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RESEARCH ARTICLE

BIOGAS SEPARATION BY POLYMER-BASED MEMBRANES

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ABSTRACT

Generation of combustible biogas from anaerobic digestion of food waste is an interesting and developing alternative for the production of a cheap source of energy. In the present work, Torlon polyamide-imide based membrane films were studied for biogas separation. In pure Torlon polymeric membrane, the methane content increased from 62% in feed biogas to 94% methane in retentate. But, there was about 3.7% methane loss into the permeate stream. In a mixed matrix membrane of Torlon-Zif8(20%), the methane content enriched from 62% in feed biogas to 96% methane in retentate, with no loss (0%) of methane into the permeate stream. Thus, this paper describes important development in the application of membranes to purify biogas and enrich its energy/calorific value.

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INTRODUCTION

Fossil fuel (coal, oil and natural gas) reserves are fast depleting and the impact of global warming on the Earth is increasing. According to the 2018 BP (British Petroleum company) Statistical Review of World Energy, global total reserve levels, by fossil fuel, are now: 1035 billion tonnes of coal, 193.5 trillion cubic meters of natural gas, and 1,696.6 billion barrels of crude oil. While these numbers may seem large at a glance, at today's level of extraction BP's estimated proved reserves of coal would be exhausted in 113-151 years, the last cubic meter of natural gas will finish in 2069, and the entire crude oil reserves will deplete by 2067 [1, 2]. In such a scenario, it is important for academic research centers and industries to focus attention of development of alternate sources of energy like renewable wind, solar, hydrogen, hydroelectricty or nuclear energy. One such cheap source of energy for combustion in small to large scale domestic cooking stoves is 'biogas'. Biogas is produced from the anaerobic digestion of organic food/agricultural/municipal waste. When complex organic matter is subject to anaerobic digestion (absence of oxygen) by group of microbes using multi-enzymes, it breaks down via hydrolysis, fermentation, acidogenesis, acetogenesis, methanogenesis to form biogas and residual sludge.

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Biogas comprises methane, hydrogen, carbon dioxide, water vapour and trace quantities of hydrogen sulphide or ammonia or siloxanes. Biogas (methane and hydrogen) is a source of heat energy. The composition and quality of biogas depends upon the organic waste from which it is derived. Biogas typically has a calorific value of 35-44kJ per gm (4800-6900 kcal/m^3), comparable to kerosene, petrol, diesel and LPG and higher than charcoal. Hydrogen and methane are the combustible gases while acid gases like carbon dioxide and hydrogen sulphide reduce the overall calorific value and sometimes cause corrosion problems. Therefore, removal of CO_2 and H_2S from biogas would enrich the CH_4 content and calorific value of the product biogas. Extraction and purification of natural gas is an expensive process. The purification mainly involves separation of carbon dioxide from methane which is usually achieved by absorption/desorption in amine based solvents or Selexol or by adsorption in zeolites or by polymeric membranes under high feed pressure conditions. Natural gas is transported via pipelines to commercial use for combustion for energy generation. But, natural gas reserves are limited and thus, biogas can serve as a cheap and re-generable source of energy. Raw biogas exhibits a significantly lower Wobbe index (heating value) compared to natural gas. Therefore, biogas upgrading is essential. According to the latest 2015 data, there are 17,240 biogas plants and 367 biomethane plants in Europe [3].In India, the production of biogas was 20,757 lakh cubic meters in 2014-15 which is equivalent to 6.6crore domestic LPG cylinders or 5%

of LPG consumption in the country [4]. The majority of biogas plants in Australia are associated with municipal waste treatment facilities. Treating agriculture, biowaste, industrial, landfill and sewage feedstocks, there are 135 biogas plants in Australia [5]. Biogas can be used for heating purposes like lighting cooking stoves or heat transfer in industrial processes or hot water boiler for generating steam for processes, use as a fuel in a gas engine to generate heat or electricity, use as compressed gas to run motor vehicles, room/space heating and transforming into cleaner fuels like syngas for producing ethanol, methanol (by syngas fermentation), gasoline, jet fuels(by Fischer-Tropsch synthesis) and supply of upgraded biomethane into natural gas pipeline system [6,7]. Limitations of biogas are presence of carbon dioxide, hydrogen sulphide and other impurities that reduce its overall calorific value, purity, quality and can cause corrosion problems in compressor, pipelines and transportation or combustion equipment, restriction to near on-site use, disposal of sludge, organic overload when feedstock exceeds biodegradation capacity of microbes and hydraulic overload when the hydraulic retention time is not enough to allow sufficient multiplication of anaerobic microbes leading to decrease in their concentration or eventual wash out causing stoppage of biogas formation and accumulation of VFA (volatile fatty acids) in the digestor. It is therefore important that all liquid inputs, as well as solid inputs, to a digester are measured and recorded [8].

