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WEENTECH Proceedings in Energy 5 (2019) 195-205

4th International Conference on Energy, Environment and Economics, ICEEE2019, 20-22 August 2019, Edinburgh Conference Centre, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

Comparative evaluation of the effect of pore size and temperature on gas transport in nano-structured ceramic membranes for biogas upgrading

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Abstract

As a result of rising economies and environmental constraints, the demand for clean and renewable sources of energy is fast increasing. Biogas is a renewable form of energy that fits all expectations in terms of delivery, cost, and greenhouse emissions reduction. Biogas utilization is advantageous because it is a means of creating wealth from daily human, agricultural, household and municipal waste that could otherwise be polluting the environment as waste is deposited on a daily basis which are potential biogas sources; it is not dependent on weather conditions as other renewable forms (solar and wind). Biogas can also be compressed, stored and transported, and therefore easily responds to changes in demand. This paper entails the use of nano-structured membranes to upgrade biogas (which contains primarily methane and carbon dioxide). The benefits of membranes include their compact structure and ease of usage with low maintenance, their low running costs and minimal loss of the upgraded gas. 15nm, 200nm and 6000nm membranes were used to ascertain the flux of the model biogas mixture passing through it under various operating conditions. In each case, the exit flowrate of methane was higher than that of carbon dioxide and this is attributed to the pore sizes of the membrane and its ability to filter the heavier gases. The results show that the molecular weight of the gases also play a role in their permeation rate as it follows the Knudsen regime.

Keywords: Biogas upgrading; Sustainable; Nano-structured; Ceramic; Membrane; Carbon capture

https://doi.org/10.32438/WPE.8319

Manuscript History

Receipt of completed manuscript: 12 March 2019

Receipt of Revised Manuscript: 11 April 2019

Date of Acceptance: 13 April 2019

Online available from: 12 November 2019

1. Introduction

The world's population is fast increasing and the demand for energy will have to increase to support this growth. By 2040, world population is estimated to reach 9.2 billion people, which is 1.8 billion more than the current population, and global energy demand to increase by nearly 25% [1]. Biogas holds a promising future in the sustainable supply of low-cost energy that will also help reduce greenhouse gas emission, which has been a major concern worldwide [2]. Greenhouse emissions are the release of gases (especially CO_2, CH_4 and nitrous oxide) into the atmosphere that causes an effect known as global warming. Global warming is strongly linked to various problems associated with climate change and environmental degradation which have negative effects on the economy, ecosystems and most importantly, human life [3]. For these reasons, the retrieval and upgrade of biogas is a major subject in energy production and a solution to various challenges relating to clean energy.

Biogas is the gas given off from the anaerobic breakdown of organic waste materials [4]. This gas can be very useful in our everyday life as it can be used as fuel for transportation, heating and electricity. Biogas may be used directly but in order to fully harness its potential as a fuel, cleaning and upgrading must be done to remove contaminants. This would increase the heating value of the fuel and make its application vast in many fields including injection into the natural gas grid. Currently, biogas is being upgraded by various techniques including scrubbing, pressure swing adsorption, membrane and cryogenic.

The use of biogas as opposed to other fuels has many advantages in that it is a clean and renewable source of energy. Biogas generation is not reliant on external factors as the production process occurs in nature. Environmental concerns are also diminished as waste is efficiently managed and the atmosphere is made cleaner and more conducive, the cost of waste management becomes an investment as produced biogas becomes an alternative source of energy that can be used locally and exported for income generation.

The main project deliverable will be an enhanced, multi-technique nano-structured membrane unit that integrates existing proven technologies for use in biogas production facilities. One of the prime goals is to demonstrate long-term performance and reliability under simulated industrial conditions.

The main objectives are:

1. To reduce greenhouse gas emissions and the effect of global warming by utilizing biogas. This is clean and renewable source of energy.
2. To harness biogas as source of energy and lessen reliance on other fossil fuels. This would also reduce the cost of importation of fossil fuels since biogas is available in abundance
3. To create wealth from waste by upgrading biogas generated from organic waste materials
4. To increase the efficiency of the overall process in terms of energy consumption, purity and recovery of bio-methane produced.

