Bioresource Technology 243 (2017) 1207–1215

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Review

Cascading biomethane energy systems for sustainable green gas production in a circular economy

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ARTICLE INFO

Keywords:
Anaerobic digestion
Macro-algae
Microalgae
Power to gas
Biomethane

ABSTRACT

Biomethane is a flexible energy vector that can be used as a renewable fuel for both the heat and transport sectors. Recent EU legislation encourages the production and use of advanced, third generation biofuels with improved sustainability for future energy systems. The integration of technologies such as anaerobic digestion, gasification, and power to gas, along with advanced feedstocks such as algae will be at the forefront in meeting future sustainability criteria and achieving a green gas supply for the gas grid. This paper explores the relevant pathways in which an integrated biomethane industry could potentially materialise and identifies and discusses the latest biotechnological advances in the production of renewable gas. Three scenarios of cascading biomethane systems are developed.

1. Introduction

It is evident that future EU legislation will become more focused on the use of advanced biofuels to further the reduction of greenhouse gas (GHG) emissions in the energy sector. The most recent EU directive proposals have suggested a progressive reduction in first generation (food based) biofuels by 2030; with an increasing share in renewable, low-carbon transport fuels (including electric vehicles) from 1.5% in 2021 to 6.8% by 2030, with advanced biofuels to make up at least 3.6% by that time (EC, 2016). This will require a significant overhaul of the current energy system which is predominantly fossil fuel based. Sustainability will become a more significant issue in terms of biofuels contributing towards set EU renewable energy supply (RES) targets. At present, on a whole life cycle analysis basis, GHG emissions must be reduced by 60% compared to the fossil fuel displaced to count as a renewable transport fuel, with a further increase to 70% scheduled for 2021 (EC, 2016). Thus, biofuels must not only be a renewable energy source but must also be truly sustainable in future energy systems.

Biogas and biomethane have repeatedly been highlighted as renewable fuels of significant merit. Biogas (consisting of 50–70% methane and 30–50% carbon dioxide) generated from anaerobic digestion (AD) can be used directly for the production of electricity and heat in a CHP plant. Biogas can also be upgraded to biomethane (> 97% methane), and in turn provide a substitute for fossil-natural gas. Biogas and biomethane systems are predominantly focused on second generation biofuel substrates (such as non-edible crops, agricultural biomass and waste residues) and include for many wider benefits including; a form of waste treatment; a method of utilizing the existing grid infrastructure sustainably; and an alternative source of revenue for farmers.

Reductions in emissions in electricity and large industry are covered by The EU Emissions Trading Scheme (ETS) with obligations imposed on companies. Emissions reductions in the transport, agriculture and heat sectors are known as Non-ETS sectors. Here the obligations are imposed on member states. Increased production of green electricity has no impact on emissions reductions for member states. Thus biomethane systems can contribute to emissions reductions in non-ETS or ETS sectors depending on end use. From a policy perspective this is extremely significant.

The preferred end-use of biomethane typically varies by country, dependent on the set framework conditions of that country. For instance, Sweden utilises biomethane primarily as a transport fuel – as a consequence of the financial incentives available and limited natural gas grid coverage (IEA Bioenergy Task 40 and Task 37, 2014). Besides providing a potential gaseous transport fuel for bus fleets and heavy goods vehicles (HGVs), biomethane can supply renewable heat to large industry energy users and feed high efficiency combined heat and power (CHP) units. To date, biogas for electricity has been the predominant energy output from AD; by the end of 2015 there were 17,376 biogas plants in Europe producing 60.6 TWh (European Biogas

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http://dx.doi.org/10.1016/j.biortech.2017.07.115
Received 23 June 2017; Received in revised form 19 July 2017; Accepted 21 July 2017
Available online 23 July 2017
0960-8524/

Association, 2016). However, as biomethane can be injected to the gas grid and/or used as a transport fuel, it can be viewed as a more flexible energy carrier than biogas-CHP achieving higher final energy output efficiencies (SEAI, 2017). As of 2015, there were 459 biomethane plants in Europe, with significant growth in the UK in particular where 43 new plants built were built (European Biogas Association, 2016).

However, the onus to provide a renewable source of energy and decarbonise our future energy systems through such methods could put a significant constraint on both arable and agricultural land; currently there is 0.2 ha of arable land per person on the planet (Murphy and Thamsiriroj, 2011). In 2050, the world's population is expected to grow to 9.4 billion, with an energy demand three times larger than the energy demand of 2001 (Tabassum et al., 2017). Increases in population will increase demand for food and use of land for bioenergy will ultimately drive up the price of food production. As a consequence, identified technologies such as digestion of maize silage may become less favourable pathways for the production of biomethane. Nonetheless biomethane can play a key role in the integration of future energy systems. Advanced, third generation biofuels such as macro-algae (seaweeds) and micro-algae are gaining more traction as potential feedstocks. Generating gaseous fuel from non-biological origin through power to gas (PtG) systems is also seen as a pathway with significant potential (Persson et al., 2014). In providing for a decarbonised future energy system, there is significant potential for cascading bioenergy systems, whereby various biomethane technologies can be integrated with the majority of by-products valorised.

The aim of this paper is to identify the latest biotechnological advances for the production of renewable gas (biomethane) and to illustrate how these technologies could potentially be integrated in future cascading bioenergy systems in the transition to a low carbon economy. Three specific illustrative examples are developed.

