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Novel esterification reaction from biomass product by coupled acetate membrane and catalysts for ethyl lactate separation

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Abstract

This study presents the effect of combined membrane separation and heterogeneous catalysts for the production of ethyl lactate solvent. The enhanced process is a flat sheet cellulose acetate membrane and cation-exchange resin catalyst. A methodology based on catalyst and acetate membrane impregnation in the presence of an sweep gas at low pressure with the aim of obtaining a higher yield of the ester product have been developed. The esterification reaction was carried out at the temperature of 60 $^{\circ}$C. The ester product gave a percentage yield of up 75%. The ion chromatogram of the ester product obtained in the catalyst and membrane impregnation was compared with the esterification product of the batch esterification reaction. The gas chromatograph NIST library spectra of the ester product indicated the structure of ethyl lactate (45) on the mass spectra which was in accordance with the commercial ethyl lactate. Products obtained on dowex 50W8x and amberlyst 36 resin catalysts were found to elute faster at 1.503 and 1.527 min respectively in contrast to those using amberlyst 15 and amberlyst 16. In all, the percentage yield of the ethyl lactate can be improved using cellulose acetate membrane. Amberlyst 36 and dowex 50W8x cation-exchange resins were revealed as the most effective catalysts for the esterification process involving lactic and ethanol to produce ethyl lactate in contrast to other cation-exchange resins that were used in the study. The results further confirms effectiveness of cellulose acetate membrane in the selective removal of the water from the esterification product.

Key words: Cellulose acetate membrane, esterification, cation-exchange resin, ethyl lactate, lactic acid and characterisation.

1. Introduction

The world's energy consumption has increased tremendously over the recent years due to increase population and daily requirement. For sustainable development, there must be minimum energy consumption giving maximum benefits to human life and environment. This can be obtained via green, clean, and renewable energies in industries which can reduce energy consumption by using process intensification, hybrid technology, novel equipment and techniques that can transform energy to clean solvents. The separation and purification technology has the advantages to produce useful products or to recover useful materials from the waste by the separation processes such as reactive extraction, adsorption and pervaporation [1]. The development of renewable fuels has attracted a lot of attention over the last few years due to the depletion of petroleum reserves and increased environmental concerns [2]. Ethyl lactate has shown a lot of promise as a powerful non-toxic replacement for toxic, halogenated and petroleum-based solvents such as toluene, hexane, n-methylpyrrolidone (NMP), acetone and xylene [3],[4] that have dominated U.S.A and the world market over the years [5],[6]. In the past decade, there has been an increasing demand for using bio renewable materials instead of petroleum based feedstock for the production chemicals, driven by environmental concerned and sustainability. Research has shown that bio-based product is one of the major pillars of the sustainable economy. However, nature produces over 170 billion tons of the biomass products per year by means of photosynthesis. Out of this, 75% of these products belong to the carbohydrates, while 3-4% of these compounds are used by humans for food and non-food purposes [7]. Biomass products are organic matters in which solar energy is stored through chemical bonds including trees, crops and animal manure. In contrast to other renewable energy sources, biomass is the only renewable feedstock that can be converted into energy and chemical products. Esterification reaction is widely used in the chemical industries. However, esters can be classified into different category ranging from aliphatic to aromatic with various substitutions and multifunctional groups. Different synthesis routes have been used for the production of esters, but most of these do not meet the standard that is applied in the chemical industry. Recently, the synthesis of alkyl esters of lactic acid including ethyl lactate has attracted a lot of attention due to the fact that they can be obtained from renewable sources. A lot of work have described this synthesis by heterogeneous catalysis using amberlyst 15 heteropolyacids and dowex 50W, however, the process is limited by equilibrium resulting in a conversion of only 35% [6]. Alkyl lactates are high boiling point liquids and can be used as solvents and plasticizers for cellulose

plastics and vinyl resins, among other applications. They also take part in cosmetic and herbicidal formulations and are used as skin whitening products. Esterification of an acid catalyzed reaction which traditionally is carried out over mineral acids. The problem is that these catalyst are corrosive, toxic, non-reusable and often hard to remove from the products. This problem can be overcome by the used of a solid acid catalyst including heterogeneous catalysts. Many of the solid acid catalyst cause a lot of drawback including poor thermal stability, poor regeneration ability, low turnover numbers and low specific surface area [2]. Maximizing the reaction conversion at equilibrium (which represents the maximum attainable conversion) is one of the most significant criteria for reaction optimization together as well as catalytic activity, selectivity and kinetics. Indeed, maximizing the equilibrium conversion needs a large number of experiments to be carried out in order to screen all operating conditions including the nature of solvent, the solvent phase volume ratio, the initial substrate concentration, the pH and temperature needed. To overcome these problems, various predictive methods which explains the thermodynamics for reactions in two-phase media have been developed in order to evaluate conversion at equilibrium [8]. Ethyl lactate can be produced from the reversible esterification of biomass fermented ethanol and lactic acid. 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 [9]. Biomass-based feedstock provides a more sustainable alternative, but conversion possibilities and technologies must be realized to offer practical and economically possible sources of production [10]. Hydrogen is an important industrial feedstock for the production of fuels and other chemical, fuel cell applications and purification of hydrogen is an important unit operation. Hydrogen separation using membranes has emerged as an important technology and inorganic membrane has attracted a lot of application in hydrogen separation contrast to polymeric membrane with limited permeance and selectivity [11]. Esterification reactions with both membranes and heterogeneous catalyst can be carried out at different temperatures in the presence and absence of a catalyst. Membrane reactors can incorporate both separation and reaction in one single unit. It can also be described as an intensive reactive system [12]. Membrane-based separation technologies has been successfully employed over the years in several industrial applications [13] including food, biotechnology, pharmaceutical and in the treatment of industrial effluents and has also replaced a lot of conventional technologies due to a number of advantages including reliability, simple to operate, absence of moving parts and ability to tolerate fluctuations in flow rate and feed composition [14]. Membrane technology has attracted a lot of attention from several industrial sectors and academics in their research due to the fact that the technology gives the most relevant means of reducing costs and environmental problems [15]. The use of membranes 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 [16],[17]. Generally, esterification reactions are usually limited by equilibrium and therefore do not reach completion [18],[19], Although the traditional method of solving equilibrium problems in esterification reactions involve the addition of an excess amount of alcohol to the reaction system however, using a membrane can result in higher conversion by shifting the chemical equilibrium towards the formation of the product by in-situ removal of water from the reaction mixture [16].

