Gas Transport and Characterization of Inorganic Ceramic Membrane for Lactic Acid Esterification

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Abstract - **Ethyl lactate is an important organic ester, which is biodegradable in nature and widely used as food additive, perfumery, flavor chemicals and solvent. Inorganic porous ceramic membrane has shown a lot of advantages in the equilibrium process of ethyl lactate separation. In this work, the transport characteristic of carrier gas including Nitrogen (N_2), Helium (He), Argon (Ar) and Carbondioxide (CO_2), with α-Al_2O_3 inorganic ceramic membrane used for ethyl lactate separation was investigated, at the pressure drop of 0.01-0.09bar and 298K. The carrier gas flow rate was molecular weight dependent in the order: He > Ar > N_2 > CO_2 with respect to pressure drop. The membrane pore size distribution was analysed using Scanning electron microscope coupled with energy dispersive x-ray analyser (SEM-EDXA).**

Keywords - **Esterification, Ethyl lactate, Inorganic Ceramic Membrane, Gas Transport Mechanism and Permeability.**

I. INTRODUCTION

Ethyl lactate is a biodegradable and non-toxic material with an excellent solvent property which could potentially replace halogenated and toxic solvents for a broad range of consumer and industrial uses, corresponding up to 80% of worldwide solvent consumption [1]. This solvent is said to have a significant share in the global solvent market, which is about 30 million pounds per year [2]. The industrial manufacture of esters by esterification of acid with alcohol was first performed in a continuous stirred tank reactor (CSTR) and later in a catalytic distillation column in the presence of cation-exchange resins [3]. Currently some studies have focused on the water-permeable membrane reactor which has to do with liquid-phase reversible reactions including esterification reactions [3], [4] and [5].

Among the membranes considered, inorganic membranes have been found to be the perfect membrane for the esterification reaction process because they can allow heterogeneous catalysts to be deposited easily on the surface of the membrane; this results in an increase in the purity of

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products since side reactions and corrosion problems can be avoided [6]. Inorganic membranes have attracted important attention in different fields including academic and industry [7]. These membranes can be prepared using different methods including sol-gel, chemical vapour and sintering processes [8]. However, inorganic ceramic membrane composed of two materials such as aluminum oxide (Al_2O_3) and zirconium dioxide (ZrO_2), other materials include titanium dioxide (TiO_2) and silicon dioxide (SiO_2). The transport behavior of gases through inorganic ceramic membrane can be explained using various mechanisms such as viscous flow, Knudsen diffusion, surface diffusion and molecular sieving mechanism. Knudsen diffusion mechanism takes place when the mean free path of the diffusing gas molecules is greater than the pore size of the membrane [9]. Gas permeability can also be described in terms of solution-diffusion mechanism, i.e.

$$Permeability\ (P) = solubility\ (S)\ x\ diffusivity\ (D) \quad (1)$$

Where diffusivity explains the rate at which gases move across the membrane and solubility describe the interaction between the membrane surface and the permeating gas molecule [8], [10]. The transport of gases across the pore space of membrane has been a subject of numerous studies in the development of separation process involving membrane [16].

II. EXPERIMENTAL

Fig 1 shows a schematic diagram of a simple gas permeation setup. The gas transport through a porous inorganic ceramic membrane was performed using single gases including carbondioxide (CO_2) helium (He), nitrogen (N_2) and Argon (Ar) at different gauge pressure (Bar) and room temperature (298K).

The gas transport was performed at room temperature of 298K between the pressure drops of 0.01 – 0.09bar. The flow meter (L/min) was used to determine the gas flow rate. The inner and outer radius of the membrane was 7mm and 10mm respectively, whereas the total length of the membrane was measured to be 36.6cm. The membrane was prepared using a similar procedure as that proposed by Gobina 2006 [15]. The characterisation of the membrane pore size distribution was examined using SEM-EDXA to determine the morphology and the elemental composition of the membrane support before and after modification was also analysed.
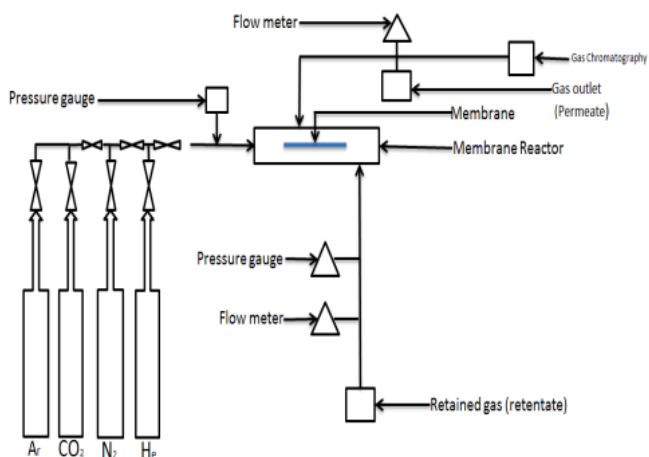
Fig. 1. Schematic diagram of gas permeation setup.