2. Macro-algae in future gaseous fuel production

2.1. Sourcing seaweeds for digestion

The possibility of exacerbating the food v. fuel debate has meant that alternative feedstocks, free from land based production, must be sourced for future biofuels. Advanced biofuels will play increasingly important roles in provision of transport fuel up to 2050. Third generation biofuel sources, such as macro-algae (seaweed), can be farm cultivated at sea and achieve higher growth rates than traditional biomass crops (Dave et al., 2013). This seaweed can be digested for biomethane, offering a more sustainable alternative to second generation biofuels sources (Czyrnek-Delêtre et al., 2017). The initiation of a seaweed biofuel industry will likely focus on seaweeds of natural stocks, however harvesting this particular resource on beaches may be laborious, expensive and potentially have implications on biodiversity (Stagnol et al., 2013). Cultivation of seaweeds for biomethane production will become the preferential method however the economic feasibility, practicality, environmental impact, and governance and regulation for such cultivation projects must be explored (Roberts and Upham, 2012). One method of interest is combining seaweed cultivation with existing fish farms, known as integrated multi-trophic aquaculture (IMTA). The advantage of IMTA is that a form of bioremediation occurs, in that the seaweed absorbs the nutrient-rich waste produced from the fish in their growth, whilst increasing the growth productivity of the seaweed (Jacob et al., 2016). From a life cycle assessment (LCA) perspective, offshore cultivation of seaweed for energy production can be environmentally advantageous and play a significant role in mitigating climate change (Seghetta et al., 2017). However, previous studies have shown that sizable resources of seaweed are required to have an impact on overall energy; in order to achieve 1.25% of energy in transport in the EU from seaweed, a resource of 168 Mt of seaweed would need to be coupled with 13 Mt of farmed salmon (Jacob et al., 2016). Nonetheless, the harvest and reuse of excess nutrients in seaweed cultivation associated with fish farms not only provides a regenerative economy, but also redirects emitted carbon to a closed loop bioenergy system that can moderate eutrophication (Czyrnek-Delêtre et al., 2017). Future methods for cultivation may involve the coupling of facilities with off-shore wind farms. The structures of the wind turbines can act as a framing system for seaweed cultivation; further research is required prior to development of such an application (Roberts and Upham, 2012).

2.2. Varied composition of seaweeds

Seaweeds are typically rich in carbohydrates and have low lignin content, thus can be particularly suitable as a feedstock for AD. Green, red and brown algae have different carbohydrate composition; typically 25–60%, 30–60%, and 30–50% dry weight, respectively (Sambusiti et al., 2015). However, the exact composition of different seaweed species ultimately depends on the time of its harvest and this will be an essential component in the logistics of future seaweed biomethane systems. Seasonal variation necessitates a specific harvest time for different seaweeds as the total biomethane production can vary by up to 30% (Adams et al., 2011). Seasonal variation in the growth conditions, for example, temperature, nutrient availability and sunlight not only alter the carbohydrate content of seaweeds but also the concentrations of ash and protein (Tabassum et al., 2016b). A study, pertaining to the seaweed *L. digitata* in Ireland, indicated that the specific methane yields (SMY) expressed per unit volatile solid (VS) obtainable from an August harvest could be 40% higher than a December harvest. This is due to a higher carbohydrate content, a more suitable C/N ratio, a lower ash content and a lower associated salt content (Tabassum et al., 2016b). The study also indicated a higher VS content per unit wet weight in August. When it is considered that in August a higher wet weight resource of seaweed is available as compared to that in December, the increase in total energy yield per unit wet weight is significantly more substantial than would be expressed by the SMY (Tabassum et al., 2016b). In contrast, the recommended harvest of *L. digitata* in the neighbouring island of Britain was reported as a month earlier, with optimal biomethane yields in July (Adams et al., 2011). The concentration of polyphenols in seaweed can also have a considerable impact on the SMY as they can inhibit the enzymatic processes undertaken in digestion. This was illustrated in a study on the species *A. nodosum*, whereby high concentrations of polyphenols had more of a detrimental effect on the SMY than the ash content (Tabassum et al., 2016c). In such cases, harvesting should occur at a time of year when the polyphenol levels are lower in the seaweed; early spring and late autumn (Tabassum et al., 2016c).

Ultimately, different seaweed species can have very different characteristics, thus each much be investigated on its own merits with regards to carbohydrate content, polyphenol concentrations, sulphur content, C/N ratio and the presences of heavy metals (McKennedy and Sherlock, 2015). Not all seaweeds will be applicable to AD and gaseous fuel production. For instance *A. nodosum*, a brown seaweed, has been described as having higher polyphenol content and being more difficult to degrade (Allen et al., 2015). Other species such as *F. serratus* and *H. elongate* have low density and sparse growth on rocky coastlines which could make scaling up to a commercially viable system more difficult to achieve. Thus, the full logistics of a specific seaweed biofuel system in a specific geographic and climatic zone must be determined prior to deployment.

2.3. Preservation of seaweed

Another logistical issue in achieving a seaweed biomethane industry is supplying a secure supply of feedstock for the digester year round. Drying seaweeds to preserve them is energy intensive and if reliant on fossil resources will affect the sustainability of such methods. In temperate oceanic climates (such as Britain and Ireland) sun-drying may not be suitable due to precipitation levels. A novel approach involves the ensiling of seaweed, similar to methods in the ensiling of crops on farms. A study by Herrmann et al. (2015) showed promising results for the ensiling of five seaweed species (*U. lactuca*, *A. nodosum*, *L. digitata*, *S. polyschides*, *S. latissima*) that were macerated (particle size 2–4 cm) and stored in glass jars at 20 °C for up to 90 days. Despite low initial lactic acid bacteria numbers, ensiling of seaweeds, for the majority of species investigated, increased the available biomethane yield available from the biomass. It was noted that the use of the silage effluent generated was important for methane production. The SMY on a VS basis for the five seaweed species both fresh and ensiled ranged from 186 to 423 L CH_4 kg^{-1} VS. A more recent study investigated three seaweeds (*Gracilaria vermiculophylla*, *Ulva rigida* and *S. latissima*) cultivated from an IMTA system for their ensiling properties (Cabrita et al., 2017). The results again suggested that different seaweeds would present different fermentation patterns when ensiled. *S. latissima* was shown to present a homo-lactic fermentation and could be preserved effectively. Ensiling in essence can act as both a storage mechanism and as a pre-treatment process. The combined preservation and storage of seaweed feedstocks is an essential step towards a sustainable seaweed based biofuel industry.

