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UPGRADING BIOGAS TO BIOMETHANE BY USE OF NANO-STRUCTURED CERAMIC MEMBRANES

Priscilla Ogunlude *, Ofasa Abunumah, Ifeyinwa Orakwe, Habiba Shehu, Firdaus Muhammad-Sukki and Edward Gobina

Department Centre for Process Integration and Membrane Technology, School of Engineering, Robert Gordon University, Sir Ian Wood Building, Garthdee Road, Aberdeen AB10 7GJ, United Kingdom

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ABSTRACT

In order to meet the demands of growing economies while considering environmental implications, the use of clean and renewable sources of energy has increasingly become of interest. Biogas utilisation is a means by which these rising needs can be met. This involves the use of waste materials; which are deposited on a daily basis by agriculture, sewage, household, to produce energy that may be used for heating, electricity, transportation and other daily needs. This paper would look into the use of nano-structured ceramic membranes for the upgrading of biogas to a high value fuel that can be used for a variety of purposes. The use of membranes offers great advantages including low running costs, high efficiency and the elimination of the need for phase change of the gas. Experiments were carried out using membranes of different pore sizes (15nm, 200nm and 6000nm) to ascertain which would be the most suitable for use in terms of permeability and yield of product gas. The 15nm membrane showed the greatest exit flow of methane compared to carbon dioxide and a mechanism approaching an ideal knudsen regime. Taking into account the effect of molecular weight and viscosity, these results show that the smallest membrane pore size of 15nm had a greater impact on the flow mechanism and thus improvement can be made by modification of the membrane to achieve a mechanism of surface diffusion of the particles.

1. INTRODUCTION

Biogas is evolved from the anaerobic digestion of biogradable materials such as human or animal waste, food scraps, cotton, wool, wood and other organic sources. The biogas obtained can be used directly as a fuel but in order to fully harness its potential, it can be cleaned and upgraded to a point where its heating value is very high, and impurities are removed such that it can be injected into the national gas grid.

The treatment or upgrading of biogas is essential because: (i) the presence of CO_2 in the gas reduces the power output from the engine, takes up space when biogas is compressed for storage and causes freezing problems when the compressed gas undergoes expansion at valves and metering points (ii) traces of H_2S can produce H_2SO_4 which corrode pipes, fittings, etc. (iii) moisture reduces the heating value of the biogas and causes corrosion. Nonetheless, several safety aspects need to be considered during the treatment and utilization of biogas. It is very crucial to be aware of the associated risks and to minimize them. The most common risks include flammability, poisoning (due to the presence of H_2S), suffocation and the risks associated with high pressures and temperatures. However, the advantages include the fact that biogas is lighter than air and any gas leakage would rise upward. Moreover, upgraded biogas has a greater temperature of ignition than both petrol and diesel so the possibility of a fire or explosion is reduced (Svenskt Gastekniskt Center, 2012).

The advantages of utilizing biogas are numerous; biogas upgrading technology can turn the cost of waste management into a revenue opportunity. Turning waste into a renewable source of energy by this upgrading process will reduce dependence on importation of fossil fuels, reduce greenhouse gas emissions, improve environmental quality, increase local jobs and provide revenue by export thereby boosting the economies. The benefits cannot be overstretched as even the digestate from anaerobic digestion offers an opportunity to recycle nutrients in the food supply, reducing the need for both petrochemical and mined fertilizers. Research has proven that upgraded biogas shows lower carbon intensities compared to other vehicle fuel (Penev et al., 2016; Scarlat, Dallemand, & Fahl, 2018).

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* Corresponding author:
Priscilla Ogunlude
email: p.ogunlude@rgu.ac.uk

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Currently, American liquified natural gas (i.e. methane) is being exported to counties like China, India and Japan who still rely on coal for power generation but wish to substitute their coal for clean gas (Weinstein, 2019). Thus, this technology can be implemented on a large scale for the export of upgraded biogas to other countries without knowledge, infrastructure and expertise, this would provide revenue for the economy as well as an abundance of jobs. This highlights one of the advantages of biogas compared to other forms of renewable energy such as solar and wind that cannot be stored and transported.

This paper would introduce a novel method for the upgrading of biogas to a clean and useful fuel replacing fossil fuels. The use of nano-structured membrane technology would be implemented, where biogas components pass through the membrane as the feed gas to observe the separation characteristics at various operating conditions for three different membrane pore sizes.

