

Development of Catalytic Membrane Reactors for Esterification of Lactic Acid and Hydrogenation of Water for Oxygen Removal

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Abstract— Membrane separation processes have shown a lot of advantages in various separations including esterification of lactic acid with ethanol to produce ethyl lactate as well as the removal of dissolved oxygen from sea water for industrial process applications. In this work, the single gas behaviour with porous ceramic membrane was carried out to study the permeation properties of gases through the membrane at the gauge pressure range of 0.10 -1.00 bar and between the temperature range of 298 – 413 K. The single gases used for the investigation include; argon (Ar), helium (He), nitrogen (N₂), carbon dioxide (CO₂), oxygen (O₂) and hydrogen (H₂). The gas permeance with respect to the kinetic diameter showed a non-molecular sieving mechanism of transport. The gas flux was found to increase with increase in gauge pressure in the order; H₂ > He > O₂ > N₂. The transport of the various species showed a linear dependence with the inverse square root of molecular weight confirming Knudsen flow mechanism of transport.

Keywords— Ceramic membrane, Permeation, Temperature, Kinetic diameter, Molecular weight

I. Introduction

Lactic acid is the simplest hydroxyl carboxylic acid with an asymmetric carbon atom. It can be obtained from biomass, petroleum or natural gas. Lactic acid can also be produced through the fermentation process or through chemical synthesis of several carbohydrates including glucose from starch [1]. Copolymers and polymers of lactic acid are known to be eco-friendly compatible due to their degradability [2]. Ethyl lactate which is obtained from the esterification process of lactic acid and ethanol are high boiling point liquid. Ethyl lactate is used as a commercial solvent in different industries including pharmaceutical and food industries for flavouring and preservation purposes. This solvent can replace a lot of hazardous petrochemical solvents including volatile organic compounds, toluene, benzene and xylene and as such, there is need for solving the equilibrium limitation problems in the production of this solvent to obtain a higher conversion [3], [1]. The conventional method of producing ethyl lactate is by the esterification of lactic acid with ethanol catalysed by homogeneous catalysts. The esterification reaction is a reversible reaction in which the yield is controlled by thermodynamic equilibrium [4]. The use of homogeneous acid catalyst such as sulphuric acid and hydrochloric acid causes problems including acid contamination of the ester product, low reaction rate and equipment corrosion [5]. Aside from thermodynamic equilibrium limitation, reaction yield can also be limited by other factors such as mass transfer

and heat that is generated during esterification. Such limitations can be removed by altering the reaction design.

Nowadays, some investigations have focused on the use of heterogeneous catalyst and water-permeable membrane reactors applied to liquid-phase reversible reactions. Among the membranes considered, inorganic ceramic membranes are a perfect candidate due to many advantages such as: (a) corrosion problems could be avoided and it is easier to deposit heterogeneous catalysts (b) continuous operations are possible (c) there is no need for catalyst to be removed from the reaction products by decantation or filtration and (d) the purity of the desired product is higher since side reactions can be eliminated or are less significant.

The use of membranes to selectively eliminate water from the reaction product during esterification of lactic acid is yet another important application that has attracted a lot of attention [6], [7]. Although the traditional method of solving equilibrium problems in esterification reactions involve the addition of an excess amount of alcohol to the reaction system, using a membrane can result in higher conversion by shifting the chemical equilibrium towards the formation of the product by in-situ removal of water from the reaction mixture [8].

The term “dissolved oxygen” refers to the presence of free non bonded oxygen molecule present in water [16]. The presence of dissolved oxygen in surface water, seawater or ocean is termed a contaminant with reference to water quality needed for downhole water injection usually done to maintain reservoir pressure and therefore enhance the production of hydrocarbon [9] [12] [14]. Dissolved oxygen can be removed by both physical and chemical means. Some of the methods involve the traditional use of gas stripping towers, large vacuum tower deaerators and oxygen scavengers [17]. These methods had disadvantages of being bulky, having very high tower which causes motion problems and also the problems associated with addition of chemicals [17]. These resulted in the requirements of floating systems to meet smaller footprint [13]. There is a need to develop compact deaerating systems, and membrane technology can help address this problem.