1.1 Absorption by Scrubbing

Figure 1 shows a schematic flow diagram of a water/chemical scrubbing system for CO_2 removal. Water scrubbing is used to eliminate CO_2 and H_2S, which are more soluble in water than CH_4. The absorption procedure is purely physical; normally biogas is pressurized and passed through the base of a packed column while water is sustained on the top and the process is carried out counter-currently. The water which exits the column with retained CO_2 and/or H_2S can be recovered and reinjected again to the scrubber. Recovery is done by de-pressuring or stripping with air in a similar manner [5]. Stripping with air is not suggested when high amounts of H_2S are handled because hydrogen sulphide is heavier than air

and extremely combustible. In the case where cheap water can be utilized, for instance, outlet water from a sewage treatment plant, the most cost-effective technique is not to re-circulate the water [6].
On the other hand, scrubbing can be done using organic solvents like mixtures of methanol and dimethyl ethers of polyethylene glycol [7]. This method relies on the principle of solubility and is similar to the process of water scrubbing. The disparity between water and polyethylene glycol is that CO_2 and H_2S are more soluble in polyethylene glycol which brings about a lower solvent demand and diminished pumping [8].

The use of chemical scrubbers for absorption includes the development of reversible chemical bonds between the solute and the solvent. Recovery of the solvent, consequently, includes breaking of these bonds and this requires a relatively high energy input. Aqueous solutions of alkaline salts and amines are typical solvents used [7].

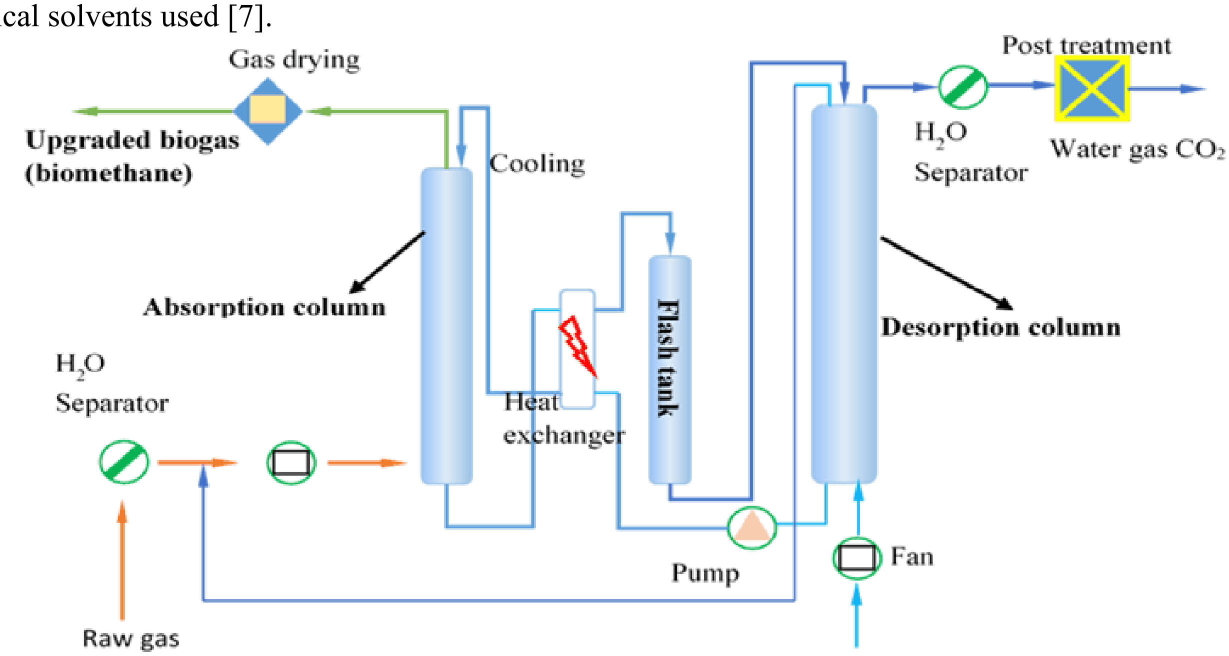

Fig. 1 Water and Organic Solvent Scrubbing for CO_2 Removal [9]

1.2 Pressure Swing Adsorption

Figure 2 shows a schematic diagram describing the pressure swing adsorption for CO_2 removal. Pressure swing adsorption (PSA) is used to separate gas mixtures according to the components' molecular characteristics and attraction to an adsorbent material. Absorption materials, like zeolites or initiated carbon, are utilized as a molecular sieve, specially adsorbing the target gas at high pressure. The procedure then swings to low pressure to desorb the adsorbent material. This process depends on the principle that under high pressure, gases have a tendency to be pulled in to solid surfaces or are "adsorbed". Afterwards, the gas is discharged or desorbed when the pressure is reduced [5, 10]. Pressure swing adsorption processes can be used to separate gas mixtures because each component would be adsorbed at different paces. Operating two vessels simultaneously permits consistent build-up of the target gas and permits the pressure distributing evenly throughout the process, in which the gas flowing out of the vessel being depressurized is utilized to pressurize the next vessel [7, 8].