For biogas enrichment, S.Basu et.al.reviewed membranes based on CO_2/CH_4 separation [6] . PRISM® membranes are commercially available membranes for CO_2/CH_4 separation for natural gas upgrading. At present, polyimide membranes are commercially available from a few manufacturers: Medal (Air Liquide), IMS (Praxair) and UBE Industries Ltd. M.Harasimowicz, et.al.studied commercial UBE membranes for simulated binary and ternary biogas [9]. A.G. Chmielewski et.al.provided a short review and studied commercial polyimide hollow fiber modules from UBE for biogas from agricultural waste in Poland [10]. In both studies, while biogas enrichment was achieved, there was about 10% methane loss in the permeate in lab-tests and 3.5-5% methane loss in field tests. A list of membranes for CO_2/CH_4 separation is provided in supplementary section. On the campus of IICT, there is a medium sized biogas plant. Food and vegetable waste is weighed (maximum 150kg) and dumped into a digestor tank. In this tank, microbes biodegrade the waste (anaerobic digestion) and release biogas. The biogas collects in an overhead balloon. This biogas is compressed to about 4bar pressure and sent through pipelines to cooking stoves. This biogas serves as a cooking gas to the canteen in the institute.
In the present work, an isobaric gas permeation system operating in isochoric mode was setup and connected to a bypass from the biogas pipeline in the plant. The gas separation performance of three polymer-based membranes was experimentally studied.

Theory: A gas separation membrane is a robust material that provides selective permeation of one gas from a mixture, owing to its microscopic structure and properties. A membrane is characterized by permeability and selectivity.

Permeability of a gas through a membrane is defined as the flux normalized by the pressure driving force.

$$P_i = D_i \cdot S_i = \frac{(Flux)_i}{\Delta p_i / l}$$

Permeability is related to the product of the diffusivity D_i (dependent on molecular size of gas relative to pores in membrane) and the adsorption coefficient S_i (dependent on adsorption/condensability of gas in membrane) of the penetrant gas molecule in the membrane [11,12]. This is called the solution-diffusion model. P_i is the permeability of gas i, through the membrane, Δp_i is the partial pressure difference of gas i across the thickness of the membrane and l is the thickness of the membrane. Permeability of a membrane can be a function of operating temperature and pressure and is a measure of the intrinsic productivity of the membrane material. The commonly used unit of permeability is Barrer.

$$1\,\text{Barrer} = 10^{-10}\,\frac{\text{cm}^3(\text{STP})\cdot\text{cm}}{\text{cm}^2\cdot\text{sec}\cdot\text{cm Hg}} \qquad \text{.....(2)}$$

Smaller and more adsorbing gases have higher permeability than larger gas molecules in the membrane. In the presence of nanoparticles in the membrane, size-based exclusion of larger gas molecules occurs in addition to solution-diffusion in the mixed matrix membrane. Gas permeation tests can be carried out with pure gases or mixed gases. The ratio of the permeabilites of pure gases at the same pressure and temperature is defined as ideal selectivity α. For a mixed gas feed, the separation factor β of a membrane is the ratio of the mole fractions of gas i to gas j in permeate divided by the ratio of mole fractions in the upstream.

$$\text{Selectivity } \alpha = \frac{P_i}{P_j} \qquad \text{..... (3)a}$$

$$\text{Separation factor } \beta = \frac{\left(\frac{yi}{yj}\right)permeate}{\left(\frac{xi}{xj}\right)feed} \qquad \text{.....(3)b}$$

Membrane fabrication: In this section, fabrication of three membranes is described- Torlon pure polymeric membrane, Torlon-Zif8(10%) mixed matrix membrane and Torlon-Zif8(20%) mixed matrix membrane. Polymer Torlon® AI-10 polyamide-imide was purchased from Solvay advanced polymers, India. Solvent NMP n-methyl 2-pyrrolidone (99%, anhydrous, 328634_1L) and Basolite® Z1200 ZIF-8 nanoparticles were purchased from Sigma-Aldrich, India (Zif8 powder: density 0.35gm/cm^3, BET surface area 1810m^2/gm, pore volume 0.63cm^3/gm).

