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Can power to methane systems be sustainable and can they improve the carbon intensity of renewable methane when used to upgrade biogas produced from grass and slurry?

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Abstract

The recast of the renewable energy directive (RED recast) considers power to gas (P2G) an advanced transport biofuel if a 70% greenhouse gas savings as opposed to the fossil fuel displaced is achieved. Power to methane systems can store electricity as gas and the system can be optimised in sourcing CO_2 from biogas to upgrade biogas to biomethane. The crucial question in this work is whether P2G systems can be sustainable and if they can improve the sustainability of biomethane systems using traditional upgrading systems. This work evaluates a comparative lifecycle assessment of grass and slurry (50:50 wet weight equivalent to 80:20 volatile solid weight) biomethane using P2G and/or amine scrubbing as an upgrading method. The sustainability of P2G upgrading systems is heavily dependent on the carbon intensity of the source of electricity. Using a 41% decarbonised electricity mix the sustainability was reduced using P2G and would not be deemed sustainable under criterion set by the RED recast. Maintaining a maximum of 2% fugitive CH_4 emissions, using 74% slurry (wet weight) in a grass slurry feedstock, allowing for 0.6 t carbon sequestration per hectare per annum in grasslands and using an electricity mix with 85% renewable electricity the whole system including P2G upgrading could satisfy the GHG savings of 70%. However, the tradition system employing amine scrubbing had higher levels of sustainability.

Keywords: life cycle assessment; sustainability criteria; advanced biofuels; power to gas; biological methanation; co-digestion.

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1 Introduction

The transition from fossil fuels to renewable decarbonised energy needs evidence of sustainability and of a significant reduction in environmental impacts. The recast of the Renewable Energy Directive (RED recast) states that advanced biofuels should make up at least 3.6% of transportation fuels by 2030. These advanced biofuel systems must meet a threshold of 70% greenhouse gas (GHG) savings as compared to the fossil fuel displaced [1]. It is unlikely that biomethane produced from mono-digestion of crops such as maize will meet this criterion: however, maize is not considered as a source of advanced biofuel. Perennial ryegrasses are included in the list of sources of advanced biofuels, but mono-digestion of grass is unlikely to meet the strict sustainability criteria of 70% GHG savings set for transport biofuels. However, it is likely that when grass is co-digested with slurry at certain ratios sustainability may be achieved. This is due to the methane emission credit obtained by avoiding the open storage of raw manure. When slurry is stored in an open tank fugitive methane emissons occur; methane has a global warming potential (GWP) of 21 times that of CO_2 in a 100 year time frame. In anaerobic digestion systems the slurry is not open to the atmosphere and these emissions are thus avoided. When biogas is combusted it releases CO_2 (21 times less GWP than CH_4) whilst displacing the emissions from a fossil fuel. The credit for digesting manure is given as 14.6% of the methane content of the slurry stored using methodology developed by the European Commission Joint Research Centre (JRC) [2, 3]. Mono-digestion of slurry is carbon negative, however, slurries have low volumetric energy content, produce a low specific methane yield and as such are uneconomic [4].

A recent paper by the authors described a techno-economic analysis (TEA) of co-digesting grass silage with manure and injection of the produced renewable methane to the gas grid [5]. Using water for agriculture, especially for biofuel production creates pressure on water usage due to irrigation and land use change [2]. The United Nations reported that 70% of potable water is used for irrigation purposes in agriculture [6]. However, those problems have not been an issue in Ireland as 90% of agricultural land are grass and Ireland has the lowest water stress index in the world [7] due to the

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plentiful availability of rainfall throughout the year. Three upgrading scenarios were assessed: 1. amine scrubbing, 2. amine scrubbing + ex-situ biological methanation, and 3. ex-situ biological methanation. The amine scrubbing upgraded the biogas to biomethane (renewable methane) in scenario 1 by removing the CO_2. Scenario 2 & 3 offer CO_2 capture. In Scenario 2 the CO_2 from the amine scrubber is sent to an ex-situ biological methanation unit to produce renewable methane. In Scenario 3 an amine scrubber is not used and the biogas is sent to an ex-situ biological methanation unit to upgrade biogas. First, the electrolyser splits water into hydrogen and oxygen (Eq. 1); the hydrogen then reacts with carbon dioxide to produce renewable methane (Eq. 2) [8].

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ $\Delta Hr = 286$ kJ/mole (at 25° C, 1 bar) (1)

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ $\Delta H = -165$ kJ/mole (2)

The results of the TEA analysis [5] concluded that Scenario 1 amine scrubbing was the cheapest method to upgrade biogas followed by Scenario 3 (ex-situ methanation). Using both amine scrubbing and ex-situ methanation as described in Scenario 2 was the most expensive method investigated. The sustainability analysis of such systems has not previously been assessed in the scientific literature to the authors' knowledge. This innovation in this paper is the assessment of whether P2G scenarios can improve the sustainability of a biomethane system and whether a P2G system can meet the sustainability criteria for advanced biofuels when used as an upgrading system of a biogas system digesting slurry and grass; furthermore the work examines at what ratio of grass silage to slurry, greenhouse gas emission savings of biomethane exceeds 70% GHG saving as compared to the fossil fuel displaced

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A *cradle-to-gate* LCA was carried out including for grass cultivation, ratios of grass and slurry in the digester, methane slippage at biogas plants, and hydrogen production from electrolysis. The three primary scenarios evaluated are as follows:

Scenario 1 (S1): Grass cultivated and transported to the biogas facility within a 10-km radius, while slurry transported within 3 km. Biogas produced from the plant was upgraded by an amine scrubber. The CO_2 from the biogas was emitted to the atmosphere after upgrading.

Scenario 2 (S2): Similar to S1 with an addition of the CO_2 sent to ex-situ biological methanation where it is reacted with hydrogen from an electrolyser to produce more renewable methane.

Scenario 3 (S3): Similar to S1 with the change that amine scrubber is not used and the entire upgrading process was undertaken by ex-situ biological methanation where hydrogen from an electrolyser combines with CO_2 to produce more renewable methane.

The objectives of the paper are to assess: the parameters (including ratios of grass to slurry in feedstock, methane slippage, and sequestration of carbon in grasslands) that will allow slurry grass biomethane systems be considered sustainable; the parameters with the greatest impact on the sustainability of P2G systems, in particular the share of renewables in the electricity grid mix; and the optimum combination of parameters that allow sustainability of biomethane and P2G systems.

2 Methodology

2.1 System boundaries and functional unit

A *cradle-to-gate* LCA boundary was used to measure the environmental impacts in this study. The system boundaries included: the cultivation of grass including fertilizers and machinery associated with cultivation; transportation of grass silage, dairy slurry and digestate (organic fertilizer) to and

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from the biogas facility; biogas production by anaerobic digestion (AD); upgrading by amine scrubbing; electrolyser for hydrogen production; and ex-situ biological methanation (Figure 1). The grass silage used in this study is assessed at 25,344 t/a cultivated in a land area of 634 ha (40 t/ha/a). The least distance needed to cultivate this volume of grass silage corresponds to a radius of 3.17 km. In the base case, 10 km was considered for transporting grass to the biogas plant and digestate back to the fields.

Previous work by the authors [5] assessed injection of the renewable methane to the gas grid at 8 bar. This paper examines transportation fuel with compression to 250 bar. The functional unit used in this study was one MJ of compressed renewable gas. The data from this work was compared with fossil fuel comparators (FFC) from the RED recast. Based on the guidelines of the RED recast, the emissions from the manufacturing of equipment and machinery within the biogas facility were not considered [1].

