

## NOVEL APPLICATION OF GAS TRANSPORT PROPERTIES WITH CERAMIC MEMBRANE FOR VOC EMISSION AND LACTIC ACID ESTERIFICATION

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### ABSTRACT

Ethyl lactate is an environmentally friendly solvent which is obtained from the esterification of lactic acid and ethanol generated from biomass through a fermentative process. Membrane separations have shown a lot of promise in numerous esterification processes including ethyl lactate and in the recovery of CO<sub>2</sub> emissions from flue gas. This arises due to its cost-effective separation approach. The membrane can also act as a catalyst. In this work, the investigation of gas transport through inorganic ceramic membrane was carried out at a gas pressure range of 0.10-1.00 bar and temperature of 373 K. The gases used for the permeation tests were: carbon dioxide (CO<sub>2</sub>), nitrogen (N<sub>2</sub>), helium (He) and argon (Ar). The gas permeance was found to initially decrease and remain relatively constant with respect to gauge pressure at 373 K indicating a transition to Knudsen flow mechanism of gas transport through the ceramic membrane. Scanning electron microscopy (SEM) coupled with energy dispersive x-ray analyser was used for the characterisation of the quality and chemical composition of the support. The SEM image of the support showed a dense surface after the dip-coating process indicating a defect-free support.

**Keywords:** Lactic acid, gas permeance, characterization, Ethyl lactates and transport mechanism.

### INTRODUCTION

Membrane processes have shown a lot of advantages in improving the yield of equilibrium-limited reactions by in-situ selective removal of water from the product during esterification reaction. 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 (Li et al. 2014). Ceramic membranes possess high thermal, mechanical and chemical stabilities and have shown promises in various applications in biochemistry, food, pharmacy and waste water treatment in contrast to organic membranes (Zhu, Fan and Xu 2010). The driving force for transport through the membrane involves the removal from the permeate side by introducing a vacuum or employing a sweep gas (Budd et al. 2004).

### LITERATURE REVIEW

Lactic acid is one of the most essential organic acids with a broad range of applications in environmental protection, pharmaceutical, agriculture and food (Li et al. 2010). Polymers derived from lactic acid such as polylactic acid have shown a lot of promise as biodegradable and biocompatible polymer material and have been employed in different processes including

drugs delivery system, internal bone fixation and surgical suture (Li et al. 2010). The synthesis of polylactic acid from lactic acid requires a high purity lactic acid. Different techniques including solvent extraction, electro dialysis and adsorption have been employed in order to achieve a high purity lactic acid for fermentation process (Khunnonkwao et al. 2012). However, due to low volatility of lactic acid, and its affinity to water during fermentation process, none of these purification techniques have successfully produced high-purity lactic acid. The esterification reaction is a reversible reaction in which the yield is controlled by thermodynamic equilibrium generally recognized as a limiting process for obtaining high purity lactic acid (Li et al. 2010). Membrane separation processes have gained an increasing attention for use in several esterification reactions because it is easy to operate and inexpensive. Ceramic membranes are better in terms of mechanical strength, thermal and chemical stability in contrast to polymeric membranes. However, all these advantages make them significant in some essential heterogeneous catalytic reactions, specifically under harsh operating conditions including high acidic temperature and pressure (Jiang et al. 2013). Both membrane selectivity and permeability play a major role in the successful use of membrane for industrial separations.

Gas transport through porous ceramic membrane basically depends on viscous flow, Knudsen diffusion, capillary condensation, surface diffusion and molecular sieving mechanisms (Li and Liang 2012). Moreover, the transport mechanisms of vapours through porous inorganic ceramic membrane are more complex. In explaining the permeation mechanisms of vapours of alcohol (such as ethanol) and ketones surface adsorption mechanism is usually employed which generates a blockage for gas-phase transport (Li and Liang 2012). However, surface diffusion sometimes contributes so much to the total flux of the adsorbed molecule across the membrane. Knudsen diffusion is said to be the dominant flow mechanism with regards to gas flow across inorganic membrane with smaller pores of several nanometre in size (Uchytel, Schramm and Seidel-Morgenstern 2000). The Permeation properties of single gases have been investigated as a function of temperature and the effect of pressure for the characterisation of the gases with the membrane (Poshusta, Noble and Falconer 1999). Li et al. (2014) carried out an investigation on the experimental and modeling study of gas transport through a composite ceramic membrane which consists of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. In their study, the gas permeance was found to decrease with increase in gauge pressure indicating limitation due to mass transfer of gas transport through the ceramic membrane.

