

Bioconversion of carbon dioxide in anaerobic digesters for on-site carbon capture and biogas enhancement – A review

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Abstract

Energy consumption of the water sector presents an increasing energy demand, contrary to GHG mitigation aims. As a result, research aimed at capturing emitted CO₂ and at developing treatment technologies with a low energy demand and increased renewable energy production has increased, leading to a surge in implementation of anaerobic digestion (AD). Valorisation of the biogenic CO₂ emitted with biogas AD (estimated at over 1 MtCO₂ per annum for the UK water and organic waste sectors), presents an opportunity to further reduce carbon footprint and support energy supply decarbonisation. This paper reviews bioconversion of CO₂ into CH₄ in ADs (without addition of H₂) as a means to valorise CO₂ emissions. The review has concluded this to be a promising solution to reduce carbon footprint and uplift renewable energy production. However, in order to increase readiness for implementation (1) the mechanisms of CO₂ utilisation need to be elucidated, including the sources of additional H₂ needed, (2) studies need to report more thoroughly the conditions of CO₂ injection and (3) trials where ADs are integrated with gas to liquid mass transfer technologies need to be performed.

Keywords

Anaerobic digestion, bioconversion, carbon dioxide, greenhouse gas, valorisation

1. Motivation and targets for greenhouse gas reduction

Carbon dioxide (CO₂) concentration in the atmosphere has increased from 280 ppm in the preindustrial era to *ca.* 400 ppm in 2017 (NOAA, 2017), with an average rise of 2 ppm per year during the last decade (IEA, 2013a). This rise has been attributed to anthropogenic emissions (IEA, 2013a; United Nations, 1998), leading to legislation targeting GHG reduction both at national and international levels. The Kyoto Protocol, signed in 1997 and effective since 2005, was the first treaty stating legally binding GHG reduction targets. It was divided into two commitment periods, 2008-2012 and 2013-2020, stating a GHG reduction target of 4.7% for industrialised countries as a group for the first phase. A combined GHG reduction target of 8% was stated for European countries (EU-15), which was further distributed in a burn-sharing agreement (Fig. 1). The Kyoto Protocol has in turn led to the development of national legislation in each specific country, aimed at compiling or tightening the stated targets. For example, a GHG reduction target of 12.5% when compared against the 1990 baseline was agreed for the UK as part of the Kyoto Protocol, while an additional legally binding GHG target was set by the Climate Change Act 2008, which stated a 80% reduction below base levels by 2050 (34% by 2020).

Fuel combustion related CO₂ emissions for countries with emission targets in the first commitment period (Annex I Kyoto Parties) reduced from 8,270 to 6,874 megatons CO₂ (MtCO₂) between 1990 and 2013 (Fig. 2 (a)) (IEA, 2015), which implied a 16.9% reduction and hence compliance with the 4.6% target. The UK CO₂ emissions were reduced by 18.1% compared to the baseline by 2013 (IEA, 2015), with a drop from 547.7 MtCO₂ in 1990 to 448.7 MtCO₂. Despite these positive trends, there is a need for further GHG mitigation efforts, since part of the goals for the Kyoto Protocol first commitment period were achieved

by utilising emissions trading schemes (EEA, 2012) or as a consequence of the global economic recession (IEA, 2013a), rather than due to operation of industrial processes in a more sustainable manner. Furthermore, equivalent world CO₂ emissions experienced an increase of 56% for the same period, increasing from 20,623 to 32,190 MtCO₂ (Fig. 2 b) (IEA, 2015), which was attributed to a combined growth in population (35%) and in per capita gross domestic product (GDP) (60%) (IEA, 2015). The World Energy Outlook estimated in its New Policies Scenario that global electricity demand will increase by 70% over 2010 levels by 2035 (IEA, 2012), with CO₂ emissions from combustion of fossil fuel reaching 37,200 MtCO₂ even when the announced GHG mitigation commitments are implemented (IEA, 2013b). As a response, decarbonisation of energy supply is identified as one of the most pressing needs to improve carbon footprint and mitigate climate change (DECC, 2012a). Carbon intensity of energy supply was reduced by 8% for Annex I Kyoto Parties between 1990 and 2013 (Fig. 2 (a)) (IEA, 2015). However, this parameter remained almost constant at a world level for the same period (56.2 tCO₂·TJ⁻¹ on 1990 and 56.8 tCO₂·TJ⁻¹ on 2013 (IEA, 2015)) (Fig. 2 b), evidencing that sustainable energy generation has not yet been achieved at a global level. The share of energy with fossil fuel origin has indeed remained relatively constant over the last 40 years, constituting over 80% of the world energy supply (IEA, 2013a).

Energy consumption of the water sector presents an increasing energy demand, contrary to GHG legislation aims. Electricity demand of this sector accounts for *ca.* 3% in UK (Rothausen and Conway, 2011). Energy usage for operation of water and wastewater treatment sites at a UK level increased from 8,290 GWh in 2007/2008 (Water UK, 2008a) to 9,016 GWh in 2010/2011 (Water UK, 2012), in part as a consequence of the tightened quality standards resulting from the endorsement of the Water Framework Directive in 2000 (European Commission, 2009; Georges et al., 2009). Emissions of CO₂ are expected to

increase by over 110,000 tonnes per year (Georges et al., 2009) from energy demand and emissions from additional processes needed to upgrade more wastewater treatment plants to meet the most recent quality standards. As a result, the potential of the water sector to contribute towards GHG emissions mitigation has been highlighted at national (e.g. UK (DEFRA, 2008), USA (USEPA, 2012)) and global level (McGuckin et al., 2013). This has in turn led to a surge in research aimed at capturing emitted CO₂ and at developing treatment technologies with a low energy demand and increased renewable energy production. An important strategy towards mitigating GHG emissions is the implementation of anaerobic digestion (AD), which is regarded favourably due to the production of renewable energy and the stabilisation of waste into a digestate that can be used as a fertilizer, which offsets GHG emissions from usage of energy with fossil fuel origin (DEFRA, 2007). The last few decades have seen a rapid surge of research aimed at further improving AD performance, in order to increase renewable energy generation and contribute to decarbonise energy supply. The operation of ADs leads to formation of CO₂ with the biogas, which, if captured and valorised, could further improve the carbon balance of the AD process. Biogenic CO₂ emissions are not accounted for in carbon inventories. However, its reduction is considered as a negative release to be deducted from overall carbon emissions, which makes carbon management strategies for biogenic CO₂ suitable to mitigate carbon footprint (Byrns et al., 2013). This review quantifies the CO₂ emissions associated with biogas from AD, both in the water and organic waste sectors, in the UK. Then, the possibility of further enhancing the AD process by on-site bioconversion of biogas sourced CO₂ (without H₂ addition) is reviewed.

2. Identification and quantification of CO₂ emissions from the water and organic waste sectors

Emissions of GHG from the water sector have been estimated to account for 3-10% of total world emissions (McGuckin et al., 2013), which evidences the potential for this sector to

contribute towards GHG mitigation (McGuckin et al., 2013; USEPA, 2012). To illustrate, emissions of GHG from the UK water sector were estimated to be over 5 MtCO₂ equivalents (MtCO₂e) during 2010-2011 (Water UK, 2012), which accounts for *ca.* 1% of the total national GHG emissions (CIWEM, 2013). Approximately 56% of the emissions were attributable to wastewater treatment (2005-2006 data (DEFRA, 2008)). Biogenic CO₂ emissions resulting from UK wastewater treatment have in turn been estimated at 2 MtCO₂ per annum (Byrns et al., 2013), which if reduced would contribute to reduce the sector's carbon footprint. Specific sources of biogenic CO₂ emissions were previously quantified by Byrns et al., (2013) at a UK level (Table 1). Aerobic wastewater treatment was identified as the main source of CO₂, with a contribution of 1-1.1 MtCO₂ per annum from activated sludge or biological filters. Emissions of CO₂ with the biogas generated in ADs were estimated at 0.27 MtCO₂ per annum (Byrns et al., 2013), when considering a total sludge production of 1,762,000 tonnes as dry solids (Water UK, 2008b) of which 66% is anaerobically digested. Combustion of methane (CH₄) from biogas in combined heat and power (CHP) engines or flares was quantified as 0.5 MtCO₂ per annum. Energy recovery by combustion of sludge was estimated responsible for the annual emission of 0.26 MtCO₂. Considering these figures, the contribution of aerobic wastewater treatment towards on-site biogenic CO₂ emissions is three to four times higher than that of sludge incineration or of CO₂ confined in biogas produced by ADs. However, biogas CO₂ was identified as the direct emission most easily available to be recovered within the wastewater treatment flowsheet (Byrns et al., 2013), due to a concentration up to 40 times higher than the CO₂ generated in aerobic processes (Table 1). Furthermore, the point source nature of this stream would reduce the costs for capture, when compared with emissions from open systems such as activated sludge. The development of carbon management strategies for biogas derived CO₂ (CO₂ inherent in biogas and from combustion of CH₄) would imply a *ca.* 38% reduction in the release of biogenic CO₂ from the

UK water sector (0.77 MtCO₂ per annum) (Table 1). This potential for avoidance of CO₂ emissions in the water sector relates to current AD infrastructure and will further increase as biogenic CO₂ emissions rise in response to the higher implementation of this technology.

