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Batch Process Esterification of Lactic Acid Catalysed by Cation-exchange Resins for the Production of Environmental-friendly Solvent

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Abstract—**In this work, batch wise esterification of lactic acid and ethanol was carried out using different cation-exchange resins including amberlyst 15, amberlyst 16, dowex 50W8x and amberlyst 36 as heterogeneous catalysts. The Zeiss EVO LS10 Scanning electron microscopy/energy dispersive x-ray analyser (SEM/EDXA) was used to examine the surface morphology of the resin catalysts before and after the esterification reaction process. The EDXA of the catalysts showed the presence of sulphur with the highest peak on the spectra. The SEM of the commercial resin catalysts showed a clear surface with no crack before the esterification reaction. Amberlyst 36 showed a greater thermal stability after the esterification reaction process. The order of the surface integrity from the SEM morphology of the resin catalysts after the esterification process was Amberlyst 36 > dowex 50W8x. Gas chromatography equipped with mass spectrometry (GC- MS) detector was used to analyse the reaction products. Ion 45 on the mass spectra confirmed that the esterification product was in accordance with the library mass spectra of the commercial ethyl lactate solvent. The agitation time was found to increase with increase in concentration indicating a non-mass transfer limitation at 60 ºC. The reaction product catalysed with amberlyst 36 was found to elute at faster at 1.441 min in contrast to the commercial ethyl lactate solvent at 2.124 min indicating a higher reaction rate of the resin catalysts.**

Key words: Esterification, lactic acid, cation-exchange resin, ethyl lactate, chromatogram and ethanol.

I. INTRODUCTION

Ethyl lactate is a biodegradable and non-toxic material with excellent solvent properties which could potentially replace halogenated and toxic solvents for a broad range of consumer and industrial uses. In the food industry, approximately 85% of the estimated 50,000 tons/yr of ethyl lactate manufactured worldwide is being used for food product, while the remaining percentage is used in other industries such as textile, cosmetic, leather and pharmaceutical industries [1]. The esterification reactions involving lactic acid with alcohols are not only used in the manufacture of the corresponding esters, but are also used in lactic acid purification process [2]. Esterification reaction of carboxylic acid with alcohol in the presence of heterogeneous catalysts has been widely investigated. 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. Currently some studies have focused on the water-permeable membrane reactor which has to do with liquid-phase reversible reactions including esterification reactions [3]. Among the membranes considered, inorganic ceramic membrane 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 increase in the purity of products since side reactions and corrosion problems can be avoided [4].

According to Altiokka and Citak [5], several researchers have shown a lot of interest on the investigation of the esterification reactions between carboxylic acids and alcohols catalysed with acids. However, both heterogeneous and homogeneous catalysts have been used for this reaction. While a cation-exchange resin in the acid form can serve as heterogeneous catalyst, mineral acids such as sulphuric and hydrochloric acids are known as an example of the homogeneous catalysts [5]. Based on the heterogeneous and homogeneous approaches, the esterification reactions in the presence of ion-exchange resins can be explained using several kinetic models including Langmuir Hinshelwood (LH), Eley-Rideal (ER) and pseudo-homogeneous (PH) models [6-8]. Although the PH model does not consider the sorption effect on the resin by various components in the reactant mixture, the ER and LH models consider the sorption effects in their reactions kinetics [6]. The ER and LH model takes place when a reaction occurs between an adsorbed and the non-adsorbed reactant species. Cation-exchange resins are polymers with larger pores which are made of styrene divinyl-benzene copolymer with sulfonic acid functional groups that enables the strong acidity of the catalysts [9]. Although this catalyst possesses some outstanding properties such as excellent porous medium and surface acid site characteristics, cation-exchange resin does not only work as a catalyst in esterification reaction, but also affect the equilibrium conversion due to their swelling nature [10]. These acid catalysts sometimes exhibit some drawback of low activity for the reactions that require high acid strength,

