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Purification of Gases Using Nanoporous Inorganic Membranes

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Abstract : *The application of membranes has gained acceptance in the chemical and process industries for separation and purification for over three decades and is currently being practiced for natural gas processing, waste water treatment among others. A crack-free composite membrane was employed in this paper. Scanning electron microscopy (SEM) observation was carried out to characterize the membrane. The operational parameters such as feed flow rate, permeation pressure, permeation temperature, kinetic diameter and gas molecular characteristics are examined at 25 ^0C to 450 ^0C and 0.05 to 1.0 barg feed pressure. The performance of gas selectivity is also provided. Separation factor of 2.554 was obtained for H_2/CO_2 at 450 ^0C and 0.8 barg. Activation energies of 1.0 and 0.42 kJ/mol were also obtained for H_2 and $CO_2/CO/H_2$ gas mixtures at 1.0 barg.*

Keywords: composite membranes, gas permeation, separation factor, activation energy.

1 Introduction

Membranes for gas separation are basically barriers that are selective to specific components in a feed gas mixture and is driven by a pressure difference across the membrane and are widely used for purification in the industries. Membranes can be classified into inorganic and organic/inorganic (hybrid) systems. The organic ones are further divided into biological and polymeric constituents, while the inorganic membranes can be divided into metallic and ceramic (porous and non-porous) membranes [1]. The International Union of Pure and Applied Chemistry (IUPAC) classified porous membranes as; Micropores 0.5 - 2 nm, mesopores is 2 - 50 nm and macropores is > 50 nm [2, 3]. In all cases, some considerations on productivity and separation selectivity, mechanical integrity, and membrane's durability at the operating conditions needs to be taken into account against cost issues [1], because the importance of each of these requirements differs with their applications. Infarct, permeability and selectivity are the main basic properties of a membrane. It can be elaborated that; the higher the permeability, the lower the membrane area is required. Also, the higher the selectivity, the more efficient the process, the lower the driving force required to attain a separation and therefore the lesser the operating cost of the separation system [1]. On one hand, the technical merits of inorganic membranes include chemical stability in wide pH, high thermal stability, long term durability as well as high structural integrity. Some of the demerits include the fact that they are expensive, and have low hydrothermal stability. On the

other hand, the technical merits of polymeric membranes include the fact that they are cheap. The demerits of polymers are that they are prone to denature and be contaminated, they are structurally weak, and they are not stable [1] which hinders the use of such membranes for gas separation at high temperature. It is for these reasons that inorganic material membrane is receiving an ever increasing attention [4]. Inorganic membranes are commonly made from metal oxide or sintered metal, palladium metal, zeolite among others [1].

Gas transport through inorganic membranes depends on pore size and pore size distribution, membrane materials as well as the interaction between the diffusing gases and the membrane [5]. The main transport mechanisms are viscous flow, Knudsen diffusion, surface diffusion, multi-layer diffusion, capillary condensation, molecular sieving and Solution-diffusion transport mechanism [6, 7, 8]. Numerous factors influencing gas permeation across inorganic membranes have been recognised in many literatures [1-8] which are however very heterogeneous in nature which pose challenges to researchers in order to arrive with research conclusion.

The separation of gas mixtures is now a significant component in industries such as natural gas processing plant [9], pharmaceuticals, food, waste water treatment and biochemistry among others [10]. Membrane technology has gained acceptance for gas separation and recovery. This includes carbon dioxide separation from fuel gas [11], hydrogen separation/recovery for fuel cell application [12], hydrogen sulphide separation from natural gas [13] and recovery of helium and methane from bio-gas [9]. The inorganic ceramic membranes are environmentally benign, cost-effective and energy efficient. Research is necessary to enhance more robust membrane materials that are capable of upholding their properties for long under demanding conditions. These membranes are in the form of a tubular or flat sheet [14].

In this paper, a crack-free composite membrane was employed in order to examine its operational parameters such as permeation pressure, permeation temperature, kinetic diameter and gas molecular characteristics at 25 ^0C to 450 ^0C and 0.05 to 1.0 bar feed pressure. The performance of gas selectivity is provided in the results.

