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Authors	Wu, Benteng;Lin, Richen;O'Shea, Richard;Deng, Chen;Rajendran, Karthik;Murphy, Jerry D.
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Production of advanced fuels through integration of biological, thermo-chemical and power to gas technologies in a circular cascading bio-based system

Benteng Wu [a,b], Richen Lin [a,b,*], Richard O'Shea [a,b], Chen Deng [a,b], Karthik Rajendran [c], Jerry D. Murphy [a,b]

[a] MaREI Centre, Environmental Research Institute, University College Cork, Cork, Ireland
[b] School of Engineering, University College Cork, Cork, Ireland
[c] Department of Environmental Science, SRM University-AP, Amaravati, Andhra Pradesh, 522502, India

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ABSTRACT

In the transition to a climate neutral future, the transportation sector needs to be sustainably decarbonized. Producing advanced fuels (such as biomethane) and bio-based valorised products (such as pyrochar) may offer a solution to significantly reduce greenhouse gas (GHG) emissions associated with energy and agricultural circular economy systems. Biological and thermochemical bioenergy technologies, together with power to gas (P2G) systems can generate green renewable gas, which is essential to reduce the GHG footprint of industry. However, each technology faces challenges with respect to sustainability and conversion efficiency. Here this study identifies an optimal pathway, leading to a sustainable bioenergy system where the carbon released in the fuel is offset by the GHG savings of the circular bio-based system. It provides a state-of-the-art review of individual technologies and proposes a bespoke circular cascading bio-based system with anaerobic digestion as the key platform, integrating electro-fuels via P2G systems and value-added pyrochar via pyrolysis of solid digestate. The mass and energy analysis suggests that a reduction of 11% in digestate mass flow with the production of pyrochar, bio-oil and syngas and an increase of 70% in biomethane production with the utilization of curtailed or constrained electricity can be achieved in the proposed bio-based system, enabling a 70% increase in net energy output as compared with a conventional biomethane system. However, the carbon footprint of the electricity from which the hydrogen is sourced is shown to be a critical parameter in assessing the GHG balance of the bespoke system.

1. Introduction

1.1. Advanced transport biofuel production: pressures and policy

The transportation sector is one of the largest and fastest growing energy consumers, and one of the most difficult sectors to decarbonize [1]. Although there are projections of a rapid increase in Electric Vehicles (EVs), there is still uncertainty in decarbonizing high-power transport vehicles (such as airplanes, ships and long-haul trucks). To decarbonize the transportation sector in a sustainable way, the European Union (EU) legislation and directives have set an ambitious goal to promote advanced biofuels. According to the European Union recast Renewable Energy Directive (2018/2001), advanced biofuels, including biomethane, refer to those which either do not use agricultural land or compete with food. As such typical advanced fuels include for those produced from animal slurries, food waste and other organic wastes and for macroalgae (seaweed) and microalgae [2]. The recast Renewable Energy Directive (2018/2001) introduces an obligation on European

List of abbreviations: EV, Electric Vehicle; EU, European Union; CNG, Compressed natural gas; LNG, Liquid natural gas; GHG, Greenhouse gas; AD, Anaerobic digestion; GWP, Global warming potential; DIET, Direct interspecies electron transfer; P2G, Power to gas; DES, Deep eutectic solvent; IL, Ionic liquid; MIET, Mediated interspecies electron transfer; GAC, Granular activated carbon; WAS, Waste activated sludge; FW, Food waste; VFA, Volatile fatty acid; TS, Total solid; VS, Volatile solid; LHV, Lower heating value; PEF, Primary energy factor; TEA, Techno-economic analysis; LCA, Life cycle assessment.

* Corresponding author. MaREI Centre, Environmental Research Institute, University College Cork, Cork, Ireland.
E-mail address: richen.lin@ucc.ie (R. Lin).

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transport fuel suppliers to ensure that the share of renewable energy in the transportation sector is not less than 14% by 2030; meanwhile the contribution of advanced biofuels should climb from at least 0.2% in 2022 to 3.5% in 2030 [2]. However, advanced biofuels in the transportation sector are not commercialized, with the exception of biomethane generated from slurries and organic waste with numerous examples in Sweden [3]. Electrification of lightweight private vehicles is seen as the future with advancing sales particularly in Norway. EVs are not seen by the authors as an application for heavy goods vehicles (such as haulage and coaches). Natural gas technologies are currently one of the most effective alternatives to diesel in the heavy-duty sector [4]. There are now more than 3600 compressed natural gas (CNG) and more than 200 liquid natural gas (LNG) refuelling stations in Europe, of which more than 10% are fuelled by biomethane [5]. CNG is suitable for automobiles at a significantly lower price than petroleum, while LNG shows a huge potential in medium- and long-distance transport (such as long-distance haulage trucks and maritime vehicles) due to its higher density, easier storage and transportation as compared with CNG [6]. The Alternative Transport Fuel Infrastructure Directive (2014/94/EU) states that by the end of 2020, Member States should ensure the establishment of a sufficient number of CNG (at least every 150 km) and LNG (at least every 400 km) refuelling points to sustain the circulation of all CNG and LNG vehicles across the EU [7]. Therefore, gaseous biofuels will have commercially available vehicles and distribution systems (including natural gas infrastructure) in place or at the very least a route to being in place. Optimising the sustainable and economic production of gaseous biofuels is therefore the crucial issue for reducing greenhouse gas (GHG) emissions of haulage.

1.2. Anaerobic digestion: an effective way to produce advanced biofuels

Recent advances have demonstrated that anaerobic digestion (AD) is a feasible and effective bioconversion technology for gaseous biofuel (biogas) production from various feedstocks, such as grass, cattle slurry and seaweed [8–10]. AD involves the decomposition and degradation of organic material under anaerobic conditions by different microbial consortium (including hydrolytic bacteria, acidogenic bacteria, acetogenic bacteria, and methanogenic archaea), finally resulting in the production of an energy rich gas mixture (typically contains 60% methane and 40% carbon dioxide).

AD is more than a technology for production of renewable energy. It is one of the most effective solutions to treat organic wastes [8]. It can reduce GHG emissions significantly; in particular reduction of fugitive methane (global warming potential (GWP) of 28) emissions from open slurry storage tanks can result in GHG negative transport biofuel as only CO_2 (GWP of 1) is emitted from the exhaust [11]. AD can supply organic biofertilizer to amend soil quality or generate nutrients for algal cultivation [12]. AD can also boost the economy in rural areas by providing employment and act as a platform that can combine different technologies to achieve a circular bioeconomic system.

Over the past decade, AD plants have witnessed a significant growth in Europe, mainly boosted by the favorable support programs from several EU Member States (Fig. 1). By the end of 2017, there were 17,783 AD plants and 540 biogas-upgrading plants in Europe, producing approximately 19,352 GWh of biomethane [13]. However, the increase in the rate of new AD plants in recent years has decreased greatly as there are still serious challenges in proving the sustainability of biogas and biomethane production.

1.3. Challenges faced by traditional anaerobic digestion

The first challenge is the degradability of feedstocks. While food waste and grass silage have been shown to have greater than 90% biodegradability [14,15], feedstocks such as algae, slurry and lignocellulosic feedstock can generate less than 50% of theoretical yield even at prolonged retention times [12,16]. With more than 70% of biogas produced from agricultural feedstock in Europe [13], the success of biogas production highly depends on the availability, composition and degradability of these agricultural feedstocks. There is a vast array of feedstocks available for AD; Allen et al. [17] documented the biomethane potential of 83 substrates including crop residues, livestock slurries, algae, and lignocellulosic biomass. The resource of the biomethane industry is dependent on the abundance and availability of these feedstocks [18,19]. Not all these feedstocks are ideal; lignocellulosic biomass is slow to degrade due to its recalcitrant physicochemical properties [20]. Feedstock pretreatment can enhance the biodegradability of these readily available but hard-to- degrade feedstocks. Pretreatment can be primarily classified into physical, chemical and biological approaches. Carrere et al. [21] highlighted the effectiveness of pretreatment in enhancing biogas production. Despite the enhancement of biogas production from a technological perspective, there are still many issues that need to be addressed, such as high operating cost, low recovery efficiency, formation of toxic co-products, and loss of fermentable components [22].

The second challenge is the overall conversion efficiency from “field to wheel” of feedstock; a significant amount of unutilized energy may remain in digestate. The readily degraded organics are utilized by microbes in digestion while the remaining solid organics are typically the recalcitrant and lignin components. Generally, digestate from AD is land-spread as biofertilizer or used as soil conditioner depending on the source and hygiene standards [23]. However, large digesters generating large quantities of digestate require significant areas of land to assimilate the nutrient loads. This process is ideally assessed using a nutrient management plan to negate potential for eutrophication, and environmental damage to soil and water quality [24]. There is potential to combine AD with other technologies to recover the energy in digestate in a circular economy and cascading bio-based system. Recent studies have shown that thermochemical technologies are a promising way to generate energy from solid digestate and offer the potential to produce extra energy in the form of syngas, bio-oil and biochar [12,25]. Due to its high specific area and considerable electrical conductivity, biochar can be potentially applied as an additive in AD to boost microbial

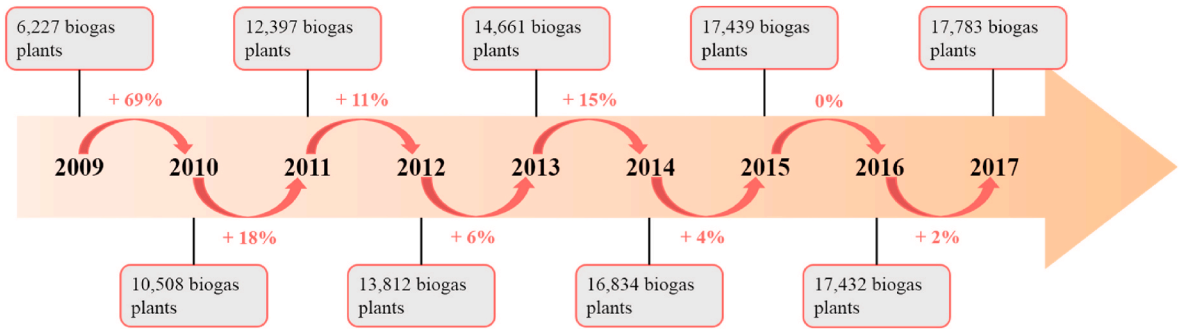


Fig. 1. Evolution of the number of biogas plants in Europe [13].

interactions and enhance AD performance [26,27]. Electrically conductive carbonaceous materials (such as graphene, carbon cloth and activated carbon) have been demonstrated to promote direct interspecies electron transfer (DIET) between acetogens and methanogens in AD, thereby enhancing biogas production [28,29]. However, the associated high cost (such as expensive graphene) may limit their practical application. Alternatively, renewable and cost-effective biochar derived from thermochemically treated digestate may have the potential to promote DIET. This characteristic has rarely been evaluated in AD systems. High quality biochar can act as a bridge coupling biological AD and thermochemical technologies, leading to the development of a future circular bioeconomy system.

