Biogas Purification

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Effective Purification of Biogas by a Condensing-Liquid Membrane**

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In a time of limited reserves of fossil fuels, the problem of biogas utilization becomes a fundamental question.[1] For example, the city of Prague in central Europe with 1.25 million inhabitants requires 35 million liters of diesel per year for its 1180 buses. Diesel is expensive and significantly increases air pollution, mainly with aromatic hydrocarbons (including naphthalenes and alkyl benzenes) and carbon black. Biogas occurs as a result of anaerobic digestion of organic waste, and consists mainly of methane, carbon dioxide, and a small amount of corrosive gases (water vapor, hydrogen sulfide, ammonia, and mercaptanes). Therefore, biogas has the potential of becoming an alternative to classical fuels.[2]

Unfortunately, the composition of biogas, typically 50–70 vol% methane and 30–50 vol% carbon dioxide,[3] depends on its origin and on the season. Consequently, it is most commonly used in ancillary combined heat and power plants connected to biogas sources, such as farms or sewage plants,[4] where a change in the composition of biogas is not a problematic element. If we think about biogas as a fuel, the best alternative seems to be the purification of biogas produced in sewage plants, because it generally has the highest methane content and is easily accessible. Various residual compounds (water vapor, hydrogen sulfide, siloxanes, mercaptanes) present in biogas have already been described[5,6] with complex analysis.[7,8] Many different methods have been attempted to purify biogas to engine-fuel quality.[9] Water scrubbing, polyethylene glycol scrubbing, or molecular sieves are used to remove carbon dioxide. Pressure-swing absorption[10] is also very common. Hydrogen sulfide, which is problematic because of its corrosive effect, is captured on impregnated active coal or by absorption.[11]

Membrane separation represents the latest approach to biogas purification. Polymeric membranes made of silicone rubber[12] and cellulose acetate have already been described.[13] Polyimide membranes[14,15] are very popular and polyether block amide membranes have also been tested.[16] Most of these membranes are effective for CH_4/CO_2 separation, but the majority of them cannot be used for biogas purification because they are destroyed by aggressive gases. Nevertheless, they have already been applied for inert gases.[17] A very promising method of gas separation is represented by ionic-liquid membranes. Their main advantages are high fluxes through membranes and a very good selectivity.[18] Many different ionic liquids have been used to separate methane from carbon dioxide[19–21] and their effectiveness has been proved. However, ionic liquids appear to be too expensive for biogas treatment on an industrial scale, their hygroscopic properties lead to water degradation of the ionic liquid, and certain biogas compounds may cause their fast degradation. Moreover, their low chemical reactivity cannot preclude accumulation of unfavorable substances in membranes. That is why membrane processes for biogas treatment do exist[22] but do not employ liquid membranes.

We have proposed a new method of membrane separation called the "condensing-liquid membrane" (CLM).[23] This type of membrane has a significant advantage over the usual liquid membrane. Unwanted and toxic gases are removed from its continuously refreshed surface with condensed water to avoid contamination of the permselective membrane; furthermore, condensed water passing through the membrane ensures selectivity of the whole separation. The CLM is in fact a liquid (water in this case) condensing on a porous hydrophilic membrane as a result of the temperature difference of the membrane and water-saturated biogas feed. The main difference between the CLM and an immobilized liquid membrane lies in the fact that the condensing membrane is being regenerated during its continuous operation. The feed mixture of gases (raw biogas from a sewage plant, see Table 1) is saturated by water vapor.

The porous membrane (the optimal pore size must be found) has to be cool enough to make the liquid condense in its pores. In our case study, the feed biogas was thermostated at 27 °C and the porous membrane at 14 °C. Various operational conditions were followed and their effect on the separation of methane from unwanted gases was monitored.