It can be seen from Fig 3 that the gas flux through the porous membrane increases linearly with gauge pressure at 298K for all the gases. These results corroborate with a similar results by Tomita et al [11]. The order of the gas molecular weight was represented as CO_2 (44) > Ar (40) > N_2 (28) > He (4). Helium gas has the lowest molecular weight but exhibited a higher flux with the gradient of 0.0123 whereas CO_2 with the higher molecular weight exhibited a low flux with a low gradient of 0.0056. Although Nitrogen and Argon have different molecular weights, their respective flux and gradient were close. These also suggest that Knudsen mechanism of transport was responsible for the gas flow through the porous ceramic membrane since this mechanism has a relationship with the gas molecular weight.

III. RESULTS AND DISCUSSION

The gas kinetic diameter was plotted against permeance to determine the flow mechanism of the single gases. Table 1 shows the different gases with their respective kinetic diameter (Å). The result obtained in Fig 2 showed that helium gas with the lowest kinetic diameter recorded the highest permeability. If the membrane had any molecular sieving properties, then CO_2 would have been next to He. However, N_2 with the higher kinetic diameter exhibited a higher permeance than CO_2 indicating that the gas transport through the membrane was not based on molecular sieving mechanism, but there could be another flow mechanism that was responsible for the flow of these gases. The order of the gas kinetic diameter is represented as N_2 > Ar > CO_2 > He.
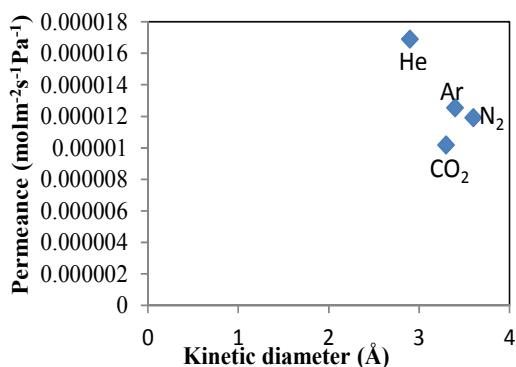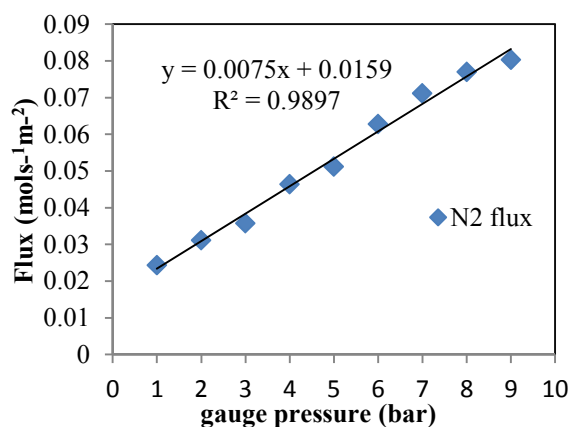

Fig. 3a. N_2 gas flux (mol m^{-2} s^{-1}) against gauge pressure (bar)

Fig. 2. Effect of kinetic diameter with the gas permeace at 0.03bar gauge pressure.
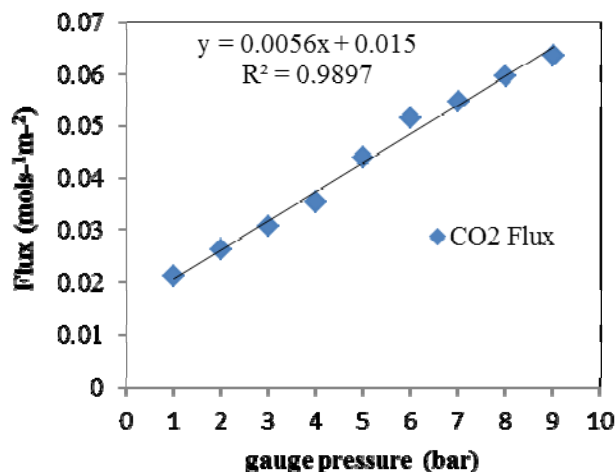
Fig. 3b CO_2 gas flux (mol m^{-2} s^{-1}) against gauge pressure (bar)