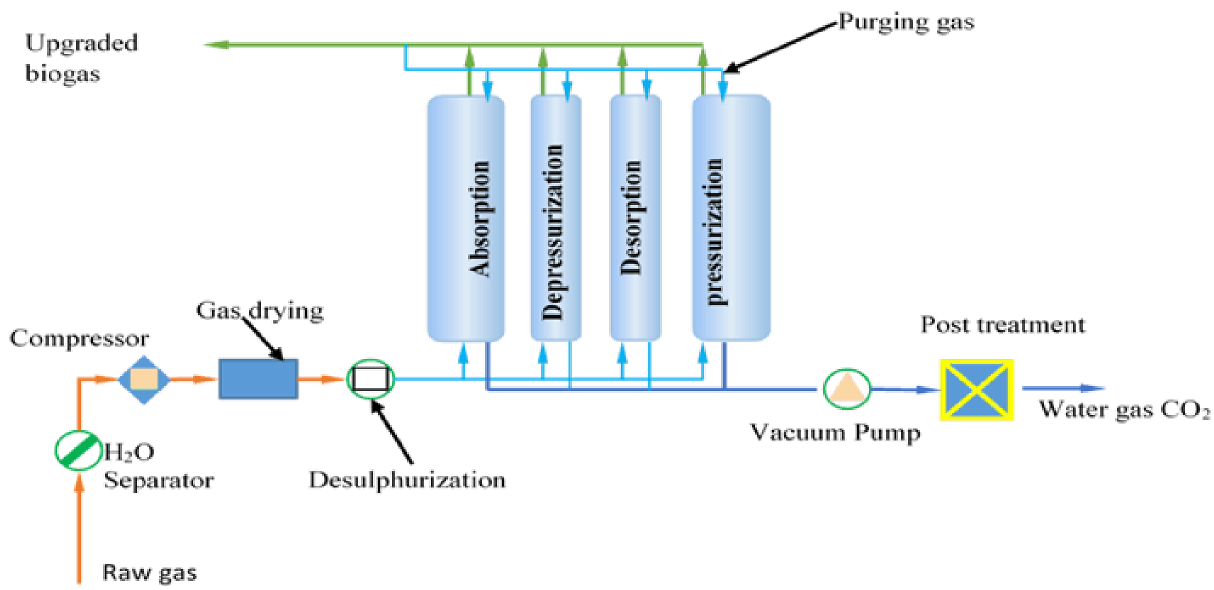

Fig. 2 Pressure Swing Adsorption Technology for CO_2 Removal [9]

1.3 Membrane Purification

Figure 3 shows a schematic diagram describing gas transport membrane separation process. In membrane purification, the gas mixture is passed through a thin membrane (film) which restricts the passage of some of its components [5]. Solid membranes can be built as hollow fibre modules that provide a large surface area. There are two membrane separation strategies: high pressure gas separation and gas-liquid adsorption. The high-pressure separation specifically separates hydrogen sulphide and carbon dioxide from methane while the gas-liquid adsorption uses micro-permeable hydrophobic films; the carbon dioxide and hydrogen sulphide break up into the fluid while methane remains a gas and is collected [7,8].

