

# Cation-exchange resin Characterisation and Carrier gas Performance with Mesoporous Silica Membranes for Ethyl lactate Separation

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**Abstract**— In this work, characterisation of cation-exchange resins including Dowex 50W8x and Amberlyst 16 and carrier gas transport properties with mesoporous silica membranes has been investigated. The SEM of the resin catalyst was investigated in order to determine the surface morphology of the resin before the esterification process. The scanning electron microscopy (SEM) morphology of the resin catalysts showed a defect-free resin. The carrier gas permeation properties with silica membrane was also analysed between the gauge pressures drop of 0.01 - 1.00 bar and temperature range of 353 – 413 K. The membrane was coated twice with silica. The gas flux was found to increase with respect to gauge pressure. The  $R^2$  values of argon, nitrogen, helium and carbon dioxide was in the range of 0.8866 - 0.9873. The permeance increased with molecular weight in the order  $He > Ar > N_2 > CO_2$ . The permeance of the four gases was also found to decrease with increase in temperature at the gauge pressure of 0.7 bar. These observations indicate a Knudsen mechanism of gas transport.

**Keywords**— Ethyl lactate, cation-exchange resin, carrier gas, silica membrane, permeation and gas flux.

## I. INTRODUCTION

Ethyl lactate (EL) is an important organic solvent produced from biomass and considered to be biodegradable. It can be used as food additives (can be found in soy products, wine and beer), agricultural processes (used in cadmium and copper removal from the contaminated soil), flavor chemicals and perfumery. Catalytic membrane reactor, a process that combines heterogeneous catalytic reaction with membrane separation, has shown a lot of advantages in the equilibrium process of ethyl lactate separation.

One of the major challenges faced by the petrochemical industry involves the replacement of traditional petroleum-derived solvents [1]. EL is one of the most promising solvent among these alternative organic solvents with excellent properties, and is a major member of the lactate ester family [2]. The USA Food and Drug Administration (FDA) has approved the use of EL in food products due to its low toxicity [3],[2]. Ethyl lactate solvent can be employed in the removal of silicon oil, greases and adhesives in cleaning several metal surfaces for coating and fabrication applications. This solvent can also be found in soy products, wine and beer, and is being recommended for use in the food industries for many years [4]. Despite the numerous qualities of some alternative

solvents the use of EL in large scale industrial processes is very limited [4],[2]. The worldwide demand of ethyl Lactate solvent is estimated to be roughly 130, 000 to 150, 000 tons per annum. However, the global consumption of this solvent is expected to increase rapidly in the nearest future [5].

Lactic acid and ethanol esterification reaction is a reversible reaction in nature; hence, the conversion of lactic acid is limited by equilibrium [6]. The production of EL from the esterification process of lactic acid with the respective alcohol in the presence of a catalyst suffers the major drawback of purity and low conversion [7] due to chemical equilibrium [8]. Several researchers have shown a lot of interest on the selective removal of product from the reaction system by distillation process [8]. However, the use of membranes and membrane technologies for the selective removal of product to shift the equilibrium towards higher yield of the product in equilibrium limiting reaction system have attracted a lot of attention [9], [10].

Membrane-based separation technologies have been successfully employed over the years in several industrial applications [11] including food, biotechnology, pharmaceutical and in the treatment of industrial effluents [11]. Membranes may be classified into organic and inorganic categories and the different configurations include: dense, porous and composite membranes [12],[13]. Currently, ceramic porous inorganic membranes have been widely employed in different fields such as chemical and petrochemical, bioengineering, and environment engineering [14]. Compared to other membranes, ceramic membranes can withstand the effect of thermal, mechanical and chemical stability. The ceramic membranes being use possess an asymmetric structure made up of a support layer such as  $\alpha$ -alumina and zirconia with fine porous layer which controls the permeation flux [14].