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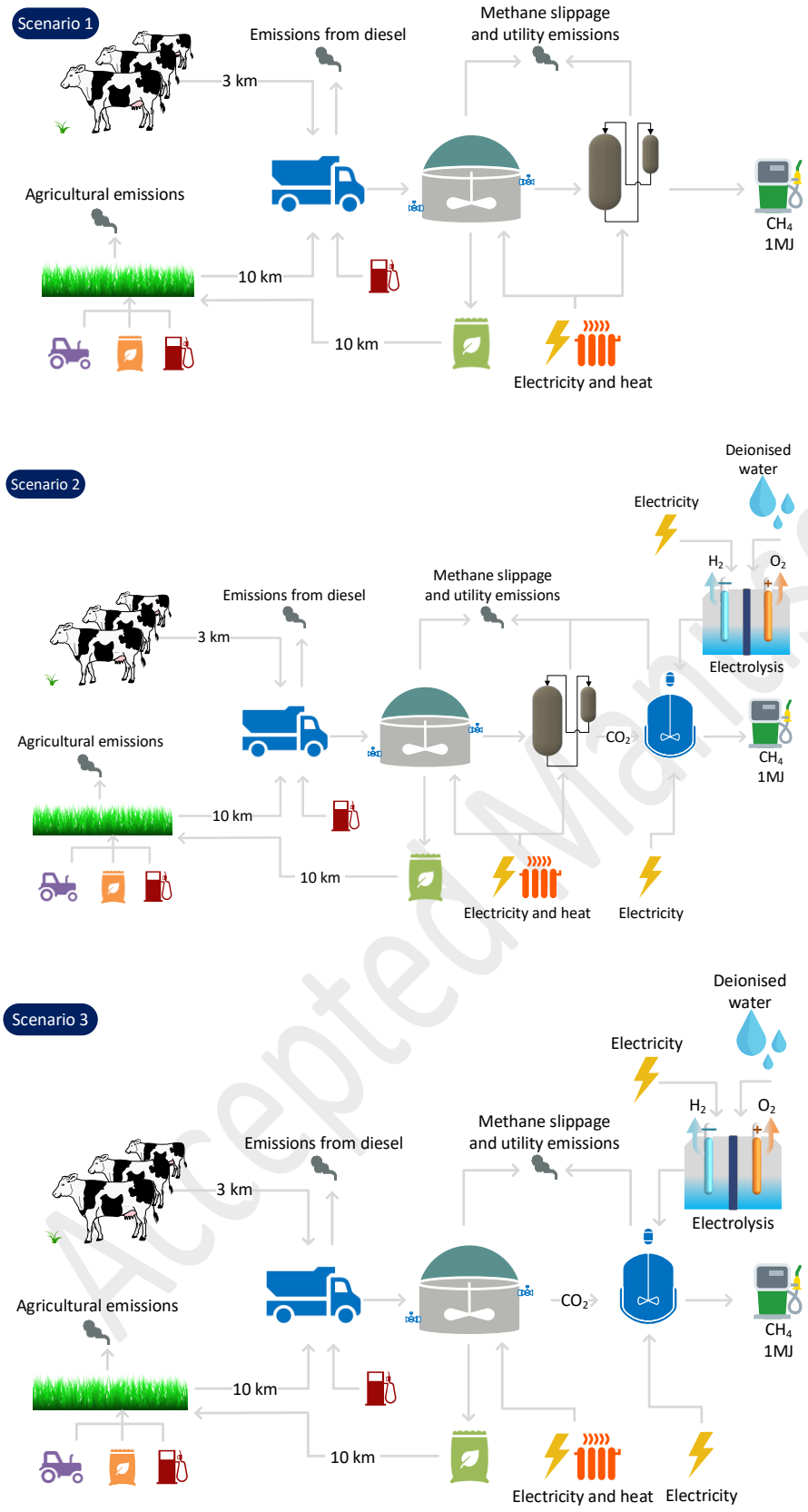


Figure 1: System boundaries of three scenarios

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2.2 Life cycle inventory

The data for diesel supply, deionised water, and fertilizers were gathered from the proprietary software package GaBi [9].

2.2.1 Biogas plant, amine scrubber and ex-situ biological methanation

The data for the feedstocks, biogas plant, amine upgrading and ex-situ biological methanation were based on Vo et al. [5]. For the base case scenarios, grass silage and slurry was used at a ratio of volatile solids (VS) of 80:20 [5]. The processing capacity of the biogas plant was assessed with a total feedstock supply of 53,064 t/a consisting of 27,720 t/a dairy slurry and 25,344 t/a grass silage. It was assessed that approximately a 50:50 wet weight ratio is equivalent to an 80:20 VS ratio (VS of grass silage and dairy slurry are 28% and 6.7% of wet weight [5]). The digestate (organic fertilizer) production is equivalent to 44,539 t/a. About 84% of the VS loaded to the system were converted to biogas in the digesters, which had a retention time of 40 days. The biogas plant produced 3.3 million m^3 renewable methane/a and 3.2 million m^3 CO_2/a; broadly equivalent to 122.5m^3 biogas/t at 51% methane content or 62.2 m^3 CH_4/t. The base case scenarios assumed a 2% fugitive methane emission of the total methane produced from the biogas system. The sources of fugitive emissions includes: leakages from the digesters; short-term substrate storage; upgrading of biogas; digestate storage and the pressure release valve [10]. To compress the purified methane to 250 bar and use it as a transportation fuel, 0.35kW_eh electricity is needed per m^3 of renewable methane produced.

The input data including for electricity, heat, amine scrubbing and biological methanation were adapted from Vo et al. [5]. To upgrade the biogas via amine scrubber, 0.55 kWh heat per m^3 raw biogas [11] was used. The consumption of heat in the process was based on natural gas (Ireland steam) taken from GaBi [9]. The input data for utilities used in three scenarios are summarised in Table 1. It should be noted that the energy produced from Scenario 1 is just from the biogas produced in the AD plant, whilst the energy produced from Scenario 2 and 3 are from the AD plant and the methanation

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upgrading where CO_2 in the biogas is converted to CH_4. As such the energy produced from Scenario 2 and 3 is roughly double that of Scenario 1.

Table 1: Parasitic energy demand for the three scenarios

	Scenario 1		Scenario 2		Scenario 3	
Energy produced - MJ (LHV):	116,500,442		225,561,198		229,561,534	
	Heat (kWh)	Electricity (kW_eh)	Heat (kWh)	Electricity (kWeh)	Heat (kWh)	Electricity (kW_eh)
Biogas production	957,169	1,149,008	957,169	1,149,008	957,169	1,149,008
Amine upgrading	3,556,268	141,930	3,556,268	141,930	-	-
Ex-situ biological methanation	-	-	0	2,985,840	0	3,088,800
Compression		1,132,643		2,192,956		2,231,848

2.2.2 Grass silage cultivation

Smyth *et al.*[12] carried out a comprehensive study on energy requirements of grass silage production in Ireland. From a single hectare of land, about 12 t dry solids (DS) of baled grass silage can be produced in a year at a dry solids content of 30% [4]. This corresponds to 40 t/ha/a wet weight from 634 ha. The crop production process encompassed cultivation and harvesting. The agricultural inputs for the grass cultivation include fertilisers, lime, and herbicides. Diesel is used in agricultural machinery for different activities including ploughing, sowing, harrowing, rolling and application of fertilisers. The emission data associated with agricultural machinery usage were included in the LCA.

The digestate from the biogas plant was assumed to be applied to the pasture land as organic fertiliser replacing synthetic fossil fuel based fertiliser. Smyth *et al.* [12] calculated the amount of nitrogen needed for grass cultivation as 259.37 kg N/ha/a. The maximum permittable nitrogen load on farmland from an organic fertiliser is 170kg N/ha/year [13]. Thus, synthetic fertilizer of 89.37 kg

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N/ha/a is still required. On a wet weight basis, grass silage and dairy slurry contain 4 and 3 kg N/t respectively [5]. During anaerobic digestion, 6% of nitrogen is used for growth of microbes [14]. This corresponds to 3.89 kg N per ton of digestate (Appendix 1). Therefore, 43.65 t digestate was applied in one ha of grass; for 27,674 t/a digestate the area corresponds to 634 ha. The extra 16,865 t/a digestate was assumed to be spread on adjoining agricultural land. For the impact assessment, the GHG emissions from digestate storage, transportation, and field application were included in the assessment.

The benefits of digestate as a biofertiliser include avoiding the production of synthetic fertiliser and associated emissions. The commonly used synthetic fertilisers in Ireland are Calcium Ammonium Nitrate (CAN), Potassium Chloride and Triple Superphosphate [15]. The GHG emissions to produce 1kg of CAN, Potassium Chloride and Triple Superphosphate are 979g, 210g and 232g CO_2 eq., respectively [9]. Using digestate avoids the GHG emissions from producing synthetic fertilisers. According to ISO 14044, whenever possible the system expansion should be applied for the process which produces more than one product. Thus, system expansion was applied in this research. Table 2 shows the total amount of nutrients needed, nutrients from digestate and the amount of nutrients that were substituted by the synthetic fertilisers in the grass field.

Table 2. Inputs for grass silage production, nutrients from digestate and synthetic fertiliser

	Total nutrients required (kg/ha/a) [12]	**Nutrients from digestate (kg/ha/a)**	**Nutrients substituted by synthetic fertiliser (kg/ha/a)**
Nitrogen	259.37	170	89.37
Phosphorous	38.75	26	12.75
Potassium	308.75	66	242.75
Herbicide	0.72		
Seed	3.125		
Lime	1500		

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Spreading of lime on the field leads to CO_2 emissions; an emission factor of 0.12 was used [16]. GaBi lacks the data for herbicide application, harrowing, rolling and energy needed to produce grass seed. Hence, the data from Smyth *et al.* [12] was used.

Nitrous oxide (N_2O) is a GHG that has a GWP 298 times higher than that of CO_2 [17]. In Ireland, applying fertilizer and emissions from animal wastes corresponds to 90% of N_2O emissions [18]. N_2O is formed in the soil by nitrification and denitrification processes.

Phosphate (PO4-P) is deemed to be discharged to the surface water at 1% of total P content in inorganic and organic fertilisers [19]. Indirect and direct N_2O emissions from synthetic and organic fertiliser were also calculated following the IPCC's guideline (Tier 1 method) [16]. The direct emission factor (EF) of N_2O-N by applying synthetic fertilisers as well as organic fertiliser is one percent of total N.