2 Experimental

2.1 Membrane preparation and characterization
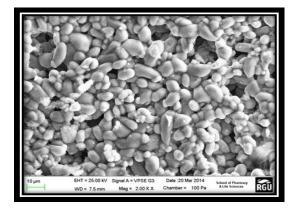
Porous alumina support of tubular configuration supplied by Ceramiques Techniques et Industrielles (CTI SA) France, consisted of (77% alumina + 23% TiO2) and an average pore diameter of 15 nm was employed for this experiment. The alumina support consisted of 7 and 10 mm internal and outer diameter respectively. It possesses a permeable length of 348 mm and 45% porosity (Fig. 1). A pressure 0.05 to 1.0 barg and temperatures of 25 ^{0}C (298 K) to 450 ^{0}C (723 K) were applied.

Figure 1: Porous tubular alumina support.

The surface and cross-sectional morphologies of the support were analysed by scanning electron microscopy (SEM) (Zeiss EVO LS10) shown in Fig. 2. The gas species used consisted of single gases (CH_4, CO_2, H_2, He, N_2, Ar) and ternary gas mixture ($CO_2/CO/H_2$) (10/30/60) (BOC UK) with 99.999 (% v/v) purity.
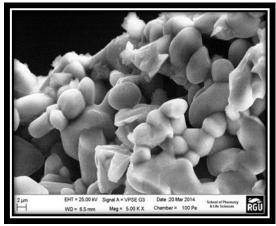

Figure 2: SEM images of the support surface and cross-section.

Gas species permeation was measured using the permeation test apparatus (Fig. 3) with the retentate valve fully opened. The tubular stainless steel membrane reactor is enclosed with a heating tape jacket, and the permeate flow tube was connected to the flowmeter to metre the gas flow rate. Gas permeance was obtained using equation (1) [13].

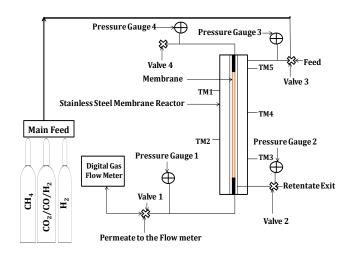$$Q = \left(\frac{q}{A \, \Delta P} \right) \qquad (1)$$

Where Q is the Permeance (mol m^{-2} s^{-1} Pa^{-1}), q is the molar flow (mol/sec), A is the membrane area (m^2), and ΔP is the pressure difference (Pa) across the membrane.

Gas selectivity was also considered in this experiment. Therefore, the membrane select a particular gas and reject others to pass through. The selectivity of the membrane was also obtained using equation (2) [13].

$$S_{ij} = Q_i/Q_j \qquad (2)$$

Where S_{ij} is the selectivity of i to j, Q_i is the permeance of i (mol m^{-2} s^{-1} Pa^{-1}), Q_j is the permeance of j (mol m^{-2} s^{-1} Pa^{-1}).

TM = Thermocouple

Figure 3: Schematic Diagram for the permeation Test.

3 Results and discussion

3.1 Effect of permeation pressure

Figs. 4 and 5 shows the effect of feed pressure on the permeation rate of helium, carbon dioxide, hydrogen, methane and ternary mixture of $CO_2/CO/H_2$. At relatively low pressure, permeation is normally restricted to Knudsen diffusion mechanism [9]. However, as the pressure increased substantially, permeation of gases exceed Knudsen diffusion boundary and moved to viscous diffusion mechanism. Basically, permeation can be increased with proper material selection as stated under section 1 (introduction).
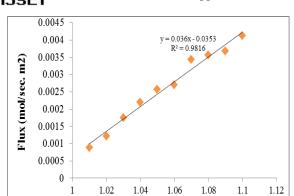
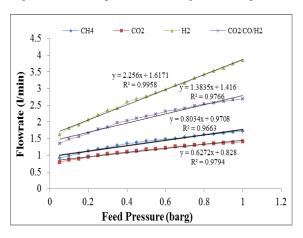Figure 4: Helium permeate flux against feed pressure at 25 ^{0}C.

