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Esterification of maleic acid and butanol using cationic exchange resin as catalyst

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Abstract. Dibutyl maleate is a perfumery ester used as an intermediate in the production of paints, adhesives, and copolymers. Esterification of maleic acid and butanol was studied in presence of acidic cation exchange resin as a catalyst. The objective of this work was to test the suitability and efficacy of heterogeneous catalysts such as Indion 225H and Amberlyst-15 in the synthesis of dibutyl maleate. Various parameters deciding the conversion of reaction such as mole ratio, catalyst loading, molecular sieves, speed of agitation and effect of temperature were optimized for the maximum rate and conversion. The activation energy was calculated as 71.5 kcal/mol. Diffusivity value D_{AB} (maleic acid in n-butanol) at 80 °C was calculated as $5.08 \times 10^{-10} \text{ m}^2/\text{s}$ and effective diffusivity (D_{e-A}) was calculated as $5.08 \times 10^{-11} \text{ m}^2/\text{s}$. Solid–liquid mass transfer coefficient (k_{sl-A}) was calculated as $6.77 \times 10^{-6} \text{ m/s}$ for the particle size of Amberlyst-15 as 0.5 mm.

Keywords. Esterification; dibutyl maleate; ion exchange resin; Indion 225H; Amberlyst-15.

1. Introduction

Esters are derived from the reaction between carboxylic acids and organic alcohols. The liquid phase esterification reaction has a significant role in chemical industry due to its wide applications as plasticizers, adhesives, pharmaceutical intermediates, pesticides and in polymerization of monomers.^{1–6} In the past few years, various esterification reactions catalyzed by inorganic acid, Lewis acid, organometallic compounds, and solid acids, were investigated by researchers to understand the reaction mechanism. Earlier, homogeneous catalysts such as H_2SO_4 , *p*-toluene sulphonic acid, sodium hydrogen sulphate and HCl were used for producing the ester at a faster rate. However, separation of this catalyst requires more steps and also it generates a large amount of waste that made the process tedious. Hence ion-exchange resin is a versatile material for the replacement of the homogeneous acid catalysts. Use of heterogeneous catalysts are of high importance due to their non-corrosive and eco-friendly nature, easy to separate and no washing as of homogeneous acid is required. These catalysts affect the equilibrium conversion due to their selective adsorption of reactants.^{4–12} Cation-exchange resins such as Dowex, Amberlyst series are

manufactured mainly by sulfonation of ethylbenzene first, followed by cross-linking with divinylbenzene. Sulphonic acids have an effective catalytic activity and cause fewer side reactions. These co-polymer beads are prepared by pearl polymerization technique to get macroreticular or macroporous resin.^{4,6} The application of ion exchange resin as a catalyst for esterification reaction is well explored earlier by researchers. Various researchers have investigated the mechanism of heterogeneous catalysts using ion exchange resin. Yadav and Thathagar studied the kinetics of esterification of maleic acid with ethanol over various cationic exchange resins like Amberlyst-36, Amberlyst-15, Indion-170, Amberlyst-18, Amberlite IR 400, and DTP/K-10.¹ Dange and Rathod reported esterification reaction involving butyric acid and methanol over the Amberlyst-15 catalyst. Kinetic data were tested for pseudo-homogeneous model, Langmuir-Hinshelwood model and Eley-Rideal model.² State of art work has been published by M. M. Sharma on the use of cationic ion exchange resin as catalyst.⁴ Gangadwala *et al.*, have determined the intrinsic reaction kinetics of esterification of acetic acid with n-butanol in presence of Amberlyst-15.⁵ Yadav and Krishnan have investigated the synthesis of methyl anthranilate from

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anthranilic acid and methanol using eco-friendly heterogeneous catalysts like ZSM-5, acid treated clays such as filtrol-24 and K-10, ion exchange resins such as Nafion-H, Indion-130, Amberlyst-15 and Amberlyst-18.⁸ Although various reports are available on synthesis of ester using ion exchange resin, a limited work has been carried out on synthesis of dibutyl maleate with ion exchange resin as catalyst. Dibutyl maleate has wide applications as a plasticizer for vinyl resins and used for various copolymer applications. It is also used in plastisols, dispersions, coatings and adhesives.

M Bengi Taysun *et al.*, compared the performance of Amberlyst-15-dry, Amberlyst-5-wet, Amberlyst-131H+ for esterification of maleic acid with butanol using deep eutectic solvents with 1:10 molar ratio of maleic acid to butanol. However, the effect of various parameters was not well-explored and fixed to comparison at only one condition.¹³ Hence the current investigation is an attempt to explore the utilization of ion exchange resin for the synthesis of dibutyl maleate by a possible screening of various ion exchange resins and to maximise the conversion by optimizing the various parameters.