The indirect N_2O emissions were calculated from the atmospheric deposition (ATD) of N volatilised from the managed soil, N_2O (ATD)-N, Eq. (3) and from N leaching/runoff from managed soils in regions where leaching/runoff occurs Eq. (4) [16]:

$$N_2O\ (ATD)\ (kg\ N_2O/a) = (FSN*0.1 + FON*0.2) * 0.01*44/28 \quad (3)$$

Where:

FSN = annual amount of synthetic fertiliser N applied to the soil in kg N/a

FON = annual amount of organic N added to the soil in kg N/a

$$N_2O\ (kg\ N_2O/a) = (FSN + FON) * 0.3 * 0.0075*44/28 \quad (4)$$

FSN = annual amount of synthetic fertiliser N applied to the soil in regions where leaching/runoff occurs, kg N/a.

FON = annual amount of animal manure, compost, sewage sludge and other organic N added to the soil in regions where leaching/runoff occurs, kg N/a.

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Using manure as a feedstock in AD reduces the GHG emission, as methane is processed and captured in a controlled environment. Using the dairy slurry provides a methane credit of 14.6% of the biomethane potential [10]. The biomethane potential of the dairy slurry is 239 L CH_4/kg VS [4].

2.2.3 Electrolyser

Proton exchange membrane (PEM) was selected as an electrolyser in this study as it was deemed most suitable to handle the fluctuations of the wind electricity [8]. To consume the CO_2 produced from S2 (5,953 t/a) and S3 (6,201 t/a) [5], 1,082 t/a (S2) and 1,127 t/a (S3) H_2 is needed. The electrolyser plant (termed the distributed electrolyser plant [20]) can be built beside a biogas plant thus negating the need for storage.

Götz et al. [21] concluded in their review paper that the total energy consumed to produce 1 m^3 H_2 from PEM technology varies between 3.75 and 7.5 kWh. Marshall et al. [22] conducted an experiment and found an energy consumption of 3.75 kWh/Nm^3 H_2 from PEM technology. In addition to this, Barbir [23] used the number 6.6 kWh/Nm^3 H_2 for PEM in his study. In the future, the average energy consumption to produce 1m^3 H_2 could reduce to 4.3 kWh [24]. Therefore, this study used a conservative approach of 4.4kWh electricity to produce 1m^3 H_2. This equates to 49 kWh electricity to produce 1kg H_2 (ca. 75% conversion efficiency) (Appendix 2). Hydrogen is produced closer to the biogas facility and hence the compression of 1 bar was used.

Deionised water is necessary for smooth operation of the electrolyser [25]. The deionised water used in this study was assumed to be produced via reverse osmosis. GaBi professional database [9] provided the life cycle inventory (LCI) data for the production of deionised water. According to Eq. (1), 9.09 kg water is needed to produce 1 kg H_2. However, in reality, the water consumption is 25% higher [23]; therefore, 11.36 kg water was used to produce 1kg H_2.

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2.2.4 Electricity mix

This work assessed the LCA for the plants that will be built after 2020. Therefore, in the base case, an electricity mix from 2020 from EirGrid (Irish electricity utility) was used for all the electrical needs [26]. This projected electricity mix could be divided into steady evolution and low carbon living. The difference between these two electricity mixes are a 1.4% higher renewable share in low carbon living. This study used a conservative approach of steady evolution. This includes 41% renewables spread as follows: 36.3% wind electricity, 2.2% biomass/landfill gas, 2% hydropower, and 0.7% PV. The remaining electrical demand (59%) is met by fossil fuels, including natural gas (37.8%), hard coal (7.9%), peat (2.85%), distilled oil and heavy fuel oil (9.19%) and waste (0.74%). The GHG emissions from this 2020 electricity mix are 117g CO_2 eq. /MJ.

2.3 Life cycle impact assessment

The GaBi software (Leinfelden-Echterdingen, Germany, version 8.2) [9] was used to perform the LCA of the three scenarios. The assessments were based on midpoint life cycle impact assessment method as recommended by the European Union Joint Research Centre (JRC) on LCA in the European context; these conform to ISO 14040 and 14044 requirements [27, 28].

The environmental impacts assessed in this study include global warming potential (GWP), acidification potential, freshwater eutrophication potential, particulate matter emission (PM2.5) and ozone depletion potential.

2.3.1 Global warming potential (GWP)

Greenhouse gases (GHG) such as CO_2, CH_4 and N_2O trap heat in the atmosphere at different capacities due to radiative forcing. GWP refers to the equivalent amount of GHG released to the atmosphere from a process, expressed in terms of kg CO_{2eq}. The IPCC developed this metric to compare global warming impacts of different GHGs. The different GHGs were converted to $CO_{2eq.}$ as CO_2 corresponds

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to the most abundant GHG with uniformity in reporting. The GWP reporting period used in this study is 100 years (GWP 100).

2.3.2 Acidification potential

Acidifying substances such as sulphur oxides, nitrous oxides and ammonia increase the hydrogen ion concentration in the atmosphere which leads to acid rain. Acidification potential measures the amount of acids emitted as mole H^+ eq. This is a relative unit for different acids measured.

2.3.3 Freshwater eutrophication potential

The excess nutrient release from a process leads to augmentation of the aquatic ecosystem. This results in environmental issues such as eutrophication. Eutrophication potential measures amount of excess nutrient released as kg $P_{eq.}$

2.3.4 Particulate matter \ Respiratory Inorganics

This category measures the fine particulate matter (PM2.5 eq.), a critical environmental impact category that affects human health. An intake fraction concept was used to calculate this impact category [2].

2.3.5 Ozone depletion potential (ODP):

ODP expresses the potential degradation of gases on the ozone layer compared with trichlorofluoromethane (CFC-11), which is set at an ODP of 1.

2.4 Sensitivity analysis

The effects of four crucial factors were assessed. Three of these related to the biogas system: CO_2 sequestration in the soil; ratio of slurry and grass silage in the feedstock; the fugitive emissions in the

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biogas facility. The fourth relates to the power to gas system and is seen as the critical parameter in such systems; the carbonisation level of the electricity.

2.4.1 CO_2 sequestration in soil

The base case did not include for carbon sequestration by photosynthesis in the LCA; the rational for this is expanded upon in section 3.1. Within the grass silage production, carbon is captured by the grass and the soil; grasslands are identified as a CO_2 sink source [29]. Kiely et al. [30] showed that the Irish grassland soil has a large potential for carbon sequestration. Rastogi et al. [31] reviewed the factors that effect the emission of CO_2 from the soil and concluded that tillage practise releases CO_2 back to the atmosphere from the soil. Davidson and Ackerman [32] stated that cultivation of previously untilled soil usually led to the emission of CO_2 from the soil to the atmosphere. Pinheiro et al. [33] conducted research to compare CO_2 emissions from different types of tillage practices and found that tillage systems have a negative effect on soil carbon stock. However, grasses are perennial, and tillage is not necessary. Grasslands may be reseeded every 4 to 8 years in theory (and less often in practice); direct sowing is recommended for grasslands [12]. Earlier studies [34, 35] reviewed carbon sequestration rates of temperate grasslands across the EU. The results from their study showed that CO_2 sequestration varied between 0.6 and 8.7 t C/ha/a. In the sensitivity analysis the CO_2 sequestration from the soil was considered conservatively at 0.6 t C/ha/a. This equates to 2.2 t CO_2/ha/a.

2.4.2 Feedstock

In the base case, grass and slurry were used on an 80:20 VS basis. Using slurry as a feedstock reduces the GHG emissions due to the mitigation of methane emitted from open storage systems [2]. For the sensitivity analysis, 60:40 VS ratio of grass silage and slurry was evaluated for S1, S2 and S3. The mass and energy balance data was obtained based on the modified process using SuperPro designer (Intelligen Inc., Scotch Plain, NJ, V10) [5]. The amount of grass silage for the variations was maintained at 25,344 wet weight t/a (7,603 tDS/a at 30% DS and 7096 t VS/a at 28% VS). The amount of slurry

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varied depending on the VS ratio used. If grass silage accounted for 60% of the VS in the feedstock and dairy slurry 40% of the VS in the mix, then the wet weight of dairy slurry (6.7% VS) per year would be 70,607 t. This yields a ratio of 26:74 grass silage to slurry ratio on a wet weight basis. The utilities consumption and energy production data were presented in Appendix 3.

2.4.3 Fugitive methane emissions

The fugitive emissions in a biogas plant can vary between 1% and 7% of the produced biomethane [10]. The base cases assumed 2% methane fugitive emissions, while the sensitivity analysis evaluated 6% methane fugitive emissions.

2.4.4 Carbonisation level of the electricity

The primary or theoretical purpose of converting power to gas is to store the excess renewable electricity and convert to a renewable decarbonised gaseous energy vector. To ensure sustainability, the share of renewables in the electricity grid should be significant. Generating hydrogen from brown electricity produces brown hydrogen and as such is not deemed renewable. The majority of renewable electricity such as wind and solar are intermittent sources. This is also the reason why higher penetration of intermittent renewable electricity in the grid is not easy. Earlier studies investigated the possibilities of higher penetration of renewables in the grid. The results concluded that flexibility of the grid and external storage were the two factors that can help achieve higher penetration of renewables in the grid [36] [37]. The International Energy Agency (IEA) forecasts that the global renewable electricity share by 2050 will be between 57% and 71%; this needs a strong policy support [38]. Denmark for example plans for 100% renewable electricity by 2050 [39].