Upgrading biogas to natural gas-grade biomethane effectively and economically is the third challenge in generating renewable transport biofuel from AD systems. Biogas generally contains 60–70% methane (CH_4) and 30–40% carbon dioxide (CO_2), thus it cannot be directly used in the transportation sector without removing CO_2 to achieve more than 95% (volume ratio) of CH_4 [30]. Various conventional upgrading technologies, including membrane separation, scrubbing (absorption methods) using water or chemicals, pressure swing adsorption with zeolities, activated carbon or carbon molecular sieve and cryogenic separation, are used to upgrade biogas [31]. However, the relatively high costs either from membranes, or addition of chemicals, application of high pressure, or intensive energy consumption, and methane loss are still constraints for their further development [32]. Sustainable ways for CO_2 capture and transformation to fuel including photoautotrophy by algae [33], photocatalysis by specific metal oxides [34], electroreduction by renewable electricity [35] and bioconversion by methanogens [36] represent potential "green" novel approaches to biogas upgrading. Power to gas (P2G) technology based biological methanation can upgrade biogas to biomethane by using hydrogen produced from curtailed or constrained intermittent renewable electricity (such as from wind or solar energy) described by the stoichiometric equation: $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ [36]. Optimised biological P2G systems can lower operational energy and cost and minimize fugitive CH_4 loss [37,38].

1.4. Towards a bespoke circular cascading bio-based system

To address the challenges outlined above, new strategies are required which integrate technologies in circular economy cascading systems. Different energy conversion technologies (such as pretreatment, pyrolysis, biogas upgrading, and algae cultivation) coupled with AD have been investigated; most of these investigations showed beneficial effects in terms of energy gains [1,33,36,39]. Pretreatment processes to improve the biodigestibility of feedstock have been shown to enhance biomethane production, particularly for lignocellulosic biomass [21,40]. Preliminary economic analysis of a system coupling hydrothermal pretreatment with AD suggested a discounted payback period of 4.8 years, 27% lower than the AD process without pretreatment [41].

However such a system does not deal with the large quantities of digestate produced, which for a vibrant biogas industry will necessitate large tracts of agricultural land to deal with the nutrient load of land spread of digestate [42]. Transportation and land application of digestate is a logistical and economic barrier to the industry. By coupling biological AD and thermochemical technologies, solid digestate from AD effluent can be converted into biochar, bio-oil and syngas, reducing the agricultural land required for land application of digestate and enhancing digestate valorisation [1]. The pyrolysis-AD system could produce 42% more electricity compared with the individual AD system [43].

Biogas cannot be directly used in the transportation sector; it needs to be upgraded to biomethane for such use. With integration of AD and biogas upgrading technologies, biogas can be utilized as an advanced biofuel to decarbonize the transportation sector (particularly long distance heavy transport not readily suited to electrification) rather than to generate heat or electricity. Techno-economic analysis revealed that from an economic perspective, the coupling of AD and amine scrubbers (traditional physio-chemical biogas upgrading) exhibited the cheapest production cost of biomethane, while from a sustainability or decarbonization perspective, renewable biomethane produced from *ex-situ* biomethanation showed a great advantage due to reuse of CO_2 [44]. Detailed discussion is found in Sections 2, 3 and 4.

A reduction in investment costs is critical to promote the integration of AD and P2G technologies. P2G is an early stage technology with expectations of significant improvements in technology, cost and resource. An economic assessment in 2020 is speculative. For example the 2020 EU hydrogen strategy (COM/2020/301 final) anticipates significantly reduced costs of renewable electricity and electrolysers, the key drivers for the development of hydrogen; electrolyser costs are expected to halve by 2030 as compared with that of today (2020) [45].

Some of the elements of the systems proposed are of themselves at low technology readiness levels. The proposed integration of the elements into a circular cascading bio-based system has not been realised yet. There is a lack of research on such systems, in which different biomass processing technologies are integrated with a goal of achieving the maximum production of advanced biofuels, increasing net energy output of the entire system, and optimising economic value obtained from the same amount of starting biomass. The objective of the paper is to propose and undertake a preliminary energy and carbon analysis of an integrated bio-based system generating renewable advanced biofuel, minimising land spread and operating as a biological battery for otherwise curtailed electricity. The system is embryonic for a detailed economic analysis.

1.5. Objectives

This paper offers a perspective on advanced gaseous biofuel produced through the integration of biological, thermochemical and power to gas systems in a circular cascading bio-based system incorporating carbon capture and use. Although individual bioenergy technologies have been studied with regards to improving energy production and sustainability, studies outlining the potential of circular cascading biosystems have been sparse. The research gaps still lie in: (1) developing highly efficient and environmentally friendly feedstock pretreatment methods; (2) identifying practical and sustainable ways to incorporate high-quality digestate derived biochar in AD or biogas upgrading systems to enhance biomethane production; and (3) integrating biological treatment (AD), electrofuels (P2G) and thermochemical technologies to achieve optimal biomethane production and digestate valorisation. The paper seeks to address the above research gaps by proposing an integrated circular cascading biobased system with optimised mass balance and energy yield, thereby facilitating future deployment of sustainable bioenergy systems.

The paper is structured as follows:

- Section 2 examines enhanced biogas production through feedstock pretreatment by novel deep eutectic solvents (DESs) and biochar-based DIET.
- Section 3 examines enhanced biogas upgrading via P2G systems and incorporation of biochar in biological methanation.
- Section 4 presents perspectives on an integrated circular bio-based system for advanced biomethane production, including the calculations of mass balance and energy analysis of the system.

2. Enhancement of biogas production efficiency

Generally, biogas production can be enhanced in two ways: (1) improving the digestibility of feedstock; (2) stabilizing and enhancing the AD process. Herein, studies on feedstock pretreatment to increase digestibility and methods to stimulation DIET in order to stabilize and enhance AD efficiency have been reviewed focusing on the application

of deep eutectic solvents and digestate derived pyrochar.

2.1. Feedstock pretreatment

Pre-treating recalcitrant feedstock has proven an efficient way to increase biogas production efficiency, particularly for lignocellulosic biomass [46,47]. The hydrolysis of polysaccharides to smaller molecules (such as mono sugars) is typically the rate-limiting step in the multiple reactions of AD, primarily attributed to the presence of the high content of lignin [18]. Lignin blocks hydrolysis of biomass because of its inherent structural resistance and rigidity and as such withstands oxidative stress and microbial access [22,48]. Conventional pretreatment methods (such as physical, alkaline, and steam explosion) have widely been investigated to improve biogas production [40,49]. A bioeconomy process coupling hydrothermal pretreatment with AD has been evaluated to decarbonize the production of whiskey using biogas to replace natural gas to produce combined heat and power [41]. By pre-treating whiskey by-products, biogas produced from pre-treated by-products could cover 100% of electrical energy demand and 25% of thermal energy demand of the conventional whiskey production process. Indeed, the electricity generated was equivalent to 446% of that required at the distillery. Overall, the process lead to a 61% reduction in energy associated CO_2 emissions. However, several technological challenges still remain with respect to hydrolysis efficiency, chemical addition, and generation of toxic inhibitors [40,49]. Pretreatment technologies for removing lignin can be classified into three generations; their benefits and drawbacks are summarized in Table 1. First-generation pretreatment methods (such as alkali, organosolv, and oxidative) show relatively high efficiency in removing lignin, but the need for rigorous conditions results in the loss of hemicellulose and cellulose. In addition, the potential formation of inhibitors and high operating costs can significantly hinder their practical application [50,51]. The effect of mechanical pretreatment on AD of grass *Hybrid Pennisetum* has been investigated; results revealed that biomass particle size reduction increased methane production by 2.5–8.2% and shortened the digestion time by 7.1–35.7% [52]. Alkaline pretreatment with NaOH was also adopted to treat *Hybrid Pennisetum*; with different NaOH solutions (2–8% w/w), temperatures (35 °C, 55 °C and 121 °C) and treatment times (24 h and 1 h); all treated groups showed significant removal of lignin (58.9–84.8%) [53]. The highest biomethane production of 302 mL/g VS, a 21.0% increase compared with the control, was obtained at treatment conditions of 35 °C, 2% NaOH and 24 h. However, adverse impacts on AD performance were observed at treatment conditions of 6% NaOH and 8% NaOH, in which high Na^+ concentrations reduced biomethane production by 3.2–7.3% [53]. Ionic liquids (ILs), categorized as the second-generation pretreatment technology, have demonstrated significant potential as efficient solvents for lignin removal. Gao et al. [54] used four kinds of ILs to pre-treat water hyacinth, mango leaves, spruce, and rice straw at different temperatures (100 °C, 120 °C and 140 °C) and times (2 h and 4 h); results showed that lignin removal rates in the range of 15.4–64.8% were achieved depending on the pretreatment time, temperature, biomass type, and ILs. With the selection of the optimal solvent based on lignin removal, treatment at 120 °C and 2 h improved biomethane yields (mL/g carbohydrates) from water hyacinth, mango leaves, spruce, and rice straw by 63.9%, 65.4%, 65.9%, and 70.4% compared with that of the control, respectively [54]. Studies on the integration of ILs and AD technology to produce biomethane are rather sparse, possibly resulting from its low economic feasibility, due to the complicated steps in preparation, the high cost of solvent materials and difficulties in reuse [55]. Furthermore, their low biodegradability, toxicity and high solubility of cellulose and hemicellulose lead to potential obstacles to incorporation with biological processes [55].

DESs are mixtures of hydrogen bonding donors (such as urea, acetic acid and glycerol) and hydrogen bonding acceptors (such as choline chloride, proline and glycine). Due to the hydrogen bonding interaction, they can be used as liquid solvent under ambient conditions [56]. DESs have been suggested as a "green" substitute for ILs in dissolving lignin due to their advantageous attributes including: easy and fast synthesis without the requirement of purification; high stability; high biocompatibility; high biodegradability; renewable nature; ease of recycling and reuse; and low price [57,58]. DESs are competent in removing large amounts of lignin, while leaving cellulose more or less in place, as demonstrated in Table 2. DESs have recently been extensively investigated in removal of lignin to improve enzymatic hydrolysis, but less has been done with respect to integrating this novel pretreatment with AD to improve biogas production. As recycling is not a significant barrier for DESs and the residual DESs in biomass can be biodegraded by microbes [56,59], therefore the combination of DESs pretreatment and AD should be a cost-effective and environmentally friendly approach to enhance biogas production, especially from lignin-rich biomass. Yu et al. [60] used choline chloride and hot water ($ChCl/H_2O$, mass ratio of 1:2) to pre-treat palm leaf sheaths; 53.6% of lignin removal was achieved, resulting in a significant enhancement of biogas production via AD (increased from 0.8 to 261.8 mL CH_4/g biomass). Nonetheless, the loss of hemicellulose accompanied with lignin removal should be addressed, and the feasibility of combining DESs and AD requires further research before its practical implementation.

Table 1
A comparison between different generations of lignin removal pretreatment methods to improve AD performance [40,49,50,58].