Process intensification is defined as the improvement of a process at different scales and units of operation [20]. In the pervaporation membrane process, a thin polymer film is brought in contact with liquid solvent (feed) and permeate which dissolves and permeate through the membrane by diffusion mechanism along a concentration gradient. Although the transport behaviour of gases through a membrane is the same as that of porous ceramic membrane, the transport of gases through polymeric membrane depends on several factors including the nature of the polymer material, nature of crosslinks, cross link density and the temperature of the polymer. Among the different factors, the most predominant factor that strongly affects the transport process is the nature of the polymer material [21]. The permeate vapour can be condensed and collected or release as desired. The chemical potential across the membrane serves as the driving force for the process. The driving force can be created by the application of a vacuum on the permeate side of the reactor to maintain the permeate vapour pressure lower than the partial pressure of the feed liquid or by using a sweep gas flow [22]. Pervaporation when used for reactions such as esterification process, offers the opportunity to shift the chemical equilibrium by removing the product (water) from the reaction medium. However, reactor pervaporation hybrid method overcomes chemical equilibrium of the process and therefore leads to an increased yield of the product [23]. The important of incorporating pervaporation with esterification reaction is because the method is energy intensified approach as it uses less energy consumption compared to other conventional methods including packed bed reactor (PBR) and reactive distillation column (RDC). Distillation and packed bed reactors consumed high energy depending on the vapour-liquid equilibria of the system and require number of separation units for the product separation [1]. Cellulose acetate membrane was chosen among other membranes for this study because this membrane has a lot of advantages in the solving thermodynamic equilibrium problems esterification reaction due to its high permeability, high selectivity, increase in yield of ester product, cost lost, ease of operation, mechanical stability

and can allow heterogeneous catalysts can be deposited easily on the surface of the membrane. The membrane is also selective for the removal of water from the esterification reaction medium.

In the present study, a novel technology for the process intensification of lactic acid and ethanol using a flat sheet cellulose acetate membrane impregnated with different cation-exchange resin catalysts, for the separation of ethyl lactate solvent have been addressed. By incorporating a carrier gas on the permeate side of the reactor, a shift in the equilibrium for improved yield of the ester product at different temperatures and relatively low pressure can be achieved.

2. Experimental procedure

2.1 Chemicals and Materials

The flat sheet cellulose acetate membrane support with the thickness of 0.035 mm, effective membrane area of 0.0155m^2 and 150 mm x 150 mm dimension was supplied by Good fellow, Cambridge Limited, England, UK. The carboxyl methyl cellulose, boric acid, lactic acid (80 % purity), ethanol (99 % purity) and ethyl lactate (98 % purity) were all purchased from Sigma Aldrich, UK. The deionized water was supplied by Center for Process Integration and Membrane Technology (CPIMT), RGU, UK. The resistivity of the instrument was set at 18.9 mΩ cm. The cation-exchange resins were amberlyst 16, amberlyst 15, dowex 50w8x and amberlyst 36 (Sigma Aldrich, UK).

2.2 Pervaporation of resin catalysts impregnated cellulose acetate membrane

Prior to the analysis, two layers were prepared i.e the catalytic and the separation layers. Chemicals for the two layers were prepared separately before being mixed together to obtain a homogeneous solution. The cellulose acetate membrane was then immersed into the liquid. The significance of coating the support surface was to obtain a thin layer on the surface of the support so as to be effective in the removal of water from the esterification system when in contact with the reactants. The separation layer was prepared as thus: the carboxyl methyl cellulose (CMC) with weight of 0.5wt% was measured into a 100 mL beaker and 50 mL of deionized water was used to dissolve the solid CMC. The solution was the allowed to stir for 10 hours in order to attain a homogeneous mixture. The catalytic layer was prepared separately by weighing 2wt% boric acid into a 100mL beaker and adding a 50 mL of the deionized water to the beaker containing boric acid and allowed to stir for 10 hours to dissolved the boric acid (in a tablet form). After 10hrs, the solution containing the CMC was poured in to the beaker containing the boric acid solution. The two solutions (catalytic and separation solutions) were allowed to mixed together while stirring for 3hrs in order to obtain a homogenous mixture. A similar method to that of Nigiz et al. [24] was adopted for the preparation of the cellulose acetate membrane with slight modification in the solvent composition. The composition of the CMC and boric acid solvents that were used for the preparation of the catalytic and separation layers are presented in Table 1.

Table 1: Composition of solvents used for the cellulose acetate membrane preparation.

Substance	Amount (mL) and g
Carboxyl methyl cellulose (CMC)	5g
Boric acid	2g
Deionized water	50mL
Beaker	100mL

After 3hrs, the cellulose acetate membrane was immersed into the solution consisting of the CMC, boric acid and deionized water and was allowed in the solution for a further period of 3min to allow a uniform coating. After 3 minutes, the membrane was taken out of the solution and allowed to air dry for 3 days at room temperature before the esterification reaction. The importance of drying the cellulose acetate membrane in air was for the homogenous solution of the catalyst to penetrate into the porous structure of the acetate sample in order to obtain a uniform coating on the surface and also to avoid the acetate membrane burning in the oven during drying. A similar method

by Collazos et al. [25] was adopted for the catalysts preparation. Figure 1a and b shows the pictorial view of the cellulose acetate membrane (1a) and resin catalysts (1b) before process intensification and figure 1c shows the stainless steel flat sheet membrane reactor-separator.

(a)

(b)

(c)
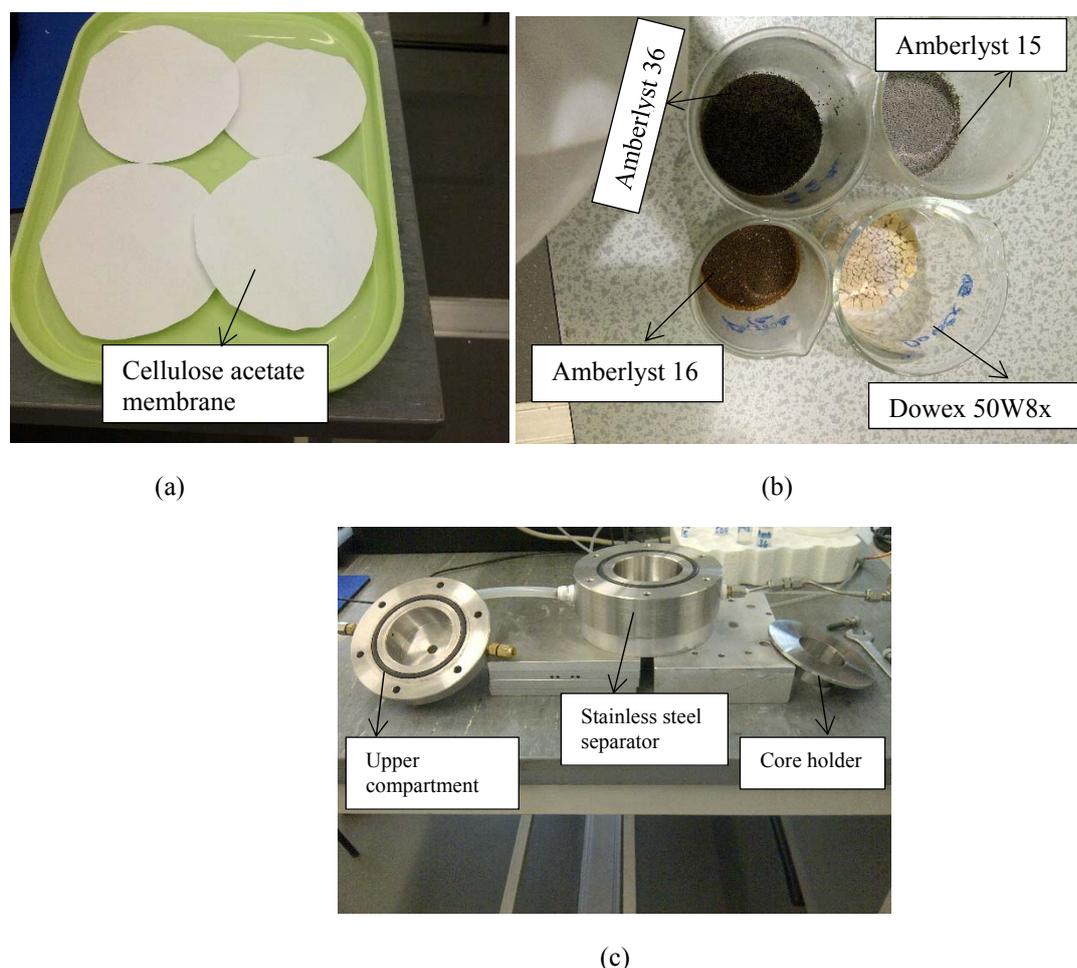
Figure 1: Pictorial view of the cellulose acetate membrane (a) and resin catalysts (b) before process intensification and stainless steel flat sheet membrane separator (c).

