Copernican Letters®Vol 6/2015

ISSN: 2082 968X

Use of membranes in the implementation of the "Power to gas" concept

Maciej Szwast[1]

Department of Chemical and Process Engineering, Warsaw University of Technology, Poland

Abstract

This paper presents the possibility of membrane use in the Power to Gas concept.
Power to Gas is a concept of electrical energy conversion into the gaseous methane by well known Sabatier reaction. This reaction needs pure reagents such as carbon dioxide and hydrogen. The polymeric dense membranes could be used to obtain pure carbon dioxide from the stream of biogas or flue gas. The products of this reaction are methane and water. For methane dewatering one could also use polymeric membranes.
The paper presents literature data as well as the Author's own research results.

Keywords: Power to gas, Sabatier reaction, membrane processes, gas separation

Each of the global economies needs a regular supply of energy for its development. Thus, the access to energy resources is the subject of policies pursued and often also wars waged throughout the world.

At present, energy is generated from raw materials such as: hard coal, brown coal, crude oil, natural gas, peat, shale and radioactive elements. However, there are a lot of problems related, e.g. the depletion of resources or the impact of extraction and exploitation on the environment. It should be remembered that using most of the aforementioned energy sources results in production of such compounds as carbon oxides, sulfur oxides and dusts e.g. PM2.5 (solid particles whose diameter is not bigger than 2.5 μm). With the increasing global demand for energy (see Table 1) [1], the environmental pollution is growing as well.

Table 1. Global demand for primary energy in the so-called reference scenario, expressed in million tonnes of oil equivalent [1].

Energy source	1971	2003	2010	2020	2030
Coal	1439	2582	2860	3301	3724
Crude oil	2446	3785	4431	5036	5546
Natural gas	895	2244	2660	3338	3942
Nuclear energy	29	687	779	778	767
Water energy	104	227	278	323	368
Biomass and wastes	683	1143	1273	1454	1653

[1] Corresponding author email: *M.Szwast@ichip.pw.edu.pl*

Other renewable sources	4	54	107	172	272
Total	5600	10723	12389	14402	16271

For years the European Union has been managing programmes aimed at increasing the efficiency of energy generation as well as increasing the share of non-conventional sources in energy production with minimizing the negative effects of exploitation of traditional sources. Among the conventional energy sources, natural gas appears to be the most environment friendly (see Table 2) [2].

One of the requirements imposed by the European Union on the Member States is to increase the share of unconventional energy in total energy production. Currently, in Poland the rate is approx. 9% and is anticipated to reach 15% by 2020. Unconventional energy sources include mostly biogas plants, wind power plants and photovoltaic plants. In particular, the last two sources are very much dependent on weather conditions and seasons. Consequently, there are periods of increased and lowered energy production, which are always difficult to predict. In countries such as Poland, where the share of such resources is small, irregularity of energy production does not significantly affect the national energy system. On the other hand, countries with a large share of wind power and solar energy systems (e.g. Germany and Austria, where the share of conventional energy is approx. 30%) have to face a problem of maintaining constant energy production throughout the energy system. Within the next years, this issue will have to be addressed by other countries which are increasing the share of renewable energy in overall production.

Table 2. Amount of air pollutants emitted in the combustion process of various types of fuels [kg/teracalorie] [2].

Contamination	Natural gas	Furnace oil	Coal
Carbon dioxide	21100	29500	37400
Carbon monoxide	72	59	374
Nitrogen oxides	166	806	823
Sulfur dioxide	1.1	2 020	4664
Solid particles	12.6	151	4939
Formaldehyde	1.350	0.396	0.398
Mercury	0.000	0.013	0.029

One of the possible solutions to the problem of the fluctuating energy supplied to the system is its storage during overproduction periods and consumption in underproduction periods. Construction of pumped storage power plants is a method of energy storage which has been in use for many years. However, the current landscape adaptability does not permit to build enough such plants to meet the energy demand. Storage of electrical power in batteries is inefficient either. Among all the possible forms of energy storage the best and the most beneficial one is the form of gas – hydrogen or methane. It is these two gases that may store large quantities of energy and enable its long exploitation [3].