Generation	Typical technologies	Advantages	Disadvantages
First	Physical Steam-explosion Alkaline Oxidative Organosolv Liquid hot water	Extensively investigated Mature Relatively efficient	Negative energy balance Low recovery efficiency Generation of toxic co-products Loss of available components
Second	Ionic liquids	High thermal stability Low viscosity Excellent lignin removal efficiency	Troublesome to synthesize Expensive raw materials Poor biodegradability Toxic Difficult to recycle Loss of available components Volatile
Third	Deep eutectic solvents	Easy to synthesize Cost-competitive High stability Good lignin removal efficiency Biocompatible Biodegradable Non-toxic Easy to recycle	High viscosity Rarely investigated

2.2. Direct interspecies electron transfer

The efficiency and stability of AD are fundamentally determined by interspecies electron transfer among different microbial groups [28]. Developing accessible approaches to enhance electron transfer efficiency offers another route to improve biogas production efficiency. In the past few decades, the recognition of interspecies electron transfer in AD was based mainly on mediated interspecies electron transfer (MIET), in which hydrogen or formate is used as the electron carrier [65]. However, a critical requirement for MIET is that the metabolites must be maintained at low concentrations to make the reaction thermodynamically favorable [28,66]. For example, obligate proton-reducing acetogenic bacteria produce hydrogen in a reaction that is not favorable in the presence of a high hydrogen partial pressure. A syntrophic association is

Table 2
Lignin removal by different deep eutectic solvents (DESs).

Biomass	DES	Molar ratio[a]	T (°C)	Time (h)	Lignin removal (%)	Hemicellulose loss (%)	Cellulose loss (%)	Reference
Palm leaves	ChCl: H_2O	1:2[b]	180	0.5	53.6	10.8	4.8	[60]
Xylose residue	ChCl: formic acid	1:1.5	120	2	63.5	82.5	20.0	[61]
Xylose residue	ChCl: 1,4-butanediol	1:2	120	2	54.0	76.1	11.3	[61]
Xylose residue	Betaine: lactic acid	1:2	120	2	81.6	93.2	12.0	[61]
Rice straw	ChCl: formic acid: acetic acid	1:1:1	130	2	43.6	60.1	–	[62]
Switchgrass	BTMAC[c]: lactic acid	1:2	140	2	63.4	80.8	4.5	[63]
Switchgrass	BTEAC[d]: lactic acid	1:2	140	2	56.5	66.0	5.9	[63]
Wheat straw	ChCl: MEA[e]	1:6	70	9	71.4	42.1	6.3	[64]
Wheat straw	ChCl: DEA[f]	1:8	90	12	73.5	15.4	2.0	[64]
Wheat straw	ChCl: MDEA[g]	1:10	90	12	44.6	10.4	1.4	[64]

Note.
[a] Molar ratio between hydrogen bonding donors and acceptors in DESs.
[b] Mass ratio.
[c] Benzyltrimethylammonium chloride.
[d] Benzyltriethylammonium chloride.
[e] Monoethanolamine.
[f] Diethanolamine.
[g] Methyldiethanolamine.

formed between hydrogenotrophic methanogenic archaea and acetogenic bacteria via MIET, which allows the process to occur. Recent studies discovered that some bacteria (such as *Geobacter* species) can directly transfer electrons to methanogens (such as *Methanosarcina* species) without the need of hydrogen or formate as an electron carrier [67,68]. Such DIET processes offer thermodynamic and metabolic advantages to methane production from specific VFAs (such as propionic acid and butyric acid) as compared to conventional indirect electron transfer. For example, propionate oxidation to acetate via DIET pathway can yield 239 kJ/mol more energy (Eq. (2)) as compared to that via hydrogen diffusion (Eq. (1)) [1]; $\Delta G^{0'}$ is computed under the following conditions (T = 298.15 K, pH = 7, pressure = 1 atm, and [reactants] = 1 M).

$$\text{MIET: } CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2 \ \Delta G^{0'} = +71.6 \text{ kJ/mol} \quad (1a)$$

$$\text{DIET: } CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 6H^+ + 6e^- \ \Delta G^{'} = -167.4 \text{ kJ/mol} \quad (2)$$

This cell-to-cell electron exchange strategy between microorganisms has been recognized as "DIET" [67,69]. In general, electrically conductive pili (e-pili) or extracellular c-type cytochrome are indispensable to the natural transfer of electrons between species [70]. E-pili is suggested to be capable of functioning long-distance electron transport due to its metallic-like conductivity [71]. Extracellular c-type cytochrome derived electron transfer is another option for achievement of DIET without e-pili, however, cytochrome has been reported to be insufficient to allow long-distance electrical connections [72]. In a methanogenic digester, many bacteria are unable to act like *Geobacter* species in generating e-pili and thus facilitating DIET [73]. The addition of electrically conductive materials such as biochar, granular activated carbon (GAC), carbon cloth, graphite, and carbon-based nanomaterials (such as graphene and carbon nanotubes) provides a shortcut to compensate the deficiency or absence of e-pili, since syntrophic acetogens and methanogens can attach to these conductive materials and use them as electron conduits to exchange electrons for biomethane production [74,75]. This kind of electron transfer exhibits a more efficient and faster strategy compared with MIET (as shown in Eqs. (1) and (2)), ultimately accelerating the conversion of organic substates to biomethane.

The recent applications of carbon-based conductive materials in AD systems are summarized in Table 3. The addition of various conductive materials during AD has demonstrated the capability to increase biogas yield and production rates by 13.1–72% and 20.4–72%, respectively (as can be seen in Table 3). As a specific type of biochar, pyrochar is produced from pyrolysis of biomass including solid digestate in an oxygen-free environment. The physicochemical properties of pyrochar can be adjusted through controlled process conditions, offering potential advantages over expensive carbon-based conductive materials (such as graphene) [76]. Owing to the properties of high specific surface area and electrical conductivity, pyrochar can be potentially used as an additive to stimulate DIET and promote AD performance (Table 3). Li et al. [77] used sawdust based pyrochar to achieve stable and efficient biomethane production in thermophilic (55 °C) digestion of waste activated sludge (WAS) and food waste (FW); they demonstrated that the presence of pyrochar greatly reduced the lag time of CH_4 production and increased CH_4 production rate. Meanwhile, DIET was established between bacteria and methanogens, thus facilitating the syntrophic oxidation of butyrate and acetate [77]. In the presence of pyrochar, the syntrophic oxidation of volatile fatty acids (VFAs) was investigated when co-digesting dewatered activated sludge and FW [78]. The authors claimed that due to the accelerated DIET between bacteria *Anaerolineaceae* and methanogen *Methanosaeta*, the syntrophic degradation of butyrate to acetate was unaffected even under a high hydrogen partial pressure; the results showed that the lag time was shortened by 27.5–64.4% and the maximum methane production rate was enhanced by 22.4–40.3% [78]. Economical and conductive pyrochar with proper physicochemical properties may be capable of connecting bacteria and archaea like a bridge, which enables the possibility of accelerating DIET and improving biomethane production efficiency. The application of digestate derived pyrochar in anaerobic digestion has attracted attention due to not only the increased biomethane production compared with that of AD alone, but also other synergistic advantages, such as digestate valorisation and reduction of agricultural land requirement for managing digestate [12,79]. Deng et al. [1] coupled AD with pyrolysis through addition of pyrochar (produced from forest residue and solid digestate) to the digester to improve the biomethane yield from seaweed. The AD results demonstrated that the promotion effect of cost effective pyrochar (average price ca. €3/kg) on improving biomethane yield was comparable to that of expensive graphene (purchase price ca. €644/kg). The mass balance and energy analysis of this integrated system showed obvious synergies between AD and pyrolysis as biomethane production improved by 17% and digestate mass reduced by 26%; this leads to a slight increase in the net energy of the system, a reduction in digestate to be managed and a corresponding reduction in agricultural land requirement [1]. Ambaye et al. [80] adopted sewage sludge digestate derived pyrochar to enhance AD of fruit waste; more than 27% improvement in biomethane yield was achieved compared to that of the

Table 3
Summary of recent applications using carbon-based conductive materials to engineer direct interspecies electron transfer in anaerobic digestion systems.

Material	Substrates	Mode	T (°C)	Main contributions highlighted	Reference
Graphene	Ethanol	Batch	37	CH_4 production rate increased by 25.0%	[28]
			55	CH_4 production rate increased by 26.4%	[28]
Graphene	Glycine	Batch	37	CH_4 production rate increased by 28%	[75]
Carbon cloth	Butanol	Semi-continuous	37	CH_4 production rate increased by 59%	[81]
Carbon cloth	Leachate	Continuous	33	CH_4 production rate increased by 29.2%	[82]
GAC[a]	WAS[b]	Batch	37	CH_4 production increased by 13.1%	[83]
GAC	Acetic acid + ethanol	Batch	35	CH_4 production increased by 31% and its production rate increased by 72%	[84]
Pyrochar	Oil	Batch	35	CH_4 production increased by 32.5%	[74]
Pyrochar	Glucose	Batch	37	CH_4 production increased by 72%	[27]
Pyrochar	Chicken manure	Batch	35	CH_4 production increased by 69%	[85]
Pyrochar	Dairy manure	Batch	20	CH_4 production increased by 26.5% and its production rate increased by 20.4%	[86]
			35	CH_4 production increased by 24.9% and its production rate increased by 32.3%	[86]
			55	CH_4 production increased by 24.7% and its production rate increased by 50.5%	[86]

Note.
[a] Granular activated carbon.
[b] Wasted activated sludge.

Table 4
Pyrochar based *in-situ* biogas upgrading during anaerobic digestion: source, conditions, effects, and characteristics.

Pyrochar source	AD conditions	Effects of pyrochar on biogas quality	Highlighted characteristics of pyrochar	Reference
Corn stover	Thermophilic batch mode at 55 °C Feedstock: primary sludge Pyrochar dosage: 1.82–3.06 g/g TS of feedstock	CH_4 content in biogas enhanced by 20.4–29.3%; maximum CH_4 content reached 81.3–87.3%	Surface area; pore volume; alkalinity; alkaline earth metals	[79]
Corn stover	Thermophilic batch mode at 55 °C Feedstock: sewage sludge Pyrochar dosage: 1.82–3.64 g/g TS of feedstock	CH_4 content in biogas enhanced by 30.3–42.4%; maximum CH_4 content reached 88.5–96.7%	Surface functional groups; alkali and alkaline earth metals; ash content	[88]
Corn stover	Thermophilic semi-continuous mode at 55 °C Feedstock: sewage sludge Pyrochar dosage: 1.4–3.6 g/g VS of feedstock	CH_4 content in biogas enhanced by 13.7–25.3%; maximum CH_4 content reached 95%	Hydrophobicity; surface functional groups; alkalinity; alkali and alkaline earth metals; ash content	[91]
Pine	Thermophilic semi-continuous mode at 55 °C Feedstock: sewage sludge Pyrochar dosage: 1.4–3.6 g/g VS of feedstock	CH_4 content in biogas enhanced by 0.7–9.1%; maximum CH_4 content reached 84%	Alkalinity; alkali and alkaline earth metals	[91]
Walnut shell	Thermophilic batch mode at 55 °C Feedstock: food waste Pyrochar dosage: 0.96–3.83 g/g VS of feedstock	CO_2 removed by 40–96%; maximum CH_4 content reached 77.5–98.1%	Ash content, particle size; alkali and alkaline earth metals	[92]

control. These findings indicate that renewable pyrochar derived from solid digestate can improve the net energy output of the AD process.

