Regenerated cellulose based carbon membranes for CO₂ separation; Durability and aging under miscellaneous environments

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ABSTRACT

Predictive models regarding the aging effect on membrane separation properties are required to estimate the membrane life time with acceptable permeability and selectivity for the respective application. The current article is reporting an insight into this topic regarding the aging of regenerated cellulose-based carbon hollow fibres (CHF) mounted in a membrane module when they were exposed to real biogas in three different fields. CHF were exposed to biogas for almost one year with H_2S content extending from 0-2400 ppm, and gas permeation tests for single gases, N_2, CO_2, CH_4, and O_2 were analysed periodically at the membrane production facility. CHF storage methods under miscellaneous dry environments like air, vacuum, CO_2, etc. were studied. The air flow through bore side of the CHF under controlled conditions had a regenerative effect on the membrane permeability, and the membrane performance was quite steady until after 150 days under laboratory environment.

Key words: Carbon membrane; gas separation; biogas; module housing; H_2S exposure

1   Introduction

Carbon molecular sieve (CMS) membranes were first reported by Koresh and Soffer in the 1980s, and after a couple of years, the first company called Carbon Membranes Ltd. was based in Israel [1]. As of now, extensive attempts involve the development of new strategies for producing CMS membrane with improved CO_2-CH_4 separation performance, finding cheaper and environmentally friendly raw materials. Most of the work reported has been performed at laboratory scale and, to the best of our knowledge, very limited work has been reported on the actual industrial exposure of CMS membranes when in contact with H_2O, H_2S, higher

hydrocarbons, aromatic compounds and aging of carbon membranes under these harsh environments. CMS membranes appear to be vulnerable to oxidation, humidity and pore blockage resulting in pore constrictions that make it hard for gas molecules to permeate through the membrane [2].

Carbon membranes are known to age, and extended exposure to various molecules such as H_2O and O_2 change the effective pore size by physical or chemical sorption, hence modifying the performance of the membrane. The vulnerability of CMS membranes to water is a complex phenomenon. Carbon surfaces are basically hydrophobic; however, the microporous walls of the carbon membrane will quickly become partially covered with an oxygen containing functional group which hence results in the membrane having a hydrophilic character. Therefore, once the first layer of water molecules is adsorbed, adsorbate-absorbate interactions promote further adsorption of more water through hydrogen bonds [3, 4]. This results in a reduction in capacity of the membrane, and hence is a serious problem for the industrial application of carbon membranes as most feed streams contain some humidity. Jones et al. [5] reported that performance losses were minimum for carbon membranes prepared at 550 °C as compared to the one pyrolyzed at 500 °C when tested in the range of 23-85 % humidity. Xu et al. [6] have recently reported the importance of physical aging showing that physical aging appears to be the leading source for rapid changes of transport properties at the early stage after the membrane fabrication. It may happen due to shrinkage of pores over time to achieve a thermodynamically stable state. Wenz et al. [7] has recently reported the postsynthetic modification method to suppress the physical aging by tuning the pores of carbon membranes. Chemical sorption involves chemical bonds, usually C-O bonds, and the bonding forces here are stronger than van der Waals forces (physical bonding), making removal of these components more complex and energy demanding [8, 9].

Okamoto et al. [10] carbonized asymmetric hollow fiber membrane of a polyimide from 3,3′,4,4′-biphenyltetracarboxylic dianhydride and aromatic diamines in the N_2 atmosphere at 500-700 °C. Carbon membranes prepared at 600-630 °C showed good stability in the separation of propylene/propane and 1,3-butadiene/n-butane. The membranes hardly changed the performance, when stored for 1 week at room temperature. Campo et al. [11] have described the flat sheet carbon molecular sieve membrane produced from commercially available cellophane paper which is regenerated cellulose obtained by the viscose process. The authors claim the membrane showed no signs or aging upon exposure to oxygen and water. It has been shown that storing carbon membranes in an inert environment such as nitrogen prior to use is advantageous [9].

MemfoACT AS, a spin-off company from the Norwegian Univ. of Science and Tech. founded in 2008 (closed in 2015) produced an efficient and compact system for biogas upgrading to fuel quality bio-methane based on carbon hollow fibres (CHF) membranes using deacetylated cellulose acetate (CA) as precursor. These membranes were exposed to real biogas at three different biogas fields in Norway, Field 1 (F1) with H_2S <5 ppm in the feed gas, Field 2 (F2) also with H_2S <5ppm and Field 3 (F3) with H_2S: 150-2400 ppm in the raw biogas. CHF installed, demonstrated excellent initial performance, but a significant drop (up to 70 % in CO_2 permeance) was observed after one year of exposure at F1. This highlights the importance of concern with respect to aging for the carbon membrane. Anderson et al. [12] has reported the effect of H_2S on polyfurfuryl alcohol based carbon membranes. It is important to understand the stability and aging of CMS membranes when stored under different conditions (static aging) and while in operation (dynamic aging). The experience of CHF to mentioned conditions and their effect on membrane performance is important to understand for the actual industrial applications of CHF and is the motivation and focus of the current work. It is however important to stress that the current study reports the performance of regenerated cellulose based CHF membranes at low pressure The high pressure process is discussed elsewhere [13]. Real biogas exposure results also indicated that the membrane was mechanically stable at actual industrial conditions. However, the brittleness of hollow fibers remained a challenge. The mechanical strength of carbon membranes may be enhanced using some fillers in the precursor [14]. The challenges experienced with the regenerated cellulose derived CMS membranes may be different that of other precursors. As an example, Zhang et al. [15] has reported the excellent stability of a polyimide based precursor for carbon hollow fibre membranes when operated over 100 bar It is hence important to remember that CMS is not a single material but a family of materials where the achieved separation properties may be determined by choice of precursors and processing conditions. Detailed characterization of the CMS membranes studied here, are more closely reported in references [16-18] using FTIR and SEM.

