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REVIEW

Gas permeation processes in biogas upgrading: A short review

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Biogas upgrading is a widely studied and discussed topic. Many different technologies have been employed to obtain biomethane from biogas. Methods like water scrubbing or pressure swing adsorption are commonly used and can be declared as well established. Membrane gas permeation found its place among the biogas upgrading methods some years ago. Here, we try to summarize the progress in the implementation of gas permeation in biogas upgrading. Gas permeation has been already accepted as a commercially feasible method for CO_2 removal. Many different membranes and membrane modules have been tested and also some commercial devices are available. On the other hand, utilization of gas permeation in other steps of biogas upgrading like desulfurization, drying, or VOC removal is still rather rare. This review shows that membrane gas permeation is able to compete with classical biogas upgrading methods and tries to point out the main challenges of the research.

Keywords: biogas upgrading, membranes, gas permeation, CO_2 removal

Introduction

Biogas is a result of anaerobic digestion of organic waste. It contains mainly methane, carbon dioxide, water vapor, and many different trace compounds, which depends on the origin of the biogas. The high methane content draws a lot of attention to biogas because it makes it utilizable as a biofuel similarly to e.g. butanol from ABE fermentation (Kujawska et al., 2015). Utilization of biogas is contemporary a widely discussed topic due to the exploitation of fossil fuels resources (Wellinger & Lindberg, 1999).

Biogas may be produced from cattle manure or vegetable waste on farms, in sewage plants after the waste water treatment or in landfills. The concentration of methane varies from 50 vol. % (landfill gas) to 70 vol. % (sewage plant biogas). The rest is mainly carbon dioxide, water vapor, and unwanted compounds:

i) siloxanes, present in sewage plant biogas, arise from silicone added to cosmetics;

ii) sulfur compounds (hydrogen sulfide, mercaptanes), products of anaerobic digestion of proteins;

iii) ammonia, present in agricultural biogas, originate from urine present in manure;

iv) volatile organic compounds, mostly hydrocarbons, but also oxygenated or halogenated organic compounds, are mostly rests from urban waste or products of incomplete decomposition of natural waste (Rasi et al., 2007).

All these compounds cause that biogas cannot be used as a substitute for natural gas without any pretreatment. To make biogas utilizable, the content of methane has to be increased to at least 95 vol. % and all trace compounds and water vapor have to be removed. Therefore, many different methods of biogas upgrading have been developed. Classical methods of biogas upgrading were described in literature many times (Ryckebosch et al., 2011).

Biogas upgrading process usually consists of the following steps:

i) drying – water vapor removal;

ii) desulfurization;

iii) removal of other trace compounds (ammonia, siloxanes);

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iv) carbon dioxide removal.

Drying is normally performed by cooling biogas below its dew point. Desulfurization occurs by adsorption or biological processes (Abatzoglou & Boivin, 2009). Carbon dioxide removal is achieved by physical or chemical absorption (scrubbing), cryogenic distillation, or membrane separation (Kárászová et al., 2011). Siloxanes are removed by adsorption on different sorbents (Schweigkofler & Niessner, 2001).

Here, we focused on membrane separations used in biogas upgrading. Although membrane separation was put aside for a long period of time, referring to its low efficiency and high investment costs, the situation has overturned and membrane separations have become more employed in the purification of biogas in recent years. Membrane separation is a compact process with very low space requirements contrary to e.g. water scrubbing. The membrane system can be placed in a mobile container and brought directly to the sewage plant, landfill, or farm. Moreover, membranes do not consume much energy and also the membrane materials became cheaper and more available after all the years of research.

