Esterification of Lactic Acid and Ethanol using Heterogeneous Catalysts for the Production of a Bio-based Chemical

O Edidiong, S Habiba and *E Gobina

Abstract— In this work, the batch process esterification reaction was carried out at 80 °C using different types of heterogeneous catalysts. The heterogeneous resin catalysts used for the analysis were amberlyst 15, amberlyst 36, amberlyst 16 and dowex 50W8x. The esterification product was analysed using autosampler gas chromatograph coupled with mass spectrometer (Agilent technology 7890B). The surface morphology of the resin catalysts after the esterification process was examined using scanning electron microscopy (The Zeiss EVO LS10) coupled with energy dispersive analysis of x-ray (The Oxford INCA System) (SEM/EDAX). The SEM of amberlyst 36 and 16 showed a defect-free surface in contrast to amberlyst 15 and dowex 50W8x. The EDAX spectra of the resin catalysts confirmed the presence of elements including carbon, oxygen, sulphur, and aluminium. Amberlyst 36 exhibited a large pore after the esterification process in contrast to other catalysts. Sulphur showed the highest peak on the EDAX of the resin. Dowex 50W8x and amberlyst 36 resin catalysts were found to elute faster at 1.523 and 1.527 min respectively in contrast to amberlyst 15 and amberlyst 16 at 1.521 and 1.503 min respectively. The increasing order of the retention time after the esterification process at 80 °C was dowex 50W8x > amberlyst 36 > amberlyst 15 > amberlyst 16. The liquid nitrogen adsorption at 77 K (Quantachrome 2013) was used to determine the surface area, pore size and the total pore volume of the cation-exchange reins. The BET surface area of the resin catalyst was found to be higher (14.302 m^2/g) with hysteresis loop confirming a good interaction of the catalysts with the reactant solvent.

Key words: Cation-exchange resin, esterification, ethyl lactate, ethanol, adsorption and characterisation.

I. INTRODUCTION

The Chemical industries is currently faced with a lot of problems including the use of homogenous acid catalysts in solving the chemical equilibrium limitations of esterification reaction involving a carboxylic acid and alcohol to produce organic esters and water as the by-product. In the past decade,

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organic solvents including chloroform, carbon tetrachloride and benzene have shown a lot of environmental and health problems which have resulted in their removal from general use as petrochemical solvents because of their carcinogenic and toxic effects [1]. Volatile organic compounds (VOCs) including toluene and hexane, have been implicated in the production of photochemical smog, whereas chlorofluorocarbons (CFCs) have been removed from their general use [1]. The major reason for replacement chemicals has been to avoid the environmental impact resulting during separation. However, a lot of research effort has been made on the replacement of VOCs and chlorinated solvents.

Ethyl lactate (EL) has shown a lot of promise as a powerful non-toxic replacement for petroleum-based solvents that have dominated U.S and the world market over the years [2, 3]. EL has proven to replace numerous halogenated and environmentally damaging toxic chemicals including carcinogenic methylene chloride, chloroform, acetone, xylene and chlorofluorocarbons (CFCs) due to its high solvency properties [4,5,6]. Ethyl lactate may be obtained from the esterification reaction including lactic acid and ethanol in the absence or presence of catalysts. Recently, 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 due to chemical equilibrium [7,8]. In the synthesis of ethyl lactate, water is also obtained as a by-product. However, water does not only cause the thermodynamic equilibrium limitations, but also hydrolyses the ester resulting in an hindrance in the reaction efficiency [9]. Aside from thermodynamic equilibrium limitation, reaction yield can also be limited by other factors such as mass transfer and heat that is generate during the esterification. These limitations can be eliminated by altering the reaction design to enhance the reaction yield [10].