The main goal is to analyse the flow characteristics of biogas through a membrane in order to measure the permeability and selectivity of the gas components through various pore sizes and determine the flow/transport mechanisms of biogas components.

2. LITERATURE REVIEW

2.1 Current Technologies

The current state-of-the-art technologies for biogas upgrading include absorption, adsorption, membrane separation and cryogenic separation. Absorption may be by physical or chemical scrubbing. In the case of water scrubbing, biogas is injected into the bottom of the absorption column where carbon dioxide is absorbed by water that runs from the top at high pressure. The absorption column is filled with random packing to increase the gas-liquid-contact. The counter current flow of gas and liquid is necessary to achieve a high process efficiency. During the process, carbon dioxide and some methane are physically absorbed in water and the selectivity of the process depends on the much higher solubility of carbon dioxide compared to methane in water. Finally, the carbon dioxide is then released from the water again in the desorption column, by using air at atmospheric pressure as stripper medium. The process of chemical scrubbing is similar to the water-scrubbing process, however the solubility of carbon dioxide in an organic solvent is increased by about five times compared to water. This means that the volume of solvent that is requires in the system is significantly reduced.

The pressure swing adsorption method may also be used to remove the unwanted constituents of biogas by changes in pressure within a system that cause each gas to move or be adsorbed at different rates. The adsorbents may be of the equilibrium type, which adsorbs more of carbon dioxide than methane. It may also be of the kinetic type, adsorbing carbon dioxide at a faster rate than methane due to con- trolled diffusion rates. Some examples of adsorbent materials which are commonly used include activated carbons, natural and synthetic zeolites, titanosilicates, silica gels and carbon molecular sieves.

Membrane technology involves the use of a barrier that restricts the flow of some components of biogas which allows the resultant gas to be stripped of the restricted gas. Cryogenic technology is still relatively new and works at very high pressures and low temperature to permit the separation of gases. Research has shown that membrane technology and absorption are the most economical and efficient methods that possess high potential for scaling up to achieve an efficient and profitable means of upgrading because of their high gas recovery and minimal loss of gas. Currently, absorption by chemical scrubbing is widely used to upgrade biogas, but this results in a significant amount of waste products that need to be properly disposed of thereby increasing costs. In this research, the use of membrane technology is explored as an effective and efficient means of upgrading biogas. The energy consumption is relatively lower than the conventional upgrading processes as they do not consume energy in the latent heat of evaporation and the possibility of methane slip or losses is minimal. Other advantages are that they are compatible with temperature sensitive materials and are not chemically altered, separation does not involve phase change, other reactions can be processed simultaneously due to the versatility of membranes, there is a high efficiency of separation, they are simple to operate and membranes have high selectivity and permeation rate (Scott & Hughes, 2012).

2.2 Membrane Gas Transport Mechanisms

The mechanism of gas transport in membranes are derived from Graham's law and Fick's law (Shehu, Okon, Orakwe, & Gobina, 2018). Graham's law states that the rate of diffusion of a gas is inversely proportional to the square root of its molecular weight. In mathematical form (Domenico De Meis, 2017):

$$\frac{Rate\ a}{Rate\ b} = \left({}^{M_b}/_{M_a}\right)^{1/2} \tag{1}$$

Where,

Rate a and Rate b denote the rate of diffusion of the first gas and second gas respectively,

M_a and M_b are the molar masses of gases a and b in g mol^{-1} respectively.

Fick's law relates the molar flux to the concentration gradient through the membrane thickness. This can be written in mathematical form as (Domenico De Meis, 2017):

$$F_i = \frac{P_e}{L}(P_1 - P_2)A \qquad \left(\frac{mol}{s}\right) \tag{2}$$

Where,

P_e is the permeability, mol m^{-1} s^{-1} Pa^{-1}

L is the length, m

P_1, P_2 is the pressure at point 1 and 2 respectively, Pa

A is the permeation area, m^2

Gas transport in membranes can take place through several mechanisms including Hagen-Poiseuille flow, Knudsen diffusion, surface diffusion, capillary condensation and molecular sieving.

