Carbon membranes for oxygen enriched air –Part I: Synthesis, performance and preventive regeneration

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Highlights:

- Regenerated cellulose precursor was carbonized to make carbon membranes
- O_2 permeability increased exponentially with increase in operating temperature
- O_2/N_2 selectivity was between 17-20 for all operating temperatures (23-68 °C)
- Thermal, chemical, and online-electrical regeneration methods were investigated

Abstract

Chemisorption of oxygen on the active sites of carbon layers limits the use of carbon membranes in air separation application. A novel online electrical regeneration method was applied to prevent the active sites on carbon surface to be reacting with O_2 while the membrane was in operation. This method reduced the aging effect and the membrane showed relative stable performance with only 20% loss in O_2 permeability and 28% increase in O_2/N_2 selectivity, over the period of 135 days using various feeds containing H_2S, n-Hexane and CO_2-CH_4 gas. The carbon membranes reported here were produced at the pilot-scale facility by the carbonization of regenerated cellulose under optimized conditions to achieve good air separation properties. The permeation properties of the membranes were tested by single gas separation experiments at 5 bar feed pressure (50mbar permeate) and temperature range 20-68 °C. It was observed that O_2 permeability is increasing exponentially with increase in operating temperature without significant loss in the O_2/N_2 selectivity. The O_2 permeability of 10 Barrer *(1 Barrer =2.736E−09* $m^3(STP)m/m^2$ *bar h)* with O_2/N_2 selectivity of 19 was achieved at 68

°C. Thermal (80 °C), chemical (propylene) and online-electrical (10V DC) regeneration approaches were studied to lessen the aging effect on carbon membranes.

Key Words: Carbon hollow fibers, oxygen-enriched air, online electrical regeneration

1. Introduction

At present, the air separation market to produce pure oxygen (O_2: 95-99.99%) is dominated by cryogenic fractionation and pressure swing adsorption because current membranes are not capable of economically producing membranes with comparable purity [1]. The separation is based on the difference in permeation rates of oxygen and nitrogen through the membrane, and the performance of polymeric membranes is restricted by the trade-off between permeability and selectivity [2]. Polymeric materials may have a high permeability for O_2, but rather low O_2/N_2 selectivity (usual range 2-8), and the maximum permeate purity achievable for O_2 with these membranes seems to be 30-60% [3].

Carbon is one class of material that can offer improved performance due to molecular sieving effect. In molecular sieving, the available pore size is below the kinetic diameter of one of the gas components in the feed. This characteristic of the material increases selectivity by reducing the rotational degrees of freedom of nitrogen versus oxygen in the diffusion (kinetic) transition state. Carbon membranes (CM) can be prepared by carbonization of the precursor membranes at high temperature (550 – 850 °C) under vacuum or in an inert environment (Ar, He or N_2). Gas permeation properties of CM are affected by the type of precursor and carbonization conditions. Many authors have reported high selectivity and permeability of carbon membranes (CM) compared to polymeric membranes for air separation [4-7].

Although CM have reported better performance compared to polymeric membranes, the operational stability and aging are the important issues to be considered for the implementation of these carbon membranes. CM usually age very rapidly due to physical aging (pore shrinkage to achieve a thermodynamically stable structure and or physical adsorption of gas molecules) and or chemical aging (chemical bonding, usually C=O bonds) [8-11]. This aging effect may seriously reduce the permeability of a membrane and hence it is still a major problem for the industrial application of CM in air separation where the membrane is exposed to O_2 all the time.

Several techniques have been reported to achieve a stable performance of CM under oxygen environment. Menendez et al. [11] used *thermal regeneration* and found that thermal treatment of membranes at 120 °C in a vacuum could remove oxygen-containing surface groups from activated carbons. However, the regenerative effect is very brief because it leaves a surface with reactive carbon sites that can re-adsorb oxygen very quickly even at room temperature. *Chemical regeneration* requires an addition of a chemical (gas) to restore the membrane performance. Jones and Koros [12] tested purging of propylene at about 10 bar to restore the membrane performance, however, the permeance of O_2 was not successfully recovered.

Lie et al. [13] studied *electrothermal regeneration* to enhance the permeation of CO_2 in iron-doped flat-sheet CM. They applied a direct current of 30mA (17.5V) on the iron-doped CM and studied the effect of pulsating electrothermal regeneration (i.e. electric current set to "on" and "off" periodically). After electrothermal regeneration, the CO_2 permeability was 65% higher compared to initial value because the sorption of gases in carbon matrix was reduced, while diffusivity was increased to a considerable extent. Nevertheless, the membrane without any regeneration showed 60% loss in permeance of CO_2.

The aim of the current study has been to exploit further the electrically conductive nature of CM to enhance or stabilize the performance of the membrane. The present paper focuses on the novel online-regeneration method to prevent the reactive/adsorption sites by supplying continuous electric current. The effect of "online electrical regeneration (regeneration parallel with separation process)" on carbon hollow fiber membranes has not been fully explored, and there is not much information available on this topic. Hence, an online regeneration (DC: 44-55 µA, 10V) was tested in this study to achieve a stable performance of CM in air separation application. In addition, thermal and chemical regeneration methods were also pursued to find an effective, simple, and economical solution to restore the membrane performance. The term "Preventive electrical regeneration" (PER) is used for the electric regeneration in this study. PER means a continuous supply of electrical potential during membrane operation to prohibit the molecules adsorbing on the membrane surface.

2. Theory and background

2.1. Structure of carbon molecular sieve

Carbon molecular sieve (CMS) is derived from organic thermosetting precursors by heat treatment in vacuum or in an inert environment. Geiszler and Koros [14] reported that an inert gas (Ar, He or N_2) atmosphere resulted in more open, but less selective CMS matrix compared to vacuum carbonization. They explained this with acceleration in the carbonization process due to increased gas phase heat and mass transfer. By increasing the final temperature in polyimide carbonization from 550°C to 800 °C (in vacuum of He gas), the authors observed a decrease in permeance while selectivity increased. Precursors for CMS include thermosetting resins, graphite, coal, pitch, plants and synthetic polymers [15].

Bisco and Warren [16] introduced the concept of turbostratic order for graphitic carbons. The carbon consists of turbostratic groups, where each group has several graphite layers stacked together roughly parallel and equidistant, but with each group having a random orientation as shown in figure 1(a). Packing imperfection between the stacked layers contains slit-like pores which give rise to the molecular sieving structure and have a bimodal pore size distribution. The edges of adjacent stacked layers are believed to make the slit-like ultra-micropores (≤0.7nm), while micropores (0.7-2nm) are formed between the planes due to the random orientation of the adjacent carbon sheets [6]. The gases may diffuse through the pores, or they may adsorb on the walls and travel through the pores by a mechanism known as surface flow [17]. The bigger, more strongly adsorbed molecules may also block the pores of smaller molecules in a phenomenon known as competitive adsorption or selective surface flow. This results in reverse selectivity; the smaller components are thus retained.

