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Pervaporation study of Propionic Acid with Ethanol using heterogeneous catalyst in integrated Esterification-Pervaporation system

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Abstract : Pervaporation can be used to enhance the yield of esterification reactions via selective removal of water from the product mixture. Esterification of propionic acid with ethanol over the ion exchange resin, Dowex 50Wx8-400 and sulfuric acid with and without pervaporation has been studied. Various parameters such as, catalyst loading (0.05 to 0.25 mL using H_2SO_4 and 7.11 to 27.11 g using Dowex 50 Wx8-400), effect of molar ratio (1:1 to 1:2.5), and temperature (40 to 70°C) were analyzed. The change in standard enthalpy and entropy of the reaction under same condition were estimated to be 36.07 kJ mol^{-1} and 127.53 J mol^{-1} K^{-1}. Characterization analysis of ion exchange resin was performed using scanning electron microscope (SEM-EDEX) and X-ray differaction (XRD).Using pervaporation-assisted esterification 68% enhancement in the conversion of ethyl propionate was achieved.

Keywords : Dowex 50Wx8-400, pervaporation, batch esterification, propionic acid, ethanol.

Introduction

Process intensification involves imperatives like make it small, combine and use of alternative driving forces. Pervaporation used as the emerging separation techniques based on the principles of process intensification. Phase change through membrane is employed for separation of components present in low concentration in the feed streams. Pervapoation technique differ from other membrane process such as Ultra filtration (UF), Microfiltration (MF) and Reverse osmosis (RO) with respect to its applications in areas of close boiling mixtures, similar size molecules and non volatile solute components.

Pervaporation has been recently employed in the form of hybrid system with reactors where the reactor mass is pumped into the pervaporation system. This leads to the separation of one of the products of reactions and hence intensifying a reversible reaction (based on Le-Chatelier's principle). After inventing of selective and permeable membranes, which selectively remove only the desired component, has resulted to increase in yield and separation with continuous production in the hybrid process. This leads to a reduction in the size of the plant as well as increase the driving force for production.

In recent years, pervaporation has been used as a strong, effective and novel energy – efficient technique in separation and purification industry. Various types of membranes have been used in pervaporation process by various authors i.e.poly dimethyl isiloxane membrane,[1] PVA (Poly vinyl alcohol) / porous composite ceramic membrane,[2] PVA-PES (Poly vinyl alcohol – polyether solfone),[3] PERVAP 2201,[4]embedded nano-iron

polysulfone membrane,[5]blended membrane PVA-Pectin.[6]Pervaporation has also been studied as an efficient process for the separation of organic mixtures (liquid) which are more difficult to separate by another application of other processes such as distillation, etc. Azeotropic mixture, close boiling point mixtures etc. has been separated by pervaporation process without any additional heat loads or external substances.

Pervaporation in recent years have found application in petrochemical, pharmaceutical, purification industries, biochemistry, environment, chemical, food, cosmetic industry, chemistry, waste removal plant, etc. Reactions like esterification and etherification have been recent in the list of the potential applications of pervaporation own to their lower yield as these reactions are equilibrium reactions. Reaction parameters such as temperature, concentration and type of catalysts and using excess of reactant have been the parameter that needs to be optimized by extensive research, for higher yield.Simultaneous removal of the product of the reaction leads the reaction to move in a forward direction, as according to the Le chatelier's principle, and hence resulting increase in the conversion.

Study for the comparison of conversion of with and without pervaporation of benzyl alcohol and acetic acid using p-toluene-sulphonic acid, employing GFT membrane (GFT Pervap 1005) was employed.[7]Without pervaporation, conversion of the acid remains constant at approx 0.45, however, with pervaporation aided esterification (PAE), the conversion was found to increase with time and reach to an approximate conversion of 0.60. The Esterification reaction of acetic acid with ethyl alcohol using an acidic ion exchange resin catalyst (Amberlst-15) in a packed bed reactive distillation column operated in both batch and continuous modes, at temperature between 323 and 343 K.[8] In the formation of ethyl acetate, activation energy was found to be 104.123 kJ kmol^{-1}. It has been reported by various researchers, that continuous mode gave the highest ethyl acetate production compare to batch mode. Rate of reaction and equilibrium constants were calculated from conversions at equilibrium and were found to be almost constant over the range of experiments carried out. Effect of catalyst loading, the effect of initial water concentration, effect of temperature was also studied. The equilibrium constant was found to be approximately $K_{eq} = 4.0 \pm 0.2$ at 353 K. The parameters of the Arrhenius equation, activation energy, frequency factor were also determined for the forward reactions at different temperatures.

Esterification of adipic acid with methanol over Amberlyst 15 catalyst was performed to determine the effect of temperature (313, 323, 333 K), catalyst loading (5%, 7%, 10%) and alcohol to acid molar ratio (10:1, 15:1, 20:1).[9]Esterification of acrylic acid with methanol using Amberlyst 15 for synthesis of methyl acrylate.[10]Modeling and simulation of moving bed reactor (SMBR) was implemented and the optimal point of operation was determined. It was found that about 12 mol of methanol /mol of methyl acrylate was needed to obtain 98% conversion of acrylic acid. Esterification of ethanol and lactic acid using Amberlyst 15 in PERVAP 2201.[11] It was observed that in studies on dilute lactic acid esterification (nEtOH/nHL1 =2, T$_{reaction}$ = 348.15 K, TPV = 342.15 K, A/Vo =23m^{-1}, catalyst = 2wt %), water weightfraction in the reactor continuously decreases with time and ethyl lactate weight fraction continuously increases with time. It is due to the shifting of the conversion beyond the equilibrium conversion due to the water removed by pervaporation. [3]Lactic acid and iso-propanol as raw materials for the esterification reaction using sulfuric acid as a catalyst were used. Polyvinyl alcohol-polyether sulfone (PVA-PES) composite hydrophilic membrane was used for pervaporation-assisted esterification. Several parameters such as, initial mole ratio of Iso-propanol over lactic acid, the ratio of the effective membrane area over the volume of the mixture, process temperature variation and catalyst concentration were discussed.