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swelling of the catalyst in the reaction medium and also difficulties of applying reaction temperature above 100 ºC [11]. Resin catalysts have been successfully applied in the liquid-phase acid catalysed reactions especially in the reactions involving water and lower alcohols [11] because they possess several advantages including allowing continuous operation in the reactor, removal of the catalyst for the reaction product, increase product purity and reaction intermediate can be isolated since side reactions can be eliminated. Furthermore, cation-exchange resin can discriminate between small and large molecules [12]. The most popular cation-exchange resins for ester production include amberlyst 35, dowex 50Wx, amberlyst 15 and amberlyst 36 [13]. However, in recent years, a lot of research has focused on the use of cation-exchange resin for esterification process because of their selectivity and reactivity. Additionally, they are relatively cheap and can be used repeatedly over a long period [13]. Although the traditional method of solving equilibrium problems in esterification reactions involve the addition of an excess amount of alcohol to the reaction system [14], 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 [15]. However, membrane can lose their performance easily during esterification reaction as a result of being attack by homogeneous acids catalyst. As such, heterogeneous solid catalysts including cation-exchange resin have been employed for esterification in order to solve the degradation problems of inorganic ceramic membranes [16]. According to Sharma et al. [17], the kinetics of the esterification reaction products can be analysed using two methods; either by titration or using GC with a choice of detector and carrier gas. Using the GC-MS, the product can be analysed by matching the retention time of the reaction product to the retention time of the commercial ethyl lactate. Sharma et al. [17] applied both methods in the analysis of the esterification product (propyl nonanoate) with flame ionisation detector (FID) as the detector and nitrogen as the carrier gas. Zhang et al.[3] studied the kinetics of esterification of lactic acid with ethanol catalysed by different cation-exchange resin. In their study, the order of the resin catalytic activity was D002 < D001 < Amberlyst-15 < NKC < 002. Sanz et al. [18] studied the esterification of lactic acid with ethanol and methanol catalysed by cation-exchange resin. They found out that amberlyst 15 is the most suitable catalyst for the esterification process. Sharma et al. [17] also studied the effect of particle size and amount of catalyst on the esterification reaction using gel type Dowex 50W8x as solid catalyst and found that internal mass-transfer resistance could be neglected and the conversion could be improved in a small particle size of the resin. In this study, the esterification reaction of lactic acid and ethanol catalysed by amberlyst 15, amberlyst 16, amberlyst 36 and dowex 50W8x cation-exchange resin catalysts was carried out at 60 ºC to determine the product distribution using the retention time and the peak area.

II. EXPERIMENTAL

An 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 also purchased from Sigma-Aldrich, UK.

Helium gas (99.98 % purity) was used as carrier gas and was obtained from BOC, UK. Before the experiments, the fresh commercial resins were rinsed with deionised water and ethanol and were oven dried at 65 ºC for 24 hrs to remove poisonous substances and moisture completely. A similar method to that of Zhang et al. [3] was adopted with some modification in the reaction temperature, drying time as well as lactic acid and ethanol concentration. Agilent technologies 7890B autosampler Gas chromatography (GC) system coupled with Agilent technologies 5977A mass spectrometry detector (MSD) was used to determine the kinetics of the esterification reaction product. A microliter syringe (Hamilton HM80300 microliter ™ syringe) was used for sample preparation before it was inserted into the GC vial for injection. Fig. 1 shows the GC-MS instrument that was used for the esterification analysis.

Fig. 1. Agilent technologies 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.

As part of the quality control measures, a blank analysis was carried out in order to clean the GC column prior to the sample analysis. Ar and N_2 gas were used as the detector gases. A capillary column with the column dimensions of 30 m x 250 µm x 0.25 µm was used for the analysis and at the rate of 10 ºC/min, at 63.063 kPa. The Helium gas temperature was set at 40 ºC 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 program at 40 ºC with the holding time of 2mins at maximum operating temperature of 25 ºC. The sample scanning rate was 9.773 mins. The solvent analysis was set on split mode with the split ratio of 50.0. The sample vial was carefully cleaned prior to each analysis. The sample was carefully inserted into the sample rage embedded in the injector port of the GC-MS where the carrier gas transfers the solvent to the GC column. The NIST GC software program was used for data collection. Both quantitative and qualitative analysis of the reaction product in the presence of each cation-exchange resin at 60 ºC were performed in triplet and 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 other to examine the

thermal stability and mechanism strength of resin catalyst before and after the esterification process.