## METHODOLOGY

### Permeation test

The gas permeation tests were carried out using four gases namely nitrogen (N<sub>2</sub>), argon (Ar), helium (He) and carbon dioxide (CO<sub>2</sub>). A similar method to that of Poshusta, Noble and Falconer 1999, was adopted and modified by changing the gauge pressures and temperature. The membrane was mounted into the stainless steel reactor which encloses the membrane. The support was dip-coated once prior to the analysis. The inner and outer radius of the porous alumina ceramic support was 7 mm and 10 mm respectively. The total length of the support was 36 cm. The weight of the ceramic support before and after modification was 48.3 g and 49.0 g respectively. However, the actual weight of the support after the modification process was 0.7 g. The membrane preparation was carried out based on a method that is patented (Gobina 2006). Prior to the SEM analysis, the ceramic support was fractured and a fragment of the sample was used for scanning electron microscopy (SEM). Figure 1 shows the gas permeation setup.

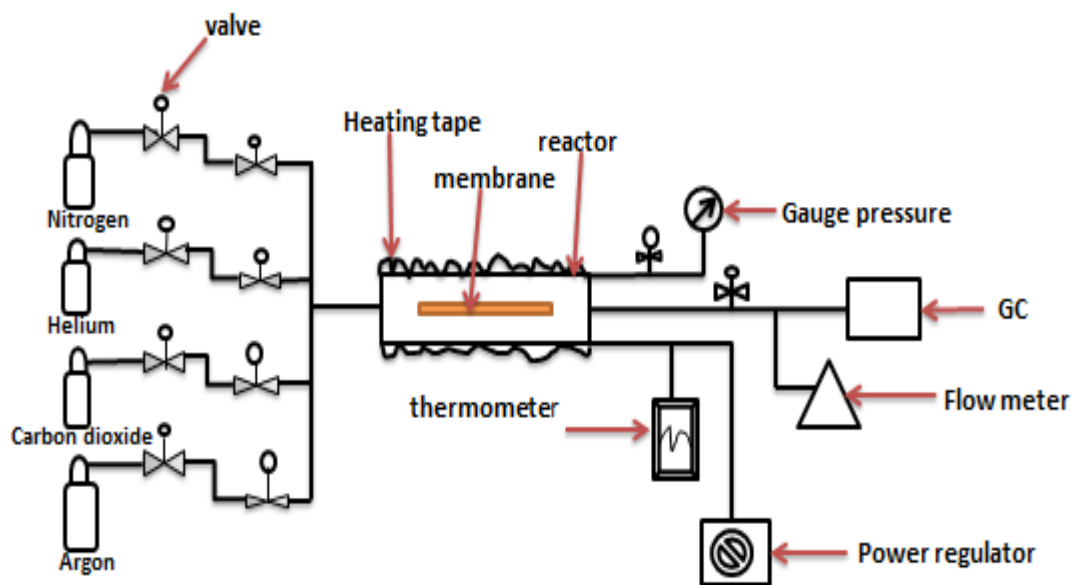


Figure1: Schematic diagram of gas permeation setup.

## RESULTS

The characterisation of the membrane morphology was carried out to examine the pore size distribution of the support and membrane after the dip-coating process. Figure 2 shows the SEM image of the inner surface of the dip-coated and uncoated membrane support.