The intensification process by pervaporation was performed for the removal of water from the reaction mixture as shown in figure 2. The reactor was made up of two stainless steel compartments. The experimental setup consist of a gauge pressure, valve, gas cylinder, flow meter, O-ring seal, reactor upper and lower compartment, core holder, stainless steel reactor, gas cylinder, gas chromatograph, cellulose acetate membrane/cation-exchange resin. The gas was used as a sweep gas on the permeate side of the reactor to help in the chemical equilibrium shift to the forward reaction to improve the conversion of the ester product that is produced. Though a lot of work has used vapour on the permeate side of the reactor however, the conversion of the ester product is still low. Thus this work try a novel method of using a sweep gas with very low pressure on the permeate side of the stainless steel separator to improve the conversion of the ester product. The pressure from the sweep gas serves as a driving force for the selective removal of water from the reaction mixture. The valves was used to control the flow of the sweep gas when varying pressure at each stage as the sweep gas flows through the reactor. The flow meter was used to detect the flow rate. The resultant ester product passes through the permeate side of the reactor and through the flow meter to the GC-MS. The cellulose acetate membrane weighing 1.5g was placed in between the lower compartment of the separator and the core holder. 0.5g of each cation-exchange catalyst was impregnated on the cellulose acetate membrane. After the addition of the cation-exchange resin catalysts, the core holder and the rubber gasket was placed on the reactor and the reactant solvents consisting of the lactic acid and ethanol solutions which had been prepared separately were then added to the reactor through the openings of the core holder. The molar ratio of lactic acid to ethanol was 2:3wt% and were heated at 60 °C before transferring to the stainless steel separator. The experimental set up was based on a similar work carried out by Siti Khadijah et al. [26].
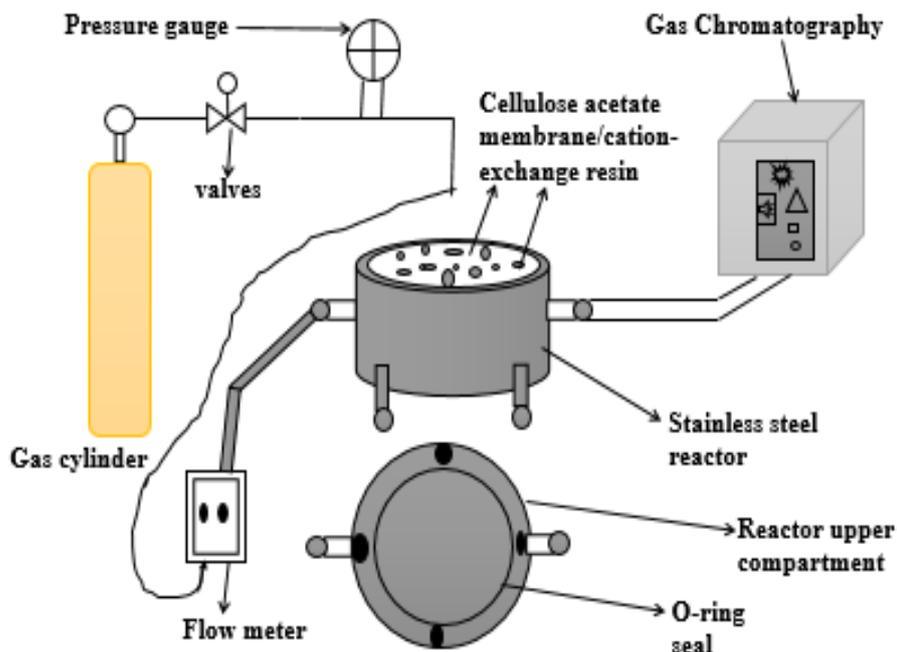
Figure 2: Schematic diagram for cellulose acetate membrane process intensification setup.

2.3 FTIR-ATR

The FTIR-ATR equipment shown in figure 3 was also used to determine the presences of functional groups in the samples. A Thermo Scientific Nicolet iS10 FTIR spectrometer (FTIR, Fisher Scientific Ltd, Bishop Meadow Road, Loughborough, UK) equipped with a PIKE 15337 Attenuated Total Internal detector (ATR, PIKE Technologies, Shelton, USA) was used for the analysis. All the spectra were recorded from 400 to 4000 cm^{-1} at room temperature using the double-side forward-backward acquisition mode. A total number of 32 scans were co-added and the signal was averaged at an optical resolution of 4cm^{-1} using the transmission measurement of the potassium bromide plate containing about 1mg of the sample. A similar method to that of Karimi et al. [27] was adopted for the FTIR analysis. Figure 3 depict the pictorial view FTIR-ATR that was used for the analysis.
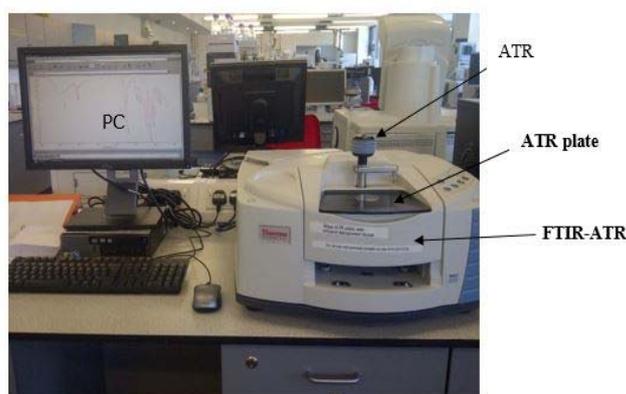
Figure 3: Pictorial view of the FTIR-ATR instrument.