Very little work on the esterification of monocarboxylic acid with lower alcohols have been found in literature and till date there has been no work on the pervaporation aided esterification of propionic acid using Dowex 50Wx8-400 with ethanol as alcohol. In the present work, propionic acid and ethanol was used for ester production. The effect of temperature, catalyst dosage, ethanol/propionic acid molar ratios, and percentage yield were also investigated.[12]Dowex 50Wx8-400 and sulfuric acid were used as catalyst. Investigations were built up through use of homogeneous and heterogeneous catalyst.[13]

Experimental

Esterification reaction was studied in a jacketed tank reactor. Ethanol, propionic acid and catalyst (Dowex 50Wx8-400 and sulfuric acid) were of analytical grade and obtained from Sigma Alderich, India. The
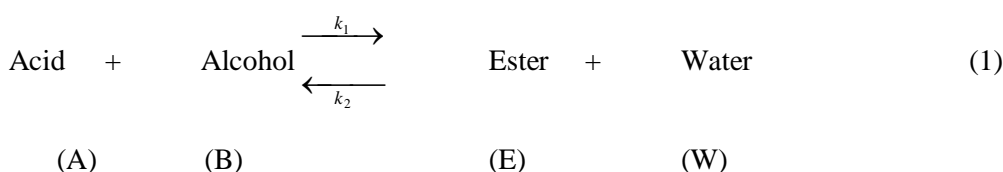
reagents were heated separately before being fed into the reactor. Samples were withdrawn at definite time interval to determine the concentration of reacting components. Esterification kinetics was performed at various temperatures (40, 50, 60 and 70 °C). Catalyst concentration varied from 11.3 to 28.2 g L^{-1} in the case of Dowex 50Wx8-400 and 0.17 to 0.83 wt% in the case of sulfuric acid. Molar ratios were varied as 1:1; 1:2; 2:3; 3:2 in the experiments on esterification studies and 1:1 to 1:2.5 in the pervaporation aided esterification studies. Reaction components were determined by gas chromatography (NUCON GC 5700) using packed column at oven temperature of 453 K, injector temperature of 423 K and detector temperature of 453 K. The pervaporation setup consists of a 3L heating jacketed stainless steel reactor with digital temperature and pressure indicator. Membrane module is of SS having size of test cell: 240mm x 180mm x 25mm and having an active membrane area of 0.0155m^2.

In the hybrid system the various parameters were employed as; temperature: 313, 323, 333 and 343 K; catalyst (Dowex 50Wx8-400) concentration 11.3-28.2 g L^{-1} and molar ratios: 1:1 to 1:4. Polyvinyl alcohol-polyether sulfone (PVA-PES) membrane was employed in the pervaporation setup.

Results and discussion

General pervaporation-aided esterification kinetics[14]

The reaction between propionic acid and ethanol was represented as

$$\text{Acid} \quad + \quad \text{Alcohol} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \quad \text{Ester} \quad + \quad \text{Water} \tag{1}$$

(A)   (B)   (E)   (W)

Reactions were carried out in the presence of catalysts. Homogeneous catalysts (sulfuric acid, HCL, p-tolune sulfonic acid) or heterogeneous catalyst (Amberlyst™ 15, Amberlyst™ 36, Amberlyst™ BD 20, and Amberlyst™70, Amberlite IR-120, Amberlyst 36[15-17] were used in the reaction.

Where, A is propionic acid, B is ethanol, E is ethyl propionate and W is water. Esterification is highly reversible reaction therefore pseudohomogeneous kinetic model has been used to analyze the behavior of the reaction. So the reaction rate equation can be written for forward and backward rate constants as follows:

$$r_w = k_f C_A C_B - k_b C_E C_W \tag{2}$$

where r_w is the reaction rate of water permeation (mol kg^{-1} h^{-1}), C_A, C_B, C_C, C_D are the concentration of propionic acid, ethanol, ethyl propionate and water in g mol lit^{-1} at a particular time. k_f and k_b are the forward and backward reaction rate constants. Generally the rate constants are function of activation energy and reaction rate constant.

$$r_w = k_0 \exp\left(-\frac{E_a}{RT}\right)\left(C_A C_B - \frac{1}{Keq} C_E C_W\right) \tag{3}$$

The homogeneous esterification reaction rate equation without a catalyst

In pervaporation reactor, hydrophilic membrane (water selective) is used, so water is continuously removing from the permeate side of the perveporation reactor because is a continuous mode reactor so water balance in pervaporation reactor can be written as follows:

$$\frac{dC_W}{dt} = \left(k_f C_A C_B - k_b C_E C_W\right) - \frac{S}{V} J_W \tag{4}$$

where S is effective membrane area (m^2), V is the volume of the reaction mixture(m^3) of and Jw is the permeate water flux (kg m^{-2} h^{-1}).

The relation between flux and feed water concentration can be written as

$$J_W = k_{PV1} C_W - k_{PV2} C_W{}^2 \qquad (5)$$

The concentrations of ethyl propionate, ethanol and propionic acid in permeate side were negligible as compared to water.Hence the material balance of ethyl propionate, propionic acid and ethanolwas as follows:

$$\frac{dC_E}{dt} = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = \left(k_f C_A C_B - k_b C_E C_W \right) \qquad (6)$$

The effect of catalyst in the rate equation

$$A + B + C \Leftrightarrow E + W + C \qquad (7)$$

where C represents the catalyst amount in the esterification reaction.

Reaction rate constants for forward and backward reactions are taken as:

$$k_f = k_0 \exp\left(-\frac{E_a}{RT}\right) \qquad and \qquad k_b = k_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (8)$$

In the integrated pervaporation unit with the reactor, simultaneous removal of the product from the reactor needs to be subtracted from the equation accounting for the change of product concentration in the reaction mass.Hence, the overall rate of disappearance of component B can be given by:

$$-\frac{dC_B}{dt} = \left(k_f C_A C_B C_C - k_b C_E C_W C_C \right) \qquad (9)$$

$$-\frac{dC_B}{dt} = k_1 C_C \left(C_A C_B - \frac{C_E C_W}{K_{eq}} \right) \qquad (10)$$

where $\quad K_{eq} = \frac{k_f}{k_b} = \frac{\left(C_E C_W\right)}{C_A C_B} \qquad (12)$

K_{eq} is equilibrium constant which is the proportion of forward and backward reaction rate constants so,

$$-\frac{dC_B}{dt} = k_{obs} \left(C_A C_B - \frac{C_E C_W}{K_{eq}} \right) \qquad (13)$$

wherek_{obs}depends on the catalyst concentration and reaction temperature. Thus, in the pervaporation aided esterification process, the change in water concentration may be represented by Eq. (14).

$$\frac{dC_w}{dt} = k_{obs} \left(C_A C_B - \frac{C_E C_W}{K_{eq}} \right) - \frac{S}{V} J_W \qquad (14)$$

Water flux is a complex parameter which depends on membrane area, temperature and composition/concentration. For a fixed membrane and temperature of operation (as in the present case), the flux may be represented as a linear function of the components involved in the transfer. For PVA-PES membrane employed in the present study and low concentration of water, flux may be defined mathematically as

$$J_w = \alpha[W] \qquad (15)$$

α is proportionality constant and [W] gives the water concentration. The similar expression may be written for other components also but since the membrane is highly selective for water, the flux of other components needs not to be considered.