Several researchers have shown a lot of interest on the selective removal of one or more product from the reaction system by distillation process in the presence of homogeneous catalysts. Esterification is an extensively used reaction especially in the chemical industries including adhesive, solvent of paints, pesticides emulsifier, fragrances and flavour and also in pharmaceutical, food industries as well as the production of biodiesel [11]. Esterification reactions are typically slow and need several days attain equilibrium in the absence of a catalyst [12]. The use of homogeneous catalysts including sulphuric acid (H_2SO_4), hydrochloric acid and (HCl) have cause a lot of negative impact such as corrosion of the esterification equipment,

miscibility with the reaction medium, and environmental pollution [11,13]. The environmental effect and the safety aspects for the production of chemicals are the major issues to ensure the sustainability of the industrial production. However, numerous industrial esterification processes over the world are still performed under homogeneous conditions. In spite of the numerous esterification studies with heterogeneous catalysts, only very few studies consider the effect of adsorption, reaction and diffusion in the heterogeneous system in contrast to the homogeneous system. As such, the reaction mechanisms and the rate expression are more complicated in contrast to that of the homogeneous catalyst [14]. Amberlysts solid heterogeneous catalyst are commercially available non-hazardous and reusable catalysts which are made up of styrene-divinyl benzene matrix coupled with sulfonic acid groups as active sites but they exhibit low thermal stability and hence can be used in high temperature reactions [13]. According to Sharma et al. [15], the kinetics of the esterification reaction products can be analysed using two methods; either by titration or using gas chromatography (GC) with a choice of detector including flame ionization (FID) and thermal conductivity as well as carrier gas including hydrogen, helium, argon and nitrogen. However, very few studies have considered the use of mass spectrometry (MS) detector.

In this work, the batch-wise esterification process of lactic acid and ethanol in the presence of cation-exchange resin was carried out using the GC-MS, the activity of the different catalyst for the removal of water from the esterification process was determine. The reaction kinetics was analysed by comparing the retention time and the peak area of the reaction product for the different catalyst.

II.   EXPERIMENTAL

A. Materials

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. Helium gas (99.98% purity) was supply by BOC, UK. The deionised water used for the washing of the catalysts was supply by the Centre for Process Integration and Membrane Technology (CIPMT), Robert Gordon University (RGU), Aberdeen, United Kingdom.

B. Method and Procedure

Fig. 1 shows the batch process esterification reaction set-up. Prior to the esterification process, the fresh commercial resins were rinsed with deionised water and ethanol and were oven dried at 65 ^{o}C for 24 hrs to completely remove any poisonous substances and moisture. 30 mL amount of lactic acid with 5g of the different cation-exchange resins were charged into the reactor and heated to 80 ^{o}C. After the desired temperature has been research, 50 mL of ethanol which has been heated separately using the heating mantle was added to the mixture in the reactor. The stirring and heating of the reaction mixture was achieved using a

magnetic hot plate with a stirrer. About 1 mL of the reactant mixture was taken out for analysis with the GC-MS analysis using helium gas (99.98% purity) as the carrier gas. A similar method to that of Jogunola et al. [16] was adopted for the catalysts preparation process. 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. As part of the quality control measures, a blank analysis was carried out in order to clean the GC column prior to the analysis. The NIST GC software program was used for data collection. The quantitative analysis of the reaction product in the presence of each cation-exchange resin at 80 ^{o}C was performed in duplicate for repeatability and the chromatogram, mass spectra, retention time and peak area were compared.
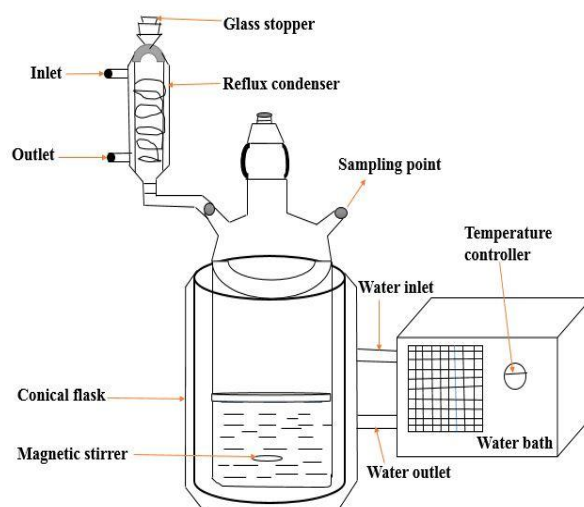

Fig 1. Batch process esterification reaction set-up.