2.2.1 Hagen-Poiseuille

This mechanism comes to play when the pore diameter is large compared to the mean free path of the gas molecules (λ). Here, the gas permeance is inversely proportional to the gas viscosity (Domenico De Meis, 2017; Oyama, 2011).

$$P_e = \frac{\varepsilon\eta r^2}{8\mu RT} P_{av} \quad (\text{mol m}^{-1}\text{ s}^{-1}\text{ Pa}^{-1}) \tag{3}$$

Where,
Ɛ is the porosity, dimensionless
µ is the viscosity, Pa s
η is the shape factor assumed equal to the reciprocal tortuosity, dimensionless
R is the universal gas constant, J K^{-1} mol^{-1}
r is the pore radius, m
T is the temperature, K
P_{av} is the mean pressure, Pa

2.2.2 Knudsen Diffusion

This may occur when the pore size is larger than that of the gas molecules but smaller than its mean free path (λ). There is elastic collision between the gas molecules and the pore wall and therefore no interaction between them. The permeance is given as (Domenico De Meis, 2017; Oyama, 2011):

$$P_e = \frac{2\varepsilon\eta r v}{3RT} \quad (\text{mol m}^{-1}\text{ s}^{-1}\text{ Pa}^{-1}) \tag{4}$$

Where,
Ɛ is the porosity, dimensionless
η is the shape factor assumed equal to the reciprocal tortuosity, dimensionless
r is the pore radius, m
v is the molecular velocity, ms^{-1}
R is the universal gas constant, J K^{-1} mol^{-1}
T is the temperature, K

2.2.3 Surface Diffusion

This occurs at low temperatures where contact between the gas molecules and inner surface is so strong compared to their kinetic energy such that the molecules cannot escape. The permeance is given as (Domenico De Meis, 2017; Oyama, 2011):

$$P_{SD} = P_O \exp\left(\frac{-\Delta Ha - \Delta Esd}{RT}\right) \tag{5}$$

Where,
P_0 is the pressure, Pa
(-ΔHa – ΔEsd) is the energy barrier for diffusing molecules to permeate through the membrane, J m^{-1} s^{-1}
R is the universal gas constant, J K^{-1} mol^{-1}
T is the temperature, K

2.2.4 Capillary Condensation

Capillary condensation usually occurs at higher gas pressures with temperatures lower than the critical temperature. Therefore, condensed gas molecules are transported across the pores of the membrane (Uchytil, Petrickovic, Thomas, & Seidel-Morgenstern, 2003; Uhlhorn, Keizer, & Burggraaf, 1992):

$$\frac{\rho RT}{M}\ln\frac{P_t}{P_o} = -\frac{2\sigma\cos\theta}{r} \tag{6}$$

Where,
r is the density, kg/m^3
M is the gas molecular weight, kg mol^{-1}
q is the contact angle
P_t is the total pressure, Pa
s is the interfacial tension, N/m
r is the radius, m
R is the universal gas constant, J K^{-1} mol^{-1}
T is the temperature, K
P_o is the vapor pressure, Pa

2.2.5 Molecular Sieving

This mechanism separates the molecules by their size using membrane pores of similar size of the molecules. The typical pore sizes for molecular sieving are less than 2nm (Nagy, 2019; Rackley, 2017).

$$J_s(T) \sim \rho q_{sat} D_S^0(0)(1-\theta)^{-1}\exp(-E_{D,S}/RT)d\theta/dx \tag{7}$$

Where,
J_s(T) is the flux at temperature T, mol/s
r is the density, kg/m^3
q_{sat} is the saturated molar volume, m^3/mol
D_s^o(0) is the limiting surface diffusivity, m^2/s
q is the fraction of available adsorption sites that are occupied, dimensionless
$E_{D,S}$ is the surface diffusion activation energy, kJ/mol
R is the universal gas constant, J K^{-1} mol^{-1}
T is the temperature, K

3. METHODOLOGY

This research involved the use of a shell-and-tube system. Three different membrane modules of different pore sizes were studied with the membrane fitted into center of the tube sealed with graphite seals. Methane and carbon dioxide gases analyzed under different temperatures and pressures.

3.1 Experimental Set-up

The experimental set-up used in this work is shown in Figure 1 and Figure 2 shows the different views of the membrane support. The experimental set-up contains a gas cylinder (4) with regulator (3) which contains the feed gas, this can be sent to the membrane. It contains a heat regulator (5), pressure gauge (1), temperature indicator (7), volumetric meter (6), the membrane module that has been sealed to prevent leakage of gas and covered in heating tape with insulation (2) with an exit line through which the outlet gas flows to the fume cupboard. This chamber was set up to determine the flux of each gas through the membrane under different operating conditions.