The principal objective of the described study is hence to obtain a better understanding of the durability and aging of the cellulose derived carbon membrane performance when exposed to real field biogas and H_2S. In the current work the aging effect on the performance of CHF when stored under different conditions is also reported, such as vacuum, open air, CO_2 atmosphere, dark place and cold place (4 °C). CHF membranes were exposed to field biogas for maximum 350 days and the membrane performance was measured before and after the exposure. Lab-scale study of *dynamic aging* (membrane under controlled conditions and a continuous gas flow through the membrane), *static aging* (membrane lying inside the lab, no control of the

flow) and *intermediate aging* (mix of the dynamic and static aging, further discussed below) using bore side-feed configuration is also presented. The gas permeation results indicate that dynamic aging under certain environments is helpful preventing the membrane performance better than static aging.

2   Experimental

2.1   Carbon hollow fibers preparation

The precursor for CHF was prepared using cellulose acetate (CA, M_W 100,000 from ACROS Organics Belgium) by the dry/wet phase inversion process in a pilot scale spinning set up delivered by Philos Korea. Process details are described elsewhere [19]. A dope consisting of CA mixed with N-methylpyrrolidone (NMP: purity >99.5% from Merck Norway) and polyvinylpyrrolidone (PVP: M_W 10,000 from Sigma Aldrich Norway) was used to spin CA hollow fibers. CA hollow fibers were deacetylated batch-wise with a mix solution of NaOH (>99% from VWR Norway) in short chain alcohol. Then deacetylated CA hollow fibers were carbonized at 550 °C under N_2 flow in a tubular furnace. The carbonization protocol had a heating rate of 1 °C/min with several dwells and the final temperature of 550 °C for 2hrs. Figure 1 shows the schematic of carbonization process to form carbon hollow fibers from cellulose precursor. The detailed description of carbonization process can be found in reference [20].
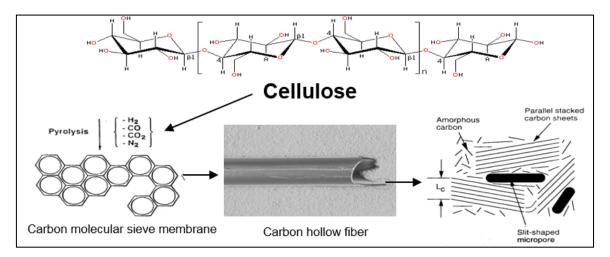

Figure 1: Regenerated cellulose precursor to form carbon hollow fibers

2.2   CHF storage environments and conditions

The carbon fibers were stored in different environments before mounted in a module.

2.2.1   Storage in air (ambient temperature)

Different air environments were tested at ambient temperature (21±2 °C):

- Stored in open air inside lab
- Rolled in plain paper lying on open shelf
- Rolled in plain paper lying inside cabinet (dark place; a chemical storage cabinet with dimension as; H: 1990 x W: 1000 x B: 435 MM)
- Rolled in aluminum foil lying on open shelf
- Rolled in aluminum foil inside cabinet (dark place)
- Rolled in tightly packed aluminum foil lying on open shelf
- Rolled in tightly packed aluminum foil lying under dark fume hood
- Rolled in plain paper lying under dark fume hood

2.2.2   Storage under vacuum (ambient temperature)

- Stored under vacuum lying inside ABS tube
- Stored in vacuum bag in dark place inside cabinet
- Stored in vacuum bag under the light

2.2.3   Storage under CO$_2$ atmosphere (ambient temperature)

- Stored under CO$_2$ lying inside ABS tube

2.3   Gas permeation experiments

2.3.1   Gas permeation tests in laboratory

The issues of porosity and surface polarity also come into play when considering the orientation of the membrane in relation to the feed stream. Generally, for the modules described here, the gas is fed into the membrane using a shell side flow configuration, having permeate gas coming from bore side. But in the study of dynamic aging, feed air was transported through the membrane using bore side feed to understand the most influential conditions which promote aging and the most critical time for aging depending on the environment the membrane is exposed to.

Two identical modules (M1 and M2 with an effective area of 0.02 m^2 for each module) were prepared and tested using a continuous (dynamic) flow of air. The feed pressure used in this study was slightly above atmospheric pressure (1.4bar) at 24 °C temperature in a standard

pressure-rise set up as described in [21, 22]. Permeability tests were carried out on each module separately and were recorded at different time intervals. Each test was carried out over a time span (650 hrs) until linearity was established. This ensured that the aging process continued with a constant flow of air through the system. No other gases were tested for these two modules.