Engineering aspects

Generally, two types of membrane processes are employed in biogas upgrading: gas permeation and membrane contactors (Scholz et al., 2013a). Gas permeation membranes are available as membrane modules: envelope type modules, spiral wound modules and hollow fibers, which are the most common. Scholz et al. (2013a) presented a table of commercial membrane materials used for CO_2 recovery, among which PDMS had the highest CO_2 permeability (2700 barrer) but poor CO_2/CH_4 selectivity (3.4), and polycarbonate had the highest selectivity (32.5) but negligible CO_2 permeability (4.2 barrer). This problem of selectivity and permeability trade-off complicates the application of membrane processes in industrial scale. The feasibility of membrane processes was studied in detail e.g. by Scholz et al (2015) who optimized the membrane separation process for CO_2 removal from biogas. The calculation was done for cellulose acetate and polyimide membranes assuming the carbon dioxide permeance of 60 GPU and CH_4/CO_2 selectivity of 60, and the carbon dioxide permeance of 20 and CO_2/CH_4 selectivity of 60 for cellulose acetate and polyimide membranes, respectively. Scholz et al. (2015) attempted to find the economic optimum rather than the energetic one, considering investment and operational costs. They used the Robeson correlation to determine the optimal membrane parameters. From their calculations, the following conclusions can be made. Three membrane stages are the maximum for the industrial process. Application of a three stage process with commercially available membranes showed good performance. Furthermore, for the optimal membrane material, the development and product launching costs must justify the application of such membrane, or in other words it is not reasonable to develop expensive sophisticated membranes for processes like CO_2 removal. In another work, Scholz et al. (2013b) proved that membrane processes can improve the current conventional processes effectiveness without increasing their costs. The authors modeled three hybrid processes where membrane separation was combined with amine scrubbing, a cryogenic process and pressurized water scrubbing. In most cases, investment costs for the hybrid process were the same as those for the simple process without membrane separation. A combination of a classical procedure with membrane separation makes even the cryogenic process of carbon dioxide removal more competitive to well established processes like water scrubbing. Makaruk et al. (2010) published an optimization algorithm for membrane process integration in a biogas plant. Two configurations able to cover the energy consumption of the biogas plant itself and to produce CNG (compressed natural gas) simultaneously were suggested: one stage membrane process combined with a CHP plant and two stage process with a gas burner.

The mentioned advantages of membrane separations are supported also by older works. For example Baker (2002) showed that membrane separation processes are useful in small and medium scales (up to 50000 $m^3\ h^{-1}$, normal conditions).

Many published works have been dedicated to CH_4/CO_2 membrane separation. Two models of economical effectiveness of membrane gas permeation were presented by Corti et al. (2004), who found that membrane separation is comparable to absorption and the only problem consists in the investment costs.

An interesting approach to the assessment of membrane performance was introduced by Brunetti et al. (2014), who defined the so called permeation number (Θ), a determining parameter for the membrane module performance:

$$\Theta = \frac{\Pi_{CO_2} A p^{\text{feed}}}{x_{CO_2}^{\text{feed}} Q^{\text{feed}}} \quad (1)$$

where Π_{CO_2} is the membrane permeance for CO_2, A is the membrane surface area, p^{feed} is the feed pressure, $x_{CO_2}^{\text{feed}}$ is the CO_2 mole fraction in feed, and Q^{feed} is the feed flow rate. The permeation number reaches values form 0 to 25. A low permeation number means low recovery of the target substance and high concentration of the permeate and vice versa. The permeation number is a powerful tool of membrane assessment because it can be used to:

i) estimate the membrane area needed to perform separation of the given feed stream when membrane material of particular permeance is chosen;

ii) find the optimal membrane material when the size of the installation is defined;

iii) calculate the optimal feed flow rate under the required pressure, composition of the feed and known membrane material.

Biogas upgrading is a widely discussed topic now, which led to many new membranes being designed, as the authors say, for biogas purification. However, only a negligible number of these membranes has been really tested with raw biogas.

Separation of CO_2

Separation of CO_2 by membranes is a very popular and widely studied topic. Many works including complex reviews have been already published. For this reason, we do not want to present the well-known and well cited works but we want to focus on works on biogas purification. Unfortunately, as it was mentioned before, in many works the keyword biogas appears in title only.

Promising membrane materials for CO_2 separations were summarized e.g. by Brunetti et al. (2010). The most employed membranes are:

i) polyimides (PI);
ii) facilitated transport membranes;
iii) mixed matrix membranes (MMMs);
iv) carbon molecular sieves (CMS);
v) polyethyleneoxide (PEO);
vi) liquid membranes (LMs).

Polyimide membranes have been applied many times. Wind et al. (2004) used polyimides to purify natural gas and proved that crosslinked PI has better selectivity and permeability than cellulose acetate or Matrimid usually employed for the separation of complex gas mixtures. Harasimowicz et al. (2007) tested polyimides with a ternary mixture of CH_4 (68 vol. %), CO_2 (30 vol. %), and H_2S (2 vol. %) and they were able to achieve a retentate methane concentration of 94 vol. % while polyimide was found highly permeable also for H_2S. Polyimide membranes have already reached their pilot plant application. Miltner et al. (2010) built their pilot plant for biogas upgrading in Margarethen Moos, Austria. The membrane separation unit is situated after the pretreatment step (refrigeration and desulfurization) and consists of hollow fiber aromatic polyimide modules. The plant produces biomethane of fuel quality, which is subsequently compressed and used as CNG. The off gas from the plant is brought to a combined heat and power plant unit to be processed.