3. Enhancement of biogas upgrading to biomethane

3.1. Pyrochar based in-situ biogas upgrading

For biogas to be used in the transportation sector, CO_2 and CH_4 must be separated with the aim of achieving a natural gas-like specification (above 95% methane content). The biogas upgrading process has to generate a high methane content, and to be sustainable with a low energy consumption and minimal methane loss. Apart from existing commercially available biogas upgrading technologies (mentioned in Section 1.3) pyrochar has recently been investigated as a means to *in-situ* sequester CO_2 during AD due to its high content of monovalent and divalent cations, which can facilitate carbonation reactions (such as $K_2O + 2CO_2 + H_2O \leftrightarrow 2KHCO_3$) [87,88]. Moreover, its high porosity also offers a large surface area for CO_2 capture [89,90].

Table 4 shows recent studies adding pyrochar in digesters to upgrade biogas *in-situ*. Shen et al. [88] successfully established an *in-situ* biogas upgrading system with the addition of corn stover pyrochar during AD of sludge, achieving more than 90% CH_4 content and less than 5 ppb H_2S. They revealed that due to the comparatively higher surface area (105 m^2/g) and content of alkali metals (14.2 wt% of K_2O, 4.2 wt% of MgO and 3.9 wt% of CaO in the ash after combustion of pyrochar), the CO_2 removal efficiency reached 86.3% and the CH_4 purity was 42.4% higher than the control digester with no addition of pyrochar. In a study by Shen et al. [91], two types of pyrochar (corn stover pyrochar and pine pyrochar) were applied in a continuous two-stage AD system under thermophilic conditions (55 °C). Results showed that compared with the control, the addition of corn stover pyrochar enhanced the CH_4 proportion in biogas by 13.7–25.3%, with a maximum CH_4 composition of 95%; while pine pyrochar showed relatively inferior performance but still improved the CH_4 content by 0.7–9.1% [91]. One possible explanation for this discrepancy was based on the surface functional groups. Compared with pine pyrochar, corn stover pyrochar exhibits an extremely low O/C ratio, indicating its high hydrophobicity which is suggested as an ideal characteristic for CO_2 adsorption. The inorganic element content may be another reason. With the addition of K-dominant corn stover pyrochar, the digester had a higher alkalinity (2300–3500 mg/L) than that of Mg-dominant pine pyrochar (1900–3000 mg/L), enabling more CO_2 to be captured to form bicarbonate/carbonate by base cations released from pyrochar [91]. Linville et al. [92] developed an *in-situ* biogas upgrading technology with the help of walnut shell pyrochar to sequester CO_2 during AD of FW at mesophilic and thermophilic conditions. Due to its strong porous

structure and high cation content (31 wt% of Ca, 8.4 wt% of Mg and 23.4 wt% of Na in the ash post combustion of pyrochar), biochar amended digesters removed 40–96% of CO_2 resulting in 77.5–98.1% concentration of CH_4 in biogas.

It should be noted that despite the high removal of CO_2 achieved, the higher dosage of pyrochar could lead to a decrease in biomethane production, which was caused by higher concentrations of mono- and divalent cations released from biochar into the solution of the reactor [92]. Hence, before implementation, the dosage of pyrochar in AD systems should be optimised to achieve the maximum CO_2 sequestration and biomethane production. Moreover, despite its low price (average ca. €3/kg) [1], the design of the reactor configuration to retain pyrochar within the digester should be considered in future research to enhance the sustainability of this process. During the sequestration process, most of the CO_2 was captured or fixed in biochar, and then was subsequentially sequestered in the soil when applied as a fertilizer. An alternative approach will be discussed below whereby CO_2 may be converted to a renewable fuel at mild operational conditions (such as standard atmospheric pressure, mesophilic or thermophilic conditions).

3.2. Power to gas based biogas upgrading

P2G, as a new biogas upgrading technology, is based on the CO_2-type hydrogenotrophs that can convert H_2 and CO_2 together into CH_4 as described by the following reaction ($\Delta G^{0'}$ is computed at: T = 298.15 K, pH = 7, pressure = 1 atm, and [reactants] = 1 M) [18,44]:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \; \Delta G' = -130.7 \text{ kJ/mol} \quad (3)$$

During this process, the CO_2 in biogas can be combined with hydrogen preferably sourced from renewable electricity. In an ideal P2G system the electricity used would be otherwise curtailed or constrained and as such the system is a chemical energy methodology for storing intermittent renewable electricity in the form of hydrogen, when supply is greater than demand [93,94]. Hydrogen can be generated from splitting water into hydrogen and oxygen using electricity via electrolysis. The hydrogen when biologically reacted with CO_2 in a bioreactor practically doubles the methane output of the biogas system, whilst upgrading biogas to biomethane.

In 2018, the European Biogas Association estimated that approximately 13.5 billion m^3 of CO_2 from existing biogas and biomethane plants could be methanised by P2G; this highlights the huge potential and resource for this technology [13]. Biological methanation is designed in two categories, *in-situ* and *ex-situ*, which have been proven in lab-scale under mesophilic and thermophilic conditions. In the *in-situ* process, H_2 is introduced into the conventional anaerobic digester to bind to the endogenous CO_2, which is then converted into CH_4 by hydrogenotrophic methanogens [18]. Wang et al. [95] revealed that this technology could achieve an approximate 99% biomethane content when the primary parameters (such as pH and hydrogen partial pressure) were fully controlled and monitored at optimal levels. However, a serious constraint of *in-situ* technology is the impaired equilibrium between methanogenesis and acetogenesis caused by high hydrogen partial pressure. This can be seen in the thermodynamics of obligate proton reducing acetogenic bacterial degradation of VFAs; for example the oxidation of propionate (Eq. (1)) and butyrate (Eq. (4)) to acetate ($\Delta G^{0'}$ is computed at: T = 298.15 K, pH = 7, pressure = 1 atm, and [reactants] = 1 M) [36]:

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2 \; \Delta G' = +71.6 \text{ kJ/mol} \quad (1b)$$

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2 \; \Delta G' = +48.3 \text{ kJ/mol} \quad (4)$$

To keep these reactions thermodynamically feasible, the hydrogen partial pressure should be maintained at a quite low level (less than 10 Pa) [96], which conflicts with the essential design concept of *in-situ* technology. Thus, efficient interspecies hydrogen transfer between acetogens and hydrogenotrophs is critical to prevent the inhibition of acetogenesis caused by the addition of exogeneous hydrogen. This highlights the potential role of conductive materials in *in-situ* biomethanation systems, which can alter the methanogenesis process from a hydrogen diffusion process to a DIET process. As described in Section 2.2 (and Eqs. (1) and (2)) pyrochar can stimulate DIET between acetogenic bacteria and methanogenic archaea and enhance the AD performance. Therefore, the introduction of pyrochar in digesters during *in-situ* biogas upgrading may alleviate the suppression of acetogenic bacterial oxidation of VFAs caused by high hydrogen partial pressure, thereby enhancing the stability and efficiency of the whole upgrading system.

Another major challenge is the increasing pH due to the reduction in CO_2 leading to lower levels of bicarbonate. As can be seen in Eq. (5), CO_2 dissolved in the solution in the reactor is dissociated to H^+ and HCO_3^-. The consumption of CO_2 in hydrogenotrophic methanogenesis then results in a decrease of H^+ level (Eq. (6)), thus increasing the pH of the process. Inhibition of methanogenesis occurs when the pH level reaches 8.5 [97]. Therefore, co-digestion with acid-containing wastes (such as food waste and whey) and the addition of economically viable materials with strong buffering capacity may provide a feasible solution for this challenge.

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \quad (5)$$

$$4H_2 + H^+ + HCO_3^- \rightarrow CH_4 + 3H_2O \quad (6)$$

As described in Section 2.2, pyrochar can stimulate DIET between acetogenic bacteria and methanogenic archaea and enhance the AD performance. Therefore, the introduction of pyrochar in the anaerobic digester during *in-situ* biogas upgrading may alleviate the inhibition of acetogenic bacterial oxidation of VFAs caused by high hydrogen partial pressure, thereby enhancing the stability of the whole upgrading system. Moreover, the high content of cations within pyrochar ensures a strong buffering capacity [76], which may counteract rising pH associated with *in-situ* biogas upgrading. However, the understanding of the application of pyrochar in the process of *in-situ* biomethanation is still largely speculative. Fundamental research in the laboratory is necessary to back up this hypothesis.

The *ex-situ* concept of biological methanation, in which CO_2 from external sources (including from biogas and from other sources) and H_2 are introduced into a separate bioreactor containing enriched or pure hydrogenotrophic methanogens, has been developed to overcome the constraints of the *in-situ* process [37]. Since the *ex-situ* strategy relies on a separate system in the absence of biomass feedstock (such as food waste), unstable degradation of VFAs caused by high partial hydrogen pressure is not of issue and as such the biological methanation process is easier to control. There are only gaseous feedstocks and such biological processes are dominated in taxonomy by hydrogenotrophic methanogens, such as *Methanothermobacter wolfeii* [37]. However, a critical technical challenge is the effective solubilisation of H_2 in *ex-situ* systems,

which limits its availability to the methanogens. As the solubility rate of H_2 in water at 55 °C is only 0.7 mmol H_2/L/bar, which is 24 times less than CO_2, the low gas-liquid mass transfer rate of H_2 becomes the decisive step for efficient *ex-situ* biogas upgrading [36]. Recent studies have demonstrated that the gas-liquid mass transfer rate is highly related to the reactor configuration, mixing intensity, gas recirculation rate, and the employed gas diffusion device [36,98,99]. The operating temperature also influences the efficiency of biomethanation. Guneratnam et al. [37] revealed that increasing temperature (55 °C–65 °C) could make the *ex-situ* biological methanation system more efficient; over 90% CH_4 content was steadily obtained at a yield of 0.45 $L_{CH4}/L_{reactor}$/day. Moreover, other studies revealed that the formation of biofilm could play a positive role in accelerating the biomethanation process. Porte et al. [100] used trickling biofilter reactors for *ex-situ* biomethanation under thermophilic condition; the authors achieved a stable biogas output with a high purity of biomethane (>97%) at a steady rate of greater than 1.7 $L_{CH4}/L_{reactor}$/day, due to the formation of biofilm localized with robust hydrogenotrophic methanogens that enabled a fast and efficient conversion process. Luo et al. [101] revealed that pyrochar-added AD could increase the proportion of archaea and set them in tightly bound fractions; the selective enrichment of functional microorganisms in both the internal and external biochar enhanced the resistance of the reactor to acid stress. Another study also observed the facilitated colonization of archaeal microorganisms induced by pyrochar-added AD [102]. From this aspect, pyrochar presents potential to serve as the filler or carrier to support the formation of biofilm in the *ex-situ* system because of its rough surface and internal porous structure. This hypothesis has been recently proved by Yang et al. [103], who introduced two types of pyrochar (derived from corn straw and digestate) in *ex-situ* biomethanation systems; results revealed that both types of pyrochar significantly accelerated the biomethane production rate and improved the biomethanation efficiency, which was suggested to be ascribed to their large specific surface area and surface functional groups that favoured the immobilization of hydrogenotrophic methanogens. However, this study was conducted in batch mode with a five-day experiment period, in which the hydrogen partial pressure was initially set at a fixed value but gradually decreased with the progress of the biomethanation process. The lack of data regarding continuous application of pyrochar in *ex-situ* biomethanation systems suggests the need for further research.