The useful information that can be obtained from this study is a calculation of the flow rate in accordance with the Reynolds number (R_e). Using this information, the pressure drop can also be calculated due to a change in thickness of the boundary layer [23]. The pressure at the feed end including the pressure loss was estimated and compared to that of the experimental feed pressure applied to assess the pressure loss due to aging. Three different types of pressure are considered when evaluating the estimated feed pressure. They are the pressure loss due to sudden contraction, i.e., the flow going from the inlet tube to the entrance of the membrane. Secondly, the friction losses within the membrane due to the gas flow through the fibre. Thirdly, the loss due to the expansion from the permeate side to the atmosphere. The estimated feed pressure at the feed side was calculated using a Fanning-type expression [24].

2.3.1.1   *Intermediate aging (Aging with no feed flow)*

Following a period of 28 days, permeation tests were conducted on Module 1 as a function of dynamic aging. The pump was then disconnected from the module at the feed end and the module was exposed to the atmosphere, undergoing a period of static aging (ambient temperature). A vacuum remained on the permeate side of the module, to prevent the adsorption of air on the remainder of the gas unit. Thus, this combination of dynamic and static aging was termed intermediate aging.

2.3.2   *Real biogas field exposures (small scale pilot plant)*

2.3.2.1   *Field 1 (F1)*

Some of the CHF membrane modules exposed to F1 were modified using chemical vapor deposition (CVD), oxidation and reduction process. All other membrane modules studied in this article are non-modified carbon hollow fibers prepared as described in section 2.1. In total 31 modules of the area ranging from 0.5-2 m^2 of each module were installed on F1 biogas plant for a period ranging from 25 to 212 days to separate biomethane from raw biogas mixture. Gas permeation measurements were performed with pure gas (CO_2 and N_2) at the membrane production facility, using 5 bar feed pressure against vacuum on permeate side in ambient temperature (closed-volume setup). These permeation tests on the membrane module were

conducted before and after the module was exposed to biogas field, and the results were analyzed to evaluate the aging effect of real biogas on CHF. Figure 2 shows the process diagram of F1 and F2. F3 was similar but had no H_2S removal system.

The composition of a biogas depends strongly on the substrate type and the digestion conditions. Table 1 shows the biogas source and contents of biogas produced on three different fields. The biogas, in all three cases, was fully saturated with water. However, the water was removed from the feed gas, before exposed to membranes, to keep it below %RH of 30 which is considered as a safe relative humidity for carbon membranes [5]. Proteins and other sulfur containing materials produce H_2S in the digestion process which is a poisonous and corrosive gas. It was expected that high loading of H_2S may cause the chemisorption and ultimately reduce the performance of the membrane. Therefore, the H_2S contents were reduced to <20 ppm (fuel standard requirement) in field F1 and F2. Table 1 shows the loading of H_2S in different fields and the amount of H_2S exposed to the membranes.

Table 1:
Biogas source and its composition in different fields

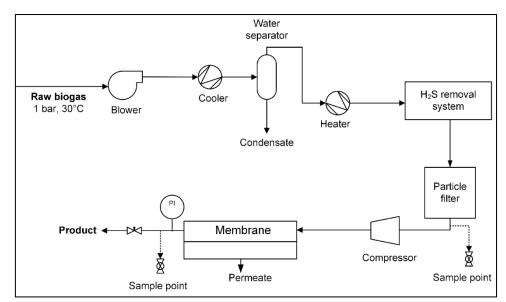| Biogas source	Food waste F1	Food waste, fish oil F2	Sewage, municipal waste F3
Component		(mole %)	
Methane (CH_4)	64 ± 3	62 ± 6	59 ± 3
Carbon dioxide (CO_2)	30 - 35	32 - 44	38- 44
Nitrogen (N_2)	< 1	< 1	ca. 2
Oxygen (O_2)	ca. 0	ca. 0	ca. 1
H_2S feed loading (ppm)	150-1000	0-2000	150-2400
H_2S at membrane inlet (ppm)	<5	<5	150-2400
H_2O in feed, 35 °C (g/Nm^3)	~32	~32	~ 32
H_2O at membrane inlet (%RH)	~20	10	~20

Figure 2: Biogas separation process using CHF membrane at Field 1, 2 and 3. (F3 did not have H_2S removal system)

2.3.2.2 Field 2 and Field 3

One membrane module with an effective area of 0.08 m^2, which had been gas permeation tested for single gas CO_2, N_2, O_2 and CH_4 in the laboratory, was installed at F3, where the CHF were exposed to a real biogas containing H_2S from 150-2400 ppm. H_2S concentration was varying each day depending upon the source of biogas in the anaerobic digester. After 30 days, the module was brought back to the laboratory and tested for the above-mentioned single gases and installed again at F3. After exposure of 120 days at F3, the module was tested for single gas and installed at F2 where less concentration of H_2S (<5 ppm) was present, as the biogas was passing through the adsorption column containing silica gel for H_2S removal. After continuous exposure of 100 days at F2, the CHF membrane module was tested for single gases in the laboratory. After the tests, it was again installed at F3 for additional 50 days for high concentration exposure of H_2S. The reason for this procedure was to understand if biogas containing less concentration could regenerate the hollow fibers effected by high concentration of H_2S.