2.4 SEM/EDAX

The cellulose acetate membrane and resin catalysts were characterised using the Zeiss EVO LS10 scanning electron microscopy coupled with the energy dispersion analysis of x-ray (Oxford instrument INCA EDAX system). It was used to determine the morphological characteristics and the elemental composition of compounds

respectively on the cellulose acetate impregnated cation-exchange resin catalysts. Both the surface and cross sectional images of the cellulose acetate membranes were scanned at same magnification of 5000 X and the working distance of 8.0 mm and the chamber maintained at a pressure of 100 Pa while the electron energy was set at 20.00kV. Permeation measurement were also carried to determine the gas flow rate. Figure 4 shows the SEM (a) and EDAX (b) instrument that was used to obtain the SEM micrograph of the membrane and cation-exchange resin catalysts.

2.5 Gas Permeation

Gas permeation with α-alumina nano-porous support was also carried out using five different gases which were identified as capable of serving as carrier gases for the analysis of esterification reaction with the GC-MS to determine the percentage conversion. The five different carrier gases that were used for the analysis include: argon (Ar), helium (He), hydrogen (H_2), carbon dioxide (CO_2) and nitrogen (N_2). The carrier gases were supplied by BOC, UK, with a purity of at least 99.99% v/v. The gas permeation experiment, were conducted at the gauge pressure range of 0.10 -1.00 bar and at 298 K. The different carrier gases were feed into the reactor through the feed gas opening where the gases interact with the membrane and exit through the permeate. The flow rate of the gases was obtained using a flow meter by varying gauge pressure. The esterification product was quantified using the Agilent 7890B Gas chromatography coupled with 5977A Mass Spectrometry Detector (Agilent Technologies, Santa Clara, USA) with helium (99.99 % v/v) as the carrier gas.
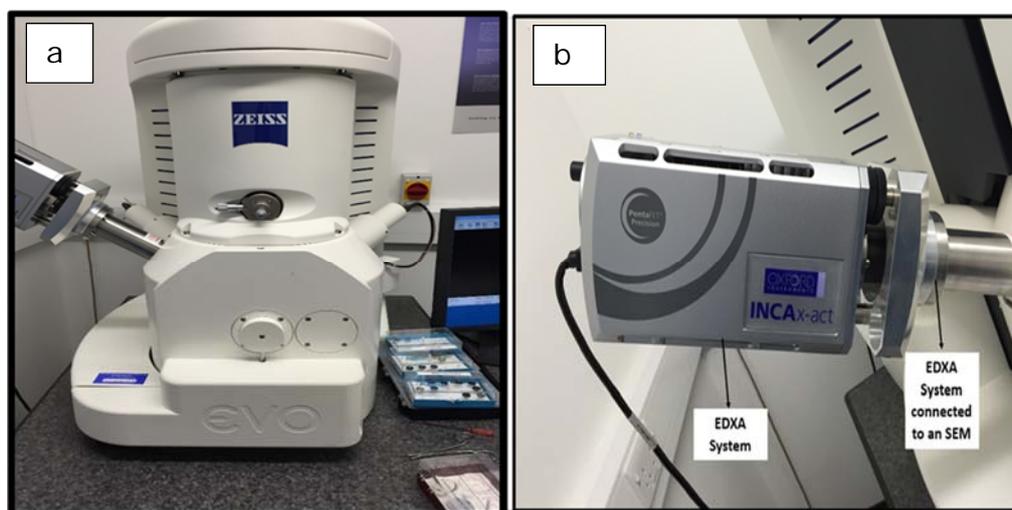
Figure 4: Pictorial vie of the Zeiss EVO LS10 scanning electron microscopy (a) and energy dispersion analysis of x-ray (b).

3. Results and discussion

3.1 GC-MS Results

Figure 5 present the chromatogram results of the ester product for cellulose acetate membrane impregnated with the amberlyst 36 (5a), dowex 50W8x (5b), amberlyst 16 (5c) and amberlyst 15 (5c) cation exchange resin at 60 ºC. The structure of the ethyl lactate was detected using the NIST mass spectra library software program. From figure 5a-d, it was found that the gas chromatograph NIST library spectra of the ester product indicated the structure of ethyl lactate (45) on the mass spectra which was in accordance with the commercial ethyl lactate. From figure 5a and b, it was observed that products obtained for dowex 50W8x and amberlyst 36 resin catalysts were found to elute faster at 1.766 and 4.460 min with the peak area of 914127648 and 78565354 m^2 respectively in contrast to that of amberlyst 15 and amberlyst 16 with the retention of 1.847 and 1.745 min and the peak area of 1129522313 and 851486410 m^2 in figure 5c and d respectively. It was also observed that amberlyst 15, 16 and dowex 50W8x elute faster after 1min in contrast to amberlyst 34 which eluted after 4 min. The ester product gave a good conversion rate of up 75% at 60 ºC which was in accordance with the literature value.

The conversion of the cellulose acetate membrane impregnated with each cation-exchange resin to obtain the resultant ester product was calculated using the following formula:

$$\text{Conversion (\%)} = \frac{C_o - C_i}{C_o} * 100\ \%\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(1)}$$