2.4. Risk of chloride and heavy metal accumulation

As indicated, seaweeds are a potential future feedstock for digestion, however by their nature, they possess higher salt (sodium chloride) concentrations than more traditional AD feedstocks. Small additions of seaweed in co-digestion have previously been shown to inhibit methanogens and result in the build-up of volatile fatty acids (VFAs) (Akunna and Hierholtzer, 2016). To overcome such difficulties the operational conditions of the digester, in terms of organic loading rate (OLR) and hydraulic retention time (HRT), must be carefully selected. Providing an acclimatised inoculum is also very beneficial. Previous studies have indicated that the chloride salt tolerance can be increased from 10 g L^{-1} to over 30 g L^{-1} by adapting the inoculum (Roberts et al., 2016). This is of significance in that there may not be a need for a pre-washing step for seaweed prior to digestion. Evidence from continuous digestion trials have reported that increasing the OLR for seaweed reactors can increase the rate at which chloride will accumulate, and despite the possibility of tolerance at high chloride levels ($>$ 17 g L^{-1}) the system must be continuously monitored (Tabassum et al., 2016a).

Seaweeds may also bioaccumulate heavy metals which can inhibit the digestion process and affect the digestate quality, making it unsuitable for land spreading if heavy metal concentrations are too high (Cogan and Antizar-Ladislao, 2016). The accumulation of heavy metals in seaweeds occurs due to the significant metal sorption capacity of the algal cells (associated with alginate) and the presence of chemical groups susceptible to metal binding such as the carboxyl and sulphonate groups (Lodeiro et al., 2005). Previous literature has investigated the enhancement of seaweed digestion in a leach bed reactor coupled with an alkaline/autoclave treatment of leachate in a two phase system to reduce the influence of heavy metals (Nkemka and Murto, 2012); methane yields were enhanced as compared to the digestion of raw seaweed and improved heavy metal mobilisation was achieved. An imminodiacetic acid (IDA) cryogel has also been previously analysed for the removal of heavy metals (cadmium, copper, nickel, zinc) in leachate derived from seaweed hydrolysis with removal efficiencies ranging from 41% to 79% for zinc and cadmium respectively (Nkemka and Murto, 2010).

2.5. Opportunities in digestion

To initiate the deployment of seaweed as an AD feedstock, it may be beneficial to explore the role of certain species as co-feedstock in the short term. Often this may be at low volumes, however, co-digestion of seaweed and other feedstocks (such as food waste or slurry) can provide a mutual synergy by improving the nutrient balance in digestion (Oliveira et al., 2014). One such example in literature is the digestion of *Ulva Lactuca* (a green seaweed commonly referred to as sea lettuce that washes up in bays and estuaries as a result of eutrophication) with dairy slurry. *Ulva Lactuca* contains high concentrations of hydrogen sulphide (H_2S), the same toxic gas present in slurry storage pits on farms. As an environmental risk and a hindrance to the amenity of a bay, the green seaweed must be removed. Digestion of green seaweeds may become the preferable waste management option as a viable energy resource can be extracted. Yields of 250 L CH_4 kg^{-1} VS have been reported previously in literature, equivalent to 100 m^3 CH_4 t^{-1} of dried seaweed (Allen et al., 2013). In rural, coastal communities, the addition of other feedstocks such as grass silage and slurry from farmers may improve the potential biomethane yield by optimising the C/N ratio in digestion. Previous literature has demonstrated that both natural stock seaweed and farm cultivated seaweed can also be co-digested successfully with slurry. The co-digestion of *L. digitata* and *S. Latissima*, in the ratio 66% single species seaweed VS with 33% farm slurry VS, was previously shown to operate successfully at an OLR of 4 kg VS m^{-3} d^{-1}, achieving SMYs of 261 L CH_4 kg^{-1} VS and 252 L CH_4 kg^{-1} VS, respectively (Tabassum et al., 2016a). This can be considered a high OLR for mesophilic anaerobic digestion and outperformed the mono-digestion of slurry at an OLR of 4 kg VS m^{-3} d^{-1} which achieved SMYs of 55 L CH_4 kg^{-1} VS. As such, this study gives a promising outlook for the future application of seaweed biomethane systems. The SMY achievable from particular species of seaweeds are particularly variable depending on the method of cultivation, time of harvest, method of preservation, preparation and digestion conditions; SMYs in the range of ca. 100–500 L CH_4 kg^{-1} VS have been reported in previous literature reviews (McKennedy and Sherlock, 2015). The main barrier with respect to commercialising seaweed biomethane systems in the future will most likely involve the high costs of seaweed cultivation (Tabassum et al., 2017).

3. Micro-algae and the circular economy

3.1. Micro-algal biomass

Microalgae can play a significant circular economy role in biomethane systems. The unicellular algae species is not only a potential AD feedstock, but also can serve as a means of biogas upgrading and a method of removing excess nutrients from digestate (Xia et al., 2015; Xia and Murphy, 2016). From a biofuels perspective, microalgae have been primarily used for the transesterification of lipids for biodiesel production (Zhu et al., 2017). However, use of microalgae as a feedstock for biogas production may be more favourable than for biodiesel for a number of reasons: the low dry solids content are suitable for digestion systems negating the need for drying as would be the case with biodiesel production; the lack of need for a particular species, nor singularity of species; and the level of contamination with higher trophic life forms as would be found in open algal ponds is not of issue for anaerobic digestion (Murphy et al., 2015). Even if microalgae are used for biodiesel production, the remaining residues post lipid extraction can still be utilised in a biohydrogen and biomethane system (Jankowska et al., 2017), improving the energy balance of the overall biorefinery process (Neves et al., 2016). Microalgae, as a biofuel source, possess a number of advantages over more traditional biofuel sources including higher growth productivity, cultivation without land requirement and potential CO_2 mitigation through sequestration (Passos et al., 2014).