2. Experimental

2.1 Materials

Maleic acid and n-butanol were procured from S.D. Fine Chem Mumbai, India and Loba Chemie respectively. Acidic ion exchange resin (Indion 225H & Amberlyst-15 of Rohm and Haas Co.) was obtained from S.D. Fine Chem Mumbai. Molecular Sieves (4A° type), from S.D. Fine Chem Mumbai was used in the reaction.

2.2 Experimental setup and method

The reactions were carried out in a batch reactor of 100 mL capacity equipped with 4 baffles. The reactor was continuously stirred by using a three blade glass turbine impeller driven by an electrical motor. The reaction contents were well-stirred and the speed of agitator was varied using a speed controller. The temperature of the reaction was maintained at a constant value by using a thermostatic water bath. The catalyst was dried at 70 °C for 2 h before use. A measured quantity of maleic acid and butanol were added to the reactor and allowed to reach a desired temperature. Cationic exchange resin and molecular sieves were added and zero time sample was collected. Butanol was taken in far excess over maleic acid to drive the equilibrium of the reaction towards ester formation. Very small amount of sample was withdrawn at a higher frequency at first half hour and at a definite interval thereafter for 4 h of time.

2.3 Methods of analysis

2.3a Gas chromatographic analysis: The liquid samples were analyzed using a gas chromatograph Model GC2010 Shimadzu Plus for quantitative determination of dibutyl maleate and water formed in the reaction. Column SH-RXi-5 Sil MS (30 m × 0.25 mm i.d, 0.25 μm film thickness) was used. Helium was used as carrier gas. The initial column temperature was set at 50 °C with a hold time of 1 min to obtain prolonged retention for early eluting peaks. The column temperature was increased to 280 °C with temperature gradient maintained at 30 °C/min. At final column temperature of 310 °C, hold time of 5 min and temperature gradient at 15 °C/min, dibutyl maleate eluted at a retention time ranging from 11.73 to 12.96 min.

2.3b Infra-red spectroscopy: The product liquid samples were analyzed using infrared spectrometer (FTIR 1-S Affinity- Shimadzu make) to determine the functional groups present, through infrared spectrum. Spectrometer details are; wavenumber range is 400–4000 cm⁻¹ with Michelson interferometer (30° incident angle) and DLATGS detector equipped with temperature control mechanism.

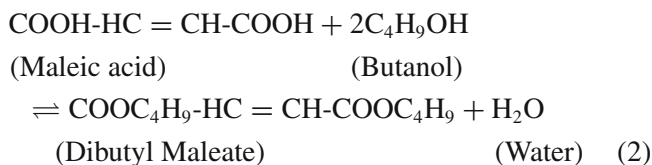
2.3c Titrimetric analysis: Samples were taken out at known intervals of time from the reaction mixtures and were titrated using alcoholic 0.01 N KOH using phenolphthalein indicator to calculate the acid value. Acid value was calculated for each sample taken out at intervals. Dibutyl maleate obtained was expressed in terms of percent conversion as given in equation 1.

$$\% \text{ conversion} = \frac{(a_{v1} - a_{v2})}{a_{v2}} \times 100 \quad (1)$$

Where a_{v1} is an acid value (mg KOH/g) of the reaction mixture at beginning and a_{v2} is an acid value (mg KOH/g) of the reaction mixture at an individual time interval.

3. Results and Discussion

In the present work, a dicarboxylic acid *i.e.*, maleic acid reacts with n-butanol in presence of an acidic catalyst to produce monobutyl maleate and further reacts with n-butanol to produce dibutyl maleate. As per the reaction stoichiometry, one mole of maleic acid reacts with two moles of n-butanol to give the product of one mole of dibutyl maleate along with one mole of water, where water is the by-product of the reaction. As mentioned earlier, butanol was used in excess of maleic acid to shift the equilibrium towards the forward direction of ester formation. The reaction is represented as below:



Various reactions were carried out with reaction conditions altered to study the effect of catalysts, temperature, the speed of agitation, acid to alcohol ratio, catalyst loading and amount of molecular sieves.

All experiments were performed thrice to check the reproducibility of the experiments. The conversion obtained with this analysis for the effect of various parameters was found with 2% deviation in the results which are reported in appropriate figures.