4. Perspective: an integrated circular cascading bio-based system

In the future, it is the perspective of the authors that the production of advanced biofuels will involve system optimization and integration within circular cascading bio-based systems complete with carbon recycling. As a platform technology, AD is a proven technology to produce renewable green gas from a wide assortment of feedstocks. The integration of AD with thermochemical technologies may show merits over a simple AD process. These include for: higher overall energy production through valorisation of the solid component of anaerobic digestate; and incorporating renewable pyrochar (derived from digestate) in both the AD process and in biogas upgrading. The literature is focused on the application of pyrochar in AD systems without emphasizing the number of roles it can undertake in an expanded integrated circular cascading system for advanced biomethane production. This paper proposes advanced gaseous biofuel production in an integrated circular cascading bio-based system including for biological, thermochemical and P2G systems (Fig. 2). AD is recognized as the core element, whilst intermediate products generated at each stage are adopted as the starting point of a new stage to maximize the environmental and economic benefits. The chemical reactions in the sequential processes are presented in Table 5.

As shown in Fig. 2, DESs can efficiently enhance the accessibility of wet organic feedstock especially lignocellulosic biomass to microorganisms, thus stimulating the production of biogas. *Ex-situ* biological methanation is chosen over *in-situ* due to the outlined merits of the *ex-situ* technology in Section 3.2. Pyrochar derived from pyrolysis of the solid component of digestate is used both in the AD process and in the *ex-situ* biogas upgrading processes. Pyrochar can play a significant role in

Table 5
Reactions of different processes in an integrated circular cascading bio-based system including for biological, thermo-chemical and power to gas systems.

Process	Reaction
Pretreatment	$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$
Enhanced anaerobic digestion	$nC_6H_{12}O_6 \rightarrow 3nCH_4 + 3nCO_2$
Ex-situ biogas upgrading	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$
Pyrolysis	$(C_6H_{10}O_5)_n \rightarrow$ pyrochar + bio-oil + syngas
Overall	$2(C_6H_{10}O_5)_n + 12nH_2 \rightarrow 6nCH_4 + 5nH_2O +$ pyrochar + bio-oil + syngas

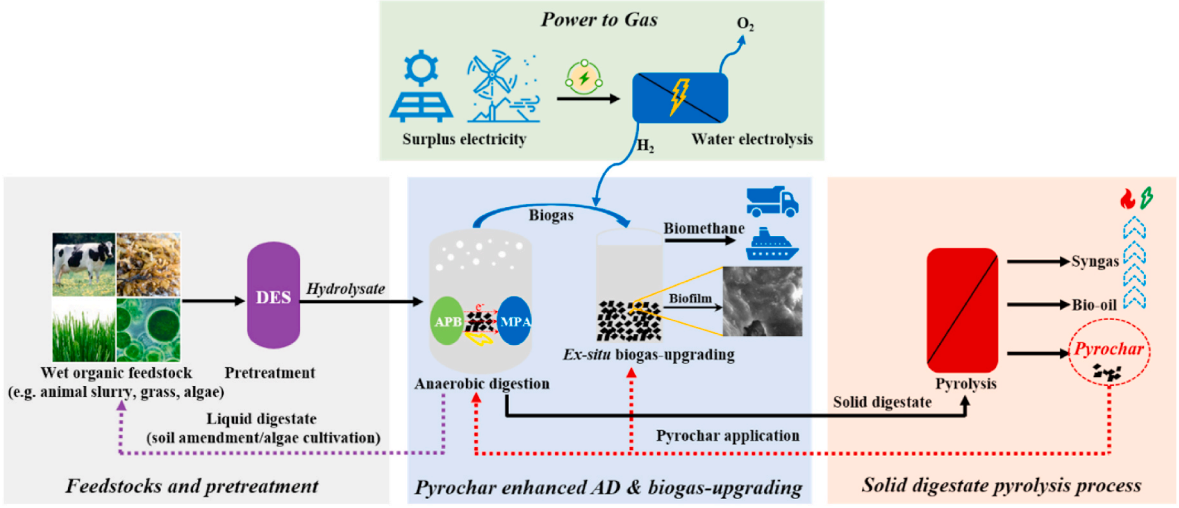


Fig. 2. Advanced gaseous biofuel production in an integrated circular cascading bio-based system including for biological, thermo-chemical and power to gas technologies (DES: deep eutectic solvents; APB: acid producing bacteria; MPA: methane producing archaea; the image of biofilm is reproduced with permission from Ref. [101] Copyright 2015, Elsevier Co.).

Table 6
Various assumptions made for the calculations of a conventional biomethane system and a circular cascading bio-based system.

Item	Components	Assumptions	Note
A conventional biomethane system			
Feeding	Cattle slurry	Dry solid (DS) = 8.75%; volatile solid (VS) = 6.69%	[15]; fed at a VS mass ratio of 1:1
	Grass silage	DS = 29.27%; VS = 26.84%	
Conventional AD system	Specific methane yield of feedstock	0.308 Nm^3 CH_4/kg/VS	[15]
	Biodegradability index of feedstock	74%	[15]
	Methane content in biogas	60%	CO_2 residue
Digestate segregation process	Electrical energy consumed	3.5 kWh_{el}/t digestate	[106]
	Moisture in solid digestate	70%	[107]
Amine scrubber biogas upgrading system	Methane content in the upgraded biogas	96%	
	LHV of CH_4	10 kWh/Nm^3 CH_4	[43]
Energy consumption of AD system	Thermal energy	25.54 kWh_{th}/t feedstock; heating feedstock from 15 °C to 37 °C ($E_{th} = C_p \times m \times \Delta T$)	[1]
	Electrical energy	10 kWh_{el}/t feedstock	[108]
Energy consumption of amine scrubber biogas upgrading system	Thermal energy	0.45 kWh_{th}/Nm^3 biogas input	[109]
	Electrical energy	0.09 kWh_{el}/Nm^3 biogas input	[109]
A circular cascading bio-based system			
Pyrochar enhanced AD system	Biodegradability index of feedstock	89%	[27]
	Methane content in biogas	70%	[91]; residual CO_2
Ex-situ biogas upgrading system	Methane content in the upgraded biogas	96%	[36]
	Electrical energy required to produce hydrogen	4.4 kWh_{el}/Nm^3 H_2	[110]
Solid digestate drying process	Moisture in solid digestate	70%	[107]
	Thermal energy consumption	Heating water and digestate from 25 °C to 100 °C and water evaporation at 100 °C	[111]
Dried digestate pelletizing process	Electrical energy consumption	150 kWh_{el}/t TS	[112]
Pelletized digestate pyrolysis process (500 °C)	Pyrolysis parameters	Temperature = 500 °C; residence time = 10 min	
	Bio-oil production	58.4 wt% (55% of water) of TS	[43]
	Syngas production	8.8 wt% of TS; 69.8 NL/kg TS	[43]
	Pyrochar production	32.8 wt% of TS	[43]
	LHV of syngas	4.36 kWh/Nm^3	[43]
	LHV of bio-oil	6.0 kWh/kg	[43]
	Electrical energy required	0.25 kWh_{el}/kg TS	[113]
Energy consumption of AD system	Thermal energy	25.54 kWh_{th}/t feedstock; heating feedstock from 15 °C to 37 °C ($E_{th} = C_p \times m \times \Delta T$)	[1]
	Electrical energy	10 kWh_{el}/t feedstock	[108]
Energy consumption of *ex-situ* biogas upgrading system	Thermal energy	0.01 kWh_{th}/Nm^3 CH_4 output	[44]
	Electrical energy	0.58 kW_{el}/Nm^3 CH_4 output	[44]

supporting DIET and as such in stimulation, immobilization of microbes, buffer potential, and biofilm growth. After AD, the remaining matter in the digestate is mechanically separated into liquid and solid components, in which dried solid digestate can be pyrolyzed into value-added products (such as syngas, bio-oil and pyrochar) to generate more utilizable energy, while liquid digestate can be valorised for soil amendment or algae cultivation [33,42].

4.1. Methods and calculations

To evaluate the sustainability of the entire system, an energy analysis and a mass analysis are assessed, based on the assumptions outlined in Table 6. Essential assumptions are as follows:

(1) The assumed biogas plant is fed with a mixture of cattle slurry and grass silage at a VS mass ratio of 1:1.
(2) Although DESs are considered efficient in enhancing the biomass biodegradability, research in its application in AD systems is still in its infancy. Therefore, the energy analysis of the system excludes the likely benefits of DESs pretreatment.
(3) The energy content of biomethane, bio-oil and syngas is calculated by lower heating value (LHV). Moreover, the primary energy consumption considered in this circular bio-based system includes the operation of AD (both electrical and thermal energy), *ex-situ* biogas upgrading (both electrical and thermal energy), hydrogen production (electrical energy), digestate segregation (electrical energy), drying the solid digestate after the centrifuge (thermal energy), pelletizing of dried solid

BOX 1
Calculations of a conventional biomethane system including AD and amine scrubber biogas upgrading processes for the production of biomethane.

Parameters of a conventional biomethane system

Conventional AD system

The assumed biogas plant is fed with cattle slurry and grass at a VS mass ratio of 1:1. A VS mass ratio of 1:1 equates to a wet weight ratio of 4:1; since slurry has a 6.69% VS content while silage has a 26.84% VS content. The corresponding biomethane yield is assumed as 0.308 Nm^3/kg VS which is equivalent to a 74% biodegradability index. Biogas contains 60% of CH_4 with the residual dominated by CO_2. With reference to Table 6:

- $TS = \frac{8.75\% \times 80 + 29.27\% \times 20}{100} \approx 12.85\%$
- $VS = \frac{6.69\% \times 80 + 26.84\% \times 20}{100} \approx 10.72\%$
- Biogas production $= \frac{10.72 \text{ t VS/day} \times 0.308 \text{ Nm}^3\text{/kg VS} \times 1000 \text{ kg/t}}{0.6} \approx 5{,}503 \text{ Nm}^3$ biogas/day

Energy consumption of the AD system is based on its electrical energy demand (10 kWh_{el}/t feedstock) and thermal energy requirement for heating the water in feedstock from 15 ºC (average ambient temperature) to 37 ºC (digester temperature):

$$E_{Heat} = m \times Cp \times (T_{AD} - T_a)/3600 \quad (5)$$

Where E_{Heat} (kWh_{th}/day) is the energy requirement of increasing the water from 15 °C to 37 °C; m (kg/day) is the mass of feedstock; Cp is the water specific heat equal to 4.18 kJ/kg/°C; T_{AD} is the digester temperature, assumed as 37 °C; and T_a is the average ambient temperature, assumed as 15 °C. The specific heat of solids in feedstock is assumed conservatively to be the same as the specific heat capacity of water.