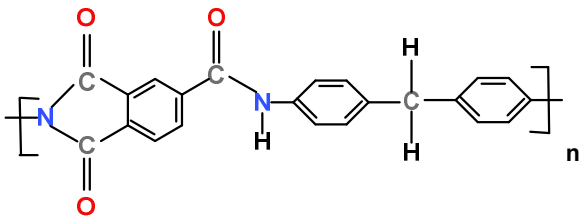

Figure 1. Molecular structure of polymer Torlon® AI-10 repeat unit

Torlon® AI-10 is a polymer prepared by reacting trimellitic anhydride acid chloride with 4,4'-methylene dianiline. Polyamic acid intermediate is formed that gets converted into imide groups upon thermal or chemical imidization. In this work, we have used only Torlon® AI-10 (Figure 1). Its glass transition temperature was measured to be 175°C and density 1.1969gm/cc. The viscosity of the Torlon AI-10 solution in NMP is a parameter to define the molecular weight and it is

1.00Pa.s (23°C, 25% in NMP, ±300mPa.s). A special feature of Torlon® polymeric membranes is inter-chain hydrogen bonding between hydrogen of amide group and carbonyl oxygen between neighboring chains that keeps the chain packing very rigid. Torlon AI-10 based membrane can provide gas separation upto 75-100psia gas pressure.Zif-8 is zeoliticimidazolate framework-8 which aremicroporous nanoparticles composed of zinc tetrahedrally co-ordinated to four 2-methyl-imidazolate linkers. Commercially available Zif-8 has a structural aperture of 3.4Å size that allows small gas molecules like carbon dioxide and hydrogen to pass through but cannot fit larger methane to pass through it. Therefore, it was attempted to increase gas separation factor by incorporating Zif8 particles into polymer Torlon. Fabrication of pure Torlon® membrane: A solution of the polymer 4gm Torlon (18weight%) in NMP 18gm (n-methyl 2-pyrrolidone) was prepared by magnetic stirring for 6 hours and let stand at room temperature for 18 hours. The clear brown solution was poured onto a clean glass plate and drawn cast into a film with a graduated glass rod, which is called solution casting. The glass plate with the film was placed in a convection oven (Memmert UF110) at 90°C for 24 hours. Complete evaporation of solvent dried the film. The film was peeled off the glass plate. Unsupported defect free film was obtained. The polymeric membrane is flexible and strong. The area of the yellow transparent film was 320cm^2 for 0.09mm thickness (400cm^2 for 0.07mm).

Fabrication of Torlon with 10% ZIF-8 mixed matrix membranes: For preparing 10% Zif8 in Torlon, a solution of the polymer Torlon 4gm (19weight%) in NMP 17gm (n-methyl 2-pyrrolidone) was prepared in a glass jar by magnetic stirring for 6 hours and let stand at room temperature for 18 hours. A solution of 0.5gm of ZIF8 in 4gm NMP was prepared in a glass vial and sonicated for 20 minutes two times over 24 hours. Sonication provided a homogeneous milky white dispersion of ZIF8 particles in NMP. Soon after second sonication, the ZIF8 solution was mixed with the polymer solution by stirring with a spatula for 2 minutes and allowed to stand for 30minutes for air bubbles to disappear. The mixed solution was poured onto a clean level glass plate and drawn cast into a film with a graduated glass rod. Soon after casting, the plate was placed in a convection oven and left at 90°C for 24 hours. Complete evaporation of solvent dried the membrane. Unsupported defect free film was carefully peeled off the glass plate. This area of this yellow semi-transparent film was about 380cm^2 (0.07mm thickness). The novel mixed matrix membrane film is flexible, strong and has 11% Zif8 in Torlon polymer. Fabrication of Torlon with 20% ZIF-8 mixed matrix membranes: For preparing 20% Zif8 in Torlon, a solution of the polymer Torlon 4gm (19weight%) in NMP 17gm (n-methyl 2-pyrrolidone) was prepared in a glass jar by magnetic stirring for 6 hours and let stand at room temperature for 18 hours. A solution of 1gm of ZIF8 in 6gm NMP was prepared in a glass vial and sonicated for 20 minutes two times over 24 hours. Sonication provided a homogeneous milky white dispersion of ZIF8 particles in NMP. Soon after second sonication, the ZIF8 solution was mixed with the polymer solution by stirring with a spatula for 2 minutes and allowed to stand for 30minutes for air bubbles to disappear. The mixed solution was poured onto a clean level glass plate and drawn cast into a film with a graduated glass rod. Then, the plate with the film was placed in a convection oven and left at 90°C (60% fan, 40% flap in oven). After about 2 hours, the film gets peeled off the glass plate and it was left in the oven at 90°C for 24 hours. Complete evaporation of solvent dried the membrane. Unsupported defect free film was obtained. The novel mixed matrix film is flexible, strong and has 20% Zif8 in Torlon polymer. The area of the yellow opaque film was about 260cm^2 and it is curled from edges with 0.08mm thickness. In-depth material characterization was performed on these fabricated membranes and reported in an earlier paper[13]. The techniques included Differential Scanning Calorimetry, Thermo Gravimetric Analysis, Differential Mechanical Thermal Analysis, Fourier Tranform Infra-Red spectroscopy, X-Ray Diffraction, Scanning Electron Microscopy, Field Emission-Scanning Electron Microscopy and Universal Testing Machine measurements. Pure gas and mixed gas permeation results were also reported in the earlier paper [13].

