Bioresource Technology 247 (2018) 7–13

Contents lists available at ScienceDirect

Bioresource Technology

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

Influence of operating pressure on the biological hydrogen methanation in trickle-bed reactors

Timo Ullrich[a,*], Jonas Lindner[a], Katharina Bär[b], Friedemann Mörs[b], Frank Graf[b], Andreas Lemmer[a]

[a] University of Hohenheim, State Institute of Agricultural Engineering and Bioenergy, Garbenstraße 9, 70599 Stuttgart, Germany
[b] DVGW Research Center at Engler Bunte Institute of Karlsruher Institute of Technology, Engler-Bunte-Ring 1, 76131 Karlsruhe, Germany

ABSTRACT

In order to investigate the influence of pressures up to 9 bar absolute on the productivity of trickle-bed reactors for biological methanation of hydrogen and carbon dioxide, experiments were carried out in a continuously operated experimental plant with three identical reactors. The pressure increase promises a longer residence time and improved mass transfer of H_2 due to higher gas partial pressures. The study covers effects of different pressures on important parameters like gas hourly space velocity, methane formation rate, conversion rates and product gas quality. The methane content of 64.13 ± 3.81 vol-% at 1.5 bar could be increased up to 86.51 ± 0.49 vol-% by raising the pressure to 9 bar. Methane formation rates of up to 4.28 ± 0.26 $m^3\,m^{-3}\,d^{-1}$ were achieved. Thus, pressure increase could significantly improve reactor performance.

1. Introduction

Power-to-gas technology allows the conversion of electrical energy to synthetic natural gas (SNG) via electrolytic hydrogen production and its subsequent conversion together with carbon dioxide to methane and water (Clegg and Mancarella, 2015). This process is beneficial in many ways. Firstly, a significant quantity of electrical energy, produced by fluctuating renewable energy sources including wind and solar power, is able to be managed and stored (Leonzio, 2017). Another advantage is the high specific energy density of SNG (1.200 kWh m^{-3} at 200 bar). A longer storage period from minutes to months is also possible because of the existing high storage capacities in the gas grid (Kirchbacher et al., 2017). Thus, the well established gas grid can be used as a powerfull energy storage and transportation system for electric energy.

The production of SNG with the power-to-gas technology is a two-step process. First, electrical energy is transformed into oxygen (O_2) and hydrogen (H_2) by electrolysis of water. In the second step, H_2 is converted with an external CO or CO_2 source to methane (CH_4) via methanation (Götz et al., 2016). The methanation reaction can take place either in catalytic or biological reactors. Catalytic processes usually operate at temperatures between 200 and 550 °C, pressures of up to 100 bar and have a very high methane formation rate (MFR), which describes the specific methane yield, calculated as a function of the reactor volume. In order to achieve the same output, significantly larger reactor volumes are necessary for a biological reactor (Barbarossa and Vanga, 1992; Bartholomew, 2001). A typical value for evaluating the performance of a reactor is the gas hourly space velocity (GHSV). It refers to the incoming gases and according to Götz et al. (2016) the efficiency at the same MFR of biological reactors with GHSV of up to 300 h^{-1} is significantly lower than that of catalytic ones with GHSVs up to 5000 h^{-1}.

On the other hand, the catalytic processes has some disadvantages compared to the biological pathway. For example, nickel catalysts which are commonly used in the thermochemical power-to-gas technology, demand high purity standards of the feed gases (Barbarossa and Vanga, 1992; Bartholomew, 2001). Sulphur and sulphur-containing components are known catalyst poisons for the nickel catalysts used in catalytic methanation (Bartholomew, 2001; Götz et al., 2016). For many applications, the feed gas must be cleaned before injection into the methanation reactor (sulphur content ≪ 1 ppm) (Götz et al., 2016). In contrast, the biological methanation process appears to be very robust, meaning that it will not be affected by impurities of the feed gases or infections with foreign organisms (Götz et al., 2016; Liew et al., 2016; Seifert et al., 2013). Even minor disruptive components such as sulphur and oxygen were found to have no effect on the biological methanation (Bartholomew, 2001; Götz et al., 2016). Seifert et al. (2013) investigated the conversion of real gases (synthesis gas, biogas and flue gas) by *methanothermobacter marburgensis*. Methane formation

* Corresponding author.
E-mail address: t.ullrich@uni-hohenheim.de (T. Ullrich).

http://dx.doi.org/10.1016/j.biortech.2017.09.069
Received 7 July 2017; Received in revised form 7 September 2017; Accepted 8 September 2017
Available online 11 September 2017
0960-8524/