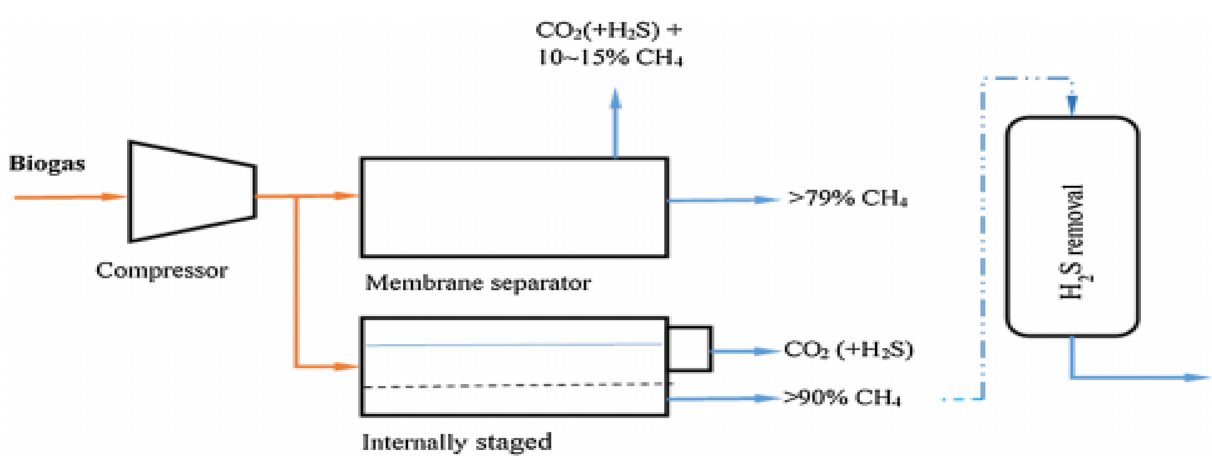

Fig. 3 *Membrane Separation Process [9]*

1.4 Cryogenic Separation

Figure 4 shows a flow diagram describing the cryogenic separation process for gas separation. This purification process separates CH_4 from CO_2, H_2S and all different biogas contaminants. This is possible because every contaminant condenses at an alternate temperature-pressure domain. This process works at low temperatures, close to -100^{O}C, and at high pressures of close to 40 bars. Operation requirements are maintained by utilizing a direct arrangement of compressors and heat exchangers. At the end, the refining section splits CH_4 from alternate contaminants, predominantly H_2S and CO_2. However, this process is expensive relative to other means of gas separation [5, 7, 8].

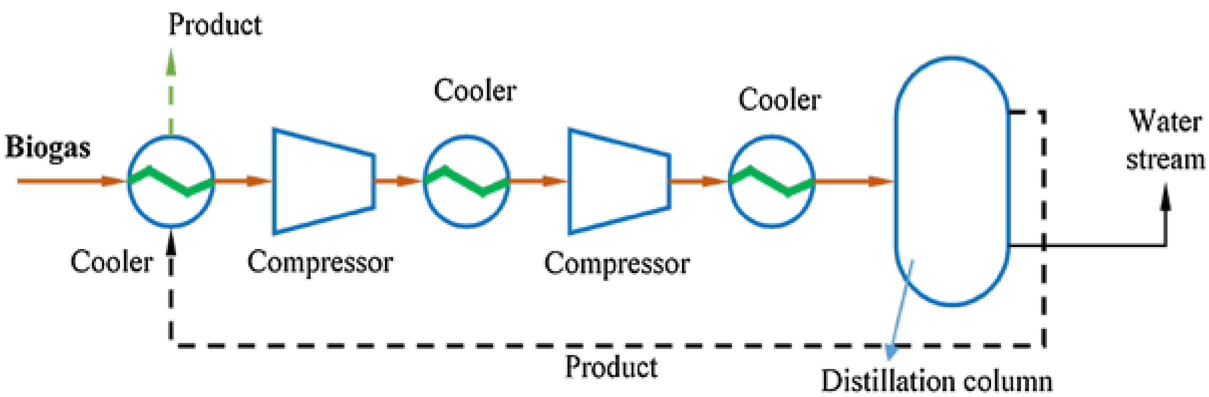

Fig. 4 Cryogenic Gas Separation Process [9]

Table 1 Comparison of current biogas upgrading techniques [7]

	Cryogenic	PSA	Water Scrubbing	Physical Scrubbing	Chemical Absorption	Membrane Separation
Consumption for raw biogas (kWh/Nm^3)	0.76	0.23-0.30	0.25-0.30	0.2-0.3	0.05-0.15	0.18-0.20
Consumption for clean biogas (kWh/Nm^3)	na	0.29-1.0	0.3-0.9	0.4	0.05-0.25	0.14-0.26
Heat consumption(kWh/Nm^3)	na	none	none	<0.2	0.50-0.75	none
Heat demand (°C)	-196	na	na	55-80	100-180	na
Cost	high	medium	medium	medium	high	high
CH_4 losses (%)	2	<4	<2	2-4	<0.1	<0.6
CH_4 recovery (%)	97-98	96-98	96-98	96-98	96-99	96-98
Pre-purification	yes	yes	optional	optional	yes	optional
H_2S co-removal	yes	possible	yes	possible	contaminant	possible
N_2 and O_2 co-removal	yes	possible	no	no	no	partial
Operation pressure (bar)	80	3-10	4-10	4-8	atmospheric	5-8
Pressure at outlet (bar)	8-10	4-5	7-10	1.3-7.5	4-5	4-6