2.3.2.2.1 Difference between steel housing and ABS housing

Stainless steel (SS) with all its advantages, is still a costly material to use commercially in membrane assembly. To achieve an economical solution for module housing, Acrylonitrile Butadiene Styrene (ABS) material was used to make a CHF module. Both SS (effective area: 0.05 m2) and ABS (effective area: 0.015 m2) modules were installed at F3 for high concentration exposure of H_2S, and gas permeation tests for single gases, CO_2, N_2, and CH_4

were performed before and after exposure to analyze the aging effect on membranes inside both materials.

3   Results and Discussion

3.1   Aging under different conditions

The difficulty in carrying out any type of aging experiment on bundles of these CHF in a module is that the membranes cannot be tested immediately after carbonization, as the time required to prepare the modules is a minimum of 6 hours. The epoxy resin requires this duration of time to set. Placing the module directly in the gas testing unit under vacuum, would cause distortion of the epoxy resin, break the seal and hence the gas would permeate through the fibers as well as the module resulting in an inaccurate evaluation of permeability.

The first permeation tests were thus carried out 9 days after the CHF had been prepared. It has been reported by Menendez *et al*. [8] that the permeability values of carbon membranes drops by nearly 50 % after 1 day due to aging and following a certain period of time, then the reactive sites are saturated and then permeability remains constant. Hence, the aging reported in the current work is investigated after an aging of 9 days. Membranes in which the permeability varies due to severe aging, is not an option for large-scale use. Thus, following module assembly, mounting the module into the gas permeation unit and allowing time for a short evacuation period, the fibers had already undergone a significant aging, and it will be of interest if high performance can be recovered.

The aging effect on the CO_2 permeability of carbon membrane stored under different conditions is shown in figure 3 and summary of the results is presented in table 2. To analyze the performance stability of the stored CHF, the gas permeation properties were measured systematically during this storage period. CHF after carbonization were rolled in a plain paper and kept on an open shelf inside the lab for all batches until the first module was prepared and permeation test was performed. Figure 3(a) presents the four sets of CHF which are rolled in plain paper and then stored at different conditions. The decline in CO_2 permeability is fastest for the fibers lying on an open shelf, whereas slowest in the fibers stored inside the cabinet, which decelerated the chemisorption phenomena by reducing the O_2 supply inside the cabinet. Apparently, membrane performance losses here are due to chemisorption of O_2, rather than other contaminants.

Figure 3(b) shows the CO_2 permeability loss over time for CHF rolled inside aluminum foil and stored under different conditions. Coldness (4 °C) was not helpful in preventing or slowing the performance loss of the membranes. Not surprisingly, the identical effect as fig. 3(a) was

observed for the CHF rolled in aluminum foil and stored inside the cabinet. In all cases, membrane performance becomes constant after all unstable sites on carbon had reacted or stabilized by the formation of oxygen surface groups.

Table 2:
Effect of storage conditions and storage time on CO_2 permeability of regenerated cellulose-based CFM

Storage conditions	Duration (days)	CO_2 permeability loss (%)	Fig. No.
Rolled in plain paper			
On shelf	42	98.5	3(a)
Inside cabinet	50	93.5	3(a)
Under fume hood in darkness	68	99.7	3(a)
Rolled in aluminum foil			
On shelf	70	96.9	3(b)
Inside cabinet	42	85.1	3(b)
Under fume hood in darkness	68	91.4	3(b)
Inside fridge (4 °C)	21	66.7	3(b)
Under vacuum			
In Vacuum bag inside cabinet	56	88.0	3(c)
In ABS tube under vacuum	56	55.4	3(c)
In vacuum bag under light	26	91.2	3(c)
Under CO_2 at 1 bar	23	86.0	3(d)
Open air inside lab	37	96.0	3(d)

The storage of CHF under vacuum was helpful in keeping the membrane performance to some extent. Fig. 3(c) illustrates the change in CO_2 permeability when CHF were stored under vacuum in different conditions. Fibers stored inside an ABS tube under vacuum slowed down the aging effect until first 28 days and then performance remained constant for next 32 days. First permeation test was performed 10 days after the carbonization and then fibers were stored under vacuum, which explains that some reactive sites of carbon surface had formed oxygen surface groups during first 10 days reducing CO_2 permeability from 74 to 33 Barrer, however applying vacuum helped in slowing down and further preventing chemisorption of O_2, when stored inside ABS tube. CHF stored in vacuum bag did not help to prevent the aging and that was due to small leakages present in vacuum bags. Figure 3(d) shows the aging comparison for CHF stored under CO_2 atmosphere and in open air. It was observed that fibers stored under CO_2 environment lost the performance faster than fibers stored under open air inside the lab. Hayashi et al. [25] reported a membrane carbonized at 700 °C and they studied the stability of membrane in air at 100 °C for 30 days. They observed that permeances decreased in the initial