The benefits of developing carbon management strategies for AD derived CO₂ are even higher when considering the increasing implementation of AD for treating alternative substrates (e.g. manure, organic waste). To illustrate, the number of ADs treating the organic fraction of municipal solid waste in Europe increased from 53 in 1999 (De Baere, 2006) to 244 in 2014 (De Baere and Mattheeuws, 2012), which implied an increase in treating capacity from 1,037,000 to 7,750,000 t·annum⁻¹ (De Baere and Mattheeuws, 2012).

Attending to this capacity, emissions of biogas CO₂ from European ADs treating the organic fraction of municipal solid waste can be estimated at *ca.* 1.46 MtCO₂ per annum if a biogas yield of 300 m³ biogas·tonne⁻¹ (Georges et al., 2009) with 65% CH₄ concentration is considered. Within the UK, the number of AD sites outside of the water sector increased from two in 2005 (NNFCC, 2016a; WRAP, 2012) to 316 in 2016 (NNFCC, 2016b). Table 2 compiles information of the current AD infrastructure in the UK outside of the water sector (up to May 2016), where size is considered as per electricity generation capacity and CO₂ emissions have been estimated based on an electrical yield of 2.1 kWhe·m⁻³ biogas (energy yield of 6.1 kWhe·m⁻³ biogas with 35% CHP electrical efficiency) and a biogas composition of 65% CH₄ and 35% CO₂ (0.63 kg CO₂·m⁻³ biogas at standard conditions). Emissions of CO₂ with biogas from UK ADs outside of the water sector are hence estimated at 0.75 MtCO₂ per annum (industrial sites not accounted), with ADs treating community waste accounting for 58% (Table 2). Biogenic CO₂ emissions from ADs, both within and outside of the water sector, are expected to further increase because of the government support towards the use of AD (DEFRA, 2011; DEFRA, 2007) and the UK legal requirement to reduce by 2020 the biodegradable waste derived to landfill to 35% of 1995 level. Sequestration or valorisation of

biogas CO₂ would hence further increase the carbon benefits of the AD process, contributing towards energy supply decarbonisation. This in turn would help mitigating the negative trend in GHG emissions of the water sector and reducing the carbon footprint of the organic waste sector.

3. Options for implementation of carbon capture and storage or valorisation strategies in the water and organic waste sectors

Carbon capture and storage (CCS) in geological or oceanic reservoirs is proposed as one of the most cost effective technologies for CO₂ management both at UK and worldwide level. Its economic feasibility is further enhanced when coupled with enhanced gas or oil recovery (DECC, 2012a). The International Energy Agency has estimated that CCS has the potential to provide a sixth of the carbon emission reduction targets required by 2050 (IEA, 2014), and the feasibility of a commercial-scale implementation of CCS and the availability of storage capacity in the UK seabed have been evidenced (DECC, 2012a). The existence of clusters of centralised emission sources (power and industrial plants) close to a potential storage site (DECC, 2012a) has raised the possibility of installing a shared CO₂ transportation infrastructure, which would benefit from the pipeline's economy of scale and hence reduce overall transport costs. However, the performance of a similar preliminary assessment comparing the location of AD sites and potential CO₂ reservoirs in the UK (Fig. 3 b), evidences the particular transportation challenge to be addressed in sectors like water or organic waste, where individual sites are scattered. The development of a common pipeline infrastructure for handling CO₂ emissions of the water and organic waste sectors appears unrealistic and alternative strategies for management of biogas CO₂ emissions are hence required (Cheah et al., 2016). Particularly appealing are those that promote on-site CO₂ valorisation as opposed to off-site storage, since they avoid transport and compression of CO₂. Potential opportunities for biogenic carbon sequestration have been discussed by

leading practitioners of the sector, such as in the technology strategy board in 2011 (NERC, 2011), where the carbon sequestration potential of biochar and algae, amongst others, were discussed. The need for further basic research (proof of concept) and for increasing technology readiness before a widespread implementation can be considered were stated. Byrns et al. (2013) further studied on-site carbon management alternatives and identified utilisation of CO₂ for growth of algae and addition of CO₂ to anaerobic processes for its bioconversion to CH₄ by methanogenic *Archaea* as the most economically feasible options. Both alternatives would have a double benefit in GHG emissions, since they imply a direct uptake of CO₂ and an increase in renewable energy production associated with the digestion of the grown algae or the bioconversion of CO₂ to CH₄. This increase in renewable energy production places these carbon management strategies in a leading position when compared with carbon storage alternatives, since they aim for CO₂ valorisation as opposed to storage or sequestration. Besides, an increase in renewable energy production would contribute towards the decoupling of energy demand from combustion of fossil fuels, main source of GHG anthropogenic emissions (IEA, 2013a). Furthermore, it is in line with the government commitments to expand energy recovery from waste through AD (DEFRA, 2007) and to provide 15% of the UK energy and 10% of the energy used in the transport sector from renewable sources by 2020 (Directive 2009/28/EC). The following sections of this review focus on the direct addition of CO₂ to ADs for its bioconversion to CH₄ by methanogenic *Archaea* (without addition of H₂), for which previous studies investigating bioconversion of CO₂ to CH₄ in anaerobic processes, possible mechanisms of CO₂ utilisation and potential impacts in operation of ADs are reviewed.

4. State of the art of bioconversion of CO₂ in ADs as an on-site carbon management strategy

4.1 Previous evidence

Bioconversion of CO₂ to CH₄ has been studied for different systems and applications, including, among others, electrochemical bioreactors (Jeon et al., 2009), fixed bioreactors enriched with hydrogen (H₂) (Lee et al., 2012), bioconversion in deep subsurface aquifers (Leu et al., 2011) or biogas upgrading units (Martin et al., 2013). Investigations considering onsite CO₂ bioconversion to CH₄ as a GHG management strategy in anaerobic processes and without addition of exogenous H₂ are, however, scarce (Table 3) and the focus of this review. Studies addressing bioconversion of CO₂ into CH₄ in a sewage sludge matrix were first reported in the 1990's. Sato and Ochi, (1994) measured associated increases in CH₄ production when the CO₂ concentration in the headspace of ADs was controlled both in laboratory and pilot scale units. Increases of up to 30% in specific CH₄ yield were reported when maintaining headspace CO₂ concentrations of 60% v/v in semicontinuous operating ADs treating waste activated sludge. The extent of CO₂ uptake or the mechanisms by which this could be biotransformed into CH₄ were not thoroughly investigated. Alimahmoodi and Mulligan, (2008) explored the impact of enriching with CO₂ the influent to a laboratory scale upflow anaerobic sludge blanket (UASB) reactor. A CO₂ pressure of $1.01 \cdot 10^5$ Pa was maintained in the influent storage tank to achieve a higher CO₂ dissolution. It was estimated that 69-86% of the CO₂ dissolved could be utilised in the process. Salomoni et al., (2011) measured a 25% increased specific CH₄ yield when continuously injecting CO₂ at a load of $0.49 \text{ m}^3 \cdot \text{d}^{-1}$ into the first stage of a two-phase anaerobic digestion (TPAD) process and a CO₂ uptake of up to 46% of that injected was estimated. Bajón Fernández et al. (2014) observed an enhancement of CH₄ production in batch ADs enriched with CO₂ of up to 13% and 138% for units treating food waste and sewage sludge, respectively. An associated reduction of CO₂ emissions of up to 11 and 34% was estimated for ADs treating food waste and sewage sludge, respectively. Koch et al., (2015) reported a 20% increased CH₄ specific yield when flushing the headspace of batch sewage sludge ADs with a gas containing 20% CO₂ as

opposed to flushing with pure N₂ (g). Bajón Fernández et al., (2015b) recorded an assimilation of 0.55 kg of exogenous CO₂ when injecting CO₂ every 48 hours during 77 days in a food waste pilot scale AD. In this case, CO₂ was contacted with the digesting material through a bubble column installed in the AD recirculation loop and each injection increased by 4.0E-3 kmol CO₂·m⁻³ the CO₂ dissolved concentration inside of the AD. Al-mashhadani et al., (2016) observed a 109% increase in the cumulative CH₄ production of kitchen waste ADs enriched daily with pure CO₂.

The references available have evidenced that a significant benefit in CH₄ production and CO₂ uptake can be achieved when injecting exogenous CO₂ (e.g. sourced from biogas) in ADs, without a need for exogenous H₂ addition. However, despite the increasing literature available on the topic (Table 3), the majority of previous references constitute a proof of concept for conversion of CO₂ to CH₄ in anaerobic processes, while critical knowledge gaps have not yet been fully addressed. In particular, the mechanisms for CO₂ utilisation, the source of electrons for CO₂ reduction if exogenous H₂ is not added to the system, the criticality of gas to liquid mass transfer for implementation in scaled-up systems and the poor reporting of conditions at which CO₂ was injected have not been rigorously addressed so far. These aspects and other further research needed before a widespread full scale implementation can be considered are discussed in the following sections.