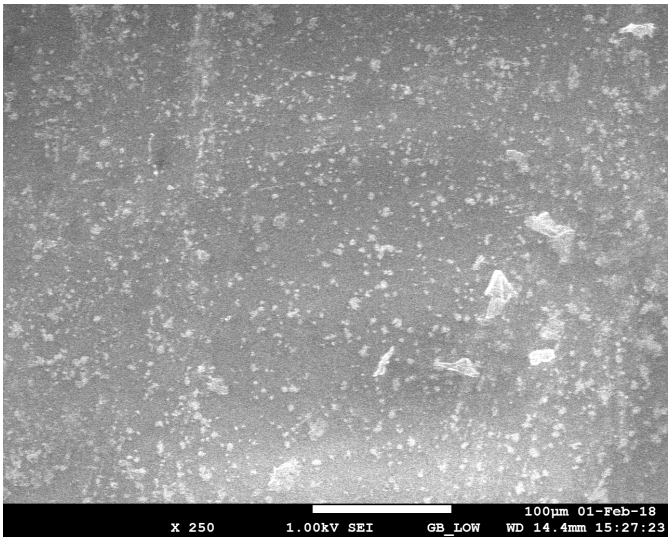

Figure 2. FE-SEM of Torlon –Zif8(20%) mixed matrix membrane dense film

From field emission-scanning electron microscopy image of Torlon-Zif8(20%) membrane as in figure 2, we can observe well-dispersed nanoparticles of Zif8 perfectly embedded in polymer Torlon. There is good adhesion between Zif8 particle and polymer. There are no defects or gaps or cracks at single particle-polymer interface and no agglomeration.

Experimental procedure

An isochoric gas permeation system was used to measure composition of permeate and retentate streams from a membrane to calculate its separation factor. The system is depicted is Figure 3. The composition of the feed gas was measured by directly connecting a steel bottle to the biogas pipeline and collecting the biogas. The collected stream was sampled by a syringe through a rubber septum in the end of the steel bottle and injected into a gas chromatograph to determine its composition. The feed gas line was connected to an available pressure regulated by-pass from the pipeline of the biogas plant. The feed pipe is connected to a gas inlet valve and an upstream pressure gauge to read the feed gas pressure. The feed valve is connected to the membrane permeation cell. The membrane cell has a permeate outlet below the membrane from which the permeate gas (gases which can pass through the membrane) is collected in a steel bottle with a rubber septum at its end. The membrane cell also has a retentate outlet above the membrane from which the retentate gas (gases which cannot pass through the membrane) is collected in a steel bottle with a rubber septum at its end.

