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Simultaneous hydrogen sulphide and carbon dioxide removal from biogas by water–swollen reverse osmosis membrane

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ABSTRACT

Biogas is a suitable alternative fuel if unwanted impurities are removed to avoid corrosion of the inner parts of an engine. A recent breakthrough in biogas purification showed that a thin hydrophilic composite membrane can create the selective water swollen barrier able to remove unwanted sour gases such as carbon dioxide and hydrogen sulphide owing to significantly higher water solubility of the latter in comparison to methane. This work presents the use of water–swollen membranes for the simultaneous removal of carbon dioxide, hydrogen sulphide and water vapour from agro-biogas. Up to 82 vol.% of carbon dioxide and 77 vol.% of hydrogen sulphide were successfully removed from the feed stream at a pressure of 220 kPa. The selection of the most suitable thin hydrophilic composite membrane based on the knowledge of its basic characteristics is discussed. SEM analysis showed that the surface of the best performing composites changed significantly upon swelling by water. It was found that a compact structure of the upper selective thin layer after the swelling by water is fundamental for obtaining a selective water–swollen membrane. The next key factor is a high porosity of the membrane support. A detailed comparison of various systems and their performance is presented.

1. Introduction

In spite of the increasing attention for alternative sources such as wind and solar energy, classical combustible energy carriers still play an essential role in the current society. The energy consumption has continuously risen [1–3] and the energy supply plays a fundamental role for the sustainability of the modern age to ensure the current quality of the human life [3,4]. Nowadays, the energy demand is supplied by fossil fuels for approximately 88% [5]. However, fossil fuels pollute the atmosphere by emissions of greenhouse gases like carbon dioxide, sulphur dioxide, and nitrogen oxides [6]. Fossil fuels reserves are limited resources. In this context, an intensive search for alternative renewable fuels is needed to find a solution to the growing energy challenges [3,7,8] from the economic as well as the environmental point of view [9]. A biowaste such as a wastewater contains a lot of energy that might be exploited in the form of methane [10,11]. Biomass has also been recognized as a possible renewable energy source [6]. Biogas, an example of a gaseous biofuel, which can be obtained from biomass via a biochemical way, seems to be a very good candidate for the replacement of fossil fuels [12]. For example, natural gas can be replaced directly by biogas if the latter contains a sufficiently high amount of methane [5].

Raw biogas consists mainly of methane, carbon dioxide, and a small amount of various residual compounds, such as water vapour, hydrogen sulphide, ammonia, siloxanes, and mercaptanes [7]. Biogas contains typically 50–70 vol.% of methane and 30–50 vol.% of carbon dioxide, depending on its origin and on the season [7]. Biogas thus needs to be purified to become the “energy of the future” at engine-fuel quality [1]. Many different methods for carbon dioxide removal from biogas exist, namely water scrubbing, polyethylene glycol scrubbing, absorption of contaminants using molecular sieves, or pressure-swing absorption [7]. Carbon dioxide removal is an important operation to enhance the heating value of the gas [13]. Further, hydrogen sulphide has to be captured from biogas (i.e. by absorption or using active coal) both because of its high toxicity and because of its corrosive effect [7,13].

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Newly, biogas purification can be realized by the membrane separation technology [7,13,14]. The tested polymeric membranes have been made from silicone rubber, cellulose acetate, and polyimide [7,13–16]. At the current state of the art, upgrading of biogas with polymeric membranes is commercially competitive with the conventional technologies for carbon dioxide and hydrogen sulphide removal, such as pressure swing adsorption, temperature swing adsorption or amine scrubbing [17,18]. However, most of the membranes suffer damage by aggressive gases [7,13,14,18,19] and it is necessary to pre-treat the raw biogas and remove water vapour and also the potentially harmful compounds, namely hydrogen sulphide, ammonia and siloxanes.

The need to minimize the costs of biogas upgrading leads a continuous search for new and more effective membrane materials [19]. One of the possibilities is the use of water–swollen membrane for simultaneous carbon dioxide and hydrogen sulphide removal from the biogas stream [7,8]. Conventional biogas purification methods require removal of water vapour from the biogas stream. However, it is well known that the solubility of quadrupolar carbon dioxide and polar gases in water is significantly higher than that of methane. Under appropriate conditions the polyamide layer of thin film composite reverse osmosis membranes is able to create a thin film of water, which can then perform as a perfect selective membrane for separation of polar gasses from methane [8]. The great advantage of this membrane separation is that unwanted and toxic gases, including water vapour itself, are removed from its continuously refreshed surface, thus avoiding contamination of the permselective membrane. Furthermore, the condensed water passing through the membrane ensures good permselectivity of the whole separation [8].

