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Research Paper

LOW PRESSURE SEPARATION TECHNIQUE OF BIOGAS INTO CH_4 AND CO_2 EMPLOYING PDMS MEMBRANE

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ABSTRACT

Continuous research has been going on to find out easy and cheap technique for separation of biogas employing membrane technology. Work has been carried out to find the best suited membrane for gas separation with low operational pressure and cost. Membrane gas separation technique is very advantageous as it doesn't require huge infrastructure for plant set up due to low pressure requirement for the process and availability of membrane at a reasonable cost. This technique has generated immense commercial interest. This paper deals with an advanced separation technique employing poly dimethylsiloxane (PDMS) hollow fiber membrane module. The results clearly show that, PDMS double membrane module in series gave the upgraded methane with 93 % purity and carbon dioxide with 96% purity.

KEYWORDS: Biogas, Methane, Carbon dioxide, Membrane Separation Technique.

1 INTRODUCTION

Environmental issues due to emission of pollutants from combustion of fossil fuels have assumed global proportions. The use of fossil fuels for generation of electricity contributes to a number of environmental problems all over the world[1]. Thus there is a real need for development of a sustainable & renewable energy source to fulfill the increasing energy demand. In the long term context, it has become mandatory to think of renewable sources of energy. New techniques are being developed for effective and proper utilization of renewable energy. Techniques for generation of biogas were established four decades ego and all of us are well acquainted with it. Almost in every village household biogas plants has been set up. In order to increase the calorific value of the biogas, it is necessary to remove CO_2 from it.

This paper deals with the performance enhancement of Biogas plant employing membrane for separation of CH_4 and CO_2. The membrane gas separation based process aims at upgrading the biogas to substitute natural gas using low pressure (up to 3 bar) and distributing the substitute natural gas in the natural gas network. The by-product of the membrane gas separation process is a stream rich in CO_2 which could be liquefied to produce very pure, industrial CO_2. [2] After liquefaction, the remaining biogas components, which include CH_4, are recycled into the membrane gas separation process, thereby minimizing the loss of biogas. Both gases have very high industrial value. Bio-Methane also known as SNG has been used as a substitute of vehicle fuel and also can be used to produce electricity. Carbon dioxide can be used as green house gas & in supercritical fluid application, carbonated drinks and ice making industries. [3]

Biogas Generation

Table No: 1.1 Composition of Biogas[4]

Substrate	Symbol	Percentage
METHANE	CH_4	50-70
CARBON DIOXIDE	CO_2	30-40
HYDROGEN	H_2	5-10
NITROGEN	N_2	1-2
WATER VAPOUR	H_2O	0.3
HYDROGEN SULPHIDE	H_2S	20-20,000 ppm

Biogas generation includes anaerobic digestion process of biomass by certain bacteria. The composition of biogas is given in the table 1.

The produced biogas is a colorless, odorless and flammable gas which having an energy content of 20 MJ/m^3 .The ratio of methane to carbon dioxide varies depending on the input materials (feedstock) and the completeness of the process. The biomass used in this process has high moisture content, such as animal dung, sewage sludge, crop byproducts, and organic waste from household and industry [5]. The gas coming out from biogas plant has CH_4, CO_2, H_2, N_2, H_2S and traces of water, as given in above table and hence biogas has a comparatively less calorific value than natural gas.

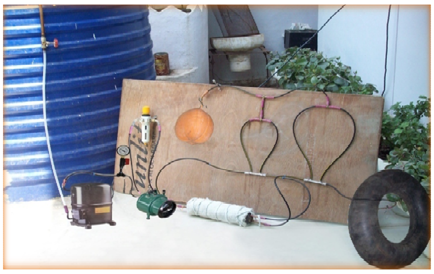
2. EXPERIMENTAL DETAILS:

2.1 Materials

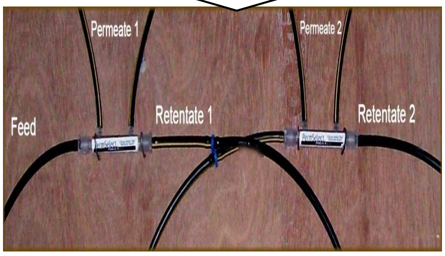
Biogas is obtained from the biogas plant running on kitchen waste, the membrane material used for this project was hydrophobic, dense, polymeric hollow fiber membrane made up of silicon cured with platinum.. The membrane was purchased from Med Array Inc. USA (Permselect). The size of the membrane is 10 cm^3 i.e. PDMSXA-10 [6]. For analysis purpose CH_4 gas analyzer and CO_2 gas analyzer are used. Apart from this Gas flow meter, Compressor, Moisture separator, Heater, pipe connectors and pressure guage is used for the experiment