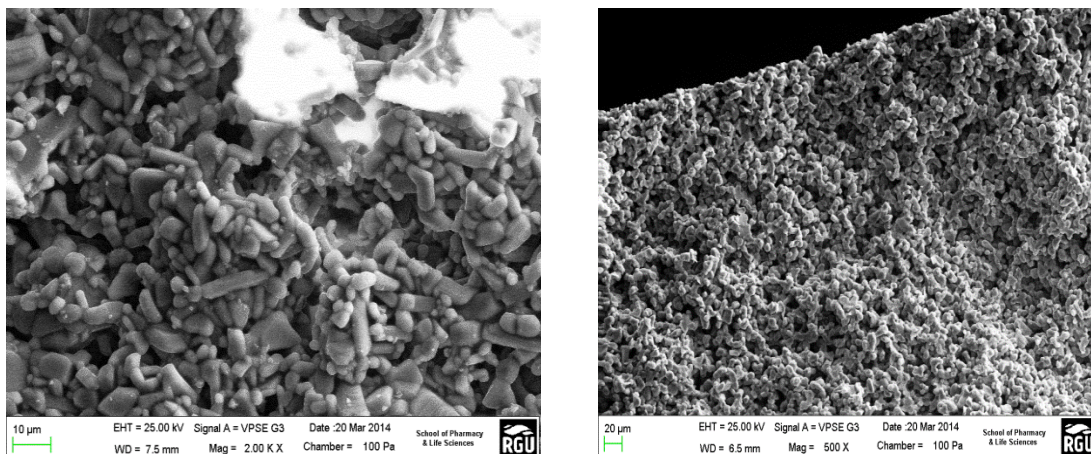


Figure 2a and b: SEM of the inner surface image of the dip-coated and uncoated ceramic support.

Figure 3 shows the gas permeance ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) against the feed gas gauge pressure (bar) to investigate the effect of pressure on flow rate through the dip-coated membrane at 373 K.

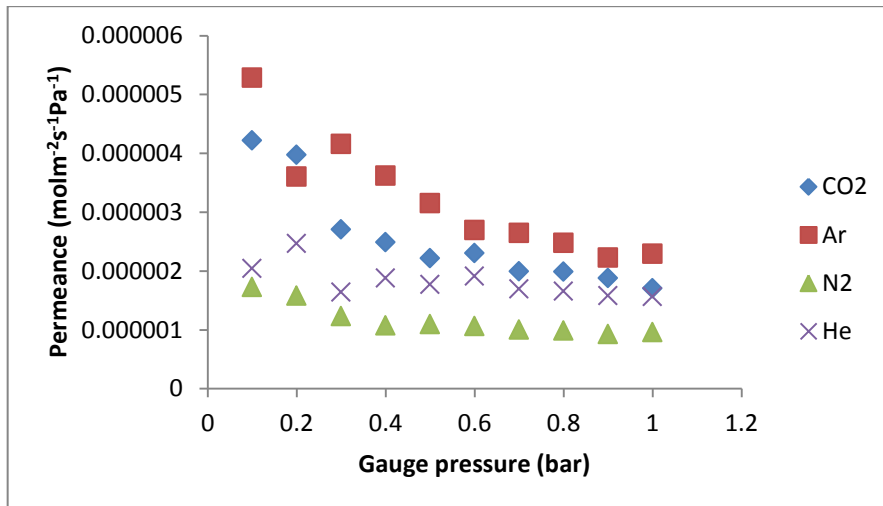


Figure 3: Gas permeance (molm<sup>-2</sup>s<sup>-1</sup>Pa<sup>-1</sup>) against gauge pressure (bar) at 373 K

Table 1 shows the molecular weight (g/mol), the kinetic diameter (Å) and the inverse of square root of the molecular weight of the four gases.

Table 1: Gases with their respective molecular weight (g/mol), Kinetic diameter (Å) and the inverse of square root of their molecular weight.