4.2 Possible mechanisms of CO₂ utilisation in the digestion process

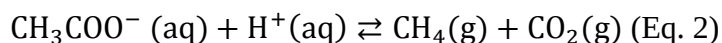
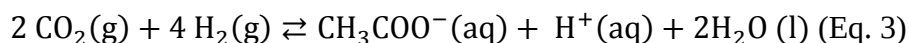
The complexity and multiplicity of reactions involved in ADs means that it is difficult to identify the mechanisms by which additional CO₂ could be utilised and bioconverted to CH₄. Potential benefits in carbon footprint associated with bioconversion of CO₂ in anaerobic processes have been reported as an overall term in which all the reactions where CO₂ could be utilised or produced are included (Alimahmoodi and Mulligan, 2008; Bajón Fernández et al., 2014), without specifically considering the individual reactions. While this approach

enables proof of concept for conversion of CO_2 to CH_4 , it prevents elucidation of the mechanisms of CO_2 utilisation, which limits understanding of the substrates in which the concept could be implemented and does not provide a robust scientific basis for a widespread implementation. Oh and Martin (2016) developed one of the few studies that addresses thermodynamic efficiency of the proposed carbon utilisation mechanisms in ADs. This section aims to review the mechanisms by which CO_2 could be utilised and to identify impacts other than CH_4 production that CO_2 injection could have in the AD process.

4.2.1 Biological bioconversion to CH_4

There is conflicting information in the literature regarding the means by which CO_2 can be bioconverted to CH_4 in an anaerobic process, with references supporting both an increase in hydrogenotrophic or acetoclastic methanogenesis. The mechanism based on hydrogenotrophic methanogenesis (Eq. 1) relies on the reduction of CO_2 with H_2 by hydrogenotrophic *Archaea*. The mechanism supporting a boost of acetoclastic methanogenic activity (Eq. 2) after CO_2 addition, relies on the higher substrate availability (VFAs) for this reaction to take place as a consequence of homoacetogenesis (Eq. 3) being encouraged via the Wood-Ljungdahl pathway (Salomoni et al., 2011). Utilisation of CO_2 by the Wood-Ljungdahl pathway consists on its reduction in the methyl branch and carbonyl branch (Fig. 5) that constitute this mechanism of CO_2 fixation. In the methyl branch one molecule of CO_2 is reduced to formate, which is the precursor for the formation of a methyl group in the shape of methyl- H_4 -folate after reduction with four more electrons. In the carbonyl branch, one molecule of CO_2 is reduced by two electrons to carbon monoxide. The methyl and carbonyl groups are then condensed with coenzyme A to form acetyl-CoA, which can be assimilated as cellular carbon or converted to acetyl-phosphate, which in turn leads to acetate formation. Acetoclastic methanogenesis (Eq. 2) would then be encouraged because of a

higher substrate availability. The steps in the Wood-Ljungdahl pathway are summarised in Fig. 5 and can be further consulted in the review by Ragsdale and Pierce, (2008).



Previous investigations on CO₂ bioconversion in ADs have focused on proving the potential to achieve an improved CH₄ production, without the mechanisms by which additional CO₂ could be utilised being thoroughly investigated. Previous work supporting both an increase in hydrogenotrophic or acetoclastic methanogenesis can be found. Alimahmoodi and Mulligan, (2008) studied the impact of bioconversion of CO₂ in the CH₄ production and CO₂ uptake capacity of a laboratory scale UASB reactor. External CO₂ gas was injected in three types of synthetic influents containing a different proportion of short-chain volatile fatty acids (VFAs): (1) acetic acid, (2) acetic, propionic and butyric acids and (3) propionic and butyric acids. In every case, a higher CH₄ production rate was observed when the influent was enriched with CO₂. The improvement was more noticeable for the system containing solely acetic acid. This was attributed to additional CO₂ being reduced to CH₄ by hydrogenotrophic methanogens (Fig. 4), which were considered able to utilise VFAs as an alternative supply of H₂.

Several references contradict this by supporting a boost of acetoclastic methanogenesis after injecting CO₂ in ADs. Francioso et al., (2010) and Salomoni et al., (2011) studied the influence of injecting CO₂ into the first stage of a TPAD process at laboratory and pilot scale, respectively. The 40-46% CO₂ uptake observed in both cases was attributed to an increased carbon assimilation by the Wood-Ljungdahl pathway, which leads to formation of acetate

that can in turn be utilised in acetoclastic methanogenesis (Fig. 4). It must be remarked that the study of Salomoni et al., (2011) was performed in a TPAD system, where a good phase separation (based on pH, VFA levels and produced gas composition) was achieved. In this scenario, no methanogenic activity was expected in the first reactor (acid phase), where the CO₂ was injected, hence it is unlikely that hydrogenotrophic methanogenesis was the reason for the utilisation of additional CO₂. However, the TPAD with CO₂ injection system was compared with a control single phase AD system, preventing a clear understanding of the contribution of CO₂ conversion and of phase separation to the increased CH₄ formation. Bajón Fernández et al., (2014) reported a substrate dependant response of ADs to an injection of CO₂, with higher benefits in CH₄ production observed in sewage sludge digesters compared with food waste units. Since the ammonia (NH₃) concentration observed in food waste ADs reached reported toxicity levels for obligate acetoclastic methanogens, the higher benefit in sewage sludge ADs was attributed to an increase in the activity of these methanogens as a response to CO₂ injection. Mohd Yasin et al., (2015) observed an initial increase in acetate formation in methanogens enriched from WAS and sparged with CO₂, with a later consumption of acetate and CH₄ gas formation. This was attributed to CO₂ being utilised by the Wood-Ljungdahl pathway to produce acetate and the subsequent use of acetate by acetoclastic methanogens for CH₄ production. However, in no case was experimental evidence provided to support the proposed hypothesis (e.g. microbial community analyses, carbon isotopes measurements). Previous references proposing a reduction of exogenous CO₂ via homoacetogenesis (Figure 5) or hydrogenotrophic methanogenesis have not thoroughly investigated the need for a reducing agent. Several potential sources of electrons have been proposed: availability of H₂ due to a shift of the bicarbonate equilibrium when dissolving exogenous CO₂ (Bajón Fernández et al., 2015b), oxidation of ammonia to nitrogen gas (Oh and Martin, 2014) or utilisation of VFA as sources of hydrogen and electrons (Alimahmoodi

and Mulligan, 2008). Reported increases of H_2 concentration in the headspace of pilot scale food waste ADs enriched with CO_2 (Bajón Fernández et al., 2015b) and of VFA concentration following CO_2 injection in acetogenesis reactors (Francioso et al., 2010), support electron availability for CO_2 reduction without the need for external H_2 addition. However, further investigation on the electron sources for CO_2 reduction is required before the mechanisms of utilisation of exogenous CO_2 in ADs can be elucidated.

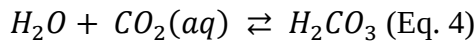
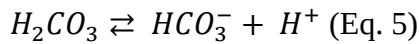
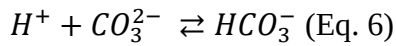
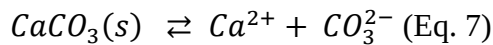
The need to understand the mechanisms by which CO_2 can be transformed into CH_4 in ADs is required to understand the types of systems in which CO_2 bioconversion could be applied with benefits. Acetoclastic methanogenesis can be severely inhibited in ADs where substrate degradation leads to high NH_3 concentrations (e.g. manure, food waste) (Banks et al., 2012; Demirel, 2014; Vavilin et al., 2008) resulting in lower contribution to total CH_4 production than the commonly accepted 70% (Conrad, 1999). If coupling of homoacetogenesis by the Wood-Ljungdahl pathway and acetoclastic methanogenesis proves to be the mechanism of CO_2 bioconversion, the inhibition of this pathway in protein rich substrates could be a limit for implementing CO_2 bioconversion in ADs in sectors like organic waste, unless NH_3 concentration could be reduced. Further information therefore needs to be gathered regarding the CO_2 fate, with emphasis on the possibility of a substrate dependant response based on the predominance of different methanogenic communities (Bajón Fernández et al., 2014). This in turn would contribute to determining the substrates and industrial sectors in which it could be successfully applied and the potential GHG savings achievable if a widespread implementation could be achieved.

4.2.2 Chemical utilisation pathways

Dissolution of additional CO_2 in an aqueous media leads to formation of carbonic acid (Eq. 4), which in turns dissociates to protons (H^+) and bicarbonates (HCO_3^{2-}) (Eq. 5). The majority of the H^+ formed is then neutralized by reacting with carbonates (CO_3^{2-}) (Eq. 6), further

increasing the concentration of HCO_3^- . Part of the HCO_3^- can in turn be converted to CO_3^{2-} , however, under the pH conditions present in ADs, the HCO_3^- form is expected to dominate.

Part of the CO_2 injected into ADs has the potential to react chemically to form or dissolve carbonated compounds. Calcium carbonate (CaCO_3) can form in anaerobic processes, leading to a reduced specific methanogenic activity (Chen et al., 2008). Addition of CO_2 to a media containing calcium (Ca^{2+}) has the potential to precipitate CaCO_3 . However, at the pH conditions present in ADs (6.5 - 7.5), an increased solubility of this compound is expected because of the impact of CO_2 dissolution in CO_3^{2-} concentration, which would displace the CaCO_3 equilibrium to the ionized form (Eq. 7) and contribute to reduce potential loss of specific methanogenic activity.



