Bioresource Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

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

Review

An overview of microbial biogas enrichment

Nabin Aryal[a,b], Torben Kvist[b], Fariza Ammam[c], Deepak Pant[d], Lars D.M. Ottosen[a,*]

[a] Biological and Chemical Engineering, Aarhus University, Hangovej 2, DK-8200 Aarhus N, Denmark
[b] Danish Gas Technology Centre, Dr. Neergaards Vej 5B, DK-2970 Horsholm, Denmark
[c] Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, United Kingdom
[d] Separation and Conversion Technology, Flemish Institute for Technological Research (VITO), Boeretang 200, Mol 2400, Belgium

ARTICLE INFO

Keywords:
Methane enrichment
Biogas upgrading
Methanation
Hydrogenation
In-situ
Ex-situ and Bioelectrochemical System

ABSTRACT

Biogas upgrading technologies have received widespread attention recently and are researched extensively. Microbial biogas upgrading (biomethanation) relies on the microbial performance in enriched H_2 and CO_2 environments. In this review, recent developments and applications of CH_4 enrichment in microbial methanation processes are systematically reviewed. During biological methanation, either H_2 can be injected directly inside the anaerobic digester to enrich CH_4 by a consortium of mixed microbial species or H_2 can be injected into a separate bioreactor, where CO_2 contained in biogas is coupled with H_2 and converted to CH_4, or a combination hereof. The available microbial technologies based on hydrogen-mediated CH_4 enrichment, in particular *ex-situ*, *in-situ* and bioelectrochemical, are compared and discussed. Moreover, gas-liquid mass transfer limitations, and dynamics of bacteria-archaea interactions shift after H_2 injection are thoroughly discussed. Finally, the summary of existing demonstration, pilot plants and commercial CH_4 enrichment plants based on microbial biomethanation are critically reviewed.

1. Introduction

Methanation is the production of methane (CH_4) by thermo-chemical, catalytic and/or biological processes. The catalytic process, referred to as Sabatier process, is already in commercial use and usually performed by reacting hydrogen (H_2) with either carbon monoxide (CO) or carbon dioxide (CO_2) applying predominately nickel catalysis at higher temperatures 500–600 °C (Muñoz et al., 2015). Biogas is a CH_4-rich mixture of gas produced anaerobically by breaking down organic matters, such as energy crops, plant biomass, animal manure, agricultural residues, waste water treatment sludge and other sources of organic waste, in a biological process called anaerobic digestion (AD). The process is mediated by both mesophilic and thermophilic methanogenic microorganisms. AD is a well-established and mature technology. There are several limitations like high operating cost, expensive feedstocks and especially upgrading expenses. AD usually requires significant financial incentives and subsidies to compete with traditional fossil fuel-based energy technologies (Benjaminsson et al., 2013). Nevertheless, it is a key energy source in the emerging market for global renewable energy resources, and considered a key enabling technology for the transition to fossil fuel independency. It is estimated that global commercial biogas facilities and its role as an alternative energy carrier will become progressively important. Currently biogas production in Europe asserts to about 14 billion m^3 in natural gas equivalent and is expected to increase up to 28 billion m^3 in natural gas equivalent (European Biogas Association, 2013).

Typically, biogas contains a mixture of 40–60% CH_4 and 60–40% CO_2, traces of hydrogen sulfide (H_2S), ammonia (NH_3), H_2, oxygen (O_2), nitrogen (N_2) carbon monoxide (CO), hydrocarbons, volatile organic compounds (VOC) and siloxanes (Börjesson and Mattiasson, 2008). In anaerobic organic carbon degradation processes, biogas is generated in a complex process which involves four phases: (i) hydrolysis, (ii) acidogenesis, (iii) acetogenesis/dehydrogenation, and (iv) methanogenesis, all accomplished by syntrophic interaction of different archaeal-bacterial consortia as shown in Fig. 1. Additionally, in acidogenesis, some facultative anaerobes, for example *Ruminococcus, Paenibacillus, Streptococci* etc. convert soluble monomers to various gaseous and soluble metabolic products, for example VFAs, alcohols, CO_2, and H_2 (Ziganshin et al., 2013). Likewise, in acidogenesis, some facultative anaerobes for example *Clostridium, Ruminococcus, Paenibacillus, Streptococci* etc. convert soluble monomers to various gaseous and soluble metabolic products, *viz* alcohol, VFA, CO_2, and H_2. Subsequently, in acidogenesis, microbes like *Aminobacterium, Acidaminococcus*, *Desulfovibrio* etc. convert monomers into acetic acid and H_2. Finally, in the methanogenesis step, CH_4 is produced from both hydrogenotrophic methanogenic archaea utilizing H_2 and CO_2 or by aceticlastic