2.2 Experimental Set-up

A small biogas plant running on kitchen waste installed by the Appropriate Rural Technology Institute (ARTI) Pune is used in this set up. The system for separation was developed on the plywood board by fixing all necessary accessories. Compressor, pressure gauge with ball valve, gas flow meter, moisture separator, pre-heater and membrane module was attached in a series. Two way & three way connectors for pipe connections; plastic pipe was used for connecting the all the accessories. Gas storing bags (bladder and tube) were used for collecting samples for analysis. Gas leakages were checked with the help of soap solution.



Photograph 2.1: Experimental set up for CH_4 and CO_2 gas separation



Photograph 2.2: Close up of membrane module connection in series

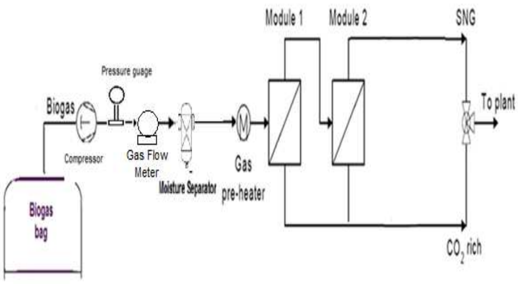


Figure – 2.1 : Process flow diagram for biogas separation through membrane module

2.3 Experimental Procedure

1. Bio-gas outlet was attached to compressor.
2. In compressor, the gas was stored and released at 1.6 bar pressure through pressure valve which was attached immediate next to compressor.
3. Gas flow meter for flow rate measurement was attached next to pressure valve.
4. Constant flow rate was maintained at 7.8 lit/hr as seen on gas flow meter.
5. Moisture separator was placed next to gas flow meter to remove the moisture content of Bio-gas
6. It was then passed through gas pre heater to maintain the temperature between 33-40 ^{o}C.
7. The heated Bio-gas was then passed through first membrane module.
8. The retentate of first module (R-1) was passed to second module and retentate of second module (R-2) was collected separately for analysis.
9. The permeate of first membrane module (P-1) and second membrane module (P-2) were separately collected for analysis.

2.4 Analytical methods for biogas:

Analytical testing for biogas was necessary to find out the biogas composition before feeding to membrane and percent purity of CH_4 as a retentate and CO_2 as permeate after processing through membrane module.

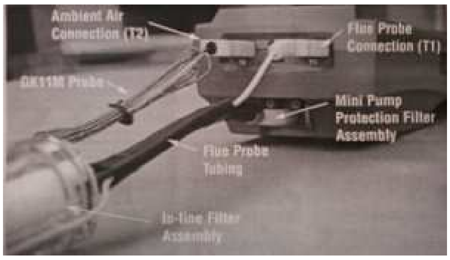
The instrument involved in the analytical testing of biogas was mentioned below

1. CO_2 - gas analyzer
2. CH_4 - gas analyzer

In this project, the above mentioned gas analyzer were used. This was very handy and with the help of same one can directly obtain the gas percentage on the site itself. For determination of $CO_{2,}$ a CO_2 gas analyzer was used. For determination of $CH_{4,}$ CH4 gas analyzer was used. The readings were taken for biogas in before and after processing through membrane.

2.4.1 CO_2 Gas Analyzer:

The CO_2 Gas Analyzer named SUMMIT 714 'A' - flue gas analyzer was used for the analysis of carbon dioxide percentage in feed biogas as well as in permeate collected



Photograph -3.1: CO_2 - Gas Analyzer

Procedure for determination of % CO_2 by using CO_2 gas analyzer:

Step 1: Connect ambient air connection as shown in Photograph - 3.1 to port named T-2 for temperature measurement. It gave the both atmospheric as well as gas temperature.

Step 2: Connect one part of flue probe tubing named Flue probe to T-1 as shown in Photograph 3.1 from which CO_2 enters inside the gas analyzer.

Step 3: Connect other end of flue probe tubing to the gas holding bag or directly attached to gas line.

Step 4: Keep In-line filter assembly always horizontal for best result as shown in Photograph 3.1.

Step 5: Start SCROLL button and wait for screen appears

Step 6: After 10 – 15 second the result was shown on the screen 1.

Step 7: Note down the result (% CO_2) for calculation purpose.