3.1 Screening of catalysts

Cationic ion exchange catalysts like Indion 225H and Amberlyst-15 were used to understand the efficacy of the reaction. During the reaction, n-butanol was used as an excess reactant and maleic acid as limiting reactant to drive the equilibrium towards formation of an ester. The condition used for screening of the catalyst was mole ratio of 1:4 for maleic acid to butanol, the temperature of 80 °C with a catalyst loading of 2% and a speed of agitation of 300 rpm. The results are shown in Figure 1 which is expressed as the conversion of maleic acid for these two heterogeneous catalysts. It was found that Amberlyst-15 gave a higher conversion of 48% as compared to Indion 225H with 44% conversion for the reaction time of 4 h. The chemical activity which is expressed as meq/g for Indion

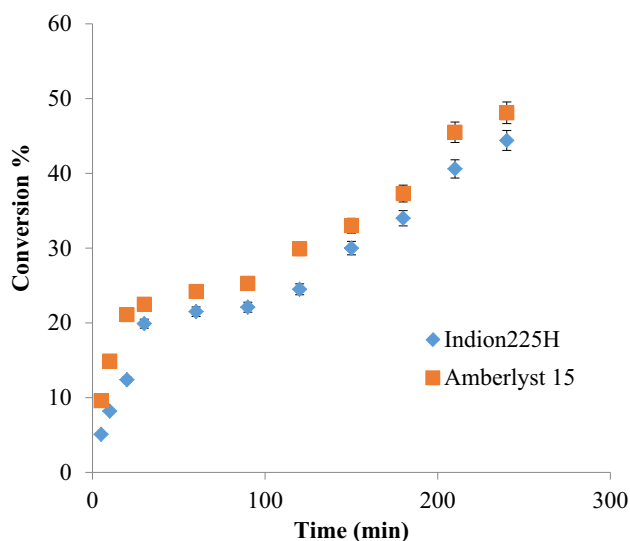


Figure 1. Effect of different catalyst on conversion of maleic acid at 80 °C, catalyst loading 2%, the speed of agitation 300 rpm, maleic acid to butanol mole ratio 1:4.

225H and Amberlyst-15 are 1.8 and 4.7 respectively which means Amberlyst-15 was found to be more active. Yadav and Thathagar carried out the esterification reactions of maleic acid and ethanol on Amberlyst-15 and Indion-130 as well as Dange and Rathod investigated the esterification reaction involving butyric acid and methanol over Amberlyst-15 as a catalyst. Yadav and Kulkarni also performed the synthesis of isopropyl lactate using Indion -130, Amberlyst-36, Amberlyst-15, Amberlite-120, Dowex 50W, Filtrol-44, DTPA/K-10, where they observed that Amberlyst-36, Amberlyst-15 and Indion-130 were most effective.¹⁴ Although M. Bengi Taysun *et al.*, used Amberlyst-15 for esterification of butanol and maleic acid, the conversion obtained was only 8% as they have not performed the reaction at optimized conditions.¹³

Further reactions in this present work were carried out with Amberlyst-15 as the catalyst where only one parameter was varied at a time under the otherwise similar experimental conditions. The properties of cation exchange resins like Indion 225H and Amberlyst-15 are given in Table 1.

3.2 Effect of acid to alcohol ratio

As per the reaction stoichiometry, 1:2 mole ratio of maleic acid to n-butanol is required to perform the reaction. However, to alter the reaction equilibrium, use of an excess of alcohol is recommended to increase the rate of forward reaction and improve the formation of ester. Thus, the mole ratio of maleic acid to n-butanol was also varied as 1:3, 1:4, and 1:5 keeping other parameters at a constant value. The results are plotted as shown in Figure 2 at reactions conditions as 4% of catalyst, 4% molecular sieves, reaction temperature 80 °C and speed of agitation as 300 rpm.