3.2. Cultivation and availability of nutrients

From a sustainability perspective, the cultivation system, nutrient source and cultivation location are the key factors in generating microalgae biofuels (Chia et al., 2017). Two types of system have been proposed for autotrophic microalgae cultivation; open raceway ponds and closed photobioreactors (Zhan et al., 2017). The advantages and disadvantages of the various growth systems for micro-algae have previously been outlined in literature (Moreno-Garcia et al., 2017). From a commercial viewpoint, open raceway ponds are most commonly utilised as they are relatively inexpensive (as compared to photobioreactors) but are only suitable for certain microalgae species and have lower growth productivity (Chia et al., 2017). Photobioreactors are closed systems that avoid culture contamination and have a variety of configurations (e.g. tubular, flat plate).

Previous literature has indicated that cultivation at site specific locations can reduce the overall microalgae production costs; however, the location of the microalgae must be strategically favourable so that nutrients and a suitable source of light are readily available and the energy can be also exploited locally (Moreno-Garcia et al., 2017). The nutrient source for microalgae cultivation can potentially be provided by digestate, an important by-product of the AD process, most commonly used as a bio-fertiliser by farmers. In essence, the typical biogas systems using crops for biogas and utilising the digestate for fertilisation is a circular economy. However, combining digestate with microalgae cultivation may be opportunistic for farmers and AD developers to broaden the circular economy into a cascading bioenergy system. Microalgae need the nutrients to grow; the digestate may need nutrient removal or reduction for safer land application to avoid eutrophication. Microalgae cultivation on digestate has been demonstrated in previous literature for the variety of different digestion feedstocks with successful results (Ayre et al., 2017; Massa et al., 2017). Using the nutrients provided from digestate significantly reduces the cost of microalgae cultivation, as these nutrients would otherwise need to have been purchased externally (Xia and Murphy, 2016). Factors of consideration in cultivating microalgae in digestate are the turbidity and ammonia nitrogen levels, as if either is high, microalgae growth can be inhibited; while other features such as the phosphorus and carbon limitations, bacterial contamination and pollutants must also be monitored (Xia and Murphy, 2016). Pretreatments for the liquid portion of digestate, such as ammonia stripping and activated carbon adsorption, have shown some positive results in reducing optical density and promoting microalgal growth, negating the need for water dilution (Marazzi et al., 2017).

3.3. Digestion of microalgae

Numerous strains of microalgae have been reported in terms of their cultivation conditions, harvesting technique and subsequent SMYs generated from digestion. The recorded range of SMY is wide from ca. 100 to 550 L CH_4 kg^{-1} VS (Jankowska et al., 2017). Microalgae are not regarded as a straightforward feedstock for digestion and the SMY will depend on the macromolecular composition and cell wall characteristics (González-Fernández et al., 2012; Passos et al., 2014). With high protein content, the digestion of microalgae can lead to inhibiting levels of ammonia which can affect the productivity of methanogens (Passos et al., 2014). However, microalgae will most likely be co-digested to improve the nutrient balance. High carbon co-feedstocks such as barley straw, beet silage or brown seaweed have been investigated for such purposes (Herrmann et al., 2016). For instance, the co-digestion of *Arthrospira platensis* and *Laminaria digitata* was reported to operate successfully at a high OLR of 4 kg VS m^{-3} d^{-1} as opposed to mono-digestion of the microalgae which could not be operated above 1 kg VS m^{-3} d^{-1} (Herrmann et al., 2016).

Besides a low C/N, microalgae can often have alginate and laminarin in the cell walls which are not easily degradable and thus pre-treatments may be required (Moreno-Garcia et al., 2017). Extensive literature reviews have been made for the different pre-treatments available for microalgae and the effect said pre-treatments have on the SMY (Jankowska et al., 2017; Neves et al., 2016). Pre-treatment methods have been investigated to increase biomass solubilisation generally in biomethane potential assay (BMP) tests and include for thermal (solubilisation of microalgae by high temperature treatment), mechanical (physically disruption of the cell walls), chemical (acid or alkali reagent addition to solubilise microalgae) and biological (addition of enzymes to promote hydrolysis) methods; with all methods designed to attack the cell walls (Passos et al., 2014). Ideally the pre-treatment should have a low energy requirement. Enzymatic methods potentially have the most scope as a pre-treatment with low energy input. Recent studies have shown up to 15% increase in methane yield was achievable when microalgae were pre-treated with a particular enzyme mix (cellulase, glucohydrolase and xylanase) as compared to a control (Passos et al., 2016).

3.4. Novel biogas upgrading method

Microalgae need, in addition to nutrients and light, a source of CO_2 for growth. Previous literature has looked at sources of CO_2 such as coal power plants. For a 1 GWe coal power plant producing 6.77 Mt CO_2 per annum it was calculated that 2.69 Mt VS of microalgae could be produced in a closed cultivation system (tubular or flat plate photobioreactor) (Jacob et al., 2015). Alternatively, with a lower CO_2 capture efficiency it was estimated that 1.68 Mt VS of microalgae could be produced from an open raceway pond system. Such methods may provide an intermediate CO_2 source for microalgae in the transition to renewables.

In a future energy system where AD is widely deployed, the CO_2 for microalgae can come from biogas (ca. 30–50% CO_2), which is ultimately a by-product of upgrading. However, for every mol of CO_2 captured by the microalgae, 1 mol of oxygen (O_2) is released through oxygenic photosynthesis (Meier et al., 2017). This can have an adverse effect in relation to the biomethane quality produced; specifications for biomethane injection to the gas grid will have a low O_2 tolerance level (less than 1% (molar) in the UK) (GreenGas Certification Scheme, 2013). Nonetheless biogas upgrading via microalgae cultivation should be capable of producing sufficient biomethane gas grid quality with the right technology. Previous studies have highlighted the use of external absorption columns with high rate algal ponds in successfully upgrading biogas to biomethane as illustrated in Fig. 1. Bahr et al. (2014) illustrated a system that recirculated liquid from an algal pond to an external adsorption column using an alkaliphilic bacterial consortium which could completely remove H_2S and 90% of the CO_2, while limiting the concentration of O_2 in the upgraded biogas to 0.2% sufficient for natural gas grid injection. This type of photosynthetic biogas upgrading is achieved by microalgae fixing the CO_2 using light energy and sulphur-oxidizing bacteria using the resultant O_2 to oxidise H_2S to sulphate (Toledo-Cervantes et al., 2017).