Table 1: Composition of biogas before and after separation.[a]

Compounds	Unit	Feed	Retentate	Permeate
flow rate of streams	$mL\,min^{-1}$	10.08	8.88	1.30
sum of aromatic hydrocarbons	$mg\,m^{-3}$	87.1	7.92	23.8
sum of chlorinated and aliphatic hydrocarbons	$mg\,m^{-3}$	8.26	2.00	3.80
sum of siloxanes	$mg\,m^{-3}$	130	9.10	13.0
hydrogen sulfide	vol%	0.34	0.19	1.34
water	vol%	3.40	2.51	16.5
carbon dioxide	vol%	27.2	21.3	67.6
methane	vol%	67.6	76.0	14.5

[a] Measured at a feed flow rate of 10 $mL\,min^{-1}$ of raw biogas at 27 °C with the porous membrane at 14 °C. The minor gases are also dissolved in condensing water.

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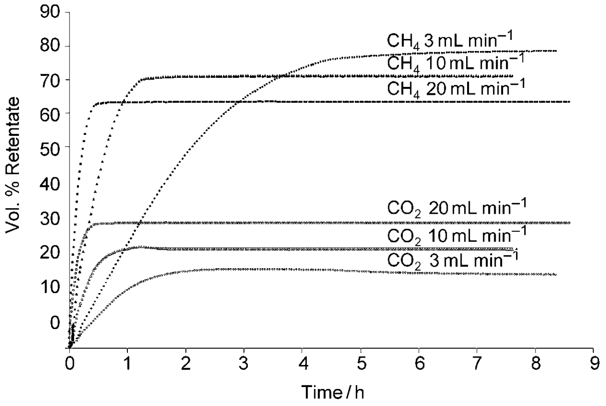

Figure 1. Dependence of kinetics of separation on feed flow rate ($\Delta p = 200$ kPa). The breakthrough pressure difference of the CLM is 280 kPa.

As can be seen from Figure 1, the feed flow rate played a crucial role in the separation of the components by a CLM. With higher feed flow rate, the steady state is achieved more quickly; however, as the residence time of biogas in the permeation cell is shorter, the methane concentration in the retentate is lower. In other words, if the residence time is shorter, a smaller amount of preferentially permeating components (carbon dioxide, hydrogen sulfide) is able to penetrate through the CLM.

The driving force of the separation is the difference in chemical potential, which in our case is a function of concentration and pressure. The cell in which the CLM is placed is well thermostated and its active membrane area is 133 cm^2. The speed of the separation is represented by the permeation flux of all components present in the feed. The permeation flux of component i (J_i) is defined as the number of liters or kilograms permeating through a membrane per square meter per hour. The permeation fluxes of the main biogas components in our laboratory-scale apparatus at a pressure difference of 200 kPa are $J_{\mathrm{CH_4}} = 1.31\,\mathrm{L\,m^{-2}\,h^{-1}}$ and $J_{\mathrm{CO_2}} = 6.12\,\mathrm{L\,m^{-2}\,h^{-1}}$ through a hydrophilic porous Teflon membrane with 65% porosity, pore diameter 0.1 µm, membrane thickness 30 µm, and initial feed flow rate 10 mL min^{-1}. The real separation factor is $\alpha = 4.67$, which is higher than the value so far published with a polyimide membrane ($\alpha = 3.95$).[24] The optimal conditions must therefore be further investigated to balance the cost-effectiveness of the industrial process.