Inorganic membranes have attracted a lot of attention in various fields including industry and academia, due to the great potential they have shown in various applications [10]. They possess high thermal, mechanical and

chemical stabilities and show promise in various applications in biochemistry, food, pharmacy and waste water treatment in contrast to organic membranes [11].

The aim of this study is to select and characterize the membrane by employing a permeation study. The knowledge of the findings will be applied for the production of ethyl lactate from lactic acid and for the removal of dissolved oxygen for Process applications

II. Material and Methodology

II.1 Materials

A 15nm pore size commercially available tubular ceramic membranes consisting of 77% alumina + 23% TiO₂, purchased from Ceramiques Techniques et industrielles (CTI SA) France were used for this initial experimental study. The support has a 7 mm inner diameter and 10 mm outer diameter, with a total length of 368 mm of which 318 mm is the permeable length. Figure 1 shows the pictorial diagram of the silica membrane. The six gases used for the permeation tests include nitrogen (N₂), argon (Ar), helium (He), carbon dioxide (CO₂), oxygen (O₂) and hydrogen (H₂) as shown in fig. 2. The gases were supplied by BOC, UK.



Fig. 1 Picture of the 15nm pore size commercial ceramic membrane.

II.2 Methods

The permeation test was carried out at the feed pressure drop of 0.10 – 1.00 bar and between the temperature range of 298 – 413 K. The support modification process was carried out based on the procedure developed by Gobina (2006) [15]. Figure 2 shows the experimental setup for the single gas permeation tests.

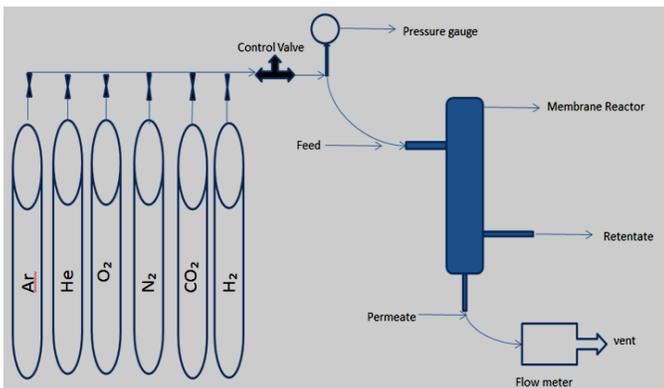


Fig. 2 Experimental setup for the gas permeation test

III. Results and Tables

Figure 3 presents the relationship between the gas permeance ($\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$) and the kinetic diameter of Ar, He, N₂ and CO₂ at 0.4 bar and 413K. From figure 2, it was found that the gas

permeance was not in a precise order of their kinetic diameter. Generally, gas molecule with the higher kinetic diameter should have exhibited a lower permeance in a precise order of N₂ (3.64 Å) < Ar (3.40Å), CO₂ (3.30Å) < He (2.60Å) for a molecular sieving flow mechanism as shown in table 1. However, CO₂ (3.30Å) with a lower kinetic diameter exhibited a lower permeance than N₂ and Ar with a higher kinetic diameter of 3.64 Å and 3.40 Å respectively indicating that gas flow was not based on molecular sieving mechanism.

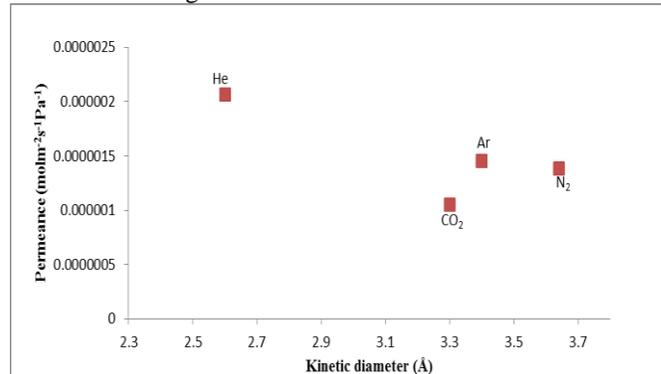


Fig. 3 Permeance ($\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$) against kinetic diameter (Å) at 0.4 bar and 413 K.

