

Hydrodynamic Performance in Mesoporous Silica Membrane for Lactic Acid and Esterification

O Edidiong, S Habiba, K Mohammed, O Adesola, N Ngozi, O Ifeyinwa and *E Gobina

Abstract—Ethyl Lactate has a lot of applications in different industries including food, pharmaceutical and agricultural processes. The esterification process of lactic acid and ethanol is a highly-equilibrium-controlled reaction. The selective removal of one of the reaction products can be improved using membrane. In this work, the hydrodynamic performance of silica membrane with single carrier gases was analysed to determine the flow mechanism of the gases at the gauge pressure range of 0.01 to 1.00 bar and a temperature of 140 °C. The results showed that the gas flux increases with increase in gauge pressure indicating Knudsen mechanism of gas transport. The R^2 value for the four gases used (CO_2 , He, Ar and N_2) were in the range of 0.98 – 1.00. The gas permeance was found to decrease with respect to the gauge pressure in the order $\text{N}_2 > \text{Ar} > \text{He} > \text{CO}_2$ confirming non-Knudsen mechanism of gas transport. Gases with higher kinetic diameter showed a higher permeance indicating a non-molecular sieving mechanism of gas transport. The gas permeance with respect to viscosity indicates viscous mechanism of gas transport. The decreasing order of the gas viscosity with respect to gas permeance was $\text{CO}_2 < \text{He} < \text{Ar} < \text{N}_2$.

Key words: Esterification, Ethyl lactate, Gas permeation, Lactic acid, Transport mechanism.

I. INTRODUCTION

Ethyl lactate esterification can be carried out in liquid-phase reversible reaction between lactic acid and ethanol in the presence of an acid catalyst [1].

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O. Edidiong is a research student with Centre for process Integration and Membrane Technology (CPIMT), School of Engineering, The Robert Gordon University Aberdeen, AB10 7GJ, United Kingdom. (e-mail: e.p.okon@rgu.ac.uk).

S. Habiba is a research student with Centre for process Integration and Membrane Technology (CPIMT), School of Engineering, The Robert Gordon University Aberdeen, AB10 7GJ, United Kingdom. (e-mail: h.shehu@rgu.ac.uk).

K Mohammed is a research student with Centre for process Integration and Membrane Technology (CPIMT), School of Engineering, The Robert Gordon University Aberdeen, AB10 7GJ, United Kingdom. (e-mail: m.n.kajama@rgu.ac.uk).

O Adesola is a research student with Centre for process Integration and Membrane Technology (CPIMT), School of Engineering, The Robert Gordon University Aberdeen, AB10 7GJ, United Kingdom. (e-mail: a.o.orimoloye1@rgu.ac.uk).

N Ngozi is a research student with Centre for process Integration and Membrane Technology (CPIMT), School of Engineering, The Robert Gordon University Aberdeen, AB10 7GJ, United Kingdom. (e-mail: n.c.nwogu@rgu.ac.uk).

O Ifeyinwa is a research student with Centre for process Integration and Membrane Technology (CPIMT), School of Engineering, The Robert Gordon University Aberdeen, AB10 7GJ, United Kingdom. (e-mail: i.r.orakwe@rgu.ac.uk).

E. Gobina is the Director of Centre for process Integration and Membrane Technology (CPIMT), School of Engineering, The Robert Gordon University Aberdeen, AB10 7GJ, United Kingdom. (*Corresponding Author e-mail: e.gobina@rgu.ac.uk. Phone No.: +44(0)1224262348).

