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# Cellulose-based carbon hollow fiber membranes for high-pressure mixed gas separations of $CO_2/CH_4$ and $CO_2/N_2$



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#### ABSTRACT

Carbonized cellulose -based hollow fiber membranes were prepared by dry-wet spinning phase inversion method, followed by carbonization and evaluated in terms of gas separation performance for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/ CH<sub>4</sub> mixtures, under flow conditions. Permeability and real selectivity were measured for both mentioned mixtures, in a temperature range of 25 °C to 60 °C, a differential pressure range of 8 bar(a) to 20 bar(a) and a CO<sub>2</sub> concentration range from 5% v/v to 15% v/v. The highest yielding mixture selectivity values were 42 for CO<sub>2</sub>/ N<sub>2</sub> at 10% v/v CO<sub>2</sub>, 25 °C & 8 bar(a) and around 150 for CO<sub>2</sub>/CH<sub>4</sub> at the same conditions, whereas the respective CO<sub>2</sub> permeabilities were 110 and 45 Barrer. Additionally, experiments of varying head pressure, while maintaining differential pressure, transmembrane pressure, at 8 bar(a), have revealed that  $CO_2/N_2$  separation factor can be further enhanced with real selectivity being raised to 55 and permeability to 180 at 20 bar head pressure. The same approach had negligible effect on  $CO_2/CH_4$  separation. This is an important finding by taking into consideration that natural gas treatment, i.e. sweetening and purification processes, is energetically and economically convenient if it takes place under the conditions, where the NG stream is extracted from the wells, or after a decompression. Moreover, Process simulation indicates that a two-stage system using the developed carbon membranes is technologically feasible to produce 96% methane with a low methane loss of < 4%. Further improving membrane gas permeance can significantly reduce the specific natural gas processing cost which is dominated by the membrane-related capital cost.

#### 1. Introduction

Natural gas has been a popular energy source for many decades. It is and will be the major energy input for houses and industries worldwide [1]. Natural gas has been established as one of the best fuels because of its availability, multifacility and thanks to the fact that it is a cleaner energy source compared to coal and crude oil. At the same time, new natural gas reservoir types, like shale formations, bursts onto the scene [2] by providing new reserves to be exploited by the industry.

The economic size of the natural gas industry is one of the biggest worldwide. Natural gas supplies 22% of the energy used worldwide, and makes up nearly a quarter of electricity generation, as well as playing a crucial role as a feedstock for industry. Natural gas is a versatile fuel and its growth is linked in part to its environmental benefits relative to other fossil fuels, particularly for air quality as well as greenhouse gas emissions. EIA forecasts that dry natural gas production in USA for 2021 will be 87.48 Bcf/d [3]. Natural gas consumption worldwide is over 3.87 trillion cubic meters per year [4]. Before the natural gas becomes ready for use, gas separation processes are required, and these separations are by far the largest industrial gas separation applications.

Depending on the raw natural gas wells' derivation; oil wells, gas wells, and condensate wells; different separation processes are required. Whatsoever the source of the natural gas, once separated from crude oil (if it is present), it commonly exists in mixtures with other hydrocarbons. Natural gas is typically at least 90 per cent methane, plus any other hydrocarbons, such as ethane, propane, butane and pentanes. Additionally, raw natural gas contains water–vapor, carbon dioxide ( $CO_2$ ), hydrogen sulfide ( $H_2S$ ), nitrogen ( $N_2$ ), helium (He), and other compounds like  $H_2$ , Ne and Xe, in traces [5]. Among all the

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components, which must be separated from  $CH_4$ ,  $H_2S$  and  $CO_2$  are classified as two major components that must be removed because of their ability to create serious problems during transportation and storage of natural gas. This separation process is called natural gas sweetening.

Raw NG needs further purification to meet quality standards specified by major pipeline transmission and distribution companies. Two major processes in raw NG processing are gas dehydration and gas sweetening. In gas sweetening, more research attention has been focused on the removal of CO<sub>2</sub>, due to its abundance in the raw NG, than H<sub>2</sub>S. CO<sub>2</sub> removal will enhance the energy content (calorific value) of NG, decrease the volume of gas to be transported through pipelines and cylinders, prevent atmospheric pollution and reduce pipeline corrosion [6]. Removal methods that are commonly used for CO<sub>2</sub> include cryogenic distillation, adsorption, and membrane separation. Today the growth rate of membrane separation is higher than any of these aforementioned methods. Some economic advantages of membrane gas separation, which makes it attractive for industrial applications, are the ability to achieve higher efficiency of separation (more capital efficient), the yield of faster separation (which is coupled with the simplicity of operation in modern compact modules) and the high space economy.

Based on the anticipated capacity, there is the necessity for the development of new, economically efficient, technologies for the natural gas purification, so that any NG producing country keeps and increases its role on the world energy map. It is worth noting that Government of Norway, together with Equinor, Shell and Total, started the Northern Lights project for developing an "open source" service for transport and storage of European emitted  $CO_2$ , where the separation activities will play a significant role in the overall objectives [7].