Dissolved CO_2 can also react with aqueous ammonia leading to a higher dissolution of CO_2 and formation of ammonium carbonated compounds, which is industrially exploited in processes aimed at CO_2 capture for carbon mitigation (Bai and Yeh, 1997; Zhuang et al., 2012). Within the possible reaction products, ammonium salts of bicarbonate (HCO_3^-), carbamate (NH_2CO_2^-) and carbonate (CO_3^{2-}) anions are the most likely species to be formed, with their relative abundance being highly dependent on pH and the free NH_3 and absorbed CO_2 ratio (Mani et. al. 2006). At the high CO_2 loading expected when injecting exogenous CO_2 in an AD and the low free NH_3 concentration expected from a pH of 6.5-7.5 (majority NH_4^+), ammonium bicarbonate is the species most likely to be found in the solution. Due to

the very high solubility of ammonium salts, ammonium bicarbonate precipitation is not expected to occur under the AD operational conditions, although requires further investigation to determine if precipitation would occur in ADs with a high NH_3 concentration (e.g. treating food waste or manure) and enriched with CO_2 .

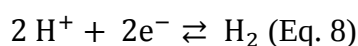
The study of the potential formation of ammonium precipitates is of particular interest when considering the fertiliser properties of NH_4HCO_3 (Zhuang et al., 2012), which could enhance the soil conditioning or fertiliser potential of AD digestate. Furthermore, the high concentrations of NH_3 resulting from hydrolysis of protein rich substrates, leads to toxicity for acetoclastic methanogenesis in ADs (Banks et al., 2011; Chen et al., 2008; Rajagopal et al., 2013). Therefore, processes with potential to reduce free NH_3 levels would be beneficial.

4.3 Other potential impacts of CO_2 injection in ADs

Aside from the reported increase in CH_4 production and uptake of CO_2 , which will benefit renewable energy production and carbon footprint, CO_2 could influence the AD process in other manners, as discussed below.

4.3.1 Increase in H_2 levels

Injection of CO_2 in ADs has the potential to alter H_2 concentration in several ways. On one hand, utilisation of additional CO_2 by hydrogenotrophic methanogens (Eq. 1) or homoacetogenesis (Eq. 3) would imply a consumption of H_2 . On the other hand, dissolution of CO_2 in aqueous media alters the carbonate equilibrium, increasing the concentration of HCO_3^- and releasing H^+ as per Eq. 5. Due to the low oxidation reduction potential (ORP) characteristic of ADs, typically - 200 mV to - 400 mV (Fetzer and Conrad, 1993; Gupta et al., 1994), the H^+ released can react with available electrons to form H_2 (Eq. 8). The overall impact in the AD H_2 concentration would be determined by the extent to which both individual processes take place.



The role of H_2 as an intermediate and electron carrier in several reactions of the AD process makes its concentration influence the relative abundance of other intermediate (e.g. VFAs) or end products (e.g. CH_4) (Cord-Ruwisch et al., 1997). When moderate, an increase in H_2 will be buffered by H_2 consuming metabolisms, i.e. hydrogenotrophic methanogenesis, homoacetogenic acetogenesis or sulphate reducing reactions. However, in cases where the H_2 assimilatory capacity of the system is saturated, several unfavourable effects for the digester operation have been reported, namely inhibition of fermentation reactions by obligate syntrophic bacteria and a shift in the regeneration pathway of the cofactor nicotinic adenine dinucleotide (NAD) (Collins and Paskins, 1987; Harper and Pohland, 1986). In the first case, propionic and butyric acid degradation reactions are thermodynamically favoured at H_2 partial pressures below 10^{-4} atm and 10^{-3} atm, respectively (Cord-Ruwisch et al., 1997; Harper and Pohland, 1986; Kidby and Nedwell, 1991). Higher H_2 concentrations will hence hinder degradation of higher VFAs into acetic acid, leading to an accumulation of the former and to a reduction of pH that can inhibit methanogenesis (Harper and Pohland, 1986). In the second case, a shift in the regeneration pathway of the reduced form of nicotinic adenine dinucleotide (NADH) will also contribute to an acidification of the digesting media. As part of the catabolic reactions taking place in AD (Fig. 6), NAD is reduced to NADH during the oxidative decarboxylation of pyruvic acid to acetyl CoA (Harper and Pohland, 1986). Re-oxidation of NADH for the process to continue is accomplished by the reduction of H^+ and release of H_2 gas (Collins and Paskins, 1987). An increase in the H_2 concentration of an AD hinders this regeneration pathway and necessitates different electron disposal mechanisms. Both the fermentation of acetyl-CoA to butyric acid (Harper and Pohland, 1986) and fermentation of pyruvic acid to propionate, lactate or butyrate as opposed to acetate (Collins and Paskins, 1987) have been reported as alternative NADH regeneration pathways at

elevated H₂ concentrations. The slower assimilation of these VFAs can lead to their accumulation and to a pH drop in the system.

Al-mashhadani et al., (2016) highlighted the need to understand the impact that CO₂ addition in ADs has in H₂ production, as both the mechanisms proposed for utilisation of exogenous CO₂ (hydrogenotrophic methanogenesis or homoacetogenesis via the Wood-Ljungdahl pathway) use H₂ as a co-substrate. Within previous references studying bioconversion of CO₂ in ADs (Table 3) only Bajón Fernández et al., (2015b) reported H₂ concentrations over long-term experiments. Periodic injections of CO₂ in food waste pilot scale ADs were reported to increase the H₂ concentration in the headspace by 2.5 fold when compared to control units (no CO₂ addition), leading to a baseline concentration of 320±153 ppm with peaks over 600 ppm. This H₂ formation was attributed to the dissolution of CO₂ in the aqueous media or to a boost of acetogenesis. In that study the H₂ concentration was reported to reach a new baseline with periodic CO₂ injections, rather than a continuously increasing trend, which was attributed an increased utilisation of H₂ via the Wood-Ljungdahl pathway.

4.3.2 Ammonia stripping

Several studies have investigated the possibility of controlling NH₃ inhibition in ADs treating substrates with a high protein content (e.g. food waste) by stripping it with biogas (Abouelenien et al., 2010; Guštin & Marinšek-Logar, 2011; Serna-Maza et al., 2014; Walker et al., 2011). Significant reductions in free NH₃ levels in the digesting material have been reported, particularly when digestate temperature is maintained over 70°C and lime or sodium hydroxide are dosed in order to maintain pH close to 10 (Guštin and Marinšek-Logar, 2011; Serna-Maza et al., 2014). The possibility of coupling NH₃ toxicity control with CO₂ bioconversion to CH₄ in ADs was introduced by Budzianowski, (2012).

Although findings reported for NH_3 stripping with biogas are likely to be transferable when utilising CO_2 concentrated streams (e.g. impact of temperature, pH and gas flowrate in removal performance), at the typical pH found in ADs (6.5 - 7.5) the ammonia-ammonium equilibrium is shifted toward ca. 100% ionized form (NH_4^+) making it unavailable for gas stripping. Besides, any pH drop associated with a dissolution of CO_2 would modify the equilibrium between total ammonia nitrogen (TAN) and free ammonia nitrogen (FAN) (Anthonisen et al., 1976), further displacing the equilibrium towards the ionized form and influencing the availability of free NH_3 for it to be degassed.

4.3.3 Alteration in alkalinity levels

Dissolution of CO_2 is not expected to alter total alkalinity since it releases the same amount of positive (H^+) and negative equivalents (CO_3^{2-} and HCO_3^-), as demonstrated mathematically by Pankow (1991). However, in presence of a high amount of inorganic cations or NH_3 , carbonated precipitates may be formed, leading to a modification of the alkalinity available in the liquid phase. This would be reflected in soluble alkalinity analysis when done in supernatant after centrifugation (majority of solids removed), but would not increase or reduce the total alkalinity available within an AD. In agreement with this, Francioso et al., (2010) reported that total alkalinity was not affected when injecting CO_2 into the first stage of a TPAD.

4.3.4 Increase in dissolved CO_2 levels

Injection of CO_2 in ADs may increase CO_2 dissolved levels in the final digestate if not fully utilised in the AD process. If this is the case, additional CO_2 could be released in later stages of the sludge treatment process, contributing towards uncontrolled GHG emissions. From previous studies assessing the potential benefits of bioconversion of CO_2 in anaerobic processes (Table 3) Alimahmoodi and Mulligan, (2008) reported dissolved CO_2 concentrations in the system effluent for various influent CO_2 levels. Dissolved CO_2

discharged with the effluent of the operated UASB reactor appeared fairly constant, with discharge rates of 0.3-0.7 g CO₂·d⁻¹ for influent dissolved CO₂ rates of 8.6-25.1 g CO₂·d⁻¹ for a system containing acetic acid as only VFA (Alimahmoodi and Mulligan, 2008). Effluent CO₂ was estimated by applying carbonate equilibrium reactions for a measured pH and alkalinity. Bajón Fernández et al., (2015b) reported similar dissolved CO₂ levels between a control AD and a test AD enriched with CO₂ three times a week.

Understanding the rate of utilisation of exogenous CO₂ within an AD process is needed to determine the frequency by which CO₂ could be injected into the system, which is required before a full-scale implementation can be considered. Bajón Fernández et al., (2014) and Al-mashhadani et al., (2016) reported the pH evolution in ADs treating sewage sludge and kitchen waste, respectively, stating that any initial acidification of the system related with CO₂ injection was overcome within 24-48 hours. Bajón Fernández et al., (2014) attributed this recovery in pH to dissolved CO₂ levels returning to those prior to the gas injection, which was supported by a later operation of a pilot scale chemostat by the same research group (Bajón Fernández et al., 2015b). In these three studies the pH drop observed following a CO₂ injection was between 0.1 and 0.6 units and did hence not hinder process performance.