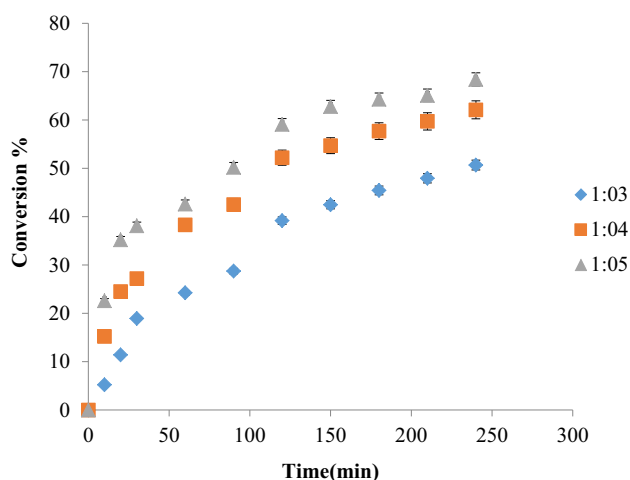
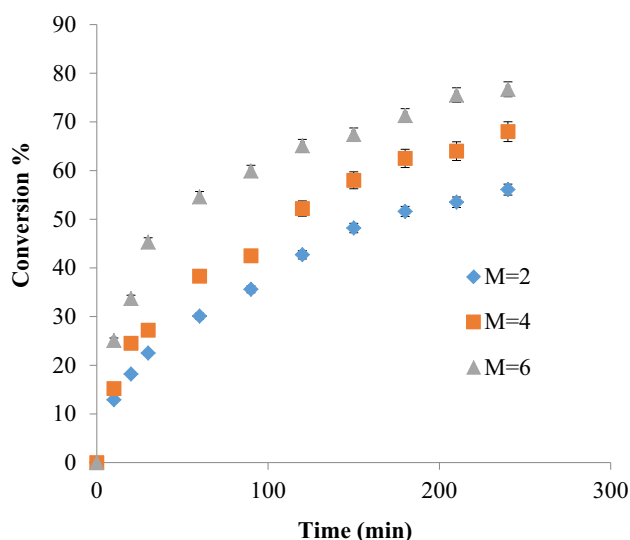
It was found that the concentration of n-butanol has an influence on the conversion. As the amount of alcohol was increased, the conversion of maleic acid also increased from 50% to 62% with an increase in the mole ratio of maleic acid to n-butanol at 1:3 to 1:4 at optimum conditions of temperature, the speed of agitation and catalyst loading. Beyond 1:4 there was no appreciable effect on the conversion. Thus, mole ratio of 1:4 for maleic acid to butanol was considered to be optimum.

3.3 Effect of catalyst loading

The effect of catalyst loading for Amberlyst-15 on the conversion of maleic acid and n-butanol was investigated by varying the catalyst loading from 2%, 4% and 6% based on the total weight of the reactants at a temperature of 80 °C, using 4% molecular sieves and

Table 1. Characteristics of cation exchange resin used.

Properties	Indion 225H	Amberlyst-15
Shape	Beads	Beads
Size (mm)	0.3–1.2	0.5
Polymer type	Macro-reticular	Macro-reticular
Matrix	Styrene divinylbenzene copolymer	Styrene divinylbenzene copolymer
Weight Capacity (mEq/g)	1.8	4.7
Porosity (%)	–	36
Surface area (m ² /g)	–	34.85
Temperature Stability	393 K	393 K
Functional group	sulfonic acid	sulfonic acid
Cross linking (% DVB)	–	20

**Figure 2.** Effect of mole ratio on conversion of maleic acid at a catalyst loading 4%, molecular sieves 4%, temperature 80 °C, the speed of agitation 300 rpm.**Figure 3.** Effect of Catalyst Loading on conversion of maleic acid at a mole ratio of maleic acid to butanol 1:4, temperature 80 °C, the speed of agitation 300 rpm, molecular sieves 4%.

speed of agitation as 300 rpm keeping the mole ratio of maleic acid and n-butanol as 1:4. Fresh resin was used for each new trial. The conversion of maleic acid as a function of time with different catalyst loading is shown in Figure 3. It was observed that the conversion of maleic acid increases proportionally with catalyst loading. Increase in the catalyst loading means more active sites available for the reaction, which gave an increase in conversion. The change in the conversion of maleic acid was observed from 68% to 77% when catalyst loading was varied from 4% to 6%. Thus, no significant change in conversion was observed when catalyst loading was varied from 4% to 6%, may be due to unavailability of sufficient substrate for the reaction. Hence optimum catalyst loading was taken as 4% for further experiments.

3.4 Effect of agitation speed

In solid-liquid catalytic reaction, two types of mass transfer resistances exist which include solid liquid interface and other is intraparticle diffusion.^{7,14} Also the diffusion of A from the bulk liquid phase to the exterior of the catalyst surface through the liquid film surrounding the catalyst particle is represented by solid-liquid mass transfer coefficient k_{sl-A} .⁸ Amongst two resistances, external mass transfer resistance can be reduced by increasing the turbulence in reaction medium; that can be done by varying the speed of agitation. Thus, the effect of speed of agitation was studied at different agitation speed between 100 rpm to 500 rpm to understand the influence of external mass transfer resistance. The reaction conditions were mole ratio of maleic acid to butanol at 1:4, 4% catalyst loading, temperature 80 °C and 4% molecular sieves. Figure 4 shows that conversion increases from 55% to 62% when agitation speed is varied from 100 rpm to 300 rpm. Further increase in the agitation speed to 500 rpm shows an increase