Membrane separation systems possess many advantages, such as low capital and operating costs, small footprint, being environmentally friendly, no moving parts for the separation and exhibiting process flexibility, which implies a great potential in subsea application [8]. However, there are still several drawbacks of commercially available polymeric membranes (cellulose acetate (CA), cellulose triacetate (CTA) and polyimide (PI)) used for high pressure natural gas sweetening, namely mainly the relatively low separation performance (i.e., low CO<sub>2</sub>/CH<sub>4</sub> selectivity and low CO<sub>2</sub> permeance) due to membrane compaction and plasticization (polymeric membrane materials are suffering from plasticization phenomena by condensable CO2 molecules). These issues lead to high costs due to a large required membrane area and short lifetime, which indicates the need of development of novel, high performance membrane materials. In addition, the commercial polymeric membranes have the limitation of the trade-off issue between permeability and selectivity in gas separation processes, as depicted in the Robeson plot [9].

Currently, polymeric membrane technology development focuses on incorporation of inorganic particulates to yield filled hybrid polymer composite membranes, named as mixed matrix membranes (MMMs) [10,11]. MMMs are composed of homogeneously interpenetrating polymeric and inorganic particles. A promising example could be the carbon nanotubes (CNTs) reinforced polyvinyl amine (PVAm) / polyvinyl alcohol (PVA) in a blended fixed-site-carrier (FSC) membrane, a system which was developed and tested for  $CO_2$  removal from high pressure natural gas recently [12]. This membrane presented a good separation performance at moderate pressure (up to 40 bar) operation and relatively good long-term durability while being exposed to different impurities [12,13].

On the other hand, inorganic membranes, which are significantly more durable and with less environmental impacts compared to polymeric, shall play an increasingly important role in different membrane separation processes in the coming decades, including gas separation [14]. Among other types of inorganic membranes, such as ceramic, zeolite, alumina based, metallic supported and glass membranes [15-18], carbon membranes provide a series of advantages mainly thanks to the low production cost, the high selectivity performance and the established knowledge of the controlled porous structure development [19,20]. Recently, MXene membranes, a young family of 2D materials, and supported graphene oxide membranes are also reported as promising materials for gas separation applications [21–23].

Carbon membranes are ultra-microporous inorganic membranes, prepared mainly by carbonization of polymeric precursors, and present good mechanical strength [24], moderate modulus and high gas selectivity performance, mainly for hydrogen and carbon dioxide [25,26]. In fact, carbon molecular sieve membranes (CMSMs), which present excellent separation performance and stability, seem to be promising candidate materials for  $CO_2/CH_4$  and  $CO_2/N_2$  separations. Different polymeric precursors, mainly polyimides (PI) and cellulose derivatives, have been used so far for the preparation of high gas selective carbon membranes [27,28].

During the last decades extensive work has been done, focusing on the study of synthesis & modification of different polymeric precursor membranes and on the study of different pyrolysis environments. On the other hand only few are the works in literature, which focus on the investigation of the optimum pressure conditions for gas-selective carbon membranes [29–31]. In these works both polymeric and carbon membranes have been investigated, concerning their gas separation properties, by single gas and gas mixture measurements, at feed pressures up to about 40 bar. It must be noted that the investigation of the gas permeability and selectivity performance through inorganic membranes under high-pressure environments is an active topic that is of increasing importance during the last two decades [32].

In our work we present, among others, gas permeability and selectivity data of feed pressures up to 30 bar, by additionally taking into consideration the effect, that application of different pressure differences has, on the permeability/selectivity performance of  $CO_2/CH_4$  and  $CO_2/N_2$  gas mixtures, as well as the effect of varying feed pressure by keeping constant, at 8 bar, the pressure difference between feed and permeate streams (differential experiments). This could be characterized as the continuation of our previous works [33–35], where only single gas differential permeability measurements were studied.

#### 2. Experimental section

#### 2.1. Materials

Microcrystalline cellulose (MCC, Avicel PH-101), glycerol (> 99%, FG grade) and DMSO ( $\geq$  99%, FG grade) used in this work were purchased from Sigma-Aldrich. The ionic liquids of EmimAc were provided by the Institute of Process Engineering, Chinese Academy of Sciences (IPE-CAS). The EmimAc was directly used for cellulose dissolution without any treatment, and the product purity was confirmed by 1H and13C nuclear magnetic resonance (NMR) spectroscopy [36]. Tap water was used as non-solvent in coagulation and rinsing baths.

#### 2.2. Fabrication of carbon hollow fiber membranes

A well-known dry – wet spinning method was employed to fabricate cellulose hollow fibers. The dried cellulose hollow fibers were carbonized in a tubular horizontal split tube furnace by applying a specific carbonization protocol, up to 600 °C, by applying a carbonization protocol under a  $CO_2$  purge gas with 80 ml/min continuous flow. In specific, the carbonization protocol was: 1) heating from ambient temperature up to 120 °C with a heating rate of 1 °C/min, 2) isothermal stay at 120 °C for 2 h, 3) heating from 120 to 200 °C with a heating rate of 1 °C/min, 4) isothermal stay at 200 °C for 2 h, 5) heating from 200 to 340 °C with a heating rate of 4 °C/min, 6) isothermal stay at 340 °C for 2 h, 7) heating from 340 to 600 °C with a heating rate of 3 °C/min, and 8) isothermal stay at 600 °C for 2 h. The system cooled down naturally and the prepared CHFMs were taken out when the temperature had cooled to below 50 °C. Details, concerning the carbon hollow fiber



Fig. 1. Scheme of membrane testing rig for gas separation measurements under continuous flow.

preparation process and the overall study of the spinning parameters for the fabrication of these carbon hollow fiber membranes, are available in our recent work [26]. The studied carbon hollow fiber membranes in the current work were prepared based on the same condition as the batch "d" reported in our previous work [26].

