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EVALUATION OF POSSIBLE APPLICATIONS OF MEMBRANE SEPARATORS FOR PURIFICATION OF GAS FROM UNCONVENTIONAL DEPOSITS

1. INTRODUCTION

Part of the gas associated with oil production is considered to be waste due to its too low quantity or composition. As a consequence it is flared. Economically, managing of such small amounts of gas is unprofitable therefore they are utilized. According to the literature sources [1] about 8% of gas extracted with oil is utilized in this way. Gas flaring cannot be treated as a good solution as it has a negative environmental impact, the installations wear away and the respective costs increase. The amount of gas flow and its composition determine the way in which the field is managed. Frequently, the resources of the produced gas are too small as compared to the related costs and the field remain unmanaged. Some conventional fields, and certainly a majority of unconventional shale gas fields, have relatively poor flows and the production from a developed field may be viewed in a perspective of a dozen or so years. Another unknown is the gas composition; apart from methane the gas may also contain other hydrocarbons, hydrogen, carbon dioxide, nitrogen, hydrogen sulfide, etc. The parameters of gas supplied to the gas network are strictly determined by the operator who may reject gas fuel which does not meet specific requirements. Many scientific and industrial centers realize research works on gas cleaning methods, and membrane gas separators are one of the possible solutions.

2. BASIC CHARACTERISTIC OF MEMBRANES

The analyses of membranes, new materials in particular, which have been conducted over the last years cause that membrane separators became one of the most prospective technologies. The asymmetrical membranes are recommended for industrial purification of gases.

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They should be highly permeable and highly selective; their surface layer should be thin and dense whereas the inner layer thick and porous. Figure 1 illustrates the typical structures of various types of membranes. They were grouped into the following categories with respect to the cross-section of their microstructure [1]:

– Symmetrical membranes (homogeneous, porous, with cylindrical pores);
– Asymmetrical membranes (porous, porous with thickened surface layer, composite);
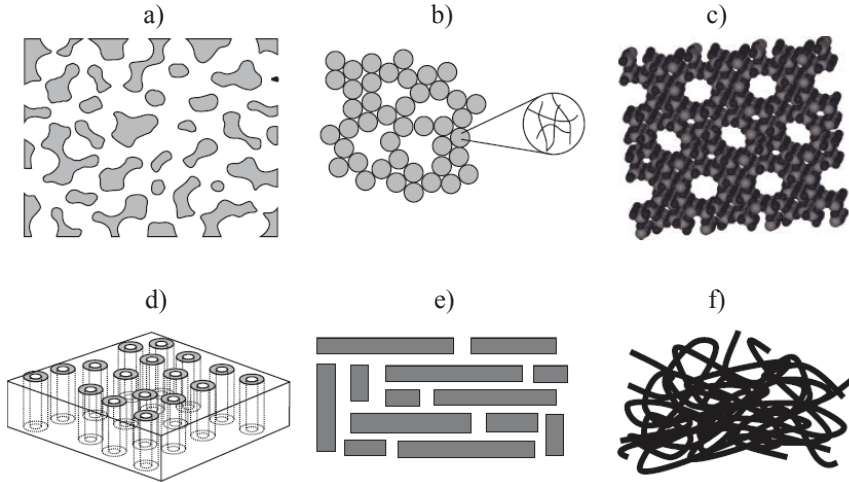

Fig. 1. Exemplary structures of various types of membranes – a) microporous glass, b) silica, c) zeolite, d) carbon nanotubes, e) carbon layers, f) polymers [5]

Six major processes can be distinguished in membranes used for industrial purposes [1]:

– Microfiltration – process takes place in pores of 0.2 to 10 μm, at a pressure of 0.1 to 0.3 MPa the high velocity of a few to a dozen m/h can be obtained.
– ultrafiltration (molecular filtration) – process takes place in molecular sieves, membranes and other porous materials, whose pore size is close to that of individual molecules. Ultrafiltration is a time-consuming process requiring high pressures.
– Reverse osmosis – process with induced diffusion through a semipermeable membrane separating two solutions of different concentration. Opposite to the spontaneous osmosis, reverse osmosis takes place from a higher concentration solution to a lower concentration solution. This leads to the increasing concentration difference in both solutions. This process has to be initiated by exposing the membrane to a pressure of a higher value and directed oppositely to the direction of osmotic pressure, which is naturally present in the system.
– Electrodialysis - the migration of ions in electrical field with the participation of membranes (diaphragms) of exchangeable anion-cation properties. Membranes let the anions and cations in but selectively stop the opposite ions.
– Gas separation – gravitational separation process.