This method of biogas upgrading has been patented recently [20]. The contact of the thin hydrophilic composite (TFC) membrane surface with water causes swelling of the polyamide thin film. In order to achieve the spontaneous condensation of water, the temperature of the TFC membrane must be below the dew point of the raw biogas feed. Interestingly, the heat of evaporation of the liquid phase from the permeate side of the membrane helps to cool the membrane surface. The function of the water–swollen thin film composite membrane was previously proven for the high-pressure type of RO membrane and the subject of the present manuscript is to test also a low-pressure membrane meant for brackish water (much less expensive compression work would be used) and to compare the results. In particular, the possibility to use the polyamide composite membranes for simultaneous removal of both carbon dioxide and hydrogen sulphide from agro-biogas has been experimentally studied in the present manuscript.

2. Experimental

2.1. Materials and membrane preparation

Commercial TFCs Reverse Osmosis (RO) membranes of two suppliers were tested. The TFC membrane specifications are displayed in Table 1. The first two TFCs supplied by Sterlitech Corporation (further denoted as *Sterlitech I* and *Sterlitech II*) were used for preliminary tests with binary mixtures of methane and carbon dioxide. The third TFC membrane supplied by Sterlitech Corporation was denoted as the *low pressure RO membrane* and was originally produced for low pressure brackish water desalination. The last used TFC membrane, supplied by Koch Membrane System Inc., was indicated as the *high pressure RO membrane*.

Table 1
The specifications of thin film hydrophilic composite (TFC) membranes.

Supplier	Product code	Our designation
Sterlitech Corporation	YMAKSP3001	*Sterlitech I*
Sterlitech Corporation	YMACM53001	*Sterlitech II*
Sterlitech Corporation	YM70UBSP18	*Low pressure membrane*
Koch Membrane System Inc.	KM8011395	*High pressure membrane*

A circular area of 124.6 cm^2 was cut out from the flat sheet TFC membranes. Three millilitres of deionized water were spread with a brush on the membrane skin layer before closing the permeation cell, according to the previous experience to achieve water–swollen layer on the composite [8].

All single gases were supplied by Linde gas with a stated purity of at least 99.995%. Pure methane and pure carbon dioxide were mixed with a stream containing carbon dioxide and 10,000 ppm of hydrogen sulphide to obtain an agro-biogas model mixture with 940 ppm of hydrogen sulphide.

2.2. Membrane characterisation

2.2.1. SEM and EDX analysis

Elemental analysis was carried out on the Tescan Indusem with Quantax 200 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) analyzer from producer Bruker. The EDX system consists of an XFlash detector 5010 operated with an accelerating voltage of the electron beam in the range from 5 to 30 kV. The necessary accelerating voltage dependeds on the thickness of the deposited layer. SEM/EDX analysis provides a superior imaging quality and rapid and nondestructive quantitative elemental results directly in the live image. Due to the relatively high energy of the electrons, SEM/EDX equipment typically probes the surface at a depth between 1 and 2 μm.

2.2.2. Membrane support porosity

Composite membranes were pre-dried at 40 °C before porosimetry measurements were carried out on a top-rating high-pressure mercury porosimeter AutoPore III (Micromeritics, USA), which performs high-pressure mercury intrusion up to 400 MPa. The porosimetry determination of the membrane support is described in detail in the literature [21].

2.3. Apparatus and measurement

The laboratory-scale biogas separation apparatus used in the present work is shown in Fig. 1. The feed stream is prepared by mixing CH_4, CO_2, and H_2S using Bronkhorst mass flow controllers. Firstly, a preliminary test was carried out with a dry feed stream to check the separation performance of a virgin composite membrane. Secondly, the feed stream was saturated with water in a two-stage humidifier filled with a total of 24 mL deionized water and was fed through the first stage of the humidifier at laboratory temperature. The second stage of the humidifier was heated to reach a higher water saturation pressure. The temperature and humidity of the feed stream was measured by HygroFlex 4 system with HC2 sensor (Rotronic). The combined feed stream was then fed into the permeation cell. The water swollen surface was continuously refreshed during the measurement by the condensing water, thanks to the fact that the permeation cell (described in detail in the previous work [8]) was cooled. After leaving the permeation cell, the residual humidity in both permeate and retentate streams was removed in the cold traps (at −15 °C) to avoid humidity inside the backward pressure controller (Bronkhorst) and the IR gas analyser (Aseko Air LF®, CZ). Methane and carbon dioxide content were analysed by infrared sensors, and hydrogen sulphide and oxygen by electrochemical sensors, respectively. The maximal applied feed pressure was 500 kPa (absolute), while the permeate carrier gas (i.e. nitrogen) was always at atmospheric pressure. All