An effective area of 9.0 cm<sup>2</sup> contained 6 hollow fiber membranes was constructed in a 3/8-inch Swagelok<sup>®</sup> stainless steel tubing sealed by LOCTITE<sup>®</sup> EA 3430 epoxy adhesive.

#### 2.3. Gas permeation measurements

Gas separation studies under continuous flow were performed with the rig of Fig. 1. The membrane module was connected to the four terminals of the rig and kept at the desired temperature by a heating tape element, controlled by a YUMO d-Tron 316 PID temperature controller, while the pressure drop across the membrane was regulated by two Bronkhorst back pressure regulators BPR1 & 2 at the retentate (head-pressure) and the permeate side, respectively. The membrane feed stream concentration was regulated through proper adjustment of flow rates by Bronkhorst mass flow controllers (MFC2 for CO2 & MFC3 for  $CH_4$  or  $N_2$ ), while keeping the total feed stream at 100 ccSTP/min. Helium was used as the sweep gas for sweeping the permeate side of the membrane, with a flow rate of 30 cc/min, controlled by mass flow controller MFC1 in Fig. 1. All flow rates were measured with a Supelco Optiflow 520 bubble flow meter at the exit to atmosphere. Gas concentrations were measured with a SRI 8610C gas chromatograph equipped with a fused silica capillary column and a TCD detector.

Selectivities (i.e. gas separation factors) were calculated from the following equation:

$$S = \frac{(y_{gas1}/y_{gas2})_{permeate}}{(y_{gas1}/y_{gas2})_{feed}}$$
(1)

where  $y_i$  are the gas concentrations expressed as % v/v.

Permeability of each gas was calculated from the equation:

$$Pe_i = \frac{y_i \cdot Q \cdot dx}{A \cdot dP_i} \tag{2}$$

Where  $Pe_i$  is the permeability of gas *i* in Barrer (where 1 Barrer =  $10^{-10}$  cm<sup>3</sup> (STP) · cm · cm<sup>-2</sup> · s<sup>-1</sup> · cmHg<sup>-1</sup>), *Q* is the volumetric flow rate at

the permeate exit (cm<sup>3</sup> (STP) s<sup>-1</sup>),  $y_i$  the concentration of gas *i* in the permeate stream (net number, % v/v concentration of feed gas stream), *A* the effective area of the membrane (in cm<sup>2</sup>), dx the thickness of the membrane's separation layer (in cm) and  $dP_i$  the partial pressure drop across the membrane for gas *i* (in cmHg). In all gas permeation tests the surface area of the membrane was 9.4 cm<sup>2</sup> and thickness of the separation layer was  $4.5 \times 10^{-3}$  cm.

#### 3. Results and discussion

## 3.1. Structural characteristics of cellulose precursor and derived carbon hollow fiber membranes

The cellulose hollow fiber precursor membranes present a symmetric structure, as dried carrier, with outer diameter of 490  $\mu$ m and 80  $\mu$ m thickness, according to SEM images of Fig. 2a-b. Analogous is the observed structure of the derived carbon hollow fiber membrane, but with shrinkage. In specific, both diameter and thickness are recorded with an average reduction of about 40% (Fig. 2c-d) with average outer



Fig. 2. Cross-sectional SEM images of cellulose precursor (a, b) and the derivative carbon hollow fiber membranes (c, d).

diameter of 290 µm and thickness of 45 µm.

#### 3.2. Mixed-gas $CO_2/CH_4$ and $CO_2/N_2$ separation properties

The capability of a membrane to separate gas mixtures is reported in literature mainly in terms of two separation factors: the ideal selectivity factor and the mixture selectivity factor. The first, ideal selectivity  $a_{ij} = \frac{P_i}{P_i}$ , is defined as the ratio of the permeabilities  $P_i$  and  $P_j$  of two pure gases, measured separately under the same conditions, with i being the most permeable gas. The second, real selectivity (Eq. (1)) is the result of the online analysis of the membranes' permeate gas streams, 1 and 2, as monitored by using a gas chromatography analysis or/and gas analyzers. However, the ideal and real separation factors, which are measured using single gases or their mixtures, can be significantly different. Usually the ideal selectivity overestimates the real ability of the membrane in the reference gas couple separation [37]. There are also many the cases that unusual permeation behavior has occurred in mixed-gas experiments, different considerably from what was observed in single-gas experiments. Same examples of this behavior, where reported by Sedigh et al., Centeno et al. and Ogawa et al. [38-40].

In any case, what really matters is the membrane's selectivity property of a real binary mixture feed and of multicomponent mixtures which are closer to what exists in the industrial processes.

The most important parameters which determine the membrane performance are the temperature at which the separation takes place, applied pressures and gas concentrations. The effect of these parameters on permeability and selectivity performance are studied and discussed in the current work.

#### 3.2.1. Temperature influence

The temperature effect on both  $CO_2/CH_4$  and  $CO_2/N_2$  mixtures through the studied carbon hollow fiber membranes was studied over a temperature range of 25–60 °C by keeping the feed gas stream of both above mentioned mixtures constant (10%v/v  $CO_2$  in  $CH_4$  gas mixture and 10%v/v  $CO_2$  in  $N_2$  gas mixture). Fig. 3 shows the permeability values of  $CO_2$  and  $CH_4$  and of  $CO_2$  and  $N_2$ , respectively, as a function of temperature.