2.2. Electrical regeneration

The continuous medium of graphene sheets makes the CMS membranes electrically conductive. As shown in figure 1(b), each sp^2-hybridized carbon atom combines with three other sp^2-hybridized atoms to form a series of hexagonal structures, all located in parallel planes. The fourth valency, that is, the free delocalized electron, is oriented perpendicular to this plane as shown in fig. 1(b). Unlike the sigma (σ) orbital, it is non-symmetrical and is called by convention a pi (π) orbital [18].

An adsorbed gas, such as CO_2, may be quickly and efficiently desorbed by the passage of a direct current (DC), thereby allowing for a low-energy, electric swing separation system with operational simplicity [19]. The van der Waals forces between the carbon skeleton and the adsorbent are disrupted or perhaps reversed by the electric current. This interaction most likely results from the quadrupole moment and the free electrons of CO_2. As a result, adsorbed CO_2 is released or repulsed from the micropore surface and desorption occurs. The same effect may apply to other adsorbed gases.

Electrothermal desorption is a process where the heat is generated inside the adsorbent. Hence, the heat and mass flux directions are the same, i.e. from solid to the fluid, as opposed to traditional thermal regeneration. Petkovska and Mitrovic [20] reported that electrothermal desorption is more energy efficient than conventional desorption because the fluid temperature can be substantially lower than the adsorbent temperature determining the adsorption equilibrium. They also showed that same direction of heat and mass fluxes results in better desorption kinetics. The ohmic heating enhancing desorption, probably discourage adsorption at the pore entrances. For this reason, optimization of current cycle time, to stabilize or increase the permeability of relevant gas is believed to be important.

The electrical resistance R (Ω) can be evaluated from media resistivity and its dimensions [21] as shown in equation 1.

$$R = \frac{\rho L}{e\ell} \qquad (1)$$

Where ρ is electrical resistivity of the material (Ωm), L is the length of material (m), e is the width (m) and ℓ is the thickness (m). Resistivity is defined as resistance times cross sectional area for the current flow, divided by the resistor length [22].

Electro-swing adsorption has also been reported, this is a process that takes place on beds of activated carbon material [23] and on activated carbon honeycomb monoliths [24]. In the latter process [24], an electrical current was applied to the activated carbon resulting in a localized heating of the material, which is referred to as the Joule effect. This heating, in turn, caused desorption of CO_2, much the same mechanism as thermal swing adsorption. Electro-swing adsorption had been applied commercially for removal of volatile organic compounds but not yet for gas separation processes [25].

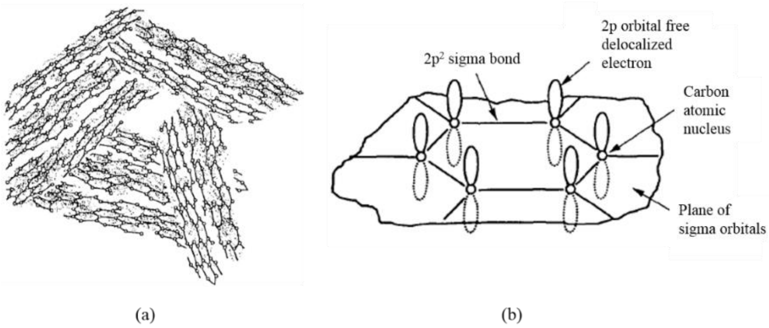

Figure 1: (a) Structure of turbostratic graphite (b) Schematic of sp^2 *hyberdized structure of graphite sheet showing 2p free electrons [18]*

The rationale behind the study of preventive electrical regeneration (PER) was to add ohmic heating (Ohm's law) to desorb the molecules and prevent new adsorption. Electric potential is a very strong driving force compared to pressure. It was presumed that while introducing elecric current, the cross coupling of driving force and mass flow would enhance the membrane flux by reducing the adsorption of gas molecules on the pore edges.

3. Experimental

3.1. Preparation of carbon membranes

Carbon hollow fiber membranes were produced at a semi-commercial scale production plant by carbonization of regenerated cellulose precursor. Through an organized study of both precursor and carbonization parameters, protocols were developed for dope solution formation and carbonization process which are described elsewhere [13, 26]. Cellulose acetate (CA), which is a biodegradable semi synthetic polymer (M_w: 100,000, ACROS, Belgium) was dissolved in 1-Methyl-2-pyrrolidone (NMP: Mw 99.13, Merck, Germany), and then mixed with polyvinylpyrrolidone (PVP: M_w 10,000, Sigma-Aldrich®, Norway) to make a dope solution. CA hollow fibers were synthesized using dry-wet spinning process using NMP and water mixture as bore solvent. The prepared CA hollow fibers were then treated with a mixture of NaOH and short chain alcohol to deacetylate the fibers. A tubular horizontal furnace (Carbolite®, 3 zones split furnace) was used to carbonize the deacetylated hollow fibers. These deacetylated CA hollow fibers were carbonized at 550 °C under N_2 flow using heating rate of 1 °C/min with several dwells and the final temperature of 550 °C for 2hrs. Carbonization protocol is shown in fig. 2 and procedure details can be found in the patent [27]. The pilot-scale module construction procedure for CM is reported elsewhere [28]. 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 [13, 22, 29] using FTIR and SEM.

3.2. Gas permeation tests

Carbon hollow fibers (effective area of 0.004 m^2) were mounted in an in-house made module, using stainless steel tubing and Swagelok® fittings. Gas permeation properties were tested using shell side feed configuration with single pure gases N_2 and O_2 at 5 bar feed pressure and vacuum on the permeate side. A set of temperature values, 20, 25, 35, 45 and 68 °C was applied to measure the temperature effect on O_2 and N_2 permeances. A standard pressure-rise setup with LabView® data logging was used for all tests. The experiments were run for several hours to ensure that steady state was obtained. For each set of the permeation tests with one temperature set point, the O_2 was run for ca. 2 hours followed by N_2 which was ca. 3 hours. Then system was evacuated overnight before next set of experiments were started. The gas permeance P was calculated using equation 2.

$$\mathrm{P} = \frac{9.828\mathrm{V} \cdot (dp/dt)}{\Delta P \cdot A \cdot T} \qquad (2)$$

Here, V is the permeate side volume (cm^3) that can be measured with a pre-calibrated permeation cell as reported by Lin et al. [22, 30], dp/dt is the collection volume pressure increase rate (mbar/s) and A is the total active area of membrane (cm^2), ΔP (bar) the pressure head and T (K) is the temperature for experiment. The ideal selectivity is defined as the ratio of the pure gas permeances as shown in equation 3.