Where C_o and C_i represents the initial concentration of lactic acid and ethanol that were used as reactant solvent and the final concentration of the ester product yield that was obtained from the GC-MS analysis at determined reaction time respectively.
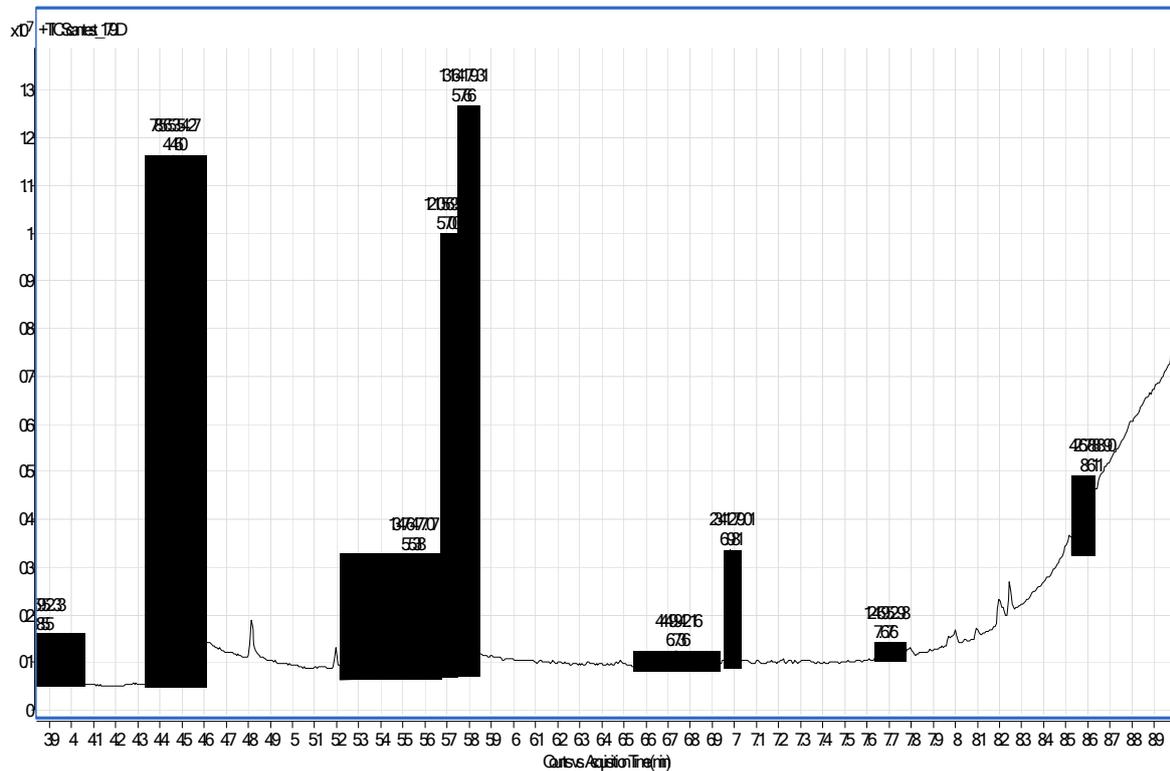
Figure 5a: Esterification reaction product cellulose acetate/amberlyst 36 at 60 ºC.
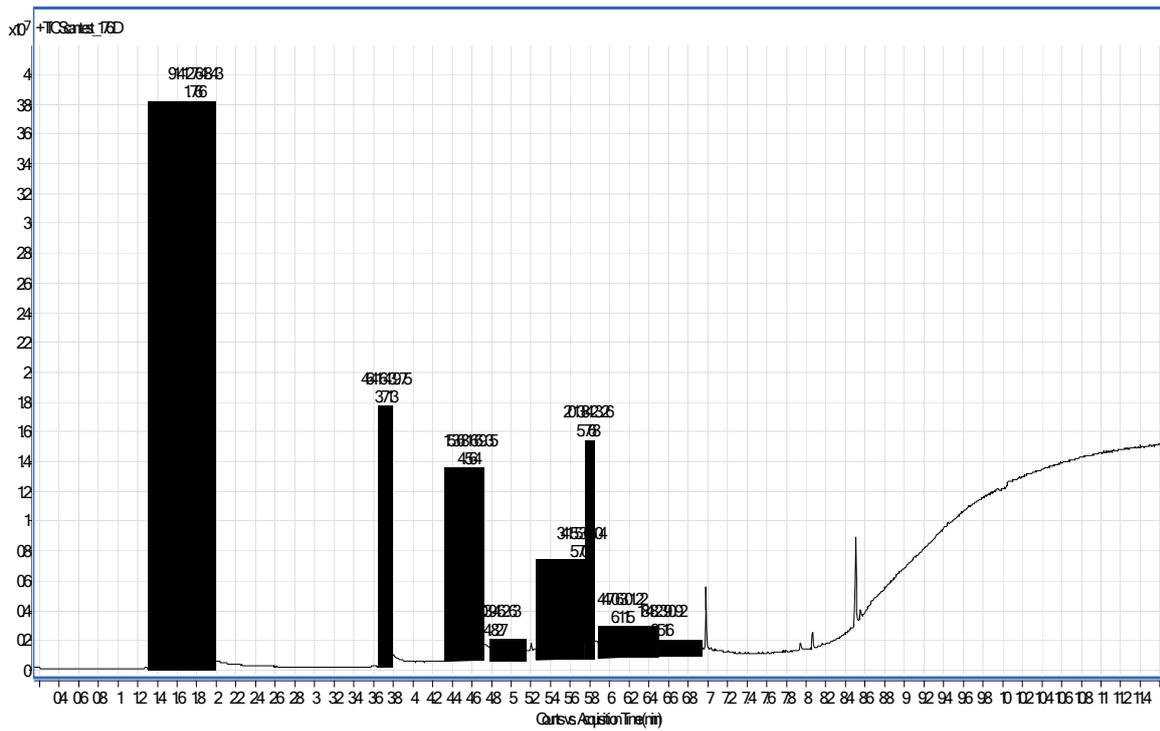
Figure 5b: Esterification reaction product cellulose acetate/dowex 50W8x at 60 ºC.
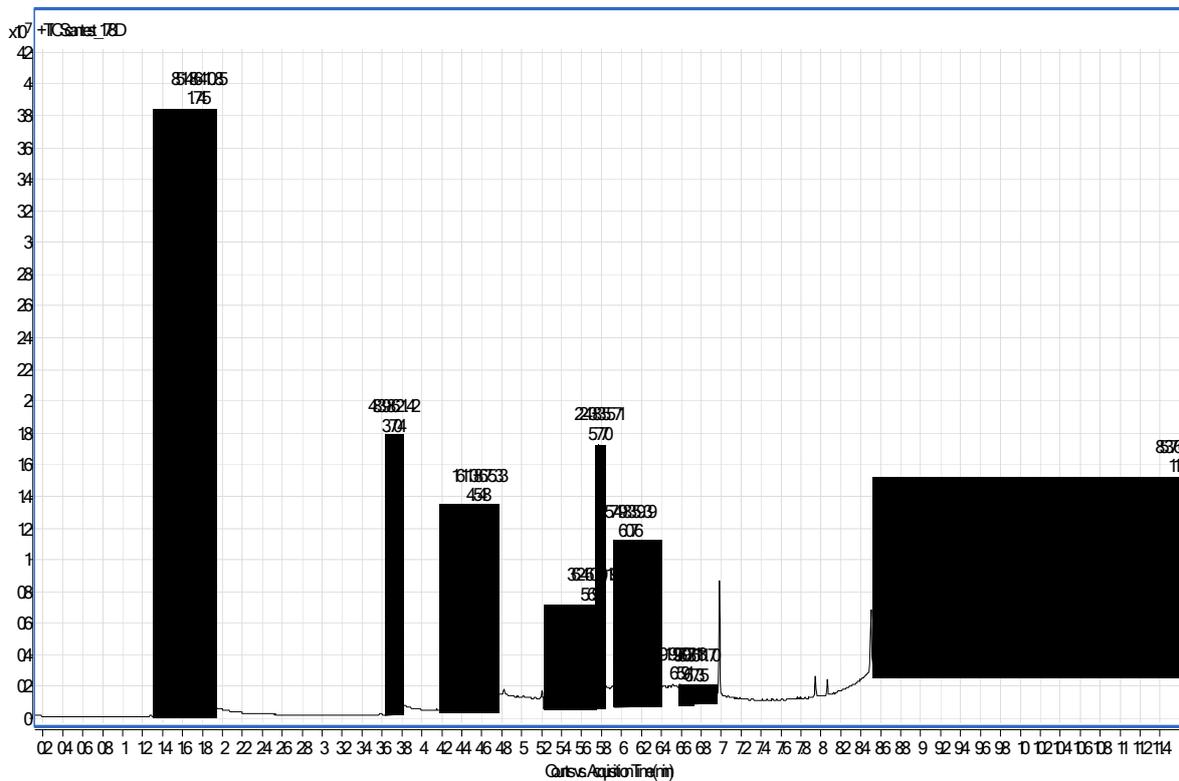
Figure 5c: Esterification reaction product cellulose acetate/amberlyst 16 at 60 ºC.
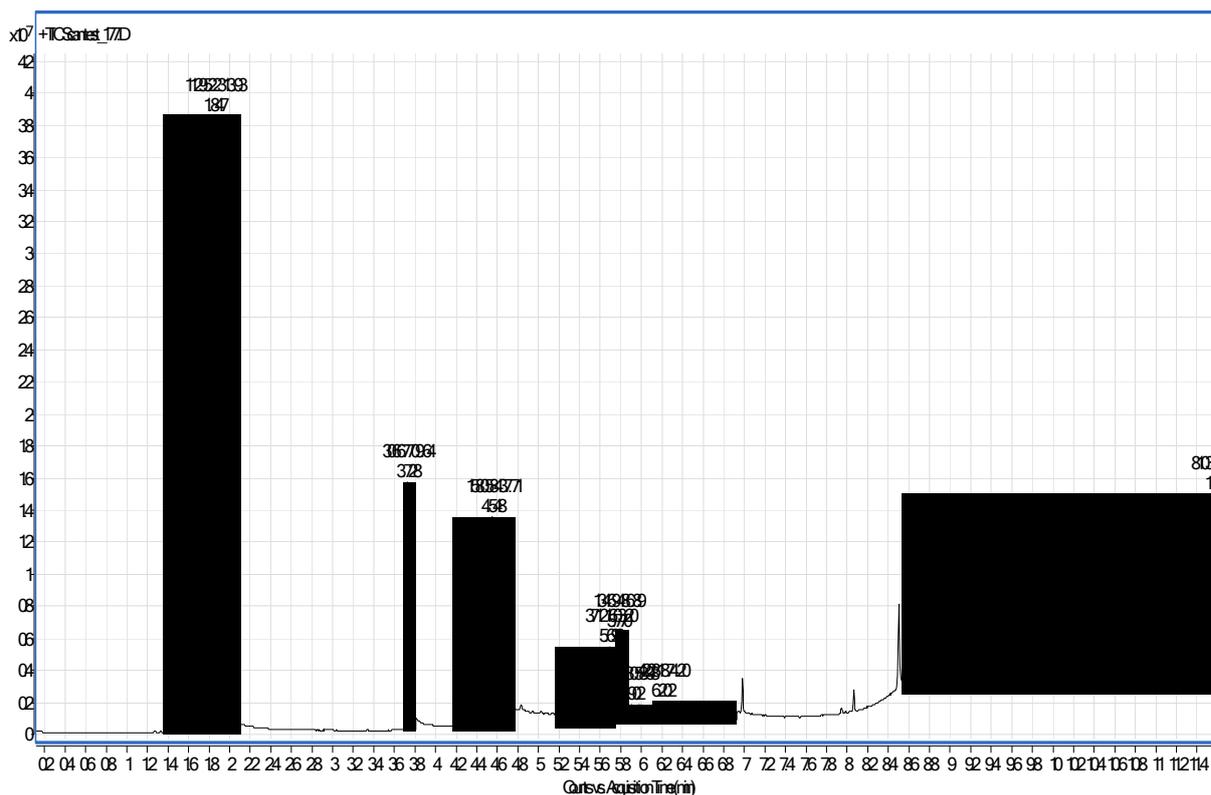
Figure 5d: Esterification reaction product cellulose acetate/amberlyst 15 at 60 °C.