Lactic acid is the simplest hydroxyl carboxylic acid with an asymmetric carbon atom. It can be obtained from biomass, petroleum or natural gas liquid and coal. Copolymers and polymers of lactic acid are known to be eco-friendly and compatible. Due to their biodegradability, they can be used as alternative petrochemical polymers [1]. Ethanol can be obtained from various biomass crops including starch crops (cassava and corn), cellulosic feedstock (e.g grasses, agricultural residues and wood) and sugar crops (e.g sugar beet and sugar cane). USA is the leading country in the ethanol market with about 59 % share of the global manufacture, followed by Brazil with 24 % share [1]. Ethyl lactic is a solvent which can be obtained through the esterification process of lactic acid and ethanol. Ethyl lactate is an important organic solvent which are produced from biomass and are considered to be biodegradable. It can be used as food additives, agricultural processes (used in cadmium and copper removal from the contaminated soil), solvent, flavour chemicals and perfumery. It can also be used in the pharmaceutical industry as a dispersing/dissolving excipient for several biological compounds without destroying the pharmacological activity of the active ingredient. It serves as a desirable coating for polystyrene and can also act as paint remover. This solvent has the ability to dissolve a lot of polyurethane resin because of its high solvency properties which has made it an excellent cleaner for the polyurethane industry [2]. Ethyl lactate can replace environmentally damaging solvents including toluene, acetone, N-methyl pyrrolidone and xylene.

The use of inorganic ceramic membrane 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 [3]. Inorganic porous ceramic membranes with the pore size greater than 0.3 nm are normally used as sieve for larger molecules and particles. Materials such as zirconia, zeolite, metals, glass, alumina and carbon membranes are used as commercially porous inorganic membrane. Other materials used for the manufacture of inorganic membrane also include; titania, tin oxide, cordierite and silicon nitride. Although inorganic membranes are generally expensive in contrast to the organic polymeric membrane, they have a lot of advantages in gas separation including well defined stable pore structure, chemical inertness and wear resistant [4]. The function of the membrane during esterification reaction is to selectively remove water from the reaction mixture as well as driving the reaction towards completion [5]. Although esterification reactions are usually limited by equilibrium and as such do not reach completion. However, using a membrane can result in higher conversion by shifting the chemical equilibrium towards the formation of the product by removal of water from the reaction mixture [6].

Gas separation is a membrane process whereby a pressurized gas mixture interacts with the membrane at one side (high pressure side) with the other side kept under vacuum or at low pressure using an inert sweep gas. The driving force (i.e partial or total) is a pressure difference through the membrane [7]. The transport mechanism through porous membrane can be explained using various transport mechanisms based on the membrane material and the average pore size. The different mechanisms of gas transport through ceramic membrane include: Knudsen diffusion, Poiseuille or viscous flow, capillary condensation, surface diffusion and molecular sieving [7].

Knudsen mechanism takes place when the mean free path of the diffusing gas molecules is greater than the pore size of the membrane [8]. In this mechanism, random collision occurs between the molecules of the gas and the pore wall, than between each permeating gas molecules. In capillary condensation mechanism of transport, partial condensation within the pores occurs as a result of low vapour pressure. However, the condensed feed component diffuses faster through the pores of the membrane resulting in separation [9].

Poiseuille flow also known as viscous flow occurs if the pore radius of the membrane is larger than the mean free path of the permeating gas molecule [10]. In this case more collision will take place between the permeating gas molecules (molecule-molecule collision) than between the molecule and the pore wall of the membrane. In surface diffusion, the adsorption of gas molecules are considered to be on the surface and move on the surface by jumping between the minimum potential energy generated on the membrane pore surface. Moreover, the diffusing gas molecules that bound on the surface may withdraw from their state of adsorption to the gaseous state if their kinetic energy is greater than their sorption energy [8]. For molecular sieving to occur, the membrane must have pore diameters which are roughly the same as those of the gas molecules to be separated [11].

II. EXPERIMENTAL

The permeability of the single gases with inorganic ceramic membrane was carried out using four different gases which serve as carrier gases for esterification reaction including argon (Ar), helium (He), carbon dioxide (CO₂) and nitrogen (N₂). A similar method to that of Poshusta, Noble and Falconer 1999 [12], was adopted and modified by changing the gauge pressures and temperature. The effective length of the inorganic mesoporous silica membrane was measured to be 36.6 cm. The inner and outer radius the membrane was 7 and 10 mm respectively. The permeability experiment was carried out at the gauge pressure of 0.10 -1.00 bar and temperature of 140 °C (413 K). The membrane preparation was carried out based on the patented method by Gobina 2006 [13]. The membrane dip-coating process was carried out once. Figure 1 shows the schematic diagram of the dip-coating process. These consist of silica solution, measuring glass cylinder, membrane support, magnetic stirrer, electric heating plate and control knob.