$$\alpha_{\mathrm{A/B}} = \frac{\mathrm{P_A}}{\mathrm{P_B}} \qquad (3)$$

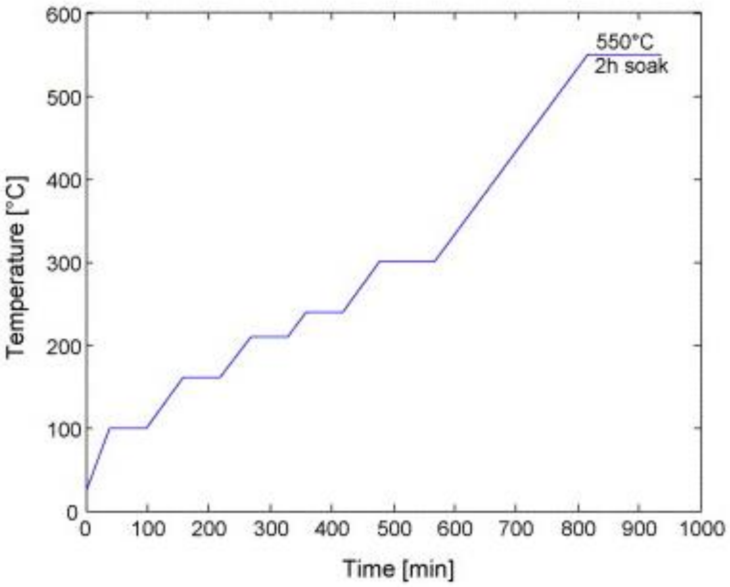

Figure 2: Carbonization protocol based on [27, 31]

3.3. Aging and regeneration of carbon membranes

To study the enhanced aging effect on CM, the membrane was exposed to a biogas containing three different concentrations of H_2S as shown in table 1.

Table 1: Different gas mixtures used to enhance the aging effect on CM

Gas mixture name	Gas composition
Synthetic biogas (SBG)	40ppm H_2S in a CO_2-CH_4 mixture
Worst case gas (WCG)	1% H_2S and 0.1 % n-Hexane in biogas mixture
Real biogas field exposure (RBG)	250ppm H_2S in biogas (source: microbial digestion of slurry from waste water)
Air exposure during the storage period	Ambient air with average relative humidity 40%

3.3.1. Thermal and chemical regeneration

Adsorption is an exothermic phenomenon; and as a consequence the desorption is an endothermic phenomenon and energy must be supplied to desorb the adsorbents [22]. A membrane module with stainless steel housing was prepared using two carbon hollow fibers (0.0004m^2 effective area) in the module. Single gas experiments for pure O_2 and N_2 were performed at 30 °C (2 bar feed pressure and vacuum on permeate side) to measure the reference permeability values. After determining the initial permeability values of these two gases, both sides (shell and bore) of the membranes were exposed to WCG for 24 hours. The permeability of pure gases was measured again to examine the possible aging effects in the membrane.

The membranes were regenerated chemically using propylene. The CM were flushed with propylene gas for 24 hours and the single gas permeation tests were performed systematically after the exposure to detect any change in membrane performance. After single gas tests, thermal regeneration was applied by heating the membrane module. The module was heated up to 80 °C and kept at this temperature for 24 hours to desorb the adsorbed gas molecules in the pore structure of the membrane. Then final gas permeation tests were performed at 30 °C to see the effect of thermal regeneration.

3.3.2. Electrical regeneration

Two new membrane modules with Acrylonitrile Butadiene Styrene (ABS) housing were prepared containing two carbon hollow fibers (4 cm^2 effective area, OD: 198μm, wall thickness, ℓ: 31μm) in each module. A conductive glue (Eccobond 56C) was applied between carbon hollow fibers and Swagelok® fittings on each end of the module. The electric power source was connected (Alligator clips) to the external of the Swagelok ® fitting containing conductive glue on both sides of one module as shown in figure 3. The second module (reference module) was not connected to electric current. The conductive glue was not gas tight enough at high pressure, hence another set of Swagelok® unions were connected to a non-conductive glue on the outer section of the module. Teflon tubings were used for feed, retentate and permeate flows. Single pure gases were tested to determine the initial permeability of the membranes.

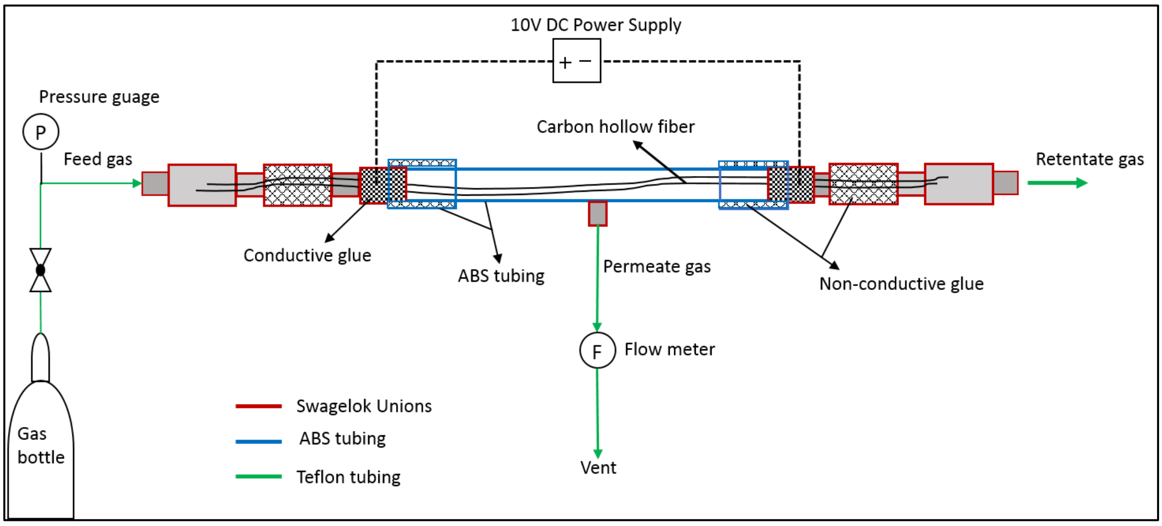

Figure 3: Experimental setup for electrical regeneration of carbon hollow fiber membrane module

Both modules with CM were exposed on both sides (shell and bore side) to WCG for four days. Then "preventive electrical regeneration" (PER) was performed on one module and the second module was used as reference (RM) module (no electrical treatment). PER was conducted using a direct current (DC) power source and an applied voltage of 10 V which corresponds to about 45-55 µA measured amperage on carbon fibers. The current was continuously applied during the whole exposure.