III.   APPARATUS

The esterification reactor contains a three-necked conical flask of 500mL capacity fitted with a condenser, a thermometer and a sampling device as shown in figure 2. The temperature of the reaction system was controlled using a thermometer to ensure a constant temperature. The reaction mixture was mixed using a magnetic stirrer and the stirrer speed was controlled from the heating system at the frequency of about 400-800 rpm. The water from the reaction product was removed by connecting two vaccum pumps to the openings of the reactor i.e both the inlet and the outlet water flow. The inlet water flows through the pipe to flush the system while the out let water displace the waste water from the reaction system. The mixture was left in the reactor with a magnetic stirrer to mixture the solution together before the analysis. About 1mL of the reaction product was withdrawn from the reactor simultaneously for the qualitative and quantitative analysis. A standard solution was made from the mixture with serial dilution for analysis with GC-MS.
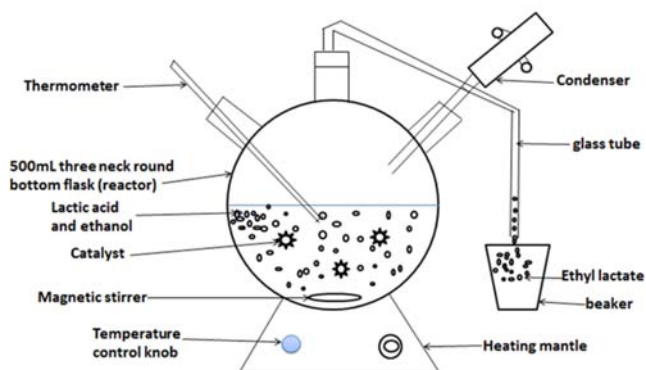
Fig. 3. GC chromatogram for commercial ethyl lactate solvent.

Fig. 2. Batch process experimental setup
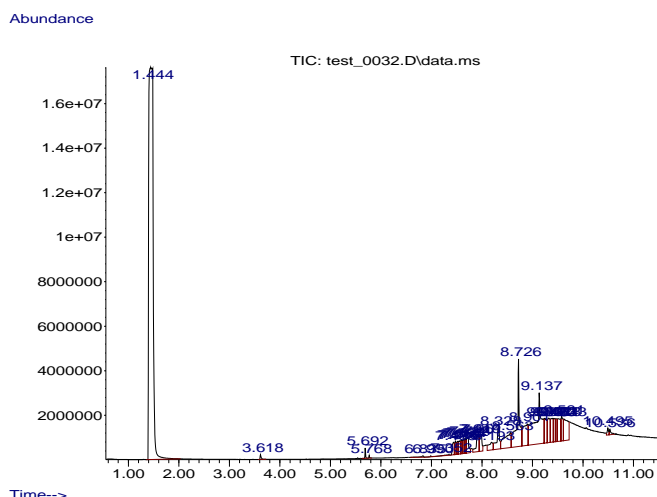
Fig. 4. GC-chromatogram of reaction product catalysed by Amberlyst 36 at 60ºC.

IV.   RESULT AND DISCUSSION

Fig. 3,4,5,6 and 7 presents the chromatogram results of the commercial ethyl lactate and the reaction product in the presence amberlyst 36, 16, 15 and Dowex 50W8x resin catalysts. From the chromatogram results, the mass spectra of the reaction product were generated from the highest peak in the chromatogram using NIST software program of the GC system. From the mass spectra of the reaction product, ion 45 exhibited the structure of ethyl lactate solvent as shown in fig. 8. This was in accordance with the library spectra of the commercial ethyl lactate solvent as shown in fig. 9 which also confirm that the produced esterification reaction product can be used for industrial purposes.
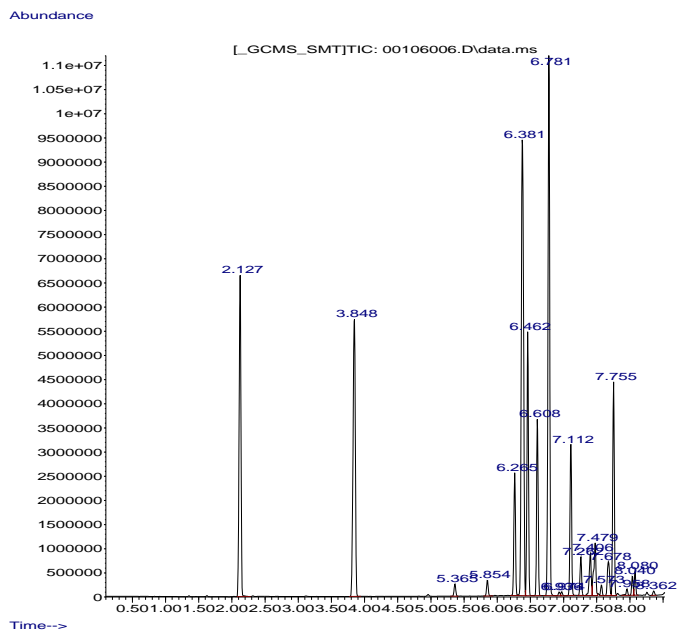
Table 1: Comparison of Retention time and Peak area for the commercial ethyl lactate and reaction product for Amberlyst 36 at 60 ºC.