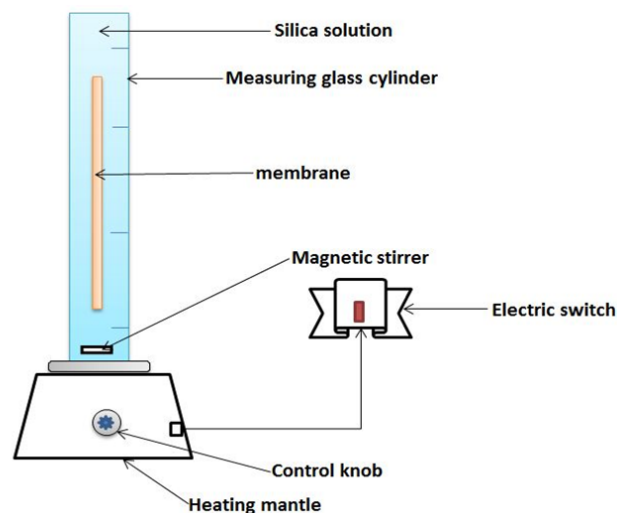


Fig. 1. Schematic diagram of the membrane dip-coating process.

Figure 2 shows the permeation setup for the permeability analysis Okon et al. [14].

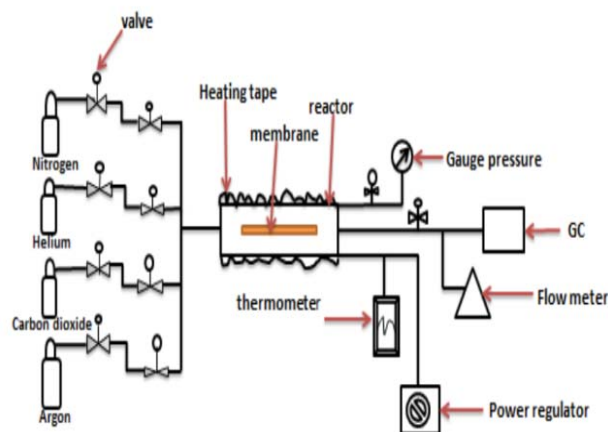


Fig. 2. Schematic diagram of gas permeation setup.

III. RESULT AND DISCUSSION

The graph of the permeance ratio against the gauge pressure drop was plotted for argon, helium, nitrogen and carbon dioxide gases. From figure 3, the experimental selectivity of the gases were found to be higher than the Knudsen selectivity at 0.10 – 1.00 bar and 413 K.

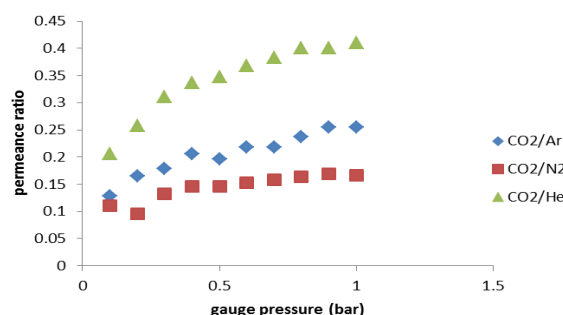


Fig. 3. Permeance ratio against gauge pressure (bar) at 413 K.

Figure 4 shows the graph of the gas Flux ($\text{mol m}^{-2} \text{s}^{-1}$) against the gauge pressure at 413 K. From figure 4, it was observed that the flux of the four gases increases with respect to the gauge pressure. Nitrogen and helium gases with the molecular weight of 28g/mol and 4g/mol respectively showed a higher flux in contrast to CO_2 gas with higher molecular weight of 44g/mol as shown in Table 1. The R^2 value of gas with 1.00 indicates a good correlation of the graph. Although CO_2 gas seems to show the least permeance among other gases as shown in figure 4, the R^2 was higher than other gases. It was also suggested that there could be another mechanism of transport responsible for the flow of CO_2 gas. The order of the gas flux was given as $\text{CO}_2 < \text{He} < \text{N}_2 < \text{Ar}$.