One of the characteristic properties of microporous membranes is the activated gas transport [41]. It has been found that gas flux *J*  $(mol/m^2 \cdot s)$  through a microporous material increases as a function of temperature according to:  $J \propto exp\left(\frac{-E_{act}}{RT}\right)$ , where  $E_{act}$  (*kJ/mol*) is the



**Fig. 3.** Permeability of  $CO_2$  and  $CH_4$  vs. temperature for 10%v/v  $CO_2$  in  $CH_4$  gas mixture, and of  $CO_2$  and  $N_2$  vs. temperature for 10%v/v  $CO_2$  in  $N_2$  gas mixture. Pressure difference across the membrane was kept constant at 8 bar.

apparent activation energy. Although activated diffusion of gases, such as He, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>, depends on pore size, the accurate relation between activation energy and pore size is not known. The activation energy is usually mentioned as "apparent" activation energy ( $E_{act}$ ) [42], to "underline" the impact of the isosteric heat of sorption. Depending on micropore size and gas molecule size, activation energies usually fluctuate from around 2 to 40 kJ/mol, according to literature [42,43].

In our system the "apparent" (sorption contributed) activation energy values for the studied gases, produced by implementing the Arrhenius analysis, were calculated equal to 8.9 and 12 kJ/mol for CO<sub>2</sub> in the cases of CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> mixtures respectively, and 23.7 and 23.1 kJ/mol for CH<sub>4</sub> and N<sub>2</sub> respectively. It must be noted that the above values have resulted from the respective permeance values of CO2, CH4 and N2, as calculated from mixed gas selectivity experiments and not from single gas permeability experiments. The higher values of CH<sub>4</sub> and N<sub>2</sub> imply that in these cases a greater barrier for diffusion exists for these gas species [44]. The calculated activation energy of the three studied gases provides positive values and is implying that the transport mechanism of the examined gas species is mainly controlled by the molecular sieving mechanism. In Fig. 3 it is apparent that in both cases the dependence of CH<sub>4</sub> and N<sub>2</sub> permeability on temperature is a linear increase, whereas CO2 permeability follows an almost linear increase.

At the same time, as temperature increases from 298 to 333 K, selectivity decreases from approximately 150 to 50 for 10% v/v  $CO_2$  in  $CH_4$  and from about 45 to 25 for 10%  $CO_2$  in  $N_2$  gas mixtures (Fig. 4).

This behavior can be explained by the fact that although in all studied gases ( $CO_2$ ,  $CH_4$  and  $N_2$ ) the effect of temperature on their permeability values is positive; the grade of this effect is recorded higher for  $CH_4$  than in  $CO_2$  in the case of  $CO_2$  in  $CH_4$  mixtures and also higher for  $N_2$  than in  $CO_2$  in the case of  $CO_2$  in  $N_2$  mixtures. Therefore, by increasing the temperature the  $CO_2$  permeability increases but the  $CH_4$  and  $N_2$  permeabilities increases farther, as they are multiplied by higher factor, and overall the  $CO_2/CH_4$  and  $CO_2/N_2$  selectivities decrease, as it is shown in Fig. 4.

#### 3.2.2. Transmembrane pressure influence

By keeping a constant permeate pressure of 1 bar, the influence of transmembrane pressure (dP) [45] on membrane separation performance was investigated by varying the total feed pressure from 9 to 21 bar. As shown in Table 1, for  $CO_2$  and  $CH_4$ , as well as for  $CO_2$  and  $N_2$ , permeability dependence on applied total transmembrane pressure at 25 °C is similar, with a slightly decreasing  $CO_2$  permeability and almost



Fig. 4. Separation factors (selectivities) vs. temperature for  $10\% v/v CO_2$  in  $CH_4$  and  $10\% v/v CO_2$  in  $N_2$ . Pressure difference across the membrane was kept constant at 8 bar.

#### Table 1

Permeability and separation factor (selectivity) of  $CO_2$  vs. total transmembrane pressure, for 10%v/v  $CO_2$  gas mixture in  $CH_4$  and  $N_2$ , respectively. Temperature was kept constant at 25 °C.

dP (bar)	Permeability (barrer)				Selectivity	
	$CO_2$ in $CH_4$	CH4	$CO_2$ in $N_2$	$N_2$	$\rm CO_2/CH_4$	$\rm CO_2/N_2$
8 12	45.07	0.315	108.83	2.43	146.98 131.42	44.77 39 73
16	37.01	0.295	98.66	2.69	128.08	33.51
20	35.12	0.343	93.59	2.51	104.17	37.19

stable N2 and CH4 permeabilities.

A similar behavior has been reported in numerous other works, both for zeolite-type and for microporous carbon membranes [46–48]. As the main separation mechanism of the studied carbon membrane is this of molecular sieving, the observed systematic decrease of  $CO_2$  permeability with transmembrane pressure increase, could be attributed to pore blocking by the larger gas molecules (CH<sub>4</sub> and N<sub>2</sub>), which makes diffusion of CO<sub>2</sub> slower at higher pressures, in contrast with lower pressures where the partial pressure of the competitive gas is lower.

Furthermore, as transmembrane pressure increases from 8 to 20 bar (a), selectivity drops from 150 to 100 for 10% v/v  $CO_2$  in  $CH_4$  and from 45 to 35 for 10%  $CO_2$  in  $N_2$  gas mixtures (Table 1). This behaviour has also been reported by other researchers, who mention a decrease up to 30% in  $CO_2/CH_4$  in 50:50  $CO_2/CH_4$  mixtures at 35 °C and at a pressure difference of 20 bar [30].