Xia et al. (2015) previously outlined a CO_2 biofixation method by microalgae, using a bicarbonate/carbonate cycle that offered energy and cost savings over traditional upgrading systems. Recent studies have indicated that despite microalgae not performing photosynthesis in darkness (at night), high levels of CO_2 could still be removed in such upgrading processes (removal efficiencies between 89 and 93%) (Meier et al., 2017). This would potentially allow for continuous 24 h operation of indirect biogas upgrading.

Upgrading biogas through microalgae cultivation in digestate is an exemplary case of the circular economy in action. However, application at full scale will involve further challenges such as controlling the microalgae species to maintain high growth rates, negating the inhibitive effects of microalgae on the AD process, assessing the geographical and seasonal constraints of microalgae growth and technology costs (Zhu et al., 2016).

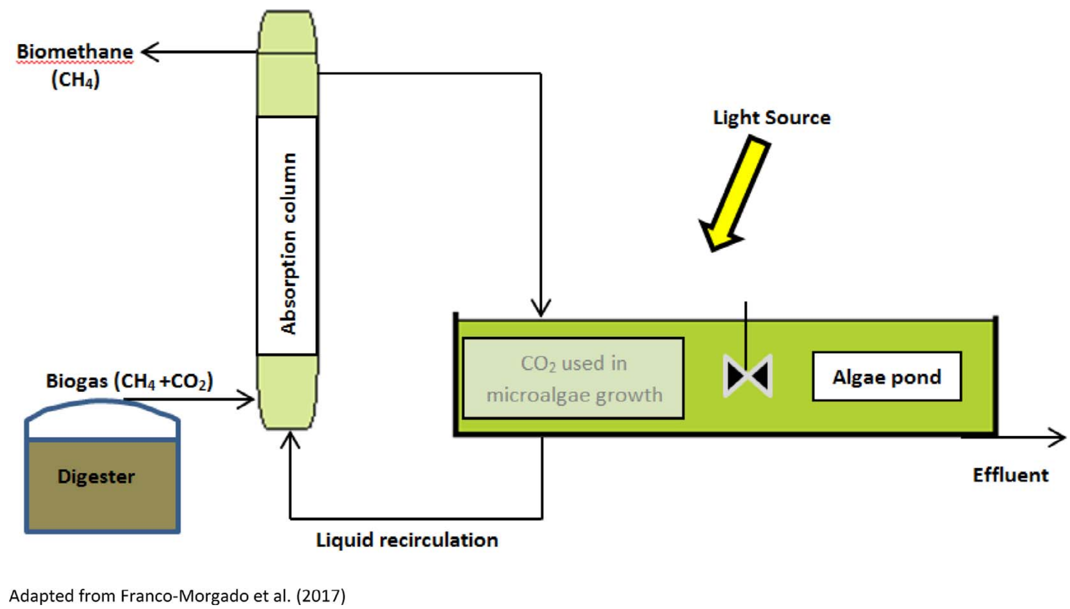

Fig. 1. Microalgae biogas upgrading system. (See above-mentioned references for further information.)

4. Gaseous fuel from non-biological origin – power to gas

4.1. Electrolysis for power to hydrogen

Power to Gas (PtG) is an emerging smart grid concept whereby surplus renewable electricity is converted into gaseous form for storage purposes. In changing the energy vector, the output gas from PtG can be hydrogen (PtH) or methane (PtM). The technology in its simplest form involves electrolysis to split water into its components: hydrogen (H_2) and O_2. This route is technically less complex than PtM and has been studied in detail in previous literature (Gahleitner, 2013).

Three main technologies are reported for electrolysis: the alkaline electrolyser, the polymer electrolyte membrane (PEM) and the solid oxide electrolysis cell (SOEC). Alkaline electrolysis is at a higher technology readiness level (TRL) than PEM or SOEC and thus is currently cheapest to deploy (Götz et al., 2016) and is commercially available with modules up to 2.5 MW_e (Schiebahn et al., 2015). However, higher process efficiencies may be potentially viable in PEM and SOEC in the future. When evaluating electrolysis units, the most important features from a PtG perspective include efficiency of conversion to H_2, flexibility for a cold start up, and operational lifetime (Götz et al., 2016). Alkaline and PEM are considered low temperature technologies; SOEC is a high temperature process at the lowest TRL of the three and is expected to improve the efficiency considerably (Parra and Patel, 2016). PtG requires a quick start up time from the perspective that the system will potentially only operate when the price of electricity is sufficiently cheap to produce financially sustainable gas. PEM is a faster technology than alkaline but the cost is a big factor as the technology require noble catalysts (Pt, Ir, Ru) (Schiebahn et al., 2015). Any future enhancements in electrolysis will depend on the SOEC technology which is currently at a low TRL. Since SOEC operates at a much higher temperature range the operation should be continuous if possible; since start up and shut down at such high temperatures could lead to thermal stress in the system (Schiebahn et al., 2015). Table 1 gives an overview of the different electrolyser technologies available for PtG.

In essence, the limitation with the PtH pathway in future energy systems is the lack of current infrastructure to carry and store H_2 gas; and subsequently the high cost of construction required with such a development. Natural gas grid infrastructure is prevalent in countries such as France, the UK, Ireland, Germany, Italy and the Netherlands. However, the input of H_2 into the EU grids is regulated, reported as low as 2% in some cases (Persson et al., 2014). This is primarily due to; the difference in volumetric energy content at standard temperature and pressure between H_2 and methane (12 MJ/m^3 v. 36 MJ/m^3), the higher losses associated with H_2 leakage due to its low molecular weight, and the tendency of H_2 to cause embrittlement in existing pipelines (Qadrdan et al., 2015). Thus, storing vast amounts of H_2 is logistically challenging at present.