3.2 Experimental Procedure

A leak test was conducted prior to each experiment. At the inlet, the methane gas to be analysed was fed in at a predetermined pressure and readings were recorded while operating at thermal stability of 100°C respectively. The stability of the flow meter confirmed that a steady constant driving force was being maintained.

At the outlet, there was also a flow meter to measure the flow of the outgoing gas. The flux was then obtained given that both inlet and outlet flow rates were measured.

FIGURE 1: Experimental set-up showing all equipment including; pressure gauge(1), membrane module covered with heating tape(2), gas regulator(3), gas cylinder(4), heat regulator(5), volumetric meter(6) and temperature indicator(7).

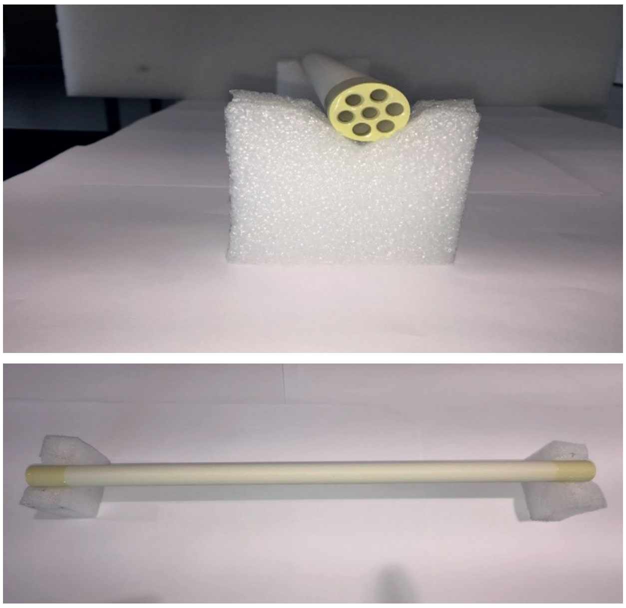

FIGURE 2: Top view (above) and side view (below) of a membrane.

The experiment was carried out at 0.2, 0.6, 1.0, 1.4, 1.8, 2.2, 2.6 and 3.0 bar.

The membrane module was flushed prior to changing the type of gas flowing through e.g. to enable us to measure the flow characteristics of carbon dioxide gas by repeating the procedure. By comparing the flow characteristics of the different gases, the perm-selectivity of the membrane was measured.

Additionally, to note how the membrane module would separate the two gases, a gas mixture containing a known composition of both gases and maintained at a set pressure would be analysed by passing the mixture through the chamber to measure the total permeation across the module and measuring how fast the outlet pressure increases. By checking the outlet gas composition, we would also measure how much of the exit gas from the total permeation is methane versus carbon dioxide which would enable us to figure out how well the membrane will separate the gases in an industrial application.

4. RESULTS AND DISCUSSION

The following set of graphs show the relationship between pressure drop and the ratio of CH_4 and CO_2 gas flowrate at set temperatures. The behaviour of the gases which is based on their molecular weight is typical of the Knudsen regime where the pore size is larger than that of the gas molecules but smaller than its mean free path (λ). There is elastic collision between the gas molecules and the pore wall and therefore no interaction between them thus permeability using these membranes are found to be in acceptable range. On the other hand, for selectivity using pure gases, the separation factor is defined by the ratio of permeability coefficient of gas A to gas B whilst the theoretical (Knudsen) separation factor is defined by:

