



The performance of carbon membranes in the presence of condensable and non-condensable impurities

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ARTICLE INFO

Article history:

Received 30 November 2010
Received in revised form 30 March 2011
Accepted 6 April 2011
Available online 18 May 2011

Keywords:

Carbon membranes
Carbon dioxide
Hydrogen sulphide
Water
Carbon monoxide
Hydrocarbons

ABSTRACT

To fully assess the suitability of nanoporous carbon (NPC) membranes for industrial applications such as carbon capture, it is necessary to understand the impact of impurities commonly present in the feed streams upon the membrane performance. In this work, the effect on the performance of a NPC membrane upon exposure to condensable impurities typically found in natural gas (e.g. water, hexane and toluene) and non-condensable impurities typically found in synthesis gas (e.g. H₂S and CO) has been determined in laboratory experiments. Small reductions in the permeance (less than 30%) and minimal reductions in selectivity have been observed, with the greatest impact at 35 °C and less impact at 100 °C. The performance of a NPC membrane upon exposure to real synthesis gas produced from air-blown coal gasification, as part of the Mulgrave Capture Project, has also been determined. The combined higher concentrations of impurities in these pilot plant experiments resulted in a greater impact on performance at 100 °C with a reduction in CO₂ permeance of around 40% and in CO₂/N₂ selectivity of around 25%. However, these relatively limited reductions in membrane performance suggest that such carbon membranes still offer some promise for pre-combustion applications.

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1. Introduction

Nanoporous carbon (NPC) membranes, made from the pyrolysis of polymers at high temperatures, have shown high selectivities when tested in the laboratory [1–6], which gives them promise as a new generation of gas separation membranes. In order to further assess the suitability of NPC membranes for industrial applications, it is necessary to test the performance of these membranes in the presence of impurities that commonly exist in industrial feed gases.

The focus of this research is in assessing NPC membranes for the separation of carbon dioxide (CO₂) as part of the carbon capture and geological sequestration process for reducing greenhouse gas emissions [7]. As such, the impurities tested in this work relate to (1) CO₂ separation from methane (CH₄) as part of CO₂ capture from natural gas and (2) CO₂ separation from nitrogen (N₂) as part of CO₂ capture from air-blown synthesis gas production. The condensable impurities studied include water and hydrocarbons. The non-condensable impurities studied were hydrogen sulphide (H₂S) and carbon monoxide (CO).

Water is in equilibrium with natural gas when produced from a reservoir. Similarly, water will be present in synthesis gas pro-

duction because of the water gas shift reaction. Due to problems when operating membrane processes with such a humid feed, gas streams are often dehydrated using established technologies such as glycol dehydration or a solid desiccant [8]. If the water tolerance of the membrane process can be increased by using materials such as nanoporous carbon instead of polymers, this will decrease the amount of pre-treatment required and therefore the cost.

To specifically address the impact of water vapour on the performance of NPC membranes, several studies have used a humidified feed [9–12]. These studies all conclude that flux or permeance is decreased with increasing humidity. At lower humidity levels, the water is adsorbed onto the surface of the carbon. At higher humidity levels, the water fills the pores of the surface leading to a significant reduction in the adsorption of other gases.

Condensable hydrocarbons are an omnipresent part of the natural gas processing system. Even reservoirs which are largely comprised of methane will have some heavier and aromatic hydrocarbons (usually termed “gas condensate”). The majority of the gas condensate will condense out in one or a series of upstream pressure separation vessels but there will invariably be some small carry-over into the gas stream. As such, gas processing facilities using the traditional polymeric membranes are equipped with expensive pre-treatment equipment to remove these condensable impurities. Synthesis gas can also contain hydrocarbons due to byproduct reactions in the gasifier. At the research level, hexane (C₆H₁₄) or heptane (C₇H₁₆) is commonly used to simulate the

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Table 1
The concentration of condensable impurities in the feed gas based on the operating temperature of the saturating vessel containing the liquid impurity.

Component	Vessel temperature (°C)	Impurity concentration (mol%)	Water % relative humidity at 35 °C membrane temperature	Water % relative humidity at 100 °C membrane temperature
Water	5	0.07	13	1
Water	10	0.09	18	1
Water	25	0.24	47	3
Hexane	5	0.61	–	–
Hexane	10	0.78	–	–
Hexane	25	1.55	–	–
Toluene	5	0.09	–	–
Toluene	10	0.12	–	–
Toluene	25	0.25	–	–

impact of heavier hydrocarbons whilst toluene (C₇H₈) is used to simulate the impact of aromatic hydrocarbons.