stage of the oxidation but were regenerated by a post-heat-treatment at 600 °C for 1-4 h. Lagorsse et al. [9] studied the effect of air on CMS membrane and reported that the formation of new constrictions arising from chemisorption of oxygen had a noticeable influence on penetrants with critical dimensions close to the critical pore size resulting in higher loss of the N_2 permeance as compared to CO_2 and similar behavior was observed in this study.
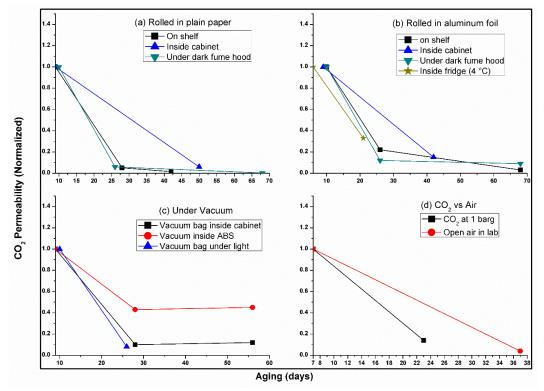

Figure 3: Storage of CHF under different environments

3.2 Dynamic, intermediate and static aging

The aim of this study was to understand the aging phenomena when membranes are lying under ambient environment (air). The more focus of the work was about the collective permeance of air through the membrane. The individual O_2 and N_2 permeabilities were not measured in these experiments. In the figure 4, the scatter plot is to show the trend of air permeability through the membrane. The results showed that both modules are following the same trend.

The slope for aging is hard to define as many variables are involved here. The degree of freedom can be reduced by controlled environment as in dynamic aging in this study. With bore feed orientation as depicted from the graph in figure 4, there is only a slight change in permeability over a time of 650 hours. The slight changes between each module are most likely

attributed to the variation in fiber diameter and hence wall thickness, as slight variations in the pre-treatment stages can result in variations of the membrane permeability. It is evident that there is no decrease in permeability, indicating that this dynamic source of air has an inhibitory effect on aging. Following, approximately 100 hours of aging, there is an increase in permeability and after 200 hours of aging, there is a stabilization period, in which the permeability remains within a range of 50-60 Barrer. The air flow under controlled environment had a regenerative effect on the membranes to restore the permeability which was lost due to physical aging (narrowing of pores due to matrix shrinkage and/or pore clogging caused by dust and moist) during first nine days until the module was prepared and installed for testing. Some studies have shown that high fractional free volume polymer precursor based carbon membranes may change pore structure due to physical aging, like glassy polymer membranes [6, 26]. After recovering the permeability, controlled environment helped to keep it at a constant value. Physical aging at this point would be considered zero in this case. The rate of physical aging depends on the ratio of the driving force, i.e. the displacement of the specific volume from its equilibrium value, and the relaxation time for the sample, which is a function of temperature and the material's current free volume state.

As shown in figure 5, there was no significant change in permeability over an 11-day period following a 27-day period of dynamic aging. The temperature was then monitored and recorded in accordance with the room temperature (22-25 °C) at the time of each experiment. From the presented results in fig. 5, it can be seen that the dynamic atmosphere had an inhibitory effect on the aging process.
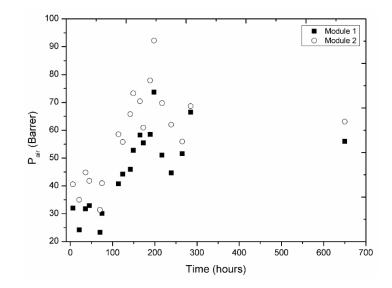

Figure 4: Permeability values for air as a function of time (dynamic aging). Two similar modules were tested to ensure validity of the study
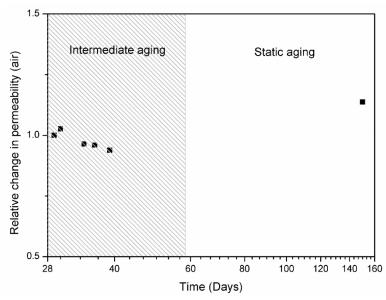
Figure 5: Permeability values of air as a function of time for Module 1 containing carbon membranes previously used in the dynamic aging study

3.2.1 Pressure drop calculations

Given the similarity in velocity and inner diameters of both module 1 and 2, the Reynolds number of 423 and 442 were evaluated respectively, which shows that flow is laminar [27]. The quantified pressure values at various points of the membrane are correlated to give Δp^2 in Pa^2, as shown in Table 3. From the data shown in Table 3, it is evident that the estimated feed pressures, p_{est}, of 1.35×10^5 and 1.38×10^5 Pa are within close range of the experimental feed pressures, p_{exp}, of 1.40×10^5 Pa for module 1 and 2, respectively. This indicates that the flow rate is maintained and the accumulation of a boundary layer due to adsorption of molecules such as O_2 present in the air flow is minimized. Hence, aging of the membrane is reduced using this type of flow system.