Figure 5: Gas flow rates against feed pressure at 450 ^{0}C.

Based on the order of the kinetic diameter of the gases starting from the largest is Ar > N$_2$ > CO$_2$ > He (3.70 > 3.64 > 3.3 > 2.60) [9]. It can be seen in Fig. 6 that nitrogen having a kinetic diameter of (3.64 Å) is permeating at a rate that is higher than carbon dioxide with lower kinetic diameter. It can be seen from Fig. 6 that the membrane did not exhibit molecular sieving flow mechanism.
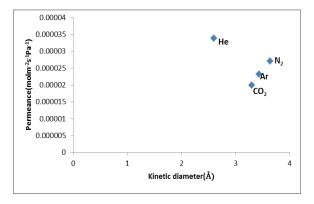

Figure 6: Permeance against gas kinetic diameter at 25 ^{0}C.

3.2 Effects of activation energy on ceramic supports.

The permeation activation energy can be defined as shown in the following equation [7];

$$Q = Qo \exp \left(\frac{-Ea}{RT} \right) \tag{3}$$

Where Ea is the apparent activation energy (kJ/mol) which is composed of the required energy for diffusion in pores and heat of adsorption, R is the gas constant (8.314 J.K^{-1}.mol^{-1}) and T is the permeation temperature (K).

Fig. 7 depicts the relationship between permeance and reciprocal temperature at 1.0 barg. The result reveals that both single and mixture gases with hydrogen decreased with permeation temperature. From Fig. 7, the activation value for hydrogen and CO$_2$/CO/H$_2$ mixture were calculated to be 1.0 and 0.42 kJ/mol, which almost corroborates with the literature [15] for permeation through silica-gamma alumina membrane.
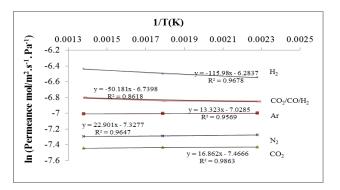

Figure 7: Relationship between Permeance and Reciprocal Temperature at 1.0 barg.

Fig. 8 shows the influence of permeation temperature on hydrogen selectivity (H$_2$/CO$_2$, H$_2$/N$_2$, H$_2$/CH$_4$ and H$_2$/Ar) at feed pressure 0.8 barg. From the graph, a highest separation factor of 2.554 was obtained from H$_2$/CO$_2$ at 450 ^{0}C which implies that more hydrogen is recovered from CO$_2$ than for H$_2$/N$_2$, H$_2$/CH$_4$ and H$_2$/Ar.
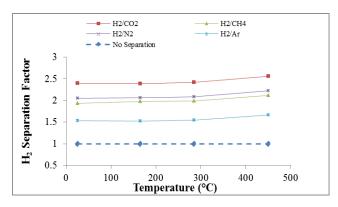

Figure 8: Hydrogen separation factor as a function of temperature across porous alumina support at feed pressure 0.8 barg.

4 Conclusions

Membrane technology for gas separation and purification particularly in remote locations such as offshore gas treatment is receiving substantial attention due to their uniqueness e.g. light weight. Membrane also possesses limited parts which make its processes less risky in operation. In this paper, Nanoporous tubular alumina membrane was used to examine the operational parameters such as feed flow rate, permeation pressure, permeation temperature and kinetic diameter at 25 ^{0}C to 450 ^{0}C and 0.05 to 1.0 barg feed pressure. Scanning electron microscopy (SEM) observation was carried out to examine the membrane performance and was found to be defect free. Hydrogen flow rate of 3.852 l/min was obtained at 450 ^{0}C and 1.0 barg. Also, separation factor of 2.554 was obtained for H_2/CO_2 at 450 ^{0}C and 0.8 barg. These membranes can be used preferably at higher temperature for separating hydrogen from other hydrocarbons.

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