Table 2: Electrical regeneration of CM and exposure to different gases (reported in consecutive days from left to right). Single gas tests are O_2 and N_2

Single gas tests	WCG	Single gas	WCG	Single gas	RBG	SBG
PER module	4 days, 10V	no voltage	14 days, 10V	no voltage	14 days, no voltage	no voltage
RM module	4 days, no voltage	no voltage	14 days, no voltage	no voltage	14 days, no voltage	no voltage

Table 2 shows the steps followed during electrical regeneration of the CM. As shown, single gas tests (O_2, N_2) were performed for both the PER module (which is going to be regenerated electrically and current is on during the test) and reference module (RM). Then both modules were exposed to WCG for four days, with PER under 10V and RM without any current. After four days voltage supply was turned off on PER module, and both modules were tested for single gases. After the single gas tests, both modules were again exposed to WCG for 14 days keeping voltage supply "on" for PER module, and then tested again for single gases afterward.

The CM modules were then installed at a real biogas plant for 14 days and exposed to the real biogas containing 250ppm H_2S. The modules were disconnected from the biogas plant and reconnected to the synthetic biogas in the laboratory for several days. The membrane modules were then tested for single gases again to check if a stable performance had been achieved after the preventive electrical regeneration.

The electrical resistance of the carbon fibers was measured by a handheld Ohm meter to calculate the specific conductivity of the membranes. Carbon fibers obtained at different soak temperatures (550 °C. 650 °C, 750 °C) were used to measure the electric conductivity.

4. Results and discussion

4.1. Experimental findings

The impact of temperature on O_2 and N_2 permeability at constant pressure and feed flow rate is plotted in fig. 4. The results reported are from pure gas permeation experiments. He et al. has performed the mixed gas experiments on the same type of CM (same protocol) and results indicated that the membrane performance is same or even higher in some cases for mixed gas as compared to single gas separation [32]. Singh et al. [33] also confirmed that pure gas permeation properties were within 3% of mixed gas permeation properties for the pyrolyzed hollow fibers. The trend in fig. 4 shows that O_2 permeability is increasing exponentially with increase in temperature which is also comparable with an Arrhenius law type effect. The high permeability is a result of high diffusivity and high solubility as well, and the increase in O_2 permeability here indicates a more open molecular matrix aiding O_2 flux. Whereas, change in N_2 permeability is quite modest with an increase in temperature. Figure 5 represents the selectivity of O_2/N_2 at varying temperatures. The carbon matrix is comprised of relatively large pores interconnected by constrictions of negligible thickness that approach the dimensions of diffusing molecules. In this case, penetrant molecules require characteristic activation energies to overcome the resistance at the constrictions. Hence, a small increase in activation energy in form of high temperature increased the activated diffusion of O_2 and N_2. Permeation experiments were performed at 20, 35, 45, 50 and 68 °C in order of increasing temperature. Finally, the experiment at 25 °C was performed (shown in fig. 5) to see if the microporous structure of the membrane had changed after a ten hours direct exposure of the O_2 and finally altering the permeation properties. It was observed that O_2/N_2 selectivity increased to 31 as compared to values at 20 and 30 °C, which are 17 and 18 respectively. However, the membrane permeability for O_2 increased slightly as compared to the value at 20 °C and to some extent decreased for N_2. The small numerical value for the N_2 permeability causes this to be more vulnerable to fluctuation in the leak-rate of the setup (measured at the beginning of the test series). Hence the measured value of an O_2/N_2 selectivity of 31 at 25°C is most likely an experimental out-layer. Fresh carbon membranes, prepared with similar protocol, were tested at 25°C and an O_2 permeability of 32 Barrer was measured and O_2/N_2 selectivity was 10.

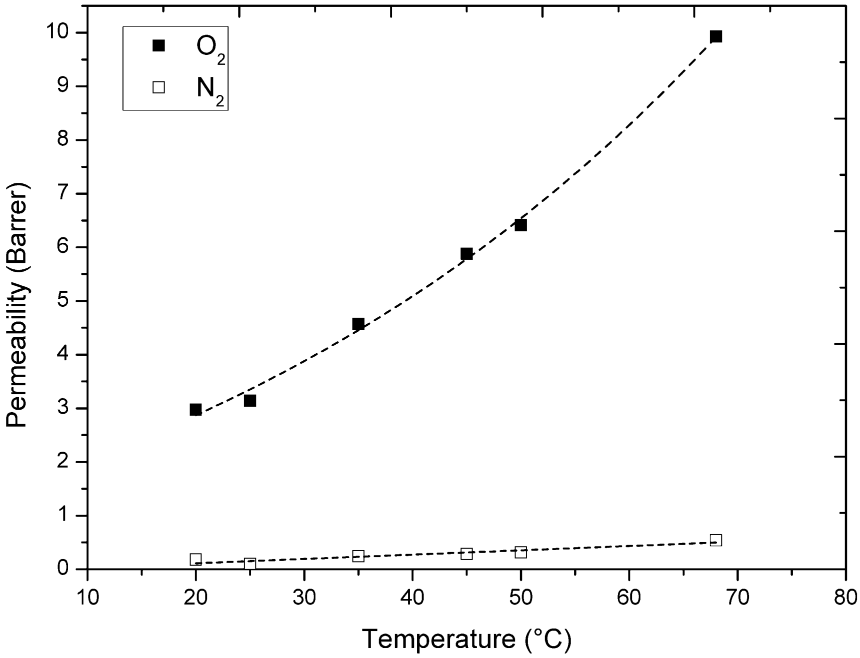

Figure 4: Effect of temperature on O_2 and N_2 permeability (P:5bar)

Hayashi et al. [34] exposed the CM (carbonized at 700 °C) to air at 100 °C for 1 month and observed that membrane permeance increased with increasing permeation temperature. They concluded that O_2 in the air reacts with the membrane and forms oxygen-containing functional groups, which are continuously decomposed to CO_2. The formation and removal of surface oxides gradually restructure the carbon layer and somewhat narrow the micropores permanently. This effect was observed in the present study as well by inclined in selectivity of O_2/N_2 without losing O_2 permeability when the membrane was tested at 25 °C as shown in figure 4 and 5. As explained earlier, the permeance test at 25 °C was performed after the membrane had gone through many exposures of O_2, N_2, and vacuum (6 days) at different temperature and pressure conditions which helped the membrane micropores to restructure. The effect of temperature was not significant on the permeability of N_2 as it was observed for

O_2. Figure 6 presents the Robeson upper bound (2008) and as can be seen, the membrane performance for all experiments reported here, are in the commercially attractive region [2].