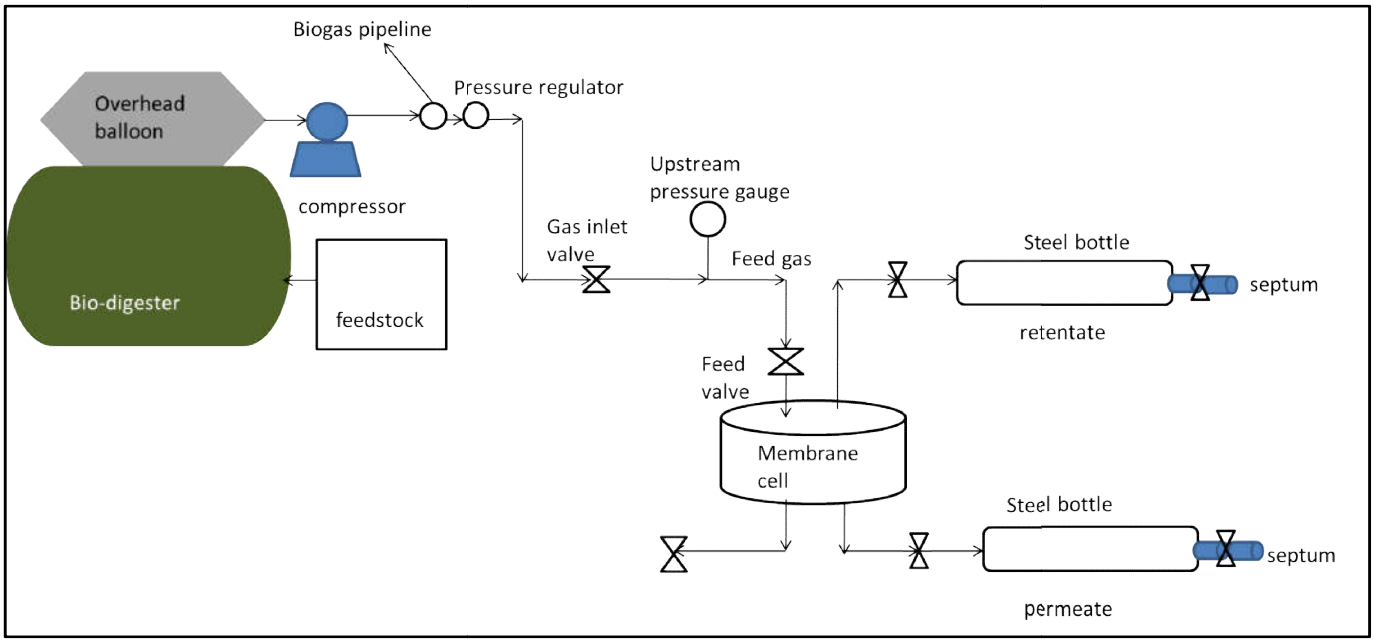

Figure 3. Schematic diagram of biogas separation by membranes

Table 1. Gas chromatograph analysis of streams from biogas membrane separation tests

	Sample	Composition
1	Feed biogas	8.05%H_2, 62.53%CH_4,29.41% CO_2, <1%H_2S
2	Torlon membrane permeate	21.28%H_2, 74.97%CO_2, 3.76% CH_4
	Torlon membrane retentate	94.47%CH_4, 4%H_2, 0.76% CO_2, 0.74% H_2S
3	Torlon-Zif8(10%) membrane permeate	20.64% H_2,76.28% CO_2, 3.08%CH_4
	Torlon-Zif8(10%) membrane retentate	95.19%CH_4, 3.5%H_2, 0.59% CO_2, 0.7% H_2S
4	Torlon-Zif8(20%) membrane permeate	22.71% H_2,77.29% CO_2, 0%CH_4
	Torlon-Zif8(20%) membrane retentate	96.57%CH_4, 3.08%H_2, 0.35% CO_2,<1%H_2S

A dense membrane film was tightly sealed in the gas permeation cell made of stainless steel with a sealing O-ring. The permeation cell and collection bottles were fitted into the system as in figure 3. The feed gas pressure was controlled at 55-58psia while downstream remained at atmospheric pressure (14.7psia). When the feed valve is opened, gas contacts the membrane. First, there is an experimental time lag noted in which the gas transport through the membrane is transitioning from unsteady state to steady state. Then, the permeate gas starts flowing out downstream slowly. For each membrane, the experiment lasted 2.5hours (duration of collection of permeate and retentate streams). At the end of each experiment, the inlet valves of the steel bottles were closed, the bottles were disconnected from the system and analysed for composition in a gas chromatograph machine. The gas samples were extracted from the bottles in syringes through rubber septum. The sample in the syringe was immediately injected into GC. The calibrated GC provides areas of peaks corresponding to different gases present in each stream. The gas chromatograph machine was Agilent 7820A GC system with a Newchrom® 16214 column inside it. GC oven temperature was 60°C and thermal conductivity detector was maintained at 150°C. Helium was used as carrier gas. Area% of different gases as a function of retention time were obtained.

RESULTS

The feed biogas contained 8.05% hydrogen, 29.41% carbon dioxide, 62.53% methane and less than 1% hydrogen sulfide. This feed gas was passed through three membrane films. The smaller gases permeated through the membranes and were collected downstream in permeate.

The remaining larger gases were collected in the retentate. From pure Torlon membrane at 58psia feed gas, the permeate contained 21.28% hydrogen 74.97% carbon dioxide and product loss of 3.76% methane. The retentate was enriched with 94.47% methane, 4% hydrogen, 0.76% carbon dioxide and 0.74% hydrogen sulphide. From Torlon-Zif8(10%) mixed matrix membrane at 56psia feed gas, the permeate contained 20.64% hydrogen 76.28% carbon dioxide and product loss of 3.08% methane. The retentate was enriched with 95.19% methane, 3.5% hydrogen, 0.59% carbon dioxide and 0.70% hydrogen sulphide.