It is to be remarked that the majority of previous studies (Table 3) fail to report enough detail with regards to the conditions at which CO₂ was injected. The potential contribution towards carbon footprint reduction of CO₂ bioconversion in ADs can only be quantified if the assimilation of exogenous CO₂ in the system is determined. This in turn requires a greater reporting of the conditions at which CO₂ is injected, the achieved dissolved CO₂ levels and the partial pressure of CO₂ in the gas injected.

4.4 Potential implications of a full-scale application

Implementation of CO₂ bioconversion in ADs at full-scale would lead to benefits on the renewable energy generation capacity of the process and on its carbon footprint, being the latter enhanced both due to the direct CO₂ uptake and to the offset of energy with fossil fuel origin. The discrepancy currently found in available literature (Table 3) prevents a clear quantification of the benefits attainable in full-scale systems. A study reporting a full mass balance of an AD with exogenous CO₂ injection and no H₂ addition is still lacking. Only a high level preliminary assessment of the additional benefits achievable can be completed based on available literature data. Uptakes of CO₂ between 3 and 98% have been reported (Table 3) with typically 40-50% when considering ADs operating continuously. If the solubility of CO₂ in the anaerobically digesting material is considered to be 1071 mg·L⁻¹, based on values for aqueous solutions at mesophilic conditions, an uptake of 40% of CO₂ in an influent saturated with a partial pressure of CO₂ of 1 atm would imply a normalised CO₂ assimilation of 0.43 kg CO₂ per tonne substrate treated. This figure could be significantly increased if CO₂ were to be dissolved periodically in the bulk of the AD unit (e.g. by a potential use of gas mixing systems). Previous studies provide an initial indication of the frequency by which CO₂ injection could be performed (Bajón Fernández et al., 2014; Bajón Fernández et al., 2015b; Sato and Ochi, 1994), based on that within 24- 48 hours an AD enriched with CO₂ could recover its previous state. However, the rate at which ADs can assimilate exogenous CO₂ has not been thoroughly investigated yet, which would determine the frequency of CO₂ injection in order to ensure that dissolved CO₂ levels in the effluent are not raised.

Further environmental benefits are envisaged when the increase in CH₄ production resulting from CO₂ bioconversion is considered. Previous literature presents a variable range of benefits (Table 3 and (Oh and Martin, 2016)), again evidencing the need of a full mass balance of the system studied to be presented. An increase in CH₄ yield of 30% when

considering continuously operated ADs has been reported (Table 3), which could raise CH₄ yield by 54 m³ per tonne of substrate treated when considering a base value of 180 m³·tonne⁻¹ (300 m³ biogas·tonne⁻¹ (Georges et al., 2009) with 60% CH₄ concentration). An offset of CO₂ emissions from prevention of energy usage with fossil fuel origin of 536 g CO₂·kWh⁻¹ (IEA, 2013a) can be considered. This would imply that an increase of 54 m³ CH₄·tonne⁻¹ offsets the emission of 101 kg CO₂ per tonne of substrate treated, when considering an energy yield from CH₄ of 10 kWh·m⁻³ and a CHP electrical efficiency of 35%. Additional incentives to study the potential of CO₂ bioconversion in ADs are present when considering the support of the UK government towards an increase of renewable energy production and the feed-in tariff schemes, which currently support renewable energy from ADs with a total capacity greater than 500 kW with 5.70 p·kWh⁻¹ (Ofgem, 2017).

5. Requirement for further work

The potential of CO₂ bioconversion in ADs to act as an on-site carbon management strategy while enhancing renewable energy production has been experimentally evidenced (Table 3). However, several aspects need to be addressed in order to increase readiness for implementation. Examination of the literature presents conflicting information regarding the mechanisms of utilisation of additional CO₂, being proposed both an enhancement of the hydrogenotrophic (Alimahmoodi and Mulligan, 2008) and acetoclastic (Bajón Fernández et al., 2014; Francioso et al., 2010) routes of CH₄ formation. The higher increase in CH₄ formation reported by Bajón Fernández et al., (2014) in sewage sludge ADs than in food waste units, supports a boost of acetoclastic methanogenesis since NH₃ concentration in food waste ADs reached toxicity levels for obligate acetoclastic methanogens. The benefits reported by Salomoni et al., (2011) in a TPAD system were attributed to a utilisation of CO₂ via the Wood-Ljungdhal pathway, as a good phase separation was observed and hence no hydrogenotrophic methanogenesis in the first stage AD (point of CO₂ injection) was

expected. Besides, Mohd Yasin et al., (2015) observed an initial increase in acetate formation in methanogens enriched from WAS and enriched with CO₂. These literature evidences support reduction of CO₂ via homoacetogenesis, an increase of acetate formation and an encouragement of acetoclastic methanogenesis. However, further validation of mechanisms proposed is required (e.g. microbial community analysis, carbon isotopes) and investigation of the pathways by which the additional H₂ required for homoacetogenesis is sourced. Furthermore, part of the CO₂ has the potential to remain in unstable forms that can be released in the later treatment of digestates. Investigation of the potential of additional CO₂ to form carbonated precipitates and to increase CO₂ dissolved levels in the final digestates is essential to confidently determine benefits in carbon footprint reduction. A more consistent reporting in literature of the conditions of CO₂ injection (gas to liquid contact system, CO₂ partial pressure, dissolved CO₂ levels...) is also required to make studies comparable and quantify benefits in carbon footprint.

Byrns et al., (2013) identified the need for the benefits of CO₂ bioconversion in ADs to be demonstrated in full-scale trials. While the proof of concept has been developed at laboratory or pilot scale by injecting CO₂ through internal tubing (Salomoni et al., 2011), gas mixing lines (Sato and Ochi, 1994), diffusers (Bajón Fernández et al., 2014) or bubble columns (Bajón Fernández et al., 2015b), there is no study addressing the practicalities of an up-scaled implementation. The possibility of utilising already existing gas mixing systems of ADs to inject additional CO₂ would ease full scale implementation and enable retrofitting CO₂ enrichment of ADs without incurring in additional pumping costs. However, the risk of diluting the AD's headspace with undissolved CO₂ needs to be considered, since variations in biogas quality would lead to a detriment in the performance of CHP engines. In particular, the need for contacting CO₂ with digestate or substrate material while achieving a significant CO₂ gas to liquid mass transfer needs to be addressed in order to replicate at full-scale the

benefits evidenced with laboratory or pilot ADs. It is postulated that CO₂ would be preferably utilised in dissolved form, which requires a better understanding of CO₂ gas to liquid mass transfer in fluids of complex rheology like anaerobically digested substrates (Bajón Fernández et al., 2015a).

6. Concluding remarks

Bioconversion of CO₂ in ADs (without addition of external H₂) has the potential to reduce the carbon footprint of the water and organic waste sectors, with a concomitant increase in renewable energy generation and hence a contribution towards energy supply decarbonisation. However, in order for bioconversion of CO₂ in ADs to become a full-scale solution, the mechanisms of CO₂ utilisation and the technologies for contacting CO₂ (g) and digesting fluids with an efficient mass transfer need to be further investigated. Besides, a more thorough reporting of the CO₂ injection conditions (including partial pressure of CO₂) is required to confidently quantify benefits in carbon footprint.

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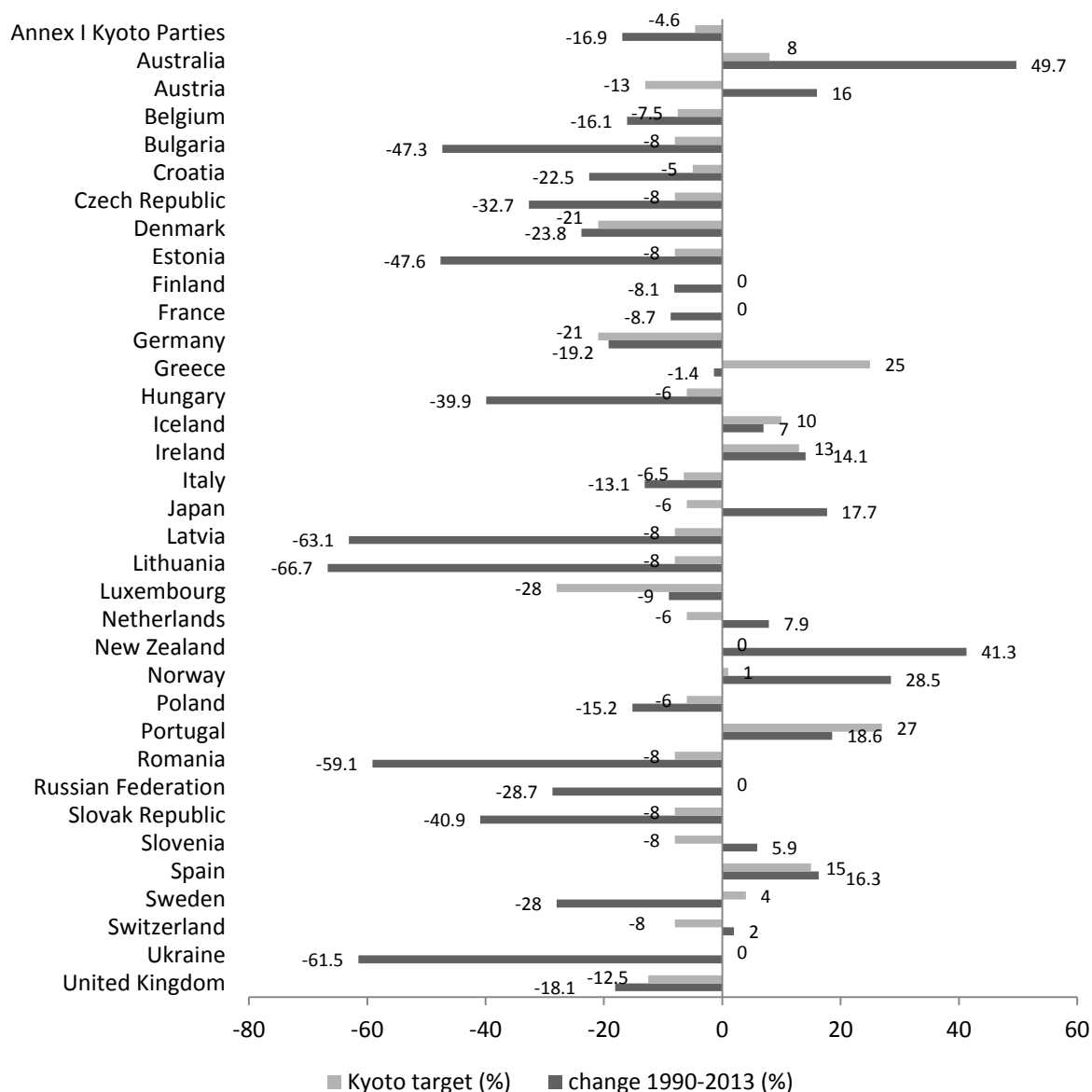
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Note: Annex I Kyoto Parties includes Australia, Austria, Belarus, Belgium, Bulgaria, Canada, Croatia, Cyprus, the Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Japan, Latvia, Liechtenstein, Lithuania, Luxembourg, Malta, Monaco, the Netherlands, New Zealand, Norway, Poland, Portugal, Romania, Russian Federation, the Slovak Republic, Slovenia, Spain, Sweden, Switzerland, Turkey, Ukraine, the United Kingdom and the United States (IEA, 2015).