C. Equipment

Fig. 2 shows the GC-MS instrument that was used to detect and identify esterification reaction product. Ar and N2 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 ^{o}C/min, at 63.063 kPa. The sample was heated at the column temperature of 300 ^{o}C. The Helium gas temperature was set at 40 ^{o}C with the flow rate of 1.2 mL/min and equilibration time of 0.25 mins. The Helium gas inlet pressure was 100 psi. The oven temperature was program at 40 ^{o}C with the holding time of 2 mins at maximum operating temperature of 250 ^{o}C. The sample scanning rate was 9.773 mins. The solvent set in split mode with the split ratio of 50.0. The resin catalysts were also analysed by SEM/EDXA (The Zeiss EVO LS10) in other to examine the surface morphology of resin after the esterification process. The BET surface area and the BJH pore size of the resin catalyst were determined using Quantachrome 2013 liquid nitrogen physisorption method at 77 K.

Fig 2. 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

The concentration for the ethyl lactate solvent was calculated using the formular:

$$C_1V_1 = C_2V_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .....(1)$$

Making C_2 the subject of the formular:

$$C_2 = \frac{C1V1}{V2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots ..\ldots ......(2)$$

Where C_1 is the initial concentration of ethyl lactate (gdm^3), V_1 = Volume of the reactant (dm^3), V_2 = known volume (dm^3) and C_2 = final concentration (g/dm^3).

The effect of the internal diffusion of the cation-exchange resin can be estimated using the following equation

$$\varphi = \frac{r_o^2 k}{9D_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .(3)$$

Where φ = the thiele modulus, k = rate constant (mol g^{-1}s^{-1}), De = effective diffusion coefficient (m^2 s^{-1}) and r_o= radius of the catalyst particle (m). If φ is less than 1, the internal mass transfer can be ignored [4].

The conversion of ethyl lactate solvent in esterification reaction can be obtained using the following equation:

$$\text{Conversion (\%)} = \frac{C_0 - C_i}{C_o} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots ..(4)$$

Where C_o and C_i represents the initial acid concentration and the final acid concentration at determined reaction time respectively [5].

III. RESULT AND DISCUSSION

A. Retention time and Peak Area

Table 1 shows the retention time and peak area comparison of the esterification product catalysed by the different resin catalysts at 80 ^{o}C. From table 1, it was also found that the retention of the esterification product increase with respect to the peak area. Dowex 50W8x and amberlyst 36 showed a higher retention time at 1.527 and 1.523 min with the peak area of 142522149.5 and 138638054.1 m2 respectively in contrast to amberlyst 15 and amberlyst 16 which were found to elute first at 1.521 and 1.503 min with the peak area of 149055537.3 and 119782347.8 m2 respectively as also shown chromatogram in Fig. 3a-d. Although dowex 50W8x resin was found to elute first at 1.523min, from the spectra of the esterification product catalysed by dowex 50W8x as shown in figure 3d, it was found that only a few peaks were found on the spectra. However, amberlyst 36 and amberlyst 16 resins exhibited a retention time of up to 10.490 and 10.502 min respectively suggesting the strong catalytic performance of the resin catalysts in the thermodynamic process of lactic acid esterification to produce ethyl lactate. Also from Fig. 3a – d, it was found that amberlyst 36, 15 and 16 showed more peaks on their respective chromatogram in contrast to dowex 50W8x. The GC-MS of the esterification reaction product was in accordance with that of the commercial ethyl lactate confirming the structure of the ethyl lactate. The increasing order of the retention time of the resin catalysts after the esterification process at 80 ^{o}C was dowex 50W8x > amberlyst 36 > amberlyst 15 > amberlyst 16. A similar work was also obtained in our previous study at 60 ^{o}C [17].