From Torlon-Zif8(20%) mixed matrix membrane at 55psia feed gas, the permeate contained 22.71% hydrogen 77.29% carbon dioxide and no product loss 0% methane. The retentate was enriched with 96.57% methane, 3.08% hydrogen, 0.35% carbon dioxide and traces of H_2S. Methane was not able to permeate through Torlon-Zif8(20%) mixed matrix membrane due to size based exclusion. The results are presented in table 1 and figure 4. The separation factor for CO_2/CH_4 separation was calculated using equation 3b.

The mechanism of gas permeation in pure Torlon membrane is by solution-diffusion mechanism [11] wherein permeability is theoretically equal to the product of diffusivity and adsorption coefficient. The mechanism of gas permeation in Torlon-Zif8 mixed matrix membranes is a combination of solution-diffusion and size based exclusion mechanisms. The CO_2/CH_4 separation factors of the membranes were calculated using equation 3b).

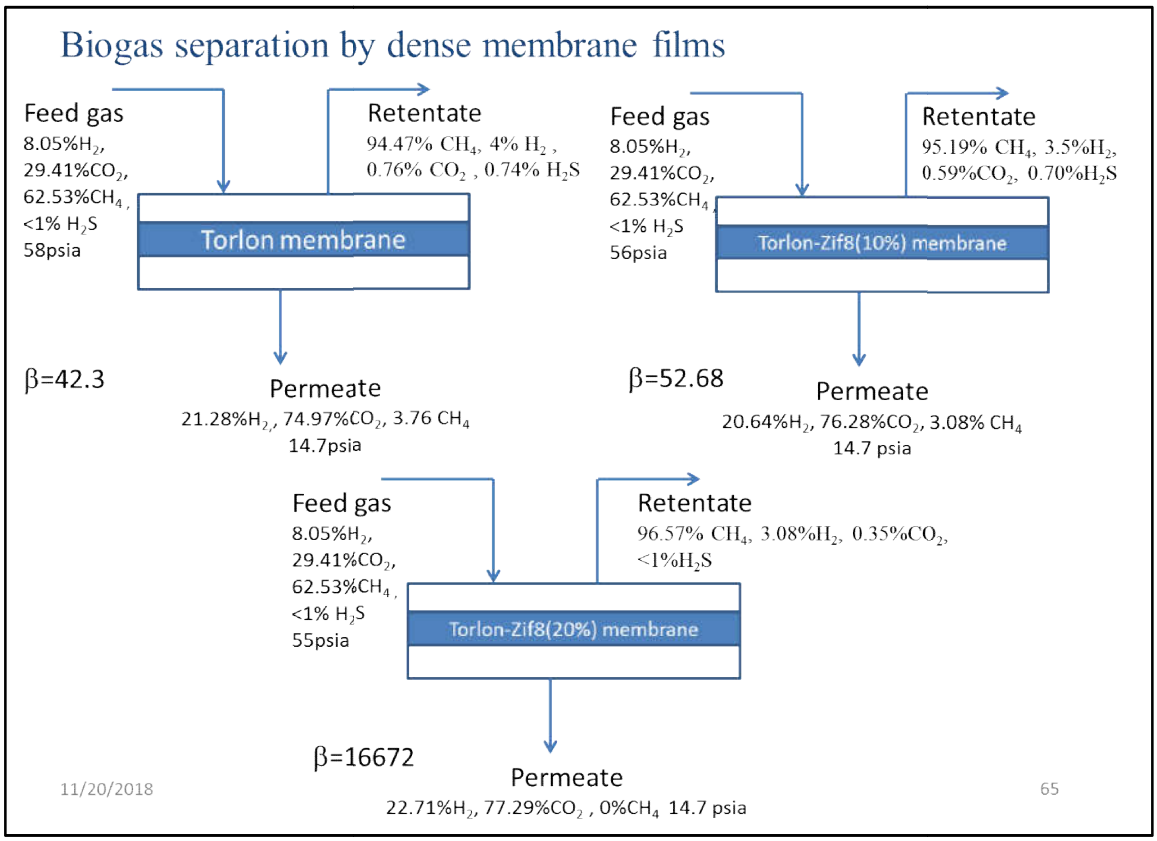

Figure 4. Results of biogas separation by Torlon, Torlon-Zif8(10%) and Torlon-Zif8(20%) dense membrane films

DISCUSSION

The physical parameters of the involved gases are listed in Table 2.