Facilitated transport membranes were used by Deng and Hägg (2010), who employed a polyvinylalcohol membrane with implemented amine groups. CO_2 reacted with the amine group in the membrane which resulted in facilitated transport. The tested mixture of CH_4 and CO_2 was saturated with water vapor. A model mixture of 65 vol. % of CH_4 and 35 vol. % of CO_2 was used. The membrane showed rather low permeance of 0.55 GPU for CO_2 and the selectivity of 30 under the feed pressure of 1 MPa. The authors designed an optimized two stage recycled biogas upgrading process based on the obtained results. The device should be capable of upgrading 761 m^3 h^{-1} (at normal conditions) of biogas using the membrane surface of 1440 m^2. The obtained biomethane was of fuel quality (CH_4 > 98 vol. %).

Carbon molecular sieves were employed for example by Vu et al. (2002), who prepared two different hollow fiber membranes by coating polyimide matrix with CMS. The membrane was tested with a binary mixture of 90 vol. % of CH_4 and 10 vol. % of CO_2 with interesting results in regard to selectivity and permeability. The membrane consisting of 6FDA/BPDA-DAM polyimide and CMS showed the CO_2 permeance of 12 GPU and the selectivity of 80. The membrane consisting of Matrimid® 5218 and CMS showed the CO_2 permeance of 25–30 GPU and the selectivity of 80. Both results are highly promising but some experiments with biogas are needed.

Mixed matrix membranes consist of inorganic micro- or nanoparticles and polymeric membranes. Added particles enhance the permeability and selectivity of the membranes compared to the polymeric ones and improve their mechanical stability. PEBAX® with implemented particles of polyhedral oligomeric silsesquioxane (POSS) was prepared by Li and Chung (2010), who tested the membrane with a CH_4 and CO_2 mixture and obtained results close to the Robeson plot, however, more experiments are needed. Molecular sieve SAPO 34 was implemented in a polymerized room temperature ionic liquid by Hudiono et al. (2011). According to the obtained results, the addition of a molecular sieve shifted the transport properties of the membrane close to the Robeson upper bound limit. Mixed matrix membranes were applied for biogas upgrading by Ozturk and Demirciyeva (2013), who used PI and polyether imide (PEI) polymers combined with an 3 Å, 4 Å, and 5 Å zeolite. The prepared membranes were tested with a binary mixture first. The best selectivity (40) was achieved with PI with 30 mass % of the 4 Å zeolite at the feed pressure of 0.3 MPa. The highest CO_2 permeability (40 barrer) was achieved with PEI with 30 % of the 4 Å zeolite at 0.8 MPa. Concerning the permeability, the results are not really interesting. The results obtained in experiments with biogas were unfortunately not presented in terms of selectivity and permeability. The only fact stated by the authors was that the presence of water vapor decreased the selectivity and increased the permeability of the membranes. Membranes consisting of tetraorthosilicate and polyvinyl acetate were used by Quéchulpa-Pérez et al. (2014). Unfortunately, although the work has the word biogas in its title, it contains a highly sophisticated introduction about the biogas upgrading and alternative fuels but the only results published deal with the membrane structure and model binary mixture separation results are pre-

sented. It was shown that up to 80 % of CO_2 was removed from the feed stream.

Polyethylene oxide has generally high affinity to CO_2 because of the ether functional group. Important work dealing with PEO membranes was published by Lin and Freeman (2004). They found that the crystalline phase present in PEO has an unfavorable influence on gas transport properties of the membrane. Permeability of CO_2 through an amorphous polymeric phase was twelve times higher than that through a semicrystalline phase. Nylon based tetraamide T6T6T blocks and groups of terephtalic acid were used to suppress the crystalline phase in the polyethylene oxide by Husken et al. (2010). The added substances caused a decrease of the melting temperature of the polymer and improved the transport properties of the membrane for CO_2. Kim and Park (2011) reached the absolute lack of the crystalline phase by adding 4,4-dichlorphenyl sulfon and bisfenol into PEO, which led to random PSF–PEO copolymers. Transport properties of the resulting membrane were worse than those obtained for pure PSF, which was probably caused by the PEO–PSF interphase. Hollow fiber membranes consisting of a combination of polyimide and polyethylene oxide were investigated by Suzuki et al. (1998). Unfortunately, the membrane was not stable for a long time losing its initial properties after one month. A polyether–ether ketone (PEEK) membrane was used by Molino et al. (2013a) to separate biogas. PEEK is a commercially produced membrane manufactured by PoroGen Corp. known by its good chemical durability and high separation effectiveness. Hollow fiber module PEEK-SEP^{TM}S1 was employed in an experiment performed directly at the ENEA biogas – biomethane plant. First, the ternary mixture of 54.4 vol. % of CH_4, 44.6 vol. % of CO_2, and 1 vol. % of N_2 was used. The pressure varied from 0.3–2 MPa and the feed flow rate varied from 18 kg h^{-1} to 96 kg h^{-1}. The retentate contained 95 vol. % of CH_4. In a subsequent work (Molino et al., 2013b), a two stage membrane separation process with the PEEK membrane was designed and tested with biogas from different sources. Biogas compressed to 3.2 MPa was brought to the first stage providing retentate of 95 vol. % of CH_4. The permeate from the first stage was brought to the second stage and enriched to 85 vol. % of CH_4. The technology seems to be highly perspective for biogas upgrading.