Table 3:
Data correlating the pressures at various sections of the membrane. These values have been used to estimate the feed pressure, p_{est} and compared with the experimental feed pressure, p_{exp}.

Module	Δp^2 (Pa^2)	Δp (Pa)	p_{est} (Pa)	p_{exp} (Pa)
1	8.35×10^9	9.14×10^4	1.35×10^5	1.40×10^5
2	9.16×10^9	9.57×10^4	1.38×10^5	1.40×10^5

3.2.2 Static study

Figure 6 illustrates the data recorded for the static aging experiment. The first permeation test was not carried out until 9 days of aging had occurred. As mentioned earlier, during module

assembly, mounting the module into the gas permeation unit and allowing time for a short evacuation period, the fibers had undergone a significant aging. CHF used to prepare this module, Module 3, were prepared from the same batch as those used in Module 1 and 2, and thus were expected to have similar performance. Fibers were stored in the lab environment all the time.

As depicted in figure 6, the permeability of module 3 decreased exponentially as fibers underwent a further period of aging between day 10 and day 141. However, from day 41 to day 141, the change in permeability remained very small. The relatively small fluctuation in permeability from day 41 to 141 indicates that the largest effect of aging had occurred, and the permeability was relatively stable for this membrane after day 41.
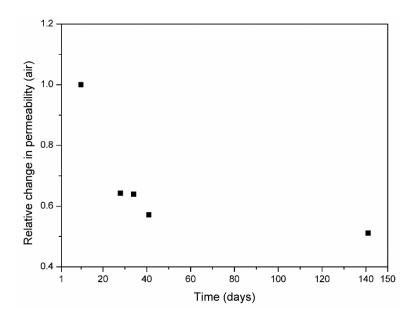

Figure 6: Permeability data plotted as a function of time, for the static aging study.

Analysis of the changes in permeability from day 41 to day 141 appears quite similar for the membranes exposed to intermediate aging followed by static aging. However, the average decrease in permeability from day 1 for the module that is exposed to the only static environment is hard to determine from the slope of permeability as a function of time, as shown in figure 6. Only a good enough estimation can be made by considering the slope from day 41 to 141. But that estimation is not good enough to understand the life expectancy of the membrane. From the fig. 5 and 6, apparently, it can be expected that the membranes exposed to the static environment are aging at a rate faster than those previously exposed to a dynamic air supply and then to a static environment. Hence, this confirms the positive effect that a dynamic air source has on slowing down the aging process. However, as mentioned previously,

in order for this to be a viable process for industry, the process of aging should be kept to a minimum. Although a dynamic air flow has this effect, financially, the cost of this process should be evaluated before applying it at large scale.

3.3 Real biogas exposure

This chapter presents the results of exposing the carbon membranes to biogas from three different plants F1-F3.

3.3.1 Exposure to F1

Table S1 in supporting information summarizes the permeability loss of CO_2 and N_2 after CHF exposed to real biogas with H_2S < 5ppm. It can be seen in figure 7 and table S1 in supportin information that most of the modules lost CO_2 permeability in the range of 20-50 %, even though the exposure time for these modules is varying from 25-210 days. It explains that after oxygen adsorption (whether during module preparation or in a later stage) CHF start stabilizing without further loss in performance. Membrane modules showing 20 % loss after 210 days may have lost the performance already and close to saturation point before they were tested the first time for gas permeation.
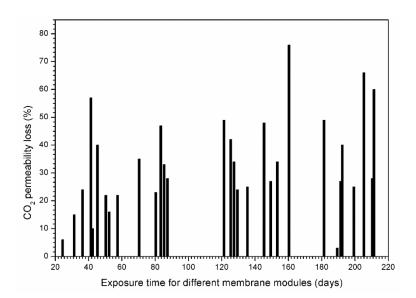

Figure 7: Percent loss in CO_2 permeability for different CHF modules in different exposure time at F1

3.3.2 Exposure to F2 and F3

Fig. 8 shows the change in permeability of N_2, CO_2, CH_4 and O_2 with the time for CHF exposed to F2 (H_2S: <5 ppm) and F3 (H_2S: 150-2400 ppm). Results indicate that after 30 days with high

H_2S concentration, CHF lost 22 % CH_4 permeability, however, CO_2 permeability increased resulting in good membrane performance for CO_2-CH_4 separation, and so did increase the O_2 and N_2 permeabilities. It can be speculated that CH_4 molecules filled the carbon micropores and prevented the access to oxygen, thus resulting in enhanced performance of the membrane. However, after four months with a high concentration of H_2S, CHF showed degraded performance with 70 % loss in CO_2 permeability, which may be the result of micropore blockage. Adsorption onto activated carbon is one of the methods that is used to clean the biogas when pressure swing adsorption (PSA) is used to upgrade the biogas. The reason for decreased performance of carbon membrane at F2 may be the high loading and adsorption of H_2S on carbon. Consequently, regeneration of carbon membrane is needed to restore the lost performance. The membrane module was then installed at F2 with low H_2S for regeneration and it was observed that after 100 days exposure, membrane recovered 40 % CO_2 permeability without any extra regeneration treatment. O_2, N_2, and CH_4 permeabilities were also increased. Again, exposure of 50 days at F3 showed no effect on CO_2 permeability, whereas N_2 and CH_4 permeabilities were decreased. O_2 permeation was not measured for the final experiment. It can be assessed from the exposure at F2 and F3, that high H_2S concentration reduced the membrane performance, but in some way, membrane regenerated itself to some extent under real biogas conditions. CHF membranes need to be regenerated during separation process and this extra step adds complexity and cost to the process. Anderson et al. [12] has reported the effect of H_2S on polyfurfuryl alcohol based carbon membranes. The PFA based carbon membranes showed that CO_2 permeance was reduced by 7% in the presence of H_2S (partial pressure: 0.3 kPa) in the feed when membrane was performing at 35 °C for almost 5 hrs. The loss in CO_2/N_2 selectivity was only 2%.