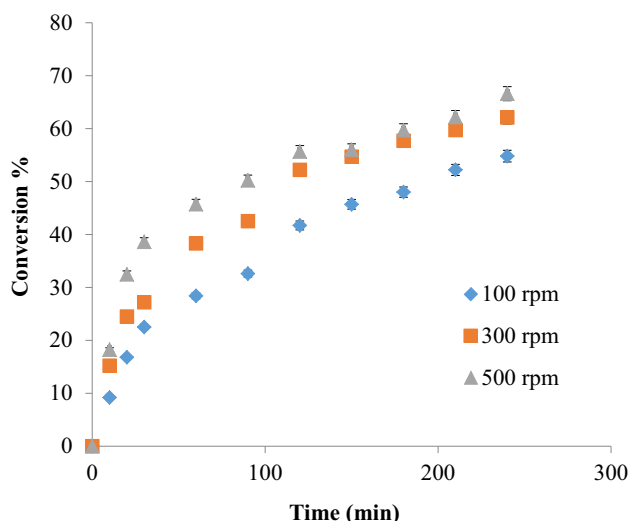


Figure 4. Effect of the speed of agitation on conversion of maleic acid at catalyst loading 4%, temperature 80 °C, maleic acid to butanol mole ratio 1:4, molecular sieves 4%.

in conversion to 66%. This marginal increase in the conversion from 62% to 66% at 300 rpm and 500 rpm may be because of the decrease in mass transfer resistance due to increase in the turbulence. Hence the stirrer speed of 300 rpm was selected as optimum and further experiments were carried out at 300 rpm. Since n-butanol (B) was taken in excess, there may be a possibility of diffusional resistance of maleic acid (A) through the liquid film around the catalyst and through the pores. Hence liquid phase diffusivity values D_{AB} (maleic acid in n-butanol) was required which was calculated by Wilke Chang equation.¹⁵

D_{AB} at 80 °C was calculated as $5.08 \times 10^{-10} \text{ m}^2/\text{s}$ and effective diffusivity (D_{e-A}) is calculated as $5.08 \times 10^{-11} \text{ m}^2/\text{s}$ from $D_{e-A} = D_{AB} \varepsilon / \tau$ where ε and τ are taken as 0.3 and 3, respectively.¹ The values of solid-liquid mass transfer coefficient k_{sl-A} was calculated by assuming Sherwood number, $sh = (K_{sl}d_p)/D = 2$ where D is diffusivity. k_{sl-A} was calculated as $6.77 \times 10^{-6} \text{ m/s}$ for the particle size of Amberlyst-15 as 0.5 mm.^{9,14} Yadav and Thathagar, Yadav and Krishnan described the influence of intraparticle diffusion which was varied with particle size. They reported the values of mass transfer coefficient k_{sl-A} as $4.34 \times 10^{-5} \text{ m/s}$ and $1.857 \times 10^{-3} \text{ cm/s}$ respectively.

Similar study was also reported for the synthesis of diethyl maleate using Indion-170 where no external diffusion effect was observed for stirrer speed ranging from 500 to 1000 rpm.¹ Dange and Rathod also studied the effect of stirrer speed in the range of 100 to 400 rpm and found that the mass transfer coefficient was almost negligible at 300 rpm. In the study undertaken by Ali *et al.*, it was found that in the reaction of 2-propanol

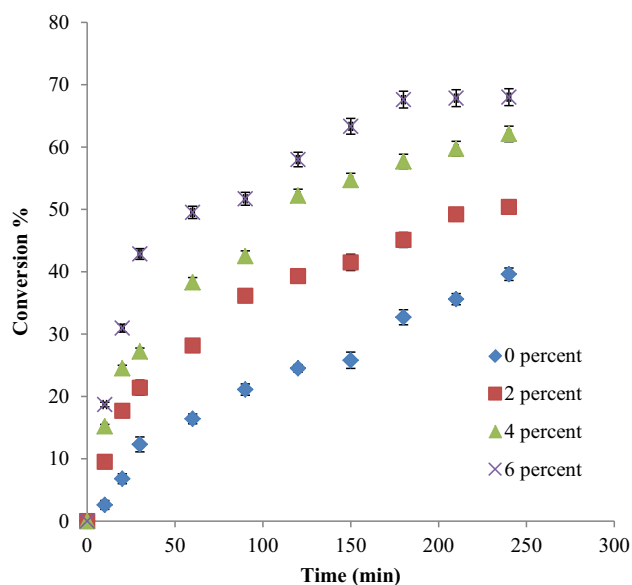


Figure 5. Effect of molecular sieves (0%, 2%, 4% and 6%) on conversion of maleic acid at a mole ratio of maleic acid to butanol 1:4, Catalyst loading 4%, temperature 80 °C, the speed of agitation 300 rpm.