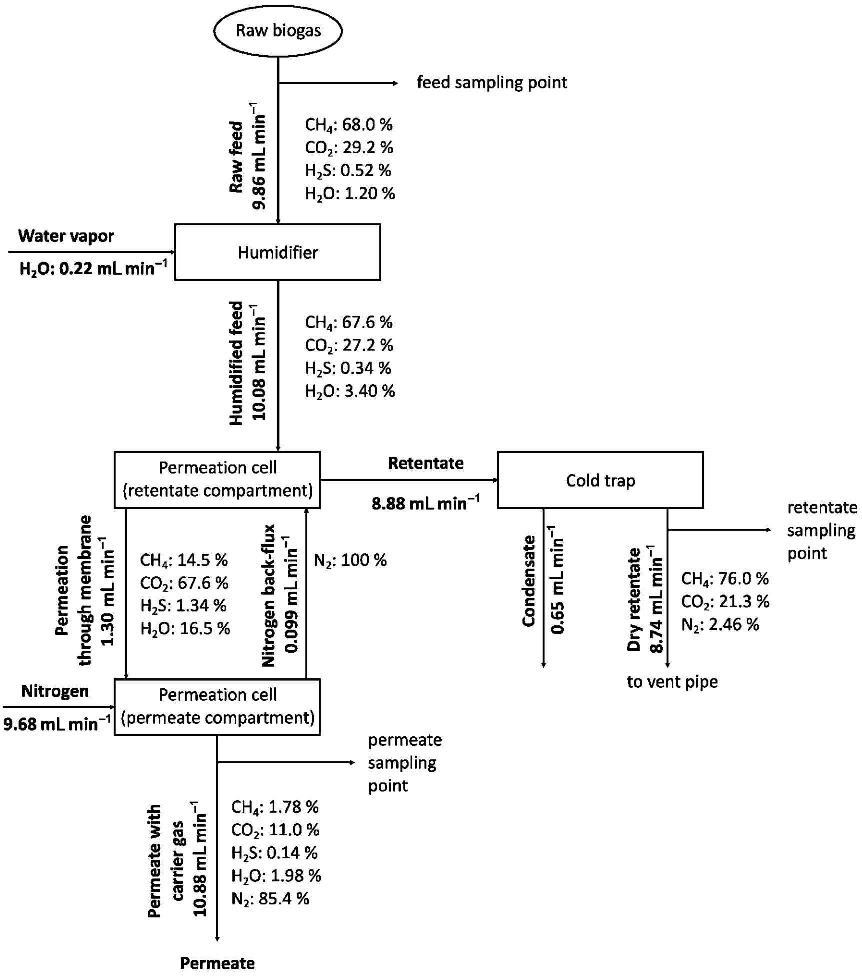

Figure 2. Flow diagram of molar balance of the separation of raw biogas. All fluxes are expressed as volume flow rates under normal conditions, assuming ideal-gas behavior for all components.

Because of a demand for the lowest cost of separation, a membrane suitable for biogas treatment has to be as cheap as possible. Following the idea of the CLM, water seems to be the ideal liquid from the processing point of view. Its presence in all types of biogas, which is usually seen as a disadvantage, thus changes into an indisputable advantage and necessity. The selectivity of the condensing membrane is given by the different solubilities of methane and carbon dioxide in water. Other minor compounds present in raw biogas (hydrogen sulfide, mercaptanes, and siloxanes) are much more soluble in water than methane. Porous hydrophilic Teflon is a support on which water is able to condense and is not involved in the separation. The CLM is able to separate more undesirable components from biogas in one separation step. Water vapor from biogas is used to refresh the membrane because it condenses on the feed side of the membrane and is partially removed from the permeate side of the membrane by sweeping gas (nitrogen). Thus, the CLM is a new and revolutionary change in biogas upgrading.

The whole separation process is described as a flow sheet in Figure 2, in which the molar balance of all streams is displayed. The molar balance is executed on the basis of an oriented graph formed by four knots and 10 streams. This balance respects the law of conservation of matter and Avogadro's law. Six balanced components are used. The obtained balance equations form a system of 43 linear equations solved by an elimination method. By their solution, the flow rates and composition of all streams are obtained. Calculations are based on analyses of raw biogas, retentate, and permeate. Moreover, the results correspond to the measured flow rates of nitrogen and raw biogas. The obtained results are also presented in Figure 2. The hydrogen sulfide, mercaptanes, and siloxanes are mostly removed from the feed stream by condensing water (see Table 1). In case of enough long membrane modules (larger membrane area) it would be possible to enrich raw biogas up to natural-gas quality (minimum 95% of methane content).