Table 1: Comparison of retention time and peak area of the esterification product catalysed by the different catalysts at 80 ^{o}C

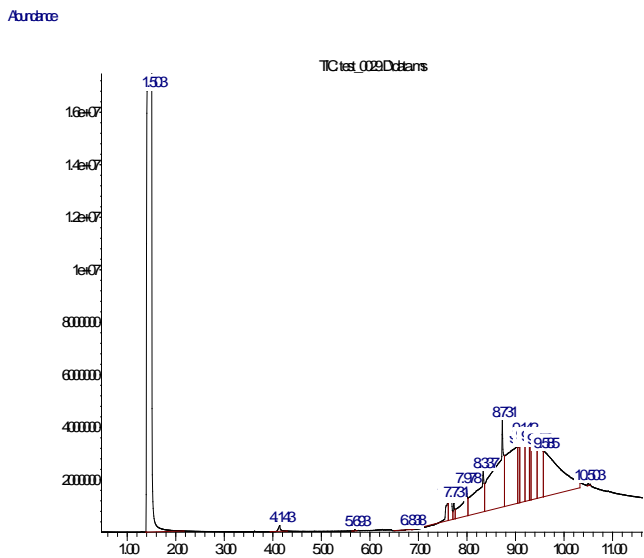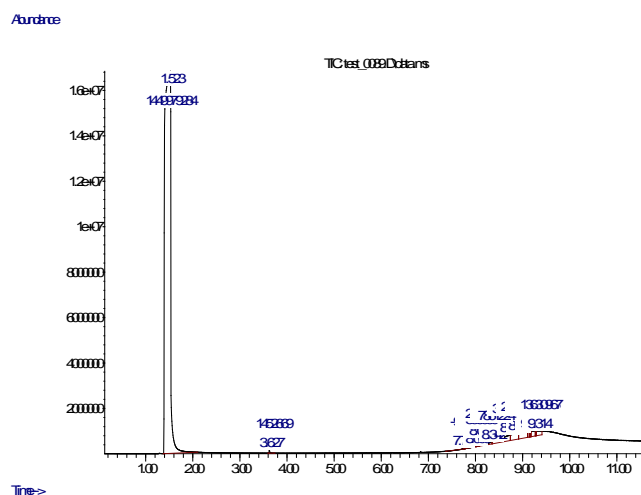| Catalysts	Retention time (min)	Peak Area (m^2)
Amberlyst 15	1.521	149055537.3
	4.169	1761909.18
	7.738	4826559.45
	9.218	113978453.4
Amberlyst 16	1.503	119782347.8
	4.143	9286786.17
	8.731	283366480.1
	10.502	23075482.13
Amberlyst 36	1.527	138638054.1
	3.628	98634990
	7.975	97944520.42
	8.726	121332143.6
	10.490	14091694.59
Dowex 50W8x	1.523	142522149.5
	3.627	78276693.15

Fig 3a. Chromatogram of the esterification product catalysed by amberlyst 16 at 80 °C.
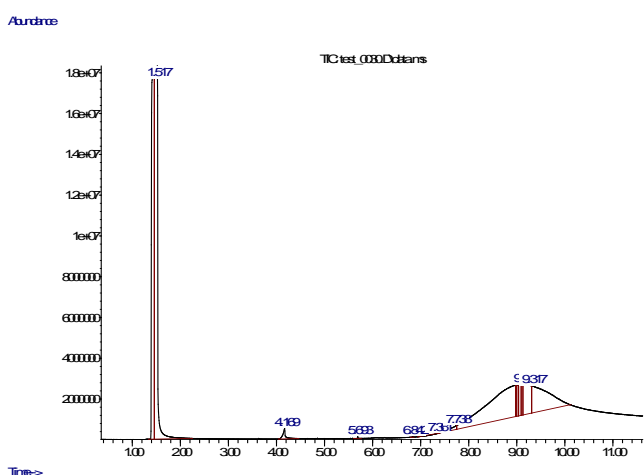