Scanning electron microscopy (SEM) imaging of untreated and treated Dowex 50Wx8-400 catalyst

Scanning electron microscopy (SEM) image analysis was done to examine the morphological changes in the Dowex 50Wx8-400 catalyst, before and after treatment.[18]The untreated and treated catalyst was initially coated with a thin layer of gold using a sputter coater (Quorum-SC7620 Sputter Coater). The coated samples were observed with a scanning electron microscope (ZEISS EVO 18) at an acceleration voltage of 10 KV and 500X magnification.

The images of the pure form of catalyst are shown in Fig. 1. It was found that all the samples had no pores therefore no water could be absorbed on the inner surface of the catalyst. As the temperature was increased in the range of 40 to 70°C, agglomeration was observed.
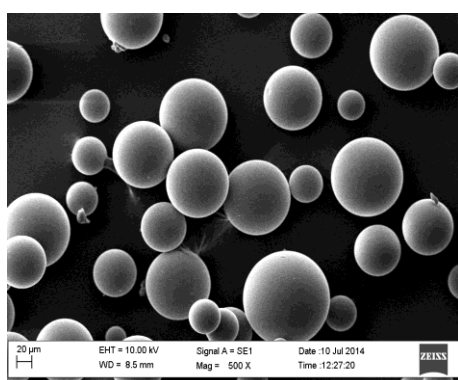
Figure 1.SEM micrographs of pure Dowex 50Wx8-400 (as received). The surface was scanned at an acceleration voltage of 10 KV at a magnification of 500X.

Energy-dispersive X-ray spectroscopy (EDAX) analysis

The energy-dispersive X-ray spectroscopy(EDAX) analysis was performed to determine chemical compositions in a "spot mode" in which the beam is localized on a single spot manually chosen within the field of view. The EDS detector was capable of detecting elements with atomic number equal to or greater than six. The intensity of the peaks in the EDS is not a quantitative measure of elemental concentration. Also, relative amounts can be inferred from relative peak heights. The results of the analysis were given in Table 1 and Table 2, respectively.

Table 1.Weight % of catalyst (chemical composition)

	C-K	O-K	S-K
At pure	60.64	24.42	14.95
40°C	58.66	26.41	14.93
50°C	59.92	27.51	12.57
60°C	60.26	27.13	12.6
70°C	59.58	22.4	18.02

Table 2.Atomic % of catalyst (chemical composition)

	C-K	O-K	S-K
At pure	71.71	21.64	6.62
40°C	69.77	23.58	6.65
50°C	70.26	24.22	5.52
60°C	70.61	23.86	5.53
70°C	71.66	20.22	8.12

X-ray diffraction (XRD) analysis

Fig. 2 shows the X-ray diffraction analysis to determine the crystallinity index (CrI) of untreated and treated Dowex 50Wx8-400 catalyst using an X-ray diffractometer (X'pert PRO, PANalytical). The diffractometer is equipped with a Cu Ka radiation source (k = 0.154 nm) set at 45KV and 30 mA and scanned the samples at a step size of 2 degree, between the grade range (2h) of 20 degree to 76 degree. X- Various crystalline forms, known as phases, of compounds present in powdered and solid samples were identified and quantitatively determined. Identification is achieved by comparing the X-ray pattern or "diffractogram" – obtained from an unknown sample with an internationally recognized database containing reference pattern for more than 70,000 phases.
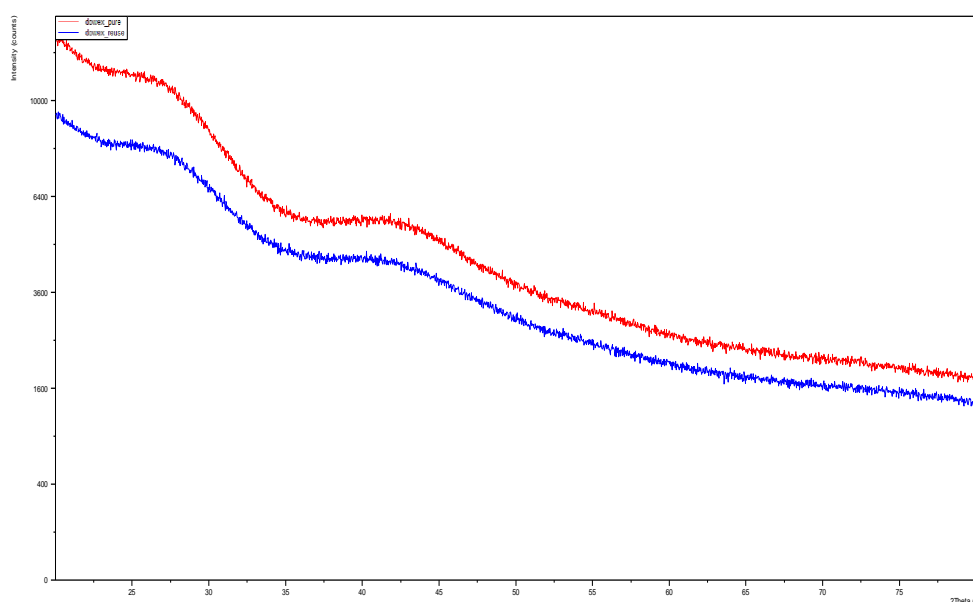
Figure 2. X-ray diffractograms of untreated and treated at 60°C, Dowex 50Wx8-400 catalyst Scan range was set to 2θ= 20° to 76° and samples were scanned at a rate of 2°/min.

Esterification of propionic acid with ethanol using Dowex 50WX8-400 as catalyst: Batch studies

The reaction between propionic acid and ethanol is affected by various parameters such as temperature, concentration of reactants, molar ratio and catalyst concentration. Thus these parameters need to be optimized. K_{eq} was determined by running the reaction for 24 hours at specific temperature and obtaining equilibrium conversion. K_{eq} values were obtained to be 2.55, 2.97, 4.16 and 5.72 at 40, 50, 60 and 70 ^{o}C, respectively.The molar ratio of 1:1 and catalyst wt % of 0.17 was employed in the studies. To understand the thermodynamics of the reaction, equilibrium complexation constant was plotted vs. temperature to determine the entropy and

enthalpy of reaction. $\ln K = \dfrac{-\Delta H^o}{RT} + \dfrac{\Delta S^o}{R}$ (7)

ln$K$ vs. *1/T* was plotted and enthalpy is calculated as 36.07 kJ mol^{-1}. The positive value of ΔH^o indicates the reaction is endothermic. The entropy ΔS^o of this reaction is found by the same equation to be 127.53 Jmol^{-1} K^{-1}(Fig. 3).