with acetic acid, external mass transfer limitation was negligible at a stirrer speed above or equal to 500 rpm, where the stirrer speed was varied in a range from 50 to 900 rpm.¹⁶ Researchers also reported a negligible impact of speed of agitation on the overall rate of reaction in the range of 12 to 33 rps. Hence the esterification reactions were carried out at a higher stirrer speed of 16.7 rps.¹⁷

3.5 Effect of addition of molecular sieves

In this investigation, molecular sieves (4A° type) were added in a range of 2%, 4%, 6% (w/w) to study the effect of water produced in the esterification reaction.^{1,2} One experiment is also performed without addition of molecular sieve to identify the variation in conversion. All these experiments were carried out at a mole ratio of maleic acid to butanol 1:4, agitation speed of 300 rpm and catalyst loading of 4% (w/w) at a temperature of 80 °C. Figure 5 shows an increase in the conversion of dibutyl maleate from 40% to 68%, with an increase in molecular sieves, however the reaction conversion is investigated to be lower at 40% without addition of molecular sieves. This indicates the adsorption of produced water in the pores of molecular sieves. As there was a marginal change in the conversion of dibutyl maleate after 4% (w/w) molecular sieves, it was taken as optimum. Liu *et al.*, reported the deactivation of catalyst occurs with water as the by-product.¹² Dange and

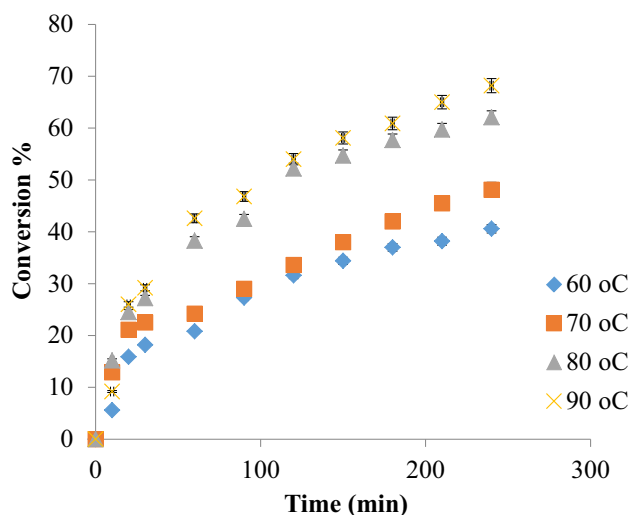


Figure 6. Effect of temperature on conversion of maleic acid at maleic acid to butanol mole ratio 1:4, Catalyst loading 4%, the speed of agitation 300 rpm, molecular sieves 4%.

Rathod carried out esterification reactions using molecular sieves and reported the increase in the conversion of methyl butyrate on increasing molecular sieves to the reaction mixture.²

3.6 Effect of temperature

Effect of temperature was studied by performing reaction at 333 K, 343 K, 353 K and 363 K for 4 h with Amberlyst-15 as a catalyst, mole ratio of maleic acid to butanol 1:4, Catalyst loading 4%, with continuous agitation at 300 rpm. Figure 6 depicts higher values of conversion with increasing temperature. This is due to more collisions within the reactants which have sufficient energy to break the bonds in between the reactant molecules to form products.

There was no appreciable change in the conversion beyond 353 K, therefore, it was taken as an optimum value. Further, the plot of $-\ln(1 - X_A)$ vs time as in Figure 7 indicates a straight line behaviour alike pseudo-first order behaviour.⁸ Thus, the rate constants for the forward reaction at different temperatures are represented in Table 2.

The rate constant was expressed in terms of Arrhenius equation, which is as follows

$$k = k_0 e^{-E/RT} \quad (3)$$

where k is Rate constant, k_0 is frequency factor, E is activation energy and R is Gas constant ($1.98 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}$).

The Arrhenius plot to calculate the rate constant for forward reaction in the temperature range of 333–363 K gives the regression coefficient of 0.94 as shown

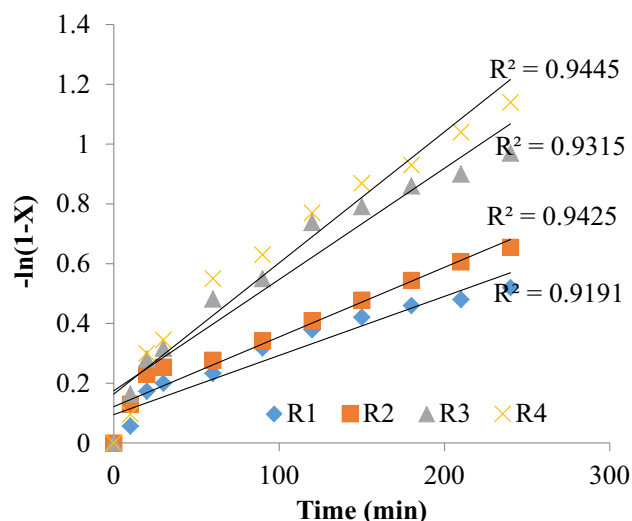


Figure 7. Plot to calculate rate constants at various range of temperatures 333–363K.

