possible via an existing gas grid. This implies that if renewables cannot supply a set amount of CH_4 to achieve further production processes, it can be topped up. Similarly, basic building block chemicals, such as formate (chemically) or acetate (biologically), can be produced from CO_2 . Acetate in particular can be of interest, due to its universal use by microorganisms.

The production of high-value compounds that will create economic value for the overall process is essential to equilibrate the costs of the production process of the basic intermediates. The CH_4 can be used by methanotrophs to produce a wide array of outcomes, from fuels to food, such as commercial microbial protein products (e.g., Feedkind™ by

Calysta) (www.calysta.com). New metabolic pathways need to be considered that lead to net incorporation of additional CO_2 , while consuming CH_4 , essentially implying that products with a lower electron density (not fuels) are favoured. This principle can be understood, assuming a reaction not yet engineered, i.e. the formation of acetate from CH_4 (Eq. (4)).



Evidently, acetate will not deliver high economic returns, but could be considered as intermediate in the production of higher-value chemicals, such as 2,3-butanediol [103] or succinic acid [104], some of the key building block chemicals in demand today. The production pathways release part of the incorporated CO_2 relative to the degree of reduction associated with the target compounds, and this can be calculated for many compounds [105].

An alternative to enable diverse production from CH_4 is to perform first a chemical looping process, such as “super-dry” reforming (Eq. (5)) [55]



This is an outstanding approach to combining previously produced CH_4 with available CO_2 , and to follow this through with a microbial CO-based production process. There are several other options that blend CCU more creatively with other elements than carbon and oxygen.

In this conceptual approach, the pinnacle is the production of microbial protein from CO_2 , where the protein-rich microbial biomass is the product itself. Considering today’s meat footprint, ranging between 2–150 kg CO_2 equivalents per kg of meat, depending on the LCA study and type of meat [106], such an approach could have a major impact. Hence, it is important to identify processes that can rapidly combine available renewable energy and CO_2 into intermediates, and subsequently use them in a secondary, CO_2 capturing process to obtain an array of attractive products for the current and future bio-based economy.

Conclusions

The full potential of H_2 , produced through water electrolysis, driven by renewable energy sources, such as photovoltaics, extends beyond mere use as a fuel. Here, the opportunities of an electricity-driven hydrogen bio-based economy for the future have been highlighted. First, H_2 can be considered a central molecule to produce building block chemicals, following the CH_4 -route. Because CH_4 as such, produced via biomethanation of CO_2 , has insufficient value to compete with inexpensive fossil derived CH_4 , it should be used as energy and carbon source to produce bio-based high-value/commodity chemicals. Secondly, H_2 can serve as a carbon-neutral source to produce high-quality third-generation protein products, i.e. microbial protein, making use of recovered nutrients and enabling net carbon fixation. Both approaches can be combined in a temporal framework of electrification in the 21st century to maximise the utilisation potential of the discontinuous nature of renewable energy supply.

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