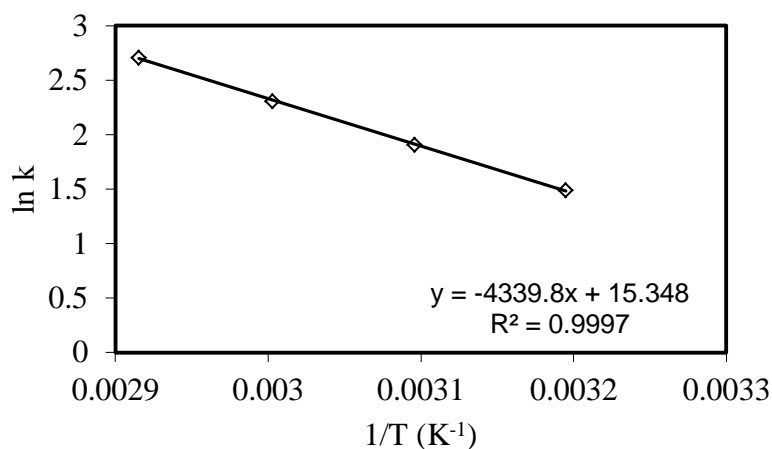Figure with y-axis "ln k" from 0 to 3, x-axis "1/T (K^{-1})" from 0.0029 to 0.0033. Equation shown:
$$y = -4339.8x + 15.348$$
$$R^2 = 0.9997$$

Figure 3.Plot of lnk versus 1/T usingreaction conditions: propionic acid/ ethanol molar ratio 1:1; temperature 40 to 70 ^{o}C; catalyst loading 0.11 gL^{-1} (Dowex 50Wx8-400).

Without a catalyst, the conversion is very low (< 20 %) (Fig. 4) and it takes long time to achieve the equilibrium conversion. In the presence of catalyst (sulfuric acid and Dowex 50Wx8-400), the conversion increases to 56.4% in the case of sulfuric acid and 41.67% in the case of Dowex 50WX8-400. Homogeneous catalysts were found to provide higher conversion in the lowest volume employed. Even though the volume % and weight % are not comparable, yet it may be thought that presence throughout the media of the mono catalyst may result in higher equilibrium conversion (X_{eq}). The reason of the research on the use of heterogeneous catalyst in place of homogeneous catalyst has been due to corrosive nature and difficult separation of the homogenous catalyst from the reaction mass of the later. Further challenge, is that due to presence in such a low concentration there are challenges in heterogeneous catalyst, on the other hand it does not suffer from such disadvantages and could be easily removed from the reaction mass by filtration. There is a need for a solid catalyst that provides higher surface area and is cheap. Various heterogeneous catalysts have been employed as found in available literatures. In most of all Amberlite products or other ion exchange resins were used for esterification or in coupled pervaporation experiments, however, the challenges of reusability or the high cost always surrounds the usability of these catalysts for commercial purpose. On the other hand, Dowex 50Wx8-400 resin was strong acid cation with sulphonic group fine mesh of hydrogen form. It has a large surface area and good reusability (as in the result of reusability are discussed in later sections). The efficiency of this catalyst is also high as compared to other heterogeneous catalyst. Fig. 5 and 6 shows the effect of catalyst concentration, (sulfuric acid and Dowex 50WX8-400) on the conversion of propionic acid + ethanol. It was found that as the catalyst concentration was raised from11.3 to 28.2 g L^{-1},X_{eq} increased from 56.38 to 60.4% and 41.67 to 53.14%, when sulfuric acid and Dowex 50WX8-400 were used as catalyst, respectively. The equilibrium conversion could have increased with further increase in catalyst concentration but it can be seen that increase in conversion diminishes with every change in catalyst concentration. So further increase in would affect the economy and safety of the process (particularly sulfuric acid, which is corrosive in nature). The catalyst affects both the forward and reverse reaction but does not affect the equilibrium constant of the reaction. Due to this reason, on addition of catalyst, the rate and rate constant k$_1$, both increase with the same factor. Since, catalyst does not affect the equilibrium constant, hence the reverse reaction rate constant also increase by the same factor as of forward reaction.[6]
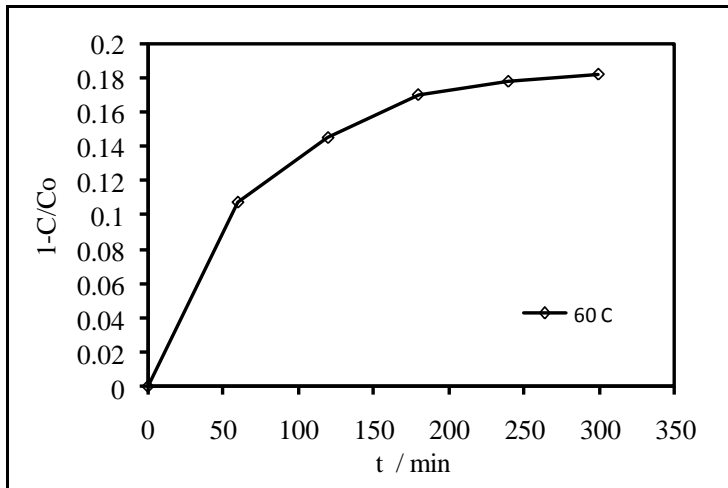
Figure 4.Plot of conversion versus time on theesterification of propionic acid and ethanol at conditions:T = 60°C, molar ratio 1:1, without catalyst
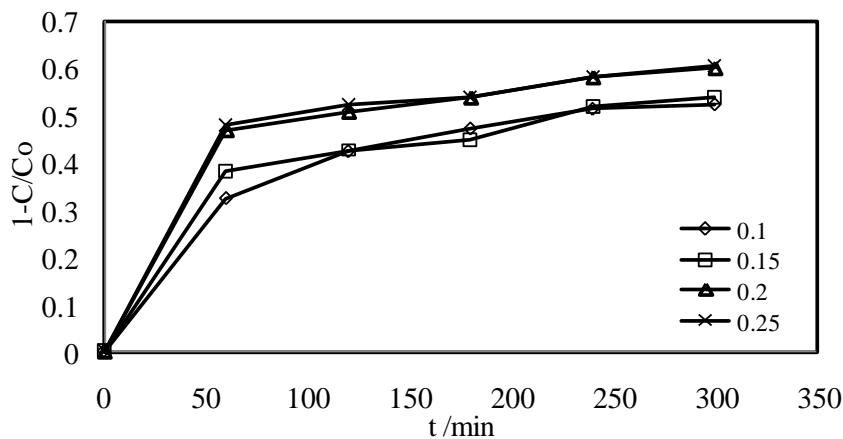

