



Initial Study of Batch Process Esterification of Lactic acid and Ethanol Catalysed by Cation-exchange resins and Carrier Gas Permeation

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Abstract: The permeation properties of single gases were analysed between the gauge pressure range of 0.01-1.00 bar at a temperature of 60 °C. The four gases used for the permeation test were He, Ar, N₂ and CO₂ gases. The gas flux was found to exhibit a linear dependent on the inverse square root of the molecular weight indicating Kundsens mechanism of gas transport through ceramic membrane. The gas kinetic diameter relationship with the gas flow rate showed a non-molecular sieving mechanism of gas transport. The order of the gas flux in relation to the inverse square root of molecular weight was He > Ar > N₂ > CO₂. The four catalysts used for the esterification process were amberlyst 36, amberlyst 16, amberlyst 15 and dowex 50W8x. The SEM surface morphology of the amberlyst 36, amberlyst 16 and dowex 50W8x showed a defect-free surface indicating good resistance to lactic acid after the esterification process. The order of the thermal stability of the resin catalysts after the esterification process was amberlyst 36 > amberlyst 16 > dowex 50W8x > amberlyst 15. The esterification of lactic acid and ethanol to produce ethyl lactate as the product was carried out to determine the catalytic activity of the resin catalysts at different temperatures. The qualitative analysis of the reaction product was carried out using an autosampler connected to a gas chromatograph coupled with mass spectrometer. The highest peak on the chromatogram of the reaction product identifies ethyl lactate and is in agreement with that of commercial ethyl lactate.

Keywords: Esterification, ethyl lactate, cation-exchange resin, membrane and gas permeation.

I. Introduction

Organic esters are an important class of chemicals and have shown a wide range of applications in different areas including perfumes, pharmaceuticals, flavours and chemicals intermediates [1],[2]. Besides the numerous applications, esters from nonedible crops and alternative sources are potential candidates in carbon emission reduction. In order to ascertain the future energy supplies and offset the environmental impact, low-carbon technologies will play a major role with this regards. In addition to the energy efficiency, different types of renewable energy, nuclear power, carbon capture/storage as well as new technologies must be widely developed in order to reach the emission targets. Esterification reactions can be performed in the absence of catalyst even though the reaction are in worst cases very slow due to the fact that the reaction rate depends on the autoprotolysis (transfer of proton) of the carboxylic acid group [3]. Generally, esterification does not reach completion and may require days or months to attain equilibrium in the absence of catalyst [2],[4]. In order to increase the reaction rate in esterification process, homogeneous and heterogeneous catalysts are normally employed for the liquid-phase esterification reaction. While cation-exchange in the acid form can serve as heterogeneous catalysts, the mineral acid can be given as the example of the homogeneous catalysts.

Despite the strong catalytic effect, the use of homogeneous catalysts including hydrochloric and sulphuric acids has a lot of drawback including corrosion of equipment, existence of side reactions and need to deal with acid with the acidic waste which constitutes environmental problems. A lot of research have employed heterogeneous catalysts as an alternative catalyst because of their numerous advantages including good chemical and physical properties, high selectivity and thermal stability and shows no corrosion problems [2] and [3]. The use of membranes to selectively remove water from the reaction product in an equilibrium limited reaction to shift the equilibrium towards the higher conversion of product has attracted an increasing attention [5]. Although the traditional method of solving equilibrium problems in esterification is by reactive distillation, current research have shown that the shifting of chemical equilibrium in esterification reaction can be accomplished using a membrane reactor by selectively removal of water from the reaction product [6].

Membranes can be prepared using different methods including self-assembly, spray coating, dip-coating and vapour deposition [7]. The mechanism of gas transport through membranes is generally divided into 5 groups: surface diffusion, capillary condensation, Knudsen diffusion, viscous flow and molecular sieving mechanisms [8]. Viscous flow mechanism takes place if the pore radius of the membrane is larger than the mean free path of the permeating gas molecule. Surface diffusion mechanism occurs when the adsorption of the permeating gas molecule occurs on the pore surface of the membrane material thereby increasing the gas transport performance. Knudsen mechanism takes place if the molecules of the gas collide more frequently with the pore walls than with each other [9]. Separation by molecular sieving mechanism takes place when the pore dimension of the inorganic ceramic membrane approaches those of the permeating gas molecules. However, in capillary condensation mechanism, separation can take place in the pores of the membrane with mesoporous layer in the presence of condensable gas species [9].