3.2 Gas Permeation rate

Figure 6 depicts the graph of Ar, He, H_2, N_2, and CO_2 carrier gas flow rate (mols $^{-1}$) against the gauge pressure (bar) at 298 K. From the results obtained in figure 6, it was found that the carrier gas flow rate increases with respect to the gauge pressure. It was observed that the lighter molecular weight gases tend to permeate faster than the heavier molecular weight gases. He and H_2 gas flow rate was assumed to be based on Knudsen flow mechanism of gas transport since this gases exhibited a higher permeation rate with respect to their low molecular weight (4 mol/g) and H_2 (2 mol/g) [28],[29]. The order of the gas flow rate with the α-alumina support membrane at 298 K was found to be He (4 mol/g) > H_2 (2 mol/g) > N_2 (28 mol/g) > Ar (40 mol/g) and CO_2 (44 mol/g). Although hydrogen gas is not compatible with the mass spectrometry detector when used as a carrier gas, however, it was found that this gas also exhibited a higher permeation rate with the support membrane at 298K. From the result obtained, it was also confirmed that H_2 gas can be used as the carrier gas since it is compatible with gas chromatography couple with flame ionisation detector.
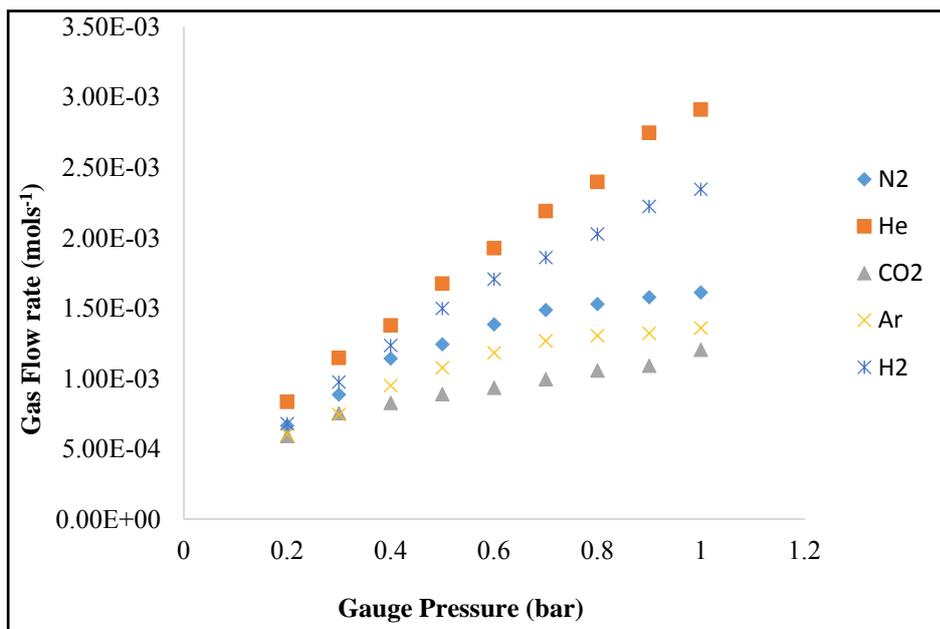
Figure 6: Effect of gas flow rate (mols^{-1}) on gauge pressure (bar) at 298K.

