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APPLICATION OF MEMBRANE TECHNOLOGY FOR SEPARATION CO_2 FROM NATURAL GAS

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Abstract: Natural gas consists of a mixture of hydrocarbons with the largest share of methane, and non-hydrocarbon impure components such as N_2, CO_2 and H_2S. In order to fulfill the gas market requirements, it is necessary to separate these unwanted components from the natural gas stream. There are several available technologies for the separation of CO_2 from natural gas, such as: polymeric membranes, cryogenic distillation, absorption and adsorption.

In this paper is presented the mechanism of CO_2 separation using membrane technology, as well as the process of separation CO_2 depending on the number of membranes in the system for a typical gas reservoir in Serbia.

Keywords: CO_2 separation; polymeric membranes; membrane modules;

1 INTRODUCTION

Natural gas is a mixture of hydrocarbons with the highest proportion of methane and variable amounts of non-hydrocarbon components such as acid gases (CO_2, H_2S). The average composition of natural gas in Serbia expressed in mol% is: 96,184 of C_1, 1,624 of C_2, 0,508 of i-C_4, 0,018 of n-C_4, 0,018 of i-C_5, 0,012 of n-C_5, 0,019 of C_{6+}, 0,99 of N_2 and 0,471 of CO_2 (Srbijagas-a). To meet market specifications, the natural produced gas must meet certain requirements such as composition, calorific value, and pressure. The maximum allowed value of CO_2 in the gas can be 2 mol%, while the value of N_2 is 3 mol% (Srbijagas-b). Removing impurities from natural gas increases the calorific value and reduces the volume of gas for transport. Available technologies for separation CO_2 from natural gas are membranes, cryogenic distillation, absorption, and adsorption. The removed CO_2 and N_2 can be injected into hydrocarbon reservoirs in order to increase the

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recovery of oil and gas reservoirs, and thus reduce greenhouse gas emissions into the atmosphere.

2 SEPARATION MECHANISM IN POLYMERIC MEMBRANES

Gas separation using membrane technology works on the principle of creating two streams of input mixture, retentate stream and permeate stream (Spillman, 1995). The retentate filtration represents the portion of the input mixture retained in the membrane, and contains the material that has separated, while the permeate stream represents the portion of the input mixture that has passed through the membrane. Factors influencing gas separation using membrane technology are the share of CO_2 in the mixture, membrane material and the operating conditions (Peters et al, 2011). Polymers, such as polyimides, polysulfones, polyethersulfones, cellulose acetates, polycarbonates, are most often used for membrane production (Songolzadeh et al, 2014). Cellulose acetate and polyimide are the most widely used for CO_2 separation from natural gas (Zhang et al, 2013).

A solubility-diffusion model is used to analyze transport through nonporous dense polymeric membranes (Peters et al, 2011). The total flow *Ji* through the membrane of the *i*-th gas component, is based on Fick's law, where the driving force of movement through the membrane represents the difference of partial pressures along the membrane (Hussain, 2017), and is expressed as:

$$J_i = \frac{D_i \cdot K_i}{l}\left(p_f x_i - p_p y_i\right) \tag{1}$$

Where:

J_i - total volumetric flow of the *i*-th gas component [$m^3 \cdot m^{-2} \cdot h^{-1}$],
D_i – diffusion coefficient [$m^2 \cdot s^{-1}$],
K_i – sorption coefficient [$m^3 \cdot m^{-3} \cdot bar^{-1}$],
l – thickness of the membrane [m],
p_f – pressure of feed gas [bar],
p_p – pressure of permeate gas [bar],
x_i – volume fraction of feed gas,
y_i – volume fraction of permeate gas.

Membrane performance in a gas separation depends on selectivity and permeability of the membrane material.

Permeability is the ability of membranes to leak gases (Rufford et al, 2012). The permeability unit is Barrer (1 Barrer=$7{,}5005 \cdot 10^{-18}$ $m^3 \cdot m \cdot m^{-2} Pa^{-1} \cdot s^{-1}$). The basic equation for permeability (Pi) of gases through the membrane shows that it is the product of the diffusion coefficient (Di) and the solubility coefficient of the i-th component (Ki) (Alqaheem et al, 2017):

$$P_i = D_i \cdot K_i \tag{2}$$

Diffusion coefficient Di $[m^2 \cdot s^{-1}]$ represents the mechanism of movement of gas molecules within the membrane, and is a function of the size of gas molecules, i.e. with increasing molecule size the diffusion coefficient decreases due to greater interaction with polymers compared to small molecules (Rufford et al, 2012; Baker, 2006).