II. Design and procedure

The four gases used for the carrier gas permeation tests include nitrogen (N_2), argon (Ar), helium (He) and carbon dioxide (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 at 393K. 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 was carried out based the procedure developed by Gobina [10]. Aqueous lactic acid 99.9 wt% and ethanol 99.9 wt% solutions were purchased from sigma-Aldrich, UK and were used as received without further purification. The catalysts used in the experiments were commercial solid cation-exchange resins purchased from Sigma-Aldrich, UK. Before the esterification process, the fresh commercial resins were rinsed with deionised water and ethanol and were oven dried at 65 °C for 24 hrs to remove any poisonous substances and moisture completely. A similar method to that of Zang *et al.* [6], was adopted and modified for the esterification process. Fig.1a and b shows the batch reactor esterification and single gas permeation experimental setup respectively.

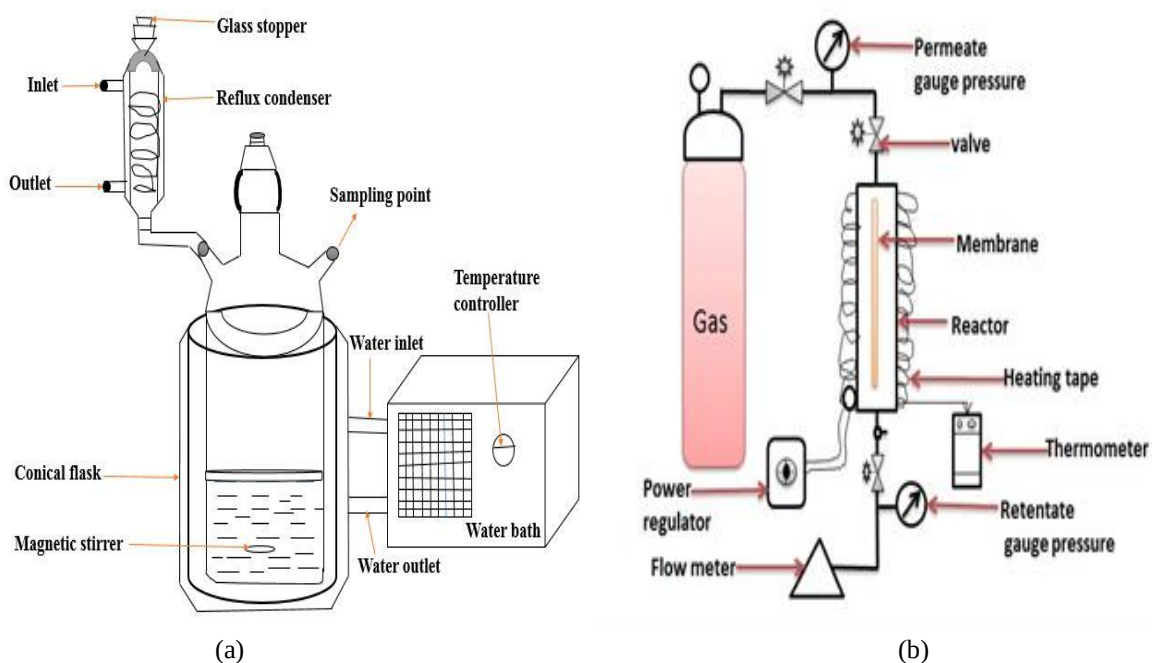


Fig. 1a-b: (a) batch reactor esterification and (b) gas permeation experimental setup.

Figure 2 shows the GC-MS instrument that was used to detect and identify the esterification reaction product. A capillary column with dimensions of 30 m x 250 μm x 0.25 μm was used for the analysis. The heating was done at the rate of 10 °C/min, at 63.063 kPa. Helium gas (99.98 % purity) was used as carrier gas. The Helium gas temperature was set at 40 °C with the flow rate of 1.2 mL/min and equilibration time of 0.25 mins, while the inlet

pressure was 100 psi. The oven temperature was programmed at 40 °C with the holding time of 2 mins at the maximum temperature of 25 °C. The solvent analysis was set on split mode with the split ratio of 50.0. The NIST GC software program was used for data collection. The qualitative analysis of the reaction product was carried out in the presence of each cation-exchange resin at 60 °C. The chromatogram, mass spectra, retention time and peak area were compared with that of the commercial ethyl lactate solvent. The resin catalysts were also analysed using SEM/EDXA in order to examine the thermal stability after the esterification process.