A non-adsorbable gas like H_2 or He could be used in purging the membrane for removal of contaminants, but this is adding cost and extra line to the process for the treatment. Another alternative is N_2, however in ultra-microporous membranes, the kinetics of transport of N_2 may be too slow and if separation application does not involve N_2, then nitrogen itself will constitute a contaminant that could take a couple of hours to leave the pore structure of the membrane [9]. The objective of this purging study by exposing membrane to real biogas stream with high and low H_2S concentration was to regenerate and clean the membrane by removing contaminants adsorbed physically. Thus, the additional cost could be avoided in the industrial application of carbon membranes.
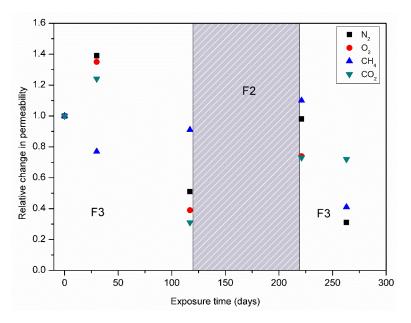
Figure 8: Relative change in permeability of N_2, CO_2, O_2 and CH_4 when CHF are exposed to high H_2S concentration

3.3.3   *Effect of module material housing*

As mentioned earlier, the focus of this study is to make the CHF membranes viable and economical for industrial applications. The exposure to high H_2S concentration was to understand if CHF can survive this harsh condition and H_2S removal unit could be used after membrane separation, which would reduce the cost of the unit because of less gas flow on retentate as compared to feed flow. The intention to study the SS housing and ABS housing was primarily to understand the effect of H_2S and aging of the membrane and finally to reduce the cost of the module. Biogas primarily deals with CO_2-CH_4 separation, but before the gas is exposed to the membrane, pretreatment is performed to remove impurities like H_2S and water. The same task is performed for natural gas separation, so research published on natural gas upgrading can also be applied to biogas upgrading. Schell et al. [28] studied a process for biogas treatment using cellulose acetate spiral-wound membranes for 18 months and reported that no significant differences were seen between the permeation of landfill gas with and without pretreatment, however, the authors suggested that gas pretreatment could prolong the service lifetime of membranes.

The internal corrosion of carbon steel in the presence of hydrogen sulfide represents a significant problem for both oil refineries and natural gas treatment facilities. Surface scale formation is one of the important factors governing the corrosion rate. The scale growth

depends primarily on the kinetics of scale formation which is proportional to the sulfide concentration.

One module with SS-housing and one with ABS-housing were installed at F3 with high H_2S concentration and single gas permeation tests were performed in the lab afterwards. Figure 9 shows the SS-module and single gas permeation results for N_2, CO_2, and CH_4. Both N_2 and CO_2 were stable for the first 20 days and then N_2 permeability started increasing, whereas CO_2 remained almost constant for first two months. CH_4 permeability increased 2.4 times within first 24 hours and results were same even after 18 days before it dropped very quickly in the next 10 days. The reason for the loss in CH_4 permeability may be the pore clogging with H_2S and CO_2. Only CO_2 was tested after 30 days and it can be seen that CO_2 permeability started declining after two months of exposure at F3 until the membrane lost 90 % of CO_2 permeability in 350 days. In comparison with figure 8, here the membrane module is exposed to only high H_2S concentration so more chances of pore clogging which resulted in 90 % loss of CO_2 permeability. However, in figure 8, exposure to F2 with low H_2S concentration had a regenerative effect on the membrane and CO_2 permeability loss was 25 % after 260 days.
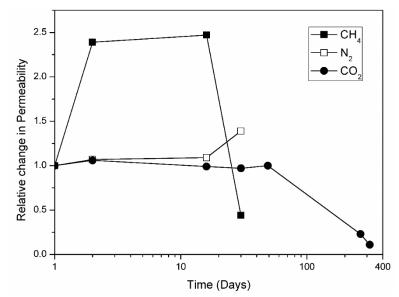