Sorption coefficient Ki $[m^3 \cdot m^{-3} \cdot bar^{-1}]$ represents the number of molecules dissolved in the membrane material, i.e. the energy required to dissolve individual components in the polymer, and is proportional to the size of the molecules (Rufford et al, 2012).

Equation (1) can be expressed as:

$$J_i = \frac{P_i}{l}\left(p_f x_i - p_p y_i\right) \tag{3}$$

The separation efficiency of the gas components, represents the selectivity, αi,j, (Rufford et al, 2012), and is expressed as the ratio of the permeability of the gases, where Pi represents the more permeable gas and Pj the less permeable gas of the binary mixture (Freeman, 1999):

$$\alpha_{i,j} = \frac{P_i}{P_j} = \left[\frac{D_i}{D_j}\right] \cdot \left[\frac{K_i}{K_j}\right] \tag{4}$$

The parameter D_i/D_j represents the ratio of the diffusion coefficients of the two gases and can be characterized as a membrane selectivity based on the mobility of individual molecules (Baker, 2006). K_i/K_j denotes the ratio of the solubility coefficients of two gases and characterizes the selectivity of membranes based on solubility.

It is important that polymers have high values of permeability and selectivity, because in this way the required surface area of the membrane for gas treatment is reduced and its purity is increased (Freeman, 1999). However, in practice polymers that are highly permeable have low selectivity and vice versa.

The permeability of cellulose acetate is about 60 GPU $(1GPU = 7{,}501 \cdot 10^{-12}\ \mathrm{m}^3 \cdot \mathrm{m}^{-2} \cdot \mathrm{Pa}^{-1} \cdot \mathrm{s}^{-1})$, and the value of selectivity in laboratory conditions for CO_2/CH_4 is 40, while in practice this value is twice lower (CO_2 moves through the membrane 20 times faster than CH_4) (Rufford et al, 2012). Table 1 shows the values of CO_2/CH_4 permeability and selectivity for different polymers (Alqaheem et al, 2017).

Table 1 Permeability and selectivity values for different polymers

Material	P_{CO_2}(Barrer)	α_{CO_2/CH_4}
Cellulose acetate	2,4	22,1
Polyimide (Matrimid 5218)	5,5	28
Polyimide (6FDA-durene)	456	16
Polyimide (6FDA-TBAPB)	42	25,7
Polysulfone	5,6	22,4
Polycarbonate	6,5	22,4

3 CHARACTERISTICS OF MEMBRANE MODULES

The membrane modules represent the geometry of the membrane, as well as its position in relation to the flow of input fluid and permeate (Berk, 2009). Membranes can be structurally made as: tubular modules, plate and frame modules, spiral-wound, hollow fiber, and capillary modules. The most used CO_2 separation membranes are hollow fiber modules. Spiral membranes have also been used, but to a much lesser extent. The criteria that are considered when choosing a module are: membrane area per unit volume of the module, low costs per unit surface area of the membrane, energy consumption, and maintenance (Berk, 2013; Nagy, 2019).

Hollow fiber membrane modules (Figure 1) consist of a very large number of hollow fibers assembled in a module. There are two modes of gas flow through the membrane, i.e. from the inside of the fiber to the outside, and vice versa (Berk, 2013). The main advantage is the compactness of the membrane with hollow fibers.