* Corresponding author.
E-mail address: ldmo@eng.au.dk (L.D.M. Ottosen).

https://doi.org/10.1016/j.biortech.2018.06.013
Received 7 April 2018; Received in revised form 5 June 2018; Accepted 6 June 2018

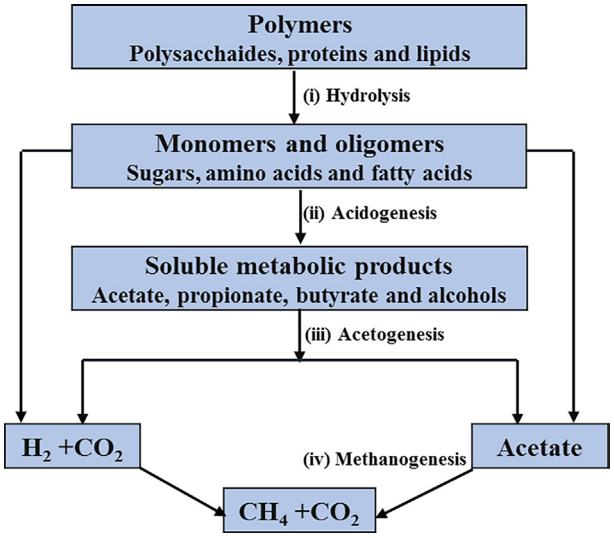

Fig. 1. The conventional approach of anaerobic degradation of organic matter to produce CH_4.

methanogenic archaea via consumption of acetic acid (Angelidaki et al., 1993).

Methanogenesis can be driven by three major pathways: (i) the CO_2 reduction (Wood Ljungdahl) pathway, (ii) the acetotrophic (aceticlastic) pathway and (iii) the methylotrophic pathway. These pathways are differentiated by the nature of the substrate and the energy source used for CH_4 production (Garcia et al., 2000; Liu and Whitman, 2008). The Wood Ljungdahl (WLP) also named hydrogenotrophic pathway is the most widespread and metabolically efficient pathway so far reported for energy generation and carbon fixation (Lever, 2016; Sousa et al., 2013). Although it is present in both archaea and bacteria, some metabolic differences were found in the methyl branch of the WLP in the archaeal phylum including enzymes and cofactors involved in the reduction of CO_2 to CH_4 (Borrel et al., 2016). Furthermore, the WLP in archaea can be involved in the reverse oxidation of organic compounds to regenerate reducing equivalents. For instance, *Thermacetogenium phaeum*, a syntrophically acetate oxidizing bacterium, was describe to use at least part of the WLP enzymes including CODH and tetrafolate-linked redox enzymes to oxidize acetate (Hattori et al., 2005). In the acetotrophic pathway, acetate is split into a methyl group and CO. The former one is used for CH_4 production while CO is oxidized to generate the required reducing power. The methylotrophic pathway involves C-1 compounds such as methyl-amines and/or methanol which could be used both as carbon and energy source. One molecule of C-1 compound is oxidized to generate electrons for the generation of three molecules of CH_4 (Costa and Leigh, 2014). The AD should have a balanced process in all four stages; otherwise it could lead to failure of methanation. For example, rapid acidogenesis stages might cause high acidity due to high accumulation of VFA, thus resulting in the inhibition of methanogenic microorganism due to reduced pH at high VFA concentration. Simultaneously, a rapid methanogenic process could be limited in the hydrolysis stage. (Luo and Angelidaki, 2013a).