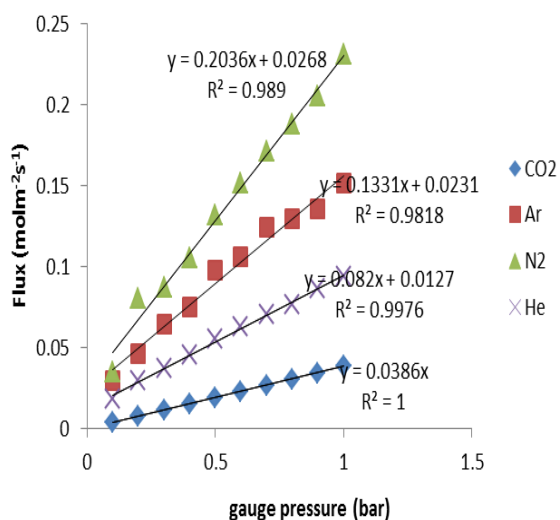


Fig. 4. Gas flux ($\text{molm}^{-2} \text{s}^{-1}$) against gauge pressure drop (bar) at 413 K

The gas flux was calculated using the formula:

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

J = flux ($\text{mols}^{-1} \text{m}^{-2}$), Q = flow rate of the gases (mol/sec), A = membrane surface area (m^2).

Figure 5 shows the relationship between the permeance ($\text{molm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) and the kinetic diameter (\AA) of N_2 , CO_2 , He and Ar gas at the gauge pressure of 0.5 bar and 413 K. From the result obtained in figure 5, it observed that the gas flow was not based on molecular sieving mechanism since the gas flow did not follow the order of the kinetic diameter. N_2 and Ar gases with a close kinetic diameter (as shown in Table 1) showed permeance flow which did not reflect that of molecular sieving mechanism.

The order of the gas kinetic diameter from the highest was given as $\text{N}_2 > \text{Ar} > \text{CO}_2 > \text{He}$. In the case of molecular sieving mechanism, He and CO_2 gases with the lowest kinetic diameter would have been close to each other with a higher permeance value while N_2 and Ar with a higher kinetic diameter would have been close to each other with a lower permeance. It was suggested that there could be another mechanism of transport that was responsible for the flow of the gases at 0.5 bar and 413 K.

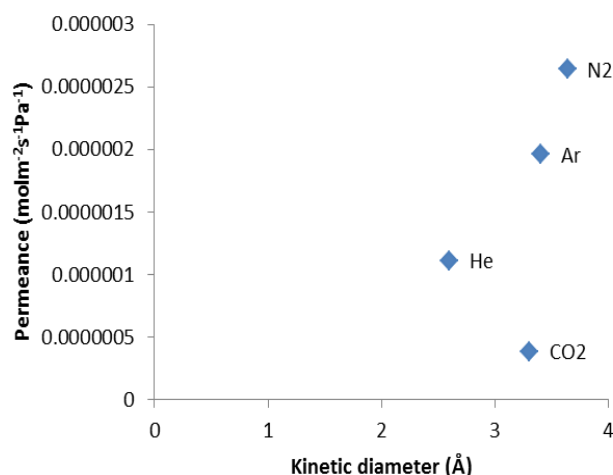


Fig. 5. Gas permeance ($\text{molm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) against kinetic diameter at 0.5 bar and 413 K

Table 1 shows the molecular weight (g/mol), viscosity (Pas^{-1}) and Kinetic diameter (\AA) of the four gases.

Table I: Molecular weight, Viscosity and Kinetic diameter of N_2 , Ar, He and CO_2 .

Gases	Molecular weight (mol/kg)	Gas viscosity (Pas^{-1})	Kinetic diameter (\AA)
Nitrogen	28	15	3.64
Argon	40	17.81	3.4
Helium	4	20	2.9
Carbon dioxide	44	22.7	3.3

The relationship between the gas permeance and inverse of the gas viscosity was also plotted at the gauge pressure drop of 0.7 bar and 413 K. From figure 6, it was observed that gases with highest viscosity value showed the least permeance which suggests that the gas flow through the silica membrane was based on viscous mechanism.