Table 2. Rate constant values for butanol at different temperatures.

Temperature (K)	Rate Constant k_1 (min^{-1})
333	1.3×10^{-3}
343	2.6×10^{-3}
353	5×10^{-3}
363	6.6×10^{-3}

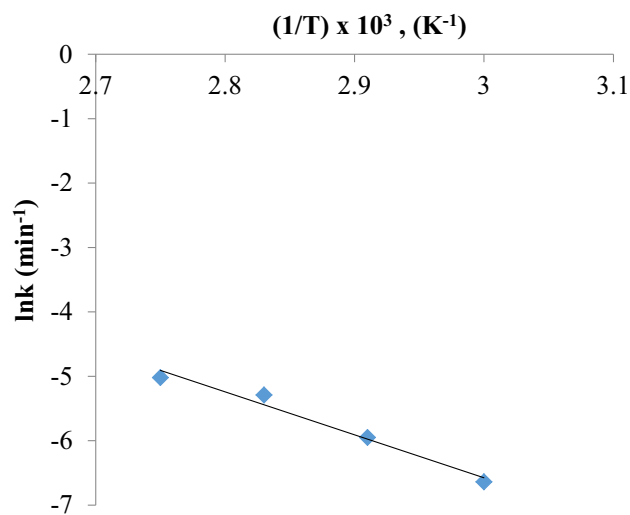


Figure 8. Arrhenius plot of $\ln k$ versus $(1/T) \times 10^3$, Catalyst loading 4%, the speed of agitation 300 rpm, maleic acid to butanol mole ratio 1:4.

in Figure 7. A plot of $\ln K$ versus $1000/T$ was plotted as in Figure 8, and the energy of activation was calculated as 71.5 kcal/mol which represents a kinetically controlled reaction. There is an increase in the