- Primary energy requirement of the AD system = 100 t/day × 10 kWh_{el}/t feedstock × 2.3 (PEF of electricity) + 100 t/day × 1000 kg/t × 4.18 × (37 – 15) °C ÷ 3600 × 1.1 (PEF of natural gas) ÷ 0.9 (boiler efficiency) ≈ 5,422 kWh/day

Digestate segregation process

After AD, the feedstock is converted into biogas and digestate. The digestate is segregated by decanter centrifuge, with energy consumption of 3.5 kWh_{el}/t digestate (fresh matter).

- $m_{digestate} = m_{feedstock} - m_{biogas} = 100 - \frac{5503 \times 0.4 \times 44\ (CO_2) + 5503 \times 0.6 \times 16\ (CH_4)}{22.4 \times 1000} \approx 93.32$ t/day
- Primary energy requirement of digestate segregation = 93.32 t/day × 3. 5 kWh_{el}/t digestate × 2.3 (PEF of grid electricity) ≈ 751 kWh/day

Amine scrubber biogas upgrading system

Assume that the biogas produced from conventional AD system is upgraded by a conventional upgrading method (amine scrubber) while the biogas loss is not considered in this assessment. The methane content in the upgraded biogas is considered as 96% with residual CO_2. Assume that the LHV of CH_4 is 10 kWh/Nm^3 CH_4.

- Biomethane output = 5503 × 0.6 ≈ 3,302 Nm^3/day
- Primary energy content of upgraded biogas = 3302 × 10 = 33,020 kWh/day

Energy consumption of the amine scrubber biogas upgrading system is based on its electrical energy demand (0.09 kWh_{el}/Nm^3 biogas input) and thermal energy demand (0.45 kWh_{th}/Nm^3 biogas input).

- Primary energy requirement of the amine scrubber biogas upgrading system = 5503 Nm^3 biogas/day × 0.09 kWh_{el}/Nm^3 biogas × 2.3 (PEF of electricity) + 5503 Nm^3 biogas/day × 0.45 kWh_{th}/Nm^3 biogas × 1.1 (PEF of natural gas) ÷ 0.9 (boiler efficiency) ≈ 4,166 kWh/day

Total net energy output of a conventional biomethane system

Total net energy output of a conventional biomethane system is considered as the difference between total output energy and total input energy. Total output energy refers to the total primary energy of upgraded biogas (E_O'). Total input energy includes the primary energy consumption during the operation of AD (E_{I1}'), amine scrubber biogas upgrading (E_{I2}') and digestate segregation (E_{I3}'). With reference to Table 6:

- E_{I1}' = 5,422 kWh/day
- E_{I2}' = 4,166 kWh/day
- E_{I3}' = 751 kWh/day
- Total net energy output = E_O' – E_{I1}' – E_{I2}' = 33020 – 5422 – 4166 – 751 = 22,681 kWh/day

BOX 2
Calculations of a circular cascading bio-based system including biological, thermo-chemical and power to gas systems for the production of advanced biomethane.

Parameters of a circular cascading bio-based system

Pyrochar enhanced AD system

The biodegradability index of feeding after addition of pyrochar is assumed to be enhanced from 74% to 89%. The methane content in biogas is assumed as 70% with residual CO_2.

With reference to Table 6 and Box 1:

- Biogas production $= \dfrac{10.72\ \text{t VS/day} \times 1000\ \text{kg/t} \times 0.308\ \text{Nm}^3\text{/kg VS} \times (0.89 \div 0.74)}{0.7}$
  $= 5{,}673\ \text{Nm}^3$ biogas/day

Energy consumption of the AD system is based on its electrical energy demand and thermal energy requirement. With reference to Box 1:

- Primary energy requirement of the AD system = 100 t/day × 10 kWh_{el}/t feedstock × 2.3 (PEF of electricity) + 100 t/day × 1000 kg/t × 4.18 × (37 – 15) °C ÷ 3600 × 1.1 (PEF of natural gas) ÷ 0.9 (boiler efficiency) ≈ 5,422 kWh/day

Digestate segregation process

Digestate is considered to be separated by decanter centrifuge, in which a 3.5 kWh_{el}/t digestate (fresh matter) of energy is consumed.

- $m_{Digestate} = m_{Feedstock} - m_{Biogas} = 100 - \dfrac{5673 \times 0.3 \times 44\ (CH_4) + 5673 \times 0.7 \times 16\ (CO_2)}{22.4 \times 1000} \approx 93.82$ t/day
- Primary energy requirement of digestate segregation = 93.82 t/day × 3.5 kWh_{el}/t × 2.3 (PEF of grid electricity) ≈ 755 kWh/day

Ex-situ biogas upgrading system

The methane content after *ex-situ* biogas upgrading is assessed as 96%. The volume of input biogas is 5,673 Nm^3/day, including 3,971 Nm^3/day of CH_4 and 1,702 Nm^3/day of CO_2. Hydrogen is introduced at a recommended stoichiometric ratio of 4 : 1 (H_2 : CO_2). The energy requirement of hydrogen production is considered at 4.4 kWh_{el}/m^3 H_2 based on the mainstream electrolysis technology of alkaline electrolysis. Theoretically, the volume of CH_4 (X Nm^3), CO_2 (Y Nm^3), and H_2 (Z Nm^3) in upgraded biogas should satisfy the following equations:

$$X + Y = 5{,}673 \quad (1)$$
$$Z = 4Y \quad (2)$$
$$X \div (X + Y + Z) = 0.96 \quad (3)$$

Hence,

- Biomethane output ≈ 5,626 Nm^3 CH_4/day
- H_2 residue ≈ 188 Nm^3 H_2/day
- CO_2 residue ≈ 47 Nm^3 CO_2/day
- Primary energy content of upgraded biogas = 5626×10 = 56,260 kWh/day
- Primary energy requirement of hydrogen production
  = 1702 Nm^3/day × 4 × 4.4 kWh_{el}/m^3 × 0 (PEF of curtailed electricity) = 0 kWh/day (scenario 1)
  = 1702 Nm^3/day × 4 × 4.4 kWh_{el}/m^3 × 1 (PEF of renewable electricity) ≈ 29,955 kWh/day (scenario 2)
  =1702 Nm^3/day × 4 × 4.4 kWh_{el}/m^3 × 2.3 (PEF of grid electricity) ≈ 68,897 kWh/day (scenario 3)

For energy consumption of the *ex-situ* biogas upgrading system, it is based on its electrical energy demand (0.58 kWh_{el}/Nm^3 CH_4) and thermal energy demand (0.01 kWh_{th}/Nm^3 CH_4).

- Primary energy requirement of the *ex-situ* biogas upgrading system = 5626 Nm^3 CH_4/day × 0.58 kWh_{el}/Nm^3 CH_4× 2.3 (PEF of electricity) + 5626 Nm^3 CH_4/day × 0.01 kWh_{th}/Nm^3 CH_4× 1.1 (PEF of natural gas) ÷ 0.9 (boiler efficiency) ≈ 7,574 kWh/day

Solid digestate drying process

Assume that the moisture in solid digestate is 70%. Energy consumption of drying solid digestate is based on the thermal energy requirement of heating the water and digestate from 25 °C to 100 °C and water evaporation at 100 °C:

$$E_{Heat} = m \times Cp \times (T_{Final} - T_{Initial})/3600 \quad (5)$$

Where E_{Heat} (kWh_{th}/day) is the energy requirement of increasing the water and digestate from 25 °C to 100 °C; m (kg/day) is the mass of solid digestate; Cp is the water specific heat equal to 4.18 kJ/kg/°C; T_{Final} is

final temperature, assumed as 100 °C; and $T_{Initial}$ is the initial temperature, assumed as 25 °C. The specific heat of solids in digestate is assumed conservatively to be the same as the specific heat capacity of water.

$$E_{Evaporation} = m_{water} \times Lv/3600 \quad (6)$$

Where $E_{Evaporation}$ (kWh_{th}/day) is the energy requirement of water evaporation at 100 °C; m_{water} (kg/day) is the mass of water in the solid digestate; Lv is the latent heat of vaporization (2256 kJ/kg).

- Quantity of solid digestate = $\frac{12.85 \text{ t TS} - (10.72 \times 0.89) \text{ t VS destroyed}}{1 - 0.7} \approx 11.03$ t/day
- Quantity of water in solid digestate = 11.03 × 0.7 ≈ 7.72 t/day
- E_{Heat} = 11.03 t/day × 1000 kg/t × 4.18 kJ/kg/°C × (100 – 25) °C/3600 ≈ 961 kWh_{th}/day
- $E_{Evaporation}$ = 7.72 t/day × 1000 kg/t × 2256 kJ/kg ÷ 3600 ≈ 4,838 kWh_{th}/day
- Primary energy requirement for drying solid digestate = (961 + 4838) × 1.1 (PEF of natural gas) ÷ 0.9 (boiler efficiency) ≈ 7,088 kWh/day

Dried solid digestate pelletizing process

Dried solid digestate is pelletized to make the storage and loading of digestate for pyrolysis efficient. The energy consumption of the pelletizing step is considered as 150 kWh_{el}/t TS.

- Primary energy requirement of pelletizing = (11.03 – 7.72) t/day × 150 kWh_{el}/t TS × 2.3 (PEF of grid electricity) ≈ 1,142 kWh/day

Pelletized digestate pyrolysis process (500 °C)

The pyrolysis process is assumed as slow pyrolysis (temperature and residence time is 500 °C and 10 min, respectively). The production of bio-oil, syngas and pyrochar are assumed as 58.4 wt% (55% of water), 8.8 wt% and 32.8 wt% of TS, respectively. The syngas yield is considered as 69.8 NL/kg TS while the LHV of syngas and bio-oil is assumed as 4.36 kWh/Nm^3 and 6.0 kWh/kg, respectively. The energy requirement of the pyrolysis process is considered at 0.25 kWh_{el}/kg TS.

- Bio-oil production = (11.03 – 7.72) t TS/day × 58.4 wt% × (1 – 0.55) ≈ 0.87 t/day
- Syngas production = (11.03 – 7.72) t TS/day × 8.8 wt% ≈ 0.29 t/day
- Pyrochar production = (11.03 – 7.72) t TS/day × 32.8 wt% ≈ 1.09 t/day
- Primary energy content of bio-oil = 0.87 t/day × 1000 kg/t × 6 kWh/kg ≈ 5,220 kWh/day
- Primary energy content of syngas = (11.03 – 7.72) t TS/day × 69.8 NL/kg TS × 4.36 kWh/Nm^3 ≈ 1,008 kWh/day
- Primary energy requirement of pyrolysis process = (11.03 – 7.72) t TS/day × 1000 kg/t × 0.25 kWh_{el}/kg TS × 2.3 (PEF of grid electricity) ≈ 1,903 kWh/day

Total net energy output of a circular system

Total net energy output of the circular cascading system is equal to the total output energy minus the total input energy. Total output energy includes the primary energy output of upgraded biogas (E_{O1}), bio-oil (E_{O2}) and syngas (E_{O3}). Total input energy considered in this system includes the primary energy consumption of the operation of AD (E_{I1}), *ex-situ* biogas upgrading (E_{I2}),digestate segregation (E_{I3}), drying of solid digestate (E_{I4}), pelletizing of dried digestate (E_{I5}), pyrolysis of dried digestate (E_{I6}), and hydrogen production (E_{I7}).