TABLE 1
GAS MOLECULAR WEIGHT AND THEIR RESPECTIVE KINETIC DIAMETER

Gases	Molecular weight (g/mol)	Kinetic diameter (Å)
Helium (He)	4	2.60
Argon (Ar)	40	3.43
Nitrogen (N_2)	28	3.64
Carbondioxide (CO_2)	44	3.30
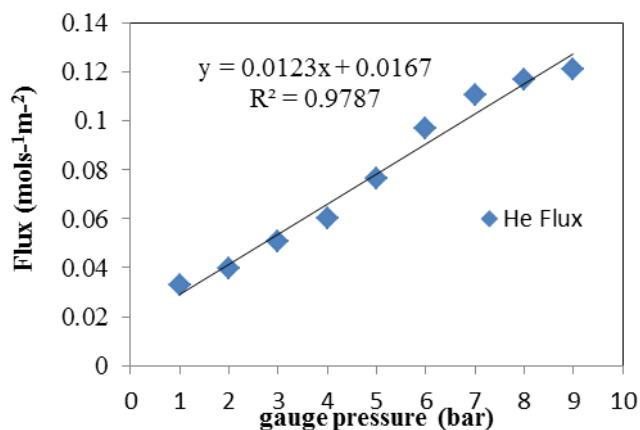
Fig. 3c He gas flux (mol m^{-2} s^{-1}) against gauge pressure (bar)
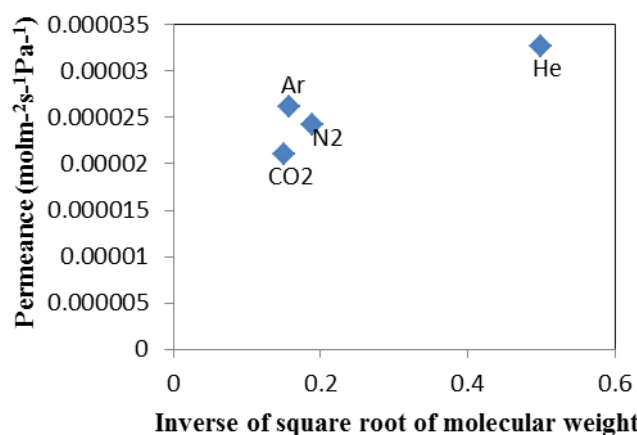

Fig. 4. Gas permeance (molm^{-2}s^{-1}Pa^{-1}) against Inverse of square root of the gas molecular weight.
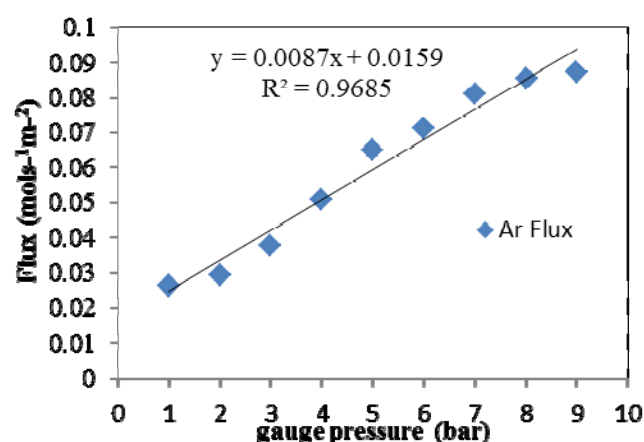

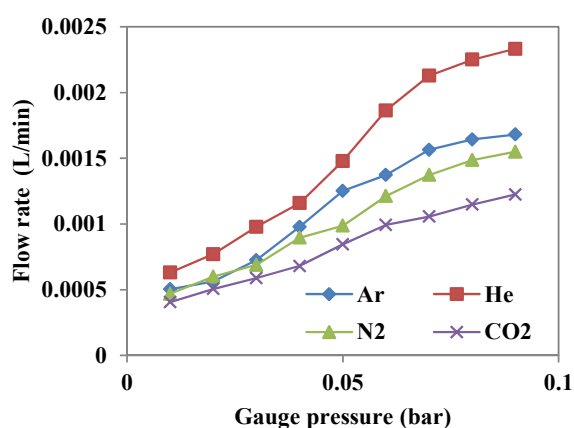Fig. 3d. Ar gas flux (mol m^{-2} s^{-1}) against gauge pressure (bar)

Fig. 5. Flow rate (L/min) of Ar, He, N$_2$ and CO$_2$ against gauge pressure (bar)

A linear equation was obtained for all the gases with the gradient of the graph being less than 1. R^2 values indicating good fit of data were obtained for the gases. The gas flux was calculated using the following equation:

$$J = \frac{Q}{A} \qquad (2)$$

Where J = flux (mol s^{-1} m^{-2}), Q = flow rate of the gases (mol s^{-1}), A= membrane surface area (m^2).

