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Evaluation of a membrane permeation system for biogas upgrading using model and real gaseous mixtures: The effect of operating conditions on separation behaviour, methane recovery and process stability

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ABSTRACT

In this paper, the enrichment of methane by membrane technology was studied by employing (i) a model as well as (ii) a real biogas mixture produced on a laboratory-scale. Thereafter, the endurance of the process was tested at an existing biogas plant. The commercial gas separation module under investigation contained hollow fiber membranes with a polyimide selective layer. During the measurements, the effect of critical factors (including the permeate-to-feed pressure ratio and the splitting factor) was sought in terms of the (i) CH_4 content on the retentate-side and (ii) CH_4 recovery, which are important measures of biogas upgrading efficiency. The results indicated that a retentate with 93.8 vol% of CH_4 – almost biomethane (>95 vol% of CH_4) quality – could be obtained using the model gas (consisting of 80 vol% of CH_4 and 20 vol% of CO_2) along with 77.4% CH_4 recovery in the single-stage permeation system. However, in the case of the real biogas mixture, ascribed primarily to inappropriate N_2/CH_4 separation, the peak methane concentration noted was only 80.7 vol% with a corresponding 76% CH_4 recovery. Besides, longer-term experiments revealed the adequate time-stability of membrane purification, suggesting such a process is feasible under industrial conditions for the improvement of biogas quality.

1. Introduction

Biogas is a mixture generated from organic matter via the process known as anaerobic digestion (Patinvoh et al., 2017; Pavi et al., 2017). Basically, it consists of methane, carbon dioxide and other (trace) compounds such as N_2, H_2S, water vapour, etc. (Weiland, 2010). Given its valuable CH_4 content, it has been widely applied to replace fossil fuels (such as natural gas) and contribute to sustainable energy, i.e. heat and electricity production (Ge et al., 2016). Though it can be utilized after partial purification, i.e. in Combined Heat and Power (CHP) systems, upgrading to biomethane is also an option (Ferella et al., 2017; Miltner et al., 2017; Morero et al., 2017). In this latter case, the sufficient separation of impurities is required, making the subsequent use of biomethane possible (i) in the transportation sector as a vehicle fuel or alternatively, (ii) it may be fed into the natural gas grid once quality requirements are met (Chen et al., 2015; Makaruk et al., 2010).

Biogas cleaning can rely on a range of physical, chemical and biological techniques that include, but are not limited to, (i) condensation, (ii) absorption based on components such as amines, ionic liquids (Albo et al., 2010), (iii) pressure swing adsorption (PSA), (iv) bio-scrubbing, i.e. for hydrogen sulfide elimination, and (v) membrane separation (Bauer et al., 2013; Ryckebosch et al., 2011). This latest option employing membrane contactors and polymerized membranes as permselective barriers has gained remarkable attention in recent years (Albo et al., 2014; Albo and Irabien, 2012). The several reasons behind are portability, relatively simple scalability, sufficient selectivity and stability of modules, advantageous energy requirements, etc. (Basu et al., 2010; Niesner et al., 2013). Although membrane gas separation is

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regarded as a mature technology and various modules are available on the market supplied by several companies, most of them were not originally intended for biogas-separation purposes but rather to process other gaseous mixtures, i.e. natural gas (Makaruk et al., 2010). Thus, once such membrane has been adopted for biogas upgrading, however, careful assessment of their separation behaviour as well as optimization of operating conditions should be carried out, i.e. due to the different compositions of gas streams handled, to be able to meet biomethane specifications.

So far, various "membrane-powered" applications have been developed and thoroughly evaluated in terms of biogas enrichment, most of which are designed from polymeric membranes, i.e. cellulose acetate (CA), polydimethylsiloxane (PDMS), polysulfone (PSf) and polyimide (PI) (Scholz et al., 2013). A contemporary membrane system, in order to provide biomethane as a substitute for natural gas, should be capable of providing at least 95% CH_4 purity with 90% CH_4 recovery (Brunetti et al., 2015). Typically, the raw biogas that is subjected to purification contains approximately 50–70% methane, 30–50% carbon dioxide, lower quantities of nitrogen and water, and trace amounts of substances such as H_2S, depending on its source, e.g. a farm, sewage sludge digester, landfill, etc. (Rasi et al., 2007, 2011). In general, the performance of a given membrane system that deals with such gaseous streams will strongly depend on the operating conditions, namely the (i) pressure gradient across the membrane module (assisting the driving force), (ii) retentate (R) to feed (F) flow ratio (R/F) known as the splitting factor, (iii) separation temperature, and (iv) feed-gas composition, etc., which play a major role (Bakonyi et al., 2013a,b).