Figure 4 depicts the relationship between the gas Flux ($\text{molm}^{-2}\text{s}^{-1}$) and the inverse of gas viscosity (Pas^{-1}) at 0.1 bar and 413K. It can be seen from figure 3 that He gas exhibited a higher permeation rate in contrast to other gases. The decreasing order of the gas viscosity as shown in figure 3 is given as CO₂ (15) < Ar(17.81) < He(20) < N₂(22.7). Although the N₂ gas possesses a higher viscosity value, it was found that Ar with the lower viscosity than that of N₂ showed almost the same flux as the N₂ gas indicating that the gas transport is not based on viscous flow mechanism of gas transport which has an inverse flux relationship with the gas viscosity.

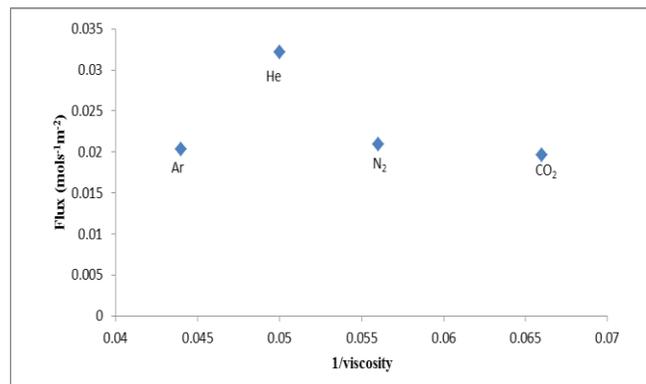


Fig. 4 Gas Flux ($\text{molm}^{-2}\text{s}^{-1}$) against inverse viscosity (Pas^{-1}) at 0.1 bar and at 413 K.

Table 1 Gases with their respective viscosity, inverse viscosity, kinetic diameter, molecular weight and inverse molecular weight values.

Gases	1/viscosity (Pas) ⁻¹	Gas viscosity (Pas)	Kinetic diameter (Å)	Molecular weight (MW) (g/mol)	1/√MW (mol/g) ^{-1/2}
Ar	0.044	17.81	3.40	40	0.158
He	0.05	20	2.60	4	0.50
CO ₂	0.066	15	3.30	44	0.151
N ₂	0.056	22.7	3.64	28	0.189
O ₂	0.049	20.4	3.00	32	0.031
H ₂	0.110	8.80	2.89	2	0.50

Figure 5 shows a graph of flux (mols⁻¹m⁻²) plotted against gauge pressure (bar). It was observed that the flux increases with an increase in gauge pressure. The order of the single gases flux were H₂ > He > O₂ > N₂. H₂ with the lowest molecular weight of 2, tend to flow faster than the other gases. This is followed by Helium with a molecular mass of 4. It was expected that N₂ with molecular weight 28 will follow suit, but in this case it was oxygen with a molecular weight 32. O₂ permeated faster than N₂ because it has a lower kinetic diameter compared to that of N₂. This goes further to explain that various transport mechanism could occur in parallel during gas permeation through a membrane. In this case, the gas transport mechanisms involved were both viscous flow and molecular sieving. It is viscous flow because the gas flux increased with increasing pressure, and molecular sieving because it allowed the permeation of oxygen with a lower kinetic diameter than N₂.

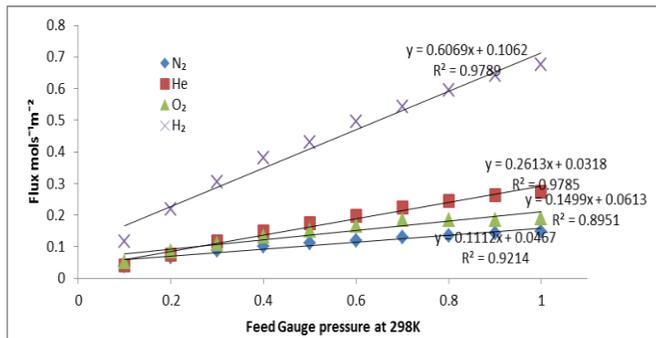


Fig. 5 Gas Flux (mols⁻¹m⁻²) against feed gauge pressure (bar) at 298 K.