In summary, a new method for raw biogas purification and carbon dioxide separation by a CLM was developed. The separation is based on the different solubility of components of raw biogas in a very thin, continuously refreshed water layer on/in a hydrophilic porous membrane. The permeation flux of each component of biogas depends on the feed flow rate of the gases and pressure and temperature differences between the upstream and downstream side of the CLM. The selectivity of the CLM increases with a lower feed flow rate. The molar balance based on 43 linear equations confirmed the high potential of this method to upgrade raw biogas to natural-gas quality. The CLM can also be used under unfavorable conditions in which other polymeric membranes could be contaminated or destroyed by aggressive substances.

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[1] R. Dewil, L. Apples, *Energy Convers. Manage.* **2006**, *47*, 1711–1722.

[2] W. Kossmann, U. Pönitz, et al.: Biogas basics. Biogas Digest 1, project of Information and Advisory Service on Appropriate Technology (ISAT).

[3] S. Rasi, A. Veijanen, J. Cintala, *Energy* **2007**, *32*, 1375–1380.

[4] W. Xiao, W. Yao, Z. Jun, C. Miller, *Bioresour. Technol.* **2010**, *101*, 4042–4047.

[5] F. Osorio, J. C. Torres, *Renewable Energy* **2009**, *34*, 2164–2171.

[6] C. Jury, E. Benetto, J. Koster, B. Schmitt, J. Welfring, *Biomass Bioenergy* **2010**, *34*, 54–66.

[7] E. Wheless, J. Pierce, *Siloxanes in Landfill and Digester Gas Update*, SWANA 27th Landfill Gas Conference, March 22–25, **2004**.

[8] M. Schweigkofler, R. Niessner, *Environ. Sci. Technol.* **1999**, *33*, 3680–3685.

[9] M. Schweigkofler, R. Niessner, *J. Hazard. Mater.* **2001**, *83*, 183–196.

[10] N. Abatzoglou, S. Boivin, *Biofuels Bioprod. Biorefin.* **2009**, *3*, 42–71.

[11] T. Ahrens, P. Weiland, *Landbauforsch. Voelkenrode* **2007**, *1*, 71–79.

[12] F. Wu, L. Li, X. Zhihong, T. Shujuan, Z. Zhibing, *Chem. Eng. J.* **2006**, *117*, 51–59.

[13] H. M. Ettouney, G. Al-Enezi, S. E. M. Hamam, R. Hughest, *Gas Sep. Purif.* **1994**, *8*, 31–38.

[14] J. Zhang, J. Lu, W. Liu, Q. Xue, *Thin Solid Films* **1999**, *340*, 106–109.

[15] J. D. Wind, D. R. Paul, W. J. Koros, *J. Membr. Sci.* **2004**, *228*, 227–236.

[16] S. Sridhar, R. Suryamurali, B. Smitha, T. M. Aminabhavi, *Colloids Surf. A* **2007**, *297*, 267–274.

[17] F. F. Krull, C. Fritzmann, *J. Membr. Sci.* **2008**, *325*, 509–519.

[18] A. Corti, D. Fiaschi, L. Lombardi, *Energy* **2004**, *29*, 2025–2043.

[19] X. Hua, T. Jianbin, A. Blasig, S. Youqing, M. Radosz, *J. Membr. Sci.* **2006**, *281*, 130–138.

[20] J. E. Bara, C. J. Gabriel, E. S. Hatakeyamaa, T. K. Carlisle, *J. Membr. Sci.* **2008**, *321*, 3–7.

[21] P. Scovazzo, D. Havard, M. McShea, S. Mixon, D. Morgan, *J. Membr. Sci.* **2009**, *327*, 41–48.

[22] A. Makaruk, M. Miltner, M. Harasek, *Sep. Purif. Technol.* **2010**, *74*, 83–92.

[23] "Upgrade of biogas from sewage plant or from agriculture by methane and the apparatus": P. Izak, M. Poloncarzova, J. Vejrazka, PV 2010-437, **2010**.

[24] M. Harasimowicz, P. Orluk, G. Zakrzewska-Trznadel, A. G. Chmielewski, *J. Hazard. Mater.* **2007**, *144*, 698–702.