Scenario 1:

- E_{O1} = 56,260 kWh/day
- E_{O2} = 5,220 kWh/day
- E_{O3} = 1,008 kWh/day
- E_{I1} = 5,422 kWh/day
- E_{I2} = 7,574 kWh/day
- E_{I3} = 755 kWh/day
- E_{I4} = 7,088 kWh/day
- E_{I5} = 1,142 kWh/day
- E_{I6} = 1,903 kWh/day
- E_{I7} = 0 kWh/day

Total net energy output = $E_{O1} + E_{O2} + E_{O3} - E_{I1} - E_{I2} - E_{I3} - E_{I4} - E_{I5} - E_{I6} - E_{I7}$ = 56260 + 5220 + 1008 – 5422 – 7574 – 755 – 7088 – 1142 – 1903 – 0 = 38,604 kWh/day

Scenario 2:

- E_{I7} = 29,955 kWh/day

Total net energy output = $E_{O1} + E_{O2} + E_{O3} - E_{I1} - E_{I2} - E_{I3} - E_{I4} - E_{I5} - E_{I6} - E_{I7}$ = 8,649 kWh/day

Scenario 3:

- E_{I7} = 68,896 kWh/day

Total net energy output = $E_{O1} + E_{O2} + E_{O3} - E_{I1} - E_{I2} - E_{I3} - E_{I4} - E_{I5} - E_{I6} - E_{I7}$ = –30,292 kWh/day

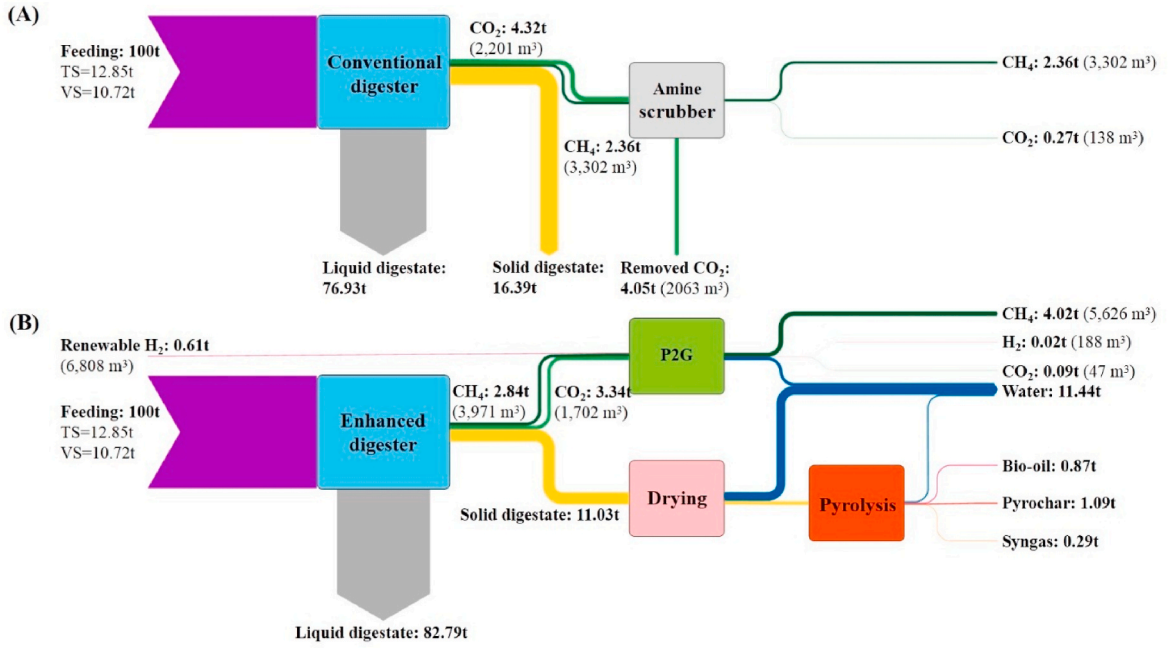


Fig. 3. Mass balance of (A) the conventional biomethane system and (B) the proposed circular cascading bio-based system based on one-day operation process (P2G: power to gas).

Table 7
Total net energy output of three scenarios in a circular cascading bio-based system.

Item	Components	Scenario 1[a]	Scenario 2[b]	Scenario 3[c]
Total output energy	Upgraded biogas (kWh/day)	56,260	56,260	56,260
	Bio-oil (kWh/day)	5220	5220	5220
	Syngas (kWh/day)	1008	1008	1008
Total input energy	AD (kWh/day)	5422	5422	5422
	Ex-situ biogas upgrading (kWh/day)	7574	7574	7574
	Digestate segregation (kWh/day)	755	755	755
	Drying of solid digestate (kWh/day)	7088	7088	7088
	Pelletizing of dried digestate (kWh/day)	1142	1142	1142
	Pyrolysis of pelletized digestate (kWh/day)	1903	1903	1903
	Hydrogen production (kWh/day)	0	29,955	68,896
Total net energy output	–	38,604	8649	−30,292

[a] Hydrogen from curtailed electricity
[b] Hydrogen from renewable electricity
[c] Hydrogen from non-renewables

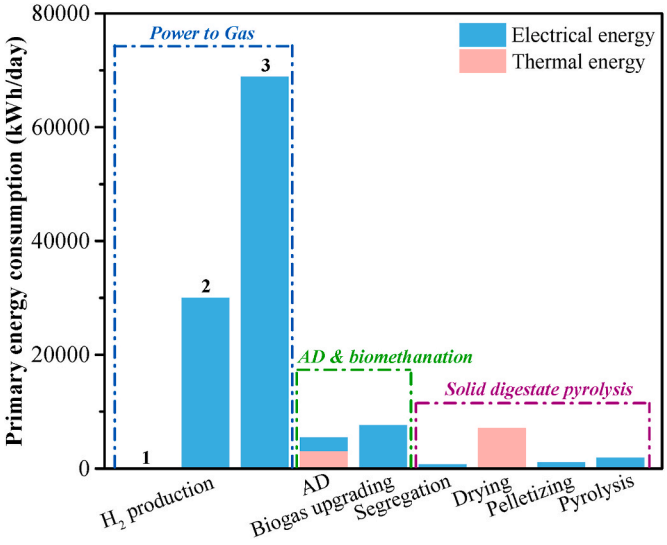


Fig. 4. Primary energy consumption of different processes in the proposed circular cascading bio-based system (1, 2 and 3 represent scenario 1, 2 and 3, respectively). Scenario 1: hydrogen from curtailed electricity (Primary Energy Factor (PEF = 0)); scenario 2: hydrogen from renewable electricity (PEF = 1); and scenario 3: hydrogen from non-renewables (PEF = 2.3) [105].

digestate (electrical energy), and pyrolysis of pelletized digestate (electrical energy).

(4) To compare the potential energy benefits of the proposed system, a conventional biomethane system including AD and amine scrubber biogas upgrading processes is assumed. The main energy consumption considered in this conventional system contains the operation of AD, amine scrubber biogas upgrading and digestate segregation.

(5) Considering the difference between primary energy consumption (covering consumption of the energy sector itself, losses in energy conversion and distribution processes, and the final energy consumed by end users) and final energy consumption (the total energy consumed by end users), the energy requirement of all processes is converted to primary energy consumption in the calculations. The volume of gases (such as hydrogen, biogas and syngas) is normalized to standard temperature (0 °C) and pressure (1 atm_{abs}). Natural gas is assumed to provide thermal energy in a boiler with an efficiency of 90% [104]. The primary energy factor (PEF) of natural gas, grid electricity, and renewable electricity is considered as 1.1, 2.3, and 1.0, respectively [105].

Box 1 shows the detailed calculations of mass and energy balance of a conventional biomethane system, where AD and amine scrubber biogas upgrading processes are adopted. Box 2 presents detailed calculations of the integrated circular cascading bio-based system utilizing three

scenarios, which deal with the energy input from hydrogen using three different assumptions in three different scenarios:

- ➢ Scenario 1: All hydrogen used for *ex-situ* biogas upgrading comes from water electrolysis, with the assumption that only curtailed or constrained electricity is used. Thus the electricity consumption of hydrogen production is not counted in the calculations of total net energy output (PEF = 0). Use of a PEF of zero is warranted as the electrical energy used by the electrolysis system would have been wasted in the absence of the system being assessed.
- ➢ Scenario 2: All hydrogen used for *ex-situ* biogas upgrading is assumed to be sourced from water electrolysis using renewable electricity (PEF = 1). It is assumed that sufficient renewable electricity can be supplied in a future where a high penetration of renewable generators is present in the electricity network as outlined in International Energy Agency Energy Technology Perspectives 2017 [114]. This renewable electricity could consist of curtailed and constrained electricity such as from wind farms, based on the data from Vo et al. [115], who suggests that the curtailed wind energy in Ireland in 2020 will be in the range of 2175–2535 GWh_{el}/annum due to a mismatch of supply and demand. Additionally, in order to achieve sufficient run hours of such a P2G system, some of the renewable electricity may also be purchased from an energy supplier through the use of guarantees of origin, as outlined in work by McDonagh et al. [116].
- ➢ Scenario 3: All hydrogen used for *ex-situ* biogas upgrading is assumed to be sourced from water electrolysis using non-renewable electricity (PEF = 2.3).

4.2. Results and discussion

The one-day mass balance of the integrated circular cascading bio-based system is shown in Fig. 3. Combined with pyrochar enhanced AD and *ex-situ* biogas upgrading, 100 t of wet organic feedstock can produce 5626 Nm^3 of renewable biomethane per day (Box 2), which is 70% more than that (3302 Nm^3) of the conventional biomethane system (Box 1). Vo et al. [115] also highlighted the significant enhancement effect on biomethane production from the integration of AD and *ex-situ* biomethanation (6.64 Mm^3 upgraded biogas/year with a 97% methane content) compared with that from the integration of AD and amine scrubber (3.44 Mm^3 upgraded biogas/year with a 96% methane content); this is a 95% increase. Moreover, adopting pyrolysis as the post-treatment approach for digestate is a significant way to optimize economic benefits of the whole system. By means of pyrolyzing, 3.31 t of dried digestate can produce 1.09 t of pyrochar, 0.87 t of bio-oil and 0.29 t of syngas, of which bio-oil can be upgraded into high-grade transport fuels through catalytic technologies [117] and syngas can be used directly for combined heat and power [25]. It is worth noting that the solid digestate pyrolysis process can result in a significant reduction in the digestate mass (11%) as 11.03 t of solid digestate is finally converted to 2.25 t of valuable by-products (namely biochar, bio-oil and syngas), which significantly reduces the agricultural land requirement for digestate spread, transportation cost and greenhouse gas emissions related to digestate application. Similar results were reported by Deng et al. [1] who proposed a bioenergy system integrating AD and pyrolysis to enhance gaseous biofuel production from seaweed; results revealed that 26% of the digestate mass could be valorised to produce biochar, bio-oil and syngas, and an increase of 17% in biomethane production and 10% in bio-oil yield could be achieved compared with individual AD and pyrolysis systems. The liquid digestate (82.79 t/day) rich in nutrients such as nitrogen and phosphorus could be applied as a land bio-fertilizer or used for algae cultivation.