2.4.2 CH_4 Gas Analyzer

The CH_4 Gas Analyzer named Technovation Infrared Analyzer - PIR-89 'A' was used for the analysis of methane percentage in feed biogas as well as in retentate collected.

Photograph -3.2: CH_4 Gas Analyzer

Procedure for determination of % CH_4 by using CH_4 gas analyzer:

Step 1:Switch on the instrument by using power switch and then pump was used to switch on the

internal pump in which draw the sample whose concentration was to be measure.
Step 2: The potentiometer was used to ZERO the instrument.
Step 3: This potentiometer was used to calibrate the instrument and wait for 2-3 minutes.
Step 4: To take a reading of sample gas, it can be drawn into the instrument by pressing the pump switch.
Step 5: Gas sucked through hose tube into the sensor.
Step 6: Reading of gas was noted after 1-2 minutes as the display stabilized.
Step 7: Note down the reading in % and used for calculations.
Step 8: Purge the instrument with fresh air after used.

3. RESULT AND DISCUSSION:

At 1.6 bar pressure

As per the analytical procedures of CO_2 and CH_4, purity percentage of CO_2 and CH_4 in feed, permeate and retentate for single membrane module and double membrane module were noted down and tabulated below table. The pressure was maintained at 1.6 bar, accordingly the gas flow rate was 7.8 lit / hr recorded on gas flow meter. Temperature was maintained constant at 33^O Celsius.

Table No: 3.1: Reading of feed composition, permeate and retentate for Single membrane module at 1.6 bar pressure

SINGLE MEMBRANE MODULE									
PRESSURE	FLOW RATE	FEED COMPOSTION			PERMEATE-1		RETENTATE -1		
BAR	Lit/Hr	CH_4 %	CO_2 %	Other %	CO_2 %	Other %	CH_4 %	CO_2 %	Other %
1.6	7.8	61	36	3	91	9	86.9	9.7	3.4

Table No 3.2: Reading of feed composition, permeate and retentate for Double membrane module at 1.6 bar pressure

DOUBLE MEMBRANE MODULE											
PRESSURE	FLOW RATE	FEED COMPOSTION			PERMEATE-1		PERMEATE -2		RETENTATE -1		
BAR	Lit/Hr	CH_4 %	CO_2 %	Other %	CO_2 %	Other %	CO_2 %	Other %	CH_4 %	CO_2 %	Other %
1.6	7.8	61	36	3	92	8	100	0	93.6	3.9	2.5

Table No: 3.3: Percent removal efficiency of single and double membrane module at 1.6 bar pressure

Pressure	Flow rate	Single module		Double module		
(bar)	(lit/hr)	% removal efficiency for P-1	% removal efficiency for R-1	% removal efficiency for P-1	% removal efficiency for P-2	% removal efficiency for R-2
1.6	7.8	85.24	20.32	84.44	99.20	34.15

The above table indicated that the double membrane module can separate CH_4 and CO_2 more efficiently than single membrane module. The percent removal efficiency of permeate -1 and retentate-1 for the single membrane module was 85.24 % and 20.32 % respectively where as the percent removal efficiency of permeate -1, permeate -2 and retentate-2 for double membrane module was 84.44%, 99.20 % and 34.15% respectively. Hence from the above table it was observed that the percent removal efficiency increases from 20.32 % to 34.15 % in retentate and from 85.24% to 91.82 % in permeate.

At 1.8 bar pressure

Similarly, purity percentage of CO_2 and CH_4 in feed, permeate and retentate for single membrane module were noted down and tabulated below in table

Table No: 3.4: Reading of feed composition, permeate and retentate for Single membrane module at 1.8 bar pressure

SINGLE MEMBRANE MODULE									
PRESSURE	FLOW RATE	FEED COMPOSTION			PERMEATE-1		RETENTATE -1		
BAR	Lit/Hr	CH_4 %	CO_2 %	Other %	CO_2 %	Other %	CH_4 %	CO_2 %	Other %
1.8	9.5	62	35	3	92	8	87	9.4	2.83

The single membrane module wasn't enough to separate the CH_4 and CO_2 as per desired percentage. Hence there must be need of second module attached in series to increase the purity percentage of CH_4 and CO_2. The % R of permeate of single membrane module was 84.52% and for retentate was 21.35%. Hence in order to increase the % removal efficiency (%R), the double membrane module has to be used.
Percentage purity of CO_2 and CH_4 in feed, permeate and retentate for double membrane module were noted down and tabulated below in table.
The pressure was maintained at 1.8 bar, accordingly the gas flow rate was 9.5 lit / hr recorded on gas flow meter. Temperature was maintained constant at 33^O Celsius.