na: not available

The advantages of membrane technology over other methods are briefly highlighted in table 1 above; there is a low possibility of methane loss via the process, a good possibility of removing other contaminants in the gas stream (such as H_2S,N_2,O_2), no heat consumption and this would in turn have a massive impact on total running costs thereby dismissing the initial high cost of installation.

2. Problem identification and basic principle

Due to fast growing economies, the demand for energy is increasing daily without options for more sources of energy to sustain the economies. In fact, the current energy sources such as petroleum, coal and other fossils are known to emit carbon dioxide as a by-product of their processing. Carbon dioxide is a greenhouse gas and when emitted into the atmosphere leads to global warming which has adverse effects on climate change that can cause disasters and lead to loss of life and properties.

Biogas holds a promising future to solving these challenges as it utilizes these gases as a renewable fuel to meet economic demand and prevent emissions that cause global warming. In this article, the use of nano-structured membranes would be utilized for the biogas upgrading process would be studied.

The current methods of upgrading biogas are detailed in the previous section. Currently, chemical scrubbing is most widely used on an industrial scale, however, the process of using scrubbers is energy consuming and requires the use of toxic chemicals which are non-recyclable, this results in a significant amount of waste products that need to be properly disposed of thereby increasing costs. In this study, 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. In general, membranes are classified as either polymeric or inorganic membranes. Polymer membranes have been studied over time for use in gas separation. However, due to demands for use of membranes in acidic environments, inorganic ceramic membranes which do not suffer these chemical limitations are being considered [11]. Material selection to achieve the desired performance of membranes require good knowledge of chemical properties and transport phenomena which will be involved in the specific application. In this study, ceramic membranes are used which have high permeability, are suitable with temperature sensitive materials without being chemically altered, do not involve phase change, and they are simple to operate [11]. Nevertheless, the challenge with this technology is its low selectivity. Material enhancers would be used to deliver an enhanced, multi-technique nano-structured membrane unit with improved selectivity that integrates existing proven technologies for use in biogas production facilities and demonstrate long-term performance and reliability under simulated industrial conditions. The first step, which is detailed in this paper, is to observe the behaviour and flow mechanism of the gases as they flow through the membranes under various conditions of temperature and pressure using different pore sizes.

3. Proposed Technology

A membrane is a permeable or semi-permeable phase which controls the flow of compounds and hence provides one product with less of certain components and another product concentrated in these components [12]. The performance of a membrane is defined by its flux and selectivity.

The flux is also known as the permeation rate and it is the flowrate per unit area at which the fluid passes through the area of the membrane. Selectivity refers to the concentration of component passing through the membrane versus the concentration in the feed [13]. Aside high flux or permeability and selectivity, membrane materials should possess other properties such as chemical resistance, thermal stability, mechanical stability and stable operation

This set up will allow us to measure the permeability of a single gas through the nano-structured membrane. At the inlet, a pressurized gas for analysis would be fed in at constant pressure, the flow meter would check that a steady constant driving force is maintained. At the outlet, a flow meter would also measure the flow of the outgoing gas. This would give an estimate of what the permeability of the membrane is given that both inlet and outlet rates are measured. The membrane module would then be flushed to enable us to measure the flow characteristics of another gas of interest by repeating the procedure. By comparing the flow characteristics of the different gases, the perm-selectivity of the membrane can be found.

In further studies, 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 pass through the chamber to measure the total permeation across the module by measuring how fast the outlet pressure increases. By checking the outlet gas composition, we can 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. Methodology

The experimental set-up used in this work is shown in the figure 5. This 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.