Porous membranes can have different pore size including microporous with the pore size  $< 2$  nm, mesoporous with 2-50 nm and macroporous  $> 50$  nm [15]. Materials including  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$  are the most frequently used materials for ceramic membranes. Basically, the macroporous layer provides the mechanical support, while the mesoporous layer which is the middle layer links the pore size differences between macroporous (support layer) and the microporous (top layer) where the actual separation occurs [16]. Ceramic membranes can be prepared using different methods including sol-gel, sintering, chemical deposition and dip-coating methods [13]. The dip-coating technique has been widely employed to fabricate ceramic membranes with microporous layer on the porous support and is also a convenient membrane preparation technology. Generally the conventional dip-coating process involves two major steps: support dipping and support withdrawal [17].

The suitability of a ceramic membrane depends on the membrane selectivity and permeability [18]. However, gas transport through porous ceramic membrane can be explained using different mechanisms of transport including surface diffusion, viscous flow, molecular sieving and Knudsen diffusion [19]. Viscous flow occur if the pore radius of the membrane is larger than the mean free path of the permeating gas molecule, in this case more collision will take place between the molecule and the pore wall of the membrane

than between the permeating gas molecules. Knudsen diffusion is likely to be the mechanism controlling the rate of transport if the mean free path of the permeating gas molecule is greater than the pore size of the membrane [20]. Molecular sieve occurs when the diameter of the gas molecule is roughly the same as the pores of the membrane. Surface diffusion mechanism enables permeation in such a way that the gas is strongly adsorbed on the on the pores of the membrane [20]. In capillary condensation mechanism, separation can takes place in the pores of the membrane with mesoporous layer in the presence of condensable gas specie [21].

## II. EXPERIMENTAL

The four gases used for the carrier gas permeation tests include; nitrogen ( $\text{N}_2$ ), argon (Ar), helium (He) and carbon dioxide ( $\text{CO}_2$ ). The gases were supplied by BOC, UK. The permeation test was carried out at the feed pressure drop of 0.10 – 1.00 bar and temperature between 353 - 413 K. The membrane support was dip-coated twice before the permeation analysis. The effective length of the membrane was 36.6 cm, while the inner and outer radius of the membrane was 7 and 10 mm respectively. The support modification process was carried out based on the procedure developed by Gobina (2006) [22]. Figure 1 shows the single gas permeation setup. The surface morphology was also examined using SEM at the magnification of 10  $\mu\text{m}$  and 100  $\mu\text{m}$  respectively.

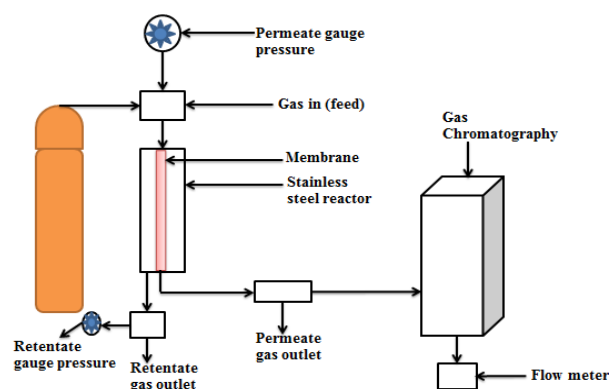


Fig. 1. Schematic diagram of gas permeation setup.

## III. RESULTS AND DISCUSSION

Figure 2 presents the relationship between the permeance ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) and temperature (K). From fig 2, it was found that the gas permeance decreases with temperature at 0.70 bar. Li et al. [23] obtained a similar result with alumina silica membrane at different temperatures. He gas recorded the highest decrease with temperature in contrast to other gases. In our previous work carried out on the silica membrane with the carrier gases at 1<sup>st</sup> dipping [24], He gas with the least molecular weight also exhibited some deviation from the trend indicating that the gas flow was based on Knudsen mechanism of gas transport.