The gas flux was calculated using the following equation:

$$J = \frac{Q}{A} \quad (1)$$

Where J = flux (mol m⁻² s⁻¹), Q = flow rate of the gases (mol s⁻¹) and A= membrane surface area (m²)

Figure 6 shows a plot of permeance against feed gauge pressure. It was observed that the permeance of the single gases decrease with increase in gauge pressure. Knudsen flow mechanism was predominant in this case. Helium gas showed a bit of deviation between 1000 - 3000 Pa, which is attributed to a different type of gas flow mechanism.

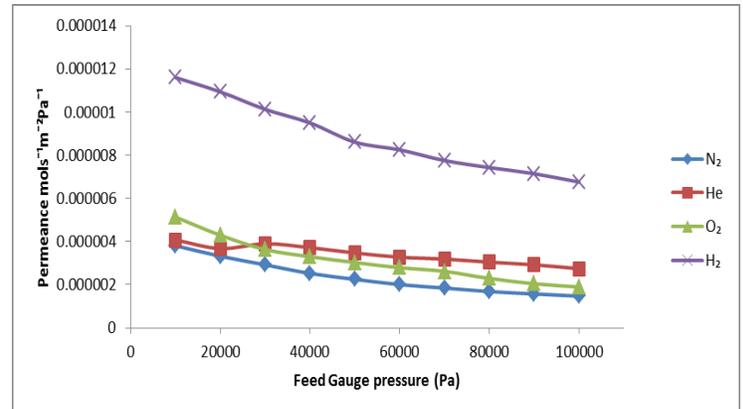


Fig. 6 Permeance (mols⁻¹m⁻²Pa⁻¹) against feed gauge pressure (Pa) at 298 K

Figure 7 shows the flow rate of H₂, He, O₂ and N₂ as a function of the inverse square root of their molecular weights at 0.5 bar gauge pressure. The graph shows that the order of permeation was H₂ > He > O₂ > N₂. It was also observed that the H₂ gas had the highest flow rate compared to other gases. It found that O₂, N₂ and H₂ gases showed a linear dependence with the inverse square root of molecular weight indicating Knudsen flow mechanism whereas He was suggested to be controlled by another mechanism. This was attributed to the surface diffusion mechanism of gas transport which explains that gases with the least molecular weight would permeate faster through the very tiny pores of the membrane than the higher molecular weight gases.

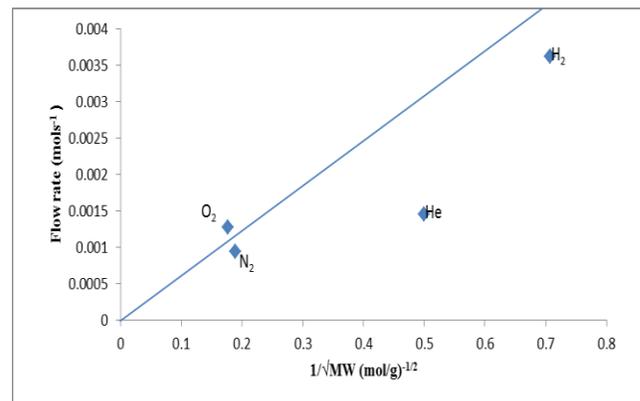


Fig. 7 Flow rate (mols⁻¹) against Inverse square root of molecular weight (mol/g)^{-1/2} at 0.5 bar and at 298 K.

IV. Conclusion

The permeation behaviour of single gases with porous ceramic membrane was achieved using Knudsen diffusion with some contribution of viscous flow and molecular sieving transport mechanisms. The flow rate of O₂, N₂ and H₂ gas showed a linear proportionality with the inverse square root of gas molecular weight indicating Knudsen flow mechanism except for He gas. The gas flux was found to increase with respect to the feed gauge

pressure. The permeance of the gas decreases as the feed gauge pressure increases. The gas viscosity relation with flux showed a non-viscous mechanism of transport. H₂ gas with least molecular weight exhibited a higher flux in contrast to other gases.

Nomenclature

J = flux (mol m⁻² s⁻¹)
Q = flow rate of the gases (mols⁻¹)
A = membrane surface area (m²)

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