Fig. 2: Agilent 7890B autosampler Gas chromatography (GC) system coupled with Agilent technologies 5977A mass spectrometry detector (MSD) at the Centre for Process Integration and Membrane Technology (CPIMT), RGU.

III. Results and Discussion

Fig. 3 depicts the mass spectra of the esterification product catalysed by amberlyst 36 at 60 °C. From Figure 3, it can be seen that ion number 45 with the highest peak reflected the structure of the ethyl lactate compound which was in accordance with that of commercial ethyl lactate compound from the NIST of the GC-MS. Although the peaks of at 45 identifies that of the ethyl lactate, other ions in the spectra were represented by their respective compounds including propyl ester (42), 2,4-pentanediol (43), 1-chloro-1fluoro-ethane (44), acetonitrile(46), acetone (56), hydroxylamine-o-methyl (58), formic acid (75) and acetic acid (89).

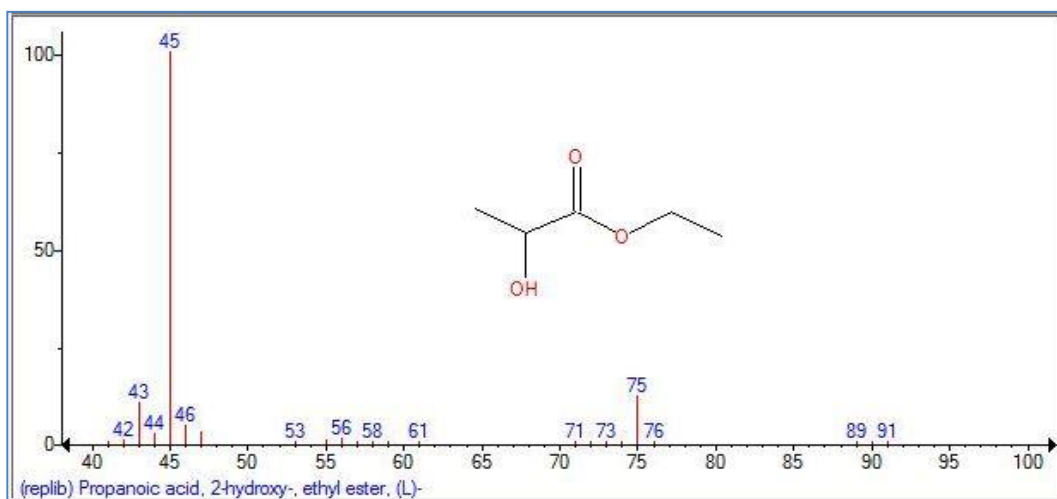


Fig 3: Mass Spectra of the esterification product catalysed by amberlyst 36 at 60 °C.

Fig 4 shows the relationship between the mass abundance and retention time (min) of the esterification product catalysed by amberlyst 36. From figure 4, it was found that the retention time of ethyl lactate for the resin catalyst increases with respect to their peak area. The first peak was found to elute at 2.125 minutes with the peak area of

Fig. 6 depicts the SEM surface morphology of the different resin catalysts after the esterification process. The different catalysts were examined at different magnifications in order to compare the surface morphology after the esterification process at 80 °C. From the SEM surface image of the resin catalysts, amberlyst 36 (6a), amberlyst 16 (6b) and dowex 50W8x (6d) showed a defect-free surface indicating good resistance property to lactic acid after esterification process, although there were some tiny white crystalline artifacts on the surface of amberlyst 36 and amberlyst 16. Amberlyst 15 (6c) and dowex 50W8x were found to exhibit larger pores in figure 6b and 6c. However it was also found that amberlyst 15 (6c) exhibited some defects on the surface after the esterification process suggesting a lower resistance to lactic acid and temperature at 200 μm magnification. The order of the thermal stability of the catalysts after the esterification process was amberlyst 36 > amberlyst 16 > dowex50W8x > amberlyst 15. Future experiments will continue the carrier gas membrane process with the esterification reaction to study the combined reactor-separator process for enhancing the yield of ethyl lactate.