Gases	Molecular weight (g/mol)	Inverse square root of the gas molecular weight	Gas kinetic diameter (Å)
Helium (He)	4	0.50	2.60
Argon (Ar)	40	0.158	3.40
Nitrogen (N <sub>2</sub> )	28	0.189	3.64
Carbon dioxide (CO <sub>2</sub> )	44	0.151	3.30

Figure 4 shows the gas flow rate (molsec<sup>-1</sup>) against the gas Kinetic diameter (Å) to investigate the effect of kinetic diameter on the gas transport through the dip-coated membrane at 373 K.

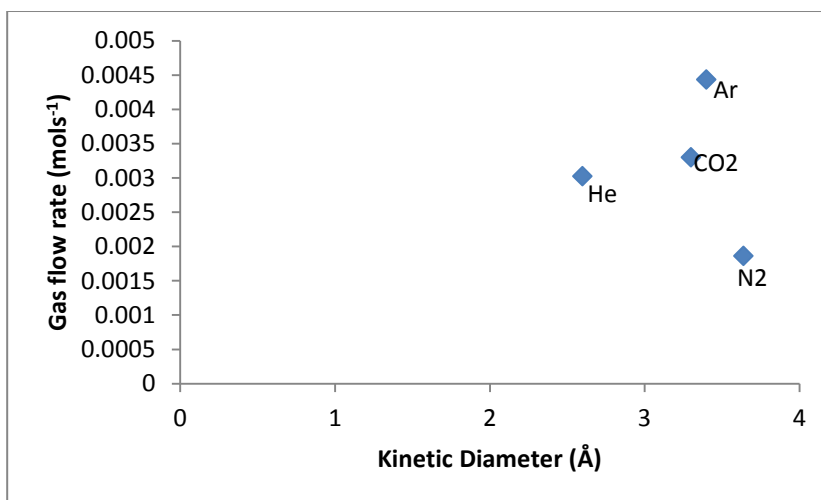


Figure 4: Gas flow rate (mol s<sup>-1</sup>) against Kinetic diameter (Å) at 373 K

Figure 5 shows gas flow rate (mol/sec) of Ar, N<sub>2</sub> CO<sub>2</sub> and He gases against the feed gas gauge pressure (bar) at 373 K.

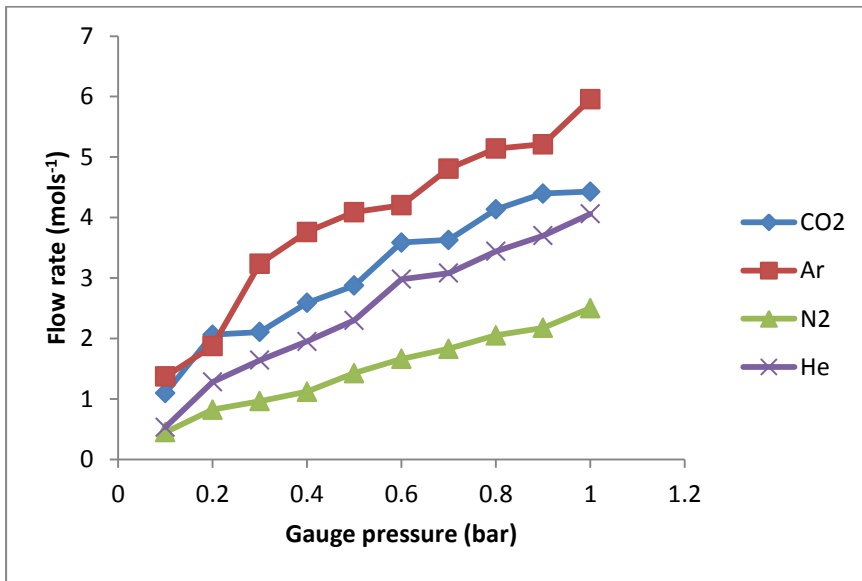


Figure 5: Gas flow rate (mol s<sup>-1</sup>) against Gauge pressure (bar) at 373 K

Figure 6 shows gas flow rate (mol s<sup>-1</sup>) of Ar, N<sub>2</sub> CO<sub>2</sub> and He gas against the inverse of the square root of the molecular weight (g/mol) of the four gases at 373 K to determine the relationship between the gas molecular weight and flow rate.