– Pervaporation – separation process of liquid chemical mixtures where polymeric membranes („dense' or „ceramic') of diameter below 5 nm are commonly applied. The resulting separation stems from differences in the solubility of particular components in the diaphragm (sorption) and differences in their diffusion through the membrane. This technique does not require lowering of pressure on the permeate (substance separated from the solution) side though is used for enhancing it. Pervaporation is an alternative of reverse osmosis. Among the advantages of this method is its high selectivity, efficiency in diluted mixtures. Besides it is environmentally friendly, e.g. the cost of production of unhydrous ethanol can be reduced by about 25 to 50% as compared to distillation with azeotropic factor or dehydration with the use molecular sieves, mainly thanks to the lower energy requirements.

The parameters which are crucial for the correct operation of membranes are: selectivity, permeability and mechanical strength. The common applications of membrane separators are listed in table 1.

Table 1

Applied membrane separators [1,2,4]

Process	Separated components
Oxygen enrichment, generation of neutral gases	O_2/N_2
Hydrogen recovery through refining	H_2/hydrocarbons
Ammonia purification	H_2/N_2
Regulation of synthetic gases ratio	H_2/CO
Removal of acidic gases	CO_2/hydrocarbons
Water removal	H_2O/hydrocarbons
Removal of acid gases	H_2S/hydrocarbons
Separation of helium	He/hydrocarbons
Helium recovery	He/N_2
Hydrocarbon recovery, contamination control	hydrocarbons/air
Drying of air	H_2O/air

3. THEORETICAL FORMULAS FOR FLUID FLOWING THROUGH MEMBRANES

A few models of gas mixture flows through porous membranes were worked out. They make us better understand this effect and properly select the separating material. The quantitative gas flow can be defined as an amount of molecules which penetrate a unit of surface in a unit of time. It has been accepted that the molecular flow J is in line with the Fick's First Law:

$$J = -D\frac{dc}{dx} \tag{1}$$

where:

D is diffusion coefficient, $c(x)$ – concentration, x – thickness of membrane. If a linear concentration of gradient is assumed along the membrane, the flow may be approximated with the following equation:

$$J = D\frac{C_2 - C_1}{L} \tag{2}$$

where:

$C_1 = c(0)$ and $C_2 = c(L)$ are concentrations of molecules on both sides of the membrane, L – thickness of membrane, as shown in figure 2.

The efficiency of membranes made of different materials is frequently compared with the use of permeability k, which does not depend on the thickness of the membrane but on flow J:

$$k = \frac{JL}{p_2 - p_1} \tag{3}$$

Making use of equation (2) we can write

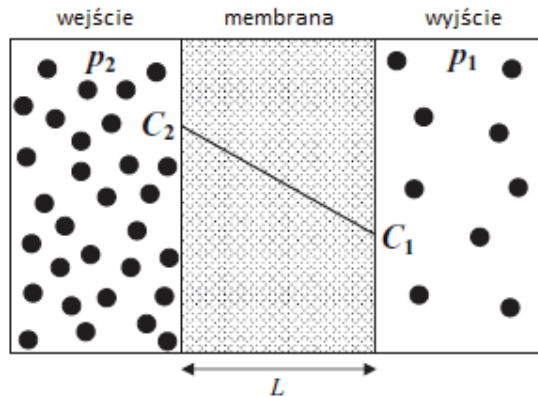$$k = D\frac{C_2 - C_1}{p_2 - p_1} \tag{4}$$

Fig. 2. Gas flow through membrane of constant concentration gradient along its thickness L [5]