Figure 5.Effect of catalyst (Sulphuric acid) on the esterification of propionic acid and ethanol at conditions:T= 60°C; $C_{catalyst}$ = 0.17-0.83 wt% of propionic acid
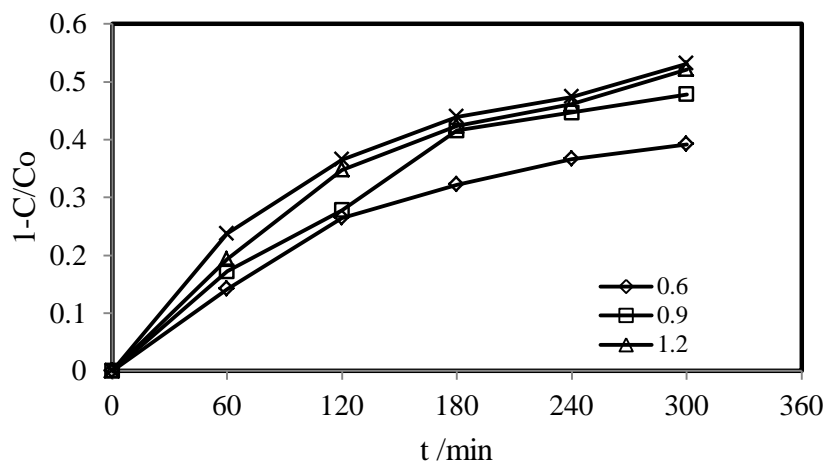

Figure 6.Effect of catalyst (Dowex 50Wx8-400)on the esterification of propionic acid and ethanol at conditions:T=60°C; $C_{catalyst}$ = 11.3-28.2 gL^{-1}of propionic acid

Esterification was studied in the temperature range of 40 to 70°C. The high temperature was not employed due to temperature restriction posed by boiling point of ethanol. $X_{eq}$was found to increase with increase in temperature. X_{eq} raised from 48.46% to 58.72 % as temperature was varied in the mentioned range during the esterification of propionic acid (ethanol + sulfuric acid) (Fig. 7). The acceleration of feed molecules with increasing the temperature is the major factor of higher production of products in forward direction. So, rate constant k is increased with the increase in temperature. Though in backward reaction temperature also influence the reaction rate, but accelerating of the reaction rate constant with the increase of the temperature for the forward reaction was faster than the backward process.The ultimate influence of the temperature is to lead to higher forward rate and hence higher ester formation.
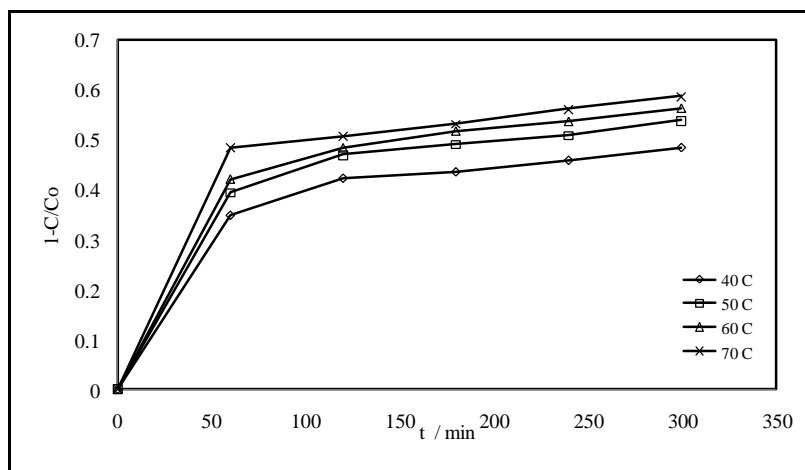
Figure 7.Effect Effect of temperature on the esterification of propionic acid and ethanol at conditions:T = 40-70°C; $C_{catalyst}$ = 0.17 wt% (Sulphuric acid) of propionic acid.

A Xeq increase from 15.3% to 45.92% as the temperature was raised from 40 to 70°C for esterification using Dowex 50Wx8-400 as catalyst (Fig. 8). Among the two catalysts, the percentage increase in Dowex 50Wx8-400 is higher as compared to the sulfuric acid, increase in temperature being in the same range. In the case of solid catalyst, the complexation is dependent on the surface interaction, whereas in the case of homogenous liquid catalyst, the ease to access and interact with the reactant molecules could be the obvious reason for the above result.The effect of temperature and catalyst on the yield on the ester is shown in (Fig. 9 & 10). Yield increases from 40.26% to 65.07% as the temperature was raised from 40 to 70°C to 1:1 acid to alcohol molar ratio of the reactants and at 60°C, yield increases from 44.29 to 74.2% as the catalyst loading was raised from 11.3-28.2 g L^{-1}, respectively.
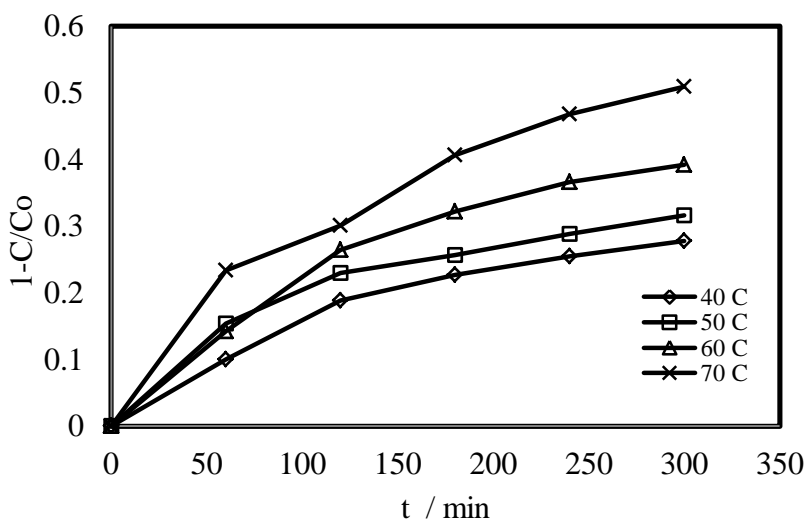