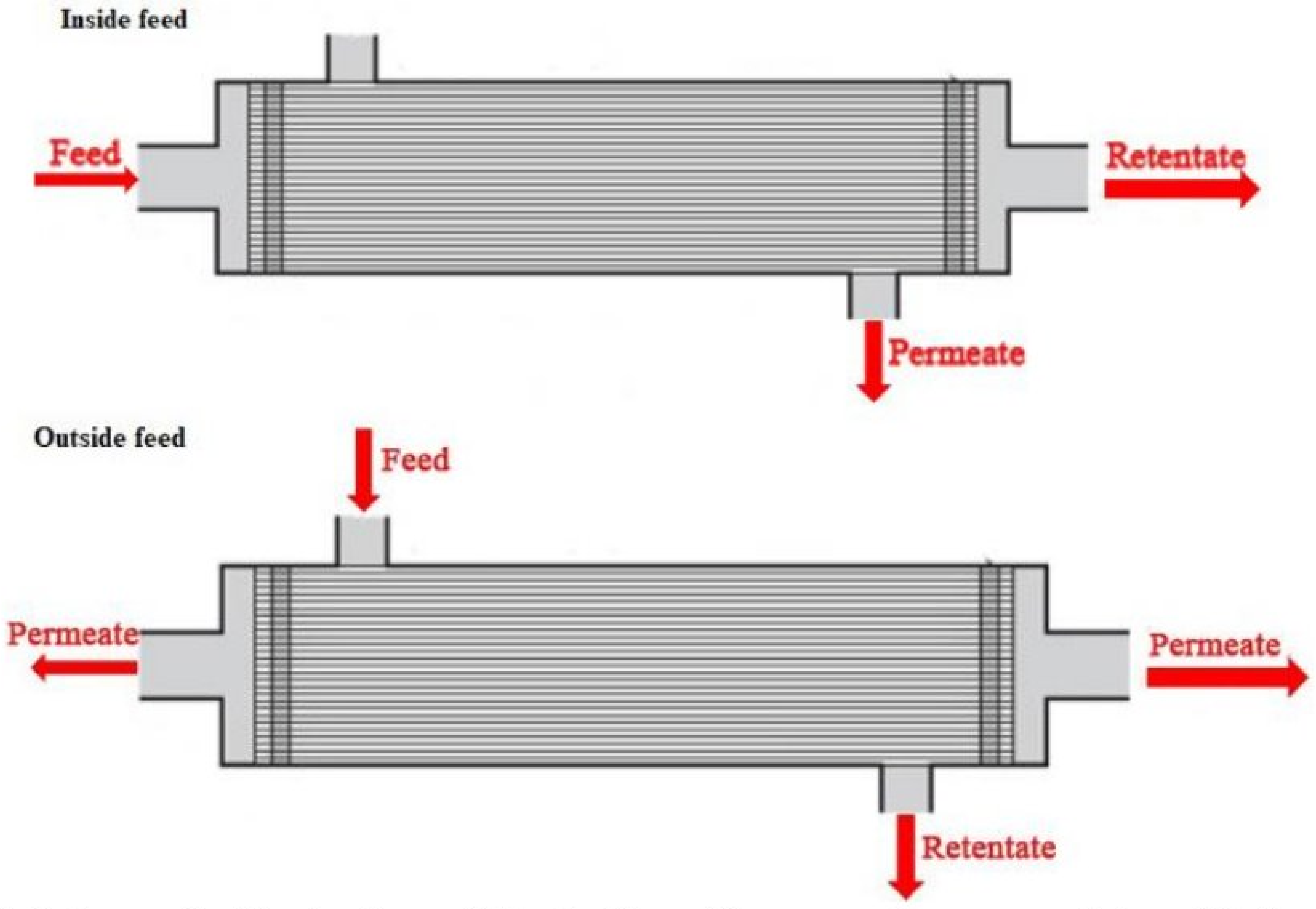

Figure 1 Schematic illustration of the hollow fiber membrane module with the feed on the inside and on the outside of the fibers (adopted from Rackley, 2017)

Spiral membranes, shown in Figure 2, consist of two membrane sheets separated by a porous polymeric material (permeate spacer), and thus regulate retentate flow (Berk, 2009). The membrane sheets are glued on three sides and form an envelope or leaf that is open at the ends and is connected to the central tube (Kidnay and Parrish, 2006). The central tube has a perforated structure, and represents a permeate collector (Berk, 2013).

