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Biocatalytic methanation of hydrogen and carbon dioxide in a fixed bed bioreactor

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HIGHLIGHTS

- Biological conversion of CO_2 and H_2 into CH_4 was studied in a fixed bed reactor.
- Two solid state bioreactors in series connected to a recirculation system.
- A maximal methane productivity of 6.35 $l/l_{reactor}$ d was achieved.
- Effective methane production can be obtained with relatively simple reactor structure.
- The used nutrient source was simple, and no precise basal medium was needed.

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ABSTRACT

Biocatalytic methanation of H_2 and CO_2 was studied in a fixed bed reactor system consisting of two solid state bioreactors in series connected to a recirculation system. Bioreactors were packed with a mixture of vermiculite shales and granular perlite material as a support material. A maximal methane productivity of 6.35 $l/l_{reactor}$ d was achieved at a hydrogen feed rate of 25.2 $l/l_{reactor}$ d, while hydrogen conversion rate was 100%. However, stable operation of the reactor at this efficiency remains to be achieved. Very simple reactor design, constructed from low cost materials, and the idea of exploiting waste material as a robust source of nutrients for methanogens makes this study very interesting regarding the overall usability and suitability of the system as part of a decentralized energy system.

1. Introduction

The greenhouse effect, climate change, awareness of the continuing depletion of fossil fuel reserves, increasing energy demands and the environmental impacts of current energy sources have together stimulated the search for sustainable, alternative energy sources and innovative fuel technologies (IPCC, 2011; Naik et al., 2010; Omer, 2008). In order to meet forecasted energy demands and reduce environmental impacts, a readily available, carbon neutral or carbon free energy source is needed. Although renewable energy has taken great leaps forward, many alternative energy solutions are still plagued by low efficiencies, high costs, or technological and especially market barriers (Delucchi and Jacobson, 2010; Ellabban et al., 2014; REN21 Secretariat, 2014; Sovacool, 2009). Another major problem concerns renewable energy storage. Wind and solar energy are currently prohibitively expensive to store. Renewable energy is not a viable option unless energy can be stored on a large scale (Lindley, 2010). The other renewable electricity source is hydro power. The Nordic (Finland, Sweden and Norway) power system is dominated by hydro power. There is a high correlation between precipitation levels and the cost of electricity on the Nordic power market (NordREG, 2013). Heavy rains lower the electricity prices, while the filled reservoirs provide only a limited buffer mechanism to regulate hydro power production. Climate change and extreme weather events will probably affect the long-term planning of hydro power, which makes hydro power utilization more difficult in the future (Nordic Council of Ministers, 2012). The common feature for all of these renewable electricity sources is that the power plants are located away from large consumer groups, demanding transmission network capacities.

'Synthetic', microbially produced methane obtained via the methanation of hydrogen produced by electrolysis using

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renewable electricity is one option to mitigate climate change. Methanation is particularly advantageous in that the reaction occurs with the aid of CO_2, which is consequently not discharged into the atmosphere during the production cycle, but converted into methane. This results in a completely closed, CO_2 cycle. The production of methane (CH_4) by methanogenic archaea is a well-known natural process, called biological methanogenesis.

Carbon dioxide (CO_2) and hydrogen (H_2) are converted into methane (CH_4) and water by the Sabatier reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \quad \Delta H = -165.0\ \text{kJ/mol}$$

This reaction chain can be catalyzed biologically at lower temperatures by hydrogenotrophic methanogens (Liu and Whitman, 2008; Thauer et al., 2008) or inorganically at elevated temperatures and pressures in the presence of nickel catalyst. Hydrogen is produced by splitting water into oxygen and hydrogen via electrolysis.

A variety of several different methodologies of biological conversion of CO_2 to CH_4 have been presented over the years (Rittmann et al., 2013). Commonly this conversion has been achieved using fermentation processes carried out either in liquid medium or on moist solid particles in a number of different types of reactor designs (Rittmann et al., 2013). Due to the low solubility of supply gases (in particular H_2), an efficient supply of gases to the microorganisms is a decisive factor in a process using gaseous substrates. Mechanical agitation or stirring is the most common way of enhancing the transfer of gases and other substances in the bioreactor. However, agitation consumes high amounts of energy and leads to high operation costs.

Burkhardt et al. (2015) used a trickle bed reactor in order to improve material transfer in the biofilm. In this reactor type, microorganisms are immobilized on the surface of a packed bed inside a reactor chamber not filled with liquid, but only sprinkled with a limited amount (Decressin, 1998). Using this type of reactor, a three phase system is created (biofilm–liquid phase–gas phase), improving material transport (gases released and transported to the biofilm) and increasing the methanation and volumetric efficiency of the system.

Solid state bioreactors have also been used. In these reactor types, the microorganisms are immobilized on solid particles inside the reactors. The high surface-to-volume ratio of the particles provides large contact areas between the microorganisms and the gas and liquid phase, and no additional mechanical power input is needed (Rittmann et al., 2013). Jee et al. (1987, 1988) reported that efficient CH_4 production from H_2 and CO_2 could be achieved using a solid support such as a porous ceramic or granular support in a fixed bed reactor. Both granular and cylindrical shapes were used.