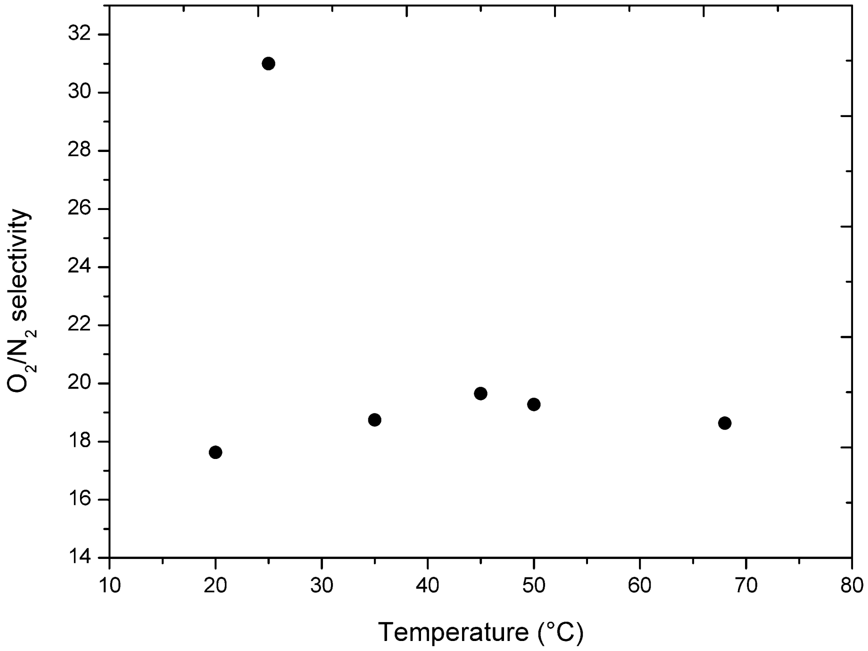

Figure 5: Effect of temperature on O_2/N_2 selectivity (P:5bar)

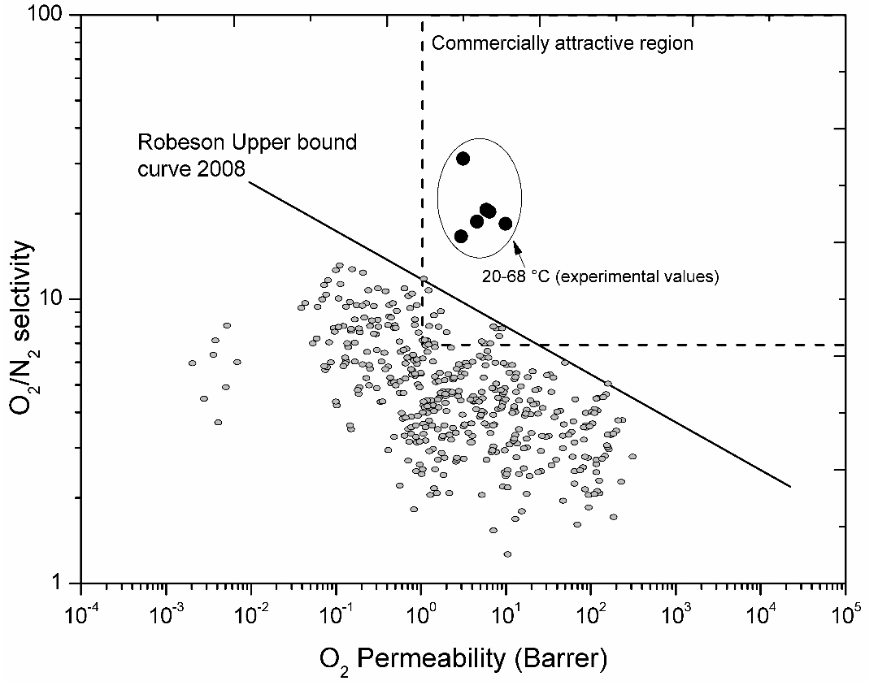

Figure 6: O_2 permeability and O_2/N_2 selectivity of CM with respect to Robeson upper bound curve (2008) [2]

4.2. Regeneration

The permeation results referring to recently prepared membranes could be very misleading if the change in results is very fast over time (aging). A better evaluation could be achieved by adding a dimension of time to the membrane performance plot. To attain a commercially attractive membrane life, a stable performance is essential, and it can be achieved by membrane regeneration process. A few techniques were used here to restore the membrane performance.

4.2.1. Thermal and chemical regeneration

Results for the change in permeability of O_2 and N_2 after WCG, propylene exposure and thermal regeneration of CM are presented in figure 7. After 24 hours exposure of WCG, the permeabilities of O_2 and N_2 declined by 30% and 40%, respectively. Chemisorption sorption occurs only on active sites; therefore, it might be that the O_2 had already penetrated the micro and ultra pores of the carbon structure and occupied a large fraction of the active sites and formed covalently bounded O-bridges with the carbon. However, further blockage of pores occurred by physiosorption when H_2S, CO_2 and hexane molecules were present in WCG and adsorbed on the carbon surface. The strong aging may be explained by both a strong physiosorption of bigger molecules on the carbon surface and chemisorption in the matrix.

Flushing the module with propylene for 24 hours could partially (ca. 10%) restore the lost permeability for both O_2 and N_2, but selectivity decreased further. Propylene acted as a cleaning agent by removing adsorbed compounds from carbon surface and the exposure broadened the membrane pores, thus reducing the resistance to the transport of O_2 and N_2. Physiosorption is usually a reversible process and heat of adsorption is low, therefore, the increase in permeability might be only due to the desorption of physically adsorbed molecules. The propylene may interact with carbon matrix in two ways: Firstly, it may act as a solvent, dissolving some or all the permeants that are sorbed in a carbon matrix. Compounds that possess π-bonds may also interact in another way: The high electron density in the π-bonds may cause repulsion between the π-cloud of the olefin and the π-cloud of the graphene layers making up the micropore. The result may be pore expansion and increased permeability [35, 36]. This may also explain the slight increase in permeability of O_2 and N_2 over the exposure of propylene.

Thermal treatment of the membrane at 80 °C for 24 hours could not regain the lost flux. Instead, the permeability values for both O_2 and N_2 decreased. It might be that all the reactive sites cleaned by propylene were occupied again by the adsorption O_2 which blocked the pores and ultimately decreased the permeability of both gases. The thermal limitations of the used epoxy in module construction prevented the use of elevated temperature in this study. Jones et al. [12] also reported that 90 °C thermal regeneration was ineffective to restore the membrane permeation properties. The oxygen chemisorbed on carbon can only be removed as CO or CO_2 at 600-800 °C. However, at this elevated temperature, the carbon structure may be changed in two ways: sintering (pore narrowing/closure) and gasification (pore widening). A stable epoxy at elevated temperatures for module construction could have helped to develop some thermal regeneration methods for the restoration of the membrane permeation properties.