When the inlet pressure is considerably higher than outlet pressure ($p_2 \gg p_1$) and inlet concentration is considerably higher than that on the outlet ($C_2 \gg C_1$), the permeability may be expressed in the following way:

$$k = \frac{C_2}{p_2}D \tag{5}$$

Introducing the solubility coefficient **S** defined as:
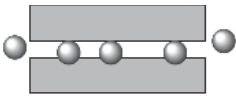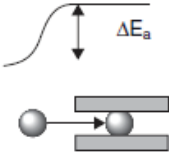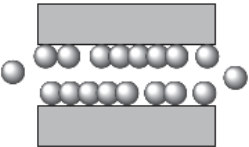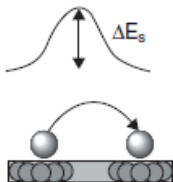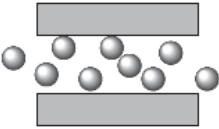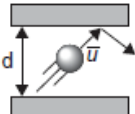
$$S = \frac{C_2}{p_2} \tag{6}$$

permeability (5) can be written as:

$$k = SD \tag{7}$$

The ability of a membrane to separate molecules A and B from their mixture is called selectivity or separation coefficient defined as a permeability for molecules A to permeability for molecules B ratio [5] $\alpha_{A/B} = k(A)/k(B)$.

Gases undergo diffusion both in porous and nonporous membranes due to the operation of various flow mechanisms. In table 2 we have various mechanisms by which molecules are transported, depending on the pore size. In very narrow pores, gases are separated using the molecular sieves mechanism which can be treated as an example of activated diffusion. This type of diffusion is considered as most popular for nonporous polymeric membranes [5]. When bigger pores are involved, (activated) surface diffusion takes place or Knudsen diffusion is observed.

Table 2

Exemplary flow mechanisms through the membrane [5]

Mechanism	Schematic	Process
Activated diffusion		Energy barrier ('choking') ΔE_a
Surface diffusion		Energy barrier(adsorption) ΔE_s
Knudsen diffusion		Velocity and direction

Surface diffusion dominates in the area between activated diffusion and Knudsen diffusion. The model describing this type of flow has elements of transport in gaseous and liquid phase in the polymeric porous membrane. When the number of pores decreases below a certain level which depends on the material of the membrane and gas permeability, the coefficient of gas permeability reaches the value of free molecular flow (Knudsen diffusion) especially for organic gases. Surface diffusion is also a form of activated diffusion and the energy barrier ΔE_S is the required energy which a molecule must possess to enable its transport from one side of porous surface to the other. Having assumed that the energy barrier is proportional to the adsorption enthalpy, the following dependence for the surface diffusion can be written:

$$D_s = D_{s1}\exp\left(\frac{-aq}{RT}\right)$$ (8)

where:

D_{S1} is the coefficient depending of the frequency of vibrations of adsorbed molecules to the surface and the distance between the diffusion sides.

q (>0) is adsorption heat

a proportionality constant (0<a<1), so aq is an energy barrier separating both sides of the membrane.

R – individual gas constant,

T – temperature.

In the case of surface diffusion the gas concentration may be described with the Henry Law:

$$c = Kp$$ (9)

where:

K – depends on temperature and is defined from the relation $K=K_0 exp(q/RT)$,

K_0 – is the proportionality constant.

As the solubility is a concentration to pressure (from eq. 6) ratio, then it is equivalent to the coefficient from the Henry Law:

$$S_S = K_0\exp\left(\frac{q}{RT}\right)$$ (10)

By substituting dependences described with formulas (8) and (10) to equation (7) we have the permeability:

$$k_S = k_{s1}\exp\left(\frac{(1-a)q}{RT}\right)$$ (11)

where: k_{s1} is constant, 0<a<1, total permeability lowers with the increase of temperature and the increase of diffusion results in lower concentration on the surface.

The Knudsen diffusion depends on the gas pressure and average free distance of moleculœs; for gaseous phase it is observed in pores of 10 Å to 500 Å [5]. In this area the average

distance available for molecules in a gaseous phase λ much exceeds the pore diameter d. The Knudsen number defined as $K_n = \lambda/d$, is commonly used. It characterizes penetration of substances through the pores. If K_n is much smaller than unity ($K_n \ll 1$) the flow has a laminar character. If K_n is many times higher than unity ($K_n \gg 1$), the Knudsen diffusion takes place. The flow has a transient character for K_n close to unity ($K_n \approx 1$). The Knudsen diffusion can be defined with the equation:

$$D_K = \frac{d}{3\tau} w \qquad (12)$$

where

τ – sinuosity of pores,

w – average molecular velocity.