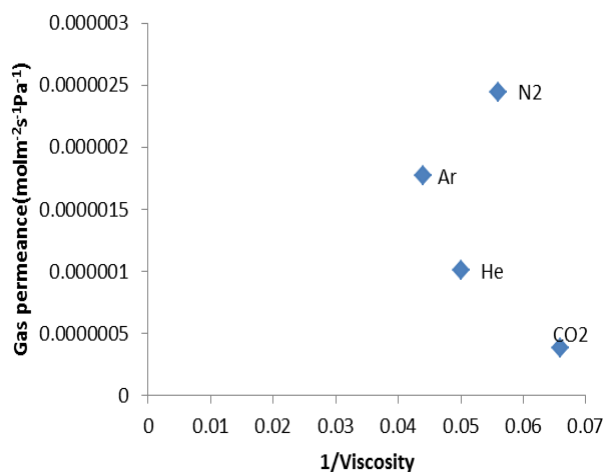


Fig. 6. Gas permeance ($\text{molm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) against $1/\text{viscosity}$ (Pas^{-1}) at 0.7 bar and 413 K.

The relationship between the gas permeance and the gauge pressure drop was also obtained as shown in figure 7. From the results obtained in figure 7, it was found that the gas permeance decreases with respect to gauge pressure indicating gas-phase mass transfer limitation. It was found that N₂ showed an increase at 0.2 bar before decreasing. The order of the gas permeance with respect to the gauge pressure drop was N₂ > Ar > He > CO₂.

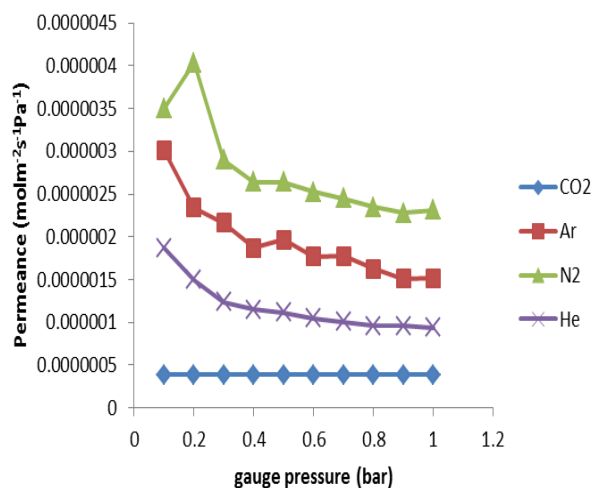


Fig. 7. Gas permeance (molm⁻² s⁻¹ Pa⁻¹) against gauge pressure (bar) at 413 K.

Figure 8 presents the relationship between the gas flow rate (mols⁻¹) and the inverse square root of the gas molecular weight for the four gases. For a gas transport to be described by Knudsen flow mechanism, the hydrothermal membrane would have exhibited a linear dependence of flow rate on the inverse square root of the molecular weight for the four gases McCool et al. [14]. However, from figure 8, it was found that there was no linear dependence between the flow rate and the inverse square root of the gas molecular weight as expected for gas transport that is dominated by Knudsen mechanism indicating that the gas flow was based on another mechanism of transport.

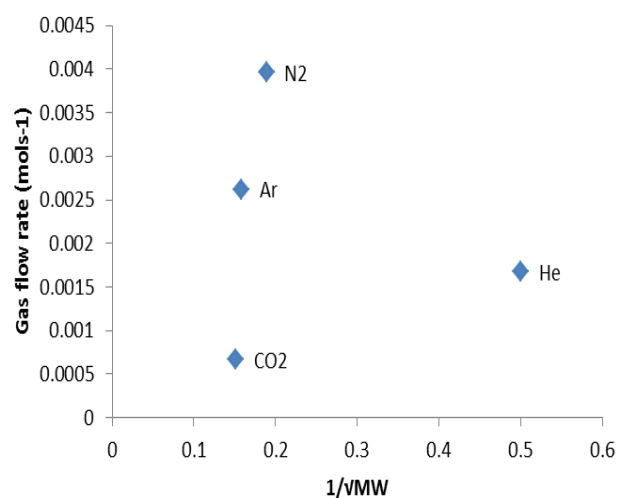


Fig. 8. Gas flow rate (mol s⁻¹) against inverse square root of the gas molecular weight at 0.9 bar and at 413 K.