An advantage of methane over hydrogen is that it is safer to store and that its storage tanks are better sealed. In addition, in contrast to hydrogen, methane can be pumped directly to a gas grid and become a source of energy on an instant basis.

Therefore, the reasonable question is how to store electrical energy in the form of gas – hydrogen or methane. The above issue is addressed in the title concept Power to Gas.

Power to Gas concept

The Power to Gas (P2G) concept is a technology that converts electrical power to energy stored in a gaseous fuel, such as hydrogen or methane. There are three methods in use to achieve this. The stage shared by all three methods is water electrolysis to hydrogen and oxygen. Electrical power is put to the process of electrolysis, and the resulting product is fuel in the form of hydrogen. In the first method to implement this concept, the resulting hydrogen is a ready-to-use product which can be stored. The second method of P2G implementation is to enrich biogas with hydrogen produced from electrolysis. The third method which will be the subject of further considerations, involves a chemical reaction of synthesis hydrogen with carbon dioxide. One of the products of this reaction is methane.

The chemical reaction commonly called methanization of carbon dioxide was described by Sabatier in 1902. The equation of the reaction is as follows:

$$4\,H_2 + CO_2 \leftrightarrow CH_4 + 2\,H_2O + \Delta H \qquad (1)$$

where ΔH is enthalpy of the reaction and equals -165 kJ/mol.

The Sabatier reaction is a catalytic reaction at elevated temperature (approx. 400^{o}C) using catalysts such as Rh, V or Cu.

The process of carbon dioxide methanization in the Sabatier reaction with the use of hydrogen produced by an electrolyser is of a relatively low efficiency. The average efficiency of the process is 50%. From the point of view of thermodynamics it is a low value. However, facing the possible waste of the whole excess energy produced by solar and wind power plants, this value could be considered acceptable. The efficiency of energy conversion may be increased by partial heat recovery during the process.

The Power to Gas concept implemented as methanization of carbon dioxide is presented in Fig. 1, which shows supply sources of carbon dioxide and engineering tasks required for implementing this concept.

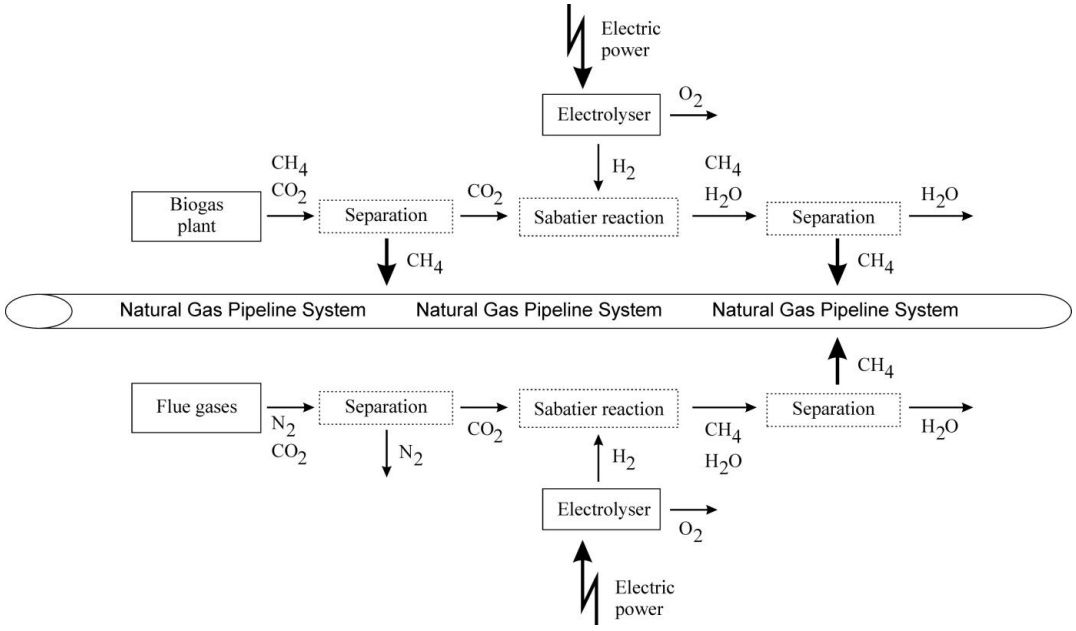

Fig. 1. General concept of Power to Gas implemented by mechanization of carbon dioxide.