Equation (12) shows that the result of separation should depend on differences of molecular velocities (or molecular masses) of particular components. The average molecular velocity can be calculated from the Maxwell equation:

$$w = \left(\frac{8RT}{\pi m}\right)^{1/2} \qquad (13)$$

where: m is molecular mass.

Substituting (13) to (12) we obtain a diffusion coefficient in the form:

$$D_K = \left(\frac{d}{3\tau}\right)\left(\frac{8RT}{\pi m}\right)^{1/2} \qquad (14)$$

The Knudsen flow may be expressed with the equation [5]:

$$J = n\pi d^2 \Delta p D_K / 4RTL \qquad (15)$$

where:

n – surface concentration of pores of diameter d,

Δp pressure drop along the membrane of thickness L.

The following expression for flow J and permeability coefficient k was obtained from above dependences [5]:

$$J = \left(n\pi^{\frac{1}{2}} d^3 \Delta p / 6\tau L\right) / \left(2 / mRT\right)^{1/2} \qquad (16)$$

$$k = \left(n\pi^{\frac{1}{2}} d^3 / 6\tau\right) / \left(2 / mRT\right)^{1/2} \qquad (17)$$

The following equations show that the separation selectivity in Knudsen diffusion is characterized by: $\alpha_{ij} = (M_j/M_i)^{1/2}$ i.e. highest separation selectivity is observed for lightest and heaviest gases, e.g. hydrogen and butane ($\alpha = 5.4$). In the case of gases of similar mass, e.g. O_2/N_2 $\alpha \approx 1$, the selectivity of membrane is very low.

4.   SELECTED TECHNOLOGICAL MEMBRANE SOLUTIONS

Membranes are separators commonly applied in gas industry. They consist of thousands of high quality hollow fibers, the ends of which are disposed on a resin surface in steel, stainless tubes. Such a construction provides tightness and protects the fibers against mechanical damaging.

Membranes are made of high quality synthetics which can withstand high pressures, temperatures and plastic deformations. Membranes are highly selective for CH_4/CO_2, thanks to which 98% methane concentration can be obtained at a level of 98% with about 0.5% losses.

The membrane technology is also effective as far as energy consumption is concerned. The MT-Membrane Technology uses about 0.2 to 0.25 kWh/m³. Another advantage of this solution is the easy adjustability of the installation to the varying gas streams and gas composition. This type of solution is applicable to flow rates of 250 to 2000 m³/h [3].

The management of unconventional gas deposits is connected with numerous unknowns as far as extraction goes. Gas composition is one of the factors determining gas destination and funds to be incurred for surface installation. The present experience shows to a considerable share of methane in the produced shale gas. Prior to sending it to the customers, gas has to be purified, and membrane separators can be successfully used for this purpose. The gas yield from the well is another important factor as it basically influences the size of the installation. The analysis of the gas production plot shows to significant flows at the initial stage of extraction, which results from the fracturing operation and the evoked gas flow to the well. The analysis of gas production in the successive years reveals that the flows had a decreasing tendency though remained on a constant level over long time perspective. Such a production characteristic induces flexible planning of the surface part of the system of gas preparation, both as far as construction and functionality go. Attention should be paid to the issue of redimensioning of production equipment and payback period. These restrictions in view, it seems reasonable to apply module solutions thanks to which large amounts of gas can be purified at the initial stage. Then, by separating and by replacing modules to a different site, the smaller amounts of gas from unconventional deposits would be possible.

The principle of membrane separator presented in figure 3 is based on selective permeability through the membrane surface. A pressure is exerted on the membrane module by a mixture of gases, the molecules of which are separated on the molecular level while the gas is passing through the membrane fibers. In the course of separation of the preliminarily purified gas some of its components, e.g. carbon dioxide or water penetrate the pores of the membrane (separated gases) methane flows along the membrane (purified gas). The permeability coefficient for gas depends on its solubility in membrane and depend of its structure. Therefore, some gases penetrate the membrane faster than other.