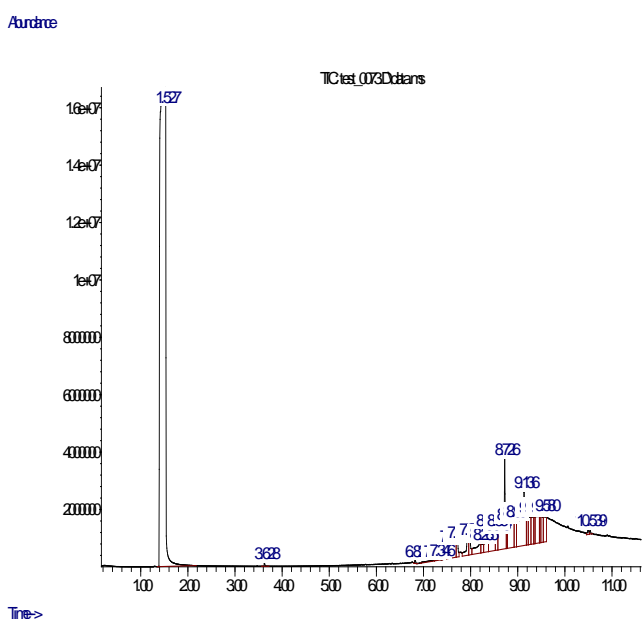Fig 3b. Chromatogram of the esterification product catalysed by amberlyst 15 at 80 °C.

Fig 3c. Chromatogram of the esterification product catalysed by amberlyst 36 at 80 °C.

Fig. 3d. Chromatogram of the esterification product catalysed by dowex 50W8x at 80 °C.

### A. Effect of Reaction Temperature

Prior to the esterification analysis, the resin catalysts were rinse before the esterification reaction. During the rinsing of the catalysts with deionised water and ethanol, amberlyst 36 and dowex 50Wx8 showed a higher activity in contrast to amberlyst 16 and amberlyst 15. The increasing other of the catalytic activity was dowex 50Wx8 > amberlyst 36 > amberlyst 16 > amberlyst 15. The batch reactor experiments were carried out at different temperatures of 60, 80 and 100 °C to determine the effect of the temperature on the different catalysts. It was observed that amberlyst 15 resin catalysts showed some degradation with respect to temperature.

B. Effect of Catalyst Loading

Prior to the esterification analysis, 5g of the four different catalysts were loaded at each temperatures of 60, 80 and 100 °C. The catalyst loading varied in mole ratio of 1:2 and 2:3 weight %. From the result obtained, it was found that the higher the catalyst loading, the faster the equilibrium was reached, due to the increasing number of acid sites available for the reaction to take place. A similar result was obtained by Sanz et al, [18]. Amberlyst 15 hydrogen was found to react most with the lactic acid and ethanol at each catalysts loading in contrast to other resin catalysts.

Fig. 4a and b shows the SEM/EDXA of the amberlyst 36 and 16 resin catalysts after the esterification process at 80 °C respectively. From Fig. 4a, it can be seen that, the SEM image of amberlyst 36 showed a defect–free surface. However, amberlyst 16 (4b) exhibited crack on the surface confirming the low resistance of the resin catalyst to temperature after the esterification process. From fig. 4a and b, it was also found that the EDAX of the resin catalysts showed the presence of the different elements on the spectra including sulphur (S), carbon (C), silicon (Si), Titanium (Ti) and oxygen (O). As expected, sulphur exhibited the highest peak on both the spectra of the esterification product catalysed by amberlyst 36 and 16 in contrast to other elements. Also carbon and oxygen were also found to