Some impurities present in the biogas may have significant adverse impact on its utilization, e.g. making the gas corrosive and induce salt accumulation on process equipment, and increase emissions and hazards for human health (Song et al., 2017). Moreover, contaminants reduce the density, calorific value and wobbe index (WI) of biogas (Jin et al., 2017). Removing these contaminants is necessary in order to increase specific heat, minimize corrosion, and to assure quality required for injection in gas grid network systems. Currently, various biogas upgrading (understood as technologies to remove unwanted molecules from the gas) methods are commercialized, in particular water scrubbing, chemical adsorption, pressure swing absorption, membrane separation and cryogenic separation (Kadam and Panwar, 2017). Among these technologies, water scrubbing is the predominately applied technique accounting for almost 40% of the total upgrading plants (Angelidaki et al., 2018). In a water scrubber, CO_2 is absorbed in water leaving behind enriched CH_4, and the absorbed CO_2 is released back to the atmosphere. Nonetheless, similar to other upgrading technologies, water scrubbing is energy intensive and corrosive to equipment, thus adding extra operating costs to methanation processes. Another important drawback of conventional methods to upgrade biogas is the loss of CO_2 from the gas. Biogas constitutes an excellent source of quite concentrated CO_2 in a completely reduced atmosphere (no oxygen at all) and is therefore very well suited as a carbon source for CO_2 utilization, which will be a quite unique source in future energy systems without fossil fuels. Hence, biological methanation is an attractive alternative for biogas upgrading since as a biological method it is eco-friendly, cost-effective, low energy demanding (Luo and Angelidaki, 2013b; Roy et al., 2015), and makes use of a valuable CO_2 source instead of wasting it immediately. Furthermore, impurities, like H_2S, NH_3, H_2 and CO, may also be utilized by bacteria to upgrade biogas into CH_4 (Zeppilli et al., 2017).

Recently, an increasing number of academic research efforts have been dedicated towards the microbial CH_4 enrichment. In this review, a summary of microbial biogas enrichment is provided. Firstly, H_2 mediated biogas enrichment, in particular *in-situ* and *ex-situ* techniques are reviewed, followed by a brief summary of bioelectrochemical CH_4 enrichment processes from biogas. Finally, large-scale commercial biogas plants based on microbial technique and future research perspectives for advancing microbial enrichment approaches for biogas upgrading are discussed.

2. Biogas enrichment in anaerobic digestion

Biological CH_4 enrichment is an emerging concept for high volumetric CH_4 production combined with a conventional biogas plant. The enrichment process is carried out either with *in-situ* injection of H_2 inside the anaerobic digester or with H_2 injection in a separate reactor called *ex-situ*, where biogas is upgraded. H_2 might be produced on site by electrolysis, using renewable electricity from wind turbines or photovoltaic as power. Several European countries along with Denmark have periodically surplus of electricity produced from wind turbines. Storing excess of electricity in H_2 and use it to directly upgrade biogas constitutes an attractive approach for these countries (Sharman, 2005; Sovacool, 2013). Mixed microbial consortia, widely known as hydrogenotrophic methanogenic archaea, produces CH_4 utilizing CO_2 as a carbon source and externally supplied H_2 as an electron source (Muñoz et al., 2015). Additionally, H_2 mediated methanation would consume CO_2 from biogas plant and, therefore, improve energy density for further utilization, such as transport sector and gas grid injection. Importantly, non-converted 5–30% H_2 by volume with CH_4, would improve combustion properties of biogas as fuel without adverse impact on engines and other appliances (Akansu et al., 2004), but could on the other hand constitute a problem in relation to grid quality compliancy.

Fig. 2 *Ex-situ* and *In-situ* approach for biogas enrichment.

2.1. In-situ enrichment

In-situ biogas upgrading allows efficient use of AD avoiding extra infrastructure for post gas treatment. Nevertheless, direct H_2 injection may affect the performance of methanogens due to increasing H_2 partial pressure, which may result in inhibition of VFAs (propionate and butyrate) degradation (Agneessens et al., 2017; Fukuzaki et al., 1990). A recent study however showed that added H_2 only penetrates less than 1 mm from saturation into an active methanogenic substrate indicating that only a very small fraction of fermenting microorganisms will actually uptake H_2, even in the event of massive *in situ* H_2 addition inside the reactor (Garcia-Robledo et al., 2016). It appears that the