Figure 9: Single gas permeability for CHF in a stainless-steel module housing

Figure 10 presents the effect of ABS-housing and results for single gas permeation are very like figure 9 except CH_4 permeability, which seems declining slower in the case of ABS-housing. The reason expected here could be the H_2S concentration varying every day on biogas field F3 (150 -2400 ppm). So, the physical aging (clogged micro pores) effect was slightly different for both modules. Results from figure 9 and 10 show that ABS-housing has the same

effect as SS-housing and it could be used for making modules of CHF. If CHF module needs to be modified with heat treatment processes like thermal regeneration or CVD for pore tailoring, then temperature limitations for ABS-housing and sealing epoxy should be measured. However, ABS housing is suitable for electrothermal regeneration since ABS is non-conductive.
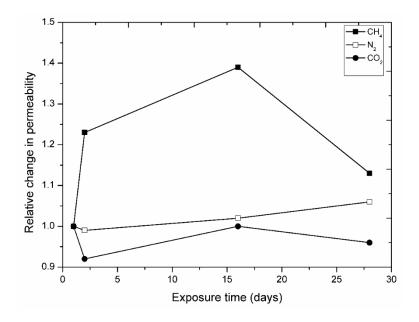

Figure 10: Single gas permeability for CHF in ABS module housing

4   Conclusions

Regenerated cellulose based carbon hollow fibers CHF were stored under different environments. Membranes stored in lab condition and CO_2 atmosphere lost the CO_2 permeability by more than 80 % within the first 30 days. CHF stored in ABS tube under vacuum were stable after losing 65 % CO_2 permeability in one month, and fibers lost their permeability very fast when stored in air at low temperature (4 °C).

Dynamic aging, as defined earlier "aging under controlled environment and continuous gas flow through the membrane", had a promising regenerative effect on the membranes to recover some permeability. The fibers which underwent dynamic aging were not susceptible to static aging anymore. They showed the same performance even after 128 days when stored in the laboratory environment. In total, 31 modules of area 0.5-2 m^2 for each module were used to separate biogas in actual biogas field for days ranging from 25-212. Most of these modules lost 40 % permeability of CO_2 within a few days after installation and were stable afterwards. CHF were mechanically stable at 20bar in real industrial conditions.

Further real gas exposure was performed in two biogas fields by exposing CHF to the H_2S in the sequence high-low-high concentrations. Adsorption of H_2S on carbon membrane may significantly reduce the performance over time. It was observed that the membranes installed at high H_2S (150-2400 ppm) concentration lost CO_2 permeability by up to 65 % in 125 days, and 55 % of this lost permeability was regenerated by exposing membrane to a biogas field with low H_2S (<5 ppm) concentration for 100 days. When this membrane was installed again on high concentration field, the CO_2 permeability was stable for the next 50 days. The biogas-field results showed that high loadings of H_2S increase the aging effect on carbon membranes. Hence, the pre-treatment of biogas is required to bring down the H_2S contents before the upgrading process.

However, it is important to note that aging behavior of carbon membranes may depend on the precursor and the manufacturing conditions used. Carbon membranes with e.g. different structure and surface chemistry will behave differently as shown by other researchers. Thus, it would be useful in the future study to do a direct comparison of carbon molecular membranes from different precursors and manufacturing conditions to better understand the behavior of CMS in biogas application.

Module casing, SS-housing or ABS-housing did not affect the membrane performance significantly. If CHF module needs to be modified with heat treatment processes like thermal regeneration or CVD for pore tailoring, then temperature limitations for ABS-housing and sealing epoxy should be measured. However, ABS housing is suitable for electrothermal regeneration since ABS is non-conductive.

Acknowledgements

Appendix A. Supporting Information

The summary of data associated with aging of carbon membranes is supplied as supporting information.

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Supporting information

Table S1:
Loss in CO_2 permeability of the membranes after exposure to the real biogas at F1

No.	Membrane Area	CO_2/CH_4 Selectivity	Loss in CO_2 permeability	CO_2/CH_4 Selectivity	Exposure time
	m^2	Before exposure to F1	(%)	After exposure to F1	(days)
1	1.7	22	-57%	42	42
2	1.5	22	-6%	42	25
3	1.5	27	-15%	22	32
4	1.4	31	-24%	30	37
5	1.6	26	-35%	39	71
6	1.5	28	-22%	28	51
7	1.7	36	-33%	43	86
8	1.6	35	-28%	49	88
9	1.6	49	-10%	56	43
10	1.4	39	-48%	57	146
11	1.5	49	-34%	68	128
12	1.4	38	-24%	58	130
13	1.1	44	-22%	57	58
14	1.7	59	-40%	71	46
15	1.1	46	-34%	62	154
16	1.1	43	-76%	31	161
17	0.9	32	-44%	59	190
18	0.8	61	-25%	72	200
19	1.0	58	-40%	42	193
20	0.7	53	-66%	58	206
21	1.0	42	-27%	51	150
22	1.0	58	-60%	44	212
23	1.5	53	-16%	34	53
24	1.7	51	-47%	47	84
25	1.5	48	-25%	54	136
26	1.4	39	-49%	45	122
27	1.4	42	-42%	53	126
28	0.9	57	-28%	70	211
29	1.0	43	-27%	59	192
30	1.9	46	-23%	51	81
31	1.1	49	-49%	49	182