exhibit a higher peak on the spectra of amberlyst 36. However, S and O were suggested to occur from the sulfonic acid functional group on the structure of the resin catalysts whereas, other element including Si, Ti and carbon were suggested occur as the results of some contaminant or impurities from the lactic acid and solvent used as the reactant solvent in the esterification process.
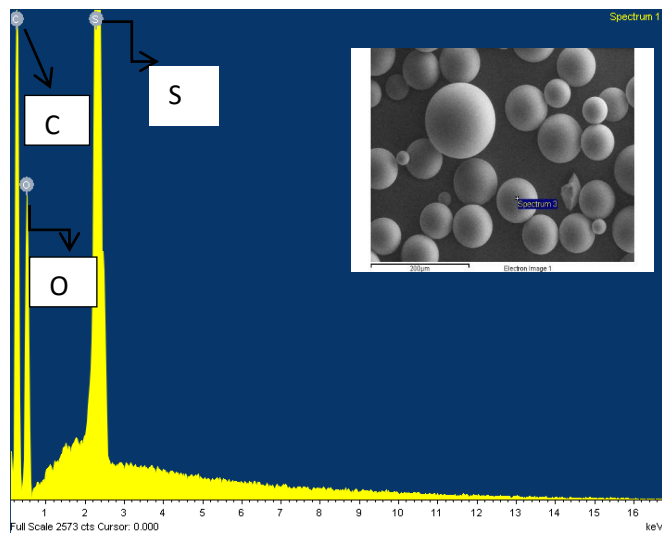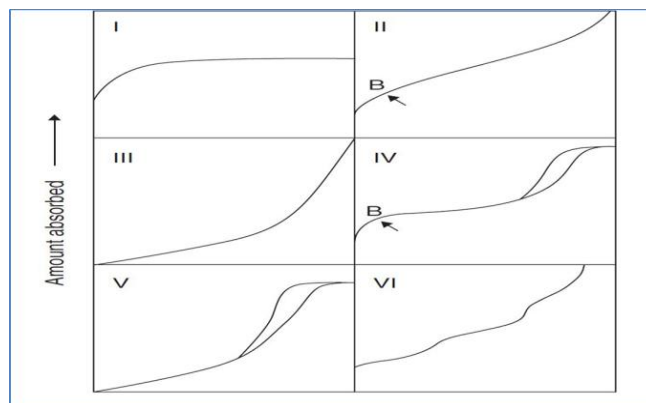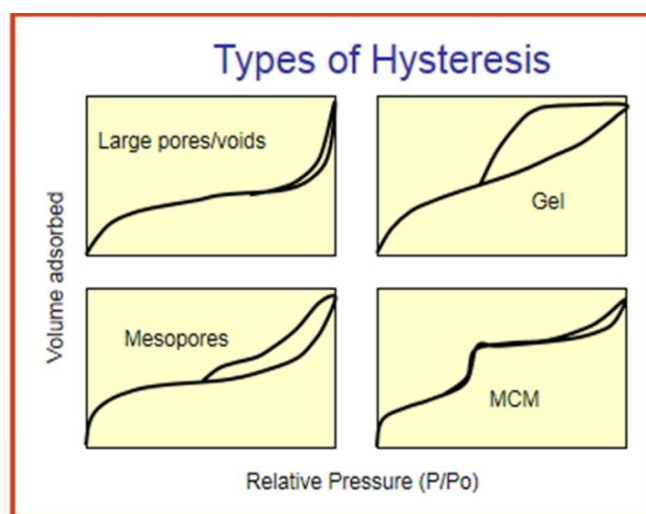

(a) Amberlyst 36
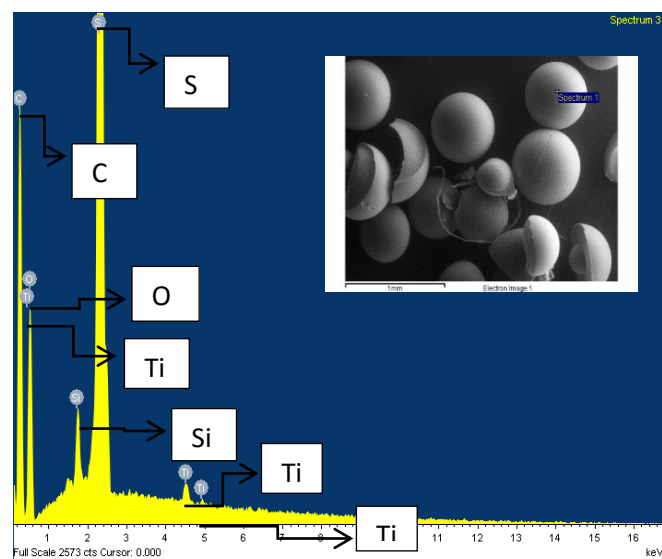
(b) Amberlyst 16

Fig. 4a and b. SEM/EDXA images and spectra of the amberlyst 36 (a) and SEM/EDXA images and spectra of amberlyst 16 (b) after esterification reaction at 80 ^{o}C.

According to Smart et al. [19], the different types of physisorption isotherms and hysteresis can be explained as shown in Fig 5a and b respectively.

(a)

(b)

Fig. 5a and b. Types of physisorption isotherms (5a) and Types of hysteresis (5b).