Retention time Ethyl lactate/reaction product		Peak Area of Ethyl lactate/reaction product	
Commercial ethyl lactate	Reaction Product with amberlyst 36	Commercial Ethyl lactate	Reaction Product catalysed by amberlyst 36
2.127	1.444	13152320	107063789
3.846	3.618	14006785	129264

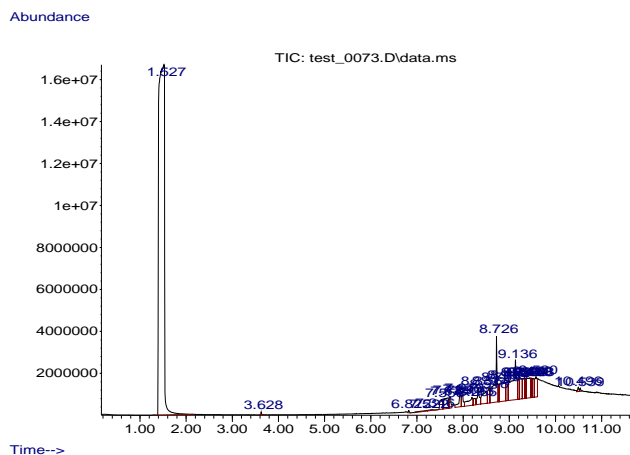|			
5.365	5.692	446352.4	5600390
5.854	8.726	57427.69	21436293
6.265	9.137	4295677	100636546
6.381	10.436	22542187	14917454

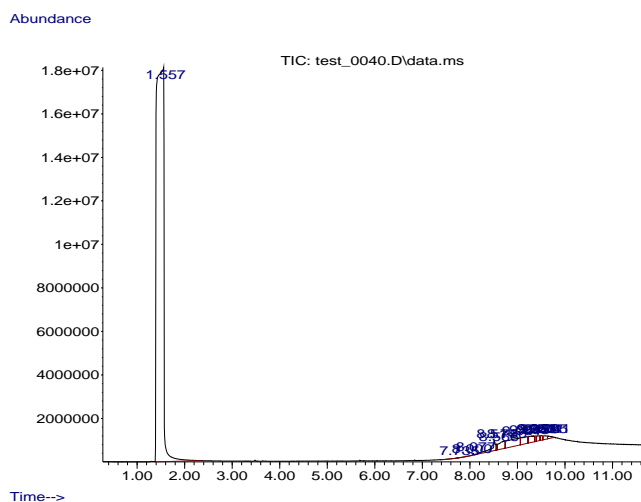Fig. 5. GC chromatogram of commercial ethyl lactate solvent catalysed by Dowex 50W8x at 60 ºC.

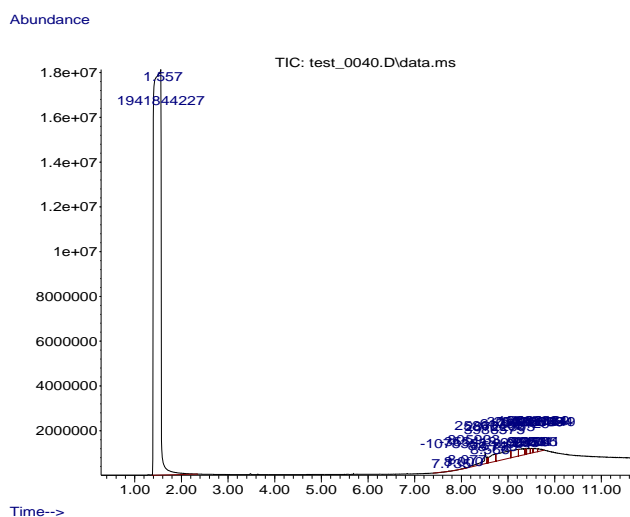Fig. 6. GC chromatogram of commercial ethyl lactate solvent catalysed by Amberlyst 16 at 60ºC.