#### 3.2.3. Concentration influence

CO<sub>2</sub> concentrations of 5, 10 and 15%, in CH<sub>4</sub> and N<sub>2</sub> mixtures, were chosen in order to investigate the selectivity fluctuation. For these CO<sub>2</sub> concentrations, and at a temperature of 25 °C, no pronounced changes in selectivity were observed (Table 2), neither for  $CO_2/CH_4$ , nor for CO<sub>2</sub>/N<sub>2</sub> gas mixtures. Slight CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> permeability changes, as shown in Table 2, are understood as a weak fluctuation. Gas permeability is dependent on both gas diffusivity and sorption coefficient (Pe =  $D \times S$ ). At a given transmembrane pressure (i.e., 8 bar) in this work, gas diffusivity (D) is much less influenced by feed gas concentration as it is kinetically dominated by operating temperature. Whereas gas sorption coefficient (S) decreases with increasing feed pressure for carbon membranes based on gas adsorption measurement reported by Fu et al. [41]. Therefore, the CO<sub>2</sub> sorption coefficient decreases with increased CO<sub>2</sub> partial pressure (i.e., increasing feed CO<sub>2</sub> concentration at a constant total feed pressure), which leads to the decrease of CO<sub>2</sub> permeability. However, due to a less competing sorption of N<sub>2</sub> comparing to CH<sub>4</sub> [49], the influence of CO<sub>2</sub> concentration on its permeability in the CO2/N2 gas mixture is not as obviously as indicated in Table 2.

### 3.2.4. Head pressure influence while keeping constant transmembrane pressure

The constant differential pressure gas permeability/selectivity

#### Table 2

 $CO_2$  permeability and separation factor (selectivity) vs.  $CO_2$  concentration, for  $CO_2$  in  $CH_4$  and  $CO_2$  in  $N_2$  gas mixtures. Pressure difference across the membrane was kept constant at 8 bar and temperature was kept constant at 25 °C.

Feed	Permeability (barrer)				Selectivity	
(%)	CO <sub>2</sub> in CH <sub>4</sub>	CH4	$CO_2$ in $N_2$	$N_2$	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>
5 10 15	93.87 85.53 82.07	0.63 0.68 0.67	134.15 108.83 111.82	2.90 2.43 2.92	149.87 127.37 129.52	43.99 44.77 38.23



Fig. 5.  $CO_2$  and  $CH_4$  (up) and  $CO_2$  and  $N_2$  (down) permeability vs. total head pressure for 10% v/v  $CO_2$  in  $CH_4$  and  $N_2$  gas mixture, respectively. Pressure difference across the membrane was kept constant at 8 bar and temperature was kept constant at 25 °C.

technique is a very useful, unique, tool for the determination of the ideal working pressures at both sides of a membrane in a specific gas separation application. Studying the different gas species involved in a process and scanning a wide range of head (feed) pressures, from mbar up to some tenths of bars, one can define the optimum operating window where the membrane exhibits the highest yield and efficiency for the specific gas separation application [35]. The permeability values, presented below, for CO<sub>2</sub> and CH<sub>4</sub> as well as for CO<sub>2</sub> and N<sub>2</sub>, were calculated from mixture selectivity experiments, as a function of head pressure. These data are shown in Fig. 5 ("up" and "down" respectively). In contrast with what is observed for respective single gas permeabilities [33–35], through microporous carbon membranes, here a continuous decrease of CO<sub>2</sub> permeability is observed in the case of CO<sub>2</sub>/CH<sub>4</sub> gas mixture experiments.

This decrease could be attributed to competition for sorption sited by  $CH_4$  molecules [30] and the same explanation could also justify the drop of  $N_2$  and  $CH_4$  permeabilities. It must be noted that differential pressure between the two sides of the membrane was kept constant at 8 bar during the increase of the head pressure from 9 to 26 bar in any case.

Although both  $CO_2$  and  $CH_4$  permeabilities were recorded to decrease by increasing head pressure, the respective measured  $CO_2/CH_4$  selectivity was found to fluctuate in a non-linear way by forming a maximum at about 11 bar (Fig. 6). In fact, this maximum cannot be noted as a clear feature, indicating a trend, since the experimental error bars are sufficiently large. However, as is shown in Fig. 6, in the case of  $CO_2/N_2$  selectivity measurements, a distinctively different behavior is



**Fig. 6.**  $CO_2/CH_4$  and  $CO_2/N_2$  separation factor (selectivity) vs. total head pressure for 10% v/v  $CO_2$  in  $CH_4$  and  $N_2$  gas mixture, respectively. Pressure difference across the membrane was kept constant at 8 bar and temperature was kept constant at 25 °C.

observed, which seems to be linked to the respective permeability variation, depicted in Fig. 5 (down).

In specific, as is shown in Fig. 5, concerning the effect of head pressure on the partial permeability of each gas in the  $CO_2/N_2$  mixture, a linear decrease in permeability of both gases is first observed at head pressures up to 14 bar, whereas above 14 bar, only for  $CO_2$ , a distinct increase in permeability is observed up to 17 bar, followed by a smooth decrease and equilibration at head pressures of 26 to 28 bar. In other words, only for  $CO_2$  a clear permeability maximum was observed at the differential head pressure of 17 bar. Similarly, by increasing the head pressure from 8 to 30 bar(a), whereas maintaining transmembrane pressure at 8 bar(a), the  $CO_2/N_2$  selectivity rises from an initial value of approximately 45 to a maximum of approximately 56, reaching it at the head pressure of 18 bar. This value remains almost constant in the head pressure region between 18 and 24 bar(a), and then decreases again (Fig. 6).