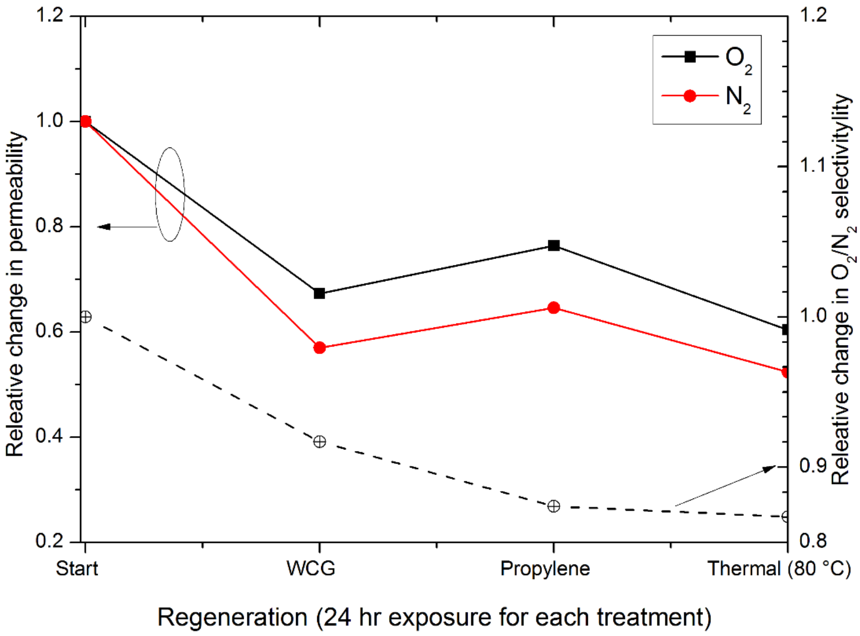

Figure 7: Relative change in permeability and selectivity of O_2/N_2 after chemical and thermal treatment

4.2.2. Electrical regeneration

The final carbonization temperature had a significant effect on the specific conductivity of the material. The conductivity of resulting carbon increased with increase in soak temperature as shown in table 3. The results in table 3 shows that 550 °C is too low temperature to yield electrical conductive carbon fibers. The resistivity of the carbon hollow fibers, used in PER, was 0.022 Ωm (from Eq. 1) which was somewhat higher than reported for activated carbons that is in the range 0.001-0.006 Ωm [37]. The resistivity can be used as measure of porosity. Increasing the porosity causes the drop-in electron flow. For characterizing carbon that have been treated in different ways, resistivity is therefore a possible rapid indicator. The high resistivity of CM may be defined by the high degree of porosity.

Electrical regeneration with 10V DC yielded a positive effect for the permeability of O_2 when applied while membrane was in operation and being exposed to WCG, as shown in figure 8.

Table 3: Final soak temperature and specific conductivity of resulting carbon fibers

Soak Temperature (°C)	Specific conductivity ($1/\Omega\cdot m^3$)
550	83
650	5520
750	112000

The permeability of O_2 increased by 15% but the effect did not last long. Later, the membrane was stored in air for five days and the membrane lost some of the permeability. After repetition of the electrical regeneration along with WCG exposure did not gain the lost permeability but rather it declined and lost 20% of the initial value after exposed to WCG for 12 days. Almost similar effect was observed for N_2 with 5% increased permeability in the first attempt of electric regeneration, as shown in figure 9. It might be that the applied voltage in 2nd electrical regeneration treatment was not enough to disrupt the van der Waals forces between carbon structure and adsorbed gases like O_2 and CO_2.

Although, the lost performance was partially regained after 10 days' exposure to RBG and remained steady for next 3 months. But the observed phenomenon is still unclear with respect to how the electric current desorbs the absorbed gases.

The effect of applied current was instantaneous, indicating that electrostatic repulsion was also active. Desorption or an instantaneous change would not result only by Ohmic heating. Therefore, some other factors could also be contributing in the results. One explanation for this opposite behavior of current could be that electro potential driving force and cross coupled mass transfer were influencing the flux through the membranes. Deconvolution of electric field effects and heating effects on permeation is a challenging task. Mixed gas tests with applied current will probably provide more insight to this problem. The permeability of N_2 dropped in a continuous way after the first electrical regeneration till the end of the run (130 days) by losing 60% of the initial value.

The effect of PER was not significant compared to the RM and it might be the WCG being too potent to be counter effected by the electric potential as conductivity of the fibers was already too low. Nevertheless, the electrical regeneration performed in this study kept the permeance of O_2 quite stable and only 20% drop in O_2 permeability was recorded during 138 days of different exposures and storage. The O_2/N_2 selectivity was 28% higher than the fresh membrane. The decreased flux of N_2 in PER may be explained by the effect of electric field. With an electric field, cross coupling is generated, which reduces the effective pore size (effect is larger for N_2) but stimulates desorption from pore walls (favorable for O_2 transport).

In the reference module, as shown in fig. 9, N_2 permeance was almost doubled after 4 months resulting 45% drop in O_2/N_2 selectivity. The results from the module exposed to PER showed that the overall performance was enhanced due to the online electrical regeneration, however, the performance of RM reduced gradually over time.

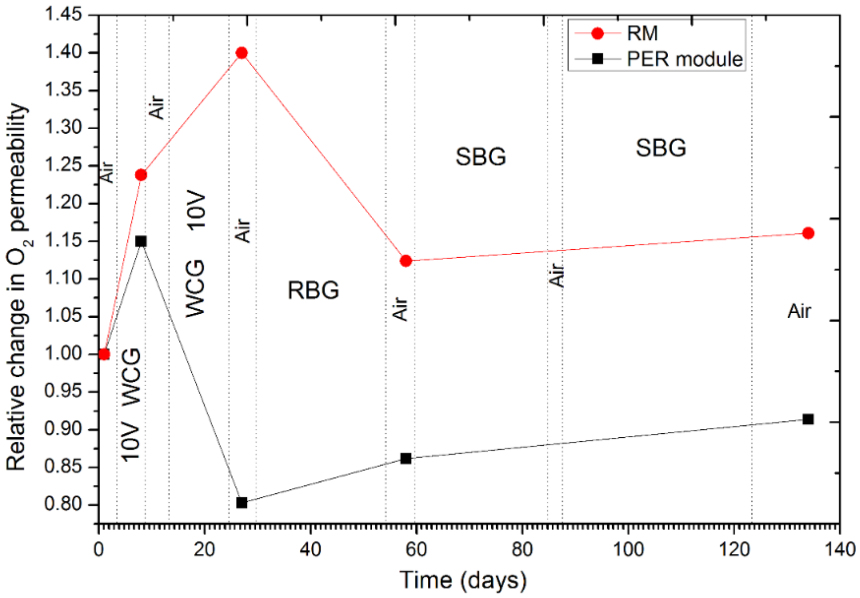

Figure 8: Aging of CM under different environments and effect of electrical regeneration on O_2 permeability