According to some scientific concepts, carbon dioxide is the cause of greenhouse effect. Legal requirements impose reduction of its emissions, so methods of its management are extremely valuable. Hence, for the Sabatier reaction, carbon dioxide may be derived from two sources: from biogas, where carbon dioxide is a major component which reduces the energy value of biogas, or from exhaust gases produced practically in all industries.

If carbon dioxide is to be derived from biogas, it is necessary to separate it from methane. If it is derived from exhaust gas, it must be separated from other components, in particular from nitrogen. At a later stage, dehydration of methane flux resulting from the Sabatier reaction is a method shared by both sources of carbon dioxide production.

Such gas and vapor mixtures may be separated with the use of various methods known to the process engineering. Among such methods there are: absorption, adsorption and cryogenic methods. Membrane techniques could also be successfully applied for separation of such mixtures. It is this method that the further part of the paper will focus on.

Membrane separation of gases and vapors

Polymer membranes are mostly used to separate volatile matter (gas and vapor). Pore-free dense membranes with the solution-diffusion model of mass transfer play a special role in this case. Each of the gas components, under the influence of different partial pressures on both sides of the membrane, is subject to solution in membrane material as well as to diffusion through the membrane and the subsequent desorption. The individual components of volatile mixtures (gases and vapors) have different sorption and diffusion coefficients depending on the polymer material. This diversification affects the ability of the membrane to separate mixture components.

The main parameters of membrane used to separate gas components are its permeability P of a selected component and selectivity α. The first of these parameters, which is a product of the sorption coefficient S and diffusion coefficient D of a selected component (equation 2) describes the membrane transfer capacity. The higher the coefficients the higher the flux of mass, which is beneficial in terms of the process.

$$P = S \cdot D \tag{2}$$

The selectivity coefficient describes how efficient the membrane is in separating components of a mixture, and is defined as follows:

$$\alpha^*_{A/B} \stackrel{\text{def}}{=} \frac{\frac{x_A}{x_B}}{\frac{y_A}{y_B}} \tag{3}$$

where x is a mole fraction of component A or B, respectively, for the permeate, and y is a mole fraction of component A or B, respectively, for the feed. This coefficient, for ideal conditions, can be also derived from:

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{4}$$

From the perspective of the process, also this membrane parameter should achieve as high values as possible. However, for polymer membranes there is a correlation between permeability and the selectivity. An increase in one of these values causes a drop in the other. These limitations may be overcome by the use of the so-called Mixed Matrix Membranes, which in their structure have inorganic solid particles in addition to polymers. This study will not elaborate on that, though.

Membranes used to implement the Power to Gas concept

In the implementation of the Power to Gas concept the task that has to be performed is separation of gas and vapor mixtures (see Fig. 1). Mixtures to be separated are as the following: CH_4 and CO_2, N_2 and CO_2, as well as CH_4 and H_2O (dehydration). Obviously, it should be noted that both mixture produced in a biogas plant and a mixture of exhaust gases coming from chimneys are not pure bicomponent mixtures. They also contain other compounds, but their separation from the main flux will not be discussed here. Also, it should be remembered that, in addition to the products of the Sabatier reaction – equation (1) – the gas flux leaving the reactor may contain a non-reacted carbon dioxide or hydrogen.

Table 3 shows in the tabular form, the various polymer membranes which can potentially be used for separation of the aforementioned gas mixtures and dehydration of the methane stream. Attention is focused on the aforementioned main parameters of membranes, i.e. permeability (expressed in the unit of barrer) and selectivity of membranes.