The base case used a 2020 electricity mix from the EirGrid. Even though the level of renewable was 41% which is relatively admirable and a significant improvement over the last 20 years, the mix is still 59% fossil or brown. However, in future scenarios there is an absolute necessity to decarbonise electricity through increasing the share of renewable sources. The EirGrid projection for 2040 was evaluated. This 2040 projection could be divided into four categories including steady evolution, low

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carbon living, slow change, and consumer action. Low carbon living was assessed in the sensitivity analysis. The share of electricity from different sources are as follows: fossil natural gas sources (24.5%), with the remaining 75.5% renewable and consisting of: wind (50.4%), PV (18%), biomass and landfill gas (including biogas CHP) (4.1%), hydro (1.2%), ocean energy (1.3%) and energy from waste (0.5%). The electricity from biomass and landfill gas were split equally for landfill gas and biogas CHP. The emissions for different electricity sources were retrieved from GaBi [9], excluding ocean energy. As GaBi lacks the data for wave and tidal energy, the data from Uihlein [40] was used. The GWP, ozone depletion and freshwater eutrophication per kWh of wave energy are: 43.7 $gCO_2eq.$, 1.8g CFC-11 eq. and 0.16 mg P eq. respectively. The carbon intensity for the electricity 2040 mix is 38.5 gCO_2eq/MJ electricity produced; this is 33% of the carbon intensity of the 2020 modelled mix. A theoretical 100% renewable electricity mix (with 75% from wind electricity and 25% from other renewable sources) was also assessed in this sensitivity analysis.

3 Results and discussions

3.1 Carbon balance

A carbon balance analyses was undertaken to understand the flow of carbon from grass cultivation to the production of methane and associated emissions when released back to the atmosphere. Wall et al. [4] previously calculated the chemical formula of grass silage and dairy slurry based on dry solid content as $C_{30}H_{50}O_{23}$ and $C_{22}H_{34}O_{19}$ respectively. Based on volatile solids content, carbon accounts for 46.27% and 43.85% of grass silage and slurry respectively. The dairy slurry has a lower volatile solids content (6.7%) than grass silage (28%) [4]. The photosynthesis process results in sequestration of 130 kg carbon for every ton wet weight of grass silage produced, it equates to 475 $kgCO_2/t$ wet weight. In 1 ha of grassland, ca. 40 wwt (wet weight tonne) grass silage is produced, which holds 5,182 kg C (19 t CO_2) in the above ground grass which is cut for silage. Further carbon is sequestered in the soil below the grass [12, 41]. Likewise, a wet weight ton of dairy slurry has 29 kg carbon (107 kg CO_2). Figure 2

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shows the carbon balance for different scenarios used in this study on a 1t wet weight slurry and 1t wet weight grass basis. Scenario 1, which does not capture carbon dioxide in the upgrading process releases 43% carbon in the form of methane, 39.5% as CO_2, and the digestate holds 18.5% of the carbon. Using power-to-gas systems, S2 and S3 capture CO_2 and release 79.5% of the carbon in methane with the remaining carbon held in digestate. The amount of carbon released from CO_2 in S1 and S2 decreased from 39.5% to less than 0.07% respectively. S2 and S3 have a higher percentage of carbon that can be used for energy compared with S1, due to CO_2 capture. In this work in the base case study, the CO_2 sequestered by photosynthesis and the CO_2 emission due to methane combustion were not considered in the LCA calculations as the absorption and emission would be in theory neutralized by each other. Therefore, the emissions from combustion of renewable methane are set to zero.

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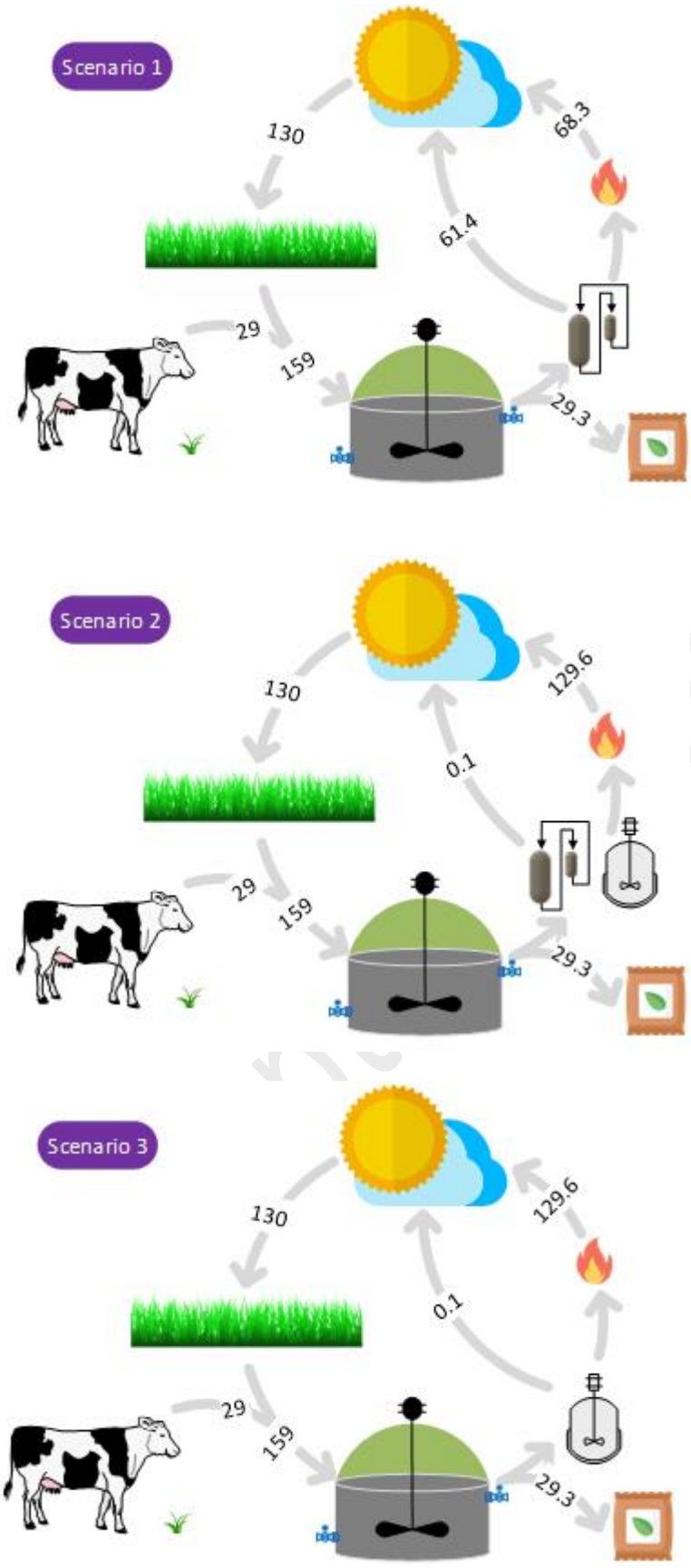


Figure 2: Carbon balance in three scenarios based on 1 ton of slurry and 1 ton of grass on a wet weight basis.

3.2 Life cycle impact assessment

3.2.1 Process contributions

Figures 3 & 4 show the process contributions as a percentage of different impact categories. There are different processes in the whole chain including silage production, transportation, biogas production, upgrading by amine, electrolysis and biological methanation. Of the different processes, electrolysis is a dominant contributor for all categories except eutrophication impact. The electrolysis process alone contributes to 80% of GHG emissions; 86% of acidification; 70% of ozone depletion and 85% of particulate matter (S2 and S3). This high-impact is due to the significant consumption of electricity (0.235 kW_eh/MJ biomethane or 0.357 kW_eh/MJ hydrogen) as it converts electricity to hydrogen. In essence the carbon intensity of the hydrogen is increased beyond that of the electricity by the reciprocal of the efficiency in converting electricity to hydrogen expressed as a decimal. The Irish 2020 grid mix contains 41% renewables and 59% fossils. This high amount of fossil electricity leads to higher environmental impacts.

Grass silage cultivation contributes the most to freshwater eutrophication and GWP in S1 (45%). Eutrophication is due to the nutrient value of the fertiliser and its potential leakage of phosphorous (in inland waterways), while the GHG emissions are from fertiliser production, fieldwork activities and emissions from applying fertilisers.

For all scenarios, the share of GWP contributions were split between the biogas production, compression, upgrading by amine and biological methanation (Figure 3). It should be noted that the amount of methane produced in S2 and S3 is significantly increased by power-to-gas upgrading, which reduced the emissions per functional unit. Using the slurry as a co-digestion substrate mitigates GWP at the rate of 29% in S1, 4% in S2 and S3. When the digestate was applied at other fields, the credit for avoiding synthetic fertiliser production for S1 is 6%, and 0.8% for S2 and S3. For the digestate applied at the grass fields, the credit was automatically calculated in GaBi for grass cultivation process. For S1, the fugitive methane emissions correspond to 29% of the GWP, which is significant. This

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highlights the importance in reducing fugitive emissions to reduce the GWP. The use of diesel in the transportation contributes 41% in S1, 4% in S2 and S3 to PM2.5 and 31% in S1, 2.5% in S2 and S3 to acidification.