Speaking about the CO_2 recovery, ionic liquid membranes must be mentioned because they represent a significant trend in membrane separation. The definition and classification of liquid membranes were made by Krull et al. (2008). In the last few years, mainly liquid membranes containing ionic liquids became very popular. Ionic liquids are suitable for liquid membranes preparation because of their specific physical and chemical properties. A complex review on gas separation was presented by Kárászová et al. (2014). Classical supported ionic liquid membranes, presented e.g. by Scovazzo et al. (2009), have very good CH_4/CO_2 selectivity and permeability but they can hardly be transformed to a membrane module and utilized in a full scale industrial processes because of their poor mechanical stability. On the other hand, gelled structured ionic liquid membranes seem to solve the problem of liquid membrane stability without losing the main advantages usually ascribed to liquid membranes such as high permeation flux. Voss et al. (2009) created a gelled ionic liquid membrane of $[C_6mim][Tf_2N]$ using 12-hydroxystearic acid as a low molecular gelator. The resulting membrane had CO_2 permeability of 650 barrer. Gu and Lodge (2011) designed a sophisticated triblock copolymer in the $[emim][Tf_2N]$ ionic liquid and obtained ionic liquid membranes with the CO_2 permeability of 1000 barrer at the experimental pressure of 207 kPa. The use of ionic liquid membranes is limited also by the lack of models predicting the ionic liquid membrane transport properties and scale up of the ionic liquid membrane processes (Kárászová et al., 2013). Unfortunately, no ionic liquid membrane was tested in a real biogas separation process although their gas separation properties predestine them for such application.

Another approach to liquid membranes was presented by Poloncarzova et al. (2011), who designed a condensing water membrane supported in hydrophilized porous PTFE. The membrane separates polar gases from biogas (CO_2, H_2S) as they are more soluble in water than CH_4. The principle is as follows: a thin water layer trapped in pores of the porous support works as a membrane. The membrane was integrated in a sweeping gas permeation setup. The feed (biogas) was humid and tempered to 27 ℃, the membrane itself was tempered to 14 ℃ and humidity from the feed condensed on the porous support from the feed side and withdrawn by the sweeping gas from the permeate side so the water layer was refreshed continually. The tested biogas contained 67.6 vol. % of CH_4 and the retentate was enriched to 76.7 vol. % of CH_4. The technology was upgraded in a subsequent work of the group (Kárászová et al., 2012), where the hydrophilized porous support was replaced by a commercial thin film composite reverse osmosis membrane. The polyamide thin film on its top was swollen by water so the resulting membrane was pressure stable. Moreover, the layer was much thinner than that of the condensing water membrane and it showed much better separation properties. Dolejš et al. (2014) tried to apply the principle in other materials but the obtained CH_4/CO_2 selectivity was not satisfactory. The authors also tested the original TFC membrane with a ternary mixture of CH_4, CO_2, and H_2S obtaining a good selectivity of 18. The membrane became a part of the biogas separation technology CLEARGAS.

Membrane separation of biogas trace compounds

Although carbon dioxide is usually the component separated from biogas by membranes, also other compounds present in biogas can be subjects of separation experiments.

Separation of hydrogen sulfide was presented in an early work of Heilman et al. (1956). Polymeric membranes of dialkyl siloxane introduced in an US patent (Porter, 1970) were designed to separate H_2S from natural gas under high pressures. Orme and Stuart (2005) reported on polyphosphazene membranes convenient for natural gas sweetening with very high H_2S permeability (1130 barrer) and selectivity of 60 for a CH_4/H_2S mixture.

The possibility of siloxane separation using a membrane was mentioned by Ajhar and Melin (2006). PDMS membrane was found to be selective for D4 siloxane and a nitrogen mixture.