The analysis of the data contained in Table 3 confirms the earlier remark about the correlation between the membrane permeability and the membrane selectivity. The remark mainly refers to gas mixtures rather than gas and vapor (e.g. water) mixtures. What is noticeable is that membranes with a high selectivity coefficient are relatively low permeable. Both of the parameters must be taken into account when designing the membrane process. A high selectivity membrane generates purer products. On the other hand, with a high permeability membrane it is possible to run the process in a more cost-effective way and achieve more products at the same energy cost. The membrane installation design must therefore compromise between product quality and cost-effectiveness of the process.

The data included in Table 3 referring to the characteristics of the various membranes have been achieved in laboratory conditions on samples of a small area. Unfortunately, the commercial selection of membranes for gas separation is not so extensive. This is due to the technical difficulty to manufacture large area membranes out of these materials. Such difficulties include for instance defects in a thin selective layer of the membrane. Such defects preclude the membrane from being used for the purpose of separating gas components.

Table 3. Membranes used to implement the Power to Gas concept.

CO_2 / N_2 separation				
Material	$\alpha_{CO2/N2}$ [-]	P_{CO2} [barrer]	P_{N2} [barrer]	
BPDA–mDDS/PEO1(80)	58	3.8	0.066	[4]
PSF-BPFL	40	10	0.25	[5]
PC–AP	26.3	9.48	0.361	[6]
Poly(dimethyl-phenyl-(1-propyl-prop-2-ynyl)-silane)	21.6	54	2.5	[7]
6FDA–FDA/HFBAPP	23.4	465	19.9	[8]
6FPT–BPA	13.5	18.53	1.37	[9]
CO_2 / CH_4 separation				
Material	$\alpha_{CO2/CH4}$ [-]	P_{CO2} [barrer]	P_{CH4} [barrer]	
Matrimid®52 18 + CMS (100%) – Mixed Matrix	200	44	0.22	[10]
6FDA-1,5-NDA	49	22.6	0.46	[11]
6FDA-DAM + ZIF-90 (15%) – Mixed Matrix	37	720	0.05	[12]
6FDA-durene	16.1	458	28.4	[13]
Poly(dimethylsiloxane) PDMS	3.17	3800	1198	[14]
H_2O / CH_4 separation				
Material	$\alpha_{H2O/CH4}$ [-]	P_{H2O} [barrer]	P_{CH4} [barrer]	
Nafion® 117	4100000	410000	0.1	[15]
Polyimide	14000	640	0.045	[16]
Pebax® 1074	6060	50000	8.25	[17]

Own research on membrane production

A team under the supervision of the Author has been involved in development research aimed at developing a technology that produces membranes for gas separation on an industrial scale. With regard to the Power to Gas concept, the Author's team has developed large-area membrane modules which have properties as indicated in Table 4.

Table 4. Properties of membranes developed to implement the Power to Gas concept.

CO_2 / N_2 separation				
Material	$\alpha_{CO2/N2}$ [-]	P_{CO2} [barrer]	P_{N2} [barrer]	
Pebax 1074	35.4	125	0.28	[18]
Pebax 1074 / PEO	26	35.6	1.37	[19]
CO_2 / CH_4 separation				
Material	$\alpha_{CO2/CH4}$ [-]	P_{CO2} [barrer]	P_{CH4} [barrer]	
Pebax 1074	15.5	125	0.12	[18]
Pebax 1074 / PEO	18.5	27.8	1.5	[19]

Summary

Polymer membranes for gas separation are potentially largely applicable to the Power to Gas concept. The role of these membranes is to separate carbon dioxide from methane (biogas plants) or from nitrogen (exhaust gas) and dehydrate the methane flux. The challenge engineers and technologists are facing is to develop, on an industrial scale, membranes that meet the process requirements. The Author's research identifies the group of Pebax copolymers as the ones about which there are great expectations regarding the industrial uses.