3.2.2 Global warming potential

The GWP in S1 was the lowest at 34 g CO_{2eq} per MJ. Scenario 3 reduced the GWP by 3.2% as compared to Scenario 2, which used both amine scrubbing and biological methanation in upgrading. However, the GWP of S2 (124 g CO_{2eq} per MJ) and S3 (120 g CO_{2eq} per MJ) were approximately 3.5 times higher than S1. The use of 2020 Irish grid mix (with 41% green electricity) for the hydrogen production in the electrolysis led to this high GWP. It may be said that P2G does not improve the sustainability of biomethane systems when used to upgrade biogas if the source of electricity is 59% brown.

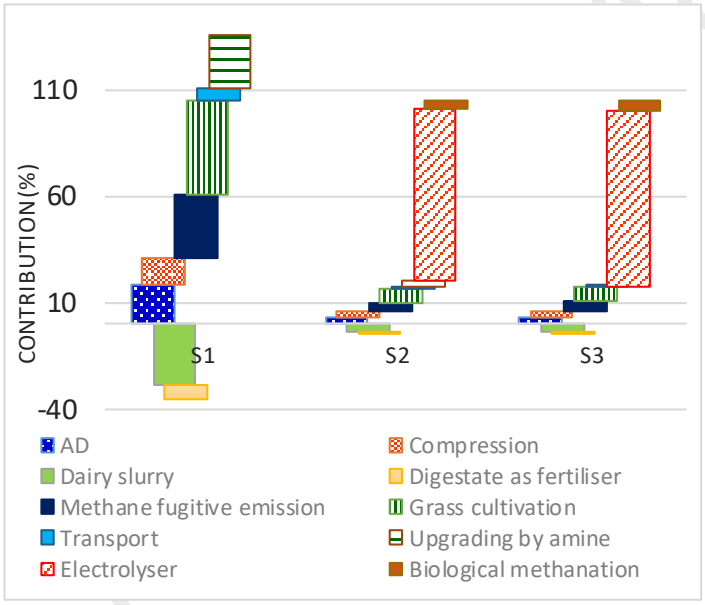


Figure 3. Percentage contributions of S1, S2 and S3 to global warming potential.

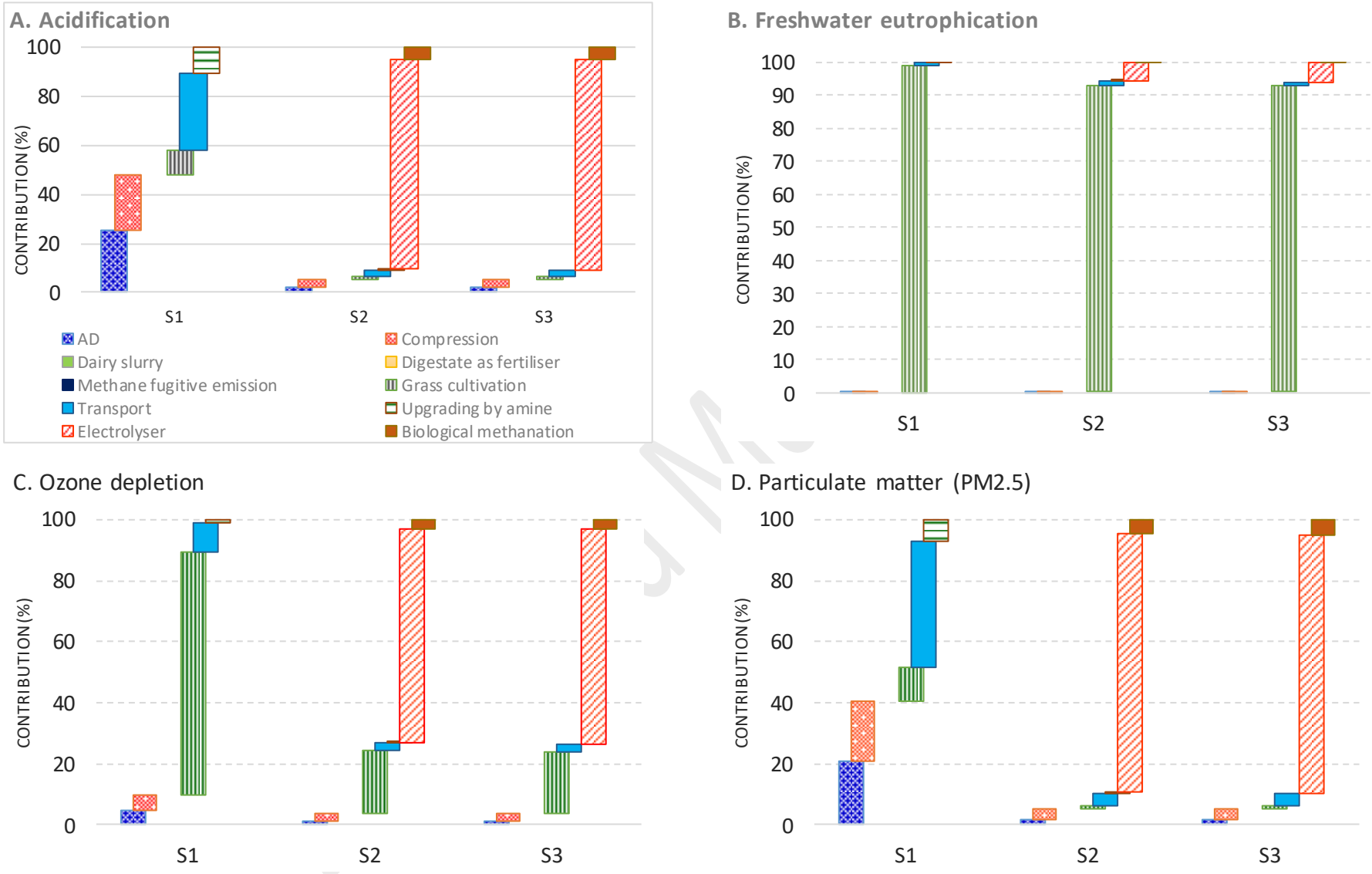


Figure 4: Percentage contributions of different processes to impact categories

3.2.3 Other environmental impact categories

The accumulated exceedance method was used to calculate the acidification potential, which is expressed as mole H^{+}_{eq} [2]. The major contribution to acidification potential is sulphur dioxide (43% - 68%) and nitrogen oxides (31%-46%) (Figure 5). The emission of nitrogen oxides was 10% higher than sulphur dioxide in S1, but N_2O was 25% lower than sulphur dioxide in S2 and S3. Nitrogen oxides in S1 are due to transportation; a major share of sulphur dioxide in S1 is emitted from biogas production and compression. Overall, biogas production, compression, and transport of grass in S1 have contributions of the same order to acidification potential. The acidification of S2 and S3 are six times higher than that of S1. The use of grid electricity in the electrolyser resulted in higher emissions of sulphur dioxide, which affected the acidification potential for S2 and S3.

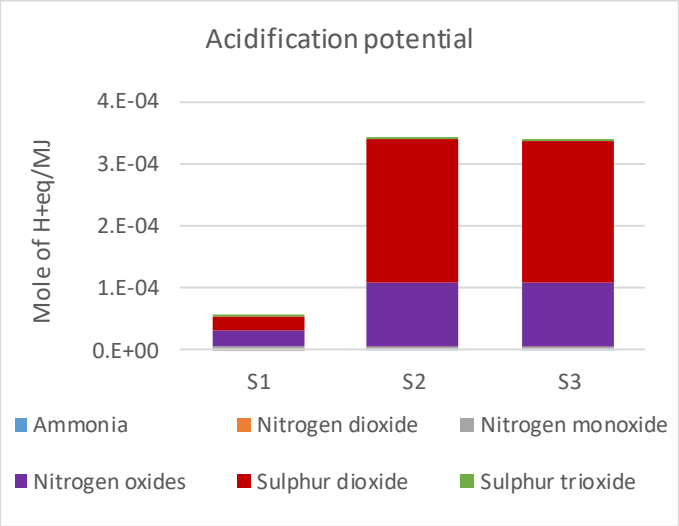


Figure 5. The contribution of different substances to acidification potential

In all scenarios, the grass silage production is the main contributor to freshwater eutrophication potential. Among the five impact categories, only freshwater eutrophication potential in S1 is higher than that of S2 and S3 (Table 3). This impact is due to the phosphate emission from phosphate fertiliser to the fresh water in grass cultivation. The reason for higher potential in S1 is the almost doubling of renewable methane output in S2 and S3.

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The larger consumption of deionised water and electricity used in the electrolyser had a high impact on the ozone depletion potential (Table 3). Moreover, the production of calcium ammonium nitrate fertiliser also contributes to this category. $PM_{2.5eq}$ effects the local atmosphere due to the contribution of potassium chloride fertiliser. The transportation of grass from the field to the biogas plant also contributes to this impact category.