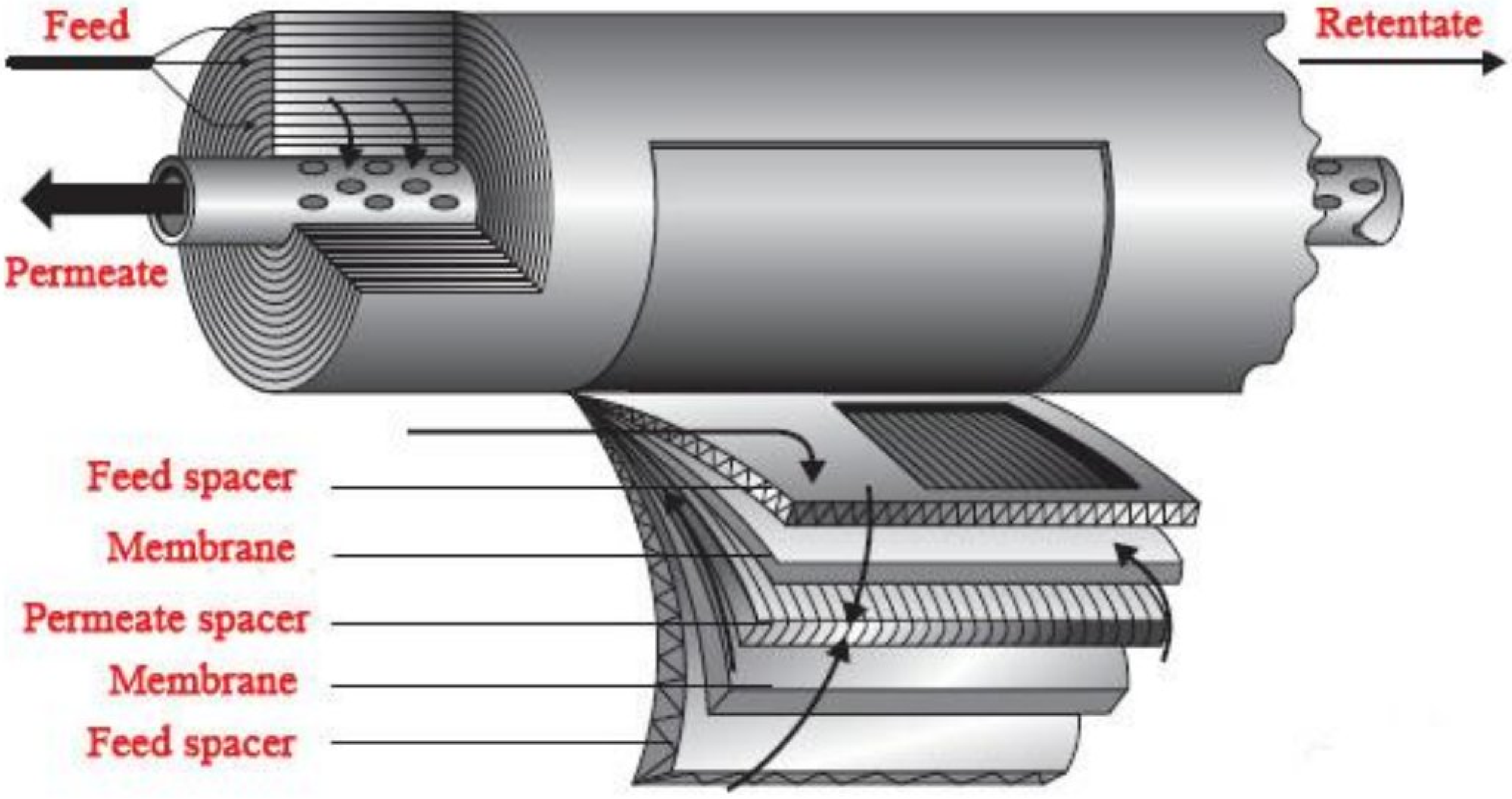

Figure 2 Schematic illustration of the spiral membrane module (Rackley, 2017)

4 THE POSSIBILITY OF APPLICATION OF MEMBRANE MODULES

A certain number of gas reservoirs in Serbia contains CO_2. A special problem is the presence of CO_2 in small gas reservoirs that produce gas for purpose of using it as a compressed natural gas - CNG. Small gas reservoirs are particularly sensitive to the economics of production due to their size, so it is necessary to find an adequate solution for separation CO_2. One of the solutions is considered in this paper, and that is using the membranes.

The paper considers the separation of 7% CO_2 from natural gas from a small reservoir in Serbia. Table 2 shows the component composition of typical gas reservoir.

Table 2 Component composition of natural gas

Component	y_i
C_1	0,88
C_2	0,03
C_3	0,02
CO_2	0,07

Figures 3 and 4 show a schematic process of separation CO_2 from natural gas depending on the number of membranes in the system. If a plant with one stage of membrane is used for natural gas treatment (Figure 3), the share of methane in the natural gas stream of about 90,2% is achieved. To increase the purity of the natural gas, a multi-stage procedure is used, which affects the complexity of the process, as well as the increase in costs. The purity of the natural gas in the case of a double stage membrane (Figure 4) is about 98,7%, while plants with a system of three or more membranes produce a gas purity of over 99% (Kidnay and Parrish, 2006; Tabe-Mohammadi, 1999).