In the respective diagram for  $CO_2/CH_4$  (Fig. 6) the same behaviour can be observed, but less pronounced, with a similar selectivity enhancement from the initial value of 138 to a maximum of 146 at 11 bar (a).

The formation of a maximum in single gas permeability vs. pressure diagrams has been reported so far for several gas-membrane combinations. For example, H. Rhim and S. Wang [50] have observed such maxima for CO<sub>2</sub> and ethane permeation through porous Vycor glass and K. Lee and S. Hwang for water and Freon 113 through the same membrane [51]. All above mentioned maxima were attributed to condensation of the adsorbed phase. However, in an earlier work in our lab [35] it was shown that such single gas permeability maxima can also be observed for CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, above the critical temperature, i.e. at temperatures where condensation is not possible. In particular, CO<sub>2</sub> permeability through a porous carbon membrane at 34 °C was found to form a maximum at 22 bar head pressure, while pressure difference across the membrane was held constant at 1 bar. This observation could not be attributed to condensation, but was explained as the consequence of a change in density of the adsorbed phase, which resembles a confined fluid with liquid-like properties. Proof for this explanation is provided by neutron scattering in another work of Th. A. Steriotis et al. [52] which revealed that the adsorbed  $CO_2$  phase undergoes four state changes, the first of which occurs at the low pressure of 5 bar (monolayer coverage).

Furthermore, based on the ideal permeability vs. head pressure data for  $CO_2$ ,  $CH_4$  and  $N_2$ , in this earlier work in our lab [35], the emerging

ideal CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivities, calculated as respective ideal permeability ratios, show a clear maximum at a head pressure of approx. 5 bar. This maximum is far more pronounced for CO<sub>2</sub>/N<sub>2</sub> than for CO<sub>2</sub>/CH<sub>4</sub> (see supplementary data), which could explain the same observation for real selectivity vs. head pressure diagrams in Fig. 6. In the work of Melnichenko et al. [53] it was further shown that the density of the adsorbed CO<sub>2</sub> phase depends on pore radius and forms a maximum for pore diameters of approx. 10 nm.

Based on this fact, the described observation of permeability and selectivity maxima could be explained as the result of the coexistence of two parallel  $CO_2$  permeation paths in the tested carbon membranes: One through pore diameters where no significant  $CO_2$  densification can occur and one through pore diameters where significant  $CO_2$  densification occurs. As head pressure increases, the contribution of permeation through the first path would result in a continuous permeability drop, typically expected for micropore filling permeation through the second path would have a maximum, as observed in our earlier work [35]. Combination of both contributions would result in a local  $CO_2$  permeability maximum for  $CO_2/N_2$  as the one observed in Fig. 5 (down) at 17 bar. This permeability fluctuation, in form of a local maximum, results in the respective maximum in the real selectivity vs. head pressure diagram of Fig. 6.

#### 3.3. Stability of carbon membranes

Physical aging, mainly in high free-volume polymer membranes, is one of the main hurdles limiting their application in gas separation. Although little work has been done on studying the aging on carbon membranes, in some works it has been pointed that there are significant issues related to the performance stability of carbon membranes [54–57]. Although timing depended, aging in carbon molecular sieve membranes has not been mentioned yet in literature, chemical aging and sorption-induced aging studies of carbon membranes in different environments have already been reported to cause property changes versus time [58]. The three major mechanisms which affect the carbon membranes' aging phenomenon are the adsorption of water vapour, the existence of oxygen which reacts with carbon and the adsorption of easily condensable gases [59].

The storage conditions could play an important role to the gas permeability stability. As Menendez and Fuertes found, carbon membranes stored in air, dry or humid, suffered a rapid permeability loss, whereas when the storage environment was nitrogen or propene the damage was negligible [60,61]. This behavior was explained by the approximation that in the first case the chemisorption of oxygen, instead of the moisture physisorption, is the reason behind the permeability decrease. Exposure to organic contaminants was also found to affect the carbon membrane permeability performance [62]. Lagorsse et al. made a thorough investigation on the effects of exposure to air and humidity on the performance of commercialized carbon hollow fiber membranes, supplied by Israeli Carbon Membranes Ltd. [63].

Our membrane module was kept in inert environment, protected by any moisture concentration and air environment. Based on this fact, in our study only the strong adsorption of gas molecules into small pore constrictions, causing pore blocking, could be the reason for the observed membrane behaviour. This was the reason that a mild treatment method was applied for the regeneration of the studied carbon hollow fiber membrane module.

In specific, after all aforementioned gas separation tests and additional membrane storage for two months, membrane performance regeneration was attempted by mild heating to 90 °C under helium flow for 24 h. The regenerated membrane was then tested again with both 10% CO<sub>2</sub> gas mixtures at 25 °C and 8 bar differential pressure and stored for another two months. Additionally, the single helium permeability at 25 °C and at feed pressure of 2 bar was measured equal to 410.2 Barrer.