Scenario 1 has two times higher potential in freshwater eutrophication than S2 and S3. Acidification potential and particulate matter (PM2.5eq) are higher in S2 and S3 than S1 (Table 3). The renewable methane production is almost doubled in S2 and S3, which reduced the environmental impacts because of grass production. In contrast, the use of the electrolyser in S2 and S3 resulted in higher *other* categories compared with S1.

Table 3. Impacts of different scenario to impact categories per MJ

Impact categories	Unit	S1	S2	S3
GWP	gCO_2eq	34	124	120
Acidification	Mole of H+ eq.	5.31E-05	3.41E-04	3.38E-04
Eutrophication freshwater	kg P eq.	8.09E-07	4.46E-07	4.39E-07
Ozone depletion	kg CFC-11 eq.	1.42E-14	2.81E-14	2.80E-14
Particulate matter	kg PM2.5 eq.	2.91E-06	1.63E-05	1.62E-05

3.3 Sensitivity analyses

3.3.1 Carbon sequestration in soil.

Each ha of grassland produces 40 wwt grass silage. To produce 1MJ of renewable methane the area under grass cultivation needed for S1, S2, S3 was 0.0544 m^2; 0.0281 m^2 and 0.0276 m^2. Using an alternative metric, the gross energy production per hectare is 183, 356 and 362 GJ/ha/a for S1, S2 and S3 respectively. The sensitivity analysis considered sequestering 2.2 t CO_2 ha^{-1} a^- into the soil.

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Sequestering the CO_2 reduced the GWP of S1, S2 and S3 to 22, 118 and 114 g CO_2eq./MJ respectively. When compared with the base case, carbon sequestration in the soil lowers the GWP of S1 by 35%, S2 and S3 by 5%.

3.3.2 Co-digestion of grass silage and slurry at different ratios

In the base case, the ratio of grass silage and slurry was 80:20 on a VS basis. The ratio of the slurry was increased to 40% on a VS basis in the sensitivity analysis to check its effect on GWP. The result shows that the GWP of 60% VS grass silage and 40% VS slurry ratios was 19 gCO_2eq/MJ (S1). The base case reported a GWP of 34 gCO_{2eq}/MJ; thus, increasing the slurry from 20% to 40% VS in the mix decreased the GWP by 43.4% (S1-IS). Increasing the slurry also increases the amount of nitrogen in the digestate. Replacing the fossil fertilizer with biofertilizer increases the GHG emission savings. The methane credit increased from 29% to 102% due to the higher portion of slurry used and the methane slippage from open slurry holding tanks displaced. However, the GWP savings did not increase proportionally to slurry added. Slurry suffers from high water content (91.2%) leading to higher electricity and heat parasitic demand lowering the potential reduction in GWP. The GHG credit for replacing fossil fertilisers increased from 6% to 24%. This shows that slurry contributes significantly in reducing GHG emissions in a biogas plant.

However, this increased slurry did not have a significant effect on the GWP reduction in S2 and S3; the GWP in S2 and S3 were 118 and 117 gCO_{2eq}/MJ, respectively. When comparing with the base cases, the GHG reduction varied from 2.5% to 5%. Electricity used to produce H_2 accounted for 80% of the GHG emissions in S2 and S3 and as such the emissions credit from slurry has a lesser effect on the overall system including P2G. Therefore, increasing slurry content of the feedstock is not an effective method to reduce GHG emission in S2 and S3.

3.3.3 Methane fugitive emissions

Increasing the fugutive methane emissions from 2% to 6% in the sensitivity analysis increased the GWP for all the scenarios. The GWP for S1, S2 and S3 at 6% fugitive emissions were 57, 138 and 137

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gCO_2eq/MJ. When compared with the base case, increasing the fugitive emissions increased the GWP by 40% in S1, 10% in S2 and S3 respectively. Minimizing the methane emissions plays an important role in reducing the GHG emissions of the biogas plant. IEA Bioenergy [10] recommeded measures to reduce methane slippage including gas tight digestate tanks, or complete degradation, frequent leakage control surveys, avoidance of open handling and storage of digestate under anaerobic conditions, and gas management.

3.3.4 Electricity

The base case scenarios used the Ireland electricity mix projected for 2020, which contains 41% renewable electricity. In the sensitivity analysis, the proposed 2040 grid mix containing 75.5% renewable electricity was evaluated. The GHG results of S1, S2, and S3 when consuming 75.5% renewable electricity were 28, 49 and 45.5 gCO_2eq/MJ. Replacing the 41% renewable electricity mix with the 75.5% renewable electricity reduced the GWP 1.2-fold in S1 and 2.5 times in S2 and S3. Thus, as expected greening of the electricity, will green the hydrogen used in the power to gas process significantly improving the renewable methane in S2 and S3. Increasing the level of renewables in the electricity grid did not increase the GHG savings for S1 at the same rate as it did in S2 and S3. This is due to the reason that for S1, the electricity is used as a utility satisfying parasitic demand, while for the other scenarios it is the precursor for hydrogen production, which is the source of almost half the renewable methane.

3.3.5 Greenhouse gas savings

The RED recast proposed to use 94 gCO_2eq/MJ as a fossil fuel comparator (FFC) for transportation [1]. The data from the base case and all sensitivities were compared to the RED recast (Table 4).

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Table 4: Greenhouse gas savings of sensitivity analysis in comparison with fossil fuel comparator from the EU.

	Scenario	Name	GWP (CO_2eq)	GHG Savings with RED recast (%)
S1	Base case	S1	34	64
	CO_2 sequestration in the soil	S1-S	22	77
	60 GS: 40 Slurry (VS basis)	S1-IS	19	80
	6% fugitive emissions	S1-6%	57	39
	2040 -75.5%renewable electricity	S1- Green75.5%	28	70
	Optimum	S1-Optimum	3.9	96
S2	Base case	S2	124	-32
	CO_2 sequestration in the soil	S2-S	118	-26
	60 GS: 40 Slurry (VS basis)	S2-IS	118	-26
	6% fugitive emissions	S2-6%	138	-47
	2040 -75.5%renewable electricity	S2- Green75.5%	49	48
	Optimum	S2-Optimum	38	60
S3	Base case	S3	120	-28
	CO2 sequestration in the soil	S3-S	114	-21
	60 GS: 40 Slurry (VS basis)	S3-IS	117	-25
	6% fugitive emissions	S3-6%	137	-46
	2040 -75.5%renewable electricity	S3-Green75.5%	45.5	52
	Optimum	S3-Optimum	35	63

Note: The negative value indicates those scenarios had higher GWP than the FFC. The green colour represents those scenarios that meet the GHG emission savings in comparison with RED recast, while the red colour represents the scenarios that did not meet the RED recast criteria. Optimum case includes 2% fugitive methane emissions, 60:40 slurry grass, CO_2 sequestration and 75.5% green electricity

Among the various sensitivities assessed, only S1 meets the sustainability criteria under the following conditions: 1. Carbon sequestration of 0.6t C/ha/a in the soil; 2. Increasing the slurry from 20% to 40% on a VS basis; 3. Electricity grid mix from 2040 with 75.5% renewables; 4. Under the combination of these conditions (Optimum). The optimum conditions in S2 and S3 could save only 60% and 63% GHG emissions. These conditions did not satisfy the RED recast of 70% GHG savings. The questions posed in this paper are "*Can power to methane systems be sustainable and can they improve the carbon intensity of renewable methane when used to upgrade biogas produced from grass and slurry?"* An answer at this stage is no and not even with electricity at 75.5% renewable. It is necessary to find out under what conditions power to gas systems can be deemed sustainable when used to upgrade biogas.