Figure 8.Effect of temperatureon the esterification of propionic acid and ethanol at conditions:T= 40-70 °C; $C_{catalyst}$ = 11.3gL^{-1}(Dowex 50Wx8-400) of propionic acid.
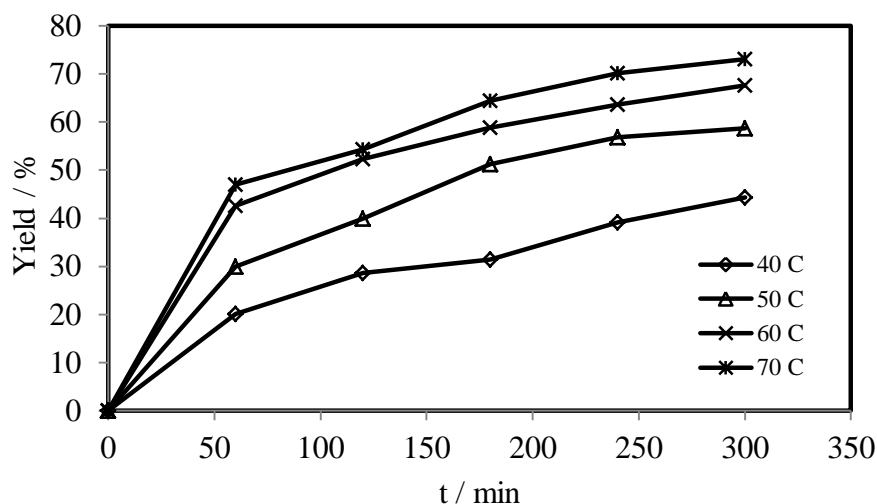
Figure 9.Effect of temperature yield onthe esterification of propionic acid and ethanol at conditions:T= 40-70°C; $C_{catalyst}$ = 11.3gL^{-1}(Dowex 50Wx8-400) of propionic acid.
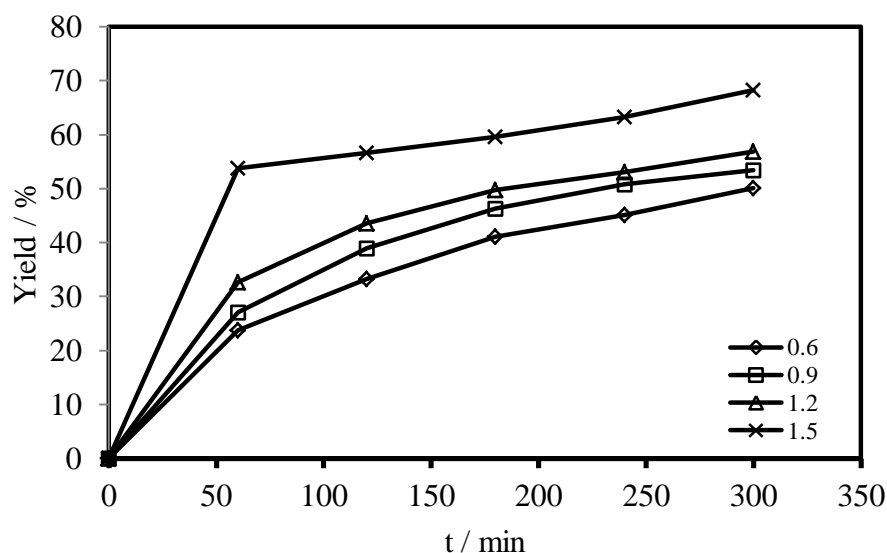

Figure 10.Effect of catalyst (Dowex 50Wx8-400)loadingyield onthe esterification of propionic acid and ethanol at conditions:T= 60°C; $C_{catalyst}$ = 11.3gL^{-1}of propionic acid.

Using the reactant in excess could be the way to increase the equilibrium conversion. However, this could lead to a dilution of the product stream, still the range of using the reactant in excess needs to be determined. Four different molar ratios 1:1, 1:2, 2:3, 3:2 was tried for the esterification reaction of propionic acid with ethanol using sulfuric acid and Dowex 50Wx8-400 as catalyst. It was observed that as the molar ratio of alcohol was raised, the conversion increases from 29.5 to 39.2 and 39.58 to 53.38% in the sulfuric acid (Fig.11) and Dowex 50Wx8-400 catalysts (Fig. 12), respectively. Raising the molar ratio to 2:3 though provide higher conversion compared to when 1:1 molar ratios, but were lower than when 1:2 molar ratios were used. Increasing acid molar ratio over the ethanol results in lowest X_{eq}among the four molar ratios chosen.X_{eq} was found to be 41.2% and 39% using sulfuric acid and Dowex 50Wx8-400 catalysts, respectively.
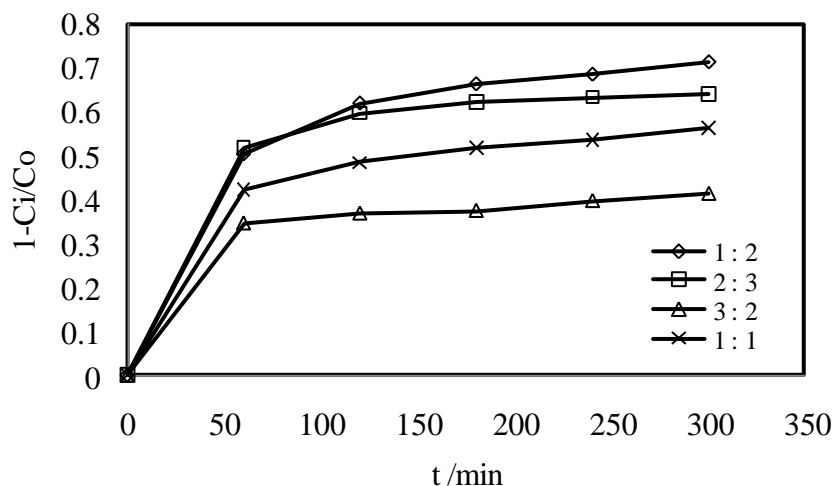
Figure 11.Effect of molar ratios onthe esterification of propionic acid and ethanol at conditions:T = 60°C; $C_{catalyst}$ = 0.17wt% (Sulphuric acid) of propionic acid.