Gas	Kinetic diameter (Å)	Critical temperature (K)
Hydrogen	2.89	33.2
Carbon Dioxide	3.3	304.1
Methane	3.8	190.4
Hydrogen Sulfide	3.6	373.5

The kinetic diameter represents the size of gas molecules and the critical temperature represents the adsorption/ condensability of gas molecules. These two parameters play a role in the overall permeability of a gas through a membrane. We observe that hydrogen and carbon dioxide are smaller in size while methane and hydrogen sulphide are larger gas molecules. Due to this size difference, the permeate from the membranes is rich in H_2 and CO_2 while the retentate is rich in CH_4. We observe that the retentate streams from the studied membranes contain 98-99% flammable gas (methane + hydrogen) which is high purity biogas. The product loss is low. It is also important to note that Torlon-Zif8(20%) acts as a perfect membrane because no methane is able to permeate through this membrane. Based on gas permeation data collected on these membranes, the following plots (figure 5a,b,c) of variation of permeability as function of kinetic diameter of gas penetrant were obtained. The performance of the studied membranes is plotted on the Robeson upper bound curve for CO_2/CH_4 separation in figure 6 [16, background re-printed with permission from Elsevier, license no. 4234710132221). The performance of Torlon-Zif8(20%) membrane exceeds the upper bound curve because methane is not able to permeate through this membrane.

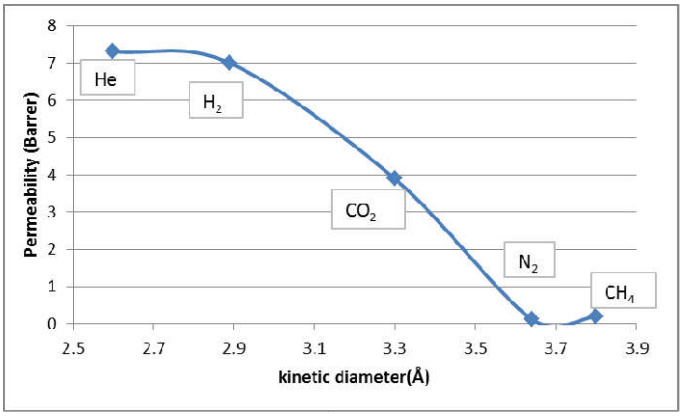

Figure 5a. Variation of gas permeability as a function of size in pure Torlon dense membrane film

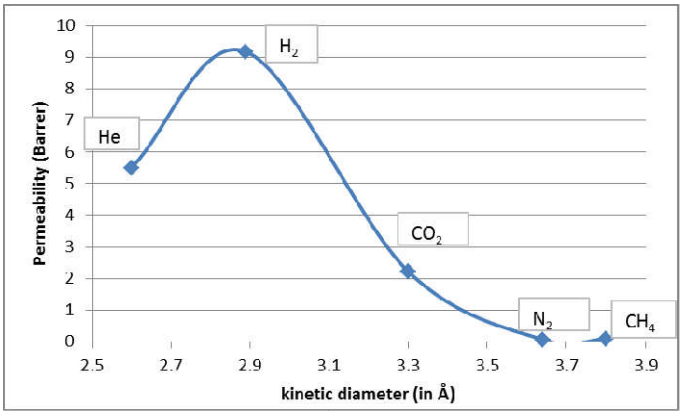

Figure 5b. Variation of gas permeability as a function of size in Torlon-Zif8(10%) mixed matrix dense membrane film

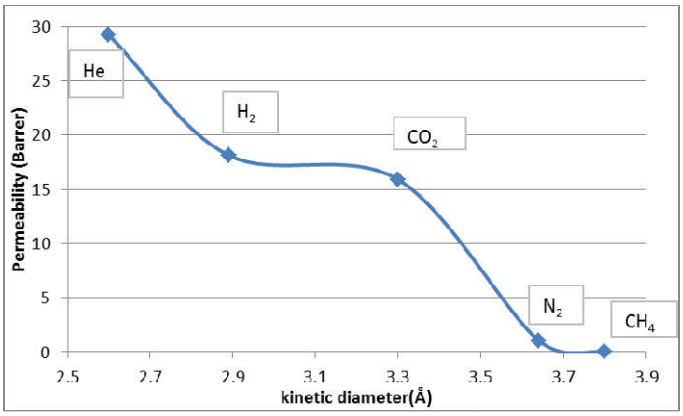

Figure 5c.Variation of gas permeability as a function of size in Torlon-Zif8 (20%) mixed matrix dense membrane film

The performance of the studied membranes is plotted on the Robeson upper bound curve for CO_2/CH_4 separation in figure 6 [16, background re-printed with permission from Elsevier, license no. 4234710132221). The performance of Torlon-Zif8(20%) membrane exceeds the upper bound curve because methane is not able to permeate through this membrane.