Fig. 7. GC chromatogram of commercial ethyl lactate solvent catalysed by Amberlyst 15 at 60ºC.
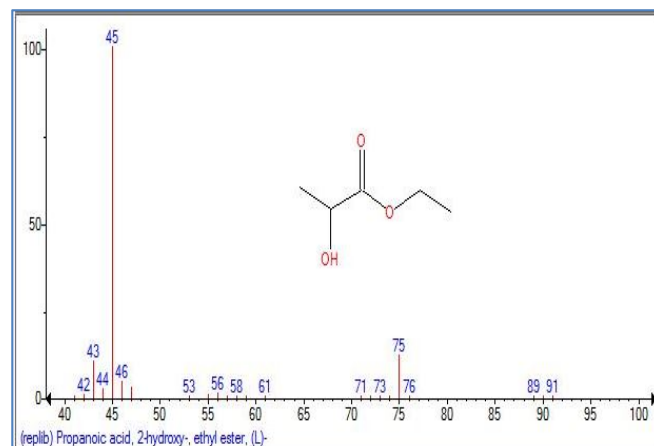

Fig. 8. Mass spectra for reaction product catalysed by Amberlyst 36 at 60 ºC

Figure 9 presents the Library of spectra for the commercial ethyl lactate solvent. The mass spectra/chromatogram results for the commercial ethyl lactate and the reaction product were compared in order to investigate the reaction kinetics using the retention time and their peak area. Table 1 and 2 presents the retention time and the peak area of the reaction product and that of the commercial ethyl lactate. From table 1 and 2, can be seen that there was appearance of peaks at 1.444 min whereas for the commercial ethyl lactate, the peak elution started at 2.127 min. This difference can be attributed to the presence of catalyst in the solvent thereby fastening the rate of the reaction product. At the retention time of 3.846 min for commercial ethyl lactate elution, the reaction product was found to elute at 3.618 mins and also at 6.383min for the commercial ethyl lactate, the reaction product in the presence of resin catalyst was found to elute at 10.436 mins. It was suggested that faster elution of peaks in the reaction product was due to the presence of the cation-exchange resin thereby speeding up the rate of the reaction in the reaction product at 60 ºC. Comparing the peak area in table 1, it was found that of the reaction product catalysed by amberlyst 36 was larger than that of the commercial ethyl lactate which was also attributed to the resin activity. Although some work has been carried out on the reaction kinetics of the esterification reaction, only very few studies have attempted to kinetically model the esterification product using the retention time and the peak area of the reaction product. A similar results was also obtained for amberlyst 15, 16 and Dowex 50W8x at 60 ºC.
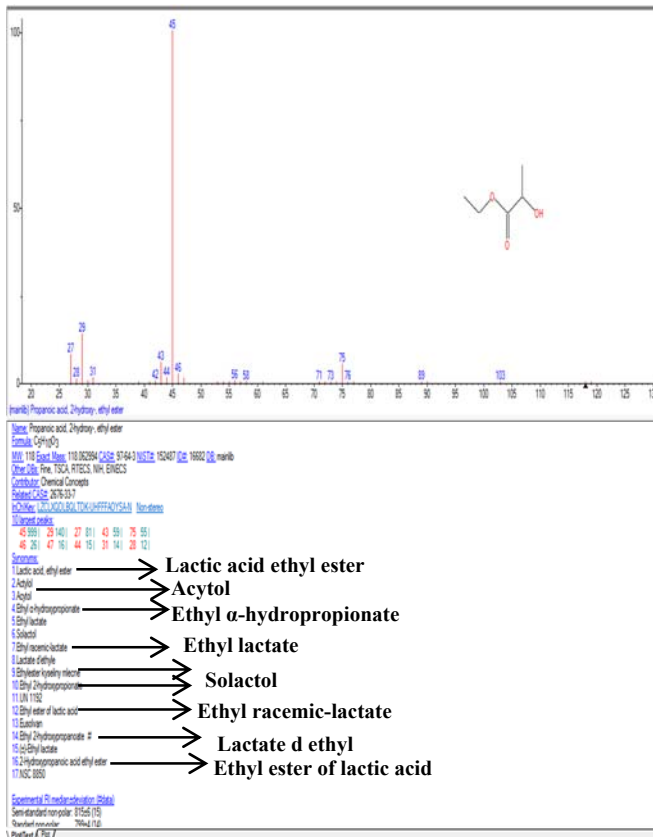
Fig. 9. MS Library spectra for ethyl lactate solvent.