Figure 7 shows the flow rate (mol s<sup>-1</sup>) of Ar, N<sub>2</sub>, CO<sub>2</sub> and He against the inverse of the viscosity (Pa s<sup>-1</sup>) at 373 K to determine the relationship between the gas viscosity and the flow rate.

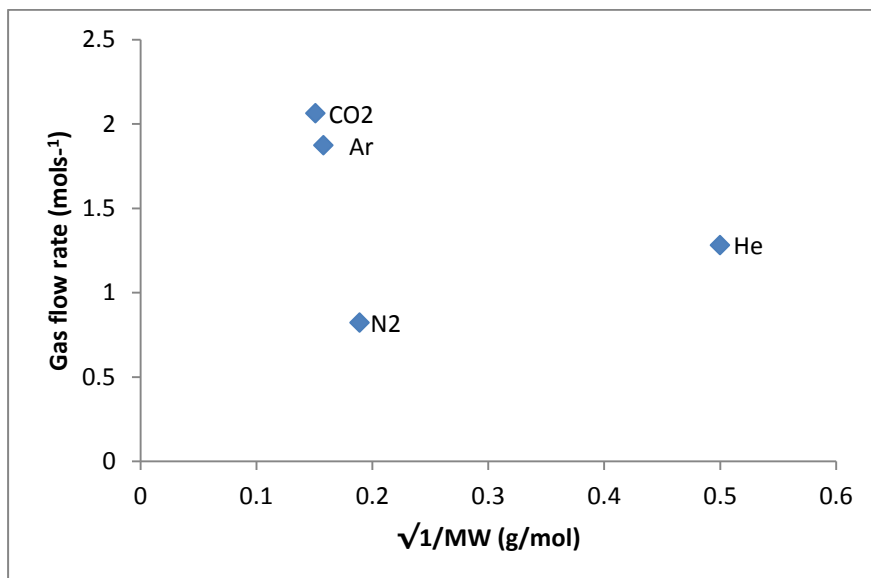


Figure 6: Gas flow rate (mol s<sup>-1</sup>) against √1/MW (g/mol) at 373 K

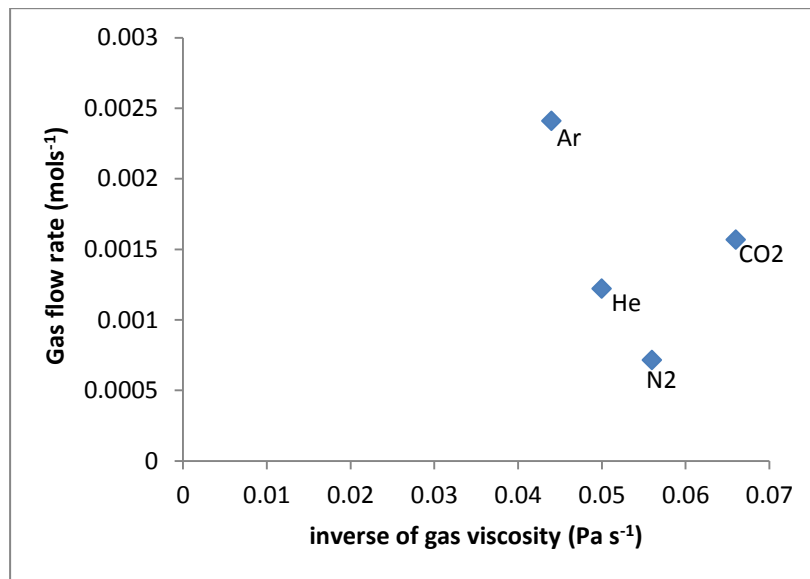


Figure 7: Gas flow rate (mols<sup>-1</sup>) against the inverse of the gas viscosity (Pa s<sup>-1</sup>) at 373 K.