Fig 4 shows the plot of permeance against the inverse of the square root of the gas molecular weight. The graph obtained was not a straight line graph as expected for Knudsen flow mechanism.

The flow rate was also plotted against the gauge pressure to further observe the flow mechanism. It can be seen from Fig 5 that the gas flow rate increases with respect to gauge pressure. Helium gas showed the highest increase compared to other gases, which means; Helium gas was more permeable to the ceramic membrane compared to other gases. Considering the gas molecular weight as shown in Table 2, the result obtained showed that at the higher gauge pressure, the gas flow rate was molecular weight dependent in the order; He > Ar > N$_2$ > CO$_2$ with respect to pressure, indicating Knudsen mechanism of transport.

The gas permeability (mol m s^{-1} m^{-2} Pa^{-1}) was plotted against the mean pressure (bar). From the results obtained for the straight line in Fig 6, it was assumed that viscous flow was very low or approximately zero and as such viscous flow was neglected. However, Knudsen flow seems to be valid which indicate Knudsen mechanism of transport. These results corroborate with a similar result by Julian et al. [12] but in their case, Knudsen number was very high and as such was neglected.
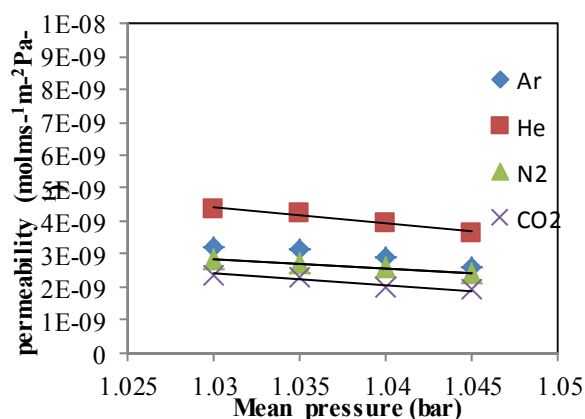

Fig. 6. Gas Permeability (mol m s^{-1} m^{-2} Pa^{-1}) against mean pressure (bar).

The straight line equation from the graph shown in Fig 6 is represented as:

$$F = \alpha + \beta.Pm \qquad (3)$$

Where F = permeability (mol m m^{-2} s^{-1} Pa^{-1}), α = constant representing viscous flow, β = constant representing Knudsen flow and P$_m$ = mean pressure (bar) [13].

The constant representing Knudsen and viscous flow can be further calculated using the following equation:

$$\alpha = \frac{k_v}{R.T.\mu.L} \qquad (4)$$

Where α = constant representing viscous flow (mol m^2 s^{-1}), K$_v$ = the intrinsic permeability corresponding to viscous flow (m^2), R = gas molar constant (J mol^{-1} K^{-1}), T = temperature (K), μ = gas viscosity (Pa.s), L= membrane thickness (m)

$$\beta = \frac{4\nabla}{3.R.T.L} k_{nv} \qquad (5)$$

Where β = constant representing Knudsen flow (m^2/s), $\overline{v}$= mean molecular velocity (Pa s^{-1}), T = temperature (K), R = gas molar constant (J mol^{-1} K^{-1}), L = membrane thickness (m), K$_{nv}$ = intrinsic permeability corresponding to Knudsen flow (m) [12].

The membrane pore radius and the mean free path with the gases were also determined. From Table 2, the results obtained showed that the membrane pore radius for the gas was all smaller than the mean free path, indicating Knudsen mechanism of transport. These results corroborate with a report by Benito et al [13], Pandey and Chauhan [14]. According to them, Knudsen diffusion is the dominate mechanism, if the membrane pore radius is smaller than the mean free path of the molecules and this is also significant for membrane with small pore radius <10nm for a free-defect membrane support. The results showed that the membrane pore radius with the gases was less than 10nm indicating a free-defect membrane and Knudsen flow as the dominant mechanism of transport.
The membrane pore radius was calculated using the formula:

$$\tau\rho = \frac{16.A.\mu}{3.B} \sqrt{\frac{8RT}{\pi M}} \qquad (6)$$

Where r$_p$ = membrane pore radius (m), α = constant representing viscous flow from the permeability graph, β = constant representing Knudsen flow from the permeability graph, μ = gas viscosity (Pa.s), M = gas molecular weight (g/mol), π = 3.141 [12].