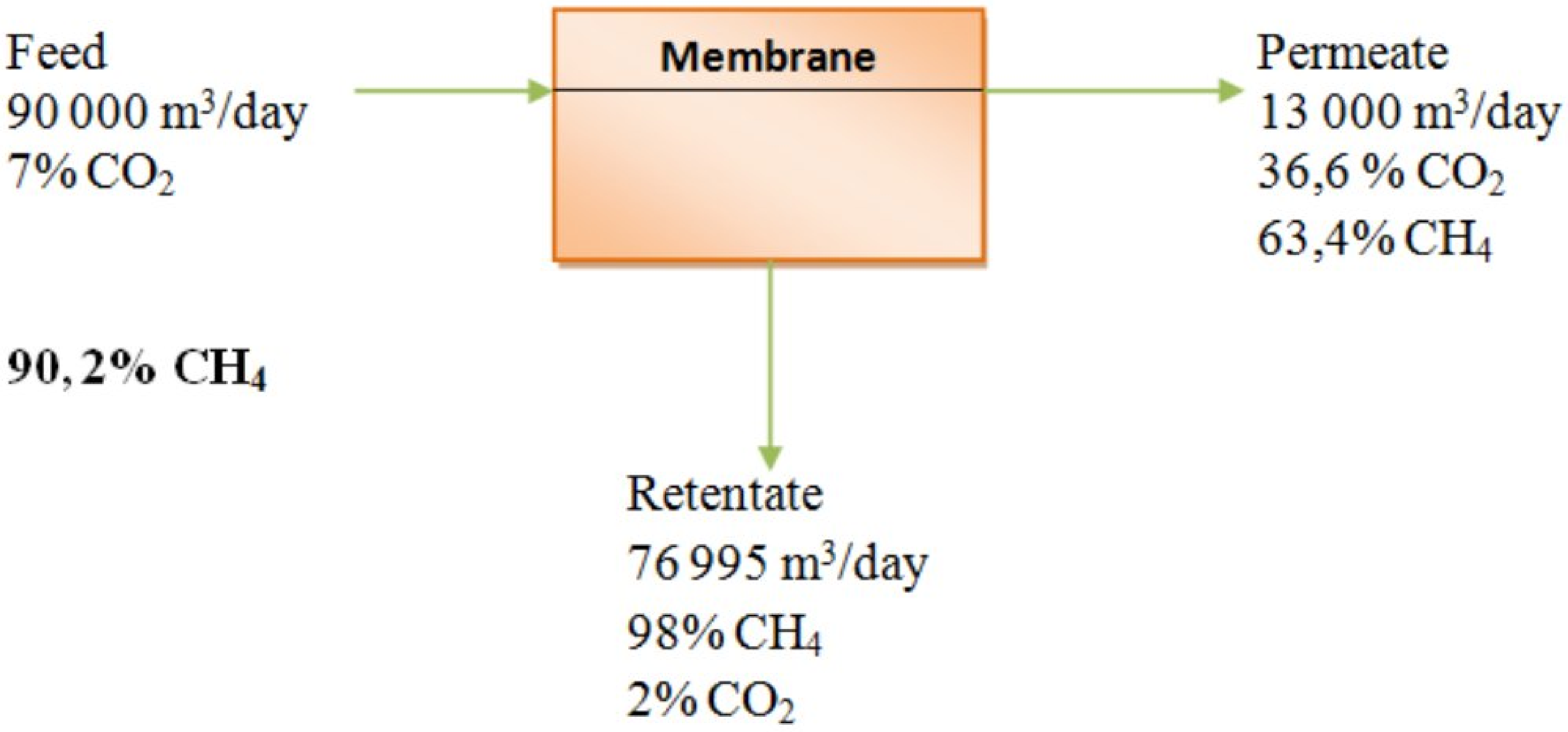

Figure 3 One stage membrane separation process

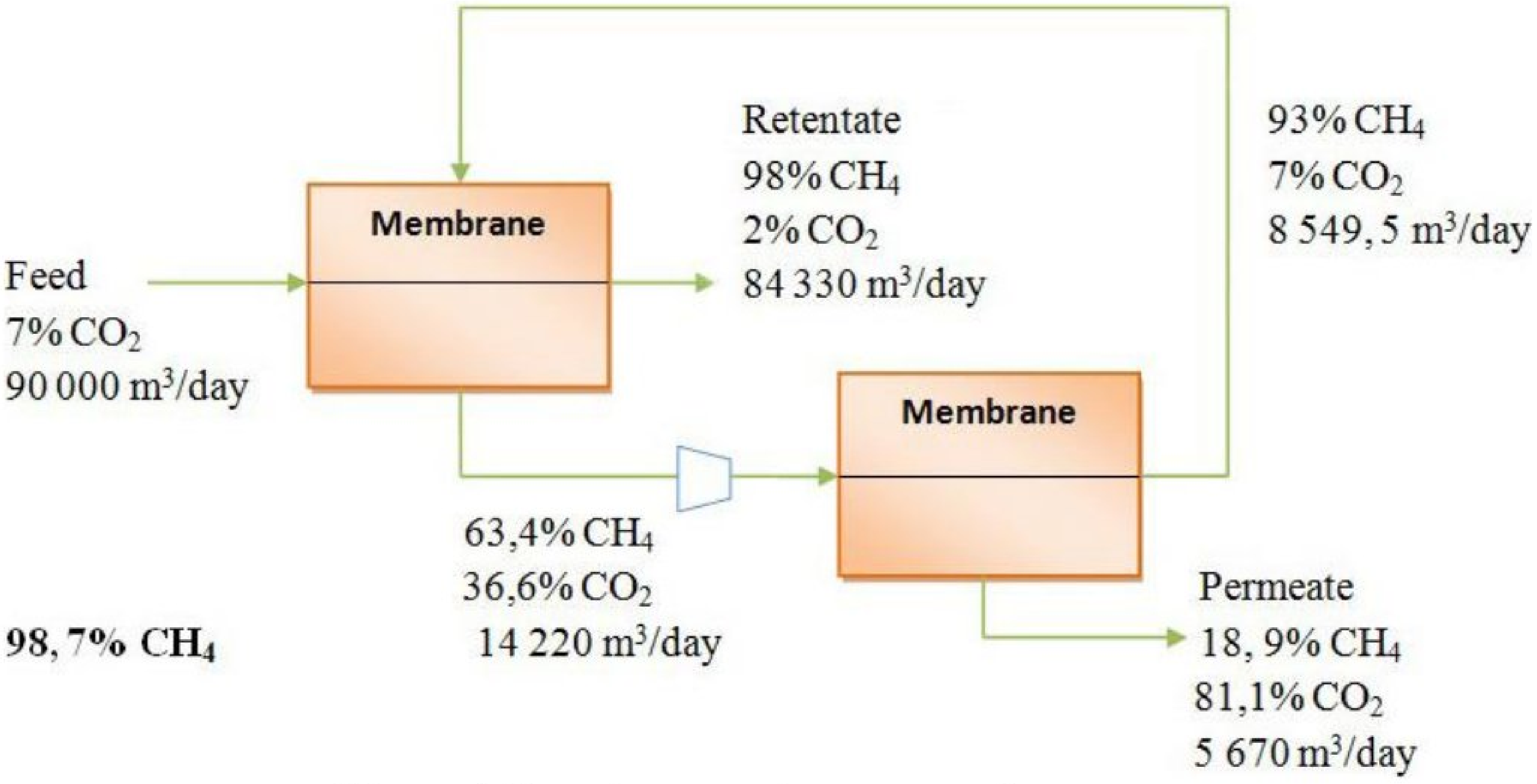

Figure 4 Two stage membrane separation process

The process is fully automated, which increases control and simplifies process management. Small capital and operational investments are required, which significantly reduces costs. Membranes are also used for a number of other processes such as dehydration and removal of H_2S from the natural gas stream. Also, one of the advantages is certainly the lifespan of the membranes (> 5 years) (Alqaheem et al, 2017; Ji and Zhao, 2017). The main disadvantage of the membrane is the previous gas treatment because it is necessary that the natural gas contains as few impurities as possible.

5 CONCLUSION

In order to satisfy the characteristics of the gas, it is necessary to remove unwanted components. In this paper, the mechanism of gas separation in membranes is given. The main advantage is the easy use and control of the process, as well as small capital investments. The efficiency of the gas separation process is influenced by the selectivity and permeability of the membrane material. Polymers are used for membranes, of which cellulose acetate and polyimide are most often used for the separation of CO2 from natural gas.

It is desirable that the polymers have the highest possible values of permeability and selectivity, because in this way the required membrane area for the treatment of a certain amount of gas is reduced, and the purity of the gas is increased.

In the paper is analyzed the separation of CO_2 depending on the number of membranes in the system. In order to achieve greater purity of the gas, systems with more membrane are used, which increases the complexity of the process and costs. The share of methane in the natural gas stream in a one stage membrane is 90,2%, in a two-stage membrane about 98,7%, while in a system with three or more membranes gas of over 99% purity is produced.

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