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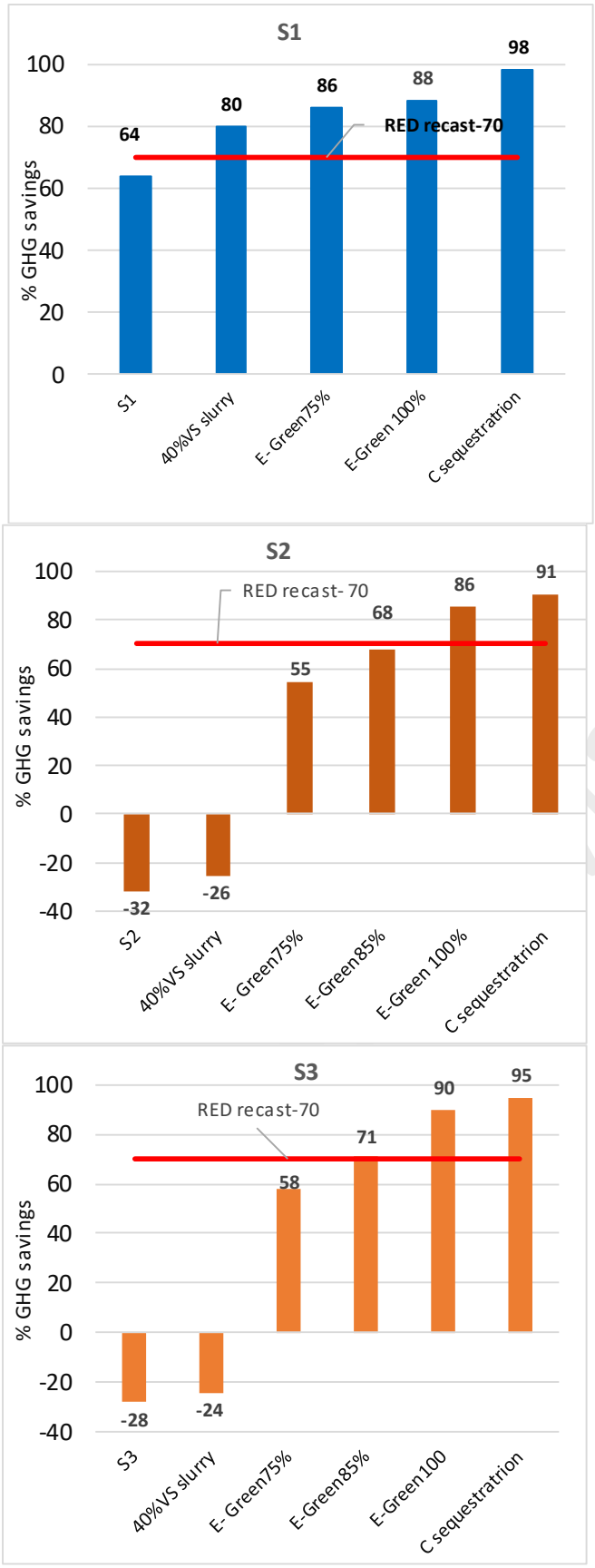


Figure 6: Cumulative (left to right) percentage GHG savings (e. g C sequestration for S1 included electricity 100% green and 60:40 grass slurry)

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To examine this, the share of renewables in the electricity grid was increased from 75.5% to 85% to 100%, which obviously had a positive effect on the GHG savings (Figure 6). With greening electricity S2 and S3 can both surpass the 70% GHG savings criteria. When the electricity for the processes are 100% renewable, the GHG saving for S3 increased from -24% (40% VS slurry, 40% renewable electricity) to 90%. This shows that the share of renewables in the grid is crucial for P2G to be considered as an upgrading choice for renewable methane production to meet the RED recast sustainability criteria.

One element which needs future work is whether the carbon capture and replacement (termed e_{ccr} in the RED recast) may be deemed a carbon credit. This would greatly improve the sustainability of S2 and S3, which capture CO_2 from the biogas system and reuse it to make methane. In this paper no credit is applied.

3.4 Data comparison with literature

Figure 7 shows the data comparison from this study to the earlier studies reported in the literature. To meet the RED recast of 70% GHG savings, the GWP of renewable methane should be less than or equal to 28 gCO_2eq/MJ.

The GWP of the grass silage and slurry production (S1) is higher than the seaweed, ley crop and cereal crop; but is comparable with maize. If only grass is used as a feedstock, it produces more GHG than when co-digested with slurry; the GWP drops from 49.7 (only grass) to 34 (S1 50:50 grass silage slurry on a wet weight basis) and to 19 gCO_2eq/MJ (S1-IS allowing for carbon sequestration in grass lands). This shows the importance of slurry in decreasing the GWP of renewable methane. The fugitive emissions from the biogas plants have a considerable impact on the GWP. When comparing the literature that used open digestate storage (Biowaste-O, Maize-O) [1] and 6% fugitive emissions (this study) with the GWP of closed digestate storage (Biowaste-C, Maize-C) [1] and 2% methane slippage

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(this study), the latter had lower GHG emissions. This means that reducing the methane slippage is another key factor in reducing the GHG emissions.

The GWP of catalytic P2G (when not used as an upgrading unit) in the literature was 113 gCO_{2eq}/MJ [42]. When the biological methanation is considered as an upgrading unit, the GWP was 133 gCO_{2eq}/MJ (this study). When more renewable electricity was used in S2 and S3, the GWP of those two-scenarios decreased significantly to 45 and 49 gCO_2eq/MJ as in S2-Green75.5% and S3-Green75.5% and to 30.5 and 27 gCO_2eq/MJ as in S2-Green85% and S3-Green85%. This further drops to 1.8; 8.87; 5.08 gCO_2eq/MJ For S1; S2 and S3, respectively if electricity is 100% green and carbon sequestration into soil was considered. Similar results were reported in the literature for a P2G unit, which consumed wind electricity, and generated a GWP between 6 and 29 gCO_{2eq}/MJ [42].

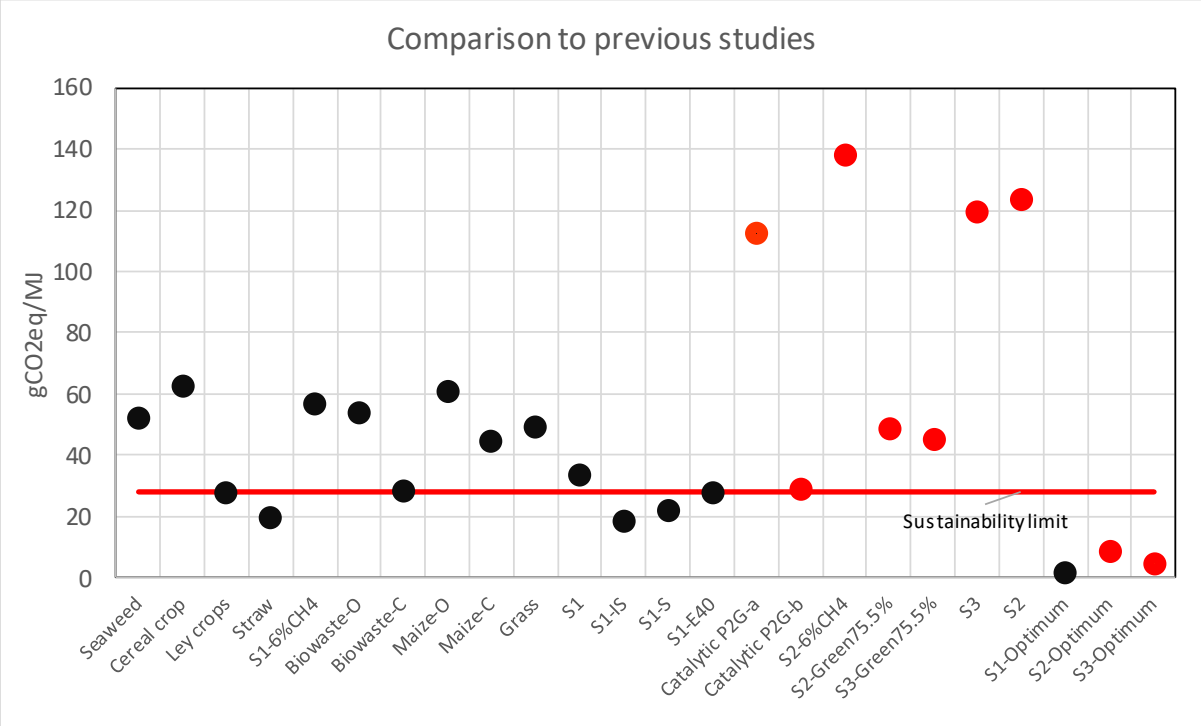


Figure 7: Comparison of output to previous studies on sustainability of biomethane systems
Note:
O- open digestate storage; C- Close digestate storage;
Seaweed [43]; cereal crop [44]; biowaste – O & C, maize whole plant – O&C [1]; ley crops, straw [45]; grass [34]; catalytic P2G-a&b[42], of which P2G –b consumed wind electricity; all S scenarios – this study. The red dots are for the processes involved P2G, the black dots are for biogas plants with traditional upgrading units.

4 Conclusion

The question posed in this paper is "*Can power to methane systems be sustainable and can they improve the carbon intensity of renewable methane when used to upgrade biogas produced from grass and slurry?"* The biogas system considered a grass silage slurry system. According to the recast renewable energy directive, biofuels need to have a 70% GHG savings as compared to the fossil fuel displaced on a whole life cycle analysis to be considered as an advanced transport biofuel. This paper undertook a life cycle assessment of biomethane with and without carbon utilisation in a P2G system.

The optimised biogas system in terms of sustainability included for larger percentages of slurry than grass silage to avail of the carbon credit in displacing open storage of slurry, minimisation of methane slippage, and allowing for carbon sequestration in the soil. This system readily met the 70% GHG savings criteria.

The P2G system was heavily influenced by the source of electricity. The carbon intensity of the hydrogen is increased beyond that of the electricity by the reciprocal of the efficiency in converting electricity to hydrogen expressed as a decimal. As the electrolysis efficiency was assumed at 75%, the hydrogen had a 33% higher carbon intensity than that of the electricity. To meet the RED recast sustainability criteria, the carbon intensity of the electricity needed to be less than 15%. Thus, the answer to the question posed is that power to gas systems can be sustainable but are unlikely to improve the sustainability of biomethane systems when they are used to upgrade biogas, if the electricity supply has an element of fossil fuel.