Over the preceding years, our group has been conducting research into gaseous biofuels (hydrogen and methane) production as well as their subsequent separation. As a result, membrane bioreactors (MBR), as integrated approaches, have been designed (Bakonyi et al., 2017; Szentgyörgyi et al., 2010). Besides, ex-situ tests with regard to the evaluation of gas upgrading were performed as well (Bakonyi et al., 2013b). In the light of preliminary experiments, hollow fiber membranes (HFMs) made of PI are shown as applicable candidates in terms of gas upgrading (Bakonyi et al., 2013b; Szentgyörgyi et al., 2010). Though previous information concerning biogas purification using certain PI membranes is available in the literature (Harasimowicz et al., 2007), an in-depth examination of the particular one employed in this study, to the best of our knowledge, has not been yet reported. Hence, in this work, the thorough evaluation of a commercialized membrane made of PI – a polymer with the potential to be utilized in CH_4/CO_2 separation (Baker and Low, 2014) – was aimed to study. The main scope of investigation was laid down to reveal the operating circumstances under which biomethane may be produced. Over the course of the assessment, model and real biogas mixtures were applied to determine how the composition affects the efficiency of purification. Afterwards, the time-stability of the gas permeation process was analysed over a series of longer-term experiments to obtain information concerning its applicability with regard to possible industrial implementation. To the best of our knowledge, such experimental results are not found in the literature for this PI membrane module and hence, this work is believed to exhibit added value and contribute to the development of anaerobic digestion technology.

2. Experimental setup

Biogas purification measurements were performed on a membrane module (UBE-CO5, Ube Industries, Ltd.) designed for natural gas separation. It contains composite hollow fibers membranes composed of a PI selective layer. Since a number of module features, i.e. the active surface area and thickness of the membrane are unknown, the gas permeability, measured in the recognised non-SI unit of Barrer, cannot be calculated to characterise the separation process. Therefore, an experimental, pressure-normalized volumetric gas flow rate is reported according to Eq. (2). The module was installed into a high-pressure gas separation membrane system, referred to as GSMS (Fig. 1). The schematic drawing of the GSMS and its most essential technical details can be found in our earlier paper (Bakonyi et al., 2013b). The permeate and retentate were quantified by digital mass flow meters (Bronkhorst EL-FLOW® Select), which had undergone preliminary calibration. To obtain the exact flow rate of mixtures throughout the separation process, a correction factor was provided by Fluidat® (https://www.fluidat.com, Bronkhorst®). This took into account the exact composition of the permeate and retentate streams in terms of CH_4, CO_2 and N_2 as determined according to Section 3.

The gas separation experiments were carried out at a temperature of 30 °C unless otherwise stated, first by using a binary (model) mixture composed of 80 vol% methane and 20 vol% carbon dioxide (SIAD Hungary Kft., Hungary) (Table 1). Afterwards, real biogas – from a continuously operated anaerobic membrane bioreactor system – as documented by Szentgyörgyi et al. (2010) – was collected over a period of time, compressed into a gas cylinder and subsequently tested. Recently, together with our industrial partner, work has commenced on the valorization of landfill-deposited organic waste fractions, i.e. to generate biogas. As a part of that line of research, the assessment of methane purification by membrane technologies is a distinct goal. In accordance with a summary in the paper of Brunetti et al. (2015), the nitrogen content in biogas can vary considerably (1–17 vol%). Hence, to simulate realistic conditions and typical compositions of landfill-derived biogas, enrichment of the real gaseous mixture (pressurized in the external tank, as noted above) by N_2 was conducted. As a result, the final composition was as follows: 70 vol% CH_4, 19.8 vol% CO_2, 9.2 vol% N_2 and approx. 1 vol% unidentified minor impurities.

As can be observed in Tables 1 and 2, the effect of the main membrane operating parameters – namely the (i) feed pressure to permate pressure ratio (p^F/p^P) and (ii) the splitting factor (R/F) defined as the retentate flow rate relative to the total feed flow rate – on (i) methane concentration on the side of the retentate and (ii) methane recovery was sought (Figs. 2–5). All data presented in this work were obtained under steady-state permeation conditions,

Fig. 1. Image of the gas separation membrane system (left-hand side) with the PI membrane module installed (right-hand side).