Fig. 1. Kyoto GHG reduction targets for the 2008-2012 commitment period and percentage change in CO₂ emissions from fuel combustion between 1990 and 2013.

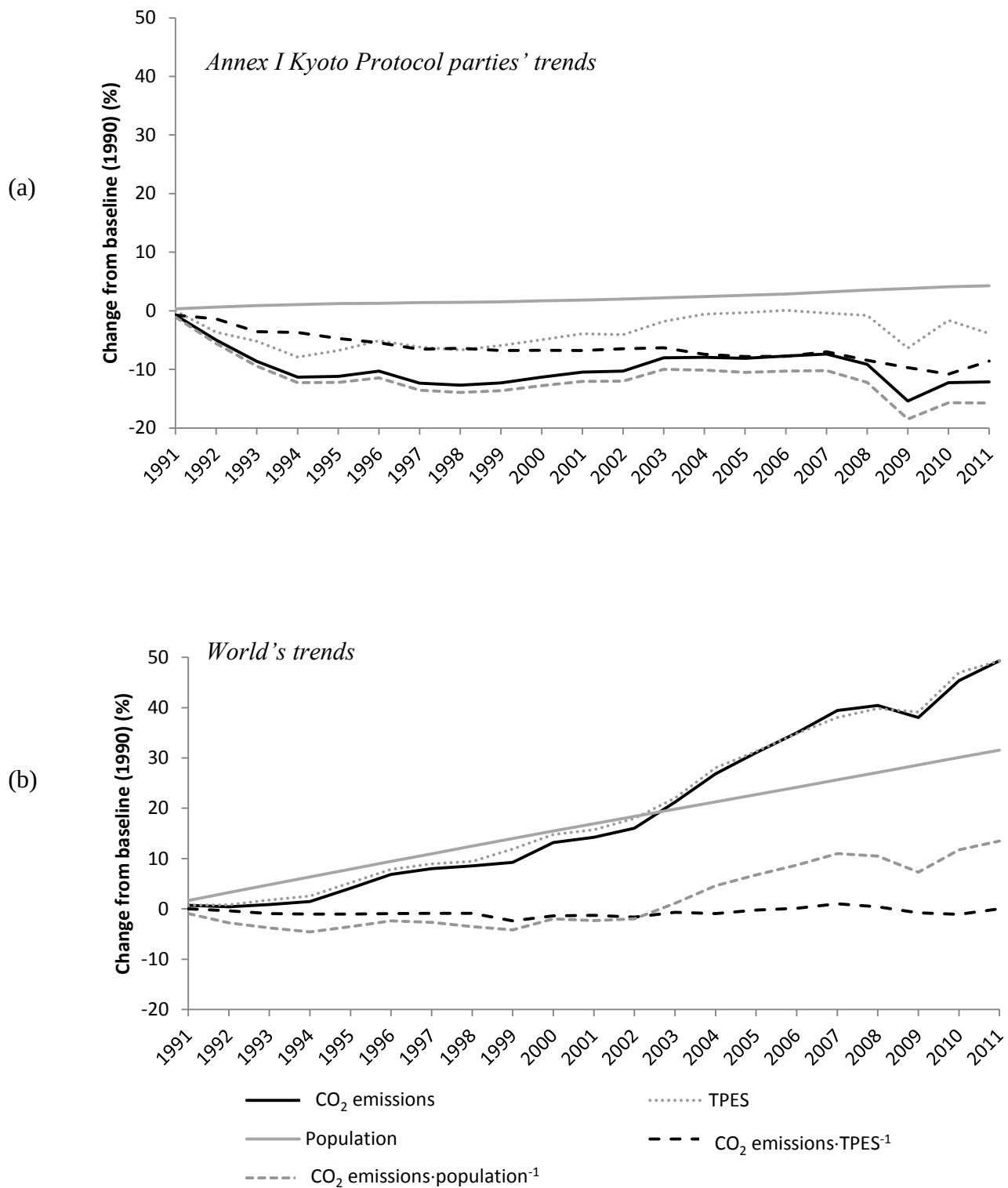


Fig. 2. (a) Annex I Kyoto Protocol parties' and (b) world's trends in CO₂ emissions from fuel combustion, energy demand and population growth for the period 1990 to 2011. TPES: total primary energy supply. Source: (IEA, 2013a).

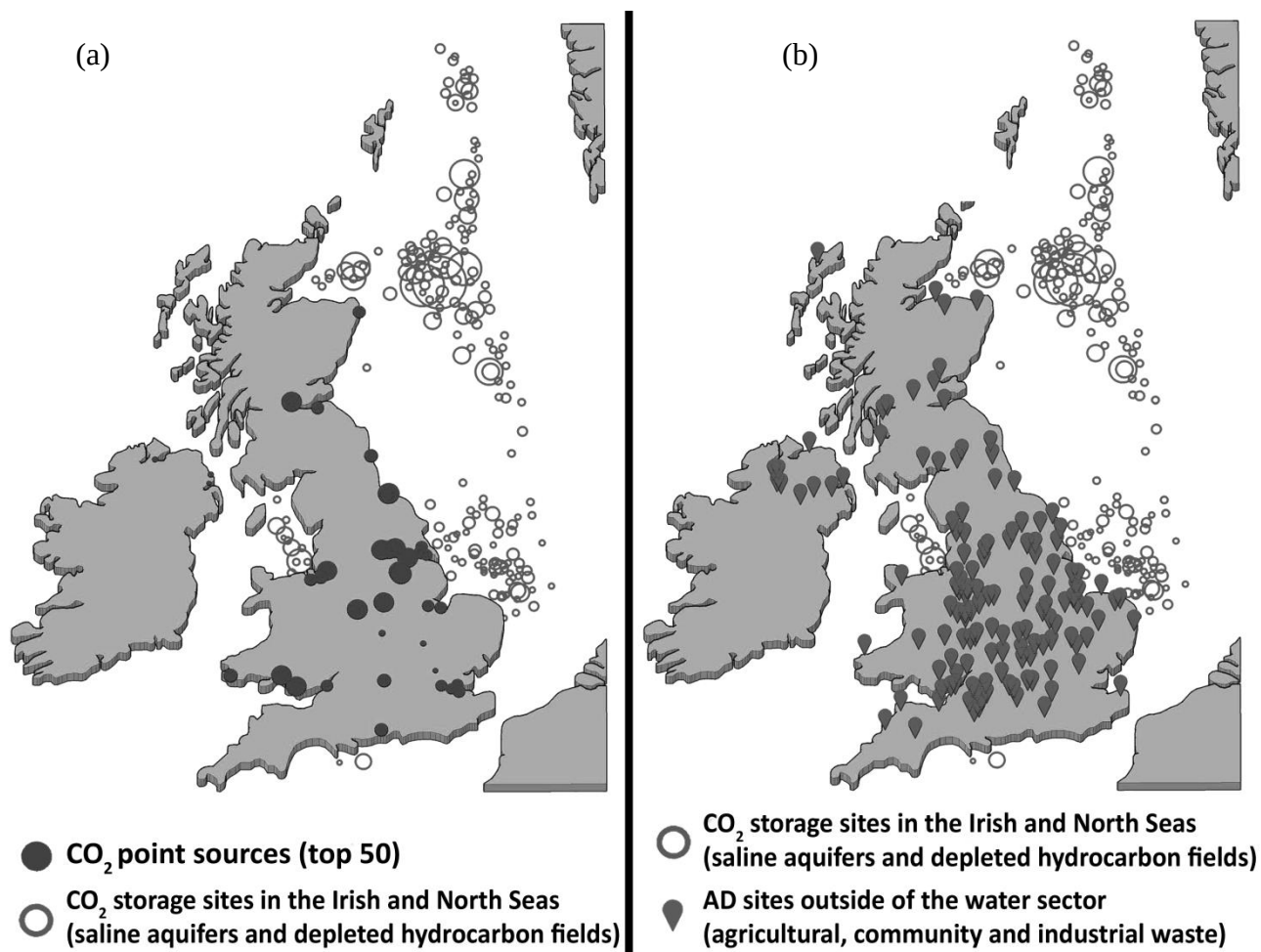


Fig. 3. (a) Main CO₂ emitters (power and industrial plants) in the UK and location of potential CO₂ storage sites, adapted from DECC (2012a). (b) AD sites in UK outside of the water sector and location of potential CO₂ storage sites. Adapted from NNFCC (2016a) and DECC (2012).