Membranes for ammonia removal were reported e.g. by Tan et al. (2006), who used PVDF hollow fiber modules or by Xie et al. (2009) who tested hydrophobic PTFE flatsheet membranes.

However, none of the membranes mentioned above was directly used or at least suggested for biogas separation.

Available membrane separation technologies for biogas upgrading

Evonik Industries produces a hollow fiber module of polyimide P84® called Sepuran® Green. Sepuran® Green is implemented in the biogas membrane technology used by Enivitech Ind. The technology consists of biogas desulfurization by active carbon adsorption, pre-drying, filtration and compression to 1–2 MPa. The technology is capable to process 10–1000 $m^3\ h^{-1}$ (at normal conditions) of biogas and produce biomethan of a 99 vol. % concentration. The technology is available as a container setup (Evonik Industries, 2015).

BORSIG offers biogas upgrading technology which also contains a desulfurization step and a spiral wound module membrane module for CO_2 separation (BORSIG Membrane Technology, 2015).

Another commercial membrane module is called *Perm*Select®. It is a hollow fiber membrane module of PDMS. The membrane enables to separate CO_2, H_2S, and H_2O in one step. It is also possible to implement molecular sieves into the membrane (PermSelect, 2015).

The Air Liquide MEDAL® – BIOGAZ system uses hollow fiber membrane modules. BIOGAZ unlike other technologies uses VOC removal for biogas pretreatment. Here, CO_2, O_2, H_2S, and H_2O are removed from biogas by permeation. The module is capable to process biogas compressed to 1.37 MPa in the amount of 28 $m^3\ min^{-1}$ (normal conditions) and retentate containing 1 vol. % of CO_2 in the amount of 14 $m^3\ min^{-1}$ (normal conditions) (Air Liquide, 2015).

Air Products launched PRISM® membrane modules. These hollow fiber modules are capable, after a suitable pretreatment, to process 60 $m^3\ h^{-1}$ (normal conditions) of raw biogas at 1.2 MPa and produce 33.6 $m^3\ h^{-1}$ (normal conditions) of high purity (99.7 vol. %) biomethane (Air Products and Chemicals, 2015).

The CLEARGAS (Energoklastr, 2015) system is a container setup employing spiral wound polyamide membrane modules. It is able to produce biomethane in one separation step without any pretreatment. The system can process up to 2000 $m^3\ h^{-1}$ (normal conditions) of raw biogas, which has to be compressed to 0.6 MPa only. The system employs a liquid water membrane which recreated during the separation process by condensing the humidity present in biogas on the polymeric membrane and its evaporation from its other side. The setup is based on a WSTFC membrane.

DMT Environmental Technology introduced the Carborex® MS system for biogas upgrading. A case study of this system was presented by Lems et al. (2014). The multistage technology as a "plug-and-play" setup consists of desulfurization performed by active carbon adsorption, compression of biogas, drying of biogas by cooling, filtration, and membrane separation of CO_2 using the Carborex membrane modules. The technology is capable to process up to 800 $m^3\ h^{-1}$ of biogas (normal conditions), while the retentate contains up to 99.6 vol. % of CH_4. The off gas (permeate) of the technology is compressed to 1.5 MPa and cooled to –35 °C, so pure CO_2 is obtained.

Conclusions

The membrane gas permeation has already found its place in biogas upgrading because of its compactness and low energy consumption. At least seven commercial technologies utilizing membrane separation are available. So the first goal, to make gas permeation equal to e.g. water scrubbing or diethanol amine (DEA) scrubbing has thus been accomplished. There is no reason to look for new membrane materials for CO_2 separation. The problem of trace compounds as hydrogen sulfide, VOC or siloxanes has to be solved now. Trace compounds represent an ideal challenge for membrane separation. They are present in low concentration and methods like active carbon adsorption produce dangerous waste. Therefore, some tasks have to be solved:

i) to find chemically durable membranes for biogas desulfurization;

ii) to find membranes suitable for the separation of such a disparate group of substances like siloxanes;

iii) to implement available membranes for VOC re-

moval in biogas upgrading.

Desulfurization of biogas is complicated by membrane fouling caused by pure sulfur produced by oxidation of the S^{2-} anion.

Membrane separation of siloxanes is limited by their chemical variability. Siloxanes can be either linear or cyclic and their chain length also varies, which results in significant differences in chemical and physical properties, e.g. melting point, viscosity, etc.

A similar problem occurs in VOC separation as VOC present in biogas originate from different chemical groups.

Solution of all the mentioned tasks could result in biogas upgrading technology consisting of membrane modules only. Such technology is simple and compact with low energy consumption, and as such it is worth to try.

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