**Fig. 7.** Up: CO<sub>2</sub> and CH<sub>4</sub> or N<sub>2</sub> permeability, for 10% v/v CO<sub>2</sub> in CH<sub>4</sub> or N<sub>2</sub>, respectively, at 25 °C and 8 bar pressure difference, initially and after purging with He at 90 °C for 24 h and after purging with He at 90 °C for 24 h second time. Down: Respective separation factors (selectivities).

Thereafter, a second regeneration step was applied and membrane testing was repeated. As can be seen in Fig. 7, the regeneration steps, not only recover, but enhance permeability for all gases, while selectivity is maintained for  $CO_2/N_2$ , but declines for  $CO_2/CH_4$  gas separation. This could be attributed to the fact that in the beginning the membranes were cleaned by applying high vacuum, but without the existence of a higher than the ambient temperature and under continuous flow of a gas carrier like the inert and highly diffusive helium.

#### 3.4. Feasibility analysis for natural gas sweetening

Finally, the Robeson plot (see Fig. 8) describes in the log–log plot of selectivity vs. permeability the upper bounds of  $CO_2/CH_4$ . By adjusting the studied gaseous separation parameters, at most of the investigated conditions CHFMs show good permeation performances that are above the Robeson upper bound of  $CO_2/CH_4$  separation.

Compared to the literature, results of our work have are mentioned in the same region of the 2008 Robeson plot with other recent works such as: 1) this of Tseng and Ita, who prepared carbon molecular sieve membranes by using poly(p-phenylene oxide) (PPO) casting dope as the carbon segment-forming agent in the previously obtained olyimide (PI)



**Fig. 8.**  $CO_2/CH_4$  Robeson plots of 2008. Data labels present: Head pressure (bar (a)), permeate pressure (bar(a)) and temperature (°C).

and polyetherimide (PEI) derived CMS membranes [64], 2) this of Chua et al., who applied thermal annealing in air and incorporating  $\beta$ -CD and  $\beta$ -CD-ferrocene in order to change the molecular structure and improve the CO<sub>2</sub>/CH<sub>4</sub> gas-pair separation and stability of polyimide membranes [65], 3) this of Swaidan et al. who studied thermally-rearranged (TR) (440 °C) and carbon molecular sieve (CMS) membranes (600, 630 and 800 °C) derived from a polyimide of intrinsic microporosity (PIM-6FDA-OH) [66], and more recently: 1) this of Zainal et al., who studied PEG/ PEI carbon membranes which were synthesized on an alumina support coated with an  $Al_2O_3$  intermediate layer [67], 2) this of Ismail et al., who prepared carbon membranes from P-84 (BTDA-TDI/MDI) polymeric solution which was sprayed on the alumina disk with an incorporation of intermediate layer. The derivative membrane was carbonized at 700 °C under nitrogen atmosphere with a heating rate of 3 °C/min [68], and 3) this, again, of Ismail et al., who prepared defect free alumina disk supported membranes, by one-step spray coating technique, by using commercial co-polyimide BTDA-TDI/MDI (P84) and after carbonization at 700 °C under N<sub>2</sub> gas flow [69].

However, in order to develop an energy-efficient and cost-effective carbon membrane process for high-pressure natural gas sweetening, process design and operating parameter optimization are also crucial. Therefore, a two-stage carbon membrane system for  $CO_2$  removal from a 10 mol.%  $CO_2$  contained natural gas was designed to investigate the technology feasibility on achieving the required  $CH_4$  purity of > 96 mol.% with a low methane loss of < 4% (see Fig. 9).

The detailed simulation basis is listed in Table S1, and the cost model reported by He et al. [70] was employed to estimate the specific natural gas processing cost. The 1st-stage carbon membrane will be used to produce high purity sweet NG, whereas the 2nd-stage membrane unit is applied to capture  $CO_2$ , and also achieve a low methane loss due to its greater greenhouse effect. The 2nd-stage retentate (i.e., Retentate 2) can be either mixed with the 1st-stage retentate as final product or recycled back to the 1st -stage feed if the  $CH_4$  purity cannot reach the purity requirement of sweet NG.

Different scenarios by changing the operating pressures were investigated by HYSYS simulation integrated with ChemBrane (for the customized membrane unit [70]). The power demand of compressors and the required membrane area were obtained for estimation of annual capital related cost (CRC) and operating expenditure (OPEX).

#### 3.4.1. The 2nd-stage permeate pressure influence

Based on the experimental data from Section 3.2.4, process simulation by varying the second stage feed and permeate pressure with a constant transmembrane pressure of 8 bar was conducted.



Fig. 9. Process flow diagram of a two-stage carbon membrane system for natural gas sweetening.

#### Table 3

The influence of the 2nd-stage permeate pressure at a constant transmembrane pressure of 8 bar on the membrane-based CRC and OPEX corresponding to the required membrane area and power demand.

Feed 2 (bar)	Permeate 2 (bar)	Membrane area (×10 <sup>5</sup> m <sup>2</sup> )	Power demand (kW)	CRC *(M\$)	OPEX (M \$)
9	1	6.71	723.0	6.95	0.405
10	2	7.24	675.9	7.50	0.379
11	3	8.00	601.4	8.28	0.337
12	4	8.57	574.3	8.88	0.322
13	5	9.02	562.6	9.34	0.315
14	6	9.50	559.5	9.83	0.313

\* : Membrane lifetime of 5 year.