$$\propto_{A/B} = \sqrt{\frac{MW_B}{MW_A}}$$

Where MW_B AND MW_A are the molecular weights of B and A respectively

The Figures 4 and 5 show that the 200nm and 6000nm membranes, which have very large pore sizes, do not approach ideality (i.e. the orange line depicting ratio of the square root of the molecular weight of gases) compared to the 15nm membrane. Instead, the larger pore-sized membranes show that the gas selectivities are farther away from the ideal knudsen selectivity and show a viscous flow which does not fall into the desired selectivity range. The blue plot shows the degree of selectivity of the membrane to methane gas which increased as the membrane pore decreased as the highest selectivity reached for the 6000, 200 and 15nm membranes were 1.55, 1.57 and 1.61 respectively. This means that in order to achieve higher membrane selectivity, a reduction in the pore size of the membrane is necessary. Selectivity above the knudsen range (i.e. the orange line) is desirable for effective separation of the biogas mixture. From Figure 3, it can be seen that the 15nm membrane was able to achieve the highest degree of selectivity at 1 bar compared to the selectivity values derived from other larger pore sized membranes. The results also indicate that the flux of methane through the membrane is greater than that of carbon dioxide using these membranes and portrays a good potential for upgrading of biogas which is a mixture of both. In all cases studied, the gas flux is dependent on the gas molecular weight as the heavier, CO_2 gas molecules showed lower permeability through the membrane compared to the lighter, CH_4 gas. This distinctive feature makes this technology viable for gas separation.

5. CONCLUSIONS

This research proposes membrane technology as an efficient means to transform biogas and shows good permeability characteristics for the gases studied. The results from experiments show that the molecular weight of the gases determines their permeation rate. In the case

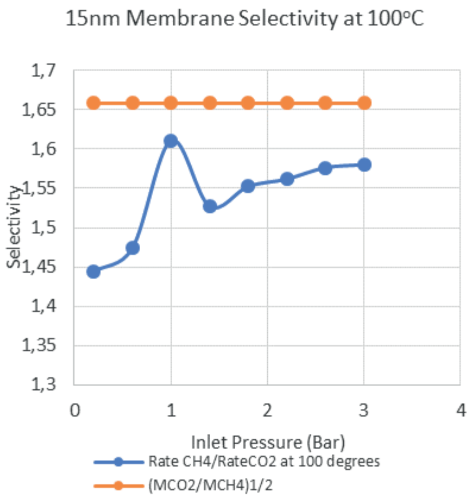

FIGURE 3: Effect of pressure drop on gas ratios at 100 degrees through a 15nm membrane.

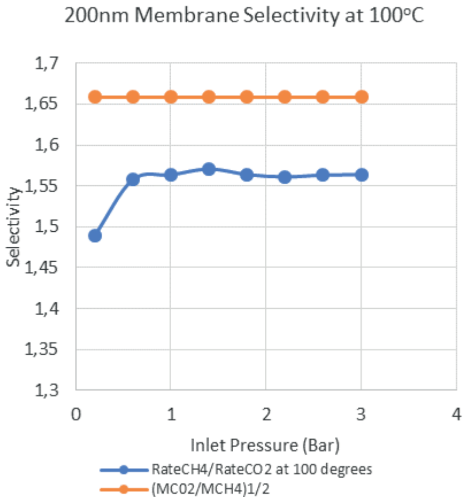

FIGURE 4: Effect of pressure drop on gas ratios at 100 degrees through a 200nm membrane.

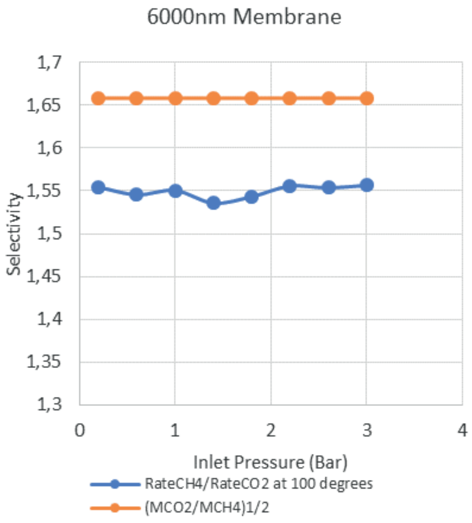

FIGURE 5: Effect of pressure drop on gas ratios at 100 degrees through a 6000nm membrane.

where the pore size is large, as in the 200nm and 6000nm membrane, there is viscous flow through the pores which is undesirable because the selectivity of the membrane is reduced. However, where membranes of smaller pore size is used, pressure drop across the membrane caused the gases to diffuse at different rates through the pores, showing increased selectivity to methane gas thus proving that gas separation can take place.

It can also be deduced from these results that the 15nm membrane shows the greatest separation efficiency as the flux of CO_2 is restricted compared to CH_4; and the ratio of methane flowrate to carbon dioxide approaches the ideal knudsen regime. An inverse relationship was observed between permeance and molecular weight of the individual gases which also confirms Knudsen flow mechanism.

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