Table No: 3.5: Reading of feed composition, permeate and retentate for Double membrane module at 1.8 bar pressure

DOUBLE MEMBRANE MODULE											
PRESSURE	FLOW RATE	FEED COMPOSTION			PERMEATE -1		PERMEATE-2		RETENTATE -1		
BAR	Lit/Hr	CH_4 %	CO_2 %	Other %	CO_2 %	Other %	CO_2 %	Other %	CH_4 %	CO_2 %	Other %
1.8	9.5	62	35	3	92	8	100	0	93.56	3.11	3.11

Table No: 3.6
Percent removal Efficiency of Single and Double membrane Module at 1.8 bar pressure

Pressure	Flow rate	Single module		Double module		
(bar)	(lit/hr)	% removal Efficiency for P-1	% removal Efficiency for R-1	% removal efficiency for P-1	% removal efficiency for P-2	% removal efficiency for R-2
1.8	9.5	84.52	21.35	84.52	99.18	38.51

The above table indicated that the double membrane module can separate CH_4 and CO_2 more efficiently than single membrane module. The percent removal efficiency of permeate -1 and retentate-1 for the single membrane module was 85.24 % and 20.32 % respectively where as the percent removal efficiency of permeate -1, permeate -2 and retentate-2 for double membrane module was 84.44%, 99.20 % and 34.15% respectively. Hence from the above table it was observed that the percent removal efficiency increases from 20.32 % to 34.15 % in retentate and from 85.24% to 91.82 % in permeate.

At 2 bar pressure

Similarly, purity percentage of CO_2 and CH_4 in feed, permeate and retentate for single and double membrane module were noted down and tabulated below table the pressure was maintained at 2 bar, accordingly the gas flow rate was 11.3 lit / hr recorded on gas flow meter. Temperature was maintained constant at 33^O Celsius

Table No: 3.7: Reading of feed composition, permeate and retentate for Single membrane module at 2 bar pressure

SINGLE MEMBRANE MODULE									
PRESSURE	FLOW RATE	FEED COMPOSTION			PERMEATE -1		RETENTATE -1		
BAR	Lit/Hr	CH_4 %	CO_2 %	Other %	CO_2 %	Other %	CH_4 %	CO_2 %	Other %
2	11.3	64	33	3	92.5	7.5	88.2	9.68	7.8

Table No: 3.8: Reading of feed composition, permeate and retentate for Double membrane module at 2 bar pressure

DOUBLE MEMBRANE MODULE											
PRESSURE	FLOW RATE	FEED COMPOSTION			PERMEATE-1		PERMEATE -2		RETENTATE -1		
BAR	Lit/Hr	CH_4 %	CO_2 %	Other %	CO_2 %	Other %	CO_2 %	Other %	CH_4 %	CO_2 %	Other %
2	11.3	64	33	3	92.2	7.8	100	0	94.2	3.9	1.9

Table No: 3.9: Percent removal Efficiency of Single and Double membrane Module at 2 bar pressure

Pressure	Flow rate	Single module		Double module		
(bar)	(lit/hr)	% removal efficiency for P-1	% removal efficiency for R- 1	% removal efficiency for P-1	% removal efficiency for P-2	% removal efficiency for R-2
2	11.3	86.73	21.17	84.91	98.62	30.13

The above table indicated that the double membrane module can separate CH_4 and CO_2 more efficiently than single membrane module. The percent removal efficiency of permeate -1 and retentate-1 for the single membrane module was 86.73 % and 21.17 % respectively where as the percent removal efficiency of permeate -1, permeate -2 and retentate-2 for double membrane module was 84.91%, 98.62% and 30.13% respectively. Hence from the above table it was observed that the percent removal efficiency increases from 21.17% to 30.13% in retentate and from 86.73 % to 91.77% in permeate.

3.1 Densities of co$_2$ and ch$_4$ with respect to temperature and pressure:

The above Percent removal efficiency calculations need densities at different pressure for the conversion of gases from gram to liter. The flow meter wasn't available for the measurement of permeates and retentate collected in liters. To overcome the problem, the conversions of gram to liter were needed and for that purpose the densities of methane and carbon dioxide was calculated. By using molecular weight, pressure, gas constant and temperature, density was calculated.