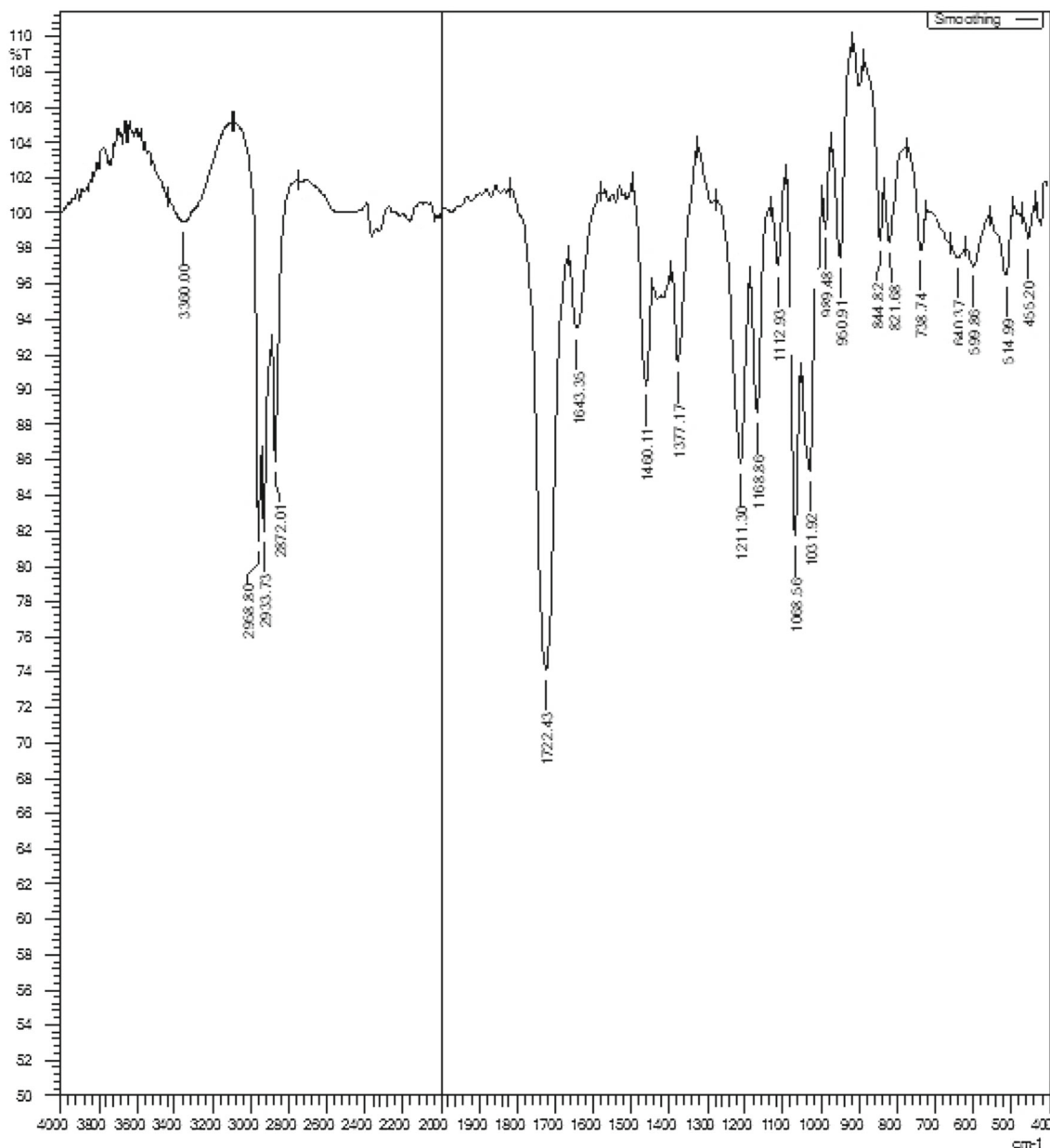


Figure 9. IR spectrum of dibutyl maleate. IR (cm^{-1}): $\nu(\text{CH}=\text{CH})$, 961; $\nu(\text{C}-\text{O})$, 1213; $\nu(\text{C}-\text{O}-\text{C})$, 1210; $\nu(\text{CH}$ and $\text{CH}_2)$, 2900.

value of the equilibrium constant with an increase in the temperature which indicates that the reaction is endothermic in nature. The earlier work done by Yadav and Thathagar reported the activation energy as 14.2 kcal/mol for the esterification reactions of maleic acid and ethanol carried out with Indion-170.¹ Yadav and Krishnan calculated the activation energy as 18.176 kcal/gmol for the synthesis of methyl anthranilate from anthranilic acid and methanol using heterogeneous catalysts like Indion-130.⁸ The activation energy for the current investigation is quite high that indicates the sensitivity of the reaction rate with temperature.

3.7 Determination of functional groups

Further liquid samples were analyzed using infrared spectrometer (FTIR 1-S Affinity- Shimadzu make) to determine the functional groups present, through infrared spectrum as shown in Figure 9. The characteristic peak at 961 cm^{-1} can be attributed to $=\text{CH}$ - out-of-plane deformation in $\text{CH}=\text{CH}$ - structure. The band near 1168 cm^{-1} may be due to C-O-C anti-symmetric stretch for the ether linkage. The band at 1210 cm^{-1} confirms the C-O-C stretching in dibutyl maleate as ester linkage. The presence of carbonyl group is confirmed

from the peak near 1722 cm^{-1} which appears relatively red shifted from the expected position of 1740 cm^{-1} because of the presence of unsaturation in the molecular structure. The peak near 2900 cm^{-1} is attributed to the symmetric and asymmetric stretching of $-\text{CH}$ and $-\text{CH}_2$ groups in aliphatic chain. This result confirms the synthesis of dibutyl maleate by using Amberlyst-15.

4. Conclusion

The esterification of maleic acid and butanol in presence of cationic ion exchange resin was successfully carried out in presence of Amberlyst-15. The rate of esterification increases with an increase in temperature over a range from 60°C to 90°C where 80°C was found to be optimum. The conversion was optimum at a stirrer speed of 300 rpm, which was found to be effective for eliminating external diffusion effect. A maximum conversion of 76% was found for catalyst loading and the addition of molecular sieves as 4% (w/w). Diffusivity values D_{AB} (maleic acid in n-butanol) was calculated at 80°C as $5.08 \times 10^{-10}\text{ m}^2/\text{s}$ and effective diffusivity as $5.08 \times 10^{-11}\text{ m}^2/\text{s}$. The energy of activation was found to be 71.5 kcal/mol. Mass transfer coefficient (k_{sl-A}) was calculated as $6.77 \times 10^{-6}\text{ m/s}$ for the particle size of Amberlyst-15 as 0.5 mm.

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