TABLE II
MEMBRANE PORE RADIUS (M) AND MEAN FREE PATH (M) FOR THE GASES

Gas molecule	mean free path (λ) m	pore radius (m)
Ar	3.15E-04	4.72E-12
He	3.63E-04	1.09E-11
N$_2$	2.96E-04	4.45E-12
CO$_2$	1.11E-04	2.22E-12

IV. MORPHOLOGY OF MEMBRANE

The SEM image of the modified membrane was also obtained as well as the EDXA spectra of the membrane. The image was focused at 200μm. Fig 7 shows the surface image of the modified α-Al$_2$O$_3$ ceramic membrane. The pore of the membrane was found to reduce after modification. This could indicate the effect of support on the pores of the membrane. This result corroborates with a similar study by Tomita et al. [11].
The EDXA results obtained showed that the elemental composition of the modified membrane consists of elements such as silicon (Si), titanium (Ti), bromine (Br), oxygen (O) and zirconium (Zi). However, Ti and O showed a higher concentration. This could indicate that the membrane support was initially coated with TiO$_3$ and subsequently coated with SiO$_2$ and ZrO$_2$.
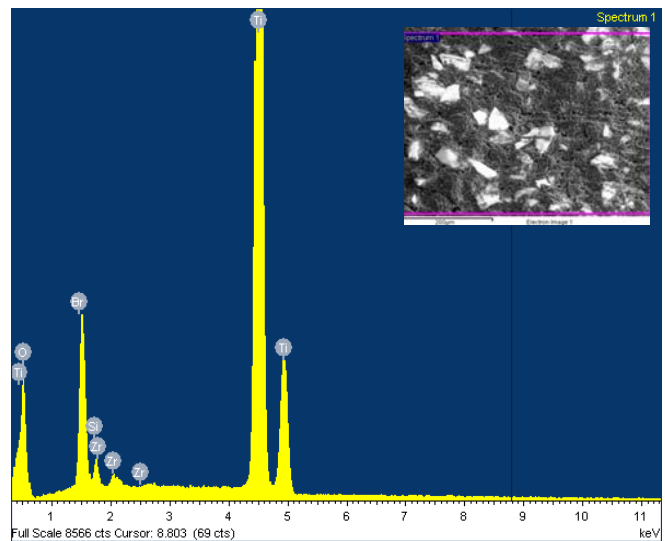

Fig. 7. SEM images and the EDXA spectra of the modified α-Al$_2$O$_3$ support.

V. CONCLUSION

The permeation tests to determined the characterisation of gases with ceramic membrane for ethyl lactate production was achieved using Knudsen flow mechanism. The gas flux through the membrane increases linealy with gauge pressure at 298K indicating a good fit of the data. Nitrogen with the higher kinatic diameter exhibited a higher permeance than CO$_2$ suggesting that the gas flow was not based on molecular seiving mechanism. The membrane pore radius was smaller the mean free path indicating Knudsen

mechnism of transport. The SEM of the membrane shows a decrease in size after modification while the EDXA showed that the ceramic membrane was initially coated with TiO_3 and subsequently with SiO_2 and ZrO_2.

NOMENCLATURE

Symbols

A   = Surface area of the membrane (m^2)

D   = Diffusivity ($m^2 s^{-1}$)

F   = Permeability (mol m $m^{-2} s^{-1} Pa^{-1}$).

J   = Flux (mol $s^{-1} m^{-2}$)

K_{nv} = Intrinsic permeability corresponding to Knudsen flow (m)

K_v = the intrinsic permeability corresponding to viscous flow (m^2)

L   = Membrane thickness (m)

M   = Gas molecular weight (g/mol)

P_m = Mean pressure (bar)

Q   = Gas flow rate (mol s^{-1})

R   = gas molar constant (8.314 J $mol^{-1} K^{-1}$)

S   = Solubility (mol $m^{-3} Pa^{-1}$)

T   = Temperature (Kelvin)

Greek Symbols

Å   = Angstrom

α   = Constant representing viscous flow (mol $m^{-2} s^{-1}$)

β   = Constant representing Knudsen flow ($m^{-2} s^{-1}$)

μ = Viscosity (Pa^{-1}.s)

$\overline{v}$ = Mean molecular velocity (Pa s^{-1})

λ   = Mean free path (m)

r_p = Membrane Pore radius (m)

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