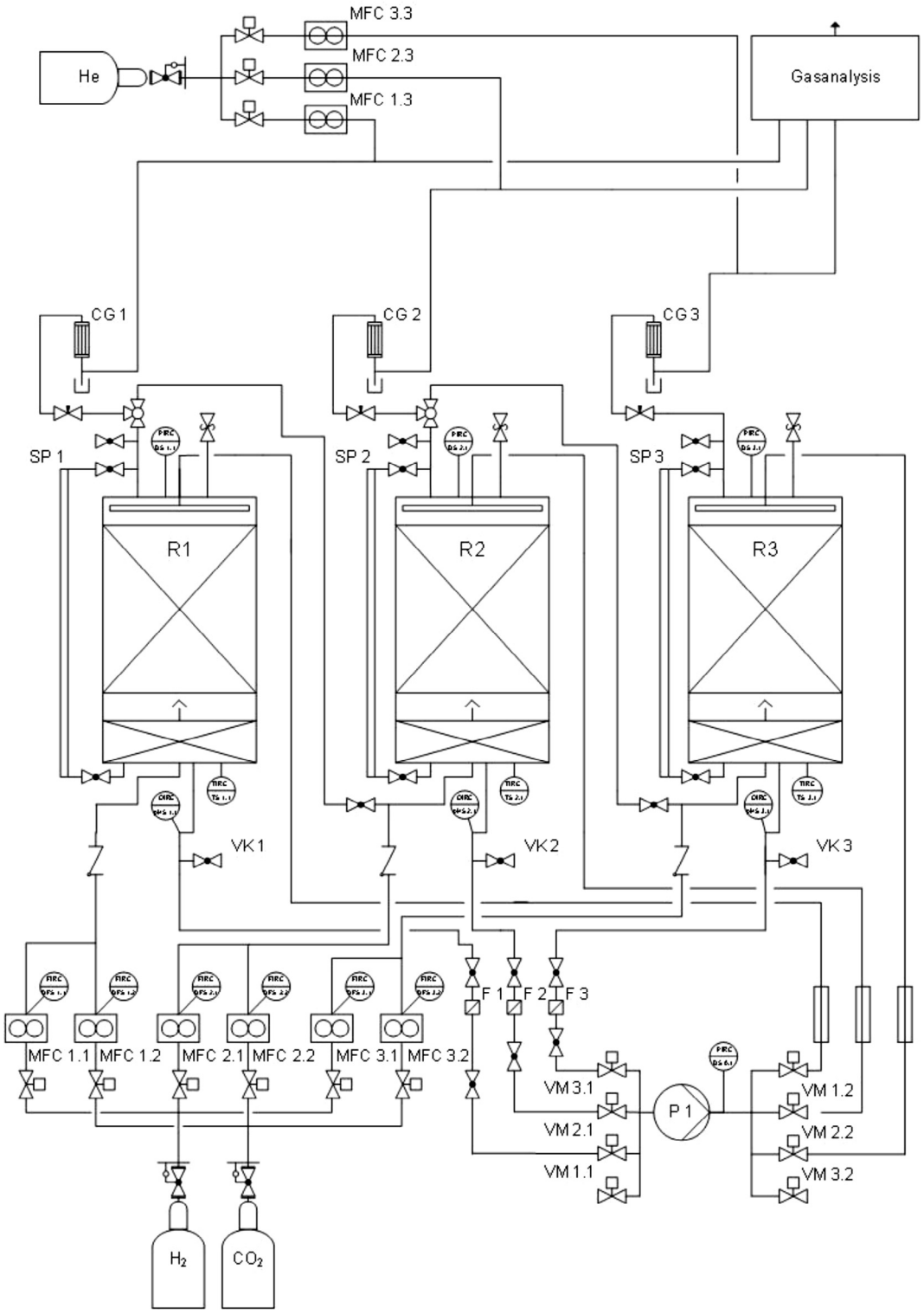

Fig. 1. Piping and instrument diagram of the test facility with the three trickle-bed reactors (R1–R3), the injection of the educt gases CO_2 and H_2 (MFC 1.1–MFC 3.2), the circulation unit of the nutrient solution (P 1, VM 1.1–VM 3.2), the gas analysis and the gas quantity measurement (MFC 1.3–MFC 3.3) with He as the tracer-gas.

was not affected by the presence of sulfur components or short chain hydrocarbons. Furthermore, some of these components can be partly removed by biological methanation (Bartholomew, 2001; Götz et al., 2016). For example, Strevett et al. (1995) investigated the reaction behavior of hydrogen-sulfite (H_2S) containing biogas and showed that even H_2S was also degraded.

Biological methanation is not only more robust against impurities than the catalytic reaction; it is also more flexible in relation to load changes. Immediate load changes from 100% to 0% were achieved as well as re-start after standstill times of up to 23 days. In contrast, a minimum load is often required for catalytic processes (Götz et al., 2016).

Besides these advantages, the biological methanation has the disadvantage, that large reactors are required due to the low volume related productivity (Götz et al., 2016). The literature indicates a limitation of the MFR due to slow transition of the feed-gases into the