Fig. 10 shows a plot of the solvent concentration against agitation time at the esterification temperature of 60 °C. From fig. 10, it was found that the solvent concentration increases with increase in agitation time (sec). According to Nie et al. [19], the effect of external mass transfer diffusion limitation between the liquid components and the resin catalyst can be avoided by increasing the agitation time of the esterification reaction. The stirring time was set between 400 – 800 rotation per minute (rpm). The stirrer time was found to be stable above 400 rpm. It was suggesting that with the stirring time above 400 rpm, there was no resistance to external mass transfer limitation and as such, all further experiments were performed at 800 rpm.
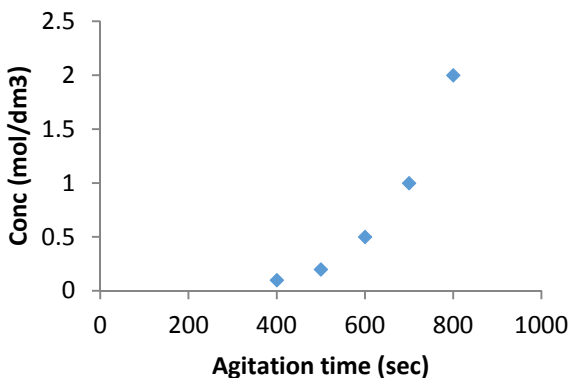

Fig. 10. Concentration (mol/dm^3) against agitation speed (sec).

Fig. 11 (a-d), presents the SEM images of the fresh commercial resin catalysts before and after esterification at

60 °C. It can be seen that the surfaces of dowex 50W8x (11a) and amberlyst 36 (11b) before the esterification reaction showed a very smooth surface indicating that the resin catalysts were defect-free. A similar result was obtained by Zhang et al [3]. From fig. 11c (Dowex 50W8x after esterification) it was observed that the catalysts exhibited some tiny bubble-like structure which was attributed to the effect of temperature of the resin catalyst after the esterification process. However, from fig. 11d (Amberlyst 36 after esterification) it was found that amberlyst 36 showed no sign of crack on the surface indicating that this catalyst has a greater thermal stability at 60 °C in contrast to the dowex 50W8x catalyst at the same temperature.
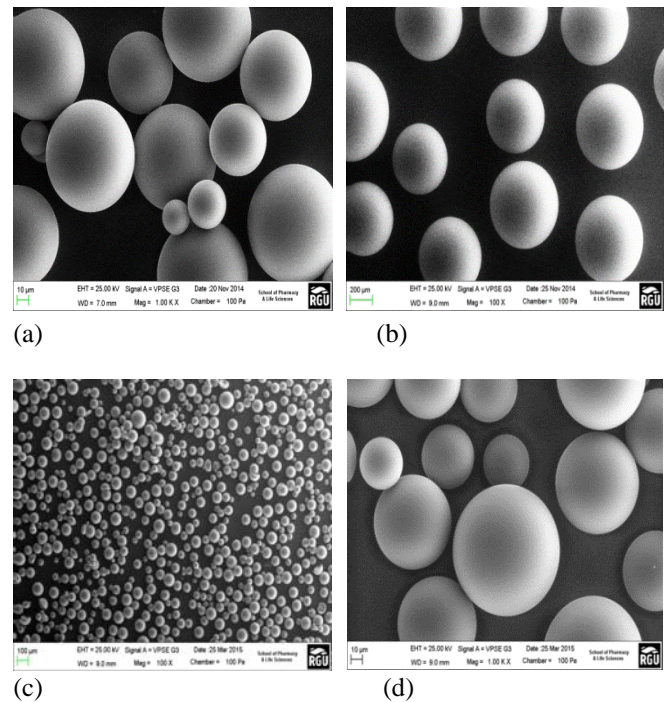

Fig. 11. 11a (Dowex 50W8x before), 11b (Amberlyst 36 before), 11c (Dowex 50W8x after) and 11d (Amberlyst 36 after): SEM surface morphology of Amberlyst 36 and Dowex 50W8x resin catalysts before and after esterification reaction at 60 °C.