3.3 SEM/EDAX

Figure 7 shows the SEM images of the fresh cellulose acetate membrane before the pervaporation process and after impregnation with the cation exchange resin catalysts. The cellulose acetate membrane micrograph was focused at 1000X and 500X magnifications respectively for comparison. From the SEM image of the fresh cellulose acetate membrane in figure 7a, it was found that the cellulose acetate membrane exhibited large pores with a thread-like form on the surface. However, in figure 7b, it can be seen that the membrane pores were reduced after the pervaporation process. It can be seen that there was also some tiny white particles on the membrane surface which was attributed to the cation-exchange resin and reactant solvents that were impregnated on the membrane surface.

(a)

(b)
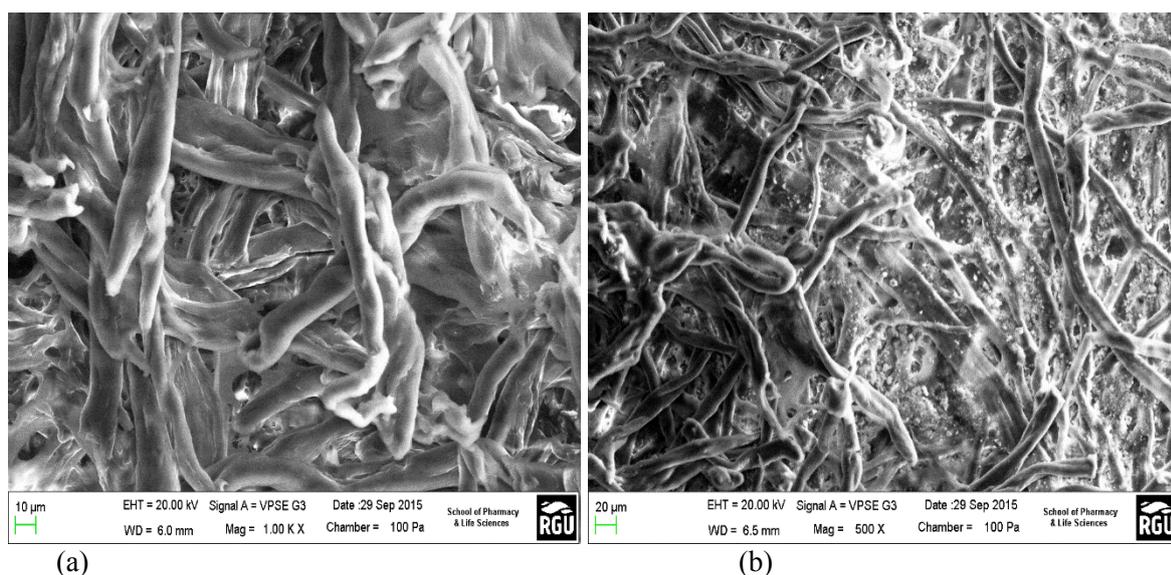
Figure 7: SEM images of fresh cellulose acetate membrane before (a) and after pervaporation process with cation exchange resin (b).

Also, the SEM/EDAX micrograph of the resin catalyst before and after pervaporation was also determined as shown in figure 7c and d respectively. The images were examined at 100X magnification with the scale of 100 µm. From figure 7c, it can be seen that the catalysts exhibited a clear surface as was expected for a fresh cation exchange resin catalysts. However, after the process intensification, it was found that the catalysts exhibited some cracks on the surface as shown in figure 7d. It was suggested that this defect could be due to the chemical reactions taking place on the catalyst surface. The distance between the ends of the pores (Pa) and the respective angle (Pb) at each position was also evaluated for the sample. From figure 7c, it was found that at position 2 (PaR2), the distance between the ends of the pores was found to be 505.9 µm while the angle was 349.5 º. However, in figure 7d, it was found that at same position, there was an increment (742.9 µm) in the measured distance and the respective angle (350.3 º). This increment was attributed to the defect on the surface of resin catalyst. The EDAX of the cation exchange resin was also determined. From the result obtained in figure 7c, it was found that the fresh cation-exchange resin exhibited different elements including carbon (C), oxygen (O) and sulphur (S). Whereas after the pervaporation process, the cation-exchange resin exhibited different elements including carbon (C), oxygen (O), sulphur (S) and aluminium (Al) as shown in figure 7d.
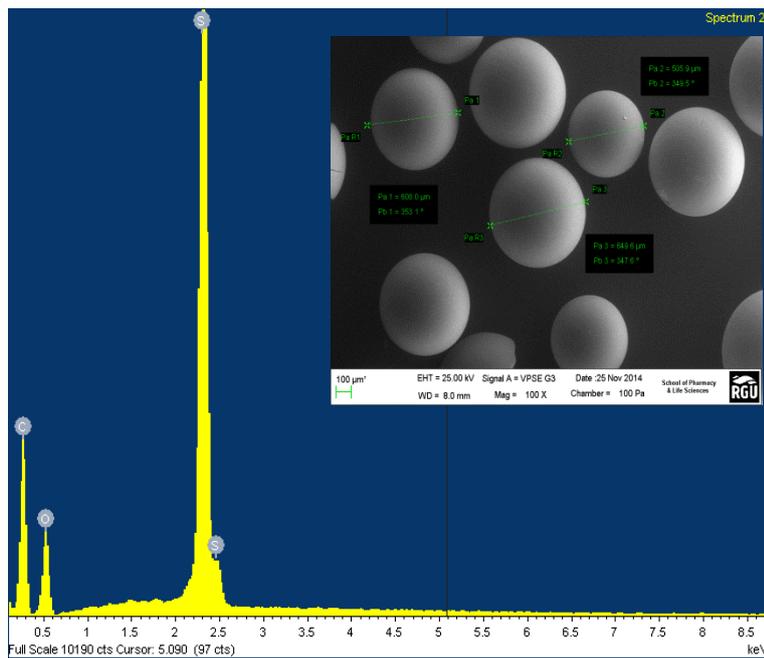
Figure 7c: SEM/EDAX micrograph of the cation exchange resin before pervaporation.
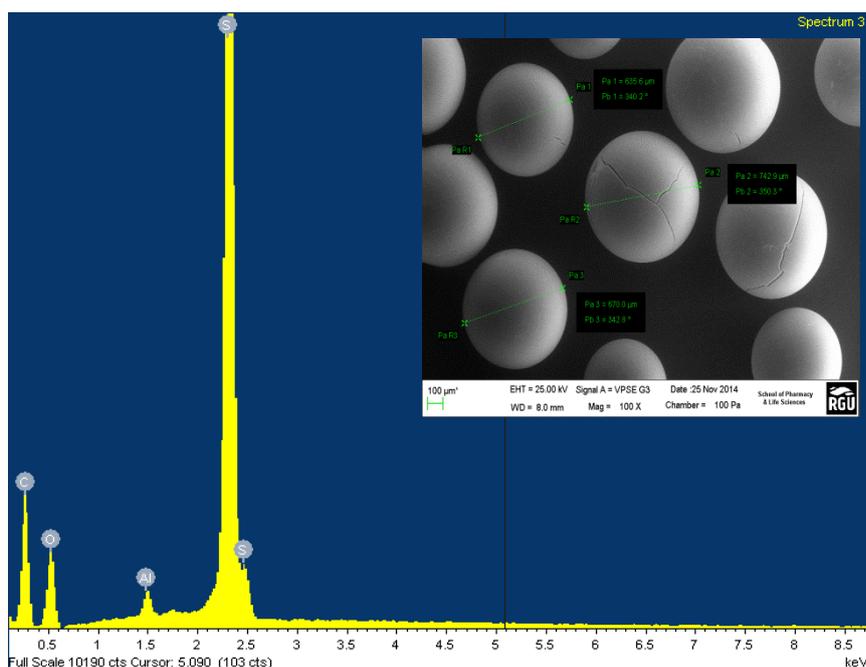
Figure 7d: SEM/EDAX micrograph of the cation exchange resin after pervaporation process.