Figure 4 illustrates the schematics of the gas cleaning process with the use of a membrane gas separator. The produced gas may be a mixture of various components, e.g.

methane, carbon dioxide, hydrogen, sulfides, nitrogen, oxygen, steam, etc. First, the raw gas is preliminarily purified: is heated and dried, the sulfides are removed with the activated carbon filter. Then the preliminarily purified gas is compressed with a compressor to about 16 bar. For increasing the efficiency of the installation, part of thermal energy generated at the stage of compression is used at the further stage. The third step is drying. Excessive heat has to be removed from the system by cooling the gas mixture to lower the dew point of the steam and other gases which could be potentially condensed. This effect is achieved by a heat exchanger which cools down the gas with water supplied to the cooler, thus preventing gas condensation at further stages. Another step is gas heating. For optimizing separation properties of membranes, gas is heated up to a temperature of about 35 °C. Bearing in mind that contaminations could possibly deteriorate the permeability of membranes, gas undergoes a three-stage cleaning operation prior to being sent to the membrane module. The oil, aerosol and solid molecules are stopped as first on the microfilter, then the adsorption filter with activated carbon seizes other molecules and finally the third microfilter catches the remaining contaminations which managed to pass through till that point.
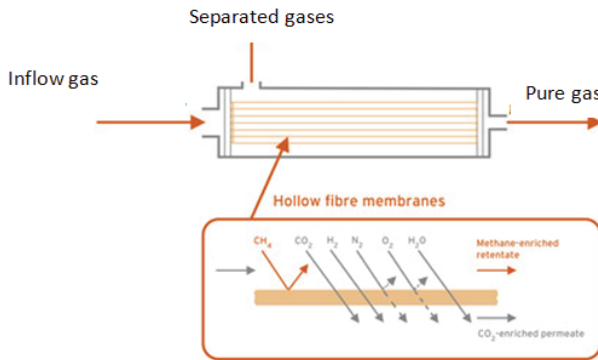

Fig. 3. Schematic of membrane separator operation [3, modified]

The last step lies in separation of gases on membranes. The number of connections inside the module depends on the required degree of methane-removal. Figure 4 illustrates a three-step separator [3] for separating carbon dioxide and methane. Its principle is as follows:
- at the first stage membrane fibers separate the gas to methane and carbon dioxide;
- at the second stage the separation is continued – inlet gas (CH_4 + smaller amounts of CO_2) flows through the membrane and another separation takes place – inlet gas of satisfactory purity is directed to further use, carbon dioxide goes to the compressor (step 2).
- at the third stage the gas separated at stage 1 is purified again. The inlet gas with methane content is directed to the compressor; the separated gas (containing less than 0.5 % CH_4) is utilized.
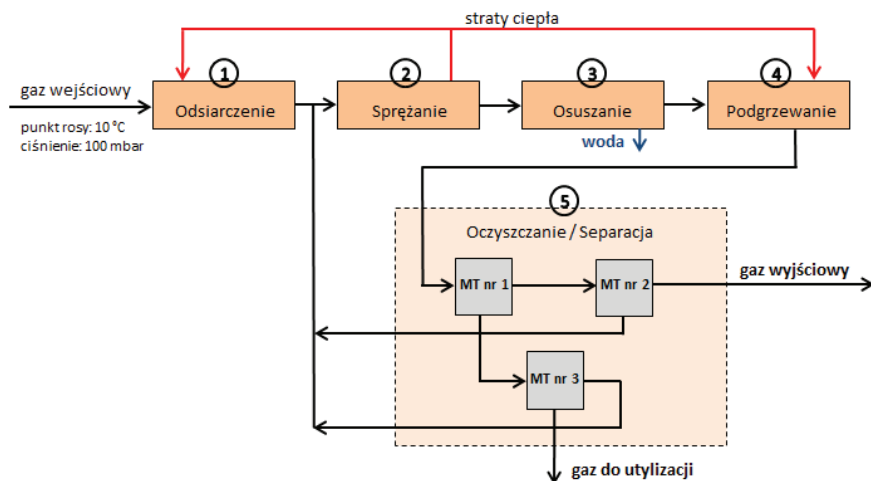
Fig. 4. Schematic of qualitative gas processing [3, modified]

5. SUMMING UP

- Membrane separators are frequently used for the filtration and purification of gases. The developing membrane technology, especially the life membranes, their applicability and possibility of linking with other technological modules, which may contribute to the growing popularity of this solution in industry.
- Membrane separators can be used in module installations specializing in purification of gas from unconventional sources. They can be easily adjusted to the varying gas stream parameters and gas composition. This option is economical because of the low cost of exploitation of membrane separators and high efficiency of gas cleaning.

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