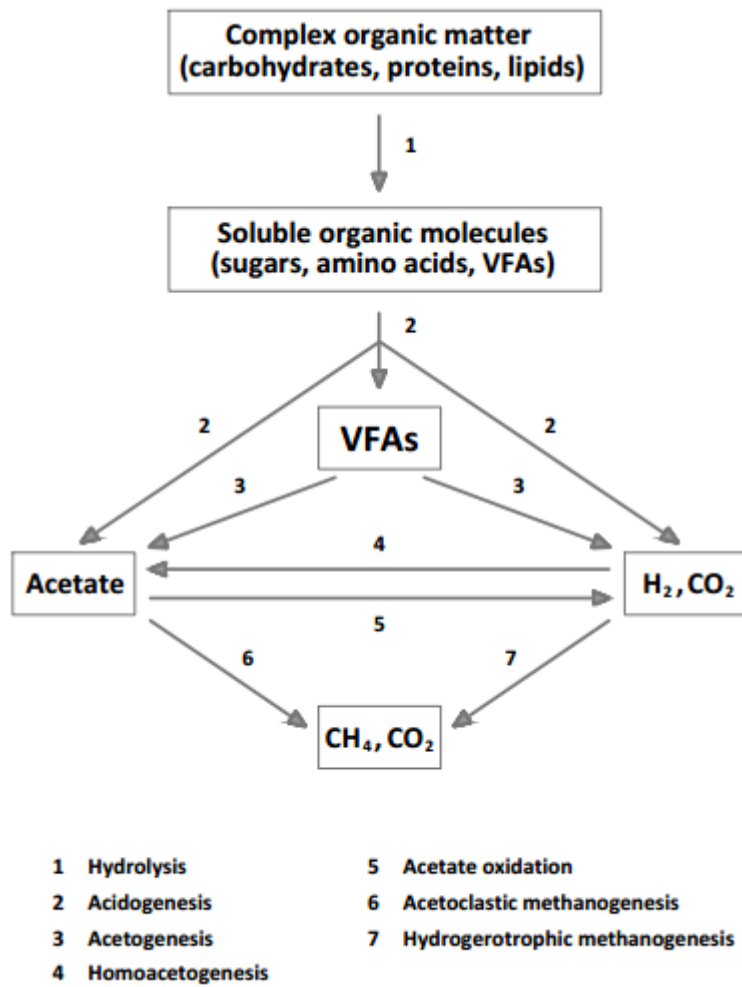


Fig. 4. Schema of stages of the anaerobic digestion process.

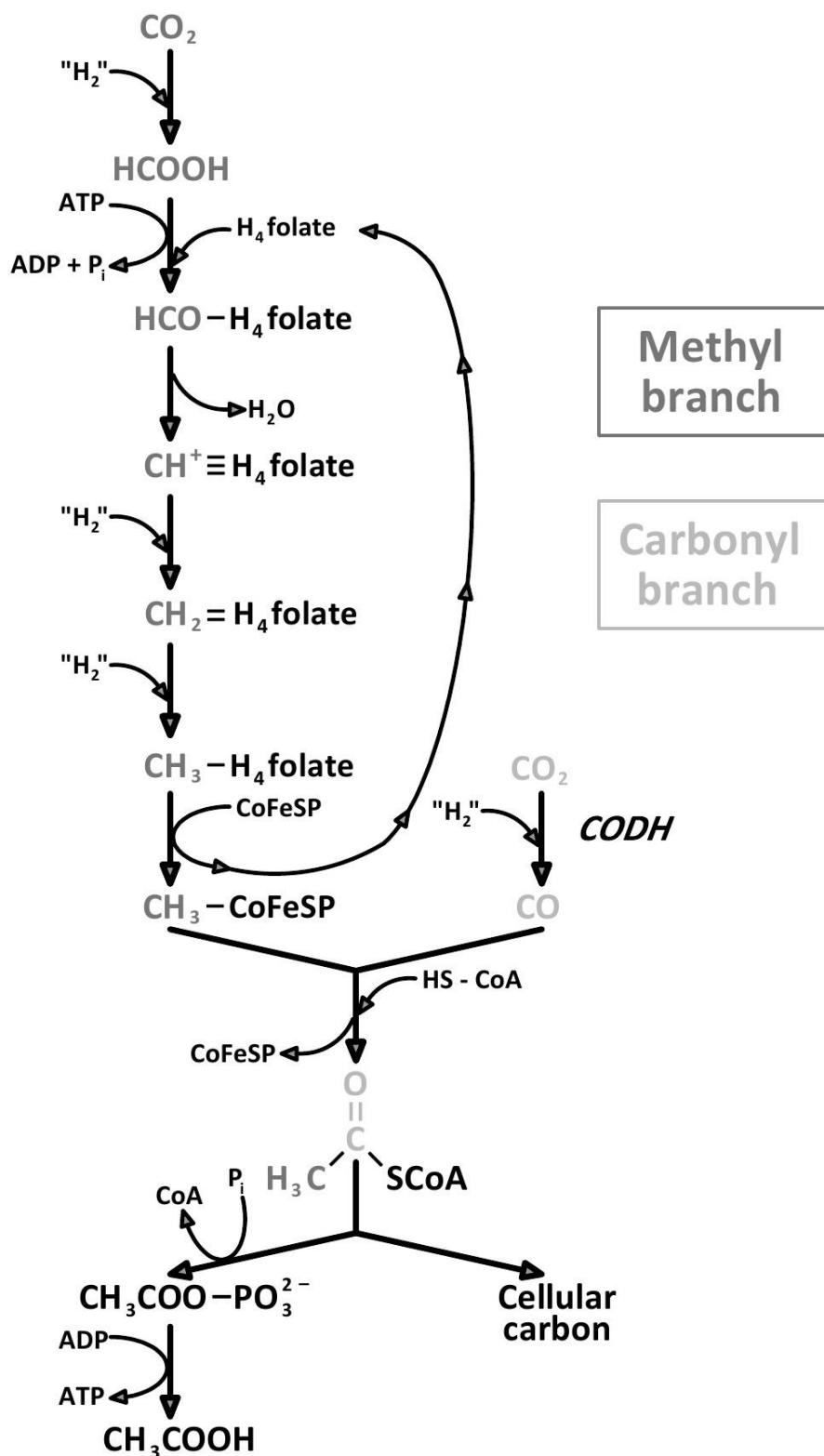


Fig. 5. Wood-Ljungdahl pathway for homoacetogenic acetogenesis. “H₂” is used to represent requirement of two electrons and two protons. Adapted from Ragsdale and Pierce, (2008).