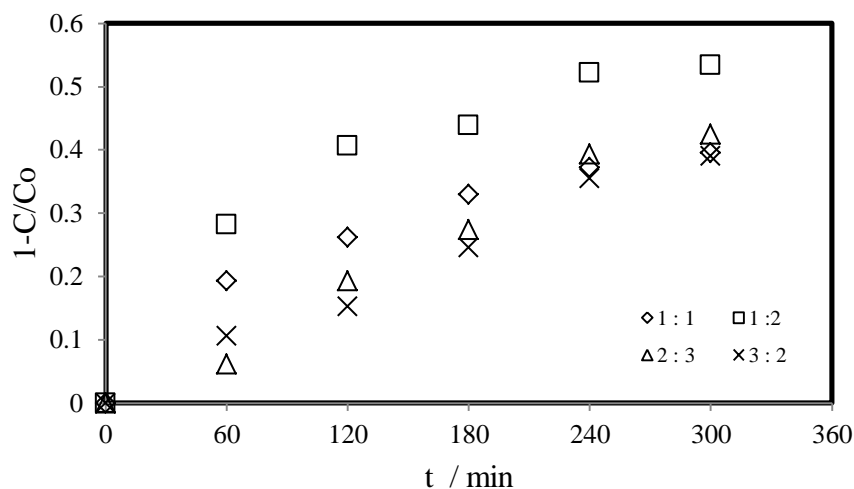**Figure 12. Effect of molar ratios onthe esterification of propionic acid and ethanol at conditions:T= 60°C; $C_{catalyst}$ = 11.3gL^{-1}(Dowex 50Wx8-400) of propionic acid.**

Pervaporation aided esterification

For the modeling and design of pervaporation membrane coupled esterification reactor, for the esterification of propionic acid with ethanol using Dowex 50Wx8-400 as catalyst, different parameters is to be determined. Presence of product of reaction in reversible reactions decreases the equilibrium conversion (X_{eq}). Coupling with pervaporation removes the product of reaction which leads to increase in conversion. Effect of temperature on pervaporation aided esterification is shown in (Fig. 13). Increase in temperature increases equilibrium conversion both in simple and pervaporation aided esterification. However the equilibrium conversion in membrane reactor hybrid is higher than system without pervaporation. X_{eq} increases from 32.53 to 49%; 39 to 54%; 50 to 56.9% and 62 to 68% in esterification without and with pervaporation, temperature being increased by 10°C increment from 40 to 70°C. The esterification reaction is endothermic in nature; hence increase in temperature shall increase the conversion. This leads to more product formation and hence, brings the role of back reaction step to lessen the rate. This effect could be lowered by the presence of membrane that simultaneously removes the product of the reaction. But it is desirable that the membrane should resist to the temperature of operation of the reactor streams. Further the research on the effect of temperature on membrane performance is important. The results obtained show that the temperature has a positive influence in the membrane-reactor hybrid system. Thus, membrane favors higher permeation at higher temperature. The

increase in thermal energy of molecules or the flexibility of polymeric chains of membrane or the increase in diffusivity with temperature may be the reason for the findings in the present experiments.
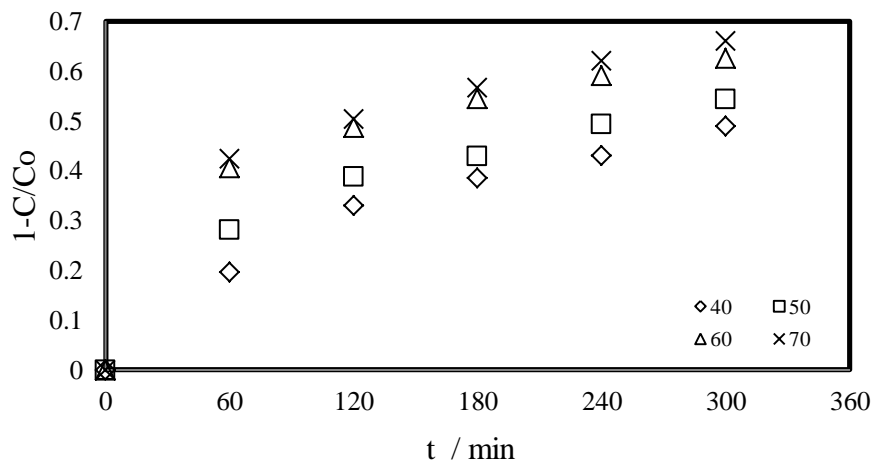

Figure 13.Effect of temperature onthe esterification assisted pervaporation reactor of propionic acid and ethanol at conditions:T = 40–70°C; $C_{catalyst}$= 11.3 gL^{-1}(Dowex 50Wx8-400) of propionic acid

Effect of catalyst concentration on the yield of ester is shown in (Fig. 14). Yield increases from 23 to 68% as the catalyst concentration was raised from 11.3-28.2 g L^{-1}, for 1:1 acid to alcohol molar ratio at 70°C. Percentage conversion is higher in pervaporation aided esterification. X_{eq}in without and with pervaporation system is 41.67%, 47.85%, 52.19, 53.14% and 56.9%, 58.83%, 62.09% and 65.05%, respectively. Yield may be enhanced by using higher catalyst loading. Using higher catalyst loading, the activation energy of reaction decreases and reaction rate could accelerate. However, catalyst, either homogeneous or heterogeneous does not affect the reaction equilibrium. In pervaporation, increasing the catalyst loading, enhanced the conversion and water was kept low through permeation on the permeate side quickly. So in pervaporation, the simultaneous steps results in higher conversion in comparison of without pervaporation.
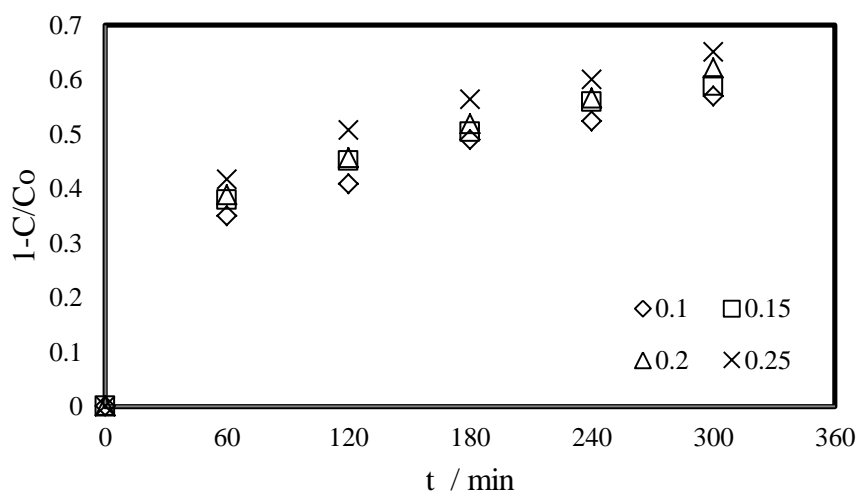