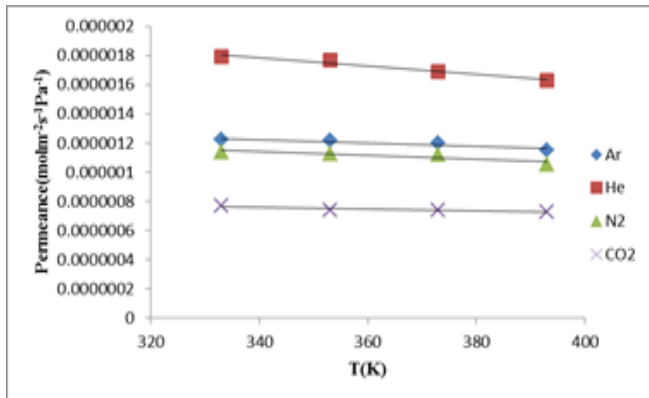


Fig. 2. Permeance ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) against temperature (K) at 0.70 bar and between 353 – 413 K.

The activation energy of the transport of Ar, He, N<sub>2</sub> and CO<sub>2</sub> gas was calculated using the Arrhenius equation:

$$Q = Q_0 \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

Where  $Q$  = Permeance ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ),  $Q_0$  = pre-exponential factor,  $E_a$  = activation energy (K J mol),  $R$  = universal gas constant ( $\text{J mol}^{-1}\text{K}^{-1}$ ),  $T$  = temperature (K) [25], as can be seen in table 1.

TABLE 1 GAS, MOLECULAR WEIGHT AND ACTIVATION ENERGY VALUES

Gases	Molecular weight (g/mol)	Activation Energy (K J mol)
He	2	$-2.49 \times 10^{-9}$
Ar	40	$-8.314 \times 10^{-9}$
CO <sub>2</sub>	44	$-4.98 \times 10^{-9}$
N <sub>2</sub>	28	$-8.314 \times 10^{-9}$

Figure 3 depicts the relation between the gas permeance ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) against temperature ( $^{\circ}\text{C}$ ) at a lower gauge pressure of 0.4 bar and between the temperature of 353 – 413 K. From Fig 3, it can be seen that the gas permeance decrease with respect to temperature. It was found that He and N<sub>2</sub> gas showed a deviation from the trend with a slight increase for He gas with also a slight decrease for N<sub>2</sub> gas at 80  $^{\circ}\text{C}$  suggesting Knudsen mechanism of gas transport. There was a slight difference for He and N<sub>2</sub> gas permeance with respect to temperature in  $^{\circ}\text{C}$  (Fig 3) when compared at the same temperature in Kelvin (Fig 2). It can be seen from Table 1 that the calculated activation energy for the four gases was less than 1.

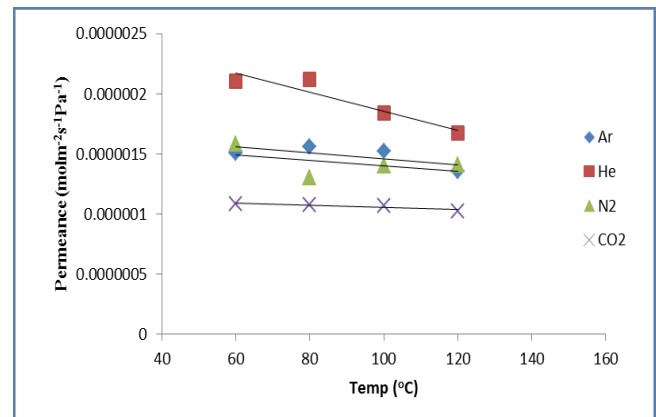


Fig. 3. Permeance ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) against temperature ( $^{\circ}\text{C}$ ) at 0.4 bar.