In the present study, another type of fixed bed packing material was used. In order to make the technology suitable for widespread use and for decentralized energy systems, simple low-cost technology using inexpensive materials is required. In this study, biological conversion of CO_2 and H_2 into CH_4 was studied in a fixed bed reactor packed with vermiculite shales and granular perlite material. The idea of mixing shale and granular type materials was to obtain a structure that prevents compaction. Vermiculite and perlite are also common and cheap materials, widely used in construction because of their light weight and outstanding insulating characteristics. The objectives were to investigate the operational conditions of biological conversion of CO_2 and H_2 into CH_4, the dynamics and stability of this kind of reactor system, and process efficiency when two fixed bed reactors were connected in series. Two bioreactors in series configuration was used because in previous studies it has been shown that several reactors in series configuration may increase treatment stability, treatment efficiency and provide advantages in process control (Alitalo et al., 2013).

2. Methods

A schematic of the methane bioreactor system is presented in Fig. 1. The reactor system consisted of two solid state bioreactors in series connected to a recirculation system. Heating system and supply gas sources (H_2 and CO_2) were also attached to the reactor regime.

Bioreactors were constructed from sections of a polypropylene pipe with a diameter of 75 mm and height of 500 mm. The effective volume of the two-reactor (serial) system was 4.0 l. A nylon inlet tube for CO_2 and H_2 delivery was fitted to the upper part of the pipe. The lower part was provided with two outlet tubes, one for gas collection and the other for possible maintenance procedures such as water recycling. The lower part of the pipe was covered with a 10 cm thick layer of pebble stones (3–10 mm) and the rest of the bioreactor was filled with a solid support. Prior to the filling, 9 l of solid support was produced by mixing 7.2 l/(957.6 g, particle size 2–4 mm) vermiculite with 1.8 l/(207 g, particle size 2–6 mm) perlite and adding 10.5 g wood ash, 0.2 g hydrated cobalt sulfate ($CoSO_4 \cdot 7H_2O$), and 0.2 g hydrated nickel chloride ($NiCl_2 \cdot 6H_2O$). The specific surface area of the support material was 37.44 m^2/g. The nutrient content of wood ash was 356, 93, 31.8 and 24.2 g/g of Ca, K, Mg and P, and 244, 2470, 6490 and 2200 mg/g of Cu, Fe, Mn and Zn, respectively. Before packing, this solid support mixture was moistened with 1.7 l of water. Each reactor was packed with 2.4 l of this moistened solid mixture.

After packing, the reactors were flushed with the mixed gas overnight to provide anaerobic conditions. The next day each bioreactor was inoculated with a 2 l aqueous slurry of methanogens, obtained from an earlier bioreactor cultivation and stored in a mixture of CO_2 and H_2, by pumping through the inlet of the upper part of the bioreactor.

Recirculation was with outlet liquid medium from the 10-l collector tank of the bioreactor. Recirculation was carried out automatically at a rate of 1000 ml/72 h (in batches once in every 72 h) and the calculated average retention time of the reactor was 144 h. An additional recirculation was carried out with nutrient-supplemented recirculation medium. On days 20 and 41 both reactors were recycled with 500 ml of recirculation medium containing 0.5 g/l Na_2S and 1.0 g/l $NH_4CO_2NH_2$. On day 32, Reactor I was recycled with 500 ml of filtered wood ash water suspension and Reactor II with 500 ml recirculation medium to which 0.5 g/l of Na_2S and 1.0 $NH_4CO_2NH_2$ had been added. Ash water suspension was prepared by mixing 100 g/l wood ash to water. Recirculation pumps and water circulation pumps were diaphragm pumps manufactured by Hücon (Part 13 of 3010). Diaphragm

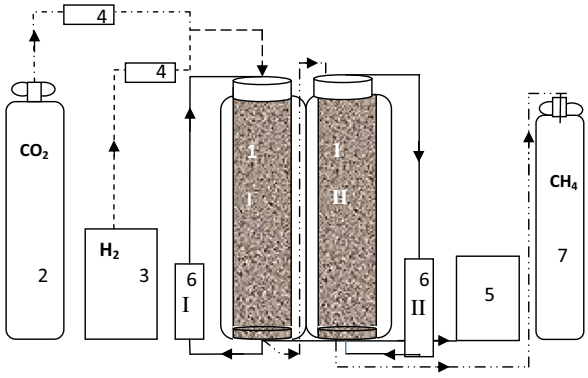

Fig. 1. Schematic of a pilot scale plant for biological methanation. (1) Bioreactors I and II connected in series, (2) CO_2 source, (3) hydrogen generator, (4) mass flow controller, (5) circulating heat water system, (6) recirculation tanks I and II, (7) CH_4 storage.