Table 7 presents the total net energy output in three scenarios. A daily energy production of 56,260 kWh, 5220 kWh and 1008 kWh and can be expected from upgraded biogas, bio-oil and syngas respectively. The daily parasitic demand of the AD plant and *ex-situ* biomethanation process is considered as 5422 and 7574 kWh of primary energy, respectively, while the primary energy consumption of digestate segregation is modelled as 755 kWh/day. The total primary energy consumption of drying, pelletizing, and pyrolysis of solid digestate is considered as 10,133 kWh/day.

In scenario 1, if hydrogen is only generated from curtailed or constrained electricity, integrating AD, *ex-situ* biogas upgrading and digestate pyrolysis can produce a net energy yield of 38,604 kWh per day, which is equivalent to an increase of 70% compared with that of a conventional biomethane system (22,681 kWh/day). The increase in total net energy production demonstrates the strong synergy between different parts of this circular cascading bio-based system through enhancing the biomethane production efficiency and increasing the value of co-products. As mentioned earlier, Ireland in 2020 is expected to have more than 2175 GWh_{el}/annum of curtailed electricity from wind farms. The electricity consumption to meet the hydrogen demand in the proposed system is calculated as 10.93 GWh_{el}/annum (365 days per annum is considered), which makes up less than 0.5% of total expected curtailed electricity in Ireland. Nonetheless, if the capacity of this system increases significantly, curtailed electricity alone may be insufficient to provide hydrogen. Vo et al. [115] highlighted that if the potential CO_2 in biogas produced from typical wet organic feedstocks (such as grass, algae, animal slurry) in Ireland was used in a P2G system, 1722 MNm^3/annum of H_2 would be consumed, which equates to 7653 GWh_{el}/annum of electricity [44]. In this context, H_2 produced from expected curtailed electricity in 2020 would be able to contribute 28.4% of the required electricity.

In scenario 2, all hydrogen is derived from renewable electricity sourced from the grid. This is based on a bid price for electricity and as such includes electricity that could have been curtailed or constrained but also includes for electricity that would not have been curtailed or constrained but is less than the price bid. The circular cascading bio-based system in scenario 2 outputs a net energy yield of 8649 kWh per day, which equates to 38% of the net energy output of a conventional biomethane system. The expanded system including electrolysis reduces the net energy efficiency of the system when electricity from renewables are included in the system as per scenario 2. The system including electrolysis does have other benefits (further GHG saving of the transportation sector using an advanced transport fuel, grid balancing of electricity networks, and utilization of otherwise curtailed electricity). The curtailed electricity from wind or solar energy potentially offers an alternative way to increase the economic feasibility of P2G based biological biogas upgrading, which is heavily dependent on the cost of electricity [44]. McDonagh et al. [118] using the software package PLEXOS modelled a bidding strategy by a wholesaler of 5c/kWh of electricity, which would result in a yearly average purchase price of 3.5c/kWh as it would capture curtailed electricity or electricity produced at times of low demand. It has been shown that two different tools can be used in Ireland to minimize the carbon footprint of the electricity drawdown for hydrogen production, namely (1) wind forecasting and (2) bid price; electricity is cheap at times of excessive production associated with wind electricity on windy days [93]. Policy and incentives are necessary to reduce the cost of the electricity used in the electrolysis process, thereby improving the financial sustainability of P2G based biogas upgrading systems.

In scenario 3, hydrogen is assumed to be produced from water electrolysis using non-renewable electricity. This significantly reduces the sustainability of the circular cascading bio-based system, as 68,896 kWh/day of energy is consumed in hydrogen production, leading to a negative net energy output (−30,292 kWh/day). The rationale for this scenario is that in the event of high wind power production and low electricity demand the need to turn off the supporting fossil fuel power plants is negated as the fossil fuelled electricity may be sent to electrolysis removing the need for ramp down or turn off of the fossil fuelled systems.

The foregoing evaluation of scenarios 1, 2 and 3 highlight the variability in sustainability analysis of P2G based upgrading systems

depending on the carbon intensity of the electricity source [10]. It is hard for the proposed circular bio-based system to be sustainable with fossil fuel electricity used in hydrogen production, even combining its strong synergy and complementarity between different parts.

Fig. 4 compares the primary energy consumption of different processes in the bio-based system. Excluding the primary energy consumed by producing hydrogen (scenario 1), the parasitic energy demand of AD and of biogas upgrading processes account for a large proportion of total primary energy consumption (54.4%), while segregation, pelletizing and pyrolysis of digestate make up 15.9% (Fig. 4). Monlau et al. [43] suggested that an increase of 42% electrical energy could be achieved with the integration of pyrolysis and AD technologies compared with AD alone. It should be noted that the calculation was based on a series of assumptions which would lead to different results than here, for example: the electrical energy consumption of the pyrolysis process was not considered; neither were primary energy factors for heat and electricity taken into account to unify the primary energy baseline. Deng et al. [1] when considering the primary energy factors, found only 0.1% more net energy was gained in the pyrolysis-AD system as compared to AD in stand-alone operation. Reducing the energy consumption of drying solid digestate exhibits a huge potential to improve the overall energy output of this bio-based system as 29.7% of primary energy is consumed in solid digestate drying process. Interestingly, 6228 kWh/day of thermal energy can be expected from bio-oil and syngas produced from pyrolysis process, providing an ability to satisfy 88% of primary energy consumed in the solid digestate drying process.

Scenario 1 (PEF = 0) shows that the maximum net energy gain of the proposed circular cascading bio-based system in this study can be improved by 70%. The mass and energy analyses reveal that the proposed system benefits greatly through the utilization of curtailed electricity, digestate valorisation, and the positive effect of pyrochar addition on AD and *ex-situ* biomethanation. However, if this system is further expanded to a much larger scale, its sustainability may be weakened due to the carbon footprint of fossil based electricity leading to non-renewable hydrogen, leading to a negative net energy gain (scenario 3).

However, the EU published a hydrogen strategy in 2020 (COM/2020/301 final) which highlights that the production of renewable hydrogen is a priority for a climate-neutral Europe [45]. Costs of renewable hydrogen are expected to drop considerably with for example electrolyser costs expected to halve by 2030 compared with those of today (2020). In some regions where renewable electricity is cheap (and will become cheaper with scale of decarbonised electricity production), renewable hydrogen is expected to be cost-competitive against fossil-based hydrogen in 2030 [45]. Based on improved efficiencies and scale of intermittent renewable electricity (such as large offshore wind farms) and technology advances in electrolysers, if it is postulated that the primary energy factor of electricity to produce hydrogen could decrease to 0.5 (a combination of curtailed and renewable electricity), then the net energy output of the proposed bio-based system could be improved by 4.2% as compared with that of the conventional biomethane system.

The merits of (1) production of pyrochar from digestate with bespoke properties to trigger DIET in AD, (2) further utilization of pyrochar as the buffer for stabilization of the biomethanation process and/or as the biocarrier for growth of microorganisms, and (3) the utilization of curtailed electricity to produce renewable biomethane through the reaction of hydrogen with carbon dioxide, represent strong synergies between the different elements in scenario 1. Furthermore, bio-oil and syngas derived from digestate, increased biomethane production with pyrochar addition, and improved biomethane output using curtailed electricity and CO_2 in biogas, highlight the energy output advantage of scenario 1. Scenario 1 is proposed as a climate neutral integrated cascading bio-based system with an optimised mass balance and energy yield, which should be encouraged as a model for future deployment of a sustainable efficient bioenergy system.

4.3. Future perspectives

Until now, most of the technologies in this proposed bio-based system are investigated at laboratory scale and their integration is still in its infancy. However, the potential environmental and economic benefits of integrating these technologies are highly promising, for instance the reduction of GHG emission in transportation sectors, valorisation of digestate, enhancement of renewable biomethane production, and facilitation of intermittent renewable electricity. Current developments on enhancing biomethane production are significant, nevertheless, there are still many challenges that need to be overcome. More insights are required in the following areas:

(1) Delignification can efficiently accelerate the hydrolysis of biomass by reducing inherent structural recalcitrance and rigidity, enhancing subsequent biomethane production. Using DESs derived from green and cheap solvents (such as ChCl/urea) may be a desirable and cost-effective pretreatment method as it can efficiently remove lignin from recalcitrant biomass. However, the literature is very sparse in discussing combinations of DESs pretreatment and AD. Minimisation of losses of fermentable hemicellulose during DESs pretreatment needs investigation as does the biodegradability and biocompatibility of DESs in AD.
(2) Most of the literature focuses on the application of pyrochar derived from raw biomass in AD rather than from digestate. For future valorisation of pyrochar, digestate derived pyrochar and its influence on the performance and stability of a long-term run AD system should be investigated. Since the properties of pyrochar are adjustable by modifying production conditions (such as temperature, residence time and digestate type) suitable parameters of digestate pyrolysis should also be identified to produce specific kinds of pyrochar that can be used for promoting DIET, sequestrating CO_2 or attaching microbes. Furthermore, adopting digestate derived pyrochar as the carrier or supporter of microorganisms in *ex-situ* biogas upgrading process needs in-depth research before implementation.
(3) Integrating AD, *ex-situ* biogas upgrading, and digestate pyrolysis with carbon reuse can efficiently enhance total biomethane production and has great potential to increase the net energy output. However, the sustainability of the system heavily relies on the electricity source for hydrogen production and may be adversely affected by the use of non-renewable hydrogen derived from fossil fuels especially when numerous systems are applied in a large geographic area. In addition, the energy consumption in relation to drying solid digestate needs to be significantly reduced, thereby allowing for increased sustainability.
(4) The energy analysis of the circular cascading system shows its advantage in enhanced bioenergy production. However, in-depth techno-economic analysis (TEA) and life cycle assessments (LCA) are critical to evaluate the economic and environmental feasibility associated with the production of biomethane. TEA can assist in the scale-up of the experimental work by assessing factors which are essential for financial profitability and other economic indicators. LCA can contribute to evaluating environmental related parameters (such as carbon balance) in the defined system. The authors recommend efforts to promote systematic laboratory work, which can be extended to pilot-scale, and finally to commercialise the entire system.

5. Conclusion

Producing advanced gaseous biofuels in a sustainable biorefinery scheme is necessary to sustainably reduce GHG emissions from haulage. Integrating AD, *ex-situ* biogas upgrading and digestate pyrolysis may be a promising strategy to produce renewable biomethane in a circular cascading bio-based system. Pyrochar derived from digestate pyrolysis

can be used to enhance the efficiency of both biogas production and upgrading in the AD system. Biomethane production is shown to increase by 70% through adopting P2G biogas upgrading technologies (biomethanation). The energy analysis suggests that the symbiosis of AD, P2G and digestate pyrolysis is capable of increasing final net energy output by 70% as compared with a conventional biomethane system if the electricity used to produce hydrogen is assumed to be otherwise curtailed. However, if the hydrogen is sourced from renewable electricity guaranteed by renewable certificates or connected directly to a wind farm (or photovoltaic array) then the net energy return is reduced to 38% of the conventional biomethane system. As such electricity source is a major influencer on the benefits of the bespoke system. Future research is needed to validate the technical and economic feasibility of the proposed circular system before commercial application.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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