Fig. 12 present the EDXA of the resin catalysts before esterification and after the esterification reaction process. These figures explain the elemental composition of the resin catalysts before and after the esterification process. From fig. 12a, elements including carbon (C), oxygen (O) and sulphur (S) before the esterification process are identifiable. However, from fig. 12b, it can be seen that carbon (C), oxygen (O), aluminium (Al) and sulphur (S) are present. It was observed that although the same elements were found to reflect in the spectra of the resin after esterification, sulphur was found to exhibit a higher peak in contrast to other elements. It was also observed that Al was found on the spectra of the resin catalyst after the esterification reaction process which was as a result of the solvent from the esterification reaction. Sulphur was also found to appear twice on the spectra of the resin catalysts after esterification. This was attributed to the sulfonic acid functional group of the resin catalysts.
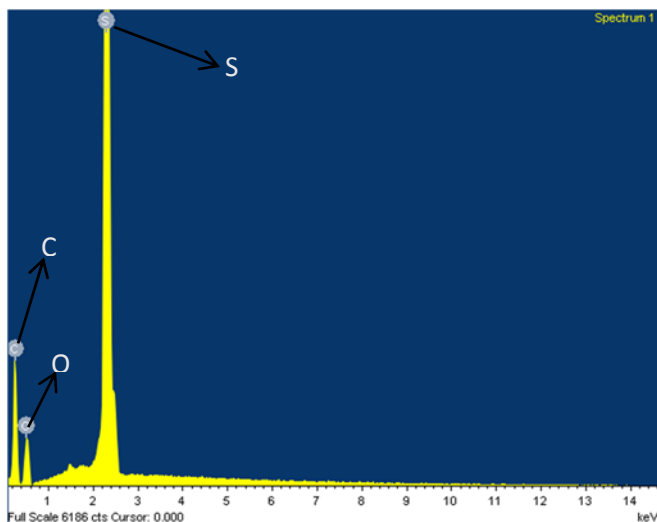
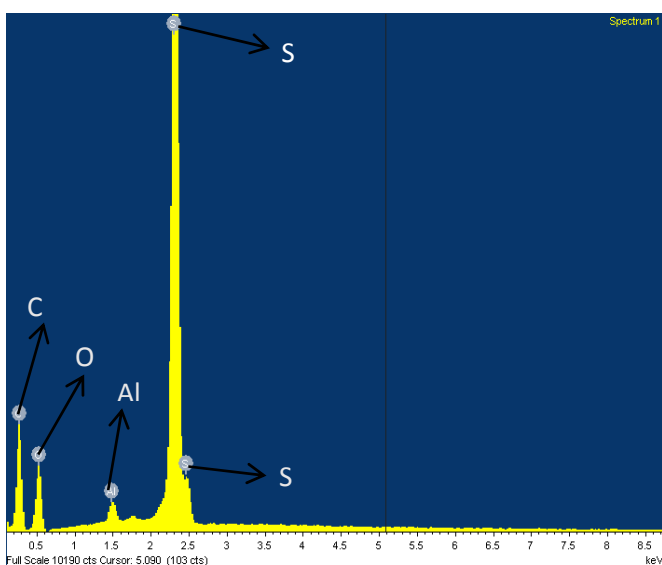Fig. 12a. EDXA of the resin catalysts before esterification reaction.

Fig. 12b. EDXA of the resin catalyst after esterification reaction.

V.   CONCLUSION

The batch process esterification reactions of lactic acid and ethanol catalysed by cation-exchange resin catalysts for the production of environmentally-friendly solvent was achieved. The SEM surface of the cation-exchange before esterification showed a defect-free surface whereas the surface of the catalyst after esterification showed a bit of crack indicating the effect of temperature on the surface of the resin catalyst. The mass spectra result generated from the ion chromatogram of the reaction product confirm the presence of ethyl lactate solvent which matches the library spectra of that of the commercial ethyl lactate used as the reference sample. The SEM results of the amberlyst 36 confirm that the catalyst has more resistance to temperature in contrast to Dowex 50W8x. This also suggests that the produced reaction product with amberlyst 36 can be used for industrial purposes. The order of the catalytic activity with respect to the SEM analysis was amberlyst 36 > Dowex 50W8x. The EDXA of the resin catalysts showed sulphur as

the highest peak both before and after the esterification process. The concentration of the reaction product was found to increase with increase in the agitation time.

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