## DISCUSSION

From results obtained in Figure 2, it was found that the inside surface of the ceramic support showed a clear surface which could indicate that the support was defect-free. The surface support was focused at the magnifications of 2000 x with the scale of 10  $\mu\text{m}$  for the dip-coated and 500 x with the scale of 20  $\mu\text{m}$  for the uncoated membrane.

From Figure 3, it was found that the permeance of the four gases decreases with gauge pressure. However, the decrease observed for Ar gas was more rapid with the gauge pressures, but subsequently slowed after 0.40 bar. Helium gas also showed a slight increase at 0.20 bar although it was not as obvious as that of Ar gas. This irregularity was attributed to the effect of temperature on the coated silica membrane. The decreasing order of the gas permeance from the least was  $\text{N}_2 < \text{He} < \text{CO}_2 < \text{Ar}$ . The gas permeance due to Knudsen diffusion was calculated using the formula:

$$P = \frac{2 \varepsilon d_p}{3 \tau \delta} \sqrt{\frac{2}{\pi M_w R T}} \quad (1)$$

Where  $P$  = permeance ( $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ),  $T$  = temperature (K),  $\delta$  = the membrane thickness (m),  $M_w$  = gas molecular weight (g/mol),  $R$  = gas molar constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $\varepsilon$  = porosity (%),  $d_p$  = pore diameter (m),  $\pi$  = constant (3.142) and  $\tau$  = tortuosity (Araki et al. 2007).

The results obtained in Figure 4 shows that He, CO<sub>2</sub> and Ar gases exhibited a higher flow rate in contrast to N<sub>2</sub> gas. N<sub>2</sub> has a higher kinetic diameter as shown in Table 1. In the case of molecular sieving mechanism, the gas molecule with the higher kinetic diameter should exhibited a lower flow rate precisely in the order:  $\text{N}_2$  (3.64 Å) < Ar (3.40 Å) < CO<sub>2</sub> (3.3 Å) < He (2.60 Å). However, from the results obtained, it was found that the gas transport across the coated silica membrane was due to another mechanism of gas transport. The order of the gas flow showed in Figure 4 was given as  $\text{Ar} > \text{CO}_2 > \text{He} > \text{N}_2$ .

From the results obtained in Figure 5, the flow rate of the four gases was found to increase with the pressure drop as the gases permeate differently. Ar and CO<sub>2</sub> with high molecular

weight of 40 and 44 g/mol precisely permeate faster in contrast to N<sub>2</sub> and He gas with low molecular weight of 28 and 4 g/mol respectively. The flow mechanism in this case was attributed to Knudsen mechanism of gas transport.

According to Araki et al. (2007), the linear dependence of flow rate on the inverse of square root of the gas molecular weight suggest the fact that the gas transport through silica membrane is due to Knudsen mechanism of transport. However, from Figure 6, the results obtained did not show the linear dependence of flow rate with the inverse square root of the molecular weight. This indicates that the gas flow was controlled by another mechanism of gas transport and Knudsen flow mechanism.

The order of the gas viscosity was given as Ar (22.9 Pa s<sup>-1</sup>) > He (20.0 Pa s<sup>-1</sup>) > N<sub>2</sub> (17.81 Pa s<sup>-1</sup>) and CO<sub>2</sub> (15.0 Pa s<sup>-1</sup>). He gas with a higher viscosity showed a lower flow rate than CO<sub>2</sub> with the least viscosity. This indicates that the gas flow was not based on Knudsen mechanism of transport.

## CONCLUSIONS

The gas transport behaviour through a ceramic membrane support was non-Knudsen transport mechanism. The gas permeance was found to be decrease with increase in gauge pressure. Ar gas decreased rapidly with gauge pressure, but subsequently slowed after 0.40 bar. The gas flow with respect to gas viscosity indicates another mechanism of gas transport. The SEM image of the ceramic support indicates a defect-free membrane support. The gas flow rate with respect to the gas kinetic diameter was not in accordance with the molecular sieving mechanism of gas transport. The flow rate relationship with the inverse square root of the gas molecular weight did not show a linear graph for the gas flow.

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