The designed membrane system was found to be technologically feasible to achieve the separation requirement of 96 mol.% CH<sub>4</sub> with methane loss of < 4%. The compressor power demand, the required membrane areas, the annual CRC related to membrane unit ( $$50/m^2$ ) and OPEX (only electricity is included at a cost of \$0.07/kWh) are listed in Table 3.

It can be seen that the annual CRC (only including the 2nd-stage membrane unit) is increasing with the increase of feed pressure, while the OPEX decreases. However, the overall specific cost increases due to the dominating effect from CRC. Therefore, a lower head pressure is preferred for the 2nd-stage of such membrane system. It should be noted the capital cost related to compressors and other equipment were not included as those cost should be similar for all the scenarios investigated here.

3.4.1.1. The 2nd-stage feed pressure influence. Even though both CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity decrease with the increase of feed pressure while keeping constant permeate pressure of 1 bar as indicated in Table 1, the gas flux is still increasing due to the significantly enhanced driving force at high feed pressure. This will on one hand lead to the reduction of the required membrane area to accomplish a specific separation requirement, but on the other hand may increase the power demand for recompression of the Permeate 1 stream to a higher pressure before feeding to the 2nd-stage unit. Therefore, process simulations on varying the 2nd-stage feed pressure were conducted to investigate its influence on system performance, and the results are shown in Fig. 10. These results were expected from our hypothesis of the decrease of membrane area and increase of power demand as indicated in the insert of Fig. 10. It is worth nothing that OPEX related to the compressor power demand is much lower compared to the annual CRC related to the 2nd-stage membrane unit. Thus, a higher pressure (21 bar) for the Feed 2 will be beneficial to minimize total specific NG processing cost.

Moreover, the low OPEX is mainly due to the high selectivity of this carbon membrane, and thus future focus on improving gas permeance should be conducted to significantly reduce the membrane capital cost and thus the annual CRC for natural gas sweetening.

3.4.1.2. The 1st -stage feed pressure influence. The pressure of raw NG produced from gas wells may vary in different regions, and thus it is important to identify the optimal pressure for the application of this carbon membrane. Therefore, process simulations by changing the 1ststage feed pressure from 21 to 90 bar and Keeping constant transmembrane pressure of 20 bar in the 2nd-stage were performed, and the results are shown in Fig. 11. It can be found that the specific NG processing cost is reduced when the membrane system for CO<sub>2</sub> removal is operated at a higher feed pressure, which is mainly due to the significantly reduced membrane area (see Table S2). It should be noted that high pressured testing at > 30 bar has not been conducted in the current work, and the gas permeability used for simulation was obtained by extrapolating the fitting model based on the experimental data in Figs. 3 and 5. Moreover, the annual CRC (including compressors cost) is found to be much higher compared to the OPEX. Therefore, bringing down the membrane unit cost by enhancing gas permeance is crucial in order to applying carbon membrane technology for high pressure natural gas sweetening, and future work related to mixed gas permeation and field testing on carbon membranes at higher pressure of up to 90 bar is required.

#### 4. Conclusions

Carbon molecular sieve hollow fiber membranes were prepared from cellulose based hollow fiber precursors. The prepared CHFM present high mixture selectivity values of 42 for  $CO_2/N_2$  at 10% v/vCO<sub>2</sub>, 25 °C & 8 bar(a) pressure difference and between 130 and 150 for CO<sub>2</sub>/CH<sub>4</sub> at the same conditions, whereas the respective CO<sub>2</sub> permeabilities were 110 and 45 Barrer. Additionally, at constant differential pressure of 8 bar, mixture selectivity experiments have revealed that  $CO_2/N_2$  separation efficiency can be further enhanced by raising pressure at both sides of the membrane, with real selectivity being raised to 55 and permeability to 180. Increasing the operating temperature decreases the CO<sub>2</sub>/CH<sub>4</sub> selectivity due to a faster increment of CH<sub>4</sub> permeability than  $CO_2$ ; whereas in the case of  $CO_2/N_2$  separation, a slight decrease is observed. The achieved CO2/CH4 separations at all tested conditions of different head pressures and feed concentrations surpass the 2008 Robeson upper bound. The regeneration of the carbon membrane was successfully achieved by applying heating under helium flow for 24 h. Process simulation indicates that the two-stage carbon membrane system is technologically feasible to produce 96% methane with a low methane loss of < 4%. The specific natural gas processing cost is



Fig. 10. The influence of the 2nd-stage feed pressure on the membrane-based CRC and OPEX. The Insert is the influences of feed pressure on the required membrane area and the compressor power demand.

very much dependent on the membrane-related capital cost, and thus improving gas permeance for this carbon membrane can significantly reduce the cost. Overall, the developed novel CHFMs from cellulose precursors present a potential applicability in high-pressure natural gas sweetening or other gas separation processes.

#### CRediT authorship contribution statement

Dionysis S. Karousos: Methodology, Investigation, Formal analysis. Linfeng Lei: Methodology, Investigation, Formal analysis. Arne Lindbråthen: Methodology, Supervision, Writing - review & editing. Andreas A. Sapalidis: Writing - review & editing. Evangelos P. Kouvelos: Writing - review & editing. Xuezhong He: Supervision, Project administration, Investigation, Writing - review & editing. Evangelos P. Favvas: Supervision, Writing - review & editing.

#### **Declaration of Competing Interest**

There are no conflicts to declare.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2020.117473.



Fig. 11. The influences of the 1st-stage feed pressure on CRC, OPEX and specific NG processing cost.

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