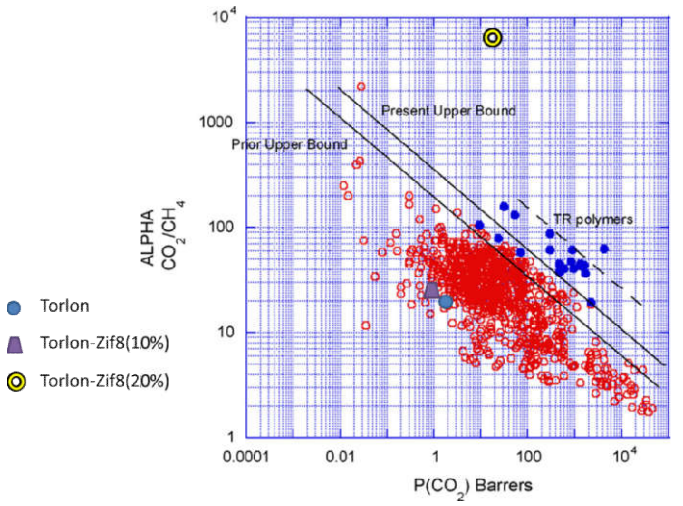

Figure 6. Gas separation performance of studied membranes on the Robeson upper bound curve for carbon dioxide-methaneseparation(background re-printed with permission from Elsevier)

Conclusion

Producing energy from nonfossil-fuel sources is necessary to meet fuel shortages in future. One such source of heat energy is biogas generated from anaerobic digestion of organic food and vegetable waste. On-site biogas purification measurements were performed in an isochoric membrane gas permeation system. The methane content in the biogas got enriched from 62% in feed to 94-96% in retentate stream. Three polymeric membranes with varying amount of nanoparticles were studied. Torlon-Zif8(20%) membrane showed excellent separation of H_2 and CO_2 from CH_4. Thus, this study demonstrated that membrane technology can be employed to increase the purity of biogas.

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Supplementary information

Literature survey on selected membranes for carbon dioxide-methane separation

S.no.	Polymer	Permeability CO_2 (Barrer)	Selectivity CO_2/CH_4	Reference
1	PVSH doped polyaniline	0.029	2200	16
2	Polypyrrole 6FDA/PMDA(25/75)-TAB	3.13	140	16
3	Polyimide TADTO/DSDA(1/1)-DDBT	45	60	16
4	Poly(diphenyl acetylene)3a	110	47.8	16
5	Polyimide 6FDA-TMPDA/DAT(1:1)	130.2	38.9	16
6	Poly(diphenyl acetylene)3e	290	31.5	16
7	Polyimide 6FDA-TMPDA	555.7	22.7	16
8	Polyimide 6FDA-durene	677.8	20.18	16
9	PIM-1	2300	18.4	16
10	PTMSP	19000	4.42	16
11	A-2 UBE Polyimide commercial hollow fiber module	CH_4 enrichment from 55-85% to 91-94.4%		9
12	A-2 UBE commerical Polyimide hollow fiber module	CH_4 enrichment from 60% to 80% CH_4 enrichment from 54% to 90%		10
13	Torlon®	0.47	36	18
14	Polyphenylene oxide PPO	75.8	6.89	10
15	PMDA-ODA polyimide (pyromelliticdianhydride/4,4-oxydianailine)	3.55	37.8	10
16	PMDA-MDA polyimide (pyromelliticdianhydride/methylene dianiline)	4	43	10
17	6FDA-MDA polyimide (4,4-hexafluoroisopropylidene-diphthalic anhydride/methylene dianiline)	19	45.2	10
18	6FDA-IPDA polyimide (4,4-hexafluoroisopropylidene-diphthalic anhydride/isopropylidenedianiline)	30	42.8	10
19	6FDA-ODA polyimide (4,4-hexafluoroisopropylidenediphthalic anhydride/4,4-oxydianailine)	16.7	48	10
20	6FDA-DAF polyimide (4,4-hexafluoroisopropylidene diphthalic anhydride/diaminofluorene)	32.2	51	10
21	6FDA-MPD polyimide (4,4-hexafluoroisopropylidene-diphthalic anhydride/m-phenylenediamine)	11	58	10

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