A comparison between the effect of toluene exposure on polymeric polyimide membranes compared with NPC membranes also made from polyimide, revealed that the drop in permeance and selectivity is more significant for the polymeric membrane due to the irreversible compaction of the polymeric membrane caused by plasticisation [13]. Conversely, in other studies of exposing NPC membranes made from polyimide to trace amounts of hexane and toluene, larger reductions in the permeances and slight reductions in selectivity were observed [14,15]. However, these performance reductions were reversed upon regenerating the NPC membranes using pure propylene [14] or high temperature nitrogen [15] suggesting that the impurities are only physically adsorbed to the nanoporous carbon.

Non-condensable impurities are impurities that remain in a gaseous form upon contact with the NPC membrane and may impact on the performance of the membrane by physical adsorption and pore blocking or by chemically reacting with the carbon. In the case of CO₂ removal from natural gas, hydrogen sulphide (H₂S) is present due to sulphide producing bacteria present in the reservoir. Similarly, H₂S is present in syngas from the sulphur producing bacteria present in the original hydrocarbon source (such as coal). Another component present in synthesis gas is carbon monoxide (CO), which is known for poisoning catalyst materials due to its reactivity.

Table 2
Syngas composition from the pre-combustion capture pilot plant.

Gas species	mol%
CO ₂	13.95
H ₂	11.67
N ₂	59.96
CO	11.45
CH ₄	2.52
H ₂ O	0.11
H ₂ S	~0.05
Heavier hydrocarbons (propane, ethane, etc.)	~0.21

Table 3
Baseline performances of the NPC membranes used to test the change in performance in the presence of condensable and non-condensable impurities. All data measured at 35 °C.

Membrane		1	2	3	3
Used to test		Condensable impurities 35 °C	Condensable impurities 100 °C	Non-condensable impurities and pilot plant 35 °C	Non-condensable impurities and pilot plant 100 °C
CO ₂ permeance	mol/m ² s Pa × 10 ⁻¹⁰	22.4 ± 1.2	12.2 ± 0.7	26.5 ± 1.8	36.7 ± 2.5
CH ₄ permeance	mol/m ² s Pa × 10 ⁻¹⁰	1.4 ± 0.1	1.7 ± 0.1	–	–
N ₂ permeance	mol/m ² s Pa × 10 ⁻¹⁰	–	–	2.2 ± 0.2	6.4 ± 0.4
CO ₂ /CH ₄ selectivity		16.5 ± 1.2	7.2 ± 0.5	–	–
CO ₂ /N ₂ selectivity		–	–	12.0 ± 0.8	7.6 ± 0.5

Traditional polymeric membranes are susceptible to plasticisation upon prolonged exposure to H₂S [16]. It has also been shown that H₂S reduces the performance of palladium-based membranes, which are traditionally used in synthesis gas purification, due to the formation of surface sulphides that block H₂ adsorption sites [17]. If NPC membranes could be shown to be resistant to H₂S whilst also removing some H₂S into the CO₂ stream for sequestration, savings could be made in terms of the H₂S removal systems required.

Whilst there is little known specifically of the effect of H₂S and CO on the performance of NPC membranes, there have been several studies on the adsorption of these gases on activated carbon. Adsorption isotherms of various gases on activated carbon revealed that the volume of gas adsorbed is as follows H₂S > CO₂ > CH₄ > CO > H₂, with all gases following the Langmuir model of adsorption [18]. Likewise, for dual gas experiments, CO₂ adsorbed more than CO, H₂S adsorbed more than CO₂ and CO₂ adsorbed more than CH₄ [18]. It has also been shown that when H₂S is reacted with adsorbed oxygen upon activated carbon, elemental sulphur is formed, which in the presence of water can form sulphuric acid [19].

The first objective of this research is to test the performance of NPC membranes in the laboratory in the presence of water, hexane and toluene at concentrations higher than those previously reported. The second objective is to report on the laboratory performance of these membranes in the presence of the non-condensable impurities—H₂S and CO. Finally, the membranes were tested in a pre-combustion pilot plant using a real synthesis gas manufactured from the air-blown gasification of Australian brown coal to evaluate how a mixture of H₂S, CO, water and trace hydrocarbons affects performance.

2. Experimental

The NPC membranes used in this research work were made from the pyrolysis of PFA at 550 °C under a flow of ultra high purity argon. The details of the manufacturing technique are described elsewhere [7].

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