Table 1
Comparison of electrolyser technologies for PtG.[a]

	Alkaline	PEM	SOEC
Technology readiness level (TRL)	High (commercial)	High (commercial)	Low (laboratory)
H_2 production (m^3/h)	< 760	< 450	–
Charge carrier	OH^-	H_3O^+/H^+	O_2^-
Cell temperature (°C)	40–90	20–100	800–1000
Cold start time	Minutes to hours	Seconds to minutes	–
Potential efficiency (% LHV)	< 70%	< 74%	> 90%
Potential costs[b] (€/kWhe)	500–1000	500–2000	–

[a] Adapted from Götz et al. (2016), Schiebahn et al. (2015) and Vo et al. (2017a).
[b] Allowing for now and potential reductions in the future.

4.2. Methanation for power to methane

PtM has the advantage of providing a means to maximise the use of existing infrastructure, by increasing the share of renewable gas in the natural gas grid. For the PtM pathway to be deployed, a source of CO_2 and a methanation phase are necessary in addition to electrolysis. The methanation step can be catalytic or biological; both methods adhere to the Sabatier process of combining H_2 and CO_2 (at a ratio of 4:1) to produce methane and water. The Sabatier reaction is described in Eq. (1) (Persson et al., 2014).

For catalytic methanation, a form of catalyst, typically nickel-based is used (Rönsch et al., 2016). Catalytic is deemed less robust than biological methanation as it is more susceptible to contaminants; it operates in the temperature range of 200–500 °C with pressures of 1–100 bar (Götz et al., 2016).

$$CO_2(g) + 4H_2(g) => CH_4(g) + 2H_2O(g) + \text{heat } \Delta Hr = -165 \text{ kJ/mole} \quad (1)$$

For biological methanation, hydrogenotrophic methanogenic archaea (as opposed to catalysts) are used for the conversion of H_2 and CO_2 to methane, and the process can be "in-situ" or "ex-situ". For in-situ methanation systems the conversion of H_2 and CO_2 to methane can be accomplished within the digester. H_2 is injected directly into the digester and combines with the CO_2 in the biogas. The in-situ method provides a means of increasing the methane concentration in the biogas from the digester but not to a standard high enough for direct natural gas grid injection, thus a biogas upgrading step is still required post methanation (Luo et al., 2012). However, ex-situ systems rely on an external reactor where both H_2 and CO_2 are introduced. With efficient transfer of H_2 to the liquid medium; a sufficiently high standard biomethane can be achieved for gas grid injection (Ahern et al., 2015). The gas-liquid solubility of H_2 is often the bottleneck for such systems and is currently overcome by high rate agitation, making the process energy intensive (Götz et al., 2016).

The source of CO_2 for PtM can be provided by traditional biogas plants, large CO_2 emitters in industry (such as distilleries), or sludge digesters in wastewater treatment plants (WWTPs). Ideally the CO_2 source should be concentrated and of low cost. Biogas typically contains 30–50% CO_2. As biomethane facilities become more prevalent in the EU, the scrubbed CO_2 from the upgrading process can be utilised directly in the methanation phase. Current literature is now focused on maximising the future potential for PtM by identifying suitable geographical locations through modelling. Factors considered include for CO_2 source, the location of the gas grid, existing biogas sites and construction constraints (Schneider and Kötter, 2015). For instance, in Ireland, PtG was found to be limited by the amount of curtailed electricity as opposed to the quantity of CO_2 potentially available from biogas production (Vo et al., 2017b). Future PtM systems will most likely operate on biogenic CO_2 sources, however the transition to decarbonisation should include for CO_2 derived from fossil fuels as an intermediate process, since emissions savings will still be possible (Meylan et al., 2017).

4.3. PtG demonstration and key technology components

Currently, PtG technologies are being demonstrated for proof of concept. Laboratory studies of ex-situ biological methanation reported that a methane content of 90% could be achieved at 65 °C, with a production rate of 0.45 L $CH_4/L_{reactor}$/day and with the methanothermobacter species dominant for thermophilic biogas upgrading (Guneratnam et al., 2017). On a larger scale, two projects aiming for commercial viability with regards to PtG with biological methanation are the Electrochaea – BioCat project (Denmark) and MicrobEnergy – BioPower2 Gas project (Germany); both utilise biogas systems as the source of CO_2 (Bailera et al., 2017).

PtG systems are still considered to be at a relatively low TRL despite some recent uptake in Germany. However, its future potential is considered significant particularly as a control function for the electrical grid. The capability to utilise curtailed electricity in real time and produce gaseous fuel is an appealing feature. The technology costs, particularly electrolysis and methanation, must become more defined while the levels of curtailed electricity become apparent in future years. Some costs studies have already been undertaken (Benjaminsson et al., 2013). As PtG systems contain many inputs and outputs, it is suggested that the technology needs to utilise the full value chain in order to make it financially viable (Breyer et al., 2015). For instance, oxygen generated through the electrolysis process can be a valuable monetary by-product if integrated with a gasification plant for example. Alternatively the oxygen could be used at a WWTP for aeration. The end use for oxygen will be site specific but should integrate with other technologies where possible. Previous literature from Germany has indicated that the introduction of PtG systems can potentially transition to a 100% renewable energy system for specific regions at lower cost (Kötter et al., 2016). It can also contribute to the decarbonisation of energy. There is a viewpoint that more renewable energy in the heat and transport sectors needs to be provided – this can be facilitated by PtG. A study looking at excess solar energy in Germany indicated that 370 MWe of PtG capacity could utilise 30% of the excess available resource in 2015; this PtG capacity would equate to ca. five hundred 300 kW electrolysers and three hundred 700 kW electrolysers coupled with anaerobic digesters distributed in the region (Estermann et al., 2016).