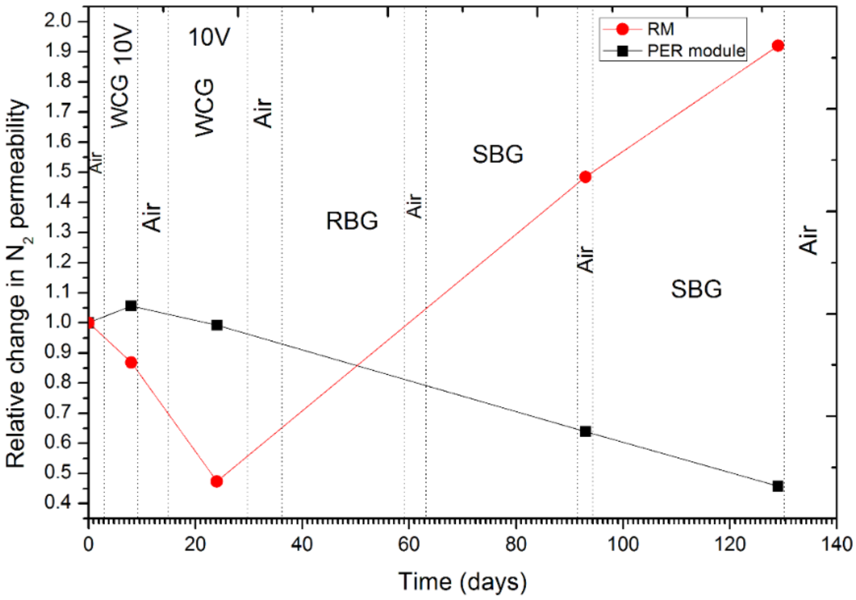

Figure 9: Aging of CM under different environments and effect of electrical regeneration on N_2 permeability

5. Conclusions

Regenerated cellulose-based carbon hollow fiber membranes produced at the pilot-scale plant demonstrated competitive air separation properties. Experimental results showed that elevated temperature operations increase O_2 permeability without significant loss in O_2/N_2 selectivity. The prepared CM had reasonable performance over a time span of about 5 months under harsh environments (air, H_2S, n-Hexane, CO_2, CH_4). Online preventive electrical regeneration (PER) enhanced the O_2 permeability by eliminating the aging effect on the membrane and the O_2/N_2 selectivity was also increased.

When choosing a regeneration method, both energy demand and ease of operation are key factors. Offline regenerations (thermal and chemical) has the severe drawback of potential plant shut down. If this interruption must be avoided, then one needs to have two sets of membranes. One set can be regenerated while other is in use. Both interruption of a process and or having a double set of membranes mean extra cost.

Thermal treatment up to 80 °C was not very effective and use of very high temperature would result in possible burnout of the carbon matrix. Chemical regeneration requires the use of an additional chemical (if the regenerating gas/vapor is not present in the feed stream), with the subsequent evacuation of that gas/vapor after use, and offline operations.

"Preventive" electric regeneration is the most promising method if its regeneration efficiency is reasonable because it operates constantly online but requires a small amount of energy (0.86 μW/fiber·m) and simple equipment. It also has the possibility of high heating rates. Deconvolution of electric or magnetic field effects and heating effects on permeation is a challenging task. Mixed gas tests with applied current will probably provide more insight to this problem.

However, it is important to note that aging behavior of CM may depend on the precursor and the manufacturing conditions used. Carbon membranes with e.g. different structure and surface chemistry will behave differently as also shown by other researchers.

Acknowledgement

The authors would like to thank The Department of Chemical Engineering at NTNU for providing the possibility to work with this article.

References

[1] R.W. Baker, Future Directions of Membrane Gas Separation Technology, Ind. Eng. Chem. Res. 41(6) (2002) 1393-1411. **DOI:** 10.1021/ie0108088

[2] L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320 (2008) 390-400. http://dx.doi.org/10.1016/j.memsci.2008.04.030

[3] B.D. Bhide, S.A. Stern, A new evaluation of membrane processes for the oxygen-enrichment of air. I. Identification of optimum operating conditions and process configuration, J. Membr. Sci. 62 (1991) 13-35. http://dx.doi.org/10.1016/0376-7388(91)85003-N.

[4] C.W. Jones, W.J. Koros, Carbon molecular sieve gas separation membranes-I. Preparation and characterization based on polyimide precursors, Carbon 32(8) (1994) 1419-1425. doi: http://dx.doi.org/10.1016/0008-6223(94)90135-X

[5] W. Shusen, Z. Meiyun, W. Zhizhong, Asymmetric molecular sieve carbon membranes, J. Membr. Sci. 109(2) (1996) 267-270. doi: http://dx.doi.org/10.1016/0376-7388(95)00205-7.

[6] J.E. Koresh, A. Sofer, Molecular Sieve Carbon Permselective Membrane. Part I. Presentation of a New Device for Gas Mixture Separation, Sep. Sci. Technol. 18(8) (1983) 723-734. doi: 10.1080/01496398308068576.

[7] H. Hatori, Y. Yamada, M. Shiraishi, H. Nakata, S. Yoshitomi, Carbon molecular sieve films from polyimide, Carbon 30(4) (1992) 719-720. doi: http://dx.doi.org/10.1016/0008-6223(92)90192-Y.

[8] S. Lagorsse, F.D. Magalhães, A. Mendes, Aging study of carbon molecular sieve membranes, J. Membr. Sci. 310 (2008) 494-502. doi: http://dx.doi.org/10.1016/j.memsci.2007.11.025.

[9] L. Xu, M. Rungta, J. Hessler, W. Qiu, M. Brayden, M. Martinez, G. Barbay, W.J. Koros, Physical aging in carbon molecular sieve membranes, Carbon 80 (2014) 155-166. https://doi.org/10.1016/j.carbon.2014.08.051

[10] G.B. Wenz, W.J. Koros, Tuning carbon molecular sieves for natural gas separations: A diamine molecular approach, AIChE J. 63(2) (2017) 751-760. https://doi.org/10.1002/aic.15405

[11] I. Menendez, A.B. Fuertes, Aging of carbon membranes under different environments, Carbon 39(5) (2001) 733-740. doi: http://dx.doi.org/10.1016/S0008-6223(00)00188-3

[12] C.W. Jones, W.J. Koros, Carbon molecular sieve gas separation membranes-II. Regeneration following organic exposure, Carbon 32(8) (1994) 1427-1432. doi: http://dx.doi.org/10.1016/0008-6223(94)90136-8.