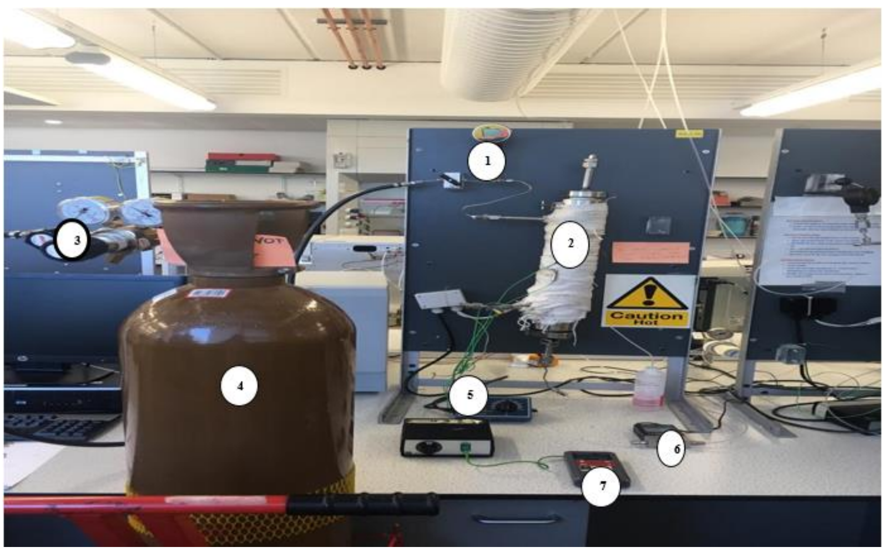

Fig. 5 Experimental set-up showing all equipment including; pressure gauge (1), membrane module covered with heating tape (2), gas regulator (3), gas cylinder (4), heat regulator (5), volumetric meter (6) and temperature indicator(7)

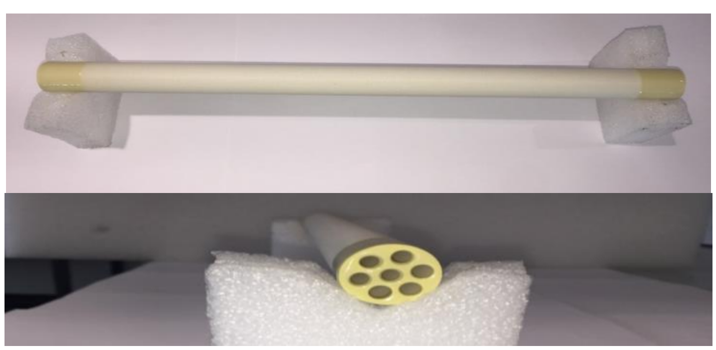

Fig. 6 *Top view(above) and side view(below) of a membrane*

A leak test was conducted prior to each experiment. At the inlet, the methane gas to be analyzed was fed in at 0.2 bar and readings were recorded while operating at thermal stability of 20ºC, 50ºC, 70ºC and 100ºC respectively. 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. The experiment was repeated at 0.6, 1.0, 1.4, 1.8, 2.2, 2.6 and 3.0 bar.

The membrane module was flushed 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.

5. Results and Discussion

5.1 Effect of Pressure Drop on Permeate Flowrate for different Temperatures and Membrane Pore Sizes

The set of graphs below show the relationship between the exit flowrate and inlet pressure for each gas used in the experiment.

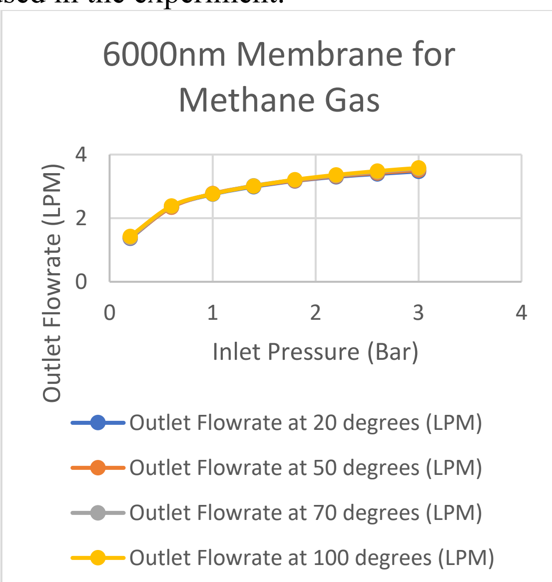

Fig. 7 Effect of pressure drop on the flowrate of methane gas at various temperatures through a 6000nm membrane