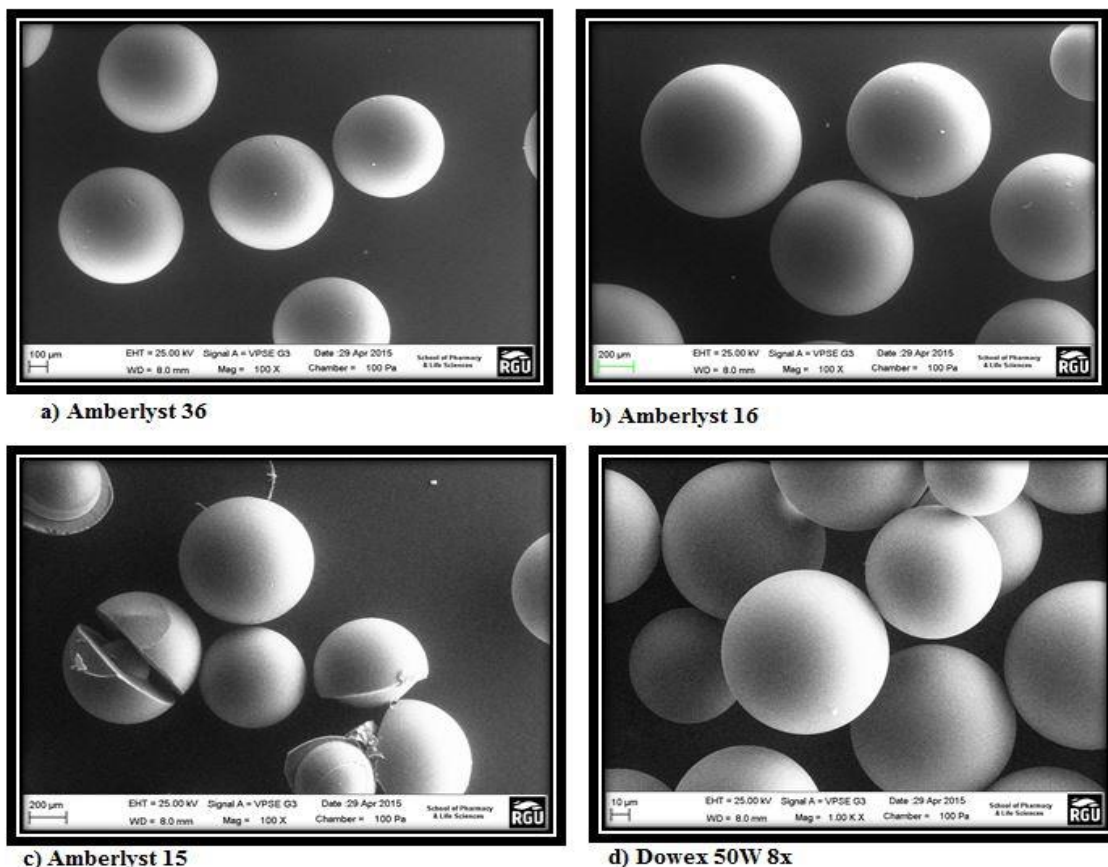


Fig. 6a (amberlyst 36), 6b (amberlyst 16), 6c (amberlyst 15) and 6d (Dowex 50W8x): SEM surface morphology of the cation-exchange resin catalysts after esterification.

IV. Conclusion

The batch process esterification of lactic acid with ethanol catalysed by cation-exchange resin and studies using carrier gas permeation with membrane was successfully determined. The mass spectra of the reaction product reflect the structure of ion number 45 confirming the presence of ethyl lactate compound using the NIST library spectra of GC-MS. Other compounds including acetic acid, formic acid-propyl ester and acetone were also detected on the spectra. The retention time of ester product was in 2.145 – 7.754 minutes. The gas flow rate with respect to the gas kinetic diameter showed a non - molecular sieving mechanism. Ar, CO₂ and N₂ gas showed a linear relationship with the gas flux exception of He gas. The retention of the reaction product was found to increase with mass abundance with their respective peak area. He gas flux with respect to the gas molecular weight showed a deviation from the linear line. Amberlyst 15 resin exhibited some crack on the surface after the esterification reaction process confirming the low resistance of the catalyst with respect to temperature. Future experiments will continue the carrier gas membrane process with the esterification reaction to study the combined reactor-separator process for enhancing the yield of ethyl lactate.

V. References

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