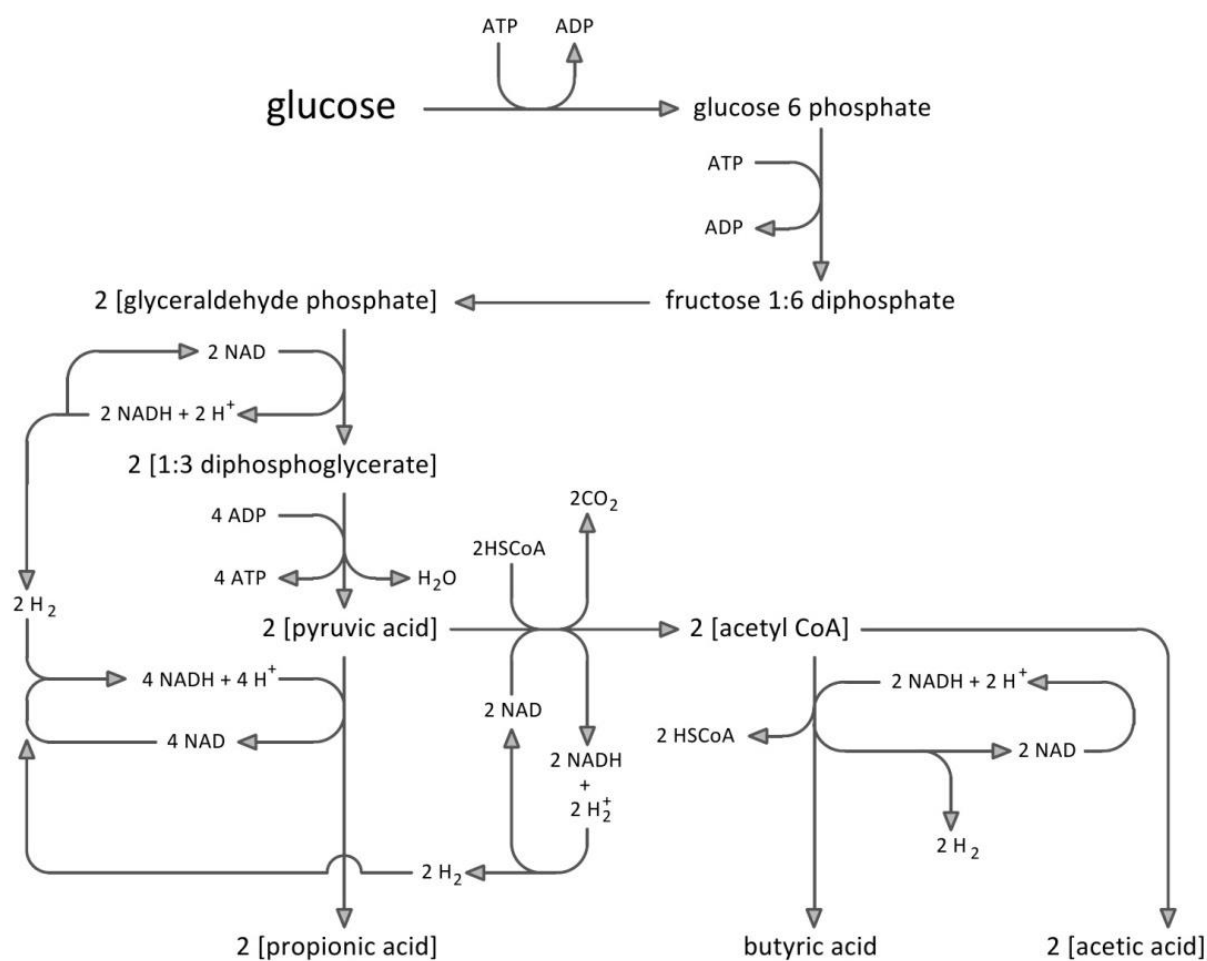


Fig. 6. Hydrogen-regulated catabolic pathways in anaerobic processes, exemplified for glucose.

Adapted from Harper and Pohland, (1986).

Table 1. Estimated biogenic CO₂ emissions in UK from wastewater treatment. Source: Byrns et al., (2013).

	CO ₂ production (MtCO ₂ ·annum ⁻¹)	CO ₂ concentration (%v/v)	confined stream
Aerobic treatment	1-1.1	0.8	No
Biogas of anaerobic digestion	0.27	35	Yes
Combustion of biogas (CHP or flares)	0.5	8-15	Yes
Incineration of sludge	0.26	^(a)	Yes

^(a) Dependant of amount of air used for incineration.

Table 2. Number of AD sites outside of the water sector currently in UK classified per electrical production capacity and associated CO₂ emissions contained in the biogas produced. Industrial ADs have not been considered. Capacity data (kWe) extracted from NNFCC (2016b).

Electrical capacity range (kWe)	Agricultural waste			Community waste		
	Number of sites ^(a)	Combined capacity (kWe)	CO ₂ produced with biogas (tonnes CO ₂ ·year ⁻¹)	Number of sites ^(b)	Combined capacity (kWe)	CO ₂ produced with biogas (tonnes CO ₂ ·year ⁻¹)
kWe ≤ 250	73	12,515	32,316	14	1,987	5,131
250 < kWe ≤ 500	91	44,290	114,366	25	12,298	31,756
500 < kWe ≤ 1000	12	10,290	26,571	13	12,400	32,020
1000 < kWe ≤ 2000	19	27,611	71,298	28	46,282	119,510
2000 < kWe ≤ 3000	5	12,922	33,367	11	28,200	72,819
kWe > 3000	4	15,150	39,121	15	65,250	168,490

^(a) Four AD sites registered as operational but without reported electricity production capacity has not been accounted for.

^(b) Two AD sites registered as operational but without reported electricity production capacity have not been accounted for.

Table 3. References addressing CO₂ bioconversion in anaerobic systems without addition of H₂.

Substrate treated	Anaerobic system used	Scale of the reactor	Operational conditions	CO ₂ injection	y _{CO₂} ^(c)	Increase in CH ₄ yield or production rate	Increase in CH ₄ content of the biogas	CO ₂ uptake	Mechanism of CO ₂ utilisation suggested	Ref.
Waste activated sludge	Single phase AD	6 L	T = 35°C; HRT ^(b) = 10.8 d; semicontinuous operation of the ADs	Daily CO ₂ enrichment with gas mixing line		30% increased specific CH ₄ yield (m ³ CH ₄ · kg VS ⁻¹) with CO ₂ concentrations of 60% v/v	-	-	-	(Sato and Ochi, 1994)
Synthetic solutions	UASB reactor	1 L working volume	T = 35°C	Dissolved in the influent to unit, which was treated with KOH to maximise the dissolution	1	CH ₄ rate increased from ca. 3.5 gCOD·d ⁻¹ to ca. 7 gCOD·d ⁻¹ for a system with acetic acid as solely VFA	-	69-86%	Hydrogenotrophic methanogenesis	(Alimahmoodi and Mulligan, 2008)
Stabilised sludge	TPAD	Ten units of 1.8 L working volume per phase	T = 25°C in first phase and T = 42°C in second phase; HRT for each phase = 6 days	Continuous injection of 1.5 L CO ₂ ·d ⁻¹		-	-	Up to 40% of input	Transformation of CO ₂ into short-chain VFAs by Wood-Ljungdahl pathway	(Francioso et al., 2010)
Synthetic solution, simulating stream from EOR ^(a) process	Two-phase reactor	2 L	T = 35°C, pH of 2.5-4.5	CO ₂ was present in the initial waste stream, without additional CO ₂ being injected		-	-	Up to 98% CO ₂ removal	Hydrogenotrophic methanogenesis	(Alimahmoodi and Mulligan, 2011)

Mixed primary and secondary sludge	TPAD	580 and 630 L working volume for first and second phase, respectively	T = 25°C in first phase and T = 42°C in second phase; HRT first stage = 8.3 d and HRT second stage = 9.0 d	Continuous CO ₂ injection in bottom of the first phase via internal tubing; CO ₂ load = 0.49 m ³ ·d ⁻¹ (0.035 m ³ CO ₂ ·h ⁻¹ ·m ⁻³ working volume)	1	25% increased specific CH ₄ yield (0.279 to 0.35 m ³ CH ₄ ·kg VSS ⁻¹)	64% average CH ₄ content vs 60% of the control	46% of the input (229 L·d ⁻¹)	Transformation of CO ₂ into short-chain VFAs by Wood-Ljungdahl pathway	(Salomoni et al., 2011)
Food waste or sewage sludge	Single phase AD	0.7 L working volume	T = 38°C, batch mode	Saturation at start of batch process via Pyrex diffusers	0.3, 0.6, 0.9	- Food waste ADs: Up to 13% increased CH ₄ yield - Sewage sludge: 2.0-2.4 fold increase in CH ₄ production during 24 hours following CO ₂ injection	Concentration not altered	- Food waste: 3-11% - Sewage sludge: 8-34%	Transformation of CO ₂ into short-chain VFAs by Wood-Ljungdahl pathway followed by acetoclastic methanogenesis	(Bajón Fernández et al., 2014)
Food waste	Single phase AD	106 l working volume	T=38.5°C, semicontinuous mode	CO ₂ injection three times a week with a bubble column installed in digestate recirculation loop	1	20% increased CH ₄ production rate (m ³ CH ₄ ·(kg VS _{fed} ·d) ⁻¹)	Concentration not altered	0.55 kg CO ₂ over trial period (77 d)	Transformation of CO ₂ into short-chain VFAs by Wood-Ljungdahl pathway followed by acetoclastic methanogenesis	(Bajón Fernández et al., 2015)
Digested sewage sludge	Single phase AD (only inoculum)	0.4 L working volume	T= 40°C	Flushing gas on commencement of batch tests	0.2	20% higher specific CH ₄ yield	-	-	-	(Koch et al., 2015)
WAS enriched for methanogens	Single phase AD	0.03 L working volume	T= 37°C	CO ₂ injection for 5 min.	1	0.128 m ³ CH ₄ ·kg VS ⁻¹)	-	-	Transformation of CO ₂ into short-chain VFAs by Wood-Ljungdahl pathway followed by acetoclastic methanogenesis	(Mohd Yasin et al., 2015)
Digested sewage sludge	Single phase AD (only inoculum)	0.4 L working volume	T= 38°C	Flushing gas on commencement of batch tests	1	30% increased specific CH ₄ yield	-	-	-	(Koch et al., 2016)
Kitchen waste	Single phase AD	-	T= 35°C	CO ₂ injection 5 min a day through microporous ceramic diffuser (20 µm size pores)	1	109% increased specific CH ₄ yield	-	-	Hydrogenotrophic methanogenesis or transformation of CO ₂ into short-chain VFAs by Wood-Ljungdahl pathway, with	(Al-mashhadani et al., 2016)

additional H₂ being generated
from a faster hydrolysis of
the sugary components in
the feedstock

^(a) Enhanced oil recovery.

^(b) Hydraulic retention time.

^(c) CO₂ molar fraction.



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Bioconversion of carbon dioxide in anaerobic digesters for on-site carbon capture and biogas enhancement - A review

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