5. Integration of bioenergy systems

5.1. Cascading second and third generation biomethane systems

Integration of bioenergy technologies is fundamental to the decarbonisation of the future energy sector. Greater than 70% GHG emissions savings for transport biofuels will be required by 2021; this may be further increased after this time. This paper has focused on the advanced pathways available for generating renewable gas from AD including for – seaweeds, micro-algae and PtG, all third generation biofuels free from direct or indirect land use. Even for advanced systems such as seaweed biomethane, the future GHG emissions targets may be difficult to meet. Thus cascading systems will be required. By-products that result from the advanced bioenergy systems must be further integrated, ensuring the use of the full supply chain and circular economy concepts including for cascading bioenergy. For instance, gasification (with the methanation of syngas) is an additional technology that can be used to generate biomethane and is typically applied at a much larger (MW) scale than AD. Although such a process is considered a second generation biofuel, in terms of generating the quantities of renewable gas required for future energy systems, gasification of woody crops or wood chips may play a significant role. Well-to-wheel analysis of gasification-methanation for use as a transport fuel in heavy duty engines has indicated that emissions savings of up to 67% were possible as compared to diesel (Alamia et al., 2016). Recent studies have focused on potentially reducing the capital investment and operating costs of gasification-methanation facilities such as the Gothenburg Biomass Gasification (GoBiGas) project (Haro et al., 2016). The concept of combining AD and gasification has also been considered in prior work. Li et al. (2015) investigated separating H_2 from syngas produced from gasification as a method of upgrading biogas from AD (via a Sabatier process) to generate additional biomethane. Alternatively, by-products of the AD process such as solid digestate can provide a source of feedstock for gasification, along with woody crops such as short rotation coppice (SRC) willow grown on marginal lands. The liquid portion of the digestate can be used as a biofertiliser for the SRC willow. In a bioenergy system with PtG, the O_2 produced from electrolysis may be utilised in the gasification process to increase the energy value of the syngas, whilst negating the need to purchase an external O_2 supply. There are potential limitations to this as the scale of a biogas facility is typically much smaller than a gasification facility; however it may be such that a number of biogas systems with PtG serve one larger gasification/methanation facility. Three scenarios of cascading biomethane systems are illustrated below.

5.2. Integrated algae biomethane production system

Fig. 2 shows an integrated biomethane energy system that utilises both macro- and micro-algae. The concept revolves round an IMTA system that provides a sufficient seaweed biomass feedstock for digestion. Micro-algae is cultivated in an outdoor raceway pond with liquid digestate effluent (collection post digestion process) used as a nutrient medium for cultivation. The carbon source (CO_2) for the microalgae is taken from the biogas generated by the digester, and thus indirectly

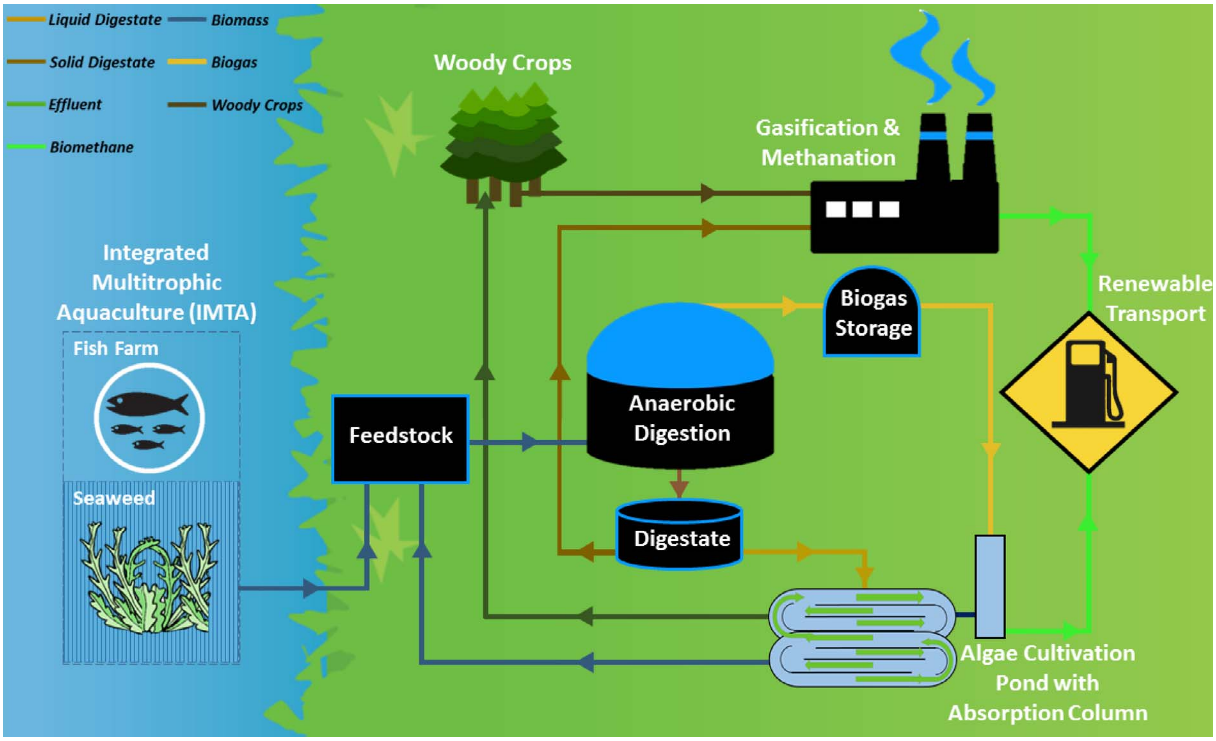

Fig. 2. Integrated biomethane energy system that utilises both macro- and micro-algae.