[13] J.A. Lie, M.-B. Hägg, Carbon membranes from cellulose: Synthesis, performance and regeneration, J. Membr. Sci. 284 (2006) 79-86. doi: http://dx.doi.org/10.1016/j.memsci.2006.07.002.

[14] V.C. Geiszler, W.J. Koros, Effects of Polyimide Pyrolysis Conditions on Carbon Molecular Sieve Membrane Properties, Ind. Eng. Chem. Res. 35(9) (1996) 2999-3003. **DOI:** 10.1021/ie950746j

[15] S.M. Saufi, A.F. Ismail, Fabrication of carbon membranes for gas separation––a review, Carbon 42(2) (2004) 241-259. https://doi.org/10.1016/j.carbon.2003.10.022

[16] J.W. Biscoe, B. E., An X-Ray Study of Carbon Black, J. Appl. Phy. 13(6) (1942) 364-371. doi: 10.1063/1.1714879

[17] J.E. Koresh, A. Soffer, Mechanism of permeation through molecular-sieve carbon membrane. Part 1.-The effect of adsorption and the dependence on pressure, J. Chem.

Soc. Faraday Transactions 1: Physical Chemistry in Condensed Phases 82(7) (1986) 2057-2063. doi: 10.1039/F19868202057

[18] H.O. Pierson, Handbook Of Carbon, Graphite, Diamond and Fullerenes-Properties, Processing and Applications, NOYES, New Jersey, 1993.

[19] T.D. Burchell, R.R. Judkins, M.R. Rogers, A.M. Williams, A novel process and material for the separation of carbon dioxide and hydrogen sulfide gas mixtures, Carbon 35(9) (1997) 1279-1294. https://doi.org/10.1016/S0008-6223(97)00077-8

[20] M. Petkovska, M. Mitrović, Microscopic modelling of electrothermal desorption, The Chem. Eng. J. Biochem. Eng. 53(3) (1994) 157-165. https://doi.org/10.1016/0923-0467(92)02768-E

[21] A. Subrenat, P.L. Cloirec, Adsorption onto Activated Carbon Cloths and Electrothermal Regeneration: Its Potential Industrial Applications, J. Environ. Eng. 130(3) (2004) 249-257. doi/abs/10.1061/(ASCE)0733-9372(2004)130:3(249)

[22] J.A. Lie, PhD. Thesis (ISBN 82-471-7191-0): Synthesis, performance and regeneration of carbon membranes for biogas upgrading – a future energy carrier, NTNU, Trondheim 2005.

[23] S.H. Moon, J.W. Shim, A novel process for CO2/CH4 gas separation on activated carbon fibers - electric swing adsorption, J. Colloid Interface Sci. 298(2) (2006) 523-528. DOI: 10.1016/j.jcis.2005.12.052

[24] R. Ribeiro, C.A. Grande, A.E. Rodrigues, Electrothermal performance of an activated carbon honeycomb monolith, Chem. Eng. Res. Des. 90(11) (2012) 2013-2022. doi: 10.1016/j.cherd.2012.03.010

[25] C.A. Grande, R.P.L. Ribeiro, E.L.G. Oliveira, A.E. Rodrigues, Electric swing adsorption as emerging CO2 capture technique, Energ. Proced. 1(1) (2009) 1219-1225. https://doi.org/10.1016/j.egypro.2009.01.160

[26] J.A. Lie, M.-B. Hägg, Carbon membranes from cellulose and metal loaded cellulose, Carbon 43(12) (2005) 2600-2607. doi: http://dx.doi.org/10.1016/j.carbon.2005.05.018

[27] T.B. Edel Sheridan, Jon Arvid Lie, May-Britt Hagg,, Carbon Membranes from Cellulose Esters,: U.S. patent: 8394175 , 2013.

[28] S. Haider, A. Lindbråthen, J.A. Lie, I.C.T. Andersen, M.-B. Hägg, CO2 separation with carbon membranes in high pressure and elevated temperature applications, Sep. Purif. Technol. 190 (2018) 177-189. doi: https://doi.org/10.1016/j.seppur.2017.08.038.

[29] X. He, M.-B. Hägg, Structural, kinetic and performance characterization of hollow fiber carbon membranes, J. Membr. Sci. 390-391(Supplement C) (2012) 23-31. doi: https://doi.org/10.1016/j.memsci.2011.10.052.

[30] W.-H. Lin, R. H. and Chung, T.-S., Gas transport properties of 6FDA-durene/1,4-phenylenediamine (pPDA) copolyimides, J. Polym. Sci. B Polym. Phys. 38 (2000) 2703-2713. doi: 10.1002/1099-0488(20001101)38:21<2703

[31] M.-B.H. Jon Arvid Lie, Carbon Membranes, U.S. patent: 20100162887 A1, 2010.

[32] X. He, J.A. Lie, E. Sheridan, M.-B. Hägg, Preparation and Characterization of Hollow Fiber Carbon Membranes from Cellulose Acetate Precursors, Ind. Eng. Chem. Res. 50(4) (2011) 2080-2087. doi: 10.1021/ie101978q.

[33] A. Singh-Ghosal, W.J. Koros, Air separation properties of flat sheet homogeneous pyrolytic carbon membranes, J. Membr. Sci. 174(2) (2000) 177-188. doi: http://dx.doi.org/10.1016/S0376-7388(00)00392-6.

[34] J.-i. Hayashi, M. Yamamoto, K. Kusakabe, S. Morooka, Effect of Oxidation on Gas Permeation of Carbon Molecular Sieving Membranes Based on BPDA-pp‘ODA Polyimide, Ind. Eng. Chem. Res. 36(6) (1997) 2134-2140. doi: 10.1021/ie960767t

[35] Y. Finkelstein, A. Saig, A. Danon, J.E. Koresh, Encapsulation of He and Ne in Carbon Molecular Sieves, Langmuir 19(2) (2003) 218-219. **DOI:** 10.1021/la026671n

[36] J.E. Koresh, On the flexibility of the carbon skeleton, J. Chem. Soc. Faraday Transactions 89(6) (1993) 935-937. doi:10.1039/FT9938900935[37] A. Subrenat, J.N. Baléo, P. Le Cloirec, P.E. Blanc, Electrical behaviour of activated carbon cloth heated by the joule effect: desorption application, Carbon 39(5) (2001) 707-716. doi: 10.1016/S0008-6223(00)00177-9