Figure 4 depicts the relation between the permeance ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) of the four gases and the inverse square root of the gas molecular weight at 0.50 bar and at 353 K. According to Lu et al. [26] gas transport is described by Knudsen flow mechanism if there a linear dependence of permeance on the inverse square root of the gas molecular weight. From Fig 4, it can be seen that Ar, CO<sub>2</sub> and N<sub>2</sub> gas flow were attributed to Knudsen flow mechanism whereas He gas flow is suggested to be controlled by another mechanism of gas transport.

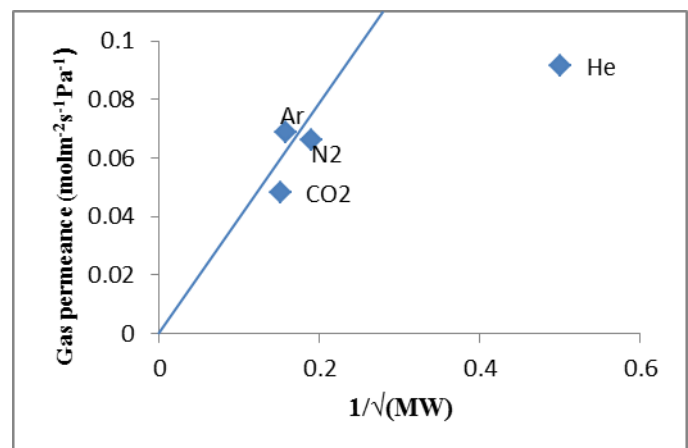


Fig. 4. Permeance ( $\text{molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ ) against inverse of molecular weight at 0.50 bar and at 353 K.

Figure 5 presents the relationship between the flux ( $\text{molm}^{-2}\text{s}^{-1}$ ) of Ar He, N<sub>2</sub> and CO<sub>2</sub> and the gauge pressure (bar). From Fig 5, it was found that the gas flux increase linearly with respect to gauge pressure at 353 K for He. For Ar, N<sub>2</sub> and CO<sub>2</sub> however, inertial forces become dominant above a gauge pressure of about 0.7 bar. This was more noticeable for Ar and N<sub>2</sub>. It was also observed that Ar and N<sub>2</sub> gases therefore exhibited the least R<sup>2</sup> values at 353 K. Although Ar gas molecular weight is higher than that of N<sub>2</sub> gas, it was assumed that at higher temperature, N<sub>2</sub> gas flux may supersede that of Ar gas. CO<sub>2</sub> and He gases exhibited a higher R<sup>2</sup> values at 353 K suggesting less contribution of inertial forces. The increasing order of the gas flux was: He > Ar > N<sub>2</sub> > CO<sub>2</sub>.

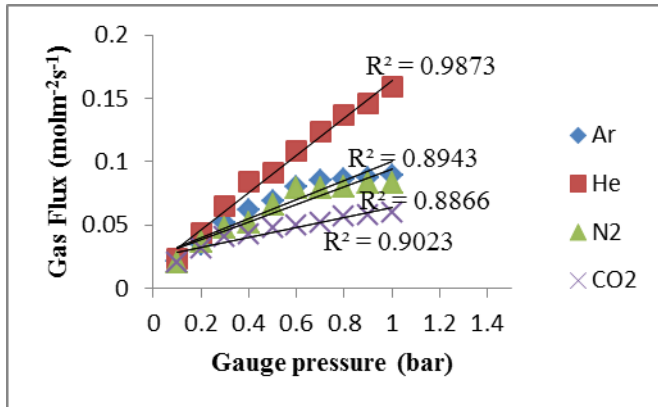


Fig. 5. Gas flux ( $\text{mol m}^{-2} \text{s}^{-1}$ ) against gauge pressure (bar) at 353 K