Fig. 6a and b depicts the Liquid nitrogen adsorption of the resin catalyst at 77K. From Fig. 6a, it was found that the BET curve of the resin catalysts showed a flat curve with a very small hysteresis loop on the curve indicating a type IV physisorption isotherm [18],[20]. The BET surface area of the resin catalyst was found to be high (14.302 m2/g) confirming a good interaction of the catalysts with the reactant solvent during the esterification reaction process. A similar result was also obtained in our previous study [21]. However, the results were found to be in the range of that reported in the literature for this type of mesoporous material [22].

From Fig. 6b, it was observed that the pore size of the resin catalysts was found to be 33.839 nm, while the pore volume of the resin catalyst was found to be 0.137cc/g. It was found that the material exhibited a higher pore size in the mesoporous range of 2-50 nm, which was in accordance with the International Union of Pure and Applied Chemistry (IUPAC) classification of physisorption isotherm for mesoporous material [23]. From the BET and BJH results, it was suggested that the material was suitable in solving the equilibrium problem of esterification reaction.
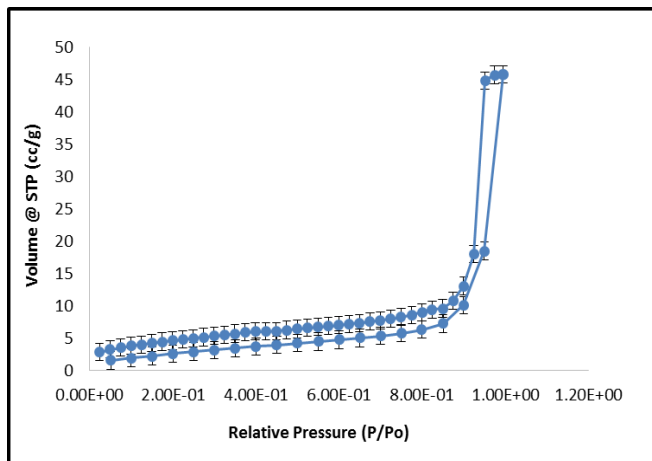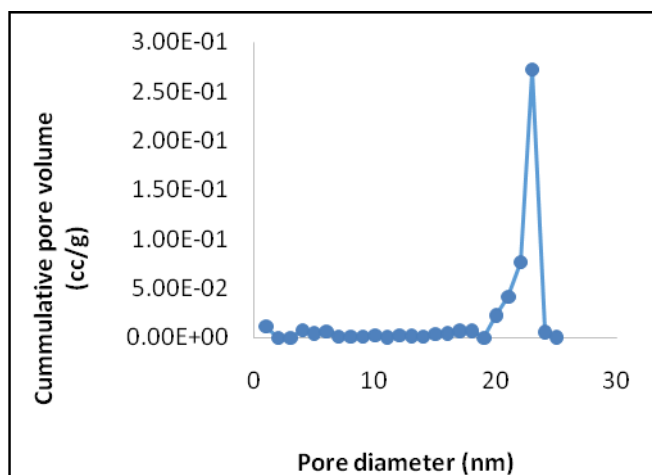
Fig. 6b. BET isotherm for amberlyst 15 at 77K.

Fig. 6a. BJH curve for amberlyst 15 at 77K.

IV. CONCLUSION

The esterification of lactic acid and ethanol in the presence of heterogeneous catalysts for the production of a bio-based solvent was successfully carried out in a batch mode. The elution time of the resin catalysts was found to increase with respect to the peak area. Amberlyst 36 and dowex 50 showed a higher elution time. Amberlyst 36 and amberlyst 16 showed much peaks on the spectra in contrast to other catalysts confirming a higher catalytic effect of the reins for the equilibrium shift in the esterification process. Amberlyst 36 was found to be a good catalyst for solving the solving the equilibrium limitation problems in the esterification of lactic acid to produce ethyl lactate. The EDAX of the resin catalysts showed different elements on the spectra including carbon, sulphur, silicon and oxygen. Sulphur was found with a higher peak on the spectra in contrast to other elements. The BET surface area and BJH pore size of the resin catalysts were found to be large confirming a mesoporous material with hysteresis based on the IUPAC classification.

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