Figure 14.Effect of catalyst (Dowex 50Wx8-400)onthe esterification assisted pervaporation reactor of propionic acid and ethanol at conditions:T = 60°C; $C_{catalyst}$ = 11.3-28.2 gL^{-1}of propionic acid

In the results of the esterification, it was discussed that higher alcohol is beneficial in terms of ester yield. So for further studies 1:1, 1:1.5, 1:2, 1:2.5 molar ratios have been used in (Fig. 15). So in the pervaporation study only effect of increase in molar ratio of alcohol studied. For a fixed molar ratio,X_{eq} in without pervaporation is 21.5% lower than system with pervaporation. Increase in molar ratio has been found to

increase the X_{eq} in both with and without pervaporation. Increase in molar ratio of 1:1 to 1:2.5, increases X_{eq} by 15 %.
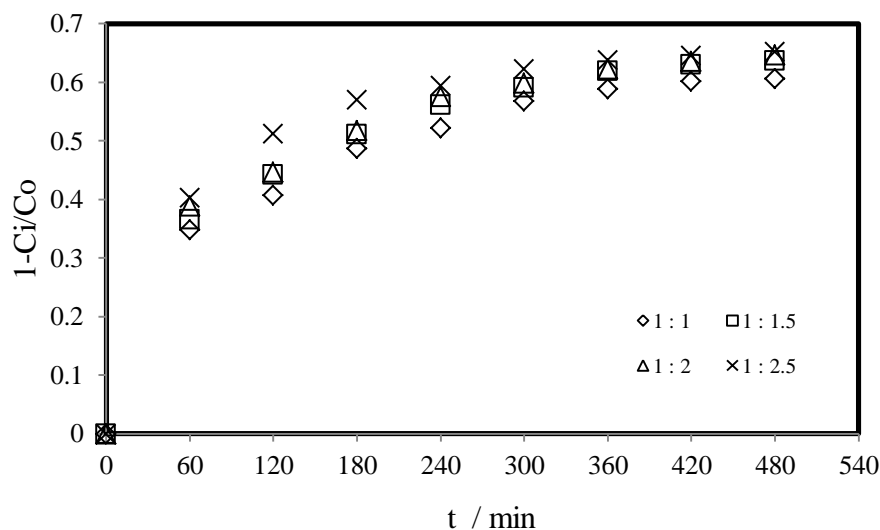

Figure 15.Effect of molar ratios onthe esterification assisted pervaporation reactor of propionic acid and ethanol at conditions:T= 60°C; $C_{catalyst}$ = 11.3gL^{-1}(Dowex 50Wx8-400) of propionic acid.

Reusability

Many heterogeneous catalysts have been employed in various research works for reuse of catalyst, but Dowex 50Wx8-400 catalyst gives remarkable results through various acids and ethanol mixture. As we can see the (Fig. 16), in first experiment 52 ester % was obtained, then in 2, 3 and 4th experiment overall ester % were decreased by 4 % i.e. 48 % approximately.
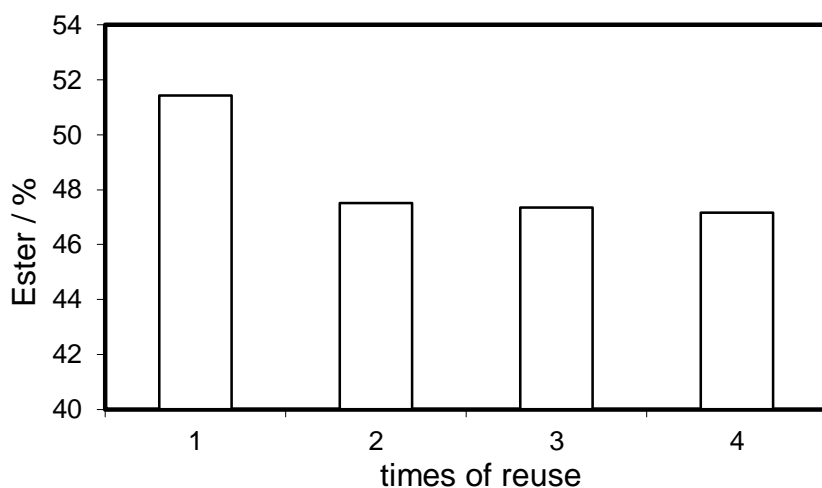

Figure 16. Reusability of Dowex 50Wx8-400 catalyst using 60°C temperature and 0.11 gL^{-1}catalyst loading

Conclusion

Batch reactor of three necks round bottom flask with heating mental was fabricated and used as initial to perform esterification lof propionic acid and ethanol at stirrer speed of about 800 rpm. An ion exchange resin Dowex 50Wx8-400 and sulphuric acid were used as catalyst for the study. Sulphuric acid was a strong acid catalyst and performs better than other homogeneous acid catalyst, but main disadvantage is its corrosive nature, so in the present study a heterogeneous catalyst Dowex 50Wx8-400 was used to carry out the pervaporation studies.

PVA-PES membrane enhances the pervaporation properties by selective removal of water from the reaction medium. Integrated esterification – pervaporation based reactor has a great influence to the operating parameters. Higher temperature and higher alcohol volume may result in higher ester conversions. Effect of catalyst loading has been also performed to investigate the influence of catalyst in reaction medium and results conclude that increasing the catalyst gives a higher conversion of ester.

SEM – EDEX and XRD analysis were performed to investigate the structural properties and composition of the catalyst. The reusability of the catalyst was also carried out to examine the catalyst efficiency and performance and it was found that a little deviation has been determined in efficiency in each run but overall it was tremendous to run 4-5 analysis.

Acknowledgement

Nomenclature

ΔS^o	Enthalpy
ΔH^o	Entropy
K_{eq}	Equilibrium constant
$T_{reaction}$	Reaction temperature
T	Temperature
x_D	Rate of product
k_1	Rate constant for forward direction
k_2	Rate constant for backword direction
C_{cat}	Catalyst concentration
J_H	Flux (water)
S/V	Surface of membrane and volume of reaction mixture ratio
α	Propertionality constant
K	Kelvin (temperature)
CrI	Crystallinity Index
T	Temperature
X	Conversion
X_{eq}	Equilibrium conversion

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