Figure 6 present the relation between the gas permeance ( $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ) and the gas Kinetic diameter ( $\text{\AA}$ ) at 353 K and at 0.1 bar. The order of the gas kinetic diameter is given as  $\text{N}_2$  ( $3.64 \text{\AA}$ ) < Ar ( $3.40 \text{\AA}$ ),  $\text{CO}_2$  ( $3.30 \text{\AA}$ ) and He ( $2.60 \text{\AA}$ ). From the result obtained in figure 6, it was found that the permeance of the four gases were not in accordance with their kinetic diameter.  $\text{N}_2$  with the least kinetic diameter exhibited a higher permeance than  $\text{CO}_2$ . This result does not reflect molecular sieving flow mechanism. Additionally, He gas with the kinetic diameter of  $2.60 \text{\AA}$  exhibited a higher permeance in contrast to other gases suggesting a strong adsorption due to surface diffusion mechanism on the membrane pore walls thereby resulting in an increase in permeation rate at 0.1 bar and at 353 K. The order of the gas permeance with respect to kinetic diameter as shown in Fig 6 was  $\text{He} > \text{Ar} > \text{N}_2 > \text{CO}_2$ .

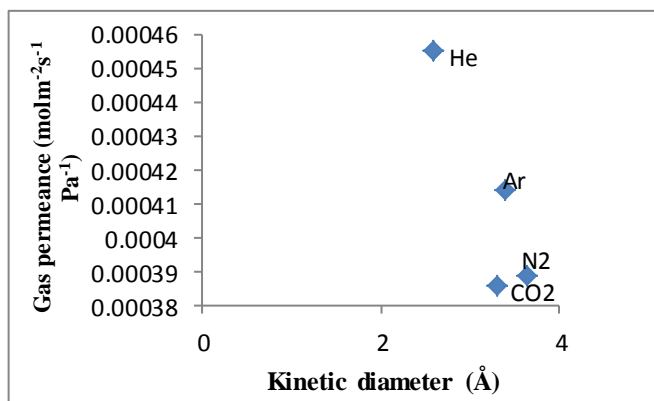


Fig. 6. Permeance ( $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ) against Kinetic diameter ( $\text{\AA}$ ) at 0.1 bar and 353 K

Figure 7 shows the SEM surface morphology of the esterification Dowex 50W8x (7a) and Amberlyst 16 (7b) resins catalysts. From figure 7a and b, it was observed that the resin catalysts had a free-defect surface before. It was also observed from figure 7a that the crystallinity on the surface of Dowex 50W8x resin catalyst suggest the effect of sulfonic acid group from which the structure of the solid catalyst is made up of indicating a strong catalyst effect in contrast to

Amberlyst 16 resin catalyst. These results will be compared to the surface image of the resin catalyst after esterification reaction.

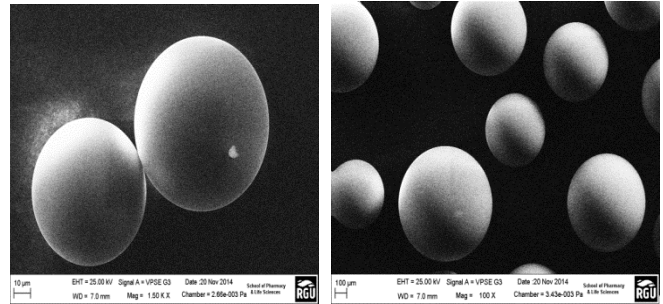


Fig. 7a (Dowex 50W8x) and 7b (Amberlyst 16): SEM surface morphology of the fresh resin catalyst before esterification.

#### IV. CONCLUSION

The carrier gas permeation properties with inorganic silica membrane and cation-exchange resin characterisation were determined. The rate of transport was described by Knudsen flow with some contribution of viscous and surface diffusion mechanisms. The silica membrane exhibited a linear flux in the range of 0.8866 – 0.9873 indicating viscous flow mechanism. The gas permeance decreases with respect to temperature at 0.4 and 0.7 bar. The SEM surface images of the resin catalysts exhibited a clear surface indicating that the resin was defect-free. He gas with the least kinetic diameter exhibited a higher permeance indicating a non-molecular sieving mechanism of gas transport.

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