IV. CONCLUSION

Gas permeation performance in mesoporous silica membrane for lactic acid and ethanol esterification at the 413 K and 0.10-1.00 bar pressure drop was determined. The gas transport was tested using Knudsen, viscous and molecular sieving mechanisms. The best fit was found to be based on viscous flow. However, the theoretical Knudsen selectivity was found to be higher than the experimental selectivity indicating that some Knudsen flow was also occurring. The order of the gas permeance with respect to the gauge pressure drop was found to be N₂ > Ar > He > CO₂.

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REFERENCE

- [1] Pereira CS, Rodrigues AE. Ethyl Lactate Main Properties, Production Processes, and Applications. *Alternative Solvents for Natural Products Extraction*. Springer; 2014. p. 107-125.
- [2] Pereira CS, Silva VM, Rodrigues AE. Fixed bed adsorptive reactor for ethyl lactate synthesis: Experiments, modelling, and simulation. *Separation Science and Technology*. 2009; 44(12):2721-2749.
- [3] Asthana N, Kolah A, Vu DT, Lira CT, Miller DJ. A continuous reactive separation process for ethyl lactate formation. *Organic process research & development*. 2005; 9(5):599-607.
- [4] Ismail AF, David L. A review on the latest development of carbon membranes for gas separation. *Journal of Membrane Science*. 2001; 193(1):1-18.
- [5] Jafar JJ, Budd PM, Hughes R. Enhancement of esterification reaction yield using zeolite A vapour permeation membrane. *Journal of Membrane Science*. 2002; 199(1):117-123.
- [6] Delgado P, Sanz MT, Beltrán S. Isobaric vapor-liquid equilibria for the quaternary reactive system: Ethanol water ethyl lactate lactic acid at 101.33 kPa. *Fluid Phase Equilibria*. 2007; 255(1):17-23.
- [7] Vercauteren S, Keizer K, Vansant E, Luyten J, Leysen R. Porous ceramic membranes: preparation, transport properties and applications. *Journal of Porous Materials*. 1998; 5(3-4):241-258.
- [8] Lee D, Oyama ST. Gas permeation characteristics of a hydrogen selective supported silica membrane. *Journal of Membrane Science*. 2002; 210(2):291-306.
- [9] Basu A, Akhtar J, Rahman M, Islam M. A review of separation of gases using membrane systems. *Petroleum Science and Technology*. 2004; 22(9-10):1343-1368.
- [10] Benito JM, Conesa A, Rubio F, Rodríguez MA. Preparation and characterization of tubular ceramic membranes for treatment of oil emulsions. *Journal of the European Ceramic Society*. 2005; 25(11):1895-1903.
- [11] Poshusta, J.C., Noble, R.D. and Falconer, J.L. (1999). Temperature and pressure effects on CO₂ and CH₄ permeation through MFI zeolite membranes. *Journal of Membrane Science*, 160(1), pp. 115-125.
- [12] Gobina, E. (2006). Apparatus and Method for separating gases. United State patent. Patent No.7,048,778B2.. Robert Gordon University, Aberdeen, UK.
- [13] Okon E, Shehu H, Gobina E. Novel Application of Gas Transport Properties with Ceramic Membrane for VOC Emission and Lactic Acid Esterification. *European Journal of Engineering and Technology* vol. 2014; 2(2).
- [14] McCool BA, Hill N, DiCarlo J, DeSisto WJ. Synthesis and characterization of mesoporous silica membranes via dip-coating and hydrothermal deposition techniques. *Journal of Membrane Science*. 2003; 218(1-2):55-67