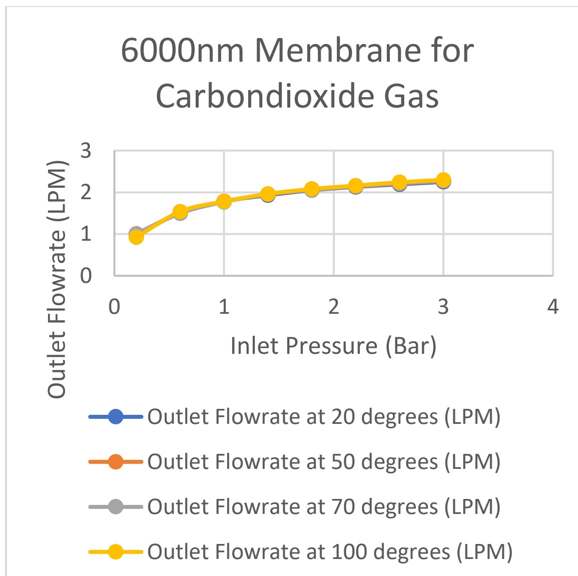

Fig. 8 Effect of pressure drop on the flowrate of carbon dioxide gas at various temperatures through a 6000nm membrane

It was observed that as pressure increases the exit flowrate of each gas steadily rises (as in figures 7 and 8). In terms of temperature, between 20 and 100^{0}C, the effect is negligible with no significant change in the exit flowrate of each gas which shows that the performance of the membrane was not affected by changes in operating conditions

5.2 Gas Comparison

The set of graphs below show a comparison of the effect of pressure drop on methane and carbon dioxide outlet flowrate at set temperatures.

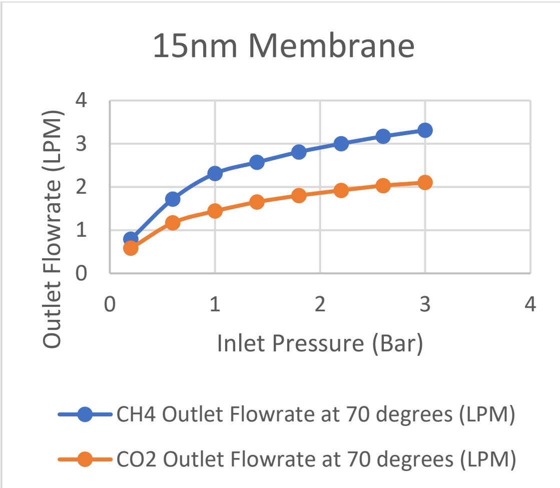

Fig. 9 Effect of pressure drop on methane and carbon dioxide flowrate at 70 degrees through a 15nm membrane

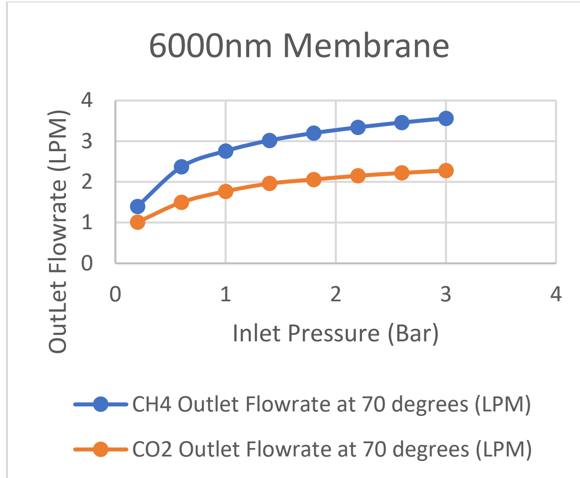

Fig. 10 Effect of pressure drop on methane and carbon dioxide flowrate at 70 degrees through a 60000nm membrane

It can also be seen from the figures 9 and 10 that the exit flowrate of each gas increases with increasing pore size as the 6000nm membrane show very high exit flowrate compare to the 15nm membranes, this is attributed to the large pores that allow carbon dioxide to flow along with methane without any restriction.

5.3 Gas Ratios

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.