3.4 FTIR-ATR Results

Figure 8 shows the percentage transmittance (%) against the wavenumber (cm^{-1}) for dowex 50W8x cation-exchange resins after esterification at 60 °C. From the result obtained in figure 8, the peaks at 3400 and 3003 cm^{-1} were assigned to symmetric and asymmetric O-H bond C-H respectively from the structure of ethanol which was one of the reactant solvent of the reaction. A strong band was found at 1723cm^{-1} which was attributed to C=O group carboxylic acid functional group that explains the successful interaction of the lactic acid with the reaction mixture. Two bands at 1455 and 1380 cm^{-1} were assigned to asymmetric aromatic bands of C=C while the bands at 1211, 1124, 1044, 1017, 934 and 754 cm^{-1} were attributed to C-H which was assigned to bands of C-H functional group.
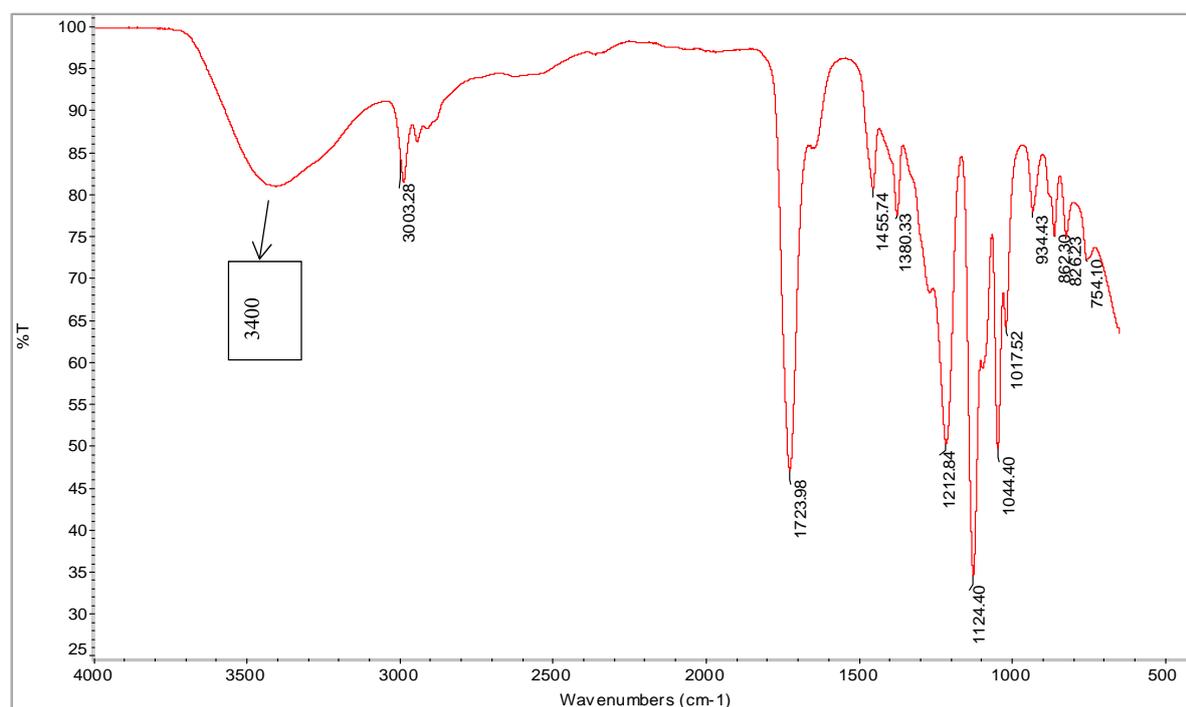
Fig. 8: FTIR spectra of esterification reaction product catalysed by dowex 50W8x at 60 °C and the wavelength region of 500 – 4000 cm^{-1}.

Conclusion

The novel method of lactic acid and ethanol esterification in the presence of flat sheet cellulose membrane and catalysts for ethyl lactate conversion to obtain a high yield of the ester product was successfully achieved. The ester product gave a high yield of up to 75 % confirming the effectiveness of the acetate membrane impregnated resin catalysts in the production of ethyl lactate solvent. The FTIR analysis of the solvent showed different functional groups including C=O, C-H, and O-H bonds on the spectra which were suspected to occur from the reactant molecules of carboxylic acid functional group and hydroxyl functional group. The GC-MS analysis of the ester product for cellulose acetate membrane impregnation with amberlyst 16 and amberlyst 36 showed the elution time at 1.745 and 4.460 min. The SEM of the cellulose acetate membrane before process intensification showed a clear surface image with some whitish particle on the surface after the process. The SEM micrograph of the cation-exchange resin also exhibited a plain surface before the process intensification with some cracks on the surface after the process intensification. The distance between the ends of the pores for the SEM image of the crack sample exhibited an increment of 742.9 µm with the respective angle 350.3°. In all, the percentage conversion of the ethyl lactate has been improved using cellulose acetate membrane impregnated with amberlyst 36 and amberlyst 16 cation-exchange resins. The study has revealed the most effective catalysts for the process

intensification involving lactic and ethanol to produce ethyl lactate as amberlyst 36 and amberlyst 16 cation-exchange resins in contrast to other that were used in the study. The results further confirms effectiveness of cellulose acetate membrane in the selective removal of the water from the esterification product.

Acknowledgement

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