LITERATURE

[1]. Stańczyk K., *Czyste technologie użytkowania węgla*. Główny Instytut Górnictwa, Katowice 2008, ISBN 978-83-61126-15-7, in Polish.
[2]. Łucki Z., Misiak W., *Energetyka a społeczeństwo. Aspekty socjologiczne.* Wydawnictwo Naukowe PWN, Warszawa 2010, ISBN 978-83-01-16346-4, in Polish
[3]. Specht M., Baumgart F., Feigl B., Frick V., Sturmer B, Zuberbuhler U., Sterner M., Waldstein G., Storing bioenergy and renewable electricity in the natural gas grid, FVEE, AEE Topics (2009).
[4]. Yoshino M., Ito K., Kita H., Okamoto K.-I., Effects of hard-segment polymers on CO2/N2 gas-separation properties of poly(ethylene oxide)- segmented copolymers, J. Polym. Sci. Part B: Polym. Phys. 38 (2000) 1707-1715.
[5]. Kazama S., Teramoto T., Haraya K., Carbon dioxide and nitrogen transport properties of bis(phenyl)fluorene-based cardo polymer membranes, J. Membr. Sci. 207 (2002) 91-104.
[6]. Aguilar-Vega M., Paul D.R., Gas transport properties of polycarbonates and polysulfones with aromatic substitutions on the bisphenol connector group, J. Polym. Sci. Part B: Polym. Phys. 31 (1993) 1599-1610.
[7]. Stern S.A., Polymers for gas separations: the next decade, J. Membr. Sci. 94 (1994) 1-65.
[8]. Chun B.-W., Ishizu C., Itatani H., Haraya K., Shindo Y., Characterization, Gas permeability of a three-component polyimide series, J. Polym. Sci. Part B: Polym. Phys. 32 (1994) 1009-1016.
[9]. Xu Z.-K., Dannenberg C., Springer J., Banerjee S., Maier G., Novel poly(arylene ether) as membranes for gas separation, J. Membr. Sci. 205 (2002) 23-31.
[10]. Vu D.Q., Koros W.J., Miller S.J., Mixed matrix membranes using carbon molecular sieves: I. Preparation and experimental results. J. Membr. Sci. 211 (2003) 311–334.
[11]. Wang R., Cao C., Chung T.S., A critical review on diffusivity and the characterization of diffusivity of 6FDA-6FpDA polyimide membranes for gas separation, J. Membr. Sci. 198 (2002) 259–271.
[12]. Bae T.-H., Lee J.S., Qiu W., Koros W.J., Jones C.W., Nair S., A high-performance gas-separation membrane containing submicrometer-sized metal–organic Framework Crystals, Angewandte Chemie International Edition 49 (2010) 9863–9866.
[13]. Liu Y., Chng M.L., Chung T.-S., Wang R., Effects of amidation on gas permeation properties of polyimide membranes, J. Membr. Sci. 214 (2003) 83–92.
[14]. José N.M., Prado L.A.S.A., Yoshida I.V.P., Synthesis characterization, and permeability evaluation of hybrid organic–inorganic films. Journal of Polymer Science Part B: Polymer Physics 42 (2004) 4281–4292.
[15]. Chiou J.S., Paul D.R., Gas permeation in a dry Nafion membrane, Ind. Eng. Chem. Res. 27 (1988) 2161–2164.
[16]. Mulder M., *Basic Principles of Membrane Technology*, 2nd ed., Kluwea Academic Publishers, Dordrecht 1996. ISBN 978-94-009-1766-8.

[17].Potreck J., Nijmeijer K., Kosinski T., Wessling M., Mixed water vapor/gas transport through the rubbery polymer PEBAX® 1074, J. Membr. Sci. 338 (2009) 11–16.
[18].Szwast M., Makaruk A., Harasek M., Gas separation membranes made of PEBA block copolymer, ACEE 4 (2012) 107-111.
[19].Szwast M., Polak D., Zalewski M., Technologia wytwarzania membran wspomagających proces magazynowania energii elektrycznej w postaci substytutu gazu ziemnego, materiały 8. Kongresu Technologii Chemicznej, Rzeszów 2015, e-copy, in Polish