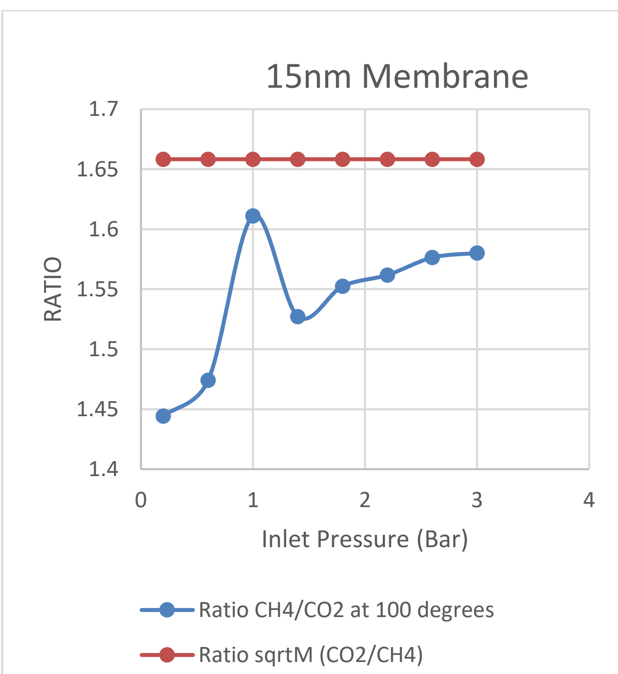

Fig. 11 Effect of pressure drop on gas ratios at 100 degrees through a 15nm membrane

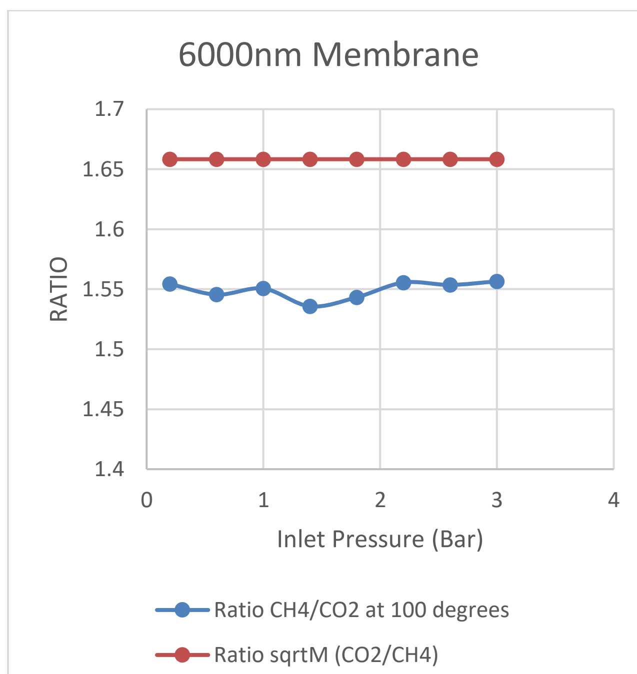

Fig. 12 Effect of pressure drop on gas ratios at 100 degrees through a 6000nm membrane

Figures 11 and 12 show that the membrane with larger pore size of 6000nm membrane does not approach ideality (i.e. the orange line depicting ratio of the square root of the molecular weight of gases) compared to the smaller sized 15nm membrane pores. Thus, gas separation using the 6000nm membrane would be cumbersome compared to using membranes with smaller pore size as described by Domenico in his findings [14].

5. Conclusions

- The experiments show that pressure has a greater influence on the gas flow through membranes compared to temperature with no significant changes in the graphs from 20 – 100^{o}C
- The flux of methane through the membrane is greater than that of carbon dioxide in regular pore geometry and depicts a greater potential for separation/upgrading of biogas which is a mixture of both.
- Results also show that flux is dependent on the gas molecular weight, kinematic viscosity and viscosity as the heavier, larger and more viscous gas CO_2 did not pass through the membrane as quickly as the lighter, smaller and less viscous CH_4 gas. This agrees with Keizer et al's model that molecular size is a determining factor in considering the rate of permeation of gases [15].
- It has been identified from the experiments that the 15nm membrane shows the greatest efficiency as the flux of CO_2 is restricted compared to CH_4; and the ratio of CH_4 flowrate to CO_2 approaches the ideal knudsen regime with optimization at 1 bar. Thus, the experiments illustrate good separation of the greenhouse gases present in biogas that would increase the heating value of the fuel making it easily adapted for other processes.
- By modifying the membrane to obtain a lower pore size a surface diffusion mechanism is expected because the contact between gas molecules and the inner surface would be very strong leading to an increase in overall efficiency of the process. It is therefore recommended that further investigation on ceramic membranes should be carried out using membrane pore sizes less than 15nm.

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