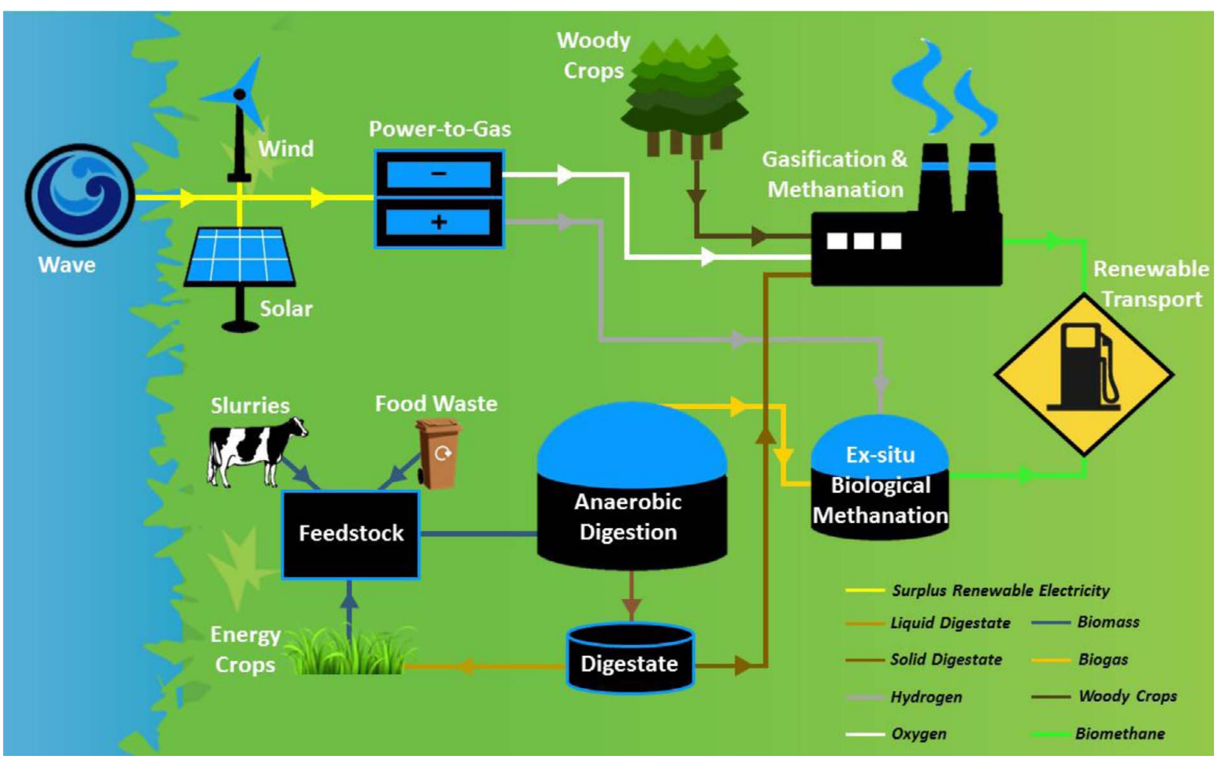

Fig. 3. Integrated biomethane energy system that utilises PtG technologies from surplus renewable electricity.

upgrades the biogas to biomethane through the use of an absorption column as outlined in literature (see detail in Fig. 1). The micro-algae biomass in this scenario would be co-digested with the IMTA-derived seaweed. The effluent wastewater from the raceway pond could potentially be applied to SRC willow as a fertiliser whilst the willow provides a remediation step removing impurities in the wastewater and protecting ground water or aquifers from pollution. The SRC willow is suitable for a gasification plant (gasification with methanation of syngas) to further increase the biomethane output from this scenario. The solids portion of the digestate separated from the digester may also be gasified. The biomethane produced can be injected into the natural gas grid and used as a renewable gaseous transport fuel.

5.3. Integrated community biomethane production system with power to gas

Fig. 3 shows an integrated biomethane energy system that utilises PtG technologies from surplus renewable electricity. In this scenario, it is assumed the digester is community based with feedstocks such as energy crops, food waste and slurries from the surrounding region. This may be representative of a seasonal shift in available feedstocks for digestion. Biogas produced from the digester is sent to an ex-situ biological methanation reactor where it is combined with the H_2 produced from electrolysis. The electrolysis unit is fed with electricity from renewable devices such as wind turbines, solar and/or tidal devices. The H_2 reacts with the CO_2 in the biogas (Sabatier reaction) in the methanation reactor and produces biomethane removing the need for the costs of a traditional biogas-upgrading unit. In this scenario the solid and liquid portions of the digestate are also separated, however, the liquid is now used as a biofertiliser for the energy crops by the farmer. The solids are sent to a gasification plant for further energy conversion along with woody crops. Additional integration is provided by rerouting of the O_2 stream, available from electrolysis, to the gasification process. The biomethane produced can again be used as a renewable gaseous transport fuel.

5.4. Cascading biomethane production system with algae and power to gas

A further integrated scenario can combine the previous two scenarios. The digester can incorporate the algae feedstock associated with IMTA along with food waste and slurries from the surrounding region. By day, biogas may be upgraded by the micro-algae system. By night, biogas may be sent to an ex-situ biological methanation reactor where it is combined with the H_2 produced from electrolysis. This has the serendipitous advantage in that micro-algae grow by day where typically electricity is more likely to be surplus by night when demand for electricity is low as the populace sleep.

6. Conclusions

Three integrated biomethane scenarios were developed. Scenario 1 considered seaweed digestion, with biogas upgrading via microalgae (which also acted as a co-feedstock) and gasification of solid digestate, with the liquor digestate applied to woody crops (for gasification) completing the circular economy approach. Scenario 2 illustrated that power to gas could be coupled with gasification through use of oxygen from electrolysis, whilst hydrogen from electrolysis could be used to upgrade biogas via ex-situ biological methanation. A third scenario could combine the two allowing for natural growth of algae by day and the tendency for electricity to be surplus by night.

Acknowledgements

This work was funded by Science Foundation Ireland (SFI) through the Centre for Marine and Renewable Energy (MaREI) under Grant No. 12/RC/2302. The work was also co-funded by Gas Networks Ireland (GNI) through the Gas Innovation Group and by ERVIA and the International Energy Agency Bioenergy Task 37 “Energy from Biogas”.

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