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References

[1] EC. Directive of the European parliament and of the council on the promotion of the use of energy from renewable sources (recast). In: Commission E, editor.2017. Available from: http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:52016PC0767, accessed 05.12.2017.
[2] Agostini A, Battini F, Giuntoli J, Tabaglio V, Padella M, Baxter D, et al. Environmentally sustainable biogas? The key role of manure co-digestion with energy crops. Energies. 2015;8:5234-65.
[3] Giuntoli J, Agostini A, Edwards R, Marelli L. Solid and gaseous bioenergy pathways: input values and GHG emissions. Report EUR. 2014;26696.
[4] Wall DM, O'Kiely P, Murphy JD. The potential for biomethane from grass and slurry to satisfy renewable energy targets. Bioresource technology. 2013;149:425-31.
[5] Vo TTQ, Wall DM, Ring D, Rajendran K, Murphy JD. Techno-economic analysis of biogas upgrading via amine scrubber, carbon capture and ex-situ methanation. Applied Energy. 2018;212:1191-202.
[6] The United Nations. Water for feed security. 2014. Available from: http://www.un.org/waterforlifedecade/food_security.shtml, accessed 12.12.2017.
[7] McKiernan; P. Agriculture, Food and GHGs. 2013. Available from: https://www.epa.ie/pubs/reports/air/airemissions/Ire_GHG_Emissions_1990_2012_P_McKiernan.pdf, accessed 12.12.2017.
[8] Vo TTQ, Xia A, Rogan F, Wall DM, Murphy JD. Sustainability assessment of large-scale storage technologies for surplus electricity using group multi-criteria decision analysis. Clean Technologies and Environmental Policy. 2017;19:689-703.
[9] Thinkstep AG. GaBi ts, software and database contents for Life Cycle Engineering, Professional Version. Stuttgart. Available from: http://www.gabi-software.com/uk-ireland/index/, accessed 2018.
[10] Liebetrau J, Reinelt T, Agostini A, Linke B, Murphy JD. Methane emissions from biogas plants: Methods for measurement, results and effect on greenhouse gas balance of electricity produced. 2017. Available from: http://www.ieabioenergy.com/wp-content/uploads/2018/01/Methane-Emission_web_end_small.pdf, accessed 12.2017.
[11] Bauer F, Persson T, Hulteberg C, Tamm D. Biogas upgrading–technology overview, comparison and perspectives for the future. Biofuels, Bioproducts and Biorefining. 2013;7:499-511.
[12] Smyth BM, Murphy JD, O'Brien CM. What is the energy balance of grass biomethane in Ireland and other temperate northern European climates? Renewable and Sustainable Energy Reviews. 2009;13:2349-60.
[13] Lukehurst CT, Frost P, Al Seadi T. Utilisation of digestate from biogas plants as biofertiliser. IEA bioenergy. 2010:1-36.
[14] Giuntoli J, Agostini A, Edwards R, Marelli L. Solid and gaseous bioenergy pathways: input values and GHG emissions. Report EUR. 2015;26696.
[15] Teagasc. Fertiliser Types. Available from: https://www.teagasc.ie/crops/soil--soil-fertility/fertilizer-types/, accessed 11.12.2017.
[16] De Klein C, Novoa RS, Ogle S, Smith KA, Rochette P, Wirth TC, et al. N2O emissions from managed soils, and CO2 emissions from lime and urea application. IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme. 2006;4:1-54.
[17] EPA U. Understanding Global Warming Potentials. Available from: https://www.epa.gov/ghgemissions/understanding-global-warming-potentials, accessed 12.12.2017.
[18] Teagasc. Nitrous Oxide. Available from: https://www.teagasc.ie/environment/climate-change/nitrous-oxide/, accessed 12.12.2017.
[19] van der Werf HMG, Kanyarushoki C, Corson MS. An operational method for the evaluation of resource use and environmental impacts of dairy farms by life cycle assessment. Journal of Environmental Management. 2009;90:3643-52.

Accepted Manuscript

[20] U.S . Department of Energy. Central Versus Distributed Hydrogen Production. Available from: https://energy.gov/eere/fuelcells/central-versus-distributed-hydrogen-production, accessed 07.01.2018.
[21] Götz M, Lefebvre J, Mörs F, McDaniel Koch A, Graf F, Bajohr S, et al. Renewable Power-to-Gas: A technological and economic review. Renewable Energy. 2016;85:1371-90.
[22] Marshall A, Børresen B, Hagen G, Tsypkin M, Tunold R. Hydrogen production by advanced proton exchange membrane (PEM) water electrolysers—Reduced energy consumption by improved electrocatalysis. Energy. 2007;32:431-6.
[23] Barbir F. PEM electrolysis for production of hydrogen from renewable energy sources. Solar Energy. 2005;78:661-9.
[24] James B, Colella W, Moton J, Saur G, Ramsden T. PEM Electrolysis H2A Production Case Study Documentation. National Renewable Energy Laboratory (NREL), Golden, CO (United States); 2013. Available from: https://www.hydrogen.energy.gov/pdfs/h2a_pem_electrolysis_case_study_documentation.pdf, accessed 15.08.2017.
[25] Carmo M, Fritz DL, Mergel J, Stolten D. A comprehensive review on PEM water electrolysis. Int J Hydrogen Energy. 2013;38:4901-34.
[26] SONI Ea. Tomorrow's Energy Scenarios 2017: Planning our Energy Future. 2017. Available from: http://www.eirgridgroup.com/site-files/library/EirGrid/EirGrid-Tomorrows-Energy-Scenarios-Report-2017.pdf, accessed 02.03.2018.
[27] EU-JRC. Handbook–General Guide for Life Cycle Assessment–Detailed Guidance. Publication Office of the European Union, Luxembourg. 2010.
[28] International Organization for Standardization. Environmental Management: Life Cycle Assessment: Principles and Framework: ISO; 1997.
[29] Scurlock J, Hall D. The global carbon sink: a grassland perspective. Global Change Biology. 1998;4:229-33.
[30] Kiely G, Leahy P, Lewis C, Xu X, Sottocornola M. SoilC-Feasibility of Grassland Soil Carbon Survey. 2017.
[31] Rastogi M, Singh S, Pathak H. Emission of carbon dioxide from soil. Current Science. 2002;82:510-7.
[32] Davidson EA, Ackerman IL. Changes in Soil Carbon Inventories Following Cultivation of Previously Untilled Soils. Biogeochemistry. 1993;20:161-93.
[33] Pinheiro ÉFM, de Campos DVB, de Carvalho Balieiro F, dos Anjos LHC, Pereira MG. Tillage systems effects on soil carbon stock and physical fractions of soil organic matter. Agricultural Systems. 2015;132:35-9.
[34] Korres NE, Singh A, Nizami AS, Murphy JD. Is grass biomethane a sustainable transport biofuel? Biofuels, Bioproducts and Biorefining. 2010;4:310-25.
[35] Jones M, Donnelly A. Carbon sequestration in temperate grassland ecosystems and the influence of management, climate and elevated CO2. New Phytologist. 2004;164:423-39.
[36] Hohmeyer OH, Bohm S. Trends toward 100% renewable electricity supply in Germany and Europe: a paradigm shift in energy policies. Wiley Interdisciplinary Reviews: Energy and Environment. 2015;4:74-97.
[37] Denholm P, Hand M. Grid flexibility and storage required to achieve very high penetration of variable renewable electricity. Energy Policy. 2011;39:1817-30.
[38] Guandalini G, Robinius M, Grube T, Campanari S, Stolten D. Long-term power-to-gas potential from wind and solar power: A country analysis for Italy. Int J Hydrogen Energy. 2017;42:13389-406.
[39] The Danish Government. The Danish Climate Policy Plan: towards a low carbon society. 2013. Available from: https://ens.dk/sites/ens.dk/files/Analyser/danishclimatepolicyplan_uk.pdf, accessed 27.02.2018.
[40] Uihlein A. Life cycle assessment of ocean energy technologies. The International Journal of Life Cycle Assessment. 2016;21:1425-37.

Accepted Manuscript

[41] Saggar S, Hedley C, Mackay A. Partitioning and translocation of photosynthetically fixed 14C in grazed hill pastures. Biology and Fertility of Soils. 1997;25:152-8.
[42] Parra D, Zhang X, Bauer C, Patel MK. An integrated techno-economic and life cycle environmental assessment of power-to-gas systems. Applied Energy. 2017;193:440-54.
[43] Czyrnek-Delêtre MM, Rocca S, Agostini A, Giuntoli J, Murphy JD. Life cycle assessment of seaweed biomethane, generated from seaweed sourced from integrated multi-trophic aquaculture in temperate oceanic climates. Applied Energy. 2017;196:34-50.
[44] Buratti C, Barbanera M, Fantozzi F. Assessment of GHG emissions of biomethane from energy cereal crops in Umbria, Italy. Applied energy. 2013;108:128-36.
[45] Uusitalo V. Potential for Greenhouse Gas Emission Reductions by Using Biomethane as a Road Transportation Fuel. Acta Universitatis Lappeenrantaensis. 2014.

Accepted Manuscript