Density can be calculated by following formula, [7]

$$\text{Density}\ (\rho) = \frac{\text{Molecular Weight of gas}}{\text{Gas constant}} \times \frac{\text{Presuure}}{\text{Temperature}}$$

For Example:

Density of CO $_2$ at pressure 1.6 bar & Temp 33^0 C

$$\text{Density}\ (\rho) = \frac{44}{0.08314} \times \frac{1.6}{306} \qquad \frac{\text{kg/kmol}}{\left[\frac{\text{m}^3\text{Bar}}{\text{kmol. K}}\right]} \times \frac{\text{Bar}}{\text{K}}$$

Density of CO_2 = 2.76 kg/m^3

Densities of CH_4 and CO_2 at different pressure and temperature can be calculated and shown in table below:

Table No: 3.1.1 Densities of co$_2$ and ch$_4$ with respect to temperature and pressure

Sr. no.	Pressure(bar)	Temperature(^{0}C)	Density of CH_4(kg/m3)	Density of CO_2(kg/m3)
1	1.6	33	1.006	2.767
2	1.8	33	1.132	3.1131
3	2.0	33	1.257	3.459

3.2 Comparison of different membrane with PDMS membrane:

As per the literature review, different types of membrane was studied and compared with the PDMS membrane. The following table no 6.3 shown the comparison of different membranes with PDMS with their pressure requirement, temperature needed and the type of business whether the membrane suites for the large scale production or small scale production.

Table No 3.2.1: Comparison of different membrane with PDMS membrane

Sr. No	Membrane Type	Pressure Required (Bar)	Temp Required (^{0} Celsius)	Business Type
1.	Zeolite and Inorganic Molecular Sieve Membranes	18-26	27- 98	Large Scale
2	Microporous Glass-Ceramics membrane	7- 8	200- 500	Large Scale
3	Carbon Molecular sieves Membrane	8-16	50- 60	Large scale
4	Asymmetric membrane based on Matrimid® and polysulphone blends	12 – 14	65-95	Large scale
5	Hydrophobic silica membranes	7-10	400-600	Large scale
6.	Polysulfone hollow fiber membrane	10-16	40-90	Large Scale
7	Poly tetra fluoro ethylene (PTFE) Hollow fiber membrane	34-40	60-70	Large scale
8	PDMS Membrane	1-3	33-40	Small scale

From above table, it was clearly distinguished that PDMS membrane was very useful for the separation of biogas than other membrane used for the separation. PDMS membrane required very less pressure and temperature for the operation and can be used for small scale business. [2], [8],[9],[10],[11],[12],[13]

3.3 Silicone permeability coefficients:

Silicon permeability coefficient of CO_2 and CH_4

Table No: 3.3.1: Silicone permeability coefficients

SR NO	GAS NAME	FORMULA	SILICONE PERMEABILITY COEFFICIENT (Barrer)*
1	Carbon dioxide	CO2	3250
2	Methane	CH4	950

*1 Barrer = 10-10 cm^3 (STP) · cm /cm2 · s · cm-Hg

Methane coefficient = 950

Carbon dioxide coefficient = 3250

Separation Factor Ratio of membrane

= 3250/950

= 3.42

The ratio of the permeability coefficient i. e separation factor was calculated 3.42, and that gives the clear indication of separation of both the gases through the silicon membrane.

4. CONCLUSIONS:

In biogas feed, percentage of methane and carbon dioxide was 62 % and 35 % respectively. By using single membrane module, the percentage of the methane and carbon dioxide was upgraded to 87 % and 92% from 62 % and 35 % respectively with some impurities. Hence to obtain higher percentage of methane and carbon dioxide individually, a second membrane module was attached in series. The result obtained from double membrane module is 93% and 96% of methane and carbon dioxide respectively. Hence by using two PDMS membrane module in series gave the upgraded methane with 93 % purity which can be stored in the cylinder and used as SNG which could be directly sold to the market at the rate of Rs 20 / kg whereas the carbon dioxide with 96% purity which can be stored in the cylinder and directly sold in the market at the rate of Rs 60/kg. Both gases can be stored in the cylinder by using bottle filling technique.

According to the experimentation, the rate of gas flow was directly proportional to pressure used in the system up to certain limit. Feed pressure can also affect permeation rates as membrane structure can change under pressure. By comparing the result obtained from calculation, it was observed that up to a certain limit (i.e up to 1.8 bar) pressure, the percent removal efficiency increases and gave better separation of both gases i. e. CH_4 and CO_2. The optimum pressure for the PDMS membrane was found to be 1.8 bar. Further increase in pressure i. e. above 1.8 bar, percent removal efficiency suddenly decreases. Hence to improve the overall efficiency of the process, the optimum pressure must be used.

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